EARTH & SPACE SCIENCES
UNIVERSITY of WASHINGTON

Δ*IsoLab

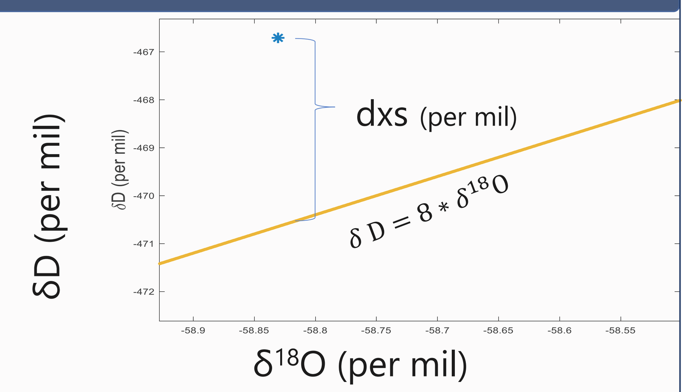
Improved Precision of $\Delta^{17}O$ Measurements by Laser Spectroscopy

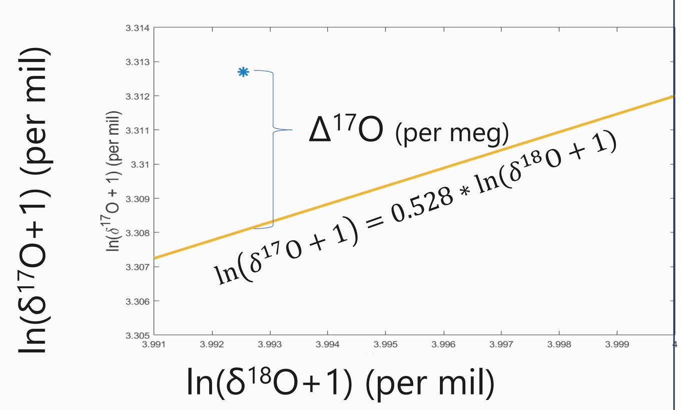
Lindsey Davidge, Eric Steig, Andrew Schauer

with Tyler Jones, Valerie Morris, Bruce Vaughn (INSTAAR)

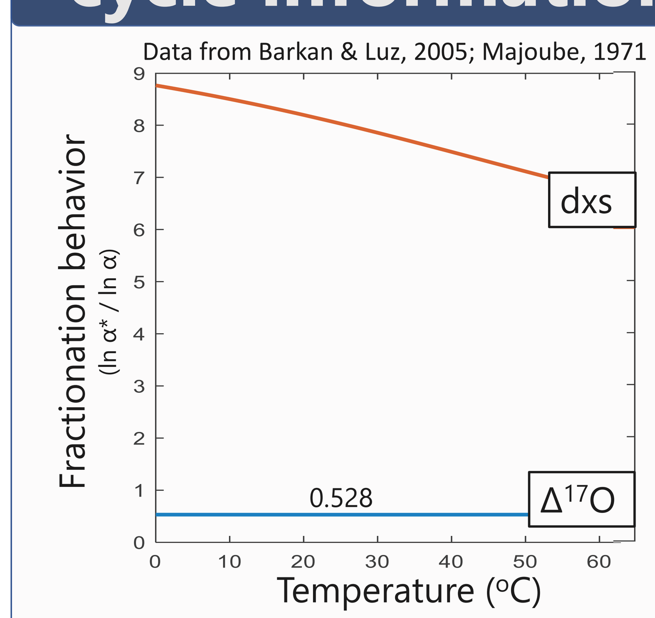
$\Delta^{17}O$ and dxs reflect kinetic fractionation

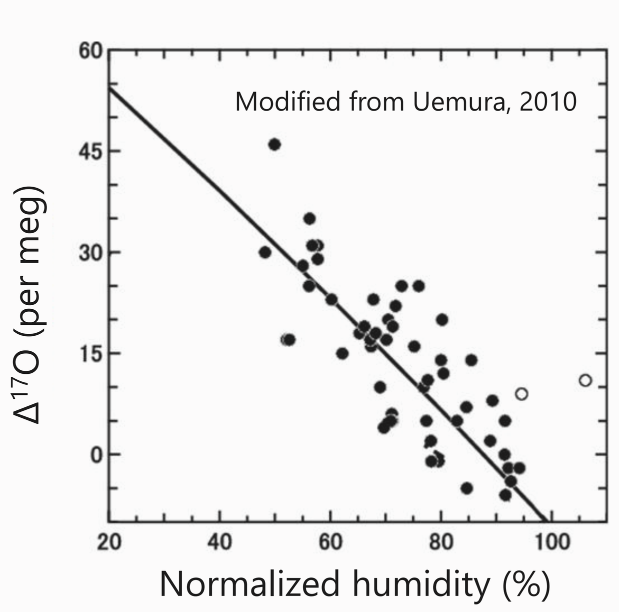
$\Delta^{17}O$ and dxs are calculated from corresponding measurements of $\delta^{17}O$ and $\delta^{18}O$ or δD and $\delta^{18}O$, respectively. Both $\Delta^{17}O$ and dxs record the difference from equilibrium fractionation behavior. Kinetic fractionation records from ice cores can inform past hydrologic cycle conditions.





$\Delta^{17}O$ should provide new hydrologic cycle information

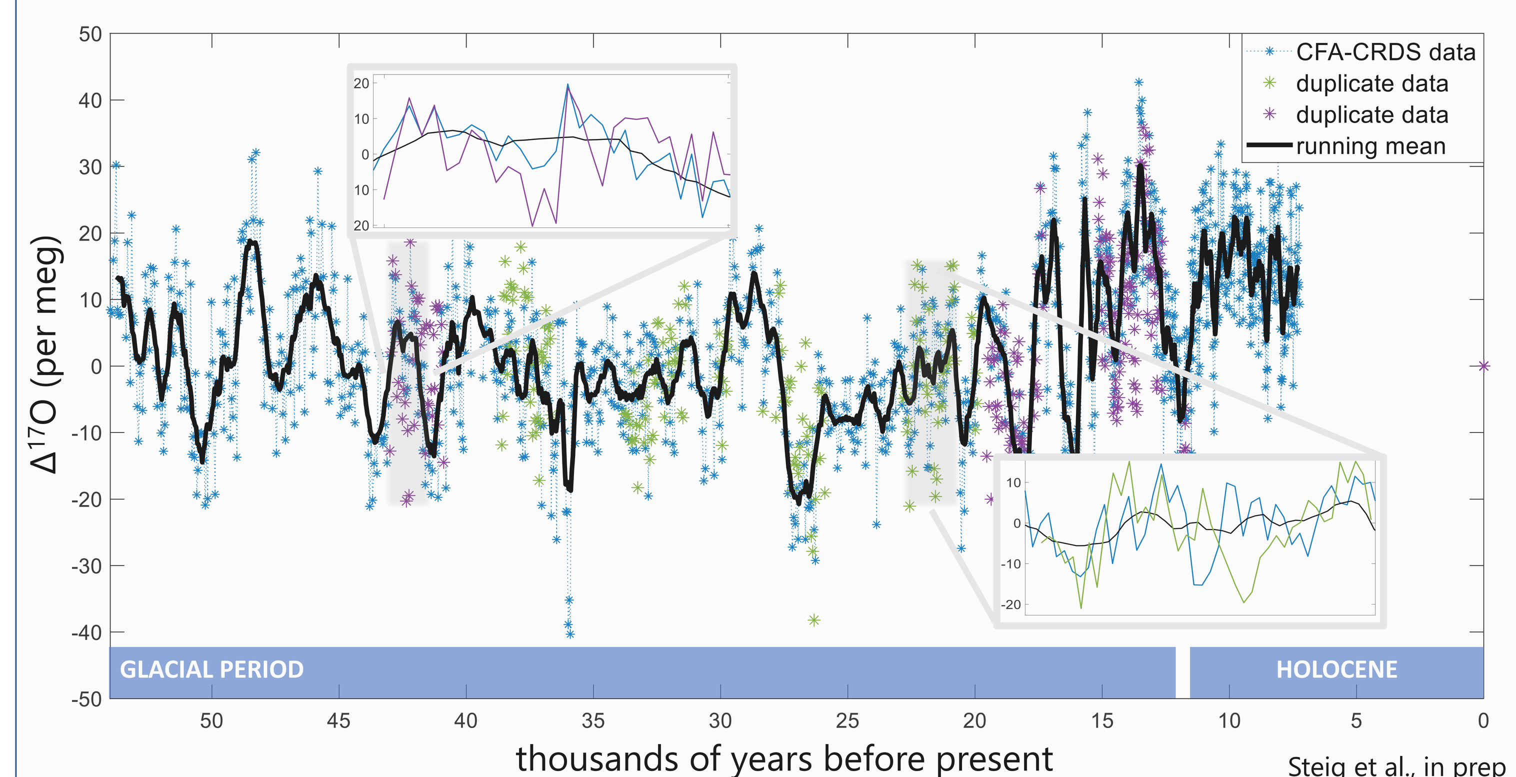




$\Delta^{17}O$ should reflect different climatic conditions than dxs:

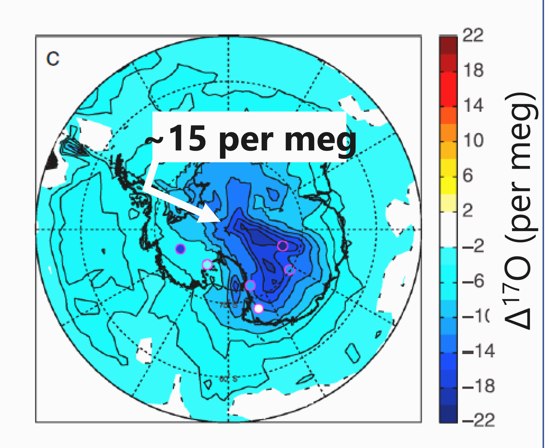
- $\Delta^{17}O$ is less sensitive to temperature than dxs
- $\Delta^{17}O$ observations are strongly correlated to humidity at low latitudes
- Improved spatial and temporal resolution of corresponding $\Delta^{17}O$ and dxs records are needed to better understand the implications of $\Delta^{17}O$ for paleoclimate.

CFA-CRDS improves $\Delta^{17}O$ measurement efficiency & measurement resolution



Data from the South Pole ice core shows great potential for high-resolution $\Delta^{17}O$ measurements:

- $\Delta^{17}O$ shift during glacial-interglacial transition generally agrees with modeled expectations
- Duplicate ice core measurements generally agree within 12 per meg (1σ)

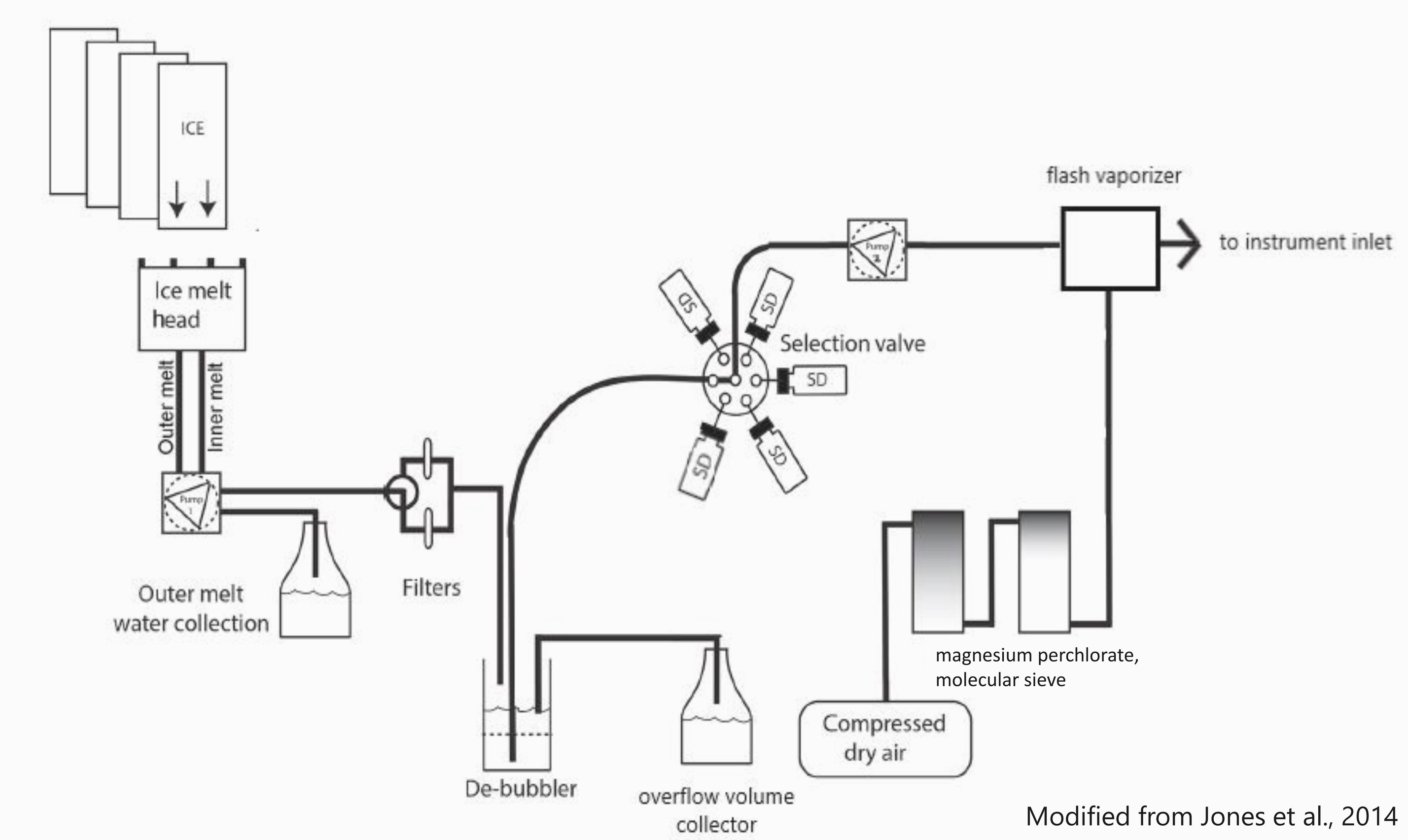


Our goal: improve precision for $\Delta^{17}O$, maintain high resolution

- $\Delta^{17}O$ measurement precision at South Pole is as good as 6 per meg, but consistently only <12 per meg
- Duplicate core measurements suggest some high-frequency signals are reproducible, but signal-to-noise ratio could be improved (see inset, above)

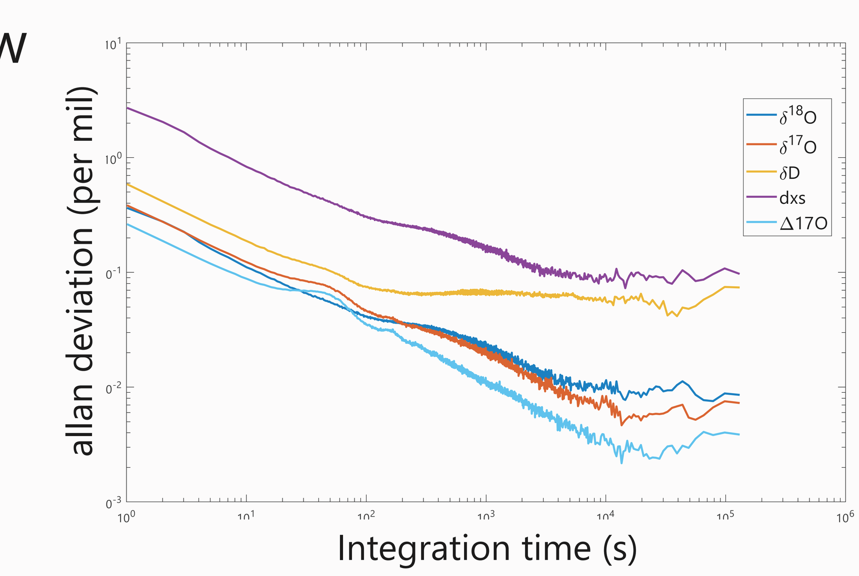
New CFA system was designed to optimize $\Delta^{17}O$ measurement

- Custom vaporizer uses low-volume flash vaporizer tee (Gkinis et al., 2010) to minimize memory effects and ensure instantaneous sample evaporation
- Bubbles and particulate (>0.2μm) are removed, then sample is metered into vaporizer by peristaltic pump



Improved $\Delta^{17}O$ measurement precision

- Consistently achieves <6 per meg precision for $\Delta^{17}O$ with 4000s integration time
- Currently using new CFA system to test reproducibility of measured $\Delta^{17}O$ from ice cores



References:

Allan, D. W. (1966). Statistics of atomic frequency standards. *Proceedings of the IEEE*, *54*(2), 221–230. https://doi.org/10.1109/PROC.1966.4634

Barkan, E., & Luz, B. (2005). High precision measurements of17O/16O and18O/16O ratios in H2O. *Rapid Communications in Mass Spectrometry*, *19*(24), 3737–3742. https://doi.org/10.1002/rcm.2250

Gkinis, V., Popp, T. J., Johnsen, S. J., & Blunier, T. (2010). A continuous stream flash evaporator for the calibration of an IR cavity ring down spectrometer for isotopic analysis of water. *Isotopes in Environmental and Health Studies*, *46*(4), 463–475. https://doi.org/10.1080/10256016.2010.538052

Jones, T. R., White, J. W. C., Steig, E. J., Vaughn, B. H., Morris, V., Gkinis, V., … Schoenemann, S. W. (2017). Improved methodologies for continuous-flow analysis of stable water isotopes in ice cores. *Atmospheric Measurement Techniques*, *10*(2), 617–632. https://doi.org/10.5194/amt-10-617-2017

Jouzel, J., & Merlivat, L. (1984). Deuterium and oxygen 18 in precipitation: Modeling of the isotopic effects during snow formation. *Journal of Geophysical Research*, *89*(D7), 11749. https://doi.org/10.1029/JD089iD07p11749

Majoube, M. (1971b). Oxygen-18 and deuterium fractionation between water and steam, *J. Chim. Phys. Phys. Chim. Biol.*, 68(10), 1423–1436.

Schauer, A. J., Schoenemann, S. W., & Steig, E. J. (2016). Routine high-precision analysis of triple water-isotope ratios using cavity ring-down spectroscopy. *Rapid Communications in Mass Spectrometry,* 30, 2059-2069. https://doi.org/10.1002/rcm.7682

Schoenemann, S. W., Steig, E. J., Ding, Q., Markle, B. R., & Schauer, A. J. (2014). Triple water-isotopologue record from WAIS Divide, Antarctica: Controls on glacial-interglacial changes in $^{17}O_{excess}$ of precipitation: WAIS LGM-Holocene 17Oexcess Record. *Journal of Geophysical Research: Atmospheres*, *119*(14), 8741–8763. https://doi.org/10.1002/2014JD021770

Steig, E. J., Gkinis, V., Schauer, A. J., Schoenemann, S. W., Samek, K., Hoffnagle, J., … 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*, *7*(8), 2421–2435. https://doi.org/10.5194/amt-7-2421-2014

Uemura R, Matsui Y, Yoshida N, Abe O, Mochizuki S (2005). Isotopic fractionation of water during snow formation: Experimental evidence of kinetic effect. Polar Meteorol Glaciol 19:1–14.