KEYWORDS: ***Radiocarbon dating – Accelerator mass spectrometry – Plasma-chemical extraction***

# RADIOCARBON DATING OF ANCIENT PICTOGRAMS WITH ACCELERATOR MASS SPECTROMETRY

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**Abstract**. After its introduction over five decades ago, radiocarbon dating is still the primary means for providing archaeological chronology. A review of the plasma-chemical extraction technique that permits direct AMS $^{14}C$ dating of ancient rock paintings is presented. Low-temperature and low-pressure argon and oxygen plasmas, coupled with high vacuum, remove carbon-containing material in pictogram paints without contamination from inorganic carbon in the rock substrates ($CaCO_3$) or mineral accretions ($CaC_2O_4.nH_2O$). The pictogram samples dated so far generally conform to age ranges expected on the basis of archaeological inference. This technique was also used on standard materials of known $^{14}C$ activity; results agreed within statistical uncertainty with previously determined ages. To establish that the method and apparatus do not have a significant live carbon background, $^{14}C$-free samples were measured as well. Chemical pre-treatment with ~1 M NaOH and ultra sonication at 50°C to remove possible contaminants is routine; HCl treatment normally used in dating archaeological charcoal to dissolve limestone is unnecessary with our approach. Almost all the radiocarbon determinations from our laboratory so far support the conclusion that the plasma-chemical technique produces viable ages for rock paintings, regardless of the pigment used. However, the technique must remain provisional until confirmed by another independent means. So far, we have dated rock paintings from Angola, Arizona, Australia, Belize, Brazil, California, Colorado, France, Guatemala, Idaho, Mexico, Missouri, Montana, Russia, Texas, Utah, Wisconsin and Wyoming. New results are presented.

## Introduction

Radiocarbon dating of rock paintings has produced exciting results during the 1990s. Over the past decade, our team at Texas A & M University collaborating with others has utilised the plasma-chemical technique (e.g., see Russ et al. 1990; Hyman and Rowe 1997) for extracting organic material in pictograms from numerous parts of the world in order to obtain radiocarbon dates for the paintings. Some of these rock paintings had strong archaeological inference with which to place the paintings into a reasonably secure chronology for comparison with the radiocarbon analyses. These comparisons are very useful to test the validity of our technique. Some of the pigments were charcoal; others were iron oxides or manganese oxides. But other samples were also dated, including a painted Egyptian pottery sample. In this paper I summarise these and other 'test' samples along with recent radiocarbon dates for rock paintings from the Texas A & M University group. New results continue to support the general validity of the radiocarbon dates by this technique, with an uncertainty of perhaps ± 100–250 years BP, depending on the specific circumstances of the individual cases.

## Universal standard for reporting the ages of rock paintings

Watchman (1999) recently called for a universal standard for the experimental publications reporting the ages of petroglyphs and rock paintings. With the number of rock painting dates rapidly increasing, that plea is more important than ever. I emphasise guidelines in addition to those set forth by Watchman and duplicate some of his here. To be able to critically examine the new findings in the future, we need experimental dating papers to contain the following:

(1) Cultural aspects of fieldwork and study. See Ward and Tuniz (2000: 5) for their suggestions for research pro-to-cols.
(2) Archaeological rationale for taking a sample for dating. This information is usually better supplied by the archaeologist(s) involved, rather than the chronogra-phers themselves, but is important and should be included.
(3) Description of how the samples were taken, including sample size (surface area removed, weight of sample), equipment used, etc.
(4) Description of the sample, including such information as: pigment composition (if known); pigment colour; accretionary minerals (if known); rock type pictogram is painted on; etc.
(5) Description of any pre-treatment used. Chemical pre-treatment and reaction system backgrounds should be measured and reported. Lawson and Hotchkis (2000: 27) discuss the effect of chemistry background and its importance to a radiocarbon date.
(6) Mass of carbon extracted from a sample and analysed for radiocarbon. This is critical and has been generally

ignored in the literature so far. See Lawson and Hotchkis (2000) for a good discussion. This can have a strong effect on the accuracy and reliability of the dates.

(7) Radiocarbon laboratory analysis number.

(8) Radiocarbon determination with ±1σ uncertainty (and possibly ±2σ uncertainty as well).

(9) A calibration program should be used to convert a radiocarbon age determination (years BP) to a calendar date range.

A striking example of the importance of items 7–9 is illustrated by a recent study of archaeological peyote dates (Terry et al. submitted). They measured radiocarbon ages on all three of the extant excavated peyote specimens from Shumla Caves, Texas. The three peyote samples had statistically indistinguishable radiocarbon ages (5160 ± 45; 5200 ± 35; 5210 + 335 years BP), with a weighted mean of 5195 ± 20 BP. We wanted to compare our three internally consistent Shumla Caves dates with radiocarbon measurements reported earlier (Furst 1989; Bruhn et al. 2002). However, previous reports of radiocarbon results for archaeological peyote contained no detailed sample and processing documentation. Furst (1989) mentioned that a direct radiocarbon date on one of the peyote specimens from Shumla Caves 'unexpectedly added six millennia' to the oldest age then thought to apply to archaeological peyote. This comment refers to an oblique reference to a date of A.D. 810 for a plaited mat found with peyote at the Cuatros Cienegas CM-79 shelter (Adovasio and Fry 1976). So the radiocarbon age is six millennia earlier than that, but 6000 radiocarbon years or 6000 calendar years? This distinction makes a large difference of ~700 years.

Similarly, Bruhn et al. (2002) radiocarbon dated two of the three Shumla Caves peyote specimens, but reported only 'a mean age of 5700 years'. They did not report the two individual radiocarbon dates and their corresponding uncertainties. Nor did they indicate any type of units for years, i.e., whether radiocarbon years BP or calendar years. This omission is significant, as the calibrated date differs from the uncalibrated date by over 700 $^{14}$C years. In the absence of such essential documentation, one cannot tell whether their unreported dates were internally consistent, or whether one date may have agreed with our three internally consistent dates (Terry et al. submitted). Carefully specified radiocarbon laboratory identification numbers, raw radiocarbon dates, calibrated dates, whether the dates are corrected for ′$^{13}$C, etc., are absolutely crucial when reporting radiocarbon results.

(10) Inclusion of failed attempts at dating as well as successful attempts and reason(s) for failure, i.e., too little carbon for AMS analysis, or as has been even more common in our work, when the background rock is seriously contaminated with organic carbon, etc.

(11) Inclusion of rejected dates and reasons for rejection. There is a need for such detail if rock art chronology is to advance scientifically.

(12) Techniques need to be independently tested whenever possible. This last item has become more and more important as time goes on. There have been no statistically satisfactory agreements between independent inter-laboratory dating comparisons for rock art so far. In the best case the disagreement was about 400 years from two laboratories with similar techniques on the same pictogram — well outside statistical agreement (Nelson et al. 1995; Watchman and Jones 2002). In the worst cases, differences of many millennia were observed (Pettitt and Bahn 2003 versus Valladas and Clottes 2003; Rowe and Steelman 2003 compared to Watanabe et al. 2003).

Virtually everyone who has published radiocarbon dates has been somewhat negligent in not providing all essential information, a condition that we should all strive to overcome.

**Texas A & M University experimental procedure**

*Sample collection*

We remove small samples of pigment from rock paintings from a surface area of approximately 2 cm × 2 cm for non-charcoal pigments (iron oxide/hydroxide[s] and manganese oxide/hydroxides) and as little as 1 mm × 1 mm for charcoal pigmented paintings. We routinely wear rubber gloves and use surgical scalpels with a new blade for each sample. The samples, including part of the underlying rock and accretionary mineral matter in addition to the pigments, are collected on and wrapped in aluminium foil, then stored in sealable plastic bags. These are taken to Texas A & M University (hereafter referred to as TAMU) where they are kept in a desiccator until ready for analysis. We examine each sample with an optical microscope to ensure that no extraneous material is included in a sample to be dated. Issues regarding successful pictogram dating are sampling techniques used; amount of sample available for analysis; ratio of pigment to rock in a small sample; amount of remaining organic material in the pigment; and presence or lack of an organic binder/vehicle or pigment originally in the sample. Also important are considerations of the aesthetics of paint removal, i.e., taking the samples so as to cause minimal damage.

*Chemical pre-treatment*

Once again, rubber gloves are worn to avoid contamination during all handling of samples. Procedures for chemically pre-treating archaeological charcoal vary slightly from laboratory to laboratory around the world; but all involve treatment with acid (usually hydrochloric acid, HCl) and base (sodium hydroxide, NaOH) (e.g., see Bowman 1990 and Taylor 1987). In the usual procedure, limestone is dissolved with acid to remove any $^{14}$C-free carbonates. Next, NaOH is used to dissolve the humic acid fraction that may be present. The sample is then re-acidified to prevent adsorption of atmospheric carbon dioxide ($CO_2$) caused by the NaOH. However, at TAMU, we routinely eliminate both the acid washes as we have shown them to be unnecessary with our plasma-chemical extraction technique. Our plasmas do not extract the carbon from carbonate and oxalate; only the carbon in the organic material is removed.

To remove any potential humic acids (contamination) from the sample, we immerse samples in about 5 ml of ~1 M NaOH and place them in an ultrasound bath for ~1 hour at 50 ± 5°C. After the NaOH wash/ultra sonication treatments, the supernatant should be colour-less, indicating all humic and fulvic acids have been removed. Otherwise, the NaOH treatment is repeated until a colourless solution results.

Since the NaOH adsorbs water and carbon dioxide from the atmosphere, samples are then placed in ~15 ml of doubly distilled, de-ionised water and sonicated at 50° ± 5°C for ~1 hour. This water wash is repeated to thoroughly rinse NaOH from the sample. Adsorbed carbon dioxide and water from the air do not affect the plasma dating technique, but sample extraction time is increased if they are present due to the number of argon plasmas necessary to remove those adsorbed species. Finally, the samples are dried in an oven set at 110°C. The samples are then ready for plasma extraction.

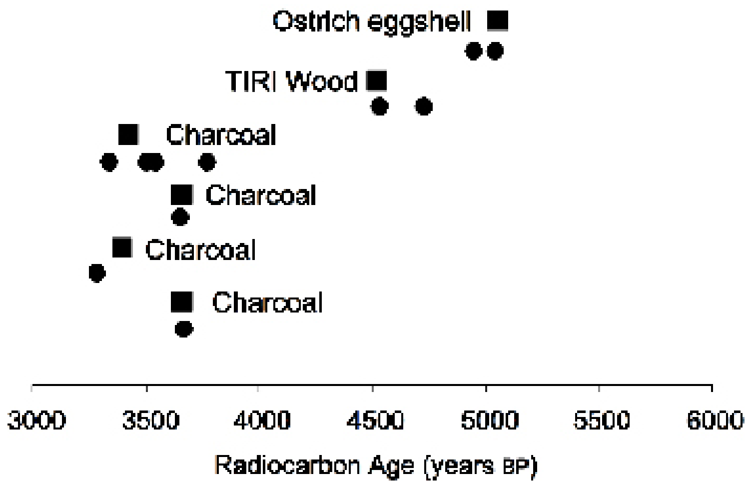


***Figure 1.*** *Comparison of our plasma-chemical AMS results (circles) with $^{14}C$ content previously determined at other laboratories (squares). Agreement is within the expected statistical variation except for one charcoal date.*

*Plasma-chemical treatment*

The plasma-chemical method we use to extract organic carbon from ancient rock paintings will be presented here. Ultra-high purity bottled argon and oxygen (99.999%) is used for all plasmas; the gases are passed through a cold-trap (dry-ice/ethanol slurry) to ensure removal of organic contaminants and water from the gases and transfer line before entering the system proper.

Rotary pumps are sufficient to maintain vacuum conditions (~$10^{-4}$ torr), but there is a problem with oil back streaming into the system (Steelman et al. in press). Our latest system uses an oil-free turbo molecular pump that easily reaches pressures of ~$10^{-6}$ torr. Low temperature oxygen plasmas are used to pre-clean the reaction chamber before introduction of each sample and these are repeated until ≤0.001 mg carbon, as $CO_2$, is generated. Samples are introduced into the chamber via a copper-gasketed, stainless steel flange-sealed port under a flow of argon (99.999%) to prevent atmospheric $CO_2$, aerosols or organic particles from entering the system. After the chamber is resealed and the sample degassed under vacuum and heat, low temperature argon plasmas are used to desorb $CO_2$ molecules from the sample and chamber walls by inelastic collisions of the non-reactive, but energetic argon species. Adsorbed $CO_2$ on a sample is thus reduced to ≤0.001 mg carbon by vacuum pumping.

Then, a low temperature (<175°C), low-pressure (~1 torr oxygen) plasma is run to oxidise the carbon in the charcoal paintings to $CO_2$. Running the plasmas at low-temperature ensures that decomposition of any inorganic carbon present (limestone and calcium oxalate) is prevented because the heat generated is well below their decomposition temperatures. Oxidising plasmas react only with organic carbon present in the samples, leaving any substrate rock and accretionary carbonates and oxalates intact — as has been demonstrated in earlier publications from TAMU (e.g. Russ et al. 1992; Chaffee et al. 1994). Solid carbon dioxide from a sample is flame sealed into a glass tube cooled by immersion in liquid nitrogen (-194°C), after the water had been frozen out in a trap consisting of dry ice and ethanol at -58°C. Finally, the gas is sent for radiocarbon analysis. We have utilised the accelerator mass spectrometry laboratories at the Center for Accelerator Mass Spectrometry Lawrence Livermore National Laboratory (CAMS), the Australian Nuclear Science and Technology Organisation, and at the University of Arizona.

**Verification studies on plasma-chemical technique**

During the past decade, we have made numerous attempts to verify whether the plasma-chemical extraction technique produces valid radiocarbon dates. The first type of test was the analysis of materials that had been previously measured by other radiocarbon laboratories. Although none of these was on rock paintings, examples included: charcoal, International Wood Standard (TIRI) and ostrich eggshell samples. For the eggshell, the plasma was used to clean the sample by removing possible organic contamination, and then the carbon from the shell was released as $CO_2$ by phosphoric acid dissolution. These results all produced agreement with the previous age determinations within expected statistical variation as illustrated in Figure 1. Two analyses appear outside ~±1σ uncertainties; that number of deviant values is expected because of statistical uncertainty alone. These results on samples of known $^{14}C$ content support the general validity of the plasma-chemical technique for radiocarbon dating.

We also performed radiocarbon analyses on materials that were too old to contain significant radiocarbon. Examples are Albertite (coal), Axel-Heiberg wood and commercial graphite. Our background measurements were insignificant compared with the background level of 0.0009 mg modern carbon obtained at the Australian Nuclear Science and Technology Organisation AMS laboratory (Ewan Lawson,

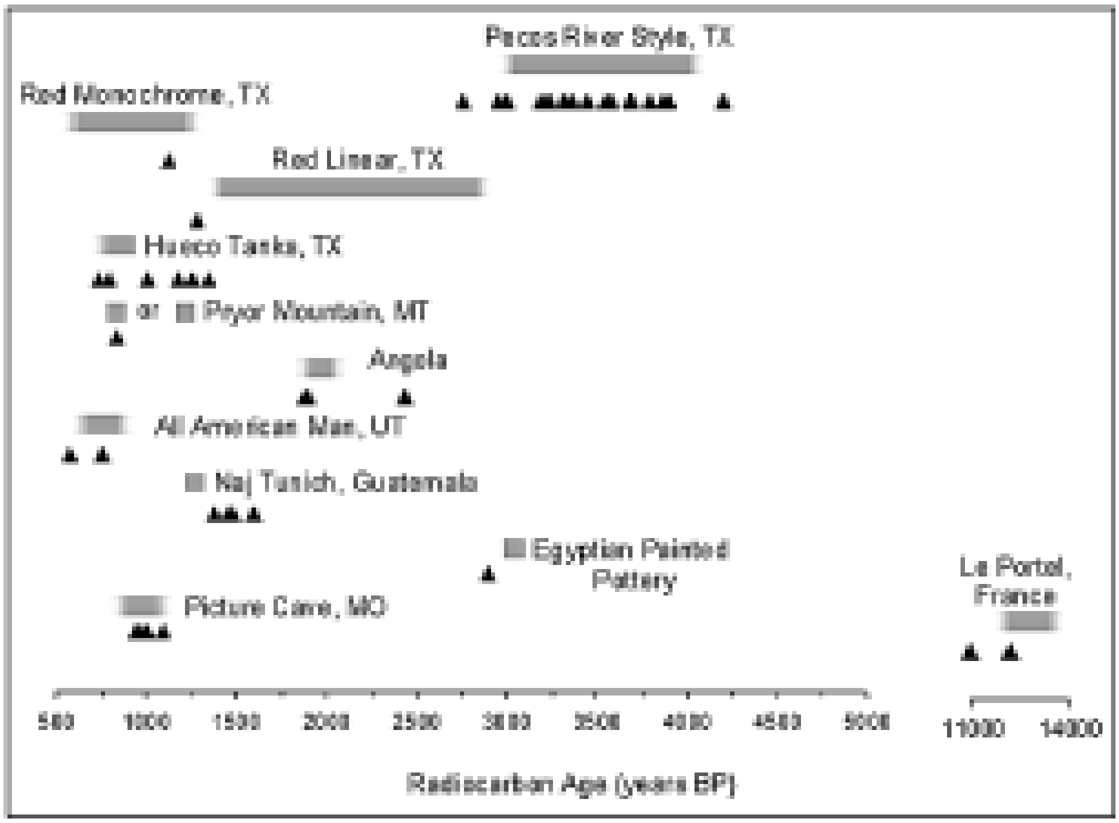


***Figure 2.*** *Comparison of our plasma-chemical AMS results (triangles) with $^{14}C$ content previously determined at other laboratories (rectangles). Agreement is within the expected statistical variation. There are two points that overlap for the Red Linear style. There are five dates, some overlapping for the Picture Cave pictograms. The older dates for the Hueco Tanks pictograms are almost certainly older than the expected range, calling into question that estimate inferred from archaeology (Hyman et al. 1999).*

pers. comm. 1998). The Lawrence Livermore accelerator mass spectrometry laboratory also indicated no significant background of modern carbon in plastic fibres that had been measured at >49 900 radiocarbon years BP (Miller et al. 2002).

We have also radiocarbon-dated pictogram samples from various parts of the world for which age ranges were available based on archaeological inference. Although these inferences were generally not stringent, our results generally agreed with the archaeologists' assertions. These comparisons are shown in Figure 2. Finally, we have measured replicate dates on several different paintings to check internal precision. These results suggest a 1σ uncertainty of ~±10% in our ages. More recently we dated a sample of an Egyptian painted pottery fragment; our radiocarbon ages when calibrated *barely* overlapped with the known age at ± 2σ as indicated in Figure 2 (Robert Brier, pers. comm. 1999). In general, all tests that we have made at present support the validity of the plasma-chemical extraction procedure.

**New age determinations**
***United States of America***

*Arizona:* Only one pictogram site is known along the San Pedro River, the only continuous flowing waterway in south-eastern Arizona on whose margins are numerous archaeological remains and petroglyph sites. Three charcoal pictograms were sampled, but because the paint layer was thin and diffuse, only one of those contained enough carbon to get a radiocarbon date. A radiocarbon date of 2370 ± 150 years BP was obtained for an anthropomorphous image on a fallen rock on the shelter floor (Steelman et al. in press). The relatively large uncertainty derives from the small sample size. This study demonstrated the subtle balance between collecting enough material for reliable radiocarbon analysis and minimising the damage to paintings during sampling. We typically err on the side of taking too little, while ensuring minimal damage to paintings.

*Colorado:* Accelerator mass spectrometric analysis yielded an uncalibrated radiocarbon age of 3160 ± 110 years BP (CAMS-41467) on a black, non-charcoal pigmented pictogram sample from Falls Creek Shelter, Colorado. We also subjected a sample of unpainted rock near the black painting to the plasma process as a background check. That sample yielded carbon at 19.7% of the pictogram carbon, indicating that the rock itself was contaminated with organic matter. Since the background sample was too small for an accurate radiocarbon analysis, we did not send it to an AMS laboratory for measurement. A background of 19.7% is significant, however, and must be taken into account. That was done first by making two extreme assumptions: (1) that the background consists of modern carbon and (2) that the background consists of infinite age carbon, i.e., no live radiocarbon remains. This gives the ultimate range of ages, but the assumptions are probably unrealistically restrictive.

| Sample | $A_m$ | $A_x$ (assumed) | $A_s$ | Age, years BP |
|---|---|---|---|---|
| Pictogram | 0.6748 | --- | --- | 3160 ± 110 |
| Background 1 | | 1.0 (modern) | 0.5950 | 4170 |
| Background 2 | | 0.0 ($^{14}C$-free) | 0.8403 | 1400 |
| Background 3 | | 0.7700 (assuming2100 years BP) | 0.6514 | 3440 |
| Background 4 | | 0.4999 (assuming 5570 years BP) | 0.7177 | 2660 |

***Table 1.*** *Calculated radiocarbon ages assuming different activities for the ~20% background contamination.*

The relationship between a 'true' radiocarbon activity and the measured one when contaminated is given as (Bowman 1990: 27–8):

$$A_m = fA_x + (1-f)\, A_s$$

(Where $A_m$ is the measured radiocarbon activity, $A_x$ is the activity of the contamination (background), $A_s$ is the activity of the 'true age' of the sample and $f$ is the fraction of contamination (0.197) in the measured material).

Using that equation, Table 1 gives the sample ages for different assumptions for the 'age' of the background contamination. If the first extreme assumption (modern 1950 carbon) is used, a corrected radiocarbon age of 4170 years BP is obtained; with the assumption of a radiocarbon-free background, the age is calculated to be 1400 years BP. Neither of the two extremes is likely. If we adopt the midpoint of the two extremes as more likely, we get an age estimate of 2785 years BP. Unfortunately we have no information concerning the age of the background at the Falls Creek location in order to make a more accurate assessment. In the Lower Pecos region of Texas, however, Russ et al. (1996, 1999) dated accretionary calcium oxalate deposits on limestone rock, finding an age range from 2100 to 5570 years BP. If the Falls Creek background was represented by one of those ages, then the estimate of the age of the painting would lie between 3440 and 2660 years BP, respectively.

The most *secure* conclusion at the present time is that the age of the Falls Creek black rock painting falls between 1400 and 4170 years BP. But, with more reasonable estimates (based on dated background samples from other areas) of the age of the background contamination, the age might more likely lie between 2660 and 3440 years BP. This latter age range overlaps with the age expected on the basis of archaeological inference, i.e., Pueblo II.

*Missouri:* Diaz-Granados et al. (2001) reported four radiocarbon dates on charcoal pigments from three drawings in Picture Cave in north-eastern Missouri (Diaz-Granados et al. 2001: Table 1). These samples contained sufficient charcoal carbon for AMS $^{14}C$ analysis; four statistically indistinguishable ages were obtained, ranging from 940 ± 80 to 1090 ± 90 BP for a weighted average of 995 ± 45 BP. These black motif samples (red and white paintings are also present in the cave) fall into a time frame that associates them with the prominent Cahokia complex in the region about 1000 years ago. Arguments against significant 'old wood' and 'fossil charcoal' factors were given in the paper, and these strengthen confidence in the age estimates. A recent charcoal pigment removed from a fifth painting there, a black painting of a 'warrior', yielded an AMS radiocarbon date of 965 ± 35 years BP (unpublished date). This age agrees with the four previous plasma-chemical extraction/accelerator mass spectrometry radiocarbon measurements on three other images located in Picture Cave. There is no statistical difference in any of the ages. From these results, we conclude that there was a flurry of painting at this time in Picture Cave. These dates agree with the archaeologically inferred age range of about 1000 years BP (Diaz-Granados 1993).

*Montana:* In 2002, pigment samples were extracted from three prehistoric pictograms in the Big Belt Mountains of west-central Montana. The samples were radiocarbon dated using plasma-chemical extraction and accelerator mass spectrometry (Scott et al. submitted). The three dates, although at separate sites were statistically indistinguishable and yielded a weighted average age of 1220 ± 30 years BP, which calibrates to ~ A.D. 690 to 890. This corresponds to the early Late Prehistoric period on the northwestern plains. An oxalate accretion overlying a painted area in Big Log Gulch provided a minimum age of 1440 ± 45 years BP for the rock art under the oxalate crust. The dated images at the four sites fall within the Foothills Abstract rock art tradition.

*Texas - Pecos River style:* The Lower Pecos River region in Texas contains the striking Pecos River style of polychrome pictograms. They are often large, reaching several metres in height or length. Nineteen samples of red and black inorganic pigmented Pecos River style paintings have been dated previously by AMS radiocarbon analysis (Russ et al. 1990, 1992; Chaffee et al. 1993, 1994; Ilger et al. 1996; summarised in Hyman and Rowe 1997). The ages, ranging between 2750 and 4200 BP, are in general agreement with the age range based on archaeological inference of 3000 to 4000 BP. However, replicate analyses indicate an uncertainty in precision of perhaps ± 200–250 BP and contamination effects cannot be ruled out totally. Concurrent analysis of unpainted rock near the dated pictograms allows the assessment of potential contamination.

Radiocarbon age estimates obtained from six portions of a pictogram from 41VV75 yielded 3690 ± 80, 3790 ± 60, 3900 ± 60, 3310 ± 50, 3440 ± 50 and 2340 ± 80 years BP. Different pre-treatments were used for the different aliquots of the painting sample. The last one was rejected as a low outlier; the others fell well within the range of previous Pecos River style ages (Hyman and Rowe 1997). The spread in the ages confirms an uncertainty in the radiocarbon dates obtained from inorganic pigments of the order of ± 200–250 years BP (Pace et al. 2000).

Radiocarbon analysis of a pictogram sample from Mystic Shelter gave an age of 3920 ± 120 years BP, at the upper end of the twenty or so Pecos River style paintings we have dated previously. Of the two samples taken from the Cedar Springs Shelter only one had enough carbon to produce a radiocarbon date, 3010 ± 100 years BP, and falling within the expected range for the Pecos River style of paintings (3000–4000 years BP; Turpin 1990).

Recently, four more dates on Pecos River style were obtained from samples at the White Shaman Shelter (Steelman and Rowe unpubl. data, 2000). These dates were surprisingly recent, with an average age of 1960 ± 220 years BP, compared to the other Pecos River style pictograms. A fifth sample did not yield enough carbon for a date. We are currently preparing polished sections to determine whether any of the four pictograms dated had been over-painted, thus yielding more recent dates because of a newer painted surface. For the moment, the young ages are not understood. It may be, of course, that the style extended over a longer time period than indicated by our earlier dates or by the archaeological inference. A majority of the earlier dates have come from a single shelter, 41VV75. Only five other shelters were represented in the Pecos River style pictogram dates prior to these White Shaman figures. See also the San Vicente, Mexico, discussion below, where other Pecos River style pictograms were also recently dated. The relatively recent dates at White Shaman reduce the agreement between our dates and the archaeological inference for the style.

*Texas - Red linear style:* A sample of a black deer of unidentified style, about 10 cm long, was dated at 1280 ± 80 BP (Rowe in press). The motif is located in site 41VV75 of the Lower Pecos River region, a site dominated by many badly degraded Pecos River style paintings. However, the deer is of unknown genre; its size indicates Red linear style, but it is more complicated than the usual stick figures of that style, and possibly belongs to the Pecos River style. The age is indistinguishable from either the single date, 1280 ± 150 years BP, obtained on a Red linear figure or the one date, 1125 ± 85 years BP, obtained on another Red monochrome figure (Ilger et al. 1994, 1995, respectively). Rowe (in press) suggests that the pictogram is Red linear style based on its age.

*Wisconsin - Arnold Cave:* A sample from a charcoal rock painting at the Arnold Cave site 47Cr560 was radiocarbon dated (Steelman et al. 2001). The painting, which resembled a caribou because of the orientation of the tines on its antlers, was of interest because caribou have not been found in the Arnold Cave region since the end of the Pleistocene, c. 10 000 years ago. However, the accelerator mass spectrometry radiocarbon (AMS) date, 1260 ± 60 years BP, is inconsistent with that interpretation. Another sample of a deer painting was also taken, but unfortunately, did not yield enough carbon for a radiocarbon measurement.

*Wyoming:* A charcoal drawing in Lower Canyon Creek Cave was sampled for radiocarbon dating. Whereas other samples that do not contain charcoal typically yield ~100 μg of organic carbon, the charcoal-pigmented rock painting gave an unusually large (for us) amount of carbon, 852 μg. The large amount of carbon produced gives us added confidence in this age determination (550 ± 50 years BP; Steelman and Rowe unpubl. data, 2000). The radiocarbon measurement is on a shield-bearing 'warrior' and although it is ~100 years older than Larry Loendorf (pers. comm. 2000) would have predicted, it is within the expected age range. It is conceivable that we may be experiencing the 'old charcoal' effect (Schiffer 1986), always a potential problem when dating charcoal. Three other paint samples with iron oxide pigments were taken in Wyoming, one at Lower Canyon Creek Cave and two from the Mack site. Unfortunately, none of these contained enough carbon for dating.

***Australia -*** *Mitchell-Palmer, Queensland:* Our AMS radiocarbon results from charcoal rock drawings from the Mitchell-Palmer limestone zone have identified each drawing as dating to late Holocene times (David et al. 2001). Confidence in these determinations is heightened by the similarity of results from two adjacent samples from Alcove Cave (both 'modern'), and by the results from the three infilled anthropomorphs from Hay Cave, which overlap at two standard deviations. These three anthropomorphs were positioned in close proximity to each other within the cave, and were drawn by following similar artistic conventions.

***Belize:*** A single radiocarbon date has been obtained on a Mayan charcoal rock painting from the Actun Ik Cave in Belize. It dated to 1100 ± 60 BP (Rowe et al. 2001), considerably more recent than the Guatemalan paintings at Naj Tunich (see Fig. 2), but in accordance with expected ages for Maya paintings.

***Brazil -*** *Toca do Serrote da Bastiana:* At present, nine samples have been radiocarbon dated from Toca do Serrote da Bastiana, Brazil, and nearby shelters (Rowe and Steelman 2003). Some of these samples were taken by other researchers in Brazil and were sometimes too small for our purposes. All the measured ages (Fig. 3) are far less than the ~30 000–40 000 years BP determined by Watanabe et al. (2003) for a pictogram in Toca do Serrote da Bastiana. We have no scientific reason to doubt the validity of our dates. Watanabe et al. used thermoluminescence (TL) and electron spin resonance (ESR) to date calcite deposition over the painting. We suggested that the use of TL and ESR for dating calcite deposited in this arid, open-air shelter may suffer from the incorporation of undissolved carbonate particles into the calcite layer as it formed. Incorporation of solid carbonate would make the calcite layer appear older than its true deposition time because the shelter's limestone rocks are millions of years old.

***Guatemala -*** *Cueva de la Pinturas:* A panel of polychromatic red, black and yellow pictograms from Cueva de la Pinturas in Guatemala was found to contain substantial amounts of fine fibres. These fibres were extracted and radiocarbon dated to >49 900 years BP (along with scanning electron microscopic imaging), which indicated that they were post-1940s plastic made from fossil fuel. An alternative explanation that the samples were natural fibres older than 50 000 years is most unlikely. The AMS $^{14}C$ measurement confirms the low background of modern carbon in our

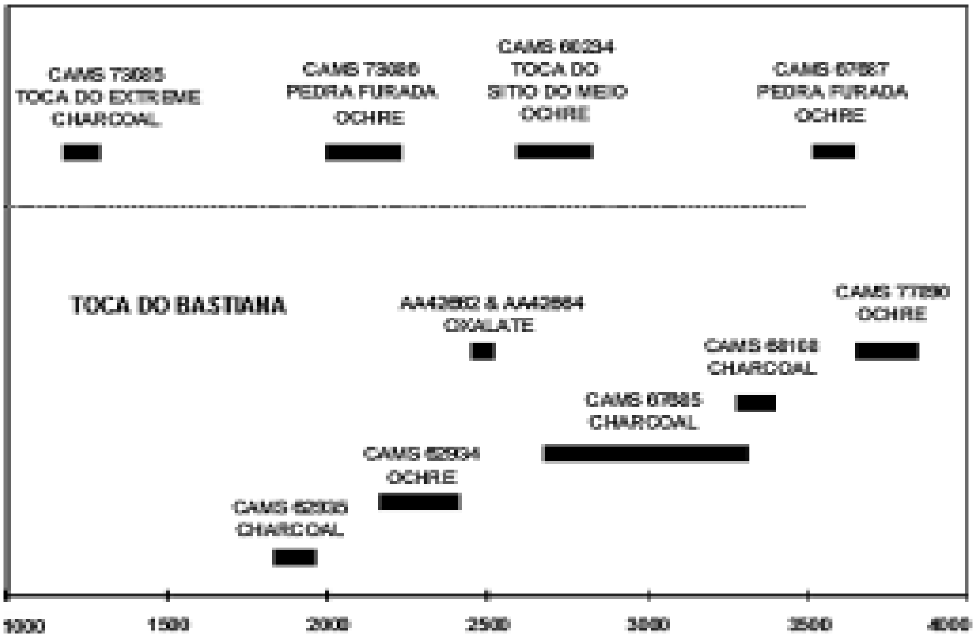


***Figure 3.*** *Radiocarbon results for rock paintings at Toca do Bastiana and other nearby rockshelters (from Rowe and Steelman 2003). All radiocarbon dates shown here are at least an order of magnitude smaller than the TL and ESR dates. The ochre painting with CAMS ID# 77890 is the pictogram dated by Watanabe et al. (2003)*

plasma-chemical procedure. A second pictogram sample was collected, but with care to avoid fibres. Nonetheless, it too was found to be seriously contaminated, likely with some fossil fuel organic carbon, yielding 20 430 ± 130 radiocarbon years BP. This rock art panel is obviously too contaminated to provide a reliable radiocarbon date for the paintings (Miller et al. 2002).

***Guatemala -*** *Diablo Rojo:* A polished cross-section of paint from a red anthropomorphous image called 'Diablo Rojo' in Guatemala reveals a black paint layer underneath the surface red paint. Charcoal from this black layer was radiocarbon dated to 3030 ± 45 years BP (Steelman and Rowe, unpubl. date). Complication arises because the visible painting of Diablo Rojo is a red ochre layer painted on top of the dated charcoal layer. That means that the red layer was painted some indeterminate time more recently than the charcoal layer. Whether the elapsed time between the painting of the charcoal layer and the overlying red one was short (months or years) or long (centuries) is difficult to ascertain. The black layer may underlie the red one throughout the painting or it may only occur in the sampled area of the red painting. It is conceivable that Diablo Rojo was simply painted over a previous charcoal painting of another totally independent figure. Further sampling with additional cross-sections should answer that question. The radiocarbon measurement probably represents the maximum time of its painting; the actual red painting may be much younger. Nonetheless, iconography of the image had led us to suspect that the image would be Olmec, consistent with the date obtained. However, for the reason given above the reported age, 3030 ± 45 years BP cannot be considered an accurate indication of the time of painting.

***Mexico -*** *Pecos River style:* Three samples from two shelters in northern Mexico were collected for radiocarbon dating. They were found to contain significant carbon background in the natural rock, and the sample from the Abrigo Diego shelter was too highly contaminated to permit the measurement of a valid age. The samples from the San Vicente shelter were calculated assuming that the background (20% for San Vicente 2; 15% for San Vicente 3) was either 1280 years BP (the youngest radiocarbon age we have determined on any pictogram from the Lower Pecos River region) or 4200 years BP (the oldest radiocarbon age we have determined on any pictogram from the Lower Pecos River region). The ages obtained were 1930 +170/-480 and 2500 ± 255 years BP, respectively. As with the White Shaman date above, the younger of these age estimates is more recent than the other Pecos River style pictogram dated so far (Hyman and Rowe 1997; Pace et al. 2000), ranging from 2750 to 4200 years BP for some 21 samples.

***Russia:*** Samples from three charcoal rock paintings from Ignatievskaya Cave in the southern Ural Mountains, Russia, were radiocarbon dated (Steelman et al. 2002). Relatively old antiquity was expected from the other imagery in cave with some paintings thought to be more than 10 000 years old. One charcoal painting, for example, resembled a mammoth. However, the radiocarbon age of that motif was 7370 ± 50 years BP. If that motif were actually a representation of a *live* mammoth it would place mammoth extinction in the Ural Mountains nearer to the present than had been supposed. Another sample of a drawing of lines radiating from a central focus was also dated. Its age was a few hundred years older than the 'mammoth': 7920 ± 60 years BP. Another charcoal line gave an age of 6030 ± 110 years BP. A red ochre painting of a woman did not contain enough organic material to obtain a viable date. Radiocarbon dates on pictograms in

Ignatievskaya Cave obtained so far indicate that they are more recent than had been supposed.

***Spain:*** Carbon was extracted from charcoal paint samples collected from megalithic monuments in north-west Iberia. Nine AMS radiocarbon dates on these paints established their ages to be within 1000 years of each other, centred at approximately 5000 years BP (Steelman et al. submitted). These radiocarbon dates fall within the proposed time period expected for north-west Iberia megalithic culture. This agreement lends general confidence in our method for dating rock paintings.

## Conclusion

The radiocarbon age determinations obtained at TAMU during the past decade and a half indicate that the plasma-chemical/accelerator mass spectrometry technique for determining the ages for rock paintings has the potential to produce accurate and reliable results. The technique is the only one directly applicable to rock paintings that have been painted with carbon-bearing, inorganic iron and manganese oxides/hydroxides, as well as charcoal. Organic carbon in the basal rock and mineral accretions associated with rock paintings is the major remaining impediment to our technique routinely giving accurate and reliable ages, along with the uncertainty of the identity of the materials being dated. With the background reduced or removed, the potential exists for this new technique to provide archaeologists with ever more reliable and accurate chronological information. Future work will focus on this problem. No other technique currently used for dating rock paintings is as generally applicable as the plasma-chemical one. Many dates for rock paintings have now been measured. Those done on inorganic pigmented paintings are provisional until confirmed independently. And those determined on charcoal pigments suffer from the uncertainty brought about by the old wood and old charcoal effects.

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