Subaerial Diagenesis of Carbonate Sediments: Efficiency of the Solution-Reprecipitation Process

Abstract. *Interaction between percolating groundwaters and aragonitic carbonate sediments within the vadose zone of the coral cap of Barbados, West Indies, results in dissolution of aragonite and concurrent reprecipitation as low-magnesium calcite. Comparison of the ratios of strontium to calcium in groundwater, aragonitic carbonate, and recrystallized calcite indicates that locally the solution-reprecipitation process is operating at an efficiency greater than 90 percent.*

The transformation of aragonite to calcite can take place through a process of solution-reprecipitation (*1*) or recrystallization *in situ* (*2*). During large-scale solution-reprecipitation, other factors being equal, the relative rates of groundwater movement determine the extent of calcium carbonate mobility in the aquifer system. A high rate of percolation in the vadose zone (zone of aeration) may lead to complete transport of calcium carbonate to the water table. This would result only in the dissolution of aragonite with no concurrent reprecipitation of calcium carbonate as low-magnesium calcite. High rates of groundwater movement therefore lead to the development and retention of cavities in aragonitic limestones. With moderate rates of percolation, however, dissolution of aragonite and reprecipitation of calcium carbonate as low-magnesium calcite would occur concurrently.

Several investigators (*3*) have inferred from petrographic relationships in subaerially exposed Pleistocene carbonates that calcium carbonate from the solution of aragonite is reprecipitated as low-magnesium calcite. A more rigorous demonstration of the efficiency of the solution-reprecipitation process seems desirable, and the island of Barbados, West Indies provides a "natural laboratory" for study of this process.

Six-sevenths of the island's surface consists of a coral cap averaging 70 m in thickness and constructed from reef-tract terraces of different Pleistocene age (*4*). Most of this coral cap is above the water table. Relatively impermeable rocks underlie the cap and restrict the vertical movement of groundwater, thereby producing the major aquifer for the island.

In the southern part of the island, in Christ Church Ridge, local groundwater is both topographically and structurally isolated from other groundwaters of the island (Fig. 1). Rainwater which has fallen on an aragonitic terrane is the only contributor to the groundwater.

The maximum elevation of Christ Church Ridge is 113 m. The vadose zone has a maximum thickness of about 60 m at high elevations on the ridge and thins with decreasing elevation to less than 3 m thick near the coast. Above elevations of about 30 m, groundwater movement under conditions of concentrated conduit flow occurs within an integrated drainage net in "groundwater stream" channels at the base of the coral cap. On occasion, these channels are deeply incised into the impermeable underlying sedimentary rocks. Water thickness in these underground stream channels is up to 3 m. When these subsurface streams reach sea level they feed into a fresh-water lens (of variable thickness) which floats above a prominent coastal salt-water body.

The coral-cap aragonite contains approximately 6 to 8 parts of strontium per thousand, and calcite which replaces the aragonite contains 2 to 3 parts per thousand strontium (*5*). If the calcite is locally reprecipitated after the solution of aragonite, the excess strontium must remain in the groundwater. By measuring the strontium content of unrecrystallized carbonates, the strontium content of recrystallized carbonates, and the ratio of strontium to calcium in the locally isolated water, one can estimate the efficiency of the solution-reprecipitation process. If only solution of aragonite were occurring in this area, the ratio of strontium to calcium in the groundwater should be no greater than that of aragonite. Any increase over the value for aragonite in this ratio of the groundwater would indicate that some calcite is being reprecipitated locally within the rock. The efficiency of the solution-reprecipitation process (E) may be expressed in terms of ratios of strontium to calcium.

$$E = \frac{(\mathrm{Sr/Ca})_{\mathrm{Groundwater}} - (\mathrm{Sr/Ca})_{\mathrm{Aragonite}}}{(\mathrm{Sr/Ca})_{\mathrm{Groundwater}} - (\mathrm{Sr/Ca})_{\mathrm{Calcite}}} \qquad (1)$$

An atomic absorption spectrophotometer (Perkin-Elmer model 303) was used for cation analysis of carbonate rocks, groundwater, and other natural waters. The calcium and strontium content of Christ Church groundwater samples is given in Table 1. The pos-

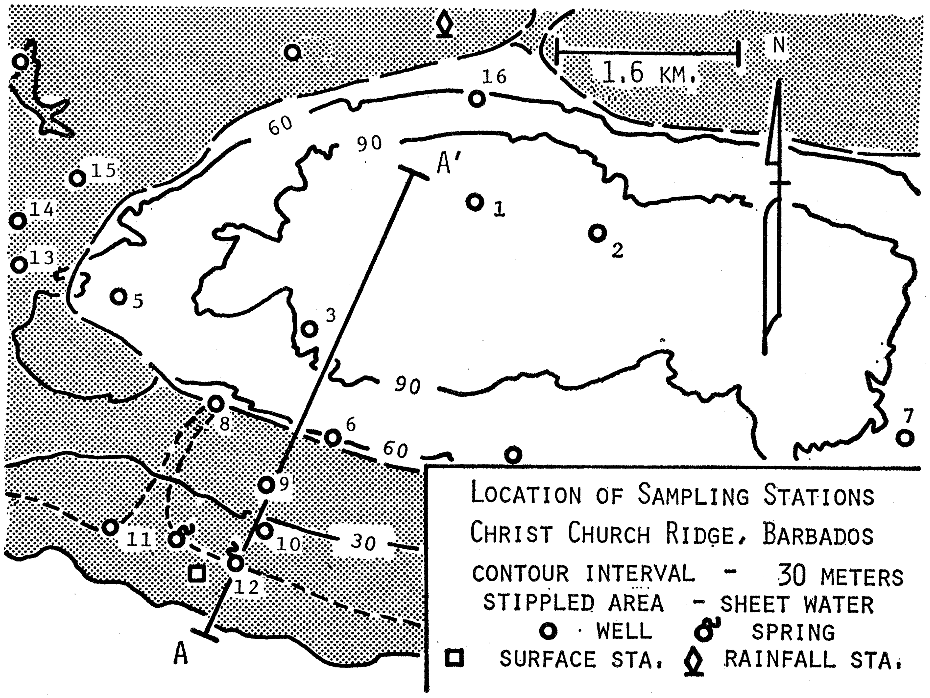

Fig. 1. Location of sampling stations, Christ Church Ridge, Barbados. Topography is indicated with 30-m contour interval. A-A' denotes line of section, Fig. 2. Well No. 4 is slightly east of map area.

sible sources for calcium and strontium in the waters are summarized in Table 2.

Rainwater samples were collected once a week for 6 weeks. The concentration of strontium and calcium in rainwater analyzed is sufficiently small that no correction need be applied to observed data (Table 2).

Analysis of successive soil leachates for strontium and calcium reveals that a strontium adjustment for possible contribution by soils should be undertaken. Calcium constitutes the greater part of cation loss after application of fertilizer to Christ Church soils (*6*). The hypothetical assumption was made that all the calcium in the groundwater originates from soil-seepage. Leachate samples representative of effluents from Christ Church soils under stable conditions of wet-season leaching after application of fertilizer were diluted with redistilled water at the atomic absorption spectrophotometer until their calcium content was equivalent to that of the groundwater samples. The strontium content of these diluted leachates was applied as a soil-seepage correction to observed strontium concentrations (Table 1).

A similar adjustment was made for the strontium contribution by salt-water encroachment. It was assumed that all the sodium in the groundwater is due to seawater dilution. Barbados seawater was diluted at the atomic absorption spectrophotometer with redistilled water until the sodium content of the seawater was equivalent to that of Christ Church groundwaters. The strontium content of these diluted seawaters was applied as a correction of seawater dilution to observed strontium concentrations (Table 1).

Similar adjustments can be applied to the calcium data and are generally less than 10 percent of the observed values. However, because such adjustment of the observed concentrations would increase the calculated efficiency of the solution-reprecipitation process, we did not do so. That is, all adjustments that were undertaken were made to

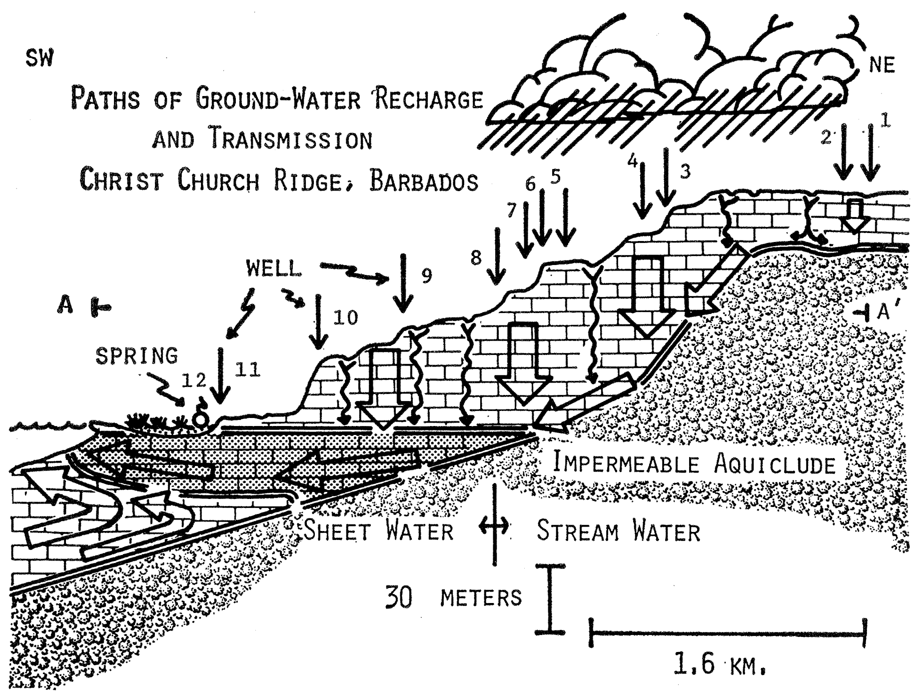

Fig. 2 (left). Paths of groundwater recharge and transmission, Christ Church Ridge, Barbados. Although some water percolates through the vadose zone (large vertical arrows), substantial volumes of surface runoff may pass through sinkholes and fissures (wavy arrows) directly to the phreatic zone during times of heavy rain. The net result is to make our estimates of solution-reprecipitation efficiency minimum estimates for percolating waters.

Table 1. Strontium and calcium content of groundwater, groundwater ratios of strontium to calcium and efficiency of solution-reprecipitation, Christ Church Ridge, Barbados, W.I. P, pumped sample; B, collected with bottle sampler; W, physically collected in well at the water table; S, spring; epm, equivalents per million; dates of collection, 12 to 19 August 1966 (15–13B, 19 September 1967).

Sample	Maximum strontium component			Adjusted Sr (ppm)	Observed Ca (ppm)	Adjusted Sr/Ca (epm × 10^3/epm)	Efficiency* (%)
	Observed (ppm)	Soil-seepage (ppm)	Seawater dilution (ppm)				
503P	0.46	0.61		0	68	0	
16–6B	0.69	0.63		0.04	68	0.27	
15–13B	1.43	0.41	0	1.02	75	6.23	
16–17B	0.89	0.55	0	0.34	59	2.65	
629W	1.5	0.41	0	1.09	44	11.3	36
15–2B	4.0	0.32	0.04	3.64	33	50.4	88
16–15B	3.3	0.49	0.05	2.76	48	26.3	76
15–9B	4.9	0.53	0.065	4.31	54	36.5	83
15–11B	11.4	0.43	0.12	10.85	43	115.3	94
15–8B	8.4	0.50	0.10	7.80	52	68.5	91
565B	14.2	0.77	0.15	13.28	81	74.9	92
15–23S	8.6	0.51	0.12	7.97	55	66.2	91
539P	2.2	0.72	0.04	1.44	72	9.1	16
449B	1.68	0.74	0.04	0.9	77	5.3	
437B	1.56	0.82	0.03	0.71	81	4.0	
11–23P	0.96	0.55		0.41	75	2.5	

* Percentage of efficiency calculated by Eq. 1.

Table 2. Strontium, calcium, and ratios of strontium to calcium (epm Sr × 10^3/epm Ca) in aragonitic carbonate, recrystallized calcite, and Barbados rainfall, soil seepage, and seawater. Aragonitic sand; *Montastrea annularis* coralline aragonite, and recrystallized calcite from Christ Church Ridge, Barbados (*5*). Rainfall from average of two rainfall-station composite monthly samples, 1966 (Constant and Waterford). The composite monthly samples were prepared by mixing weekly samples for each station in proportion to the amount (in millimeters) of weekly precipitation. Soil seepage, leachates from soil-seepage experiments with rainwater; 63F, north flank and crest of Christ Church Ridge; 42F, south slope and western nose of Christ Church Ridge. Analysis for Sr by atomic absorption spectrophotometry; Ca calculated from principle of seawater constant proportions for Barbados seawater; 19.542 ppt Cl (Mohr-Knudsen method).

Source	Ratio Sr/Ca	Ca (ppm)	Sr (ppm)
Aragonitic sand	7–9	400 × 10^3	6–8 × 10^3
Montastrea annularis			
Coralline aragonite	7–8	400 × 10^3	5.9–7.0 × 10^3
Calcite	2.3–3.5	400 × 10^3	2.0–3.1 × 10^3
Rainfall, July	3.6	1.65	0.013
Rainfall, August	4.5	4.14	0.041
Soil seepage 63F	3.1	210	1.4
Soil seepage 42F	4.4	225	2.2
Seawater	8.8	417	8.0

bias the data against the conclusion reported.

Rainwater can reach the base of the coral cap through various paths (Fig. 2). Under the normal pattern of intermittent showers, percolation of rainwater through the coral cap and interaction with aragonite results in a groundwater with a high ratio of strontium to calcium. We attempted to study this path of water movement. However, during heavy rains, surface runoff into sinkholes and fissure recharge to the water table limits appreciable interaction of groundwater with aragonite in the vadose zone of the coral cap. In addition, the ratio of strontium to calcium in groundwater for a well in a lower aragonitic terrace is somewhat reduced by low-strontium groundwaters which have percolated through higher, more calcitic terraces.

Thus, having reasons to believe that the efficiency estimates represent minimal estimates, we base our conclusions on six wells, one on the western nose (539P), and five on the south slope of Christ Church Ridge (629W, 16-15B, 15-2B and 15-8B). All have anomalously high strontium concentrations. Adjusted ratios of strontium to calcium in the water from these six wells average 34, in contrast to the ratio of 9 or less that would be expected if solution of aragonite were the only process acting in this area. We conclude that reprecipitation of calcium carbonate in the form of low-magnesium calcite is occurring concurrently with dissolution of aragonite above the water table. We estimate that the solution-reprecipitation process is operating at an efficiency greater than 90 percent.

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Lysosomal Stability during Phagocytosis of Aspergillus flavus Spores by Alveolar Macrophages of Cortisone-Treated Mice

Abstract. *Control mice and those treated with cortisone were exposed to aerosols of viable spores of* Aspergillus flavus. *Fifteen to 20 minutes later, animals were killed, and alveolar macrophages were obtained by tracheobronchial lavage. Electron-microscopic examination of these cells revealed that, whereas the lysosomes of control macrophages showed extensive attraction and fusion with the phagocytic membranes surrounding spores, the lysosomes of macrophages from animals treated with cortisone revealed little, if any, interaction. This diminished lysosomal response in forming phagocytic vacuoles may be important in the subsequent development of hyphal bronchopneumonia which frequently occurs in cortisone-treated mice exposed to spores of* A. flavus.

The increase in the incidence of severe systemic human infections with opportunistic fungi, such as *Aspergillus* (*1*), has prompted us to investigate the pathogenesis of pulmonary aspergillosis (*2, 3*). After a brief exposure to aerosols of viable spores of *A. flavus,* mice become highly susceptible to lethal hyphal bronchopneumonia if they have previously been treated with drugs such as cortisone or with cytotoxic agents considered to be associated with the development of fatal human aspergillosis (*2*). In contrast, normal control mice exposed similarly to *A. flavus* spores are resistant to this infection (*2*). This experimental model is being used in investigations of the cellular mechanisms involved in the enhanced susceptibility to secondary mycotic disease. Unlike the alveolar macrophages from exposed control mice, acid phosphatase is not released from the particulate fraction into the supernatant fraction of macrophages from cortisone-treated mice 8 hours after their exposure to spores (*3*). These data support the hypothesis (*4*) that corticosteroids may act by stabilizing lysosomal membranes. We now report ultrastructural observations which further support this hypothesis.

White female mice (Carworth Farms strain 1) weighing, on the average, 20 g were used. The experimental mice received 5 mg of cortisone acetate subcutaneously 2 days before they and untreated control mice were exposed to spores. Animals were exposed to aerosols of viable spores of *A. flavus* for 5 minutes in an exposure chamber (*3*). Mice were killed by aortic transection 15 to 20 minutes after removal from the exposure chamber. Alveolar macrophages were obtained by lavage of the lungs three or four times with 1.0 ml of either isotonic saline (0.89 percent) or sucrose ($0.25M$) through a 23- or 26-gauge needle inserted into the trachea (*3*). In the first experiment, washings obtained from 20 control mice exposed to spores were pooled for fixation, dehydration, and embedding, as were those from 12 animals treated with cortisone. In a second experiment, the washings obtained from 17 control mice and from 16 cortisone-treated mice were used similarly. In a third experiment, washings were obtained from cortisone-treated and control mice that were not exposed to spores. The washings obtained from each group were separately fixed in 2 percent phosphate-buffered osmium tetroxide at *p*H 7.4 and 0° to 4°C for 1 to 2 hours. Each milliliter of cell suspension was mixed in 1 ml of OsO_4 such that the final concentration of osmium was 1 percent. The cell suspensions were then centrifuged at 500 rev/min for 10 minutes, and the supernatants were decanted. The pellets were resuspended and dehydrated in a series of graded ethanols, treated with propylene oxide, and infiltrated in Epon 812. For each step in dehydration, it was necessary to resuspend and centrifuge the pellets. After infiltration, the cells were pipetted into No. 00 gelatin capsules and centrifuged at 1000 rev/min for 15 minutes. These capsules were then filled with Epon and polymerized in an oven at 45°C for 24 hours and at 60°C for 48 hours. Silver or gold sections cut with