Progress in automated extraction and purification of *in situ* ^{14}C from quartz: Results from the Purdue *in situ* ^{14}C laboratory

Nathaniel Lifton^{1,2,*}, Brent Goehring^{1,**}, Jim Wilson³, Thomas Kubley², Marc Caffee²

1 Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana, 47907, USA. E-mail: nlifton@purdue.edu

2 Department of Physics and Astronomy and Purdue Rare Isotope Measurement Laboratory (PRIME Lab), Purdue University, 525 Northwestern Avenue, West Lafayette, Indiana, 47907, USA.

3 Aeon Laboratories, LLC, 5835 North Genematas Drive, Tucson, Arizona, 85704, USA. E-mail: jim.wilson@aeonlaboratories.com

* *Corresponding Author*

** Now at: Department of Earth and Environmental Sciences, Tulane University, 6823 St Charles Avenue, New Orleans, Louisiana, 70118, USA. E-mail: bgoehrin@tulane.edu

Abstract

Current extraction methods for *in situ* ^{14}C from quartz [e.g., 1, 2, 3] are time-consuming and repetitive, making them an attractive target for automation. We report on the status of *in situ* ^{14}C extraction and purification systems originally automated at the University of Arizona that have now been reconstructed and upgraded at the Purdue Rare Isotope Measurement Laboratory (PRIME Lab). The Purdue *in situ* ^{14}C laboratory builds on the flow-through extraction system design of Pigati et al. [2], automating most of the procedure by retrofitting existing valves with external servo-controlled actuators, regulating the pressure of research purity O_2 inside the furnace tube via a PID-based pressure controller in concert with an inlet mass flow controller, and installing an automated liquid N_2 distribution system, all driven by LabView[®] software. A

separate system for cryogenic CO_2 purification, dilution, and splitting is also fully automated, ensuring a highly repeatable process regardless of the operator. We present results from procedural blanks and an intercomparison material (CRONUS-A), as well as results of experiments to increase the amount of material used in extraction, from the standard 5 g to 10 g or above. Results thus far are quite promising with procedural blanks comparable to previous work and significant improvements in reproducibility for CRONUS-A measurements. The latter analyses also demonstrate the feasibility of quantitative extraction of in situ ^{14}C from sample masses up to 10 g. Our lab is now analyzing unknowns routinely, but lowering overall blank levels is the focus of ongoing research.

Keywords: carbon-14; cosmogenic; carbon isotopes; automation techniques

1.0 – Introduction

Extracting in situ cosmogenic ^{14}C (in situ ^{14}C) from quartz is a challenging endeavor: minute quantities of ^{14}C must be extracted and purified from quartz samples while maintaining scrupulous isolation from ubiquitous atmospheric/organic ^{14}C . Building on procedures developed for extraction of in situ ^{14}C and stable carbon species from meteorites and basaltic glasses [e.g., 4, 5-7], Lifton et al. [1] presented techniques for quantitative extraction of in situ ^{14}C from quartz using degassed lithium metaborate (LiBO_2) as a flux to dissolve quartz at 1100°C in a stream of Research Purity O_2 (99.999%), oxidizing all C-species to CO_2 . Although workable, these techniques are quite labor-intensive and time-consuming, requiring up to ca. 20 man-hours to process a quartz sample into a graphite target for analysis by accelerator mass spectrometry (AMS). Alternate methods published to date that involve high-temperature extraction of ^{14}C from quartz are similarly time-consuming [e.g., 2, 3, 8, 9]. Automating these procedures would make lab personnel more efficient and increase analytical reliability, offering the potential for significantly increasing lab throughput and helping to raise the profile of in situ ^{14}C as a tool for surficial process studies.

After significant effort, the in situ cosmogenic ^{14}C laboratory at the Purdue Rare Isotope Measurement Laboratory (PRIME Lab) is now operational, with fully automated procedures for extraction and CO_2 purification. Below we describe the design and implementation of these automated systems, and present some early results.

2.0 – System Description

The Purdue in situ ^{14}C laboratory has two identical high-temperature extraction systems and one CO_2 purification system, based on the flow-through design and procedures described in

Pigati et al. [2] which were modified from the original recirculating in situ ¹⁴C system of Lifton et al [1] (Figs. 1 and 2a). Each extraction system consists of three major parts: (1) a tube furnace capable of reaching >1200°C, fitted with a dedicated 5 cm o.d. mullite tube; (2) a U-shaped secondary combustion furnace packed with 2 mm diameter fused quartz beads set at ca. 1000°C; and (3) a single cryogenic coil trap (Fig. 1). Each is maintained at high vacuum with turbo pumps backed by dry scroll pumps. The mullite tube has borosilicate glass polished socket joints sealed to each end with o-ring ball joint end caps to enable easy access. A 12 mm glass nipple extends at right angles from the glass sections on each side of the tube to connect the tube to the vacuum system via Cajon[®] fittings. Glass fritted tubes (coarse porosity) are installed between the nipples and the rest of the vacuum system to guard against particulate contamination. These frits also slow the movement of oxygen through the mullite tube, minimizing the possibility of disturbing the sample during extraction. Oxygen flow is controlled with an MKS Instruments 1479A mass flow controller with a range of 0-20 standard cubic centimeters (mL)/minute (sccm), and tube pressure is maintained between 0-100 torr via an MKS Instruments 640B pressure controller.

We follow a two-day extraction process similar to that of Pigati et al. [2]. We summarize the process here. The first day is dedicated to 1) flame-cleaning carbon-bearing contaminants from the quartz sleeve that lines the furnace tube to prevent condensation of LiBO₂ on the tube itself, and 2) fusing and degassing 20 g of LiBO₂ in a 50 mL Al₂O₃ sample boat. After cooling overnight, the boat is retrieved from the furnace and placed in a laminar flow hood using flame-cleaned quartz implements. The sample is loaded on top of the fused LiBO₂, and the boat is returned to the furnace tube. After evacuating the extraction system with the furnace at 180°C for

90 minutes, the boat is heated to 500°C in a stream of Research Purity O_2 at ca. 50 torr for 1 hour to remove atmospheric contaminants, and then oxidized in O_2 at 1100°C for 3 hours.

Approximately 4-6 tube volumes of Research Purity O_2 are bled slowly through the furnace tube at approximately 50 torr pressure during the high-temperature extraction step, carrying evolved sample gases through the secondary combustion furnace before condensable gases are collected in the coil trap. These gases are then transferred to a borosilcate glass breakseal for loading into the separate purification system to isolate the evolved CO_2 component.

The purification system removes water, halides, nitrogen and sulfur species using a combination of cryogenic separation with variable temperature traps and a Cu mesh/Ag wool furnace held at ca. 475°C. The amount of purified CO_2 is then measured in a known volume, diluted with ^{14}C -free CO_2 to approximately 0.4 mg C-equivalent. A small aliquot of the diluted mixture is split into a 12 mL Exetainer[®] for offline $\delta^{13}\text{C}$ measurement at the Purdue Stable Isotope Facility (PSI), and the remainder transferred to a second breakseal for transfer to the graphitization system. Graphitization system design and procedures are based on those of Santos et al. [10, 11], using H_2 reduction of CO_2 over an Fe catalyst at 580°C, with $\text{Mg}(\text{ClO}_4)_2$ as a water trap. The graphitization system comprises 8 reactors: 6 for low-level analyses and 2 with larger volumes intended for graphitization of AMS standards (Fig. 2b).

2.1 – System Automation

The original implementation of the extraction system at the University of Arizona [1, 2] required manual operation of all valve and liquid nitrogen procedures. The repetitive and time-consuming nature of the processes makes automation attractive; automating multiple extraction systems would maximize sample throughput. At Arizona existing systems were retrofitted for

automation rather than building new systems. This required custom design and implementation of equipment to automate three key aspects of the systems: valve operation, temperature control, and liquid nitrogen (LN) transfer. Each system is operated using LabView[®] software in a Windows 7 environment, linked to a dedicated enclosure housing custom-designed control electronics (Fig. 2c) that include data acquisition and digital input/output modules. Considerable effort has been devoted to optimizing design reliability and efficiency of each system.

2.1.1 – Valve actuators

A variety of valves facilitate the movement of gases through the system. Most of the valves are glass valves with Viton[®] o-ring seals (Kimble-Chase HI-VAC with glass plug); these are supplemented by Swagelok SS-4BK bellows-sealed stainless steel valves. Edwards Vacuum backing-roughing valves are used to switch between high- and low-vacuum states. Given the range of valve types and sizes, special purpose electromechanical actuators were designed to open and close the valves via commands from the control system (Fig. 2d and e). Each actuator uses a servo-loop-controlled gear-motor to translate electronic speed and direction commands into mechanical motion. Detector switches send position information back to the control system. Gate valves above the turbo pump inlets are operated pneumatically.

A mechanism to crack breakseals in the purification process was also designed and implemented. This is accomplished by first scoring the breakseal circumference at a predetermined distance from the bottom end (to ensure proper placement in the tube cracker). The breakseal is then cleaned with ethanol-moistened lint-free wipes and inserted into the bottom of the tube cracker mechanism. The tube cracker consists of a Swagelok[®] 3/8" (ca. 0.9 cm) o.d. x 12" (ca. 30.5 cm) long stainless steel flexible tube with Cajon[®] fittings on the ends, and a glass

plug in the bottom fitting. The flexible tube is held securely on either side of the scored portion of the breakseal via bushings in holes bored through two plastic blocks – the upper block is fixed to the servo motor housing and the lower one is attached to the motor spindle. When activated the lower block rotates approximately 60° and cracks the breakseal at the scored location, then returns to its original position.

2.1.2 – Temperature control and monitoring

Two main aspects of temperature control are automated. For the extraction systems, the main tube furnace is interfaced to the control electronics by an RS-232 via USB connection, and operated via software. The control electronics for the purification system operate the variable temperature traps (VTTs), which allow the separation of gas species based on characteristic phase transition temperatures. Each VTT contains a cold finger surrounded by a heater coil and enclosed within a sealed tube filled with helium. A type T thermocouple is attached to the cold finger. With the helium-filled tube submerged in liquid nitrogen, power to the heater coil is then controlled using the temperature feedback from the thermocouple. The cold finger temperature is maintained at any desired temperature from -196 to -100°C.

2.1.3 – Liquid N₂ transfer

Transferring LN to and from needed locations in each system is the most difficult aspect of the procedures to automate; condensation being a constant concern. LN is transferred from a pressurized 200 L supply dewar through insulated Teflon tubing to fill dewars on various cold traps or VTTs. This is accomplished via a manifold containing a series of solenoid valves that which are rated for cryogenic service. The amount of LN in the supply dewar is monitored by weight as measured with a 300 kg load cell assembly. Filling and emptying of individual dewars

is controlled using LN level sensors comprising three 1 M Ω carbon-composition resistors in series, positioned with resistors at empty, nominal, and full levels within each dewar. Certain cold traps need to be alternately filled, emptied, and warmed. Dewars stationed on those traps are emptied using a small shop vacuum cleaner via a drain manifold fitted with cryogenic solenoid valves. Cold traps are warmed gently using heat guns capable of temperatures <100°C.

2.2 – PRIME Lab

Although these automated systems were operational at Arizona in late 2009, they were disassembled and moved with Lifton to PRIME Lab in 2010. A new laboratory layout there required reconfiguration of the systems. In addition, several design changes were made to simplify the procedures and increase overall robustness of the automated operation. These included adding the pressure controller to each extraction system and removing the central two of four original VTTs from the purification system. By modifying our procedures slightly we were able to achieve similar levels of CO₂ purity with only two VTTs, as evidenced by the agreement of our results for the CRONUS-A intercomparison material with those of previous analyses [12] (Section 3.3). In addition, experiments were conducted using slightly positive He pressure when opening the extraction system furnace tubes to prevent atmospheric incursion. All systems are now operational at PRIME Lab.

3.0 – System Operation and Initial Results

The automation of the PRIME Lab in situ ^{14}C systems has enabled extremely consistent process conditions within each system from run to run. For example, the amount of O₂ bled through each extraction system during the 1100°C step varies only by < 0.2% between runs.

Similar process reproducibility is observed in the other steps of extraction and purification as well.

Automation has allowed for significant reduction in overall process times. The LiBO_2 pretreatment on the first process day now only takes ca. 3.5 hours, compared to ca. 5 hours previously. Similarly, the sample extraction on the second day now takes ca. 6-7 hours, compared to ca. 8 hours before automation. Sample purification takes ca. 3.5 hours, comparable to before automation, but can now run unattended, and the H_2 -reduction graphitization is significantly faster than the previous Zn reduction process (Section 3.1).

Our initial characterization of these systems comprised three series of tests: graphitization blanks, process blanks, and analyses of the CRONUS-A intercomparison material [12]. We report on each of these below. Results are reported in terms of $^{14}\text{C}/\text{C}_{\text{total}}$ following Hippe and Lifton [13], which for in situ ^{14}C is a more appropriate method of data reduction and reporting than traditional fraction modern (F_m) or percent modern carbon (pMC). All uncertainties are reported as 1σ .

3.1 – Graphitization blanks

Our new graphitization systems rely on H_2 reduction of CO_2 over an Fe catalyst [e.g., 10, 11] instead of Zn reduction [14] which is used at the University of Arizona. The advantage of H_2 reduction over Zn is primarily speed; graphitization typically is completed in < 2 hours with H_2 instead of ca. 18-20 hours for Zn in our Arizona systems. We also use a constant mass of Fe for all samples (3.0 ± 0.1 mg) regardless of carbon mass, in contrast to a Fe:C ratio of ca. 2.0 in Arizona.

Previous experience with graphitization suggests an inverse dependence of the measured $^{14}\text{C}/^{13}\text{C}$ ratio (or F_m) on the mass of carbon in the sample for both Zn and H_2 -based systems [e.g., 1, 15, 16]. Given the procedural differences between previous and current systems, we conducted experiments to determine the mass dependence of the blank associated with our graphitization process. Aliquots of the ^{14}C -free CO_2 we use for dilution were prepared in sizes ranging from 0.14 to 2.0 mg C. Results follow the expected $1/M$ dependence; the blank $^{14}\text{C}/\text{C}_{\text{total}}$ [corresponding to “f” in Eq. 25 of 15], associated with graphitization of the typical diluted sample size of ca. 0.4 mg C is ca. 3×10^{-15} (Table 1; Fig. 3).

3.2 – Process blanks

Procedural blanks were conducted on initial startup of each extraction system and subsequently interspersed with CRONUS-A and unknown samples. Each blank analysis consisted of the full set of procedures normally utilized for extraction and purification of a quartz sample, but without adding any quartz. The initial set of extractions using the first extraction system (Line 1) involved opening the furnace tube to air during sample insertion and removal, following previous procedures [1, 2, 9, 17], while a second set maintained a slow flow of Research Purity He (99.9999%) through the furnace tube at slightly above atmospheric pressure while open to prevent atmospheric incursion (Table 2, Fig. 4). An initial set of blanks on the second extraction system (Line 2) used only the He flow procedures.

Results from the initial set of process blanks on Line 1 yielded a mean blank of $(1.64 \pm 0.45) \times 10^5$ ^{14}C atoms ($n=7$) (Fig. 4). Six of the seven initial blanks were within 1σ of the mean; one (PISC-35) was within 2σ . The $>27\%$ coefficient of variation (COV – mean divided by standard deviation) indicates significant room for improvement. The source of the variability is not

obvious from procedural considerations. We attempted to mitigate this variability by slowly back-flushing the furnace tube with Research Purity He during insertion and removal of the sample boat and quartz sleeve. Results of this second set of procedural blanks yielded a mean value of $(1.84 \pm 0.38) \times 10^5$ ¹⁴C atoms ($n = 3$), indistinguishable from the previous mean value but with a slightly lower COV of 20.4% (Fig. 4). Reasoning that the He procedure did not appear detrimental to the results, and given the potential for limiting atmospheric C contamination in the extraction systems with this method, we continued to use the He procedure going forward. A third set of process blanks for Line 2 with this procedure yielded a somewhat higher mean blank value of $(2.27 \pm 0.06) \times 10^5$ ¹⁴C atoms, but with excellent reproducibility (COV = 2.7%) (Fig. 4). Identical procedures were used on both systems, leaving the source(s) of the differences between the two systems unclear. Overall backgrounds for the two extraction systems are similar to previous systems [1, 2, 9, 17].

3.3 – CRONUS-A analyses

Intercomparison materials generated as part of the Cosmic-Ray Produced Nuclide Systematics on Earth (CRONUS) project were used to compare extraction system yields with previous results from in situ ¹⁴C labs at Arizona, Lamont-Doherty Earth Observatory, and ETH-Zurich [12] (Table 3, Fig. 5). Initial tests used the standard 5 g of quartz used in those procedures [1, 2, 9, 17], both with and without He flushing. Results with and without He are indistinguishable from those presented in Jull et al. [12]. We then explored the possibility of using larger sample sizes to allow increased AMS ratios, to yield results farther above background levels than possible with 5 g samples (4:1 LiBO₂:quartz). Both 10 g (2:1 LiBO₂:quartz) and 20 g (1:1 LiBO₂:quartz) sample sizes were attempted. 10 g sample sizes yielded results that were indistinguishable from those using 5 g, but the 20 g analysis was

significantly lower (Fig. 5). This suggests that 10 g sample sizes allow full recovery of in situ ^{14}C , while 20 g results in incomplete recovery. The 20 g result is likely due to the higher viscosity of the melt with the lower LiBO_2 :quartz ratio, leading to slower dissolution and/or CO_2 degassing rates. In theory, longer extractions at the 1:1 ratio could extract the in situ ^{14}C fully, but our extraction times are limited by the corrosiveness of the LiBO_2 vapor – longer times typically lead to structural failure of our Al_2O_3 sample boats and/or the quartz sleeve that shields the furnace tube from the vapor. The mean of 5 and 10 g samples is $(6.89 \pm 0.04) \times 10^5$ ^{14}C atoms/g ($n = 6$, COV 0.6%), compared to $(6.93 \pm 0.44) \times 10^5$ ^{14}C atoms/g ($n = 23$, COV 6.3%) in Jull et al. [12], demonstrating the increased reproducibility of our automated systems, as well as the efficacy of our purification procedures with only 2 VTTs. 5-10 g sample sizes are now in routine use in our lab.

4.0 –Conclusions

Initial operation of the PRIME Lab in situ ^{14}C laboratory indicates that much of the promise of automation has been achieved. Automating the extraction and purification procedures has enabled increased sample throughput and improved reproducibility, as evidenced by faster procedures and highly reproducible CRONUS-A analyses on quartz sample masses up to 10 g. Procedural blank levels can still be improved, but early results are comparable to previous work on previous manually operated systems. Improving the blank and improving overall system reliability is a priority for ongoing work. Based on these initial results, we are now measuring unknowns routinely.

262 **Acknowledgements**

263 The authors would like to acknowledge support from NSF grant EAR-1153689, and valuable
264 assistance from Adam Hudson (Arizona), Casey Beel (Purdue), and the PRIME Lab staff.

265

References

1. Lifton, N., A. Jull, and J. Quade, A new extraction technique and production rate estimate for in situ cosmogenic ^{14}C in quartz. *Geochimica Et Cosmochimica Acta*, 2001. **65**(12): p. 1953-1969.
2. Pigati, J., N. Lifton, A. Jull, and J. Quade, A simplified in situ cosmogenic ^{14}C extraction system. *Radiocarbon*, 2010. **52**(2-3): p. 1236-1243.
3. Hippe, K., F. Kober, L. Wacker, S. Fahrni, S. Ivy-Ochs, N. Akcar, C. Schluchter, and R. Wieler, An update on cosmogenic in situ ^{14}C analysis at Zürich. *Nuclear Instruments and Methods B*, 2013: p. 1-19.
4. Jull, A., D. Donahue, and T. Linick, Carbon-14 activities in recently fallen meteorites and Antarctic meteorites. *Geochimica Et Cosmochimica Acta*, 1989. **53**: p. 2095-2100.
5. Jull, A., D. Donahue, T. Linick, and G. Wilson, Spallogenic ^{14}C in high-altitude rocks and in Antarctic meteorites. *Radiocarbon*, 1989. **31**(3): p. 719-724.
6. des Marais, D., Light element geochemistry and spallogeneis in lunar rocks. *Geochimica Et Cosmochimica Acta*, 1983. **47**: p. 1769-1781.
7. Des Marais, D.J. and J.G. Moore, Carbon and its isotopes in mid-oceanic basaltic glasses. *Earth and Planetary Science Letters*, 1984. **69**: p. 43-57.
8. Hippe, K., F. Kober, H. Baur, M. Ruff, L. Wacker, and R. Wieler, The current performance of the in situ ^{14}C extraction line at ETH. *Quaternary Geochronology*, 2009. **4**(6): p. 493-500.

- 286 9. Goehring, B.M., I. Schimmelpfennig, and J.M. Schaefer, Capabilities of the
287 Lamont-Doherty Earth Observatory in situ ^{14}C extraction laboratory updated. *Quaternary*
288 *Geochronology*, 2013: p. 1-18.
- 289 10. Santos, G., J. Southon, K. Druffel-Rodriguez, S. Griffin, and M. Mazon, Magnesium
290 Perchlorate as an Alternative Water Trap in AMS Graphite Sample Preparation: A Report
291 on Sample Preparation at KCCAMS at the University of California, Irvine. *Radiocarbon*,
292 2004. **46**(1): p. 165-174.
- 293 11. Santos, G., M. Mazon, J. Southon, S. Rifai, and R. Moore, Evaluation of iron and cobalt
294 powders as catalysts for ^{14}C -AMS target preparation. *Nuclear Instruments and Methods in*
295 *Physics Research Section B: Beam Interactions with Materials and Atoms*, 2007. **259**(1):
296 p. 308-315.
- 297 12. Jull, A.J.T., E.M. Scott, and P. Bierman, The CRONUS-Earth inter-comparison for
298 cosmogenic isotope analysis. *Quaternary Geochronology*, 2013: p. 1-8.
- 299 13. Hippe, K. and N.A. Lifton, Calculating isotope ratios and nuclide concentrations for in
300 situ cosmogenic ^{14}C analyses. *Radiocarbon*, 2014. **56**(3): p. 1167-1174.
- 301 14. Slota, P., A. Jull, T. Linick, and L. Toolin, Preparation of small samples for ^{14}C
302 accelerator targets by catalytic reduction of CO. *Radiocarbon*, 1987. **29**(2): p. 303-306.
- 303 15. Donahue, D., A. Jull, and L. Toolin, Radiocarbon measurements at the University of
304 Arizona AMS facility. *Nuclear Instruments and Methods in Physics Research B*, 1990.
305 **52**: p. 224-228.

- 306 16. Santos, G., J. Southon, S. Griffin, S. Beaupre, and E. Druffel, Ultra small-mass
307 AMS ^{14}C sample preparation and analyses at KCCAMS/UCI Facility. Nuclear Inst. and
308 Methods in Physics Research, B, 2007. **259**(1): p. 293-302.
- 309 17. Miller, G., J. Briner, N. Lifton, and R.C. Finkel, Limited ice-sheet erosion and complex
310 exposure histories derived from in situ cosmogenic ^{10}Be , ^{26}Al , and ^{14}C on Baffin Island,
311 Arctic Canada. Quaternary Geochronology, 2006. **1**(1): p. 74-85.

List of Figures

Fig. 1: Schematic of PRIME Lab in situ ^{14}C extraction systems. Al_2O_3 sample boat is placed inside the furnace tube in a precleaned fused quartz sleeve (single-use). Research Purity O_2 is bled through the tube via a mass flow controller (MFC) calibrated for 0-20 standard mL (cc)/min, while a pressure of ca. 50 torr is maintained in the tube via a pressure controller (PC). All evolved carbon species are oxidized to CO_2 in the O_2 stream within the quartz bead combustion furnace. CO_2 is then trapped for offline purification in the coil trap cooled with liquid nitrogen.

Fig. 2: A) PRIME Lab in situ ^{14}C extraction (left side of lab frame) and purification (right side of frame) systems. B) PRIME Lab ^{14}C graphitization reactors. C) Control electronics for the purification system. Extraction systems have similar enclosures. D) Valve actuator assembly for glass valves, with guide rods and limit switch circuitry. E) Valve actuator assembly for SS-4BK valves, with bracket for circuitry. Valve travel between open and closed positions is too small for limit switches. Instead, a prescribed time interval is used for opening and a current limit associated with increased torque at closure stops the actuator.

Fig. 3: Plot showing mass dependence of graphitization systems, with best-fit equation.

Fig. 4: Process blanks from both extraction systems. System 1 blanks include runs with and without positive pressure He backfilling the furnace tube during tube opening. System 2 blanks only include He backfilling procedures. Mean and standard deviation indicated for each set of samples.

Fig. 5: Results for CRONUS-A intercomparison material, for different masses of quartz as indicated. 5-10 g of quartz give indistinguishable results which are also indistinguishable from results presented by Jull et al. [12], while 20 g has a significantly lower yield indicating incomplete recovery.

1 **Table 1 - Mass dependence of graphitization blank**

Sample Number	Mass C <i>mg</i>	¹⁴ C/ ¹³ C <i>10⁻¹³</i>	¹⁴ C/C _{total} <i>10⁻¹⁵</i>
PISC-57	0.401	2.863 ± 0.440	3.013 ± 0.463
PISC-58	0.644	2.597 ± 0.206	2.733 ± 0.217
PISC-59	1.137	1.978 ± 0.189	2.082 ± 0.199
PISC-60	2.030	2.449 ± 0.180	2.577 ± 0.190
PISC-61	0.413	2.841 ± 0.490	2.990 ± 0.516
PISC-62	0.141	3.911 ± 0.858	4.116 ± 0.903
PISC-63	0.210	3.299 ± 0.011	3.472 ± 1.109
PISC-64	0.312	3.364 ± 0.558	3.540 ± 0.587

2 **Note:** δ¹³C = -46.1‰

3

1 **Table 2 - Extraction system blanks**

Sample Number	CO ₂ Yield <i>10⁻² mL</i>	Diluted CO ₂ <i>10⁻¹ mL</i>	AMS CO ₂ Split <i>10⁻¹ mL</i>	¹⁴ C/ ¹³ C <i>10⁻¹²</i>	δ ¹³ C ‰	¹⁴ C/C _{total} <i>10⁻¹⁴</i>	¹⁴ C <i>10⁵ at</i>
PISC-15	3.585 ± 0.220	7.786 ± 0.080	7.070 ± 0.074	1.087 ± 0.044	-45.7	0.900 ± 0.072	1.882 ± 0.150
PISC-18	3.364 ± 0.220	7.699 ± 0.080	6.960 ± 0.073	1.202 ± 0.077	-45.9	1.021 ± 0.098	2.111 ± 0.202
PISC-24	2.668 ± 0.222	7.723 ± 0.080	6.992 ± 0.073	0.922 ± 0.041	-44.5	0.788 ± 0.047	1.389 ± 0.098
PISC-28	2.509 ± 0.222	7.776 ± 0.080	7.061 ± 0.074	8.960 ± 0.037	-45.6	7.590 ± 0.044	1.341 ± 0.092
PISC-31	3.904 ± 0.222	7.897 ± 0.082	7.152 ± 0.074	1.198 ± 0.043	-45.6	1.077 ± 0.050	2.038 ± 0.105
PISC-33	3.281 ± 0.221	8.269 ± 0.085	7.482 ± 0.775	1.081 ± 0.047	-46.3	0.953 ± 0.054	1.865 ± 0.119
PISC-35	1.593 ± 0.220	18.20 ± 0.182	16.52 ± 0.166	0.421 ± 0.012	-48.2	0.258 ± 0.024	0.878 ± 0.106
						<i>Mean</i>	<i>1.643 ± 0.451</i>
PISC-36 ^a	2.879 ± 0.221	7.389 ± 0.0767	6.699 ± 0.0701	0.976 ± 0.023	-45.5	0.843 ± 0.031	1.434 ± 0.062
PISC-41 ^a	2.872 ± 0.223	7.785 ± 0.0806	7.045 ± 0.074	1.155 ± 0.022	-46.0	1.031 ± 0.031	1.911 ± 0.064
PISC-42 ^a	2.751 ± 0.222	7.763 ± 0.080	7.216 ± 0.075	1.276 ± 0.036	-46.1	1.158 ± 0.043	2.174 ± 0.090
						<i>Mean</i>	<i>1.839 ± 0.375</i>
PISC-47 ^{a,b}	2.273 ± 0.220	7.622 ± 0.079	6.896 ± 0.072	1.301 ± 0.053	-46.6	1.184 ± 0.059	2.180 ± 0.122
PISC-49 ^{a,b}	2.495 ± 0.220	7.566 ± 0.078	6.804 ± 0.071	1.365 ± 0.061	-46.3	1.252 ± 0.068	2.300 ± 0.138
PISC-53 ^{a,b}	2.448 ± 0.223	7.543 ± 0.078	6.825 ± 0.071	1.352 ± 0.052	-46.4	1.238 ± 0.058	2.266 ± 0.117
PISC-55 ^{a,b}	2.299 ± 0.219	7.655 ± 0.079	6.861 ± 0.072	1.361 ± 0.054	-46.3	1.247 ± 0.061	2.320 ± 0.125
						<i>Mean</i>	<i>2.267 ± 0.062</i>

2 **Notes:** All analyses done on Extraction system 1 except as indicated.

3 a Backflow with He slightly above atmospheric pressure during furnace tube opening

4 b Extraction Line 2

1

2 **Table 3 - CRONUS-A analytical results**

Sample Number	Mass quartz <i>g</i>	CO ₂ Yield <i>10⁻¹ mL</i>	Diluted CO ₂ <i>10⁻¹ mL</i>	AMS CO ₂ Split <i>10⁻¹ mL</i>	¹⁴ C/ ¹³ C <i>10⁻¹¹</i>	δ ¹³ C ‰	¹⁴ C/C _{total} <i>10⁻¹³</i>	[¹⁴ C] <i>10⁵ at g⁻¹</i>
PISC-16	5.023	0.758 ± 0.023	8.013 ± 0.083	7.301 ± 0.076	1.659 ± 0.032	-43.9	1.720 ± 0.033	7.042 ± 0.185
PISC-17	5.008	0.797 ± 0.023	7.992 ± 0.082	7.218 ± 0.075	1.633 ± 0.026	-44.0	1.692 ± 0.028	6.924 ± 0.166
PISC-30	10.031	1.318 ± 0.025	8.754 ± 0.090	7.980 ± 0.082	2.877 ± 0.029	-41.6	3.013 ± 0.031	6.895 ± 0.112
PISC-32	20.058	2.196 ± 0.031	10.480 ± 0.107	9.444 ± 0.096	4.159 ± 0.048	-40.0	4.376 ± 0.051	6.058 ± 0.097
PISC-37 ^a	5.030	0.768 ± 0.023	8.424 ± 0.087	7.818 ± 0.081	1.544 ± 0.036	-43.5	1.600 ± 0.038	6.829 ± 0.208
PISC-38 ^a	10.001	1.217 ± 0.025	8.645 ± 0.089	8.021 ± 0.083	2.911 ± 0.030	-41.7	3.048 ± 0.032	6.891 ± 0.113
PISC-39 ^a	10.004	1.207 ± 0.025	8.661 ± 0.089	8.031 ± 0.083	2.842 ± 0.029	-42.0	2.974 ± 0.031	6.730 ± 0.111
<i>Mean (no PISC-32)</i>								6.885 ± 0.043

3 **Notes:** Uncertainty in quartz mass = ± 0.2 mg

4 a Backflow with He slightly above atmospheric pressure during furnace tube opening

5

6

Figure 1

Lifton et al.
Progress in automated extraction and purification of in situ ^{14}C from quartz

Fig. 1

Figure 2

Lifton et al.
Progress in automated extraction and purification of in situ ^{14}C from quartz

Fig. 2

Figure 3

Lifton et al.
Progress in automated extraction and purification of in situ ^{14}C from quartz

Fig. 3

Figure 4

Lifton et al.
Progress in automated extraction and purification of in situ ^{14}C from quartz

Fig. 4

Figure 5

Lifton et al.
Progress in automated extraction and purification of in situ ^{14}C from quartz

Fig. 5