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DIRECT RADIOCARBON DATING OF ROCK ART

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ABSTRACT. In ^{14}C dating of pictographs, we use a low-temperature oxygen plasma coupled with high-vacuum techniques to selectively remove carbon-containing material in the paint without contamination from the rock substrate, even if limestone ($CaCO_3$). In addition to one previously published measurement, we analyzed two more pictograph samples, which are in accord with archaeological inference. A sample of known age charcoal, also processed by our method, matched the control. This technique produces little mass fractionation, the maximum $\delta^{13}C$ being 0.16‰ from the untreated sample. Limestone decomposition does not occur during our procedure. Although the technique development is in its infancy, these new results demonstrate that our non-destructive technique has great potential for producing accurate ^{14}C ages.

INTRODUCTION

Pictographs occur worldwide, but until recently (*e.g.*, van der Merwe, Sealy & Yates 1987; Loy *et al.* 1990; Russ *et al.* 1990, 1991; Valladas, Cachier & Arnold 1990) archaeologists assumed that such artifacts could not be dated directly (Leroi-Gourhan 1965; Barnes 1982). Instead, indirect methods were used to give relative ages: superpositions of style; depiction of temporally sensitive elements; dating deposits that cover the art *in situ*; dating deposits that contain exfoliated fragments of the painted surfaces (Kirkland & Newcomb 1967; Breuil 1979; Sieveking 1979; Pfeiffer 1982). However, the lack of direct chronometric methods have made it difficult to relate these graphics to associated archaeological artifacts and, thus, known cultural sequences. Here we present a progress report on our new technique (Russ *et al.* 1990, 1991) for ^{14}C dating pictographs with results from three samples of Pecos River style rock paintings and one of known age charcoal. The pictograph dates, 3865 ± 100; 3355 ± 65; 3000 ± 70 BP, concur with archaeological inference. Our determination of the age of a previously dated charcoal sample was in perfect agreement with the earlier age.

Direct ^{14}C dating of pictographs requires that 1) organic material was incorporated into the paints, and 2) this carbonaceous matter can be extracted without contamination from other sources. The paint pigments themselves are inorganic, primarily iron and manganese oxides, at least in the Lower Pecos (Zolensky 1982). To facilitate attachment of the pigments to the substrate wall, an organic binding medium is often used (Rudner 1983; Loy *et al.* 1990). This organic binder can be dated, or in some cases, the charcoal used as pigment (van der Merwe, Sealy & Yates 1987; Valladas, Cachier & Arnold 1990). The organic phase must be extracted from a sample that contains a portion of the rock substrate along with the surface painting. In the Lower Pecos region, the substrate is limestone ($CaCO_3$). Thus, the most profound source of potential contamination is the inorganic carbon of the substrate and the calcite and gypsum ($CaCO_3$, $CaSO_4 \cdot 2H_2O$) accretion which sometimes occurs on the pictographs.

METHODS I - SAMPLE DATING

We use a radiofrequency (RF) generated low-temperature (~175°C), low-pressure (~1 torr) oxygen plasma to separate the organic matter from the carbonate substrate by oxidizing the organic material to carbon dioxide (CO_2). This type of plasma has long been known to have a catalytic effect in oxidizing virtually all types of carbonaceous materials (Gleit & Holland 1962; Gleit 1965; Hollahan 1966). The atomic oxygen and excited molecular species produced in the discharge readily react with organic matter in the paint, forming CO_2 and H_2O. In the otherwise mild conditions, the already fully oxidized carbonate rock is unaffected. The gaseous products can be separated by freezing on a liquid nitrogen (LN_2) cold finger. Thus, the plasma allows the selective removal of the organic phase leaving the substrate intact. Once extracted, the organic component can be analyzed by accelerator mass spectrometry (AMS), enabling these pictographs to be ^{14}C dated for the first time.

Vacuum System

The apparatus and procedure have been described earlier (Russ *et al.* 1991). Although the basic design remains the same, we have made changes to the system and in the operating procedure for future runs, based on the results of experimental tests conducted during the past several months. We repeat the procedure here and incorporate the specific changes that have been made to improve it. To minimize contamination by atmospheric CO_2, we built a Pyrex high-vacuum chamber, 27 cm long and 10 cm in diameter. This was placed between two external rectangular copper electrodes (14 cm × 20 cm with 3-cm holes drilled on 4.5-cm centers) bent to conform to the curvature of the chamber. In our earlier work (Russ *et al.* 1990, 1991), the electrodes were connected to an International Plasma Corporation RF generator (13.6 MHz, 150 watt maximum power). Now we are using a Plasma-Therm, Inc., RF generator (27.2 MHz, 1500 watt maximum power). The electrodes, however, are identical. In our present apparatus, all pumping is accomplished with oil-less pumps. Two LN_2 sorption pumps achieve pressures of $\sim 10^{-5}$ torr in the system; an ion pump is used to obtain high vacuum (10^{-7} torr). Pressures are measured only when the plasma is not being run, using a CVC Products GT-340 A thermistor gauge and a Bayard-Alpert ionization gauge. The gauges are separated from the plasma chamber by an all-metal valve with a copper gasket. Leak tests are routinely performed to ensure high-vacuum integrity. Our prior use of ultra-pure bottled oxygen has been discontinued due to concern that the bottled oxygen may contain traces of organic material or CO_2. Instead, a CuO furnace was added to the system, which produces pure oxygen when heated to ~900°C. In the previous apparatus design, samples were inserted into the chamber after blowing an opening in the glass. To eliminate the possibility that organic material was introduced from the flame or the glass blowing, we now use a 7 cm ConFlat blank flange with a copper gasket, through which the sample is placed into the chamber.

Plasma Chamber Cleansing

Before introducing the sample into the chamber, a series of steps are carried out to thoroughly cleanse the interior walls of any possible organic contamination: 1) the chamber is rough-pumped down to $\sim 10^{-3}$ torr with the first LN_2 pump before opening the second to achieve a pressure of $\sim 10^{-5}$ torr; 2) oxygen is introduced to a pressure of ~1 torr by raising the CuO furnace to ~900°C; 3) the RF generator is set to 250 watts and a plasma produced with a matching network keeping the reflected power at <5% of the incident power level; 4) the plasma is maintained for 2 h; 5) the RF generator is turned off and the system pumped back down to $\sim 10^{-5}$ torr using the LN_2 pumps. This procedure is repeated until no CO_2 is released, ensuring clean surfaces. During the cleaning phase, heating tapes keep the collection arm and cold finger at ~180°C. The oxygen plasma treatment oxidizes all organic contamination in the chamber to CO_2 and H_2O; the heating and subsequent vacuum pumping prevents adsorption of the gases onto the glass surfaces. The plasma chamber is not in contact with any organic materials; all surfaces seen by the plasma are either borosilicate glass or metal. Thus, there is little chance of contamination from the plasma chamber itself after cleansing by this plasma operation. Residual atmospheric CO_2 contamination is minimized by evacuating the reaction chamber to a pressure of $\sim 10^{-7}$ torr before introducing plasma oxygen. We had previously calculated that an atmospheric pressure of 65 torr was sufficiently low that CO_2 would cause only a 1 ppm increase of the ^{14}C concentration, assuming no leak in the system. As a second precautionary measure, we now open our vacuum system only to pure argon or nitrogen atmospheres, so that our system is subjected to little atmospheric CO_2.

Sample Analysis

No special sample preparation is necessary other than that common to all ^{14}C dating. Samples were placed in aluminum foil when collected, brought to the laboratory and photographed in both black and white and color. Then the samples were wrapped in clean aluminum foil and placed into a vacuum desiccator. This was evacuated with a LN_2 sorption pump and filled with pure argon. The samples are stored under argon until removed for study. The samples are examined under an optical microscope, all visible contamination removed and the painted surface carefully scraped off. Every attempt is made to keep the sample exposed primarily to argon until placed in the plasma chamber, which is itself being flushed with argon or nitrogen. The samples are placed on a Pyrex glass plate, 15 cm × 3 cm, near the center of the plasma chamber after unbolting the 7 cm ConFlat blank flange, which is rebolted after sample insertion. The system is pumped with the two LN_2 pumps until the pressure is low enough that the ion pump can be engaged ($\sim 10^{-5}$ torr). Heating tapes on the collection arm and cold finger are kept at ~180°C during the entire pumping phase. Infrared lamps also heat the sample chamber to accelerate outgassing and to prevent gases from adsorbing on the walls. Once high vacuum is obtained, the heating devices are removed and the resulting pressure monitored after closing the valve to the ion pump to insure no leaks. The system is then ready to begin plasma production. Oxygen from the CuO furnace is admitted into the system to a pressure of ~1 torr. Application of the RF potential across the external electrodes produces a glow discharge that is maintained for a few hours. The products formed by the reaction of the organic phase of the paint with the oxygen plasma (CO_2 and H_2O) are collected in the extraction finger by cooling with liquid nitrogen and sealed off. The finger is then sent to an AMS facility for determination of the ^{14}C content.

METHODS II - PROCEDURE VALIDATION

Establishing Limestone Stability in the Plasma

Limestone, at least $CaCO_3$, which is the primary (~97% or greater) component of Lower Pecos limestone, does not decompose in the oxygen plasma. Powdered $CaCO_3$ was placed into the plasma vacuum chamber and thoroughly cleaned by subjecting it to an oxygen plasma. Then possible CO_2 production from $CaCO_3$ decomposition was monitored as the power of the system was raised from an initial value of 75 watts. No measurable $CaCO_3$ decomposition occurred in our system even at 350 watts, well above our operating power of 100 watts.

We measured the temperature of the $CaCO_3$ in the chamber during plasma operation as a function of both plasma power and oxygen pressure in order to determine the approximate sample temperature during a plasma run and to optimize our operating conditions for future extractions. Over a pressure range of 0.5 to 2.0 torr, the temperature decreased monotonically as the pressure was increased, falling ~40°C per torr. Similarly, the rate of production of CO_2 from oxygen plasma treatment of graphite fell as oxygen pressure was increased. Figure 1 shows the increase in limestone temperature as the power of the system was raised from 75 watts up to 350 watts at oxygen pressures of 0.8 and 1.4 torr. At an oxygen pressure of 0.8 torr, the temperature is ~160°C at ~75 watts. This corresponds to an initial CO_2 production from graphite of ~ 0.021 cc min^{-1}. The reproducibility for setting the power is probably about ± 5–10 watts, which corresponds to temperature uncertainties of ± 10°C.

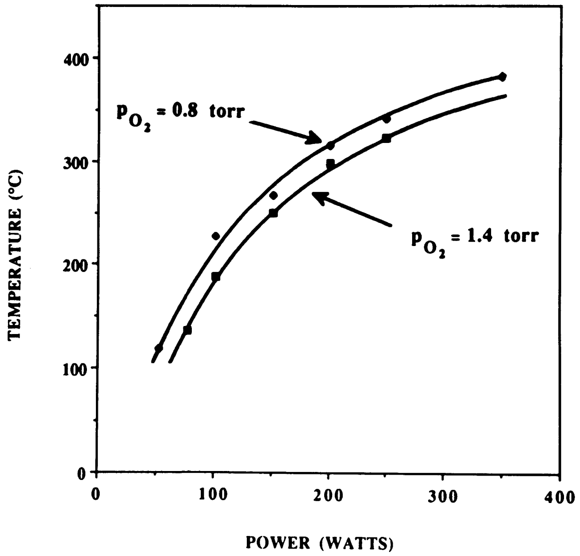

Fig. 1. Limestone temperature *vs.* system power. The temperature increases as the power is increased.

Although the limestone from the Lower Pecos region that we analyzed is comprised primarily of $CaCO_3$, it also contains a small component (<3%) of $MgCO_3$. We measured the $MgCO_3$ content of three limestone samples by atomic absorption and found values of 1.1, 3.1 and 2.2%. We are presently conducting experiments on the plasma decomposition conditions for $MgCO_3$.

Isotopic Fractionation

With the assistance of Professor E. Grossman, Department of Geology, Texas A&M University, we have measured the isotopic fractionation of carbon introduced by a typical plasma run. To do this, we placed a sample of charcoal of previously measured $\delta^{13}C$ into the plasma chamber and treated it as a normal sample to be dated. The CO_2 was collected at five different times as the oxygen plasma was applied. Analyses of the carbon isotopes were carried out on a Finnegan MAT-251 isotope ratio mass spectrometer. We summarize the data in Table 1. Our technique causes little isotopic fractionation for charcoal; the maximum change seen was only 0.16‰.

TABLE 1. Mass fractionation effects measured on charcoal treated to the plasma technique

Plasma exposure time (h)	$\delta^{13}C$	Cm^3 CO_2
No exposure to plasma	−7.53 ± 0.04‰	
0–0.25	*	0.32
0.25–1.25	−7.69 ± 0.04‰	1.6
1.25–2.25	−7.60 ± 0.04‰	1.2
3.25–4.25	*	0.85
4.25–5.25	−7.61 ± 0.04‰	0.86

*These samples leaked when sealed to the mass spectrometer and could not be analyzed.

RESULTS AND DISCUSSION

Our first pictograph sample gave an age of 3865 ± 100 BP (Russ *et al.* 1990), in accord with the archaeologically inferred onset of the Pecos River style, at 4100–3200 BP (Turpin 1991). We have since dated two additional samples of Pecos River style pictographs, yielding ages of 3355 ± 65 BP (Russ, Hyman & Rowe 1991a) and 3000 ± 70 BP (Russ, Hyman & Rowe 1991b). We also analyzed a sample of charcoal that had been dated earlier by Tamers (personal communication 1990), using the usual combustion and AMS techniques, at 3655 ± 60 BP. The charcoal sample was carried through our plasma procedure. The age we obtained, 3665 ± 65 BP, was in perfect agreement with the previous age. Whereas this constitutes a limited test, the result validated our confidence in the technique. In the future, we intend to repeat the test, adding limestone to other aliquots of this same charcoal sample. Table 2 lists the ages and the laboratory and site numbers for the samples we have dated.

TABLE 2. Site numbers, laboratory numbers and radiocarbon dates for three Pecos River style pictograph samples and a charcoal sample of known age

Site	Texas A&M	Beta Analytic	AMS	Years BP
41VV75	75-1	Beta-33586	ETH-5909	3865 ± 100
41VV576	576-1	Beta-39107	ETH-6962	3355 ± 65
41VV576	576-3a	Beta-39946	ETH-7047	3000 ± 70
	KAC-1	Beta-40497	ETH-7165	3665 ± 65
				3655 ± 60*

*Previously determined age given by Tamers (personal communication 1990).

Although all of the pictograph ages were consistent with archaeological estimates, the color of the plasma during the extraction of the organic carbon from the paint of the third sample showed evidence of slight atmospheric contamination. Since the second and third pictograph samples both yielded less CO_2 than the first pictograph or the charcoal sample of known age, they were more susceptible to possible adsorption of atmospheric gases. Adsorbed CO_2 would cause these samples to appear younger than they actually are. We are continuing to investigate the extent of the effect and how to minimize it. The adsorbed CO_2 can be reduced markedly by exposing the sample of limestone brought along with the paint sample to a low-temperature *argon* plasma. Argon, an inert, non-reactive gas, will not oxidize the organic material; so it does not react with organic carbon to form CO_2. Rather, the energetic argon plasma bombards the surface of the limestone grains, knocking adsorbed CO_2 off and allowing it to be pumped away. It will be possible, in this way, to clean the limestone of adsorbed CO_2 so that subsequent exposure to an oxygen plasma results in the production of CO_2 only from the oxidation of the pictograph paint binder. Preliminary experiments are promising and this work continues.

We are now confident that the potential problem of atmospheric adsorption can be readily overcome by the combination of high-vacuum techniques coupled with pretreatment with an argon plasma to ensure removal of adsorbed CO_2. Further, we demonstrated that we operate well below the plasma power level at which $CaCO_3$ decomposes, and that the dates obtained were not influenced by mass fractionation.

CONCLUSION

Our new method for the extraction of organic carbon from pictographs without contamination from the rock substrate is applicable to the direct radiocarbon dating of rock paintings throughout the world. It does not depend on the presence of a particular organic substance in the paint, since it will extract any organic material used. It is also independent of the substrate rock, working even on pictographs painted on limestone. The new technique will allow these fascinating, enigmatic graphics to take on a more important role as a critical component of cultural history. That these graphics had a major function in prehistoric societies is apparent. Yet without a chronometric age, assigning these artifacts to a specific culture is tentative. Further, the reactivity of low-temperature oxygen plasmas in oxidizing organic carbon is not limited to pictographs, but is germane to most materials previously dated by ^{14}C. Although our technique has passed the tests to which we have subjected it, continued research is needed before the method is proven to be practicable in providing accurate and reliable ages. We are engaged in an experimental program designed toward that end.

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