

Kinetics of the Dissolution of Calcium Fluoride

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Previous investigations have shown that small amounts of various metal ions inhibit the rate of dissolution of calcite in water saturated with CO_2 . As this effect was considered to be general in nature, corresponding experiments with other heavily soluble salts were highly desirable.

This paper describes the results obtained by dissolving fluorite in water. The rate of dissolution is not controlled by mass transfer and becomes negligible at a concentration of CaF_2 considerably lower than the solubility of the mineral, thus giving the impression of an apparent equilibrium. Y^{3+} and Sc^{3+} are effective inhibitors, Ba^{2+} and Ca^{2+} show a similar but much weaker effect. F^- inhibits the process more than a corresponding stoichiometric excess of Ca^{2+} does. EDTA reduces the rate at lower concentrations of CaF_2 , but promotes the dissolution at higher concentrations. $\text{C}_2\text{O}_4^{2-}$ promotes the dissolution process, the effect of CN^- is similar but less pronounced. The initial rate of dissolution is influenced by the negative ions examined, but not by the positive ones.

The kinetics of the dissolution of calcite in water saturated with CO_2 to form $\text{Ca}(\text{HCO}_3)_2$ have been investigated by Erga and Terjesen¹ and by Terjesen, Erga, Thorsen, and Ve.² Additions of several metal ions in concentrations ranging from 10^{-3} to 10^{-7} M were found to inhibit the rate of dissolution. The inhibiting effect of an ion increased with decreasing solubility of its metal carbonate.

The empirical eqn. (1) indicates how the rate of dissolution is affected by the inhibitor.

$$\frac{dC}{dt} = k \frac{C_{\text{real}}^*}{C_{\text{app}}^*} (C_{\text{app}}^* - C) \quad (1)$$

In eqn. (1) C = the concentration of $\text{Ca}(\text{HCO}_3)_2$, C_{real}^* = the solubility of $\text{Ca}(\text{HCO}_3)_2$ in pure water saturated with CO_2 at atmospheric pressure, C_{app}^* = the apparent equilibrium concentration of $\text{Ca}(\text{HCO}_3)_2$ observed, t = the time and k = a constant.

Eqn. (1) shows that with no inhibitor present, meaning that $C_{\text{real}}^* = C_{\text{app}}^*$, the dissolution process is described by a first-order rate equation until the

solution is saturated with $\text{Ca}(\text{HCO}_3)_2$. With inhibitor present eqn. (1) is still of the first order, but the rate of dissolution now becomes close to zero at C_{app}^* which is smaller than the solubility, thus giving the impression of the reaction approaching an apparent equilibrium. Concentrations higher than the apparent equilibrium were observed only after extremely long times of reaction. The initial rate of dissolution was not affected by the addition of inhibitor.

As it was conjectured that the inhibiting effect observed might be general in nature, further experiments with other salts were highly desirable. During the experiments with calcite, the pH and the activity coefficients in the solution changed with increasing concentration of $\text{Ca}(\text{HCO}_3)_2$, and the surface area of the calcite particles was reduced because of dissolution. An approximate method of correcting for the changing surface was developed, but the variations of the two other variables could not readily be taken into account. These difficulties are to a great extent avoided when dissolving a salt with a very low solubility. It was thus decided to use CaF_2 which has a solubility of only 21.3×10^{-5} moles per litre at 40°C ³ and is supplied in the form of fluorite of high purity, suitable for preparation of particles required by the experimental method. Calculations showed that a solution of CaF_2 in water could be considered as completely dissociated in Ca^{2+} and F^- ions.

The first exploratory experiments on the kinetics of the dissolution of CaF_2 were carried out by Ylvisaker,⁴ his results have been of great value to the authors in planning the experiments described in this paper.

EXPERIMENTAL

Apparatus. Most experiments were carried out by stirring a suspension of fluorite particles and water in the stainless steel vessel used in the calcite experiments.² Some runs were carried out in a perspex vessel of similar dimensions. The vessel was equipped with a two-blade stirrer, four baffles, and a specially shaped bottom to prevent settling of particles. Liquid samples for analysis could be extracted through a sintered glass filter. Constant temperature was maintained by a thermostatically controlled electric heating coil around the vessel. The electrical conductivity of the solution was measured with a conductometer CDM2d and a measuring cell CDC 104, both units manufactured by Radiometer, Copenhagen.

Materials. Most of the experiments were carried out with particles made from selected pieces of natural fluorite from Drag quarry in Fauske, Norway. Spectrographical and chemical analysis showed the following composition: Ca=51.33 % (Stoichiometrically 51.33 %), Y=0.06 %, Mg=0.01 %, Si=0.01 %, Al=0.01 %, Fe=0.01 %, Yb=0.001 %, F=48.57 % (Stoichiometrically 48.67 %). Some experiments were carried out with synthetic fluorite prepared from analytical grade CaCO_3 and HF according to a procedure described by Brauer.⁵ The precipitated CaF_2 was melted in a graphite crucible to transfer it to a form suitable for the manufacture of particles. Analysis of the melted material showed: Ca=51.15 %, Sr=0.1 %, Al=0.01 %, Si=0.01 %, Mg=0.01 %, Ba=0.01 %, F=47.4 %. The rest was CO_3^{2-} which was not determined quantitatively.

Fluorite particles. The fluorite was ground in a ceramic ball mill and sieved through stainless steel sieves. Only particles of the fraction $-50+70$ mesh U.S. standard sieve series were used in the experiments. The sieving was carried out according to the A.S.T.M.⁶ procedure.

As in the experiments with calcite^{1,2} it proved necessary to stabilize the reactivity of the particles by removing adhering dust, sharp edges and amorphous surface layers through a pre-treatment. After washing several times with distilled water until the suspension appeared to be clear, 200 g particles were stirred with 10 litres of 0.1 N HCl

at 40°C for 4 h in the perspex vessel. The particles were then thoroughly washed with distilled water to remove the acid, and finally dried at 60°C.

The surface area of the particles was estimated to be 86 cm²/g by a simple microscopic method.

Procedure. The water used in the experiments was purified by distillation followed by a treatment with a combined an- and cationic ion-exchange resin. 10 litres of water containing a known quantity of the electrolyte to be investigated for inhibiting effects were used in each experiment. In most experiments, the stirrer was rotated at 370 rpm. When the temperature in the vessel was stabilized at 40°C, the electrical conductivity was recorded and 50 g fluorite particles added. The change in concentration of CaF₂ as a function of time was followed partly by recording the electrical conductivity of the solution and partly by extracting liquid samples and determining the amount of Ca²⁺ by titration with EDTA and Indikator-Puffertabletten Merck.⁷

Calculations. Corresponding values of concentration C and time t recorded during an experiment were fitted to a polynomial of the form

$$C = a_0 + a_1 \ln t + \dots + a_5 (\ln t)^5 \quad (2)$$

The values of the constants a_0, a_1, \dots, a_5 giving the least square deviation between the observed and calculated values of C were calculated by means of an electronic computer. By differentiation of eqn. (2) with respect to time, an expression for the rate of dissolution as a function of time was obtained. The rate of dissolution as a function of concentration could then be calculated from eqn. (2). In some experiments the rate of dissolution was calculated by graphical differentiation of curves visually fitted to the experimental points.

RESULTS

Dissolution in pure water. Fig. 1 shows among others a plot of the concentration of CaF₂ as a function of time for 2 experiments carried out in pure water at 40°C. The points are reasonably well described by the same smooth

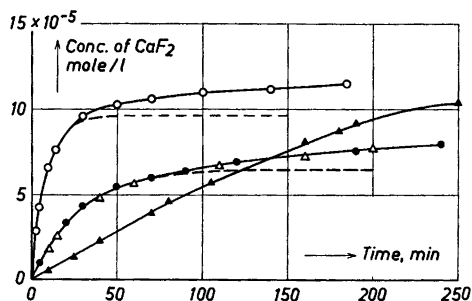


Fig. 1. The concentration of CaF₂ as a function of time.

●: Pure water. △: Reproducibility of experiments with pure water. ▲: 10⁻⁶ M EDTA. ○: 10⁻⁵ M Na₂C₂O₄.

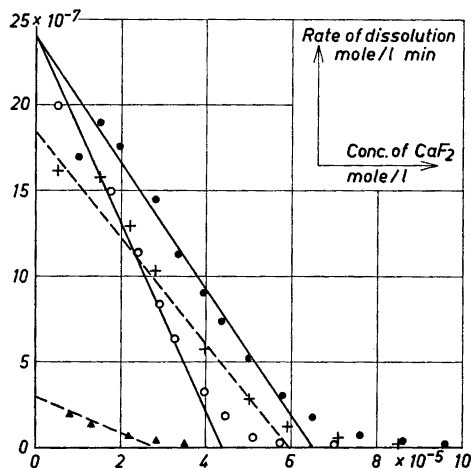


Fig. 2. The rate of dissolution as a function of the concentration of CaF₂.

●: Pure water. ○: 1.9 × 10⁻⁴ M CaCl₂. +: 10⁻⁵ M BaF₂. ▲: 10⁻⁴ M BaF₂.

curve, and the differences between the concentrations measured in the experiments give a typical example of the reproducibility of the experiments. Concentrations measured at times greater than 250 min are not shown graphically because of the very low rates of dissolution in this region. After 24 h the concentration had risen to 11×10^{-5} M which is still far less than the solubility of CaF_2 .

The upper curve on Fig. 2 shows the rate of dissolution for these experiments as a function of concentration. In the region up to 5.5×10^{-5} M CaF_2 , the rate is described by a first order equation of type (1). Insertion of $k \cdot C_{\text{real}}^*/C_{\text{app}}^* = 3.69 \times 10^{-2} \text{ min}^{-1}$ and $C_{\text{app}}^* = 6.5 \times 10^{-5}$ M into eqn. (1) followed by integration yields the lower dotted curve on Fig. 1. Near the apparent equilibrium concentration the rate is higher than predicted by eqn. (1), and the dissolution proceeds at higher concentrations at a steadily decreasing rate, being only a small fraction of the initial rate. The existence of an apparent equilibrium concentration, which is considerably lower than the solubility of CaF_2 , might in analogy with the calcite experiments be explained by assuming the presence of an inhibitor. Ylvisaker⁴ had shown that Y^{3+} was an efficient inhibitor to the dissolution of fluorite. As the particles made from naturally occurring material were found to contain a small amount of this element, it was decided to make particles from very pure synthesized fluorite. The rate of dissolution observed with these particles was, however, in close agreement with the results previously obtained. By experiments carried out in the perspex vessel, metal ions from the walls of the steel vessel were proved to have no inhibiting effect.

The influence of temperature upon the rate of dissolution was investigated in the range from 20°C to 60°C. Fig. 3 shows that the apparent equilibrium concentration remained practically unchanged whereas the rate of dissolution increased substantially with temperature. Concentration had very little effect upon the relative rates of dissolution measured at different temperatures. The rate constants of the first order rate equations describing the first part of the experiments are plotted according to the Arrhenius equation on Fig. 4. The activation energy is thereby calculated to be 13.9 kcal/mole, indicating that the rate of dissolution is controlled by a process taking place on the surface of the fluorite rather than by mass transfer.

Increasing the stirrer speed to 575 rpm produced no change in the rate of dissolution at concentrations lower than the apparent equilibrium. At 10×10^{-5} M CaF_2 the higher stirrer speed doubled the rate of dissolution and at 14×10^{-5} M it was 4 times the rate observed at 370 rpm. Experiments with different inhibitors and promoters added all showed the same effect of variation of the stirrer speed. The theoretical rate constant of mass transfer from the particles to the bulk of the solution at the lower stirrer speed, calculated according to Harriott,⁸ is 0.9 per minute or 24 times as high as observed in the experiments. If the rate of dissolution were controlled by mass transfer, the observed rate constant should have been of the same order of magnitude as predicted by the theory of mass transfer. Furthermore, the influence of the stirrer speed should then, in contrast with the experimental evidence, have been more pronounced at the lower concentrations of CaF_2 . Considerable experimental efforts were made to investigate this highly unexpected effect

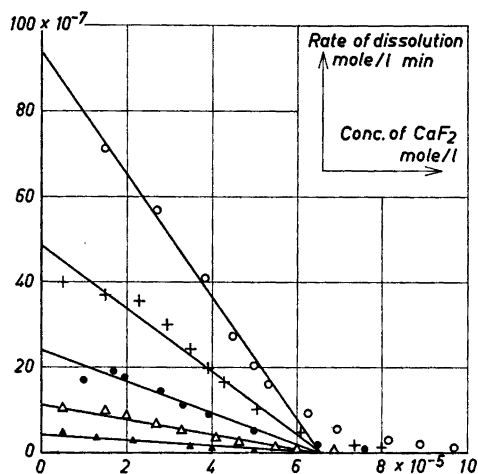


Fig. 3. The rate of dissolution as a function of the concentration of CaF_2 at different temperatures.

○: 60°C. +: 50°C. ●: 40°C. △: 30°C. ▲: 20°C.

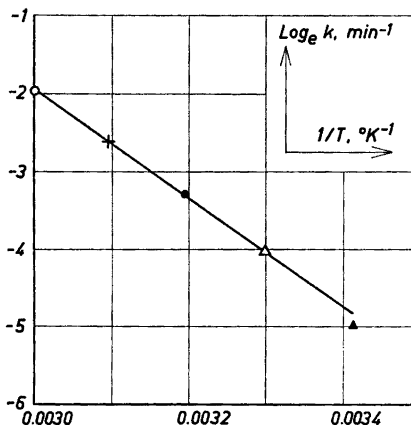


Fig. 4. The natural logarithm of the rate constant k as a function of the inverse absolute temperature.

○: 60°C. +: 50°C. ●: 40°C. △: 30°C. ▲: 20°C.

of stirring; it was, however, not possible to prove beyond doubt that it was not caused by fine dust produced by mechanical wear of the particles, the amounts of dust increasing with the stirrer speed.

Dissolution in presence of EDTA. Addition of a small amount of the complexing agent ethylenediamine-tetraacetic acid (EDTA) had proved very efficient in neutralizing the effect of inhibitors during the calcite experiments. Calculations showed that the small amounts of Y^{3+} dissolving from the fluorite would be quantitatively bound by 10^{-7} moles of the disodium salt of EDTA. Several experiments were carried out where fluorite was dissolved in solutions containing varying amounts of this salt. The reproducibility of these experiments was not satisfactory. Fig. 1 shows the results of a typical experiment in which the concentration of disodium EDTA was 10^{-6} M. The rate of dissolution is in the beginning of the experiment independent of the concentration of CaF_2 and considerably lower than in the reference experiment with pure water. On the other hand it decreases more slowly with increasing concentration of CaF_2 , and the concentration has after 48 h of reaction reached 15.6×10^{-5} M. This is, however, still substantially less than the solubility of CaF_2 .

EDTA-experiments therefore, together with the experiments with synthesized material, suggest that the somewhat unexpected rates of dissolution observed for the dissolution in pure water are not caused by inhibition.

The effects of NaCl and BaCl₂. An experiment with 5×10^{-5} moles of NaCl per litre added produced no changes in the rate of dissolution from the experiments with pure water. This shows that the inhibiting effect is not caused by

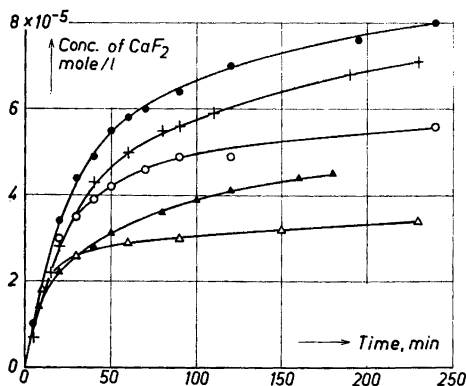


Fig. 5. The concentration of CaF_2 as a function of time.

●: Pure water. +: 10^{-5} M BaF_2 . ○: 1.9×10^{-4} M CaCl_2 . ▲: 10^{-6} M ScCl_3 . △: 10^{-6} M YCl_3 .

the addition of electrolytes as such and opens the possibility of investigating the effect of positive or negative ions separately by adding them as chlorides or sodium salts.

BaCl_2 was tested because it is an electrolyte of the same type as CaF_2 . The initial rate of dissolution was not affected by concentrations up to 10^{-4} M BaCl_2 , the apparent equilibrium concentration of CaF_2 was, however, slightly reduced by increasing concentrations of BaCl_2 . This very small effect may be explained either as caused by an action of the Ba^{2+} ions or by inhibiting impurities possibly present in the salt.

The effects of Ca^{2+} and F^- . The purpose of these experiments was to investigate the influence of a nonstoichiometric composition of the solution. The concentrations are plotted on Fig. 5. Fig. 2 shows that the initial rate of dissolution is not affected by Ca^{2+} ions; the apparent equilibrium concentration is, however, reduced. F^- ions, added as BaF_2 , cause a significant reduction in the initial rate and reduce the apparent equilibrium concentration more than the same amount of Ca^{2+} ions does. As Ca^{2+} and F^- have a different influence upon the initial rate of dissolution, their action cannot be correlated by means of the solubility product of CaF_2 .

The effect of $\text{C}_2\text{O}_4^{2-}$ and CN^- . The concentrations of CaF_2 as a function of time with 10^{-5} M $\text{Na}_2\text{C}_2\text{O}_4$ added are plotted on Fig. 1. Fig. 6 shows the rate of dissolution for this experiment as well as for others with smaller amounts of $\text{Na}_2\text{C}_2\text{O}_4$ added. $\text{C}_2\text{O}_4^{2-}$ ions are seen to promote the dissolution process; the initial rates as well as the apparent equilibrium concentrations are increased. Integration of the first order rate equation gives the upper dotted curve on Fig. 1.

Experiments with higher concentrations of $\text{Na}_2\text{C}_2\text{O}_4$ resulted in further increases in initial rate and apparent equilibrium concentration. At the highest concentration, 2.5×10^{-4} M $\text{Na}_2\text{C}_2\text{O}_4$, precipitation of CaC_2O_4 occurred when the total concentration of Ca^{2+} dissolved was approximately 19×10^{-5} M. The solubility product of CaC_2O_4 was reached when 1.7×10^{-5} moles CaF_2 per litre had dissolved. It was, however, not possible to detect any change in the rate at this point. The results of these experiments are not shown because formation of associated CaC_2O_4 molecules in the solution makes the observed

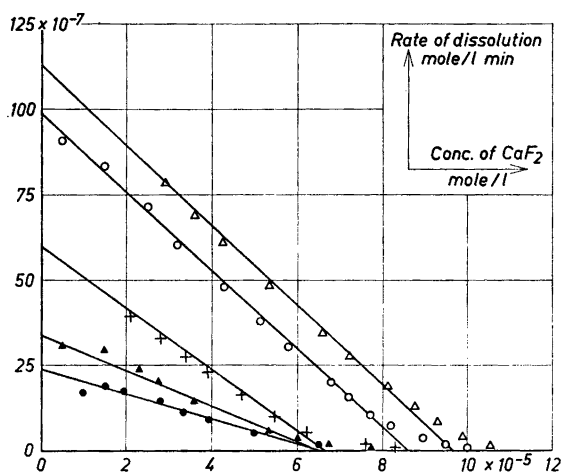


Fig. 6. The rate of dissolution as a function of the concentration of CaF_2 at different concentrations of $\text{Na}_2\text{C}_2\text{O}_4$.

Δ : 10^{-5} M $\text{Na}_2\text{C}_2\text{O}_4$. \circ : 5×10^{-6} M $\text{Na}_2\text{C}_2\text{O}_4$. $+$: 10^{-6} M $\text{Na}_2\text{C}_2\text{O}_4$. \blacktriangle : 10^{-7} M $\text{Na}_2\text{C}_2\text{O}_4$. \bullet : Pure water.

rates of dissolution a result of two opposing effects, *viz.* the promoting action of the $\text{C}_2\text{O}_4^{2-}$ ions and the inhibiting action of a stoichiometric surplus of F^- ions.

A possible explanation of the effect of $\text{C}_2\text{O}_4^{2-}$ ions could be the formation of complexes with inhibitors present in the system. Stable complexes are formed between one Y^{3+} ion and 1, 2, and 3 $\text{C}_2\text{O}_4^{2-}$ ions, and calculations based on the stability constants obtained by Feibush *et al.*⁹ show that when 10^{-4} M CaF_2 or less is dissolved, the corresponding amount of Y^{3+} ions present as impurities is quantitatively bound as complexes when 10^{-6} moles $\text{C}_2\text{O}_4^{2-}$ or more are added. As the rate of dissolution is increased by increasing the concentration of $\text{C}_2\text{O}_4^{2-}$ ions beyond 10^{-6} M, the promoting effect of these ions could not be explained as a result of complexes formed with Y^{3+} . Another argument against this explanation is the very different effect of the complexing agent EDTA.

CN^- showed the same kind of effect upon the rate of dissolution as did $\text{C}_2\text{O}_4^{2-}$, experiments with 10^{-4} M KCN giving results very similar to those obtained with 10^{-6} M $\text{Na}_2\text{C}_2\text{O}_4$.

The effects of Y^{3+} and Sc^{3+} . The concentrations measured in experiments with 10^{-6} moles of Y^{3+} and Sc^{3+} per litre added are plotted as a function of time on Fig. 5. These ions are very efficient inhibitors, their effect being stronger than that of a concentration of Ca^{2+} 200 times as high. It will be seen that Sc^{3+} is the more efficient inhibitor in the beginning of an experiment while Y^{3+} is more efficient at higher concentrations of CaF_2 .

Fig. 7 shows that a concentration of Y^{3+} as low as 10^{-8} M reduces the apparent equilibrium concentration of CaF_2 without appreciably affecting

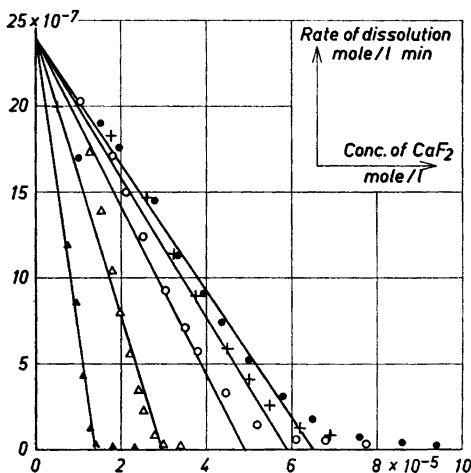


Fig. 7. The rate of dissolution as a function of the concentration of CaF_2 at different concentrations of YCl_3 .

●: Pure water. +: 10^{-8} M YCl_3 . ○: 10^{-7} M YCl_3 . △: 10^{-6} M YCl_3 . ▲: 10^{-5} M YCl_3 .

the initial rate of dissolution. It appears that the inhibiting effect of Y^{3+} upon the dissolution of CaF_2 is very similar to the one previously observed with calcite.^{1,2}

DISCUSSION

It is very difficult at the present stage to provide complete theoretical explanations of either the somewhat unexpected rate of dissolution observed with pure water or the effects of different ions.

A striking difference between the positive and the negative ions capable of influencing the rate of dissolution is that the former do not seem to affect the initial rate at all. Ylvisaker⁴ tested several positive ions; these are listed in Table 1 in order of decreasing effects as inhibitors. A comparison between Ca^{2+} and the three ions which proved to be efficient inhibitors, Y^{3+} , Sc^{3+} , and Cu^+ , reveals some common features which are possibly characteristic for the inhibitors. They have crystalline ionic radii which do not differ very much from that of Ca^{2+} , they form heavily soluble fluorides and show a tendency towards formation of complexes with F^- . It should, however, be noted that the promoting $\text{C}_2\text{O}_4^{2-}$ ions also form a heavily soluble salt and a complex with the oppositely charged ion of the CaF_2 .

The results also show that a stoichiometric excess of F^- has a much greater effect on the rate of dissolution than has a corresponding excess of Ca^{2+} , and that the effect of F^- is strong already at the start of an experiment, whereas that of Ca^{2+} is not. Seen in conjunction with the behaviour of negatively charged promoters and positively charged inhibitors, discussed above, these observations indicate that the role played by Ca^{2+} and F^- in the dissolution mechanism must be different.

Table 1. Properties of metal ions examined.

Metal ion	Effect as inhibitor	Crystalline ionic radius, ¹⁰ Å	Crystalline structure of fluoride ^{11,12}	Possibility of formation of complex with F ⁻¹³	Solubility product at 25°C ¹⁴
Y ³⁺	strong	0.93	cubic	good	(heavily soluble)
Sc ³⁺	»	0.81	rhomb.	good	»
Cu ⁺	medium	0.96	—	uncertain	»
Ba ²⁺	weak	1.35	cubic	good	7.8 × 10 ⁻⁷
Ca ²⁺	»	0.99	cubic	good	8.6 × 10 ⁻¹³
Zn ²⁺	weak or uncertain	0.74	monocl. or tricl.	bad	3.2 × 10 ⁻³
Cu ²⁺	»	0.72	monocl.	uncertain	(slightly soluble)
Mn ²⁺	»	0.80	tetrag.	good	8.0 × 10 ⁻⁶
Bi ³⁺	»	—	cubic	bad	(heavily soluble)
Cd ²⁺	»	0.97	cubic	bad	2.4 × 10 ⁻²
Na ⁺	none	0.95	tetrag. or cubic	good	10 ⁻²

The experiments have shown that the rate of dissolution is controlled by processes taking place on the surface of the dissolving fluorite or in the liquid layer very close to it. A quantitative analysis of the action of an inhibitor must then be based upon knowledge of the amount of inhibitor adsorbed in these regions. The results of adsorption measurements, using the radioactive isotope ⁴⁶Sc as a tracer, will be described in a future paper to appear in this journal.

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