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THE REPLACEMENT OF CALCITE BY FLUORITE: A KINETIC STUDY[1]

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ABSTRACT

Calcium carbonate mineral specimens were transformed to fluorite in NH_4F solutions. With calcite single crystals, the combination of epitaxy and the anisotropy of the reaction led to the formation of elongated hexagonal etch pits. The reaction rate was shown to be directly proportional to the F^- concentration and the surface area. The initial reaction rates were used to obtain estimates of the effective surface area, as contrasted to the geometrical surface area, for porous specimens. Comparison of the experimental rate curves with theoretical rate curves showed that the rate of reaction at the phase boundary was an important, if not the only, rate determining step.

INTRODUCTION

The reaction of fluoride-bearing solutions with calcite minerals has received considerable attention. Grayson (1956) suggested the use of HF to preserve carbonate fossils by conversion to CaF_2 pseudomorphs. Honjo and Minovra (1967) described a technique for preparing nannofossils for electron-microscopic examination based on using HF to remove clay while replacing calcite with fluorite. Kovachy (1964) and Mamillan (1964) described the use of ammonium bifluoride in the cleaning of stone. Ames (1961) demonstrated, in a laboratory study, that field occurrences of fluoride replacement did not require the action of HF. Trautz and Zapanta (1961) noted the formation of a 0.3 mm thick layer of CaF_2 on a large cleavage rhomb of calcite which had been immersed for two months in 2 percent NaF solution. The mechanism of pseudomorphic replacement was examined by Glover and Sippel (1962) who proposed that the $(10\bar{1}1)$ plane of calcite became the (110) plane of fluorite. Gard (1964) confirmed this hypothesis by electron microscopy and indicated that the reaction was epitaxial. From a kinetic study on polished calcite single crystal surfaces immersed in HF, Glover and Sippel (1962) concluded that the reaction rate was limited by diffusion through a coherent layer of strained pseudomorph. This layer reached a maximum thickness that was inversely related to the concentration of HF. The increased stress of the growing layer resulted in its rupture, causing repetition of the film growth-film rupture cycle. The reaction rate was approximately four times greater for 1 percent than 20 percent HF. It also was observed

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that crystals greater than 0.5 mm in size tended to shatter during the transformation process.

Our interest in the topochemistry of calcite led to a kinetic study on large calcite and aragonite specimens in an attempt better to understand the replacement mechanism and the dependence of the reaction on fluoride ion concentration. Preliminary experiments with several fluoride salts indicated that NH_4F solutions, which by hydrolysis are weakly acidic, gave convenient reaction times.

EXPERIMENTAL METHODS

Materials. In addition to the large single crystals of Iceland Spar which were used for the bulk of the experiments, a selection of calcite mineral specimens representing a range of porosities and surface areas was employed. To study the effect of lattice parameter change on the reaction rate, both fine-grained and single crystal aragonite were employed. A materials description, together with the results of X-ray analyses, are given in Table 1. *Baker Analyzed* grade NH_4F was dissolved in distilled water in the preparation of all reagent solutions.

TABLE 1. CALCITE AND ARAGONITE SAMPLE ANALYSES

Sample	Location	X-ray analysis	
		Before NH_4F treatment	After NH_4F treatment
Aragonite-microcrystalline[a]	New York	aragonite	fluorite
Aragonite-single crystal[a]	Spain	aragonite	fluorite
Caen Stone[b]	Bermuda	calcite[c]	fluorite
Coquina[b]	Florida	calcite	fluorite
Iceland Spar[a]	Mexico	calcite	fluorite
Limestone[b]	Bedford-Indiana	calcite	fluorite
Marble[b]	Toronto	calcite	fluorite
Travertine[b]	Italy	calcite	fluorite
Travertine[a]	New York	calcite	fluorite

[a] From Ward's Natural Science Establishment.
[b] Collected locally.
[c] Contained 10 percent Maliss Clay.

Experimental Procedure. The specimens were immersed in stirred solutions of NH_4F at 25±2°C. The volumes used were sufficient to assure a maximum reduction in fluoride concentration of less than 5 percent after complete replacement.

Partially replaced specimens were washed in water, ethanol, and ether, then dried to constant weight. The percent reaction was calculated from the loss in weight, based on the assumption that the only reaction was the conversion of calcite to fluorite. This procedure was checked by removing the pseudomorphic layer from a partially reacted single crystal and calculating the percent reaction independently from the amount of calcite left and the amount of fluorite formed. All methods gave results in agreement within an average deviation of ±1 percent. Some specimens on sectioning showed an unreacted core corresponding to *ca.* 1 percent of the original specimen even though the weight loss corresponded to 100 percent pseudomorphic conversion. This error was traced to mechanical losses of CaF_2 from the surface of the transformed specimen.

DESCRIPTION OF THE SOLID PHASES

All specimens treated retained their original dimensions during the kinetic runs, though in 1.0 *F* NH_4F the calcite crystals occasionally developed cracks and some surface puckering.

Etching. The calcite single crystals displayed an interesting anisotropy of reaction which yielded etch figures. The fundamental etch figure on the cleavage plane is a rhombus whose sides are parallel to the cleavage rhomb edges (Baer and Lewin, 1968). The etch figures formed in NH_4F are considerably different from those formed in solutions of the other ammonium halides, which gave the fundamental figure. The reaction was followed with time from 15 minutes to as long as 36 days. The attack rate of the solution species on the calcite is most rapid in the *c*-axis direction. This is evidenced by substantial rounding of two of the corners of the residual core of unreplaced calcite, and is strikingly demonstrated in the cross-section of a partially converted specimen (Fig. 1). A similar anisotropy of reaction was observed by Giardini and Salotti (1969) on cleavage rhombohedra in the calcite-hydrogen reaction.

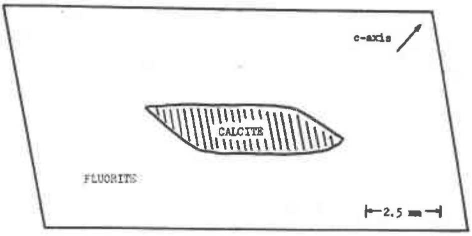

FIG. 1. Tracing of a photomicrograph of a cross-section of a calcite single crystal partially converted to fluorite showing the effect of a markedly greater rate of attack in the direction of the *c*-axis than along other directions.

The initial etch figures were boat-shaped, the deepest part of the etch pit running along the direction of emergence of the *c*-axis from the interior of the crystal. With time, the "prow" of the boat transformed from an acute angle to a right angle while the sides of the pit deepened (Fig. 2a). Eventually, well-shaped elongated hexagonal pits were formed (Fig. 2b). For short times, the development of the etch figure could be observed through the thin film of CaF_2 epitaxially formed on the calcite substrate. This layer was sufficiently thin to generate interference colors. As the reaction progressed, however, the film became opaque and had to be removed in order to see the etch pits. Occasional portions of the surface were observed to be covered in part with small unstrained cubic fluorite crystals which showed no birefringence. This contrasted with the material removed from the major part of the surface, which showed marked strain as reported by Glover and Sippel (1962).

The reaction also was carried out with vigorous stirring in the vicinity of the crystal surface in an attempt to disturb the epitaxial film and thus change the etching morphology. Even with most vigorous stirring, no change in etch pit shape was observed.

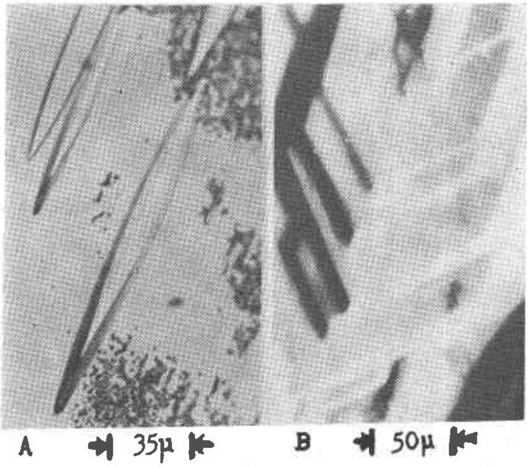

FIG. 2. Etch pits on the cleavage face of calcite crystals immersed in NH_4F. A. Crystal etched 1 hour in 0.5 *F* NH_4F with surface fluorite layer removed to reveal the deepening of the "prow" of the boat-shaped pit and the development of a right angle in the lower pit. B. Crystal etched 10 days in 0.1 *F* NH_4F with transformed layer removed to show well-formed hexagonal pits.

EXPERIMENTAL RESULTS

Kinetics of Calcite Transformation. The transformation reaction was followed with time for cleavage rhombs of calcite at concentrations of 1.0, 0.5, and 0.05 *F* NH_4F. Results are given in Figure 3. The reaction

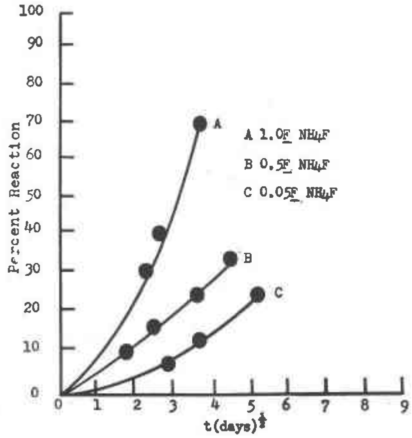

FIG. 3. Rates of reaction of calcite crystals with NH_4F as a function of concentration. The rates corresponding to the initial slopes are: 0.05 *F*, 0.5 percent per day; 0.5 *F*, 2.5 percent per day; and 1.0 *F*, 5.0 percent per day.

rate increased with increasing NH_4F concentration, a trend opposite to that reported for HF by Glover and Sippel (1962).

The specific surface area of the specimen also was an important factor in determining the reaction rate. For two specimens of differing surface area cleaved from the same single crystal, a specimen of specific surface area 2.7 cm^2/g required 14 days to reach 50 percent conversion while one with a specific surface area of 4.1 cm^2/g required 10 days to attain the same conversion in 1.0 *F* NH_4F. A selection of calcite minerals, ranging from very dense marble with large grains to a very friable fine-grained coquina was treated in a like manner. The results for marble, limestone, travertine (N.Y.) and Iceland spar are given in Figure 4.

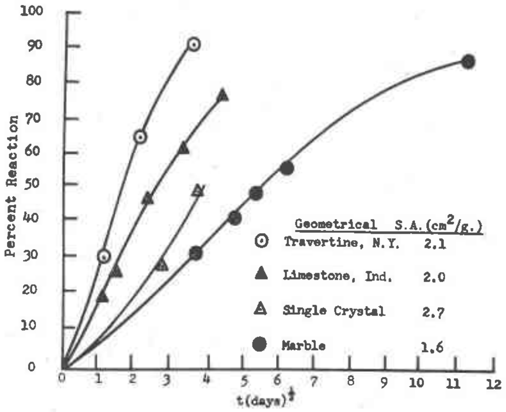

FIG. 4. The rates of reaction of calcite minerals with 1.0 *F* NH_4F. The geometrical surface areas listed correspond to those calculated from the external dimensions with no correction for porosity.

Kinetics of Aragonite Transformation. As discussed above, the mechanism of the calcite to fluorite transformation is believed to involve the layer by layer epitaxial build-up of a new CaF_2 lattice with the calcium ions occupying approximately the same sites in the fluorite as in the original calcite. Since the lattice parameters and crystallographic symmetry of aragonite differ markedly from those of calcite, it was of interest to investigate the kinetics of this pseudomorphic transformation. Both single crystals and fine-grained aragonite were used. Both gave well-formed pseudomorphs in 1.0 *F* NH_4F. Fluorite layer samples taken from the converted single crystals displayed considerable birefringence.

Two regular parallelepipeds of fine-grained aragonite of widely differing specific surface area were cut from the same section of a large specimen. The kinetic data with these specimens and with single crystals

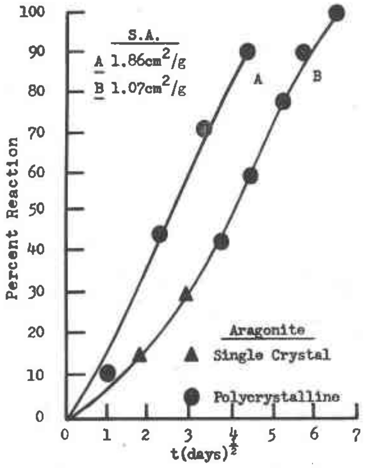

FIG. 5. The rates of reaction of aragonite specimens with 1.0 F NH_4F.

demonstrated that specimens of the same surface area reacted at the same rate, and that the rate was directly proportional to the specific surface area (Fig. 5).

DISCUSSION

Rate Law. Considering the reaction rate of fluoride ions with calcite and aragonite to be controlled by both the rate of diffusion of fluoride ions from the bulk solution of fixed concentration c through the growing layer of fluorite of relative thickness D, and the rate of reaction at the phase boundary, the overall rate of formation of fluorite is given by,

$$\frac{dN_f}{\rho dt} = \frac{A dD}{dt} = \frac{k_1 c A}{k_2 D + k_3} \tag{1}$$

where ρ is the molar density of fluorite, A the surface area of the specimen, and N_f the number of moles of fluorite formed. Integrating we obtain,

$$k' D^2 + k'' D = t. \tag{2}$$

Thus for short times, D is small, and

$$k'' D \cong t,$$

which is identical to the limiting law for reaction at a phase boundary (Jost, 1952). For long times,

$$k' D^2 \cong t,$$

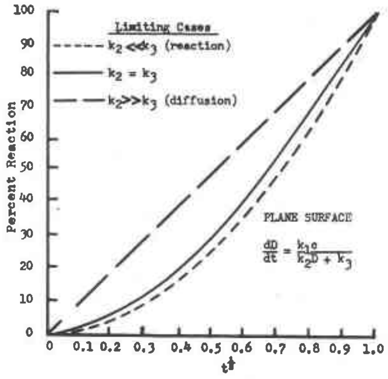

FIG. 6. Calculated reaction rate curves for a plane specimen.

which is the ordinary parabolic law for a reaction limited by diffusion through a barrier layer (Wagner, 1933). The limiting cases for the general rate law (eq. 1) are plotted in Figure 6.

Surface Area. The experimentally measured quantities are percent reaction and time. Percent reaction will be directly proportional to the film thickness. The phase boundary area, however, will be constant only for an infinitely thin wafer. For any other shape, the boundary area varies with time in a manner dependent on the specimen geometry and the percent reaction is not linearly related to the film thickness. For a cube with edges of length s, and a depth of replacement Δ,

$$\%R = 1 - \left(\frac{s - 2\Delta}{s}\right)^3 \times 100$$

Defining the relative thickness of the replaced layer as $D = \Delta/s$.

$$\%R = k\left(D - 2D^2 + \frac{4}{3}D^3\right) \tag{3}$$

and

$$A = 6(s - 2\Delta)^2$$

The relative area, A/s^2, thus varies as a function of the relative thickness:

$$\frac{A}{s^2} = 6(1 - 4D + 4D^2) \qquad 0 \leqq D \leqq \tfrac{1}{2}$$

To investigate the effect on the operational parameter ($\%R$) of the changing surface area of a cubic specimen, the kinetic equation was manipulated as follows: An arbitrary ratio of $k':k''$ was selected, and the k's were numerically evaluated from equation (2) by adopting the normalizing condition that $t=1$ (arbitrary units) when $D=0.5$. Using these values equation (2) then was solved to show how D varies with t during the course of the reaction. Since equation (3) shows how the percent reaction varies with D, numerical substitution permits the form of the variation of $\%R$ with t to be calculated. This was done for a range of $k':k''$ ratios, with the results shown in Figure 7. The *shape* of the curve is of interest, for as the Figure shows, it permits one to differentiate between purely diffusion controlled kinetics (c-shaped curve) and kinetics where reaction at a phase boundary is the rate controlling factor (s-shaped curve).

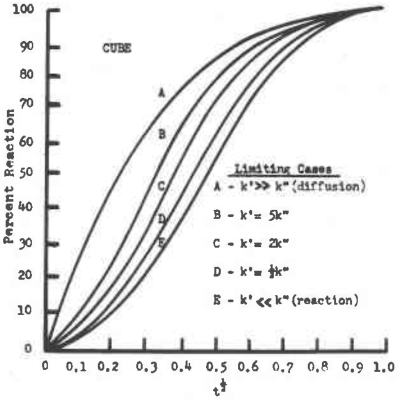

FIG. 7. Calculated reaction rate curves for a cube. The normalization procedure sets the time for completion of the reaction at unity. This compresses the time scale but does not affect the significant feature of the shape of the curves, viz., the presence or absence of an inflection point.

When the data for the several aragonite specimens were replotted as percent reaction divided by the surface area per gram of aragonite in the untreated sample, a single curve was obtained (Fig. 8). The same procedure when applied to nonporous marble and single crystal calcite specimens also gave a single curve (Fig. 8).

Mechanism. Examination of the experimental curves (Figs. 4 and 5) indicates that in general a plot of percent reaction vs. $t^{\frac{1}{2}}$ gives an s-shaped curve. Since a c-shaped curve is predicted for the diffusion limited case, the experimental data indicate that for macroscopic specimens the reaction rate is not purely diffusion controlled. The data do not permit one to judge what role, if any, diffusion plays. One can only state that the rate of reaction at the phase boundary is either the rate-determining step or a strongly rate-influencing step. This reaction rate at the phase boundary may be controlled by the migration of the exchanging species through the very thin epitaxial layer of fluorite.

Comparison of the computed curves for the plane specimen (Fig. 6) and the cube (Fig. 7) indicates that the effect of changing surface area becomes significant mainly when the reaction has gone relatively far. This accounts for the fact that when the data for various calcite specimens of different shapes and for various aragonite specimens are plotted in terms

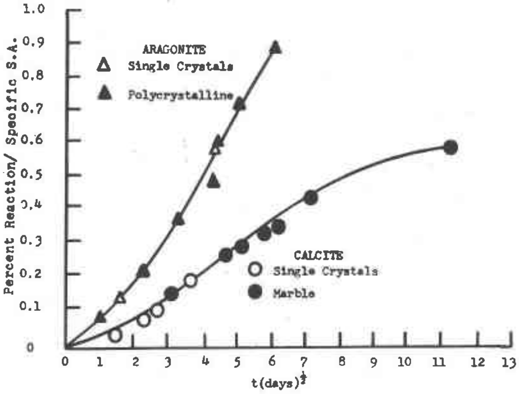

FIG. 8. The effect of surface area on the rate of reaction of calcite and aragonite with 1.0 *F* NH_4F.

of percent reaction divided by the surface area per gram, the data conform to a common curve for a common polymorph. This procedure was not applicable to very porous specimens such as Indiana limestone and New York travertine. Here the variation of the surface area with time was not susceptible to simple analytical description. Nevertheless, it seems that the *initial* reaction rates for calcium carbonate minerals immersed in NH_4F can be employed to yield an accurate estimate of the *effective surface area* as contrasted to its geometrical surface area. This can be done by comparing the initial rate of a given specimen to that for a nonporous standard at the same concentration of NH_4F, both having the same external dimensions.

In Table 2 the times to reach 30 and 50 percent reaction are used to calculate the surface areas of calcite minerals. The geometrically measured surface of a cube of non-porous marble is used as a standard. For

TABLE 2. RELATIVE SURFACE AREAS OF CALCITE MINERAL SPECIMENS

Specimen	Geometrical S. A.	S.A. based on time to reach 30% reaction	S.A. based on time to reach 50% reaction	$\frac{\text{Effective } S.A.}{\text{Geometrical } S.A.}$
Caen Stone	2	8	7	4
Coquina	1½	—	44	30
Limestone	2	8	11	5
Travertine (Italy)	1.7	2	2	1
Travertine (N.Y.)	2	20	18	10
Marble	1.5	1.5	1.5	1

a sample specimen, *s*,

$$S.A.\ (\text{sample}) = S.A.\ (\text{marble}) \left(\frac{t^{s}_{N\%}}{t^{m}_{N\%}}\right).$$

Concentration. The present work demonstrates that the rate of fluorite formation in NH_4F solutions is directly proportional to the fluoride ion concentration. Glover and Sippel (1962), on the other hand, found that the formation rate of fluorite films on calcite single crystals immersed in HF was about four times greater in 1 percent than in 20 percent reagent. It also was noted that there existed a maximum film thickness, in the absence of external forces, for a given concentration of HF and that this maximum was 50 percent greater for 1 percent HF than for 20 percent HF. No explanation was offered for these observations.

Bell, Bascombe, and McCoubrey (1956) studied the dissociation of HF in concentrated solutions and showed that the concentration of F^- ions decreased rapidly with increasing HF concentration in the 10–50 percent range due to the formation of polymeric species such as HF_2^-, $H_2F_3^-$, and $H_3F_4^-$, whereas the hydrogen ion concentration increased. These observations, plus the present results, suggest that the rate of fluorite formation is reduced in the more concentrated HF solutions due to a reduction in the concentration of fluoride ions, and that the formation of fluorite requires the direct action of fluoride ions rather than HF or any polymeric species. The decreased stability of the fluorite film with increasing HF concentration reported by Glover and Sippel (1962) may have been due to high local CO_2 pressures caused by increased acidity.

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