METHODOLOGICAL ISSUES IN THE ^{14}C DATING OF ROCK PAINTINGS

R. E. M. HEDGES,[1] CHRISTOPHER BRONK RAMSEY,[1] G. J. VAN KLINKEN,[1] P. B. PETTITT,[1] CHRISTINA NIELSEN-MARSH,[1] ALBERTO ETCHEGOYEN,[2] J.O. FERNANDEZ NIELLO,[2] M. T. BOSCHIN[3] and A. M. LLAMAZARES[3]

ABSTRACT. Chemical and isotopic analyses have been made of pigment samples from two separate rock art sites in Argentina. The purpose of the study has been to establish the feasibility of extracting carbonaceous material from the samples which will permit reliable radiocarbon dates for the time of painting. The two sites, Catamarca and Rio Negro, present quite different problems. Most of the paper is concerned with Catamarca, and here we have shown that the paint pigments contain very little or no organic binder; but they do contain calcium oxalate derived from local cacti, and calcium carbonate derived probably from local plant ash. We describe a method to purify carbon extracted from the calcium oxalate, and present the dates obtained on both components. We show that, though rare, natural deposits containing both calcium oxalate and calcite do occur, but that they are very distinct in both ^{13}C and ^{14}C compositions; and we argue that they are very unlikely to contaminate the pigments to such an extent that the ^{14}C dates are altered. For the Rio Negro site we show that the ground for the paint pigments contains carbon derived from fires burnt inside the cave, and discuss how analytical methods provide information to develop a strategy for extracting material, from both ground and pigment, for more reliable dating.

INTRODUCTION

Rock paintings are among the most difficult archaeological artifacts to date reliably and directly using radiocarbon, because their composition is generally unpredictable and complex, and their large surface areas are deliberately exposed to the environment. Also, the availability of material for experimental purposes is usually very limited. Furthermore, rock art is hardly ever clearly associated with other material that could be reliably dated for comparison.

The most favorable case, so far, is when microscopic pieces of charcoal, recognized in the SEM from their morphology, can be recovered and pretreated by standard methods (for charcoal) (Valladas *et al.* 1992; McDonald *et al.* 1990), but these are exceptions. Attempts to extract and date biomolecules (*e.g.*, protein) putatively used in binders remain controversial (Loy *et al.* 1990; Nelson 1991) and are undoubtedly technically extremely difficult to perform satisfactorily. Where massive quantities of the paint survive well, as in the lipids present in beeswax, samples can be reliably pretreated to exclude subsequent contamination (Nelson *et al.* 1995). Diagenetic deposits, such as oxalates, where they underlie later paint layers, have also been "dated" in situations where the internal stratigraphic consistency of dating can be tested (Watchman and Campbell 1996). Finally, techniques have been reported (Russ *et al.* 1990) which oxidize the most labile carbon using a glow discharge in O_2 gas, and which apparently give dates in accordance with archaeological expectations.

We undertook the work described here in order to assess how well rock painting materials would lend themselves to chromatographic separation and direct ^{14}C on-line measurement of the separated peaks. Too little is known about the potential of rock paintings for chromatography (either gas phase of volatile derivatives, pyrolysis, or liquid phase) for this to be carried out without a great deal of preliminary work. As a rule, most paint pigments are likely to be inorganic (elemental carbon is an exception), restricting ^{14}C dating to the surviving traces of organic binders, which probably were

[1]Oxford Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, Oxford University, 6 Keble Road, Oxford OX1 3QJ, United Kingdom
[2]Laboratorio TANDAR, Departamento de Física, Comisión Nacional de Energía Atómica, Avda. del Libertador 8259, 1429 Buenos Aires, Argentina
[3]Facultad de Filosofia y Letras, Universidad de Buenos Aires, Moreno 350 (1091) Buenos Aires, Argentina

protein or carbohydrate based, rather than lipid-based. However, in the attempts to understand the materials used, the dating attempts described in this paper have not been on binders, but on the pigment itself or on stratigraphically related organic material.

In any case, in any reliable dating of rock painting it is necessary to 1) identify a carbonaceous component which can be extracted and which has an obvious chronological relationship to the act of painting, and 2) show that the extraction and purification techniques avoid or remove contaminants. The exposure of surfaces containing organic materials to the elements for millennia almost certainly leads to the inclusion of fungi, algae, lichens and microbes, as well as including insect deposits, plant exudations, soil soluble organic matter, and so on.

This paper describes work on rock art at three sites. One (Apollo 11 in Namibia (Wendt 1976)) did not involve actual sampling of the material (believed to be charcoal drawing on portable sandstone slabs and loosely associated with features dated at *ca.* 27 ka BP). However, experiments involved in assessing its potential for dating are of interest, and are described in the Appendix. The other two sites (here referred to as Rio Negro and Catamarca, from their provinces) are both in Argentina, of comparatively recent age, but present very contrasting problems. Most work has been done on the Catamarcan sites, and this is described first.

Catamarcan Rock Art Sites

Several rock art sites from the eastern slope of the Sierra de Ancasti or El Alto in the Ancasti department are known (de la Fuente 1979; Segura 1988). These site are located 80–90 km from San Fernando del Valle de Catamarca, the capital of Catamarca province, 500–900 m above sea level (asl), corresponding to the biosystem known as Bosque Subtropical Chaqueño (Marchetti and Prudkin 1983). Archaeological research has so far identified 25 sites in the area, 23 with rock art as the only archaeological remains, and 2 with stone constructions (Llamazares).

In general style, some rock paintings unmistakably resemble the incised patterns of pottery of the Aguada culture (dated by ^{14}C from *ca.* 500–900 cal AD), which flourished in several valleys of the Northwestern region of Argentina. Many of the rock art sites in the Ancasti area consist of granite boulders, weathered by aeolian forces to hollow shells, which act as small shelters or caves. The pigment is thickly applied to a very rough surface, and therefore can be obtained in large samples (up to 300 mg of material). The site most studied here, called La Candelaria Cave (28°41'16"S, 65°27'40"W) is in fact a water-worn cave in metamorphic rock. In all cases, the pigments are predominantly white, or grey or buff, contrasting with the darker color of the granite. The incisions in the black-fired polished Aguada pottery are filled with pigment whose main component, on the strength of one analysis, is calcite.[4] Therefore, not only the designs, but also the colors in the pottery decoration are reflected in the rock paintings. Many sites contain apparently separate designs, and could have been worked over many centuries. In some cases figures overlap.

Chemical and Isotopic Composition

Preliminary work on two samples of white pigment showed that, following routine acid-base-acid treatment of the bulk material, they contained 1–2% carbon, and gave a ^{14}C date of *ca.* 1000 BP. (In retrospect (see below) most or all of the carbon should have been removed by such treatment; the fact that it was not shows that the routine acid treatment had not dissolved all the oxalate present.) Of particular interest was the δ^{13}C value of the combusted pretreated material of –11‰. Given that

---

[4]Collection under study by Ines Gordillo, at the Ethnographic Museum of the University of Buenos Aires

carbonates would have been removed by the pretreatment, this implies that most of the remaining carbon is derived from a C4 photosynthetic pathway. CAM plants are in abundance in the region, and therefore are likely to be involved directly, or via a food chain. Prickly Pear (*Opuntia spp.*) is very common in this area and, more than other succulents and cacti, contains mucilaginous tissue which in modern times is added as a binder to pigments and inorganic extenders to make a paint. We concluded that a similar usage could account for the $\delta^{13}C$ value found here.

Fresh samples as well as other non-pigment deposits were obtained, including a non-anthropogenic white deposit accumulating around a water seep. The pigments and natural deposits were analyzed by infra red (IR) spectrometry. This showed that all the pigments contained gypsum (calcium sulfate), whewellite (calcium oxalate) and quartz in varying proportions. Many also contained calcite (calcium carbonate). The main features of the non-paint deposits were carbonates and quartz, but the spectra (both IR and Raman) were complex and difficult to interpret.

No detectable lipid material was obtained from extraction with methanol/chloroform, and pyrolysis-GC/MS on the bulk material produced no useful signal. After careful treatment with dil HCl, to decompose calcite and dissolve whewellite, the residue contained <10% of the original carbon content. Therefore, if any *substantial* portion of the carbon content was present as binder, it was lost or rendered soluble during treatment with dilute HCl. Further work is necessary to see if any material ascribable to binder, such as prickly pear mucilaginous tissue, can be identified. IR spectrometry did not disclose any signal ascribable to purely organic material in the pigment.

Using standards, the estimates of oxalate and carbonate content as provided by IR are in fair agreement (~30%) with the estimate based on the carbon extracted chemically. Carbonate and oxalate could account for up to 90% of the total carbon, and certainly account for 50% (the uncertainty is due to potential losses in collecting carbon from carbonate and oxalate) (Table 1). It is likely that there is some unaccounted carbon that analytical methods so far have failed to discover.

The Occurrence of Whewellite (Calcium Oxalate)

Calcium oxalate is precipitated as kidney stones and as raphides in plant cells, and can be produced by algae and lichens. The occurrence of calcium oxalate layers on exposed rocks, frequently limestone, is well known (Russ *et al.* 1996; Watchman 1990) and is presumably due to metabolic processes on photosynthetically derived Krebs cycle metabolites in algae or lichens. In general, the $\delta^{13}C$ of oxalic acid resembles that of the bulk photosynthesizing material, or may be somewhat heavier (*cf.* the ^{14}C NOX standard with that for a C_3 plant). However, the range of oxalate $\delta^{13}C$ values recovered from lichens can be quite large (−35‰ to −14‰ as quoted in Lange and Zeigler (1986)).

For consideration for ^{14}C dating, the questions to be asked are:

1. Is the whewellite deliberately collected to compose the pigment, or is it deposited naturally?
2. If deliberately collected, is it extracted from plants, or collected from a natural deposit?
3. Could the pigment contain a subsequent addition of naturally deposited oxalate?
4. How can the oxalate component be selectively extracted, leaving behind possible contaminants as humic acids, detritus, *etc.*?

Two non-painting white deposits were also sampled from the cave, one (called LC1) clearly still forming from an evaporating water seep. The other has given results (not discussed here) that suggest it may be an obliterated painting. Analysis of LC1 showed it to contain some carbon (mainly as carbonates), but 50 times less whewellite than in the pigment samples. The isotopic composition is

also completely different. Therefore, whewellite can form naturally in this environment, but in very low abundance, and the natural deposit can be recognized from its $\delta^{13}C$ signal (Table 1).

We conclude the whewellite was deliberately collected, most likely by processing from local cacti, which contain abundant whewellite. Raphides extracted from a dried herbarium specimen of a local cactus (*Trichocereus terchekii*) (*achuma* in Spanish) had a $\delta^{13}C$ value of −9.7‰, a value similar to that for bulk tissue sampled from local cacti, including *Opuntia*, and also similar to that for the calcium oxalate extracted from the paint (see Table 1). While this answers questions 1 and 2 above, 3 must still be addressed. An addition of *ca.* 5% modern whewellite (say from a natural deposit) to pigment whewellite in the paint is necessary to significantly change (*i.e.*, by >50 yr) the ^{14}C age of the pigment. Unfortunately, such an addition would be too low to be detected with a measurement of $\delta^{13}C$, despite the recognizable difference (10‰) in the bulk values between natural and pigment oxalates. However, the concentration of whewellite in the richest natural deposit we could find is 50 times less than in the pigment, while there is a complete and obvious spatial separation between the thick application of pigment and those areas where white deposits have formed naturally. In summary, we are able to show that the two different origins of oxalate which occur at La Candelaria can be distinguished, but their admixture cannot be detected at the level required for reliable ^{14}C measurement. However, we believe the extracted oxalate from the paint will give valid ^{14}C dates because the natural oxalate deposits contain too little oxalate and are too well spatially separated to be able to contaminate the pigment to a significant extent.

Purification of Calcium Oxalate

Assuming that whewellite represents the carbon isotopic composition of plants contemporary with the making of the pigment, it is necessary to extract the oxalate selectively from other carbonaceous material. We have found the apparatus shown in Figure 1 to be effective. The system is purged with N_2 at approximately atmospheric pressure and a flow rate of 1 mL s^{-1}. Dilute (2M) H_2SO_4 is introduced to the sample *via* a syringe and serves to release CO_2 from carbonate in the sample. This can be collected in the trapping loop if desired. Alternatively, carbonates can be removed from the sample beforehand. A 0.5 M solution of $KMnO_4$ is then introduced, which quantitatively releases CO_2 from oxalates present. Water vapor and CO_2 are swept by the N_2 flow through the system where water is trapped and the CO_2 collected in a GC-type transfer loop. In our case we have found it convenient to take the transfer loop to our combined continuous-flow CHN analyzer and mass spectrometer (Europa Roboprep and 20/20 mass spectrometer (Hedges *et al.* 1992)), where the gas is further purified, and measured in total quantity and for $\delta^{13}C$, and collected for accelerator mass spectrometry (AMS) dating. Using laboratory controls, this system works satisfactorily at the 100–1000 µg level, with $\delta^{13}C$ values valid to at least ±1‰.

A similar system has also been used for collecting CO_2 from calcite, using 1M HCl in place of permanganate and sulfuric acid. A similar chemical approach has very recently been published by Gillespie (1997).

Isotope Results on Carbon from the Paint and Natural Samples

Only one pigment sample so far has been extensively studied. Different fractions have been examined. These comprise the whole sample (no chemical pretreatment), the acid-base-acid treatment for the preliminary work, and carbon extracted from carbonate and from oxalate. The results obtained are tabulated in Table 1.
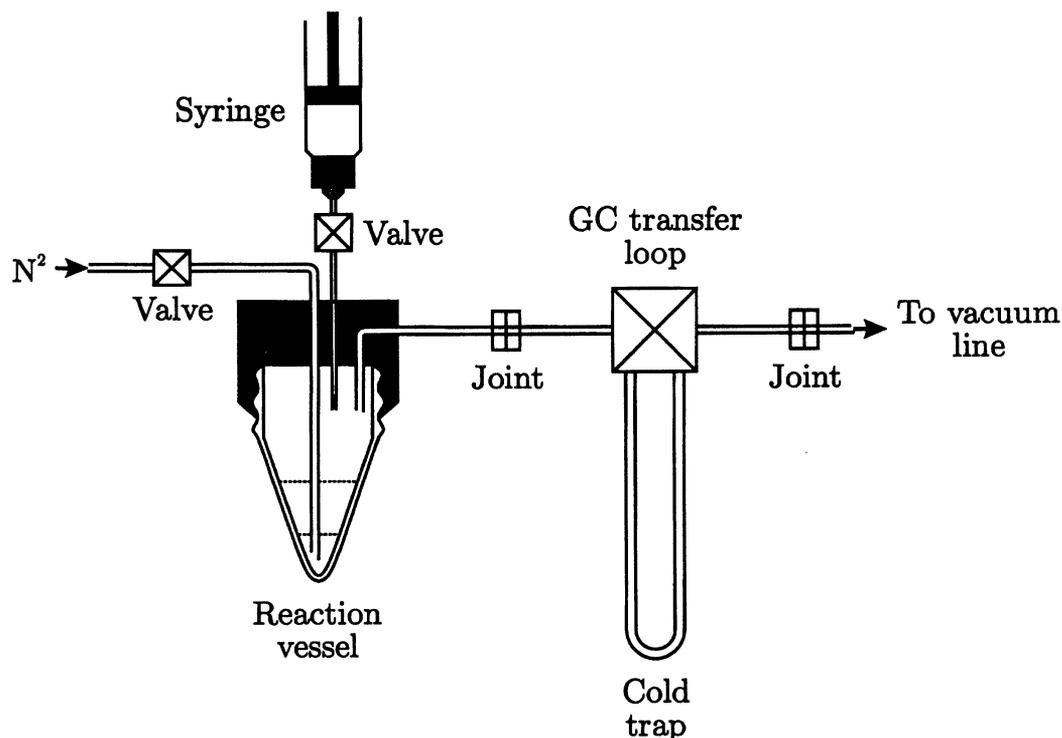
Fig. 1. Schematic of the apparatus used to extract and collect CO_2 from carbonates and oxalates. The system operates with a flow of N_2 at about one atmosphere pressure. The syringe delivers either HCl or H_2SO_4 (for carbonates), or H_2SO_4 + $KMnO_4$ solution (for oxalates) to the sample. Evolved CO_2 is swept into the cold trap, which forms part of a conventional gas chromatographic transfer loop. This can be demounted and the trapped CO_2 + water, *etc.*, is injected directly into a CHN analyzer for purification and analysis and mass spectrometric measurements.

TABLE 1. Results on Cave Paint Samples from La Candelaria*

	Original sample	Fresh sample (LC2)	Natural deposit (LC1)
Total carbon content	--†	7%	3%
Total C δ^{13}C	--	−17‰	+1‰
Total C ^{14}C date	--	1330 ± 50 (OxA-6942)	108% M (OxA-7167)
A/B/A C content	4%	--	--
A/B/A δ^{13}C	−10‰	--	--
A/B/A ^{14}C date	1000 ± 80 BP	--	--
Calcite carbon content	--	1.6%	0.6%
Calcite δ^{13}C	--	−23‰	+4.5‰
Calcite ^{14}C date	--	1310 ± 110 (OxA-6943) 1390 ± 75 (OxA-7169)	108% M (OxA-7168)
Oxalate carbon content	--	2.2%	0.04%
Oxalate δ^{13}C	--	−10.3‰	−26‰
Oxalate ^{14}C date	--	1195 ± 45 (OxA-6941)	too small to date

*The unusual δ^{13}C values for LC2 calcite and LC1 oxalate were replicated in separate extractions.
†Data not obtained

DISCUSSION

The ^{14}C dates of both natural sample fractions are modern, as would be expected. The $\delta^{13}C$ value for LC1 carbonate is fairly typical for an inorganic equilibrium with the atmosphere. Clearly the oxalate has formed from carbon derived through an entirely different pathway than that for the paint (LC2), and its $\delta^{13}C$ value is consistent with a C_3-based photosynthetic pathway, presumably due to algae or lichens.

The three ^{14}C dates obtained from LC2 fractions are in good agreement with each other (although they seem significantly older than those from the original sample). It is a little surprising that the carbonate component seems to have no subsequent exchange with atmospheric CO_2 in the last 1000 yr. Because this carbonate component had a very unusual $\delta^{13}C$ value, it was extracted twice (samples were small— *ca.* 100 µg of C), and isotopic measurements replicated well. Clearly, the carbonate is not of diagenetic or geological origin. A possible explanation of the $\delta^{13}C$ value is that C_3 plant ash such as K_2CO_3—*e.g.,* from wood fires—was added to the pigment, and that reaction with gypsum has produced calcite. We are not aware of any work which has characterized $\delta^{13}C$ values for plant ash carbon, but one might expect ash carbonate to be slightly enriched with respect to plant cellulose, and a value of −23‰ is therefore quite consistent with this idea. Other explanations, such as bacterial processing from inorganic carbonates, seem very much less likely. This interesting insight into the production of the pigment warrants further investigation.

We have presented arguments that calcium oxalate carbon can be extracted in pure form from the paint samples, and that the calcium oxalate very likely was originally extracted and prepared from local CAM cacti, so that the ^{14}C date should refer accurately to the time of preparing the painting, provided subsequent oxalate contamination has occurred. We argue that while such contamination is conceivable, it is very unlikely to be sufficient to affect the date significantly. Furthermore, the good agreement with the carbonate fraction argues for the validity of the dating.

We believe the results show that the methodology is now suitable for dating several parts of one painting, paintings which have a stratigraphic relationship, and also some paintings which can be "dated" on other evidence. (One example being an image of a horseman, and therefore post-Columbus.) Such results would properly test the validity of the method for dating. We do not know what precision is necessary; perhaps the main phase of painting was fairly short-lived, and an accuracy of *ca.* 50 yr might not be sufficient to demonstrate the time between overlapping paintings.

It should be borne in mind that some kind of binder could well have been used, and might still be present; the use of mucilaginous tissue from the same cactus that also provides the plant oxalate would seem an obvious source. Such material, if it could be extracted and purified in sufficient quantity, is to be preferred to oxalate for dating, since it should be chemically distinguishable from possible *in-situ* contaminants (unlike oxalate, which here is only distinguishable on the basis of its $\delta^{13}C$ value). However, so far we have failed to detect the presence of any such component—especially in sufficient quantity; further analysis is required. Samples of candidate plant tissues have been collected to make comparisons using chromatographic and mass-spectrometric methods. But the quantity of extractable binder would need to be quite large in order to obtain sufficient carbon, even from a 300-mg sample, to produce a ^{14}C date with sufficient precision to make a valid comparison with that from the oxalate component.

Rio Negro Rock Art Sites

Samples were taken from only one rockshelter, Loncoman Cave (40°47′33″S, 70°10′51″W). Although there are 21 sites with paintings in the region, the short time for field work did not allow us to visit more sites. Loncoman Cave is currently being archaeologically excavated and the stratified findings—including an important number of remains of prepared pigments that are submitted for chemical analyses at the Buenos Aires University—provide indirect chronological data for the assessment of both engraved and overpainted motifs. These suggest hypotheses concerning the age the art at the site. Continuous archaeological research in the region since 1978 has been able to determine an indigenous settlement sequence which started 2700 yr ago, according to ^{14}C dates (Boschin and Cuadernos 1988), and which continued to the 19th century, according to historical sources. Both the stylistic features of the motifs engraved and overpainted and the relationship between the art and the stratified materials suggest a late chronology. Very probably this type of rock art was executed immediately before or contemporaneously with the Spanish conquest of South America.

The shelter is a natural erosional feature in an outcrop of the relatively soft tuff, and the inner surface has been engraved as well as painted. The paint is thinly applied, and contains bright pigments (purple and yellow). We know through recent historical records that the Argentine Patagonia indigenous people elaborated their painting by adding lipids to the inorganic mineral pigments as a binding medium. As with the Catamarcan sites, a preliminary measurement was made on acid-base-acid pre-treated bulk material which contained *ca.* 1% carbon, and two separate samples gave ^{14}C ages of 2–3 millennia BP.

On a subsequent visit to Loncoman Cave (by REMH, JOFN and MTB), it was noted that the interior of the shelter is strongly blackened, and that the painting is essentially on blackened rock, so that paint samples are likely to include the black rock (here called "black patina"). The black patina was found to contain *ca.* 1% carbon, and so could be a significant contaminant. In any case, the black patina essentially forms a layer covering the unaltered tuff, so that there is a stratigraphic relationship between the black patina, engravings in the tuff, and painting on the surface, which needs to be resolved. Therefore, the question of dating the paint became one of understanding the formation and relative chronology of the black patina.

The Composition of the Black Patina

Samples of black patina and the underlying tuff were taken and their carbon isotopic contents measured, both for total and the residue after alkali extraction. There was insufficient material to date the alkali-soluble components (Table 2).

TABLE 2. Isotopic Results from Samples from Loncoman Cave

	Paint sample 1	Paint sample 2	Black patina	Underlying tuff
Total C%	--	--	1.3%	0.14%
Total δ^{13}C	--	--	−18.5	−24.5‰
Total ^{14}C age	--	--	1590 BP	1830 BP
A/B/A fraction: C content	1%	2%	0.9%	0.1%
A/B/A fraction: δ^{13}C	−23‰	−18‰	−19‰	−20‰
A/B/A fraction: ^{14}C date	1540 BP	3300 BP	1220 BP	2140 BP

These results show that the black patina is enriched in C with respect to the underlying tuff, which is very porous and likely to contain humic acids. This does not rule out the possibility that the extra carbon is derived from an accumulation of humics during evaporation. The $\delta^{13}C$ of the patina is distinctly enriched in ^{13}C over that of the presumed humic material in the tuff, as well as having a younger ^{14}C date. The less soluble carbonaceous material in the tuff has an older date, which would be expected for humic material. The reverse is the case for the black patina.

Further tests on the patina were made to identify the carbonaceous material, and to confirm that it has the same distribution as the black coloration. Electron microprobe analyses showed that the black patina did not differ significantly from the underlying tuff in such elements as iron and manganese (although there was increased calcium sulfate). Optical reflectance microscopy was able to identify the dark material as largely elemental carbon in the form of vitrinite and inertinite. The quantity observed was estimated to account for *ca.* 1–2% carbon (that is, it could account for all the carbon measured chemically). The micromorphology of the black deposits suggests both woody particles and cooked inorganic material. The interpretation is of a low pressure thermal event involving carbon; this almost certainly corresponds to fires in the shelter. This interpretation was further investigated by subjecting both whole samples of the patina, and samples after treatment with HF + HCl, to pyrolysis-GC/MS analysis. In summary, the results are somewhat surprising in that extremely little volatile material was observed. Some aromatic carbon structures, consistent with a firesmoke and ash deposit, were detected, but quite definitely less than might have been expected. Possibly, the surface exposure of the material to air for some millennia can account for this. In any case, given the anthropogenic nature of the site, the fact that the black patina is not observed in analogous situations where fires can be ruled out, the elimination of alternative possibilities, and the clear association with a thermal carbon deposit, the conclusion that the black patina carbon is wholly or mainly due to fire-smoke is inescapable.

Chemical (Organic) Composition of the Paint

Analysis of the paint organic composition has been difficult and is so far inconclusive. No detectable lipid material was extracted with methanol-chloroform. One paint sample (which also contained the black patina material) produced a weak but rich spectrum of aliphatic hydrocarbon peaks when subjected to pyrolysis-GC/MS. This included C27, C29 and C31 alkanes, indicative of higher plants. Protein-derived material was not observed. A second paint sample, after treatment with HCl, yielded a very impoverished spectrum from which nothing could be identified. Unfortunately, the quantity of material available severely limits the extent to which different analytical methods can be used. The $\delta^{13}C$ values of the bulk paint material are similar to that of the patina wood-smoke (which may compose a substantial proportion of the carbon present anyway). Note that the sample with the highest C% has somewhat isotopically heavier carbon—perhaps indicating a greater content of protein.

CONCLUSION

The dating of the cave (rockshelter) paintings in Rio Negro has first required us to understand the carbon isotopy of the underlying substrate, the "black patina". The carbon content of the patina is liable to be mixed with any sampled paint to an unacceptable degree. Analysis, using techniques of reflection microscopy as applied to coalified material, combined with pyrolysis-GC/MS, of the black patina shows that most, if not all, of it is very probably formed from fire smoke. The $\delta^{13}C$ values are consistent with carbon derived from local woody material. It should be possible to decide on suitable chemical pretreatment to prepare samples for a ^{14}C date of the time-averaged use of fire.

Our preliminary result, based on the alkali insoluble components, suggests a date of *ca.* 1000 BP—which implies an earlier use of fire in the cave.

Although the paint is stratigraphically above the black patina, and is therefore younger than the time when the patina begun to form, it is not necessarily younger than when the patina stopped forming, so that a "date" for the patina is not simply related to the date for the paint. Further careful sampling might better elucidate the stratigraphic relationships; for example, they should allow comparison of patina dates immediately below the paint with dates from exposed patina. The identification of organic material in the paint is still very far from being achieved—there appears to be very little volatile material detected by Py-MS. At present the status of the two paint "dates" (they have not been given laboratory OxA references) remains unresolved. The date of 3300 BP, which is surprisingly old for this site, may indicate underlying older firesmoke in the sample.

REFERENCES

Boschin, M. T. 1988 Arqueología del "Area Pilcaniyeu", Sudoeste de Río Negro, Argentina. *Cuadernos* (Instituto Nacional de Antropología, Buenos Aires) 11: 99–119.

de la Fuente, N. 1979 Arte rupestre en la región de Ancasti, provincia de Catamarca. *In* Jornadas de Arqueología del NOA. *Antiquitas* (Buenos Aires) 2: 408–418.

Gillespie, R. 1990 On the use of oxidation for AMS sample pretreatment. *Nuclear Instruments and Methods* B52: 345–347.

_____1997 On human blood, rock art and calcium oxalate. *Antiquity* 71: 430–437.

Hedges, R., Humm, M., Foreman, J., van Klinken, G. and Bronk, C. 1992 Developments in sample combustion to CO_2, and in the CO_2 ion source system. *In* Long, A. and Kra, R. S., eds., Proceedings of the 14th International *14C* Conference. *Radiocarbon* 34(3): 306–311.

Lange, O. L. and Zeigler, H. 1986 Different limiting processes of photosynthesis in lichens. *In* Marcelle, R., Clijster, H. and van Poucke, M., eds., *Biological Control of Photosynthesis*. Dordrecht, Netherlands: 147–161.

Llamazares, A. M. 1996 (ms.) Research report presented to CONICET (National Council for Scientific and Technological Research). Buenos Aires.

Loy, T., Jones, R., Nelson, D., Meehan, B., Vogel, J., Southon, J. and Cosgrove, R. 1990 Accelerator radiocarbon dating of human blood proteins in pigments from late pleistocene art sites in Australia. *Antiquity* 64: 110–116.

Marchetti, B. and Prudkin, N. 1983 *Atlas Total de la República Argentina*. Centro Editor de América Latina, Buenos Aires.

McDonald, J., Officer, K., Jull, A. J. T., Donahue, D., Head, J. and Ford, B. 1990 Investigating *14C* AMS: Dating prehistoric rock art in the Sydney sandstone basin, Australia. *Rock Art Research* 7: 83–92.

Nelson, D. E. 1993 Second thoughts on a rock art date. *Antiquity* 67: 893–895.

Nelson, D. E., Chaloupka, G., Chippindale, C., Alderson, M. S. and Southon, J. R. 1995 Radiocarbon dates from beeswax figures in the prehistoric rock art of northern Australia. *Archaeometry* 37 (1): 151–156.

Russ, J., Hyman, M., Shafer, H. and Rowe, M. 1990 Radiocarbon dating of prehistoric rock paintings by selective oxidation of organic matter. *Nature* 348: 710–711.

Russ, J., Palma, R. L., Loyd, D. H., Boutton, T. W. and

Coy, M. A. 1996 Origin of the whewellite-rich rock crust in the lower Pecos region of Southwest Texas and its significance to paleoclimate reconstructions. *Quaternary Research* 46: 27–36.

Segura, A. B. 1988 El arte rupestre del Este de Catamarca. *Las pictografías de La Candelaria, Departamento Ancasti, provincia de Catamarca.* Universidad Nacional de Catamarca. Facultad de Humanidades. Catamarca, Buenos Aires.

Valladas, H., Cachier, H., Maurice, P., Bernaldo de Quiros, F., Clottes, J., Valdes, V. C., Uzquiano, P. and Arnold, M. 1992 Direct radiocarbon dates of prehis-

toric paintings at the Altamira. *Nature* 357: 68–70.

Watchman, A. 1990 A summary of occurrences of oxalate-rich crusts in Australia. *Rock Art Research* 7: 44–50.

Watchman, A. and Cambell, J. 1996 Microstratigraphic analysis of laminated oxalate crusts in northern Australia. In 2nd International Symposium on the oxalate films in the conservation of works of art, Milan 1996: 409–422.

Wendt, W. E. 1976 'Art Mobilier' from the Apollo 11 Cave South West Africa. *South African Archaeological Bulletin* 31: 5–11.

APPENDIX: RECOVERING CHARCOAL AND GRAPHITE FROM SIMULATED ROCK DRAWINGS

This exercise was stimulated by an examination of two designs, apparently in charcoal—although there is no direct evidence for this—found on sandstone tablets at the Late Stone Age site of "Apollo 11" in Namibia. The drawings are small (*ca.* 8 cm across and *ca.* 2–3 cm^2 in total area) and, by their association, may perhaps date from 26,000 BP (Wendt 1976). Their dating by AMS-^{14}C was considered, and as a preliminary study, we carried out experiments to see how much of the drawing would need to be sampled.

We measured the quantity of carbon per unit area required to produce both faint and emphatic drawings on smooth and rough surfaces of sandstone which were chosen from a museum collection. The carbon was applied using a graphite pencil. We measured the fraction of carbon so deposited that could be recovered by scraping the surface, and combusting the product in a CHN analyzer. We also measured the amount of carbon recovered by scraping a "control" surface away from the drawing. Renewed scraping of the already scraped layer gave a somewhat lower but still significant yield. The results are summarized in the table below.

TABLE 3. Results of Experiments to Recover Carbon from Drawings on Rock Surfaces

Surfaces studied:	Unglazed terra-cotta; fine-grained and coarse-grained sandstones
Quantity of graphite needed to cover 100 mm^2:	~1000 μg carbon (when heavily shaded)
Quantity recovered from scraping 100 mm^2:	300–600 μg
Quantity total scraped material from 100 mm^2:	5–15 mg (only *ca.* 3% is carbon)
Quantity of carbon recovered from 100 mm^2 of clear surface (no graphite applied):	30–100 (μg carbon)
To discriminate graphite from surface contaminants:	
Effect of pretreating with acid/alkali/acid:	30% loss of charcoal; 70% loss of surface contaminant

The quantity of carbon recovered from the "control" surfaces, which had previously been blown free of superficial dust, was surprisingly high (Table 3). Taking this together with the quite low recovery of carbon recovered by surface scraping of the drawing, the possibility of ^{14}C dating of a sample only containing carbon from the drawing is evidently quite low. In the case of the Apollo 11 material, which has the increased difficulty of a potentially very low ^{14}C content, an area of >50 mm^2 would need to be sampled, which would cause unacceptable destruction. In any case, without differentiation from surface "dirt" carbon, the date would be meaningless, especially in the context of an dating an artifact potentially several ^{14}C half-lives old. In our experiments, some differentiation could be achieved by treating the scraped material with NaOH, with the rationale that the surface dirt carbon contains more alkali-extractable material. This improved the drawing carbon/dirt carbon by a factor of 2 to 3—this is not enough to be reliably useful.

Of course, this is only one indication of the degree of superficial carbonaceous material on rock that is liable to be included when a rock painting or drawing is sampled; the museum specimens are not necessarily representative. However, it is evidence that argues for great caution, and for careful design of control tests, when sampling and "dating" this kind of material. It also suggests that chemical methods for differentiating charcoal carbon from the "dirt" carbon (for example, oxidation with permanganate (Gillespie 1990) need first to be considered and developed).