How Well Do We Know δ^{13} C of Atmospheric CO₂? Estimates of Uncertainty, Inter-Laboratory Comparisons, and Calibrations to Carbonate Primary Standards

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Measurements of stable isotopes of carbon dioxide are very useful for partitioning fluxes of CO_2 between the terrestrial biosphere and oceans. However, in models that determine these fluxes, small changes in isotopic values have large effects. Therefore the utility of the models depends on robust quality assurance/quality control (QAQC) of isotopic data. Measurement uncertainty must be reduced as much as possible, a normal criterion for isotopic measurements. In addition, a consistent scale, traceable over decades, must be established and maintained. This is a task that is not commonly addressed by the isotopic community. The Stable Isotope Lab at University of Colorado/INSTAAR has been measuring isotope of CO_2 from the NOAA Carbon Cycle Group's Cooperative Global Air Sampling Network since 1990. Here we present results of ongoing QAQC, including evidence to show the consistency of our scale over time. We also present a method for dynamic calculation of the uncertainty of our flask measurements, reflecting instrument performance and yielding varying uncertainties over time.

Comparison experiments with other stable isotope laboratories suggest that our δ^{13} C scale is offset by approximately 0.03 per mil. Overall there is far less agreement in δ^{18} O scales. Much of the discrepancy between laboratories is due to the inadequate calibration of CO₂-in-air to carbonates, the international primary standards. We have designated a mass spectrometer for calibrations, and its customized extraction system enables direct comparison of CO₂-in-air standards to CO₂ evolved *in situ* from carbonates and CO₂ equilibrations with water. Here we present results which prove the capability of the combined extraction systems to compare CO₂ from different sources. This new capability should enable us to resolve our offsets.



Figure 1. The top panel shows δ^{13} C of CO₂ at Mauna Loa, plotted by sample date, with error bars reflecting the measurement uncertainty. Bottom panel, the δ^{13} C of the "trap" tank run on the corresponding day, with error bars reflecting the standard deviation of three replicates. The trap tank allows us to follow instrument performance and confirm the consistency of our isotopic scale.