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Geochimica et Cosmochimica Acta 71 (2007) 2250–2263
Geochimica et Cosmochimica Acta
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Evidence of rainfall variations in Southern Brazil from trace element ratios (Mg/Ca and Sr/Ca) in a Late Pleistocene stalagmite

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Received 10 August 2006; accepted in revised form 8 February 2007; available online 16 February 2007

Abstract

Trace element ratios in the Bt2 stalagmite from Botuverá cave, Southern Brazil, are explored as a proxy for changes in the local rainfall recharge during the last 116 ky. BP Mg/Ca and Sr/Ca ratios, measured with an electron microprobe, are significantly positively correlated with one another throughout the entire record, and vary in a way that is very consistent with variations of $\delta^{18}O$ in the same speleothem during the last glacial period. We suggest that prior calcite precipitation in the vadose zone of the cave system is the main factor affecting the incorporation of Mg and Sr into calcite of the stalagmite. This interpretation is supported by trace element correlation patterns and by results from a hydrochemistry study performed in a cave located in the same region and in a similar environmental setting. Therefore, we conclude that higher (lower) Mg/Ca and Sr/Ca values are associated with lower (higher) levels of recharge into the karstic aquifer, as such conditions lead to an increase (decrease) in the volume of calcite precipitated in the unsaturated zone above the cave during dry (wet) climate periods.

Trace element variations point to generally dryer (wetter) conditions during lower (high) phases of summer insolation in the southern hemisphere. These periods coincide with decreased (increased) activity of the South American summer monsoon, as revealed by $\delta^{18}O$ stalagmite records. In addition trace element variations show that rather wet conditions persisted throughout most of the last glacial period from approximately 70 to 17 ky BP. We suggest that during this period the glacial boundary conditions, especially ice volume buildup in the northern hemisphere, played an important role for monsoon rainfall intensification in the region.

1. INTRODUCTION

Speleothems have become an important archive for studying climate change in the Late Pleistocene and Holocene. Most commonly, the oxygen isotope ratios of speleothem calcite have been used as a proxy for changes in the isotopic composition of rainfall of a particular region. Then, depending on the specific local relationships between climate and the $\delta^{18}O$ of rainfall, $\delta^{18}O$ of the speleothem may be interpreted in terms of mean temperature (Linge et al., 2001) or of rainfall source (Cruz et al., 2005a) or amount (Burns et al., 2000; Fleitmann et al., 2003). But speleothems contain a number of other, less-frequently utilized, chemical proxies for climate. For one, trace element ratios such as Mg/Ca and Sr/Ca have the potential to reveal changes in karst-water processes that may be climate related. For example, studies utilizing drip water modern monitoring programs performed in karst systems in

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doi:10.1016/j.gca.2007.02.005

different environments around the world (Fairchild et al., 2000; Tooth and Fairchild, 2003; Musgrove and Banner, 2004; McDonald et al., 2004) suggest that Mg/Ca and Sr/Ca ratios reflect the meteoric water infiltration rate in the vadose zone of caves, and that they, therefore, can be used to estimate relative variations in amount of rainfall. The relationships between climate parameters and trace element ratios obtained from studies such as these have been used to infer past hydrological changes from speleothems on decadal to subannual (Huang et al., 2001; Fairchild et al., 2001; Baldini et al., 2002; Treble et al., 2003; Johnson et al., 2006) to long-term time scales (Verheyden et al., 2000; Li et al., 2005).

In subtropical Brazil, stable oxygen and carbon isotope studies on cave stalagmites have provided new insight into the understanding of changes in rainfall regimes (Cruz et al., 2005a) and temperature (Cruz et al., 2006a) during the Late Pleistocene. They allow us to infer seasonal changes in the relative contribution of summer monsoonal and winter extratropical precipitation, because the speleothem $\delta^{18}O$ records the relative proportion of more depleted moisture from distant sources in the Amazon Basin and more enriched moisture from the nearby Atlantic Ocean (Cruz et al., 2005a). To date, the $\delta^{18}O$ records from stalagmites have revealed increases in the summer monsoon precipitation during periods of higher summer insolation, due to the influence of changing land-sea temperature contrast on the atmospheric circulation over South America. However, $\delta^{18}O$ variations in stalagmites from the Brazilian subtropics are not direct proxies of changes in the mean rainfall accumulation, because the amount effect is not the dominant factor controlling the isotopic composition of rainwater infiltrating down into the caves (Cruz et al., 2005b). Furthermore, in regions with a typical bimodal precipitation regime such as the study site, variations in $\delta^{18}O$ of rainfall and consequently of cave speleothems reflect primarily the relative contribution of monsoonal rainfall (60% of annual accumulation today) versus extratropical rainfall (40% of annual accumulation today). In this case, the paleorainfall amount cannot be determined from $\delta^{18}O$ of speleothems because an increase in the more isotopically depleted monsoon rainfall (average $\delta^{18}O$ of precipitation of about $-7‰$) might be compensated by a decrease in more enriched extratropical rainfall (average $\delta^{18}O$ of precipitation of about $-3‰$) and vice-versa.

In the present paper we use Mg/Ca and Sr/Ca ratios in a stalagmite that grew approximately continuously during the last 116 ky BP to infer past variations in the relative amounts of rainfall in Southern Brazil.

2. STUDY SITE

Stalagmite Bt2 was collected in Botuverá cave, a 1200 m long cave located in Southern Brazil (27°13′24″S; 49°09′20″W, Fig. 1). The sample is a 70 cm tall stalagmite that was active when collected. The sample is from the end of the cave's main gallery, 300 m from its only entrance and 110 m below the surface. Previous work indicates no relevant depositional hiatus in Bt2 during the last 116 ky BP (Cruz et al., 2005a).

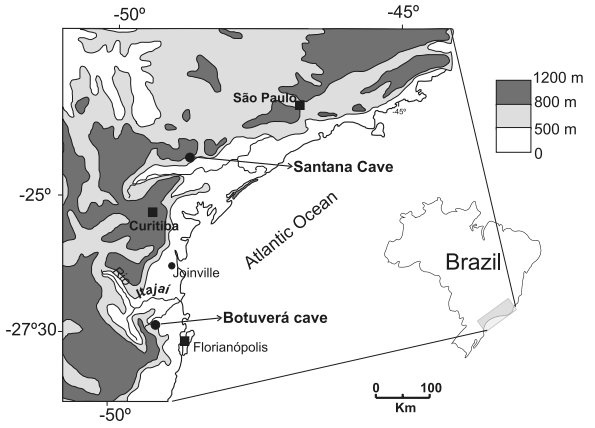

Fig. 1. Location map of the study sites in southeastern Brazil. Botuverá (1) and Santana (2) caves are located at the transition between the Atlantic coastal plain and the Serra do Mar and Serra Geral plateaus. The altitude at the surface above the caves varies from 230 to 700 m a.s.l.

The present-day climate in the cave site is sub-tropical humid, with nearly saturated mean relative humidity and rainfall that is uniformly distributed throughout the year (Rao and Hada, 1990). The mean annual precipitation (MAP) from 1911 to 1966 at a meteorological station 40 km from Botuverá Cave and at similar altitude was 1752 mm (Climerh-Epagri, 2004, pers.com). The external mean annual temperature (MAT) between 2000 and 2001 was 18.9 °C, respectively, in close agreement with measured cave MAT of 19.0 °C (Zilli and Rabelo, 2001). The cave entrance is located at the transition between the Atlantic coastal plain and the Brazilian plateaus at an altitude of 250 m. The flora of the area is a predominantly dense, tropical Atlantic rainforest growing in mature, meters-thick, clay-rich soils.

Because of a lack of observational temperature records for the study site we used NCEP/NCAR reanalysis data (derived from the closest grid cell, centered at 27.5°S/50°W; Kalnay et al., 1996). The analysis showed that, relatively cold conditions prevail during the austral winter (June–August) and mean surface temperature drops to 13.9 °C near the cave site. The summer mean temperature (December–February) averaged 20.8 °C between 1968 and 1996. On average the temperature difference between the warmest and coldest month in the region (February and July) is ~12 °C, but the annual temperature range can vary from ~7 °C to 25 °C (Cruz et al., 2006a).

Approximately 60% of annual average precipitation occurs during late spring and summer (October–March) and is linked to northwesterly low-level moisture transport from the Amazon basin related to the South American Monsoon system (Zhou and Lau, 1998; Gan et al., 2004). The remaining precipitation occurs from the late fall to early spring (April–September) and is mostly associated with the passage of extratropical cyclones along the subtropical Atlantic coast (Vera et al., 2002). The increases in the frequency and

intensity of the cyclones are associated with a northward displacement of the subtropical jet, which leads to an enhancement in the extratropical circulation. The relative contribution of extratropical precipitation decreases moving north of Botuverá cave, while the percentage of monsoonal precipitation increases (Fig. 2). These differences in the regional rainfall distribution are very important when comparing speleothem records from different caves in subtropical Brazil, as we will do here by using samples from Botuverá and Santana caves (Fig. 1). The comparison of the $\delta^{18}O$ speleothem records from these caves indicates a steep north–south gradient in $\delta^{18}O$ of rainfall, which is interpreted as reflecting different relative contributions of extratropical and monsoonal precipitation to the two locations. For some time periods, more pronounced negative $\delta^{18}O$ anomalies occur in the northern part and more positive anomalies in the southern part of the region, which appear to be associated with more abundant monsoonal and extratropical rainfall, respectively (Cruz et al., 2006b).

Also pertinent to this study are the results of a four year long hydrochemistry monitoring program performed in Santana cave (24°31′51″S; 48°43′36″W; (Karmann et al., under review in Chemical Geology), which has 6300 m of mapped galleries and is located about 300 km north of Botuverá cave.

3. METHODS

The Bt2 age model is constrained by 20 U–Th ages measured at the Berkeley Geochronology Center (USA), using conventional chemical and thermal ionization mass spectrometry (TIMS) techniques. Samples preparation and experimental procedures used for geochronology of Bt2 stalagmite was described in detail by Cruz et al. (2005a).

Layer thickness in Bt2 was digitally measured on images obtained from a CCD camera by using the Image-Pro software. We used transmitted light and reflected light images for the transparent and the non-transparent portions of the stalagmite (Fig. 5a). Because Bt2 has quite thick layers, mean thickness of 1.3 mm, it was possible to precisely delimit individual layers from magnified images.

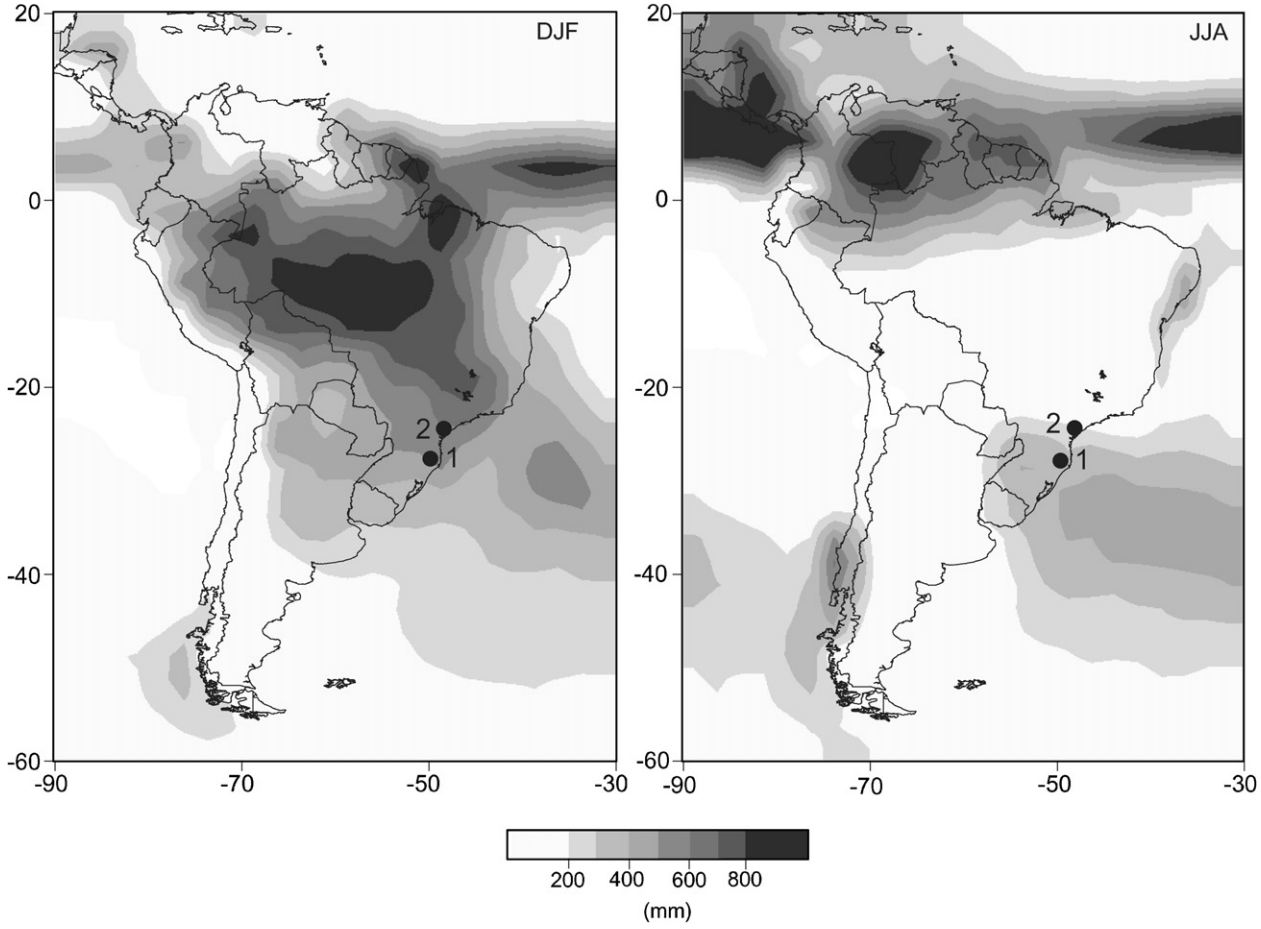

Fig. 2. Long-term mean (1979–2000) Climate Prediction Center Merged Analysis of Precipitation (CMAP, Xie and Arkin, 1997) seasonal precipitation totals (in mm) for December–February (left) and June–August (right). Precipitation over SE Brazil in DJF is related to the southward expansion and intensification 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 the text: 1, Botuverá Cave; 2, Santana cave.

Compositional microanalysis was conducted in two steps, using instrumentation within the Department of Geosciences, Electron Microprobe/SEM Facility at the University of Massachusetts. First, the Ca and Mg contents were determined using the Cameca SX50 electron microprobe, a four wavelength-dispersive spectrometer instrument automated via Cameca's SXRayN50 software. Analyses were performed at 15 kV, 15 nA using a defocused beam (10 μm beam diameter) and 20 s count times. Analyses were taken in 1 mm increments through each of the 12 sections used to cover the entire stalagmite. At the 1.1 wt.% concentration level for Mg (the approximate average in the unknown), the analysis yields a precision of ±0.03 wt.% (2σ).

Trace element analyses for Sr were performed using the Cameca SX-Ultrachron electron microprobe. This unique instrument is a five wavelength-dispersive spectrometer instrument that was developed for high spatial resolution and count precision, and operates via Cameca's PeakSight™ software automation system. This instrument is equipped with high-sensitivity spectrometers, including both "large" PET (LPET) and "very large" PET (VLPET) monochromators. The analytical line used for Sr is Sr Lα. Typically, this will be run using a TAP monochromator with low pressure P-10 flow proportional counters. SrLα is found at the low wavelength end of a TAP spectrometer, allowing very high counting efficiency, approximately 10× the count rate of the same line on PET (SrLα is found at the high wavelength end of a PET spectrometer), but having the distinct disadvantage of relatively low spectral resolution. In the case of Sr in Ca-carbonate, the influence of CaKα (2nd-order) on SrLα is substantial. The Ultrachron high intensity spectrometers, however, permit Sr to be run on PET, eliminating the spectral overlap issue. Count precision was enhanced by integrating counts from multiple spectrometers: PET, 2 LPET, and 2 VLPET; all flow-proportional P-10 at ~3 bars total pressure with Be detector windows except for the PET spectrometer at ~1 bar with polypropylene; and polypropylene column separation windows except for the LPET spectrometers which use mylar. With this arrangement, the average SrLα count rate is more than 2× greater than the count rate using a single TAP at 1 bar (P-10 and polypropylene windows). All Sr analyses were done directly next to the points analyzed for Ca and Mg, using a 15 kV, 100 nA beam, defocused to 10 μm. A 100 s counting time was used. The calculated counting precision for a single-point analysis with five-spectrometer integration for Sr is 29 ppm (2σ) at a concentration of 200 ppm, with a detection limit of 50 ppm.

4. RESULTS

Time series of Sr/Ca and Mg/Ca ratios (weight %) of the Bt2 speleothem are presented in Fig. 3. Sr/Ca and Mg/Ca ratios (x10^3) vary from 0.16 to 1.25 and from 19.86 to 50.5, respectively. These values are within the range of those found in similar studies on stalagmites (Verheyden et al., 2000; Li et al., 2005). The Mg/Ca and Sr/Ca ratios are positively correlated with one another ($r^2 = 0.55$) and show a pattern that is coherent with southern hemisphere summer insolation and stable oxygen isotope ratios during the last 116 ky BP (Cruz et al., 2005a). This pattern is characterized by a general increase in trace elements ratios and $\delta^{18}O$ values during low insolation phases and vice-versa. However, there are some significant differences in the long-term variability of trace element ratios throughout the last glaciation. For instance, the positive relationship between Mg/Ca, Sr/Ca and insolation is less clear from 70 to 17 ky BP.

Anomalies (total mean − individual values) of trace-element ratios and oxygen stable isotopes for Bt8 and St8 (Cruz et al., 2006b) are plotted in Fig. 4 in order to provide a more realistic comparison of the temporal variability between records. Differences in trends of normalized trace element ratios are marked by pronounced alternations from positive to negative anomalies from 116 to 70 ky BP and a predominance of negative anomalies from 70 to 17 ky BP, except for discrete positive anomalies in periods of low insolation in Bt2 (Fig. 4). In comparison, positive anomalies of $\delta^{18}O$ in the second period are still prevalent at periods of high insolation in Bt2, but interestingly they are almost absent in St8 from Santana Cave and in the trace element records. After 15 ky BP positive trace element anomalies again become predominant (Fig. 4).

5. DISCUSSION

5.1. Climate signal of Sr/Ca and Mg/Ca ratios

Factors that might affect the incorporation of Sr and Mg in speleothem calcite include changes in the composition of drip water, the temperature cycle of the cave atmosphere and the growth kinetic effects (Huang and Fairchild, 2001; Huang et al., 2001; Treble et al., 2003; Treble et al., 2005). Huang and Fairchild (2001) found that under karst-analogue experimental conditions, the partition coefficient for Sr ($D_{Sr} = (Sr/Ca)_{calcite}/(Sr/Ca)_{solution}$) may depend on speleothem growth rate, in agreement with a number of experimental studies of the incorporation of Sr into calcite (e.g. Tesoriero and Pankow, 1996). In contrast, the distribution coefficient for Mg, D_{Mg}, appears to be dependent on temperature (Huang and Fairchild et al., 2001). The same study reported that changes in growth rates exert a strong control on Sr/Ca or Sr variations in speleothems in the absence of significant variations in drip water composition. Fast growth rates may increase the Sr/Ca ratios in speleothems (Huang and Fairchild, 2001; Treble et al., 2003). However, substantial Sr/Ca variations due to growth kinetics alone require a speleothem growth range that is not observed in nature, especially over short time periods (Fairchild et al., 2006).

Fig. 6 presents a comparison between growth rates, layer thickness, carbon isotopic composition and Mg/Ca, Sr/Ca ratios of Bt2 stalagmite. Variations in Bt2 elemental ratios are not as consistent with the growth rates as they are with $\delta^{18}O$ and summer insolation. In fact, growth rates are in phase with Mg/Ca, Sr/Ca ratios between 70 and 17 ky BP and out of phase in the intervals between 114 to 84 ky BP; 83 to 73 ky BP; and after 3 ky BP. Hence, we conclude that growth rate alone does not exert a major control on trace element ratios in Bt2.

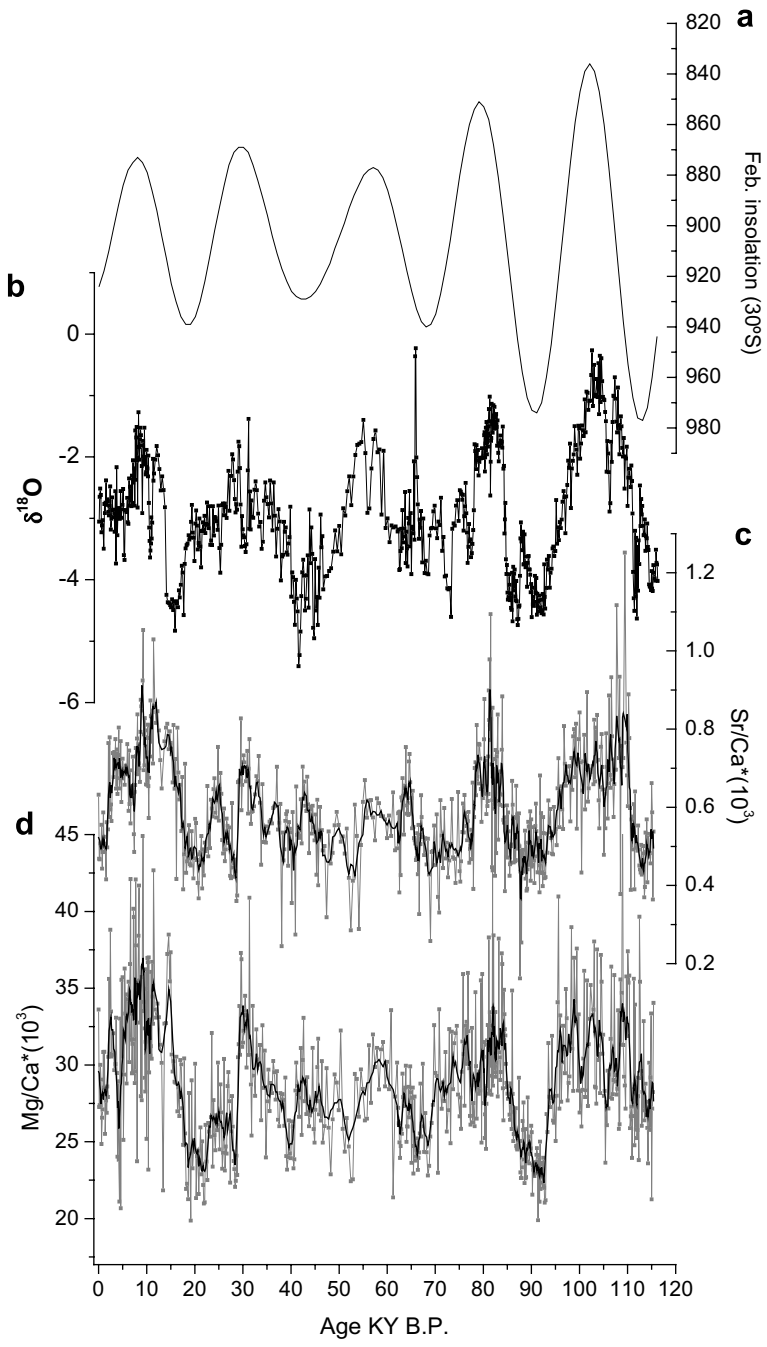

Fig. 3. Comparison between (a) February insolation at 30 °S (Berger and Loutre, 1991; the insolation axis is reversed); (b) Bt2 stalagmite ratios of oxygen isotopes; (c) Sr/Ca and (d) Mg/Ca ratios. The solid black lines in (c) and (d) are 5-points running mean.

Variations in trace elements of speleothems may be due to the same process that causes layer thickness to vary because of growth kinetics (Treble et al., 2005). A relative enrichment in the calcite Mg/Ca ratio is attributed to the relative increase of Mg adsorbed onto non-lattice sites compared with Mg incorporated into lattice sites (Mucci and Morse, 1983; Treble et al., 2005). These crystallographic features may be linked to climate changes because samples with higher crystal defect density and more irregular morphology along the growth surface reflect periods when drip rates are at their lowest or cease completely (Frisia et al., 2000; Treble et al., 2005).

Growth kinetics may be a relevant mechanism affecting the Mg/Ca ratios because Bt2 stalagmite is marked by significant variations in texture and primary structure along the growth axis. Along its 70 cm long axis, Bt2 consists of a lower part marked by 11.7 cm of thinner layers of predominantly non-transparent columnar crystals; a central part mainly consisting of thickly laminated, transparent columnar crystals, which abruptly give way to predominantly

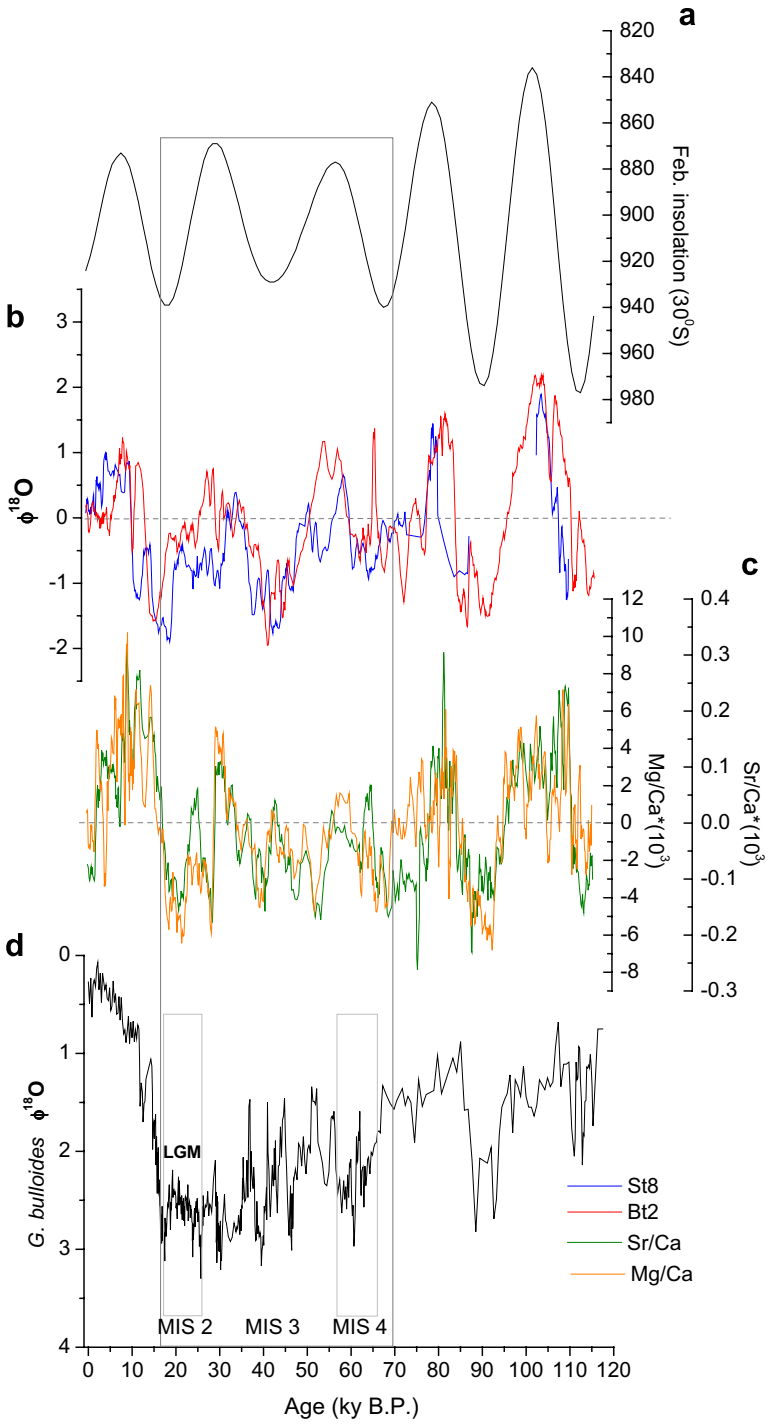

Fig. 4. (a) February insolation at 30°S (the insolation axis is reversed); (b) $\delta^{18}O$ anomalies for Bt2 (Cruz et al., 2005a) and St8 (Cruz et al., 2006b) stalagmites; (c) Mg/Ca and Sr/Ca anomalies for Bt2 stalagmite; (d) $\delta^{18}O$ of planktonic foraminifera in the core MD95-2040 from Iberian Margin in North Atlantic (Abreu et al., 2003). Note the predominance of low trace element and more positive values of $\delta^{18}O$ of planktonic foraminifera during the MIS4 to MIS2 (marked with rectangles).

non-transparent columnar crystals and thinner layers in the upper part of the sample (Figs. 5 and 6). This upper contact marks the beginning of the Holocene period at 9.75 cm from the top of the stalagmite. The transparent character is apparently associated with a low density of microscopic cavities, which mark the contacts between layers. Such cavities are not as visible at terminations of crystals in the transparent part of Bt2 as they are within its non-transparent portions (Fig. 5).

Variations in texture and structure are in general consistent with trace element ratios in Bt2, with lower and higher values corresponding to portions mainly consisting of

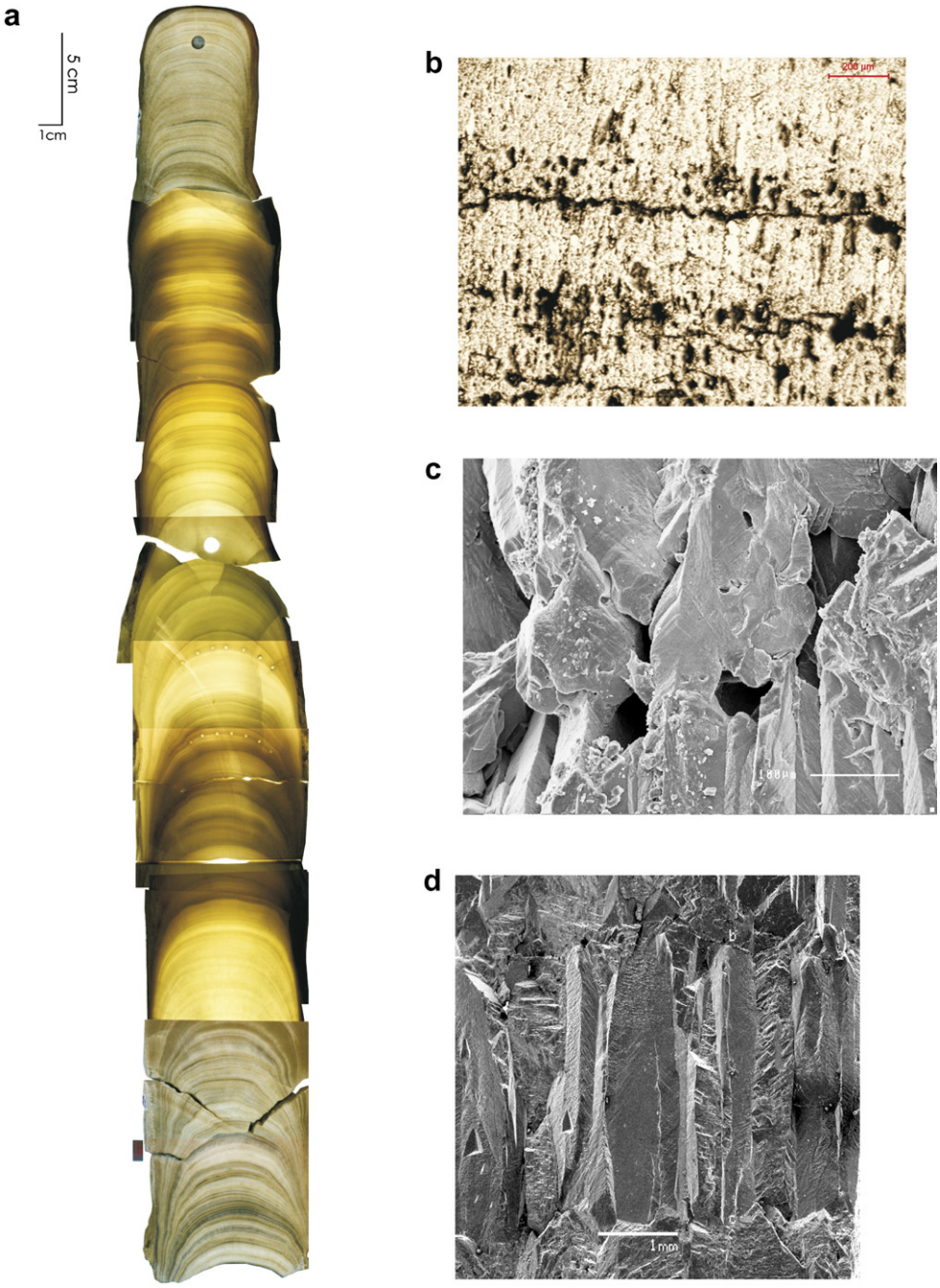

Fig. 5. (a) CCD camera image showing predominantly transparent and, thicker layers (transmitted light), respectively, and non-transparent and thinner layers (reflected light), respectively, in the central portions and extremities of Bt2 stalagmite; (b) petrography microscope image (parallel nicols) showing a high alignment of cavities that define typical layers in the upper and lower portions of Bt2; (c) detail of the cavities formed in the terminations of columnar crystals; (d) SEM image of large columnar crystals showing regular morphology typical of layers in central portion of Bt2.

transparent/thicker layers and non-transparent/thinner layers, respectively (Figs. 5 and 6). Exceptions to this relationship are found between 116 to 110 ky BP, 85 to 72 ky BP, 17 to 11 ky BP and after 3 ky BP. Thus, it might be possible that growth kinetics could produce significant fluctuations in Mg/Ca, Sr/Ca ratios of Bt2 that are superimposed on the insolation trend such as the negative anomalies ratios that persisted between 70 and 17 ky BP (Fig. 4). Nevertheless, environmental changes are still captured in the Mg/Ca, Sr/Ca ratios of Bt2, independent of the extent to which this mechanism affects its geochemical composition, because thicker layers resulting from more continuous growth are linked to wetter periods and more prolonged rainy seasons and vice-versa.

Although a large number of experimental studies have shown that temperature exerts an important control on

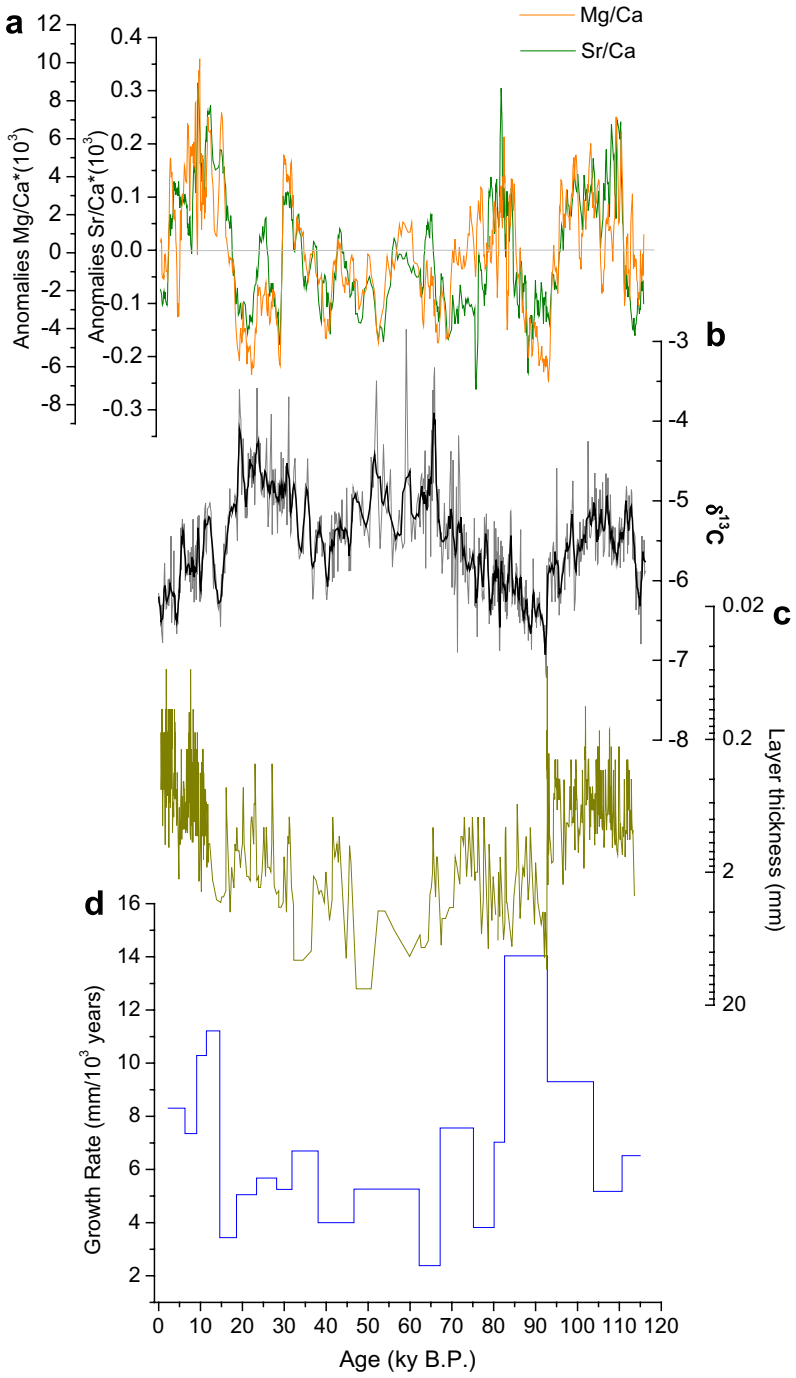

Fig. 6. Comparison between (a) Anomalies of Mg/Ca and Sr/Ca ratios calculated for Bt2 stalagmite and (b) $\delta^{13}C$ variations and; (c) Layer thickness; (d) Growth rates in the same speleothem. The solid black line in (b) is a 5-points running mean.

Mg incorporation into calcite (Morse and Bender, 1990; Rimstidt et al., 1998), its influence on the speleothem composition is generally considered negligible on annual timescales because temperature in most caves, including Botuverá, is nearly constant throughout the year. On the much longer timescales of our study, temperature within the cave might have varied by 3–6 °C, enough to cause some variability in the Mg/Ca ratios. Similar values of trace element ratios during the Last Glacial Maximum and the late Holocene, however, do not support a major control by temperature in Bt2. The strong correlation observed between Sr/Ca and Mg/Ca ratios in our study argues for a single mechanism controlling both, such as calcite precipitation in the karst system above the cave, which would strongly influence the chemistry of karst waters.

A change in the chemistry of the water forming the speleothems is often considered to be a dominant factor for speleothem records that show Mg and/or Sr variations

(Verheyden et al., 2000; Baldini et al., 2002; McMillan et al., 2005; Li et al., 2005; Johnson et al., 2006). Drip water composition is closely linked to hydrological conditions in the cave system because processes controlling carbonate dissolution and precipitation are highly dependent on the rate at which meteoric water infiltrates down in the soil-bedrock profile (Fairchild et al., 2000; Musgrove and Banner, 2004; Tooth and Fairchild, 2003). In this context, decreased water levels in the vadose aquifer above the cave can enhance air ventilation through the fractures or proto-conduit networks and trigger CO_2 degassing, while promoting prior calcite precipitation (PCP) during dry periods. Ca is preferentially incorporated into calcite precipitated in the vadose zone right above the cave (D_{Sr} and $D_{Mg} \ll 1$), resulting in higher Sr/Ca and Mg/Ca in drip waters (Huang and Fairchild, 2001). This process is likely to produce coherent variations in these trace element ratios in speleothems.

A four year long hydrochemistry monitoring program performed in nearby Santana cave (Fig. 1), reveals that prior calcite precipitation is most likely the dominant process affecting the drip water composition (Karmann et al., under review). Because the Santana cave system shows very similar climatic, hydrogeological and environmental (e.g. soil and vegetation cover) characteristics, it provides an excellent analogue for understanding the dissolution–precipitation processes taking place at 110 m depth in Botuverá cave, where Bt2 was collected. Hydrochemical parameters measured in rimstone pools, cave rivers and at drip sites with contrasting discharge and located at depths from 100 to 300 m in the Santana cave system show clear synchronous variations that are related to seasonal changes in rainfall recharge. A fast and synchronous trace element response to rainfall variations is still possible in relatively thick unsaturated aquifers above the Santana cave because of the high connectivity between flow paths in the cave due to piston flow mechanisms. This is also evident from studies of dissolved organic carbon and O and D stable isotope studies on soil and drip waters performed in the same cave (Cruz et al., 2005b; Cruz et al., 2005c).

In Santana cave, lower Mg/Ca and Sr/Ca ratios are found following rainfall associated with the South American monsoon in Southern Brazil, which peaks between December and February (Fig. 7). Simultaneous and relatively rapid variations in $\delta^{18}O$ (Cruz et al., 2005b) and Mg/Ca and Sr/Ca ratios (Karmann et al., under review) of water from drip sites with a large range in mean discharge and located at different depth below the surface revealed that processes such as drip CO_2 degassing are unlikely to significantly affect the isotopic composition of drip waters or stalagmite calcite in relative deep caves such as Santana and Botuverá. Otherwise, different responses of infiltrated waters with different residence time and degassing rate would be expected between slow and fast drip flows speleothems. Indeed, lower ratios are more consistent with variations in rainfall amount than drip discharge. On the other hand, it is possible that drip CO_2 degassing may be responsible for some secondary shifts in the Mg/Ca and Sr/Ca ratios of Bt2.

The PCP is well illustrated by the Santana cave system, where different types of water samples show an significant exponential decrease of Ca in solution relative to both Mg and Sr (Figs. 8a and b). The observed Sr/Ca and Mg/Ca curves are very consistent with model behavior of drip solution under conditions favorable for PCP in a karst unsaturated zone (Fairchild et al., 2000). In summary, the PCP mechanism in the Pérolas–Santana System is independent of water type (river, drip, pools) and location within the system. The only exceptions are the waters from runoff and soil sites, where no relationship between these trace element ratios was observed, because the epikarst waters were always non-saturated in respect to calcite. In addition, a positive correlation between Mg/Ca and Sr/Ca appears to be independent of bedrock composition (Fig. 8c). The bedrock composition influences the absolute values of ratios, as demonstrated by different slopes of Mg/Ca and Sr/Ca curves in Fig. 8c.

In contrast, prior calcite precipitation does not appear to be an important mechanism for $\delta^{13}C$ variations in Bt2. Johnson et al. (2006) have reported that PCP and drip water CO_2 degassing are dominant mechanisms on $\delta^{13}C$ variations in stalagmites from China and that they affect the $\delta^{13}C$ and Mg/Ca and Sr/Ca ratios in the same direction. Conversely, the negative relationship between $\delta^{13}C$ and Mg/Ca and Sr/Ca ratios found in most of the Bt2 record suggests that both mechanisms are not controlling the $\delta^{13}C$ variations in the same stalagmite (Fig. 6). This supports our previous interpretation that $\delta^{13}C$ variations are primarily linked to soil processes (Cruz et al., 2006a).

Because the trace element ratios also show a coherent positive covariation pattern during the last 116 ky BP in the Bt2 stalagmite, we interpret that PCP is the main process controlling the incorporation of Sr and Mg in the calcite. Therefore we can relate the trace element variations to the level of the unsaturated aquifer above the cave, a factor that is directly dependent on local rainfall conditions. Since PCP is dependent on the degree of ventilation in the vadose zone, we infer that this process is less effective when the rainfall recharge events are more intense and more evenly distributed throughout the year. In this case, the residence time of water in the karst aquifer is, on average, lowest, and PCP is lessened. Furthermore, geochemistry variations in Bt2 are likely coupled to the hydrological changes due to the combined effects of PCP and kinetic mechanisms related to speleothem growth rates. The second one may play a secondary role on Mg/Ca and Sr/Ca variations of Bt2.

5.2. Rainfall variations and climate forcing of South American summer monsoon in Southern Brazil

Based on the above discussions we propose that trace element variations in the Bt2 record are closely linked to rainfall variations in Southern Brazil during the Late Pleistocene. Lower values of Sr/Ca and Mg/Ca ratios correspond to wetter conditions (Fig. 7). Thus, the regional climate variability inferred from this relationship is characterized by relatively wet and dry periods coinciding with high and low incoming summer solar radiation in the southern hemisphere (Figs. 3 and 4). The striking resem-

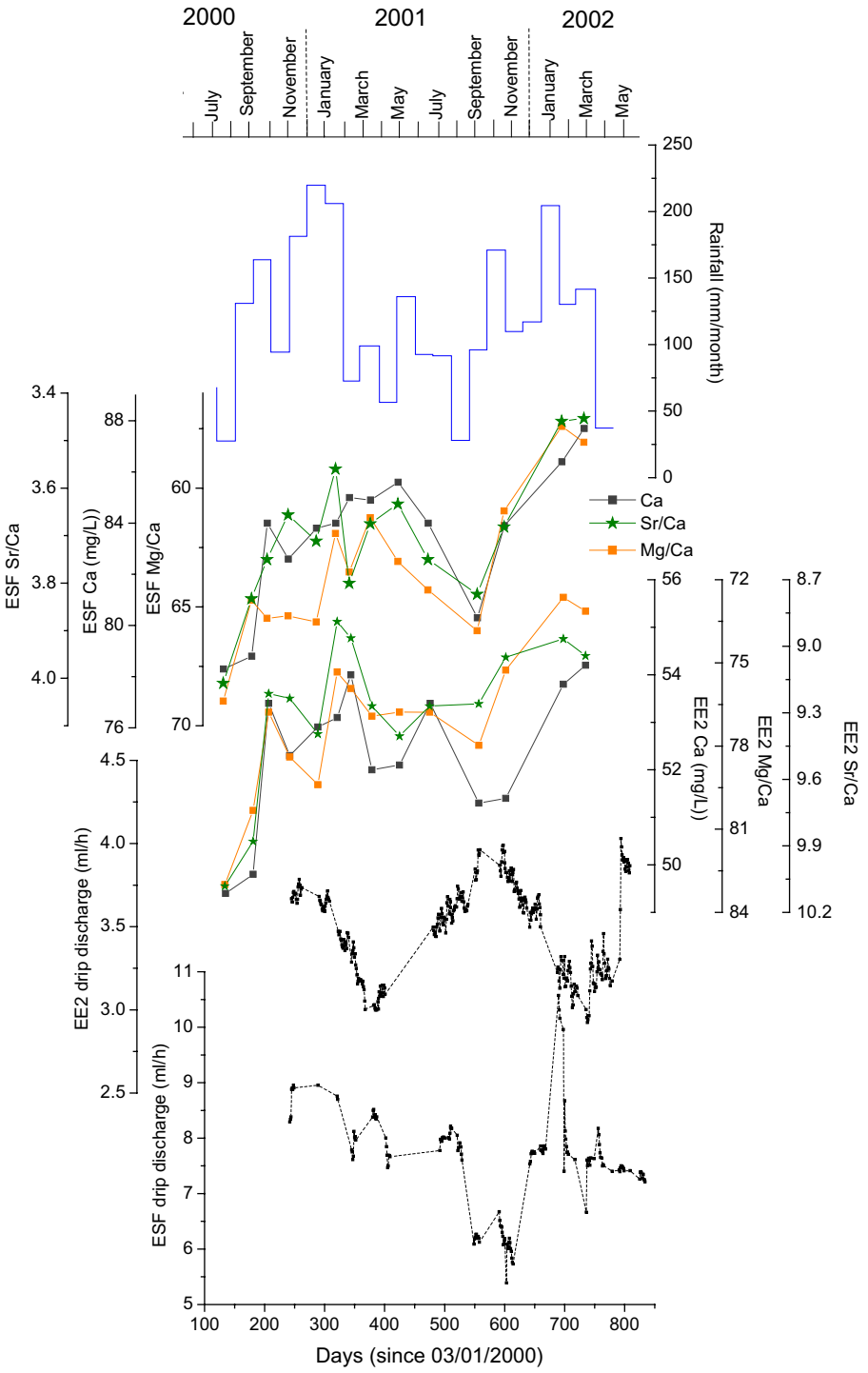

Fig. 7. Comparison between Ca, Sr/Ca, Mg/Ca and drip discharge variations at ESF and EE2 sites located 100 and 300 m below the surface in Santana cave, respectively (Karmann et al., under review). Time-series of Ca, Sr/Ca, Mg/Ca follow approximately the variations in monthly rainfall amount in the cave site. Similar variations in the Sr/Ca, Mg/Ca ratios between drips showing such different hydrological behavior indicate that CO_2 degassing during dripping is not the dominant process controlling the Sr/Ca, Mg/Ca in cave drip water and consequently in speleothems from caves in southern Brazil.

blance between trace element ratios and the $\delta^{18}O$ record (Cruz et al., 2005a) in the same stalagmite also suggests that changes in annual rainfall amount are closely related to atmospheric circulation and the relative seasonal contribution of South American summer monsoon (SASM) and extratropical rainfall, respectively.

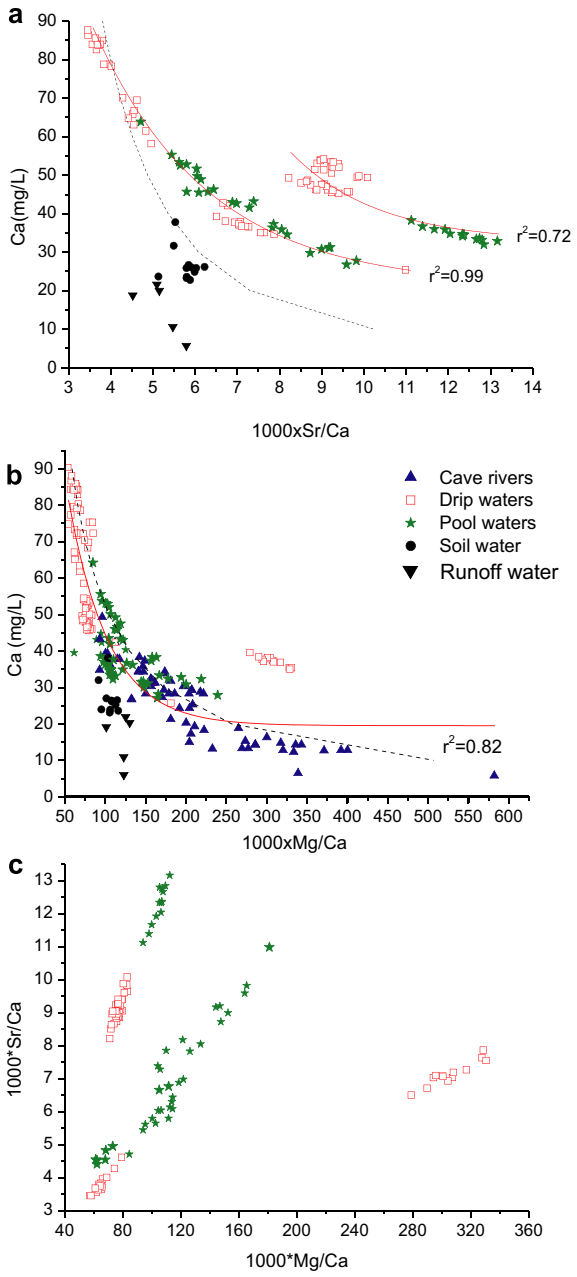

Fig. 8. (a) Ca vs. Sr/Ca; (b) Ca vs. Mg/Ca; (c) Mg/Ca vs. Sr/Ca for samples collected during a monitoring program performed in Santana–Pérolas, a cave system also located in subtropical Brazil (Karmann et al., under review). Dotted lines are prior calcite precipitation trend (Fairchild et al., 2000) calculated using partition coefficients of 0.0284 and 0.058 obtained from Mg/Ca and Sr/Ca in water and modern speleothem samples from the same cave site.

The present multi-proxy comparison suggests that the increases in local rainfall recharge reflect periods of enhanced monsoon rainfall in the region during high summer insolation phases, as manifested by lower values of both $\delta^{18}O$ and trace element ratios in Bt2 (Fig. 4). In addition, relatively dry conditions, indicated by higher trace element ratios during low insolation phases, can only be caused by reduction in summer monsoon rainfall, since a decrease in the isotopically-enriched extratropical winter rainfall would result in more negative $\delta^{18}O$ values in the Bt2 stalagmite. This is especially true during the full glacial times when weak positive or even negative trace element anomalies are observed, despite periods of low insolation (between 63 to 50 ky BP and 36 to 24 ky BP), when one would expect to see strong positive anomalies (Fig. 4).

Hence, the notion of longer and more intense summertime rainfall during full glacial times is supported by synchronous negative anomalies in both trace element ratios and $\delta^{18}O$ in Bt2, but also in the St8 stalagmite from Santana cave (Cruz et al., 2006b; Fig. 4). Negative anomalies in $\delta^{18}O$ are even more evident in the St8 record, probably because the more northerly location of Santana cave receives a larger proportion of isotopically depleted summer monsoon rainfall when compared to Botuverá cave (Rao et al., 1996). The weaker correspondence of trace element variations with insolation trends between 70 ky BP and 17 ky BP suggests that other factors contributed to the excess of monsoon rainfall during this time period.

5.3. Influence of summer insolation forcing on climate in the Brazilian subtropics during glacial periods

Since a consistent relationship between trace elements, stable oxygen isotopes and summer insolation is maintained during the Late Quaternary, we can infer that insolation is the most important low-frequency forcing, leaving a distinct imprint on reconstructed rainfall amount and meridional atmospheric circulation in the Brazilian subtropics. There is clear evidence for increased (decreased) regional monsoonal convection during periods of high (low) southern hemisphere summer insolation. This relationship is maintained by differential heating of land and ocean, which in turn exerts a major control on the intensity and location of the South American summer monsoon. This monsoon system is connected with the South Atlantic Convergence Zone (SACZ) and consequently determines the spatio-temporal variation of summertime rainfall in Southern Brazil and the La Plata Basin, both on modern time scales (Paegle and Mo, 2002; Díaz and Aceituno, 2003; Gan et al., 2004) and during the Late Pleistocene (Cruz et al., 2005a; Wang et al., in press). This is also consistent with the southerly shifts in the location of the ITCZ, which increased the rainfall in northeast Brazil during high summer insolation phases (Wang et al., 2004). However, insolation alone cannot explain the excessive monsoon rainfall as indicated by exceptionally low trace element ratios from 70 ky BP to 17 ky BP (Fig. 4). An additional external climate forcing must at times amplify the southward moisture transport to the South American subtropics.

Others factors that might have caused an enhancement of the South American summer monsoon during the last glaciation are the atmosphere–ocean interactions in the south Atlantic and a remote control by northern hemisphere glacial boundary conditions, sea and land ice cover and temperature, on the ITCZ position. The former mechanism involves meridional displacements of the confluence region between the cold Malvinas and the warm Brazil currents, centered around 30°S on the southwest Atlantic coast (Robertson

and Mechoso, 2000; Wainer and Venegas, 2002). Today, on interdecadal time scales, positive rainfall anomalies in southern Brazil are linked to enhanced SACZ activity caused by warmer sea surface temperatures (SST) resulting from southward movement of the Brazil current. However, such a major control of the SSTs on the SACZ convection in southern Brazil during the Late Pleistocene seems very unlikely, because SST during glacial times remained cooler than during the Holocene, as pointed out by $\delta^{18}O$ records of planktonic foraminifera off the Brazilian coast (Arz, 1998). Therefore, variations in South Atlantic SSTs do not seem able to explain the excess of monsoon rainfall observed in the region during Marine Isotope Stages 4, 3 and 2.

A teleconnection to the high northern latitudes is primarily a result of northern hemisphere ice sheet volume and its effects on trade winds, meridional SST gradients and ITCZ displacements. According to simulations by Chiang et al. (2003; 2005), glacial conditions at high northern latitudes are transmitted to the tropics through strengthened northeasterly trades over the North Atlantic, which increase the latent heat flux, that in turn leads to the progressive cooling of SSTs from the subtropical to the tropical North Atlantic. The resulting interhemispheric SST gradient highly favors a southward shift of the ITCZ during periods such as the last glacial maximum, ~21 ky BP (Chiang et al., 2003). This mechanism resembles meridional ITCZ displacements observed in eastern tropical Brazil during boreal winter on interannual-decadal timescales today (Nobre and Shukla, 1996). A similar shift of the ITCZ can also result from a reduced Atlantic thermohaline circulation during stadial phases, but in this case the meridional mode response of the tropical Atlantic SSTs is due to the combined effect of larger inland ice-volume over the northern hemisphere and increased freshwater flux on ocean heat transport (Claussen et al., 2003). Nevertheless, the rainfall distribution over South America would be affected in both cases due to the anomalous transport of moisture into the Amazon Basin, which results from a more southerly position of the ITCZ.

Our record reveals that the glacial boundary conditions in the northern hemisphere impacted convective rainfall in the southern hemisphere by reinforcing the moisture transport from the Amazon Basin to southern Brazil during MIS 4–MIS 2. This hypothesis is broadly supported by the coincidence of lower trace element ratios in Bt2 with lower SSTs in the subtropical north Atlantic, as indicated by heavier $\delta^{18}O$ in planktonic foraminifera (Fig. 4). The mechanism to explain lowered SSTs in this region is associated with increased NE trade winds within the region climatologically influenced by the Azores high in the subtropical North Atlantic as a result of melting icebergs during periods of more pronounced ice buildup during the last glaciation (Moreno et al., 2002; Abreu et al., 2003).

On the basis of the previous description it is possible to infer that the ice-volume effect on the ITCZ displacement induced anomalous cross-equatorial moisture flow, which lead to higher land precipitation in the southern hemisphere during a considerable part of the last glaciation. Intensified deep convection in the Amazon basin is often associated with an anomalous upper-tropospheric anticyclonic circulation over the central part of the continent. This intensified anticyclonic circulation aloft, combined with a strengthened Chaco low at the surface tends to reinforce the northwesterly low-level flow of warm and humid air masses from the Amazon region southward during wet monsoon episodes in the subtropical plains of southern Brazil and Uruguay (Díaz and Aceituno, 2003; Gan et al., 2004).

6. CONCLUSIONS

The striking similarity between trace element ratios in the Bt2 stalagmite record indicates a dominant control of prior calcite precipitation on the Sr and Mg ratios incorporated into the calcite cave formations and secondarily by growth kinetics. This PCP mechanism is consistent with previous results from a cave hydrochemistry monitoring program in subtropical Brazil. Therefore the Mg/Ca and Sr/Ca ratios of Bt2 represent changes in hydrological conditions associated with changes in the rate of rainfall recharge and water level in the system throughout the year. Based on this evidence we were able to reconstruct relative variations in amount and seasonal distribution of rainfall for the last glacial cycle in southern Brazil.

The good match of Mg/Ca and Sr/Ca ratios with summer insolation confirms that the rainfall amount in the region is primarily forced by insolation precession during the last 116 ky BP in such a way that wet and dry periods coincide with high and low austral summer insolation phases, respectively. The fact that the trace element ratios also correlate with $\delta^{18}O$ variations indicates that changes in rainfall amount are in general driven by the time-varying influence of the two dominant atmospheric circulation patterns, which determine the relative contribution of rainfall by the South American summer monsoon and extratropical regimes, respectively.

The Bt2 trace element record suggests a new scenario for the paleoclimate in southern Brazil, featuring a predominantly wet last glacial period. The rainfall excess in the study region is likely caused by the glacial conditions in the northern hemisphere, which lead to enhanced moisture flux and moisture convergence into the southern hemisphere tropics during the South American summer monsoon season. Because more intense monsoon rainfall in the Brazilian subtropics depends on an increase in the poleward transport of low-level tropical moisture, we suggest increased moisture availability and higher convective activity at least in part of the Amazon Basin during the last glaciation. In order to evaluate this problem, however, more studies based on independent records of paleo-rainfall from low-latitude South America are needed.

ACKNOWLEDGMENTS

The authors wish to thank Kathleen Johnson and two anonymous referees and the Associate Editor Miriam Bar Matthews for their insightful suggestions and comments.

REFERENCES

Abreu L., Shackleton N. J., Schonfeld J., Hall M., and Chapman M. (2003) Millennial-scale oceanic climate variability of the

Western Iberian margin during the last two glacial periods. *Mar. Geol.* **196**, 1–20.

Arz, H., 1998. Dokumentation von kurzfristigen Klimaschwankungen des Spätquartärs in Sedimenten des westlichen äquatorialen Atlantiks. Berichte, Fachbereich Geowissenschaften, Universität Bremen **124**, 96 p. (in German).

Baldini J. U. L., McDermott F., and Fairchild I. J. (2002) Structure of the 8200 year cold event revealed by a speleothem trace element record. *Science* **296**, 2203–2206.

Berger A., and Loutre M. F. (1991) Insolation values for the climate of the last 10 million years. *Quaternary Sci. Rev.* **10**, 297–317.

Burns S. J., Matter A., Frank N., and Mangini A. (2000) Speleothem-based paleoclimate record from northern Oman. *Geology* **26**, 499–502.

Chiang J. C. H., and Bitz C. M. (2005) Influence of high latitude ice cover on the marine intertropical convergence zone. *Clim. Dynam.* **25**, 477–496.

Chiang J. C. H., Biasutti M., and Battisti D. S. (2003) Sensitivity of the Atlantic Intertropical Convergence Zone to the last glacial maximum boundary conditions. *Paleoceanography* **18**(4). doi:10.1029/2003PA00091.

Claussen M., Ganopolski A., Brovkin V., Gerstengarbe F.-W., and Werner P. (2003) Simulated global-scale response of the climate system to Dansgaard/Oeschger and Heinrich events. *Clim. Dynam.* **21**, 361–370. doi:10.1007/s00382-003-0336-2.

Cruz Jr., F. W., Burns S. J., Karmann I., Sharp W. D., Vuille M., Cardoso A. O., Ferrari J. A., Silva Dias P. L., and Viana, Jr., O. (2005a) Insolation-driven changes in atmospheric circulation over the past 116 ky in subtropical Brazil. *Nature* **434**, 63–66.

Cruz Jr., F. W., Karmann I., Viana, Jr., O., Burns S. J., Ferrari J. A., Vuille M., Moreira M. Z., and Sial A. N. (2005b) Stable isotope study of cave percolation waters in subtropical Brazil: implications for paleoclimate inferences from speleothems. *Chem. Geol.* **220**, 245–262.

Cruz Jr., F. W., Karmann I., Magdaleno G. B., Coichev N., and Viana, Jr., O. (2005c) Influence of hydrological and climatic parameters on spatial-temporal variability of fluorescence intensity and DOC of karst percolation waters in the Santana Cave System, southeastern Brazil. *J. Hydrol.* **302**, 1–12.

Cruz, Jr., F. W., Burns S. J., Karmann I., Sharp W. D., Vuille M., and Ferrari J. A. (2006a) A stalagmite record of changes in atmospheric circulation and soil processes in the Brazilian subtropics during the Late Pleistocene. *Quaternary Sci. Rev.* **25**, 2749–2761.

Cruz Jr., F. W., Burns S. J., Karmann I., Sharp W. D., and Vuille M. (2006b) Reconstruction of regional atmospheric circulation features during the Late Pleistocene in subtropical Brazil from oxygen isotope composition of speleothems. *Earth Planetary Sci. Lett.* **248**, 494–506.

Díaz A., and Aceituno P. (2003) Atmospheric circulation anomalies during episodes of enhanced and reduced convective cloudiness over Uruguay. *J. Clim.* **16**, 3171–3186.

Fairchild I. J., Borsato A., Tooth A. F., Frisia S., Hawkeswirth C. J., Huang Y., McDermot F., and Spiro B. (2000) Controls on trace element (Sr–Mg) compositions of carbonate cave waters: implications for speleothem climatic records. *Chem. Geol.* **166**, 255–269.

Fairchild I. J., Baker A., Borsato A., Frisia S., Hinton R. W., McDermott F., and Tooth A. F. (2001) High-resolution, multiple trace-element variation in speleothems. *J. Geol. Soc. London* **158**, 831–841.

Fairchild I. J., Smith C. L., Baker A., Fuller L., Spötl C., Mattey D., and McDermott F. (2006) Modification and preservation of environmental signals in speleothems. *Earth Sci. Rev.* **75**, 105–153.

Fleitmann D., Burns S. J., Muldelsee M., Neff U., Kramers J., Mangini A., and Matter A. (2003) Holocene forcing of the Indian monsoon records in the stalagmite from Southern Oman. *Nature* **300**, 1737–1739.

Frisia S., Borsato A., Fairchild I. J., and McDermott F. (2000) Calcite fabrics, growth mechanisms and environments of formation in speleothems (Italian Alps and SW Ireland). *J. Sediment. Res.* **70**, 1183–1196.

Gan M. A., Kousky V. E., and Ropelewski C. F. (2004) The South American monsoon circulation and its relationship to rainfall over West-Central Brazil. *J. Climate* **17**, 47–66.

Huang Y., and Fairchild I. J. (2001) Partitioning of Sr^{2+} and Mg^{2+} into calcite in karst-analogue experimental solutions. *Geochim. Cosmochim. Acta* **65**, 47–62.

Huang Y., Fairchild I. J., Borsato A., Frisia S., Cassidy N. J., McDermott F., and Hawkesworth C. J. (2001) Seasonal variations in Sr, Mg and P in modern speleothems (Grotta di Ernesto, Italy). *Chem. Geol.* **175**, 429–448.

Johnson K. R., Hu C., Belshaw N. S., and Henderson G. M. (2006) Seasonal trace-element and stable-isotope variations in a Chinese speleothem: the potential for high-resolution paleomonsoon reconstruction. *Earth Planetary Sci. Lett.* **244**, 394–407.

Kalnay E., Kanamitsu M., Kistler R., Collins W., Deaven D., Gandin L., Iredell M., Saha S., White G., Woollen J., Zhu Y., Chelliah M., Ebisuzaki W., Higgins W., Janowiak J., Mo K. C., Ropelewski C., Wang J., Leetmaa A., Reynolds R., Jenne R., and Joseph D. (1996) The NCEP/NCAR 40-year reanalysis project. *Bull. Am. Meteorol. Soc.* **77**(3), 437–471.

Karmann, I., Cruz Jr., F. W., Viana Jr., O., Burns, S. J. Climate influence on trace element geochemistry of waters from Santana–Pérolas cave system, Brazil. Chemical Geology, under review.

Li H.-C., Ku T.-L., You C.-F., Cheng H., Edwards R. L., MA Z.-B., Tsai W.-S., and LI M.-D. (2005) $^{87}Sr/^{86}Sr$ and Sr/Ca in speleothems for paleoclimate reconstruction in Central China between 70 and 280 kyr ago. *Geochim. Cosmochim. Acta* **69**(16), 3933–3947.

Linge H., Lauritzen S. E., Lundberg J., and Berstad I. M. (2001) Stable isotope stratigraphy of Holocene speleothems: examples from a cave system in Rana, northern Norway. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* **167**, 209–224.

McDonald J., Drysdale R., and Hill D. (2004) The 2002–2003 El Niño recorded in Australian cave drip waters: implications for reconstructing rainfall histories using stalagmites. *Geophys. Res. Lett.*, 31. doi:10.1029/2004GL02085.

McMillan E., Fairchild I. J., Frisia S., Borsato A., and McDermott F. (2005) Annual trace element cycles in calcite-aragonite speleothems: evidence of drought in the western Mediterranean 1200–1100 yr BP. *J. Quaternary Sci.* **20**, 423–433.

Moreno A., Nave S., Kuhlmann H., Canals M., Targarona J., Freudenthal T., and Abrantes F. (2002) Productivity response in the North Canary Basin to climate changes during the last 250,000 yr: a multi-proxy approach. *Earth Planetary Sci. Lett.* **196**, 147–159.

Morse J. W., and Bender M. L. (1990) Partition coefficients in calcite: examination of factors influencing the validity of experimental results and their application to natural systems. *Chem. Geol.* **82**, 265–277.

Mucci A., and Morse J. W. (1983) The incorporation of calcite overgrowths: influences of growth rate and solution composition. *Geochim. Cosmochim. Acta* **47**, 217–233.

Musgrove M., and Banner J. (2004) Controls on the spatial and temporal variability of vadose dripwater geochemistry: Edwards Aquifer, central Texas. *Geochim. Cosmochim. Acta* **68**, 1007–1020.

Nobre P., and Shukla J. (1996) Variations of sea surface temperature, wind stress, and rainfall over the tropical Atlantic and South America. *J. Clim.* **9**, 2464–2479.

Paegle J. N., and Mo K. C. (2002) Linkages between summer rainfall variability over South America and sea surface temperature anomalies. *J. Clim.* **15**, 1389–1407.

Rao V. B., and Hada K. (1990) Characteristics of rainfall over Brazil: annual variations and connections with the Southern Oscillation. *Theor. Appl. Climatol.* **42**, 81–90.

Rao V. B., Cavalcanti I. F. A., and Hada K. (1996) Annual variation of rainfall over Brazil and water vapor characteristics over South America. *J. Geophys. Res.* **101**, 26,539–26,551.

Robertson A. W., and Mechoso C. R. (2000) Interannual and interdecadal variability of the South Atlantic convergence zone. *J. Clim.* **128**, 2947–2957.

Tesoriero A. J., and Pankow J. F. (1996) Solid solution partitioning of Sr^{2+}, Ba^{2+} and Cd^{2+} into calcite. *Geochim. Cosmochim. Acta* **60**, 1053–1063.

Tooth A. F., and Fairchild I. J. (2003) Soil and karst aquifer hydrological controls on the geochemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland. *J. Hydrol.* **273**, 51–68.

Treble P., Shelley J. M. G., and Chappell J. (2003) High resolution subannual records of trace elements in a modern (1911–1992) speleothem from southwest Australia. *Earth Planetary Sci. Lett.* **16**, 141–153.

Treble P. C., Chappell J., and Shelley J. M. G. (2005) Complex speleothem growth processes revealed by trace element mapping and scanning electron microscopy of annual growth layers. *Geochim. Cosmochim. Acta* **69**, 4855–4863.

Vera C. S., Vigliarolo P. K., and Berbery E. H. (2002) Cold season synoptic-scale waves over subtropical South America. *Mon. Weather Rev.* **130**, 684–699.

Verheyden S., Keppens E., Fairchild I. J., McDermott F., and Weis D. (2000) Mg, Sr and Sr isotope geochemistry of a Belgian Holocene speleothem: implications for paleoclimate reconstructions. *Chem. Geol.* **169**, 131–144.

Wainer I., and Venegas S. A. (2002) South Atlantic multidecadal variability in the climate system model. *J. Clim.* **15**, 1408–1420.

Wang X., Auler A. S., Edwards R. L., Cheng H., Cristalli P. S., Smart P. L., Richards D. A., and Shen C.-C. (2004) Wet periods in northeastern Brazil over the past 210 kyr linked to distant climate anomalies. *Nature* **432**, 740–743.

Wang, X., Auler, A. S., Edwards, R. L., Cheng, H., Ito, E., Solheid, M., in press. Interhemispheric anti-phasing of rainfall during the last glacial period. Quaternary Science Reviews.

Zhou J., and Lau K. M. (1998) Does a monsoon climate exist over South America? *J. Clim.* **11**, 1020–1040.

Zilli, A., Rabelo, L., 2001. Monitoramento climático do ambiente cavernícola para determinação da capacidade de visitação turística da caverna Botuverá. Relatório final de atividades, Fundação o Boticário de Proteção a Natureza- MacArthur Foundation-Grupo de Estudos Espeleológicos do Paraná. Curitiba-Brasil, 19 p. (in Portuguese).

Associate editor: Miryam Bar-Matthews