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# A GEOCHEMICAL SURVEY OF THE NATURAL WATERS OF BELIZE, CENTRAL AMERICA

by

Anthony D. Marfia

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Geosciences

Western Michigan University Kalamazoo, Michigan April 2003 Copyright by Anthony D. Marfia 2003

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Finally, I am grateful to the many Belizeans who provided me with transportation, food, shelter and great conversation.

Anthony D. Marfia

# A GEOCHEMICAL SURVEY OF THE NATURAL WATERS OF BELIZE, CENTRAL AMERICA

## Anthony D. Marfia, M.S.

## Western Michigan University, 2003

A geochemical survey of the natural waters in Belize, Central America was carried out to compliment routine water quality analysis and to identify processes affecting water quality. The objective of this research was to provide a geochemical assessment of natural waters throughout Belize by examining select major ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>), and stable isotopes of carbon (<sup>13</sup>C), oxygen (<sup>18</sup>O) and hydrogen (<sup>2</sup>H).

The dominant geology relevant to this investigation comprises a varied landscape of carbonates and clastic sediments in a subtropical rainforest/savannah climate. Stable oxygen and hydrogen isotope ratios shows high d-excess (10 to 40.8 %), suggesting a significant secondary continental vapor flux mixing with incoming vapor from the sea. Model calculations indicate that moisture derived from continental evaporation contributes between 9-16% during the July-August atmospheric vapor load in the region, while evaporation contributes 20-35% towards total evapotranspiration.  $\delta^{13}$ C values between -7.4 and -17.4% for the dissolved inorganic carbon (DIC) indicates both open and closed system DIC evolution.  $\delta^{13}$ C values in conjunction with concurrent magnesium and sulfate dissolution indicates dedolomitization occurring in several samples.

## TABLE OF CONTENTS

ACKNOWLEDGMENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
CHAPTER	
I. INTRODUCTION	1
Purpose of the Study	1
Description of the Study Site	2
II. METHODOLOGY	5
Collection and Analysis of Ground and Surface Samples	5
Sampling Episodes	5
Field Sampling	5
Stable Isotope Analysis	6
Ion Analysis	6
III. RESULTS AND DISCUSSION	7
Chemical and Isotopic Analyses	7
Stable Oxygen and Hydrogen Isotopes	7
The $\delta D$ - $\delta^{18}O$ relationship and d – excess	7
Analysis of Stable Carbon Isotopes of Dissolved Inorganic Carbon and Select Ions	14
Dissolved Inorganic Carbon	14
Gypsum Dissolution	15

# Table of Contents—continued

Dedolomitization	17
CONCLUSIONS	20
APPENDIX	
Additional Laboratory Analyses and Sampling Data	21
BIBLIOGRAPHY	26

# LIST OF TABLES

1.	Chemical and Isotopic Data of Groundwater (GW) and Surface Water (SW) from Belize, Central America	8
2.	Percentage of evaporated mainland derived vapor estimated to be contributing to the atmosphere during July-August in Belize	13

# LIST OF FIGURES

1.	Map of Belize, Central America, showing sampling locations.	3
2.	Crossplot of $\delta D$ -vs- $\delta^{18}O$ and regression line for surface and groundwaters sampled from Belize, Central America.	9
3.	Crossplot of <i>d-excess</i> vs. $\delta^{18}$ O showing that most of the water samples from Belize, Central America plot above 10, the <i>d-excess</i> value for the MWL.	9
4.	Crossplot of $\delta^{13}C_{DIC}$ -vs- dissolved inorganic carbon, for surface and groundwater from Belize, Central America.	16
5.	Crossplot of Ca <sup>2+</sup> -vs- SO <sub>4</sub> <sup>2-</sup> for surface and groundwater samples from Belize, Central America. The regression line represents samples within 25% of the SO <sub>4</sub> <sup>2-</sup> / Ca <sup>2+</sup> molar ratio.	16
6.	Crossplot of $\delta^{13}C_{DIC}$ - vs - Mg <sup>2+</sup> . The regression line excludes the outlier (GW3) enclosed by the circle (see text).	18
7.	Crossplot of $SO_4^{2^-}$ -vs- $\delta^{13}C_{DIC}$ for surface and groundwater samples identified in figure 5.	18

#### CHAPTER 1

#### **INTRODUCTION**

## Purpose of the Study

The isotopic compositions of oxygen and hydrogen in water, modified by meteoric processes, are useful tracers for determining groundwater origin. Carbon isotope ratios of dissolved inorganic carbon traces multiple carbon sources, and enables us to identify biogeochemical processes in the hydrosphere (Clark and Fritz, 1997).

Reports indicate that 69% of Belize's rural population has access to safe drinking water (UNICEF, 1997). Contamination of aquifers is known to exist in several locations through increasing agrichemical use and the dissolution of sulfaterich minerals (Day, 1996; Alacron *et al.*, 1998). The expansion and improvement of countrywide water quality monitoring is national policy for Belize (UNICEF, 1997).

The purpose of this study is to understand hydrogeologic process governing water quality in Belize, Central America. We report the stable isotope ratios of hydrogen, oxygen and carbon and select ion (Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>) concentrations of ground and surface waters in Belize. The analyses presented are essential in understanding important atmospheric and geochemical processes affecting water quality. Being the first of its kind from this region, this research adds significant knowledge regarding water resources management.

## Description of the Study Site

Belize lies in the subtropical geographical belt at 15 degrees 53' to 18 degrees 30' north latitude (figure 1). Rainfall in Belize increases with elevation and more southerly latitude and is largely affected by the topographic bulk of the Maya Mountains. Orographic lifting of the Easterly Trade Winds, thermal convection and cyclones result in rainfall totals ranging from 130 cm./yr in the north and 450 cm/yr. in the south (Miller 1996, Heyman and Kjerfve, 1997). The wettest months of the year are June – September while the driest months are February - April.

The escarpment bounded Maya Mountains are encircled by lower units of mostly Cretaceous carbonate sedimentary rocks with some well-developed karst (Miller, 1996). North of the mountains, 200-300m limestone hills terminate into primarily Paleocene-Eocene carbonate formations extending northward as rolling plains. Insoluble clays, carbonates, marls and poorly consolidated sands provide the most recent sedimentation of the typically flat north (Miller, 1996). Highly permeable limestone hills and ridges dominate the southern slopes of the Mayas.

Uplifting and NE-SW faulting of the Yucatan platform defines the N-NE course for surface water drainage north of the mountains. Calcareous sediments in the north have shown high permeabilities where tested (Hartshorn, 1984). Hydraulic conductivities typical of well-developed karst terrains are typical in many areas. Streams draining the east and southeast slopes of the Mayas form well-developed branching patterns with relatively straight, steep courses in the mountains. Slowed surface drainage through clastic sediments is typical upon nearing coastal zones.

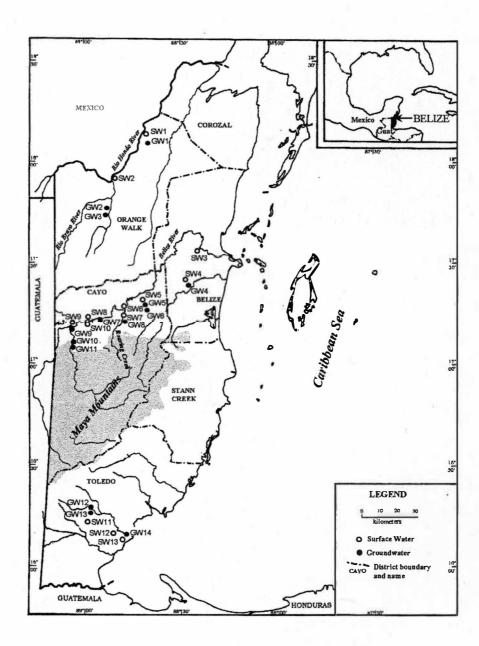


Figure 1. Map of Belize, Central America, showing sampling locations

Agricultural contamination of the northern karst aquifers is an increasing concern in the Orange Walk district (Day, 1996). Hand pumps in some rural villages in the karst areas are reported to yield pathogens responsible for severe illness (Panton, pers. comm.). Sulfate concentrations as high as 450 mg/L have been detected in wells in S. Antonio, Orange Walk (Hartshorn, 1984).

#### CHAPTER 2

#### **METHODOLOGY**

Collection and Analysis of Ground and Surface Samples

## Sampling Episodes

In January 1998, an initial survey of ground and surface waters from various locations throughout Belize was conducted. Analysis of the stable isotopes of dissolved inorganic carbon ( $^{13}C_{DIC}$ ), oxygen ( $^{18}O$ ) and hydrogen ( $^{2}H$ ) signaled geochemical processes requiring further investigation. A reconnaissance survey during July – August 1998, whose data is the focus of this discussion, was conducted with analysis of the above isotopes and augmented through examining select major ions ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$ ).

## Field Sampling

13 surface and 14 groundwater samples were collected from locations throughout Belize (figure 1). Surface samples were collected from streams and rivers. Groundwater samples were collected from public supply wells after purging a minimum of three estimated casing volumes. Samples were filtered through disposable, in-line 0.45 μm filters and cooled until laboratory analysis. DIC samples were prepared in the field and analyzed using a gas evolution technique (Atekwana and Krishnamurthy, 1997).

## Stable Isotope Analysis

Oxygen isotope ratios were measured via the carbon dioxide equilibration technique of Epstein and Mayeda (1953) and the hydrogen isotope measurements were made via the uranium reduction method of Freidman (1953). Isotope measurements were made at the Stable Isotope Laboratory at Western Michigan University. Isotopic ratios were measured using a Micromass Optima-isotope ratio mass-spectrometer and are expressed in  $\delta\%$  where (for  $^{13}$ C):

 $\delta^{13}C_{Sample}$  =((  $R_{Sample}$  -  $R_{Standard}$ ) /  $R_{Standard}$ ) x 1000 where  $R = ^{13}C/^{12}C$   $\delta^{18}O$  and  $\delta D$  values are reported with respect to VSMOW and  $\delta^{13}C$  of DIC values are reported with respect to PDB. DIC concentrations are expressed as "mg/C/L".  $\delta^{13}C_{DIC}$  and DIC concentrations have an analytical precision of 0.1‰ and 1%, respectively. The precision of the  $\delta$  values for oxygen and hydrogen are 0.1‰ and 1‰, respectively.

### Ion Analysis

Ion analysis was conducted at the Michigan State University – Kellogg
Biological Station Water Quality laboratory. Calcium and magnesium concentrations
were determined via atomic adsorption spectrophotometery, while sulfate was
analyzed by ion chromatography.

#### **CHAPTER 3**

## **RESULTS AND DISCUSSION**

## Chemical and Isotopic Analyses

## Stable Oxygen and Hydrogen Isotopes

Mean  $\delta D - \delta^{18}O$  values are -12.4‰ and -3.9 ‰ for surface water and -13.8 ‰ and -4.4‰ for groundwater samples (table 1). The  $\delta D - \delta^{18}O$  relationship for all surface and groundwater samples is shown in figure 2. Similar isotopic values between surface and groundwaters is not surprising due to high hydraulic conductivities in karst regions.

## The $\delta D$ - $\delta^{18}O$ relationship and d – excess

The  $\delta D$  -  $\delta^{18}O$  relationship for all samples is defined by the following least squares regression equation:

$$\delta D = 7.5 \, \delta^{18} O + 17$$

A slope of 7.5 is close to the slope of the Meteoric Water Line (MWL), given by  $\delta D = 8\delta^{18}O + 10$  (Craig, 1961). However, the intercept of 17 is higher than that of the MWL. The intercept is often referred to as the deuterium-excess (*d-excess*), defined as  $d = \delta D - 8\delta^{18}O$  (Dansgaard, 1964). The *d-excess* is a useful proxy for identifying secondary processes influencing the atmospheric vapor content in the evaporation-

Table 1.

Chemical and Isotopic Data of Groundwater (GW) and Surface Water (SW) from Belize, Central America. Ions and DIC concentrations in mg/L

Sample	Description	SO <sub>4</sub> <sup>2</sup> -	Ca <sup>2+</sup>	Mg <sup>2+</sup>	δ <sup>18</sup> Ο‰	δD‰	δ <sup>13</sup> C‰	DIC as Carbon
SW1	S. Antonio, O.W Rio Hondo Rvr.	1114	423.0	70.1	-3.4	-16	-8.3	42.8
		818	358.1	56.0	-3.4	-10 -1	-11.8	48.2
SW2	Rio Bravo / Rio Hondo River confl.	244.5	137.7	28.8	-3.3 -4.2	NA	-11.8	23.9
SW3	Ladyville - Belize Rvr.		5.8	2.2	-4.2 -4.8	-19	-13.2 NA	5.4
SW4	Belize Zoo - pond	6 5.6	100.7		-4.8 -3.9		-13.9	51.5
SW5	Cotton Tree - Rock Dondo Creek			3.1		-14		
SW6	Belize Rvr at West. & Humm. hwys.	16.8	43.9	7.6	-4.0	-18	-16.3	24.4
SW7	Roaring Crk. at West. & Humm. hwys.	4.5	73.2	9.1	-3.9	-12	-14.0	44.2
SW8	Belize River at Blackman	13.1	51.0	10.0	-5.2	-24	-14.5	25.9
SW9	S. Ignacio, Cayo - Belize Rvr.	3.7	11.6	2.9	-4.8	-20	NA	7.7
SW10	Blackman - open spring	3.4	122.0	17.2	-4.3	2	-14.1	78.4
SW11	S. Antonio, Toledo - stream	1.7	72.7	6.8	-4.1	-19	-15.9	36.1
SW12	Punta Gorda - Joe Taylor Creek	155.1	217.1	10.6	-3.6	-15	-17.4	15.4
SW13	Punta Gorda - stream	3.2	56.6	9.8	-3.3	-11	NA	28.7
GWI	S. Antonio, Orange Walk - supply well	1632	593.2	89.8	-5.0	-30	-7.4	76.4
GW2	Mayan open pit well	21.8	61.8	10.0	-4.7	-24	-17.1	24.5
GW3	Prog. for Belize - supply well (470')	47.9	172.4	53.2	-5.5	-23	-15.9	112.9
GW4	Sanctuary - supply well (100')	1.7	51.7	2.8	-4.4	-11	NA	13.1
GW5	Cotton Tree - hand pump well	3.5	162.3	8.4	-3.7	-6	-13.7	88.7
GW6	Cotton Tree - supply well	20.9	142.1	11.9	-3.9	-12	-14.4	80.3
GW7	Teakettle - supply well	4.4	109.7	10.0	-4.1	8	-15.0	59.0
GW8	Belmopan - supply well	8.8	117.5	12.2	-4.3	-13	-12.5	71.6
GW9	S. Ignacio, Cayo - supply well	14.2	43.2	4.5	-4.7	-22	-16.5	22.2
GW10	S. Antonio, Cayo - hand pump well	57.6	186.9	18.5	-3.7	-15	-11.8	79.3
GW11	S. Antonio, Cayo - supply well	520.4	287.6	7.8	-4.3	-19	-13.8	71.3
GW12	S. Antonio, Toledo - hand pump well	10.3	14.6	2.2	-4.3	-2	-14.3	82.4
GW13	S. Antonio, Toledo - supply well (450')	35.9	33.6	14.4	-4.6	-15	-10.9	75.8
GW14	Punta Gorda - supply well (80')	43.1	123.1	11.9	-4.4	-9	-14.6	53.8

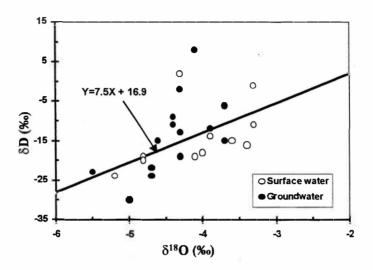


Figure 2. Crossplot of  $\delta D$  -vs-  $\delta^{18}O$  and regression line for surface and groundwaters sampled from Belize, Central America.

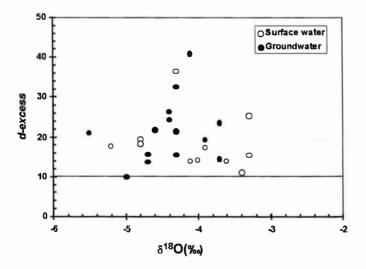


Figure 3. Crossplot of *d-excess* vs.  $\delta^{18}$ O showing that most of the water samples from Belize, Central America plot above 10, the *d-excess* value for the MWL.

condensation cycle in nature (Craig, 1961; Merlivat and Jouzel, 1979; Gat et al., 1994; Machavaram and Krishnamurthy, 1995). For all cases not influenced by secondary processes, the *d-excess* approximates the y-intercept of the MWL, which is 10. It is known that *d-excess* contributions from secondary processes such as open surface evaporation from large water bodies can alter the *d-excess* of the original vapor mass (Machavaram and Krishnamurthy, 1995).

The *d-excess* -  $\delta^{18}$ O relationship for surface and groundwater samples is shown in figure 3. The *d-excess* values ranging from 10 to 40.8 % (Table 1) with averages of 18.0 and 21.4% for surface and groundwater samples, respectively, suggest a substantial secondary moisture flux into the atmosphere. A significant admixture of a secondary moisture flux with atmospheric moisture is probably occurring through both inland water evaporation and plant respiration. Flooded lowlands and lagoons in the swampy north, tropical landscapes covering most of the south and coastal mangrove swamps all provide optimal conditions for this process to occur. Monthly climate data from Belize report evapotranspiration rates of approximately 200 mm/month during July-August (Walker, 1973). This is roughly half of the average rainfall totals (440mm./mo) over the same period.

Transpiration has no effect on the *d-excess*, since it is believed to return moisture to the atmosphere isotopically identical to the local precipitation left behind (Gat and Matusi, 1991). Here, we estimate the role of evaporation by using the high *d-excess* in water samples. An evaluation of *d-excess* in precipitation via evaporation requires that we determine the isotopic composition of the evaporated flux. The

Craig-Gordon evaporation model (Craig and Gordon, 1965) is useful in calculating the isotopic composition of the evaporated moisture component. An approximation of this equation, which calculates the isotopic signature of the evaporated flux ( $\delta_E$ ) for either the hydrogen or oxygen isotopes, is:

$$\delta_{\rm E} = (\delta_{\rm W} - h \delta_{\rm A} - \epsilon)/(1-h)$$

 $\delta_W$  and  $\delta_A$  are the isotopic compositions of surface water from which evaporation takes place, and the isotopic composition of incoming atmospheric moisture, respectively. The relative humidity, h, is normalized to the saturated vapor pressure at the temperature of the surface water. Equilibrium and kinetic fractionation factors are defined by  $\epsilon = \epsilon_{eq} + \epsilon_k$ , both expressed in permil. The equilibrium fractionation factor ( $\epsilon_{eq}$ ) is expressed as  $(1 - \alpha) \times 10^3$ , where  $\alpha$  is the water-vapor fractionation factor @ 25°C. The kinetic fractionation factor ( $\epsilon_k$ ) is given as  $(1-h)\theta$  C<sub>k</sub> where  $\theta$  is a weighting factor and C<sub>k</sub> is a model dependant kinetic constant (Majoube, 1971).

 $\delta_{W}$ , the isotopic ratio of surface water prior to evaporation has a  $\delta^{18}O = -5\%$  and a  $\delta D = -32\%$ , based on IAEA World Meteorological Precipitation monitoring data (Rozanski *et al.*, 1993; IAEA, 2001). The isotopic ratio of incoming vapor ( $\delta_{A}$ ) was calculated from the oxygen isotope values of seawater:  $\delta^{18}O = 0.5\%$  (Teal *et al.*, 2000) and a *d-excess* of 8 for July precipitation, adopted from IAEA contour maps, resulting in  $\delta D$  of -8% (IAEA, 2001). Kinetic and equilibrium fractionation factors were calculated at 25°C using the above equations to define  $\delta_{A}$ = -11.8 % for the oxygen and -86.6% for the hydrogen isotopic compositions of incoming vapor.

The equilibrium fractionation factor in the Craig-Gordon model ( $\varepsilon_{eq}$ ) was obtained for a temperature of 25°C: 9.3 ‰ for  $\delta^{18}O$  and 76‰ for  $\delta D$ . The kinetic fractionation factor was calculated to be 3 and 2.6 ‰, respectively, for  $\delta^{18}O$  and  $\delta D$ , assuming the following:  $\theta = 1$ , h = .80 and  $C_k = 15$ ‰ (oxygen) and 13‰ (hydrogen). (Gat *et al.*, 1994).

Our model proposes the following: incoming vapors from the Caribbean Sea are mixed with an evaporated moisture flux from the Belize mainland, resulting in high *d-excess* in precipitation. Two different humidity values of 75 and 85% were used in these calculations. The following mass balance equation was used to calculate the percent contribution of mainland evaporation to total atmospheric vapor:

$$E\% = 1 - [(d_b - d_e) / (d_x - d_e)] \times 100$$

Where:

E% = the contribution of mainland evaporation

 $d_b = d$ -excess value for Belize precipitation

 $d_e = d$ -excess value for mainland evaporation flux

 $d_x = d$ -excess value for incoming vapor

The results for the two humidity values are given in table 2. The *d-excess* value of 20.4‰ for Belize precipitation ( $\delta^{18}O = -4.2\%$  and  $\delta D = -13\%$ ) was taken from a central sampling location near Belmopan (Figure 1). Our study shows that evaporation from the mainland can contribute between 9 and 16% towards the total precipitation in the region. The following equation can be used to calculate the contribution of evaporation to the secondary vapor flux ( $\%E_{sv}$ ):

Table 2.

Percentage of evaporated mainland derived vapor estimated to be contributing to the atmosphere during July-August in Belize.

Hum -idity	$\delta^{18}O_E$	$\delta D_{E}$	d-excess	Percent of Mainland Evaporation in Belize Precipitation
0.75	-33.8	-182.6	87.7	16%
0.85	-48.7	<b>-24</b> 6.6	143	9%

$$E_{sv}\% = (E\% \times p) / ET$$

E is the contribution of the evaporated component to atmospheric moisture, p is the total measured precipitation and ET is the amount of moisture returned to the atmosphere through evapotranspiration. Precipitation in July has been measured at approximately 440 mm/month of which approximately 200 mm is returned to the atmosphere through evaportranspiration (Walker, 1973). Taking the range of 9 – 16% for E, our study shows that the contribution of evaporation to the total secondary vapor flux can be between 20 and 35%. A steady state evapotranspiration model in the Amazon basin estimated that evaporation accounted for between 20-40% of the total evapotranspiration flux in a tropical rainforest (Gat and Matsui, 1991). Our estimates of evapotranspiration over mainland Belize are in good agreement with these, although admittedly, more detailed work needs to be carried out.

Analysis of Stable Carbon Isotopes of Dissolved Inorganic Carbon and Select Ions

## Dissolved Inorganic Carbon

Results of  $\delta^{13}C_{DIC}$  and dissolved inorganic carbon (DIC) are shown in table 1. The formation of DIC and its isotopic ratio values is typically initiated by the dissolution of  $CO_2$  from root respiration and decomposing vegetation in the soil zone. Carbon isotope values ( $\delta^{13}C$ ) for vegetation are expected to average about -26 ‰ and -13 ‰ in landscapes hosting  $C_3$  and  $C_4$  vegetation, respectively (Deines, 1980). Although  $C_4$  crops, corn and sugarcane, are grown in several areas, their influence on

the  $\delta^{13}$ C of DIC should be minimal since a majority of the land in Belize remains uncultivated and consists of  $C_3$  type vegetation. Recharging groundwater DIC is further affected by carbonate dissolution and the degree of openness to soil  $CO_2$ . The openness of the groundwater system and the contributions to the DIC pool is reflected in the  $^{13}$ C of the DIC (Clark and Fritz, 1997). Under fully open system conditions, DIC is controlled by the hydrolysis of soil  $CO_2$  alone, enriching DIC  $\approx$  9‰, to approach a value of -17‰. Under closed system conditions, final DIC is composed of carbonate and soil  $CO_2$ , equally (Clark and Fritz, 1997). Assuming that the  $\delta^{13}$ C of carbonates is 0‰,  $\delta^{13}C_{DIC}$  will approach -13‰. However, the presence of dissolving dolomite can result in  $\delta^{13}C_{DIC}$  above this range.

 $\delta^{13}C_{DIC}$  values and DIC concentrations range from -7.4 to -17.1‰ and 5.4 to 112.9 mg C/L, respectfully (Table 1).  $\delta^{13}C_{DIC}$  vs. DIC (mgC/L) for Belize surface and groundwaters is shown in figure 4. In general, increasing DIC accompanies higher  $\delta^{13}C_{DIC}$ . This supports a DIC model initially under open system conditions, and evolving towards higher  $\delta^{13}C$  through carbonate dissolution. Surface water samples typically had less DIC compared to groundwater: mean concentrations of 33.3 and 65.1 mg C/L, respectively. Despite the differences in DIC, their  $\delta^{13}C_{DIC}$  values were similar: -13.9‰ for surface waters and -13.7 ‰ for groundwaters.

## Gypsum Dissolution

Gypsum dissolution is an important process in the evolution of natural waters.

The dissolution reaction for gypsum is:

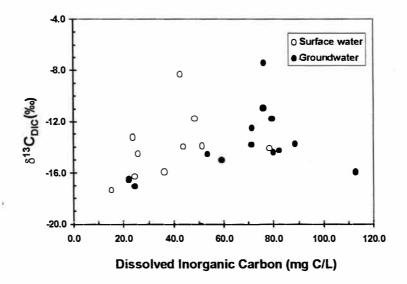


Figure 4. Crossplot of  $\,\delta^{13}C_{DIC}$  -vs- dissolved inorganic carbon, for surface and groundwater from Belize, Central America.

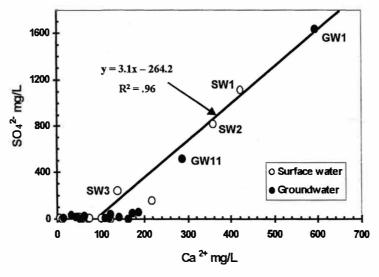


Figure 5. Crossplot of  $Ca^{2+}$ -vs-  $SO_4^{2-}$  for surface and groundwater samples from Belize, Central America. The regression line represents samples within 25% of the  $SO_4^{2-}$ /  $Ca^{2+}$  molar ratio.

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

The concentrations of sulfate (1.7 to 1632 mg/L) and calcium (5.8 to 593 mg/L) are given in Table 1. The sulfate-calcium relationship for surface and groundwaters is shown in Figure 5. A clustering of data at low sulfate values indicates that changes in concentrations of calcium are associated with relatively minor changes in the sulfate concentrations. However, for some samples, there is a linear increase between sulfate and calcium. Samples within 25% of the sulfate/calcite molar ratio for gypsum dissolution (2.4) were chosen to represent geochemical conditions dominated by gypsum dissolution (SW1, SW2, SW3, GW1, GW11). The regression line in Figure 5 shows the sulfate and calcium relationship of these samples. A slope of 3.1 for these samples approximates the theoretical slope of a gypsum solution in equilibrium. Here, we suggest that gypsum dissolution is causing the precipitation of oversaturated calcite through the common ion effect, thereby controlling the quantities of dissolved calcium and sulfate.

### Dedolomitization

Figure 6 shows the relationship between  $Mg^{2+}$  and  $\delta^{13}C_{DIC}$  for all samples. The outlying data point (GW3) contains isotopically light  $^{13}C_{DIC}$ . One likely explanation is the addition of  $CO_2$  through bacterially mediated reactions. Support for this hypothesis is indicated by the high DIC concentrations (112.9 mg/L) and low  $\delta^{13}C_{DIC}$  value (–15.9%) of this sample. In general, increasing magnesium concentrations are

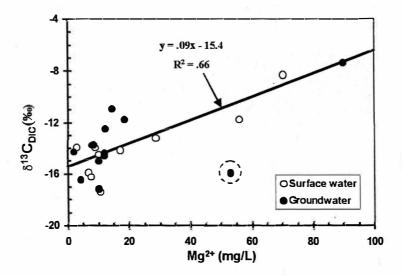


Figure. 6. Crossplot of  $\delta^{13}C_{DIC}$  - vs - Mg  $^{2+}$ . The regression line excludes the outlier (GW3) enclosed by the circle (see text).

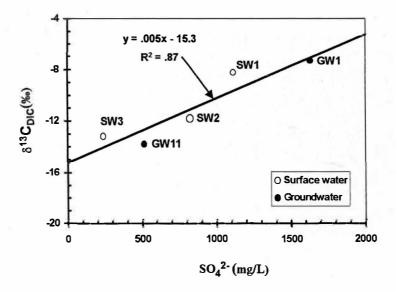


Figure 7. Crossplot of  $SO_4^{\,2^*}\text{-vs-}\,\delta^{13}C_{DIC}$  for surface and groundwater samples identified in figure 5.

accompanied by higher  $\delta^{13}C_{DIC}$  values, suggesting the incongruent dissolution of dolomite.

Figure 7 shows the relationship between  $\delta^{13}C_{DIC}$  and  $SO_4^{2-}$  for the 3 surface and 2 groundwater samples identified in Figure 5, as those with significant gypsum dissolution. The regression line indicates a strong linear relationship between  $\delta^{13}C_{DIC}$  values and sulfate concentrations. Neither the precipitation of calcite nor the gain of dissolved gypsum should significantly influence  $\delta^{13}C_{DIC}$  values, whereas the incongruent dissolution of dolomite does effect the  $\delta^{13}C_{DIC}$ . This is clear from the following equations:

$$Ca^{2+} + CO_3^{2-} + CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + CaCO_3 + 2H_2O$$

$$Ca^{2+} + HCO_3^{-} + CaMg(CO_3)_2 + H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^{-} + CaCO_3 + OH^{-}$$

Increases in δ<sup>13</sup>C<sub>DIC</sub> attributed to the incongruent dissolution of dolomite and concurrently dissolving gypsum suggests that dedolomitization (the dissolution of gypsum/anhydrite driving the precipitation of calcite and dissolution of dolomite) is the dominant geochemical reaction in some samples. This is consistent with the geochemical modeling carried out in other carbonate landscapes (Plummer *et al.*, 1990; Lòpez-Chicano *et al.*, 2001). The utility of dedolomitization as a proxy for groundwater evolution in Belize seems promising, although based upon the limited sampling and analyses presented in this study.

#### **CHAPTER 4**

### **CONCLUSIONS**

A survey of the ground and surface waters from Belize, Central America was carried out to study and improve upon the current knowledge of atmospheric and geochemical processes governing the regional hydrology. Based upon the analysis of the stable isotope ratios of hydrogen, oxygen and carbon and select ion (Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>) concentrations, the following conclusions can be made:

1) Oxygen and hydrogen isotope measurements show *d-excess* values between 10 and 40.8 ‰, suggesting a secondary vapor flux through evaporation. 2) A Craig-Gordon evaporation model estimated evaporation contributions to atmospheric vapor at 9-16%, while evaporation contributes 19-35% to total evapotranspiration. 3)  $\delta^{13}C_{DIC}$  values and DIC concentrations suggest open-closed carbonate dissolution in surface and ground waters. 4)  $\delta^{13}C_{DIC}$  values in conjunction with dissolved ion concentrations indicate dedolomitization occurring in several samples.

Detailed investigations along these lines are warranted to understand important geochemical processes affecting water quality.

# Appendix

Additional Laboratory Analyses and Sampling Data

## Additional data from the reconaissance survey

			Alk. as						
Sample	Temp	pН	HCO3	Cl- N	1O3-N	Na+	K+	Dol SI	Ca SI
SW1	33	7.4	34	11	1.3	10.8	0.7	-3.14	-1.58
SW2	28	7.3	421	7.9	0.9	4.6	0.4	0.63	0.55
SW3	32	7.6	189	6.7	0	4.7	0.6	0.21	0.25
SW4	27	7.5	187	7.7	0.1	6.4	1.5	-0.14	0.12
SW5	28	7.6	98	3.6	0	3.1	0.5	-0.21	0.36
SW6	25.5	7.9	250	2.9	0.1	5.3	0.7	0.66	0.66
SW7	28	7.8	70	5.2	0.1	4.3	0.5	-1.51	-0.65
SW8	27	7.6	256	5.6	0.6	3.4	0.4	0.36	0.45
SW9	27	7.6	126	8.9	0.3	5.3	1	-0.58	-0.1
SW10	28	7.9	290	15.1	0.1	8.2	0.7	0.73	0.93
SW11	28	7.4	150	36	0.2	15.8	0.7	0.06	0.18
SW12	30	7.5	265	32	0	12.7	1.9	1.24	0.82
SW13	32	7.7	264	42	0	15.4	2.1	1.53	0.97
GW1	30	7.2	155	7.9	0	4.6	0.2	-1.22	-0.18
GW2	28	7.9	281	16.1	- 1	8	1.1	1.3	0.96
GW3	29.5	7.8	501	5	0	95.1	6.9	0.07	0.24
GW4	28	7.2	132	9.1	0.1	5.8	0.9	-1.42	-0.41
GW5	29	7.2	403	8.6	1	4.4	0.6	0.28	0.43
GW6	26.5	7.2	404	60.2	33	36.5	8	0.35	0.49
GW7	26.5	7.5	387	19	5.2	10	0.7	0.46	0.84
GW8	27	7.6	323	7.9	2.8	4.1	0.2	0.72	0.69
GW9	29	7.6	440	17.2	0	6.2	0.4	1.07	0.98
GW10	29	7.4	417	17	0.5	9.3	0.6	0.64	0.66
GW11	32	7.4	170	16.9	0.3	12.9	2.6	-0.23	0.07
GW12	27.5	7.5	506	38.8	1.2	16.9	0.7	1.66	0.9
GW13	28	7.5	328	39	0	7.4	1.9	1.52	0.98
GW14	27	7.4	405	10	0.7	19	2.1	0.33	0.16

Isotopic results of the initial survey (January 1998) are listed below

Sample	$CO_2 \mu$ moles	δ <sup>13</sup> C‰ δ <sup>18</sup> O‰ δ <sup>2</sup> H ‰		
Ponded or Stagnant				
Maya Well (25' open pit well)	112.6	-17.3	-4.7	-21
Chanona Farm roof collection	ND	ND	-4.2	-13
Zoooff hummingbird-surface pool	ND	ND	-3	-2
Cave #2 San Miguel, Rio Grande (Toledo)	37.7	-16	-5.2	NA
Cave #1 (3km. from San Miguel)	35.6	-15.6	-4.9	NA
Streams and Rivers				
Chanona Creek stream-sw of belmopan	trace	NA	-4.3	-16
Rio On pools in the Maya Mtns.	trace	NA	-4.9	-20
Mopan roiver @ S. Jose Succotz	39.5	-13.3	-5.1	-23
Haulover Bridge-Belize River	26	-14	-2.6	<b>-</b> 6
Ladyville-Belize River	26.4	-15	-3.5	-2
Belcan Bridge-Belize City	14.8	-15.3	-2	1
Swing Bridge @ entrance to carib.	16	-13.8	-1.8	-1
City Pump-15 miles upstream of BC	28.6	-13.8	-3.6	-11
Columbia-Rio Grande	48.2	-14.6	-5.2	<b>-</b> 19
San Miguel	34.8	-14.4	-5	-19
Big Falls	38.4	-14.2	-5	-19
S. Pedro, Columbia,(Rio Grande) Bridge	26.7	-15.7	-5.3	NA
S. Miguel, Rio Grande (Toledo)	38.5	-15.4	-5.1	NA
Mafredi Ford	40.1	-14.2	-3.8	-12
Sivasey Bridge	5.2	-14.5	-4.7	-16
Wells				
Rio Bravo, 460 ft @ Programme for Belize	122	-16.6	-5.6	-20
Sanctuary-across from zoo-100'well	26.8	-14.9	-3.8	-15
Bella Vista-50' hand pump well	4.2	-17.7	-3.7	-12
S. Antonio (Cayo) Shallow Well	89.5	-11.8	-4.6	-26
S. Antonio (Cayo) water supply well	76.1	-13.6	-4.3	-21
Douglas Village, (Orange Walk) hand pump	76.2	-13.2	-4.2	NA
S. Antonio (Orange Walk) water supply well	78.2	-8.3	-5.2	NA

Carbon Isotope values for select soils samples and one aquifer carbonate sample are listed below.

5	Soils	Carbon-13	
N	Maya Well	-27.3	
I	Belmopan	-27.0	
	CottonTree	-23.8	
(	Cayo	-30.3	
	Blackman	-28.8	
2	Zoo	-20.6	
9	S Antonio OW	-28.8	
1	Mean:	-26.7	
S	StDev:	3.4	
•	Carbonates		
	Prog from Belize	0.0	
1	repeat	-0.2	
1	repeat	0.5	
1	repeat	0.7	
1	repeat	1.0	
]	Mean:	0.2	
;	StDev:	0.4	

## Cleansing of samples containing hydrogen sulfide gas

The Samples below were analyzed for Carbon-13. Mass Spectrometery readings indicated contamination. The cleansing of these samples was achieved through the removal of H<sub>2</sub>S gas by heating the sample gas with CuO at 900 deg. C.for 3 hours. The following series of reactions is thought to occur:

$$2CuO \rightarrow Cu + O_2$$

$$H_2S + 2O_2 \rightarrow SO_3 + H_2O$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$Cu + H_2SO_4 + \frac{1}{2}O_2 \rightarrow CuSO_4 \cdot H_2O$$

Sample	Pre-treated delta C-13	gas yield/ micromoles
SW3 SW4 SW9	-5.1 ND -12.3	21.6 15 20.3
GW4	-12.5	18.5
	Post-treated delta C-13	gas yield/ micromoles
SW3	-14.5	10.9
SW4	-17.4	12.8
SW9	-16.3	5.7
GW4	-16.5	10.2

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