PART X

Dating Rock Art: Technological Advances and Applications
ABSTRACT

This chapter includes a brief description of radiocarbon dating rock images with accelerator mass spectrometry. Analytical techniques used to identify inorganic mineral and organic pigments found worldwide are discussed. One challenge to dating rock paintings is small sample sizes and minimal organic material. Plasma chemistry is used to date both charcoal and inorganic pigmented paintings. Calcium oxalate accretions can, in ideal situations, provide minimum and maximum ages, but typically provide minimum ages only. Recommendations for reporting radiocarbon dates will be offered. More research applied to dating rock art using multiple techniques is required. We provide case studies from various continents.

Direct dating [of rock art] must always be performed to check archaeological hypotheses and address particular problems. Aimless dating would only provide unrelated data that would have to wait until they could be corroborated by other methods. (Clottes et al. 1992:128–129)

The inclusion of rock art studies alongside other archaeological specialties is crucial for developing a synergistic approach to studying past cultures. At many sites, rock
art images have been cataloged with detailed descriptions as part of important and extensive recording projects, but without chronological information there is no way to directly relate the images to each other or the people who created them. In the past, rock art studies were neglected by mainstream archaeology, often relegated to providing attractive book covers for publishers. That situation was dictated by two assumptions held by most archaeologists: it was presumed impossible to directly date rock art with confidence or to interpret the cultural meanings associated with images.

The publication of this volume, the plethora of rock art papers in archaeology journals, and presentations at conference meetings all demonstrate the exciting research that is current in the field of rock art, particularly in the area of radiocarbon dating. Many advances have been made in interpreting rock art images in many locations (e.g., Lewis-Williams and Dowson 1988; Turpin 1991; Boyd 2003; McDonald and Veth 2009; Kaiser et al. 2010; Pettitt et al. 2010). Radiocarbon dating of rock art also makes it possible for images to be studied in association with excavated cultural materials. Alternatively, relative ages or approximate age ranges for some distinct genres of rock art have been possible using methods such as superimpositioning and stylistic analyses (Pettitt and Bahn 2003; McDonald and Veth 2008; Mulvaney 2009). These relative methods will continue to be crucial to rock art studies, as it is not possible or even desirable to directly date every image studied.

**Paint on a Rock Canvas**

Pictographs – painted images on boulders and cave and rock-shelter walls – provide spectacular evidence of prehistoric cultures worldwide. However, if the pigment is not charcoal, the only organic material in the paint is most likely a binder or vehicle that was added to an inorganic pigment. After hundreds or thousands of years, the amount of organic material in a paint layer remaining on a rock wall is minuscule. Rowe discussed the attempts to chemically identify organic materials used in paints (Rowe 2001b); since then, various researchers have worked on this problem at specific sites (Mori et al. 2006; Vazquez et al. 2008; Livingston et al. 2009; Mazel et al. 2010).

Because pictographs are painted on mineral canvases, thin mineral accretions often cover painted images over time, making it virtually impossible to physically separate a paint layer from surrounding minerals when collecting a sample (Figure 32.1). These accretions can cause paintings to look faded, when, in fact, these accretions encase the paint and may have prevented erosion of the paint from a rock surface. In the case of limestone substrates, these accretions are predominantly calcium carbonate mixed with lesser amounts of calcium oxalate, both of which contain carbon that differs in age dramatically and may have little or no relation to the age of the art. In most rock art samples, and all painted on limestone, carbonates far outweigh the amount of carbon associated with the actual paint. In many cases, organic carbon comprises a very small fraction of the total sample carbon (e.g., <0.01 percent). Acid treatment, used traditionally in archaeological radiocarbon dating, may not be sufficient to remove calcium oxalate sometimes present and care must be taken to ensure complete removal of carbonates (Hedges et al. 1998; Armitage et al. 2001).
The introduction of accelerator mass spectrometry (AMS) in the late 1970s greatly reduced the amount of carbon necessary for radiocarbon analysis, which made it possible for the first time to date small paint samples. For radiocarbon ($^{14}$C) to be used as a chronometer or “clock,” paint must be composed of organic material temporally related to the painting event: charcoal pigment, for example, or an organic binder/vehicle added during paint manufacture. Since 1990, over 200 radiocarbon dates have been obtained on rock paintings worldwide.

**Figure 32.1** A polished section of a rock painting showing an accretion layer (a), principally calcium carbonate and calcium oxalate, which formed over the pigmented paint layer (b). Layer (c) is the limestone rock upon which the image was painted.

*Radiocarbon Dating*

Willard F. Libby published the first radiocarbon ages in the December 23, 1949 issue of *Science* with a “curve of knowns” (Arnold and Libby 1949). For “his method to use carbon-14 for age determinations in archaeology, geology, geophysics, and other branches of science” (Nobel Foundation 1964:587), Libby was awarded the Nobel Prize in Chemistry in 1960. As the principal technique used to establish chronologies within the past 50,000 years, radiocarbon dating has revolutionized archaeological research since the 1950s. However, it was not until the late 1980s that radiocarbon dating was first successfully applied to rock art studies (Hedges et al. 1987; van der Merwe et al. 1987). More recently, the premier place occupied by radiocarbon dating
in archaeology was emphasized in an article, “The 10 Greatest Archaeological Discoveries of the Twentieth Century” (Fagan 1999:34). Fagan wrote, “And then there is the eleventh discovery [radiocarbon dating]: a spectacular find from the laboratory of a chemist, not the dig of an archaeologist. Its impact is so great that we list it separately: the single greatest archaeological discovery of the century.”

Theory
Radiocarbon dating is based upon the presence of the radioactive isotope, $^{14}$C, in all once-living organic materials. Radiocarbon ($^{14}$C) is produced naturally in the upper atmosphere by cosmic ray bombardment. When these cosmic particles interact with atmospheric gases, thermal neutrons are produced which in turn react with $^{14}$N to form radiocarbon via an n-p nuclear reaction. Upon formation, $^{14}$C rapidly combines with oxygen to form $^{14}$CO$_2$ and within hours mixes with atmospheric carbon dioxide initiating the carbon cycle. Radiocarbon enters the biosphere through photosynthesis and, subsequently, the food chain. A dynamic equilibrium is established between the atmosphere, hydrosphere, and biosphere with a known amount of $^{14}$C present in all living organisms due to the approximately steady rate of $^{14}$C production and the constant known decay rate of the radioisotope. But, once a plant or animal dies (and there is no exchange or uptake of $^{14}$C from the environment), the level of $^{14}$C then decreases due to radioactive decay. Radiocarbon decays by emission of a beta particle back to $^{14}$N, following first-order kinetics. Using the Libby half-life of 5,568 years, the rate equation simplifies to an age equation of:

$$t = -8.033 \ln \left( \frac{A}{A_0} \right)$$

where $A$ is the activity of $^{14}$C atoms at time, $t$, and $A_0$ is the initial activity of $^{14}$C atoms at time zero. Thus, by measuring the remaining amount of $^{14}$C atoms in a sample, we can calculate the age by solving for time ($t$) or “years ago” since the sample was living.

Traditionally, the $^{14}$C concentration of a sample was determined by measuring its radioactivity. Known as conventional techniques, these methods count the number of beta decays emitted from a sample. Current conventional radiocarbon dating is usually performed by gas or liquid scintillation counters. To obtain sufficient counts of beta decay for a precision of ±1% or ±80 years BP (before present), typically 5–10 grams of carbon are needed. There is only one $^{14}$C atom for every trillion $^{12}$C atoms in a pre-bomb modern sample. And, for every minute of count time, less than 14 $^{14}$C atoms will decay in a 1 gram sample of modern carbon (Taylor 1987). The development of low-background liquid scintillation counters reduced sample sizes to 250 mg, and mini-gas counters reduced sample sizes to ~100 mg, but with extended counting times on the order of days (Bowman 1990). With the onset of AMS, conventional radiocarbon laboratories have steadily declined in number.

Instead of measuring the decay products of $^{14}$C, an alternative and more efficient approach is to directly measure the amount of $^{14}$C relative to one of carbon’s stable isotopes using mass spectrometry. A mass spectrometer separates individual particles by the differences of their mass-to-charge ratio. But, this cannot be accomplished
using traditional mass spectrometry because the $^{14}\text{C}^+$ signal is completely masked by interfering isobars from $^{14}\text{N}^+$, $^{13}\text{CH}^+$, and $^{12}\text{CH}_2^+$. The use of a high-energy mass spectrometer and a cesium sputter ion source in the late 1970s eliminated these interferences (Bennett et al. 1977; Nelson et al. 1977; Muller et al. 1978). A basic schematic of an AMS instrument is shown in Figure 32.2.

Accelerator mass spectrometry revolutionized archaeological dating, and now allows the routine measurement of samples as small as 100 $\mu$g pure carbon, and even the measurement of samples as small as 50 $\mu$g carbon in special cases. Routine AMS analysis achieves an analytical precision of better than 0.5 percent for samples with less than 1 mg carbon, so that ages pertaining to the past 12,000 years are reproduced with an analytical confidence of a few decades (Scott and Harkness 2000). AMS thus provides the means for dating valuable artifacts where sampling must be minimized to limit destruction or for dating material where only a small amount of sample exists.

There are over 30 AMS instruments throughout the world and many of them are dedicated to $^{14}\text{C}$ analysis.

**Practice**

When an archaeological artifact is radiocarbon dated, it typically undergoes four separate steps: (1) removal of a sample from a bulk artifact for analysis; (2) chemical pretreatment to remove contamination or isolation of sample-specific chemical compounds; (3) conversion of the carbon to a measurable form; and (4) measurement of $^{14}\text{C}$ to determine age. The most widely used methods for steps 2 and 3 are acid–base–acid (ABA) treatments, followed by combustion of the sample.

---

**Figure 32.2** Schematic of an accelerator mass spectrometry (AMS) instrument. This technique allows samples as small as 50 $\mu$g carbon to be radiocarbon dated.
using high temperatures. AMS is often used for step 4. Furthermore, radiocarbon results are typically (5) calibrated to a calendar age range and (6) should be reported with detailed information in the literature.

**Sampling rock paintings**

While small sample size is the main technological advance of AMS, there is concern that in many applied contexts there is a limit below which the ultra-small carbon sample cannot be assumed to truly represent a particular event or natural process of interest (Scott and Harkness 2000). Amounts of organic carbon contained in pictograph paint samples vary from 100 μg to 1 mg, depending upon the type and amount of material removed from a painting. Samples yielding less than ~50 μg carbon should be viewed with extreme caution, if not outright skepticism, unless supported by other data. Besides the capability of the AMS to obtain accurate measurements, there should be concern for identifying the dated material and its association with the cultural “event” being dated.

In our studies, we remove relatively small samples – an approximate surface area of 2 cm² for non-charcoal pigments and as little as 1 mm² for charcoal pigments – from rock paintings using surgical scalpels with a new sterile blade for each sample. If possible, we prefer to take many very small samples spread across a rock painting in order to minimize visual impact on a painting. And, furthermore, we seek small samples that are apparently on the verge of spalling from the walls. Paint samples, including part of the underlying rock and accretion, are collected over and wrapped in aluminum foil (Plate 24), then stored in sealable plastic bags. Samples of unpainted rock directly adjacent to paint samples and on similar rock are also collected to investigate the background levels of organic contamination in the rock substrate. We examine each sample under magnification to ensure no extraneous material is included. Rubber gloves are worn throughout sampling and during later handling in the laboratory to avoid contamination.

Image aesthetics and information content are taken into consideration during sampling with consultation from archaeologists and site owners/managers. Research questions should be discussed among all researchers to determine the best sampling locations. Often on-site discussions are the most useful, as the environment and condition of the sampling location can be observed first-hand. Of the utmost importance, proper recording of sites must be accomplished prior to sampling. In addition, proper documentation of the sampling process, such as photographs of specific sampling locations, as well as entire panels before and after sampling, should be included with site reports (see McDonald and Steelman 2008).

Sometimes pictographs are contaminated with organic materials. Visual examination under a stereoscope and physical removal of obvious intrusive non-pictograph materials, such as rootlets and lichen, should be undertaken prior to chemical pretreatment. Organic contamination in the rock from unknown natural sources is also a concern. To detect and account for this, we collect unpainted rock samples adjacent to a paint sample and encourage all researchers to follow this procedure. We process background samples in exactly the same manner as paint samples to determine the amount of natural or background carbon contamination in the rock. We have observed contamination levels ranging from nil to amounts equal to corresponding
paint samples. This effect is sometimes negligible; in other instances, an age determination for a painting is rendered impossible, as it was for attempts to date pictographs at Canyon de Chelly, the Grand Canyon, at La Pulsera in Mexico, and in Arkansas (Steelman and Rowe, unpublished data). Conversely, in Australia, high levels of background carbon probably indicated previous (now no longer visible) painting episodes which predated the visible art by several millennia (McDonald and Steelman 2008).

**Chemical pretreatment**

Chemical pretreatment procedures for archaeological samples typically involve an acid–base–acid wash sequence with hydrochloric acid and sodium hydroxide solutions. The first acid treatment dissolves carbon-containing minerals, such as limestone. Sequential base washes remove soil organic matter (SOM) contamination, such as humic and fulvic acids. A final acid wash removes absorbed carbon dioxide from the base solution. When combustion is used, acid pretreatments are necessary to remove any carbon-containing minerals, such as carbonates, which will decompose at temperatures above 750°C (Johnston 1910; Armitage et al. 2001). Carbonate contamination is 14C-free (dead carbon) and will result in an older measured age than the true age of a sample, sometimes near the limit of detection at ~50,000 years BP. For rock art studies, another concern is that acid washes may not completely remove oxalate minerals, which are commonly associated with rock surfaces (Hedges et al. 1998; Armitage et al. 2001).

In our laboratory, both acid pretreatments may be excluded because of our use of plasma oxidation pretreatment (see below) whereby the mild temperatures of this pretreatment are below the decomposition temperatures of both carbonates and oxalate minerals (Russ et al. 1990) and the ultra high vacuum conditions of the plasma sample chamber remove absorbed CO2. This allows us to successfully date smaller samples, much of which might otherwise be dissolved during acid–base–acid treatments. Carbon that would be lost in the traditional pretreatments is retained in our technique and is available for oxidation to CO2.

There has been little investigation as to whether humic acids are present in pictograph samples, as they are in many archaeological artifacts buried in soils. Fortunately, in the meager experiments that have been done, there is no evidence that these are a problem (Pace et al. 2000). But more work will be necessary to resolve this question with confidence. We routinely use a pretreatment of base to ensure the removal of any potential humic acids present.

**Combustion and plasma oxidation**

Traditional radiocarbon dating utilizes high temperatures to combust samples in the presence of oxygen. Samples are typically loaded into quartz tubes with copper oxide, sealed, and combusted at ~900°C to make carbon dioxide.

Alternatively, for rock art paint samples, we utilize a custom-built plasma oxidation apparatus that produces a glow discharge by radio frequency (RF) capacitive coupling with two external copper electrodes on either end of a glass sample chamber. Oxygen
plasma exposures convert organic material in a paint sample to carbon dioxide and water, while leaving the solid carbon-containing minerals intact (see more detailed description of the technique below).

**Graphitization and AMS measurement**

Carbon dioxide is then subsequently reduced over a metal catalyst to make a graphite target (Wilson 1992) and loaded into a sample wheel in the ion source. From an AMS measurement, results are reported in years BP (years before present), representing $^{14}$C years before 1950 AD (time zero), and follow the conventions of Stuiver and Polach (1977). The standard counting error associated with the mass spectrometer is quoted as 1σ after the radiocarbon age.

**Calibration**

Calibration curves that convert $^{14}$C years BP to calendar year ranges have been constructed by radiocarbon dating tree-ring sequences (Bowman 1990; Stuiver and Pearson 1993; Taylor 1997). These corrections are done using either the intercept method or Bayesian statistics with computer programs, such as OxCal (Bronk Ramsey 2009) or CALIB (Stuiver and Reimer 1993) which use data from Stuiver et al. (1998) and Reimer et al. (2009).

**Reporting radiocarbon results**

Better documentation of rock art dating has been called for by Watchman (1999) and Rowe (2001a). Unfortunately, many results have been published with too few experimental details (some with none at all) to make possible a serious evaluation of the techniques. To be able to critically examine new findings in the future, we need experimental dating papers to contain the following:

1. **Archaeological rationale for taking a sample for dating.** This information is usually better supplied by the archaeologist(s) involved, rather than the chronographers themselves, but it is important and should be included.
2. **Sites** should be properly recorded prior to sampling with cultural aspects of fieldwork and study taken into consideration. See Ward and Tuniz (2000:5) for their suggestions of research protocols.
3. **Site numbers and site descriptions.**
4. **Image description** (scale photo or drawing, if possible), as well as a description of the sample, including such information as pigment composition (if known), pigment color, accretion minerals (if known), geology of rock substrate, and so on.
5. **Description of how the samples were taken,** including sample size (surface area removed and sample mass) as well as equipment used.
6. **Description of any pretreatment used.** Chemical pretreatment and reaction system backgrounds should be measured and reported.
Microgram amounts of carbon recovered for AMS $^{14}$C measurement. This is critical and has been generally ignored in the literature so far. This can have a strong effect on the accuracy and reliability of the dates.

Radiocarbon laboratory identification numbers.

Raw radiocarbon dates with $\pm 1\sigma$ uncertainty.

Whether the dates are corrected for $\delta^{13}$C or were calculated using a value of $-25\%$.

Calibrated dates with the computer program accessed, as well as whether the intercept or Bayesian statistics methods were used.

Unsuccessful results, whether reporting the number of samples that did not contain sufficient amounts of carbon for dating or rejected dates that appear absurd or non-viable due to other lines of evidence.

**DATING ROCK ART**

Numerous methods have been employed since about 1984 to radiocarbon date rock art paintings. Rowe (2012) has compiled references on the topic, some of which we will profile here. Several other methods of note are optically stimulated luminescence dating of wasp nests superimposed over paintings (Roberts et al. 1997) and the use of U/Th dating of associated calcite accretionary deposits (Genty et al. 2005; Plagnes et al. 2010).

**Charcoal pigments**

In 1987, the first radiocarbon dates for rock art on two charcoal pictographs from South Africa were determined on the Oxford AMS (Hedges et al. 1987; van der Merwe et al. 1987). Acid was used to dissolve the carbonates and the remaining charcoal was radiocarbon dated. This date was independently followed quickly by others from several laboratories and rock art locales (Loy et al. 1990; McDonald et al. 1990; Russ et al. 1990; Valladas et al. 1990, 1992). Not all these early techniques have stood the test of time (e.g., Nelson 1993; Gillespie 1997).

In western European Paleolithic caves, both French and Spanish researchers have concentrated on determining the age of spectacular rock paintings by dating charcoal pigments – charcoal being the principal ingredient used by ancient artists to make black paints. In addition, some of the dates are on charcoal from fire remains found directly below the paintings, which are located in dark zones of caves. More than 60 dates have been obtained by Hélène Valladas, Jean Clottes, and co-workers (see Clottes 2001; Valladas 2003; Valladas et al. 2006; Clottes and Geneste in Chapter 33 of this volume). They adopted the standard procedure for dating archaeological charcoal, using acid to remove carbonates and combustion to collect carbon for AMS dating. As the age of a few of the Paleolithic paintings is near the limit of detection for radiocarbon dating, this is impressive work.

Most dates obtained on pictographs worldwide have been on charcoal pigmented paintings. There are about 150 publications on dating charcoal pigment in rock art that involve at least six laboratories (Rowe 2012). As in all archaeological applications where charcoal is dated, caution is advised in interpreting these dates due to the old
wood and old charcoal effects. For instance, wood used to make charcoal may have died long before it was burned (Schiffer 1986). Similarly, charcoal may have been produced hundreds of years before it was used to create an image on a cave wall (Bednarik 1994). A clear example of old charcoal was illustrated by a study in which the Rowe group radiocarbon dated an historical charcoal writing “Mr. C.B. Ross” to 1310 ± 460 years BP (OZC437: David et al. 1999). Nearby, the characters “C Ross 1894” were engraved. The Ross family is known to have been in that region since the late 1800s and the writing style is similar in both cases. One would have expected the historic charcoal graffiti to date from ∼1894 AD, i.e. to return a young result in radiocarbon terms. However, two samples of near-surface charcoal found on the shelter floor had been previously radiocarbon dated to 690 ± 90 (ANU-4812) and 1,470 ± 170 (ANU-5154) years BP, indicating that older charcoal was readily available to modern people. Radiocarbon dates on charcoal pictographs should be considered as maximum ages for painted images unless these two effects can somehow be ruled out.

Organic binders/vehicles in inorganic pigmented paintings
In pictographs worldwide, inorganic pigments are more frequent than charcoal: reds, oranges, browns, and yellows are usually iron oxide/hydroxide minerals of various oxidation states and degrees of hydration, and black is often a manganese oxide/hydroxide, instead of charcoal. These inorganic minerals cannot be radiocarbon dated because they do not contain carbon related to the production of a painting. However, pictographs with inorganic pigments potentially can be radiocarbon dated if organic material was added to the paints initially and enough of that organic material has survived in order that measurements can be made with sufficient accuracy and reliability. Our plasma oxidation method provides a direct technique for dating pictographs with inorganic pigments (see Rowe 2009 for a recent review of the technique).

We have had limited success (∼50 percent) when dating inorganic pigments at various locations around the world. There is no way of knowing whether there is sufficient carbon remaining in a sample for reliable radiocarbon measurement or whether any organic material was indeed added to the paint in the first place. An archaeologist needs to be aware that a sample can be collected, hours of analysis time spent in the laboratory, funds spent, with no results.

When dating an inorganic pigmented painting, we do not know what material is being analyzed. In many cases, sufficient amounts of carbon for 14C measurement are collected from paint samples and negligible amounts of carbon are found in adjacent unpainted rock samples (backgrounds). So, we know that the organic material being dated is associated with the paintings; however, we cannot ascertain what that material might be. Many materials have been suggested as a binder or a vehicle to make suitable paints; these include animal oils, blood, egg whites, egg yolks, honey, milk, plant juices, plant resins, oils, and urine – but almost always without chemical analysis for confirmation (Barnes 1982; Rowe 2001b).

Another problem, probably of much less severity, is natural variation in δ13C values of organic material used in paint preparation. Unless told otherwise, AMS laboratories assume a δ13C value of −25‰, the average value exhibited by wood and charcoal as the most commonly dated archaeological material. If enough organic carbon is
removed from a pictograph sample to allow measurement of the $\delta^{13}$C, that effect can be corrected by stable isotope measurement. Organic carbon from many typical organic sources will have values close to $-25\%$ and will not overly affect the age of the painting. On the other hand, if the values differ significantly (such as for cacti), the age may well be skewed $-100$ $^{14}$C years BP.

**Beeswax**

Canadian researcher Erle Nelson and his co-workers presented over 135 radiocarbon dates from beeswax rock art, uniquely occurring in northern Australia (Nelson et al. 1995, 2000; see Taçon et al. 2010). This is the largest collection of radiocarbon data collected on a corpus of rock art. Their age determinations ranged from modern to $-4,000$ years old, with the bulk of the ages being less than 750 years old. A duplicate measurement for one of the dated beeswax figures was also conducted (Watchman and Jones 2002). The techniques (pretreatments) of both researchers varied enough that they probably constitute independent determinations. However, agreement between their results was not completely satisfactory: Nelson and colleagues returned $4,040 \pm 90$ years BP, while Watchman and colleagues returned $4,460 \pm 80$ years BP. One would have expected statistical agreement, but even when calibrated the two radiocarbon results do not overlap at 2 standard deviations; so clearly more work is needed.

**Fibers**

Fibers that have been incorporated into wet paint are sometimes found when examining paint samples under magnification. The fibers should contain material that is contemporary with the painting event to provide reliable ages. Watchman and Cole (1993) found sufficient fibers in paint samples from northeastern Australia to radiocarbon date them; however, the fibers were not abundant enough to identify their source. The primary disadvantage of this method is that such fibers are only rarely found in paints. A thorough search under magnification should be made for any paint samples for which radiocarbon dates are sought. Finding fibers in inorganic pigmented paintings would provide a means of independently testing our plasma oxidation method for mineral-based paints.

**Blood**

Loy et al. (1990) radiocarbon dated extracted blood residues from Australian rock paintings, but this work was subsequently questioned by one of the senior authors (Nelson 1993) and by the later work of Gillespie (1997). To our knowledge, no further dating of rock paintings has been attempted using this technique.

**Oxalate coatings**

Alan Watchman has used oxalate minerals associated with rock art to determine relative ages (Watchman 1991). Our research groups and those of Jon Russ and collaborators (Russ et al. 1999; Steelman et al. 2002; Rowe and Steelman 2003; Ruiz et al.
2006) have also dated oxalate accretions. Since calcium oxalate (CaC$_2$O$_4$) is a mineral formed from atmospheric carbon, the age of carbon in oxalate accretions is contemporaneous with its formation. By radiocarbon dating calcium oxalate strata overlying and underlying pigment layers, it is possible to determine maximum and minimum ages for a pictograph. Russ et al. (1999) have published oxalate dates associated with Texas Pecos River style inorganic pigmented pictographs; and their results are consistent with radiocarbon dates obtained using plasma oxidation on organic material in paints from these same sites. However, the age ranges generated in dating oxalates are too large to confirm the accuracy of the plasma oxidation results.

**Excavated materials**

Although not a direct measurement of the age of a painting, the identification of spalled rock art samples in excavated, dated, stratigraphic layers permits minimum and maximum ages to be estimated. Numerous researchers have used this approach. A few examples include the Serra de Capivara National Park in Piauí, Brazil (Pessis 1999; Prous 1999) and from North America at a site near Crater Lake in Central Oregon on the Columbian Plateau, as well as at Bernard Creek rock-shelter in Hells Canyon on the Snake River (Keyser 1992:18). While stratigraphy is a common tool used in archaeology for relative dating, caution should always be exercised. Erosion, burrowing animals, and human activity can redeposit and mix stratigraphic layers such that more recent artifacts (and particularly small ones) may be reworked below older ones.

**Our Work Using Plasma Oxidation**

The Rowe archaeological chemistry group at Texas A&M University developed the method of plasma oxidation to extract organic matter from ancient paint samples for radiocarbon dating. Steelman has continued this work in her laboratory at the University of Central Arkansas, as has Ruth Ann Armitage at Eastern Michigan University. Plasma oxidation has successfully dealt with many issues surrounding rock art dating. To test any new analytical technique, standards with known amounts of analyte ($^{14}$C) are measured. Unfortunately, no real standard for dating a pictograph exists. Instead, we have used (1) $^{14}$C-free samples; (2) non rock art samples with previously measured dates; and (3) pictographs archaeologists can place within a limited time-span based on archaeological inferences as approximations of standards. Results for pictographs with inferred time-spans are shown in Figure 32.3.

From the use of hydrogen plasmas to restore metallic artifacts by chemically reducing them (Vepřek et al. 1987), Rowe hypothesized that oxygen plasmas could be used to successfully collect organic carbon from rock art paint samples (Russ et al. 1990). The main advantage is that the inorganic rock substrate would not decompose during exposure to oxygen plasmas. Plasma oxidation negates the use of extensive acid pretreatments because plasma temperatures (<150°C) are below the decomposition temperatures of both carbonates and oxalate minerals and only organic material is removed for radiocarbon measurement (Johnston 1910; Russ et al. 1992). In addition, plasma oxidation is preferable because acid washes may not completely remove
oxalate minerals, which are commonly associated with rock surfaces (Hedges et al. 1998; Armitage et al. 2001). Plasma oxidation is ideal for samples in which only a trace amount of organic material remains because extensive acid pretreatments used in conjunction with combustion are avoided, minimizing the loss of organic material during wet chemical pretreatment steps.

Our laboratories employ a custom-built plasma oxidation apparatus to convert organic material to carbon dioxide for accelerator mass spectrometry (AMS) radiocarbon dating. Glow discharges are produced by radio frequency (RF) capacitive coupling with two external copper electrodes on either end of a glass sample chamber. A plasma is an electrically excited gas composed of neutral atoms, both negative and positive molecular and atomic ions, and electrons. Neon signs and fluorescent lights are plasmas commonly used by society. Electrons gain kinetic energy from an oscillating electric field, while the temperatures of the gas components are increased by elastic collisions between the electrons and the gas. Electrons are thermally isolated from the gas components by their very large mass differences. Temperatures of the plasma gas thus can remain near ambient temperatures; at the same time, the electrons are sufficiently energetic to break molecular bonds (Hollahan and Bell 1974). The active species in a plasma allow reactions, which would normally occur only at high temperatures, to proceed at low temperatures. Oxygen plasmas convert organic matter to carbon dioxide and water, which we collect by freezing the products with liquid nitrogen for AMS radiocarbon dating.

We have obtained dates from over 30 pictographs painted with red or black inorganic pigments from Arizona, Brazil, Mexico, Montana, Texas, Utah, and Wyoming. Replicate measurements on the same image suggest an uncertainty of ±250 years BP.

![Figure 32.3](image-url) Early plasma oxidation studies on paint samples with inferred ages from cultural occupation at sites or stylistic analyses.
for inorganic pigmented paintings. Almost all successful dates on paintings with inorganic pigments were those on limestone walls; we find that sandstone almost invariably contains too much organic contamination to yield reliable results.

We have dated approximately 60 charcoal pictographs from Angola, Arizona, Australia, Belize, Brazil, California, France, Guatemala, Missouri, Texas, Utah, and Wisconsin. Replicate measurements in our laboratory suggest that an uncertainty of ±100 years BP or less is possible for charcoal dates, depending upon the amount of carbon sampled.

There have been only two independent dates for pictographs dated using plasma oxidation. In one case, Russ and his co-workers dated oxalate accretions surrounding a pigment layer of a Texas Pecos River style pictograph; these oxalate dates bracket the radiocarbon results for paintings of the same style (Russ et al. 1999). Unfortunately, in the other case of Brazil rock paintings, there is a complete disagreement between results from our laboratory and results from thermoluminescence dating methods (Steelman et al. 2002; Rowe and Steelman 2003; Watanabe et al. 2003). However, oxalate dates and plasma oxidation dates from the Texas A&M University laboratory do temporally agree (Rowe and Steelman 2003). The need for additional independent studies cannot be overemphasized.

CONCLUSIONS AND FUTURE WORK

For the field of rock art dating to mature, there is a dire need for more research practitioners to use multiple independent methods. Multi-laboratory efforts to date the same pictographs via different analytical techniques should be embraced and encouraged by archaeological and scientific communities. Material analyzed for radiocarbon dating must relate to the event of interest; in our case, the creation of a painted image on a rock surface. With 14C AMS analysis, organic material in the paint must first be separated and collected from other carbon-containing interferences that will affect the age determination.

Archaeologists need to realize that chemists, geologists, and other rock art dating “experts” do not have all the answers. We have seen rock art researchers cling to dates as if they are the gospel truth, simply because it is a number from a dating “expert,” even when there has been considerable evidence that the dates were questionable. As dating researchers, we are just as fallible as anyone else. And we are definitely only as good as our samples. Although most of the dates have withstood the test of time, some have not. Caution should be exercised in the study of rock art chronology. Independent inter-laboratory studies are essential for full, complete confidence in the ultimate reliability of the dates.

ACKNOWLEDGMENTS

We wish to thank the many collaborators and rock art researchers who have guided us to rock art sites and proposed interesting projects. Special thanks are due to Jo McDonald and Peter Veth for compiling and editing this volume. Karen Steelman wishes to thank her undergraduate research students at the University of Central
Arkansas; Marvin Rowe wishes to thank his former graduate students who worked to date rock paintings in his laboratory at Texas A&M University.

REFERENCES


McDonald, J., and Steelman, K., 2008 Rock Art Dating Results from the Calvert and Carnarvon Ranges, Western Desert. Report to the Australian Institute of Aboriginal and Torres Strait Islander Studies.


Watchman, A.L., and Jones, R., 2002    An Independent Confirmation of the 4 ka Antiquity of a Beeswax Figure in Western Arnhem Land, Northern Australia. Archaeometry 44:145–153.