International Journal of Mass Spectrometry 284 (2009) 142–151

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Characterizing the binders in rock paintings by THM-GC–MS: La Casa de Las Golondrinas, Guatemala, a cautionary tale for radiocarbon dating

Andrew Livingston[a], Eugenia Robinson[b], Ruth Ann Armitage[a,*]

[a] Department of Chemistry, 225 Mark Jefferson, Eastern Michigan University, Ypsilanti, MI 48197, USA
[b] Director of the Proyecto Arqueológico del Área, Department of Sociology, Anthropology, and Criminal Justice, Montgomery College, Rockville Campus, 51 Mannakee Street, Rockville, MD 20850, USA

ARTICLE INFO

Article history:
Received 29 February 2008
Received in revised form 1 December 2008
Accepted 2 December 2008
Available online 11 December 2008

Keywords:
Rock paintings
Rock art
THM-GC–MS
Radiocarbon dating

ABSTRACT

Chemical characterization of the organic material in rock paintings is an important new direction in directly determining the age of such artifacts. Using plasma-chemical oxidation and accelerator mass spectrometry, radiocarbon dates (6250–5550 cal B.C. and 1500–900 cal B.C.) were obtained for two red-pigmented pictographs from La Casa de Las Golondrinas, the largest recorded rock art site in the Guatemalan Highlands. While the dates fell within or near the 6000-year span of human activity at the site, plasma-chemical oxidation yielded significant amounts of carbon from the unpainted tuff samples that were collected for comparison with the paint. The presence of organic material not related to the paint will render a radiocarbon date irrelevant at best. Qualitative analyses using thermally assisted hydrolysis/methylation (THM)-GC–MS were undertaken to clarify the nature of the organic matter in these paint samples from Guatemala and to determine if any binder could be identified in the paint samples. Results of the analyses show only small differences in composition between the paint samples and unpainted substrate. The older date is not related to a binder, but more likely to humic acids derived from soil organic matter that were not removed by the standard chemical pretreatments; that date, then, should not be considered anthropologically relevant to placing the painting activity in time. The results demonstrate the importance of collecting both appropriate substrate and paint samples for any attempt to date rock art. The THM-GC–MS method we describe has demonstrated excellent potential as a rapid screening method for the comparison of substrate and paint samples to determine which ones have the best chance of yielding a reliable direct radiocarbon date.

1. Introduction

Compositional analysis of paintings by chromatographic and mass spectrometric methods is typically undertaken in order to understand the technology employed by the artist, often to inform conservation or to place the painting into an art historical context. Rock paintings are of interest to both archaeologists and art historians, as they are a visual window into the cultures of the past. Such paintings are unique archaeological artifacts, in that they are not a part of the stratigraphic record and are subsequently difficult to place in time. An understanding of the composition of these materials is important for dating the paintings, as direct methods such as radiocarbon analysis must be utilized. Such organic materials as charcoal, bone, wood, leather, and fabric are now routinely placed into the chronology of archaeological sites using conventional radiocarbon dating. In the late 1970s, accelerator mass spectrometry (AMS) was shown to be applicable to small and very old organic materials for determining absolute ^{14}C content [1,2]. It is important to know as much as possible about the nature of the material being dated, particularly for small samples – such as those from rock paintings – where contamination can play a significant role.

1.1. Radiocarbon dating and rock paintings

Before the advent of radiocarbon analysis by AMS, several grams of material were necessary to obtain a reliable decay count using conventional methods. This was a severe limitation for dating rock paintings, as it would have required completely destroying a painting in order to date it. With AMS, samples as small as 100 μg or even less can be reliably analyzed, making direct dating of rock paintings a possibility. The first report of direct radiocarbon analysis of rock art was from a charcoal-pigmented painting in South Africa [3]. Charcoal-based pigments, rich in organic carbon, are ideal substances for radiocarbon dating. Clottes et al. [4] reported the first use

---

* Corresponding author. Tel.: +1 734 487 0290; fax: +1 734 487 1496.
E-mail addresses: alivings2@emich.edu (A. Livingston), eugenia.robinson@montgomerycollege.edu (E. Robinson), rarmitage@emich.edu (R.A. Armitage).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.12.008

of AMS to determine the age of charcoal from Paleolithic rock paintings in France, where significant work continues [5–10]. In North America in the early 1990s, AMS was used directly on samples of charcoal from rock paintings [11,12] and illustrated the so-called "old charcoal" problem. These AMS analyses were undertaken on relatively large (e.g., milligram-sized samples) portions of charcoal paint, which were subjected to the destructive acid–alkali–acid pretreatment typically used on much larger charcoal samples prior to radiocarbon analysis to remove contamination. When charcoal is not present as a pigment in rock art, other organic materials that are easily identified – including beeswax [13] and plant-fiber inclusions [14,15] – have also been used to determine the direct age of rock art by AMS.

Most rock art, unfortunately, has been rendered not in either charcoal or beeswax, but in paint made with a pigment (often red ochre, or iron oxide) mixed with a binder or vehicle to make the paint flow and adhere. Russ et al. [16–19] developed a plasma-chemical oxidation (PCO) method whereby the small amounts of organic carbon remaining from the binder or vehicle in a red pigmented rock painting are selectively removed via oxidation from the inorganic carbon-bearing substrate (in this case, limestone); the carbon dioxide was subsequently radiocarbon dated using AMS. The PCO–AMS technique has since been used to date other inorganic-pigmented paintings [20–29], charcoal paintings [30–35], and oxalate accretions [36] from around the world.

The PCO–AMS technique for radiocarbon dating rock art remains experimental because of the many challenges that exist. The most significant of these comes from extraneous or inherent organic material present in rock painting samples that is not associated with the activity of creating the painting. For instance, soil humic acids can be deposited in or on rock surfaces over time; the age of this contamination is not related to that of the paint, and their presence in paint samples results in erroneous ages. Sometimes human interaction with paintings leaves behind organic material that influences the measured radiocarbon age. When a painting from the Great Gallery in Utah was dated to more than 32,000 years old using the PCO–AMS method, it was found that hydrocarbon contamination was present in the sample, probably due to the application of kerosene to enhance the visibility of the image for photography [37]. This extreme case exemplifies the importance of understanding the origin of the material being dated, and determining that such contamination is not present in either the unpainted rock substrate or the paint itself.

1.2. Characterizing rock painting binders

Understanding the nature of binders in rock paintings is important for conservation, learning about the artists' technology, and especially for dating. Typically, studies have targeted either alone or in combination, lipids [38,39] and proteins [40–42]. Seldom is the analysis directly related to dating a painting. Pecos River genre paintings from Texas are well dated using the PCO–AMS method, yet the binder has not been identified. Studies using gel electrophoresis [19], Raman and FTIR spectroscopies [43–45], and amplification and sequencing of extracted DNA [46] indicated that a binder may have been present in at least some of the Pecos River samples, though subsequent gas chromatography–mass spectrometry [39] and re-examination of the DNA work [46,47] have raised questions about the earlier findings. Controversies over the nature of the organic material that is being dated – exemplified by the work at Laurie Cave in Australia [48–51] – have raised concerns about directly dating rock art without characterization.

Most of the characterization work on rock paintings has not been done in association with radiocarbon analysis. Hedges et al. [52] demonstrated its importance nearly a decade ago. A recent and significant example is the work of Mori et al. [53], wherein characterized proteins were purified and directly dated by AMS. Quantitative analysis of specific classes of compounds (e.g., lipids, proteins, or carbohydrates) by a method like GC–MS or LC–MS would be preferred for characterizing such binders. Small, minimally destructive samples of the pictographs are all that can typically be taken, and that material consists primarily of inorganic substrate and possibly accretion, with only a small portion of paint with even less binder present. Because large amounts of paint such as was obtained by Mori et al. [53] are seldom available, a balance must be struck between a complete quantitative characterization and retaining enough material for a reliable date, while still minimally affecting the integrity and aesthetic quality of the paintings. Qualitative comparisons of the organic material present in the unpainted substrate and the paint will provide evidence for, and clues to the nature of, the binder that has long been presumed to be present. Thermally assisted hydrolysis/methylation (THM)-GC–MS

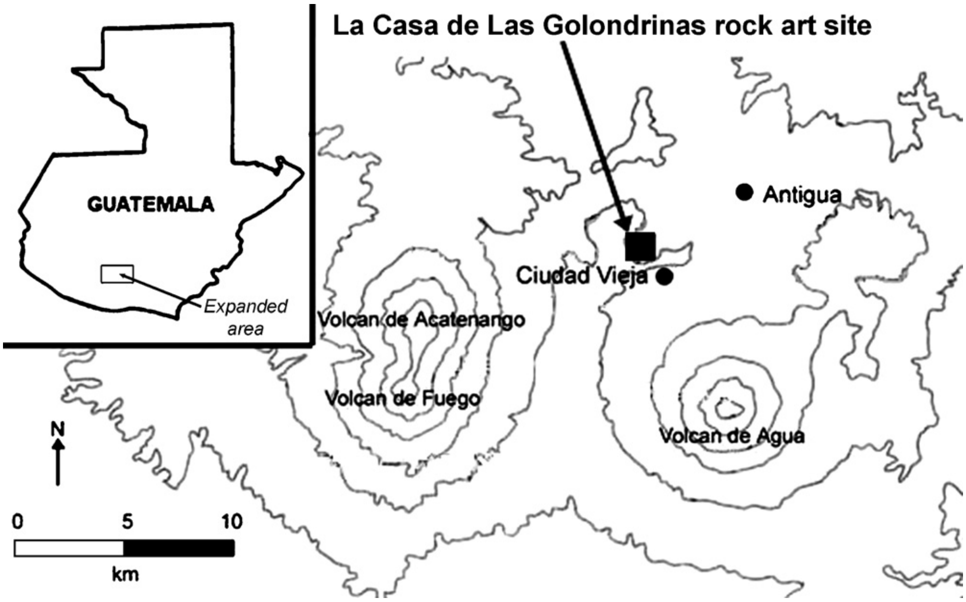

Fig. 1. Map showing approximate location of La Casa de Las Golondrinas in the Guatemalan Highlands.

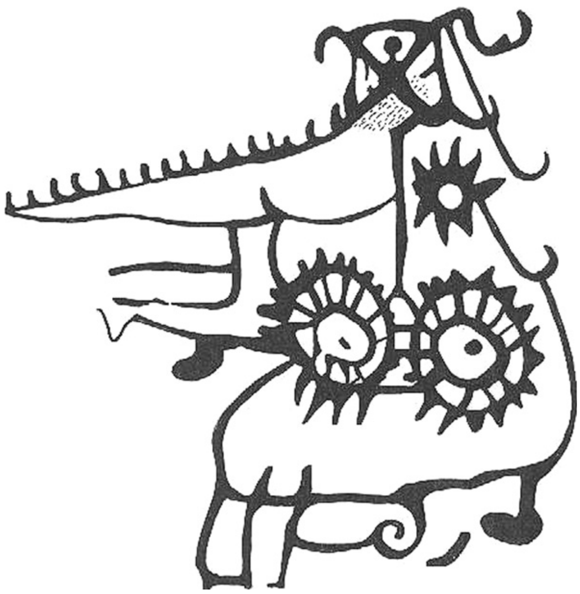

Fig. 2. Drawing of one of the painted images (#8) sampled at La Casa de Las Golondrinas for dating and binder characterization.

is one method that provides this type of qualitative analysis. It has been applied to rock paintings and related residues [52,54–56] in the past, and yields an overview of the composition of the organic material under study. Raman spectroscopy, another method for obtaining such qualitative comparisons of paint samples, has the advantages of being nondestructive (to the microsamples) and able to identify inorganic pigments and minerals as well. However it has significant limitations in studying complex mixtures of organic compounds, particularly those of biological origin. Direct mass spectrometric studies would be ideal for such studies in the future.

1.3. La Casa de Las Golondrinas, Guatemala

La Casa de Las Golondrinas (The House of the Swallows) is located in the Central Highlands of Guatemala in the Antigua Valley near Ciudad Vieja (Fig. 1). The site is the largest recorded rock art site in the Highlands, with more than 225 painted images on the steep volcanic tuff walls; a drawing of one of the paintings is shown in Fig. 2. The site's location, nestled amongst the volcanoes of the Highlands and surrounded by springs, rivers and lakes, indicate that it was likely an important one in the Mesoamerican ritual landscape. Humans have been active in the Antigua Valley for at least the past 6000 years, based on paleoenvironmental and archaeological studies [57]. While there are glyphs and images at La Casa de Las Golondrinas that correspond to known Mayan Late Postclassic iconography (1200–1520 A.D.), most of the images are not datable based on their style or content. The original project sought to use the PCO–AMS technique to directly radiocarbon date samples of the paintings, thereby placing them into the 6000-year sequence of human occupation in the region.

2. Materials and methods

2.1. Materials: rock painting samples from La Casa de Las Golondrinas

The original intent of the project was solely to determine the age of the rock art at La Casa de Las Golondrinas. Samples were collected in August 2003 by one of us (Robinson) with the aid of Dr. Marvin Rowe, Texas A&M University, Lic. Marlen Garnica, co-director of the project and Coordinator of the Archaeology Program at San Carlos University, Guatemala City; and Ramiro Martinez, an archaeologist interested in rock art. Gloves were worn during sample collection to prevent contamination; a fresh pair was used each time a new area was sampled. Samples were removed by scraping the painted surface with a sterile scalpel blade and collecting the resulting powder or flakes of paint onto cleaned aluminum foil. The foil was folded around the samples, and then the packets were wrapped in additional foil and sealed into zip-top plastic bags. The samples collected or planned are listed in Table 1; only those in bold were a part of the chemical analyses reported here. In the case of Sample #4, the white and red paint was easily removed from the heavily eroded painting. In all others, the paint was extremely difficult to remove from the volcanic tuff surfaces, resulting in very small, flake-like samples. Typically, a sample about $3\ \mathrm{cm}^2$ is necessary for radiocarbon analysis by the PCO–AMS method. For Samples #3 and #13, portions of the unpainted substrate were collected as well for comparison. Ideally, substrate samples should have been collected for all of the paint samples, but the difficulties in sampling the hard volcanic tuff made this impossible for the majority of the paintings.

Table 1
Rock painting samples collected from La Casa de Las Golondrinas; those in bold were a part of the chemical characterization study.

Sample number	Location	Description
1	Area B, painting 8	Planned but not collected
2	Area E, painting 18	Small flake of red pigment
3B	**Area E, group 12, painting 64**	**Red pigment with calcite**
3C	**Next to 3B**	**Unpainted substrate for Sample 3B**
4	**Area C, ∼1 m below painting 8**	**White and red pigment mixed**
5	**Area D**	**Red pigment, very small sample**
6	**Area C, painting 16, the Crab**	**Red pigment, small sample**
7	**Area E, painting 86**	**Red pigment, v. small sample**
8	**Area E, painting 50**	**Pink pigment from rayed eyes**
9	n/a	Gourd sample (not paint)
12	**Area A, painting 16**	**Red pigment, small sample**
13	**Area A, painting 23**	**Heavily weathered red pictograph**
13B	**Next to sample 13**	**Unpainted substrate for #13**
14	Area A, painting 16	Monkey with tail, very small sample
15	Area B, painting 1	Blue paint

The materials collected were then transferred to our laboratory at Eastern Michigan University for plasma-chemical oxidation. Upon inspection, two of us (AJL and RAA) determined that the samples were likely too small to yield reliable radiocarbon dates. We determined that the materials collected would at least provide an opportunity to combine chemical characterization of the organic material with the plasma-chemical oxidation technique, something that had not been done in a systematic manner before.

2.2. Methods: plasma-chemical oxidation and accelerator mass spectrometric dating

The paint samples were evaluated visually to determine which ones were most likely to provide sufficient carbon for an AMS radiocarbon date. All samples were examined microscopically at 10×, and any extraneous material like fibers and insect parts were removed. The samples were then pretreated by sonicating in either a base wash (1 M NaOH, 50 ± 5 °C, 60 min) to remove humic acid contamination (a standard procedure in radiocarbon analysis of charcoal-pigmented paintings) or deionized water to remove surface soil and dust. After drying the samples, the material was placed into a clean glass boat and placed into the plasma-chemical oxidation chamber. The chamber was maintained at a vacuum pressure

Table 2
Pretreatment and plasma conditions and results for paint and tuff samples from La Casa de Las Golondrinas.

Sample	Pretreatment	Plasma conditions	Results	Radiocarbon results
Sample 3B paint	DI water rinse	n/a	–	–
Sample 3C unpainted tuff	DI water rinse	30 min Ar, 75 min O_2	130 μg C	–
Sample 4 paint	DI water rinse	30 min Ar, 61 min O_2	45 μg C	CAMS #116948, 3010 ± 90 BP
Sample 5 paint	DI water rinse	n/a	–	–
Sample 6 paint	DI water rinse	n/a	–	–
Sample 7 paint	DI water rinse	60 min O_2	7 μg C	–
Sample 8 paint	NaOH rinse	60 min O_2	40 μg C	CAMS #127361, 6890 ± 160 BP
Sample 12 paint	DI water rinse	60 min O_2	8 μg C	–
Sample 13 paint	NaOH rinse	n/a	–	–
Sample 13B unpainted tuff	NaOH rinse	30 min Ar, 60 min O_2	60 μg C	–

of $\sim 10^{-7}$ Torr. Vacuum integrity checks (VICs) prior to plasma-chemical treatment indicated that no significant leaks were present in the system. We assume, as a worst case scenario, that all pressure increase during the 60-min VIC arises from carbon dioxide; as long as the pressure increase corresponds to less than the contamination background in the accelerator mass spectrometer (typically 0.5–1 μg C), the increase is considered inconsequential. All gases were of ultra-high purity grade (99.999 + %). Initially, we applied a 30-min Ar plasma (p_{Ar} = 200 mTorr, RF power = 40 W) to the samples to sputter away any surface-adsorbed atmospheric CO_2. Dr. Rowe, the originator of the plasma-chemical method for dating rock art, has since eliminated using Ar plasmas for surface cleaning, as little effect was noticed in the resulting radiocarbon dates (personal communication, 2005). Following or in lieu of Ar plasmas, then, a 60-min O_2 plasma ($p_{o_2} = 1$ Torr, RF power = 100 W) was applied. The oxygen plasma has been shown to react with organic carbon in the paint samples at a sufficiently low temperature (~150 °C) that the inorganic oxalates and carbonates present are unaffected [20]. Ideally, 100 μg of carbon as carbon dioxide is preferred to obtain a reliable radiocarbon date. If at least 45 μg C was produced from a paint sample, it was collected by cooling a glass finger on the plasma system with liquid nitrogen. The glass tube was then sealed off and sent to the Center for Accelerator Mass Spectrometry at the Lawrence Livermore National Laboratory for radiocarbon analysis. Pretreatment and plasma conditions and radiocarbon results for the Golondrinas samples are listed in Table 2.

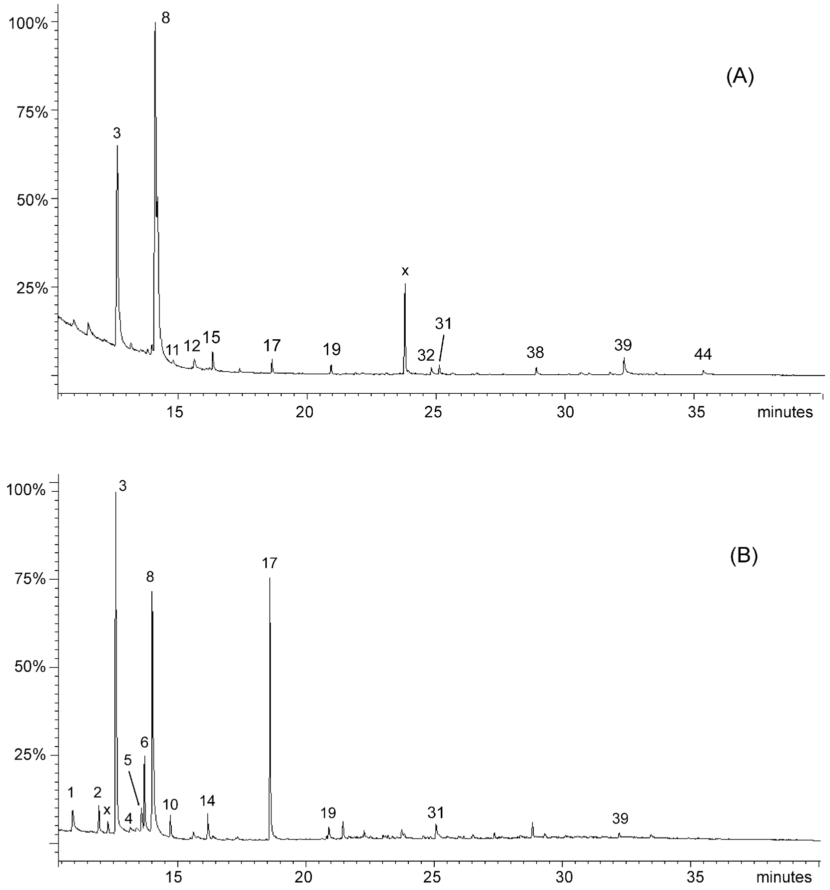

Fig. 3. Total ion chromatograms for unpainted tuff samples from La Casa de Las Golondrinas: (A) #3C and (B) #13B.

2.3. Methods: thermally assisted hydrolysis/methylation-GC–MS

Chemical characterization of the organic matter found in the paint samples from La Casa de Las Golondrinas was carried out because so few of the samples yielded sufficient CO_2 for an AMS radiocarbon date, and because the substrate samples yielded large amounts of carbon.

THM-GC–MS was carried out using a Varian 3800-CP gas chromatograph equipped with a Chromatoprobe$^{\text{TM}}$ sample inlet system. Similar to a pyrolyzer, the Chromatoprobe allows for the introduction of solid samples into a ballistically heated injection port. While this technique is much slower and limited to a maximum temperature of 400 °C, a comparison by Brown-Sinha [58] showed that the Chromatoprobe system yielded results indistinguishable from those obtained with a standard pyrolyzing unit [56]. A small portion of the paint or substrate sample – sufficient to be seen – was placed into a clean glass vial. Approximately 1 μL of the derivatizing agent, tetramethylammonium hydroxide (25% in methanol, Alfa Aesar) was added to the sample, which was then placed into the Chromatoprobe and inserted into the injector port. The injector, held at 40 °C initially, was programmed to 85 °C to desolvate and then heated rapidly (at the maximum rate of 200 °C min^{-1}) to the derivatization temperature of 300 °C. The resulting THM thermochemolysis products were swept under splitless conditions by a flow of 9.3 psi UHP helium onto the VF-5ms column (Varian, Inc.: 5% phenyl PDMS stationary phase, 30 m long × 0.25 mm i.d., 0.25 μm film thickness). The GC oven was held at 40 °C for 5 min, then increased at a rate of 6.5 °C min^{-1} to a temperature of 250 °C, at which it was held for 10 min. A Saturn 2200 ion trap mass spectrometer in electron impact ionization mode, over the range of m/z 35–650, served as a detector. The ion trap was held at 150 °C, while the transfer line and manifold were maintained at 170 °C and 35 °C, respectively. Identification was carried out using standards along with the NIST 2002 mass spectral database, and an additional database, Mass Spectra of Geochemicals, Petrochemicals and Biomarkers (J.W. DeLeeuw, ISBN 0471647985, published by Wiley–VCH).

3. Results and discussion

3.1. Plasma-chemical oxidation results and radiocarbon dates

The two samples, #3 and #13, that had substrate collected for comparison were particularly troublesome for radiocarbon dating. Plasma-chemical oxidation revealed that significant amounts of organic matter – indeed, enough for an AMS radiocarbon date – were present in the unpainted tuff. The PCO sample preparation method was first proposed as a viable method for radiocarbon dating rock paintings because it was selective for organic carbon in the presence of inorganic carbon [14–17]. One of the significant drawbacks to the method, long acknowledged by the originators of the method [59], is that the plasma oxidizes all organic material present without discrimination between the age-diagnostic carbon present in the binder and that which resides on the surface as a result of groundwater deposition or biogeochemical activity from bacterial or lichen colonies on the surface. Depending on the source of this contaminating material, it may be either older or younger than the binder, thus rendering the resulting radiocarbon date meaningless.

The plasma yields were quite low for the two dated samples, #4 and #8, at the absolute minimum that we will consider submitting for AMS radiocarbon analysis, and gave quite different ages, though both fell within or near the 6000-year range over which the Golondrinas site was utilized. Unpainted tuff from these specific locations was not provided. We were therefore unable to determine if the radiocarbon dates for these samples were reliable based on their plasma-oxidizable carbon content. Comparison of the composition of the organic material in the other unpainted substrate samples to that of the paint samples was extremely important to determining the relevance of the measured radiocarbon dates.

3.2. THM-GC–MS results

3.2.1. Substrate samples-unpainted

Only two samples of unpainted tuff substrate were provided. Both yielded significant amounts of carbon by the PCO–AMS method (Table 2), indicating that the paint samples associated directly with these backgrounds were unlikely to yield reliable radiocarbon dates. In the past, this was attributed to an unknown source of contamination; this study is the first to directly compare PCO–AMS results to chemical analyses of the same samples. Fig. 3 shows the total ion chromatograms for the two unpainted substrate samples from La Casa de Las Golondrinas. The compounds are identified by number in Table 3, and mass spectra for some of the compounds, with database identifications, are shown in Fig. 4.

Methoxymethylbenzene and N,N-dimethylbenzenemethanamine are observed in all samples and blanks with TMAH present and are thus not diagnostic. Siloxanes and phthalates are contaminants from the PDMS stationary phase, septa, etc. and are identified in the chromatograms with a letter “x” rather than an identifying number. The compounds endogenous to the unpainted substrate are predominantly short chain fatty

Table 3
Peak identification for chromatograms.

Peak number	Identification
1	Hexanoic acid, methyl ester (C6:0)
2	1-Ethoxyoctane
3	Methyoxymethylbenzene
4	4-Methoxy-2-butenoic acid, methyl ester
5	Heptanoic acid, methyl ester (C7:0)
6	2-Ethyl-1-hexanol
7	Butanedioic acid, dimethyl ester
8	N,N-dimethylbenzenemethanamine
9	2-Ethyl-hexanoic acid, methyl ester
10	N,N,2-trimethylbenzeneamine
11	Methylbutanedioic acid, dimethyl ester
12	Benzoic acid, methyl ester
13	Nonanal
14	Octanoic acid, methyl ester (C8:0)
15	N,N,4-trimethylbenzenemethanamine
16	Methylhexofuranoside
17	Nonanoic acid, methyl ester (C9:0)
18	3,5-Dimethoxyphenol
19	Decanoic acid, methyl ester (C10:0)
20	1,2,3-Trimethoxybenzene
21	1,2,4-Trimethoxybenzene
22	Trimethyltriazinetrione
23	Unknown, bp = 219m/z
24	Diethylcarbamodithioic acid, methyl ester
25	2-Ethyl-6-hydroxybenzoic acid, methyl ester
26	Hexamethylinositol
27	Octanedioic acid, dimethyl ester
28	1-Chlorodecane
29	3,4-Dimethoxybenzaldehyde
30	Methyl-4-tert-butylbenzoate
31	Dodecanoic acid, methyl ester (C12:0)
32	1,4-Benzenedicarboxylic acid, dimethyl ester
33	Nonanedioic acid, dimethyl ester
34	3,4,5-Trimethoxybenzaldehyde
35	3,4-Dimethoxybenzoic acid, methyl ester
36	Unknown, bp = 91m/z
37	Tetradecanoic acid, methyl ester (C14:0)
38	Pentadecanoic acid, methyl ester (C15:0)
39	Hexadecanoic acid, methyl ester (C16:0)
40	2,3,4,6-Tetramethoxystyrene
41	Hexadecenoic acid, methyl ester (C16:1)
42	Heptadecanoic acid, methyl ester (C17:0)
43	Octadecenoic acid, methyl ester (C18:1)
44	Octadecanoic acid, methyl ester (C18:0)

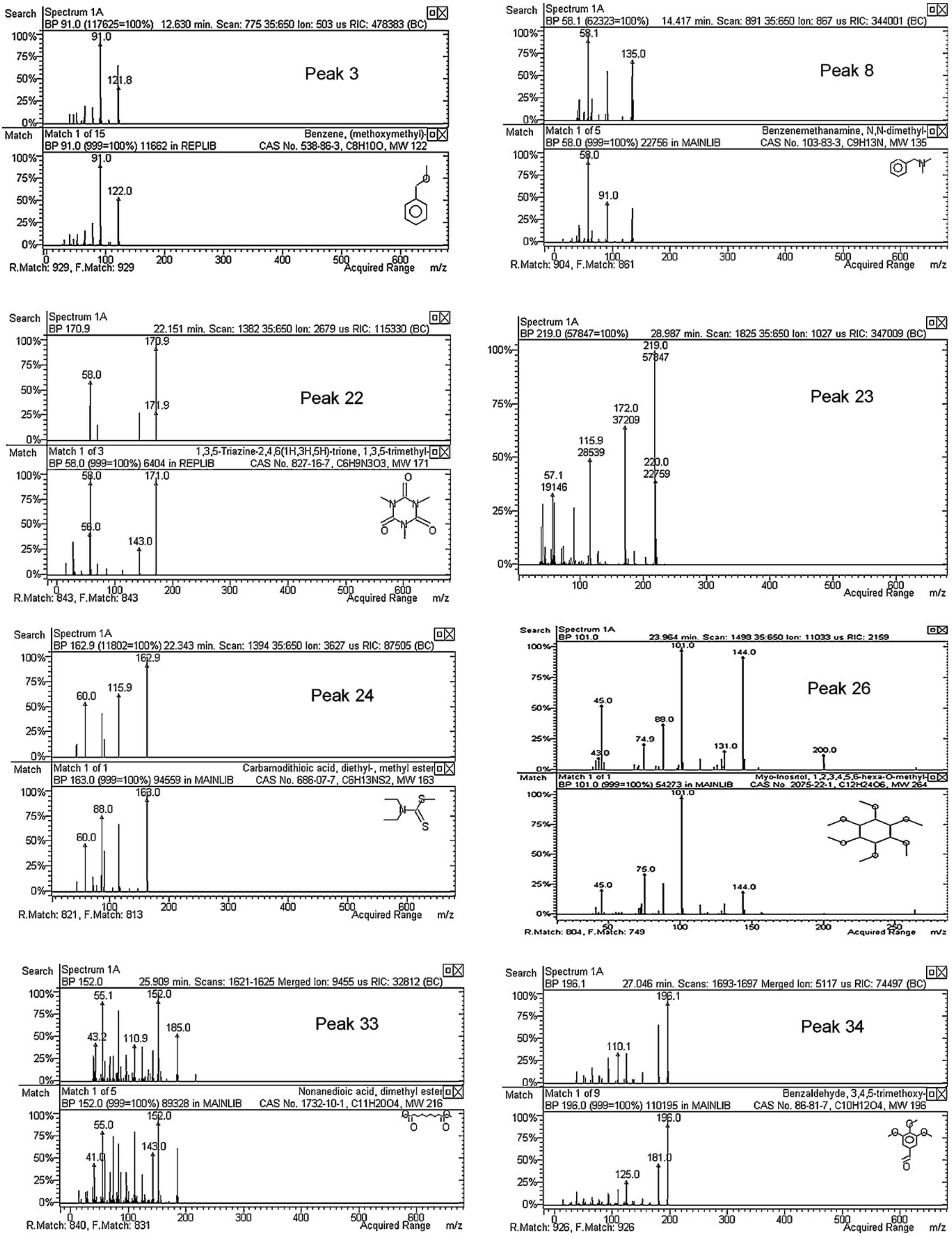

Fig. 4. Selected mass spectra for the compounds listed in Table 3, with database matches shown for comparison.

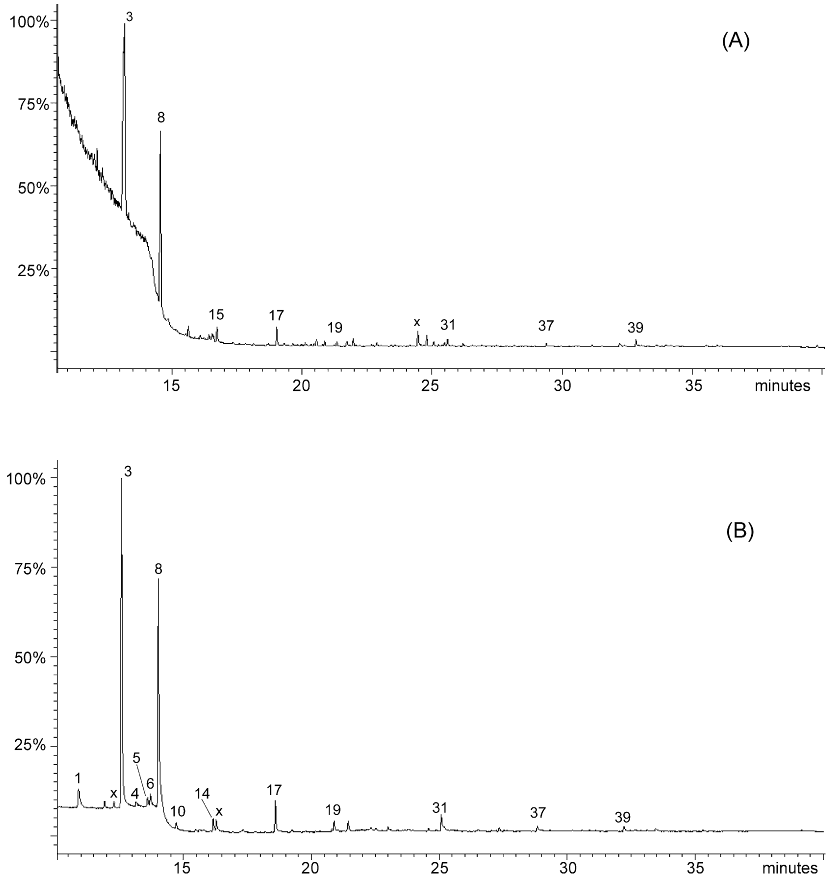

Fig. 5. Total ion chromatograms for paint samples from #3 (A) and #13 (B).

acids ($C_{6:0}$–$C_{12:0}$), though Sample #3C shows the presence of some longer chain lipids. These fatty acids may be derived from soils or originate from such biological contamination as bacteria, fungi, and lichen on the tuff surfaces. Methyl derivatives of phenolic compounds, associated with humic substances, were not observed in either of the substrate samples. A quantitative comparison by Spades and Russ [39] showed that lipid concentrations in rock paintings from the 41VV75 site in Texas were no higher than that of the unpainted substrate limestone, indicating that though lipids were present in the paint their presence was not indicative of a binder. The lipids were likely the source of the CO_2 produced by the PCO method.

3.2.2. *Paint samples*

Fig. 5 shows the total ion chromatograms (TICs) resulting from the THM thermochemolysis of the paint Samples #3B and #13. There are few significant differences between the composition of the unpainted tuff (#3C, Fig. 3A) and paint (#3B, Fig. 5A). Ideally, a marker compound, specific to a binder would be observed in the paint and not in the substrate. As has already been stated, lipids are poor qualitative biomarkers for rock paintings, as they can originate from sources not related to the binder. Proteins (as amino acid derivatives) and carbohydrates might be better markers, though they are far more susceptible to leaching and degradation than the hydrophobic lipids. Differences in the TICs in Figs. 3 and 5 are primarily in the background and may have more to do with day to day variability than with compositional differences in the two materials. No binder is obviously present in the red pigment Sample #3B.

Similarly, the composition of the paint in Sample #13 (shown in the TIC in Fig. 5B) and that of the substrate are qualitatively the same. Nonanoic acid (peak 17) appears to be present in significantly larger quantities in the substrate than in the paint; quantitative extraction and derivatization would confirm this, though it would not identify the source of this compound. The chromatograms indicate that no evidence of a binder is present in the paint from Sample #13 either. This could mean that a binder was once present and has since decayed or that something like water was utilized as vehicle for the pigment by the artists who made these images. Samples #3B and #13 were poor candidates for radiocarbon analysis, and they illustrate the utility of using qualitative THM-GC–MS as a screening method for selecting – or eliminating – samples for further PCO–AMS.

The composition of Sample #4, which yielded a radiocarbon date of 1500–900 cal BC (95.4% probability, calibrated using the IntCal04 dataset [60] using OxCal v.3.10 [61,62]) by the PCO–AMS method [63] is shown in the total ion chromatogram in Fig. 6. The methyl ester of diethylcarbamodithioic acid (peak 24) was the major compound observed in the TIC for Sample #4; this compound has been observed as an environmental contaminant in other THM thermochemolysis studies [64]. This same compound was also present in several other samples run within a few days of each other, as is the unknown compound (peak 23) with a base peak at m/z 219. These contaminants are unlikely to have been present on the native paint sample and probably originated either from the instrument or from the sample preparation for the THM-GC–MS and were thus not present in the plasma-oxidized material that yielded the radiocarbon date.

Of particular interest in Sample #4 are peaks 16 and 26, which are both carbohydrates. Long chain fatty acids, including unsaturated $C_{18:1}$, were also observed, as was trimethyltriazinetrione, a nitrogen-containing compound. These compounds might be

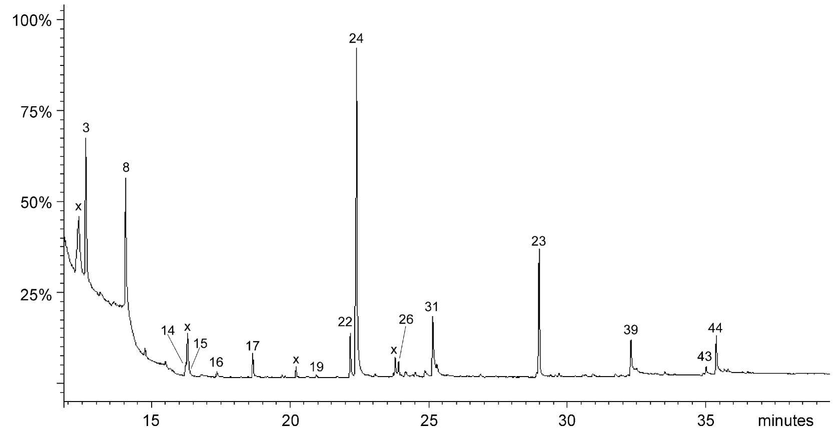

Fig. 6. Total ion chromatogram for paint Sample #4, which yielded a date of 3010 ± 90 uncalibrated radiocarbon years before present.

indicative of a plant- or animal-derived binder. Definitive characterization of that binder requires a quantitative comparison between the paint and a substrate sample from that same area of the rock art panel to rule out the possibility that the carbohydrates and lipids do not have an environmental origin. Therefore, although the measured date fell within the rather wide 6000-year range for the Golondrinas site, we cannot state categorically that the organic material extracted by the plasma and subsequently dated was actually relevant to age of the desired event, the creation of the painting. These results show the importance of understanding the composition of the paint and its substrate when applying the PCO–AMS method to radiocarbon date rock art not made with a readily identifiable organic constituent like charcoal.

Sample #8 was more problematic. The radiocarbon date for #8 fell at the outermost limit for the expected range at the site. The total ion chromatogram for #8 is shown in Fig. 7. A large number of compounds were observed in #8, including fatty acids (C_6–C_{18}, $C_{18:1}$) and a number of methyl derivatives of phenolic compounds characteristic of humic acids from soil organic matter, even though the sample was washed with base prior to dating (and analysis). Treatment of rock painting samples with 1 M NaOH is supposed to remove humic acids; this is part of the standard acid–alkali–acid pretreatment for charcoal and other macroscopic artifacts prior to radiocarbon dating [6,8,65]. Charcoal pigments are particularly susceptible to contamination from water-borne soil organic matter, and the importance of treating such samples prior to dating has long been established [6,8,9]. Pace et al. [66] showed that the base treatment was not detrimental to the dating of the red pigmented Pecos River genre paintings of Texas. The general effect of the treatment on what likely is only a trace amount of binder – rather than macroscopic amounts of cellulose and lignin from charcoal – is not well understood. Studies underway in the Armitage laboratory show that carbohydrates from plant-derived binders in particular are significantly leached out by this treatment.

The age of soil organic matter is not related in any way to that of the paint; it can be older or younger than the binder, and probably is made up of both younger and older carbon, which is why it must be removed prior to dating the paint. Thus a radiocarbon date for a humic-contaminated binder is at best irrelevant for placing the paint in time. To determine if the compounds observed in the TIC for Sample #8 were consistent with soil organic matter from the site, it would be best to examine the composition of the soil itself. Unfortunately, no soil sample was collected during sampling. Instead, the humic fraction extracted from Sample #9, a gourd that was buried as part of a cache at the site, was subjected to THM-GC–MS. All of the compounds derived from humic acids (peaks 20, 21, 29, 34, 35, and 40 in Fig. 7) observed in Sample #8 were also found in the humic fraction from the gourd. Therefore in the case of the paint Sample #8, we believe that the measured radiocarbon date is most probably linked to the soil-derived humic substances that were not completely removed by the standard alkaline pretreatment. Further work to understand and optimize chemical pretreatments for these kinds of paintings is ongoing.

Samples #7 and #12 yielded almost no carbon dioxide when subjected to the PCO method. Samples #5 and #6 were not plasma treated because they were deemed too small to yield measurable carbon. The qualitative results for these paint samples are summarized in Table 4. Although little organic matter was expected to be

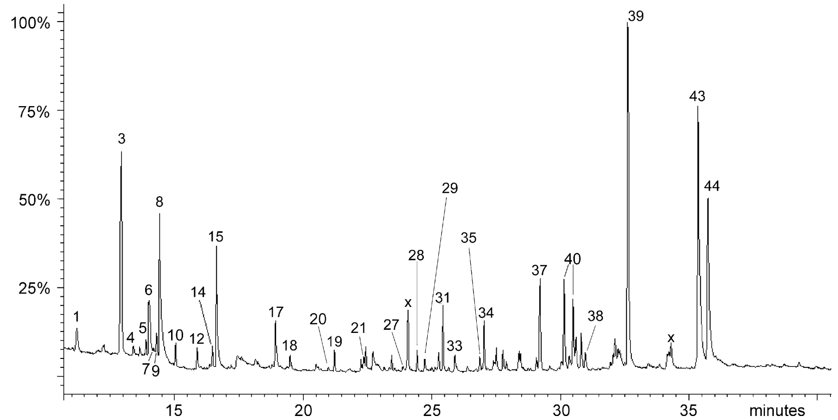

Fig. 7. Total ion chromatogram for paint Sample #8, which yielded a date of 6890 ± 160 uncalibrated radiocarbon years before present.

Table 4
Comparison of the qualitative compositions of the other Golondrinas paint samples investigated.

Identification	Paint samples			
	#7	#12	#5	#6
Methyoxymethylbenzene	x	x	x	x
2-Ethyl-1-hexanol			x	
N,N-dimethylbenzenemethanamine	x	x	x	x
Benzoic acid, methyl ester		x		
Nonanal	x			
Octanoic acid, methyl ester (C8:0)		x		
N,N,4-trimethylbenzenemethanamine	x			
Methylhexofuranoside	x			
Nonanoic acid, methyl ester (C9:0)	x	x	x	
Decanoic acid, methyl ester (C10:0)	x	x	x	
Trimethyltriazinetrione	x		x	
Unknown, bp = 219 m/z	x			
Diethylcarbamodithioic acid, methyl ester	x			
2-Ethyl-6-hydroxybenzoic acid, methyl ester	x			
1-Chlorodecane			x	
Methyl-4-tert-butylbenzoate		x		
Dodecanoic acid, methyl ester (C12:0)	x	x	x	
1,4-Benzenedicarboxylic acid, dimethyl ester		x	x	
Nonanedioic acid, dimethyl ester	x	x	x	
N,N′-diethyl-6-methoxytriazinediamine	x			
Unknown, bp = 91 m/z		x	x	
Tetradecanoic acid, methyl ester (C14:0)		x	x	
Pentadecanoic acid, methyl ester (C15:0)		x	x	
Hexadecanoic acid, methyl ester (C16:0)	x	x	x	
Hexadecenoic acid, methyl ester (C16:1)			x	
Heptadecanoic acid, methyl ester (C17:0)			x	
Octadecenoic acid, methyl ester (C18:1)	x	x	x	
Octadecanoic acid, methyl ester (C18:0)	x	x	x	

present in Sample #7 based on the plasma results, the qualitative results showed, amongst several lipids, one carbohydrate and two nitrogen-containing compounds. The reason for the discrepancy between the two analyses may be related to the surface-selective nature of the plasma-chemical oxidation process and the bulk characterization obtained from THM-GC–MS. Depth profiling studies using a surface-sensitive technique like secondary ion mass spectrometry would aid in understanding how the composition of the paint differs spatially within the sample, and further clarify how the plasma-chemical oxidation actually affects the composition.

For the most part, both Samples #7 and #12 had compositions similar to the other samples from La Casa de Las Golondrinas. Sample #12 consisted mainly of fatty acids at relatively low concentrations, consistent with the plasma-chemical oxidation results. Sample #5, had it been larger (only a small 2 mm^2 flake was provided), might have been a good candidate for radiocarbon analysis, as there were significantly more of the longer chain and unsaturated lipids present in this sample, possibly indicative of a binder. Again, though, it is difficult to know without comparing the composition to that of the substrate from that specific area of the rock face. No significant signal (aside from the non-diagnostic methoxymethylbenzene and N,N-dimethylbenzenemethanamine) was obtained for replicate analyses of Sample #6.

Ideally, a marker compound or class of compounds would be isolated from rock painting samples like those from La Casa de Las Golondrinas and then directly dated by accelerator mass spectrometry. Sampling limitations typically preclude this kind of treatment. Direct AMS dating of lipids (specifically $C_{16:0}$ and $C_{18:0}$) extracted from pottery sherds has proven that even this approach may not be sufficient to unquestionably date residues like rock paintings [67].

4. Conclusions

This study illustrates the importance of understanding the origin of organic matter in rock paintings, especially when attempting to apply direct radiocarbon dating to place the paintings in time. The work presented here is by no means the final word on the feasibility of using PCO–AMS to date rock art. It should be viewed as a cautionary tale in selecting appropriate paint and substrate samples for future analyses. We have shown here that THM-GC–MS has potential as a screening method for choosing which rock painting samples to subject to further study with the PCO–AMS sample preparation and dating methodology. Much work remains in this area, as there is significant archaeological interest in directly dating rock art.

Acknowledgements

The authors thank Marvin Rowe, Marlen Garnica, and Ramiro Martinez for their help in collecting the samples for this study and their support throughout the project. Funding for the project was provided by a Research Grant (#7527-03) from the National Geographic Society. One of us (RAA) was supported by a Faculty Research Fellowship from the EMU Provost's Office, while another (AJL) received two EMU Honors College Undergraduate Fellowships to carry out the analyses. Financial support was also provided by the EMU Chemistry Department, the Sellers' Fund, and the EMU College of Arts and Sciences.

References

[1] D.E. Nelson, R.G. Korteling, W.R. Stott, Science 198 (1977) 507.
[2] C.L. Bennett, R.P. Beukens, M.R. Clover, H.E. Gove, R.B. Liebert, A.E. Litherland, K.H. Purser, W.E. Sondheim, Science 198 (1977) 508.
[3] N.J. Van der Merwe, J. Sealy, R.S. Yates, Afr. J. Sci. 83 (1987) 56.
[4] J. Clottes, J. Courtin, H. Valladas, Rock Art Res. 9 (1992) 122.
[5] J. Clottes, A. Beltran, J. Courtin, H. Cosquer, Antiquity 66 (1992) 583.
[6] H. Valladas, Meas. Sci. Technol. 14 (2003) 1487.
[7] H. Valladas, J. Clottes, Antiquity 77 (2003) 142.
[8] H. Valladas, N. Tisnerat-Laborde, H. Cachier, M. Arnold, F.B.d. Quiros, V. Cabrera-Valdes, J. Clottes, J. Courtin, J.J. Fortea-Perez, C. Gonzalres-Sainz, A. Moure-Romanillo, Radiocarbon 43 (2001) 977.
[9] H. Valladas, H. Cachier, P. Maurice, F. Bernaldo de Quiros, J. Clottes, V.C. Valdes, P. Uzquiano, M. Arnold, Nature 357 (1992) 68.
[10] H. Valladas, H. Cachier, M. Arnold, Rock Art Res. 7 (1990) 18.
[11] P.R. Geib, H.C. Fairley, J. Field Archaeol. 19 (1992) 155.
[12] M.M. Farrell, J.F. Burton, N. Am. Archaeol. 13 (1992) 219.
[13] D.E. Nelson, G. Chaloupka, C. Chippendale, M.S. Alderson, J.R. Southon, Archaeometry 37 (1995) 151.
[14] N. Cole, A. Watchman, Rock Art Res. 9 (1992) 27.
[15] A. Watchman, N. Cole, Antiquity 67 (1993) 355.
[16] J. Russ, M. Hyman, H.J. Shafer, M.W. Rowe, Nature 348 (1990) 710.
[17] J. Russ, M. Hyman, H.J. Shafer, M.W. Rowe, Plasma Chem. Plasma Process. 11 (1991) 515.
[18] J. Russ, M. Hyman, M.W. Rowe, Radiocarbon 34 (1992) 867.
[19] J. Russ, M. Hyman, M.W. Rowe, Arch. Nat. Sci. 1 (1993) 127.
[20] S.D. Chaffee, M. Hyman, M.W. Rowe, in: J. Steinbring, A. Watchman, P. Faulstich, P.S.C. Taçon (Eds.), Time and Space: Dating and Spatial Considerations in Rock Art Research, vol. 8, Australian Rock Art Research Association, Melbourne, Australia, 1993, p. 67.
[21] S.D. Chaffee, M. Hyman, M.W. Rowe, N. Coulam, A. Schroedl, K. Hogue, Am. Antiq. 59 (1994) 769.
[22] S.D. Chaffee, L.L. Loendorf, M. Hyman, M.W. Rowe, Plains Anthropol. 39 (1994) 195.
[23] S.D. Chaffee, M. Hyman, M.D. Rowe, in: D. Whitley, L.L. Loendorf (Eds.), New Light on Old Art: Recent Advances in Hunter-Gatherer Rock Art, University of California Press, Berkeley/Los Angeles, 1994, p. 9.
[24] W.A. Ilger, M. Hyman, M.W. Rowe, Bull. Texas Archaeo. Soc. 65 (1994) 337.
[25] R.A. Armitage, M. Hyman, M.W. Rowe, L.L. Loendorf, J.R. Southon, Kiva 65 (2000) 253.
[26] W. Ilger, M. Dauvois, M. Hyman, M. Menu, M.W. Rowe, J. Vézian, P. Walter, Préhistoire Ariègeoise 50 (1995) 231.
[27] W.A. Ilger, M. Hyman, J. Southon, M.W. Rowe, Radiocarbon 37 (1995) 299.
[28] K.L. Steelman, M.W. Rowe, V.N. Shirakov, J.R. Southon, Antiquity 76 (2002) 341.
[29] S.D. Chaffee, M. Hyman, M.W. Rowe, in: F.G. Bock (Ed.), American Indian Rock Art, vol. 19, American Rock Art Research Association, San Miguel, CA, 1993.
[30] R.A. Armitage, J.E. Brady, A. Cobb, J.R. Southon, M.W. Rowe, Am. Antiq. 66 (2001) 471.
[31] R.A. Armitage, B. David, M. Hyman, M.W. Rowe, C. Tuniz, E. Lawson, G. Jacobsen, Q. Hua, Rec. Aust. Mus. 50 (1998) 285.
[32] R.A. Armitage, M. Hyman, M.W. Rowe, in: G. Ward, C. Tuniz (Eds.), Australian Rock Art Research Association, Lucas Heights, Melbourne, Australia, 2000.
[33] R.A. Armitage, M. Hyman, J. Southon, C. Barat, M.W. Rowe, Antiquity 71 (1997) 715.
[34] B. David, R.A. Armitage, M.W. Rowe, E. Lawson, in: S.M. Freers, A. Woody (Eds.) Am. Indian Rock Art 27 (2001) 106.

[35] M. Hyman, K. Sutherland, R.A. Armitage, J. Southon, M.W. Rowe, Rock Art Res. 16 (1999) 75.

[36] K.L. Steelman, R. Rickman, M.W. Rowe, T.W. Boutton, J. Russ, N. Guidon, in: K. Jakes (Ed.), Archaeol. Chem.: Mater. Methods Mean. 831 (2002) 22.

[37] S.D. Chaffee, M. Hyman, M.W. Rowe, Stud. Conserv. 39 (1993) 161.

[38] C. Pepe, J. Clottes, M. Menu, P. Walter, C. R. Acad. Sci. Paris, Serie II 312 (1991) 929.

[39] S. Spades, J. Russ, Archaeometry 47 (2005) 115.

[40] D.A. Scott, M. Newman, M. Schilling, M. Derrick, H.P. Khanjian, Archaeometry 38 (1996) 103.

[41] L. Rampazzi, L. Campo, F. Cariati, G. Tanda, M.P. Colombini, Archaeometry 3 (2007) 559.

[42] L. Rampazzi, F. Cariati, G. Tanda, M.P. Colombini, J. Cultur. Heritage 3 (2002) 237.

[43] H.G.M. Edwards, L. Drummond, J. Russ, Spectrochim. Acta A 54 (1998) 1849.

[44] H.G.M. Edwards, L. Drummond, J. Russ, J. Raman Spectrosc. 30 (1999) 421.

[45] H.G.M. Edwards, E.M. Newton, J. Russ, J. Mol. Struc. 550–551 (2000) 245.

[46] R.L. Reese, M. Hyman, M.W. Rowe, J.N. Derr, S.K. Davis, J. Archaeol. Sci. 23 (1996) 269.

[47] E.J. Mawk, M. Hyman, M.W. Rowe, J. Archaeol. Sci. 29 (2002) 301.

[48] R. Gillespie, Antiquity 71 (1997) 430.

[49] T.H. Loy, Antiquity 68 (1994) 147.

[50] T.H. Loy, R. Jones, D.E. Nelson, B. Meehan, J. Vogel, J. Southon, R. Cosgrove, Antiquity 64 (1990) 110.

[51] D.E. Nelson, Antiquity 67 (1993) 93.

[52] R.E.M. Hedges, C.B. Ramsey, G.J. Van Klinken, P.B. Pettitt, C. Nielsen-Marsh, A. Etchegoyen, J.O. Fernandez Niello, M.T. Boschin, A.M. Llamazares, Radiocarbon 40 (1998) 35.

[53] F. Mori, R. Ponti, A. Messina, M. Flieger, V. Havlicek, M. Sinibaldi, J. Cultur. Heritage 7 (2006) 344.

[54] C. Saiz-Jimenez, B. Hermosin, J. Anal. Appl. Pyrolysis 49 (1999) 349.

[55] C. Saiz-Jimenez, B. Hermosin, J. Anal. Appl. Pyrolysis 49 (1999) 337.

[56] S. Fezzey, R.A. Armitage, J. Anal. Appl. Pyrolysis 77 (2006) 102.

[57] D. Freidel, E. Robinson, J. Jones, Paper presented at the Society of American Archaeology Meeting, TX, USA, 2007.

[58] J. Brown-Sinha, M.S. Thesis, Eastern Michigan University (2007).

[59] M. Hyman, M.W. Rowe, Am. Indian Rock Art 23 (1997) 1.

[60] P.J. Reimer, M.G.L. Baillie, E. Bard, A. Bayliss, J.W. Beck, C.J.H. Bertrand, P.G. Blackwell, C.E. Buck, G.S. Burr, K.B. Cutler, P.E. Damon, R.L. Edwards, R.G. Fairbanks, M. Friedrich, T.P. Guilderson, A.G. Hogg, K.A. Hughen, B. Kromer, G. McCormac, S. Manning, C.B. Ramsey, R.W. Reimer, S. Remmele, J.R. Southon, M. Stuiver, S. Talamo, F.W. Taylor, J.v.d. Plicht, C.E. Weyhenmeyer, Radiocarbon 46 (2004) 1029.

[61] C. Bronk Ramsey, Radiocarbon 37 (1995) 425.

[62] C. Bronk Ramsey, Radiocarbon 43 (2001) 355.

[63] E. Robinson, M. Garnica, R.A. Armitage, M.W. Rowe, in: J.P. Laporte, B. Arroyo, H.E. Mejía (Eds.), XX Simposio de Investigaciones Arqueologicas en Guatemala, 2006, Ministerio de Cultura y Deportes, Guatemala City, 2007, p. 959.

[64] D. Fabbri, S. Prati, I. Vassura, J. Environ. Monit. 4 (2002) 210.

[65] M.J. Head, G. Jacobsen, C. Tuniz, Radiocarbon 38 (1996) 46.

[66] M.F.N. Pace, M. Hyman, M.W. Rowe, J.R. Southon, in: F.G. Bock (Ed.), American Indian Rock Art, vol. 24, American Rock Art Research Association, San Miguel, CA, 2000, p. 95.

[67] A.W. Stott, R. Berstan, R.P. Evershed, C. Bronk-Ramsey, R.E.M. Hedges, M.J. Humm, Anal. Chem. 75 (2003) 5037.