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Chemical Geology 220 (2005) 245–262

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

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Stable isotope study of cave percolation waters in subtropical Brazil: Implications for paleoclimate inferences from speleothems

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Received 19 September 2004; received in revised form 25 March 2005; accepted 4 April 2005

Abstract

We analyze the interannual monthly variability of oxygen isotope ratios in data from IAEA stations along the Atlantic coast of South America between 23° and 34° S to evaluate the influence of parameters such as temperature, rainfall amount and moisture source contribution on meteoric water recharging two karst systems in subtropical Brazil. In addition, a 2 year monitoring program performed on soil and cave drip and rimstone pool waters from sampling sites with contrasting discharge values and located at 100 and 300 m below the surface in the Santana Cave System (24°31′ S; 48°43′ W), is used to test the influence of hydrologic and geologic features on the temporal variations of seepage water $\delta^{18}O$.

Interannual monthly variations in $\delta^{18}O$ of rainfall reflect primarily regional changes in moisture source contribution related to seasonal shifts in atmospheric circulation from a more monsoonal regime in summer (negative values of $\delta^{18}O$) to a more extratropical regime in winter (positive values of $\delta^{18}O$). Variations in groundwater $\delta^{18}O$ indicate that the climatic signal of recent rainfall events is rapidly transmitted through the relatively deep karst aquifer to the cave drip waters, regardless of location of collection in the cave. In addition, the data also suggest that water replenishment in the system is triggered by the increase in hydraulic head during periods when recharge exceeds the storage capacity of the soil and epikarst reservoirs. Significant perturbations in the groundwater composition, characterized by more positive values of $\delta^{18}O$, are probably connected to an increased Atlantic moisture contribution associated with extratropical precipitation. This implies that the $\delta^{18}O$ of speleothems from caves in this region may be a suitable proxy for studying

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doi:10.1016/j.chemgeo.2005.04.001

tropical–extratropical interactions over South America, a feature that is intrinsically related to the global atmospheric circulation.

Keywords: Karst; Speleothem; Stable isotopes; Drip hydrology; Brazil; Paleoclimate

1. Introduction

Stable oxygen isotope ratios from carbonate stalagmites offer potential records of continental climate change because they can provide long, high resolution and well-dated archives for the Late Pleistocene and Holocene (Gascoyne, 1992; Lauritzen and Lundberg, 1999). The climate signal captured by $\delta^{18}O$ of stalagmites (and other speleothems) is mainly generated by the isotopic ratios of meteoric water, which feeds these formations. Because carbonate deposition in the cave environment generally occurs in isotopic equilibrium with seepage water from which they are formed, it is possible to associate the $\delta^{18}O$ of speleothems with the climate processes that affect rainwater isotopic composition (Linge et al., 2001).

Under conditions of isotopic equilibrium, the oxygen isotope ratios of stalagmites can, depending on local conditions, be an independent proxy of temperature variations (Lauritzen, 1995) and/or hydrological balance (Bar-Matthews et al., 1997). In certain regions it is possible to link stalagmite isotopic variations with changes in mean atmospheric circulation, which allows reconstructing climate variability on a larger scale. For example, temperature variability derived from stable isotopes recorded in Greenland ice cores have been related to changes in the location and intensity of the Asian monsoon over China (Yuan et al., 2004) and Southern Oman (Burns et al., 2000; Fleitmann et al., 2003). However, the type of paleoclimatic information contained in $\delta^{18}O$ in speleothems varies regionally and needs to be determined in each case by identifying the relative importance of all factors affecting the isotopic composition of rainwater during precipitation and subsequent recharge events in karst systems.

To assess the climate forcing on stable isotope ratios in meteoric waters over subtropical regions, such as the present study site, is a challenging task because its composition may be affected by seasonal variations in temperature, rainfall amount and moisture source. As a consequence, the mechanisms explaining the isotope variability in rainwater are sometimes ambiguous because the seasonal cycles of temperature display fluctuations that could counterbalance the rain intensity effect (Rozanski and Araguás-Araguás, 1995). Furthermore, rainfall events along the Atlantic coast of subtropical South America are not only influenced by summer tropical convection but also by extratropical winter precipitation (Vera et al., 2002). This seasonal interplay suggests an additional controlling factor due to changing moisture source contributions from both the Amazon Basin and the Atlantic Ocean. Therefore, an evaluation of modern regional patterns of isotopic variability in rainfall is essential when attempting to interpret the climate signal provided by the $\delta^{18}O$ of speleothems.

Annual or quasi-annual growth layers, recognized in stalagmites from caves located in different environments worldwide, can contain potential information on climate and vegetation variations (Genty et al., 2001; Polyak and Asmerom, 2001). Interannual climate anomalies related to ENSO events and expressed as layer thickness variability (Brook et al., 1999), were recently also identified in speleothem $\delta^{18}O$ profiles by using modern laser techniques (McDermott et al., 2001). However, just how rapid changes in meteoric $\delta^{18}O$ may be incorporated into stalagmites, formed mostly by slow drip water, is still unclear.

Monthly monitoring of cave seepage waters from relatively shallow systems (<50 m) suggests that in some cases the oxygen isotopes ratio remains constant throughout the year due to the mixing of waters in the karst system and corresponds approximately to the mean composition of rainfall recharge events (Yonge et al., 1985; Caballero et al., 1996). This mixing implies that the water stored in the aquifer is old enough to prevent seasonal changes in rainwater $\delta^{18}O$ from being recorded in stalagmites. The attenuation in the $\delta^{18}O$ signal of rainfall events is also confirmed by high frequency monitoring, although small daily isotopic variations can be observed during more intense recharge, when the storage capacity of the aquifer is reached and the shallow groundwater rapidly reach the cave drip sites (Perrin et al., 2003). Therefore, it is likely that the seepage water composition can respond differently to events of infiltration waters in different cave systems due to variations in rock cover thickness and drip hydrology characteristics.

The present study aims to investigate the climate forcing on the isotopic signature of rainfall in subtropical Brazil and how the isotopic signal is transmitted to a variety drip sites, which exhibit very contrasting discharges and are located at depths between 100 and 300 m above the cave roof. A key question of this work is how the $\delta^{18}O$ response to rainfall recharge in a relative deep karst aquifer is modulated: i) Is response completely buffered due to its greater storage capacity and consequently a larger proportion of older reservoir water, or ii) Are more pronounced variations with relatively rapid response seen?

2. Study area and sampling sites

The stable isotopic composition of soil and seepage water was monitored systematically in the Santana cave area (24°31′ S; 48°43′ W) which is located in Iporanga municipality, 350 km south of São Paulo City, southeastern Brazil and approximately 100 km from the Atlantic coastline (Fig. 1a). Samples of seepage water and modern speleothems were also collected in Botuverá cave (27°13′ S; 49°09′ W), located 300 km apart, in order to make a regional comparison. These caves developed in low metamorphic grade limestones of the Meso- to Neoproterozoic Açungui and Brusque Groups, respectively (Cam-

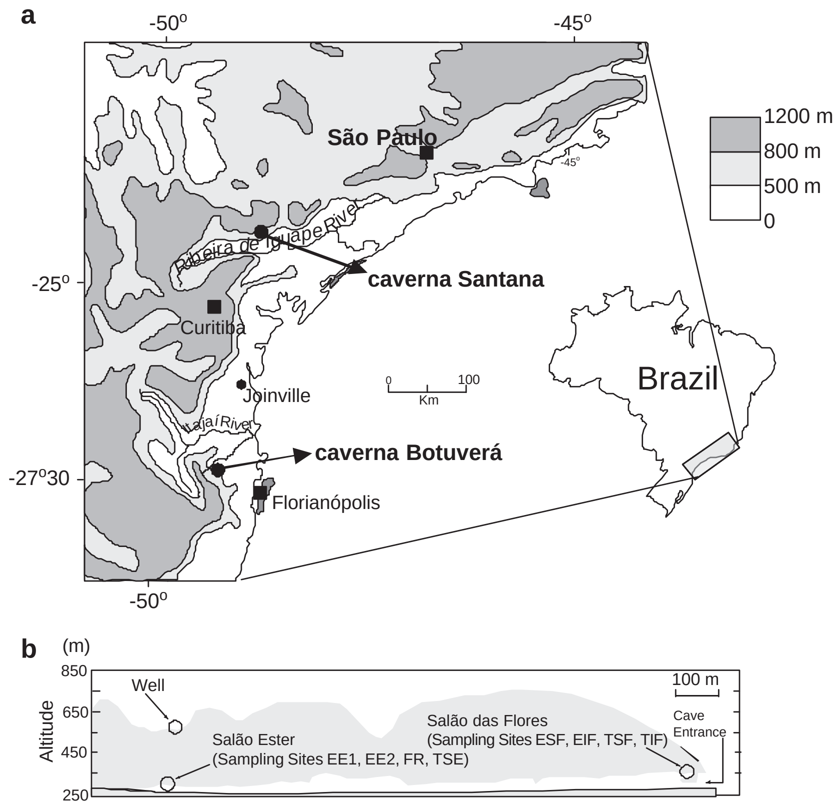

Fig. 1. Location map of the study sites in south and southeastern Brazil. (a) Caves are located at the transition between Atlantic coastal plain and the Serra do Mar/Serra Geral plateaus. (b) Cave longitudinal profile of Santana Cave showing the location of the sampling sites with depth and distance from entrance.

panha and Sadowski, 1999). The present-day climate above both cave sites is sub-tropical humid, with high mean relative humidity and rainfall that is relatively uniformly distributed throughout the year (Rao and Hada, 1990). The sites are located at the transition between the Atlantic coastal plain and the Brazilian plateaus of Serra do Mar and Serra Geral, at elevations from 250 to 550 m (Fig. 1a). Dense tropical Atlantic rainforest covers both areas and is locally associated with clayey soils that are a few meters thick.

The average annual precipitation from 1972 to 2003 at a meteorological station located 7 km from the Santana cave entrance was 1631 mm (source DAEE: www.daee.sp.gov.br). A difference of 67% is observed between the average monthly rainfall amount during the wettest months in austral summer, 198 mm, (December, January and February) and during the driest months in austral winter (June, July, August), 74 mm. Convection during the wetter period is related to the South American Summer Monsoon (SASM), with low-level air masses from the Amazon Basin reaching the region (Gan et al., 2004). A smaller but still important fraction of rainfall events occurs during the winter and early spring months, when incursions of drier and cooler air from midlatitudes affect the climate over the region (Vera et al., 2002). Precipitation at this time of year is primarily associated with extratropical cyclonic activity with an increased contribution of moisture from the Atlantic Ocean.

The average annual temperature measured outside the Santana and Botuverá caves during 2000 and 2002 were 18.6 and 18.9 °C, respectively. These values are equal or very close to the average temperature measured at the cave sampling sites, which are 18.6 ± 0.1 and 19.0 ± 0.1 °C, respectively. The relative humidity in both caves is always 100%.

The Santana karst system exhibits significant topography and therefore variations in the vadose zone thickness along the direction (NE–SW) of the cave axis, which is marked by the presence of the cave river (Fig 1b). The cave has 6.3 km of predominantly horizontal conduits and is densely decorated by carbonate cave formations. Analyses of $\delta^{18}O$ and δD were performed on waters from runoff, soil and eight different sampling sites in this cave. The sampling took into account various hydrological conditions represented by aquifer thicknesses ranging from 100 to 300 m, and mean drip water discharge ranging from 55 to 3.5×10^5 ml/h (Table 1). The soil water was sampled from a well at 4–5 m depth, which is located approximately above the Salão Ester in order to obtain a percolating water profile from surface to cave.

Four cave sites (ESF, EIF, TSF, TIF) are closely distributed around the Salão das Flores, a fossil tributary passage that connects to the cave river. These sites are located 100 m below the surface, 35 m above the river level at the main gallery and 150 m from the cave entrance. The other four sites

Table 1
Resume of isotopic oxygen composition for rain, soil and drip waters collected in Santana cave area

	Depth from the surface (m)	Discharge		*n*	$\delta^{18}O$ range	Δ ($\delta^{18}O$)	$\delta^{18}O$ (mean)	$\delta^{18}O$ CV (%)
		(ml/h)	CV (%)					
Rainwater		–	–	27	−0.71 to −7.28	6.57	−3.57	62
Soil water	4–5	–	–	12	−4.38 to −5.59	1.21	−5.09	8.0
Drip waters								
ESF	100	120.99	12.7	17	−4.36 to −5.86	1.50	−5.41	7.8
EE2	300	55.09	8.1	17	−4.42 to −5.88	1.46	−5.39	8.5
EE1	300	470.51	15.2	15	−4.54 to −5.85	1.31	−5.47	7.1
EIF	100	818	>200	8	−4.57 to −5.88	1.31	−5.36	8.8
FR	300	3.5×10^5	9.0	14	−4.64 to −5.69	1.05	−5.32	7.1
Rimstone pools								
TSF	100	–	–	9	−4.4 to −5.69	0.19	−5.27	7.5
TIF	100	–	–	10	−4.62 to −5.5	0.88	−5.29	6.2
TSE	300	–	–	11	−4.83 to −5.77	0.93	−5.55	5
Total (cave waters)		–	–	101	−4.36 to −5.88	1.52	−5.34	7.5

*Intermittent flow.

(EE1, EE2, TSE, FR) in the Salão Ester are 300 m below the surface and about 1500 m from the cave entrance. In both locations, with exception of EIF, the sampling sites were active throughout the year. ESF, EE1, EE2 and EIF are stalactite drip waters characterized by lower discharge when compared to FR, which is a small waterfall in the cave (Table 1). TSF, TSE and TIF are sites where water accumulated in small travertine pools on the cave floor and which are fed by water from ESF, EE2 and EIF stalactites, respectively. Modern active speleothem samples representing different morphologies that are related to drip waters and travertine pools were collected at both cave sites.

3. Methods

Water samples were taken monthly for most of the time between March 2000 and March 2002. Surface and cave water samples for stable isotope analyses were collected in 15 ml amber glass bottles. Bottles were previously cleaned with detergent and dilute perchloric acid and rinsed with deionized water. Soil water samples were pumped out from the well using a Low Flow Waterra inertial pump with high-density polyethylene tubes previously cleaned with dilute HCl. Samples from rain events were collected in previously cleaned plastic recipients after rinsing them with rainwater before collection. These samples were immediately transferred to the sampling bottles to avoid evaporation.

Precipitation and stalactite discharge measurements were done automatically using a Davis automatic tipping bucket gauge coupled to an Onset Logger, model Hobo for 8000 events. The discharge values were continuously recorded by the loggers at the slowest drip water flows (EE2 and ESF), at a time interval of 17–21 days for EE2 and 8–12 days for ESF, depending on the flow changes during the year at each site. At other cave sites, discharge corresponds to the elapsed time needed to fill a known volume. Temperature and relative humidity (RH) were measured automatically, every 30 min, using an Onset Hobo RH-Temp logger H8-series at Salão Ester and Salão das Flores in the cave and at the surface near the water-sample collection sites (under forest climatic conditions).

Analysis for stable isotopes of carbonates were carried out using CO_2 gas extracted from powdered carbonates in a high vacuum line, after reaction with 100% phosphoric acid at 25 °C for one day, and cryogenically cleaned, according to the method described by McCrea (1950), at the stable isotope laboratory (LABISE) of the Universidade Federal de Pernambuco, Brazil. The released CO_2 was analyzed for O and C isotopes in a double inlet, triple collector SIRA mass spectrometer, using the BSC reference gas (Borborema skan calcite) that was calibrated against NBS-18, NBS-19 and NBS-20 standards. The analytical reproducibility for both $\delta^{18}O$ and $\delta^{13}C$ is ± 0.02‰. Results are expressed in the notation δ‰ (per mil) in relation to the international PeeDee Belemnite (PDB) scale.

Determination of $\delta^{18}O$ for waters samples was performed at the stable isotope laboratory (CENA) of the Universidade de São Paulo, Brazil; and some samples were also analyzed at University of Waterloo, Canada. The water samples analyzed at CENA were prepared by equilibration with CO_2 overnight at 25 °C (Epstein and Mayeda, 1953). After being cryogenically purified in a high vacuum line, the CO_2 is transferred to a Finnigan Delta Plus mass spectrometer for $^{18}O/^{16}O$ measurements. A maximum deviation of 0.3‰ was permitted for $\delta^{18}O$ of all water samples. The results are given in per mil relative to the SMOW standard.

The discussion of interannual rainfall isotopic variability is based on the weighted mean values of monthly rainwater accumulations from two IAEA stations in Brazil, Rio de Janeiro and Porto Alegre,

Table 2
Data description of IAEA stations over subtropical Atlantic coast of South America

IAEA Stations	Geographic position	Period of collection	Minimum of months	Maximum of months
Rio de Janeiro		1961–1976; 1983–1987	12	19
Porto Alegre		1965–1969; 1973–1983	9	15
Buenos Aires		1961–1964; 1978–1991	12	17

and one in Argentina, Buenos Aires. Collection periods and the minimum and maximum number of samples for each month are shown in Table 2.

4. Results

4.1. Isotopic composition of regional precipitation

The $\delta^{18}O$ values of karst waters in the study area can best be understood by considering the isotopic values of regional precipitation. The rainwater isotopic composition from the IAEA-GNIP database for stations located along the Atlantic coast of South America reveals significant spatial and temporal differences (Fig. 2). The isotopic signature of rainfall at tropical sites north of 20° S is primarily influenced by the amount of rainfall (Vuille et al., 2003), and is characterized by a decrease in ^{18}O with increasing amounts of rainfall, as clearly observed at the Rio de Janeiro station (Fig. 2). This empirically observed relationship is typical for rainfall associated with deep convection in the tropics (Gat, 1996). In contrast, the lack of correlation between rainfall amount versus $\delta^{18}O$ at Porto Alegre and Buenos Aires (Fig. 2) indicates that other processes control variations in rainfall composition over the subtropics.

Although temperature varies considerably through the year, with amplitudes of 10.1 and 13.66 °C between winters and summers months in Porto Alegre and Buenos Aires, respectively, local temperature changes do not seem to play an important role on rainfall $\delta^{18}O$ values (Fig. 3a). Contrary to the expected tendency predicted by Rayleigh-type distillation model (Dansgaard, 1964), or the observed trend for most mid- to high-latitude sites, the isotopic composition of rainfall in the study area is relatively more enriched during winter months and early spring and more depleted in summer rainfall are observed at all IAEA-GNIP stations (Fig. 3a and c). This pattern agrees with simulations by the ECHAM-4 and GISS II models which show only a slight influence of temperature in most regions of South America $\delta^{18}O$ (Vuille et al., 2003).

A seasonal change in the moisture source for precipitation along the Atlantic coast south of Rio de Janeiro (~23°S) is the apparent cause for the lack of a significant correlation between rainfall amount and monthly $\delta^{18}O$ at subtropical coastal stations. The amount effect is only evident at Rio de Janeiro because this location remains under highly convective tropical climatic conditions all year long, while this is not the case for the stations further south. The significant dependence of rain $\delta^{18}O$ on the precipitation

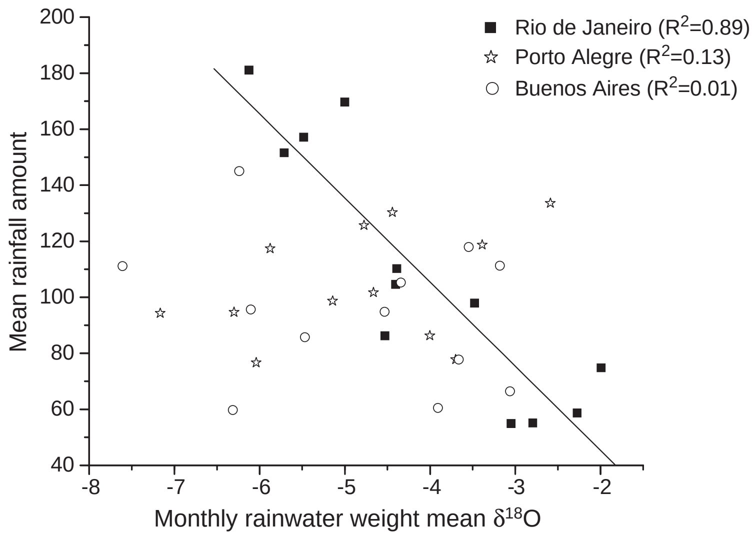

Fig. 2. The relationship between monthly rainwater $\delta^{18}O$ weighted mean values and monthly rainfall amount for IAEA stations in Rio de Janeiro, Porto Alegre and Buenos Aires.

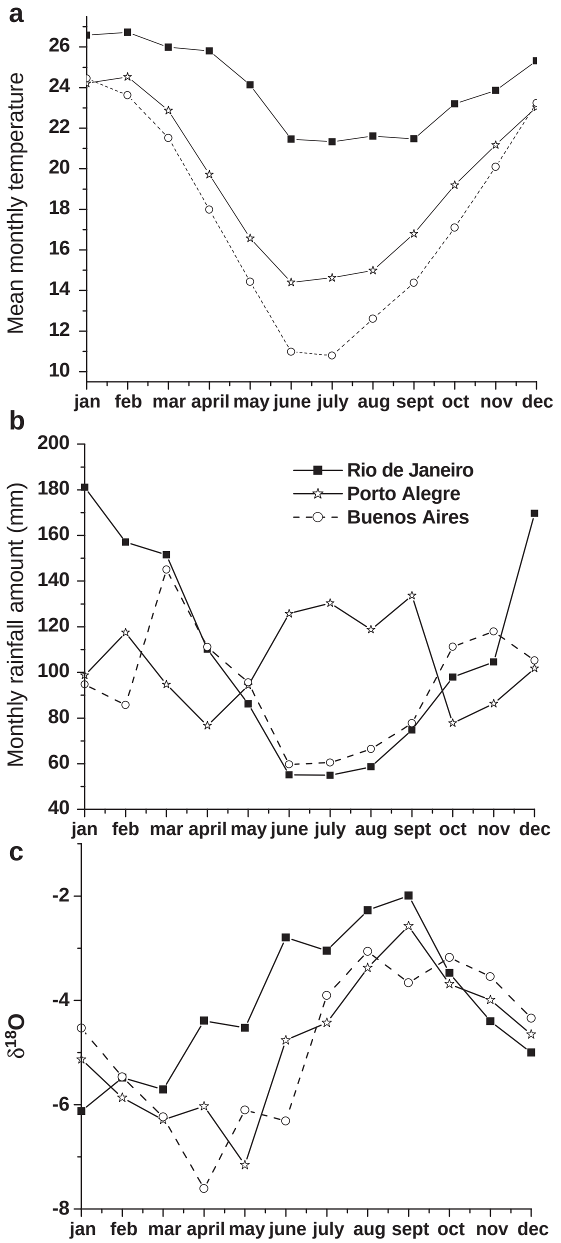

Fig. 3. Data from IAEA stations Rio de Janeiro, Porto Alegre and Buenos Aires (IAEA/WMO, 1994), (a) monthly temperature, (b) monthly rainfall amount, (c) weight mean monthly $\delta^{18}O$.

amount at IAEA stations in Rio de Janeiro and toward lower latitudes in Central and Amazon Basin in Brazil is characteristic of areas dominated by the South American Summer Monsoon (SASM) activity (Vuille et al., 2003). On the other hand, the coincidence of more positive values of $\delta^{18}O$ with the rainiest period in Porto Alegre during winter and early spring cannot be attributed to temperature or precipitation rainout effects (Fig. 3b and c).

The driving mechanism behind seasonal variations in isotopic composition of rainfall over subtropical regions is probably linked to seasonal changes in the relative contribution of: (1) more enriched moisture advected from the nearby Atlantic mainly during winter to early spring and (2) higher percentages of isotopically-depleted, continental moisture originating over the Amazon basin and transported south by a low level jet (Fig. 4a). The former source is associated with incursions of extratropical air masses circulation into the region, for example during episodes of enhanced cyclonic activity over the Atlantic Ocean, with winter storm tracks progressing north along the coastal region (Vera et al., 2002). The later source, on the other hand, reflects tropical water vapor transported south during the summertime active phase of the SASM (Garreaud and Wallace, 1998). The Amazonian moisture is increasingly distilled along its southward trajectory to the coast, resulting in typically more negative $\delta^{18}O$ values for austral summer rainfall (Fig. 4a) as compared to the more enriched precipitation associated with intensified cyclonic activity in the Atlantic Ocean (Fig. 4b).

Temporal variations of the rainwater isotopic composition at the subtropical sites suggest a seasonal dependence of $\delta^{18}O$ on mean atmospheric circulation patterns over South America. The monthly rainfall $\delta^{18}O$ changes progressively from the most negative values between April and May to the most positive values between September and October in both Porto Alegre and Buenos Aires (Fig. 3c). Although the amount effect is not the dominant factor affecting the rainwater composition at these sites, it is nonetheless apparent that the seasonal cycle of $\delta^{18}O$ follows the annual migration of deep monsoonal convection over the subtropical Atlantic coast. There is a clear association between the decreasing (increasing) isotopic trend and the concurrent onset (demise) of convection related to SASM activity over the region, in September–October and April–May, respectively (Gan et al., 2004). Beginning in April, the South American Monsoon System starts to weaken as the center

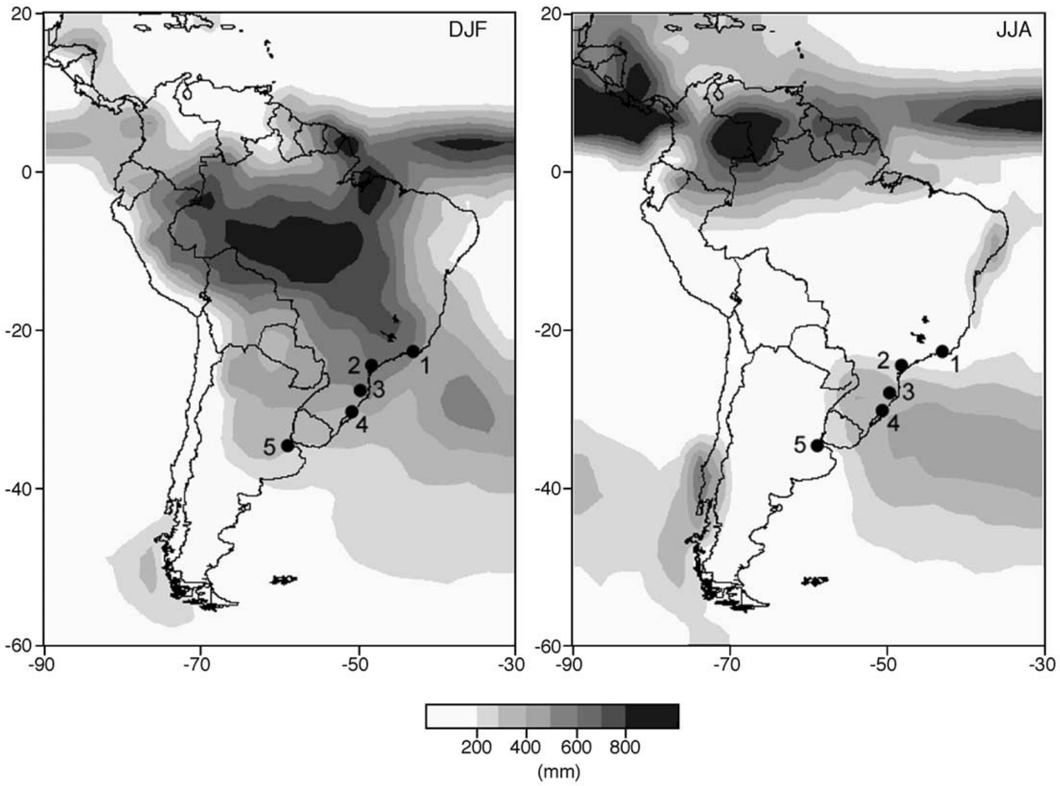

Fig. 4. Long-term mean (1979–2000) Climate Prediction Center Merged Analysis of Precipitation (CMAP,Xie and Arkin, 1997) seasonal precipitation totals (in mm) for December–February (left) and June–August (right). Precipitation over SE Brazil in DJF is related to the southward expansion and intensification of the South American summer monsoon, while in JJA precipitation is of extratropical nature and associated with midlatitude cyclonic activity over the South Atlantic. Numbers in figure indicate locations mentioned in text: 1—IAEA station in Rio de Janeiro, Brazil; 2—Santana cave; 3—Botuverá Cave; 4—IAEA station in Porto Alegre, Brazil; 5—IAEA station in Buenos Aires, Argentina.

of activity of deep convection retreats northwestward; by this time the contribution of Atlantic moisture to convection is enhanced. The enriched δ^{18}O between June and September is marked by increased baroclinic activity as well as an enhanced frequency of offshore cyclones transporting enriched Atlantic moisture inland (Vera et al., 2002). However, positive anomalies of precipitation are more frequently observed at the end of the winter and in early spring (August–September), favored by higher water vapor content (Rao et al., 1996). Thus, these differences in the moisture source contribution allow us to infer interannual changes in the precipitation behavior by using the quite distinct seasonal signal of δ^{18}O during rainfall recharge events in the karst aquifer of the studied region.

4.2. Isotopic composition of precipitation and local percolating waters

The local meteoric water line (LMWL) obtained from 27 values of δD and δ^{18}O of rainwater samples collected nearby Santana cave has a slope of 7.77 (Fig. 5), which is very close to the world meteoric water line (WMWL). The rainwater exhibits a range of δ^{18}O from -7.28‰ to -0.71‰, which is relatively large compared with soil (-4.38‰ to -5.59‰, n=sand 12) cave water (-4.36‰ to -5.88‰, $n=101$) (Table 1). The narrow range observed for groundwater and the similarity between soil and cave drip water composition reflects attenuation of the seasonal rainfall isotopic variation due to mixing of recharge water from different events in the system.

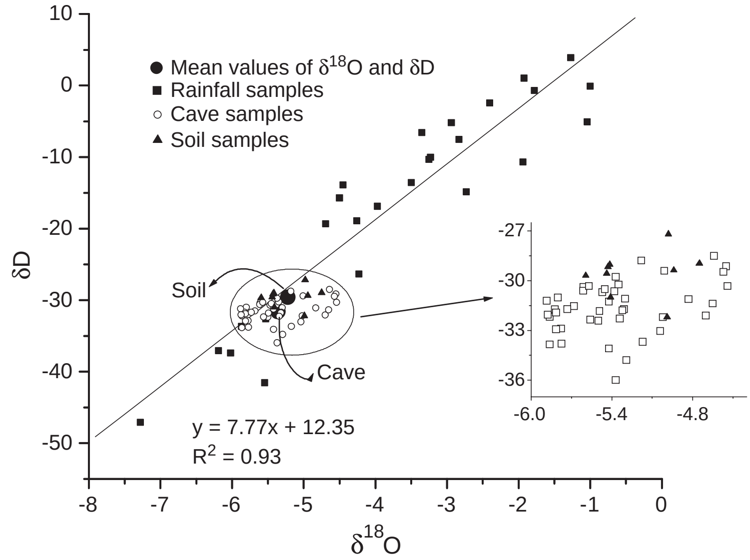

Fig. 5. The $\delta^{18}O$ and δD composition of rainwater, soil and dripwaters from Santana cave area (2000–2002).

Both soil and cave water isotopic compositions fall on the LMWL, which indicates negligible effects of rainfall evaporation near the surface, or during transit from the surface to the cave (Fig. 5), as observed in karstic regions of Caribbean islands (Jones and Banner, 2003). The similarity between mean $\delta^{18}O$ of cave water (5.34‰, $n = 101$) and the annual weighted mean $\delta^{18}O$ observed at IAEE stations (Vuille et al., 2003), as well as the close position of the seepage waters to Global Meteoric Water Line (GMWL), indicate that changes in $\delta^{18}O$ of cave dripwaters feeding the speleothems are associated with the isotopic composition of rainfall. Non-evaporative conditions can also be assumed for the cave environment given the marked similarity of $\delta^{18}O$ of water accumulated in rimstone pools and their corresponding drips, for example ESF → TSF, EE2 → TSE and EIF → TIF (Table 1). This suggests favorable conditions for deposition of speleothems close to isotopic equilibrium with their parental water; otherwise an evaporative enrichment of $\delta^{18}O$ in pool waters should be expected.

4.3. Drip water hydrology characteristics

The investigation of flow characteristics in karst-infiltrated waters is important for understanding environmental factors controlling the cave water isotopic composition (Genty and Deflande, 1998). Two dripping stalagmites corresponding to seepage flow were monitored in cave sites at 100 and 300 m below the surface in order to evaluate the effect of rainfall recharging and mixing with percolation waters in the aquifer. Previous studies showed that because the dynamic of karst seepage flow is largely influenced by storage capacity, the response in drip discharge is sometimes buffered and the seasonal and interannual isotopic signal completely dampened (Yonge et al., 1985; Ayalon et al., 1998; Perrin et al., 2003). However, descriptions of hydraulic features from high-resolution discharge measurements in cave drip waters at depths below 100 m were not reported in previous studies. Therefore, it is very important to study the flow characteristics under increased hydraulic head during extreme rainfall recharge events.

Fig. 6 presents the results of mean daily discharge for ESF and EE2 drip waters, measured during approximately two years by use of an automatic tipping-bucket gauge. The drip discharge shows strong control by rock cover thickness in Santana cave, which varies from 100 m at ESF to 300 m at EE2. The timing of increased drip rate relative to the onset of rainfall events is influenced by soil cover and a limestone micro-fissure network that in some cases can promote a time lag of

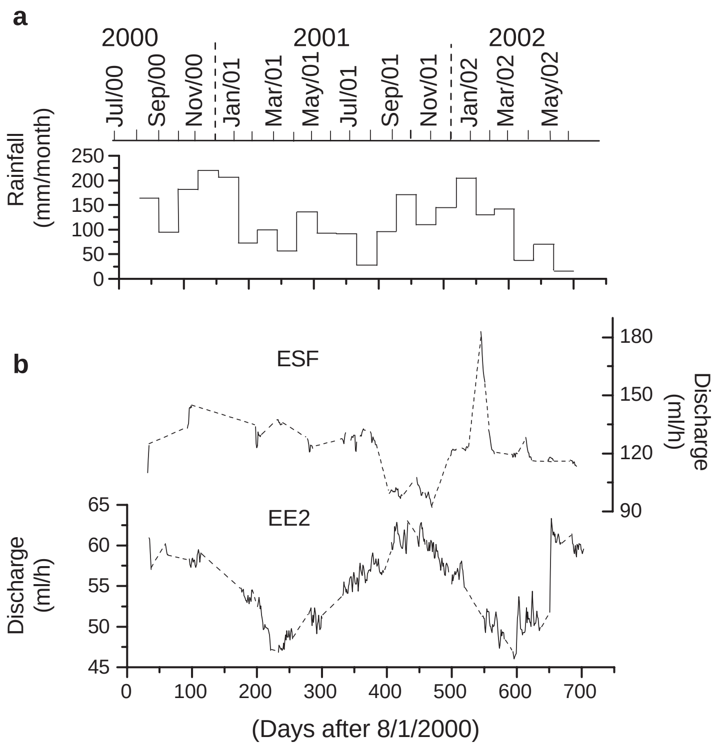

Fig. 6. (a) Monthly rainfall variations; (b) Drip discharge variation with time for slow drip waters at ESF Site, located at 100 m from surface and EE2 sites, located at 300 m from surface. Dashed lines mark periods without measurements.

several months before rain water infiltration events start to affect the drip discharge and its average composition of stalactites (Genty and Deflande, 1998; Ayalon et al., 1998).

Variations in discharge of ESF stalactites ranged between 92 and 182 ml/h (Table 1). The response time of the mean drip discharge to changes in precipitation was estimated as a week to a month, based upon comparisons of ESF discharge and rainfall variations (Fig. 6). For EE2 stalactites the drip discharge ranged from 46 to 63 ml/h and showed no correspondence with monthly rainfall. The variations and changes in EE2 drip discharge were very regular over the 2 years (Fig. 6).

The EE2 discharge curve in Fig. 6 is asymmetric, characterized by a longer rising limb of 7 months and a shorter recession limb of 5 months. During the 2 years, the maximum and minimum drip discharge values occurred in October and March respectively, despite differences in the timing of the rainiest months in the 2 years. Rainwater is gradually stored in the fissured aquifer and that the discharge increases at the beginning of rainy season as a result of an increase in hydraulic head.

Rapid drip discharge variations that characterize the secondary peaks in the ESF curve appear to be associated with extreme events of water infiltration in the system (Fig. 7a to d). Despite the short observation time of 1 week–20 days for continuous discharge monitoring at the ESF site, a lagged response of a few days from mean daily discharge to the most important flood events (Fig. 7a, c, d), or a continuous decrease in discharge during periods without significant events (Fig. 7c) is apparent. On the other hand, there is no correspondence between EE2 mean daily discharge variations and rain events, which indicates that the signal of individual infiltration events is greatly dampened by the thicker aquifer feeding the EE2 stalactite.

Although seasonal variations are not evident at mean time EE2 dripping, the high-frequency discharge variability seems to be approximately syn-

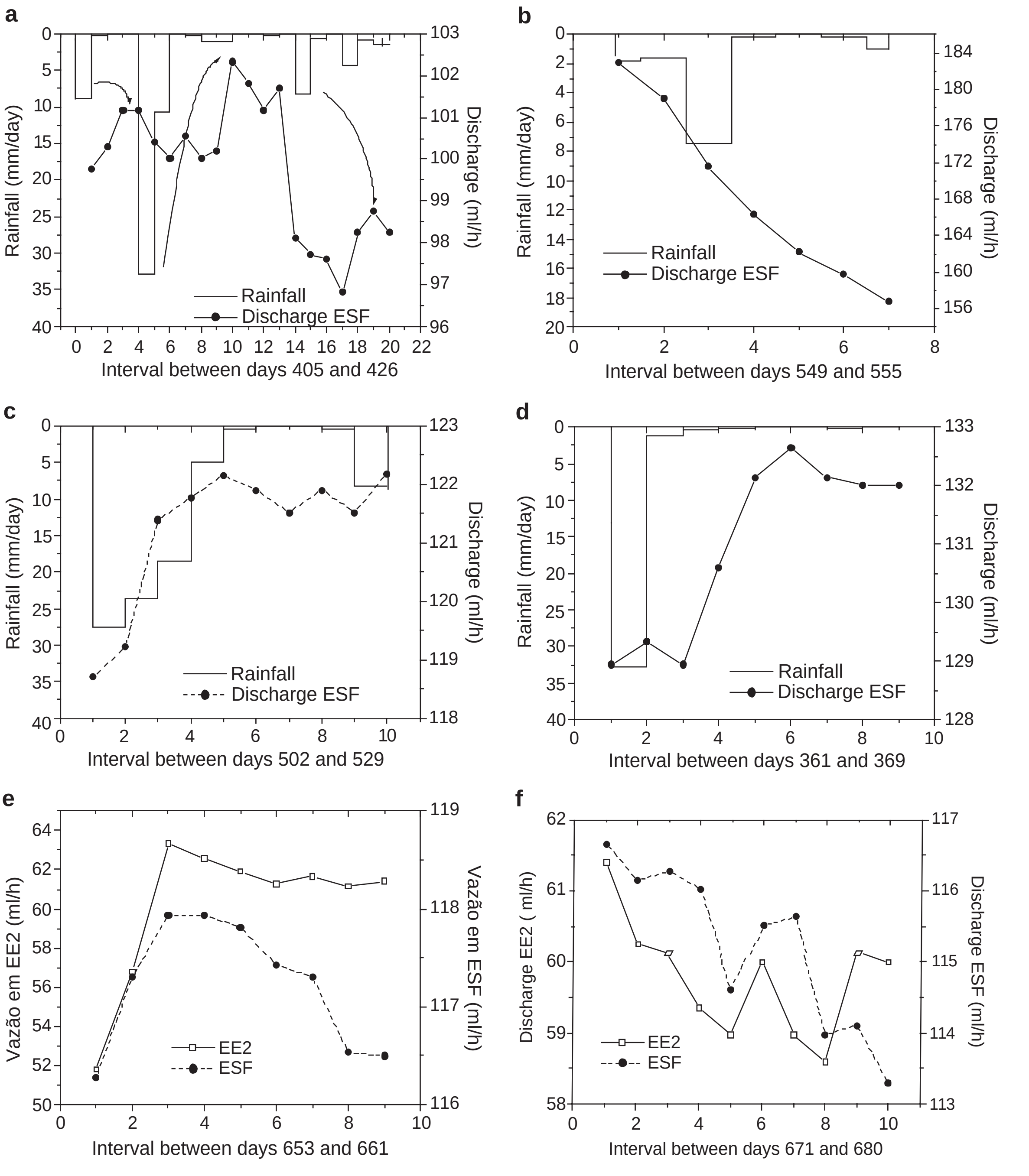

Fig. 7. a–d: ESF dripping discharge vs. daily rainfall. e–f: Stalactite dripping discharge between ESF (100 m depth) and EE2 (300 m depth) sites.

chronous between EE2 and ESF drip discharges (Fig. 7e and f). The two time series are significantly correlated at the 95% confidence level during 11 of the 18 common intervals, with a lag varying from 3 days to less than 1 day (Fig. 8a to d). These correlations imply that non-linearities in discharge are ob-

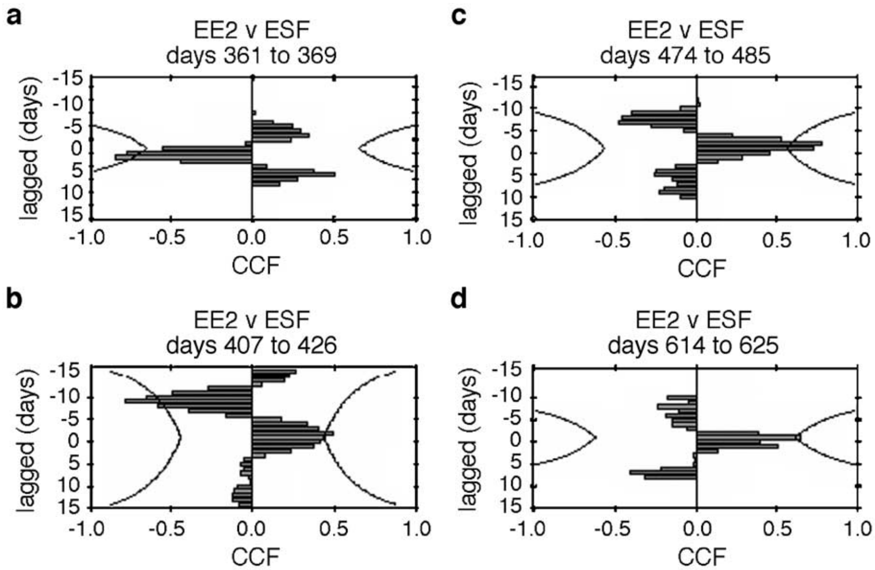

Fig. 8. Cross correlation graphics of discharge data for EE2 and ESF. The black line represents the confidence level of 95% for analysis.

served in response to rainfall recharge within the karst system, as evidenced in the drip hydrology study by Baker and Brunsdon (2003) in Stump Cross Caverns, England. The mechanism explaining this behavior in drip discharge might be coupled to an increase in hydraulic head during high infiltration events. In the case of large storm events the storage capacity in the soil and epikarst zone is exceeded and a significant amount of water can percolate into deep zones of the karst system (Perrin et al., 2003). Furthermore, the lack of correlation observed in the remaining intervals could be due to the short observational time or periods without relevant flood events.

4.4. Temporal and spatial variations of $\delta^{18}O$ for soil and drip waters

The results of the monitoring program for groundwater in the aquifer overlying Santana cave is characterized by remarkable similarities in $\delta^{18}O$ values among sampling sites (Fig. 9). Over 2 years the time-series variations showed a surprising correlation between $\delta^{18}O$ of cave drip water and soil water, even for very contrasting mean discharges elsewhere in the cave, which varied from 55 to 3.5×10^5 ml/h and depths from 100 to 300 m (Table 1). Homogenization of the isotopic composition seems to take place close to the surface.

During the monitored period, the oxygen isotopic composition of percolating waters exhibited enrichment in $\delta^{18}O$ between days 138 and 216 (August–September/2000) and also between days 293 and 385 (December/2000–March/2001) of about 0.5‰ and 1.5‰, respectively (Fig. 9). The former period is coincident with late winter and early spring rainfall events, while the later period was associated with higher rainfall amounts during the summer months and consequently reflects more effective aquifer recharge. The more pronounced isotopic peak in summer represents an enrichment of approximately 1.5‰ relative to the bulk cave water mean isotopic composition (−5.34‰). However, it is lagged by 1 month compared to the onset of the rainy season. An abrupt decrease of 0.5–0.7‰ in $\delta^{18}O$ values within this period, at day 353, is probably due to the lack of relevant flood events (daily rainfall < 15 mm) in February/2001 (Fig. 9).

By contrast, the values of $\delta^{18}O$ for the period from days 479 to 744 (June/2001–March/2002) were essentially constant within analytical errors, even during important wet season recharge events between October/2001 and February/2002. This implies that perturbations in the groundwater isotopic composi-

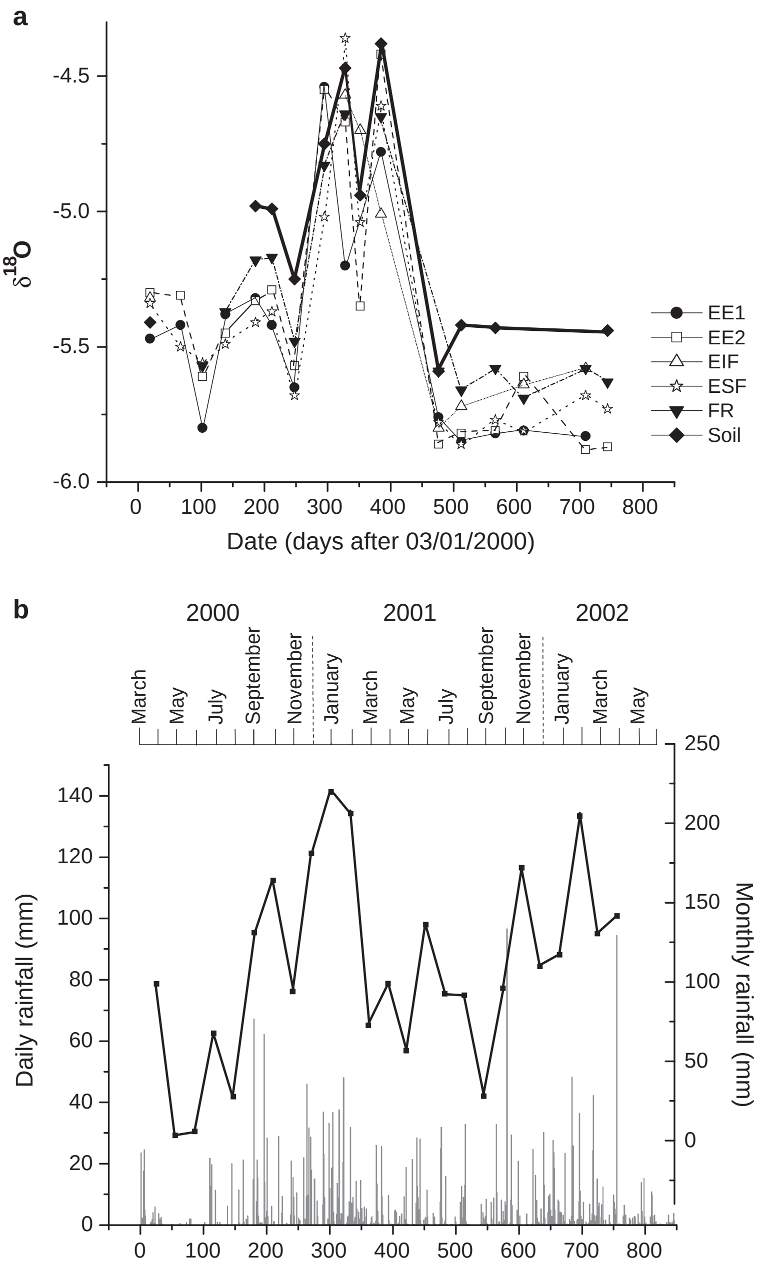

Fig. 9. (a) Time series of $\delta^{18}O$ for soil and drip waters at 300 m deep (EE1,EE2, and FR sites) and at 100 m deep (ESF and EIF sites) in Santana cave system. (b) Monthly rainfall amount.

tion are associated with variations in the moisture source contribution rather than the amount of recharge in the system. It is interesting to note that during this period the soil water is ~0.5‰ enriched relative to the cave water.

4.5. Present-day calcite speleothems

Isotopic equilibrium conditions between calcite deposition and its parental water have been tested in the literature by comparing observed cave tempera-

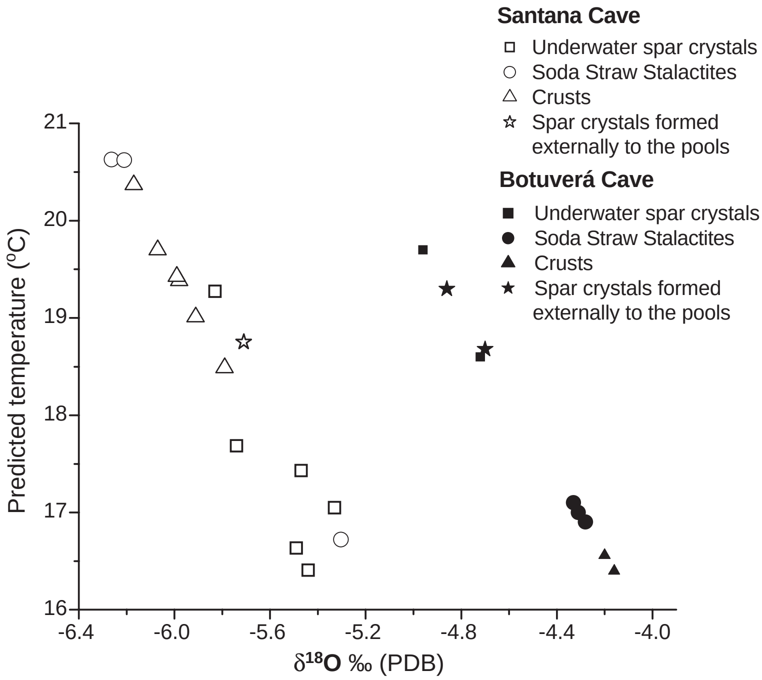

Fig. 10. $\delta^{18}O$ (PDB) of modern speleothems vs. the predicted temperature calculated from the equation of Craig (1965). The graphic shows more positive values of $\delta^{18}O$ for speleothems from Botuverá cave in comparison with ones from Santana cave. Note that the predicted temperature is roughly similar according to the morphology type but different between groups. The average temperature measured in cave sampling sites is 18.6 and 19.0 °C in Santana and Botuverá caves, respectively. See explanation in the text.

tures and isotopic measurements with the predicted values of temperatures obtained through the equation of Craig (1965):

$$T_P = 16.9 - 4.2\left(\delta^{18}O_{calcite} - \delta^{18}O_{water}\right) + 0.13\left(\delta^{18}O_{calcite} - \delta^{18}O_{water}\right)^2$$

Ideal environmental conditions for calcite deposition in isotopic equilibrium are assumed from this approach when the predicted temperatures are similar to the present day cave temperatures (Thompson et al., 1976; Desmarchelier et al., 2000).

Modern calcite speleothem samples collected in Santana and Botuverá caves were soda straw stalactites, crusts deposited on the tipping bucket gauge used for discharge monitoring in the caves, spar crystals formed under water in rimstone pools and over external parts of rimstone pools. The mineralogy of all morphology types was confirmed by X-ray diffraction (XRD).

The predicted temperatures were estimated for Santana Cave by combining the values of $\delta^{18}O$ of each morphology group with its respective parental water, while for Botuverá cave the mean value of drip waters was used (Fig. 10). An error of ± 1.26 °C is estimated for the predicted temperatures based on combined analytical reproducibility of standards for $\delta^{18}O$ in water (± 0.3‰) and calcite samples (± 0.02‰).

In Fig. 10, the relationship between the $\delta^{18}O$ of speleothems and the predicted temperature is presented. Speleothem samples from Botuverá cave are approximately 1‰ more enriched than the ones from Santana Cave. The observed difference is consistent with the more positive $\delta^{18}O$ values of cave waters in Botuverá cave: − 4.28 ± 0.28‰ (SMOW, $n = 12$), in comparison to − 5.34 ± 0.40‰ (SMOW, $n = 101$) at Santana cave.

The predicted temperatures range from 16.4 to 20.6 °C and from 16.4 to 19.7 °C, for Santana and Botuverá caves, respectively (Fig. 10). In both caves, temperature estimates are clustered according to sample morphology. However, there is a significant difference in temperature between groups of speleothem samples; some are a few degrees above or below the measured temperature in the caves and lie beyond the error of estimate. For Santana cave, the crusts and the spar crystals exhibit temperatures which are similar to the one observed in the cave, 19 °C. The soda straw stalactites and the underwater spar crystals showed values which are a few degrees above and below the observed cave temperature, respectively. For Botuverá cave, the soda straw stalactites and both underwater and external spar crystals exhibit temperatures consistent with the observed temperature in the cave, 18.7 °C. The crusts soda straw stalactites and underwater spar crystals showed values which are a few degrees above and below the observed cave temperature, respectively.

5. Discussion

5.1. Hydrological processes and the climate forcing on $\delta^{18}O$ of cave drip-waters

The time-series variations of groundwater samples indicate that the climatic signal embedded in the isotopic composition of recent rainfall accumulations can be rapidly transmitted through the karst aquifer to the stalactites dripping in the cave, as observed from late winter to summer in the first year of monitoring (Fig. 9). This result shows that the response of δ^{18}O in seepage waters to recharge events is not completely dampened when mixed with waters in the aquifer, in contrast with other studies (Yonge et al., 1985; Caballero et al., 1996; Perrin et al., 2003). The simultaneous variations in δ^{18}O among sampling sites also suggest that effective mixing does not significantly influence the response of the drip-water composition to rainfall infiltration; otherwise different responses of infiltrated waters due to variations in aquifer thickness and time of residence should be expected between slow and fast drip flows, as reported by Ayalon et al. (1998).

Comparison of daily average values of discharge in slow drip water with daily rainfall accumulations demonstrates that a linear response of discharge to individual recharge events is highly dependent on the depth from the surface. Therefore, a significant correlation between discharge and precipitation amount is observed at 100 m below the surface, but not at 300 m. In contrast, the discharge correlation between ESF and EE2 sites for most intervals suggests that a greater hydraulic connectivity is achieved during more intense rainfall events, when the storage capacity in the soil and epikarst zone is exceeded and the water accumulated in the upper parts reaches the whole karst profile in a short time interval. These results, in combination with the synchronous variations observed in δ^{18}O of groundwater, demonstrates that rapid variations in both discharge and isotopic composition are triggered by the increase in hydraulic head by a piston flow mechanism rather than preferential flow (Tang and Feng, 2001). This mechanism can promote a very efficient hydraulic conductivity between contrasting drip flows in a karst system, because during periods of more intense recharge the matrix water becomes completely mobile and may bypass the epikarst subsystem through a more prominent fracture network and conduits reaching the drip water reservoirs adjacent to the cave roof (Perrin et al., 2003).

Further evidence for a drip water control by moisture source variability comes from the regional tendency of increased δ^{18}O values at higher latitude, observed in both cave drip water and modern speleothems from Santana Cave (24°31′ S) and Botuverá Cave (27°13′ S). The mean δ^{18}O values in the former cave are -5.34 ± 0.40‰ (SMOW, $n=101$) and -5.72 ± 0.31‰ (PDB, $n=19$), while in the later cave they are -4.28 ± 0.28‰ (SMOW, $n=12$) and -4.49 ± 0.42‰ (PDB, $n=12$), for drip water and modern speleothems, respectively. This suggests a larger contribution of Atlantic moisture and a decrease in Amazonian moisture farther south.

The systematic difference in the isotopic composition of about 0.5‰, observed between soil water and slower drip water sites during drier periods suggests that an important fraction of more enriched rainwater is stored in epikarst, while the other part percolate into the fractured aquifer feeding the drip water in the cave, for example between day 185 and 211, August and September/2000. The recharge of relatively enriched meteoric water coincides with extratropical precipitation during winter and early spring of 2000 (source CPTEC/INPE:www.cptec.inpe.br/clima).

The close match between all isotope curves during the wettest period (between days 290 and 385, Fig. 9) suggests that the hydraulic pressure exerted by water accumulated in shallower parts of the infiltration path leads to a rapid hydraulic response of the whole karst system and homogenization of the groundwater isotopic composition at more positive $\delta^{18}O$ values. In addition, the lag of approximately 1 month between the major shifts in the isotopic composition of groundwater and the beginning of the wet season in December/2000, indicates that a certain recharge threshold is required for the enriched water, stored in the epikarst, to reach the deepest part of the aquifer, probably under piston flow conditions. A similar response to flood events was also observed at the same sampling sites through a synchronous increase in dissolved organic matter concentration in the system a few months after the rainy periods (Cruz et al., 2005a). This implies that when increased hydraulic connectivity is reached due to increased hydraulic head, the soil constituents can be rapidly transported via water to stalactite drips.

The phase represented by a more negative and stable groundwater isotopic signal between the days 477 and 743 (Fig. 9) may be associated with a less significant recharge contribution from rainfall events with Atlantic signature as indicated by negative anomalies of winter/spring precipitation (source CPTEC/INPE:www.cptec.inpe.br/clima) even during important precipitation events, such as between October/2001 and March/2002 (days 600 and 750). During this time groundwater $\delta^{18}O$ reflects the isotopic composition of monsoonal rainfall. Thus the main perturbations of groundwater $\delta^{18}O$ can be attributed to an increased contribution of Atlantic source water to regional precipitation. This evidence agrees with the local climatology at Santana cave site, in which the rainiest and the driest months coincide with the monsoonal and extratropical regimes, whose optimum occurs during the summer and winter season, respectively (Gan et al., 2004).

5.2. Implications for isotopic paleoclimatic studies on speleothems

Results of this study have broad implications for paleoclimatic studies from stable oxygen isotopes on speleothems. Several factors need to be considered when interpreting speleothem records from subtropical South America or from other regions with similar climatic and hydrogeologic characteristics.

Interannual variations of rainfall $\delta^{18}O$ from IAEE stations along the subtropical Atlantic coast allow us to associate the drip water oxygen ratios with changes in rainfall patterns from a typical monsoon-related to a more extratropical regime based on seasonal differences in the isotopic signature of moisture sources contributing to regional precipitation. The results show that the $\delta^{18}O$ of speleothems from caves in this region may be a suitable proxy for tropical–extratropical air–mass interaction over southeastern South America, a feature that is intrinsically related to global atmospheric circulation modes. In addition, an eventual increase in the influence of the South American Monsoon System, characterized by more negative values of $\delta^{18}O$ in water and speleothems, would suggest an enhancement in summer rainfall. However, changes in paleorainfall amount cannot be detected based on relative differences in isotopic composition from such speleothems, as the amount effect is not a dominant controlling factor in this region. The relationships between moisture source region and rainwater $\delta^{18}O$ have been also used to interpret changes in rainfall patterns over subtropical Brazil for the last 116,000 years B.P. from the Bt2 speleothem oxygen isotope record (Cruz et al., 2005b).

Temporal variations of soil and drip water $\delta^{18}O$ in Santana cave are useful for understanding the processes controlling the resolution of climate signals retained in isotopic ratios of rainfall infiltrating in a relatively deep karst profile. The fast restoration observed in the isotopic composition of drip water in the cave does not only depend on the exchange rate between newly infiltrated water and the older reservoir stored in the system, but also on the hydrological regime in which seepage flow occurs during periods of more effective recharge. This suggests that intrannual and interannual shifts in climate can be inferred from the isotopic composition of speleothems. However, the distribution of more immobile water, efficiently transported from less permeable reservoirs in soil and epikarst to the aquifer, when the recharge capacity is reached, must be considered in order to avoid unrealistic residence time estimates in karst aquifers. Otherwise the age of the aquifer would be older than predicted by the models describing the water transport (Bethke and Johnson, 2002).

The very similar values of $\delta^{18}O$ from drip water and pool water in Santana cave indicates that the isotopic exchange with the cave atmosphere is not significant and that evaporative conditions are very limited. This is in agreement with the results obtained by Ingraham et al. (1990) for Carlsbad Cavern, who pointed out that cave water vapor $\delta^{18}O$ is controlled by the pool water composition. Such evidence suggests ideal environmental conditions for the deposition of cave secondary carbonates in isotopic equilibrium with their parental water. Thus, the oxygen isotopic ratios of speleothems can be linked to the rainfall composition.

Temperature estimates based on the equation of Craig (1965) from $\delta^{18}O$ values from modern speleothems and drip water are mostly concordant with the measured cave temperature within the estimated errors and indicate approximate conditions for isotopic equilibrium between speleothems and cave seepage water (Fig. 10). These conditions are in agreement with results of Hendy's tests performed on ancient stalagmites from both Santana (Cruz, 2003) and Botuverá caves (Cruz et al., 2005b). Slight discrepancies (less than 2 °C) among measured and calculated temperatures in few samples suggest that some fluctuations in $\delta^{18}O$ may be derived from uncertainties about age of speleothems and chemical composition and crystallographic controls (Dickson, 1991).

6. Conclusions

Seasonal variations in moisture source contribution are the major control of oxygen isotope ratios of drip waters within the Santana cave system. The aquifer feeding the stalactites has a similar mean isotopic composition as rainfall during summer and fall, which is related with the South American Monsoon System. Although the local karst aquifer is thicker than those usually reported in cave seepage hydrology studies, rapid perturbations of groundwater $\delta^{18}O$ were observed. Such shifts in the isotopic composition are associated with rainfall events that occur during winter and spring. These events have a greater contribution of Atlantic moisture and therefore more positive $\delta^{18}O$ values.

Our results indicate a relative rapid variation of the drip-water composition in the cave, which is more dependent on the behavior of the increased hydraulic head during periods of effective recharge into the system than on the simple mixing of waters from different recharge events. The synchronicity of the isotopic curves from soil and cave dripping sites confirms that the $\delta^{18}O$ of seepage water is independent of drip discharge. Therefore the isotopic signal of water collected at drip sites from 100 to 300 m depth appears to be related in a non-linear fashion with rainwater input into the karst. Distinctive short-term climate events may therefore be recorded not just in groundwater, but possibly also in the speleothems, as suggested by Baker and Brunsdon (2003).

Acknowledgements

We thank the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP), Brazil, for financial support of this research (Grant 99/10351-6 to I. Karmann and scholarship to F.W. Cruz Jr.). We thank Jurandir Santos and PETAR State Park Staff Cave and Botuverá's cave guides for supporting field work at Santana and Botuverá cave sites, respectively. **[LW]**

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