Variations in Atmospheric $^{13}$C/$^{14}$C Ratios within a Radiocarbon Preparatory Lab and Implications for AMS Measurements

Kimberly Arias1,2, Alexandra Hedgpeth3, Karis McFarlane3
1Stem Teacher and Researcher Program, 2California Polytechnic State University, San Luis Obispo, 3 Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory

Introduction

At CAMS, we focus on measuring carbon isotopes ($^{12}$/$^{13}$C) for a variety of applications. High precision radiocarbon AMS measurements are used for measuring atmospheric radiocarbon. The problem with performing high precision radiocarbon AMS measurements is that there’s almost always background contamination introduced during preparation for the AMS. For graphite preparation, dry ice is used in an isopropyl-dry ice mixture to condense H2O in the CO2 extraction and reduction lines. Dry ice is composed of $^{12}$/$^{13}$C and releases carbon into the atmosphere as it sublimes. The dry ice for preparation is held in containers inside and outside the lab. We believe this may be a possible source of background contamination during the graphite preparatory phase for AMS. This experiment will provide data for quality control for ultra precise measurements at CAMS, LLNL. We measured the $^{13}$C/$^{14}$C ratios of air at multiple locations within the graphiteization lab and compared them across the lab and to atmosphere to test the following hypotheses:

H1: $^{13}$C/$^{14}$C ratios of lab air vary from atmosphere.
H2: $^{13}$C/$^{14}$C ratios vary across sites within the lab.

We found that air in the graphite lab varies from atmosphere and at different sites within the lab. The dry ice containers are releasing depleted $^{13}$C and $^{14}$C into the lab air and affect lab sites close to them. This could lead to contamination when weighing out samples when CO2 can remain adsorbed to the sample during preparation. It is recommended that the dry ice containers be removed from the lab to reduce background contamination levels.

Methods

1. Using a PFP (Figure 2), air samples were taken at locations inside and outside the lab (Figure 5).
2. Air samples from the PFP were evacuated into the extraction line (Figure 3) to isolate CO2.
3. CO2 was reduced to graphite in the reduction line (Figure 4).
   \[ \text{CO}_2 + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \]
4. Graphite samples analyzed using the HVEC 10 MW Model FN Tandem Van de Graaff Accelerator.

Results

The average $^{13}$C and $^{14}$C ($^{13}$C and $^{14}$C depletion, respectively) measurements for air at different lab sites are seen in Table 1 (Results):

- At sites 1 and 4, where dry ice containers are located, $^{13}$C and $^{14}$C is low. This is possibly because fossil fuel derived CO2 (dry ice) is depleted in $^{13}$CO2 and contains no $^{14}$CO2, and can cause a dilution effect, changing the ratio of atmospheric concentrations of carbon isotopes.
- $^{13}$C and $^{14}$C for site 3 are just above the averages for atmosphere ($^{13}$C=−8.5 ‰ and approximately $^{14}$C=10 ‰, respectively). This implies that the air at this site is mostly unaffected by outside factors and the small amount of $^{13}$C and $^{14}$C is a result of air from the lab mixing with outside air.
- At site 1, $^{13}$C and $^{14}$C measurements lie between those of site 2,3, and 4. This is likely a result of air from the dry ice site mixing with non-depleted air in the lab. This demonstrates the large differences between sites 1 and 2 as they are in close proximity to each other (188 inches apart).

The results imply that the dry ice containers are affecting the $^{13}$C and $^{14}$C ratios within the graphite lab causing the air to become more depleted in $^{13}$C and $^{14}$C. This could cause contamination when samples are first weighed out, at a site close to the dry ice container, into tubes that are exposed to lab air. The tubes are evacuated to 0 atm and torched closed, but CO2 can remain adsorbed to the sample. The variability between the lab sampling sites can lead to uncertainty in the level of background contamination. We recommend that the dry ice container be removed from the lab to further minimize contamination in the area around it.

Table 1. Average $^{13}$C and $^{14}$C measurements for air samples at different lab sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>$^{13}$C ‰</th>
<th>$^{14}$C ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dry Ice Container</td>
<td>$-18.7 \pm 0.0$</td>
<td>$-304 \pm 2$</td>
</tr>
<tr>
<td>2</td>
<td>Extraction Line</td>
<td>$-12.5 \pm 0.0$</td>
<td>$-111 \pm 3$</td>
</tr>
<tr>
<td>3</td>
<td>Back Door</td>
<td>$-9.2 \pm 0.0$</td>
<td>$-3 \pm 3$</td>
</tr>
<tr>
<td>4</td>
<td>Front Door</td>
<td>$-21.4 \pm 0.0$</td>
<td>$-403 \pm 2$</td>
</tr>
</tbody>
</table>

Discussion

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References


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