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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_4 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_4 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.

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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 stables 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 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, SO_4, Mg/Ca and Sr/Ca, saturation index for calcite, pH, pCO_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–Perólas 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^2 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