



Technical note: Studying Li-metaborate fluxes and low-temperature combustion/high-temperature extraction systematics with a new, fully automated *in situ* cosmogenic ^{14}C processing system at PRIME Lab

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15 **Abstract.** Extraction procedures for *in situ* cosmogenic ^{14}C (*in situ* ^{14}C) from quartz require quantitative isotopic yields while maintaining scrupulous isolation from atmospheric/organic ^{14}C . These time- and labor-intensive procedures are ripe for automation; unfortunately, our original automated *in situ* ^{14}C extraction and purification systems, reconfigured and retrofitted from our original systems at the University of Arizona, proved less reliable than hoped. We therefore installed a fully automated stainless-steel system (except for specific glass or fused-quartz components) incorporating more reliable valves and improved actuator designs, along with a more robust liquid
20 nitrogen distribution system. As with earlier versions, the new system uses a degassed Li-metaborate (LiBO_2) flux to dissolve the quartz sample in an ultra-high-purity oxygen atmosphere, after a lower-temperature combustion step to remove atmospheric/organic ^{14}C .

We compared single-use high-purity Al_2O_3 vs. reusable 90%Pt/10%Rh (Pt/Rh) sample combustion boats. The Pt/Rh boats heat more evenly than the Al_2O_3 , reducing procedural blank levels and variability for a given LiBO_2 flux. This
25 lower blank variability also allowed us to trace progressively increasing blanks to specific batches of fluxes from our original manufacturer. Switching to a new manufacturer returned our blanks to consistently low levels on the order of $(3.4 \pm 0.9) \times 10^4$ ^{14}C atoms.

We also analyzed the CRONUS-A intercomparison material to investigate sensitivity of extracted ^{14}C concentrations to the temperature and duration of the combustion and extraction steps. Results indicate that 1-hr combustion steps
30 at either 500 or 600°C yield results consistent with the consensus value of Jull et al. (2015), while 2 hr at 600°C results in loss of ca. 9% of the high-temperature ^{14}C inventory. Results for 3 hr extractions at temperatures ranging from 1050°C to 1120°C and 4.5 hr at 1000°C yielded similar results that agreed with the nominal value as well as with published results from most laboratories. On the other hand, an extraction for 3 hr at 1000°C was judged to be incomplete due to a significantly lower measured concentration. Based on these results, our preferred technique is
35 now combustion for 1 hr at 500°C followed by a 3 hr extraction at 1050°C. Initial analyses of the CoQtz-N intercomparison material at our lab yielded concentrations ca. 60% less than those of CRONUS-A, but more analyses of this material from this and other labs are clearly needed to establish a consensus value.



1 Introduction

40 Extracting *in situ* cosmogenic ^{14}C (*in situ* ^{14}C) from quartz is challenging in that minute quantities of ^{14}C must be extracted and purified from quartz samples while preventing contamination by ubiquitous atmospheric/organic ^{14}C . These extraction and purification procedures are time-consuming and labor-intensive when done manually – as such they are attractive targets for automation. Lifton et al. (2015) presented results from the initial automated *in situ* ^{14}C extraction and purification systems at the Purdue Rare Isotope Measurement Laboratory (PRIME Lab), reconfigured and retrofitted from our original glass systems at the University of Arizona. As hoped, the automation of key
45 components of our *in situ* ^{14}C lab indeed led to increased throughput and reproducibility. While the overall timeline of the extraction, purification, and graphitization was still ca. 3 days, a single person was able to operate both automated extraction systems, the automated purification system, and the manual graphitization system simultaneously, boosting sample throughput significantly over the purely manual systems.

50 These automated systems comprised two independent extraction systems and a separate CO_2 purification system. A separate system for converting CO_2 to graphite was not automated. This required custom design and implementation of equipment to automate three key aspects of the systems: servo-based valve actuators, temperature control for cryogenic gas purification, and liquid nitrogen (LN) transfer. While these automated systems improved throughput over our original purely manual systems, they also required manual transfer of sample gas between separate extraction, purification, and (manual) graphitization systems.

55 However, in terms of overall reliability of operation, the limitations of retrofitting our original designs ultimately became apparent. For example, the glass high-vacuum valves are not precision components – no two are precisely the same. The valve actuators thus had to adapt to differences in resistance to motion arising from variations in valve stem and valve bore diameters, as well as to different lengths of travel to adequately seat each valve. As originally designed, the valve actuators accommodated these variations well, but the mechanical settings at which each
60 operated properly tended to creep over time, such that sometimes during active processes individual valves might not indicate that they are closed or open, or might indicate a closed position but not be seated properly and allow leakage across the valve. Without actively checking on the system status when this happened, the sample gas could be pumped away by accident, or a process could be interrupted (which could lead to system damage).

65 Similarly, the LN distribution system in that system was ultimately problematic. LN was transferred from a pressurized 200 L supply dewar through insulated Teflon tubing to fill dewars on various cold traps. Filling and emptying of individual dewars was controlled using LN level sensors comprising three resistors in series, positioned with resistors at empty, nominal, and full levels within each dewar. During the processes, certain cold traps needed to be alternately filled and emptied. Dewars stationed on those traps were emptied using a small shop vacuum cleaner via a drain manifold fitted with cryogenic solenoid valves. Particularly at times of high humidity (not as
70 much of an issue in arid Arizona as in Indiana), ice condensation in those dewars could cause the drain tubing to clog and interrupt the process sequence. Also, sometimes when a particular dewar was filled and emptied multiple times in a process sequence, the resistor string would not register the proper voltage during a fill cycle to trigger shutoff of LN flow, and the dewar would overflow continuously unless an operator was present to close the main



75 supply dewar valve manually. Thus, although sample throughput and repeatability was considerably improved over manual operation, system reliability was not at the point where one could generally leave a system in unattended operation.

We thus recently purchased and installed a customized Carbon Extraction and Graphitization (CEGS) system from Aeon Laboratories, LLC, similar to that of Goehring et al. (2019) at Tulane University. The largely stainless-steel system (except for specific sections requiring glass or fused-quartz components) incorporates more reliable valves and improved actuator designs compared to our original system, as well as a robust and efficient liquid nitrogen distribution system. The new system, controlled by a flexible and extensible modular software package written in C#, follows a similar procedure to that of Lifton et al. (2015), using a degassed Li-metaborate (LiBO₂) flux to dissolve the quartz sample in a Research Purity (RP) O₂ atmosphere. In addition, all sections of the new system are connected, so that one can extract all evolved carbon species as CO₂ from a quartz sample, purify and precisely measure the resulting gas yield, and convert the CO₂ to graphite for AMS analysis – all without human intervention. Below we describe key differences relative to the system of Goehring et al. (2019), then present baseline results from the now fully operational system, including procedural blanks and analyses of established intercomparison materials, for both our original single-use high-purity aluminum oxide and new reusable 90%Pt/10%Rh sample boats.

90 **2 Purdue CEGS design and operation**

The Purdue CEGS (PCEGS) comprises three main modules: two extraction modules and a collection/purification/graphitization module (main CEGS module) (Fig. 1), following the general design of Goehring et al. (2019) but with an additional extraction module. However, the PCEGS differs from the latter system in two key aspects. First, the two PCEGS extraction modules (Tube Furnace 1 [TF1] and Tube Furnace 2 [TF2]) are connected in parallel, each accommodating a high-temperature resistance furnace with a mullite furnace tube and evacuated by separate vacuum systems distinct from the main CEGS vacuum system (Fig. 1). On the other hand, the Goehring et al. (2019) system comprises one tube furnace in series with the CEGS, evacuated by a single vacuum system. Our design allows each PCEGS extraction module to run processes independently of those controlled by the other modules, enabling increased flexibility in system operations. The other key difference is that condensable gases evolved on the PCEGS during an extraction procedure in either furnace are trapped in a compact borosilicate glass coil trap held at LN temperature (-196°C) instead of the variable temperature trap (VTT) used for this purpose on the Goehring et al. (2019) system (Figs. 1, 2). The compact coil trap (ca. 3.5 cm diameter x ca. 10 cm tall) derives from our previous larger coil trap designs (e.g., Lifton et al., 2001; Pigati et al., 2010; Lifton et al., 2015), which consistently demonstrated quantitative trapping of minute CO₂ quantities from O₂ carrier gas. This compact design ensures similarly reliable CO₂ trapping through a 9 mm o.d. x 7 mm i.d. inlet downtube delivering process gases directly to the base of the trap before passing through a constriction connecting the downtube to a 6 mm o.d. x 4 mm i.d. coiled section and outlet tube (Fig. 2). The total length of the trap submerged in LN when operating is ca. 55 cm (ca. 5 cm of the downtube and the ca. 50 cm coil).



110 Other than incorporating a U-shaped secondary oxidation furnace (9 mm o.d. x 7 mm i.d. filled with 2 mm quartz beads, held at ca. 900°C) from the Lifton et al. (2015) system instead of an inline granular quartz oxidation furnace of the Goehring et al. (2019) design, the rest of the PCEGS utilizes similar hardware to that of the latter. However, our six-reactor graphitization manifold is configured in front of the main purification and measurement process path to achieve a shorter footprint than the linear configuration of the Tulane system (Fig. 1), allowing the first extraction module and the CEGS module to fit onto our existing lab frame and benchtop.

115 We implement a two-day extraction procedure with the PCEGS similar to those of Lifton et al. (2015) and Goehring et al. (2019), utilizing a lithium metaborate (LiBO_2) flux to dissolve the quartz and release the *in situ* ^{14}C at 1100°C. The first day's procedures involve degassing the LiBO_2 flux and preparing the purified quartz for extraction, while the second day is the extraction/purification/graphitization procedure. Once started, the Day 1 LiBO_2 degassing process operates on the selected extraction module (either TF1 or TF2) completely independently of the main CEGS module. The Day 2 process, on the other hand, requires control from the main CEGS module to allow sample collection, purification, measurement, dilution, and graphitization. In practical terms, we execute a Day 1 process on one extraction module, then the next day start a Day 1 process on the second extraction module. The Day 2 process for the first extraction module can then be run without interruption from the main CEGS module. The Day 1 and Day 2 processes are then subsequently cycled between the two extraction modules. This comfortably allows for PCEGS throughput of 4-5 samples per week.

130 On Day 1, a quartz sample is pretreated with 50% (v:v) HNO_3 :18 M Ω water for at least 90 min in an ultrasonic bath, rinsed thoroughly in 18 M Ω water, then dried in a vacuum oven overnight. A sample boat (either single-use high-purity Al_2O_3 or reusable 90%Pt-10%Rh) containing ca. 20 g of pre-fused LiBO_2 beads (melting point 845°C) is placed inside a flame-cleaned fused quartz sleeve in the mullite furnace tube (with borosilicate glass o-ring ball joint end seals), using flame-cleaned implements. The 24-inch-long (60.96 cm) quartz sleeve (replaced after every sample) extends beyond the furnace hot zone, protecting the furnace tube from LiBO_2 vapors that evolve from the fused sample at high temperature. The aggressively reactive vapors etch the interior of the sleeve within the hot zone of the furnace, instead of the furnace tube itself (Fig. 3). To prevent atmospheric CO_2 or other contaminants from entering the furnace tube when it is opened, the tube is first backfilled with Research Purity He (99.9999%) to 20 torr above ambient atmospheric pressure. The He is then slowly bled through the tube while open to atmosphere. Once closed again, the furnace tube is evacuated to $<5 \times 10^{-3}$ torr, isolated, and 50 torr of RP O_2 is subsequently added. The furnace is then heated to the extraction temperature (typically 1100°C for 1 hour while O_2 is bled through with a mass flow controller and automated metering valve to maintain the tube pressure and to flush out any evolved contaminants to the vacuum pump. The tube is then cooled and evacuated overnight.

140 On Day 2, approximately 5 g of the pretreated quartz sample is evenly distributed over the now-solid LiBO_2 in the boat and returned to the furnace, evacuated to $<5 \times 10^{-3}$ torr, isolated, and 50 torr RP O_2 is added again. The sample is then heated to 500°C for one hour to combust and remove atmospheric/organic contaminants, while bleeding O_2 across the sample as before and exhausting to the vacuum system. After that hour, the 500°C tube furnace is evacuated to $<5 \times 10^{-3}$ torr. Subsequently, 50 torr of RP O_2 is admitted into the tube furnace and the sample/flux is



145 heated to 1100°C and held at the high temperature for three hours to dissolve the quartz and release any trapped carbon species. During extraction the O₂ pressure in the tube typically rises to ca. 60 torr.

After the extraction procedure completes, the evolved gases are bled with RP O₂ through the secondary oxidation furnace to ensure any carbon species released during extraction are completely oxidized to CO₂ before collection in the compact coil trap cooled with LN. During this step, the tube pressure at the end of the extraction step is
150 maintained during the bleed (to prevent excess LiBO₂ vaporization) while the furnace cools to <800°C (to ensure complete melt solidification), before shutting off additional O₂ inflow and slowly evacuating all tube gases through the secondary furnace and coil trap. The condensed gases are then transferred to the purification section to remove water, halogens, and nitrogen and sulfur oxides. The gas is transferred cryogenically with LN first into the variable temperature trap (VTT) and the incondensable gases are evacuated. The VTT is then warmed to -145°C for 10
155 minutes, while the evolved CO₂ is passed through a Cu mesh/Ag wool trap held at 600 °C and frozen with LN into the measurement chamber (MC) (Fig. 1). The CO₂ yield is then measured manometrically as equivalent mass of C (µg), and typically diluted to ca. 300 µg C with ¹⁴C-free CO₂. A ca. 9 µg C split is collected in a pre-evacuated Exetainer[®] vial for stable C isotopic analysis offline, and the remaining sample is transferred cryogenically to one of the six graphite reactors (Fig. 1). The sample then undergoes hydrogen reduction (with Research Purity H₂ –
160 99.9999%) to filamentous C (graphite) on an Fe catalyst, with water trapped by Mg(ClO₄)₂ (Southon, 2007; Santos et al., 2004). Procedural background samples are run after approximately every 7-10 unknown samples, using identical procedures without adding quartz.

Finally, the graphite is packed into an Al cathode for ¹⁴C measurement by Accelerator Mass Spectrometry (AMS) at PRIME Lab. Sample ¹⁴C/¹³C ratios are measured relative to Oxalic Acid II (NIST-4990C). Stable carbon isotopic
165 ratios were measured at the University of California at Davis Stable Isotope Facility (stableisotopefacility.ucdavis.edu) using isotope ratio mass spectrometry (Lifton et al., 2015). Measured *in situ* ¹⁴C concentrations are calculated from the resulting ¹⁴C/C_{total} after subtracting representative procedural background ¹⁴C values, following Hippe and Lifton (2014). Measurement uncertainties are presented at the 1σ level unless otherwise noted.

170 3 Initial Experiments

Once the PCEGS was operational, we began to characterize its performance in terms of procedural blank (background) values as well as measurements of intercomparison materials such as CRONUS-A (Jull et al., 2015). We also characterized the mass-dependence of graphitization blanks. Since publication of Lifton et al. (2001), we and other labs using LiBO₂ for extraction (e.g., Goehring et al., 2019; Lamp et al., 2019; Fülöp et al., 2010) had used
175 single-use high purity sintered Al₂O₃ combustion boats for our flux + samples. On the other hand, laboratories that implemented flux-free *in situ* ¹⁴C extractions have either used Pt (e.g., Hippe et al., 2009, 2013; Lupker et al., 2019) or fused quartz vessels (Fülöp et al., 2015, 2019). The labs using flux-free processes typically report blanks on the order of 1-3x10⁴ ¹⁴C atoms (e.g., Lupker et al., 2019; Fülöp et al., 2019), while the labs using flux-based extractions have reported blanks on the order of 1-2x10⁵ ¹⁴C atoms (e.g., Lifton et al., 2015; Goehring et al., 2019; Lamp et al.,
180 2019). Goehring et al. (2019) deduced that the differences in ¹⁴C backgrounds between the flux and flux-free



extraction systems lay at least in part with the sintered Al_2O_3 boats reacting with the flux to release small and variable amounts of persistent contaminant ^{14}C during the extraction process. They described assessing boats of alternate construction, and reported a promising process blank result of ca. 4×10^4 ^{14}C atoms from an initial experiment with a reusable 90%Pt:10%Rh alloy boat.

185 Our initial PCEGS experiments utilized the single-use Al_2O_3 combustion boats, but in the meantime, we also obtained a set of 90%Pt:10%Rh (hereafter Pt/Rh) combustion boats from Heraeus Precious Metals North America LLC (www.pt-labware.com). We thus compared results using both types of boats, for both blanks and intercomparison samples. The solidified LiBO_2 +sample melt is cleaned from the Pt/Rh boats between samples by overnight ultrasonication at 40°C in 10% (v:v) reagent grade HNO_3 :18 M Ω water in sealed 1L polypropylene
190 bottles, followed by thorough rinsing in 18 M Ω water and drying in a gravity oven.

3.1 Graphitization blanks

The mass-dependence of the PCEGS graphitization blanks was assessed by graphitizing aliquots of ^{14}C -free CO_2 in masses ranging from ca. 50 $\mu\text{g C}$ to 1000 $\mu\text{g C}$ (Table 1). As with previous studies using either Zn or H_2 as the reducing agent for CO_2 to C (e.g., Donahue et al., 1990; Lifton et al., 2001, 2015; Goehring et al., 2019), we observe
195 an inverse relationship between sample mass and the measured $^{14}\text{C}/\text{C}_{\text{total}}$. This relationship is well-characterized by the equation (adjusted $R^2 = 0.994$)

$$B_g = (1.243 \pm 0.045) \times 10^{-13} / \text{mass} + (1.301 \pm 0.050) \times 10^{-15} \quad (1)$$

Correction of the measured $^{14}\text{C}/\text{C}_{\text{total}}$ for the graphitization blank (B_g) follows Eq. 6 of Donahue et al. (1997).

3.2 Procedural blank comparison

200 Initial experiments with the new system involved procedural blanks with our original single-use Al_2O_3 boats in concert with measurements of intercomparison materials (Section 3.3). Subsequently, we switched to reusable 90%Pt/10%Rh sample boats, with associated measurements of procedural blanks and intercomparison materials for a range of experimental conditions.

3.2.1 Al_2O_3 boats

205 The first set of blanks and intercomparison samples processed on the PCEGS with Al_2O_3 boats involved a more aggressive than normal Day 2 combustion step to more thoroughly remove any potential organic C that might remain on the etched sample grains. This was motivated by Nichols and Goehring (2019) who found evidence of modern ^{14}C contamination by laurylamine used in froth flotation mineral separation techniques that was not removed completely by their original etching procedure. Although we had not observed evidence of this issue with
210 *in situ* ^{14}C results from our lab, we tested a low-temperature combustion procedure of 2 hr. at 600°C , reasoning that Hippe et al. (2013) utilized a 2 hr. at 700°C combustion step with no apparent demonstrable effects on their results relative to combustions for 1 hr. at 500°C . This more aggressive combustion step was then followed by our normal 1100°C flux fusion for 3 hr.



Initial procedural blank experiments largely utilized TF1, and progressively increased from ca. 6.50×10^4 to 1.03×10^5 ^{14}C atoms with a mean of $(8.79 \pm 1.64) \times 10^4$ ^{14}C atoms, while a single blank from TF2 yielded ca. 1.14×10^5 ^{14}C atoms (Table 2, Fig. 4). The source of the time-dependent increase was not identified before switching to the Pt/Rh boats, but these values still represent an improvement over blank values presented in Lifton et al. (2015) by ca. 30-70%.

3.2.2 Pt/Rh boats

On switching to the Pt/Rh boats, we also reverted to our original procedure utilizing a 500°C combustion step for 1 hr. It was immediately obvious that the Pt/Rh boats heat much more uniformly than the Al_2O_3 , based on dramatic differences in the flux's corrosive effects on the quartz sleeves between the two types of boats (Fig. 3). The sleeves used with the Al_2O_3 boats were corroded mainly above and below the boat, as well as at the ends of the heated zone where the LiBO_2 vapor condenses in ca. 5 cm-wide bands (Fig. 3a). The rest of the heated portion of the sleeve is only lightly corroded and remains transparent. However, when using the Pt/Rh boats, the LiBO_2 evenly corrodes the sleeve interior over the entire hot zone length (Fig. 3b). It thus appears that the more efficient heat conduction of the metal boats leads to more aggressive heating of the flux and sample than in the Al_2O_3 boats. Experiments with the Pt/Rh boats at extraction temperatures of 1000°C and 1050°C resulted in significantly less corrosion of the sleeve than at 1100°C (Fig. 3b).

Initial procedural blanks using the Pt/Rh boats were dramatically lower than those using the Al_2O_3 boats, with much better reproducibility, averaging $(4.08 \pm 0.66) \times 10^4$ ^{14}C atoms (1σ) (Table 3, Fig. 4). Different combinations of combustion (500°C and 600°C – 1 hr) and extraction temperatures/times (1100°C – 3 hr, 1000°C – 3 hr and 4.5 hr) were investigated as well (Table 3) (corresponding to intercomparison experiments described in Section 3.3), with no significant effect on blank results. This supports the hypothesis of Goehring et al. (2019) that a significant component of Al_2O_3 procedural blanks derived from the sintered ceramic boats themselves. The improved blank reproducibility using the Pt/Rh boats allows us to identify background signals that previously we were unable to resolve. After this initial set of analyses depleted most of the bottle of Ultra-Pure grade LiBO_2 (Claisse C-0611-00, Batch C-10001), we switched to a new bottle of Pure grade LiBO_2 (Claisse C-0610-00, Batch C-17000-10). We reasoned that Pure and Ultra-Pure grades only differ in metal impurity content – both are pre-fused, spherical beads and thus should be essentially functionally equivalent for our application.

However, subsequent blanks with the new bottle increased in both CO_2 yield (ca. 1.5 μg to ca. 4 μg C-equivalent) and ^{14}C content (ca. $(1.51 \pm 0.31) \times 10^5$ ^{14}C atoms) (Table 3, Fig. 4). Although these values were higher than the initial measurements, they were reproducible on both TF1 and TF2, so we continued with normal system operation. Subsequently, though, the CO_2 yields and ^{14}C content inexplicably jumped again to new 'stable' values of ca. 6.6 μg C-equivalent and $(2.66 \pm 0.07) \times 10^5$ ^{14}C atoms, respectively, using TF1, with a similar but slightly lower result with TF2. At that point we tested a second bottle of Pure grade LiBO_2 (Claisse C-0610-00, Batch C-19000-10 – purchased at the same time as Batch C-17000-10) on procedural blanks in TF1 (PCEGS-94) and TF2 (PCEGS-95), with even higher results of $(3.21 \pm 0.10) \times 10^5$ and $(3.63 \pm 0.15) \times 10^5$ ^{14}C atoms, respectively. The higher blanks



250 from Batch C-19000-10 also exhibited higher CO₂ yields (ca. 8-9.5 μg C-equivalent). In fact, the CO₂ yields from each extraction module tracked the ¹⁴C atoms quite linearly for all these experiments, with similar regression fits to each (R² values of 0.955 and 0.970 for TF1 and TF2, respectively – Fig. 5)

At that point we paused normal system operations and conducted more basic experiments to try to isolate the source of the increased blanks – was it in the system overall or the LiBO₂? Two procedural blanks with everything except for the LiBO₂ (boat-sleeve only) – one boat cleaned in 10% v:v HCl, and the other in 10% v:v HNO₃ – both yielded 255 ca. 2.0 x 10⁴ ¹⁴C atoms. This indicated that the LiBO₂ was the source of the high blank, although the nature of that source and why the blank increased with time is unclear.

We then obtained a new bottle of Ultra-Pure grade LiBO₂ (Claisse C-0611-00, Batch C-19001-10); two blanks from that bottle from TF2 (PCEGS-98 and 99) yielded values comparable to PCEGS-95 – ca. 3.6-3.7 x 10⁵ ¹⁴C atoms, and ca. 8-9 μg C-equivalent yields (Fig. 4, Table 3). Finally, we tried a blank with the remainder of the original bottle of 260 Ultra-Pure grade LiBO₂ (Claisse C-0611-00, Batch C-10001). This experiment (PCEGS-100) exhibited CO₂ yield and ¹⁴C content comparable to our original tests: 2.2 μg C-equivalent and 4.76 ± 1.12 x 10⁴ ¹⁴C atoms. In consultation with Claisse technical support, we were unable to identify any chemical change in their product or manufacturing process that could have led to the progressively increasing blanks. As such, we identified another vendor, SPEX CertiPrep. We purchased a similar prefused Ultra-Pure grade LiBO₂ from them (FFB-0000-03, Lot 265 240920D-2904) and ran a blank on each extraction module. CO₂ yields were comparable to those of the original Claisse Ultra-Pure batch, and ¹⁴C contents were slightly improved over that material: ca. 2.5 μg C-equivalent and ca. 3.6 x 10⁴ ¹⁴C atoms (Table 3, Fig. 4). Subsequent blanks with the new SPEX LiBO₂ were generally comparable to or better than those initial measurements, ranging from ca. 2.4 x 10⁴ to 5.0 x 10⁴ ¹⁴C atoms (mean: (3.38 ± 0.92) x 10⁴ ¹⁴C atoms), and similar to recently published blank measurements from other *in situ* ¹⁴C laboratories using Pt sample 270 boats (e.g., Lupker et al., 2019; Goehring et al., 2019) (Table 3, Fig. 4). Regardless of the ultimate cause of the unexplained blank behavior with the more recent bottles of Claisse LiBO₂, we are proceeding with the SPEX Ultra-Pure LiBO₂ as our preferred flux.

Late in this process we also discovered that the temperature controller for TF2 was miscalibrated at high temperature setpoints, reading 1120°C on an independent Type-S thermocouple probe when set to 1100°C. Independent 275 measurement of the lower temperatures for the combustion steps in TF2 agreed with the setpoints – only the extraction temperatures exhibited the offset. We subsequently adjusted the setpoint temperatures for extractions to achieve the desired temperature on that furnace (1080°C setpoint for 1100°C actual, and 1035°C setpoint for 1050°C actual). No such problem was observed with TF1. Results from both blanks and intercomparison materials (Section 3.3 below) do not appear to indicate any significant effect from the 20°C excess temperature in the affected TF2 280 experiments (Figs. 4 and 6, Tables 3 and 4).

3.3 Extraction experiments with intercomparison materials

While we worked to isolate and understand the source(s) of the time-dependent procedural blanks on our new system, we also set out to better understand the effects of different combustion temperatures/durations on the



285 amount of ^{14}C extracted from the well-studied CRONUS-A intercomparison material (Jull et al., 2015). In addition,
since the more uniform heating of the Pt/Rh boats rendered the LiBO_2 flux more broadly aggressive toward the
fused quartz sleeves at 1100°C , we tested whether it would be possible to lower the extraction temperature and still
achieve full ^{14}C recovery from CRONUS-A. We also initiated measurements at PRIME Lab of the *in situ* ^{14}C
content of the CoQtz-N intercomparison material (e.g., Binnie et al., 2019) using both types of boats.

3.3.1 CRONUS-A – Al_2O_3 boats

290 Initial experiments with the Al_2O_3 boats used CRONUS-A to test whether the more aggressive combustion
procedure described in Section 3.2.1 (2 hr at 600°C) followed by a 3 hr fusion at 1100°C might affect the measured
in situ ^{14}C concentrations significantly. Results from both TF1 and TF2 yielded ^{14}C concentrations on the order of
10% below the consensus value for the material and outside the uncertainty band (Table 4, Fig. 6), suggesting
diffusive loss of *in situ* ^{14}C during the more aggressive low-temperature combustion step. We thus subsequently
295 abandoned that more aggressive procedure in favor of the original 1 hr at 500°C combustion step of Lifton et al.
(2001) (also Section 3.2.2).

3.3.2 CRONUS-A – Pt/Rh boats

Our efforts with the Pt/Rh boats largely focused on optimizing extraction temperature and time, again using
CRONUS-A as a benchmark (Table 4, Fig. 6). We varied combustion and extraction temperatures/durations, using
300 corresponding background corrections appropriate for the procedures used and allowing for the observed procedural
blank time-dependence.

The experiments with extractions for 3 hr at 1100°C and 1120°C , and 4.5 hr at 1000°C (PCEGS-44, 46, 50, 90, 104,
105, 106, 133 – Table 4, Fig. 6) yielded a mean and standard deviation of $(7.08 \pm 0.17) \times 10^5$ ^{14}C atoms g^{-1} (1σ). An
additional extraction test for 3 hr at 1000°C (PCEGS-47) yielded a ^{14}C concentration about 8% lower than this
305 mean, but still within the nominal range of results in Jull et al. (2015). However, we judge this extraction as likely to
be incomplete as it is outside of the 2σ uncertainty of our mean Pt/Rh CRONUS-A analyses, and as such do not
consider this further. Another test with a combustion step of 1 hr at 600°C and a normal 1100°C extraction (PCEGS-
50) yielded a result ca. 4% below the mean above using a 500°C combustion temperature but within 2σ of that
mean, and still well within the Jull et al. (2015) range. Excluding PCEGS-50 from the mean above does not
310 significantly change the mean nor these conclusions. After discovering the furnace controller miscalibration for TF2,
we also tested CRONUS-A results for TF2 at 1100°C (PCEGS-105), and found them indistinguishable from the
Pt/Rh mean. Finally, given the less aggressive corrosion of the quartz sleeve from tests at 1050°C (Fig. 3b), we also
tested CRONUS-A extraction for 3 hr at 1050°C (PCEGS-106), with results indistinguishable from our overall
Pt/Rh mean (Table 4, Fig. 6). We thus have switched to a 3 hr at 1050°C extraction temperature/duration going
315 forward.

Our CRONUS-A results are consistent with the consensus value and range of Jull et al. (2015), $(6.93 \pm 0.44) \times 10^5$
 ^{14}C atoms g^{-1} , as well as with the mean of our previous results at PRIME Lab (Lifton et al., 2015): $(6.89 \pm 0.04) \times$



10⁵ ¹⁴C atoms g⁻¹. In addition, these new results are consistent with recent measurements by Lupker et al. (2019),
Fülöp et al. (2019), and Lamp et al. (2019) (Fig. 6). Like those other studies, they also disagree with the CRONUS-
320 A measurements of Goehring et al. (2019), for reasons yet to be determined (Fig. 6).

3.3.3 CoQtz-N

Our three results for the CoQtz-N intercomparison material spanned the period discussed in this work (Table 4). An
initial analysis using an Al₂O₃ boat and the more aggressive 2 hr combustion at 600°C returned a lower
concentration (2.48 ± 0.06) × 10⁵ ¹⁴C atoms g⁻¹ than the two Pt/Rh experiments at 500°C/1100°C (TF1) and
325 500°C/1120°C (TF2), which agree within 1σ measurement uncertainties and yield a mean value of (2.62 ± 0.04) ×
10⁵ ¹⁴C atoms g⁻¹. Interestingly, the Al₂O₃ result with the more aggressive combustion step is only about 5% lower
than the Pt/Rh mean CoQtz-N result (uncertainties overlap at 2σ), vs. 9% lower than the nominal value for the Al₂O₃
analyses of CRONUS-A. The source of this difference is not clear, but likely reflects intrinsic differences in
diffusive properties of the quartz from each sample.

330 We only found one other study in which *in situ* ¹⁴C had been measured in CoQtz-N (Schiffer et al., 2020), but that
study provides incomplete experimental details and only a plot of concentrations vs. quartz mass without any
tabulated data. The four measured values presented for 1 g of CoQtz-N appear to span concentrations ca. 3 × 10⁵
over 4 × 10⁵ ¹⁴C atoms g⁻¹ – well above our measured values. The source of this discrepancy merits further
investigation but currently is difficult to evaluate without complete experimental details.

335 4 Conclusions

This study details key characteristics of and procedures in use for the new *in situ* ¹⁴C extraction system at PRIME
Lab (PCEGS), and presents results of initial testing of procedural blanks and intercomparison materials. We
compare results using the original single-use Al₂O₃ sample boats employed since Lifton et al. (2001) with those
from a new set of reusable 90%Pt/10%Rh alloy sample boats.

340 It is clear from these experiments that the reusable Pt/Rh boats provide distinct advantages over the Al₂O₃ boats,
supporting suggestions of Goehring et al. (2019). First, the Pt/Rh boats heat much more aggressively than the
sintered Al₂O₃ ceramic boats, likely leading to more uniform heating of the contents. The Pt/Rh boats also appear to
reduce or eliminate a significant component of the blank variability associated with the sintered ceramics, perhaps
associated with small amounts of atmospheric carbon potentially incorporated into the ceramics during manufacture.
345 Taken together, the aggressive uniform heating and purity of the Pt/Rh alloy allow for improved analytical
reproducibility, allowing robust identification of systematic influences on background signals that we were
previously unable to resolve with the Al₂O₃ boats.

Using the Pt/Rh boats, we demonstrated that time-dependent increases in procedural blanks were tied directly to
specific batches of LiBO₂ fluxes manufactured by Claisse. The time-dependence did not appear to reflect flux
350 purity, but rather some presently unknown characteristic of the Claisse fluxes appears to have changed since the
original batch we used for our early experiments. Subsequent analyses with LiBO₂ from an alternate supplier, SPEX



CertiPrep, yielded consistently low procedural blanks on the order of $(3.4 \pm 0.9) \times 10^4$ ^{14}C atoms, and we have switched to that flux going forward.

355 We also analyzed two intercomparison materials as part of our initial experiments, to confirm compatibility with earlier results from this lab as well as from others. Using both Al_2O_3 and Pt/Rh boats, we focused mainly on CRONUS-A, but also made initial measurements for our laboratory of the newer CoQtz-N intercomparison material. We first tested CRONUS-A in Al_2O_3 boats using a more aggressive combustion procedure than typically used (2 hr at 600°C vs. 1 hr at 500°C) and found significantly lower ^{14}C concentrations from the high-temperature extraction relative to the nominal value of Jull et al. (2015), likely due to diffusive loss during the more aggressive low-
360 temperature step. Abandoning that aggressive procedure in favor of the shorter 500°C combustion, and switching to the Pt/Rh boats, we then explored various time-temperature combinations for the high-temperature extraction step with CRONUS-A. Results for 3 hr extractions at temperatures ranging from 1050°C to 1120°C and 4.5 hr at 1000°C yielded similar results, in agreement with the consensus value as well as with published results from most laboratories, including those using our previous extraction system (Lifton et al., 2015). On the other hand, an
365 extraction for 3 hr at 1000°C yielded a significantly lower concentration than the other analyses in this study, suggesting incomplete extraction for those conditions. Based on these results, our preferred technique is now combustion for 1 hr at 500°C followed by a 3 hr extraction at 1050°C .

The initial analysis of CoQtz-N at PRIME Lab used the more aggressive combustion step, but displayed less diffusive loss (relative to our analyses with Pt/Rh boats) than did CRONUS-A with that procedure, suggesting
370 variable low-temperature diffusion behavior among samples. Subsequently, internally consistent results were achieved with CoQtz-N using Pt/Rh boats, with approximately 60% lower ^{14}C concentrations than CRONUS-A. However, additional analyses of this material from this and other labs are clearly needed to work toward a consensus value.

Declaration of competing interests

375 The authors declare that they have no conflict of interest.

Acknowledgments

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380 Author contributions

This study was conceived by NL and JW. Sample preparation and analysis was done by NL and AK. NL analyzed the data and wrote the manuscript, with contributions from AK and JW.

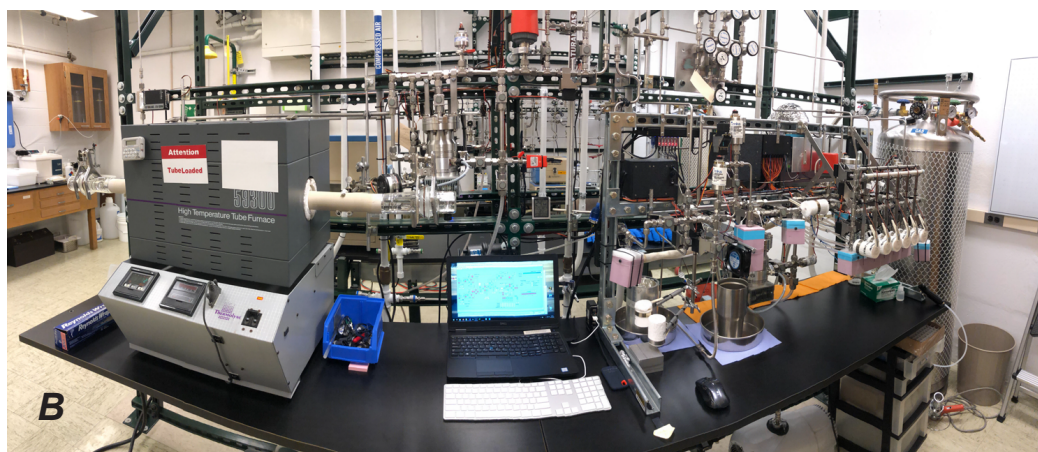
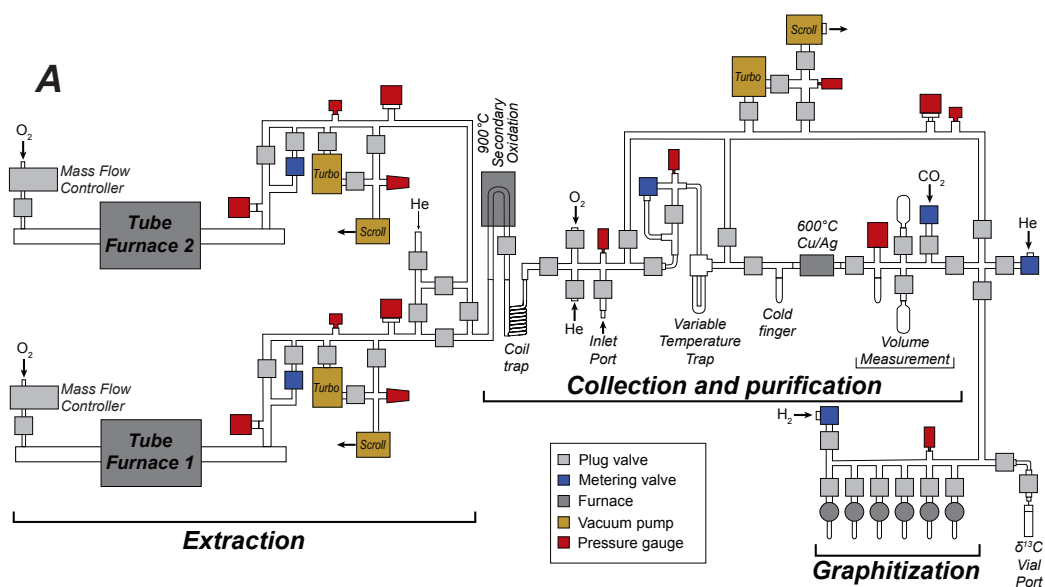


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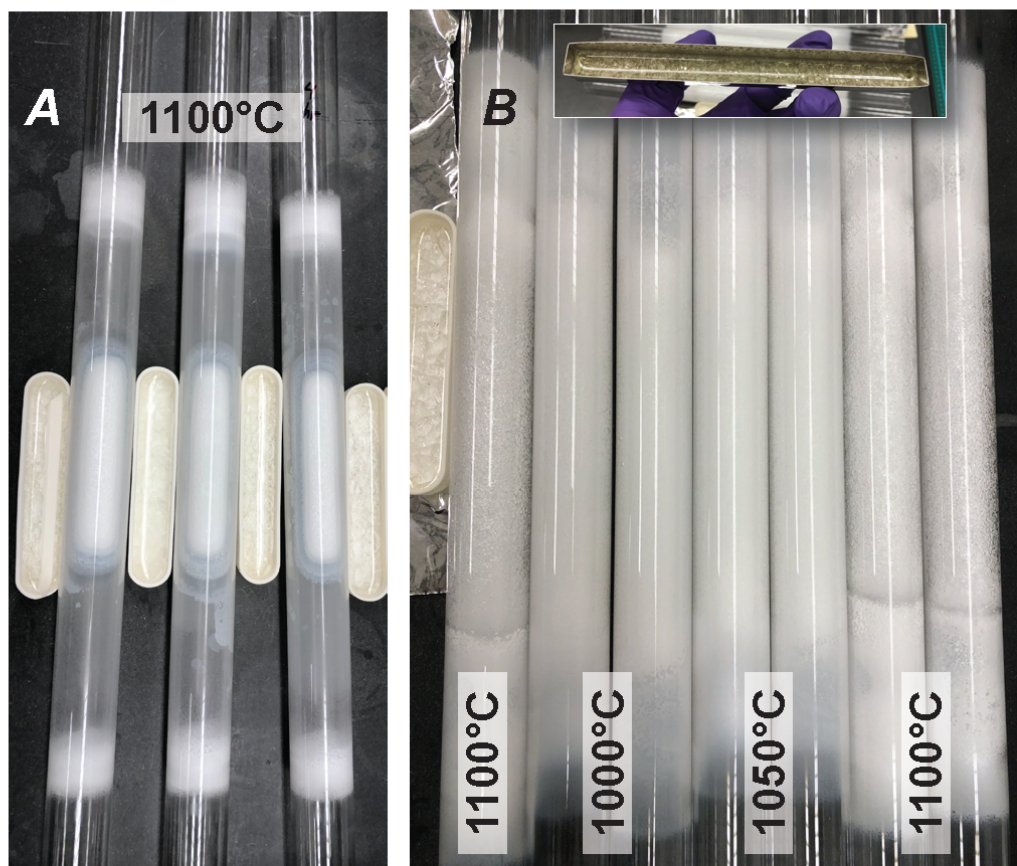


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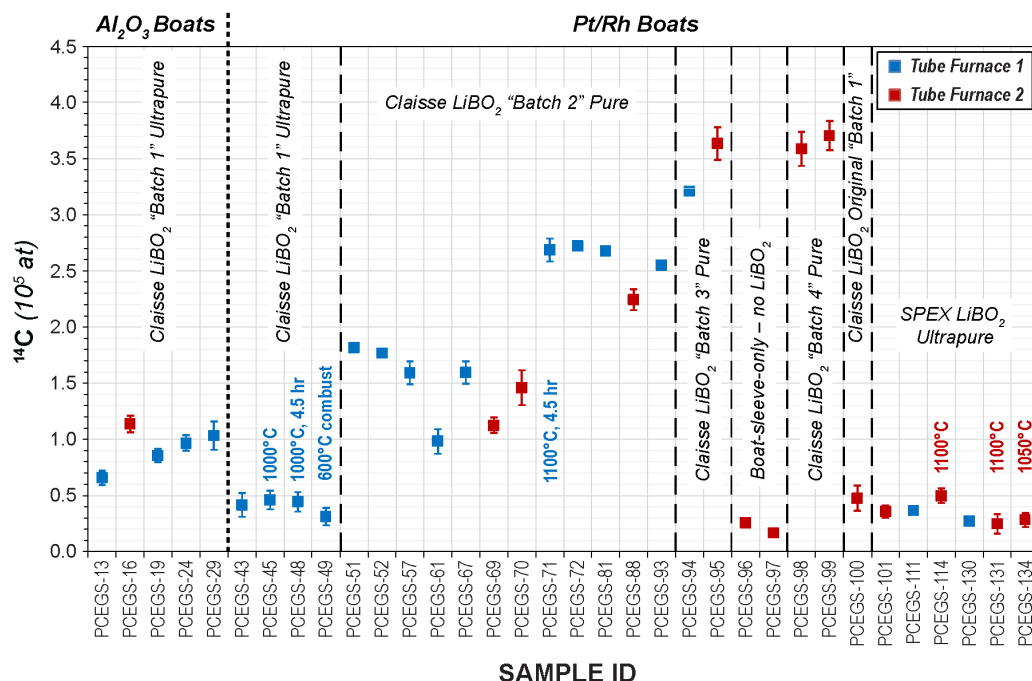
Figure 1: A) Schematic and B) photo of the Purdue Carbon Extraction and Graphitization System (PCEGS).



450 **Figure 2: Compact borosilicate glass coil trap, consisting of a 9 mm o.d. x 7 mm i.d. inlet downtube (on the left), connected to a tightly coiled 6 mm o.d. x 4 mm i.d. section with subsequent outlet tube. Scale on bottom is in cm.**



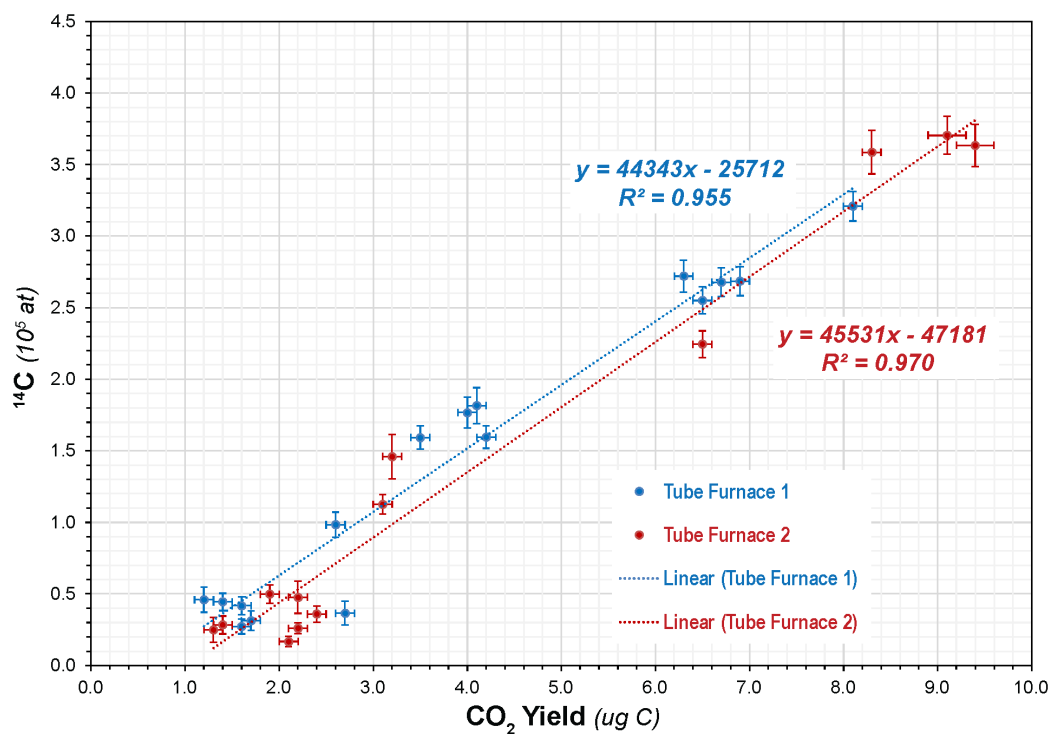
455 **Figure 3: Comparison of quartz sleeve corrosion from LiBO_2 for (A) Al_2O_3 boats and B) Pt/Rh boats (inset), after the high temperature fusion step (3 hr) at the temperatures indicated. Note the significantly greater corrosion associated with the Pt/Rh boats vs. the Al_2O_3 , indicating more even heating in the former, and noticeably milder corrosion from the 1050°C and 1000°C runs. The Al_2O_3 boat on the left side of B) is holding the sleeves in place but also serves as a comparison to A).**



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Figure 4: Procedural blank results for Al_2O_3 and Pt/Rh boats (1σ uncertainties). All blanks using Al_2O_3 boats used a 2 hr at 600°C combustion step followed by a 3 hr extraction at 1100°C (1120°C for Tube Furnace 2 due to a miscalibration at the 1100°C setpoint). All Pt/Rh Tube Furnace 1 runs were a 1 hr at 500°C combustion step followed by a 3 hr extraction step at 1100°C , except as indicated. Tube Furnace 2 combustions with Pt/Rh boats were also 1 hr at 500°C , but extractions were at 1120°C due to the miscalibration, except as indicated.

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470 Figure 5: Linear fit between CO₂ yield in µg C vs. procedural blank in ¹⁴C atoms, for Tube Furnaces 1 and 2 (1σ uncertainties shown).

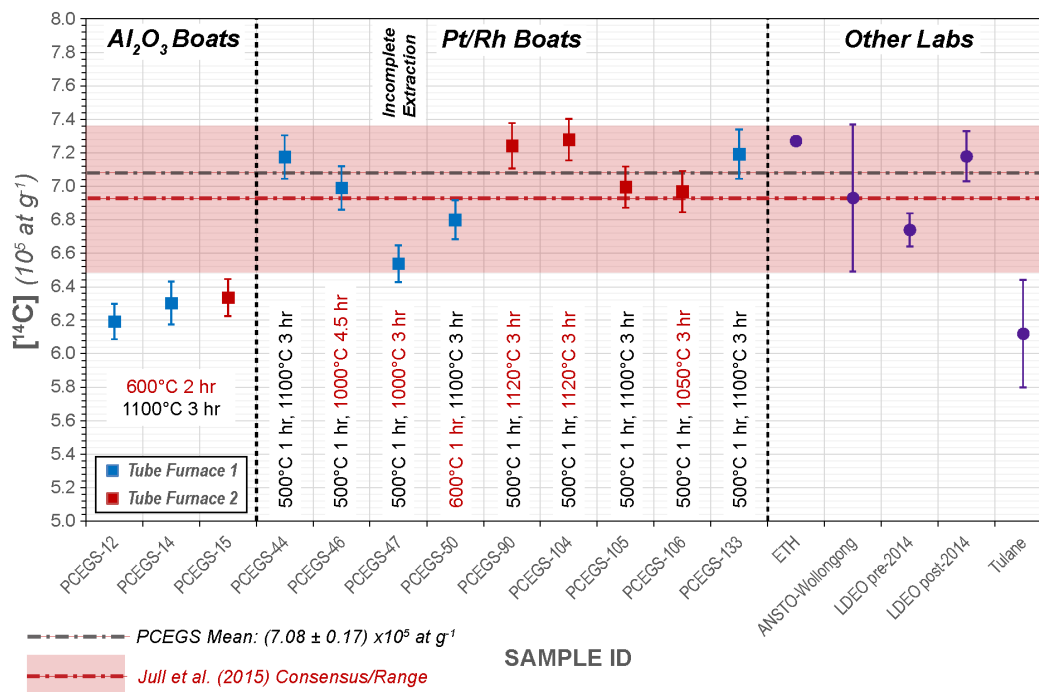


Figure 6: CRONUS-A results with experimental details (1σ uncertainties) from this study, with mean values from other studies for comparison.

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Table 1: Graphitization Blanks

SAMPLE	PCEGS #	PLID ^a	Mass C μg	¹⁴ C/ ¹³ C 10 ⁻¹³	¹⁴ C/C _{total} ^b 10 ⁻¹³
DILGAS-300	PCEGS-20	202001597	309.2 ± 3.8	1.5882 ± 0.1829	1.6709 ± 0.0019
DILGAS-300	PCEGS-21	202001598	339.6 ± 4.1	1.4773 ± 0.1817	1.5543 ± 0.0019
DILGAS-50	PCEGS-33	202100561	48.4 ± 0.6	3.7096 ± 0.4990	3.9024 ± 0.0053
DILGAS-100	PCEGS-34	202100562	92.6 ± 1.2	2.4291 ± 0.4102	2.5554 ± 0.0043
DILGAS-200	PCEGS-35	202100563	198.9 ± 2.4	1.9322 ± 0.2480	2.0326 ± 0.0026
DILGAS-500	PCEGS-36	202100564	523.5 ± 6.3	1.4752 ± 0.1897	1.5519 ± 0.0020
DILGAS-700	PCEGS-37	202100565	696.0 ± 8.4	1.4390 ± 0.2788	1.5138 ± 0.0029
DILGAS-1000	PCEGS-38	202100566	1,000.2 ± 12.1	1.4068 ± 0.1852	1.4799 ± 0.0020
DG-05072021	--	202101467	304.7 ± 3.7	2.1203 ± 0.2686	2.2305 ± 0.0028

Notes

a PRIME Lab ID

b δ¹³C averages -45.6 ± 0.2 ‰_{VPDB}

Table 2: Al₂O₃ Procedural Blanks – all used 2 hr combustion at 600°C and 3 hr extraction at 1100°C, unless otherwise noted

SAMPLE	PCEGS #	PLID	C yield μg	Diluted C Mass μg	AMS C Mass μg	δ ¹³ C ‰ _{VPDB}	TF1		¹⁴ C 10 ¹⁴ atoms
							¹⁴ C/ ¹³ C 10 ⁻¹²	¹⁴ C/C _{total} 10 ⁻¹⁴	
PB1-10012020	PCEGS-13	202001590	2.8 ± 0.1	308.2 ± 3.7	299.2 ± 3.6	-45.0 ± 0.2	0.5673 ± 0.0466	0.4256 ± 0.0494	6.5763 ± 0.7667
PB1-10272020	PCEGS-19	202001596	3.0 ± 0.1	310.4 ± 3.8	301.3 ± 3.7	-45.4 ± 0.2	0.6857 ± 0.0357	0.5502 ± 0.0379	8.5621 ± 0.5995
PB1-12032020	PCEGS-24	202100567	4.2 ± 0.1	308.6 ± 3.8	299.6 ± 3.6	-46.2 ± 0.2	0.7579 ± 0.0506	0.6252 ± 0.0534	9.6735 ± 0.8351
PB1-12152020	PCEGS-29	202100568	3.7 ± 0.1	303.8 ± 3.7	294.9 ± 3.6	-44.9 ± 0.2	0.8080 ± 0.0541	0.6784 ± 0.0572	10.3334 ± 0.8796
TF2									
PB2-10162020 ^a	PCEGS-16	202001593	4.0 ± 0.1	303.7 ± 3.7	294.8 ± 3.6	-45.2 ± 0.2	0.8731 ± 0.0460	0.7467 ± 0.0487	11.3708 ± 0.7547

Notes

a 1120°C extraction due to furnace miscalibration at 1100°C setpoint



490 **Table 3: P/Rh Procedural Blanks – All used 1 hr combustion at 500°C and 3 hr extraction at 1100°C, unless otherwise noted**

SAMPLE	PCEGS #	PLID	C Mass µg	Diluted C Mass µg	AMS C Mass µg	δ ¹³ C ‰(VPDB)	¹⁴ C/ ¹³ C 10 ⁻¹²	¹⁴ C/C _{total} 10 ⁻¹⁴	¹⁴ C 10 ⁴ atoms
TFI									
PB1-02042021	PCEGS-43	202100569	1.6 ± 0.1	300.8 ± 3.7	292.0 ± 3.6	-46.3 ± 0.2	0.4275 ± 0.0389	0.2768 ± 0.0412	4.1740 ± 0.6240
PB1-02092021 ^a	PCEGS-45	202100571	1.2 ± 0.1	300.6 ± 3.7	296.0 ± 3.6	-42.9 ± 0.2	0.4523 ± 0.0555	0.3051 ± 0.0588	4.5979 ± 0.8879
PB1-02202021 ^b	PCEGS-48	202100574	1.4 ± 0.1	304.1 ± 3.7	295.2 ± 3.6	-46.1 ± 0.2	0.4407 ± 0.0374	0.2912 ± 0.0397	4.4399 ± 0.6071
PB1-022232021 ^c	PCEGS-49	202100575	1.7 ± 0.1	304.1 ± 3.7	295.1 ± 3.6	-45.2 ± 0.2	0.3582 ± 0.0426	0.2047 ± 0.0452	3.1213 ± 0.6897
PB1-03232021	PCEGS-51	202101468	4.1 ± 0.1	315.8 ± 3.8	306.5 ± 3.7	-43.8 ± 0.2	1.2488 ± 0.0737	1.1467 ± 0.0779	18.1577 ± 1.2520
PB1-03252021	PCEGS-52	202101469	4.0 ± 0.1	307.8 ± 3.7	298.8 ± 3.6	-44.6 ± 0.2	1.2531 ± 0.0644	1.1446 ± 0.0680	17.6652 ± 1.0711
PB1-04062021	PCEGS-57	202101474	3.5 ± 0.1	304.2 ± 3.7	295.3 ± 3.6	-43.9 ± 0.2	1.1538 ± 0.0484	1.0438 ± 0.0513	15.9198 ± 0.8064
PB1-04152021	PCEGS-61	202101478	2.6 ± 0.1	305.1 ± 3.7	296.2 ± 3.6	-44.4 ± 0.2	0.7731 ± 0.0535	0.6423 ± 0.0566	9.8250 ± 0.8742
PB1-04292021	PCEGS-67	202101479	4.2 ± 0.1	307.8 ± 3.7	298.8 ± 3.6	-44.4 ± 0.2	1.1447 ± 0.0466	1.0340 ± 0.0493	15.9575 ± 0.7850
PB1-05252021 ^d	PCEGS-71	202101639	6.9 ± 0.1	316.7 ± 3.9	307.4 ± 3.7	-44.8 ± 0.2	1.7682 ± 0.0572	1.6911 ± 0.0605	26.8532 ± 1.0157
PB1-06012021	PCEGS-72	202101640	6.3 ± 0.1	311.8 ± 3.8	302.7 ± 3.7	-45.7 ± 0.2	1.8171 ± 0.0637	1.7401 ± 0.0672	27.2047 ± 1.1013
PB1-06192021	PCEGS-81	202101649	6.7 ± 0.1	308.5 ± 3.8	299.4 ± 3.6	-42.3 ± 0.2	1.8025 ± 0.0573	1.7310 ± 0.0607	26.7745 ± 0.9950
PB1-07242021	PCEGS-93	202101661	6.5 ± 0.1	306.9 ± 3.7	297.9 ± 3.6	-45.2 ± 0.2	1.7384 ± 0.0544	1.6577 ± 0.0575	25.5091 ± 0.9372
PB1-08062021	PCEGS-94	202101662	8.1 ± 0.1	310.3 ± 3.8	301.2 ± 3.7	-44.7 ± 0.2	2.1215 ± 0.0576	2.0626 ± 0.0608	32.0902 ± 1.0248
PB1-10222021	PCEGS-111	202102037	2.7 ± 0.1	305.0 ± 3.7	296.0 ± 3.6	-45.1 ± 0.2	0.3905 ± 0.0514	0.2389 ± 0.0544	3.6539 ± 0.8329
PB1-11192021	PCEGS-130	202102056	1.6 ± 0.1	302.1 ± 3.7	293.2 ± 3.6	-45.8 ± 0.2	0.3348 ± 0.0320	0.1796 ± 0.0341	2.7205 ± 0.5175
TF2									
PB2-05112021 ^e	PCEGS-69	202101637	3.1 ± 0.1	309.1 ± 3.8	300.1 ± 3.7	-44.6 ± 0.2	0.8523 ± 0.0405	0.7260 ± 0.0429	11.2509 ± 0.6798
PB2-05132021 ^e	PCEGS-70	202101638	3.2 ± 0.1	307.2 ± 3.7	298.2 ± 3.6	-42.6 ± 0.2	1.0608 ± 0.0951	0.9477 ± 0.1005	14.5966 ± 1.5576
PB2-07142021 ^e	PCEGS-88	202101656	6.5 ± 0.1	304.3 ± 3.7	295.4 ± 3.6	-45.5 ± 0.2	1.5619 ± 0.0557	1.4711 ± 0.0588	22.4454 ± 0.9380
PB2-08112021 ^e	PCEGS-95	202101663	9.4 ± 0.2	304.9 ± 3.7	295.9 ± 3.6	-45.3 ± 0.2	2.4222 ± 0.0865	2.3766 ± 0.0912	36.3332 ± 1.4618
Boat-HCl ^e	PCEGS-96	202101663	2.2 ± 0.1	305.2 ± 3.7	296.2 ± 3.6	-45.8 ± 0.2	0.3249 ± 0.0228	0.1697 ± 0.0246	2.5962 ± 0.3770
Boat- HNO ₃ ^e	PCEGS-97	202101669	2.1 ± 0.1	304.9 ± 3.7	296.0 ± 3.6	-45.1 ± 0.2	0.2671 ± 0.0226	0.1091 ± 0.0244	1.6671 ± 0.3729
PB2-08312021 ^e	PCEGS-98	202101670	8.3 ± 0.1	307.3 ± 3.7	298.3 ± 3.6	-45.9 ± 0.2	2.3763 ± 0.0903	2.3272 ± 0.0951	35.8579 ± 1.5277
PB2-09022021 ^e	PCEGS-99	202102024	9.1 ± 0.2	303.4 ± 3.7	294.5 ± 3.6	-45.0 ± 0.2	2.4769 ± 0.0767	2.4350 ± 0.0809	37.0417 ± 1.3107
PB2-09082021 ^e	PCEGS-100	202102025	2.2 ± 0.1	306.0 ± 3.7	297.0 ± 3.6	-43.9 ± 0.2	0.4575 ± 0.0692	0.3102 ± 0.0732	4.7589 ± 1.1240
PB2-09282021 ^e	PCEGS-101	202102026	2.4 ± 0.1	313.1 ± 3.8	303.9 ± 3.7	-44.6 ± 0.2	0.3796 ± 0.0328	0.2287 ± 0.0350	3.5907 ± 0.5509
PB2-10262021	PCEGS-114	202102027	1.9 ± 0.1	302.2 ± 3.7	293.3 ± 3.6	-45.4 ± 0.2	0.4763 ± 0.0398	0.3287 ± 0.0422	4.9805 ± 0.6425
PB2-11232021	PCEGS-131	202102057	1.3 ± 0.1	304.4 ± 3.7	295.5 ± 3.6	-45.6 ± 0.2	0.3183 ± 0.0541	0.1627 ± 0.0572	2.4830 ± 0.8728
PB2-12022021 ^f	PCEGS-134	202102060	1.4 ± 0.1	301.9 ± 3.7	293.0 ± 3.6	-45.9 ± 0.2	0.3420 ± 0.0394	0.1871 ± 0.0417	2.8326 ± 0.6326

^a 1000°C extraction, 3 hr



495
b 1000°C extraction, 4,5 hr
c 600°C combustion, 1 hr
d 1100°C extraction, 4,5 hr
e 1120°C extraction due to furnace miscalibration at 1100°C setpoint
f 1050°C extraction

500



Table 4: Intercomparison samples – All analyses used 1 hr combustion at 500°C and 3 hr extraction at 1100°C, unless otherwise noted

SAMPLE	PCEGS #	PLID	Mass Quartz g	C yield µg	Diluted mass C µg	AMS Split Mass C µg	$\delta^{13}\text{C}$ ‰ <i>VPDB</i>	$^{14}\text{C}/^{13}\text{C}$ 10^{-11}	$^{14}\text{C}/\text{C}_{\text{total}}$ 10^{-13}	^{14}C 10^6 at	$[^{14}\text{C}]$ 10^5 atoms g^{-1}	^{14}C Blank 10^4 atoms
CRONUS-A												
<i>Al₂O₃^a</i>												
CRA-09172020	PCEGS-12	202001589	5.0549	24.7 ± 0.3	306.4 ± 3.7	297.4 ± 3.6	-41.6 ± 0.2	1.9916 ± 0.0210	2.0868 ± 0.0222	3.1303 ± 0.0535	6.1925 ± 0.1058	7.5692 ± 1.4042
CRA-10072020	PCEGS-14	202001591	5.0008	25.5 ± 0.4	377.6 ± 4.6	366.5 ± 4.4	-42.9 ± 0.2	1.6313 ± 0.0242	1.7048 ± 0.0256	3.1519 ± 0.0639	6.3028 ± 0.1279	7.5692 ± 1.4042
CRA-10132020	PCEGS-15	202001592	5.0556	25.7 ± 0.4	303.2 ± 3.7	294.3 ± 3.6	-42.2 ± 0.2	2.0829 ± 0.0239	2.1819 ± 0.0252	3.2033 ± 0.0562	6.3361 ± 0.1113	11.3708 ± 0.7547
<i>Pt/Rh</i>												
CRA-02062021	PCEGS-44	202100570	5.0415	26.3 ± 0.4	303.0 ± 3.7	294.1 ± 3.6	-43.1 ± 0.2	2.3000 ± 0.0297	2.4085 ± 0.0313	3.6174 ± 0.0656	7.1753 ± 0.1300	4.1740 ± 0.6240
CRA-02112021 ^b	PCEGS-46	202100572	5.0099	26.2 ± 0.4	302.4 ± 3.7	293.5 ± 3.6	-42.1 ± 0.2	2.2316 ± 0.0296	2.3390 ± 0.0313	3.5020 ± 0.0649	6.9902 ± 0.1295	4.4399 ± 0.8879
CRA-02182021 ^c	PCEGS-47	202100573	5.0048	25.3 ± 0.4	303.9 ± 3.7	295.0 ± 3.6	-43.4 ± 0.2	2.0817 ± 0.0236	2.1776 ± 0.0249	3.2722 ± 0.0558	6.5381 ± 0.1115	4.5979 ± 0.6071
CRA-02252021 ^d	PCEGS-50	202100576	5.0630	23.1 ± 0.3	302.4 ± 3.7	293.5 ± 3.6	-42.0 ± 0.2	2.1861 ± 0.0251	2.2910 ± 0.0265	3.4425 ± 0.0589	6.7993 ± 0.1163	3.1213 ± 0.6897
CRA-07172021 ^e	PCEGS-90	202101658	5.0250	30.3 ± 0.4	309.6 ± 3.8	300.5 ± 3.7	-42.6 ± 0.2	2.3751 ± 0.0296	2.4891 ± 0.0312	3.6395 ± 0.0685	7.2428 ± 0.1362	22.4454 ± 0.9380
CRA-10072021 ^e	PCEGS-104	202102030	5.0568	25.9 ± 0.4	303.5 ± 3.7	294.6 ± 3.6	-42.9 ± 0.2	2.3318 ± 0.0268	2.4425 ± 0.0283	3.6810 ± 0.0628	7.2793 ± 0.1241	3.5907 ± 0.5509
CRA-10092021	PCEGS-105	202102031	4.7910	24.9 ± 0.3	304.5 ± 3.7	295.6 ± 3.6	-43.0 ± 0.2	2.1205 ± 0.0240	2.2197 ± 0.0253	3.3516 ± 0.0591	6.9955 ± 0.1234	3.7317 ± 1.7660
CRA-10122021 ^f	PCEGS-106	202102032	4.7458	25.2 ± 0.4	306.0 ± 3.7	297.0 ± 3.6	-43.1 ± 0.2	2.0775 ± 0.0261	2.1740 ± 0.0275	3.3071 ± 0.0587	6.9686 ± 0.1237	2.8326 ± 0.6326
CRA-12012021	PCEGS-133	202102059	5.0281	25.3 ± 0.4	303.2 ± 3.7	294.3 ± 3.6	-43.8 ± 0.2	2.2933 ± 0.0369	2.3997 ± 0.0389	3.6163 ± 0.0743	7.1922 ± 0.1477	3.1872 ± 0.6600
CoQiz-N												
<i>Al₂O₃</i>												
CQN-10222020 ^a	PCEGS-18	202001595	5.0112	7.5 ± 0.1	307.2 ± 3.7	298.2 ± 3.6	-44.6 ± 0.2	0.8281 ± 0.0133	0.8549 ± 0.0140	1.2412 ± 0.0303	2.4768 ± 0.0604	7.5692 ± 1.4042
<i>Pt/Rh</i>												
CQN-05012021	PCEGS-68	202101480	5.0525	7.0 ± 0.1	307.9 ± 3.7	298.8 ± 3.6	-43.6 ± 0.2	0.9122 ± 0.0134	0.9444 ± 0.0142	1.3071 ± 0.0419	2.5870 ± 0.0830	15.1188 ± 3.1330
CQN-10052021 ^c	PCEGS-103	202102029	5.0289	6.2 ± 0.1	304.7 ± 3.7	295.7 ± 3.6	-45.3 ± 0.2	0.8673 ± 0.0164	0.8954 ± 0.0173	1.3321 ± 0.0317	2.6488 ± 0.0630	3.5907 ± 0.5509

Notes

- a 2 hr at 600°C combustion
- b 4.5 hr at 1000°C extraction
- c 3 hr at 1000°C extraction
- d 1 hr at 600°C combustion
- e 3 hr at 1120°C extraction
- f 3 hr at 1050°C extraction