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Dolomitization of the Hope Gate Formation (north Jamaica) by seawater: Reassessment of mixing-zone dolomite

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Abstract—Deposition of the Hope Gate Formation, which forms a prominent reef terrace along the coastline of north Jamaica, took place near the Pliocene-Pleistocene boundary, based on $^{87}Sr/^{86}Sr$ ratios of a mineralogically unaltered biolithite. $^{87}Sr/^{86}Sr$ ratios of some isolated dolomite samples are consistent with coeval seawater values, but most samples are less radiogenic. Dolomite crystals are characterized by relatively narrow ranges in strontium concentration (300 ± 50 ppm) and $\delta^{18}O$ (+3.1 ± 0.4 per mil PDB), both of which are consistent with precipitation from seawater (using a $D_{Sr} = 0.06$), but not with precipitation from mixed water. The observed range in $^{87}Sr/^{86}Sr$ can be explained if both surface seawater and seawater that had interacted with underlying Miocene chalk were responsible for dolomite precipitation. Lowered $\delta^{13}C$ values of Hope Gate dolomite (+0.9) relative to precursor biolithites (+3.0) suggest that the oxidation of organic carbon, possibly accompanying sulfate reduction, also modified the seawater that caused dolomitization. Because the concentration of magnesium in seawater exceeds the concentration of either calcium or bicarbonate, and because seawater is nearly calcite-saturated, precipitation of dolomite causes undersaturation with $CaCO_3$. Replacement of $CaCO_3$ by dolomite thus proceeds automatically if the difficulty in nucleating and/or growing dolomite can be overcome. Porosity is generated because the volume of dolomite precipitated is less than the volume of $CaCO_3$ dissolved as long as large amounts of new CO_2 are not supplied. Dolomitization by seawater can thus be self-sustaining, following porosity channels generated by the process itself, as long as the seawater "pump" is maintained.

INTRODUCTION

THE ZONE OF MIXING between seawater and meteoric water is one hydrogeochemical environment which has been advocated to account for extensively dolomitized rocks. The Hope Gate Formation of north Jamaica (LAND, 1973) was one of the first examples described where mixing-zone dolomitization was proposed. Although the applicability of the mixing-zone model to larger scale, more ancient examples has been questioned (*e.g.*, HARDIE, 1987), no author, to my knowledge, has proposed an alternative explanation for the Hope Gate Formation. Additionally, many other Quaternary and late Cenozoic dolomites, similar to the Hope Gate in both petrography and geochemistry, have subsequently been described (SUPKO, 1977; SIBLEY, 1980; KALDI and GIDMAN, 1982; WARD and HALLEY, 1985; AHARON *et al.*, 1987; HUMPHREY, 1988). Most authors have advocated dolomitization in the mixing-zone for these occurrences, but some have proposed dolomitization by normal or evaporated seawater. Because of virtually identical petrography and geochemistry, a single explanation presumably applies to all.

Two new lines of evidence have stimulated a reassessment of the mixing-zone hypothesis as applied to the Hope Gate Formation. First, $^{87}Sr/^{86}Sr$ ratios not only "date" the time of deposition of Hope Gate biolithites to approximately the Plio-Pleistocene boundary, older than was previously assumed, but $^{87}Sr/^{86}Sr$ analyses of the dolomite also prove that significant amounts of yet "older" strontium were incorporated in most of the dolomite which now constitutes the rocks. The allochthonous strontium must have been derived from underlying units. Secondly, the discovery of dolomite forming in modern Jamaican reefs from near-normal seawater (MITCHELL *et al.*, 1987) suggests other models. The possibilities that Hope Gate dolomite is marine in origin, or that an original marine precipitate was modified by subsequent interaction with meteoric water, must also be considered.

LATE CENOZOIC EVOLUTION OF NORTH JAMAICA

During the Cenozoic, central and western Jamaica consisted of a carbonate platform which accumulated mostly foraminiferal packstones and wackestones, including local scleractinian biolithites. Toward the end of the Oligocene and beginning of the Miocene, a shelf margin approximately 10 km south of the present north coast shed reef debris onto a north-facing slope on which pelagic chalk (the Miocene Montpelier Formation) accumulated. $^{87}Sr/^{86}Sr$ ratios of chalk which is subaerially exposed, and chalk which has been recovered in piston cores taken offshore in water depths up to 4200 m (LAND, 1979), range from .7083 to .7088 (Table 1). Because it is unlikely that erosion has removed much overburden, the highest ratios probably record the end

Table 1. Analytical data for Miocene chalk

Sample	$^{87}Sr/^{86}Sr$	$\delta^{13}C$	$\delta^{18}O$	% dolomite
Onshore outcrop sample				
A	0.70845	−8.0	−3.5	0
F	0.70834	+0.6	+1.7	0
M′	0.70851	−0.3	+0.1	5
8a	0.70883	0.0	−1.2	0
8c	0.70883	−1.7	−0.9	0
S2	0.70847	1.9	3.6	100
Offshore samples				
477	0.70847	+1.3	+0.8	0
628	0.70838	+1.4	+0.3	0
458	0.70850	+1.3	+0.3	0

Sample locations from Fig. 1 and LAND, 1979, his Fig. 1.

of sedimentation, perhaps as the result of uplift, which is thought to have occurred in Late Middle Miocene at approximately 12 Ma (HENDRY, 1987; LAND, 1991). Biolithites of the Hope Gate Formation were deposited unconformably on the Miocene Chalk (Fig. 1), which has undergone considerable meteoric modification since uplift (LAND, 1979).

METHODS

$^{87}Sr/^{86}Sr$ data were obtained by dynamic multicollection on samples immersed for 72 hours in three rinses with 0.2 N sodium acetate to remove exchangable strontium, rinsed several times with distilled water, and dissolved in dilute acetic acid prior to isolation of strontium by column chromatography. Replication is better than 30 ppm, and within-run precision is better than 20 ppm. Carbon and oxygen isotopes were determined by phosphoric acid digestion at 25°C relative to PDB, and are reproducible to ±0.2 per mil. Mineralogy was determined by X-ray diffraction. Calcium, magnesium, and strontium were analyzed by inductively coupled argon plasma atomic emission spectroscopy, and replicates and multiple analyses of the NBS #88b standard indicate precision better than ±5%.

THE HOPE GATE FORMATION

Age

In 1968, while searching for fossil sclerosponges (HARTMAN and GOREAU, 1970) the late T. F. Goreau chanced upon a small outcrop of "chalky" *Halimeda* grainstone (quarry B-1 of LAND, 1973, his Fig. 1), which contains deep water species including *Halimeda cryptica.* The grainstone appears to have been a local sand channel within the reef, which became so densely cemented by Mg-calcite marine cement as to almost entirely preclude subsequent diagenesis. Not only are the primary textures, mineralogy, and bulk chemistry of both allochems and cement preserved in these samples, but the original $^{87}Sr/^{86}Sr$ cannot be very different from the ocean in which Hope Gate reefs grew. Except for this small outcrop, the Hope Gate formation is entirely dolomite plus calcite.

Fourteen analyses from several samples, using various dissolution techniques involving various pretreatments to minimize extraneous strontium, yield an $^{87}Sr/^{86}Sr$ ratio of 0.709064 ± 0.000014. When compared to the value for modern seawater obtained during the interval when these analyses were being accumulated (0.709167 ± 0.000016, 16 analyses), it is clear from known secular changes in ocean $^{87}Sr/^{86}Sr$ (DEPAOLO, 1986; HODELL *et al.*, 1990) that the seaward-most exposures of the Hope Gate Formation must have been deposited in latest Pliocene or earliest Pleistocene time. Exposure surfaces of the Hope Gate formation exhibit extensive microkarst, local karst collapse features, and locally extensive horizontal (water-table) caves which display multiple levels of occupation. These geomorphic features are much more in accord with exposure for approximately 2 Ma subsequent to deposition as evidenced by the $^{87}Sr/^{86}Sr$ data, than would be true if the Hope Gate had a late Pleistocene age as previously supposed (LAND, 1973).

Petrography

The petrography of Hope Gate biolithites is virtually identical to other late Cenozoic dolomites which have been described (*e.g.*, SIBLEY, 1982). Fine-grained, sub-micron-sized dolomite mimetically replaces red algae and benthic foraminifera, and single crystals replace echinoderm allochems, faithfully preserving internal microarchitecture (Fig. 2). Mimetic replacement suggests that dolomite replacement occurred while the allochems were still Mg-calcite, and that dolomite nucleated syntaxially on the skeletal crystals and grew into voids (some submicroscopic) generated by dissolution of the Mg-

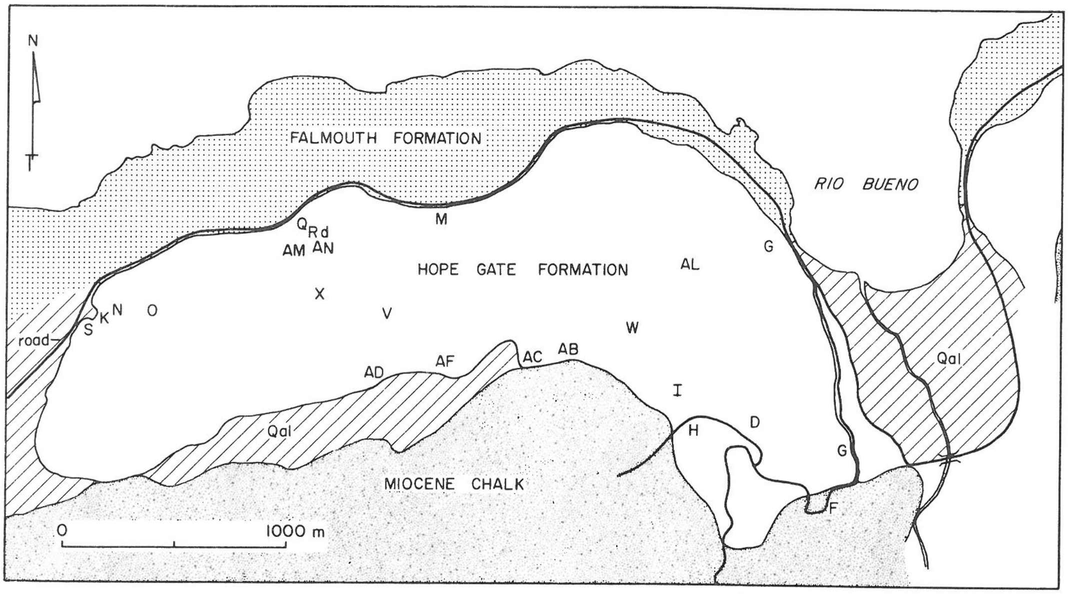

FIG. 1. Map of the study area along the north central coast of Jamaica showing locations of the samples analyzed. Hope Gate reefs form a geomorphic terrace deposited unconformably on chalk of the Middle Miocene Montpelier Formation. The Hope Gate Formation is overlain unconformably by the Falmouth Formation, a reef terrace formed 125,000 years ago during the last interglacial stage when sea level was six meters above its present level.

calcite substrate. Similarly, originally micritic areas are preferentially dolomitized. Since Mg-calcite micrite dominates modern Jamaican biolithites (*e.g.,* LAND and MOORE, 1980), epitaxial nucleation of dolomite on primary Mg-calcite is again suggested (see MITCHELL *et al.,* 1987, their Fig. 4).

The coarsest-grained (<100 microns) "limpid" dolomite isopachously lines aragonite dissolution voids and large primary intergranular pores, many of which were subsequently filled by spar calcite. The average chemistry of the spar calcite ($\delta^{18}O = -3.5$, $\delta^{13}C = -6.7$, $^{87}Sr/^{86}Sr = 0.70884$) is consistent with precipitation from meteoric water, some of the $CaCO_3$ being derived autochthonously from dissolution of aragonite within the reefs themselves, but most being allochthonous from the Miocene chalk.

The presence of intimately associated "sparry" calcite and "limpid" dolomite cements (ignoring minor subsequent cave and soil features), together with relatively low strontium and sodium concentrations of the dolomite, constituted the primary petrographic and geochemical arguments for mixing-zone dolomitization (LAND, 1973). Rare alternating zones of calcite and dolomite (LAND, 1973, his Fig. 9; WARD and HALLEY, 1985, their Fig. 5; HUMPHREY, 1988, his Fig. 4) seem to support the hypothesis that precipitation of limpid dolomite was associated with meteoric influx. But the volume of "limpid" dolomite in the reefs is small, and alternating zones of calcite and dolomite are rare. It is the origin of the fine-grained mimetic dolomite which preceeded the pore-filling dolomite and spar calcite, and which constitutes most of the dolomite in the rocks, which is the primary issue.

FIRST-CYCLE MIXING-ZONE PRECIPITATION OF DOLOMITE

Table 2 presents data collected subsequent to 1973, mostly from localities shown in Fig. 1. In order to test the hypothesis that Hope Gate dolomite was a first-cycle precipitate from mixtures of seawater and meteoric water, the composition of meteoric water which might have been available to infiltrate the reefs must be constrained. Hope Gate reefs grew on uplifted Miocene chalk which was subsequently considerably modified by meteoric diagenesis (LAND, 1979). We can estimate the composition of meteoric water which accompanied diagenesis of the chalk and is hypothesized to have discharged through Hope Gate reefs. Specifically, the $^{87}Sr/^{86}Sr$ of the water would have reflected the $^{87}Sr/^{86}Sr$ of the surficial chalk. Rain infiltrating the chalk would have rapidly become saturated with the most soluble phases, probably fine nannofossils,

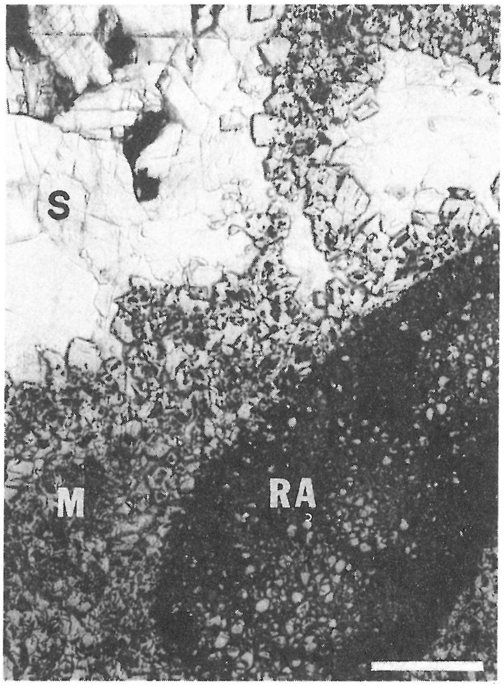

FIG. 2. Back-scattered electron micrograph of typical Hope Gate biolithite. Red algal grain (RA) was replaced mimetically by extremely fine-grained dolomite, suggesting that the dolomite directly replaced Mg-calcite. Matrix dolomite (M) is somewhat coarser-grained and probably also grew epitaxially on primary Mg-calcite micrite. Coarse "limpid" dolomite fills a moldic pore formed by the dissolution of an aragonite allochem and is overlain by spar calcite (S) of meteoric origin. A few dolomite crystals are zoned, and "hollow" rhombs are common, probably formed by epitaxial growth of a more stable phase and subsequent dissolution of the more Ca-rich and defect-ridden core. Scale bar is 100 microns.

near the land surface, and therefore would have an $^{87}Sr/^{86}Sr$ of about 0.7085 (Table 1). This is exactly the ratio found today in the Pear Tree river, a small river just east of the study area, having its headwaters in the Miocene Montpelier Formation.

The ionic composition of meteoric water in Hope Gate time, controlled by the partial pressure of CO_2 in the soil and the bedrock lithology, would probably have been similar to the ground water in this area today, which contains between 40 and 75 ppm dissolved calcium (O'NEIL, 1964; F.A.O., 1974). Groundwater today contains about 20 ppb Sr (O'NEIL, 1964), yielding a molar Sr/Ca ratio of about 0.00032, only slightly higher than the Sr/Ca ratio of outcropping (altered) chalk (LAND, 1979, his Fig. 4). In Hope Gate time, the recently uplifted chalk would have contained approximately 1200 ppm Sr (LAND, 1979, his Table 2), yielding a Sr/Ca of .0014. Judging from studies of Holocene aquifers where mineralogic stabilization reactions are in progress (HARRIS and MATTHEWS, 1968; BUDD, 1988) the Sr/Ca of groundwater is several times elevated over the Sr/Ca of the host sediments because of the precipitation of low-strontium calcite. Therefore, accepting a calcium concentration of the water of about 75 ppm, and a molar Sr/Ca about three times that of the primary chalk, meteoric water in Hope Gate time is estimated to have contained at most 0.5 ppm Sr.

$^{87}Sr/^{86}Sr$ data

Combining estimates of the Sr/Ca ratio in meteoric water infiltrating Hope Gate reefs, and its strontium isotopic composition, Fig. 3 depicts possible mixtures which could account for the observed strontium isotopic composition of Hope Gate dolomite. If Hope Gate dolomite is a first-cycle precipitate from mixtures of seawater having a $^{87}Sr/^{86}Sr$ ratio of 0.70906 and meteoric water having an $^{87}Sr/^{86}Sr$ of 0.7085, then precipitation of dolomite must have taken place from a wide range of mixtures, from essentially pure seawater to mixtures containing only a few percent seawater. Most samples, however, could have precipitated in the range of 10 to 40% seawater, similar to the range of overlapping dolomite supersaturation and calcite undersaturation predicted from theoretical solubility equilibria for mixtures of seawater and meteoric water (PLUMMER, 1975). The most radiogenic samples, those inconsistent with mixing-zone precipitation, might be explained if meteoric water had undergone rock/water interaction with the Hope Gate reefs (say by aragonite dissolution) prior to mixing, thus shifting the $^{87}Sr/^{86}Sr$ ratio of the meteoric water toward coeval seawater values. The increased strontium concentrations which would result from this scenario are not substantiated, however, and no gradients of increased $^{87}Sr/^{86}Sr$ toward the present coast (away from the Miocene chalk) have been detected (Table 2).

Strontium concentration data

The range in strontium concentrations of Hope Gate dolomite is quite restricted (Table 2, Fig. 4). Unfortunately, lack of assurance of the distribution coefficient for strontium between dolomite and solution makes interpretation of this fact somewhat tenuous. Known Holocene marine dolomite (BEHRENS and LAND, 1972; PATTERSON, 1972; MITCHELL *et al.*, 1987) contains approximately 600 ppm Sr. Given a constant molar Sr/Ca for seawater of

Table 2. Analytical data for Hope Gate dolomite and limestone

Sample	f_{Mg}[1]	ppm Sr	$^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$	$\delta^{13}\mathrm{C}$	$\delta^{18}\mathrm{O}$	% dolomite[2]
Dolomite concentrates						
C			0.70899	1.0	3.1	60
D			0.70901	1.6	3.3	50
G	0.417	240	0.70901	0.8	2.9	45
I	0.416	330	0.70907	1.6	3.4	70
K	0.429	270	0.70897	1.6	3.4	95
M	0.419	270	0.70901	1.6	3.5	70
Mc	0.421	295	0.70897	1.1	3.2	95
N	0.419	295	0.70897	1.6	3.6	90
Qrd	0.387[3]	285	0.70906	−2.6	2.5	60
Q30	0.416	325	0.70895	0.2	3.2	90
Q40	0.419	305	0.70892	0.1	3.3	85
Q45	0.389[3]	340	0.70893	0.3	2.9	65
W	0.419	295	0.70904	0.8	3.2	45
X	0.416	435	0.70889	0.8	2.9	45
AB	0.346[3]	220	0.70900	−0.9	2.2	55
AF	0.421	270	0.70888	−0.7	2.5	55
AM	0.429	330	0.70884	0.6	3.2	70
AN	0.435	325	0.70889	0.4	2.3	45
Limestones						
H			0.70884	−10.1	−2.9	trace
O			0.70884	−8.3	−3.3	5
V			0.70881	−9.4	−3.3	5
AC			0.70881	−4.6	−1.6	trace
AL			0.70889	−6.5	−2.6	trace
AD			0.70892	−9.6	−2.6	5

[1] Molar Mg/(Ca + Mg).
[2] Before concentration by leaching with EDTA.
[3] Still contained detectable calcite by X-ray diffraction.

0.0092, this transforms to a distribution coefficient of 0.14 (based on the Sr/Ca of dolomite, not Sr/[Ca + Mg]), nearly identical to the distribution coefficient for calcite which applies to most biogenic marine calcite and to rapidly precipitated laboratory calcite (KINSMAN, 1969). This is not surprising since strontium in the dolomite lattice probably substitutes almost entirely for calcium and not for magnesium. Because the distribution coefficient of strontium in calcite is known to be lower than 0.14 under conditions of slower, more nearly equilibrium precipitation (LORENS, 1981), it is logical to suppose that a lower distribution coefficient might also apply to dolomite precipitated under more nearly equilibrium conditions. Figure 4 shows that Hope Gate dolomite could have precipitated as a first-cycle phase from solutions containing more than about 50% meteoric water using a distribution coefficient of 0.14. Alternatively, marine-dominated solutions are required, and mixing-zone conditions precluded, if distribution coefficients as low as 0.05 apply.

Oxygen isotope data

One of the most puzzling aspects of Hope Gate (and other Quaternary) dolomite is the relatively uniform and $^{18}\mathrm{O}$-enriched compositions in comparison to presumed normal marine precipitates. Average Hope Gate $\delta^{18}\mathrm{O}$ dolomite is approximately +3.1 (PDB), whereas dolomite having a slightly more Ca-rich composition, and interpreted to have precipitated from normal seawater (MITCHELL *et al.*, 1987; LUND, 1989), is between 0.0 and +2.0. Oxygen isotope data thus do not support significant involvement of first-cycle meteoric water in the precipitation of Hope Gate dolomite. Two possible explanations could account for the somewhat $^{18}\mathrm{O}$-enriched composition of Hope Gate dolomite relative to presumed marine precipitates:

1) The dolomite-water fractionation factor used (+3.8 relative to calcite, which includes the differences in phosphoric acid fractionation factors between the two minerals at 25°C, *i.e.*, ΔPDB) is too low, and should be closer to 4.5 or even 5 per mil.

2) Hope Gate dolomite precipitated from mixtures of seawater and/or meteoric water which had been buffered toward $\delta^{18}\mathrm{O}$-enriched values because of rock/water interaction with underlying strata.

Figure 5 demands that if the second explanation is correct, then the most enriched dolomites must have precipitated from about half seawater and half

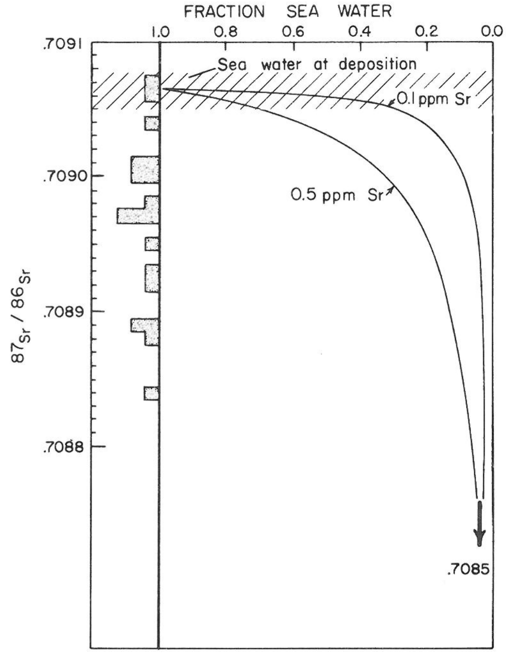

FIG. 3. Fraction of seawater ($^{87}Sr/^{86}Sr = 0.70906$) and meteoric water ($^{87}Sr/^{86}Sr = 0.7085$) necessary to precipitate Hope Gate dolomite (analyses from Table 2 presented as a histogram on left) for two assumed strontium concentrations of meteoric water (0.1 and 0.5 ppm). The range of mixtures characterized by overlapping dolomite supersaturation and calcite undersaturation is typically between 0.1 and 0.5, depending on variables such as CO_2 partial pressure and K-dolomite (PLUMMER, 1975). All but the most radiogenic dolomite samples could have precipitated under appropriate mixing conditions. Some samples contain large amounts of allochthonous (Miocene) strontium, whereas others contain none.

meteoric water which had been buffered at $\delta^{18}O = +3.5$ (SMOW) by reaction with the Miocene chalk. In the case of Jamaica, this scenario is possible, considering that the $\delta^{18}O$ of the original chalk was approximately +1 (Table 1, and LAND, 1979, his Table 1), and that water which reached equilibrium with the chalk at 25°C would have a $\delta^{18}O$ slightly greater than +3. In the case of other Quaternary localities, however, where large upflow masses of reactive pelagic carbonates are absent, this explanation is less satisfactory. In addition, such large ^{18}O-enrichments have never been documented in modern meteoric aquifers, and would require extremely low water/rock ratios.

If the fractionation factor between dolomite and calcite is larger than 3.8 per mil, then Hope Gate dolomite could have precipitated directly from seawater, as well as from mixtures of seawater and/or meteoric water which had undergone substantial chalk/water interaction. The oxygen isotopic data in no way support significant involvement of first-cycle meteoric water in dolomite precipitation. If mixtures of meteoric water and seawater were involved, oxygen isotopic data demand not only that the $\delta^{18}O$ of the mixtures was similar to, or slightly enriched relative to, modern surface seawater, but that the mixtures did not vary more than about 1.5 per mil over the time Hope Gate dolomite precipitated. It is difficult to understand how mixtures of seawater and rock-buffered meteoric water could maintain such limited compositional ranges over the duration of Hope Gate dolomitization.

Other data

Other chemical parameters which have been analyzed include $\delta^{13}C$ of both dolomite and calcite,

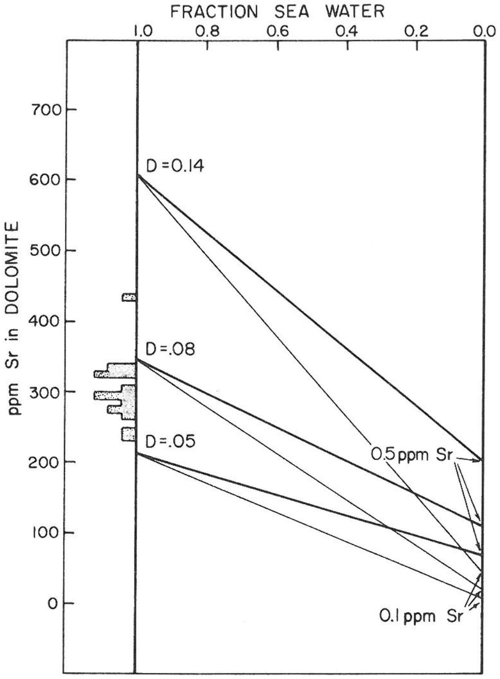

FIG. 4. Strontium concentration in Hope Gate dolomite (data from Table 2 presented as a histogram on left axis) versus fraction seawater in meteoric water-seawater mixtures for three different distribution coefficients, D ($m[Sr/Ca]_{dolomite} = D * m[Sr/Ca]_{water}$), and two assumed strontium concentrations in meteoric water (0.1 and 0.5 ppm). Hope Gate dolomite could have formed as a first-cycle mixing-zone precipitate in the range 10 to 50% seawater if $D = 0.14$. Marine-dominated mixtures must have been responsible if lower D's apply, unless Sr/Ca ratios of mixtures were elevated due to the dissolution of Sr-rich aragonite and Mg-calcite in the primary reefs. The relatively narrow range of strontium values observed, and their generally non-radiogenic nature, dispute such a scenario.

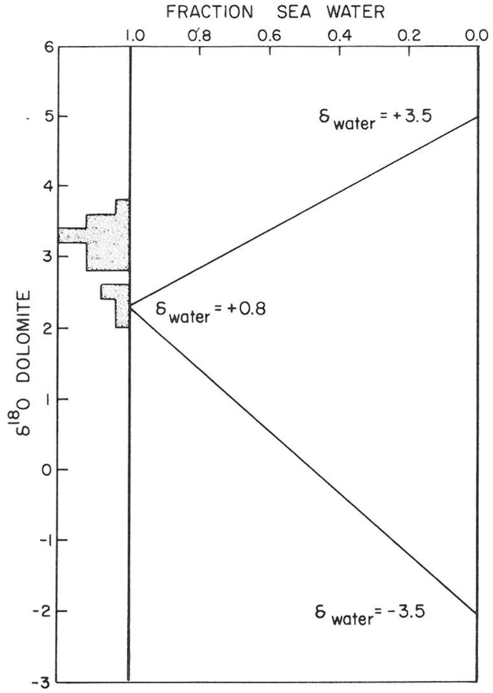

FIG. 5. $\delta^{18}O$ of Hope Gate dolomite (data from Table 2 presented as a histogram on the left axis) versus fraction seawater ($\delta^{18}O = 0.8$ SMOW). Mixing lines are shown for both first-cycle coastal meteoric water (−3.5 SMOW), and for water buffered at 25°C by primary Miocene chalk (+3.5 SMOW). Equilibrium dolomite precipitates could be heavier than the values calculated if the dolomite-water fractionation factor used (+3.8 PDB relative to calcite) is actually larger. In either case, precipitation of Hope Gate dolomite from mixtures of seawater and first-cycle meteoric water is precluded. If meteoric water is involved, the water must have been buffered to relatively ^{18}O-enriched values by the ^{18}O-enriched Miocene chalk.

and a few sodium determinations. The average $\delta^{13}C$ of Hope Gate dolomite is +0.9 (PDB), as compared to +3.0 for the precursor reefs (LAND, 1973, his Table 2) and +1.5 for the original Miocene chalk (LAND, 1979, his Table 1). Subaerially exposed Miocene chalk today has a wide range of $\delta^{13}C$ values, averaging −2.3. Clearly, Hope Gate dolomite precipitation incorporated additional ^{12}C than was present in the precursor sediments, a scenario consistent with (but not unique to) meteoric-marine mixing. Too many variables exist, however, to constrain a narrow range of mixtures. The average $\delta^{13}C$ of Hope Gate calcite (−6.7) is very different from Hope Gate dolomite (+0.9), and proves that the bulk of the fine-grained dolomite cannot be a meteoric precipitate co-genetic with (meteoric) calcite.

Limited sodium analyses support substantially less sodium in Hope Gate dolomite (*ca.* 500 ppm) than in modern marine examples (>1000 ppm, LAND and HOOPS, 1973). Too much uncertainty exists in assuring that sodium is a lattice constituent, and in assigning a distribution coefficient, to use sodium to constrain the magnitude of possible meteoric-marine mixing. If kinetic factors affect the distribution coefficient of strontium in carbonates, then similar factors likely affect distribution coefficients for other elements, including sodium.

One final relevant calculation is the volume of water necessary to accomplish the required diagenesis. As previously documented (LAND, 1973, p. 76), Hope Gate diagenesis involved not only the elimination of primary aragonite and Mg-calcite, but the addition of approximately 15% by volume dolomite cement which reduced average porosities from about 20% to about 5%. Using PHREEQE (PARKHURST *et al.*, 1980) and a pK-dolomite of 17.23, a minimum of 67 cm^3 of seawater (0.15 cm^3 dolomite/2.224 cm^3 dolomite precipitated per liter of seawater, Table 3) is required to precipitate 15 volume percent dolomite in one cm^3 of reef. Assuming a mixture of 20% seawater and 80% meteoric water, approximately ⅓ liter is required, involving approximately 2500 exchanges of pore water using an average porosity during cementation of 12%. If the reefs grew and underwent diagenesis in an interval of 80,000 years (80 m thick reef which grew at a rate of one meter per 1000 years, LAND, 1974), then only one pore volume exchange would need to occur every 30 years (assuming the modelled equilibrium was achieved) to accomplish the observed dolomite cementation. Even allowing for only 1% efficiency of dolomite precipitation, a flow rate of three pore volumes per year is hardly excessive, especially in this relatively high relief setting.

Based on these data (and assumptions), Hope Gate dolomite apparently could have precipitated from mixtures of approximately 20% meteoric water and seawater, provided (1) that a distribution coefficient for strontium of 0.14 applies; (2) that all the meteoric water was buffered to relatively ^{18}O-enriched values by interaction with the underlying reactive chalk, but that some was buffered back to coeval $^{87}Sr/^{86}Sr$ values; and (3) that the range of mixtures which caused precipitation was quite restricted. These relatively uniform conditions must have been maintained over sufficient time for at least 2500 pore volume exchanges to take place.

STABILIZATION OF PRIMARY MARINE DOLOMITE IN METEORIC WATER

The finding that dolomite is forming from seawater in modern and late Pleistocene biolithites

Table 3. Results of equilibrating seawater[1] with calcite + dolomite[2]

	Open to CO_2		Closed to CO_2	
	Cal + Dol	Cal + Dol + C[3]	Cal + Dol	Ca + Dol + C[3]
pH	7.51	7.52	6.79	6.16
pCO_2	−3.50	−3.50	−2.07	−0.78
Dol ppt'd[4]	2.224	2.318	2.206	2.273
Cal dissv'd[4]	2.451	2.398	2.462	2.427
porosity[5]	0.227	0.080	0.256	0.154

[1] from PARKHURST *et al.* (1980, p. 55). pH = 8.32, $pCO_2 = 10^{-3.50}$. PHREEQE was modified to calculate activity coefficients by the B-dot method. Simulations using PHRQPITZ (PLUMMER *et al.*, 1988) produce similar results.

[2] pK dolomite = 17.23, pK calcite = 8.51.

[3] 0.015 moles organic carbon, which resulted in reduction of approximately 25% of the original sulfate. This would produce dolomite with a $\delta^{13}C$ of approximately −1.3 (assuming −20 organic matter), which is more ^{13}C depleted than is actually observed. Increasing sulfate-reduction would result in dolomite progressively more depleted in ^{13}C, and eventually, no increase in porosity.

[4] cm^3 per kilogram of water using a molar volume of 65.64 cm^3 $mole^{-1}$ for Hope Gate dolomite (based on unit cell measurements by X-ray diffraction) and 36.94 cm^3 $mole^{-1}$ for calcite.

[5] cm^3 per kilogram of water. Increasing sulfate reduction results in increased dolomite precipitation and decreased calcite dissolution. Changes in pK dolomite and/or dolomite stoichiometry cause only minor changes in the amount of porosity produced.

(MITCHELL *et al.*, 1987), and the observation of extensive hydrodynamic flow of seawater through both modern and late Pleistocene reefs (LAND *et al.*, 1989), suggests another possible origin for Hope Gate dolomite involving meteoric water. If considerable amounts of dolomite, similar to that observed forming today (MITCHELL *et al.*, 1987; LUND, 1989), had been emplaced contemporaneously with deposition, by direct precipitation from seawater, the dolomite might have recrystallized when meteoric water infiltrated the reefs as they grew seaward. No "water volume" problem exists to accomplish porosity reduction because of demonstrably adequate (although not explained) flow of seawater through the reefs (LAND *et al.*, 1989). This scenario can be modelled using an algorithm evolved from that presented by LAND (1980) or advocated by BANNER and HANSON (1990).

The original dolomite is presumed to have contained 600 ppm Sr having an $^{87}Sr/^{86}Sr$ ratio of 0.70906, and to have a $\delta^{18}O$ of +2 and a $\delta^{13}C$ of +2. Using values for meteoric water of 0.1 ppm Sr, $^{87}Sr/^{86}Sr$ = 0.7085, $\delta^{18}O$ = +1.3, and $\delta^{13}C$ = −25, the results of the simulation are shown in Fig. 6.

Because of the rock/water ratio of the constituents modelled (12% porosity), oxygen is most sensitive to modification, and carbon least sensitive. Fifty pore-volume exchanges of fluid of any reasonable oxygen isotopic composition are sufficient to equilibrate primary dolomite with the imposed water assuming that equilibration takes place during each pore volume exchange. Clearly, the water which was responsible for precipitation of the dolomite that now constitutes the rocks must have been in oxygen isotopic equilibrium with the existing dolomite. Even granted that sufficient volumes of mixed water having a $\delta^{18}O$ of +1.3 were available, approximately 150 pore volume exchanges are necessary to lower $^{87}Sr/^{86}Sr$ ratios to average Hope Gate values (0.70896), 500 to lower the strontium content to Hope Gate values using a $D = 0.06$, and more than 2000 pore volume exchanges to reach acceptable $\delta^{13}C$ values.

Therefore, using basic conservation-of-mass requirements and reasonable approximations of possible solution compositions, an original marine dolomite could have been reset to the values observed today in the Hope Gate Formation only if several thousand pore volume exchanges took place in order to satisfy the carbon mass-balance. Except for $\delta^{13}C$, the water involved must have been in equilibrium with the observed dolomite ($\delta^{18}O_{water}$ = +1.3, 6 ppm Sr if $D = 0.06$, and $^{87}Sr/^{86}Sr$ between 0.70916 and 0.70884). These constraints are not too different from those demanded by direct precipitation from mixed waters. Except for the most rock-dominated component (carbon), the dolomite must essentially be an equilibrium precipitate from the water which caused stabilization (recrystallization). Except in the case of the most rock-dominated component, carbon, the precursor composition was not important.

DIRECT PRECIPITATION FROM MODIFIED SEAWATER

The two scenarios outlined above are not satisfactory for several reasons. Although the oxygen

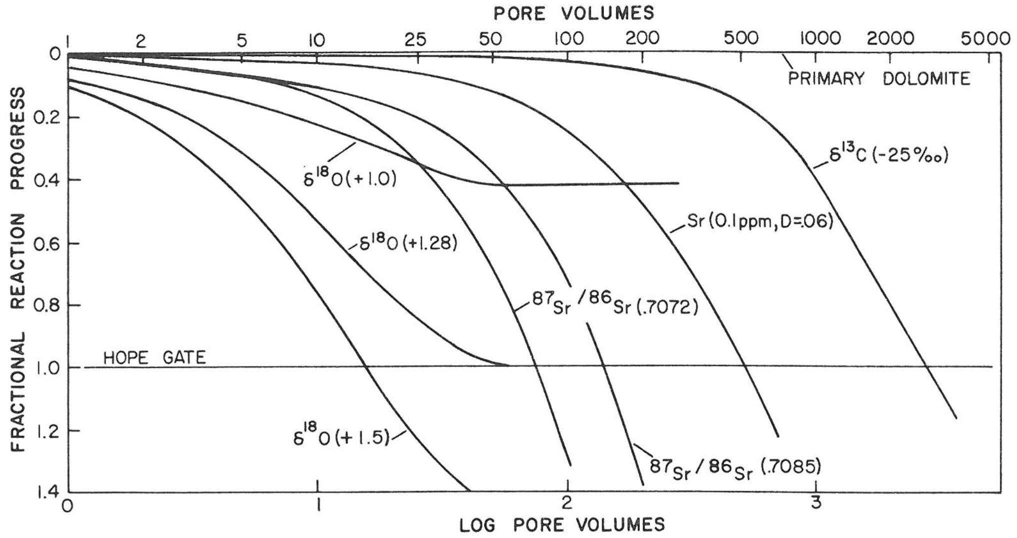

FIG. 6. Modelled evolution of dolomite chemistry as an initial marine precipitate (PRIMARY DOLOMITE, FRACTIONAL REACTION PROGRESS = 0) is recrystallized by meteoric water. REACTION PROGRESS is relative to observed average Hope Gate dolomite composition (FRACTIONAL REACTION PROGRESS = 1.0). In order to "reset" $\delta^{13}C$ values, for which rock/water ratios are highest, the $\delta^{18}O$ of the imposed water, together with its strontium concentration and $^{87}Sr/^{86}Sr$ ratio, must be in equilibrium with the replacement product. Several possible water compositions are shown. Therefore, except for the component with the highest rock/water ratio, no difference between primary precipitation and replacement can be discerned.

isotopic fractionation between dolomite and water is not known with certainty, it is unlikely that water more depleted in ^{18}O than modern surface seawater could have precipitated Hope Gate dolomite. Therefore, either seawater was the dolomitizing solution, or seawater and/or meteoric water buffered to elevated $\delta^{18}O$ values by reaction with Miocene chalk is required. The limited range of $\delta^{18}O$ dolomite values observed (Fig. 5), the lack of correlation of $\delta^{18}O$ with other measured variables (Table 2), and the unlikelihood of large volumes of rock-buffered (^{18}O-enriched) meteoric water being available, all make it difficult to invoke mixtures of seawater and meteoric water.

A similar conclusion can be reached with respect to strontium concentrations in the dolomite. Many authors have advocated a distribution coefficient for strontium in slowly precipitated dolomite (and calcite) considerably lower than 0.14, and values of 0.06 (BAKER and BURNS, 1985) or even lower (BAKER *et al.*, 1982; VAHRENKAMP and SWART, 1990) have been suggested. If a distribution coefficient of 0.06 is appropriate, then precipitation of Hope Gate dolomite from near-normal seawater is possible, and precipitation from meteoric/marine mixtures ruled out (Fig. 4). The precipitation of low-strontium dolomite directly from seawater may not be unreasonable, as the precipitation of low-strontium calcite from seawater has been documented (FREEMAN-LYNDE *et al.*, 1986; SALLER, 1986).

The $^{87}Sr/^{86}Sr$ data, however, demand that allochthonous (presumably Miocene) strontium be incorporated in most of the dolomite crystals. The apparent need to precipitate dolomite from seawater, and simultaneously to import extraneous strontium, can be achieved if the seawater had been modified by interaction with underlying Miocene chalk. There is no reason to suppose that unmodified surface seawater must be the sole agent of dolomitization. In fact, Jamaican surface seawater apparently precipitates more Ca-rich ($Mg_{0.38}$) and Sr-rich (600 ppm) dolomite than the dolomite that characterizes the Hope Gate Formation. Seawater which had interacted with Miocene chalk would have been characterized by $^{87}Sr/^{86}Sr$ ratios approaching those of the chalk, and slightly elevated strontium and $\delta^{18}O$ relative to seawater in which the reefs grew. Only the increased strontium concentration of seawater which had been modified by chalk/water interaction appears to be incompatible with this hypothesis. Either the strontium concentration of seawater resulting from chalk/water interaction did not rise because of rapid back-precipitation of calcite at a $D = 0.14$, or a distribution coefficient of strontium in dolomite somewhat less than 0.06 may apply (BAKER *et al.,* 1982; VAHRENKAMP and SWART, 1990).

One further modification of seawater is compatible with these data and may have favored dolomitization. Small amounts of organic carbon in the underlying chalk and in Hope Gate reefs themselves may have undergone oxidation, possibly accompanying sulfate reduction. Many cases of dolomite precipitation in organic-rich marine sediments have been reported (*e.g.,* GARRISON *et al.,* 1984). Both increased alkalinity and reduction in sulfate concentrations may favor dolomite precipitation (BAKER and KASTNER, 1981). The slightly ^{13}C depleted values of Hope Gate dolomite relative to the precursor sediments suggest that the oxidation of organic carbon (not necessarily soil carbon), possibly accompanying sulfate reduction, was involved in the dolomitization process. Massive sulfate reduction (and, of course, methanogenesis) is precluded by the paucity of organic matter in these high energy deposits, and by relatively small changes in $\delta^{13}C$ that took place as the precursor sediments were dolomitized relative to the large change in Mg/Ca which occurred.

The coincidence of calcite undersaturation and dolomite oversaturation has been one of the strengths of the mixing-zone model, permitting replacement to take place as dolomite precipitates occupy voids caused by calcite dissolution (PLUMMER, 1975). Seawater is grossly oversaturated with dolomite because of its high Mg/Ca ratio, but is much closer to calcite saturation. Once precipitation of dolomite is initiated, calcite undersaturation is necessitated. The rate-limiting step is certainly dolomite precipitation, not calcite dissolution. Provided that large quantities of new CO_2 are not introduced, the volume of calcite dissolved exceeds the volume of dolomite precipitated (Table 3). In this way precipitation of dolomite from seawater generates porosity, and dolomite "fronts" can continue to advance at the expense of limestones. As long as the "pump" is maintained, fresh seawater is continuously funnelled into porous zones at the sites of reaction and in more porous, previously dolomitized strata. Porosity (and permeability?) should continue to increase as long as the reaction proceeds, and dolomitization by circulating seawater can thus proceed to completion, and then advance as a "front" into adjacent limestones. Calcite undersaturation is also favored by small amounts of sulfate reduction in carbonate sediments (WALTER and BURTON, 1990) and by aerobic respiration and sulfide oxidation. Thus, calcite undersaturation in seawater can be achieved in several ways other than as a result of dolomite precipitation, and the need for mixing with meteoric water is diminished.

The precipitation of dolomite from seawater may be an extremely common phenomenon, as evidenced by numerous pore water analyses which show lowered Mg/Ca ratios with increased depth (*e.g.,* GEISKES, 1981), and the relatively common occurrence of dolomite in deep-sea sediments (*e.g.,* LUMSDEN, 1988). In the absence of an advective seawater pump, the amount of dolomite formed is limited by diffusion (*e.g.,* COMPTON and SIEVER, 1986), so that dolomite is rarely an abundant phase in modern sediments, although it may be much more common than is currently recognized.

Near-normal seawater is hypothesized to have dolomitized Hope Gate reefs. Thermal buoyancy, dispersion due to meteoric discharge, tidally induced flow, and/or yet undocumented (geostrophic?) forces (LAND *et al.,* 1989) circulated seawater through the reefs. The presence of a massive seawater pump, whatever its cause, is the primary cause of massive dolomitization. In the case of the Hope Gate Formation, some of the seawater had undergone previous chalk/water interaction so as to achieve lowered $^{87}Sr/^{86}Sr$ ratios (Fig. 7). Increased alkalinity, possibly accompanied by minor sulfate reduction, and evidenced by slight ^{13}C depletion is also likely. Extensive sulfate reduction is not supported by the generally rock-buffered character of the carbon isotopic data and is not evidenced in water analyses where active dolomitization by seawater is hypothesized (FANNING *et al.,* 1981).

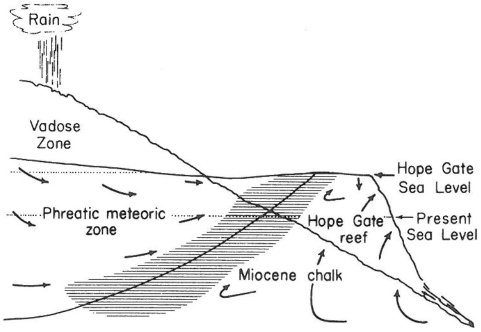

FIG. 7. Cross section of the study area showing the inferred environment of dolomitization. Dolomite precipitated in Hope Gate reefs from coeval surface seawater and from seawater which had interacted with underlying Miocene chalk. Emplacement of meteoric spar followed dolomitization (Phreatic meteoric zone). Precipitation of small amounts of coarse-grained "limpid" dolomite spar in the mixing-zone one (horizontal pattern) may also have taken place.

CONCLUSION

Meteoric water was probably not involved in the precipitation of most Hope Gate dolomite. It is difficult to accept that relatively large volumes of water having a $\delta^{18}O$ near +1 and more importantly, a limited range in $\delta^{18}O$ of only about one per mil could have been generated as the result of mixing seawater with rock-buffered meteoric water. The oxygen isotopic data strongly support seawater as being the dolomitizing agent. If a distribution coefficient for Sr in dolomite near 0.06 is accepted, strontium concentration data are also consistent with seawater as the dolomitizing solution, provided that "slow" precipitation is invoked. Again, a relatively narrow range of data argues against mixing of disparate solutions. A few of the $^{87}Sr/^{86}Sr$ ratios also support coeval seawater as the sole agent of dolomitization, but many values prove that import of allochthonous strontium took place. Circulation of seawater through underlying units to derive the extraneous strontium is the most reasonable explanation. Modified seawater may be a more effective dolomitizing agent than is surface seawater, accounting for the chemical differences between Hope Gate dolomite and modern Jamaican dolomite (MITCHELL *et al.,* 1987).

In Hope Gate time, surface seawater may have precipitated minor (?) amounts of dolomite ($Mg_{.38}$) similar to that observed in modern Jamaican reefs (MITCHELL *et al.,* 1987). This extremely metastable phase was subsequently replaced by, or syntaxially overgrown by, the more stable phase ($Mg_{.42}$) characteristic of the rocks today. Presumably, the more stoichiometric phase was favored by some combination of slower precipitation, and/or precipitation from sulfate-depleted and/or otherwise "modified" seawater. The removal of "organic coatings" or "crystal poisons" (phosphate?) in oxygen-depleted seawater may have provided suitable substrates on Mg-calcites and Ca-rich ($Mg_{.38}$) dolomite for epitaxial dolomite nucleation and crystal growth, and is another "modification" which cannot be discounted.

Subsequent infiltration of the reefs by meteoric water resulted in dissolution of all metastable phases which had not been replaced by dolomite (aragonite, Mg-calcite, and $Mg_{.38}$ dolomite) and the emplacement of meteoric spar. The "hollow rhombs" (Fig. 2), and perhaps even the calcite-dolomite intergrowths (LAND, 1973, his Fig. 9; WARD and HALLEY, 1985, their Fig. 5; HUMPHREY, 1988, his Fig. 4) may be due to the preferential dissolution of the more unstable $Mg_{.38}$ phase followed by epitaxial nucleation of meteoric spar. If this is true, then alternating calcite-dolomite zones do not provide conclusive evidence for mixing-zone conditions.

RELEVANCE TO OTHER DOLOMITES

The Hope Gate Formation is remarkably similar to many other late Cenozoic dolomites in the Caribbean, including those from the Netherlands Antilles (LAND, 1973; SIBLEY, 1982), Mexico (WARD and HALLEY, 1985), Grand Cayman Island (B. JONES, pers. commun.), Barbados (HUMPHREY, 1988), and the subsurface of the Bahamas (SUPKO, 1977; SWART *et al.,* 1987; VAHRENKAMP, 1988). Based on very limited data, nearly coeval deposits in the Pacific and Indian oceans are also known (AISSAOUI, 1986; AHARON *et al.,* 1987, and refs. therein). Limited $^{87}Sr/^{86}Sr$ data from several of these deposits (AHARON *et al.,* 1987; SWART *et al.,* 1987; VAHRENKAMP, 1988; unpubl. data) support dolomitization of coeval or older strata by seawater at a time not too different from the Pliocene-Pleistocene boundary. It is tempting to invoke an "event" to account for these very similar deposits, widely separated in space, but apparently not widely separated in time.

SIBLEY (1980) suggested a climatic "event" to account for the Pliocene Seroe Domi dolomite of Bonaire. Changes in sea-level are a more appealing world-wide "event" which might trigger dolomitization. Several authors (KALDI and GIDMAN, 1982; WARD and HALLEY, 1985; VAHRENKAMP, 1988) have suggested that dolomitization was triggered by a fall in sea level. The transition from marine (deposition and dolomitization) conditions to meteoric (stabilization and spar emplacement) conditions is certainly favored by such circumstances. Alternatively, a transgression followed by a period of relatively stable aggradation may favor dolomitization, as porous sediments accumulate rapidly, and as coastal hydrology (including seawater circulation) stabilizes.

We should be careful, however, not to generalize about the contemporaneity of these very similar Cenozoic deposits at this stage of our knowledge. Similarity in $^{87}Sr/^{86}Sr$ data from dolomite support neither contemporaneous deposition nor contemporaneous dolomitization, and allochthonous strontium seems to characterize many dolomites (Fig. 3; GAO and LAND, 1991). Clearly, continued investigation of the effects of modified seawater on the dolomitization process, both in the laboratory and in the field, is warranted. Especially important is an increased understanding of the behavior of more stoichiometric phases, such as are found in the subsurface of the Bahamas (VAHRENKAMP, 1988), which exhibit very low strontium concentrations and maintain enriched ^{18}O signatures. If these phases can also be shown to be due to primary precipitation from, or stabilization in, near-normal seawater (Land, 1985), then reassessment of a great many ancient examples will be necessary.

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