RADIOCARBON DATING OF HISTORICAL PARCHMENTS

Fiona Brock

Research Laboratory for Archaeology and the History of Art, University of Oxford, Dyson Perrins Building, South Parks Road, Oxford OX1 3QY, United Kingdom. Email: fiona.brock@rlaha.ox.ac.uk.

ABSTRACT. A range of pretreatment methods was applied to 6 known-age historical parchments to investigate the most suitable methods for effectively removing contamination and ensuring accurate radiocarbon dates while minimizing unnecessary destruction of potentially valuable historical documents. The methods tested included an acid wash, different concentrations of acid-base-acid (ABA) pretreatments, the current routine ABA method applied at the Oxford Radiocarbon Accelerator Unit (ORAU) that includes an additional bleach treatment, and extraction of collagen. The C:N atomic weight ratio of the untreated and pretreated parchment fractions was observed to be a useful indicator of the presence or successful removal of contaminants. The pretreatment methods that produced the most accurate ^{14}C dates and acceptable C:N ratios were found to be ABA protocols (without bleach) and collagen extraction; solvent washes and acid pretreatments alone were not sufficient to remove all contaminants and produce reliable ^{14}C dates. The inclusion of a base wash did not affect the ^{14}C dates of the samples, but did favorably influence the C:N ratio of the final product.

INTRODUCTION

Parchment is a collagen-based writing medium made from processed, but untanned, skins of cattle, sheep, and goats. Parchment superseded papyrus as the writing medium of choice in the 2nd century AD (Edwards et al. 2001), and from roughly the 5th to 15th centuries AD almost all documents were written on parchment (Berger et al. 1972), including most of the written history of Europe (Ghioni et al. 2005). Parchments provide a wealth of information for archaeologists and historians, both from the information recorded (including historical records, legal documents and property deeds, and music manuscripts and artwork) and also relating to the processes involved in the manufacture of the parchment itself.

Methods of parchment manufacture are often not recorded and have evolved over time (see Kennedy and Wess 2003 for a review). Once a hide had been removed from the animal, it may have been dried or cured to reduce the moisture content, thus avoiding putrefaction during transport or before processing. Curing may have involved air-drying, or wet or dry salting. When ready for processing, the hide may have been washed (traditionally with fresh- or seawater, but historical records detail a range of substances used including excrement; Kennedy and Wess 2003) before being soaked in a solution containing lime ($Ca(OH)_2$) to remove hairs and other non-collagenous materials. Lime that was not subsequently washed out of the parchment reacted with carbon dioxide in the air to form calcium carbonate, several polymorphs of which have been detected within historical specimens (Edwards et al. 2001; Kennedy et al. 2004a). Liquors containing vegetable infusions were also used to remove hairs in ancient times (Reed 1972). After liming, hair and fat were removed by scraping with blades, before the parchment was "finished" with a variety of processes including mechanical thinning, bleaching, dyeing, surface cleaning, and polishing. Various substances are recorded as having been applied to the surface of parchments to remove fats, and improve appearance and the adhesion of ink, including lime, chalk, and ash (Strlič et al. 2009) and egg yolk and flour (Edwards et al. 2001). Poorer quality parchments were sometimes treated with chemical preparations such as sodium sulfite suspended in natural oils (Edwards et al. 2001) and fish glue was also used to "size" parchments (Thompson 1956).

Parchment is a complex, inhomogeneous material, and its chemistry and state of preservation can be affected by a range of external factors such as environmental pollution, harsh cleaning, improper conservation, and restoration (Badea et al. 2008). Collagen degrades over time via oxidation,

hydrolysis, and biological attack, especially in hot, humid conditions (Kennedy and Wess 2003). As the collagen degrades, parchment loses strength, becomes brittle and deteriorates. Gelatinization can also occur (sometimes observed as translucency within a parchment) whereby the collagen triple helix unravels to form random coils of gelatin (Weiner et al. 1980). As parchment ages, it can also collect surface deposits that darken the material (Kennedy et al. 2004b).

While some parchments are inscribed with a date, many are not, and these are often dated using paleographical and codicological techniques. Such methods can often only provide broad age ranges, maybe to within a century (Santos et al. 2010). Radiocarbon dating is often not used to date parchments for a variety of reasons, in particular: the requirement for destructive analysis of valuable samples; uncertainty over the most effective pretreatment techniques, especially for poorly preserved pieces, in order to ensure that dating can be completed with accuracy and precision; and (often unfounded) concerns about the accuracy and potential precision of ^{14}C dates for such materials. But ^{14}C dating is a potentially powerful technique for dating parchments—especially as they were usually written on within a relatively short time period after manufacture (assuming the absence of palimpsests)—complimenting traditional, non-destructive techniques, for samples dating from periods for which the calibration curve is favorable. Manuscripts from the 13th to 15th centuries, for example, can often be dated with excellent precision, while those from AD 1650–1950 may not benefit from ^{14}C dating.

Although samples of the Dead Sea Scrolls were used by Libby to test the accuracy of ^{14}C dating during the initial development of the technique, and Berger et al. (1972) subsequently investigated the feasibility and accuracy of the method by dating English historical legal documents, ^{14}C was rarely used for dating parchments until the advent of AMS dating, which required much less material than earlier conventional methods. Subsequently, ^{14}C dates for more of the Dead Sea Scrolls (Bonani et al. 1992; Jull et al. 1995; Rasmussen et al. 2001, 2009), the Vinland Map (Donahue et al. 2002), and several Spanish historical manuscripts (Santos et al. 2010) have been published, with the dates generally being in good agreement with paleographical estimates or known ages.

Careful sampling and pretreatment protocols must be followed to ensure accurate ^{14}C dates for parchments. When sampling, attention needs to be paid to areas of localized degradation (especially around the edges of a manuscript, from where samples are generally available for destructive analysis) and the state of preservation of the parchment. Pretreatment procedures need to be tailored to suit individual parchments sufficiently to remove contaminants that may be of a different age from the parchment and may therefore result in erroneous dates if not completely removed, and to produce an accurate date without causing unnecessary destruction. Such contaminants include those added to the parchment during processing (e.g. carbonates formed following liming, egg, flour, and fish glue, although many of these may be of the same age as the parchment), and conservation materials applied subsequently. The effective removal of castor oil applied to the Dead Sea Scrolls prior to dating, for example, has been the subject of much discussion (Rasmussen et al. 2001, 2003, 2009; Carmi 2002).

Lipids from a variety of sources may also be present within parchments, ranging from those from the original skin that were not removed during processing or that have originated from microbial decay, to those added during processing, conservation, or simply from handling over time (especially at the corners and edges) (Ghioni et al. 2005; Strlič et al. 2009). Such lipids all have potentially different ages and it is hard to distinguish between sources, so it is advisable for pretreatment procedures to include a solvent wash to remove them. However, ultrasonication in solvents may be too harsh for more fragile samples, and simple washing or Soxhlet extractions may be more suitable (Rasmussen et al. 2009).

Published pretreatment methods initially involved only washing with cold dilute acid (Berger et al. 1972), but have subsequently generally involved an acid-base-acid (ABA) sequential wash, varying in concentration from very mild (e.g. 0.05M HCl and 0.01M NaOH; Bonani et al. 1992) to much stronger (e.g. 0.5M HCl, 0.1M NaOH; Santos et al. 2010). The strength of solutions, temperatures, and times involved are often varied during pretreatment according to the ability of individual samples to withstand treatment. Samples that have deteriorated over time may be brittle and very delicate during pretreatment and fragile, poorly preserved specimens (especially those that are gelatinized or partly gelatinized; Bonani et al. 1992; Jull et al. 1995) and those from hot, humid environments (e.g. the Dead Sea Scrolls) are particularly susceptible to dissolution in base washes. Santos et al. (2010) suggest (based upon evidence from a single sample) that the base wash can be reduced to a minimum to avoid sample loss.

Hedges et al. (1989) grouped parchment together with leather and bog bodies as collagen-based materials that had undergone additional chemical processing during manufacture or burial, and proposed a collagen-based protocol for their pretreatment. (Although no specific details are given, the authors suggest that following an initial treatment to break down cross-linking of protein with organic acids and aldehydes derived from tanning agents, gelatin can subsequently be extracted and treated as for bone.) The only published record of a "collagen" extraction from parchment for dating is that of Donahue et al. (2002), who observed that extraction by washing in 0.25N HCl and then dissolving in hot 0.01N HCl gave the same date (and $\delta^{13}C$ value) for the Vinland Map as an ABA-based pretreatment with a weak base step.

The routine pretreatment method for parchment samples at the Oxford Radiocarbon Accelerator Unit (ORAU) currently employs an ABA sequence followed by a sodium chlorite bleach wash (Brock et al. 2010). Although the original reason for inclusion of the bleach step is not recorded, it is likely that, by grouping parchment with leather and bog-bodies (as mentioned above), the bleach was required to break down cross-links of protein within the sample with organic acids and other organic substances, thus enabling the removal of contaminants such as humic acids and those added during the tanning process. However, this step may not be necessary for parchment, which has not been tanned during its manufacture, and for the majority of European samples that have not been buried, and may risk unnecessary destruction of sample.

This paper presents results from a study investigating the most suitable methods for pretreating parchments, ensuring minimum starting weights (to reduce the need for destructive analysis) and good yields, while still providing accurate ^{14}C dates. A range of pretreatment methods and conditions was applied to 6 known-age historical parchments in various states of preservation. Particular attention was paid to the necessity for a base wash (especially for parchments known to have been stored in collections, museums, and archives for the duration of their existence) and a final bleach step (as currently applied at ORAU), and investigating whether collagen extraction is a viable alternative to ABA procedures.

SAMPLES

Six known-age British historical parchments, thought to date from the 14th to 19th centuries and in various states of preservation, were used in this study. Ideally, due to the nature of the calibration curve, this study would have included more earlier (i.e. pre-16th century) samples, but despite extensive enquiries no further known-age samples were available in the quantities required for experimental analysis.

Sample P1 consisted of 3 small pieces of parchment thought to date from the 14th century. The fragments were gray/black in color and mottled in appearance on one side, but were fairly sturdy.

Sample P2 was known to date from AD 1769. The parchment was cream/light brown in color with a slight mottled appearance, and was fairly well preserved. Ink was present, and could not be avoided for some sampling. Sample P3, inscribed with AD 1832, was cream colored with some ink present and was generally in very good condition. Samples P2 and P3 had originally been donated to researchers at Cardiff University ~AD 2000 by the National Archives of Scotland for use in studies into the structure of historical parchments. The results of these studies are published by Kennedy et al. (2004a,b) and Ghioni et al. (2005), in which the samples are referred to as USH02 and USH06, respectively.

Samples P4 and P5 were a page and cover, respectively, of the Morrison of Cadeby cartulary, from Lincolnshire. The volume comprised a collection of loose folia, including deeds to properties owned by the family, and is thought to date from the late 16th century. The page (P4) was in very poor condition, thin and crumbly, possibly moldy, and mostly stained black and purple. Some ink may have been present. In contrast, the cover (P5) was stained gray but was sturdy and in much better condition.

Sample P6, from AD 1649, was quite clean and cream colored, although very light and fragile.

METHODS

Each sample was subjected to up to 5 different pretreatment protocols depending on the amount of material available and the fragility of the samples, as well as being dated without any prior treatment. The methods applied were designed to reflect those published in the literature (e.g. Bonani et al. 1992; Donahue et al. 2002; Rasmussen et al. 2009; Santos et al. 2010) as well as current methods applied at ORAU (Brock et al. 2010). Starting weights were deliberately kept small to demonstrate their effectiveness, with 3–10 mg used for most methods (although up to 90 mg was used for collagen extraction procedures). Due to the limited amount of material available for each parchment sample, it was not possible to repeat specific pretreatment protocols to obtain replicate measurements for individual samples.

Except for those samples dated with no pretreatment, all samples were initially subjected to a sequential solvent wash to remove lipids and potential conservation treatments designed taking into consideration several published methods (Donahue et al. 2002; Ghioni et al. 2005; Rasmussen et al. 2009; Strlič et al. 2009; Santos et al. 2010) as follows: hexane (45 °C, 1 hr); acetone (45 °C, minimum of 1 hr); $2 \times$ 1:1 methanol:chloroform (room temperature, 1 hr each). Samples were then left to air-dry overnight or longer to ensure complete removal of the solvents before subsequent treatments were applied.

The pretreatment methods applied were as follows:

- **Acid only**: HCl (0.5M, 30 min). Samples were checked to ensure they were still intact after 20 min before leaving for a further 10 min in the acid.
- **"Mild" ABA**: HCl (0.5M, 30 min); NaOH (0.1M, 20 min); HCl (0.5M, 1 hr).
- **"Strong" ABA**: HCl (0.5M, 30 min); NaOH (0.2M, 20 min); HCl (0.5M, 1 hr).
- **ABA + bleach**: HCl (0.5M, 30 min); NaOH (0.1M for P4, P6; 0.2M for P2, P3, P5, 20 min); HCl (0.5M, 1 hr); sodium chlorite $NaClO_2$ (2.5% w/v for P3, P4, P6; 5.0% w/v for P2, P5; at pH 3 and 75 °C for up to 25 min depending on the fragility of the sample) (Method ACJ in Brock et al. 2010).

- **"Collagen" extraction** (based on method AG for bone pretreatment without ultrafiltration applied at ORAU; Brock et al. 2010): HCl (0.5M, 3 rinses over ~18 hr); NaOH (0.1M, 30 min); HCl (0.5M, 15 min); gelatinized in pH 3 solution at 75 °C for 20 hr and resultant solutions filtered using a 45–90 μm Ezee-filter™ (Elkay, UK).

All treatments were carried out at room temperature unless otherwise stated, with thorough rinsing with ultrapure Milli-Q™ water between each stage. Washes were removed from samples by decanting, except for sample P4 during the ABA procedures, when the sample was Ezee-filtered to reduce sample loss. Following pretreatment, samples were freeze-dried and weighed, before being combusted, graphitized, and AMS dated following routine ORAU procedures as described by Brock et al. (2010).

RESULTS AND DISCUSSION

All samples survived all pretreatment protocols applied to them, although P6 appeared slightly fragile after the initial acid washes, and P4 released a purple color upon washing with base solution. Sample yields, C:N atomic weight ratios, $\delta^{13}C$ values, and ^{14}C dates are presented in Table 1. Due to the limited amount of material available for each parchment, each result given is a single measurement. For all samples, the highest yield was generally achieved with the milder ABA treatment, or with the acid-only treatment. It should be noted that the high yields recorded for P2 and P3 following "mild" and "strong" ABA pretreatments are thought to be caused by instabilities with the balance used on 1 specific day, rather than addition of material to the samples during pretreatment. Ink on P2 and P3 was not removed during the solvent washes, but was by acid treatment.

As parchment is thought to contain ~90–95% collagen (Kennedy and Wess 2003; Badea et al. 2008), it can be assumed that the C:N atomic weight ratio of the pretreated samples is a good indicator of quality and contamination removal according to the acceptable range of ~2.9–3.5 proposed for bones by Ambrose (1990). van Klinken (1999) observed the average C:N ratio for collagen measured at ORAU to be ~3.3. Untreated samples often had high C:N ratios, indicating the necessity for pretreatment prior to dating (e.g. 4.4 for P6 and 4.6 for P4; Table 1). The "best" C:N ratios (~3.2–3.3 according to ORAU's average value; van Klinken 1999) were observed for the samples that had undergone either of the "mild" or "strong" ABA treatments (without bleach) or collagen extraction, and also for the acid-only protocol for P2 and P3.

In general, the results indicate that parchments require a certain level of pretreatment prior to dating, as evidenced by high C:N ratios and inconsistent dates for untreated samples. Although none of the samples were lost in the base wash, this step did affect the C:N ratio of some samples (most notably P4 and P5) without influencing the dates of any of the samples. Samples given an additional bleach wash after the ABA pretreatment produced lower yields and, for reasons unclear, these fractions often had higher C:N ratios (sometimes above the acceptable range of 2.9–3.5; Table 1) than those produced following ABA methods. Although collagen extraction unsurprisingly resulted in the lowest yields of any of the pretreatment methods applied, the products gave consistently good C:N ratios, and the ^{14}C dates were in good agreement with expected ages and those achieved with ABA pretreatments.

The results for P1 are difficult to interpret, due to uncertainties over the expected age of the sample. When the samples were initially sourced for this study, they were thought to date from the 14th century, although this was later revised to the 17th century. However, dates measured following both ABA methods calibrate to give age ranges predominantly from the 15th century or earlier (Figure 1). The C:N ratios of both pretreated fractions remained high (3.5 and 3.7), although the

Table 1 ^{14}C ages, pretreatment yields, and associated data for different untreated and pretreated parchment samples. Note that δ^{13}C values in italics indicate samples containing less than half the %C of the associated standards, and which therefore may not be entirely accurate.

Sample	Method	% yield	%C	C:N	δ^{13}C (‰)	^{14}C age (BP)	Lab code OxA-
P1	Mild ABA	81.9	45.2	3.5	−22.5	436 ± 26	X-2457-41
	Strong ABA	91.3	45.9	3.7	−22.3	416 ± 27	X-2457-42
P2	Untreated	100	42.4	3.7	−23.0	Not dated	
	Acid only	90.8	42.6	3.3	−22.5	Not dated	
	Mild ABA	105.1	43.3	3.3	−22.3	Not dated	
	Strong ABA	101.9	42.9	3.3	−22.4	Not dated	
	ABA + bleach	84.3	43.1	3.4	−22.0	166 ± 23	25919
	Collagen	71.3	44.0	3.3	−22.3	169 ± 23	26010
P3	Untreated	100	?	3.4	−21.1	Not dated	
	Acid only	82.2	42.2	3.2	−22.1	Not dated	
	Mild ABA	105.5	42.0	3.2	−22.2	Not dated	
	Strong ABA	84.2	42.5	3.2	−22.1	Not dated	
	ABA + bleach	85.9	41.4	3.2	−21.6	177 ± 23	25921
	Collagen	64.6	44.2	3.3	−22.6	140 ± 23	25920
P4	Untreated	100	36.0	4.6	*−22.2*	459 ± 25	X-2479-15
	Solvent only	52.6	37.7	3.8	−21.2	395 ± 29	X-2464-40
	Acid only	57.7	43.7	3.7	−21.7	315 ± 23	X-2453-42
	Mild ABA	96.2	43.0	3.4	−21.7	314 ± 24	X-2453-43
	Strong ABA	79.3	44.7	3.5	−22.4	348 ± 26	X-2457-43
	ABA + bleach	59.6	46.0	3.6	−22.7	334 ± 25	25798
P5	Untreated	100	38.6	3.7	−23.1	320 ± 26	X-2478-41
	Acid only	100.6	42.8	3.6	−22.8	361 ± 23	X-2459-54
	Mild ABA	81.7	42.4	3.4	−22.6	309 ± 23	X-2459-55
	Strong ABA	83.8	41.1	3.3	−22.6	364 ± 25	X-2459-57
	ABA + bleach	52.4	44.5	3.5	−23.2	345 ± 25	25734
	Collagen	46.7	44.5	3.3	−22.6	338 ± 23	25733
P6	Untreated	100	42.2	4.4	*−23.6*	324 ± 25	X-2479-16
	Acid only	80.9	43.9	3.4	−22.8	256 ± 28	X-2464-41
	Mild ABA	87.4	43.6	3.3	−22.6	219 ± 28	X-2464-42
	Strong ABA	69.3	41.6	3.3	−22.7	215 ± 29	X-2464-43
	ABA + bleach	75.6	43.8	3.6	−23.7	306 ± 26	25799

value for the untreated sample is not known, suggesting that some contamination may still be present, which may in turn be influencing the ^{14}C ages. No additional material was available for further analysis.

Samples P2 and P3 were impossible to date precisely due to their positions on the calibration curve and so although all the different pretreatments were applied to both samples, only the routine ORAU ABA + bleach treatment and collagen extraction fractions were dated (Figure 2). Three of these fractions gave calibrated age ranges as expected, but the ABA + bleach treatment does not appear to produce an accurate calibrated ^{14}C date for sample P3 (Figure 2). All pretreatments gave good yields, even collagen extraction (71% and 65%, respectively; Table 1). C:N ratios of 3.7 and 3.4 for the untreated material were reduced to 3.2 or 3.3 by all methods except ABA + bleach for P2 (3.4), indicating that even for such clean-looking, well-preserved samples, some pretreatment is necessary.
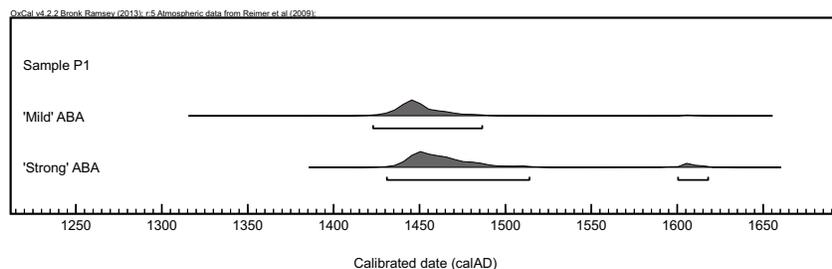
Figure 1 OxCal v 4.2.2 (Bronk Ramsey 2009) plot of calibrated ^{14}C dates for sample P1 following "mild" and "strong" ABA treatments. Horizontal bars show the 95.4% highest probability density ranges.
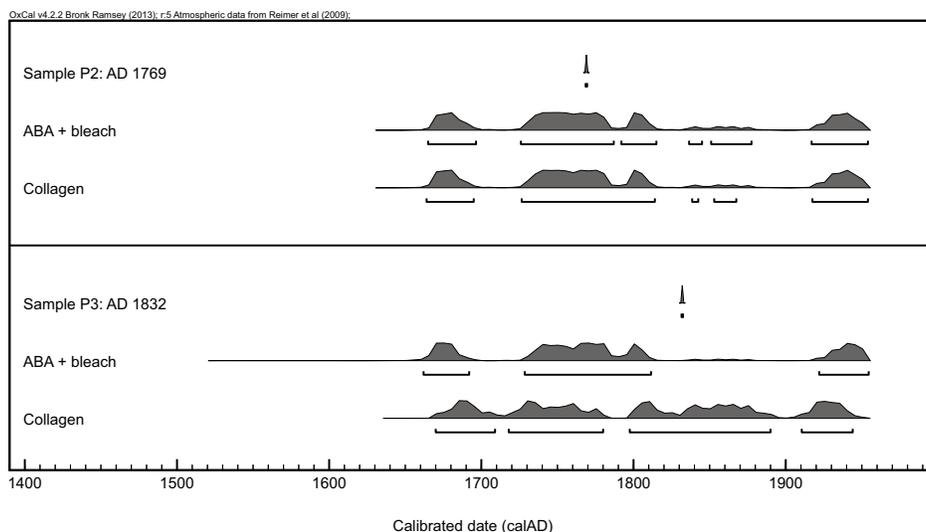

Figure 2 OxCal plots of calibrated ^{14}C dates for fractions of samples P2 and P3 following ABA + bleach pretreatment or collagen extraction. Horizontal bars show the 95.4% highest probability density ranges.

Untreated material from P4 had a high C:N ratio of 4.6 and produced an older date than all other fractions (Figure 3). However, the contamination was not wholly removed from this sample by solvent washing alone according to the C:N ratio, and only the ABA pretreatments gave acceptable C:N ratios (3.4 and 3.5; Table 1). All dates measured for sample P5 (including the untreated sample) are acceptable given that it is thought to come from the 16th century (Figure 3), and acceptable C:N ratios are observed for all treated samples except that which underwent the acid-only treatment. Unfortunately, given the nature of the calibration curve during the 16th century, it is impossible to give a more precise date for the cartulary (or to determine if the cover is older than the page as expected), and conclusions relating to the relative accuracies achievable with the different pre-treatment methods are limited for these 2 samples.

All the pretreated fractions of P6 produced acceptable date ranges when calibrated, compared with the untreated fraction, which was slightly too old and had an elevated C:N ratio of 4.4 (Figure 4; Table 1). Simulated dates for AD 1649 (also shown in Figure 4) indicate the range of potential cali-brated ages for this sample, demonstrating that the ABA + bleach pretreatment does not give such an erroneous date as the calibration plot may suggest.
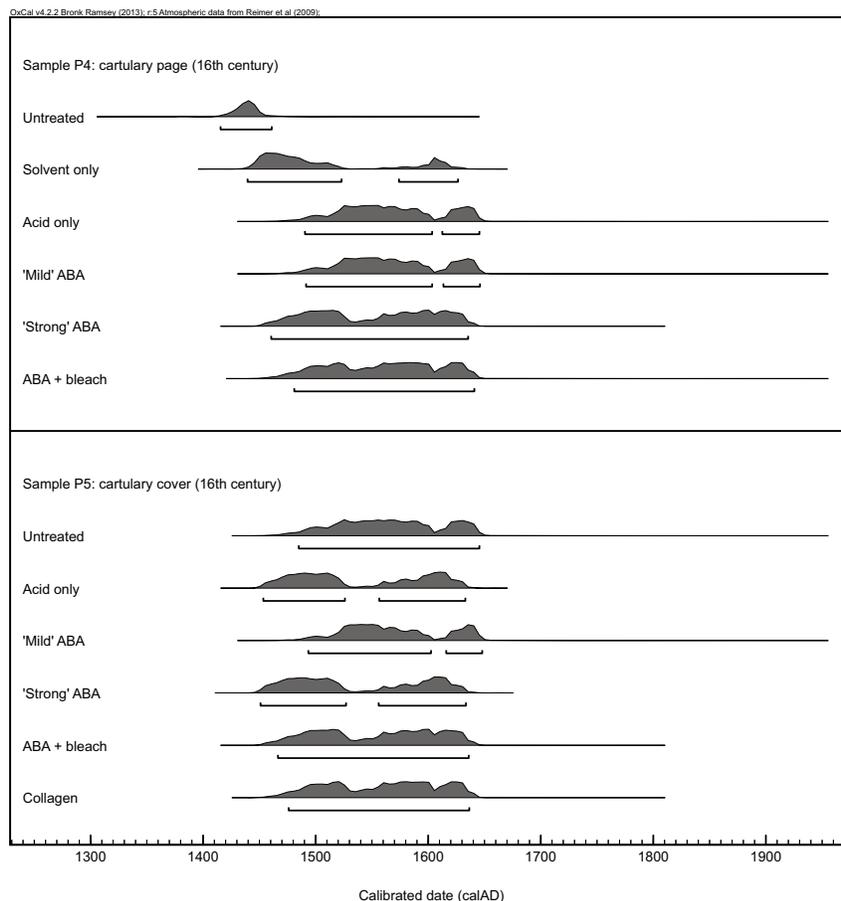
Figure 3 OxCal plot of calibrated ^{14}C dates of untreated and pretreated fractions of samples P4 and P5, a page and the cover from the Morrison of Cadeby cartulary, respectively, thought to date from the 16th century. Horizontal bars show the 95.4% highest probability density ranges.

This study demonstrates the survival potential of parchments undergoing "stronger" pretreatment protocols, that solvent washes and acid-only treatments may not be sufficient for thorough cleaning of parchaments prior to ^{14}C dating, and that the C:N ratio of a parchment can be a useful indicator of the presence or removal of contaminants. However, the limitations of the age and amount of available material for the parchments studied here must be acknowledged. Further tests need to be carried out on older (preferably pre-AD 1500) parchments with known ages on steeper parts of the calibration curve (ideally with sufficient material available for replicate measurements to be made for each pretreatment protocol studied), to be able to conclude which pretreatment method(s) provide the most accurate dates.

The reason(s) for the variation in C:N ratios of the fractions that underwent a bleach wash following ABA pretreatment is unclear. However, because of this, and because of the potential for unnecessary sample destruction by the harshness of the technique, the ORAU standard method for pretreating parchments is now being adjusted to include a strong ABA sequence (0.5M HCl and 0.1–0.2M NaOH) without a subsequent bleach step (ORAU lab code ACP). The bleach step will continue to be applied to leather samples and bog bodies as per Hedges et al. (1989) and Brock et al. (2010).
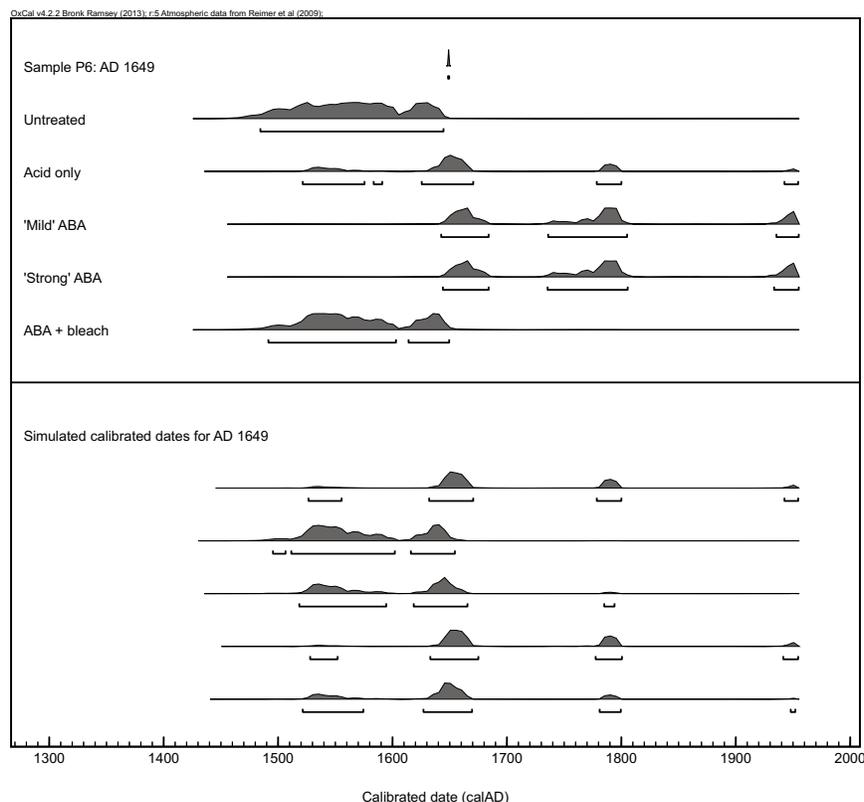
Figure 4 OxCal plot of calibrated ^{14}C dates of untreated and pretreated fractions of sample P6, as well as 5 simulated dates for a sample dating to AD 1649. Horizontal bars show the 95.4% highest probability density ranges.

CONCLUSIONS

The 6 historical parchments included in this study survived pretreatment conditions better than expected, and no samples were completely lost, even with relatively strong (0.2M) base washes or bleaching, or during collagen extraction procedures. As parchment consists predominantly of collagen, the C:N atomic weight ratio of the untreated and treated fractions can give a useful indication of the presence or successful removal of contamination for a sample when using the acceptable range of ~ 2.9–3.5 first proposed for bones by Ambrose (1990).

The results of the study demonstrate that most, if not all, parchments require some form of pretreatment prior to ^{14}C dating to ensure accurate dating. Such pretreatment requires thorough solvent and acid washes as a minimum. ABA treatments with very weak (e.g. 0.01M) HCl may not be strong enough to remove contaminants effectively. Although the base washes did not appear to affect the dates of the samples in this study, their application did result in an improvement to the C:N ratios, and is therefore recommended (with caution) for all but the most fragile of parchment samples. Accurate dates can be measured on samples undergoing an acid-base-acid pretreatment with starting weights of as little as 2–4 mg. Dating extracted collagen fractions from parchments is possible for samples of ~10 mg or less, but the additional work involved in this method is probably not justified given that ABA pretreatments have been shown to result in accurate dates and acceptable C:N val-

ues. Based on the C:N ratios observed in this study, and the potential for unnecessary sample destruction, the additional bleach step has been removed from the routine parchment pretreatment protocol applied at ORAU.

Further work dating 15th century and older known-age parchments with different pretreatment methods (ideally where sufficient material is available for multiple measurements) is, however, required to support the conclusions of this study, and to more clearly identify the method(s) that will result in the most accurate ^{14}C dates.

ACKNOWLEDGMENTS

REFERENCES

Ambrose SH. 1990. Preparation and characterization of bone and tooth collagen for isotopic analysis. *Journal of Archaeological Science* 17(4):431–51.

Badea E, Miu E, Budrugeac P, Giurginca M, Masic A, Badea N, Della Gatta G. 2008. Study of deterioration of historical parchments by various thermal analysis techniques complemented by SEM, FTIR, UV-VIS-NIR and unilateral NMR investigations. *Journal of Thermal Analysis and Calorimetry* 91(1):17–27.

Berger R, Evans N, Abell JM, Resnik MA. 1972. Radiocarbon dating of parchment. *Nature* 235(5334):160–1.

Bonani G, Ivy S, Wölfli W, Broshi M, Carmi I, Strugnell J. 1992. Radiocarbon dating of fourteen Dead Sea Scrolls. *Radiocarbon* 34(3):843–9.

Brock F, Higham T, Ditchfield P, Bronk Ramsey C. 2010. Current pretreatment methods for AMS radiocarbon dating at the Oxford Radiocarbon Accelerator Unit (ORAU). *Radiocarbon* 52(1):103–12.

Bronk Ramsey C. 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon* 51(1):337–60.

Carmi I. 2002. Are the ^{14}C dates of the Dead Sea Scrolls affected by castor oil contamination? *Radiocarbon* 44(1):213–6.

Donahue DJ, Olin JS, Harbottle G. 2002. Determination of the radiocarbon age of parchment of the Vinland Map. *Radiocarbon* 44(1):45–52.

Edwards HGM, Farwell DW, Newton EM, Rull Perez F, Jorge Villar S. 2001. Application of FT-Raman spectroscopy to the characterisation of parchment and vellum, I; novel information for palaeographic and historiated manuscript studies. *Spectrochimica Acta Part A* 57(6):1223–34.

Ghioni C, Hiller JC, Kennedy CJ, Aliev AE, Odlyha M, Boulton M, Wess TJ. 2005. Evidence of a distinct lipid fraction in historical parchments: a potential role in degradation. *Journal of Lipid Research* 46(12):2726–34.

Hedges REM, Law IA, Bronk CR, Housley RA. 1989. The Oxford accelerator mass spectrometry facility: technical developments in routine dating. *Archaeometry* 31(2):99–113.

Jull AJT, Donahue DJ, Broshi M, Tov E. 1995. Radiocarbon dating of scrolls and linen fragments from the Judean Desert. *Radiocarbon* 37(1):11–9.

Kennedy CJ, Wess TJ. 2003. The structure of collagen within parchment – a review. *Restaurator* 24(2):61–80.

Kennedy CJ, Hiller JC, Lammie D, Drakopoulos M, Vest M, Cooper M, Adderley WP, Wess TJ. 2004a. Microfocus X-ray diffraction of historical parchment reveals variations in structural features through parchment cross sections. *Nano Letters* 4(8):1373–80.

Kennedy CJ, Vest M, Cooper M, Wess TJ. 2004b. Laser cleaning of parchment: structural, thermal and biochemical studies into the effect of wavelength and fluence. *Applied Surface Science* 227(1–4):151–63.

Rasmussen KL, van der Plicht J, Cryer FH, Doudna G, Cross FM, Strugnell J. 2001. The effects of possible contamination on the radiocarbon dating of the Dead Sea Scrolls I: castor oil. *Radiocarbon* 43(1):127–32.

Rasmussen KL, van der Plicht J, Doudna G, Cross FM, Strugnell J. 2003. Reply to Israel Carmi: "Are the ^{14}C dates of the Dead Sea Scrolls affected by castor oil contamination?" *Radiocarbon* 45(3):497–9.

Rasmussen KL, van der Plicht J, Doudna G, Nielsen F, Højrup P, Stenby EH, Pederson CT. 2009. The effects of possible contamination on the radiocarbon dating of the Dead Sea Scrolls II: empirical methods to remove castor oil and suggestions for redating. *Radiocarbon* 51(3):1005–22.

Reed R. 1972. *Ancient Skins, Parchments and Leather.*

New York: Seminar Press.

Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Buck CE, Burr GS, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Hajdas I, Heaton T, Hogg AG, Hughen KA, Kaiser KF, Kromer B, McCormac FG, Manning SW, Reimer RW, Richards DA, Southon JR, Talamo S, Turney CSM, van der Plicht J, Weyhenmeyer CE. 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP. *Radiocarbon* 51(4): 1111–50.

Santos FJ, Gómez-Martínez I, García-León M. 2010. Radiocarbon dating of medieval manuscripts from the University of Seville. *Nuclear Instruments and Meth-ods in Physics Research B* 268(7–8):1038–40.

Strlič M, Cigić IK, Rabin I, Kolar J, Pihlar B, Cassar M. 2009. Autoxidation of lipids in parchment. *Polymer Degradation and Stability* 94(6):886–90.

Thompson DV. 1956. *The Materials and Techniques of Medieval Painting*. New York: Dover Publications.

van Klinken GJ. 1999. Bone collagen quality indicators for palaeodietary and radiocarbon measurements. *Journal of Archaeological Science* 26(6):687–95.

Weiner S, Kustanovich Z, Gil-Av E, Traub W. 1980. Dead Sea Scroll parchments: unfolding of the collagen molecules and racemization of aspartic acid. *Nature* 287(5785):820–3.