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EXPERIMENTAL DETERMINATION OF PARTITION COEFFICIENTS FOR CALCIUM, STRONTIUM, AND BARIUM IN ARAGONITE PRECIPITATED FROM SEA WATER AT LOW TEMPERATURES

A DISSERTATION

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DOCTOR OF PHILOSOPHY

ΒY

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EXPERIMENTAL DETERMINATION OF PARTITION COEFFICIENTS FOR CALCIUM, STRONTIUM, AND BARIUM IN ARAGONITE PRECIPITATED FROM SEA WATER AT LOW TEMPERATURES

APPROVED DISSERTATION COMMITYEE

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ABSTRACT

The partition of calcium, strontium, and barium has been measured between sea water and precipitates of aragonite at low temperatures and atmospheric pressure. The distribution of calcium, strontium, and barium between the solution and precipitate approximates the Doerner-Hoskins relationship, thus surface equilibrium is maintained between solution and solid during the coprecipitation process. The partition of calcium and strontium between precipitates of aragonite and sea water approximates more closely the logarithmic distribution law than that of the calcium and barium distribution.

Aragonite was precipitated from sea water by the addition of dilute solutions of sodium carbonate. Barium was quantitatively separated by ion-exchange techniques and both strontium and barium were analyzed by flame spectrophotometry.

The partition coefficient K_{Sr}^{A} ++ is 1.29 ± 0.04 at 25° C, 1.20 ± 0.03 at 35° C, and decreases to 1.15 ± 0.02 at 45° C. The partition coefficient K_{Ba}^{A} ++ is 3.16 at 25° C, 2.78 at 35° C, and 2.71 at 45° C. The strontium content of the inorganically precipitated aragonites ranges

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from 9,200 to 10,200 ppm, and barium ranges from 96 to 113 ppm.

Many marine organic and inorganic aragonites contain amounts of strontium similar to those predicted from the distribution data. Recent marine non-skeletal aragonites which contain less strontium than those precipitated in the laboratory might be considered organic in origin.

The barium content of naturally occurring aragonites appears not to conform to the predicted values of determined partition coefficients. The low level of barium content in modern marine aragonites cannot, therefore, be interpreted by the results of distribution coefficient data.

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EXPERIMENTAL DETERMINATION OF PARTITION COEFFICIENTS FOR CALCIUM, STRONTIUM, AND BARIUM IN ARAGONITE PRECIPITATED FROM SEA WATER AT LOW TEMPERATURES

INTRODUCTION

Purpose of Investigation

The purpose of this study is to investigate the distribution of the alkaline-earths, calcium, strontium, and barium, between aragonite (CaCO3) and the natural sea water from which it is precipitated. This series of low temperature experiments hopefully may provide criteria useful for differentiating between inorganic and biogenic aragonites precipitated from sea water. Another objective of this work is to provide criteria to evaluate naturally occurring aragonite to determine whether it is a primary precipitate from sea water or if it has undergone alteration and may be considered secondary.

The coprecipitation of strontium and barium in calcium carbonate is evaluated at various temperatures using partition coefficient theory. If the partition coefficients are known from laboratory experiments as a function of temperature, we then have a relationship between the three variables (composition of liquid, composition of

solid, and temperature) which may be applied to naturally occurring aragonite. Lowenstam (1961) has shown that the strontium to calcium ratio in sea water has remained essentially constant during the last 2.0-2.5 X 10⁸ years. Since the composition of sea water can be assumed constant and the strontium and barium concentration can be measured on naturally occurring aragonite, then the established relationship between the three variables allows us to evaluate the temperature at which a given aragonite was formed.

Previous Investigations

McIntire (1963) has given a comprehensive review of theory and experimental data relative to trace element partition coefficients in geological environments. It is notable in this review that experimentally determined partition coefficients are largely for systems other than carbonate.

Some information on the low temperature coprecipitation of strontium with aragonite can be obtained from the following papers: Goldberg (1957), Odum (1957), Zeller and Wray (1956), Cloud (1962), and Kinsman (1965).

Goldberg (1957) has stated that the ratio of strontium to calcium in aragonite precipitated from sea water was higher than the ratio in sea water, in other words, the distribution coefficient was greater than unity. Odum (1957) has reported values of strontium coprecipitated with calcium carbonate precipitated from sea water at 0.54

to 1.48. However, temperature, mineralogy, and other details were not reported. Zeller and Wray (1956) precipitated aragonite, calcite, and vaterite under conditions of controlled temperature, pH, and impurity ion concentration. Their purpose was to study the factors affecting the formation of the various crystalline forms of calcium carbonate.

Cloud (1962) precipitated aragonite, containing a trace of calcite, from sea water of the Bahama Banks. Three samples were precipitated by the removal of carbon dioxide. The semiquantitative spectrographic analyses of the aragonites showed the strontium content to be 5,000 to 10,000 ppm.

Kinsman (1965) reported on the coprecipitation of strontium with aragonite from sea water. Values of K_{Sr}^{A} determined were: 15° C - 1.16 ± 0.04; 45° C - 1.04 ± 0.03; 60° C - 0.97 ± 0.03; 80° C - 0.88 ± 0.03.

The distribution of barium between aragonite and its coexisting saturated aqueous solution has been previously investigated in a semiquantitative manner (Cloud, 1962). Semiquantitative spectrographic analyses for trace elements, which included barium, were reported on three precipitates. These precipitates were mainly aragonite with a trace of calcite which had been precipitated from sea water by removal of carbon dioxide. The barium content was reported to range between 100 and 500 ppm.

EXPERIMENTAL TECHNIQUES

Precipitation of Aragonite from Sea Water

The most important factors in conducting a series of experiments of this type are: (1) controlling the polymorphic form of the precipitated phase at the prevailing experimental conditions, and allowing only a single solid phase to form, (2) equilibrium crystallization, (3) permitting only experimental conditions that reasonably approximate calcium carbonate precipitation in nature, and (4) having a sufficient yield of solid formed for proper handling.

Calcium carbonate can be artificially precipitated in the laboratory by a variety of methods. Some of the more common techniques are: (1) the removal of CO_2 from sea water and the degassing of a saturated calcium carbonate solution, (2) the decomposition of organic acid salts or hydrolysis of certain ions to yield the carbonate radical which in turn may act as precipitant for the calcium ions present in the solution, and (3) the decomposition of various salts.

The degassing of a saturated calcium carbonate

solution seemed most appropriate for this investigation. This technique is superior to the others mentioned in that there are no additional ions added to the precipitating solution. Crocket and Winchester (1966) used this method for the coprecipitation of zinc with calcium carbonate.

In order to test this procedure artificial sea water was prepared (Lyman and Fleming, 1940). Precipitations were carried out in one liter florence flasks. The flasks were supported in a ten gallon polyethylene water bath whose temperature was controlled by immersion heaters regulated by a Thermistemp (Model 71) thermoregulator. Each flask was continuously stirred by means of magnetic Teflon-coated bars and magnetic stirring motors placed immediately below the bath. Temperature could be controlled within one-half of a degree at approximately 25° C, and within one degree above 40° C. Experiments were run at 25° C, 35° C, and 45° C.

To saturate the sea water, one gram of analytical reagent grade calcium carbonate was placed in a liter of sea water. The P_{CO_2} was increased by bubbling carbon dioxide through the solution for about three hours. The solution was then filtered through a previously weighed fritted glass crucible and the undissolved solid calcium carbonate could then be dried and weighed. The solution, now with a known amount of dissolved calcium carbonate, was tightly stoppered and stored in the refrigerator until

needed.

The artificial sea water was measured into a one liter flask fitted with a tube through the stopper that would project above the level of the water bath. The sea water was sealed from the atmosphere by means of a rubber tube and clamp on the tube. The solution could be stirred by means of a magnetic bar previously placed in the flask and a stirring motor under the constant temperature water bath. When the sea water had reached the temperature of the bath, it was opened to the atmosphere. Continued stirring caused a degassing of the solution with a resulting precipitation of aragonite after about six hours at 25° C, and one-half hour at 45° C.

The relevant carbonate equilibria in this technique are given below in equations (1), (2), and (3).

$$CO_2(aq) = CO_2(gas)$$
(1)

$$CO_2(aq) + H_2O = H_2CO_3$$
 (2)

$$2HCO_3^{-} = H_2CO_3 + CO_3^{-}$$
 (3)

Loss of carbon dioxide from an aqueous solution by stirring results in (1) shifting to the right, which, in turn, requires that (2) shift to the left, which finally results in (3) moving to the right with consequent production of the carbonate ion and precipitation of calcium carbonate.

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Many problems were encountered with this procedure and eventually it was abandoned altogether. At the maximum, only about 0.4 grams of calcium carbonate could be dissolved at room temperature in the sea water, and commonly less. The recoverable precipitate was generally less than fifty percent. Also, many of the trial runs yielded no solid at all for which no explanation is available.

The removal of carbon dioxide from sea water also causes the precipitation of aragonite. Cloud (1962) passed air through a saturated solution of sodium hydroxide to take up carbon dioxide and then allowed the CO_2 free gas to bubble through a column of sea water. The effect was to carry CO, out of the sea water, thereby raising the pH, moving the carbonic-acid equilibria to the right and bringing about the precipitation of calcium carbonate. Precipitates were formed in four experiments at room temperature (approximately 24° C), all of which were aragonite with a trace of calcite. These experiments lasted from thirteen days to several months with 400 to 600 ml of sea water. A maximum of 22 mg and as little as 9.5 mg of precipitate was formed. The 22 mg of calcium carbonate separated represents 4.7 percent of the original calcium which precipitated. It is felt that this yield is too small for practical use.

Another method that was considered for the laboratory precipitation of aragonite was the decomposition of

organic acid salts to yield carbonate ions. The selection of a particular salt must be governed by the rate of decomposition at the temperature of the particular experiment. This technique has been used by several authors, (Bodine et al., 1965; Holland et al., 1963, 1964), generally at elevated temperatures with trichloroacetic or formic acid. By this method it is possible to insure relatively slow bicarbonate production in order to maintain homogeneity in the solution during carbonate precipitation. A serious drawback for this study would be the introduction of various ions not normally found in sea water. Various unknown reactions might occur.

The addition of dilute sodium carbonate to natural sea water was chosen as the technique for the precipitation of aragonite for this study. Kinsman (1965) reported on the precipitation of aragonite from sea water by the addition of sodium carbonate solutions and supplied the author with details of his technique.

Thirty-five gallons of sea water were collected from the Gulf of Mexico off Galveston, Texas. The water was filtered, placed in covered plastic containers, and stored away from the light to depress bacterial and algal growth.

Various strengths of sodium carbonate solutions (up to 600 mg sodium carbonate per liter) and differing lengths of time (one to twenty hours) for the addition

of the carbonate solutions were tried.

It was found that solutions containing approximately 600 mg of sodium carbonate per liter could saturate the sea water with carbonate ions over a reasonably long time. At this concentration, complete mixing of the solutions is possible over a period of many hours before nucleation begins. More concentrated solutions caused immediate precipitation in the vicinity of the carbonate solution drops as they were added to the sea water.

The techniques for the precipitation of aragonite from sea water are as follows. Into the one liter reaction flasks were measured 600 ml of sea water. The sea water had been filtered soon after it was collected and was also filtered a second time just before each experiment. The flasks were then placed into the constant temperature water bath. The neck of the flask projected well above the surface of the water and was left open to the atmosphere.

After the sea water had equilibrated with the water bath at the desired temperature, 125 ml of sodium carbonate solution were added dropwise over a period of three to four hours. The solution was allowed to stir for a minimum of three hours after the first addition of carbonate solution.

A second 125 ml portion of sodium carbonate solution was then added dropwise to the sea water over a similar period of three to four hours. Precipitation normally began several hours after this final step. Stirring continued

during the entire experiment, i.e., from the time the reaction vessels were placed in the constant temperature water bath until they were removed at the end of the experiment.

The pH was monitored during experimental runs to verify the buffering capacity of the solution during the experiment. During a few runs the pH was taken at the start of the experiment, after the addition of the first aliquot of sodium carbonate, after further sodium carbonate addition, and finally past the precipitation point. The maximum pH value observed was 8.7, after the addition of the second aliquot of sodium carbonate. Thereafter, the pH fell as precipitation ensued, finally stabilizing near 8.4.

At the end of each run the flasks were removed from the water bath and quickly filtered. The separation of the precipitate and its coexisting fluid was done rapidly to avoid contamination by material precipitated at temperatures between that of the experiment and room temperature. The solid was washed twice, dried, and weighed.

The absolute amount of solid carbonate which is recoverable from this process is a few tenths of a gram. This is adequate for a portion to be X-rayed and also to be chemically analyzed.

Using these procedures it was possible to recover approximately fifty-eight percent of the calcium in

solution. Fifty percent of the total calcium is precipitated at the end of approximately 50 hours and fifty-eight percent is recovered after 140 hours. It was decided that 60 hours would be a satisfactory upper limit for the experiments.

Slight modification of the above procedures was found necessary for those experiments in which the distribution of calcium and barium between sea water and precipitated aragonite was investigated. Large amounts of barium were incorporated in the precipitate when the sodium carbonate solution was added to the sea water over a short period of time. Figure 1 shows approximately 1500 ppm barium in those aragonites which had precipitated from solution that had sodium carbonate added for 9 hours at 25° C. For those aragonites precipitated from solutions which had sodium carbonate added at a slower rate, the total amount of barium was less. A value of 112 ± 23 ppm barium was found for precipitates formed when sodium carbonate was added to sea water over a 36 hour period or longer (Figure 1). Aragonites precipitated from solutions to which sodium carbonate was added over a period of less than 36 hours must contain appreciable barium as interstitially trapped ions. Experiments in which the distribution of calcium and barium between sea water and precipitated aragonite was investigated, therefore, had 250 ml of sodium carbonate added for a minimum of 36 hours.



BARIUM INCORPORATED IN ARAGONITE VERSUS TIME Na₂CO₃ (250 ml) ADDED TO SEA WATER

Also, more vigorous stirring was used on these runs to insure equilibrium.

Optical Examination of Precipitates

Research biological microscopes with high magnification and resolution were used to check the precipitates for overall crystal habit, the presence of more than one carbonate phase, and possible liquid inclusions within the individual crystals. Precipitates from ordinary runs at 25°, 35°, and 45° C were examined optically using an oil immersion objective lens.

The carbonates and sulfates of both strontium and barium were looked for. Crystal habits specifically looked for were acicular aragonite, calcite rhombohedra, hexagonal plates of μ -CaCO₃, and the rosettes or spherulitic variety of vaterite. Along with crystal habit, other optical properties (such as index of refraction) were used in order to explore the possibility of other phases present.

In all examined precipitates, nearly all observed crystals were the needle-like aragonite forms. The only other crystal forms seen were calcite rhombs, and these were rare. Visual estimates were made of the proportions of calcite present. Strewn slides were prepared from four randomly chosen experiments at each temperature under investigation. Fifty fields of view were counted for calcite rhombs on each of the twelve slides. The X50 objective was used. Spot checks were run on three additional slides prepared from three different experiments. On the average, there were approximately 800 individual crystals in each separate field of view on all slides. There was an average of one calcite rhomb per 13 fields of view in the total, 600 fields of view examined. This is a general average of one calcite crystal per 10,000 crystals or 0.01 percent calcite.

The proportion of calcite was approximately equal in all precipitates examined and seems to be independent of temperature or percentage of calcium carbonate precipitated at a given temperature.

Measurements were made on precipitates from all temperatures. The range of crystal lengths was two to twenty microns. The average size was less than ten microns. There appeared to be no noticeable increase in average crystal size with increased temperature.

With reasonably high magnification (using the X100 objective) and good resolution, it is possible to examine the individual crystals with transmitted light. Many individual crystals were thus examined for the presence of liquid inclusions that might take the form of bubbles or other shapes. The examined aragonite needles appeared to be clear and free from inclusions.

The general conclusions drawn from the optical work are that the precipitates are acicular aragonite that

range from two to twenty microns in length (average length less than ten microns) and are relatively free from inclusions. Traces of calcite are present.

X-ray Analysis of Precipitates

The precipitates were identified by X-ray diffraction analysis. The powder was sprinkled onto a vaselinecoated glass slide and allowed to stand for five minutes until the solid was firmly bonded to the slide. The slide was then inverted and tapped gently in order to remove excess material. This randomly-oriented material was analyzed with a Norelco X-ray diffractometer. Nickelfiltered Cu (K alpha) radiation was used. The copper-target X-ray tube was operated at forty kilovolts and twenty milliamps. The diffractometer scan was made from 4° two theta to 60° two theta.

Because calcium carbonate can exist in at least three polymorphic forms (calcite, aragonite, and vaterite), these minerals were specifically looked for on the X-ray diffractograms. Other minerals might possibly form in a series of experiments of this type. For example, hydrates of calcium: $CaCO_3 \cdot H_2O$ and $CaCO_3 \cdot 0.65 H_2O$. These minerals were looked for, but were not found. Other carbonate minerals such as huntite (Faust, 1953) were looked for but not found.

From X-ray analysis it was concluded, after all

X-ray peaks were identified, that the only carbonate precipitated was aragonite. This conclusion is supported by the data of Kinsman (1965) which show vaterite, calcite, and the mono-hydrate of calcium carbonate present only below 15° C and one hundred percent aragonite above 30° C.

Simkiss (1964) examined the precipitates from artificial sea water and showed that aragonite precipitates when the solution contains CaCl₂, MgCl₂ and NaCl. Calcite is formed when the solution contains only NaCl and CaCl₂. In the absence of magnesium but in the presence of NaCl, KCl, NaSO₄ and NaCl₂, the precipitate was found to be composed of calcite plus vaterite. Simkiss' data indicates that aragonite precipitated from normal sea water.

Recent work (Lowenstam, 1954; Turekian and Armstrong, 1960; Chave, 1962; and Davies and Hooper, 1962) has shown that quantitative results can be obtained by X-ray diffraction techniques on the polymorphic composition of calcium carbonate. Lowenstam (1954) and Turekian and Armstrong (1960) measured the peak heights of the calcite and aragonite lines and quote an accuracy of ± 10 percent. Chave (1962) measured the integrated line intensity and claims an accuracy of ± 5 percent for the concentration of calcite and aragonite. Davies and Hooper (1962) measured integrated line intensity on the diffractometer patterns and according to the authors the proportion of calcite and aragonite can be determined to within one percent of the

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total.

Preliminary optical and X-ray examination showed the precipitates to be essentially aragonite with traces of calcite. Therefore, in order to establish the lower limit of detectability of calcite intermixed with aragonite, artificial mixtures were prepared. One-half, one, two, and five percent by weight of calcite was mixed with aragonites precipitated at 25°, 35°, and 45° C. It was assumed that the precipitated calcium carbonate was one hundred percent aragonite from X-ray and optical examination. Calcite is present in the precipitates in trace amounts. The most intense peaks for calcite and aragonite are located at 29.4 and 26.2° two theta respectively. As each of these peaks is free from interference of less intense reflections of the other mineral, their presence was considered diagnostic of the two minerals.

In the case of the two-percent and five-percent calcite-aragonite mixtures, several calcite peaks were clearly visible on the diffractogram. The X-ray examination of the one-percent calcite-aragonite mixture contained only one calcite peak, the (104). This peak (3.035 Å) is the strongest of the calcite group and is located at 29.4° two theta and is free from interference from aragonite peaks. Generally the most intense peak of the aragonite precipitate (3.395 Å) can be set at near one hundred percent on the chart recorder with a scale factor of 4 X 1.0. At

this setting, however, no calcite peaks can be observed. If the scale factor is increased to 4 X 0.6, a large number of the strong aragonite peaks are off scale but the strongest peaks of calcite, especially (3.035 Å), can be observed. At these instrument settings, the strongest calcite peak has, compared to the strongest aragonite peak, a relative height of approximately 0.04. No calcite peaks were observed on the diffractogram of the one-half percent calcite-aragonite mixture.

It is felt from the relatively easy detection of one-percent calcite mixed with the precipitates that any calcite within the one-percent range would be detected by X-ray examination.

D.T.A. Examination of Precipitates

Several precipitates were run in the high-sensitivity sample holder of an R. L. Stone (Model 13M) D.T.A. unit. It was hoped that traces of phases other than aragonite could be detected. Artificial mixtures of onehalf-percent, one-percent, and two-percent calcite were also run. There were slight indications of endothermic reactions other than aragonite even on the one-half-percent calcite-aragonite mixture but these were not clear or easily interpreted. In general the results were not satisfactory and it seems that it is not possible to detect very small amounts of calcite in the presence of aragonite using this equipment.

Aging of Precipitates

The nucleation and crystallization periods of these experiments are relatively short, especially as compared to those in nature. There is a possibility that some of the precipitates may be in a poorly crystalline state or may be truly amorphous immediately after precipitation.

To see if other phases might appear on aging the precipitates, the following experiment was performed. Solids were precipitated from sea water at 25°, 35°, and 45° C. Instead of removing the reaction vessels from the constant temperature water bath and separating the liquid and solid as usual, the vessels were left in the bath for a period of time. At each temperature, the precipitate was allowed to remain in contact with its coexisting liquid for 24 hours and also for 168 hours. After this aging process, the solids were removed and X-rayed. At the end of both aging periods (24 and 168 hours) the X-ray and optical examination showed no trace of other phases appearing.

It is therefore concluded that under the experimental conditions, aragonite was precipitated from sea water at 25°, 35°, and 45° C, in a reasonably well ordered crystalline state and undergoes no observable structural change during the experiment or immediately afterwards.

> Separation of Barium by Ion Exchange Because of the difficult analytical problems

involved in the detection of small amounts of barium in the presence of large amounts of calcium and strontium, satisfactory separation techniques have been devised only recently (Strelow, 1968; Andersen and Hume, 1968). The quantitative concentration and separation of barium from calcium, strontium, and other cations for purposes of analysis was done by ion exchange methods (Andersen and Hume, 1968).

The ion exchange resins used were Dowex 50W-X12 sulfonated polystyrenes. This strong-acid cation exchange resin was Analytical Grade (AG) of 200 to 400 mesh particle size. Borosilicate glass tubes of 1.4 cm diameter were used as columns. Each column contained twenty-five grams of resin for a total length of approximately 30 cm.

The column was prepared by passing through 100 ml of a saturated calcium chloride solution which had previously been stripped of strontium and barium by ion exchange. The flow rate through the column is kept at one milliliter per minute at room temperature (20-22° C) for all solutions. By this process the column was converted to the calcium form.

The sample was then passed through the cation exchange resin. Those samples from which barium was separated were solutions of the precipitated aragonites and sea water. The sample was followed through with 20 ml of 0.01M, pH 5.0 ammonium acetate buffer wash solution.

Calcium is eluted with 500 ml of pH 5.0, 0.02M cyclohexane-1, 2-dinitrilotetracetic acid (CyDTA). Many of the divalent and trivalent metals in sea water are concentrated on the resin and then removed by the chelating agent, CyDTA, with the calcium fraction. The calcium fraction was discarded.

Strontium was next eluted with pH 6.5, 0.02M CyDTA. The first 60 ml collected contained all the strontium.

The eluent was then changed to 0.01M EDTA in a pH 10.0 ammonia-ammonium chloride buffer. The first 10 ml that come through the column are discarded. The following 35 ml contain all of the barium which was retained by the column. The 35 ml barium fraction was evaporated on a hot plate to approximately 6 ml and then diluted to 10.0 ml for aspiration into the spectrophotometer flame. The pH of the barium fraction is decreased to approximately six during this evaporation step.

Once strontium had been removed from the exchange column there was no need to use as selective a reagent as the expensive CyDTA simply to recover the barium from the column, according to Andersen and Hume (1968). Therefore, EDTA at pH 10.0 was used to elute the barium fraction. There are no appreciable differences in the elution behavior of EDTA or CyDTA under the conditons of the experiment.

The column is regenerated for the next sample by

passing through about 100 ml of the saturated calcium chloride solution.

Artificial mixtures containing known amounts of calcium, strontium, and barium were successfully separated using these techniques. Less than one percent loss or gain of material was found during these separations. Blank samples were processed by the usual techniques as a check for barium in reagents and as a background in the flame analyses for barium.

Flame Spectrophotometry for Strontium

and Barium and Analytical Errors

The dilution-addition method for the analysis of strontium was used for the solutions of the aragonites of this experiment. The flame photometric determination of strontium in sea water and marine products is outlined by Chow and Thompson (1955).

A Zeiss Model PMQ II Spectrophotometer with a flame attachment exploying a hydrogen-oxygen gas flame was used to measure quantitatively strontium and barium. Table 1 gives the instrument parameters for both strontium and barium.

One of the drawbacks inherent in the flame photometric method of determining element concentration is the matrix effect. The emission intensity from a given element may depend on the nature and concentration of the accompanying elements in the sample. The matrix effects are largely

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TABLE	1

INSTRUMENT PARAMETERS AND ANALYTICAL DATA FOR THE FLAME PHOTOMETRIC DETERMINATION OF STRONTIUM AND BARIUM

Element	Wave- length (mµ)	Back- ground (mµ)	Tube	Slit Width (mm)	Gas
Sr	460.7	454	Photo- multiplier	0.03	Hydrogen Oxygen
Ba	553.7		Photo- multiplier	0.10	Hydrogen Oxygen

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overcome by sufficient dilution of the sample and residual matrix effects are corrected by an addition technique. The addition or spiking technique is the adding to the sample of known amounts of element being measured. The resulting plot of intensity versus concentration defines the upper region of a working curve characteristic of the given sample matrix mixed with differing amounts of test element. The shape of the curve for lower concentrations of the element is deduced by extrapolation from the known position to zero intensity, thus defining at the same time the point of zero concentration.

The extrapolation to zero intensity is simplified by choosing a concentration for a standard such that, if the standard is set at 100, the sample which has had no test element added to it reads in the range of twenty to thirty-five percent transmission. Before plotting, the intensities obtained are corrected for background by reading emissions to the left or right of the chosen line, or both.

Minimum slit widths are used to obtain the best resolving power and thus decrease or eliminate line interference from other elements.

Standards were prepared from Johnson, Matthey & Co., Ltd., spectrographically standardized solutions. Appropriate dilution of these strontium chloride and barium chloride standards was made to yield solutions of varying

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concentration.

The precipitated aragonites were dissolved in a minimum of hydrochloric acid (2 ml of concentrated HCl in 25 ml of distilled water), and diluted with distilled water to 100 ml.

Approximate concentrations of strontium in each sample were obtained by first setting 30 ppm standards at near full scale on the spectrophotometer recorder and reading each element at its most sensitive wavelength. These approximate concentrations were used as a guide for addition of increments of standard solutions to each sample.

For the quantitative measurement of strontium, four 5 ml aliquots of each sample solution were placed in 25 ml volumetric flasks. The first flask was diluted to the mark with distilled water. The second was diluted to volume with a 5 ppm strontium standard solution. The third flask was diluted to the mark with a standard twice as concentrated as the second flask, or 10 ppm Sr⁺⁺, and the fourth with a dilution three times as concentrated as the solution added to the second flask. The concentration of the fourth flask was such that it would read approximately eighty percent with a 30 or 40 ppm standard set at one hundred percent total transmission.

The net intensity of strontium in each aliquot (total intensity minus the reading of the background and blank solution) was plotted aginst concentration in each sample. The concentration of the aliquot with no standard solution added was set at an arbitrary point on the graph. A smooth curve was drawn through the points and the curve was extrapolated to zero intensity. This located the point of zero concentration. The concentration of the sample could then be read as the difference between the zero point of concentration and the point arbitrarily chosen for the sample diluted only with distilled water.

The determined concentration of strontium was converted to a percentage of the original aragonite as follows:

(a) 100 mg of sample dissolved and diluted to100 ml (called sample solution) = 1 mg of sample/ml.

(b) 5 ml of sample solution diluted to 25 ml =
5 mg of sample/25 ml = 200 mg of sample/liter = 200 ppm
of sample (in 5 ml of sample solution).

(c) If 2.0 ppm strontium is found in 5 ml of sample solution then

 $\frac{2.0 \text{ ppm Sr}^{++}}{200 \text{ ppm sample}} \times 100\% = 1.00\% \text{ Sr}^{++}/\text{sample}$

Precision of the flame spectrophotometric analyses of strontium and barium was measured by comparison of replicate determinations of a single sample, as well as the analyses of duplicate samples. The precision and comparison of analyses were expressed in terms of the standard deviation and the relative standard deviation or coefficient of variation, C.V., which is computed by the expression:

$$C.V. = \frac{S.D.}{X} \times 100\%$$

S.D. = the standard deviation \overline{X} = the arithmetic average of the measured values

Table 2 shows the precision with which strontium can be measured in a single sample. These samples are precipitated aragonites from Runs 1, 2, 5, 13, and 17. The 100 ml solutions of these precipitates were repeatedly analyzed by the standard-addition technique. The precision for the repeated analyses of an individual sample is demonstrated by inspection of both the standard deviation and coefficient of variation.

The figures of Table 3 are the results of two identical experiments run simultaneously. The variations between these samples are considered the results of random and determinate errors in the analytical procedures. These errors include volumetric determinations of solutions at all steps of the procedure, the mechanical separation of the liquid and solid phases, and the errors in the actual photometric determination of strontium. The solutions of
Trial	Run 1	Run 2	Run 5	Run 13	Run 17
1	10,100	10,100	10,000	9,600	9,400
2	10,100	10,100	10,100	9,500	9,400
3	10,000	10,100	10,100	9,600	9,400
X	10,100	10,100	10,100	9,600	9,400
S.D.	71	• •	71	71	• •
C.V.(%)	0.70	•••	0.70	0.74	• •

PRECISION OF REPLICATE ANALYSES OF STRONTIUM BY FLAME SPECTROPHOTOMETRY IN PPM STRONTIUM

TABLE 2

T.	A	B	L	Ε	3
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PRECISION OF ANALYSES FOR DUPLICATE EXPERIMENTS IN STRONTIUM (PPM)

Tricl	Exper	iment 7	
	Run 1	Run 2	
1	10,300	10,100	
2	10,600	10,200	
3	9,900	10,400	
Arithmetic Mean (\overline{X}) .	• • • • • • •	• • • • • • •	10,200
Standard Deviation ((S.D.)		230
Coefficient of Varia	tion (C.V.) in	0	2.25

each trial were made up individually from the sample solutions.

The standard deviaiton for the data of Table 3 is 230 ppm strontium. It is assumed that this value, along with the error for the quantitative analysis for calcium (mentioned in the next section) represents the bulk of analytical uncertainties in the computation of the partition coefficients. If we take the standard deviation of Table 3 (230 ppm strontium) and the standard deviation of Table 5 (3 ppm calcium), add and subtract these values to the quantities used to calculate all partition coefficients, we will get an estimate of the precision of the partition coefficients. If these analytical errors are added to and subtracted from all quantities and the partition coefficients recalculated, we obtain ±0.02 for all coefficients.

Flame Spectrophotometry for Barium

The flame photometric determination of barium is simplified by the quantitative separation and concentration of barium (Andersen and Hume, 1968). Calcium particularly gives spectral interference in the detection of barium. This ion as well as most others are removed by the ion exchange technique. Andersen and Hume (1968) investigated the flame photometric determination of both strontium and barium. The emission characteristics were examined in the reagents and eluents used and high sensitivity and accuracy were found.

Table 4 shows the results of five runs in the determination of barium. The precision of repeated analyses is very high. Similar analytical errors were found on duplicate runs for barium as previously indicated for runs involving strontium. Partition coefficients recalculated using the uncertainties of these duplicate runs gave a dispersion of approximately ±0.03 for all coefficients.

Titration of Calcium with EDTA

The quantitative determination of calcium in sea water was by the standard titration using EDTA [(Ethylenedinitrilo) Tetra-acetic Acid] using Cal-Red [2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylaxo)-3-naphthoic acid] as an indicator (Szabo, 1967).

One of the major problems involved in the analysis of calcium in sea water is the presence of magnesium and strontium. Sea water contains large amounts of magnesium as compared to calcium (five to one molar ratio), and, therefore, possible error in the calcium determination due to the presence of magnesium in the titrating volume must be considered.

The calcium plus strontium concentration is determined after magnesium has been precipitated quantitatively as hydroxide. This determination requires special care because the magnesium hydroxide precipitate present in the titration volume hinders the observation of the color

Trial	Run 25	Run 27	Run 29	Run 33	Run 39
1	112	112	109	105	100
2	112	112	109	105	100
3	112	113	109	105	100
X	112	112	109	105	100
S.D.	••	0.71	• •	• •	• •
C.V. (%)	• •	0.63	• •	• •	••

:

PRECISION	OF	REPLICATE	ANALYSE	S OF	BARIUM	ΒY
FLAME	SPEC	CTROPHOTOM	ETRY IN	PPM	BARIUM	

TABLE 4

change at the end point. To improve the end point detection and to eliminate the coprecipitation of calcium and/or EDTA by the magnesium hydroxide, the aliquot of the sea water sample was diluted with distilled water (one to fourteen by volume). In addition, ninety-nine percent of the EDTA volume required for complexing calcium was added before the buffer, and the precipitation of magnesium was carefully controlled by dropwise addition of the sodium hydroxide.

A ten milliliter precision burette was utilized for the titration of the combined calcium and strontium solutions.

The calcium concentration in each sample was calculated by subtracting the result of the flame spectrophotometric strontium determination from the combined calcium and strontium titration results.

In the process for calcium analyses in sea water, interference of trace elements other than strontium may result. In fact, a whole group of elements such as barium, aluminum, iron, zinc, cobalt, nickel, and copper can form complexes with EDTA. The usual way to cope with this problem is by masking undesirable ions. A combination of two masking agents was used. To each sample, 30 mg of hydroxylamine hydrochloride were added before the buffer. Also, 30 mg of potassium cyanide were added after the sample was buffered.

The precision with which calcium was determined by

titrating with EDTA is indicated in Table 5.

Sea water was run eleven times with a range of 378 to 390 ppm calcium and an arithmetic average of 383. The standard deviation and relative standard deviation (coefficient of variation) are 3 ppm calcium and 0.9 percent, respectively.

TABLE	5
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PRECISION	0F	REF	LIC	CATE	TITRATION	FOR
CA	LC1	UM	IN	SEA	WATER	

Trial	Volume	0.026N EDTA (m1)		Calcium (%)		Calcium (ppm)
1		6.21		0.0383		383
2		6.20		0.0384		384
3		6.21		0.0383		383
4		6.20		0.0384		384
5		6.15		0.0380		380
6		6.34		0.0390		. 390
7		6.16		0.0380		380
8		6.11		0.0378		378
9		6.21		0.0383		383
10		6.22		0.0383		. 383
11		6.26		0.0386		386
Range	••••	• • • • • •	•••	• • • •	• •	. 378-390
Arithmetic M	dean (X)	• • • • • •	•••		• •	. 383
Standard Dev	viation	(S.D.)	•••		••	. 3.0
Coefficient	of Vari	ation (C.V.)	in %.		• •	. 0.9

PARTITION COEFFICIENT THEORY

General

Partition coefficient relationships are specific statements of the more general law which governs the distribution of components between phases (liquid-liquid, liquid-solid). These relationships are based on the observation that a growing crystal traps minor element impurities in its structure. The amount of impurities trapped in this way is related to the amount of the impurity in the fluid from which the crystal is growing. The ratio of the amount of the impurity in the liquid to the amount trapped in the solid is called a partition coefficient. If the partition coefficient is known, then a measurement of the amount of the trace element in the solid will enable one to compute the amount that existed in the fluid when the crystal was growing.

These partition or distribution coefficients are dimensionless constants and are characteristic of each mineral species and each chemical element for a given set of conditions. These coefficients are dependent upon: (1) temperature, (2) pressure, (3) composition of the

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solid phase, and (4) major changes in the composition of the liquid. They are independent of: (1) concentration of the trace component, as long as the concentration is low, and (2) presence of other trace elements in the system.

The equilibrium distribution of the trace element between the coexisting liquid and solid phase tends to approach either of two limiting laws: (1) homogeneous distribution where the trace element is uniformly and homogeneously distributed throughout the solid, or (2) logarithmic distribution in which the distribution is inhomogeneous, with the trace element being more concentrated near the center or near the surface of the crystal. This is an equilibrium between the crystal and solution which is attained for the surface only and not the entire crystal.

Homogeneous Distribution

If the entire crystal is in equilibrium with the solution, the distribution of the trace element between the solid and coexisting liquid solution follows the Berthelot-Nernst distribution law:

$$k = \frac{C_s}{C_1}$$
(4)

k = partition coefficient
C_s = concentration of the trace
 component in the solid

C₁ = concentration of the trace component in the liquid

In the application of this law it is assumed that: (1) the liquid and solid solutions are dilute enough with respect to the microcomponent so that variations in its content do not affect the thermodynamic properties of the solutions, (2) the components are in equilibrium both between phases and throughout each phase, and (3) the microcomponent distributed between the phases is in the same ionic or molecular state.

A generally more convenient form of the distribution law was introduced by Henderson and Kracek (1927). This form of the homogeneous distribution law is particularly useful in cases involving the substitution of a trace ion for a major ion:

$$D = \frac{\left|\frac{\mathrm{Tr}}{\mathrm{Cr}}\right|_{\mathrm{S}}}{\left|\frac{\mathrm{Tr}}{\mathrm{Cr}}\right|_{\mathrm{I}}}$$
(5)

D = homogeneous partition
 coefficient

Tr = concentration of "tracer" or microcomponent

Cr = concentration of "carrier"

or macrocomponent

 $\left(\frac{Tr}{Cr}\right)_{s}$ = ratio of tracer to carrier in the solid phase $\left(\frac{Tr}{Cr}\right)_{1}$ = ratio of tracer to carrier in the liquid phase

For values of D greater than unity, the precipitate is enriched in the trace element; for values of D less than unity, the solution is enriched in the trace element.

Logarithmic Distribution

A second condition of precipitation may be realized in which equilibrium between crystal and solution is attained for the surface only and not the entire crystal. Doerner and Hoskins (1925) considered the case in which it becomes increasingly difficult, for a crystal growing from a solution or melt, to maintain equilibrium between the interior of the crystal and the liquid. This metastable equilibrium results in large part because of the slow rate of diffusion of ions through solids.

The Doerner-Hoskins equation may be written in the form:

$$\log \frac{\left(\frac{m_{Tr}^{L}++\right)_{i}}{\left(\frac{m_{Tr}^{L}++\right)_{f}}} = K \log \frac{\left(\frac{m_{Cr}^{L}++\right)_{i}}{\left(\frac{m_{Cr}^{L}++}{m_{Cr}^{L}++}\right)_{f}}$$
(6)

K = logarithmic partition coefficient

$$\begin{pmatrix} m_{Tr}^{L} + + \end{pmatrix}_{i} = \text{concentration of trace ion in the} \\ \text{initial solution} \\ \begin{pmatrix} m_{Tr}^{L} + + \end{pmatrix}_{f} = \text{concentration of trace ion in the} \\ \text{final solution} \\ \begin{pmatrix} m_{Cr}^{L} + + \end{pmatrix}_{i} = \text{concentration of carrier or macro-} \\ \text{component in initial solution} \\ \begin{pmatrix} m_{Cr}^{L} + + \end{pmatrix}_{f} = \text{concentration of carrier or macro-} \\ \text{component in final solution} \end{cases}$$

If K is greater than unity, the precipitate is enriched in trace element. If K is less than unity, the solution is enriched in the trace component.

Some of the major assumptions underlying the application of this partition coefficient are: (1) the dissolution and recrystallization of the precipitate are negligible, (2) the diffusion of the microcomponent in the solid phase is negligible, and (3) the precipitate forms from an essentially saturated solution.

DISCUSSION AND RESULTS

Coprecipitation of Calcium, Strontium, and

Barium in Aragonite

The coprecipitation of calcium, strontium, and barium with aragonite precipitated from sea water was carried out at 25°, 35°, and 45° C. All experiments were performed in a constant temperature water bath. Forty-two isothermal and isobaric experiments were conducted in which the effects of the following were investigated: (1) temperature, (2) sodium carbonate addition to the sea water, and (3) length of time for precipitation. Table 6 lists the experimental conditions and results for the distribution of calcium and strontium between aragonite and sea water. Table 7 is also a tabulation of the experimental parameters and distribution coefficients for calcium and barium between aragonite and sea water.

For each flask in each run, apparent values were calculated for the partition coefficient D, according to the homogeneous distribution law, and for K, according to the logarithmic distribution law. These values are included as part of Table 6 and Table 7. The precision

10 12 12 12 14	ЧУХ4V078	Run Num- ber
8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Temperature (°C)
160 200 200 160 200	120 200 180 200 200 200 160 180	Na2CO3 Added (mg/250 m1)
383 383 380 382 385 385 385	383 383 384 383 385 385	Calcium in Starting Solution (ppm)
304 276 254 214 191	306 298 248 230 209 188 181	Calcium in Final Solution (ppm)
0.21 0.28 0.33 0.39 0.44	0.20 0.22 0.31 0.40 0.40 0.51	Fraction Calcium Precipitated
7.9 7.2 7.2	7.9 7.1 7.1 7.1 7.1	Strontium in Starting Solution (ppm)
υ υ υ υ υ υ υ υ υ υ υ υ υ υ υ υ υ υ υ	2.0 89615990	Strontium in Final Solution (ppm)
0.24 0.31 0.45 0.51	0.24 0.26 0.42 0.48 0.56 0.62	Fraction Strontium Precipitated
9,500 9,500 9,500 9,500	10,100 10,100 10,100 10,000 10,100 10,200 10,200	Strontium in Precipitate (ppm)
1.17 1.15 1.18 1.22 1.22	1.23 1.23 1.25 1.25 1.27 1.29 1.32 1.37	K ^A Sr ⁺⁺
1.19 1.19 1.23 1.26 1.31 1.40	1.26 1.32 1.35 1.59	$D_{Sr^{++}}^{A}$

EXPERIMENTAL CONDITIONS AND DISTRIBUTION COEFFICIENTS FOR STRONTIUM AND CALCIUM PRECIPITATED IN ARAGONITE FROM SEA WATER TABLE 6

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115 116 117 21 221 23	Run Num- ber
4 4 4 4 4 4 4 4 5 5 5 5 5 5 5 5 5 5 5 5	Temperature (°C)
160 200 200 180 180 180 180	Na2CO3 Added (mg/250 ml)
383 383 383 383 383 383 383 383 383 383	Calcium in Starting Solution (ppm)
309 284 284 198 273 206	Calcium in Final Solution (ppm)
0.19 0.25 0.40 0.48 0.48 0.48 0.48 0.47	Fraction Calcium Precipitated
7.9 7.9 8.1	Strontium in Starting Solution (ppm)
3453345556 922363052	Strontium in Final Solution (ppm)
0.22 0.22 0.28 0.28 0.28 0.28 0.28 0.28	Fraction Strontium Precipitated
9,300 9,300 9,200 9,200 9,200 9,200 9,200 9,200	Strontium in Precipitate (ppm)
1.13 1.13 1.13 1.13 1.15	K ^A Sr ⁺⁺
1.15 1.20 1.21 1.22 1.24 1.24 1.24 1.24 1.24 1.22	D ^A Sr ⁺⁺

TABLE 6--Continued

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30 32 33 34 35	24 25 28 29	Run Num- ber
\$\$\$\$\$\$\$\$ \$\$ \$\$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	25 25 25 25	Temperature (°C)
160 180 160 180 180	160 180 200 180 200 200	Na2CO3 Added (mg/250 ml)
383 381 380 385 385 385 382	383 383 381 384 385	Calcium in Starting Solution (ppm)
341 328 315 308 295 265	345 326 297 284 266	Calcium in Final Solution (ppm)
0.11 0.14 0.17 0.20 0.22 0.22 0.30	0.10 0.15 0.22 0.22 0.26 0.31	Fraction Calcium Precipitated
34444 363351	44 44 44 24 44	Barium in Starting Solution (ppm 10 ⁻³)
31 31 26 23 22 22	30 27 18 16 10	Barium in Final Solution (ppm 10 ⁻³)
0.24 0.31 0.40 0.47 0.52 0.52	0.25 0.37 0.44 0.56 0.64	Fraction Barium Precipitated
99 106 107 105 113 101	109 112 111 111 112 111 111 109	Barium in Precipitate (ppm)
2.41 2.49 2.58 2.80 2.98 3.29	2.75 2.88 2.78 3.31 3.35 3.88	K ^A Ba++
2.62 2.79 3.17 3.48 5.10	3.03 3.39 4.52 7.15	D ^A Ba++

TABLE 7

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EXPERIMENTAL CONDITIONS AND DISTRIBUTION COEFFICIENTS FOR BARIUM AND CALCIUM PRECIPITATED IN ARAGONITE FROM SEA WATER

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41 42	Run Num- ber
44444 55555555555555555555555555555555	Temperature (° C)
160 180 160 160 200 200	Na_2CO_3 Added (mg/250 ml)
387 383 383 382 384 384 381	Calcium in Starting Solution (ppm)
344 296 286 276 244	Calcium in Final Solution (ppm)
0.11 0.22 0.25 0.25 0.25 0.28 0.32 0.32	Fraction Calcium Precipitated
444 44 44 44 44	Barium in Starting Solution (ppm 10 ⁻⁹)
33 28 19 14 13	Barium in Final Solution (ppm 10 ⁻³)
0.25 0.33 0.60 0.68	Fraction Barium Precipitated
101 96 98 98 96	Barium in Precipitate (ppm)
2.44 2.34 2.83 2.81 2.81 2.84	K ^A Ba++
2.67 3.52 3.52 4.53 4.53	D ^A Ba++

TABLE 7--Continued

with which the distribution coefficients, $K_{Sr^{++}}^A$, $D_{Sr^{++}}^A$, $K_{Ba^{++}}^A$, and $D_{Ba^{++}}^A$ can be measured was taken as the sum of all analytical uncertainties. To make the best estimate for which distribution law was most closely followed, during each individual run, the apparent values of D and K were plotted versus the fraction of total calcium which had precipitated. The constancy of either D or K with fraction calcium precipitated was taken to indicate that individual crystals of aragonite are either homogeneous throughout, or they follow a logarithmic composition variation with crystal radius.

The distribution law most closely followed in the partition of calcium and strontium between aragonite and sea water is seen on inspection of Figures 2 through 4. These figures are the apparent values of $K_{Sr^{++}}^A$ and $D_{Sr^{++}}^A$ versus the percent of total calcium precipitated with aragonite at 25°, 35°, and 45° C. At 25°, 35°, and 45° C the apparent values of both K and D increase with an increase in the fraction of calcium precipitated. However, D values increase at a much greater rate than the K values. Because neither K nor D is strictly independent of the percent of calcium carbonate which had precipitated, it is assumed that neither equation (2) nor equation (3) fully expresses the partition mechanism. The slight increase of K values as compared with those values of D at a given temperature suggest that the limiting case of





APPARENT VALUES OF K^A_{Sr}++ AND D_{Sr}++ VERSUS PERCENT OF TOTAL CALCIUM PRECIPITATED IN ARAGONITE AT 25° C









APPARENT VALUES OF $K_{Sr^{++}}^A$ and $D_{Sr^{++}}^A$ versus percent of total calcium precipitated in

ARAGONITE AT 45° C

the logarithmic distribution law is a better approximation to the results of these precipitation experiments.

McIntire (1963) states:

The homogeneous and logarithmic distributions may be considered limiting cases. In any system in which crystals are growing from a liquid, particularly in nature, the distribution followed may well fall between these two extremes.

Previous studies (Holland et al., 1963 and 1964) of the coprecipitation of strontium with aragonite and calcite at 90° and 100° C showed that early formed crystals do not react with the solution, and that only surface equilibrium is maintained between the precipitates and the solution. Therefore, the logarithmic distribution coefficient adequately describes the $(Ca,Sr)CO_3$ solid solution at approximately 100° C. This being the case at higher temperatures, then the logarithmic law almost certainly would be followed at the lower temperatures of this study as reaction and diffusion rates are lower.

Figures 5 through 7 are graphic representations of the data of Runs 24 through 42. All three figures are the apparent values of both distribution laws plotted against the fraction of calcium which had precipitated as aragonite in the experiments.

At all temperatures investigated the logarithmic distribution appears to be followed. The distribution of calcium and barium between sea water and precipitated aragonite approaches the logarithmic law less closely







APPARENT VALUES OF K^A_{Ba++} AND D^A_{Ba++} VERSUS PERCENT OF TOTAL CALCIUM PRECIPITATED IN ARAGONITE AT 35° C



FIGURE 7

APPARENT VALUES OF K^A_{Ba++} AND D^A_{Ba++} VERSUS PERCENT OF TOTAL CALCIUM PRECIPITATED IN ARAGONITE AT 45° C

than that of calcium and strontium. This is demonstrated by the dependency of $K_{Ba^{++}}^A$ upon the total calcium precipitated. There is an increase of $K_{Ba^{++}}^A$ as the total amount of solid phase increased, and this rate of change is greater than in the case of $K_{Sr^{++}}^A$. The reason for the closer conformity of $K_{Sr^{++}}^A$ to the logarithmic distribution law may be the larger size of the barium ion compared to the strontium ion which causes different diffusion rates in the growing crystal.

Cloud (1962) has demonstrated that aragonites precipitated from sea water by the removal of carbon dioxide contain approximately 100 to 500 ppm barium. These experiments were run over periods of many months. The amounts of barium found in the aragonites of the current study range from 96 to 113 ppm and are in agreement with the findings of Cloud (1962). The strontium content found by Cloud (1962) was 5,000 to 10,000 ppm. These values are in good agreement with the strontium content of the aragonites from this series of experiments. The strontium content ranges from 9,200 to 10,200 ppm.

Trace elements may occur in minerals in several ways. In the common case, the trace element substitutes for a normal atom at a regular lattice position. Less commonly, interstitial solid solution may occur or the trace element can occupy a position between regular lattice points of the mineral. Other possible modes of occurrence

for trace elements in minerals are surface adsorption and occlusion.

In the case of surface adsorption, foreign ions are held in a diffuse layer at the surface of the mineral as a result of the attraction of the surface atoms. The importance of surface adsorption increases with surface area and thus is particularly important where the mineral occurs as an aggregate of very fine grains approaching colloidal dimensions.

The solution chemistry of barium as well as strontium is not complicated by extensive complexing and neither cation undergoes a change in oxidation state (Cotton and Wilkinson, 1967). The three methods that have been used to precipitate aragonite from sea water (Cloud, 1962; Kinsman, 1965) all indicate by their similar trace element contents that general equilibrium between the solid and liquid phase has been maintained. The coprecipitation of strontium and barium with aragonite probably involves simple substitution for calcium atoms at regular structural positions as well as interstitial incorporation of trace ions. That interstitial incorporation is an important mechanism is indicated by the decrease in the partition coefficients with increasing temperature.

Surface adsorption or occlusion of strontium and barium within aragonite might be indicated by an appreciable change in the K and D values with a reduction in crystal

To test this idea, aragonites from Run 6 and Run 26 size. were placed in agate mortars. A few drops of five percent hydrochloric acid were placed on the aragonite. The precipitate was ground in the mortar for thirty seconds and then washed with distilled water and redried. A visual estimate was made that the particle size had been reduced by fifty percent and the weight loss was approximately twenty-five percent on both precipitates. The partition coefficients were calculated once again on the aragonite. The original value, before grinding, on Run 6 was $K_{Sr^{++}}^A =$ 1.32 and on Run 26 was $K_{Ba}^{A} + = 2.78$. The recalculated values are: Run 6, $K_{Sr^{++}}^A = 1.31$ and Run 26, $K_{Ba^{++}}^A = 2.78$. These values are within the actual measured analytical error of ± 0.02 and indicate that the compositional gradient of strontium and barium along the crystal radius is within limits of precision of the experiments.

The absolute amount of strontium was found to be larger than barium by a factor of one hundred. A possible explanation lies in the physical size of the strontium and barium ions. The ionic radius for strontium (+2) is 1.13 Å, barium (+2) is 1.35 Å, and calcium (+2) is 0.99 Å. The difference between ionic radii of calcium and strontium is twelve percent and between calcium and barium is twentyseven percent. Barium is some nineteen percent larger than strontium and the large difference in ionic radii between barium and calcium prevents barium ions from entering the aragonite structure in very large amounts. Figure 8 is a plot of average $K_{Sr^{++}}^A$ values from Table 6 versus temperature of precipitation. Figure 9 is a graph of the average $K_{Ba^{++}}^A$ values of Table 7. The ninety-five percent confidence interval for $K_{Sr^{++}}^A$ values are shown on Figure 8.

The average K_{Sr}^A ++ value for aragonites at 25° C, of Figure 8, is 1.29 ± 0.04. Five of the measured values are within the stated limits at 25° C. At 35° C, K_{Sr}^A ++ = 1.20 ± 0.03 and four of the six measurements are within the stated limits. At 45° C, K_{Sr}^A ++ = 1.15 ± 0.02 with eight of the nine values within the ninety-five percent interval.

The average K_{Ba}^{A} ++ value for aragonites at 25° C, of Figure 9, is 3.16. At 35° C, K_{Ba}^{A} ++ = 2.78. At 45° C, K_{Ba}^{A} ++ = 2.71. Since the numerical value of each K_{Ba}^{A} ++ value is more strongly dependent upon the absolute amount of precipitate than the K_{Sr}^{A} ++ values, the limit of ± 0.03 is the analytical uncertainty of each K_{Ba}^{A} ++ value and not the average at each temperature.

The values of K_{Sr}^A and K_{Ba}^A of Figures 8 and 9 indicate an inverse relationship with temperature and can be partially explained by surface equilibrium. Some of the trace elements in aragonite may be present as interstitially trapped ions. The nonsubstitutional incorporation of these ions would be expected to decrease with increasing temperature as diffusion rates away from the growing crystal









surface would increase. Surface equilibrium would be easier to attain at higher temperatures which would mean a decrease in surface adsorbed ions.

Comparison to Natural Aragonites

The mean annual temperatures typical of modern carbonate sedimentation areas fit within the temperature range (25-45° C) investigated. For example, the average temperature of bank water west of Andros Island does not vary much during the year (Cloud, 1962). During January through March, water temperatures range between 24° C and a little over 25° C. Temperatures rise to an average of about 31° C during July and August. Average temperature declines to approximately 24° C in November.

Modern marine carbonate samples were supplied to the author by Dr. William Ham, of the Oklahoma Geological Survey. All samples are essentially one hundred percent aragonite. The oolitic sand as well as other samples were hand picked, under the microscope, for impurities before analysis. All samples were treated with chlorox for twenty-four hours in order to remove any organic matter. Because the nucleus of many oolites is made of all types of materials, the oolite sample was placed in an agate mortar and slightly crushed. The outer portions were considered to be pure aragonite and were hand picked after crushing. The outer portion or shell was re-examined. Tables 8 and 9 are samples of and analytical data for

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RECENT MARINE CARBONATE SAMPLES

Sample	Location	
Cymopolia	Dasycladacean Algae, Bermuda	
<u>Halimeda</u>	Codiacan Algac (green algae), Bermuda	
Oculina	Stony coral, North Lagoon (50 feet deep), Bermuda	
Porites	Stony coral, Harrington Sound (6 feet deep), Bermuda	
Acropora palmata	Stony coral, Dry Rock reef (2 to 5 feet deep), Key Largo, Florida	
Oolitic sand	South Cat Cay, Bahamas	

Sample	Туре	Mineralogy ^a	Strontium (ppm)	Barium (ppm)
A	Algae	Aragonite	10,250	14
В	Algae	Aragonite	10,000	20
С	Stony Coral	Aragonite	5,400	10
D	Stony Coral	Aragonite	8,100	8
Ε	Stony Coral	Aragonite	6,800	6
F1	Oolite (bulk) ^b	Aragonite	10,000	10
F2	Oolite (shell) ^C	Aragonite	10,100	10

TABLE 9

ANALYTICAL DATA FOR RECENT MARINE CARBONATE SAMPLES

^aX-ray data.

^bHand picked.

^CHand picked outer portions after slight crushing.

the recent marine carbonates.

At the present time, it is widely believed that oolites represent the inorganic precipitation of aragonite in nature. Kahle (1965) reported strontium analyses of oolites from Cat Cay, Bahamas as 10,080 ppm. Zeller and Wray (1956) found pseudo-oolites from the Bahamas with 10,600 ppm strontium. Oolites from Hogsty Reef, Bahamas, contained 10,000 to 10,100 ppm strontium (Milliman, 1967). The oolitic sample from the shoal of south Cat Cay, Bahamas (Table 9) contains 10,000 ppm strontium.

The values from this study of the strontium content for inorganically precipitated aragonites are approximately 9,200 to 10,200 ppm. These figures reflect the strontium values of aragonites precipitated from sea water from 25° C to 45° C. Other workers, Odum (1957), Cloud (1962), and Kinsman (1965), who have artificially precipitated aragonites, record similar amounts of strontium (close to 10,000 ppm). All of these observations, both laboratory experiments and analyses of natural material, indicate that an inorganically precipitated aragonite contains approximately 10,000 ppm strontium, in the marine environment.

Aragonite-forming organisms contain a wide range of strontium. The stony corals (Table 9) contain 5,400 to 8,100 ppm strontium. Algal aragonites have high strontium contents, 10,000 to 10,250 ppm strontium. Milliman (1967) presents strontium values of aragonite organisms (green
algae, corals, mollusks, and others) which contain 2,000 to 9,000 ppm.

Kahle (1965) reports forty-three Pleistocene coral specimens from the Florida Keys that contained an average of 10,055 ppm strontium. These corals were one hundred percent aragonite. It is possible, therefore, for some biological specimens to contain strontium values almost identical to those predicted for inorganically precipitated aragonites. In the case of some algae and corals it would appear that any biochemical fractionation affects the incorporation of strontium into the aragonite test very little.

It may be possible to put some limits on the origin of recent marine non-skeletal aragonite grains. If the strontium content of these grains (lumps, pelletoids, and aggregates) were in the vicinity of 10,000 ppm strontium, the origin might be organic or inorganic. However, if the grains were unaltered and the storntium content were below this value, it might be considered organic in origin as no inorganically precipitated aragonites to date contain much less than 10,000 ppm strontium.

The barium content of inorganically precipitated aragonites from this study ranges from 96 to 113 ppm. These values are in agreement with the aragonites Cloud (1962) precipitated from sea water. However, these values differ from the reported values in natural material.

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barium content of inorganically precipitated aragonites from this study ranges from 96 to 113 ppm.

(6) The inverse correlation of the partition coefficients with temperature may be explained partially by the nonsubstitutional incorporation of strontium and barium in aragonite and the surface equilibrium of the trace elements during crystal growth.

(7) The strontium content of recent marine nonskeletal aragonites may be interpreted to some degree in terms of partition coefficients determined in the laboratory. Since no inorganically precipitated aragonite to date contains much less than 10,000 ppm strontium, any non-skeletal aragonite which was unaltered and which contained less strontium might be considered organic in origin.

(8) The barium content of naturally occurring aragonites appears not to conform to the predicted values of determined partition coefficients. The low level of barium content in modern marine aragonites cannot, therefore, be directly interpreted by the results of this study.

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