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Oxygen isotope values of precipitation and surface waters in northern Central America (Belize and Guatemala) are dominated by temperature and amount effects

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ABSTRACT

An understanding of the climatic controls on precipitation $\delta^{18}O$ is required to interpret isotopic records of paleoclimate and paleoaltimetry. However, variations in precipitation $\delta^{18}O$ in time and space are only poorly known in northern Central America. To test the hypothesis that precipitation and surface water $\delta^{18}O$ values are dominated by temporal and spatial amount effects, we analyzed $\delta^{18}O$ in surface waters collected from Guatemala and Belize, and in precipitation from the Global Network for Isotopes in Precipitation database for Veracruz, Mexico, and San Salvador, El Salvador. Herein we show that the dominant controls on $\delta^{18}O$ values of precipitation and surface waters are fairly simple. Temporally, the dominant control on precipitation $\delta^{18}O$ values is the amount effect, whereby there is an inverse correlation between rainfall amount and $\delta^{18}O$. Precipitation $\delta^{18}O$ values decrease by 1.24‰ per 100 mm increase of monthly rainfall. Spatially, only two variables – distance from the coast and mean catchment altitude – explain 84% of the surface water $\delta^{18}O$ variability. Surface water $\delta^{18}O$ values show an altitude effect of −1.9 to −2.4‰ km^{-1} and a continental effect of 0.69‰ per 100 km once corrected for altitude effects. A decrease in surface water $\delta^{18}O$ by 3 to 4‰ from the Caribbean Sea to the Pacific Ocean is evident as an isotopic rain shadow on the Pacific slope. Our data also show that river waters in this humid tropical environment are good proxies for $\delta^{18}O$ values of precipitation in northern Central America. The Guatemala/Belize surface water line is defined as $\delta D = 8.0 \times \delta^{18}O + 8.7$, which is similar to the meteoric water line at San Salvador of $\delta D = 8.1 \times \delta^{18}O + 10.9$. Spatial variability in $\delta^{18}O$ values is interpreted to reflect 1) progressive rainout of Caribbean-sourced air masses upon traverse of Central America, and 2) the temperature-dependent equilibrium fractionation between vapor and condensate related to the altitude effect. The data show that the northeast trade winds are the dominant moisture source to Central America, mixing with Pacific-derived moisture west of the cordilleran divide.

1. Introduction

1.1. Background and project rationale

Stable isotope values of tropical precipitation are important indicators of modern climate dynamics (Johnson and Ingram, 2004; Vuille and Werner, 2005; Cobb et al., 2007), and vary due to several climate "effects" including the amount, continental, temperature, and altitude effects (Dansgaard, 1964; Rozanski et al., 1993). $\delta^{18}O$ values of modern precipitation are valuable tools for understanding regional climate dynamics and moisture sources (Friedman et al., 2002; Aggarwal et al., 2004) and for tracking changes in atmospheric circulation on modern and Quaternary time scales (Charles et al., 1994; Alley and Cuffey, 2001; Schmidt et al., 2007). In the tropics, precipitation $\delta^{18}O$ has been used to understand the effects of the El Niño/Southern Oscillation (Vuille et al., 2003; Cobb et al., 2007; Lachniet, 2009b), for understanding monsoon dynamics (Johnson and Ingram, 2004; Vuille et al., 2005), and for modeling rainout processes across continents (Grootes, 1993; Vuille and Werner, 2005; Lachniet et al., 2007). Understanding the effects of modern climate dynamics on $\delta^{18}O$ values of precipitation is essential for understanding past climates, as revealed by tropical and high latitude ice cores (Thompson et al., 2000; EPICA-community-members, 2004; NGRIP-Members, 2004), lake sediment (Hodell et al., 2008; Seltzer et al., 2000), and cave calcite speleothems (Fairchild et al., 2006; Lachniet, 2009a).

Stable isotope values of authigenic minerals have also been used to estimate paleoaltimetry, as summarized in several recent reviews (Poage and Chamberlain, 2001; Blisniuk and Stern, 2005; Rowley, 2007; Rowley and Garzione, 2007). However, knowledge of atmospheric circulation is required to interpret stable isotope values of authigenic minerals, because variations in air mass rainout may result in $\delta^{18}O$ variations in the absence of an altitude effect. Such variations

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in air mass history may have a large effect on tropical rain δ^{18}O values (Vuille and Werner, 2005; Schmidt et al., 2007; Sturm et al., 2007), and are important in areas that contain orographic barriers that result in isotopic rain shadows. Isotopic rain shadows in the lee of mountain ranges were suggested to be characteristic of regions with one dominant wind direction (Blisniuk and Stern, 2005), but have only been previously documented in the mid-latitude westerly regions. The presence of isotopic rain shadows in the lee of tropical mountain ranges has not been clearly demonstrated.

The process by which air masses become depleted in heavy isotopes (^{18}O, ^{2}H) in precipitation is due to isotopic distillation. Rayleigh distillation models relate the δ^{18}O value of precipitation to two dominant variables: temperature, which controls the equilibrium fractionation (α) between vapor and condensate, and the fraction of moisture removed from a given air mass (f). Rayleigh distillation can be modeled according to

$$R = R_o f^{(\alpha - 1)}$$

where R is the isotopic ratio and R_o is the initial isotopic ratio (Clark and Fritz, 1997). The climatically-relevant parameters for precipitation δ^{18}O values are the vapor condensation temperature and fraction of moisture remaining (f), which itself is related to the drop in temperature of the air mass over time that is required to provoke progressive condensation. The actual δ^{18}O value of tropical precipitation, and hence surface waters, is also related to variations in moisture sources and in-cloud microphysical processes (Bony et al., 2008; Risi et al., 2008). In reality, precipitation δ^{18}O variability also results from changes in moisture source, moisture recycling, and moisture mass mixing.

Networks of precipitation collection stations have been established to investigate the climate controls on δ values (IAEA/WMO, 1998). However, knowledge of the climatic controls on precipitation δ^{18}O values on a regional scale is hampered by the lack of a sufficiently-dense network of precipitation sampling stations. This problem is particularly acute in mountainous regions where δ^{18}O values of precipitation may vary dramatically over short distances due to altitude effects and microclimates, and in developing countries where financial considerations prohibit stable isotope sampling efforts. These problems may be partially overcome by the dense spatial sampling of non-evaporative surface waters (Kendall and Coplen, 2001), which in humid tropical Central America have been demonstrated to be good proxies for δ^{18}O and δD values of rainfall (Lachniet and Patterson, 2002; Lachniet and Patterson, 2006). Such a protocol may allow quantitative estimation of the isotope/climate gradients, as well as to test hypotheses of the controls on δ values. Such an analysis is important in Central America, for example, because an estimated 80–90% of the

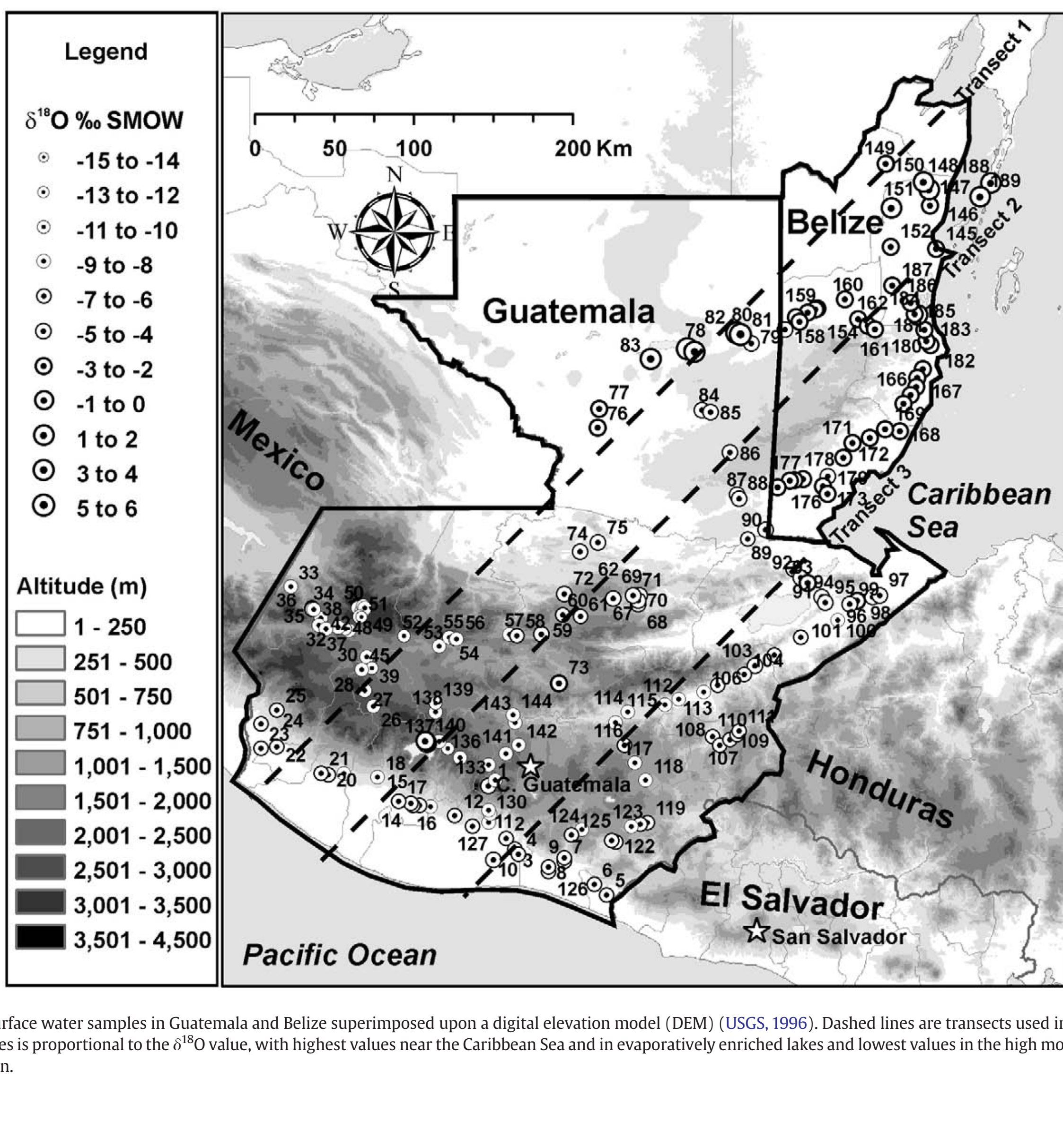

Fig. 1. Map of surface water samples in Guatemala and Belize superimposed upon a digital elevation model (DEM) (USGS, 1996). Dashed lines are transects used in Fig. 7. The size of the sample circles is proportional to the δ^{18}O value, with highest values near the Caribbean Sea and in evaporatively enriched lakes and lowest values in the high mountains and along the Pacific Ocean.

population relies upon groundwater for drinking water (Bundschuh et al., 2007b), that is ultimately derived from precipitation. Further, an understanding of the climate controls on surface waters is required for prudent water resource management (Bergstrom and Cardona, 2007) and effective exploitation of hydrothermal energy (Birkle and Bundschuh, 2007).

Based on our previous results from southern Central America (Lachniet and Patterson, 2002; Lachniet and Patterson, 2006; Lachniet et al., 2007), we hypothesize that spatial variations in surface water δ^{18}O values are controlled primarily by rainout along a path away from the Caribbean Sea. To test this hypothesis, we sampled 186 waters in Guatemala and Belize (Fig. 1), spanning the entire breadth of Central America from the Caribbean Sea to the Pacific Ocean. Additionally, we analyzed the temporal rainfall δ^{18}O variability in two isotope monitoring stations at Veracruz, Mexico, and San Salvador, El Salvador (IAEA/WMO, 1998) to evaluate the amount effect and to provide context for the surface water analyses. Herein, we show a decrease in δ^{18}O values from the Caribbean Sea to the Pacific Ocean, the presence of a well-developed isotopic rain shadow, and a well-constrained altitude effect. Temporally, δ^{18}O variation is dominated by the amount effect. Our results provide valuable calibration data for regional-scale general circulation models that attempt to model δ^{18}O variations in areas of mountainous topography.

1.2. Physiography and climate of Guatemala and Belize

Guatemala and Belize, in northern Central America (Fig. 1), consist of broad Caribbean lowlands and volcanic and sedimentary highlands (with altitudes reaching 4220 m atop Tajamulco volcano) (Marshall, 2007; Bundschuh et al., 2007b). The volcanic and sedimentary cordilleras are separated by the Motagua fault zone and parallel the Pacific Coast, with large areas above 2500 m altitude (Fig. 1). The broad karst lowlands (Day, 2007) along the Caribbean and Yucatan Peninsula (the Petén) are typically <500 m altitude, with the exception of the Maya mountains in eastern Guatemala and southwestern Belize. The cordilleras span the length of Guatemala without significant gaps, such as are common farther north in Mexico (Tehuantepec Gap), Costa Rica/Nicaragua (Papagayo Gap) and Panama (Canal Zone) (Xie et al., 2005). The lack of gaps forces air masses to ascend over the Guatemalan cordilleras, which are oriented approximately perpendicular to the dominant NE trade wind direction. Because most of the region is mountainous, rainfall is quickly fed into stream systems where runoff is high (Bundschuh et al., 2007b). In lowland areas, base flow may be an important contributor to stream discharge.

The climate of Guatemala (Portig, 1965; Bundschuh et al., 2007b) is humid tropical and varies due to geographic location. The study area is influenced by the North Atlantic subtropical high pressure cell (boreal winter), and borders the warm waters of the Western Hemisphere Warm Pool (Wang and Enfield, 2003). Regional atmospheric circulation is dominated by the north easterly trade winds and moisture convergence in the Intertropical Convergence Zone (ITCZ) during the boreal summer, when southern hemisphere southeasterly trade winds are displaced north of the equator and converge with the northeast trade winds (Barlow et al., 1998). Near-surface winds in Guatemala (Fig. 2) are related to topography and convergence over the high cordillera (INSIVUMEH, 2009). On the Pacific slope, onshore winds are primarily southerly, converging with the easterly trade winds near the cordilleran crest. This wind configuration suggests that convection over the cordilleras is an important control on mean annual wind direction that supplies both Pacific and Caribbean moisture to the country, consistent with the regional circulation (Barlow et al., 1998).

Seasonality is expressed most strongly in terms of rainfall variation. Most locations (INSIVUMEH, 2008) on the Pacific slope and interior of Guatemala experience a boreal summer wet season from May to November, and a winter dry season. Puerto Barrios on the Caribbean Coast is wet year round, but experiences a precipitation maximum in summer (Fig. 2) and again during the late Fall. The wet season is dominated by the migration of the Intertropical Convergence Zone over Central America (Portig, 1965; Hastenrath, 1967; Hastenrath, 2002; Poveda et al., 2006). The Pacific coast experiences a short mid-summer drought (Poveda et al., 2006) during July and August (*e.g.* at Huehuetenango and Guatemala City). The zone of highest rainfall (Fig. 2) midway up the Pacific side of the volcanic cordillera likely reflects orographic precipitation associated with rising Pacific air masses. Microclimates in the deep valleys of southeastern Guatemala (as at La Fragua) show low rainfall totals.

Mean annual temperature varies from 26.6 to 27.4 °C near sea level at Puerto Barrios (Caribbean Coast) and Puerto San José (Pacific Coast), respectively, to 14.2 °C in Todos Santos Cuchumatán at 2480 m (Fig. 2). Temperature seasonality is typically less than 5 °C, in marked contrast to the large precipitation seasonality, with a peak in the spring before the arrival of the ITCZ. The temperature lapse rate is -5.7 °C km^{-1} with the altitude of the 0 °C isotherm at 4844 ± 230 m, based on analysis of Guatemala climate data (INSIVUMEH, 2008).

1.3. Previous stable isotope research in Guatemala and Belize

There have been few isotope climatology studies in Guatemala and Belize. A basic summary of station δ^{18}O characteristics was presented for Central and South America (Rozanski and Araguás-Araguás, 1995), with a demonstration of altitude, amount, and continental effects. Surface water samples from Belize were analyzed for δ^{18}O and δD (Marfia et al., 2004), and for geothermal studies (Birkle and Bundschuh, 2007). Isotope values of the Zuníl geothermal field on the Pacific slope of western Guatemala show that most spring waters fall near the Global Meteoric Water Line (GMWL) (Fournier et al., 1982; Birkle and Bundschuh, 2007). Deep geothermal waters show increased δ^{18}O and δD values relative to the GMWL, indicating mixing between meteoric and altered geothermal waters. δ^{18}O and δD values of Ca–HCO_3- and Na–HCO_3-type waters from thermal springs near San Marcos (Pacific slope of northwestern Guatemala) plot on the meteoric water line and have δ^{18}O values of -10.4 to -11.0‰ (Marini et al., 1998). The low spread in δ^{18}O values is indicative of groundwater homogenization. Michatoya river spring waters near Lago Amatitlán plot on the GMWL with δ^{18}O values of -8 to -10‰ (Giggenbach, 1992; Birkle and Bundschuh, 2007). A local meteoric water line of $\delta D = 7.6 \times \delta^{18}O + 6.7$ was defined based on meteoric waters from the Pacific slope of eastern Guatemala (Tecuamburro Volcano) (Janik et al., 1992; Birkle and Bundschuh, 2007). These data also show an altitude effect of -3.0‰ km^{-1} ($r = -0.81$). A water line based on those samples of presumed meteoric origin (Giggenbach, 1992; Janik et al., 1992; Marini et al., 1998) yields a MWL of $\delta D = 7.9 \times \delta^{18}O + 8.9$.

2. Methods

We analyzed the Guatemala and Belize surface waters for δ^{18}O and δD at the Stable Isotope Laboratory at the University of Saskatchewan. The samples were collected between June 9 and 19, 2007 for Guatemala and February 16 through 22, 2008 for Belize. The waters were sampled along the road network by dropping a bucket from bridges. In a few cases, tap water was collected where surface waters were not present, a cave drip water from Lanquín Cave (Bundschuh et al., 2007a) was collected, and several springs and lakes were also sampled. The samples were collected in 30 ml Nalgene bottles with no air headspace, with the cap sealed by electrical tape. Sample elevations ranged from sea level to 3700 m.

δ^{18}O and δD values were determined on a ThermoElectron high-temperature conversion elemental analyzer (TC/EA) using a continuous

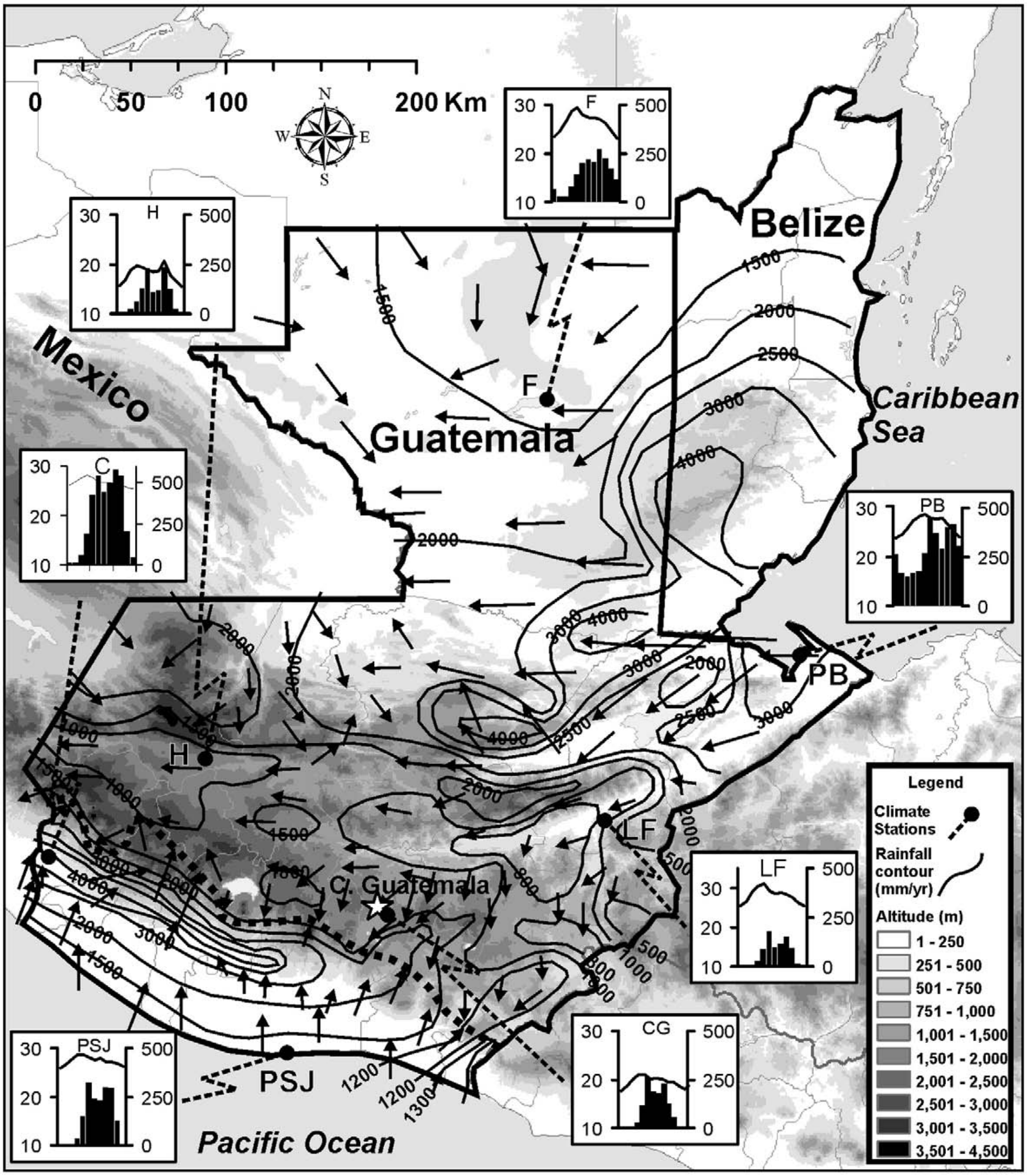

Fig. 2. Climate map for Guatemala. Mean annual precipitation isohyets (in mm), wind vectors, superimposed upon a digital elevation model. The contour intervals were digitized from the original base map (INSIVUMEH, 2009). Mean annual wind direction for Guatemala shows that the trade winds are primarily northeasterly on the Caribbean slope and are channeled by surface topography. On the Pacific slope winds are onshore southerlies. The dotted line is the zone of wind convergence and is oriented approximately along the Cordilleran Crest. Selected climate stations are: Catalina (C), Huehuetenango (H), Puerto San José (PSJ), Puerto Barrios (PB), Ciudad de Guatemala (CG), La Fragua (LF), and Flores (F), and their monthly climate data (*x*-axis) in the graphs are monthly median temperature (line, in °C; left *y*-axis) and monthly rainfall (bars, in mm; right *y*-axis).

flow pyrolysis technique. Approximately 10 µl of water was injected via septa into the TC/EA with a GC PAL auto-sampler using a 10 µl syringe, which was reacted in a ceramic column lined with glassy carbon and packed with glassy carbon fragments at 1450 °C and reduced to CO and H_2 gases. The gases were carried by high purity helium and separated in a gas chromatograph at 90 °C and interfaced with a Delta Plus XL mass spectrometer via a Conflo-III open split. δ values were determined by analysis relative to four internal standards that were calibrated to VSMOW, SLAP, and GISP standards. Repeated injections and analysis was done to ensure a minimal memory effect, and final δ values are reported in standard δ-‰ notation, with precisions better than ± 0.3‰ for $\delta^{18}O$ and 3‰ for δD. Deuterium excess values (d) were calculated by $d = \delta D - 8 \times \delta^{18}O$.

Physiographic data for each sample were gathered in the field and in a Geographic Information System (GIS). Variables tabulated include latitude, longitude (and their UTM derivatives), sample altitude, stream head altitude and spatial coordinates, median stream altitude, mean catchment altitude, catchment area, distances from the Pacific Ocean and Caribbean Sea for sample location and stream heads (measured along a NE/SW axis comparable to trade wind direction), stream length above the sample, estimated mean annual precipitation at the sampling location, and estimated cumulative rainfall amount (m^3) along one of three precipitation transects (Fig. 1) away from the Caribbean Sea to approximate the passage of air masses borne by the northeasterly trade winds. We determined mean catchment altitude, because it is the most climatically-relevant altitude parameter as it takes into account drainage basin hypsometry, and is commonly used for paleoaltimetry studies (Stern and Blisniuk, 2002; Blisniuk and Stern, 2005; Rowley and Garzione, 2007). The stable isotope and physiographic data for the water samples are shown in the Supplementary materials.

A subset of data containing only rivers was analyzed statistically by linear and multiple regression (Brown, 1993; Brown, 1998), similar to previous efforts (Lachniet and Patterson, 2006). Multiple regression allows for the simultaneous regression of several physical parameters against $\delta^{18}O$ values, and provides a matrix ($n \times p$) consisting of n samples and p variables (measurements). Correlation of variable and statistical significance (we accepted correlations with p-value <0.05) matrices were constructed using MatLab (Mathsoft, 2004). Multiple regression returns an equation of the general form

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + \ldots + b_xX_n$$

where Y is the predicted dependent variable, b_0 to b_x are partial regression coefficients, and X_1 to X_n are independent variables (Brown, 1993; Brown, 1998). Many of the physiographic parameters are co-linear, *e.g.* the distances from the coasts are co-linear with cumulative precipitation and with each other. Co-linearity may give artificially robust statistics if multiple co-linear variables are included in the regression model. In contrast, selection of variables that are not co-linear will maximize the accuracy of the predicted regression model while worsening the statistical fit.

3. Results and interpretation

3.1. Precipitation $\delta^{18}O$

3.1.1. Temporal $\delta^{18}O$ variability

To provide an understanding of the seasonal variation in rainfall $\delta^{18}O$ values, we statistically analyzed GNIP (IAEA/WMO, 1998) data from the two nearest stations in El Salvador and Mexico, to define local meteoric water lines (LMWL) and seasonal amount effects. The station at San Salvador, El Salvador (13.7°N, 89.12°W, 651 masl) is located on the Pacific slope ~80 km SE of the border with Guatemala and 26 km from the Pacific coast (Fig. 1). The data cover January 1968 to August 1984 with significant gaps between July 1981 and May 1983 ($n = 95$), and little or no $\delta^{18}O$ data is available for the December to March dry season when precipitation is scarce. Veracruz, Mexico (19.2°N, 96.13°W, 16 masl) is located 600 km northwest of Guatemala on the Gulf of Mexico, with data spanning April 1962 to December 1988 ($n = 130$), also with significant monthly gaps. The local meteoric water lines are $\delta D = 8.1 \times \delta^{18}O + 10.9$ for San Salvador and $\delta D = 7.1 \times \delta^{18}O + 6.3$ for Veracruz (Fig. 3). The lower slope and intercept of the Veracruz LMWL suggests that these samples have been enriched in ^{18}O, possibly due to raindrop evaporation beneath cloud base, although $\delta^{18}O$ values less than −2‰ fall closely on the global meteoric water line.

Weighted mean annual average $\delta^{18}O$ values are −6.5‰ for San Salvador and −4.0‰ for Veracruz. The seasonal cycle in $\delta^{18}O$ ranges from −1.2 to −7.8‰ in San Salvador, with lowest values during the May to November wet season when monthly rainfall totals exceed 250 mm. Similarly, the seasonal cycle for Veracruz ranges from +0.3 to −5.3‰ with lowest values in the June to November wet season when monthly rainfall totals commonly exceed 300 mm. The higher annual $\delta^{18}O$ at Veracruz relative to San Salvador is likely related to its location near the main moisture source (Gulf of Mexico and Caribbean Sea), and to evaporative effects on raindrops beneath the cloud base. Seasonal variation in $\delta^{18}O$ values demonstrates clear amount effects (Fig. 4) at both stations, most clearly observed in monthly $\delta^{18}O$ averages. The magnitude of the amount effect is −1.25‰ ($r = -0.90$) and −1.24‰ ($r = -071$) per 100 mm of monthly rain for Veracruz and San Salvador, respectively. Because $\delta^{18}O$ data from southern Central America (El Salvador, Costa Rica, Panama) do not correlate to air temperature, it is clear that the dominant control on the temporal variations in rainfall $\delta^{18}O$ near our study area is precipitation amount. In contrast, data from Veracruz do show a temperature effect of −0.58‰/°C ($r = -0.83$). The presence of combined amount and temperature effects is common in subtropical latitudes (Bowen, 2008), and the location of Veracruz in the trajectory of cold air surges from North America (Schultz et al., 1998) may influence the seasonal temperature and isotope values.

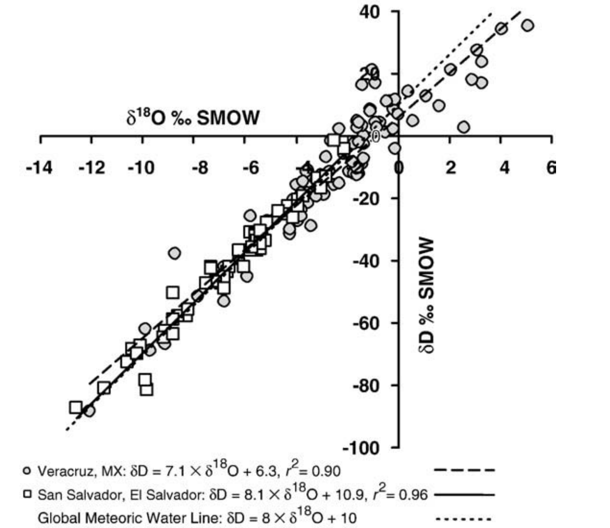

Fig. 3. $\delta^{18}O$ and δD data for Veracruz, Mexico (grey filled circles), and San Salvador, El Salvador (open squares), define local meteoric water lines. Monthly δ values for Veracruz indicate some evaporative effects and skews the local meteoric water line to a lower slope and deuterium intercept, whereas δ values for San Salvador plot closely on the global meteoric water line (dotted line).

3.2. Surface water $\delta^{18}O$

3.2.1. Surface water line

To answer whether surface water δ values are suitable proxies for precipitation, we compared the surface water line (SWL) to the GMWL (Fig. 5). The Guatemala/Belize SWL is defined as $\delta D = 8.0 \times \delta^{18}O + 8.7$, nearly identical to the GMWL of $\delta D = 8 \times \delta^{18}O + 10$ (Dansgaard, 1964), and very close to the LMWL for San Salvador. Surface water $\delta^{18}O$ values range from −12.0 to +5.2‰, averaging −6.0 ± 3.1‰ (one σ) for a total range of 17.2‰. Highest $\delta^{18}O$ values occur in the Petén lakes, that exhibit a clear evaporative trend from a source water with a $\delta^{18}O$ value of approximately −3.0‰. The evaporative lakes were not used in the calculation of the Guatemalan surface water line or in the linear and multiple regressions discussed below. The similarity of the meteoric and surface water lines shows that surface waters in northern Central America are good proxies for the isotopic composition of rainfall. The data also suggest that hydrothermal fluids are not a prominent water source to Guatemalan rivers despite the presence of active volcanism and numerous hydrothermal systems in the region (Birkle and Bundschuh, 2007).

3.2.2. Spatial isotope effects

There is a clear geographic variation in $\delta^{18}O$ values that appears dominated by 1) distance from the coasts, with highest (lowest) values along the Caribbean (Pacific), and 2) altitude effects, with highest (lowest) values in the lowlands (highlands) (Figs. 1 and 6). This variation is apparent in a plot of $\delta^{18}O$ vs. distance from the Pacific Ocean (Fig. 6), which exhibits a clear "Nike Swoosh"$^{(TM)}$ pattern. $\delta^{18}O$ values decreased from −3‰ on the Caribbean coast, to −11‰ along the cordilleran crest, and subsequently increased to −7‰ along the Pacific coast. There is no trend in deuterium excess, indicating that

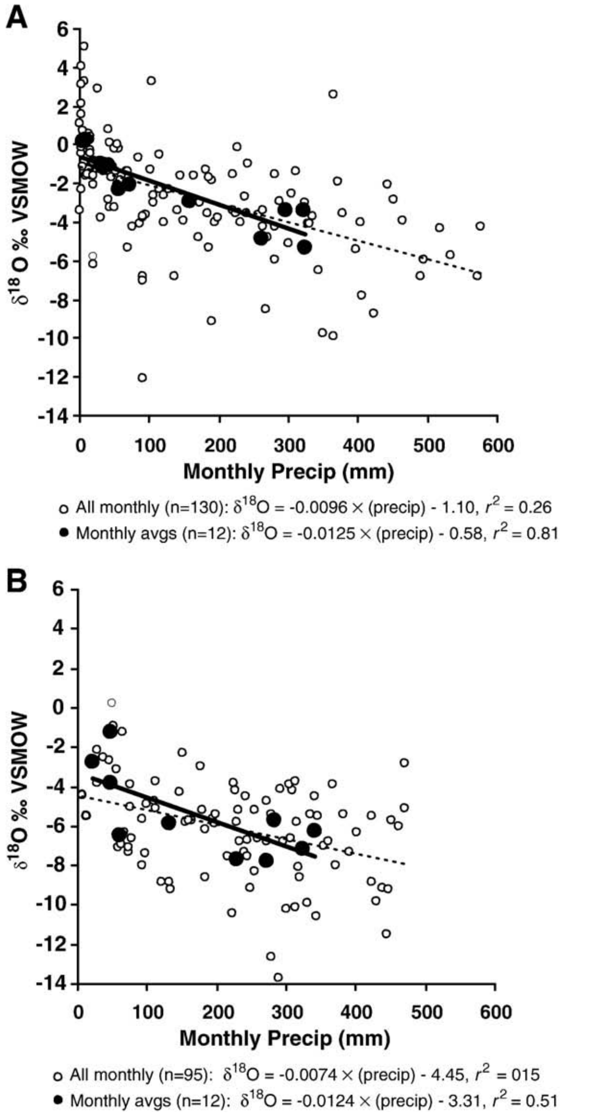

Fig. 4. The amount effect in rainfall at Veracruz, Mexico (A), and San Salvador, El Salvador (B). The mean monthly δ^{18}O/precipitation gradients are −1.25 and −1.24‰ per 100 mm of rain, respectively.

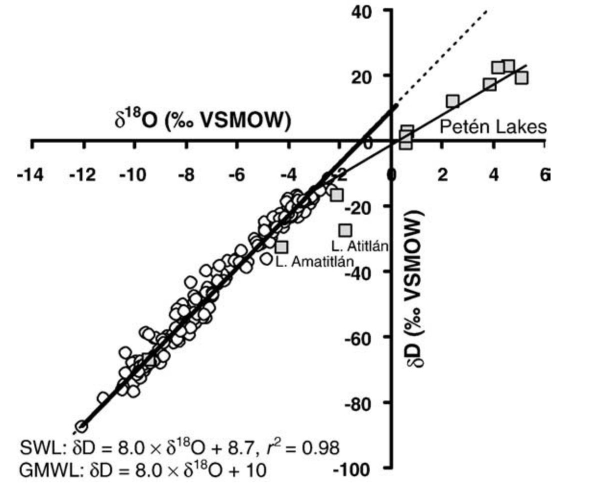

Fig. 5. δ^{18}O/δD plot showing the Guatemala and Belize surface water samples (circles) and surface water line (SWL, solid black line). The data plot on the GMWL, with the exception of lakes (filled squares) which plot along evaporation slopes with higher δ^{18}O and δD values. The Petén lakes have the highest δ^{18}O values, and their evaporation trend line suggests an initial δ^{18}O value of −3‰ where it intersects the SWL. The SWL and GMWL are highly similar, which suggests that river waters in Guatemala and Belize are good proxies for the δ^{18}O of precipitation.

moisture recycling is not a dominant factor controlling surface water δ^{18}O values, contrary to the postulation by others for Belize (Marfia et al., 2004). Lower δ^{18}O values along the isthmian crest are readily apparent in Fig. 6, because the highest peaks are aligned parallel to the Pacific coast. A plot of δ^{18}O vs. distance from the Caribbean Sea shows the same cross-Central America δ^{18}O decrease, but not the pronounced minimum because the cordillera and Caribbean coastline are not parallel. Because the spatial variation in δ^{18}O is most clearly captured by distance from the Pacific Ocean, we use this variable in subsequent analyses and plots.

The distance/δ relationship is plotted for three transects in Fig. 7 (see Fig. 1 for locations). δ^{18}O values decrease away from the Caribbean Sea, which is a prominent moisture source to Guatemala and Belize as air masses are advected with the northeasterly trade winds. δ^{18}O values are lower (by 3 to 4‰) on the Pacific side of the cordillera, demonstrating a clear isotopic rain shadow (Blisniuk and Stern, 2005). Linear regression of the measured δ^{18}O values shows a continental effect of 1.25‰ 100 km^{-1} ($r = +0.82$; Table 1). The effect is hypothesized to reflect rainout of Caribbean-sourced air masses as they traverse the isthmus, and contains an imprint of the altitude effect associated with the high cordilleras. To test this hypothesis, cumulative precipitation was estimated for the three δ^{18}O transects assuming a NE to SW passage of Caribbean moisture. The correlation between cumulative precipitation and δ^{18}O is $r = -0.86$, -0.78, and -0.65 for transects 1, 2, and 3, respectively. Thus, the decreasing δ^{18}O values with distance away from the Caribbean Sea may be best interpreted as air mass rainout along the trajectory of Caribbean-sourced moisture, and is a manifestation of Rayleigh distillation as the fraction (f) of moisture in an air mass changes (Dansgaard, 1964; Rozanski et al., 1993; Rozanski and Araguás-Araguás, 1995).

Surprisingly. there is a *positive* correlation between surface water δ^{18}O and estimated mean annual precipitation at the collection site ($r = +0.47$, $p = < 0.01$), in contrast to the well-established negative correlation of the amount effect evident in seasonal and interannual δ^{18}O precipitation values in Central America (Lachniet and Patterson, 2002; Lachniet and Patterson, 2006) and other areas in the tropics

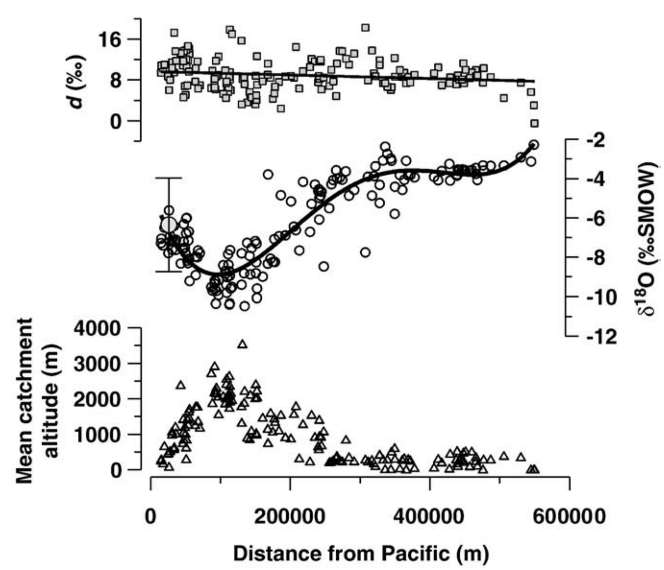

Fig. 6. Plot of surface water δ^{18}O, d, and mean catchment altitude vs. distance from the Pacific Ocean. The data show lowest δ^{18}O values in the high Cordillera that parallel the Pacific coast, and a general decrease in δ^{18}O values across Central America. The grey circle is the San Salvador annual weight-averaged δ^{18}O with one standard deviation error bars.

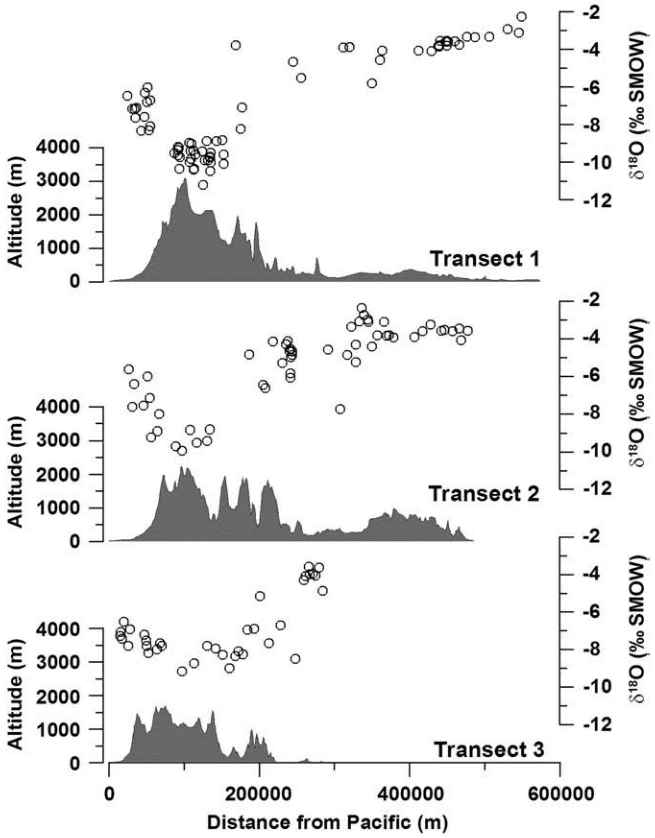

Fig. 7. Surface water $\delta^{18}O$ (circles) and topography (grey shaded profiles) along three transects across Guatemala. See Fig. 1 for locations. The Caribbean Sea is to the right and the Pacific Ocean is to the left.

(Dansgaard, 1964; Rozanski et al., 1993). The positive correlation between estimated mean annual precipitation and surface water $\delta^{18}O$ values demonstrates that regional rainout is a more important control than local rainout amount for spatial variation in surface water $\delta^{18}O$.

The clear $\delta^{18}O$ minimum over the high cordillera is evidence for a clear altitude effect (Fig. 7). Minimum $\delta^{18}O$ values appear related to the altitude of the Cordilleran crest, with values reaching −10 to −11‰ for transect one (crest at ~3000 m), −9 to −10‰ for transect two (crest at ~2000 m), and −8 to −9‰ for transect three (crest at ~1500 m). Assuming a $\delta^{18}O$ value of −4.0‰ at the base of the mountain prior to uplift, this results in a $\Delta(\delta^{18}O)$ of 6 to 7‰ for a 3000 m altitude change, 5 to 6‰ for 2000 m of altitude change, and 4 to 5‰ for 1500 m altitude change. Fig. 8 shows raw and 500-m-binned $\delta^{18}O$ data plotted against mean catchment altitude, which is the most climatically-relevant altitude for $\delta^{18}O$ values (Rowley and Garzione, 2007). The altitude effects of −2.4‰ km^{-1} (binned, $r=-0.99$) and −2.5‰ km^{-1} (raw data, $r=-0.85$) are clearly expressed. There is some scatter in the $\delta^{18}O$ values for a given altitude, which may be related to local microclimates, possible groundwater influence that is biased to certain altitudes, or geographic source uncertainty.

3.2.3. Linear and multiple regression

The linear correlations between $\delta^{18}O$ values and physiographic variables are shown in Table 1. Surface water $\delta^{18}O$ is most strongly correlated to mean catchment altitude ($r=-0.85$), median altitude ($r=-0.83$), and sample ($r=0.80$)and stream head distance from the Pacific ($r=0.82$). The results of the multiple regression indicate that only a few physical variables dominate $\delta^{18}O$ values of Guatemalan surface waters. Allowing the statistics to determine the best fit to the data while ignoring co-linearity of variables, an equation relating $\delta^{18}O$ values to latitude, mean catchment altitude, stream head easting and northing, and estimated mean annual precipitation can explain 86% of the $\delta^{18}O$ variability (Table 2). This statistical best-fit equation can be constructed using the coefficients and intercept in the table. Using mean catchment altitude (proportional to temperature via the lapse rate) and estimated cumulative precipitation (proportional to f) returns an equation with adjusted $r^2=0.73$ (not shown).

We also created a physically-based regression using only those parameters most strongly related to temperature and f: mean catchment altitude and sample distance from the Pacific (adjusted $r^2=0.84$). The results of this multiple regression indicate that just sample distance from the Pacific and mean catchment altitude explain 84% of the Guatemala surface water $\delta^{18}O$ values, somewhat remarkable given the complexities that control precipitation $\delta^{18}O$. From the multiple regression results, we define a best-estimate regression equation for surface water $\delta^{18}O$ values in northern Central America:

$$\delta^{18}O_{sw} = \left(-1.7082 \times 10^{-3} \times \text{catchment altitude}\right) + \left(7.1421 \times 10^{-6} \times \text{Distance}_{\text{Pacific}}\right) - 6.08\left(\text{adjusted } r^2 = 0.84\right),$$

where altitude and distances are in meters.

Because the cross-Guatemala distance/$\delta^{18}O$ slope contains an imprint of altitude, we corrected the $\delta^{18}O$ values by removal of an altitude effect of −1.71‰ km^{-1} (Fig. 9), determined from the partial regression coefficients. This correction allows evaluation of the spatial $\delta^{18}O$/distance correlation without the imprint of the altitude effect. The altitude-corrected gradient of 0.69‰ 100 km^{-1} ($r=0.74$, $p=<0.01$), is lower than that determined for the uncorrected $\delta^{18}O$ values of 1.25‰ 100 km^{-1}. Once corrected for mean catchment altitude, the data do not show a $\delta^{18}O$ increase along the Pacific slope (as in Figs. 6 and 7). The correlation between $\delta^{18}O$ and distance from the Caribbean Sea is weaker but still statistically significant ($r=-0.48$, $p=<0.001$).

4. Discussion

4.1. The amount effect in precipitation

The seasonal variability in monthly $\delta^{18}O$ values from Veracruz, Mexico, and San Salvador, El Salvador clearly show an amount effect on precipitation δ values. The gradients of the amount effect (expressed as ‰ per 100 mm of rainfall) of −1.24‰ and −1.25‰ are smaller than the gradients constrained for the amount effect in Panama (−2.85‰) and Costa Rica (−1.86‰). The smaller magnitude of the amount effect in northern Central America and Mexico may be due to a smaller fraction f of rainout of air masses. Alternatively, the change in $\delta^{18}O$ for a given % of f remaining increases as the total amount of f decreases, so that the larger gradients in Panama and Costa Rica may represent greater amounts of prior rainout upwind of the sampling stations.

4.2. Seasonality influences on surface water $\delta^{18}O$ values

Because of the seasonal variation in precipitation $\delta^{18}O$ values, there is likely to be a seasonal bias in the surface water $\delta^{18}O$ values, which were collected for Belize during the dry season ~8 months after the wet season sampling for Guatemala. Are the data from the two countries comparable? To answer this question, we compared the Belize data to only those Guatemalan surface waters located in lowland regions around the Maya mountains and near the Caribbean Coast. Because the Guatemalan samples are both farther inland and have higher mean catchment altitudes than in Belize (1003 m vs. 377 m, respectively), it is reasonable that the mean $\delta^{18}O$ values are different for Belize ($\delta^{18}O=-3.5\pm0.4$‰) and Guatemala ($\delta^{18}O=-5.3\pm1.5$‰). However, after correcting for both distance and altitude effects – using the results of the physical basis multiple regression described above – it is clear that

Table 1
Correlation matrix for linear regressions.

Correlation matrix	$\delta^{18}O$	Longitude	Latitude	Sample alt.	Stream head alt.	Median alt.	Mean catchment alt.	Catchment area	Dist from Carib	Dist. from Pacific	Stream head easting	Stream head northing	Stream head dist. from Caribbean	Stream head dist from Pacific	Stream Length	Estimated MAP	Cumulative Precip	δD
(r)	(‰, SMOW)	(dec. deg.)	(dec. deg.)	(m)	(m)	(m)	(m)	(km^2)	(m)	(m)			(m)		(m)	(mm)	(m^3)	(‰, SMOW)
Longitude (dec. deg.)	0.76																	
Latitude (dec. deg.)	0.74	0.68																
Sample alt. (m)	−0.72	−0.61	−0.34															
Stream head alt. (m)	−0.79	−0.74	−0.55	0.68														
Median alt. (m)	−0.83	−0.74	−0.50	0.89	0.94													
Mean catchment alt. (m)	−0.85	−0.74	−0.51	0.88	0.85	0.94												
Catchment area (km^2)	*0.04*	*0.15*	*0.15*	−0.16	*0.07*	*−0.03*	*−0.04*											
Dist from Carib (m)	−0.72	−0.98	−0.59	0.63	0.73	0.74	0.74	−0.16										
Dist. from Pacific (m)	0.80	0.83	0.97	−0.45	−0.65	−0.62	−0.62	0.16	−0.76									
Stream head easting	0.78	0.94	0.67	−0.59	−0.81	−0.78	−0.75	*−0.04*	−0.92	0.80								
Stream head northing	0.75	0.68	0.98	−0.37	−0.58	−0.54	−0.54	*0.07*	−0.59	0.96	0.70							
Stream head dist from Caribbean (m)	−0.72	−0.98	−0.57	0.64	0.72	0.75	0.75	*−0.15*	0.99	−0.75	−0.92	−0.58						
Stream head dist from Pacific	0.82	0.82	0.94	−0.47	−0.69	−0.65	−0.64	*0.04*	−0.75	0.97	0.84	0.97	−0.74					
Stream Length (m)	*0.02*	*0.07*	*0.08*	*−0.14*	0.22	*0.08*	*−0.01*	0.71	*−0.07*	*0.08*	*−0.15*	*−0.01*	*−0.06*	*−0.07*				
Estimated MAP (mm)	0.47	0.20	0.19	−0.45	−0.30	−0.39	−0.42	−0.09	*−0.16*	0.24	0.21	0.26	−0.17	0.30	*−0.02*			
Cumulative Precip (m^3)	−0.73	−0.99	−0.63	0.63	0.73	0.75	0.75	−0.16	1.00	−0.79	−0.93	−0.63	0.99	−0.78	*−0.07*	−0.16		
δD (‰, SMOW)	0.99	0.74	0.71	−0.74	−0.78	−0.83	−0.85	0.03	*−0.70*	0.78	0.75	0.73	−0.70	0.80	*0.00*	0.53	−0.71	
d (deuterium excess)	*−0.12*	−0.17	−0.18	*−0.10*	*0.07*	*0.00*	*0.00*	*−0.07*	*0.16*	−0.17	−0.16	*−0.15*	*0.15*	*−0.14*	*−0.11*	0.38	0.17	*0.05*

Values in italics are not statistically significant at the 0.05 level.

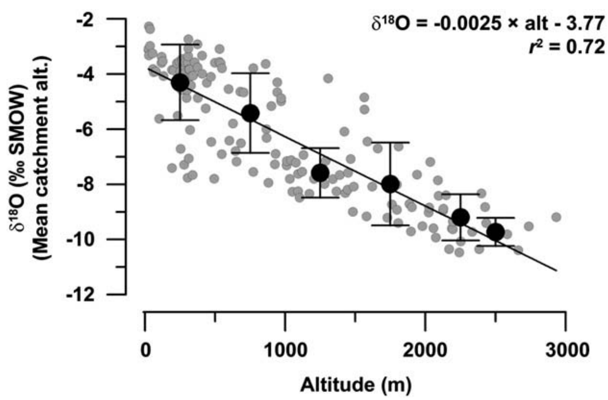

Fig. 8. The altitude effect on Guatemalan surface water, in a plot of mean catchment altitude against δ^{18}O. The raw δ^{18}O data (grey circles) are plotted with δ^{18}O values averaged within 500 m altitudinal bins (black circles) with one σ error bars. There is a clear δ^{18}O decrease with altitude of 2.4 to 2.5‰ km^{-1}.

the corrected δ^{18}O values from Belize (-2.2 ± 0.6‰) and Guatemala (-2.5 ± 1.2‰) have similar means and overlapping ranges. Thus, there does not appear to be a large effect of seasonality on the surface waters from Guatemala and Belize.

We found clear relationships between altitude and distance from the coasts on the δ^{18}O values of northern Central American surface waters. How would seasonality affect these relationships? The δ^{18}O value of streams would be expected to show a muted, and perhaps lagged, response to rainfall δ^{18}O variation (Rowley and Garzione, 2007). Because the river δ^{18}O values should reflect the amount- and altitude-weighted δ^{18}O of precipitation falling on the drainage basin (Rowley and Garzione, 2007), they would tend to be biased towards the wet season. Evidence that this is the case is the perfect overlap of the weighted average δ^{18}O at San Salvador and the Pacific coast streams sampled in our study (Fig. 6). Given that most of the region experiences a similar seasonal cycle in precipitation amount with a May to November wet season, we would expect the relationships determined in this paper to remain robust in broad detail if the samples were collected at different times of the year. However, we would expect the absolute values of the surface water "isoscape" to vary on a seasonal basis, with lower values following the wettest periods. Evidence that the altitude/distance control on the δ^{18}O of surface waters is robust in time and space is also shown by nearly identical spatial variations in surface water δ^{18}O from southern Central America (Lachniet and Patterson, 2002; Lachniet and Patterson, 2006; Lachniet et al., 2007), despite the samples having been collected some 5° of latitude south of the current study area and at different times.

4.3. Surface water δ^{18}O values as indicators of climate processes

Our results show that surface water δ^{18}O values in humid tropical environments may be suitable proxies for the δ^{18}O values of precipitation, as evidenced by the similarity of surface and meteoric water lines (Figs. 3 and 5), and the near perfect overlap of δ^{18}O in Pacific slope surface waters and weighted mean precipitation in San Salvador (Fig. 6). From this observation, we infer that most river water is supplied by high intensity rain storms during which relative humidity and rainfall rate are sufficiently high to minimize rain drop evaporation.

The results from the multiple regression are both simple and powerful to elucidate the climatic controls on surface water δ^{18}O values. Only two physically-plausible physiographic variables – mean catchment altitude and distance from the Pacific – account for 84% of the isotope variability in Guatemala and Belize, and are themselves explicitly linked to the two dominant terms (α, and f) in Rayleigh distillation. The catchment altitude should be proportional to the mean condensation temperature of air masses above the drainage basin. This temperature effect controls the equilibrium fractionation (α) of oxygen isotopes between vapor and condensate. The distance from the Pacific Ocean is inversely proportional to cumulative rainfall amount of Caribbean-sourced air masses. Our data strongly suggest that upwind rainout amount (f) in air masses is a dominant control on at-a-site δ^{18}O values, which can explain the positive correlation between surface water δ^{18}O and estimated mean annual precipitation at the sampling location. This is consistent with results from tropical South America (Vuille and Werner, 2005; Sturm et al., 2008) that show a strong influence of the amount effect and air mass history on the δ^{18}O of precipitation. Recent work has suggested that rainout amount may be of lesser importance than raindrop evaporation,

Table 2
Stepwise multiple regression results for Guatemala and Belize surface water δ^{18}O data.

Variable	Statistical best			Physical Basis		
	Coefficient[a]	*T*-ratio	*p*-value	Coefficient	*T*-ratio	*p*-value
Longitude (dec. deg.)						
Latitude (dec. deg.)	1.6307800	4.431300	0.000			
Sample altitude (m)						
Stream head altitude (m)						
Median stream altitude (m)						
Mean catchment altitude (m)	−0.0014878	−10.168600	0.000	−0.00170816	−14.0	0.000
Catchment area (km^2)						
Distance from Caribbean (m)						
Distance from Pacific (m)				0.00000714	11.0617	0.000
Stream head easting	0.0000030	2.550200	0.012			
Stream head northing	−0.0000078	−2.080200	0.039			
Stream head dist. from Caribbean (m)						
Stream head dist. from Pacific (m)						
Stream Length (m)						
Estimated mean annual precip. (mm)	0.000434504	5.401800000	0.0000			
Cumulative Precip (m^3)						
Intercept	−20.096			−6.080		
RMSE	0.88			0.96		
r^2	0.87			0.84		
r^2 adjusted	0.86			0.84		
F-statistic	203.4			410.8		
Probability of *F*-statistic	0.00			0.00		

[a] All coefficients are statistically significant at the <0.05 level.

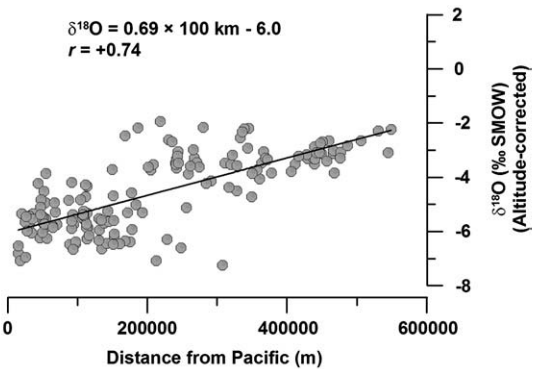

Fig. 9. Corrected surface water $\delta^{18}O$ shows the cross-Guatemala gradient with the altitude effect removed. The data show the depletion in heavy isotopes with distance from the Caribbean Sea, and is interpreted to reflect increasing fractions of moisture removed from air masses as they traverse the cordillera.

moisture entrainment, isotopic exchange between raindrops and vapor, and other microphysical processes within clouds (Bony et al., 2008; Risi et al., 2008). However, our data do not support this suggestion on a spatial and time-integrated scale, although they may be important for individual rain events. Rather, our data support a large-scale temperature and rainout amount control on the $\delta^{18}O$ values of tropical precipitation that is consistent with the classical interpretation of the amount effect as being dominated by Rayleigh distillation processes.

A striking result from our study is the 3–5‰ $\delta^{18}O$ decrease in values from the Caribbean Sea to the Pacific Ocean. High $\delta^{18}O$ values on the Caribbean coast is evident in the mean $\delta^{18}O$ values of waters from Honduras, where several cold springs have values of −3 to −7‰ (Birkle and Bundschuh, 2007). The cross-Guatemala $\delta^{18}O$ decrease is similar to those in Panama and Costa Rica (Lachniet et al., 2007), where surface waters and stalagmites had $\delta^{18}O$ values ~4–5‰ lower on the Pacific side of the isthmus (Lachniet et al., 2007). Our data are also consistent with a ~4–6‰ decrease in δ values from the windward to the leeward side of the southern Andes (Stern and Blisniuk, 2002). For comparison to locations cited in the review by Blisniuk and Stern (2005), the cross-Guatemala $\delta^{18}O$ change of 3–5‰ is less than the 5–8‰ decreases across the Sierra Nevada (altitudes ~3000 m) and the 6–7‰ decreases across the Cascades (~3000 m), but similar to a decrease of ~4–5‰ across the New Zealand Alps. A lower gradient in Guatemala/Belize may be due to mixing of moisture with high $\delta^{18}O$ derived from the Pacific Ocean, a relatively smaller fractional rainout amount of the air mass in this high humidity climate, or mixing of recycled water from upstream sources. The wind vector data and prominent rainfall maximum on the Pacific side of the volcanic cordillera (Fig. 2) indicates a Pacific moisture source contribution. As this moisture has not crossed an orographic barrier, it is likely to have higher $\delta^{18}O$ values than incoming Caribbean moisture. Taken as a whole, it appears that orographic rainfall in high cordilleras oriented approximately perpendicular to the moisture transport vector is approximately equally-efficient in distilling air masses of heavy isotopes in both tropical and extra tropical locations. A major implication of the cross-Central America $\delta^{18}O$ decrease is that the $\delta^{18}O$ value of surface waters – and by inference rain waters – in the humid tropics is controlled by the cumulative rainout of air masses upwind of the sampling or collecting station (Rozanski and Araguás-Araguás, 1995). Such transport involves the atmospheric export of freshwater across Central America that helps to maintain the salinity contrast between the ocean basins (Zaucker et al., 1994; Liu and Tang, 2005).

Our data also demonstrate that an isotopic rain shadow is a robust feature of stable isotope transects across Central America (Blisniuk and Stern, 2005), as is evident in Fig. 9. $\delta^{18}O$ transects in Guatemala appear to display characteristics of both situations A and B of (Blisniuk and Stern, 2005) whereby there is an altitude effect on both sides of the cordillera, but that spillover of ^{18}O-depleted moisture to the Pacific slope imparts lower $\delta^{18}O$ values there. The altitude-corrected gradient in Guatemala/Belize of −0.69‰ per 100 km is an order of magnitude larger than that in the Amazon Basin of −0.075‰ 100 km^{-1} (Salati et al., 1979), and twice as large as that defined globally of −0.2 to −0.4‰ per 100 km (Dansgaard, 1964; Rozanski et al., 1993). The larger gradients in northern Central America can be best explained by the orographic effect, whereby air masses advected across Guatemala undergo large amounts of rainout as the air mass is lifted over the high mountains (Poage and Chamberlain, 2001; Blisniuk and Stern, 2005), resulting in delivery of moisture with low $\delta^{18}O$ values to their lee. In contrast, low relief in the Amazon Basin precludes an orographic effect. Additionally, *d* in the Amazon indicates substantial moisture recycling, which returns rainfall back to the atmosphere and decreases the spatial $\delta^{18}O$ gradient. In contrast, *d* in Guatemala and Belize does not provide evidence for moisture recycling. The suggestion for such recycling in Belize (Marfia et al., 2004) is not consistent with our data, and we suggest the presence of methodological problems with their stable isotope data.

The magnitude of the altitude effect defined by surface waters in Guatemala of −1.9 to −2.4‰ km^{-1} is slightly less than that observed in Panama (−1.9 to −3.1‰ km^{-1}) and the global isotopic lapse rate of −2.8‰ km^{-1} (Poage and Chamberlain, 2001). Comparison to the eastern slope of the Andes indicates that the altitude effects are nearly identical (−1.5 to −2.4‰ km^{-1}) (Gonfiantini et al., 2001). These altitude effects are equivalent to temperature effects of −0.33 to −0.43‰/°C, based on the lapse rate of −5.7 °C km^{-1}.

Our results have implications for the interpretation of isotopic paleoclimate records near high cordilleras, and for reconstruction of paleoaltimetry in tropical regions. Although not yet applied to Central America, paleoaltimetry studies will benefit from the isotope data contained within this paper. Because Caribbean-derived moisture appears to be a dominant factor in the delivery of low-$\delta^{18}O$ vapor to the Pacific side of Central America, terrestrial and marine proxy records on either side of the isthmus that are sensitive to freshwater delivery, *e.g.* stalagmites (Lachniet et al., 2007), lake sediment (Hodell et al., 1995; Hodell et al., 2008), marine sediment (Benway and Mix, 2004; Benway et al., 2006), and corals (Linsley et al., 1994), will contain an imprint of the air mass history. Although our data clearly show that the transport of moisture across Central America is reflected in surface water and precipitation $\delta^{18}O$ values, it is unclear how $\delta^{18}O$ will respond to changing climate dynamics. For example, low $\delta^{18}O$ values of precipitation on the Pacific slope may result either from 1) enhanced air mass rainout on the Caribbean slope, yet be unrelated to rainfall amount on the Pacific slope, or 2) increased rainfall on the Pacific slope unrelated to rainfall on the Caribbean coast, or 3) some combination of the two. These scenarios are consistent with modern climate dynamics in Central America, where stations on the Caribbean and Pacific coasts exhibit anti-phased rainfall responses to ENSO (Waylen et al., 1994; Waylen et al., 1996; Poveda et al., 2006), even while moisture transport is increased during El Niño events (Schmittner et al., 2000).

Despite the potentially complex controls on the $\delta^{18}O$ values of tropical precipitation and surface waters, our data show that just two variables, distance from the Pacific Ocean and mean catchment altitude, can explain 84% of the spatial isotopic variability. Our results have implications for the interpretation of paleoclimate records from Central America, for geothermal studies, as well as for the interpretation of paleoaltimetry from $\delta^{18}O$ values of authigenic materials, in that they demonstrate the presence of an isotopic rain shadow in the lee of a humid tropical climate mountain range. Further investigations into the temporal variation in Central American waters will refine the climate interpretations, and allow for additional insight into modern climate dynamics.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2009.05.010.

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