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CATALYSIS, INHIBITION, AND THE CALCITE-ARAGONITE PROBLEM

II. THE VATERITE-ARAGONITE TRANSFORMATION

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ABSTRACT. The kinetics of the vaterite-aragonite transformation in aqueous solution were studied to determine the factors involved in aragonite formation. The reaction involved the solution and equilibration of vaterite and subsequent nucleation and growth of aragonite. Extent of reaction was monitored by time-lapse photography. The effect of various geologically common ions was studied.

Effects of various ions are specific. Sulfate is a strong inhibitor of aragonite formation, while magnesium is weakly so. Strontium catalizes aragonite formation in solutions in which strontianite is supersaturated. Ionic strength catalizes aragonite formation.

Comparison with data on calcite formation (Bischoff and Fyfe, 1968) suggests that the predominance of either polymorph in natural environments is determined primarily by magnesium ion concentration. In sea water, the concentration of magnesium ion is sufficient to explain the precipitation and persistence of aragonite. Magnesian calcite is suggested as a metastable intermediate phase during the aragonite-calcite transformation in sea water.

INTRODUCTION

This discussion is the second of two papers concerned with the process of calcite and aragonite formation in near surface environments. The preceding paper (Bischoff and Fyfe, 1968) dealt with the process of calcite formation as interpreted from the kinetics of the aragonite-calcite transformation in aqueous solution. The present paper deals with the process of aragonite formation as interpreted from the kinetics of the vaterite-aragonite transformation in aqueous solution. The purpose and underlying principles of such an approach are discussed in the preceding paper and need no elaboration here.

Vaterite, a hexagonal polymorph of calcium carbonate, is metastable with respect to calcite and aragonite at near surface conditions (Deer, Howie, and Zussman, 1962, p. 226). Consequently, aqueous solutions equilibrated with vaterite will be supersaturated with both calcite and aragonite. By inhibiting the formation of calcite in such solutions, in this case by adding $MgCl_2$, aragonite will form from the vaterite, and the kinetics of aragonite formation can then be studied.

Certain restrictions on the study of the vaterite-aragonite reaction decreased the degree of quantification possible with the previous calcite-aragonite study. Firstly, the supply of vaterite was extremely limited, necessitating an experimental operation amenable to small portions of vaterite. Thus, the reaction was monitored by time lapse photography using a petrographic microscope and a glass cell reaction vessel which

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accommodated 0.1 milliliter solution and 0.003 gram vaterite. Analysis of the solution for calcium ion was unfeasible due to small solution volume, and, since the solubility product of vaterite is unknown, no calculation of the distribution of ionic species could be made. Secondly, the inhibition of calcite formation dictates certain restrictions on the solution chemistry. For example, small additions of KOH resulted in the removal of the inhibiting Mg^{++} as $Mg(OH)_2$ and the formation of calcite instead of aragonite. Additionally, solutions equilibrated with high CO_2 pressures so accelerated calcite formation as to overcome the inhibiting effect of the Mg^{++}, unless such high concentrations of $MgCl_2$ were used that $MgCO_3$ was supersaturated.

It was possible, nevertheless, to study the effect of varying ionic strength, varying amounts of $CaCl_2$, $MgCl_2$, $SrCl_2$, and K_2SO_4, and varying amounts of vaterite. It was also found that the reaction could be observed in natural sea water, the reaction requiring approximately one week.

The purpose of studying this reaction was to compare the factors controlling aragonite formation with those controlling calcite formation and to make geologically pertinent inferences.

PROCEDURES AND VARIABLES

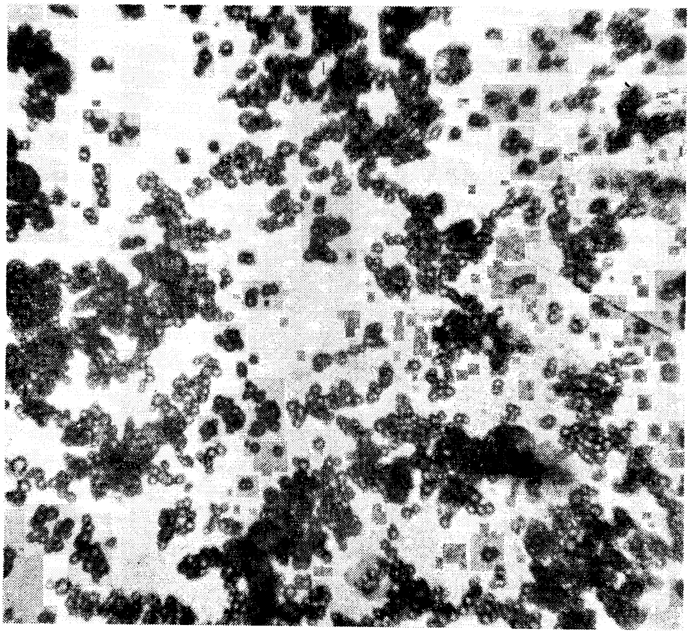
Pure spherulitic vaterite (pl. 1-A) was prepared by slowly adding 50 milliliters of concentrated NH_4OH to one liter of concentrated $CaCl_2$ solution through which CO_2 gas was bubbling. The resulting precipitate was filtered, rinsed with distilled water, dried, and stored in a capped bottle.

Solutions were prepared in the same way as for the aragonite-calcite study but with each having a standard concentration of 0.0005 molal $MgCl_2$ for calcite inhibition. Solutions of the following salts with respective molalities were prepared: KCl, 0.001, 0.01, 0.05; $CaCl_2$, 0.0005, 0.00075, 0.001; $SrCl_2$, 0.00015, 0.0003, 0.0005; K_2SO_4, 0.002, 0.005, 0.01; $MgCl_2$, 0.00015, 0.0003, 0.005, 0.001, 0.01, 0.05; natural sea water; and a special solution of 0.054 $MgCl_2$ and 0.028 K_2SO_4.

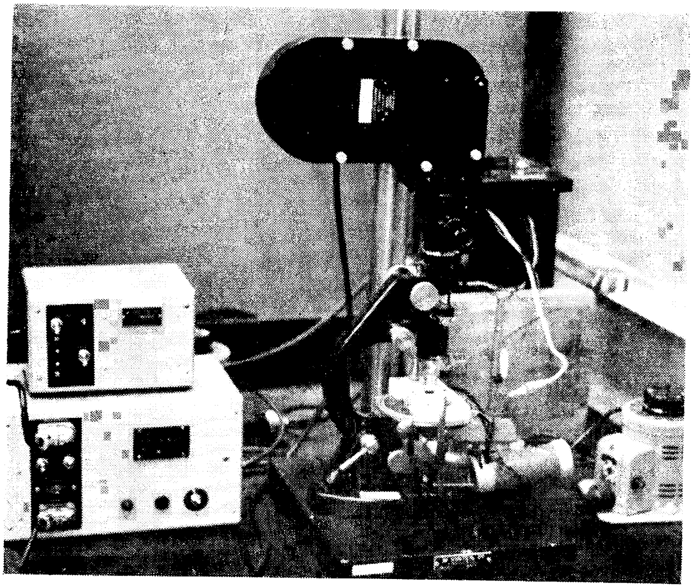
The reaction was studied by means of time lapse photography using a Mark III Mitchell-Vinten 16 millimeter movie camera and intervelometer in conjunction with a petrographic microscope. The reaction vessel was a quartz glass cell with a ¼-inch light path and a 0.1 milliliter solution capacity. The cell was inserted in an aluminum plate which rested above a silver plate, mica insulator, and nichrome wire heating coil, all of which were enclosed in an insulating teflon chassis. Temperature was controlled by a thermocouple, located next to the cell, and the nichrome coil regulated by a Wheelco thermostat apparatus (see pl. 1-B).

Solution and vaterite were injected into the cell by syringe, and the cell sealed by a teflon lined swedge lock. Runs were made at 94°C, and photographs were taken every 15 minutes.

PLATE 1



A. Vaterite spherules (X150) at beginning of reaction.

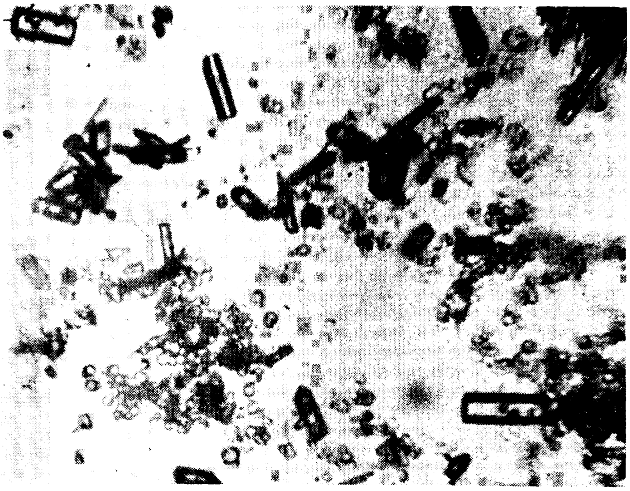


B. Photographic and temperature control apparatus.

DATA AND DISCUSSION

Films of the reactions were observed on a table viewer (pl. 2). Plots of percent aragonite against time (fig. 1-7) were constructed by noting the frame at which the last vaterite was seen to disappear (± half an hour) and then working backward and visually estimating the frames for 75, 50, and 25 percent aragonite. The visual estimate errors are approximately plus or minus five percent aragonite (or plus or minus half an hour).

Plate 2



Vaterite partially transformed to aragonite (X150) in $MgCl_2$-K_2SO_4 solution.

A series of additional experiments was carried out with varying volume of solution, varying glass surface area, and varying amounts of initial vaterite. Aragonite formation rate in these experiments was varied only by the amount of initial vaterite, suggesting that aragonite nucleates on the surface of vaterite.

The general form of the curves (time squared relationship) as with the aragonite-calcite data show that the reaction proceeds at a continually increasing rate, indicating a process controlled by nucleation and growth of aragonite. If vaterite solution were rate controlling the reaction rate would be either constant or would slow with time. Thus it is inferred that vaterite solution and equilibration are rapid with respect to the bulk reaction and provide a constant supersaturation for aragonite. In all runs except those in sea water aragonite crystals are remarkably similar in size and habit. Based on the shape of the curves and dependence of aragonite formation on the amount of vaterite, all arguments and conclusions regarding general nucleation and growth processes applied to calcite apply to aragonite (Bischoff and Fyfe, 1968). Thus, solution rate of vaterite is not rate controlling, nucleation takes place on the vaterite surface, and growth takes place on a fixed number of sites on each crystal, such as point or edge defects.

The various ions, however, have a considerably different effect on aragonite formation, as compared with calcite formation.

KCl.—The pattern of the KCl curves (fig. 1) suggest an ionic strength catalysis. Similar runs with 0.05 molal NaCl and 0.05 molal indicate the general nature of the catalysis. Slopes of plots of percent aragonite against time squared were calculated and plotted against the square root of the ionic strength (fig. 2 and table 1).The same straight line relationship results, as for the calcite data, suggesting a general ionic strength catalysis for crystallization processes. Work in progress indicates ionic strength catalyzes the nucleation process, but more data is needed before conclusive statements can be made.

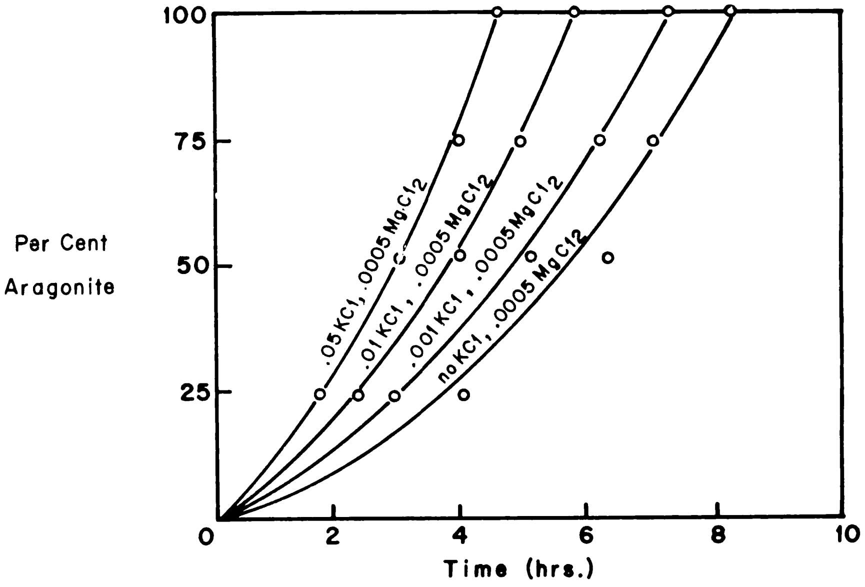


Fig. 1. Effect of KCl on aragonite formation from vaterite.

$CaCl_2$.—Calcium ion, for the concentration range of $CaCl_2$ studied (fig. 3), has little or no effect on the rate of aragonite formation. Ionic strength for the $CaCl_2$ solutions ranges only from about 0.00345 to 0.00518 (table 1), so the total expected variation in rate of reaction will be within the errors of the reaction plots. It remains to be explained, however, that the $CaCl_2$ reaction rates are slower than predicted for their ionic strengths. The plots should lie between those for 0.001 KCl and 0.01 KCl.

If, as suggested for calcite formation, a rate controlling process for aragonite formation were a reaction between a calcium and bicarbonate ion, $CaCl_2$ would be a significant catalyst.

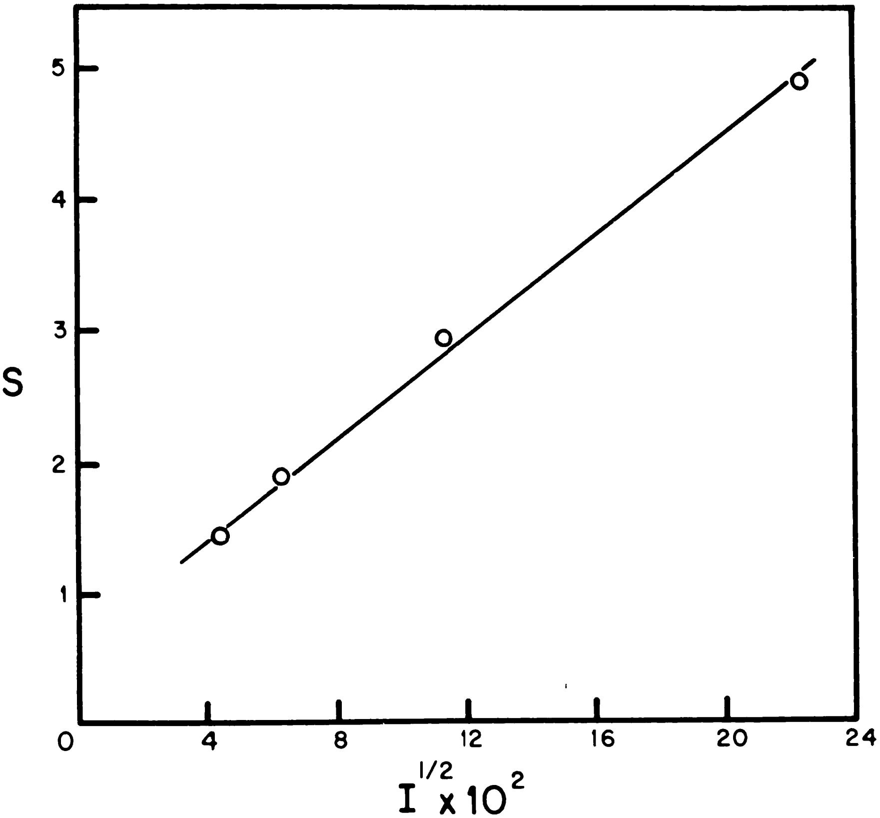


Fig. 2. Relationship of rate of aragonite formation, S, and ionic strength.

The analogous reaction for aragonite formation might well be a simple combination of calcium and carbonate ions. In such a case, the rate of reaction would be proportional to the activity product of Ca^{++} and $CO_3^{=}$, the supersaturation inferred to be constant in all runs. The data, however, are only permissive for such a conclusion.

$MgCl_2$.—Curves for $MgCl_2$ solutions (fig. 4) indicate a very mild inhibition of aragonite formation but only at concentrations above magnesite saturation (approx 0.005 molal Mg^{++} in solutions equilibrated with aragonite). There are no time lags as with calcite formation in the presence of Mg^{++}, and thus, no indication of an absorption-removal process.

K_2SO_4.—Sulfate ion (fig. 5) inhibits the rate of aragonite formation, and from the pattern of the curves the inhibition must be of a different nature than for calcite inhibition. No habit modification of aragonite was noted. Qualitatively, the degree of sulfate inhibition on both polymorphs is comparable enough to discard sulfate as an important factor in determining polymorphic form in natural environments. Sulfate will, however, retard the diagenetic transformation of aragonite to calcite.

TABLE 1

Ionic strength values for solutions equilibrated with aragonite and atmospheric CO_2

Solution	I	$I^{1/2}$
0.0005 $MgCl_2$	0.0023	0.0447
0.0005 $MgCl_2$ 0.001 KCl	0.004	0.0632
0.0005 $MgCl_2$ 0.01 KCl	0.0133	0.115
0.0005 $MgCl_2$ 0.05 KCl	0.0521	0.223
0.0005 $MgCl_2$ 0.0001 $CaCl_2$	0.00345	0.058
0.0005 $MgCl_2$ 0.00075 $CaCl_2$	0.0044	0.066
0.0005 $MgCl_2$ 0.001 $CaCl_2$	0.00518	0.072

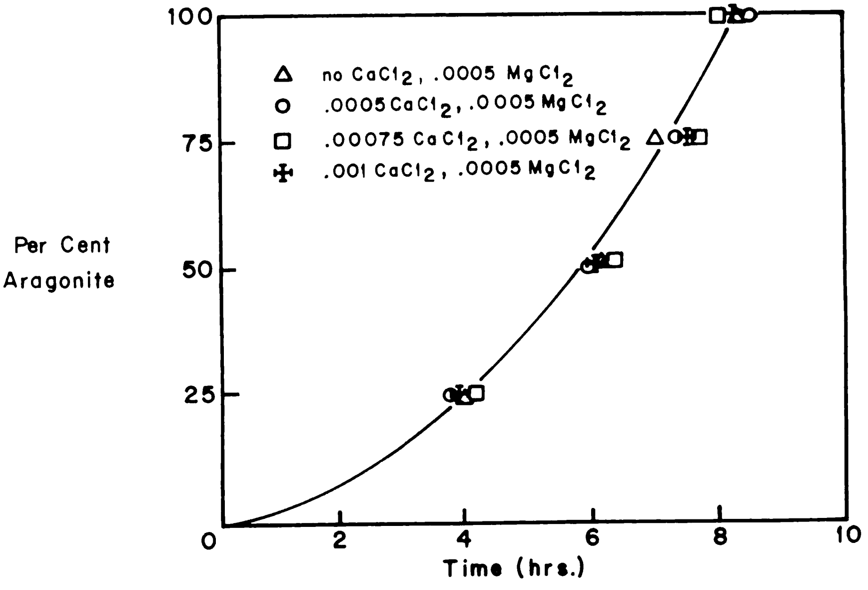


Fig. 3. Effect of $CaCl_2$ on aragonite formation.

$SrCl_2$.—Strontium ion (fig. 6) catalizes the formation of aragonite but only when present in concentrations above saturation of strontianite (approx 0.0003 molal Sr^{++} in solutions equilibrated with aragonite). Production of seed nuclei of strontianite isomorphous with aragonite

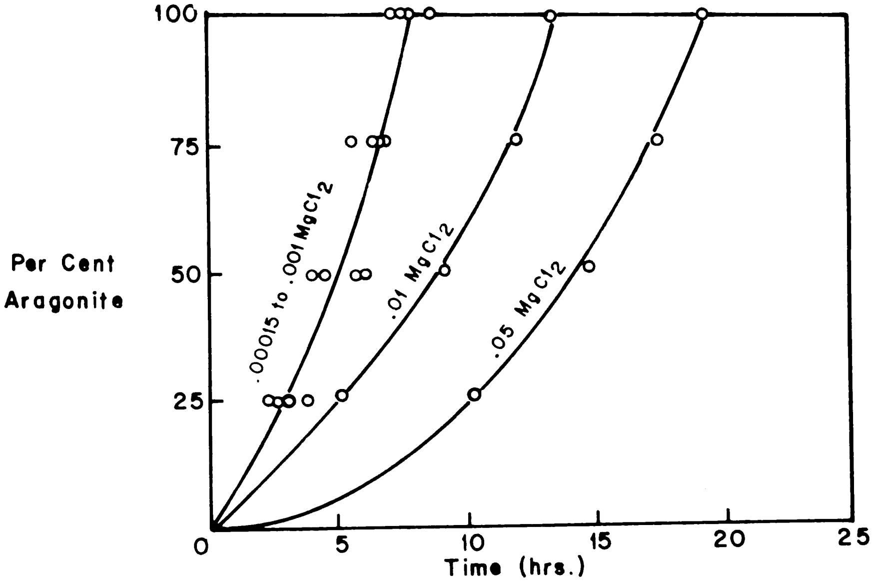


Fig. 4. Effect of $MgCl_2$ on aragonite formation.

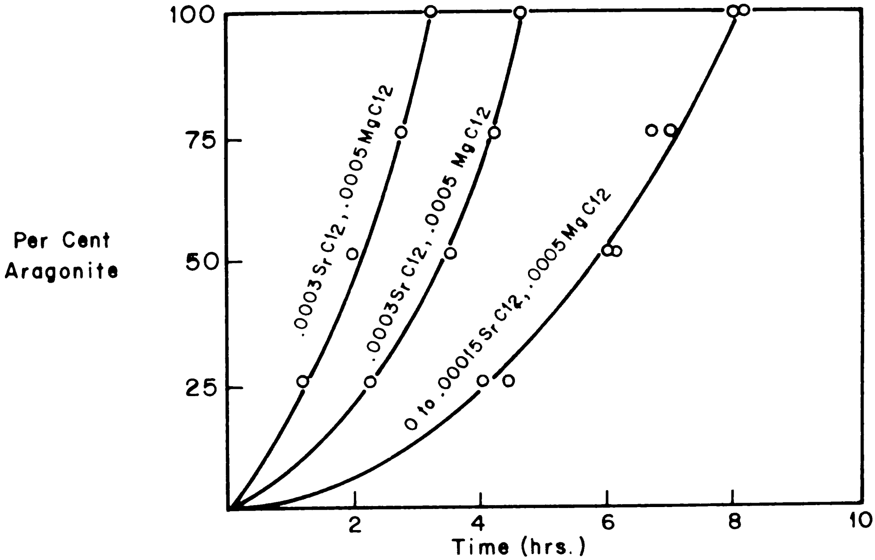


Fig. 5. Effect of K_2SO_4 on aragonite formation.

is suggested as the catalizing process. Much emphasis has been placed on the role of strontium ion both in inducing aragonite nucleation and "stabilizing" aragonite (Johnston, Merwin, and Williamson, 1916; Zeller and Wray, 1956). Although the inducing effect is evidently real,

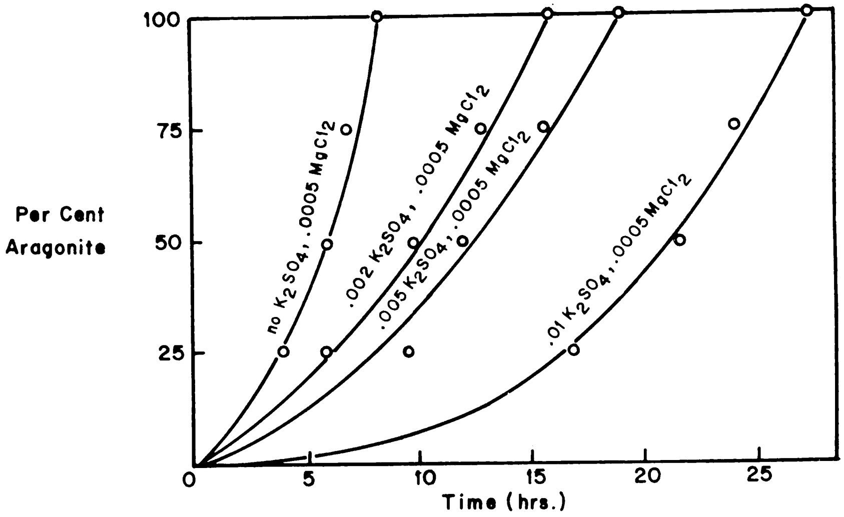


Fig. 6. Effect of $SrCl_2$ on aragonite formation.

it is questioned whether strontium is sufficiently concentrated in natural environments to exert a controlling effect. For example, sea water concentration of strontium is about 0.000092 molal (Goldberg, 1965).

Sea water.—The reaction in sea water (fig. 7) required about 100 hours, with the resulting aragonite having a stunted, equant habit, in contrast to the needle habit in the other experimental runs. Of the major ions in sea water, only magnesium and sulfate inhibit the formation of aragonite, so to determine if these ions are solely responsible for the slowness of the reaction in sea water, a solution 0.054 molal $MgCl_2$ and 0.028 molal K_2SO_4 was prepared (that is, a solution with sea water molalities of magnesium and sulfate). The vaterite-aragonite reaction in this solution (fig. 7) was considerably faster than natural sea water, indicating the inhibition of aragonite by some minor component of sea water. Kitano and Hood (1956) have shown that various dissolved organic substances in sea water have marked effects on rates of calcium carbonate precipitation. It is not unreasonable that some dissolved organic component of sea water is responsible for the slowness of aragonite formation in this work.

CONCLUSIONS ON ARAGONITE FORMATION

Under the conditions of the experiments, aragonite nucleates on the vaterite surface and grows on point or edge defects, analogous to calcite nucleation and growth. In contrast to calcite formation, there appears to be no fundamental rate controlling process involving the Ca^{++} and HCO_3^- ions. The rate controlling step may be a simple calcium and carbonate combination. The data, however, are not conclusive for such a mechanism.

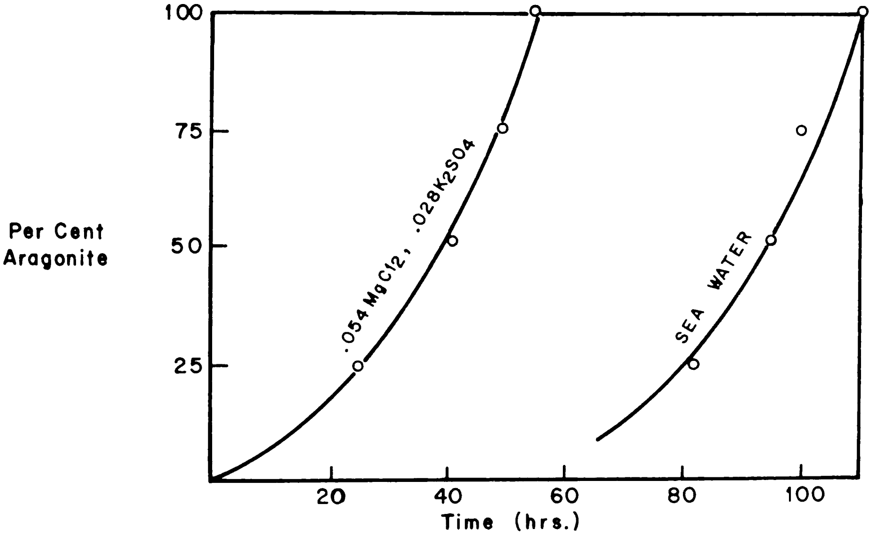


Fig. 7. Plots of vaterite-argonite transformation in natural sea water and in artificial solution of magnesium and sulfate ions at sea water molality.

Sulfate is a strong inhibitor of aragonite formation, while magnesium is a very weak inhibitor. Strontium ion, when concentrated sufficiently to precipitate strontianite, accelerates aragonite formation, probably by providing seed nuclei.

GEOLOGICAL IMPLICATIONS

A comparison of the mode of crystallization of calcite and aragonite suggests a few generalizations about the factors controlling the predominance of one polymorph over the other in natural environments.

Calcite will predominate in those environments in which calcite forms at a faster rate than aragonite or transforms from aragonite at a rapid rate. Thus, low pH (that is, high HCO_3^-), high calcium, high ionic strengths, and low sulfate and, particularly, low magnesium will be most conducive to calcite predominance in modern environments.

Aragonite predominance will be in those environments where aragonite forms faster than calcite and in which the rate of transformation to calcite is extremely slow. The only critical factor would be concentration of Mg^{++}, and a review of modern carbonate environments, particularly the non-marine, supports the generality that predominance of aragonite is correlated with high magnesium concentration (Bischoff, ms). Sea water has sufficient magnesium to account for the precipitation and persistence of aragonite.

Recent observations in marine environments have indicated the occurrence of inorganically precipitated high magnesian calcite (Von der Borch, 1965; Friedman, 1965; Milliman, 1966). Some of this magnesian calcite may have formed from transformation of aragonite. It would seem, judging from the ability of the nascent calcite nuclei to remove magnesium ion from solution, that high magnesian calcite would form from aragonite in sea water, given sufficient time. The magnesium carbonate content of such a calcite, however, would have to be less than some value between 10 to 14 mole percent. (Solubility studies indicate that calcite of magnesium carbonate contents above the range of 10 to 14 mole percent are metastable with respect to aragonite, Berner, 1967.) Deep drilling off the Florida coast by the Joint Oceanographic Deep Earth Sampling Program (J. C. Hathaway, personal communication) indicates the disappearance of high magnesian calcite with depth, and replacement by low magnesian calcite and dolomite, suggesting, supplementarily with the experimental data, the following scheme of $CaCO_3$ precipitation in sea water:

1. Precipitation of aragonite (high or low magnesian calcite crystallizes too slowly to compete due to Mg^{++} inhibition).
2. Aragonite solution and slow crystallization of high Mg calcite ($<$10-14 mole percent $MgCO_3$), possible cementation.
3. High Mg calcite solution and slow crystallization of low Mg calcite and/or dolomite and possible cementation.

Removal of aragonite from the marine environment into a subaerial environment would remove the magnesium inhibition of calcite and result in a rapid transformation to calcite and possible cementation and lithification.

Acknowledgements are included in the first paper of this series (Bischoff and Fyfe, 1968, p. 79).

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