

Long-term performance of a dual-laser absorption spectrometer for the measurement of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ of CO_2

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The SICAS is a dual-laser absorption spectrometer which measures the mole fraction of the four most abundant isotopologues (626, 636, 627 and 628) of CO_2 on dry, atmospheric samples (see figure 1). Samples are calibrated with a set of gas mixtures of known isotope compositions

Absorption spectra SICAS

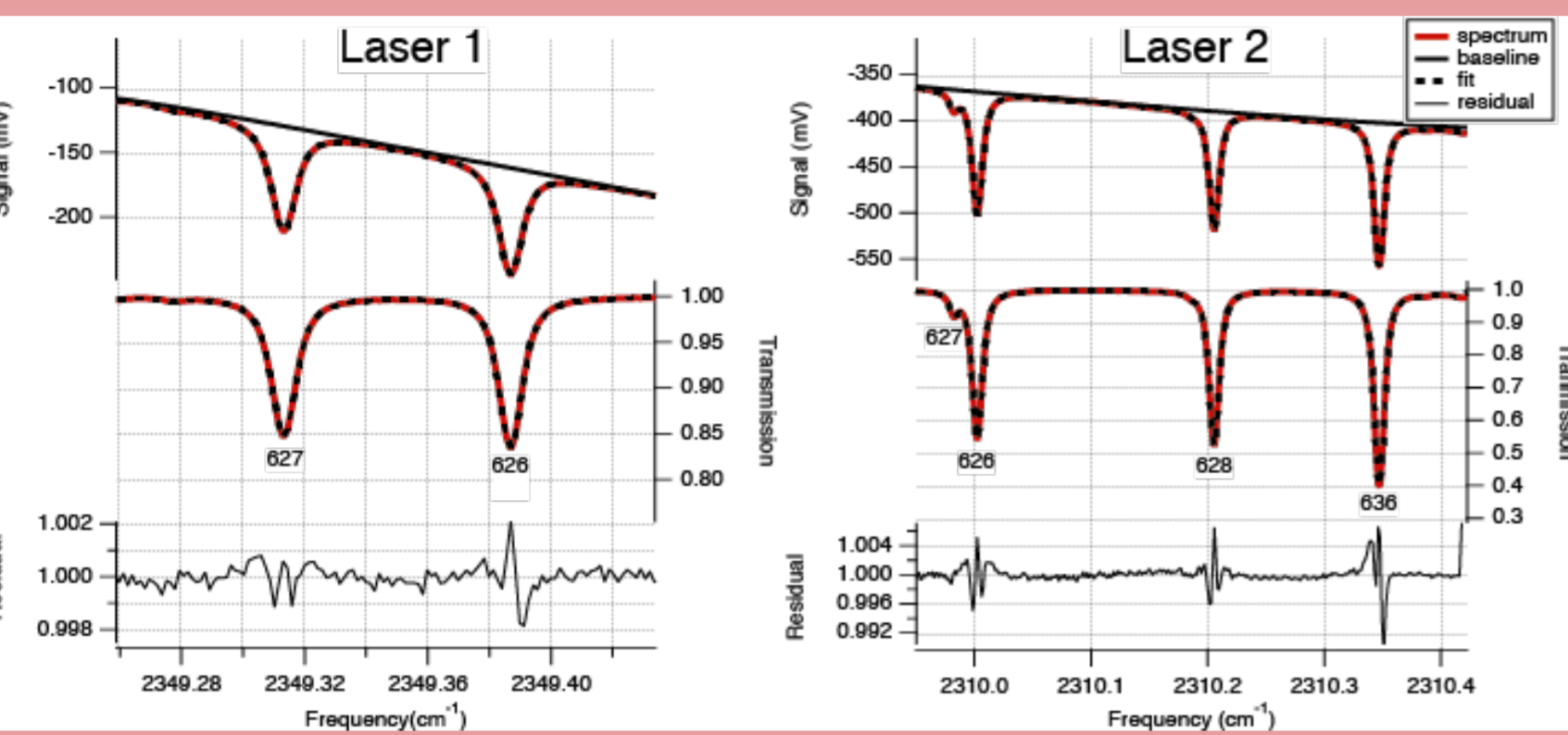


Figure 1 Typical absorption spectrum, transmission spectrum and residual for laser 1 (left) for measurement of 627 and 626 and laser 2 (right) for measurement of 626, 628 and 636. The residuals show systematic deviations at the line positions. These deviations are primarily due to the use of the Voigt line shape function in the spectral fitting model, rather than a more complex line shape function such as Hartmann–Tran.

and CO_2 mole fractions. The calibration method used is the isotopologue method as described in Steur et al. (2021), based on direct calibration by isotopologue amounts, described by Griffith (2018). A quality control cylinder (QC) is used as a 'known unknown' to monitor the measurement quality of a measurement series as well as the long-term measurement quality.

The results of long-term monitoring over the period 2020 - now of the QC are shown in figure 2, also with respect to the WMO/GAW inter-laboratory compatibility goals for the Northern Hemisphere (Crotwell et al., 2020).

Measurement results of the quality control tank over period 2020 - now

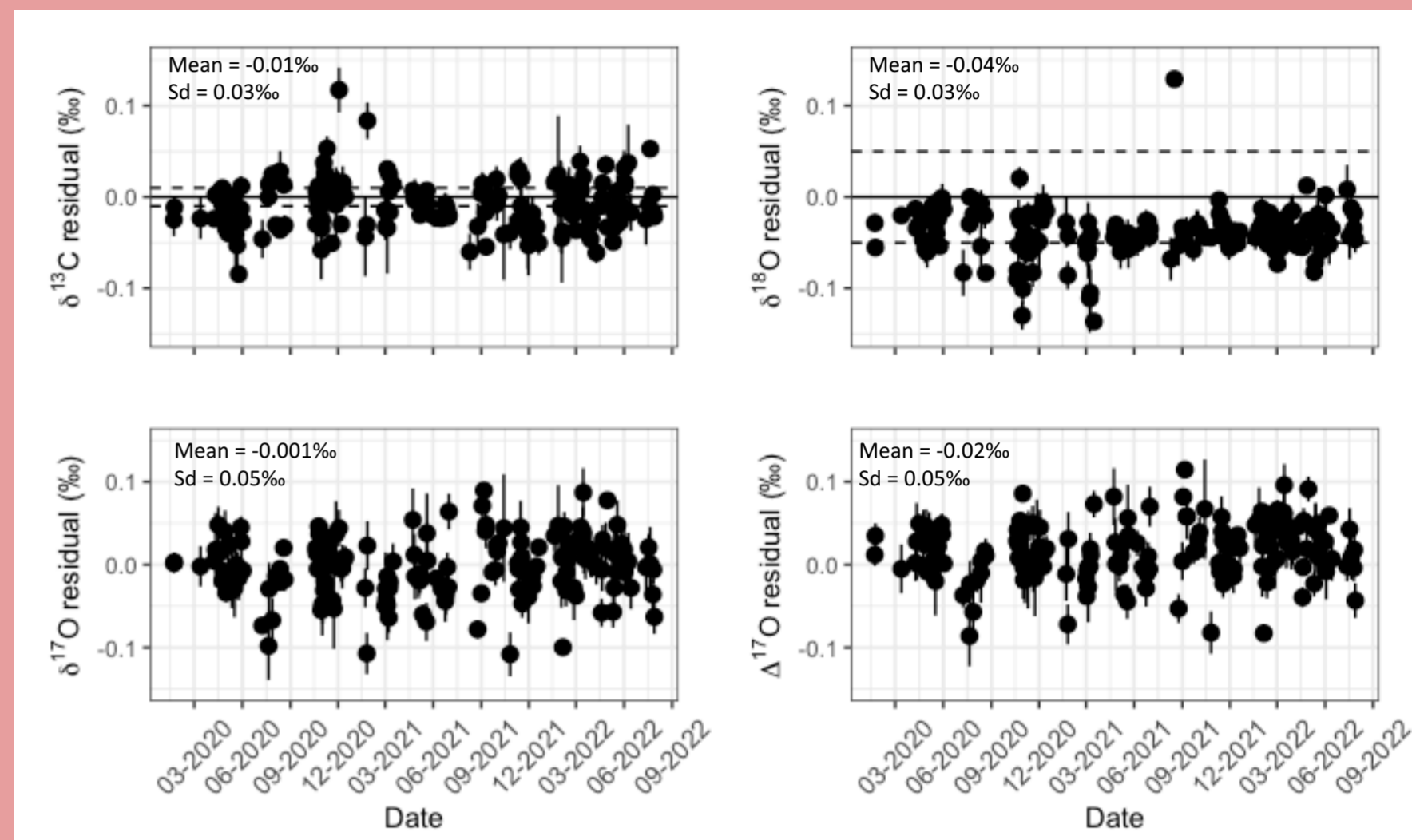


Figure 2. All measurements (top left $\delta^{13}\text{C}$, top right $\delta^{18}\text{O}$, bottom left $\delta^{17}\text{O}$, bottom right $\Delta^{17}\text{O}$) of the quality control tank over the period 2020 – now. The mean and standard deviation of the measurement series over the full measurement period are shown in the upper left corners of the graphs. The dotted lines show the WMO/GAW inter-laboratory compatibility goals for the Northern Hemisphere.

Calibration with high pressure gas tanks

For daily calibration of measurements we use high pressure gas cylinders (40L Luxfer aluminum, max. pressure of 200 bar) filled with natural air from the roof of our institute. We are aiming for an even spread of CO_2 mole fractions of our reference cylinders that bracket the range of CO_2 mole fractions of our samples to correct for the varying and non-linear residuals of the measured isotopologue mole fractions with respect to the actual mole fractions that occur due to imperfect line fitting. The references used in the period 2020 – now are shown in figure 3 (including the QC).

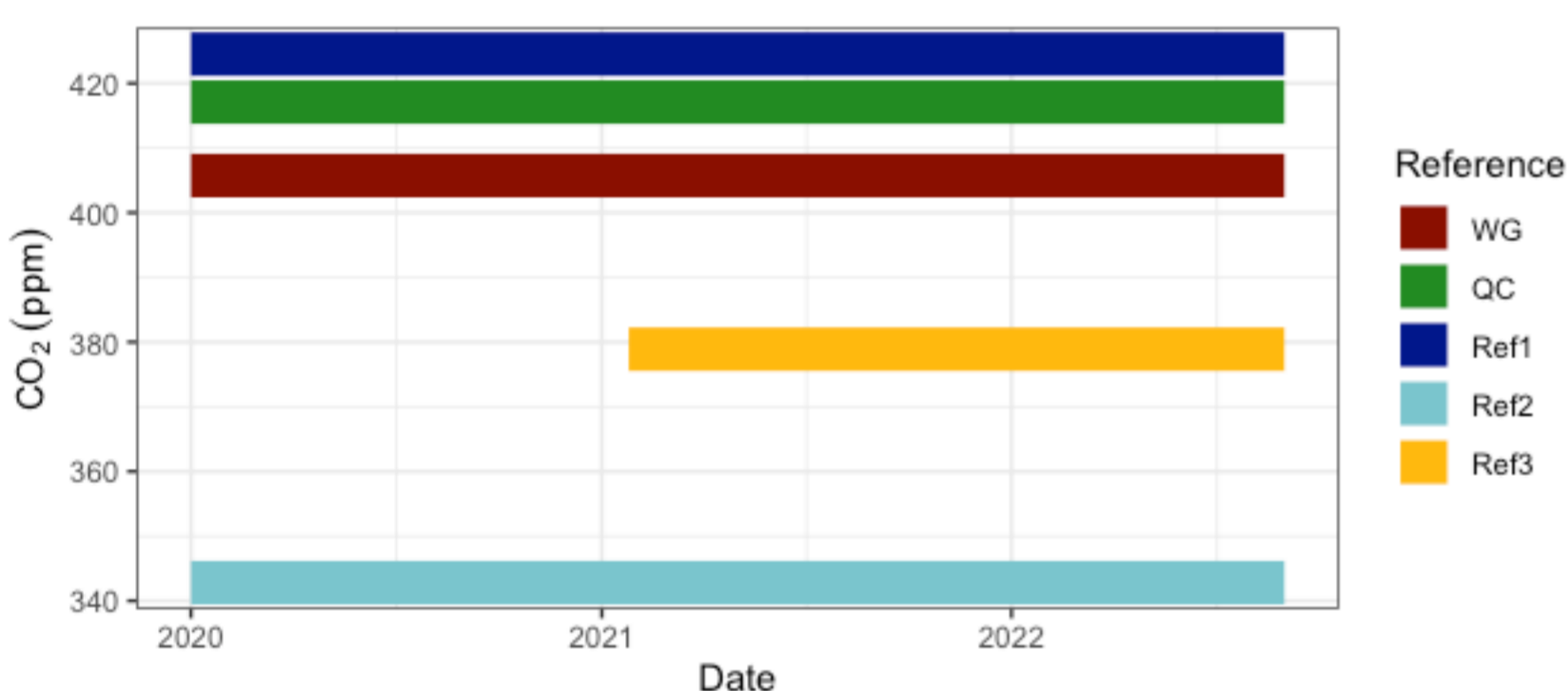
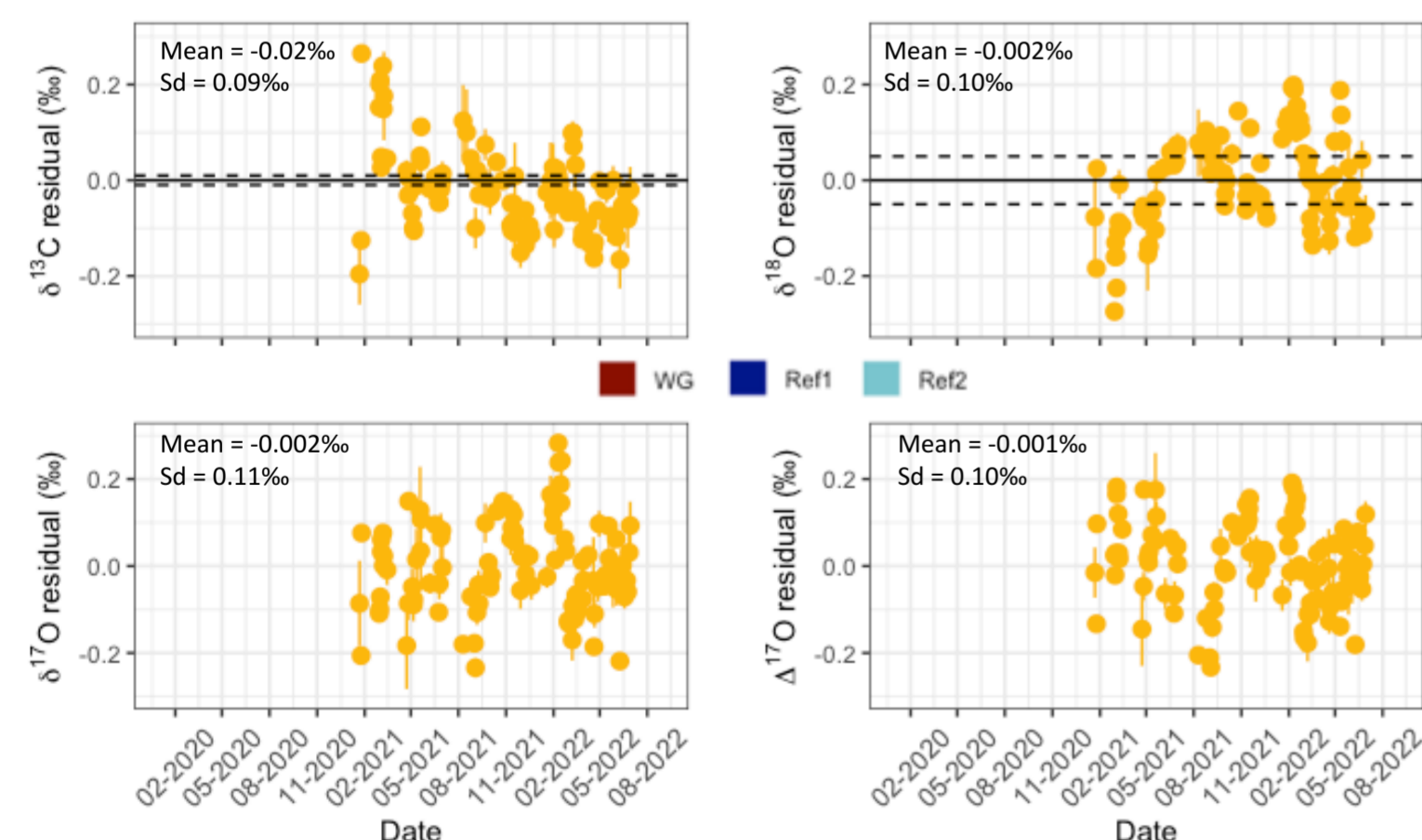


Figure 3. The reference cylinders and their CO_2 mole fractions that were included in the measurements during the period 2020 – now.

Consequences of interpolation and extrapolation

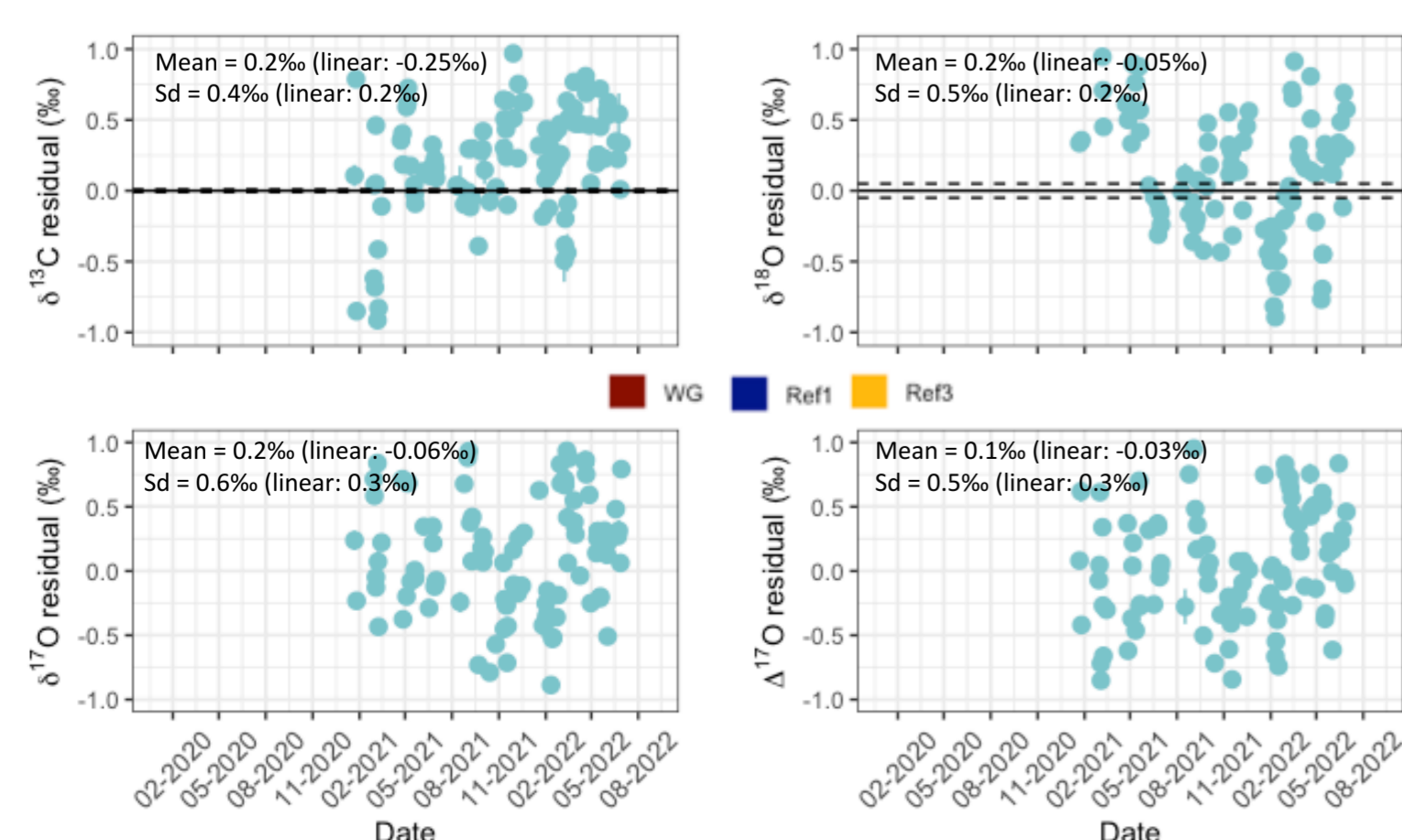
Results of interpolation to calibrate measurements of reference 3 (378.9 ppm), using WG, reference 1 and reference 2.



Although reference 3 is bracketed by the WG and reference 1, the low density of references induces higher uncertainty on the longer time scale.

Figure 4. Reference 3 measurements calibrated using a quadratic calibration curve based on WG, reference 1 and reference 2 measurements.

Results of extrapolation to calibrate measurements of reference 2 (342.81 ppm), using WG, reference 1 and reference 3.



Extrapolation of the calibration curves induces very high uncertainty over the longer time scale and should therefore be avoided.

Figure 5. Reference 2 measurements calibrated using a quadratic calibration curve based on WG, reference 1 and reference 2 measurements. In brackets the mean and standard deviation of a linear calibration.

Measurement of reference materials on the SICAS – ongoing work

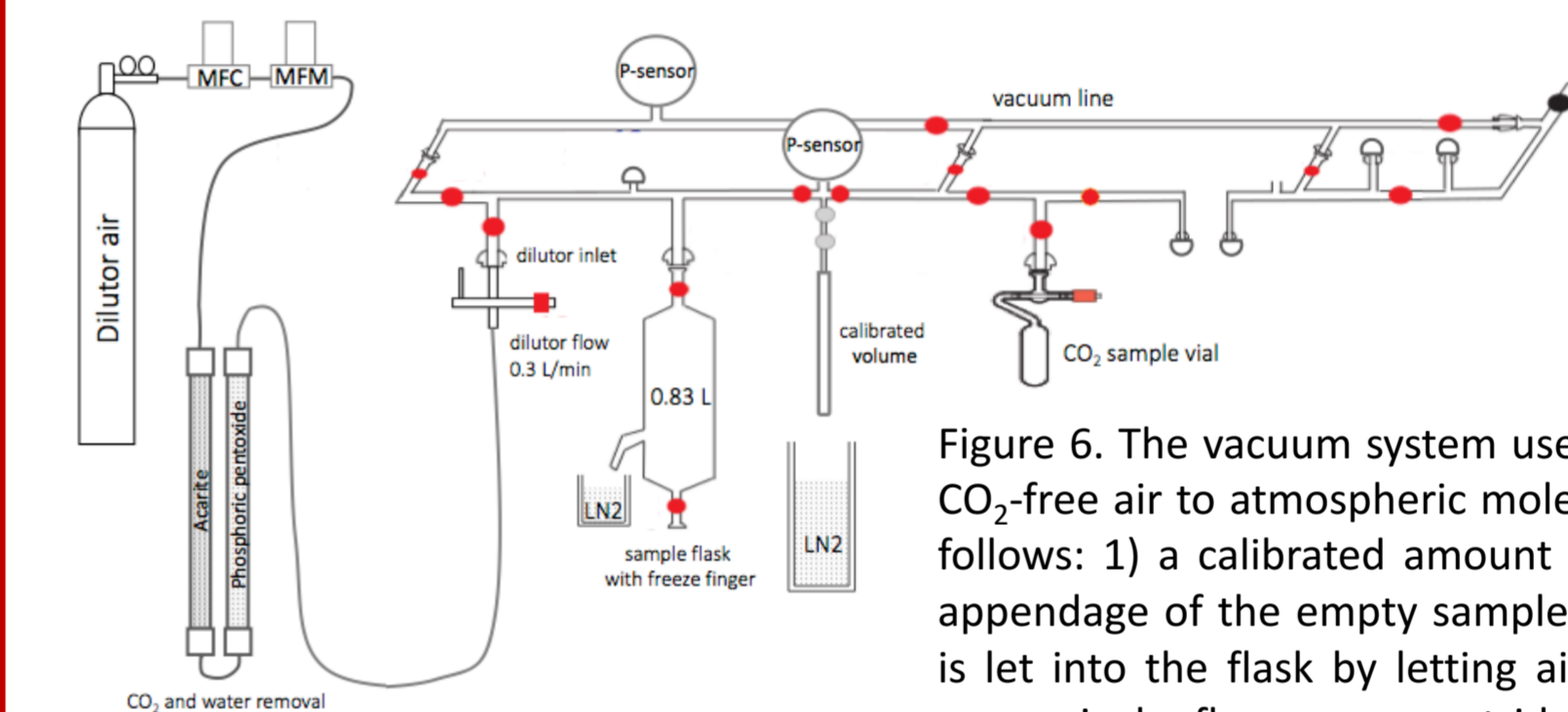


Figure 6. The vacuum system used for dilution of pure CO_2 into CO_2 -free air to atmospheric mole fractions. The procedure is as follows: 1) a calibrated amount of pure CO_2 is frozen into the appendage of the empty sample flask using LN_2 2) CO_2 -free air is let into the flask by letting air from a pressurized cylinder successively flow over a cartridge with Ascarite, to remove the CO_2 , and a cartridge with phosphoric pentoxide, to remove all remaining water, and let it flow into the sample flask until the preferred sample pressure is reached 3) the sample flask is closed and put to rest for at least twelve hours to assure complete mixing of the CO_2 with the CO_2 -free air.

Our reference cylinders were measured for their isotope composition at the MPI-BGC in Jena, and therefore linked to the JRAS-06 scale. For direct linkage to the VPDB($-\text{CO}_2$) scale we want to be able to measure CO_2 produced from the reaction of calcium carbonates and phosphoric acid on the SICAS. We developed a dilution system to produce gas mixtures composed of pure CO_2 and CO_2 -free air with CO_2 mole fractions in the atmospheric range. Measurement of various calcium carbonate references on the SICAS are shown in figure 7. The results show that the variance in between batches of different phosphoric acid reactions and between diluted samples it still too high to link the SICAS directly to the VPDB($-\text{CO}_2$) scale.

Reference material	HGJC	IAEA-603	MAR-J1	NBS-19	USGS-44
$\delta^{13}\text{C}$	-4.28	2.46	1.96	1.95	-42.08
$\delta^{18}\text{O}$	-13.92	-2.37	-2.1	-2.20	-15.66

Table 1. Assigned values of the reference materials that were measured on the SICAS. The $\delta^{13}\text{C}$ of USGS-44 is the value as measured at BGC-IsoLab in Qi et al. (2020).

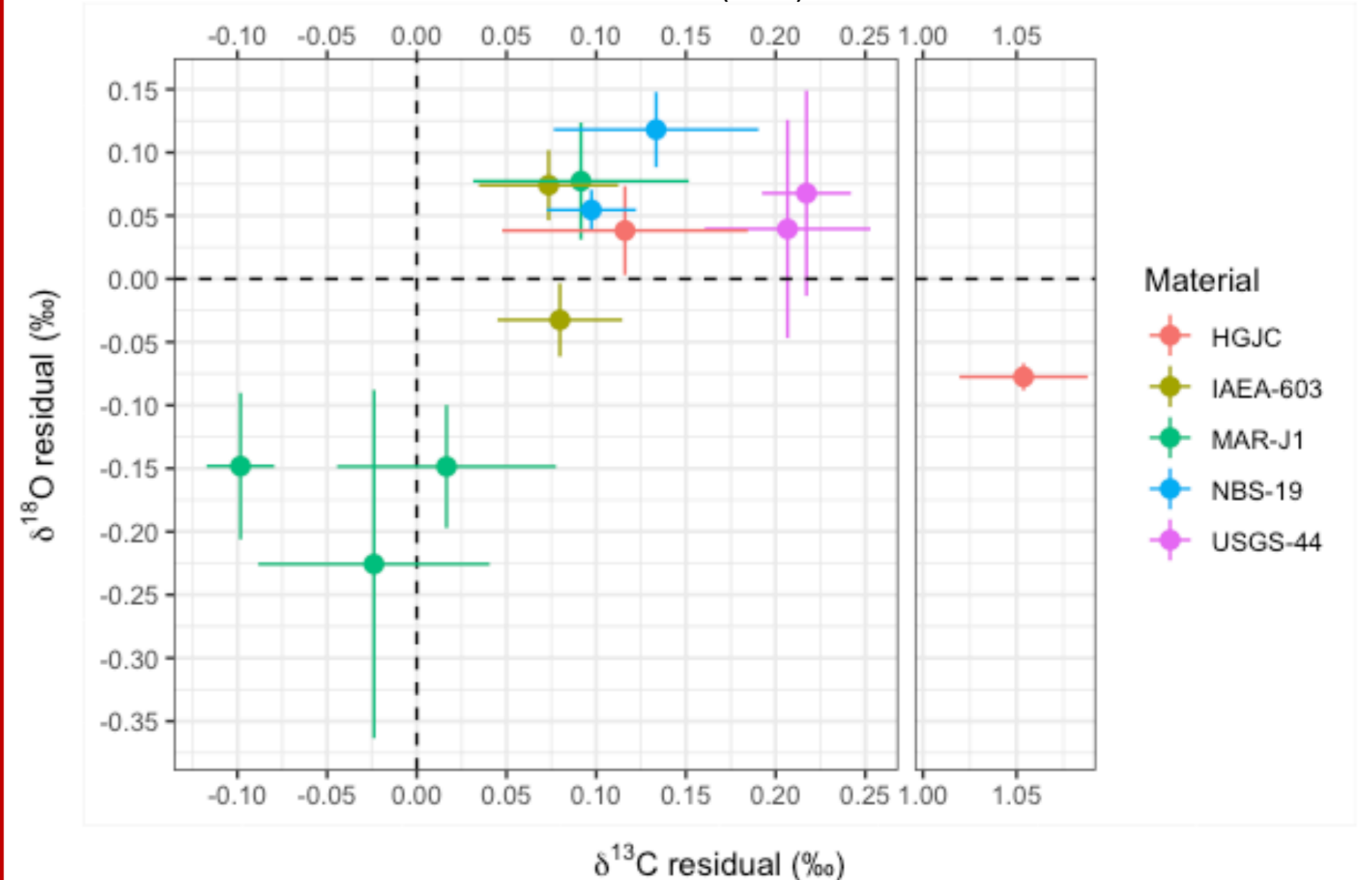


Figure 7. Residuals of measured reference materials on the SICAS. Every data point corresponds to a series of samples produced from pure CO_2 of the same phosphoric acid reaction.