

FLUORITE FORMATION FROM DILUTE
AQUEOUS SOLUTIONS OF F^- ON
CARBONATE MINERALS AND ROCKS AT
ROOM TEMPERATURE AND PRESSURE

By

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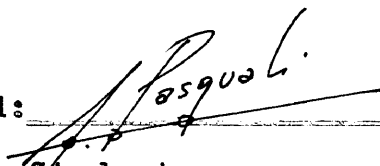
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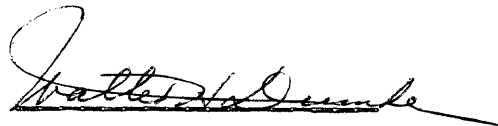
A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Geochemistry.

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ABSTRACT

A laboratory investigation of the formation of fluorite on the surface of calcite, dolomite, carbonate rocks fragments, and pores of carbonate rocks discs was performed to apply results to the elucidation of processes in the natural environment.

The effects of changes of F^- concentration, host mineral surface area, diffusion of ions, pH of reacting solutions, time of reaction, and ionic strength of reacting solutions were investigated. The concentration of the replacing anion (F^-) in solution was changed from 0.002 N to 0.012 N F^- in its reaction with calcite at pHs of 5 and 10. The surface area for calcite was varied from 16 to 178 sq cm. The diffusion of ions through the CaF_2 layer formed on the surface of calcite was studied as the thickness of CaF_2 varied from 0 to 1.5×10^{-3} cm. The pH of reacting solutions was changed from 2 to 10 in the reaction

with calcite and dolomite. Reactions were followed in time up to 50 days for calcite at the pH of 10. Ionic strength of reacting solutions was varied from 0.078 to 0.501 with calcite in the reaction.

The results of studies mentioned above were correlated with Ca^{45} tracer studies to give a partial description for the reaction mechanism.

The rate of CaF_2 formation is directly proportional to mineral surface area and F^- concentration; indirectly proportional to pH; and essentially uninfluenced by ionic strength and diffusion of ions. Calcite reacts faster than dolomite, and limestones react faster than dolostones. Rocks react more slowly than their freshly broken major minerals.

Further work should be done on a) the detailed behavior of the minerals dolomite, ankerite, and magnesite; b) the effect of different ions; c) the effect of surface aging on reactivity; and d) the possibility of defining interstitial solutions in terms of the rock variables of carbonate rocks that contain them.

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INTRODUCTION

The general purpose of this study is to analyze heterogeneous equilibria involving carbonate minerals and dilute aqueous solutions of ions which react to form a new mineral species. This work was done experimentally by studying a suitable heterogeneous reaction. The specific reaction of CaF_2 formation was selected on the bases of reasonable rate (Bisque and Lemish, 1960, p. 42) and natural occurrence (Currier, 1937, p. 364). The particular purposes of this study are (a) to study the variables involved and their importance, (b) to find a correlation between mineral behavior and rock behavior, and (c) to develop a mechanistic description for the interpretation of results.

This study is presented in 4 main parts, LITERATURE REVIEW, THE REACTION, EXPERIMENTAL WORK AND INTERPRETATION, NOTES ON MECHANISM. The literature review attempts to give an idea of the conditions in which fluorite is formed in

nature from calcite and dolomite and to give an idea of what pertinent knowledge the literature of surface chemistry has to offer to the student of geologic problems involving heterogeneous reactions. The section on the reaction is a brief exposition of the theoretical elements of fluorite formation from calcite and dolomite, with the purpose of giving the reader an introduction to the problem. The experimental section has a suitable descriptive title. The chapter on mechanism explains with experimental evidence what the author feels can be said at this moment about the steps in the mechanistic description of the fluorite-formation reaction. The appendix contains examples of pertinent calculations referred to throughout the text, and data whose importance does not justify their space requirements in the text.

LITERATURE REVIEW

Three papers refer specifically to the laboratory formation of fluorite. Grayson (1956, p. 71-78) reported the replacement of calcareous fossils by HF to form fluorite with the accurate preservation of the original shape of the fossil, and suggested a detailed investigation of this reaction. Bisque and Lemish (1960, p. 42) had noted marked differences in reactivities of carbonate rocks with F^- . Ames (1961, p. 730-739) published the results of a detailed laboratory investigation of the formation of fluorite from calcite. Ames' work consisted in passing 6 liters of solution containing NaF through columns made up by 50 grams of calcite and studying the influence of the different variables; pH, from 7 to 12; temperature, from 15°C to 90°C; flow rate; F^- concentration, from 0.01 N to 0.1 N F^- ; and calcite surface area, from 0.01 to 0.17 sq m. The results of Ames' work are presented graphically (1961, p. 735),

and their significance explained through the text (1961, p. 732-736). Ames used columns for reaction vessels and has not reported checking CaF_2 formation or pH of solutions along points of the columns. These factors and flow rates make it very difficult to consider the kinetics of the reaction in terms of time; a repetition and extension of his work, performed in better defined and controlled environments, is desirable.

The geologic literature affords some determinations of the abundance of fluorine in the different natural environments. Crustal rocks contain an average of 700 ppm of F as compared with 200 ppm of Cl (Mason, 1958, p. 44). Sea water contains 1.3 mg per l F^- (Mason, 1958, p. 187). The earth as a whole contains 2.7 atoms of F per 10,000 atoms of Si (Mason, 1958, p. 202). The F^- content of river waters varies from 0.02 to 0.6 mg per l (Gautier and Clausmann, in Clark, 1959, p. 73); spring waters contain up to 7.6 mg per l F^- (De Gouvernain, in Clark, 1959, p. 194). Compounds of F have also been reported from gaseous emanations as HF and SiF_4 , the gases from the Vesuvius contain 0.11 mg of F per l of gas (Scacchi, in Clark, 1959, p. 262).

Fluorite bedding-replacement deposits are formed by replacement of either calcite or dolomite by fluorite in certain favorable horizons of a sedimentary geologic section.

Deposits of this type are common in New Mexico (Johnston, 1928, p. 51) and in Illinois (Currier, 1937, p. 364); the most important deposit is found in the Cave In Rock district of Illinois.

In New Mexico (Johnston, 1938, p. 51-52), the fluorspar occurs replacing certain favorable beds which are cut by minor faults. The capping bed is generally a massive shaly limestone, the replaced bed a medium-grained limestone, and the floor a dolostone bed. The fluorspar is here associated with calcite, quartz, barite, galena, pyrite, chalcopyrite, and specularite; although the geologic setting (Johnston, 1928, p. 13) and wall rock alteration indicate a lack of uniformity of formation conditions, the suites of minerals indicate mesothermal to epithermal deposits.

In Illinois (Currier, 1937, p. 367), the fluorite bedding-replacement deposits occur in the Fredonia limestone member which is oölitic. The top of the replacement zone is a shale bed. Currier (1937, p. 364) describes the deposits as a replacement of limestone with the preservation of bedding and cross bedding. The ore is generally banded, the darker bands formed by replaced impure rock, and the lighter bands formed by the CaF_2 brought in by solutions and emplaced in the voids made available because fluorite has a smaller molar volume than calcite. In this connection

Grogan (1949, p. 615) believes that the reduction in volume is due to a stoichiometric replacement reaction and to solution of limestone by mineralizing fluids.

The limits of mineral bodies (Currier, 1937, p. 369) are ordinarily marked by a thinning of mineralization and by an increase in impurity of ore, the residual carbonate grains in the impure bands being ferriferous, probably ankeritic. Currier (1937, p. 364) describes the replacement as stoichiometric, probably caused by HF contained in hydrothermal solutions.

The formation of CaF_2 from solid CaCO_3 (calcite) and F^- in aqueous solutions represents an example of a heterogeneous reaction. A reaction is heterogeneous when two or more phases are present, in this example solid and liquid phases, and also gaseous phase if CO_2 is evolved at the reaction sites. A proper understanding of what is involved in the study of this reaction, or any other heterogeneous reaction, necessitates a minimum knowledge of what is known about the structure and chemical behavior of solid surfaces. The following brief introduction to surface chemistry should aid in elucidating the methods.

Surface of crystalline materials should be looked at in 3 dimensions, for there is a depth action of surface distortion (Weyl, 1953, p. 156). This surface distortion

is caused, at least partly, by the unbalance of electric forces at the surface of an ionic crystal that has not yet rearranged. The depth of this distortion layer is a cause of controversy among the workers in the field; Weyl (1953, p. 156) asserts it to be of the order of several hundred atoms or 3000 A; Leise (in Thomson, 1953, p. 196) has not found any distortion on calcite, Finch (in Thomson, 1953, p. 196) has found an amorphous layer on calcite when the gross surface makes a considerable angle with the cleavage; and Samuels (1960, p. 83) takes the amorphous layer of crystalline materials to be 50 A thick on metallograpically polished surfaces.

The surface-distorted film on crystals is a coating of material that is amorphous (Weyl, 1953, p. 158), and, that going from the surface into the body of the solid, the film increases in crystallinity. The distorted coating is believed to be caused by polarizable ions (Weyl, 1953, p. 159). Generally cations are smaller and less polarizable than anions. At the surface of a crystal more anions per cation than stoichiometry predicts are needed to prevent the very high potential otherwise developed by cations. The electron clouds of anions are deformed and attracted towards the cations; cations are then partially shielded from the environment, and the surface of the crystal as a whole has negative

charge (Weyl, 1953, p. 154).

Crystals are characterized by surface energies which are different for every kind of crystal and greatly depend on the previous history of the crystal. Surface energy, expressed in terms of units of energy per unit of area, is defined as the energy required to form 1 sq cm of new surface in presence of its saturated vapor (Gregg, 1951, p. 233). The formation of this new area is achieved in two steps (Adamson, 1960, p. 235): the cleaving of the solid to expose a new surface, and the rearrangement of the atoms on the new surface to their equilibrium position. As the surface of a solid increases, its surface energy increases together with an increase in availability of crystal components to its reactive environment.

Weyl (1953) mentions 4 types of changes which can lower the surface energy of a homogeneous crystal: (a) polarization of surface ions (p. 152), (b) distortion of surface structure and formation of an electric double layer (p. 155), (c) excess of anions over cations (p. 155), and (d) sorption of molecules and anions (p. 158).

Polarization of surface ions of the crystal occurs when the electron clouds of the anions in the crystal are attracted toward adjacent cations with the effect of obtaining a surface with strong localized positive potentials and dis-

persed weak negative potentials instead of the original checkered strong positive and strong negative fields (Weyl, 1953, p. 153). In a crystal where the anion is not polarizable as in CaF_2 , the surface energy to form the first crystal from a solution of F^- and Ca (II) ions is great, and in this case a supersaturation of 500 percent is necessary before the first crystal is formed (Weyl, 1953, p. 155).

Distorting the surface structure and forming an electric double layer occur when the polarization of the surface ions is accompanied by a geometrical dislocation not having any cation in the extreme outer layer (Weyl, 1953, p. 155). The result is a weakly negatively charged surface instead of a checkered field of strong positive and strong negative charges.

The stoichiometric excess of anion over cations occurs when some extra anions are attached to the outer layer of a crystal when the crystal is precipitated from solution (Weyl, 1953, p. 155); the purpose of the extra anions is to screen the high potentials of cations on the crystal surface. The result is a surface with cations whose electric energy has been partially neutralized.

The sorption of molecules and of anions occurs when the crystal is put into an environment which contains chemical species which can be adsorbed on the surface of the crystal

by its high positive potentials (Weyl, 1958, p. 158). The result is a screening of high potentials and a lowering of the surface energy.

Reactions in solutions at a solid surface interface occur in a series of steps (Laidler, 1950, p. 152): (a) diffusion of reacting ions to the solid surface, (b) adsorption of ions on the surface, (c) reaction on the surface, (d) desorption of unused ions, and (e) diffusion of unused ions to the body of the solution. Any one, or any combination of these processes can be rate determining. Depending on what steps are rate determining. The rate expression takes different forms. If the rate of transport of ions to the solution is the slowest process, the parabolic law holds (Gregg, 1951, p. 277), $F^2 = \frac{k}{t}$ (where F = amount of product formed, t = time of reaction, and k = a constant). If the rate of transport of ions to the solution is the slowest process, and the film of product is repeatedly cracking and healing, the logarithmic law holds (Gregg, 1951, p. 277) $F = k \log (1 + k_2 t)$ where k_1 and k_2 are constants). If a combination of processes is rate determining, complex mathematical expressions for the rate expression result.

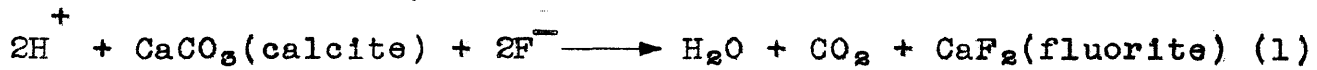
Reactions in solutions at a solid surface do not start immediately over the whole surface. Reactions start by a process called nucleation, which is the formation of tiny

particles of product on spots of the solid surface which have high potential energies, such as edges, corners, or kinks in the steps on the faces (Gilman, 1960, p. 137-138). Nuclei are formed at a limited rate so that the reaction goes slowly at first (Gregg, 1951, p. 279), the rate increases until the surface is completely coated with products, if these products do not interfere with the transport of ions. The rate at which nuclei are formed is dependent on the following factors: (a) the amount of area, and the structure of the crystal (Gregg, 1951, p. 278); (b) the crystallographic direction of advance in the crystal (Gregg, 1951, p. 274; (c) the ions present in solution and their concentration (Keith and Gilman, 1960, p. 1); (d) the ambient temperature (Gregg, 1951, p. 279); (e) the previous history of the crystal represented by amount and kind of molecules adsorbed (Weyl, 1953, p. 151); and, (f) the closeness to attainment of surface equilibrium with its environment (Gregg, 1951, p. 278).

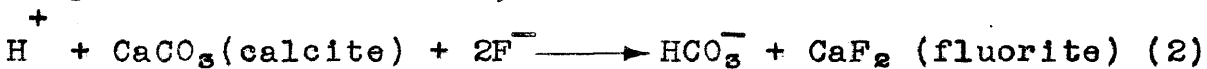
THE REACTION

The fluoride ion (F^-) attacks the surface of calcite (or dolomite) to replace a carbonate ion (CO_3), forming the new mineral species fluorite (CaF_2). Three equations can be written to describe the stoichiometry of this transformation depending at which pH the reaction occurs,

at pHs lower than 4,



at pHs between 4 and 10,



at pHs higher than 10,

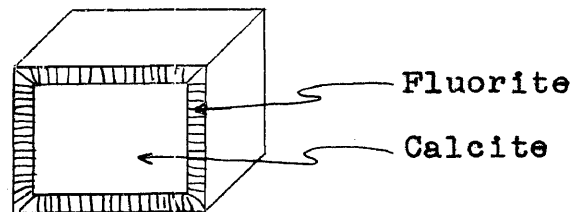
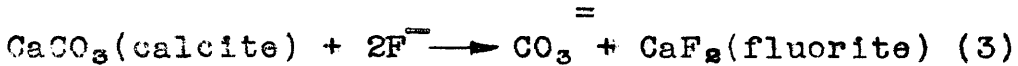
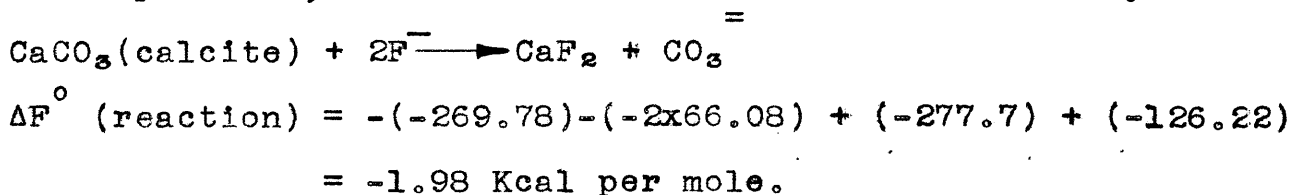


Figure 1: Calcite coated with fluorite.

Calcite is consumed as the reaction proceeds, and fluorite forms on the calcite surface as a layer of small crystals. After reaction, the grains seem to retain their shape; however, under the microscope the retention of shape does not hold.

If, from the above equation (3) the assumption is made that every Ca (II) ion in the calcite structure will go to form part of the fluorite structure, a considerable reduction in volume of the solid phase must occur. One g mole of calcite has a volume of 36.9 cu cm, whereas 1 g mole of fluorite has a volume of 24.5 cu cm, the reduction of the original volume being 33.6 percent.

A thermodynamic calculation of the free energy of the reaction shows that the reaction is spontaneous at 25°C and 1 atm pressure, if all substances are at unit activity.



Data are in kilocalories per g mole (Garrels, 1960, p. 225-228).

If the assumption is made that dilute aqueous solutions react with dolomite forming CaF₂ and release all Mg (II) ions into solution as indicated by the equation below, CaCO₃, MgCO₃(dolomite) + 2F⁻ → CaF₂ + 2CO₃⁼ + Mg⁺⁺, then the reduction in volume of the original solid phase for the transformation is 61.7 percent.

EXPERIMENTAL WORK AND INTERPRETATION

METHODS

Most experiments consisted of reacting a weighed quantity of mineral with 500 ml of a dilute aqueous solution of F^- , buffered at a desired pH, in nalgene bottles. The solutions were kept in contact with the atmosphere either by having a hole drilled through the cap or by not tightening the cap. The average pressure in the laboratory is 620 mm of Hg, and the average temperature is 23.5° C.

The solids used in the reactions--calcite, dolomite, and carbonate rocks--were broken with a glazed porcelain mortar and pestle, and sieved. The different sieved fractions were washed with demineralized water and dried before being weighed and used in reactions.

The reaction solutions were prepared by using proper amounts of analytical-grade chemicals previously dried and diluting them with demineralized water. The reactions were initiated by dropping the solids into the various solutions

and shaking the bottle until all grains settled to the bottom. At different times of reaction, aliquots of the solution were taken and analyses made for F^- , Ca (II) ion, Mg (II) ion, and the pH measured, as the particular case required.

The F^- concentration was determined colorimetrically (with a Beckman model B spectrophotometer) using the reaction of F^- in decolorizing the 2-(p-Sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate-Zirconium lake (Bellack and Schouboe, 1958, p. 2032). The accuracy of the method is 3 percent in the interval 0 to 1.4 mg per l F^- under the present work conditions. Aliquots of reaction solutions were diluted to place them within the F^- concentration range of the method.

The concentrations of Ca (II) ion and of Mg (II) ion were determined by titration with ethylenediaminetetraacetic acid (versene or EDTA) either 0.025 M or 0.00125 M depending on the amounts present (Bisque, 1961, p. 113-122). The smallest amount easily detectable was 1×10^{-5} moles of either Ca (II) ion or Mg (II) in a 10-ml aliquot.

The H (I) ion-concentration determinations were made with a Beckman electronic pH meter, which was calibrated periodically with standard buffer solutions.

AREA DEPENDENCE

The effect of the change in surface area of the calcite upon the rate of CaF_2 formation was studied. The area of the calcite surface was varied by (a) changing sieved-size fraction of 1-g samples of material, and (b) changing sample size of the -40+60 sieved-size fraction. The area of samples was calculated from geometric data of the grains assuming a cubic model (see appendix for example of surface area calculation, p. 48). The reacting solutions were analysed for F^- after 48 hours. The results obtained are plotted in figure 2 (p. 17). The rate of CaF_2 formation was directly proportional to calcite area, as also shown by Ames (1961, p. 735) at a pH of 9.

 F^- CONCENTRATION DEPENDENCE

The dependence of the rate of the CaF_2 formation on F^- concentration ranging from 50 to 220 mg per l (0.002 to 0.012 N F^-) was studied at pHs of 5 and 10. The range of F^- concentration was selected to approximate natural solutions and correlate results with Ames' work (1961, p. 735).

The investigation at pH 5 consisted of reacting 1-g

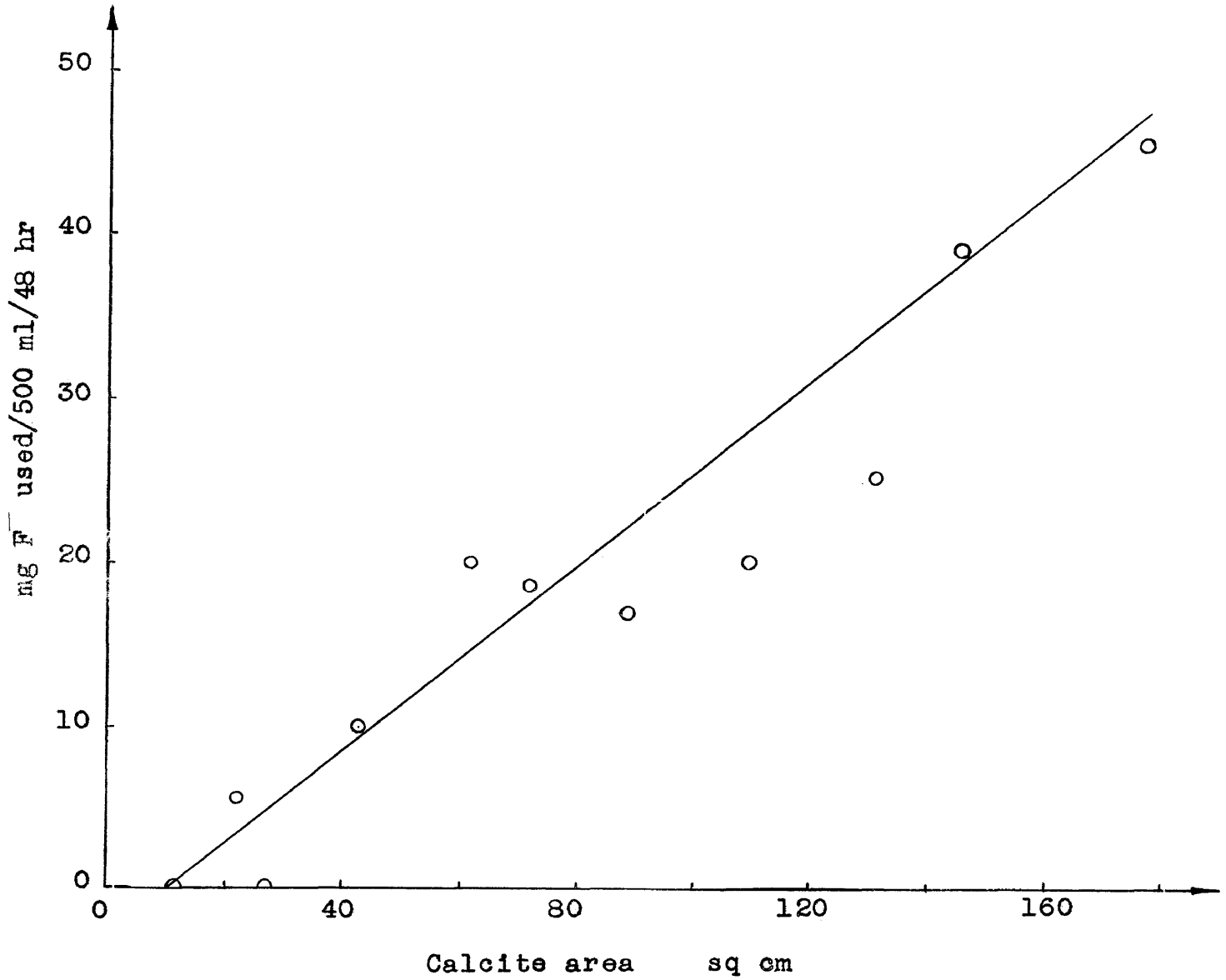


Figure 2: Area dependence. The reaction solutions were buffered at pH 5 with the NaOH-KHC₈O₄H₄ buffer system. The ionic strength of solutions is 0.078.

samples of -20+40 mesh calcite with 500 ml of solutions buffered with the NaOH-KHC₈O₄H₄ system at an ionic strength of buffer of 0.068 (see appendix for example of ionic strength calculation, p. 49) show a direct dependence of rate of CaF₂ formation with the original F⁻ concentrations.

The investigation at pH 10 was done under the same conditions except for the buffer system. The buffer system was NH₄OH-NH₄Cl with an ionic strength of 0.012. The results are plotted in figure 4 (p. 20) for a reaction time of 11 days. The linear relationship of rate of CaF₂ formation with original F⁻ concentration is again seen in figure 4 (p. 20) and in figure 3 (p. 19).

TIME DEPENDENCE

The reaction was followed by taking aliquots of the solutions in contact with the host minerals at different times and analyzing for F⁻. This analysis was done by reaction of 1-g (-20+40-mesh) calcite samples using reacting solutions at F⁻ concentrations of 200, 150, and 100 mg per l. The solutions were buffered at pH 5 with the NaOH-KHC₈O₄H₄ system with 0.068 ionic strength. The results of this work are plotted in figure 5 (p. 21). This figure

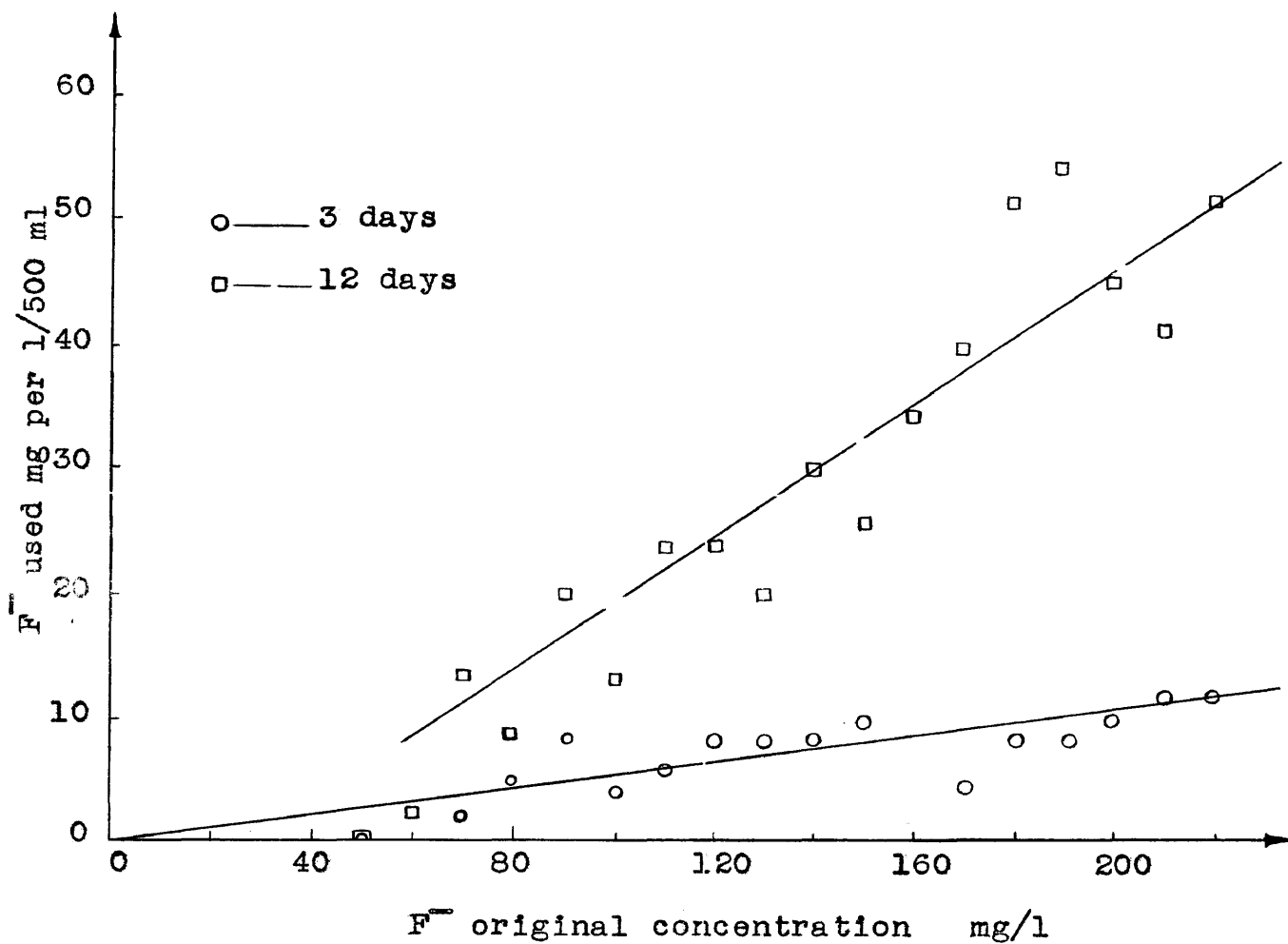


Figure 3: F⁻ concentration dependence at pH 5. The reacting solutions were buffered with the NaOH-KHC₈O₄H₄ buffer system with an ionic strength of 0.068. Samples of calcite used were 1 g of the -20+40-mesh fraction.

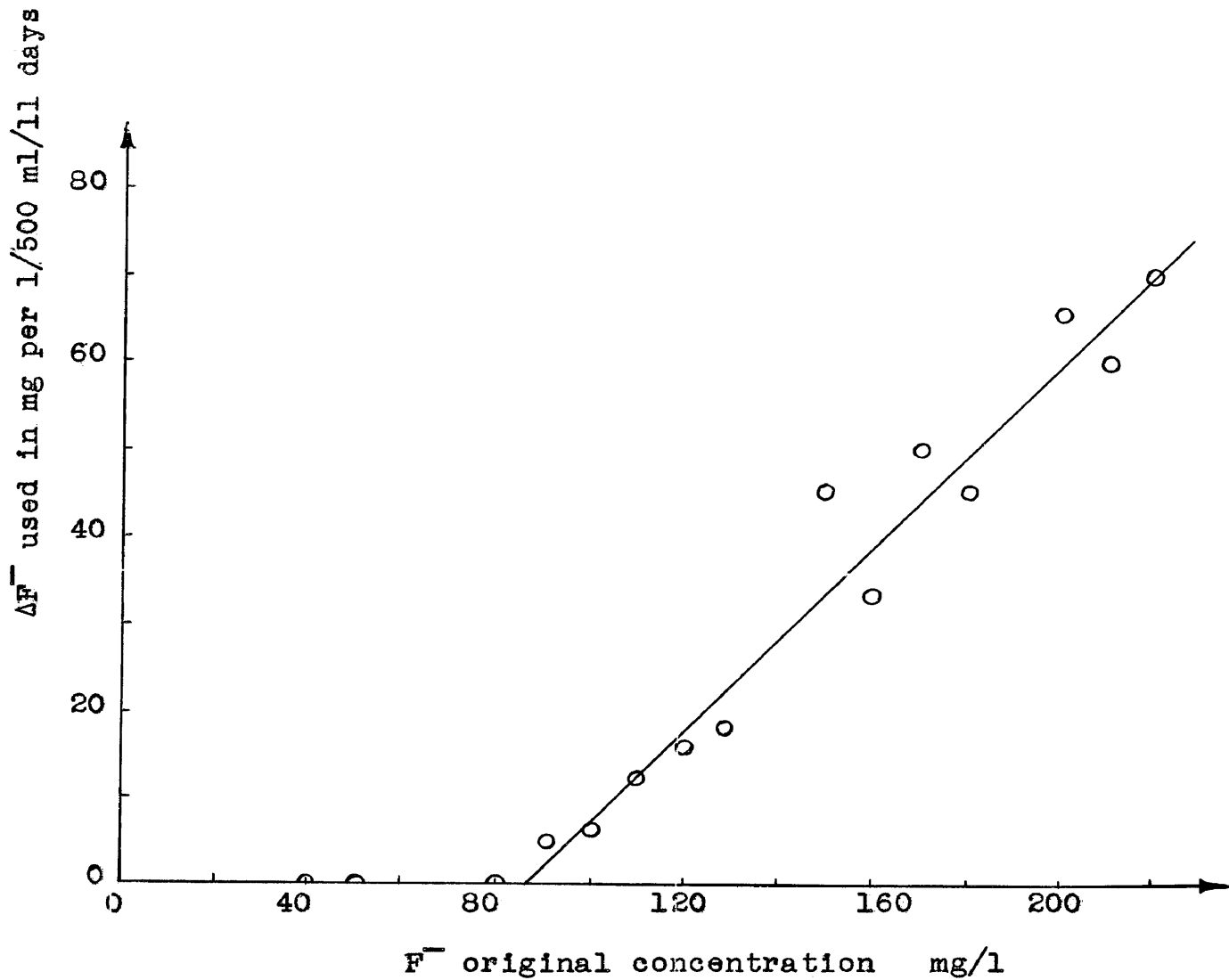


Figure 4: F⁻ concentration dependence at pH 10. The reacting solutions were buffered with the NH₄OH-NH₄Cl buffer system with an ionic strength of 0.012. Samples of calcite used were 1 g of the -20+40-mesh fraction.

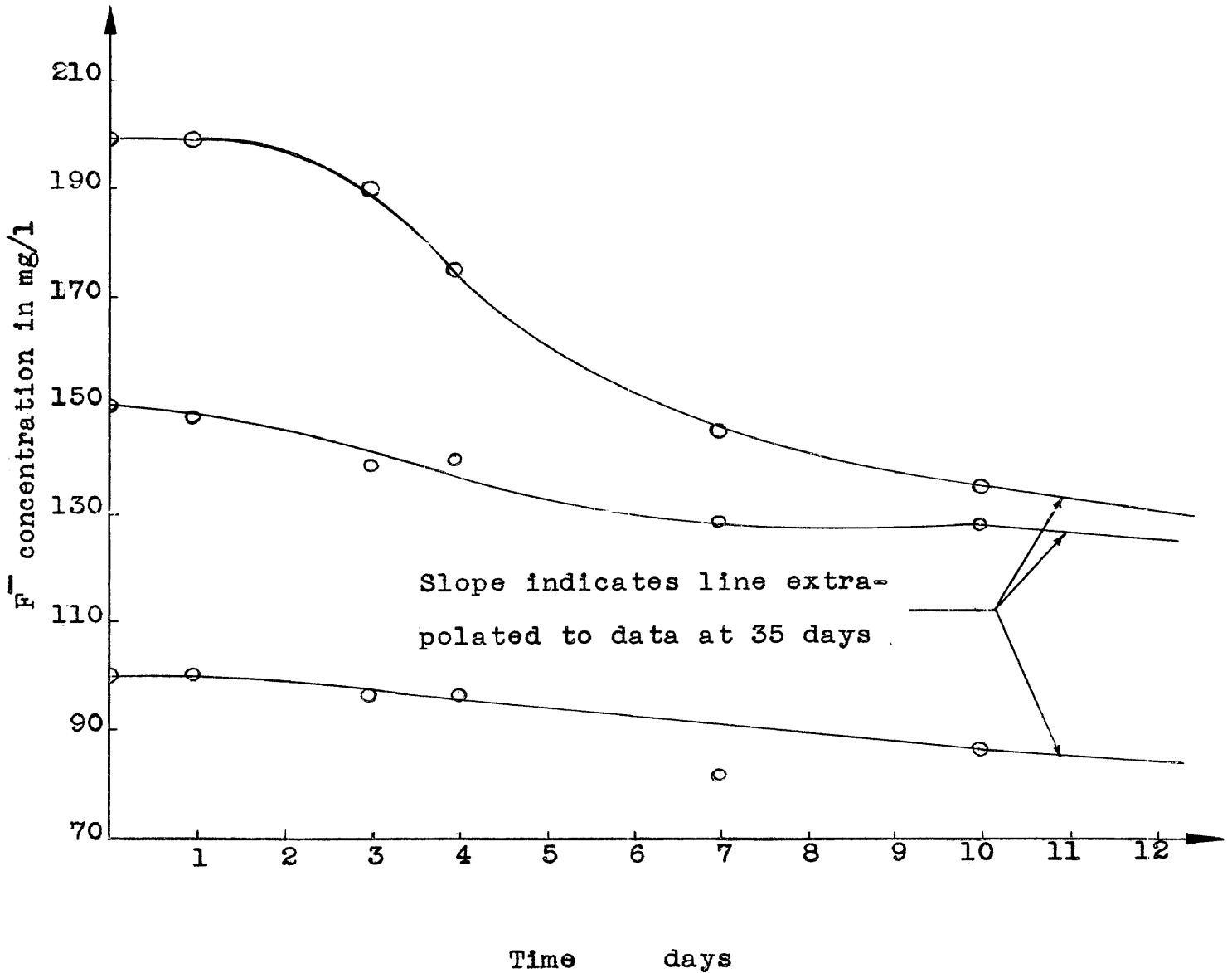


Figure 5: Reaction versus time. The reaction solutions were buffered at pH 5 with an ionic strength of the NaOH- $KHC_2O_4H_4$ buffer system. Samples of calcite used were 0.5 g of the -20+40-Mesh fraction.

shows that the reaction starts out slowly, probably because of the slow nucleation process. At reaction time of 2 to 3 days (see fig. 5 referring to 200 mg per l original F^- concentration curve, p. 21) nucleation became unimportant since most of the CaF_2 is formed by adding crystals. The reaction rate reaches a maximum at 4 to 5 days, and from then on the reaction rate decreases because of decreasing F^- concentration in the solution (see influence of F^- concentration change, p. 16).

INFLUENCE OF DIFFUSION

The effect of the CaF_2 film developed on the surface of calcite grains upon the diffusion of reacting ions or the rate of CaF_2 formation was studied for the first 10 days of reaction. The reaction solutions buffered at pH 5 with the $NaOH-KHC_8O_4H_4$ system with ionic strength of 0.068 had F^- concentrations of 200, 150, and 100 mg per l. Solutions were reacted with 1-g samples of calcite (-20+40 mesh).

Aliquots of solutions were taken at different times; analysed for F^- ; and replenished to reproduce the volume, the F^- concentration, and the buffer concentration of the original solution at zero reaction time.

Results are illustrated in figure 6 (p. 24). From these plots it may be observed that the thickness of CaF_2 , assumed to be uniform and dense (see appendix for calculations, p. 51), up to 1.5×10^{-3} cm has no effect on the rate of reaction. If the diffusion of Ca (II) ions from the surface of the calcite to the reaction sites on CaF_2 crystals would be rate determining, the rate of CaF_2 formation after nucleation should then decrease as the diffusion distance increases; the rate does not decrease, indicating that the diffusion of Ca (II) is not rate determining. A similar reasoning applies to F^- diffusion if CaF_2 growth occurs on the inner surface of the CaF_2 layer or directly on the calcite surface, indicating that the diffusion of F^- ions is not rate determining.

INFLUENCE OF IONIC STRENGTH

The effect of change in ionic strength (see appendix for sample calculation, p. 49) was studied at pHs of 5 and 8 by reacting 1 g of -20+40-mesh calcite samples with 500-ml reaction solutions at F^- concentrations of 150 and 200 mg per l.

At pH 5 the ionic strength of 150 mg per l F^- solutions

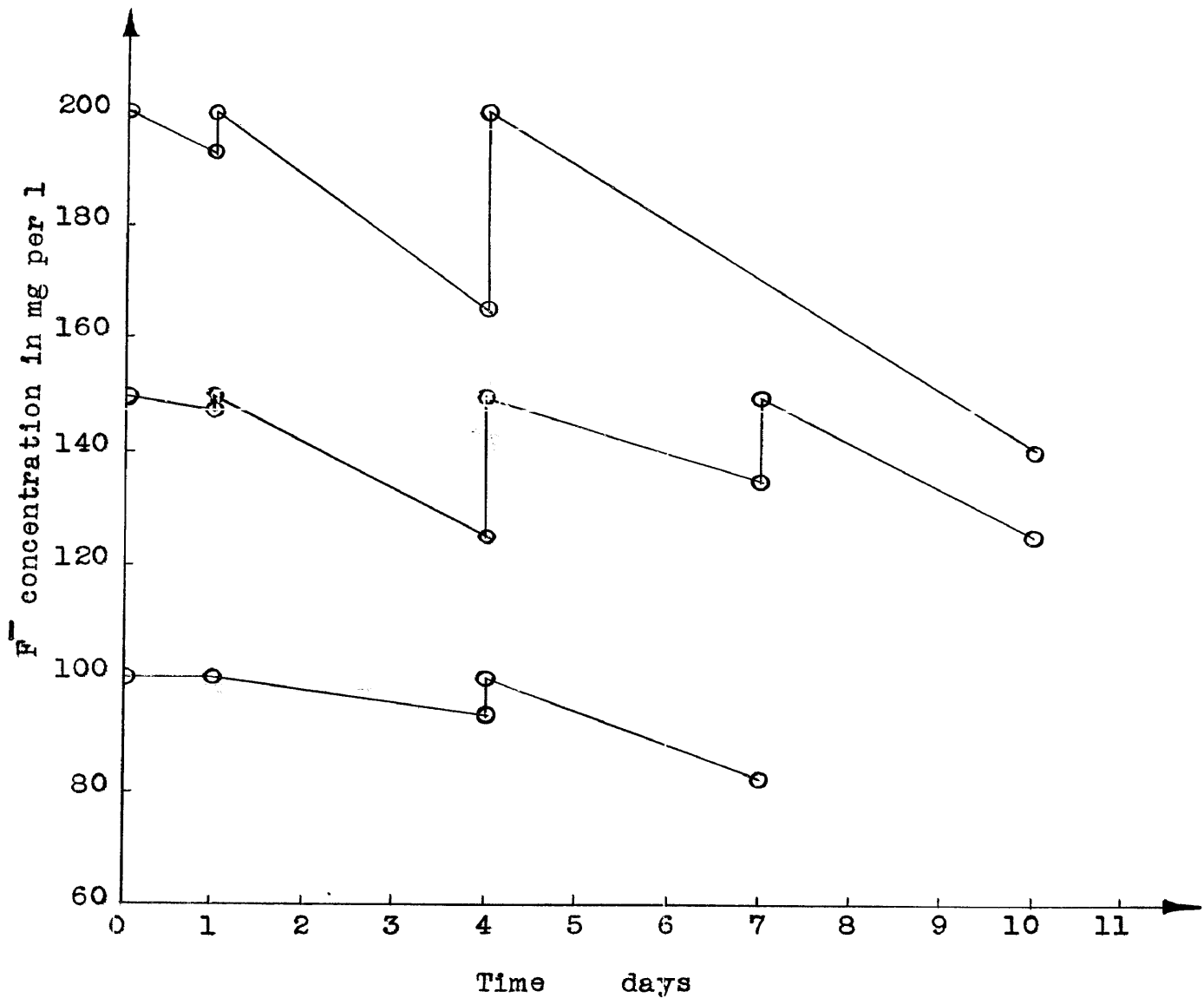


Figure 6: Effect of diffusion. The reaction solutions were buffered at pH 5 with an ionic strength of 0.068 of the NaOH-KHC₈O₄H₄ buffer system. Samples of calcite used were 0.5 g of the -40+60-mesh fraction. The connecting lines follow the F^- concentration of the solutions as the solutions react and are replenished.

was changed from 0.078 to 0.144 by changing the concentration of the buffer system NaOH-KHC₈O₄H₄. No change in the rate of CaF₂ formation with the change in ionic strength was observed when reaction solution aliquots were analyzed at 7 and 14 days of reaction time, as also observed by Ames (1961, p. 734).

A similar study at pH 8, reacting 0.5 g (-40+60 mesh) calcite samples with solutions that contained 200 mg per l F⁻ in which the ionic strength was adjusted with KCl from 0.111 to 0.501, resulted in no detectable change in rate of CaF₂ formation with change in ionic strength when analysed at 2 and 4 days of reaction time.

The fact that the ionic strength of the solution has little or no effect on the rate of CaF₂ formation means (Laidler, 1950, p. 126) that the reaction intermediate is a neutral molecule, or a chemical species as ionic as the starting material (Hine, 1956, p. 53) if the reaction involves a homogeneous equilibrium. In this case, the reaction is heterogeneous and nothing can be said about the intermediate at this point, because nothing definite is known about the reactants and products of the rate-determining step.

pH DEPENDENCE

The effect of the pH of reacting solutions on the rate of CaF_2 formation was studied using both calcite and dolomite. The pH was varied from 2 to 10 in steps of 1 pH unit by using different buffering systems at approximately the same ionic strength (see appendix for buffer-system, table 4, p. 54). Reaction solutions, 500 ml in volume, with a 150 mg per l F^- concentration, were reacted with 1-g -20+40-mesh samples of both calcite and dolomite.

When calcite was used for equilibrations, aliquots of reaction solutions were taken at 2 and 4 days of reaction time. The results of this work (see fig. 7, p. 29) do not fall into a smooth curve and give only a general indication that the rate of CaF_2 formation increases as pH decreases.

The reason for the scattering of data is that a given buffering system covers, at most, 3 pH units; and when passing from a buffering system to another the influence of the difference in the kind of ions overshadows the influence of H (I) ion concentration.

In the pH-dependence study using calcite for equilibration, the reaction vessels were checked macroscopically periodically up to 44 days after the initiation of the reaction. The calcite crystals were completely disintegrated

at pH 2; their shape seriously damaged at pHs 3 and 4; and their shape retained at pHs of 5 and greater. At pHs of 2 and 3, the crystals of CaF_2 grew in radiating needles on many remains of calcite grains. In connection with the macroscopic examination of samples, no violent evolution of CO_2 was observed until pHs lower than 5. This result is contrary to experimental results described by Ames (1961, p. 736).

When dolomite was used for equilibrations, samples were analyzed at 19 days of reaction time for F^- , Ca (II), and Mg (II). The results obtained from analyses of F^- are plotted in figure 7 (p. 29). The results of Ca (II) and Mg (II) determinations are tabulated in the appendix (see p. 55).

The results plotted in figure 8 (p. 30) indicate that the different kinds of ions do not influence the CaF_2 formation from dolomite as much as the CaF_2 formation from calcite, since a smooth curve may be drawn through the various points. These results may be related to the much lower reactivity of dolomite with respect to calcite in dilute aqueous solutions of F^- .

The reaction systems in which dolomite was used in the pH study were macroscopically observed up to 29 days of reaction time. No violent evolution of CO_2 resulted at any pH from 2 to 10, and the original shape of dolomite grains

was retained in the same pH interval. The system at pH 2 had fluorite growing in radiating needles around nuclei formed in the body of the solution and completely detached from the dolomite grain surface.

At this point a comment on the pH dependence study made by Ames (1961, p. 735) is in order, who reports a change of CaF_2 formation with pH based on solutions flowing through columns. It is very likely (see p. 37) that the solutions that were passed through the columns had their influent pH changed to equilibrium pH before going through the entire column. If this be the case, the pH dependence of the CaF_2 formation reported by Ames (1961, p. 735) would measure, for every initial pH studied, the influence of the changing pH from its original value to its equilibrium value in the portion of his reaction column in which the equilibrium pH was attained. No evidence or indication was presented in Ames' work (1961, p. 730-739) to the effect that pH was measured or controlled along points of the reaction column.

Ca (II) ION MOBILITY

A 0.5-g -40+60-mesh sample of calcite in 10^{-4} M HCl aqueous solution would change the pH of the solution more

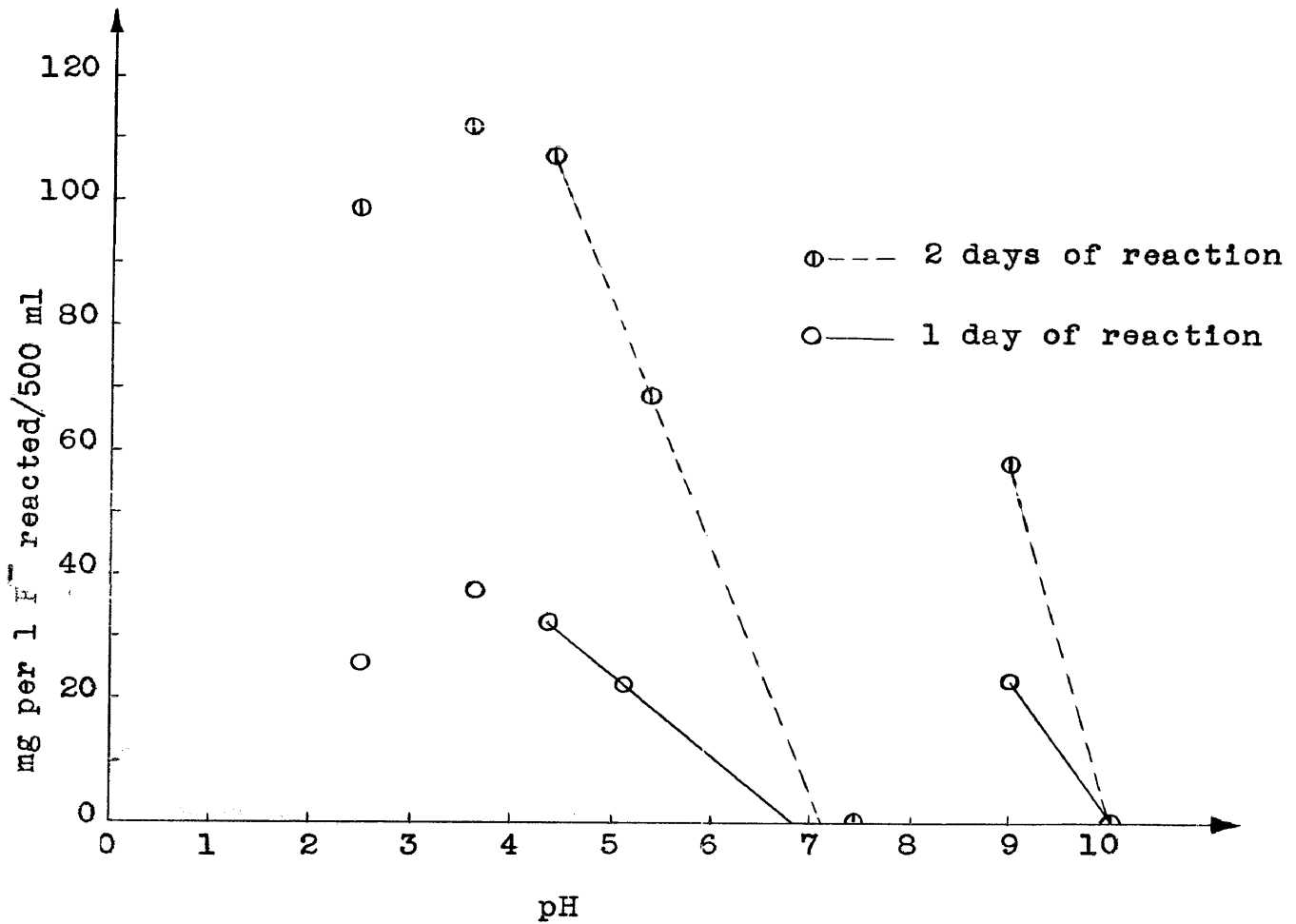


Figure 7: pH dependence of calcite. The reaction solutions contained 150 mg per 1 F^- , had an ionic strength of 0.078, and were buffered at the desired pH (see p. 54 for a listing of buffer systems). Samples of calcite used were 1 g of the -20+40-mesh fraction. Points are connected when they represent the same buffer system.

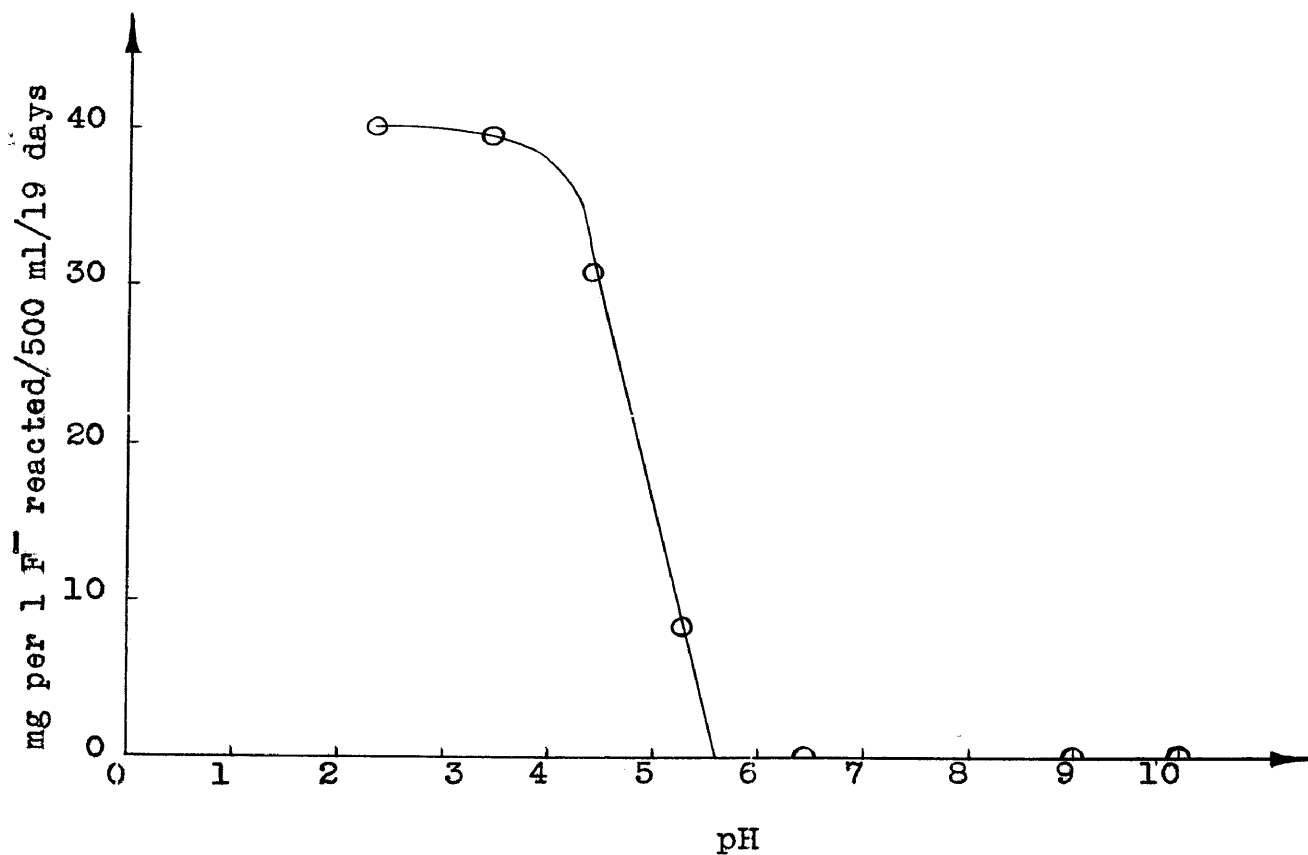


Figure 8: pH dependence of dolomite. The reacting solutions contained 150 mg per l F⁻, had an ionic strength of 0.078, and were buffered at the desired pH (see p. 54 for a listing of buffer systems). Samples of dolomite were 1 g of the -20+40-mesh fraction.

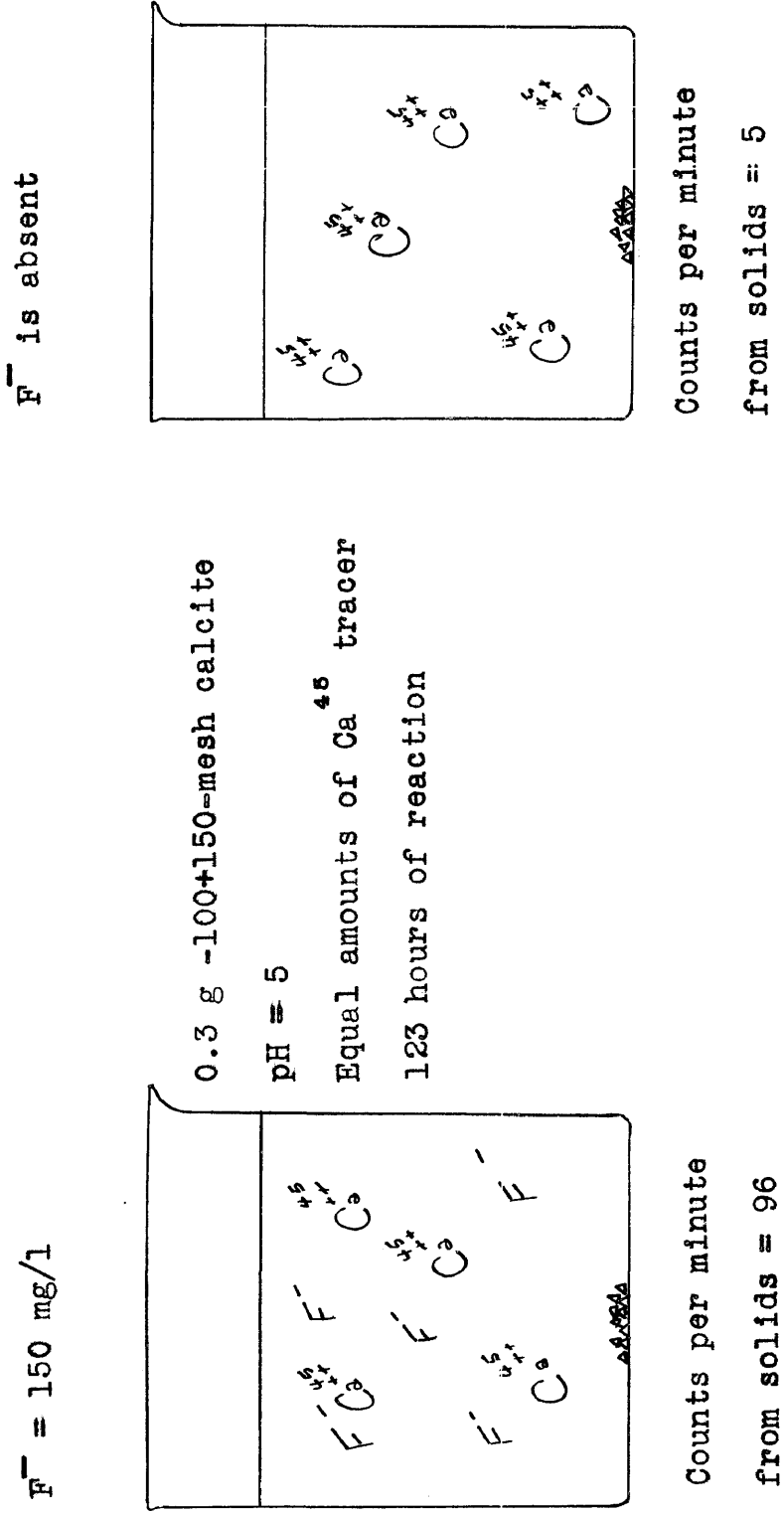


Figure 8a: Diagrammatic representation of the Ca^{45} tracer experiment.

slowly than an identical sample which had 100 mg per l F^- added to it as shown by the 2 curves in figure 9 (p. 33). This effect should be due to the increase in rate of calcite structure breakdown making more CO_3 available for the following reaction which influences pH, $CO_3 + H^+ = HCO_3^-$.

It was thought that if CO_3 and Ca (II) ions were made apparently more available with F^- present, it must have been due to the CaF_2 formation at sites other than on the calcite surface. If the Ca (II) ions are utilized "in place", as Ames (1961, p. 737) has asserted, the CO_3 availability would have been lowered by shielding the calcite surface from solution. The point needed investigation.

For clarification the CaF_2 formation was made to occur in solutions that contained radioactive Ca^{45} so that the solubility product of CaF_2 was not exceeded.

Samples of -100+150-mesh calcite weighing 0.3 g were reacted with 2 sets of solutions; one set contained 150 mg per l F^- , and the other set contained no F^- ; all solutions were buffered at pH 5 (with 0.068 ionic strength of NaOH- $KHC_8O_4H_4$ buffer system) and contained the same amounts of Ca^{45} tracer.

At 5 and 123 hours of reaction time, members of the 2 sets of solutions were filtered to obtain an essentially "infinitely" thick layer of solid (Friedlander and Kennedy,

1960, p. 203).

Solids were mounted on a planchette, and counts obtained from a Geiger-Muller counter were recorded (see appendix, p. 53).

At 123 hours of reaction time, the counts for the solid reacted with the solution containing F^- was 96 counts per min above background; whereas for the solid that reacted with the solution containing no F^- the counts were 5 counts per min above background. The results indicate clearly, contrary to Ames' assertions (1961, p. 737-738) presented without evidence, that the Ca (II) ion in its reaction to form CaF_2 at pH 5 goes through a stage in which it is free to move in solution. It is in this step that the F^- , being unable to differentiate between Ca (II) isotopes, includes the radioactive Ca^{45} in the structure of resulting CaF_2 .

Ames (1959, p. 829-841) has reported a similar tracer study where Ca^{45} was used to investigate the mobility of Ca (II) ions in replacing solid $Ca^{45} CO_3$ by phosphate ions. The result reported was the complete retention of Ca^{45} within the calcium (II) phosphate formed; however supporting evidence was not presented.

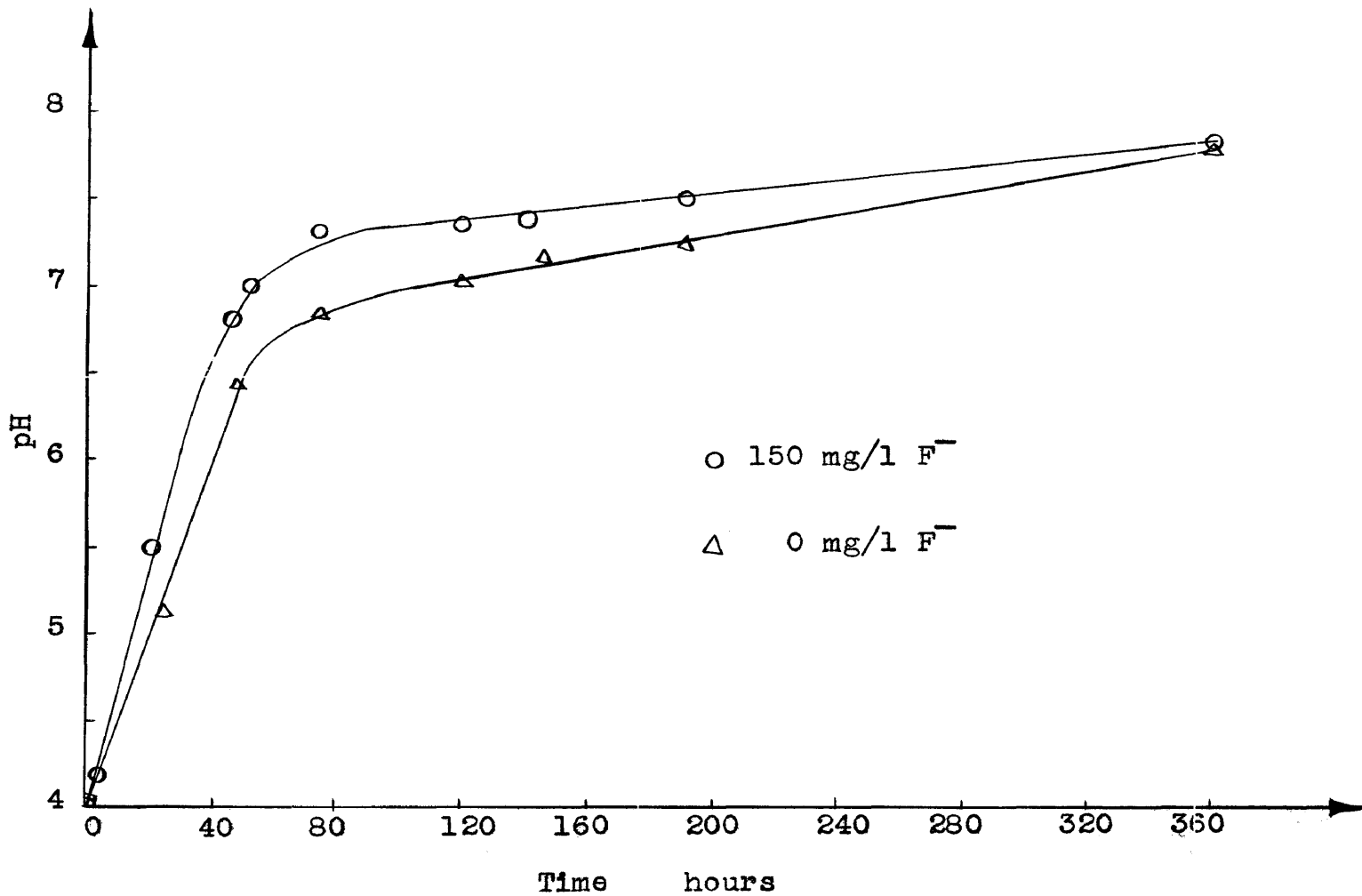


Figure 9: Effect of F⁻ on pH change. Both 500-ml solutions were set at pH 4 with 1×10^{-4} M HCl.

ROCKS

After some knowledge of the behavior of calcite and dolomite was acquired, experiments were devised to compare their behavior with rocks. Two types of experiments were performed: equilibration of rock fragments with F^- solutions, and the flow of F^- solutions through rock discs.

Fragments

In the equilibration of rock fragments with F^- solutions, hand specimens of carbonate rock were broken, sieved, washed with demineralized water, and weighed, as in the preparation of pure minerals. The weighed 1-g (-20+40-mesh) rock samples were equilibrated with 500 mg per l F^- solutions buffered at pH 5 with an ionic strength of 0.068 of the NaOH-KHC₈O₄H₄ buffer system. Aliquots of reaction solutions were taken after 10 days of reaction time and analyzed for F^- . The results are summarized in table 1 (p. 35) where reactivities of dolomite and calcite are included for comparison.

As can be seen on table 1 (p. 35) there is a correlation between reactivity and types of rocks; limestones and dolostones fall into two distinct reactivity groups. The correlation between reactivities of rocks and minerals is less

clear. The experiment indicates that the reactivity of rocks is, at least in these cases, considerably less than that of their major pure component, pointing out the importance of rock variables in the chemical behavior of rocks.

Table 1

| <u>Material</u> | <u>Ca (II): Mg (II)</u> | <u>Insoluble resi- due percent</u> | <u>$\Delta F^{\text{---}}$ mg per l per 500 ml per 10 days</u> |
|-----------------|-------------------------|--|---|
| Calcite | | 0 | 38 |
| Dolomite | 1:1 | 0 | 16 |
| Marble | 200 | 0 | 22 |
| 8A | 1:1 | .4 | 3 |
| 11A | 1:1 | 19.5 | 2 |
| 12A | 1:1 | 1.6 | 1 |
| 18B | 19:1 | 6.7 | 15 |
| 23A | 65:1 | 2.2 | 15 |
| 26B | 83:1 | 4.5 | 17 |

Rocks 8A to 26B are from the carbonate rocks collection of the Geochemistry Section of the Chemistry Department of Colorado School of Mines: analyses on these rocks were done by Mr. G.E. Manning. The marble comes from Marble, Colorado.

The lower reactivity of rocks with respect to their major pure minerals may be due to the fact that rocks will preferentially break around rather than through grains. Rocks then present to reactive solutions surfaces that are closer to the environmental thermodynamical equilibrium (less surface imperfections per unit area) than do the corresponding surfaces of pure freshly fractured minerals. The resulting expected effect would be a decrease in the rate of nucleation reaction causing this process to be rate determining for a longer period. Intergranular surfaces in rocks tends to offset this effect in an amount dependent upon the permeability and grain size of the rock.

Discs

Rocks under study were cored and discs cut for permeability studies with dilute aqueous solutions of F^- . Discs were attached to Pyrex tubing (54mm ID) with Lakeside Cement, a head was applied to them with buffered (ionic strength 0.068 of NaOH-KHC₈O₄H₄ buffer system) 150 mg per l F^- solution, and the rate of flow measured for 6 days.

The effluent solution was analyzed for F^- , Ca (II) ion, and Mg (II) ion. Tables 6 and 7 in the appendix (p. 55) contain data concerning the rocks used and their behavior. Permeability decreases with time for the calcite rocks, but

for rock C, a dolostone, the 61-percent theoretical reduction in volume from dolomite to fluorite causes the permeability to start increasing after 20 hours of flow and to attain 2.2 its original value in 90 hours.

It is to be noted that the pH of effluent solutions (see table 7, p.56) is for rocks of reasonably low permeabilities, between 8.35 and 8.97 (rock B had a sizeable pore transecting the disc). The influent solution was buffered at pH 5.

These results mean that the original pH of solutions introduced into carbonate rocks is unimportant because the solutions come to equilibrium with the carbonate minerals within the first 0.5 cm of rock traversed; this fact also means that the partial pressure of CO_2 in carbonate rock interstitial solutions is a quantity rapidly fixed by the rock. If the CO_2 partial pressure were high, the part of the carbonate rock in contact with these CO_2 -rich solutions would dissolve away, and a few cm of penetration into the rock would obliterate the effect of the CO_2 partial pressure.

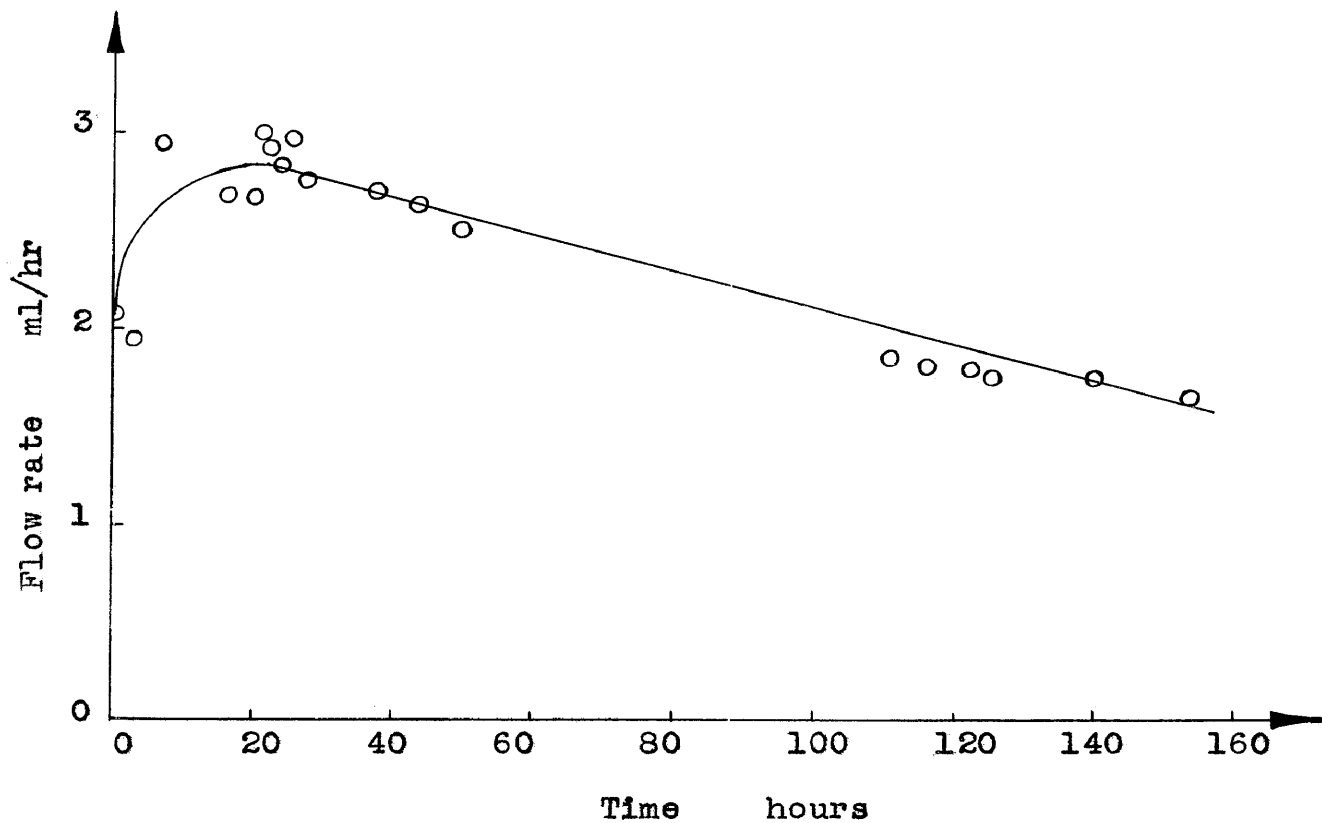


Figure 10: Permeability change of a limestone. The influent solution contained 150 mg per l F^{--} , was buffered at pH 5, and had an ionic strength of 0.078. A disc of rock C was used (see appendix, p. 55).

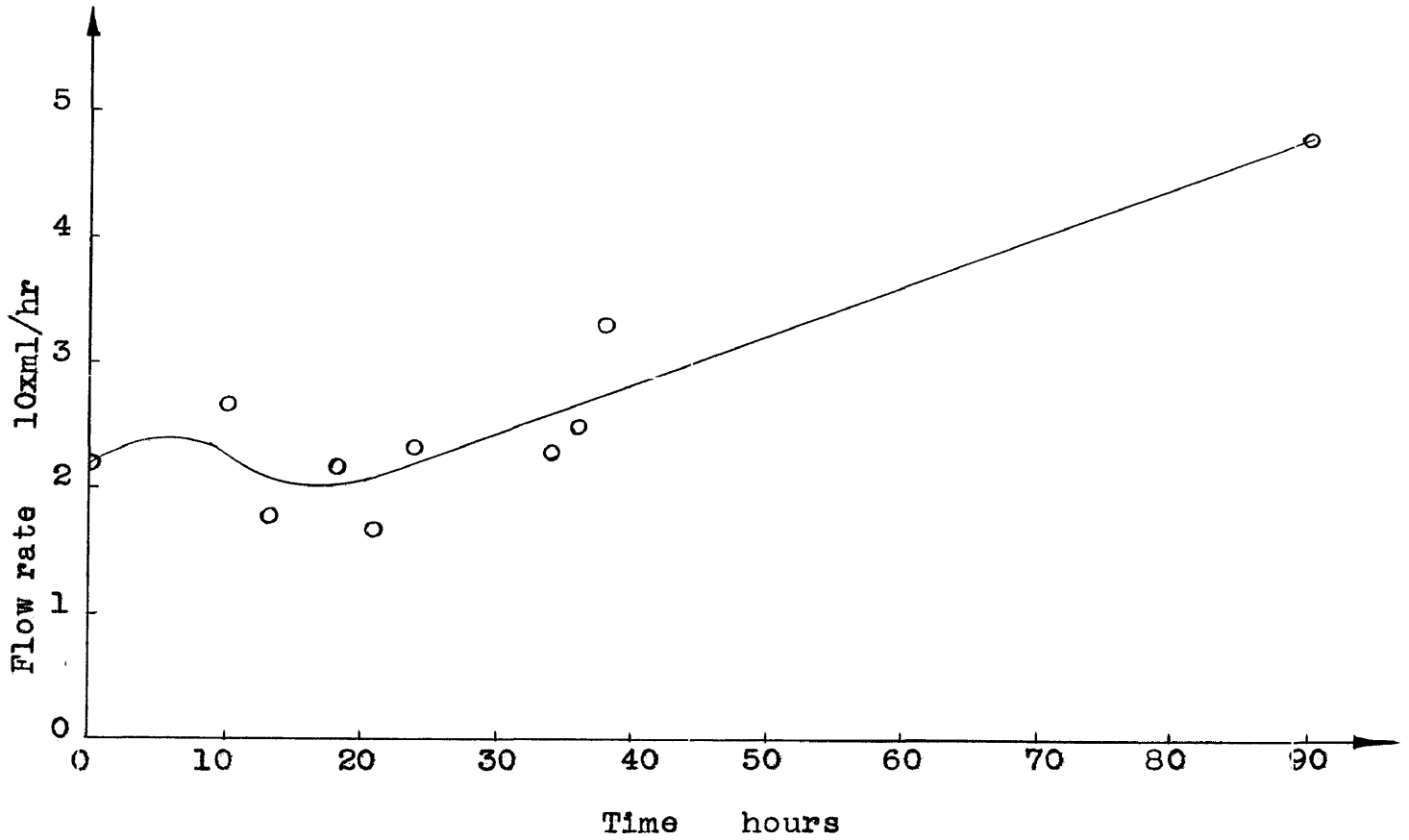


Figure 11: Permeability change of a dolostone. The influent solution contained 150 mg per l F^- , was buffered at pH 5, and had an ionic strength of 0.078. A disc of rock D was used (see appendix, p. 55).

NOTES ON MECHANISM

Sufficient work has not been done to define the mechanism for the CaF_2 formation from dilute aqueous solutions of F^- on the surface of carbonate minerals, hence the work "notes" in the title of this section. There has been enough data gathered however to justify the discussion of some steps in a mechanistic description of the process.

In a heterogeneous reaction where the phases are a liquid and a solid, a series of steps is necessary to have any continuous reaction (Laidler, 1950, p. 154): (a) Diffusion of ions to the surface, (b) adsorption of ions to the surface, (c) reaction at the surface, (d) desorption of liberated ions from the surface, and (e) diffusion of liberated ions away from the surface.

Referring specifically to the reaction of aqueous dilute F^- on the surface of calcite the reaction steps are as follows: (a) diffusion of F either as F^- or HF_2^- to the surface

of calcite, (b) the adsorption of ionic F to the calcite surface, (c) the reaction of Ca (II) ions with F^- ions to form fluorite, (d) desorption of $CO_3^{=}$, or HCO_3^- , depending on solution pH, into the body of solution.

The diffusion of F^- in the nucleation process and the diffusion of F^- and Ca (II) ions in forming CaF_2 on nucleated sites are found to be unimportant in determining CaF_2 formation rate (see discussion on p. 22).

The reaction at the calcite surface is attained first only at certain spots of high potential energy and with the aid of considerable supersaturation of F^- , for much energy is needed to form a small grain of CaF_2 as indicated by Weyl (1953, p. 155). This step is the nucleation process; from the moment the calcite surface has its first nucleus of CaF_2 , 2 surfaces and 2 distinct manners of CaF_2 formation are present simultaneously until all the calcite surface is covered with CaF_2 .

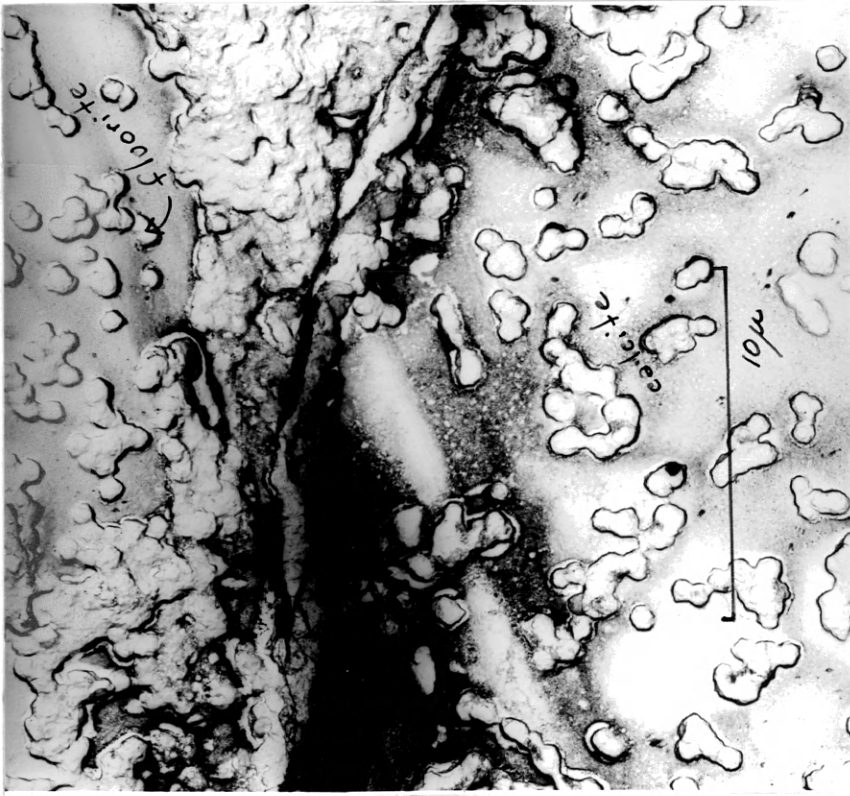
The nucleation process keeps going on independently until all favorable sites on the calcite surface have been nucleated, or the F^- is essentially depleted. This process is slow (see fig. 5, p. 21) and rate determining at the beginning of the reaction, probably because of its high-energy and entropy requirements.

The second process of CaF_2 formation takes place at the

surface of CaF_2 crystallites formed during nucleation. This process is faster than the nucleation process because no energy is required to form a minimum amount of solid CaF_2 from solution. This process becomes rate determining as soon as enough CaF_2 crystallites are formed.

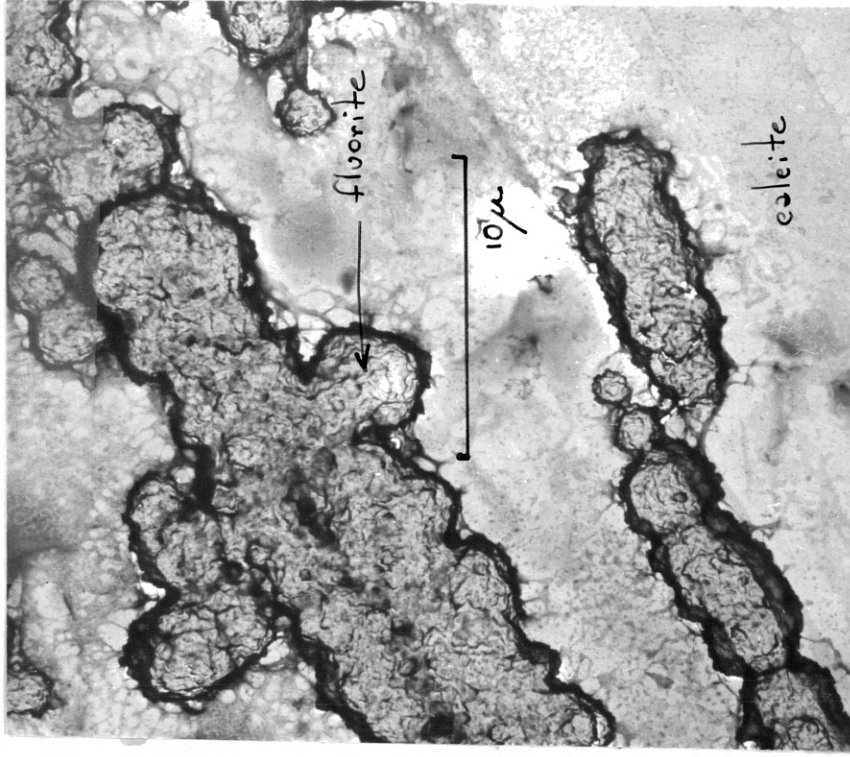
For the reaction to occur on the surface of the fluorite, both F^- and Ca (II) ions must migrate to it; in this step of the mechanism the Ca (II) ions of calcite become relatively free in solution and compete with radioactive Ca^{45} (II) ions if previously placed in solution (see p. 28, 31, 32). In this process of CaF_2 formation on the surface of CaF_2 there is no desorption of unused ions.

Evidence for the differentiation of the CaF_2 formation processes is afforded by electron photomicrographs 1 and 2 (p. 43) where crystallites on the surface of calcite are shown to increase in size with reaction time.



Electron photomicrograph 1:

CaF₂ crystallites at 1 hour reaction time with 200 mg per l F⁻ buffered at pH 5. The reacting solution has an ionic strength of 0.08.



Electron photomicrograph 2:

CaF₂ crystallites at 12 hours reaction time with 200 mg per l F⁻ buffered at pH 5. The reacting solution has an ionic strength of 0.08.

SUGGESTIONS FOR FURTHER STUDY

The need for further study is obvious. A mechanism for the CaF_2 formation has not been worked out in detail; correlation between the behavior of minerals and rocks is only in its early stages; and basic understanding of how natural solutions are affected by rocks as they react is deficient to say the least.

Enlightening work could immediately begin with the study of:

- (a) the detailed behavior of the minerals dolomite, ankerite, and magnesite.
- (b) the effect of the presence of different ions.
- (c) the effect of the mineral-surface equilibrium on reactivity, this might be done by aging newly broken mineral surfaces before reacting them with F.
- (d) the conditions of a solution flowing through a rock in terms of rock variables and viceversa. This might be accomplished by flowing known solutions through discs of analyzed rocks.

CONCLUSIONS

This investigation has led to the following certain conclusions:

1. The rate of CaF_2 formation on calcite from dilute aqueous solutions of F^- is directly proportional to the surface area of calcite.
2. The rate of CaF_2 formation on calcite from dilute aqueous F^- solutions is directly proportional to the F^- concentration.
3. The rate of CaF_2 formation on calcite from dilute aqueous solutions of F^- starts out slowly because of the slow nucleation process and then accelerates because of the faster method of CaF_2 formation on the surface of fluorite crystallites already formed.
4. Diffusion of ions through (intracrystalline diffusion) the CaF_2 layer coating the calcite crystals

- is not important at least up to 1.5×10^{-3} cm of thickness of CaF_2 formed.
5. Ionic strength has very little effect on the rate of CaF_2 formation in the range of values from 0.078 to 0.5.
 6. The pH of solutions is not a very important variable in the evaluation of the rate of CaF_2 formation from calcite and dilute aqueous F^- solutions. Generally, the rate of CaF_2 formation decreases with increasing pH for both calcite and dolomite in dilute F^- aqueous solutions.
 7. In the formation of CaF_2 from dilute F^- aqueous solutions, no violent evolution of CO_2 is observed down to a pH of 5 for calcite, and down to a pH of 2.5 for dolomite.
 8. In the formation of CaF_2 from dilute F^- aqueous solutions the shape of grains of calcite was destroyed up to a pH of 4, whereas grains of dolomite were not affected down to a pH of 2.5.
 9. In the CaF_2 formation from dilute F^- aqueous solutions the Ca (II) ion is mobile at least in one step of the mechanism as evidenced by Ca^{45} tracer studies.
 10. Dolomite is less reactive than calcite to dilute

aqueous F^- solutions.

11. In all cases of this study carbonate rocks were less reactive than samples of the pure rock forming minerals. This effect is due to (a) the relatively higher surface free energy of freshly fractured mineral crystals and (b) rock variables.
12. Limestones and dolostones used in this study react markedly differently, the former being much more reactive to dilute aqueous F^- solutions.
13. Because of rapid equilibration of interstitial solutions with carbonate rock minerals, the effects of original CO_2 partial pressure and original pH are negligible.
14. Nongeologic literature has been overlooked by most geologists in their attempts to explain geologic processes.

APPENDIX

CALCULATION OF CALCITE SURFACE AREA

Nomenclature:

A = area of 1 g of calcite

a = edge of the cube of the average grain

v = volume of an average grain

V = volume of 1 g of calcite

Assumptions:

The average grain is a cube

The edge of the average grain is 1/30 in.

Data:

Density of calcite = 2.71 g per cu cm

Weight of calcite sample = 1 g

Seive size = -20+40

Calculations:

$$a = \frac{1 \text{ in.}}{30} \frac{2.54 \text{ cm}}{1 \text{ in.}} = 8.46 \times 10^{-3} \text{ cm}$$

$$v = (8.46 \times 10^{-8})^3 = 6.03 \times 10^{-22} \text{ cm}^3$$

$$V = 1 \text{ g} \frac{1 \text{ cm}^3}{2.71 \text{ g}} = 0.369 \text{ cm}^3$$

$$\text{number of grains in 1 g} = \frac{0.369 \text{ cm}^3}{6.03 \times 10^{-22}} = 610 \text{ grains}$$

$$A = (6) (8.46 \times 10^{-8})^2 (610) = 26.2 \text{ cm}^2 / 1 \text{ g of } -20+40\text{-mesh calcite}$$

Table 2

| <u>Seive size</u> | <u>Average seive size</u> | <u>A</u> |
|-------------------|---------------------------|----------|
| -20+40 | 30 | 26.2 |
| -40+60 | 50 | 44.5 |
| -60+80 | 70 | 61.9 |
| -80+100 | 90 | 72.2 |
| -100+150 | 125 | 111.5 |

CALCULATION OF IONIC STRENGTH

Ionic strength is defined as one-half the sum of the product of the stoichiometrical molality of each ion into the square of its charge or valence, summed for all ions in solution (Rossini, 1958, p. 343).

Data:

0.01 molal NaF

0.024 molal NaOH

0.056 molal $\text{KHC}_8\text{O}_4\text{H}_4$

Calculations:

$$\begin{aligned} \text{Ionic strength} &= \frac{(0.01)(1)^2 (\text{F}^-)}{2} + \frac{(0.01+0.024)(\text{Na}^+)}{2} + \\ &+ \frac{(0.056)(1)^2 (\text{K}^+)}{2} + \frac{(0.056)(1)^2 (\text{KHC}_2\text{O}_4\text{H}_4)}{2} \\ &= 0.078 \end{aligned}$$

The ions H^+ , OH^- , and HF_2^- are not considered in this calculation because their concentration is negligible with respect to the concentrations of the ions considered.

CALCULATION OF F^- EQUILIBRIUM CONCENTRATION

Nomenclature:

a = activity

m = molality

P = partial pressure

Data (Garrels, 1960, p. 54-56):

Ionic strength = 0.1

$$P(\text{CO}_2) = 10^{-3.5} \text{ atm} \quad (1)$$

$$m(\text{H}_2\text{CO}_3) = 10^{-1.5} P(\text{CO}_2) \quad (2)$$

$$a(\text{H}^+) m(\text{HCO}_3^-) = 10^{-6.3} m(\text{H}_2\text{CO}_3) \quad (3)$$

$$a(\text{H}^+) m(\text{CO}_3^{2-}) = 10^{-10} m(\text{HCO}_3^-) \quad (4)$$

$$m(\text{Ca}^{++}) m(\text{CO}_3^{2-}) = 10^{-7.5} \quad (5)$$

$$m(\text{Ca}^{++}) m^2(\text{F}^-) = 10^{-9.78} \quad (6)$$

Calculations:

The combination of all the equations given in the data
 the expression $a(H^+) m(F^-) = 10^{-11.73}$ results. A graphical
 representation of this last equation is found in figure 12
 (p. 52).

CALCULATION OF THICKNESS OF CaF_2 LAYER

Assumptions:

The CaF_2 layer is uniformly thick

The CaF_2 layer has no porosity

Data(see figure 6, p. 24):

51 mg F^- consumed in 10 days

0.5 g of -40+60-mesh calcite used (area=22.25 cm^2)

density of fluorite = 3.1 g per cm^3

Calculations:

$$51 \text{ mg } F^- \frac{78.08 \text{ mg of } CaF_2}{38.0 \text{ mg of } F^-} = 105 \text{ mg of } CaF_2 \text{ formed}$$

$$\text{volume of } CaF_2 \text{ formed} = 0.105 \text{ g } \frac{1 \text{ cm}^3}{3.1 \text{ g}} = 0.034 \text{ cm}^3$$

$$\text{thickness of } CaF_2 = \frac{0.034 \text{ cm}^3}{22.25 \text{ cm}^2} = 1.51 \times 10^{-3} \text{ cm}$$

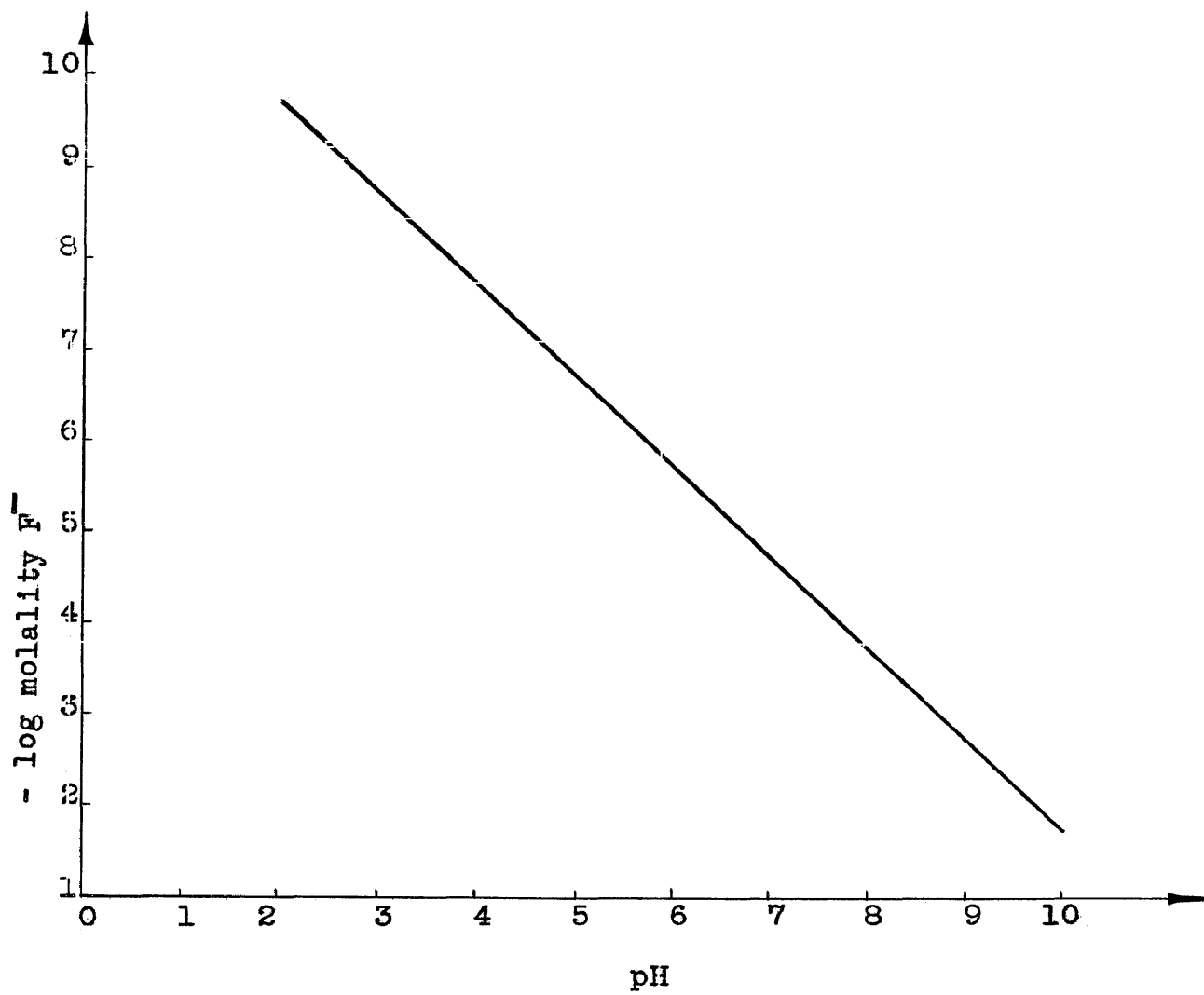


Figure 12: Calculated equilibrium F^- concentration at different pHs (see p. 50).

DATA ON Ca^{45} TRACER STUDIES

The 0.3-g -100+150-mesh calcite samples were reacted with 4 solutions, 2 solutions containing no F^- and the other 2 containing 150 mg per l F^- , for an equivalent amount of time. The solutions used for reaction (250 ml) were buffered at pH 5 with the $\text{NaOH-KHC}_8\text{O}_4\text{H}_4$ buffer system at an ionic strength of 0.068. To every solution the same amount of Ca^{45} tracer was added, this amount being less than the amount of Ca (II) ion needed to exceed the CaF_2 solubility product.

At 5 and 123 hours, the solids from a solution containing no F^- and the solids from a solution that originally contained 150 mg per l F^- , were filtered and deposited uniformly, each on a planchette. The planchettes were counted separately in a Geiger-Muller counter and results recorded. For every sample counted a total of at least 2,000 counts was obtained to ensure a less than $2\frac{1}{2}$ percent statistical error. In table 3 the counts obtained are presented.

The background on a basis of 9,287 total counts was 35.5 counts per minute.

Table 3

| <u>Original F⁻ mg per l</u> | <u>Counter shelf</u> | <u>Total counts</u> | <u>Total time min</u> | <u>Counts/min corrected for background</u> |
|--|--------------------------|---------------------|---------------------------|--|
| 150 | 2 | 2,000 | 30.90 | 29.2 |
| 0 | 2 | 2,002 | 46.57 | 7.5 |
| 150 | 4 | 2,203 | 16.50 | 96.0 |
| 0 | 4 | 2,201 | 54.42 | 5.0 |

TABLE OF BUFFER SYSTEMS

The following table lists the buffer systems that were used in the study of the effect of pH on the rate of CaF₂ formation on the surfaces of calcite and dolomite.

Table 4

| <u>pH</u> | <u>Buffer system</u> | <u>Ionic strength of buffer</u> |
|-----------|---|---------------------------------|
| 2 | Na ₂ SO ₄ -NaHSO ₄ | 0.068 |
| 3 | HCl-KHC ₈ O ₄ H ₄ | 0.068 |
| 4 | NaOH-KHC ₈ O ₄ H ₄ | 0.068 |
| 5 | NaOH-KHC ₈ O ₄ H ₄ | 0.068 |
| 6 | NaOH-KHC ₈ O ₄ H ₄ | 0.068 |
| 7 | Na ₂ SO ₃ -NaHSO ₃ | 0.068 |
| 8 | Na ₂ SO ₃ -NaHSO ₃ | 0.068 |
| 9 | NH ₄ OH-NH ₄ Cl | 0.068 |
| 10 | NH ₄ OH-NH ₄ Cl | 0.068 |

DATA ON THE pH VARIATION WITH DOLOMITE

In the study of the effect of pH on the rate of CaF_2 formation on the surface of dolomite, Ca (II) and Mg (II) ions concentrations in the reaction solutions were determined after 8 days of reaction time. Table 5 lists the results obtained.

Table 5

| pH | Ca ⁺⁺ (moles per 1×10^4) | Mg ⁺⁺ (moles per 1×10^4) |
|-----|--|--|
| 2.0 | 12.5 | 15.0 |
| 3.1 | 8.7 | 10.0 |
| 4.1 | 8.2 | 8.7 |
| 5.0 | 5.0 | 6.2 |
| 6.1 | 2.5 | 2.5 |
| 6.7 | 1.5 | 1.7 |
| 9.3 | 0.15 | 0.2 |
| 9.8 | 0.1 | 0.1 |

DATA ON ROCK DISCS

Table 6

| Rock | Ca ⁺⁺ : Mg ⁺⁺ | Insol. res. percent | Hydro. pressure cm of water | Thickness cm |
|------|-------------------------------------|------------------------|--------------------------------|-----------------|
| A | 8.7 | 2.96 | 90 | 0.40 |
| B | 1.3 | 17.70 | 90 | 0.60 |
| C | 20.5 | 24.20 | 90 | 0.35 |
| D | 1.0 | 0.93 | 90 | 1.60 |

Table 7

| <u>Rock</u> | <u>Orig. F⁻</u> <u>mg/l</u> | <u>Eff. F⁻</u> <u>mg/l</u> | <u>Ca</u> <u>mol./l</u> | <u>Mg</u> <u>mol./l</u> | <u>Flow rate</u> <u>ml/hr</u> | <u>Eff. pH</u> |
|-------------|---|--|----------------------------|----------------------------|----------------------------------|----------------|
| A | 150 | --- | ----- | ----- | 0.00 | ---- |
| B | 150 | 149 | 2×10^{-4} | 2×10^{-4} | 1,800.00 | 5.00 |
| C | 150 | 39 | 1.5×10^{-2} | 2×10^{-4} | 2.50 | 8.97 |
| D | 150 | 41 | 0.7×10^{-2} | 0.75×10^{-2} | 0.25 | 8.35 |

Table 7 lists the average chemical analyses of effluent solutions. Rock A is a lithographic limestone and had no detectable permeability.

DESCRIPTION OF CALCITE AND DOLOMITE

Calcite of suboptical quality (100 percent CaCO_3) was used in this study. This calcite was purchased from Ward's Natural Science Establishment Inc.

The dolomite used in this study came from a dolomite marble of unknown locality. This marble is 99 percent $\text{CaCO}_3, \text{MgCO}_3$, the remaining 1 percent is fine-grained muscovite that concentrates in the -80+100-seive fraction. This fraction has not been used.

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