

Calibration of stable isotope ratios in atmospheric CO₂: Improving the traceability chain.

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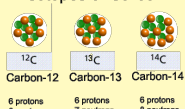
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Introduction: the importance of stable isotopes

The accurate measurement of the relative abundances of the rare stable isotopes in natural materials is an important tool in a large range of scientific applications, ranging from biomedicine through hydrology to greenhouse gas and paleoclimate studies.

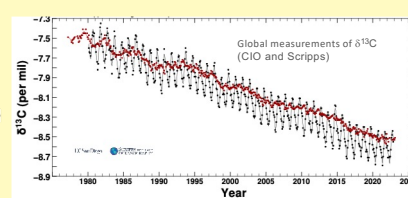
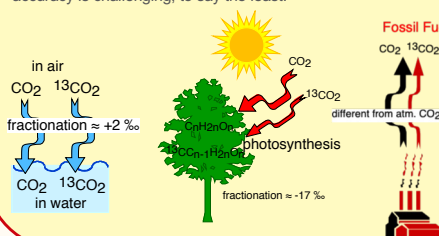
The small variations in these relative abundances, for example for the ¹³C and the ¹⁸O isotopes in atmospheric CO₂, give important information about the origin, transport, phase transitions and uptake of the respective molecules. Prerequisite is, however, that the measurements are highly precise and accurate, and properly calibrated.

Isotopes of Carbon



Isotopes in atmospheric CO₂: requiring the utmost precision and calibration stability

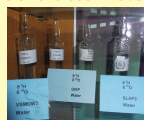
The isotope measurements of atmospheric CO₂ give valuable additional insight into the so-called carbon cycle, the processes of exchange and uptake of CO₂ between atmosphere, ocean, land, and the anthropogenic production of CO₂ from fossil fuels. However, due to the size of the atmosphere, the isotope signals of these sources and sinks get diluted, and precise and accurately (and long term) calibrated measurements are of crucial importance. The average annual trend of $\delta^{13}\text{C}$ in atmospheric CO₂ is only $\approx -0.025\text{‰}$ / yr, meaning calibration accuracy and stability should be at the $\leq 0.01\text{‰}$ level. Transferring the isotope ratio of the original carbonate reference material through pure CO₂ into CO₂-in-air with that level of accuracy is challenging, to say the least.



Why are isotope delta measurements special?

All physical and chemical processes, including the measurement process, influence the relative abundance of stable isotopes, therefore such measurements have been designed to be "double relative": the isotope ratio of rare to abundant isotope in a sample material is compared to that same ratio in a reference material. Depending on the field of study, different choices of reference materials have been made.

The absolute isotope abundances of substances could and still cannot be determined accurately enough. The required and achieved precision in the measurement of relative differences between samples is much higher. Therefore, measurements of stable isotopes are still artefact-based and these artefacts form the basis of the relative measurement scales. For example, a specific calcium carbonate is the material of choice for carbon and oxygen isotopes.



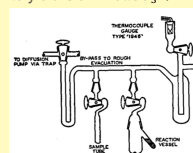
A measurement result is usually expressed as a δ -value, in this example $\delta^{13}\text{C}$ of a sample related to a Reference Material:

$$\delta^{13}\text{C}(\text{‰}) = \left(\frac{R_{\text{sample}}(^{13}\text{C}/^{12}\text{C})}{R_{\text{RM}}(^{13}\text{C}/^{12}\text{C})} - 1 \right) \times 1000$$

Since the difference between sample and reference for natural materials is very small, δ -values are usually small numbers, and expressed in ‰

Reference Material for CO₂

The Reference Material for all carbon materials, including atmospheric CO₂ is a calcium carbonate (IAEA-603). This RM must be converted with a 100% efficiency using phosphoric acid to yield CO₂: $\text{CaCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} + \text{CO}_2$

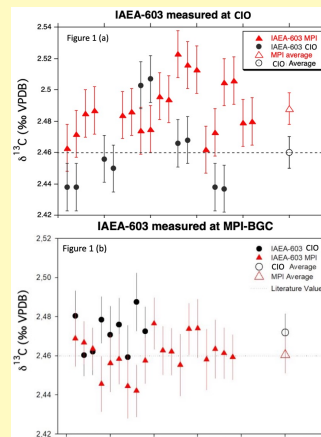


Original system by McCrea (1950)



Systems in practice at MPI-BGC and CIO

The reliability of the results of the phosphoric acid reaction with the carbonate RM is tested by comparing the results of a series of preparations between the two expert labs CIO and MPI-BGC. To separate the reaction from the measurements, CO₂ was produced at MPI-BGC and sent to CIO to compare with the locally produced CO₂ (a) and vice versa (b). The results are in figure 1. The agreement between the labs is approaching the 0.01‰ level.



Calibrating atmospheric CO₂ isotope measurements

Isotope measurements of atmospheric CO₂ were, and still are, performed on flasks from which the CO₂ is cryogenically extracted.

Originally, the pure CO₂ from the calcite RM serves as calibration tool (Calibration scheme A). Figure 2 shows $\delta^{13}\text{C}$ measurements in Lütjewad station, performed this way.

As the cryogenic extraction is a potential source of fractionation, more and more labs use CO₂-in-air as RM nowadays. The MPI-BGC produces such a CO₂-in-air RM: JRAS-06. Several NMI's plan a similar product (Calibration scheme B).

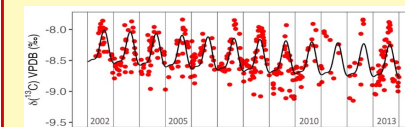
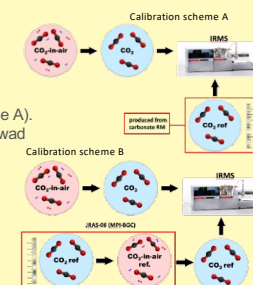


Figure 2: $\delta^{13}\text{C}$ measurements performed by IRMS on flasks sampled at Lütjewad station under 'background' conditions. Calibration has been performed using scheme A.

More recently, CO₂ stable isotope measurements became possible directly in air, by Laser Absorption Spectroscopy (LAS). Since 2017, we have been analysing flasks from Lütjewad using LAS (figure 3A). Recently, we have installed a dedicated LAS instrument at Lütjewad, for (semi-)continuous isotope measurements (figure 3B). For calibration, CO₂ extraction is no longer needed, and we rely on a CO₂-in-air RM (Calibration scheme C).

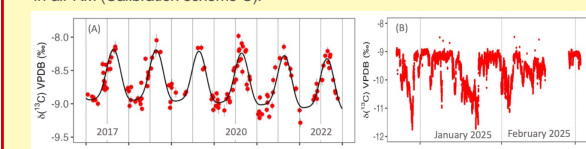


Figure 3: $\delta^{13}\text{C}$ measurements performed by LAS on flasks sampled at Lütjewad station under 'background' conditions (A). Recently, we have installed a LAS instrument at Lütjewad for continuous measurements (B). Calibration is performed using scheme C.

In all schemes, dilution and extraction of CO₂ play a profound role. The best way to scrutinize those processes for fractionation is a 'closed loop' experiment, as sketched here: start with pure CO₂, dilute it, and extract it again. The combined employment of IRMS and LAS helps to detect possible fractionation effects in either of the two processes. At CIO, this 'closed loop' experiment is currently executed.

