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 \textsuperscript{230}Th dating provides potential records for atmospheric \textsuperscript{14}C reconstruction. In this preliminary work, we investigate the isotopic composition (\(\delta^{18}O\) and \(\delta^{13}C\)) 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 \(\textsuperscript{14}C\) concentration in the atmosphere during the nuclear tests period based on the Bomb\textsubscript{13}SH\textsubscript{1-2} curve. Our results show that the speleothem dead carbon proportion is less than 20\% between 1932 and 1992 AD while \(\delta^{13}C\) 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 \textsuperscript{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 \textsuperscript{CO}\textsubscript{2} than that of the cave atmosphere. This leads to \textsuperscript{CO}\textsubscript{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-water that form speleothems, for instance, can be related to the \(\delta^{18}O\) 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 \textsuperscript{13}C-depleted \textsuperscript{CO}\textsubscript{2} and, to a lesser extent to carbon isotopes from the cave bedrock (Genty et al., 2001; McDermott, 2004; Dreybrodt and Scholz, 2011). Additionally, \textsuperscript{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 \textsuperscript{14}C measurements in speleothems and varved records, which also correlate calendar years with atmospheric \textsuperscript{14}C concentration, allow for the extension of the Northern Hemisphere calibration curve to cover the 50 ky of the \textsuperscript{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 CO2 to the speleothem composition has to be accurately determined. Besides the atmospheric carbon component, both soil biogenic CO2, 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 14C free carbonate to the system. The so-called “dead carbon” proportion (dcp), as shown in eq. (1), relates the measured radiocarbon activity (a14C) of the speleothem carbonate with the coeval atmospheric activity (a14Cam) (Genty and Massault, 1997).

\[ \text{dcp} = \left(1 - \frac{a_14^{\text{Cam}}}{a_14^{\text{Cmol}}} \right) \times 100\% \]  

(1)

The reliability of speleothem 14C records can only be assessed through comparisons with other independent geochronology methods such as 230Th dating. Provided that the dcp can be accurately determined for modern speleothems and is constant in time, atmospheric 14C 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 stalagmitic from South Africa and observed radiocarbon fluctuations linked to variations in the geomagnetic field. Similarly, Holmgren et al. (1994) mention an increased production of 14C as one of the possible reasons for the observed deviations between 230Th and radiocarbon dates obtained from a stalagmite collected in Botswana. Both examples illustrate the potential use of speleothems as records for the atmospheric 14C 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). δ18O 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 δ18O 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 14C 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 14C 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 Unai (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 Unaí. The central Brazil (16°19′25.68″S, 46°59′3.48″W). 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.
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 $\sim700$ 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 bursrs. 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 $^{230}$U-$^{232}$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 ± 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$_3$PO$_4$. 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

![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.](image-url)
Table 1

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>238U (ppb)</th>
<th>232Th (ppt)</th>
<th>230Th/232Th (atomic ×10^-6)</th>
<th>δ 234U* (measured)</th>
<th>230Th/238U (activity)</th>
<th>230Th Age (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(uncorrected)</td>
<td>(corrected)</td>
<td>(corrected)***</td>
<td>(corrected)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GT1-1</td>
<td>4526 ± 24</td>
<td>236 ± 5</td>
<td>132 ± 4</td>
<td>1172 ± 5</td>
<td>0.0004 ± 0.0000</td>
<td>21 ± 1</td>
</tr>
<tr>
<td></td>
<td>4534 ± 27</td>
<td>2455 ± 51</td>
<td>24 ± 1</td>
<td>1335 ± 6</td>
<td>0.0008 ± 0.0000</td>
<td>37 ± 5</td>
</tr>
<tr>
<td>GT1-6</td>
<td>4711 ± 26</td>
<td>57 ± 1</td>
<td>1147 ± 30</td>
<td>1005 ± 5</td>
<td>0.0008 ± 0.0000</td>
<td>46 ± 1</td>
</tr>
<tr>
<td>GT1-17</td>
<td>4093 ± 8.3</td>
<td>791 ± 16</td>
<td>114 ± 4</td>
<td>1025 ± 2.5</td>
<td>0.0013 ± 0.0000</td>
<td>72 ± 2</td>
</tr>
<tr>
<td>GT1-23</td>
<td>4441 ± 19</td>
<td>142 ± 3</td>
<td>637 ± 15</td>
<td>1078 ± 4</td>
<td>0.0012 ± 0.0000</td>
<td>65 ± 1</td>
</tr>
<tr>
<td>GT1-28</td>
<td>1841 ± 6.3</td>
<td>56 ± 2</td>
<td>975 ± 35</td>
<td>1008 ± 4.2</td>
<td>0.0018 ± 0.0000</td>
<td>97 ± 2</td>
</tr>
</tbody>
</table>

U decay constants: λ238 = 1.55125 × 10^-10 (Jaffey et al., 1971) and λ234 = 2.82206 × 10^-6 (Cheng et al., 2013). Th decay constant: λ230 = 9.1705 × 10^-6 (Cheng et al., 2013). *δ234U = (234U/238U)activity – 1)×1000. **δ234Uinitial was calculated based on 230Th age (T), i.e., δ234Uinitial = δ234Umeasured x e^λ234 x T. Corrected 230Th ages assume the initial 230Th/232Th atomic ratio of 4.4 ± 2.2 × 10^-6. Those are the values for a material at secular equilibrium with the bulk earth 232Th/238U 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.

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 234U–230Th 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 interdigitated 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 forming discontinuous lenses. The speleothem δ13C values vary between −14 and −9.0‰ and δ18O between −10 and −4‰ (Fig. 5b). The δ13C and between −7 and −4.5‰ for δ18O over the last millennium. Wortham et al. (2017) have studied these stable isotope ratios in Tamboril cave and found similar values between −11.5 and −8‰ for δ13C and between −7 and −4.5‰ for δ18O over the last millennium. At decadal timescales, the δ13C record presents similar variations to those observed in δ18C (Fig 5b). It is noteworthy that excursions in the δ18O values are often correlated with δ13C variation, suggesting that the

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).
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 $-8.02$ ($\varepsilon_{CO_2(g)-HCO_3^-}$) (Mook, 1986) thus yielding a $\delta^{13}C$ enrichment of ca. 8‰ in HCO$_3^-$. 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 $\sim -11$‰ 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 $\sim -11$‰.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>LACUFF</th>
<th>UGA</th>
<th>$^{230}$Th date (AD)</th>
<th>Modelled date (AD)</th>
<th>$pMC$</th>
<th>Distance from the edge (mm)</th>
<th>$dcp$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GT1-1</td>
<td>170272</td>
<td>33210</td>
<td>1992 ± 1</td>
<td>1993</td>
<td>109.80 ± 0.39</td>
<td>0.6</td>
<td>4.1 ± 0.1</td>
</tr>
<tr>
<td>GT1-6</td>
<td>170191</td>
<td>31219</td>
<td>1982 ± 5</td>
<td>1982</td>
<td>113.41 ± 0.46</td>
<td>5.6</td>
<td>9.3 ± 0.6</td>
</tr>
<tr>
<td>GT1-12</td>
<td>170192</td>
<td>31220</td>
<td>1966 ± 1</td>
<td>1963</td>
<td>132.73 ± 0.43</td>
<td>16.6</td>
<td>9.4 ± 9.4</td>
</tr>
<tr>
<td>GT1-17</td>
<td>170194</td>
<td>31222</td>
<td>1946 ± 1</td>
<td>1941</td>
<td>96.56 ± 0.34</td>
<td>27.5</td>
<td>1.62 ± 0.37</td>
</tr>
<tr>
<td>GT1-28</td>
<td>170273</td>
<td>33211</td>
<td>1941 ± 1</td>
<td>1932</td>
<td>96.91 ± 0.52</td>
<td>32</td>
<td>1.27 ± 0.55</td>
</tr>
<tr>
<td>GT1-32</td>
<td>180135</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
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 $6.1 \pm 5.6\%$, 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 $(15 \pm 5)\%$ 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. 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.
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.quageo.2019.02.010.


