

MINERALOGICAL STABILIZATION OF HIGH-MAGNESIUM CALCITE: GEOCHEMICAL EVIDENCE FOR INTRACRYSTAL RECRYSTALLIZATION WITHIN HOLOCENE PORCELLANEOUS FORAMINIFERA¹

DAVID A. BUDD AND ERIC E. HIATT

*Department of Geological Sciences
University of Colorado
Boulder, Colorado 80309*

ABSTRACT: Mineralogical stabilization of porcellaneous foraminifera is known to consist of chemical change without textural alteration at any scale. However, the nature of the alteration process has not been fully reconciled. Porcellaneous foraminifera from the freshwater diagenetic zone of two small islands in the Schooner Cays, Bahamas, are in the midst of Mg loss and $\delta^{18}\text{O}$ change with no textural alteration at any scale. These data indicate that the mineralogical stabilization process, or recrystallization, is a repetitive *intracrystal* incongruent dissolution-precipitation reaction. Each recrystallization produces a calcite with a slightly lower Mg content than its predecessor. The rate of stabilization is dependent on time and hydrologic flux; older phreatic-zone material is the most altered and younger vadose-zone material is the least altered.

Numerical modeling of the chemical diagenesis indicates that the molar water : rock ratio of a single recrystallization is < 1 , and the resultant precipitate is not in equilibrium with the ambient pore waters. Repetitive recrystallizations, however, eventually yield a mineralogically stable low-Mg calcite (LMC) that is in equilibrium with the bulk pore waters. Complete mineralogical stabilization to LMC should occur at cumulative molar water : rock ratios of about 16 and will require ten to hundreds of recrystallizations, each reducing Mg content by no more than 0.1 mole %. The large number of recrystallizations with incrementally small chemical changes per recrystallization makes alteration of these foraminifera significantly different from single-step recrystallization of other types of bioclasts.

The simultaneous modeling of Mg concentrations and oxygen isotopic compositions requires a Mg partition coefficient (D_{Mg}) between 0.0001 and 0.0003. These values are two orders of magnitude less than that generally assigned to calcite precipitation from a large fluid reservoir, and they suggest that D_{Mg} is dependent on the type and scale of reaction, though the nature of that dependency is unknown.

INTRODUCTION

Porcellaneous foraminifera are a unique type of high-Mg calcite (HMC) bioclast in that they can undergo mineralogical stabilization to low-Mg calcite (LMC) without any textural change in the micron-sized crystals that constitute their shell walls (Towe and Hemleben 1976). HMC-to-LMC alteration in all other types of HMC bioclasts is widely regarded to result in both chemical and textural alteration at some scale (e.g., Sandberg 1975; Richter 1979, 1984; Manze and Richter 1979; Neugebauer 1979; Brand and Veizer 1980; Blake et al. 1982; Oti and Muller 1985; Turner et al. 1986). Different degrees of textural change occur in HMC bioclasts due to differences in skeletal architecture (Walter 1985; Turner et al. 1986), solution chemistry (Walter 1983), or diagenetic setting (Richter 1984), but only porcellaneous foraminifera are known to exhibit no textural changes at any scale.

Understanding the chemical processes that result in the mineralogical stabilization of porcellaneous foraminifera is important because of the lack of textural alteration that occurs in these grains. Towe and Hemleben (1976) have suggested a cation-exchange reaction, whereas Turner et al. (1986) have suggested congruent dissolution of the most soluble HMC phase with a concomitant precipitation of LMC. More recently, Bischoff and Mazzullo (1990) have suggested incongruent dissolution of HMC with or without LMC precipitation. The diversity of opinions expressed by these previous workers is in part due to their

observations of $\delta^{18}\text{O}$ changes relative to Mg loss. Towe and Hemleben (1976) had no isotopic data, Turner et al. (1986) noted $\delta^{18}\text{O}$ changes concurrent with Mg loss, and Bischoff and Mazzullo (1990) reported that isotopic and Mg changes may or may not be concurrent.

The conflicting results and conclusions of Towe and Hemleben (1976), Turner et al. (1986), and Bischoff and Mazzullo (1990) indicate that the timing of isotopic exchange relative to Mg loss, the nature of the HMC-to-LMC reaction mechanism, and the relationships between chemical change, reaction mechanism, and texture have not been fully reconciled for porcellaneous foraminifera. The purpose of this paper is to address these issues using Holocene porcellaneous foraminifera that are undergoing HMC stabilization by freshwater diagenesis on 700-year-old islands in the Schooner Cays, Bahamas. These foraminifera are composed of less Mg-rich HMC phases than unaltered foraminifera, and they exhibit both Mg and $\delta^{18}\text{O}$ changes without textural alteration. The textural and chemical data presented imply a repetitive, intracrystal recrystallization process involving incongruent dissolution-precipitation. Numerical modeling of the chemical diagenesis illustrates that water-rock interaction during the recrystallization process is more complex than suggested by previous workers.

SETTING

Porcellaneous foraminifera for this study were collected from Wood and Water cays, two Holocene islands within the Schooner Cays oolitic tidal-bar belt, Bahamas (Fig. 1). Wood Cay is 625 m long and about 125 m wide; Water

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TABLE 1.—Calculated oxygen and carbon isotopic compositions of diagenetically altered foraminifera, Wood and Water cays

Rock Sample	LMC Calcite ¹		% Arag ² (±1 σ)	% LMC (±1 σ)	% HMC (±1 σ)	Measured ³		Calculated HMC ⁴		Error
	δ ¹⁸ O	δ ¹³ C				δ ¹⁸ O	δ ¹³ C	δ ¹⁸ O	δ ¹³ C	
S1-V	-3.9	-1.0	36 ± 2	35 ± 6	29 ± 5	-2.02	+2.69	-3.1	+4.8	±0.4
S2-V	-3.9	-1.2	39 ± 2	35 ± 2	26 ± 3	-1.91	+2.27	-3.2	+3.5	±0.4
S2-P8	-4.8	-0.8	42 ± 4	43 ± 4	15 ± 3	-2.27	+2.20	-3.3	+4.1	±0.3
S4-WT	-5.0	0.6	52 ± 2	19 ± 5	29 ± 5	-1.47	+3.02	-3.1	+1.8	±0.8
S4-P7	-4.0	2.3	54 ± 3	29 ± 2	17 ± 3	-1.33	+3.78	-3.2	+3.7	±0.3
S8-V24	—	—	27 ± 3	0 ± 5	73 ± 3	-1.59	+4.09	-2.4	+3.9	±0.7
S8-V6	-4.9	-5.9	5 ± 5	0 ± 5	95 ± 5	-1.48	+4.35	-1.6	+4.3	±0.4
S8-P5	-4.8	-0.5	23 ± 3	48 ± 3	29 ± 3	-2.98	+1.84	-2.9	+3.5	±0.5
S8-P12	-3.7	1.5	24 ± 2	51 ± 2	25 ± 2	-2.47	+2.75	-3.0	+3.5	±0.4
T2-P4	-3.3	2.6	35 ± 3	40 ± 4	25 ± 6	-2.00	+3.60	-3.7	+3.8	±0.7
T3-V2	-3.7	1.6	11 ± 3	64 ± 2	25 ± 2	-3.10	+2.61	-3.2	+4.3	±0.7
T3-P5	-4.2	1.8	29.5 ± 5	53 ± 4	17.5 ± 3	-2.65	+3.16	-3.6	+4.9	±0.4
							Mean	-3.0	+3.9	
							1σ	±0.5	±0.8	

¹ Isotopic composition of diagenetic pore-filling LMC from Budd and Land (1990).

² All aragonite is assumed to have a uniform isotopic composition of δ¹⁸O = +0.7‰ and δ¹³C = +4.6‰, PDB (Budd and Land 1990).

³ Measured isotopic composition of the HMC (foraminiferal tests), aragonite (ooid coatings on tests) and LMC (intrapartical cement in tests) mixture; 4 to 6 foraminifera per measurement, one measurement per sample.

⁴ Isotopic composition of the HMC calculated using equation 1, as explain in Methods.

Cay is more equidimensional, with an average diameter of about 200 m. Elevations range from 0.5 to 2.5 m above sea level. All sediment and rock on Wood and Water cays are composed of well sorted, medium-grained ooid sand. Porcellaneous foraminifera are the dominant HMC bioclasts in the sediments, but they are a minor constituent, averaging only 0.8% by volume in thin-section point counts of the sediment (Budd 1984).

Small freshwater lenses occur on Wood and Water cays. The thickness and extent of the lenses are greatest immediately after the rainy season. Maximum lens thickness, as defined by the 1.0 ppt isohaline (2.9% seawater), was 1.25 m on Water Cay and 1.0 m on Wood Cay. Further details on the hydrology and hydrochemistry of the lenses can be found in Budd (1988a).

The presence of the freshwater lenses results in freshwater diagenesis being an active process on the islands. The dominant diagenetic processes are dissolution of the aragonitic ooids and precipitation of LMC cement. These processes and their resultant products have been documented in detail by Budd (1988a, 1988b) and Budd and Land (1990).

Radiocarbon ages of the outermost cortical layers of ooid sand collected from the water table on each island indicate that the islands are less than 700 years old (Budd 1988b). These ages establish the maximum possible duration of freshwater diagenesis on the islands. The two dates on Wood Cay (Fig. 2) also suggest that Wood Cay is younger to the north, which is also the direction of island accretion, as evidenced by paleo-beach ridges and current spit growth.

METHODS

Rock samples from both the freshwater vadose and phreatic zones were recovered on the two islands by coring with a portable drill and by hand sampling, as described by Budd (1988b). Polished thin sections of these

rock samples generally contained one to two foraminiferal grains per section, and these thin sections were used for initial textural observations and electron microprobe analyses. For detailed textural analyses and isotopic determinations, individual foraminifera were hand-picked from disaggregated portions of the rock samples.

Complete foraminiferal tests were examined in polished thin sections of epoxy-impregnated rock samples using transmitted light and back-scatter electron microscopy (BSEM). Individual crystals in the shell walls of hand-picked foraminifera were examined by scanning electron (SEM) and transmission electron (TEM) microscopy. For the SEM analyses, individual grains were first broken and lightly etched in 0.1% acetic acid for 15 to 25 seconds. For the TEM analyses, grains were crushed and ultrasonically disaggregated in acetone and then mounted on carbon films.

Oxygen and carbon isotopic compositions of individual HMC foraminifera could not be determined directly because of contamination by LMC cement in the chambers of the foraminifera and oolitic coatings of aragonite surrounding the grains. Estimates of the carbon and oxygen isotopic compositions of the HMC had to be calculated assuming a three-component mineralogical mixture. Four to eight foraminiferal grains from a single rock sample were analyzed together so that there was sufficient material to first determine the relative abundances of HMC, LMC, and aragonite. The foraminifera were first crushed and ground, then the mineralogical composition of the resultant powder was determined using x-ray diffraction (XRD) peak-area ratios (Milliman 1974). Four to six separate XRD analyses of each powder were averaged to increase precision. The accuracy of each mineralogical analysis is about 5%, as determined on known mineralogical mixtures. The powders were then roasted at 400°C for 1 hour, then reacted on-line for 20 minutes in a common-acid bath of 100% phosphoric acid at 90°C, and the resultant CO₂ gas was analyzed on a VG Isogas SIRA

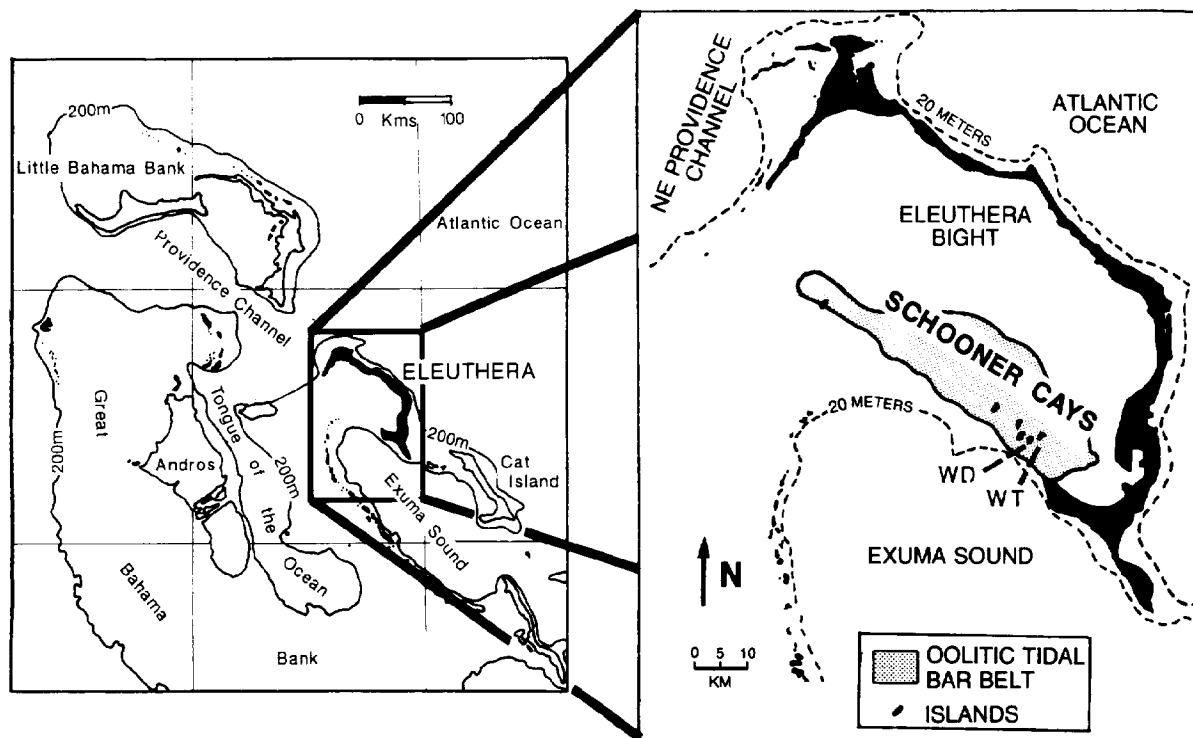


FIG. 1.—Location of the study area. Wood and Water cays (WD and WT) are in the southern portion of the Schooner Cays oolitic tidal-bar belt.

Series II mass spectrometer. Isotopic ratios were corrected for ¹⁷O and the resultant data is reported in permil (‰) relative to the PDB scale. Precision is better than 0.1‰ for both C and O isotope values, as determined by replicate analyses of laboratory standards.

The isotopic composition of the HMC fraction of the analyzed powders was calculated by the following mass-balance equation:

$$(\% \text{ LMC})(\delta_{\text{LMC}}) + (\% \text{ Arag})(\delta_{\text{Arag}}) + (\% \text{ HMC})(\delta_{\text{HMC}}) = \delta_{\text{measured}} \quad [1]$$

The isotopic composition of the oolitic aragonite component (δ_{Arag}) was assumed to be equivalent to the isotopic composition of the aragonitic ooid sand of the adjacent subtidal shoal ($\delta^{18}\text{O} = +0.7\text{‰}$ PDB, $\delta^{13}\text{C} = +4.6\text{‰}$ PDB; Budd and Land 1990). The isotopic composition of the intraparticle LMC cement in each powder was assumed to be equivalent to the isotopic composition of LMC cement in the same rock sample, which was reported by Budd and Land (1990). All of these parameters and the calculated isotopic composition of the HMC foraminifera are given in Table 1.

The assumptions given above regarding the isotopic composition of the aragonite and LMC components are reasonable and justifiable. The simple and short diagenetic history and the water-buffered chemistry of all cements (Budd and Land 1990) suggest that the bulk isotopic composition of intraparticle LMC cement in 4 to 8 foraminiferal grains from a single rock sample should be similar to the bulk isotopic composition of interparticle

LMC cement in the same rock sample. The only reason for the two to be dramatically different would be if the isotopic composition of one was partially rock-buffered and the other was not, but such is not the case. Similar arguments apply to the isotopic composition of the ara-

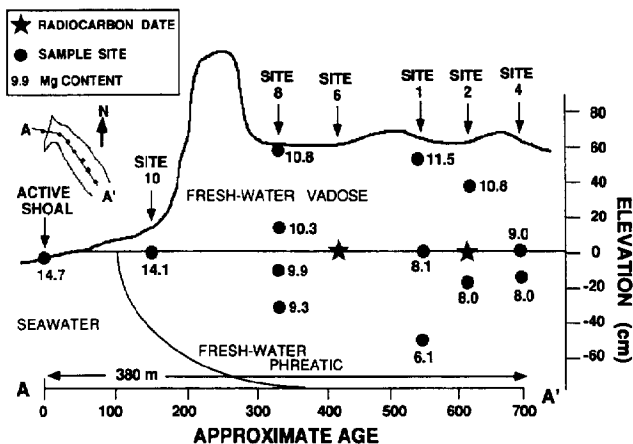


FIG. 2.—Mg content (mole %) of soritid foraminiferal tests on Wood Cay. Samples are plotted relative to the water table and with respect to the approximate age of island at that position. Ages are extrapolated from two radiocarbon dates (stars) and the assumption that the actively accreting northeastern edge of the island has a contemporary age. At any one age, Mg content in the phreatic zone is less than Mg content in the vadose zone. In the phreatic zone, Mg content also tends to lessen with increasing sediment age and, by inference, with increased duration of freshwater diagenesis.

TABLE 2.—Mg content of diagenetically altered foraminifera, Wood and Water cays

Rock Sample ¹	Mole % Mg in Individual Forams ($\pm 1\sigma$)	N*	Mean Mole % Mg for all Forams in the Sample
S1-V	10.2 \pm 0.4	9	11.5 \pm 0.6
	12.8 \pm 0.4	13	
S1-WT	8.1 \pm 1.3	11	8.1 \pm 1.3
S1-Pc	6.1 \pm 0.2	10	6.1 \pm 0.4
	6.0 \pm 0.3	25	
S2-V	11.5 \pm 0.2	4	10.8 \pm 1.9
	10.9 \pm 0.5	4	
	10.4 \pm 1.7	16	
	10.3 \pm 0.6	24	
S2-P8	8.9 \pm 0.3	4	8.0 \pm 0.7
	7.1 \pm 0.6	9	
S4-WT	9.0 \pm 1.6	12	9.0 \pm 1.6
S4-P7	8.6 \pm 1.2	10	8.0 \pm 1.8
	7.4 \pm 1.3	11	
S8-V24	12.3 \pm 1.3	10	10.8 \pm 2.5
	10.4 \pm 1.4	10	
	9.7 \pm 1.7	7	
	10.1 \pm 1.2	11	
S8-V6	10.5 \pm 1.1	9	10.3 \pm 1.6
	10.6 \pm 0.3	5	
S8-P5	9.2 \pm 0.8	21	9.9 \pm 0.9
	10.0 \pm 0.7	10	
S8-P12	8.5 \pm 1.3	17	9.3 \pm 1.5
	14.0 \pm 0.7	8	
S10-WT	14.3 \pm 0.4	7	14.1 \pm 0.8
	7.4 \pm 0.6	4	
S23-P5	7.4 \pm 0.6	4	7.4 \pm 0.6
T2-P4	6.2 \pm 1.0	4	7.0 \pm 1.4
	8.0 \pm 0.8	4	
T3-V2	6.8 \pm 0.5	4	8.4 \pm 1.8
	9.7 \pm 0.9	4	
	7.0 \pm 1.6	4	
	8.1 \pm 0.2	4	
T3-P5	8.1 \pm 0.2	4	8.1 \pm 0.2
T4-WT	5.9 \pm 1.8	5	5.9 \pm 1.8

¹ S = Wood Cay, T = Water Cay, WT = water table, P = phreatic, V = vadose.

* Number of electron microprobe analyses per foraminifera.

gonite component. The aragonite associated with the foraminiferal grains represents small bulk samples of oolitic aragonite. There is no reason for the isotopic composition of one bulk sample of recent oolitic aragonite to differ significantly from another when both were collected in essentially the same locality.

The uncertainty in mineralogical analyses coupled with the uncertainty in the measured isotopic values yields a compounded uncertainty of ± 0.3 to 0.8% PDB in the calculated isotopic composition of the HMC, as determined using the equations of Till (1974, p. 79). Although the calculated $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for the bioclasts have high uncertainties, it is assumed that trends in the isotopic composition of the altered shells are real.

Magnesium contents of the foraminifera were determined by electron microprobe analysis using a JEOL JXA-8600 Superprobe. Operating conditions were a 15 kV electron beam, 0.015 microamp current, a spot size of 5 or 10 μm , and 40-second count times. Calcite and dolomite standards were used for Ca and Mg calibrations, and both elements were determined by wave-length dispersive analysis. Detection limits were 0.03 wt % MgO

(0.05 mole % Mg). Analytical precision is about $\pm 1\%$ with an accuracy of 3% or less for Mg. Four to 25 spots were analyzed for each foraminifer, and one to three foraminifera were analyzed per rock sample. Both the average Mg content of each foraminifer and the average Mg content of all foraminifera in a rock sample are reported (Table 2).

Unaltered foraminifera collected in a sand sample from the crest of an active subtidal shoal adjacent to Wood Cay were also analyzed. The foraminifera were hand-picked from the sediment sample, and their texture and Mg content were studied by the same techniques described above. Stable isotopic compositions of the unaltered foraminifera were determined directly because the grains were fresh, were not coated by aragonite, and contained no intraparticle LMC cement.

RESULTS

Unaltered Foraminifera

The dominant porcellaneous foraminifera recognized in these sediments are *Archais* and *Peneroplis*. Unaltered tests of these foraminifera from the adjacent subtidal shoal exhibit the typical microstructure of porcellaneous foraminifera, namely a three-dimensional array of randomly oriented crystals with a surface veneer of tangentially oriented crystals (Towe and Cifelli 1967; Hemleben 1969). Individual crystals are rod-like, with lengths of 1.5 to 2.0 μm and diameters less than 0.2 μm (Fig. 3A). Unaltered tests have average Mg contents of 14.8 mole %, and average $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of -0.5% and $+3.6\%$, respectively (Table 3).

These Mg and isotopic compositions are compatible with compositions documented elsewhere in the Bahamas for porcellaneous foraminifera (e.g., Blackmon and Todd 1959; Canova et al. 1986). Electron-microprobe x-ray maps of Mg abundance within the shell walls indicate that Mg is uniformly distributed (Fig. 4A, B).

Altered Foraminifera

The average Mg content of individual porcellaneous foraminifera from the freshwater diagenetic zones of Wood and Water cays range from 5.9 to 14.3 mole % (Table 2). Mg contents are lower in phreatic-zone foraminifera (5.9 to 9.9 mole %) than in vadose-zone foraminifera (10.3 to 14.3 mole %). Within the phreatic zone on Wood Cay, the Mg contents of the foraminifera are lowest in older sediments, as shown in Figure 2. Electron-microprobe traverses across individual shells (Fig. 5) indicate that Mg is distributed fairly uniformly throughout individual foraminifera regardless of Mg content. No diagenetic reaction fronts between original HMC and LMC or less Mg-rich HMC occur. Average Mg contents of individual foraminifera are thus representative of the entire shell.

The Mg content of individual crystals could not be measured directly, because more than one crystal is included in a 5- μm electron-microprobe analysis. Instead, the Mg content of individual crystals had to be assessed from electron-microprobe x-ray maps made at high mag-

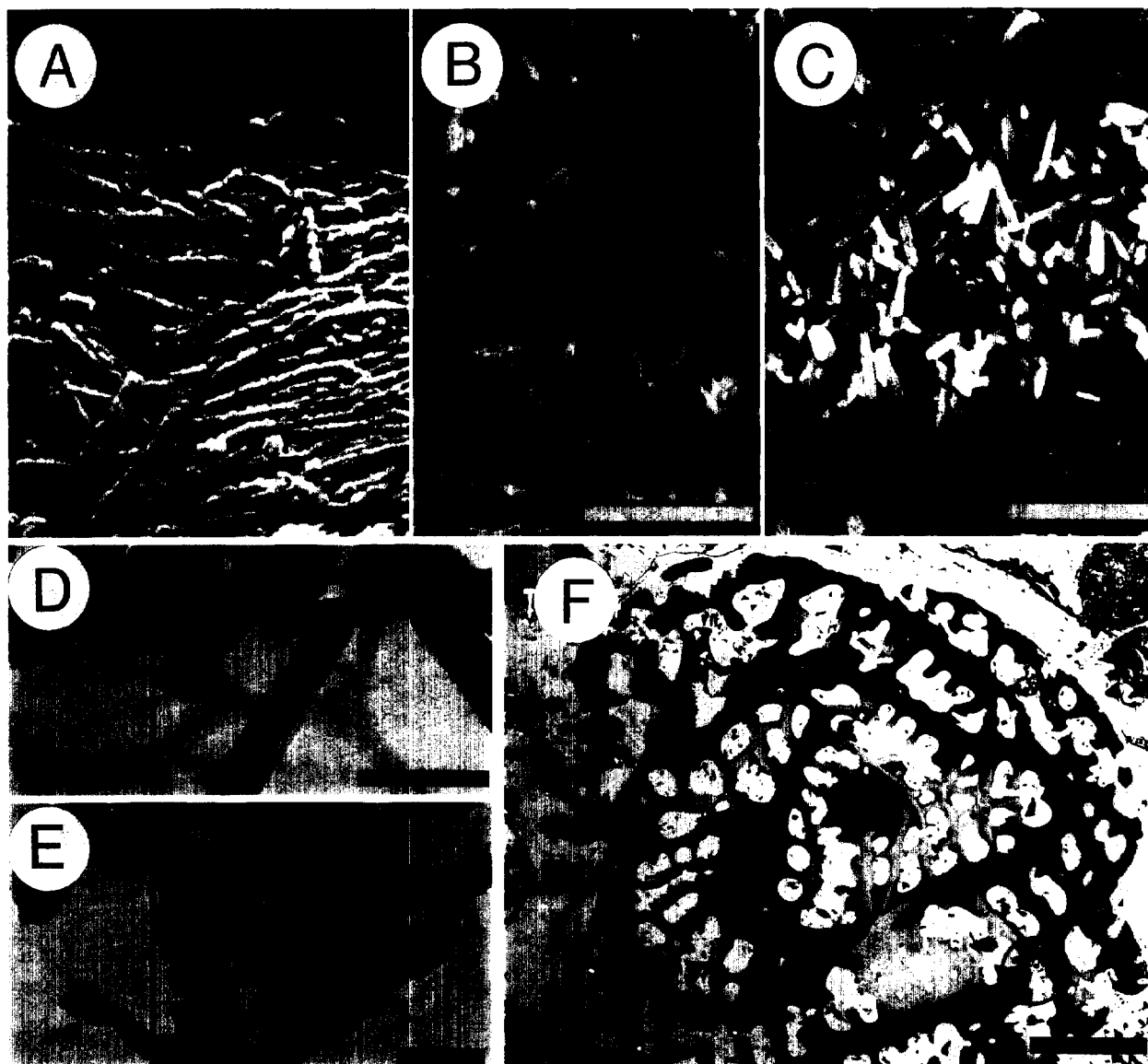


FIG. 3.—A) SEM photomicrograph of pristine, rod-like HMC needles in test of an unaltered foraminifer from the active shoal north of Wood Cay. Scale bar = 2 μm . B and C) SEM photomicrographs of seemingly unaltered rod-like crystals of calcite in tests of Mg-depleted foraminifera from the phreatic zone of Water Cay. Both scale bars = 2.0 μm . D) TEM photomicrograph of rod-like crystals from an altered phreatic-zone foraminifer. Where crystals do not overlap each other or the underlying carbon film, they exhibit a relatively uniform internal consistency in contrast (arrows), suggesting structural homogeneity. Scale bar = 0.25 μm . E) TEM photomicrograph of crystals from another altered foraminifer test. Note that where crystals do not overlap, they are not perfect rods but rather seem to consist of blocky equant subcrystals (arrows). Scale bar = 0.25 μm . F) BSEM photomicrograph of a foraminifer with macroscopic biomoldic porosity (black), LMC cement in intraparticle chambers of the foraminifer (white), and undissolved shell wall (gray). Scale bar = 200 μm . Foraminifera from the same rock samples as B, C, D, E, and F have average Mg contents of 8.1, 6.1, 10.8, 6.1, and 7.0 mole %, respectively.

nification with a 1- μm diameter beam (Fig. 4C to 4F). The distribution of Mg on these maps is too homogeneous for a mixture of LMC crystals and unaltered HMC crystals. Rather, these maps suggest that all crystals within a foraminiferal shell have similar Mg contents, and that these Mg contents are reasonably approximated by individual microprobe analyses and the average Mg content of the respective shell. That is, foraminifera with average Mg contents of 6.1 and 10 mole % Mg, respectively, are

composed of crystals that are also about 6.1 and 10 mole % Mg (Fig. 4C to 4F).

Thin sections, SEM, and TEM analyses revealed no systematic textural differences between unaltered and altered foraminifera. All foraminifera displayed the typical honey-brown color and porcellaneous texture in thin section, regardless of Mg content. Foraminifera with reduced Mg contents consist of the same micron-sized, rod-like crystals that compose unaltered tests (Fig. 3B and C). In

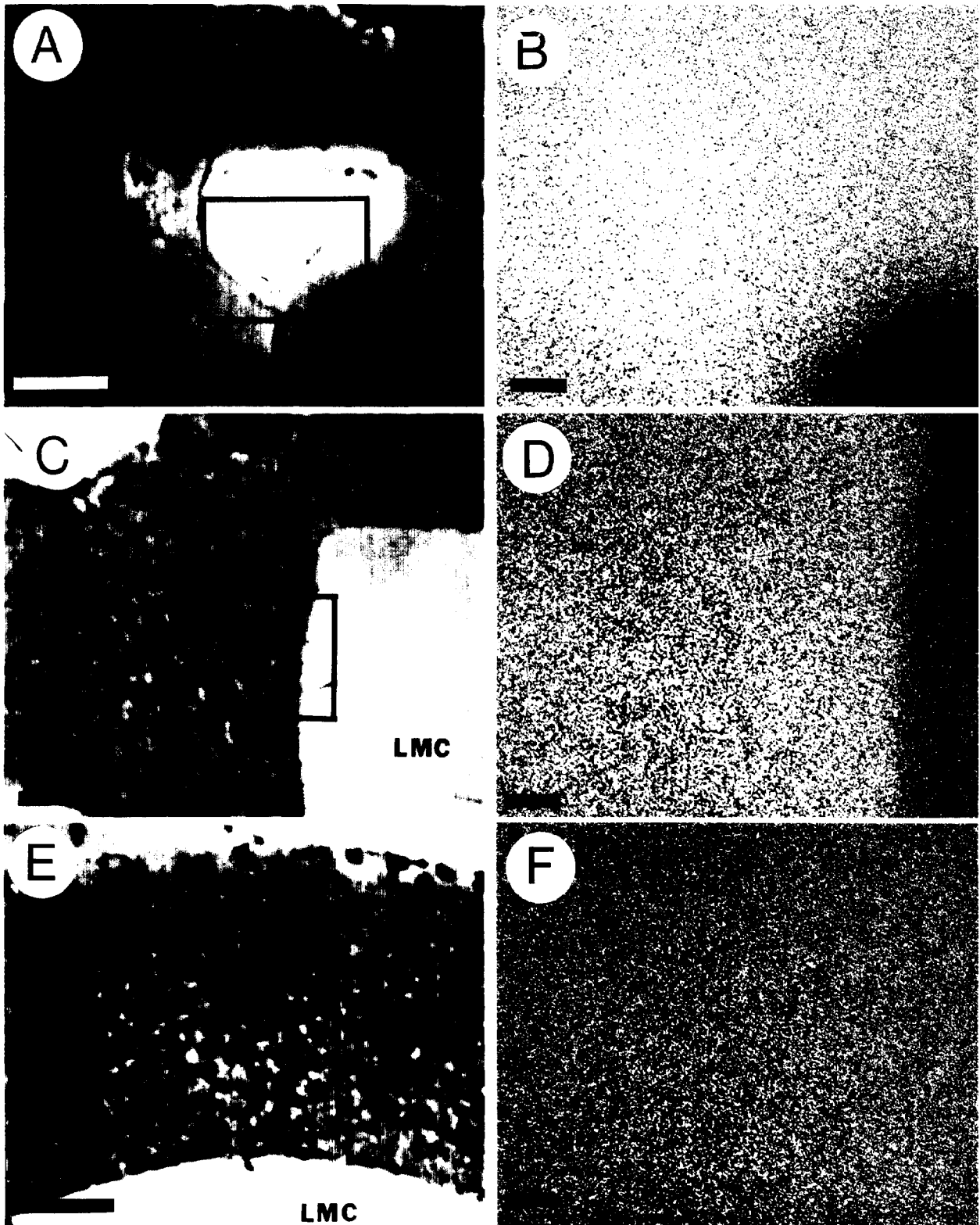


FIG. 4.—A, C, and E) BSEM photomicrographs of unaltered (A) and altered (C, E) foraminiferal tests with 14.8 ± 0.2 , 10.4 ± 0.1 , and 6.1 ± 0.2 mole % Mg, respectively. Scale bars = $10 \mu\text{m}$; LMC = low-Mg calcite cement. Black boxes outline fields of view shown in B, D, and F. B, D, and F) Same foraminifera as in A, C, and E, respectively but as high-resolution x-ray maps of Mg content. Each Mg dot map was generated with a $1\text{-}\mu\text{m}$ diameter beam, 24-minute exposure, and identical photographic processing. All scale bars = $2 \mu\text{m}$, which is the approximate length of individual crystals within the foraminifera. Dot density decreases with decreasing Mg content but is uniform within the foraminifer of each map.

TABLE 3.—Stable isotopic compositions and Mg content of unaltered foraminifera from active, Subtidal Shoal Crests, Schooner Cays, Bahamas

Stable Isotopes			
Analysis No.	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Number of Shells Analyzed
1	-0.54	+3.64	6
2	-0.53	+3.62	4
3	-0.47	+3.70	2
4	-0.55	+3.41	7
Mean	-0.52	+3.62	
1 σ	± 0.03	± 0.06	

Mg Contents		
Mole % Mg in Individual Forams ($\pm 1\sigma$)	N*	Mean Mole % Mg for all Forams
15.3 \pm 0.8	5	14.8
15.1 \pm 0.3	4	
15.1 \pm 0.6	5	
14.1 \pm 0.6	4	
15.2 \pm 1.0	5	
14.6 \pm 0.3	7	
14.3 \pm 0.7	8	

* Number of electron microprobe analyses per foraminifera.

TEM, the crystals of altered foraminifera exhibit a relatively uniform contrast (Fig. 3D), indicating no evidence for pronounced structural variations. The only possible textural difference in individual crystals that was noted occurred in a few crystals from a single foraminifer. Some of the rod-like crystals in this grain had slightly irregular shapes and showed internal variations in contrast that suggest blocky subcrystals, as shown in Figure 3E.

Evidence for the precipitation of LMC in the altered foraminiferal tests is limited to fine-crystalline LMC cement in the chambers of the tests (Fig. 3F). No micritic LMC crystals were observed within the walls of any foraminiferal shells.

Calculated isotopic compositions of altered foraminifera are given in Table 1. The mean $\delta^{13}\text{C}$ value for all 12 individual estimates is +3.9‰ with a range from +1.8 to +4.8‰ (PDB). Given the uncertainties in the calculations, these $\delta^{13}\text{C}$ data are taken to indicate no change in the carbon isotopic composition of the altered foraminifera relative to the unaltered foraminifera. The mean $\delta^{18}\text{O}$ value for all 12 individual estimates is -3.0‰ with a range from -1.6 to -3.7‰ (PDB). These data are distinctly more negative than the $\delta^{18}\text{O}$ value of the unaltered foraminifera. In addition, oxygen isotopic values decrease with decreasing Mg content (Fig. 6).

Foraminifera collected at some water table sites on Water Cay exhibited complete dissolution of HMC crystals and the formation of partial biomoldic pores or macromolds (Fig. 3F). Every foraminifer that exhibited these partial biomolds had reduced Mg contents and texturally unaltered rod-like crystals in the remaining portions of the test. The nature and possible significance of these biomolds are discussed by Budd (1992) and are not given any further consideration in this paper.

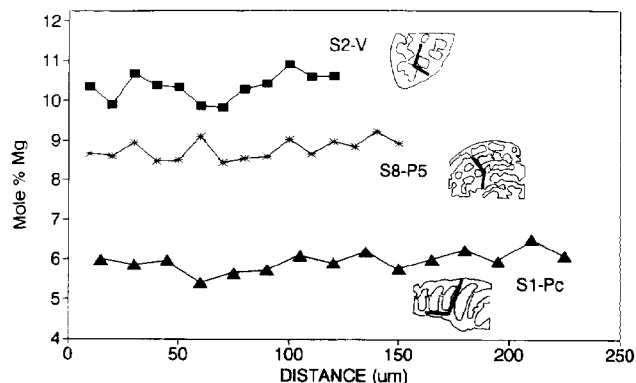


FIG. 5.—Mg content through the shell walls of individual foraminifera. These electron-microprobe traverses (5- μm spots) indicate fairly uniform Mg content throughout each shell. Insets are sketches of each foraminifer showing the path of the traverses; sample numbers refer to the rock sample from which the foraminifera were extracted.

DISCUSSION: THE ALTERATION PROCESS

Towe and Hemleben (1976) proposed a multi-stage alteration process for the mineralogical stabilization and textural recrystallization of porcellaneous foraminifera. Stage 1 involves a loss of Mg with no observable change in crystal habits even at the submicron scale. Stable LMC is the end product of this stage. Stage 2 consists of a recrystallization of the LMC crystals from their original rod-like shapes to a welded mosaic of equant, micrite-sized crystals. Not all fossil porcellaneous foraminifera necessarily attain the second stage. Towe and Hemleben

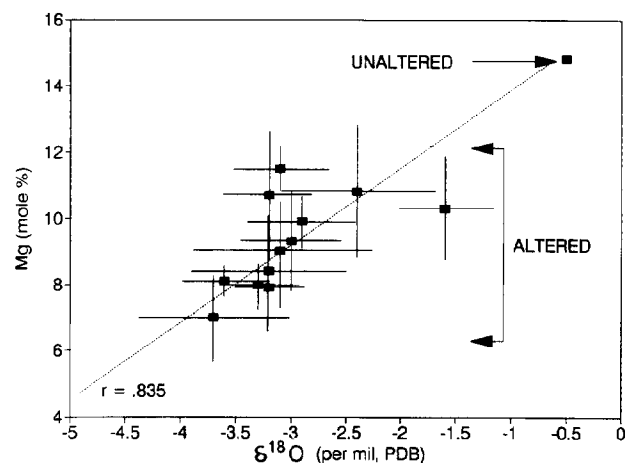


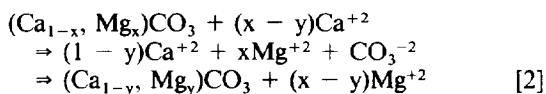
FIG. 6.—Cross plot of average Mg content for all foraminifera in a single rock sample versus calculated $\delta^{18}\text{O}$ of foraminifera from the same sample. Vertical error bars represent one standard deviation in average Mg content; horizontal error bars reflect the combined effects of uncertainty in mineralogical analyses and the measured isotopic values. In spite of the relatively large uncertainties, the uniformly more negative $\delta^{18}\text{O}$ values of altered foraminifera relative to unaltered foraminifera does suggest $\delta^{18}\text{O}$ changes concurrent with Mg loss. Line of organic correlation (Till 1974, p. 100) has a correlation coefficient of 0.835.

(1976) observed foraminifera in the terminal state of both stages and in the process of conversion from stage 1 to 2.

Porcellaneous foraminifera from the Schooner Cays are, to our knowledge, the first documented examples of foraminifera in the midst of Towe's and Hemleben's Stage 1 alteration. Mineralogical stabilization is occurring with *no* change in crystal habit. All but one sample consist exclusively of elongate crystal laths, regardless of Mg content. In the sole exception, some crystal laths consisting of blocky, equant subcrystals are also present (Fig. 3E). These laths may be the first indications of a stage 2 recrystallization, but their isolated occurrence is inconclusive.

The stage 1 HMC-to-LMC alteration of the Schooner Cay foraminifera is interpreted to be incremental, occurring through the formation of successively less Mg-rich HMC phases rather than as a single HMC-to-LMC alteration. As explained in the results, the high-resolution Mg maps (Fig. 4) suggest that all crystals within altered foraminifera are still HMC phases, but that they have less Mg than their unaltered precursors. Alteration of individual crystals is therefore to less Mg-rich HMC phases. Incremental changes are evidenced by the lateral variation in Mg contents of foraminifera on Wood Cay (Fig. 2). Mg loss is least in the vadose zone and greatest in the phreatic zone, particularly in the older portion of the island where freshwater alteration has occurred for the longest period of time. This suggests that the more water-rock interaction a foraminifera has experienced, the lower its Mg content will be. The loss of Mg must occur over a period of time in successive, incremental steps.

Each incremental HMC-to-LMC alteration must be a dissolution-reprecipitation process. Dissolution and reprecipitation is necessitated by the fact that cation (Mg) and anion ($\delta^{18}\text{O}$) chemistries are both changing. The oxygen isotopic shift is inconsistent with the cation-exchange mechanism suggested by Towe and Hemleben (1976). An incongruent reaction in the form of



is required so that oxygen isotopic exchange can occur in the carbonate ion. This reaction, written above in its simplest form, conserves CO_3 , which is necessary given the lack of change in crystal habit and volume. The initial value of x is 0.148; the final value is about 0.02 (Budd and Land 1990). The value of y is less than that of x , and the value of $x - y$ is inversely proportional to the total number of dissolution-precipitation reactions that occur in the complete alteration of HMC to LMC.

The repetitive dissolution-reprecipitation alteration of these HMC foraminifera must also be an intracrystalline process, because the altered calcites retain the same crystal habit as their predecessors. An extracrystalline alteration into the surrounding intraparticle fluid is precluded, because dissolution into that fluid would result in either new LMC crystals formed as some distance from their predecessors, or just a LMC calcite rim on an otherwise unaltered HMC crystal. The first alternative leads to tex-

tural alteration, and both result in chemical heterogeneity. Neither is an attribute of the porcellaneous foraminifera. Only an intracrystal alteration can result in preservation of crystal habit while the entire crystal is chemically changed.

Interpreting the alteration of the porcellaneous foraminifera to occur by an incongruent dissolution-precipitation reaction is not a surprising conclusion, as incongruent recrystallization at the microscale has been argued for all types of HMC bioclasts (e.g., Land 1967; Schroeder 1969; Plummer and MacKenzie 1974; Sandberg 1975; Richter 1979; Neugebauer 1979; Brand and Veizer 1980; Blake et al. 1982; Oti and Muller 1985; Turner et al. 1986). What is significant is that the data presented here indicate that incongruent alteration does not necessarily mean textural change, nor does it necessarily mean one-step alteration.

It is unlikely that all HMC bioclasts stabilize to LMC in separate chemical (Stage 1) and textural (Stage 2) steps as do porcellaneous foraminifera. The various types of HMC bioclasts are known to have marked differences in their relative solubility and reactivity (Bischoff et al. 1983; Walter 1985), and such differences probably result in different alteration paths in different grain types (e.g., Turner et al. 1986). Thus, porcellaneous foraminifera may be the only HMC bioclasts that experience different stages of Mg loss and textural change.

The possibility of separate chemical and textural alterations in other types of HMC bioclasts, however, can only be assessed unequivocally by examining bioclasts with intermediate Mg contents that are undergoing mineralogical stabilization in well-constrained settings such as the Holocene Schooner Cays. Few such examples are documented; the literature is dominated by examples of Pleistocene or older bioclasts that are both LMC and texturally altered (e.g., Sandberg 1975). It is generally assumed that the chemical and textural alterations in these pre-Holocene bioclasts were synchronous, but because these alterations are complete, the assumption is impossible to prove.

NUMERICAL SIMULATION OF THE CHEMICAL ALTERATION

Conceptual Basis

A numerical simulation of the chemical changes observed during the HMC-to-LMC alteration of porcellaneous foraminifera was developed in order to evaluate the number of recrystallization events and extent of water-rock interaction necessary to attain the observed chemistries.

The basis for the simulation is the quantitative water-rock interaction model of Banner and Hanson (1990). Their model simultaneously calculates variations in both trace-element concentrations and isotopic compositions that occur during recrystallization. In each iteration, their model "dissolves" the solid into a specified amount of water and then "precipitates" a new solid from the solute. Stable isotopic and trace-element compositions of the

new solid are determined by mass-balance calculations using appropriate fractionation factors and partition coefficients. Successive iterations react the solid produced in the previous iteration with another increment of the original solution. In this manner, the chemical evolution of the solid during repeated recrystallizations can be tracked. The specific mass-balance equations are given in the computer programs (OXCARB and INTERACT) of Banner and Hanson (1990).

The Banner and Hanson model does not require any specific geometric relationship between the recrystallizing solid and associated fluid phase. All that is important is the molar ratio of the two, as determined by porosity. The numerical simulation performed herein is thus not a test of any particular geometric scenario between solid and solution, nor is it dependent on any particular reaction mechanism. However, a general geometric scenario can be envisioned. The solid phase is an individual crystal and the solution is the fluid in some type of intracrystal reaction zone. Intracrystal solutions have been described by other workers as an intragranular messenger film (Brand and Veizer 1980), a thin reaction zone (Pingitore 1982), and an interphase boundary layer (Machel 1990). In the case of the Schooner Cay foraminifera, the intracrystal reaction zone might occur as a front that moves through a crystal, as an envelope that passes inward through a crystal, or as a diffuse entity in an intracrystal pore network. The simplest scenario, a single reaction zone, is shown in Figure 7.

Although only one reaction zone is shown in Figure 7, multiple reaction zones of varying geometries may exist within a crystal. Multiple zones would increase the reactive surface area and thus increase the rate of intracrystal recrystallization relative to dissolution on the external surface of the crystal. Varied geometries and multiple reaction zones can be accounted for in the simulation by varied porosities, as explained in a following section.

Due to the "bulk-foraminifer" nature of the isotopic data, the results of the numerical simulation must be extrapolated to all foraminifera in a single rock sample. Such an extrapolation is justifiable because Mg content is relatively uniform throughout each shell (Figs. 4 and 5) and all foraminifera within a rock sample have similar average Mg contents (Table 2). These observations suggest that all foraminifera crystals within a particular rock sample are caught at about the same point in the alteration processes. Time and hydrologic setting are the controlling factors, as indicated by the lateral variability in Mg contents on Wood Cay (Fig. 2). The recrystallization of all crystals within a single shell, and all foraminifera within a single rock sample, apparently proceeds at approximately the same rate and in association with the same ambient fluids. Each crystal thus has a composition similar to its neighbors.

The Banner and Hanson (1990) model is a good approximation of the HMC-to-LMC alteration of Schooner Cay foraminifera. First, it simulates the repetitive recrystallization of a mineral in the presence of an aqueous phase, which is the very process by which the foraminifera

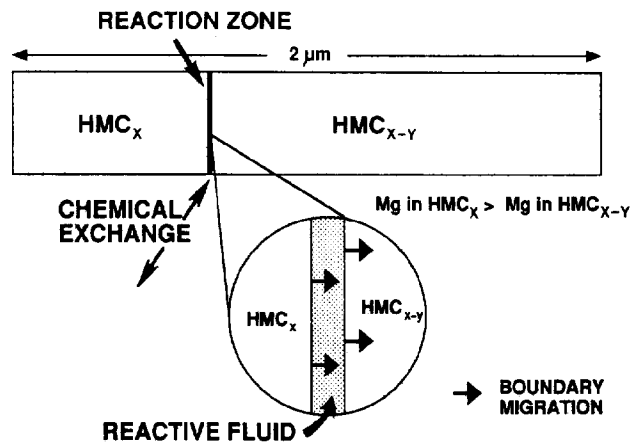


FIG. 7.—Schematic representation of a single HMC crystal with a single intracrystal reaction zone. The reaction zone migrates through the crystal and the fluid within the zone may chemically exchange with the ambient pore fluids surrounding the crystal. The number of zones, their cumulative size, and the number of chemical exchanges per recrystallization event determine the effective porosity. Figure modified from Brand and Veizer (1980) and Pingitore (1982).

are undergoing diagenesis. Second is the model's aforementioned applicability to the simulation of a single crystal's alteration. Last, the diagenetic product of each incremental recrystallization is not in chemical equilibrium with the initial solution introduced at the beginning of each iteration, which mimics the bulk-solution disequilibrium concepts of Brand and Veizer (1980), Pingitore (1982), and Machel (1990). Such concepts are important attributes of any type of intracrystal or intragranular recrystallization model.

The numerical simulation, however, is not a perfect imitation of nature. The most notable shortcoming is the complete resetting of the initial fluid chemistry prior to each iteration of the model. Some degree of chemical exchange must occur between the diagenetic fluids within the crystal and the aquifer pore fluids, otherwise aqueous Mg would build up within the intracrystal reaction zone and eventually quench the recrystallization. In nature, the chemical exchange is widely regarded to occur by diffusion (Pingitore 1982), a process that results in some chemical differences being maintained between the reaction-zone fluid and the bulk solution. The complete chemical exchange between reaction-zone fluid and aquifer pore waters that is incorporated into the numerical simulation probably overestimates the effect of diffusion transport and isotopic exchange between the two fluids. The results of the simulation are thus approximations that err toward a more open, water-buffered system. This means that the number of recrystallization events necessary to achieve a specific Mg and $\delta^{18}\text{O}$ composition are minimized.

Simulation Inputs

Inputs to the numerical simulation consist of the chemistry of the initial calcite, the temperature, the carbon isotopic enrichment factor ($\epsilon_{\text{HCO}_3\text{-Calcite}}$), the chemistry of

TABLE 4.— Numerical simulation input parameters

	Initial Calcite ¹	Initial Water ²
$\delta^{18}\text{O}$	-0.5‰ PDB	-2.6‰ SMOW
$\delta^{13}\text{C}$ (PDB)	3.6‰	-8.7‰, -14‰
HCO_3^-	—	305 ppm, 730 ppm
Ca	—	50 ppm, 70 ppm
Mg	36,800 ppm (14.8 mole%)	2 ppm, 10 ppm
Temperature	—	25°C
$\epsilon_{\text{HCO}_3^- \text{-Calcite}}$	-2.3‰ ³	
D_{Mg}	1.0×10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5} and	
	3.0×10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5}	
Effective Porosity	0.05%, 0.5%, 5%, 50%	

¹ Unaltered foraminifera from Table 3.

² Measured values from Budd (1988a) and Budd and Land (1990).

³ From Turner (1982).

the initial water, the porosity, and the Mg partition coefficient. The latter three are discussed separately in the following sections. All input parameters and their sources are given in Table 4.

Initial Water Chemistry.—The chemistry of the initial water was chosen to reflect the range of pore-water chemistries on Wood and Water cays, as reported by Budd (1984, 1988a) and Budd and Land (1990). Freshwaters collected shortly after the rainy season in November 1981 had a mean $\delta^{18}\text{O}$ value of -2.6‰ SMOW, which is compatible with tropical oceanic rainfall (Budd and Land 1990). Dissolved inorganic carbon (DIC) in the freshwaters of these islands have $\delta^{13}\text{C}$ values of -2.2‰ to -14‰ PDB, with a mean of -8.7‰ (Budd and Land 1990). The HCO_3^- contents of the same waters range from 190 to 730 ppm, with a mean of 305 ± 80 ppm (Budd 1984, 1988a). Simulations were run with mean bicarbonate and mean $\delta^{13}\text{C}$ values, and maximum bicarbonate and most negative $\delta^{13}\text{C}$ values. The latter combination maximizes the effect of the water in the model results.

Input values for the Ca and Mg content of the initial waters were chosen to reflect vadose and phreatic pore waters. The freshest waters on Wood and Water cays (< 200 ppm Cl) have Ca and Mg contents ranging from 50 to 100 ppm and 5 to 16 ppm, respectively (Budd 1984, 1988a). Because all of these waters were collected in the phreatic zone and the dominate source of Mg is admixed seawater (Budd 1988a), it is reasonable to assume vadose-zone waters might have less Ca and Mg. Two sets of initial Ca and Mg concentrations were thus used in the calculations (Table 4). The set with the higher Mg and Ca values is the average of the freshest phreatic-zone waters and the set with the lower Mg and Ca values approximates a possible vadose-zone water. Higher or lower Ca and Mg contents, which still reflect the observed pore-water data, do not significantly alter the results of the simulations.

Effective Porosity.—Porosity is an important parameter in the Banner and Hanson (1990) model because it determines the water : rock ratio of each recrystallization, which in turn determines the number of recrystallizations necessary to achieve a given set of Mg and $\delta^{18}\text{O}$ values. For example, intracrystal porosities of 0.05% and 0.5%

TABLE 5.— Reaction zone porosity, chemical exchange scenarios, and resultant effective porosities for input to the numerical simulations

Reaction Zone Porosity	Number of Chemical Exchanges	Amount of Crystal Reacted between Exchanges	Effective Porosity
0.05%	0	100%	0.05%
0.05%	10	10%	0.50%
0.05%	100	1%	5.00%
0.05%	1000	0.1%	50.00%
0.5%	0	100%	0.50%
0.5%	10	10%	5.00%
0.5%	100	1%	50.00%
5.0%	0	10%	5.00%
5.0%	10	1%	50.00%

yield the same predicted chemistries at 522 and 52 recrystallizations, respectively. Variations in porosity produce only minor differences in the chemical evolution of the solid and in the cumulative water : rock ratio necessary to attain any specific chemistry (Banner and Hanson 1990, their fig. 5).

The water : rock ratio of an individual reaction, however, is dependent not only on porosity but also on the extent of chemical exchange between the water in the intracrystal reaction zone and the surrounding parent fluid. The Banner and Hanson (1990) model requires an exchange between iterations, but not during an iteration. Chemical exchange (diffusion) during a single recrystallization event may occur and can be accounted for in the simulations by inputting effective porosity in place of porosity. For example, a crystal with multiple reaction zones might have a porosity of 1%. If no exchanges occur during a single recrystallization, then effective porosity also equals 1%. However, if four chemical exchanges occur between the reaction zones and the parent fluid as those zones move through the crystal, then the effective porosity becomes the sum of the original plus the additional pore volumes. In this case, the effective porosity would be 5%. The five-fold difference between effective porosity and porosity means a five-fold increase in the water : rock ratio of each simulated recrystallization, and a five-fold decrease in the total number of recrystallizations required to achieve a specific crystal chemistry.

Table 5 lists a number of possible scenarios involving reaction-zone porosities and chemical exchanges during a single recrystallization of a 2- μm -long crystal. The resultant range in effective porosity in these various scenarios is 0.05 to 50%. At one end of this range, a small reaction zone moves through the entire crystal with no chemical exchanges between the fluid in the zone and the ambient pore waters. This yields an effective porosity dependent only on the size of the reaction zone. Alternately, there are up to 1000 chemical exchanges. In these cases, the zone recrystallizes a fraction of the crystal, then a chemical exchange occurs between the fluid in the reaction zone and the ambient pore water. The new fluid then reacts with a second fraction of the crystal, followed by another chemical exchange, and so on. The effective porosity for these multiple chemical exchange scenarios

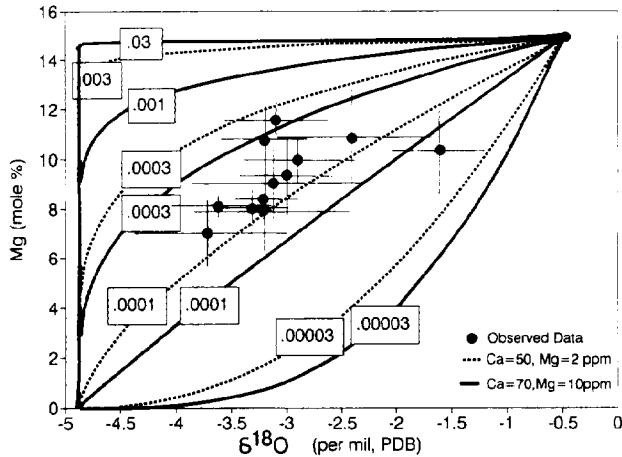


FIG. 8.—Results of numerical simulation of Mg and $\delta^{18}\text{O}$ alteration during intracrystalline recrystallization. Simulation results are shown for six different D_{Mg} values and two sets of initial water compositions. Results are independent of effective porosity (i.e., if all other variables are constant, curves for all effective porosities overlap one another). See Table 4 for remainder of input parameters. The numerical simulations that match the observed data the best are those with a D_{Mg} value between 0.0001 and 0.0003. Observed data and error bars are from Figure 6.

reflects both reaction zone porosity and the number of exchanges during a single iteration of the model. Reaction-zone porosities and the number of chemical exchanges were chosen, in part, so as to examine effective porosity over four orders of magnitude.

Mg Partition Coefficient.—Simulations were run with a number of different Mg partition coefficients (D_{Mg} ; Table 4) due to the uncertainty of an appropriate D_{Mg} value for intracrystal recrystallization. Partition coefficients are phenomenological values (Mucci and Morse 1990), meaning that a specific value is only applicable to a specific process under specific conditions. For example, the value of D_{Mg} is known to depend on temperature (Katz 1973; Mucci 1987) and the Mg/Ca ratio of the solution (Mucci and Morse 1983). As a result of these uncertainties, a range of D_{Mg} values was used in the simulations. The largest D_{Mg} value considered was 0.03, the approximate value proposed by Mucci and Morse (1983) for calcite cement precipitated from a large reservoir of fluid at 25°C and at Mg/Ca ratios less than one.

Model Results

Results of the numerical simulations with varied D_{Mg} values are shown in Figure 8. The only simulations that match the observed data points use a D_{Mg} between 0.0003 and 0.0001. At larger values of D_{Mg} , the rate of Mg loss is too slow relative to $\delta^{18}\text{O}$ changes. At smaller values of D_{Mg} , Mg loss is too rapid relative to $\delta^{18}\text{O}$ changes. The error introduced into the simulation by complete chemical exchange between the reaction-zone fluid and ambient pore waters also means that the 0.0003 and 0.0001 values are maximums. Incomplete chemical exchange would mean a large Mg/Ca ratio in the reaction-zone

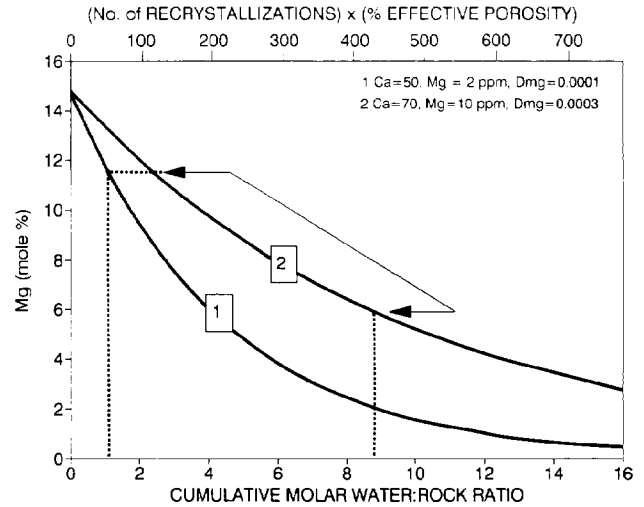


FIG. 9.—Evolution of Mg content in recrystallized calcite as a function of increasing water:rock ratio. The two curves shown correspond to the two simulations in Figure 8 that most closely bracket the observed data. Cation contents of the initial waters and D_{Mg} values for these simulations are given in the upper right corner; see Table 4 for remainder of input parameters. Arrows mark the range in observed Mg contents (Table 2); dashed vertical lines mark the least and greatest possible cumulative water:rock ratios implicated by that range. The number of recrystallizations to achieve a specific water:rock ratio is dependent on the effective porosity, as shown on the upper ordinate scale. For example, a cumulative water:rock ratio of 2 is about 10 recrystallizations if effective porosity is 10%, 100 recrystallizations if effective porosity is 1%, or 1000 recrystallizations if effective porosity is 0.1%. The curves shown can thus be related to all effective porosities.

fluids, which in turn means even lower D_{Mg} values in order to simultaneously match the observed Mg and $\delta^{18}\text{O}$ values.

The cumulative molar water-rock ratios necessary to achieve the observed Mg and $\delta^{18}\text{O}$ contents of the foraminifera are shown in Figures 9 and 10. A range of 1 to 9 yields the observed data, with narrower ranges defined by specific sets of simulation variables. Predicted $\delta^{13}\text{C}$ values are invariant over this range of water:rock ratios, even when the effect of dissolved inorganic carbon is maximized (Fig. 10). The invariant carbon but altered oxygen isotopic compositions reflect the large discrepancy between the amounts of oxygen and carbon in the fluid, and thus the lower water:rock ratios at which the $\delta^{18}\text{O}$ value of the calcite will equilibrate with the fluid.

The minimum number of times that a single crystal must recrystallize in order to match the observed data is also shown in Figures 9 and 10. Samples with the least amount of Mg (about 6 mole %) have experienced the most number of recrystallizations ($420 \div$ effective porosity). Samples with the greatest amount of Mg (about 11 mole %) have experienced the least number of recrystallizations ($50 \div$ effective porosity). The range in the number of recrystallizations that result is 1 to 8400 (Table 6). However, it is doubtful that this full range is realistic; more likely, the natural diagenetic process is approxi-

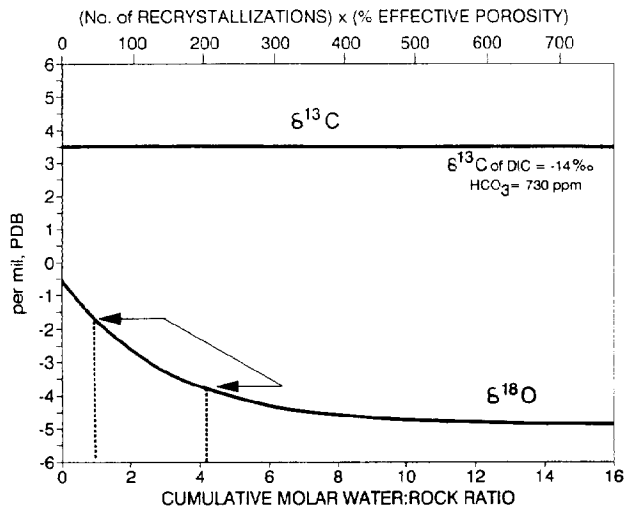


FIG. 10.—Evolution of the stable isotopic compositions of recrystallized calcite as a function of increasing water:rock ratio. The $\delta^{13}\text{C}$ curve is based on the initial water values for dissolved inorganic carbon shown below the curve. These values maximize the effect of the water in the $\delta^{13}\text{C}$ calculation. Nevertheless, calcite $\delta^{13}\text{C}$ values are invariant over the range of water:rock ratios shown. Arrows mark the range in observed $\delta^{18}\text{O}$ values (Table 1); dashed vertical lines mark the least and greatest possible cumulative water:rock ratios implicated by that range. The smaller range in water:rock ratios indicated on this figure relative to Figure 9 may, in part, be due to the uncertainties in oxygen isotopic values. The number of recrystallizations to achieve a specific water:rock ratio is dependent on the effective porosity, as shown on the upper ordinate scale. See Figure 9 for further explanation. See Table 4 for remainder of input parameters.

mated by only one or two of the effective porosities simulated.

Constraining the range in the number of recrystallizations requires further consideration of which effective porosity scenario is most reasonable. In order to do so, the number of recrystallizations per year was calculated for each effective porosity modeled (Table 6). These rates reflect the fact that the greatest amount of Mg loss occurs in older phreatic-zone material, whereas the least amount of Mg change occurs in younger, vadose-zone material (Fig. 2). An effective porosity of 50% corresponds to only one recrystallization every 83 years in the saturated zone, which is probably unreasonable given that diagenesis in general on the Schooner Cay islands is an annual occurrence associated with recharge (Budd 1988a). In contrast, the 0.05% scenario implies nearly 3 recrystallizations per year in the vadose zone, which is probably not likely given the seasonality of rainfall and the low moisture content of the vadose sediments (Budd 1984). The 0.5% and 5% effective porosity scenarios are thus considered to be the most reasonable, meaning that each crystal in a phreatic-zone foraminifera has experienced about one recrystallization every 1 to 8 years, with a total of 10 to 800 recrystallizations to explain the observed Mg contents of all altered foraminifera. One recrystallization per year in the phreatic zone (the 0.5% scenario) would be compatible with an alteration process that is triggered each year by the influx of seasonal meteoric recharge.

TABLE 6.—Relation between effective porosity, number of recrystallizations and inferred number of reactions per year to match observed data

Effective Porosity	Number ¹ of Recrystallizations to Match 11 mole % Mg	Reactions per Year to Match 11 mole % Mg in 350 years ²	Number ¹ of Recrystallizations to Match 6 mole % Mg	Reactions per Year to Match 6 mole % Mg in 700 years ³
50%	1	1/350	8.4	1/83
5%	10	1/35	84	1/8.3
0.5%	100	1/3.5	840	1/1.2
0.05%	1000	2.8/1	8400	12/1

¹ 50 ÷ effective porosity, Figure 8.

² Younger Mg-richer vadose samples, Figure 2.

³ 420 ÷ effective porosity, Figure 8.

⁴ Older Mg-poorer phreatic samples, Figure 2.

Significance

Water-Rock Interaction.—The tens to hundreds of recrystallizations that are occurring during the mineralogical stabilization of the porcellaneous foraminifera means that each recrystallization produces only a slight decrease in Mg content. On Wood Cay, the largest Mg change is from the original 14.8 mole % to 6.1 mole %. Assuming 80 to 800 recrystallizations to attain this change (Table 6), the incremental change in a single recrystallization is only 0.1 to 0.01 mole % Mg, respectively (i.e., $x - y$ in equation 2). Such incrementally small chemical changes during multiple recrystallizations clearly illustrate the unique mineralogical stabilization of these foraminifera. As stated previously, other bioclasts are not known to behave in a similar manner. For example, recrystallization (i.e., neomorphism) of aragonite is a one-step recrystallization (Sandberg and Hudson 1983; Martin et al. 1986). One boundary of the reaction zone is unaltered aragonite and the other is secondary low-Mg calcite.

The HMC-to-LMC recrystallization would intuitively seem to be a rock-buffered process in which the chemistry of the product is strongly influenced by the chemistry of the reactant (e.g., Machel 1990). However, Figure 8 indicates that a LMC will eventually develop with less than 4 mole % Mg and a water-buffered $\delta^{18}\text{O}$ value of -4.7‰ . This apparent discrepancy in the "degree of openness" (Brand and Veizer 1980) or "extent of bulk solution disequilibrium" (Machel 1990) reflects the difference in water:rock ratio during a single recrystallization event versus the cumulative effects of many recrystallizations. With effective intracrystal porosities on the order of 0.5% to 5%, the chemistry of the reaction zone will be very rock buffered (molar water:rock \approx 1:100 to 1:10) during a single recrystallization of a crystal. Disequilibrium between the resultant precipitate and the bulk solution thus occurs for a single recrystallization event. Successive recrystallization events, however, cause the cumulative water:rock ratio to rise because the amount of rock is fixed (a single crystal) but components of the bulk solution are continually introduced. Mg and $\delta^{18}\text{O}$ values change in small but irreversible amounts, and each intermediate calcite phase becomes increasingly more influenced by the bulk solution; the final diagenetic products may even approach equilibrium with the bulk solution. Figure 9

shows that the cumulative water:rock ratio at stabilization to a LMC of 4 mole % Mg is less than about 16, which is still a relatively low value. For comparison, the molar water:rock ratio for intergranular cementation in the freshwater lenses of the Schooner Cays ranges from 2000 to 10,000 (Budd and Land 1990).

Mg Partition Coefficient.—The apparent best-fit range of D_{Mg} values for the HMC-to-LMC recrystallization of these porcellaneous foraminifera is between 0.0003 and 0.0001. Only Baker et al. (1982) have reported a value of D_{Mg} of similar magnitude (0.00081), and that value was also for the recrystallization of chalk in seawater. Both sets of values are 100 times smaller than those of Mucci and Morse (1983) for direct precipitation of calcite from a large fluid reservoir. They are also 100 times smaller than the D_{Mg} value used by Budd and Land (1990) to model intergranular LMC calcite cements in the freshwater lenses of the Schooner Cays. This variability in D_{Mg} values clearly illustrates the dependence of D_{Mg} values on the type and scale of reaction.

The phenomenological conditions that result in a 100-fold difference in D_{Mg} values between HMC-to-LMC recrystallization and LMC calcite cementation *in the same setting* are unknown. Part of this discrepancy may be related to a large difference between cation activities and concentrations in the reaction zone relative to intergranular pore waters. Activities are probably significantly lower than concentrations in the ion-rich reaction zone. The partition coefficient, which is defined by concentrations, thus will be smaller than the true distribution coefficient defined by activities. The difference between the two may not be as large in the more dilute intergranular pore waters. It is also likely that the kinetics of the recrystallization process and/or cation transport in the thin reaction zone affect D_{Mg} . Partitioning probably occurs between the solid and the hydrated surface layer and between that surface layer and solution (Mucci and Morse 1983; Mucci et al. 1985), but little is known about such processes at the scale of thin reaction zones.

The scatter of observed data points in Figures 6 and 8 is not evidence for local variation in partition coefficients. Even allowing for the uncertainty in calculated $\delta^{18}O$ values, some amount of scatter is probably real and most likely reflects variation in Mg and Ca contents of the ambient pore waters. Only two sets of pore water compositions were modeled, yet lateral variability exists (Budd 1984, 1988a). Even at one point in space, the pore waters will have slightly different Mg and Ca compositions during different hydrologic cycles. The numerical simulation cannot attempt to explain each and every observed data point, nor can it yield a specific D_{Mg} value. The simulation just brackets the observed data with reasonable input data, and this in turn indicates a D_{Mg} value on the order of 0.0001 to 0.0003.

CONCLUSIONS

- 1) Holocene porcellaneous foraminifera in the freshwater diagenetic environment of the Schooner Cays, Bahamas, undergo mineralogical stabilization with *no* change in texture or crystal habit. This confirms the observations of Towe and Hemleben (1976). It is still unknown whether Mg loss without textural change occurs in other types of bioclasts. Most studies of HMC bioclasts may have examined the final products of separate Mg-loss and textural alteration stages.
- 2) The lack of change in crystal habits and the simultaneous change in Mg and $\delta^{18}O$ compositions indicate that the HMC-to-LMC alteration is a repetitive incongruent, *intracrystal* recrystallization that involves a dissolution-precipitation process.
- 3) The stabilization rate, as indicated by the amount of Mg loss, is dependent on time and hydrologic flux. Lower Mg values occur in older phreatic-zone sediments and higher Mg values occur in younger vadose-zone sediments.
- 4) Numerical modeling of Mg concentrations and isotopic compositions indicates that tens to hundreds of recrystallizations of a single crystal occur during the complete change from HMC to LMC. Each recrystallization event changes Mg contents by 0.1 to 0.01 mole %. Alteration of these HMC grains is thus significantly different from single-step alteration of other types of bioclasts.
- 5) Cumulative molar water:rock ratios ranging from 1 to 9 predict the observed Mg and $\delta^{18}O$ compositions of foraminifera from Wood and Water cays. Complete stabilization to a LMC with a water-buffered $\delta^{18}O$ will occur by a water:rock ratio of only 16. The ratio of any single recrystallization is 1:10 or less and the resultant precipitate is not in equilibrium with the bulk pore waters. The combined effects of a fixed volume of solid (a single crystal) and the influence of new volumes of water with each successive recrystallization eventually yield cumulative water:rock ratios > 1 and a final LMC that approaches equilibrium with the bulk solution. These ratios are still many orders of magnitude less than water:rock ratios of intergranular cementation.
- 6) A D_{Mg} value between 0.0001 and 0.0003 is apparent for the HMC-to-LMC recrystallization. These values are 100 times less than that apparent for cements precipitated in intergranular pores of the aquifer (Budd and Land 1990). This suggests that D_{Mg} may be dependent on the type and scale of reaction. The nature of such a dependency, however, is unknown.

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