

# Climate influence on geochemistry parameters of waters from Santana–Pérolas cave system, Brazil

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## Abstract

A four-year study of water geochemistry and hydrology was performed in a relatively deep cave system (overlying bedrock thickness varies from 100 to 300 m) as part of two monitoring programs, from June 1990 to February 1992 and from March 2000 to March 2002. The pH, saturation index for calcite, Ca and SO<sub>4</sub> concentrations, and elemental ratios of Mg/Ca and Sr/Ca were measured in surface, well and drip waters throughout the system. Despite local hydrological and geological differences among sampling sites, the monitoring revealed significant synchronous intersite variations in these parameters that are related to seasonal changes in rainfall recharge, suggesting that element ratios of speleothems formed in deep caves are capable of recording short-term climate variations.

Groundwater residence time appears to be the main factor affecting the water composition in the epikarst. Epikarstic waters are always undersaturated with respect to calcite but both saturation index (S.I.) and dissolved solids content increase substantially during drier periods because of longer residence times and longer interaction between meteoric water and limestone. By contrast, results from cave drips and rimstone pools indicate constant supersaturation for calcite and demonstrate that a major control on trace element ratios of waters in the deep vadose zone is the degree of prior calcite precipitation. This mechanism is more effective during drier periods when higher Mg/Ca and Sr/Ca values are observed in all drip and pool sites. However, variations do occur independently of the general trend of drip discharge, which suggest non-linear features in cave seepage water geochemistry. In addition, synchronous variations in SO<sub>4</sub> and Cl concentration indicate high connectivity between different water flow pathways characterized by similar response to interseasonal changes in vadose water level. Fluctuations in trace element ratios of cave streams appear to reflect increased contribution of waters flushed from the vadose fissure aquifer during very wet periods by a piston flow mechanism. Flushing episodes are also responsible for maintaining more positive saturation indices in streams even during periods of high river discharge. Our results suggest that trace elements are a potential proxy for past rainfall changes but they also reveal different scenarios for interpreting trace elements ratios of speleothems and freshwater tufa deposited in a deep cave systems located in tropical humid areas.

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**Keywords:** Paleoclimate; Hydrogeochemistry; Brazil; Karst water; Speleothems

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## 1. Introduction

Trace element geochemistry of carbonate speleothems can potentially record changes in the water recharge of karst systems in the Late Pleistocene and

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Holocene (Verheyden et al., 2000; Baldini et al., 2002), thereby providing an important complement to paleoclimate reconstructions based on oxygen isotopic measurements (McDermott, 2004). This is particularly the case for regions where the  $\delta^{18}\text{O}$  of speleothems cannot be directly related to variations in rainfall amount such as subtropical Brazil (Cruz et al., 2005a). The mechanisms by which trace element concentrations and ratios in karst waters respond to climate, however, are likely to be dependent on local environmental conditions. For example, climate interpretation from trace elements must take into account the affects of local rainfall on recharge and on dissolution and precipitation processes occurring in karst systems (Fairchild et al., 2000). Thus, monitoring programs of drip water chemistry and hydrological parameters in karst systems over time are very valuable. Previous such studies (Fairchild et al., 2000; Huang et al., 2001; Tooth and Fairchild, 2003; Musgrove and Banner, 2004; Fairchild et al., 2006) highlight the significance of factors such as residence time of percolation waters, prior calcite precipitation along cave drip waters flow paths and host rock composition on changes in element ratios of solutions forming speleothems. These studies are of great relevance for interpreting possible annual to subannual climate signals in Mg/Ca, Sr/Ca and Ba/Ca on speleothems (Roberts et al., 1998; Fairchild et al., 2001; Treble et al., 2003; McDonald et al., 2004). Yet, few multi-year studies of cave and karst water chemistry have been done, and the applicability of previous studies to different karst areas is not certain.

In particular, how trace element concentrations vary in drip waters of relatively deep caves, and whether a climate signal exists in these settings, is still an open question. It has been assumed that water geochemistry variations due to seasonal changes in rainfall are unlikely to occur in deep caves (>100 m in depth) because of the larger water reservoir above these caves stores a higher proportion of “old” waters than seen in shallow caves (<30 m in depth). On the other hand, water could also be efficiently transported from soil to cave waters in these aquifers under piston flow conditions, a mechanism produced by increased hydraulic head during periods of high water accumulation in the aquifer above the cave. This is especially true for the present study area where synchronous variations in dissolved organic matter and  $\delta^{18}\text{O}$  are observed between soil and drip waters from cave sites situated between 100 and 300 m below the surface (Cruz et al., 2005a, 2005b). However, identifying the processes controlling ionic composition of karst seepage waters is more complicated than for stable isotopes, because elemental

chemistry is additionally affected by mechanisms related to bedrock-water interaction and calcite precipitation in the vadose zone. The present work investigates possible relationships between climate, karst hydrology and the Mg/Ca, Sr/Ca and  $\text{SO}_4$  variations in drip waters above actively growing speleothems in the Pérolas–Santana cave system, subtropical Brazil. We evaluate the significance of the commonly reported dissolution and precipitation processes and their possible relationships with changes in rainfall recharge by analysing hydrochemistry (Ca,  $\text{SO}_4$ , Mg/Ca and Sr/Ca, saturation index for calcite, pH,  $p\text{CO}_2$ ) and hydrological parameters (drip and river discharge) in different compartments of the cave system such as soil cover, cave drips and rimstone pools and rivers.

## 2. Study area and sampling sites

The water samples used in the present study were collected in the Santana–Pérolas cave system (24°31'S; 48°43'W), which is located 350 km south of São Paulo city, SE Brazil, and approximately 100 km from the Atlantic coastline (Fig. 1). Pérolas Cave and Santana Cave have 1700 m and 6300 m of mapped galleries respectively (Fig. 1). The karst landscape in the area is hosted by low metamorphic grade carbonates of the Mesoproterozoic Açungui Group (Campanha and Sadowski, 1999). The bedrock is mostly fine-grained limestone (mudstones) with minor layers of metapelites and dolomites interbedded. Rock porosity is predominantly fracture and bedding plane permeability (Fig. 1). Dense tropical Atlantic rainforest covers the area and is locally associated with clayey soils that can be a few meters thick.

Allogenic rivers or drainages from the surrounding non-carbonate rocks are the most important recharge source to the main river in Pérolas and Santana cave system (P–S system). These rivers originate from mountain ridges in the Serra do Mar Plateau at elevations up to 800–1100 m and sink into the topographically depressed carbonate rocks at altitudes between 500 and 600 m, reaching the only resurgence of system at 250 m.

Allogenic runoff was sampled at site RP3 (point 1 on map of Fig. 1) just after they infiltrate into the of the P–S system. Epikarstic waters accumulating in the soil cover at the bottom of a 0.49 km<sup>2</sup> circular depression were pumped from a 5 m deep well (See Santana cave long profile, Fig. 1). The well was constructed using a 5 cm diameter PVC pipe with a bleeding filter allowing the soil water to infiltrate into its bottom at depths below 4 m. The soil at this site was a typical limestone residual, rich in clay and isolated from limestone blocks resulting in low limestone-water interaction. RP1 is located 200 m

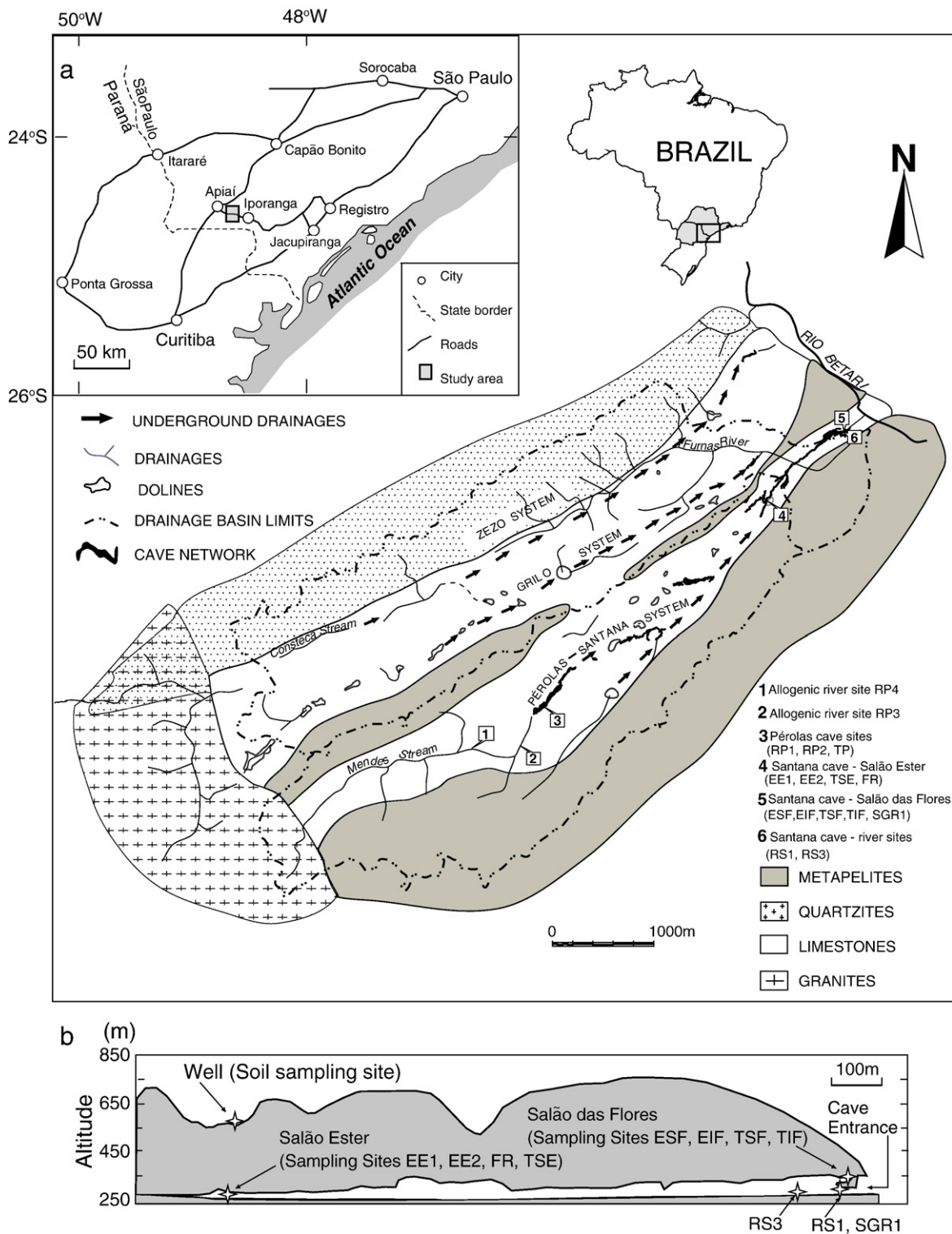


Fig. 1. (a) Map showing the location of water sampling sites along Santana-Pérolas cave system; (b) Cave longitudinal profile of Santana Cave showing the location of the sampling sites with depth and distance from entrance.

from the Pérolas cave entrance (point 2) at the recharge area zone of the P–S system. RP2 is tributary branch of Pérolas River. RS1 and RS2 are sites located near to Santana Entrance at the resurgence zone of the system (point 5).

Karst seepage water sampling was done taking into account the various hydrological conditions represented by aquifer thickness, which ranges from 100 m to 300 m (Fig. 1), and mean drip water discharge, which ranges from 55 to  $3.5 \times 10^5$  ml/h (Table 1). Five intra-cave sites (ESF, EIF, TSF, TIF, SGR1) are closely distributed around the Salão das Flores at 100 m below the surface, 35 m above the river level and 150 m from the cave entrance. The other four sites (EE1, EE2, TSE, FR) are in the Salão Ester, which is 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 low drip rates when compared to FR, which is a small waterfall in the cave (Table 1). TSF, TSE and TIF are travertine pools sites fed by waters from ESF, EE2 and EIF stalactites, respectively. The well site was chosen approximately

above the Salão Ester in order to obtain a percolating water profile from surface to the cave.

The present-day climate above the cave sites is subtropical humid, with high mean relative humidity and rainfall distributed throughout the year (Rao and Hada, 1990). The average annual precipitation (MAP) from 1972 to 2004 at a meteorological station located 7 km from the entrance of Santana cave is 1589 mm (source DAEE: [www.daee.sp.gov.br](http://www.daee.sp.gov.br)). The amount of evapo-transpiration calculated for the cave system area was approximately 1000 mm, with an estimated error of 7% (Karmann, 1994). In addition, 41% of total averaged annual accumulation occurs during the austral summer (December, January and February), which represent the wettest months in the region, while only ~15% are accumulated in the relatively dry period in austral winter (June, July, August). The average annual temperature measured outside the Santana cave during 2000 and 2002 was 18.9 °C, which is very close to the average temperature measured at the cave sampling sites (points 3 and 4, Fig. 1), which are 18.6 °C and 19.0 °C respectively. The mean daily relative humidity is very close to 100%.

Table 1  
Summary of hydrology and hydrogeochemistry parameters for the sites in Santana–Pérolas cave system

		Depth from the surface	Discharge		Sampling period	n	pH	Calcite S.I.	–log PCO <sub>2</sub>	Hardness	
			(ml/h)	CV (%)						(mg/L as CaCO <sub>3</sub> )	CV (%)
Runoff	Formation	–	–	–	*2	6	6.93±0.3	–1.6±0.46	2.26±0.5	46±16	45
Soil water		4–5 m	–	–	*2	10	6.51±0.3	–1.5±0.66	1.5±0.22	77±12	16
Drip waters											
ESF	Stalactite	100 m	120.99	12.7	*2	16	7.35±0.13	0.2±0.15	1.94±0.11	223±14	6
EE2	Stalactite	300 m	55.09	8.1	*2	16	7.97±0.12	0.2±0.07	2.77±0.13	145±4	3
EE1	Stalactite	300 m	470.51	15.2	*2	16	7.82±0.06	0.4±0.12	2.66±0.06	132±3	2
EIF <sup>a</sup>	Stalactite	100 m	818	>200	*2	11	7.9±0.25	0.4±0.23	2.67±0.26	153±35	21
FR	Waterfall	300 m	$3.5 \times 10^5$	9.0	*2	14	7.93±0.15	0.2±0.15	2.72±0.15	138±3	2
SGR1	Stalactite	120 m	–	–	*1	13	7.44±0.11	0.14±0.11	2.11±0.12	210±15	7
Total						86	7.71±0.28	0.23±0.16	2.46±0.36	167±16	10
Pools											
TSF	Rimstone	100 m	–	–	*2	14	7.83±0.18	0.3±0.16	2.6±0.2	147±14	10
TIF	Rimstone	100 m	–	–	*2	12	7.99±0.13	0.1±0.11	2.93±0.18	103±13	12
TSE	Rimstone	300 m	–	–	*2	13	8.03±0.09	0.1±0.07	3.0±0.1	101±4	4
TP	Rimstone	60 m	–	–	*1	10	7.90±0.4	–0.02±0.35	2.86±0.4	111±13	12
Total						49	7.93±0.22	0.15±0.22	2.84±0.28	116±22	19
Cave Rivers											
RS1			–	–	*1	14	7.85±0.21	–0.14±0.25	2.82±0.2	98±9.24	9
RS3			–	–	*1	14	7.85±0.21	–0.12±0.26	2.82±0.2	100±9.3	9
RP1			–	–	*1	15	7.76±0.23	–0.28±0.37	2.77±0.26	92±28	31
RP2			–	–	*1	13	7.64±0.32	–0.76±0.46	2.79±0.27	65±27	27
RP3			–	–	*1	11	7.48±0.18	–1.13±0.41	2.74±0.23	52±20	39
Total						67	7.72±0.27	–0.44±0.52	2.79±0.23	83±27	32
Furnas River						4	8.36±0.06	0.40±0.03	3.33±0.11	110±7	6

\*1 — first monitoring program: 6/29/1990 to 2/8/1992.

\*2 — first monitoring program: 3/18/2000 to 3/16/2002.

<sup>a</sup> Intermittent flow.

### 3. Methods

Monthly to trimester sampling for hydrochemistry and measurements of physical–chemical parameters were performed in two programs. The first includes sites monitored from 6/29/1990 to 2/8/1992, presented in Fig. 3 (Karmann, 1994). The second includes sites monitored from 3/18/2000 to 3/16/2002, presented in Figs. 4, 5 and 6 (Viana, 2002).

Water samples were collected in high-density Nalgene polyethylene bottles. All samples were filtered through Millipore HA2500 filters (pore size 0.45 mm) and rapidly transferred to bottles. Soil water samples were pumped out of the well using a Low Flow Waterra inertial pump with high-density polyethylene tubes. The pH and temperature were measured immediately after each collection with a digital pH-meters coupled to a temperature sensors Digisence 5985-80 and with an Orion Multi-Parameter 1230 connected to the Orion 9107 WP probe, for the first and second monitoring programs, respectively. Alkalinity was determined a few hours after sampling by the gran-titration method (Stumm and Morgan, 1981). The great majority of results show charge balance errors smaller than 5%. Samples were preserved for ion analysis by adding 2–3 drops of concentrated nitric acid after being filtered. These samples were kept refrigerated at 4 to 8 °C until analysis.

Precipitation and stalactite discharge were measured automatically using a Davis automatic tipping bucket gauge coupled to an Onset Logger, model Hobo for 8000 events. The discharge values were continuously recorded on the loggers at the slowest drip water flows (EE2 and ESF), over an interval of 17–21 days for EE2 and 8–12 days for ESF, depending on the flow changes during the year. The discharge is easily calculated by transforming the number of pulses recorded per hour in volume per hour (ml/h). At other cave sites, discharge measurements were based on the time elapsed to fill a container of known volume. The output of water from the basin ( $Q$ ) was calculated using data from the hydrograph at the Santana cave resurgence. This hydrograph is based on the monthly stage records obtained with a Stevens 68-F stage recorder (1:1 scale) installed close to the cave entrance.

All analyses were carried out at the Geosciences Institute, University of São Paulo. A Perkin Elmer (model 530) atomic absorption spectrometer (AAS) with a flame atomizer was used for cation determinations in water samples during the first monitoring program. Instrumental parameters were adjusted according to the manufacturer's recommendations and at most sensitive wavelength for each element. A Dionex ion

chromatograph (model 2010i) was used for anion determinations during both programs. The instruments performance was optimized for each set of analyses; both blanks and quality control standards were measured with every set of unknown samples, and their concentration were calculated from a calibration curve that was derived daily. All reagents analytical grade (Merck) were used as received. Solutions for calibration and quality control were daily prepared by using deionized water purified with Milli-Q Plus Water System (Millipore). The stability of analytical system was monitored by analysis of reference solution every ten samples. Experimental results obtained on triplicate samples presented standard deviation values better than 5%. Accuracy better than 5% was obtained by analyzing the quality control standard.

Ca, Mg, Sr analysis for water and for the bulk elements of soil and bedrock carbonate during the second monitoring program were made by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an ARL 3410 instrument with a CETAC ultrasonic nebulizer model U 5000 AT. Soil and rock samples were prepared by alkaline fusion of 0.25 g of powdered sample and with 0.75 g of lithium tetra metaborate material (eutectic mixture) with a 1:1000 sample dilution (method used at the Imperial College of London). Sample standard deviations were lower than 1% of three readings mean. Accuracy was assessed using the certified reference materials SPEX CLMS-2 and CLMS-4 and quantitative recoveries (95–105%) were obtained for all the studied materials.

The detection limits for all the techniques used are consistent with the conventional values reported in the literature (Skoog et al., 1998) and are negligible in comparison to the element concentrations presented in the paper. The derived parameters saturation index (SI) and  $p\text{CO}_2$  were calculated using the WATEQ program (Truesdell and Jones, 1974).  $\text{SI} = \log (\text{IAP}/K)$ , where IAP is the ion activity product  $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$  in solution (Langmuir, 1971).

### 4. Results and discussion

#### 4.1. Hydrochemical facies in the cave system

Table 1 and Fig. 2 summarize the results for relevant hydrochemical parameters. These parameters allow us to relate the physical–chemical characteristics of waters to their origin (allogenic recharge, epikarst and deep vadose reservoirs) and to dissolution–precipitation processes occurring during percolation from surface to the cave galleries.

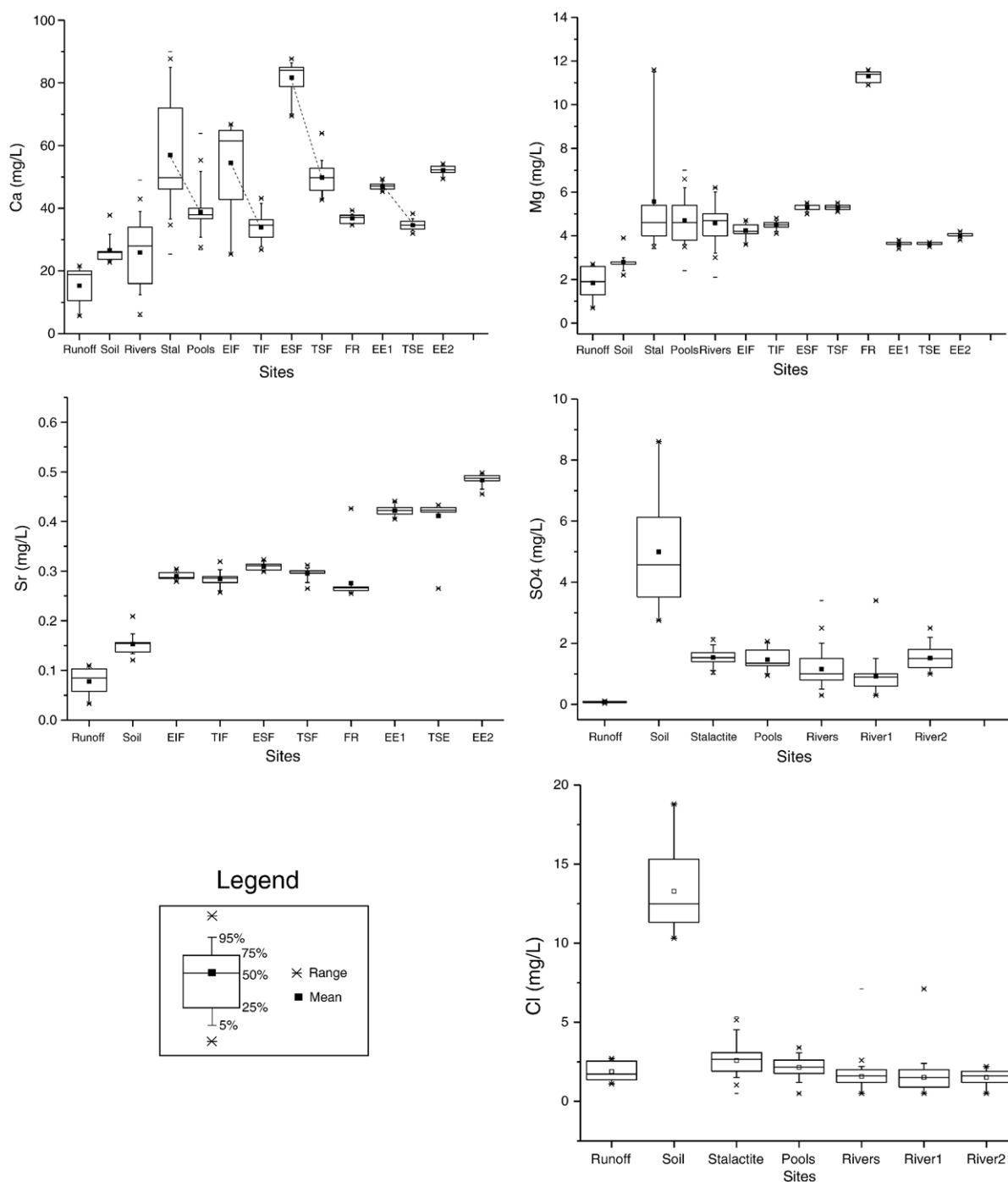


Fig. 2. Box-plot diagram of statistical properties of the Ca, Mg, Sr, SO<sub>4</sub> concentration in waters from runoff, soil, rivers, stalactites drips and rimstone pools and also at individual sites in Santana cave.

The epikarst zone (Williams, 1983) in the study area is marked by waters with high concentrations of CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub> and saturation indices for calcite that are always negative (Table 1). These hydrochemical properties of

runoff and well waters indicate that the local epikarst is a zone of carbonate dissolution. This result is also indicated by negligible contents of CaO and MgO in six samples from different soil horizons. In contrast,

carbonate precipitation is likely to prevail in the deep vadose zone as indicated by supersaturated waters in all drip sites through P–S cave system (Table 1).

The hydrochemical properties of river waters changes rapidly as the allogenic streams traverse the carbonate alluvial plain and flow to the resurgence of the P–S cave system. For example, there is a rapid increase in hardness and mean saturation indexes (S.I.) for calcite from the RP3 site to the sites located in Pérolas cave and Santana cave (Table 1, Fig. 1). Very similar values between RS1 and RS1 sites which are ~50 m apart in Santana cave indicate a good reproducibility of the hydrochemical parameters used for SI calculation.

A greater  $\text{SO}_4$  content in soil waters than in runoff waters and rivers suggests that processes occurring in epikarst, such as oxidation of sulfides of limestone bedrock, control sulfate production (Fig. 2). Sulphur is not detected in soil but it is present in bedrock samples in concentration varying from 100 to 870 ppm (five limestones samples). In the case of chlorine, higher values seen in soil waters might reflect the rain waters stored in the epikarst. Unlike  $\text{SO}_4$ , Cl concentrations are very similar between runoff, seepage and river waters, which mean that Cl in all waters is sourced primarily by rainfall. Combined sulfate and chlorine data suggests that the karst waters are well homogenized in the system after passing through the soil, as seen in the striking similarity in their concentrations between drip, pool and river waters (Fig. 2).

There are significant differences in Ca concentrations among dripwater sites and also between drip waters and their related rimstone pools (Fig. 2). Factors affecting Ca variability are apparently the depth from surface and drip water discharge. Sites located in the shallower part of cave (EIF, ESF) and with fast drips (EIF) show higher Ca variability than sites located at the deepest part of Santana Cave (FR, EE1, EE2). In addition, drip rates seem to influence significantly the intersite mean Ca concentrations. Much higher concentrations are observed at slower discharge sites, independently of the depth in the cave. In contrast, the small variability of Sr and Mg in all drip sites implies that the processes controlling Ca concentration in the system are the dominant factor in controlling Mg/Ca and Sr/Ca temporal variations in the seepage waters.

Differences in Ca are likely to result from varying degrees of prior calcite precipitation above cave, a mechanism that is very sensitive to hydrological changes in the system (Fairchild et al., 2000; Tooth and Fairchild, 2003; McDonald et al., 2004; Fairchild et al., 2006). Loss of Ca by calcite precipitation during dry periods is expected to be more significant in

shallower and faster dripping sites because their pathways are subjected to more dramatic fluctuations in aquifer level, which is consistent with our findings.

The calcite precipitation mechanism is well exemplified by the general decrease in Ca concentration of between 25 and 39% in the rimstone pools as compared to their parent stalactite drips (Fig. 2). In addition, a decrease in  $\text{PCO}_2$  induced by calcite precipitation in pool sites of between 9 and 25% ( $10^{-0.3}$  to  $10^{-0.66}$  atm) is observed, although no relevant change in pH is found. Conversely, the values of Mg and Sr remain the same because partition coefficients ( $K_D$ ) for both Mg and Sr between water and calcite are smaller than 1, which does not favor the incorporation of trace elements in the calcite. The  $K_D$  values calculated using Mg and Sr values of EE2 drip waters and a calcite coating deposited over the device to measure discharge are  $K_{\text{DMg}}=0.023$  and  $K_{\text{DSr}}=0.059$ , which are similar to the typical values reported for caves (Huang and Fairchild, 2001). However, variation in bedrock composition at the beginning of flow routes is possibly the cause of spatial differences in mean values of Mg and Sr between dripwaters. Sr (Mg) content is higher (lower) at EE1, EE2, TSE sites and lower (higher) at EIF, TIF, ESF and FR sites. Such anticorrelation behavior is consistent with the composition analyses of bedrock samples (5 samples) in which Mg varies from 0.2 to 1.7% weight and Sr from 629 to 2834 ppm in the later. High Sr values are seen in limestones with low Mg and vice-versa.

#### 4.2. Temporal variations in chemistry of the Pérolas–Santana waters

##### 4.2.1. Comparison between surface streams, underground rivers and cave seepage waters

Time-series of the first monitoring program reveal significant temporal variability in geochemistry and saturation state in the P–S waters. These differences appear to be directly linked to the changes in rainfall, which was ~20% above and ~25% below the average of austral winter (June to September) for the last 30 years during the first and second years of program, respectively (Fig. 3).

Although differences exist in hydrological characteristics between monitored sites, there is a remarkable consistency in Mg/Ca and  $\text{SO}_4$  trends among the sites especially during the first year of the program (Fig. 3). The substantial increases in  $\text{SO}_4$  concentration and Mg/Ca ratios in all waters, centered at day 125, are likely to be associated with contribution of waters flushed from the vadose aquifer above the cave rather than due to direct allogenic recharge into cave conduits because the peak

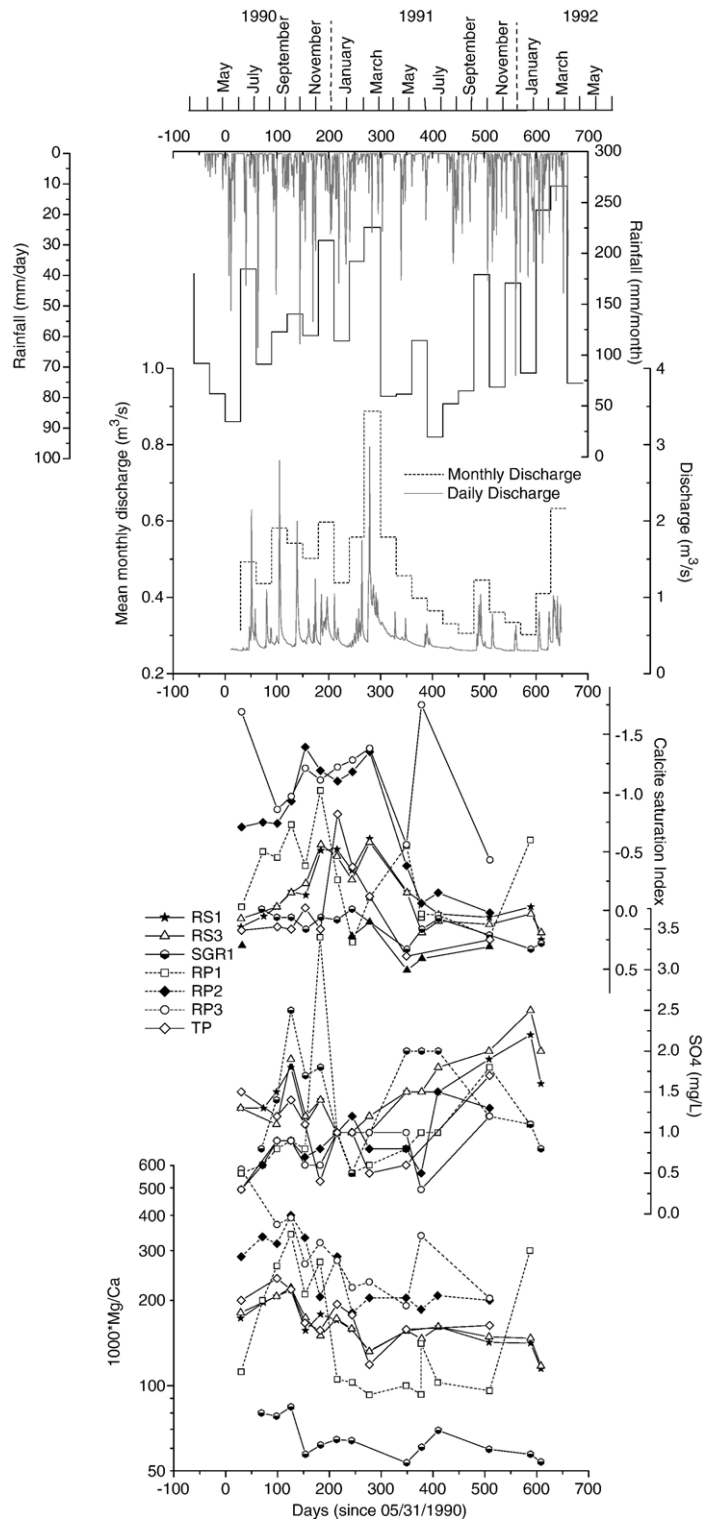


Fig. 3. Time-series of rainfall, river discharge, calcite saturation index,  $\text{SO}_4$ , Mg/Ca ratios in river and cave seepage waters during the first monitoring program, performed from May/1990 to March/1992.

concentrations occurred approximately three months after the rapid rising of the river level in Santana cave at the beginning of the rainy season (Fig. 3). Furthermore, the similarity of Cl and SO<sub>4</sub> at all sites over this period indicates that dilution is less important for river chemistry than the relative contribution of waters from vadose aquifer (Fig. 4).

Synchronous fluctuations in the chemistry of waters from sites with contrasting hydrology is a good evidence for piston flow conditions during the wettest periods when the storage capacity is reached throughout the karst aquifer and waters can be rapidly moved from the vadose zone to cave drips and small cave streams (Tooth and Fairchild, 2003). A certain recharge threshold is necessary, however, for less mobile waters from epikarst and deep vadose zone to reach different parts of cave and change the composition of small cave tributaries. Hence, this mechanism would explain the lagged response of a few months in the SO<sub>4</sub> concentration and Mg/Ca ratios in cave drips and river waters after rainfall infiltration events (Fig. 3). Therefore, the major shift in the water

composition around day 125 is consistent with the anomalous rainfall in the area during this period. This peak in concentrations at day 125 is followed by an abrupt decrease in these parameters after day 150, which persists throughout the rest of the rainy season, suggesting that much of the high alkalinity water stored in vadose aquifer was rapidly transported to rivers.

These results are in agreement with other studies performed in the Santana cave, where synchronous variations in  $\delta^{18}\text{O}$  and dissolved organic carbon (DOC) were observed at hydrologically variable drip sites located between 100 and 300 m from the surface (Cruz et al., 2005a, 2005b). In addition, relatively thick carbonate rock overlying the cave river, reaching 400 m thickness, may favor a piston flow effect because of high storage capacity of the vadose fissure zone. High storage in turn enhances the connectivity between very distinct flow routes and produces quite similar temporal variations in the chemical composition of waters. Such similarity implies that freshwater tufas and stalagmites might record coeval variations in Mg/Ca ratios and SO<sub>4</sub> in response to changes in hydrologic conditions.

Flushing episodes also impact the saturation state of river waters by maintaining S.I. values positive downstream (sites RS1 and RS3) or less negative upstream in the P–S system (site RP1, RP2 and RP3) for several weeks to months. A similar phenomenon has been reported in other hydrogeochemical studies performed on karst underground drainages (Lastennet and Mudry, 1997; Desmarais and Rojstaczer, 2002).

The second year of monitoring is characterized by minor variations in Mg/Ca ratios and the predominance of positive values of S.I. in rivers. The supersaturated waters are consistent with low-flow conditions in the rivers and a smaller proportion of subsaturated allogenic waters. Although the rainfall recharge events during this period were not sufficient to trigger pulses of vadose waters into the rivers that would change their Mg/Ca ratios, they produced significant SO<sub>4</sub> and Cl variation after day 500 (Figs. 3 and 4). Variation in the mixing ratio of allogenic waters with vadose ground waters apparently controls variations of Mg/Ca ratios in the monitored river waters in P–S system. The mixing ratio, in turn, responds to changes in rainfall.

#### 4.2.2. Comparison between soil and cave seepage waters from drips and rimstone pools

Figs. 5–7 present the time-series for Ca, Mg/Ca, Sr/Ca, SO<sub>4</sub>, and Cl of waters along a percolation profile from soil to drips and rimstone pools during the second monitoring program, performed from March 2000 to March 2002 in the deep galleries of Santana Cave.

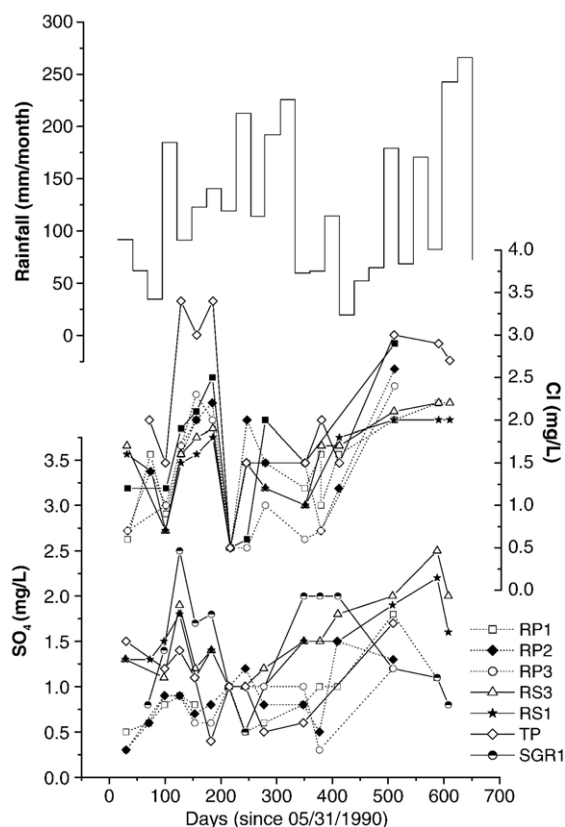


Fig. 4. Comparison between monthly rainfall amount and concentrations of Cl and SO<sub>4</sub> in river and drip waters over Pérolas–Santana cave system.

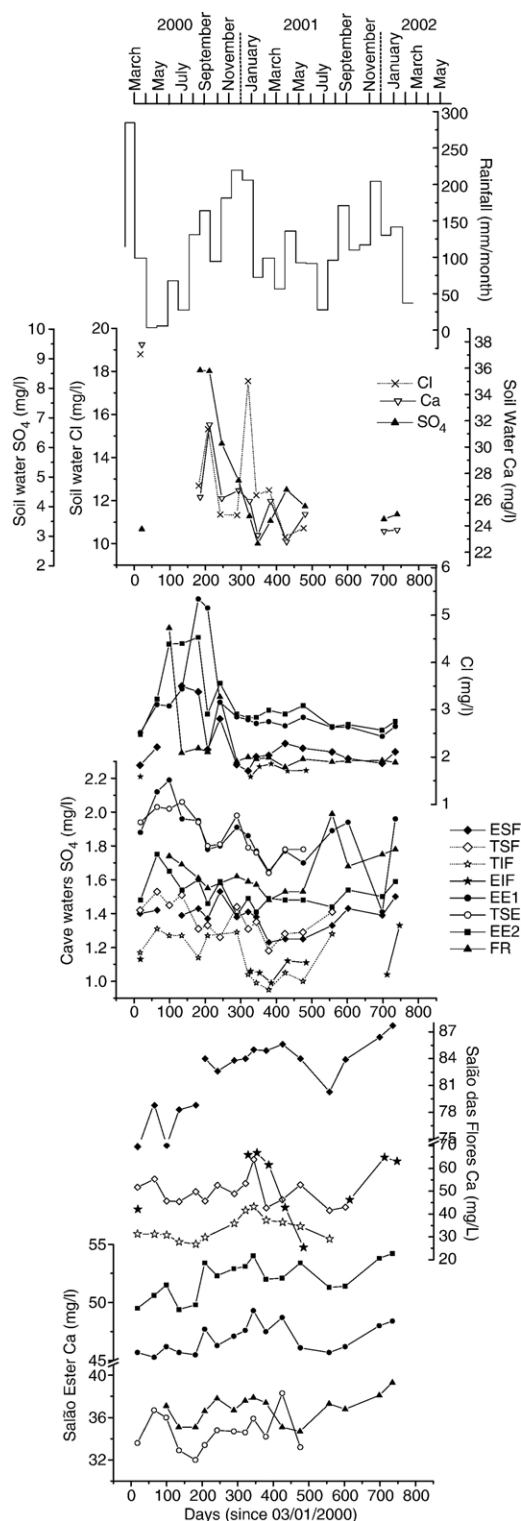


Fig. 5. Time-series of Cl,  $\text{SO}_4$  and Ca in soil water and cave seepage waters from Salão das Flores and Salão Ester in Santana cave during the second monitoring program, performed from March/2000 to March/2002.

Comparison results between soils and seepage waters is used to illustrate the major factors controlling the geochemistry of waters such as groundwater residence time and the level of vadose aquifer above the cave.

Changes in the composition of waters in epikarst, where waters never reach the saturation state for calcite precipitation, are mainly due to the effect of groundwater residence times on limestone dissolution. Dissolution is enhanced during dry periods as a result of the longer interaction of bedrock with epikarstic water, which produces a slight increase in S.I. for calcite and similar variations of Ca, Mg, and Sr values (Figs. 5 and 6). This process is evidenced by coincidence of the highest and lowest concentrations of these species in soil waters with the demise of the dry and wet seasons, respectively. In addition, a longer resident time might also favor the production of sulfate by sulfide oxidation (Mulholland, 1993). However, processes in epikarst do not seem to affect the short-term variations in drip waters as suggested by the lack of correspondence between  $\text{SO}_4$  in soil and cave waters (Fig. 5).

The relatively synchronous fluctuations of  $\text{SO}_4$  and Cl between slow and fast drips sites, together with similar mean values, is a clear indication that homogenization of karst waters occurs after water passes through the epikarst (Figs. 2 and 5). This is additional evidence to support the interconnectivity of flow routes: the approximately synchronous rainfall response in the drip discharge between the ESF and EE2 sites, even though these sites are located more than 1.5 km apart and at 100 m and 300 m below the surface, respectively (Cruz et al., 2005a). Furthermore, the coincidence of the highest values of both  $\text{SO}_4$  and Cl with the driest period, between April and August of 2001, suggests that these variations are due to reduced dilution in water stored in the deep vadose zone. On the other hand, the lack of significant variations in drip water Cl during the second year imply that this longer periods without rainfall recharge events are required to affect  $\text{SO}_4$  and Cl concentrations, as seen in the first year.

In contrast to the compositional trends in epikarst, there is a decrease (increase) in Ca concentration at the height of the dry (wet) seasons in all drip sites (Fig. 5). We argue that these fluctuations are unlikely to be caused by dilution because the low values of Ca coincide with high values of Cl in the same waters (Fig. 5). Thus, we suggest that prior calcite precipitation (PCP) in the percolation routes above the cave is the most likely process controlling Ca variability of drip waters. Ca depletion by prior calcite precipitation occurs preferentially in the dry season when air circulation is enhanced in the upper portions of the karst system due to low level

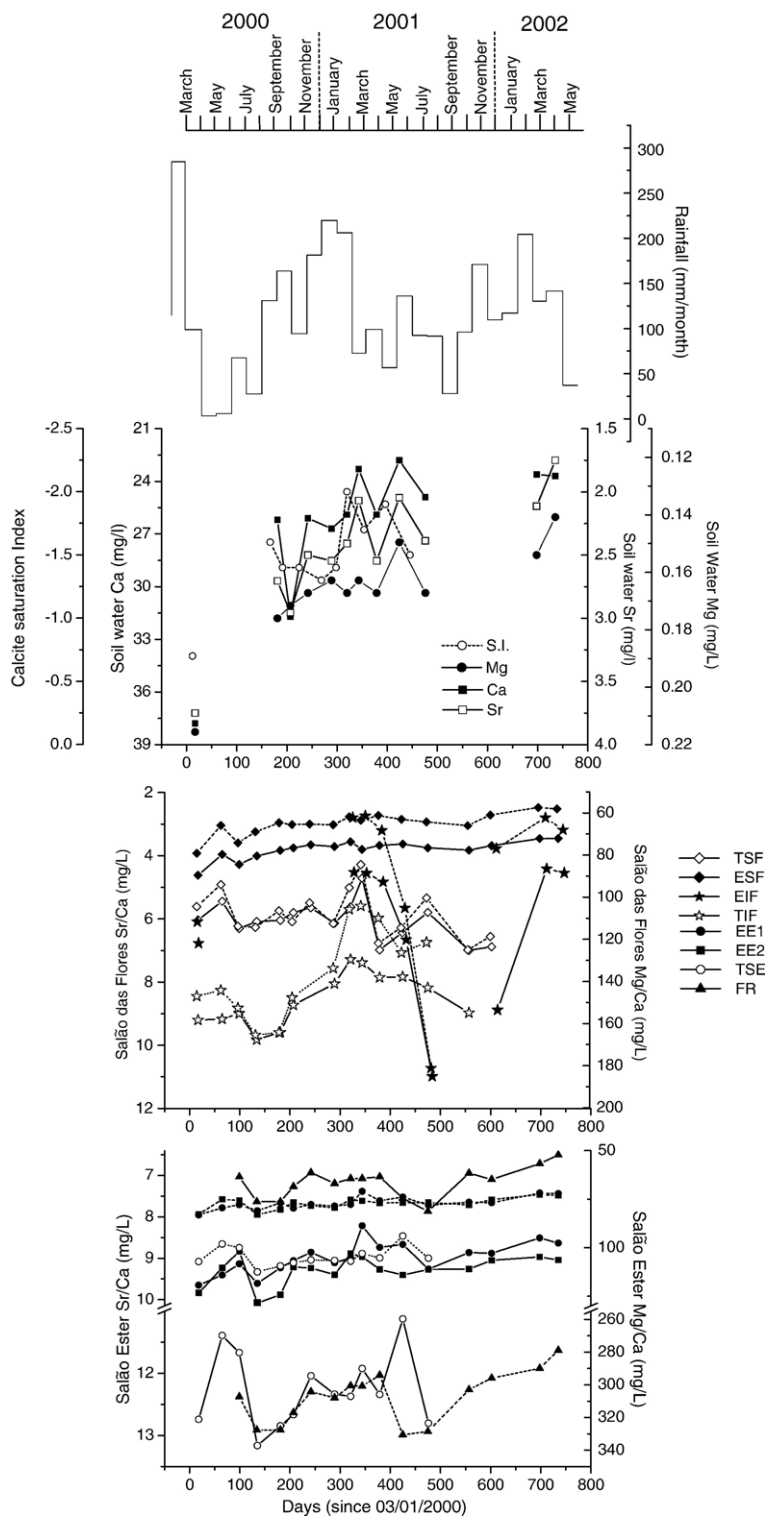


Fig. 6. Time-series of Sr, Mg, Ca and calcite saturation index for soil waters and Sr/Ca (solid lines) and Mg/Ca (dotted lines) ratios for cave seepage waters. Note: variations are not very visible at slow drips sites (ESF, EE1, EE2) because of scale. See also Fig. 6 for a more detailed scale presentation.

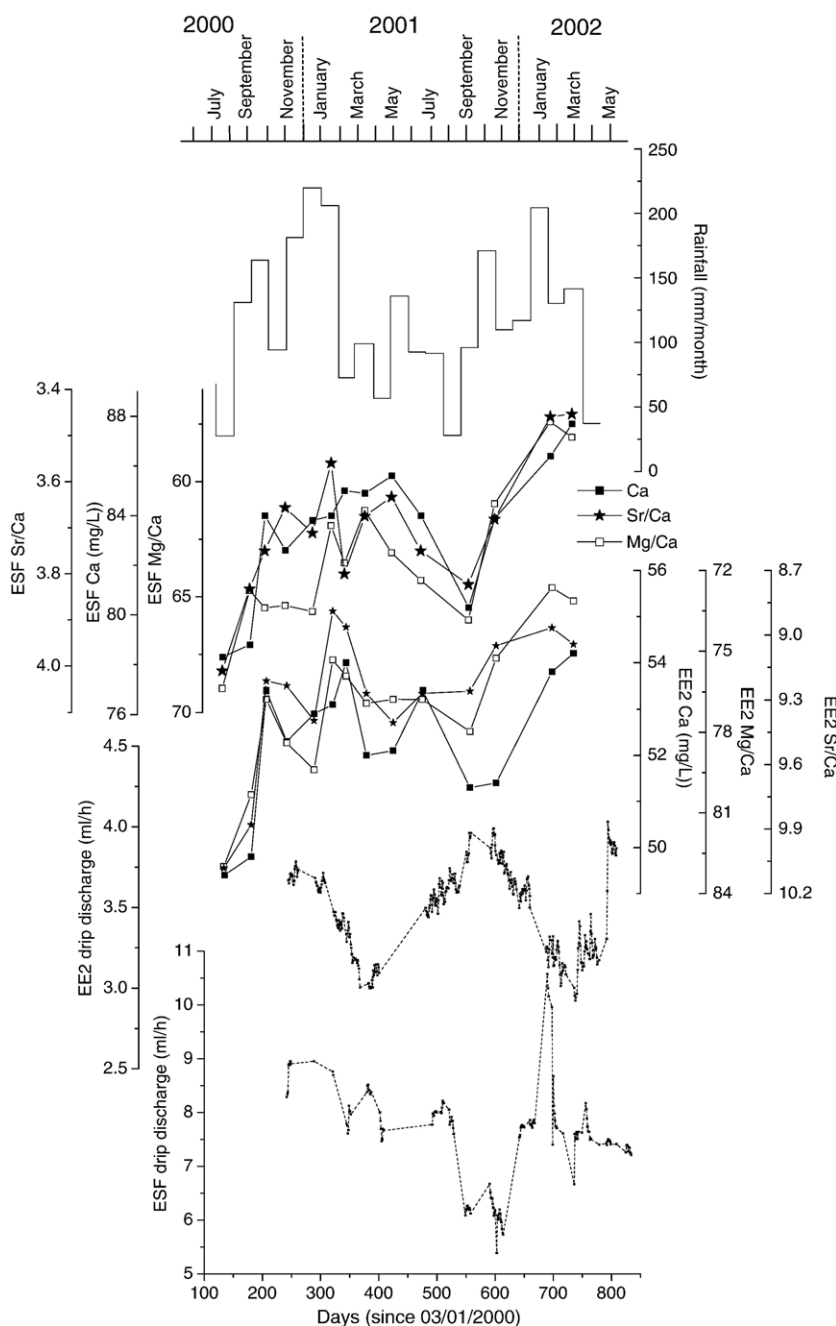


Fig. 7. Comparison between Ca, Sr/Ca, Mg/Ca and drip discharge variations at ESF and EE2 sites located 100 and 300 m below the surface in Santana cave, respectively.

of the aquifer (Fairchild et al., 2000; Tooth and Fairchild, 2003; Musgrove and Banner, 2004; McDonald et al., 2004; Fairchild et al., 2006).

A major characteristic of PCP in Santana cave is that it produces quite similar spatial variations in the Ca concentration and consequently in Sr/Ca and Mg/Ca

ratios despite substantial differences in hydrologic conditions (Fig. 7). Variations of Sr/Ca and Mg/Ca ratios are dictated by the degree of calcite precipitation because Ca is favorably incorporated in calcite crystals relative to Mg and Sr as the partitioning coefficients for both Sr and Mg are less than 1 in the low-ionic strength

waters (Mucci and Morse, 1983; Morse and Bender, 1990; Huang and Fairchild, 2001).

It is important to note that the Ca, Mg/Ca, and Sr/Ca behavior in slow drips at ESF and EE2 sites is concordant with the monthly rainfall accumulations; although they demonstrate clear differences in the general trend of drip discharge (Fig. 7). Drip discharge roughly follows the monthly rainfall at ESF, while it is more affected by piston flow mechanism at EE2. In the second case, the general trend of drip discharge is more dependent on the hydraulic pressure exerted by the water storied in the fissured/conduit reservoir and varies non-linearly with the rainfall recharge events. Therefore non-linear features previously reported for drip hydrology, dissolved organic carbon and oxygen isotopes in Santana cave (Cruz et al., 2005a, 2005b) can also be recognized in the geochemistry of the same drip waters, as suggested by Fairchild et al. (2006) for shallow conduits in an English limestone mine.

#### 4.2.3. Implications for paleoclimate studies

These findings have important implications for the interpretation of climate signals embedded in the Mg/Ca and Sr/Ca ratios of speleothems. First, geochemical variations recognized in drip waters should be reproduced in speleothems deposited in different locations in a cave and having different growth rates. Both Mg/Ca and Sr/Ca are thus not sample dependent. Second, these ratios appear to be a potential proxy for seasonal changes of past rainfall, at least in settings similar to the P–S cave system (see Discussion below). Third, in our study the observed variations cannot be accounted for by a progressive CO<sub>2</sub> degassing mechanism due to changes in drip discharge as has been suggested in other areas (Johnson et al., 2006).

Spatial variability in Santana cave waters appears to be also influenced by the type of carbonate host rock (Fig. 8a). The trends found are consistent with previously mentioned differences in the mean values of Mg and Sr in drip waters (Fig. 2), reinforcing the idea that the bedrock variations from limestones to magnesian limestones in the flow routes is the cause of spatial differences not only in their mean values but also in the slopes of Mg/Ca and Sr/Ca trends. The similar intersite temporal variations in drip composition, however, rule out an influence of bedrock type on temporal variation of Mg/Ca and Sr/Ca ratios.

Fig. 8b and c illustrate an exponential decrease of Ca in solution relative to both Mg and Sr in the great majority of monitored waters. This relationship is visible in all drip, river and pool sites except for the waters from runoff and soil sites where carbonate precipitates are not

found (Table 1). The curves are also very consistent with the modeled evolution of drip solution under prior calcite precipitation (PCP) conditions (Fairchild et al., 2000). The theoretical PCP trends were calculated by using the ESF trace element ratios as a vector starting point because it presents the highest Ca mean among drip waters and is representative of the initial vadose water composition in the system (Fig. 8b and c). In summary, PCP is recognized as the main mechanism controlling the temporal variations in elemental ratios for waters in the Pérolas–Santana System.

#### 4.3. Possible scenarios for paleoclimate reconstruction from geochemistry of speleothems and freshwater tufa in P–S cave system

Under the assumption that the processes governing modern changes in the chemical composition of waters in P–S system were also valid in the past, the Mg/Ca and Sr/Ca ratios of speleothem and freshwater tufa can potentially be used as a proxy for local paleorainfall changes. First, a reduction of rainfall recharge events during dryer periods promotes longer interaction between bedrock and percolating soil waters, which enhances bedrock dissolution in the epikarst zone and increases the concentration of Ca, Sr, Mg and SO<sub>4</sub> in karst waters. Second, dry periods lower the vadose aquifer down to levels that allows air to circulate through fracture fissures and conduits usually filled by water during wetter periods, which enhances precipitation of calcite along flow routes and increases the Mg/Ca and Sr/Ca ratios in waters forming speleothems (Fairchild et al., 2000; Tooth and Fairchild, 2003; Musgrove and Banner, 2004; McDonald et al., 2004; Fairchild et al., 2006) and freshwater tufas (Ihlenfeld et al., 2003).

On the basis of the previous discussion we can highlight some possibilities to interpret past rainfall changes based on the geochemistry of speleothems and tufas. Particularly only PCP can account for short-term changes in chemical composition of the solution forming stalactites and stalagmites in the P–S system. PCP may produce interannual to intraseasonal fluctuations in speleothems formed under fast or slow drip rates sites but the amplitude of compositional variations is substantially higher in fast flow formations deposited in shallower sites, for example in rimstones deposits at EIF site. This mechanism is apparently controlling the long term variations of Mg/Ca and Sr/Ca ratios in the Bt2 stalagmite record from southern Brazil (Cruz et al., 2007).

By contrast, all drips in deeper part of the Santana cave show smoothed temporal changes in chemistry, which could reduce the short-term variability of speleothems in

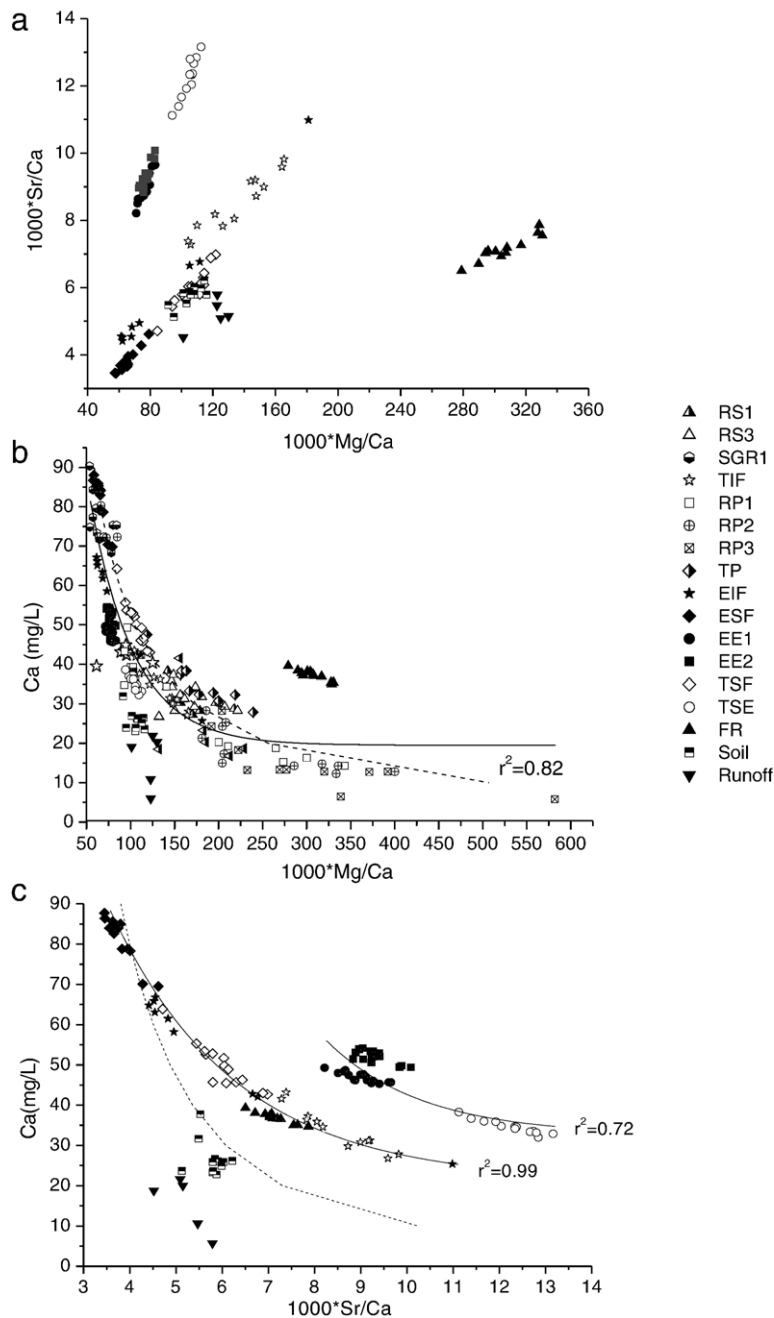


Fig. 8. (a) Mg/Ca vs. Sr/Ca for samples collected during second monitoring program; (b) Ca vs. Mg/Ca for waters collected during both monitoring programs; (c) Ca vs. Sr/Ca for waters collected during second program. Dotted lines are prior calcite precipitation trend (Fairchild et al., 2000) calculated using partition coefficients of 0.0284 and 0.058 obtained from Mg/Ca and Sr/Ca in water and modern speleothem samples at EE2 site. The vector starting points are based on trace element ratios at ESF site.

times when the dry season is not well defined. In either case, Sr/Ca and Mg/Ca ratios in speleothems formed by these waters should provide reliable information about past changes in annual rainfall distribution in subtropical

Brazil if the speleothems grow fast enough to allow sufficient sampling resolution.

Similar variations between drip and river waters during the first monitoring are consistent with water flushing

from the vadose zone into the cave river under piston flow conditions, but such a mechanism is unlikely to produce systematic short-term fluctuations in the geochemistry of carbonate formations deposited along local karst rivers under modern climatic conditions in P–S system area.

On longer time scales the rainfall driven changes in the time of residence of waters in the system might produce similar variations in trace element ratios of different types of speleothems. During dry events both groundwater residence time and extent of PCP are enhanced leading to an increase in the Sr/Ca and Mg/Ca ratios in drip waters, while the opposite tendency prevails during prolonged wet phases. These processes are thought to increase the amplitude of variation of the ratios and their background values, respectively. Furthermore, speleothems and tufas are expected to record covariations between Sr/Ca, Mg/Ca and SO<sub>4</sub> because over time all the effective geochemical processes would change the waters in the same direction over the P–S system.

## 5. Conclusions

Two hydrogeochemistry monitoring programs performed in the Pérolas–Santana cave system investigated the processes controlling dissolution and precipitation of carbonates and therefore the chemical composition of solution forming speleothems and fluvial carbonates. Changes in water geochemistry at the epikarst zone are associated with residence time of waters, while prior calcite precipitation seems to be the dominant process at deeper parts of the vadose zone above the cave. The latter is the main cause of the observed synchronous short-term variations in Ca, Mg/Ca and Sr/Ca in drip, pool and river waters in the system.

The water chemistry responds to rainwater infiltration events differently according to the hydrologic properties at each site. Hydrochemistry variations are more significant at fast than at slow drip sites because the flow pathways feeding the former are more sensitive to changes in the vadose reservoir level. In addition, variations in cave river waters are only observed during very wet periods, when the transport of Mg/Ca- and Sr/Ca-rich waters stored in the vadose zone is dominated by piston flow. Despite good correspondence with monthly rainfall totals, the temporal changes in drip water geochemistry can be independent of changes in discharge as seen at slow drip sites located in the deepest part of Santana cave. This suggests that non-linear features are also associated with trace element ratios as previously reported for drip hydrology, dissolved organic carbon and oxygen isotopes in Santana cave (Cruz et al., 2005b). We conclude that trace elements in speleothems from deep caves and areas with quite uniform

rainfall distribution can provide valuable information about climate change, but the geochemical response to climate can vary according to the type of secondary carbonate formation and time resolution.

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