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ARTIGO

## FIRST EVIDENCE OF OXALATES AND THEIR DATING IN THE ROCK SUBSTRATE OF TOCA DO BAIXÃO DO MILHO, CARACOL, PIAUÍ, BRAZIL

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### ABSTRACT

Archaeological sites in the state of Piauí, Brazil, have exhibited salt efflorescence in rock shelters. At the Toca do Baixão do Milho archaeological site, the minerals whewellite ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) and weddellite ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) were identified and radiocarbon dated. Given the relevance of the study area to the history of the Americas, radiocarbon data from Serra das Confusões, Piauí, Brazil, were compared with calcium oxalate data from Serra da Capivara National Park, Piauí, Brazil. The results indicate similarities in calcium oxalate data between the two areas and suggest that carbon-bearing minerals should be further investigated to establish a robust dataset capable of reassessing or corroborating conditional ages for the occupation of the Americas in the study area.

**Keywords:** Dating; Whewellite; Weddellite; Caracol, Piauí; Occupation of the Americas.

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## PRIMEIRA EVIDÊNCIA DE OXALATOS E SUA DATAÇÃO NO SUBSTRATO ROCOSO DA TOCA DO BAIXÃO DO MILHO, CARACOL, PIAUÍ, BRASIL

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### RESUMO

Sítios arqueológicos no estado do Piauí, Brasil, apresentam eflorescências salinas em abrigos rochosos. No sítio arqueológico Toca do Baixão do Milho, os minerais whewellita ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) e weddellita ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) foram identificados e datados por radiocarbono. Dada a relevância da área de pesquisa para a história das Américas, os dados de radiocarbono da Serra das Confusões, Piauí, Brasil, foram comparáveis aos dados de oxalato de cálcio do Parque Nacional da Serra da Capivara, Piauí, Brasil. Os resultados indicam similaridades entre as duas áreas e que minerais carbonáceos devem ser investigados mais a fundo para estabelecer um arcabouço de dados robusto que reavalie ou corrobore as idades condicionais para a ocupação das Américas na área de pesquisa.

**Palavras-chave:** Datação; Whewellita; Weddellita; Caracol; Piauí; Ocupação da América.

## PRIMERA EVIDENCIA DE OXALATOS Y SU DATACIÓN EN EL SUSTRATO ROCOSO DE TOCA DO BAIXÃO DO MILHO, CARACOL, PIAUÍ, BRASIL

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### RESUMEN

Los yacimientos arqueológicos del estado de Piauí, Brasil, presentan eflorescencias salinas en abrigos rocosos. En el yacimiento arqueológico Toca do Baixão do Milho, se identificaron y dataron por radiocarbono los minerales whewellita ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) y weddellita ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ). Dada la relevancia del área de investigación para la historia de las Américas, los datos de radiocarbono de Serra das Confusões, Piauí, Brasil, fueron comparables a los datos de oxalato de calcio del Parque Nacional Serra da Capivara, Piauí, Brasil. Los resultados indican similitudes entre las dos áreas y que se deberían investigar más a fondo los minerales carbonáceos para establecer un marco de datos sólido que permita reevaluar o corroborar las edades condicionales de la ocupación de las Américas en el área de estudio.

**Palabras clave:** Datación; Whewellita; Weddellita; Caracol; Piauí; Ocupación de América.

## CARACOL, THE GATEWAY TO SERRA DAS CONFUSÕES

The municipality of Caracol (09°16'43" S; 43°19'48" W) is home to the administrative headquarters of the Serra das Confusões National Park. The archaeological site studied here is the Toca do Baixão do Milho site, located at UTM coordinates 23E 0682260 / N 8976338. This rock shelter is about 10 m long, 8 m wide, and with a maximum height of 3 m, located at the base of a slope, at approximately 400 m above sea level (Iphan, 1997) (Figure 1 and 2). The landowner was consulted regarding access to the area. The study aimed to collect samples of secondary minerals from the rock support of the archaeological site to establish radiocarbon dates.

**Figure 1.** Toca do Baixão do Milho.

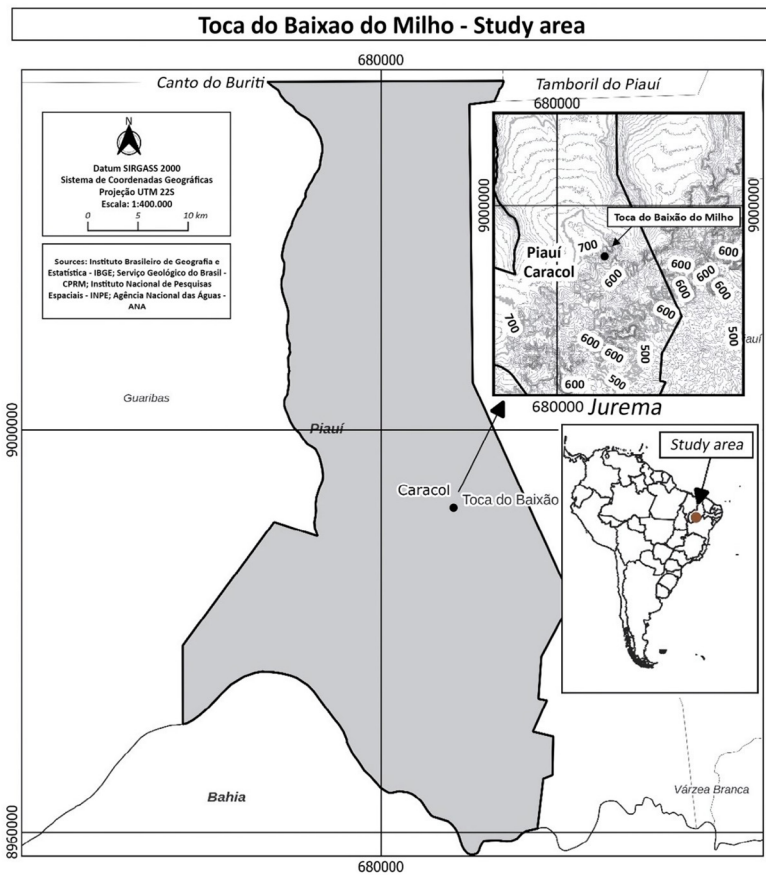


Source: Tatiane de Souza (2026).

The site is located at an intersection between the Cabeças and Pimenteiras geological formations, at altitudes close to 600 m. The Pimenteiras Formation is composed of dark gray to greenish black, partly bioturbated, shales that are rich in organic matter, with siltstone and sandstone intercalations attributed to a shallow shelf environment dominated by storms (Vaz *et al.*, 2007). According to (Caputo; Lima, 1984), silty shales with thickness exceeding 70 m and fine sandstones occur in the northeastern portion of the basin, representing pro-delta and deltaic front deposits, respectively.

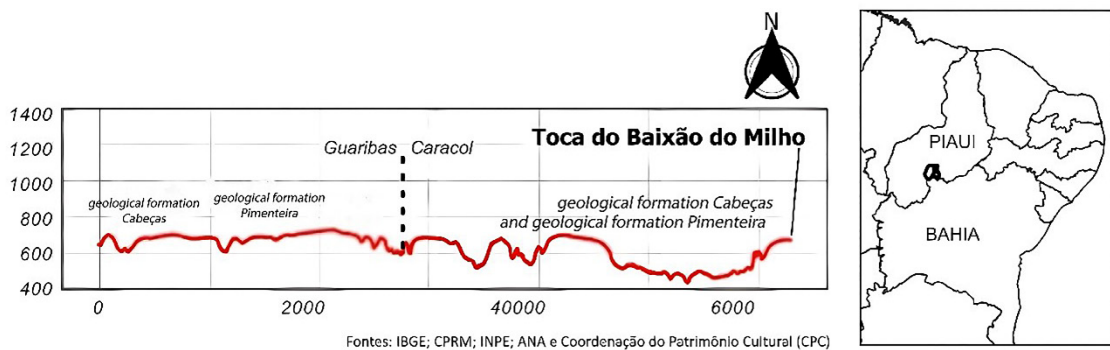
The most striking geological feature of the region is the lithostructural step located on the south-southeast boundary, which separates the Parnaíba Sedimentary Basin from the crystalline basement of the Sertaneja Depression. This step, with elevation differences of between 200 and 300 meters, is visible from the towns of Morro Cabeça no Tempo, Caracol, and São Brás do Piauí (Gonçalves, 2003) (Figure 3).

Figure 2. Site of Toca do Baixão do Milho.



Source: Carlos Rizzi (2025).

Figure 3. Lithostructural step according to the altimetric levels of Caracol and Guaribas.

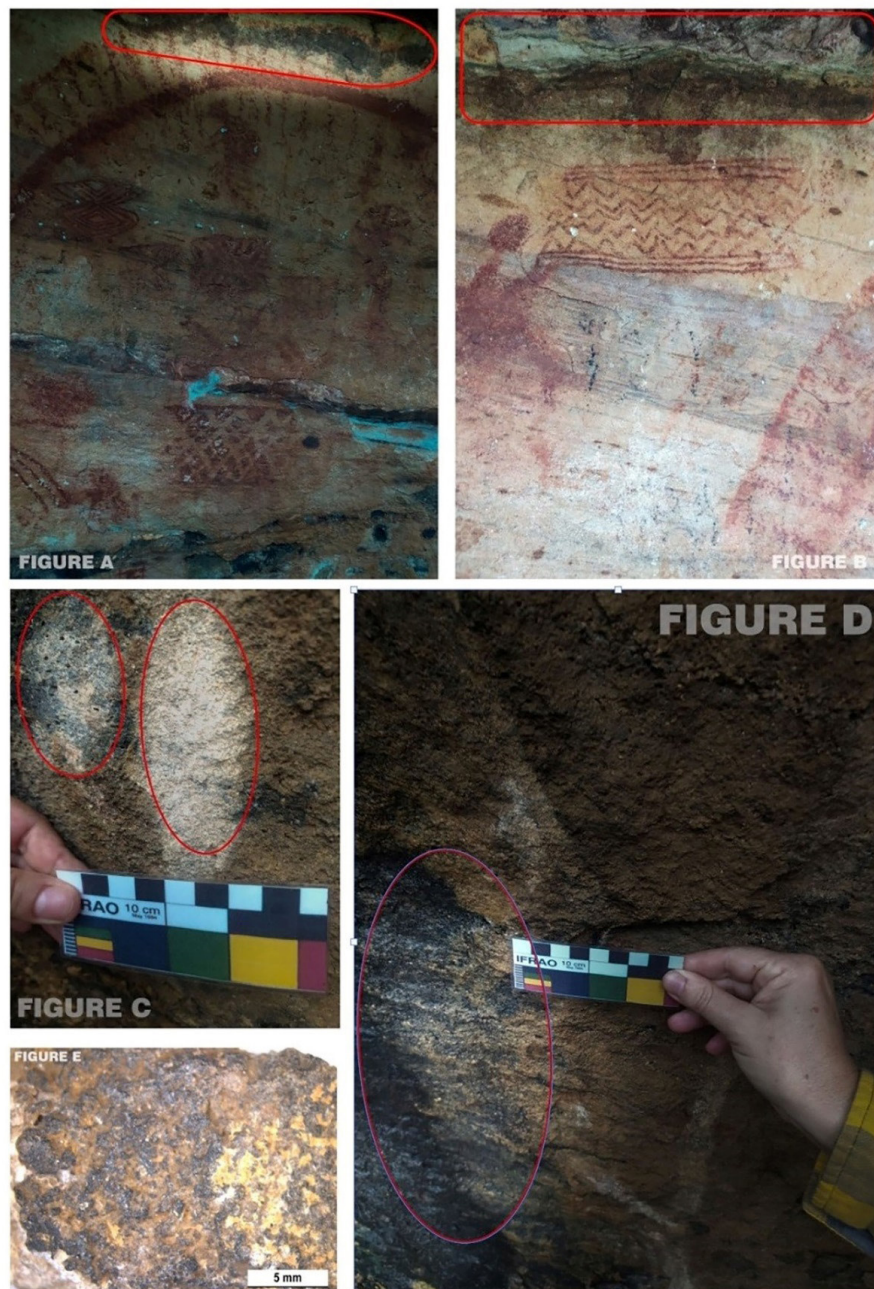


Source: Carlos Rizzi (2025).

The shelter at Toca do Baixão do Milho features rock art with a variety of motifs in different hues [colors] with the presence of possible overlapping and varied techniques suggesting complexity in the artistic interventions. The overlaps, stylistic variations, and relationships with different moments of production require further studies. However, the deposition of accretions, such as the calcium oxalate contained in whewellite, can be dated using the radiocarbon method. Lichens, microorganisms, and secondary minerals are observed in the rocky support. The oxalate sample collected is located a few meters

from the rock shelter and can also be observed above the paintings (Figure 4), indicating a process of biological and chemical alteration, which frequently results in the formation of crusts on the rock paintings, so it is possible to establish relationships between both formations for dating purposes. The main relationship between the accumulation of oxalate in the rock support and the oxalate covering the rock painting is indirect dating. Crusts of calcium oxalate (whewellite and weddellite) form over the paintings over millennia, trapping organic carbon that enables us to estimate the minimum age of the rock painting (figure 1).

**Figure 4.** A) and B) Rock art in the shelter with overlay of secondary minerals; C) Mixture of whewellite and probable calcite; D) Collection point on the rocky support; and E) whewellite seen through a binocular magnifying glass.



Source: Tatiane de Souza (2025).

Settlements in the Serra da Capivara National Park have been dated in 50,000 BP. Calcite formation on a rock-wall painting in a rockshelter yielded thermoluminescence (TL) and electron paramagnetic resonance (EPR) ages older than 35,000 BP (Watanabe *et al.*, 2003). To contribute to this ongoing debate, these researchers studied calcite deposits covering prehistoric paintings from several rockshelters. The ages obtained for these calcites are younger than 12,000 BP and suggest that the paintings could be more recent than proposed by previous studies (Guidon; Arnaud, 1991).

These new results are problematic as they are younger than the most recent occupations dated in the SCNP. If the youngest ages suggest the presence of a cultural phase that has left no trace in the excavations, such a fundamentally contradictory hypothesis needs to be tested (Guidon; Arnaud, 1991).

Dating of several rock art sites in the Serra da Capivara region was conducted using a variety of methods. In the Toca Paraguaio, dark red pigment was dated with a date of (7,606 BP, while in Boqueirão Pedra Furada, white pigment was dated of 10,715 BP, using C-ICPMS U-series to date samples of carbonate (Rosina *et al.*, 2022). Given the low  $^{230}\text{Th}/^{232}\text{Th}$  activity ratios, the obtained ages probably represent the maximum ages for the samples (Rosina *et al.*, 2022).

Other dating were conducted at Toca do Sítio do Meio, calcite, using the AMS radiocarbon method, with a result of (2,700±110 BP); at the Pedra Furada, calcite, with a result of (3,570±50) BP, (Rowe; Steelman, 2003); and at Toca do Serrote das Moendas, calcite overlying the external paintings, using the AMS radiocarbon method, with a result of (4,418+-4,783 BP) and fraction of compact calcite overlying the contact with the rocky substrate, U/Th series, (12,280 +- 10,560 BP) (Fontugne *et al.*, 2013). The Toca da Gameleirinha site, calcite with a cauliflower-like surface, was also dated by AMS radiocarbon, (7,507+-7,656 BP) and by U/Th, with a result of (12,240- 4,811) BP, (Fontugne *et al.*, 2013), in addition to Toca do Serrote das Moendas, calcite overlying external paintings, by AMS radiocarbon, (964+-1,168 BP) (Fontugne *et al.*, 2013).

For oxalate, whewellite has been identified at sites in the Serra da Capivara National Park (PI) and in northern Minas Gerais. In southeastern Piauí, it has been characterized at sites such as Toca Exu do Jurubeba and Toca do Serrote da Bastiana (Farias Filho *et al.*, 2017; Rowe; Steelman, 2003). At the latter site, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques confirmed the presence of whewellite, dated to at least (2,490 ± 30 BP). An age of (3,730 ± 90 BP, obtained via  $^{14}\text{C}$  AMS on organic material from the paint layer was also collected from the site and can be related to the organic biofilm producing the oxalate layer, rather than to evidence of a binding medium (Armitage, personal communication).

## SECONDARY MINERALS FOUND IN THE RESEARCH AREA

Whewellite ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) and weddellite ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) often occur in association and are not uncommon in geological environments (Russ *et al.*, 1995; 2000). Although a mineral is traditionally considered to be formed by inorganic processes, substances of biological origin can be classified as minerals if they meet the defined crystallographic and chemical criteria (Neves; Atencio, 2014).

The interest in oxalates in the archaeological context is due to their suitability for radiocarbon dating ( $^{14}\text{C}$ ). Since the 1990s, researchers in Australia have been using this methodology to establish chronologies at rock art sites, based on calcium oxalate samples present in mineral crusts (Watchman, 1990). The main advantage of this method is that, once precipitated, calcium oxalate preserves carbon isotopes without exchange with atmospheric, soil, or geological sources, ensuring greater

dating accuracy (Aubert *et al.*, 2022; Ruiz *et al.*, 2012; Steelman; Boyd; Trinidy, 2021; Watchman, 1987b, 1991, 2000a; 2000b; Watchman *et al.*, 2001; Watchman; O'Connor; Rhys, 2005).

Thus, ages obtained from oxalates using  $^{14}\text{C}$  are interpreted as corresponding to the period in which microbial communities were active on rock surfaces and are therefore datable as the formation of mineral crusts (Russ; Loyd; Boutton, 2000). However, some studies indicate that the carbon in oxalates derives exclusively from the biogenic activity of microorganisms, with a variable atmospheric isotopic signature.

Although the exact origin of whewellite and weddellite is not fully understood, there is evidence that these minerals are formed by distinct mechanisms, probably of biological origin, involving cyanobacteria, microstromatolytic algae, fungi, or lichens (Chaffe *et al.*, 1994; Gadd *et al.*, 2014; Lazzarini; Salvadori; 1989). Oxalate production is also involved in the biodeterioration of rock and mineral substrates, in lignocellulosic materials, and in the alteration and manipulation of cultural heritage (Pinzari *et al.*, 2010).

In Brazil, whewellite has been identified at sites in the Serra da Capivara National Park (PI) and in northern Minas Gerais. In northern Minas Gerais, in the Cavernas do Peruaçu National Park, 13 samples containing whewellite and weddellite were collected from the Abrigo Norte do Janelão site (Faria *et al.*, 2011). These minerals have also been identified at other sites in the region, such as Malhador, Janelão, and Toca Vermelha. The crusts observed at Janelão are smaller and thinner, while at Toca Vermelha they are restricted to a small area. Analyses indicated the presence of weddellite and gypsum as the main components of the white crusts (Pinheiro; Yoshida; Souza, 2006).

Despite the growing use of oxalate salts as a dating tool, the method faces criticism. The chemical composition and microstratigraphy of crusts can vary depending on the depositional environment, being influenced by factors such as rainfall, microtopography, and regional environmental changes over time (Bierman; Gillespie, 1991). Furthermore, crusts formed under similar climatic conditions but with different lithological types may have distinct compositions.

The organic components of the crust, which are generally selected for  $^{14}\text{C}$  dating because they contain carbon-bearing minerals that can be dated, such as whewellite and weddellite, are assumed to have been deposited simultaneously with the inorganic constituents. This premise underpins the accelerator mass spectrometry (AMS) dating methodology, the accuracy of which depends on the correct separation of carbonaceous components of biogenic origin. In mineral crusts and prehistoric paint, calcium oxalate can be found as hydrated minerals (whewellite and weddellite) in a mixture of other minerals. Calcium oxalate salts are highly insoluble, precipitating rapidly in the simultaneous presence of calcium and oxalate ions; however, it is important to recognize that various carbon sources may be present in the crustal organic matter (Watchman, 1991). These salts are believed to form primarily through the microbiological production of oxalic acid derived from atmospheric carbon, which reacts with calcium from the substrate or aerosols, forming oxalate. If this biogeochemical pathway is, in fact, the sole mechanism involved in the generation of these salts, radiocarbon dating would indicate the age of oxalate formation, which may or may not coincide with the application of the cave painting (Aubert, 2012).

## MATERIALS AND METHODS

The procedures used to date the rock support of Toca do Baixão do Milho are shown here considering the challenges discussed in the previous section regarding the dating of calcium oxalates. As these are radiocarbon-based analyses, it was necessary

to separate microorganisms, dust, and other organic materials present in the crust to isolate the carbon contained in the calcium oxalate.

This study used the chemical pretreatment procedures described by (Dumoulin *et al.*, 2020; Jones *et al.*, 2017), developed to isolate pure oxalates from other organic materials present in the crusts. Before applying these protocols, it was necessary to determine the sample composition using mineralogy and analytical chemistry techniques.

Mineralogical characterization began with X-ray diffraction (powder method) to identify the minerals present using a Bruker model D8 Advance da Vinci diffractometer with  $\text{CuK}\alpha$  radiation, LYNXEYE detector, and TWIN-TWIN optics. Analyses were performed at the Institute of Geosciences of USP using DiffraC-EVA software and the PDF-2 database (ICDD), version 2022. Samples were mounted on glass slides.

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). It is part of the Institute of Geosciences at USP (University of São Paulo) and was used to identify the chemical composition. Individual grains were mounted in resin and coated with a thin layer of carbon. The analyses were performed using an LEO 440 electron microscope (LEO Electron Microscopy Ltd., England) coupled to a Si (Li) spectrometer with Inca 300 software (Oxford Instruments Ltd., England), operating at 20 kV and at a working distance of 25 mm.

Raman spectroscopy was used to further characterize the chemical composition and molecular structure at the Astrobiology Laboratory of the Chemistry Institute at the University of São Paulo. The samples were analyzed directly in glass sample holders using a Renishaw inVia Reflex system coupled to a Leica DM2500 M microscope with 785 nm and 532 nm lasers (both 500 mW). Gratings of 1,200 and 2,400 lines, depending on the laser, and a cooled CCD detector were used. Data were processed with Wire 4.4 software, and baseline subtraction was performed using Fityk 1.3.1.

Once the presence of whewellite and weddellite was confirmed by all the analytical techniques, the chemical separation process for dating was conducted. The protocol, based on (Dumoulin *et al.*, 2020; Jones *et al.*, 2017;), involves two steps: (1) removal of carbonates and residual organic materials via acidification with 6N HCl (6 mol/L); and (2) dissolution of oxalate in the supernatant, isolating the minerals and organic compounds transported by the wind. The presence of oxalate and residue was monitored using Raman spectroscopy.

Note that the date proposed here refers to the rock support and not the cave paintings themselves. Although the layers of microorganisms covering the paintings may provide relevant chronological clues. For example, in research on calcium oxalate crusts associated with open air rock art on the Iberian Peninsula, radiocarbon dating of oxalate accretions was used as it may also help establish chronological limits for pictographs which, for whatever reason, cannot otherwise be dated directly (Ruiz *et al.*, 2012).

After initial characterization, about 600 mg of the calcium oxalate crust powder were submitted to the following protocol:

1. Organic decontamination: The material was introduced into a 0.5 N NaOH (0,5 N NaOH = 0,5 mol/L) solution at 60°C for one hour to remove humic and fulvic acids. After centrifugation, the supernatant was discarded, and the solid residue was extensively washed with ultrapure water until it reached neutral pH.

2. Selective dissolution: The sample was then placed in a 6 N HCl (6 N = 6 mol/L) solution at 60°C for one hour to remove carbonates and dissolve the oxalates. The supernatant containing oxalic acid was isolated, and the residue was separated. The acidic supernatant was then dried at 80°C to vaporize and remove the

HCl. To achieve better HCl removal, ultrapure water was introduced several times, followed by multiple steps to evaporate.

3. Purification: The acidic supernatant was dried at 80°C, with successive evaporation of the HCl by adding ultrapure water, until a dry powder containing the oxalate was obtained.

4. Raman verification: The final powder was analyzed using Raman spectroscopy to confirm that the carbon was present only in the oxalate phase. The separated residue was also analyzed for comparison.

The dried oxalate sample was then sealed in tubes and sent for radiocarbon dating (AMS  $^{14}\text{C}$ ) analysis, according to the procedures described by (Dumoulin *et al.*, 2020; Jones *et al.*, 2017). Separation with concentrated HCl is essential to ensure that only the calcium oxalate, and not the contaminants, is dated. Simply dating the entire crust could yield an incorrect age, often older than the actual age of the oxalate.

Our research team initiated related to the identification of secondary minerals in rock supports from rock shelters since 2020, with an interest in the influence of weathering on the production and conservation of paintings, as well as in detecting the possible participation of these minerals in the production of cave paintings. Interdisciplinary collaboration between chemistry, mineralogy, and archaeology has produced robust results in this area of research (Souza; Atencio, 2024; Souza; Atencio; Rizzi, 2023) in southern Brazil. At this time, we have also expanded our interest in radiocarbon dating of carbon-bearing minerals, given the relevance of the research context, and the results reported here have proved to be very promising.

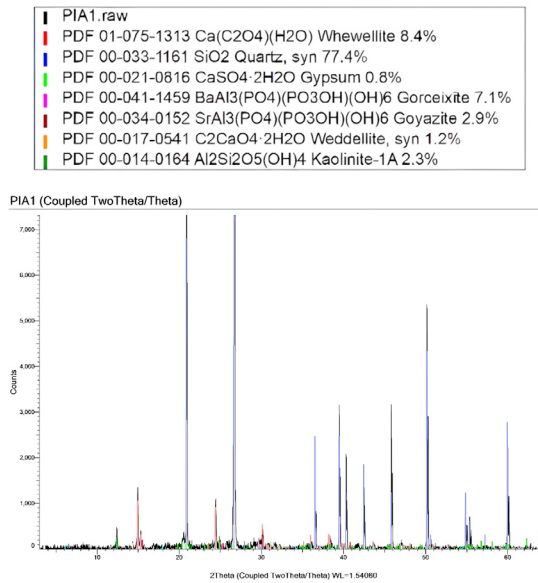
## RESULTS

### ***X-ray Diffraction (XRD)***

The results of the crystallographic analyses (Figure 5) show that the sample is composed of the oxalates whewellite and weddellite, confirming the data obtained via Raman and SEM-EDS. Moreover, associated minerals such as quartz, kaolinite, gypsum, goyazite, and goyazite were also identified. The SEM-EDS and Raman results are consistent with the XRD findings. The SEM-EDS reveals a high concentration of calcium in specific targets with XRD (Figure 5), while Raman spectra obtained from specific peaks confirm the weddellite and whewellite signature (Figure 6). The detection of these minerals, both common and accessory, is relevant not only for dating purposes but also for understanding the altered state of the rock support and the crust formation process. The mineralogical association indicates favorable conditions for the precipitation of salts such as calcium oxalates in microbially active environments, especially in humid, protected rock shelters.

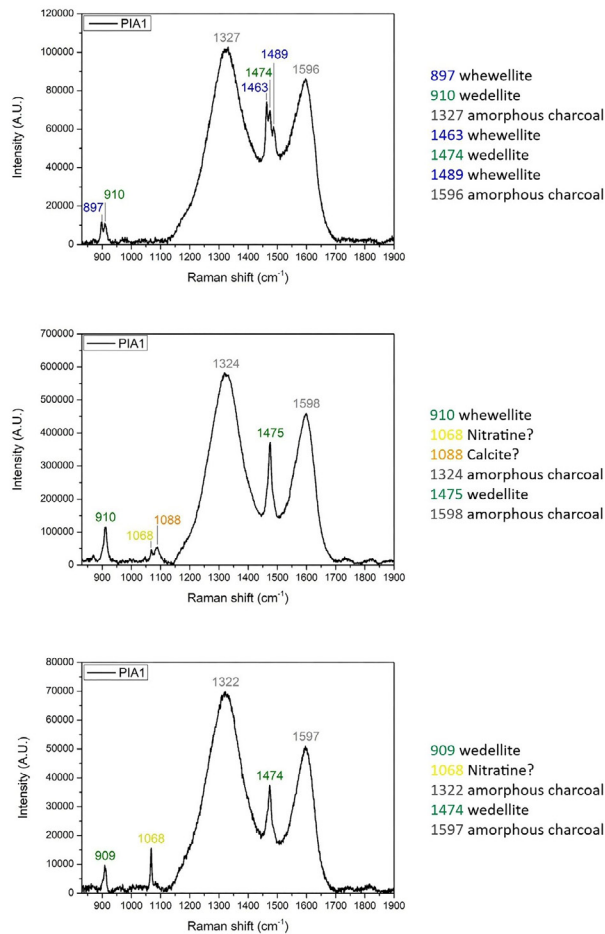
The quantification shown in X-ray diffractograms is obtained automatically by the Internal Standard Method with Corundum, or more specifically, the RIR Method — Reference Intensity Ratio. It is automatic and, in our case, unnecessary because we have minute portions of sample irradiated by X-rays. We do not aim to obtain quantitative analyses of our samples. Quantification by this method or by Rietveld only makes sense when it involves a large amount of material and is used by industry and mining, not being necessary in mineral identification studies such as the one present here. XRF was not necessary because EDS is much more efficient for chemical characterization.

**Figure 5.** X-ray diffractogram of Toca do Baixão do Milho. The identified minerals.



Source: Daniel Atencio (2025).

**Figure 6.** Raman spectroscopy results of the sample.



Source: Gabriel Gonçalves da Silva (2025).

## RAMAN SPECTROSCOPY

Raman spectroscopy analyses demonstrated the presence of two calcium oxalate species in the samples. Weddellite ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) was observed in all the analyzed samples and was characterized by the presence of intense peaks around  $910\text{ cm}^{-1}$  and  $1,474\text{ cm}^{-1}$  (Petit et al., 2018). Whewellite ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) was found in only one sample and can be recognized by the peaks at  $897$ ,  $1,463$ , and  $1,489\text{ cm}^{-1}$  (Petit et al., 2018). This abundance relationship is inverse to that observed by XRD and EDS, possibly due to the heterogeneous characteristics of the sample. In all cases, the oxalate salt peaks were observed associated with the presence of the D and G bands of amorphous carbon (Kaniyoor; Ramaprabhu, 2012). In two samples, peaks were detected at  $1,068\text{ cm}^{-1}$ , which were associated with the presence of a substance containing the nitrate ion, such as the mineral nitratine ( $\text{NaNO}_3$ ) (Huidobro et al., 2024). Finally, a weak signal at  $1,088\text{ cm}^{-1}$  in one of the samples may indicate the presence of a carbonate mineral, the most common being calcite ( $\text{CaCO}_3$ ) (Wang *et al.*, 2019).

The constant presence of amorphous carbon can be interpreted as the result of soot deposition from the burning of organic material or the intentional use of charcoal and ash, possibly of plant origin, as a source of black pigment. The presence of oxalate and nitrate salts can be interpreted as biotic in origin, as these compounds may have been formed in situ by the action of bacteria and lichens, or by accumulation caused by the percolation of water by the rocky substrate after passing through soil layers in which these biogenic compounds were present.

Studies cite that among the most common mineral deposits observed in similar situations are the crystallization of calcite ( $\text{CaCO}_3$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), in addition to calcium oxalates in their various forms, such as whewellite and weddellite. These salts can be easily detected by Raman in paintings, crusts, and rock surfaces, in combination or in isolation, as with the set of minerals observed in wall paintings.

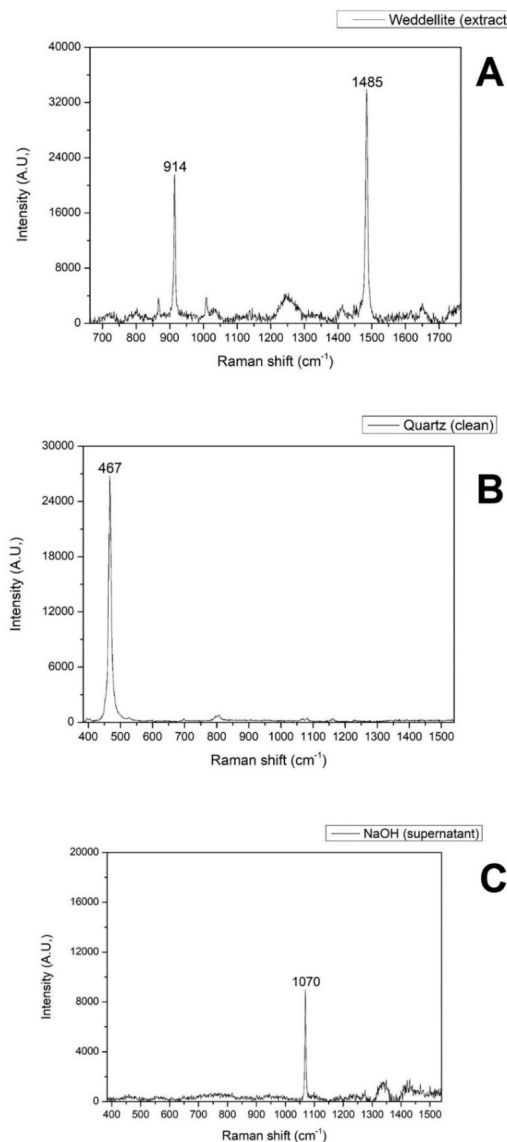
The vibrational signal corresponding to calcite appears prominently around  $1,086\text{ cm}^{-1}$ , while the peaks at  $1,373$  and  $1,583\text{ cm}^{-1}$  indicate the presence of amorphous carbon from microorganisms. Figure 7 shows that the acidification process of preparing the sample for dating eliminated the amorphous carbon present in the microorganisms of the sample, leaving only the oxalate. Oxalates are frequently observed in crusts formed by biological activity on rock surfaces. Note that calcite X-ray diffraction peaks were not located in the diffractograms, suggesting its presence in small quantities in the sample.

## RAMAN SPECTROSCOPY: OXALATE AFTER CHEMICAL SEPARATION

The chemical separation was performed using a molarity (mol/L) that indicates exactly how many particles (molecules or ions) are present in the volume, with an occurrence of  $0.6$  (mol/L) being evaluated, via successive washes with NaOH. The resulting material was again submitted to Raman spectroscopy to confirm the exclusive presence of calcium oxalate in the isolated fraction. Figure 7 shows that the chemical separation was successful, with a clean spectrum free of significant interference, such as that of amorphous carbon. Vibrational bands associated with the carbon-oxygen bonds (C=O and C-O) of the oxalate group were observed, confirming the integrity of the target compound. Previous data obtained via XRD and EDS confirm that the cation is predominantly calcium, characterizing weddellite as the main constituent of the isolated fraction. The spectrum in Figure 7 shows that the presence of purified oxalate was also confirmed by the presence of strong peaks at  $914$  and  $1,485\text{ cm}^{-1}$ , which may correspond to weddellite or other phases such as oxalate-calcium chloride heptahydrate ( $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ ), given the presence of a discrete peak at  $866$

$\text{cm}^{-1}$  (Piro *et al.*, 2018). The dried material was then sent to the laboratory for  $^{14}\text{C}$  AMS dating. The oxalate was isolated by the removal of microorganisms present in the sample. After calcium oxalate separation, the insoluble material was analyzed separately (Figure 7). The Raman spectrum of this residue revealed a predominance of quartz, with no significant signs of oxalates or organic materials. This fraction essentially represents the inorganic constituents of the crust, such as mineral dust, sediments, or amorphous silica, and confirms the effectiveness of the chemical purification protocol. Figure 7 shows the residue remaining from the oxalate separation and purification process, in which there is the presence of an intense peak corresponding to the main vibrational mode of quartz ( $467\text{ cm}^{-1}$ ), while no peak associated with oxalate is observed. The supernatant obtained after washing with  $0.5\text{N NaOH}$ , or  $0.5\text{ M}$  ( $0.5\text{ mol/L}$ ), which means 20 grams of  $\text{NaOH}$  in one liter of solution and was as equally reliable for destroying the presence of microorganisms in the sample (Figure 7).

**Figure 7.** A) Raman spectrum of oxalate after chemical separation of the sample; B) Raman spectrum of the residue separated from the oxalate; and C) The supernatant obtained after washing with  $0.5\text{N NaOH}$  or  $0.5\text{ M}$  ( $0.5\text{ mol/L}$ ), which was equally reliable for destroying the presence of microorganisms in the sample.

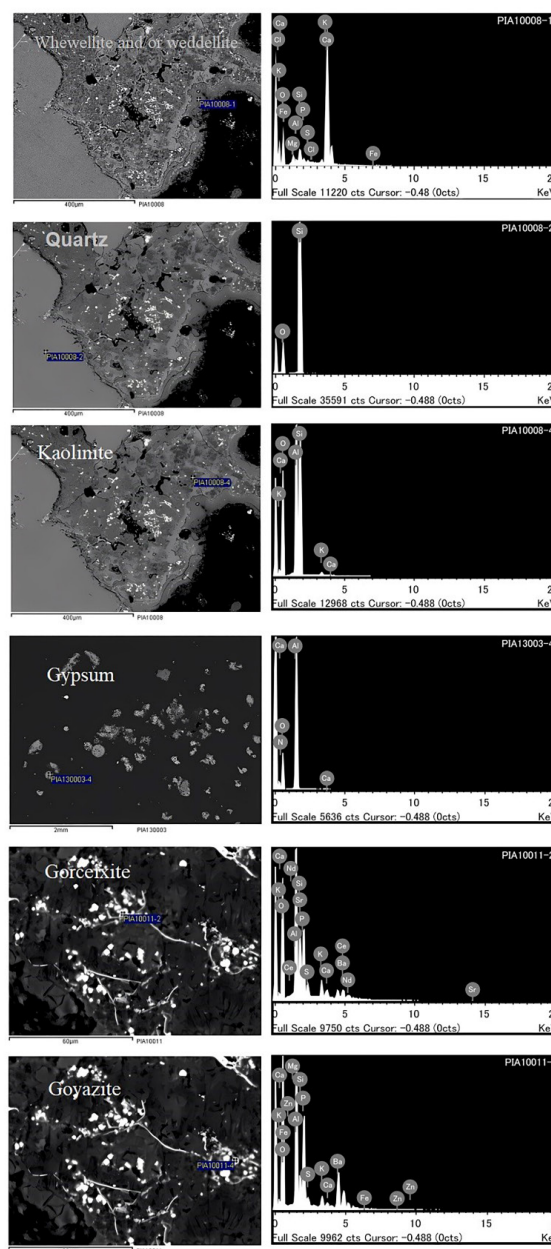


Source: Gabriel Gonçalves da Silva (2025).

SCANNING ELECTRON MICROSCOPY WITH EDS (SEM-EDS)

Analyses using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) enabled identification of the chemical elements constituting the crusts sampled at Toca do Baixão do Milho. This combination of chemical elements seen in (SEM-EDS) points to the existence of specific minerals identified both qualitatively and quantitatively according to image analysis and calculations in which the parameters describe a crystallochemical structure. The spectra obtained confirm the significant presence of calcium at the points corresponding to whewellite and weddellite, which is fundamental for the characterization of these minerals, in addition to revealing the presence of accessory minerals such as quartz, kaolinite, gypsum, gorceixite, and goyazite (Figure 8, Table 1).

Figure 8. SEM images and EDS results.



Source: Daniel Atencio (2025).

**Table 1.** Chemical composition of the sample.

Oxide	whewellite/weddellite				quartz				
	03-2	03-3	03-8	08-1	03-1	03-5	03-13	08-2	08-3
Na <sub>2</sub> O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
K <sub>2</sub> O	n.d.	0.13	n.d.	0.64	n.d.	0.24	0.16	n.d.	0.42
CaO	17.58	18.69	18.39	33.79	n.d.	0.65	2.22	n.d.	0.34
SrO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.33
MgO	0.19	0.44	1.27	2.09	n.d.	1.68	0.25	n.d.	0.14
BaO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ZnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al <sub>2</sub> O <sub>3</sub>	3.41	3.49	3.70	0.56	n.d.	6.57	0.79	n.d.	3.74
Fe <sub>2</sub> O <sub>3</sub>	0.82	0.58	0.72	0.20	n.d.	1.09	0.34	n.d.	n.d.
Ce <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nd <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SiO <sub>2</sub>	4.31	4.37	4.89	3.07	71.23	68.14	16.16	100.40	79.05
TiO <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SO <sub>3</sub>	0.32	1.47	1.04	0.44	n.d.	n.d.	0.61	n.d.	0.24
P <sub>2</sub> O <sub>5</sub>	0.77	1.32	1.03	1.14	n.d.	n.d.	0.45	n.d.	1.91
Total	27.40	30.49	31.04	41.03	71.23	78.37	20.98	100.40	87.17
Oxide	kaolinite								
	03-6	03-7	03-10	03-11	03-12	03-14	08-4		
Na <sub>2</sub> O	0.22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
K <sub>2</sub> O	0.96	2.40	0.69	0.50	3.14	2.47	0.64		
CaO	8.33	5.43	4.93	3.68	5.71	3.03	0.12		
SrO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
MgO	3.07	0.70	2.73	0.97	7.54	3.10	n.d.		
BaO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
ZnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
Al <sub>2</sub> O <sub>3</sub>	23.37	21.73	15.79	9.81	8.53	26.36	31.62		
Fe <sub>2</sub> O <sub>3</sub>	6.19	n.d.	3.86	1.22	5.59	0.40	n.d.		
Ce <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
Nd <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
SiO <sub>2</sub>	33.04	21.94	23.44	14.52	16.16	28.09	46.61		
TiO <sub>2</sub>	0.28	0.32	0.33	0.58	2.55	n.d.	n.d.		
SO <sub>3</sub>	0.69	5.79	0.31	0.34	0.45	5.62	n.d.		
P <sub>2</sub> O <sub>5</sub>	0.52	1.69	0.48	0.32	0.90	1.28	n.d.		
Total	76.67	60.00	52.56	31.94	50.57	70.35	78.99		
Oxide	gypsum		gorceixite		goyazite				
	03-4	03-9	11-1	11-5	11-2	11-3			
	n.d.	n.d.	n.d.	0.23	n.d.	n.d.			
	0.35	0.37	2.17	1.75	2.82	3.03			
	20.30	21.76	1.05	1.03	1.69	2.92			
	n.d.	n.d.	4.40	n.d.	7.28	4.04			
	0.34	0.39	n.d.	0.25	n.d.	0.51			
	n.d.	n.d.	15.93	20.15	4.44	1.15			
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
	1.26	0.97	28.52	28.48	26.06	23.34			
	0.24	0.29	0.31	n.d.	n.d.	n.d.			
	n.d.	n.d.	1.21	n.d.	2.72	1.53			
	n.d.	n.d.	n.d.	n.d.	0.71	n.d.			
	1.74	2.08	12.07	7.79	12.15	31.12			

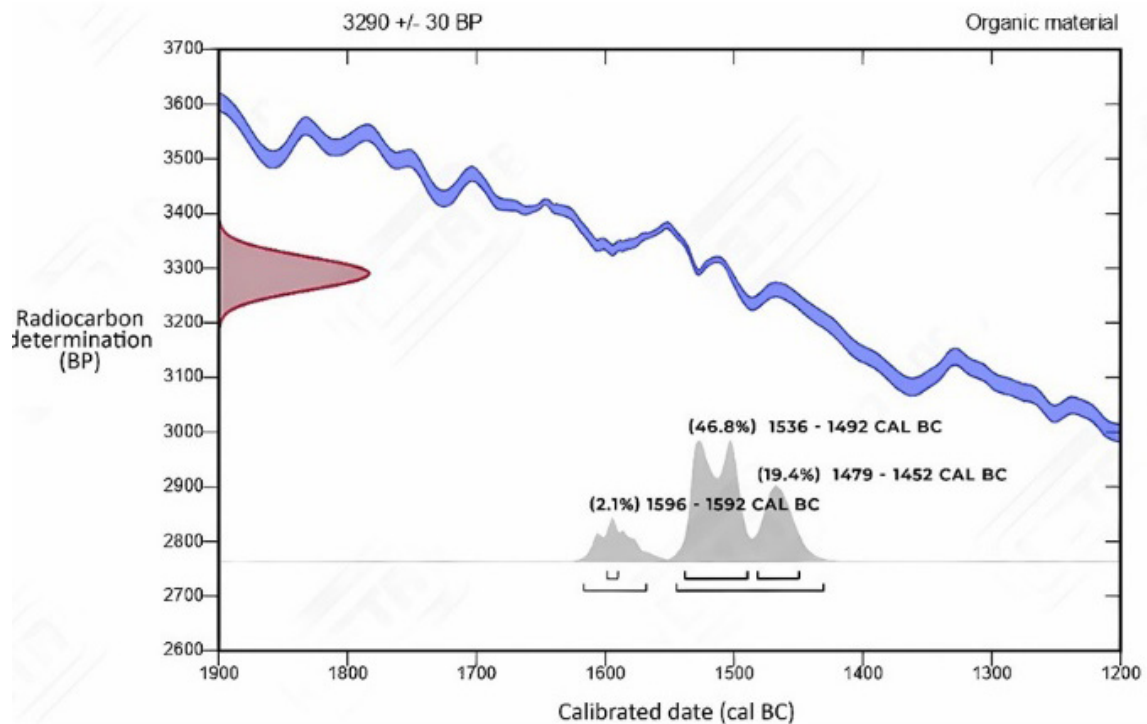
Source: Tatiane de Souza (2025).

Two phosphate minerals belonging to the plumbogummite group were identified, gorceixite,  $BaA_{13}(PO_4)(PO_3OH)(OH)_6$ , and goyazite,  $SrA_{13}(PO_4)(PO_3OH)(OH)_6$ . The joint occurrence of oxalates, phosphates, sulfates, and silicates suggests advanced weathering processes, in addition to biogenic action in crust formation. The results of the EDS analyses were significantly hampered by the nature of the material, which prevented the production of sections with flat faces, this being essential for obtaining quantitative results. The mass percentages included here are merely illustrative of the problems encountered and should not be used for calculating chemical formulas. The numbers serve only to verify the predominant chemical elements at each point analyzed and to infer the corresponding mineral (Figure 8, Table 1).

## DATING

The oxalate sample, after receiving chemical treatment, as specified in the methods section, was sent to the Beta Analytic Inc laboratory and the results are published below.

**Figure 9.** Graph showing probability ranges for the sample ages.



Source: Beta Analytic Inc.

To assess the accuracy (precision and agreement with the actual age) of radiocarbon ( $^{14}C$ ) dating, the most appropriate and widely used statistical test: the Chi-square statistic ( $X^2$  test), frequently applied in the context of Bayesian modeling, used to determine if a set of radiocarbon ages is statistically compatible with each other or suggesting contamination problems in samples from different periods. However, it was not possible to perform the test because more than one sample is required. However, it is possible to observe the general data of the dating result in tables 2 and 3.

**Table 2.** Overall result

Parameter	Value
Beta Number	763897
Radiocarbon age (BP)	3290 ± 30
δ13C (‰)	-18,7
Material	Organic
Calibration method	SHCAL20

Source: Tatiane de Souza (2026).

**Table 3.** Calibrated intervals.

Probability (%)	Age cal BC	Age cal BC	Age cal BP
79.1	1,542	1,433	3,492 – 3,383
16.3	1,614	1,570	3,564 – 3,520
46.8	1,536	1,492	3,486 – 3,442
19.4	1,479	1,452	3,429 – 3,402
2.1	1,596	1,592	3,546 – 3,542

Source: Tatiane de Souza (2026).

## DISCUSSION

Dating oxalates is always problematic as it involves removing what is not oxalate, but when compared to other methods and related studies, it can be completely reliable. The dates produced for Toca do Baixão do Milho are compatible with oxalate dating studies produced by (Steelman *et al.*, 2002) for the Toca do Serrote da Bastiana archaeological site, located in the Serra da Capivara. In this previous study, an AMS date for oxalate obtained by the plasma oxidation method produced a minimum date of (2,490 ± 30 BP). Regarding the date obtained for oxalate at Baixão do Milho, our date is compatible with that of Toca do Serrote da Bastiana, which was obtained via samples of paintings collected above the calcite dated by (Watanabe, 2003). Regarding oxalate dating, note that the dates were corresponding both in rocky support (Baixão do Milho) and in oxalates collected in paintings (Toca do Serrote da Bastiana), had similar results through different dating techniques.

These results disagreed with the age obtained by calcite dating at the Toca do Serrote da Bastiana site, established at 30,000 to 40,000 BP, which involved thermoluminescence and uranium-thorium (U-T) dating (Watanabe *et al.*, 2003). Note that in the U-T method, some of the thorium present in the sample may not have formed through uranium decay but may instead have been present since calcite precipitation. This is explained by the fact that inherited thorium contaminates the system, resulting in artificially old ages, so correction based on isotopic ratios is required, which generates problems with recrystallization and diagenesis. Moreover, calcite often has very low uranium contents and in archaeological environments (e.g., calcite associated with cave paintings, concretions on rock surfaces), there may be water percolation bringing new isotopes, precipitation in multiple overlapping phases (mixing of calcite generations), and contamination by organic matter or detrital particles.

Calcite ( $\text{CaCO}_3$ ) is a very common mineral in geological and archaeological contexts (speleothems, concretions, cave carbonates, deposits on rock surfaces, etc.), and can be dated using various methods, including  $^{14}\text{C}$  when it contains recent carbon. However, its absolute dating involves several challenges as it is highly soluble in slightly acidic water and can undergo dissolution, recrystallization, or ion exchange, opening the isotopic system and leading to the loss or gain of substances, which generates inaccurate ages. Moreover, what is present in the sample may not have formed through decay but may have been present since calcite precipitation. This contaminates the system, resulting in artificially old age; therefore, corrections based on isotopic ratios are necessary. Over time, calcite can undergo recrystallization, altering the isotope distribution, which can partially or completely reset the isotopic clock, mixing different age populations and resulting in hybrid ages that are difficult to interpret. In the case of  $^{14}\text{C}$  dating, calcite can incorporate carbon from the atmosphere, from the dissolution of ancient carbonate rocks, or from recent organic matter, which can also generate ages that are older or younger than the actual age. Therefore,  $^{14}\text{C}$  calcite dating is only reliable in very well-controlled contexts (such as recent speleothems).

Thus, the date produced from calcium oxalate is more reliable in the examined context because it is geologically less transportable and may correspond to fewer episodes of deposition and percolation of other substances. This premise guided the need for the adopted procedure of careful separation of carbonaceous components of biogenic origin.

Correcting the date established by (Watanabe *et al.*, 2003) based on a study of sample contamination and isotopic ratios would be necessary. However, the PNSC researchers preferred to adopt another strategy. They dated new calcite samples from Toca da Serra da Bastiana and other sites in the area, which had an age limit of 12,000 BP regarding Uranium-Thorium. The explanation for correcting these ages is that they are consistent with archaeological phases and traditions, mainly the Northeast Tradition, established by (Guidon, 1982; Martin; Guidon, 2010), which would present a limit of 12.000 BP.

The relevance of detecting contamination and using isotopic ratios to correct the ages established by (Watanabe *et al.*, 2003) would be of paramount importance, since contamination or the entry of foreign materials, whether modern carbon or ancient carbon (dead carbon, aging the sample), during collection or in the environment, completely alters the age and is not compatible with the recent dating established for the area. Therefore, it would be interesting to use the Isotope Exchange method, which is a chemical process in which isotopes in the sample are exchanged with the environment (e.g., carbon from groundwater), altering the original C signature and frequently observed under conditions of high humidity or temperature (Sanna *et al.*, 2010).

The criticism that researchers in the PNSC area make of oxalate dating is that it does not correspond with the stratigraphy and material culture examined in many studies (Boeda *et al.*, 2013; Boeda *et al.*, 2014; Guidon *et al.*, 1994; Parenti, 2001), as it falls far short of the correspondence between age, charcoal dating in the soil, and the characteristics of the material culture. However, it seems that they are always looking for very old sites, and not sites of more recent ages or with different aspects. Therefore, we question why researchers reject oxalate dating and have not performed it on very promising sites such as Toca do Exu da Jurubeba (Farias Filho *et al.*, 2017).

## CONCLUSION

The paintings in Caracol correspond to or are older than 3,290 +/- 30 BP, but we cannot yet specify how much older they are than that because we did not collect direct samples from the paintings and we do not even know if they contain organic material that

can be dated. However, by association with the date established for the rocky support that covers part of the paintings, the dated oxalate enables us to infer that similar ages for this type of material were identified in the Serra das Confusões and the Serra da Capivara, which opens the way for future comparisons and reformulation of dates, in addition to the investigation of other contexts that show sufficient calcite for comparison.

Although Toca do Baixão do Milho did not provide enough calcite to be dated, we agree with certain criticisms of dating by calcite identified in the region. For the Toca do Serrote da Bastiana shelter, it can be considered that recrystallization and deposition processes likely formed the calcite portion of the accretion when water containing soluble calcium carbonate coated the shelter wall. The calcite would have crystallized from solution and then have been deposited on the painting, and some older carbonate could have been incorporated into the liquid without dissolving. Another criticism raised by the authors is that even if the current radioisotope concentration in the bedrock and accretion is accurately measured, it may not accurately reflect the past environment. Therefore, in future studies in the research area, in addition to radiometric issues, there is a need to formulate studies of the geological conditions that may interfere with dating and lead to inaccuracies in the sample ages.

Seeking evidence with unbiased eyes or simply study sites in specific situations is essential. Science is an act of challenging one's own certainties, and in this sense, it is necessary to seek material that corroborates the most recent dating, or even to reformulate the established dating framework by new hypotheses, an action that will be conducted in the study of the Baixão do Milho valley.

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