High-Frequency, Field-Deployable Isotope Analyzer for Hydrological Applications

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Outline

- **Technical Overview**

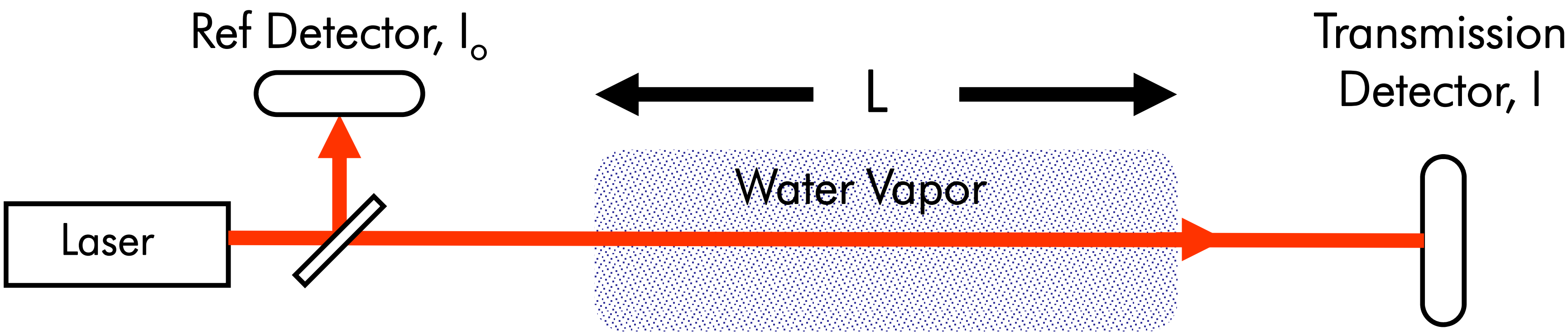
- **High-Frequency Liquid Water Isotope Analyzer**
  - Laboratory test data
  - Deployment at the H. J. Andrews Experimental Forest
  - Rain on Snow Laboratory Studies

- **Field-Deployable Water Vapor Isotope Analyzer**
  - Water Vapor Isotopic Standard Source
  - Laboratory test data
  - Preliminary Deployment at Sherman Island, California
  - Preliminary Deployment at Mauna Loa, Hawaii

- **Very High-Frequency Water Isotope Measurements**
  - Water Vapor Isotope Flux
  - Time-Resolved Liquid Water Isotope Measurements

Technical Overview

Conventional Absorption Spectrometry



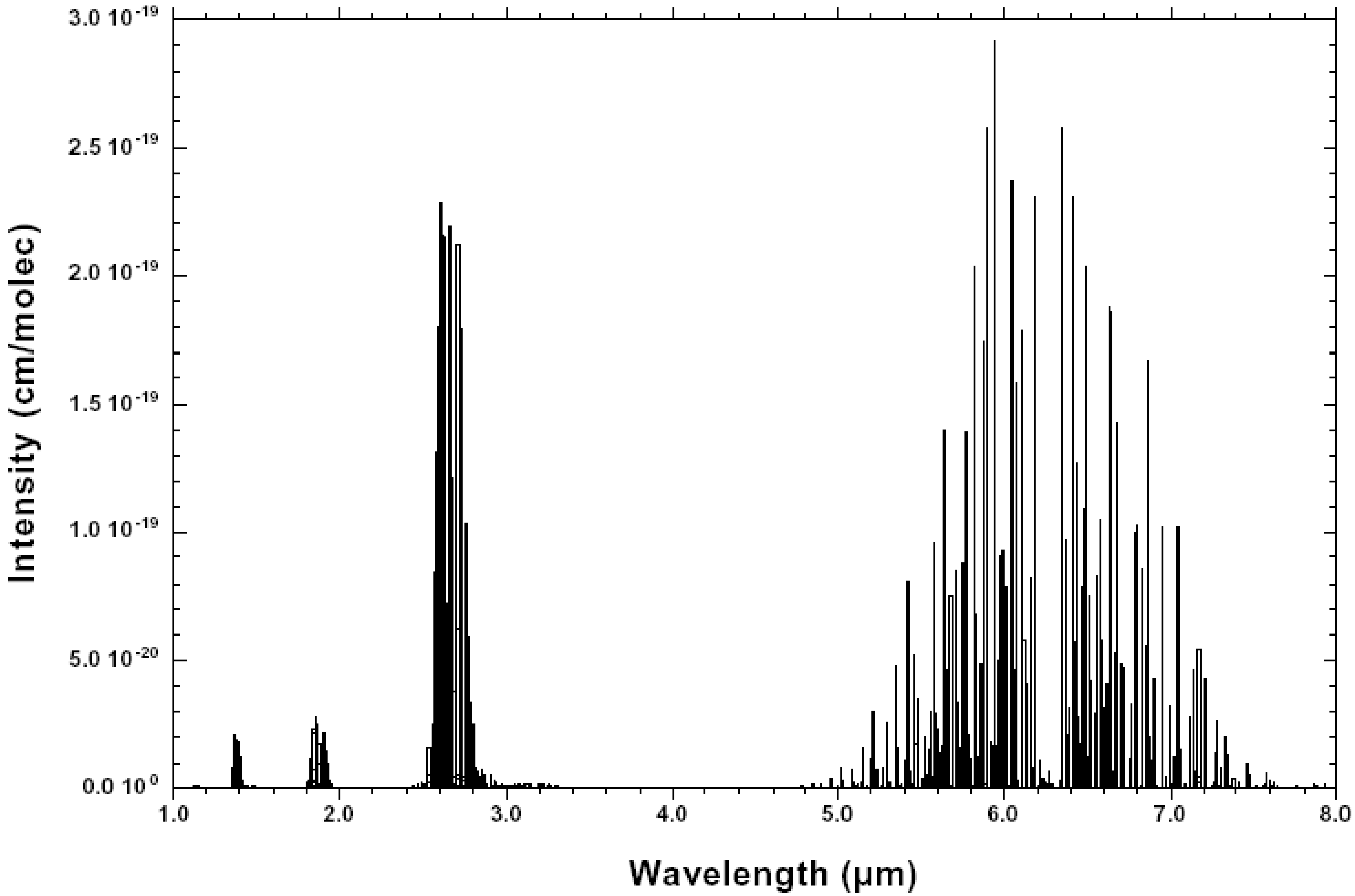
Beers Law: $\Delta I/I_o = 1\text{-exp}(-\alpha L_{eff})$

$\Delta I/I_o$	=	fractional change in laser intensity
L_{eff}	=	effective optical path length
$\alpha(\lambda)$	=	absorption coefficient, $S\ P\ \chi\ \phi(\lambda)$
S	=	absorption line strength
χ	=	mixing ratio (mole fraction)
P	=	total pressure

- 1^{st} principles measurement of species' concentration
- Different isotopes absorb at different wavelengths
- Measure molecules directly – no need for sample conversion
- Narrow linewidth laser provides extraordinary selectivity

Technical Overview

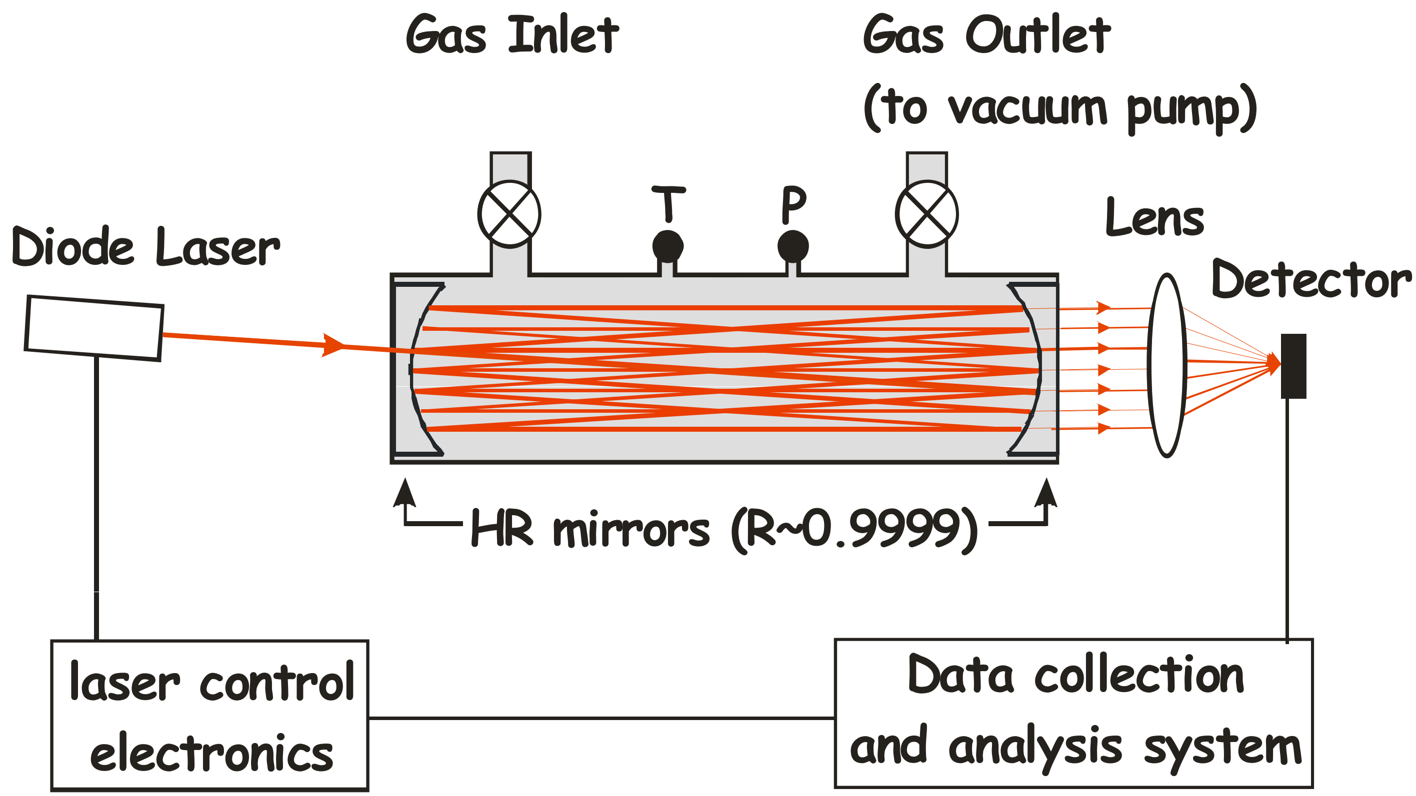
Absorption Spectrum of Water



- Mid-infrared region strongly absorbs, but is hardware limited
- Near-infrared region is readily accessible but weak absorptions
- Select isolated, proximate near-IR absorption features for isotope studies

Technical Overview

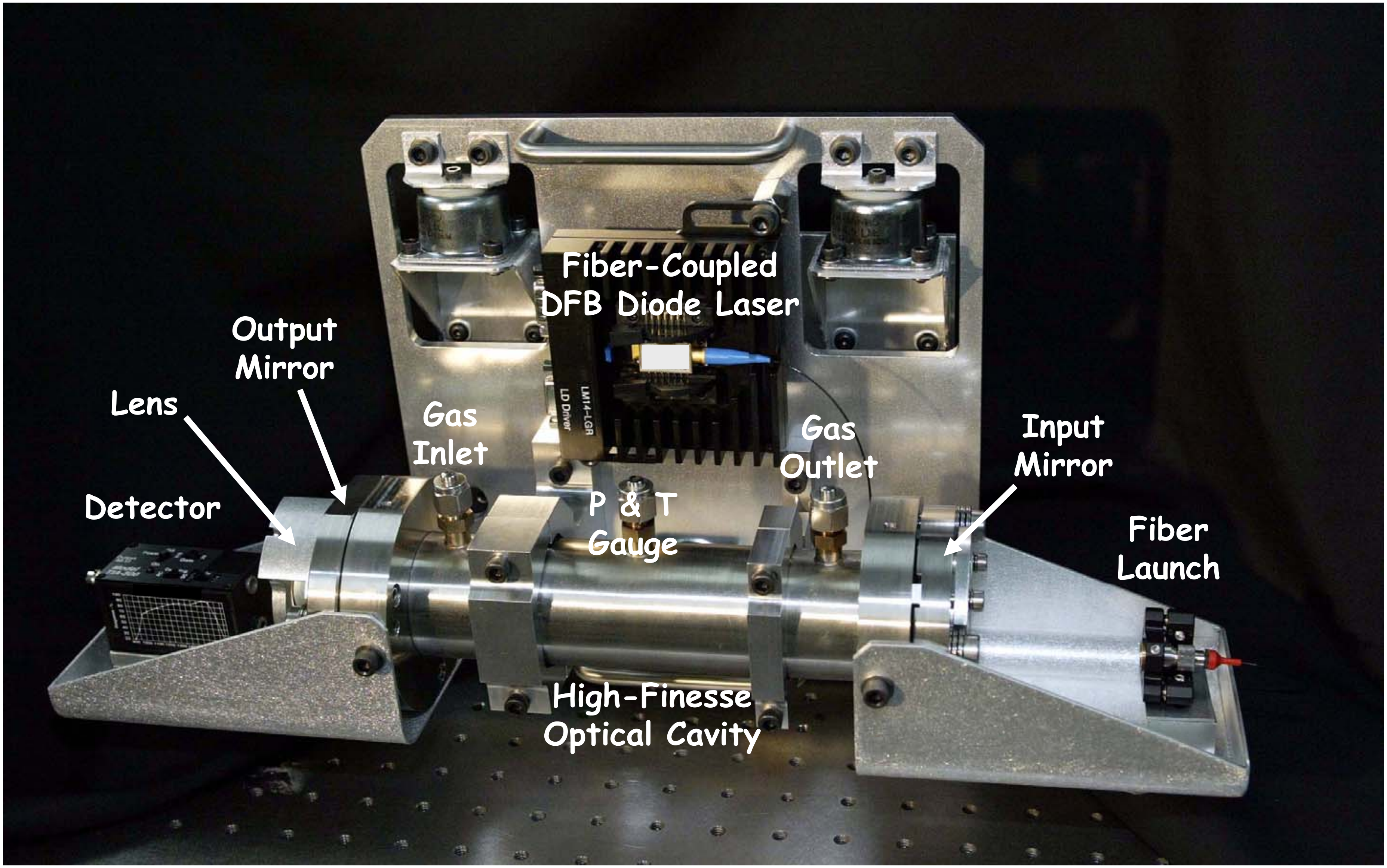
Off-Axis Integrated Cavity Output Spectroscopy



- Optical cavity provides pathlength enhancement of $L_{eff} = L / (1-R)$
- Typical R = 99.99%, L_{eff} = 10,000 meters
- Allows for the highly accurate measurement of very weak absorptions
- Extraordinarily robust - alignment insensitivity, telecom components
- Field-deployable, autonomous operation, no sample preparation
- Can measure stable isotopes of water, carbon dioxide, methane, etc…

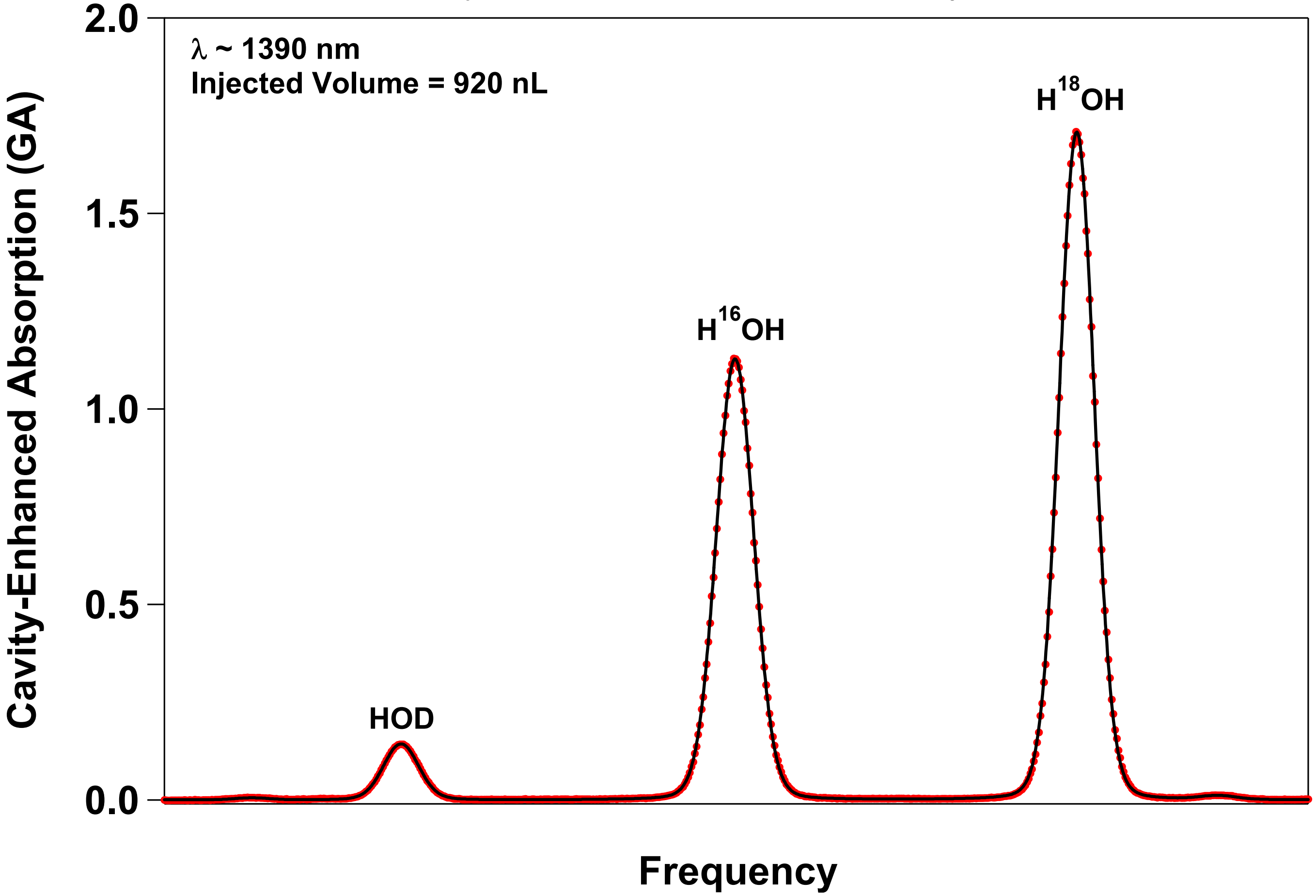
Technical Overview

Experimental Setup



Technical Overview

Measured Cavity-Enhanced Spectrum of Water



- Measure [HOD], [$H^{16}OH$], [$H^{18}OH$] → D/H, $^{18}O/^{16}O$
- Simultaneously measure both isotopes in a single laser scan
- High signal-to-noise ratio → precise isotope ratio determination
- Well characterized transitions

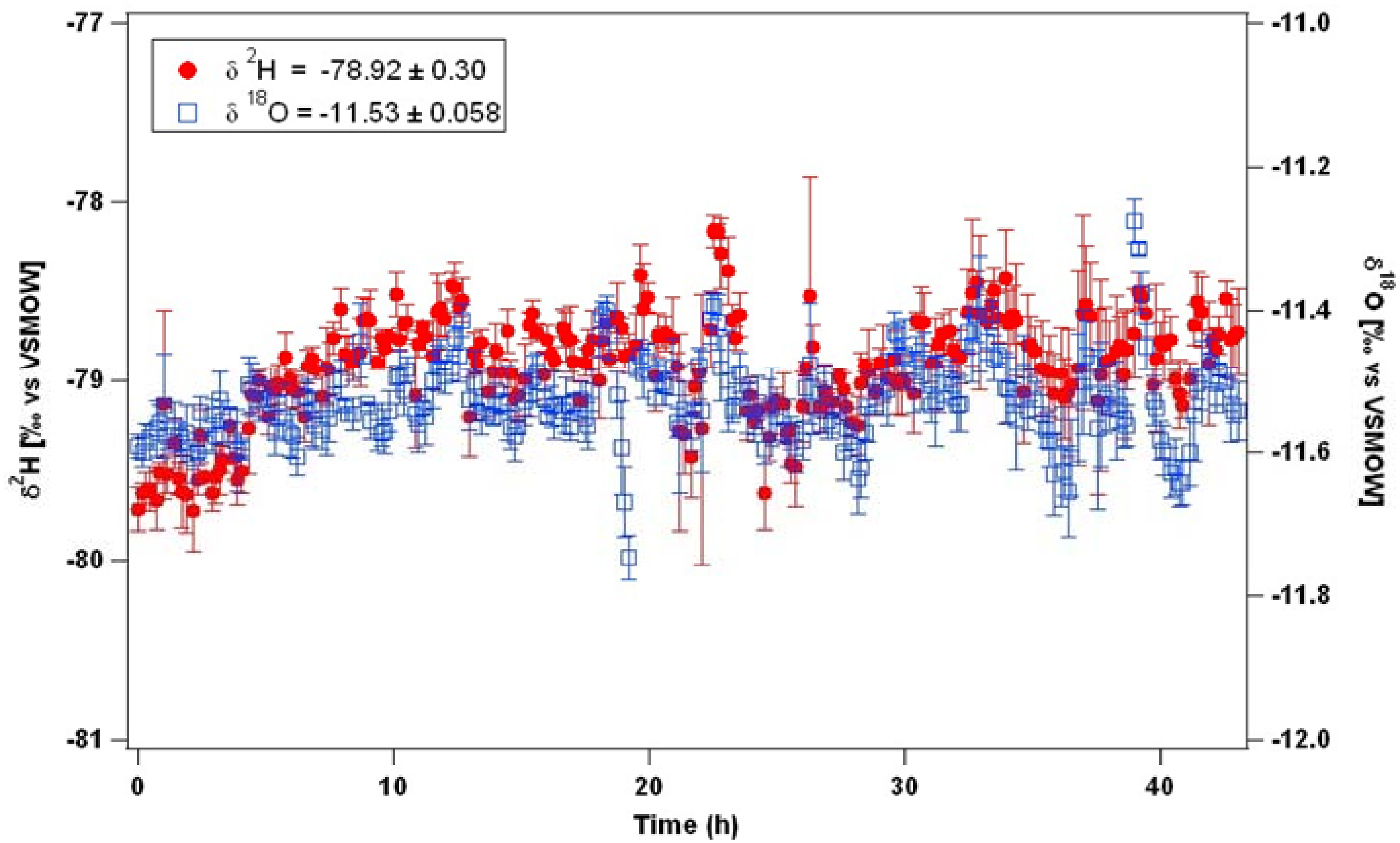
High-Frequency LWIA

Conventional LGR Liquid Water Isotope Analyzer

- Measure $\delta^{18}O$ and δD of liquid water to better than ±0.2 ‰ and ±0.6 ‰
- Approximately 30 unknown samples per day
- Widely used in hydrology, geology, and medical laboratories worldwide

High-Frequency LWIA

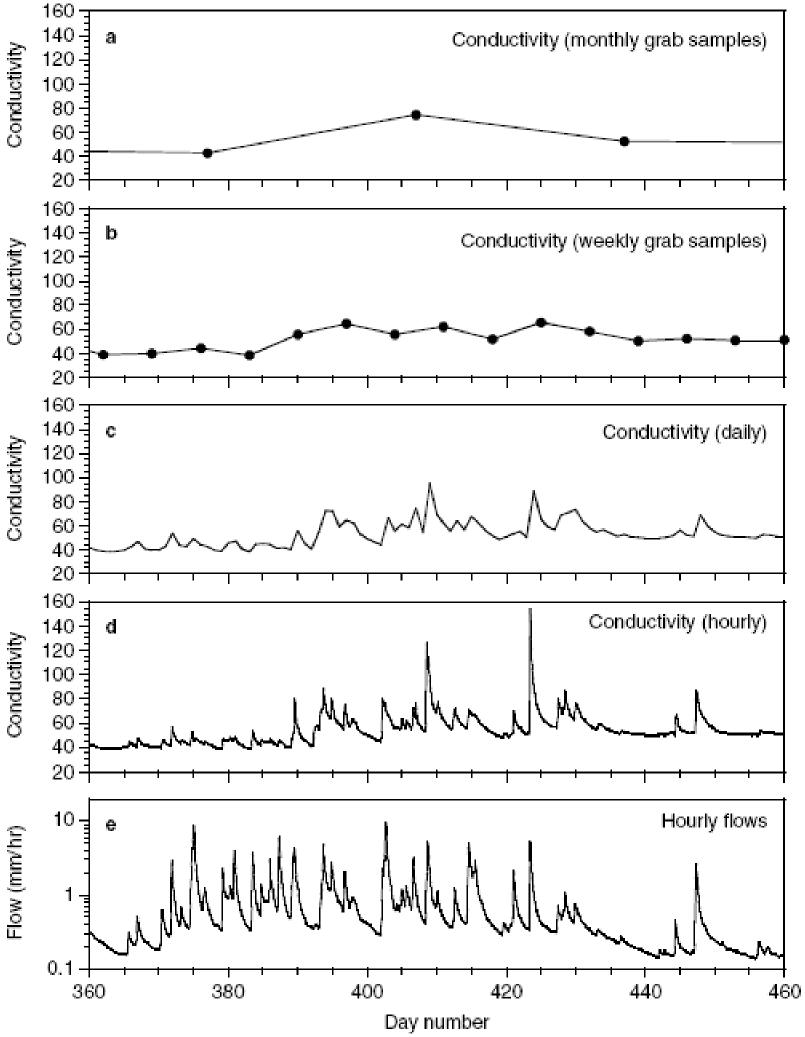
Laboratory Test Data



- Conventional LWIA requires 250 seconds/injection → 30 unknowns/day
- Improved gas conductance, evaporation, and data analysis to increase speed
- High-Frequency LWIA requires < 86 seconds/injection → 134 unknowns/day
- Measurement Precision: $\delta^{18}O$ and δD to within ±0.06 ‰ and ±0.30 ‰ (1σ)
- Accuracy verified by direct comparison to IRMS for widely varying samples

High-Frequency LWIA

H. J. A. Deployment - Motivation



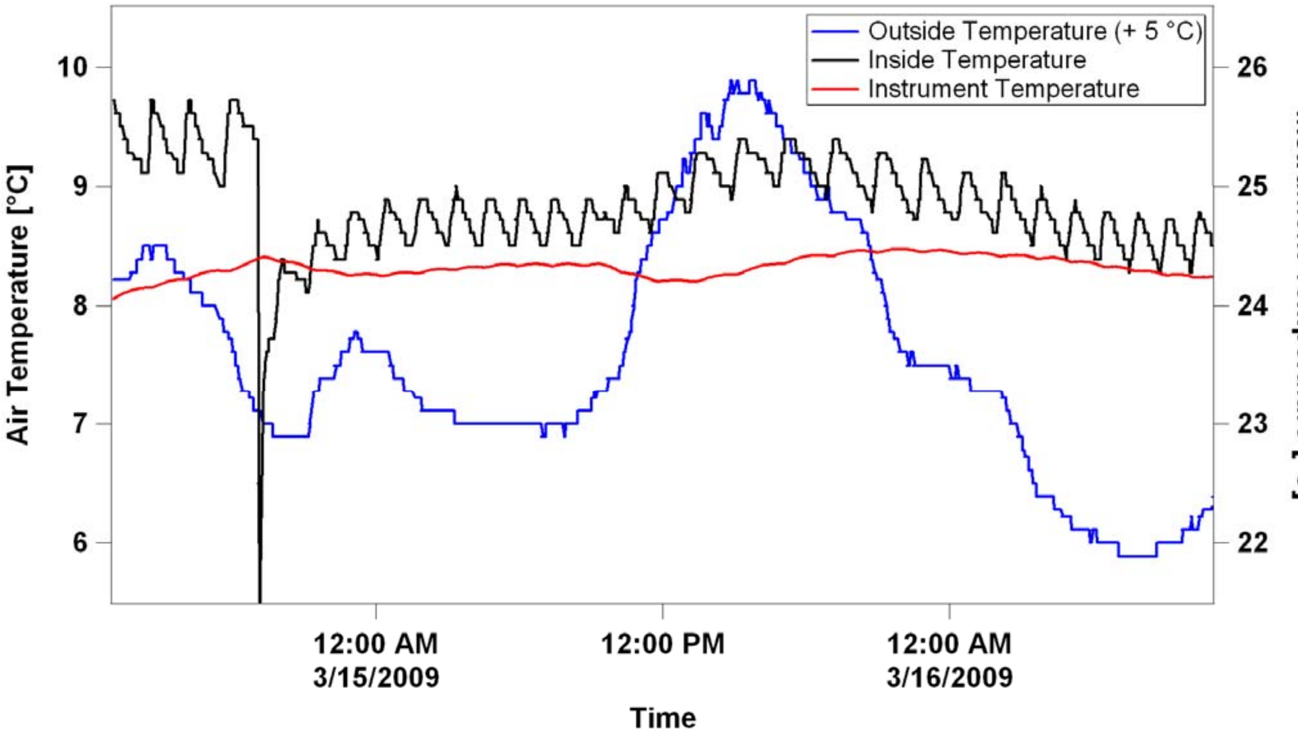
- High-frequency water flux data typically available
- Recently added high-frequency chemical data
- Want high-frequency isotope data
  - Transit time distributions
  - Precipitation studies
- "Grab" samples used for isotope data
  - High-frequency sampling for short, intense events
  - Long term data limited to much lower sampling rate
  - Cost and labor prohibitive
- Fast, field-deployable isotope analyzer required
- Work performed with Professor McDonnell (OSU)
- Figure adapted from:

  Kirchner, J. W., X. Feng, C. Neal, and A. J. Robson, 2004. The fine structure of water-quality dynamics: the (high-frequency) wave of the future. Hydrological Processes 18, 1353.

Deploy a High-Frequency LWIA for Continuous Isotope Measurements of Rain & Streams

High-Frequency LWIA

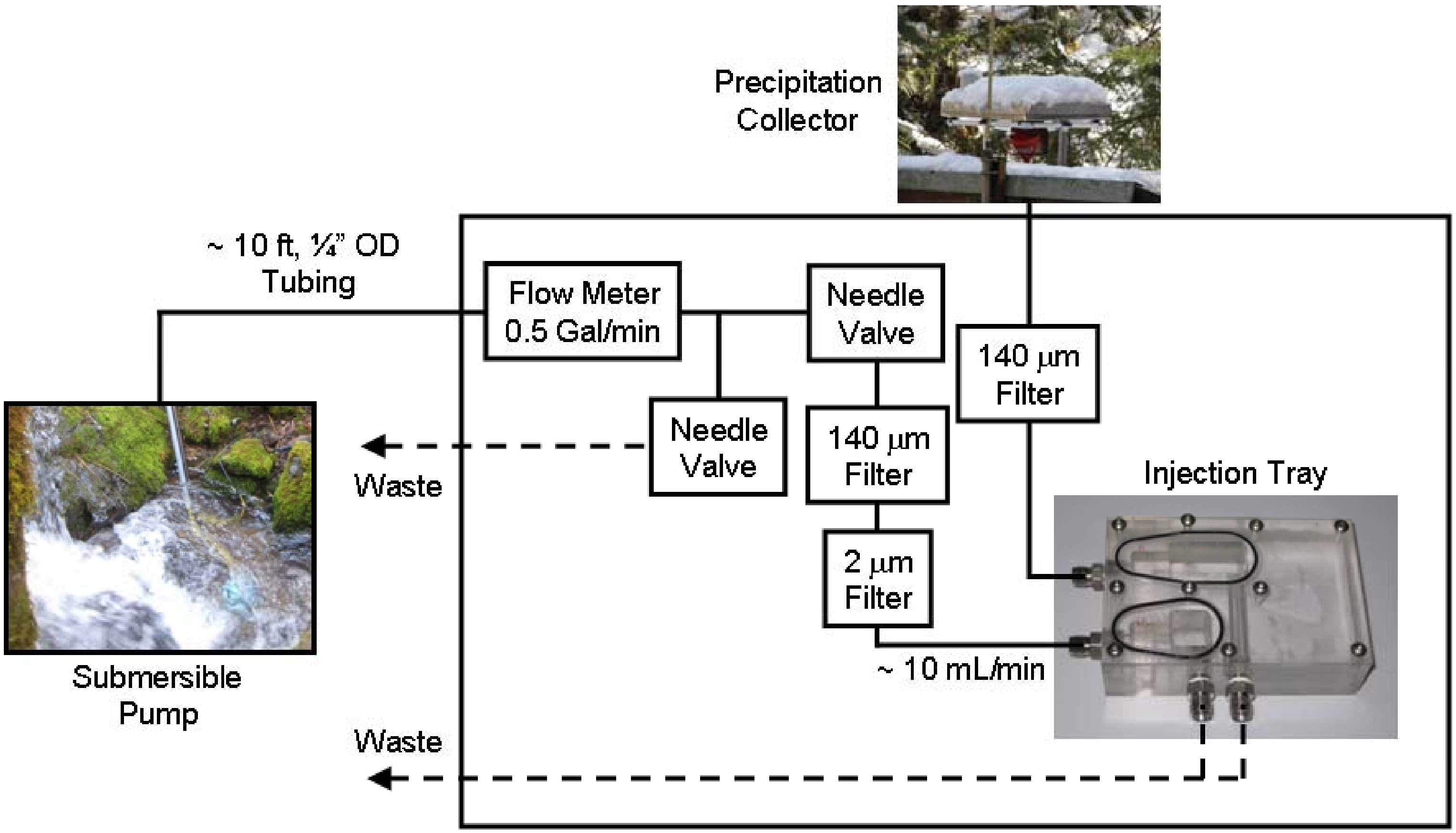
H. J. A. Deployment - Location



- Deployed in a gauging station at ~ 1 km² Watershed #1 in the H.J. Andrews
- Small propane heater in station to prevent freezing
- Enclosures to prevent debris from entering instrument or autosampler
- Collocated measurements of temperature, wind speed, rainfall, and humidity
- 4 week deployment: 3/5/09- 4/3/09

High-Frequency LWIA

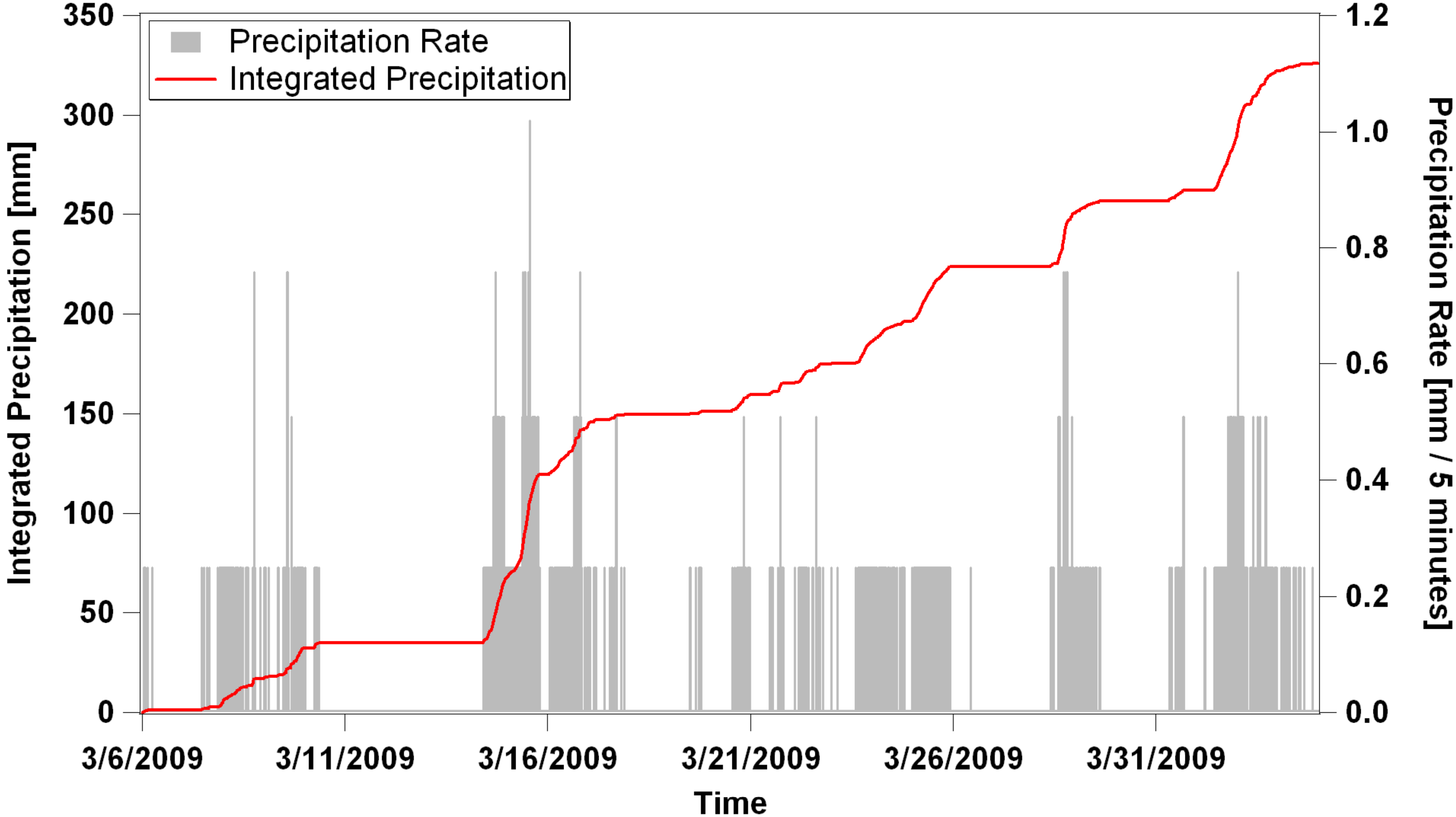
H. J. A. Deployment – Water Sampling System



- Injection tray allows external water sources to be interfaced to autosampler
- Submersible pump pushes 31 mL/s against 3 m of head
- Open split to feed and filter ~ 10 mL/min through the tray
- Precipitation (snow/rain) gravity-sampled from a rooftop 576 in^2 funnel
- Both flows passed through inline stainless steel filters to remove particulates

High-Frequency LWIA

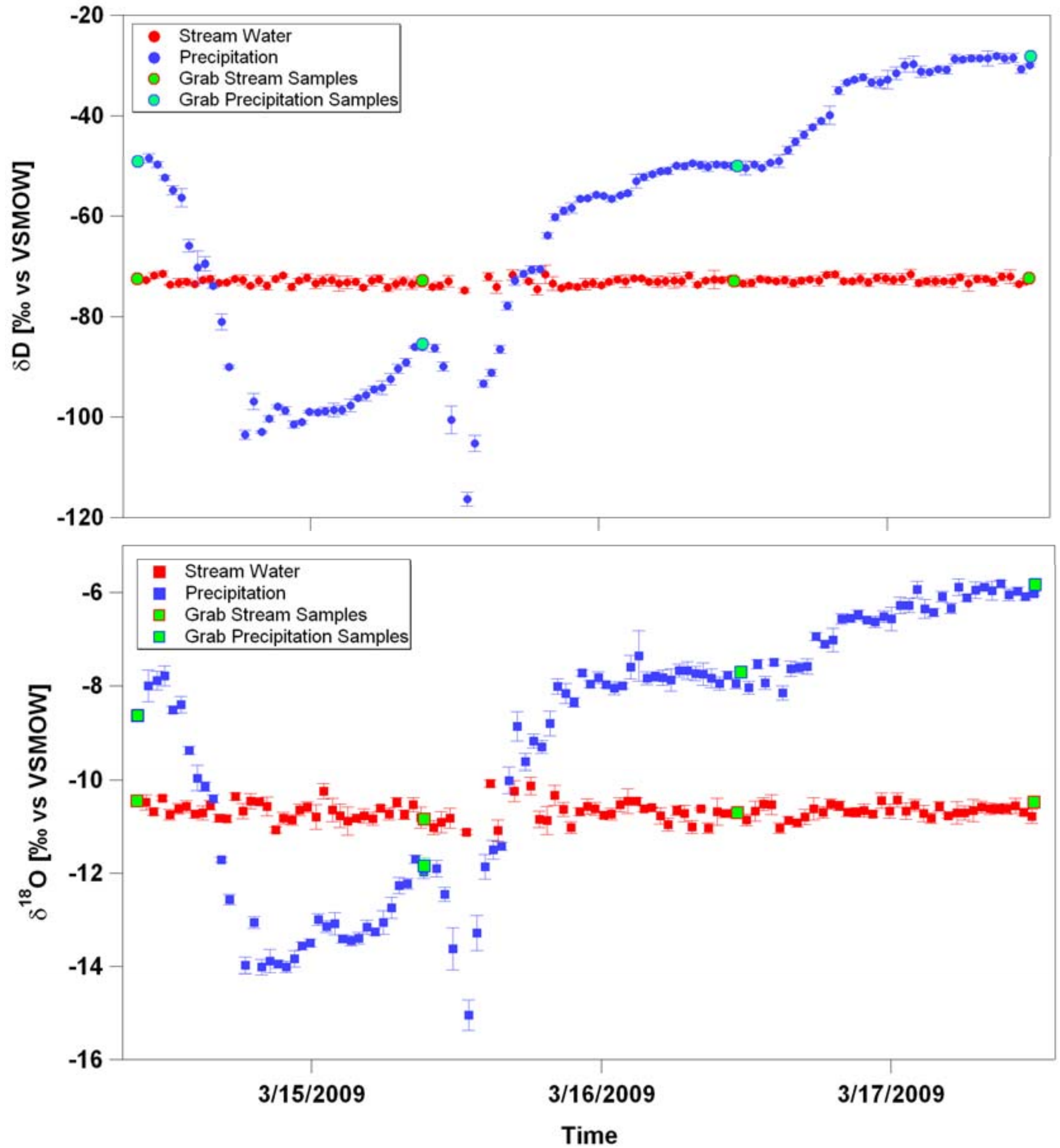
H. J. A. Deployment – 4 Major Storms

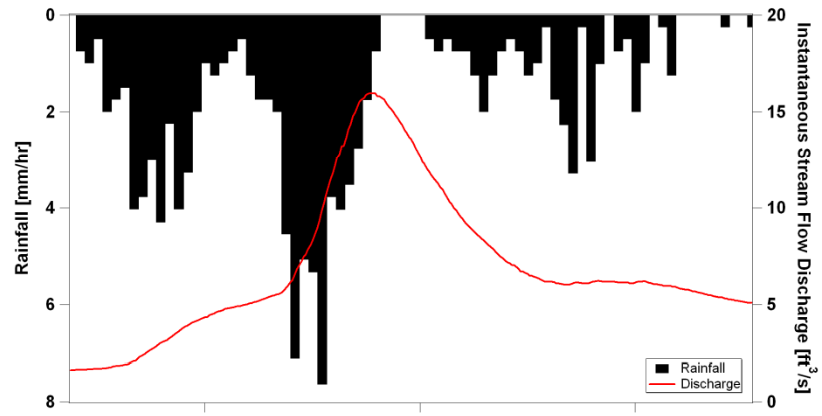


- 4 major rain events: 3/15/09, 3/25/09, 3/29/09, 4/2/09
- Amount of rainfall per storm ranged from 32 – 111 mm

High-Frequency LWIA

H. J. A. Deployment – 3/15/09 Storm

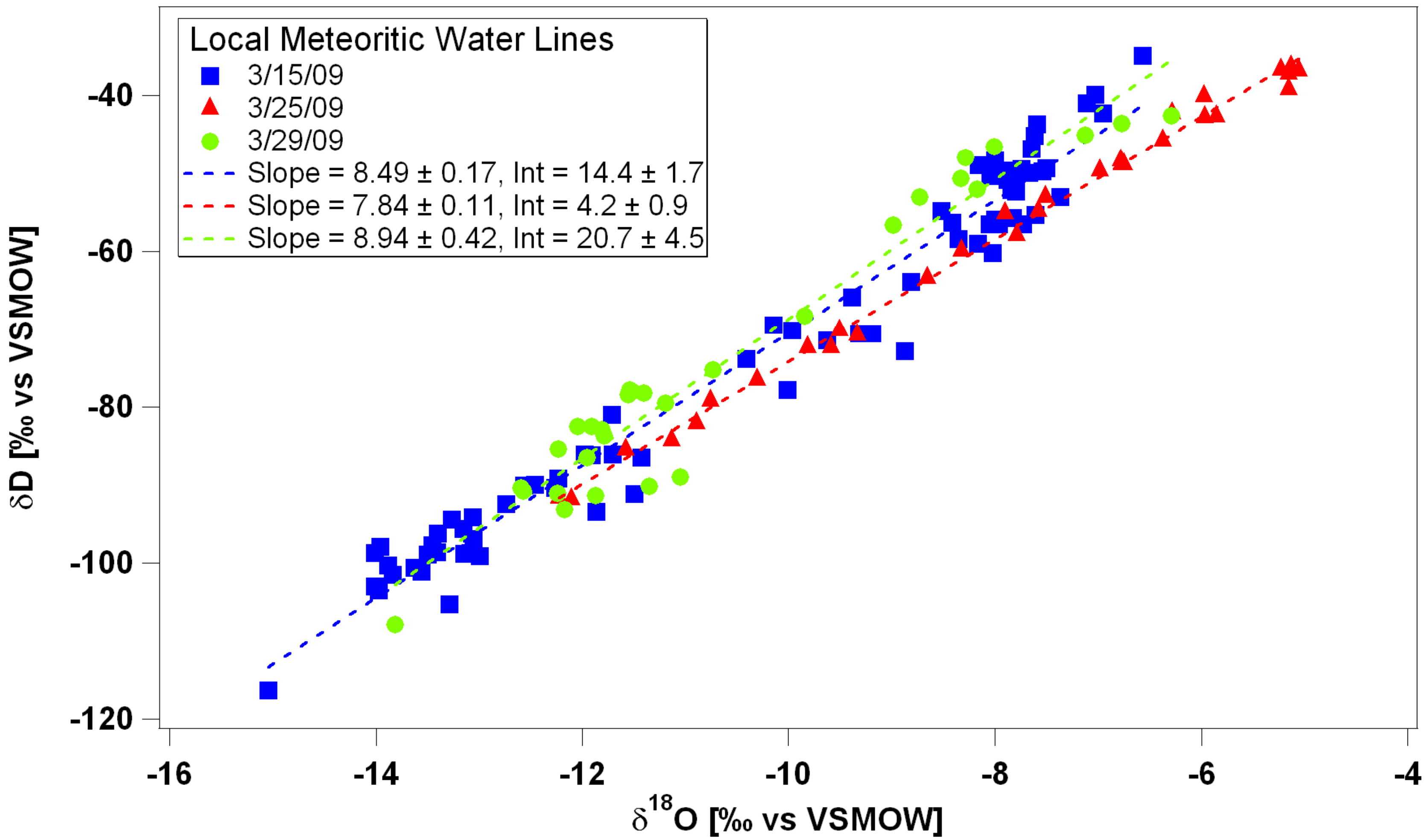




- 40 stream and 40 rain samples/day
- Large excursion in rainfall isotope ratio
- No change in stream isotope ratio
- "Old Water Paradox"
  - Pressure Pulse (flow) = immediate
  - Water stored in watershed for years
- Precipitation dynamics
- "Grab" samples every 12 – 24 hours
- Periodic servicing – septum, filters, stds

High-Frequency LWIA

H. J. A. Deployment – LMWL for 3 Rain Events



- Continuous, high-frequency data throughout long-term deployment
- Examine individual storm events
- Very limited previous studies involved using “grab” samples

High-Frequency LWIA

Rain on Snow Studies – Objective

- Rain on snow is the flood-producing runoff generation method in the Pacific Northwest
- How does rain mix with snow within the melting pack to deliver water to the ground?
- Use distinct isotopes of rain, snow, and runoff to help determine melting dynamics
- Work performed with Professor McDonnell (OSU)

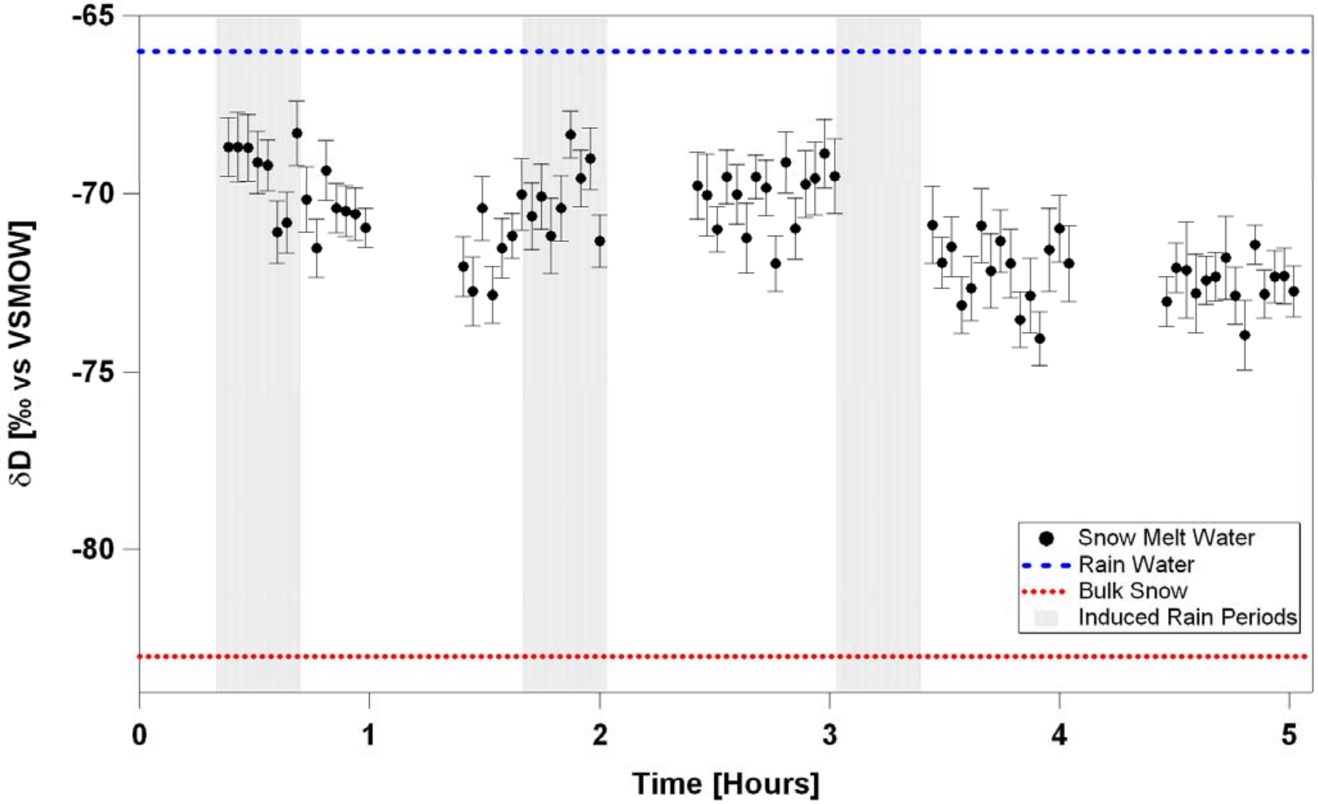
High-Frequency LWIA

Rain on Snow Studies – Experimental Method

- Snow Core: 200 mm diameter, 125 mm of water equivalent, 1512 g, from HJA Watershed #7
- "Rainfall": 10 mm/hr, 22 minute pulses spaced 1 hour apart… by a professional "rainmaker"
- Eluted water gravity-sampled into high-frequency Liquid Water Isotope Analyzer
- Analyzer sequence: 6 injections of std, 18 injections of eluted water (first 2 discarded)
- Minimal sample memory effects – each injection treated as individual analysis (no averaging)
- Measurement every 2 minutes with $\delta^{18}O$ and δD precisions of ±0.22 ‰ and ±0.8 ‰ (no averaging)

High-Frequency LWIA

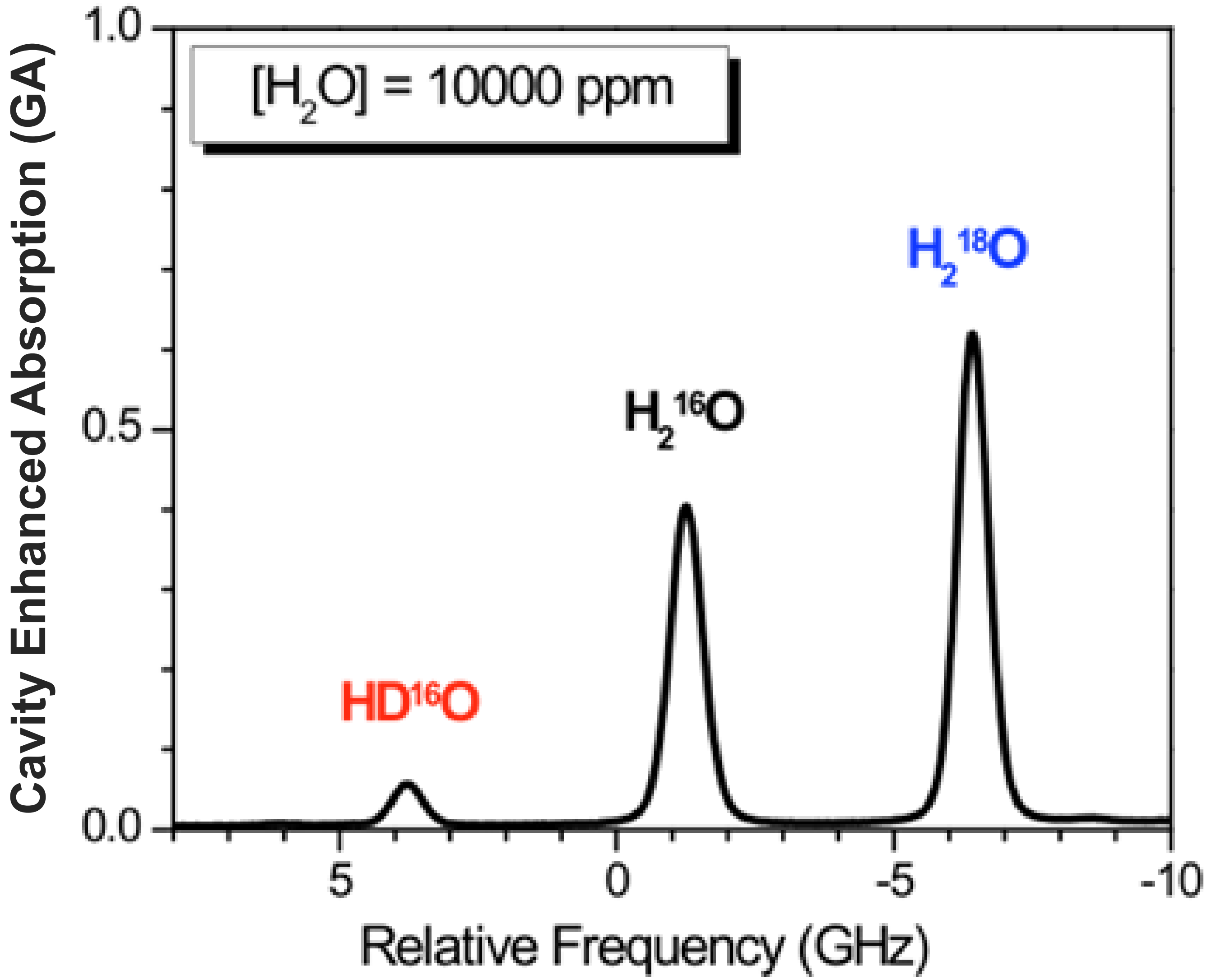
Rain on Snow Studies – Preliminary Results



- Gaps due to measurements of water standards
- Over 5 hour run, 41% of the total snow water equivalent lost due to melting
- Initially, rainfall dominates water passing through core (> 80 %)
- End of the experiment → eluted water is ~ 60 % rain water, 40 % snow melt
- High-frequency dynamics? Modeling efforts underway by McDonnell Group
- Measurements verified by comparison to "grab" samples

Field-Deployable WVIA

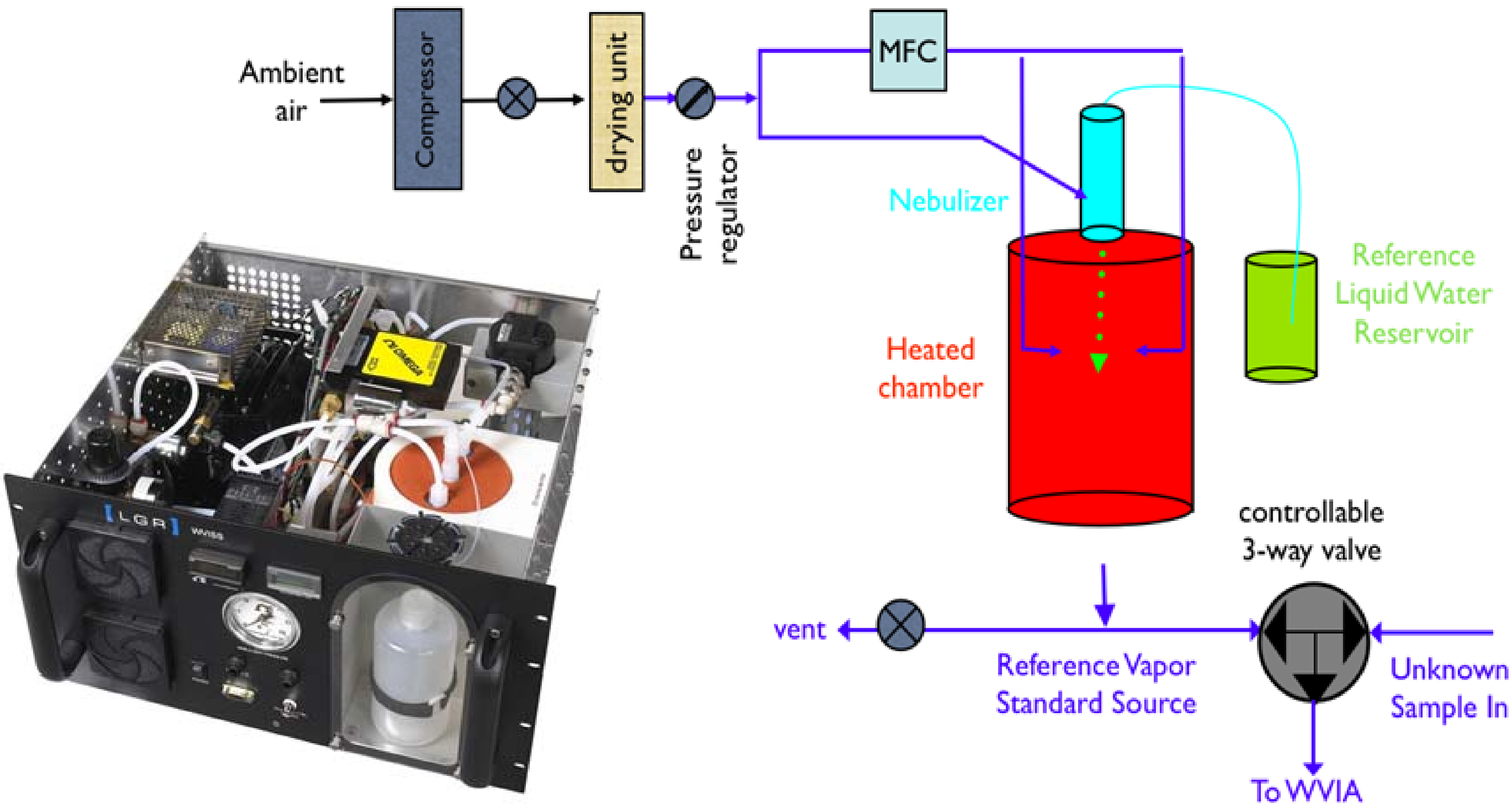
Cavity-Enhanced Spectrum



Less Sample, Higher Pressure → Better cavity and improved data analysis

Field-Deployable WVIA

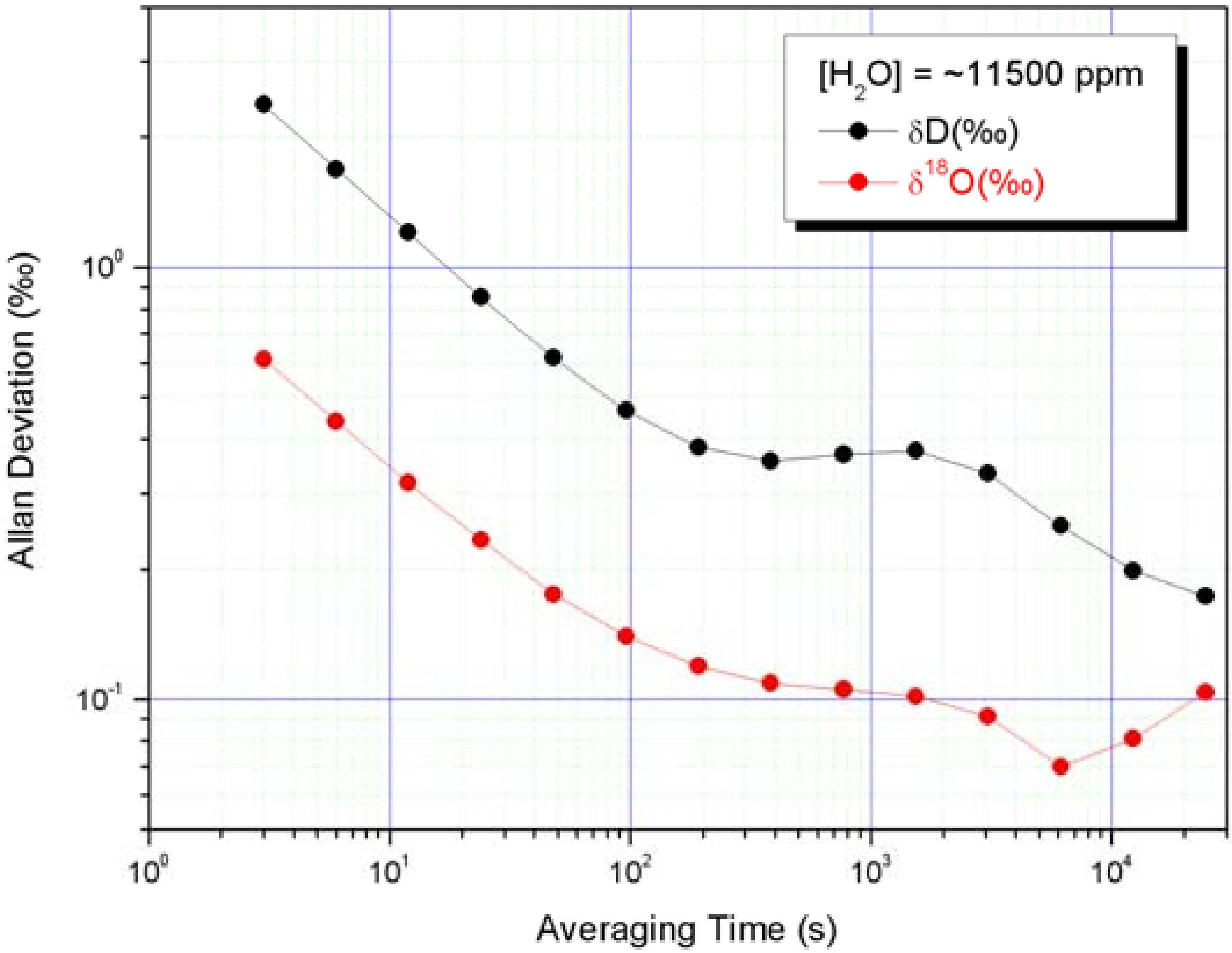
Water Vapor Isotopic Standard Source



- QUANTITATIVE evaporation with controlled water and dry air flows
- Water vapor isotope standard with controlled humidity (3000 – 30000 ppmv)
- Allows WVIA to rapidly switch between reference and sample (like LWIA)

Field-Deployable WVIA

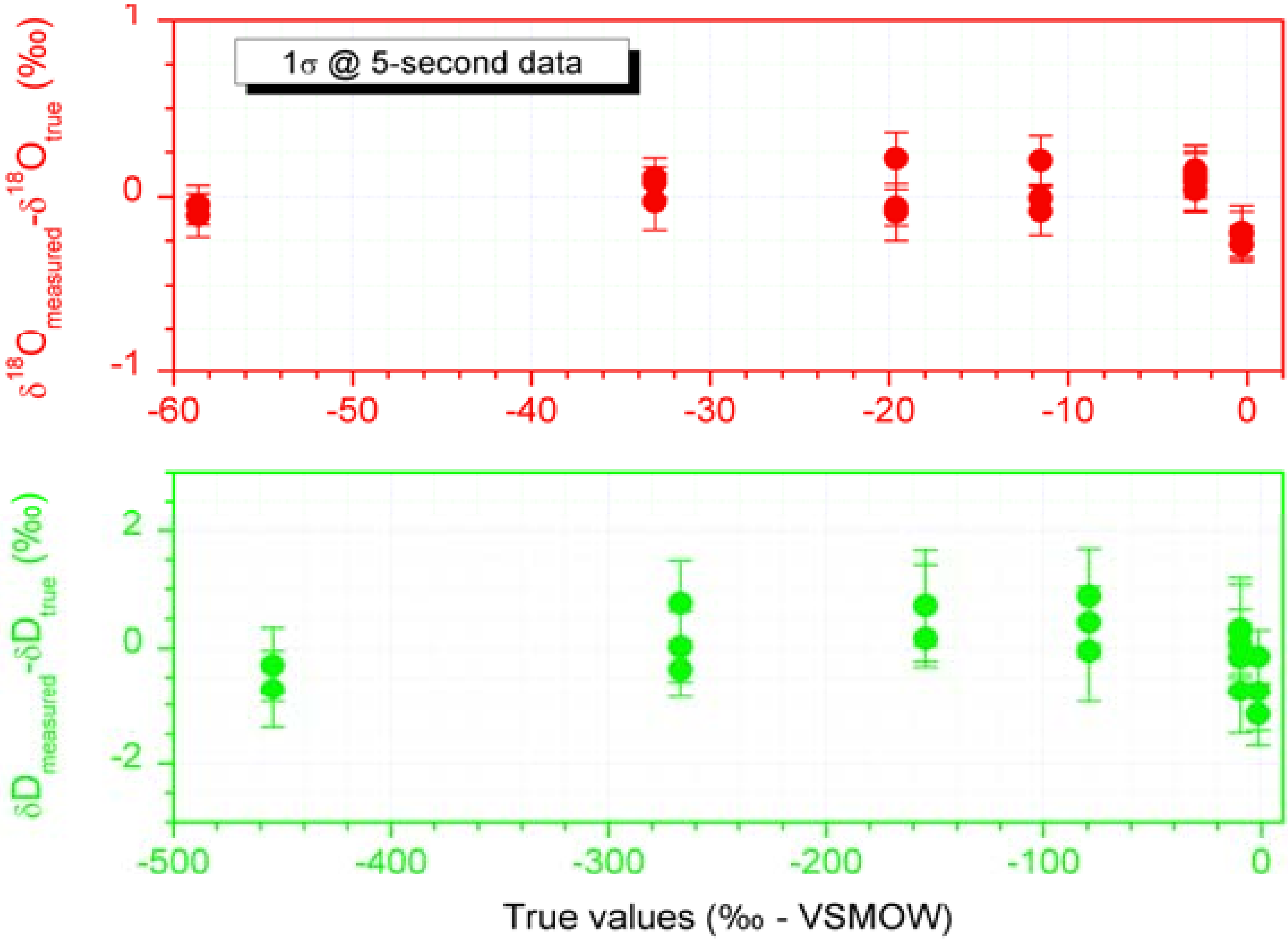
Laboratory Test Data - Precision



$\delta^{18}O$ and δD to ± 0.3 ‰ and ± 1.2 ‰ in 10 seconds

Field-Deployable WVIA

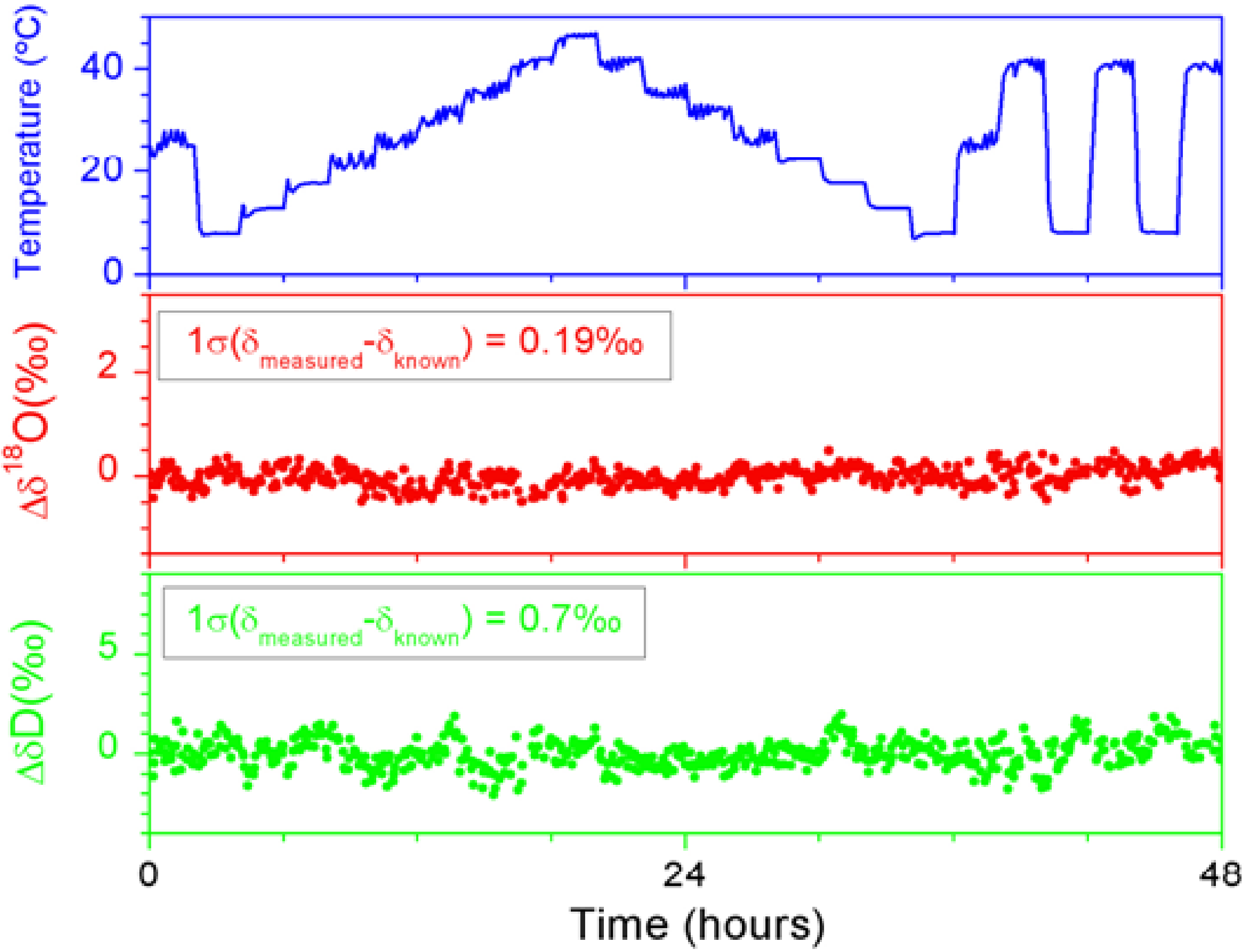
Laboratory Test Data – Accuracy



Accurate over natural water range (VSMOW → SLAP)

Field-Deployable WVIA

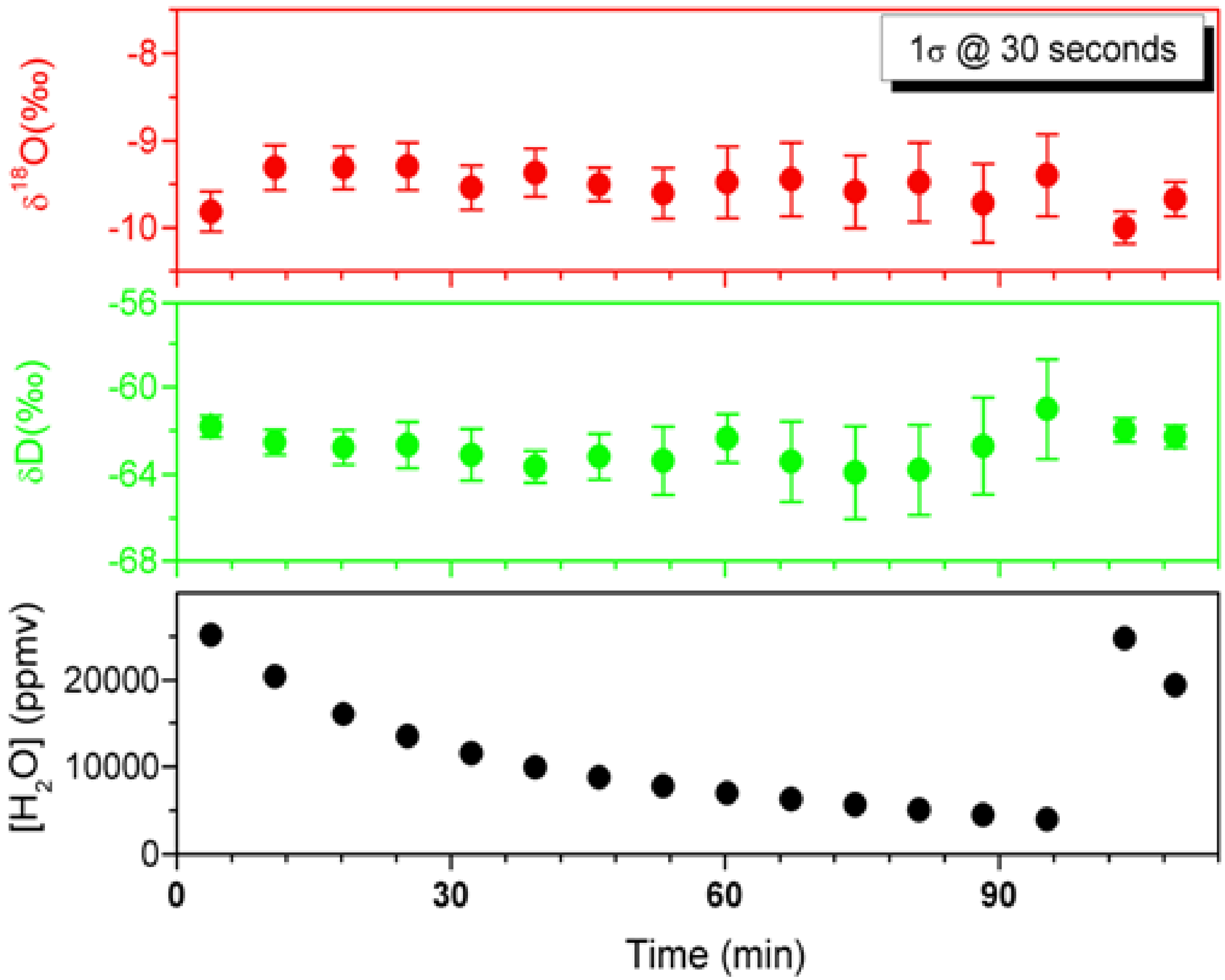
Laboratory Test Data – Thermal Stability



Stable from 5 – 45 °C

Field-Deployable WVIA

Laboratory Test Data – Concentration Invariance



No concentration dependence from 3000 – 25000 ppmv H_2O

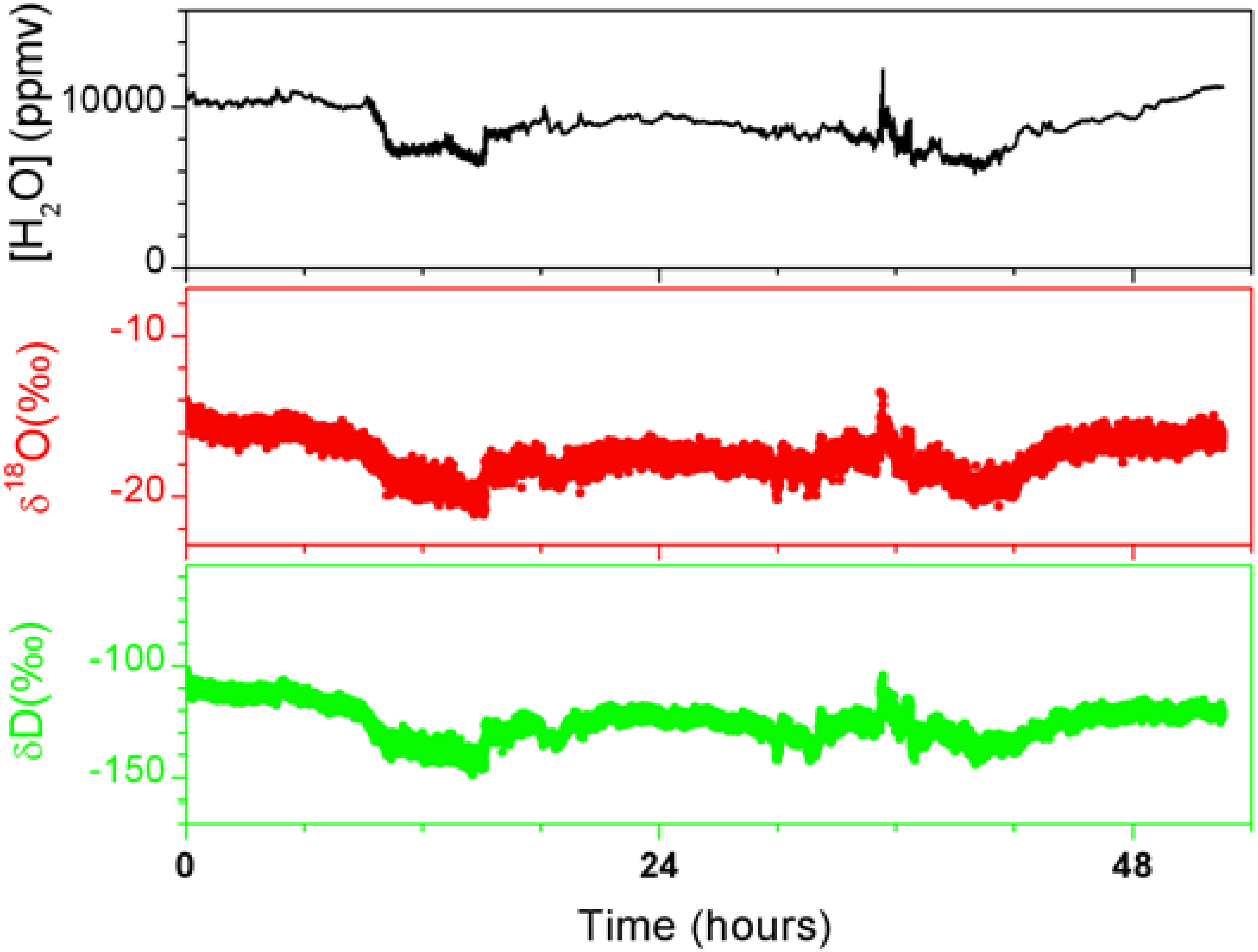
Field-Deployable WVIA

Deployment at Sherman Island - Experiment

- Deployed at Sherman Island, CA with Todd Dawson's group (UC Berkeley)
- Housed in mobile laboratory and interfaced to existing flux tower setup
- Instrument operated at a 2 Hz data rate for over 48 hours continuously
- Automatic, periodic calibration using Water Vapor Isotopic Standard Source

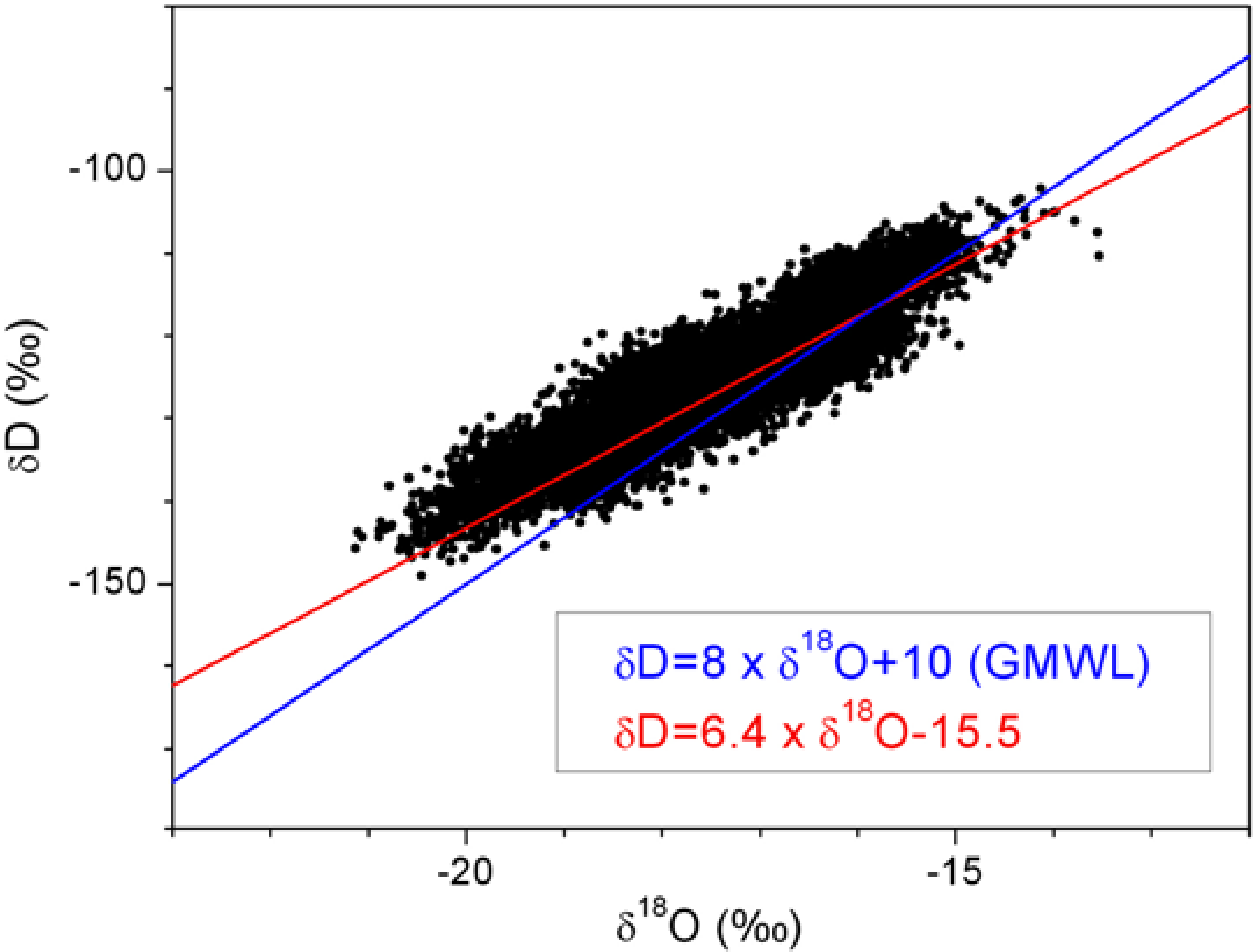
Field-Deployable WVIA

Deployment at Sherman Island – Raw Data



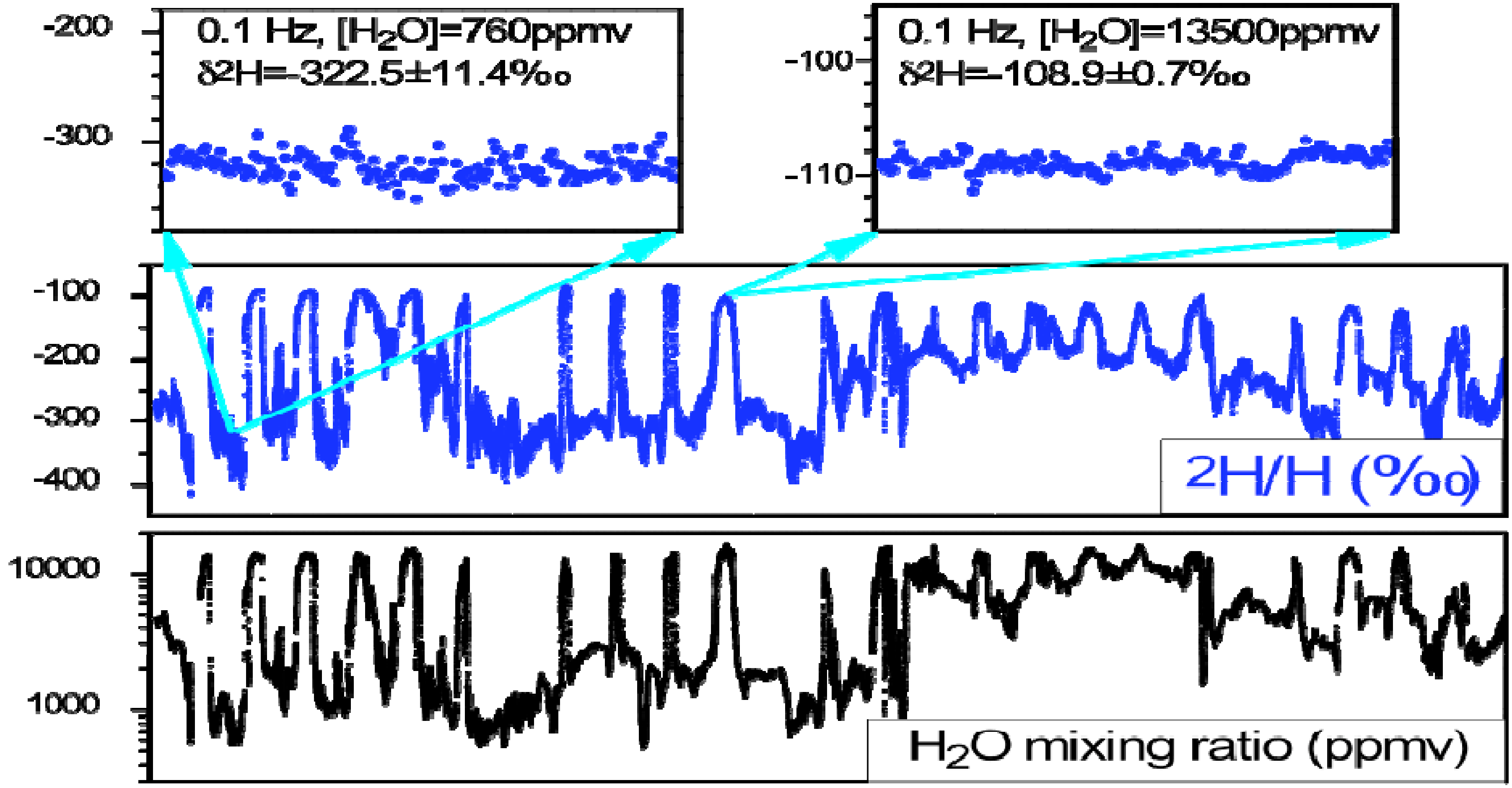
Field-Deployable WVIA

Deployment at Sherman Island – LMWL



Field-Deployable WVIA

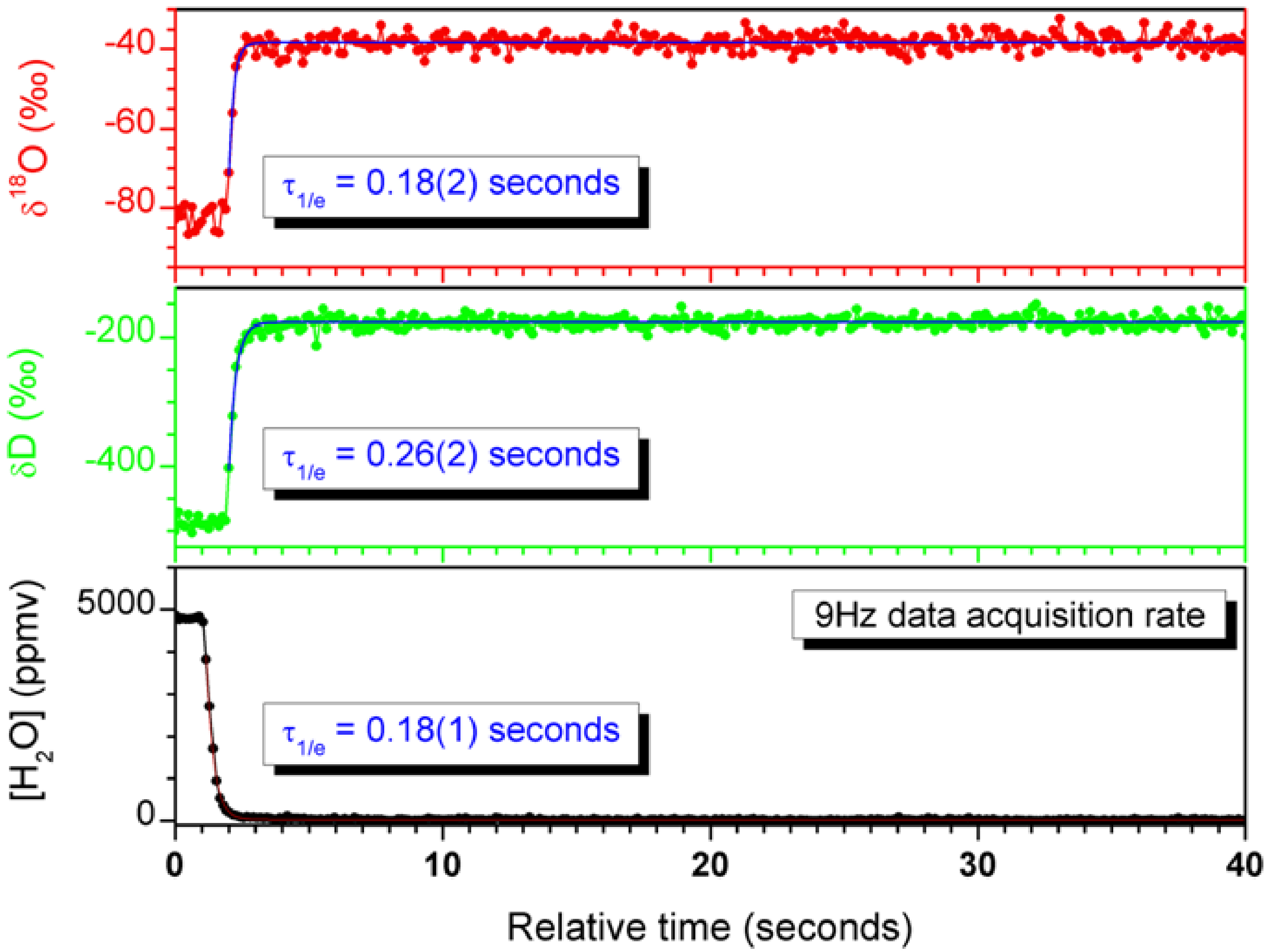
Deployment at Mauna Loa



- 25 days of continuous water vapor isotope measurements at 0.1 Hz
- Vapor concentration fluctuates between 500 – 15000 ppmv as atmospheric boundary layer moves
- Isotope ratio changes with boundary layer movement – sampling ocean air and Antarctic air
- Will incorporate these measurements into global circulation models

Very High Frequency Measurements

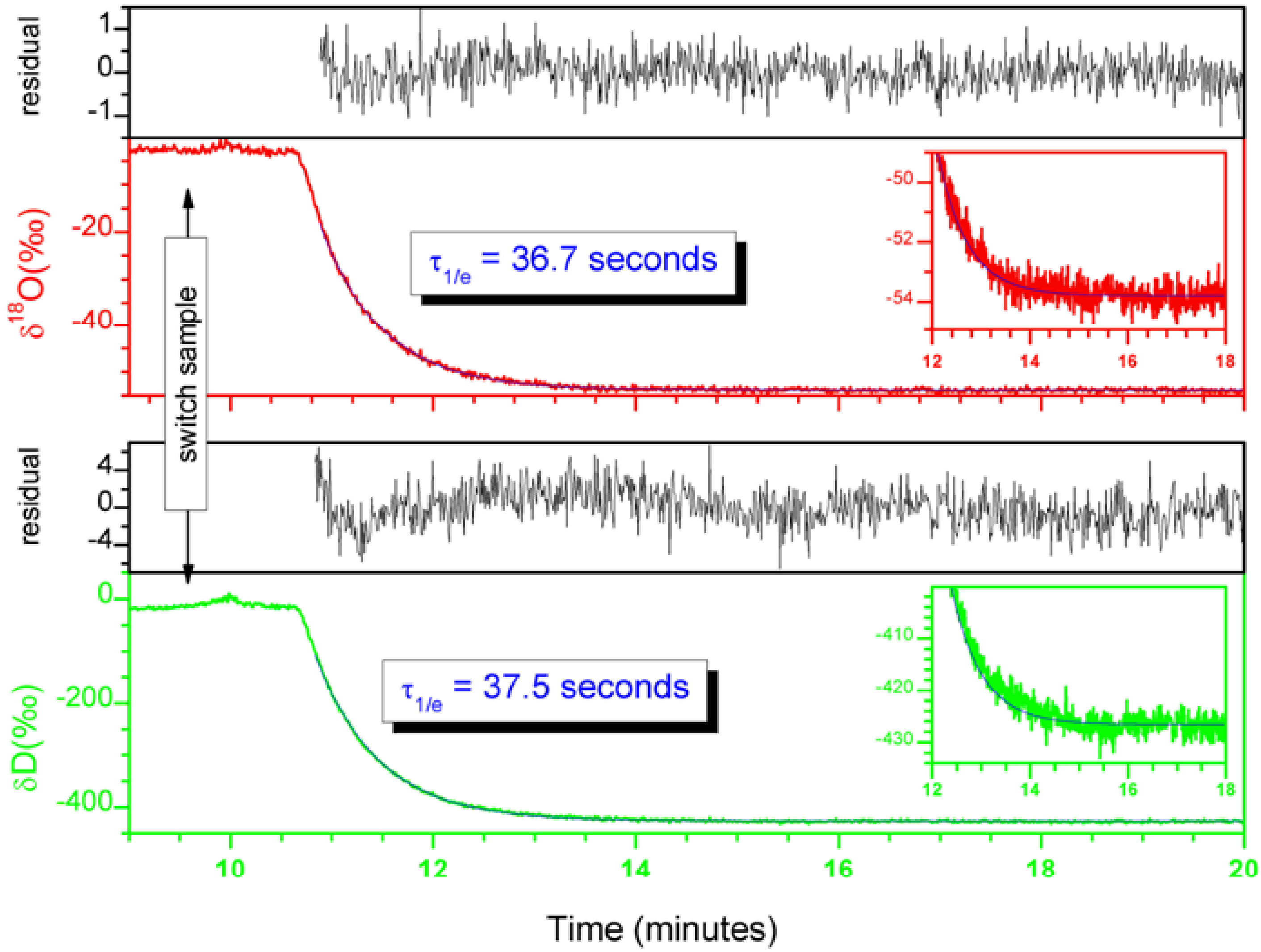
Water Vapor Isotope Flux



5 Hz Measurements → Eddy Flux Technique

Very High Frequency Measurements

Liquid Water Isotopes



Measure liquid samples every 3 minutes…

Acknowledgements

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  - Elena Berman
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  - Feng Dong
  - Brian Leen
  - Doug Baer
  - Tom Owano
  - Raymond Fellers
  - Anthony O'Keefe

- **Collaborators**
  - H.J. Andrews – Jeff McDonnell, Chris Gabrielli, and Tina Garland (OSU)
  - Sherman Island – Todd Dawson and Joe Verfaillie (UC Berkeley)
  - Mauna Loa - Joe Galewsky (UNM), Zach Sharp (UNM), David Noone (UC Boulder)

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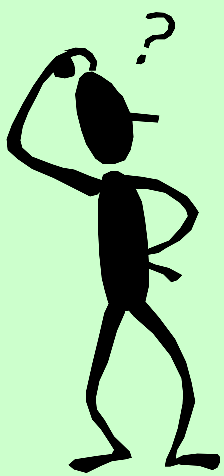
Relevant Publications/Posters

1. E. S. F. Berman, M. Gupta, C. Gabrielli, T. Garland, and J. J. McDonnell, “High-Frequency field-deployable isotope analyzer for hydrological applications,” *Water Resources Research* **45** (2009) W10201.

2. E. S. F. Berman, M. Gupta, C. Gabrielli, T. Garland, and J. J. McDonnell, “High-Frequency field-deployable isotope analyzer for hydrological applications,” *American Geophysical Union Fall Meeting* (2009) H41E-0938.

3. F. Dong, D. Baer, T. Dawson, and J. Verfaillie, “Development, Deployment, and Validation of an Isotopic Water Analyzer for High Frequency Measurements in Water Vapor and Continuous Measurements in Liquid Water,” *American Geophysical Union Fall Meeting* (2009) H41E-0947



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Thank you!