Rapid analysis of water isotope fractionation along a *Pinus spp.* branch: in-situ measurement of matrix-bound waters

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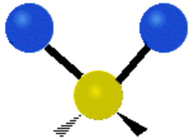
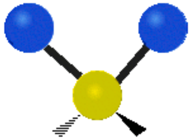
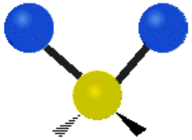
Optical spectroscopy – molecules in motion



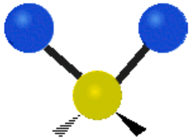
Symmetrical stretching



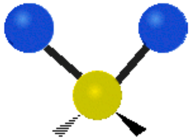
Antisymmetrical stretching



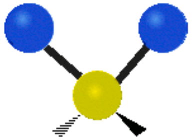
Scissoring



Rocking

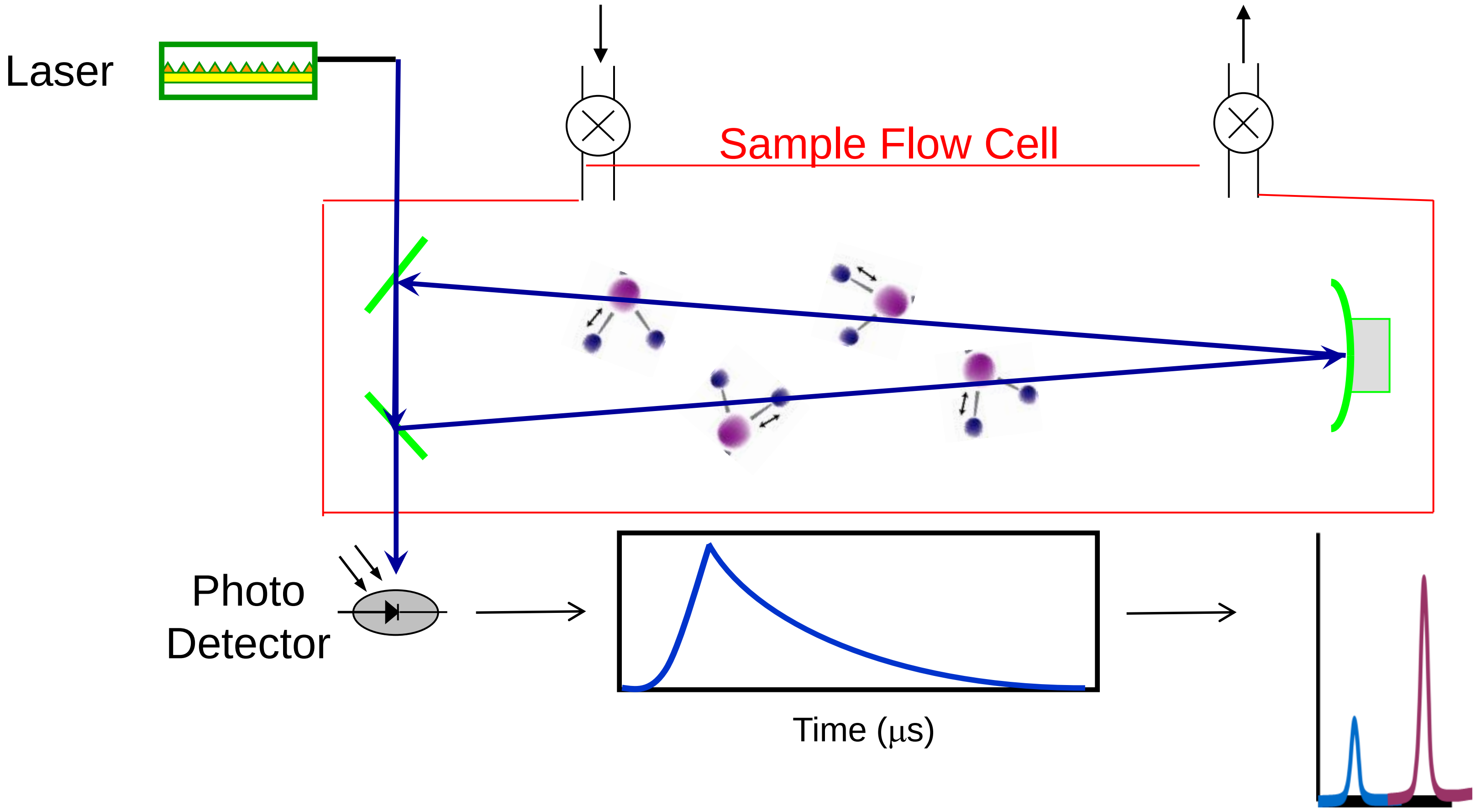


Wagging

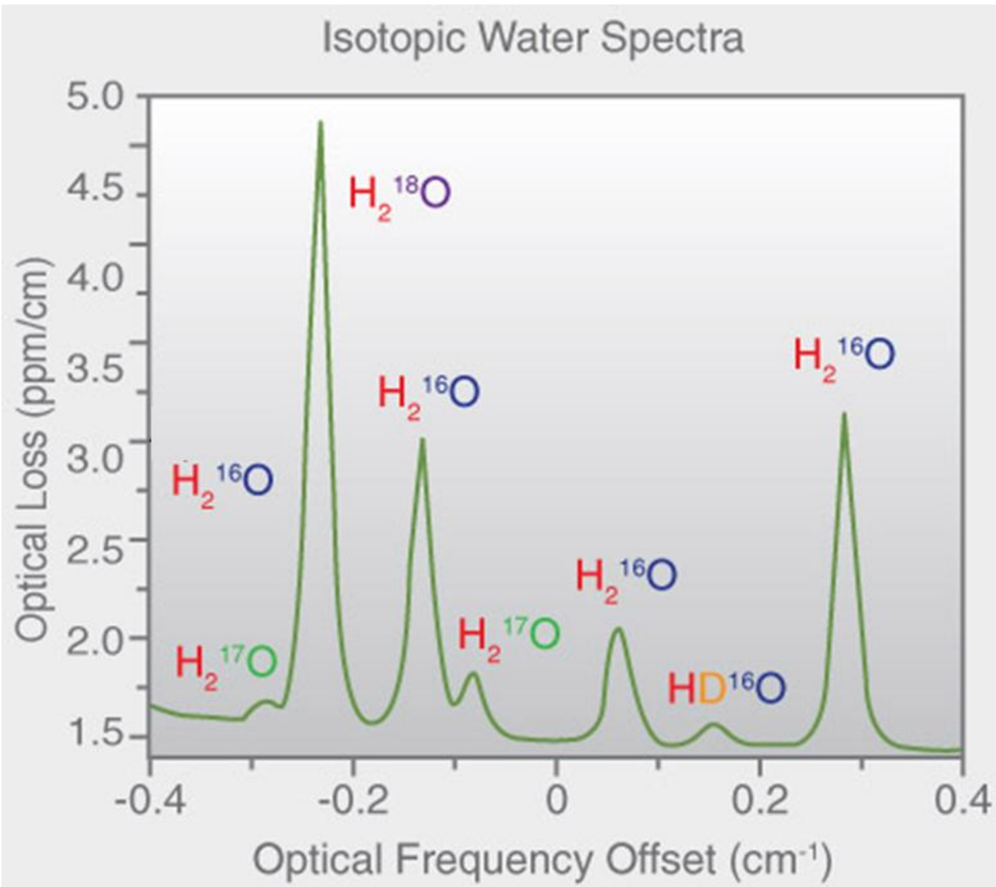


Twisting

Optical spectroscopy – Absorption of Light



Optical spectroscopy – absorption spectra



- Bond stretching frequency is affected by isotopes
- Match frequency to isotopologue
- Measure amount of each isotopologue
- Multiple isotopes of a single molecule is rapid and simple

One Analyzer, Many Applications

Small, portable and high precision gives researchers insights into:

- Hydrology
  - Watershed mapping
  - Aquifer mapping
- Oceanography
  - Water formation in the polar regions
- Ice Core Analysis
  - Precipitation and Climate records
- Atmospheric Water Measurements
  - Air mass sources and trajectories
  - Post depositional processes in ice and snow
- Ecohydrology and Evapotranspiration
  - Soil evaporation
  - Plant transpiration
- Metabolic Studies
- Food Authentication

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Extraction of Solid Samples

Cryogenic Vacuum Distillation

- Not Field Portable (until very recently)
- Hazardous Conditions and Long preparation time
- More steps increases possibility of unwanted isotopic fractionation
- Required to store samples and transport them to the lab

Cryogenic vacuum distillation
30-90 minutes per sample

CRDS
Direct measurement of Water
10-40 minutes per sample

Extraction of Solid Samples

Can it be streamlined?

- Can the extraction be amenable to field use?
- Can the extraction be faster?
- Can there be fewer manipulations?
- Can the extraction be integrated with the analysis?

Induction Module

- Solid samples are heated by induction to release water vapor (2 – 3 µL equivalent)
- A flow of dry gas directs sample vapor to water isotope analyzer L2130-*i*
- Sample preparation & analysis typically done in 5 – 15 minutes
- Rugged, low power consumption (< 200W at steady state)

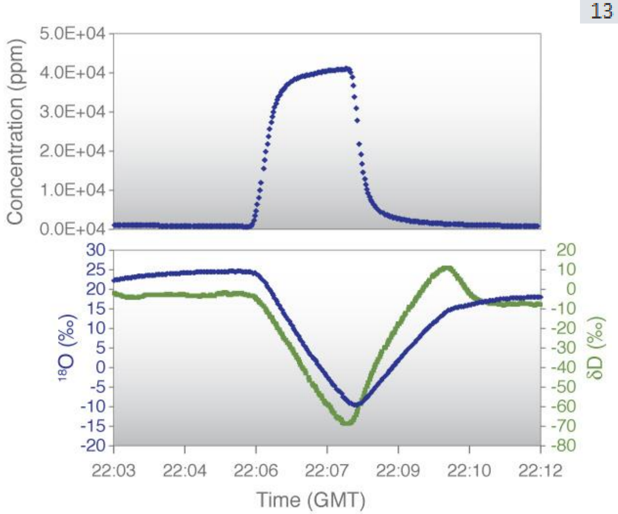
Matrix-Bound Water – Pine

- Razor blade to sample ~0.05 mm slice every cm of the branch.

- Needle cut at 3.5-cm intervals

Matrix-Bound Water – Pine

	A	B	C	D	E	F
1	Start Time	End Time	Method	Description	d(18_16)	d(D_H)
2	2011-07-08 20:28:07	2011-07-08 20:35:09	Woody Stems	Pine, stem 1.5 cm	-5.537	-56.652
3	2011-07-08 20:36:12	2011-07-08 20:43:13	Woody Stems	Pine, stem 2.5 cm	-5.184	-55.944
4	2011-07-08 20:46:47	2011-07-08 20:53:49	Woody Stems	Pine, stem 3.5 cm	-4.96	-55.205
5	2011-07-08 20:54:39	2011-07-08 21:01:39	Woody Stems	Pine, stem 4.5 cm	-4.757	-54.179
6	2011-07-08 21:02:33	2011-07-08 21:09:33	Woody Stems	Pine, stem 5.5 cm	-4.904	-53.913
7	2011-07-08 21:10:28	2011-07-08 21:17:29	Woody Stems	Pine, stem 6.5 cm	-5.156	-54.571
8	2011-07-08 21:19:13	2011-07-08 21:26:12	Woody Stems	Pine, stem 7.5 cm	-4.915	-54.7
9	2011-07-08 21:27:01	2011-07-08 21:36:27	Whole Leaf	Pine, needle, 7.5 cm, 0-3.5 cm	-26.965	-237.325
10	2011-07-08 21:38:20	2011-07-08 21:45:07	Leaf Stems	Pine, needle, 7.5 cm, 3.5-7 cm	3.649	-52.351
11	2011-07-08 21:47:08	2011-07-08 21:56:49	Whole Leaf 2	Pine, needle, 7.5 cm, 7-10.5 cm	14.863	-4.18
12	2011-07-08 21:57:16	2011-07-08 22:06:56	Whole Leaf 2	Pine, needle, 7.5 cm, 10.5-14 cm	20.706	-5.963
13						



- 98 minutes for 11 Samples
  +15 for analysis of 3 standards
- δD +/- 1.82 ‰, δ^{18}O +/- 0.23 ‰
- Obtain δD and δ^{18}O immediately

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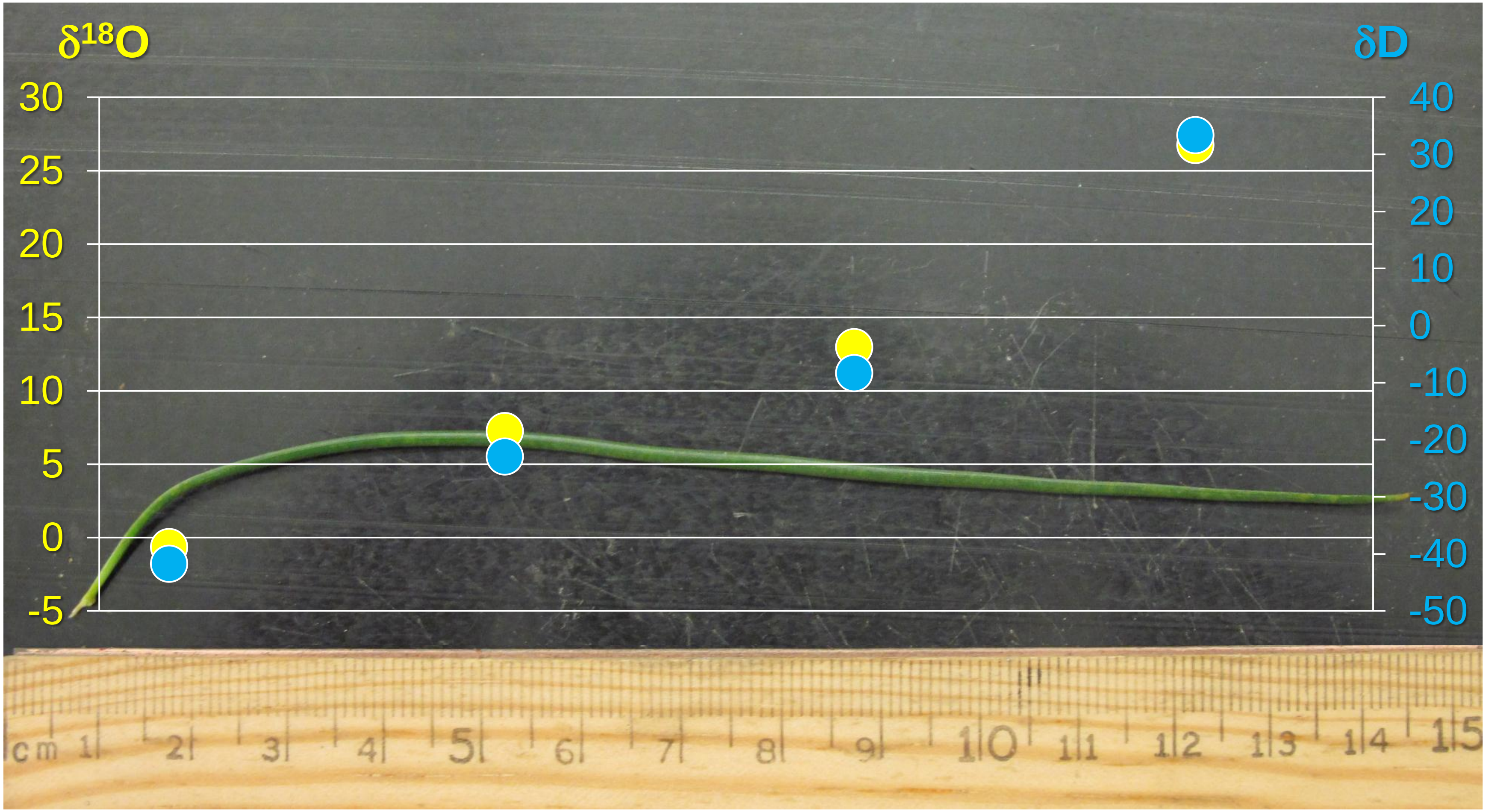
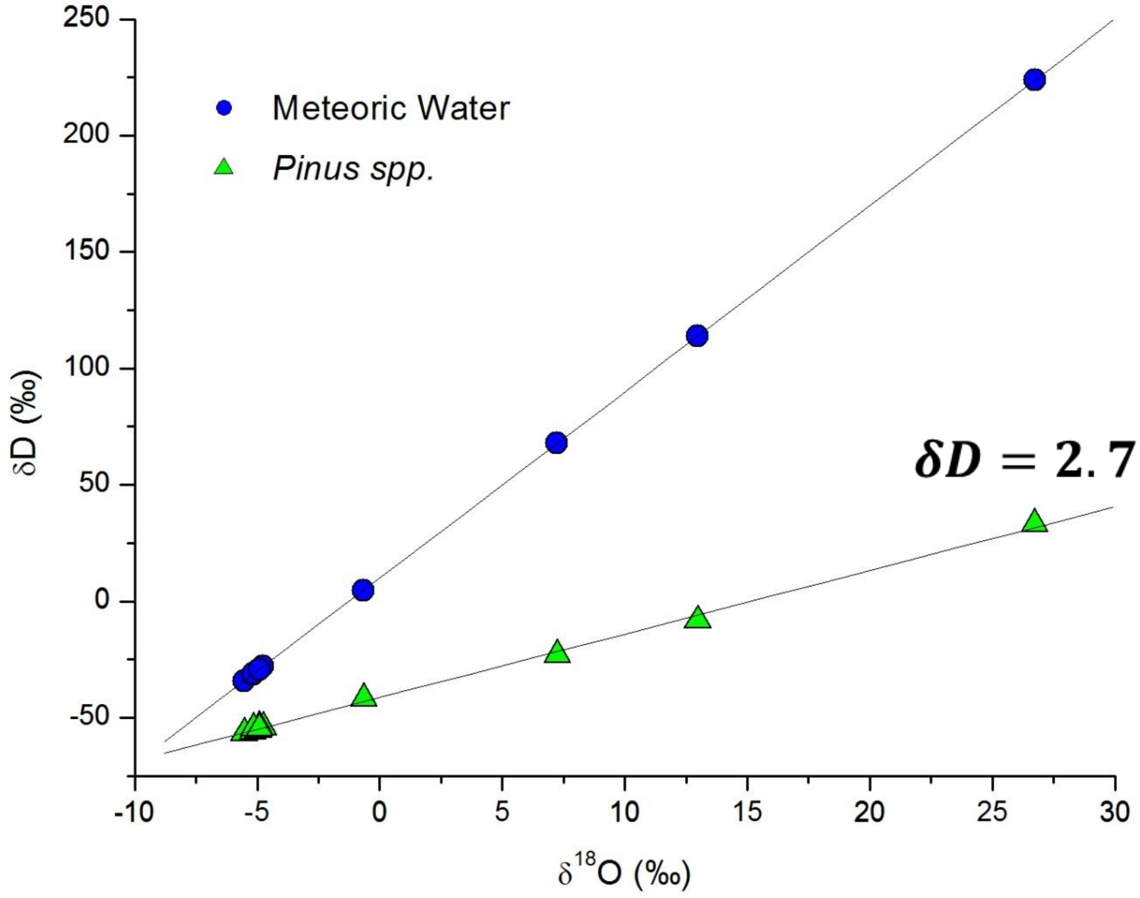
Matrix-Bound Water – Pine

Matrix-Bound Water – Pine



Matrix-Bound Water – Pine



$$\delta D = 2.73 \cdot \delta^{18}O - 41.33$$

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Matrix-Bound Water – Pine

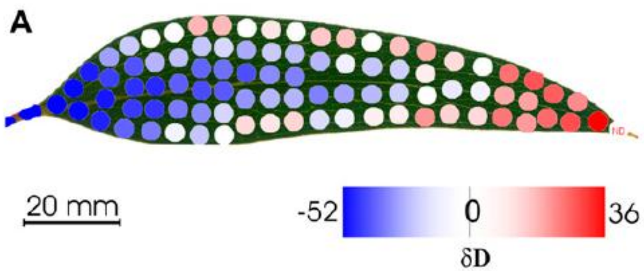
- Stem Water:
  - Little variability:
    $\delta D = -55.02 \pm 0.98$ ‰, enrichment of 0.98 ‰ / cm
    $\delta^{18}O = -5.06 \pm 0.25$ ‰, enrichment of 0.10 ‰ / cm
- Leaf Water:
  - Significant enrichment along the length of the needle:
    δD enrichment of 3.14 ‰ / cm
    $\delta^{18}O$ enrichment of 1.13 ‰ / cm
  - Cross-plot slope of 2.73 indicative of strong evaporation, in agreement with previous work (Chem. Geology 58:145-156)

Extraction of Solid Samples

Can it be streamlined?

- Can the extraction be amenable to field use? **Yes**
- Can the extraction be faster? **Yes (Minutes instead of hours, days)**
- Can there be fewer manipulations? **Yes (One Step)**
- Can the extraction be integrated with the analysis? **Yes**

Matrix-Bound Water



Plant Physiol. 143: 88-97

- Probe Water transport in soil-plant systems in the field
- Temporally
  - Different Times of day
  - Different Seasons
- Spatially:
  - Within a single leaf
  - Between Tissues
  - Between Soil and Plant
  - Between Soil Depths
  - Between Soil types
  - Between locations and individuals

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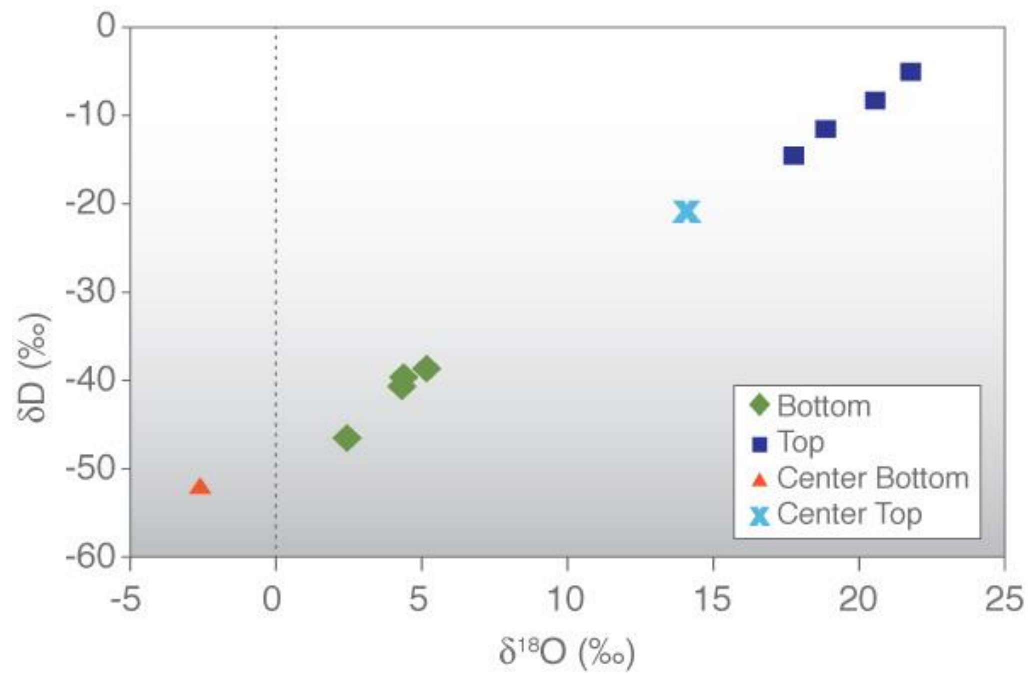
Thank You!



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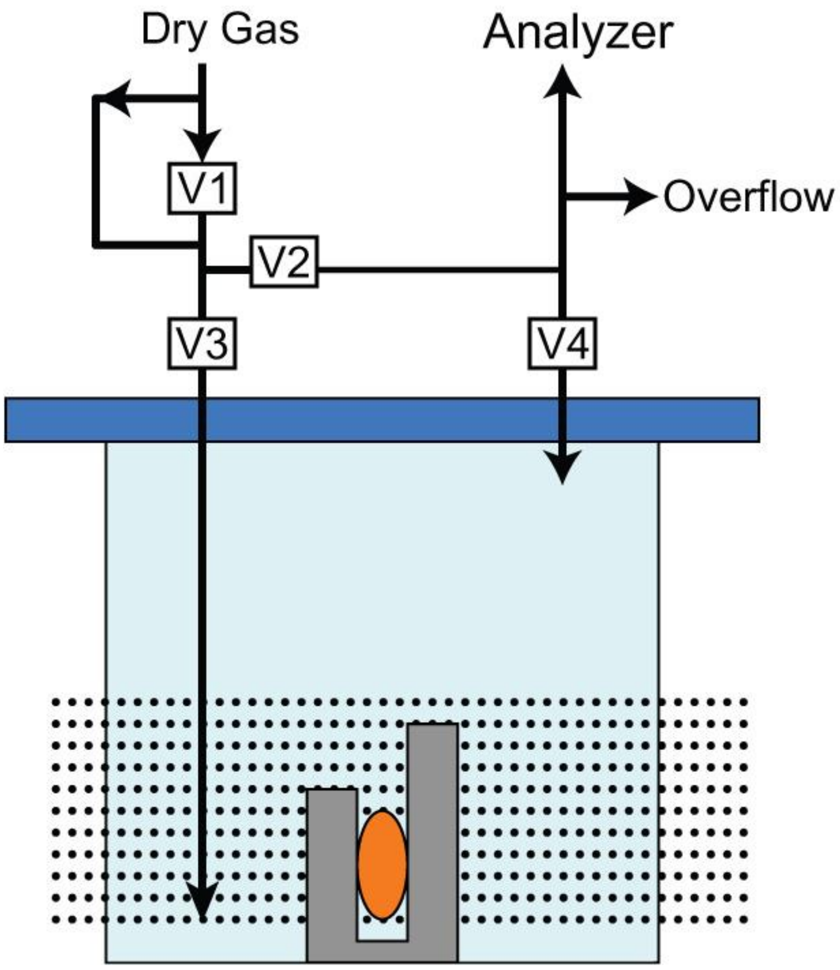
Gas Flow



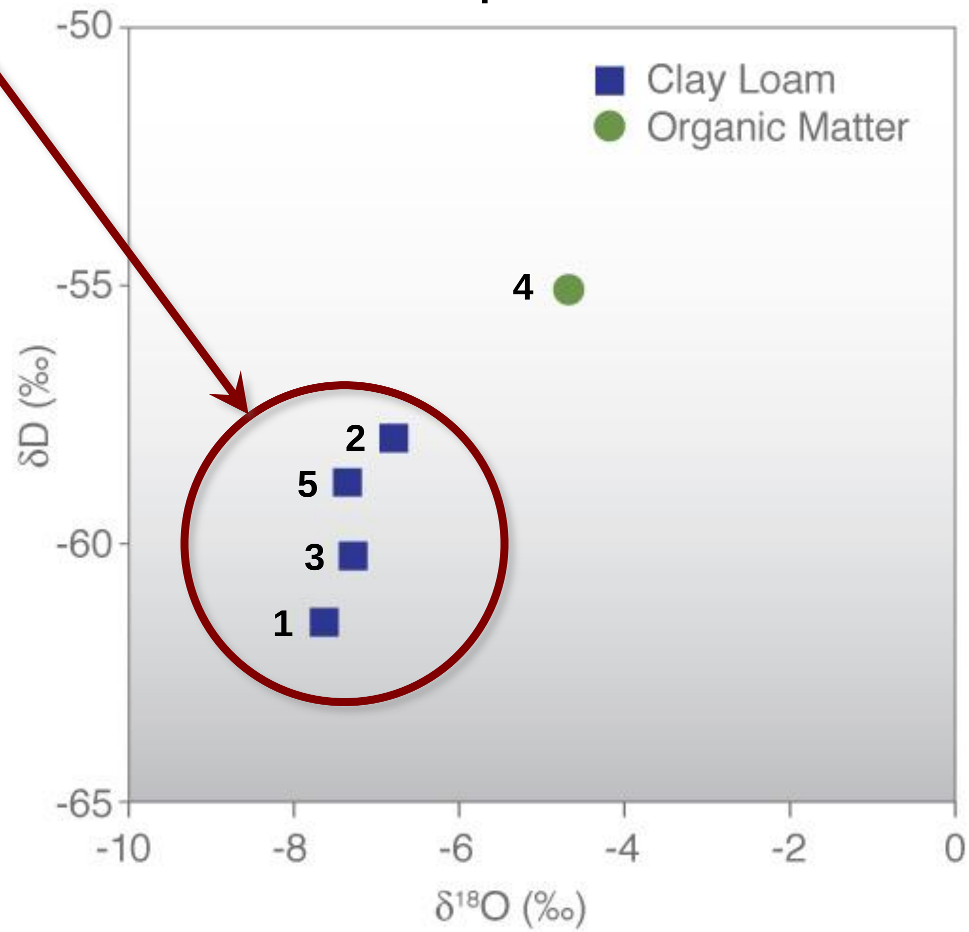
Two needles are concentric
valves are normally closed

State	V1	V2	V3	V4	Notes
Standby		X			~50 sccm by orifice @ 2.5 psi
Ready	X	X			~250 sccm @ 2.5 psi
Purge	X	X	X		Purges long line before going into vial ~300 sccm @ 2 psi
Sample	X		X	X	Flushes sample vial 50-300 sccm depending on pressure Typically 150 sccm @ 2.5 psi

Soil Measurements

- Soil water ($\delta^{18}O$, δD)
  - Mean -7.26,-59.23 ‰
  - 1σ = 0.34, 1.56 ‰
- 4 samples at ~30 cm, 1 sample at ~15 cm
- Clay loam with bits of organic matter
- Numbers indicate sequence of measurement

Soil Samples from 12”



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