



Calibration of speleothem $\delta^{18}\text{O}$ records against hydroclimate instrumental records in Central Brazil



J.S. Moquet^{a,*}, F.W. Cruz^a, V.F. Novello^a, N.M. Stríkis^a, M. Deininger^b, I. Karmann^a, R. Ventura Santos^c, C. Millo^a, J. Apaestegui^d, J.-L. Guyot^e, A. Siffedine^{f,g}, M. Vuille^h, H. Cheng^{ij}, R.L. Edwards^j, W. Santini^e

^a Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil

^b UCD School of Earth Sciences, University College Dublin, Belfield, Dublin 4, Ireland

^c Universidade de Brasília, Instituto de Geociências, Campus Universitário Darcy Ribeiro (CEP 70910-900), Brasília, Brazil

^d Instituto Geofísico del Perú, Lima, Peru

^e UMR GET (IRD) Géosciences Environnement Toulouse, CNRS-IRD-UPS, OMP, Toulouse, France

^f LMI "PALEOTRACES" (IRD/UFF/Uantof-Chili), Departamento de Geoquímica-UFF, Niterói, RJ, Brazil

^g LOCEAN (CNRS, IRD, MNHN, UPMC), Bondy, France

^h Department of Atmospheric and Environmental Sciences, University at Albany, State University of New York, Albany, NY, USA

ⁱ Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China

^j Department of Geology and Geophysics, University of Minnesota, Twin Cities, Minneapolis, MN, USA

ARTICLE INFO

Article history:

Received 6 May 2015

Received in revised form 19 January 2016

Accepted 1 February 2016

Available online 4 February 2016

Keywords:

Speleothem
Climate calibration
Stable isotopes
SAMS-SACZ
Central Brazil

ABSTRACT

$\delta^{18}\text{O}$ in speleothems is a powerful proxy for reconstruction of precipitation patterns in tropical and sub-tropical regions. The aim of this study is to calibrate the $\delta^{18}\text{O}$ record of speleothems against historical precipitation and river discharge data in central Brazil, a region directly influenced by the Southern Atlantic Convergence Zone (SACZ), a major feature of the South American Monsoon System (SAMS). The present work is based on a sub-annual resolution speleothem record covering the last 141 years (the period between the years 1870 and 2011) from a cave in central Brazil. The comparison of this record with instrumental hydroclimate records since 1921 allows defining a strong relationship between precipitation variability and stable oxygen isotope ratios from speleothems. The results from a monitoring program of climatic parameters and isotopic composition of rainfall and cave seepage waters performed in the same cave, show that the rain $\delta^{18}\text{O}$ variability is dominated by the amount effect in this region, while $\delta^{18}\text{O}$ drip water remains almost constant over the monitored period (1.5 years). The $\delta^{18}\text{O}$ of modern calcite, on the other hand, shows clear seasonal variations, with more negative values observed during the rainy season, which implies that other factors also influence the isotopic composition of carbonate. However, the relationship between $\delta^{18}\text{O}$ of carbonate deposits and rainwater is supported by the results from the comparison between speleothem $\delta^{18}\text{O}$ records and historical hydroclimate records. A significant correlation between speleothem $\delta^{18}\text{O}$ and monsoon rainfall variability is observed on sub-decadal time scales, especially for the monsoon period (DJFM and NDJFM), once the rainfall record have been smoothed with a 7–9 years running mean. This study confirms that speleothem $\delta^{18}\text{O}$ is directly associated with monsoon rainfall variability in central Brazil. The relationship between speleothem $\delta^{18}\text{O}$ records and hydroclimatic historical records allows approximation of the absolute changes in mean annual rainfall during the last millennia in the SACZ/SAMS domain.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Speleothem isotope records are considered one of the most robust proxy for precipitation in (sub)tropical regions (Fairchild et al., 2006). Because of its large karstic area, Brazil is one of the countries with highest potential for reconstruction of the South American Monsoon System (SAMS) based on speleothem isotope records (e.g. Cruz et al., 2005a, 2005b; Wang et al., 2006; Cruz et al., 2006; Wang et al., 2007;

Stríkis et al., 2011; Novello et al., 2012a, 2012b; Apaestegui et al., 2014). One of the main features of the SAMS is the South Atlantic Convergence Zone (SACZ), a NW-SE band of convective activity, which extends from central Amazon basin to the South Atlantic Ocean (Fig. 1).

The SACZ activity is widely documented in contemporaneous climatology (e.g., Robertson and Mechoso, 2000; Vera et al., 2006; Junquas et al., 2013), but its multidecadal to centennial variability remains poorly known because of the low quantity of high-resolution and precisely dated paleoclimate records within the area influenced by the SACZ (Prado et al., 2013). In South America many proxies have been analyzed to document paleoclimate variability,

* Corresponding author.

E-mail address: jean-sebastien.moquet@ird.fr (J.S. Moquet).

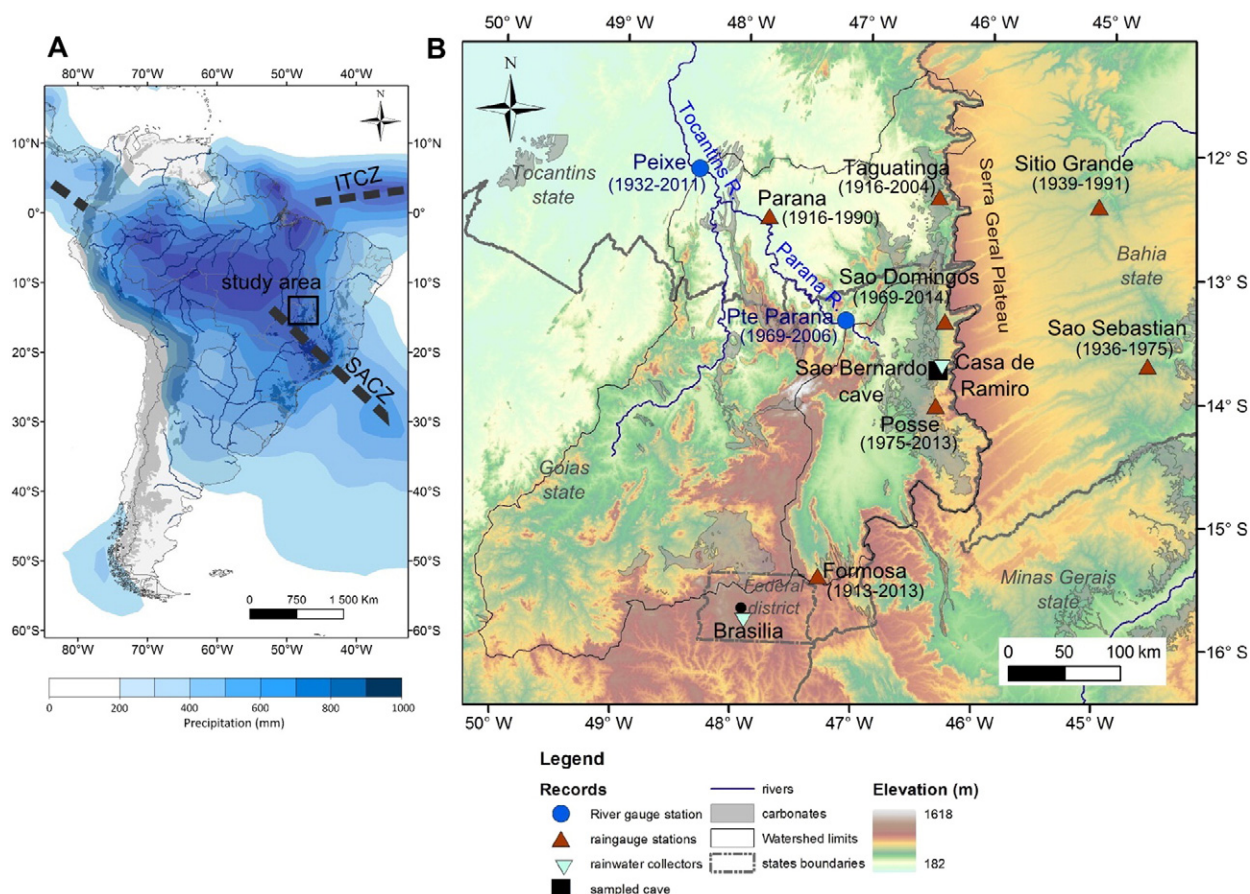


Fig. 1. A) Long-term (1979–2000) mean precipitation (in mm) for December–February (DJF) from the Climate Prediction Center Merged Analysis of Precipitation (website: <http://www.cpc.ncep.noaa.gov/>) and location of the study area. B) Location of the sampled cave, the hydrologic gauge station, the rain gauge stations and the rainwater collectors stations used in this study. Carbonate lithology is reported from CPRM geological 1/1000000 maps (2004).

including ice cores (e.g. Thompson et al., 2013), lake sediments (e.g. Cordeiro et al., 2011; Sifeddine et al., 2011), tree rings (e.g. Brien et al., 2012; Ferrero et al., 2015) and marine cores (e.g. Haug et al., 2003; Chiessi et al., 2009). Stable isotope records from carbonate speleothems, however, have been the most widely used for reconstructing paleo-precipitation variability at high temporal resolution and over timescales varying from the last millennia (Vuille et al., 2012; Novello et al., 2012a, 2012b; Apaestegui et al., 2014) to the Holocene (Strikis et al., 2011; Kanner et al., 2013) and orbital timescales (Cruz et al., 2005a, 2005b, 2006; Wang et al., 2007; Cheng et al., 2013). These proxy records also provide an ideal testbed for climate models (e.g. Vuille et al., 2003; Dias de Melo and Marengo, 2008; Braconnot et al., 2007; Khodri et al., 2009), allowing for stringent tests of their performance and ability to reproduce observed climate variability on a range of spatial and temporal scales.

Most speleothem-based paleoclimatic studies in South America focused on the carbonate $\delta^{18}\text{O}$ variability, and interpreted these changes as a function of relative changes in precipitation amount (e.g. Reuter et al., 2009; Strikis et al., 2011; Novello et al., 2012a, 2012b), changes in the relative proportion of moisture supplied from different source areas, such as the Atlantic ocean or the Amazon basin (Cruz et al., 2005a, 2006) or simply as an intensification of the monsoon regime (Kanner et al., 2013; Apaestegui et al., 2014). However, only few monitoring programs have been performed in South American caves yet (Sondag et al., 2003; Cruz et al., 2005b) and none of them attempted to calibrate the isotopic records against historical precipitation records. The calibration of speleothem $\delta^{18}\text{O}$ records as a function of climate parameter

allows determining the main environmental parameters controlling stable isotopes in speleothems in order to avoid misinterpretation of $\delta^{18}\text{O}$ records during climate reconstruction (Baker et al., 2007; Matthey et al., 2008; Jex et al., 2011; Tremaine et al., 2011a, 2011b). However, the calibration studies are usually too short to ensure that a climate relationship embedded in the $\delta^{18}\text{O}$ of carbonate speleothems is maintained and applicable to a long-term perspective. One of the reasons for this problem is that the residence time of cave percolating waters can be relatively long (Genty et al., 2014). In this context it is essential to directly establish and verify a quantitative relationship between historical climate and speleothem isotope records. However, it is very difficult to obtain well-dated speleothem records with a resolution that allows resolving interannual climate variability derived from $\delta^{18}\text{O}$ archives (Orland et al., 2014), given that most speleothems are not characterized by fast growth (rates of several $\text{mm} \cdot \text{year}^{-1}$) and present U/Th age errors larger than 10 years for the last century.

Comparing speleothem records with hydrological/climatic historical records allows investigating the coherence between speleothem $\delta^{18}\text{O}$ variations and changes in modern rainfall distribution (Yadava et al., 2004; Treble et al., 2005; Matthey et al., 2008; Cai et al., 2010; Baker et al., 2007; Jex et al., 2010, 2011). In the current literature this approach is quite common and generally performed using records that are 40–50 years long, as longer historic precipitation records are often not available. The relationship obtained over this modern calibration period is then used to estimate the magnitude of abrupt changes in absolute precipitation amounts, which may have culminated in social crisis throughout history, for instance the drought period at the time of the collapse of the Maya civilization in Mexico during the Medieval Climate Anomaly (Medina-Elizalde and Rohling, 2012).

Here we present the results of a monitoring program performed between December 2012 and June 2014 in São Bernardo cave, Central Brazil. This data set is used to support the interpretation of results from a sub-annually resolved speleothem $\delta^{18}\text{O}$ record, collected in the same cave at the monitored drip site. We then compared this well-dated record with historical records of regional rainfall and with specific river discharge from the Upper Tocantins River for the periods 1921–2010 and 1931–2010, respectively. This study allows for the first time defining the relationship between historical hydroclimatic records and a $\delta^{18}\text{O}$ record retrieved from speleothem carbonate deposits in Brazil. A major outcome of this work is that the speleothem $\delta^{18}\text{O}$ record covaries in phase with the amount of rainfall associated with SACZ activity in the central region of Brazil and that therefore the oxygen isotopic signature of speleothems can be used to reconstruct past SACZ activity.

1.1. Regional setting of São Bernardo

The São Bernardo cave (13.81°S, 46.35°W) is located in the Terra Ronca State Park (PETER) in the Paranã River sub-basin at the head of the Tocantins River basin near the border between Goiás and Bahia States in central Brazil (Fig. 1). The São Bernardo cave entrance is located at an altitude of 631 m.a.s.l.

In this area, large underground systems are formed by rivers arriving from the Serra Geral Plateau, a morphologic feature formed in the sandstones of the Urucua Formation (Cretaceous age) (Fig. 1). Large caves have developed along the trajectories of these rivers passing through Neoproterozoic carbonate formations from the Bambui group (Guyot et al., 1996). The high Mg limestone and dolostones are the main carbonate rocks that occur at the study site (CPRM, 2004). The vegetation of the region is typical savanna vegetation, called Cerrado, which is subject to fire events on a regular basis. These fires occur naturally, but since the modern colonization of the region during the 1960s, they have been accentuated by anthropogenic practices (de Campos Telles et al., 2007).

The present-day climate of the study area is tropical semi-humid with a mean annual precipitation of about 1270 mm·yr^{−1} at the meteorological station in São Domingos-GO (1971–2010, data from Agência Nacional de Aguas – ANA) close to the PETER. Most of the regional precipitation is related to convection over the larger SACZ domain, which is in turn linked to SAMS variability and associated intense convective activity over the Amazon region during austral summer (Garreaud et al., 2009; Espinoza Villar et al., 2009). The SACZ extends southeastward from the core of the continent over the Amazon basin to the South Atlantic (Vera et al., 2006) (Fig. 1A). The rainy season extends from October to April and rainfall essentially ceases between May and September. This rainfall seasonality is reflected in the discharge variation of the main drainages in the region, such as the Tocantins River (Figs. 1B and 2). Similarly, the recharge in the karst aquifers above São Bernardo cave is thought to be predominantly sourced from precipitation falling between November and March. Over the period A.D. 1977–2012, mean monthly temperature at Posse Station (The nearest meteorological station to São Bernardo Cave with air temperature data) ranges between 22.5 °C in July, and 25.8 °C in October with an annual average of 24.0 °C (Fig. 2B).

The speleothem (SBE3) has been sampled in a tributary conduit located around 250 m from the main underground river (São Bernardo River) and at about 450 m from the entrance of the São Bernardo cave. The temperature in the place where SBE3 stalagmite was collected is 24.8 °C all year long, which is very close to the mean external annual air temperature in the study area. At the monitored location the relative humidity (RH) remained constantly at 100%. RH at this level reduces the likelihood of fractionation between drip waters and stalagmite calcite due to evaporation (Mickler et al., 2004; Tremaine et al., 2011a, 2011b, Deininger et al., 2012). Cave air CO₂ concentrations varied between 1180 and 2720 ppm in the SBE3 chamber), as recorded during 5 field trips between March 2013 and June 2014.

2. Materials and methods

2.1. Rainwater isotopic signature

Rainfall samples were collected on a weekly basis between January 2012 and June 2014 by a local observer following the IAEA protocols (www-naweb.iaea.org/naweb/ih/documents/other/Sampling%20booklet%20web.pdf). The monitoring station, hereafter referred to as “Casa de Ramiro” is located at about 7 km from the entrance of São Bernardo cave (Fig. 1B).

We also used the $\delta^{18}\text{O}$ and δD values of rainwater from Global Network of Isotopes in Precipitation (GNIP) data monitored at Brasília station by the International Atomic Energy Agency (IAEA). This station is located 300 km south of the sampled cave. The two rainwater sampled stations are located in a similar rain pattern (Fig. 1A). Although the Brasília GNIP data set, collected between 1963 and 1987, is discontinuous and sparse, it can be used to discuss the possible intrinsic factors affecting the isotopic signature of rainfall on a longer time perspective.

2.2. Cave monitoring program

The São Bernardo cave was monitored between December 2012 and June 2014 for climate, stable isotope ratios of cave drip water ($\delta^{18}\text{O}$ and δD) and modern carbonate ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$). Temperature and relative humidity were monitored every 10–15 min near the place where the speleothem was sampled. The same parameters were also monitored outside the cave at the “Casa de Ramiro” station.

The drip water grab samples were collected in 8 ml Nalgene plastic bottles every 15 days by a local observer. The drip site corresponds to the same place where SBE3 was collected. Modern carbonate samples deposited on a 110 mm diameter watch glass, placed underneath the monitored drip water site, were collected and replaced throughout the hydrological cycle every 15 days to 2 months, depending on the quantity of carbonate deposited. On each watch glass, the precipitated carbonate was collected from the central part which corresponds to the drip impact zone and transformed into fine powder. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data of modern carbonate corresponds to the mean isotopic ratios of three aliquots from the same sample. The standard deviations of the three replicated analyses are less than 0.20‰ VPDB for $\delta^{13}\text{C}$ and 0.18‰ VPDB for $\delta^{18}\text{O}$.

2.3. Stable isotopes measurements and mineralogical analysis

Analysis for $\delta^{18}\text{O}$ and δD of water samples (drip water and precipitation) was carried out using a Picarro L2120-i Analyzer that simultaneously measures the isotopic ratios of hydrogen (D/H) and oxygen ($^{18}\text{O}/^{16}\text{O}$) using Wavelength-Scanned Cavity Ring-down Spectroscopy at the Stable Isotope Laboratory of the University of Brasília. Data are reported to VSMOW and precision is $\pm 0.1\text{‰}$ ($\delta^{18}\text{O}$) and $\pm 0.5\text{‰}$ ($\delta^2\text{H}$). Calibration is done by comparing the reference values to measured values of three standards provided by the IAEA (VSMOW2, NANOP, GISP) and 5 internal standards with values closer to the isotopic range of the sampled waters, with $\delta^{18}\text{O}$ ranging between -1.86 and -14.00‰ and $\delta^2\text{H}$ ranging between -1.45 and -109.00‰ . Every sample is analyzed 4 to 5 times and the first result is discarded to avoid memory effects following the IAEA recommendations.

The oxygen and carbon stable isotope analysis of carbonate samples were performed at the Stable Isotope Laboratory at the Geosciences Institute of the University of São Paulo. Oxygen and carbon isotope ratios are expressed in δ notation, the per mil deviation from the VPDB standard according to the following equation for, e.g., oxygen isotopes: $\delta^{18}\text{O} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{18}\text{O}/{}^{16}\text{O})_{\text{VPDB}} - 1] \times 1000$. The collected calcite powder was analyzed with a Gas-Bench type on-line preparation system linked to a Finnigan Delta Plus Advantage mass spectrometer. The precision of analysis is $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$.

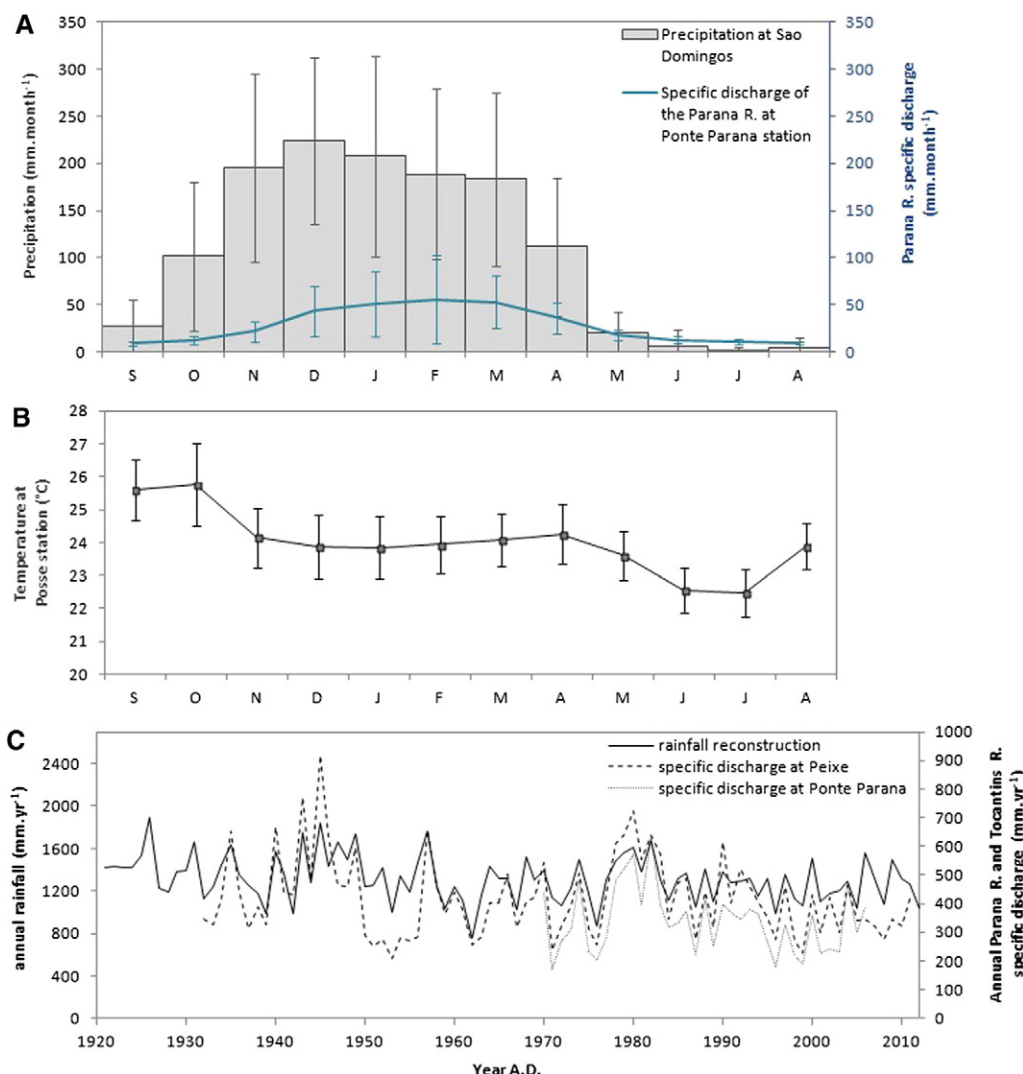


Fig. 2. A) Monthly precipitation at Sao Domingos city and Parana River monthly specific discharge at Ponte Parana gauge station averaged over the period A.D. 1971–2010 (Error bars correspond to 1 standard deviation); B) temperature at Posse station averaged over the period 1977–2012 (Error bars correspond to 1 standard deviation). C) 1921–2011 northern Goias precipitation reconstruction, 1931–2011 Tocantins specific discharge at Peixe station and 1970–2006 Parana discharge at Ponte Parana (data sources: ANA, INMET and ONS – see material and methods for details).

The samples for stable isotope analyses were collected along the longitudinal growth axis of the speleothem, from the top down to 76 mm distance from the top. The sampling interval was 0.125 mm using a New Wave micro-milling machine system with a high-speed precision drill and stereomicroscope with a charged coupled device and was carried out at the University of São Paulo. The oxygen isotope profile of SBE3 is based on 563 data points, which equals to 1 to 10 samples per year in the late and early growth history, respectively and according to the dates measurements (next section).

Samples were also drilled for Hendy tests by the same trench sampling protocol along 3 individual layers at 13, 27 and 51 mm from the top. The layers are presented as H1 ($n = 40$), H2 ($n = 36$) and H3 ($n = 23$), respectively.

Mineralogic analyses of the SBE3 speleothem were performed on 3 samples, located at 10, 70 and 125 mm from the stalagmite top, by using DRX at the Géosciences-Environnement-Toulouse (GET) Laboratory, France.

2.4. Speleothem U–Th dating

The stalagmite SBE3 was actively growing at the moment of collection in January 2012. The chronology of the SBE3 speleothem is based

on 8 U/Th dates for the last 136 years. Samples were analyzed at the University of Minnesota by using a Neptune MC-ICP-MS following the methodology described by Cheng et al. (2013). For each sample 0.1 g ($\pm \sim 0.01$ g) of carbonate powder was used and prepared by wet column chemistry to separate Th and U fractions and analyzed in the MC-ICPMS. The speleothem presents ^{238}U concentrations varying from 1583 to 3278 ppb. Low $^{230}\text{Th}/^{232}\text{Th}$ ratios (lower than 1850 ± 122.7) are reflected in the negligible correction for detrital Th content in the U/Th dates. Errors associated with the ^{230}Th corrected ages are lower than 5.3 years (Table 1).

Note that Fairchild and Baker (2012) underline that three conditions need to be met to calibrate speleothem proxies against climate records: 1) the speleothem has to be suitably sampled to prevent aliasing or other statistical issues arising, 2) it needs to be sampled at high temporal resolution, and 3) precise chronological control is necessary. The methods presented here meet all these conditions.

2.5. Rainfall record

The rainfall dataset was obtained from the National Brazilian Meteorological Institute (Instituto Nacional de Meteorologia – INMET) website (www.inmet.gov.br) and from the NOAA-GHCN-M database

Table 1
SBE3 ^{230}Th dating results. The error is 2σ .

Distance from the top along the sampling axes (mm)	^{238}U (ppb)	^{232}Th (ppt)	$^{230}\text{Th}/^{232}\text{Th}$ (atomic $\times 10^{-6}$)	$\delta^{234}\text{U}^a$ (measured)	$^{230}\text{Th}/^{238}\text{U}$ (10^{-3} activity)	^{230}Th Age (uncorrected) (year before 2012)	^{230}Th Age (corrected) (year before 2012)	$\delta^{234}\text{U}_{\text{Initial}}^b$ (corrected)	^{230}Th age (corrected) (yr AD)
3.9	3278 ± 6	96 ± 2.3	144 ± 16.0	320.5 ± 1.8	0.3 ± 0.03	21 ± 2	20 ± 2.3	320 ± 1.8	1992 ± 2.3
17.8	1652 ± 2	197 ± 4.2	61 ± 8.4	324.1 ± 1.7	0.4 ± 0.06	36 ± 5	34 ± 5.3	324 ± 1.7	1978 ± 5.3
23.1	1968 ± 3	106 ± 2.5	170 ± 13.9	323.8 ± 1.8	0.6 ± 0.04	46 ± 4	45 ± 3.7	324 ± 1.8	1967 ± 3.7
31.4	3005 ± 6	67 ± 1.7	507 ± 27.5	319.3 ± 2.3	0.7 ± 0.03	56 ± 3	56 ± 2.7	319 ± 2.3	1956 ± 2.7
38.8	2925 ± 6	19 ± 1.1	1850 ± 122.7	320.9 ± 1.9	0.7 ± 0.03	61 ± 2	61 ± 2.1	321 ± 1.9	1951 ± 2.1
57.8	2119 ± 4	34 ± 1.2	1003 ± 50.6	329.8 ± 2.2	1.0 ± 0.03	80 ± 3	80 ± 2.9	330 ± 2.2	1932 ± 2.9
64.8	1583 ± 2	93 ± 2.2	356 ± 17.2	324.7 ± 1.7	1.3 ± 0.05	104 ± 4	103 ± 4.5	325 ± 1.7	1909 ± 4.5
70.3	1992 ± 6	219 ± 4.5	252 ± 7.6	322.7 ± 2.7	1.7 ± 0.04	139 ± 3	136 ± 3.6	323 ± 2.7	1876 ± 3.6

^a $\delta^{234}\text{U} = ([^{234}\text{U}/^{238}\text{U}]_{\text{activity}} - 1) \times 1000$.

^b $\delta^{234}\text{U}_{\text{Initial}}$ was calculated based on ^{230}Th age (T), i.e., $\delta^{234}\text{U}_{\text{Initial}} = \delta^{234}\text{U}_{\text{measured}} \times e^{\lambda^{234}\text{U} \times T}$. Corrected ^{230}Th ages assume the initial $^{230}\text{Th}/^{232}\text{Th}$ atomic ratio of $4.4 \pm 2.2 \times 10^{-6}$. Those are the values for a material at secular equilibrium, with the bulk earth $^{232}\text{Th}/^{238}\text{U}$ value of 3.8. The errors are arbitrarily assumed to be 50%.

(National Oceanic and Atmospheric Administration – Global Historical Climatology Network – Monthly database) through the KNMI Climate explorer (climexp.knmi.nl). This database allows reconstructing a continuous rainfall record from 1921 to 2011, compiling data from 7 rain gauge stations (Figs. 1B; 2C). As each of these records are discontinuous, we applied a regional vector following the Brunet–Moret method with the software HYDRACCESS (Vauchel, 2005). This method, developed by the French Institute of Research for the Development (IRD), consists of the construction of a synthetic station, which takes into account the gap of the records and calculates an annual index with a mean value of 1 averaged over the entire record length. For each selected station, the annual, DJF, DJFM, NDJF, NDJM and JJA mean precipitation is downloaded into the software. When a year includes 3 rain gauge stations records, a yearly index is generated. In the present case, annual, DJF, DJFM, NDJF and NDJM rainfall records are produced for the period 1921–2011. The hydrological year is defined as the period from September to August. We then multiply the historical regional vector with the mean rainfall measured at São Domingos city station (city near the sampled site) to create a continuous long term historical rainfall record (1921–2011). Throughout this operation we assume that regional climate in the area covered by the rainfall gauge station is homogenous. This hypothesis is supported by a significant correlation between the 7 rainfall gauge records over their common period (when $n > 25$; p -value < 0.01) and by an error associated with this reconstruction lower than 15% for annual, DJF, NDJF, NDJFM records. Due to the low precipitation rate during JJA period, the error in this season is around 75%; therefore the reconstruction for these austral winter months was not considered here.

2.6. Specific discharge record

We extracted the annual, DJF, DJFM, NDJF and NDJM mean specific discharge value for each hydrological year of the Tocantins river at Peixe gauge station for the period 1931–2011 from the ANA and the Brazilian “Operador Nacional do Sistema Elétrico” – ONS (www.ons.org.br/operacao/vazoes_naturais.aspx) (Figs. 1B and 2).

In some contexts, river discharge records are longer than precipitation records (e.g. Callède et al., 2004). Calibration of paleoclimate records with discharge can be useful in such contexts (Brienen et al., 2012). To assess the relationship between hydroclimate variables and the speleothem record, we also relied on a monthly discharge reconstruction of the Paranã River at “Ponte Paranã” station for the period 1969–2006 (Figs. 1, 2). This time series is based on discharge gauging data from four stations, available from the ANA. During the period 1969–2006 the local hydrological record (“Ponte Paranã” station) is highly correlated with the regional one (Peixe station). The correlation coefficient between the two records is > 0.89 for both monsoon seasons

(DJF, DJFM, NDJFM and NDJF) and annual periods (significant at p -value < 0.001).

During the 1931–2011 period, a positive correlation coefficient is observed between rainfall and monthly specific discharge for the annual, DJF, DJFM, NDJF and NDJM records ($r > 0.74$; p -value < 0.001). An exception to this strong relationship is observed during 6 consecutive years from 1950 to 1956, when an abrupt decrease in discharge values is seen while no drop of similar magnitude is apparent in the reconstructed rainfall record. A regional rainfall analysis performed over the entire basin area indicates that a negative precipitation anomaly characterized the western side of the basin during this period. However, this rainfall anomaly was much less significant over the Paranã River basin, the eastern tributary of the Upper Tocantins basin, where the cave site is located (Fig. 1).

3. Results

3.1. Modern observations – monitoring program

3.1.1. Coherence of the water isotopes with the GMWL

The stable isotope values of local rainfall at “Casa de Ramiro” station and SBE3 drip water are shown together with the Global Meteoric Water Line (GMWL) defined by Rozanski et al. (1993) and the Local Meteoric Water Line (LMWL) calculated with data from the IAEA/GNIP Brasilia station (Fig. 3). The LMWL ($N = 115$; $R = 0.98$; $\delta^2\text{H} = (7.56 \pm 0.16) \delta^{18}\text{O} + (11.11 \pm 0.77)$) is very close to the GMWL ($\delta^2\text{H} = (8.17 \pm 0.06) \delta^{18}\text{O} + (10.35 \pm 0.65)$) defined by Rozanski

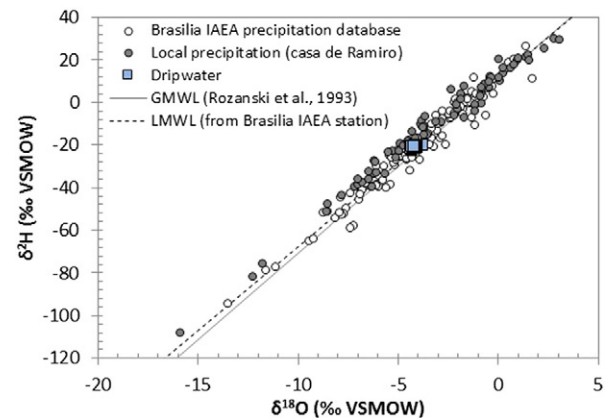


Fig. 3. Stable isotopic composition of precipitation obtained from the GNIP/IAEA database for Brasilia station, collected from 1963 to 1987, and rain and drip waters collected from 2012 to 2014. The global meteoric water line (GMWL) defined by Rozanski et al. (1993) and a local meteoric water line (LMWL) defined based on IAEA Brasilia gauge station data are very similar.

et al. (1993). The $\delta^{18}\text{O}$ values of rain samples obtained close to the cave at the “Casa de Ramiro” station vary from -15.9 to 3.1 ‰ VSMOW during the 2012–2014 period and fall on both LMWL and the GMWL, indicating that evaporative effects are not significant.

Isotope ratios of cave drip water are available for the period December 2012 to June 2014. The observed $\delta^{18}\text{O}$ values (-4.4 to -3.8 ‰ VSMOW) fall within the range of values recorded at “Casa de Ramiro station”, but they are essentially invariant throughout the monitored period. These samples plot on the LMWL and the GMWL; hence no significant evaporative influence is observed in the drip water isotopes (Fig. 3).

3.1.2. Controls of $\delta^{18}\text{O}$ variability in rainfall

The monthly stable isotope data from the IAEA station in Brasília (1963–1987) and the rainwater samples collected at “Casa de Ramiro” station from June 2012 to June 2014 are used to discuss the possible factors affecting the isotopic composition of precipitation (Figs. 4 and 5A). No significant correlation (p -value < 0.05) was observed between rain water $\delta^{18}\text{O}$ and air temperature at both stations. We observe that the rainwater $\delta^{18}\text{O}$ is significantly correlated with monthly rainfall accumulation at both stations ($r = 0.58$ and $r = 0.61$ respectively for IAEA Brasília station and Casa de Ramiro station; p -value < 0.001). In addition the slope of the linear regression (-1.6 ± 0.2 ‰ 100 mm^{-1}) is close to the value of -2 ‰ 100 mm^{-1} estimated by Rozanski et al. (1993) for monthly rainfall in tropical areas on a global scale. On the other hand the correlation between $\delta^{18}\text{O}$ and weekly rainfall accumulation at the Casa de Ramiro station is significantly higher than on a monthly basis ($n = 64$; $r = -0.72$; p -value < 0.001) (Fig. 4A). At Brasília station the monthly slope between $\delta^{18}\text{O}$ and precipitation amount is -1.6 ± 0.4 ‰ 100 mm^{-1} ($n = 132$; $r = -0.58$; p -value < 0.01) consistent with the slope calculated for the Casa de Ramiro station (Fig. 4B). Following these significant linear relationships observed at both stations, we conclude that the $\delta^{18}\text{O}$ variability in rainwater is primarily influenced by the amount effect in our study region, as generally observed for humid regions (Dansgaard, 1964; Rozanski et al., 1993; Gat, 1996; Jones and Banner, 2003; Cobb et al., 2007; Fuller et al., 2008).

3.1.3. Drip water $\delta^{18}\text{O}$ variability

During the period monitored, the rainy season at the study site lasted from November 2012 to March 2013 and from September 2013 to May 2014. Even though rainfall is highly seasonal, there was no interruption in the observed drip rate during the period analyzed, indicating that the unsaturated or vadose water reservoir above the cave can supply water to the drip site all year long. Drip water $\delta^{18}\text{O}$ values were measured biweekly between December 2012 and June 2014. We found that

these drip water oxygen isotope ratios were approximately constant throughout the hydrological cycle within the analytical error of 0.1 ‰ (Fig. 5A, B). This feature reflects the buffering effect produced by older waters stored in the vadose reservoir that feed the drip sites in the cave. The mean drip water $\delta^{18}\text{O}$ value (-4.2 ± 0.1 ‰ VSMOW, $n = 37$), however, is similar to the mean weekly weighted $\delta^{18}\text{O}$ of rainfall samples from the Casa de Ramiro station (mean = -4.5 ‰ VSMOW; $n = 64$), which implies that no significant change in isotopic composition of meteoric waters occurred, while percolating from surface to the cave. Nevertheless, drip water $\delta^{18}\text{O}$ represents a mix of recharge waters from the previous years, suggesting that the drip water isotopic signal does not necessarily reflect the rainwater isotopic composition of a single season.

3.1.4. Carbonate $\delta^{18}\text{O}$ variability along the hydrological year

$\delta^{18}\text{O}$ of carbonate samples deposited onto watch glass surfaces were collected over the course of two hydrological years. The mean $\delta^{18}\text{O}$ value of the carbonate deposited at the same location where the SBE3 stalagmite was collected is -4.10 ± 0.25 ‰ VPDB ($n = 14$) over this period. However, there is no significant correlation between $\delta^{18}\text{O}$ of drip water and $\delta^{18}\text{O}$ of carbonate. Unlike the $\delta^{18}\text{O}$ from drip water, the $\delta^{18}\text{O}$ of carbonate shows a clear seasonal variation with an amplitude of approximately 0.8 ‰, characterized by a change from lower to higher values from dry to rainy season, respectively (Fig. 5). Indeed, $\delta^{18}\text{O}$ values decrease ~ 2 months after the onset of the rainy season and start increasing ~ 2 months after its demise (Fig. 5).

We should consider that a fraction of these observed $\delta^{18}\text{O}$ changes in modern carbonate might be caused by isotope fractionation between drip water and carbonate under non-equilibrium conditions. In order to quantify this component we calculated the predicted $\delta^{18}\text{O}$ values of calcite by taking the measured values of $\delta^{18}\text{O}$ for drip water and calcite at cave temperature (24.8 °C). The drip water $\delta^{18}\text{O}$ VSMOW was converted to $\delta^{18}\text{O}$ VPDB using the following equation: $\delta^{18}\text{O}_{\text{H}_2\text{O}(\text{‰VPDB})} = \delta^{18}\text{O}_{\text{H}_2\text{O}(\text{‰VSMOW})} \times 0.97002 - 29.98$ (Lachniet, 2009). We then applied the water-calcite fractionation equation estimated by Kim and O’Neil (1997) and Johnston et al. (2013) (Fig. 6). Because aragonite is the most common mineral precipitated in São Bernardo cave (see next section), the water-aragonite fractionation equations estimated by Kim et al. (2007a) and Patterson et al. (1993) are also used. Note that the Kim et al. (2007a) equation was obtained taking into account the aragonite acid fractionation factor by Kim et al. (2007b). The results show that the expected $\delta^{18}\text{O}$ values of carbonate deposited under equilibrium conditions in São Bernardo cave, would range between -4.8 ± 0.12 ‰ VPDB (Water-aragonite; Kim et al., 2007a) to -6.0 ± 0.12 ‰ VPDB (Water-calcite; Kim and O’Neil, 1997) depending on the equation considered.

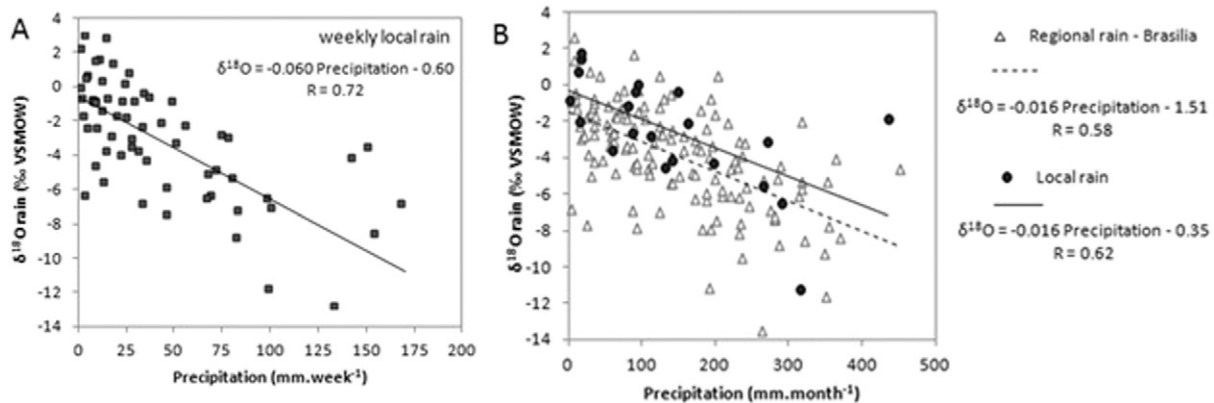


Fig. 4. A- Relationship between weekly $\delta^{18}\text{O}$ in rainfall at Casa de Ramiro station and weekly precipitation at São Domingos city. B- Relationship between monthly $\delta^{18}\text{O}$ in rainfall and monthly precipitation in Brasília (IAEA station; 1963–1987) and between monthly $\delta^{18}\text{O}$ in rainfall at Casa de Ramiro station and monthly precipitation at São Domingos city, respectively.

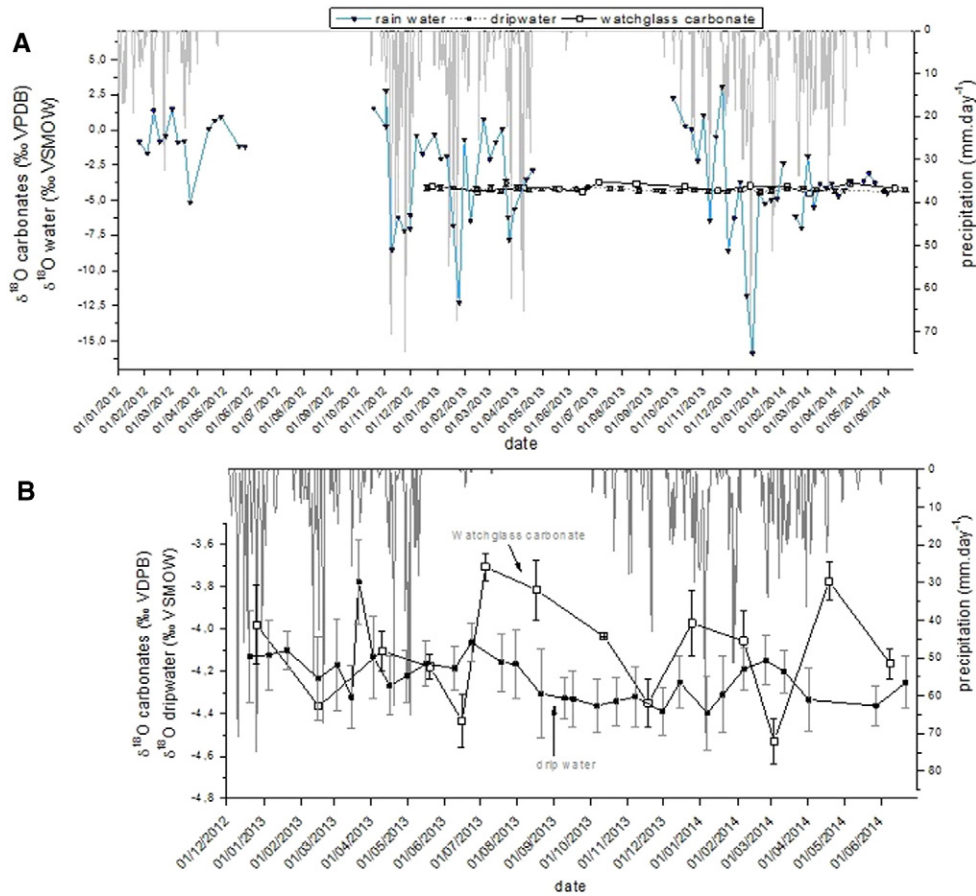


Fig. 5. A) Variability of $\delta^{18}\text{O}$ in rainwater, $\delta^{18}\text{O}$ of deposited carbonate (white points) and $\delta^{18}\text{O}$ in drip water (black points) in São Bernardo cave at the SBE3 speleothem location between December 2012 and June 2014. B) Variability of $\delta^{18}\text{O}$ of deposited carbonate (white points) and $\delta^{18}\text{O}$ in drip water (black points). For deposited carbonate, points are displayed in the middle of the period between the installation and the collection of the watchglass. In both graphs, daily precipitation at São Domingos station is shown by gray line).

These values are 0.7 to 1.9 ‰ lower than the $\delta^{18}\text{O}$ values measured in the carbonate coating precipitated on the watch glasses (-4.10 ± 0.25 ‰ VPDB, $n = 14$), suggesting that the isotope composition is in non-equilibrium conditions during carbonate precipitation.

Moreover, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of watch glass carbonate deposit are significantly correlated at $p\text{-value} < 0.05$ ($R = 0.61$; $n = 14$) along the time and following a linear regression of $\delta^{18}\text{O} = 0.35 \delta^{13}\text{C} - 0.57$ (Fig. S1 in supplemental material).

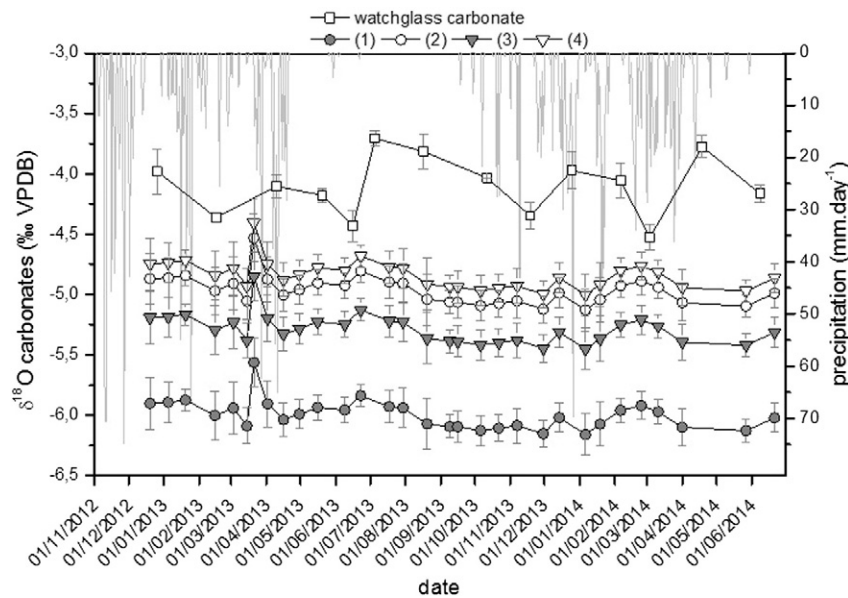


Fig. 6. Variability of $\delta^{18}\text{O}$ in deposited carbonate (white square) and calculated $\delta^{18}\text{O}$ of deposited carbonate based on drip water $\delta^{18}\text{O}$ between December 2012 and June 2014 (at a constant temperature of 24.8 °C) following the water–calcite oxygen isotope fractionation equations of (1) Kim and O'Neil (1997) and (2) Johnston et al. (2013) and following the water–aragonite oxygen isotope fractionation equations of (3) Patterson et al. (1993) and (4) Kim et al. (2007a). Daily precipitation at São Domingos station is also shown (gray line).

3.2. Speleothem isotope record

Results from DRX analysis show that the three SBE3 specimen are mainly composed by aragonite (60–90%) and microscope observations ($\times 10$ to $\times 100$) reveal that they lack evidence of dissolution or recrystallization (i.e. the observed primary layers are continuous and well preserved). Aragonite speleothems are common in dolomite host rock caves and/or in (seasonally) arid settings. This predominance of aragonite can be associated with a higher content of Mg in the epikarst as the cave is partially formed in dolomitic carbonate bedrock (Railsback et al., 1994; Bertaux et al., 2002; McMillan et al., 2005; Li et al., 2011; Wassenburg et al., 2012). We observed the presence of pristine primary white and gray layers from the top to the bottom of the speleothem; however these layers do not appear to be annual.

3.2.1. The Hendy test

The Hendy test (Hendy, 1971) can give information about the existence of kinetic processes affecting fractionation of both carbon and oxygen isotopes during speleothem deposition. The Hendy test criteria are: (1) $\delta^{18}\text{O}$ values remain constant along a single growth layer; (2) there are no simultaneous enrichments of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the speleothem carbonate (i.e., there is no correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values).

The Hendy test was performed along the longitudinal axis and from the center to the borders of 3 individual layers of the SBE3 stalagmite (Fig. S2 of the Supplementary material). The standard deviation of the $\delta^{18}\text{O}$ of the three single laminae is 0.16; 0.19 and 0.18 ‰ respectively ($n = 40, 36$ and 23 , respectively). Even though these values are close to the analytical uncertainty, a gradual increase in $\delta^{18}\text{O}$ of 0.6, 0.9 and 0.7 ‰ from the center to the border of the layers H1, H2 and H3 respectively, can be observed. The results suggest that kinetic fractionation may occur along a single layer from the center to the border of the speleothem. In addition a high positive correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is observed for all sampled layers ($r^2_{H1} = 0.83$; $r^2_{H2} = 0.78$; $r^2_{H3} = 0.81$) marked by less variable $\delta^{18}\text{O}$ than $\delta^{13}\text{C}$. The latter result may also be associated with a kinetic effect but this result is not entirely conclusive, because isotopic equilibrium could theoretically occur in the center of the speleothem at the same time that kinetic fractionation occurs at the flanks (Dreybrodt, 2008). Typically, with all other factors held constant, kinetic fractionation leads to a greater variability of $\delta^{13}\text{C}$ than $\delta^{18}\text{O}$ (Baker et al., 2007; Wiedner et al., 2008), which is apparently the case for SBE3 speleothem. On the other hand no significant correlation is observed between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ along the longitudinal sub-annual dataset ($n = 575$, $r = 0.055$), which could be due to the different processes determining the final value of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ recorded by SBE3. However, the Hendy test alone is insufficient to determine whether deposition occurred under equilibrium conditions (Mühlinghaus et al., 2009), and it may not be a conclusive test to identify kinetic

fraction occurring during speleothem growth in the cave (Kluge and Affek, 2012).

3.2.2. $\delta^{18}\text{O}$ data between 1870 and 2012 AD

During the last 141 years the $\delta^{18}\text{O}$ of SBE3 varied from -5.30 to -3.57 ‰ (mean = -4.28 ‰, range = 1.7 ‰, $n = 575$). The sub-annual and annually averaged stable isotope data used in the climate correlations are presented in Fig. 7. The annual record was averaged by year to obtain a mean annual value (VPDB‰) (Fig. 7). The high-frequency variability observed in the raw data might partially be associated with the variations seen in the seasonal carbonate deposits throughout the monitoring program at the sampled site (Fig. 7).

3.3. Stable isotopes vs. climate parameters

Based on the relationship between precipitation $\delta^{18}\text{O}$ values and the amount of rainfall the annually averaged SBE3 $\delta^{18}\text{O}$ dataset was correlated against precipitation on an annual scale and various averaging scenarios, for the monsoon season (NDJFM months) and intra-seasonally (DJF, DJFM and NDJF months). The SBE $\delta^{18}\text{O}$ dataset was also compared with the annual temperature but we found no significant correlation.

3.3.1. Correlation between the SBE3 $\delta^{18}\text{O}$ data and hydroclimate parameters

An autocorrelation test was first performed on the annual $\delta^{18}\text{O}$ SBE3 dataset ($n = 141$). This test allows identifying a pluri-annual memory in the system, which can reflect the presence of low-frequency trends in the data and may indicate storage times in the karst vadose aquifer (Jex et al., 2010). SBE3 is significantly auto-correlated (p -value < 0.01) for lags up to 8 years ($r = 0.48$). This result may reflect a buffering effect of the karstic water reservoir on the drip water $\delta^{18}\text{O}$ signature and hence also on the speleothem $\delta^{18}\text{O}$ record. In contrast, the autocorrelation test applied to the hydroclimatological records (precipitation and Tocantins River specific discharge) did not yield any statistically significant results (p -value < 0.01), regardless of the lag considered. In addition, correlations between annual $\delta^{18}\text{O}$ in SBE3 and annual and seasonal (DJF, DJFM, NDJFM) rainfall and Tocantins River specific discharge were performed. Therefore, it is reasonable to assume that the SBE3 $\delta^{18}\text{O}$ dataset reflects a multi-year average of precipitation $\delta^{18}\text{O}$ values. For this reason we applied a climate transfer function as described by Baker et al. (2007) and Jex et al. (2010). The precipitation and river specific discharge were first averaged according to the 100% average model (Jex et al., 2010):

$$W_n(t_1) = \frac{1}{n} \sum_{i=1}^n I(t_i) \quad (1)$$

whereat $W_n(t_1)$ is the smoothed climate parameter that is associated with the cave drip water in the year t_1 , t_i is the year (i.e. t_1 is the current

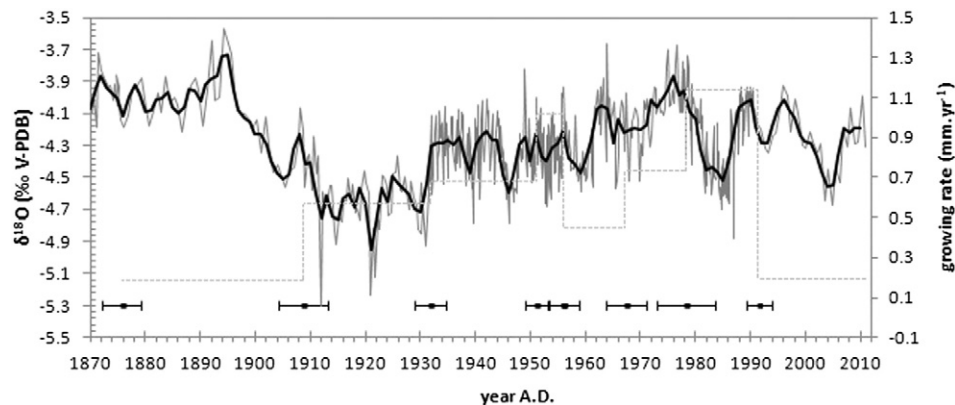


Fig. 7. $\delta^{18}\text{O}$ profiles of SBE3. Gray line: sub-annual stable isotope profile; Black line: annually averaged stable isotope profile. An analytical error of ± 0.1 ‰ is assumed on all measurements. Black points represent the 8 U/Th dates $\pm$ error (2σ) performed along the speleothem. Dashed line represents the growth rate between two dates.

year x), t_2 is the year $x-1$ and $t_i = x - (i-1)$, I_i is the raw climate parameter at year t_i (i.e. rainfall or Tocantins runoff record) and n is the number of years that contributes to the cave drip water and determines the degree of smoothing. After the smoothing the Spearman rank correlation coefficient was calculated between the processed, i.e., smoothed climate parameter records and the SBE3 $\delta^{18}\text{O}$ dataset and evaluated using the method described in Ebisuzaki (1997). Moreover, to take into account the age uncertainties of the U–Th ages of SBE3 a Monte Carlo simulation (MC) was applied. In every run of the MC a new age model of SBE3 was constructed. For this the ages were allowed to vary within their 2-sigma age uncertainty. Subsequently a new $\delta^{18}\text{O}$ record was constructed using a linear interpolation between the ages. We then calculated correlation coefficient between the new $\delta^{18}\text{O}$ record of each run of the MC and the historic data for the amount of rainfall and the Tocantins river discharge. This results in an ensemble of significant ($p < 0.05$) correlation values of which the median, minimum and maximum are reported. These analysis were performed for a smoothing of the climate parameter from 1 to 11 years, i.e. from $n = 1$ to 11 (smoothing degree).

SBE3 exhibits statistically significant correlations with annual precipitation and DJF, DJFM, NDJF and NDFM periods but correlations with the Tocantins river discharge are insignificant for most of the periods of the year and degree of smoothing (p -value < 0.05). For this reason, only results from rainfall comparison are presented in Table 2 and Fig. 8. Fig. 8 presents the correlation coefficient between the Monte Carlo SBE3 runs and the annual and seasonal rainfall parameters as a function of the number of years used for the running mean calculation (degree of smoothing). The results are shown separately for minimum, median and maximum r value measured. In each graph the results are presented for each group of months considered.

A significant negative correlation exists between the SBE record and smoothed monsoon precipitation at p -value < 0.05 when rainfall record is averaged for more than 2 years running mean ($n > 2$). The correlation coefficient increases until a maximum smoothing degree = 7 to 9 years. Furthermore, while a significant correlation is observed between $\delta^{18}\text{O}$ and annual precipitation, the r value is significantly higher when only the wet season months are considered in this correlation (DJFM, NDJF and NDFM). The maximum correlation is observed for the months DJFM and NDJFM (r minimum = -0.76 in both case; r median = -0.66 and -0.65 respectively; r maximum = -0.53 in both case; p -value < 0.05), averaged over a 7–9 years interval (Fig. 8, Table 2).

These results confirm that SBE3 $\delta^{18}\text{O}$ record reflect with high confidence the sub-decadal (7–9 years) monsoon precipitation variations.

By opposition, from the 5000 Monte Carlo runs, significant positive correlations are recorded for Tocantins river discharge using data averaged on 1–2 years ($0.26 < r$ median < 0.31 depending on the period considered; p -value < 0.05) and negative significant correlations are only recorded when averaging DJF and DJFM Tocantins discharge by 5 years (r median = -0.32 and -0.33 respectively) but only 2–3% of the MC runs were significant for this period interval. By comparison with rainfall record these results exhibits less significant r -values.

4. Discussion

The aim of this study is to investigate the relationship between an annually resolved oxygen isotope speleothem record and historical precipitation and river discharge. Data from a monitoring program have shown to be useful to complete the present analysis.

4.1. Hydrology of the karst system

Cave drip water $\delta^{18}\text{O}$ acts as a natural tracer to provide supporting evidence for groundwater residence time of karst systems (Partin et al., 2012). The flow time between surface and the cave dripping sites can be highly variable and depends on the type of porosity of the rock/soil formation (inter-granular pore space, joints and fractures, and larger conduits) above the cave (Ford and Williams, 2007). Indeed, drip water $\delta^{18}\text{O}$ signals can either reflect rapid connection between surface and cave (e.g. Cruz et al., 2005a; Van Rangelbergh et al., 2014), amount-weighted rainfall $\delta^{18}\text{O}$ integrated over previous months (e.g. Moerman et al., 2014), during several years even at shallow depths (10–50 m) (e.g. Genty et al., 2014) or even over decades (e.g. Chapman et al., 1992; Kaufman et al., 2003). At our study site the rainwater $\delta^{18}\text{O}$ values are highly variable and respond to the amount effect, while the drip water $\delta^{18}\text{O}$ remains relatively constant over the monitored period. This suggests that water residence time in the aquifer directly above the cave is at least 1.5 years, the length of our monitoring program. This result can be interpreted as an indication of a well-mixed water reservoir above a cave (e.g., Pape et al., 2010; Williams and Fowler, 2002; Fuller et al., 2008; Kluge et al., 2010; Bertrand et al., 2010; Genty et al., 2014; Feng et al., 2014). However, the monitoring period, including only two hydrological cycles, is not long enough to accurately estimate water residence time from $\delta^{18}\text{O}$ of drip water. On the other hand, the analysis of

Table 2

Best correlation coefficients (r values) and regression parameters between the annual SBE3 $\delta^{18}\text{O}$ and the seasonal to intraseasonal rainfall amount and the Tocantins R. specific discharge. The respective number of years considered for calculating the running mean and the slope of the linear regression is also reported. The period considered is 1921–2011 ($n = 91$ years). Only statistically significant r values at the 0.05% level are reported.

Periods	Unit	Precipitation						
		r	N running average years	slope	± 1 st and art deviation slope	Intercept on discharge axe	± 1 st and art deviation intercept	± 1 -Sigma standard deviation regression
			Year	mm·yr. ⁻¹ ·% ⁻¹ or mm·month ⁻¹ ·% ⁻¹		mm·yr. ⁻¹ or mm·month ⁻¹		
Annual	Median r value	-0.45	8	-1154	118	-3612	130	43
	Minimum r value	-0.56	7					
	Maximum r value	-0.36	5					
DJF	Median r value	-0.43	10	-156	14	-450	18	4
	Minimum r value	-0.55	8					
	Maximum r value	-0.36	11					
DJFM	Median r value	-0.66	8	-132	13	-354	20	5
	Minimum r value	-0.76	7					
	Maximum r value	-0.53	8					
NDJFM	Median r value	-0.65	8	-118	11	-298	20	5
	Minimum r value	-0.76	7					
	Maximum r value	-0.53	9					
NDJF	Median r value	-0.53	9	-132	13	-354	20	5
	Minimum r value	-0.66	7					
	Maximum r value	-0.41	9					

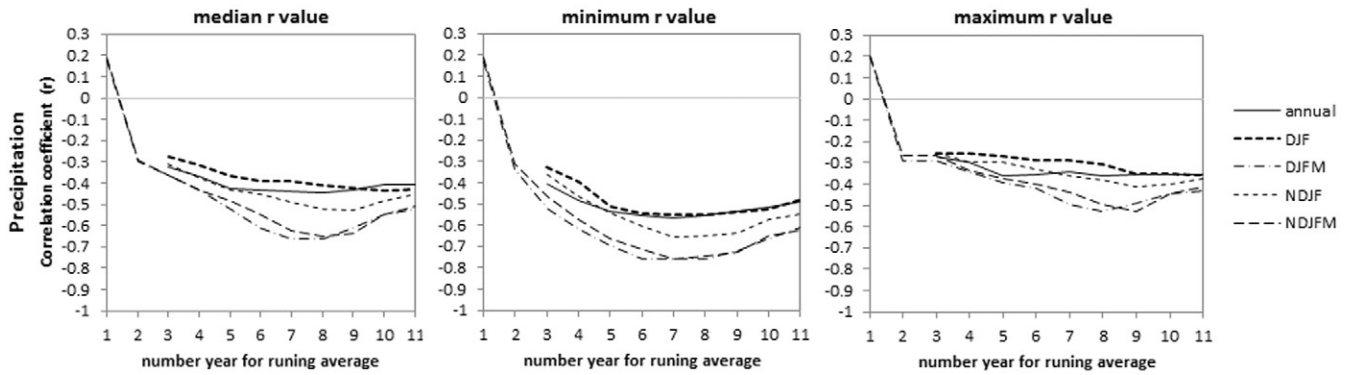


Fig. 8. Maximum, median and minimum correlation coefficient (r) between 5000 Monte Carlo runs of SBE3 $\delta^{18}\text{O}$ record and precipitation as a function of number of years included in calculating the running mean of raw hydroclimatological data ($n = 1$ to 11) for each group of months considered. Only r value significant at 0.05 level are reported.

the SBE3 isotope record (autocorrelation test and the comparison with the historical rainfall) can suggest that carbonate deposits reflect the amount of monsoon rainfall, averaged over 7 to 9 years, which would correspond to the transit time of the water between the surface and the cave point. Hence this result suggests that our speleothem, despite its high temporal resolution, does not resolve interannual climate variability and that its climatic interpretation is limited to subdecadal (7–9 year) time scales.

4.2. Isotope fractionation during carbonate deposition throughout the hydrological cycle

The predicted $\delta^{18}\text{O}$ of carbonate according to the four equations considered for calcite/aragonite–water fractionation under equilibrium conditions, showed values that are 0.7 to 1.9 ‰ lower than the $\delta^{18}\text{O}$ values measured in carbonate deposited on watch glasses. The more enriched isotope ratios observed in the watch glass carbonate suggest that the oxygen isotope composition of modern speleothems can be (i) affected by kinetic fractionation processes during its deposition or that (ii) the isotope composition of the drip water is not isotope equilibrium or (iii) both. In addition, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of watch glass carbonate deposit are significantly correlated ($R = 0.61$, $p < 0.05$; $n = 14$; Fig. S1). This suggests that during the monitoring period the carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ co-vary and can be affected by the same process. Such a process can be prior calcite precipitation (PCP) (Kluge and Affek, 2012) or Prior Aragonite Precipitation (PAP) (Wassenburg et al., 2012; Wassenburg, 2013) for example.

Although the cave air temperature remains almost constant and relative humidity remains 100% all year long, the $\delta^{18}\text{O}$ values of watch glass carbonate deposits were higher than expected for deposition under equilibrium conditions. Different reasons can explain the departure from equilibrium conditions such as the rapid calcite (or aragonite) precipitation, rapid CO_2 degassing during the bedrock dissolution and/or PCP (or PAP) may result in an isotopic disequilibrium in the deposition process of speleothems (heavier $\delta^{18}\text{O}$ values) by at least up to 0.7‰ (Mickler et al., 2006; Mook, 2006; Luo et al., 2013). Moreover, variation of minerals nature deposits (aragonite vs calcite) can also explain the $\delta^{18}\text{O}$ carbonate variation along the time. As illustrated by Fig. 6, depending on the fractioning equation used for calcite or aragonite, aragonite deposits at equilibrium can exhibit $\delta^{18}\text{O}$ signature about 1.2‰ higher than calcite deposits (Lachniet, 2015). This range corresponds to the seasonal variability of carbonate $\delta^{18}\text{O}$ observed on the watch glass deposits as well as for SBE3. However, further high-resolution analyses are necessary to test this hypothesis. This includes the analysis of the mineralogy as well as of trace elements analysis of SBE3; the Mg/Ca ratio of drip water is a crucial parameter for Aragonite precipitation. Furthermore, the cave monitoring needs to be extended, including a surface monitoring, to

investigate the mechanisms controlling the isotope fractionation in the cave and the degree of disequilibrium conditions.

4.3. The subdecadal climate signal of speleothem $\delta^{18}\text{O}$

Despite the evidence of kinetic fractionation in the São Bernardo cave, the high correlation between speleothem $\delta^{18}\text{O}$ and historical rainfall record suggests a strong relationship between the $\delta^{18}\text{O}$ values of the rainwater and the $\delta^{18}\text{O}$ values of SBE3. In fact, the apparent lack of equilibrium conditions has not disrupted the link with monsoon rainfall variability. Our findings are coherent with Mickler et al. (2006) who highlighted that for most natural speleothems a pure equilibrium fractionation cannot be assumed. As pointed out by Fairchild and Baker (2012), in areas where such disequilibrium deposition occurs, the primary climate signal is modified by kinetic fractionation or evaporation (e.g. Luo et al., 2013) but calibration is still possible (e.g. Baker et al., 2007; Matthey et al., 2008) as it is the case in the present study. Indeed, the negative correlation coefficient between the SBE3 $\delta^{18}\text{O}$ record with the historical precipitation record can be explained by either of the four following mechanisms: i) the “simple” amount effect during the formation of precipitation that is expressed by negative correlation between precipitation $\delta^{18}\text{O}$ values and the amount of rainfall. Even it is smoothed during the water transfer to the cave, the variability of the cave drip water has still the long-term $\delta^{18}\text{O}$ signature of the rain that have been precipitated during the 7 to 9 previous years (Baker et al., 2007; Jex et al., 2010). Hence, this signal is recorded by the speleothem resulting in a negative correlation between the SBE3 $\delta^{18}\text{O}$ and the historical record of the amount of rainfall. ii) PCP or PAP: Assuming that PCP or PAP is stronger during dryer periods, PCP or PAP would cause more positive speleothem $\delta^{18}\text{O}$ values during periods of little rainfall (e.g., Riechelmann et al., 2013; Kluge and Affek, 2012). Therefore, PCP or PAP would cause a negative correlation between the speleothem $\delta^{18}\text{O}$ record and a record of the history of the amount of rainfall. Hence, PCP or PAP would amplify the classical amount effect and these two processes could act together to explain the good correlation between the speleothem $\delta^{18}\text{O}$ record and the historical precipitation record. iii) PCP or PAP could either occur within the cave, which is then likely to change also the $\delta^{18}\text{O}$ of the carbon bearing species in the drip water, or already in the soil, as argued for the caves in South-East Brazil (Cruz et al., 2005a). This could favor drip waters with a high Mg concentration which can affect the mean ratio between Calcite and Aragonite (if the Mg concentration is high enough that Aragonite precipitation occurs) (Lachniet, 2015). Therefore, due to the different fractionation factors for calcite and aragonite the speleothem $\delta^{18}\text{O}$ record changes. If more (less) Aragonite is precipitated the speleothem $\delta^{18}\text{O}$ values become more positive (negative) (Fig. 6). If the degree of PCP or PAP changes the Mg concentration of the drip water, hence, if more PCP

or PAP favors Mg rich drip waters, the speleothem $\delta^{18}\text{O}$ values would be also more positive due to the higher aragonite. This is reasonable because of the Mg partition coefficient which suggests increasing Mg concentrations during the precipitation of calcite. Hence, the correlation between the speleothem $\delta^{18}\text{O}$ record and a record of rainfall history would have a negative correlation. Furthermore, this mechanism would amplify the first and the second mechanism. iv) Possible disequilibrium effects occur in terms of a changing drip rate in link with the hydrological pressure (Deininger et al., 2012; Genty et al., 2014). Higher drip rate would correspond to less disequilibrium and less enriched speleothem $\delta^{18}\text{O}$ during heavy rain season (or humid periods). Inversely, lower drip rates during dry sessions (or drier periods) would correspond to more disequilibrium and more enriched speleothem $\delta^{18}\text{O}$ because the hydrological pressure is smaller. Hence, this effect would also correspond to more negative $\delta^{18}\text{O}$ value during periods of higher precipitation.

Each of these four mechanism or a combination of them can explain the observed negative correlation between the SBE3 $\delta^{18}\text{O}$ and the historic record of the amount of rainfall. However, we cannot identify if a single mechanism dominates the isotope signature. For this further analysis on the speleothem SBE3 are necessary to illuminate this multifaceted relationships.

Using the 100% average model (Eq. 1) results in more than 60% of the $\delta^{18}\text{O}$ SBE3 variability explained by monsoon precipitation (DJFM) averaged over 7–9 years, which in turn corresponds to more than 80% of the annual precipitation over the area. The residual 40% may be related to other natural factors (e.g. kinetic fractionation, soil water evaporation) or to uncertainties in the hydroclimatological records or the chronology of the SBE3 speleothem. This first-order linear relationship is likely the result of a single source of moisture feeding the regional rainfall, transported from the Amazon basin, and nearly stable climatic conditions in the cave.

The correlation between the SBE3 $\delta^{18}\text{O}$ Monte Carlo runs and the Tocantins River discharge is less significant than with precipitation record. This result can be explain by the fact that the variations in Tocantins discharge reflect a more regional hydroclimate signal, while the precipitation is more representative of local climate, near the cave. Therefore, the use of a speleothem $\delta^{18}\text{O}$ record to reconstruct river discharge is complicated by the fact that discharge integrates both climate and physical hydrological processes that are highly heterogeneous over a large basin, while speleothems directly reflect changes in rainfall and local epikarst hydrology which cover only a small area of the Parana and Tocantins basin. Following this scenario, the positive correlations observed based on monte Carlo test, would be due to an artifact and SBE 3 is likely better “paleo-pluviometers” than “paleo-discharge meters” for this area.

Interestingly, the correlation between SBE3 $\delta^{18}\text{O}$ and the smoothed rainfall record is worse when using annual records rather than monsoon periods (Fig. 8; Table 2). This may be related to uncertainties in both rainfall data and the speleothem chronology. In addition rainfall events, which occur at the beginning and/or at the end of the monsoon season, may not contribute significantly to water recharge and to the isotopic signature of the karstic reservoir, even if they significantly contribute to the annual rainfall and surface runoff amount. Since these periods are characterized by sparse rainfall events and, particularly at the beginning of the monsoon season, low soil moisture, evapotranspiration processes may reduce water transfer from the surface to the karstic aquifer during these rainfall events. Partin et al. (2012) observed comparable effects in their rainfall drip water monitoring program. They noticed lower $\delta^{18}\text{O}$ values in drip water than in the rainfall-weighted average $\delta^{18}\text{O}$ and they hypothesized that the increased demand for moisture by plants during dry months, when less precipitation is available, might cause this effect. In our study, no evaporation processes were detectable from our measurements of drip water $\delta^{18}\text{O}$ and δH . Moreover, as the drip water is representative of the rainfall averaged over several years, it is not easy to determine the hydrology of the epikarst reservoir. Thus, complementary data and a longer monitoring period would be necessary to validate or invalidate these possible explanations.

Based on the best correlation coefficient from the “100% average” model (Eq. 1, Table 2), we apply the linear regression to the SBE3 $\delta^{18}\text{O}$ with both DJFM and annual precipitation records. The 2 standard error (SE) of the linear regression between SBE3 $\delta^{18}\text{O}$ and DJFM precipitation and annual precipitation is $10 \text{ mm} \cdot \text{month}^{-1}$ ($\pm 5\%$) and $86 \text{ mm} \cdot \text{year}^{-1}$ ($\pm 6\%$) respectively (Fig. 9 – Table 2). We emphasize that extrapolating this linear relationship back in time or applying it to other nearby speleothem records, implicitly assumes that the relationship between these parameters remained stationary in time and space and that the influence of other factors, which can contribute to $\delta^{18}\text{O}$ fractionation remained insignificant (e.g. mineralogy, drip water frequency, CO_2 degassing, pH, water alkalinity). Such hypotheses can be tested through replication of stalagmite $\delta^{18}\text{O}$ records from the same region or with other paleoclimate proxies (Wang et al., 2001).

However, this relationship does not apply to other regions of the South America where rainfall is bimodal and not exclusively related to the SAMS regime because the $\delta^{18}\text{O}$ of rainfall will be influenced by distinctly different moisture source areas (e.g. Cruz et al., 2005a, 2006) or by the intensification of the monsoon regime through the degree of rainfall upstream (Kanner et al., 2013; Apaestegui et al., 2014). The results of the present study suggest, however, that $\delta^{18}\text{O}$ records of speleothems from caves located in the region directly influenced by the SACZ in central Brazil, where the monsoon is the only rainfall regime, can be interpreted as a direct proxy of rainfall amount.

5. Conclusions

Rainfall $\delta^{18}\text{O}$ variability at our study site is mainly controlled by the amount effect and is characterized by a slope of $1.6 \text{ ‰} \cdot 100 \text{ mm}^{-1}$ on monthly timescales, comparable to previous observations in tropical regions. The $\delta^{18}\text{O}$ of drip water does not vary significantly throughout the two monitored hydrological cycles, but its mean value reflects the weighted mean of $\delta^{18}\text{O}$ of rainfall. Although the net carbonate $\delta^{18}\text{O}$ values are partially controlled by non-equilibrium isotopic fractionation, we could nonetheless observe a very significant correlation of the speleothem $\delta^{18}\text{O}$ with rainfall. The comparison with Upper Tocantins River specific discharge do not show a significant correlation during the last century, probably because river discharge is sensitive to spatial heterogeneities in rainfall over the basin during some periods.

The comparison between speleothem $\delta^{18}\text{O}$ with the historical rainfall series during the past century suggests that speleothem $\delta^{18}\text{O}$ values (approximate annual mean) is correlated to the monsoon rainfall variability above the cave, but smoothed with a 7–9 year averaging filter. The subdecadal $\delta^{18}\text{O}$ variability in carbonate is probably influenced by a relatively long residence time of stored waters in the karst reservoir. The mechanism explaining the co-variation of subdecadal $\delta^{18}\text{O}$ and precipitation can be either or conjointly explained by the amount effect rainfall print, PCP or PAP processes in both the cave and the soils or/ and the hydrological processes which would influence equilibrium and mineralogical deposits changes along the hydrological cycle. Based on the highly significant linear relationships obtained with the 100% average linear model, it is possible to propose a regional precipitation reconstruction for both the monsoon season (DJFM months) rainfall and the annual rainfall throughout the last century.

This study is the first speleothem calibration performed over the SAMS region and provides a basis upon which future research can advance paleoclimate reconstructions of SAMS and SACZ precipitation based on isotopic records. These results will be particularly valuable to support the climatic interpretation of ongoing studies based on high-resolution speleothem isotope records in the same region. Further studies are necessary to better understand the causes for kinetic fractionation processes in the caves from the same region.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.gloplacha.2016.02.001>.

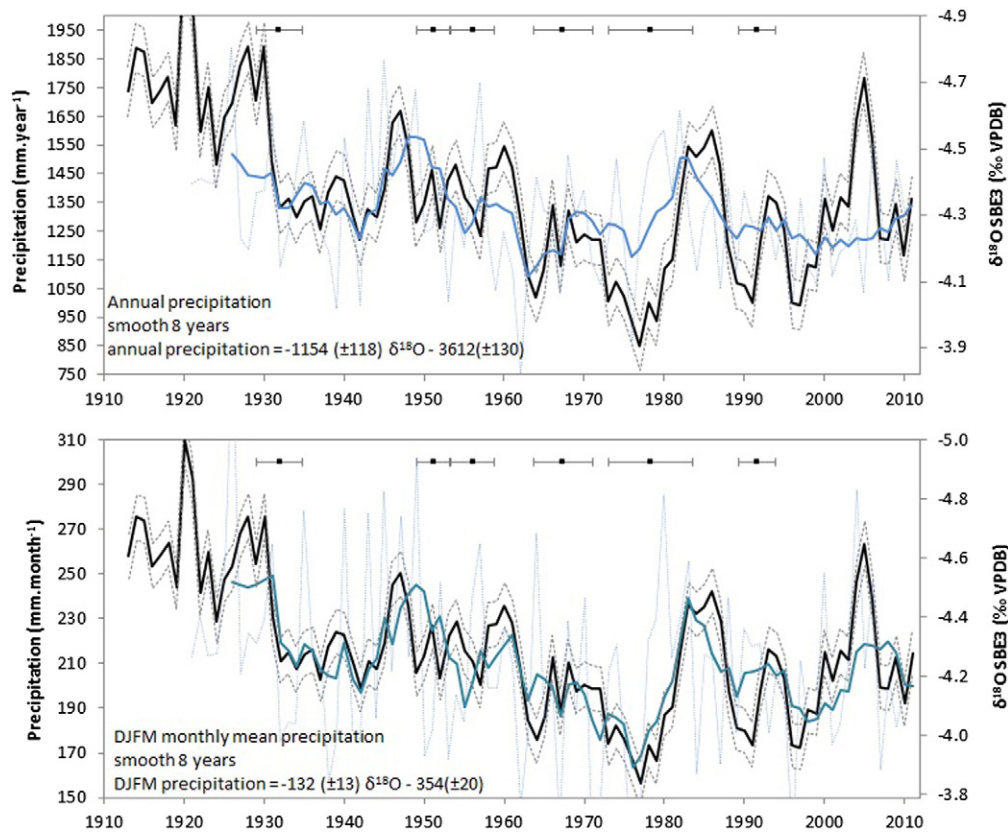


Fig. 9. Calibration of SBE3 $\delta^{18}\text{O}$ (black line) with 8 year running average annual precipitation (top) and 9 year running average DJFM precipitation amount (bottom) based on the best relationships derived from on product correlations (median r value of the Monte Carlo runs). Blue lines represent the smoothed precipitation. Blue dashed line represents the unsmoothed original precipitation. Gray dashed lines represent the error of the climatic reconstruction (± 2 standard deviation).

Acknowledgments

This research was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) grant 2011/12238-6 to Moquet, 2012/1187-4 to Karmann, 2012/50260-6, 2013/50297 to Cruz, 2011/12013-4 to Stríkis, 2012/03942-4 and 2014/10095-1 to Novello and 590172/2011-5 to PRIMO cooperative project (CNPq-IRD). It also benefited from grants from the US-NSF (1103403 to R.L.E and H.C. and 1303828 to M.V.). MD acknowledge funding by the Irish Research Council (IRC) by a Government of Ireland Postdoctoral Fellowship (GOIPD/2015/789). We thank the three anonymous reviewers for their constructive recommendations under the review process. We also thank Ramiro Hilário dos Santos for in-situ water sampling and his help during field work, Dr. Osmar Antunes for his support for carbonate stable isotope analyses in the stable isotope laboratory of the IGc-USP (Sao Paulo – Brazil), Dr. Luis Mancini and Eduardo Carvalho for the water sample stable isotope analyses in the Laboratory of Geochronology in the University of Brasília (Brazil), Dr. Damien Guillaume for carbonate mineralogical analyses at the GET Laboratory in Toulouse (France), Laia Comas Bru for providing the code for the Monte Carlo tests, Dr. Giuliano Locosselli for help during field work and in laminae counting and Dr. Guillaume Bertrand for his help in improving this manuscript. We thank the IBAMA and ICMBio for permission to collect stalagmite samples.

References

Apaestegui, J., Cruz, F.W., Sifeddine, A., Espinoza, J.C., Guyot, J.L., Khodri, M., Stríkis, N., Santos, R.V., Cheng, H., Edwards, R.L., Carvalho, E., Santini, W., 2014. Hydroclimate variability of the northwestern Amazon Basin near the Andean foothills of Peru related to the South American Monsoon System during the last 1600 years. *Clim. Past* 10, 533–561. <http://dx.doi.org/10.5194/cp-10-1967-2014>.

Baker, A., Asrat, A., Fairchild, I.J., Leng, M.J., Wynn, P.M., Bryant, C., Genty, D., Umer, M., 2007. Analysis of the climate signal contained within $\delta^{18}\text{O}$ and growth rate parameters in two Ethiopian stalagmites. *Geochim. Cosmochim. Acta* 71, 2975–2988.

Bertaux, J., Sondag, F., Roberto, S., Soubiès, F., Causse, C., Plagnes, V., Le Cornec, F., Seidel, A., 2002. Paleoclimatic record of speleothems in a tropical region: study of laminated sequences from a Holocene stalagmite in Central-West Brazil. *Quat. Int.* 89, 3–16.

Bertrand, G., Celle-Jeanton, H., Huneau, F., Looock, S., Renac, C., 2010. Identification of different groundwater flowpaths within volcanic aquifers using natural tracers for the evaluation of the influence of lava flows morphology (Argnat basin, Chaîne des Puys, France). *J. Hydrol.* 391, 223–234.

Braconnot, P., Otto-Bliesner, B., Harrison, S., Joussaume, S., Peterchmitt, J.-Y., Abe-Ouchi, A., Crucifix, M., Driesschaert, E., Fichefet, T., Hewitt, C.D., Kageyama, M., Kitoh, A., Loutre, M.-F., Marti, O., Merkel, U., Ramstein, G., Valdes, P., Weber, L., Yu, Y., Zhao, Y., 2007. Results of PMIP2 coupled simulations of the Mid-Holocene and Last Glacial Maximum – Part 2: feedbacks with emphasis on the location of the ITCZ and mid- and high latitudes heat budget. *Clim. Past* 3, 279–296.

Brienen, R.J.W., Helle, G., Pons, T.L., Guyot, J.L., Gloor, M., 2012. Oxygen isotopes in tree rings are a good proxy for Amazon precipitation and El Niño–Southern Oscillation variability. *PNAS* 109, 16957–16962.

Cai, B.G., Pumijumnong, N., Tan, M., Muangsang, C., Kong, X., Jiang, X., Nan, S., 2010. Effects of intraseasonal variation of summer monsoon rainfall on stable isotope and growth rate of a stalagmite from northwestern Thailand. *J. Geophys. Res. – Atmos.* 115, D21104. <http://dx.doi.org/10.1029/2009JD013378>.

Callède, J., Guyot, J.L., Ronchail, J., L'hôte, Y., Niel, H., De Oliveira, E., 2004. Évolution du débit de l'Amazonie à Óbidos de 1903 à 1999. *Hydrol. Sci. J.* 49, 85–97.

Chapman, J.B., Ingraham, N.L., Hess, J.W., 1992. Isotopic investigation of infiltration and unsaturated zone flow processes at Carlsbad Cavern, New Mexico. *J. Hydrol.* 133, 343–363.

Cheng, H., Sinha, A., Cruz, F.W., Wang, X., Edwards, R.L., d'Horta, F.M., Ribas, C.C., Vuille, M., Stott, L.D., Auler, A.S., 2013. Climate change patterns in Amazonia and biodiversity. *Nat. Commun.* 4.

Chiessi, C.M., Mulitza, S., Pätzold, S., Wefer, G., Marengo, J., 2009. Possible impact of the Atlantic multidecadal oscillation on the South American summer monsoon. *Geophys. Res. Lett.* 36, L21707.

Cobb, K.M., Adkins, J.F., Partin, J., Clark, B., 2007. Regional-scale climate influences on temporal variations of rainwater and cave dripwater oxygen isotopes in northern Borneo. *Earth Planet. Sci. Lett.* 263, 207–220.

Cordeiro, R.C., Turcq, B., Sifeddine, A., Lacerda, L.D., Silva Filho, E.V., Gueiros, B., Potty, Y.P., Santelli, R.E., Padua, E.O., Patchinelam, S.R., 2011. Biogeochemical indicators of environmental changes from 50 ka to 10 ka in a humid region of the Brazilian Amazon. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 299, 426–436.

- CPRM — Serviço Geológico do Brasil, 2004. Carta Geológica do Brasil ao Milionésimo.
- Cruz, F.W., Karmann, I., Viana Jr., O., Burns, S.J., Ferrari, J.A., Vuille, M., Sial, A.N., Moreira, M.Z., 2005a. Stable isotope study of cave percolation waters in subtropical Brazil: implications for paleoclimate inferences from speleothems. *Chem. Geol.* 220, 245–262.
- Cruz, F.W., Karmann, I., Magdaleno, G.B., Coichev, N., Viana Jr., O., 2005b. 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, F.W., Burns, S.J., Karmann, I., Sharp, W.D., Vuille, M., Ferrari, J.A., 2006. stalagmite record of changes in atmospheric circulation and soil processes in the Brazilian subtropics during the Late Pleistocene. *Quat. Sci. Rev.* 25, 2749–2761.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- de Campos Telles, M.P., Diniz-Filho, J.A.F., Pereira Bastos, R., Soares, T.N., Guimarães, L., Pedrosa Lima, L., 2007. Landscape genetics of *Physalaemus cuvieri* in Brazilian Cerrado: Correspondence between population structure and patterns of human occupation and habitat loss. *Biological Conservation* 139, 37–46.
- Deininger, M., Fohlmeister, J., Scholz, D., Mangini, A., 2012. Isotope disequilibrium effects: the influence of evaporation and ventilation effects on the carbon and oxygen isotope composition of speleothems — a model approach. *Geochim. Cosmochim. Acta* 96, 57–79.
- Dias de Melo, M.L., Marengo, J.A., 2008. The influence of changes in orbital parameters over South American climate using the CPTEC AGCM: simulation of climate during the mid Holocene. *The Holocene* 18, 501–516.
- Dreybrodt, W., 2008. Evolution of the isotopic composition of carbon and oxygen in a calcite precipitating $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ solution and the related isotopic composition of calcite in stalagmites. *Geochim. Cosmochim. Acta* 72, 4712–4724.
- Ebisuzaki, W., 1997. A method to estimate the statistical significance of a correlation when the data are serially correlated. *J. Clim.* 10, 2147–2153.
- Espinoza Villar, J.-C., Ronchail, J., Guyot, J.-L., Filizola, N., Noriega, L., Lavado, W., Pombosa, R., Romero, R., 2009. Spatio-temporal rainfall variability in the Amazon basin countries (Brazil, Peru, Bolivia, and Ecuador). *Int. J. Climatol.* 29, 1574–1594.
- Fairchild, I.J., Baker, A., 2012. *Speleothem Science: From Process to Past Environments*. Wiley-Blackwell.
- Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Matthey, D., McDermott, F., E.I.M.F., 2006. Modification and preservation of environmental signals in speleothems. *Earth Sci. Rev.* 75, 105–153.
- Feng, W., Casteel, R.C., Banner, J.L., Heinze-Fry, A., 2014. Oxygen isotope variations in rainfall, dripwater and speleothem calcite from a well-ventilated cave in Texas, USA: assessing a new speleothem temperature proxy. *Geochim. Cosmochim. Acta* 127, 233–250.
- Ferrero, M.E., Villalba, R., DeMembiela, M., Hidalgo, L.F., Luckman, B.H., 2015. Tree-ring based reconstruction of Río Bermejo streamflow in subtropical South America. *J. Hydrol.* 525, 572–584.
- Ford, D., Williams, P., 2007. *Karst Hydrogeology and Geomorphology*. John Wiley.
- Fuller, L., Baker, A., Fairchild, I.J., Spötl, C., Marca-Bell, A., Rowe, P., Dennis, P.F., 2008. Isotope hydrology of dripwaters in a Scottish cave and implications for stalagmite paleoclimate research. *Hydrol. Earth Syst. Sci.* 12, 1065–1074.
- Garreaud, R.D., Vuille, M., Compagnucci, R., Marengo, J., 2009. Present-day South American climate. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 281, 180–195.
- Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth Planet. Sci.* 24, 225–262.
- Genty, D., Labuhn, I., Hoffmann, G., Danis, P.A., Mestre, O., Wainer, K., Massault, M., Van Exter, S., Régner, E., Orenge, P., Falourd, S., Minster, B., 2014. Rainfall and cave water isotopic relationships in two South-France sites. *Geochim. Cosmochim. Acta* 131, 323–343.
- Guyot, J.L., Auler, A., Oga, D., Obstancias, I., Appay, J.L., 1996. Balanço hidro-geoquímico = Bilan hydro-géochimique. *Bulletin du Groupe Spéléologique Bagnols Marcoule, Hors série spécial Goiás 94 & Goiás 95. Carste de São Domingos, Goiás, Brasil*, pp. 52–57.
- Haug, G.H., Gunther, D., Peterson, L.C., Sigman, D.M., Hughen, K.A., Aeschlimann, B., 2003. Climate and the collapse of Maya civilization. *Science* 299, 1731–1735.
- Hendy, C.H., 1971. The isotopic geochemistry of speleothems-I: the calculations of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as paleoclimate indicators. *Geochim. Cosmochim. Acta* 35, 801–824.
- Jex, C.N., Baker, A., Fairchild, I.J., Eastwood, W.J., Leng, M.J., Sloane, H.J., Thomas, L., Bekaroglu, E., 2010. Calibration of speleothem $\delta^{18}\text{O}$ with instrumental climate records from Turkey. *Glob. Planet. Chang.* 71, 207–217.
- Jex, C.N., Baker, A., Eden, J.M., Fairchild, I.J., Leng, M.J., Thomas, L., Sloane, H.J., 2011. A 500 yr speleothem-derived reconstruction of late autumn–winter precipitation, northeast Turkey. *Quat. Res.* 75, 399–405.
- Johnston, V.E., Borsato, A., Spötl, C., Frisia, S., Miorandi, R., 2013. Stable isotopes in caves over altitudinal gradients: FRACTIONATION behaviour and inferences for speleothem sensitivity to climate change. *Clim. Past* 9, 99–118.
- Jones, I.C., Banner, J.L., 2003. Hydrogeologic and climatic influences on spatial and interannual variation of recharge to a tropical karst island aquifer. *Water Resour. Res.* 39. <http://dx.doi.org/10.1029/2002WR001543>.
- Junquas, C., Vera, C.S., Li, L., Le Treut, H., 2013. Impact of projected SST changes on summer rainfall in southeastern South America. *Clim. Dyn.* 40, 1569–1589.
- Kanner, L.C., Burns, S.J., Cheng, H., Edwards, R.L., Vuille, M., 2013. High-resolution variability of the South American summer monsoon over the last seven millennia: insights from a speleothem record from the central Peruvian Andes. *Quat. Sci. Rev.* 75, 1–10.
- Kaufman, A., Bar Matthews, M., Ayalon, A., Carmi, I., 2003. The vadose flow above Soreq Cave, Israel: a tritium study of the cave waters. *J. Hydrol.* 273, 155–163.
- Khodri, M., Kageyama, M., Roche, D.M., 2009. Sensitivity of South American tropical climate to Last Glacial maximum boundary conditions: focus on teleconnections with tropics and extratropics. *Developments in Paleoenviromental Research*, pp. 213–238 (pp. chap. 9).
- Kim, S.T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* 61, 3461–3475.
- Kim, S.T., Mucci, A., Taylor, B.E., 2007a. Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: revisited. *Chem. Geol.* 246, 135–146.
- Kim, S.T., O'Neil, J.R., Hillaire-Marcel, C., Mucci, A., 2007b. Oxygen isotope fractionation between synthetic aragonite and water: influence of temperature and Mg^{2+} concentration. *Geochim. Cosmochim. Acta* 71, 4704–4715.
- Kluge, T., Riechelmann, D.F.C., Wieser, M., Spötl, C., Sültenfuß, J., Schröder-Ritzrau, A., Niggemann, S., Aeschbach-Hertig, W., 2010. Dating cave drip water by tritium. *Journal of Hydrology* 394, 396–406.
- Kluge, T., Affek, H.P., 2012. Quantifying kinetic fractionation in Bunker Cave speleothems using $\text{d}47$. *Quat. Sci. Rev.* 49, 82–94.
- Lachniet, M.S., 2009. Climatic and environmental controls on speleothem oxygen-isotope values. *Quat. Sci. Rev.* 28, 412–432.
- Lachniet, M.S., 2015. Are aragonite stalagmites reliable paleoclimate proxies? Tests for oxygen isotope time series replication and equilibrium. *Geol. Soc. Am. Bull.* 127, 11–12.
- Li, T.Y., Shen, C.-C., Li, H.C., Li, J.Y., Chiang, H.W., Song, S.R., Yuan, D.X., Lin, C.D.J., Gao, P., Zhou, L., Wang, J.L., Ye, M.Y., Tang, L.L., Xie, S.Y., 2011. Oxygen and carbon isotopic systematics of aragonite speleothems and water in Furong Cave, Chongqing, China. *Geochim. Cosmochim. Acta* 75, 4140–4156.
- Luo, W., Wang, S., Xie, X., 2013. A comparative study on the stable isotopes from precipitation to speleothem in four caves of Guizhou, China. *Chem. Erde* 73, 205–215. <http://dx.doi.org/10.1016/j.chemer.2012.05.002>.
- Matthey, D., Lowry, D., Duffet, J., Fisher, R., Hodge, E., Frisia, S., 2008. A 53 year seasonally resolved oxygen and carbon isotope record from a modern Gibraltar speleothem: reconstructed drip water and relationship to local precipitation. *Earth Planet. Sci. Lett.* 269, 80–95.
- McMillan, A., Fairchild, I.J., Frisia, S., Borsato, A., McDermott, F., 2005. Annual trace element cycles in calcite–aragonite speleothems: evidence of drought in the western Mediterranean 1200–1100 yr BP. *J. Quat. Sci.* 20, 423–433.
- Medina-Elizalde, M., Rohling, E.J., 2012. Collapse of classic Maya civilization related to modest reduction in precipitation. *Science* 335, 956–959.
- Mickler, P.J., Banner, J.L., Stern, L., Asmerom, Y., Edwards, R.L., Ito, E., 2004. Stable isotope variations in modern tropical speleothems: evaluating equilibrium vs. kinetic isotope effects. *Geochim. Cosmochim. Acta* 68, 4381–4393.
- Mickler, P.J., Stern, L.A., Banner, J.L., 2006. Large kinetic isotope effects in modern speleothems. *Geological Society of America Bulletin* 118, 65–81.
- Moerman, J.W., Cobb, K.M., Martin, J., Meckler, A.N., Carolin, S.A., Adkins, J.F., Lejau, S., Malang, J., Clark, B., Tuen, A.A., 2014. Transformation of ENSO-related rainwater to dripwater $\delta^{18}\text{O}$ variability by vadose water mixing. *Geophys. Res. Lett.* 41. <http://dx.doi.org/10.1002/2014GL061696>.
- Mook, W.G., 2006. *Introduction to Isotope Hydrology*. Taylor & Francis Group.
- Mühlinghaus, C., Scholtz, D., Mangini, A., 2009. Modelling fractionation of stable isotopes in stalagmites. *Geochim. Cosmochim. Acta* 73, 7275–7289.
- Novello, V.F., Cruz, F.W., Karmann, I., Burns, S.J., Strikis, N.M., Vuille, M., Cheng, H., Edwards, R.L., Santos, R.V., Frigo, E., Barreto, E., 2012a. Multidecadal climate variability in Brazil's Nordeste during the last 3000 years based on speleothem isotope records. *Geophys. Res. Lett.* 39, L23706.
- Novello, V.F., Cruz, F.W., Karmann, I., Burns, S.J., Strikis, N.M., Vuille, M., Cheng, H., Edwards, R.L., Santos, R.V., Frigo, E., Barreto, E., 2012b. Multidecadal climate variability in Brazil's Nordeste during the last 3000 years based on speleothem isotope records. *Geophys. Res. Lett.* 39, L23706.
- Orland, I.J., Burstyn, Y., Bar-Matthews, M., Kozdon, R., Ayalon, A., Matthews, A., Valley, J.W., 2014. Seasonal climate signals (1990–2008) in a modern Soreq Cave stalagmite as revealed by high-resolution geochemical analysis. *Chem. Geol.* 363, 322–333.
- Pape, J.R., Banner, J.L., Mack, L.E., Musgrove, M.L., Guilfoyle, A., 2010. Controls on oxygen isotope variability in precipitation and cave drip waters, central Texas, USA. *J. Hydrol.* 385, 203–215.
- Partin, J., Jensen, J.W., Banner, J.L., Quinn, T.M., Taylor, F.W., Sinclair, D., Hardt, B., Lander, M.A., Bell, T., Miklavic, B., Jocsos, J.M.U., Taborosi, D., 2012. Relationship between modern rainfall variability, cave dripwater, and stalagmite geochemistry in Guam, USA. *Geochem. Geophys. Geosyst.* 13, Q03013.
- Patterson, W.P., Smith, G.R., Lohmann, K.C., 1993. Continental paleothermometry and seasonality using the isotopic composition of aragonitic otoliths of freshwater fishes. *Climate change in continental isotopic records* (eds. P. K. Swart et al.). *Geophys. Monogr. Ser.* 78, 191–202.
- Prado, L.F., Wainer, I., Chiessi, C.M., Ledru, M.-P., Turcq, B., 2013. A mid-Holocene climate reconstruction for eastern South America. *Clim. Past* 9, 2117–2133.
- Railsback, L.B., Brook, G.A., Chen, J., Kalin, R., Fleisher, C.J., 1994. Environmental controls on the petrology of a Late Holocene Speleothem from Botswana with annual layers of aragonite and calcite. *J. Sediment. Res.* 64A, 147–155.
- Reuter, J., Stott, L., Khider, D., Sinha, A., Cheng, H., Edwards, R.L., 2009. A new perspective on the hydroclimate variability in northern South America during the Little Ice Age. *Geophys. Res. Lett.* 36, L21706.
- Riechelmann, D.F.C., Deininger, M., Scholz, D., Riechelmann, S., Schröder-Ritzrau, S., Spötl, C., Richter, D.K., Mangini, A., Immenhauser, A., 2013. Disequilibrium carbon and oxygen isotope fractionation in recent cave calcite: Comparison of cave precipitates and model data. *Geochim. Cosmochim. Acta* 103, 232–244.
- Robertson, A.W., Mechoso, C.R., 2000. Interannual and Interdecadal variability of the South Atlantic convergence zone. *Mon. Water Rev.* 128, 2947–2957.
- Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. *Climate change in continental isotopic records*. *Geophysical monograph. Am. Geophys. Union* 78, 1–36.

- Sifeddine, A., Meyer, P., Cordeiro, R.C., Albuquerque, A.L.S., Bernardes, M., Turcq, B., Abrão, J.J., 2011. Delivery and deposition of organic matter in surface sediments of Lagoa do Caçó (Brazil). *J. Paleolimnol.* 45, 385–396.
- Sondag, F., Van Ruymbeke, M., Soubiès, F., Santos, R., Somerhausen, A., Seidel, A., Boggiani, P., 2003. Monitoring present day climatic conditions in tropical caves using an Environmental Data Acquisition System (EDAS). *J. Hydrol.* 273, 103–118. [http://dx.doi.org/10.1016/S0022-1694\(02\)00362-1](http://dx.doi.org/10.1016/S0022-1694(02)00362-1).
- Strikis, N.M., Cruz, F.W., Cheng, H., Karmann, I., Edwards, R.L., Vuille, M., Wang, X., de Paula, M.S., Novello, V.F., Auler, A.S., 2011. Abrupt variations in South American monsoon rainfall during the Holocene based on a speleothem record from central-eastern Brazil. *Geology*.
- Thompson, L.G., Mosley-Thompson, E., Davis, M.E., Zagorodnov, V.S., Howat, I.M., Mikhalevko, V.N., Lin, P.-N., 2013. Annually Resolved Ice Core Records of Tropical Climate Variability over the Past ~1800 Years 340. pp. 945–950.
- Treble, P.C., Chapell, J., Gagan, M.K., McKeegan, K.D., Harrison, T.M., 2005. In situ measurement of seasonal $\delta^{18}\text{O}$ variations and analysis of isotopic trends in a modern speleothem from southwest Australia. *Earth Planet. Sci. Lett.* 233, 17–32.
- Tremaine, D.M., Froelich, P.N., Wang, Y., 2011a. Speleothem calcite farmed in situ: modern calibration of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ paleoclimate proxies in a continuously-monitored natural cave system. *Geochim. Cosmochim. Acta* 75, 4929–4950.
- Tremaine, D.M., Froelich, P.N., Wang, Y., 2011b. Speleothem calcite farmed in situ: modern calibration of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ paleoclimate proxies in a continuously-monitored natural cave system. *Geochim. Cosmochim. Acta* 75, 4929–4950.
- Van Rangelbergh, M., Verheyden, S., Allan, M., Quinif, Y., Keppens, E., Claeys, P., 2014. Monitoring of a fast-growing speleothem site from the Han-sur-Lesse cave, Belgium, indicates equilibrium deposition of the seasonal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signals in the calcite. *Clim. Past* 10, 1871–1885.
- Vauchel, P., 2005. HYDRACCESS : Software for Management and processing of Hydro - meteorological data. www.mplird.fr/hybam/outils/hydraccess.
- Vera, C., Higgins, W., Amador, J., Ambrizzi, T., Garreaud, R.D., Gochis, D., Gutzler, D., Lettenmaier, D., Marengo, J., Mechoso, C.R., Nogués Paegle, J., Silva Dias, P.L., Zhang, C., 2006. Toward a unified view of the American Monsoon Systems. *Am. Meteorol. Soc.* 19, 4977–5000.
- Vuille, M., Bradley, R.S., Healy, R., Werner, M., Hardy, D.R., 2003. Modeling $\delta^{18}\text{O}$ in precipitation over the tropical Americas: 2. Simulation of the stable isotope signal in Andean ice cores. *J. Geophys. Res.* 108.
- Vuille, M., Burns, S.J., Taylor, B.L., Cruz, F.W., Bird, B.W., Abbott, M.B., Kanner, L.C., Cheng, H., Novello, V.F., 2012. A review of the South American monsoon history as recorded in stable isotopic proxies over the past two millennia. *Clim. Past* 8, 1309–1321.
- Wang, Y.J., Cheng, H., Edwards, R.L., An, Z.S., Wu, J.Y., Shen, C.-C., Dorale, J.A., 2001. High-Resolution Absolute-Dated Late Pleistocene Monsoon Record from Hulu Cave, China. *Science* 294, 2345–2348.
- Wang, X., Auler, A.S., Edwards, R.L., Cheng, H., Ito, E., Solheid, M., 2006. Interhemispheric anti-phasing of rainfall during the last glacial period. *Quat. Sci. Rev.* 25, 3391–3403.
- Wang, X., Auler, A.S., Edwards, R.L., Cheng, H., Ito, E., Wang, Y., Kong, X., Solheid, M., 2007. Millennial-scale precipitation changes in southern Brazil over the past 90,000 years. *Geophys. Res. Lett.* 34, L23701. <http://dx.doi.org/10.1029/2007GL031149>.
- Wassenburg, J.A., 2013. Holocene climate evolution in NW Morocco as recorded in aragonitic speleothems. Significance of the North Atlantic Oscillation. Institute of Geology, Mineralogy und Geophysics, Ruhr-University Bochum (PhD thesis).
- Wassenburg, J.A., Immenhauser, A., Richter, D.K., Jochum, K.P., Fietzke, J., Deininger, M., Goos, M., Scholz, D., Sabaoui, A., 2012. Climate and cave control on Pleistocene/Holocene calcite-to-aragonite transitions in speleothems from Morocco: elemental and isotopic evidence. *Geochim. Cosmochim. Acta* 92, 23–47.
- Wiedner, E., Scholtz, D., Mangini, A., Polag, D., Mühlinghaus, C., Segl, M., 2008. Investigation of the stable isotope fractionation in speleothems with laboratory experiments. *Quat. Int.* 187, 15–24.
- Williams, P.W., Fowler, A., 2002. Relationship between oxygen isotopes in rainfall, cave percolation waters and speleothem calcite at Waitomo, New Zealand. *N. Z. J. Hydrol.* 41, 53–70.
- Yadava, M.G., Ramesh, R., Pant, G.B., 2004. Past monsoon rainfall variations in peninsula India recorded in a 331-year old speleothem. *The Holocene* 14, 517–524.