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Stable isotope variations in modern tropical speleothems: Evaluating equilibrium vs. kinetic isotope effects

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Abstract—Applications of speleothem calcite geochemistry in climate change studies require the evaluation of the accuracy and sensitivity of speleothem proxies to correctly infer paleoclimatic information. The present study of Harrison's Cave, Barbados, uses the analysis of the modern climatology and groundwater system to evaluate controls on the C and O isotopic composition of modern speleothems. This new approach directly compares the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of modern speleothems with the values for their corresponding drip waters in order to assess the degree to which isotopic equilibrium is achieved during calcite precipitation. If modern speleothems can be demonstrated to precipitate in isotopic equilibrium, then ancient speleothems, suitable for paleoclimatic studies, from the same cave environment may also have been precipitated in isotopic equilibrium. If modern speleothems are precipitated out of isotopic equilibrium, then the magnitude and direction of the C and O isotopic offsets may allow specific kinetic and/or equilibrium isotopic fractionation mechanisms to be identified.

Carbon isotope values for the majority of modern speleothem samples from Harrison's Cave fall within the range of equilibrium values predicted from the combined use of (1) calcite-water fractionation factors from the literature, (2) measured temperatures, and (3) measured $\delta^{13}\text{C}$ values of the dissolved inorganic carbon of drip waters. Calcite samples range from $\sim 0.8\%$ higher to $\sim 1.1\%$ lower than predicted values. The ^{13}C depletions are likely caused by kinetically driven departures in the fractionation between HCO_3^- (aq) and CaCO_3 from equilibrium conditions, caused by rapid calcite growth. ^{13}C enrichments can be accounted for by Rayleigh distillation of the HCO_3^- (aq) reservoir during degassing of ^{13}C -depleted CO_2 .

Modern speleothems from Harrison's Cave are not in O isotopic equilibrium with their corresponding drip waters and are 0.2% to 2.3% enriched in ^{18}O relative to equilibrium values. $\delta^{18}\text{O}$ variations in modern calcite are likely controlled by kinetically driven changes in the fractionation between HCO_3^- (aq) and CaCO_3 from equilibrium conditions to nonequilibrium conditions, consistent with rapid calcite growth. In contrast to $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ values of modern calcite may not be affected by Rayleigh distillation during degassing because CO_2 hydration and hydroxylation reactions will buffer the O isotopic composition of the HCO_3^- (aq) reservoir. If the effects of Rayleigh distillation manifest themselves in the O isotopic system, they will result in ^{18}O enrichment in the HCO_3^- (aq) reservoir and ultimately in the precipitated CaCO_3 . Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

As studies of climate change have become a rapidly growing part of the Earth sciences, applications of speleothem (cave calcite deposit) geochemistry to these studies have also grown. This increased interest has come from: (1) the numerous geochemical tracers of climatic and hydrologic processes that are incorporated into speleothem calcite; (2) advances in geochronologic methods for Quaternary carbonate deposits, which allow the geochemical tracers to be put into a high-resolution time series (Musgrove et al., 2001); and (3) the widespread geographic occurrence of speleothems, including low-altitude, low-latitude terrestrial environments where other high-resolution climate records may be scarce. These tracers have been used to infer changes in paleoprecipitation, paleotemperature, and paleovegetation (Dorale et al., 1992; Winograd et al., 1992; Baker et al., 1998; Genty et al., 1998). Tropical climate change studies are of particular interest because this is where the vast

majority of tropospheric moisture originates, driving the global hydrologic cycle (Masson et al., 2000).

Most paleoclimate reconstructions apply proxy data to infer changes in some environmental parameter. Evaluating the utility, accuracy, and sensitivity of a given proxy is critical for valid paleoclimate reconstruction. Rigorous testing of the geochemical proxies preserved in corals and marine foraminifera through calibration of experimental or modern natural systems (Spero and Williams, 1988; Beck et al., 1992; Spero, 1992) has evaluated the applicability of these proxies. Despite the growing use of speleothems in paleoenvironmental reconstructions, studies that evaluate the extent to which isotopic equilibrium is reached during speleothem formation, or that attempt to calibrate speleothem isotope variations, are few (e.g., Bar-Matthews et al., 1996; Lauritzen and Lundberg, 1999; Desmarchelier et al., 2000). Speleothem proxies are inherently more complex than marine proxies, given the much wider variations in cave-water geochemistry relative to seawater and the significant kinetic isotope effects caused by rapid CO_2 degassing, rapid calcite precipitation, and cave-water evaporation. Nonetheless, terrestrial climate is ultimately of great concern for future climate predictions.

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The use of carbon and oxygen isotope records requires an evaluation of whether the isotopic composition of speleothem calcite directly reflects the isotopic composition of water and dissolved inorganic carbon upon entry into the cave. The oxygen isotope composition of the calcite can be used to infer the isotope composition of rainfall, which is climatically controlled (Dansgaard, 1964), and/or temperature at the time of speleothem formation. The carbon isotopic composition of speleothems can be used to infer the isotopic composition of atmospheric CO₂ (Baskaran and Krishnamurthy, 1993), the type of vegetation growing above the cave (Dorale et al., 1992), and the relative contributions of soils vs. aquifer limestone to the dissolved inorganic carbon that forms the speleothem (Hendy, 1971; Genty et al., 1998).

In this study, we evaluate equilibrium vs. kinetic isotope effects and determine the extent to which speleothems record variations in environmental parameters through the study of modern speleothems precipitated in Harrison's Cave, Barbados. The modern speleothems we examine include samples from the tips of actively growing stalagmites, flowstones grown since development of the cave in 1978, and speleothem calcite grown on glass plates placed under active drips in the cave. We collected the calcite precipitated under current climatic conditions and the water from which the calcite precipitated. The C and O isotopic composition of modern speleothem-drip water pairs were used to determine the extent to which isotopic equilibrium is achieved during calcite precipitation. This information can be applied to speleothem isotopic records collected from the same cave environment that are used for paleoclimatic reconstructions.

2. ISOTOPE METEOROLOGY AND HYDROLOGY OF BARBADOS

Barbados' Pleistocene limestone aquifer is well suited for studying the links between modern climate, the isotopic composition of cave drip water, and the calcite that precipitates from this water. Within this aquifer system, Harrison's Cave contains multiple speleothems that form in a variety of cave microenvironments. The island's isolated setting, removed from large-sized landmasses, and its low topographic relief, reduce the O isotopic variability of rainfall on the island. Isotopic effects that operate on larger landmasses, such as topographic and continentality effects and mixing of distant water vapor sources with significantly different isotopic compositions, have minor control on the O isotopic composition of rainfall on Barbados. In addition, the tropical location of Barbados lowers its seasonal temperature range to approximately 4°C to 5°C, limiting the effects of temperature on the O isotopic composition of rainfall. These factors combine to produce a location with ample actively growing speleothems for study, and a simplified O isotopic rainfall and groundwater system already well characterized (Jones et al., 1998; Jones et al., 2000; IAEA/WMO, 2001).

Oxygen isotopic compositions and amounts of rainfall have been measured in Barbados for the past 30 yr (IAEA/WMO, 2001) and for cave drip water data from 1997 to 2000 (this study). The seasonal distribution and oxygen isotopic compositions of rainfall on Barbados vary as a function of tropical weather patterns (Jones et al., 2000). During the dry season,

from January to April, rainfall results from local heating and rising of air, with rainfall focused over the island's central elevated portions. Most rain falls from June to December, and is associated with the seasonal movement of the low-pressure intertropical convergence zone and with passing tropical weather systems. Monthly averaged isotopic compositions of Barbados rainwater range in $\delta^{18}\text{O}$ from -4‰ to $+2\text{‰}$, with lower $\delta^{18}\text{O}$ values occurring during the wet season. Groundwaters, by contrast, have a narrower range of $\delta^{18}\text{O}$ values, with most values between -3.5‰ to -3.0‰ . This contrast reflects the effects of evapotranspiration, which limits recharge to the Pleistocene limestone aquifer to the two to three wettest months of the year (Jones et al., 2000; Jones and Banner, 2003). The isotopic composition of rainfall during these months controls the isotopic composition of groundwater and cave drip waters, including those in Harrison's Cave, resulting in groundwater with a narrow O isotopic composition (Jones et al., 2000).

3. STUDY SITES AND SAMPLE DESCRIPTIONS

Three locations were studied in Harrison's Cave for modern speleothems and drip-water collection: The Upper Passage, Crystal Droppings, and Spur 1 (Fig. 1). These sites represent the range of microenvironments found in the cave, and samples collected may record the sensitivity of speleothems to modern climatic and hydrologic variations. Low relative humidity at the site of calcite precipitation may cause high $\delta^{18}\text{O}$ values in the calcite due to evaporative ^{18}O enrichment in the cave drip water, and rapid CO₂ degassing may cause ^{13}C enrichments in the speleothem precipitated from that water (Gonzalez and Lohmann, 1988). Therefore, we would expect speleothems precipitated under high humidity conditions from relatively slow steady drips would have the highest potential for precipitation in O and C isotopic equilibrium with their corresponding drip water. Conditions at our study sites are outlined in Table 1.

We would expect that conditions in the Upper Passage sites are the most conducive to the precipitation of speleothems in isotopic equilibrium with their corresponding drip water for several reasons. Meteorological data indicate that the Upper Passage has had humidity levels close to 100% during its history. High humidity values in the Upper Passage are maintained by the presence of airflow bottlenecks on each end of the passage (Fig. 1) that act to limit air exchange. Development of the cave in 1978 to 1979 included excavation of a 5 m diameter tunnel entrance and the excavation of two ventilation shafts. Even after development, humidity in the deeper parts of the cave is above 98.2% during the day while ventilation fans operate, with the rolling steel door on the tunnel entrance open, and above 99% at night with the fans off and the door closed (Wefer, 1994). The Upper Passage sample locations are approximately 21 m below the land surface. Speleothems at this site form under high humidity conditions from relatively slow steady drips. These conditions limit evaporative ^{18}O enrichment in the drip water and may limit kinetic isotope effects caused by large variations in drip rates and the accompanying changes in drip water chemistry.

Modern speleothems were collected from four sites from the Upper Passage, BC-98-1 through BC-98-4. BC-98-1, BC-98-2 and BC-98-3 were collected from the tops of active stalagmites that are approximately 1 m in height. The drips

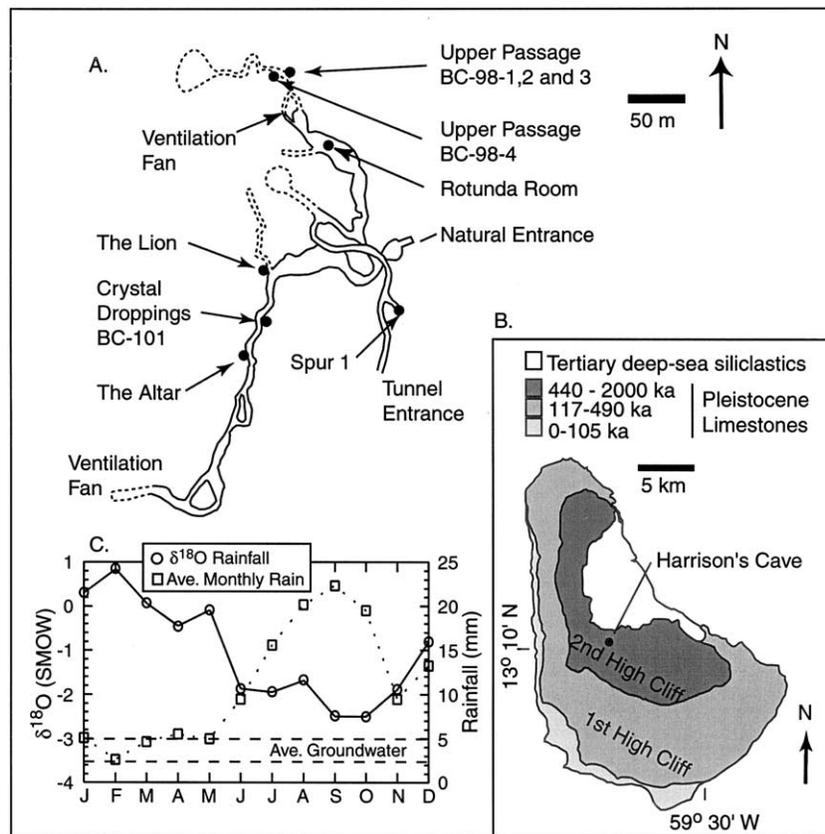


Fig. 1. (A) Map of Harrison's Cave showing the location of modern speleothem sample sites, humidity measurement sites (Wefer, 1994) and (B) the caves location on Barbados, West Indies (Hobbs, 1994). Dashed passages have not been surveyed. Harrison's Cave is located above the Second High Cliff. Limestone above the Second High Cliff ranges in age from 440 ka to 2.0 Ma, and limestone above the Second High Cliff and below the elevation of Harrison's Cave range in age from 440 to 640 ka (Banner et al., 1994). (C) Average monthly $\delta^{18}\text{O}$ values of average monthly rainfall collected on Barbados between 1961 and 1997 (IAEA/WMO, 2001) and of average monthly rainfall amounts from 1994 to 2000 (IAEA/WMO, 2001). Range of Harrison's Cave groundwater $\delta^{18}\text{O}$ values, between 3.0 and 3.5‰, indicated by dashed lines.

feeding these speleothems are slow, less than 0.3 mL/min. These speleothems occupy an area of a square meter. Ten meters away, BC-98-4 is several cm in height, precipitating from a very slow drip.

Among the sample sites studied, we would expect that conditions in Spur 1 are least conducive to the precipitation of speleothems in isotopic equilibrium with their corresponding drip water for several reasons: (1) The proximity of the room to

Table 1. Site conditions, glass plate calcite thickness, and number of samples.

Site	Drip rate (ml/min)	Drip water pH	Drip water temp. (°C)	Relative humidity (%)	Depth below surface (m)	Calcite thickness at sample location (mm)		Number of high-resolution samples Set 1, Set 2
						Plate placed 7-11-1998 Plate collected 1-31-00 Plate Set 1	Plate placed 2-1-1999 Plate collected 7-1-00 Plate Set 2	
Spur 1	0 to 18.8	7.6	27.5	97.8 to 99.6	12	0.4	NA	15, NA
Crystal Droppings	86 to 96	7.4 to 7.5	25.0 to 28.5	97.8 to 99.6	40	NA	NA	NA, NA
Upper Passage Sites								
BC-98-1	0.1 to 0.3	7.8 to 8.1	26.0 to 29.6	>98.2 ^a	21	0.4	0.6	11, 32 ^b
BC-98-2	0.1 to 0.2	8.1	25.6 to 30.0	>98.2 ^a	21	0.4	0.7	11, 27 ^b
BC-98-3	0.1 to 0.3	7.7 to 8.1	26.8 to 29.9	>98.2 ^a	21	0.3	0.8	13, 47 ^b
BC-98-4	<0.008	NA	NA	>98.2 ^a	21	<0.1	NA	NA, NA

Relative humidity, depth below surface were measured by Wefer (1994). At Upper Passage sites, BC-98-1, BC-98-2 and BC-98-3, both modern speleothem cores and glass plate calcite were sampled; at Spur 1 and BC-98-4, only glass plate calcite was sampled; at Crystal Droppings, only modern speleothem core was sampled.

^a Relative Humidity at the Upper Passage sites were assumed to be at least equivalent to the relative humidity measured at the Rotunda Room. The presence of air flow bottlenecks that isolate the Upper Passage sites suggest that relative humidity may be slightly higher.

^b Not all samples were analyzed.

the tunnel entrance (approximately 75 m) results in variable humidity ranging from 97.8% to 99.6% (Wefer, 1994), which might allow evaporative increases in the $\delta^{18}\text{O}$ values of cave drip water. More importantly, the proximity to the tunnel entrance may also allow greater ventilation, which could result in lower CO_2 concentrations in the cave atmosphere, which in turn, will promote greater CO_2 degassing from cave drip waters. CO_2 degassing is a more significant factor than evaporation of cave drip water in driving CaCO_3 precipitation in these high humidity environments. (2) Drips that are currently precipitating speleothems in this room respond to seasonal variations in rainfall rate. Drip rates ranged from approximately 0 mL/min, during the dry season, to at least 18.8 mL/min, resulting in variable calcite precipitation rates. (3) Spur 1 is much closer to the land surface (approximately 12 m) than the other sites in the cave, likely resulting in less water-rock interaction before speleothem precipitation. The combination of these variables would more likely result in speleothems with isotopic compositions that are distinct from other sites in the cave and will most likely result in disequilibrium isotope effects during calcite precipitation.

The third sampling site in the cave is Crystal Droppings. This site is located in a man-made tunnel at a depth of approximately 40 m, and approximately 250 m from the artificial cave entrance. Tunnel construction was completed in 1979 to 1980 (Hobbs, 1994). Flowstone calcite is being precipitated from a continuously flowing sheet of water on the walls of the tunnel where we measured a relative humidity of 99.6% in July 2000. Wefer (1994) measured humidity at two sites within 40 m of Crystal Droppings. At these sites, the Alter and the Lion, the relative humidity varies between 97.8% and 99.1%. Based on the close proximity of these sites to Crystal Droppings, we conclude that the three sites share the same relative humidity conditions such that Wefer's measurements are applicable to Crystal Droppings (Fig. 1).

Two types of modern speleothem samples were used in this study. Modern speleothems include cores from the tips of actively growing stalagmites and flowstones, and calcite grown on glass plates placed under active drips. Cores were taken from several actively growing speleothems in the Upper Passage in 1998. The cores are approximately 1 cm in diameter and 5 cm in length and consist of dense, translucent calcite. Calcite was sampled from the top 20 μm of the cores from the Upper Passage. Based on a long-term growth rate of 0.2 mm/yr (Mickler, 2004), the calcite was likely deposited within the year prior to coring. The Crystal Droppings core was taken in 1994 and contained 2 cm of flowstone calcite deposited on the host limestone since tunnel excavation. Two samples, one from the base and one from the top, were taken from this core.

Glass plates, prepared by frosting with a sandblaster followed by cleaning, were placed under active drips in the Upper Passage and Spur 1. The plates were left under the drips for 6 months and 18 months, and then collected. The glass plate calcite is composed of intergrown, flat-faced rhombohedral calcite crystals typically 100's of microns in diameter. Analysis of glass plate calcite yielded a record of oxygen and carbon isotope variations for the period July 1998 to July 2000.

4. ANALYTICAL METHODS

4.1. C and O Isotopic Composition of Calcite

The majority of modern calcite samples were analyzed for C and O stable isotopes at the University of Texas at Austin. Approximately 200 to 350 μg was analyzed using a Micromass Multiprep system on a Prism II dual inlet triple collector mass spectrometer. Analytical precision was 0.18‰ for $\delta^{18}\text{O}$ and 0.12‰ for $\delta^{13}\text{C}$ (2σ of 40 standard runs). Several samples were analyzed at The University of Minnesota, where 100 to 200 μg of CaCO_3 were reacted with 100% H_3PO_4 , cryogenically purified and analyzed on a Finnigan MAT delta E triple-collector mass spectrometer, method modified after McCrea (1950). Precision (2σ) was reported by the University of Minnesota as 0.2‰ for $\delta^{18}\text{O}$ and 0.13‰ for $\delta^{13}\text{C}$. For smaller samples, 20 to 40 μg of CaCO_3 were reacted using a Kiel II carbonate preparation device and analyzed on a Finnigan MAT 252 triple-collector mass spectrometer. Precision (2σ) was reported by the University of Minnesota as 0.08‰ for $\delta^{18}\text{O}$ and 0.06‰ for $\delta^{13}\text{C}$. The results of isotopic analysis are presented in conventional delta (δ) notation, defined as $\delta = (\text{R}_{\text{sample}} - \text{R}_{\text{standard}})/\text{R}_{\text{standard}} \times 1000$, where R is the ratio of $^{18}\text{O}/^{16}\text{O}$ or $^{13}\text{C}/^{12}\text{C}$. The O and C isotopic values for carbonate samples and the C isotopic values of dissolved inorganic carbon (DIC) are expressed relative to the standard Vienna Pee Dee Belemnite (VPDB).

4.2. O Isotopic Composition of Waters

Three groups have collected oxygen isotope compositions of rainwater and groundwater used in this study: (1) Rainwater $\delta^{18}\text{O}$ values have been collected on Barbados over the past 30 yr (IAEA/WMO, 2001); (2) Cave drip water and rainwater data has been collected over the past 7 yr (Jones et al., 1998; Jones et al., 2000); and (3) Cave drip waters from Harrison's Cave were collected in July 1998, February 1999, and July 2000, synchronous with deployment and collection of the glass plate experiment. In the Upper Passage water was collected by leaving a 1L wide mouth plastic bottle beneath each drip for approximately 24 h because drips were too slow to collect an adequate sample size manually. In Spur 1 and Crystal Droppings, water was collected by holding sample bottles ranging from 12 mL to 60 mL directly under the cave drips. Cave water samples analyzed in the present study were analyzed for ^{18}O using a Micromass multi-prep system and analyzed on a Prism II dual inlet mass spectrometer at the University of Texas at Austin. The O isotopic values of water samples are expressed relative to the Vienna Standard Mean Ocean Water (VSMOW) standard. Analytical precision (2σ) was 0.1‰.

4.3. Isotopic Composition of Waters

Dissolved inorganic carbon (DIC) samples were collected in the cave by filling 20 mL, amber, Volatile Organics Analysis (VOA) vials with unfiltered cave drip water with no head space and stored, dark and refrigerated, until analysis. The C isotopic composition of DIC was determined by injecting 5 mL of the cave drip water into an evacuated sample vial containing 1 mL 100% H_3PO_4 . The resulting mixture of CO_2 , water vapor, and noncondensable gases was cryogenically purified in a vacuum line. An analytical precision (2σ) of 0.1‰ was estimated by analyzing a solution of Na_2CO_3 (aq) with a known C isotopic composition and DIC concentrations similar to cave drip waters.

4.4. Equations for Determining O and C Isotopic Equilibrium

The extent to which O and C isotopic equilibrium is reached during calcite precipitation was determined using fractionation factors from the literature (Table 2 and 3). During equilibrium precipitation of calcite, the relationship between the oxygen isotopic composition of calcite and its corresponding host fluid and the temperature of formation is (O'Neil et al. (1969) as modified in Friedman and O'Neil (1977)):

$$1000 \ln \alpha_{\text{calcite-water}} = 2.78(10^{6/T} - 1) = 2.89 \quad (1)$$

where:

$$\alpha_{\text{calcite-water}} = (\delta_{\text{calcite}} + 1000)/(\delta_{\text{water}} + 1000) \quad (2)$$

Likewise, the relationship between the C isotopic composition of HCO_3^- , the dominant species in the DIC, calcite and, to a small extent,

Table 2. Equilibrium oxygen isotope fractionation factors ($1000 \ln \alpha$) at 26.6°C.

Species pair	Fractionation factor (‰)	Reference
CaCO ₃ -H ₂ O	27.73	(Kim and O'Neil, 1997)
CO ₂ (g)-CaCO ₃	12.55	(Bottinga, 1968)
CO ₂ (g)-H ₂ O	39.83	(Bottinga, 1968)
HCO ₃ ⁻ (aq)-H ₂ O (25°C)	34.0 ^a	(Uzdowski and Hoefs, 1993)
CO ₂ (g)-CO ₂ (aq)	0.8‰ ^b	(Vogel et al., 1970)

^a This value is poorly constrained and is based on a reevaluation of an experiment first conducted by McCrea (1950).

^b This value is based on the equilibrium fractionation at 0°C. The magnitude of this fractionation will be less than this value at 26.6°C.

the temperature during equilibrium calcite precipitation is (Deines, et al., 1974):

$$1000 \ln \alpha_{\text{calcite-HCO}_3^-} = 0.095(10^6/T^2) + 0.90 \quad (3)$$

where:

$$\alpha_{\text{calcite-HCO}_3^-} = (\delta_{\text{calcite}} + 1000)/(\delta_{\text{HCO}_3^-} + 1000) \quad (4)$$

Note: T in Equation 1 and Equation 3 is in Kelvin.

4.5. High-Resolution Sampling of Modern Calcite

Glass plate calcite from the Upper Passage (BC-98-1, BC-98-2 and BC-98-3) and Spur 1 were sampled at high-resolution. Glass plate calcite deposited between July 1998 and February 1999, and between February 1999 and July 2000, was collected from the Upper Passage sites. Unfortunately, the plate in Spur 1 placed in February of 1999 was broken before collection, so only the July 1998 to February 1999 time interval is available.

Approximately one square cm areas, near the locus of precipitation, on the plates were sampled in 20- μ m layers by moving the glass plate under a fixed dental drill and collecting the resulting powder for C and O isotopic analysis. The relative height of the glass plate and dental drill was monitored with the use of a digital micrometer with 1-micron resolution. The maximum thickness of glass plate calcite varied between the sites (Table 1). The thickness of the calcite decreased away from the locus of precipitation to less than 0.1 mm near the glass plate's edge, producing a calcite dome consistent with natural stalagmite formation. The area of maximum calcite thickness on the glass plates was the target of microsampling. Since the maximum calcite thickness varied between the glass plates, the time interval represented by each sample varied, estimated by assuming a constant calcite growth rate.

The lowest calcite thicknesses were seen in glass plate BC-98-4 where <0.1 mm of calcite was collected between July 1998 and February 1999. Not enough calcite grew at this site to allow the high-resolution sampling, so bulk sampling of the entire thickness of the calcite was performed.

There are three sources of error in determining the chronology of individual high-resolution glass plate calcite samples: (1) A constant calcite growth rate was assumed. It is likely that initial calcite growth rates were slower while calcite crystals were nucleating on the glass

Table 3. Equilibrium carbon isotope fractionation factors ($1000 \ln \alpha$) at 26.6°C.

Species pair	Fractionation factor (‰)	Reference
CaCO ₃ -HCO ₃ ⁻ (aq)	1.96	(Deines, et al., 1974)
CO ₂ (g)-CO ₂ (aq)	1.05	(Vogel et al., 1970)
HCO ₃ ⁻ (aq)-CO ₂ (aq)	8.79	(Mook et al., 1974)
HCO ₃ ⁻ (aq)-CO ₂ (g)	7.77	(Mook et al., 1974)

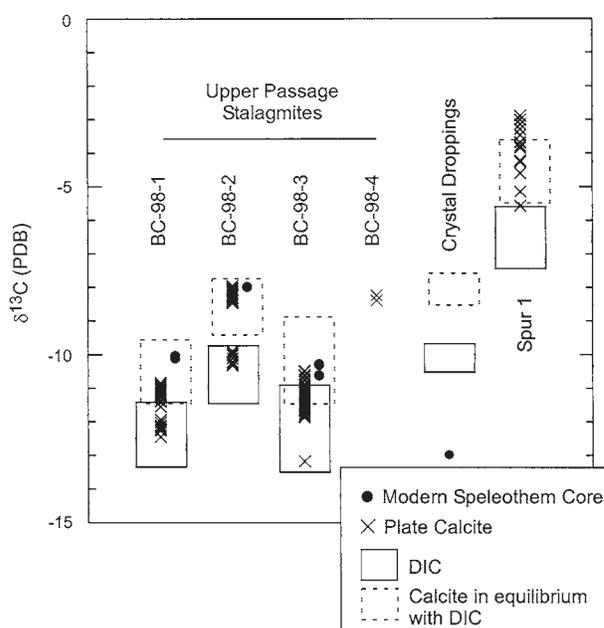


Fig. 2. Carbon isotopic composition of modern calcite and dissolved inorganic carbon (DIC) in cave drip water in Harrison's Cave, Barbados, West Indies. Solid boxes represent the range of C isotopic compositions of DIC collected at the site. The dashed boxes represent the theoretical range of C isotopic compositions of calcite precipitated in isotopic equilibrium with the corresponding drip water. All the sites, except Crystal Droppings, have precipitated calcite with a C isotopic composition consistent with equilibrium precipitation. DIC values were not obtained from the BC-98-4 site due to the slowness of the drip.

plate surface and increased until the surface of the glass plate was completely covered by calcite. (2) In Spur 1 the drip was dry when the plate was collected, indicating non deposition. This was not the case in the Upper Passage. (3) Changes in growth rate, caused by changing drip water chemistry, could not be determined between sampling trips.

4.6. Plate Retrieval Methodology

During plate retrieval, the plates were rinsed in deionized water, applied using a squirt bottle, to remove residual cave drip water from the plate surface and prevent further calcite precipitation. The plate was then tilted so the deionized water would run off, and a clean Kim-wipe was used to blot excess water from the plate edge. The plates were then stored in a clean, padded, plastic container for travel back to the University of Texas. Once back at the University of Texas, the plates were rinsed again in deionized water and allowed to dry in a hepa-filtered laminar flow hood in preparation for sample storage.

5. RESULTS

5.1. Carbon Isotopic Results for Modern Speleothems

Modern speleothems collected at Harrison's Cave show a large C isotopic variability with $\delta^{13}\text{C}$ values ranging from -13.2‰ to -2.9‰ PDB (Fig. 2). Large C isotopic variability is also seen in the composition of cave drip waters where the $\delta^{13}\text{C}$ value of drip waters varies from -13.5‰ to -5.7‰ PDB. We assessed carbon isotopic equilibrium of modern speleothems by comparing fractionation factors (Table 3) with the C isotopic composition of the modern calcite and the dissolved inorganic carbon (DIC) in the drip water at 26.6°C, the average annual air temperature of Barbados. At the pH range of 7.3 to

8.1 of the cave drip waters, the majority of DIC occurs as HCO_3^- (aq) (Plummer and Busenberg, 1982), and at equilibrium the $\delta^{13}\text{C}$ value of the CaCO_3 formed from a drip water will be 1.96‰ higher than the HCO_3^- (aq) measured as DIC of the drip water.

The carbon isotope composition of modern speleothem calcite in Harrison's Cave ranges from values that are consistent with precipitation at isotopic equilibrium, to values slightly enriched (0.8‰) or depleted (−1.1‰) in ^{13}C (Fig. 2), with Crystal Droppings being an exception. Only one of five sites tested (Spur 1) has calcite enriched in ^{13}C relative to equilibrium. At four of five sites tested (BC-98-1, BC-98-2, BC-98-3, and Spur 1), calcite samples show ^{13}C depletions relative to equilibrium. The departures from equilibrium towards both higher and lower ^{13}C values suggests that more than one mechanism may be responsible for the deviations from equilibrium.

Crystal Droppings is the only location tested with modern speleothems that are far from C isotopic equilibrium, with $\delta^{13}\text{C}$ values 4.9‰ lower than calcite predicted to be in isotopic equilibrium with the average drip water collected at the site. The Crystal Droppings site is distinct because, unlike the other sampling sites, the calcite is not precipitated from a discrete drip but rather from a film of water that may have resulted from the coalescing of many sources. In addition, the water at Crystal Droppings was sampled at a spot where it first entered the cave but before it had a chance to travel over the flowstone where the calcite sample was taken. This is in contrast with the other sampling sites, where the water enters the cave environment, flows a short distance down a corresponding stalactite, and is collected at the site of stalagmite precipitation. It is possible that the water that was collected at Crystal Droppings cannot be directly compared to its corresponding calcite because of the drip water's flow path.

5.2. Sensitivity of C Isotopes to Seasonal Changes

Glass plate calcite sampled at high-resolution at Spur 1 and the Upper Passage sites shows that these two sites respond differently to seasonal variability. The $\delta^{13}\text{C}$ values of the calcite from the Spur 1 plate show seasonal variability, $\delta^{13}\text{C}$ increasing from −5.6‰ to −2.9‰ before decreasing to −3.7‰ (Fig. 4C). The glass plate calcite in the Upper Passage shows seasonal change similar to that of Spur 1; however, the range of the variation is much less. Site BC-98-3 shows the largest variation of approximately 1.2‰ within a single plate placed between February 1999 and July 2000. In addition, the timing of the maximum $\delta^{13}\text{C}$ values varies between the Upper Passage glass plate calcite and the Spur 1 glass plate calcite. In Spur 1, where drip rates are variable and respond to changes in seasonal rainfall, the timing of the maximum $\delta^{13}\text{C}$ values closely matches that of maximum rainfall and highest drip rates. In the Upper Passage, where drip rates do not vary seasonally, the timing of the maximum $\delta^{13}\text{C}$ values lags behind the maximum monthly rainfall by approximately 4 to 7 months (Fig. 4C).

5.3. Oxygen Isotopic Results for Modern Speleothems

Modern speleothem cores and glass plate calcite collected at Harrison's Cave show lower O isotopic variability, relative to

the C isotopic system, with $\delta^{18}\text{O}$ values ranging from −5.3‰ to −3.0‰ PDB (Fig. 3). The corresponding drip waters also show lower O isotopic variability, with $\delta^{18}\text{O}$ values from −3.6‰ to −3.0‰ SMOW. None of the modern speleothems collected in Harrison's Cave precipitated in O isotopic equilibrium with its corresponding drip water. The extent to which modern speleothems attained oxygen isotope equilibrium was assessed using the full range of O isotopic composition of drip waters collected in Harrison's Cave, fractionation factors (Table 2), and the mean annual temperature of Barbados, 26.6°C. Only one site, BC-98-4 from the Upper Passage, precipitated calcite close to oxygen isotopic equilibrium with its corresponding drip water, within 0.2‰. The drip associated with BC-98-4 was much slower than the other drips studied, and the thickness of calcite collected on the plate was the lowest (Table 1).

5.4. Sensitivity of O Isotopes to Seasonal Change

High-resolution sampling of glass plate calcite grown in Spur 1 and the Upper Passage shows intra-annual O isotopic variability. Variations in the Spur 1 glass plate calcite $\delta^{18}\text{O}$ values correspond to intra-annual climate variability. The oxygen isotopic composition of the calcite increases from −4.8‰ to −4.4‰, then decreases towards lower values of −4.7‰ (Fig. 4D). The shift towards lower $\delta^{18}\text{O}$ values is closer to isotopic equilibrium with the drip water, although equilibrium is not achieved. Similar to the $\delta^{13}\text{C}$ values of the glass plate calcite from Spur 1, the timing of maximum $\delta^{18}\text{O}$ values corresponds to maximum monthly rainfall amounts and higher drip rates.

The $\delta^{18}\text{O}$ values of the Upper Passage glass plate calcite show a correspondence to intra-annual variability very similar to the $\delta^{13}\text{C}$ values. The similarities include: (1) BC-98-3 has the largest variability of the three Upper Passage sites, approximately 0.5‰ between February 1999 and July 2000; (2) The timing of the maximum $\delta^{18}\text{O}$ values of the Upper Passage sites lag behind the maximum $\delta^{18}\text{O}$ values seen in Spur 1 by 4 to 7 months; and (3) The magnitude of the $\delta^{18}\text{O}$ shift is much greater in the Spur 1 site than the Upper Passage sites (Fig. 4D).

5.5. O and C Isotopic Shift During Plate Exchange

In February of 1999, the glass plates were exchanged in the Upper Passage sites. The gap in time between glass plate collection and new glass plate deployment was only 24 h, so the oldest calcite collected on the first glass plate should have the same $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition as the youngest calcite sample from the second glass plate. The samples are essentially coeval, yet there is an isotopic enrichment seen in both ^{18}O and ^{13}C in the Upper Passage glass plates BC-98-1, BC-98-2, and BC-98-3 (Fig. 4). The largest enrichment, a $\delta^{13}\text{C}$ increase of ~2.0‰ and a $\delta^{18}\text{O}$ increase of ~0.6‰, is recorded at the BC-98-2 site.

6. DISCUSSION

Modern speleothems in Barbados have a range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values that are consistent with precipitation under isotopic equilibrium to nonequilibrium conditions. The following lines of evidence indicate the operation of kinetic isotope effects: (1)

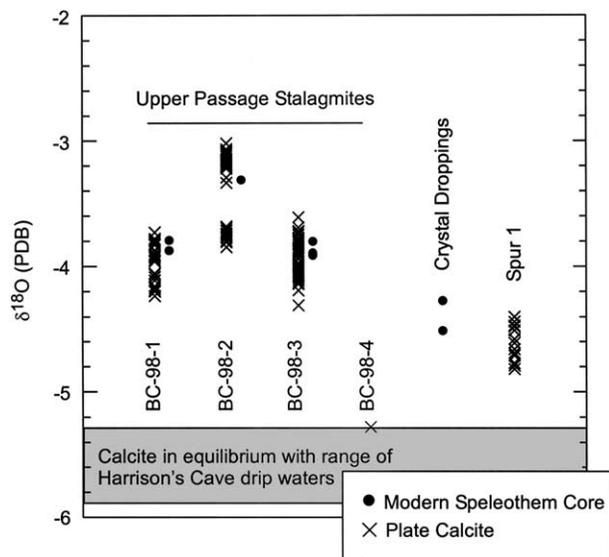


Fig. 3. Oxygen isotopic composition of modern calcite from Harrison's Cave, Barbados, West Indies. The theoretical O isotopic composition of calcite in isotopic equilibrium with the range of cave drip waters is indicated by the gray bar. Only BC-98-4 has precipitated calcite close to O isotopic equilibrium with cave water. All other sites are as much as 2.3‰ higher than equilibrium.

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition of modern speleothems depart from equilibrium values calculated from the fractionation factors from the literature, the average temperature of Barbados, and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the waters feeding the modern calcite samples. (2) There is a $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ shift during glass plate exchanges at the Upper Passage sites. It is highly unlikely that there was a fundamental change in the isotopic system during the 24 h between the placements of the glass plates. It is more likely that there was a change in the extent to which the kinetic isotope effects alter the isotopic composition of the calcite. Slight changes in the sampling location relative to the locus of calcite precipitation is likely responsible for the isotopic shifts, rather than changes in climatic conditions within or outside the cave. There is a progressive ^{13}C and ^{18}O enrichment in the calcite away from the center of the plate. These spatial isotope variations in plate calcite are detailed in Mickler (2004). (3) The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ compositions of modern calcite covary. This is a proposed criterion for kinetic isotope effects in the formation of ancient speleothems (Hendy, 1971). Here we discuss the potential mechanistic controls on the extent of kinetic and equilibrium isotope effects.

6.1. Controls on the $\delta^{13}\text{C}$ Composition of Modern Speleothems

The carbon isotope composition of modern speleothems in Harrison's Cave exhibit three ranges of values: (1) $\delta^{13}\text{C}$ values consistent with equilibrium precipitation; (2) C isotope compositions that are lower than predicted equilibrium values, but generally not lower than the $\delta^{13}\text{C}$ value of the corresponding drip water's DIC; and (3) C isotope compositions that are higher than predicted equilibrium values. Previous theoretical and laboratory studies may help explain the slight ^{13}C enrich-

ments and depletions seen in the modern calcite collected in Harrison's Cave.

6.2. Control on $\delta^{13}\text{C}$ Values Lower Than Equilibrium Values

The $\delta^{13}\text{C}$ values of modern calcite that depart from predicted equilibrium values towards lower values approach, and in some cases are equivalent to, the C isotopic compositions of DIC in its corresponding drip water (BC-98-1, BC-98-2 and BC-98-3). This process likely results from the incorporation of HCO_3^- (aq) into calcite during rapid mineral precipitation, such that isotopic fractionation is minimized (Michaelis et al., 1985). This mechanism is graphically portrayed as mechanism 1A (Fig. 5). Researchers studying kinetic isotopic behavior in rapidly precipitating calcite formation have observed similar results. Clark and Lauriol (1992) studied the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition of calcite precipitated from rapidly frozen water in both laboratory and field based studies. They suggest that the ^{13}C partitioning between calcite and DIC decreases from equilibrium conditions ($\Delta^{13}\text{C}_{\text{CaCO}_3-\text{HCO}_3^-} = 1.96\text{‰}$ to lower nonequilibrium values ($\Delta^{13}\text{C}_{\text{CaCO}_3-\text{HCO}_3^-}$ approaches 0‰) during kinetic isotope fractionation produced by rapid calcite precipitation.

6.3. Control on $\delta^{13}\text{C}$ Values Higher Than Equilibrium Values

Samples of glass plate calcite at Spur 1 show $\delta^{13}\text{C}$ values that are higher than predicted by equilibrium precipitation (Fig. 2). There are two possible explanations for this behavior: (1) The calcite is precipitating in C isotopic equilibrium with its corresponding drip water, but the full range of the $\delta^{13}\text{C}$ values of drip water DIC has not been determined by our intermittent sampling, and (2) The calcite reflects disequilibrium precipitation, likely resulting from ^{13}C enrichment of the HCO_3^- (aq) reservoir caused by CO_2 degassing.

Degassing is driven by the gradient between the P_{CO_2} of the cave drip water and the P_{CO_2} of the cave environment. The P_{CO_2} of the cave drip water is controlled by the P_{CO_2} of the soil zone, which can be ~ 2 orders of magnitude greater than atmospheric values. Large P_{CO_2} gradients engender fast degassing that may drive the dissolved inorganic carbon species away from isotopic equilibrium with respect to calcite.

The calcite dissolution/precipitation reaction can be expressed by the following equation:



CO_2 degasses from the solution into the cave environment's lower P_{CO_2} atmosphere, driving the dissolution/precipitation reaction to the right and causing speleothem CaCO_3 precipitation. The equilibrium $\delta^{13}\text{C}$ value of CO_2 (g) at 26.6°C is 7.8‰ lower than the HCO_3^- (aq) (Table 3), and the CaCO_3 is 2.0‰ higher than the HCO_3^- (aq). As degassing of ^{13}C -depleted CO_2 progresses, the reservoir of HCO_3^- (aq) will become isotopically heavier. The loss of isotopically heavy C via CaCO_3 precipitation is not enough to offset the loss of the more ^{13}C -depleted carbon via CO_2 degassing. The $\delta^{13}\text{C}$

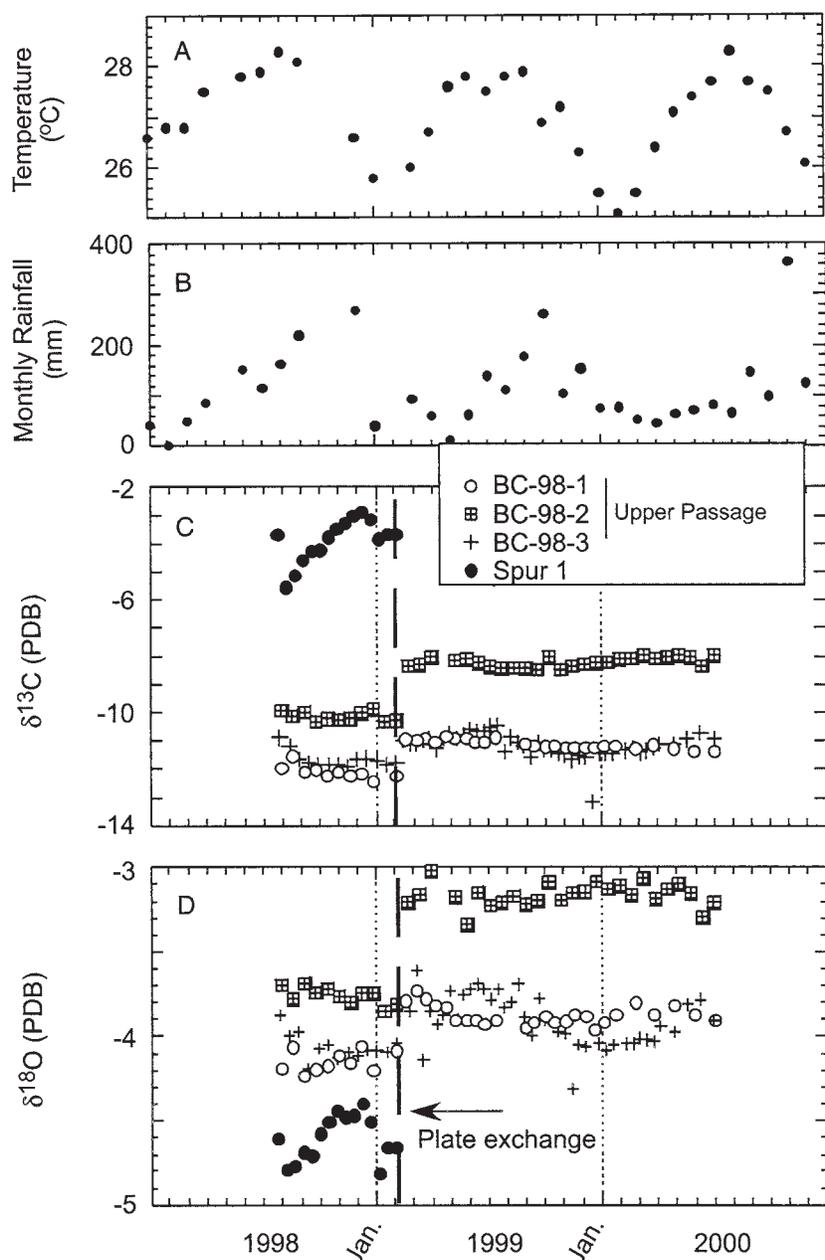


Fig. 4. (A) Monthly rainfall totals; (B) average monthly temperature collected from the Grantely Adams weather station, Barbados, and distributed by the National Climatic Data Center; (C) $\delta^{13}\text{C}$ vs. time; and (D) $\delta^{18}\text{O}$ values vs. time for the calcite grown on glass plates and sampled at high-resolution.

value of the HCO_3^- (aq) reservoir will follow Rayleigh-type distillation ^{13}C enrichment as CO_2 degassing continues (Michaelis et al., 1985; Dulinski and Rozanski, 1990). We use the term Rayleigh distillation to refer to the process by which the O and C isotopic composition of the reactant is modified by the formation of products having a different isotopic composition. These products do not react with the remaining reactant reservoir after formation. This mechanism is portrayed as mechanism 2A (Fig. 5).

The effects of Rayleigh distillation on the $\delta^{13}\text{C}$ value of the HCO_3^- (aq) reservoir can be modeled by:

$$(\delta + 1000)/(\delta_0 + 1000) = f^{(\alpha_p - 1)} \quad (6)$$

where δ is the C isotopic composition of HCO_3^- (aq), δ_0 is the initial C isotopic composition of HCO_3^- (aq), f is the fraction of HCO_3^- (aq) remaining and α_{p-r} is the equilibrium fractionation factor between the bulk product and the HCO_3^- (aq) reactant. Because the C in HCO_3^- (aq) is evenly divided between CaCO_3 and CO_2 (g) during calcite precipitation, two fractionation factors must be considered. We define a fractionation factor between HCO_3^- (aq) and a bulk product such that $\alpha_{(\text{bulk product}-\text{HCO}_3^-)}$ is $1/2(\alpha_{\text{CO}_2-\text{HCO}_3^-}) + 1/2(\alpha_{\text{CaCO}_3-\text{HCO}_3^-})$.

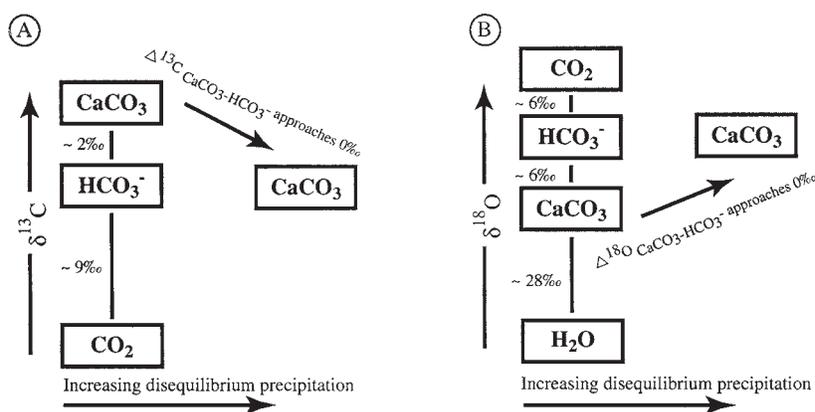
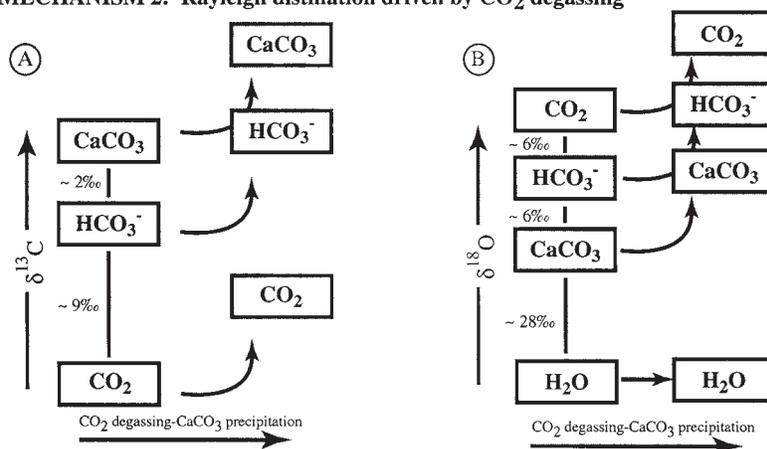
MECHANISM 1: Kinetically driven change in $\Delta_{\text{CaCO}_3\text{-HCO}_3^-}$ **MECHANISM 2: Rayleigh distillation driven by CO_2 degassing**

Fig. 5. Graphical representation of the mechanisms discussed in text to account for ^{13}C enrichments and depletions and ^{18}O enrichments, relative to predicted equilibrium values, observed in modern speleothem calcite collected on Barbados. Equilibrium fractionation values outlined in Table 2 and 3 are represented here by ‰ values between phases. In instances where no fractionation factor is listed in the tables (in the case of the O isotope system the fractionation between CaCO_3 and HCO_3^-), the fractionation factor is calculated by the difference of the other fractionation factors.

This can be used to model the evolution of the HCO_3^- (aq) reservoir (Fig. 6).

Other authors have stated that because generally less than 10% of the DIC is lost to degassing, there is a negligible change to the isotopic composition of the HCO_3^- (aq) reservoir due to the loss of isotopically light CO_2 (Hendy, 1971; Clark and Lauriol, 1992). The observations in this study, where calcite was sampled close to the site of drip impact (analogous to sampling speleothems along their growth axis), support this conclusion. If any ^{13}C enrichment was due to CO_2 degassing, the effect was small (Fig. 2). Spur 1 shows maximum ^{13}C enrichments of 0.8‰ that could result from the reaction of 24% of the HCO_3^- reservoir (Fig. 6). This is in contrast with other studies that predict large ^{13}C enrichments, $\sim 10\text{‰}$, with relatively small change in the HCO_3^- (aq) reservoir (Dulinski and Rozanski, 1990).

In summary, our results suggest that two kinetic isotope processes could cause departures from predicted equilibrium values in the $\delta^{13}\text{C}$ value of modern calcite. First, rapid calcite precipitation rates lower the $\delta^{13}\text{C}$ value of calcite by lowering

the C isotope fractionation between calcite and DIC from equilibrium values, $\Delta^{13}\text{C}_{\text{CaCO}_3\text{-HCO}_3^-} = 1.96\text{‰}$, to non-equilibrium values, $\Delta^{13}\text{C}_{\text{CaCO}_3\text{-HCO}_3^-}$ approaching 0, (Clark and Lauriol, 1992). Second, rapid CO_2 degassing could cause an increase in the $\delta^{13}\text{C}$ value of the modern speleothems through Rayleigh distillation of the HCO_3^- (aq) reservoir.

6.4. Controls on the $\delta^{18}\text{O}$ Composition of Modern Speleothems

There are distinct differences between the behavior of the O isotopic system and C isotopic system in modern speleothems in Harrison's Cave. The O isotopic compositions of modern speleothems are all higher than that predicted by the oxygen isotope equilibrium fractionation factor, and no ^{18}O depletions are observed. In addition, there are two important differences in the general fractionation behavior between the C and O isotopic systems: (1) The O isotopic composition of HCO_3^- (aq) is buffered by the O reservoir within H_2O and the moderately fast rate of CO_2 hydration/hydroxylation and dissociation (Mills

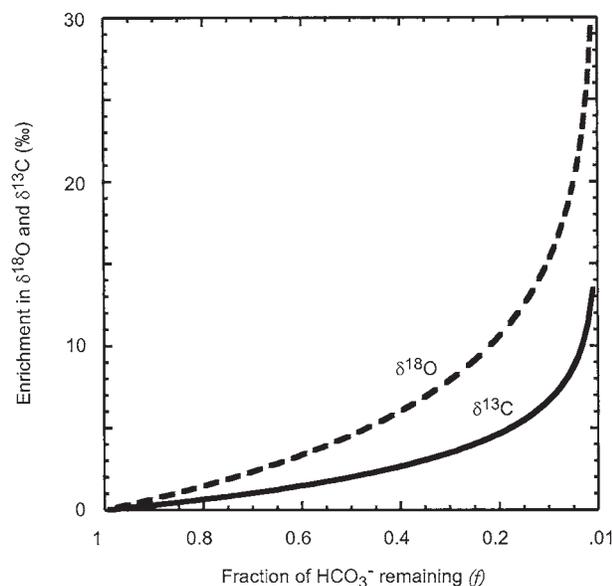


Fig. 6. Rayleigh distillation model of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of HCO_3^- (aq) during CO_2 degassing and CaCO_3 precipitation. The $\delta^{18}\text{O}$ curve does not consider CO_2 hydration and hydroxylation reactions, which would buffer the $\delta^{18}\text{O}$ composition of the HCO_3^- (aq) reservoir through isotopic exchange with the very large O reservoir held in H_2O . Thus, this is an end-member condition and the ^{18}O enrichments predicted by the model are not likely to be observed in natural systems. If Rayleigh distillation has any effect of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite, it will manifest itself as a ^{13}C and ^{18}O enrichment.

and Urey, 1940) and (2) The O isotopic composition of the HCO_3^- (aq) reservoir may not be as precisely predicted as the C isotopic composition of HCO_3^- (aq). Despite these differences, the behavior of the C isotopic system is helpful in interpreting the behavior of the O isotopic compositions of the modern calcite because the mechanisms driving calcite precipitation must affect both isotopic systems.

6.5. Control on $\delta^{18}\text{O}$ Values Higher Than Equilibrium Values

Kinetic isotope effects may be controlling the $\delta^{18}\text{O}$ values of modern calcite in the same way that $\delta^{13}\text{C}$ values are affected by the path outlined in mechanism 1A (Fig. 5). As calcite precipitation rates increase, the system departs from O isotopic equilibrium, and the $\Delta^{18}\text{O}_{\text{CaCO}_3-\text{HCO}_3^-}$ value changes from a poorly constrained equilibrium value of $\sim -6\text{‰}$ (Usdowski and Hoefs, 1993) to a disequilibrium value ($\Delta^{18}\text{O}_{\text{CaCO}_3-\text{HCO}_3^-}$ approaching 0). The $\delta^{18}\text{O}$ value of the resulting calcite will approach the $\delta^{18}\text{O}$ value of the HCO_3^- (aq) reservoir, and the modern calcite will show an ^{18}O enrichment (Clark and Lauriol, 1992). This mechanism is akin to that causing the small ^{13}C depletions observed in the same specimens (Fig. 5, mechanism 1B).

If the $\Delta^{18}\text{O}_{\text{CaCO}_3-\text{HCO}_3^-}$ value approaches 0, then the modern calcite in Harrison's Cave would show an ^{18}O enrichment of up to 6‰ relative to equilibrium values. The observed ^{18}O enrichments are 0.2‰ to 2.3‰ (Fig. 3). This suggests that either (1) $\Delta^{18}\text{O}_{\text{CaCO}_3-\text{HCO}_3^-}$ never reaches 0 during calcite precipitation and, thus, the kinetic isotope effects of direct HCO_3^- (aq)

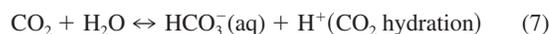
assimilation into calcite are modulated from the maximum possible effect, or (2) the O isotopic fractionation factor between HCO_3^- - H_2O is less than the 6‰ reported by Usdowski and Hoefs (1993). Clark and Lauriol (1992) report kinetically controlled ^{18}O enrichments in cryogenic calcites that average $5.5 \pm 0.5\text{‰}$. This is consistent with the $\Delta^{18}\text{O}_{\text{CaCO}_3-\text{HCO}_3^-}$ value approaching 0 and the HCO_3^- - H_2O O isotopic fractionation factors reported by Usdowski and Hoefs (1993).

6.6. Uncertainties in Bicarbonate Oxygen Isotope Fractionation Factors

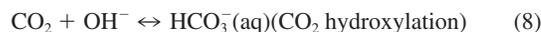
The C isotopic fractionation factors between the inorganic carbon species of interest in speleothem formation are well known; however, the O isotopic fractionation factors for DIC species are not precisely known because of difficulty in the analytical determination of their isotopic compositions. The C isotopic composition of HCO_3^- (aq) is analytically determined by quantitative conversion of the DIC (dominantly HCO_3^-) to CO_2 (g), measurement of the $\delta^{13}\text{C}$ value of this CO_2 , followed by a pH dependent correction for other minor DIC species. Because no other inorganic reservoir of dissolved carbon exists, there is no possibility of isotopic exchange reactions altering the C isotopic composition of this CO_2 . This method, however, cannot be used to determine the O isotopic composition of the HCO_3^- (aq), because as HCO_3^- (aq) is converted to CO_2 , it will continue to undergo oxygen isotope exchange reactions with H_2O via CO_2 hydration and hydroxylation (Eqn. 7 and Eqn. 8) in the reaction vessel. The O isotopic composition of the collected CO_2 will likely lie somewhere between the $\delta^{18}\text{O}$ value of the HCO_3^- (aq) and the $\delta^{18}\text{O}$ value of CO_2 in isotopic equilibrium with the H_2O . Because the O isotopic fractionation factors between HCO_3^- (aq)- CaCO_3 and HCO_3^- (aq)- CO_2 (g) cannot be precisely determined, the effect of CO_2 degassing and CaCO_3 precipitation on the O isotopic composition of HCO_3^- (aq) is impossible to determine by direct measurement and, thus, theoretical models must be used (Usdowski and Hoefs, 1993).

6.7. Potential Effect of Rayleigh Distillation on $\delta^{18}\text{O}$ Compositions

The effect of CO_2 degassing on the $\delta^{18}\text{O}$ value of calcite may be assessed using the same pathway outlined in mechanism 2A for the carbon isotopic system (see mechanism 2B, Fig. 5). The O isotopic composition of HCO_3^- (aq) is buffered by two isotopic exchange reactions with H_2O , CO_2 hydration and CO_2 hydroxylation and their corresponding reverse reactions:



and



In comparison to the rates of the CO_2 hydration and hydroxylation reactions, the protonation of CO_3^{2-} and deprotonation of HCO_3^- (aq) are nearly instantaneous (Mills and Urey, 1940), and so are not considered further. If CO_2 degassing and calcite precipitation proceed faster than the CO_2 hydration and hy-

droxylation reactions, then the HCO_3^- (aq) may deviate from O isotopic equilibrium with the water. In this case, the $\delta^{18}\text{O}$ value of the CaCO_3 may reflect the instantaneous $\delta^{18}\text{O}$ value of the HCO_3^- (aq), rather than that of the H_2O . The effect of CO_2 degassing will range from no effect when O isotope exchange reactions keep up with calcite precipitation reactions and the HCO_3^- (aq) remains in O isotopic equilibrium with H_2O , to a system governed by a Rayleigh distillation process, where the $\delta^{18}\text{O}$ value of CaCO_3 reflects the evolution of the $\delta^{18}\text{O}$ value of the bicarbonate reservoir.

We attempt to model the oxygen isotope effects of CO_2 degassing using a Rayleigh distillation approach with the following assumptions: (1) there is no oxygen isotope exchange between the DIC and the water, (2) the $\Delta^{18}\text{O}_{\text{CO}_2-\text{HCO}_3^-}$ is $\sim 6\text{‰}$, and (3) the fractionation factor between bulk products and HCO_3^- (reactant) is $2/6(\alpha_{\text{CO}_2-\text{HCO}_3^-}) + 3/6(\alpha_{\text{CaCO}_3-\text{HCO}_3^-}) + 1/6(\alpha_{\text{H}_2\text{O}-\text{HCO}_3^-})$ (in other words, in proportion to the amount of oxygen in each product). The result of this model is given in Figure 6 and suggests that CO_2 degassing could cause an ^{18}O enrichment in the resulting calcite with respect to equilibrium with water. This result, however, is only an end-member calculation because it neglects CO_2 hydration and hydroxylation reactions which will buffer the isotopic composition of the HCO_3^- (aq) reservoir and reduce the magnitude of the isotope effects of CO_2 degassing. Nonetheless, this calculation should provide the correct sign to the isotope effect of CO_2 degassing on speleothem calcite.

It may be impossible to determine the relative contributions to calcite $\delta^{18}\text{O}$ values from CO_2 degassing (Mechanism 2B, Fig. 6) vs. changes in the $\Delta^{18}\text{O}_{\text{CaCO}_3-\text{HCO}_3^-}$ due to rapid precipitation of calcite (Mechanism 1B, Fig. 6). However, both of these mechanisms of kinetic isotope fractionation should cause speleothem calcite to be enriched in ^{18}O with respect to isotopic equilibrium with drip water, and both mechanisms may be active given their apparent effects on the carbon isotope deviations from isotopic equilibrium in the same speleothem calcite samples.

6.8. High-Resolution Variations in Plate Calcite

The glass plate calcite appears to record temporal variations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values which directly, or indirectly, reflect seasonal changes in air temperature or rainfall on Barbados. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of glass plate calcite from Spur 1 correspond to changes in rainfall. This is significant because the identification of seasonally controlled changes in speleothem chemistry has the potential to aid in chronologic control and provide insights into interannual climatic variability in speleothem studies (Shopov et al., 1994; Roberts et al., 1998). In Harrison's Cave, several variables may influence the isotopic composition of the calcite. We evaluate here the potential control of seasonal changes in temperature and rainfall on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition of glass plate calcite in Harrison's Cave.

Over the time interval during which the Spur 1 glass plate collected calcite, the mean monthly air temperature dropped from approximately 28.5°C to 25.5°C (Fig. 4A). The isotopic shifts seen in $\delta^{13}\text{C}$, approximately 5‰ , are much larger than those seen in $\delta^{18}\text{O}$, approximately 0.4‰ . Although changes in temperature will affect the fractionation factors of the C spe-

cies, the effect will be much smaller ($<0.01\text{‰}/^\circ\text{C}$) than that seen in O isotopes ($0.2\text{‰}/^\circ\text{C}$). Temperature alone cannot be responsible for the magnitude of the C-isotopic shift observed. Thus, changes in monthly mean temperature are likely not the cause of the observed isotopic shifts.

The glass plates were placed before and collected after the wet season. Because the drip rate at the Spur 1 site is sensitive to changes in precipitation, it is likely that the drip rate at the site mirrors the monthly precipitation curve. The temporal variations in Spur 1 glass plate calcite O and C isotopic compositions are synchronous, although they differ in magnitude with peak isotope ratios coinciding with time of peak precipitation. Kinetic and equilibrium isotope effects previously discussed may explain the synchronous changes in calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. If increasing drip rates in Spur 1 caused an increase in calcite precipitation rates and/or an increase in the percentage of HCO_3^- (aq) incorporated into glass plate calcite, the isotopic composition of the calcite may be affected in the following ways: (1) As calcite precipitation rates increase, the $\delta^{13}\text{C}$ values of the calcite will become isotopically heavier as the HCO_3^- (aq) reservoir is enriched in ^{13}C by increased Rayleigh distillation; (2) At the same time, $\delta^{18}\text{O}$ values of calcite will become isotopically heavier as increased precipitation rates lower the fractionation between HCO_3^- (aq) and CaCO_3 . Rayleigh distillation may or may not affect the O-isotopic system because of reasons outlined in section 6.7. Thus, the observed changes in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the glass plate calcite may be caused by both kinetic and equilibrium isotope effects.

Calcite grown on the glass plates from the Upper Passage shows similar temporal isotopic variations seen in the Spur 1 glass plate calcite, but the isotopic shifts are smaller and lag behind the shifts seen in Spur 1 the glass plate calcite. Because the two sites show the same general trend in both isotopic systems, it is likely that the same mechanisms are responsible for the isotopic shifts seen in the Upper Passage and Spur 1. Differences in the magnitude and timing of the shifts are likely due to differences in hydrologic conditions at the drip sites. The drips feeding water to the Upper Passage drip sites are generally slower and do not show the variability in drip rates observed in Spur 1 (Table 1). The more consistent hydrologic conditions found in the Upper Passage drip sites result in lower O and C isotopic variability. There is likely more mixing of slow and fast flow path water feeding the Upper Passage drip sites, resulting in a smoothing of the climate signal and an averaging $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

7. CONCLUSIONS

The precipitation of speleothem calcite in O and C isotopic equilibrium with its corresponding drip water can not be assumed. This fact was known early in speleothem research, resulting in tests to identify equilibrium precipitation (Hendy, 1971). This study represents a contribution to speleothem-based climate studies by not only outlining new definitive tests for O and C isotopic equilibrium in modern speleothems, but also by determining the magnitude and direction of offsets from equilibrium. These offsets are used to propose mechanisms responsible for the nonequilibrium isotope effects observed. Mechanism 1 results in changes in the fractionation between

HCO_3^- (aq) and CaCO_3 from equilibrium towards lower values resulting in ^{13}C depletions and ^{18}O enrichments in speleothem calcite. Mechanism 2 results in both ^{13}C and ^{18}O enrichments in speleothem calcite caused by Rayleigh distillation in the HCO_3^- (aq) reservoir and the calcite precipitated from it.

This study has implications for paleoclimate studies that use ancient speleothems, deposited in the past when the water from which the speleothem precipitated cannot be directly measured. Firstly, this study demonstrates that even in areas that one may expect speleothems to be precipitated in O and C isotopic equilibrium, significant nonequilibrium isotope effects may be operating. If C and O isotopic equilibrium in modern speleothems from a cave environment can be demonstrated, then the stable isotopic composition of ancient speleothems, from that same environment, may be interpreted with greater confidence. In addition, the study of glass plate calcite is nondestructive, such that a great number of speleothem sites can be studied with no negative effect on the cave, such as breakage or drilling. Before speleothem collection, the glass plate methods outlined in this paper will allow the assessment of the extent to which calcite achieves O and C isotopic equilibrium in the modern system. This will allow the identification of speleothems best suited for paleoclimatic studies. Aside from the larger issues of data quality, this methodology is a significant contribution to cave conservation (Deines et al., 1974, Mickler, Mickler et al).

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