Tracing ground-water evolution in a limestone aquifer using Sr isotopes: Effects of multiple sources of dissolved ions and mineral-solution reactions

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ABSTRACT

Uplifted Pleistocene coral-reef terraces on Barbados, West Indies, constitute an aquifer that is built on low-permeability Tertiary pelagic rocks that overlie the Barbados accretionary prism. The downdip segments of the aquifer are composed of younger reef limestones that contain more aragonite and have higher $^{87}Sr/^{86}Sr$ and Sr/Ca ratios than the updip parts of the aquifer. Ground waters and host limestones display similar stratigraphic trends in $^{87}Sr/^{86}Sr$ and Sr/Ca. The ground waters have lower $^{87}Sr/^{86}Sr$ values, however, indicating that they acquire a significant fraction of their dissolved Sr through interaction with components of Tertiary rocks, which compose the underlying aquitard and parts of overlying soils. Geochemical modeling results indicate that ground-water evolution is controlled by (1) variations in the age and composition of the aquifer and aquitard rocks and (2) the relative roles of calcite dissolution, calcite recrystallization, and the transformation of aragonite to calcite. Sr isotopes can provide unique information for tracing ground-water evolution, which requires consideration of the multiple components and processes that make up even relatively simple limestone aquifer systems.

INTRODUCTION

Tracing the sources of dissolved constituents in ground waters is a major objective for the analysis of fluid-flow pathways and fluid-rock interaction. The Sr isotope system is one of several that have been increasingly applied to the study of ground-water evolution, diagenesis, and secular isotopic variations in Cenozoic seawater. The island of Barbados is an ideal setting for isotopic tracing of ground-water flow paths because of (1) its uplift history, (2) the relation between ages, elevations, and mineral compositions of its coral-reef terraces, and (3) its succession of nearly pure marine carbonates of Pleistocene age. Pleistocene-Tertiary hydrostratigraphic relations, resulting from the juxtaposition of pelagic and shallow-water deposits (Fig. 1), and secular variations in seawater $^{87}Sr/^{86}Sr$ outline a framework in which Sr isotopes are a sensitive indicator of the sources of dissolved constituents in Barbados ground waters. Isotopic and trace element data for ground waters, aquifer and aquitard rocks, and soils are used to develop ground-water evolution models that have implications for studies of active and ancient carbonate aquifers.

STRATIGRAPHY AND HYDROGEOLOGY OF BARBADOS

Barbados lies 150 km east of the Lesser Antilles volcanic arc. Reef limestones were deposited on upper Tertiary fore-arc pelagic strata, which have been uplifted as a result of accretionary-prism tectonics (Torrini et al., 1985). The base of exposed Tertiary rocks consists of quartzose turbidite, hemipelagite, and melange. The upper part of the Tertiary is up to 1.2 km thick and is composed of Eocene to middle Miocene biogenic and volcanogenic beds of the Oceanic allochthon. The Oceanic pelagic rocks are dominated by calcareous marlstone and chalk (Torrini et al., 1985). Shallow-water carbonate deposition began in the Pleistocene in the form of scleractinian coral-reef tracts. Successively younger reef terraces have been uplifted and exposed (Fig. 1). This Pleistocene "Coral Cap" constitutes an aquifer that is almost entirely underlain by Oceanic rocks. Ground-water flow patterns in the Coral Cap are controlled by (1) the markedly higher permeability and porosity of the Coral Cap relative to the underlying Tertiary aquitard, (2) the distribution of rainfall recharge, which is greatest in the central, elevated part of the island, and (3) the topography of the Pleistocene-Tertiary contact (Fig. 1). The age and mineralogic maturity (i.e., low-Mg calcite content) of the Pleistocene limestones increase with elevation (Matthews, 1968; Fig. 1).

Major and trace ion variations in Barbados ground waters are explained by interaction between meteoric recharge and Pleistocene limestones and soils, driven by the increase in ground-water p_{CO_2} during infiltration through soils and by the solubility differences between low-Mg calcite and aragonite (Harris and Matthews, 1968). U-series data indicate that the ground waters acquire U in part from interaction with sources that are older than their host rocks, such as limestones and soils in updip recharge areas, and underlying Tertiary rocks (Banner et al., 1991).

SAMPLES AND METHODS

Pleistocene reef carbonate rocks (predominantly corals) were sampled to cover the age range of reef tracts (Fig. 1). These rocks are composed of aragonite, low-Mg calcite, and dolomite (Table 1).[1] Tertiary Oceanic rocks are marlstone and chalk consisting of low-Mg calcite, silica, clay minerals, oxides, and volcanic ash (Saunders et al., 1984). Soils on Pleistocene terraces were sampled from a sugar cane plantation (sample SL-2) and two uncultivated sites. Barbados soils are composed of carbonate and silicate minerals (kaolinite-smectite clays; plagioclase and pyroxene sand and silt), quartz, oxides, organic matter, sea salts, and fertilizer (Harris, 1971; James, 1972; Muhs et al., 1987). Muhs et al. (1987) proposed that parent materials for the silicate and oxide fraction of the soils were Saharan dust carried by trade winds and Lesser Antilles volcanic ash. Soil analyses were performed on distilled H_2O leachates, acetic acid leachates, and complete sample dissolutions (Table 1). Ground waters were sampled from water wells, springs, and caves (drip water [sample C1] and stream waters [sample C2–C5]). These samples are Ca-HCO_3 waters (300 to 1000 mg/L TDS) that are approximately saturated in calcite and slightly undersaturated in aragonite (Banner et al., unpublished).

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[1] GSA Data Repository item 9435, Table A, an expanded version of Table 1, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301.

Data Repository item 9435 contains additional material related to this article.

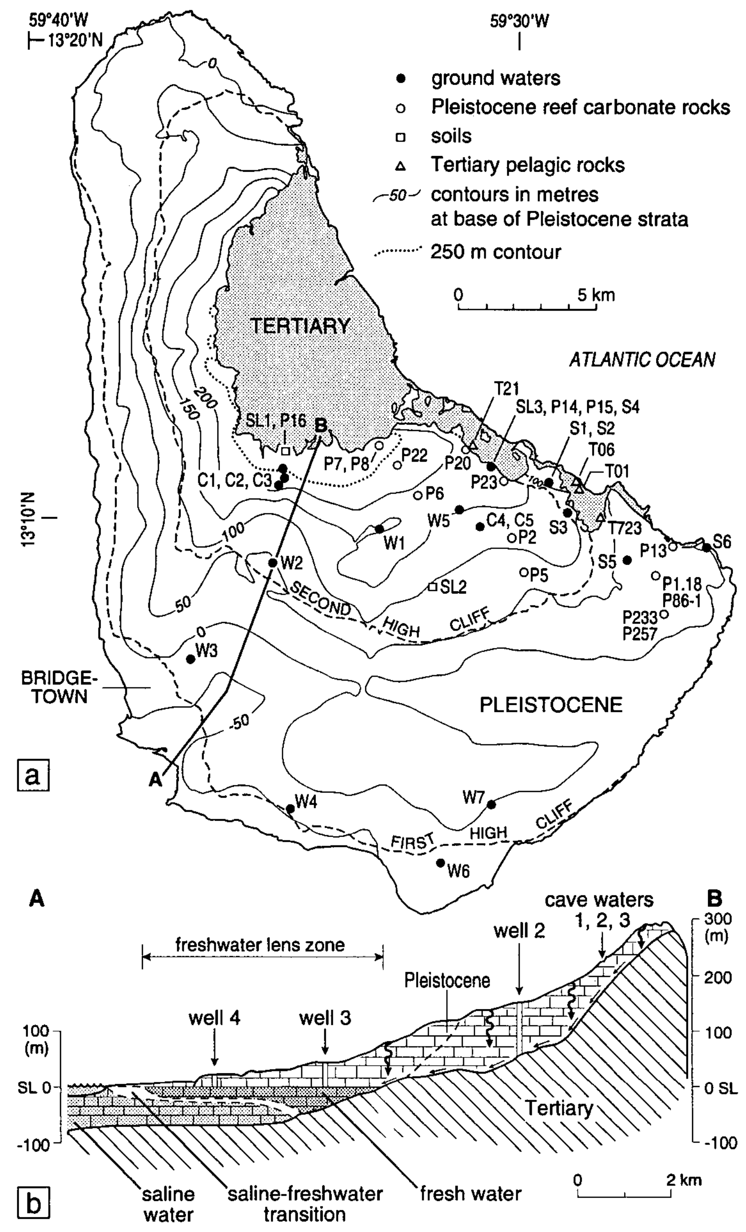

Figure 1. a: Geologic map of Barbados illustrating contours (in metres) of base of Pleistocene limestone (locally known as the Coral Cap) overlying Tertiary strata (shaded). Topography of this surface determines ground-water flow patterns and catchment boundaries in limestone aquifer (Senn, 1946, unpublished report of British Union Oil Co.). Coral-reef terraces between coast and First High Cliff range in age from 0 to 105 ka; terraces between First and Second High Cliff range from 125 to 490 ka; terraces between Second High Cliff and 150 m contour (~200 m elevation at top of Coral Cap) range from 440 to 640 ka (Mesolleia et al., 1969; Bender et al., 1979; Gallup et al., 1994). Coral composition grades from predominantly aragonite in young, coastal terraces to predominantly low-Mg calcite in old terraces in central, high-rainfall part of island (Matthews, 1968). Near-pervasive alteration of marine aragonite and high-Mg calcite has precluded radiometric age determinations for terraces older than 640 ka. Symbols indicate sites for ground-water (W, S, and C), Tertiary (T) and Pleistocene (P) rock, and soil (SL) samples in Table 1. b: Cross section A-B through Tertiary pelagic rocks and Pleistocene Coral Cap illustrates hydrogeology of Belle catchment (after Barbados Ministry of Health, 1989, unpublished report). Vadose seepage contributes to gravity flow (arrows indicate flow paths) along base of Pleistocene strata where aquifer lies above sea level (SL), and density flow occurs in coastal freshwater lenses.

RESULTS

Pleistocene limestones from low elevation have higher Sr/Ca and δ^{87}Sr values (δ^{87}Sr is defined in Table 1) than those from high elevation (i.e., updip recharge areas; Fig. 2A). The limestone δ^{87}Sr values correspond to Sr isotope stratigraphic ages of <0.3 to 1.2 Ma (determined from data of Capo and DePaolo, 1990). The validity of such ages relies on an evaluation of diagenetic effects on δ^{87}Sr values, which requires further study. Tertiary samples have $\delta^{87}\text{Sr} = -200$ to -52, consistent with Eocene to middle Miocene biostratigraphic ages for these strata (DePaolo, 1986; Saunders et al., 1984; Speed, unpublished). Barbados soil components have a large range of Sr contents and δ^{87}Sr values ($\delta^{87}\text{Sr} = -870$ to 4380). Bulk soils analyzed for this study have δ^{87}Sr and Sr/Ca values that are similar to or lower than host limestone values (Fig. 2, A and B). Complete dissolution and acid leaching yield similar δ^{87}Sr values for the soils, whereas δ^{87}Sr values for water leachates are lower for two of the three soils (Fig. 2B, Table 1). δ^{87}Sr values for a larger suite of Barbados soils are higher (-15 to 211 for complete dissolutions; Borg et al., unpublished), reflecting the wide range of values in the soils' components. Ground-water Sr/Ca ratios correlate inversely with elevation and positively with δ^{87}Sr, similar to trends for the Pleistocene limestones (Fig. 2, A and B). Harris and Matthews (1968) also found high Sr/Ca ratios in ground waters at low elevation and attributed these values to the transformation of aragonite to calcite. Despite the similar geochemical trends for the waters and their host rocks, the waters are offset to lower δ^{87}Sr (Fig. 2B).

SOURCES OF DISSOLVED Sr IN BARBADOS GROUND WATERS

The Pleistocene limestones are the most likely source of Sr in the ground waters because they constitute the aquifer and have high Sr contents, a metastable mineral composition, and a textural and chemical record of ongoing interaction with meteoric ground water (Figs. 1, 2; Matthews, 1968). Explanation of the Sr isotope variations in the waters, however, requires an additional source of Sr because some of the water samples have δ^{87}Sr values that are as much as 11 δ units lower than even the oldest (i.e., lowest δ^{87}Sr) Pleistocene limestone values. We use the Sr contents and isotopic compositions of the other components of the aquifer system (Table 1) to evaluate their contribution to the Sr budget of the ground waters.

1. *Rainfall recharge.* Average Sr concentrations in Barbados rainwater (0.016 ppm) make up only ~5% of the dissolved Sr in ground waters that have the lowest Sr concentrations.

2. *Saline fluids.* Low chloride contents of the ground waters (Banner et al., unpublished) indicate minimal mixing effects from seawater or brackish pore waters from sandstones underlying Oceanic strata (~7000 mg/L TDS; Machel and Burton, 1991).

3. *Pollutants.* Fertilizer, pesticides, sewage, organic solvents, and petroleum may significantly affect ground-water quality on Barbados. More than 90% of the fertilizer applied to Barbados soils consists of N- and K-based fertilizer. Dissolved nitrate exceeds 20 ppm in most parts of the aquifer (Barbados Ministry of Health, 1989, 1991, unpublished reports), indicating an important contribution to the ground waters from N-based fertilizer and/or sewage. The relatively low Sr contents and high δ^{87}Sr values of N- and K-based fertilizers (Table 1) indicate that

TABLE 1. BARBADOS Sr ISOTOPE DATA

Sample	Elevation (m)	Sr ppm	Sr/Ca (x 100)	$\delta^{87}Sr$	$2\sigma_m$
Ground waters					
W1	210	0.372	0.421	-14.7	1.8
W2	133	0.326	0.455	-13.1	1.1
W3	55	0.557	0.822	-14.0	1.7
W4	39	12.1	16.1	- 0.7	1.0
W5	215	0.544	0.630	---	
W6	5	11.9	11.0	- 3.8	1.4
W7	18	2.99	3.56	-11.1	1.8
C1	247	0.326	0.358	-15.1	1.0 (2)
C2	250	0.246	0.347	-20.3	1.2 (3)
C3	252	0.267	0.336	-16.6	1.4
C4	185	0.450	0.559	-11.7	1.3
C5	185	0.454	0.561	-10.9	1.6
S1	78	0.62	0.806	-12.3	1.4
S2	85	0.611	0.765	-11.4	1.7
S3	108	0.681	0.733	-13.0	1.4
S4	150	0.476	0.608	-10.4	1.6 (2)
S5	45	0.98	1.24	- 7.1	3.2 (3)
S6	0	0.96	1.05	-12.8	1.7
Rainwater*		0.016	2.58	---	
Modern seawater*		8.1	1.95	0	
Pleistocene reef carbonate rocks					
P2 (C)	170	2100	0.519	- 5.6	2.1
P5 (C/A)	160	3620	0.904	- 4.4	1.4
P6 (C)	245	2600	0.657	- 2.0	1.7
P7 (C)	310	559	0.139	- 4.5	2.8
P8 (C)	310	1480	0.365	- 5.2	1.8
P13 (A)	20	8030	2.05	---	
P14 (C)	150	1230	0.311	- 1.3	1.4
P15 (C)	150	1540	0.385	---	
Pleistocene reef carbonate rocks					
P16 (C)	300	301	0.0751	- 8.8	2.3 (2)
P20 (C)	180	2190	0.551	- 5.2	2.7
P22 (C)	275	692	0.174	- 6.5	1.7
P23 (C)	238	613	0.152	- 7.6	1.7
P233(A)	35	8200	2.15	2.0	1.5 (3)
P257(A)	35	8400	2.18	- 2.9	1.9 (3)
P1.18(D)	39	890	0.357	- 2.5	1.0 (2)
P86-1(D)	39	690	0.290	- 5.5	1.0 (3)
Tertiary pelagic sedimentary rocks					
T01	25	1220	0.390	-190.5	1.8
T06	10	1420	0.439	-198.5	2.0
T723	65	845	0.221	- 51.8	1.7
T21	178	1500	0.516	-176.0	1.8
Pleistocene soils					
SL-1 H_2O	305	0.010	0.171	-18.9	2.8
SL-1 HAc		401	0.108	-11.2	1.6 (2)
SL-1 CD		170	0.145	---	
SL-2 H_2O	160	0.009	0.357	- 3.9	1.8
SL-2 HAc		1150	0.413	- 7.2	1.8
SL-2 CD		344	0.560	---	
SL-3 H_2O	150	0.016	0.290	-12.5	3.0
SL-3 HAc		1760	0.135	-10.6	1.7
SL-3 CD		1300	0.417	- 7.9	2.1
Soil components					
Potassium fertilizer		18		4379.9	1.7
Nitrogen fertilizer		0.11		40.3	3.1
Phosphate fertilizer		520		-39.6	1.0
Saharan dust*				770 to 1060	
Volcanic ash*		185 to 214		-870 to -450	
Modern sea-spray salts (estimated)				0	

Note: $\delta^{87}Sr = [(^{87}Sr/^{86}Sr_{sample})/(^{87}Sr/^{86}Sr_{seawater}) - 1] \times 10^5$. $\delta^{87}Sr \pm 2\sigma_m$ values are for single mass spectrometer analyses, except for values followed by number in parentheses, which indicates number of replicate analyses used to determine reported $\delta^{87}Sr$ and $2\sigma_m$ values. External error (1σ) for Sr isotope standards is ± 1.3. W- well water; S- spring water; C- cave water. For Pleistocene rocks: (A)- aragonite; (C)- low-Mg calcite; (D)- dolomite. Soil leachates: HAc- 1N acetic acid; H_2O- distilled water; CD- complete dissolution. Samples, methods, and data detailed in Repository (see footnote 1 in text).

*Data from literature sources given in GSA Data Repository.

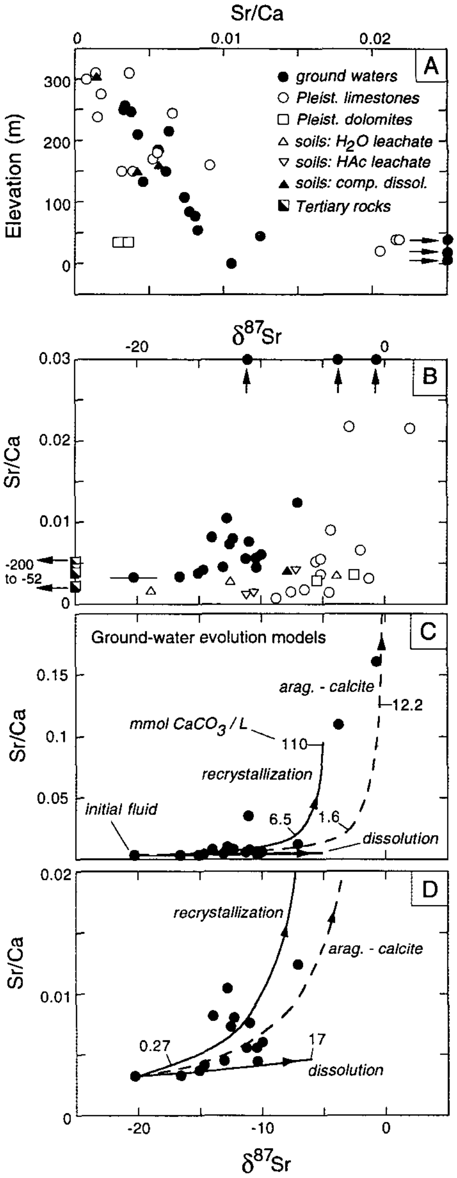

Figure 2. A: Variation with elevation of Sr/Ca weight ratio for Pleistocene carbonates, soils, and ground waters from Barbados. Three water samples from low elevations (denoted by arrows in A and B) plot off scale at Sr/Ca ratios of 0.036, 0.110, and 0.161. For clarity, only complete dissolution values for soils are shown in A. B: Sr/Ca vs. Sr isotope composition (expressed as $\delta^{87}Sr$, Table 1) in ground waters, Tertiary rocks, and Pleistocene limestones, dolomites, and soils. Modern marine carbonates and seawater have $\delta^{87}Sr = 0$. Representative analytical uncertainty is shown for one water sample. C and D: Model curves illustrating evolution of ground-water $\delta^{87}Sr$-Sr/Ca values during progressive diagenetic alteration of host Pleistocene limestones by three different processes: (1) dissolution of low-Mg calcite with 2000 ppm Sr and $\delta^{87}Sr = -5$, (2) recrystallization of same calcite, and (3) transformation of aragonite with 8500 ppm Sr and $\delta^{87}Sr = 0$ to low-Mg calcite dashed line labeled "arag.-calcite." Model calculations follow Banner et al. (1989). K_D(Sr/Ca) = 0.05. Updip ground-water sample (C2) composition was used for initial fluid in all models. Note change in Sr/Ca scale in A to D. Three waters with high Sr/Ca values not shown in D. Numbers on curves indicate amount of alteration of host rock in terms of millimoles of aragonite or calcite reacted or dissolved per litre of water. Arrows on curves indicate direction of increasing fluid-rock interaction and down-gradient direction in aquifer.

they are not a likely source of low $\delta^{87}Sr$ for the ground waters. The lack of Sr isotope data for the other pollutants precludes rigorous evaluation of their effects on ground-water isotope compositions. The greatest impact of most nonagricultural ground-water pollutants, however, occurs in the more urbanized areas along the southwest coast of Barbados, which are down gradient from the study area.

4. *Soils.* Soil components may contribute Sr with a wide range of $\delta^{87}Sr$ to the waters (Table 1). By contrast, acid-leachable Sr in the bulk soils has an isotopic composition similar to that of the Pleistocene limestones (Fig. 2B), indicating a predominantly limestone and sea-spray salt source of Sr for these soils. Sr with lower $\delta^{87}Sr$ than the Pleistocene limestones and seawater, however, may be contributed from soils, as shown by low Sr isotope values in soil water leachates and the drip water (C1). Water-exchangeable sources in the soils include salts and surfaces of minerals and organic matter. Low $\delta^{87}Sr$ values are found in soil-water leachates and the drip water from Pleistocene reef localities near the Tertiary outcrop (Fig. 1A) and may, therefore, reflect the presence of Tertiary detritus with leachable Sr (and low $\delta^{87}Sr$ values) in soils at these sites. Alternatively, volcanic ash components may constitute the water-exchangeable source of low $\delta^{87}Sr$ in the soils. Given the highly variable $\delta^{87}Sr$ values of their components, detailed sampling of Barbados soils may delineate other recharge areas with low-$\delta^{87}Sr$ sources.

5. *Tertiary rocks.* Alteration of low-Mg calcite, silica, silicate, and oxide components of the Oceanic strata may occur during ground-water flow at the base of the Pleistocene aquifer. Considering (1) the high Sr contents and very low $\delta^{87}Sr$ values of the Tertiary samples and (2) the regional hydrologic control of the Pleistocene-Tertiary contact (Fig. 1), fluid-rock interaction involving both Tertiary and Pleistocene carbonates readily accounts for the $\delta^{87}Sr$ variations in the waters. Thus, although low-permeability strata play an obvious role in governing fluid-flow paths, they may also serve as a significant source of dissolved constituents for ground waters. Such contributions from Tertiary carbonates are not discernible from the major ion chemistry of the waters.

Ground-water Sr variations are thus likely controlled by interaction of meteoric water with Pleistocene limestones, as well as by interaction with soils and Tertiary rocks.

For typical δ^{87}Sr values and Sr contents for the waters (−13, 0.4 ppm) and Pleistocene (−5, 2000 ppm) and Tertiary (−190, 1200 ppm) rocks, Sr in the ground waters can be derived from a 10:1 combination of Pleistocene and Tertiary sources. The influence of low-δ^{87}Sr Tertiary rocks and soil components on water compositions is most pronounced near older, updip recharge areas (Fig. 1, 2B); this result may be due to (1) the higher maturity of minerals in Pleistocene limestones here and (2) the potentially larger fraction of Tertiary detritus in soils in the areas proximal to Tertiary outcrops.

MODELS FOR GROUND-WATER EVOLUTION

Incorporation of Sr into Barbados ground waters via diagenetic reactions in Pleistocene limestones may occur (1) near a particular sampling site during vadose infiltration, (2) far from the sampling site in updip recharge areas, and (3) along flow paths to the sampling site. The δ^{87}Sr-Sr/Ca-elevation variations in the waters (Fig. 2) are indicative of their downdip evolution via interaction with Pleistocene limestone. To evaluate the extent to which specific carbonate diagenetic reactions control water compositions, we modeled the chemical and isotopic evolution of ground water that occurs during (1) dissolution of low-Mg calcite, (2) recrystallization of low-Mg calcite, and (3) transformation of aragonite to low-Mg calcite. The model trends (Fig. 2, C and D) encompass most of the water data and indicate that (1) at least two of these processes control water compositions in the updip part of the aquifer, (2) the extent of interaction increases down-gradient, and (3) transformation of aragonite to calcite is the dominant process in most down-dip sections. The scatter in the ground-water Sr/Ca-δ^{87}Sr trend about a given model curve is similar to the observed scatter in the Pleistocene rocks (Fig. 2B). Thus, the spread in the ground-water data may result from both the effects of fluid-rock interaction with a host rock of variable composition and the effects of multiple mineral-fluid reactions. In comparison to any single model path shown, a "multilane highway," which has a similar shape to the model path but which also has "multiple lane changes" dictated by varying host-rock minerals and composition, may more accurately represent ground-water evolution. The scatter in the water data outside of the model processes may also reflect (1) reaction with soils or the Tertiary aquitard during down-gradient water evolution or (2) our sampling of several different catchments (Fig. 1) rather than a single flow path. Thus, ground-water compositions are apparently controlled by variations in the nature of the mineral-solution reactions and in the trace element and isotope geochemistry of the rocks and soils that compose the aquifer and aquitard.

The increase in fluid-rock interaction in the lower reef terraces is a logical consequence of their more metastable minerals (Fig. 1). Despite this trend, most of the waters are not in Sr isotopic equilibrium with their host limestones (Fig. 2B). This finding suggests that fluid-rock interaction may be limited to the extent that allochthonous isotopic signatures in ground waters can persist during migration through young limestones composed, in part, of metastable minerals. Such limits on fluid-rock interaction may be imposed by thermodynamic or kinetic factors (e.g., Banner et al., 1989), including the high flow rates (>100 m/yr) and large extent of conduit flow in the aquifer (Harris, 1971), and the potential occurrence of flow paths lined with equilibrated diagenetic minerals. These results for Barbados ground waters have a bearing on generalized models for carbonate diagenesis (e.g., Meyers and Lohmann, 1985), in that these ground waters in an early diagenetic environment do not necessarily have closed-system, marine-carbonate isotopic signatures.

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