Abstract

We report on the status and capabilities of the Lamont-Doherty Earth Observatory in situ $^{14}$C extraction laboratory. In late 2006 we began, in collaboration with the AMS group at the University of Arizona, construction of a new laboratory to extract in situ cosmogenic $^{14}$C from terrestrial silicates. Long-term measurements of the process blank over the last two years give an arithmetic mean and standard deviation of $125\pm43\times10^3$ atoms $^{14}$C ($n=9$) and show significant improvement in the number of atoms, as well as stability compared to initial measurements of the process blank. We report long-term measurements of the intercomparison material CRONUS-A, which has been developed as part of the CRONUS-Earth effort to characterize inter- and intra-laboratory variability. We interpret the standard deviation (5%) of six replicate measurements of CRONUS-A as the reproducibility of in situ $^{14}$C extractions in our laboratory.

Introduction

Like the other commonly measured cosmogenic nuclides, $^{14}$C is produced in situ in earth surface materials by secondary cosmic rays. In situ $^{14}$C has a number of advantages over the other commonly measured cosmogenic nuclides: It has the shortest half-life (5730 yrs), making it uniquely suited to address a number of questions either on its own or in concert with a longer-lived nuclide (e.g., paired $^{10}$Be-$^{14}$C measurements). Production of in situ $^{14}$C in quartz is at a rate approximately three times that of $^{10}$Be
The measurement sensitivity of $^{14}$C is currently greater than all of the other cosmogenic nuclides, except for $^3$He, and the abundance of accelerator mass spectrometry (AMS) facilities with $^{14}$C measurement capability is far greater than for the other nuclides. The above factors make in situ $^{14}$C a potentially powerful tool in the study of earth surface processes.

The most promising application of in situ $^{14}$C is when it is paired with one or more longer-lived cosmogenic nuclides to investigate complex exposure histories during the past ca. 30 ka. To date only a few studies using in situ $^{14}$C have been published, all but one in the field of glacial geology (Anderson et al., 2008; Goehring et al., 2011; Miller et al., 2006; White et al., 2011), the other used in situ $^{14}$C to assess inherited $^{10}$Be (Matmon et al., 2005). Further potential applications of this paired nuclide approach are broad and include studies of soil column overturning rates/depths (Fülöp et al., 2009; Hippe et al., 2012; Lal et al., 1996), and paleoseismology (Handwerger et al., 1999). The refinement of models of nucleon scaling is another promising field for in situ $^{14}$C due to its relatively rapid achievement of secular equilibrium (Brook et al., 1995; Lifton et al., 2008). Determinations of the $^{14}$C production rates in quartz are also scarce (Dugan et al., 2008; Lifton et al., 2001; Miller et al., 2006; Schimmelpfennig et al., 2012). The paucity of studies employing in situ $^{14}$C reflects both the limited number of laboratories with in situ $^{14}$C extraction capabilities and the challenge of low-background extraction (Fülöp et al., 2010; Goehring et al., 2008; Hippe et al., 2009; Lifton et al., 2001; Pigati et al., 2010).

In 2006 we began construction of a new in situ $^{14}$C laboratory at Lamont-Doherty Earth Observatory of Columbia University (LDEO). Development of the laboratory
facilities is complete and in a stable operating mode since 2010. Here we report on progress made in the laboratory, including blank levels, improvements in precision, and measurements of a recently developed intercomparison material.

Lab Design and Extraction Procedures

All extraction, purification, and graphitization lines are based on the designs of Lifton et al. (2001) and Pigati et al. (2010). The laboratory is comprised of three main systems, a flow-through extraction line (Pigati et al., 2010), a purification line (Lifton, 2001), and dedicated in situ $^{14}$C graphitization line (Slota et al., 1987).

Extraction of in situ $^{14}$C from quartz and preparation for AMS analysis is a three-day process and follows the procedure outlined in Pigati et al. (2010). Day one consists of a 1 hour 1200°C combustion of the lithium meta-borate (LiBO$_2$) flux and alumina combustion boat to remove any surface contaminants and initially degass the LiBO$_2$. The LiBO$_2$ is used to reduce the quartz fusion temperature during the subsequent sample combustion (Lifton et al., 2001). Day one LiBO$_2$ combustion is done at 1200°C to ensure release of all potential contaminants; however, combustion at 1100°C, which is the sample combustion temperature should be equally effective. All evolved carbon species are converted to CO$_2$ under a 5 sccm flow of ultra-high-purity O$_2$ held at 50 torr (~6.7 kPa) via interaction with 2-mm quartz beads within a u-tube furnace held at 1000°C. This removes surface and atmospheric carbon contaminates from the flux as well as the combustion boat and quartz sleeve, which protects the mullite furnace tube from the volatile LiBO$_2$. On day two, ~5 g of quartz is added to the combustion boat and the sample and flux are heated at 500°C for 1 hour to remove atmospheric carbon contaminates, again in the presence of a 5 sccm flow of O$_2$. The sample is then heated at
1100°C for two hours in the presence of 50 torr (~6.7 kPa; static) of O₂, this melts the LiBO₂ and dissolves the quartz, releasing carbon. Following the initial two hour combustion, the sample is held at 1100°C for another hour in the presence of a 5 sccm flow of O₂, while a 50 torr (~6.7 kPa) tube pressure is maintained. All evolved CO₂ is collected in a liquid nitrogen-cooled coil trap and transferred to a flame-cleaned breakseal for subsequent gas purification. Day three involves the purification of the CO₂ by cryogenic removal of contaminant species (e.g. H₂O, NOₓ, SO₂, SOₓ, and halides). The total evolved CO₂ is measured using a capacitance manometer (MKS Type 622A, 0-100 torr, ±0.25% full-range precision), diluted with ¹⁴C-dead CO₂ to facilitate graphitization for AMS analysis (typical samples are only 20-50 μg of C, blanks 5-10 μg C), and split into two breakseals for AMS and δ¹³C measurement. The AMS split is then converted to graphite using catalytic reduction following Slota (1987). For data presented here, the ¹⁴C/¹³C ratio is measured by both AMS facilities.

Blank Measurements

All measurements (atoms and atoms g⁻¹) reported below were converted from fraction modern values following the procedure outlined in Hippe et al. [in press]. The δ¹³C correction included in the AMS laboratory reported fraction modern values is removed, as is reporting of the fraction modern value relative to 1950 AD. This yields carbon isotopic ratios relative to the isotopic ratio of the standard used in the AMS measurement (Ox-II here). Reported averages and uncertainties are arithmetic means and standard deviations. Sample concentrations are corrected for the long-term average blank.

Contamination from atmospheric, organic, and inorganic ¹⁴C sources is potentially a large source of the measured ¹⁴C in a sample. The measurement of
numerous process blanks with stable and low background levels is therefore critical to maximizing precision, confidence in the blank correction, and lowering the detection limit. The practice of bracketing samples, approximately every five, with measurements of the process blank are needed, because process blank measurements cannot be done simultaneously with sample extraction. Figure 1 shows the evolution of blank measurements at LDEO through time. The observed trend displays an overall reduction in background $^{14}$C by $\sim$60%. It is difficult to attribute the reduction in background to a given cause except for more thorough cleaning of the sacrificial quartz sleeve prior to insertion into the furnace, along with diligent cleaning and handling of other quartz implements entering the furnace. This conclusion is supported by the observation that blank levels show a positive correlation with the total mass of carbon evolved during the extraction procedure (Figure 2). It may however simply be due to progressive removal of contaminant carbon in the line itself through repeated use, as has been suggested for other similar $in situ$ $^{14}$C systems. Regardless of the exact cause of improvement in process blank levels, process blanks since January 2010 range between $54 \pm 13 \times 10^3$ and $179 \pm 51 \times 10^3$ atoms $^{14}$C with an average and standard deviation of $125 \pm 42 \times 10^3$ atoms $^{14}$C ($n=9$) for these blanks. Blanks from January 2010 and later are used as this represents the beginning of consistent use of the line and therefore likely represent the true characteristic value for the process blank. Our process blank level is commensurate with blank levels reported for similar line designs.
Figure 3 shows the relationship between total uncertainty and $^{14}$C concentration measured at LDEO covering a range between $10 \times 10^3$ and $680 \times 10^3$ atoms g$^{-1}$. The overall relationship is roughly an inverse exponential. At concentrations greater than approximately $100 \times 10^3$ atoms g$^{-1}$ there is no strong correlation. The observed relationship is a result of both AMS measurement uncertainty and the large influence of the blank correction on low concentration samples. At concentrations $>200 \times 10^3$ atoms g$^{-1}$, the resulting analytical uncertainty is dominated by AMS counting statistics; however, as concentrations fall below the “threshold” of $\sim 100 \times 10^3$ atoms g$^{-1}$, analytical uncertainties increase exponentially as a result of a large blank correction, in addition to any larger AMS uncertainties. From this, the effective detection limits of $\textit{in situ}$ $^{14}$C measurements for our line can be established. Two samples in particular show that concentrations below $\sim 30 \times 10^3$ atoms g$^{-1}$ yield very large uncertainties and in some cases are not statistically different from 0.

**CRONUS-A Measurements**

To assess intra-laboratory measurement variability, we measured one of the CRONUS-Earth intercomparison materials, CRONUS-A. Results of six measurements of CRONUS-A by two operators over an approximately two-year period are presented in Table 2 and Figure 4. All measurements are indistinguishable within 1-sigma uncertainties with the exception of one low measurement. The resulting mean concentration including all measurements is $652 \pm 33 \times 10^3$ atoms g$^{-1}$. We interpret the standard deviation of $\sim 5\%$ to represent the intra-laboratory reproducibility of $\textit{in situ}$ $^{14}$C extractions from samples with a similar concentration to CRONUS-A. It is possible that a lower concentration will yield more scatter; however, a lower concentration
intercomparison material (CRONUS-N) yields effectively zero $^{14}$C atoms g$^{-1}$ for the \textit{in situ} $^{14}$C concentration and therefore the relationship between scatter and concentration is unable to be established. A more recently developed intercomparison material, CRONUS-R, should yield a lower measured concentration than CRONUS-A, and hopefully greater than CRONUS-N, and may provide insight into any correlation between concentration and scatter.

Conclusions

We have successfully constructed an \textit{in situ}$^{14}$C extraction laboratory at Lamont-Doherty Earth Observatory based on the designs of Pigati (2004) and Lifton et al. (2001), significantly increasing the potential number of \textit{in situ}$^{14}$C measurements made. During the last two years, blank levels have been low, commensurate with similar laboratories, and show good stability. Potential analytical uncertainty is very good and shows little dependence on concentration above a threshold value of about $100 \times 10^3$ atoms g$^{-1}$. Intra-laboratory scatter, as determined from repeat measurements of an inter-laboratory comparison material is $\sim 5\%$. Development of the Lamont-Doherty Earth Observatory represents a significant advancement in the potential use of \textit{in situ}$^{14}$C in studies of earth surface processes and landform dating, with many applications only presently being realized.

Acknowledgements

We graciously thank the support and assistance of Nat Lifton during laboratory development. Without his knowledge none of this would have been possible. We also thank Tim Jull and the rest of the staff at the University of Arizona AMS facility, as well
as Tom Guilderson and the staff of the Lawrence-Livermore Center for AMS. This is
LDEO Publication xxxx.

References


Table 1. Process blank measurement information. Columns are the volume of CO$_2$ extracted from the sample, mass of carbon extracted, volume of the diluted sample, measured fraction modern, and number of $^{14}$C atoms. Fm values measured relative to Ox-II. All blank measurements assume a $\delta^{13}$C value of $-17.6 \pm 0.17 \%$ unless otherwise noted, which is based on numerous measurements of our dilution CO$_2$ and effectively dominates the measured $\delta^{13}$C value due to the large dilution factor. $^{14}$C measurements were either made at the University of Arizona (UA) or the Lawrence-Livermore Center for Accelerator Mass Spectrometry (CAMS).

<table>
<thead>
<tr>
<th>Date</th>
<th>AMS Lab</th>
<th>$V_{CO_2}$ (10$^2$ cc STP)</th>
<th>Mass C (µg)</th>
<th>$V_{diluted}$ (10$^2$ cc STP)</th>
<th>Fm$_{Meas}$</th>
<th>$\delta^{13}$C (%)</th>
<th>$^{14}$C (10$^3$ atoms)</th>
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<tr>
<td>7/7/08</td>
<td>UA</td>
<td>2.36±0.02</td>
<td>12.65±0.08</td>
<td>131.91±0.88</td>
<td>0.0236±0.0006</td>
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<td>903.79±54.31</td>
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<td>14.28±0.10</td>
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<td>251.56±2.13</td>
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<td>8.16±0.09</td>
<td>147.07±1.68</td>
<td>0.0051±0.0003</td>
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<td>3/5/10</td>
<td>UA</td>
<td>1.24±0.01</td>
<td>6.63±0.08</td>
<td>114.41±1.32</td>
<td>0.0057±0.0002</td>
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<td>UA</td>
<td>1.78±0.02</td>
<td>9.54±0.11</td>
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<td>0.0053±0.0001</td>
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<td>-</td>
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</table>
Table 2. Measurements of the CRONUS-A intercomparison material. Columns are as in Table 1, except showing concentrations (atoms g\(^{-1}\)), rather than total atoms. \(\delta^{13}\)C values for each sample are indicated, otherwise they are assumed to be -17.74\(\pm\)0.17 \(^\circ\)o, which is derived from the average of \(\delta^{13}\)C values measured in quartz samples, but effectively is dominated by our dilution CO\(_2\).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>AMS Lab</th>
<th>Qtz Mass (g)</th>
<th>(\text{VCO}_2) (10(^2) cc STP)</th>
<th>Mass C ((\mu)g)</th>
<th>(\text{V}_{\text{diluted}}) (10(^2) cc STP)</th>
<th>(F_m) (_{\text{Meas}})</th>
<th>(\delta^{13})C ((^\circ)o)</th>
<th>(^{14})C (10(^3) at g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRONUS-A(^1)</td>
<td>UA</td>
<td>5.0045</td>
<td>6.15(\pm)0.07</td>
<td>32.96(\pm)0.38</td>
<td>172.36(\pm)1.97</td>
<td>0.067(\pm)0.0013</td>
<td>-17.61(\pm)0.02</td>
<td>642.68(\pm)32.80</td>
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<td>CRONUS-A-2(^1)</td>
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<td>6.00(\pm)0.07</td>
<td>32.11(\pm)0.37</td>
<td>125.00(\pm)1.43</td>
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<td>6.14(\pm)0.07</td>
<td>32.89(\pm)0.38</td>
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<td>143.73(\pm)1.66</td>
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</table>

\(^1\) Blank correction based on blanks completed in 2009. All other CRONUS-A measurements are corrected for the mean blank 2010 and later.
Figure Captions

Figure 1. Plot of blank measurements versus time. Trend shows gradual improvement in blank levels and overall improvement in consistency. In all figures, errors are shown at one-sigma.

Figure 2. Blank levels versus total carbon evolved during a process blank. A correlation is observed between carbon mass and number of $^{14}$C atoms.

Figure 3. Analytical uncertainty versus sample concentration.

Figure 4. Plot of all measurements of the CRONUS-A intercomparison material. Solid line indicates arithmetic mean of all values, shading is one standard deviation, dashed line indicates two standard deviations.
Figure 1

Blank Level \((10^3 \text{^{14}C atoms})\) vs. Date

- 1/1/09
- 1/1/10
- 1/1/11
Figure 3

Uncertainty (%) vs. $^{14}$C ($10^3$ atoms g$^{-1}$)
Figure 4