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Plasma extraction and AMS 14C dating of rock paintings

Extraction par plasma et datation de peintures rupestres par mesure du C14 en spectrométrie de masse par accélérateur

Abstract. *We developed a plasma-chemical technique to remove carbon from rock paintings. This extraction is followed by accelerator mass spectrometric analysis of the 14C to yield direct estimates of the ages of rock paintings. We have demonstrated use of the technique on charcoal as well as iron and manganese pigmented paintings. Unfortunately, there are no rock paintings made with inorganic pigments that have accurately known ages. That means there are no primary standards for checking the accuracy and validity of our technique on this type of samples. To compensate for this, known age samples (charcoal and Third International Radiocarbon Intercomparison wood) were dated: these support the general validity of the technique. Also supporting the technique, the dates we obtained on numerous rock paintings agree in general with the age ranges expected based on archaeological inference. However, a date is not convincing only because it agrees with current archaeological inference. Real verification awaits confirmation by an independent technique. Future work will concentrate on the removal of background organic contamination in the basal rock and mineral accretions associated with rock paintings. Overcoming that problem will remove an impediment to our extraction technique routinely giving accurate and reliable ages.*

Keywords. *Rock paintings; radiocarbon dating; accelerator mass spectrometry; charcoal pigments; inorganic pigments.*

Résumé et conclusions. *Nous avons développé une technique combinant plasma et chimie pour extraire le carbone des peintures rupestres. L'extraction est suivie de l'analyse du C14 par spectrométrie de masse par accélérateur afin d'obtenir directement une estimation de l'âge des peintures. Nous avons démontré l'utilisation de cette technique sur le charbon de bois ainsi que sur les peintures à base de pigments de fer et de manganèse. Malheureusement, il n'y a pas de peintures rupestres à base de pigments inorganiques dont on connaisse précisément l'âge. Nous n'avons donc pas de critères de base pour vérifier la précision et la validité de nos techniques sur ce type d'échantillons. Pour pallier cela, on a daté des échantillons d'âge connu (charbon de bois et bois de la 3e campagne internationale de mesures intercomparées du radiocarbone) : la validité générale de la technique a ainsi été confirmée. Egalement à l'appui de cette technique, les dates que nous avons obtenues pour de nombreuses peintures rupestres correspondent en général aux échelles d'âge attendues grâce aux déductions archéologiques admises. Une date n'est cependant pas convaincante sur la seule base de cette correspondance. Toute vérification sérieuse dépend de sa confirmation par une technique indépendante Notre travail à venir se concentrera sur la suppression de toute contamination organique de fond sur le rocher de base ainsi que des accrétions minérales associées aux peintures rupestres. La solution de ce problème enlèvera un obstacle à notre technique d'extraction en permettant de donner des datations courantes de façon précise et fiable.*

Les dates que nous avons obtenues pour les peintures rupestres ces six dernières années prouvent que notre technique SMA appliquée à l'estimation des âges carbone 14 sur des peintures rupestres est capable de produire des résultats précis et fiables, mais des travaux complémentaires sont nécessaires. Notre technique plasma-chimique en est encore à son premier stade expérimental, mais semble fournir des datations précises à ~ + ou - 300 années 14C pour des échantillons contenant plus de 100 mg de carbone. Cette technique peut s'appliquer à des peintures rupestres de composés inorganiques à base d'hydroxydes et d'oxydes de fer et de manganèse, ainsi que de charbon de bois. Le carbone organique sur le rocher lui-même et les accrétions minérales associées aux peintures constituent encore un obstacle pour que notre technique fournisse couramment des datations précises et fiables. Si l'on réduit ou supprime ce fond, cette nouvelle technique est capable de fournir aux archéologues une information chronologique toujours plus précise et fiable. Notre travail va maintenant se centrer sur ce problème.

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During the past decade, our research laboratory has concentrated on attempts to radiocarbon date and chemically and mineralogically characterize rock paintings. To that end, we have built four different plasma chemical systems designed to permit extraction of the extremely small amounts of organic material associated with some paints used in ancient rock paintings. All systems utilize oil-free vacuum pumps and high vacuum techniques. Organic material in a painting is extracted as carbon dioxide which is then radiocarbon dated by accelerator mass spectrometry. We have access in Texas A&M University's Center for Electron Microscopy to scanning electron microscopy equipped with energy dispersive x-ray spectroscopy for chemical characterization of the micro stratigraphy of rock art cross sections. We also have a collaboration with the National Aeronautics and Space Administration Johnson Spaceflight Center at Houston for micro x-ray diffractometry for mineral analysis. DNA phylogenetic analysis is accomplished through a collaboration with Texas A&M University faculty in the Departments of Animal Science and Veterinary Pathobiology. DNA analysis is enabling us to ascertain the source of organic material added as binder/vehicle to an ancient paint.

The study of rock paintings - Introduction

The introduction of accelerator mass spectrometry (AMS) so reduced the amount of carbon necessary for a 14C date that it became possible to estimate the age of rock paintings. Van der Merwe et al. (1987) were first to directly 14C date charcoal pigment from rock paintings. Others around the world followed (e.g., McDonald et al. 1990; Valladas et al. 1990; Farrell and Burton 1992; Geib and Fairley 1992; Valladas et al. 1992; Clottes et al. 1992 a, b, c, 1994; David 1992; Chaffee et al. 1994 a; Ilger et al. 1994 a, 1995). Direct dating of rock paintings, though attempted for about a decade, must still be considered experimental. The amounts of carbon usually extracted from rock paintings are at the lower end of AMS measurement capability; our samples are often 100 mg or less, compared to the ideal of >1 mg. The "old wood problem" encountered when dating any archaeological charcoal applies to charcoal pigments as well (Schiffer 1986).

More frequently encountered than charcoal in rock paintings are inorganic pigments: reds, oranges, browns, and yellows are usually iron oxides and hydroxides and black is often manganese oxides and hydroxides (e.g. Hyman et al. 1996 a); the inorganic pigments themselves cannot be dated directly, but organic binders and vehicles can. Figure 1 shows a polished cross-section of a painting from the Lower Pecos River region of southwest Texas. It illustrates some of the problems that were anticipated when we began development of our technique to extract the organic binder/vehicle assumed to have been added to at least some inorganic paints. To accurately and reliably date rock paintings the following requirements must apply: (1) organic matter was added to the paints initially, either as pigment (e.g. charcoal) or as binder/vehicle; (2) enough organic material has survived to yield adequate carbon to date; (3) organic carbon can be extracted without also removing carbon from the atmosphere, limestone ($CaCO_3$ and $MgCO_3$), or mineral accretions (carbonates and oxalates) found both above and below rock paintings; (4) the extraction introduces little mass fractionation; (5) carbon originally added to paints does not exchange with other sources after paint application; and (6) basal rock and mineral accretions not easily separated

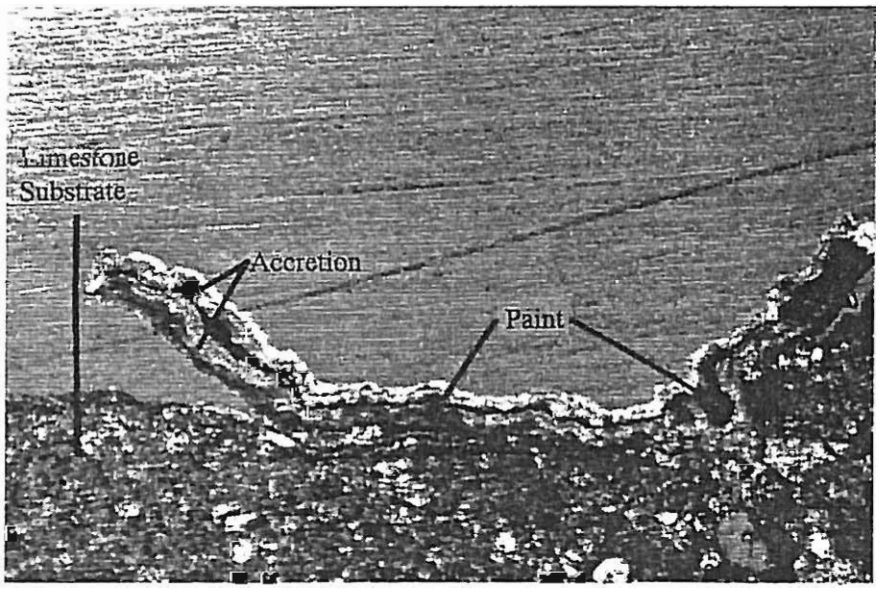

Figure 1. *Polished section of a painted sample from site 41WT75. Three principal layers are visible: (1) limestone substrate, (2) pigmented layer with black manganese oxides and hydroxides, and (3) naturally occurring accretion ($CaC_2O_4.H_2O$ and $CaCO_3$) both above and below the pigment layer.*

Section polie d'un échantillon de peinture provenant du site 41WT75. Trois couches principales sont visibles : 1. le substrat calcaire, 2. la couche pigmentée avec des oxydes et hydroxydes noirs de manganèse, 3. l'accrétion naturelle ($CaC_2O_4.H_2O$ et $CaCO_3$) à la fois sur et sous la couche de pigment.

from a pigment layer sample do not contain enough organic carbon (contamination) to invalidate a date.

To accomplish the extraction of the added organic material from the painted rock fragment, we use low-temperature (~150°C) oxygen plasmas. During the early development of our technique, we studied the following and none affect our ability to date rock paintings: O_2 and Ar sources; mass fractionation; calcium carbonate, magnesium carbonate, limestone and calcium oxalate decompositions. We have now used the technique to date charcoal pigments as well as the unknown binder/vehicles from inorganic pigment layers (Russ et al. 1990, 1992 a, b; Chaffee et al. 1993 a, b, 1994 a, b; Ilger et al. 1995 a, b, 1996). We extract whatever organic material may be present in the paint, but we do not know the material being dated.

The lack of specificity in oxidizing organic material is both the main advantage of our technique as well as a significant disadvantage. It permits us to date rock paintings presently undatable by any other technique. We do not depend upon the presence of charcoal, blood (Loy et al. 1990), plant fibers (Watchman and Cole 1993) or beeswax (Nelson et al. 1995). In only one case have we gathered information on the possible source of the organic binder/vehicle used in the paints: in two samples, one black (manganese oxide pigment) and one red (iron oxide pigment) from Pecos River genre paintings. For these we used DNA/phylogenetic analysis and found that material from an ungulate (even-toed hoofed mammals), probably bison or deer, was added to the paint (Reese et al. 1996 a, b). Further studies aimed at species differentiation are on-going in our laboratory.

Analytical Procedures

Chemical pretreatment for radiocarbon dating

We have adopted the standard NaOH treatment recommended to remove humic acids from charcoal for all our rock painting samples, whether the pigment is charcoal or inorganic. HCl treatment also suggested as standard treatment is unnecessary with our technique and may even present some problems for dating rock paintings when calcium oxalate is present in the sample (Pace 1996). Thus each rock painting sample is routinely treated with NaOH, with ultrasonication for ~1 hr at 50 ± 5°C ; wash solutions are saved. We filter the solutions through binder-free borosilicate glass filters baked overnight at ~600°C to remove organic contamination. Humic acids present will stay in solution and pass through the glass filter, removing contamination. Plasma extractions are run on dried filtrate material.

Plasma extraction for radiocarbon dating

We use a radio frequency generated low-temperature (~150°C), low-pressure (~1 torr) oxygen-plasma, coupled with high vacuum techniques, to remove organic matter in the paint leaving the substrate rock and carbonate/oxalate accretions intact (Ilger et al. 1995; 1996 and references therein). Plasma conditions are similar for all samples whether inorganic pigments or charcoal. Our early studies established the necessity for cleaning the plasma extraction system with oxygen plasmas before sample insertion to rid surfaces of adsorbed CO_2. After a sample is loaded into the plasma chamber, the chamber is evacuated to ~10-4 torr and then filled with 0.2 torr ultra-high purity Ar (99.999%). Low power Ar-plasmas are run on each sample to remove adsorbed CO_2 by inelastic collision of the unreactive, but high energy, Ar atoms and ions. We repeat this process until the amount of carbon, as CO_2, desorbed by the plasma is <1 µg. This amount of carbon has a minor effect on the sample age because the background on a typical AMS is ~2 to 4 µg carbon. Following the final Ar-plasma, the system is pumped to ~10-7 torr and left pumping for several hours. The vacuum pumps are then closed to the system and the rise in pressure for an hour or more is monitored to indicate leakage into the plasma chamber. No significant leaks were found for any of these samples.

When these precautions are followed, only negligible amounts (<1 µg carbon) of adsorbed CO_2 are released from the system surfaces or from sample surfaces during plasma extraction of a rock painting sample. After the vacuum integrity check, the chamber is filled with 1 torr ultra-high purity O_2 (99.999%). The sample is then oxidized in a low temperature plasma. The gaseous CO_2 produced by the oxygen plasma oxidation of the organic material in the paints, whether charcoal or an unidentified organic binder/vehicle, is collected and its pressure measured after the H_2O produced in the plasma reaction is removed by freezing. The CO_2 is then frozen at -194°C, sealed into a borosilicate glass finger, and sent to an AMS facility for 14C analysis of the organic material extracted from the rock painting.

Results

Samples with well characterized 14C - To test the validity of the plasma-chemical technique, we analyzed samples of known 14C content, both 14C-free and known age. The results on 14C-free samples (Albertite, IAEA wood and partially coalified Axel Heiberg wood) demonstrated that our technique did not introduce significant additional modern carbon over the AMS background levels (Ilger et al. 1995). We also dated charcoal and Third International Radiocarbon Intercomparison (TIRI) Belfast pine (B) samples of previously determined 14C ages. Figure 2 illustrates the comparison of our determinations on these

known-age materials. Agreement observed is within expected statistical variation. Two analyses appear outside ~±1σ uncertainties; that number of deviant values is expected because of statistical uncertainty alone. However, we suspect that our first determination of TIRI wood, 4,730 ± 60 years BP, may have been contaminated by the plastic bag the sample had been stored in. The first sample was an external sample in contact with a plastic bag for several years. The next two determinations, 4,530 ± 60 and 4,530 ± 70 years BP, were taken from the interior of the sample and exhibit statistical overlap with the accepted age (4,503 ± 6 (1s) years BP; Gulliksen and Scott 1995).

These results on samples of known 14C content support the general validity of the plasma-chemical technique for radiocarbon dating.

Figure 2. *Comparison of our plasma-chemical AMS results (solid symbols) with 14C content previously determined at other laboratories (open symbols). Agreement is within the expected statistical variation.*

Comparaison de nos résultats plasma-chimiques SMA (symboles noirs) avec le contenu de C14 déterminé antérieurement dans d'autres laboratoires (symboles blancs). Un bon accord apparaît dans la limite de la variation statistique attendue.

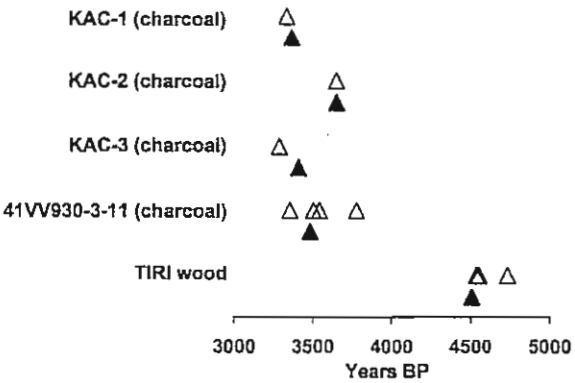

Table 1. Site sample numbers, 14C dates, AMS numbers and references for the Texas rock painting dates originating from our laboratory.

Painting site	Radiocarbon date Years BP	AMS numbers	References
Pecos River genre			
41VV75-1(c)	3865 ± 100	ETH-5909	Russ et al. 1990
41VV576-3a(c)	3000 ± 70	ETH-7047	Russ et al. 1992a
41VV576-1a(c)	3355 ± 65	ETH-6962	Russ et al. 1992a
41VV576-1b(c)	4200 ± 90	AA-7063	Chaffee et al. 1993b
41VV50-3a(c)	2950 ± 60	AA-8699	Chaffee et al. 1993b
41VV75-29A(c)	2750 ± 50	CAMS-17316	Ilger et al. 1994b
41VV75-29B	3190 ± 60	CAMS-17897	Ilger et al. 1994b
41VV75-37A(c)	2950 ± 60	CAMS-14087	Ilger et al. 1996
41VV75-37B(c)	3580 ± 60	CAMS-14088	Ilger et al. 1996
41VV75-37C(c)	3240 ± 60	CAMS-14089	Ilger et al. 1996
41VV75-37D(c)	3210 + 60	CAMS-14090	Ilger et al. 1996
41VV75-37E(c)	3550 ± 90	CAMS-17990	Ilger et al. 1994b
41VV75-37F(c)	3680 ± 60	CAMS-18206	Ilger et al. 1994b
41VV75-47A-1	3690 ± 80	CAMS-23927	Pace 1996
41VV75-47A-2	3790 ± 80	CAMS-25384	Pace 1996
41VV75-47A-3	3440 ± 50	CAMS-26762	Pace 1996
41VV75-47A-4(d)	2340 ± 80	CAMS-25368	Pace 1996
41VV75-47A-5	3310 ± 50	CAMS-25885	Pace 1996
41VV75-47A-6(c)	3900 ± 60	CAMS-25884	Pace 1996
Expected age			
Red Monochrome genre			
41VV233			
bkgd-corrected(c)	1125 ± 85(a)	CAMS-11891	Ilger et al. 1995
Expected age	650-1350		Turpin 1986
Red Linear genre			
41VV162A			
bkgd-corrected(c)	1280 ± 150(b)	AA-10549	Ilger et al. 1995
Expected age	1350-3000		Turpin 1984
Charcoal deer			
41VV75-50	1280 ± 80	CAMS-29315	Hyman et al. 1996b
Hueco Tanks			
20G-4	1180 ± 80	CAMS-29314	Sutherland et al. 1997
28A	790 ± 60	CAMS-23164	Sutherland et al. 1997
23C-1	740 ± 50	CAMS-23165	Sutherland et al. 1997
24F	1350 ± 160	CAMS-23559	Sutherland et al. 1997
12A	1250 ± 60	CAMS-23560	Sutherland et al. 1997
20K-2	1010 ± 70	CAMS-27228	Sutherland et al. 1997
20C	1250 ± 80	CAMS-25886	Sutherland 1997

(a) The background uncorrected date obtained from the AMS was 1315 ± 50 years BP.
(b) The background uncorrected date obtained from the AMS was 1280 ± 45 years BP.
(c) Not chemically pretreated
(d) Rejected because it fell well outside the range of the other dates on Pecos River genre paintings

Texas rock paintings

Dating - Table 1 summarizes the 14C dates we obtained on rock paintings in Texas. Pecos River genre rock paintings are the oldest in the Lower Pecos River region based on superposition and depiction of atlas. The figures are static, often larger than life-size, and polychrome: black, yellow, brown, reds, ranging from brown to purple to orange, and in rare instances, white (Kirkland and Newcomb 1967: 37-80). We only sample highly degraded paintings. In the interests of visual illustration, figure 3, VI shows a photograph of a Pecos River genre rock painting in good condition. This is not a painting we sampled. Dates obtained for this genre have not been corrected for possible background carbon contamination in the basal rock and mineral accretions. The spread of dates is due in part to the uncertainty introduced by the lack of such corrections. In one instance we split a sample into two aliquots, 41VV75-29A and -B. Aliquot-B was pretreated chemically in an attempt to remove at least part of the contamination carbon as compared with aliquot-A which was not pretreated. The difference in the two dates (440 years), 41VV75-29A at 2750 years BP and -B at 3190 years BP may be due to the difference in pretreatment (Ilger et al. 1994 a).

Samples 41VV75-37A-F were also from a single rock painting. A and B were not homogenized and give an indication of the spread that may be expected from differences in contamination levels in the same rock painting. C and D were splits of a homogenized sample and demonstrate that replicate analyses yield the same result for aliquots of the same sample (Ilger et al. 1996). An adjacent sample was divided into two further portions: 41VV75-37-E and -F. For sample E, an attempt was made to scrape off the accretion to yield a 'purer' pigment sample. Sample F was handled as usual without prior removal of accretion, so that the sample contained more accretion than sample E. The agreement in the ages for E and F shows that we were unsuccessful in enriching the pigment by separating the accretion, not surprising as the pigment and accretion layers are intermixed (see figure 1).

The 14C dates listed in Table 1 for the fourteen rock painting samples of the Pecos River genre lie between 2750 years BP and 4200 years BP, with the exception of 41VV75-47A-4. This date is rejected because the sample fumed and partially spilled from the tube in the chemical pretreatment step and because the date fell well outside the range of dates for other Pecos River genre paintings. Pace (1996) contends that dates for samples 41VV75-47A-3 and 5 were low due to pretreatment with HCl. Turpin (1990) argues, based on rough population estimates and the relationship of population density to information stress, that ages for the Pecos River genre should concentrate between about 3000 to 4000 years BP. In spite of the lack of background correction, our results generally fall within Turpin's estimate of the expected age range. This agreement suggests that the background correction is typically a few hundreds of years or less for this genre. Real variation between the ages of the different rock paintings is not unexpected.

The 14C dates for one sample each of two other genres located in the Lower Pecos River region, Red Monochrome and Red Linear, were corrected for background (Ilger et al. 1995). Typical examples of Red Monochrome and Red Linear paintings are shown in figures 4 and 5, VI. Red Monochrome figures are approximately life size, red static anthropomorphs and zoomorphs. The zoomorph in figure 4, VI is approximately one meter long. An unpainted rock sample from the wall near the Red Monochrome painting yielded a background with enough carbon (35% of the amount of carbon in the Red Monochrome painting sample) to be dated. This allowed correction for the background based on the weights of the background and painting samples. The shift in age of the Red Monochrome 14C date due to the background carbon was from 1315 ± 50 years BP (uncorrected) to 1125 ± 85 years BP (after correction). Red Linear paintings are small (<12 cm) stick figures, often depicting motion. They are generally red, but on occasion black. Because the amount of background contamination carbon (9% of the Red Linear painting) was too small to provide an accurate 14C date, the age was not changed; rather, extremes of modern and ancient carbon were used to increase the standard deviation to reflect the uncertainty due to contamination by the background. The uncorrected date was 1280 ± 45 years BP with an increased uncertainty after correction of ± 150 years. Both the Red Monochrome and Red Linear rock paintings yielded ages that are in agreement with the broad age ranges expected on the basis of archaeological inference. Red Monochrome genre rock paintings are constrained by the bows and arrows depicted to be more recent than ~1350 years BP, and to be older than ~650 years BP due to the lack of bison depictions (Turpin 1986). It is difficult to place temporally the Red Linear genre more accurately than older than Red Monochrome and younger than Pecos River genre, i.e., between ca. 1350 and 3000 years BP, based on superpositions (Turpin 1984). Our date for the Red Linear painting overlaps within the uncertainty with the more recent end of this range. Thus, our dates for three genres of rock paintings in the Lower Pecos region of southwest Texas are consistent with the age ranges expected based on archaeological inference.

The first charcoal pigment we saw in the Lower Pecos River region were a series of a dozen deer ~12 cm long about 40 meters from the Pecos River paintings dated and listed in table 1. A sample, taken from one of these black charcoal deer, gave a 14C date of 1280 ± 80 years BP, overlapping the ages of the Red Monochrome and Red Linear paintings we dated. At Hueco Tanks National Historic Park, Texas, all the paintings we dated were charcoal. Hueco Tanks rock paintings are considered to be of the Jornada Mogollon genre, thought to have been painted

after approximately A.D. 1050, or 900 years BP (Schaafsma 1982:197). Figure 6 is a photograph of a recurring goggled-eyed motif. About half of our Hueco Tanks rock painting dates are earlier than 900 years BP. Dates on charcoal pigments are more reliable than those on inorganic pigmented samples because the procedure for dating charcoal is well established. Because the Hueco Tanks samples consisted of charcoal pigments and were treated with sodium hydroxide to remove contamination as is done for all archaeological charcoal 14C dates, we conclude many of the rock paintings at Hueco Tanks were painted earlier than was previously generally thought.

Dates outside Texas

Table 2 contains our 14C dates on samples from outside Texas. The All American Man is a shield figure approximately one meter tall (figure 7, VII) painted in an alcove containing remains of a late Anasazi structure (site 42SA20615, Utah). Our results on a sample of the rock painting, 676 ± 46 years BP, are consistent with the archaeological context of a late Anasazi habitation and storage structure (Chaffee et al. 1994a). The date of this painting is also consistent with a number of dates from nearby Anasazi sites that range from 540 to 800 years BP (tabulated in Chaffee et al. 1994a). The superpositioning of two paints allows a relative chronology of a rock painting panel in Red Cliffs, Arizona (figure 8, VII). Whitish clay pieces were applied over a black-pigmented figure. Unfortunately, superpositioning gives no indication how much more recently the clay dots were added. Our results indicate that the clay dots were added about 500 years after the black motif was painted 1080 ± 100 14C years ago. A red rock painting in Montana, 24BH50-1a, dated at 850 + 96/-83 (Chaffee et al. 1994 b), is located near a site that has two stratified layers with cultural remains that have been dated at 850 ± 50 and 1270 ± 125 years BP. Our date overlaps the younger of those two dates.

Figure 6. *Photograph of a Hueco Tanks black and white/yellow motif. The upper figure is approximately one-half meter tall*

Hueco Tanks noir à motif blanc jaune. La figure supérieure mesure environ 50 cm de haut.

Table 2. Sites, 14C dates, AMS numbers and references for the samples of rock paintings from outside of Texas we dated.

Painting sites	Radiocarbon date, years BP	AMS numbers	References
Arizona			
Red Cliffs Ar-03-04-06-287-a	1080 ± 100(a)	CAMS-19406	Loendorf et al. 1996
Red Cliffs Ar-03-04-06-287-b	550 ± 100(a)	CAMS-19407	Loendorf et al. 1996
California			
Fern Cave, Lava Beds, tlk-2-a	840 ± 70	CAMS-27229	Armitage et al. 1997
Fern Cave, Lava Beds, tlk-2-b	230 ± 70	CAMS-27860	Armitage et al. 1997
Fern Cave, Lava Beds, tlk-2-c	330 ± 50	CAMS-27861	Armitage et al. 1997
Montana			
24BH50-1a	840+96/-82(b)	AA-8843	Chaffee et al.1994b
Expected age	850 ± 40(b)		Loendorf and Porsche 1985
Utah			
42SA1614-1a, Utah, USA	750 ± 60	AA-8359	Chaffee et al. 1994a
42SA1614-1b, Utah, USA	575 ± 70	AA-8361	Chaffee et al. 1994a
Expected age	650-950		Chandler 1990
Angola			
Mucubal 1a	2430 ± 50	CAMS-11594	Ilger et al. 1995
Mucubal 1b	1880 ± 100	CAMS-10891	Ilger et al. 1995
Mucubal 1c	1900 ± 60	CAMS-11325	Ilger et al. 1995
France			
Le Portel, Niaux type horse	12180 ± 125(c)	AA-9465	Ilger et al. 1994a
Le Portel, large horse	11600 ± 150(c)	AA-9766	Ilger et al. 1994a
Santimane, Bison	9545 ± 80	AA-9765	Chaffee et al. 1994a
Gargas, main sanctuary	10710 ± 630(c)	CAMS-4410	Ilger et al. 1994c
Bedeilhac, bichrome horse	7290 ± 340(c)	CAMS-3919	Ilger et al. 1994c
Bedeilhac, bison de diverticule	11620 ± 160(c)	CAMS-20966	Ilger et al. 1994c

(a) The older Red Cliffs sample was a black pigment (1080 years BP) that was overlain by a whitish piece of clay (550 years BP).

(b) A different site near the rock painting had been excavated and yielded two 14C dates: 850 ± 50 and 1270 ± 125 years BP. Our date is in exact agreement with the younger of these two dates.

(c) Our project to date the French/Spanish samples was intended to see how small a sample of charcoal pigment could be dated. Except for the Le Portel samples, these yielded very small amounts of carbon, often < 50 mg, always < 75 mg.

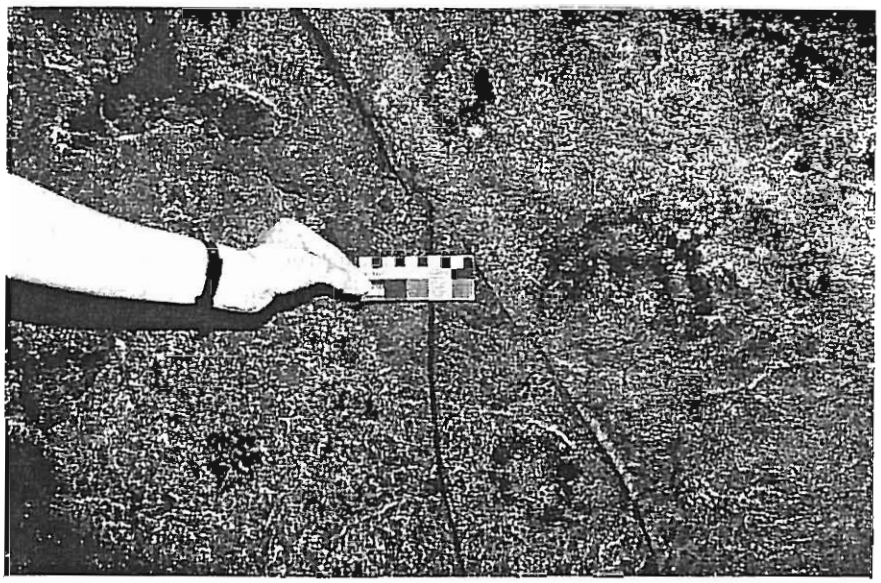

Figure 9. *The rock art panel at Fern Cave, Lava Beds National Monument, California, showing the three figures dated: two circles and a crescent, a combined image that is suggested as a recording of the 1054 A.D. supernova explosion (Brandt and Williamson 1979). The scale is 10 cm long.*

Le panneau rupestre de Fern Cave, Lava Beds National Monument, Californie, montrant les trois figures qui ont été datées : deux cercles et un croissant, image combinée suggérant la représentation de l'explosion de la supernova en 1054 av.JC (Brandt and Williamson 1979). Echelle : 10 cm de longueur.

Over twenty American painted and carved rock panels with a circle or star-like symbol and a crescent in proximity have been suggested as depictions of the 1054 A.D. supernova that resulted in the Crab Nebula. One, suggested by Brandt and Williamson (1979), is a rock painting panel in Fern Cave, Lava Beds National Monument, California (figure 9). However, a direct date of the paint-ings or carvings is the only way to judge whether the 1054 A. D. supernova is being portrayed. We dated three sam-ples from the Fern Cave panel (Armitage et al. 1997), two circles and a crescent in proximity. 14C analysis (table 2) does not permit interpretation of these images as that supernova. Skepticism is warranted for other possible depictions until they too can be dated to support or eliminate their association with the supernova.

Comparison of our results on European palaeolithic paintings (Ilger et al. 1994 a, c) with the dates obtained by Clottes, Valladas and co-workers (Clottes et al. 1992 a, b, c, 1994; Valladas et al. 1990, 1992) is difficult, in part because we are not sampling the same paintings. Our collaboration with Michel Menu (Research Laboratory of the Museums of France, Louvre, Paris) was an attempt to determine if reliable results could be obtained on very small samples. Except for the two Le Portel samples, none of our palaeolithic rock painting samples produced more than 75 mg of carbon; three produced less than 50 mg. The dateable carbon samples reported by Valladas et al. (1992) were 5 to 100 times larger than the dateable carbon extracted from our palaeolithic painting samples; Clottes et al. (1992 a, b, c) did not report the weights of the dateable carbon. The differences between our dates and those of the French workers is due to the small size of our samples. Because our samples were so small, we did not attempt chemical pretreatment, fearing sample loss. Results of Valladas et al. (1992) indicate that such pretreatment may not be important for these palaeolithic samples, because NaOH fractions yielded ages within a few hundred years of the charcoal. The smallest sample of carbon we dated (~15 mg) came from Gargas, a black negative hand in the main sanctuary # 1. If we assume that our Gargas sample is the age of the Gargas hand print dated at 26,680 years BP by Clottes et al. (1992 c), then for a 15 mg sample of carbon, incorporation of only 3.6 mg of 1950 carbon shifts the age from 26,680 years BP to the 10,710 years BP we observed. Since typical backgrounds at the University of Arizona and Lawrence Livermore AMSs are ~2 to 4 mg carbon (from oxidation and graphitization as well as the AMS background), significant improvements in graphitization and AMS backgrounds are required if reliable dates are to be obtained on samples <100 mg. Similarly, for our other palaeolithic samples, differences in our dates from those of the French may be explained by differences in sample sizes. We received a sample of charcoal pigment from Mucubal 1, Opeleva Cave, Angola that we split into two portions (Ilger et al. 1995). One portion, treated with sodium hydroxide to remove humic acids, produced a date of 2340 ± 50 years BP. Duplicate analysis of the second portion that was not pre-treated gave ages of 1880 and 1900 ± 60 years BP. These results that, as with all archaeological charcoal dating, it is necessary to show chemically pretreat charcoal pigments to obtain the most trustworthy results. We have instituted a NaOH wash as standard pretreatment of all rock painting samples to be dated.

Discussion

Six requirements for successful direct radiocarbon dating of rock paintings were listed in the introduction and will be discussed here in detail with regard to our technique.

Requirements 1 & 2

The first requirement is that organic matter was added to the paints initially and the second is that enough organic material has survived to yield adequate carbon to date. Each case must be examined individually to see whether measurable amounts of organic materials exist. This is a limitation that any technique for 14C dating rock paintings must face. Three of the four prehistoric rock painting genres in the Lower Pecos River region of Texas apparently used organic binders or vehicles. The fourth, Bold Line Geometric, remains to be studied. However, in the Olary region of South Australia, we attempted to extract organic matter from four red and white pigment samples, but found no evidence for the addition of an organic binder/vehicle. Similarly, at Hueco Tanks State Historic Park and Jaguar Cave, in far west Texas, we found insignificant levels of organic matter in red, black (non-charcoal) and white pigmented rock paintings.

Requirement 3

Organic carbon can be extracted without also removing carbon from the atmosphere, limestone (calcium and magnesium carbonate), or mineral accretions (calcium carbonates and oxalates) found both above and below rock paintings. Low-temperature plasma extraction was chosen initially because we anticipated that this would be possible. The early stages of the development of our plasma extraction technique was primarily directed toward showing this was true (Chaffee et al. 1993).

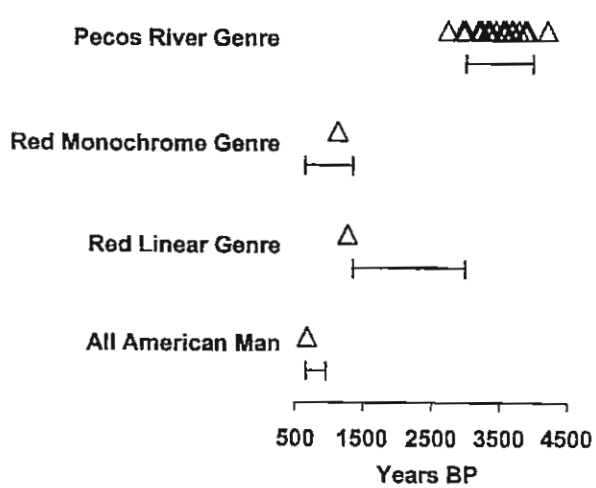

Figure 10. *Comparison of our dates with the age ranges based on archaeological inference. We agree with the archaeologically inferred ages in every instance. The triangle symbols are our determinations which are to be compared with the ranges (shaded bars) shown below them.*

Comparaison de nos dates avec les échelles d'âge basées sur des déductions archéologiques. Pour chaque cas nous trouvons une correspondance avec ces dernières. Les symboles en triangle représentent nos déterminations à comparer avec les échelles présentées en bas.

Requirement 4

Extraction does not introduce significant mass fractionation. We studied two different types of samples to demonstrate that significant mass fractionation is not produced by the plasma-chemical extraction technique. Our first study on charcoal found mass fractionation to be only 0.16" maximum (Russ et al. 1992a). In another study, collagen extracted from bone showed a total spread of mass fractionation in our technique of ~1". In neither case was mass fractionation an important component of error to the 14C date. A 1" change due to mass fractionation introduces only a 16 year error in the 14C age.

Requirement 5

Carbon in the organic matter originally added to the paint does not exchange with other sources of carbon after paint application. This can be ascertained only indirectly by comparing dates we obtained using the plasma-chemical technique on rock paintings constrained by archaeological inference. Figure 10 shows our dates on rock paintings that were previously somewhat constrained by archaeological inference. In each case, our measured dates are in general agreement with the inferred age ranges. That implies that there is no large scale exchange of the rock painting binder/vehicle organic carbon with extraneous carbon from carbonates, oxalates, ground water and the atmosphere, although the archaeological constraints are too broad to permit elimination of the effect on finer scale. We are presently conducting experiments to determine the precise binder/vehicle used to prepare the paint for two Pecos River genre rock paintings (Reese et al. 1996 a, b). Once the exact nature of the carbonaceous matter being dated can be established, the strict validity of requirement (5) will be evaluated in more detail. The fact that dates we obtained on numerous rock paintings agree in general with the age ranges expected based on archaeological inference, also supports the validity of our technique. But a given date is not convincing only because it agrees with current archaeological inference. The dates will be truly validated only when verified by independent means.

Requirement 6

Basal rock and mineral accretions associated with the rock painting do not contain enough organic carbon (contamination) to invalidate a date. Levels of organic contamination carbon in the rock and mineral accretions associated with a rock painting must be determined in each case. We have seen contamination ranging from nil to levels such that a nearby sample of unpainted basal rock is comparable to the painted sample in organic content. We corrected for background contamination in two samples (Ilger et al. 1995). Unfortunately, the archaeologically inferred age ranges are too broad to provide a

stringent test of the correction or of the technique in general. Future work in this laboratory will concentrate on methods for eliminating the contamination that sometimes thwarts attempts to date rock paintings.

Dorn (1995) listed ideal 14C dating conditions with which we concur: 1. the nature of the material to be dated is known (e.g., charcoal, beeswax); 2. independent tests have been conducted to show that the dated material yields reliable 14C ages; 3. the best method of sample pretreatment has been established; and 4. multiple ages are measured, because single ages are only suggestive. Published rock art dating papers often omit detailed experimental procedures. Thus it is difficult to evaluate whether laboratories are meeting Dorn's suggestions. Only for charcoal pigments are some investigators even close to satisfying these four requirements.

In some cases, pretreatment has been omitted because of the small sample size. Duplicates have rarely been run for comparison. French teams (Clottes et al. 1992 a, b, c; Clottes 1994) often run duplicates, with results usually in agreement; but, occasionally discrepancies are seen (e.g., Cougnac, mégaceros femelle: 19,500 ± 270 vs. 25,120 ± 390 years BP (Clottes 1994)). Evin (1996) recently reviewed French rock painting dates in this journal and concluded that, although they represent "an undeniable advance in the study of palaeolithic art... Certain limitations on the application of the carbon 14 dating method to ages of several tens of thousands of years mean that caution is necessary and the figures should not be interpreted too strictly." That call for caution holds true for all dates obtained on rock paintings, especially those studies where materials other than charcoal and possibly beeswax (Nelson et al. 1995) were dated, or when charcoal was dated without chemical pretreatment. We have found that humic acids are sometimes present in charcoal paints and that pretreatment is essential.

Summary

The dates we obtained on rock paintings during the past six years indicate that our plasma-chemical/AMS technique for estimating 14C ages on rock paintings has the potential to produce accurate and reliable results, but more work is needed. Our plasma-chemical technique is still in the early experimental stages, but appears to be yielding dates that are accurate to perhaps ~± 300 14C years for samples with >100 mg carbon. The technique is applicable to rock paintings that were painted with inorganic, iron- and manganese- oxides/hydroxides, as well as charcoal. Organic carbon in the basal rock and mineral accretions associated with rock paintings is still an impediment to our technique routinely giving accurate and reliable ages. With this 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.

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VI

Figure 3. *An example of a Pecos River rock painting, showing a composite figure approximately 2 meters tall.*

Exemple de peinture rupestre à Pecos River. On y voit une silhouette composite d'environ 2 mètres de haut.

Figure 4. *A Red Monochrome rock painting of a zoomorph, with an ~1 meter long body.*

Peinture monochrome rouge zoomorphe, montrant un corps d'environ 1 mètre de long.

Figure 5. *A Red Linear rock painting of a zoomorph approximately 10 centimeters long.*

Peinture linéaire zoomorphe rouge, d'environ 10 cm de long.

Figure 7. *A photograph of the All American Man shield-bearing figure, Utah. This unusual red, white and blue (charcoal) anthropomorph is approximately 1 meter tall. Also visible in the photograph are remains of a typical Pueblo II-Pueblo III Anasazi building.*

Le « All-American-Man » au bouclier, Utah. Cette silhouette anthropomorphe inhabituelle, rouge, blanche et bleue (charbon de bois) mesure environ 1 mètre de haut. On voit aussi des vestiges d'un bâtiment Anasi Pueblo II-Pueblo III typique.

Figure 8. *A photograph of a painted motif at Red Cliffs, Arizona showing the black figure overlain with clay dots. The central black motif is approximately three-fourths of a meter tall. According to the radiocarbon analysis, the white dots were added ~500 years after the shield was painted.*

Motif peint à Red Cliffs, Arizona, présentant une figure noire recouverte de points d'argile. Le motif central noir mesure environ 75 cm. D'après l'analyse par radiocarbone, les points blancs furent ajoutés environ 500 ans après que le bouclier eut été peint.