



## Seasonal variability in the salinity and oxygen isotopic composition of seawater from the Cariaco Basin, Venezuela: Implications for paleosalinity reconstructions

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[1] Oxygen isotope measurements ( $\delta^{18}\text{O}_w$ ) were made on seawater samples collected monthly between May 1996 and February 1997 and between December 2005 and May 2006 at various water depths at the Cariaco Basin ocean time series station ( $10^\circ 30\text{N}$ ,  $64^\circ 40\text{W}$ ). The  $\delta^{18}\text{O}_w$  values are compared with concurrent salinity measurements to assess the  $\delta^{18}\text{O}_w$ :salinity relationship in this tropical region and to determine if significant seasonal variability exists in the relationship. The  $\delta^{18}\text{O}_w$  values range from 0.88 to 1.19‰ SMOW in the upper 250 m. Our results indicate that the strongest positive linear correlation between  $\delta^{18}\text{O}_w$  and salinity in the upper 250 m occurred during the February and April 2006 upwelling season ( $R^2 = 0.95$  and  $0.94$ , respectively). The salinity:  $\delta^{18}\text{O}_w$  relationship displays significant seasonal variability which is attributed to seasonal changes in freshwater input from the Tuy, Neverí, and Unare rivers into the Cariaco Basin. Specifically, an inverse correlation ( $R^2 = 0.77$ ) exists between monthly Neverí River discharge and sea surface salinity. Our results demonstrate that significant seasonal changes in the  $\delta^{18}\text{O}_w$ :salinity relationship occur in the tropics. The data also show a distinct difference between the surface water  $\delta^{18}\text{O}_w$ :salinity relationship during the upwelling season ( $R^2 = 0.96$ ) and the nonupwelling season ( $R^2 = 0.93$ ) revealing zero-salinity end-members of  $-28.53$  (SE  $\pm 3.04$ ) and  $-8.77$  (SE  $\pm 1.33$ ), respectively. The seasonal mixing lines are an important consideration when utilizing the salinity:oxygen isotope relationship for paleosalinity reconstructions. The oxygen isotope composition ( $\delta^{18}\text{O}_c$ ) was also measured in two surface-dwelling planktonic foraminiferal species, *Globigerinoides ruber* and *Globigerina bulloides*, from biweekly sediment trap samples collected in the Cariaco Basin between November 1996 and February 1997 and May 2003 through May 2006. The large range in  $\delta^{18}\text{O}_c$  during the study period, 1.4‰ for *G. ruber* and 1.5‰ for *G. bulloides*, is attributed to changes in calcification depths of the species from 1996–1997 to 2005–2006. Using the surface water  $\delta^{18}\text{O}_w$ :salinity equations generated for the upwelling and nonwelling seasons in the Cariaco Basin, we compare measured seawater salinity with the calculated seawater salinity at various depths of calcification. The  $\delta^{18}\text{O}_w$ :salinity equation

generated from surface waters during the upwelling months yields salinity estimates that best agree with measured salinities.

**Components:** 8714 words, 8 figures, 2 tables.

**Keywords:** salinity; stable isotopes; foraminifera; paleoproxies.

**Index Terms:** 1635 Global Change: Oceans (1616, 3305, 4215, 4513); 4964 Paleooceanography: Upwelling (4279).

**Received** 24 March 2008; **Revised** 23 December 2008; **Accepted** 24 March 2009; **Published** 26 June 2009.

McConnell, M. C., R. C. Thunell, L. Lorenzoni, Y. Astor, J. D. Wright, and R. Fairbanks (2009), Seasonal variability in the salinity and oxygen isotopic composition of seawater from the Cariaco Basin, Venezuela: Implications for paleosalinity reconstructions, *Geochem. Geophys. Geosyst.*, 10, Q06019, doi:10.1029/2008GC002035.

## 1. Introduction

[2] The tropics regulate the hydrologic balance between the Atlantic and Pacific Oceans, as well as the heat balance between high and low latitudes. The sea surface temperature (SST) and sea surface salinity (SSS) gradients in the tropical Atlantic play a vital role in general ocean circulation and global climate changes [Broecker, 1995; Hughen *et al.*, 1996; Peterson *et al.*, 2000; Hoerling *et al.*, 2001]. For paleoceanographic and paleoclimatic reconstructions, the  $\delta^{18}\text{O}_w$ :salinity relationship can be used in conjunction with paleotemperature estimates from fossil shells to determine past seawater salinity changes. Such measurements of paleosalinity aid our understanding of past changes in the hydrologic cycle and ocean transport [Rostek *et al.*, 1993; Schmidt, 1998, 1999; Bigg and Rohling, 2000; Delaygue *et al.*, 2001; Oppo *et al.*, 2007]. However, paleosalinity calculations have the potential for significant error if there are uncertainties in the  $\delta^{18}\text{O}_w$ :salinity relationship for a particular region. In order to better reconstruct the paleosalinity record preserved in marine sediments it is necessary to understand the local  $\delta^{18}\text{O}_w$ :salinity relationship.

[3] The stable oxygen isotope composition in foraminiferal calcite ( $\delta^{18}\text{O}_c$ ) has long been the principle tool for estimating marine paleotemperatures [Urey, 1947; Emiliani, 1955]. However, the oxygen isotopic composition of foraminiferal calcite is a function of both calcification temperature and the oxygen isotopic composition of seawater, with the latter fluctuating on glacial-interglacial time scales because of changes in ice volume. In addition, local or regional physical factors (i.e., evaporation, precipitation, river runoff) also modify  $\delta^{18}\text{O}_w$  on shorter time scales [Fairbanks, 1989; Delaygue *et al.*, 2001]. To obtain accurate estimates of past seawater salinity it is necessary to

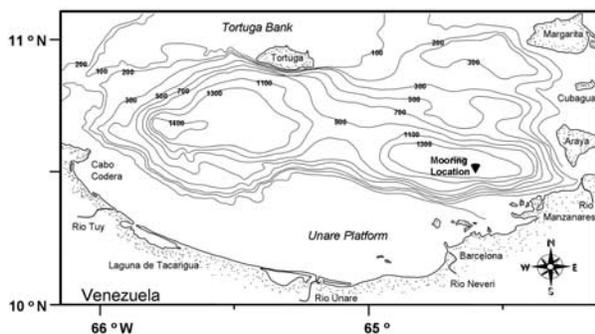
know the  $\delta^{18}\text{O}_w$  which cannot be measured directly. Thus, deconvolving  $\delta^{18}\text{O}_c$  into its constituent variables is essential for reconstructing changes in surface ocean conditions.

[4] The sediments accumulating in the Cariaco Basin provide a high-resolution record of annual to decadal-scale climate change in the tropical oceans. These sediments have been shown to record variations in fluvial input, trade wind and upwelling intensity, and the position of the Intertropical Convergence Zone (ITCZ) [Peterson *et al.*, 1991, 2000; Haug *et al.*, 2001; Tedesco and Thunell, 2003a; Black *et al.*, 2004, 2007]. Because of the considerable interest in using Cariaco Basin sediments to reconstruct past climatic and hydrologic conditions, it is vital to understand the  $\delta^{18}\text{O}_w$ :salinity relationship in this region.

## 2. Background

[5] Epstein and Mayeda [1953] were the first to observe that the  $\delta^{18}\text{O}$  of seawater in high-latitude regions influenced by glacial meltwater differed from that of the open ocean. Since then, the  $\delta^{18}\text{O}$  composition of seawater has been used to identify different water masses, track circulation patterns, and assess the freshwater balance of a region [Craig and Gordon, 1965; Fairbanks, 1982; Bauch *et al.*, 1995; Gat, 1996; Bigg and Rohling, 2000; Frew *et al.*, 2000; Schlosser *et al.*, 2002; Benway and Mix, 2004]. In addition, oxygen isotope composition in seawater has been used to assess water mass formation processes in the coastal regions of the northern North Atlantic where fresh and ocean water mix [Fairbanks, 1982; Bauch *et al.*, 1995; Frew *et al.*, 2000; Houghton and Fairbanks, 2001].

[6] The  $\delta^{18}\text{O}_w$  and salinity of surface waters have been shown to covary linearly [Östlund *et al.*,



**Figure 1.** Bathymetric map of the Cariaco Basin showing the sediment trap mooring location at 10°30'N, 64°40'W.

1987; Fairbanks *et al.*, 1992; Rostek *et al.*, 1993; Schmidt, 1999; Watanabe *et al.*, 2001; LeGrande and Schmidt, 2006]. Both salinity and  $\delta^{18}\text{O}_w$  are affected by the local evaporation and precipitation balance as well as regional ocean processes (i.e., advection, sea ice calving). For instance, equatorial surface waters typically have high salinities and high  $\delta^{18}\text{O}_w$  values ( $\sim 1\text{‰}$  higher than SMOW) because of high evaporation [Östlund *et al.*, 1987; Fairbanks *et al.*, 1992; Watanabe *et al.*, 2001; Morimoto *et al.*, 2002]. Using GEOSECS data, Wang *et al.* [1995] showed that there is very little variation in the salinity:  $\delta^{18}\text{O}_w$  relationship in the low-latitude Atlantic (40°N–40°S). However, there is regional variability in this relationship. The influences of freshwater balance and runoff [Karr and Showers, 2002] have a pronounced affect on marginal basins and coastal regions and result in large geographic variations in the salinity:  $\delta^{18}\text{O}_w$  relationship. The temporal variability in  $\delta^{18}\text{O}_w$ :salinity relationships has also been observed on seasonal [Fairbanks, 1982; Fairbanks *et al.*, 1992; Strain and Tan, 1993] and longer time scales [Rohling and Bigg, 1998].

[7] It is clear from both observations [Bigg and Rohling, 2000; G. A. Schmidt *et al.*, Global Seawater Oxygen-18 Database, 1999, <http://data.giss.nasa.gov/o18data/>] and modeling studies that distinctly different  $\delta^{18}\text{O}_w$ :salinity relationships exist in association with different water masses and source water. The latitudinal variability in the oxygen isotopic composition of seawater ranges from  $-20\text{‰}$  in the Arctic to as much as  $2\text{‰}$  in highly evaporative regions. While the G. A. Schmidt *et al.* (Global Seawater Oxygen-18 Database, 1999, <http://data.giss.nasa.gov/o18data/>) global data set of  $\delta^{18}\text{O}_w$  and salinity values covers diverse oceanic regions there is very little information on seawater  $\delta^{18}\text{O}_w$  in tropical coastal regions.

In addition, there have been few attempts to assess seasonal variability in the  $\delta^{18}\text{O}_w$ :salinity relationship in the tropics.

[8] Several recent studies report on the  $\delta^{18}\text{O}_w$ :salinity relationship in tropical regions. Benway and Mix [2004] evaluate water sources and changes in  $\delta^{18}\text{O}_w$  and salinity in the Panama Bight. They found that large changes in the isotopic composition of precipitation produce the most significant changes in the  $\delta^{18}\text{O}_w$ :salinity relationship, while freshwater fluxes from rivers and upwelling has little affect on this relationship.

[9] Morimoto *et al.* [2002] made biweekly measurements of the  $\delta^{18}\text{O}$  of coral, seawater  $\delta^{18}\text{O}$ , and salinity in the Western Pacific Warm Pool. The  $\delta^{18}\text{O}_{\text{coral}}$ :salinity displays a strong linear relationship, independent of the  $\delta^{18}\text{O}$  of precipitation and evaporation changes, and can be used for paleosalinity estimates. A similar study was conducted off of Puerto Rico, in which the  $\delta^{18}\text{O}_{\text{coral}}$ :salinity relationship was defined and used to assess seasonal changes in surface salinities during the Little Ice Age [Watanabe *et al.*, 2001]. On the basis of these studies it is clear that the  $\delta^{18}\text{O}_w$ :salinity relationship is not uniform throughout the tropics and therefore site-specific calibrations are essential.

[10] There is a long standing interest in using the sediment record from the Cariaco Basin for high-resolution climate reconstruction [Peterson *et al.*, 1991; Hughen *et al.*, 1996; Black *et al.*, 1999; Lea *et al.*, 2003; Tedesco and Thunell, 2003a]. However, the precise relationships among  $\delta^{18}\text{O}_c$ , SST,  $\delta^{18}\text{O}_w$  and salinity have not been quantified for the Cariaco Basin. This study utilizes concurrent measurements of the oxygen isotope composition and salinity of seawater collected monthly from various depths in Cariaco Basin from May 1996 through January 1997, and December 2004 through May 2005, as well as the  $\delta^{18}\text{O}_c$  of planktonic foraminifera collected in sediment traps during this period. The primary objectives of this study are to (1) calibrate the  $\delta^{18}\text{O}_w$ :salinity relationship and determine if it varies seasonally and (2) assess the reliability of this method for recording ocean salinities using the calibration with oxygen isotope measurements of planktonic foraminifera.

### 3. Regional Setting

[11] The Cariaco Basin is a 1,400 m deep basin along the continental margin of northern Venezuela (Figure 1). The basin is bounded to the north by a shallow sill ( $\sim 140$  m) which limits the exchange of

subsurface waters and results in anoxic conditions below  $\sim 275$  m water depth. High deposition rates (50–100 cm/ka) and minimal bioturbation allow for annually laminated sediments or varves to accumulate. This natural sediment trap results in a well preserved record of interannual to century-scale climate variability, comparable to that of ice core records [Hughen *et al.*, 1996; Peterson *et al.*, 2000; Lea *et al.*, 2003; Black *et al.*, 2007]. The climatology of the region is driven primarily by the seasonal migration of the ITCZ. During boreal winter and early spring, also considered the dry season, the ITCZ is in its most southerly position generating strong easterly winds that blow along the Venezuelan coast causing upwelling, minimum SST ( $\sim 22^\circ\text{C}$ ) and maximum salinities ( $\sim 37\text{‰}$ ). The ITCZ migrates to the north during summer and early fall reducing trade wind velocities. During this time, upwelling is diminished and SST increases up to  $\sim 29^\circ\text{C}$ . Increased precipitation during this time of year causes surface salinities to decrease to  $\sim 36.2$ . In addition, local river runoff from the north coast of Venezuela (the Tuy, Unare, Neverí, and Manzanares rivers) varies seasonally and affects salinities in the Cariaco Basin.

[12] The hydrography of the Cariaco Basin has been well described on seasonal to interannual time scales [Astor *et al.*, 2003; Muller-Karger *et al.*, 2004]. The North Equatorial Current (NEC) enters the Caribbean Sea from the east through the narrow Antillean passages and continues to flow westward as the Caribbean Current [Hernandez-Guerra and Joyce, 2000; Johns *et al.*, 2002]. This is the principle source of surface waters in the Cariaco Basin. Beneath Caribbean surface waters lies Subtropical Underwater (SUW) which originates in the central tropical Atlantic. The SUW is typically characterized by its location at the salinity maximum (36.88‰) [Metcalfe, 1976; Astor *et al.*, 2003, 2005]. In Cariaco Basin, the upper boundary of SUW has been observed to reach depths shallower than 50 m during the main upwelling season [Astor *et al.*, 2003; Lorenzoni, 2005]. A short-lived secondary upwelling event also occurs in the basin during July [Muller-Karger *et al.*, 2004; Astor *et al.*, 2005].

## 4. Methodology

[13] As part of the Cariaco Basin ocean time series program, hydrographic data and seawater samples collected monthly from the upper 250 m at  $10^\circ 30\text{N}$ ,  $64^\circ 40\text{W}$ . The time series study and the sampling protocols are discussed by Muller-Karger

*et al.* [2001]. Continuous profiles of temperature and salinity were measured at this location using a SeaBird CTD (SBE-25). The time series data are available via the URL <http://imars.usf.edu/cariaco>. For this study, we use samples collected from May 1996 through February 1997, and December 2005 through May 2006. The seawater samples were analyzed for the oxygen isotopic composition at Rutgers University and Lamont Doherty Earth Observatory. Measurement precision is  $\pm 0.02$  to  $0.03$  per mil.

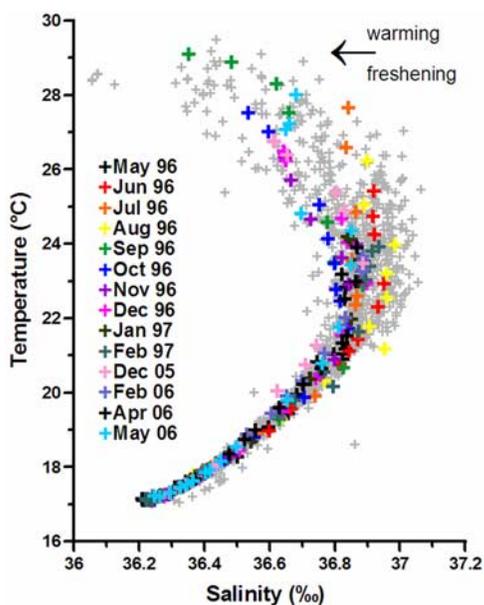
[14] The time series program also includes a mooring with five sediment traps ( $\sim 120$ , 235, 420, 810, and 1200 m) used to collect the vertical flux of particulate material at two week sampling intervals (solid triangles in Figure 1). The details of the sediment trapping program are discussed by Thunell *et al.* [2007]. This study utilizes 58 samples collected between November 1996 to February 1997, and May 2003 to May 2006. Because of a clog, sediment trap samples do not exist for May 1996 through November 1996. Each sample for this study was wet sieved at  $125 \mu\text{m}$ . Planktonic foraminiferal species *Globigerinoides ruber* (pink variety) and *Globigerina bulloides* were picked from the 212–355  $\mu\text{m}$  size fraction. The oxygen isotope analyses were carried out on a VG OPTIMA stable isotope mass spectrometer equipped with an automated Isocarb preparation system. The long-term standard reproducibility is  $0.07\text{‰}$  for  $\delta^{18}\text{O}$ .

## 5. Results

### 5.1. Seawater Salinity and $\delta^{18}\text{O}_w$ Data

[15] A composite plot of monthly temperatures and salinities from 1 to 1300 m water depth for a 10 year period of the Cariaco time series (1996–2007) is illustrated in Figure 2. These data show a distinct seasonal cycle with freshening from August through November (Figure 2) coincident with the rainy season in this region and an increase in discharge of the local rivers (Figure 3). For our study interval, the largest decrease in surface salinity occurs from August (36.90‰) to September (36.35‰) 1996, and also coincides with warmest surface temperatures (Figure 2).

[16] The freshwater budget of this region not only affects salinity but also the oxygen isotope composition of seawater. The  $\delta^{18}\text{O}_w$  values range from  $0.89$ – $1.19\text{‰}$  (SMOW) in the upper 100 m during May 1996 through February 1997 (Figure 4c) and December 2005 through May 2006. On the basis of



**Figure 2.** Temperature and salinity plot from 1–1300 m water depth during all years of the Cariaco time series (1995–2007). Beneath Cariaco surface waters lies Subtropical Underwater (SUW) located at the salinity maximum (36.9‰). The data used in this study are color coded while all other data are in grey.

these measurements the average  $\delta^{18}\text{O}_w$  in the upper 100 m is 1.04‰ (SMOW) and the average  $\delta^{18}\text{O}$  for surface waters is 1.08‰ (SMOW). The average  $\delta^{18}\text{O}_w$  for the upper 100 m for individual months varies seasonally from a low 0.97‰ in November to a high of 1.15‰ in June (Figure 4d). There is a general trend for  $\delta^{18}\text{O}_w$  to increase from the surface to the base of the mixed layer and then decrease with increasing depth below that point. The months of June and July exhibit the highest overall average  $\delta^{18}\text{O}_w$  and highest salinities (Figure 4d). A significant correlation ( $R^2 = 0.40$ ) between the average  $\delta^{18}\text{O}_w$  and the average seawater salinity is observed over the study period (Figure 4d).

[17] A comparison of  $\delta^{18}\text{O}_w$  and seawater salinity at all depths reveals a positive correlation ( $R^2 = 0.50$ ) for all months of the study except July (Figure 5a), with  $\delta^{18}\text{O}_w$  decreasing as salinity decreases. However, the slopes and zero-salinity end-members vary considerably (Table 1). For example, the zero salinity intercept of the  $\delta^{18}\text{O}_w$  versus salinity regressions range from  $-3.14$  during September 1996 to  $-21.90$  during January 1997.

## 5.2. Sediment Trap Data

[18] Time series of  $\delta^{18}\text{O}_c$  were produced for *G. ruber* and *G. bulloides* using sediment trap

samples collected during the same time periods as the seawater salinity and  $\delta^{18}\text{O}_w$  measurements (November 1996 and February 1997, and December 2005 through May 2006, Figure 6). The preservation of the planktonic foraminifera used in this study was excellent. Foraminiferal specimens of both species were present in the sediment trap samples with their spines still in tact. The  $\delta^{18}\text{O}_c$  range for *G. ruber* is 0.75‰ ( $-1.92$  to  $-1.16$ ) during 1996 and 1997 and 0.38‰ ( $-0.92$  to  $-0.54$ ) during 2005 and 2006. For *G. bulloides* the  $\delta^{18}\text{O}_c$  range is 0.53‰ with values during 1996–1997 ranging from  $-1.55$  to  $-1.02$  and during 2005–2006 from  $-1.0$  to  $-0.5$ .

[19] The lowest *G. ruber*  $\delta^{18}\text{O}_c$ ,  $-1.9$ ‰, occurs in December 1996 in conjunction with the warmest sea surface temperatures recorded in the region during the study period. Conversely, the highest *G. bulloides*  $\delta^{18}\text{O}_c$  values,  $-1.03$ ‰, occur in February 1997 when sea surface temperatures were coldest (Figure 6).

## 6. Discussion

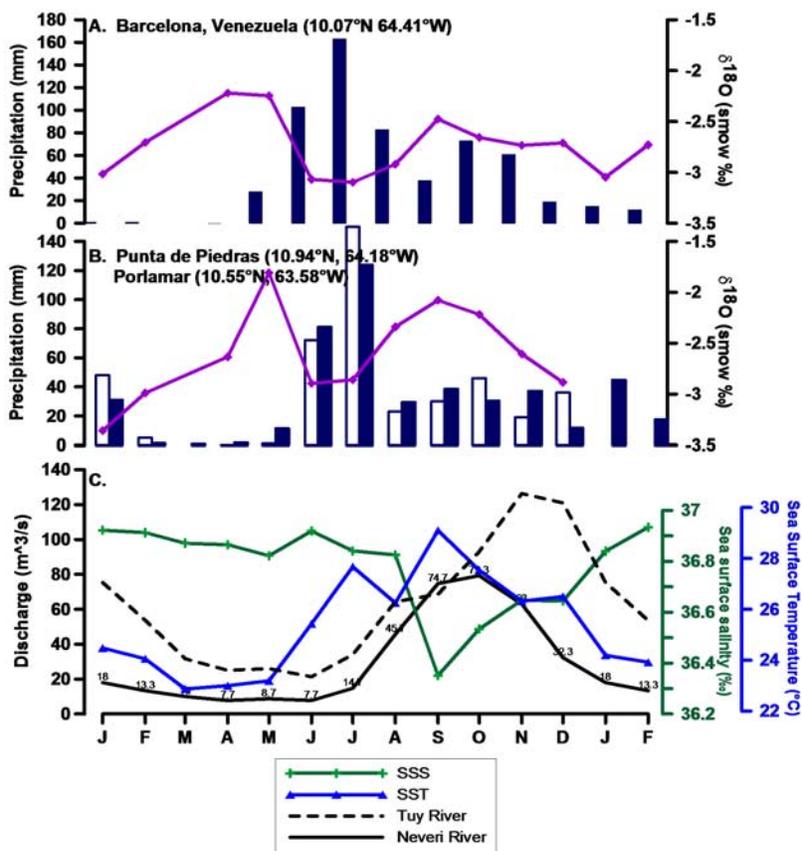
[20] The  $\delta^{18}\text{O}_w$ :salinity relationship in the Cariaco Basin is a function of changes in local and regional climate factors associated with the annual migration of the ITCZ. Specifically, the strong seasonal changes in seawater temperature and salinity in the Cariaco basin are due not only to wind driven coastal upwelling and lateral advection but also to seasonal changes in precipitation and river discharge. These processes also affect the surface  $\delta^{18}\text{O}_w$ .

### 6.1. Precipitation

[21] The oxygen isotopic composition of precipitation ( $\delta^{18}\text{O}_p$ ) is a function of the source water chemistry, fractionation during atmospheric transport, and temperature [Dannsgaard, 1964; Craig and Gordon, 1965; Gat, 1996; Schmidt, 1998]. Unfortunately, no data exists on the  $\delta^{18}\text{O}$  of precipitation in the Cariaco Basin region. Consequently, we estimate the  $\delta^{18}\text{O}$  of monthly precipitation using the global regression previously proposed by Schmidt [1998]:

$$\delta^{18}\text{O}_p = -11.88 + 0.345(T) - 0.0022(P) \quad (1)$$

where T and P are monthly mean surface air temperature ( $^{\circ}\text{C}$ ) and precipitation (mm) (Figures 3a and 3b). We calculate  $\delta^{18}\text{O}_p$  for both Porlamar, located to the northeast of the Cariaco time series



**Figure 3.** (a) Mean precipitation (histogram) and estimated  $\delta^{18}\text{O}_p$  (solid line) for Barcelona, Venezuela (1996). (b) Mean precipitation during 1996 for Punta de Piedras (blue bars) and Porlamar, Venezuela (white bars), calculated  $\delta^{18}\text{O}_p$  for Porlamar (solid line). (c) Monthly mean discharge from the Tuy and Neveri Rivers (1973–1975), SST, and SSS at Cariaco Station (1996).

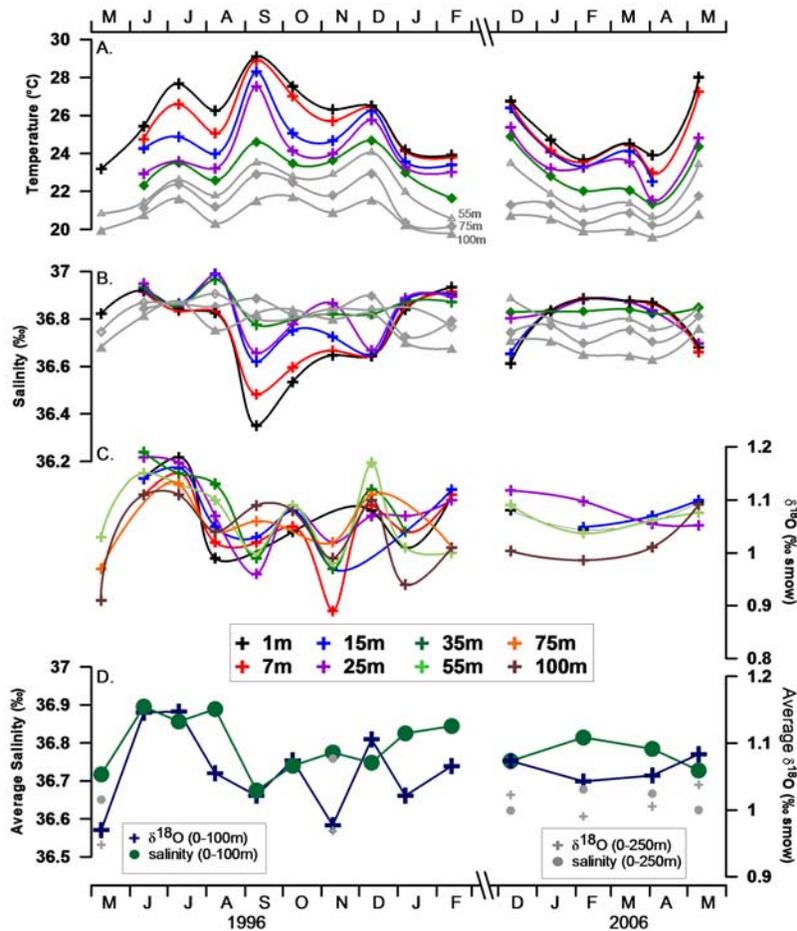
station on Margarita Island, and Barcelona, located on the mainland southeast of the Cariaco study site. On the basis of these estimates the mean annual oxygen isotopic composition of precipitation in this region is about  $-2.6\text{‰}$  with a seasonal range of  $\sim -2.0\text{‰}$  to  $-3.0\text{‰}$ . In generating this global regression the tropics are not as well represented as midlatitudes and it has been suggested that the use of this methodology for calculating  $\delta^{18}\text{O}_p$  in the tropics is tenuous [Schmidt, 1999]. However, in using this global regression our estimated values are in agreement with the mean annual  $\delta^{18}\text{O}_p$  value of  $-3.0\text{‰}$  measured in Maracay, Venezuela, approximately 330 km west of the study site (IAEA/WMO, 2006), as well as the global mean  $\delta^{18}\text{O}_p$  value of  $-2\text{‰}$  from tropical sites [Craig and Gordon, 1965].

[22] The highest precipitation recorded at Punta de Piedras ( $10^{\circ}54\text{N}$ ,  $64^{\circ}57.6\text{W}$ ), approximately 80 km northeast of the Cariaco station, during 1996 was 81 mm during June and 124 mm in July (Figure 3b). During this time the surface and

subsurface (upper 25 m) seawater salinity decreased by only 0.08 from an average 36.93‰ in June to 36.85‰ in July (Figure 4a) which is equivalent to a 0.01‰ SMOW change in  $\delta^{18}\text{O}_w$ . We conclude that precipitation in this region has a minimal effect on the oxygen isotopic composition of surface waters, similar to that reported by Craig and Gordon [1965].

## 6.2. River Input

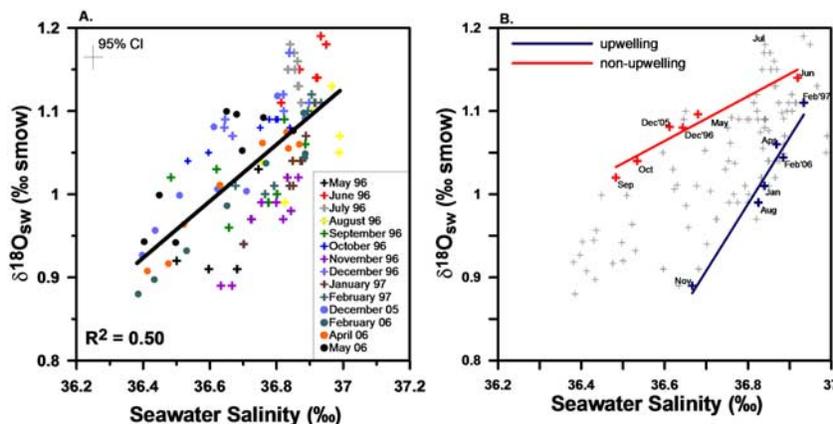
[23] The seasonal cycle of precipitation strongly influences the discharge of rivers in this region. Studies have shown that the seasonal variation in seawater salinity in the southeast Caribbean is a function of the outflow of the two largest South American rivers, the Amazon and Orinoco, rather than the local rainfall [Froelich et al., 1978; Guilderson, 1997]. Discharge from the Amazon and Orinoco is carried into the Caribbean Sea [Bowles and Fleischer, 1985; Muller-Karger et al., 1989] but is thought to have little influence on Cariaco Basin hydrography [Muller-Karger et



**Figure 4.** (a) Seawater temperature, (b) seawater salinity, and (c)  $\delta^{18}O_w$  from discrete depths at the Cariaco time series station during the study period. (d) Average salinity (dots) and average  $\delta^{18}O_w$  (crosses) for the upper 100 m for all months of the study period.

*al.*, 2004; Lorenzoni, 2005]. The local rivers influencing the Cariaco Basin include the Tuy, Unare, Neverí, and Manzanares rivers [Lorenzoni, 2005]. The average annual discharge rates for the Tuy,

Unare and Neverí Rivers are approximately 62 m<sup>3</sup>/s, 56 m<sup>3</sup>/s, and 32 m<sup>3</sup>/s, respectively [Zinck, 1977; Vorosmarty *et al.*, 1998]. River input is seasonal with highest discharge between the months of July



**Figure 5.** (a) The  $\delta^{18}O_w$ :salinity relationship for individual months of the study period. Trend line represents the composite data. (b) Surface water trends. Subsurface data are illustrated by grey crosses.

**Table 1.** The  $\delta^{18}\text{O}_{\text{sw}}$ -Salinity Relationship for the Cariaco Basin and Other Locations Where  $\delta^{18}\text{O}_{\text{sw}} = m(\text{salinity}) + b$

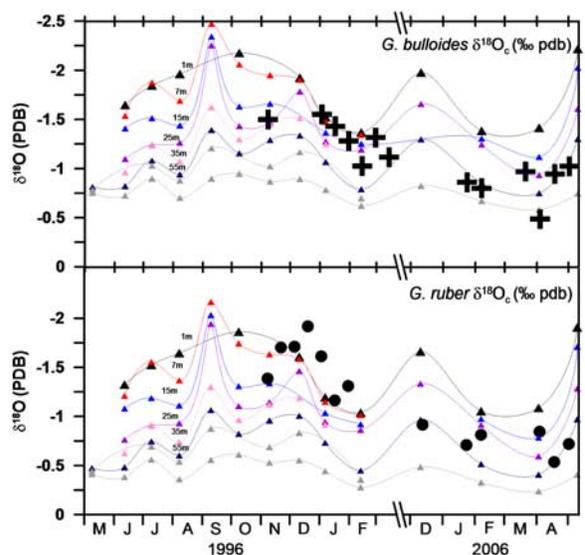
	n	Depth (m)	m	b	R <sup>2</sup>
<b>Cariaco Basin</b>					
May 1996	5	55–200	0.36 ( $\pm 0.21$ )	-12.04 ( $\pm 7.9$ )	0.47
Jun 1996	7	1–100	0.41 ( $\pm 0.24$ )	-13.97 ( $\pm 8.7$ )	0.37
Jul 1996	8	1–100	-1.20 ( $\pm 0.50$ )	45.41 ( $\pm 18.6$ )	0.49
Aug 1996	8	1–100	0.31 ( $\pm 0.16$ )	-10.24 ( $\pm 6.1$ )	0.36
Sep 1996	7	1–100	0.11 ( $\pm 0.13$ )	-3.14 ( $\pm 4.7$ )	0.13
Oct 1996	7	1–100	0.17 ( $\pm 0.03$ )	-5.12 ( $\pm 0.9$ )	0.90
Nov 1996	9	7–160	0.53 ( $\pm 0.10$ )	-18.42 ( $\pm 3.7$ )	0.79
Dec 1996	7	1–100	0.21 ( $\pm 0.10$ )	-6.64 ( $\pm 3.7$ )	0.46
Jan 1997	7	1–100	0.62 ( $\pm 0.09$ )	-21.9 ( $\pm 3.4$ )	0.90
Feb 1997	7	1–100	0.53 ( $\pm 0.10$ )	-18.36 ( $\pm 3.8$ )	0.84
Dec 2005	8	1–250	0.33 ( $\pm 0.08$ )	-11.24 ( $\pm 3.0$ )	0.73
Feb 2006	8	1–250	0.37 ( $\pm 0.03$ )	-12.68 ( $\pm 1.2$ )	0.95
Apr 2006	8	1–250	0.37 ( $\pm 0.03$ )	-12.44 ( $\pm 1.4$ )	0.94
May 2006	8	1–250	0.36 ( $\pm 0.09$ )	-11.97 ( $\pm 3.5$ )	0.79
All data	104	1–250	0.34 ( $\pm 0.04$ )	-11.48 ( $\pm 1.3$ )	0.50
Reference	Location	Depth (m)	m	b	R <sup>2</sup>
Guilderson [1997]	Barbados	1	0.17	-5.21	0.95
Watanabe et al. [2001]	Puerto Rico	1	0.20	-6.54	0.93
Weldeab et al. [2006]	western tropical Atlantic	2–50	0.49	-16.77	0.76
GEOSECS [Wang et al., 1995]	low-latitude Atlantic	1–250	0.30	-9.98	0.70
GEOSECS	global	1–250	0.50	-17.00	0.88

and December (Figure 3c). Additionally, the mouth of the Unare River is only open to the Caribbean Sea from July to December, coincident with the rainy season, and closed off by silt during the remaining months [Khandker, 1968]. The Unare and Neverí rivers to the east are considered to have the most influence on the hydrography at the Cariaco station [Lorenzoni, 2005].

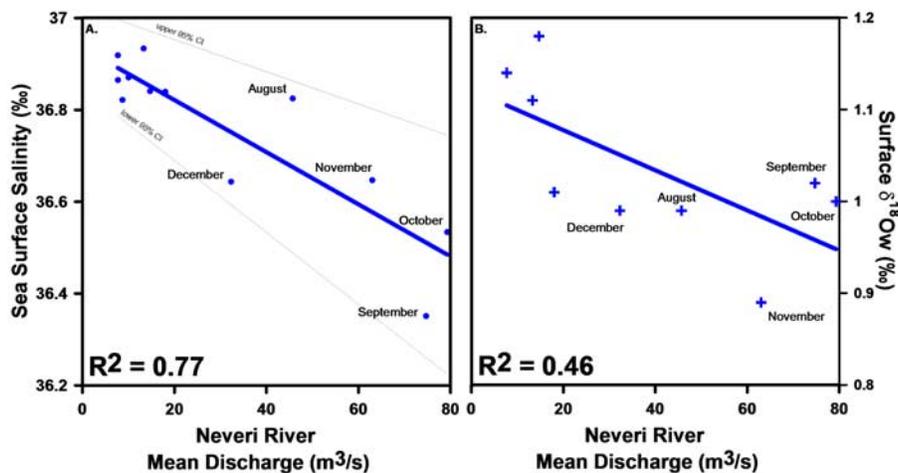
[24] Although the Tuy River has the highest annual discharge rate of the local rivers, there is still some question as to how significant an influence this river has on the Cariaco Basin. Hernandez-Guerra and Joyce [2000] found a distinct change in the direction of surface currents at 13°N in the Caribbean during the months of August and September 1997. A strong westward current is evident at 13°N, while an eastward current is observed flowing opposite the mean wind direction in the area between the coast of Venezuela and 13°N. This eastward flow could bring Tuy River water to the eastern side of the Cariaco Basin in the fall, thus influencing salinity. Transport of Tuy River water toward the eastern side of the Basin has also been observed through remote sensing ocean color images.

[25] The distinct freshening in the upper 25 m of the water column from August to September 1996 is attributed to increased riverine input to the basin (Figure 3c). The warm, low-salinity plume from

the Neverí, Unare, and possibly Tuy rivers is apparent through October. Surface waters begin to cool and become more salty in November. The Unare river plume salinity has been measured at



**Figure 6.** (top) Calculated calcite equilibrium profiles at discrete depths (colored lines) using measured seawater temperature and oxygen isotope values,  $T(^{\circ}\text{C}) = 13.2 - 4.89(\delta_c - \delta_w)$  [Bemis et al., 1998]. Crosses indicate *G. bulloides*  $\delta^{18}\text{O}_c$ . (bottom) Calculated equilibrium profile at discrete depths using  $T(^{\circ}\text{C}) = 14.9 - 4.80(\delta_c - \delta_w)$  [Bemis et al., 1998]. Dots indicate *G. ruber*  $\delta^{18}\text{O}_c$ .



**Figure 7.** Monthly (a) sea surface salinity and (b) surface  $\delta^{18}\text{O}_w$  in Cariaco Basin versus Neverí River flow rate.

~35.4 during the month of September [Lorenzoni, 2005]. Disregarding local precipitation events, a simple mass balance between the low-salinity plume from the Unare and Neverí rivers and the Cariaco surface water indicates that ~20% of the local river discharge during September is needed to decrease the surface salinity by 0.55 ‰. Monthly sea surface salinity in Cariaco Basin is highly correlated with monthly Neverí River discharge rate ( $R^2 = 0.76$ ; Figure 7). Unfortunately there are no oxygen isotope measurements for the local rivers that flow into the Cariaco Basin. Even though the outflow from the Amazon and Orinoco rivers has little effect on the Cariaco Basin hydrography the  $\delta^{18}\text{O}_w$  of the Amazon [Karr and Showers, 2002] and the Orinoco [Guilderson, 1997] river water have been measured at  $-5.5\text{‰}$  to  $-5.0\text{‰}$ , respectively. If we were to assume a  $\delta^{18}\text{O}_w$  river water of  $-5.5\text{‰}$ , and salinity 0‰ we estimate the mean annual fraction of river water at the Cariaco Station is ~2%. Though, as we highlight, the influence of rivers is dominant for only part of the year during the late summer and fall (Figure 3c).

### 6.3. The $\delta^{18}\text{O}_{sw}$ :Seawater Salinity Relationship

[26] There is a linear covariance between the  $\delta^{18}\text{O}$  of seawater and salinity for the entire data set ( $R^2 = 0.50$ ; Figure 5a and Table 1). The standard error of the slope (0.34) and  $y$  intercept ( $-11.48$ ) are  $\pm 0.03$  and  $\pm 1.23$  respectively. In order to better evaluate the effect of seasonal differences in the climate regime of the Cariaco Basin and the impact of local rivers on the isotopic composition of seawater, we examine the  $\delta^{18}\text{O}_w$ :salinity relationships for individual months (Table 1). These seasonal differences are reflected in the zero-salinity end-members.

A positive correlation exists between  $\delta^{18}\text{O}$  and salinity for all months except July 1996 (Table 1). The inverse correlation for July may be due to the brief secondary upwelling events of subtropical underwater that occur during this month [Astor *et al.*, 2003; Muller-Karger *et al.*, 2004]. This secondary upwelling also is responsible for the minor cooling in the upper 25 m from July to August (Figure 4a). Coincident with the cooling is an increase in subsurface salinities (15–35 m) reaching a maximum of 36.99‰ during the study period (Figure 4b). The highest  $\delta^{18}\text{O}_w$  value (1.13‰) during August 1996 is also measured at 35 m. However, while salinity increases at 15–35 m the  $\delta^{18}\text{O}_w$  values slightly decrease. Additionally the surface  $\delta^{18}\text{O}_w$  values decrease from July to August and this is attributed to freshwater input from local rivers.

[27] Surface  $\delta^{18}\text{O}_w$  values during September 1996 also are low in association with a warming and freshening of surface waters. The largest decrease in  $\delta^{18}\text{O}_w$  from August to September occurs in the subsurface at 25–55 m. The shallow slopes of the  $\delta^{18}\text{O}_w$ :salinity relationship observed during September ( $-3.14$ ) and October ( $-5.12$ ) are attributed to changes in freshwater input from the local rivers (Table 1 and Figure 3c). There is an overall decrease in  $\delta^{18}\text{O}_w$  from October to November for all depths, also suggesting freshwater input into the Cariaco Basin. Conversely, salinity increases slightly in the upper 25 m (Figures 4b and 4c) and the  $\delta^{18}\text{O}_w$ :salinity relationship for November does not suggest freshwater input (Table 1). There is very little difference in the  $\delta^{18}\text{O}_w$  values from 15 to 100 m during this month. The month of November is characteristically a transition month into the upwelling season as the ITCZ migrates southward.

**Table 2.** The  $\delta^{18}\text{O}_{\text{sw}}$ :Salinity Relationship for the Upwelling and Nonupwelling Seasons in the Cariaco Basin Where  $\delta^{18}\text{O}_{\text{sw}} = m(\text{salinity}) + b$

Depth	Upwelling				Nonupwelling			
	n	m	b	R <sup>2</sup>	n	m	b	R <sup>2</sup>
Surface	6	0.80 (±0.08)	−28.53 (±3.0)	0.96	6	0.27 (±0.04)	−8.77 (±1.3)	0.93
Upper 25 m average	6	0.69 (±0.24)	−24.43 (±8.7)	0.68	6	0.34 (±0.09)	−11.5 (±3.4)	0.77

[28] The annual upwelling season begins during November and December of each year [Astor *et al.*, 2003; Muller-Karger *et al.*, 2004]. Although the Neveří River discharge is declining at this time, the  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship observed during December 1996 is very similar to that of September and October suggesting additional freshwater input into this region possibly from the Tuy River (Table 1). While December surface salinities are similar to those for November, the subsurface salinities at 15–25 m decrease from November to December (Figure 4b). Concurrent with the observed freshening is also warming of subsurface waters. It is possible that upwelling initiated in November 1996 because of strong zonal winds and then briefly subsided during December allowing for lateral advection at the subsurface. The  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship determined for December 1996 is very similar to the observed surface water  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship from La Parguera, Puerto Rico [Watanabe *et al.*, 2001]. However, unlike our observations for Cariaco Basin, the seasonal trend of La Parguera surface water  $\delta^{18}\text{O}$  follows local precipitation. Nonetheless, the slope of 0.21 for the December equation is comparable to previously determined slopes from other tropical, semienclosed seas [Rostek *et al.*, 1993; Schmidt, 1999]. Watanabe *et al.* [2001] suggest that the  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship for the region near Puerto Rico may be affected by discharge from the Orinoco River. This has also been suggested for the  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship of Barbados surface waters [Guilderson, 1997]. The relationship observed in October 1996 in the Cariaco Basin is very similar to that observed in Barbados surface waters (Table 1). Given that the  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship in both regions is influenced by a freshwater component this similarity is not surprising.

#### 6.4. Surface $\delta^{18}\text{O}_{\text{sw}}$ :Seawater Salinity Relationship

[29] The surface water data reveal two distinct trends that represent the upwelling (dry) and nonupwelling (wet) seasons in the Cariaco Basin

(Figure 5b and Table 2). The zero salinity intercept of the  $\delta^{18}\text{O}_{\text{w}}$  versus salinity regression is −8.77 for the nonupwelling season and −28.53 for the upwelling months. Furthermore, the data from both December 1996 and 2005 fall on the nonupwelling trend. Taking into consideration the composite hydrographic data and the  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship or these months, upwelling likely subsided during December in both years. The standard error of  $\delta^{18}\text{O}_{\text{w}}$  for known salinity from the upwelling and nonupwelling seasons is 0.02 and 0.01, respectively. Conversely, for known  $\delta^{18}\text{O}_{\text{w}}$ , the standard error in salinity from the upwelling and nonupwelling seasons is 0.02 and 0.04, respectively.

[30] A growing number of studies have combined the oxygen isotopic and trace element composition of foraminiferal calcite in an attempt to extract the  $\delta^{18}\text{O}_{\text{w}}$  signal and reconstruct past salinity variations [Stott *et al.*, 2002; Schmidt *et al.*, 2004; Stott *et al.*, 2004; Weldeab *et al.*, 2006]. However, on the basis of other observations, it is clear that caution must be taken when reconstructing sea surface salinity since one salinity: $\delta^{18}\text{O}_{\text{w}}$  equation may not define a region.

[31] While our results for the nonupwelling season yield a salinity:  $\delta^{18}\text{O}_{\text{w}}$  relationship that is very similar to other studies in the tropical Atlantic [Guilderson, 1997; Watanabe *et al.*, 2001], the difference between upwelling and nonupwelling indicates that potential problems might arise when using the  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship for paleoclimate reconstructions, particularly in regions where the relationship varies seasonally. The samples of Watanabe *et al.* [2001] and Guilderson [1997] were collected from regions that experience pronounced hydrologic changes from precipitation and/or river input. Our equation generated from the nonupwelling season that is most similar to these studies is also generated during the wet season in Cariaco Basin, a time of enhanced hydrologic changes in the surface waters. Our data suggests that these equations are not appropriate for paleoclimate reconstructions generated from the open Caribbean [Schmidt *et al.*, 2004], a region

that is not affected by enhanced hydrologic changes from precipitation and/or freshwater discharge. In addition, *Weldeab et al.* [2006] use the available global database (G. A. Schmidt et al., Global Seawater Oxygen-18 Database, 1999, <http://data.giss.nasa.gov/o18data/>) to generate an equation for the western tropical Atlantic using seawater samples collected at 2–50 m water depth. The equation in this study (Table 1) is most similar to our equations generated during the upwelling months.

### 6.5. Planktonic Foraminiferal $\delta^{18}\text{O}$ and Salinity Estimates

[32] Both foraminifera and coral  $\delta^{18}\text{O}$  have the ability to track seasonal climate changes which is particularly important for reconstructing climate systems such as the ENSO and seasonal upwelling. Whereas coral paleothermometry relies on the accuracy of surface water relationship, studies using foraminifera for paleoclimate reconstructions must take into account the depth distribution of foraminifera, as well as consider if the sediment record is weighted toward a particular season. For example, *Tedesco et al.* [2007] showed that the oxygen isotopic composition of *G. ruber* (pink) is a good indicator of annual average SST, while *G. bulloides*  $\delta^{18}\text{O}$  primarily represents SST during the upwelling season in the Cariaco Basin.

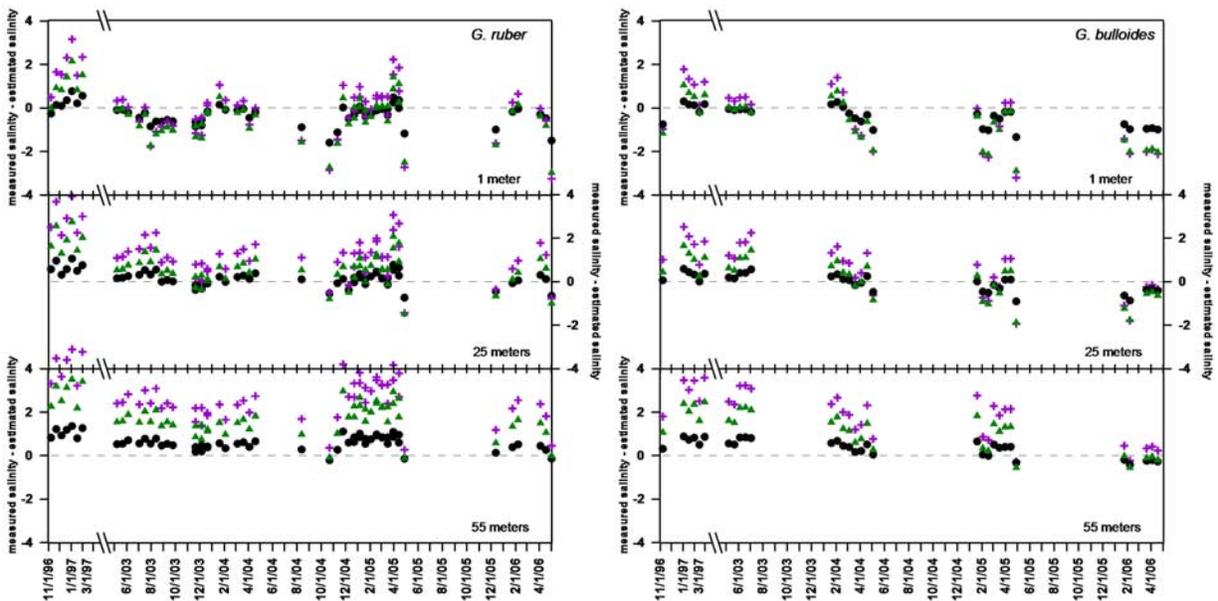
[33] In order to further evaluate the nature of the  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationships we have applied the Cariaco surface water equations for the upwelling and nonupwelling seasons to  $\delta^{18}\text{O}$  measurements made on planktonic foraminifera from the sediment trap time series. The seasonal variability in the occurrence and isotopic composition of foraminiferal species in the Cariaco basin has been previously described by *Tedesco and Thunell* [2003b] and *Tedesco et al.* [2007]. We measured the oxygen isotopic composition of *G. ruber* and *G. bulloides* collected during the months corresponding to the seawater oxygen isotope measurements. Using measured seawater temperature and  $\delta^{18}\text{O}_{\text{w}}$  we calculate calcite equilibrium profiles for *G. ruber* and *G. bulloides* utilizing the high light paleotemperature equations generated by *Bemis et al.* [1998] for *O. universa* and *G. bulloides*, respectively (Figure 6):

$$T(^{\circ}\text{C}) = 14.9 - 4.80(\delta_{\text{c}} - \delta_{\text{w}}) \quad (2)$$

$$T(^{\circ}\text{C}) = 13.2 - 4.89(\delta_{\text{c}} - \delta_{\text{w}}) \quad (3)$$

*Bemis et al.* [1998] demonstrated that the *O. universa* equation is also applicable to *G. ruber*. In addition, we use the above equations to calculate the predicted calcite equilibrium profiles for each species using measured seawater temperature and assuming an  $\delta^{18}\text{O}_{\text{w}}$  value of 0.81‰ PDB, the average for the surface waters over the entire study period (Figure 6). The two approaches yield very little difference in the equilibrium profiles. Assuming that the foraminiferal  $\delta^{18}\text{O}$  values are in isotopic equilibrium with the surrounding seawater, the depth of calcification for both species varies from the 1996–1997 to the 2005–2006 upwelling seasons. *Tedesco et al.* [2007] showed that *G. ruber* and *G. bulloides* live in the surface mixed layer but that their depth habitats vary seasonally and interannually in response to changes in hydrography in the Cariaco Basin. Overall, *G. ruber* and *G. bulloides* have higher  $\delta^{18}\text{O}$  values, suggesting they calcified deeper in the water column during December, January, and February (DJF) 2005–2006 compared to DJF 1996–1997. However, the hydrography during DJF in 2005–2006 is very similar to that in 1996–1997. The difference in calcification depth may be due to food availability rather than hydrographic conditions.

[34] To assess the accuracy of the  $\delta^{18}\text{O}_{\text{w}}$ :salinity equations generated from the composite data set and the surface water data sets for the upwelling and nonupwelling season we compare measured seawater salinity with calculated seawater salinity at various water depths. The measured seawater temperature is combined with the  $\delta^{18}\text{O}_{\text{c}}$  of *G. ruber* and *G. bulloides* for various months from 1996 to 2006 to calculate  $\delta^{18}\text{O}_{\text{w}}$ . The calculated salinities are compared to measured seawater salinities at 1 m, 25 m, and 55 m water depth (Figure 8). The estimated salinities generated from the upwelling season  $\delta^{18}\text{O}_{\text{w}}$ :salinity relationship (Table 2) for both *G. ruber* and *G. bulloides* are very similar to measured salinities at each depth. The average difference between measured and estimated salinity using this equation ranges from 0.32‰ at 25 m to 0.64‰ at 55 m for *G. ruber* and 0.32‰ at 25 m and 0.47‰ at 55 m for *G. bulloides*. Overall the largest offset between estimated salinities generated from all three equations and the measured salinities is at 55 m indicating that the oxygen isotope composition of both *G. ruber* and *G. bulloides* represent conditions in shallower water. The equation generated from the nonupwelling season with zero salinity intercept of  $-8.77$  does a poor job at accurately estimating salinity and consistently overestimates the measured value below the sur-



**Figure 8.** Difference in measured versus calculated salinities at different depths of calcification utilizing measured seawater temperature and the  $\delta^{18}\text{O}_c$  of (left) *G. ruber* and (right) *G. bulloides*. The calculated salinities are generated from three  $\delta^{18}\text{O}_w$ :salinity equations: triangles indicate the composite data set trend and the surface water trend from the upwelling (dots) and nonupwelling (crosses) seasons.

face. Interestingly there is also seasonal variability apparent in the estimated salinities. For *G. ruber*, all equations underestimate salinity in the surface water from about July through January. In contrast, for *G. bulloides*, all of the equations underestimate salinity during February through May. In addition, the *G. bulloides* record shows a general trend of decreasing salinities from 1996 to 2006, a reflection of the oxygen isotopic composition trending toward heavier values. On the basis of our data set we can extract high temporal resolution of salinity using the  $\delta^{18}\text{O}_c$  and the  $\delta^{18}\text{O}_w$ :salinity relationship generated from the upwelling season.

[35] Rohling [2007] effectively attributes the large uncertainty in paleosalinity estimates due to temporal variability in the  $\delta^{18}\text{O}_w$  versus salinity regression. Model simulations have demonstrated the potential change in the  $\delta^{18}\text{O}_w$ :salinity relationship on decadal and millennial time scales due to changes in the tropical hydrologic cycle [LeGrande and Schmidt, 2006; Oppo et al., 2007; Schmidt et al., 2007]. Herein, we demonstrate that there is significant seasonal variability in the salinity:  $\delta^{18}\text{O}_w$  relationship in the Cariaco Basin. This is important because this basin is the focus of considerable paleoclimate interest. On the basis of error propagation of various methods the uncertainty in reconstructed  $\delta^{18}\text{O}_w$  is  $\sim \pm 0.20\text{--}0.25\%$

[Weldeab et al., 2006; Rohling, 2007]. This results in a standard error in paleosalinity of  $\sim \pm 1\%$  shown in multiple studies. Assuming an uncertainty in  $\delta^{18}\text{O}_w$  of  $\pm 0.25\%$  we also calculate an error of  $\pm 1\%$  in salinity estimates using our nonupwelling equation. However, this error is reduced to  $\pm 0.3\%$  when using our equation generated from the upwelling season.

[36] Previous studies assessing the  $\delta^{18}\text{O}_w$ :salinity relationship in the tropics have made measurements on surface waters [Fairbanks et al., 1997; Watanabe et al., 2001] and further applied these relationships to reconstruct salinity using coral  $\delta^{18}\text{O}$ . In contrast studies that have collected  $\delta^{18}\text{O}_w$  and salinity at discrete depths (GEOSECS) at multiple geographic locations assess spatial variability but not temporal variability. Our data set is unique in that we are able not only able to assess the surface water  $\delta^{18}\text{O}_w$ :salinity relationship but also the seasonal variability in the  $\delta^{18}\text{O}_w$ :salinity relationship. Paleoclimate reconstructions have demonstrated that the tropics is sensitive to changes in the location of the ITCZ in the past [Peterson et al., 2000; Haug et al., 2001] and these changes have the potential to affect the  $\delta^{18}\text{O}_w$ :salinity relationship. Given that paleoclimate studies assume no temporal variability in this relationship care must be taken to avoid overestimating past

seawater salinity in a region that may have experienced intervals of enhanced climate variability, such as changes in upwelling or riverine input.

## 7. Conclusion

[37] This is the first study to evaluate both monthly and seasonal changes in the  $\delta^{18}\text{O}_w$ :salinity relationship in a tropical region. We attribute the monthly and seasonal variability in this relationship in the Cariaco Basin to changes in riverine input by the Unare, Neverí and Tuy Rivers. Furthermore, precipitation has little direct effect on the oxygen isotopic composition of surface waters in this region. For paleoceanographic and paleoclimatic reconstructions, the  $\delta^{18}\text{O}_w$ :salinity relationship can be used in conjunction with past ice volume measurements to determine paleosalinities and our calibration generated from samples collected during the upwelling season may also be useful for estimating paleosalinity from  $\delta^{18}\text{O}$  records from the Caribbean Sea. Measurements of paleosalinity will aid our understanding of past changes in the hydrologic cycle. However, as we have illustrated, the temporal variability in  $\delta^{18}\text{O}_w$ :salinity relationship is an important consideration in paleoceanographic reconstructions and one equation may not define a region.

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