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Assessing the dead carbon proportion of a modern speleothem from central Brazil

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ABSTRACT

Geographic and temporal variations in atmospheric carbon isotopic ratios are recorded in environmental proxies. In temperate regions, this may assist in the construction of datasets for the calibration of radiocarbon ages. Over the tropics, the high growth rate of speleothems combined with high precision ^{230}Th dating provides potential records for atmospheric ^{14}C reconstruction. In this preliminary work, we investigate the isotopic composition (δ^{18}O and δ^{13}C) of a speleothem from central Brazil, precisely dated by the multi-collector inductively coupled plasma mass spectrometry technique (MC-ICP-MS). Radiocarbon Accelerator Mass Spectrometry (AMS) measurements were compared to the ^{14}C concentration in the atmosphere during the nuclear tests period based on the Bomb13SH1-2 curve. Our results show that the speleothem dead carbon proportion is less than 20% between 1932 and 1992 AD while δ^{13}C values vary between −14 and −9‰. Given that the empirical radiocarbon calibration curves for the Southern Hemisphere were constructed based on limited records, we discuss the potential and limitations of Brazilian speleothems for the evaluation of atmospheric ^{14}C concentrations over the last millennia.

1. Introduction

In limestone caves, seepage water that percolates the host rock usually exhibits a higher partial pressure of CO_2 than that of the cave atmosphere. This leads to CO_2 degassing, which causes the supersaturation of water with carbonate. The deposition of secondary cave formations, known as speleothems, is induced by the precipitation of this carbonate, usually as calcite or aragonite minerals (Hendy, 1971; McDermott, 2004). These formations have the potential to record different aspects of climate variability based on elemental geochemistry and stable isotope ratios (e.g., Wang et al., 2001, 2004; Cruz et al., 2005; Lachniet et al., 2009; Novello et al., 2012; Cheng et al., 2013; Cheng et al., 2016; Stríkis et al., 2018). Stable oxygen isotopes in the cave drip-waters that form speleothems, for instance, can be related to the δ^{18}O values of precipitation and to transportation processes modifying their signature (e.g., Cruz et al., 2005). The stable carbon isotopes composition of the seepage water on the other hand, is mainly associated with soil ^{13}C-depleted CO_2 and, to a lesser extent to carbon isotopes from the cave bedrock (Genty et al., 2001; McDermott, 2004; Dreybrodt and Scholz, 2011). Additionally, ^{14}C measurements in speleothems constitute another useful proxy in paleoenvironmental studies.

In temperate regions, well defined seasons enable environmental records such as tree rings to be used for the establishment of robust chronologies. Nevertheless, these tree ring sequences are limited to certain time periods and ^{14}C measurements in speleothems and varved records, which also correlate calendar years with atmospheric ^{14}C concentration, allow for the extension of the Northern Hemisphere calibration curve to cover the 50 ky of the ^{14}C dating range of applicability (Hoffmann et al., 2010; Southon et al., 2012; Reimer et al., 2013). The Southern Hemisphere (SH) is represented by the SHCal13 curve (Hogg et al., 2013), which is primarily based on the Northern Hemisphere curve and incorporates very limited SH records. Nevertheless, in tropical regions of the SH, seasonal precipitation leads to the

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formation of annually banded speleothems. These records can potentially be used to overcome the issue of limited experimental data from the SH in the SHCal13 calibration curve but, in order to use tropical speleothems for calibration purposes, the contribution of atmospheric CO_2 to the speleothem composition has to be accurately determined. Besides the atmospheric carbon component, both soil biogenic CO_2, derived from root respiration and microbial decomposition, and carbon from limestone contribute to the composition of carbonate speleothems (Genty and Massault, 1997). The proportion of each carbon source end member depends on complex geochemical processes associated with recharge and carbonate dissolution/precipitation in karstic areas (Dorale et al., 1998; Genty et al., 2001; Lachniet, 2009). In terms of radiocarbon, the soil fraction can be either older or contemporary to the speleothem formation, but the presence of limestone will always introduce ^{14}C free carbonate to the system. The so-called "dead carbon" proportion (*dcp*), as shown in eq. (1), relates the measured radiocarbon activity ($a^{14}C_m$) of the speleothem carbonate with the coeval atmospheric activity ($a^{14}C_{atm}$) (Genty and Massault, 1997).

$$dcp = \left(1 - \frac{a^{14}C_m}{a^{14}C_{atm}}\right)100\% \quad (1)$$

The reliability of speleothem ^{14}C records can only be assessed through comparisons with other independent geochronology methods such as ^{230}Th dating. Provided that the *dcp* can be accurately determined for modern speleothems and is constant in time, atmospheric ^{14}C levels can be inferred for the last thousands of years, as they will reflect variations in radiocarbon production and distribution. As an example, Vogel (1983) analysed a stalagmite from South Africa and observed radiocarbon fluctuations linked to variations in the geomagnetic field. Similarly, Holmgren et al. (1994) mention an increased production of ^{14}C as one of the possible reasons for the observed deviations between ^{230}Th and radiocarbon dates obtained from a stalagmite collected in Botswana. Both examples illustrate the potential use of speleothems as records for the atmospheric ^{14}C concentration. The lower and lesser variable is the *dcp*, the more useful are the speleothems for the construction of radiocarbon chronologies. There is also evidence of a correlation between *dcp* and site temperature. Indeed, by comparing results from speleothems obtained from different sites, Genty et al. (1999) found out that the higher the mean annual temperatures (up to 15 °C in their study) the lower the *dcp* contribution. In this context, tropical caves, where mean annual temperatures can be higher than 20 °C, may present an advantage for this kind of study. However, this is not straightforward, since there is a gradient from external to internal cave temperatures and this will depend upon vegetation cover, as it protects the cave from the direct incidence of solar radiation. Moreover, water availability is an important factor to allow for both dissolution of limestone and the movement of carbonate into the stalagmite system.

In South America, many caves have been studied with the aim of inferring changes in climate (e.g., Wang et al., 2004; Stríkis et al., 2011; Mosblech et al., 2012; Cheng et al., 2012; Apaéstegui et al., 2018; Stríkis et al., 2018). $\delta^{18}O$ values obtained from speleothems collected in the eastern Bolivian Andes showed variations over the last 1400 years as a function of changes in precipitation regimes and two negative values of $\delta^{18}O$ were interpreted as phases of global climatic anomalies, during the Medieval Climatic Anomaly and the Little Ice Age (Apaéstegui et al., 2018). Another speleothem, collected from Santiago cave in Ecuador, was used to reconstruct the precipitation regime over the western Amazon region during the last 94 thousand years. The results showed that abrupt changes in climate were related to changes in the North Atlantic circulation (Mosblech et al., 2012). Stríkis et al. (2018) studied changes in the South American monsoon precipitation during Heinrich Stadials using speleothem records covering the 85 ky BP. In Brazil, although several studies using speleothems have been performed (e.g., Bertaux et al., 2002; Soubiès et al., 2005; Cruz et al., 2005, 2006a; 2006b), the only study employing radiocarbon analyses was inconclusive. Using an annually resolved chronological model based on layer counting, Soubiès et al. (2005) attempted to use radiocarbon dating to validate the modern age of the top of a speleothem collected in the Perolas cave, 150 km NW of Cuiabá, Mato Grosso. However, the dissolution of the carbonate host rock has hindered the *dcp* correction of the ^{14}C measurements and prevented the authors from establishing a precise chronology for the youngest segment of the speleothem.

In order to evaluate the possibility of using speleothems collected from Brazilian caves for improving the Southern Hemisphere ^{14}C calibration curve, we have analysed a modern high resolution stalagmite dated by the uranium-series disequilibrium technique and covering the last century. We discuss the limitations of such record and its potential for the evaluation of the atmospheric carbon 14 concentration over the last millennia.

1.1. Study region

The Tamboril Cave is located in central Brazil, in the municipality of Unaí (Fig. 1), Minas Gerais State (16°19′25.68″S, 46°59′3.48″W), where the mean annual temperature is ca. 24 °C and precipitation ca. 1200 mm. The cave was developed in the Dolostone unit from the Sete

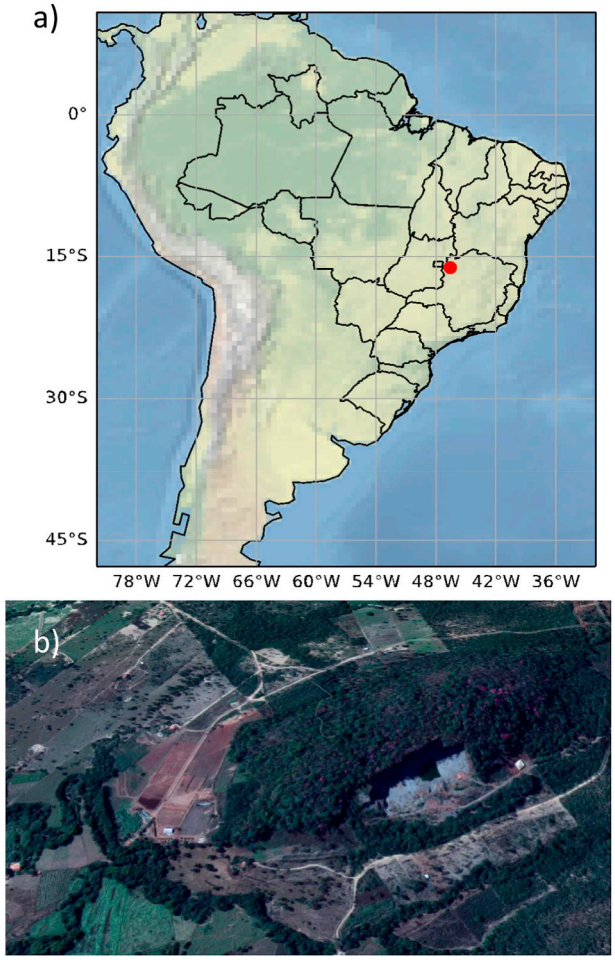

Fig. 1. a) South America map showing the study region in Minas Gerais state, central Brazil (16°19′25.68″S, 46°59′3.48″W). **b)** Google Earth image showing the location of the Tamboril Cave.

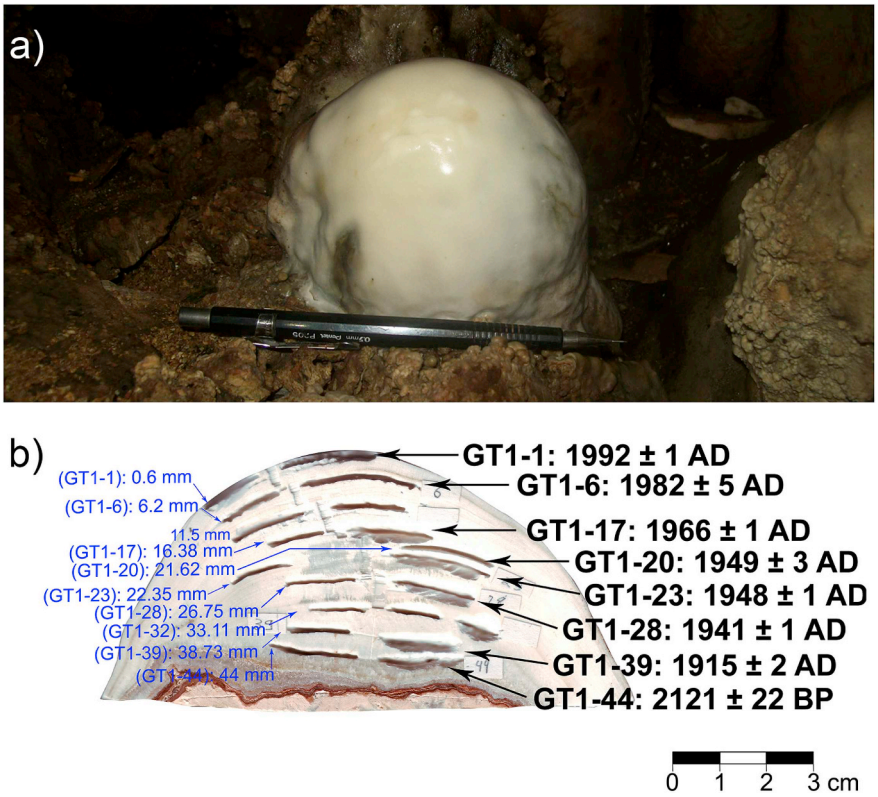

Fig. 2. a): Actively growing GT1 stalagmite at the moment of collection in the cave. **b)** ^{230}Th dates along the speleothem growth axis. A gap in growth between GT1-44 and GT1-39 can be observed.

Lagoas Formation of the Neoproterozoic sedimentary succession of the Bambui Group, characterized by unusually positive $\delta^{13}C$ values (up to + 14‰ Vieira et al., 2007). The Tamboril Cave presents a linear plan pattern forming a single large vadose conduit, being ~700 m in length. The ceiling is high, reaching up to 30 m and the cave is 55 m wide at its widest part. The cave is extensively decorated, frequently presenting large speleothems with metric sizes. The stalagmite GT1 consists of a 5 cm aragonitic, collected in April 2011 in the middle of the main conduit (Fig. 2).

2. Methods

2.1. ^{230}Th dating

Samples for ^{230}Th dating were taken in approximately 5 mm intervals along the growth axis using a hand micro drilling with dental burrs. To prevent the effects of uranium loss in the ^{230}Th ages determination, calcite sampling was performed avoiding the recrystallized portion.

The samples weighing between 150 and 300 mg were dissolved in HNO_3 and equilibrated with a $^{236}U—^{233}U—^{229}Th$ spike and then separated and purified using methods described in Cheng et al. (2013). Following the procedures described by Cheng et al. (2013), ^{230}Th ages were obtained using the multi-collector inductively coupled plasma mass spectrometry technique (MC-ICP-MS, Thermo-Finnigan NEPTUNE) available at the University of Minnesota and the Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China. Most dates present errors (2σ) of approximately 1% (Table 1). Initial ^{230}Th values were corrected with a typical bulk earth ratio, i.e. atomic ratio of $^{230}Th/^{232}Th = 4.4 \pm 2.2$.

2.2. ^{14}C analysis and dcp calculation

For radiocarbon measurements, samples were collected from the same spots where U—Th samples had been previously taken, using a micro drill (Fig. 2). Six samples were prepared at LAC-UFF, where chemical treatment followed standard procedures with etching in 0.1M HCl followed by hydrolysis in 85% H_3PO_4. The carbon dioxide produced was purified and graphitized in independently-sealed Pyrex tubes at 550 °C (Macario et al., 2015). Fossil calcite and C2 IAEA reference samples were prepared together with unknowns for quality control. The samples were measured at a 500 kV AMS system, produced by the National Electrostatics Corporation (NEC), at the Center for Applied Isotope Studies (CAIS) in Georgia, USA (Cherkinsky et al., 2010). Radiocarbon results are presented as Percent Modern Carbon (pMC) as defined by Stuiver and Polach (1977) or as Fraction Modern (FM) (Donahue et al., 1990).

The *dcp* values were obtained as in Genty and Massault (1997) using equation (1), considering the measured ^{14}C activity of the deposit and the corresponding atmospheric ^{14}C activity in the Southern Hemisphere from Hua et al. (2013).

2.3. Stable isotopes determination

For the $\delta^{18}O$ and $\delta^{13}C$ analyses, samples were milled using a conical shape burs attached to a high precision micro milling manufactured by the New Wave Research. Samples were taken along the central axis with a sampling resolution of 0.12 mm. Stable isotope analysis was carried out at the Centro de Pesquisas Geocronológicas of the Instituto de Geociências of Universidade de São Paulo (CPGeo-IGc-USP). Approximately 100 µg of powder was drilled from each sample and

Table 1
^{230}Th dating results. The uncertainties are the 2 sigma error.

Sample Number	^{238}U (ppb)		^{232}Th (ppt)		^{230}Th/ ^{232}Th (atomic $\times 10^{-6}$)		δ^{234}U* (measured)		^{230}Th/ ^{238}U (activity)		^{230}Th Age (yr) (uncorrected)		^{230}Th Age (yr) (corrected)		$\delta^{234}U_{Initial}$** (corrected)		^{230}Th Age (yr BP) (corrected)***		^{230}Th Age (yr EC) (corrected)	
GT1-1	4526	± 24	236	± 5	132	± 4	1172	± 5	0.0004	± 0.0000	21	± 1	**20**	± 1	1172	± 5	**−42**	± 1	**1992**	± 1
GT1-6	4534	± 27	2455	± 51	24	± 1	1335	± 6	0.0008	± 0.0000	37	± 1	**30**	± 5	1335	± 6	**−32**	± 5	**1982**	± 5
GT1-17	4711	± 26	57	± 1	1147	± 30	1005	± 5	0.0008	± 0.0000	46	± 1	**46**	± 1	1005	± 5	**−16**	± 1	**1966**	± 1
GT1-20	4093	± 8.3	791	± 16	114	± 4	1025	± 2.5	0.0013	± 0.0000	72	± 2	**69**	± 3	1025	± 2	**1**	± 3	**1949**	± 3
GT1-23	4441	± 19	142	± 3	637	± 15	1078	± 4	0.0012	± 0.0000	65	± 1	**64**	± 1	1078	± 4	**2**	± 1	**1948**	± 1
GT1-28	4058	± 23	145	± 3	627	± 16	1083	± 5.3	0.0014	± 0.0000	71	± 1	**71**	± 1	1083	± 5	**9**	± 1	**1941**	± 1
GT1-39	1841	± 6.3	56	± 2	975	± 35	1008	± 4.2	0.0018	± 0.0000	97	± 2	**97**	± 2	1008	± 4	**35**	± 2	**1915**	± 2
GT1-44	759	± 2	1511	± 30	349	± 7	1095	± 4	0.0421	± 0.0002	2210	± 10	**2183**	± 22	1102	± 4	**2121**	± 22		

U decay constants: $\lambda_{238} = 1.55125 \times 10^{-10}$ (Jaffey et al., 1971) and $\lambda_{234} = 2.82206 \times 10^{-6}$ (Cheng et al., 2013). Th decay constant: $\lambda_{230} = 9.1705 \times 10^{-6}$ (Cheng et al., 2013). *$\delta^{234}U = ([^{234}U/^{238}U]_{activity} - 1) \times 1000$. **$\delta^{234}U_{initial}$ was calculated based on ^{230}Th age (T), i.e., $\delta^{234}U_{initial} = \delta^{234}U_{measured} \times e^{\lambda 234 \times T}$. Corrected ^{230}Th ages assume the initial ^{230}Th/^{232}Th atomic ratio of 4.4 ± 2.2 × 10^{-6}. Those are the values for a material at secular equilibrium with the bulk earth ^{232}Th/^{238}U value of 3.8. The errors are arbitrarily assumed to be 50%. ***B.P. stands for "Before Present" where the "Present" is defined as the year 1950 A.D.

analysed with an on-line, automated, carbonate preparation system connected to an isotope ratio mass spectrometer (Thermo-Finnigan model Delta Plus Advantage). Oxygen and carbon isotope ratios are expressed in δ notation, the per mil deviation from the Vienna Peedee Belemite (VPDB) standard (Coplen, 1996).

2.4. X-ray diffraction analysis

The crystal fabric of the GT1 stalagmite consists of acicular shaped carbonate crystals, suggestive of aragonite. Localized recrystallization patches can be observed at the central portion of the speleothem, forming discontinuous lenses where a crystalline fabric exhibiting a massive habit, suggestive of calcite, replaces the main crystalline fabric. Calcitization from aragonite in speleothems is known to yield anomalously old ^{234}U–^{230}Th ages due to uranium loss (Hoffmann et al., 2009; Lachniet al., 2012). To assess the potential of uranium loss due to aragonite to calcite recrystallization, x-ray diffraction analyses were carried out in the GT1 stalagmite.

The mineralogical composition of the speleothem was determined by X-ray diffraction (XRD) in a Bruker D8 diffractometer using Cu Kα radiation, 40 kV, 40 mA, step 0.02°, 192 s/step and scanning angular range from 20 to 100° 2θ. XRD. The data were interpreted using the High Score Plus 3.0 (Panalytical) software and the Crystallographic Open Database (Gražulis et al., 2009). The analyses were performed in the Laboratório de Difração de Raios X (LDRX) Instituto de Geociências of Universidade de São Paulo.

3. Results and discussion

Calcite to aragonite recrystallization was identified in the GT1 stalagmite by X-ray diffraction analysis (Fig. 3). The Calcitization appears in two main forms: i) as irregular zones showing a vertical coalescence with the lower and upper boundaries presenting interdigited contact with the aragonite matrix. This pattern is well observed in the central part of the speleothem (Figs. 2B and 3). ii) as isolated calcite layers following the growth band, occasionally may presenting a well-defined margin (Fig. 3, left). The ^{230}Th dating of 7 spots along the top 39 mm of the stalagmite discloses a linear growth (Fig. 4) with a rate of 0.5 mm.yr^{-1}.

During recrystallization, uranium losses from the crystal lattice may reach two orders of magnitude yielding older ^{230}Th ages of several hundreds of years (Lachniet et al., 2012). However, the analytical results obtained from the ^{230}Th dating do not present any significant variation in uranium concentration within the sample (Table 1). Except for the sample GT1-39, located at the bottom of the stalagmite, the ^{238}U concentration varies from 4711 to 4058 ppb. The absence of inversion in the ^{230}Th dates covering a very narrow time interval (four dates within the interval from 1941 to 1966 AD) reinforces the idea that the aragonite to calcite recrystallization did not produce significant effects in the ^{230}Th ages.

The calendar years presented in Table 2 were generated by the StalAge algorithm based on Bayesian statistics (Scholz and Hoffmann, 2011). The Fraction Modern Carbon results of the 6 samples measured by ^{14}C-AMS are plotted in Fig. 5a together with the Bomb13SH1-2 and the SHCal13 (blue) curves and the same data multiplied by factors of 0.90 (orange) and 0.80 (grey), considering 10% and 20% *dcp*, respectively. The 4 samples relative to the bomb peak period present ^{14}C concentrations compatible with less than 20% "dead carbon" and the pre-1950 samples show 1–2% *dcp*. The speleothem δ^{13}C values vary between −14 and −9.0‰ and δ^{18}O between −10 and −4‰ (Fig. 5b). Wortham et al. (2017) have studied these stable isotopes ratios in Tamboril cave and found similar values between −11.5 and −8‰ for δ^{13}C and between −7 and −4.5‰ for δ^{18}O over the last millennium. At decadal timescales, the δ^{18}O record presents similar variations to those observed in δ^{13}C (Fig 5b). It is noteworthy that excursions in the δ^{18}O values are often correlated with δ^{13}C variation, suggesting that the

Fig. 3. X-ray diffraction sampling and results. The left-side image shows P1 to P6 samples performed in the back of the GT1 speleothem. The right-side image shows P5 and P6 sampling, between GT1-23 and GT1-28 ^{230}Th dates.

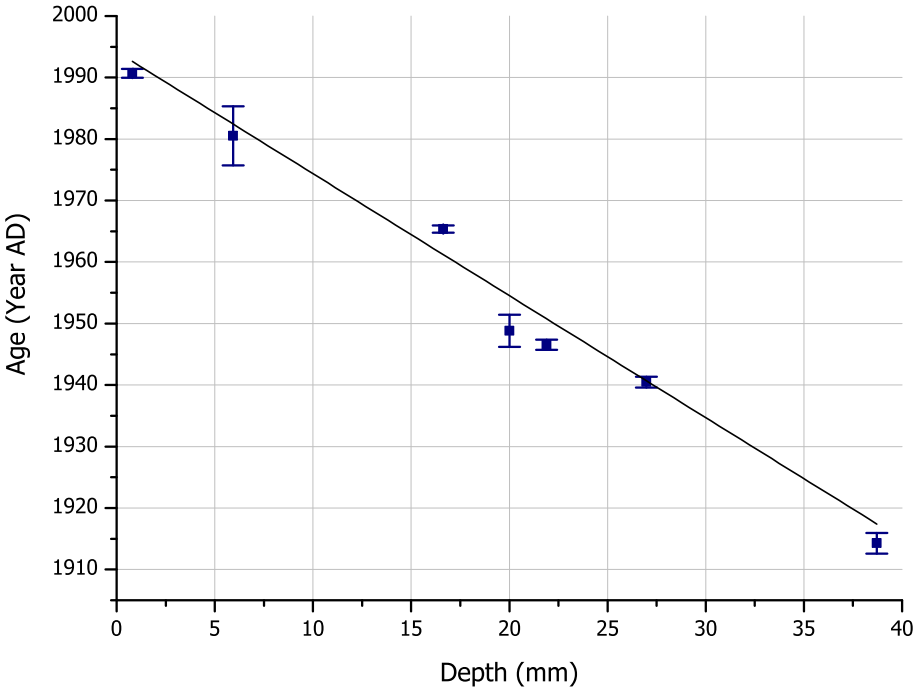

Fig. 4. Growth rate of the GT1 stalagmite based on a linear fit of ^{230}Th dates for the period 1915–1992 AD.

carbon isotopes may be associated to delayed changes in environmental parameters. For instance, while $\delta^{18}O$ fluctuations reflect changes in rainfall isotopic composition, ultimately associated with the amount of rainfall, variations in the $\delta^{13}C$ values may reflect the delayed response of soil biological activity to the changes in the hydrologic regime.

Genty et al. (2001) have studied the correlation between *dcp* and $\delta^{13}C$ of several speleothems and observed that the latter is controlled by complex geochemical and hydrologic processes. Factors that need to be taken into account include the type of vegetation cover (C3/C4 photosynthetic pathways), the type of dissolution (Hendy, 1971), karst water evolution and the isotopic fractionation effect involved along the precipitation process (Genty et al., 2001). At 24 °C the isotope fractionation factor for the reaction $CO_2 + H_2O = HCO_3^-$ is about −8.02 ($\varepsilon_{CO2(g)\text{-}HCO3\text{-}}$) (Mook, 1986) thus yielding a $\delta^{13}C$ enrichment of ca. 8‰ in HCO3-. Assuming a contribution of ^{13}C enriched from the host rock, in the Tamboril cave the $\delta^{13}C$ recorded in the speleothem GT1 of ~ −11‰ is in agreement with the end member related to C3 vegetation whose $\delta^{13}C$ values range from −32 to −20‰ VPDB (Boutton, 1996; Pessenda et al., 1996). Some sites have shown correlation between higher *dcp* and lower $\delta^{13}C$ values indicating an increase in the fraction of carbon from host rock dissolution. Generally, the $\delta^{13}C$ value of Neoproterozoic limestones ranges from −3 to +8‰ (Kaufman et al., 1991; Derry et al., 1992; Babinsky, 1993).

Over the last 90 years, the GT1 speleothem presents *dcp* values up to

Table 2
Th dates and StalAge modelled dates (Scholz and Hoffmann, 2011) and ^{14}C results for the GT1 speleothem.

Sample	LACUFF	UGA	^{230}Th date (AD)	Modelled date (AD)	pMC	Distance from the edge (mm)	dcp (%)
GT1-1	170272	33210	1992 ± 1	1993	109.80 ± 0.39	0.6	4.1 ± 0.1
GT1-6	170191	31219	1982 ± 5	1982	113.41 ± 0.46	5.6	9.3 ± 0.6
GT1-12	170192	31220		1974	120.78 ± 0.39	12	14.3 ± 0.4
GT1-17	170194	31222	1966 ± 1	1963	132.73 ± 0.43	16.6	9.4 ± 9.4
GT1-28	170273	33211	1941 ± 1	1941	96.56 ± 0.34	27.5	1.62 ± 0.37
GT1-32	180135	–		1932	96.91 ± 0.52	32	1.27 ± 0.55

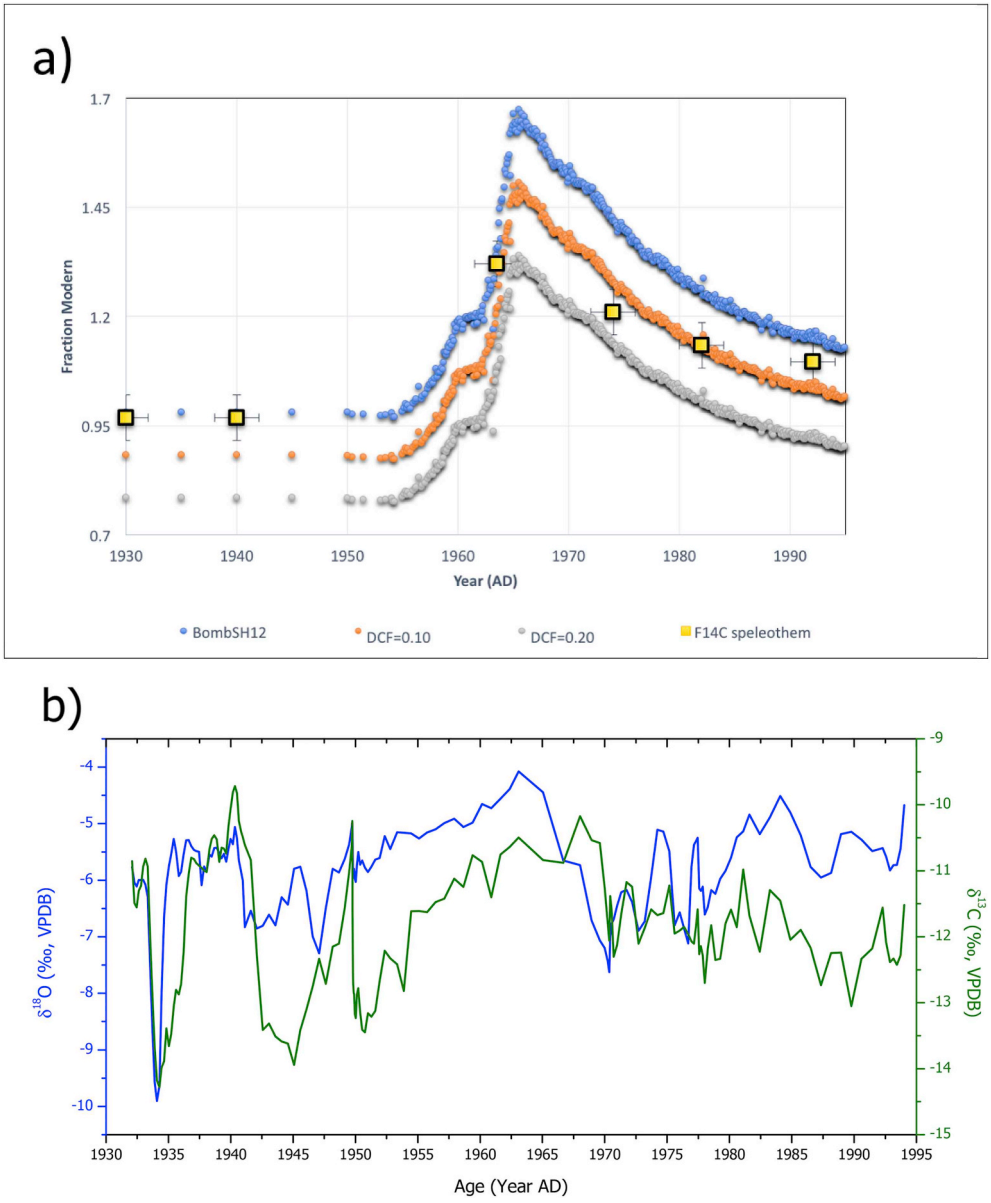

Fig. 5. a) Fraction Modern Carbon of measured samples (square) and the atmosphere* (blue), considering 10% (orange) and 20% dcp (grey); **b)** $\delta^{13}C$ (orange) and $\delta^{18}O$ (blue) values measured in the GT1 speleothem. Complete stable isotopes data are available in the supplementary material.
*SHCal13 and Bomb13SH1-2.

20%. The value from 1963 (red point in Fig. 6) is very difficult to interpret as the *dcp* in this year can assume any value from 0 to almost 20% due to the rapid increase in atmospheric ^{14}C concentration in 1963 and 1964. Neglecting such point, the results of *dcp* seem to be slightly larger for the most negative $\delta^{13}C$ values (Fig. 6). However, no strong correlation between *dcp* and $\delta^{13}C$ was observed for the studied stalagmite. Hua et al. (2012) studied a speleothem from the Christmas Islands, eastern Indian Ocean, and found no correlation between *dcp* and $\delta^{13}C$ either. Nevertheless, working with a much longer record, they were able to develop robust models based on the variability of *dcp,* what will be the next step of our research, aiming to construct speleothem-based calibration curves for the Southern Hemisphere for the last millennia. Apart from the 1963 point, our results show an average *dcp* of 6.1 ± 5.6%, representing an offset of up to 1000 ^{14}C years.

The magnitude of the *dcp* obtained in the present study is consistent with the value of (15 ± 5)% obtained by Genty et al. (2001), who compared many caves in different locations. Assuming that the *dcp* represents integrally the carbon dissolved from the host rock, it gives an accurate estimation of the contribution of the host rock in the total amount of carbon that forms the dissolved inorganic species (H_2CO_3; HCO_3^- and CO_3^{2-}). On the other hand, such variability indicates that local environmental conditions play a major role in *dcp* and building a general calibration curve with radiocarbon and Th ages could be a very complex task.

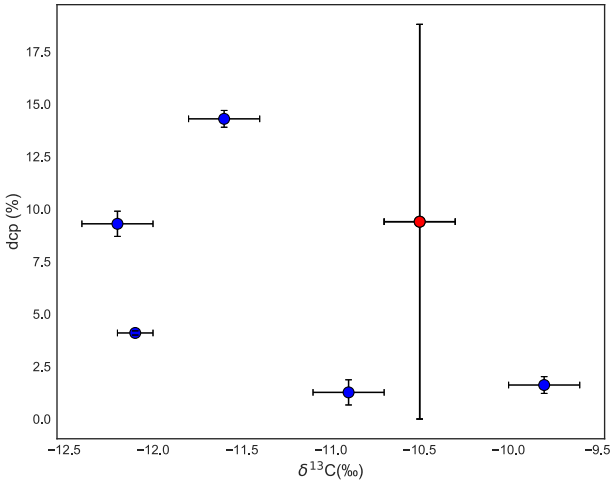

Fig. 6. Dead carbon proportion x $\delta^{13}C$ over the last 90 years in the GT1 speleothem from the Tamboril Cave. The red point marks the 1963 sample, when ^{14}C concentration varied quickly leading to a large uncertainty in *dcp*.

4. Conclusions

Speleothems presenting high growth rates are typically found in tropical caves. In the Southern Hemisphere, where ^{14}C calibration curves incorporate very limited experimental data, these structures may provide useful records for the reconstruction of the atmospheric ^{14}C content. Nevertheless, *dcp* values must be accurately assessed for the correction of non-atmospheric carbon input to the speleothems. Since these values can be extremely dependent on the local environmental conditions, this preliminary study evaluated the *dcp* of a modern speleothem collected in central Brazil. The values obtained were less than 20%, corresponding to an age overestimation of 1000 ^{14}C yr, consistent with speleothems from other regions of the world and are thus promising for atmospheric ^{14}C reconstruction studies. The absence of large *dcp* temporal fluctuations over the studied time period motivates the study of longer records from the same region. Indeed, the findings of the present paper are encouraging and the next steps will be to compare ^{230}Th chronologies to ^{14}C measurements in larger speleothems from Minas Gerais caves and to compare the latter with dendrochronologically dated fossil trees from the same region.

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Appendix A. Supplementary data

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