

## INITIAL RESULTS OF AN INTERCOMPARISON OF AMS-BASED ATMOSPHERIC $\Delta^{14}\text{CO}_2$ MEASUREMENTS

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**ABSTRACT.** This article presents results from the first 3 rounds of an international intercomparison of measurements of  $\Delta^{14}\text{CO}_2$  in liter-scale samples of whole air by groups using accelerator mass spectrometry (AMS). The ultimate goal of the intercomparison is to allow the merging of  $\Delta^{14}\text{CO}_2$  data from different groups, with the confidence that differences in the data are geophysical gradients and not artifacts of calibration. Eight groups have participated in at least 1 round of the intercomparison, which has so far included 3 rounds of air distribution between 2007 and 2010. The comparison is intended to be ongoing, so that: a) the community obtains a regular assessment of differences between laboratories; and b) individual laboratories can begin to assess the long-term repeatability of their measurements of the same source air. Air used in the intercomparison was compressed into 2 high-pressure cylinders in 2005 and 2006 at Niwot Ridge, Colorado (USA), with one of the tanks “spiked” with fossil  $\text{CO}_2$ , so that the 2 tanks span the range of  $\Delta^{14}\text{CO}_2$  typically encountered when measuring air from both remote background locations and polluted urban ones. Three groups show interlaboratory comparability within 1‰ for ambient level  $\Delta^{14}\text{CO}_2$ . For high  $\text{CO}_2$ /low  $\Delta^{14}\text{CO}_2$  air, 4 laboratories showed comparability within 2‰. This approaches the goals set out by the World Meteorological Organization (WMO)  $\text{CO}_2$  Measurements Experts Group in 2005. One important observation is that single-sample precisions typically reported by the AMS community cannot always explain the observed differences within and between laboratories. This emphasizes the need to use long-term repeatability as a metric for measurement precision, especially in the context of long-term atmospheric monitoring.

### INTRODUCTION

The radiocarbon content of atmospheric  $\text{CO}_2$  ( $^{14}\text{CO}_2$ ) is a potentially powerful diagnostic of a variety of important contemporary carbon cycle processes including fossil fuel combustion (e.g. Levin et al. 2003; Turnbull et al. 2006; Graven et al. 2009; Miller et al. 2012) and air-sea gas exchange (e.g. Krakauer et al. 2006; Naegler et al. 2006). High-precision measurement of  $\Delta^{14}\text{CO}_2$  including extraction from whole air and graphitization (e.g. Graven et al. 2007; Turnbull et al. 2007) is expensive (~US\$ 250–500 per sample) and labor-intensive, even when using accelerator mass spectrometry (AMS). This limits the capacity of any single research group to operate and maintain a large network. A more efficient way for the global research community to access a large number of atmospheric  $\Delta^{14}\text{CO}_2$  measurements is by sharing data from across many measurement programs

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(Figure 1). However, making use of the global set of measurements can only be accomplished if differences between each laboratory can be carefully quantified and eventually minimized.

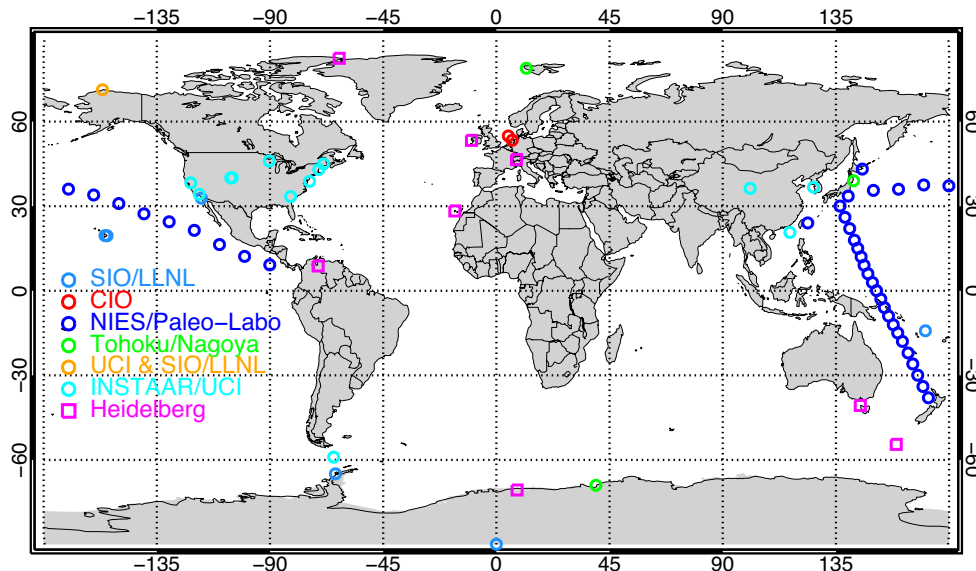


Figure 1 Map of sites where regular atmospheric  $\Delta^{14}\text{CO}_2$  AMS measurements are made by intercomparison participants (circles) and additionally the sites of University of Heidelberg (squares, Levin et al. 2010). At Barrow, Alaska, both UC Irvine and Scripps Institution of Oceanography collect air for  $\Delta^{14}\text{CO}_2$  analysis.

In 2005, the World Meteorological Organization Meeting of Experts on Carbon Dioxide Concentration and Related Measurements recommended that laboratory intercomparability of  $\Delta^{14}\text{CO}_2$  be 1‰ (Miller 2007). At the same meeting, the goals and method for the present whole air intercomparison were also established, recognizing the need for ongoing assessments of comparability between laboratories as the path towards merging international atmospheric  $\Delta^{14}\text{CO}_2$  data. The 1‰ target for interlaboratory comparability is ambitious considering that this exceeds any long-term demonstration of repeatability by any single laboratory. However, the target recognizes 2 facts. First, the early experience of the University of Colorado Radiocarbon Laboratory (CURL) had shown that the average value of graphite targets prepared from the same source air measured at the Rafter Radiocarbon Laboratory AMS ( $n = 30$ ) and University of California, Irvine AMS ( $n = 160$ ) differed by only  $0.2 \pm 0.5\text{‰}$  (Turnbull et al. 2007). Second, from the perspective of fossil fuel identification, 2‰ single-sample precision corresponds to detection of a difference from background of  $\sim 1$  ppm of fossil fuel  $\text{CO}_2$ . While this degree of random error is tolerable, the more stringent goal for interlaboratory comparability reflects the fact that laboratory calibration differences misinterpreted as geophysical gradients even at the 0.5 ppm level could significantly alter calculations of annual mean fossil fuel emissions. For example, a 0.5 ppm east/west difference in  $\text{CO}_2$  in the lowest 1 km of the atmosphere over North America corresponds, roughly, to one-tenth of US fossil fuel emissions (Committee on Methods for Estimating Greenhouse Gas Emissions 2010), or  $\sim 150$  million tons ( $1.5 \times 10^{14}\text{g}$ ) of C.

Previous intercomparison activities for the measurement of atmospheric  $\text{CO}_2$  mole fraction (Zhou et al. 2009), and  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  composition (Allison et al. 2003) have shown that the measurement of identical air can differ markedly between laboratories, even though each laboratory reports relative to the same (or traceable) scales. We find similar results in the present study for atmospheric  $\Delta^{14}\text{CO}_2$ .

## METHODOLOGY

All air used in the intercomparison was sourced from the NOAA Earth System Research Laboratory's (ESRL) Niwot Ridge, Colorado, high-pressure cylinder filling facility. One cylinder, FARI-A (First Atmospheric Radiocarbon Intercomparison) was filled on 6 July 2006 with ambient air (381 ppm) and the second cylinder was filled on 10 March 2005 with ambient air and later "spiked" with  $^{14}\text{C}$ -free fossil-fuel-derived pure  $\text{CO}_2$  to increase the mole fraction to 418 ppm and commensurately lower the  $\Delta^{14}\text{C}$ . Air from the tanks was distributed to each participating laboratory (Table 1) by filling glass or stainless steel flasks typically used by that group in air sampling. Flasks were sent to CURL where they were attached to a multiport manifold for filling from FARI-A and -B. Laboratories sent between 1 and 4 flasks for air from each of FARI-A and -B. After the flasks were attached to the manifold using custom adapters, their valves were opened and the manifold was evacuated to  $\sim 0.1$  Pa. At this stage, a valve between the manifold and roughing pump (Edwards RV3) was closed to check for any leaks. After confirming there were no leaks, the tank (either FARI-A or -B) was opened and all the flasks were filled to  $1 \times 10^5$  Pa. In order to "condition" the walls of the flasks (to minimize potential  $\text{CO}_2$  loss), the flasks were evacuated to 13 Pa and then filled again. This conditioning process was repeated once more. Finally, flasks from each group were pressurized to custom pressures corresponding to typical field filling procedures used by each laboratory. All flask valves except those being pressurized were closed, and the final pressure was adjusted using the pressure regulator of the cylinder. The filling process was identical for FARI-A and -B.

In order to check for isotopic fractionation during filling, during each manifold fill, at least 1 NOAA/ESRL flask was filled for analysis of  $\delta^{13}\text{C}$  at the University of Colorado Stable Isotope Laboratory (CU SIL). These values were compared to a direct measurement of the  $\delta^{13}\text{C}$  value of the cylinder. Three rounds of flask filling took place in February 2007, December 2007, and August 2010, although dates of  $\text{CO}_2$  extraction and AMS analysis for a given round can differ substantially between laboratories. Note that given the small amount of air available in flasks, only groups with AMS capability could participate in the intercomparison study. The much easier (and cheaper) transportation logistics for vessels filled to pressures  $< 40$  psia (276 kPa) dictated using flasks instead of sending the FARI-A and -B cylinders to all laboratories. The small fractionations observed in filling support our approach (see below).

## RESULTS AND DISCUSSION

Figure 2 and Table 2 show summary results for AMS analyses of all 3 rounds for FARI-A and -B; no outliers have been excluded. All results are  $\Delta^{14}\text{C}$  values relative to either the NIST Ox-I or Ox-II standard

$$\Delta^{14}\text{C} = F_{UN} \left( \frac{0.975}{1 + \delta^{13}\text{C}_s} \right)^2 e^{\lambda(1950-x)} - 1 \quad (1)$$

where  $F_{UN}$  is fraction modern,  $x$  is the date of sample collection, and  $s$  refers to the sample. (For simplicity, we have not included factors of 1000 in the equation and thus  $\Delta$  and  $\delta$  units are not in permil.) Note that  $\Delta^{14}\text{C}$  is equivalent to the definition of  $\Delta$  in Stuiver and Polach (1977) and  $^{14}\delta^i_{\text{N}}$  in Mook and van der Plicht (1999).  $\delta^{13}\text{C}$  values used in the  $\Delta^{14}\text{C}$  calculation were measured on-line by AMS by most groups, but other groups used off-line measurements of graphite or  $\text{CO}_2$  by isotope ratio mass spectrometry (IRMS) (Table 2).

Figure 2a shows round-by-round and aggregate results for the ambient level cylinder, FARI-A. Individual colored circles represent  $\Delta^{14}\text{C}$  values from individual flask air samples. Uncertainties in

Table 1 Participating groups.

Group nr	Group name	Extraction laboratory	Graphitization laboratory	AMS laboratory	Method references	Flask description
1	CSIRO/ANSTO	Australian Nuclear Science and Technology Organisation (ANSTO)	ANSTO	ANSTO	Fink et al. 2004; Hua et al. 2004	Borosilicate 1.5 L, 2 Teflon® or Viton® stopcocks; and borosilicate 5L, 2 Teflon stopcocks
2	CIO	University of Groningen Centre for Isotope Research (CIO)	CIO	CIO	Meijer et al. 2006	Borosilicate 2.5 L, 2 Louwers-Happert stopcocks
3	INSTAAR/UCI	University of Colorado Institute for Arctic and Alpine Research (INSTAAR)	INSTAAR	University of California, Irvine (UCI)	Turnbull et al. 2007; Lehman et al. 2013	Borosilicate 2.2 L, 2 Teflon stopcocks
4	LLNL	Lawrence Livermore National Laboratory (LLNL)	LLNL	LLNL	Graven et al. 2007	Stainless steel 4 L, dual stopcock
5	NIES/Paleo-Labo	National Institute for Environmental Studies (NIES)	Paleo-Labo	Paleo-Labo	Kobayashi et al. 2007	Borosilicate 2.5 L, 2 stopcocks
6	SIO/LLNL	Scripps Institution for Oceanography (SIO)	LLNL	LLNL	Graven et al. 2007	Spherical borosilicate 5 L, single ground-glass greased stopcock
7	Tohoku/Nagoya	Tohoku University	Nagoya University	Nagoya University	Nakazawa et al. 1993; Nakamura et al. 2004	Borosilicate 3 L, 2 stopcocks
8	UCI	UCI	UCI	UCI	Xu et al. 2007	Spherical stainless steel flask 6 L, single valve

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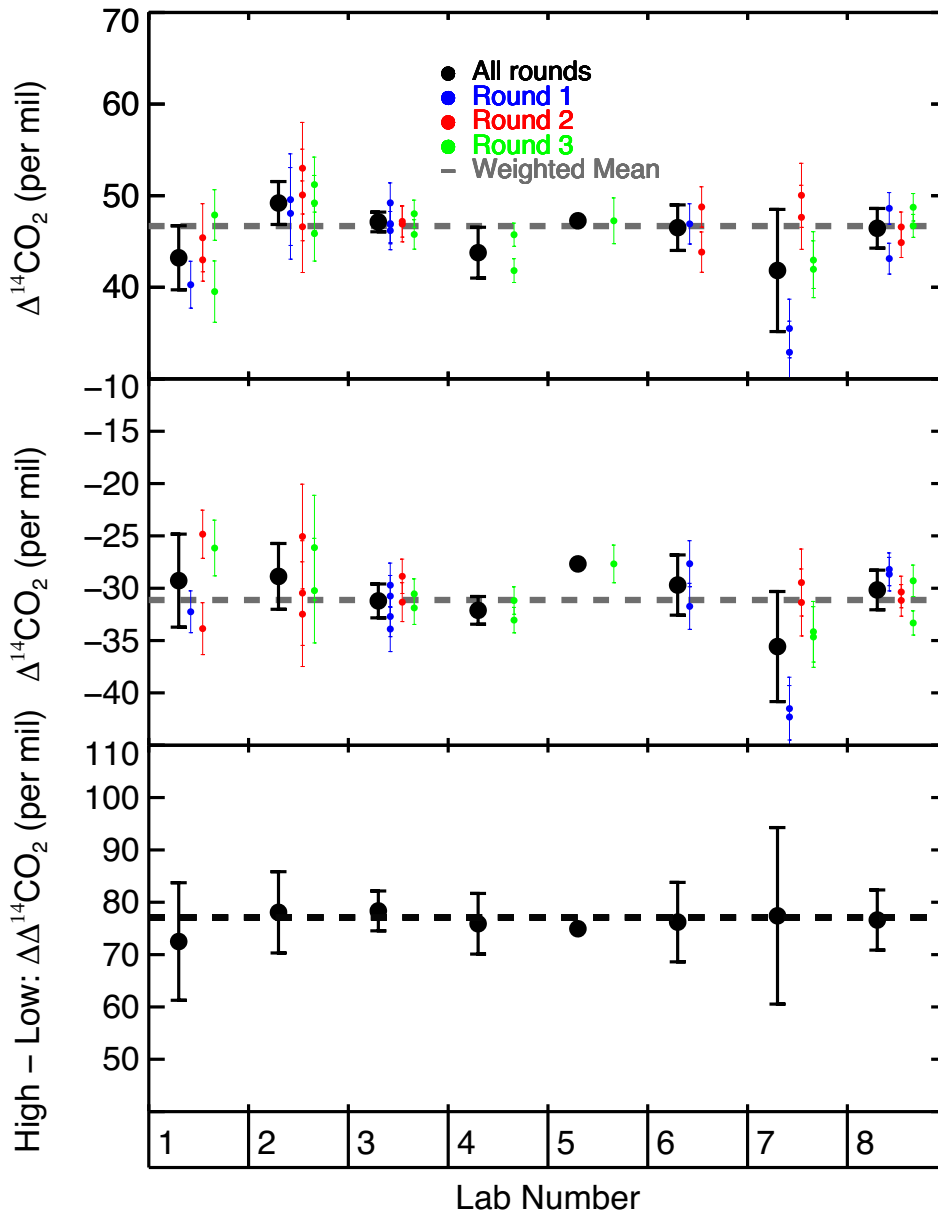


Figure 2  $\Delta^{14}\text{CO}_2$  results for ambient (A), depleted (B), and the difference (C) for all groups. For 2A and B, colored error bars for each sample represent reported uncertainty from each group, while black error bars represent the repeatability (standard deviation) of all measurements. For 2C, error bars are the quadrature-summed standard deviations of the high and low  $\Delta^{14}\text{C}$  all-round means. The gray dashed lines are the means, weighted by the inverse of the all-round variances.

Figure 2a reported by each AMS laboratory are single-sample precisions, as is normally reported, except for SIO/LLNL who reported the  $1\sigma$  reproducibility of a reference cylinder (Graven et al. 2012). For each participating group, the (unweighted) mean and standard deviation for all individual measurements was determined over all rounds. These values are plotted as the black circles and

Table 2 Mean values for FARI-A and -B.

Lab nr	All labs	1	2	3	4	5	6	7	8
<b>FARI-A</b>									
All sample mean	46.7 <sup>a</sup>	43.2	49.2	47.1	43.8	47.3	46.5	41.6	46.2
All sample $\sigma^b$		3.5	2.3	1.1	2.8	$n = 1$	2.5	6.5	2.1
Rd1		40.3	48.8	47.3	NM <sup>c</sup>	NM	46.9	34.2	45.9
Rd2		44.2	49.9	47.1	NM	NM	46.3	48.8	45.7
Rd3		43.7	48.8	46.9	43.8	47.3	NM	42.5	47.7
<b>FARI-B</b>									
All sample mean	-30.6 <sup>b</sup>	-29.3	-28.9	-31.2	-32.1	-27.7	-29.7	-35.9	-30.6
All sample $\sigma$		4.4	3.1	1.6	1.3	$n = 1$	2.9	5.1	2.0
Rd1		-32.3	NM	-31.8	NM	NM	-29.7	-41.9	-28.4
Rd2		-29.3	-29.3	-30.1	NM	NM	NM	-30.4	-30.8
Rd3		-26.2	-28.2	-31.2	-32.1	-27.7	NM	-34.4	-31.3
<b>FARI-(A-B)</b>	77.3	72.5	78.1	78.3	75.9	74.9	76.2	77.5	76.7
$\delta^{13}\text{C}$ used for normalization		EA/IRMS (graphite)	AMS	AMS	IRMS (CU-SIL)	AMS	IRMS (CU-SIL)	AMS	AMS
Working standard		OxI	OxII	OxI	OxI	OxII	OxI	OxII	OxI
$\delta^{13}\text{C}$ difference: FARI-A		-0.06	-0.01	-0.06	NM	NM	-0.07	-0.05	NM
$\delta^{13}\text{C}$ difference: FARI-B		-0.02	0.07	-0.02	NM	NM	-0.03	-0.02	NM

<sup>a</sup>Weighted by inverse variances from each laboratory (i.e.  $1/\sigma^2$ ).

<sup>b</sup>Repeatability of all measurements (i.e. standard deviation). Propagated measurement uncertainty is not included here.

<sup>c</sup>NM = Not measured.

error bars. Finally, a weighted mean value for FARI-A (gray dashed line) was calculated from these means and standard deviations, using the inverse square of the standard deviations as weights. Figure 2b displays the same information for the high  $\text{CO}_2$ /low  $\Delta^{14}\text{CO}_2$  tank FARI-B. Figure 2c shows the differences between the average FARI-A and -B results for each group, where the error bars are the quadrature sum of the standard deviations for A and B.

For FARI-A, all groups have average  $\Delta^{14}\text{CO}_2$  that overlaps with the weighted mean, given the  $1\sigma$  variability across all measurements. However, in some cases the standard deviations are large (range from  $\pm 1$  to  $\pm 7\text{‰}$ ; mean of  $\pm 5\text{‰}$ ) and the biases relative to the weighted mean range from  $-5.1$  to  $+2.5\text{‰}$ , with a root mean square error (RMSE) of  $\pm 2.8\text{‰}$ . Note that results from CIO (Lab 2) reflect a correction applied only after the initial reporting of the first 3 rounds of the intercomparison results. They discovered an error in their data treatment for these relatively small atmospheric samples, because their results were considerably higher than the weighted mean. Results now correspond better with the “All labs” average, but their result is no longer fully blind. Note also that the NIES/Paleo-Labo group results are presented, but not included in the summary. Only a single aliquot of FARI-A and FARI-B from round 3 was measured on a commercial AMS (Paleo Labo Co., Ltd.), because the Tohoku earthquake damaged the NIES AMS laboratory (NIES-TERRA). That said, the value they obtained was within  $1\text{‰}$  of the weighted mean. In terms of approaching the WMO/IAEA recommendations, 3 groups other than NIES/Paleo-Labo (INSTAAR/UCI, SIO/LLNL and UCI) have FARI-A values within  $\pm 0.5\text{‰}$  of the weighted mean, and have relatively good repeatability (JCGM 2008) across all samples:  $\pm 1.1$ ,  $2.5$ , and  $2.1\text{‰}$ , respectively.

For FARI-B, there exists a similar level of consistency across all groups relative to the weighted mean, including the presence of a wide range of between-round standard deviations (range of  $\pm 1$  to  $\pm 5\text{‰}$ ; mean of  $\pm 3\text{‰}$ ) and biases relative to the weighted mean ranging from  $-5.3$  to  $+2.9\text{‰}$ , with a RMSE of  $\pm 2.4\text{‰}$ . Among groups with results from at least 2 rounds, 4 (CSIRO/ANSTO, CIO INSTAAR/UCI, and UCI) have FARI-B values within  $\pm 2\text{‰}$  of the weighted mean, slightly outside

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of WMO/IAEA recommendations. The repeatability for FARI-B for these groups is 4.4, 3.1, 1.6, and 2.0‰, respectively.

The differences between FARI-A and -B (the “span”) reported by each group indicate whether a unit ‰ change is equivalent for all groups, even if their implementation of the scale may be offset. The spans are more similar across groups than the spread across groups for either FARI-A or -B. This is because differences from the weighted mean for Tohoku/Nagoya are low for both FARI-A and -B, by  $-5.1$  and  $-5.3$ , respectively. Note that the average deviations for Tohoku/Nagoya for FARI-A and -B are caused almost entirely by their results from round 1 (Table 2). The weighted mean span is 77.3‰ and the span of individual groups varies from this by between  $-4.8$  and  $+1.0$ ‰, with a mean span offset of just  $-1.0$ ‰.

One possible source of variability between groups and rounds that we can evaluate is the filling of flasks from the FARI-A and -B tanks, by looking at the measured values of  $\delta^{13}\text{C}$ . The differences between  $\delta^{13}\text{C}$  measured in the tanks and the control flasks averaged  $0.06 \pm 0.03$  and  $0.02 \pm 0.04$ ‰, respectively, for FARI-A and -B. Assuming that these differences resulted from small mass-dependent fractionation effects during filling of the flasks, this indicates a likely upper limit of 0.12 and 0.04‰ for  $\Delta^{14}\text{C}$  fractionation during filling. Furthermore, several labs measured  $\delta^{13}\text{C}$  in their own flasks, and average differences between the calibrated values for FARI-A and -B were all less than 0.1‰ (Table 2). In principle, any mass-dependent fractionation during flask filling (and extraction, graphitization, and AMS analysis) could be corrected by accurate  $\delta^{13}\text{C}$  measurement during AMS analysis. Nonetheless, because of the poorly defined accuracy of AMS  $\delta^{13}\text{C}$  analysis and the fact that not all labs are able to perform this measurement, confirming the absence of significant fractionation during filling is a useful step. In general, though, contamination during extraction, graphitization, and fractionation unaccounted for during AMS analysis are more likely sources of the variability observed in this experiment.

Another possible source of systematic errors between laboratories is in the implementation of the Ox-I and Ox-II scales. Although Ox-I defines the  $^{14}\text{C}$  scale and is still used by many laboratories in this experiment, Ox-II was previously agreed upon as a substitute (Stuiver 1983). It has not been established whether the international conventions regarding the  $^{14}\text{C}$  scale and its calibration are sufficiently stringent for the stated goal of 1‰ interlaboratory comparability for atmospheric  $^{14}\text{CO}_2$ . Additionally, the assigned ratio between Ox-II and Ox-I has not been established to the required sub-‰ level (Meijer et al. 2006; Turnbull et al. 2007). In the present experiment, 2 laboratories use Ox-II (excluding NIES/Paleo-Labo), but the number of Ox-I and Ox-II based analyses is not yet sufficient to draw conclusions about the impacts of using Ox-II or Ox-I.

## **CONCLUSIONS**

This intercomparison project was designed to mimic best practice procedures for assessing uncertainty below the  $\sim 3$ ‰ level. That is, regular extractions from a “target tank,” or high-pressure air cylinder, the  $\Delta^{14}\text{C}$  content of which is treated as an unknown (Graven et al. 2007; Turnbull et al. 2007; Lehman et al. 2013). In many cases (Figure 2), it is clear that single-sample precisions do not explain the variance within rounds, between rounds or between labs. This suggests that at the 1–2‰ level at which we are aiming, total uncertainty is no longer limited by counting (Poisson) statistics and that extraction, graphitization, and fractionation during AMS are also significant sources of uncertainty. Especially for studies involving the analysis of spatial or temporal differences in atmospheric  $\Delta^{14}\text{CO}_2$ , using the repeatability of air extracted from target tank as an uncertainty metric will be a more reliable indicator of uncertainty (Graven et al. 2007).

The initial results of this intercomparison suggest that it should be an ongoing, long-term exercise. As has also been seen when comparing CO<sub>2</sub> mole fractions between laboratories (Masarie et al. 2001), the level of agreement between groups can change over time. Another lesson the atmospheric <sup>14</sup>C community can learn from the CO<sub>2</sub> community is that laboratory-based intercomparisons, while valuable and necessary, are not sufficient. They need to be complemented with field-based comparisons in which different groups collect environmental air samples simultaneously so that the air collection techniques can also be included in the comparison (Graven et al. 2013). By using sampling flasks that are typically used in the field in this intercomparison, we have attempted to account for some of this variability. Field-based comparisons also provide a way that non-AMS groups needing very large amounts of air can also participate in comparisons.

In an attempt to isolate sources of existing variance among labs, aliquots of pure CO<sub>2</sub> will be distributed in the next round of the intercomparison as a way of removing variability associated with CO<sub>2</sub> extraction from whole air. We anticipate future rounds will return to distribution of air in flasks. The source of this pure CO<sub>2</sub> could be from FARI-A and -B extractions or from a near-ambient Δ<sup>14</sup>CO<sub>2</sub> pure-CO<sub>2</sub> source like that resulting from ethanol fermentation. Additionally, the laboratory of Ingeborg Levin (U Heidelberg) may provide pure CO<sub>2</sub> to participants obtained from large-volume NaOH-based extractions. New participants are welcome to join the ongoing intercomparison at any stage.

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