FIRST STATUS REPORT ON RADIOCARBON SAMPLE PREPARATION TECHNIQUES AT THE A.E. LALONDE AMS LABORATORY (OTTAWA, CANADA)

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ABSTRACT. The A.E. Lalonde accelerator mass spectrometer (3MV, HVEE) was commissioned in early 2014 at the University of Ottawa (Canada). The radiocarbon sample preparation laboratory spent the better part of 2014 undertaking a quality control program, establishing pretreatment protocols, and streamlining sample processing. In the fall of 2014, the first unknown samples were accepted and in the first year of operation well over 1000 targets (~60% unknowns) were analyzed. Here, we present an overview of sample processing protocols and results from routinely measured standards, reference, and blank materials.

KEYWORDS: radiocarbon sample preparation, AMS, Fe-only blank, status report.

INTRODUCTION

This new radiocarbon laboratory in Canada is housed in the Advanced Research Complex (ARC), University of Ottawa. Dedicated to the late Dean of the Faculty of Science and Professor in the Department of Earth and Environmental Sciences, the André E. Lalonde Accelerator Mass Spectrometry (AMS) Laboratory is currently the only AMS lab in Canada. The AMS system and sample preparation laboratories have been set up to provide routine analytical services (^{3}H, ^{10}Be, ^{26}Al, ^{129}I, actinides, etc., and, of course, ^{14}C) in an open-access environment to foster the sharing of ideas and to train researchers and students on how to process their samples from start to finish under the supervision of highly qualified personnel.

The ^{14}C sample preparation laboratory moved into the ARC in the spring of 2014 and was operational almost immediately due largely to the fact that preparations for the lab, including design and construction of the graphitization equipment (St-Jean et al. 2016, in this issue), began at least 3 yr earlier. In light of the results from the first few batches of standards and blanks for organics, collagen, and carbonates, the first unknown samples were accepted in the fall of 2014.

The pretreatment protocols are modeled after published protocols and personal communications from other well-established labs (Longin 1971; Bronk Ramsey et al. 2004; Beaumont et al. 2010; Brock et al. 2010; Staff et al. 2014; ORAU; Keck-CCAMS; ^{14}Chrono). After more than a year of analyzing unknowns, the routine pretreatment protocols are well established and therefore documented here along with results from standards run with each batch.

PRETREATMENT METHODS

Each pretreatment protocol is assigned a media code (described in detail below and listed in Table 1), which is usually decided by the researcher, but consultation is often required to ensure that the most appropriate media codes are selected. The submission form requests geographical information, which is essential for calibration and also can be useful for answering questions about preservation and possible contaminants from the natural environment or storage issues. An approximate age

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Table 1 Current routinely measured known-age standards used for quality assurance.

Media code	Standard ID	Details	Age
AAA, A, AAAB	AVR-07-PAL-37	Wood overlying Old Crow tephra (Alaska)	~125,000 BP[a]
	IAEA-C5	Two Creeks wood (Wisconsin)	11,780–11,800 yr BP[b]
B, BU	Hollis Mammoth	Associated with Valley Creek tephra (Alaska)	Middle Pleistocene[c]
	UWB	Whale bone (Ellesmere Island, Canada)	7300–7400 yr BP[d]
S, SN	IAEA-C1	Cararra marble (Italy)	Mesozoic (>50 Ma)[b]
	SIRI-K	Doublespar (Iceland)	Background
	IAEA-C2	Travertine (Bavaria, Germany)	7130–7140 yr BP[b]

[a]Reyes et al. (2010).
[b]Rozanski et al. (1990); Rozanski (1991).
[c]Constrained by ~700-ka glass-fission track age on tephra from Westgate et al. (2011) and Valley Creek tephra from Jensen et al. (2013).
[d]Based on average of 19 measurements.

range is requested in order to select the secondary standards and, to a certain extent, determine the sequence in which the samples will be run on the accelerator. Each group of samples of the same type is paired up with a process blank and a secondary standard, as shown in Table 1.

The physical pretreatment takes place in a low-dust environment and all tools are sonicated in methanol and dried prior to use. All glassware is baked at 500°C for at least 3 hr. The chemical pretreatment is performed in 13-mL Pyrex® test tubes and heating is performed in a 14L Lab Armor® waterless bead bath.

Physical Pretreatment

Samples are inspected for signs of possible contaminants (dust, soil, discolouration, shellac, preservatives), sonicated in Milli-Q® water if necessary (15 min at room temperature), and cleaned with a stainless steel surgical kit, in combination with various drill and Dremel® bits. In the case of bone (media codes B, BU), a stainless steel percussion mortar is used to crush the sample to coarse (1–2 mm) powder. Carbonate samples (media code S) are manually abraded with a drill and stainless steel Dremel bit to remove porous or recrystallized areas, and pre-etched with 0.2N HCl to remove the outer 20–30%. For small samples (e.g. forams) or powders (e.g. $SrCO_3$), no pre-etch is performed (media code SN).

Organics, Charcoal, Sediments, Wood (AAA, A, AAAB)

The standard acid-alkali-acid (AAA) pretreatment at the Lalonde AMS Laboratory follows the protocol outlined in Brock et al. (2010). Sedimentary or other carbonates are removed during the first acid wash (HCl, 1N, 80°C, 30 min), and then to remove humics, the sample undergoes rinses in an alkali solution (NaOH, 0.2N, 80°C, 30 min) until the supernatant is the color of weak tea. Any CO_2 absorbed during the alkali step is removed with a second acid wash (HCl, 1N, 80°C, 30 min). Each step is followed by three rinses in Milli-Q water. Clean samples are freeze-dried overnight.

If humic acid is not believed to be an issue, the sample is too fragile for AAA, or the submitter does not wish for humics to be removed, the sample will be assigned the media code A and will only undergo the first acid treatment of the AAA protocol before being freeze-dried overnight.

For wood, as recommended by Staff et al. (2014), the AAA-pretreated material is bleached to cellulose using a 5% $NaClO_2$ solution at 80°C. The samples are monitored and removed once the colour has turned white (30–60 min). After three rinses in Milli-Q water, the samples are freeze-dried overnight.

Bone, Teeth, Antler, and Ivory (B, BU)

The standard collagen extraction follows the Longin (1971) method and the protocol outlined in Brock et al. (2010), with modifications from Beaumont et al. (2010). The sample is first decalcified with 0.5N hydrochloric acid until translucent (3 or 4 rinses over ~18 hr, room temperature), treated with 0.1N sodium hydroxide to remove humic acid (30 min, room temperature), and 0.5N HCl again (30 min, room temperature) to remove any CO_2 that may have been adsorbed during the base wash. Each step is followed by three rinses with Milli-Q water. The samples are gelatinized at 60°C overnight in a pH 3 solution (5 mL total volume max) and filtered using a cleaned glass Whatman® autovial syringeless filter.

If required, ultrafiltration (media code BU) takes place at this stage. Ultrafilters (Vivaspin® 30kDa MWCO) are first cleaned by centrifuging with Milli-Q twice, 15 min of ultrasonic cleaning in Milli-Q, then centrifuged again three times with Milli-Q (Bronk Ramsey et al. 2004). The sample, following the filtration step of the collagen extraction, is centrifuged in the ultra-filter and the >30 kDa fraction is removed and freeze-dried.

Carbon and nitrogen content are measured by an elemental analyzer (Thermo™ Flash 1112), and if the C:N is outside the range of 2.9–3.6, the sample is deemed unsuitable for dating as it has likely undergone postdepositional alteration (DeNiro et al. 1985). If $\delta^{13}C$ and $\delta^{15}N$ are required, an aliquot of the extracted collagen is submitted to the G.G. Hatch Stable Isotope Laboratory (our partner laboratory located on the same floor in the ARC) for analysis by isotope ratio mass spectrometry (IRMS) on a Thermo DeltaPlus Advantage coupled to an elemental analyser (Vario EL Cube, Elementar) via a Conflo III interface (Thermo). Their internal standards are ($\delta^{15}N$, $\delta^{13}C$ in ‰): C-51 nicotinamide (0.07, –22.95), C-52 mix of ammonium sulfate + sucrose (16.58, –11.94), C-54 caffeine (–16.61, –34.46), and blind std C-55: glutamic acid (–3.98, –28.53). All $\delta^{15}N$ is reported as ‰ vs. AIR and normalized to internal standards calibrated to international standards IAEA-N1 (+0.4‰), IAEA-N2 (+20.3‰), USGS-40 (–4.52‰), and USGS-41 (47.57‰). All $\delta^{13}C$ is reported as ‰ vs. V-PDB and normalized to internal standards calibrated to international standards IAEA-CH-6 (–10.4‰), NBS-22 (–29.91‰), USGS-40 (–26.24‰), and USGS-41 (37.76‰). Please note that the PDB and VPDB scales are identical and interchangeable. The analytical precision is based on an internal standard (C-55), which is not used for calibration and is usually better than 0.2‰.

Acid Hydrolysis of Carbonates (S, SN)

The cleaned samples are powdered manually with a glass mortar and pestle and added to prebaked glass reaction vessels with a side-arm containing 3 mL anhydrous H_3PO_4 (see next paragraph for preparation procedure) added to the side-arm. The vessel is evacuated to vacuum baseline, the valve closed, the vessel tipped to add the acid to the carbonate powder, and the sample is left to react overnight at room temperature. The CO_2 is extracted and cryogenically purified on a glass vacuum extraction line before being sealed in a 6-mm prebaked Pyrex breakseal. We have chosen not to display a schematic of this extraction line here as this traditional method will soon be replaced with an autosampler interfaced with the new 10-port semi-automated gas cleanup line described in St-Jean et al. (2016). The gas cleanup line is

currently being tested (yield, background, memory) and results will be presented in a future publication.

Anhydrous H_3PO_4 is used as it will pump down quickly, thus allowing the technician to leak check the vessels after a much shorter evacuation time. The stock of 100% H_3PO_4 is prepared by slowly dissolving 500g of P_2O_5 in 600 mL of 85% H_3PO_4 with 10 mg of CrO_3 and heating to 180°C overnight, followed by adding 1 mL of H_2O_2 and heating to 220°C for 4.5 hr (Coplen et al. 1983). The solution is allowed to cool to 150°C and is then transferred to glass bottles with caps containing conical plastic inserts for airtight sealing.

Combustion

Pretreated, freeze-dried samples are combusted using a Thermo Flash 1112 elemental analyzer (EA) in CN mode interfaced with an extraction line to trap the pure CO_2 in a prebaked 6-mm Pyrex breakseal. Solid organic samples are weighed into a tin capsule (Elemental Microanalysis cat#D1008) and combusted using the EA. Blank tin capsules are combusted between each sample to monitor the blank and ensure no memory effect. Samples that are too small for pretreatment or do not require pretreatment are submitted for direct combustion with the media code D. While the EA will continue to be used for samples requiring C:N measurement, new semi-automated tube sealing and gas cleanup lines are now complete for sealed quartz tube combustions (St-Jean et al. 2016).

Graphitization

Samples of pure CO_2 in 6-mm breakseals are converted to elemental carbon in the presence of iron and hydrogen using semi-automated graphitization lines that were designed and built in-house (St-Jean et al. 2016). In brief, 10 breakseals are scored, loaded into Rotulex® cracker tubes, and left to pump overnight along with the reactor, which is composed of a horizontal quartz tube containing 5 mg of preconditioned (oxidized and reduced) –200 mesh (currently testing –325 mesh and various amount) iron powder (Alpha Aesar®, 99+%, CAS7439-89-6, P/N: 00737), and an empty Pyrex vertical tube pointing down for cryogenic water trapping. The CO_2 is released into the reactor by gently creating a bend at the Rotulex cracker joint to snap the breakseal, followed by transfer to the reaction volume by freezing into the water trap using liquid nitrogen. Residual noncondensable gases are pumped away, the CO_2 is heated back to room temperature to measure the pressure, and then refrozen to add hydrogen at 2.5× pCO_2 into the reaction volume. Ovens are connected and the quartz tubes are heated to a reactor inside temperature of ~550°C. The cooling bar is raised to insert the Pyrex tubes into individual cups filled with ethanol, and a closed-loop cooling system maintains the cups at –40°C for effective cryogenic water removal. The samples are left to graphitize for 3 hr, but the process is usually complete in about 2 hr. The pressure, oven temperature, and cooling cup temperatures for each sample are monitored, graphed, and recorded throughout the reaction. A memory test on the graphitization line (St-Jean et al. 2016) showed a cross-over of about 0.025% of the previous sample, which is within our standard precision of 2–3‰ and will only affect very old or very small samples. The UC Irvine reactors were tested in the same way by Southon (2007), who found a memory effect of 0.035% of the previous sample.

Graphitized samples are then pressed into targets using a pneumatic press, designed and constructed in-house. We currently use aluminum targets and copper back-pressing pins, which were found to have minimal carbon content.

AMS MEASUREMENT

^{14}C analyses are performed on a 3MV tandem accelerator mass spectrometer built by High Voltage Engineering (HVE). ^{12,13,14}C^{+3} ions are measured at 2.5MV terminal voltage with Ar stripping. The fraction modern carbon, F^{14}C, is calculated according to Reimer et al. (2004) as the ratio of the sample ^{14}C/^{12}C ratio to the standard ^{14}C/^{12}C ratio (in our case Ox-II) measured in the same data block (see paragraph below). Both ^{14}C/^{12}C ratios are background-corrected and the result is corrected for spectrometer and preparation fractionation using the AMS-measured ^{13}C/^{12}C ratio and is normalized to δ^{13}C (PDB). ^{14}C ages are calculated as –8033ln(F^{14}C) and reported in ^{14}C yr BP (BP = AD 1950) as described by Stuiver and Polach (1977). The errors on ^{14}C ages (1σ) are based on counting statistics and ^{14}C/^{12}C and ^{13}C/^{12}C variation between data blocks.

A description of the A.E. Lalonde AMS system and the analysis procedure and setup is found in Kieser et al. (2015). The HVE SO-110B ion source has a 200-position sample wheel. Because this AMS system is frequently switched to measure several different isotopes, it becomes necessary for ^{14}C samples to be measured in large batches of 100 to 200 samples each, with 6–10 pairs of Ox-II and Fe-only blanks, as well as several secondary references and process blank samples evenly distributed on the wheel. The ^{12,13,14}C^{+3} ions are measured with fast sequential injection at 92 Hz, with 90% time spent counting ^{14}C^{+3}. The total ^{14}C^{+3} counts and the average ^{12}C^{+3} and ^{13}C^{+3} currents are recorded in 30-s blocks. When a target is inserted, 10 blocks are measured regardless of counting statistics from the target; after all targets are so measured (one pass), the measurement repeats. To reach 3‰ precision on standards, usually ~10 passes, or about 100 blocks per sample, are measured in total. The AMS system is sufficiently stable to support these long-lasting cycles; the measurements of all targets included in a batch are well distributed and are averaged for normalization. The ^{12}C^{+3} current is presently limited to ≤40 μA to optimize the reproducibility of the results. Although this increases analysis time, it does not affect the accuracy or precision of the results. We are currently studying this operational limitation, which we believe to be related to the design of the instrument, as, compared with the carbon dedicated instruments with better flat-topped transmissions, the Lalonde system has the flexibility to also measure heavy elements (U, Pb, Am, etc.).

Blanks

The measurement of natural, high-purity graphite from Alfar Aesar® (-200 mesh, 99.9999%, cat#14734) typically results in F^{14}C ~0.0002 (no blank correction). This commercial graphite is included as reference only; we do not consider it as a suitable system blank because it does not include contributions from the Fe catalyst, which has an additional gettering effect from residual hydrocarbons in the source vacuum during sputtering. Instead, we always include several targets of Fe that have been conditioned on the graphitization line (oxidized and reduced) as blanks that represent any unremoved (bound) carbon impurities in the Fe catalyst as well as the small amount of contamination that occurs during graphitization, sample storage, and AMS measurement. Although using pure fossil CO_2 is commonly used as a graphitization blank, this does not allow to correct for all three isotopes of carbon present in the iron and ion source vacuum; thus, at present we use Fe-only blanks in order to correct for ^{12,13,14}C^{+3}.

Typically, the Fe-only blank produces two ^{14}C^{+3} counts per minute under ion source conditions that produce an average of 30 μA ^{12}C^{+3} from Ox-II target containing 1 mg C. Contaminations in these phases could come from several carbon sources with unknown quantity and mix. However, these are corrected in the offline AMS data reduction in which the

average result of all the Fe-only nth blocks is subtracted from the corresponding nth block of the other targets, including process blanks. Such subtraction is applied to all three isotopes of carbon, although it has little impact on ^{13}C and ^{12}C for regular samples with masses >200 µg C. The final results are then the weighted average over all blocks of the Fe-blank corrected data for each target. For making further corrections from process blanks, to account for contamination during pretreatment and CO_2 production, we are continuing to evaluate the most appropriate procedures for doing so, including a mass-balance approach.

RESULTS AND DISCUSSION

Figure 1A shows results for oxalic acid II (Ox-II), measured with each wheel for normalization, starting from the very first wheel. Figure 1B demonstrates that the majority of the Ox-II measurements are within ±1σ with tails that do not exceed ±0.02 F^{14}C. Figure 1B also illustrates the reproducibility of the precision. Data for Figure 1 are based on samples in the range of 0.5–3 mgC (typically 1–2 mg C). Ox-II samples have been measured down to 50 µg C and, although an exhaustive minimum sample size test has not yet been performed, the measurements are fairly reliable down to about 200 µg C (F^{14}C = 1.33 ± 0.007), below which point the F^{14}C continues to decrease with decreasing sample size and the precision is lower.

Each batch is paired up with an appropriate process blank (>50 ka) and a secondary standard, usually Holocene in age (Table 1). Figures 2 and 3 illustrate the results from the first year of standards routinely measured with sample batches. Table 2 is a summary of results for the first year of routinely measured standards along with other reference materials.

For organics and wood samples, two different kauri wood samples (IAEA-C4 and FIRI-B) were used during the first year, but we now use the AVR-07-PAL-37 wood (Reyes et al. 2010) as it routinely provides background ages of greater than 50,000 ^{14}C yr BP and so far it has not dated to younger than 45,000 ^{14}C yr BP (Figure 2A). IAEA-C5 (Two Creeks wood, 11,780–11,800 ^{14}C yr BP) is measured as a secondary standard for AAA batches. For the most part, IAEA-C5 is well behaved (Figure 3A), although it is affected by the process blank, causing some scatter.

For collagen extraction, SIRI-B (38,300 ± 300 ^{14}C yr BP, $n = 4$) and SIRI-C (44,100 ± 300 ^{14}C yr BP, $n = 7$)[1] were measured along with the first few bone batches, but since the ages were not true background, the Hollis Mine mammoth bone [constrained by ~700-ka glass-fission track age on tephra from Westgate et al. (2011), and Valley Creek tephra from Jensen et al. (2013)] was tested and is now used as the process blank sample as it routinely dates to greater than 45,000 ^{14}C yr BP (Table 2, Figure 2B). An in-house secondary standard has been developed from a large whale bone from Ellesmere Island (Nunavut, Canada; GSC-3055; BS-79-134; Blake 1987). The name Umingmak, for the Umingmake whale bone (UWB), comes from the Inuit name for Ellesmere Island. The current estimate of 7324 ± 39 ^{14}C yr BP for the UWB is based on 19 measurements (Figure 3B). As part of the future work for the lab, we will provide a more robust age estimate for the UWB based on a greater number of measurements and lab intercomparisons.

Carbonates and shells are analyzed along with the IAEA-C1 Cararra marble (process blank) and IAEA-C2 travertine (secondary standard). Freshly crushed IAEA-C1 routinely yields ages >50,000 ^{14}C yr BP (Figure 2C). Precrushed, stored powders have shown not to keep well,

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[1]At the time of this publication, only informal SIRI results are available.
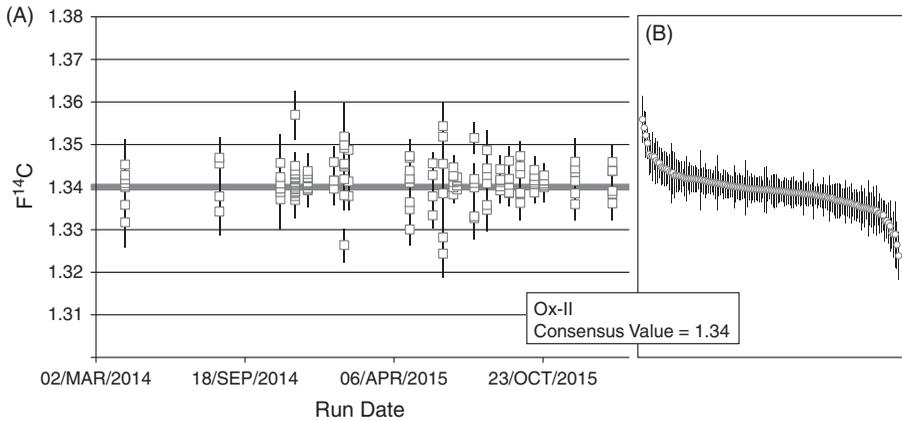
Figure 1 (A) Time series of results for the Ox-II standard (±1σ) measured from early 2014 (acceptance testing) through to late 2015. (B) Ox-II results from (A) sorted to show the distribution of data overlapping the consensus value within ±1σ, and spread of data found among the tails (±0.02 $F^{14}C$).
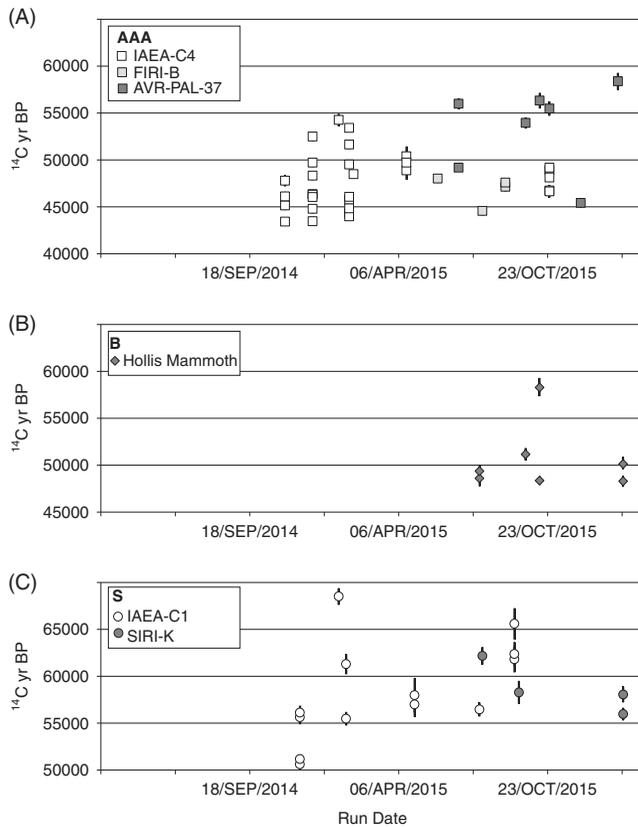

Figure 2 Results for process blanks: (A) AAA group materials, the current blank is AVR-07-PAL wood (IAEA-C4 and FIRI-B are both Kauri wood); (B) Hollis mammoth bone for samples undergoing collagen extraction (SIRI-C was used for a while as a background check, but it was not a true process blank); (C) shells and carbonates, both IAEA-C1 (Cararra marble) and SIRI-K (Icelandic doublespar), are currently used.
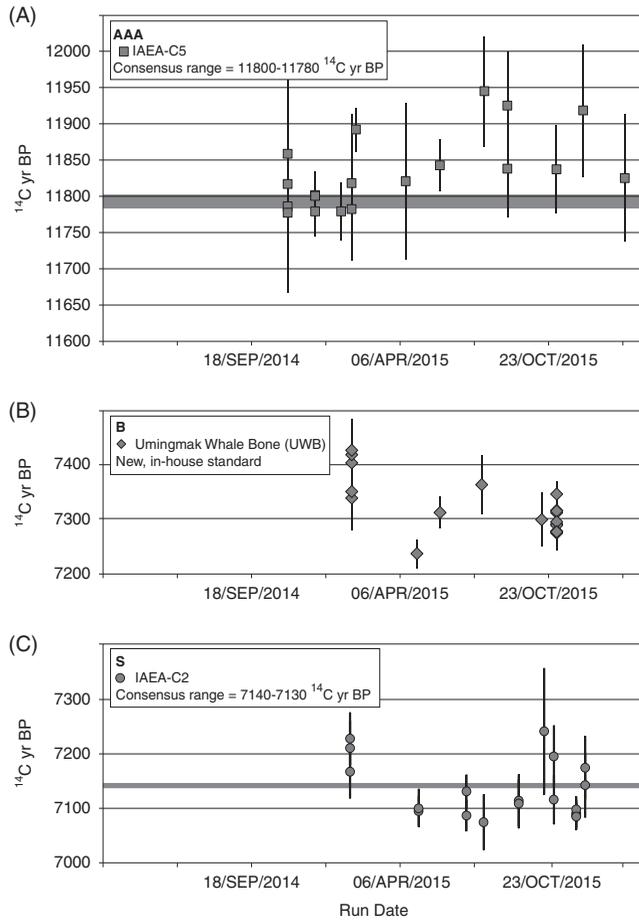
Figure 3 Results for secondary standards (A) IAEA-C5 Two Creeks wood, used for AAA materials; (B) Umingmak whale bone is an in-house standard for collagen containing materials; (C) IAEA-C2 travertine is used for shells and carbonates.

Table 2 Results for reference materials tested during the first year of operation. For samples with more than one measurement, the measured value and error are an average.

Sample	Material	n	Measured value (^{14}C yr BP)	Reference value (^{14}C yr BP)
IAEA-C1	Cararra marble	22	$53,950 \pm 780$	Mesozoic (>50 Ma)
IAEA-C2	Travertine	20	7133 ± 45	7129–7141
IAEA-C3	Cellulose	6	1.2992 ± 0.0039 (F^{14}C)	1.2941 ± 0.006 (F^{14}C)
IAEA-C4	Kauri wood	31	$47,370 \pm 450$	43,588–49,922
IAEA-C5	Two Creeks wood	19	$11,834 \pm 70$	11,780–11,800
IAEA-C6	Sucrose	3	1.5047 ± 0.0043 (F^{14}C)	1.5061 ± 0.0011 (F^{14}C)
FIRI-B	Kauri wood	4	$46,790 \pm 370$	43,588–49,922
SIRI-K	Doublespar	4	$58,630 \pm 890$	Background
AVR-07-PAL-37	Wood	7	$53,590 \pm 600$	~125,000 BP
UWB	Whale bone	19	7324 ± 39	*to be determined*
Hollis	Mammoth bone	7	$52,400 \pm 1000$	Middle Pleistocene

typically producing ages <48,000 ^{14}C yr BP (not shown), likely due to the adsorption of atmospheric CO_2. For this reason, only freshly crushed powders are used for the process blank. We have recently started testing the SIRI-K1 geologic doublespar, which shows consistent results >55,000 ^{14}C yr BP (Figure 2C). IAEA-C2 generally falls within the consensus range at 2σ (Figure 3C), again with scatter likely attributed to some variability observed with the IAEA-C1 process blank.

SUMMARY

The work presented here is based on the standards and reference materials from the first 1000 samples processed within a year or so of installation of the accelerator and getting the new sample prep lab up and running (summer 2014). The goal with presenting this early work is to demonstrate our ability to measure routine samples of varying age and material type, and to document the sample preparation protocols as they evolve with advances in knowledge. Moreover, the first status report gives a lab the opportunity to establish a baseline upon which to improve.

CURRENT AND FUTURE WORK

Below is a glimpse at the rapidly growing list of projects underway at the A.E. Lalonde AMS Laboratory:

1. Develop a protocol for $^{14}CH_4$ analysis from gas mixtures and waters;
2. Continued QA/QC testing of standards for extraction of DIC by acidification and DOC by wet oxidation, and investigation of UV oxidation methods for DOC extraction from water;
3. Integration of a CTC robotic autosampler with the semi-automated gas cleanup line (St-Jean et al. 2016) for the rapid analysis of carbonates, gas mixtures, and waters (DIC/DOC);
4. Test the use of Eeze-filters to replace decanting during pretreatment;
5. Establish a consensus value for the Umingmak whale bone (UWB) with improved statistics and lab intercomparisons;
6. Test protocols used by other labs for old charcoals: e.g. ABOx-SC (acid-base-wet oxidation-stepped combustion; Bird et al. 1999; Brock et al. 2010);
7. Thorough investigation into minimum sample size for a variety of ages;
8. Method development for small sample (<200 μg C) and compound-specific analysis, including gas source technologies; and
9. Further developing a routine for mass-balanced process blank correction.

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REFERENCES

Beaumont W, Beverly R, Southon J, Taylor RE. 2010. Bone preparation at the KCCAMS laboratory. *Nuclear Instruments and Methods in Physics Research B* 268(7–8):906–9.

Bird MI, Ayliffe LK, Fifield LK, Turney CSM, Cresswell RG, Barrows TT, David B. 1999. Radiocarbon dating of 'old' charcoal using a wet oxidation-stepped combustion procedure. *Radiocarbon* 41(2):127–40.

Blake W Jr. 1987. Geological Survey of Canada radiocarbon dates XXVI. *Geological Survey of Canada* 86(7):1–60.

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, Higham T, Bowles A, Hedges R. 2004. Improvements to the pretreatment of bone at Oxford. *Radiocarbon* 46(1):155–63.

Coplen TB, Kendall C, Hopple J. 1983. Comparison of stable isotope reference samples. *Nature* 302(5905):236–8.

DeNiro MJ, Schoeninger MJ, Hastorf CA. 1985. Effect of heating on the stable carbon and nitrogen isotope ratios of bone collagen. *Journal of Archaeological Science* 12:1–7.

Jensen BJL, Reyes AV, Froese DG, Stone DB. 2013. The Palisades is a key reference site for the middle Pleistocene of eastern Beringia: new evidence from paleomagnetics and regional tephrostratigraphy. *Quaternary Science Reviews* 63:91–108.

Kieser WE, Zhao X-L, Clark ID, Cornett RJ, Litherland AE, Klein M, Mous DJW, Alary J-F. 2015. The André E. Lalonde AMS Laboratory – the new accelerator mass spectrometry facility at the University of Ottawa. *Nuclear Instruments and Methods in Physics Research B* 361:110–4.

Longin R. 1971. New method of collagen extraction for radiocarbon dating. *Nature* 230(5291):241–2.

Reimer PJ, Brown TA, Reimer RW. 2004. Discussion: reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46(3):1299–304.

Reyes AV, Froese DG, Jensen BJL. 2010. Permafrost response to last interglacial warming: field evidence from non-glaciated Yukon and Alaska. *Quaternary Science Reviews* 29(23–24): 3256–74.

Rozanski K. 1991. Consultants' group meeting on ^{14}C reference materials for radiocarbon laboratories. February 18–20, 1991, Vienna, Austria. Internal Report, IAEA, Vienna.

Rozanski K, Stichler W, Gonfiantini R, Scott EM, Beukens RP, Kromer B, van der Plicht J. 1990. The IAEA ^{14}C intercomparison exercise 1990. *Radiocarbon* 34(3):506–19.

Southon J. 2007. Graphite reactor memory – Where is it from and how to minimize it? *Nuclear Instruments and Methods in Physical Research B* 259(1):288–92.

Staff RA, Reynard L, Brock F, Bronk Ramsey C. 2014. Wood pretreatment protocols and measurement of tree-ring standards at the Oxford Radiocarbon Accelerator Unit (ORAU). *Radiocarbon* 56(2):709–15.

St-Jean G, Kieser WE, Crann CA, Murseli S. 2016. Semi-automated equipment for CO_2 purification and graphitization at the A.E. Lalonde AMS Laboratory (Ottawa, Canada). *Radiocarbon*. This issue. DOI:10.1017/RDC.2016.57.

Stuiver M, Polach HA. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Westgate JA, Preece SJ, Jackson LE Jr. 2011. Revision of the tephrostratigraphy of the lower Sixtymile Riever area, Yukon Territory, Canada. *Canadian Journal of Earth Science* 48: 695–701.