Relationship between environmental dynamics and geochemistry of well-ventilated caves in central Brazil

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Abstract

In central Brazil, high temperatures and a strongly seasonal hydrological regime increase potential evapotranspiration, raising drought risks and threatening local ecosystems. Understanding how climate variations driven by rising global temperatures impact regional climate and water availability is crucial. Monitoring studies performed in well-ventilated caves of central Brazil revealed that changes in relative humidity and potential evaporation significantly influence the hydrological cycle, as detected through oxygen and carbon isotope ratios. This study focusing on the Lapa da Onça cave, located in the Peruaçu Kasrt canion the in northern Minas Gerais state. The study aimed to determine how temperature, relative humidity, and precipitation impact carbon and oxygen isotopy in speleothems of open cave systems.

Our findings showed that calcite deposition rates depend not only on water availability in aquifers but also on environmental conditions, closely linked to temperature. Additionally, temperature and relative humidity directly influence the isotopic behavior of carbon and oxygen. Temperature had a stronger impact on seasonal variability of $\delta^{18}O$ and $\delta^{13}C$, while relative humidity has significantly affected on iterannual variability of =$\delta^{18}O$. These parameters revealed a clear seasonal cycle, aligned with patterns of high temperature and humidity, highlighting their critical role in understanding regional hidroclimate dynamics.

1. Introduction

Speleothems are considered by the scientific community as highly precise paleoclimatic records, capable of providing high-resolution chronological information, including annual and sub-annual scales. Their chemical and isotopic variations reflect changes in climatic and environmental parameters such as temperature and precipitation depending on the local environmental conditions (FAIRCHILD et al., 2006). However, advancing research in this field requires a broader geographical distribution of records and monitoring of environmental dynamics in karst systems to more accurately relate climatic factors to geochemical and isotopic variations.

Despite global advancements, there are still few studies that connect current environmental dynamics with geochemical proxyes such as stable isotopes, trace elements, and calcite deposition rate on tropical cave site . This gap limits the reliable interpretation of paleoclimatic and paleoenvironmental records, as the hydrogeochemical responses of karst aquifers are higly dependent on local conditions. In this context new monitoring efforts are essential to prevent ambiguous or erroneous interpretations.

This study focus on Lapa da Onça, a well-ventilated cave located in the in the North of Minas Gerais State in a region occupied by the Brazilian Cerrado biome, a savannah-type vegetation characteristic of an tropical seasonal climate with dry winters and rainy summers (Stríkis et al., 2024). The primary objective of this study is to enhance our understanding of how environmental conditions, associated with cave atmosphere temperature and relativy humidity, affect the carbon and oxygen isotope signals recorded in speleothems.

2. Materials and methods

2.1. Hydrogeochemical and Isotopic Monitoring of Onça Cave

The monitoring of Onça Cave began in February 2018 and was conducted monthly until November 2019. From earlier March to December 2020, no sampling activities were conducted due to the COVID-19 pandemic. From the beginning of 2021, sampling campaigns were resumed on a monthly basis until September 2023.

The monitoring occurs at five specific points in the cave, identified as P1 to P5, with installations ranging from areas near the entrance to internal regions with active dripping, as shown in Figure 1.

Data of local rainfall, temperature, and humidity (external and cave environmet) were collected using automate data loggers manufactured by Hobbo, model U23-00, while drip rate was manually measured with stopwatches during field visits.

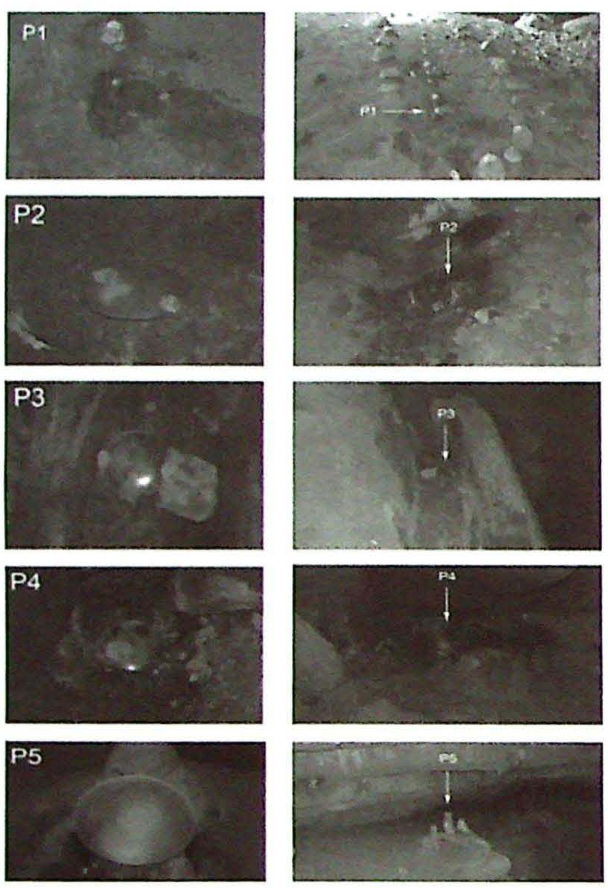

Figure 1: Hydrogeochemical monitoring points installed in Onça cave.

2.2. Calcite Sampling for Isotopic Analysis

To monitor the calcite precipitation rate and the oxygen and carbon isotopic composition of speleothems, calcite deposition experiments were carried out on artificial substrates. For this purpose, we used concave glass substrates replaced at monthly basis at the monitoring sites P1 to P5 (Figure 1). The glass substrate installed in the cave are sandblasted beforehand to create a rough surface that facilitates calcite deposition. These substrates are fixed at monitoring points using epoxy resin. Deposition rates are determined by weighing the substrates abefore and after the sampling.

Calcite samples for isotope analysis collected by scraping the glass substrate at 3 to 4 points, following the procedures outlined in STRÍKIS et al (2024).

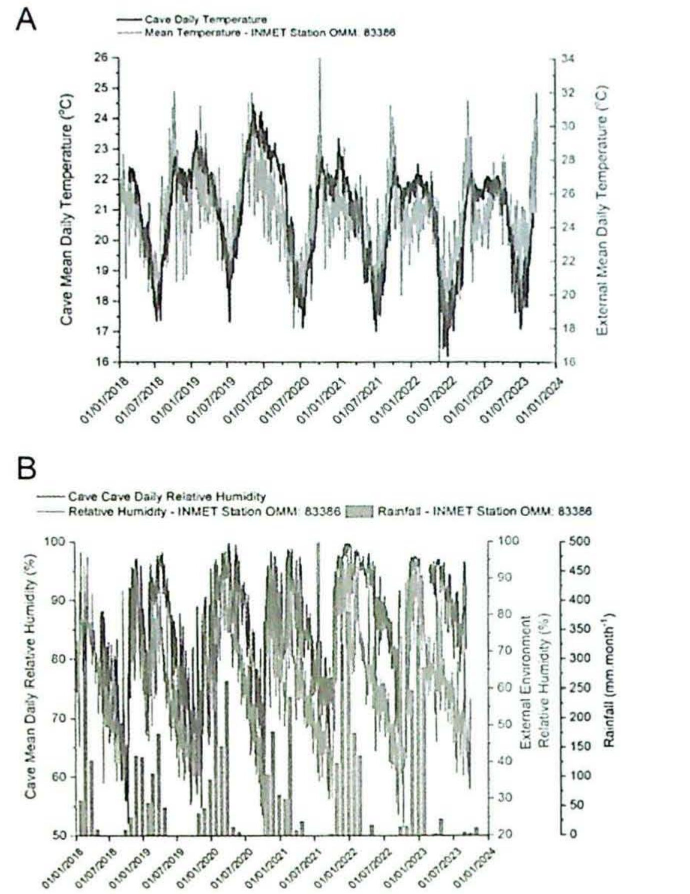

Figure 2: A) Comparison between Onça Cave daily mean temperature (black) and the external environment (red). B) Comparison between daily mean cave atmosphere relative humidity (blue) and the external relative humidity (red) and monthly precipitation (grey). Measurements from external environment were obtained from the local meteorological station from the Instituto Nacional de Meteorologia (INMET – OMM: 88336) at Januária City, located 40 km southwest of the cave.

2.3. Isotopic Analysis of $\delta^{18}O$ and $\delta^{13}C$ in Recent Carbonate

Isotopic analyses of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) were performed at LIESP-CPGEO of IGc/USP using a DeltaPlus Advantage mass spectrometer. During the process, calcium carbonate reacts with H_3PO_4, releasing CO_2. This gas is separated via gas chromatography and analyzed automatically. Isotopic ratios are measured with a precision of ±0.08 ‰ ($^{13}C/^{12}C$) and ±0.1 ‰ ($^{18}O/^{16}O$) and expressed in parts per thousand (‰) relative to the international VPDB standard. The values are corrected using international standards (NBS-18, NBS-19) and internal standards (REI, VICKS).

3. Results

3.1. Environmental Parameters of Gruta da Onça

The environmental monitoring of Onça Cave began on 02/20/2018, with temperature measurements taken at three distinct locations: near the cave entrance, in the center of the cave, and within the innermost part of the monitored cave chamber. Temperatures range from 16°C to 26°C, with lower amplitudes in the interior (16.8°C to 22.9°C). Peaks occur from October to April (21°C to 24°C), while minimum values are recorded between June and August (17°C to 19°C) (Figure 2). Seasonal control is influenced by external temperature, closely following external minimums ($r = 0.75$, p-valeu < 0.05) Relative humidity, ranging from 51% to 100%, gradually increased from 2018 to 2023, correlating with seasonality and precipitation (Figure 2). The wettest months (November to March) coincide with higher rainfall, while the driest months (June to September) show a gradual decrease in humidity (Figure 2). The relationship between internal and external temperature and humidity demonstrates environmental impacts on the cave.

3.2. Drip Rate

Drip rates measured at five points in Lapa da Onça from 19 seconds to 12 minutes and 29 seconds. To compare these points, data were normalized using the z-score, allowing for analysis of seasonal variations on a relative scale. The comparison suggest seasonal consistency, with peaks in September 2018, January, June, August, and September 2019, December 2021, and September 2022 and 2023. Drip rates respond to monthly rainfall peaks after 6 to 9 months, indicating the influence of autogenic recharge and water percolation time through the karst.

3.3. Calcium Carbonate Deposition Rate

The monitored calcite deposition rate was normalized using the z-score (). A seasonal pattern was observed, with peaks between January and May. Individual comparisons revealed a strong consistency between drip rate and calcite precipitation, although some discrepancies remains.

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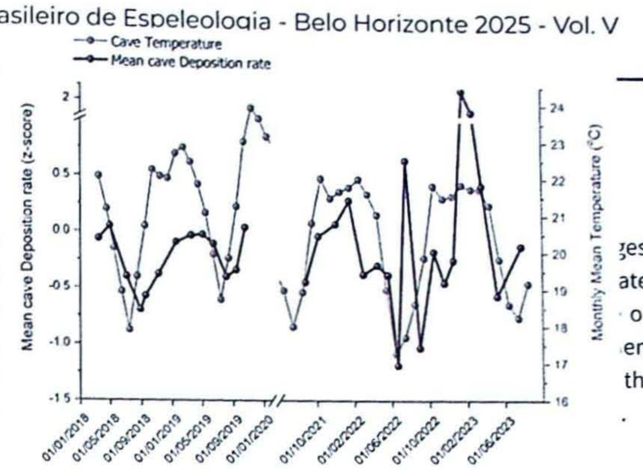

Figure 3: Comparison between cave mean deposition rate (blue) and monthly mean cave temperature (red) at Onça Cave.

3.4. Stable Carbon and Oxygen Isotopes in Recent Carbonate

Stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotopes were analyzed in 520 samples of recent carbonates collected from 130 glass slides across five monitoring points. The data, presented graphically, show consistent seasonal and interannual variations, with a trend of reduction over time. Normalized curves highlight relative variations in $\delta^{18}O$ and $\delta^{13}C$, with amplitudes ranging from -2 to 2. Both normalized averages (data on z-score) reveal similar patterns, suggesting a progressive decrease in $\delta^{18}O$ and $\delta^{13}C$ values across the five points during the monitoring period.

3.5. Relationship Between Environmental and Isotopic Parameters

The relationship between temperature, relative humidity, and isotopic values of $\delta^{18}O$ and $\delta^{13}C$ was analyzed. Rainfall was excluded as it only controls the drip rate. The comparison between temperature and cave mean $\delta^{13}C$ and $\delta^{18}O$ calculated for the five monitored point (here presented in z-score values) shows a good consistence in respec to seasonal (intrannual) variability (Figure 4A). Variations in calcite $\delta^{13}C$ and $\delta^{18}O$ exhibit a coherent relationship with cave relative humidity. Notably, lower humidity levels coincide with lower $\delta^{18}O$ values and higher temperatures during October and November, while higher humidity and elevated $\delta^{18}O$ values are observed in the cooler months from May to August (Figure 3B).

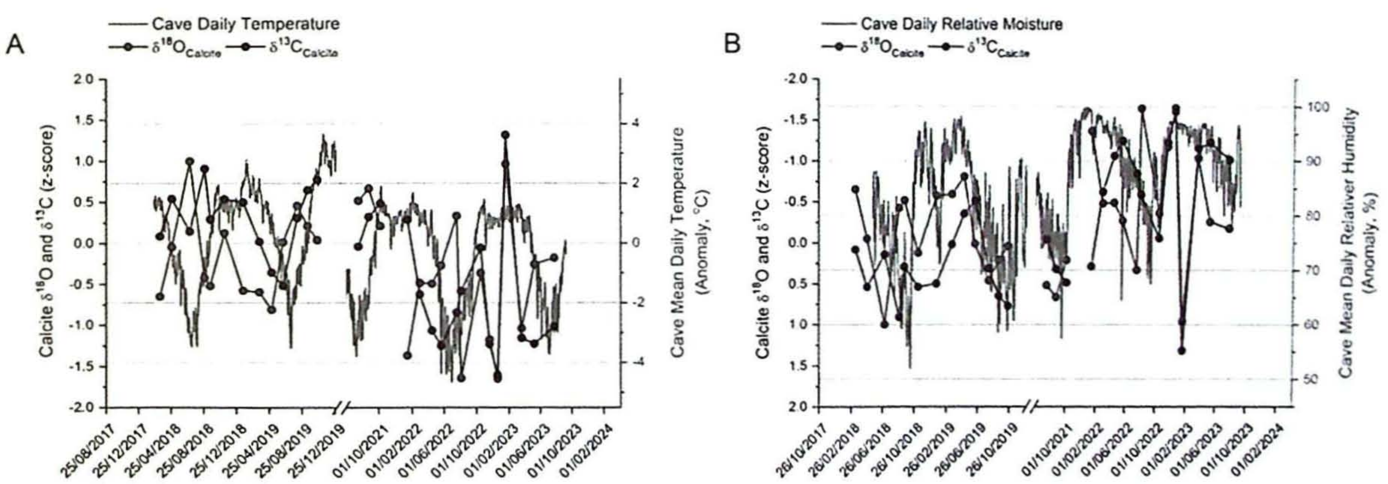

Figure 4: A) Comparison of δ18O and δ13C from calcite precipitated in artificial substrates (data on z-score) with the cave atmospheretemperature anomaly during the monitored period. B) As in «A» but with the relative humidity. Note the reversal of the Y-axis scale in the graph in B.

4. Discussion

The environmental factors influencing isotopic composition at Onça Cave cave were analyzed on a seasonal scale. The cave's average temperature fluctuates by 8.3°C, ranging from 16.2°C to 24.5°C, with maximum values occurring between October and March/April and minimum values between June and August (15.8°C to 16.2°C). This seasonal amplitude of 8.5°C is significantly higher than in confined caves, such as Lapa dos Anjos (STRIKIS, 2015), located close the Onça Cave and where variations reach only 0.5°C. Internally, the cave's temperature is more closely aligned with external minimum temperatures.

Relative humidity at Onça Cave averages around 85%, with seasonal fluctuations mirroring external conditions. This contrasts with caves of restricted air circulation, where humidity is consistently near 100% (STRIKIS, 2015; CRUZ et al., 2007). The cave's drip rate shows a delay of 6 to 9 months relative to rainfall peaks, reflecting the time required for meteoric water to percolate through the karst system.

Drip rate is crucial for $CaCO_3$ deposition but not the sole controlling factor. Temperature plays a significant role by affecting CO_2 solubility; higher temperatures decrease CO_2 solubility, promoting calcite precipitation through degassing (DREYBDROADT, 2005 ; FAIRCHILD & BAKER, 2012). This highlights the interplay between temperature and deposition rates in the cave environment.

Seasonal isotopic data ($\delta^{18}O$ and $\delta^{13}C$) show consistent cycles linked to variations in temperature and humidity, both of which influence speleothem isotopic composition. Low humidity induces kinetic fractionation, enriching isotopic values due to the preferential loss of lighter isotopes through evaporation. In the same way calcite $\delta^{18}O$ tends to present an inverse relationship with relative humidity due evaporative effects. Temperature also directly impacts isotopic fractionation, influencing calcite deposition (FAIRCHILD & BAKER, 2012). Theoretical $\delta^{18}O$ calculations align closely with observed data, confirming that temperature is the primary seasonal driver of $\delta^{18}O$ variability, although interannual variations require additional explanation.

Over the monitoring period, a gradual decrease in temperature was observed, corresponding to wetter years (Figure 4A). While lower temperatures typically increase calcite $\delta^{18}O$, the decline in $\delta^{18}O$ values between 2018 and 2023 cannot be fully explained by temperature alone (Figure 4A). In contrast the kinetic fractionation process, dirven by a decreasing in cave relative humidty results in a calcite isotope enrichemt of $\delta^{18}O$ and $\delta^{13}C$ as lighter isotopes are preferentially lost to the vapor phase. Conversely, an increse in relative humidity reduces this effect, leading to more negative $\delta^{18}O$ and $\delta^{13}C$ values.

The relationship between rising humidity and isotopic trends suggests that relative humidity plays a critical role in isotopic variability, particularly on interannual scales (Figure 4B). Temperature dominates seasonal variations, while humidity significantly influences longer-term patterns. These findings highlight the complex interactions between environmental factors shaping isotopic composition in well ventilated caves from tropical areas, like Onça Cave.

5. Conclusion

The five-year geochemical and hydrological monitoring of the Onça cave, in Central Brazil, revealed how temperature and humidity influence the geochemistry of speleothem carbonates, enabling the identification of climatic effects driven by temperature and relative humidity. The cave temperature ranges from 16.2°C to 24.5°C, adjusting with external minimums, and with maximum values occurring from October to March/April. Relative humidity shows greater variation near the entrance and smaller fluctuations in the interior, remaining consistent across monitoring points.

Drip rates, higher between June and September, respond to accumulated rainfall with a delay of several months, influencing $CaCO_3$ deposition. However, temperature also plays a critical role; as it increases, CO_2 solubility decreases, favoring solution supersaturation and calcite precipitation. Experiments with artificial substrates revealed that carbonate isotopic composition depends on drip water, temperature, and cave atmosphere relative humidity, which affect evaporation and enrich $\delta^{18}O$ and $\delta^{13}C$ values during warmer periods.

Environmental parameters display marked seasonal cycles, directly influencing the depositional and isotopic behavior of speleothems. This study contributes to understanding climatic variations and interpreting paleoclimate reconstructions based on analyses from well-ventilated caves.

Acknowledgments

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References

BUARQUE, P. F. Climatic variability of the South American Monsoon System in East-Central Brazil during the last millennium from speleothem and tree trunk records. Doctoral Thesis—São Paulo: University of São Paulo, 2019.

Dreybrodt, Wolfgang. 2005. Processes of Speleogenesis: A Modeling Approach. New York: Springer.

CRUZ F.W., et al. Evidence of rainfall variations in Southern Brazil from trace element ratios (Mg/Ca and Sr/Ca) in a Late Pleistocene stalagmite. Geochimica et Cosmochimica Acta Volume 71, Issue 9, 1 May, 2007

FAIRCHILD, I. J.; BAKER, A. Speleothem Science: From Process to Past Environments. [s.l.] Wiley since 1807, 2012.

STRÍKIS, N.M., et al. Modern anthropogenic drought in Central Brazil unprecedented during last 700 years. Nature communications,v. 15, p. 1728, 2024.

STRÍKIS, N. Activity of the South American Monsoon System in central Brazil during the last glacial period from the application of oxygen isotopes in speleothems. São Paulo: University of São Paulo, 2015.