

Continuous online field deployable high precision and high resolution water isotope analysis from ice cores

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The high temporal resolution of ice cores is currently not fully exploited with the existing water isotope analysis methods. The sampling of the core is done in a discrete mode resulting in loss of resolution and a very time consuming procedure for the analysis of the full ice core

Goals of this study

- ✓ Perform continuous water isotope analysis on an ice core
- ✓ Exploit the resolution of the core
- ✓ Field deployable system.
- ✓ Precision comparable or better to IRMS



We build an interface between a commercial CW-CRDS Infra Red Spectrometer and an ice core continuous melting system for Continuous Flow Analysis (CFA) of chemical impurities.

Boundaries

- ✓ Ability to adjust to the flow rates of the CFA system
- ✓ Deliver a continuous water vapour stream to the CRDS spectrometer at the nominal mixing ratio for optimum spectrometer performance
- ✓ 3 phase changes ice → liquid water → water vapour with zero fractionation in a continuous mode
- ✓ Semi - autonomous operation
- ✓ Minimize dead volume - Sample dispersion - Estimate Resolution

Technical Goal

From an initial liquid water stream of ≈ 0.1 ml/min we want to split off a fraction of ≈ 1 μ l/min. The micro flow should then be vaporized with 100% efficiency and the produced water vapour mixed with dry air in a controlled manner so the final product is moist air with a stable humidity level of 20.000 ppm. The system has to be adjustable to different main flows and dry air flows.

Solution

We use a fused silica 40 μ m capillary on a PEEK tee (T1 in fig. 1) to split off a micro flow from the main flow of ≈ 0.1 ml/min. Flow through the capillary is kept stable via controlling the back pressure imposed by a restriction on the waste line downstream of T1. The microflow is injected in the evaporation chamber (T2) where temperature is finely controlled at 170 °C. Upon evaporation, the water vapour stream is mixed with dry air in the evaporation chamber and transferred to the optical cavity. The flow of the moist air is finely controlled by the spectrometer's proportional valves in a feedback loop.

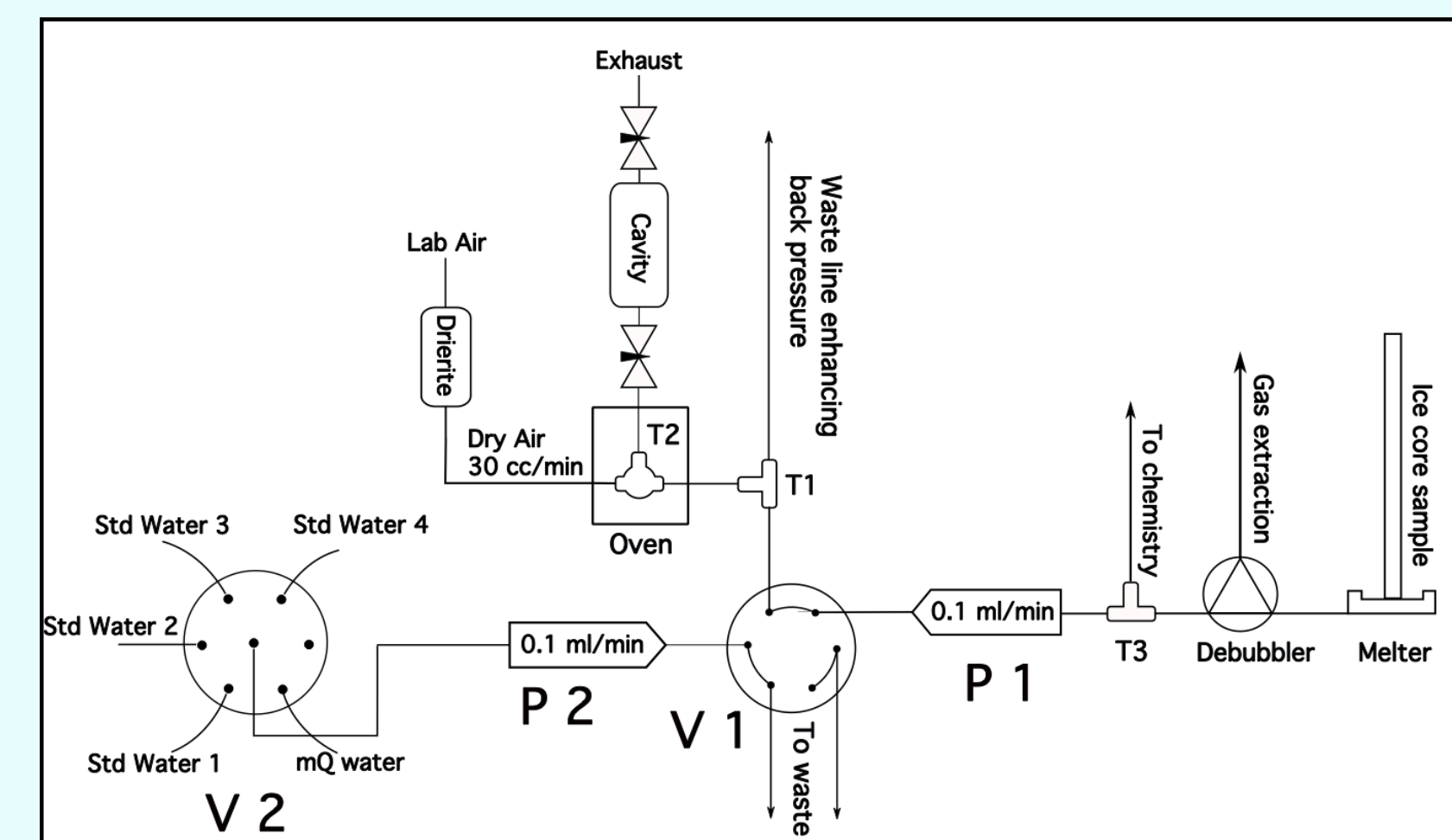


Figure 1

Allan variance test

We test the stability of the system by continuously injecting mQ Copenhagen water for a period of ≈ 16 h. Injection takes place via the 6 port selection valve (V2 in figure 1). A 6 port injection valve (V1 in figure 1) switches the system between ice core sample line and standards - mQ water. This allows for periodic calibrations with local standard waters. System shows an optimum integration time at ≈ 5000 sec after which long term instrumental drifts are observed.

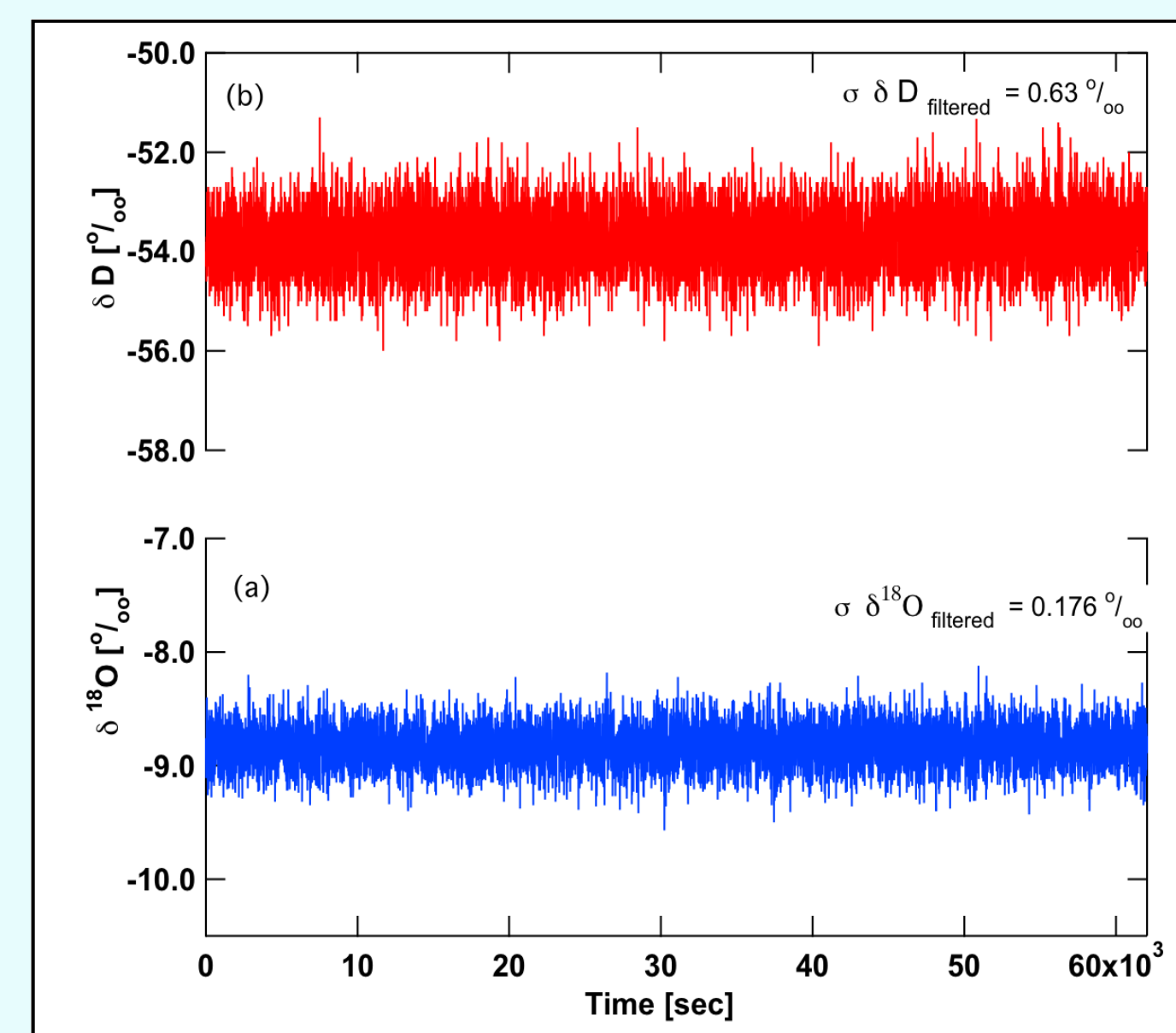


Figure 2

Water concentration:

We vary the flow rates on the peristaltic pump P2 and inject mQ water. The test reveals a dependency of the system on the water mixing ratio of the sample. We choose to perform all measurements around the linear response area of the 20 kppm.

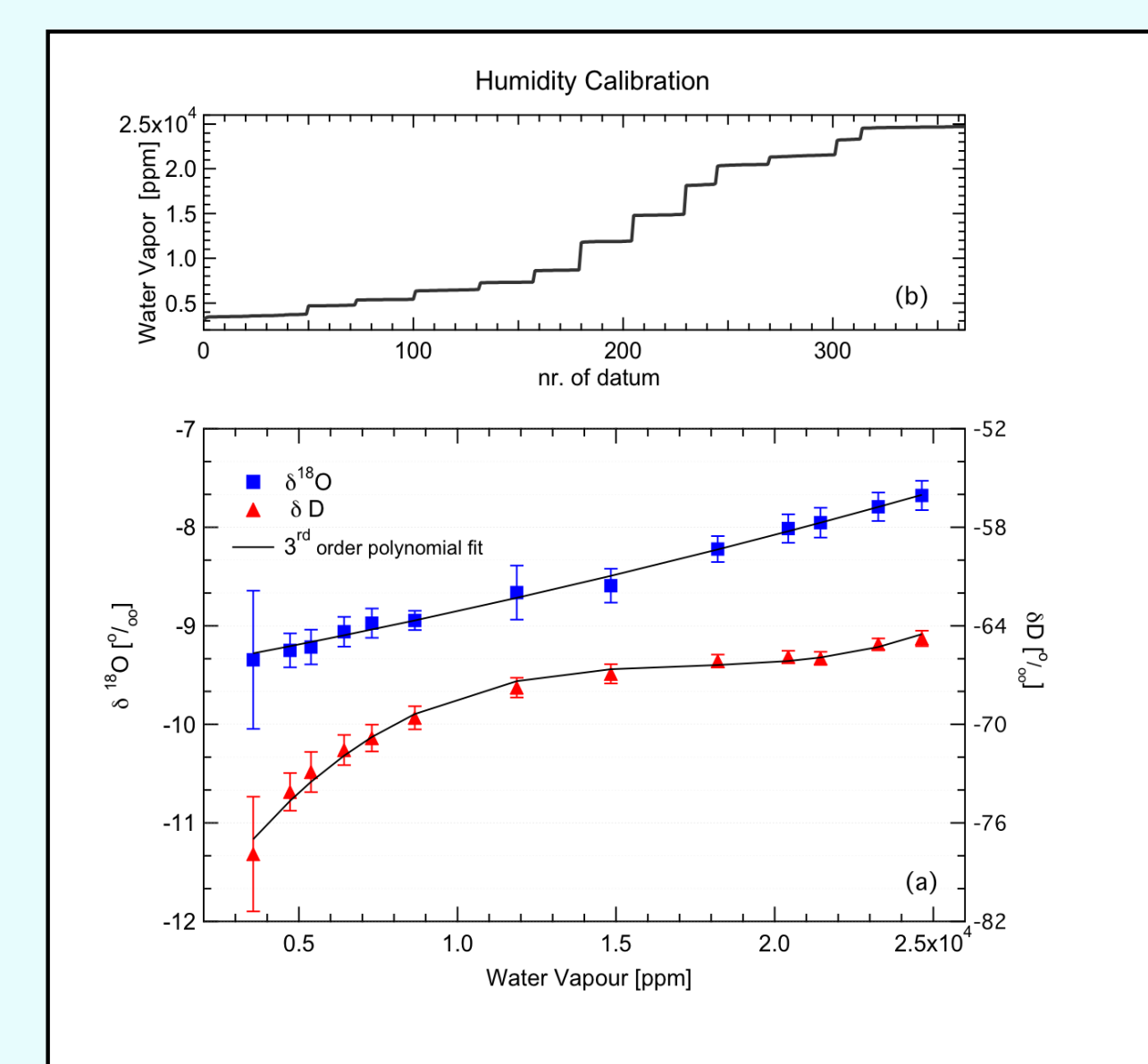


Figure 4

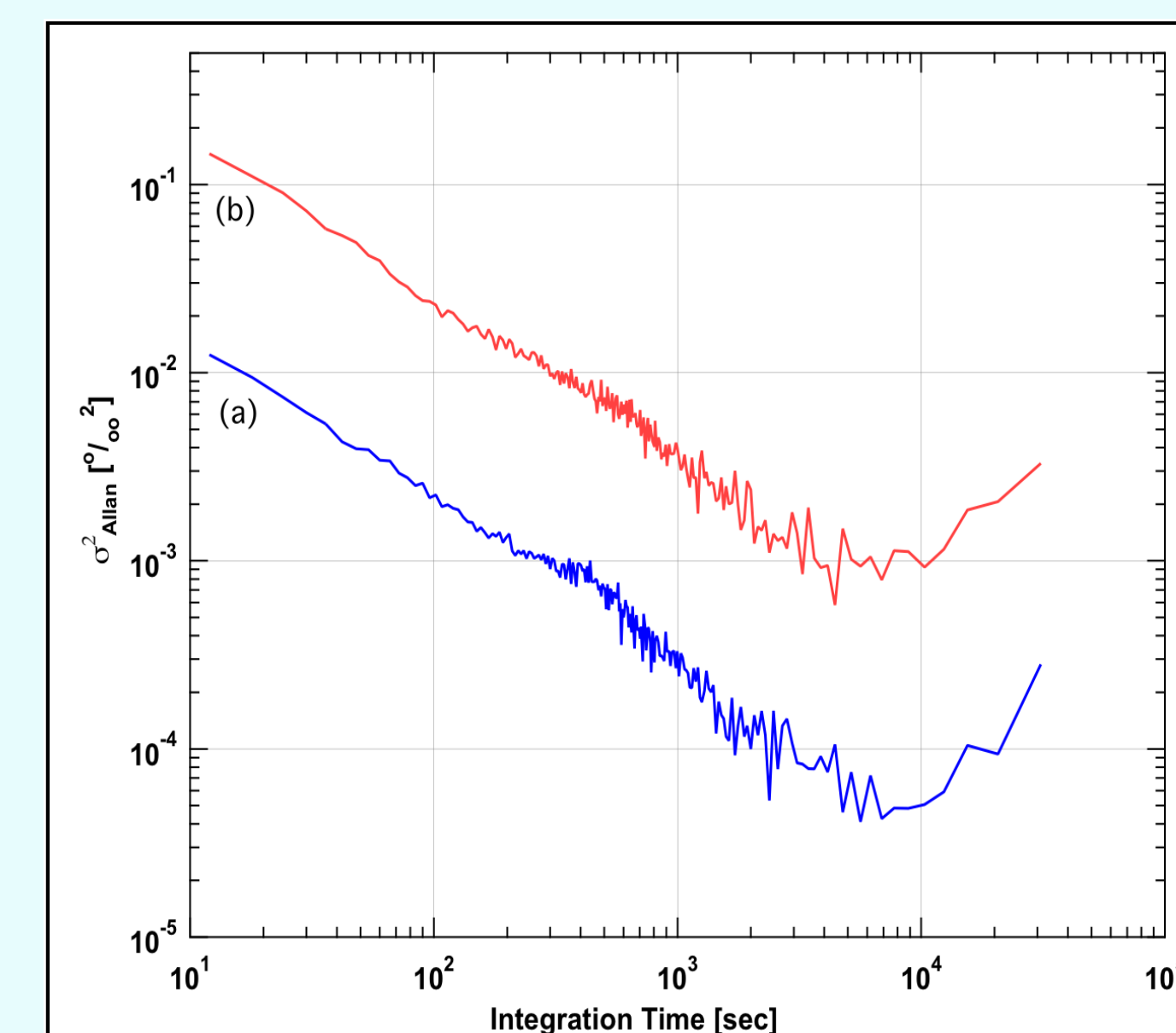


Figure 3

VSMOW calibration:

Local water standards are injected via the V2 valve. In that way we can periodically calibrate the system with respect to VSMOW. The calibration procedure takes ≈ 10 min per standard and consumes ≈ 2 ml of standard water. It can be automatized via the use of electrically actuated valves and control software.

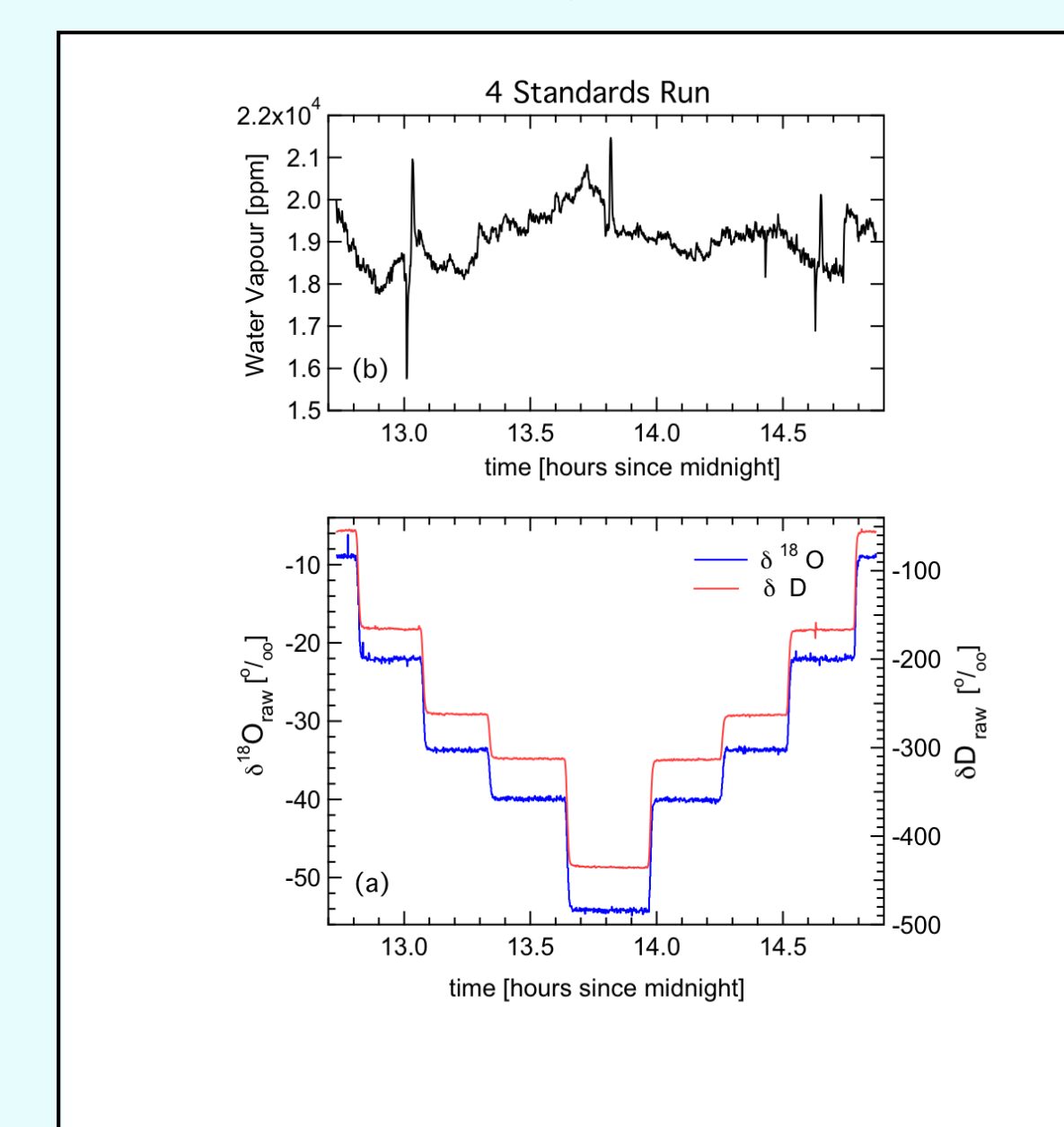


Figure 5

Sample dispersion - Memory Effects

Sample dispersion and memory effects can be characterized via the introduction of an isotopic step. The measured signal is a smoothed sigmoid curve that we assume to be the convolution of a step function with a Gaussian smoothing filter. Use of spectral methods can give an estimate of the damping of signals with different frequencies. In this case δD periodic signals with $f = 0.02$ Hz are damped by $\approx 90\%$ and are critically close to the noise level of the measurement (figure 7).

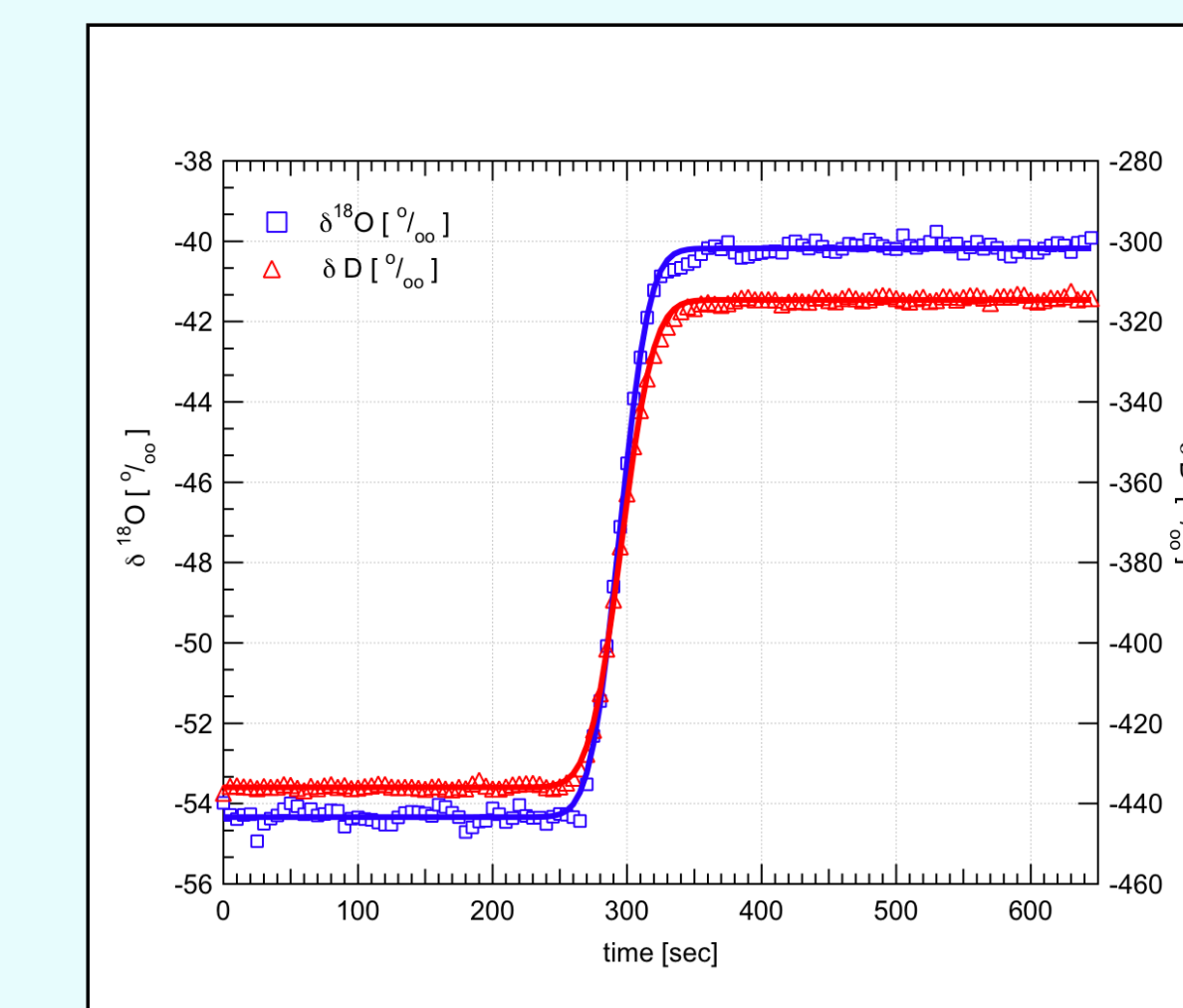


Figure 6

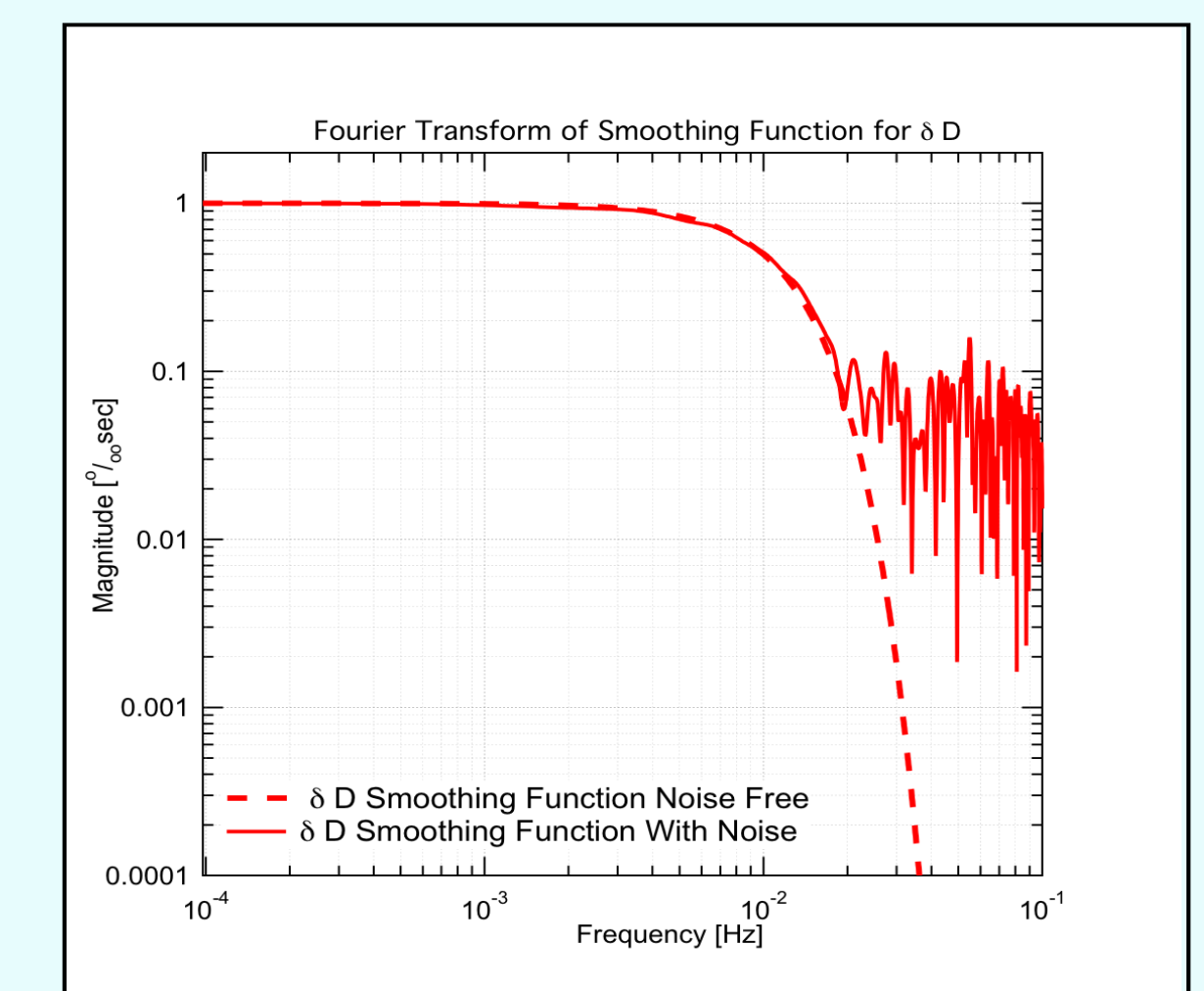


Figure 7

NGRIP melt runs:

Measurements of Holocene ice are presented in figure 8. Depth registration is done via the use of an optical encoder during the melting process. Results for $\delta^{18}O$ are compared to 5cm resolution IRMS measurements. In figure 9 we plot $\delta^{18}O$ vs δD . Results lie on the meteoric water line, an indication of an efficient evaporation step with zero fractionation.

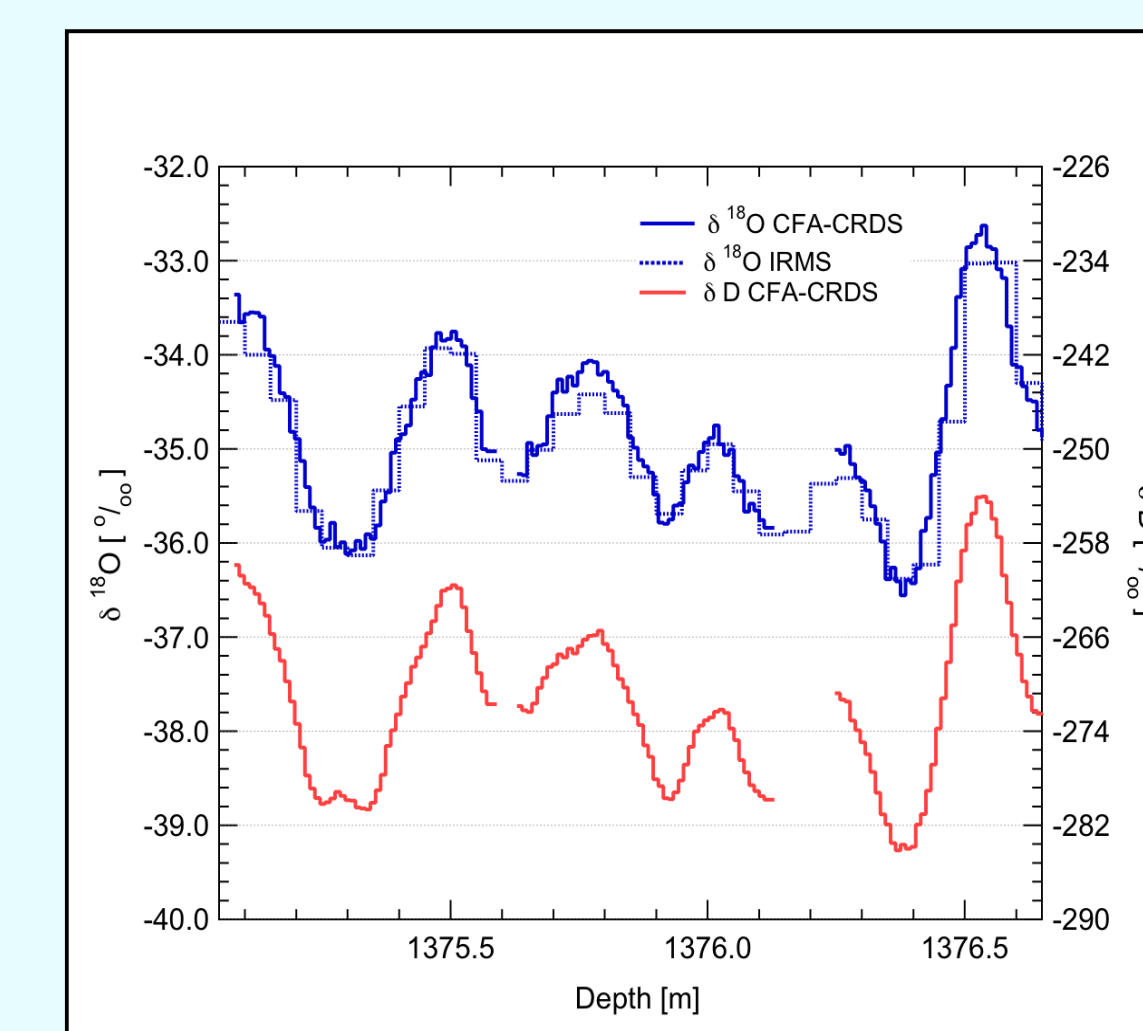


Figure 8

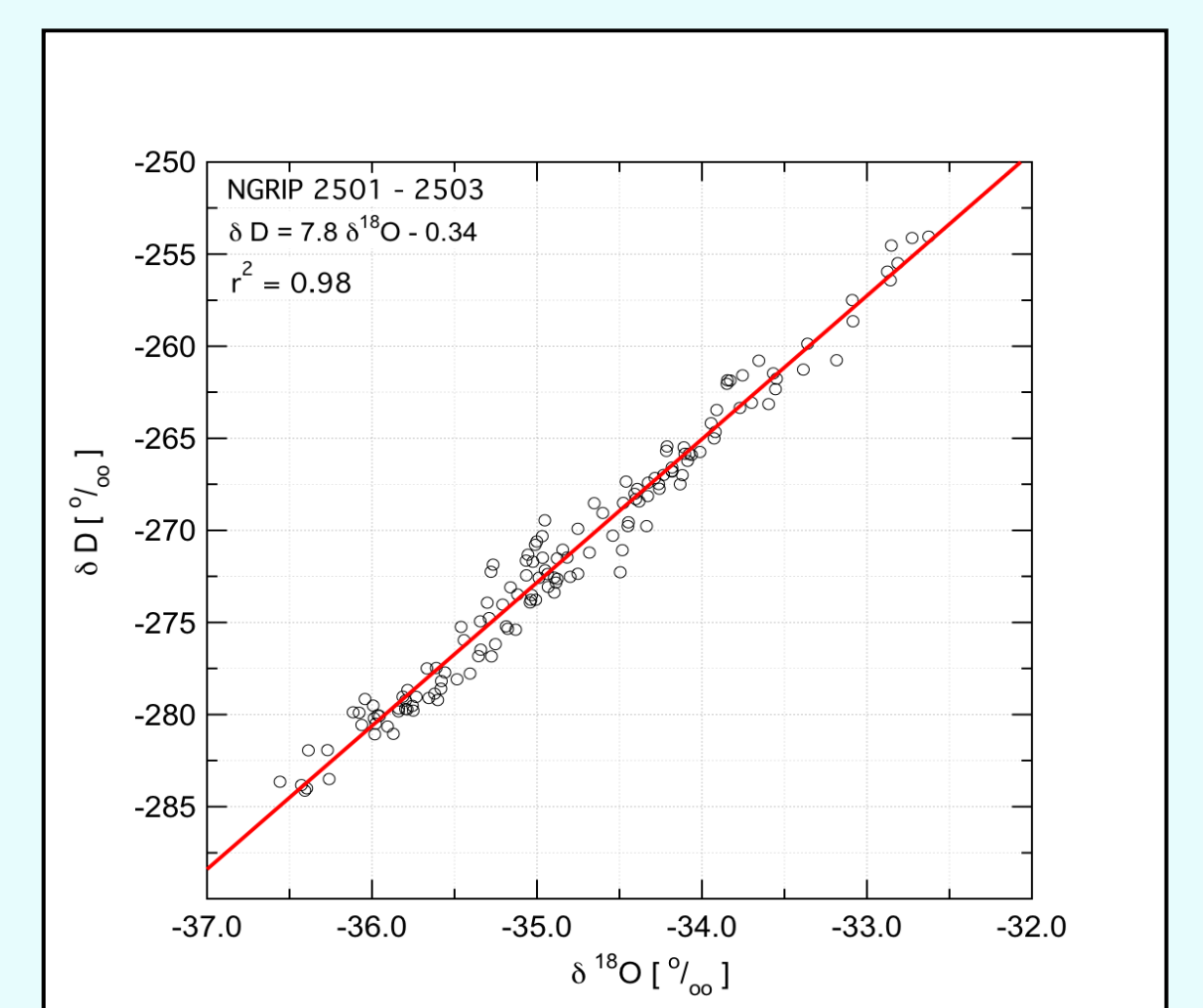


Figure 9

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