THE BARIUM CONTENT IN THE CALCAREOUS SKELETAL MATERIALS OF SOME RECENT AND FOSSIL CORALS OF THE HAWAIIAN ISLANDS

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June 1967

ABSTRACT

Seventeen samples of some living Madreporaria corals and fossil corals from a deep drilling core were obtained for determination of their aragonite-calcite ratios and analysis of their barium and calcium contents. The aragonite-calcite ratios were determined with a Temp-Pres D-1, x-ray diffraction unit, and from a standard aragonite-calcite curve obtained by analyzing known mixtures of the two minerals.

Ion exchange methods were utilized to separate barium from calcium and for its concentration to measurable quantities. The barium content was measured with a Perkin-Elmer 303 atomic absorption spectrophotometer utilizing the method of "additions." Determinations of calcium were made with a Beckman DU flame photometer.

X-ray diffraction analyses determined that all the living corals were composed entirely of aragonite. The amount of aragonite in the fossil corals decreases with depth, confirming the theory that age and increasing pressure gradually convert aragonite to calcite and at greater depths complete recrystallization occurs.

The barium concentration in the living corals varied from 5.2 ± 10% ppm to 12.5 ± 6.4% ppm. This variation in barium uptake by coral organisms cannot be attributed to differences in environmental parameters since all samples were taken from the same area. Barium was found to be concentrated from sea water by the skeletons of living corals

in very small amounts. Concentrations ranged from 1.0 to 2.2 times greater than the concentrations of the element in the sea water.

Barium in fossil corals decreased with depth, roughly following the decrease in their aragonite content, suggesting a quantitative relationship exists between barium and the amount of aragonite present. Barium may possibly act similarly to strontium as an inhibitor in the aragonite to calcite conversion. Additional work, however, would be necessary to confirm this with certainty.

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OBJECTIVES, SCOPE, AND SIGNIFICANCE OF RESEARCH

The present investigation was undertaken primarily to determine whether barium is present in the skeletons of living corals and whether a quantitative relationship exists between the barium content and the mineral composition of living and fossil corals. It has been shown by previous work that aragonitic organisms such as corals concentrate strontium in their skeletons--the incorporation of elements with an ionic radius greater than 0.99 Å appears to stabilize the aragonitic structure, a metastable polymorph of calcium carbonate. Barium has a greater ionic radius value than strontium and belongs to the same family of alkaline earth metals. For this reason, it may be similarly concentrated in the aragonitic structure.

In this study an analysis for barium was preferred upon the organic free skeletal materials of living corals and an attempt was made to relate the barium concentration to the degree of interconversion of aragonite to calcite in fossil forms.

The problem was, therefore, focussed on an apparently simple determination of the barium content in the skeletons of living and fossil corals, and the quantitative mineral determination of their aragonite and calcite contents.

The direct determination of trace elements, even with modern techniques and instrumentation, presents a number of

problems. An effective method had to be devised to separate barium, from the abundant calcium and then concentrate it in quantities that could be determined. To accomplish this, several analytical methods were considered, including a gravimetric separation which proved to be non-feasible.

Another objective was to find a feasible and reproducible means of separating barium from calcium by ion-exchange methods. Several ion-exchange methods were investigated and a number of different resins were tried.

The last objective was the quantitative determination of the mineral composition of fossil corals and the effect of depth on their mineral content. To meet this objective, the standard x-ray diffraction methods were utilized.

In summary, this part of the work attempted to determine the degree of aragonite to calcite transition that occurs following deposition of the calcareous remains of fossil Hawaiian corals and the relationship of the barium content of such calcareous deposits to increasing age. A similar study relating to the strontium content in calcareous sediments has been conducted by Siegel (1960).

INTRODUCTION

1. Previous Work

According to Goldberg (1958), "Marine animals and plants can be considered as a huge reaction area for the uptake of dissolved metallic ions." Such marine organisms have the ability to concentrate large quantities of specific ions and to utilize them in building their skeletons. The skeletons of organisms, such as corals, molluscs, and algae, are eventually abraded by wave action and are broken down to small fragments, contributing to the sediments of the nearshore area, as well as to turbidite deposits of the deeper sea.

The chief mineral of such calcareous deposits is aragonite and, according to Lowenstam (1954), the total quantity of aragonite being laid down in shallow water deposits throughout the ocean probably exceeds the amount of calcite. On the deep sea floor, however, the deposits are mostly calcite because of the predominance of pelagic foraminifera and coccoliths.

Pressures, and mainly temperatures, greater than those existing at the surface of the earth bring about the crystallographic inversion of aragonite to calcite. Thus, fossil calcareous sediments at great depth are composed mainly of calcite (Kobayashi, 1951 a, b; Jamieson, 1953; and MacDonald, 1956). This crystallographic alteration also proceeds at the surface of the earth under normal temperature and pressure,

but at a slower speed (Lowenstam, 1954). In addition, skeletons of different organisms show different susceptibilities to this process of recrystallization, with corals having the highest susceptibility, followed by molluscs, foraminifers, and echinoids. The differences in the degree of susceptibility has been attributed to differences in the concentrations of certain elements in the calcareous skeletons of these marine organisms. (Pilkey and Goodell, 1963).

Extensive studies have indicated that three factors are responsible for the inclusion of trace elements in the skeletons of calcareous organisms--skeletal mineralogy, water temperatures and the phylogenetic level of organisms. (Chave, 1954; Thompson and Chow, 1955; Swan, 1956; Odum, 1957; Lowenstam, 1959; Turekian and Armstrong, 1960; Pilkey and Goodell, 1963).

Thus, in scleractinian corals it was found that there was a tendency for trace elements such as Mn, Fe, Mg, Na, K, Sr, to be incorporated in various amounts into the skeletal material in higher concentrations than found in the adjacent sea water (Harris and Almy, 1964). Similarly, extensive studies by Clarke and Wheeler (1922), and Chave (1954), found that calcitic and aragonitic organisms concentrated magnesium in their skeletons.

Strontium was found in various quantities in the aragonitic skeletons of many marine organisms (Thompson and Chow, 1955; Odum, 1957; Lowenstam, 1959; Siegel, 1960; and

David, 1962). It was observed that the strontium-calcium ratio in such calcareous materials diminishes markedly when recrystallisation from aragonite to calcite occurs and that strontium is nearly absent when the complete inversion occurred (Odum, 1951, 1957; Thompson and Chow, 1955; Bowen, 1956; Lowenstam, 1954, 1961, 1963; Turekian and Armstrong, 1960; and Pilkey and Hower, 1960). On the basis of this, Siegel (1960) suggested that the strontium content in the skeletal material of marine organisms is a factor which inhibits the alteration of aragonite to calcite under natural geologic conditions, and such alteration rapidly takes place when most of the strontium is removed.

That strontium is exclusively held by aragonitic organisms has for a long time intrigued the imagination of geochemists seeking an explanation to this chemical-mineral relationship.

Work by Wray and Daniels (1957) presented experimental evidence that the calcium site in the aragonite lattice preferentially incorporates minor elements with ionic radii equal to, or greater than, that of calcium (0.99 A). This incorporation of elements with ionic radii greater than 0.99 A apparently tends to stabilize the aragonite structure, which is a metastable polymorph of calcium carbonate. Hence, strontium ion with an ionic radius approximately 6% greater than that of calcium and an electronegativity value equal to that of calcium is preferentially incorporated into the aragonitic structure.

According to Pilkey and Goodell (1963), the calcium in aragonite exhibits nine-fold coordination with oxygen, while in the calcite the calcium is six coordinated. In aragonite, the large nine coordinated site is more favorable for the large strontium ion while the smaller coordinated site in calcite would be rendered unstable by a large strontium ion. It has been shown, therefore, that strontium plays a very important role in the stability of the aragonite crystal.

Surprisingly, very little work has been done on barium and its possible role on the skeletal mineralogy of corals or other calcareous organisms, even though barium because of its closely related chemical properties to strontium, may be also taken up by aragonitic organisms.

Only Bowen (1956) studied both the strontium and barium content of marine organisms, (algae, molluscs, shells and corals) and has shown that barium is, indeed, concentrated in certain calcareous organisms; however, he made no distinction as to whether it is concentrated in the skeletal or the organic portion of these organisms. He did, however, show that certain plants such as brown algae favor the uptake of strontium and barium in preference to calcium, and that molluskan shells discriminate against them.

Prior to Bowen's work, only marine molluscs had been analyzed for strontium by Vinogradov (1937) and for barium by Borovik-Romanova (1939), but again with no differentiation in the area of concentration.

MATERIALS AND PROCEDURES

1. Sampling and Preparation of Specimens

A. Living corals

Samples of shallow water living Madreporaria corals were collected at Kaneohe Bay of the island of Oahu and from depths of 30 to 50 feet along the west side of Coconut Island. The samples are representative of the fauna of this area and constitute some of the most abundant shallow water corals to be found in the Hawaiian Islands. The corals collected, identified and used for analysis are listed in Table I.

Samples of living corals were placed in hydrogen peroxide for two days to destroy all of the organic matter. The samples were then cleaned, air-dried, and crushed manually using an agate mortar and pestle. They were then placed in porcelain crucibles and heated in an oven at a temperature of 350°C for 12 hours, transferred to sterilized vials and cooled in a desiccator. At this stage it was assumed that the organic matter was completely oxidized.

B. Fossil corals

Fossil coral samples were obtained from different sections of a deep hole core recently drilled at Ewa Beach, island of Oahu by the Hawaii Institute of Geophysics. Table II gives the depths from which the different samples were taken.

TABLE II. DEPTHS OF THE EWA CORE #1
FROM WHICH FOSSIL CORALS WERE COLLECTED

Sample	Depth in feet	Sample	Depth in feet
1	3	7	328
2	31	8	384
3	62	9	438
4	127	10	500
5	199	11	734
6	265	12	788

Figure 1 shows a cross-section of the Ewa #1 core (from T. K. Chamberlain, Personal Communication 1966) and the locations from which samples were obtained.

Fossil corals were treated in the same manner as the living corals to destroy any organic matter that might have been present.

E. Analytical Methods

A. X-ray diffraction studies

Outline of the method. Measurement of relative intensities of x-ray reflections provided the basis for the quantitative determinations of the mineral composition of the living and fossil corals.

According to Lowenstam (1954), the ratios of the respective principal peaks of calcite and aragonite should vary linearly with the relative percentage of

these minerals, assuming there is no preferred orientation, absorption, or other interferences. This method, simple and reasonably precise, has been outlined in a paper by Turekian and Armstrong (1960), and by Davies and Hooper (1963).

Preparation of Standards. The standards used for preparing a calibration curve were made from pure crystal calcite and pure aragonite mixed in different ratios. The coral species Pocillopora was used as the source of aragonite.

Mounting of the Samples. Each of the standards and the unknown samples was ground in a mortar, passed through a No. 100 sieve, and thoroughly mixed with a spatula. The samples were mounted into a rectangular central depression, approximately 1 mm deep and 30 mm by 30 mm in an aluminum holder. The tops of the loosely packed samples were gently levelled with a spatula at the rim of the holder. Excessive packing was avoided because of possible effects on the orientation of the crystals.

Apparatus and operating procedures. X-ray diffraction data were obtained by the use of a Temp-Pres XD-1 model proportional counter diffractometer, on which a goniometer spectrometer equipped with a geiger counter was mounted. Two patterns were run on each mixture at a scanning rate of 1 degree (2θ) per minute. A 1° beam slit, 1° detector slit, and nickel-

filtered copper Ka radiation were used. The unit was operated at 15 Kv and 25 ma. The (111) aragonite peak at 26.2, 2θ (d-spacing 3.40 A) and the (104) calcite peak at 29.4 (d-spacing 3.03 A) were used in the analysis. Maximum peak intensities were taken on the major reflection of each mineral from the recorder chart and the ratemeter. Similar runs were made for all recent and fossil coral samples.

B. Calcium and barium determination

Preparation of standards and unknowns. All the reagents used in this investigation were of analytical grade. A stock solution of calcium, 500 parts per million (ppm) was prepared by dissolving 1250.9 mg of dry calcium carbonate in 10 ml of 6N hydrochloric acid (2:1) and diluting it to one liter. Similarly, a stock solution of barium, 500 ppm was prepared by dissolving 718.4 mg of dry barium carbonate in 10 ml of 6N hydrochloric acid and diluting to one liter.

Aliquots of these stock solutions were diluted in order to prepare other standards from which working curves were made. Error may be introduced by using very dilute solutions of known standards after they have been left standing longer than 2 to 3 days. Usually an error of 2 to 3% will result from such solutions because of the absorption of the metal in solution by the walls of the container (Perkin-Elmer Co., 1965). Such errors, however, were avoided by using fresh sets

of standards each time an analysis was performed, and by running triplicate analyses and averaging the results.

Ten gram samples of living and fossil corals were dissolved in 100 ml of 5% HCl. The solutions were filtered into volumetric flasks and diluted to a liter. Filters were dried, weighed and the weight of the residue was calculated. The weight of the filtered residues was insignificant (usually less than 2 mg). The solutions were thoroughly mixed and used for separation by ion-exchange methods.

Instrumentation. Flame photometry and atomic absorption spectrophotometry were the two methods utilized for the analysis of calcium and barium, respectively. The instruments used were a Beckman DU flame photometer for calcium and a Perkin-Elmer 303 atomic absorption spectrophotometer for barium. The sensitivity of the Beckman DU flame photometer is more than adequate for the calcium's range of concentrations. Phosphorus, which is known to interfere in the determination of calcium by this method, was not present in significant amounts.

The sensitivity for the determination of barium with the Perkin-Elmer 303 atomic absorption spectrophotometer is about 3 ppm barium for 1% absorption and the detection limit is better than 1 ppm in aqueous or weak acid solutions and in the absence of interfering ions. Aluminum or phosphate, the ions that usually interfere in the determination of barium, are not present

in the skeletons of corals in detectable quantities, so interference effects were insignificant.

The instrumental parameters used throughout the determinations of calcium and barium are listed in Table III.

"Additions" method. This method is usually employed when samples either contain an unknown concentration of an element known to interfere with the analysis of a particular metal, or contain a non-interfering ion in very high concentrations.

In the analysis of barium by atomic absorption spectrophotometry, calcium or strontium do not interfere; that is, they do not absorb light in the same wavelength band. Other elements such as aluminum and phosporus that do interfere were not present in the coral samples in significant quantities. Calcium, however, in the skeletons of corals, exists in such large amounts that the intensity of the flame is altered, thus, making the direct determination of other minor elements impossible.

Suppression of such flame alteration requires almost complete removal of the interfering ion. For this reason, ion-exchange techniques described in the following section were employed for the separation of barium from calcium. Eluted fractions from such separations containing mostly barium and very little calcium,

TABLE III. INSTRUMENTAL PARAMETERS USED IN THE DETERMINATION OF CALCIUM AND BARIUM

	Calcium	Barium
Instrument	Beckman DU Flame Photometer	Perkin-Elmer 303 Atomic Absorption Spectrophotometer
Oxygen	14.00 psi	
Air Pressure		12 psi
Acetylene Pressure	---	9
Hydrogen Pressure	4.5 psi	---
Wavelength	554	276.2
Scale	0-100	10X
Source	---	9
Gain	---	5.2
Slit Width	.02	3
Range	---	Visual
Selector	0.1	---
Phototube	Blue	---
Resistor	2	---
Photomultiplier	Full	---
Zero Suppression	1	---
Bias	3	---
Sample Uptake (Rate in ml/min)	2	2

were concentrated and analyzed by atomic absorption spectrophotometry. To further eliminate other possible effects of interference from the remaining calcium or other ions present in solution, the method of "additions" was employed.

This "additions" method is based on the assumption that a linear relationship exists between instrumental readings and concentrations. In accordance with this method, three 5 ml aliquots of each unknown solution were taken. The first was mixed thoroughly with 5 ml of distilled water, the second, with 5 ml of 5 ppm barium solution, and the third, with 5 ml of 10 ppm barium solution. The known additions to the resulting 10 ml solutions were, therefore, 0.0 ppm, 2.5 ppm, and 5.0 ppm of barium. The absorptions of the three solutions were then measured three times with the Perkin-Elmer 303 atomic absorption spectrophotometer. A "working" line of average absorption vs. barium addition was plotted, and the line was extrapolated through zero absorption. The barium concentration in each of the unknown samples is given by the point at which the projected line intersects the zero absorption line (An example of a determination with this method is given on page 39).

C. Separation-Ion exchange method

Outline of the method. The selectivity characteristics of ion-exchange resins enable them to be used in

the separation of many closely related ionic species such as the alkaline earth metals. Passage of a solution containing alkaline earth metals in the ionic form, through a cationic resin results in the retention of those metals. It is then possible to seperate these ions by elution because of the differences in resin retention.

In order to determine whether separation of barium from calcium was possible with ion-exchange resin techniques, the following preliminary investigations were undertaken:

Selection of resin. Cationic resin Dowex 50W-X2 was chosen for the separation. This resin is a strong cation exchange resin. It is a synthetic cross-linked polyelectrolyte to which a large number of ion active groups are attached.) It is the end product of the copolymerization of styrene and divinylbenzene (Dow Chemical Co., 1964).

The fraction of divinylbenzene in the resin particle determines to what extent the ion-exchange resin is free to swell and shrink. The percentage of divinylbenzene in the Dowex 50W-X2 resin that was used is 2 per cent (The per cent cross linkage is indicated by an X number following the name of a particular Dow resin). Dowex 50W-X2 was chosen for the following reasons:

1. The resin remains ionized in both the acid and salt forms and shows ion-exchange behavior over a wide pH range, a property that was very desirable since the coral samples were in acidic solutions.
2. The low percentage of cross linkage in this resin affects several other of its physical-chemical properties favorably. For example, as cross linkage decreases and the resin swells, diffusion of ions within the resin becomes more rapid, giving considerably faster equilibrium rates.
3. Dowex 50W-X2 has selectivity for retaining Ba++ in preference to calcium. Its selectivity for different metals decreases as follows:

   Ba^{++} Pb^{++} Sr^{++} Ca^{++} Ni^{++} Cd^{++} Cu^{++}

   Co^{++} Zn^{++} Mg^{++} (Dow Chemical Co., 1964)

The non-exchanging ions, carbonate ions, do not have an effect on the selectivity. The selectivity of the resin for one ion over another is largely a function of the size of the ion and the barium ion being larger than calcium and strontium is preferentially held by this resin.

Selection of particle size. Different particle sizes of the Dowex 50W-X2 resin were tried in order to determine which one offered better retention of the alkaline earth metals. Although a resin of 200 to 400

mesh size has better total capacity (greatest number of ionic sites per unit volume of resin), a resin of greater particle size 50-100 mesh, was chosen. The greater particle size resin allows a more rapid flow of a solution through it.

Column Construction. For the preliminary investigations in determining whether separation of barium from calcium was possible with the ion exchange technique, a 100-ml pipette was used in place of a column.

Once the feasibility of separation was determined, larger columns were constructed from one-half inch I. D. Pyrex glass with 1/8-inch wall thickness. The five-foot column used was calibrated for its volume and then it was partially filled with 145.6 ml of the resin in wet form. The resin was supported on a bed of glass cloth and glass beads as shown in Figure 2.

Operating procedure and calibration of the separation. The method used in calibrating the separation was the following:

1. The column was filled to the proper level with resin. Then it was backwashed and drained several times to determine the exact resin volume. The height of the resin in the column was 46 inches or 145.6 ml (38 ml/ft).
2. The water in the column was drained to the top of the resin bed. 1,000 ml of feed solution containing known quantities of calcium and

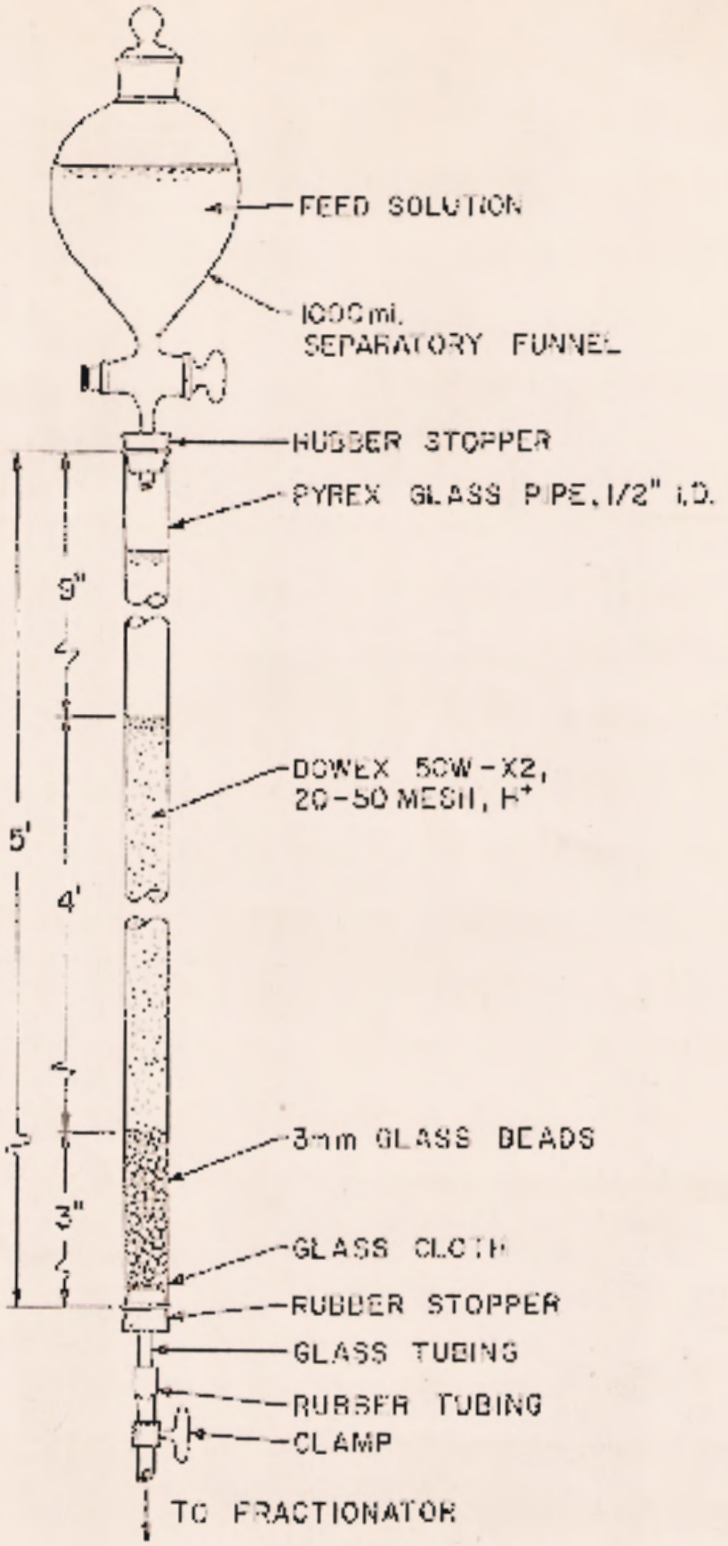

Fig. 2. Ion-exchange column used in the separation of barium from calcium.

barium was gradually and carefully introduced into the column at a constant rate to minimize disturbance of the resin bed. The passage of the feed solution was controlled to a flow rate of 2 ml/minute per square centimeter at 82°F.

3. Fifteen-ml fractions were collected with a Gilson automatic fractionator for analysis of the calcium and barium contents and for determination of the uptake by the Dowex 50W-X2 resin and the resin's loading capacity.

4. The column was rinsed with 400 ml of deionized water. The rinse flow rate was also maintained at about 2-ml per minute per square centimeter.

5. One thousand-ml of a regenerant solution of 5% HCl was then passed through the column at the same flow rate until all the ions under consideration were removed from the resin. Fifteen-ml fractions of the effluent were simultaneously collected to be analyzed for their barium and calcium contents. Enough acid was passed through the column to assure complete elution of the alkaline earth ions.

The procedure was repeated for two more solutions of known concentrations and the separation was calibrated.

D. Concentration and dilution methods

A triple increase in the concentration of barium

was achieved with the described ion-exchange method. In addition, thirty-fold concentration of the barium was achieved by controlled evaporation of the solvent of the combined eluted fractions containing barium.

Calcium was measured directly from the unknown solutions, prior to the separation, but it was also measured in the eluted fractions after the separation, in order to determine the resin's calcium-uptake and degree of recovery. In either case, due to the abundance of the element, dilution methods were employed to bring the calcium concentration within the optimum instrumental range, which for the Beckman DU flame photometer, is 0-200 ppm.

TABLE IV. X-RAY DIFFRACTION PEAK INTENSITIES OF STANDARD CALCITE-ARAGONITE MIXTURES (CORRECTED FOR BACKGROUND)

Sample No.	Composition	26.2° Peak	29.4° Peak	R
1	100% Calcite	--	71.0	100.0
2	95% Calcite 5% Aragonite	3	70.9	95.6
3	90% Calcite 10% Aragonite	3.9	68.3	94.6
4	75% Calcite 25% Aragonite	5.4	66.4	92.5
5	50% Calcite 50% Aragonite	8.5	47.7	84.9
6	25% Calcite 75% Aragonite	12.8	27.2	68.0
7	10% Calcite 90% Aragonite	15.1	12.9	46.1
8	5% Calcite 95% Aragonite	16	8	33.7
9	100% Aragonite	17	--	0.0

The errors involved in the measurement of an unknown sample from this calibration curve depend on the reproducibility of the measured intensity ratios and on the precision of the instrument. Preferred orientation of the crystals when packing into the sample holder is of little significance (Davies and Hooper, 1963). There are some errors involved, however, in the intial preparation of the sample; excessive grinding for instance may convert some of the aragonite to calcite.

In order to test the precision of the Calcite-Aragonite Ratio determination and the reproducibility of the results when small amounts of aragonite are present, standard samples were prepared which contained increasing amounts of aragonite (2.0%, 5.0%, 10%, 50%). Triplicate analyses of the same samples presented the following aragonite percentages:

TABLE V. PRECISION TESTS OF CALCITE-ARAGONITE RATIO DETERMINATION

% Aragonite In Standard	% Aragonite Found			Average % Aragonite	Dev.	% Coeff. of Variation
	1	2	3			
2%	3.0	1.9	2.5	2.5	.48	19.7
5%	4.3	5.7	6.2	5.4	.80	14.8
10%	9.3	9.7	11.1	10.1	1.12	11.0
50%	47.0	48.7	44.5	46.7	2.25	4.8

From this table, it appears that the coefficient of variation is a function of the aragonite content of the sample. Owing to the slope of the calibration curve, the error increases considerably towards both ends of the curve. For intermediate concentrations (10 to 50% aragonite), for example, the coefficient of variation by the described method is approximately 5%. It is considerably higher, however, at greater calcite concentrations and again increases with very low calcite concentrations.

There is considerable uncertainty in the low aragonite concentrations because of high noise to signal in background ratio and this is evident by the shape of the calibration curve; when results of unknown samples showed values of 5.0% or less aragonite, the samples were assumed, therefore, to be composed of pure calcite. Analysis of the unknown samples based on the standard curve, (Fig. 4), showed that all the recent corals are composed entirely of aragonite, while fossil corals from the Ewa core, were found to contain decreasing amounts of aragonite.

In Figure 5 the x-ray diffraction patterns of the first upper six samples of the Ewa core are shown. In Table VI the x-ray diffraction peak intensities for these first six samples are shown.

In Figure 6 the change in the aragonite content of fossil corals with depth is shown.

TABLE VI. X-RAY DIFFRACTION PEAK INTENSITIES OF FOSSIL CORALS FROM THE EWA CORE AND ARAGONITE CONTENT

Sample	Depth in Feet	26.2° Peak	29.4° Peak	R	% Aragonite
No. 1	3	17	6	26.0	96
No. 2	30	12.5	25.9	67.4	77
No. 3	60	8.1	41.0	83.5	52 ± 5%
No. 4	125	4.2	66.7	94.0	12 ± 11%
No. 5	198	3.1	69.8	95.7	6 ± 15%
No. 6	265	0	71.3	---	0

TABLE VII. EXAMPLE OF REPLICATE DETERMINATIONS OF NET LUMINOSITY USED IN THE CONSTRUCTION OF WORKING CURVES FOR CALCIUM; PRECISION OF THE METHOD

	ppm Ca					
Run	10	25	50	75	100	Ave.
1	7.3	15.5	30.5	43.9	58.8	
2	8.0	14.5	30.0	43.6	59.2	
3	8.2	16.0	31.4	44.2	59.6	
Ave.	7.8	15.3	30.6	43.9	59.2	
St. Dev.	.82	1.18	1.54	.34	.33	.82
Coeff. of Var. %	10.51	7.71	5.03	.29	.55	4.51

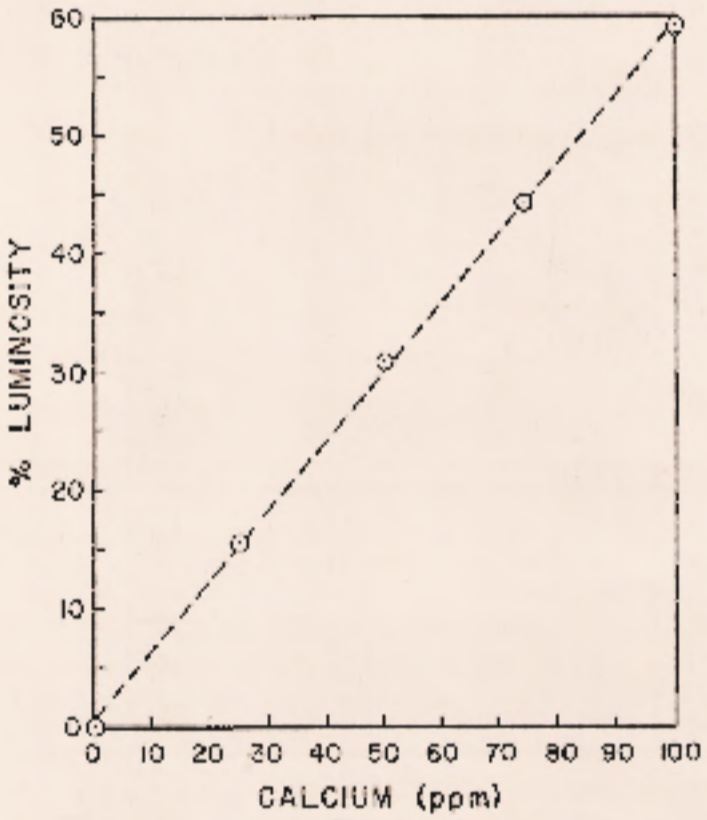

Fig. 7. Example of a working curve used in the determination of calcium.

range, however, for a linear relationship was found between the concentrations of 0-200 ppm Ca and preferably between 0-100 ppm. For this reason, all the unknown samples that were analyzed for calcium were diluted sufficiently in order to fall within the optimum concentration range.

Barium determinations utilizing the method of "additions" were made for known and unknown solutions similarly. An example of a barium determination of a known solution by this method is given in Table VIII, below, to illustrate its precision.

TABLE VIII. EXAMPLE OF REPLICATE DETERMINATIONS OF % ABSORPTION (10x expanded scale) FOR THE DETERMINATION OF BARIUM BY THE METHOD OF "ADDITIONS." PRECISION OF THE METHOD. (Standard sample containing 2.0 ppm barium.)

Run	Standard + Water	Standard + 2.5 ppm Ba	Standard + 5 ppm Ba
1	2.7	10.0	16.8
2	2.5	9.4	17.3
3	2.4	9.9	17.8
Ave.	2.5	9.8	17.3
St. Dev.	.13	.62	1.30
% Coeff. of Var.	5.36	6.32	7.51

An example of a similar determination of the barium content in an unknown sample is given in Table IX.

Extrapolation of the line joining the absorption of the three known additions through the 0-absorption line (Fig. 8), intersects it at a barium concentration value of 0.8 ppm. Equal volumes of known concentrations have been added to the unknown solution, diluting it to one-half its concentration.

TABLE IX. EXAMPLE OF REPLICATE DETERMINATIONS OF % ABSORPTION (10x expanded scale) FOR THE DETERMINATION OF BARIUM BY THE METHOD OF "ADDITIONS." PRECISION OF THE METHOD.
(Sample of Pocillopora meandrina)

Run	Pocil. + water	Pocil. + 2.5 ppm Ba	Pocil. + 5 ppm Ba
1	2.1	9.6	17.6
2	2.3	9.9	17.4
3	2.1	9.7	17.4
Ave.	2.2	9.7	17.5
St. dev.	.37	.81	1.07
% Coeff. var.	16.81	8.35	6.11

The average values of % absorption were plotted against the known additions of barium as in Figure 8.

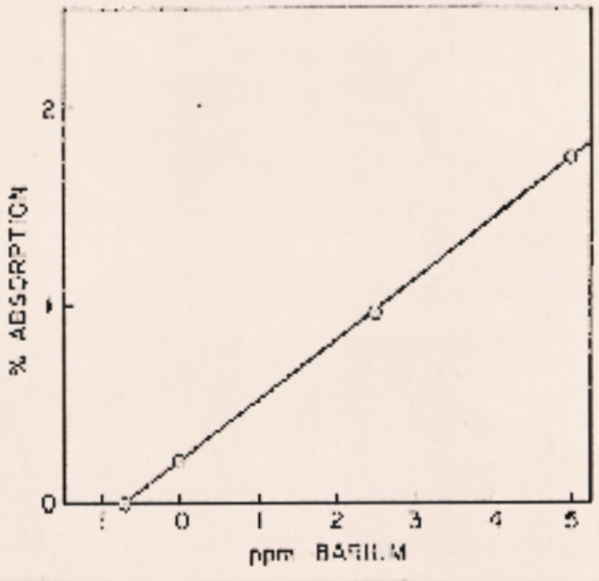

Fig. 8. Example of the determination of barium by the "additions" method.

The actual concentration, therefore, in the unknown solution is twice as much as the one found; or 1.6 ppm barium. From this value and knowing the quantity of coral that was held by the ion-exchange resin, the amount of barium in the unknown dry sample, can be calculated.

3. Separation of Standard Solutions by Ion-Exchange Method

A. Operating capacity of resin Dowex 50W-X8

Figure 9 is the total capacity curve for the ion-exchange resin, and it was obtained by analyzing the first 60 fractions collected (15 ml each), following the passage of the standard solution through the column. The total capacity of an ion-exchange resin is its uptake of a certain ion from a solution, and it is usually expressed as weight of the ion held by a unit volume of resin (Dowex, 1964). Table X gives the calcium and barium concentrations of every other fraction. The total capacity curve and the resin's operating capacity were calculated from these concentrations.

At point A of (Fig. 9) the total capacity curve, the amount of $CaCO_3$ removed by the column in the first forty fractions was:

= .600 liters x 0.1M (Molarity of feed) x 100.09

= 6.0 g of $CaCO_3$ or 2.4 g of calcium

The total amount of $BaCO_3$ removed by the column at point A was:

TABLE X. BARIUM AND CALCIUM CONTENT OF THE COLLECTED FRACTIONS FOLLOWING PASSAGE OF A STANDARD SOLUTION THROUGH THE ION-EXCHANGE COLUMN

Frac. No.	Ca in ppm	Ba in ppm	Frac. No.	Ca in ppm	Ba in ppm
1-29	0	0	46	3,600	3.6
30	25	0	48	3,900	3.9
32	27	0	50	3,950	3.9
34	25	0	52	3,900	3.9
36	27	0	54	3,950	3.9
38	26	0	56	3,950	3.9
40	25	0	58	3,950	3.9
42	720	.7	60	3,950	3.9
44	3,000	3			

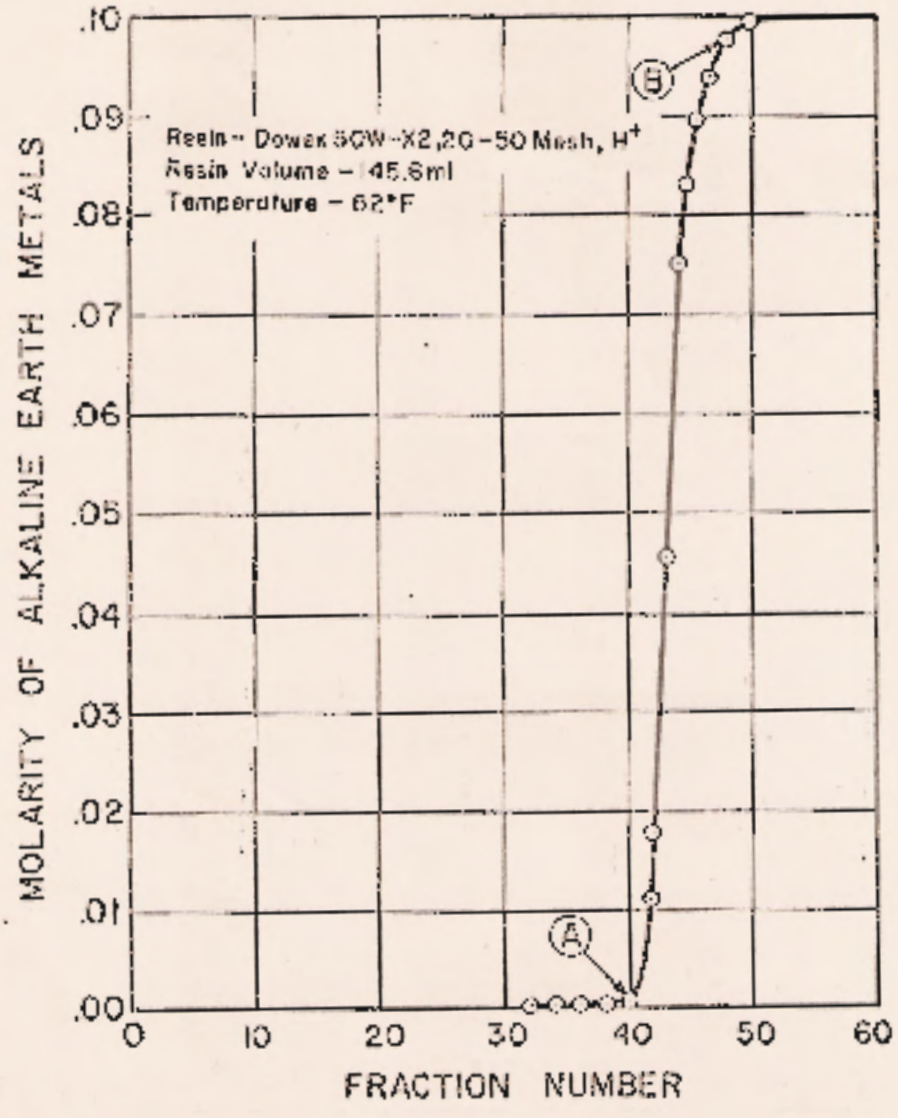

Fig. 9. Total capacity curve of the ion-exchange column.

.6 x 2.912 x 10^{-5}M (Mol. of Ba in feed sol.) x 197.37 = 344.84 x 10^{-5} = 0.00345 g of $BaCO_3$ or 0.00240 g of barium.

Barium was calculated indirectly assuming that its uptake by the resin was equivalent to the uptake of calcium. A small error, therefore, may have been introduced which, however, does not affect significantly the calculation of the resin's total capacity.

The quantities of calcium and barium removed by the column between point A and point B of the total capacity curve were calculated similarly by subtracting the concentration of the two elements in each fraction from their concentration in the feed solution. In Table XI, the total weights of calcium and barium removed by the resin in the first 45 fractions are given.

The operating capacity of the resin at point B on the loading curve is calculated as follows:

$$\frac{\text{Total amount of carbonate}}{\text{Volume of resin}} = \frac{X}{28{,}320 \text{ ml/cu. ft.}}$$

$$\frac{(6.385 + .003) \text{ gr}}{145.6 \text{ ml}} = \frac{X}{28{,}320 \text{ ml/cu. ft.}}$$

$$\text{Operating Capacity } (X) = \frac{6.388 \text{ (gr.)} \times 28{,}320 \text{ (ml/cu. ft.)}}{145.6 \text{ (ml)}} =$$

124.250 grams of CO_3/cu. ft. of resin

TABLE XI. QUANTITIES OF CALCIUM AND BARIUM HELD BY DOWEX 50W-X2 RESIN

Fraction No.	Ca in grams	Ba in grams
1-40	2.4	.002400
41	.0550	.000055
42	.0492	.000049
43	.0190	.000019
44	.0150	.000015
45	.0100	.000010
46	.0060	.000006
47	.0020	.000002
48	.0010	.000001
TOTAL	2.557200	0.002557

B. Analysis of eluted fractions

Following regeneration of the ion-exchange resin with acid, the eluted fractions were collected and analyzed for calcium and barium. Fifty fractions were analyzed for the concentration of calcium and barium. The ratio of the concentration of each fraction to the concentration of the standard feed solution (C_e/C_o), is given in Table XII.

TABLE XII. CALCIUM AND BARIUM CONCENTRATIONS IN THE ELUTED FRACTIONS COLLECTED FOLLOWING REGENERATION OF RESIN

Frac. No.	Ca in ppm	Ca in gr.	Calcium C_e/C_f	Ba in ppm	Ba in gr.	Barium C_e/C_f
1	0	0	0	0	0	0
2	40	.00060	.01	0	0	0
3	1,000	.01500	.25	0	0	0
4	3,600	.05400	.9	0	0	0
5	9,000	.13500	2.25	0	0	0
6	17,000	.25500	4.25	0	0	0
7	26,200	.39300	6.55	0	0	0
8	39,400	.57375	9.87	0	0	0
9	25,400	.38100	6.35	0	0	0
10	9,600	.14513	2.42	0	0	0
11	8,000	.12000	2.00	0	0	0
12	6,920	.10463	1.74	0	0	0
13	5,400	.08100	1.35	0	0	0
14	4,270	.06413	1.07	0	0	0
15	3,000	.04500	.75	0	0	0
16	2,700	.04050	.68	0	0	0
17	2,000	.03000	.50	0	0	0
18	1,320	.01980	.33	0	0	0
19	800	.01200	.20	0	0	0
20	615	.00923	.154	0	0	0

TABLE XII. (Continued) CALCIUM AND BARIUM CONCENTRATIONS IN THE ELUTED FRACTIONS COLLECTED FOLLOWING REGENERATION OF RESIN

Frac. No.	Ca in ppm	Ca in gr.	Calcium C_e/C_f	Ba in ppm	Ba in gr.	Barium C_e/C_f
21	328	.00492	.082	0	0	0
22	255	.00383	.064	1	.000002	.250
23	200	.00300	.005	2.2	.000033	.550
24	82	.00123	.001	3.6	.000054	.900
25	65	.00097	.001	7.0	.000060	1.75
26	41	.00061	.001	9.7	.000146	2.425
27	32	.00040	.001	10.6	.000159	2.65
28	21	.00031	.001	11.5	.000173	2.875
29	0	0	0	12.6	.000189	3.150
30	0	0	0	13.4	.000201	3.350
31	0	0	0	13.6	.000204	3.400
32	0	0	0	13.7	.000206	3.425
33	0	0	0	11.4	.000171	2.850
34	0	0	0	8.8	.000132	2.200
35	0	0	0	7.4	.000111	1.850
36	0	0	0	6.0	.000090	1.500
37	0	0	0	5.4	.000081	1.350
38	0	0	0	4.6	.000069	1.150
39	0	0	0	3.8	.000057	.950
40	0	0	0	2.9	.000044	.725

TABLE XII. (Continued) CALCIUM AND BARIUM CONCENTRATIONS IN THE ELUTED FRACTIONS COLLECTED FOLLOWING REGENERATION OF RESIN

Frac. No.	Ca in ppm	Ca in gr.	Calcium C_e/C_f	Ba in ppm	Ba in gr.	Barium C_e/C_f
41	0	0	0	2.3	.000035	.575
42	0	0	0	1.8	.000027	.450
43	0	0	0	1.8	.000027	.450
44	0	0	0	1.6	.000024	.400
45	0	0	0	1.4	.000021	.355
46	0	0	0	1.0	.000015	.250
47	0	0	0	.8	.000012	.201
48	0	0	0	.8	.000012	.200
49	0	0	0	.5	.000002	.125
50	0	0	0	.5	.000002	.125
TOTAL		2.494120			.002359	

On the basis of these results, an elution curve was constructed (Fig. 10). This graph is helpful in evaluating the degree of separation that was achieved for the standard solutions.

Due to the preference of the resin for barium over strontium or calcium, calcium appears before barium. Even though separation of the two ions was not complete, the calcium concentration in the barium containing fractions was so reduced that it was possible to measure barium.

C. Percent recoveries and efficiency of the method

The separation described was repeated three times. In Table XIII, the recovery percentage for each separation, as well as the average percent recovery for the three values, are given.

4. Calcium and Barium in Living and Fossil Corals

In Table XIV, the calcium and barium contents, the calcium/barium ratio, and the mineral compositions of all the analyzed samples are given. The amount of calcium was determined from working curves in which concentration of calcium in parts per million was plotted as a function of luminosity.

Barium concentrations were determined by the "additions" method and by extrapolation from graphs where concentrations in parts per million of barium were plotted as a function of absorption.

TABLE XIII. RECOVERY PERCENTAGES OF CALCIUM AND BARIUM

	Separation No. 1	Separation No. 2	Separation No. 3	Average % Recovery	St. Dev.	Coeff. of Variation %
Calcium held by column	2.55714 gr	2.55720 gr	2.55731 gr			
Calcium recovered	2.51110 gr	2.49412 gr	2.46780 gr			
% Ca Recovery	98.2%	94.5%	96.5%	97.4%	.69	.70
Barium held by column	0.002557 gr	0.002557 gr	0.002557 gr			
Barium recovered	0.002447 gr	0.002359 gr	0.0023166 gr			
% Ba Recovery	95.7%	92.3%	90.6%	92.8%	4.11	4.42

TABLE XIV. BARIUM AND CALCIUM CONTENTS
IN THE SKELETAL MATERIALS OF
LIVING AND FOSSIL CORALS

Specimen	Cal. %	Arag. %	Ca in ppm	Ave. Ca in ppm	Ba in ppm	Ave. Ba in ppm	(% Ba/% Ca) $\times 10^3$	Average
Pocillopora meandrina	0	100	332,000 336,000	334,000±6%	8.5 9.5	9.0±5.5%	0.0254 0.0284	0.0269
Favia hawaiiensis	0	100	334,000 336,000	335,000±3%	7.2 8.4	7.8±7.7%	0.0214 0.0251	0.0233
Porites lobata	0	100	364,000 368,000	366,000±5.4%	11.7 13.3	12.5±6.4%	0.0320 0.0363	0.0341
Montipora verrucosa	0	100	347,000 351,000	349,000±5.7%	4.8 5.7	5.2±9.6%	0.0138 0.0163	0.0149
Fungia scutaria	0	100	374,000 378,000	376,000±5.3%	6.5 7.7	7.1±8.5%	0.0173 0.0204	0.0189
Ewa Core Sample No. 1	4	96	361,000 365,000	363,000±5.5%	8.0 9.2	8.6±7%	0.0220 0.0253	0.0237
Ewa Core Sample No. 2	33	77	356,000 358,000	357,000±2.8%	6.9 7.9	7.4±6.7%	0.0193 0.0221	0.0207
Ewa Core Sample No. 3	48	52	348,000 350,000	349,000±2.8%	6.2 7.4	6.8±8.8%	0.0178 0.0212	0.0195

TABLE XIV. (continued) BARIUM AND CALCIUM CONTENTS IN THE SKELETAL MATERIALS OF LIVING AND FOSSIL CORALS

Specimen	Cal. %	Arag. %	Ca in ppm	Ave. Ca in ppm	Ba in ppm	Ave. Ba in ppm	($ Ba/$_3$Ca) x10^3	Average
Swa Core Sample No. 4	88	12	369,000 373,000	371,000±5.3%	2.3 2.9	2.6±11.5%	0.0062 0.0078	0.0070
Swa Core Sample No. 5	94	6	355,000 361,000	358,000±8.3%	--- ---	---	--- ---	---
Swa Core Sample No. 6	100	0	353,000 357,000	355,000±5.6%	--- ---	---	--- ---	---
Mean-Living Corals	0	100	--- ---	352,000	--- ---	2.3	--- ---	0.0236
Mean Fossil Corals	---	---	--- ---	359,000	--- ---	---	--- ---	---

DISCUSSION OF RESULTS

1. Barium in Living and Fossil Corals

The analysis of the calcareous skeletons of living corals revealed significance variations in their barium contents. The barium-calcium ratios were found to be on the average greater than those found in the fossil coral skeletons from the upper part of the Ewa core (Table XIV). The barium concentration in living corals varied from 5.2 ± 10% to 12.5 ± 6% ppm. The barium-calcium atom ratio (% Ba/% Ca) $x10^3$ ranged from 0.015 ± 10% to 0.034 ± 6%. Within the five Madreporaria corals that were analyzed, the species Porites lobata appears to concentrate barium in greater amount and the species Montipora verrucosa in lesser amount.

There are many conflicting opinions as to what causes differences in the uptake of an element between closely related species, and even between specimens of the same species.

Thompson and Chow (1955) analyzing the skeletons of many marine invertebrates found constant strontium-calcium atom ratios within similar types of organisms. Siegel (1960), however, analyzing Pleistocene corals for strontium, found significant variations in their strontium contents.

Swan (1956), for example, suggests that differences in the growth rates and environment are responsible for these variations. Pilkey and Goodell (1963), on the other hand, suggest that growth rates are not as important, and of the

environmental conditions, salinity is the most important.

Since the living corals that were analyzed in this work were collected in close proximity, any differences in the barium contents cannot be attributed to salinity differences, or other environmental parameters. No explanations for those differences can, therefore, be given.

Fossil corals were found to contain decreasing amounts of barium with depth, indicating that calcareous deposits lose with time not only their strontium, as has been indicated, but their barium also (Fig. 11).

Figure 11 indicates that fossil coral samples, with the aragonite partially converted to calcite, appear to contain lesser amounts of barium, and completely recrystallized fossil corals, contained no detectable barium.

2. Relationship of the Calcium and Barium Contents of Living Corals to Sea Water Concentration

According to Pilkey and Goodell (1963) when the quantity of one element is in direct proportion to that of another element in sea water, the two elements follow the same sea-water-to-skeletal material proportional relationship. The calcium concentration of sea water, however, is not in any way dependent on the barium concentration, so such a proportional relationship in the uptake of barium and calcium by coral organisms would not be expected. The available data, indeed, indicate that barium and calcium are concentrated by Madreporarian corals by different amounts and hence indepen-

antly of the sea water concentration. In Table XV, the barium-calcium ratios in the skeletons of living Madreporaria corals as related to the sea water composition and the degree of concentration of barium with respect to calcium and of concentration factors from sea water are given. On the basis of these ratios, it may be concluded that the recent corals that were analyzed concentrated barium significantly in their skeletons relative to sea water but not to the extent they concentrated calcium.

3. Barium Concentration on Fossil Corals and Relationship to Aragonite Calcite Ratios

X-ray diffraction techniques showed that all the living corals specimens were entirely composed of aragonite. The upper five specimens of fossil corals taken from the Ewa core were found to be composed of decreasing ratios of aragonite and calcite to a depth of about 270 feet. Beyond that depth all fossil corals were found to be composed entirely of calcite. The amount of aragonite appears to decrease with depth, confirming the theory that age, temperature and increasing pressure gradually convert all aragonite to calcite. Coincidentally, barium concentrations of the fossil coral samples appear to decrease with depth.

Figure 11 shows the change of the aragonite and the barium contents of the analyzed fossil corals with depth. This figure suggests that a possible relationship exists between the barium concentration of fossil corals and the

degree of their alteration to calcite. Based on the rather limited number of results a basic regression analysis was attempted on the 7040 IBM computer. The results of this regression are summarized in Table XVI, below.

TABLE XVI. RELATIONSHIP OF % ARAGONITE TO THE BARIUM CONCENTRATION

	% Aragonite (x)	Correlation Coefficient (R)	St. Error
Ba Conc. (y)	$y = \frac{x}{12.8} + 1.73$	.945	11.91

From this and Figure 12 a rather good linear relationship between aragonite content and barium concentration becomes evident.

Although these results are too limited to draw any general conclusion, they indicate the possibility that barium behaves in the same manner as has been shown for strontium (Lowenstam, 1964) in that it acts as an inhibitor of the aragonite-calcite conversion.

According to Goldschmidt (1954), however, by theoretical considerations alone, barium should be excluded from the aragonite crystal. If we assume then, that barium is not part of the aragonite lattice, it would most probably exist as $BaSO_4$, the end result of organic decomposition. $BaSO_4$, however, is insoluble in water and cannot be removed by

leaching. That no barium was found in the recrystallized fossil coral samples and that it was only found in the aragonite-rich samples excludes the possibility of its existence as an impurity in the lattice. It also suggests, in spite of Goldschmidt's arguments, that barium is part of the aragonite crystal. Whether this crystal is in its normal state or exists in a deformed state is not known.

SUMMARY AND CONCLUSIONS

On the basis of this work, the following conclusions can be drawn:

1. Separation of alkaline earth metals with ion-exchange methods is possible if a resin that has the proper selectivity characteristics is chosen. Recoveries can be better than 90%.
2. Isolation of elements found in corals in trace amounts is necessary prior to their determination by atomic absorption spectrophotometry. Although interfering ions may not be present, the determination is hindered by ions that exist in abundance which seriously alter the flame characteristics.
3. For samples that have low aragonite-calcite ratios, the quantitative determination of these minerals by x-ray diffraction has a poor precision with a coefficient of variation as high as ±20%. For higher aragonite-calcite ratios, x-ray diffraction is a reliable method for quantitative determinations.
4. The amount of aragonite decreases with depth in the fossil corals confirming the theory that age and increasing temperatures and pressures gradually convert aragonite to calcite and that at greater depths, complete recrystallization occurs.
5. The barium content in the skeletal materials of

Living corals varies considerably even in species that belong to the same family. This difference in the uptake of barium cannot be attributed to differences in the growth rates of the skeletons, in salinity differences or in other environmental conditions. It is concluded, therefore, that some coral organisms preferentially concentrate more barium, and other organisms discriminate against it, independently of environmental factors.

6. Barium is concentrated by some corals from sea water by a small factor compared to strontium which is concentrated in considerable amounts.

7. Fossil corals, in which all of the aragonite has been converted to calcite, do not contain detectable amounts of barium. Samples that contain higher amounts of aragonite also have a higher barium concentration. A linear relationship between the aragonite content and barium concentration was found. It is suggested that barium possibly behaves in the same manner as has been shown for strontium in that it acts as an inhibitor for the aragonite-calcite conversion.

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ACKNOWLEDGMENTS

Samples of the living corals that were analyzed were identified with the help o! Professor V. Brock. Dr. T. K. Chamberlain provided the samples of fossi1 cora1s and permitted reproduction of the Ewa core's cross-section. Dr. K. Pankiwsky supplied samples of pure calcite for the x-ray diffraction calibration curve. Dr. B. Cooi1 and Mr. Y. Watanabe of the Department of Plant Physiology permitted use of the Perkin-Elmer 303 Atomic Absorption Spectrophotometer. Dr. L. Swindale permitted use of instruments belonging to the Department of Soils of the University for the analyses.

The progress of this work was great1y influenced by discussions and advice received from Dr. M. Manghnani, Dr. R. Moberly, Dr. P. F. Fan, Dr. E. Her1iscka and Dr. Johanna Resig.