

Serpentine Bends Site #1:
Radiocarbon dating prehistoric soot and associated pictographs

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Abstract

At Serpentine Bends Site #1, we employed plasma oxidation followed by accelerator mass spectrometry to radiocarbon date two prehistoric rock paintings as well as soot on the shelter ceiling. Pictograph results are 2325 ± 30 ^{14}C years BP for a black line and 1315 ± 40 ^{14}C years BP for a red outline of a circle motif. We also utilized X-ray diffraction to chemically identify pyrolyzed carbon in the black stain on the shelter ceiling, confirming that it is from fire smoke. Four radiocarbon ages for the soot represent a weighted average of multiple fires, instead of a single event. The oldest result of 2740 ± 70 ^{14}C years BP is from the underlying black soot closest to the rock substrate and, as a weighted average of multiple layers, represents a minimum age for human activity at the site. Dating both pictographs and prehistoric soot provide novel methods for dating human activity within rockshelters around the world, especially when there is a lack of excavated materials for study.

1. Introduction

Performed in conjunction with rock art documentation and recording, this dating project is aimed at developing a better understanding of prehistoric occupation and art production in the Guadalupe Mountains of southeastern New Mexico (Fig. 1). Research reported in this article is part of a much larger project to document 21 rock art sites in the region, completed by Versar, Inc. and Sacred Sites Research, Inc. with funding provided by the

Carlsbad Field Office of the Bureau of Land Management through the Permian Basin Programmatic Agreement (Miller et al., 2019). As part of that project, we used the method of plasma oxidation followed by accelerator mass spectrometry (AMS) to radiocarbon date two pictographs as well as prehistoric soot on the shelter ceiling at Serpentine Bends Site #1 (LA163402). The ability to radiocarbon date rock art and place it into a temporal context is important in incorporating rock art studies alongside other archaeological artifacts in the study of past cultures.

Developed by Rowe, the method of plasma oxidation has been used to successfully AMS radiocarbon date over 300 rock paintings around the world (Russ et al., 1990; Rowe, 2012; Rowe et al., 2016; Russ et al., 2017; Armitage et al., 2020; Steelman et al., 2021). The plasma oxidation technique is particularly useful for dating rock paintings and other samples with abundant minerals. A low-temperature plasma or glow discharge is an electrically excited gas that is reactive at conditions below the decomposition temperatures of inorganic minerals. For a paint sample, the reactive oxygen plasma separates the organic components from the inorganic matrix, leaving the minerals as solid (Russ et al., 1990). The reaction products are carbon dioxide and water, which are subsequently trapped by freezing in a collection tube immersed in liquid nitrogen. We then flame-seal this collection tube with the extracted carbon for AMS radiocarbon dating.

Because some of the rock paintings at Serpentine Bends # 1 are found on black soot-stained surfaces, the primary goal for the research was to explore the possibility of radiocarbon dating the layers of soot on the rockshelter ceiling and then compare the results with dates for other rock paintings at the site. Using X-ray diffraction (XRD), we chemically identified a black stain on the ceiling as pyrolyzed carbon from fire smoke, and obtained four radiocarbon ages: 1520 ± 60 ; 1610 ± 60 ; 1870 ± 60 ; and 2740 ± 70 ^{14}C years BP. The oldest result is for an underlying soot layer closest to the rock substrate, representing older smoke stains. The variation in the radiocarbon results suggest that the soot dates represent weighted averages of multiple fires, instead of a single event. Therefore, the older age of 2740 ^{14}C years BP is a minimum age for human activity at the site. To avoid contamination from the past fires, we selected pictographs for dating that

were painted on the cream-colored limestone away from the black soot. Pictograph results are 2325 ± 30 ^{14}C years BP for a black line and 1315 ± 40 ^{14}C years BP for a red outline of a circle motif. These results agree with additional dates for line figures (zigzags and open net-like shapes) and circular forms (concentric circles, outline and infilled circles) at nearby rock art sites (Miller et al., 2019: 499).

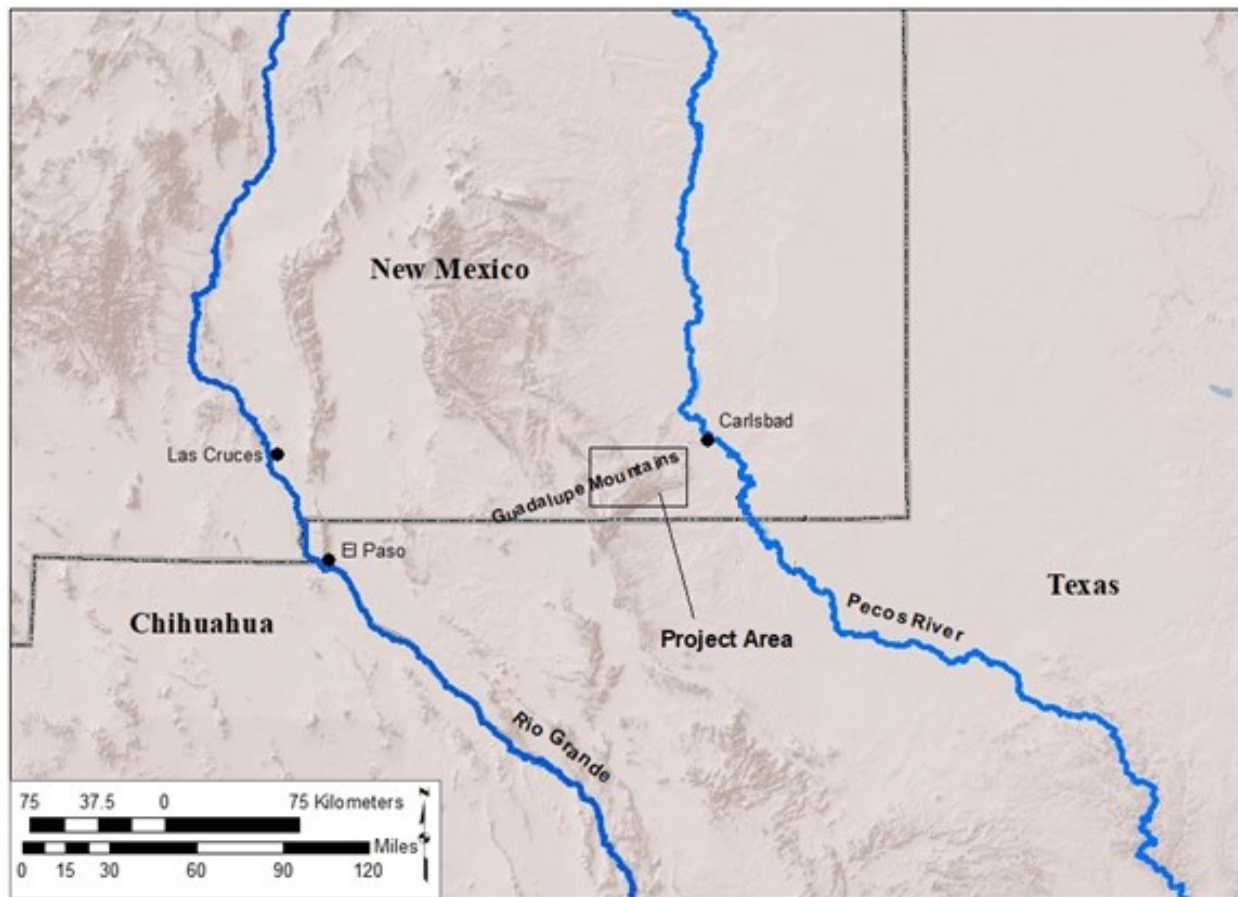


Fig 1. Location of the project area in the Guadalupe Mountains of southeastern New Mexico.

2. The Serpentine Bends #1 Site

The Serpentine Bends #1 site, located in a drainage off the main Serpentine Bends Canyon, is a rockshelter that is partially obscured by mountain laurel trees, mesquite, catclaw, acacia, and hackberry with an understory of prickly pear, sotol, and other desert plants in the surrounding landscape (Fig. 2). The rock formation containing the rockshelter is classified as Seven Rivers Formation sedimentary and metamorphic rocks (New Mexico Bureau of Geology and Mineral Resources, 2003) comprised of mixed strata of Permian age with dolomite, gypsum, anhydrite, salt, shale, siltstone, and sandstone. The rockshelter is located in a layer of dolomite, a calcium magnesium carbonate. The shelter measures 8.9 m long, with a maximum depth of 5.3 m deep and is 4.0 m high at the entrance but only 1.2 m high at the rear.



Fig. 2. Blackened ceiling of the Serpentine Bends #1 site. A painted circle, dated to 645-800 cal AD, and other elements are visible on the vertical panel below the ceiling.

A bedrock mortar, a grinding slick and at least two cupules are found on the rockshelter floor. These features are sometimes obscured by a shallow layer of sediment that results from flood activity in the canyon adjacent to the rockshelter opening. There is also a partial rock ring from a modern fire at the mouth of the rockshelter. No artifacts have been found within the scoured surface of the rockshelter during several surface recording efforts.

There are prehistoric paintings along the back wall and onto the rockshelter ceiling. The ceiling also has significant portions that are blackened, presumably by smoke from fires. While we cannot entirely rule out that the smoke blackening could be from wildfires, we suspect that the black coating is soot from man-made fires due to other human activity at the site (e.g., pictographs and groundstone). The black coating, mainly on the ceiling, obscures some paintings which led us to use DStretch software to locate additional paintings. DStretch transformation of digital photographs uses decorrelation stretch enhancement of the color separation within an image to mathematically produce exaggerated colors improving visual interpretation and feature discrimination (Harman, 2005). Some of the paintings at Serpentine Bends #1 are located on the cream-colored limestone walls and others are located in areas with soot blackening, especially on the ceiling.

Six panels of paintings were identified at the site (Miller et al., 2019: 359-366). One of these is outside the rockshelter on the canyon wall adjacent to the opening with the other five inside the rock shelter, along the walls and extending onto the ceiling. The paintings are in different shades or hues of red, maroon, yellow, orange, and black colors. All are abstract designs with at least two different styles of painting.

The most visible are concentric circle designs with the interior circle filled with a colorful paint that differs from the ring around it (Fig. 3). Some of these motifs were painted using black or red paints placed directly over (on top of) the blackened walls and ceiling, but one motif was created by applying red paint over the soot layer and then adding another area of yellow paint over the red element. The latter example demonstrates the paintings were painted over time as the soot accumulated. In part because they are colorful, these

concentric circle motifs with solid interiors are distinctive, not only because they are bold and bright, but they appear to have been finger-painted in wide swaths. These in-filled concentric forms are found at other regional sites with enough regularity to be a recognizable motif that are associated with single-color concentric circle forms or nested arcs and other curving figures. They all appear to be part of the same cultural tradition or style.

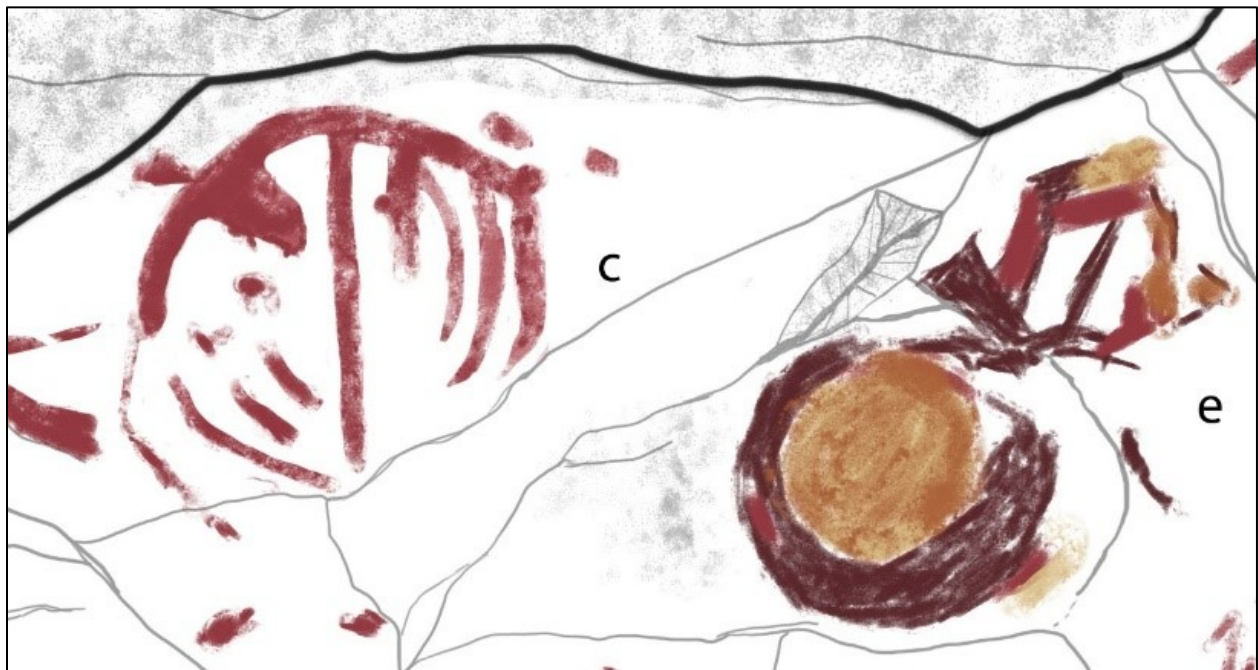


Fig. 3. The red outline of the in-filled circle (Panel 5, element e) was radiocarbon dated to 645-800 cal AD. The sample was collected from the bottom of the circle outline. The soot layer on the ceiling has been deemphasized to show the painting better; see Fig. 2 for a photograph of this panel.

The second type or style of painting at Serpentine Bends #1 includes zigzags, wavy lines, grids, open-net-like figures, and other linear motifs (Fig. 4). These figures are made with fine lines that appear to have been applied with a brush or stylus. Parts of these designs are often eroded, suggesting they were not applied with the same intensity as the solid-colored figures. Rows of dots or grids of dots appear to be associated with this type. Some of the individual motifs in this type, like zigzags, might have been made since Paleo Indian times but there is support for the fine line variety as a recognizable type in the Late Archaic in southeastern New Mexico (Miller et al., 2019: 565).

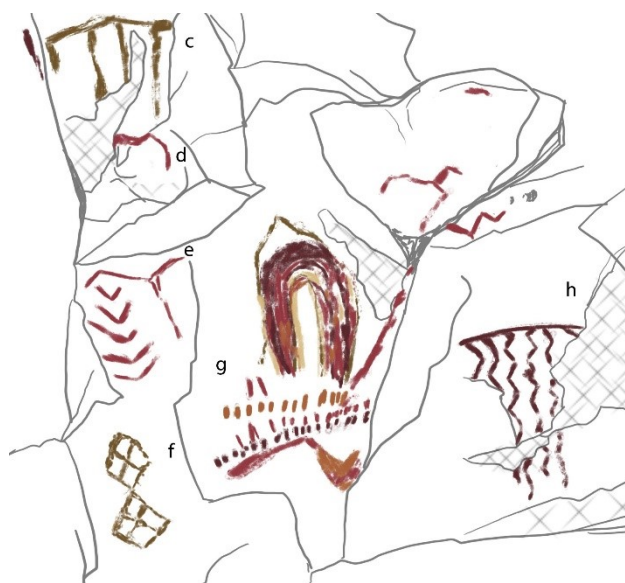


Fig. 4. Panel with intersecting lines, net-like motifs, and parallel geometric motifs at Serpentine Bends # 1. The multi-colored in-filled oval-shaped figure near the center of the panel is one of the designs that is more recent.

2.1 Rock Art Documentation

As reported in the larger study, a time-honored process was used to record the rock art at the 21 sites in the Carlsbad region (Miller et al., 2019:39-59; Loendorf et al., 1998; 2014). The contemporary practice of scientific rock art documentation is a complex, labor-intensive, and multistage program involving logistics, an extensive range of field observations, intensive recording through drawings and photographs, and the application of specialized techniques and modern technologies (e.g., DStretch photo enhancement software, GigaPan stitched images of panels, Structure from Motion 3D digital models, measured panel drawings, rock art recording forms). This process also includes the full recording of an entire site within its natural and cultural setting. Features like bedrock metates, rock shrines, and the presence or absence of medicinal plants are as important in the recoding as the drawings of the images themselves. At Serpentine Bends # 1, for example, the presence of mountain laurel trees (*Sophora secundiflora*) with seeds that contain a psychotropic drug suggest the possibility of ritual use in the shelter.

2.2 Radiocarbon Dating Pictographs

At Serpentine Bends #1, we selected two paint samples for plasma oxidation and AMS radiocarbon dating. Sample 10 was collected from black lines (element d) on Panel 2 (Fig. 5) and sample 11 was collected from a broad red arc surrounding a yellow circle (element e) on Panel 5 (Figs. 2 & 3). We selected sampling locations from motifs that would provide the most archaeological information. To minimize any visual damage to the paintings, we focused on areas that were actively spalling away from the dolomitic limestone shelter wall that would be lost to weathering and future natural deterioration of the site. In addition, we also collected a sample of unpainted rock directly adjacent to the paint sample to study the potential for organic contamination in the rock substrate. Even though these paint samples were collected on the cream-colored limestone away from the soot blackening, this control sample of unpainted limestone was especially important to ensure there was no trace contamination from previous fires in the shelter.

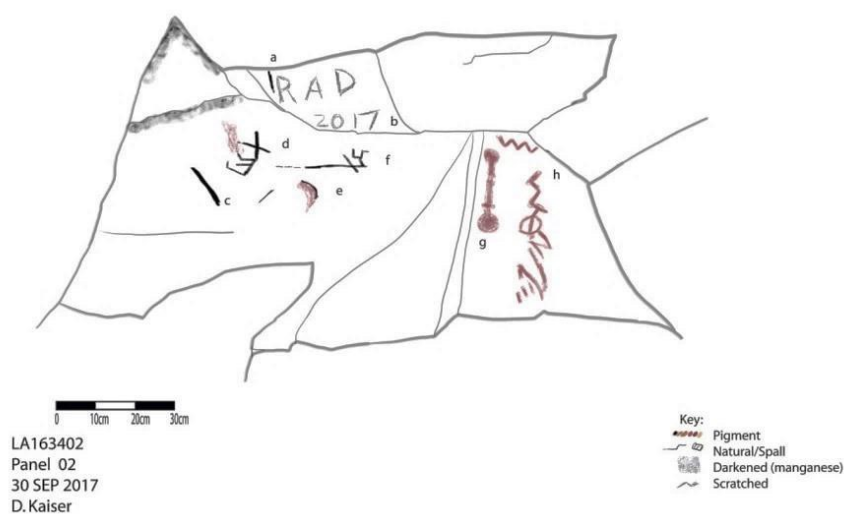


Fig. 5. Panel 2 showing element d of crossed black lines that was radiocarbon dated (sample 10). This painting dates to 475-230 cal BC.

We took before and after photographs of the sampling locations to document the sampling process. We used individual sterile surgical scalpels to collect 1 to 3 cm² samples that were wrapped in aluminum foil squares and stored in labeled plastic bags. We wore latex gloves to avoid contamination from handling, but made sure that samples were only in contact with sterile aluminum foil or scalpel blades.

A detailed description of experimental methods employed by Steelman's laboratory are provided in McDonald et al. (2014:197-198) and Miller et al. (2019:603-627; Appendix A.1). Paint and background samples were chemically pretreated with a sodium hydroxide base solution to remove any potential humic acids prior to oxidation. We utilize a radio frequency (RF) generator with two external copper electrodes on the ends of a glass sample chamber to generate a glow discharge (Fig. 6). A combination of argon and oxygen plasma exposures are used to process the samples. The oxygen plasma reacts with the organic material in the paint sample to form carbon dioxide and water, which we collect for AMS radiocarbon dating using a liquid nitrogen trap.

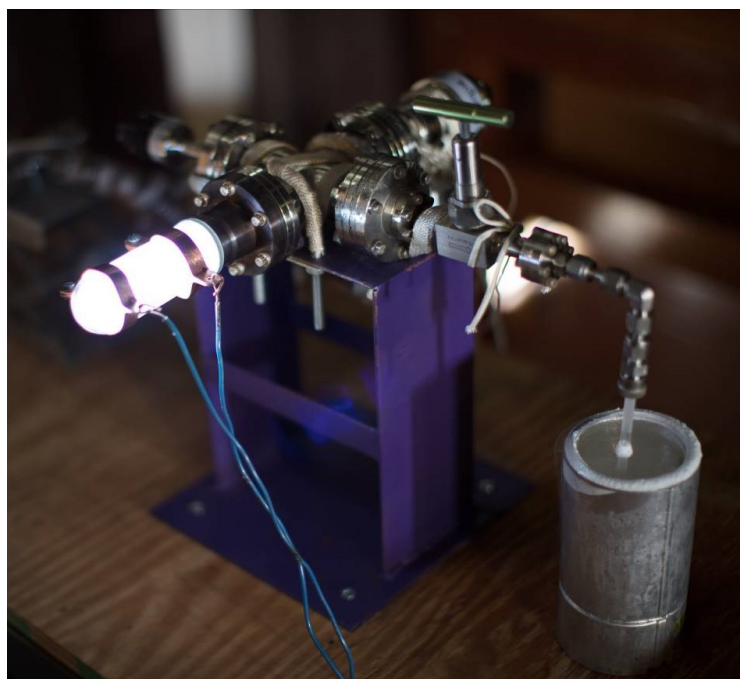


Fig. 6. Glow discharge of plasma oxidation instrument.

Results for the pictograph dating are shown in Tables 1 & 2. Stable carbon isotope ($\delta^{13}\text{C}$) values were assumed to be -25‰, as carbon dioxide samples were too small to take a split for measurement. The carbon levels in the background samples were low, suggesting that extracted carbon is inherent in the paint samples alone and contamination from the environment or prehistoric fires is negligible (Table 1). We calibrated the dates using OxCal version 4.4.2 (Bronk Ramsey, 2009, 2020) with IntCal20 curve data (Reimer et al., 2020). At Serpentine Bends #1, two ages on two different paintings located on opposite sides of the shelter had very different ages (Table 2). Black lines on the left side of the shelter had a radiocarbon age of 2325 ± 30 ^{14}C years BP, calibrated to 475-230 cal BC (95.4% probability). Red paint on the right side of the shelter had a radiocarbon age of 1315 ± 40 ^{14}C years BP, calibrated to 645-800 cal AD (95.4% probability). These two disparate ages straddle the boundary between the Late Archaic and Early Formative periods.

Table 1. Plasma oxidation data for paint and background samples.

Sample	Description	Mass (mg)	$\mu\text{g C}$	$\mu\text{g/mg}$	Shumla ID
10	black lines	10	66	7.0	70
10b	background	50	8	0.2	
11	red circle	70	86	1.0	71
11b	background	70	7	0.1	

Table 2. Radiocarbon Results at Serpentine Bends Site #1

Sample	Description	CAMS ID	^{14}C Date (BP)	Calibrated Range (cal BC/AD, 95.4% probability)	Calibrated Range (cal BP, 95.4% probability)
10	black lines	182593	2325 ± 30	475-430 cal BC (4.2%) 425-355 cal BC (84.5%) 285-230 cal BC (6.8%)	2425-2380 (4.2%) 2375-2305 (84.5%) 2230-2180 (6.8%)
11	red circle outline	182594	1315 ± 40	645-780 cal AD (95.2%) 790-800 cal AD (0.3%)	1305-1170 (95.2%) 1160-1150 (0.3%)

2.3 Characterization & Radiocarbon Dating of Prehistoric Soot

Archaeologists often have difficulty identifying the dark-colored coatings on rockshelter and cave ceilings. In many cases, the black coating is thought to be from smoke when in

fact it is from manganese-laden water that seeps out of cracks in the ceiling (Saiz-Jimenez et al., 2012; Xu et al., 2018). However, the Serpentine Bends Site #1 has a blackened ceiling that is indeed from smoke blackening (Fig. 2), based on the chemical identification of pyrolyzed carbon. Often referred to as charcoal, soot, or carbon black, pyrolyzed carbon is formed during the incomplete combustion of organic material such as plants and animal fats (Russ et al., 2017). The chemical structure of pyrolyzed carbon is similar to graphite, with covalent bonding between its graphene sheets. We use the term *soot* to describe the black powdery material of amorphous carbon that is deposited on the rock shelter surface. As there are no other diagnostic cultural features at the site (besides the rock paintings), the possibility of radiocarbon dating past occupations at the shelter using the pyrolyzed carbon on the ceiling is an interesting research question. Our plan of investigation was: (1) establish whether the black material is organic, and (2) if it is organic, use plasma oxidation to extract carbon for radiocarbon dating.

To test that the black material on the ceiling is organic, we heated three pieces of the blackened rock surfaces in a kiln with the temperature held for one hour at 600°C. As seen in Fig. 7, the black color disappeared confirming the organic nature of the black material.

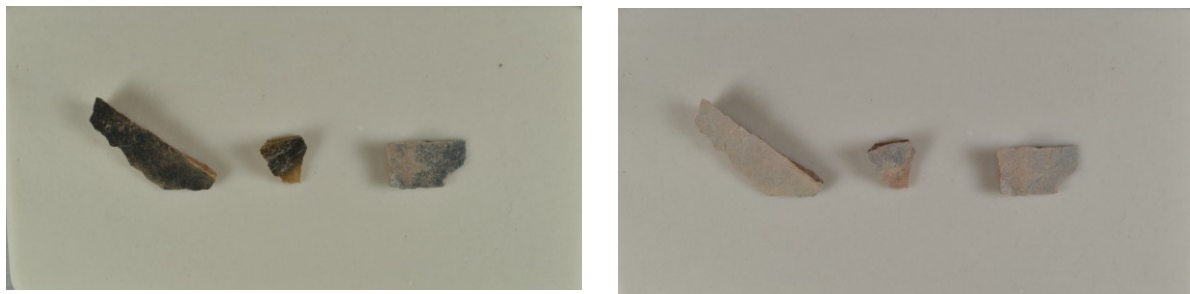


Fig. 7. Photographs before (left) and after (right) heating to 600°C in an electric kiln. The disappearance of the black color indicates that it was oxidized, supporting the assignment to organic material. For scale, each photograph is displaying 9.5 cm in width.

For chemical characterization, a sample of the blackened coating and the cream-colored limestone rock surface were analyzed separately with a Bruker D8 Advanced Bragg-Brentano X-ray diffractometer (XRD). XRD results are shown in Table 3, with observed diffraction patterns compared to the powder diffraction file (PDF) database for mineral identification. Both samples contain quartz inclusions, whewellite, dolomite, and kaolinite. The light-colored rock surface also has a minor component of gypsum. Notably, the blackened coating contains significant amounts of graphitic carbon, indicative of pyrolyzed carbon from smoke blackening.

Table 3. X-ray diffraction results.

PDF ^a	Mineral	Formula	Black Coating ^b	Background ^b
46-1045	Quartz, syn	SiO ₂	26.4%	40.2%
20-0231	whewellite, syn	CaC ₂ O ₄ ·H ₂ O	34.3%	34.6%
75-1654	Dolomite	CaMg(CO ₃) ₂	14.6%	18.5%
75-1593	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	7.8%	5.9%
76-1746	Gypsum	CaSO ₄ ·2H ₂ O	--	0.9%
75-1621	Graphite	C	16.8%	--

^aPowder diffraction file identification code.

^bPercent composition determined by XRD peak intensity.

Using plasma oxidation and AMS measurement, we obtained four radiocarbon dates on samples of soot from the ceiling at Serpentine Bends #1 (Table 4). Two were from powdered samples removed from the outer layer using a scalpel blade. Another sample was from the underneath soot layer, as close to the rock substrate as possible. And, the fourth was from an entire flake of the ceiling that had been masked with aluminum oxide to minimize any potential contribution from the basal rock (Fig. 8) (Rowe et al., 2017). Plasma oxidation is a surface oxidizing process and we only took about 100 µg of carbon for each sample. If the carbon from the surface of the soot is extracted preferentially, then it is the youngest, most recent, of the soot deposited. However, it is conceivable that the plasma penetrates throughout the entire volume of the soot, in which case the date would represent the average age of the soot deposits. Thus the dates would perhaps be best presented as minimum ages when analyzed by reaction of the masked soot surface.

For a detailed experimental procedure of the low-temperature plasma oxidation procedures by the Office of Archaeological Studies, see Rowe et al. (2016) and Loendorf et al. (2017: 3-4). No chemical pretreatment was conducted on these samples to remove any potential humic acids, as the rock art dating pretreatment process indicated that humic contamination was not present at the site. We have conducted experiments that indicate that aluminum oxide does not affect the dates obtained (Rowe and Blinman, unpublished data 2018). The isotope ratios of the carbon dioxide samples were measured directly in the ETH-Zürich AMS laboratory (Fahrni et al., 2013; Ruff et al., 2007; Wacker et al., 2013).

Results shown in Table 4 demonstrate that there were multiple fire events at the site, instead of a single event. Three aliquots from outer layers have younger ages of 1520 ± 60 , 1610 ± 60 , and 1870 ± 60 ^{14}C years BP, whereas the underlying layers of soot closest to the rock substrate is 2740 ± 70 ^{14}C years BP. As each dated aliquot contains carbon from more than one layer or fire event, the older age of 2740 ^{14}C years BP (1060-790 cal BC) is a minimum age for human activity at the site.

Table 4. Radiocarbon Results for Soot Sample

	OAS ID	ETH ID	$\mu\text{g C}$	^{14}C Date (BP)	Calibrated Range (cal BC/AD, 2σ)	Calibrated Range (cal BP, 2σ)
powdered outer layer	190128c-1	95746.1.1	43	1870 ± 60	10-260 cal AD (88.3%) 280-340 cal AD (7.1%)	1940-1690 (88.3%) 1670-1610 (7.1%)
masked outer layer	190502d-1	99754.1.1	100	1610 ± 60	260-280 cal AD (2.1%) 340-590 cal AD (93.4%)	1690-1670 (2.1%) 1610-1360 (93.4%)
powdered outer layer	190611d-2	99771.1.1	102	1520 ± 60	420-650 cal AD (95.4%)	1530-1300 (95.4%)
powdered underneath layer	191128a-1	95165.1.1	47	2740 ± 70	1060-790 cal BC (95.4%)	3010-2730 (95.4%)

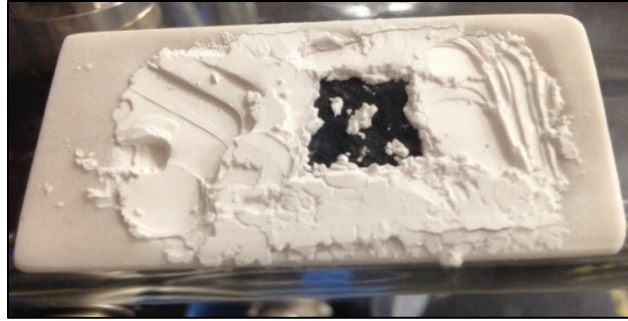


Fig. 8. Photograph of the sample where the basal rock is masked by aluminum oxide to minimize the effect of incorporation of any potential contamination from the basal rock itself.

3. Discussion

In this study, we have researched the potential to date soot on cave and rockshelter ceilings to obtain a minimum age for human activity at a site. At Serpentine Bends #1, the amount of soot on the ceiling indicates the cave had significant use with a ground level entrance and easy access. A major flood event, common to the region, apparently washed the shelter floor clean. The floor contains a grinding slick, a shallow mortar hole, two cupules and perhaps a third incipient cupule. There is also a rock ring from a modern fire near the rock shelter entrance, but no prehistoric fire features, and no charcoal to obtain an age for the site. There are no associated surface artifacts or any deposits that might be excavated to find datable materials. So, the only opportunity to learn when the site was in use is to date the pictographs and the soot covered ceiling.

3.1 Soot Samples

For the soot samples, the radiocarbon determination for these carbon aliquots is a weighted average of the deposited layers' ages, and would not reflect a single event of formation. The powdered layer taken as near the rock surface should be the earliest deposition of smoke blackening. Similarly, for the sample that was not scraped but simply masked with powdered alumina (a ^{14}C inert material), it is possible that the date obtained there represents the most recent soot deposition of that layer. However, we cannot rule

out that the entire layer was sampled by the plasma which would result in a weighted average date of layer deposition. If there had been a single fire event in the shelter, we should have obtained statistically indistinguishable ages for all of the soot samples studied. This is not what we observed (Table 4). We hypothesize that there were multiple fire events over potentially hundreds or even thousands of years. We collected carbon aliquots for dating by removing soot powder with a scalpel blade to obtain outer and underlying layers, as well as only extracting the outer surface carbon using plasma oxidation (for the masked outer layer). If the analyzed layers are not uniform, different ages would result as we observed. Even so, overlying layers will provide younger ages as any mixture of outer layers is still younger than any underlying soot. Likewise, the underlying layers of soot closest to the rock substrate represent a weighted average of older soot stains. Thus, the older age of 2740 ^{14}C years BP is a minimum age.

Importantly, the dating of ceiling soot is experimental. A previous attempt to date ceiling soot in Salt Cave, Kentucky produced a date of 3075 ± 140 ^{14}C years BP, an Archaic age, that was somewhat older but still within the range of other radiocarbon dates for fire features in the Mammoth Cave area (Bennington et al., 1962). Subsequent archaeological research in Mammoth Cave indicates that individuals were exploring the cave throughout the Late Archaic. As it is unknown if you are dating a single event or multiple layers of soot from different fire events, these ages for soot on cave and rock shelter walls are minimum ages for human activity at a site.

3.2 Pictograph Dates

For the two pictographs studied, the results are direct ages on when the paintings were created. For the red circle outline (circular forms), we obtained an age of 1315 ± 40 ^{14}C years BP. This age for the nucleated circle motif statistically agrees (overlaps at 1 standard deviation) with an age of 1380 ± 30 ^{14}C years BP for a concentric circle motif at Kee's Painted Shelter (LA 81502), located 19 km from Serpentine Bends #1 (Miller et al., 2019: 499). The Kee's figure is an eroded set of concentric circles that no longer retain a solid painted interior but there are associated concentric circles that do have infilled nuclei

in the same manner as the Serpentine Bends figure. These two dates for the same motif and a series of superimpositioning at the Ruby Canyon site (LA 148560) where circles and circular forms are found painted over zigzags offer evidence for the age of this motif in the region.

The age of the open net-like figures and zigzags at Serpentine Bends #1 is based on the date for the black abstract figure of 2325 ± 30 ^{14}C years BP. It appears to be the remnant of a net-like motif that is associated with vertically oriented zigzag or wavy line figures made with fine lines. This same motif is found at Robert's Cave (LA14288) where two of the zigzag/line motifs were processed using plasma oxidation and AMS radiocarbon dated to 2350 ± 100 and 2560 ± 80 ^{14}C years BP (Miller et al., 2019: 499). These ages are consistent with the Serpentine Bends # 1 date of 2325 ^{14}C years BP, suggesting that the fine-line, net-like and parallel wavy line figures are older than the concentric circle designs. The sample of dated figures is small, but it suggests the net and wavy line designs were made in the Late Archaic, and circles, especially nucleated circles, became more popular in the Formative. This potential trend needs to be tested at other sites across the region.

4. Conclusions

Dating both pictographs and prehistoric soot provide unique and alternate methods for dating human activity within rockshelters around the world, when there is a lack of excavated materials for study. While the rock art ages are dating a specific event with the creation of a painting, the soot date is an approximate average of fire usage at the site. At the Serpentine Bends # 1 site, it is significant that the radiocarbon ages for the soot on the ceiling fit well with the ages of the rock paintings (Fig. 9). The older age of 2740 ± 70 ^{14}C years BP represents the initial build-up of smoke stain on the ceiling with the early paintings a century or two later. A black line is 2325 ± 30 ^{14}C years BP and a red outline of a circle is 1315 ± 40 ^{14}C years BP. These pictograph dates agree with additional dates for line figures (zigzags and open net-like shapes) and circular forms (concentric circles, outline and infilled circles) at nearby rock art sites.

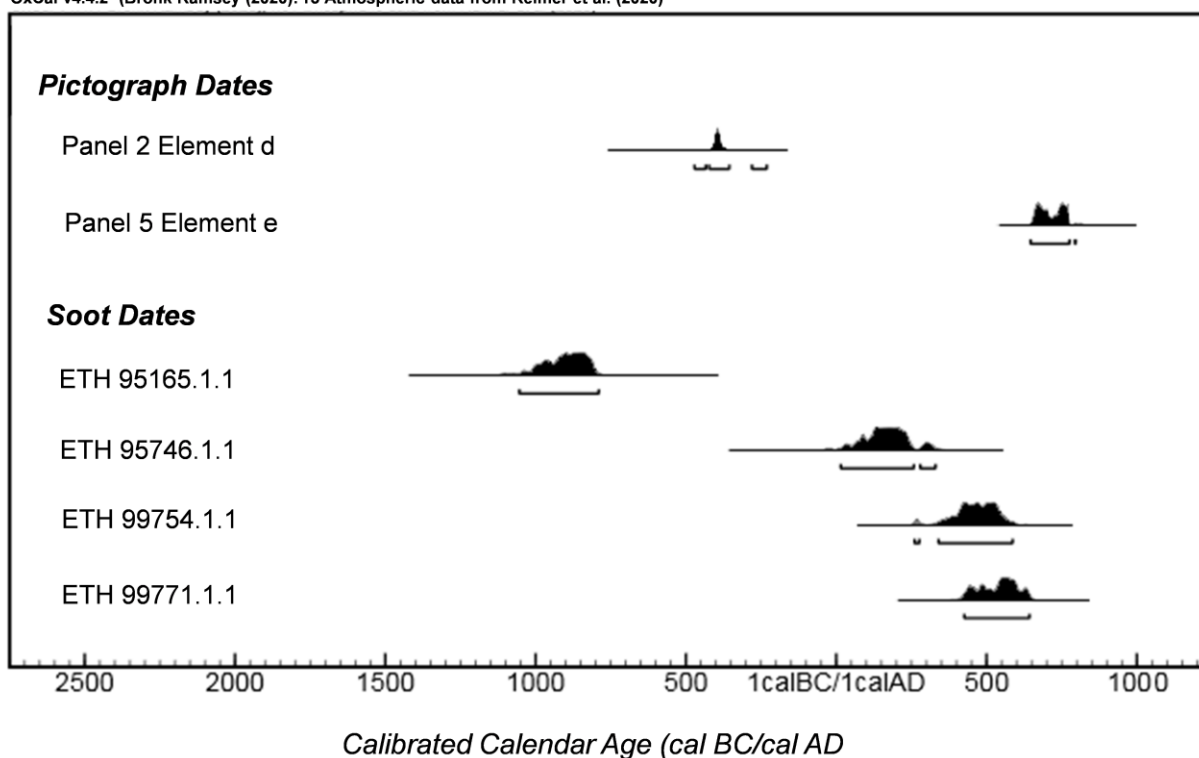


Fig. 9. Calibrated age ranges for pictograph and soot radiocarbon results.

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