

## RADIOCARBON DATING OF “OLD” CHARCOAL USING A WET OXIDATION, STEPPED-COMBUSTION PROCEDURE

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**ABSTRACT.** We present results that validate a new wet oxidation, stepped-combustion procedure for dating “old” charcoal samples. An acid–base–wet oxidation (ABOX) pretreatment procedure has been developed that is used in place of the conventional acid–base–acid (ABA) pretreatment. Combustions and graphitizations are performed in a vacuum line that is insulated from the atmosphere by a second backing vacuum to eliminate the risk of atmospheric leakage into the line at any stage of the procedure. Combustions are performed at 3 temperatures (330 °C, 630 °C and 850 °C) with a graphite target produced from the CO<sub>2</sub> evolved during each combustion step. In this way, the removal of any contamination can be monitored, and a high degree of confidence can be placed on the final age. The pretreatment, combustion, graphitization, and measurement blank for the procedure, based on the analysis of a “radiocarbon-dead” graphite, is  $0.5 \pm 0.5 \mu\text{g C}$  ( $1\sigma$ ,  $n=14$ ), equivalent to  $0.04 \pm 0.02 \text{ pMC}$  or an “age” of approximately 60 ka for a 1 mg graphite target. Analyses of a “radiocarbon-dead” natural charcoal after ABOX pretreatment and stepped combustion suggest that the total blank (including contamination not removed by pretreatment) may be higher than for graphite, ranging up to  $0.10 \pm 0.02 \text{ pMC}$ . Additional experiments confirm good agreement with accepted values for the international low-<sup>14</sup>C “New Kauri” standard ( $0.16\text{--}0.25 \text{ pMC}$ ). They also confirm excellent reproducibility, with 3 separate dates on different aliquots of a charcoal sample from Ngarrabullgan Cave (Queensland, Australia) ranging from 35.2 to 35.5 ka <sup>14</sup>C BP. It is also demonstrated that the ABOX pretreatment, in conjunction with the new vacuum line described here, is able to remove contamination not removed by the conventional ABA pretreatment, suggesting that the technique can be used to produce reliable <sup>14</sup>C dates on charcoal up to at least 50 ka.

### INTRODUCTION

Charcoal is a popular sample type for radiocarbon dating and can yield reliable dates from a large number of archaeological and geological environments. In most cases a simple acid–base–acid (ABA) pretreatment is all that is required to remove contaminants and provide reliable age estimates. However, in some cases it has been demonstrated that the ABA pretreatment does not remove all contaminants (e.g. Gillespie et al. 1992; Gillespie 1997), and the problem of ensuring the complete removal of contaminants becomes increasingly severe as the age of the sample increases. Detecting sample contamination and verifying the reliability of the ages produced also become more difficult as the age of the sample increases. In practice this means that many laboratories will only quote <sup>14</sup>C ages to about 40 ka BP (thousands of <sup>14</sup>C years Before Present), with ages greater than this generally considered to be “infinite”, or indistinguishable from procedural blanks.

The so-called “radiocarbon barrier” and the difficulty of ensuring that ages are reliable at <1% modern carbon levels has limited research in many disciplines. One such problem surrounds the timing of human occupation of the Australian continent. Early <sup>14</sup>C determinations suggested that humans first arrived about 40 ka BP (the “short” chronology summarized in Allen and Holdaway 1995; O’Connell and Allen 1998), whereas the advent of luminescence techniques in the 1980s suggested that humans may have arrived at 54–60 ka BP (the “long” chronology, Roberts et al. 1994). The large difference in ages between the short and the long chronologies is unlikely to be explained by any disparities resulting from the use of 2 independent dating techniques—<sup>14</sup>C and luminescence—representing 2 different time “clocks” (David et al. 1997). Proponents of the “long” chronology have suggested that the discrepancy is likely to be due to the influence of a small amount of contaminant-

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tion on the  $^{14}\text{C}$  dates, as contamination by 1% of modern carbon will make a “ $^{14}\text{C}$ -dead” sample have an apparent age of approximately 37 ka BP (Chappell et al. 1996). This explanation has been challenged by some archaeologists on several grounds, including the fact that although no archaeological  $^{14}\text{C}$  dates beyond 40 ka BP have been measured in Australia, a significant number of geological  $^{14}\text{C}$  dates beyond 40 ka BP are reported in the literature. It has been proposed that this would not be the case if contamination were a significant general problem (Allen and Holdaway 1995; O’Connell and Allen 1998). Resolution of this discrepancy is important for a refined understanding of early human migration and colonization of the continent as well as of the ecological effects accompanying human colonization. The production of reliable  $^{14}\text{C}$  dates on old archaeological charcoal samples can assist in this respect.

We believe that for a  $^{14}\text{C}$  date to be considered reliable at 50 ka, for example, the combined blank from natural contamination and laboratory handling should be equivalent to a  $^{14}\text{C}$  age of at least 55 ka. In addition, the ages must be reproducible within the stated error bounds, and the removal of all contamination must be verifiable. The results of this study show that these criteria can be met for charcoal, enabling the production of reliable  $^{14}\text{C}$  dates in the >40 ka BP range, using a wet oxidation pretreatment protocol to ensure removal of contaminants, and a stepped-combustion procedure to verify decontamination of the sample.

## EXPERIMENTAL TECHNIQUES

### Samples

The samples used for the verification of the procedure represent a range of natural and artificial charcoals and graphites, as listed in Table 1 and described below. They were chosen to provide information on the total blank for the procedure and to check that the ages produced are reproducible both internally and against previously generated results for well-characterized samples.

1. The Ceylon graphite is a natural geological “ $^{14}\text{C}$ -dead” graphite that is used in this study to enable an estimate of the total procedural and measurement blanks for the wet oxidation, stepped-combustion technique.
2. A sample of “ $^{14}\text{C}$ -dead” charcoal was selected to test the ability of the method to remove organic carbon contamination. The charcoal was obtained from a buried paleosol, the Coulter Pedoderm, exposed in a gully on the southwest flank of Black Mountain (Canberra, Australia). The unit is thought to have undergone pedogenesis during a period of climatic stability similar to the present, and is likely to be at least of last interglacial age. The unit is overlain by alluvial fan gravels stratigraphically equivalent to a valley-fill deposit in an adjacent valley dated by optically stimulated luminescence (OSL) to greater than 50 ka (T T Barrows and R G Roberts, unpublished data). The buried paleosol has been subject to infiltrating waters carrying organic compounds from the vegetated surface. Interactions between the charcoal and groundwater are evidenced by fine gypsum crystals deposited on the surface of some fragments.
3. An aliquot of the New Kauri standard (Hogg et al. 1995) was pyrolyzed in vacuo for this study at approximately 500 °C to produce an artificial “charcoal” with a known low  $^{14}\text{C}$  activity. Both pyrolyzed and “raw” samples of wood were used to test the pretreatment methodologies.
4. A crushed and homogenized sample of charcoal from Ngarrabullgan Cave (North Queensland, Australia) was prepared to assess the reproducibility of ages generated by the technique using charcoal from a previously dated unit. A substantial body of dates have been published for this unit, with 19  $^{14}\text{C}$  determinations spanning 28.8–34.6  $^{14}\text{C}$  ka BP (David et al. 1997).

## Pretreatment

All pretreatment steps are carried out in either a laminated flow cabinet, a HEPA-filtered clean lab, or capped vials, with all vessels and implements precleaned either by combustion overnight at 550 °C (Pyrex®) or 850 °C (quartz), or by washing with a hot solution of 0.1M  $\text{K}_2\text{Cr}_2\text{O}_7$  in a 2M solution of  $\text{H}_2\text{SO}_4$ . All water used in the pretreatments is Milli-Q® grade.

Hand-picked fragments of charcoal are crushed in a mortar and pestle and a 10–200 mg aliquot is weighed into a 50 mL capped plastic Falcon® centrifuge tube. 20 mL of 6M HCl is added to the tube, which is capped and left to stand for 1 h, after which it is centrifuged and rinsed twice with Milli-Q® water. If the sample contains appreciable mineral impurities, a 1:1 mix of concentrated HCl and HF can be used in addition to a simple acid wash and the sample is left at 60 °C overnight to dissolve mineral phases, after which the solution is rinsed as above. 50 mL of 1M NaOH is then added to the tube, which is again left to stand for 30 min before rinsing once with Milli-Q® water. These steps are designed to remove acid and base soluble organic material, respectively.

Next, 30 mL of acid-dichromate oxidant solution (0.1M  $\text{K}_2\text{Cr}_2\text{O}_7$  in a 2M solution of  $\text{H}_2\text{SO}_4$ ) is added to the tube, which is capped and heated to  $60 \pm 0.5$  °C in a temperature-regulated hot box. After 14–24 h the tube is centrifuged, the supernatant discarded, and the remaining particulate material is washed twice with Milli-Q® water. Bird and Gröcke (1997) have demonstrated that oxidation for 72 h under the above conditions will remove all organic carbon from the sample, leaving a residue of “oxidation resistant elemental carbon” (OREC). The proportion of OREC left after oxidation for 72 h depends on the nature of the charcoal and can range widely from 20 to 80%. The choice of 14–24 h is a compromise required to ensure that sufficient sample material is left for further analysis. With larger samples or denser charcoal fragments, the oxidation time can be increased to 72 h or longer.

After the final 2 rinses, the particulate material is transferred by Pasteur pipette to a capped 3 mL glass vial in Milli-Q® water. The vial is warmed on a hot plate at low temperature for 5 min, after which the supernatant, along with fine OREC and mineral impurities, is pipetted back into the centrifuge tube and a fresh aliquot of Milli-Q® water is added to the vial. The procedure is repeated until the supernatant above the sedimented particles is clear after the settling period. This step removes fine mineral impurities as well as fine OREC and also leaches some adsorbed dichromate from the surface of the larger particles. The fine residue can be kept for separate analysis if necessary. The cleaned particulate OREC is covered and allowed to dry on a hot plate for several hours, and is then weighed.

We call this pretreatment ABOX (acid-base-oxidation) to differentiate it from the conventional ABA pretreatment.

## Combustion

Significant contamination of samples from atmospheric leakage into the extraction line can potentially occur during the combustion of the sample to  $\text{CO}_2$ , or during graphitization. The Pyrex and silica vacuum extraction line developed for these analyses eliminates the possibility of atmospheric leakage by backing all the valves in the line with a second vacuum that separates the interior of the line from the atmosphere (Figure 1). Thus all valves have a pumped volume behind the O-ring through which the valve stem passes, and likewise, the sample loading and take-off points are protected by a vacuum between the inside of the line and the atmosphere. The vacuum-backed valves and metal “take-off” fittings are illustrated in Figure 2. Initial evacuation of the line is via a rotary pump, with final evacuation via a molecular drag pump backed by an oil-free diaphragm pump.

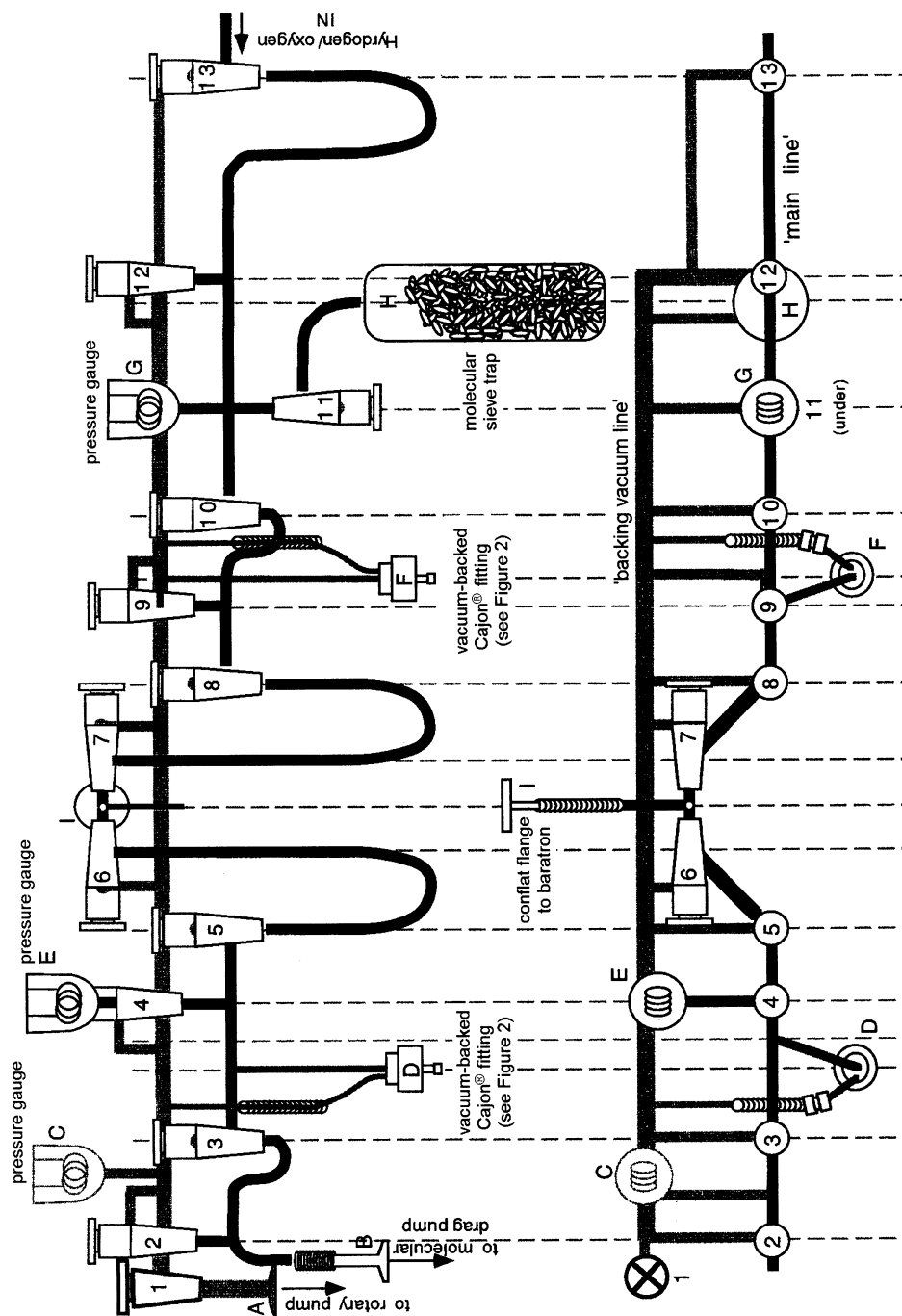


Figure 1 The combustion-graphitization line used for this study. Vacuum-backed valves (2 to 13), manufactured to specifications by Embell Scientific Pty Ltd, and vacuum-backed O-ring fittings (D and F) are shown in detail on Figure 2. The left side of the line is used for combustion of the sample, the right side for graphitizations, and the middle of the line is used for quantification of  $\text{CO}_2$  evolved and dosing both the combustion and graphitization sides with  $\text{O}_2$  or  $\text{H}_2$  as required (using a 0–1000 torr Baratron® capacitance manometer at I). The line is evacuated at valves 2, 3, and 12, with initial evacuation via a rotary pump (at A) and then via a molecular drag pump (at B).  $\text{O}_2$  and  $\text{H}_2$  is admitted via valve 13, and precleaned by sorption onto the molecular sieve at H. Monitoring of pressure is via thermal conductivity gauges at C, E, and G.

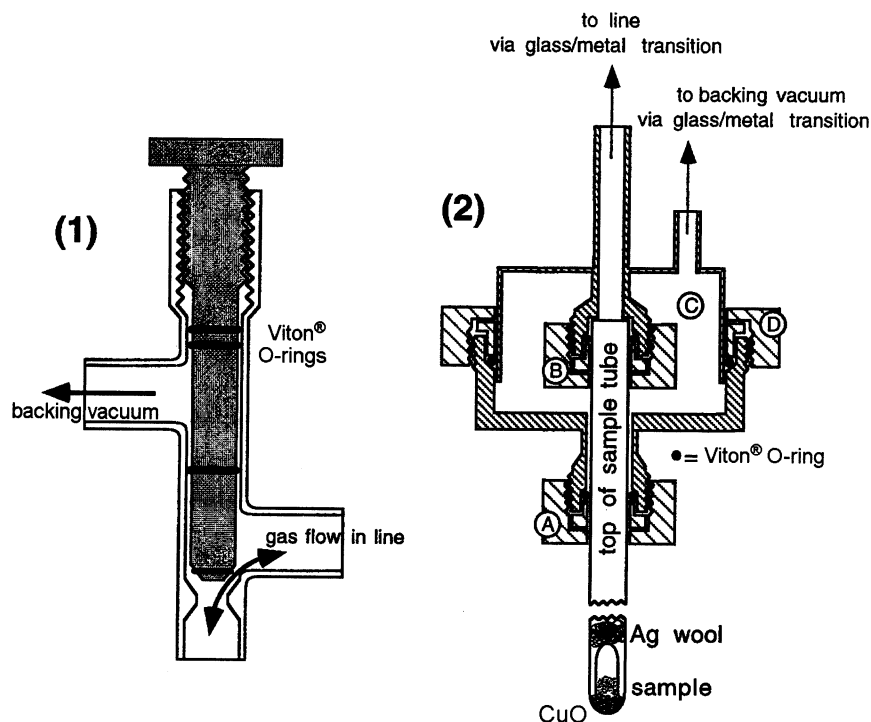


Figure 2 Diagrams of (1) a Pyrex<sup>®</sup> vacuum-backed valve, with inlets and outlets of 12 mm OD, and (2) Cajon<sup>®</sup> fittings welded together to provide a pumpable volume between the O-ring seal to the vacuum line and the atmosphere. The fittings were manufactured using: (A) 1/4 inch to 3/8 inch Cajon adaptor, drilled through to allow the passage of the 6 mm OD silica combustion tube; (B) 1/4 inch Cajon fitting with a welded "hood" of 1 inch OD, with outlets to the main vacuum line and the backing vacuum line. The pumped volume (C) is created by sealing the hood with a 1 inch Cajon fitting (D) welded to (A). All seals are made by the compression of Viton<sup>®</sup> O-rings at the locations indicated on the diagram.

Prior to loading a sample, 200 mg of combusted CuO (850 °C overnight) is weighed into a silica tube (6 mm OD  $\times$  20 cm length), and both the tube and CuO are again combusted. Approximately 5–15 mg of OREC is weighed into a small combusted silica capsule (3.4 mm OD  $\times$  10 mm length), which is pushed down the silica combustion tube to rest inverted on the CuO at the bottom (Figure 2). A plug of 0.05 mm diameter >99.9% Ag wire (Aldrich; combusted at 550 °C overnight) is pushed down the tube to rest on top of the sample. This prevents particles from being entrained into the vacuum line during pump-down and removes any halogens or sulfur produced during the combustion.

The sample tube is loaded onto the line and evacuated. Whenever the line is opened, it is back-flushed with  $\text{H}_2$  to prevent the adsorption of atmospheric  $\text{CO}_2$  onto internal surfaces. For the initial combustion step, 99.99%  $\text{O}_2$  (Linde) is first frozen onto a type 4 molecular sieve with liquid nitrogen ( $\text{N}_{2(l)}$ ). The  $\text{N}_{2(l)}$  trap is removed and replaced by a dry ice–ethanol trap (approximately  $-80^\circ\text{C}$ ) that allows  $\text{O}_2$  to sublime but will retain any carbon-bearing gas species. The sublimation is allowed to continue until a  $\text{pO}_2$  of about 0.5 atm (sufficient to oxidize about 1 mg of carbon) is present in the combustion volume. CuO does not provide available oxygen during the first combustion step at 330 °C. Excess  $\text{O}_2$  is pumped off and the molecular sieve is baked at about 200 °C until the normal background pressure is reached prior to its next use.

A furnace at 330 °C is placed around the sample and the temperature maintained for a 2 h period. Work by Cachier et al. (1989) has shown that this treatment will remove organic contaminants with minimal removal of black carbon from aerosol samples. This step serves to remove contaminants that may have been introduced during the loading procedure or that are adsorbed onto the sample surface. In practice it was found that pretreated OREC samples were partly susceptible to oxidation during this step, probably due to catalysis of the oxidation reaction by residual chromium ions on the sample surface (Mull et al. 1998). At the end of the oxidation time, the furnace is lowered, CO<sub>2</sub> is frozen with N<sub>2(l)</sub>, and excess O<sub>2</sub> is pumped off. The amount of CO<sub>2</sub> produced is measured using an MKS-Baratron® capacitance manometer (0–1000 torr). This CO<sub>2</sub> is then graphitized, as described below.

The combustion volume is then re-isolated and heated at 630 °C for 1 h. At this temperature, CuO provides the oxygen for the oxidation. As previously, the CO<sub>2</sub> produced during this combustion step is purified, measured, and graphitized. The sample is then heated at 850 °C for a further hour, with the CO<sub>2</sub> again purified, quantified, and graphitized. This last combustion step is repeated to ensure complete combustion of the sample. The quantity of CO<sub>2</sub> produced during this final step is usually negligible and is discarded.

A graphite target is generally made from the CO<sub>2</sub> produced during each combustion step (i.e., 330 °C, 630 °C, and 850 °C). In this way it is expected that any contaminants remaining after the sample pretreatment will be combusted in the 330 °C step, and that the reliability of the <sup>14</sup>C age can be assessed by the coherence of the results from the 630 °C and 850 °C steps. This is because oxidation can be expected to remove less resistant phases first, and work progressively from the outside to the interior of the particles. In the case of untreated graphite, very little CO<sub>2</sub> was produced in the 330 °C or 630 °C combustion steps, so the 3 targets were made from 3 combustions at 850 °C (850 I, II, III; Table 1).

### Graphitization

The graphitization procedure is based on the conventional technique of iron-catalyzed reduction of CO<sub>2</sub> to graphite in the presence of H<sub>2</sub> at 630 °C, with the water produced during the reaction being frozen into a dry ice–ethanol trap (Vogel et al. 1984; Kitagawa et al. 1993; Gagnon and Jones 1993). An additional step used in our procedure is a preoxidation of approximately 0.5 to 1.0 mg iron powder (Merck; 10 µm) to remove carbonaceous contaminants present in the Fe powder, or introduced during the sample loading procedure. Approximately 0.5 atm of O<sub>2</sub> is sublimed from the molecular sieve trap into the graphitization tube containing the iron powder and this is then heated to 330 °C for 2 h. Prior to graphitization, the iron powder is re-reduced with approximately 0.5 atm of 99.999% H<sub>2</sub> (Linde) at 630 °C for 2 h. The precombustion of the Fe powder does not appear to affect its catalytic action during the conversion of CO<sub>2</sub> to graphite. As for the O<sub>2</sub>, any H<sub>2</sub> used in the procedure is purified prior to use by means of the molecular sieve trap.

Sample CO<sub>2</sub> is frozen into the graphitization tube, which is then dosed with a 1.1× stoichiometric excess of H<sub>2</sub>. The graphitization is conducted at 630 °C for 16–18 h. In general, CO<sub>2</sub> produced during the 330 °C (A) and 630 °C (B) steps is graphitized in flame-sealed silica tubes offline, while the 850 °C (C) graphitization is conducted attached to the extraction line. The completeness of the graphitization for the 850 °C (C) fraction can then be checked by measuring the total pressure, and CO<sub>2</sub> pressure at the end of the reaction period. During the graphitization, water produced from the reduction of CO<sub>2</sub> by H<sub>2</sub> is frozen into a dry ice–ethanol trap placed on the bottom of the graphitization tube. The graphite that is produced is stored in vacuo until analysis by flame-sealing the graphitization tube above and below the small bucket containing the graphite and Fe powder.

In practice, the initial combustion steps as well as the preoxidation and reduction of the iron powder for graphitization occur in parallel during the day, while the graphitizations take place overnight. One sample, yielding 3 targets, can be processed per 24 h using this procedure.

### Accelerator Mass Spectrometry

The mass of graphite plus iron powder is determined as a yield check and then the graphite is pressed into 1 mm diameter holes in aluminum sample holders. These are loaded, together with 3 or 4 ANU sucrose standards, into a 32-sample wheel for insertion into an NEC multi-sample negative ion source. The  $^{14}\text{C}/^{13}\text{C}$  ratio of each sample is measured by accelerator mass spectrometry using the 14UD accelerator at the Australian National University. Although the  $\delta^{13}\text{C}$  value has not been measured, it has been assumed that ANU sucrose and charcoal have values of  $-11\text{‰}$  and  $-25\text{‰}$ , respectively, and hence a fractionation correction of  $14\text{‰}$  (equivalent to 110 yr) has been applied to each of the charcoal samples.

A blank correction of  $0.07 \pm 0.05$  pMC has also been subtracted from the measured ratios of the New Kauri and Ngarrabullgan charcoal samples, but not the Ceylon graphite analyses or the analyses of the Black Mountain charcoal samples. This blank represents the total spread of values obtained for both the Ceylon graphite and Black Mountain charcoal (as discussed below).

### RESULTS AND DISCUSSION

The results of all analyses are presented in Table 1. The analyses of Ceylon graphite (generally 3 targets per analysis) represent the combustion, graphitization, and measurement blank for the procedure. All 14 measurements are consistent with the mean value of 0.04 pMC ( $\chi^2_{\nu} = 1.2$ ) and the standard deviation of the data set is 0.02 pMC (Figure 3). This blank is at least an order of magnitude lower than the 0.7% modern carbon that would be equivalent to an age of 40 ka, and is 2–10 times

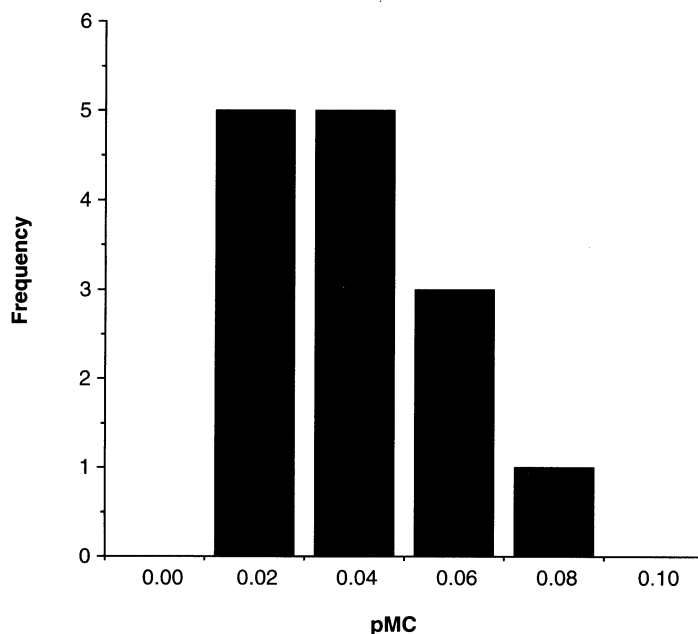


Figure 3 Histogram of blank values obtained from 14 combusted and graphitized Ceylon graphite samples

Table 1: pMC and  $^{14}\text{C}$  ages for a range of natural and artificial charcoals and graphites measured in this study. Quoted mean  $^{14}\text{C}$  ages are based upon amount-weighted pMC values for the 3 combustion fractions, and are equivalent to the "total combustion" age of the sample.

| Sample             | Description                                                        | Pretreatment   | Lab. No.                 | Fraction   | Combustion time (h) | Graphite wt (mg) | pMC <sup>a</sup> | Error (1 $\sigma$ ) | $^{14}\text{C}$ age (yr BP) | Uncertainty (1 $\sigma$ ) |
|--------------------|--------------------------------------------------------------------|----------------|--------------------------|------------|---------------------|------------------|------------------|---------------------|-----------------------------|---------------------------|
| Ceylon graphite    | Geological graphite, $^{14}\text{C}$ "dead"                        | Untreated      | ANUA-8125 <sup>b</sup>   | CI (850)   | 1                   | 0.9              | 0.03             | 0.01                | 65,160                      | +3760 / -2510             |
|                    |                                                                    |                | ANUA-8126 <sup>b</sup>   | CII (850)  | 1                   | 0.9              | 0.02             | 0.01                | 66,800                      | +4430 / -2620             |
|                    |                                                                    |                | ANUA-8127 <sup>b</sup>   | CIII (850) | 3                   | 2.2              | 0.08             | 0.02                | 57,400                      | +2030 / -1650             |
|                    |                                                                    |                | ANUA-9300 <sup>b,c</sup> | CIII (850) | 3                   | 2.2              | 0.06             | 0.03                | 59,500                      | +4760 / -3020             |
|                    |                                                                    |                | ANUA-8208 <sup>b</sup>   | CI (850)   | 1                   | 0.9              | 0.06             | 0.02                | 59,700                      | +3800 / -2530             |
|                    |                                                                    |                | ANUA-8209 <sup>b</sup>   | CII (850)  | 1                   | 0.6              | 0.04             | 0.03                | 63,500                      | +9990 / -4350             |
|                    | Untreated                                                          | Untreated      | ANUA-8210 <sup>b</sup>   | CIII (850) | 1                   | 1.1              | 0.03             | 0.02                | 64,700                      | +5510 / -3310             |
|                    |                                                                    |                | ANUA-9424 <sup>b</sup>   | CII (850)  | 1                   | 1.1              | 0.05             | 0.02                | 61,190                      | +3340 / -2310             |
|                    |                                                                    |                | ANUA-9422 <sup>b</sup>   | CI (850)   | 1                   | 0.9              | 0.05             | 0.02                | 60,710                      | +3560 / -2410             |
|                    |                                                                    |                | ANUA-9423 <sup>b</sup>   | CII (850)  | 5                   | 0.8              | 0.04             | 0.02                | 62,420                      | +3880 / -2550             |
| 95-BMtn-FAN-002    | Natural charcoal from >50 ka sediments (Barrows, unpublished data) | ABOX           | ANUA-9426 <sup>b</sup>   | CI (850)   | 1                   | 0.6              | 0.05             | 0.02                | 60,500                      | +2690 / -2110             |
|                    |                                                                    | ABOX           | ANUA-9425 <sup>b</sup>   | CIII (850) | 1                   | 0.5              | 0.03             | 0.01                | 65,700                      | +4820 / -2970             |
|                    |                                                                    | ABOX           | ANUA-9427 <sup>b</sup>   | CI (850)   | 1                   | 0.4              | 0.02             | 0.01                | 67,730                      | +5530 / -3350             |
|                    |                                                                    | ABOX           | ANUA-9428 <sup>b</sup>   | CI (850)   | 1                   | 0.1              | 0.06             | 0.02                | 59,280                      | +2940 / -2070             |
|                    |                                                                    | Untreated      | ANUA-10321               | A (330)    | 2                   | 0.5              | 1.31             | 0.09                | 34,820                      | +590 / -550               |
|                    |                                                                    |                | ANUA-10322               | B (630)    | 1                   | 0.2              | 0.50             | 0.07                | 42,520                      | +1220 / -1060             |
|                    |                                                                    |                | ANUA-10323               | C (850)    | 1                   | 0.9              | 0.19             | 0.04                | 50,360                      | +1700 / -1440             |
|                    |                                                                    |                |                          | Mean       |                     |                  | 0.56             | 0.03                | 41,660                      | +490 / -460               |
|                    |                                                                    | ABA            | ANUA-9415                | A (330)    | 2                   | 0.2              | 2.89             | 0.14                | 28,480                      | +410 / -390               |
|                    |                                                                    |                | ANUA-9416                | B (630)    | 1                   | 0.5              | 0.33             | 0.04                | 45,940                      | +1150 / -990              |
|                    |                                                                    |                | ANUA-9417                | C (850)    | 1                   | 2.4              | 0.15             | 0.02                | 52,230                      | +1430 / -1210             |
|                    |                                                                    | ABOX           |                          | Mean       |                     |                  | 0.32             | 0.02                | 46,270                      | +580 / -540               |
|                    |                                                                    |                | ANUA-9418                | A (330)    | 2                   | 0.2              | 0.91             | 0.08                | 37,720                      | +730 / -680               |
|                    |                                                                    |                | ANUA-9419                | B (630)    | 1                   | 0.6              | 0.17             | 0.03                | 51,260                      | +1780 / -1430             |
|                    |                                                                    |                | ANUA-9420                | C (850)    | 1                   | 2.0              | 0.10             | 0.02                | 55,860                      | +2210 / -1660             |
|                    |                                                                    |                |                          | Mean       |                     |                  | 0.17             | 0.02                | 51,260                      | +920 / -830               |
| New Kauri standard | Kauri wood (0.12-0.21 pMC), Hogg et al. (1995).                    | ABOX           | ANUA-6130                | C (850)    | 4                   | 1.8              | 0.11             | 0.06                | 55,060                      | +2350 / -1750             |
|                    |                                                                    | Pyrolyzed ABOX | ANUA-6129                | C (850)    | 3                   | 1.8              | 0.25             | 0.06                | 48,030                      | +2380 / -1830             |
|                    |                                                                    | Pyrolyzed ABOX | ANUA-6905                | C (850)    | 2                   | 1.4              | 0.16             | 0.06                | 51,770                      | +3960 / -2640             |
|                    |                                                                    | Pyrolyzed ABOX | ANUA-8802                | C (850)    | 1                   | 2.5              | 0.21             | 0.06                | 49,420                      | +2750 / -2040             |
|                    |                                                                    | ABOX           | ANUA-10308               | C (850)    | 1                   | 2.2              | 0.21             | 0.09                | 49,490                      | +4660 / -2930             |

| Sample          | Description                                                                                                 | Pretreatment | Lab. No.  | Fraction | Combustion time (h) | Graphite wt (mg) | pMC <sup>a</sup> | Error (1σ) | <sup>14</sup> C age (yr BP) | Uncertainty (1σ) |
|-----------------|-------------------------------------------------------------------------------------------------------------|--------------|-----------|----------|---------------------|------------------|------------------|------------|-----------------------------|------------------|
| MM25<br>XU8 (3) | Archaeological charcoal, Ngarrabullgan Cave, Queensland<br><br>See David et al. (1997) for site description | Untreated    | ANUA-9307 | A (330)  | 2                   | 0.9              | 1.98             | 0.11       | 31,510                      | +490 / -460      |
|                 |                                                                                                             |              | ANUA-9308 | B (630)  | 1                   | 1.0              | 1.52             | 0.07       | 33,630                      | +480 / -450      |
|                 |                                                                                                             |              | ANUA-8803 | C (850)  | 1                   | 2.2              | 1.25             | 0.08       | 35,200                      | +630 / -580      |
|                 |                                                                                                             |              |           | Mean     |                     |                  | 1.47             | 0.07       | 33,880                      | +400 / -380      |
|                 |                                                                                                             | HCl/NaOH     | ANUA-9309 | A (330)  | 2                   | 0.4              | 1.74             | 0.13       | 32,540                      | +630 / -590      |
|                 |                                                                                                             |              | ANUA-9310 | B (630)  | 1                   | 0.8              | 1.39             | 0.12       | 34,350                      | +720 / -660      |
|                 |                                                                                                             |              | ANUA-8804 | C (850)  | 1                   | 2.6              | 1.41             | 0.10       | 34,230                      | +600 / -560      |
|                 |                                                                                                             |              |           | Mean     |                     |                  | 1.44             | 0.08       | 34,050                      | +470 / -450      |
|                 |                                                                                                             | HCl/HF/NaOH  | ANUA-9312 | A (330)  | 2                   | 0.6              | 2.12             | 0.14       | 30,960                      | +550 / -520      |
|                 |                                                                                                             |              | ANUA-9313 | B (630)  | 1                   | 0.7              | 1.55             | 0.11       | 33,470                      | +580 / -540      |
|                 |                                                                                                             |              | ANUA-8805 | C (850)  | 1                   | 2.5              | 1.61             | 0.11       | 33,170                      | +570 / -530      |
|                 |                                                                                                             |              |           | Mean     |                     |                  | 1.68             | 0.09       | 32,850                      | +430 / -400      |
|                 |                                                                                                             | ABOX (7 h)   | ANUA-9314 | A (330)  | 2                   | 0.7              | 1.58             | 0.09       | 33,320                      | +480 / -450      |
|                 |                                                                                                             |              | ANUA-8806 | C (850)  | 1                   | 1.0              | 1.21             | 0.11       | 35,460                      | +750 / -690      |
|                 |                                                                                                             | ABOX (14 h)  | ANUA-9315 | A (330)  | 2                   | 0.6              | 1.56             | 0.09       | 33,420                      | +490 / -460      |
|                 |                                                                                                             |              | ANUA-9316 | B (630)  | 1                   | 0.8              | 1.35             | 0.09       | 34,580                      | +580 / -540      |
|                 |                                                                                                             |              | ANUA-8807 | C (850)  | 1                   | 2.0              | 1.25             | 0.11       | 35,200                      | +720 / -660      |
|                 |                                                                                                             |              |           | Mean     |                     |                  | 1.37             | 0.07       | 34,440                      | +440 / -420      |

<sup>a</sup>With the exception of the Ceylon graphites and the Black Mountain charcoal, a blank correction of 0.07 ± 0.05 pMC has been subtracted from the measured pMC for each sample.

<sup>b</sup>Negligible gas at 340 °C and 650 °C.

<sup>c</sup>Repeat measurement of ANUA-8127 after heating target in vacuo at 650 °C.

lower than commonly reported procedural blanks (Kitagawa et al. 1993; Vogel et al. 1987; Gagnon and Jones 1993). Note that 4 of the samples, ANUA-9425 to ANUA-9428, were derived from Ceylon graphite that had been subjected to the ABOX treatment before subsamples spanning a range of weights were taken for subsequent combustion and graphitization. The values obtained from these 4 samples are statistically indistinguishable from the 10 samples that were not subjected to any pre-treatment prior to combustion.

The samples spanned a range of graphite weights from 0.1 to 2.2 mg, and the corresponding amount of modern carbon that would account for the observed pMC varies between about 0.1 and 1.7  $\mu\text{g}$ , giving an average of approximately  $0.5 \pm 0.5 \mu\text{g}$  ( $1\sigma$ ,  $n=14$ , equivalent to  $\sim 60$  ka for a 1 mg graphite target). It should also be noted that calculated blanks in excess of 1  $\mu\text{g}$  were from the first 2 Ceylon graphites prepared using the combustion line, and calculated blanks for all subsequent analyses have been consistently lower. There is, however, no obvious correlation between sample weight and the measured  $^{14}\text{C}$  activity (Figure 4), suggesting that the few  $^{14}\text{C}$  atoms observed may already be present in the Ceylon graphite itself or were possibly added during target pressing.

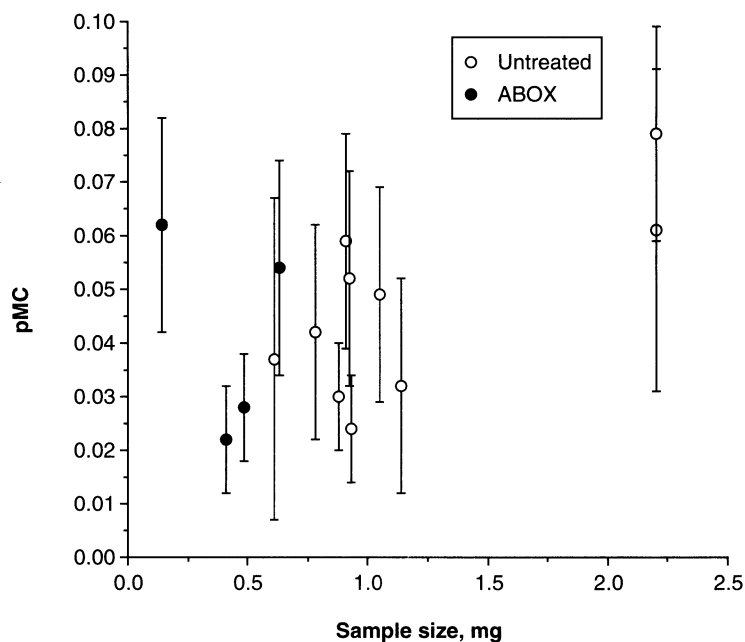


Figure 4 Plot of the relationship between sample size and pMC values for untreated and ABOX Ceylon graphite targets. Error bars represent the 68% ( $\pm 1\sigma$ ) range for overall analytical confidence.

Vogel et al. (1987) have suggested that diffusion of carbon through the walls of Vycor combustion tubes may occur during extended combustions at elevated temperature. To test this possibility for the silica tubes used in this study, samples of Ceylon graphite were combusted for 1 and 5 h (ANUA-9422 and -9423, respectively; Table 1). The resulting  $^{14}\text{C}$  ages of 60.7 and 62.4 ka BP (0.05 and 0.04 pMC, respectively) are statistically indistinguishable and indicate that diffusion of modern carbon into the tubes during combustion does not contribute significantly to the  $^{14}\text{C}$  background.

The Black Mountain charcoal sample (Figure 5) enables the estimation of the blank achievable for known “ $^{14}\text{C}$ -dead” charcoal. This sample represents a worst case in that it is overlain by a vegetated

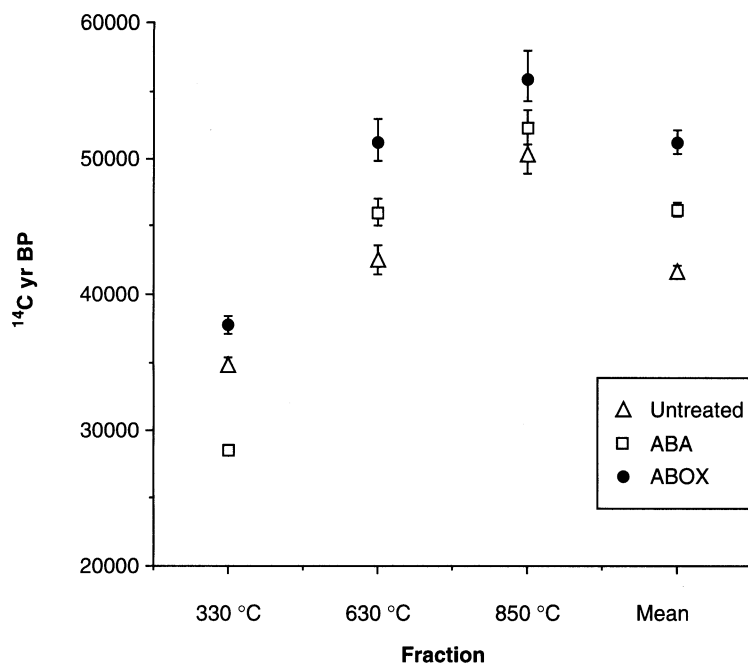


Figure 5 Variations in untreated, ABA- and ABOX-treated <sup>14</sup>C ages from Black Mountain charcoal at the 330 °C, 630 °C and 850 °C temperature fractions and amount-weighted mean ages for total combustion. Error bars represent the 68% ( $\pm 1\sigma$ ) range for overall analytical confidence. Note the consistently older ages derived using the ABOX-treatment.

soil profile and has been exposed to infiltrating waters and the organic compounds carried by those waters since deposition of the sediments and subsequent pedogenesis. This is in contrast to charcoal from Ngarrabullgan Cave, for example, which has been substantially protected from interaction with infiltrating waters (discussed below). The Black Mountain charcoal is therefore an ideal sample with which to compare the relative efficacy of the ABOX and ABA pretreatments and stepped combustion. The results suggest 2 things:

1. Neither the stepped combustion of an untreated sample nor an ABA pretreatment with stepped combustion is sufficient to remove all contaminants. The <sup>14</sup>C ages of the untreated (50.4 ka) and ABA (52.2 ka) 850 °C fractions are younger than the same fraction of the ABOX pretreated sample (55.6 ka). The weighted mean <sup>14</sup>C age (equivalent to the age that would have been obtained from complete combustion) of the untreated and ABA pretreated samples for all combustion steps (41.6 and 46.3 ka) are significantly younger at the 2 $\sigma$  level than the corresponding weighted mean age for the ABOX pretreated sample (51.3 ka).
2. The ABOX pretreatment alone does not remove all contamination, as the lower temperature fractions of the step-combusted ABOX pretreated sample have younger <sup>14</sup>C ages (37.7 and 51.3 ka) than the 850 °C fraction (55.9 ka). It therefore seems that although total combustion can produce reliable ages on charcoal, the effective limit of the <sup>14</sup>C technique will be considerably younger for samples that are analyzed by total combustion.

The results also suggest that the blank for the ABOX/stepped-combustion procedure applied to charcoal from oxidizing surficial environments may be higher than for a crystalline graphite such as the Ceylon graphite. A conservative approach to assigning a blank value to analyses of natural charcoals

would be to assume that the true blank lies between the average value obtained for the ABOX pretreated 850 °C fraction of the Black Mountain charcoal and the blank obtained for the Ceylon graphite (i.e.,  $0.07 \pm 0.05$  pMC). This blank has been subtracted from the samples discussed below. Further analysis of known “ $^{14}\text{C}$ -dead” charcoals from a variety of environments should allow a refinement of this value in future.

The results for the  $^{14}\text{C}$  New Kauri standard indicate that the pretreatment procedure does not introduce contaminants. Regardless of whether the wood was pyrolyzed in vacuo or pretreated raw, the results for this standard, which range from  $0.16 \pm 0.06$  pMC to  $0.25 \pm 0.06$  pMC (48–51.7 ka), are internally consistent and comparable within error to the accepted range of values for this standard (0.12–0.21 pMC; Hogg et al. 1995).

The series of measurements on subsamples of the homogenized charcoal from Ngarrabullgan Cave was designed to test various steps in the procedure for a typical archaeological sample. The 3 combustion steps for the 5 pretreatments returned  $^{14}\text{C}$  ages from 30.9 to 35.5 ka  $^{14}\text{C}$  BP (2.12–1.21 pMC, Table 1).

For ABOX-pretreated samples, the results indicate that consistent, reproducible ages can be obtained from the 850 °C fraction, and possibly from the 630 °C fraction, but not from the 330 °C fraction (Figure 6). The results for the step-combusted, untreated sample further suggest that for relatively uncontaminated charcoals, the 850 °C fraction of the step combustion alone can produce a reliable age. For the samples that were subjected only to an acid-base pretreatment, it is evident that minor contamination is introduced to the sample during these initial steps, most likely from adsorption of atmospheric  $\text{CO}_2$  by the alkaline solution. However, this contamination is removed during the subsequent acid oxidation step of the full ABOX procedure. No ABA-treated sample was ana-

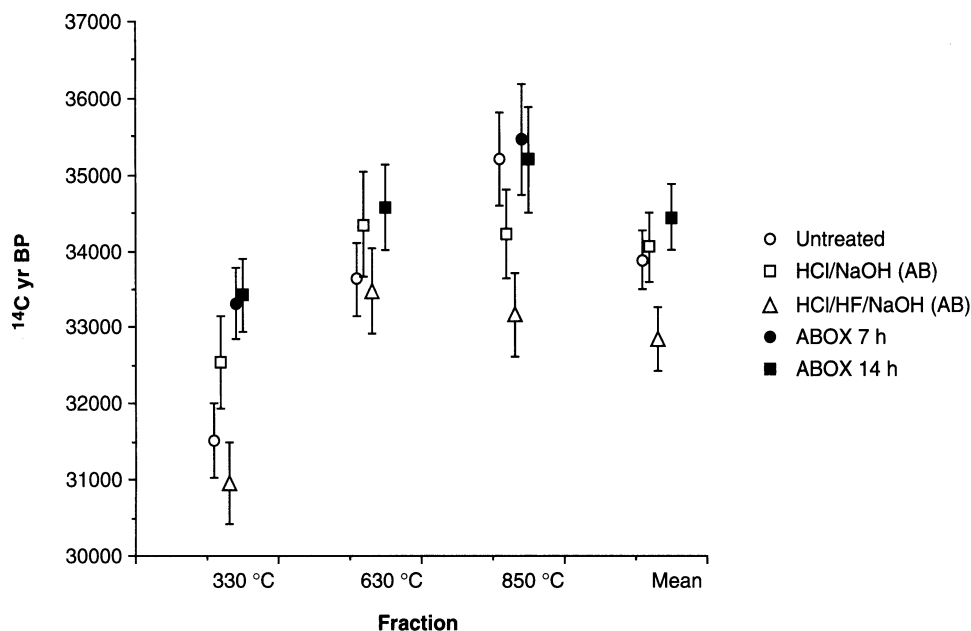


Figure 6 Variations in untreated, AB-, and ABOX-treated  $^{14}\text{C}$  ages from Ngarrabullgan charcoal at the 330 °C, 630 °C and 850 °C temperature fractions and weighted means. Error bars represent the 68% ( $\pm 1\sigma$ ) range for overall analytical confidence. Note the consistently older ages derived using the ABOX treatment.

lyzed, as the results from the untreated and ABOX-treated samples indicate that the Ngarrabullgan sample is virtually uncontaminated.

All 5 samples show a significant shift to older ages from the 330 °C to 630 °C step (Table 1 and Figure 6). However, in the case of the AB-treated samples, there is a suggestion that the ages become younger for the 850 °C fraction, possibly owing to formation of  $\text{Na}_2\text{CO}_3$ , which has a decarbonation temperature of 851 °C. The results for the 850 °C fraction of the untreated sample and of the 2 ABOX-treated samples cluster tightly between 35.2 and 35.5 <sup>14</sup>C ka BP. This age is at the upper end of the range of 19 dates on charcoal from this level of the deposit (David et al. 1997), which range from 28.8 to 34.6 <sup>14</sup>C ka BP. A sample previously analyzed from this deposit subjected to the ABOX pretreatment (without stepped combustion) also returned an age at the upper extreme of the dated sample population (OZC-733,  $35.5 \pm 0.6$  ka; Roberts et al. 1994), again suggesting that the ABOX/stepped-combustion procedure consistently removes contaminants not removed by conventional pretreatments.

## CONCLUSION

This study has demonstrated that the ABOX pretreatment is a reliable technique for removing contaminants from charcoal and that the stepped-combustion procedure can ensure that blanks are sufficiently low to enable reliable <sup>14</sup>C age determinations in the 40–50 ka time range. The production of multiple targets by stepped combustion provides an additional indicator of the reliability of age determinations in this time range.

Previous studies have demonstrated that the major source of introduced contamination in the combustion of samples for <sup>14</sup>C analysis comes from the copper oxide used during combustion (Vogel et al. 1987; Vandeputte et al. 1998). This suggests that the major contribution to reducing the overall blank for charcoal samples in this study comes from the use of stepped combustion, with oxygen employed as the oxidant at 330 °C. The stepped combustion removes contaminants present in the copper oxide and/or introduced during sample loading, and also removes contamination from samples not removed by the ABOX pretreatment. The results for the Black Mountain sample suggest that both the ABOX pretreatment and stepped combustion are required to reduce blanks to a level low enough to allow the measurement of reliable finite dates on charcoal in the 40–50 ka time range.

The other procedures used in this study, including preoxidation of the iron powder, use of molecular sieves, storage of samples in vacuo and the use of a vacuum-backed extraction line, may also contribute to overall blank reduction, but more importantly, guard against random contamination of individual samples. Based on the range of blank values obtained from “<sup>14</sup>C-dead” charcoal and graphite, it seems likely that the appropriate blank for a natural charcoal sample will vary depending on the nature of the charcoal, its degree of alteration, and the environment from which it was obtained.

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