



Atmospheric CO₂ isotope research:
History, analysis, reference materials, the SIRS project (and beyond?)

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Developments in Isotope Ratio Measurements for Gas Analysis Workshop
METAS, Bern, Switzerland | 10 October 2019

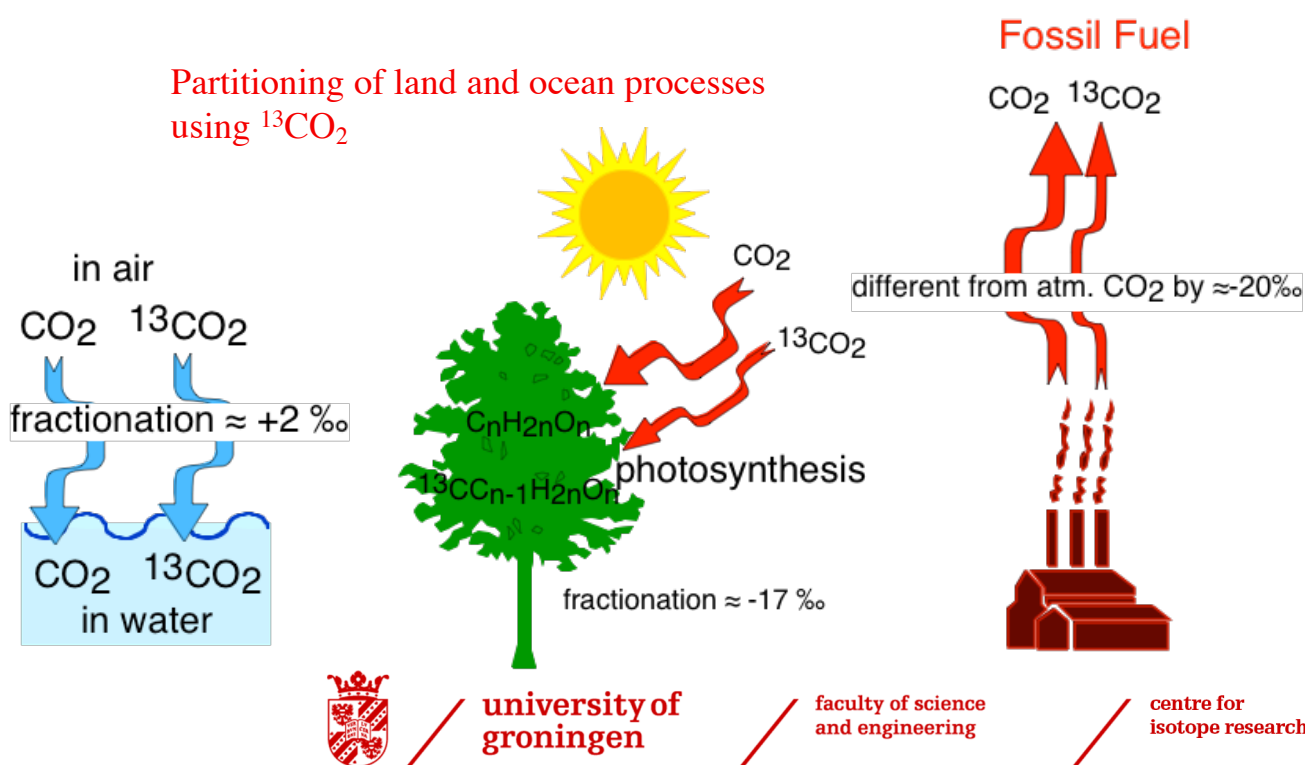
Contents:

- History of atmospheric CO₂ isotopes
- SIRS WP1: CO₂ isotopic reference materials
- SIRS WP3: Optical isotope measurements



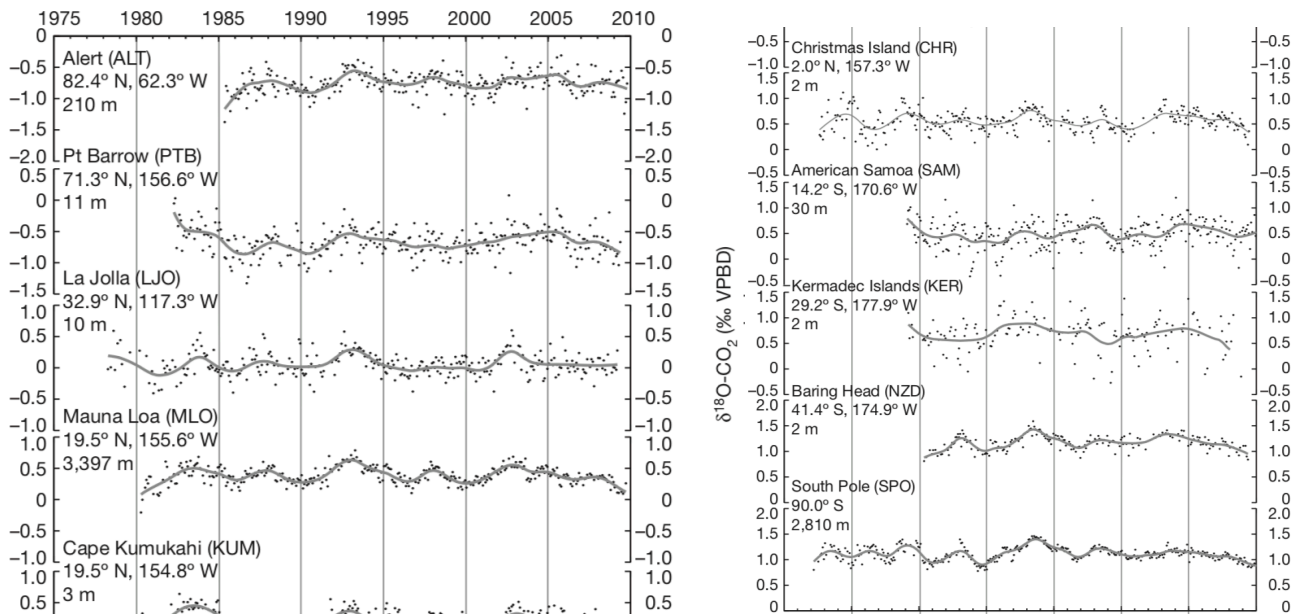
Short recall: why CO₂ isotopes?

¹³CO₂ and C¹⁸OO are valuable additional parameters in Carbon Cycle research!



$C^{18}OO$ couples the carbon and water cycles

Welp, L. R., Keeling, R. F., Meijer, H. A. J., Bollenbacher, A. F., Piper, S. C., Yoshimura, K., Francey, R. J., Allison, C. E. and Wahlen, M.: Interannual variability in the oxygen isotopes of atmospheric CO_2 driven by El Nino, *Nature*, 477(7366), 579–582, doi:10.1038/nature10421, 2011.

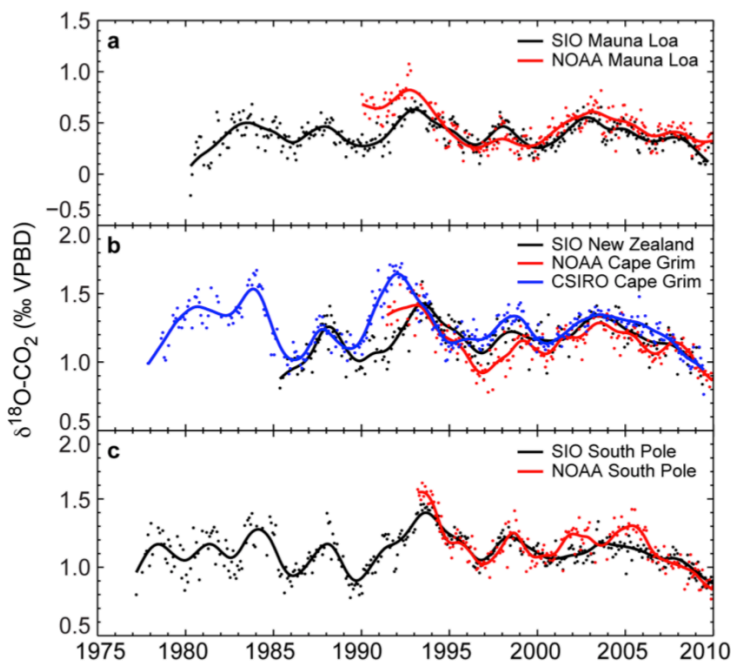


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Signals are small: good calibration and long term stability of scales is necessary



Pioneered by:
 Scripps and CIO/RUG from end
 of the 1970's
 CSIRO from end of 1970's
 NOAA came later (early 1990's)

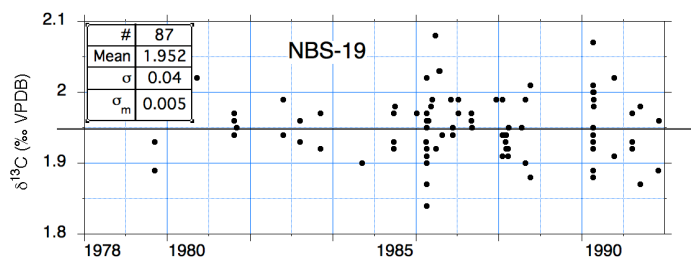
Welp, et al: Interannual variability in the oxygen isotopes of atmospheric CO_2 driven by El Nino, *Nature*, 477(7366), 579–582, 2011



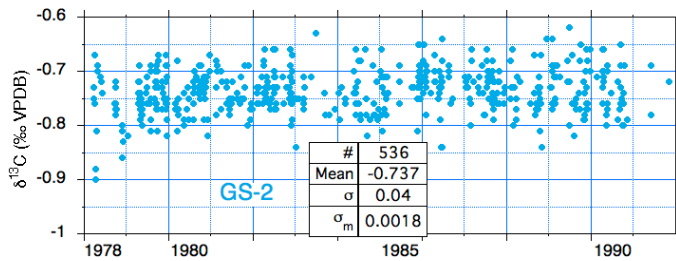
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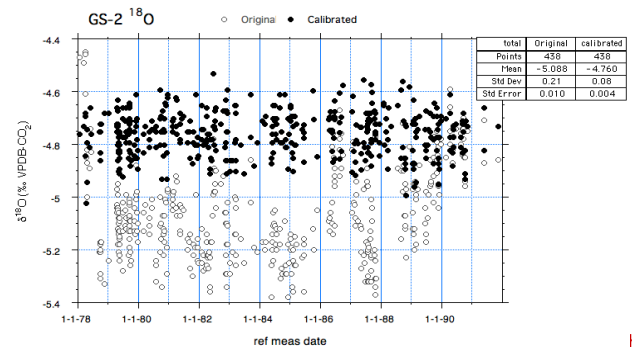
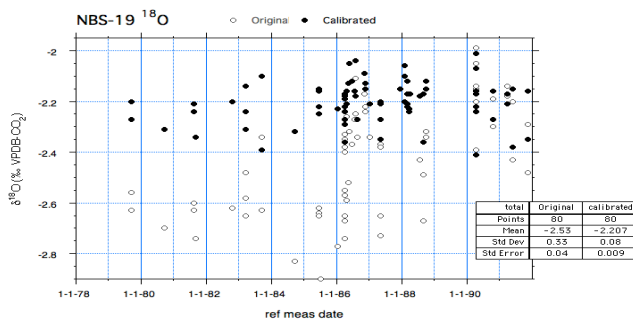
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RUG: scale calibration
based upon pure CO₂
from carbonates



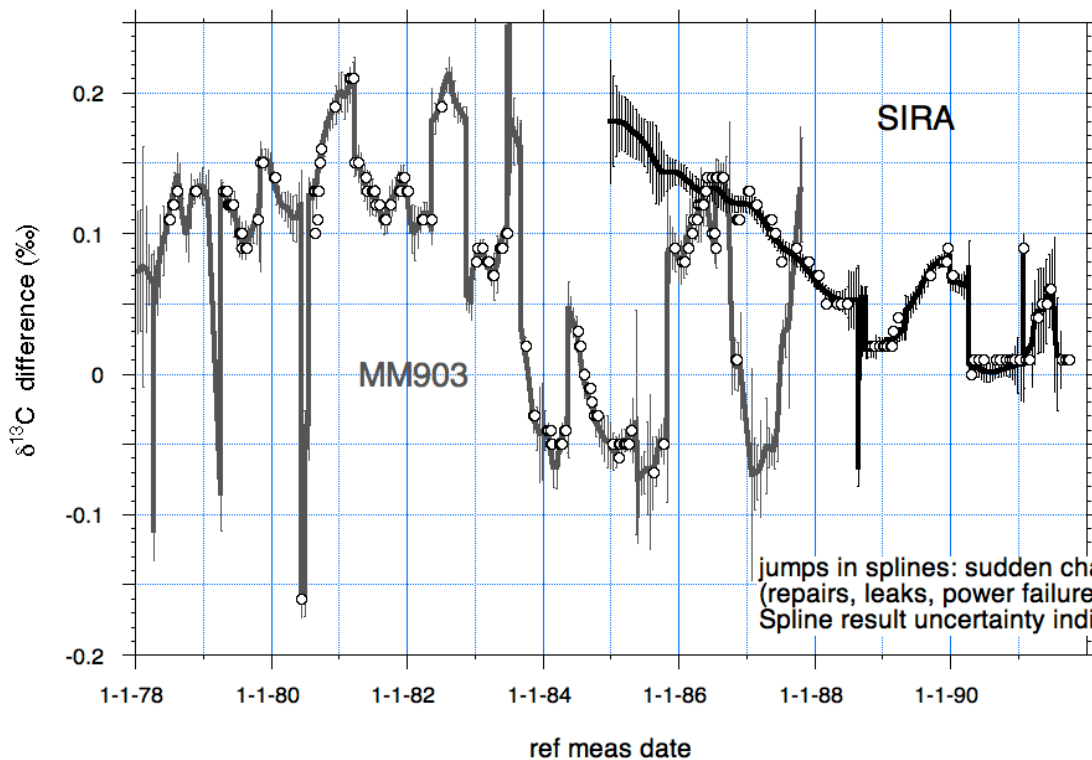
¹⁸O scale of VPDB-CO₂
coupled to the water scale



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calibration procedure: spline fits of all reference calibration data
individual points: all days with atmospheric CO₂ measurements



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Frequent intercomparisons between networks

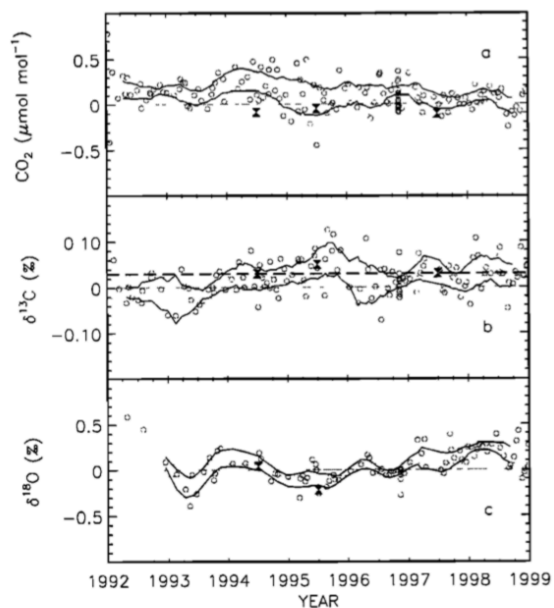
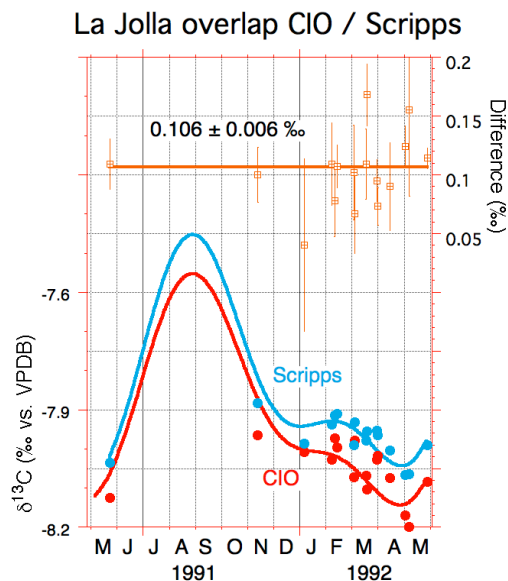


Figure 2. (a-f) Differences (CSIRO minus NOAA) betw

Masarie et al., J Geoph Res 106 (2001)

Transfer of measurements from CIO to Scripps



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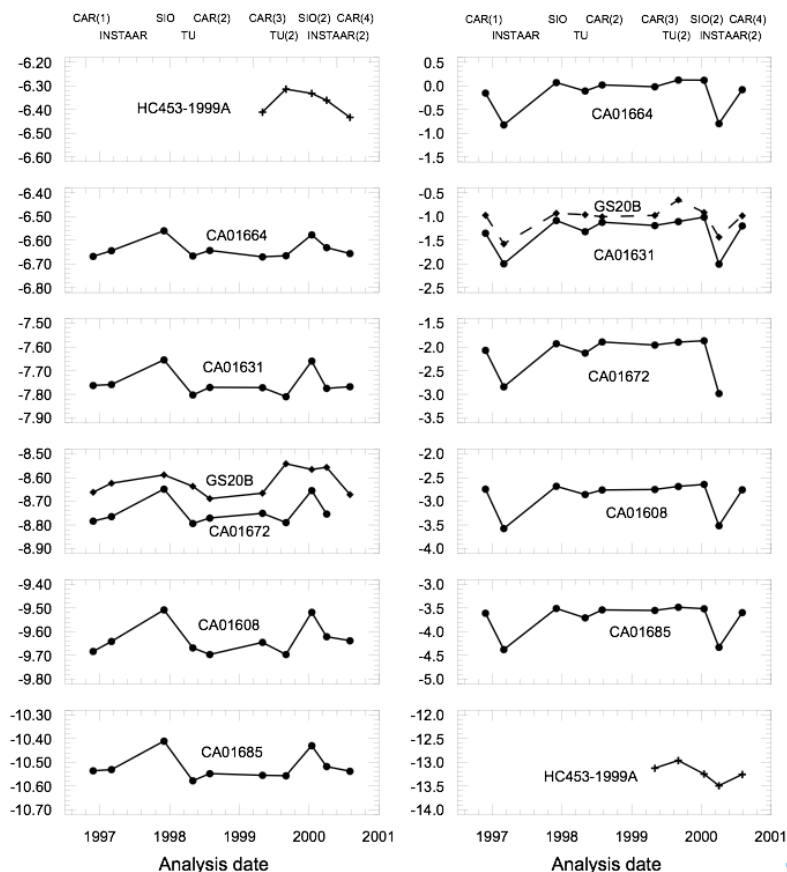
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1990's: step from pure CO₂ to "whole air" calibration

1997-2002: IAEA-CSIRO
"Classic" exercise: shipping
cylinders (and pure CO₂)
around the world

What have we learnt about stable isotope
measurements from the IAEA CLASSIC?
Allison et al, 11th WMO CO₂ Measurement Experts
Meeting: Tokyo 25-28 September 2001



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Figure 1. → Reported isotopic composition (‰) of CO₂ in the circulated CLASSIC cylinders. The six panels on the left are δ¹³C_{VPDB-CO2} and the six panels on the right are δ¹⁸O_{VPDB-CO2}.

Classic conclusions:

Ten high-pressure cylinders of chemically modified air were prepared in order to assess the comparability of CO₂ stable isotope measurements in four key laboratories. Two circulations of five of the prepared high-pressure cylinders of air and two canisters of high purity CO₂ gas between the four laboratories **have revealed significant differences in reported $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$** . The mean differences between laboratories are **significantly greater, by up to a factor of 10 or more, than the accepted target precisions** required for merging data from these laboratories. **These differences are consistent with various problems in assigning isotopic compositions onto the VPDB-CO₂ reference scale.** From repeat circulations through each laboratory, **measurements of the pure CO₂ gases relative to in-house CO₂ standards exhibit poorer consistency than those of the high-pressure cylinders of air measured relative to in-house CO₂-in-air standards** as a consequence of systematic instrument effects, such as cross contamination between sample and reference gases in the ion source of each mass spectrometer. **The influence** of these systematic effects, as well as **differences** due to cryogenic extraction systems, **are minimised by the use of air standards, subject to correct assignment of isotopic values to the standards.** Suggestions to reduce uncertainties in merged data from different sampling networks include an improved diagnostic and monitoring strategy, **GLOBALHUBS**, and development of more effective links to primary reference calibration materials. In the interim, the CLASSIC suite of gases can play a valuable role in providing consistent links between major CO₂ isotope monitoring networks over decadal timescales.



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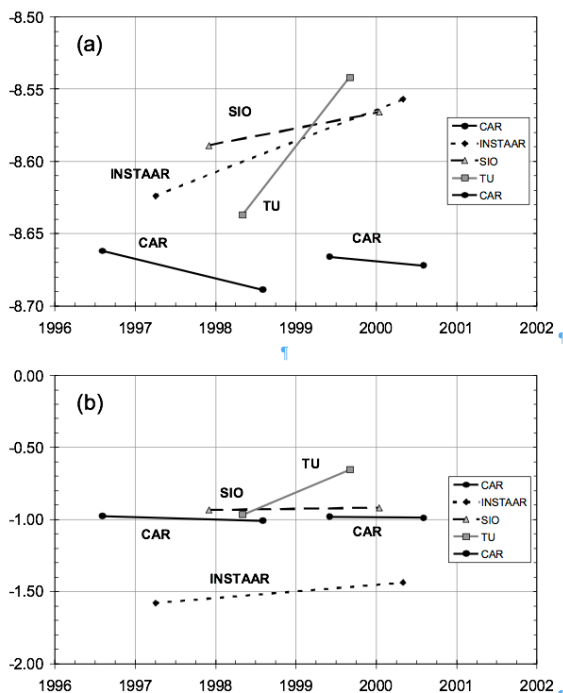


Figure 2. → Reported isotopic composition of the pure CO₂ gas in canister GS20B: (a) $\delta^{13}\text{C}_{\text{VPDB CO}_2}$, (b) $\delta^{18}\text{O}_{\text{VPDB CO}_2}$.

Pure CO₂ intercomparison was worse than the CO₂-in-air one

But: what was the true representation of “VPDB” in whole air?



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Landmark achievement

“As a result of the experiments, a new standard reference material (SRM), which consists of two 5-L glass flasks containing air at 1.6 bar and the CO₂ evolved from two different carbonate materials, is available for distribution. These ‘J-RAS’ SRM flasks (‘Jena-Reference Air Set’) are designed to serve as a high-precision link to VPDB for improving inter-laboratory comparability.”

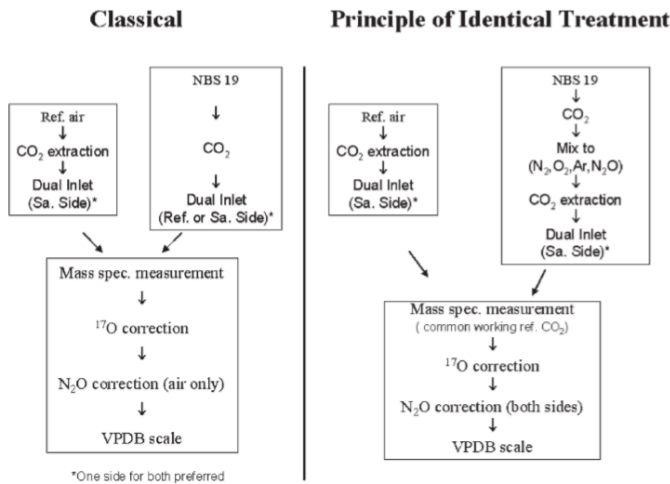


Figure 1. Comparison of the classical strategy for relating CO₂-in-air to the international VPDB scale and the one pursued in this work.

JRAS-o6 scale, tightly coupled to VPDB-CO₂

Maintained at the Max Planck for Biogeochemistry, Jena

(WMO) Central Calibration Laboratory

Heiko Moossen, successor of Willi Brand



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So, why SIRS (CO₂ part)?

- JRAS-o6 is excellent, but cannot serve an ever increasing community
- So, more streamlined production of reliable reference gases for the isotopes of CO₂ in air is necessary:
- Typically a task for NMI's
- There is a new kid on the block: optical measurements!
- SIRS will “re-invent the wheel” to some extent, but now properly documented, and aimed at routine production of reference gases, at an affordable price
- SIRS is the first project, with still “relaxed” uncertainty goals
- If successful, a follow-up will hopefully fly with stricter uncertainty goals



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Referencing CO₂ in air to VPDB



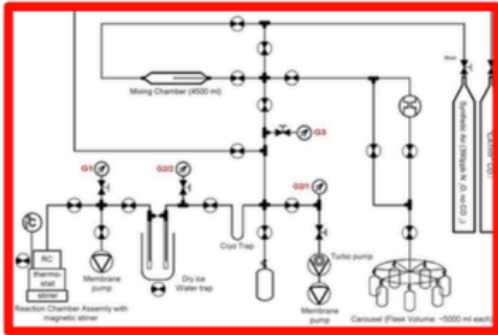
A1.3.3: - Referencing CO₂-in-air to VPDB
- Uncertainty budget



1 Syntheses = 3 x 5L Flask
(~380 ppm CO₂ in Syn. Air)



MAT 252 with BGC Air Trap (Cora): Dual Inlet measurements



ARAMIS – Acid Reaction and Air Mixing System

A1.3.3: - Referencing CO₂-in-air to VPDB
- Uncertainty budget

(WMO) Central Calibration Laboratory (MPG-Jena) instrumental for SIRS

A1.3.1: - Referencing pure CO₂ to VPDB
- Uncertainty budget

Max Planck Institute
for Biogeochemistry



Heiko.moossen@bgc-jena.mpg.de

9

SIRS overview (CO₂ part, also N₂O -> Joachim Mohn)

WP1: New reference materials for $\delta^{13}\text{C}$ -CO₂ to uphold the global measurement infrastructure



- Gas reference materials of pure CO₂ for $\delta^{13}\text{C}$ -CO₂ and $\delta^{18}\text{O}$ -CO₂
- Develop static and dynamic stable isotope reference gas mixtures of CO₂ at 400 $\mu\text{mol/mol}$ (later this morning also: Adnan ŞİMŞEK)
- Validation of reference materials and comparisons to uphold VPDB scale for CO₂- air mixtures
- Exploratory absolute measurements -> Lukas Flier



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Super ratio method (SRM) “the IRMS persons’s choice”

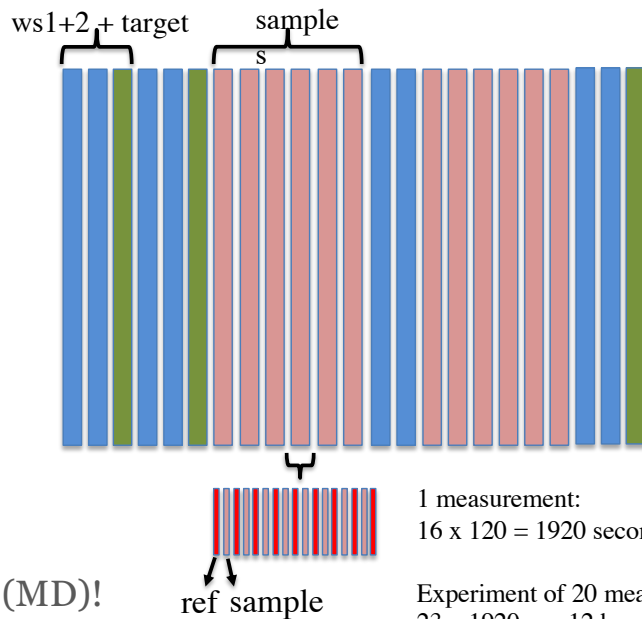
$$r^* = \frac{A_{rare}}{A_{abundant}}$$

$$R_S^* = \frac{r_S^*}{r_{ref}^*}$$

$$\delta_m^* = (R_S^* - 1)$$

$$\delta_{CAL} = (1 + \delta_{ref})\delta_m + \delta_{ref}$$

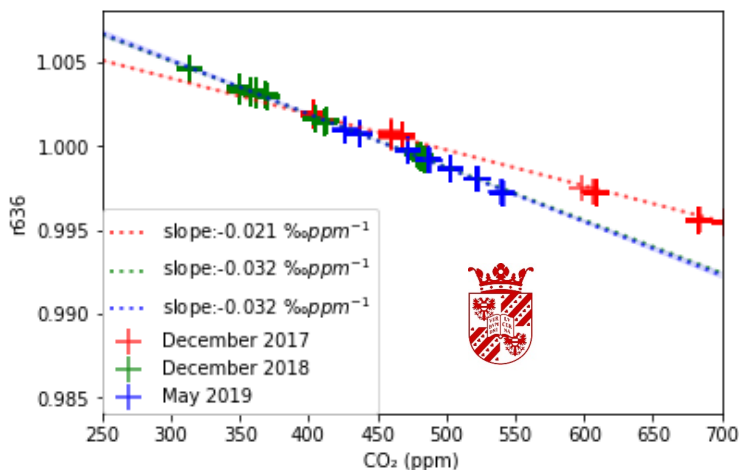
In addition however:
CO₂ Mixing ratio Dependence (MD)!



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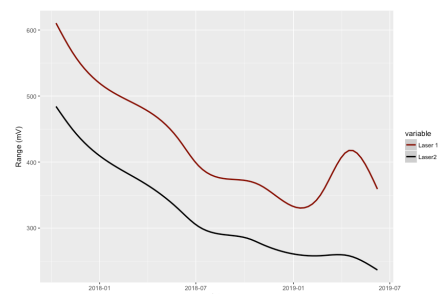
- Caused by incorrect prescription of the absorption lines
- Reduction of the slope is possible
- However, next to impossible to fully annihilate this.
- Stability is more important.

In addition, the MD is dependent on the exact composition of the “air”: Synthetic “air” with or without Ar (and N₂O), or CO₂-free natural air.

Change of MD trough time

r636	slope	st. error
Dec. 2017	-2.13E-5	6.59E-8
Dec. 2018	-3.16E-5	7.00E-8
May 2019	-3.20E-5	4.06E-7

Change of MD through time caused by cavity transmission deterioration?



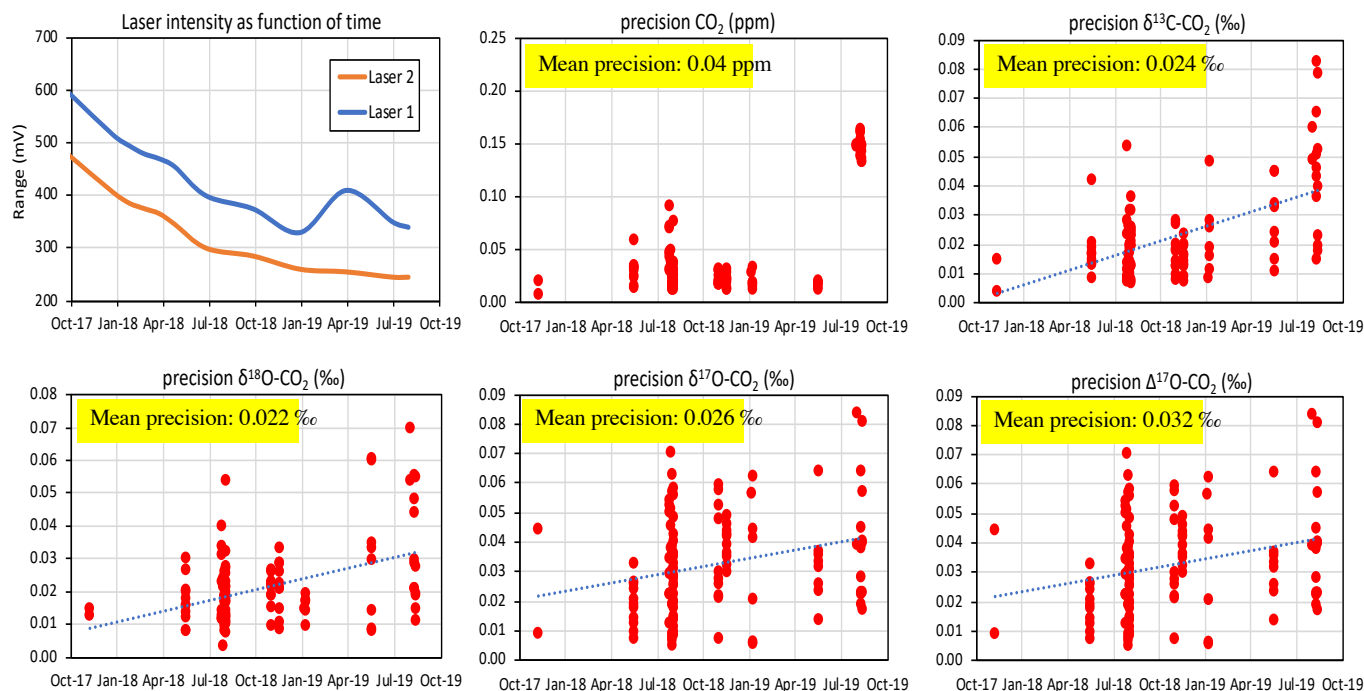
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SICAS performance over time



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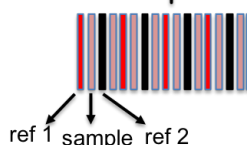
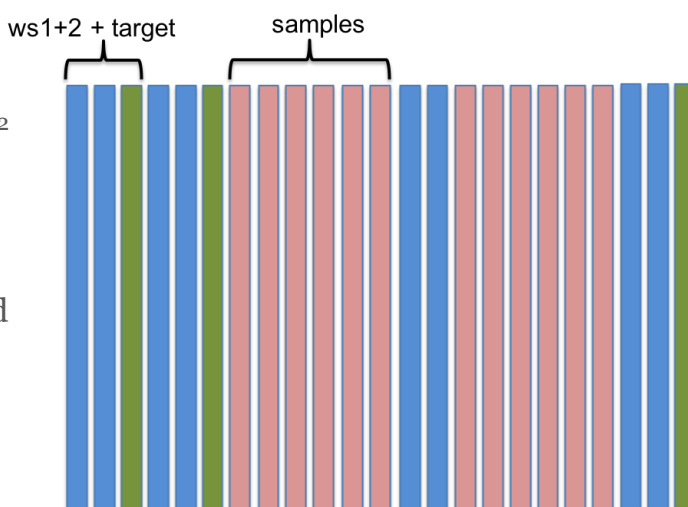
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Isotopologue Abundance Method (IAM) “The optical spectroscopist’s choice”

Two references with similar, known isotopic composition, but different CO_2 concentrations (low; 350 ppm and high; 430 ppm)

For every measurement a calibration curve is calculated for the assigned and measured isotopologue abundance

From the isotopologue abundance the isotopic composition can be calculated (following **Flores et al. 2017**)



1 measurement:
 16 x 120 = 1920 seconds

Experiment of 20 measurements :
 23 x 1920 = ~ 12 hours



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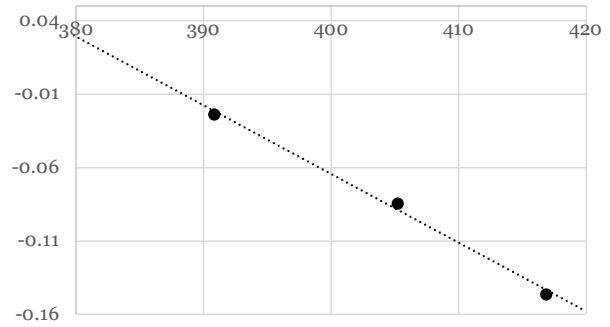
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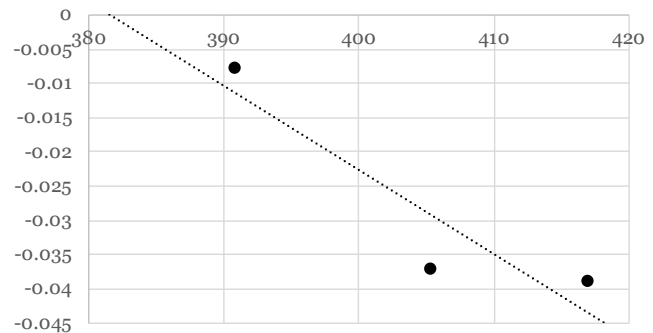
Preliminary results...

After IAM calibration (using 350 ppm and 440 ppm atmospheric cylinders, IMAU Utrecht), still some MD seems to be present...

d13C residual (‰) vs CO2 (ppm)



d18O residuals (‰) vs CO2 (ppm)



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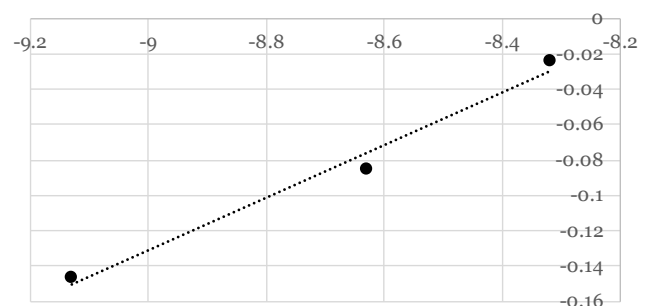
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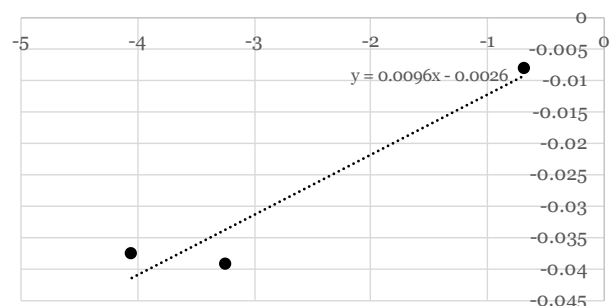
Preliminary results...

After IAM calibration (using 350 ppm and 440 ppm atmospheric cylinders, IMAU Utrecht), still some MD seems to be present...

d13C residual (per mille) vs d13C assigned (VPDB)



d18O residual (per mille) vs d18O assigned (VPDB-CO2)



... or are these scale issues in the references?

More tests are needed:



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Next steps within SIRS

Proficiency test

- Sample gases (3x)
 - CO₂ concentration within the range of 300-500ppm
 - $\delta^{13}\text{C}$ within range of -48‰ to -8‰ VPDB
 - $\delta^{18}\text{O}$ within range of -27‰ to +2‰ VPDB
- Calibration gases (2x)
 - One close to background concentrations, one with a more contaminated (depleted) signal?
- Distribution of the gases
 - Gases will be subsampled from high pressure cylinders, into sample flasks provided by the participants so pressure reducer effects are minimized

What do we want to test?

CO₂ mixing ratio dependence is one of the most challenging factors in OIRS measurements, so we will include one low (~380ppm) and one high (~430 ppm) sample

Scale contraction due to cross contamination occurs in every measurement and can be tested by including a sample with deviating isotopic composition



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Too early for conclusions, but

Considerations

The isotope super-ratio method has been developed for IRMS, because:

- A lot of common factors cancel (drifts!!), making the ratios less vulnerable and more stable

This also applies to the optical method, only:

- Several factors are not in common, and thus won't cancel (mass dependence vs absorption characteristics)

The Isotopologue abundance method implicitly corrects for mixing ratio dependence

- but is more sensitive to drifts, as all differences between the two ref gases become part of the calibration
- does it lead to a linear isotope ratio scale?



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