Developing a continuous-flow method for triple oxygen isotope analysis by laser absorption spectroscopy

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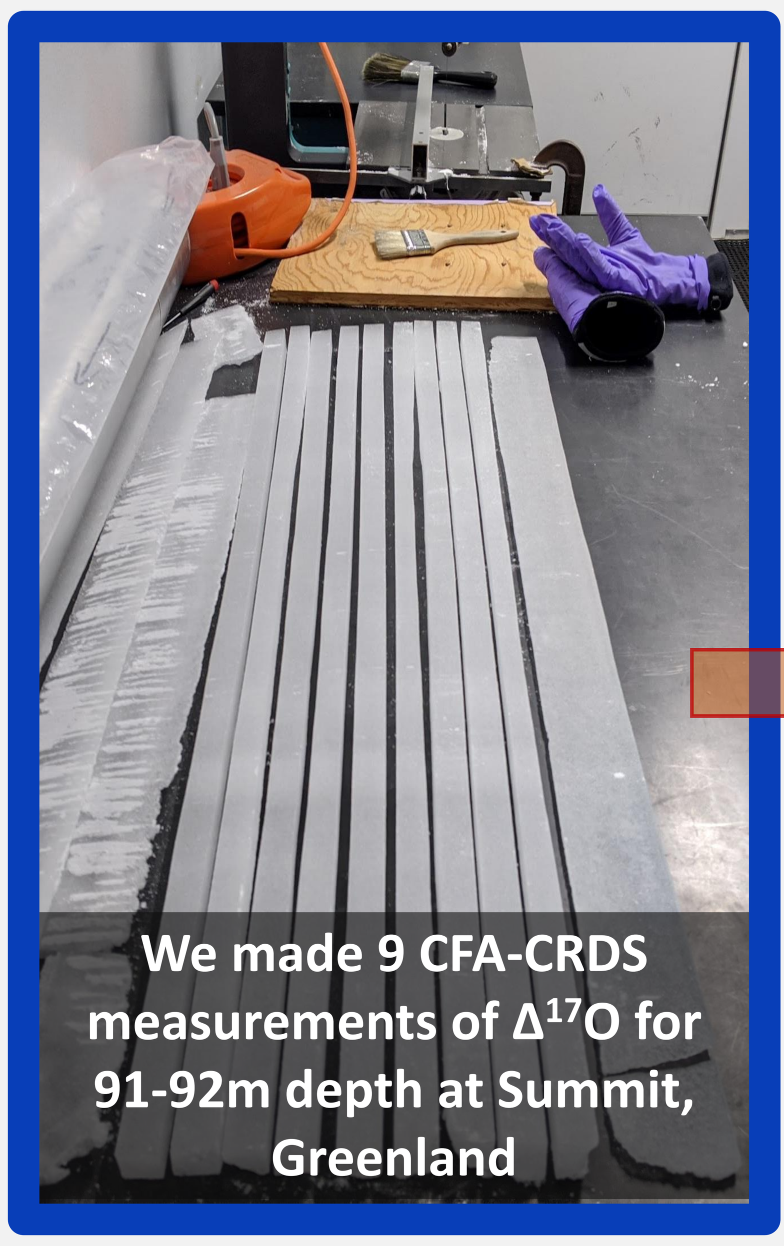
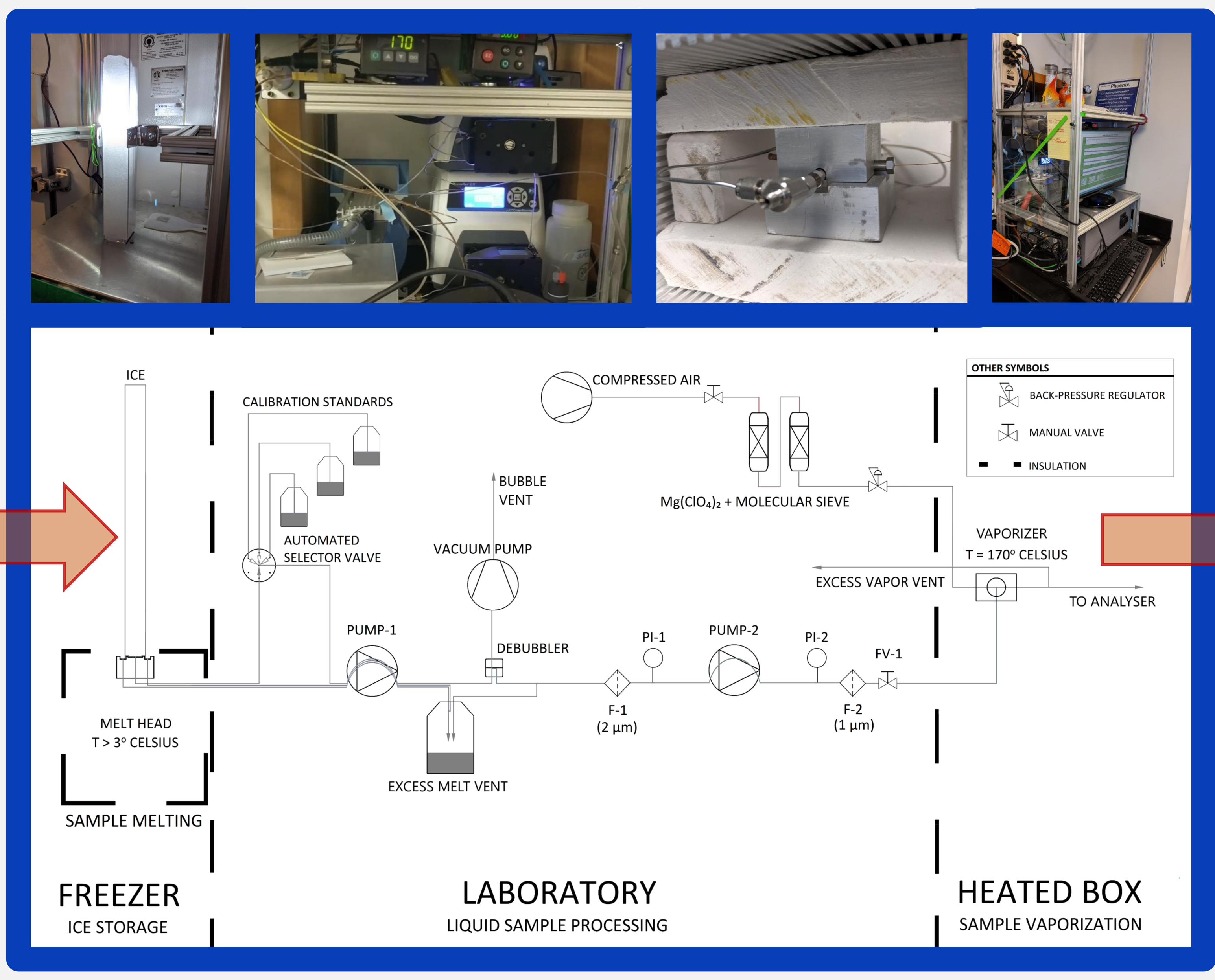
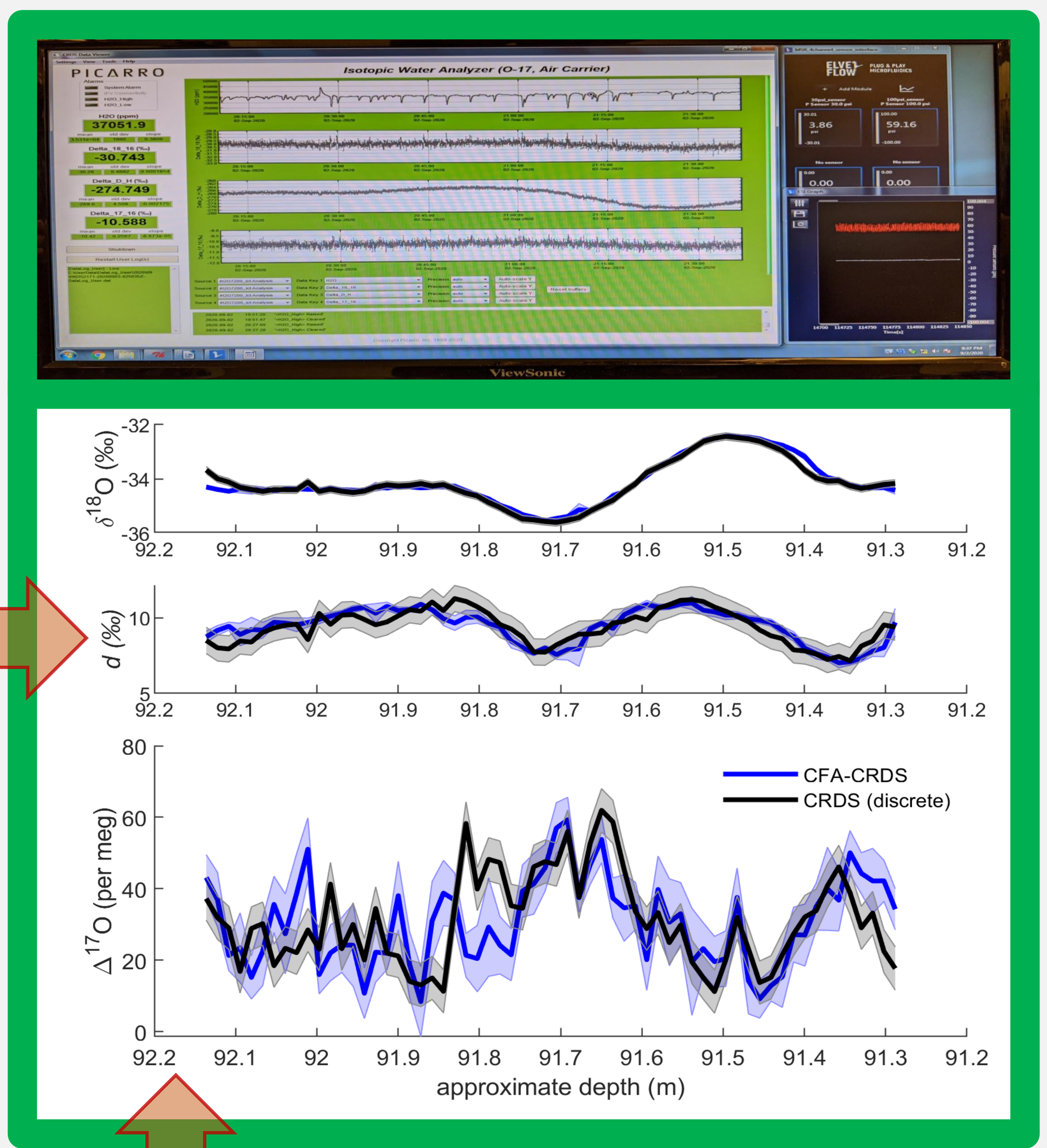






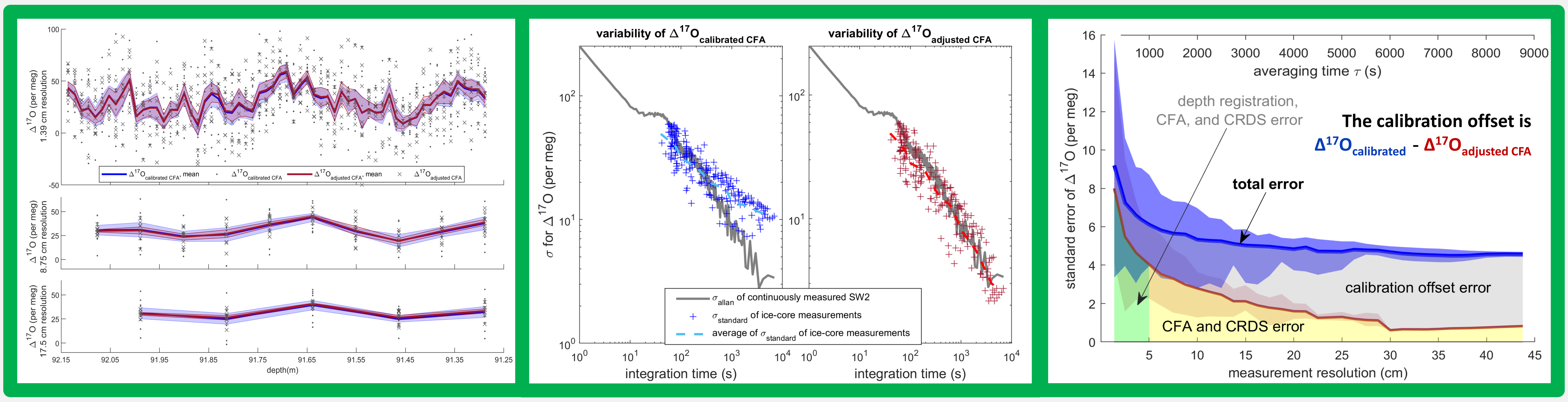
$\Delta^{17}O_{CFA\text{-}CRDS}$ agrees with $\Delta^{17}O_{discrete\text{-}CRDS}$ in magnitude, amplitude, and timing.

We designed a continuous-flow analysis (CFA) system to measure water isotopes ($\delta^{17}O$, $\delta^{18}O$, δD, *d*, and $\Delta^{17}O$) by cavity ring-down laser spectroscopy (CRDS). We measure replicate ice-core sections with this system to study the reproducibility of $\Delta^{17}O$ by CFA-CRDS and to examine the remaining sources of uncertainty in the measurement. $\Delta^{17}O$ from ice cores should provide new information about earth's climate history.

We reprocess the data with varied depth resolutions and two calibration treatments to attribute error sources.

$$\Delta^{17}O_{calibrated} = \ln(\delta^{17}O_{calibrated} + 1) - 0.528 \ln(\delta^{18}O_{calibrated} + 1) \quad \textit{for}\ \textbf{discrete}\ \textit{or}\ \textbf{CFA}$$

$$\Delta^{17}O_{adjusted\ CFA} = \Delta^{17}O_{calibrated\ CFA} + \mathrm{mean}(\Delta^{17}O_{calibrated\ discrete}) - \mathrm{mean}(\Delta^{17}O_{calibrated\ CFA})$$

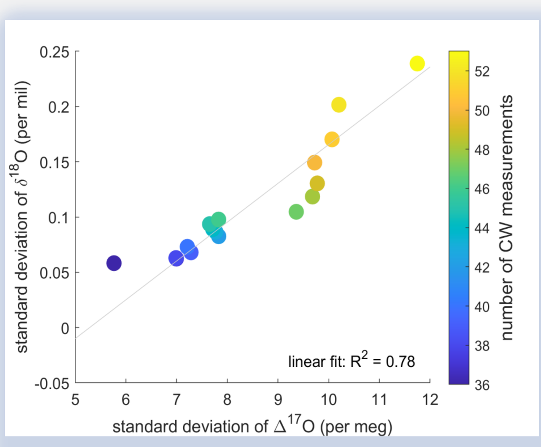


Here we show both $\Delta^{17}O_{calibrated\ CFA}$ and $\Delta^{17}O_{adjusted\ CFA}$ averaged over three depth resolutions.

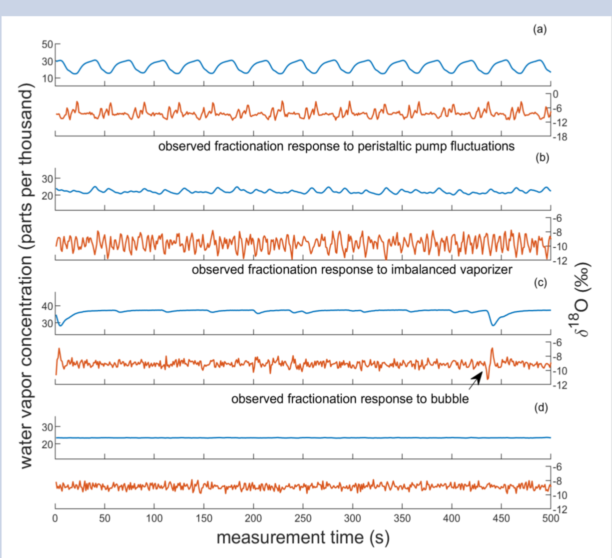
The seasonality within the ice core section is well replicated by CFA-CRDS with the expected precision.

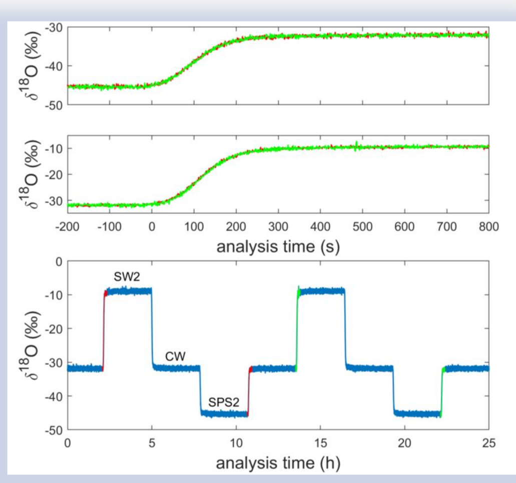
Average error is <6 per meg for τ > 1000 s, and error is limited by the calibration (not CFA or CRDS effects).

Some strategies to reduce calibration offset errors include:



Minimize fractionation of $\delta^{18}O$, since it is associated with error in $\Delta^{17}O$.





Minimize memory effects to ensure high-precision calibration data.

Ensure the system is stable over timescales long enough to measure ice samples and calibration standards.

Stack multiple CFA-CRDS measurements to average over calibration noise.

Use additional reference water measurements to identify and remove the calibration offset, as in Steig et al. (2021).

For more information, see

Davidge, L., Steig, E. J., and Schauer, A. J.: Improving continuous-flow analysis of triple oxygen isotopes in ice cores: insights from replicate measurements, AMT [preprint], https://doi.org/10.5194/egusphere-2022-60, 2022.

Steig EJ, Jones TR, Schauer AJ, Kahle EC, Morris VA, Vaughn BH, Davidge L and White JWC (2021), Continuous-Flow Analysis of $\delta^{17}O$, $\delta^{18}O$, and δD of H_2O on an Ice Core from the South Pole. Front. Earth Sci. 9:640292. doi: 10.3389/feart.2021.640292.

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