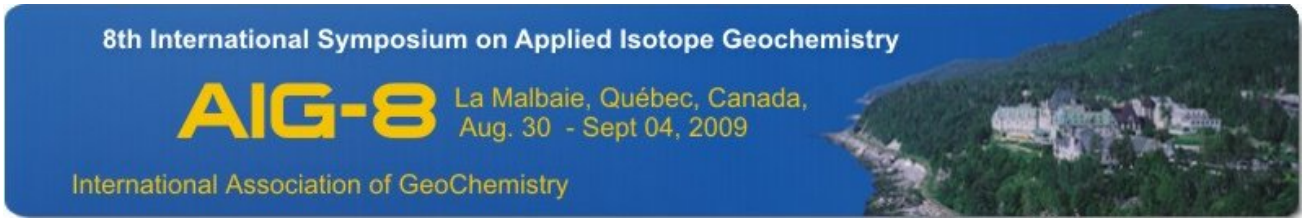


PICARRO

Isotope Measurements Transformed: Real-time, In-situ Point-of-origin Tracing with $\delta^{18}O$ and δD in Water and $\delta^{13}C$ in Complex Molecules

The World's Highest Performance and Easiest to Use Analyzers

Iain Green
Aaron Van Pelt

Picarro, Inc.

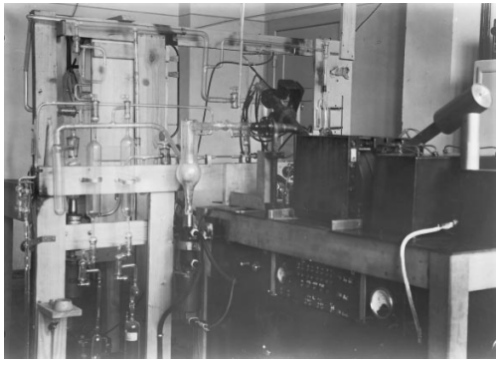
What is the evolution of a species?

10,000 BC to 2009 AD

Man: Preparing for Dinner

PICARRO

What is the evolution of a species?



1948 --- to --- Today

IRMS

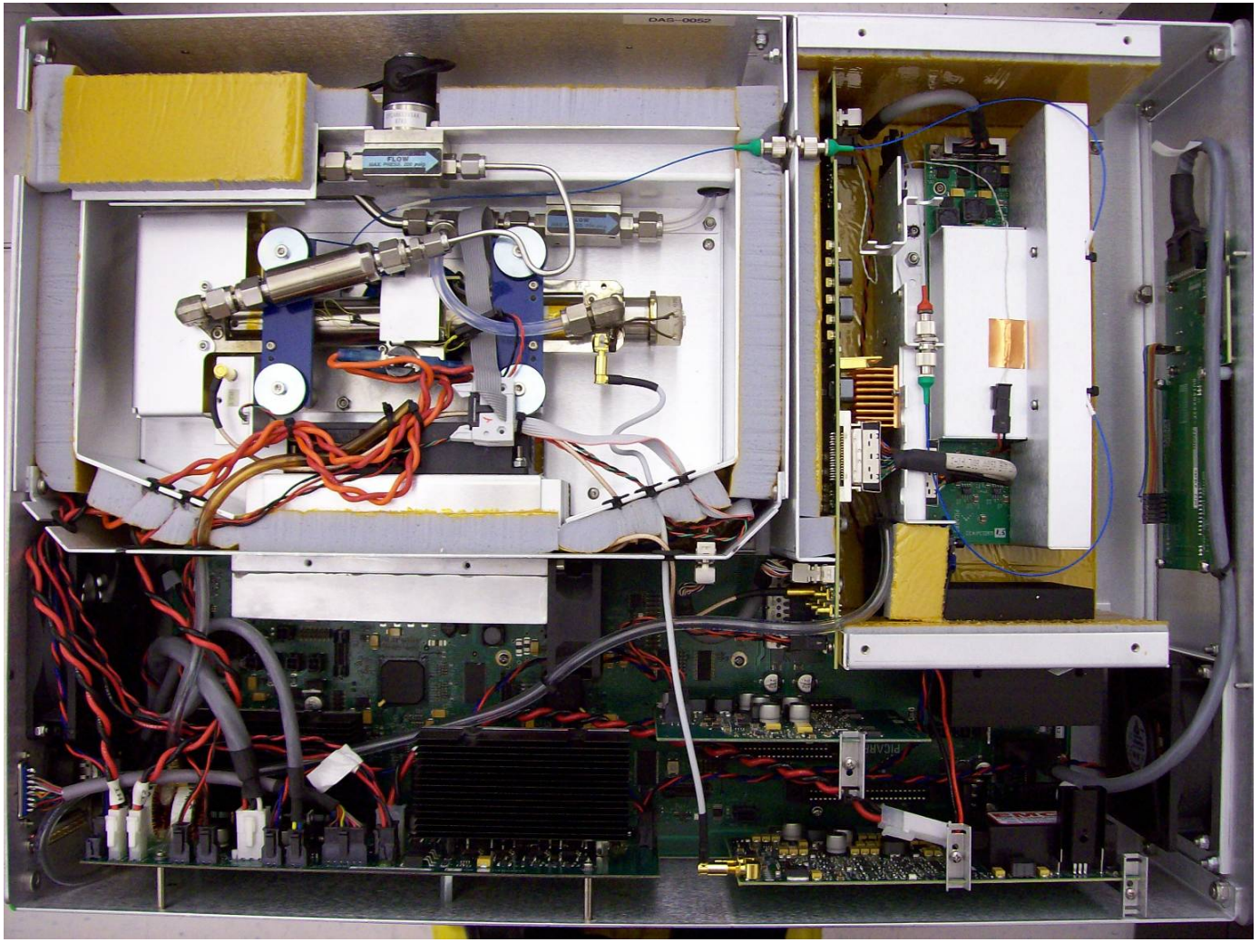
Today --- to --- Tomorrow

Optical Spectroscopy

?

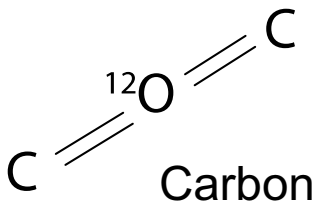
Iso CO_2 and Iso H_2O Instruments

Rugged, Compact

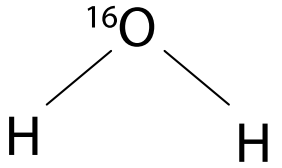


PICARRO

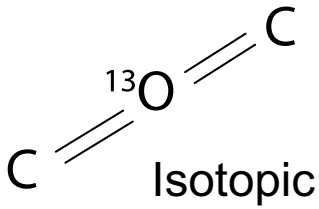
Greenhouse Gases



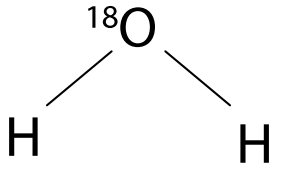
Carbon Dioxide (CO_2)



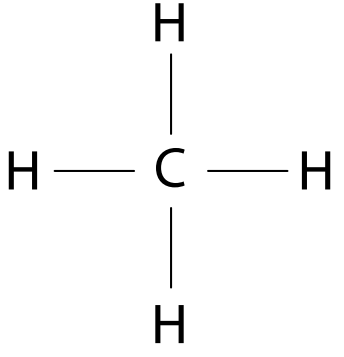
Water (H_2O)



Isotopic Carbon Dioxide ($^{13}CO_2$)



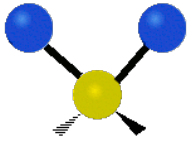
Isotopic Water ($H_2{}^{18}O$)



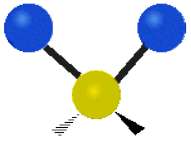
Methane (CH_4)

PICARRO

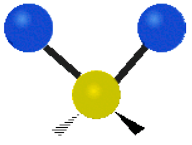
Molecules Are In Constant Motion



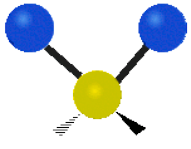
Symmetrical stretching



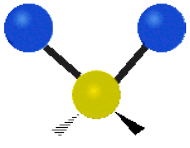
Antisymmetrical stretching



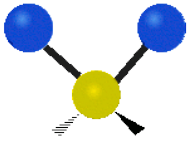
Scissoring



Rocking



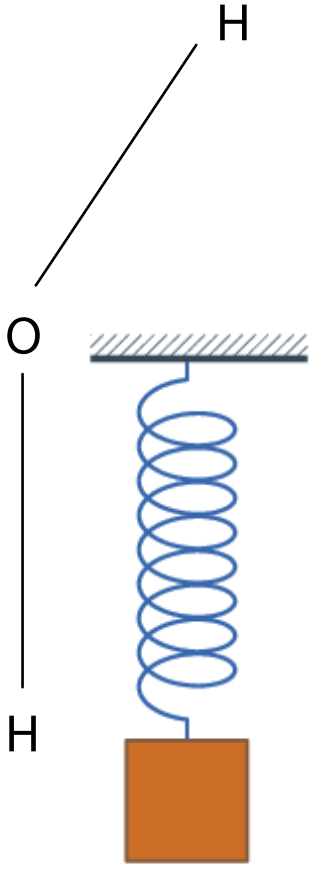
Wagging

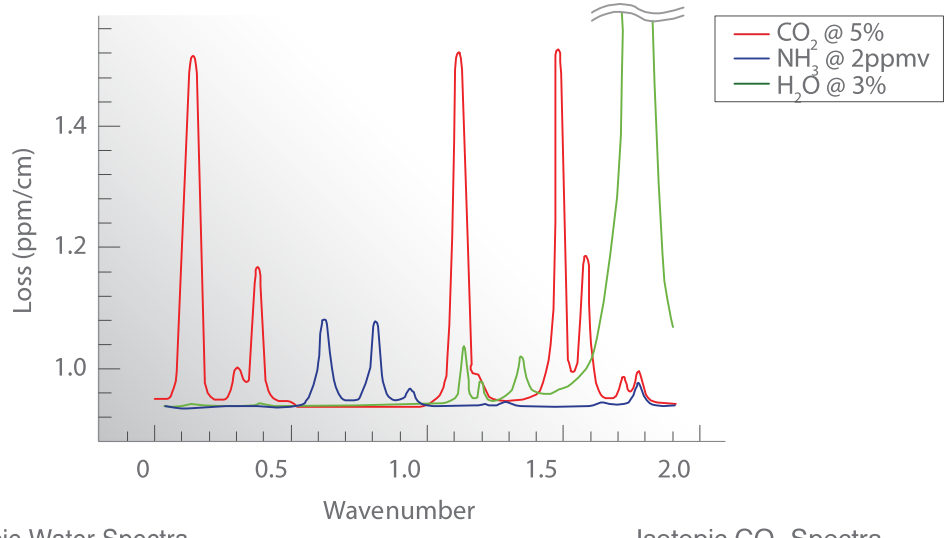


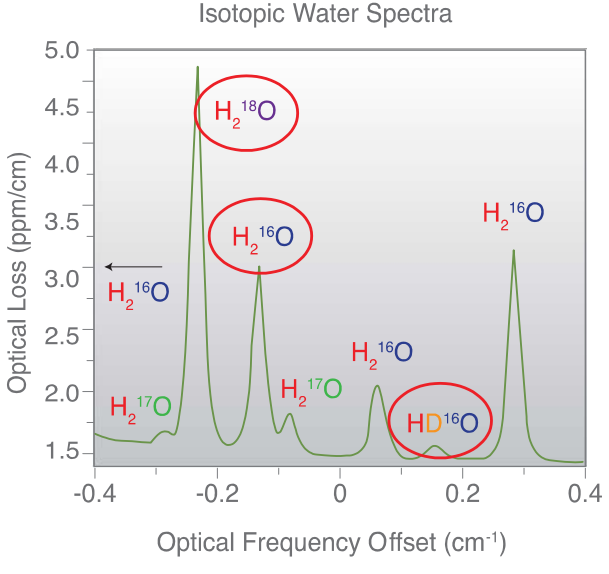
Twisting

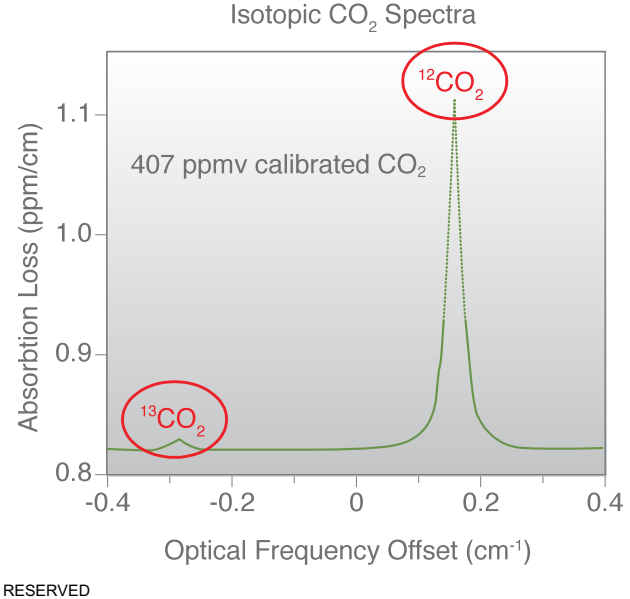
PICARRO

It's All Springs and Mirrors









PICARRO

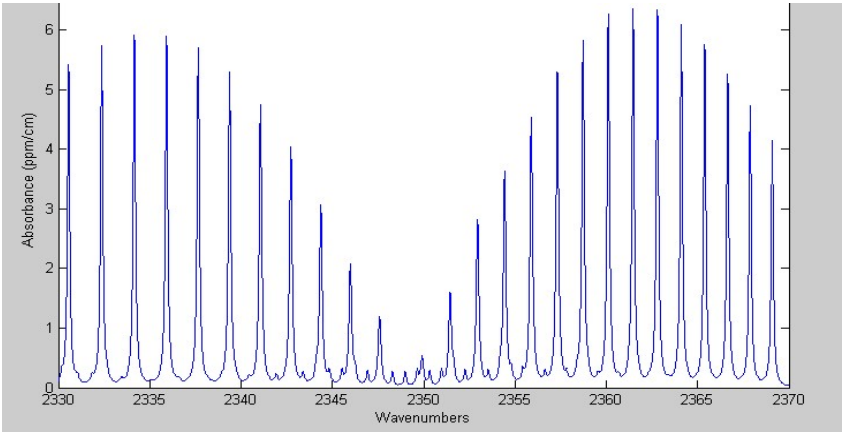
Diode Lasers Provide High Resolution

Laser sources generate very narrow spectral line-widths

- Significantly narrower than a molecule's absorption lines

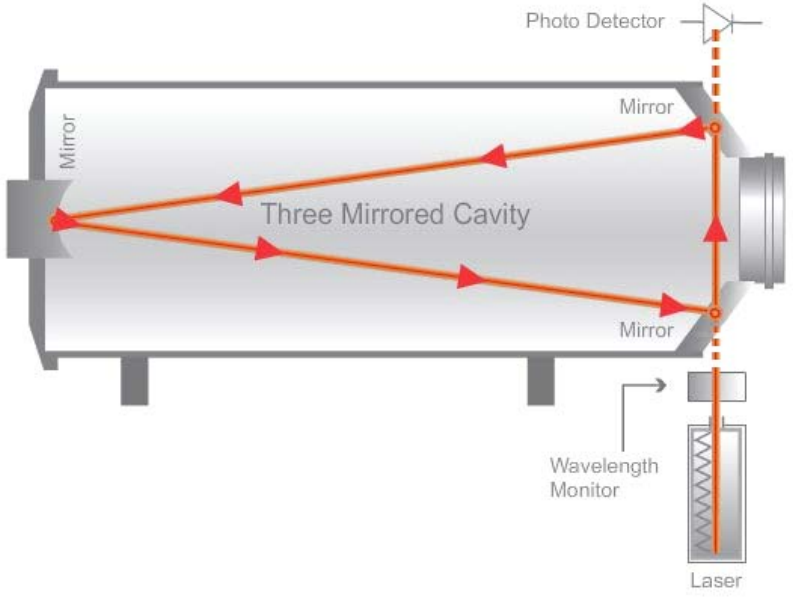
Very high resolution of closely spaced isotope lines

Complete characterization of line shapes and intensities



PICARRO

Very High Sensitivity and Precision

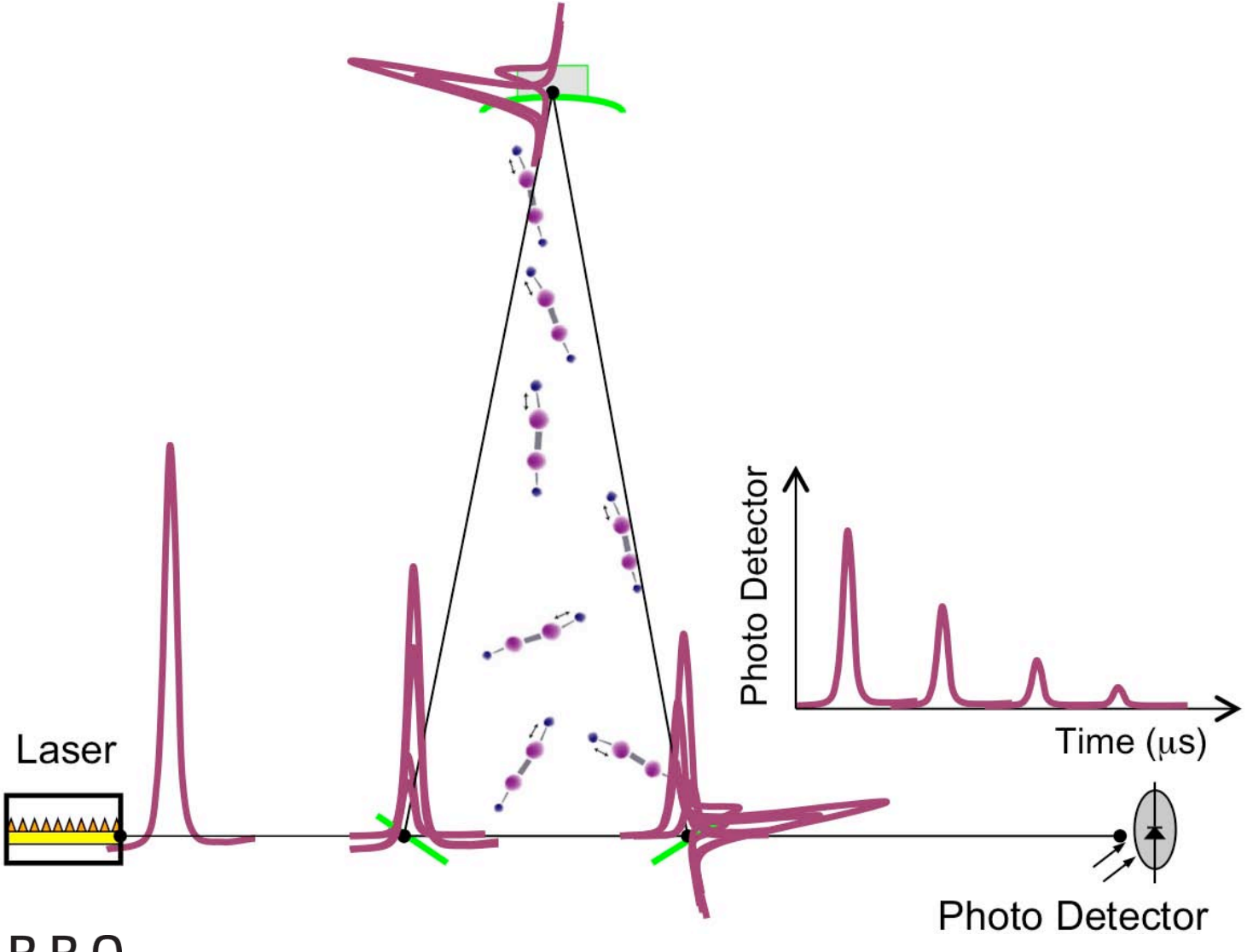


- Small, 35 cc sample cavity
- Laser intensity builds up…
- …Laser is shut off
  - Removes laser fluctuations
- Light reflects around the cavity
- **Up to 20 km pathlength**
- Cavity loss mechanisms decrease intensity each pass
- Measurement is decay rate not absolute absorbance

Time-basis and long pathlength provide high sensitivity & precision

PICARRO

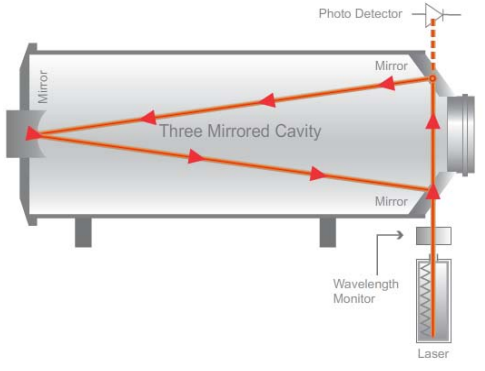
Time Based Measurement

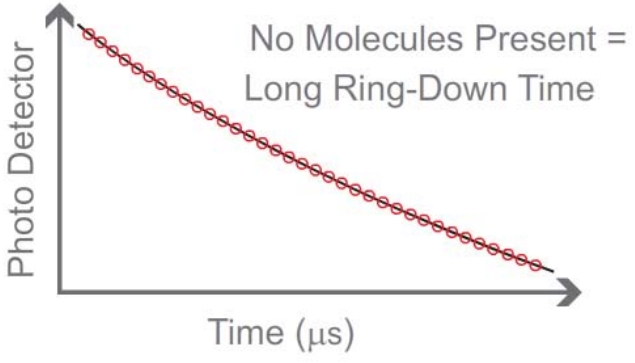


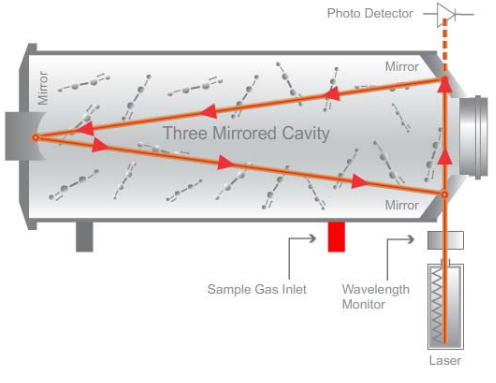
PICARRO

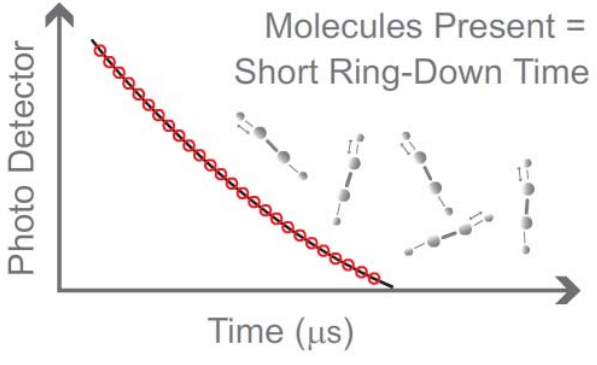
Increasing Concentration, Faster Ringdown

Absorbing species in the cavity follow Beer-Lambert Law







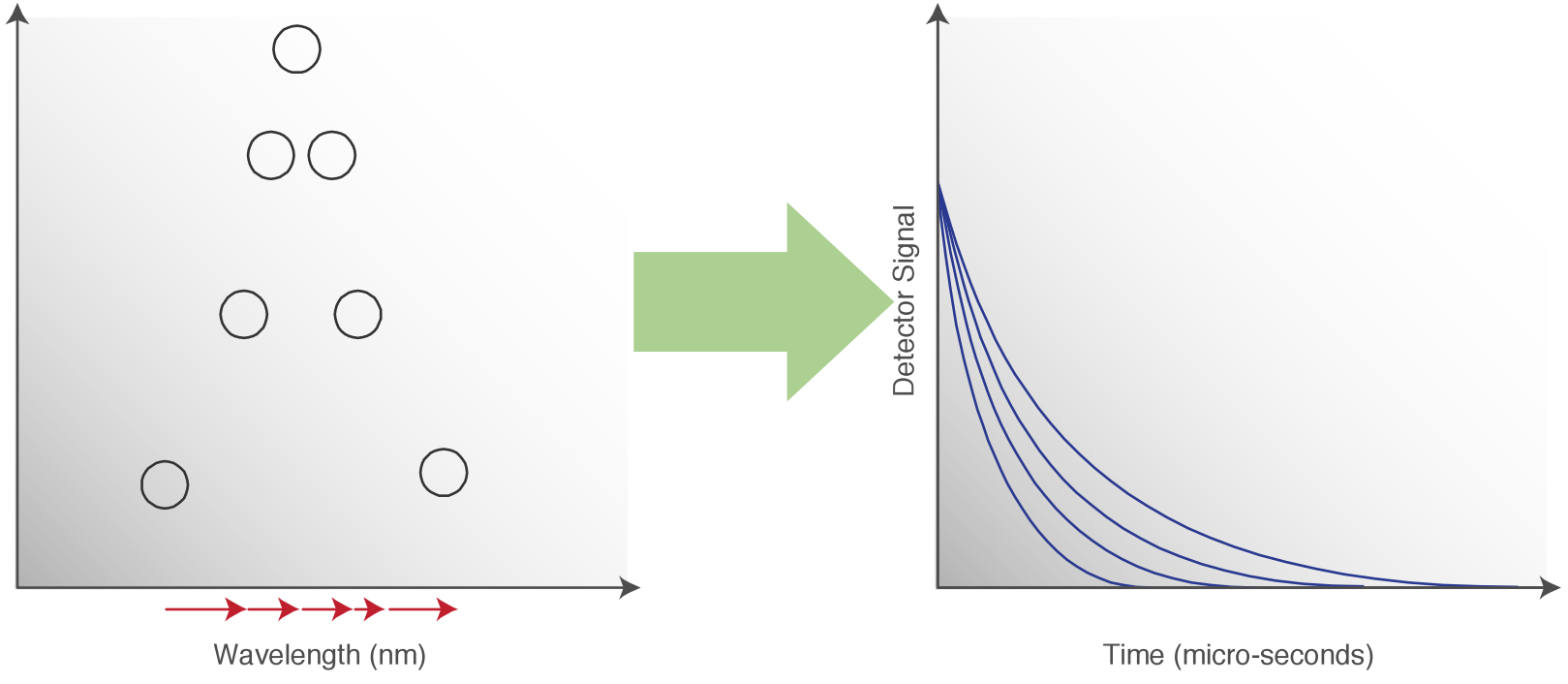


PICARRO

From Wavelength to Ringdown

Select Wavelength

Measure Ring-down

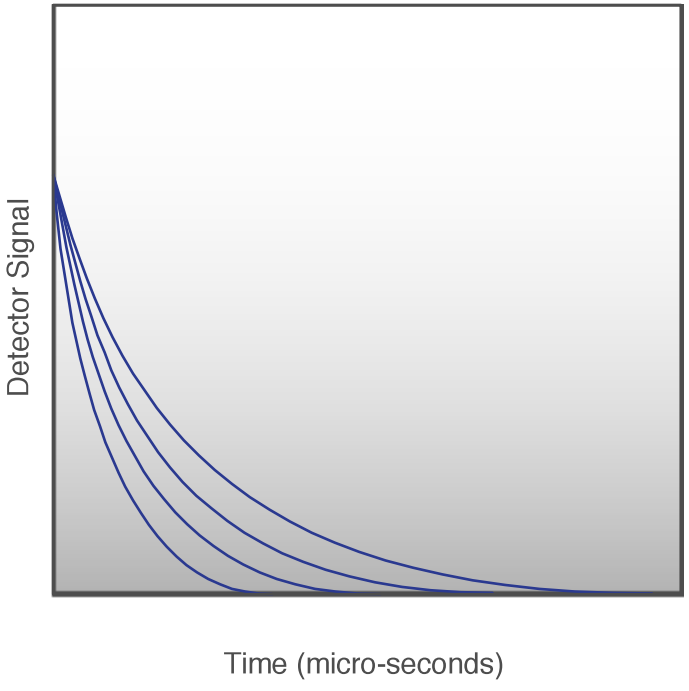


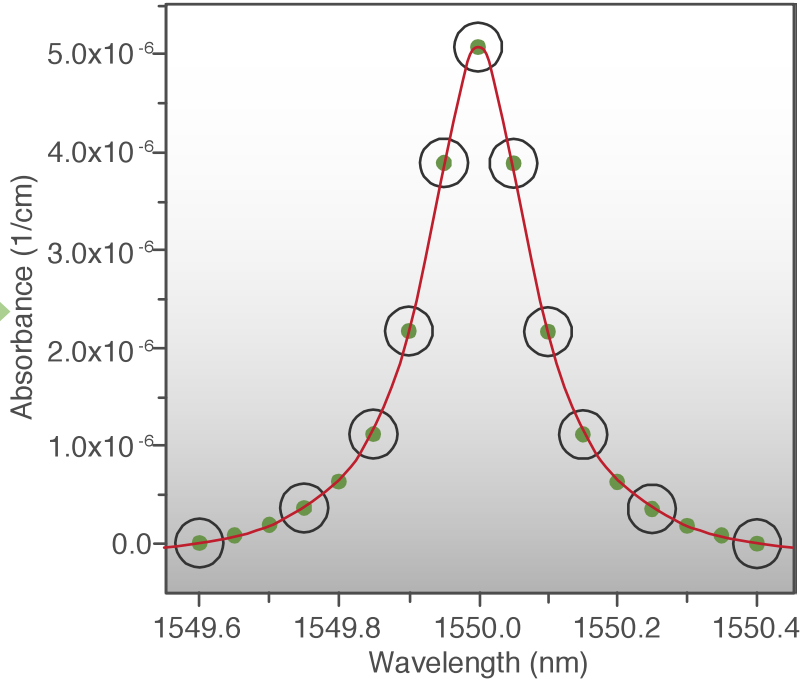
PICARRO

From Ringdown to Concentration

Ring-down

$$I_{circ}(t) = I_{circ}(t_o)\exp\left[\frac{-t}{\tau}\right]$$





PICARRO

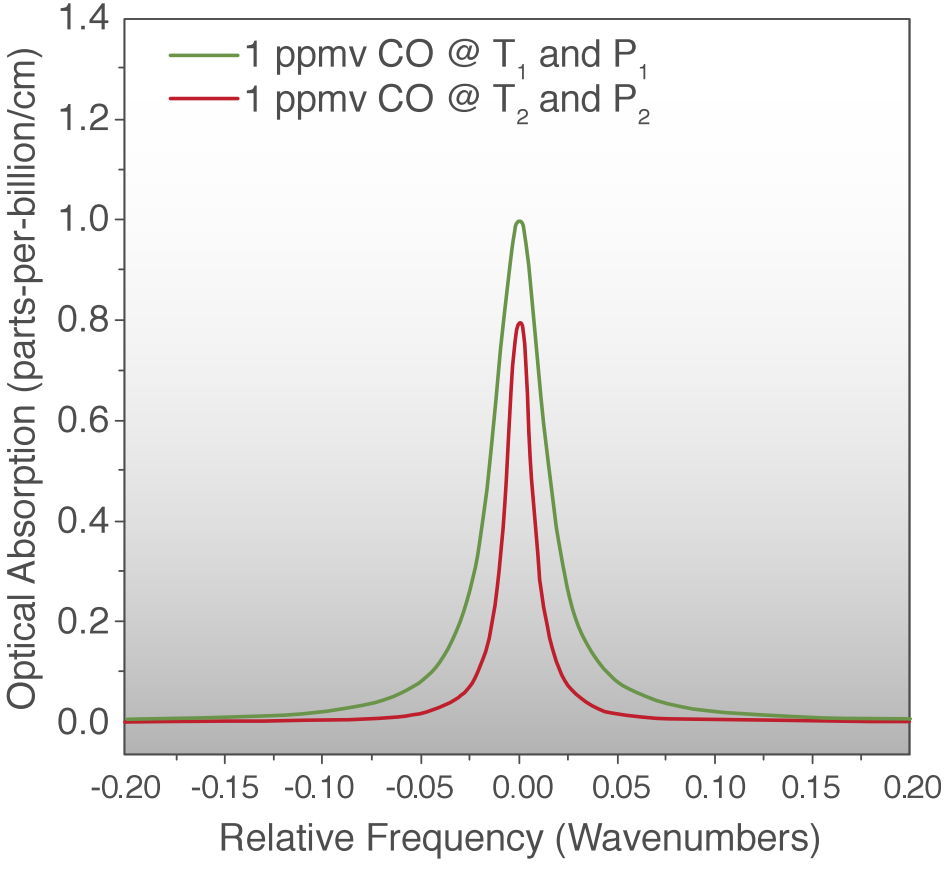
Critical to Control Temp. & Pressure

Accurate gas measurements require *stable* spectroscopic features

In a given gas matrix, only two parameters affect the lineshape

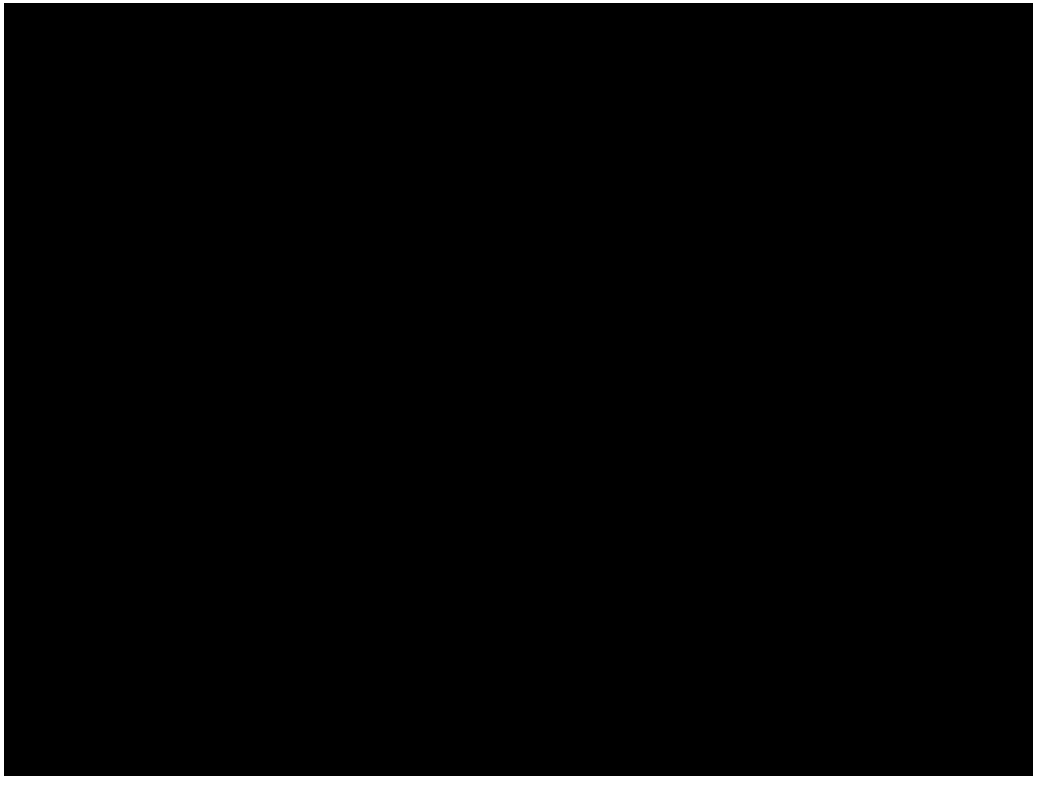
- Temperature
- Pressure

Tiny temperature and pressure instabilities means BIG concentration errors



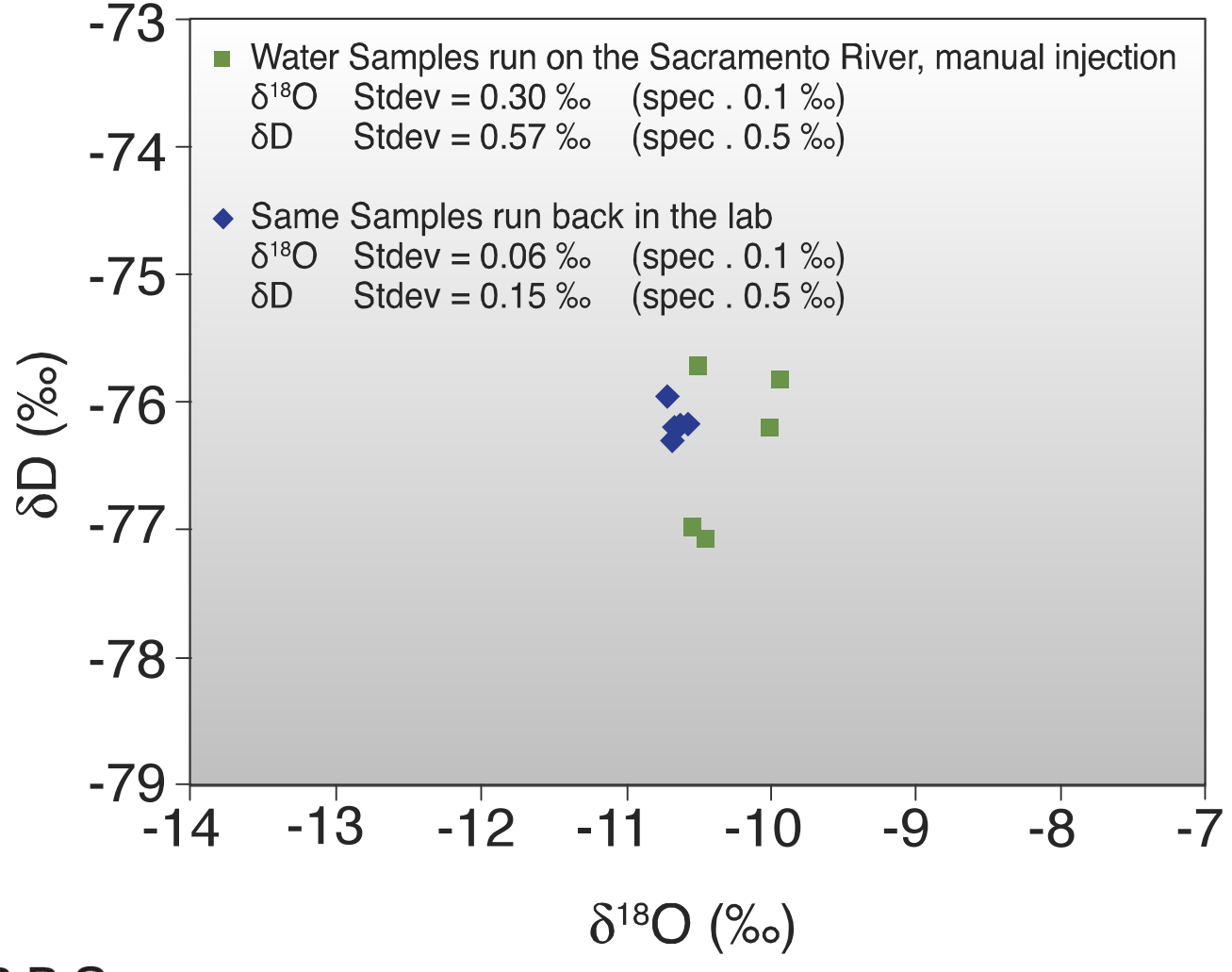
PICARRO

On The Move



PICARRO

Outstanding Data



PICARRO

Benefits of Cavity Ringdown

Low capital cost - $50K to $120K.

Low cost of ownership- $100 to $1000/year.

Small Size – as small as 17” x 8” x 23”.

Low power consumption – 100W to 400W

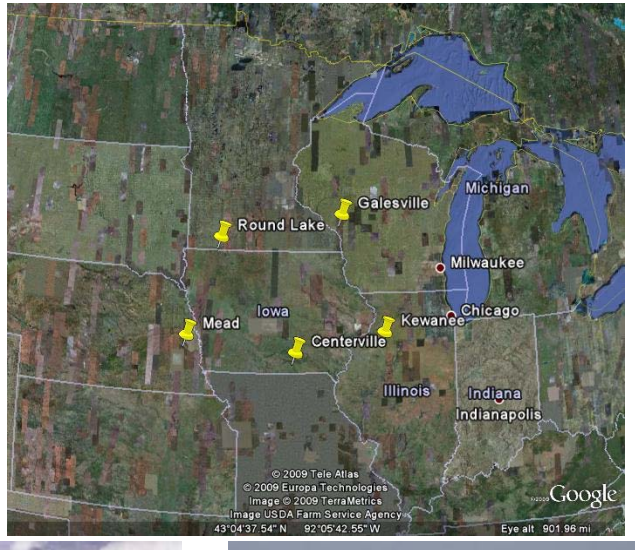
No high vacuum pumps.

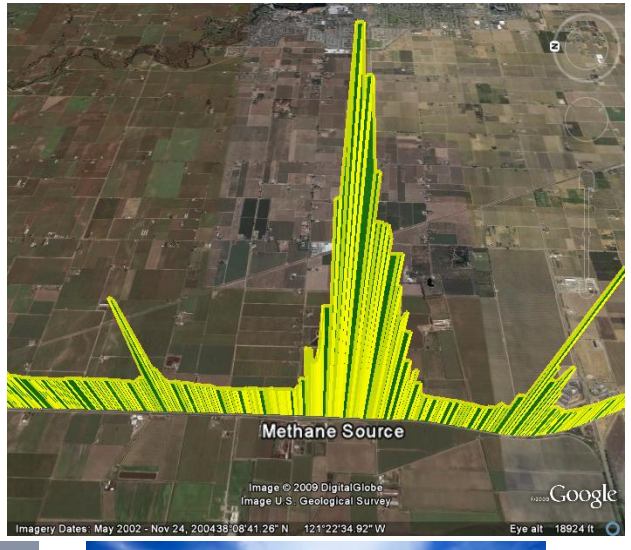
Very rugged.

Easy to Use.

Measurements All Over the World

- Global Scale
- Large Nations
- Regional Scale
- States & Small Nations
- Local Scale
- Point Sources & Sinks





PICARRO

Over 200 Systems in 32 Countries

PICARRO

PICARRO

$\delta^{18}O$ and δD in Water

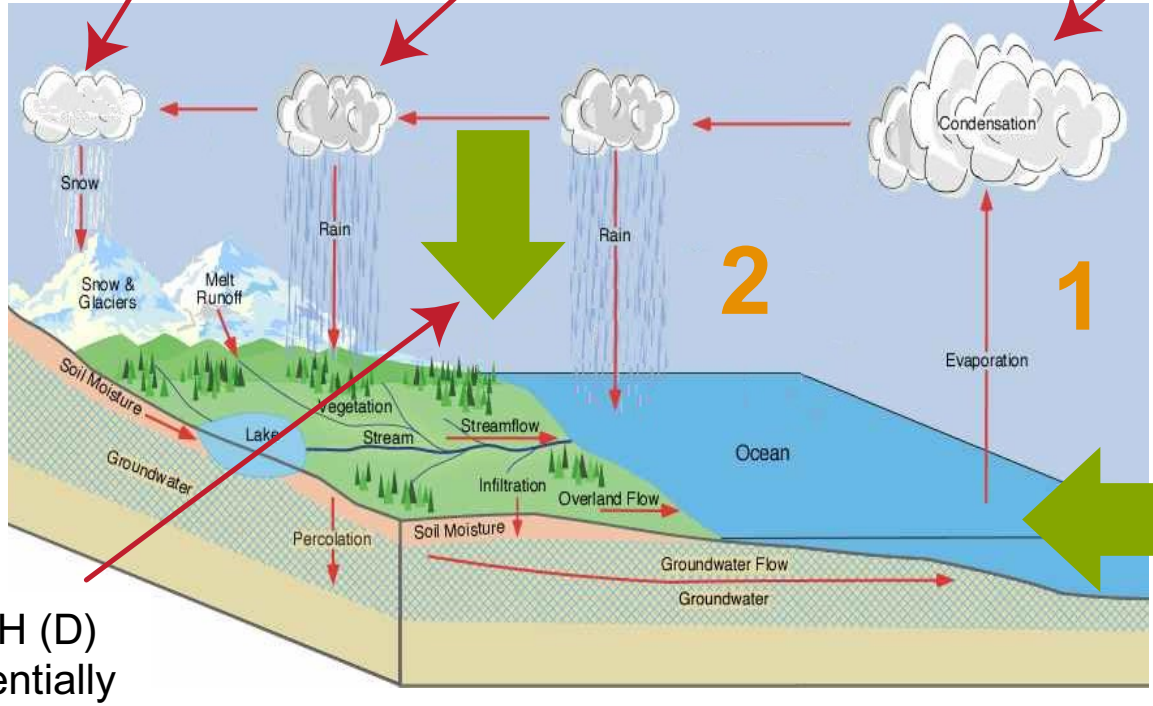
The World's Highest Performance and Easiest to Use Analyzers

Stable Isotopes in the Water Cycle

Even more enriched in light isotopes

More enriched in light isotopes

Enriched in light isotopes



^{16}O, ^{1}H preferentially vaporize

$H_2{}^{18}O$

$H_2{}^{16}O$ $H^{16}OD$

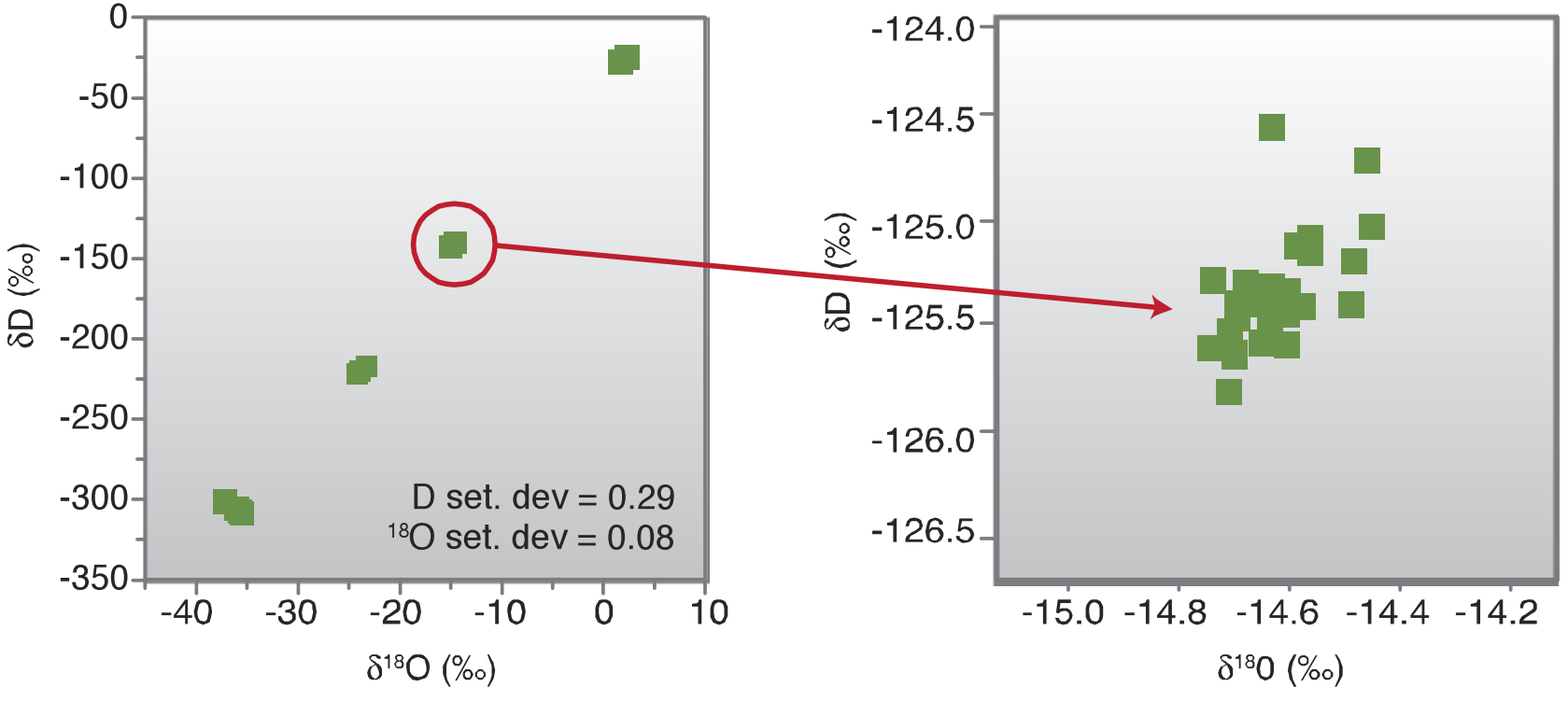
$D_2{}^{16}O$ $H^{18}OD$

^{18}O, ^{2}H (D) preferentially condense

PICARRO

Excellent Precision

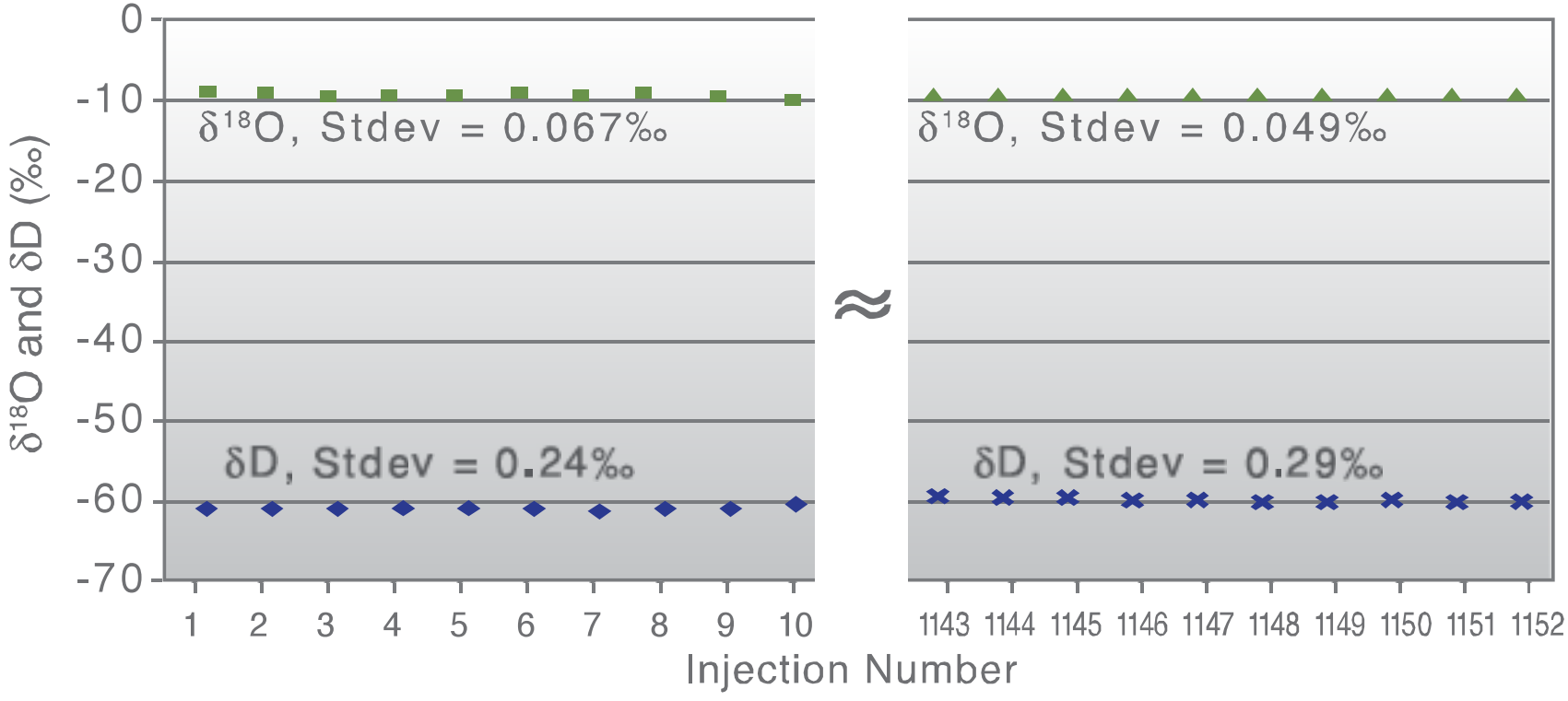
4 separate groundwater samples



PICARRO

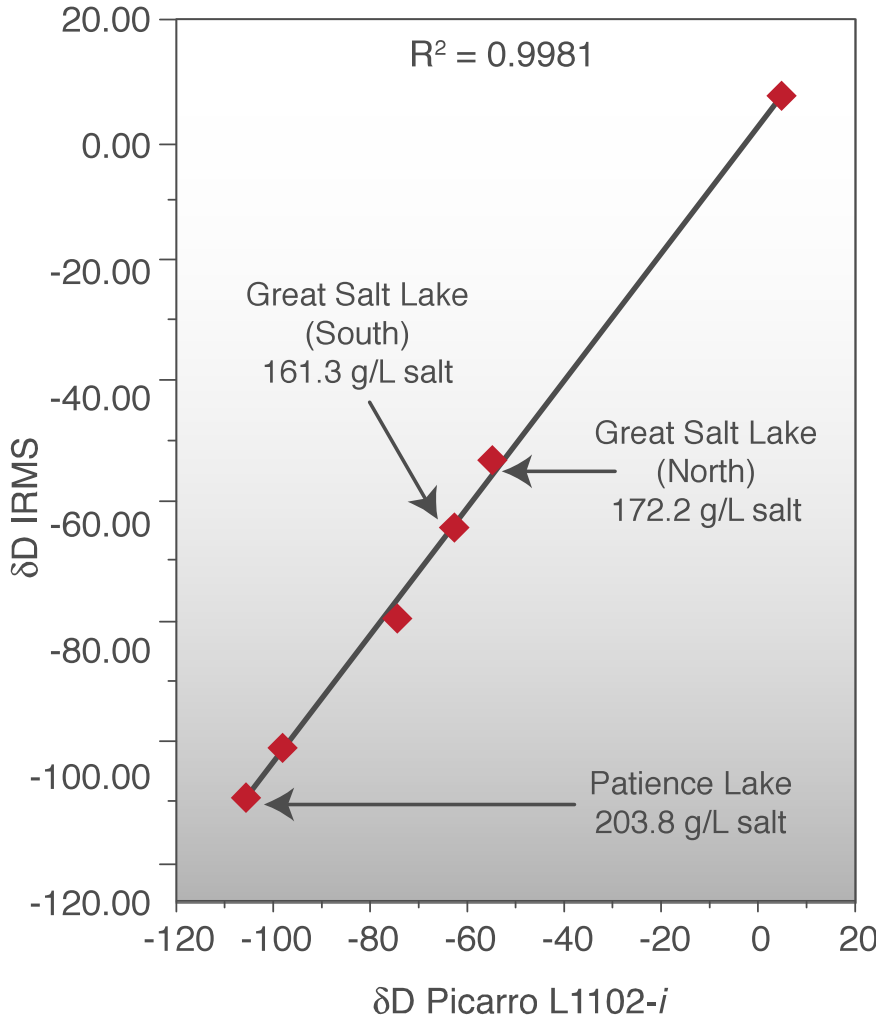
$\delta^{18}O$ and δD in Briny Samples

4% (by weight) of table salt was added to bottled water which has a characteristics of δD = -61.8 ‰, $\delta^{18}O$ = -9.6 ‰.



PICARRO

Excellent Data in Extreme Salt



Excellent comparison between Picarro L1102-*i* and IRMS data

6 samples from inland salt lakes – USA, Canada and Africa

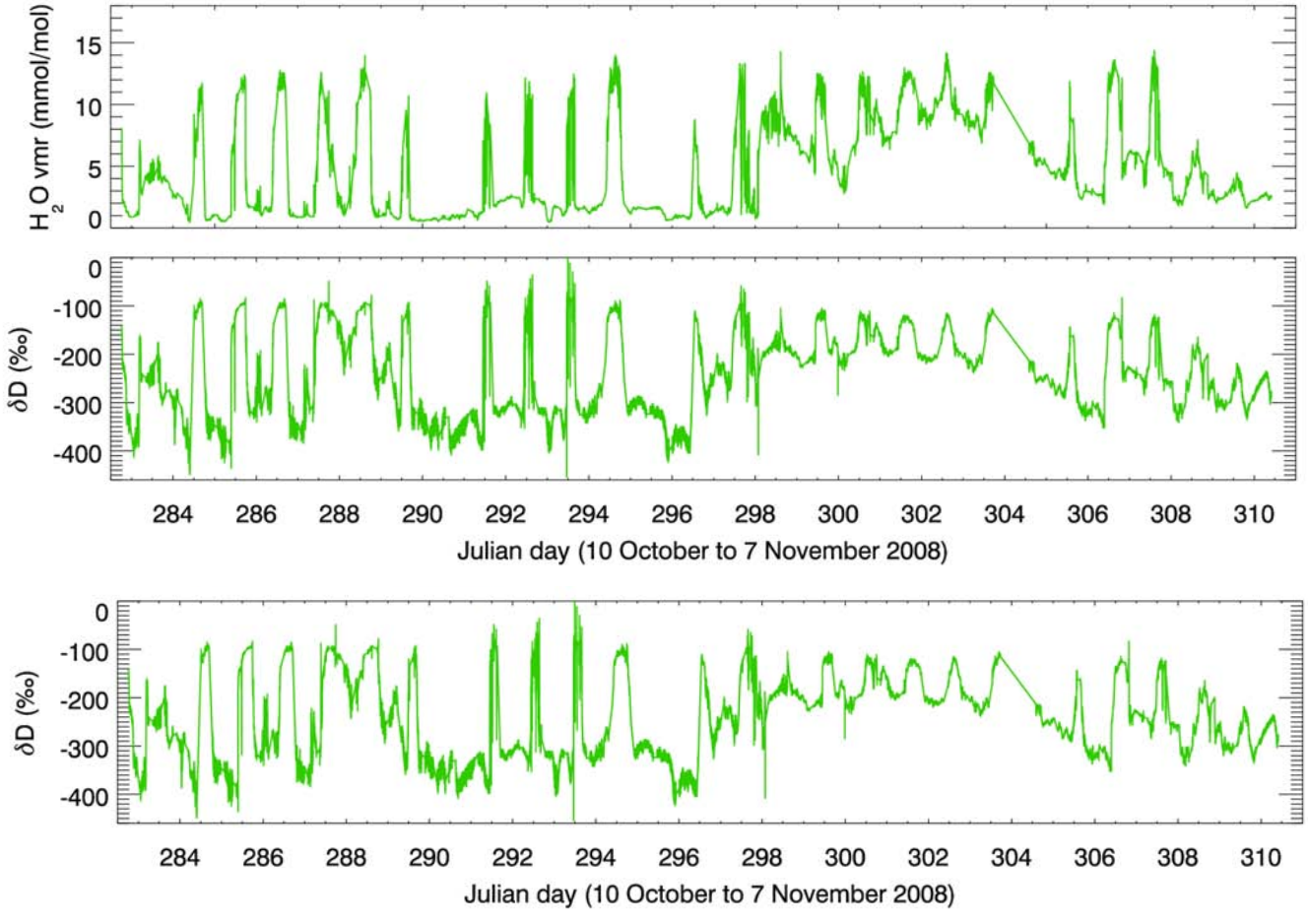
PICARRO

Picarro: On Mauna Loa, HI

David Noone with Picarro liquid/vapor isotopic water analyzer

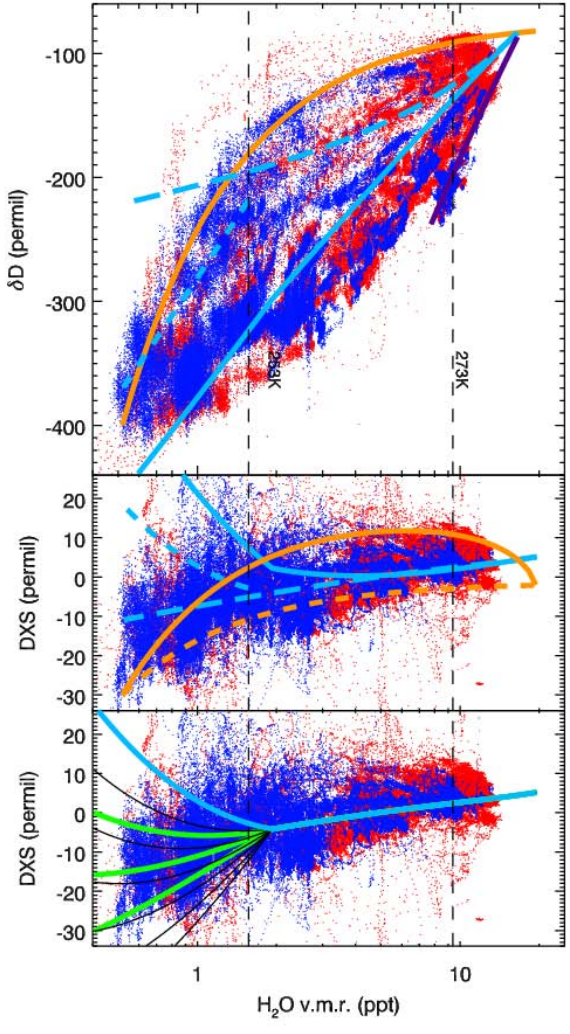
PICARRO

Mauna Loa Data



PICARRO

Mauna Loa Deuterium Excess

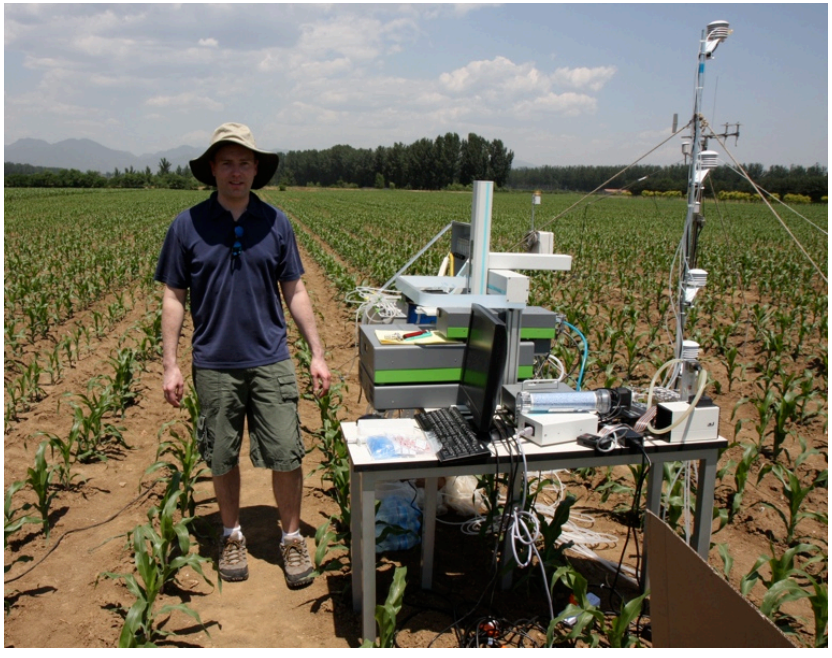


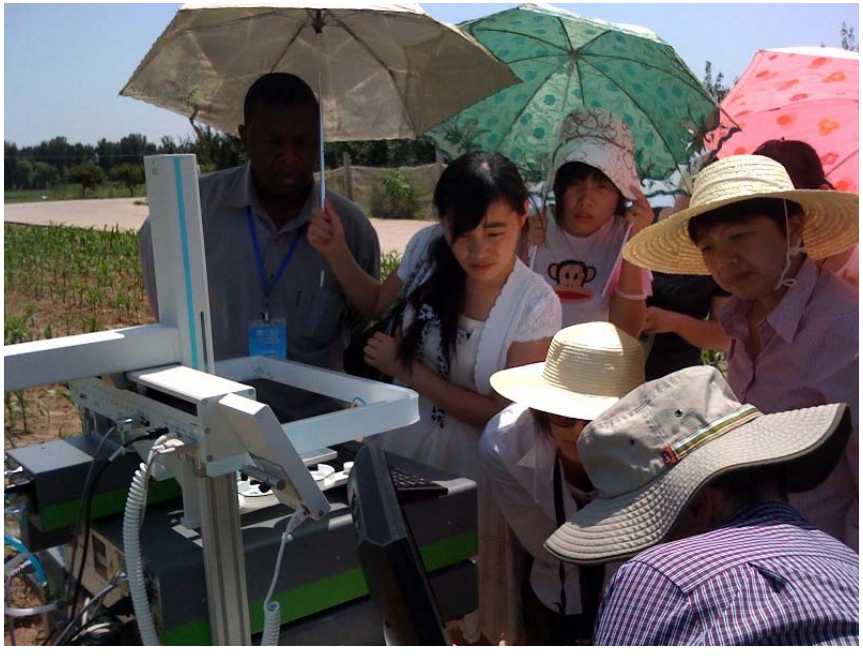
Deuterium excess - the deviation of a sample from the meteoric water line (GMWL)

- An indicator of the complexity of the air circulation
- Non equilibrium (fast) evaporation

PICARRO

Picarro: In a Corn Field Near Beijing





Picarro at FAO/IAEA Field Campaign Beijing, China

PICARRO

Food Authenticity

Fighting food fraud with science

Does your extra virgin olive oil come from a Tuscan grove? Is your cappuccino made from the finest Arabica beans? Bea Perks meets some of the scientists subjecting our food's credentials to forensic examination

A $50 Billion problem

- Wine
- Coffee
- Olive oil
- Milk

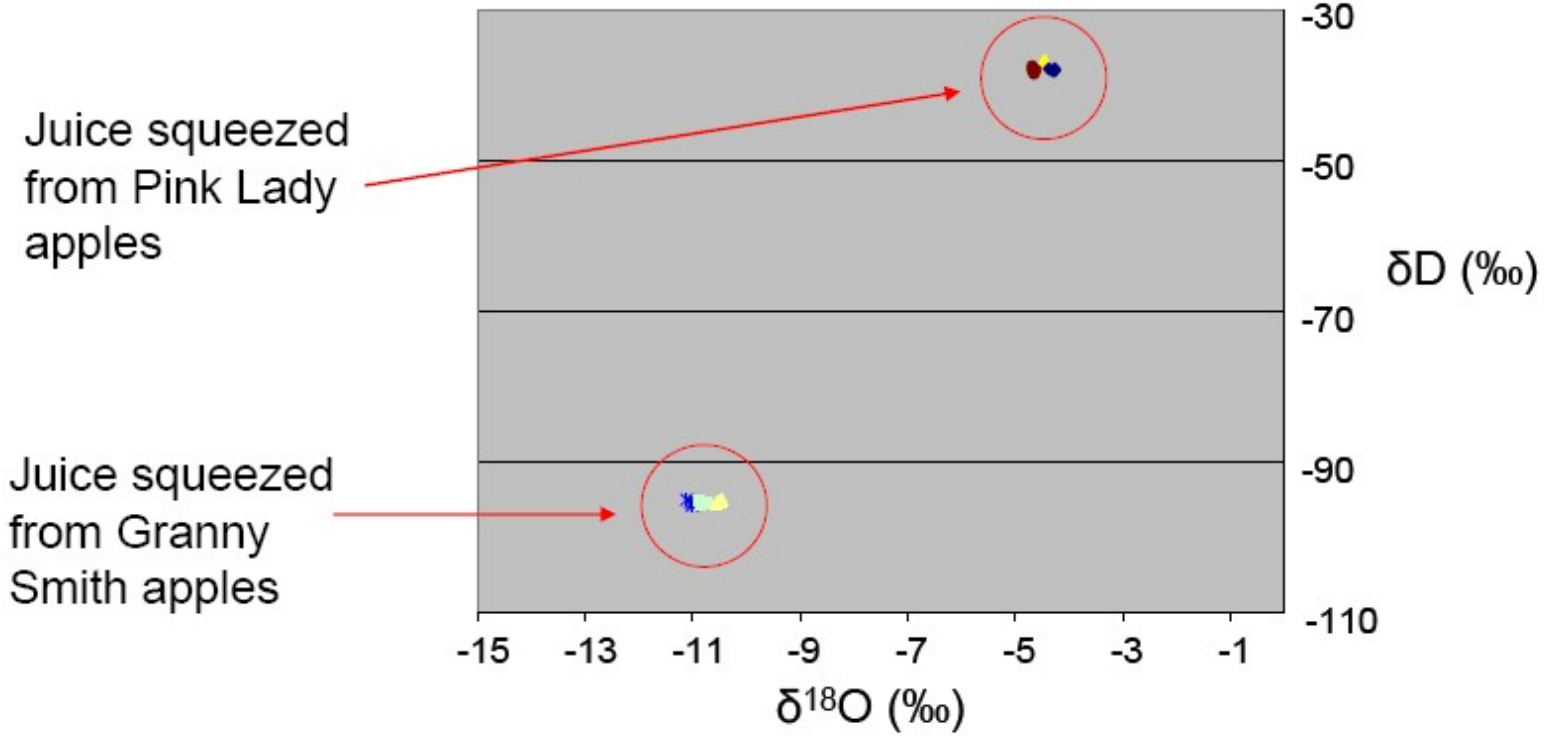
Using costly equipment and methods

- IRMS ($350,000)
- NMR ($300,000)

PICARRO

$\delta^{18}O$ and δD for Commercial Apples

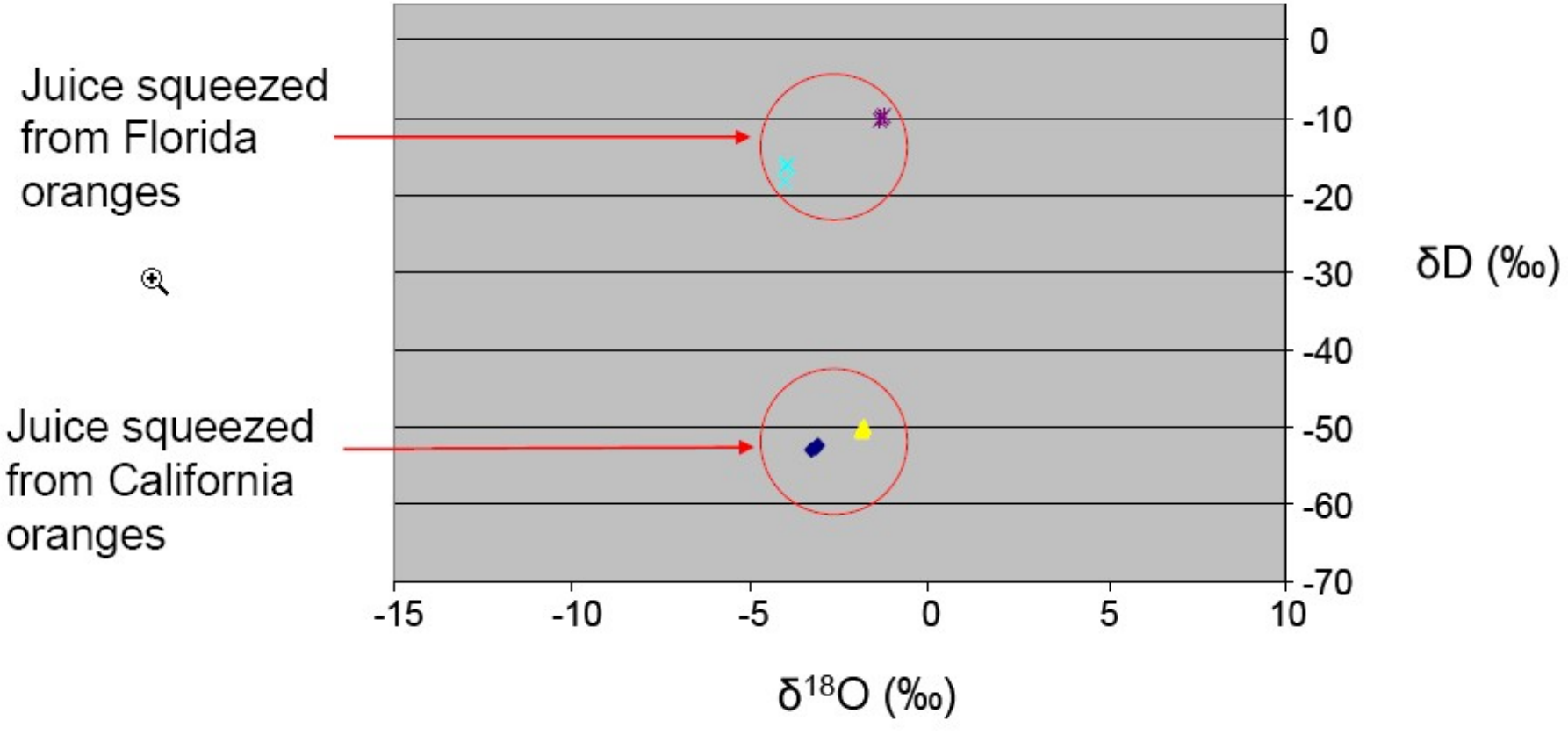
A quick screening method of using stable isotopes to distinguish the true origin and/or composition of natural food and beverage products



PICARRO

$\delta^{18}O$ and δD for Commercial Oranges

Juice was extracted from each fruit by peeling the fruit and then grinding the remaining flesh in a plastic cup.

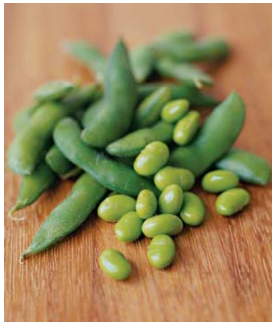


PICARRO

$\delta^{13}C$ Analysis Edible Oil Samples using *i*TOC-CRDS

The World's Highest Performance and Easiest to Use Analyzers

Isotopic Signature Variation, $\delta^{13}C$



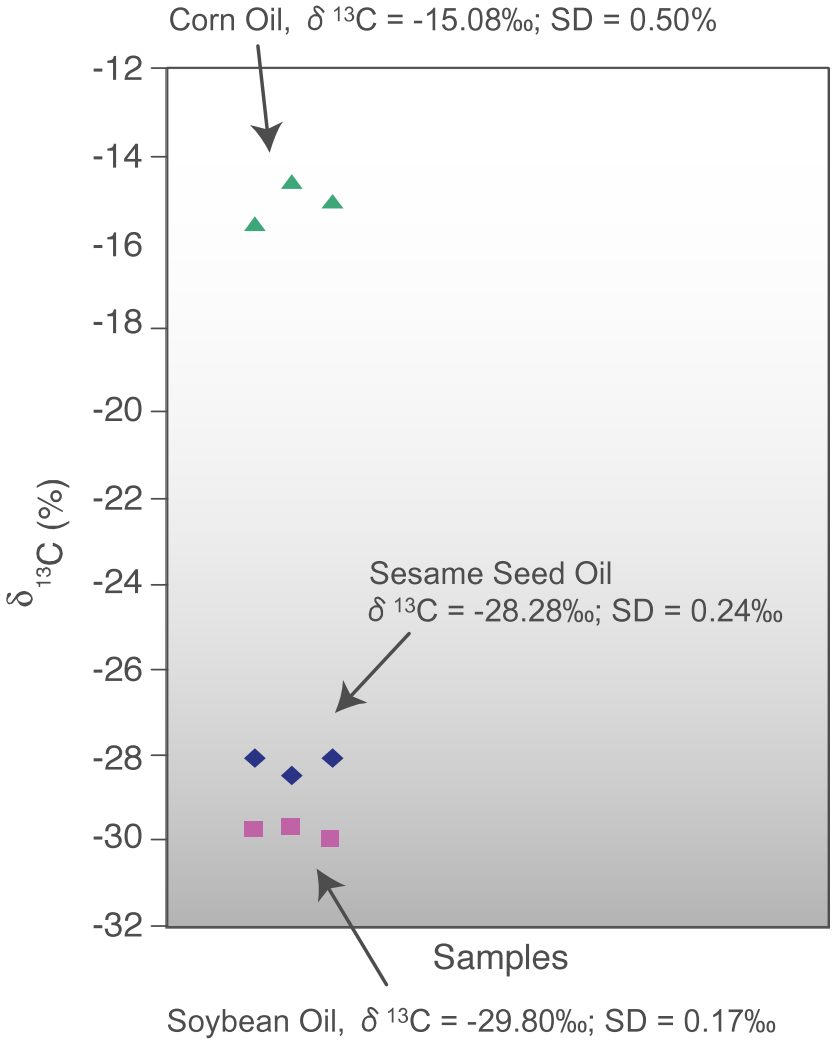
- $\delta^{13}C$ values of plant compounds are mainly influenced by the botanical origin of the plant
  - C3 plants - soy, sesame
    - Cooler, wetter
  - C4 plants - corn, sugarcane
    - Hotter, drier
- Climatic parameters can also affect $\delta^{13}C$ values
  - In particular, water stress

PICARRO

*i*TOC-CRDS: Transformational Technology

- OI Analytical's proven oxidation technology
- Picarro's acclaimed WS-CRDS
- Isotopic carbon analysis that is:
  - High precision
  - Small
  - Easy-to-use
  - Affordable

Edible Oils, 2 µl Samples



Excellent data!

Correlates well with published IRMS data:

- Same precision and accuracy

PICARRO

^{13}C Characterization of Olive Oil Origin

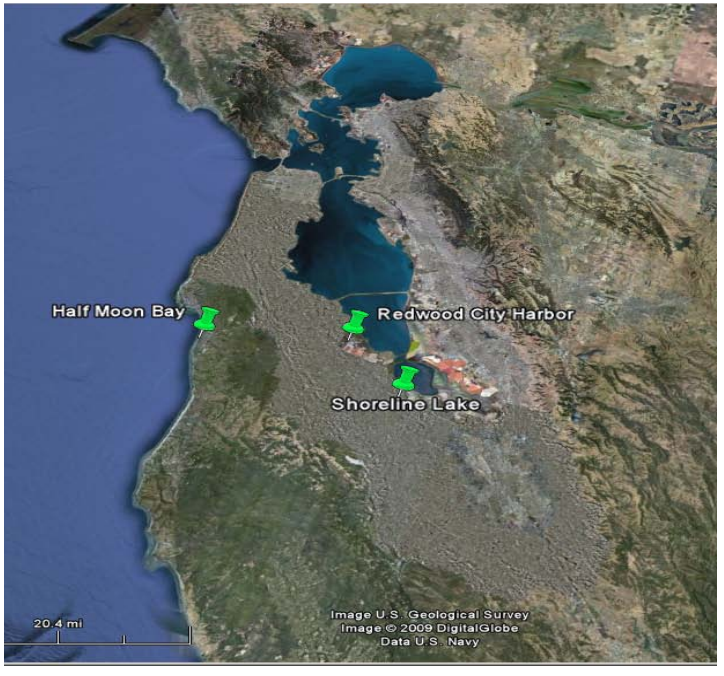
2µl Inj. Vol.	PICARRO $\delta^{13}C$ (‰)	S.D. (‰) (n=3)	IRMS $\delta^{13}C$ (‰)
Spain	-28.95	0.18	-28.94
Italy	-28.98	0.05	-29.27
Greece	-29.29	0.02	-29.21
Turkey	-30.34	0.11	-30.32
Lebanon	-29.11	0.23	-28.87
Australia	-31.23	0.01	-31.19

PICARRO

$\delta^{13}C$, Dissolved Inorganic Carbon (DIC)

Water samples collected from three San Francisco Bay Area locations :

1. Half Moon Bay (Ocean)
2. Redwood City Harbor (Bay)
3. Shoreline Lake, Mountain View (Brackish)



PICARRO

DIC Analysis

	Picarro $\delta^{13}C$ (‰)	S.D. (n=5) (‰)
Half Moon Bay Ocean Water	-1.89‰	0.24 ‰
Redwood City Harbor Bay Water	-5.58‰	0.28‰
Shoreline Lake Brackish water	-9.43‰	0.11 ‰

10% phosphoric acid added to sample

CO_2 liberated w/ N_2

$\delta^{13}C$ and CO_2 conc.

PICARRO

Watershed DIC/DOC Measurements

Stream water samples were collected from three different watersheds in SF Bay Area:

1. East Laurel Creek: feeds into the Seal Creek watershed (San Mateo Hills)
2. San Francisquito Creek: part of the San Francisquito watershed (El Corte Madera range)
3. Coyote Creek: main river of the Coyote Creek watershed (Diablo range)

PICARRO

Excellent Precision

Stream	DIC, ppm	DIC, $\delta^{13}C$, ‰	DOC, ppm	DOC, $\delta^{13}C$, ‰
E. Laurel Creek	33.7 ± 0.3	-1.8 ± 0.3	10.72 ± 0.09	-21.1 ± 0.9
San Francisquito Creek	46.1 ± 0.5	-0.8 ± 0.4	10.11 ± 0.05	-18.0 ± 0.8
Coyote Creek	93.1 ± 0.2	-1.8 ± 0.5	16.3 ± 0.3	-17.3 ± 0.6

Samples were analyzed without further prep.

4ml of water aliquot dispensed in Exetainer tubes

1ml of 5% (w/v) H_3PO_4 was added for DIC analysis

2ml of 10% $Na_2S_2O_8$ at 98°C for DOC analysis

Each sample was analyzed in six replicates

PICARRO

Thank You

Questions?

igreen@picarro.com

1 (408) 962 3942