SEMI-AUTOMATED EQUIPMENT FOR CO_2 PURIFICATION AND GRAPHITIZATION AT THE A.E. LALONDE AMS LABORATORY (OTTAWA, CANADA)

Gilles St-Jean[1] • William E Kieser[2] • Carley A Crann[1*] • Sarah Murseli[1]

[1]Department of Earth and Environmental Sciences and A.E. Lalonde Lab, University of Ottawa, 25 Templeton St., Ottawa, Ontario, K1N 6N5, Canada.
[2]Department of Physics and A.E. Lalonde Lab, University of Ottawa, 150 Louis Pasteur, Ottawa, Ontario, K1N 6N5, Canada.

ABSTRACT. New computer-controlled, semi-automatic systems were designed and built for CO_2 purification and graphitization at the A.E. Lalonde Accelerator Mass Spectrometry (AMS) Laboratory with consideration for user friendliness and high throughput. The stainless steel vacuum lines are orbitally welded to ensure clean seams with low memory. The insulated graphitization ovens with plug-in electrodes provide a hazard-free environment for operators. The closed-loop cooling system circulating low-viscosity Dynalene at –40°C provides highly efficient water trapping. The LabVIEW[TM] software features (1) pressure and temperature recording for QA/QC; (2) safety interlocks to preclude operator errors resulting in sample loss, cross-contamination, or damaging a vacuum pump; and (3) automation for leak checking, iron conditioning, and running samples. Results from the first year of routinely measured standards, reference, and background materials are reproducible and within acceptance values. In the first year of operation (commissioned in spring 2014), over 1000 targets (~60% unknowns) were produced. With new tube sealing and CO_2 purification lines, and two more graphitization lines now operational, the Lalonde AMS Laboratory is able to provide routine radiocarbon analysis (>200 µg carbon) at a capacity of more than 7000 targets per year. Most importantly, the equipment is safe and intuitive, making it ideal for education and training students to run their own samples.

KEYWORDS: graphitization, CO_2 purification, closed-loop cooling, automation, LabVIEW, orbital welding.

INTRODUCTION

To produce a sample for radiocarbon analysis by accelerator mass spectrometry (AMS), the routine common among labs is pretreatment, combustion or hydrolysis, CO_2 purification, and graphitization. The equipment, however, varies widely, especially with respect to automation. In the planning stages of the Lalonde AMS Lab, the advantages of both manual and automated systems were recognized and, since the University of Ottawa has excellent technical support with machine and electronics shops, semi-automated sample preparation equipment was designed and constructed in-house to suit the needs for research, provide timely and cost-efficient ^{14}C analytical services, and be user-friendly for the education and training of students processing their own samples.

For pretreatment, manual methods were chosen (see Crann et al. 2016, in this issue). Although continuous-flow systems have been designed for the standard acid-alkali-acid (AAA) pretreatment and collagen extraction (e.g. Law and Hedges 1990), manual methods are likely still the most common as a human element is required to record observations and to frequently make decisions such as the number of alkali washes, the duration of cellulose extraction for wood, the duration of decalcification for bone, and when to modify or abort the pretreatment so not to lose a sample should it begin to degrade.

For combustion, CO_2 purification, and graphitization, fully automated systems use an elemental analyzer or gas extraction bench to produce clean CO_2 that is transferred directly to the graphitization equipment, which in itself is automated (Aerts-Bijma et al. 2001; Wacker et al. 2010, 2013; Kato et al. 2014). Manual systems start with the evacuation of quartz tubes containing the sample, CuO, and Ag wire, which are then sealed and baked at 900°C. The tube is cracked on a graphitization line using a bellows-sealed breaker tube and the water is removed by a cold trap before the CO_2 is transferred into a reactor for graphitization. The valve

*Corresponding author. Email: radiocarbon@uottawa.ca.

operation, tube breaking, and CO_2 drying functions are performed manually. The Lalonde system is a hybrid; while we follow the steps of traditional tube sealing and graphitization methods, operation of the equipment itself is largely automated.

The AMS system on which the samples are analyzed is described in detail in Kieser et al. (2015). Aspects of this system relevant to the target preparation process are

- The ion source is a model SO-110B-200 manufactured by High Voltage Engineering, the Netherlands. Primary Cs sputtering beam energy is 7 keV and the target is well cooled by a flow of Syltherm through a cooling block immediately behind the target.
- For ^{14}C, the accelerator is operated at 2.5 MV and the C^{+3} charge state is selected for analysis, thus avoiding any interference from Li_2^- molecules

INSTRUMENTAL DESIGN

The tube sealing, CO_2 purification, and graphitization lines were constructed using many common components, as outlined in Table 1. In the subsequent section, each instrument is described from an operational standpoint, including the automated routines.

Structure

The frames are constructed with the 80/20® T-slotted aluminum building system, which is a sturdy material that is easy to cut and to connect together. T-slotted framing is light but strong, which is a necessary requirement as it houses the electrical components, computer, monitors, and the stainless steel vacuum line. For the graphitization lines, the framing also supports the cooling system, and 10 reactors with ovens.

Stainless Steel Vacuum Lines

The vacuum lines are built entirely of ½″ and ¼″ OD 316L stainless steel, using Swagelok® Micro-Fit® weld components and pneumatically actuated VCR bellows-sealed valves (Swagelok SS-4BK-VCR-1C). The stainless steel vacuum lines are orbital welded using a Swagelok SWS-M200 automated orbital welding and monitoring system in order to ensure flawless welds with smooth interior surfaces. Figure 1 shows the difference between the interior of stainless tubes that have been orbital welded versus traditional welding. The imperfections from traditionally welded joints create sites for reactions or adsorption of atoms or molecules and thus the potential for cross-contamination of samples and memory effects. In temperature critical areas, passivated stainless steel (e.g. Restek Silcosteel®) is used to eliminate active sites.

Table 1 Summary of common equipment design components described in the text.

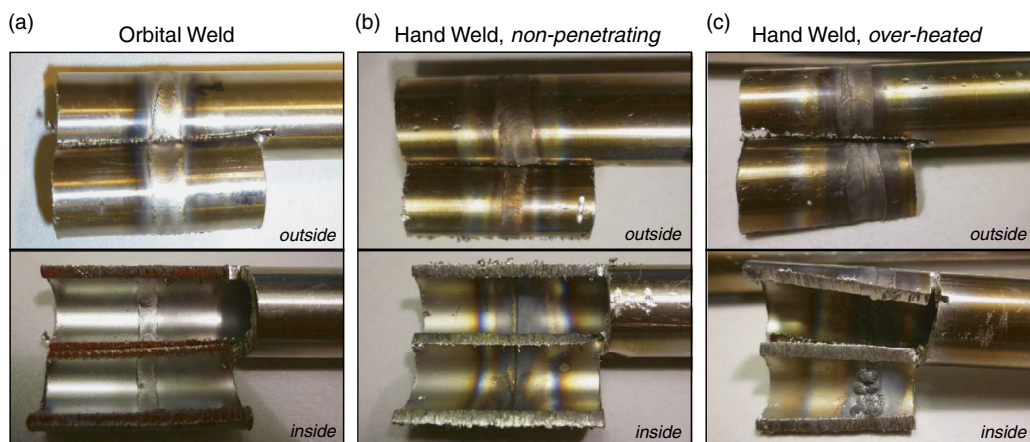|	Tube sealing	CO_2 purification	Graphitization
Structure (support frame)	✓	✓	✓
Stainless steel vacuum lines	✓	✓	✓
Software and controls	✓	✓	✓
Quantitative pressure measurement		✓	✓
Reactors			✓
Motorized cold traps		✓	✓
Ovens			✓
Automated routines	✓	✓	✓

Figure 1 Comparison of stainless steel welds: (a) smooth and complete weld by an orbital welder; (b) a nonpenetrating hand weld; and (c) an overheated hand weld.

The vacuum is achieved using a Pfeiffer HiCube® 80 Eco Turbo pumping station, which provides for oil-free pumping. This system contains an air-cooled and ready for operation HiPace® 80 turbo pump with an MVP 015 dry vacuum diaphragm backing pump. Each line is fitted with a Pfeiffer PKR 251 Compact FullRange™ Gauge read by the HiCube Display Control Unit (DCU-002) as well as the LabVIEW software. As the vacuum line can reach atmospheric pressure (new setup or with large samples), the pumping station was modified with a bypass valve (Swagelok SS-8BK-1O) to allow the diaphragm backing pump to circumvent the turbo in order to directly pump the system to a level that is safe for the turbopump (~30 mbar), thus eliminating the wait time for the turbopump to drop in speed for higher pressure pumping and the need for a secondary pump. On the graphitization line, the turbopump is also connected directly to a 1.6-L ballast volume, which allows individual reactors to be pumped directly from atmospheric pressure without causing the turbopump to trip. When initial pumping of the iron is needed, a slow pumping valve (Swagelok SS-4BK-VCR-1C) with a 1/16″ outer diameter (OD), 0.040″ inner diameter (ID) tubing has been added to the bypass to reduce the vacuum shock, thus preventing the iron from being blown out.

Software and Controls

The electronics box for each instrument houses the components for the pneumatic valves, vacuum gauges, pressure transducers, and ovens. The "brain" of the system is a National Instruments™ CompactRIO™ with specific modules (e.g. Thermocouple read, Digital I/O, etc.) interfaced to the LabVIEW control software on the computer. The CompactRIO has the capability of functioning even if communication is lost with the main computer, which is an important feature for sample protection. The system is based on National Instruments' latest LabVIEW platform (2014) compatible within multiple versions of the Microsoft® Windows® environment. It allows monitoring and data storage of operating variables to increase the QA/QC tracking of samples and processes. The software is controlled through a touch-screen monitor on all systems, while on the graphitization line a secondary monitor is used to display the pressure and temperatures (oven and cooling), and to input data. With the software accessible through the touch-screen monitor (Figure 2), the user can manually control the valves, temperature of the ovens and cooling cups, as well as the valves for the preparation gases, H_2, O_2, and Ar. Safety protocols are programmed into
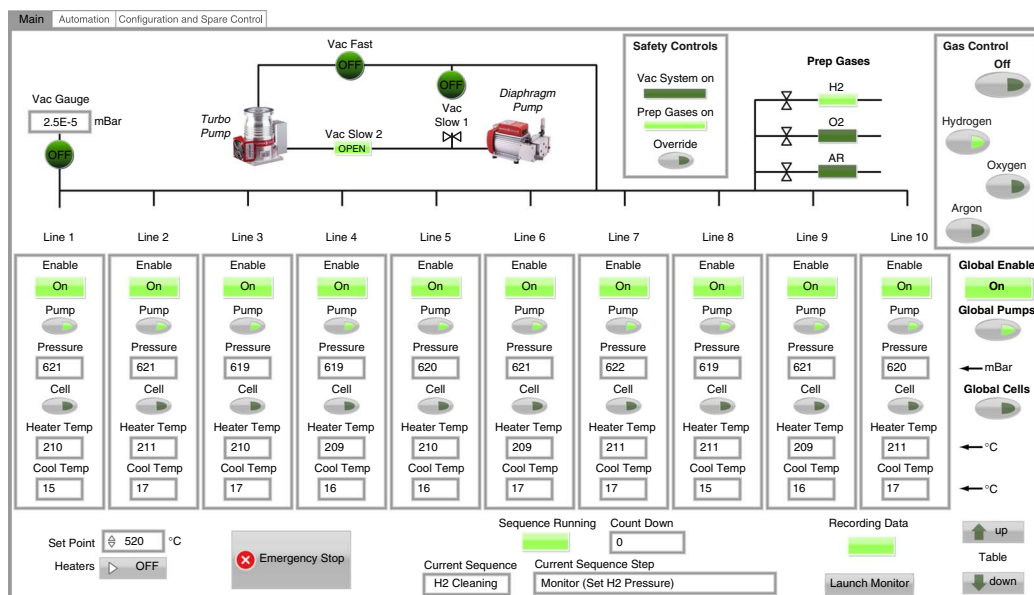
Figure 2 Main LabVIEW interface used to control the graphitization lines. The configuration presented here shows the reaction cells being filled with hydrogen through the manifold during the automated iron conditioning routine. Once the reaction cells have reached 700 mbar, the pump valves will close, the hydrogen gas is shut off, and the heaters (currently showing residual heat from the oxidation step) will ramp up to 520°C. At this stage, the *Cool Temp* is reading room temperature since the circulator pump on the cooling system is not yet turned on.

the software to prevent the user from making accidental mistakes (e.g. opening gases and pump at the same time), thus preventing sample loss and ensuring the turbopump does not experience dramatic pressure shifts.

Quantitative Pressure Measurement

The CO_2 purification and graphitization lines have calibrated volumes with solid-state absolute pressure transducers for quantitative measurement. The graphitization line has a pressure transducer on each sample reactor (Omega[TM] PX319-030A5V) to monitor the reaction and to facilitate quantitative gas filling to a maximum of 2100 mbar (pCO_2 equivalent of a 4 mg C sample plus hydrogen at $2.5 \times pCO_2$). Although much smaller samples are targeted (1 mg C), the upper range on the pressure transducer allows the quantification of a larger sample that may require splitting. However, to avoid splitting samples on the graphitization line, the appropriate sample mass for combustion is based on measured (by elemental analyzer) or estimated carbon content. Larger samples are sometimes produced during quartz tube combustion (e.g. underestimated carbon content in bulk sediment) and for this reason, each of the 10 ports on the CO_2 purification line has a calibrated volume with higher tolerance absolute pressure transducers (3400 mbar max.; Omega PX319-050A5V). Again, this issue is minimized by routinely running a quantitative analysis of unknown samples, such as soils or sediments, through the elemental analyzer.

Reactors

The volume of each reactor on the graphitization lines is 11 mL. This includes: the vertical Pyrex[®] water trap and the horizontal quartz reactor tube (both are 67 mm long; 7 mm ID; 9 mm OD), the Ultra-Torr 3/8″ tee, Micro-Fit Tribow, and pressure transducer. The reactors have a fairly standard

design (Figure 3c), except each reactor is attached to its own cracker assembly (Figure 3b) for sample introduction so that all 10 CO_2 samples can be released and trapped into the reactors at the same time. This process is much faster than transferring each sample individually from a common bellows cracker that has to be opened to atmosphere and pumped down between each sample.

Motorized Cold Traps

The CO_2 purification line and graphitization line are equipped with linear track actuators (Firgelli Automations, FA-450-TR-24-10) attached to platforms to raise and lower cold traps. The controls
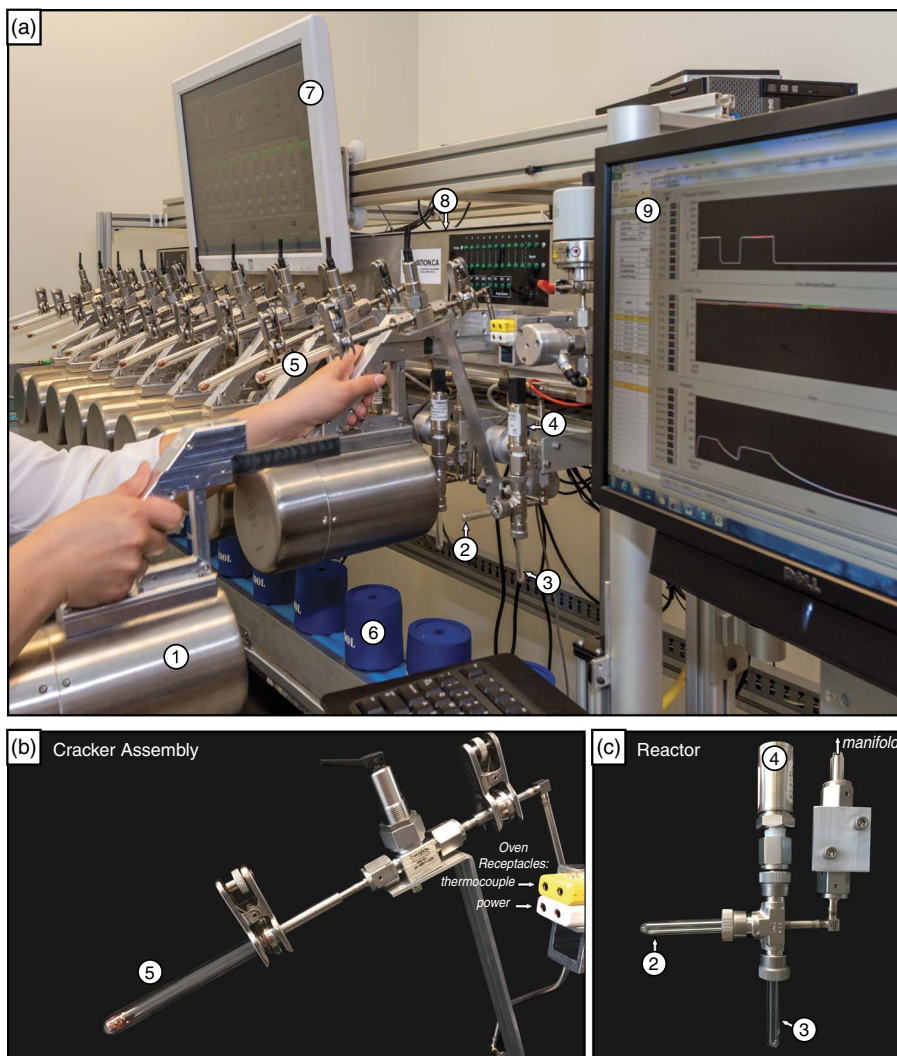
Figure 3 (a) Photograph of the graphitization line with an oven (1) removed to show the quartz reaction tube with Fe powder (2), the water trap (3), and pressure transducer (4). (5) Rotulex cracker assembly (glass joint tube with Cu turnings at the bottom to cushion the movement of the breakseal); (6) cooling cups for water removal; (7) touch-screen monitor (LabVIEW controls) mounted on rollers above the electronics box (8), and (9) the second display showing the monitoring software for pressure (top), cooling bar temperature (middle), and heater temperature (bottom). (b) and (c) show a closer look at the cracker and reactor assemblies, respectively (numbers the same as in a).

are hard wired into the electrical boxes and interfaced with the software making operation a simple touch of a button. There is also the possibility of incorporating the raising and lowering of the cold traps into the automated routines. For the CO_2 purification line, the cold trap Dewars are filled manually with either liquid nitrogen or an –80°C ethanol-liquid nitrogen slurry.

For water removal during graphitization, the motorized cold trap table (Figure 4a) has 10 cooling cups connected to a closed loop cryogenic system consisting of a chiller (FTS Systems Multi-Cool® Ultra-Low Temp Bath, MC880A1) and circulator (Oberdorfer™ Pumps, Chemsteel® Series, DC magnetic gear pump with variable speed control, SM-104). The chiller, filled with Dynalene HC-50, is capable of cooling down to –50°C; however, –40°C is sufficient to effectively remove water under the reaction conditions, as seen in the phase diagram for water (Figure 4b). This temperature is also sufficient to ensure that the water will remain frozen when the system is evacuated after graphitization is complete. The water trap tubes are changed between each use. A mix of rigid and flexible Swagelok tubing connects the entire closed-loop system where a custom lid on the chiller ensures an air-tight seal with a weekly argon flushed headspace. The chiller can be turned on automatically with a LabVIEW routine, through RS-232, that has a date/time entry allowing for the system to cool in advance of the operator arriving in the morning, thus saving time for the system to reach –40°C.

The circulator pumps the chilled Dynalene through stainless tubing in a closed-loop system until it reaches the table, where it flows in parallel through a copper coil in each of the 10 cooling cups as shown in the inset of Figure 4a. Each of the cooling cups is filled with ethanol, which is cooled to –40°C by the copper coils. A thermocouple welded to the exterior of the copper cup monitors the temperature of each of the 10 cups. The cooling system is heavily insulated to prevent heat gain. The closed-loop cooling system ensures clean, uniform cooling for water removal throughout the graphitization reaction with no need for replenishing open cup cooling baths. This also eliminates the atmospheric condensation and dripping common to open bath systems.

Ovens

The ovens were designed to be safe and easy to use. Ceramic fiber heaters (Zesta Engineering Ltd., cat#VC400J06A) are wrapped in 3.5–4 cm of glass fiber insulation, which is then packed into
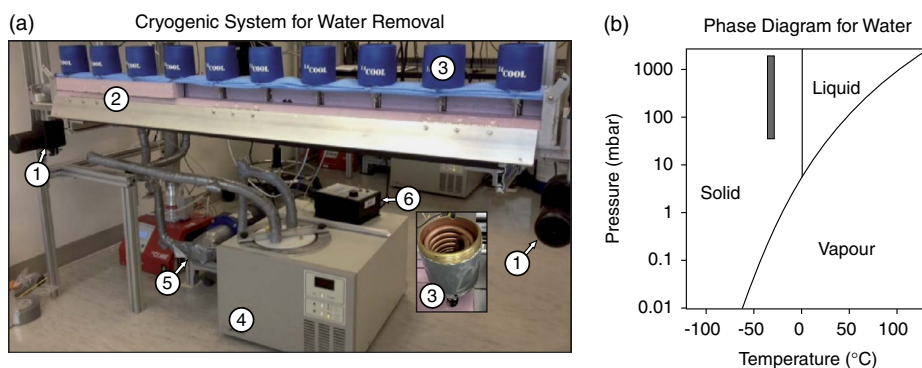

Figure 4 (a) Cryogenic system for water removal with the front cover open and part of the insulaton removed to show the feed lines to the 10 cooling cups. The labeled parts are as follows: (1) linear track actuators to raise and lower the cold trap table (2); (3) cooling cups (inset showing copper coil); (4) chiller containing Dynalene at –40°C; (5) circulator; (6) circulator speed control. (b) Phase diagram for water: the vertical gray bar denotes the temperature and range in pressure conditions experienced by the H_2O produced during the graphitization reaction.

modified 1.9-L stainless steel Bain Marie pots (Vollrath®, #78720) purchased from a kitchen supplier. When the ovens are heated to 650°C (reactor internal temperature = 550°C), the ovens are warm to the touch, but cannot cause burns. Although the ovens can achieve a temperature of 1200°C, the software will only permit a maximum temperature of 800°C. The thermocouple is calibrated to reflect the temperature inside the quartz tube (containing the Fe powder) and fitted inside each oven to where it nearly reaches the tip of the quartz tube. The ovens are programmed with a proportional–integral–derivative (PID) function to slow down the rate of heating upon nearing the set temperature in order to prevent overheating. Any break or disconnect of the thermocouple will display a default temperature of 1372°C, well above any set temperature; this disconnects the power to the ovens, thus preventing runaway heating. When the ovens are not in use, they are simply disconnected from the electronics box and stowed in a rack bolted to the side of the 80/20 frame. The thermocouple and power connections are contained within the oven handle and therefore eliminate the need for long cables to keep organized.

INSTRUMENT OPERATION

The operation of the graphitization lines is more complex than the tube sealing and CO_2 purification lines and is therefore described here in detail. The operation of the tube sealing and CO_2 purification lines are subsequently described in brief.

Graphitization

The graphitization lines are controlled through the touch-screen monitor shown in Figure 3. The vacuum schematic on the screen display is shown in Figure 2. The software currently contains the following safety interlocks:

1. *Vac slow 1* and *Vac fast* valves cannot be open when *Prep Gases* (H_2, O_2, Ar) are in use and vice versa, as the prep gases are introduced to each reactor via the pumping manifold.
2. Only one prep gas valve can be open at a time.
3. The roughing pump must back the turbo when in use; thus, the *Vac Slow 2* valve must be open when *Vac Fast* is open and *Vac Slow 1* must be closed.
4. Valves must be *Enabled* before use (valves are disabled as a safety precaution during maintenance).
5. *Emergency Stop* closes all valves and turns off heaters.

Each reactor (labeled as lines 1–10 on Figure 2) is equipped with two pneumatic valves plus a manual Swagelok toggle valve to minimize exposed volume while loading CO_2 sample breakseals (Figure 3b). The pneumatic valves are equipped with 20-μm SS sintered VCR filters and the toggle valves are equipped with 60-μm SS sintered VCR filters to prevent particles from entering the system. The *Pump* valve isolates the reactor from the pumping manifold and the *Cell* valve isolates the reactor from the breakseal cracker assembly. On the right-hand side of the display are three *Global* controls, which are used to perform a specific action on all *Enabled* lines simultaneously.

The graphitization lines can produce 10 graphite samples at a time by reduction with H_2 over an iron catalyst (Vogel et al. 1984). The entire process (outlined in Figure 5) takes approximately 6 hr, but in the future this time will be reduced after performing optimization experiments. The operation can be divided into four components: (1) vacuum check after Fe and sample loading; (2) iron conditioning; (3) sample transfer; and (4) graphitization.
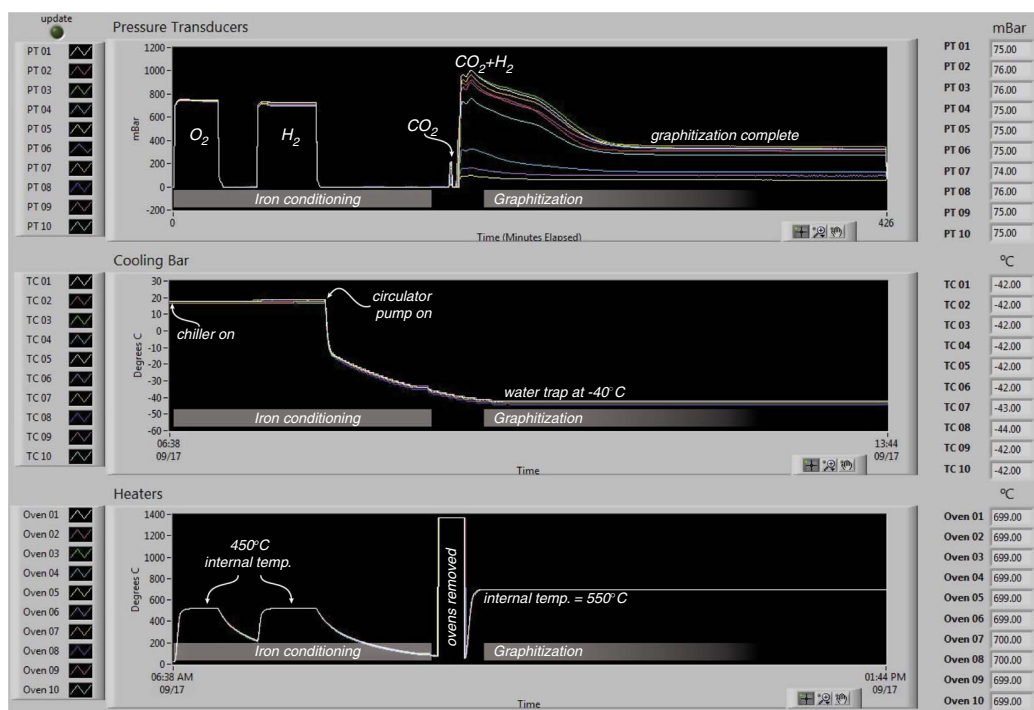
Figure 5 Monitoring software for the graphitization line. The main phases of graphitization are labeled on the plot of the pressure transducers (top), reading left to right: Fe oxidation (O_2); pumping; Fe reduction (H_2); pumping; sample release (CO_2); addition of H_2; graphitization. The middle plot shows the temperature of each cooling cup, and the bottom plot shows the temperature of each heater. Each plot shows the time in a different manner: start to finish in minutes (top); start time using 24-hr clock (middle); start time using AM/PM (bottom).

Initially, we were using 6 mg of iron powder (Alfa Aesar®, –200 mesh, 99+%, CAS7439-89-6, P/N: 00737), but we found that unless the samples had greater than 2 mg C, only part of the iron (the side closest to the Cajon® connection) would be coated with black graphite and the rest sintered into a pellet. Routine samples are now between 0.5 and 1.5 mg C where a reduction of the iron to 5 mg is warranted, also making sintering less problematic. Once the quartz tube containing the iron and the Pyrex tube for the water trap are inserted and tightened into the Cajon connections, the reactors are evacuated using *Vac Slow*. The sample breakseals (6-mm Pyrex, etched with sample numbers) are wiped clean with a Kimwipe® and methanol to remove traces of contaminants and fingerprints, scored, and, with the manual toggle valve closed to minimize the volume exposed to atmosphere, loaded into the female side (Pyrex) of the Rotulex cracker, which is clipped onto the male side (stainless steel). The Viton® O-ring separating the two sides of the Rotulex must be immaculately clean (no grease used); otherwise, there will be a leak. With the breakseal loaded, the toggle valve and cell valves are opened to pump down the entire port using *Vac Slow*. Once the pressure reaches 30 mbar, the *Vac Slow 1* valve is closed (which automatically opens the *Vac Slow 2* valve), and the *Vac Fast* valve is opened to pump the system with the turbo. An automated leak check routine ensures the vacuum drops below 10^{-3} mbar after 5 min and, if not, the routine will check how the vacuum holds for each section of the line and reports back to the user with potential locations for leaks. Once all leaks have been resolved, the ovens are slotted into place. Due to convenience, the system is left to pump overnight, although baseline vacuum (low 10^{-5} mbar range) is usually reached within an hour or

two. As shown in Figure 3, copper turnings (99+%, Alpha Aesar cat#10161) cushion the breakseal in the cracker assembly and, although the turnings have a large surface area and could potentially contribute to a memory issue, they are pumped overnight with the rest of the system and refreshed regularly.

After the graphitization line has been pumped overnight, it should reach the low 10^{-5} mbar range. If not, another leak check is performed. When the system is leak-tight, the automated iron conditioning routine is employed:

1. Fill reactors with 700 mbar O_2, bake at 520°C (reactor internal temp = ~450°C) for 20 min;
2. Ovens off, pump 20 min;
3. Fill reactors with 700 mbar H_2, bake at 520°C for 30 min;
4. Pump 1 hr; and
5. Prompt user to begin releasing CO_2 samples for graphitization.

During the pumping steps, the system is first pumped with *Vac Slow 1* until the pressure reaches 30 mbar before switching to *Vac High*. If the pressure does not reach 30 mbar within a set time, an error message prompts the operator to check on the system. Figure 6 shows the automation tab on the display, which is used to start, stop, continue, and modify the automated routines.

In preparation for releasing the CO_2 into each reactor, the ovens are removed, the pump valves are closed (by selecting *Global Pumps*) and Styrofoam^{TM} cups filled with liquid nitrogen are placed under each water trap tube and raised using the Cooling Table *UP* button on the touch-screen or by a manual switch on the electronics box. The pre-etched breakseals are

Figure 6 Automation tab on the display, generated by the LabVIEW software. In this scenario, the iron conditioning routine is at the hydrogen cleaning step.

cracked one-by-one by gently bending the Rotulex at the joint to put pressure on the glass score. The following routine is then performed:

1. The CO_2 is left to freeze for 60 s at the tip of the water trap, immersed in liquid nitrogen;
2. The cooling bar is raised 1 cm to ensure complete trapping of the CO_2 for another 60 s;
3. Cell valves are all closed (*Global Cells*) to isolate the CO_2 in the individual reactors; if there is a pressure from noncondensable gases, it is recorded in the Excel file;
4. Individually, the *pump* valves are opened briefly (few seconds max) to remove any excess noncondensable gases, then closed;
5. The liquid nitrogen is then lowered and the pCO_2 is recorded for each cell at room temperature;
6. The liquid nitrogen is again raised and steps 1 and 2 are repeated refreeze the CO_2;
7. Starting with the lowest pCO_2, H_2 is automatically added, in order from the lowest to the highest sample pCO_2, one cell at a time at 2.5 times the registered pCO_2;
8. The liquid nitrogen is lowered and the combined pressure of the CO_2 and H_2 are recorded;
9. The ovens are re-inserted and set to 650°C (reactor internal temp ~550°C); and
10. The cooling table is fully raised to immerse the water traps in ethanol cooled to –40°C.

The samples are left to graphitize for 3 hr, although we have observed from our monitoring display (Figure 5) that the pressure flat lines in well under 3 hr. The graphitization temperature of 650°C (reactor internal temp ~550°C)—determined empirically by differentiating the temperature between ports and monitoring the rate of reaction for a few batches of samples—is within the common range of 600–650°C recommended by other labs (e.g. Vogel et al. 1984; Hut et al. 1986; Arnold et al. 1987; McNichol et al. 1992; Kitagawa et al. 1993; Sie et al. 1994; Aerts-Bijma et al. 1997; Kretschmer et al. 1997; Pearson et al. 1998). Santos et al. (2007) report a graphitization temperature of 550°C for 0.1–1.0 mg C samples, although it is unclear if the reported temperature reflects the actual temperature in the reactor or if it is the set temperature of the ovens.

When the graphitization is complete, the ovens are turned off and removed. Once the reactor tubes are cool, the final pressures are recorded. The residual hydrogen is pumped away and the reactors are subsequently filled with argon to atmospheric pressure for easy removal from the line. The tubes (containing the samples) are labeled with the UOC-#### and covered with prebaked aluminum foil and Parafilm® for storage in a desiccant cabinet. Currently, the longest time the graphitized samples will sit in the desiccant cabinet does not typically exceed 2–3 weeks. With three graphitization lines now in operation and a capacity of 200 targets per sample wheel on the AMS, the graphitized samples will normally never wait more than 1–2 weeks before analysis.

Tube Sealing

The tube sealing line consists of a linear 15-port vacuum manifold, a vacuum gauge and a Dell 24″ touch screen computer with LabVIEW control for the pneumatic valves. Cajon connections hold 9-mm-OD quartz tubes, although the system is currently being adapted for 6-mm-OD quartz tubes as they are easier to seal and have less surface area. A horizontal stainless steel shield has been installed just below the Cajon connectors to protect the pneumatic tubing from the heat of tube sealing, which is performed on the 9-mm tubes with a double-tipped (National, TW-4 Flame Head, OX-4 tips) oxy-propane torch (National, 3B-B). The only

automated routine necessary on the tube sealing line is for leak checking after pumping down a new batch of quartz tubes.

CO_2 Purification

The CO_2 purification line (Figure 7) can purify 10 gas samples at a time and, as a stand-alone system, allows the graphitization line to be kept clean of dust and debris from CuO and samples. The operation can be divided into four components: (1) quartz tube cracking (sample release); (2) cryogenic purification; (3) quantitative measurement; and (4) sealing breakseals.

The 9-mm quartz breakseal tubes are scored 360° using a scoring tool, loaded into stainless steel crackers, and evacuated to 10^{-5} mbar. The crackers were designed by modeling the quartz Rotulex equivalent in stainless steel, which will withstand years of cracking quartz tubes. VCR 60-μm filters protect the valves from damage and from particles entering the system. The water trap Dewar, filled with ethanol slurry at –80°C, is raised using the motorized lift followed by the sample release in the cracker. The CO_2 passes through the water trap and is frozen in the quantitative trap using liquid nitrogen. After 2–3 min, the noncondensable gases are pumped away. The sample is isolated in the quantitative trap where the pCO_2 is measured at room temperature in the calibrated volumes and converted to mg C. For now, the ideal sample size for the ion source is 0.5–1.5 mg C; if the sample is too large, it is split at this stage. Once the purified CO_2 has been measured, it is transferred to a 6-mm Pyrex breakseal using liquid nitrogen and sealed with a single-tipped oxy-propane torch.

The automated routines on the CO_2 purification line include (1) leak checking for the cracker assembly and the Pyrex breakseals, and (2) a routine for CO_2 purification and quantitative measurement.
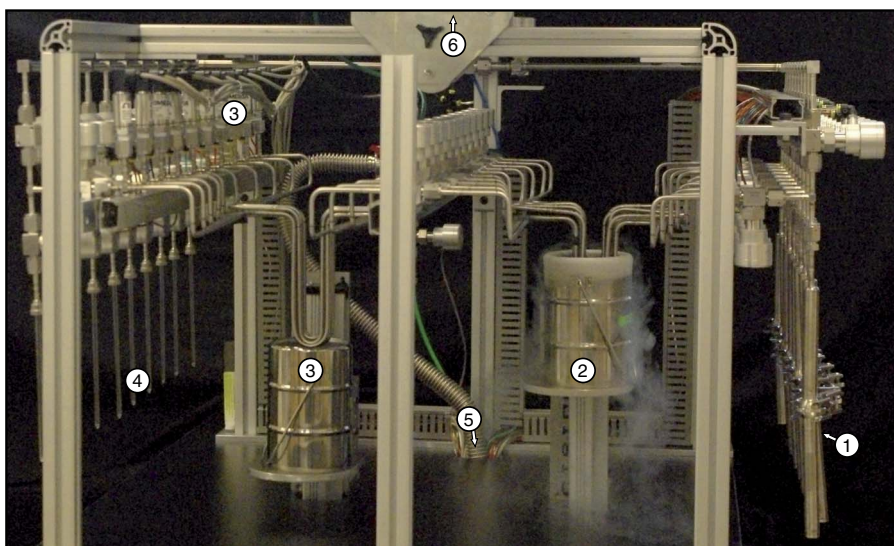

Figure 7 CO_2 purification line: (1) stainless steel Rotulex crackers containing samples in quartz breakseal tubes; (2) cleaning trap, shown here filled with liquid nitrogen, but usually filled with –80°C ethanol slurry; (3) quantitative trap consisting of a Dewar on a linear track actuator and pressure transducers; (4) Pyrex breakseals for clean CO_2; (5) vacuum tube and arrow pointing toward HiCube pumping station under the table; (6) monitor stand (on wheels connected to 80/20 frame) and arrow pointing to touch-screen monitor with LabVIEW software (not shown).

Target Pressing

Graphitized samples are front loaded into an aluminum target piece in a draft-free enclosure using a loading module, which positions the copper back-pressing pin and includes a stainless steel funnel to guide the material into the 1.3-mm-diameter hole in the target piece. The funnel is then replaced by a cap and ball bearing (4.8 mm diameter) assembly, which forms the surface of the target. The module is then placed in a pneumatic press (designed and constructed in-house), which compresses the sample material and swages the copper press pin into place behind the material, with a pressure on the pin that is adjustable up to 2.4 GPa. In between samples, the module is dismantled and dusted off with high-pressure nitrogen. After 4–5 samples, the press module pieces are sonicated in methanol and dried with high-pressure nitrogen. The funnels, ball bearings, and packing tools are in direct contact with the graphitized material and are therefore only used once before being dusted off with nitrogen and sonicated in methanol. In the ^{14}C lab, there are two sets of modules and more than 10 each of the funnels, ball bearings, and packing tools so pressing time is not hampered by cleaning. Pressed targets are screwed onto stainless steel bases, organized in numbered aluminum trays, and kept under a weak vacuum in a desiccant cabinet for no more than 2 weeks until brought to the accelerator for analysis.

RESULTS

Results from the first year of routinely measured standards, reference, and background material are reproducible and within acceptance values as shown in Table 2. For more detail, please see Crann et al. (2016). In addition to the quality control samples shown in Table 2, preconditioned (oxidized and reduced) iron is run with every wheel to monitor the blank on the iron and to create a buffer between Ox-II samples and unknowns. Typically, the Fe-only blank produces two $^{14}C^{+3}$ counts per minute under ion source conditions that produce an average 30 μA $^{12}C^{+3}$ from Ox-II targets containing 1 mg C.

Graphitization Line Memory

To assess graphitization line memory, two batches of acetanilide (background) were combusted and graphitized. The first batch was run after a batch of Ox-II (134 pMC) and the second batch

Table 2 Results for blank and reference materials tested during the first year of operation. References: IAEA (Rozanski et al. 1990; Rozanski 1991); AVR-07-PAL-37 (Reyes et al. 2010); Hollis Mine mammoth [constrained by ~700-ka glass-fission track age on tephra from Westgate et al. (2011), and Valley Creek tephra from Jensen et al. (2013)].

| Sample	Material	n	Measured value (^{14}C yr BP)	Reference value (^{14}C yr BP)	Measured value (pMC)	Reference value (pMC)
IAEA-C1	Cararra marble	15	$55,630 \pm 900$	Background	0.13 ± 0.01	0.00 ± 0.02
IAEA-C2	Travertine	14	7103 ± 42	7129–7141	41.30 ± 0.22	41.14 ± 0.03
IAEA-C3	Cellulose	6	Modern	Modern	129.92 ± 0.39	129.41 ± 0.06
IAEA-C4	Kauri wood	30	$47,660 \pm 450$	43,588–49,922	0.28 ± 0.02	0.20–0.44
IAEA-C5	Two Creeks wood	17	$11,830 \pm 70$	11,780–11,800	22.93 ± 0.19	23.05 ± 0.02
AVR-07-PAL-37	Wood	5	$54,190 \pm 590$	Background	0.12 ± 0.01	Background
Hollis Mine	Mammoth bone	5	$51,130 \pm 520$	Background	0.19 ± 0.01	Background
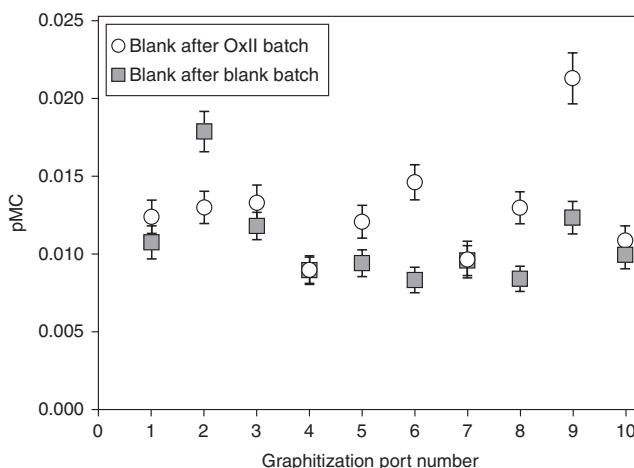
Figure 8 Memory test results for one of the graphitization lines at the University of Ottawa (referred to as G2 in the lab).

was run after the first batch (Figure 8). All of the samples were ~1 mg C, except the port 9 post-Ox-II sample, which was only 0.6 mg C. Acetanilide samples run after Ox-II were an average of 0.03 pMC higher than the second batch of acetanilide. The memory effect is therefore 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. For comparison, 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. It is therefore good practice to graphitize old or small samples after a batch of iron blanks or ^{14}C "dead" material. We do not accept samples with elevated ^{14}C, nor do we process swipes through the graphitization line (run by liquid scintillation), so there is no fear that the memory could be any higher on a different batch.

DISCUSSION AND CONCLUSIONS

In the first year of operation (2014–2015), well over 1000 targets (~60% unknowns) were produced using our prototype graphitization line, of which there are now five in operation: three at the University of Ottawa and one each at labs in Québec: the Centre d'Études Nordiques (Université Laval) and GEOTOP (Université du Québec à Montréal). Numerous students have processed their own samples, and we find that after 1–2 batches, thanks to the automation, students are able to graphitize their own samples with little supervision.

Until recently, an elemental analyzer interfaced to a manual extraction line was used to combust and purify CO_2. This setup has the advantage of obtaining C:N ratio data, although each sample takes 16 min—8 min for the sample plus 8 min for a blank (empty) capsule—an operator can only reasonably produce 20 breakseals in 1 day. With the transition toward individual sample quartz tube combustion, less operator time is required as samples can be baked and purified in large batches, as opposed to one at a time with the elemental analyzer. Either way, once the sample is ready for graphitization, the size is known and the CO_2 requires no further purification. Large batches of oxalic acid and sugar (beam tuning) can be prepared in advance during slow periods and graphitized a day or two before being run on the accelerator.

The LabVIEW software for controlling the valves, gases, ovens, and cooling systems has streamlined the graphitization process considerably as compared to manual methods. The display is very visual with open valves lighting up and closed valves staying dark, and this information is duplicated by the physical lights on the electronic panel. The user can easily scan over the vacuum system to ensure the correct valves are open or closed before continuing to the next step. So far, the software interlocks have kept the turbopumps safe and the intuitive nature of the touch-screen controls has prevented any samples from getting pumped away or cross-contaminated.

The process of graphitization is time consuming as it involves many steps, each of which require the full attention of the technician. With the semi-automated equipment at the A.E. Lalonde AMS Laboratory, much time is saved using automated routines for leak checking and iron conditioning, operator error is reduced, and the iron is always prepared in exactly the same way.

An overview on the technical specifics and operations of new semi-automated tube sealing, CO_2 purification, and graphitization lines has been presented. Crann et al. (2016) present results from the first year of ^{14}C measurements on routinely measured standards and blanks. With the new semi-automated tube sealing and CO_2 purification systems online, as well as three graphitization lines in operation, the Lalonde AMS Laboratory will be able to provide routine ^{14}C analysis (>200 µg carbon) at a capacity of more than 7000 targets per year.

FUTURE WORK

With the ^{14}C laboratory fully operational, the focus is now on adjusting equipment operation protocols and development of new techniques. Taking into consideration the points discussed by Turnbull and Prior (2010), future work includes the following:

1. Testing of iron powders (mesh size, suppliers) in light of Santos et al. (2007);
2. Identifying the factors causing iron sintering (iron mesh size, iron conditioning routine, Fe: C ratio, graphitization temperature, etc.);
3. Optimization of the iron conditioning routine (time, temperature) and graphitization reaction (temperature, Fe:C ratio) as was done by Němec et al. (2010) for the Automated Graphitization Equipment (AGE) system;
4. Reducing static cling of graphite inside reaction tube (label tubes differently, use NaOH in storage cabinet instead of desiccant cartridge, use Pyrex tubes in reactor instead of quartz);
5. Scanning electron microscope (SEM) analysis of graphite morphology under varying graphitization conditions (temperature, Fe:C ratio, irfon mesh size, C:H_2 ratio);
6. Quantify graphite yield by weighing the Fe on a microbalance before and after the reaction and comparing it to the amount of carbon in the sample as calculated by both the pCO_2 measurement;
7. Small sample development: reduction of the quartz tube volume, reduction of graphitization reactor volume (including pressure transducers), lowering of water trap temperature (Turnbull and Prior 2010), and modification and optimization of ion source; and
8. Integration of the CO_2 purification line with a headspace autosampler for carbonates, waters (DIC, DOC), and field-sampled gases; memory test on the CO_2 purification line.

ACKNOWLEDGMENTS

REFERENCES

Aerts-Bijma AT, Meijer HAJ, van der Plicht J. 1997. AMS sample handling in Groningen. *Nuclear Instruments and Methods in Physical Research B* 123(1–4):221–5.

Aerts-Bijma AT, van der Plicht J, Meijer HAJ. 2001. Automatic AMS sample combustion and CO_2 collection. *Radiocarbon* 43(2):293–8.

Arnold M, Bard E, Maurice P, Duplessy J-C. 1987. ^{14}C dating with the Gif-sur-Yvette Tandetron accelerator: status report. *Nuclear Instruments and Methods in Physical Research B* 29(1–2):120–3.

Crann CA, Murseli S, St-Jean G, Zhao X-L, Kieser WE. 2016. First status report on radiocarbon sample preparation techniques at the A.E. Lalonde AMS Laboratory (Ottawa, Canada). *Radiocarbon*, this issue. DOI:10.1017/RDC.2016.55.

Hut G, Göte Östlund H, van der Borg K. 1986. Fast and complete CO_2-to-graphite conversion for ^{14}C accelerator mass spectrometry. *Radiocarbon* 28(2A):186–90.

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.

Kato K, Tokanai F, Anshita M, Sakurai H, Ohashi MS. 2014. Automated sample combustion and CO_2 collection system with IRMS for ^{14}C AMS in Yamagata University, Japan. *Radiocarbon* 56(1): 327–31.

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.

Kitagawa H, Masuzawa T, Nakamura T, Matsumoto E. 1993. A batch preparation method for graphite targets with low background for AMS ^{14}C measurement. *Radiocarbon* 35(2):295–300.

Kretschmer W, Anton G, Bergmann M, Finckh E, Kowalzik B, Klein M, Leigart M, Merz S, Morgenroth G, Piringer I. 1997. The Erlangen AMS facility: status report and research program. *Nuclear Instruments and Methods in Physics Research B* 123(1–4):93–6.

Law IA, Hedges REM. 1990. A semi-automated bone pretreatment system and the pretreatment of older and contaminated samples. *Radiocarbon* 31(3):247–53.

McNichol AP, Gagnon AR, Jones GA, Osborne EA. 1992. Illumination of a black box: analysis of gas composition during graphite target preparation. *Radiocarbon* 34(3):321–9.

Němec M, Wacker L, Gäggeler H. 2010. Optimization of the automated graphitization system AGE-1. *Radiocarbon* 52(2–3):1380–93.

Pearson A, McNichol AP, Schneider RJ, von Reden KF, Zheng Y. 1998. Microscale AMS ^{14}C measurement at NOSAMS. *Radiocarbon* 40(1): 61–75.

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.

Santos GM, Mazon M, Southon JR, Rifai S, Moore R. 2007. Evaluation of iron and cobalt powders as catalysts for ^{14}C-AMS target preparation. *Nuclear Instruments and Methods in Physical Research B* 259(1):308–15.

Sie SH, Leaney F, Gillespie R, Suter GF, Ryan CG. 1994. Radiocarbon measurements at the CSIRO AMS facility. *Nuclear Instruments and Methods in Physics Research B* 92(1–4):35–8.

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.

Turnbull J, Prior C. 2010. Report on the 20th International Radiocarbon Conference graphitization workshop. *Radiocarbon* 52(2–3):1230–5.

Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research B* 5(2):289–93.

Wacker L, Němec M, Bourquin J. 2010. A revolutionary graphitisation system: fully automated, compact and simple. *Nuclear Instruments and Methods in Physics Research B* 268(7–8): 931–4.

Wacker L, Fülöp RH, Hajdas I, Molnár M, Rethemeyer J. 2013. A novel approach to process carbonate samples for radiocarbon measurements with helium carrier gas. *Nuclear Instruments and Methods in Physics Research B* 294:214–7.

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