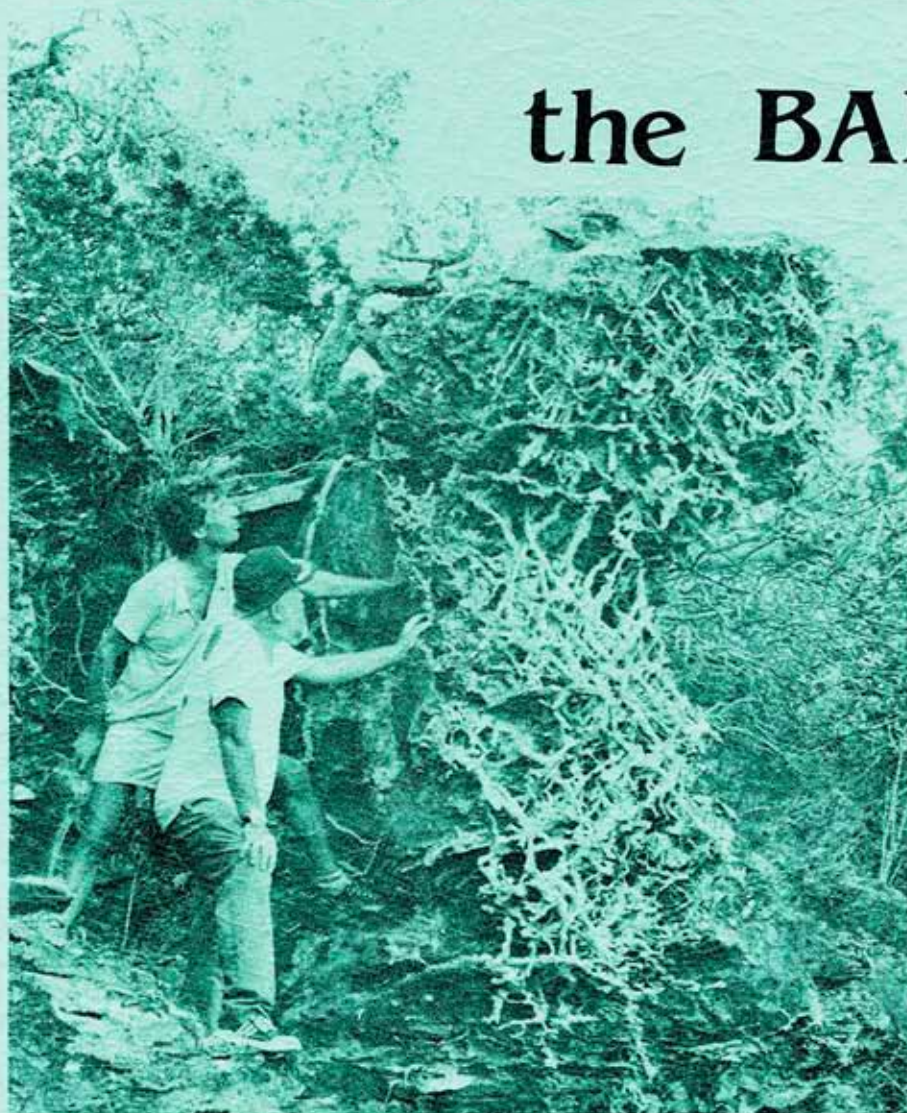


*PROCEEDINGS*  
*of the*  
**2nd Symposium on the**  
**GEOLOGY of**  
**the BAHAMAS**



*June 1984*

*CCFL Bahamian Field Station*

# DIAGENESIS OF THE CARBONATE ROCKS OF SAN SALVADOR ISLAND, BAHAMAS

Steven J. Van Kauwenbergh  
International Fertilizer Development Center  
Muscle Shoals, Alabama

and

Roger J. Bain  
Department of Geology  
The University of Akron  
Akron, Ohio 44325

## Abstract

Microprobe analyses of cements and whole-rock X-ray analyses indicate the carbonates of the island diagenetically alter in predictable patterns. Microprobe analyses of up to 3 generations of cement indicate compositional ranges in MgO content from subtidal, salt spray influenced, and early and late dune cements. Minor elemental concentrations of SrO and MgO in sparry calcite may be indicative of chemically and mineralogically maturing overburden undergoing dissolution and providing chemical constituents for cement formation.

## Introduction

Carbonate sediments may be cemented in a variety of diagenetic environments ranging from the seafloor to eolian-fresh water conditions. Cementation may occur at water-sediment interfaces, fresh water-marine water interfaces or may be a phenomenon of deeper burial. Characteristic cements with differing chemistry, mineralogy and morphology may form in each of these environments.

Marine and fresh water environments are broadly subclassified into phreatic and vadose zones. In the phreatic zones, the pore space is constantly filled with fluid. Resulting cements tend to be isopachous, that is, of equal thickness around grains. Cements forming in the vadose zone reflect the passage

of fluids through the rocks-sediments and tend to be meniscus and pendulous in nature.

Carbonate sediments cemented in the marine environment are dominated by aragonite and high Mg-calcite. Holocene limestones have shown that aragonite and high Mg-calcite are the only carbonates of significance to precipitate inorganically from seawater at shallow depths (Shinn, 1969; Alexandersson, 1972; Bathurst, 1976; James, et al., 1976). In fresh water environments sparry calcite dominates cementation. It is generally accepted that much of the cementation in carbonate rocks occurs very early in their diagenetic history and is due primarily to fresh water exposure (Milliman, 1974; Bathurst, 1976; Longman, 1980).

Although cement morphology may be one criterion for recognition of the conditions of sedimentation and/or cementation, it is not a definitive characteristic. For instance, carbonate rock cemented in a marine environment may later be exposed to fresh water conditions. Metastable components such as aragonitic or high Mg-calcite cements or grains may be dissolved or neomorphosed to stable low Mg-calcite. Mensicus and pendulous cements may then form if the rock reaches a vadose fresh water environment, marking the original cementation.

As McKee and Ward (1983) have indicated, there is no reliable petrographic indicator to distinguish ancient eolian carbonate rock from ancient ooid shoals. Even if petrographic-morphologic indicators were originally present,

these indicators may be destroyed by neomorphism of cements. It has been shown by cathodoluminescence that the minor elemental constituents of these cements may be preserved, although morphologic features may be destroyed (Grover and Read, 1978).

It was the primary purpose of this study to investigate the minor elemental chemistry of the cements of the carbonate rocks of San Salvador by quantitative microprobe analysis. X-ray diffraction study was combined with microprobe data to further place the whole-rock system in perspective. With both these methods, the history and nature of these rocks may be better examined. Hopefully these findings may be used to help analyze more ancient rock.

### Methods

On two separate occasions in the winter and spring of 1983, the island of San Salvador was visited. Over 250 samples were collected, thin sectioned and examined. Thirty of these samples were chosen for more intense study and form the basis of this paper. Samples were selected on the basis of association with unique features on the island (i.e. Watlings Castle paleosol, Cockburn Town Reef, etc.) and more broadly, to typify sedimentation and cementation characteristics of the island and carbonate environments in general. The depositional environments and samples specifically chosen for this paper are:

- 1) dunes, North Point (83-74, 83-75) Sandy Point, Watlings Quarry (above and below paleosol) C-D (2).
- 2) beach berms, French Bay, Grahams Harbour, Granny Lake (west shore 83-68, 83-67).

- 3) subtidal deposited sediments, Pigeon Creek Quarry (2), Cockburn Town Reef (backreef calcarenite).
- 4) beachrocks, French Bay, Grahams Harbour (see index map for locations).

Due to space considerations individual photomicrographs and sample analyses have been omitted. Individual rock analyses and photomicrographs may be found in Van Kauwenbergh (1984).

Bulk X-ray data, in conjunction with electron microprobe analyses, were used to typify the chemistry and mineralogy of the rocks and their cements. All microprobe analyses employed an Etech-Autoprobe System. Low specimen currents were maintained with relatively low accelerating voltage (15kv), a large beam diameter (S-10 $\mu$ ) and long count times (40 seconds) to minimize sample damage and insure reliable data. Nine elements were typically analyzed. Ca, Sr and Mg standards were meticulously analyzed before and after runs. Runs having errors on Mg and Ca standards exceeding  $\pm 2\text{wt.}\%$  were not accepted. Typical runs on Ca and Mg were made within  $\pm 1\text{wt.}\%$  deviation. All other elements were accepted at  $\pm 3\text{wt.}\%$  and were typically within  $\pm 2\text{wt.}\%$  deviation. All data was originally collected and reduced as oxide percentages utilizing the Bence-Alber empirical correction coefficients. Data was recalculated on the basis of mole % as commonly used by carbonate petrologists.

MgO and SrO concentrations have been used primarily as indicators in this study. Mg typically can be included in the 6-fold coordinated calcite structure non-stoichiometrically up to 4 mole %. Under unusual conditions MgO concentrations may be over 7%. Sr is thought to be an indicator of aragonitic

precursors to cements. Sr may be found in unaltered aragonite up to a level of 1.2 mole %.

All X-ray diffractometry was done on a Phillips-Norelco 2000 series water cooled X-ray diffraction unit with a sealed proportional counter, linear rate meter, scaler/timer and chart recorder. Radiation was Cu K alpha and a michel filter was used. Due to space considerations, all operating conditions and sample preparations of both microprobe and X-ray analyses are not given. Operating conditions, sample preparations, analysis technique and individual tables of analyses for each specimen may be found in Van Kauwenbergh (1984).

#### Diagenetic Trends

Two major diagenetic models have shaped the thinking of carbonate petrologists in recent years (Table 1). Both models use an initial sediment having mixed Mg-calcite and aragonite composition. A first cement is formed, either concurrent with, or before the loss of Mg. The loss of Mg is thought to be predominantly in the form of high Mg-calcite. After the loss of Mg, aragonite is thought to dissolve and both models culminate in a wholly low Mg-calcite product.

Although both models are reasonable, data from San Salvador indicates the situation may be somewhat more complicated. Samples were collected from the beachrocks and associated beach berms at Grahama's Harbour and French Bay. The French Bay samples reflect both the influence of the high-energy barrier reef offshore with high proportions of coral fragments

Table 1  
Diagenetic Models

Land (1967)	Gavish and Friedman (1969)
<p>Stage</p> <p>1) Initial sediment</p> <p>2) First cement</p> <p>3) Loss of Mg</p> <p>4) Dissolution-precipitation of aragonite-calcite</p> <p>5) Culmination of mineralogical changes in low Mg-calcite</p>	<p>Stage</p> <p>1) Initial sediment</p> <p>2) First cement, loss of Mg</p> <p>3) Dissolution of aragonite, occlusion of interparticle pore space, culmination of mineralogical changes in low Mg-calcite</p> <p>4) Coralline algae fragments become lighter colored, second generation calcite replaced calcite which formed in stages 2 and 3</p> <p>Mg-calcite to calcite in 7,000 to 10,000 years, all aragonite to calcite in 80,000-100,000 years</p>

and high Mg-calcite red algae. Grahams Harbour samples are much more aragonitic and reflect the high green algae components of the offshore sheltered by environment. Halimeda fragments, intraclasts, and pelecypod fragments form the bulk of the Grahams Harbour samples. In both cases, French Bay and Grahams Harbour, the beach berm rocks are much finer grained than their beachrock counterparts. The French Bay beach berm was quite friable, whereas the Grahams Harbour beach berm rock was friable to moderately indurated. Whereas the sample sets have a vastly differing mineralogy, a similar trend is seen from beachrock to the fresh water vadose altered beach berm. Although the higher proportion of aragonite in the beachrocks may be construed to be wholly from the development of their aragonitic cements, significantly, the proportion of high Mg-calcite has stayed the same or even increased slightly (Figure 1).

Microprobe data indicates MgO concentrations in the first cements from 4-7 mole %. Apparently the high Mg-calcite had not yet begun to dissolve to any great degree. This influx of Mg is attributed to be the result of leaching of brucite within the grains or unidentified organic matter. Brucite (MgO) has been identified in the structure of red algae (Weber & Kaufman, 1965; Schmaltz, 1965) and may exist to some degree disseminated in other carbonate sediments.

Further evidence of the influx of Mg is noted in samples from the Granny Lake region (Figures 2 and 3). A large (400 mm) keystone vug displaying three petrographically distinct cements was analyzed (Figure 3, sample 83-68). The first two



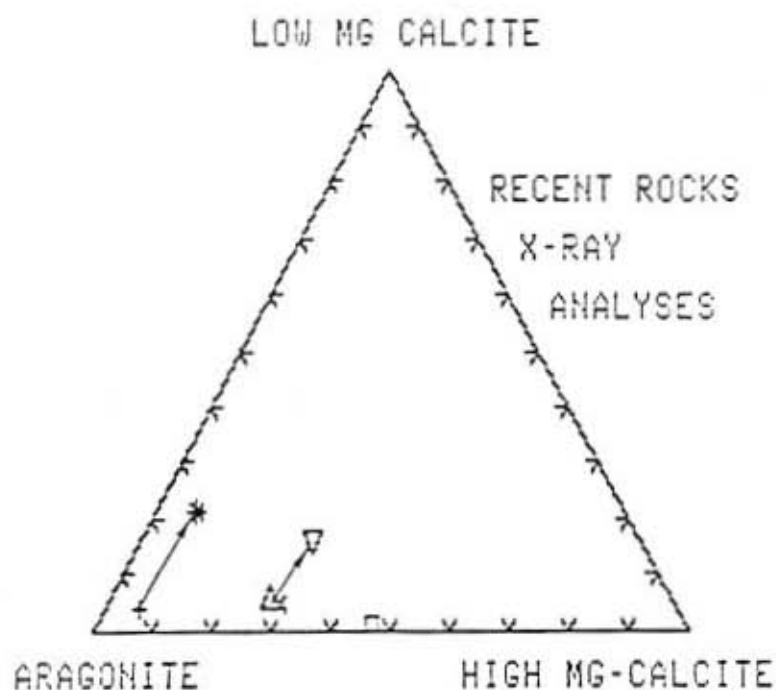


Figure 1: Triangle plot of recent rocks X-ray analyses (with recent crusts, all apices = 100% of constituent)

+ Sample no. 83-86, Grahams Harbour intertidal beachrock

\* Sample no. 83-87, Grahams Harbour beach berm

△ Sample no. 83-98, French Bay intertidal beachrock

▽ Sample no. 83-99, French Bay lithified beach berm

□ Sample no. 83-124.5, Granny Lake algal crust (dolomite component plotted with high Mg-calcite)

X Sample no. 83-275, South Pigeon Creek supra-tidal crust (dolomite component plotted with high Mg-calcite)

Note: Arrows indicate the diagenetic effect of freshwater exposure and transition in mineralogy from the beachrock to associated beach berm.

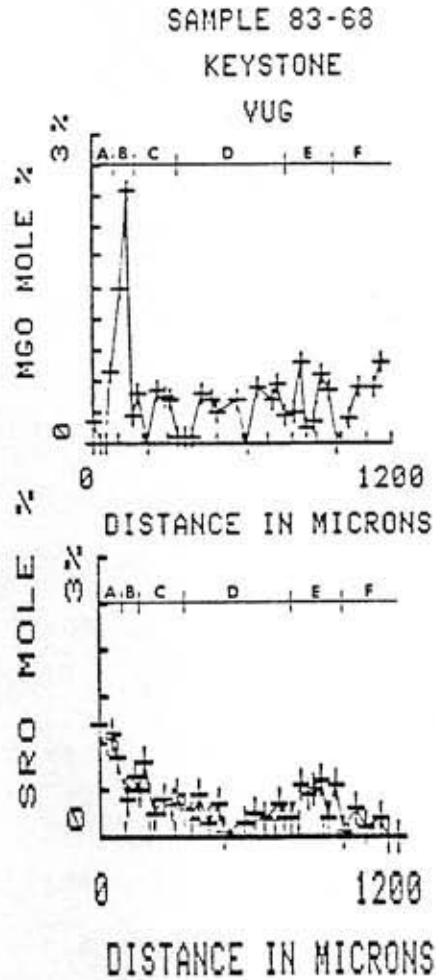


Figure 2: Microprobe analyses, Granny Lake keystone vug, sample no. 83-68, MgO and SrO concentrations vs. distance (see table 24)

- (A) Aragonitic grain
- (B) First cement, top of vug
- (C) Prismatic sparry calcite, top of vug
- (D) Coarse, equant, pore filling sparry calcite
- (E) Prismatic sparry calcite, bottom of vug
- (F) Calcitic grain

grain-rimming cements are inequant (Figure 2: B, C, E) whereas the final pore-filling sparry calcite cement is equant, indicating formation under relatively stable conditions (fresh water phreatic zone?). The first cement showed characteristic high Mg concentrations of first cements. Subsequent cements show wildly fluctuating Mg levels with characteristic drops in concentration at the culmination of each cementation episode. Such Mg fluctuations have been noted by Benson and Matthews (1971) and Benson, et al. (1972) and were attributed to the first stages of cementation in fresh vadose environment.

Fluctuations after the initial pulse of Mg were postulated to be a response to an environment that underwent significant changes with time. Such Mg influxes are also postulated here to be the result of a primary influx of Mg into the system due to dissolution of brucite and/or organic matter, dissolution of high Mg-calcite and possibly local influences as porous grains interiors with unstable mineralogies are opened to the system by dissolution of protective outer coatings. However, an influx of Mg by the addition of diagenetically fresh overburden, leachings and depletion of the source in Mg could further complicate the patterns.

Sr concentrations are much less wildly fluctuating across the vug. Aside from the initial cement where Mg is thought to "flood" the calcite structure, SrO shows a gradual decrease with minor significant decreases at cement generation boundaries to minimum levels in the center of the pore. The occurrence of high relative SrO values at the pore margins and a gradual decrease to

the center of the pore are thought to indicate that aragonite is undergoing dissolution from the inception of diagenesis rather than as a discrete stage after Mg-calcite is dissolved. Ultimately, the persistence of aragonite may be more dependent on the porosity and density of aragonite constituents rather than its relative stability with respect to high Mg-calcite. When sample 83-68 is plotted with another sample from the same area (83-67) a similar pattern is seen (Figure 3). In this plot, the SrO and MgO concentrations of morphologically similar cement have been averaged to a single point. Both samples exhibit a high MgO concentration in the first cement dropping to the second cement. The third, equant cement was not as well developed in sample 83-67. From second to third cement in sample 83-68 the trend in SrO concentrations shows an abrupt drop. This is thought to be the result of a maturing source of cement (i.e. a source composed of increasingly higher percentages of stabilized calcite).

Not only do Mg levels in sparry calcite cements fluctuate within specific sample cements but they also vary with differing depositional environments. Figure 4 is a composite plot of 14 samples having up to 3 generations of cement. Samples collected from sediments deposited in subtidal conditions show the highest Mg concentrations in their first cements (Figure 4-A). This MgO concentration may be complicated by the presence of a high proportion of red algae grains. Dune first cements (Figure 4-C) show overlaps with beach berm and subtidal sediment in first and second cements. In second generation dune cements (Figure 4-D) MgO concentrations further decrease. The lowest MgO levels are

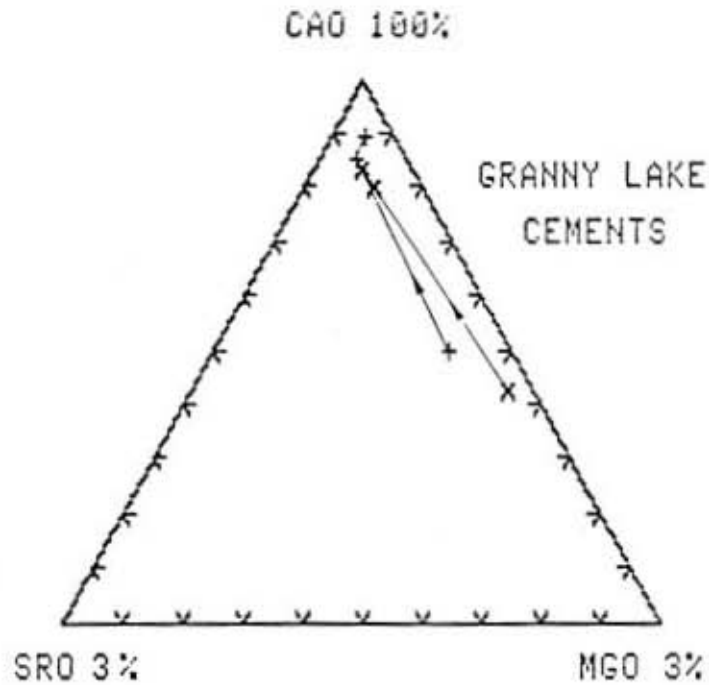


Figure 3: Triangle plot of CaO, SrO, and MgO microprobe analyses of Granny Lake cements (Note: the CaO values are from 97% to 100%)

X Sample 83-67, beach berm/dune(?) in water

+ Sample 83-68, beach berm/dune(?) on shore, with keystone vug

Note: Arrows and pathways indicate the changes in SrO, MgO and CaO concentrations with respect to the three generations of cements.

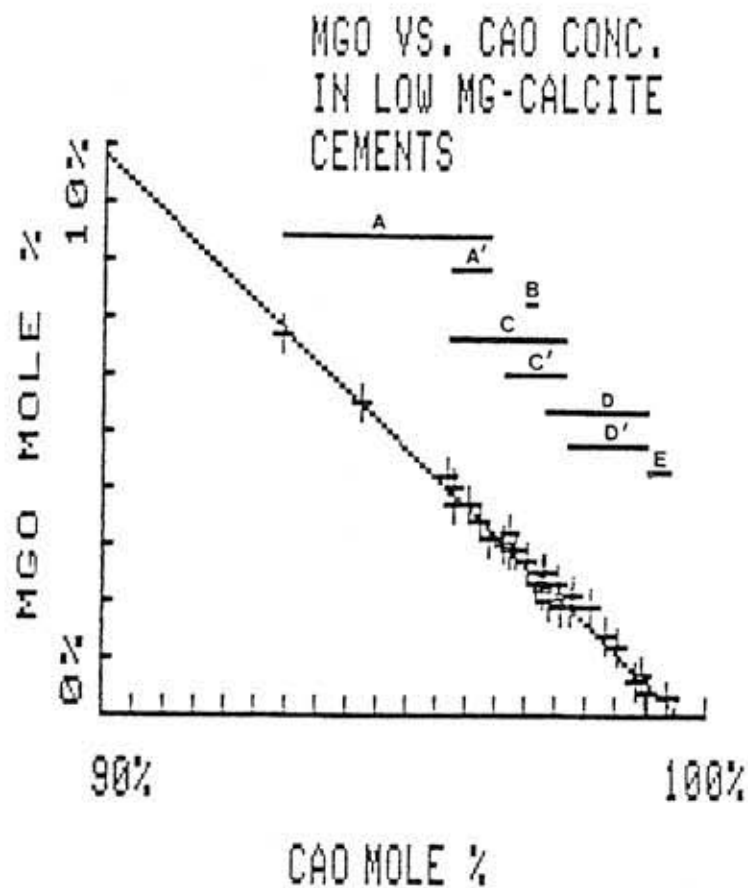


Figure 4: MgO vs. CaO microprobe analyses in all low Mg-calcite cements

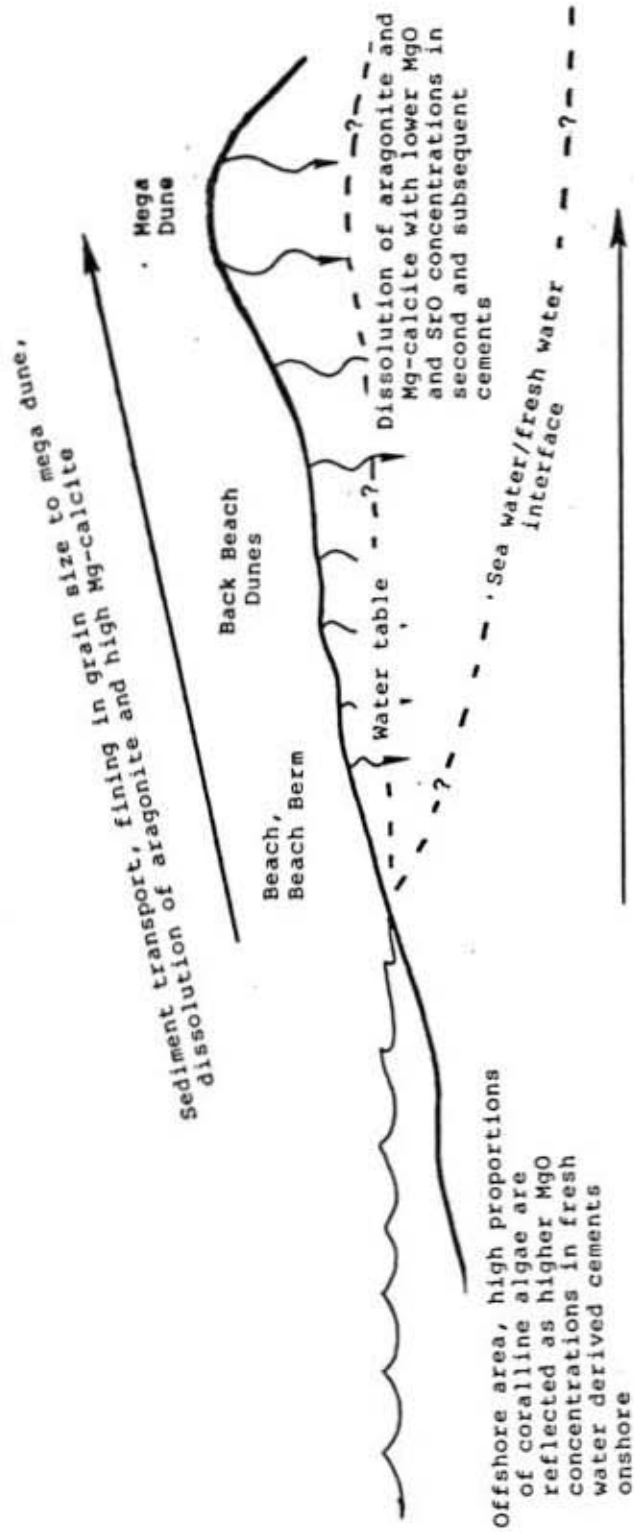
- (A) Subtidal, beach berm first cements
- (A') Subtidal, beach berm first cements without samples with a high proportion of red algal grains
- (B) Subtidal, beach berm second cements
- (C) Dune, first cements
- (C') Dune, first cements without samples 83-74 and 83-75 (possible high Mg-calcite influence from near-shore reef or salt spray influence)
- (D) Dune, second cements
- (D') Dune, second cements without samples 83-74 and 83-75
- (E) Dune and beach berm third cements

found in the third generations of cement in these examples (Figure 4-E). This situation of a general progression to lower MgO levels may be reversed when preexisting clasts are incorporated in younger sediment (Cockburn Town Reef) or fresh overburden is added to the system (lower dune facies, Sandy Point area). Higher concentrations of MgO have been found in second and third generations of cement under these conditions.

Although overlaps in MgO concentrations are exhibited in this rather limited set of samples, a general decrease in MgO concentrations can be recognized as the sediment is cemented presumably further from the paleoshoreline. Of course, the original composition and source of the sediment must be considered. With high energy conditions offshore, the sediment may contain significant proportions of high Mg-calcite red algae and the cements would reflect this influence. Low energy situations with high proportions of green algae would contain proportionally more aragonite and a lower Mg component. In this light, the composition of cements may be a useful environmental indicator when coupled with other criteria.

A general conceptual sedimentation-cementation model has been formulated (Figure 5). As marine-derived sediment is transported from the beach and possibly to dune environments, the sediment undergoes diagenesis in the fresh water vadose environment prior to lithification. Mg and Sr are leached as component grains or constituents are moved away from the beach. The amount of diagenesis before the sediment is finally deposited is complicated by factors such as original composition, climate,

Figure 5. Sedimentation-Cementation Diagenetic Model





microporosity of the original grains and residence time within the system. Second and subsequent generations of cement can also reflect these original conditions. MgO and SrO levels are further reduced as the system evolves, the cement source is depleted in Mg and Sr, and stabilizes to low Mg-calcite.

### Summary

Marine-derived carbonate sediments of mixed aragonite and high Mg-calcite compositions undergo progressive diagenesis in fresh water systems to form low Mg-calcite. The dissolution or inversion of these primary components releases indicator elements (Sr, Mg) into the system. These components will be incorporated within the cements of rocks formed in these systems.

Levels of SrO and MgO in the cement are dependent upon original composition, the amount of diagenesis that has occurred before the rock is lithified and the overall diagenetic maturity of the carbonate deposit of carbonate rock in question. Addition of diagenetically fresh overburden may cause increases in MgO concentration in subsequent generations of cement.

Progressive diagenesis cannot simply be categorized as a series of discrete steps. Carbonate diagenesis probably could be more correctly assessed as a dynamic system. Aragonite is apparently dissolving from the inception of diagenesis. The dissolution of Mg-calcite may be ultimately more dependent on the persistence of dense, relatively nonporous aragonite than its relative solubility to aragonite.

## REFERENCES

- Alexandersson, T., 1972, Intergranular growth of marine aragonite and Mg-calcite: evidence of precipitation from super-saturated seawater: *Jour. Sed. Pet.*, v. 42, p. 441-460.
- Bathurst, R. G. C., 1976, Carbonate sediments and their diagenesis, *Developments in sedimentology* no. 12, 2nd Revised Ed.: New York, Elsevier Publ. Co., 658 p.
- Benson, L. V., Achauer, C. W. and Matthews, R. K., 1972, Electron microprobe analysis of magnesium and iron distribution in carbonate cements and recrystallized sediment grains from ancient rocks: *Jour. Sed. Pet.*, v. 42, no. 4, p. 803-811.
- Gavish, E., Friedman, G. M., 1969, Progressive diagenesis in Quaternary to late Tertiary carbonate sediments: *Jour. Sed. Pet.*, v. 39, no. 3, p. 980-1006.
- Grover, G. R., Jr., and Read, J. F., 1978, Fenestral and associated vadose diagenetic fabrics of tidal flat carbonates, middle Ordovician New Market Limestone, southwestern Virginia: *Jour. Sed. Pet.*, v. 48, p. 453-474.
- James, N. P., Ginsburg, R. N., Marszalek, D. S., and Choquette, P. W., 1976, Facies and fabric specificity of early subsea cements in shallow Belize (British Honduras) reefs: *Jour. Sed. Pet.*, v. 46, p. 523-544.
- Land, L. S., 1967, Diagenesis of skeletal carbonates: *Jour. Sed. Pet.*, v. 37, no. 3, p. 914-930.
- Longman, M. W., 1980, Carbonate diagenetic features from near surface diagenetic environments: *Am. Assoc. Pet. Geol. Bull.*, v. 64, p. 461-487.
- McKee, E. D., and Ward, W. C., 1983, Eolian, in Carbonate depositional environments: *Am. Assoc. Pet. Geol. Memoir* No. 33, p. 131-170.
- Milliman, J. D., 1974, *Marine carbonates*: New York, Springer-Verlag, 375 p.
- Schmalz, R. F., 1965, Brucite in carbonate secreted by the red alga, Goniolithon sp.: *Science*, v. 149, p. 993-996.
- Shinn, E. A., 1969, Submarine lithification of Holocene carbonate sediments in the Persian Gulf: *Sedimentology*, v. 12, p. 109-144.

Van Kauwenbergh, S. J., 1984, Diagenesis of the carbonate rocks of San Salvador, Bahamas: unpublished M. S. Thesis, The University of Akron, 250 p.

Weber, J. N., and Kaufman, J. W., 1965, Brucite in the calcareous alga, Goniolithon: Science, v. 149, p. 996-997.