A COMPARISON OF CELLULOSE EXTRACTION AND ABA PRETREATMENT METHODS FOR AMS ^{14}C DATING OF ANCIENT WOOD

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ABSTRACT. We have compared accelerator mass spectrometry (AMS) radiocarbon results on wood samples at or near the limit of ^{14}C dating, pretreated with a standard acid-base-acid (ABA) protocol, with those obtained from cellulose prepared from the same samples by several modifications of the Jayme-Wise cellulose extraction method (Green 1963). These tests were carried out to determine the most efficient way to ensure low backgrounds in ^{14}C measurements of well-preserved ancient wood samples.

INTRODUCTION

Cellulose is a long polysaccharide chain that does not translocate within a tree or exchange carbon with the atmosphere following its formation. Radiocarbon dates performed on cellulose alone are therefore thought to be a good measure of past atmospheric ^{14}C. A study by Gaudinski et al. (2005) indicated that the Jayme-Wise method produces extracts that are most chemically similar to pure cellulose as compared to other cellulose extraction methods.

A batch processing protocol for Jayme-Wise cellulose extraction, developed by Leavitt and Danzer (1993) and commonly used for stable isotope measurements, involves 3 steps to isolate alpha-cellulose, each step followed by multiple water washes:

1. *Cleaning*: treatment in a Soxhlet system with toluene and ethanol to remove waxes, fats, oils, resins, and other compounds soluble in organic solvents.
2. *Isolation of holocellulose*: bleaching with a mixture of sodium chlorite and acetic acid to remove lignins.
3. *Isolation of alpha-cellulose*: treatment with strong base followed by a neutralizing acetic acid wash.

In ^{14}C studies, a major driver for using cellulose extractions has been the need to quantitatively remove resins, lignins, and other mobile wood fractions when studying ^{14}C in post-bomb and immediately pre-bomb wood. These fractions can contaminate tree rings with translocated carbon from subsequent years, which can have very different $\Delta^{14}C$ and may not be not completely removed by more conventional pretreatments, though the overall effect on measured $\Delta^{14}C$ values is relatively small (Cain and Suess 1976; Stuiver and Quay 1981).

Translocation effects are less important in studies of ancient wood where decadal- or centennial-scale $\Delta^{14}C$ changes were a few tens of per mil at most. In those contexts, cellulose extraction can be viewed as one of several strong ^{14}C pretreatment methods for removal of exogenous contamination from pollen and organic sediment fines (Brown et al. 1989; Gillespie 1990), charcoal (Bird et al. 1999), and wood (Santos et al. 2001), developed as more rigorous alternatives to the conventional acid-base-acid (ABA) or de Vries protocol (Stuiver and Quay 1981). The other techniques typically employ a variety of initial acid and base treatments rather than Soxhlet extractions, but a common feature of all of these methods is a very strong acid/oxidation step. Gillespie (1990) used dilute Schutze reagent (10% $KClO_3$ in 35% HNO_3); the ABOX method (Bird et al. 1999; Santos et al. 2001; Pigati et al. 2007) employs acid-dichromate solution (0.1M $K_2Cr_2O_7$ in 2M H_2SO_4); and acid

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Proceedings of the 20th International Radiocarbon Conference, edited by A J T Jull
RADIOCARBON, Vol 52, Nr 2–3, 2010, p 1371–1379

chlorite or hypochlorite bleaching is used in cellulose extractions and in pollen preparation for ^{14}C dating (Brown et al. 1989).

As used in many labs today, ABA involves treatment at 60–90 °C with 1N HCl and 1N NaOH, with the base washes repeated until the solutions remain clear. ABA pretreatment of wood has historically resulted in varied results and is sometimes viewed as inadequate, but comparisons of ABA with other pretreatment methods have not always involved the full rigor of the ABA protocol. For example, in radiometric labs where large volumes of reagents are required, a single long-duration base treatment may be employed (A Hogg, personal communication), as opposed to repeated washes that at least in principle might be more effective. Additionally, in some comparisons between ABA and ABOX (Bird et al. 1999; Santos et al. 2001) the acid and base treatments (AB) were carried out at room temperature (G M Santos, personal communication), and the final acid step of ABA—potentially important for removing any CO_2 absorbed under alkaline conditions—was sometimes omitted. In one study (Hatté et al. 2001) that was subsequently cited elsewhere as showing the levels of contamination remaining after ABA, the ABA was in fact deliberately carried out in a way that would maximize the uptake of modern CO_2, in order to test subsequent decontamination procedures.

In this study, we compared several variations of the Jayme-Wise cellulose extraction method against ABA pretreatment to see whether rigorous ABA could produce ^{14}C backgrounds from wood samples comparable with those obtained from cellulose. In addition, we attempted to streamline the Jayme-Wise method and thus reduce processing times for wood samples for ^{14}C measurements, to eliminate the unnecessary exposure of samples to carbon-containing reagents, and to test cellulose extraction procedures that did not require specialized Soxhlet apparatus. This report reflects the current state of an ongoing study, and the methods described here may be subject to further development and do not necessarily represent "best" techniques.

METHODS

Samples tested were well-preserved wood samples beyond or close to the limit of ^{14}C dating. Three were New Zealand kauri: cellulose from two of these (Wk5383, Wk5385) had been previously dated to >50 kyr (Turney et al. 2007) and one (OIS7) was known from stratigraphy to be >140 kyr (Marra et al. 2006). The Wk5385 sample was chosen for this study because earlier work at the Waikato ^{14}C laboratory suggested that it could not be fully cleaned even when rigorous ABA treatment was used (A Hogg, F Petchey, personal communications). The other 2 samples were woods used as background materials in our laboratory: a "Patagonia" spruce sample of unknown stratigraphic provenance from northeast Iowa, USA (S Stine, personal communication) previously dated to >50 kyr (CAMS-50039), and a conifer (probably spruce) sample collected near the Queets River mouth, Olympic Peninsula, Washington, USA, from a stratigraphic unit corresponding to oxygen isotope stage 5a or 5c (G Thackray, personal communication).

The woods were sampled as fine shavings <0.5 mm thick, cut from wood blocks with an X-Acto® knife. We typically used samples of 20–40 mg of wood—much more than we would normally use for ABA treatment—because we anticipated significant losses in the cellulose extractions. The kauri samples strongly resembled newly cut wood and produced no dust when sliced, but the Queets-A and Patagonia woods, though well preserved, were noticeably more friable.

The ABA pretreatment was carried out in 13 × 100 mm test tubes covered with vented Fisher Kim-Kap closures, on a heat block at 70 °C. Ultra-fine tip plastic pipets (Samco #233) were used throughout to minimize pipetting losses. Samples were treated with aliquots of ~6 mL of 1N HCl for 30 min, followed by successive 30-min treatments with 1N NaOH until the liquid remained clear, ending with another 30-min 1N HCl wash. Samples were then washed several times in Milli-Q® water

(15 min, 70 °C) to pH >6 to remove remaining acid, dried for 30 min at 50 °C in a vacuum oven, and the tubes were capped with gas-tight closures (Fisher TainerTop). Processing times for batches of 10–25 samples were typically 5 to 6 hr.

Isolation of holocellulose was carried out in 13-mm test tubes at 70 °C in a fume hood. Early workers recommended that acid chlorite treatment be carried out at pH 2.4 or greater for maximum bleaching efficiency (Skelly 1960), which may be why weak (buffered) acids such as CH_3COOH have traditionally been used in Jayme-Wise extractions for stable isotope measurements. However, more recent studies (Kaczur and Cawlfield 2000; Svensson et al. 2006) indicate that there is little loss of efficiency even at very low pH. The acid decomposition of sodium chlorite in the presence of chloride ion was summarized by Gordon (1982) as:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$$

Using equal volumes of 1N HCl and 1M $NaClO_2$ solution simplifies the procedure and ensures that the reaction takes place under strongly acidic conditions (pH ~1) where contamination by atmospheric CO_2 is unlikely. We found that 2.5 mL of bleaching agent and 2.5 mL of acid was sufficient to bleach up to 40 mg of wood over 4–6 hr in most cases, though bleaching times varied. For a few of the larger samples, the ClO_2 was exhausted (indicated by the disappearance of the characteristic gold color of the solution) and a second short treatment was required to fully bleach some of the larger pieces. Some ClO_2 was initially evolved into the head space of the vented caps, but very little escaped.

After bleaching, the holocellulose was washed several times with Milli-Q water (30 min, 70 °C) to pH > 6. Samples that had separated into fine fibers required centrifuging for several minutes before pipetting to help separate cellulose from liquid and thus reduce losses. The samples were then dried at 50 °C for 30 min in a vacuum oven, and the tubes were capped with gas-tight closures. For alpha-cellulose extractions, the bleached holocellulose was washed once with Milli-Q, then treated with 6 mL of 5N NaOH for 1 hr at room temperature. This was followed by a 30-min treatment with 1N HCl at 70 °C to remove any absorbed atmospheric CO_2, then multiple Milli-Q washes and drying as above.

These procedures were compared with a more traditional batch processing cellulose extraction method (X Xu, personal communication), based on the work of Leavitt and Danzer (1993) and similar to techniques used previously for ^{14}C by Linick et al. (1986). Samples were processed in Ankom™ F57 Dacron filter bags (25 μm effective pore size). Each bag was subdivided into 2 heat-sealed pouches containing individual samples, and bags were identified by unique patterns of heat-sealing lines. Up to 25 bags were placed in a 50-mm-ID (200 mL) Soxhlet apparatus and extracted with 600 mL of 2:1 mixture of >99.5% toluene and HPLC-grade ethanol and then with 600 mL of HPLC ethanol, each for ~18 hr. Subsequent processing of the bags was carried out in a 2-L beaker covered with a watch glass, on a hot plate with a magnetic stirrer. Samples were boiled gently for 2 hr in Milli-Q water and then placed in a bleaching solution (4 g of sodium chlorite and 2 mL of glacial acetic acid added to 600 mL of water) at 70 °C. An additional 4 g of chlorite and 2 mL of acetic acid were added after 3–4 hr and the treatment was continued overnight, after which the samples were washed several times with 600 mL of Milli-Q water over 3–4 hr and dried at 50 °C for 2–3 hr in a vacuum oven. For alpha-cellulose extraction, washed holocellulose samples were treated in 600 mL of 17% (weight/volume) NaOH for 1 hr at room temperature, treated at 70 °C with 1N HCl and then washed repeatedly with water and dried as above.

Further variations of the holocellulose isolation step were made by modifying both the bleaching agent and the activating acid. A 5% sodium hypochlorite solution (Chlorox), which is the traditional source of Cl_2 for chlorine-based bleaching (Long and Kalin 1992), was tested briefly as an alternative to sodium chlorite in the test tube-based protocol, though chlorite is now strongly preferred for extracting cellulose because the ClO_2 produced attacks lignin only and the reaction does not generate harmful free Cl_2. The standard batch processing Jayme-Wise method (Leavitt and Danzer 1993) uses glacial acetic acid to activate the chlorite, but mineral acids such as H_3PO_4 and HCl have been used in some ^{14}C studies (Pearson and Stuiver 1986; Long and Kalin 1992; A Hogg, personal communication), reducing the exposure of samples to carbon-containing reagents. We tested the use of H_3PO_4 and HCl as alternatives to acetic acid and ultimately chose HCl for the test tube-based method described above.

We also checked whether baking ABA-treated samples immediately prior to combustion was effective for reducing backgrounds. Samples in unsealed quartz combustion tubes prefilled with CuO and Ag, were baked in air for 1 hr or 3 hr in a muffle furnace at 160 °C or 300 °C, prior to sealing in vacuum and combustion at 900 °C. The 300 °C bake caused actual charring of the wood, and was intended to approximate the low-temperature stage of the stepped-combustion protocol of Bird et al. (1999), who found that a 330 °C combustion with a limited quantity of oxygen gas was very effective at removing contaminants remaining after ABOX.

RESULTS

A surprising result of our initial cellulose extraction tests was to reveal that a small but significant source of contamination existed: results for holo- or alpha-cellulose samples showed substantial scatter and some were elevated (by 0.1–0.5 pMC) compared to ABA-only results on the same wood. The source of the contamination was ultimately shown to be the $NaClO_2$ when a new batch was purchased, but the contamination mechanism remains unclear.

Within the obvious limitations imposed by this problem, we found no differences in ^{14}C results for OIS7 kauri, Patagonia spruce, Queets-A, and Wk5383 kauri for several variations of the cellulose extraction procedures (Table 1). Samples treated with the full Jayme-Wise alpha-cellulose protocol described above, including 2 days of Soxhlet extractions, returned results similar to those where ABA-treated wood was transferred to the Ankom bags for subsequent holo- or alpha-cellulose extractions, or samples where all processing was carried out in test tubes. In addition, we saw no significant differences between results for cellulose extractions where acetic acid, H_3PO_4, and HCl were used as chlorite activators. We also tested using a stronger acid for the final neutralization step after NaOH treatment for alpha-cellulose: 2M H_2SO_4, 2 hr at 70 °C, used by Hatté et al. (2001) to enhance the effectiveness of the final step of ABA; but saw no improvement.

Table 1 Initial ^{14}C results for OIS7 kauri, Patagonia spruce, Queets-A, and WK5383.

	Cellulose extraction[a]			^{14}C results	
Pretreatment	Activating acid/ processed in:	Cellulose fraction	Neutralizing acid for alpha-cellulose	pMC	±
ABA		None		0.20	0.13
Soxhlet	HAc/bags	Alpha	HCl	0.23	0.07
ABA	HAc/bags	Alpha	HCl	0.37	0.13
ABA	H_3PO_4/bags	Alpha	HCl	0.34	0.04
ABA	HCl/bags	Holo		0.35	0.05
ABA	HCl/tubes	Holo		0.28	0.11
ABA	HCl/tubes	Alpha	HCl	0.27	0.10
ABA	HCl/tubes	Alpha	H_2SO_4	0.31	0.12

[a] HAc: acetic acid. Note: all cellulose samples were extracted with the first (contaminated) batch of chlorite.

In spite of the presence of low-level contamination from the chlorite, these results suggested strongly that ABA treatment followed by cellulose extraction in the 13-mm test tubes was as effective as the full Jayme-Wise treatment, while taking far less time overall. Subsequent tests were therefore aimed at optimizing the test tube method described above. ABA-treated samples destined for cellulose extraction were treated with HCl and chlorite solution immediately after the last acid wash of ABA, and left overnight at room temperature. This reduced the subsequent 70 °C bleaching time to 2–3 hr and the overall processing time for holo- or alpha-cellulose production to 24–30 hr: typically from the late morning of one day to the afternoon of the next. An obvious next step would be to leave the samples at higher temperature overnight, but we have not yet tested this for fear of sample losses. (Note: we have since determined that yields for samples left bleaching overnight at 70 °C are indistinguishable from those for samples treated as above).

We tested weaker HCl and chlorite mixtures (2.5 mL of 0.25N HCl with 2.5 mL of 0.25M $NaClO_2$) but found that bleaching times increased and that 30–40 mg wood samples often required a second application of bleaching solutions. Bleaching with HCl-activated Chlorox (Long and Kalin 1992) required numerous applications of bleaching solutions following an overnight soak at room temperature, was obviously more destructive to some samples than chlorite, produced free chlorine, and left samples still only partially bleached after a full working day.

Backgrounds for holo- and alpha-cellulose extractions using the optimized test tube procedure with the new chlorite were gratifyingly lower; data from these experiments and from samples treated with ABA are shown in Figure 1. (In comparing our results with data from other studies, it is important to note that all data shown here are raw ^{14}C results: no processing line blanks or AMS "machine" backgrounds have been subtracted.) For OIS7 kauri, Patagonia spruce, Queets-A, and Wk5383 kauri, the results show little difference between pretreatment methods. Wk5383 consistently displayed slightly higher pMC values than the samples known from stratigraphy to be beyond the limit of ^{14}C dating, and may indeed be younger. Wk5385 kauri was previously measured at Waikato and found to be difficult to clean by ABA, even when treated with multiple base washes. In our tests, we found that by isolating holocellulose the background for this sample was significantly improved, though further processing to alpha-cellulose had little effect.

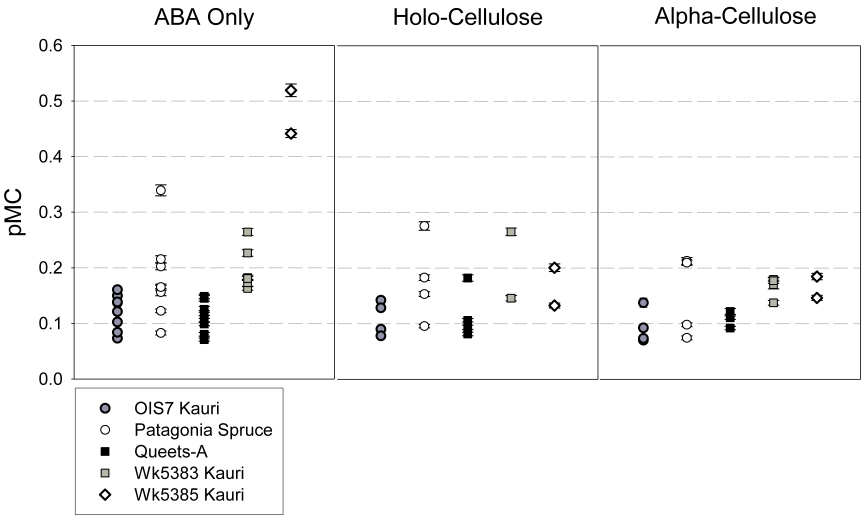

Figure 1 ^{14}C results (pMC) for wood samples treated with the standard ABA protocol, and ABA plus holo- and alpha-cellulose extractions. Note that all data are shown as raw values: no backgrounds have been subtracted.

Yields from ABA were uniformly high, but large decreases in sample mass were observed with increased processing to holo- and alpha-cellulose, particularly for the less well-preserved Queets-A and Patagonia samples. Table 2 shows average yields from test tube processing. In some cases, 30 mg or more of wood was required to produce 3 mg of alpha-cellulose, which in turn would yield about 1 mg of graphite for AMS. Furthermore, cellulose yields for a given type of wood showed significant scatter about these mean values, suggesting that wood preservation can vary significantly even within a single wood block.

Table 2 Average percent yield for samples by pretreatment method.

	ABA	Holocellulose	Alpha-cellulose
OIS7 kauri	79	35	30
Patagonia	73	16	11
Queets-A	71	15	10
WK5383	77	36	27
WK5385	76	44	33

Samples of holocellulose (and alpha-cellulose to an even greater extent) were very fluffy compared to ABA-treated wood, and sample handling problems due to static were correspondingly severe. The cellulose was particularly difficult to load into 6-mm quartz tubes for combustion, and in many cases cellulose fibers were left on the tube walls in the area where the tubes are sealed. This can lead to sealing problems as the adhering cellulose pyrolyzes in vacuum and effectively increases the melting point of the quartz. An effective solution to this problem is to burn off the stray fibers from the portion of the tubes where sealing takes place, by heating this area in air with a gas torch before attaching the tubes to the combustion vacuum line (X Xu, personal communication).

Samples that were baked just prior to combustion showed slight improvement in backgrounds in some cases (Figure 2), but the differences were small and may simply reflect random scatter. Baking for 3 hr versus 1 hr at each temperature produced no obvious increases in the ^{14}C ages. Carbon losses due to charring in the 300 °C bake (calculated from the CO_2 yields per initial mass of ABA-treated wood for charred and uncharred samples) were significant, and increased from ~30% for a 1-hr bake to ~40% after 3 hr. In marked contrast to the effect of the post-ABOX low-temperature oxygen combustion of Bird et al. (1999), charring in air had little effect on ^{14}C ages from these ABA-treated samples.

DISCUSSION

One possible candidate for the puzzling contamination of the first batch of $NaClO_2$ is absorption of atmospheric CO_2, since the jar of chlorite had been in general use in another laboratory for several months and could conceivably have been left open for extended periods. Prior to our experiments, it was used only for extractions on modern and post-bomb samples, and so the contamination was not detected. However, it is difficult to understand how any absorbed CO_2 could have been transferred to the cellulose, since the bleaching protocols involved activation under acidic conditions (strongly acidic in some cases) in part to minimize this possibility.

Hatté et al. (2001) pointed out that replacement of hydroxyl groups in wood structures by Cl^- (which does occur to some extent during chlorite delignification at low pH, e.g. Svensson et al. 2006) might lead to subsequent carboxylation via a further replacement of Cl^- by carbonate ions, but again, this second step requires alkaline conditions that were not present in our experiments. Furthermore, Hatté et al. also found that any bound CO_2 was effectively removed by subsequent treatment with 2M H_2SO_4, which did not remove the contamination we encountered.

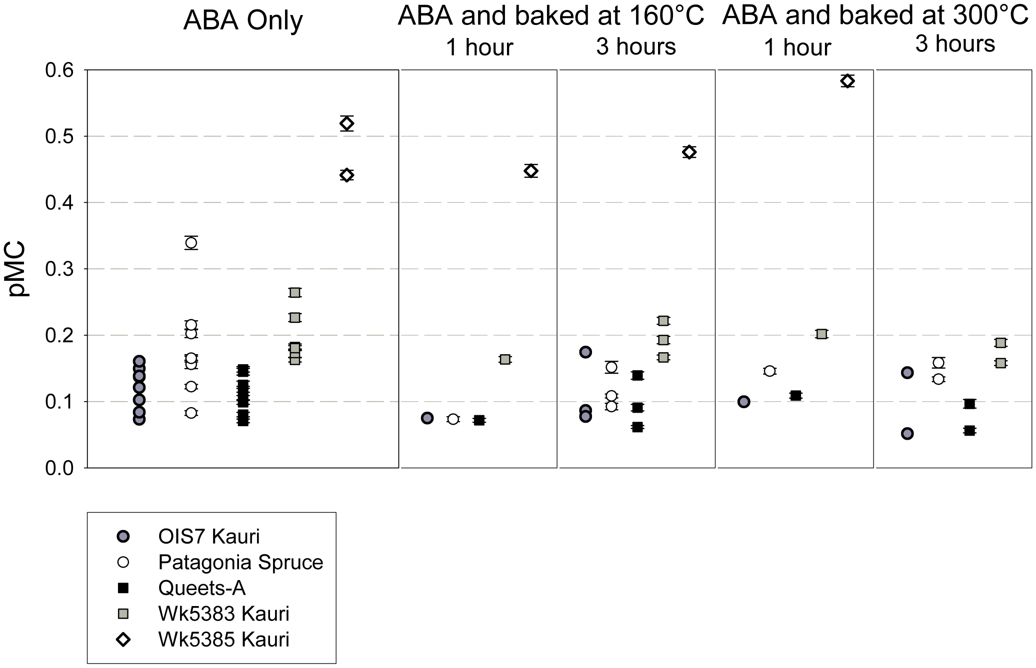

Figure 2 ^{14}C results (pMC) for ABA-treated wood samples baked in air in quartz combustion tubes just prior to sealing. (The Wk5385 sample baked for 3 hr at 400 °C was lost during graphitization.)

Our tests of cellulose extraction methods indicate that pretreatment of samples in individual 13-mm test tubes by ABA plus bleaching is effective, and appears to have several advantages over Soxhlet/bleach batch processing in the Ankom filter bags. No specialized Soxhlet equipment is required, the process takes significantly less time, any possibility of cross-contamination is removed, and labeling of samples is easier. Furthermore, the Dacron bag material consists of white matted fibers that are sometimes difficult to distinguish from adhering cellulose, which can complicate the removal of samples when the bags are cut apart after processing.

However, while the test tube method seems superior for the well-preserved woods used here, we recognize that this may not be true for more degraded samples. Processing in tubes requires many pipetting steps, and these may also require centrifugation if the samples begin to disintegrate, so that for samples with marginal preservation, batch processing in filter bags may actually be less labor intensive, and therefore preferable. If the conventional Jayme-Wise method is used for such cases, it would seem prudent to adapt it for the special requirements of ^{14}C, though the excellent cellulose ^{14}C results obtained in previous studies suggests that few serious problems exist. Nevertheless, since concerns have been raised about possible contamination by solvent residues (Long and Kalin 1992), using only ^{14}C-dead solvents rather than modern ethanol in any Soxhlet processing of old samples seems desirable (Hogg et al. 2006), though we did not test this. Our results show no disadvantages to using mineral acids for bleaching, thus avoiding unnecessary exposure of samples to organic acids.

For 4 of the 5 woods tested (OIS7 kauri, Patagonia spruce, Queets-A, and Wk5383 kauri), ^{14}C values for wood pretreated with ABA were not significantly different from ^{14}C values for holo- or alpha-cellulose extractions. However, our results for the Wk5385 kauri sample (Figure 3) clearly confirm the earlier findings of the Waikato ^{14}C laboratory. This wood contains younger contaminating material that could not be completely removed by ABA, even with multiple base treatments at high temperature, and was unaffected by subsequent 160 °C baking or 300 °C charring in air. The contamination was effectively removed by holocellulose extraction, and further processing to alpha-cellulose did not produce significantly older ages.

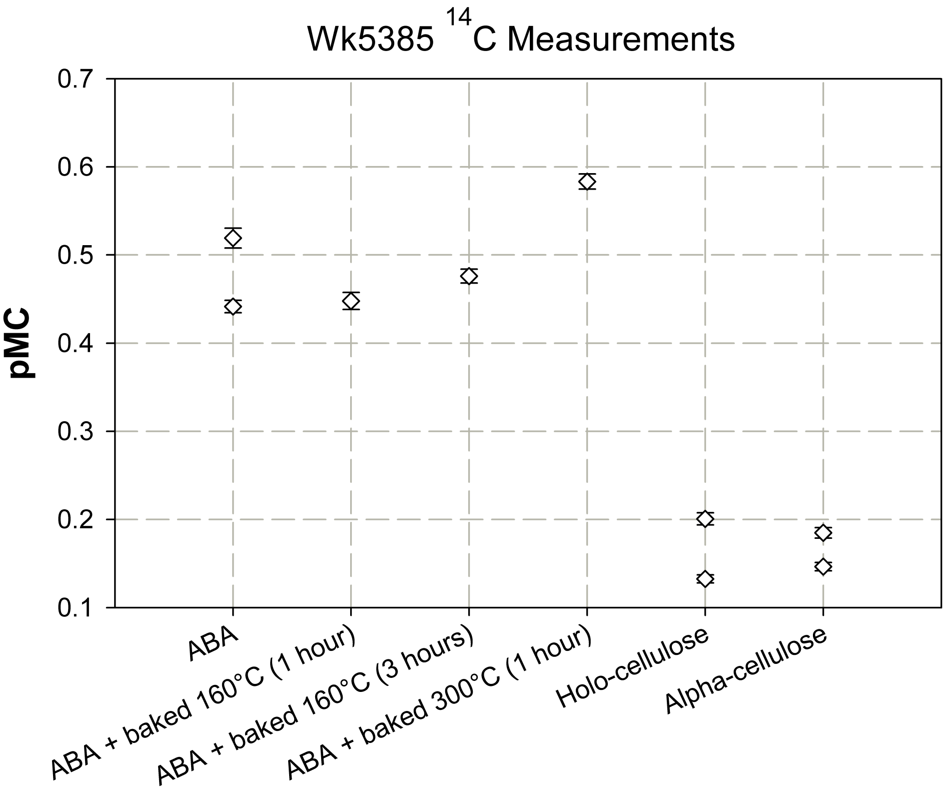

Figure 3 ^{14}C measurements on Wk5385 showed that cellulose extraction was required for removal of young contamination from this sample: ABA with or without subsequent baking was ineffective.

These tests have therefore confirmed that a subset of old wood does exist for which even rigorous ABA treatment is ineffective and more elaborate/harsh treatments are required. Given that those methods involve significant extra work and result in lower processing yields than ABA, a useful strategy for projects involving large numbers of measurements on single logs (e.g. calibration studies) would be to carry out spot-checks on inner and outer rings of ABA versus holocellulose or other pretreatment of choice. If ABA proved effective, as it did for 4 of the 5 woods tested here, it could then be used with confidence for the large-scale study.

ACKNOWLEDGMENTS

We thank Xiaomei Xu for laboratory assistance, and Glenn Thackray, Scott Stine, Alan Hogg, and Fiona Petchey for information on wood samples, pretreatment methods used in the Waikato radiocarbon lab, and previous ^{14}C results.

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