

High-resolution temporal record of Holocene ground-water chemistry: Tracing links between climate and hydrology

Jay L. Banner

MaryLynn Musgrove

Department of Geological Sciences, University of Texas, Austin, Texas 78712

Yemane Asmerom

Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131

R. Lawrence Edwards

John A. Hoff

Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455

ABSTRACT

Strontium isotope analysis of precisely dated calcite growth layers in Holocene speleothems from Barbados, West Indies, reveals high-resolution temporal variations in ground-water composition and may provide a new approach to documenting the links between climate variability and fluctuations in the hydrologic cycle such as recharge rates and flow paths. The speleothems grew in a cave that developed in a fresh-water aquifer in uplifted Pleistocene reef limestones. Three periods of ground-water Sr isotope evolution are observed: $^{87}\text{Sr}/^{86}\text{Sr}$ values decreased from 6 to 4 ka, increased from 4 to 1 ka, and decreased again after 1 ka. The Sr isotope oscillations appear to record periodic variations in the relative Sr fluxes to ground water from exchangeable soil sites vs. carbonate mineral reactions, as reflected in $^{87}\text{Sr}/^{86}\text{Sr}$ values of modern Barbados ground waters. A hydrologic model that explains changes in ground-water flow routes in karst aquifers as a function of amount of rainfall recharge can account for the speleothem Sr isotope record. Independent Holocene climate records that indicate a major period of aridity at around 1.3–1.1 ka in the American tropics correspond with periodic variations in rainfall on Barbados that are predicted by this hydrologic model.

INTRODUCTION

In spite of a developing emphasis on geochemical methods in studies of modern hydrologic systems, studies of temporal fluctuations in ground-water chemistry have been limited. Whereas Pleistocene ground-water records provide information about large temperature shifts on glacial to interglacial time scales (Winograd et al., 1992), understanding changes in the more recent past is problematic due to smaller perturbations. Relatively little is known regarding how ground waters evolve over 10 to 10^4 yr scales, yet this knowledge is required for understanding the controls of factors such as climatic variations and mineral weathering rates on aquifer development and ground-water chemistry. Studies of calcite cave deposits (speleothems) and fracture fills using C, O, and U-series isotopes have yielded insight regarding ground-water and climate evolution during the Quaternary (e.g., Harmon et al., 1978). The integration of Sr isotope variations with other tracing and dating tools appears to provide a new approach for delineating the connections between climate variability and ground-water chemistry. Strontium isotopes have not been previously applied to studies of speleothems, yet offer the advantages of (1) negligible isotope fractionation during evaporation, degassing, and temperature fluctuations, so that mineral precipitates directly reflect fluid $^{87}\text{Sr}/^{86}\text{Sr}$ values (Banner and Kaufman, 1994),

and (2) their utility as tracers of the evolution of natural waters and weathering processes (e.g., Miller et al., 1993). Barbados is a well-suited setting for examining temporal ground-water evolution because of (1) the island's isolated setting, uplift history, and consequent patterns of age and composition of the aquifer's limestones and soils (Fig. 1); (2) the absence of flooding, freezing, and glaciers, which interrupt speleothem growth (e.g., Baker et al., 1995); and (3) a range of sources of atmospheric deposition to soils and dissolved ions to ground water that are isotopically distinct (Fig. 2).

HYDROGEOLOGIC SETTING AND SAMPLES

Pleistocene coral reefs on Barbados grew on Tertiary fore-arc pelagic strata, which have been uplifted via accretionary prism tectonics (Torrini et al., 1985). Diagenesis of the Pleistocene reef limestones has led to the development of a karstic, fresh ground-water flow system (Harris and Matthews, 1968). Speleothems from Harrison's Cave, which has developed in the older, elevated part of the island (Fig. 1), were analyzed for U-series ages, Sr, C, and O isotopic compositions, and trace element concentrations. Samples BC-53 and BC-61 (0.42 and 0.73 m long stalagmites, respectively) and BC-60 (stalactite) were recovered from a room in the cave's upper passage that is overlain by 21 m of limestone (Fig. 1). BC-101 is a mod-

ern flowstone and BC-102 and BC-103 are stalagmites from the central part of the cave (Fig. 1). The speleothems are composed of white to translucent calcite. Growth layering ranges from submillimetre to centimetre in scale. Individual subsamples extracted for analysis typically correspond to 2–3 mm of growth. The ages and Sr isotope compositions for all of the speleothem samples are used to construct the temporal record shown in Figure 3, with the data for BC-61 providing the highest resolution and longest time interval.

Elemental and isotopic variations in Barbados ground waters are accounted for by interaction between rainfall recharge and Pleistocene limestones and soils (Harris and Matthews, 1968; Banner et al., 1994). Soils developed on the limestones are typically <1 m thick and are made up of carbonate and silicate minerals (kaolinite-smectite clays; plagioclase and pyroxene sand and silt), quartz, oxides, organic matter, sea-spray salts, and fertilizer (Muhs et al., 1987). Parent materials for the silicate and oxide portion of the soils are a combination of ash derived from the Lesser Antilles volcanic arc, Saharan dust carried by trade winds, and Tertiary pelagic rocks (quartz turbidites, biogenic and volcanogenic marls and chalk) exposed in northeastern Barbados (Fig. 1). Parent materials for CaCO_3 portions of the soils are Pleistocene and Tertiary carbonates. $^{87}\text{Sr}/^{86}\text{Sr}$ variations in these source materials are shown in Figure 2. Neodymium and Sr isotopic variations in Barbados soils reflect their multiple sources and the preferential weathering of low- $^{87}\text{Sr}/^{86}\text{Sr}$ carbonate and ash components (Borg and Banner, 1996).

The speleothem samples range in age from 6 ka to <18 yr. Speleothem $^{87}\text{Sr}/^{86}\text{Sr}$ values range from 0.70903 to 0.70915 (Fig. 3). The values at the high end of this range are similar to values for Pleistocene limestones and modern seawater (Fig. 3). The lowest speleothem $^{87}\text{Sr}/^{86}\text{Sr}$ values are similar to the lowest of the modern ground-water values, found in stream waters and some drip waters from Harrison's Cave. The lower speleothem $^{87}\text{Sr}/^{86}\text{Sr}$ values are also

Data Repository item 9656 contains additional material related to this article.

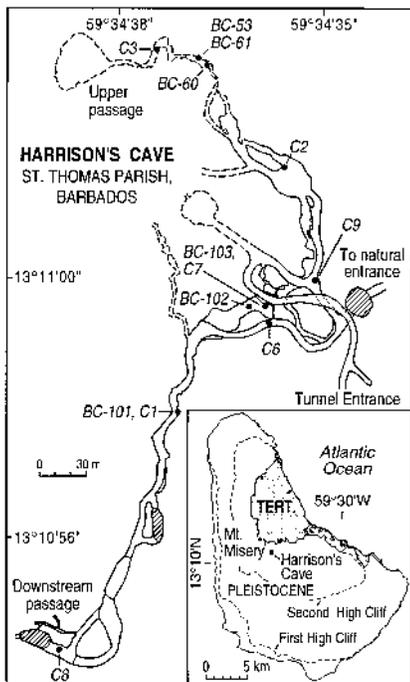


Figure 1. Map of Harrison's Cave (after Knox et al., 1978; Hobbs, 1994) and its location on Barbados, which lies 150 km east of the Lesser Antilles. Sample localities (BC = speleothem; C = cave water) correspond to designations in Banner et al. (1994) and in GSA Data Repository (see footnote 1). C2 and C3 are stream-water sampling localities; other cave water localities are drips. Dashed cave passages are those not surveyed. Reef terraces of the Pleistocene Coral Cap between coast and First High Cliff range in age from 0 to 105 ka; terraces between First and Second High Cliff range from 117 to 490 ka; terraces above Second High Cliff and below elevation of Harrison's Cave range from 440 to 640 ka (Bender et al., 1979; Gallup et al., 1994). Coral mineralogy grades from predominantly aragonite in young, coastal terraces to predominantly low-Mg calcite in old terraces in central, high-rainfall part of island. Near-pervasive alteration of marine aragonite and high-Mg calcite has precluded radiometric age determinations for terraces older than 640 ka. $^{87}\text{Sr}/^{86}\text{Sr}$ values for these undated terraces indicate that they are <2 Ma (Banner et al., 1994). Ground-water flow is from central, elevated part of island toward the coast. Flow patterns are governed by (1) high permeability and porosity of Coral Cap aquifer relative to underlying Tertiary aquitard, (2) relatively high rainfall in central part of island, and (3) topography of Pleistocene-Tertiary contact (Harris and Matthews, 1968; Banner et al., 1994).

similar to ion exchange leachate values for two soils sampled in the recharge zone of the cave (Fig. 3). Bulk Barbados soils range up to significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70890–0.71067) than the modern waters, the speleothems, and the reef limestones (Fig. 2), reflecting the several distinct sources of soil components (Banner et al., 1994; Borg and Banner, 1996). Three major periods of ground-water Sr isotope evolu-

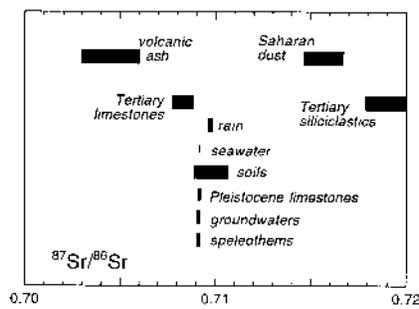


Figure 2. Strontium isotope variations in components of the geochemical cycle of the limestone aquifer of Barbados. Eolian deposition in soils comprises multiple components of (1) relatively far-traveled and high-altitude Lesser Antilles volcanic ash, Saharan dust, and rain; (2) local derivation from Tertiary limestone and siliclastic sandstone and mudstone outcrops in northeastern Barbados (see Fig. 1); and (3) sea spray salts having Sr isotope composition of seawater. Range for Tertiary siliclastics extends to $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.73. Data from Banner et al. (1994), Borg and Banner (1996), and this study.

tion are present in the speleothem record (Fig. 3). From the start of the record at ca. 6 ka until 4 ka, the $^{87}\text{Sr}/^{86}\text{Sr}$ value of ground water feeding the speleothems decreased. A sharp reversal to increasing $^{87}\text{Sr}/^{86}\text{Sr}$ occurred at 4 ka, and continued at about the same rate until ca. 1.2 ka. Growth layers younger than 1 ka record a switch to decreasing $^{87}\text{Sr}/^{86}\text{Sr}$. Mean growth rate (0.10 to 0.22 mm/yr) and rate of $^{87}\text{Sr}/^{86}\text{Sr}$ change are inversely correlated in sample BC-61 for these three time intervals. The highest speleothem $^{87}\text{Sr}/^{86}\text{Sr}$ values (>0.70913) are recorded from ca. 1.6 to 0.5 ka (Fig. 3). Average modern drip water compositions correspond with the zero-age end of the temporal $^{87}\text{Sr}/^{86}\text{Sr}$ trend (Fig. 3). A general relationship between discharge and Sr isotope composition for the modern cave waters is reflected by the increase in mean $^{87}\text{Sr}/^{86}\text{Sr}$ from streams to fast drip waters to slow drip waters (Fig. 3).

Well-developed temporal trends in the speleothem record are not found for other geochemical parameters, including Sr, K, Si, Fe, Mn, U, and P concentrations and U isotopic compositions. A general decrease in $\delta^{18}\text{O}$ (–3.0‰ to –4.3‰ Peedee belemnite) and $\delta^{13}\text{C}$ (–8.3‰ to –11.7‰) values is recorded during the period from 5.5 to 3 ka, with smaller variations after 3 ka. The lack of a direct correspondence between the temporal trends for $^{87}\text{Sr}/^{86}\text{Sr}$ and those for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is likely due to the contrast between (1) the control on ground-water $^{87}\text{Sr}/^{86}\text{Sr}$ values by variations in the sources of dissolved ions in the aquifer, and (2) the control on ground-water $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values by isotope fractionation processes that reflect variations in atmospheric and aquifer

conditions (e.g., temperature, humidity, CO_2 content, storm tracks). The trace element and C, O, and U isotope results, as well as growth-rate variations and age-determination procedures, will be presented in a separate report.

Sr ISOTOPE VARIATIONS IN THE MODERN FLOW SYSTEM

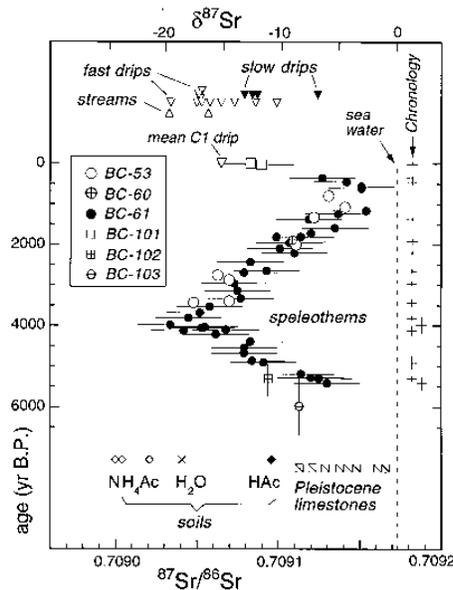
Ground waters and limestones both record increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca along the aquifer's flow path, with the trend for the waters shifted to lower $^{87}\text{Sr}/^{86}\text{Sr}$ (Banner et al., 1994). Ground waters at higher elevations in the aquifer have relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ values and likely acquire a significant portion of their Sr through interaction with low $^{87}\text{Sr}/^{86}\text{Sr}$ soil components (i.e., Tertiary carbonates, ash). Low Sr isotope values of soil leachates relative to bulk soils (Banner et al., 1994; Borg and Banner, 1996) indicate that Tertiary carbonate- and/or ash-derived Sr is preferentially removed from exchangeable sites in soils and can account for the low ground-water $^{87}\text{Sr}/^{86}\text{Sr}$ values. Evolution of ground waters toward higher $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca values along the ~10 km flow path is controlled by compositional variations in aquifer rocks and soils and the relative roles of carbonate mineral dissolution, recrystallization, and transformation (Banner et al., 1994).

MECHANISMS FOR TEMPORAL Sr ISOTOPE FLUCTUATIONS

The temporal $^{87}\text{Sr}/^{86}\text{Sr}$ trend recorded in the speleothems appears to indicate periodic variations in the fluxes from two principal end-member sources of Sr to vadose ground water. Exchangeable Sr in soils corresponds to a low $^{87}\text{Sr}/^{86}\text{Sr}$ end member, and Pleistocene limestone and/or modern seawater corresponds to a high $^{87}\text{Sr}/^{86}\text{Sr}$ end member. We evaluate below three mechanisms by which ground water may receive temporally varying fluxes (in terms of $^{87}\text{Sr}/^{86}\text{Sr}$ or Sr concentration) from these end members: (1) variations in the rate of deposition and/or weathering in soils of atmospheric components with different $^{87}\text{Sr}/^{86}\text{Sr}$ values, thereby producing varying $^{87}\text{Sr}/^{86}\text{Sr}$ values for exchangeable soil Sr; (2) variations in the rate of limestone vs. soil weathering (with a constant soil-exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ value); and (3) a combination of 1 and 2.

Temporal changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ value or in the rate of deposition or weathering of any of the several components of eolian deposition to Barbados soils may produce a temporal change in the isotopic composition and concentration of Sr released from water-exchangeable sites in the soils. This mechanism is evaluated below for each com-

Figure 3. Temporal Sr isotope variations in speleothem growth layers, compared with Sr isotope variations in modern drip and stream waters from Harrison's Cave and associated soils and limestones. Speleothem trend comprises data for stalagmites (samples BC-53, -61, -102, -103), stalactite BC-60, and flowstone BC-101 (locations given in Fig. 1). Fast and slow drip waters are defined here as those with discharge rates >0.5 L/h and <0.02 L/h, respectively. Only mean $^{87}\text{Sr}/^{86}\text{Sr}$ value for C1 drip water plotted at zero age; other water values moved up for clarity. $^{87}\text{Sr}/^{86}\text{Sr}$ values for Pleistocene limestones (from terraces that bracket the elevation of the cave) and soils are plotted relative to the abscissa only. Soil analyses are for (1) ion exchange solutions of 1N ammonium acetate (NH_4Ac) and distilled H_2O , which reflect relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ values of exchangeable Sr in soils near the cave's recharge zone, and (2) a 1N acetic acid (HAc) leachate, which reflects the high solubility of Pleistocene carbonate soil components in acidic solutions. $^{87}\text{Sr}/^{86}\text{Sr}$ values plotted are either individual analyses or the mean value of replicate analyses. Representative analytical uncertainty for all $^{87}\text{Sr}/^{86}\text{Sr}$ values (shown for BC-61 and -101 only) based on replicate analyses of samples (average $2\sigma_m = 11 \times 10^{-6}$, $n = 37$) and SRM 987 standard ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710246$; $2\sigma = 21 \times 10^{-6}$, $n = 52$). "Chronology" symbols denote U-series ages and analytical uncertainties of growth layers used to construct speleothem chronology, and are plotted relative to ordinate only. Modern flowstone (BC-101) ages based on 1978 excavation date of cave passage. Relatively large age errors on some samples (e.g., BC-102, BC-103, plotted directly on Sr isotope values) due to high Th/U values and uncertainty in initial Th isotopic composition. Sr isotope analyses conducted at University of Texas following methods of Banner and Kaufman (1994) and U-series ages by mass spectrometry at University of Minnesota following methods of Gallup et al. (1994). Sample information, analyses, and methods detailed in GSA Data Repository (see footnote 1). $\delta^{87}\text{Sr} = [(^{87}\text{Sr}/^{86}\text{Sr}_{\text{sample}})/(^{87}\text{Sr}/^{86}\text{Sr}_{\text{seawater}}) - 1] \times 10^5$. $^{87}\text{Sr}/^{86}\text{Sr}$ value of modern and Holocene seawater = 0.709173.



ponent in terms of the isotopic signature and the time scale of variation expected. Our sampling resolution of 2–3 mm growth layers corresponds to 10–30 yr, and thus cannot distinguish seasonal, annual, or other shorter-term trends.

Rainfall Composition. Rainwater Sr contents are equivalent to ~2% of the Sr in the cave waters (GSA Data Repository¹), indicating that cave water $^{87}\text{Sr}/^{86}\text{Sr}$ is not controlled by rainfall composition.

Saharan Dust. Transport of Saharan dust to Barbados by trade winds varies in response to climatic changes on seasonal and decadal scales (Prospero and Nees, 1986) and may also be expected to vary on the millennial time scale of the speleothem $^{87}\text{Sr}/^{86}\text{Sr}$ variations. The lack of any speleothem, ground-water, or soil leachate $^{87}\text{Sr}/^{86}\text{Sr}$ values above those for Pleistocene limestones (Fig. 3), however, indicates that the dust, which has very high $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 2), does not play a significant role in ground-water evolution.

Sea Spray Salts. Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ has

been constant during the Holocene (DePaolo and Ingram, 1985), but variations in the flux of sea spray to the cave's recharge zone could produce temporal changes in ground-water chemistry. Low Cl contents of drip waters (29–65 ppm) indicate that these salts contribute <10% of modern drip-water Sr in the cave. During more arid periods than present day, however, such salts may provide a larger fraction of Sr in vadose ground water. Determination of speleothem Cl and Na concentrations will help address this issue.

Fertilizer. Fertilizers have an apparently negligible effect on modern ground-water $^{87}\text{Sr}/^{86}\text{Sr}$ values (Banner et al., 1994), and no effect prior to the 20th century.

Volcanic Ash. Lesser Antilles (and to a lesser extent, Central American) volcanic eruptions have produced ash with very low $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 2) that has been incorporated into Barbados soils (Muhs et al., 1987). First order trends in Holocene eruption chronologies of Lesser Antilles volcanic centers (Simkin and Siebert, 1994) indicate that periods of high eruptive activity are not correspondingly followed by periods of declining speleothem $^{87}\text{Sr}/^{86}\text{Sr}$ values. The rapid weathering rate of volcanic ash is likely to produce a significant fraction of ground-water Sr relatively soon after depo-

sition. Such an episodic, rapidly weathered source of Sr should produce an asymmetric temporal pattern whereby a relatively large Sr flux (with very low $^{87}\text{Sr}/^{86}\text{Sr}$) to ground water is produced soon after deposition, followed by a more gradually decreasing contribution. This hypothetical trend is contrary to that observed (Fig. 3).

Tertiary Pelagic Sedimentary Rocks. Eolian transport from Eocene through Miocene strata exposed in northeastern Barbados to soils on Pleistocene reef terraces consists of weathering products of calcareous, siliceous, and volcanogenic pelagic marls and chalk with relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ values, and quartz turbidites with very high $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 2). The rate of this transport is a function of the variability of a number of climatic factors. Compared with the other sources discussed above, the proximity of these local eolian sources to the soils has likely made for relatively continuous transport to the terraces during the Holocene.

In contrast to fluctuations through time in the relative contributions of atmospheric sources of soil Sr with distinct $^{87}\text{Sr}/^{86}\text{Sr}$ values, ground-water temporal trends may result from fluctuations in the balance of Sr derived from (1) exchangeable soil Sr having a relatively constant $^{87}\text{Sr}/^{86}\text{Sr}$ value vs. (2) Pleistocene host limestone Sr. Processes that may control this balance are evaluated here.

Reef Limestone Carbonate Mineral Stabilization. If the carbonate mineral-solution reactions that are active in the modern aquifer (Banner et al., 1994) were the principal processes governing the temporal evolution of cave drip water, then the temporal trend would be unidirectional toward relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ soil exchangeable values as the Sr flux from increasingly stabilized CaCO_3 minerals decreased.

Ion Exchange Reactions in Soils. Ion exchange reactions that occur between infiltrating rainwater and soil minerals and organic matter influence soil-water $^{87}\text{Sr}/^{86}\text{Sr}$ values. Given the complex nature of these reactions, including determining the kinetic and compositional factors that will govern soil water compositions, we experimentally determined the isotope composition of Sr released from soils to ion exchange solutions. $^{87}\text{Sr}/^{86}\text{Sr}$ values of these solutions are similar to the lowest values recorded in the speleothem ca. 4 ka (Fig. 3). One hour and 24 hr NH_4Ac leachates yielded similar results.

P_{CO_2} of Soil Atmosphere. Changes in soil zone CO_2 concentrations can control the extent of dissolution of CaCO_3 in soils and host limestones. These changes are mainly driven by variations in organic productivity and degradation in soils, which in turn can

¹GSA Data Repository item 9656 (Sr isotope and concentration data, U-series ages, and additional sample and methods information) is available upon request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301. E-mail: editing@geosociety.org.

be controlled by variations in (1) rainfall and associated shifts in type and productivity of vegetation (Dorale et al., 1992), and (2) temperature (Baker et al., 1995). Temperature is unlikely to be a key factor in CO₂ production in Barbados soils, given the narrow range of mild mean temperatures between seasons (24–29 °C) and the lack of evidence for large temperature shifts (in low-altitude, Mesoamerican tropical settings) during the past 6000 yr. Variations in rainfall are discussed below.

Rainfall Rates. Ground water migrating along conduit pathways in the vadose zone reacts less with limestone than does ground water migrating by diffuse flow through matrix porosity (seepages). This is due to the shorter residence times and lower mineral-surface/fluid-volume ratio of conduit flow. A model involving changes in the routes of vadose ground-water migration as a function of rainfall has been constructed from quantitative tracer studies in karst terrains of Great Britain (Smart and Friederich, 1987). In this model, ground-water migration is predominantly along seepage routes during periods of low rainfall (i.e., low excess rainfall). During high rainfall periods, the capacity of seepage routes is exceeded and migration is predominantly by conduit flow along paths of enhanced permeability.

Application of this ground-water flow route model to the Barbados karst system suggests, in conjunction with the contrasting soil and limestone Sr isotope signatures, a climatic control on the temporal fluctuations between soil vs. limestone contributions to ground-water Sr. This model predicts that the compositional balance of cave drip waters will shift toward a soil zone signature (i.e., lower ⁸⁷Sr/⁸⁶Sr) during periods of elevated recharge (i.e., low evaporation/precipitation ratio, E/P), and toward a limestone signature (higher ⁸⁷Sr/⁸⁶Sr) during periods of diminished recharge (high E/P). The low residence time and preferred conduit pathways during high rainfall periods would lead to diminished interaction between ground water and host limestones. The increase in mean ⁸⁷Sr/⁸⁶Sr from modern stream waters to fast drip waters to slow drip waters (Fig. 3) is consistent with a flow route control on ground-water Sr isotope variations. The low speleothem ⁸⁷Sr/⁸⁶Sr values may therefore correspond to periods of relatively high rainfall, and high ⁸⁷Sr/⁸⁶Sr values to periods of low rainfall. Ground-water ⁸⁷Sr/⁸⁶Sr values during relatively dry periods may also be influenced by increased accumulation of sea-spray salts, which will impart high ⁸⁷Sr/⁸⁶Sr values (similar to the Pleistocene limestones; Fig. 2) to vadose ground water.

The inferred temporal shifts in flow

routes may also be governed by local porosity and permeability evolution in the aquifer, rather than climatic fluctuations. The oscillations in the Barbados speleothem record, however, would require reversals in the direction of this evolution. While the only extended temporal isotope records in this study are from two closely spaced stalagmites (Fig. 1), the coherence of the ⁸⁷Sr/⁸⁶Sr age trend for speleothems that represent five different ground-water drips and one flow suggests that the process(es) controlling the trend operated on at least the scale of the sample coverage (200 m). If a regional process such as climate variability controls temporal ⁸⁷Sr/⁸⁶Sr variations in karst ground water, a coherent regional isotope record could still be obscured by local differences in factors such as soil composition and in the length and configuration of flow paths.

Temporal variability in Sr isotope composition is not observed in modern drip waters at an individual location (C1, Fig. 1) for four samples taken over a 3.5 yr period (for which annual rainfall rates varied by 35%) and for eight samples taken over a four month period (for which discharge rates varied by 20%). This lack of temporal variability may reflect (1) the relatively small shifts in discharge and rainfall rates and/or or short time scale of the modern study period, or (2) the lack of applicability of our modeled links between rainfall, flow routes, and ground-water compositions. Further study of modern fluctuations in ground-water ⁸⁷Sr/⁸⁶Sr as a function of climatic variations and independent temporal ⁸⁷Sr/⁸⁶Sr records will provide tests for this model. In summary, temporal Sr isotope variations in ground water recorded by the speleothems may reflect a combination of (1) changes in the transport and/or weathering of atmospheric components to soils with distinct ⁸⁷Sr/⁸⁶Sr values, and (2) changes in the relative Sr flux from soil vs. limestone. A model involving changes in vadose flow routes as a function of rainfall recharge is consistent with the variations predicted by the second mechanism.

HOLOCENE CLIMATE FLUCTUATIONS

In order to further test the rainfall–flow route model, we examine independent records of Holocene climate fluctuations in the Caribbean and surrounding tropics. A pronounced increase in δ¹⁸O values and sulfur/CaCO₃ ratios of sediments from Lake Chichanacanab (Yucatán) during the period 1.3–1.1 ka is inferred to represent the driest period in the middle to late Holocene epoch (Hodell et al., 1995). As summarized by Hodell et al. (1995), this period coincides

with a proposed drought in this region based on archaeological evidence, increased fires in Central America, and low lake levels in Venezuela. Sediments from Lake Miragoane in Haiti record an earlier drying event between 2.5 and 1.5 ka, but this timing difference may be due to underestimation of hard-water-lake dating errors for Lake Miragoane (Hodell et al., 1995). The inferred dry period of 1.3–1.1 ka falls within the period of highest ⁸⁷Sr/⁸⁶Sr values in the Barbados speleothem record (Fig. 3). Such an interval of low rainfall and high ⁸⁷Sr/⁸⁶Sr in speleothem calcite is consistent with the predictive ground-water flow route model discussed above. Taken in the context of this model, the Barbados speleothem record (Fig. 3) indicates two principal transitions from relatively dry (high E/P) to humid (low E/P) climatic periods. The first transition began at ca. 6 ka at the start of the record, and the second ca. 1.0 ka, as discussed above. Lake records from Venezuela also indicate a transition at ca. 6–5.5 ka from arid to humid conditions, which persisted up to around 1.0 ka (Leyden, 1985). Such a transition is not observed in the Yucatán record from 6.0 to 5.5 ka. Differences among the Barbados speleothem and Mesoamerican climate records may result from (1) differences in the response of closed-basin lake conditions vs. vadose ground-water compositions to changes in rainfall (i.e., moisture balance), and (2) local climatic variability that is not discernible from present records.

IMPLICATIONS

The results of this study indicate that Sr isotopes have application for reconstructing ground-water evolution and for testing the controls on this evolution by factors such as climate variations. Further geochemical and flow modeling studies of this and other karst systems are required to evaluate the extent to which speleothem Sr records reflect local vs. regional conditions, and their potential for studies of climate variability, weathering processes, element cycling, and atmospheric transport that have been advanced by previous investigations of shorter term modern systems (Miller et al., 1993) and longer term marine records (Burke et al., 1982). High-resolution proxy records, such as the speleothem ⁸⁷Sr/⁸⁶Sr record, are needed to assess the magnitude and effects of millennial and shorter scale variations in climate on surface and ground water.

ACKNOWLEDGMENTS

We thank the following persons for assistance in the field and the laboratory: A. Mason, I. Jones, J. Mwansa, L. Barker, K. Neblett, E. Holder, T. Housh, A. Remington, F. Wefer, C. Gallup, and the staffs of Harrison's Cave, the Barbados Water Authority, and the Barbados National Trust. The manuscript was improved by comments from T. Quinn, L. Land, and an anonymous reviewer. Support was provided by the Geology Founda-

tion of the University of Texas and Mobil Research and Development (to Banner) and National Science Foundation grant EAR-9406183 (to Edwards).

REFERENCES CITED

Baker, A., Smart, P. L., and Edwards, R. L., 1995, Paleoclimate implications of mass spectrometric dating of a British flowstone: *Geology*, v. 23, p. 309–312.

Banner, J. L., and Kaufman, J., 1994, The isotopic record of ocean chemistry and diagenesis preserved in non-luminescent brachiopods from Mississippian carbonate rocks, Illinois and Missouri: *Geological Society of America Bulletin*, v. 106, p. 1074–1082.

Banner, J. L., Musgrove, M., and Capo, R., 1994, Tracing ground-water evolution in a limestone aquifer using Sr isotopes: Effects of multiple sources of dissolved ions and mineral-solution reactions: *Geology*, v. 22, p. 687–690.

Bender, M. L., Fairbanks, R. G., Taylor, F. W., Matthews, R. K., Goddard, J. G., and Broecker, W. S., 1979, Uranium-series dating of the Pleistocene reef tracts of Barbados, West Indies: *Geological Society of America Bulletin*, v. 90, p. 577–594.

Borg, L. E., and Banner, J. L., 1996, Nd and Sr isotopic constraints on weathering processes and soil sources in Barbados, West Indies: *Geochimica et Cosmochimica Acta* (in press).

Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, N. F., and Otto, J. B., 1982, Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time: *Geology*, v. 10, p. 516–519.

DePaolo, D. J., and Ingram, B. L., 1985, High-resolution stratigraphy with strontium isotopes: *Science*, v. 227, p. 938–941.

Dorale, J. A., Gonzalez, L. A., Reagan, M. K., Pickett,

D. A., Murrell, M. T., and Baker, R. G., 1992, A high-resolution record of Holocene climate change in speleothem calcite from Cold Water Cave, northeast Iowa: *Science*, v. 258, p. 1626–1630.

Gallup, C. D., Edwards, R. L., and Johnson, R., 1994, The timing of high sea levels over the past 200,000 years: *Science*, v. 263, p. 796–800.

Harmon, R. S., Thompson, P., Schwarcz, H. P., and Ford, D. C., 1978, Late Pleistocene paleoclimates of North America as inferred from stable isotope studies of speleothems: *Quaternary Research*, v. 9, p. 54–70.

Harris, W. H., and Matthews, R. K., 1968, Subaerial diagenesis of carbonate sediments: Efficiency of the solution-precipitation process: *Science*, v. 160, p. 77–79.

Hobbs, H. H., III, ed., 1994, A study of environmental factors in Harrison's Cave, Barbados, West Indies: National Speleological Foundation, 106 p.

Hodell, D. A., Curtis, J. H., and Brenner, M., 1995, Possible role of climate in the collapse of Classic Maya civilization: *Nature*, v. 375, p. 391–394.

Knox, O., Torres, A., Burch, J., and Sorensen, O., 1978, Survey of Harrison's Cave, St. Thomas Parish, Barbados: National Speleological Foundation Project (map).

Leyden, B. W., 1985, Late Quaternary aridity and Holocene moisture fluctuations in the Lake Valencia Basin, Venezuela: *Ecology*, v. 66, p. 1279–1295.

Miller, E. K., Blum, J. D., and Friedland, A. J., 1993, Determination of soil exchangeable-cation loss and weathering rates using Sr isotopes: *Nature*, v. 362, p. 438–441.

Muhs, D. R., Crittenden, R. C., Rosholt, J. N., Bush, C. A., and Stewart, K. C., 1987, Genesis of marine

terrace soils, Barbados, West Indies: Evidence from mineralogy and geochemistry: *Earth Surface Processes and Landforms*, v. 12, p. 605–618.

Prospero, J. M., and Nees, R. T., 1986, The impact of the North African drought and El Niño on mineral dust in the Barbados trade winds: *Nature*, v. 320, p. 735–738.

Simkin, T., and Siebert, L., 1994, *Volcanoes of the world: A regional directory, gazetteer, and chronology of volcanism during the past 10,000 years* (second edition): Tucson, Arizona, Geoscience Press, 349 p.

Smart, P. L., and Friederich, H., 1987, Water movement and storage in the unsaturated zone of a maturely karstified aquifer, Mendip Hills, England, in *Proceedings, Conference on environmental problems in karst terrains and their solution*: Bowling Green, Kentucky, National Water Well Association, p. 57–87.

Torrini, R., Jr., Speed, R. C., and Mattioli, G. S., 1985, Tectonic relationships between forearc-basin strata and the accretionary complex at Bath, Barbados: *Geological Society of America Bulletin*, v. 96, p. 861–874.

Winograd, I. J., Coplen, T. B., Landwehr, J. M., Riggs, A. R., Ludwig, K. R., Szabo, B. J., Kolesar, P. T., and Revesz, K. M., 1992, Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada: *Science*, v. 258, p. 255–260.

Manuscript received March 28, 1996
 Revised manuscript received July 19, 1996
 Manuscript accepted August 19, 1996

CORRECTION

Multistage evolution of Australian subcontinental mantle: Re-Os isotopic constraints from Victorian mantle xenoliths: Correction

Geology, v. 24, p. 631–634 (July 1996)

An incomplete version of Table 1 was printed with this article. The complete version is reprinted below, and this corrected version has been substituted into the article in *GSA Journals on Compact Disc*.

TABLE 1. Sr-Nd-Os ISOTOPIC AND SELECTED MAJOR AND TRACE ELEMENT DATA

Sample	Type	Al ₂ O ₃	MgO	(La/Sm) _N	$^{87}\text{Sr}/^{86}\text{Sr}$	ϵ_{Nd}	Re	Os	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	γ_{Os}	T_{RW}	T_{MA}
P7a	H	0.65	47.4	3.32	0.704 63	+1.65	0.0441	2.30	0.0935 ± 28	0.1237 ± 5	-2.68	513	668
P7b	H(PR)						0.0661	2.12	0.1504 ± 45	0.1253 ± 5	-1.42	270	431
P7c	H(PR)							4.08		0.1255 ± 3	-1.26	243	
P12a	H	0.66	46.4	1.64	0.704 87	-1.41	0.123	2.47	0.2426 ± 73	0.1241 ± 3	-2.36	450	1133
P12b	cpx				0.705 07	-1.65							
P27	H	1.09	45.2	2.59	0.704 62	-0.32	0.0199	3.03	0.0319 ± 9	0.1262 ± 2	-0.71	131	142
P29	L	1.65	43.9	3.95	0.704 06	+3.78	0.0241	1.89	0.0625 ± 19	0.1221 ± 3	-3.93	759	899
P33a	H	1.35	44.3	10.3	0.704 37	+1.01	0.2657	3.72	0.3346 ± 100	0.1246 ± 2	-1.97	386	2299
P33b	H(MSR)							3.73		0.1250 ± 3	-1.65	315	
P43	L	3.35	39.9	1.17	0.703 09	+6.92	0.0874	1.90	0.2254 ± 68	0.1264 ± 4	-0.55	113	259
P52a	L	2.51	41.0	2.80	0.704 50	+1.79	0.0298	2.21	0.0667 ± 20	0.1226 ± 4	-3.54	674	808
P52b	cpx				0.704 49	+1.44							
A6	L	5.04	35.8	0.779	0.702 87	-4.58	0.0616	0.92	0.3212 ± 96	0.1290 ± 44	+1.40		
A13a	L	4.64	37.4	0.435	0.702 55	+7.74	0.0575	2.29	0.1232 ± 37	0.1384 ± 4	+8.89		
A13b	L(PR)						0.193	4.25	0.2202 ± 66	0.1252 ± 6	-1.49	283	627
A13c	cpx				0.702 54	+8.24							
A33a	L	3.54	37.9	0.575			0.107	1.55	0.3321 ± 99	0.1301 ± 4	+2.36		
A33b	cpx				0.702 30	+10.1							
A34a	L	2.71	40.6					1.85		0.1238 ± 8	-2.60	495	
A34b	L(PR)						0.1919	1.15	0.8075 ± 242	0.1327 ± 6	+4.41		833
A37	L	3.34	39.1				0.0992	1.36	0.3539 ± 106	0.1293 ± 5	+1.75		
B-555a	GP	15.2	14.8	1.44			0.0788	0.43	0.8716 ± 262	0.1315 ± 9	+3.46		561
B-555b	GP(MSR)							0.43		0.1334 ± 11	+4.96		

Note: Abundances are in parts per million (ppm) for Ni, parts per billion (ppb) for Re and Os, and in wt% for Al₂O₃ and MgO. P = Mount Porndon; A = Anakies; B = Lake Bullenmerri. Type: H = harzburgite; L = lherzolite; GP = garnet metapyroxenite; PR = full procedure repeat; MSR = mass spectrometry repeat; cpx = acid-leached clinopyroxene mineral separate. Model ages calculated with respect to chondritic $^{187}\text{Re}/^{188}\text{Os} = 0.40076$, $^{187}\text{Os}/^{188}\text{Os} = 0.1271$ (Walker and Morgan, 1989). T_{RW} assumes sample $\text{Re}/\text{Os} = 0$. γ_{Os} = percentage difference between sample and chondritic mantle at present day. Sr corrected for mass fractionation to $^{86}\text{Sr}/^{87}\text{Sr} = 0.1194$ and reported relative to $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025$ for NBS 987. Nd corrected to $^{146}\text{Nd}/^{144}\text{Nd} = 0.72190$ and reported relative to $^{143}\text{Nd}/^{144}\text{Nd} = 0.511860$ for La Jolla. ϵ_{Nd} calculated with respect to chondritic $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$ (Goldstein et al., 1984). Uncertainties in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ are 2σ based on in-run statistics and error magnification. Re-Os determined by isotope-dilution negative-thermal-ionization mass spectrometry (N-TIMS), following desilicification and low-blank Carius tube digestion (Shirey and Walker, 1995), except P7b and P7c, which were not desilicified. Maximum Os blank = 30 pg and maximum Re blank = 45 pg. Al₂O₃, MgO, and Ni determined by XRF and (La/Sm)_N determined by inductively coupled plasma mass spectrometry (ICP-MS).