IN: Jakes, K. (Ed.). 2002. ***Archeological Chemistry***, pp. 22-35. American Chemical Society, Washington, DC.

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AMS Radiocarbon Ages of an Oxalate Accretion and Rock Paintings at Toca do Serrote da Bastiana, Brazil

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At the Toca do Serrote da Bastiana rock shelter in Brazil, a red, iron ochre pictograph of an anthropomorphic figure had become coated with a ‘calcite’ accretion over time. Using X-ray diffraction and Fourier transform infrared spectroscopy, we determined that the accretion also contains whewellite, the monohydrate of calcium oxalate, in addition to calcium carbonate. An AMS radiocarbon date on the oxalate formed from contemporaneous carbon yielded a minimum date of

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2490 ± 30 years BP for the painting. An AMS radiocarbon age of 3730 ± 90 years BP on organic material in the underlying paint layer is consistent with the oxalate result and four direct radiocarbon dates on organic matter extracted from other rock paintings in the same shelter. Our results strongly disagree with a 30,000-40,000 year old age obtained by electron spin resonance and thermoluminescence dating of the accretion.

Controversy has reigned for years about the antiquity of an early human presence in Brazil (*1-4*). Work under the supervision of Niéde Guidon and the Fundação Museu do Homen Americano suggests that humankind was present in Brazil as early as 50,000 years ago, tens of thousands of years before humans were thought to have migrated into the Americas (*5*, *6*). Whereas charcoal and quartzite flakes found at the Pedra Furada site may possibly be linked to natural phenomena *(7-9*), dates on rock art have the advantage that they are most certainly associated with a human presence (*10*). Currently, the Fundação Museu do Homen Americano has initiated research to locate proof of natural fire vestiges in the area surrounding Pedra Furada, but none has been found (*11*). Dates obtained by electron spin resonance (ESR) and thermoluminescence (TL) for the crystallization age of a 'calcite' accretion layer deposited over an ~20 cm tall red anthropomorphic pictograph in the Toca do Serrote da Bastiana shelter located in the state of Piaui further support the early arrival of humans in Brazil (Figure 1). The ESR and TL results suggest that the accretion was formed 30,000-40,000 years ago (*12*). Considering that the pictograph must have been produced prior to the 'calcite' deposition on top of it, this fascinating result would place the pictograph among the oldest dated rock paintings in the world.

In order to verify these results, we tested for calcium oxalate in the accretion layer covering the pictograph in question at the Toca do Serrote da Bastiana shelter. Calcium oxalate crusts are formed from contemporaneous carbon and are ubiquitous as accretions on limestone surfaces (*13-23*). Lichen and other bio-agents are thought to produce oxalate-rich rock crusts, although some nonbiological mechanisms have also been proposed (*13-15*, *17*, *21-24*). Oxalate crusts have been radiocarbon dated in order to obtain maximum and minimum ages for pictographs (*22*, *23*, *25-28*). We radiocarbon dated the oxalate portion of the accretion layer covering the red anthropomorphic pictograph in the Toca do Serrote da Bastiana shelter giving an age of 2490 ± 30 years. If the 30,000-40,000 TL/ESR age had been confirmed by independent means, the antiquity of this painted figure would provide strong support that a human presence was in Brazil far earlier than generally accepted. Unfortunately, that was not the case.

Our research group at Texas A&M University has begun to directly radiocarbon date rock art pigments at several rock art sites in the Serra da Capivara National Park region in collaboration with Niéde Guidon. Using the plasma extraction method to date organic material in the paints, we now have radiocarbon dates on four other images in the Toca do Serrote da Bastiana shelter: 1880 ± 60, 2280 ± 110, 2970 ± 300, 3320 ± 50 (*29* and two previously unpublished dates). In addition, organic material extracted from the pigment of the red anthropomorph in question gave a radiocarbon age of 3730 ± 90 years BP.

Background

In northeastern Brazil, the Serra da Capivara National Park region occupies an area of around 40,000 km^2 located in the southeast quadrant of the state of Piaui. On the edge of the Precambrian crystalline plain of the São Francisco River depression and the mountain ranges (*serras*) of the Permian-Devonian sedimentary basin of the Parnaiba River, the town of São Raimundo Nonato is set in an impressive landscape. For more than 200 km, cliffs formed by erosion with up to 250 m drops form a spectacular border between these two contrasting geological zones. Searches for archaeological sites have been limited to the area between S 8° to 9-1/2° latitude and W 41-1/5° to 43-1/2° longitude around the present day communities of São Raimundo Nonato, São João do Piaui, Canto do Buriti, Anisio de Abreu, and Caracol. The region's rich and diverse prehistoric art includes over 300 rock shelters containing paintings, engravings, or a combination of the two forms of expression. Certain shelters, like Toca do Boqueirão of Pedra Furada, harbor more than a thousand figures; and because many fragments of painted rock have been found buried in archaeological strata, it is estimated that 40% of the images have spalled away. However, in general, most sites are decorated with somewhere between ten and a hundred figures, but sometimes only one. With little doubt, rock art played an important role among prehistoric populations in Brazil.

With human occupation in Brazil possibly spanning as far back as 50,000 years ago, the 30,000-40,000 year old date of the Toca do Serrote da Bastiana rock painting measured by ESR and TL is feasible. Rock art images such as the 35,000-year-old paintings in Chauvet Cave in France demonstrate that rock art can remain visible for tens of thousands of years (*30*). However, it is important to note that European Paleolithic paintings are in protected underground cave environments, while the images in Brazil occur predominantly in open shelters more exposed to atmospheric weathering. In fact, the presence of painted spalled wall fragments in the excavated archaeological sediment suggests that the rock shelter surface is not a permanent canvas (*10*).

Site description

The Toca do Serrote da Bastiana shelter is small, perhaps 3-4 meters wide, with an overhang of only a few meters. It is located at a limestone outcrop where local inhabitants were, until recently, actively dynamiting the rock to process it to lime by heating on-site. That activity has damaged – and had threatened to destroy completely – the rock paintings in the shelter. There are approximately a dozen images there.

Sample Collection

During the summer of 2000, two of us (NG and MWR) visited the Toca do Serrote da Bastiana shelter for sampling. Visual examination of the ~20 cm tall red anthropomorphic motif dated by ESR and TL indicated that an area of about 1 cm^2 of the pictograph was coated with undisturbed 'calcite', the rest having been removed earlier for ESR and TL studies (*12*). The painting itself is a bright, apparently unfaded, red iron ochre color. Rubber gloves were worn throughout sampling and also during later handling in the laboratory to avoid modern contamination. A new surgical scalpel blade was used to remove the accretion layer, while we took care not to dig into the underlying paint pigment. It was easy to accomplish the removal of the accretion and it separated cleanly from the pictograph, leaving the pigment layer intact. The sample was scraped onto a clean square of aluminum foil, wrapped and placed into a sealable plastic bag. A sample of red paint from the same anthropomorphic figure as well paint samples from other images at Toca do Serrote da Bastiana were taken by Guidon and coworkers and then sent to Texas A&M for analysis.

Experimental Methods

Chemical Pretreatment

Procedures for chemically pretreating archaeological samples typically involve an acid-base-acid treatment (*31, 32*). However, we routinely eliminate both acid washes as we have shown them to be unnecessary with our plasma-chemical extraction technique. Carbonate and oxalate carbon are not extracted by the plasma; only organic material was removed for radiocarbon measurements (*33,34*). Samples are immersed in ~1 M NaOH and placed in an ultrasound bath for an hour at 50±5ºC. When the resulting supernatant was colored, subsequent NaOH washes were performed until the supernatant appeared colorless because humic acids appear brownish-yellow in NaOH. Rinsed samples are then filtered through binder-free borosilicate glass filters baked overnight at ~600ºC to remove organic contamination. Humic acids present will stay in solution and pass through the glass filter, removing unwanted organic contamination from the solid paint sample. Plasma extractions are run of dried filtrate material.

Plasma Extraction of Carbon from Pigment Samples

The plasma-chemical extraction method has been used to separate organic carbon from rock art pigment samples for radiocarbon dating and has been described in detail elsewhere (*33-40*). The main advantage of this technique is the ability of the plasma to selectively oxidize organic carbon present in a sample and leave accompanying carbonates and oxalates intact (*33, 34*). Ultra-high purity bottled argon and oxygen (99.999 %) gases were used for all plasmas. A rotary pump and a turbo molecular pump maintain vacuum conditions (~10^{-4} and ~10^{-7} torr, respectively). First, low-temperature oxygen plasmas were used to pre-clean the reaction chamber; these were repeated until $\leq$0.001 mg carbon, as CO_2, was released. Samples were introduced into the chamber via a stainless-steel, copper-gasketed, flange port under a flow of argon to prevent atmospheric CO_2, aerosols, or organic particles from entering the system.

After the chamber was resealed and the sample partially degassed under vacuum, low temperature (<150°C) argon plasmas were used to desorb CO_2 molecules from the sample and chamber walls by inelastic collisions of the non-reactive, but energetic, argon species. The amount of adsorbed CO_2 and water on the sample was thus diminished to correspond to <0.001 mg carbon equivalent as is usual in our procedure.

Next, low-temperature ($\leq$150ºC), low-pressure (~1 torr) oxygen plasmas oxidized organic components of the sample to CO_2. Decomposition of inorganic carbon present (dolomitic limestone rock and calcite/calcium oxalate accretions) was prevented by running the plasmas at low-temperature. Carbon dioxide from the sample was flame-sealed into a glass tube cooled to liquid nitrogen temperature (-194°C), after water had been frozen out with a dry-ice/ethanol slurry (-58°C), and finally sent for radiocarbon analysis at the Center for Accelerator Mass Spectrometry at the Lawrence Livermore National Laboratory (LLNL-CAMS). It was necessary to utilize an AMS measurement due to the small sample size.

Detection and Extraction of Calcium Oxalate

For the accretion covering the red anthropomorph, the presence of both calcium carbonate and calcium oxalate was confirmed by FTIR and powdered XRD. The principal minerals of the accretion layer were calcite (calcium carbonate) and whewellite (calcium oxalate monohydrate). Approximately 3 mg of the powdered sample were pressed into a KBr pellet for FTIR analysis on a Midac M2000 FTIR. The resulting spectrum shows absorption peaks consistent with the presence of oxalate, as well as a large carbonate component (Figure 2). The spectrum also indicates the presence of other constituents, probably silicates (clay or quartz). For XRD analysis, the sample was ground to a fine powder using an agate mortar and pestle. Calcite was determined to be the main constituent of the sample, with some whewellite present.

Due to the uncertainty of the relative amount of oxalate present, the entire remaining sample (~560 mg) was treated at Arkansas State University for the AMS ^{14}C and stable carbon isotope ratio (δ^{13}C) analyses to maximize the probability that sufficient oxalate would be present for viable results. To remove carbonates, the powdered sample was placed in a Teflon beaker and treated with 25 ml of dilute phosphoric acid. After the initial acid/carbonate effervescence ceased, the pH of the solution was adjusted to pH ~ 2 using concentrated phosphoric acid. This pH was maintained for several days to ensure all carbonates were removed. This phosphoric acid treatment was tested and reported in Russ et al. (*25*). A final FTIR analysis established the removal of carbonate by the disappearance of the strong absorption peak at 1405 cm^{-1} and also confirmed the presence of oxalate with absorption peaks at 1618 and 1315 cm^{-1}. The remaining sample was divided into two aliquots with approximately half sent to The University of Arizona AMS facility for ^{14}C analysis and the remaining half to T. W. Boutton at Texas A&M for the δ^{13}C measurement.

Results

An aliquot of the processed sample contained 4.45% carbon, corresponding to 23.7 % CaC_2O_4, and only 0.02 % nitrogen. The small fraction of nitrogen implies a negligible amount of organic matter (except oxalate) in the accretion sample. The remainder of the sample is most likely silicates that do not affect a radiocarbon analysis. The δ^{13}C was measured to be -11.67 ‰, in the range of values determined for oxalate crusts in the Lower Pecos River region of southwest Texas (*25*). These results are compared to the δ^{13}C values for other materials in Table I. Hedges et al. (*41*) reported a similar δ^{13}C value of -10.3 ‰ for an oxalate crust over a rock painting in Argentina. The Brazilian oxalate δ^{13}C value suggests that neither marine carbonates (δ^{13}C ~0 ‰) nor unknown organic materials ($\delta^{13}C$ typically -25‰) will have a significant effect on dating. A radiocarbon measurement on the oxalate sample gave an age of 2,540 ± 60 years BP (AA-42663 on 07-07-01), corrected for a $\delta^{13}C$ of -11.7 ‰ measured at the NSF – University of Arizona AMS Facility. A second measurement on the same graphite target gave an age of 2,470 ± 40 years BP (AA-42664 on 08-05-01), corrected for a $\delta^{13}C$ of -11.6 ‰. These two radiocarbon measurements on the same sample yielded a combined age of 2490 ± 30 years BP.

Table I. Approximate $\delta^{13}C$ values for various materials including the oxalate crust studied here

Source	*$\delta^{13}C$*	*Reference*
C3 plants	-27 ‰	*(42)*
C4 plants	-13 ‰	*(42)*
Woody tissue of C3 plants	-25 ‰	*(32)*
Marine limestones	0 ‰	*(32)*
Atmospheric CO_2 (rural)	-7.8 ‰	*(42)*
Oxalate crusts in Texas	-10.6 ‰[a]	*(25)*
Calcium oxalate sample (Boutton)	-11.67 ‰	
Calcium oxalate sample (UA AMS)	-11.7 ‰	

[a] Average value of oxalate crusts from the Lower Pecos River region of southwest Texas.

The radiocarbon results for organic matter extracted from five different pictograph paint samples taken from Toca do Serrote da Bastiana, including the ~20 cm tall red anthropomorph, are shown in Table II. The red paints contain iron ochre and the black ones are charcoal. The high uncertainty associated with 4BR312 is due to small sample size (~0.020 mg of carbon). We would not normally report a radiocarbon age on such a small sample, but the measurement is consist with the other radiocarbon results and shows that the age of the pictograph is certainly not 30,000-40,000 years old. Typically, >0.050 mg of carbon is necessary to obtain a viable radiocarbon age.

Table II. Radiocarbon Results of Paint Samples

Texas A&M	*AMS Laboratory*	*Description*	*Sample Size (mg C)*	*Radiocarbon Age (years BP)*
4BR309	CAMS-62934	Red “batonnets”	.05	2280 ± 110
4BR310	CAMS-62935	Black sloth 1	.12	1880 ± 60
4BR312	CAMS-67685	Black sloth 2	.02	2970 ± 300
4BR320	CAMS-68108	Black figure	.22	3320 ± 50
4BR366	CAMS-77890	Red anthropomorph	.07	3730 ± 90

Discussion

The radiocarbon date of 2490 years BP obtained on an oxalate accretion covering the red anthropomorph and the direct radiocarbon date on the same figure, as well as dates on four additional pictographs in the shelter, are all inconsistent with a date of 30,000-40,000 years ago determined by ESR and TL (*12*). Both dating methods, ESR/TL and oxalate radiocarbon dating, should yield equivalent dates corresponding to a similar event – the formation of a calcium carbonate and calcium oxalate accretion layer covering the pictograph. Both provide minimum ages for painting given that the pictograph must be at least as old as the calcite/oxalate crust covering it.

Re-crystallization and deposition processes most likely formed the calcite portion of the accretion when water containing soluble calcium carbonate coated the shelter wall. Formation of individual calcite layers would have occurred with multiple events throughout the entire history of the painting even up until the present time. ESR and TL measure accumulated electron traps produced as the newly formed calcium carbonate accretion is exposed to ionizing radiation. If the environmental radiation dose rate is known, then the time of crystal formation or when the accretion was deposited can be determined.

There are various proposed origins of calcium oxalate rock coatings that occur worldwide, including biological sources such as lichen, and bacteria, as well as chemical reactions of dissolved organic acids in rain aerosols at the rock/atmosphere boundary *(13-15, 17, 21-24)*. Nevertheless, the source of carbon is atmospheric, meaning that the carbon is contemporaneous with oxalate crust formation. Thus, the coating can be radiocarbon dated to determine when the oxalate was formed. Oxalate crust formation most likely occurred with multiple sequential events forming microscopic layers. A radiocarbon determination for an oxalate crust, therefore, would be a weighted average of the deposited layers’ ages. With an extreme assumption of uniform oxalate deposition starting 3730 years ago and continuing to the present, the theoretical measured ^{14}C activity, while not identical, is similar to our experimentally determined age of the oxalate accretion. In cases where such coatings are observed to cover pictograph paint layers, radiocarbon dating of the oxalate crust can constrain the production of the image by establishing a minimum age for the rock art (*22, 23, 25-28*).

Our oxalate radiocarbon determination is consistent with the era determined by radiocarbon dates on four other pictographs located in the same shelter. In fact, we have also obtained a direct radiocarbon date of 3730 ± 90 years BP on organic material extracted from the same red figure covered by the oxalate accretion. This plasma-chemical process has been verified by successfully dating known age materials and pictographs with archaeologically constrained ages (*39, 40)*.

How can the discrepancy between the two techniques, based on different assumptions, i.e., radiocarbon versus ESR/TL, be explained? Assuming for the moment that the ESR and TL dates are correct for the time of calcite crystallization, and thus the 'true' age of the oxalate should be in that general age range, we must conclude that both radiocarbon ages of the pigment and oxalate have been skewed drastically by young carbon. The most likely source of modern carbon would be biological microorganisms living in the crust. Only with the inclusion of ~73% modern carbon could we have obtained a measured date of 2490±30 years BP for the oxalate, assuming a 'true' age of 30,000-40,000 years. No bio-contamination was observed under optical microscopy and such a high amount of contamination is unlikely. We have not experienced that level of modern carbon contamination in our twelve years of radiocarbon dating.

If the oxalate radiocarbon age truly represents a minimum age of the painting, what can have affected the ESR and TL dates, making them so much older than ~2,500 years? Since ESR and TL are based on the same assumptions, agreement between the two is perhaps fortuitous. One key assumption in ESR and TL dating is that the dating signal is re-set to zero at the time of origin of the sample. In other words, the time of crystal formation corresponds to the time of interest to geologists and archaeologists (*43*). If as fresh calcite crystallized from solution and then deposited on the painting, some older particulate carbonate could have been incorporated into the liquid without dissolving. This inclusion of Precambrian calcite (>570 million years old) into freshly deposited calcite crystals would skew the ESR /TL dates to be older than the 'true' age. Since the crystallization age of the rock carbonate, possibly being incorporated as wind blown dust, would be millions of years old, a large effect could result. Some support for this scenario may be found in the presence of silicates that we saw in the FT-IR analysis, probably incorporated into the calcite/oxalate accretion as dust. In the Lower Pecos River region of Texas, Russ et al. (*25*) suggests that a silicate component in oxalate crusts is most likely the result of eolian dust adhering to surfaces when damp from dew or fog was present. The fraction of undissolved rock carbonate dust necessary for skewing the ESR and TL dates from 2,500 to 30,000-40,000 years would not be high because of the very ancient age of the rock. Another assumption of ESR and TL dating is that the environmental history of the sample needs to be determined (*43*). The uptake of radioisotopes such as uranium and thorium in the surrounding rock would increase the number of electron traps produced. Subsequent leaching of radioisotopes may have occurred. Even if the current concentration of radioisotopes in the rock substrate and accretion are accurately measured, it may not accurately reflect the past environment.

A reviewer was concerned with the possible inclusion of carbonate carbon during oxalate formation. We cannot totally rule out a fraction of the oxalate carbon arising from dissolved carbonate. But, limestone carbon cannot be the *sole* source of the oxalate carbon because of the C-14 content. The conversion of carbonate carbon to oxalate carbon would result in an oxalate radiocarbon age older than the 'true' age and our conclusion that the accretion layer is not 30,000-40,000 years old would still be valid. Russ et al. (*22*, *23*, *25*) and Watchman et al. *(26-28)* obtained radiocarbon results that suggest oxalate does not contain ^{14}C-free carbon by the superposition of multiple oxalate and known age pictograph paint layers. Furthermore, the oxalate δ^{13}C value of -11.67‰ is closer to atmospheric (-7.8‰) than to marine carbonates (~0 ‰).

Conclusions

Unfortunately, our radiocarbon dates on the oxalate crust and organic matter in the paint layer cast doubt on the exciting ESR and TL dates obtained for the red anthropomorph pictograph at Toca do Serrote da Bastiana. An AMS radiocarbon date on an oxalate crust covering the red anthropomorph yielded a minimum date of 2490 ± 30 years BP for the painting. Another AMS radiocarbon age of 3730 ± 90 years BP on organic material in the underlying paint layer is consistent not only with the oxalate result, but with four direct radiocarbon dates obtained on organic matter extracted from other rock paintings in the same shelter.

Acknowledgments

KLS was partially supported by a Regent's Fellowship from the office of the Vice-Provost for Research at Texas A&M University. Additional funding came from the Fundação Museu do Homen Americano, Brazil, and the Program to Enhance Scholarly and Creative Activities, Office of the Vice-President for Research at Texas A&M University.

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