

EXPERIMENTAL PSEUDOMORPHS: REPLACEMENT OF CALCITE BY FLUORITE

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ABSTRACT

Pseudomorphs of fluorite after calcite have been produced by treatment of cleavage rhombs of calcite with 1 to 50 per cent hydrofluoric acid. Complete pseudomorphic replacement occurs for crystals up to 1 mm in less than twenty-four hours. That strain is produced in the process is suggested by the slight birefringence and the tendency of the larger crystals to shatter.

Electron diffraction patterns of films of fluorite produced on polished calcite show that the (110) plane of fluorite is parallel to the (10 $\bar{1}$ 1) plane (cleavage plane) of calcite. Inspection of models indicates the probable orientation of the (110) plane of fluorite about the normal to the calcite surface. X-ray diffraction from the converted crystals yields broad peaks characteristic of small crystallites. Single crystal techniques reveal orientation in the bulk pseudomorph.

Proton bombardment using the (P, α , γ) reaction in fluorine shows that the rate of replacement in thin films is proportional to the square root of time for thicknesses up to 1000 Å, indicating a diffusion limited transfer through the growing film. At about this thickness the rate curve shows a sharp upward break, apparently associated with rupture of the film. A new cycle of growth then begins at the original rate. The fluorite pseudomorph has an internal surface area of 47.4 M²/gm as determined by the BET method.

We conclude that this replacement involves successive conversions of thin layers of the calcite crystal to oriented crystallites of fluorite leaving the Ca²⁺ positions nearly unchanged and leaving pore space for interchange of solution and gas.

INTRODUCTION

Niggli (1920) and later Kröhnke (1950), have classified pseudomorphism into three types: physical pseudomorphism, where atoms are slightly displaced giving a new crystal structure; exchange pseudomorphism, where one ion or atom in a crystal is exchanged for an ion or atom from the surrounding environment, and pure displacement pseudomorphism where there is complete material exchange while maintaining the macroscopic crystal form. The present work pertains to the second type, exchange pseudomorphism. In this case two fluoride ions are substituted for one carbonate ion in calcite.

Several people have observed the conversion of carbonate fossils to fluorite in the laboratory by hydrofluoric acid treatment (Cookson and Singleton, 1954; Grayson, 1956). This technique has been made the basis of improving the appearance of shells for identification of details of their anatomy since isotropic fluorite, when placed in a liquid of suitable refractive index, is transparent, showing up inclusions, air chambers and foreign material (Sohn, 1956; Upshaw, Todd and Allen, 1957). Fossil

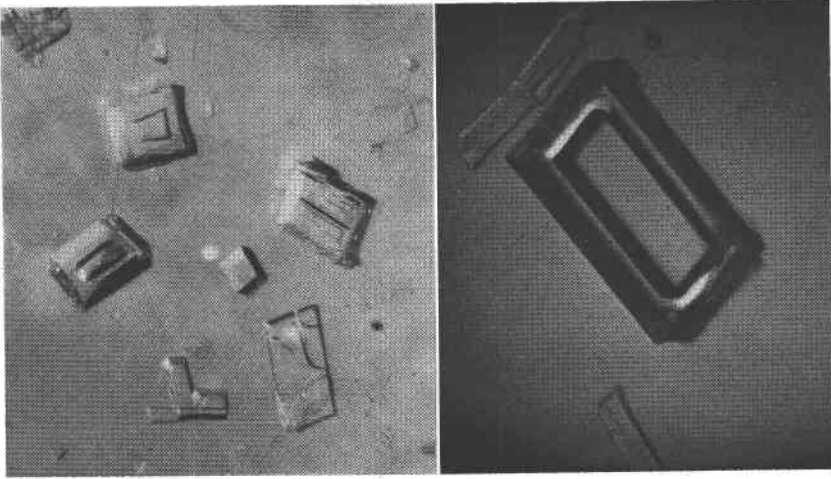


FIG. 1. (left) Partially and completely converted Iceland spar crystals showing a perfect rhomb of fluorite ($\times 15$).

FIG. 2. (right) Partially replaced single crystal of calcite in polarized light with a gypsum plate in the path ($\times 50$).

shells may often be more easily removed intact from marls by first converting them to fluorite while at the same time removing the siliceous matter (Jones, 1961).

The present study started with attempts to convert single crystals of calcite to fluorite. The observation that this transformation took place pseudomorphically in small calcite crystals led to an examination of the details of this change. The calculated volume decrease in converting calcite to fluorite is 33.5% which corresponds to a linear dimension change of 12.5%.

EXPERIMENTS

Conversion of sized fractions of Iceland spar

Experiments with 325, 325-120, 120-60, 60-35, 35-18, 18-10, 10-5, and > 5 mesh Iceland spar using concentrations of HF from 1 to 50% gave complete conversion to fluorite up to above 5 mesh (4 mm) in less than 24 hours. Above 0.5 mm (35 mesh), the crystals tend to shatter easily during or after conversion and many smaller crystals are crazed throughout their volume upon conversion. The perfect rhomb of fluorite is the exception but many can be found. The tendency of the fluorite pseudomorph to craze may be due in part to the strains set up in breaking up the Iceland spar into sized fractions. Figure 1 shows an example of a small converted rhomb which shows no signs of cracking. Along with it

are some other rhombs which are partially converted, showing the central unconverted calcite portion whose boundaries are parallel to the original surfaces. These fluorite pseudomorphs have been washed and are immersed in water. If the crystals are dried they become faintly cloudy but regain their transparency on being immersed again. A photograph of a partially converted crystal is shown in Fig. 2. Here the crystal is immersed in 10% hydrofluoric acid and is viewed with polarized light with a gypsum plate in the path.

The blue and yellow interference colors (dark and light portions of the converted rim of the crystal) indicate a slight birefringence, suggest-

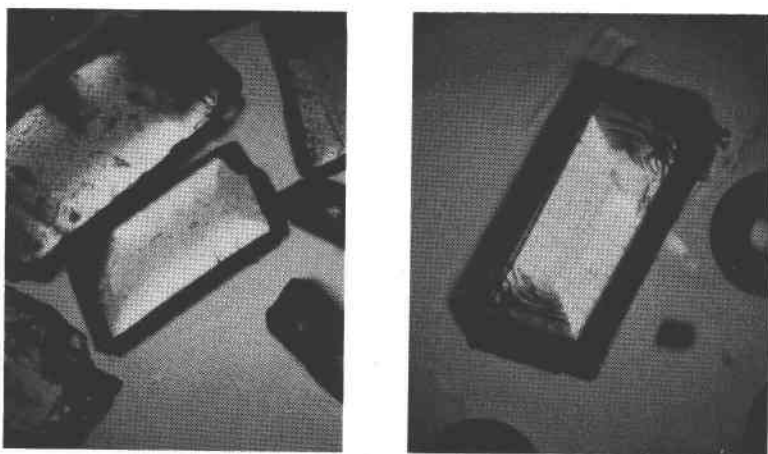


FIG. 3. Completely replaced crystals of calcite showing the "hour glass" effect. Crystal on right crazed throughout volume (crossed nicols, gypsum plate, $\times 50$).

ing strain in the structure. The fact that parallel layers of converted material have the same interference colors shows that the converted material (or strain in it) is related in orientation to the cleavage surfaces. The crystal on the right in Fig. 3 shows the crazing referred to above. Completely converted regular shaped crystals seen in Fig. 3 show the "hour glass" effect. The light and dark portions are yellow and blue in the original. Observation of the optical effect produced by compressive stress on a single crystal of fluorite of about the same size as the pseudomorphs allowed us to infer that the compressive stress in the pseudomorph was approximately perpendicular to the original $(10\bar{1}1)$ calcite plane.

If vapors from a hydrofluoric acid solution are used to convert a calcite crystal, the transition zone is less regular and the converted portion shows no birefringence (Fig. 4).

Weight loss and volume change

The weight loss as measured on the dry (105° C.) product was 23%. The calculated value for the conversion of calcite to fluorite is 22%. Several calcite grains were measured using a micrometer ocular before and after conversion to fluorite. The average change in linear dimensions was -2% which is within the range of error of the measurement. No change could be detected in the size of converted shells or in a converted limestone core approximately $3\frac{1}{2}$ " long by 1" in diameter (dimensions of core changed by less than 0.1%). Since there is a 33.5% volume decrease, there is 33.5% additional porosity in the converted material.

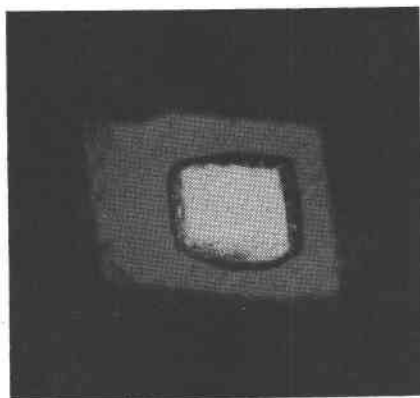


FIG. 4. Crystal of calcite partly replaced using HF solution vapors (crossed nicols, gypsum plate, $\times 50$).

Electron diffraction effects in fluorite films

Electron diffraction patterns of thin films of fluorite formed by treatment of polished calcite surfaces with 1% HF for 1 to 5 seconds have been made by J. J. Porter of this laboratory. The diffraction pattern shown in Fig. 5 is similar to a Laue pattern of a single crystal except that the spots are smeared out. This pattern is interpreted as a "fiber" pattern of fluorite oriented with the (110) plane in the plane of the film. A drawing of this pattern is shown in Fig. 6 with the "reflections" labeled. The angles between the line joining the (002) reflections and the lines from the center of the pattern to other reflections are shown in Table I along with the calculated angles.

When a model of fluorite in the (110) orientation was made with the same scale as a calcite model it was obvious on inspection that the calcium positions of the (110) plane nearly coincided with those of the calcite

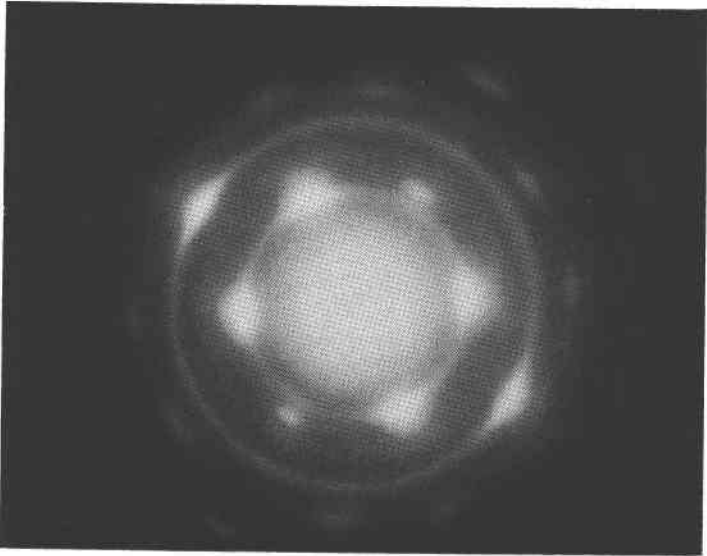


FIG. 5. Electron diffraction pattern of a thin film of fluorite formed on a polished cleavage surface of calcite.

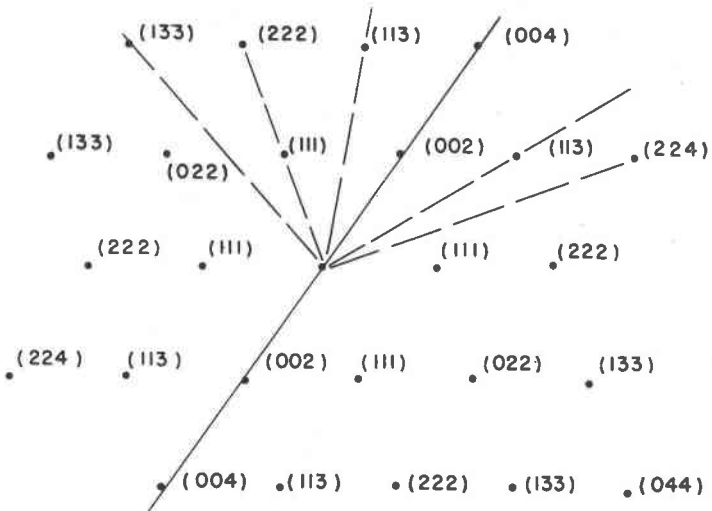


FIG. 6. Diagram of diffraction pattern (shown in Figure 5) with reflections labeled and traces of normals to reflecting planes indicated.

TABLE I. ANGLES BETWEEN NORMALS TO DIFFRACTING PLANES

Angle between	Measured angle	Calculated angle
(002), (022)	Not measured	90°
(002), (111)	55° 0'	54° 44'
(002), (113)	24° 55'	25° 14'
(002), (112)	35° 13'	35° 16'
(002), (133)	77° 7'	76° 49'

cleavage plane, and that the center of pairs of fluoride ions was nearly over the Ca^{2-} positions. A scale drawing of the superposed nets of calcium atoms of the fluorite (110) plane and the calcite cleavage plane is shown in Fig. 7. Since the area per calcium atom is actually a little larger in the fluorite (110) plane than it is in the calcite (1011) plane (21.04 sq. Å compared to 20.10 sq. Å) the major change in dimension (3.035 Å to 1.931 Å) would then have to be in a direction perpendicular to these planes. In order for this change to proceed, successive planes of calcium atoms need to be laterally shifted in changing from rhombohedral to cubic symmetry. A consistent picture of the relation of optical effects to structural change results if the major residual stress is a

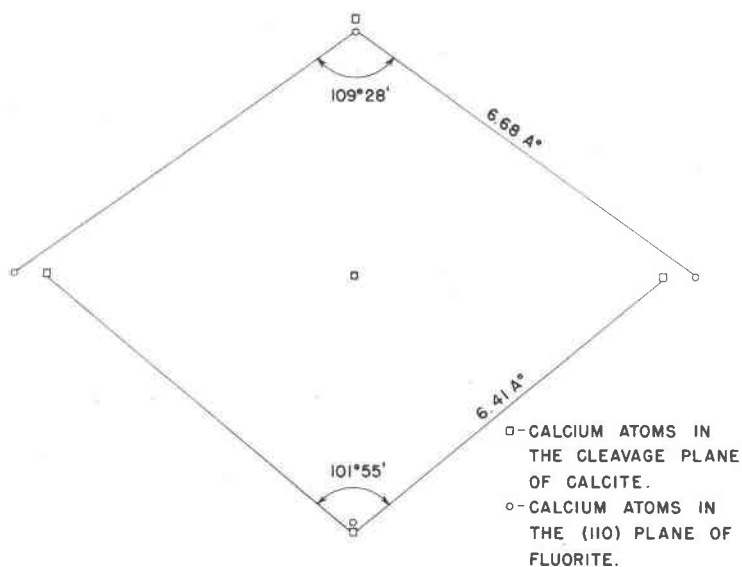


FIG. 7. Superposed nets of calcium ions in the cleavage plane of calcite and in the (110) plane of fluorite.

tensile stress in the (110) fluorite plane due to the lateral shifting of planes of calcium atoms. This is equivalent to a compression perpendicular to the (110) fluorite plane inferred from the optical data.

X-ray diffraction effects of fluorite pseudomorphs

X-ray diffraction of the converted material gave a fluorite powder pattern with fairly broad peaks. Single converted rhombs showed orientation to exist in the bulk as well as the thin films studied by electron diffraction, although the patterns were not readily interpretable, presumably because of the superposition of effects from three orientations of crystallites. Experiments with several concentrations of HF showed the particle size of the fluorite to be inversely related to the HF concentration. Table II shows this relation for HF concentrations from 1 to 10%.

TABLE II. X-RAY DIFFRACTION EFFECTS FROM FLUORITE MADE WITH VARIOUS HF CONCENTRATIONS

HF concentration in per cent	Relative (111) peak height	Relative (111) peak width at 1/2 height
1	1.6	.17
2	1.0	.30
5	.65	.44
10	.62	.41

Since free space in the pseudomorph and the small particle size of the fluorite suggest considerable internal surface, a direct determination was made by James Whalen of this laboratory, using the BET method. The result was 47.4 square meters per gram. For an average calcite particle size of 0.5 μ m this area corresponds to equidimensional units of replacing fluorite 400 Å on a side with pores of approximately 50 Å width.

Kinetics of the transformation

Rate measurements of the replacement of sized calcite particles gave results that were not repeatable. We therefore undertook a study of the kinetics of replacement by measuring the thickness of thin films of fluorite formed on calcite cleavage surfaces. Polished single crystal surfaces of calcite immersed for short times in 1-20% HF produced adherent films of fluorite which could be observed by interference colors, the thinner films producing a straw-colored reflection and the thicker films a blue color which was quite uniform over the polished surface. The method selected for measurement of the film thickness was proton bombardment using the 874 KEV resonance for the production of 6 and 7

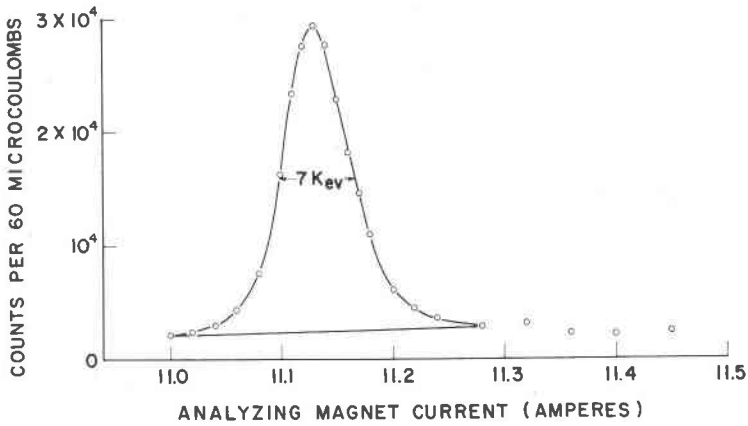


FIG. 8. Typical resonance curve of fluorite film.

mev gamma radiation from the $F^{19} (P, \alpha, \gamma) O^{16}$ reaction. Scanning over the resonance a fixed number of microcoulombs per point, one can determine the film thickness from the area under the resonance curve, the system first being calibrated by bombardment of an evaporated layer of CaF_2 of known weight. An illustration of a typical resonance curve is

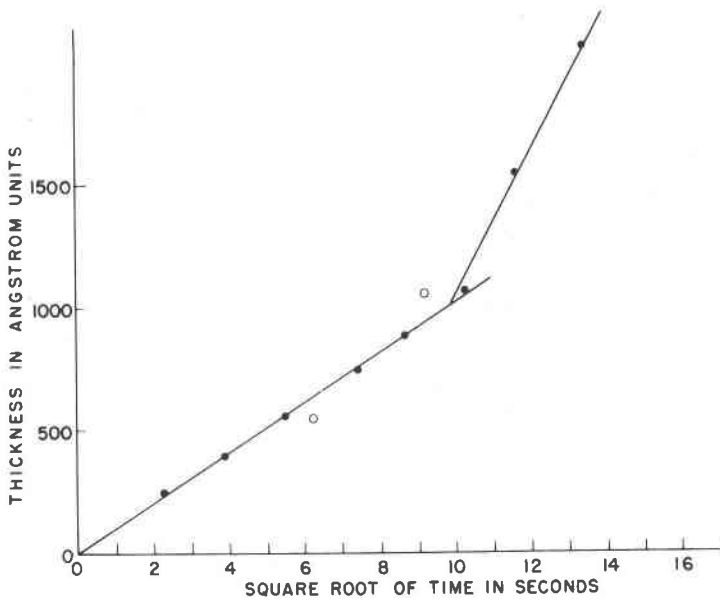


FIG. 9. Graph showing rate of growth of fluorite film in 20% HF.

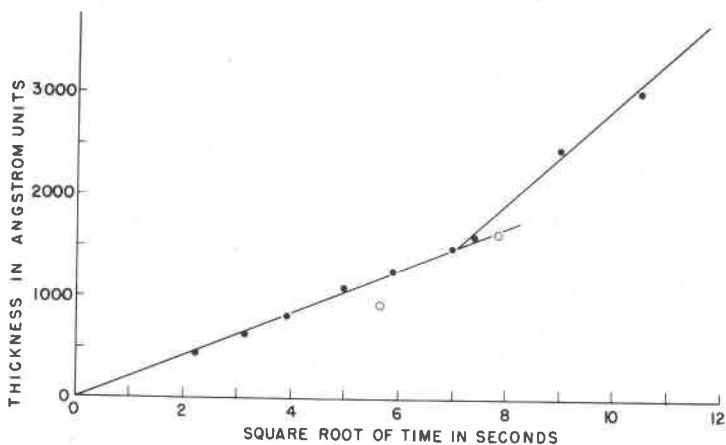


Fig. 10. Graph showing rate of growth of fluorite film in 1% HF.

given in Fig. 8. This method proved to be extremely sensitive, and was entirely suitable to the purpose. The calcite surfaces were immersed in HF solution and constantly agitated for a measured time. The thickness of the replacement film was determined in each case. Figure 9 shows the film thickness resulting from immersion in 20 per cent HF for times from 5 to 180 seconds at a constant temperature of 20° C. For times up to 100 seconds a straight line was obtained on the square root of time plot. As usual with this growth law for a film, we interpret the data to indicate that the growing film forms a protective layer and that further growth is rate-limited by diffusional transfer across the growing pseudomorph. The sharp break at 100 seconds, or 1000 Å, we interpret as rupture of the fluorite film so that the solution has again unhindered access to the calcite surface. Indeed if the point (100 seconds, 1000 Å) is displaced to the origin then the points at 135 and 180 seconds fall as shown by the open circles on the graph. Similar results were obtained by immersions in 1 per cent HF solution, also at 20° C. (Fig. 10), although the rate is apparently faster in the more dilute acid, and the break occurs at about 1500 Å. Again, however, the second "cycle" seems to overlay the first rather well. This dependence of film thickness on HF concentration is in accord with the inverse particle size, HF concentration relationship noticed in the *x*-ray diffraction experiments.

CONCLUSION

The evidence from the various techniques used shows that a single crystal of calcite is converted to many small crystallites of denser fluorite in reproducing the macroscopic form of the original calcite. This

results in 33.5% void space. Initially in the process the fluorite film grows to 1000 Å or slightly larger in thickness and is oriented in a special way with (110) fluorite=(10 $\bar{1}$ 1) calcite such that the calcium nets of the two structures roughly coincide. In the over-all process the average dimensions obtained from the measured surface area correspond to units of linear dimensions of less than one-half this thickness. One can imagine successive layers of CaCO₃ undergoing replacement and, after a critical size is reached, the strained rhombohedral unit, having the strain relieved by shifting of planes of calcium atoms forming a cubic structure. The reduction of solid volume on conversion would seem to be a necessary part of this rapid exchange pseudomorphism allowing ample free space for exchange of ions and molecules in solution.

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