THE HYDROXYLATION OF FLUORITE UNDER HYDROTHERMAL CONDITIONS

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ABSTRACT

At one atmosphere, CaF_2 hydrolyzes according to the reaction (1) $CaF_2 + H_2O = CaO + 2HF$, with a transitory, intermediate step (2), $CaF_2 + xH_2O = CaF_{2-x}(OH)_x + xHF$. Because reaction (1) is suppressed at elevated pressures, crystallization of $CaF_{2-x}(OH)_x$ is to be expected under hydrothermal conditions, but has not been reported owing to the small value of x. Experiments with CaF_2 have been carried out between 800° and 1000°C and at a $P(H_2O)$ between 300 and 500 bars using rapid-quenching techniques. Distinct shoulders on (111) and (220) X-ray reflections of CaF_2 have been observed. These are believed to represent $CaF_{2-x}(OH)_x$, with a unit cell parameter approximately 0.02 Å larger than that of CaF_2. An infrared absorption band corresponding to $(OH)^-$ (~ 3670 cm^{-1}) was observed in experiments at and above 975°C. Above 230°C, solutions in equilibrium with fluorite are known to contain more than twice as much F^- as Ca^{2+}, suggesting hydrolysis according to reaction (2). The implied value of x is extremely small, but increases with temperature in the absence of silica. CaF_2 hydrolyzes with decreasing temperature in the presence of silica because the equilibrium $SiO_2 + 4HF = SiF_4 + 2H_2O$ shifts progressively to the right, decreasing HF fugacity. Contrary to common belief, CaF_2 deviates from ideal stoichiometry under hydrothermal conditions, particularly at high temperatures.

Keywords: fluorite, hydrolysis, hydrothermal, hydroxyl, substitution, synthesis.

SOMMAIRE

Sous pression atmosphérique, le CaF_2 se hydrolyse selon la réaction (1) $CaF_2 + H_2O = CaO + 2HF$, qui est accompagnée d'une réaction intermédiaire (2), qui est transitoire, $CaF_2 + xH_2O = CaF_{2-x}(OH)_x + xHF$. Parce que la première réaction n'est pas favorisée à pression élevée, on devrait s'attendre à trouver le $CaF_{2-x}(OH)_x$ sous conditions hydrothermales, mais ce composé n'a pas été signalé à cause de la valeur très faible de x. Des expériences avec CaF_2 à 800° et 1000°C et une pression $P(H_2O)$ de 300 à 500 bars, utilisant une technique de trempe rapide, ont donné un produit ayant des satellites sur les réflexions (111) et (220). Ces réflexions satellites représenteraient le $CaF_{2-x}(OH)_x$, dont le paramètre réticulaire est environ 0.02 Å supérieur à celui du CaF_2. Une bande d'absorption infrarouge à environ 3670 cm^{-1} correspondant au $(OH)^-$ est présente dans le produit de synthèse à 975°C ou plus. A une température supérieure à 230°C, la solution en équilibre avec la fluorite contient plus de deux fois la quantité de $F^°$ que de Ca^{2+}, ce qui concorderait avec la réaction (2). La valeur de x serait très restreinte, mais augmenterait avec la température en l'absence de silice. Le CaF_2 devient hydrolysé avec diminution de la température en présence de silice à cause du déplacement progressif de l'équilibre $SiO_2 + 4HF = SiF_4 + 2H_2O$ vers la droite, et de la diminution conséquente de la fugacité de HF. Contrairement à l'opinion courante, le CaF_2 dévie de sa stoechiométrie idéale sous conditions hydrothermales, surtout à températures élevées.
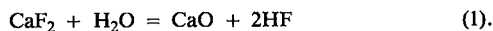
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Mots-clés: fluorite, hydrolyse, hydrothermal, hydroxyle, substitution, synthèse.
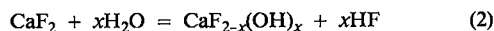
INTRODUCTION

The hydrolysis of fluorite in the presence of water vapor at temperatures as low as 100°C was first noted by Stockbarger in 1949. Since then, thermochemical calculations (*e.g.*, Balakir *et al.* 1968, Schlegel 1968) and experimental studies (*e.g.*, Bontinck 1958, Schlegel 1968) have served to confirm Stockbarger's inference, to compare the hydrolysis of fluorite to that of other fluorides, and to determine the mechanism of reaction. All studies show that, in the presence of water vapor, fluorite hydrolyzes slowly at one atmosphere according to the reaction

$$CaF_2 + H_2O = CaO + 2HF \qquad (1).$$

A transitory, intermediate step, given by the reaction

$$CaF_2 + xH_2O = CaF_{2-x}(OH)_x + xHF \qquad (2)$$

was recognized by Bontinck (1958), who established the presence of small amounts of (OH)⁻ in fluorite by infrared absorption spectroscopy; hydroxyl-stretching bands were observed to reach a maximum intensity after 3 hours and to disappear after 11 hours at 1020°C.

Despite the fact that fluorite is believed to crystallize under hydrothermal conditions in natural environments, the possible hydroxylation of fluorite at elevated temperatures and pressures has not been considered to date. Because the molar volume of the products exceeds that of the reactants, reaction (1) should not be favored at elevated pressures. The suppression of reaction (1) at elevated pressures might be expected to lead to the crystallization of $CaF_{2-x}(OH)_x$, according to reaction (2), but the presence of (OH)⁻ has never been reported in natural or synthetic fluorite.

Thermochemical calculations and experimental studies at one atmosphere suggest that the extent of hydrolysis decreases and the temperature of hydrolysis increases for alkaline earth fluorides in the series BeF_2, MgF_2, CaF_2, BaF_2 (Deadmore *et al.* 1961, Stacey *et al.* 1965, Balakir *et al.* 1968, Schlegel 1968). The hydrolysis of CaF_2 may be compared to the more extensive and better documented hydrolysis of MgF_2.

MgF_2 undergoes hydrolysis reactions analogous to those of CaF_2. At one atmosphere, MgF_2 hydrolyzes according to a reaction similar to (1), with two intermediate steps. Hydrolysis temperatures are lower for MgF_2 than for CaF_2; the reaction of MgF_2 is relatively rapid at 745°C, the lowest temperature investigated (Messier 1965). Under hydrothermal conditions, the reaction equivalent to (1) is suppressed, whereas the intermediate reactions yielding $MgF_{2-x}(OH)_x$ [equivalent to reaction (2)] and Mg(OH)F are stabilized (Crane & Ehlers 1969). Although there is no reason to suspect the existence of a calcium compound analogous to Mg(OH)F, it seems likely that $CaF_{2-x}(OH)_x$ should form under hydrothermal conditions owing to the suppression of reaction (1) at elevated pressures. At temperatures above the upper thermal stability of Mg(OH)F (765°C, 1 kbar; Crane & Ehlers 1969), the hydrolysis of MgF_2 probably involves the same steps as CaF_2. However, the hydroxylation of fluorite under hydrothermal conditions may have escaped detection owing to its very small extent, its high activation energy and possibly its failure to persist under ambient conditions. A brief experimental investigation has been undertaken to search for evidence of the hydroxylation of fluorite at high temperatures.

EXPERIMENTAL STUDIES

A series of experiments was carried out starting with optical grade CaF_2 and distilled H_2O or 10% HF solution at temperatures between 800° and 1000°C and pressures between 300 and 500 bars using cold-seal pressure vessels, sealed gold tubes and rapid-quench hydrothermal techniques. The starting material was ground in an agate mortar under ethyl alcohol for 60 minutes, washed to remove the <0.2mm fraction, and then heated at 750°C for 5 days. Solid/water weight ratios were between 2/1 and 3/1 in all experiments. Pressure vessels were heated rapidly and held at temperature for 2–24 hours.

After rapid quenching, the sealed tubes were opened immediately, and the products examined by means of optical microscopy, X-ray diffractometry and infrared absorption spectroscopy. The (111) and (220) X-ray reflections of CaF_2 (28.3° and 47.2°2θ Cu$K\alpha$, respectively) were measured against an annealed internal standard, CdF_2, which has conveniently located reflections with the same indices at 28.700° and 47.748°2θ Cu$K\alpha$ (Rosenberg 1987). The d values were obtained by averaging two or more measurements at scan rates of 1/4° or 1/8° per minute and are known to within 0.001 Å (111) and 0.0005 Å (220). Infrared absorption spectroscopy was used to examine the (OH)-stretching region; samples were prepared using the conventional KBr pellet techniques (5 mg sample in 500 mg KBr). Experimental data are summarized in Table 1.

Under the optical microscope, fluorite grains have sharp boundaries before the experiments with distilled water, but appear somewhat corroded after

TABLE 1. EXPERIMENTAL DATA: SYNTHESIS OF $CaF_{2-x}(OH)_x$

Temp. (°C)	Press. (bars)	Soln.*	Time** (Hrs.)	Cell Dimension (Å) (220)	(111)
985	345	H₂O	2.5	5.487	5.481
975	415	H₂O	4	5.485	5.475
950	407	H₂O	4	5.487	5.475
935	345	H₂O	2	5.485	5.479
935	345	10%HF	2.5	***	***
850	500	H₂O	7	***	***
850	500	10%HF	7	***	***
800	500	H₂O	24	***	***

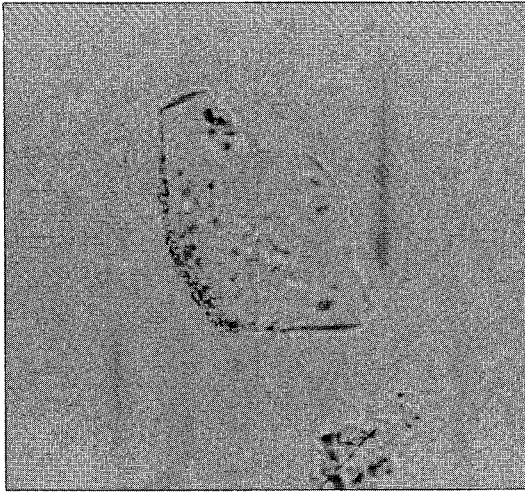* Starting solution; ** Time at temperature;
*** $CaF_{2-x}(OH)_x$ not observed.

FIG. 1. Fluorite grain (935°C, H_2O starting solution, Table 1) showing corrosion and alteration. Plane-polarized light, 700×.

FIG. 2. X-ray-diffraction patterns for experiment at 935°C (H_2O, Table 1). a) CaF_2 (111) reflection (right) at 28.3°2θ with satellite peak [$CaF_{2-x}(OH)_x$] at lower 2θ and CdF_2 (111) standard (left) at 28.7°2θ $CuK\alpha$ (Rosenberg 1987); b) CaF_2 (220) reflection at ~47.2°2θ $CuK\alpha$ with satellite peak [$CaF_{2-x}(OH)_x$] at lower 2θ.

these experiments, particularly at temperatures above 900°C (Fig. 1). The extent of corrosion varies from grain to grain within the same sample; highly corroded grains also show a slight degree of optical anisotropy. With 10% HF rather than distilled water, the grains appear equant (recrystallized) after the experiments.

Small satellite peaks appear as distinct shoulders on both the (111) and (220) X-ray reflections (Fig. 2) in the products of experiments with distilled water above 900°C. These reflections are presumed to represent $CaF_{2-x}(OH)_x$, where x is small. The mean cell parameter of hydroxylated CaF_2, based on measurements of two reflections in each of four samples (Table 1), is 5.483(2) Å, approximately 0.02 Å larger than that of end-member CaF_2 (5.463 Å, PDF 4-0864; 5.4613 Å, this study). Satellite peaks were not observed in products of experiments with 10% HF or at temperatures below 900°C. CaF_2 and its hydroxylate account for all of the observed X-ray-diffraction maxima.

Infrared absorption studies on products of experiments at 1020°C (Bontinck 1958) show weak absorption bands at 3650 and 3580 cm⁻¹, which may be assigned to structural $(OH)^-$. In the present investigation, a small, sharp $(OH)^-$ absorption band was observed at ~3670 cm⁻¹ in experiments at and above 975°C (Fig. 3). This absorption band was not observed below 975°C, probably because hydrolysis is much less extensive at lower temperatures (Bontinck 1958). Weak absorption bands corresponding to absorbed water (Wilkins et al. 1974) were observed at approximately 3450 and
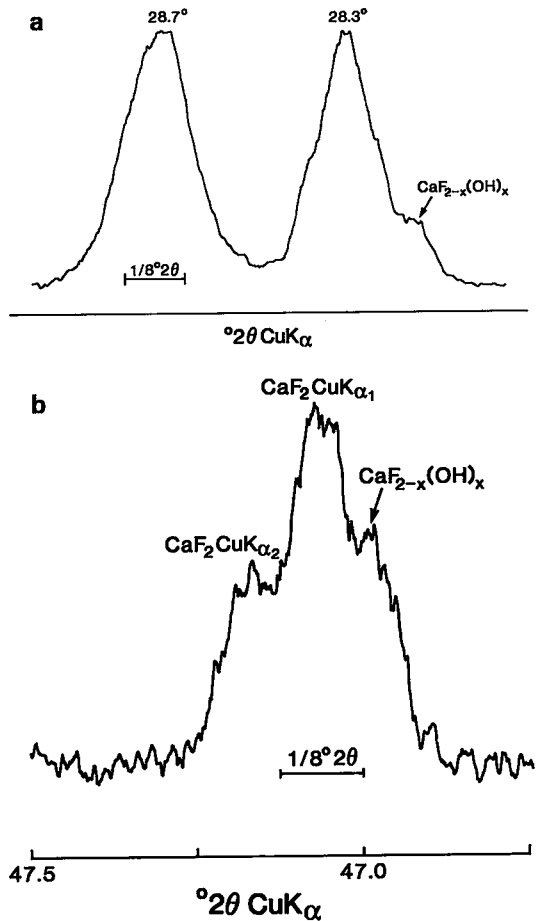
1640 cm⁻¹ in the products of all experiments except those in which 10% HF solution was used.

DISCUSSION

Phase relations

Probable phase-relations in the reciprocal ternary system $CaO-CaF_2-H_2O-HF$, based on data from Biggar (1967) and this study, are shown in a hypothetical, isothermal, isobaric diagram (Fig. 4) for temperatures above 675°C and a pressure of 1000 bars. Under these conditions, the liquid composition has been estimated to be $Ca(OH)_2$
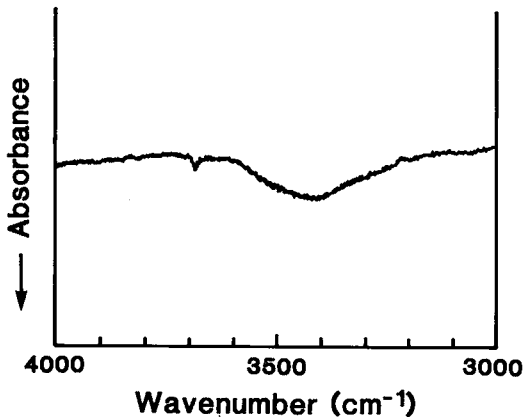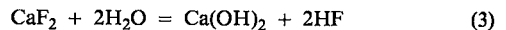
FIG. 3. Infrared absorption spectrum in the (OH)⁻ stretching region of $CaF_{2-x}(OH)_x$ synthesized at 975°C (Table 1).

69%, CaF_2 26%, H_2O 5%, whereas the composition of the vapor is almost pure H_2O (Biggar 1967). The diagram shows that CaF_2 coexists with a HF-bearing vapor phase, whereas $CaF_{2-x}(OH)_x$ may crystallize in the HF-deficient portion of the system. Inasmuch as $CaF_{2-x}(OH)_x$ has not been reported in nature, the hydroxylated form may be metastable with respect to the end member at high pressures as well as at one atmosphere (Bontinck 1958). Even if $CaF_{2-x}(OH)_x$ is stable at high pressures, it may not persist under ambient conditions.

Solubility of fluorite

In a study of the solubility of CaF_2 under hydrothermal conditions, Ellis & Mahon (1964) observed that the concentration of the fluoride ion in solution above 230°C is more than twice the concentration of the calcium ion. They suggested that the reaction

$$CaF_2 + 2H_2O = Ca(OH)_2 + 2HF \qquad (3)$$

gradually assumes greater importance with increasing temperature. Although portlandite was not actually observed in the products of these experiments, measurements of portlandite solubility (Blount & Dickson 1967) are in accord with this interpretation.

In view of the hydrolysis of CaF_2 and by analogy with that of MgF_2 (Messier 1965, Crane & Ehlers 1969), a more likely explanation for the presence of "excess" F⁻ in solution is the beginning of hydrolysis according to reaction (2), where x is very
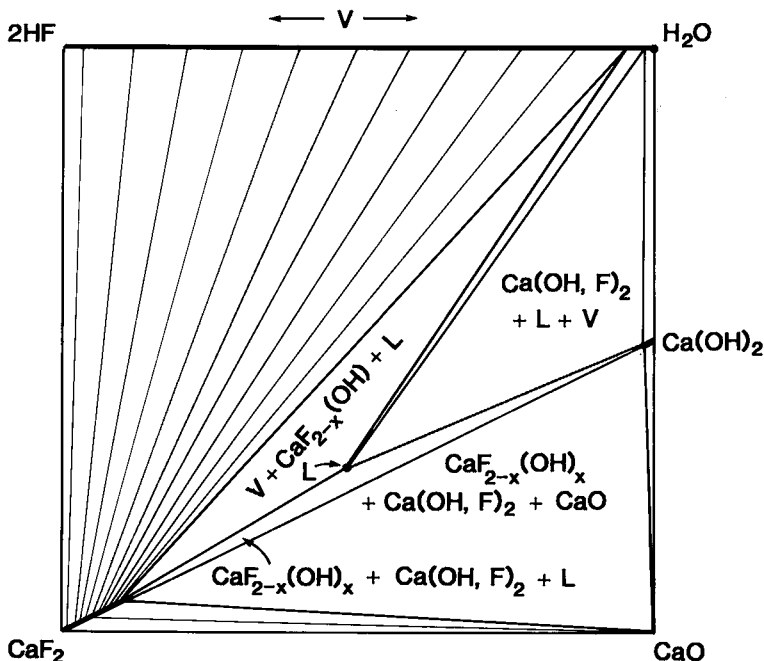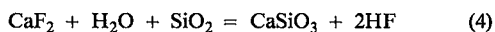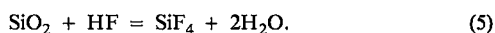

FIG. 4. Inferred phase-relations in the reciprocal ternary system $CaO-CaF_2-H_2O-HF$ at a temperature above 675°C, 1000 bars. See text.

small but increases with temperature. Solutions in equilibrium with fluorite at 350°C contain approximatey 1 ppm Ca^{2+} and 3 ppm F^- (Ellis & Mahon 1964). If the "excess" F^- (*i.e.*, 1 ppm) is attributed to reaction (2), then x, which is a measure of the extent of this reaction, would equal about 0.0001 at 350°C. Replacement of F^- by $(OH)^-$ in so few of the total available anionic sites would be difficult to detect even if substitution were confined to grain edges.

In the presence of amorphous silica, Ellis & Mahon (1964) observed that the total amount of F^- in solutions equilibrated with fluorite is much greater, and that incongruence extends to lower temperatures than in the absence of silica. They attributed these results to the reaction

$$CaF_2 + H_2O + SiO_2 = CaSiO_3 + 2HF \qquad (4)$$

although wollastonite was not actually observed in the products of their experiments. Inasmuch as concentrations of the Ca ion in solution are the same in the presence or absence of silica, whereas concentrations of the F ion are much higher in the presence of silica, it seems more likely that P_{HF} is controlled by the reaction

$$SiO_2 + HF = SiF_4 + 2H_2O. \qquad (5)$$

HF greatly predominates over SiF_4 in the vapor phase at high temperatures, but the ratio HF/SiF_4 decreases rapidly with decreasing temperatures, SiF_4 becoming a significant F-bearing molecular species below 300°C (Rosenberg 1973), resulting in a more extensive hydrolysis of CaF_2 in the presence of silica than in its absence and, therefore, a greater amount of total F in solution at low temperatures. Thus, $CaF_{2-x}(OH)_x$ should crystallize from silica-bearing solutions at low temperatures. Its absence in nature in the presence of silica is further evidence of its metastability with respect to CaF_2 at low as well as at high temperatures.

Contrary to common belief, fluorite may deviate from ideal stoichiometry under hydrothermal conditions, particularly at high temperatures. However, the slight hydroxylation of fluorite reported here is probably the product of a transitory step during hydrolysis that is promoted by elevated pressures or temperatures (or both), and preserved by rapid cooling. Thus, hydroxylated fluorite may be expected to exist as a mineral only under unusual conditions. Conceivably, it might be preserved as a product of F-metasomatism of siliceous limestone by volcanic gases at relatively low temperatures (<300°C). However, under low $P(CO_2)$, cuspidine, $Ca_4Si_2O_7F_2$ (Van Valkenburg & Rynders 1958, Burt *et al.* 1991), zeophyllite, $Ca_4Si_3O_8(F,OH)_4 \bullet 2H_2O$ (Chalmers *et al.* 1958,

Passaglia & Porcelli 1983) or a related mineral might form instead.

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