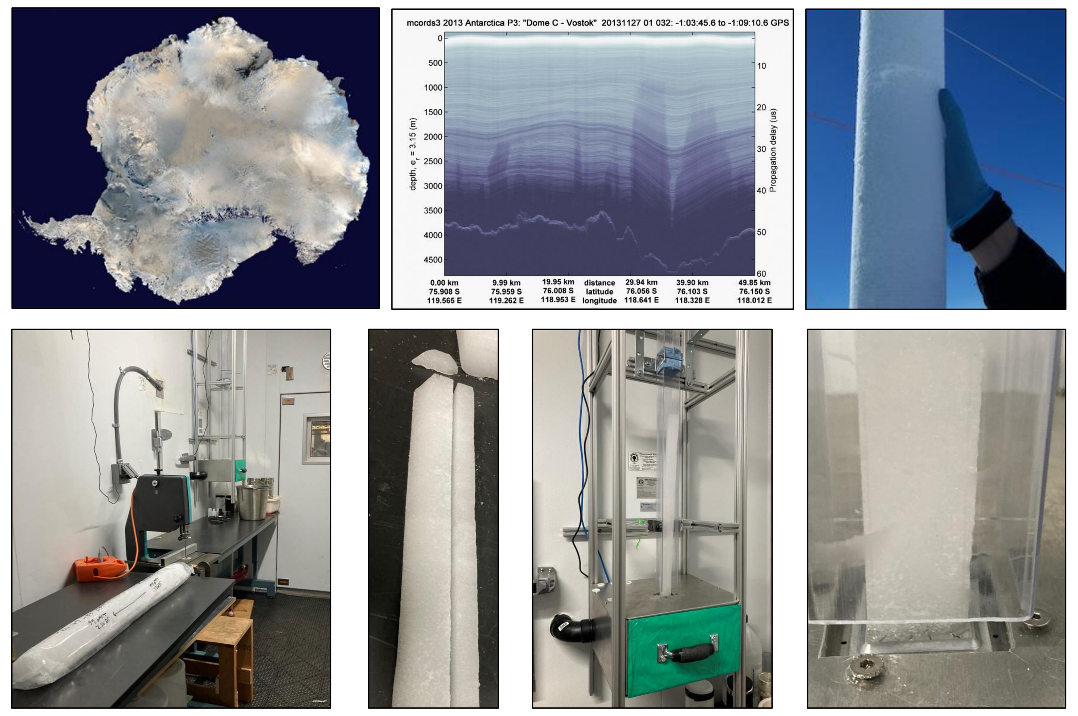
Evaluating Vaporization Methods for CFA Water Isotope Measurements

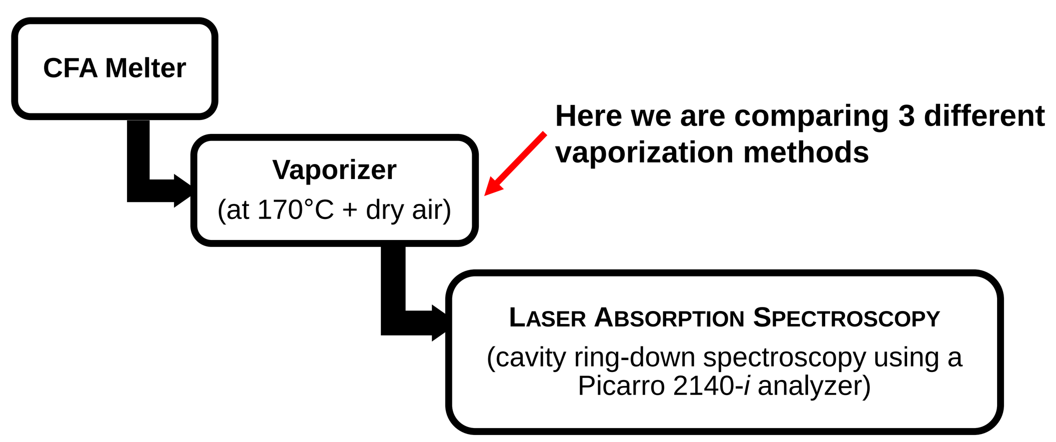
Noah Brown*, Maciej G. Śliwiński, Lindsey Davidge, Andrew J. Schauer, Eric J. Steig *IsoLab, University of Washington, Seattle, WA* (*nbrown@uw.edu)

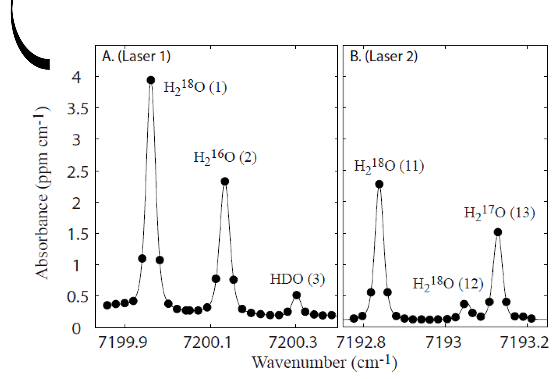
Continuous Flow Analysis (CFA) of Ice Cores



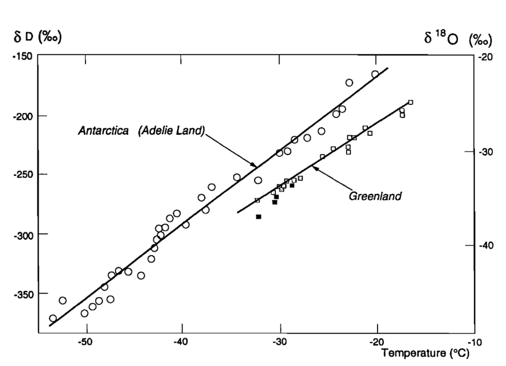
We use **CFA-CRDS** to measure **water isotopes (δD, δ^{18}O, δ^{17}O, Δ^{17}O, dxs)**

CRDS = **C**avity **R**ing-**D**own **S**pectroscopy *(a form of Laser Absorption Spectroscopy)*





From Steig *et al.* (2014)

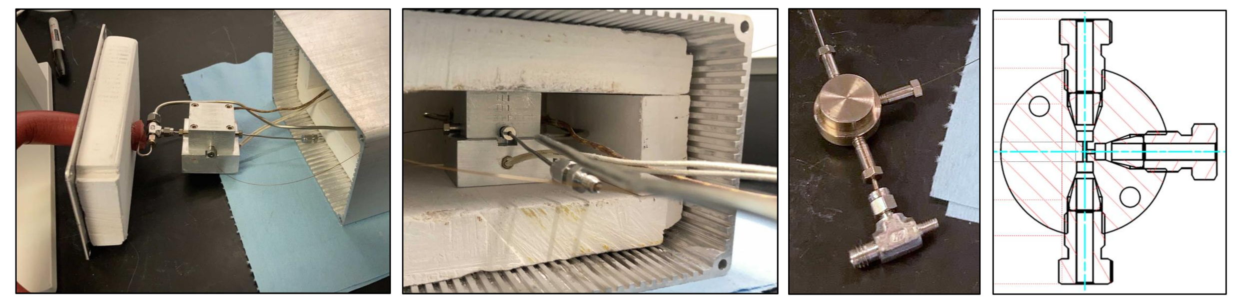


From Jouzel *et al.* (1997)

High-resolution records of variations in isotopic composition of glacial ice and climate models can be used to interpret past climate events.

Different Methods of Vaporizing Water

CFA System 1: Davidge *et al.* (2022) design



Based in-part on Gkinis et al. *(2011), Steig* et al. *(2014)*

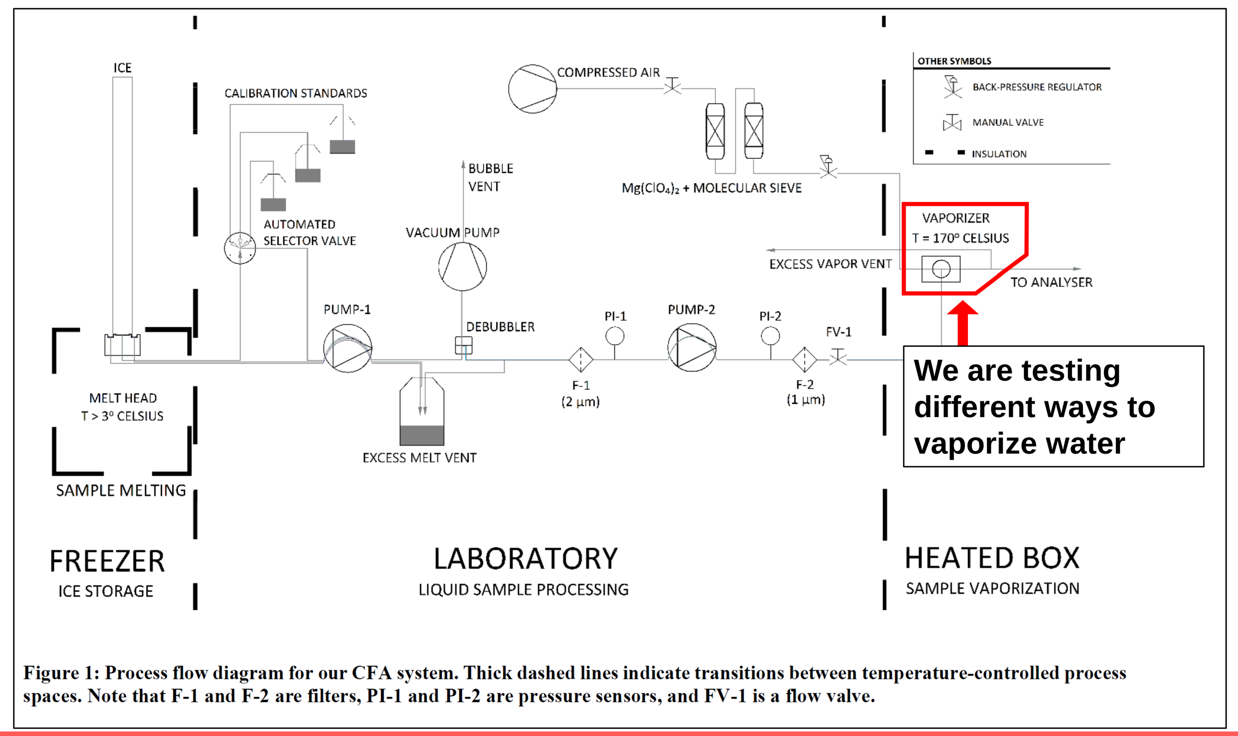
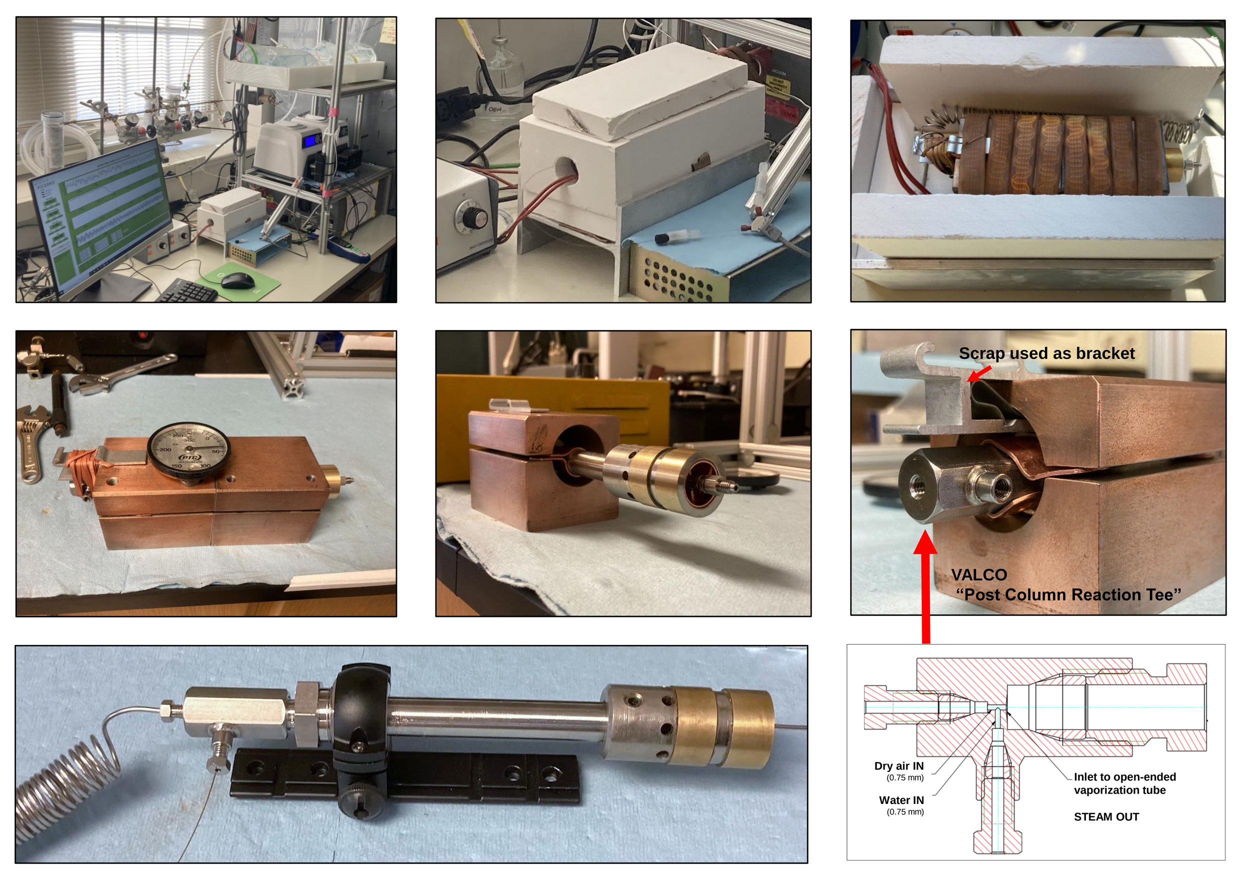
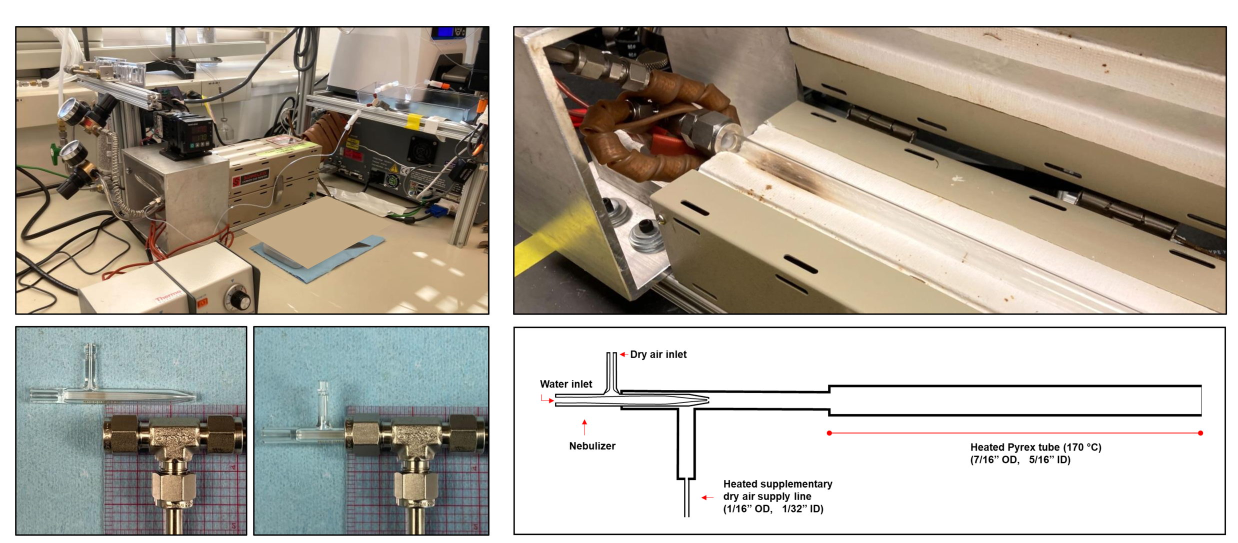


Figure 1: Process flow diagram for our CFA system. Thick dashed lines indicate transitions between temperature-controlled process spaces. Note that F-1 and F-2 are filters, PI-1 and PI-2 are pressure sensors, and FV-1 is a flow valve.

CFA System 2: Metal nebulizer

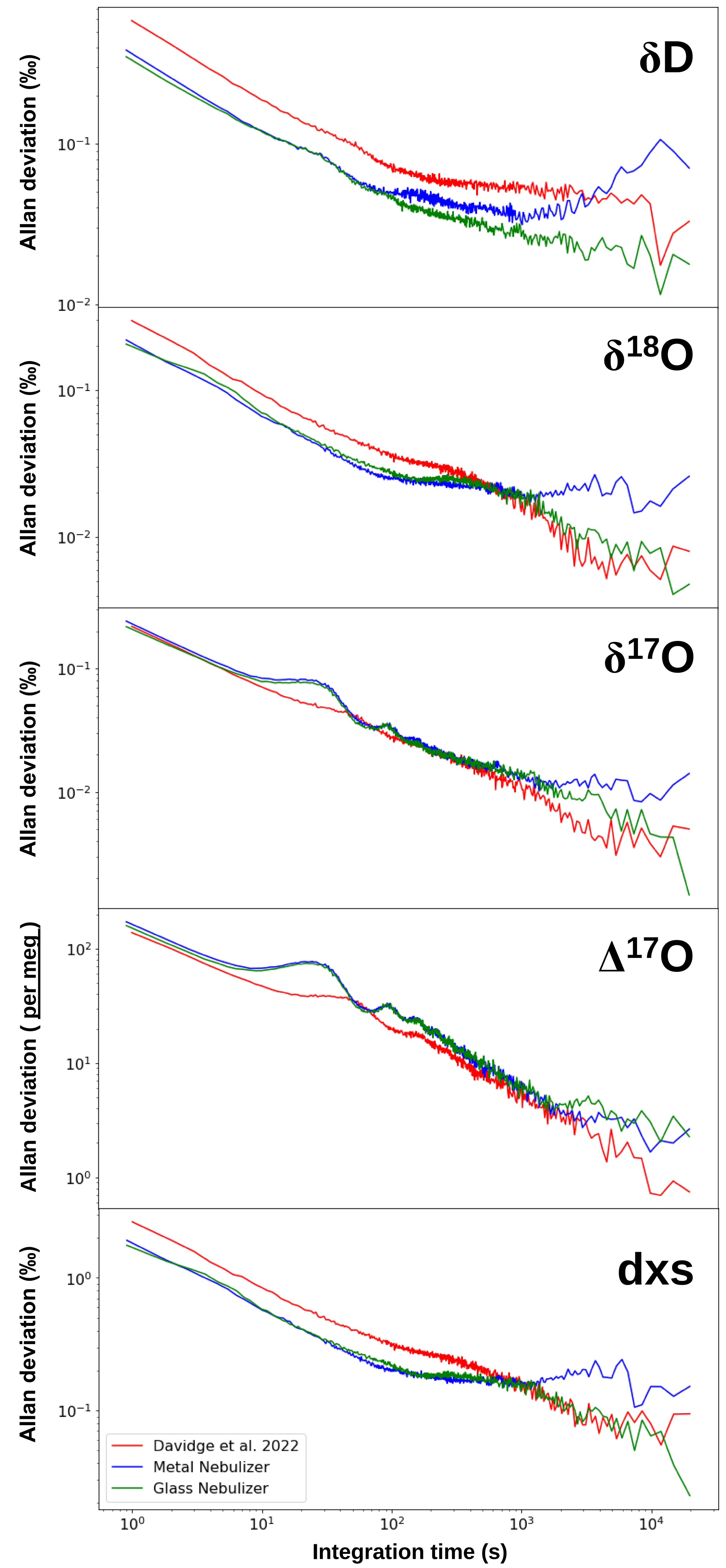


CFA System 3: Glass nebulizer *(after Jones et al. 2017)*



Stability Tests *(Allan variance analysis)*

We evaluate the relationship between precision and signal averaging time for each configuration with a 19 hour long continuous measurement of 18 MΩ water.



Select Integration Times

Summary **Allan deviation values**

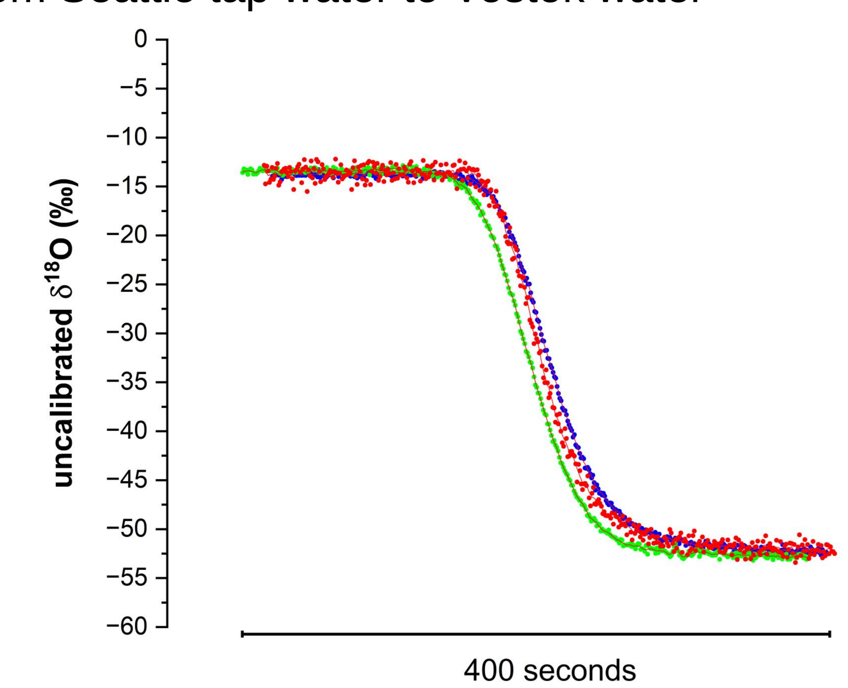
Davidge *et al.* (2022)					
Integration Time (s)	**δD (‰)**	**δ^{18}O (‰)**	**δ^{17}O (‰)**	**Δ^{17}O (per meg)**	**dxs (‰)**
10	0.200	0.100	0.074	49	0.886
60	0.095	0.042	0.040	33	0.375
600	0.052	0.022	0.015	7	0.190
3600	0.045	0.007	0.004	2	0.081

Metal Nebulizer					
Integration Time (s)	**δD (‰)**	**δ^{18}O (‰)**	**δ^{17}O (‰)**	**Δ^{17}O (per meg)**	**dxs (‰)**
10	0.124	0.071	0.086	67	0.606
60	0.055	0.029	0.036	31	0.239
600	0.038	0.023	0.016	9	0.178
3600	0.045	0.024	0.013	3	0.208

Glass Nebulizer *(1st of several designs to evaluate)*					
Integration Time (s)	**δD (‰)**	**δ^{18}O (‰)**	**δ^{17}O (‰)**	**Δ^{17}O (per meg)**	**dxs (‰)**
10	0.125	0.075	0.081	64	0.618
60	0.053	0.033	0.034	29	0.263
600	0.028	0.021	0.015	9	0.163
3600	0.023	0.011	0.001	4	0.099

Transition between two reference waters

Step from Seattle tap water to Vostok water



Initial Conclusions

- Comparable signal stability across systems.
- However, obvious 'ease-of-use' differences exist
- Wide-mouth vent extends range of operating conditions

Next step: Quantitative assessment of memory effects and evaluation of performance with ice core melt water.

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

Gkinis, V., Popp, T.J., Blunier, T., Bigler, M., Schüpbach, S., Kettner, E., and Johnsen, S.J., 2011, Water isotopic ratios from a continuously melted ice core sample: Atmospheric Measurement Techniques, v. 4, p. 2531–2542, doi:10.5194/amt-4-2531-2011.

Jones, T.R., White, J.W.C., Steig, E.J., Vaughn, B.H., Morris, V., Gkinis, V., Markle, B.R., and Schoenemann, S.W., 2017, Improved methodologies for continuous-flow analysis of stable water isotopes in ice cores: Atmospheric Measurement Techniques, v. 10, p. 617–632, doi:10.5194/amt-10-617-2017.

Jouzel, J. et al., 1997, Validity of the temperature reconstruction from water isotopes in ice cores: Journal of Geophysical Research: Oceans, v. 102, p. 26471–26487, doi:10.1029/97JC01283.

Steig, E.J., Gkinis, V., Schauer, A.J., Schoenemann, S.W., Samek, K., Hoffnagle, J., Dennis, K.J., and Tan, S.M., 2014, Calibrated high-precision ^{17}O-excess measurements using cavity ring-down spectroscopy with laser-current-tuned cavity resonance: Atmospheric Measurement Techniques, v. 7, p. 2421–2435, doi:10.5194/amt-7-2421-2014.

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