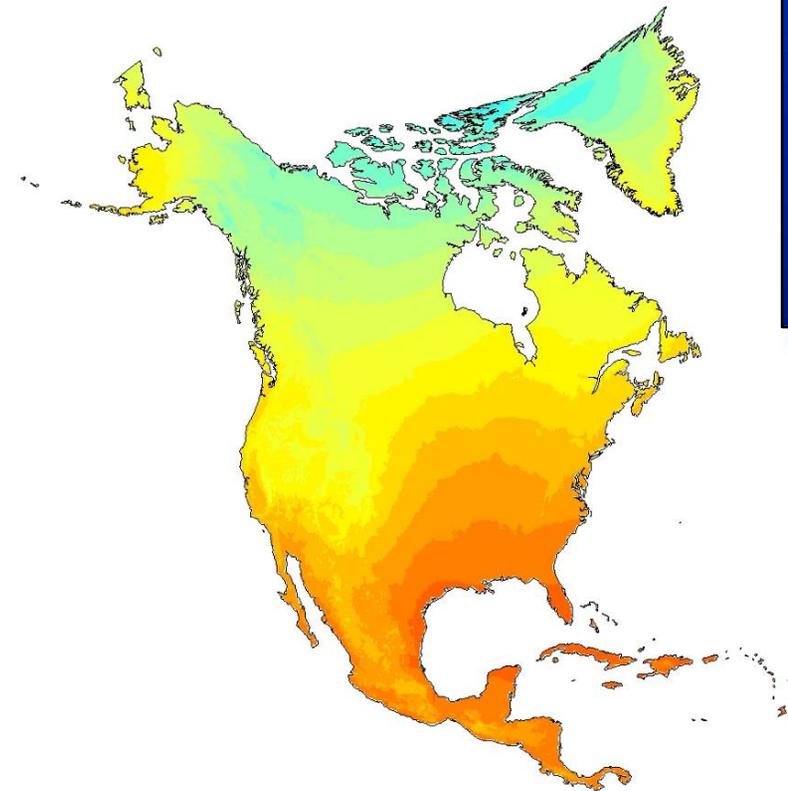
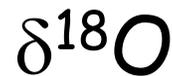


# Stable isotopes and water

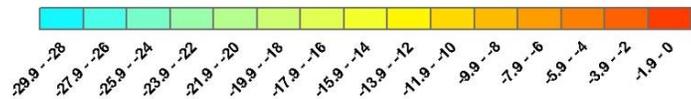
Todd Dawson  
University of California - Berkeley



IsoCamp 2016  
[21 years old - now we're legal]



$\delta^{18}\text{O}$  of Annual Precipitation



## Roadmap for today:



Look at our **BLUE PLANET** and some key PATTERNS of H and O isotope variation in meteoric waters that then end up in soils, the sub-surface, and organisms (+ I'll put a climatic and then ecological context on what we discuss)

Link some of the PROCESSES that help us understand why we see the patterns we see

Examine some data on H and O variation in "source" waters (soil, ground, etc.) used by plants and animals linking these to their "ecology" and "physiology" (**Dave Williams** will extend this to ecosystems)

Look at how H and O isotopic variation informs our work via a few case studies in plant ecology that lead to research with tree-ring's (**John Roden**), biomarkers (**Kate Freeman**) and in Oceans (**Howie Spero**)

# Where did Planet Earth's Water come from?



## Possible Sources:

✓ **Planetary Cooling** (but; pressure and out-gassing do not permit this option)

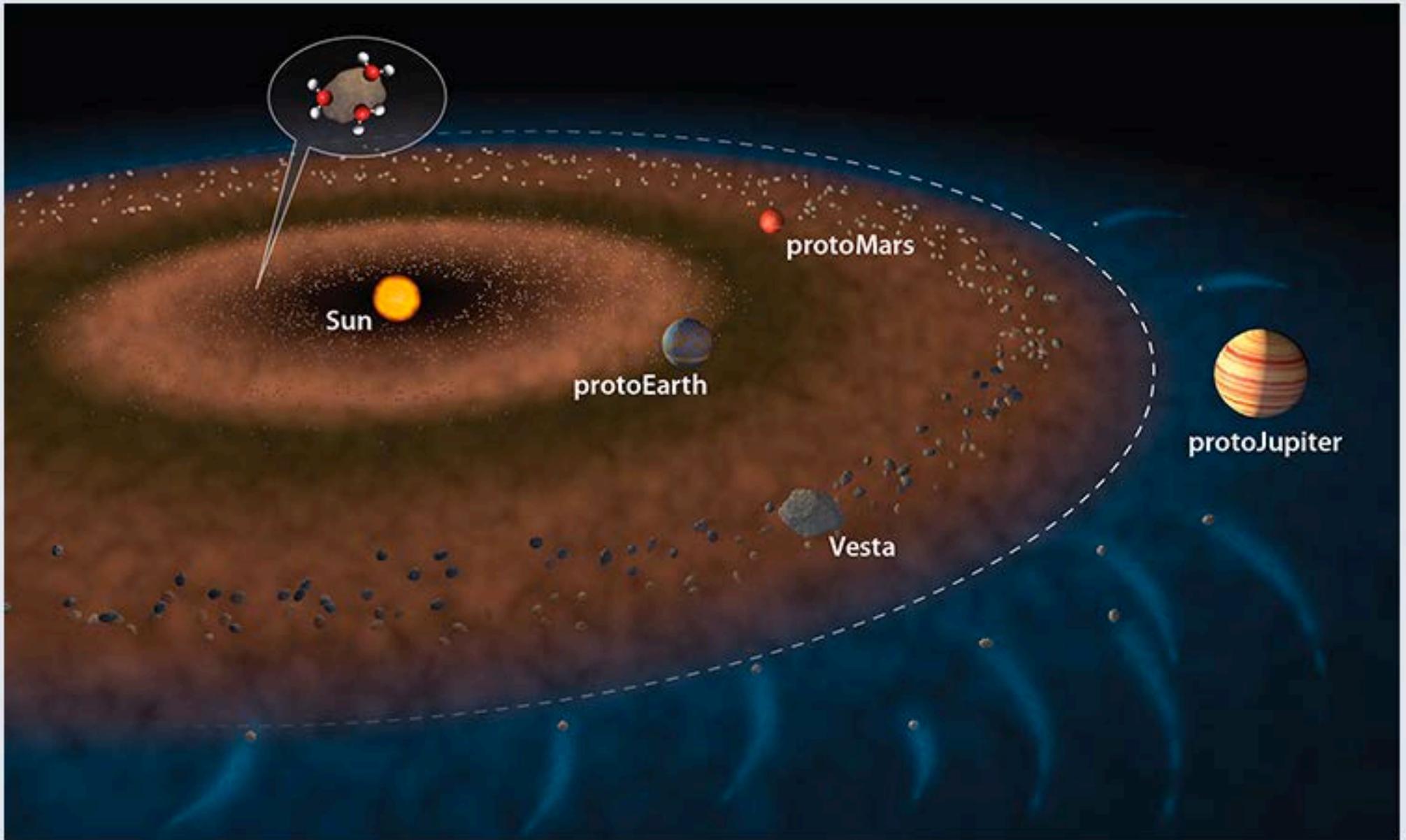
**Hydrate Minerals** (but; leakage from these is too little)

✓ **Volcanic Activity** (vapor from eruption is a source of 'rain' but this source would be too little)

**Extrplanetary Sources** (Comets, meteoroids like carbonaceous chondrites [carbon rich meteorite] can contain 3-22% water and:

→ They have the same D/H ratio (159 D : 999,840 H) as Earth's water where Comets have less water and a D/H of 320 D : 998,950 H

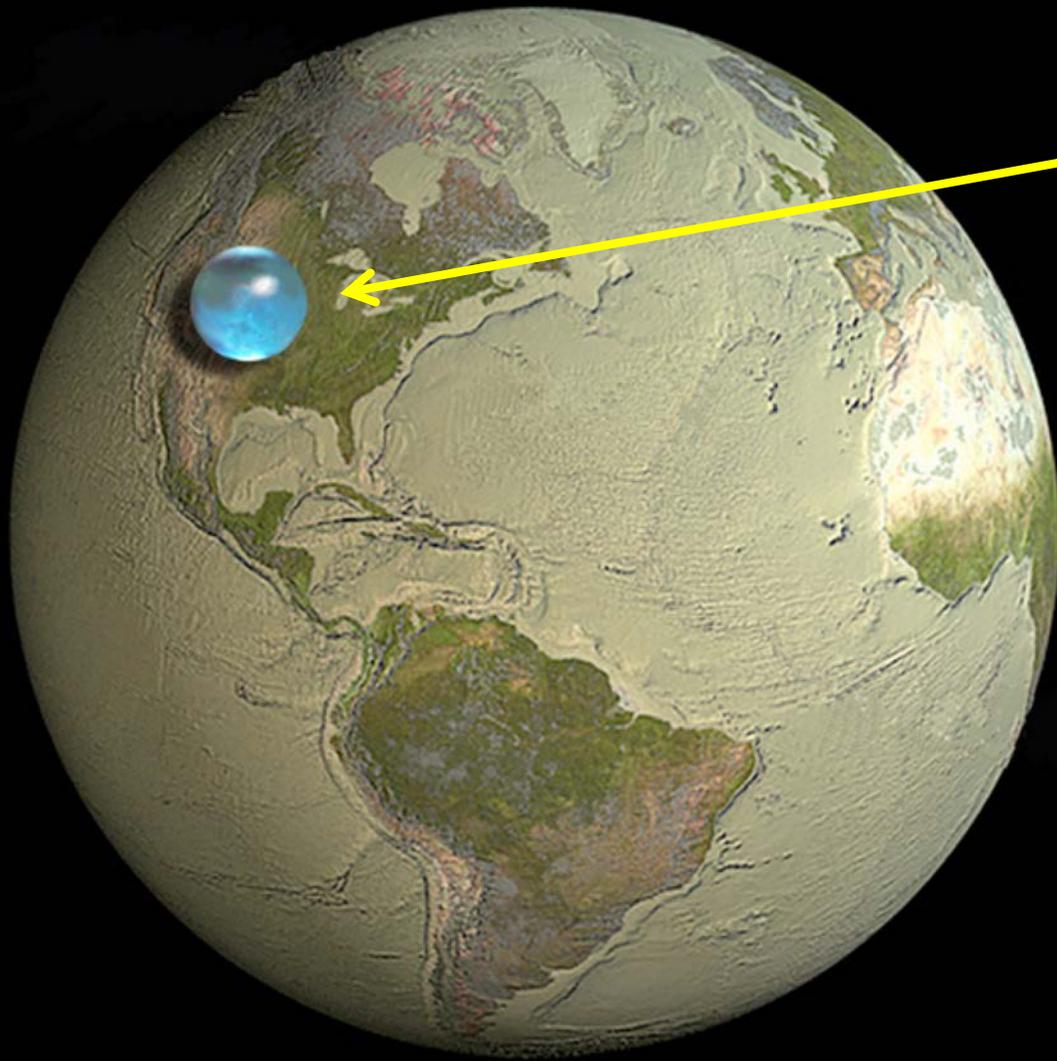
**Inheritance from Big Bang Origin** – the Earth and its Moon + carbonaceous chondrites all have the same D/H ratio suggesting a common origin of water when the planets were originally formed (samples from Apollo 15 & 17 missions)



In this illustration of the early solar system, the dashed white line represents the snow line—the transition from the hotter inner solar system, where water ice is not stable (brown) to the outer Solar system, where water ice is stable (blue). Two possible ways that the inner solar system received water are: water molecules sticking to dust grains inside the "snow line" (as shown in the inset) and carbonaceous chondrite material flung into the inner solar system by the effect of gravity from protoJupiter. With either scenario, water must accrete to the inner planets within the first ca. 10 million years of solar system formation.

(Illustration by Jack Cook, Woods Hole Oceanographic Institution)

CLOSE X



If all of Earth's water (oceans, icecaps and glaciers, lakes, rivers, groundwater, and water in the atmosphere) was put into a sphere, then the diameter of that water ball would be about 860 miles (about 1,385 kilometers), a bit more than the distance between Salt Lake City, Utah to Topeka, Kansas.

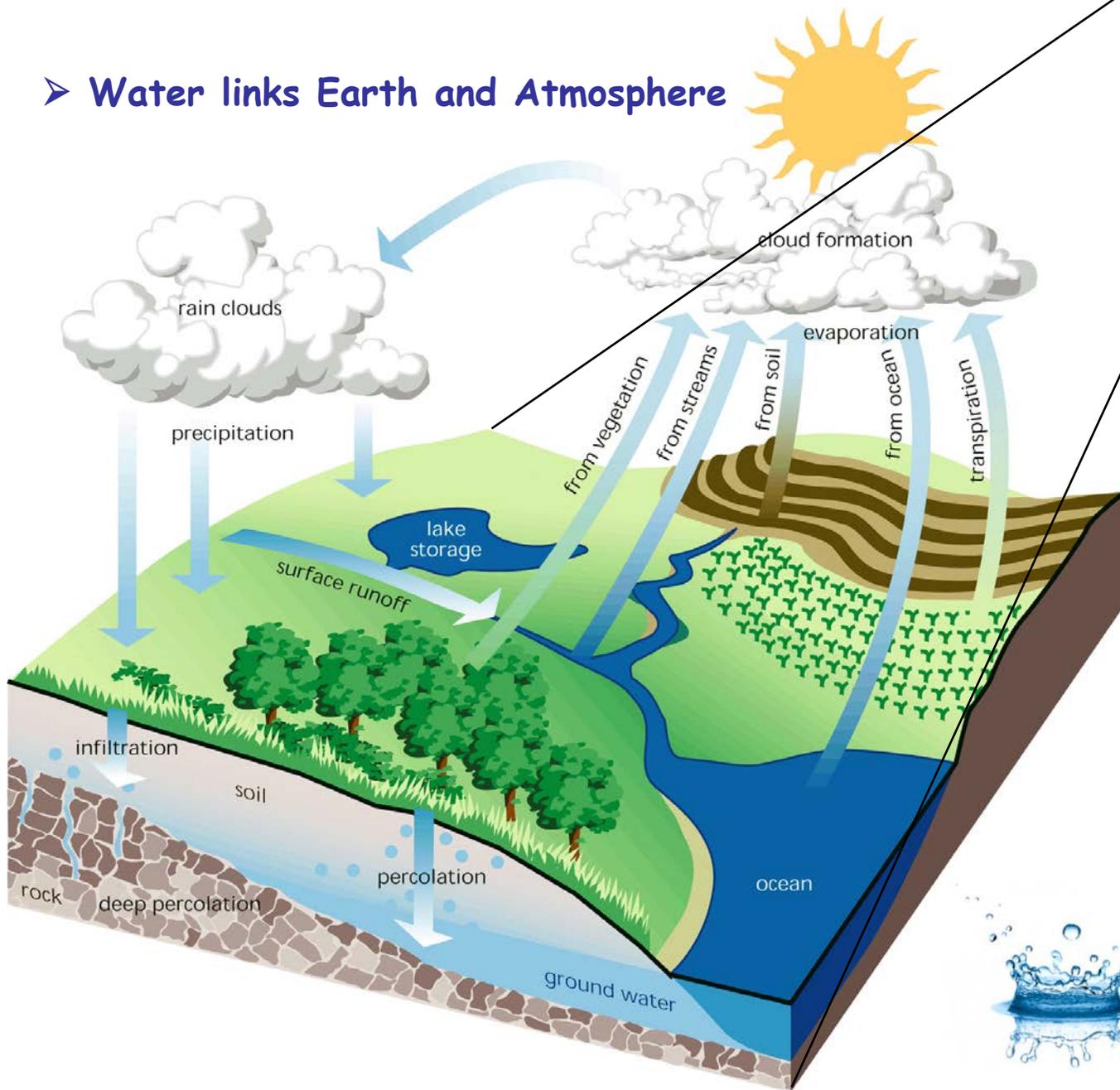
The volume of all water would be about **332.5 million cubic miles (mi<sup>3</sup>)**, or **1,386 million cubic kilometers (km<sup>3</sup>)**. A cubic mile of water equals 1.112 trillion gallons. A cubic kilometer of water equals about 264 billion gallons.

### Water on Earth



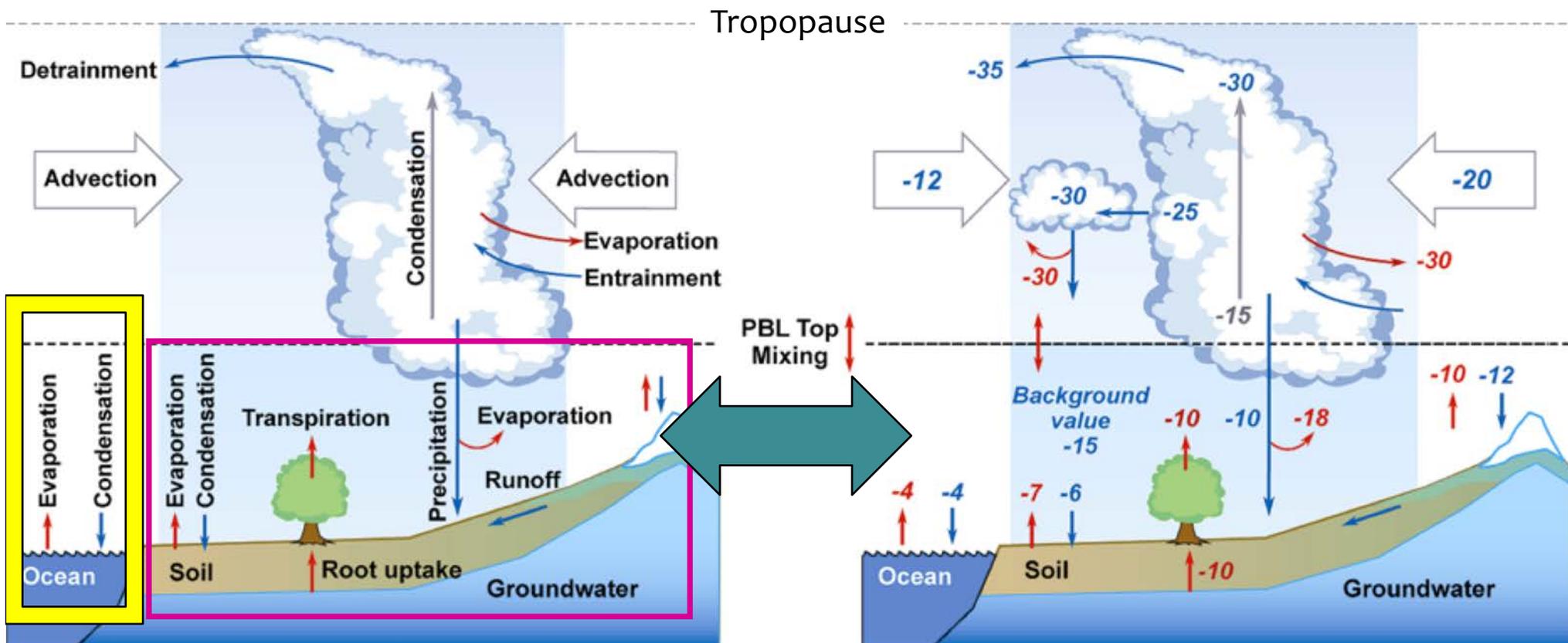
# The hydrologic cycle

➤ Water links Earth and Atmosphere



*Evaporation*  
*Condensation*  
*Sublimation*  
*Percolation*  
*Infiltration . . and*  
*Transpiration*  
*- of -*  
**PRECIPITATION**

# Water isotope partitioning by hydrologic pools & fluxes ~ coupling process to pattern ~



Values are expressed as  $\delta^{18}O$

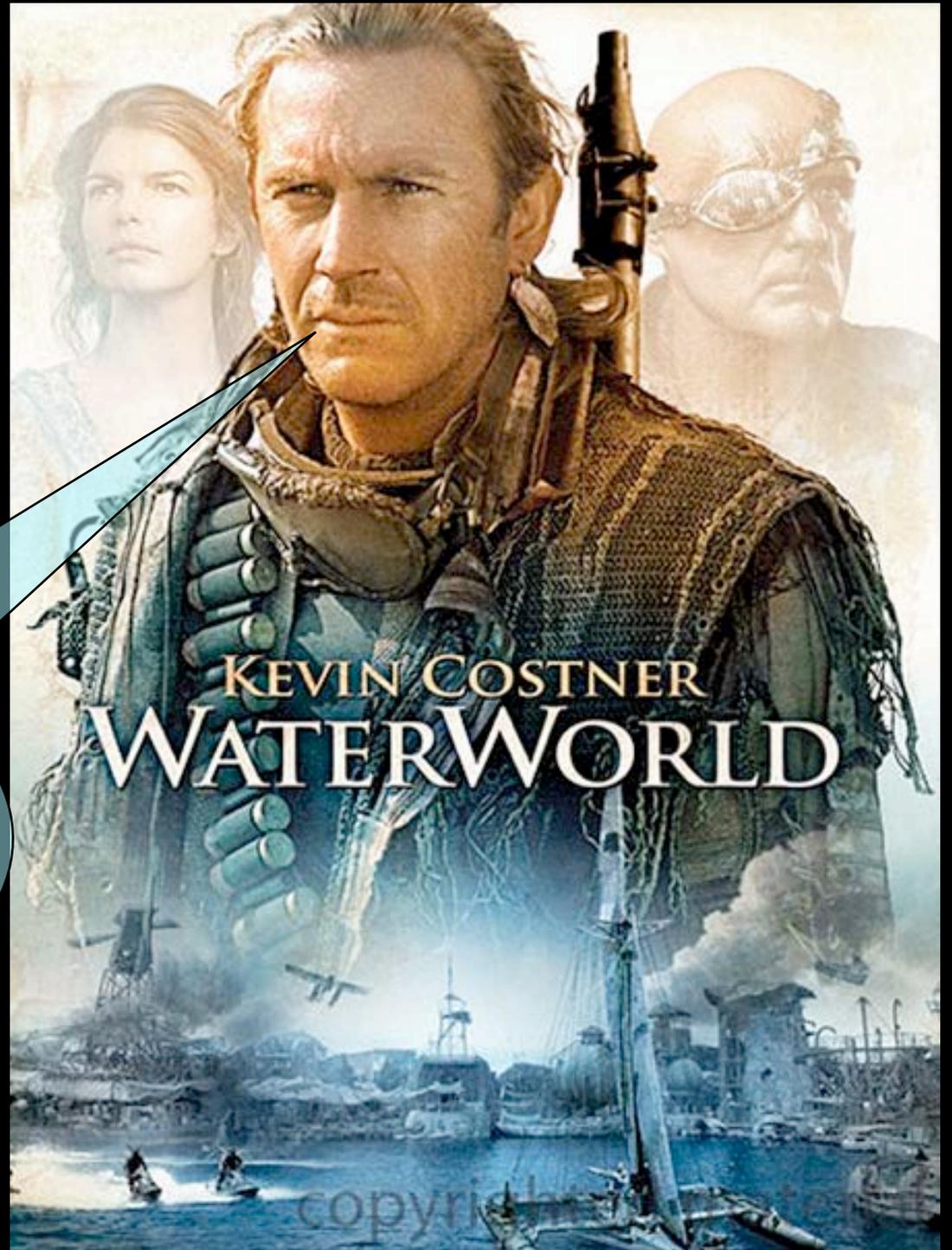
Dawson & Fung, 2011

**But what about the MAGNITUDE, MIXING and MEASUREMENT of this variation?**



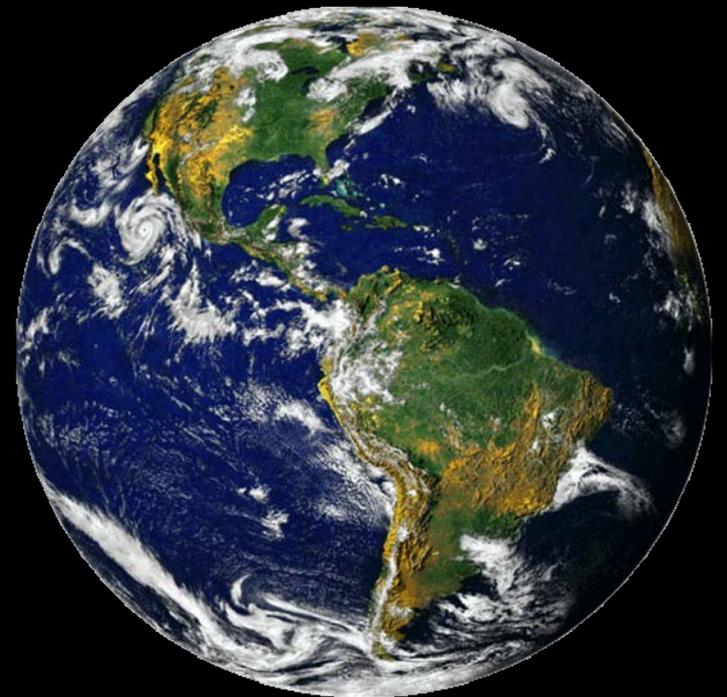
Our mission on this  
**WATER WORLD**  
is to know the  
**RULES!**

- *the mutant*



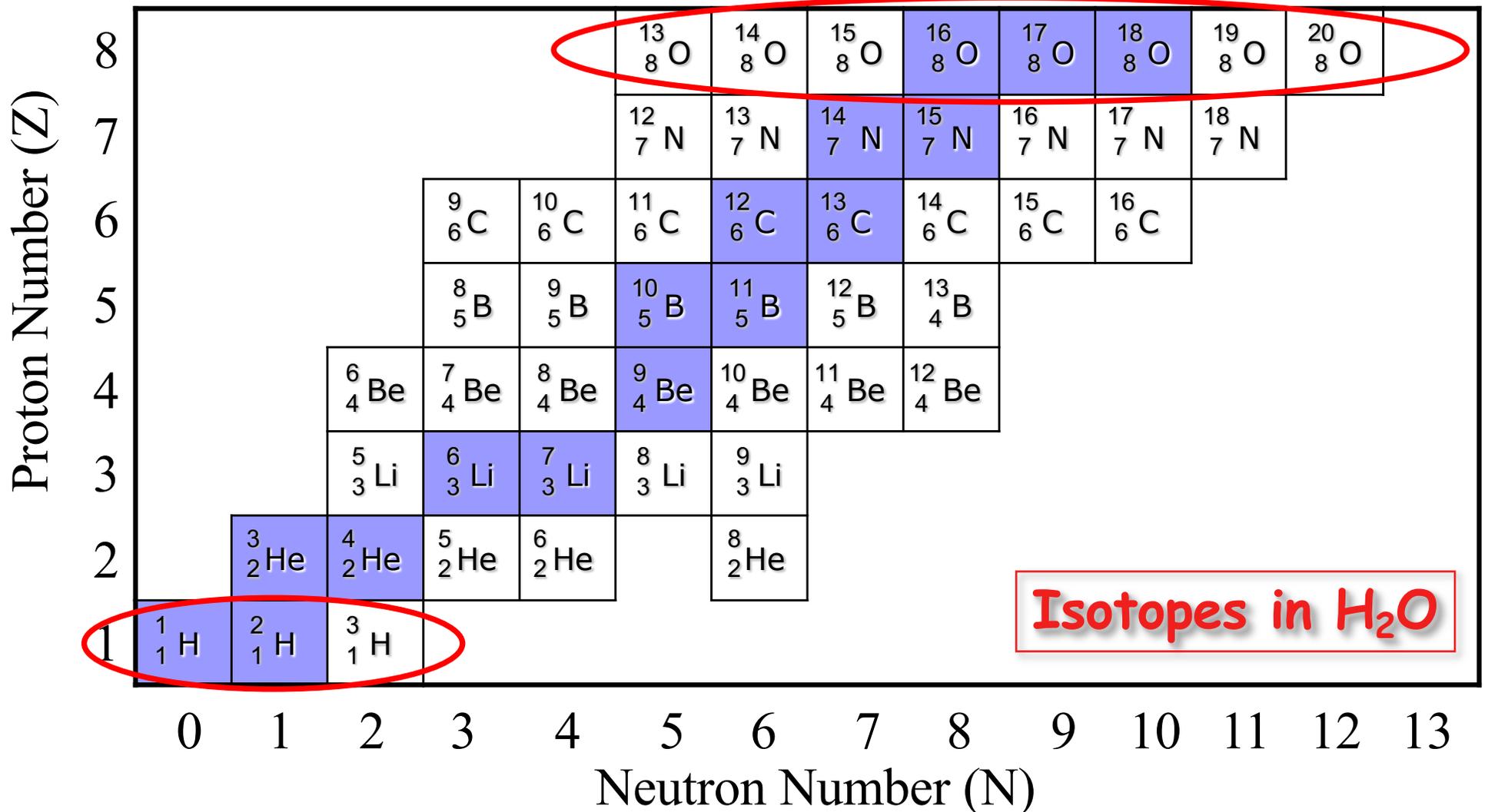
## THE FOUR WATER WORLD RULES:

1. Expect fractionation during phase changes
2. Temperature impacts the isotope composition (lower temps, great affect)
3. The isotope composition of any water is a result of fractionation, mixing or both
4. Always anticipate that equilibrium and kinetic affects could be at play



# Naturally Occurring Isotopes

The shaded squares are **stable** and the un-shaded squares are unstable or radioactive nuclides



# Isotope Natural Abundances

Hydrogen isotopes - 2 stable, 1 unstable (radioactive):

$^1\text{H}$ , protium (H)	99.984%
$^2\text{H}$ , deuterium (D)	0.0159%
$^3\text{H}$ , tritium (T)	$5 \times 10^{-6}\%$



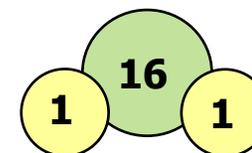
Oxygen isotopes - 3 stable, 5 unstable (radioactive):

$^{16}\text{O}$	99.630%
$^{17}\text{O}$	0.0375%
$^{18}\text{O}$	0.1995%

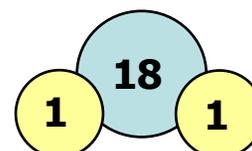
# Isotope Natural Abundances

Of nine configurations (**isotopologues**) of H & O stable isotopes in meteoric water, only three make up the majority on Earth:

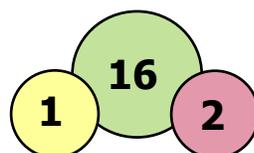
**H<sub>2</sub><sup>16</sup>O** - most common (highest vapor pressure)



**H<sub>2</sub><sup>18</sup>O** - less common



**HD<sup>16</sup>O** - least common



Note:

**Isotopologues** = identical compounds or molecules that differ in isotope composition (<sup>12</sup>C<sup>16</sup>O<sup>18</sup>O vs. <sup>13</sup>C<sup>16</sup>O<sup>18</sup>O),

**Isotopomers** = identical molecule with isotopes bonded at different locations (N<sub>2</sub>O has N[ $\alpha$ ]N[ $\beta$ ]O and the O can be on either N)

# Stable Isotope Expression: Delta ( $\delta$ ) Notation

$$\delta R \text{ in } \text{‰} = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000$$

R = isotope ratio of RARE / COMMON  
i.e. for H<sub>2</sub>O = D/H or <sup>18</sup>O/<sup>16</sup>O - a **very small** number

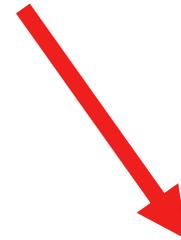
$[(R_{\text{sample}} / R_{\text{standard}}) - 1]$  is a small number - but multiplying value by 1000 allows us to express the value in **per mil** (parts per thousand ; ‰) notation (easier to use)

Delta notation is a "difference" or relative expression in relation to a standard. So, an isotope ratio in the sample equal to the standard means  $R_{\text{sample}}/R_{\text{standard}} = 1$  and  $\delta R = 0\text{‰}$  - the International Atomic Energy Association (IAEA) maintains these standards

# International Reference Standards

Isotope	Ratio Measured	IAEA Reference Standard	Abundance Ratio of reference standard
$^2\text{H}$ (D)	$^2\text{H}/^1\text{H}$ (D/H)	<b>VSMOW</b> : "Vienna-Standard Mean Ocean Water"	$155.76 \times 10^{-6}$
$^{18}\text{O}$	$^{18}\text{O}/^{16}\text{O}$	<b>VSMOW</b>	$2005.2 \times 10^{-6}$

- Reference standard was originally called SMOW but is now called V-SMOW
- Measurements are calibrated to international standards that span a wide range of values . . .



# Other International Standards

Abbreviation	Standard Name	$\delta^2\text{H}_{\text{VSMOW}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$
<b>VSMOW</b>	Standard Mean Ocean Water	0‰	0‰
<b>SLAP</b>	Standard Light Antarctic Precipitation	-428.0‰	-55.50‰
<b>GISP</b>	Greenland Ice Sheet Precipitation	-189.7‰	-24.80‰
NBS1	National Bureau of Standards 1	-47.1‰	-7.88‰
NBS1A	National Bureau of Standards 1A	-183.2‰	-24.29‰
UU-DI	Univ. Utah DI	-123‰	-16.5‰
UU-Zero	Univ. Utah "Zero" (manufactured)	-0.1‰	-0.2‰

# Variation in $\delta$ is caused by fractionation

**FOUR** factors at play:

- ★ Bond strength of and to heavy isotopes are greater
- ★ Vibrational frequencies of light isotopes are greater than heavy isotopes (defined by  $KE = mv^2/2$ ) so bonds with light isotopes break more easily
- ★ Mass differences (not really chemical differences) lead to different reaction rates and thus different representation of isotopes in product and reactant
- ★ Reactions can be bi-directional, unidirectional and along concentration gradients – all are temperature dependent (rule: **lower temps** lead to **greater isotope affects**)

# Types of Fractionation

## 1. Exchange/equilibrium

- ⊕ Complete back-reactions occur
- ⊕ Product/reactant offset by constant fractionation factor,  $\alpha$

## 2. Kinetic

- ⊕ Incomplete back-reactions or none occur
- ⊕ Product and reactant  $\delta$  can evolve in concert (**closed system**), or product composition determines reactant composition (**open system**)

## 3. Transport or Diffusive

- ⊕ Can be thought of as a special case of kinetic fractionation reaction (along a flux gradient vs. a chemical reaction that is not dependent upon a concentration gradient)
- ⊕ Incomplete back-flux is a necessary condition (rule)

# Examples of Fractionation Types

## ⊕ Exchange/equilibrium

- ⊕ Liquid droplet formation from vapor in clouds
- ⊕ Evaporation at the boundary layer (100% RH) of Ocean

## ⊕ Kinetic

- ⊕ Mineral precipitation out of magma
- ⊕ Biosynthesis (enzyme mediated)

## ⊕ Transport / Diffusion

- ⊕ Diffusion through boundary layer over water, out of leaves, through soils

During any fractionation event these are NOT mutually exclusive

For water,  
equilibrium and diffusive (kinetic) fractionation usually always occur

# Isotope fractionation of water and Rayleigh distillation

(also called Rayleigh ["raylee"] fractionation)

## What is this process?

- Fractional distillation of mixed liquids
- Exponential relation describing isotope partitioning between two reservoirs as one reservoir decreases in size

## ASSUMPTIONS:

1. Material is continuously removed from a mixed system containing molecules of two or more isotope species (e.g., H<sub>2</sub>O with <sup>18</sup>O & <sup>16</sup>O)
2. Fractionation accompanies the removal process and at any instance is described by the fractionation factor,  $\alpha$
3.  $\alpha$  does not change during the process

# Rayleigh fractionation/distillation

- **Rayleigh fractionation** occurs when a parent mass is depleted by **equilibrium fractionation** to a phase continually removed. Lord Rayleigh (J. William Strutt, 1843-1919) first used this to describe distillation of liquid rain from an air mass (in the ideal case RF is only for chemically 'open' systems that are in a well mixed thermodynamic equilibrium with finite reservoirs)
- The simple equation describing Rayleigh processes is:

$$R = R_0 f^{(1-\alpha)}$$

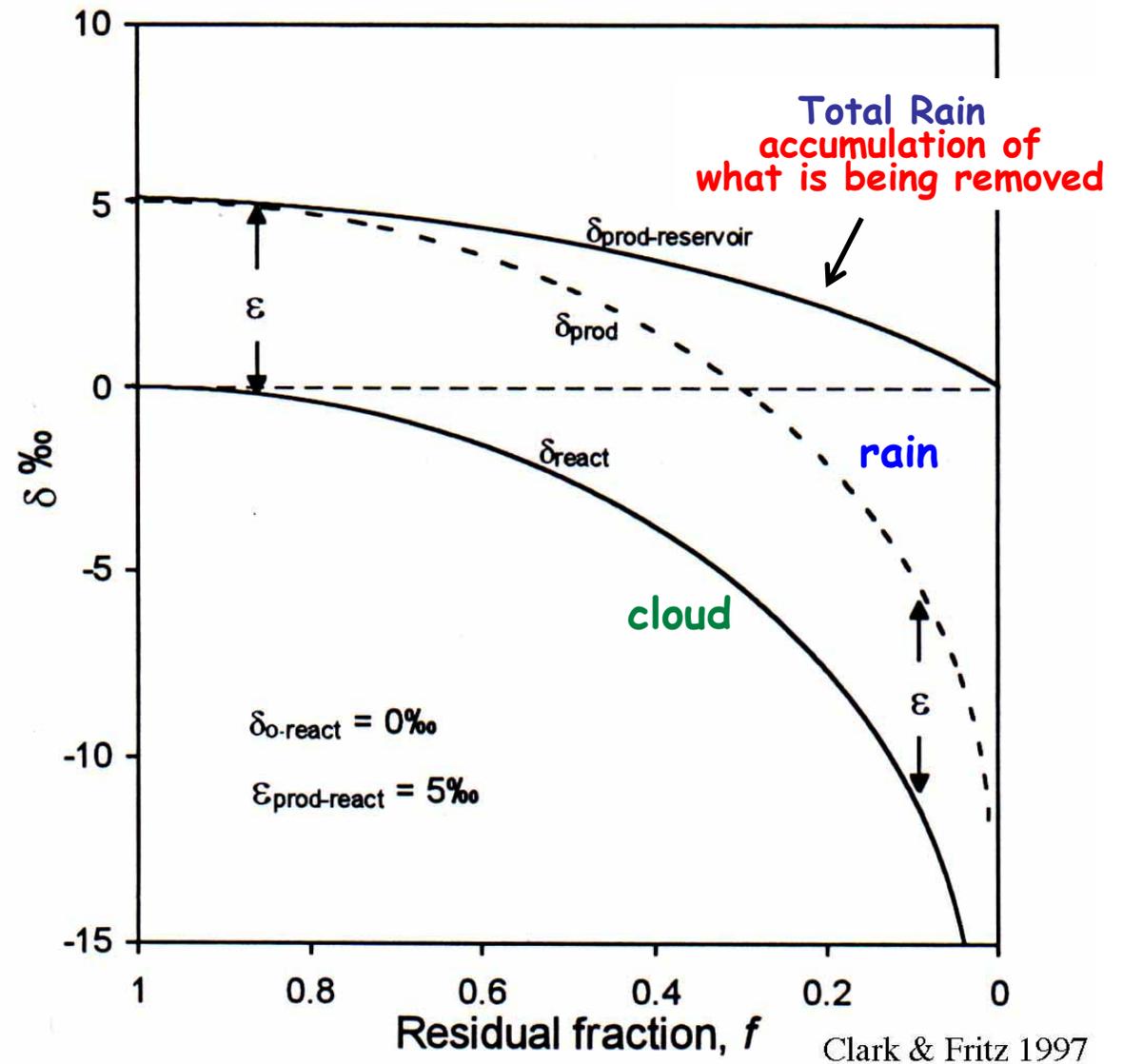
**R** and **R<sub>0</sub>** are the ratios at time "t" and at t=0

**f** is the fraction remaining at t,

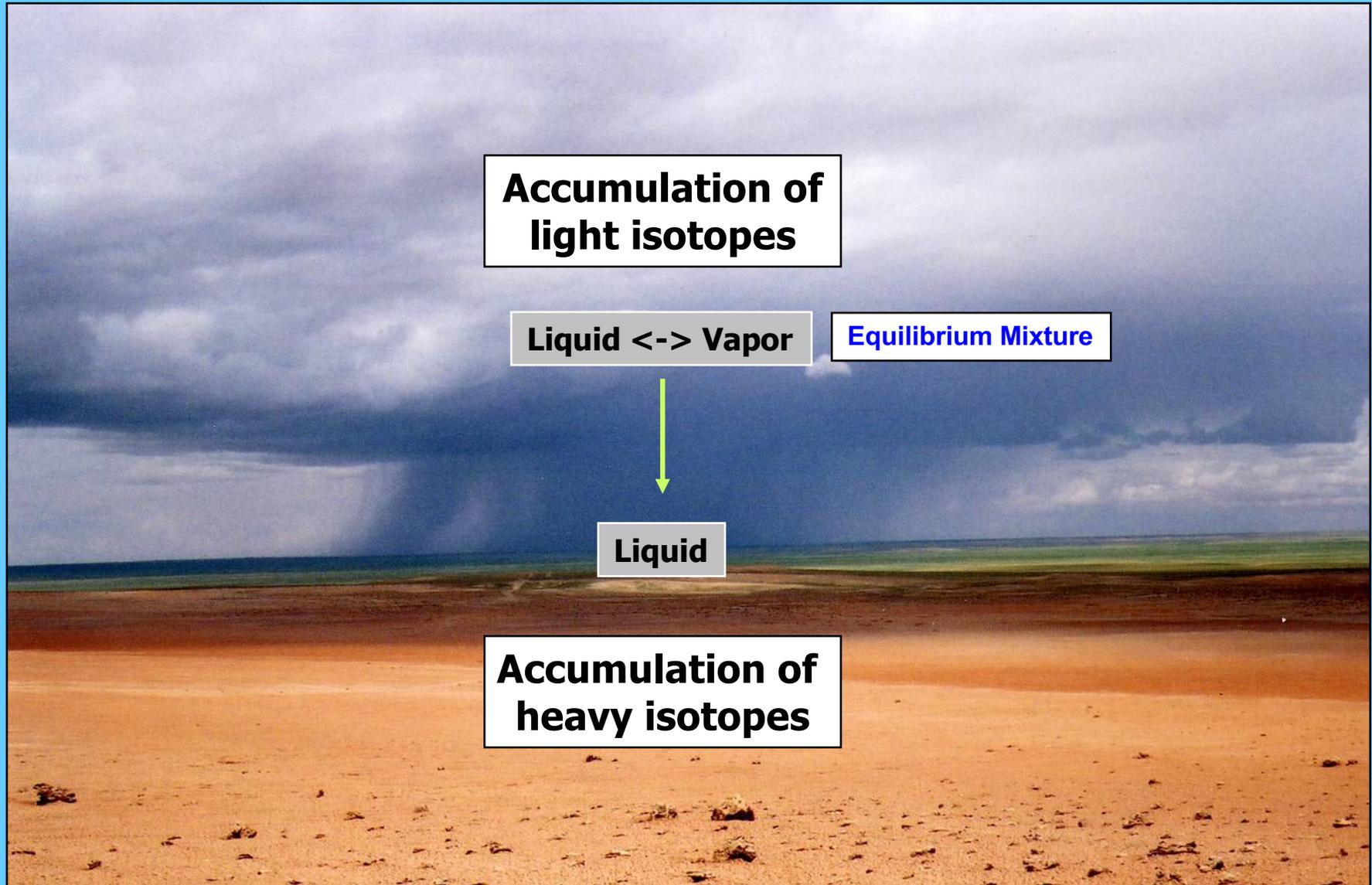
**α** is the fractionation factor

# Rayleigh fractionation from rainfall (condensation)

$\delta$  in cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the cloud. These idealized lines follow the same Rayleigh process as classical evaporation



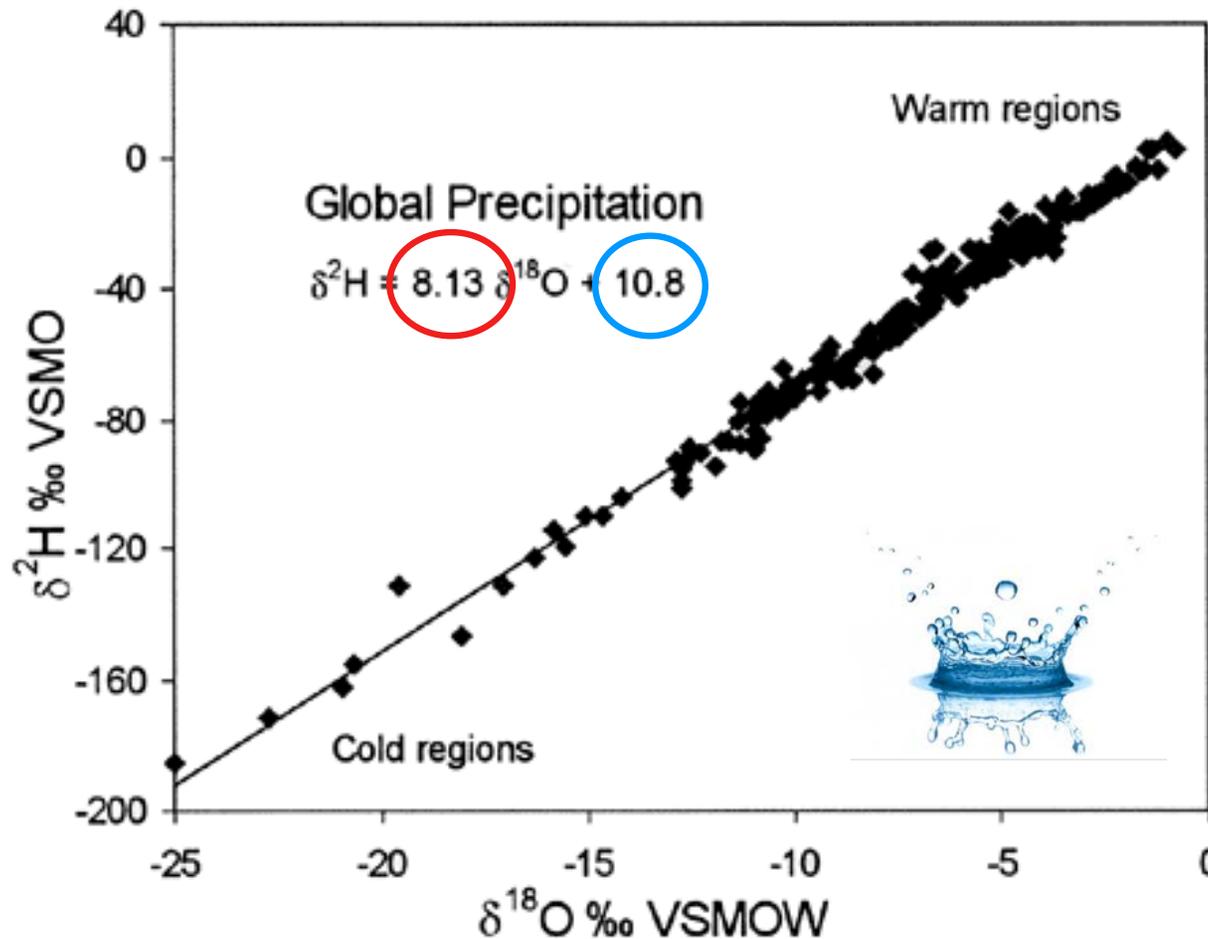
# Rayleigh Distillation in action



Generally an “open” system case

Questions?

# The Global Meteoric Water Line, GMWL



Condensation  
is an equilibrium process

so

Most precipitation  $\delta$  values  
lie along a Global Meteoric  
Water Line (GMWL) of  
slope  $\sim 8$

$$(\epsilon^{2\text{H}} / \epsilon^{18\text{O}} = 8)$$

The intercept of the  
GMWL is ca. **+10‰** not **0**  
**WHY?**

**kinetic effects in action**

# A note about equilibrium fractionation factors for water isotopes (vapor-liquid)

at 20° C

$$\oplus \epsilon^{2\text{H}} = 74\text{‰}$$

$$\oplus \epsilon^{18\text{O}} = 9.2\text{‰}$$

$$\oplus \epsilon^{2\text{H}} / \epsilon^{18\text{O}} = 8.0$$

at 80° C

$$\oplus \epsilon^{2\text{H}} = 38\text{‰}$$

$$\oplus \epsilon^{18\text{O}} = 4.5\text{‰}$$

$$\oplus \epsilon^{2\text{H}} / \epsilon^{18\text{O}} = 8.4$$

**Mass Differences**

$$\oplus ({}^2\text{H} - {}^1\text{H}) / {}^1\text{H} = 1$$

$$\oplus ({}^{18}\text{O} - {}^{16}\text{O}) / {}^{16}\text{O} = 0.125$$

$$\oplus 1 / 0.125 = 8$$

Equilibrium enrichment factors for H isotopes are ~8 x those for O isotopes

...insight into the GMWL to come

**~ Craig-Gordon Model ~**  
**Isotope Evolution during phase changes of H<sub>2</sub>O**

$$\delta_{\text{vapor}} = \delta_{\text{liquid}} - h_{\text{air}} \times \delta_{\text{awv}} - \alpha_{\text{eq}} - (1 - h_{\text{air}}) \times \alpha_{\text{k}} / 1 - h_{\text{air}}$$

- $\alpha_{\text{eq}}$  = Equilibrium fractionation factor (1.009)  
 $\alpha_{\text{k}}$  = Kinetic fractionation factor (1.0285)  
 $h_{\text{air}}$  = humidity [vapor pressure of water] in air  
 $\delta_{\text{awv}}$  = molar ratio of <sup>18</sup>O/<sup>16</sup>O (or <sup>2</sup>H/H) of atmospheric water vapor

# ~ Craig-Gordon Model ~

## Isotope Evolution during phase changes of H<sub>2</sub>O

### THREE ASPECTS of IMPORTANCE:

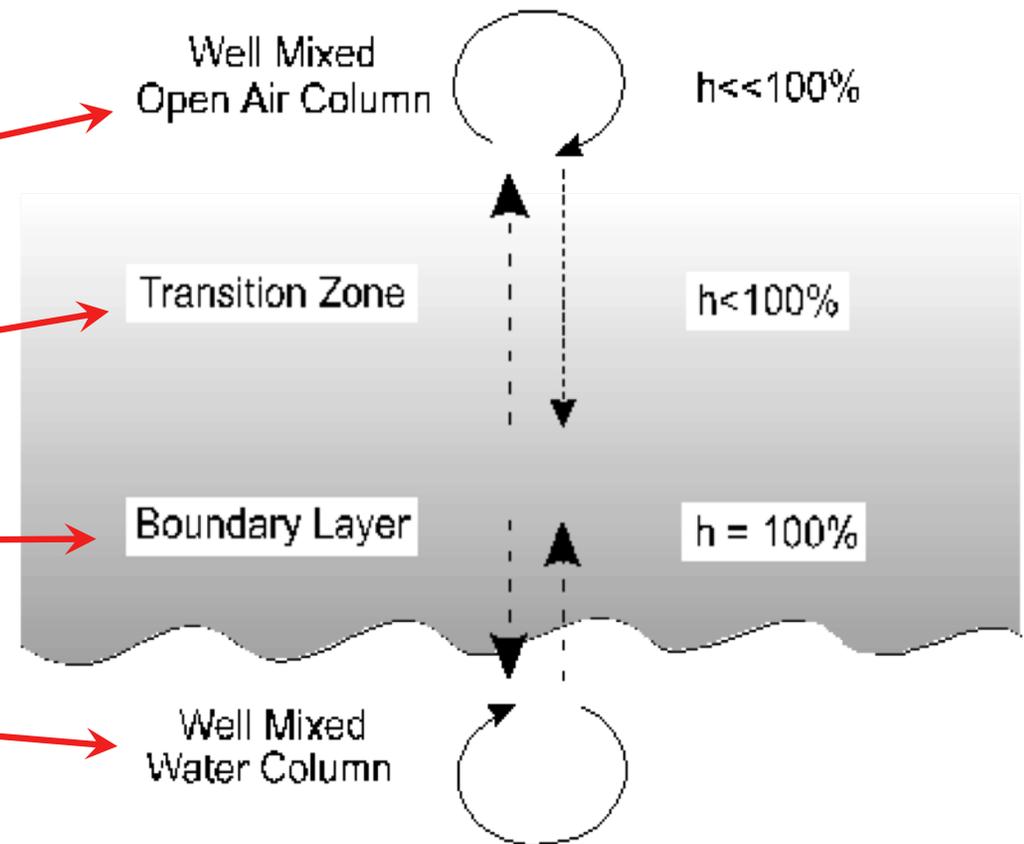
- 1) Characteristics of the model layers
- 2) Processes occurring in the model layers
- 3) Isotope Effects in the model layers

Open air

Transition zone

Boundary layer

Liquid



# ~ Craig-Gordon Model ~

## Isotope Evolution during phase changes of H<sub>2</sub>O

### Characteristics of the model layers

#### Open air

- ⊕ Well-mixed
- ⊕ Large

#### Transition zone

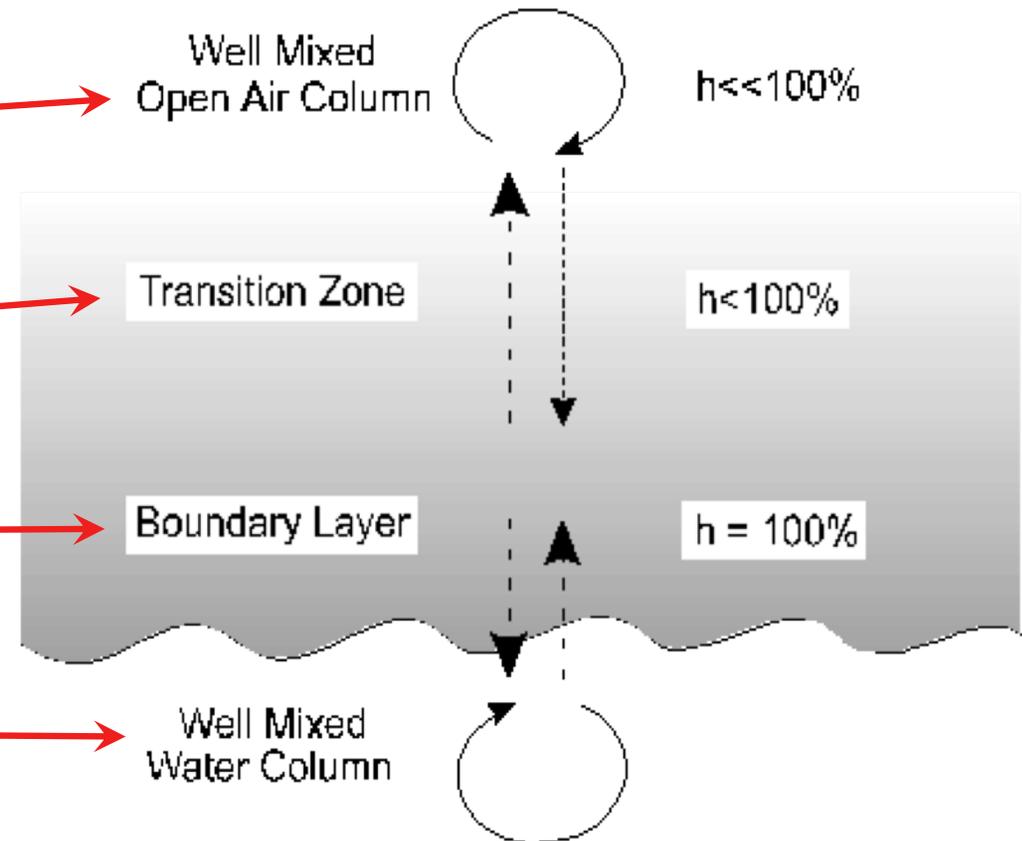
- ⊕ Unmixed
- ⊕ Decreasing humidity upwards

#### Boundary layer

- ⊕ Thin, well-mixed layer
- ⊕ 100% RH

#### Liquid

- ⊕ Large (ocean) or small body of water
- ⊕ Mixed or stratified



# ~ Craig-Gordon Model ~

## Isotope Evolution during phase changes of H<sub>2</sub>O

### Processes occurring in the model layers

#### Open air

- ⊕ Rapid mixing and removal evaporated vapor

#### Transition zone

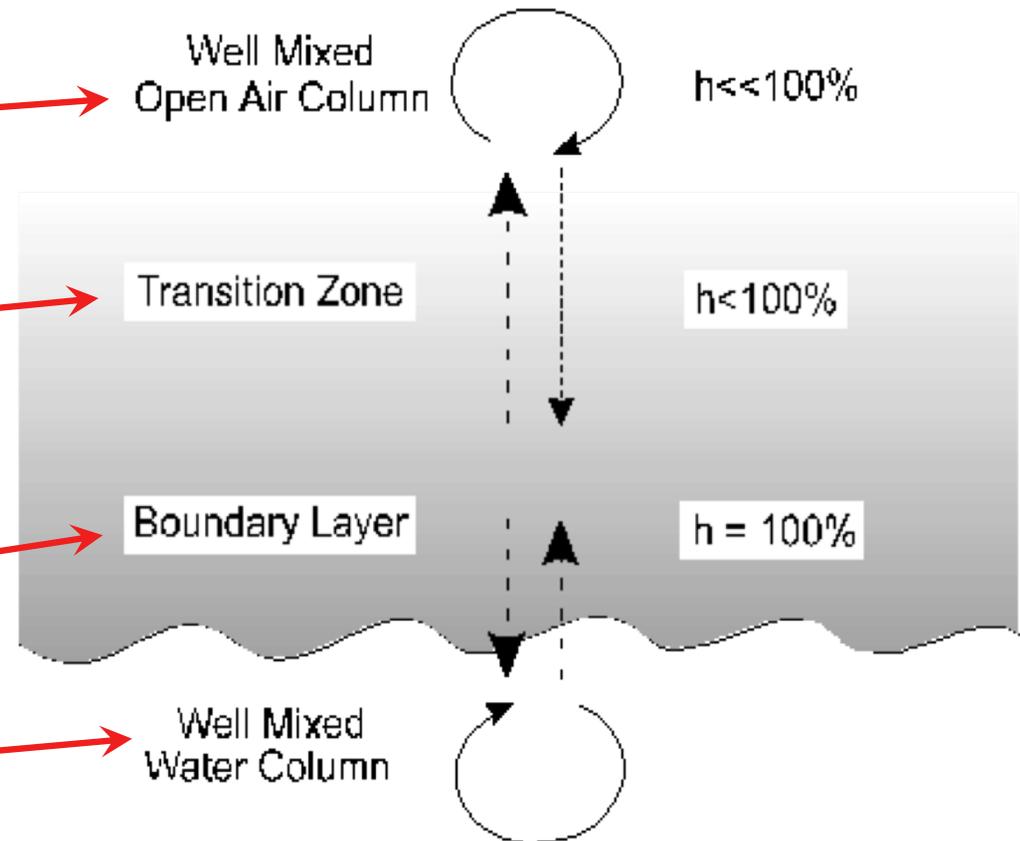
- ⊕ Diffusive transport of vapor in 2 directions
- ⊕ Net transport to open air

#### Boundary layer

- ⊕ Equilibrium exchange with liquid layer

#### Liquid

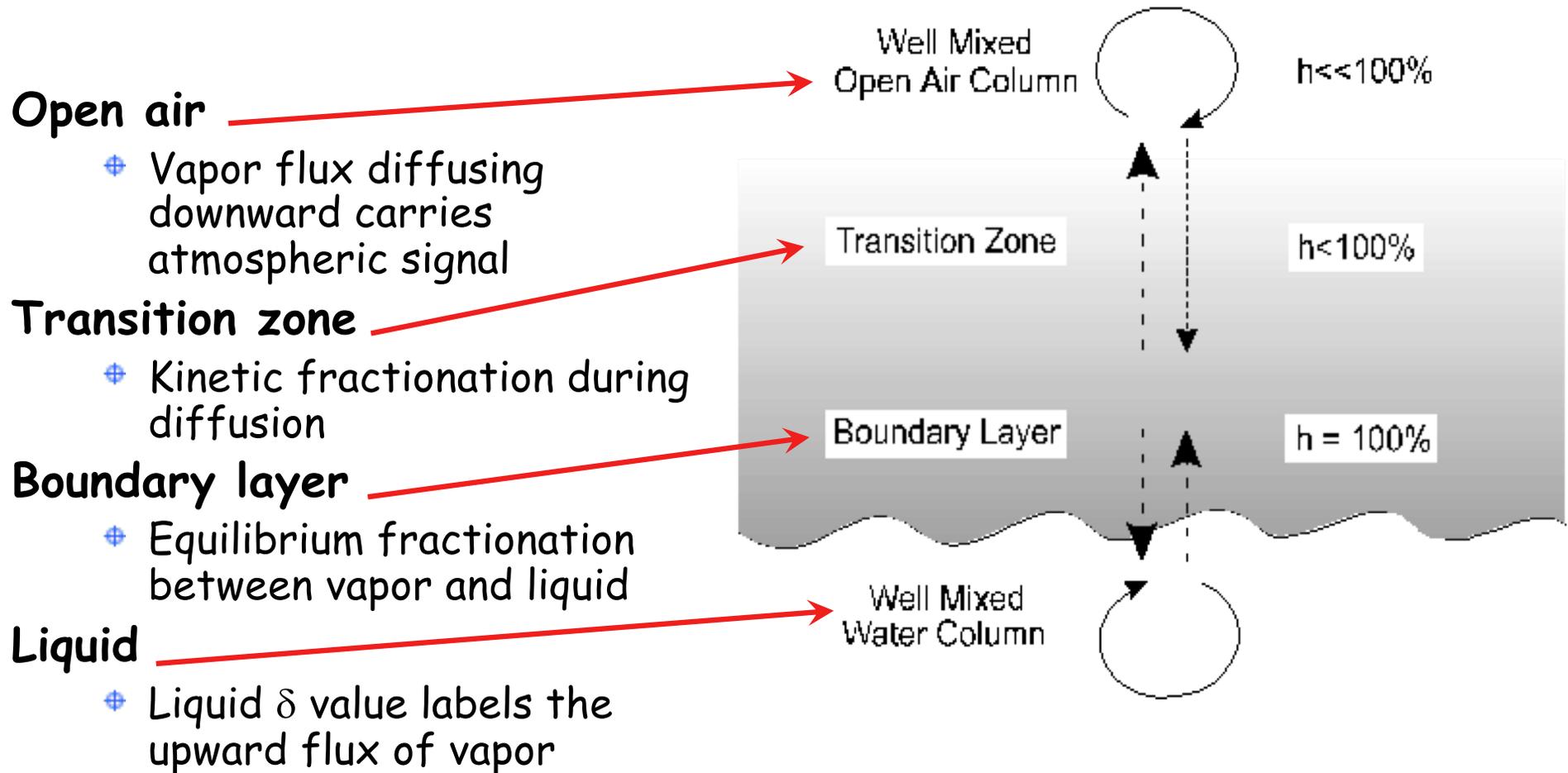
- ⊕ Rapid mixing and supply of water



# ~ Craig-Gordon Model ~

## Isotope Evolution during phase changes of H<sub>2</sub>O

### Isotope effects related to the model layers

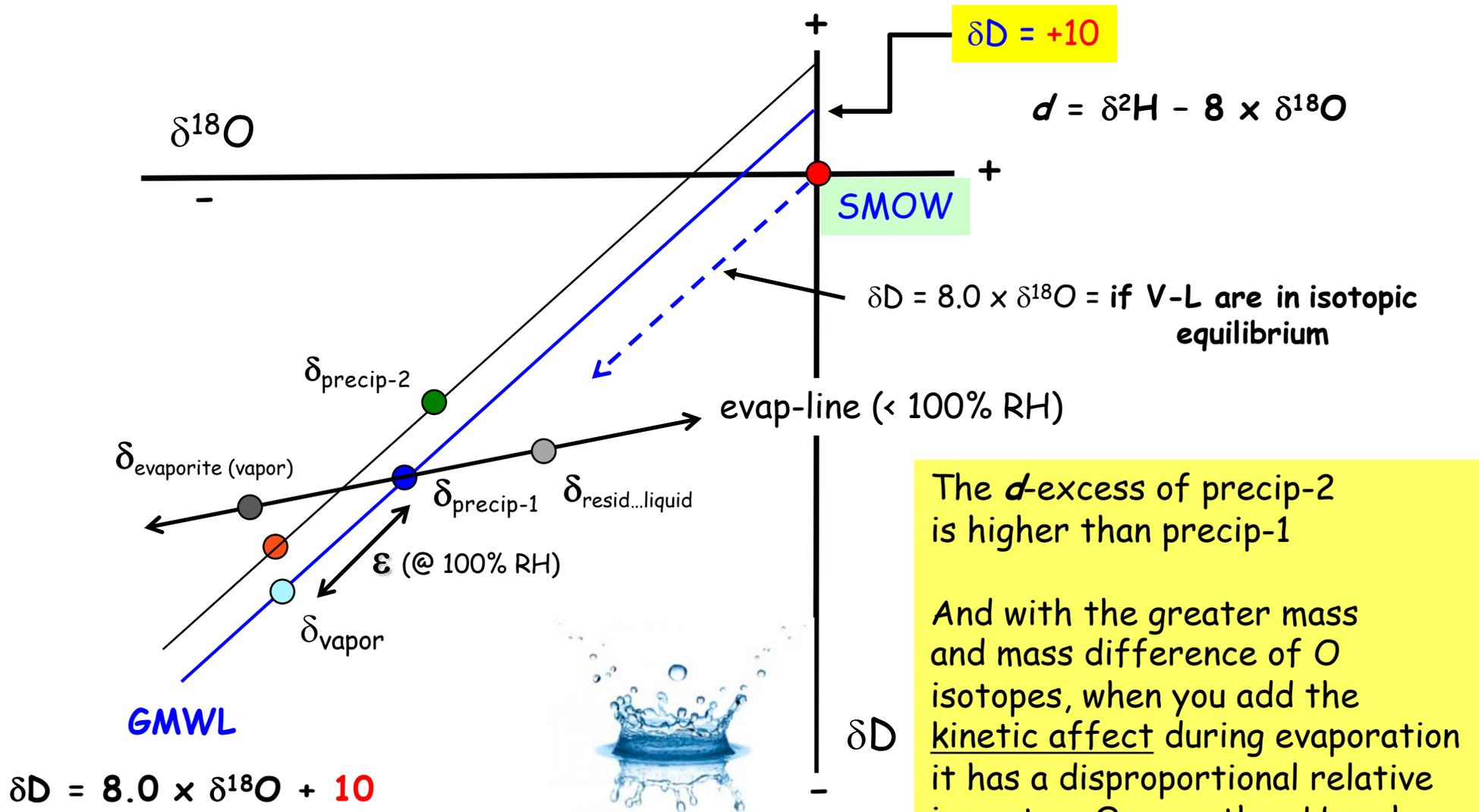


**~ Craig-Gordon Model ~**  
**Isotope Evolution during phase changes of H<sub>2</sub>O**

Remember these:

- When a portion of liquid water evaporates, the  $\delta$  value of the remaining water increases (Rayleigh distillation)
  
- The isotopic composition of the residual water depends on:
  - ⊕ The **initial composition** of the water
  - ⊕ The **fraction of the water evaporated**
  - ⊕ The **isotopic composition of the evaporative flux** (what was added to what was there)
  - ⊕ The **back-flux** of water from the atmosphere (relative size and isotopic composition)
  
- Depending on the system, this last factor can be insignificant (the ocean) or the most important factor (e.g., body/leaf water)

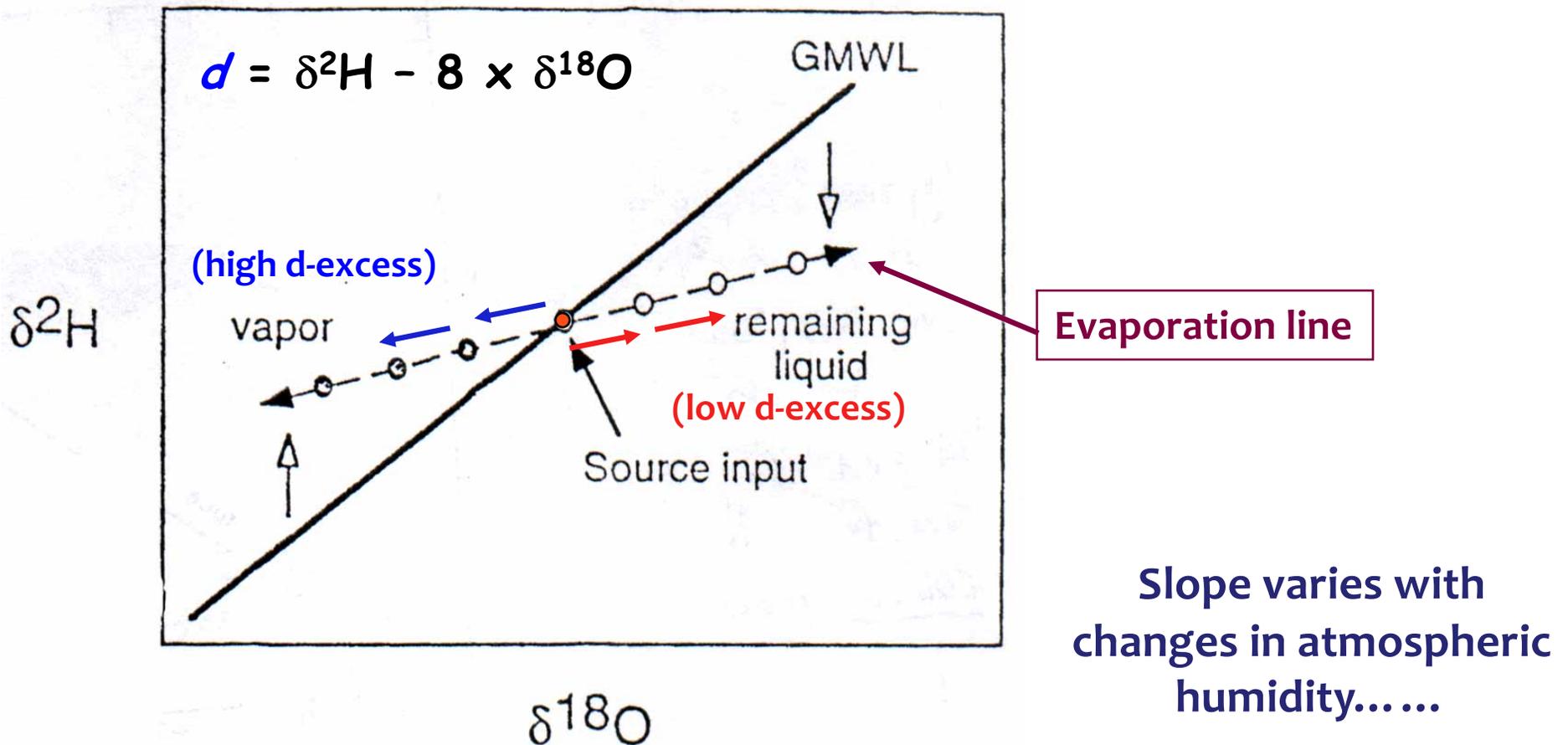
# Why doesn't the Global Meteoric Water Line intercept 0?



# d-excess & the Global Meteoric Water Line

“From the GMWL a critical tool emerged we could use to identify the occurrence of and conditions around which natural water evaporation, as well as the origin and history of air masses carrying precipitation, had occurred we termed **d-excess**”.

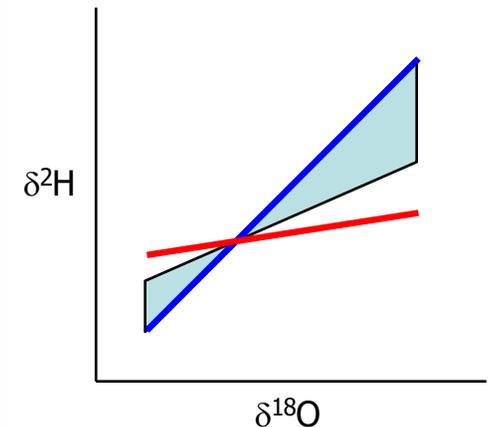
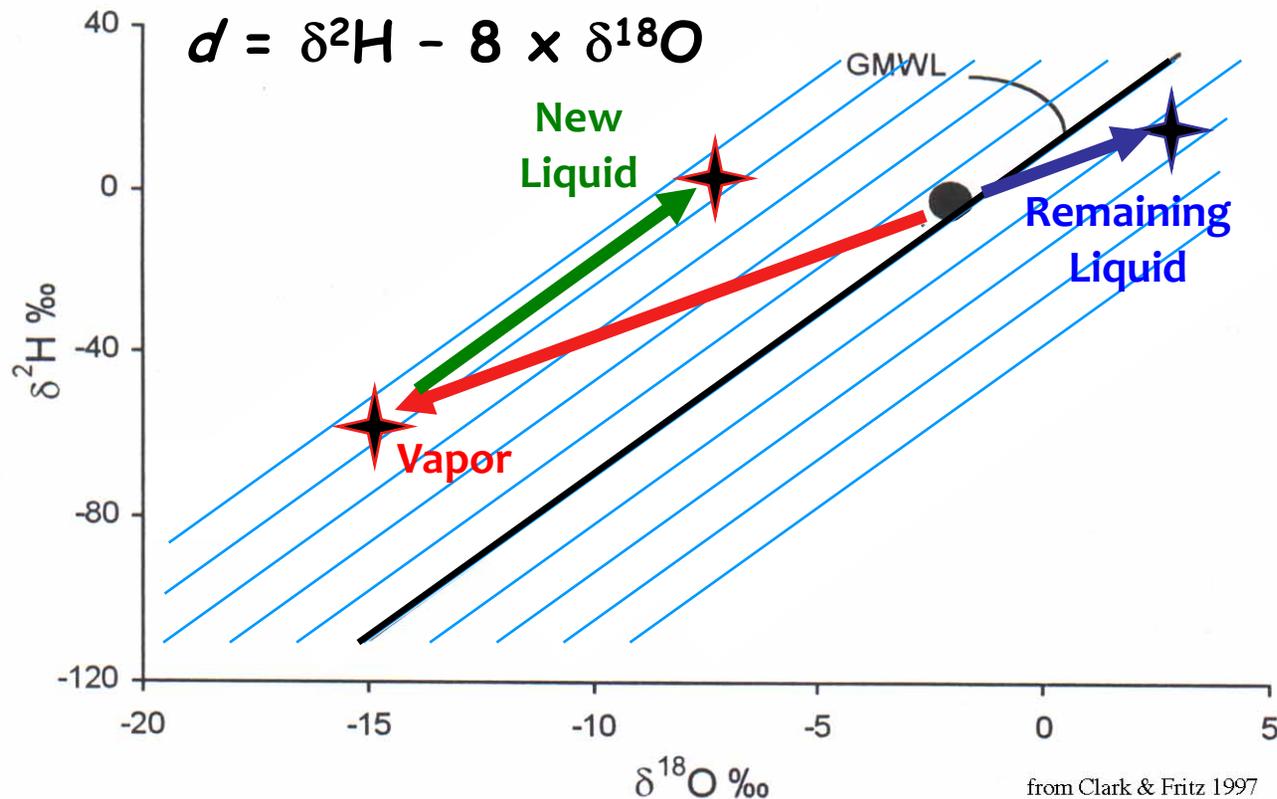
Joel Gat, 2011

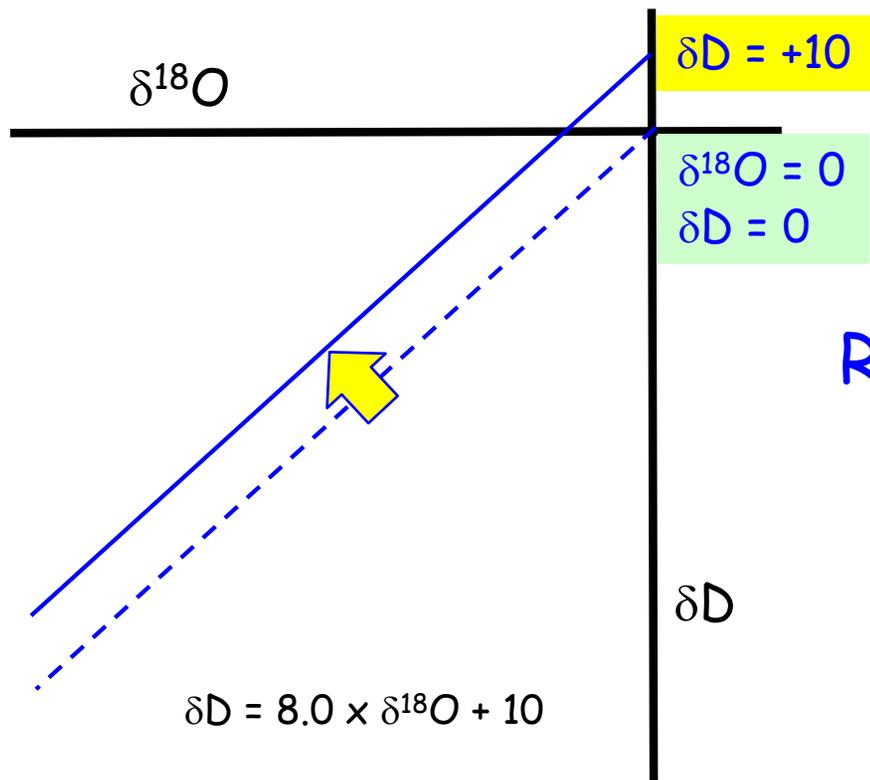


The "see-saw" affect of evaporative (kinetic) isotope fractionation (after Gat 1996)

# Deuterium Excess ( $d$ )

- ⊕ For “bodies of water”, the evaporation line can be extended to show the change in residual water  $\delta$  values and  $d$
- ⊕ As evapoconcentration proceeds the  $\delta$  values increase and  $d$  decreases (of the ‘residual’ water (see last slide))

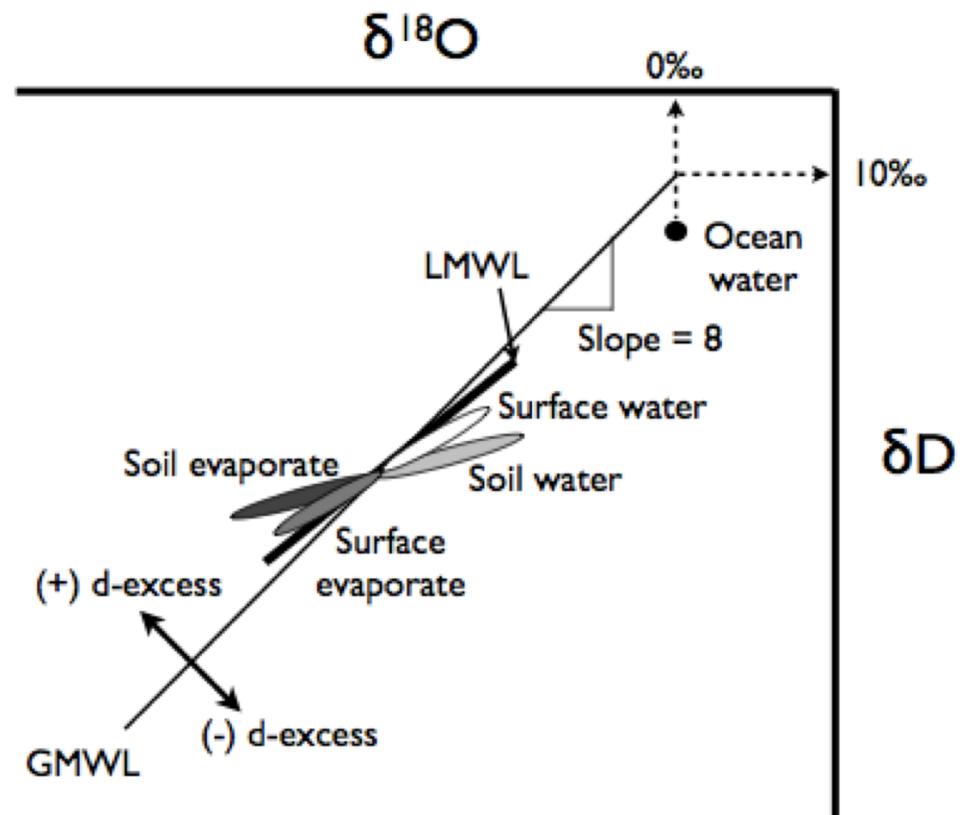




Additional kinetic processes at 81% humidity (Global average)

Equilibrium processes at 100% humidity

## REVIEW: Meteoric Water Lines

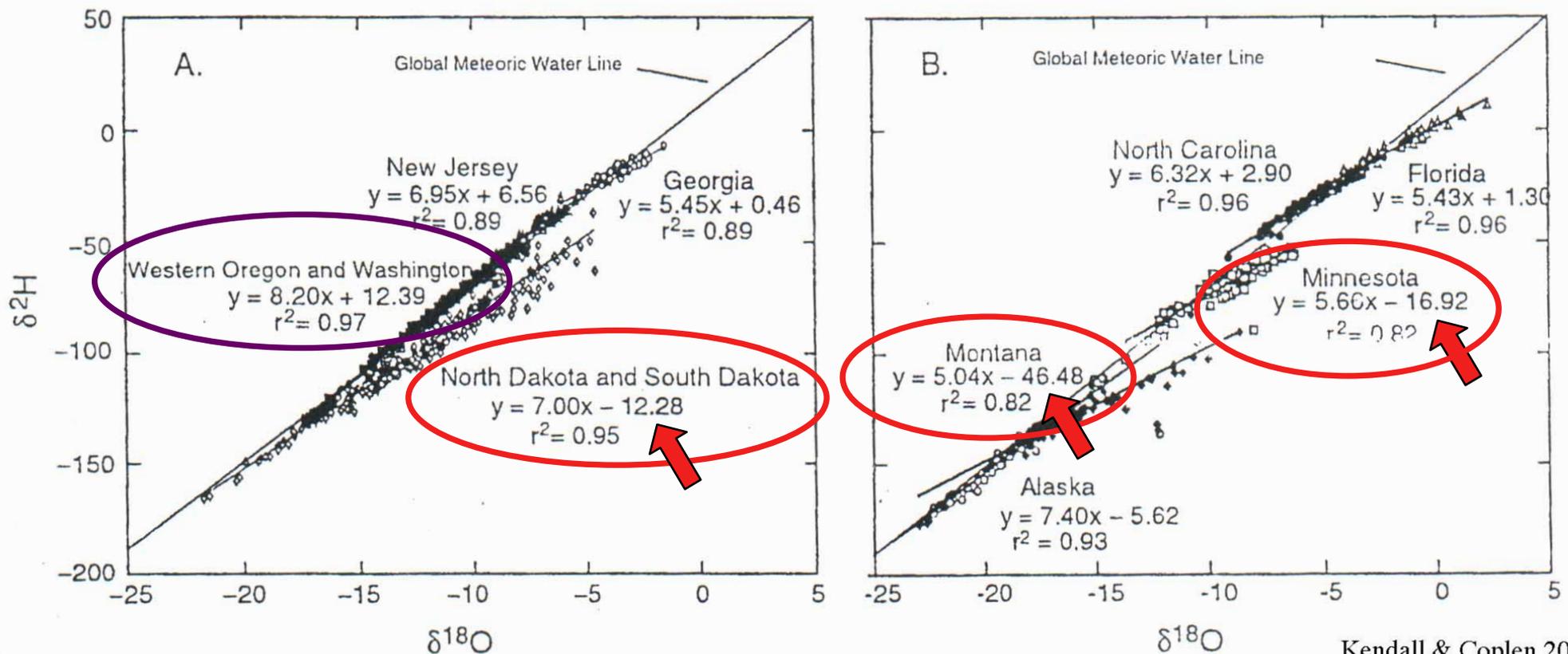


- \*Evaporation causes departures from the MWL
- \*Since mass-balance must be preserved, the liquid phase will get "heavier" if the vapor leaving is "lighter"
- \*The affect of evaporation is 'seen' more for oxygen than for hydrogen because  $\text{H}_2^{16}\text{O}$  diffuses 5.4% faster than  $\text{H}_2^{18}\text{O}$  but  $\text{HD}^{16}\text{O}$  only 2.7% faster than  $\text{H}_2^{16}\text{O}$  during evaporation (plus note that scale for O is 8X smaller than H)

From: Dawson and Simonin, 2011

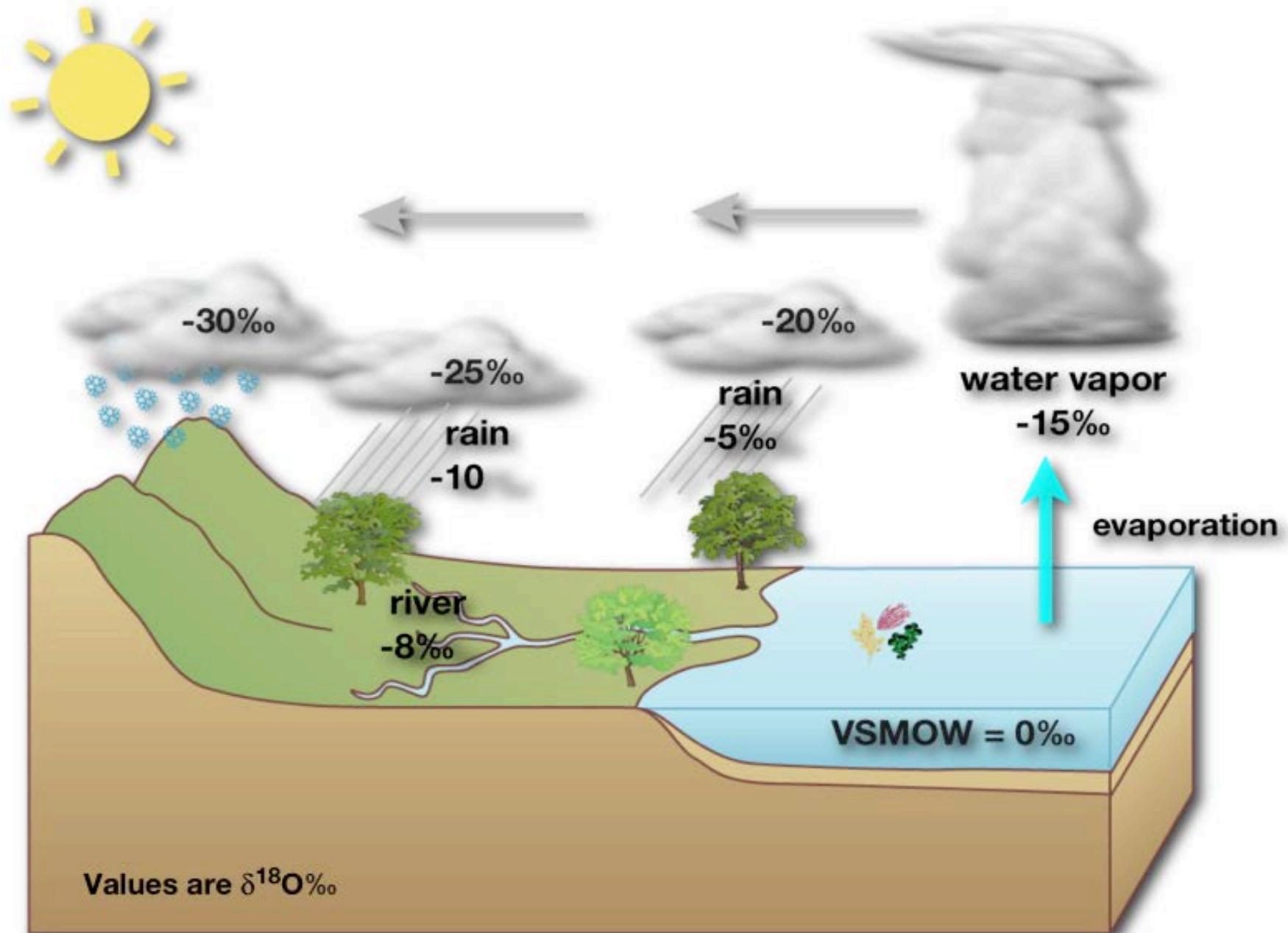
# Local Meteoric Water Lines

Coastal regions are similar to GMWL, but **continental regions** (cold) and regions with high evaporation have shallower slopes (4 to 6) and often a negative *d-excess*' (intercept) (examples below are surface waters)



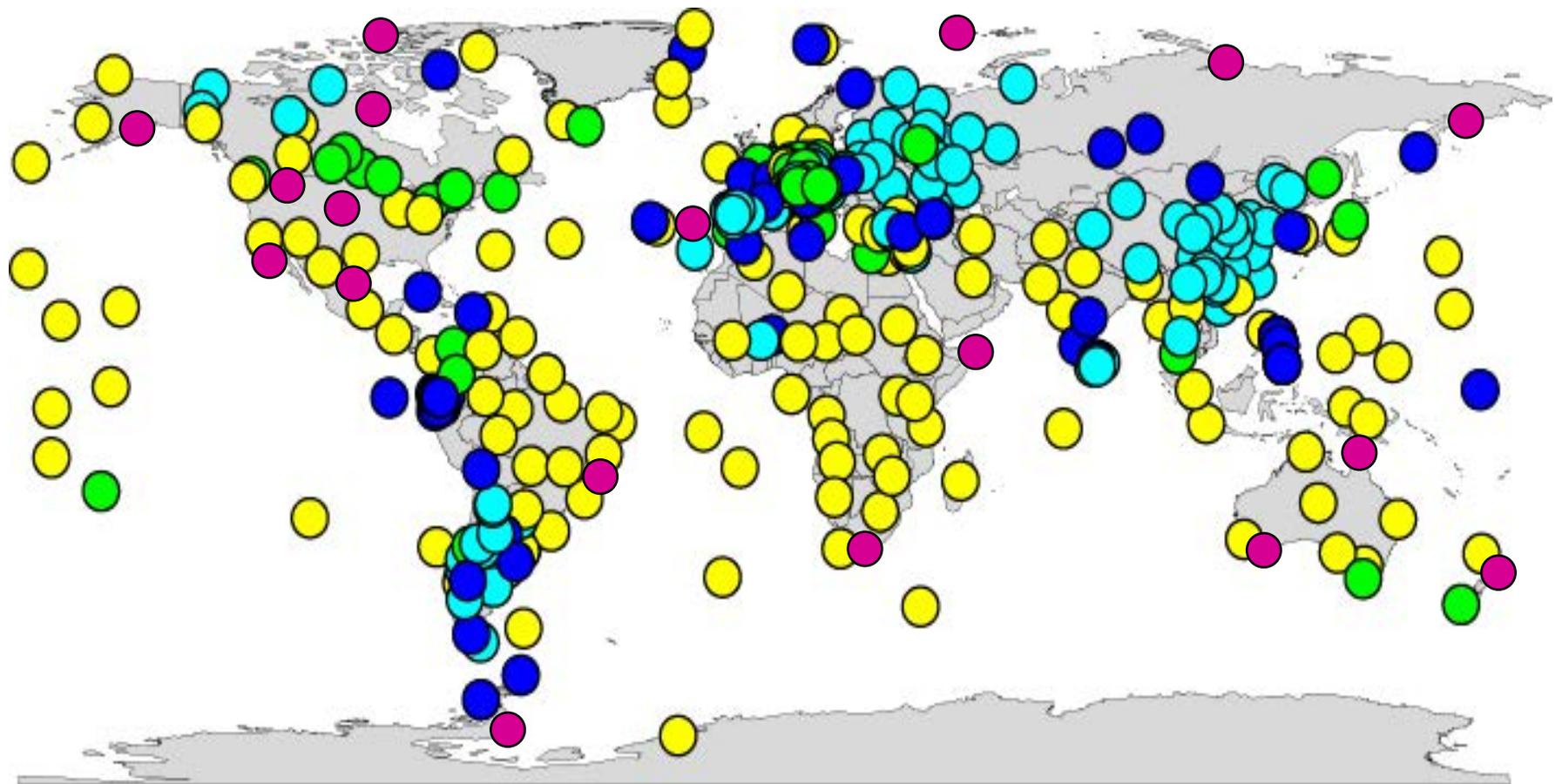
Questions?

# Spatial variability of O isotopes in hydrologic fluxes



# GNIP: Global Network for Isotopes in Precipitation

⊕ <http://isohis.iaea.org/>



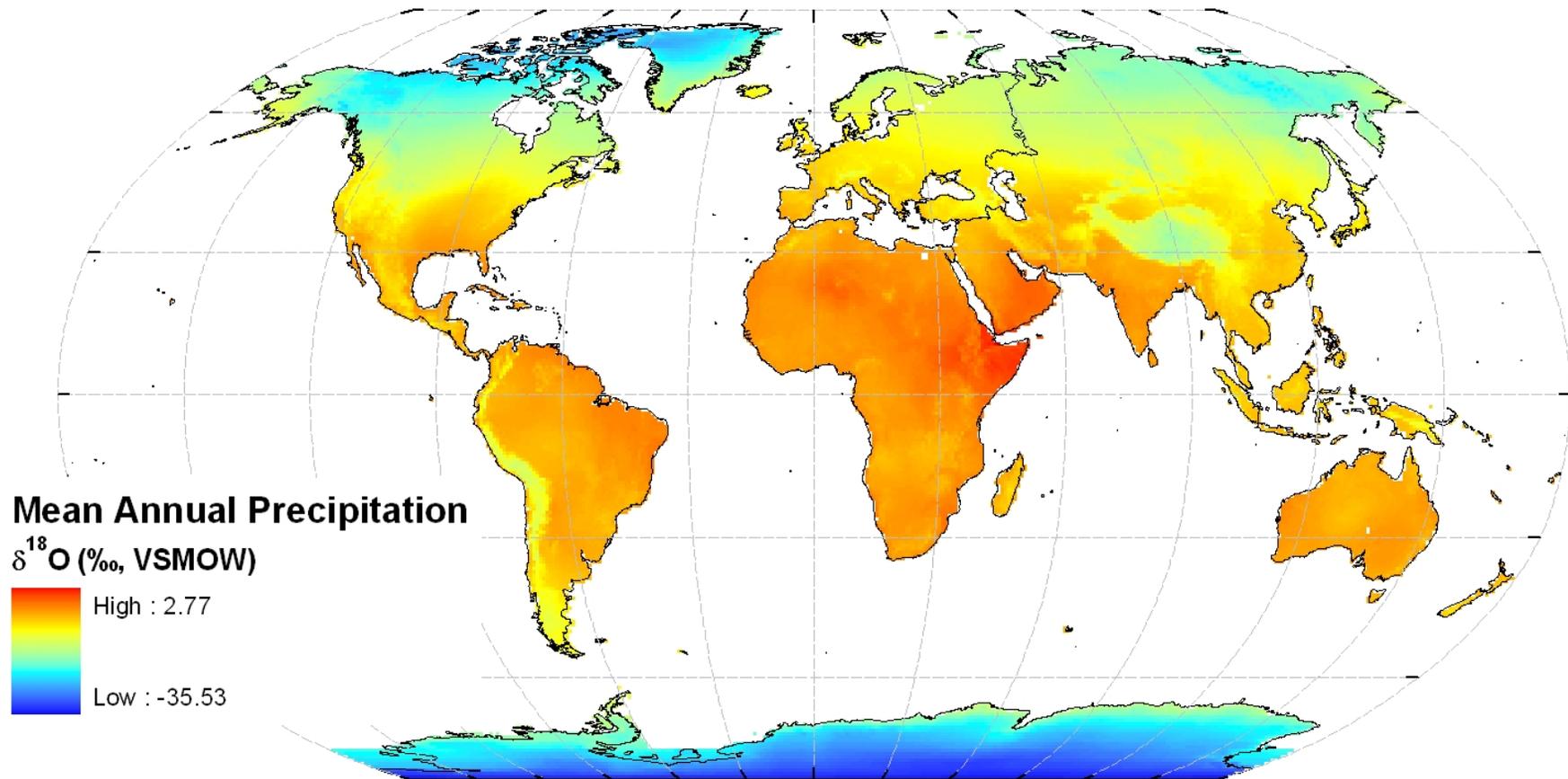
Year of First  $\delta^{18}\text{O}$  Observation

● 1960-1969 (n = 134) ● 1970-1979 (n = 47) ● 1980-1989 (n = 101) ● 1990-2000 (n = 66) ● 2007-present (n = 18)

# Stable Isotopes in Precipitation

Bowen and Revenaugh, 2003

[www.WaterIsotopes.org](http://www.WaterIsotopes.org)



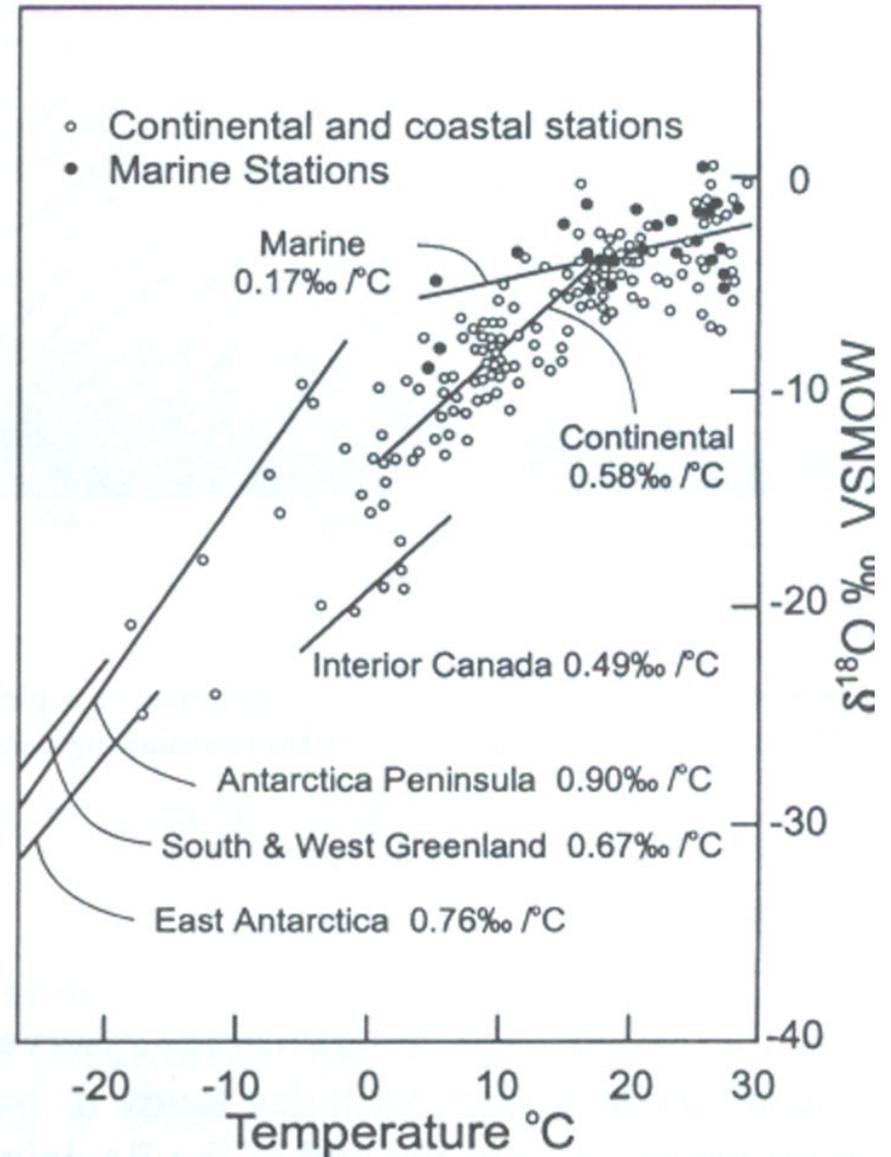
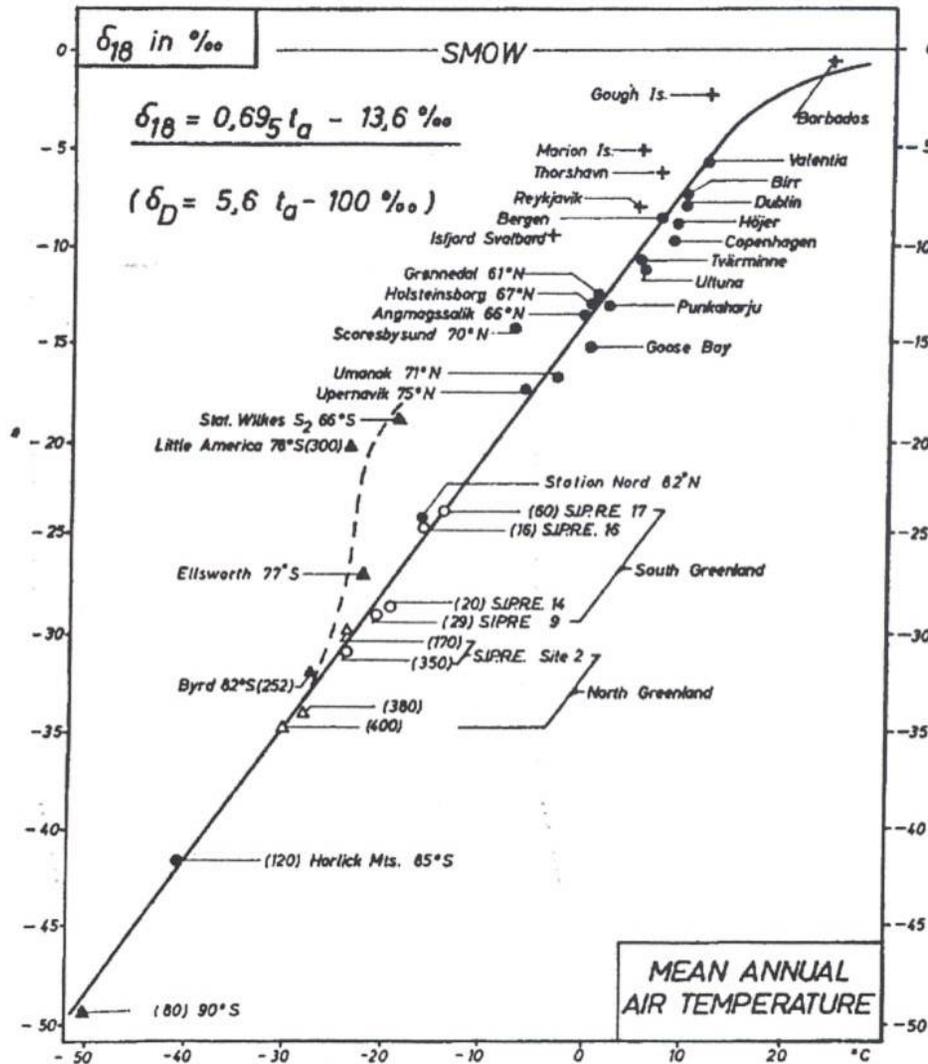
Processes behind Patterns?

# Temperature Effect

$$\delta^{18}\text{O} = 0.69 T_{\text{average}} - 13.6\text{‰}$$

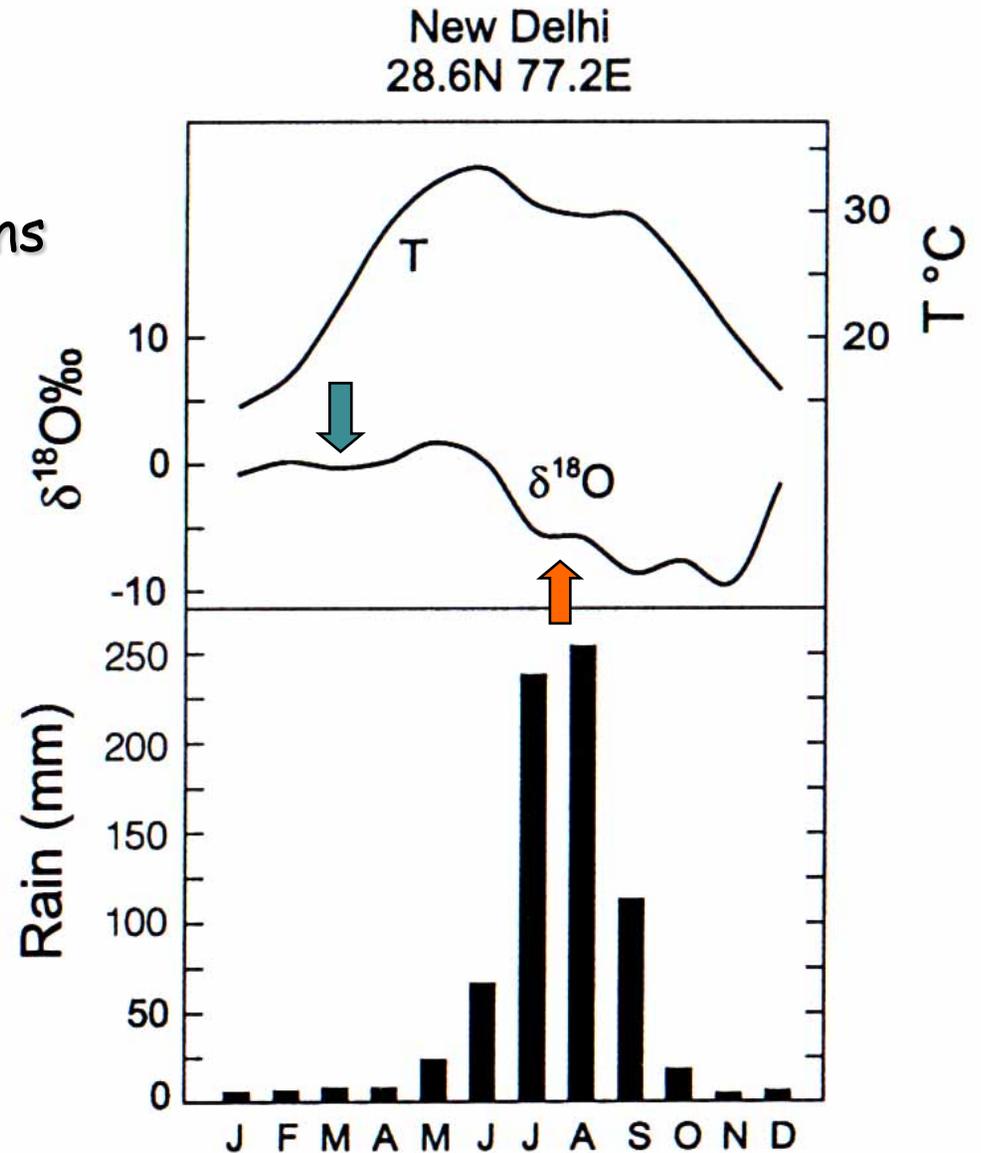
~

$$\delta^2\text{H} = 5.6 T_{\text{average}} - 100\text{‰}$$



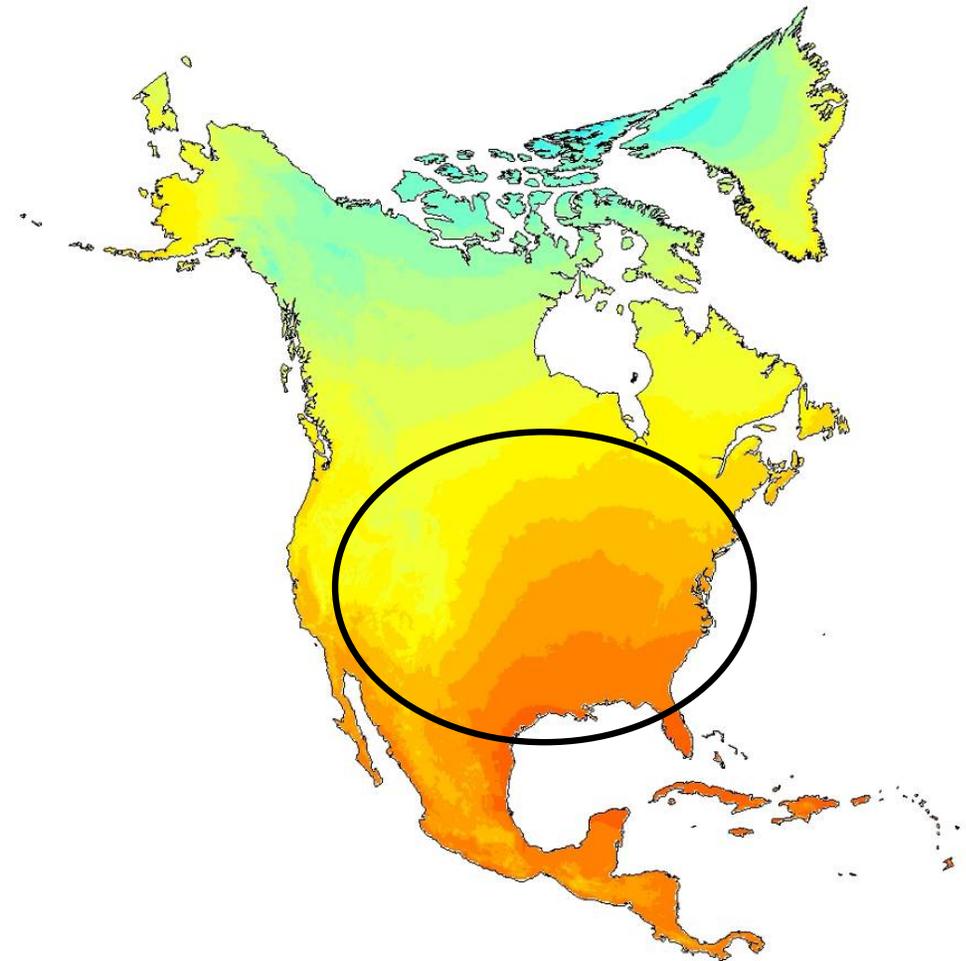
# Amount Effect

- ⊕ Precipitation isotope  $\delta$  values decrease with increasing amounts of rainfall (= rain out)
- ⊕ Generally follows the predictions of a Rayleigh model forced by lapse rate of cooling airmass

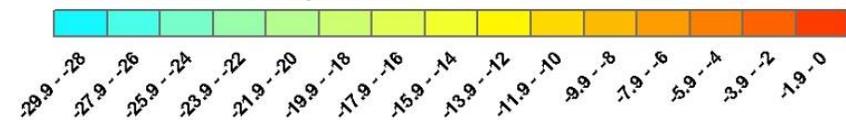


# Continental Effect

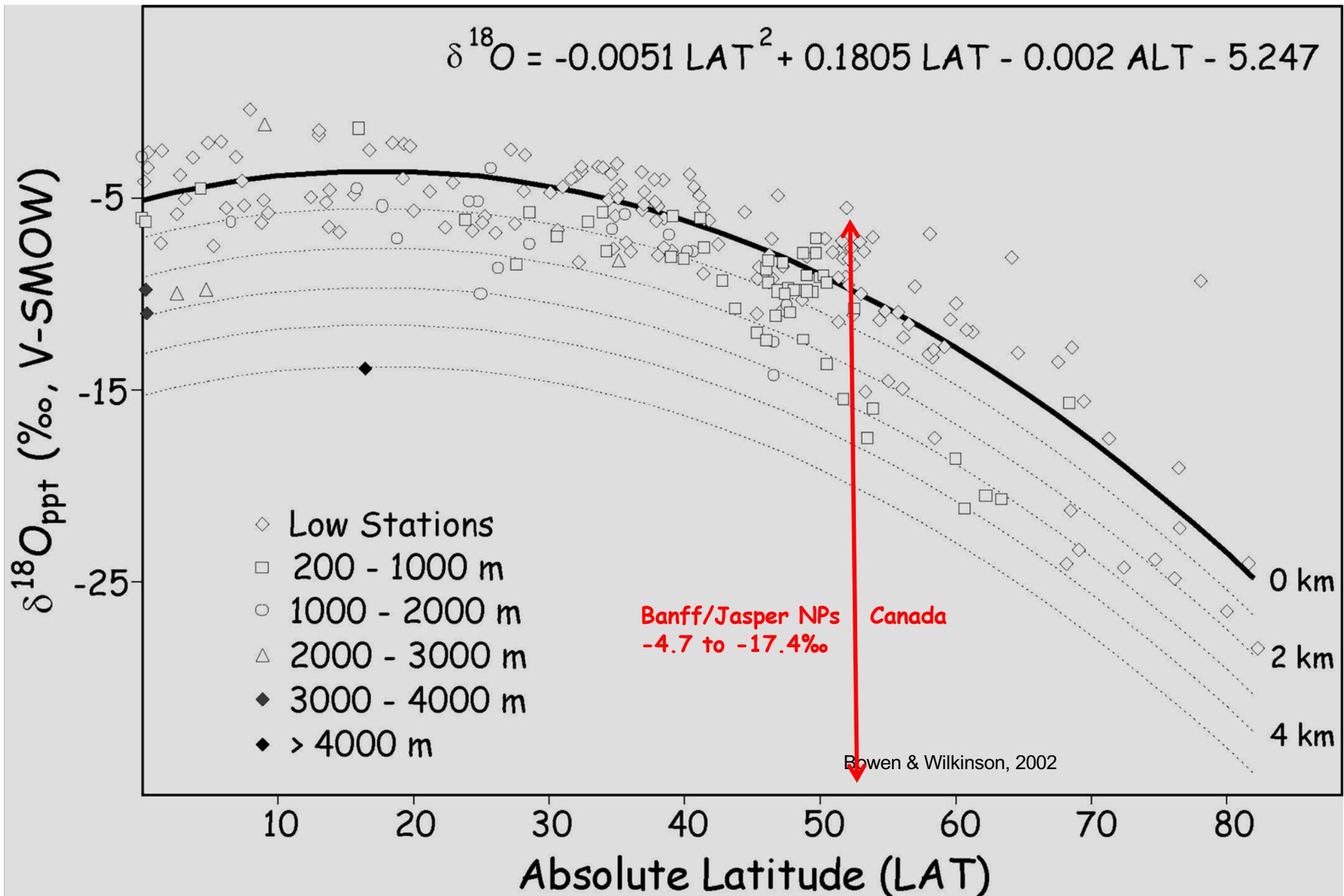
- ⊕ Precipitation isotope  $\delta$  values decrease towards **continental interior**
- ⊕ Reflects the fact that vapor is sourced from the oceans, **rains out** over the continents (+ winter precipitation [snow] is formed at **colder temperatures**)



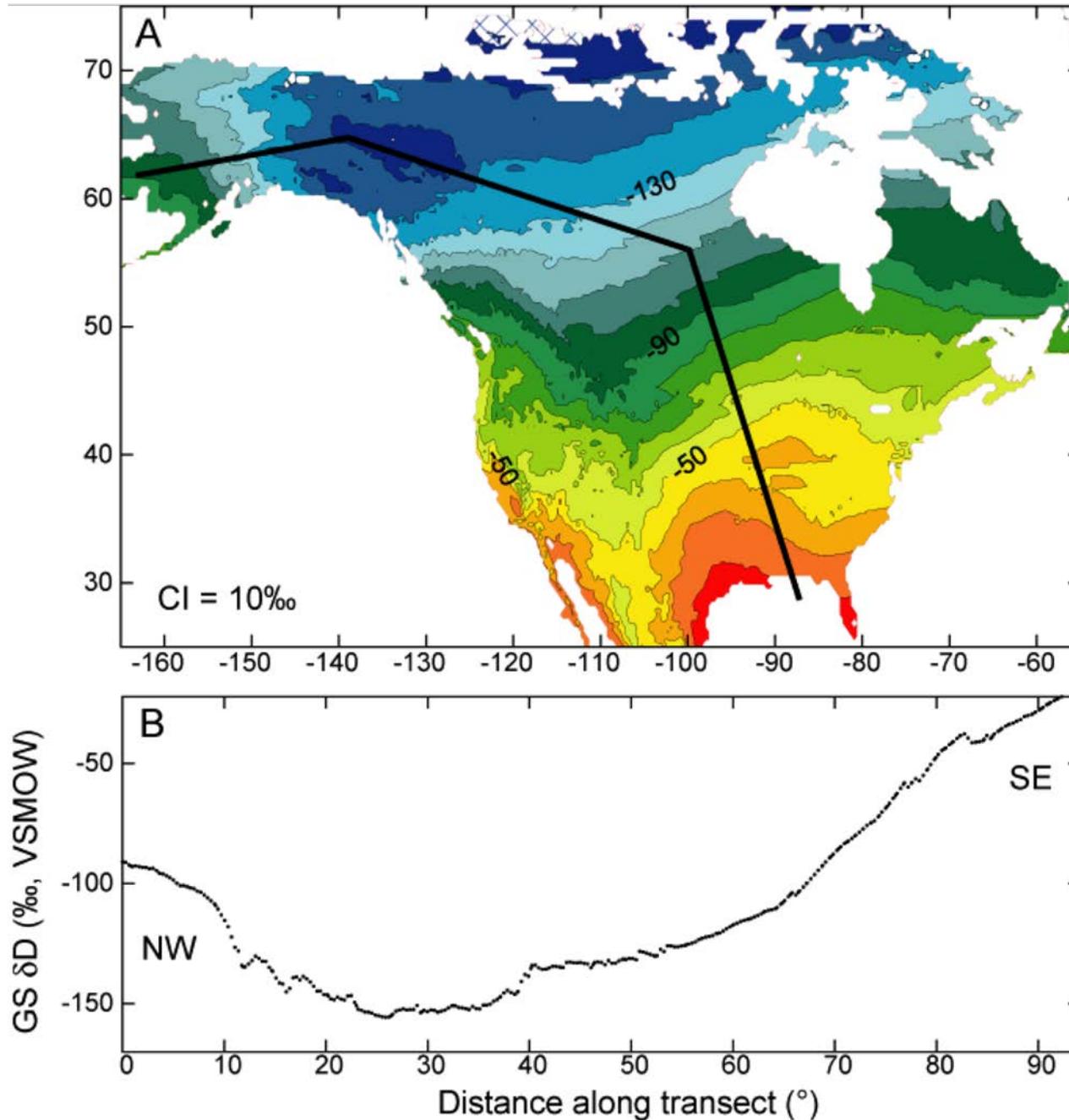
$\delta^{18}\text{O}$  of Annual Precipitation



# Latitude and Altitude Effects



# A North American IsoRoad Trip

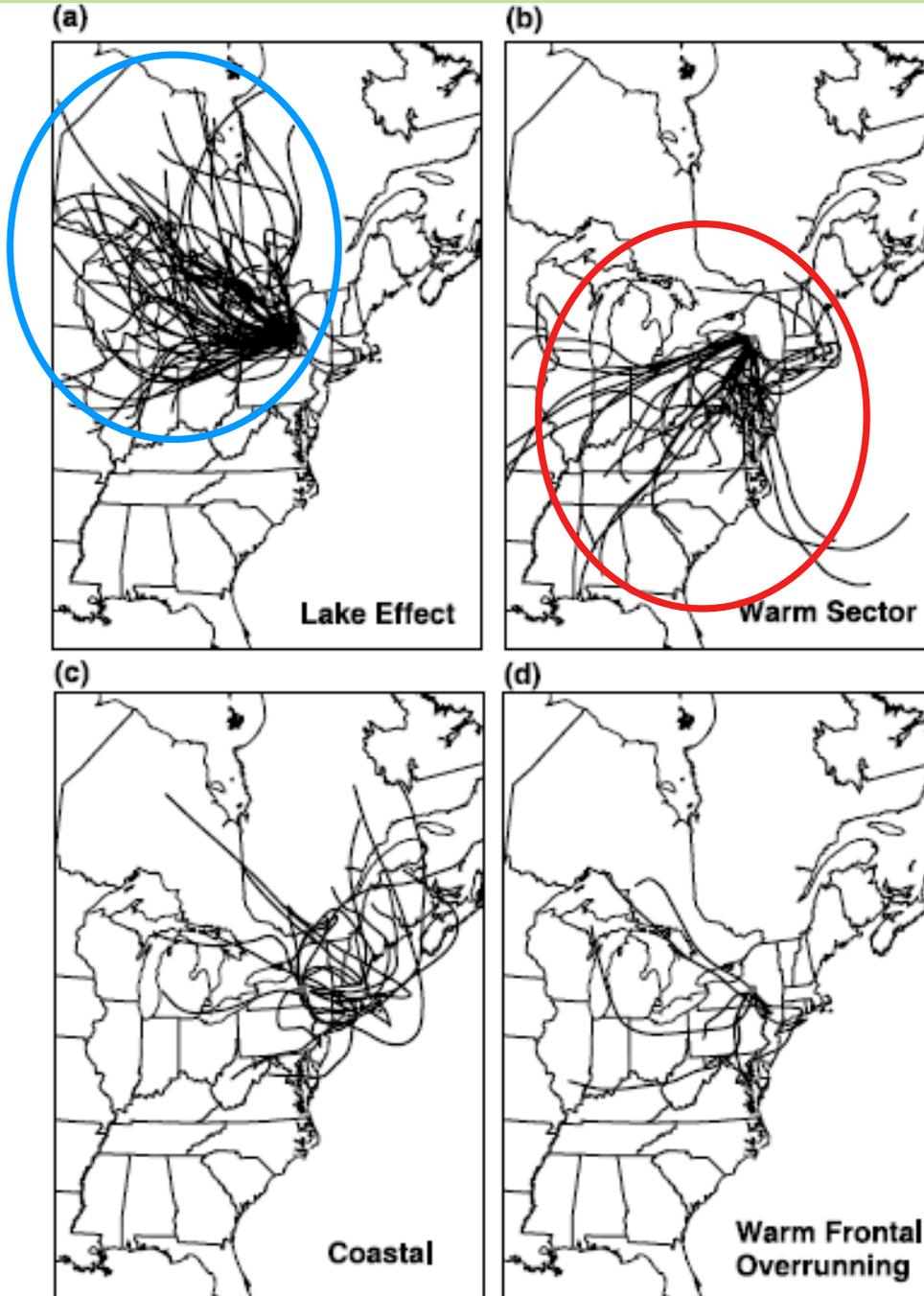


## Distillation in action:

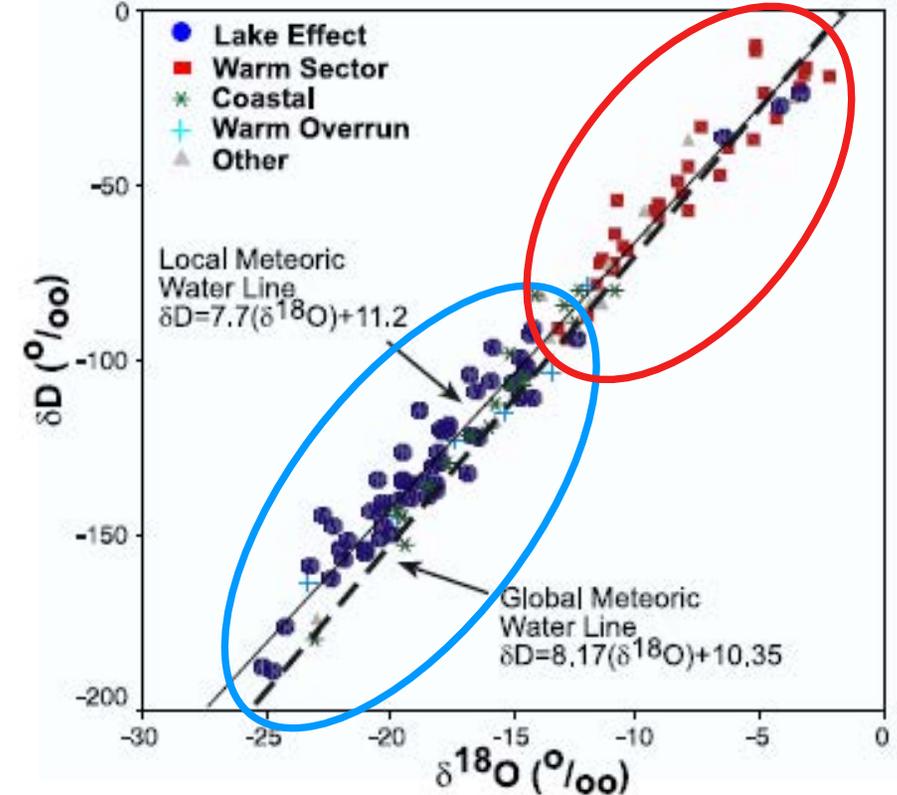
- Latitude effect
- Altitude effect
- Continentality

Bowen *et al.* (2005)  
*Oecologia* 143: 337-348

# Source Areas



Air mass history and source areas both affect precipitation isotope ratios



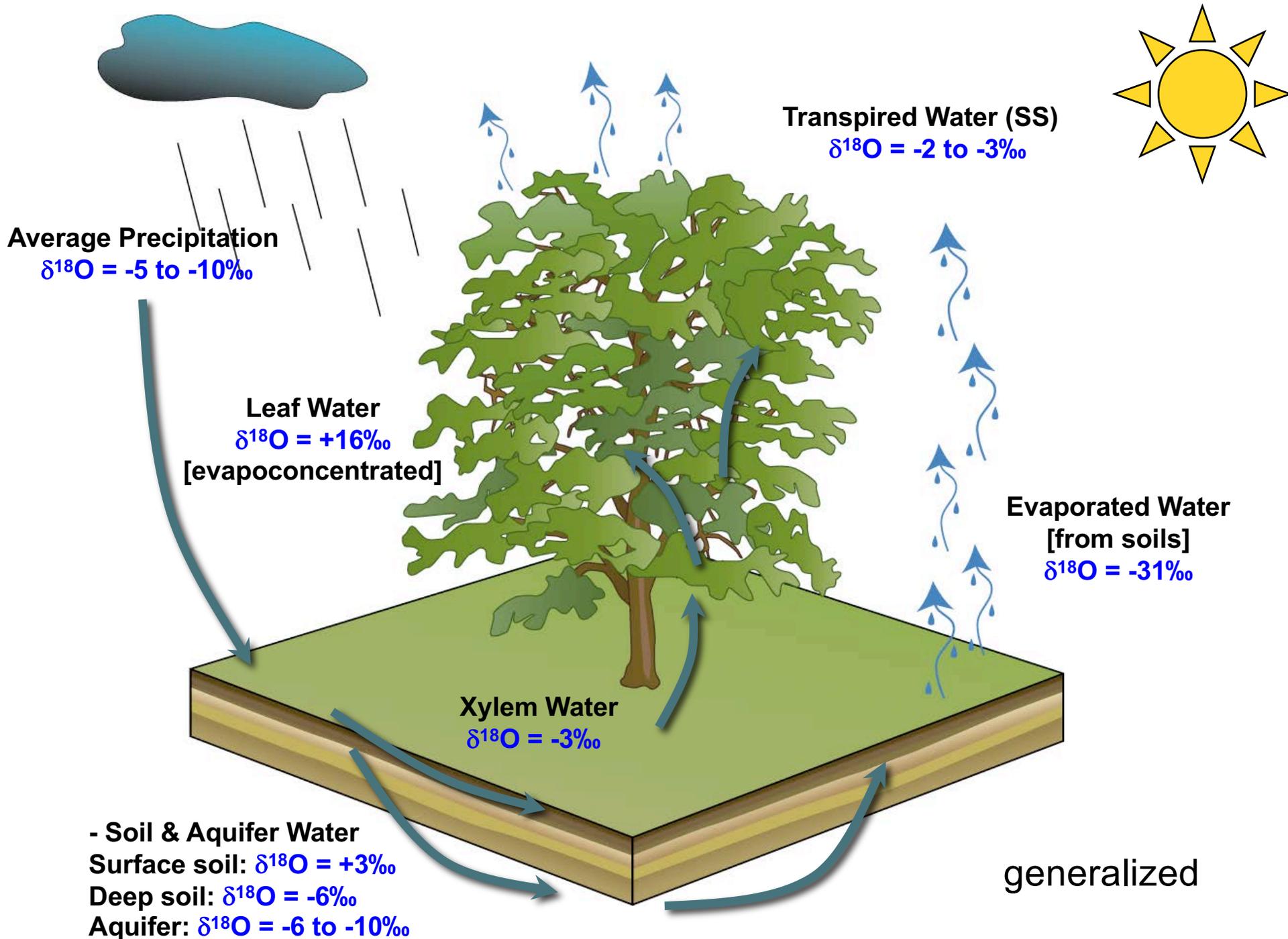
# Break Time



**Up next; following water into  
soils, plants and beyond**

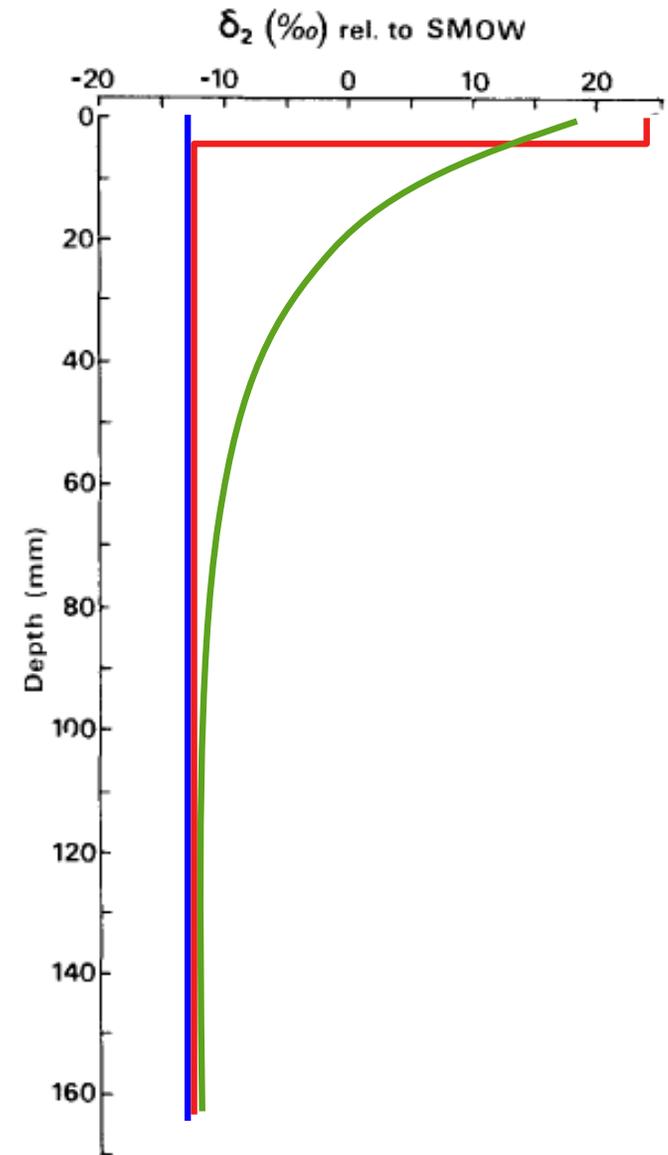
**What do we see or expect when  
analyzing soil and other sub-  
surface waters?**





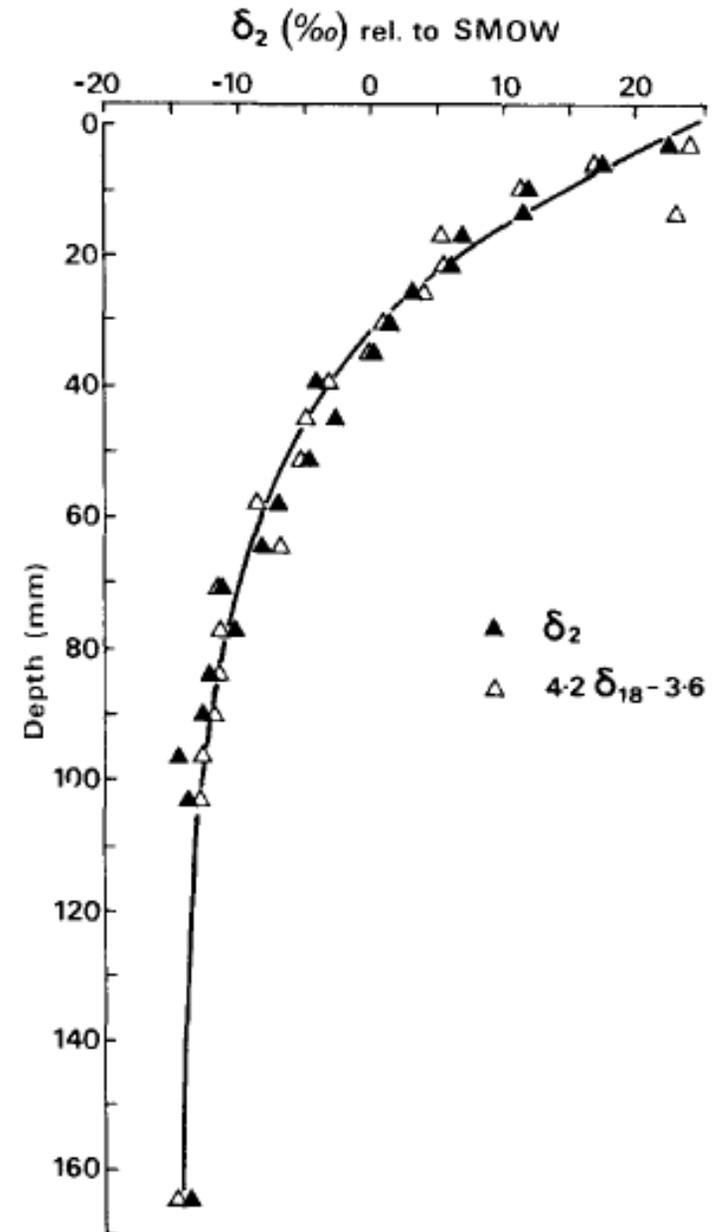
# Building a Soil Water Profile

1. Start w/dry soil
  2. Add rain and saturate
  3. Apply heat and evapoconcentrate
  4. Restore steady-state profile by diffusion
- In a saturated soil:
- ⊕ Highest  $\delta$  at surface
  - ⊕ Exponential decrease to  $\delta \approx$  precipitation  $\delta$  low in profile



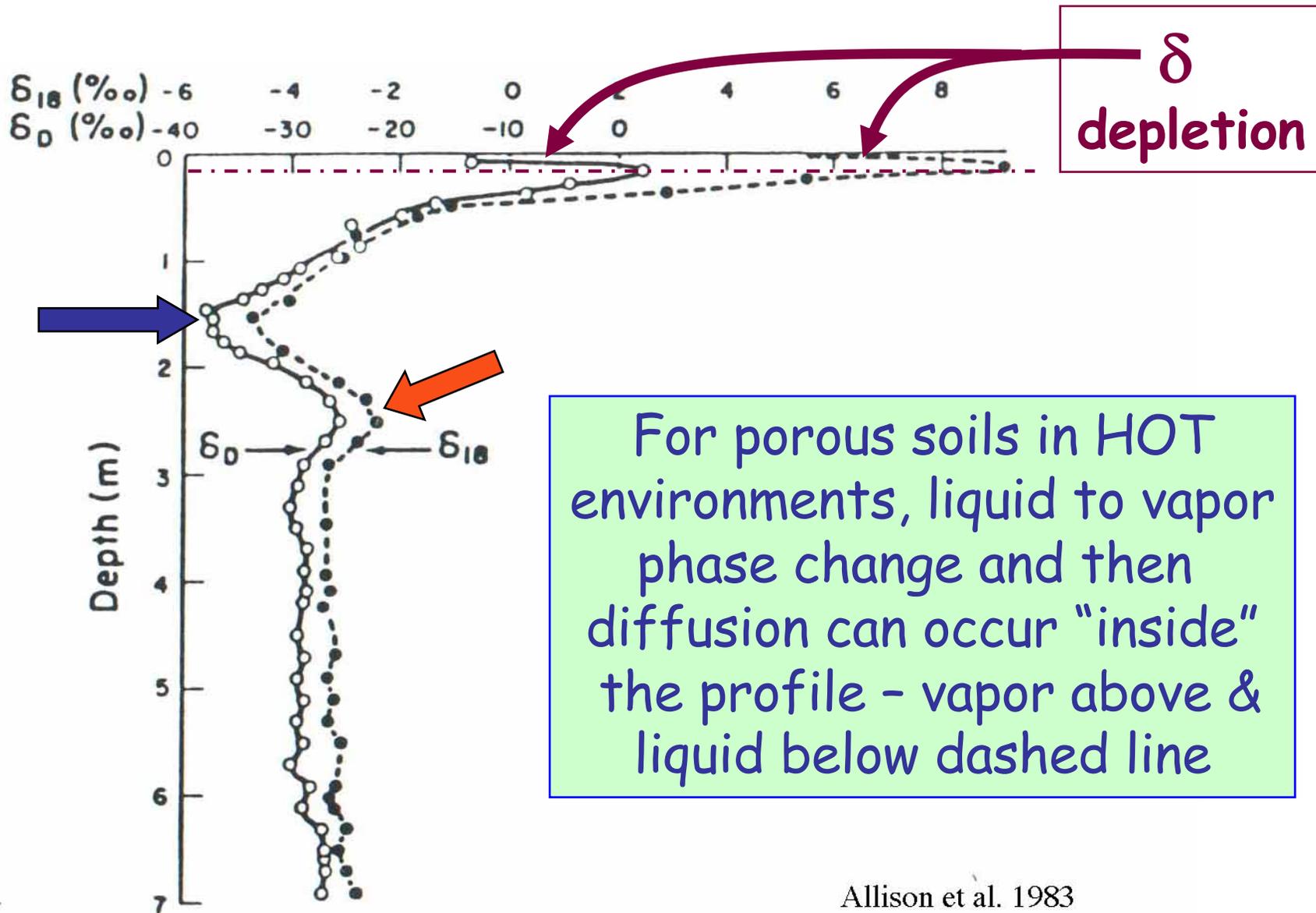
# Water in Soils

- ⊕ Soils act like reservoirs
  - ⊕ Water input
  - ⊕ Water flows through
  - ⊕ Evapoconcentration
- ⊕ But have their own flavor
  - ⊕ Not well mixed
  - ⊕ Flow rate varies widely in space and time
  - ⊕ High resistance to diffusion



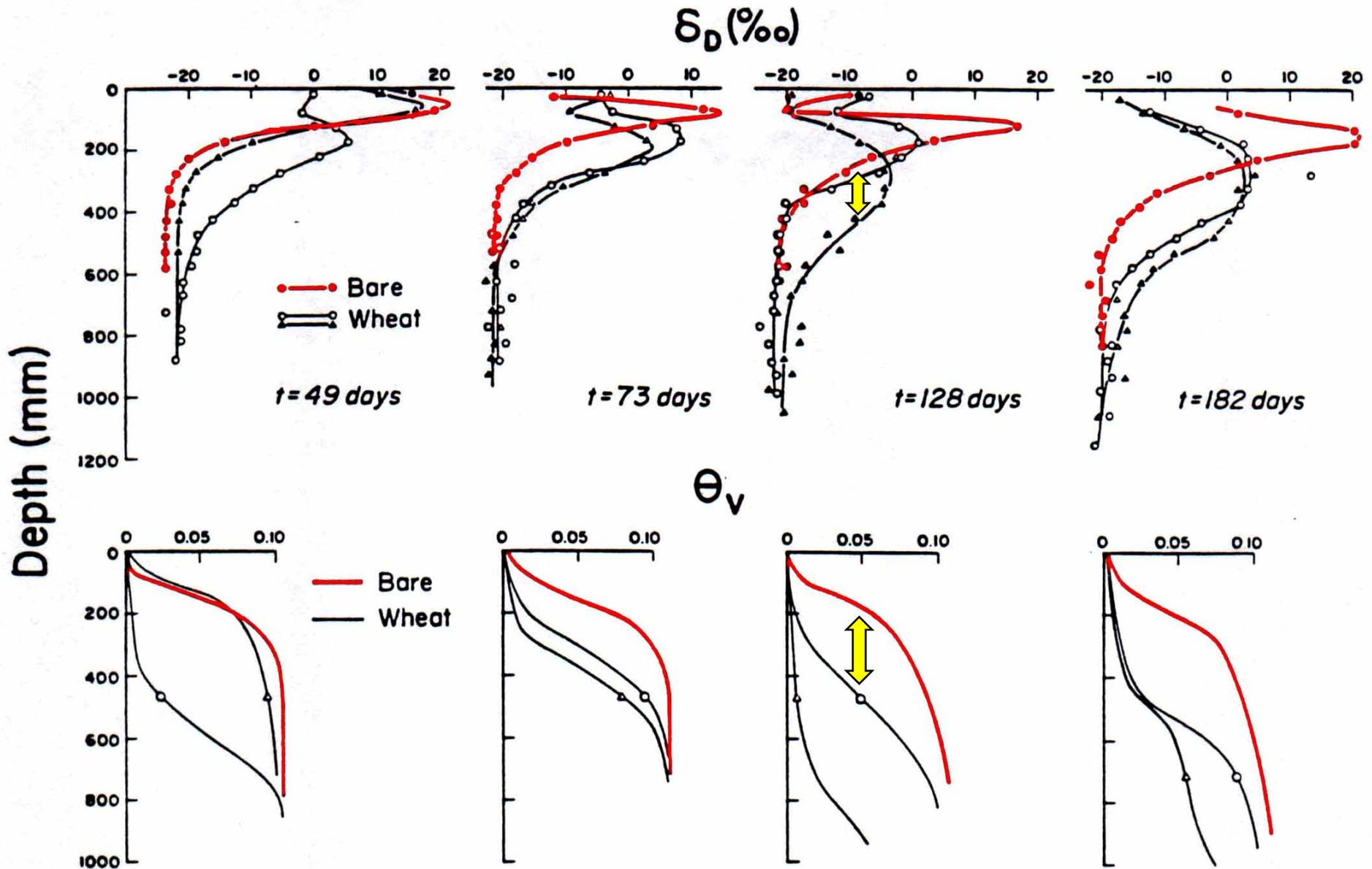
Barnes and Allison, 1988

# Soil Water Profiles



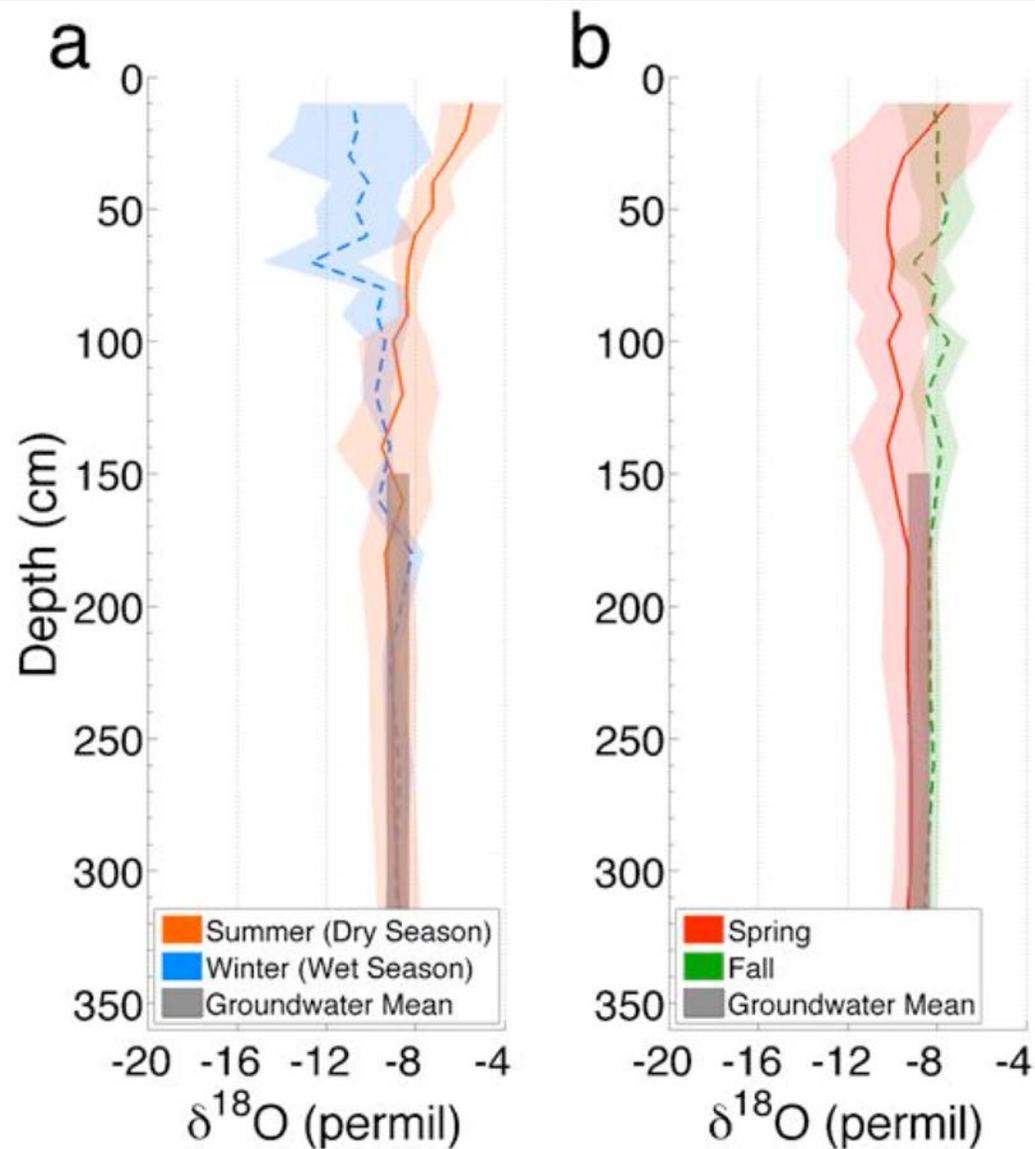
Depth profiles of  $\delta_D$  and  $\delta_{18}$  for a deep sand at Gawler, 25 km north of Adelaide.

# Soil Water $\delta^2\text{H}$ and water content ( $\theta_v$ )

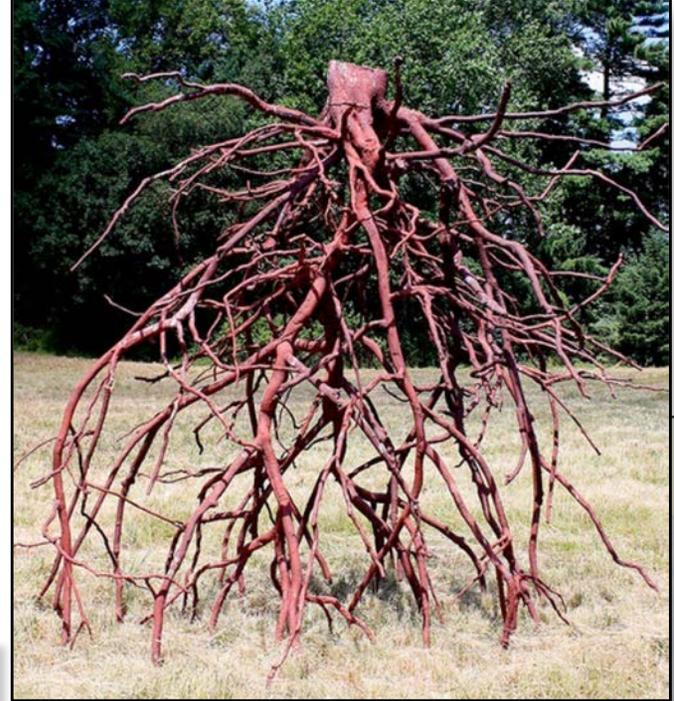


Depth profiles of  $\delta_D$  and volumetric water content  $\theta_v$  for laboratory pots, both bare and planted with wheat.

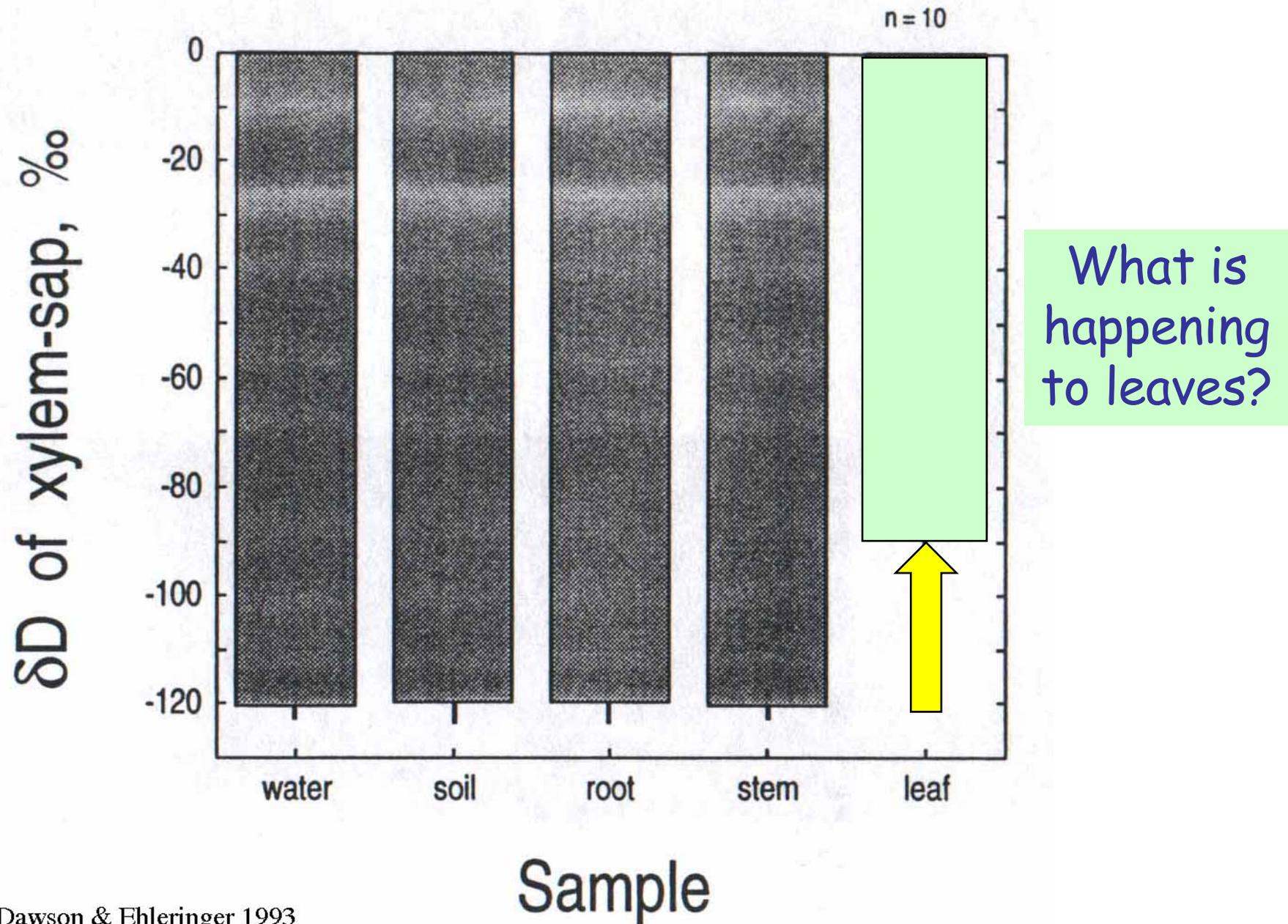
Spring (red), summer (orange), fall (green) and winter (blue) soil water oxygen isotope ratios ( $\delta^{18}\text{O}$ : lines = means; shading = 95% CI) for two periods in a mixed-species forest in N-central California (2008-2013)



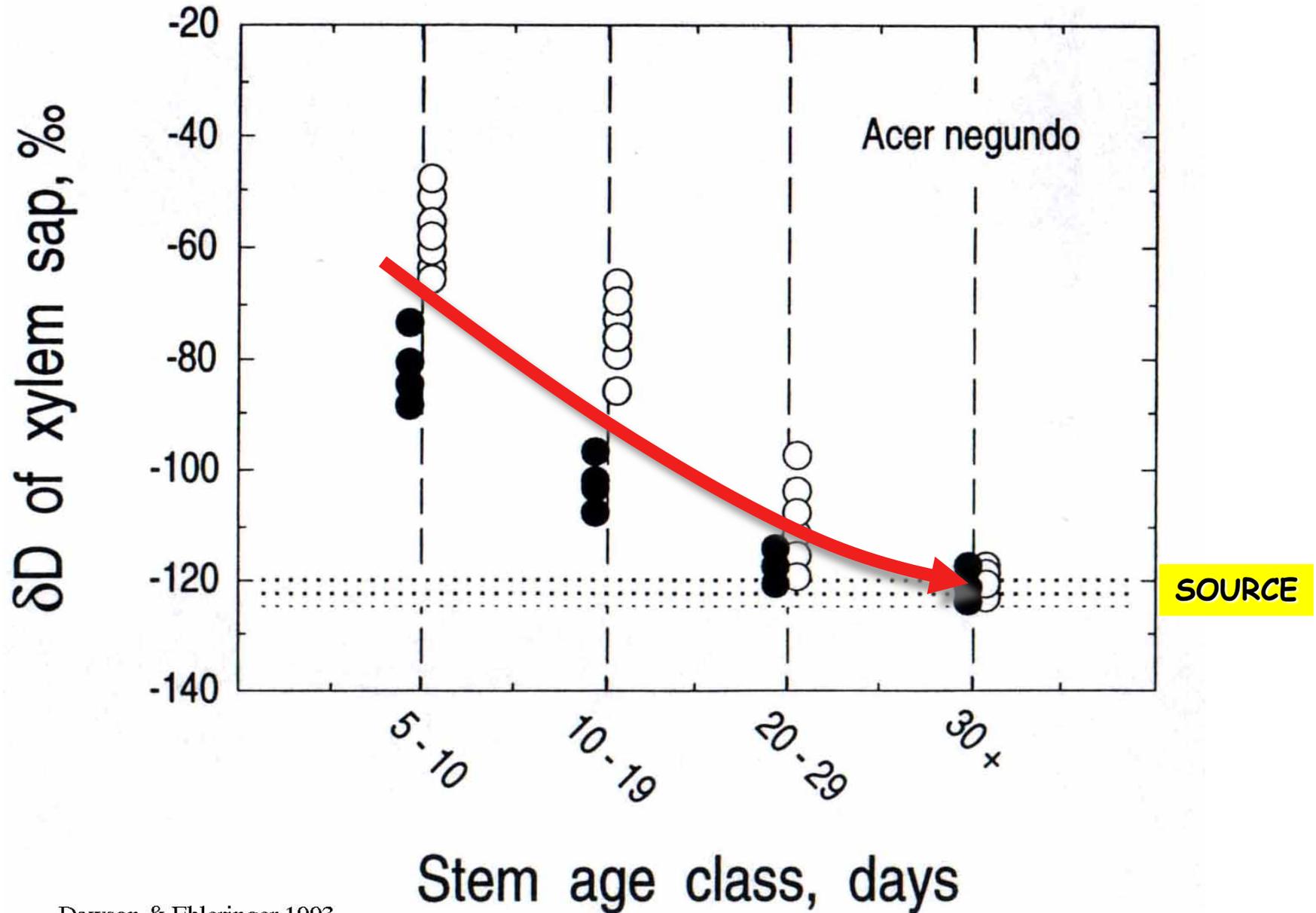
# Using D and O stable isotopes in water to identify patterns of water source utilization by plants



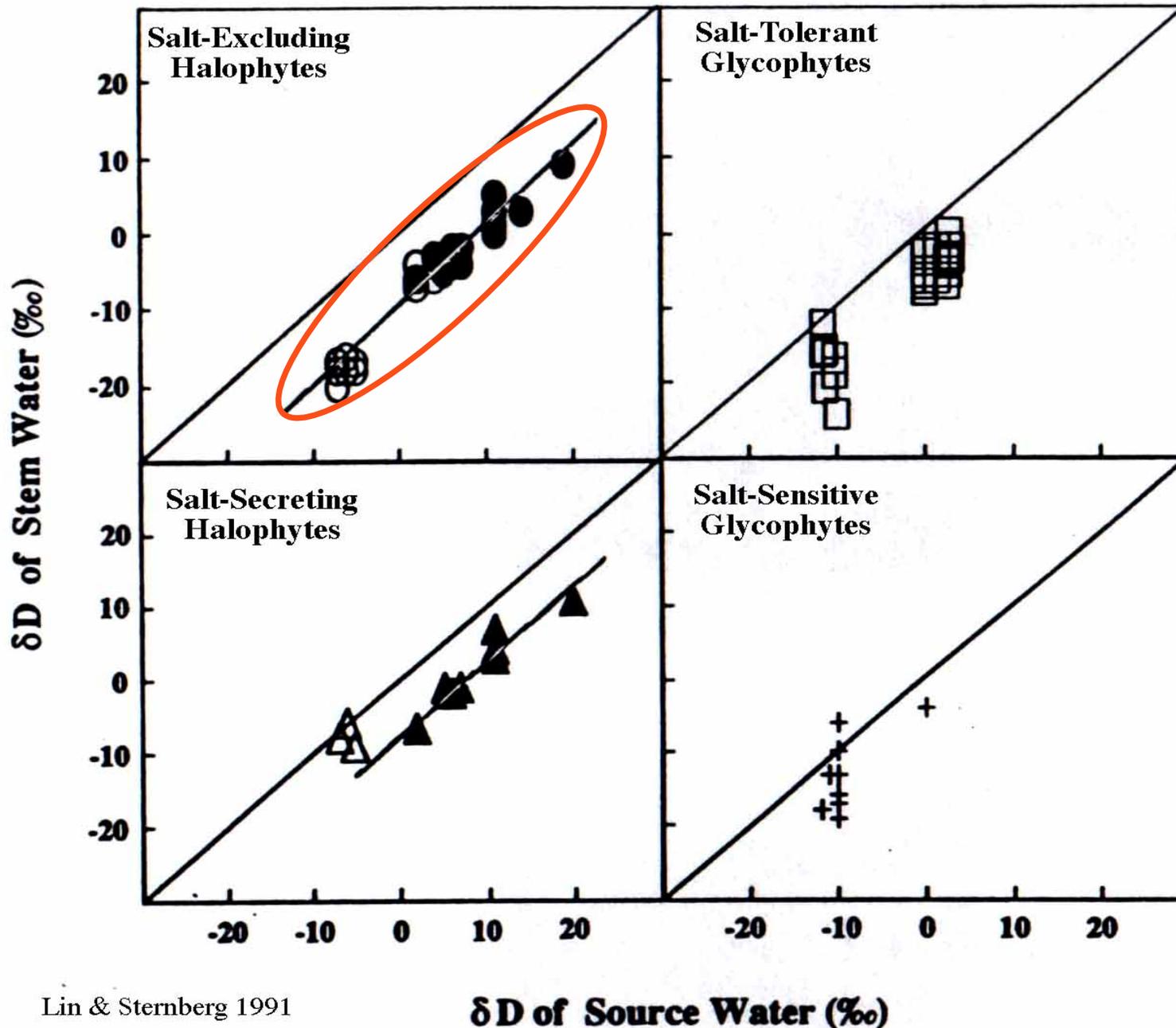
# Does Fractionation in Plant Water Exist?



# And . . . not all stems are created equally



# Fractionation Can Occur in Halophytes



Root membranes can act as isotope "filters"

Water aggregates at the outside of the root

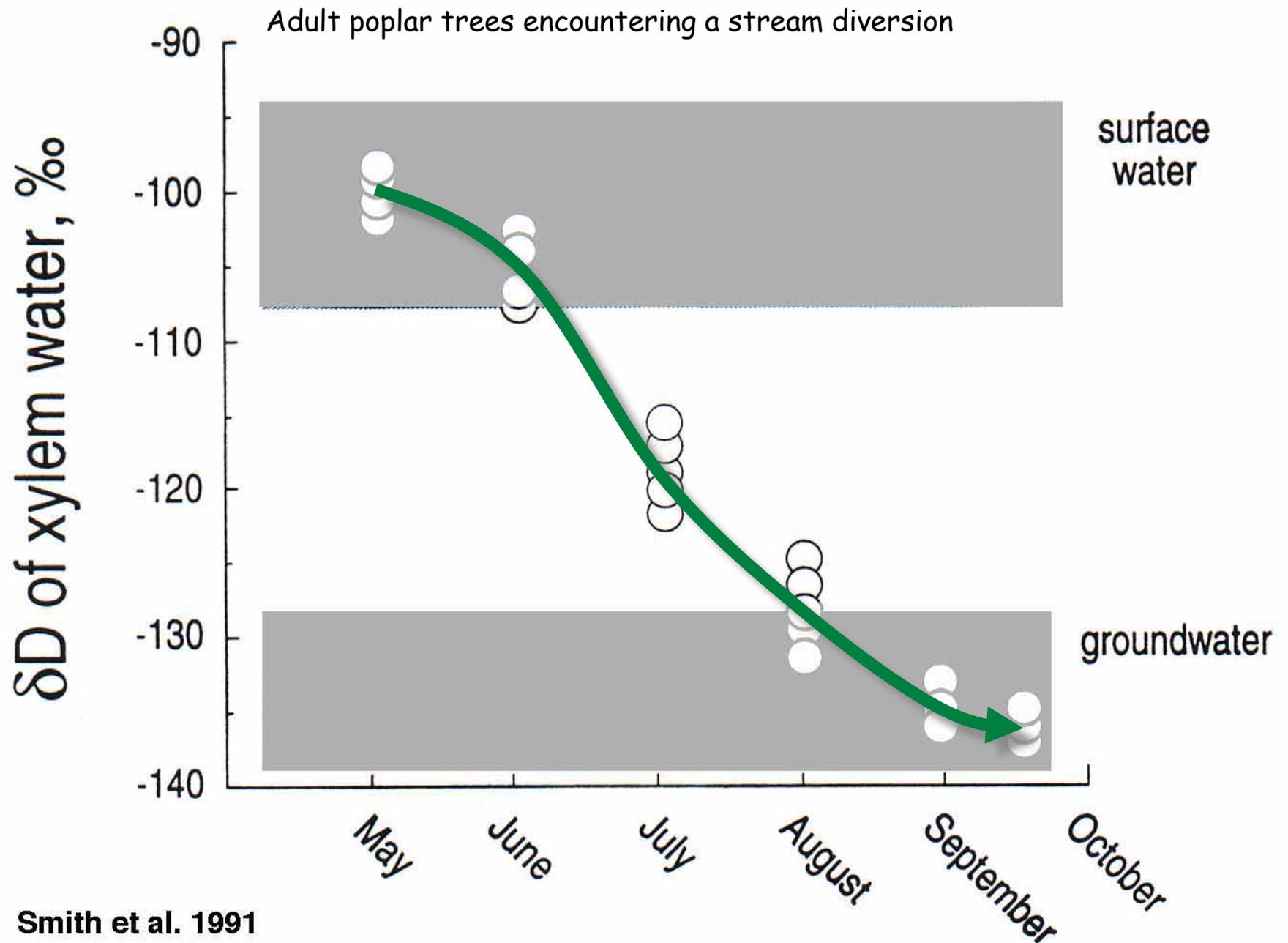
H-bonds break constantly but H-H more than D-H

D-H bonds are much stronger than H-H bonds leaving "source" water enriched relative to stem waters

# Using stable isotopes to identify patterns of water utilization by plants:

- ★ Identification of differential water-source utilization (e.g., groundwater, deep & shallow soil water, fog, rain pulses . . .)
- ★ Intra- and interspecific resource competition and community water-use patterns
- ★ Plant effects on hydrological processes (e.g., hydraulic redistribution, water cycling, transpiration vs. evaporation)

# How does water source use vary seasonally?



Are all these plants using the same water source(s)?



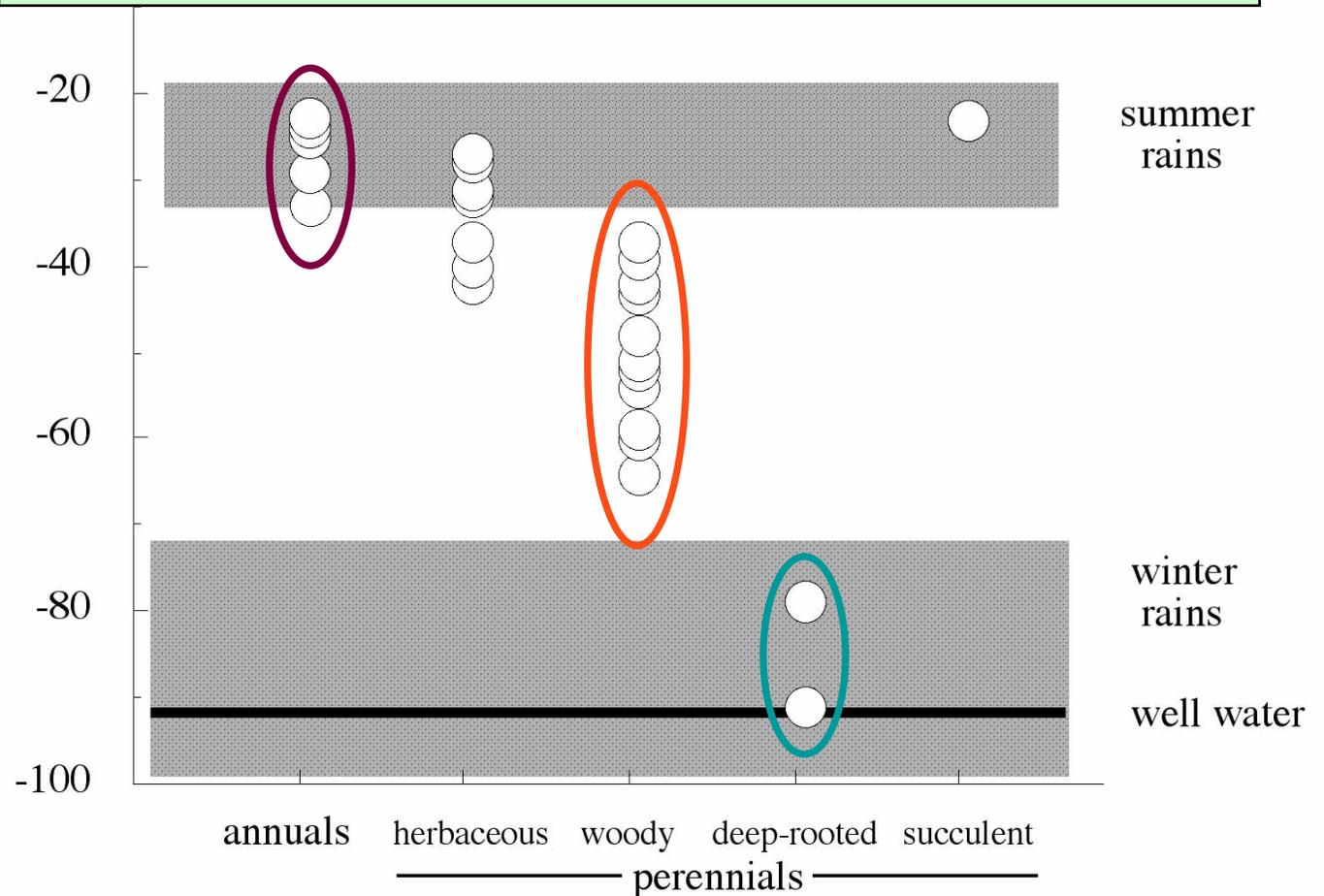
Photo: Da-Sandquist

# Interspecific Water-use Differences

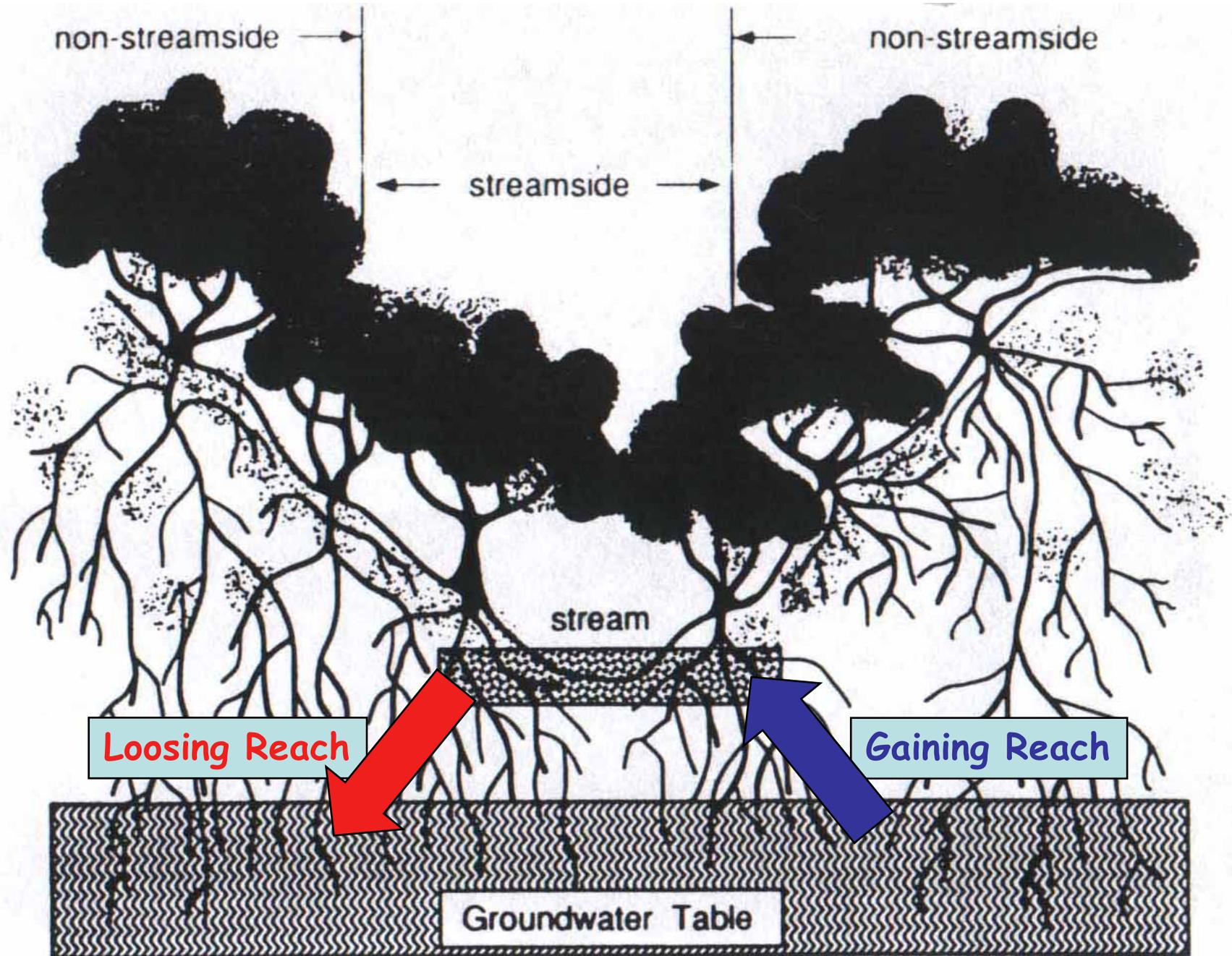
Cold desert shrub community at Stud Horse, Utah

Can this sort of niche-partitioning among species help explain the high biodiversity on this otherwise water limited desert?

$\delta D$  of xylem water (‰)



# Intraspecific Resource-use Variation



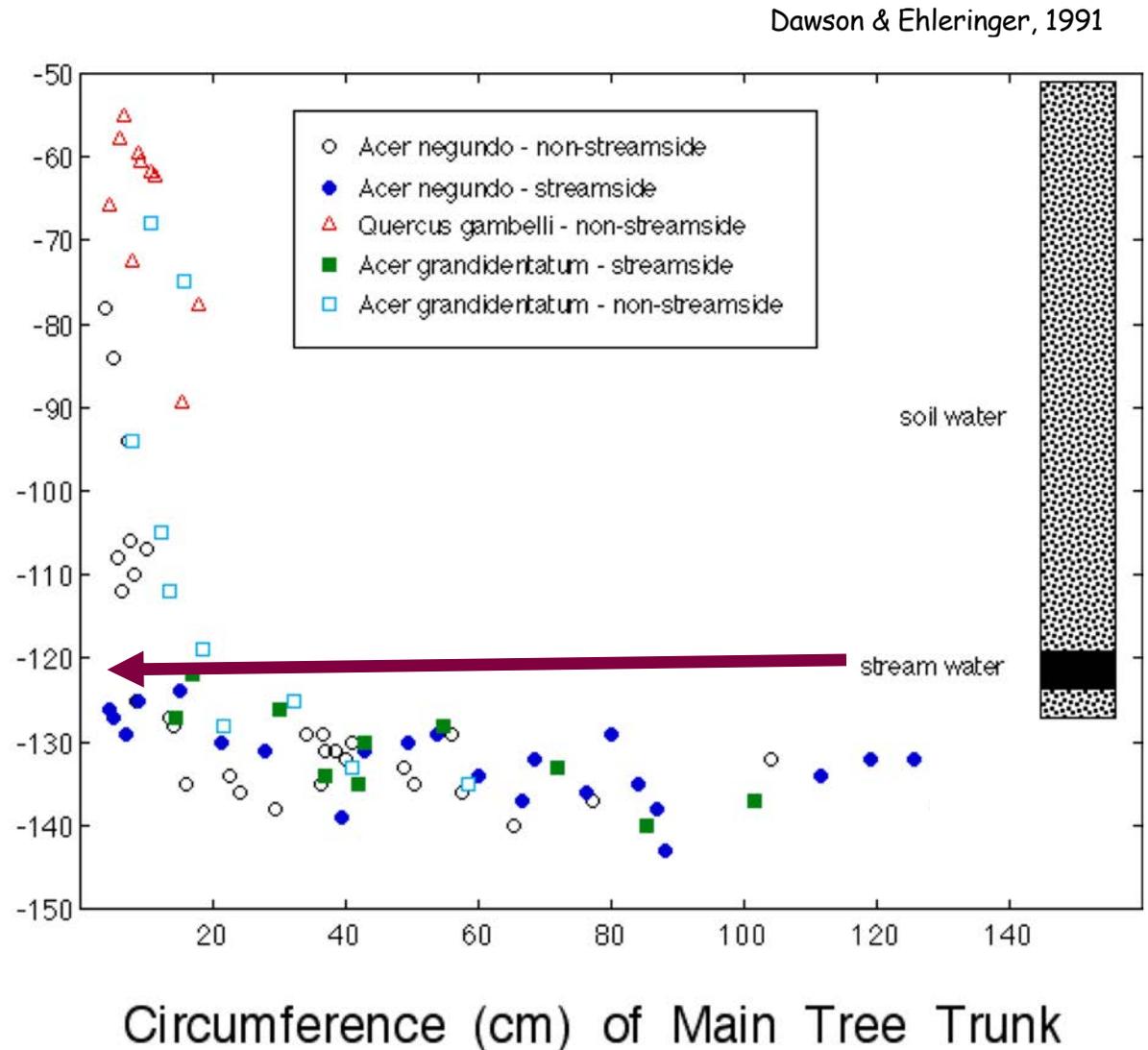
# DA! - what water sources do riparian plants use?

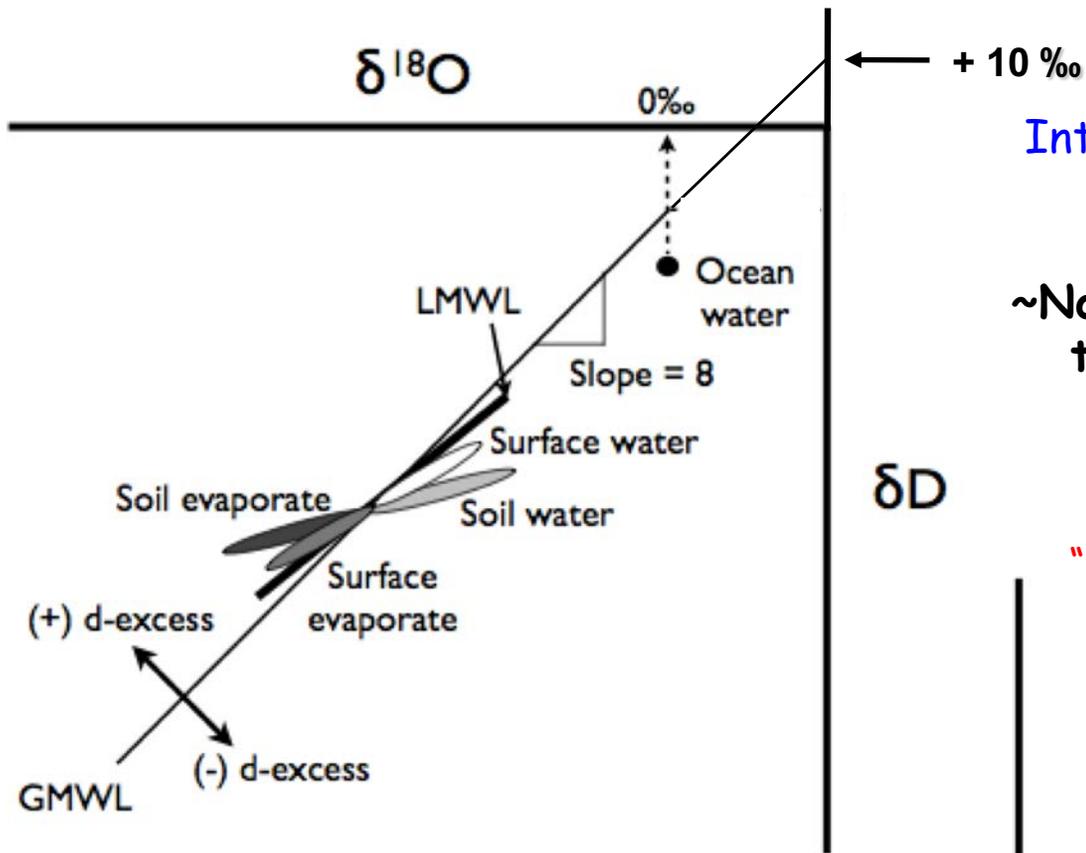
## OBSERVATIONS:

Medium-sized trees or larger of both the maple species at streamside and non-streamside sites do NOT appear to be using the stream water . . .

What's missing?

Hydrogen isotope ratio of Xylem-water, ‰

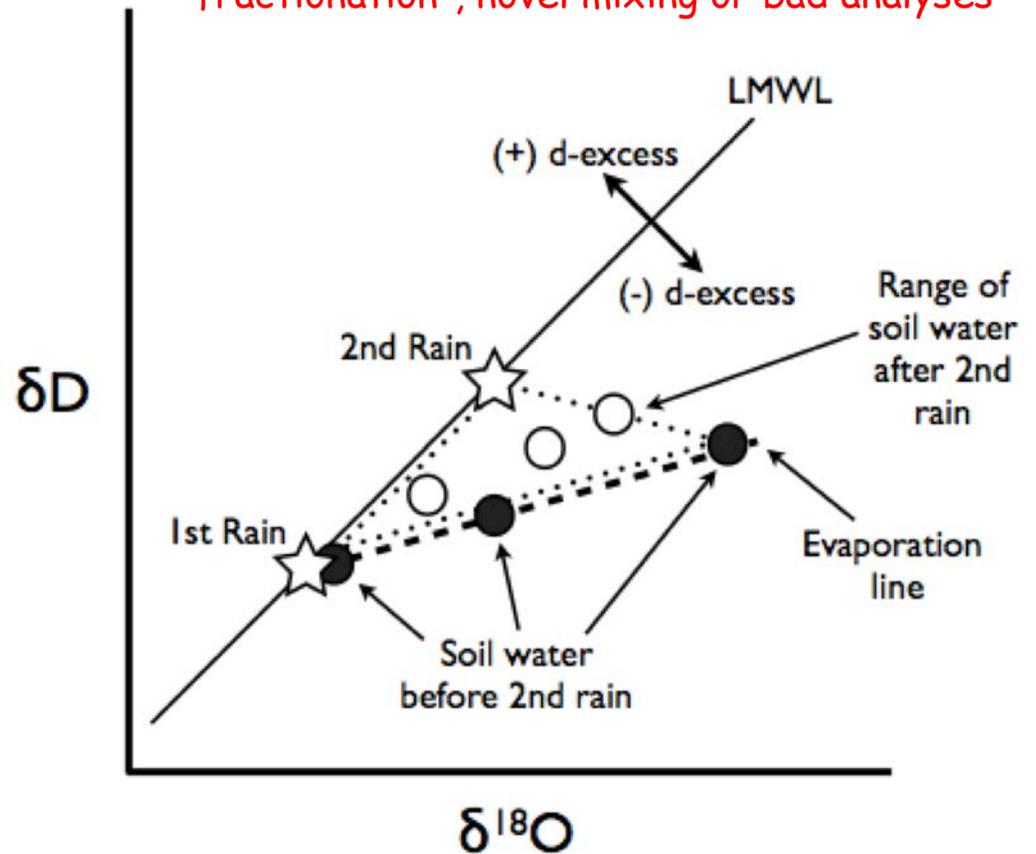




Integrating Meteoric Water Modifications into soil-plant studies

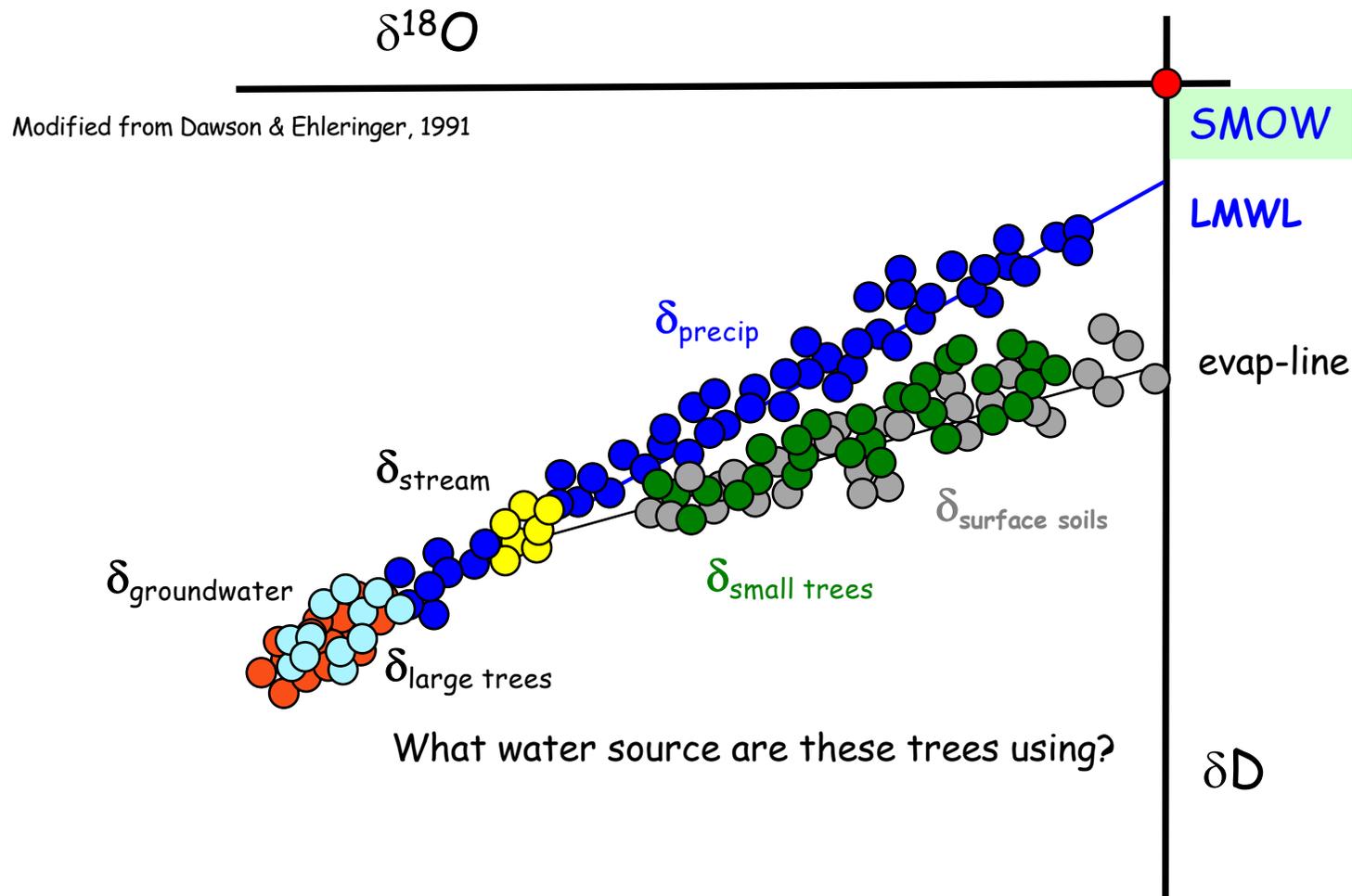
~Note the dotted-line provides a "mixing" triangle that many/most plant roots will have access to~

Falling outside this triangle implies "fractionation", novel mixing or bad analyses



From: Dawson and Simonin, 2011

# No really - what water sources do riparian plants use?

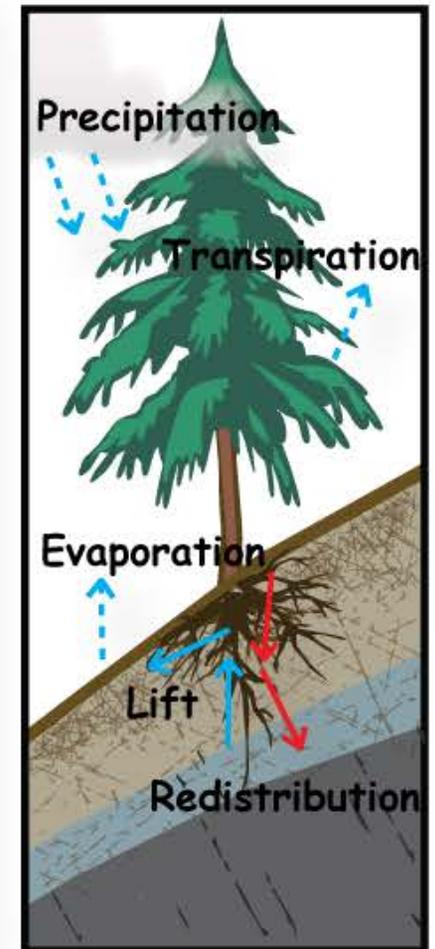
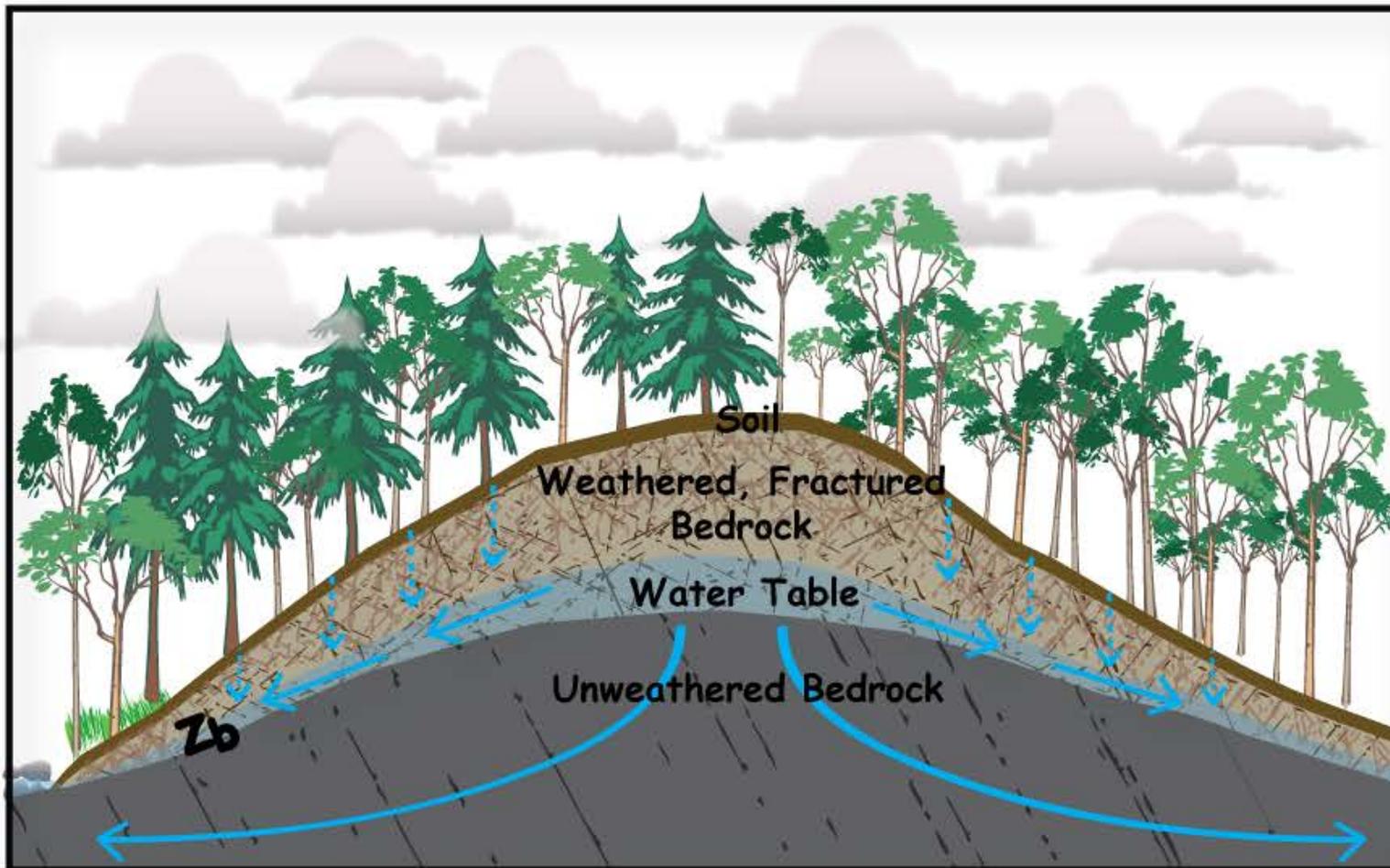


Using isotope analyses of **ALL** water sources revealed that as tree grew larger they were not using the "most likely" water source but the most reliable one!



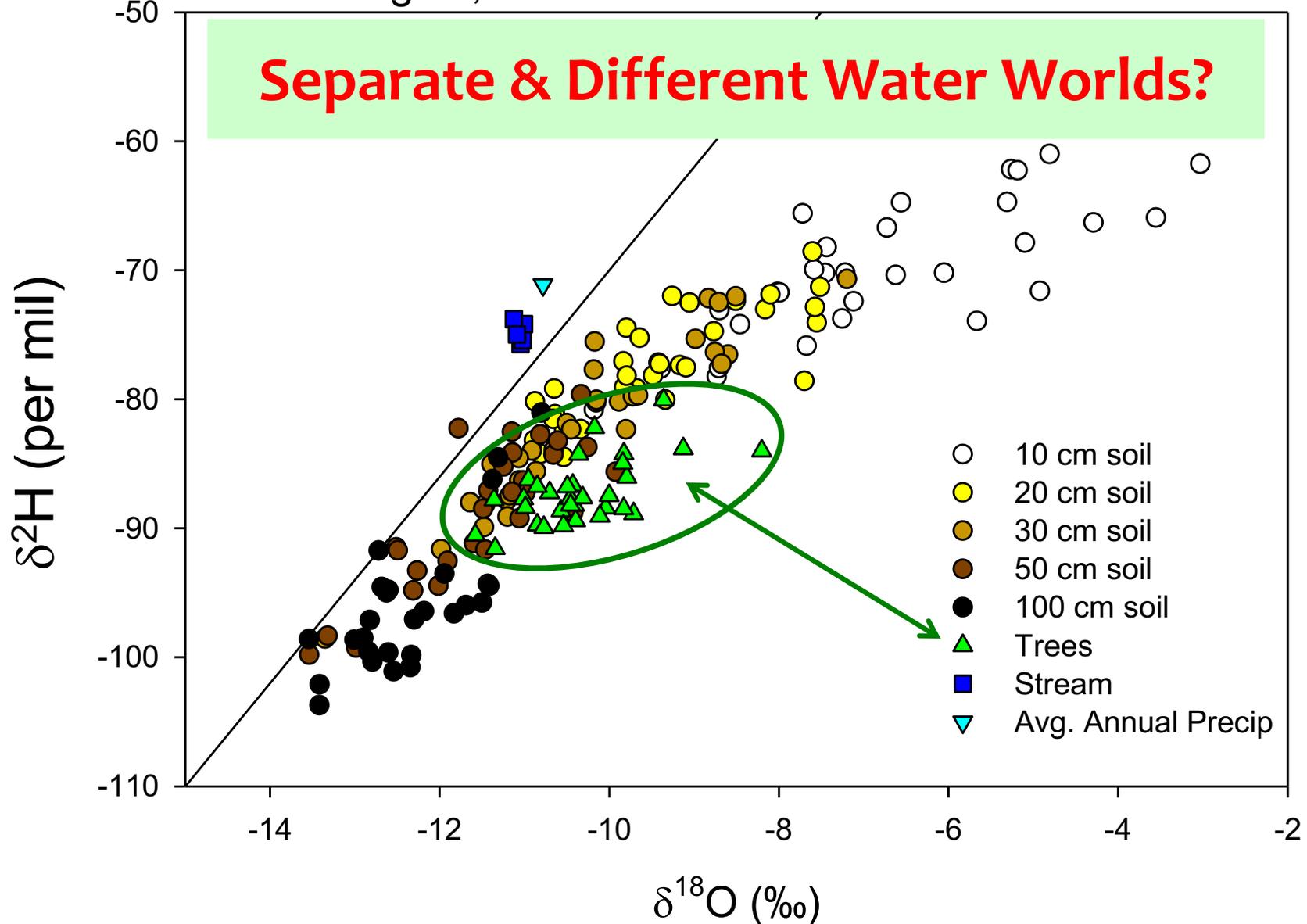
## What lies beneath?

LINKING water & watersheds to the  
Plants using isotopes



# Soil and Plant (tree) Waters Differ from the Stream Water

WS-10 August, 2005



Brooks, J.R., H. Barnard, R. Coulombe and J.J. McDonnell. 2010.

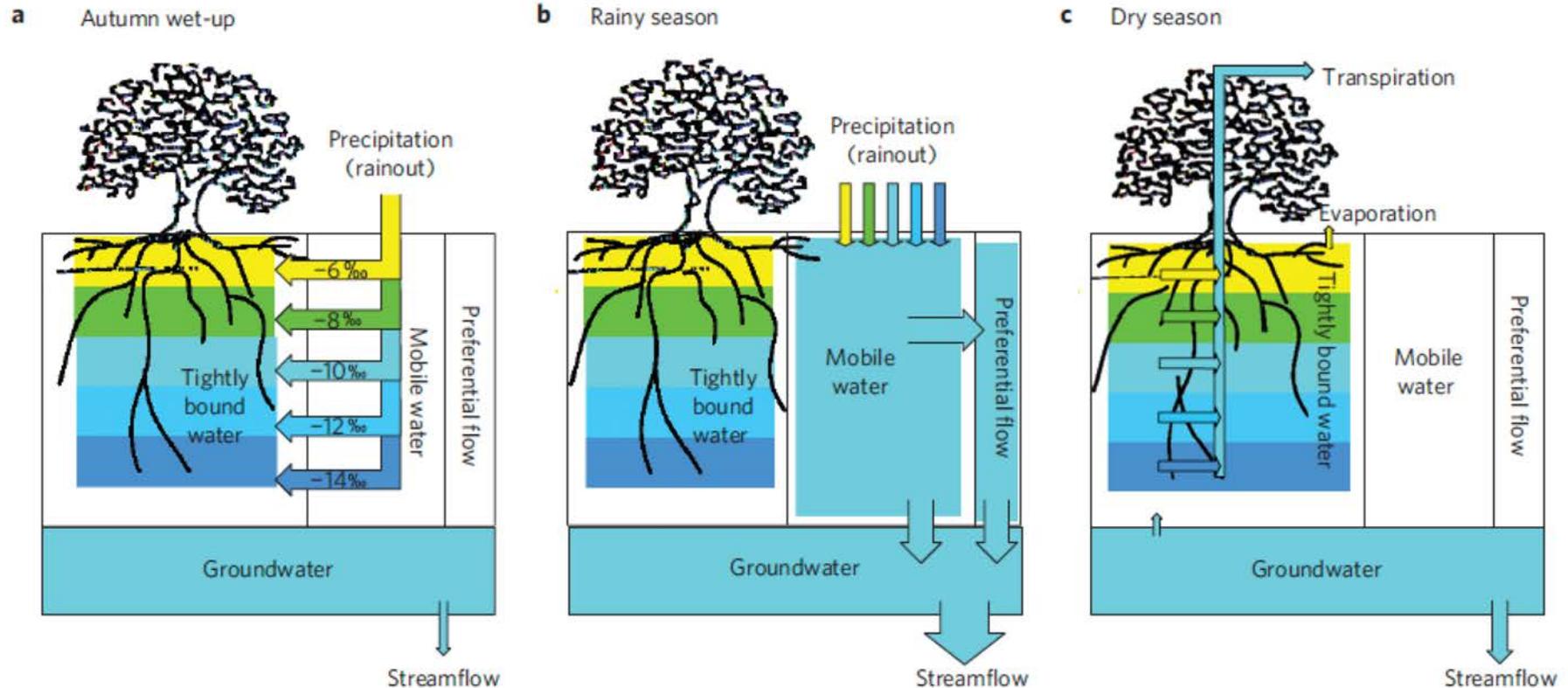
Ecohydrologic separation of water between trees and streams in a Mediterranean climate. *Nature Geoscience* 3:100-104.

Brooks, J.R., H. Barnard, R. Coulombe and J.J. McDonnell. 2010.

Ecohydrologic separation of water between trees and streams in a Mediterranean climate. *Nature Geoscience* 3: 100-104

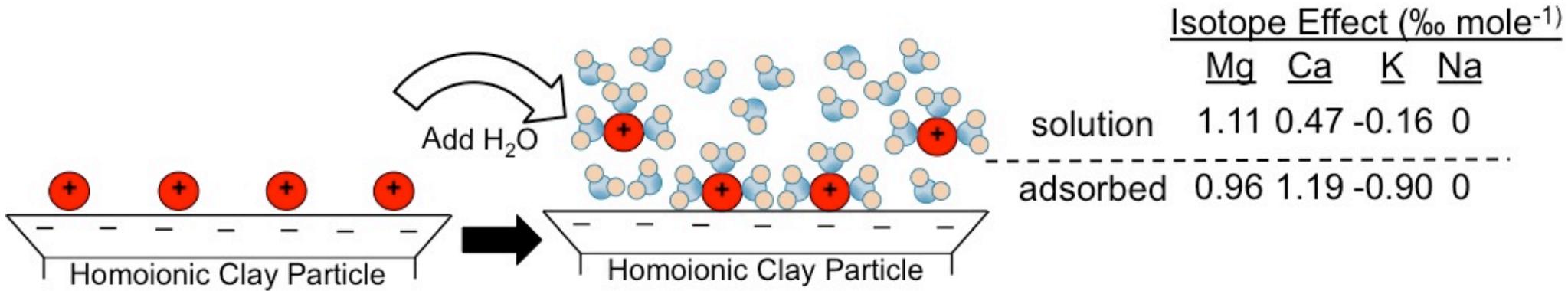
## LETTERS

NATURE GEOSCIENCE DOI: 10.1038/NCEO722

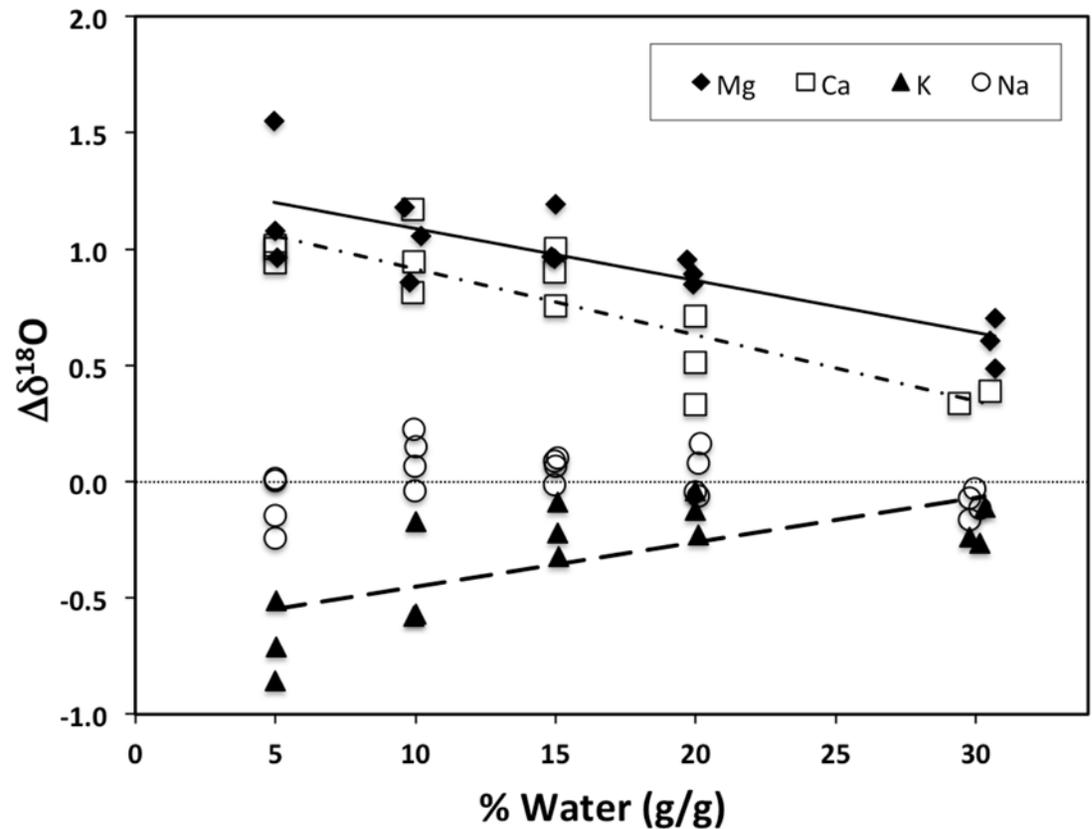


**Figure 4 | Conceptual model for water resource separation in a Mediterranean climate.** **a**, During autumn wet-up, pores within soil layers fill sequentially with progressively more isotopically depleted water as the wetting front moves to depth ( $\delta^{18}\text{O}$  values shown) and the rainout process occurs during a large soil-wetting precipitation event. **b**, During the winter rainy season, precipitation moves through the profile through larger pores and preferential flow paths. **c**, During the dry summer, large pores drain, emptying mobile and preferential flow paths. The remaining soil water is tightly bound within small pores and used by plants for transpiration.

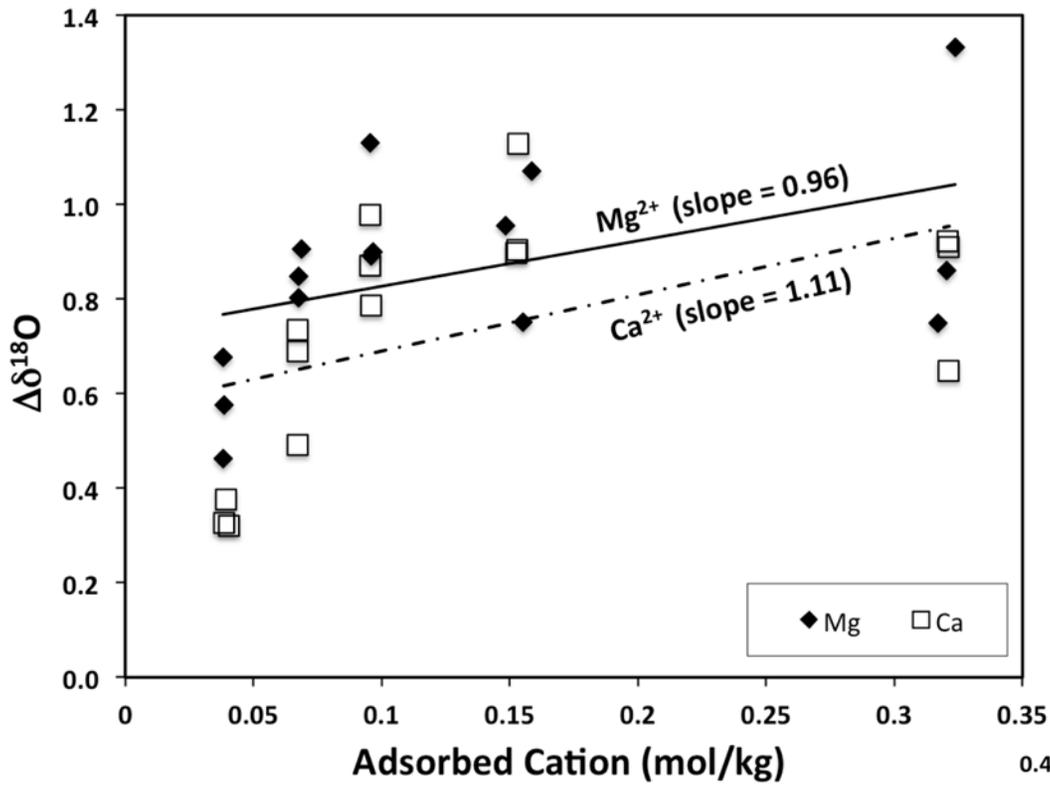
# Is subsurface fractionation known or possible?



From: Erik Oerter et al.  
Journal of Hydrology (2014)

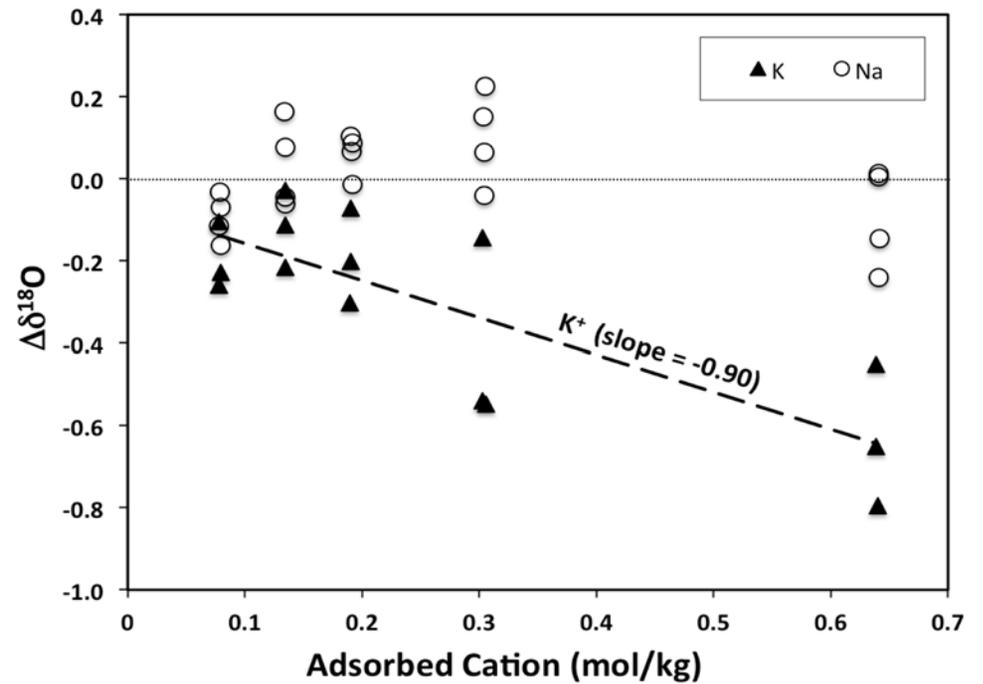


Subsurface fractionation  
appears to be possible



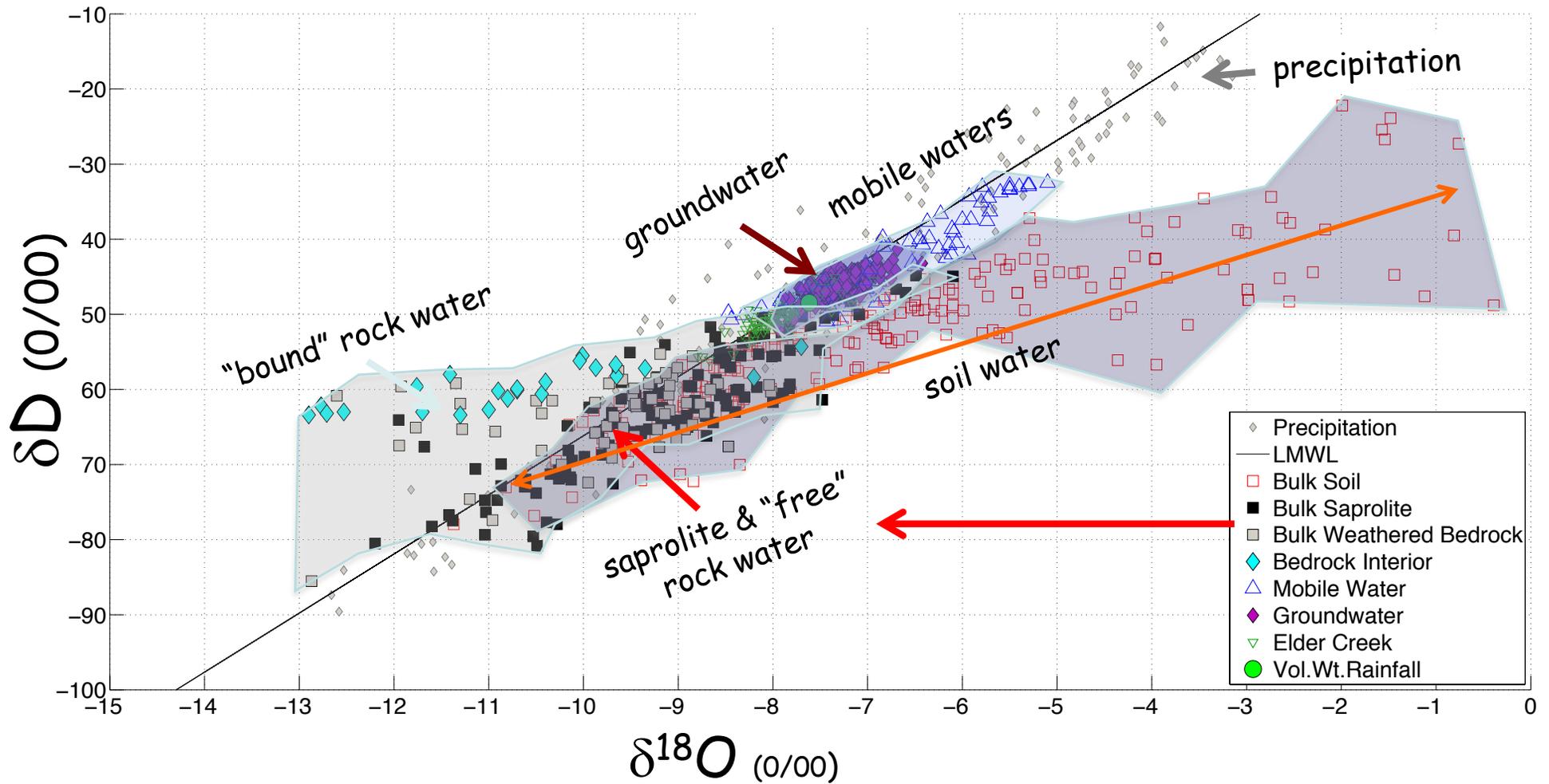
$\Delta\delta^{18}\text{O}$  = the isotope “difference” between known source water and the measured  $\delta^{18}\text{O}$  achieved after cryogenic extraction

Oerter et al. *J. of Hydrology* (2014)



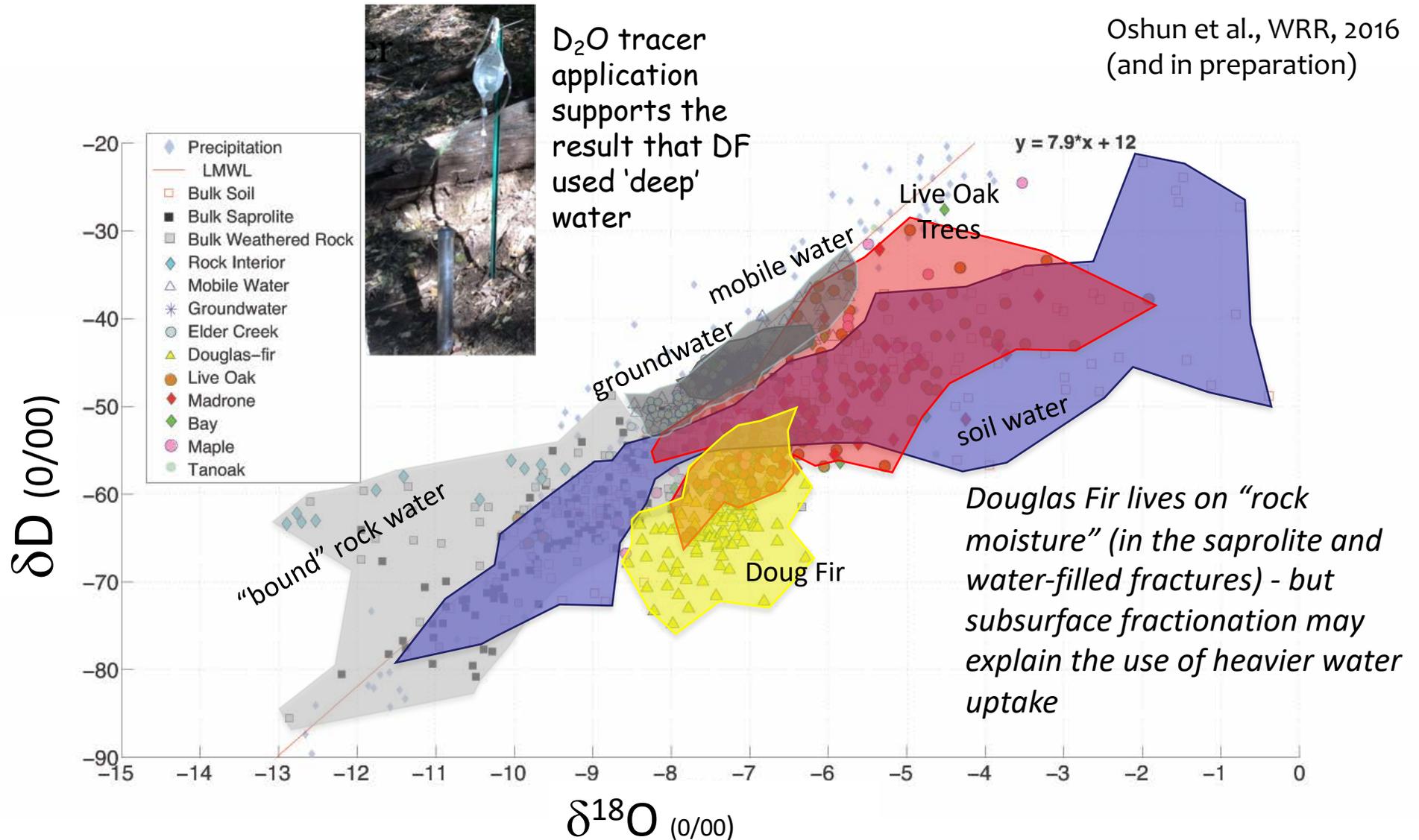
# Structured heterogeneity of water isotopes occurs in hillslopes

Oshun et al., WRR, 2016  
(and in preparation)

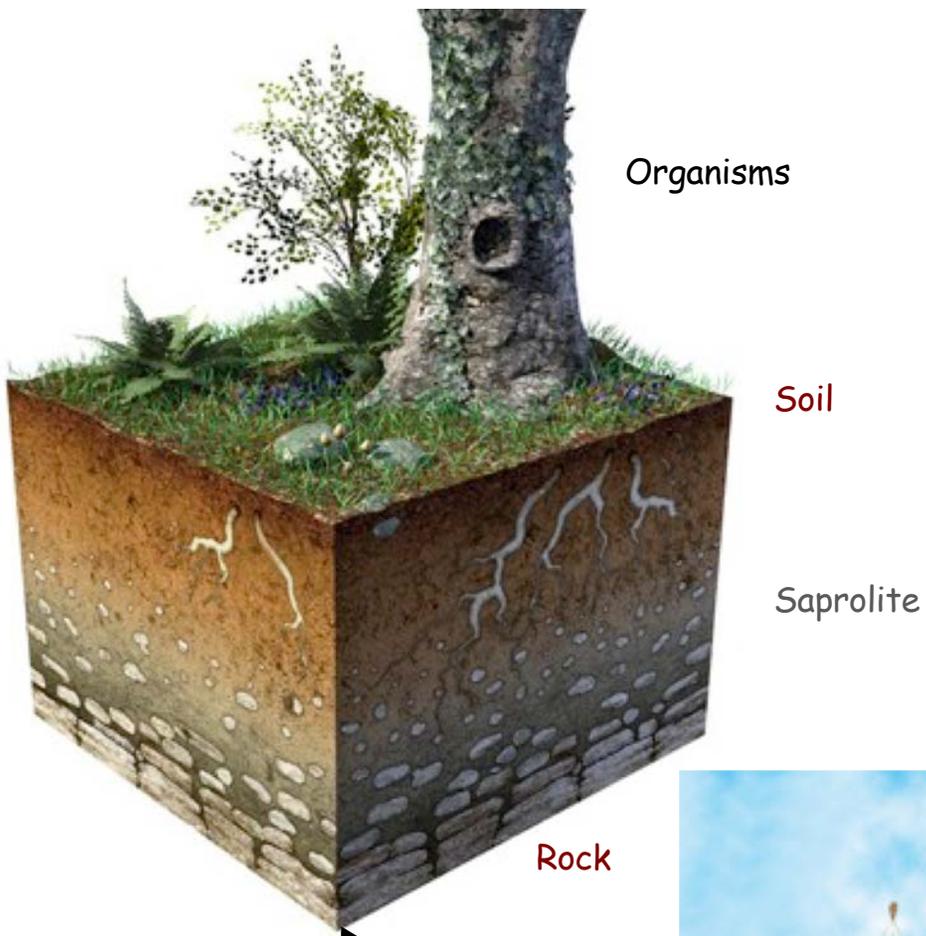


Analysis of hydrogen and oxygen isotope composition identifies several (5) different water reservoirs 'in' the hillslope that drive the hydrology and biogeochemistry

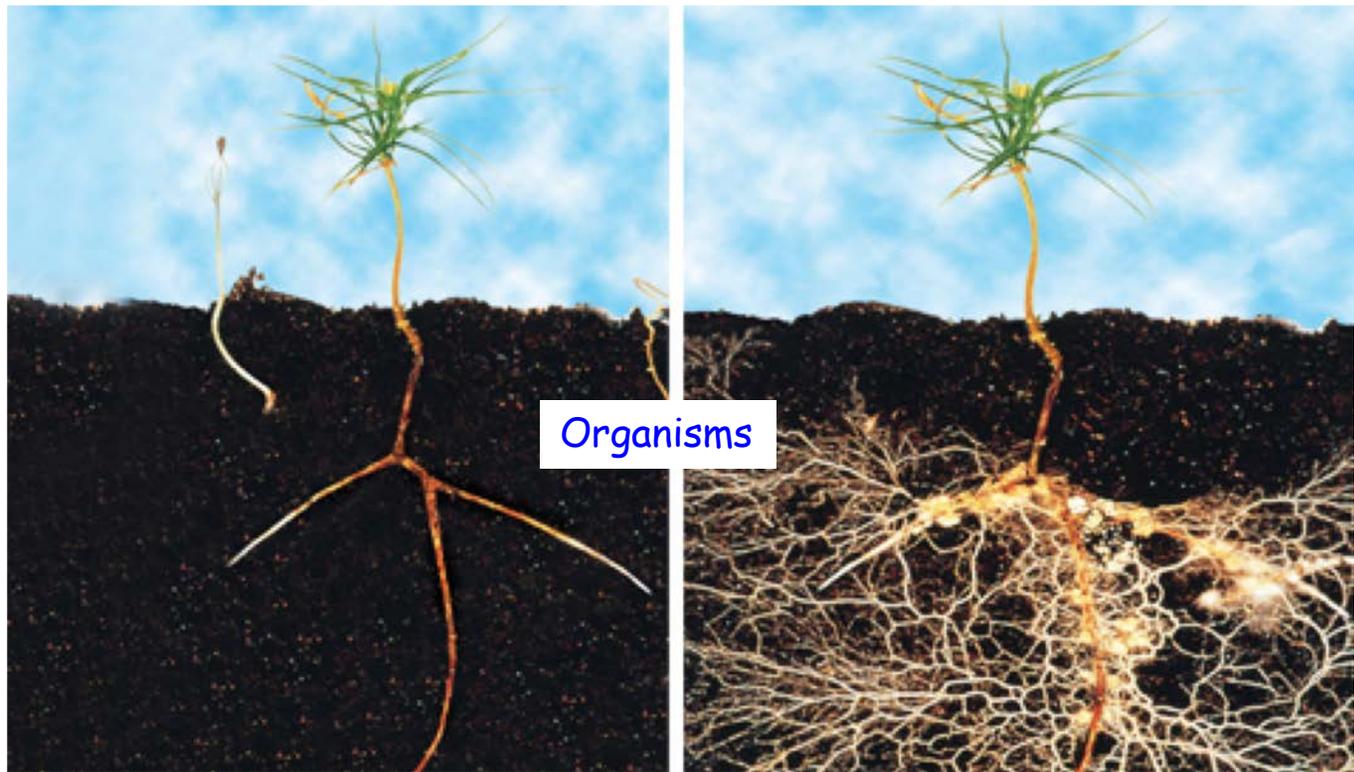
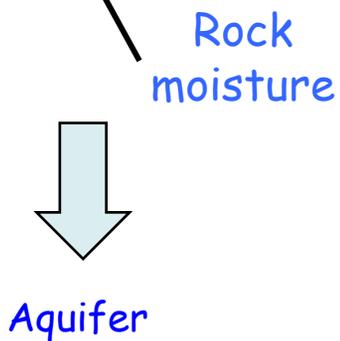
Oshun et al., WRR, 2016  
(and in preparation)



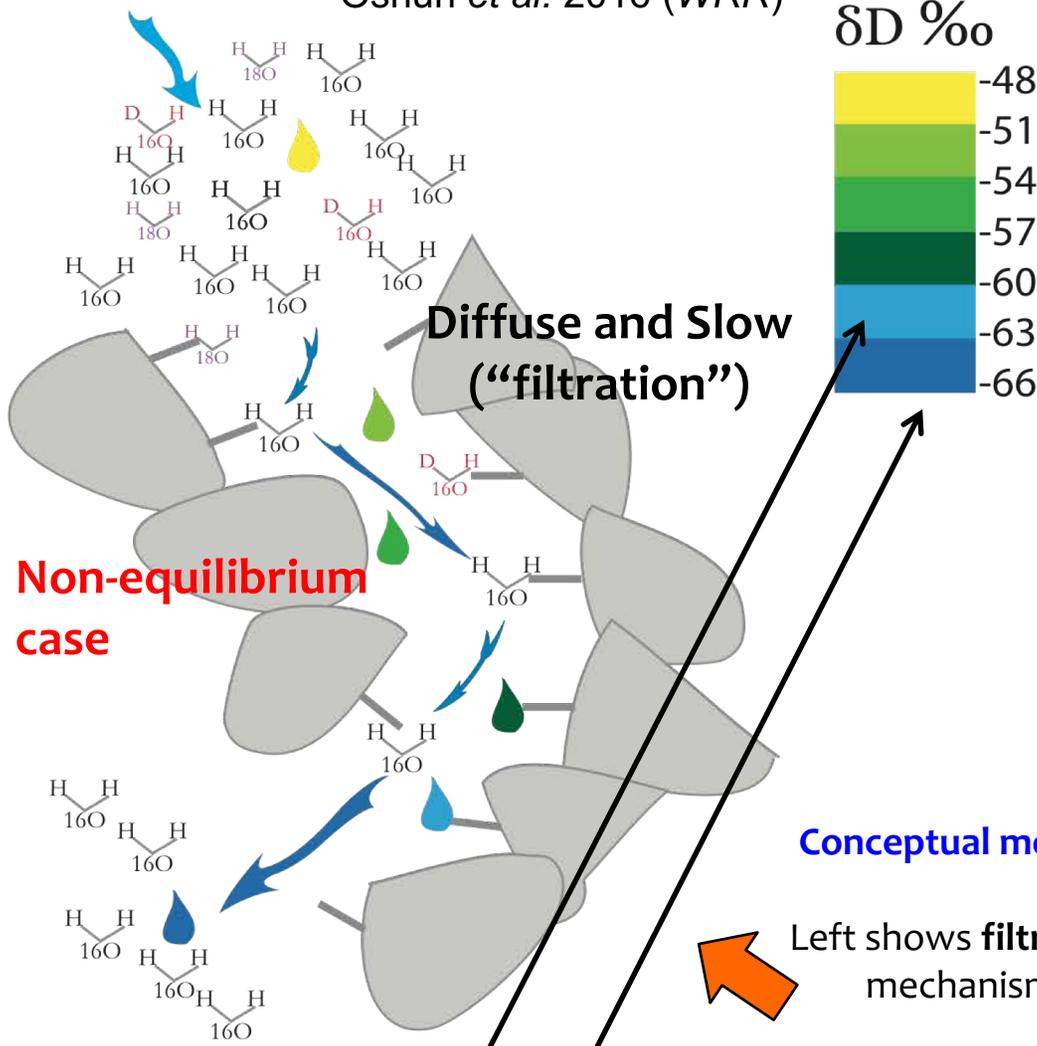
This persistently light composition of "rock water" (saprolite and rock fracture moisture) that deviate from average meteoric values suggests that **subsurface fractionation caused by physical, chemical, or biological** (fungi) mechanisms OR from the **inheritance of paleo-meteoric** "rock moisture" associated with rock uplift that can lead to large enduring isotopic differences between high and low mobility water.



The sub-surface CZ has several “compartments” and each has a role in CZ behavior



Oshun *et al.* 2016 (WRR)



**Non-equilibrium case**

**Diffuse and Slow ("filtration")**

$\delta D \text{ ‰}$



**Conceptual models**

Left shows **filtration** mechanism

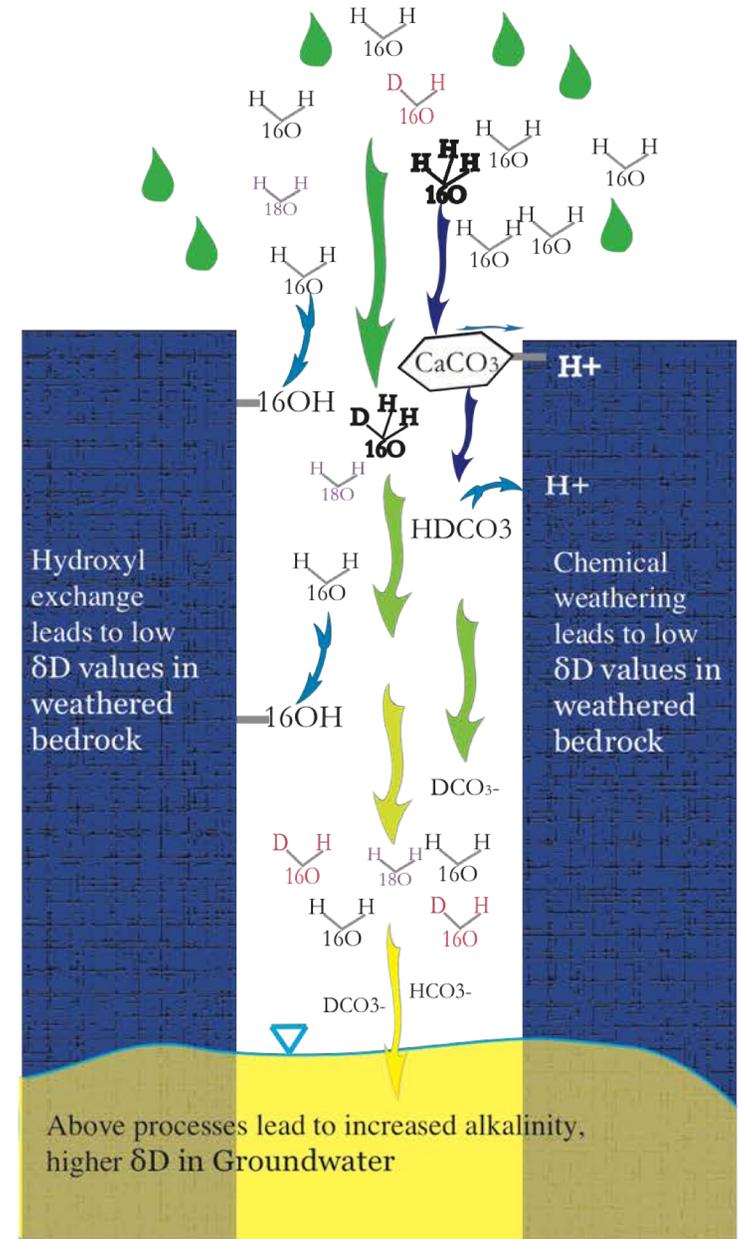
Right shows **hydroxyl exchange** and **chemical weathering**



Observed isotopic structure inside mudstone matrix

**Structured Heterogeneity**

**Advective and Fast**



**Equilibrium case**

## Important recent research focused on the subsurface

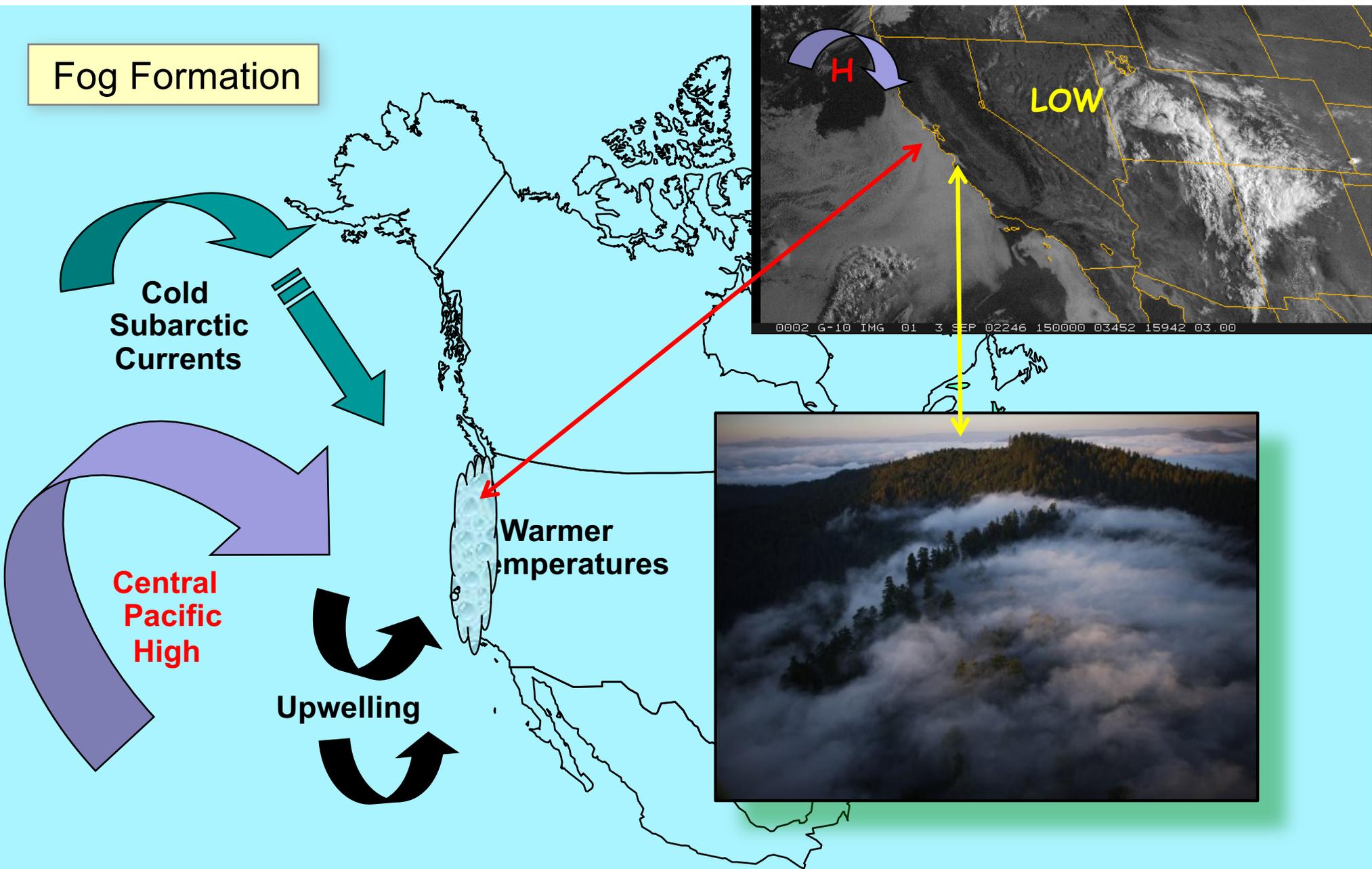
- Between 2011 and 2016 there are now nine papers suggesting, showing or modeling subsurface fractionation
- Clay-rich soils and/or very fine textured lithology (rock) appear to be most influential in either:
  - (a) preferentially holding onto a greater fraction of lighter isotopologues of water,
  - (b) providing 'reaction' surfaces that allow redox or hydroxyl reactions that lead to fractionation affects in "bound" and "mobile" phases of water, and/or
  - (c) retaining "older" water
- Clay-rich tills and mudstones contain "old" (paleo) waters from the Pleistocene with adjacent pore-waters containing modern meteoric waters (Hiscock et al. 2011 for East Anglia, UK)

Questions?



Where do the tallest trees in the world get their water?

# Fog Formation



Summer fog formation off the coast of west-central North America occurs when subsidence air moved by the Central Pacific High pressure cell meets cold water from Alaskan currents and deep water upwelling along the Pacific rim



*Gaultheria shallon*

*Polysticum munitum*

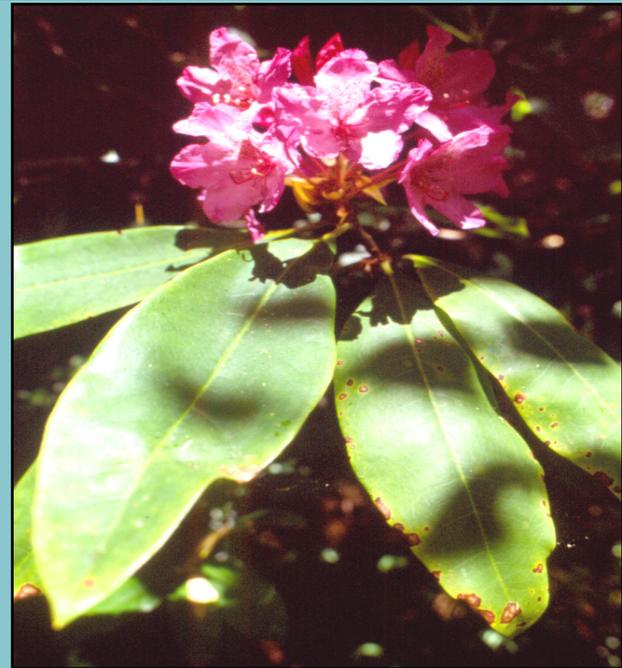


*Sequoia sempervirens*



Ewok

**Study Species**

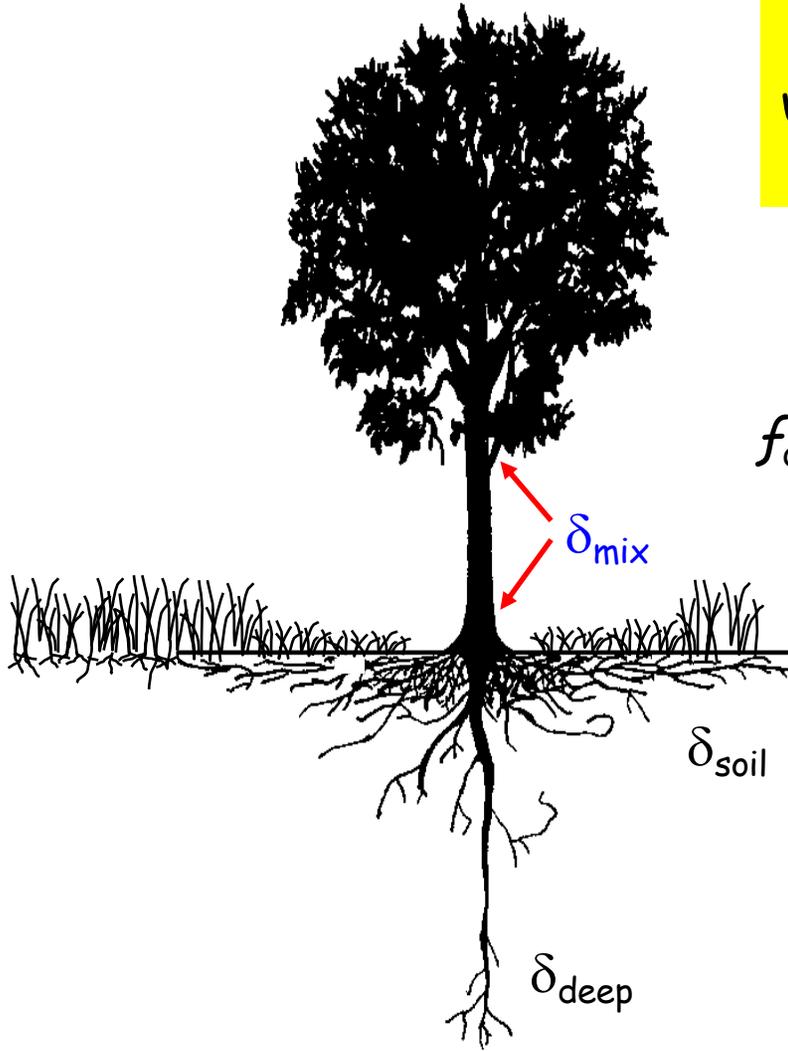


*Rhododendron macrophyllum*

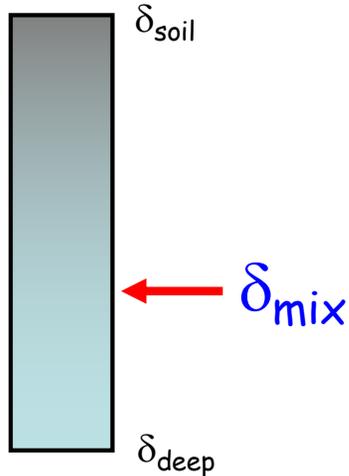
*Oxalis oregana*



One isotope, two source, linear mixing model  
where the fraction,  $f$  of deep water used is:



$$f_{deep} = \frac{\delta_{mix} - \delta_{soil}}{\delta_{deep} - \delta_{soil}}$$

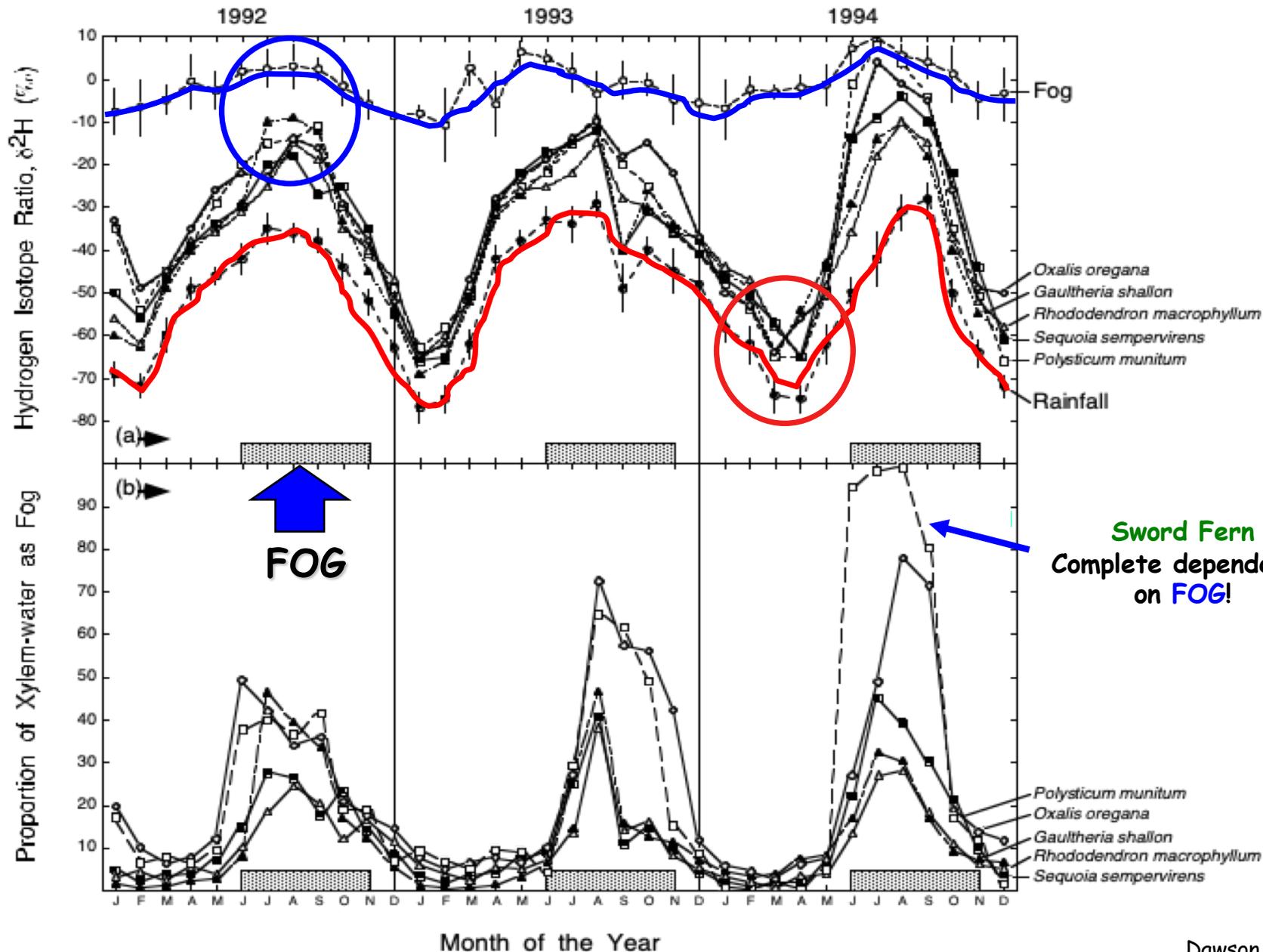


$\delta_{mix}$  = mixture

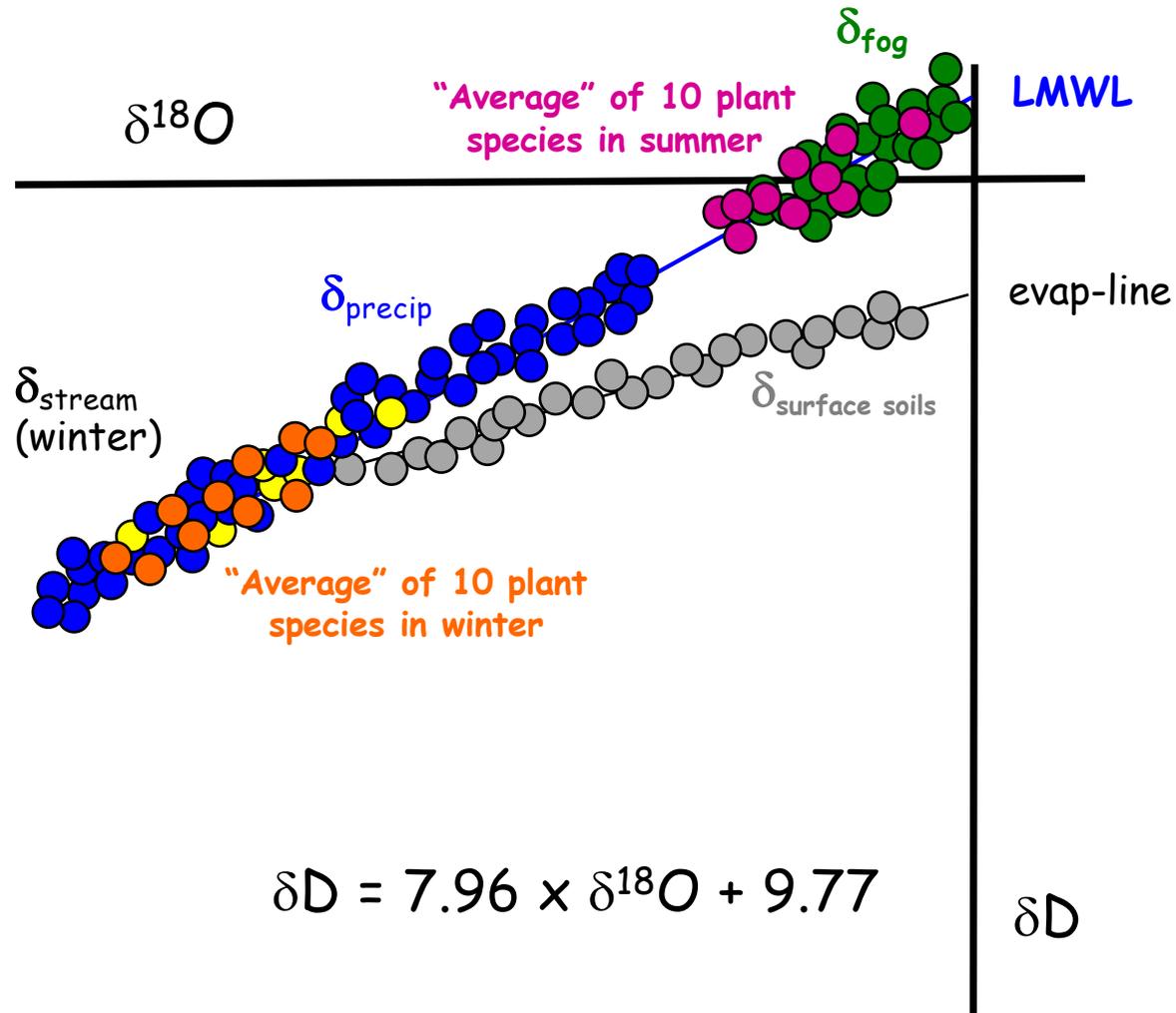
$\delta_{soil}$  = shallow soil H<sub>2</sub>O

$\delta_{deep}$  = deep soil H<sub>2</sub>O

# Do plants from Redwood-Forest Communities use Fog?



**Sword Fern**  
Complete dependence  
on **FOG!**



Using isotope analyses of **ALL** water sources revealed that in summer plants were using fog drip as their primary and most reliable water source

# Once water reaches the leaf what happens to leaf water?

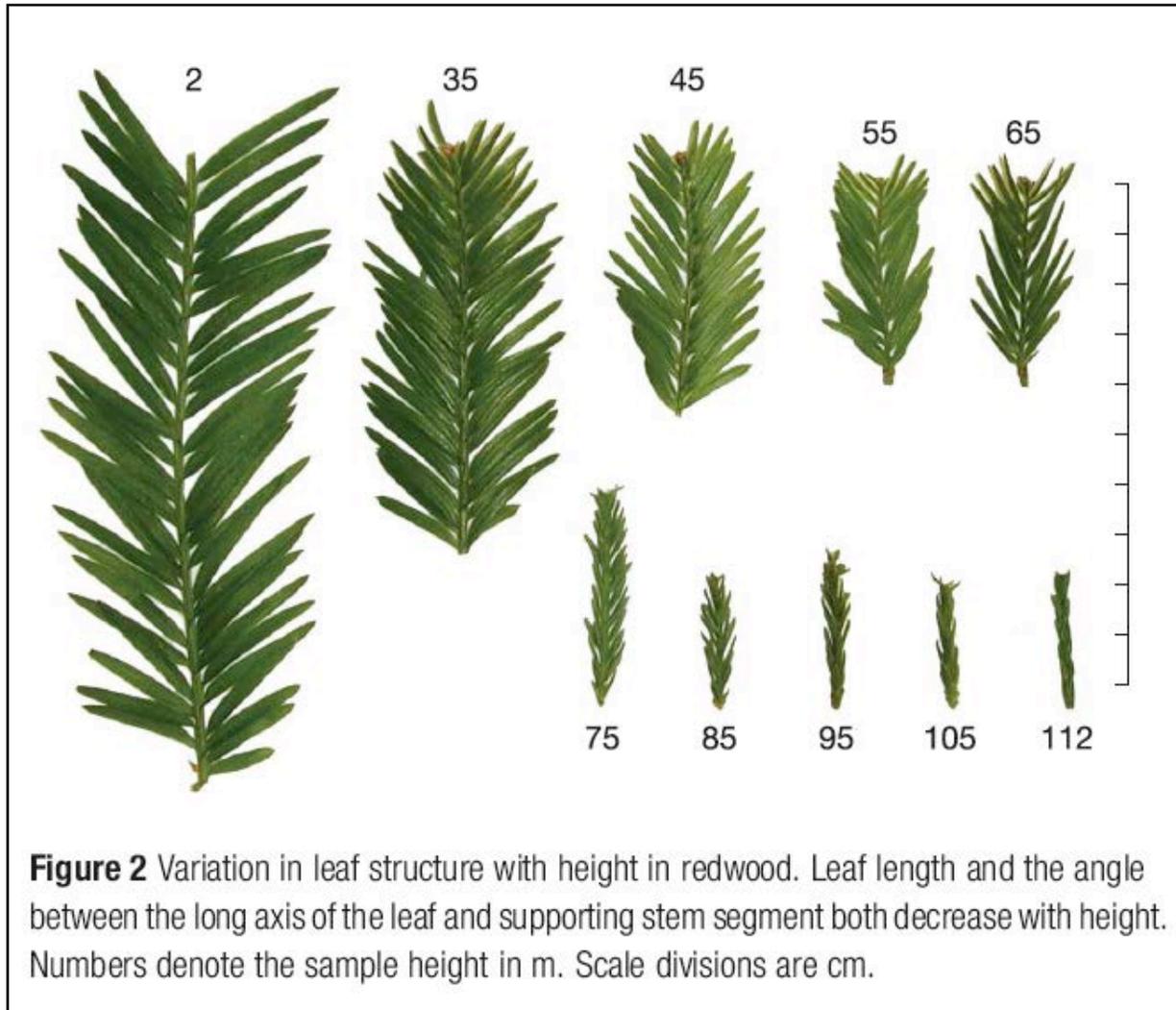


Photo: K. Simonin

Photo: G. Koch

**~ Craig-Gordon Model ~**  
**Evaporative Enrichment of Stable Isotopes in H<sub>2</sub>O**

$$R_{\text{Leaf}} = \alpha^* \left[ \alpha_k R_{\text{Xylem}} \left( \frac{e_i - e_a}{e_i} \right) + R_{\text{AWV}} \left( \frac{e_a}{e_i} \right) \right]$$

$\alpha^*$  = Equilibrium fractionation factor (1.009)

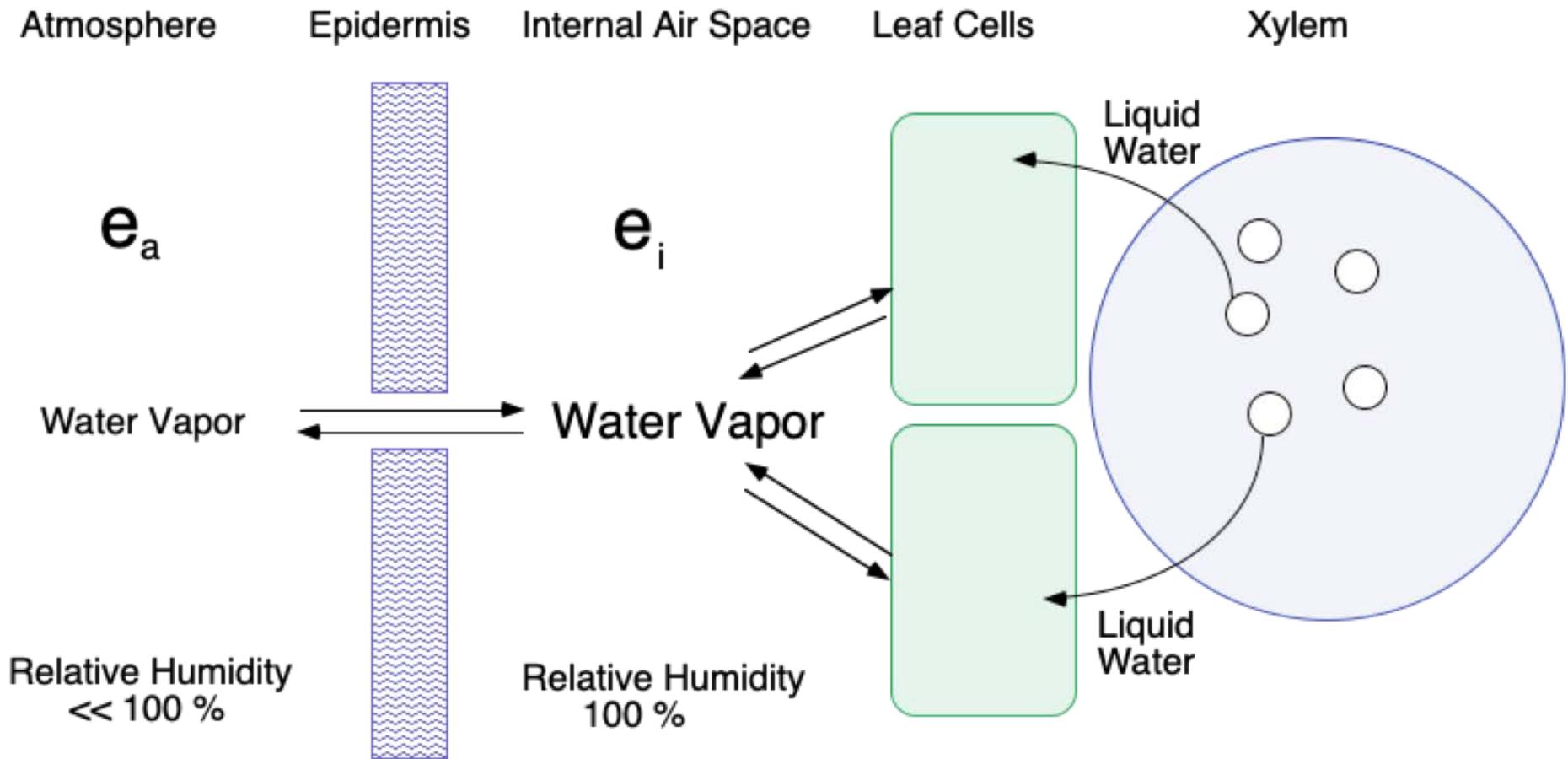
$\alpha_k$  = Kinetic fractionation factor (1.0285)

$e_i$  = vapor pressure of water in leaf intercellular space

$e_a$  = vapor pressure of water in air outside leaf

$R_{\text{AWV}}$  = molar ratio <sup>18</sup>O/<sup>16</sup>O of atmospheric water vapor

# What happens to leaf water?



What do these birds eat and drink in this resource-limited desert?

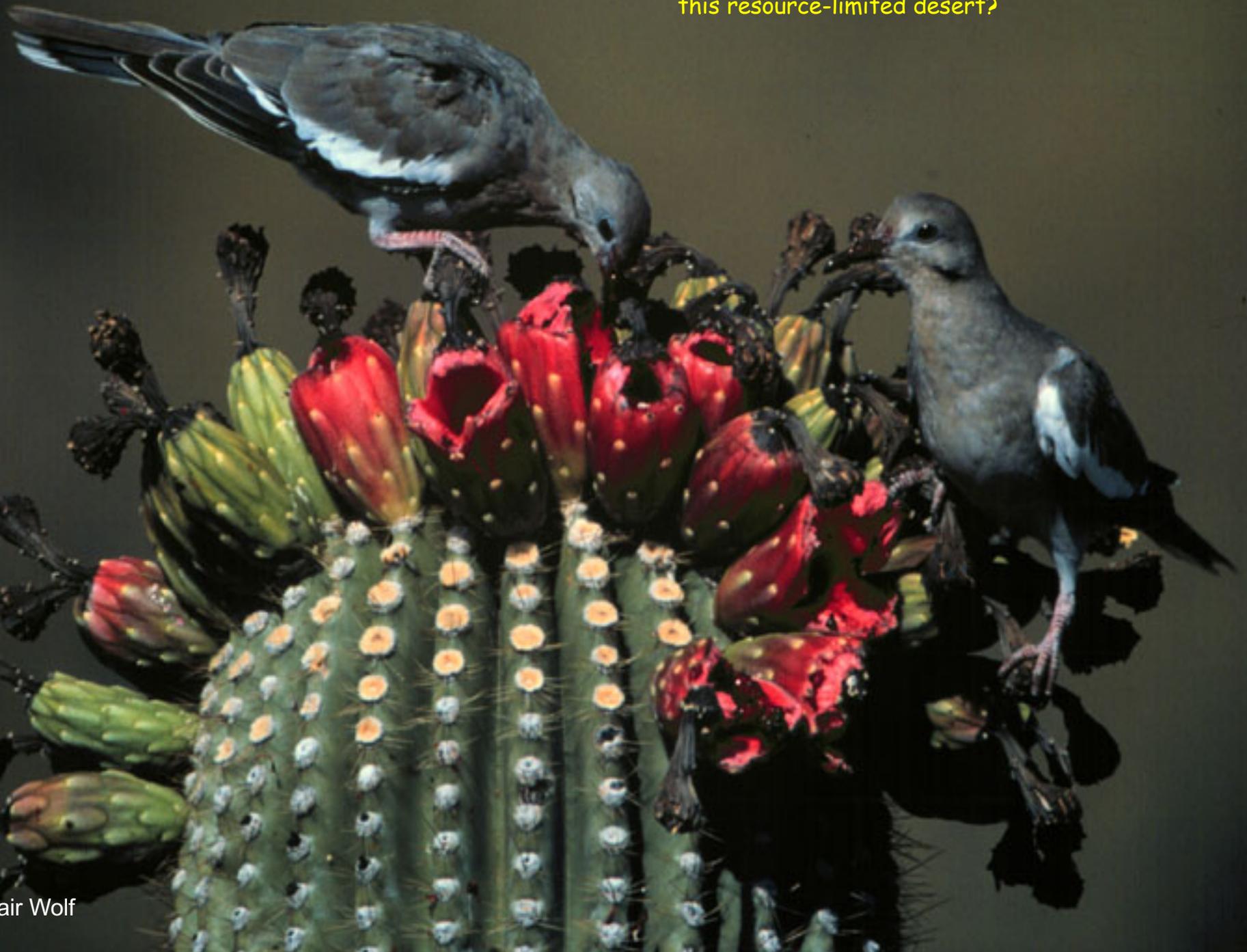


Photo: Blair Wolf

# Carbon isotope ratios of Sonoran Desert plant resources

## SAGUARO (CAM)

$\delta^{13}\text{C}$  (‰) V-PDB

Nectar:

$-12.8 \pm 0.4$  (10)

Fruit:

$-13.0 \pm 0.4$  (10)

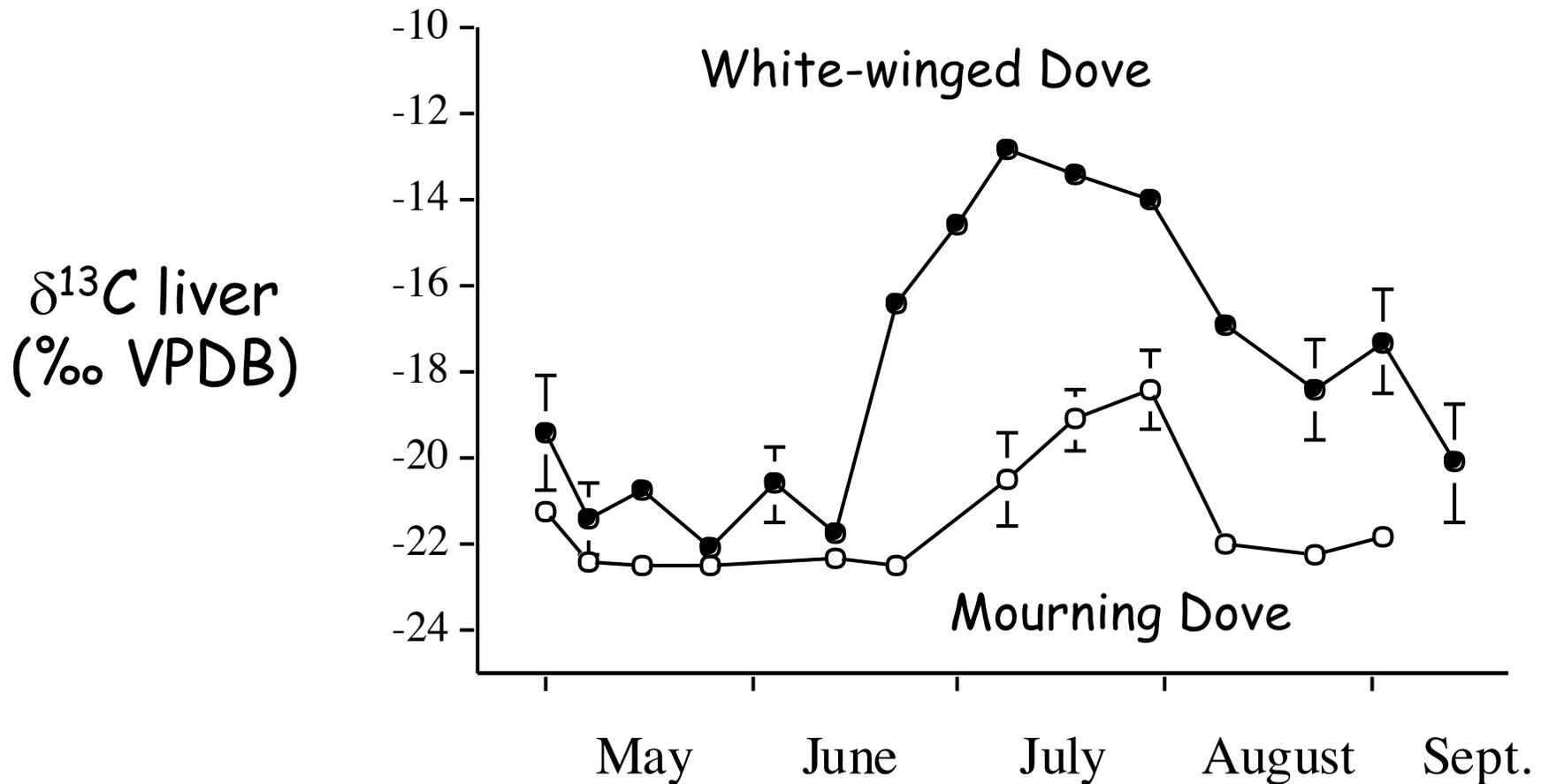
## C3 plants

Seeds\*:

$-24.9 \pm 0.3$

\*Mean value for 7 species of food plants used by doves.

# Do doves use saguaro nectar (carbon)?



It's a desert (water limited); so what do they drink?

Hydrogen isotope ratios of Sonoran Desert water resources

## **SAGUARO**

**$\delta D$  (‰) VSMOW**

Nectar

$19.6 \pm 7.5$  (n = 19)

Fruit

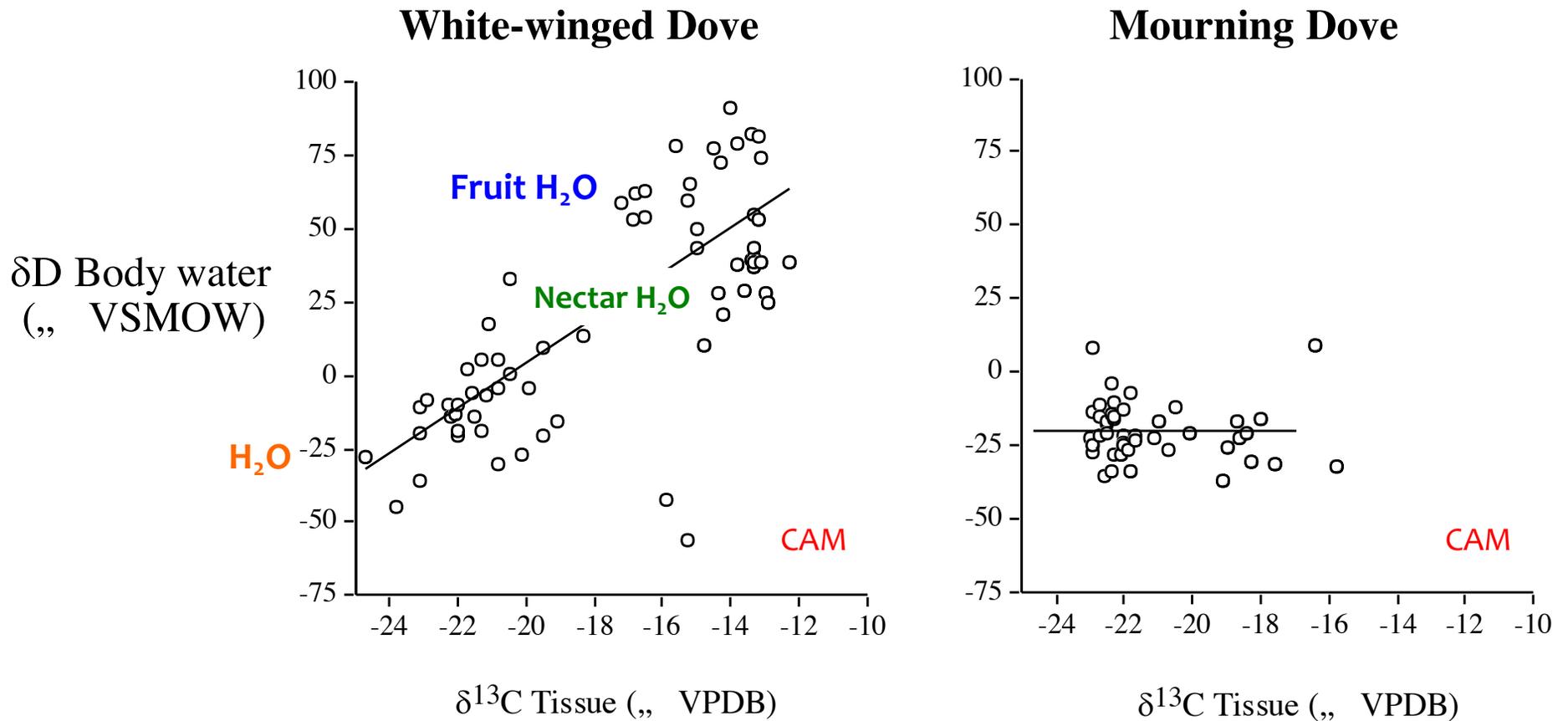
$50.5 \pm 4.7$  (n = 47)

## **WILDLIFE WATER CATCHMENTS**

Drinking water

$-20.0 \pm 5.2$

# Desert dove resource use (liver tissue & body water)



# Let's do Lunch



## Additional Examples

plus and extension to 'body' & leaf water

What about plant water relations, climate change and plant response to drought?

What can isotope data provide?

Q: In the face of climatic changes, extremes and more severe droughts will the depth of root water acquisition be a pivotal survival trait?



South African Fynbos

Q: In the face of climatic changes, extremes and more severe droughts will the depth of root water acquisition be a pivotal survival trait?



South African Fynbos

Collaborative research with Adam West @ U. Cape Town

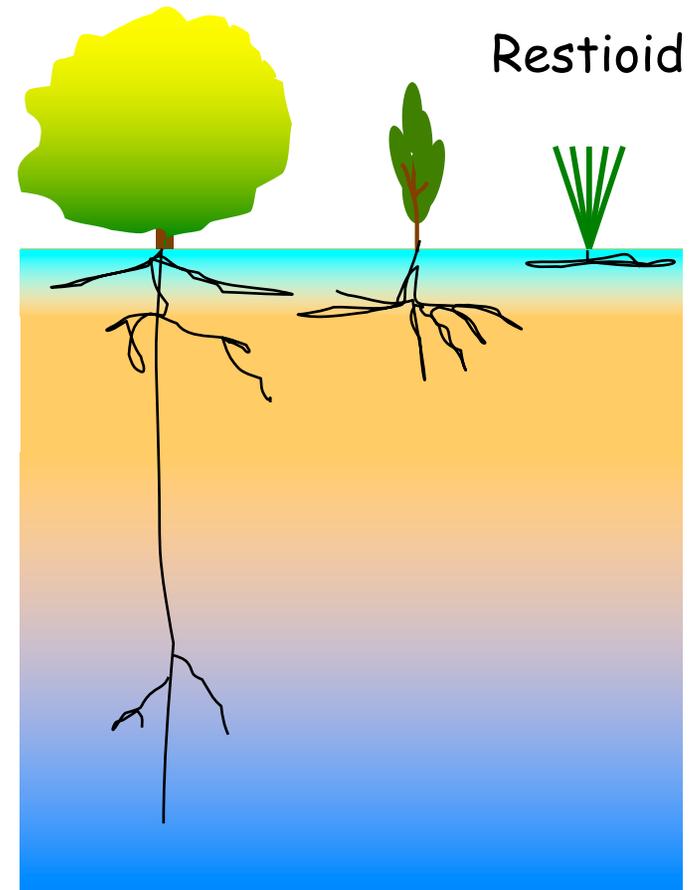
Increasing drought susceptibility



Proteoid

Ericoid

Restioid



# Experimental setup



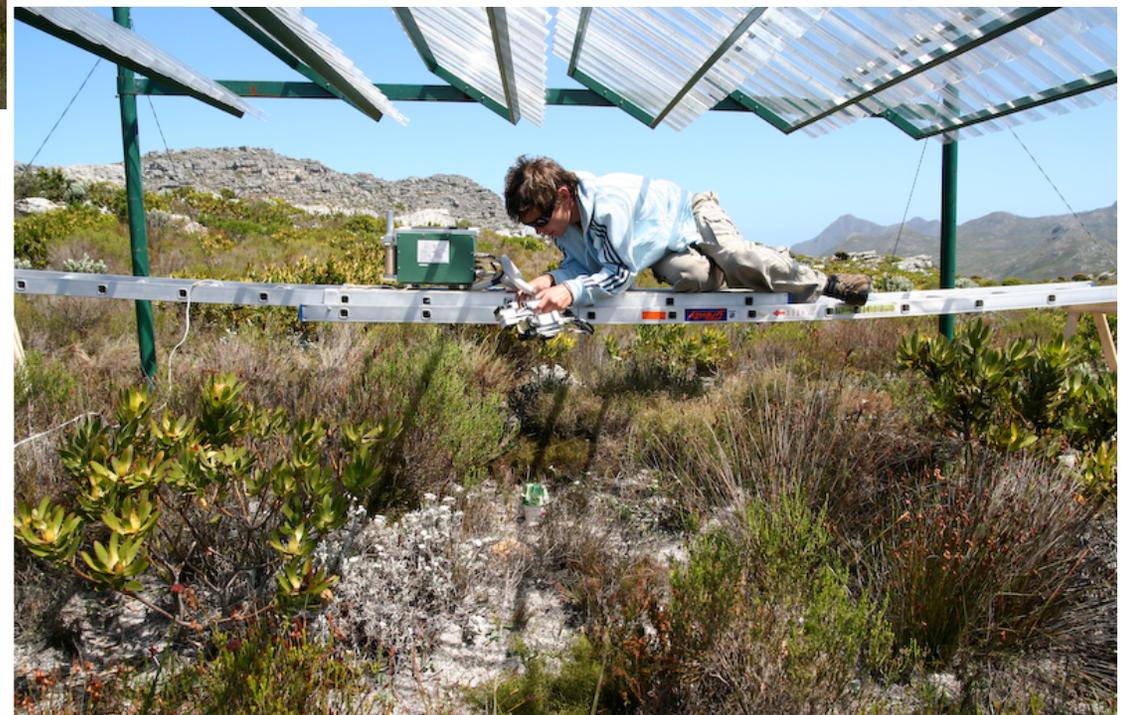
## Rain-exclusion shelters

Silvermine, TMNP

4m x 4m

100% exclusion (treatment)

0% exclusion (control)

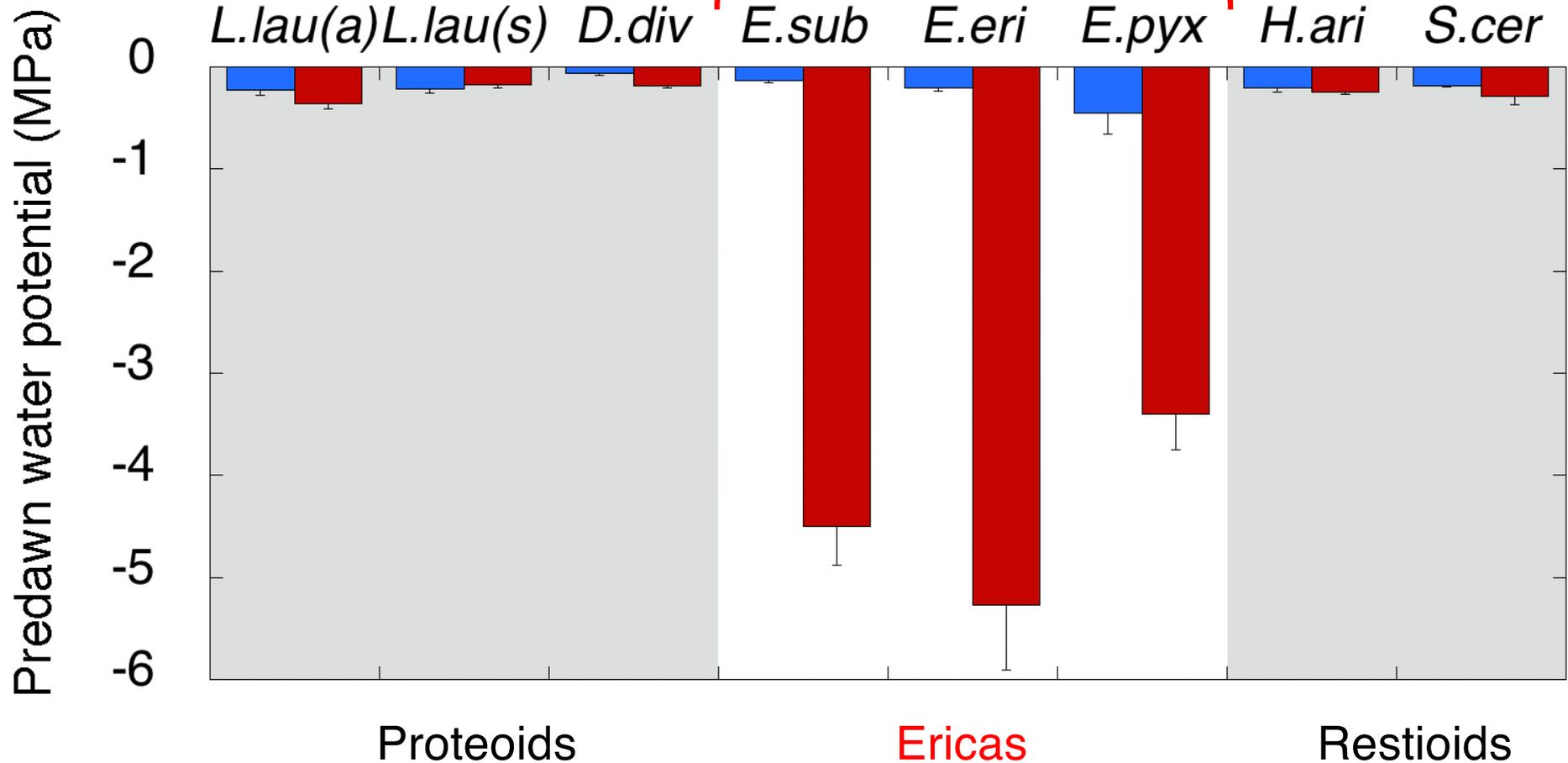


Pre-dawn water potential measurements  
on plants of the Fynbos



Photo: Adam West

# Erica's experience more severe water stress

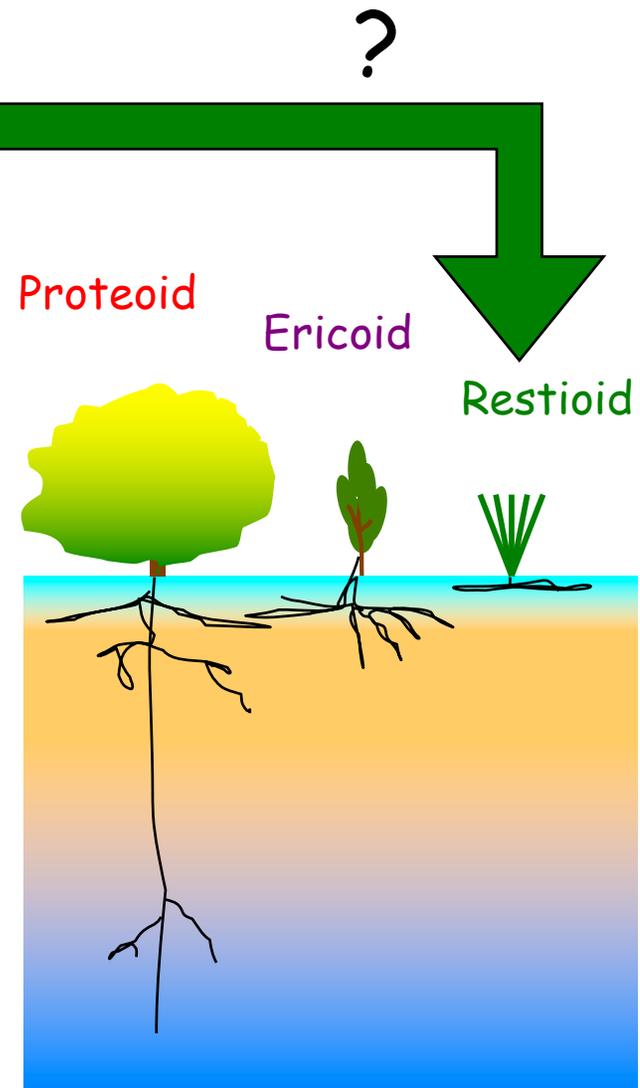
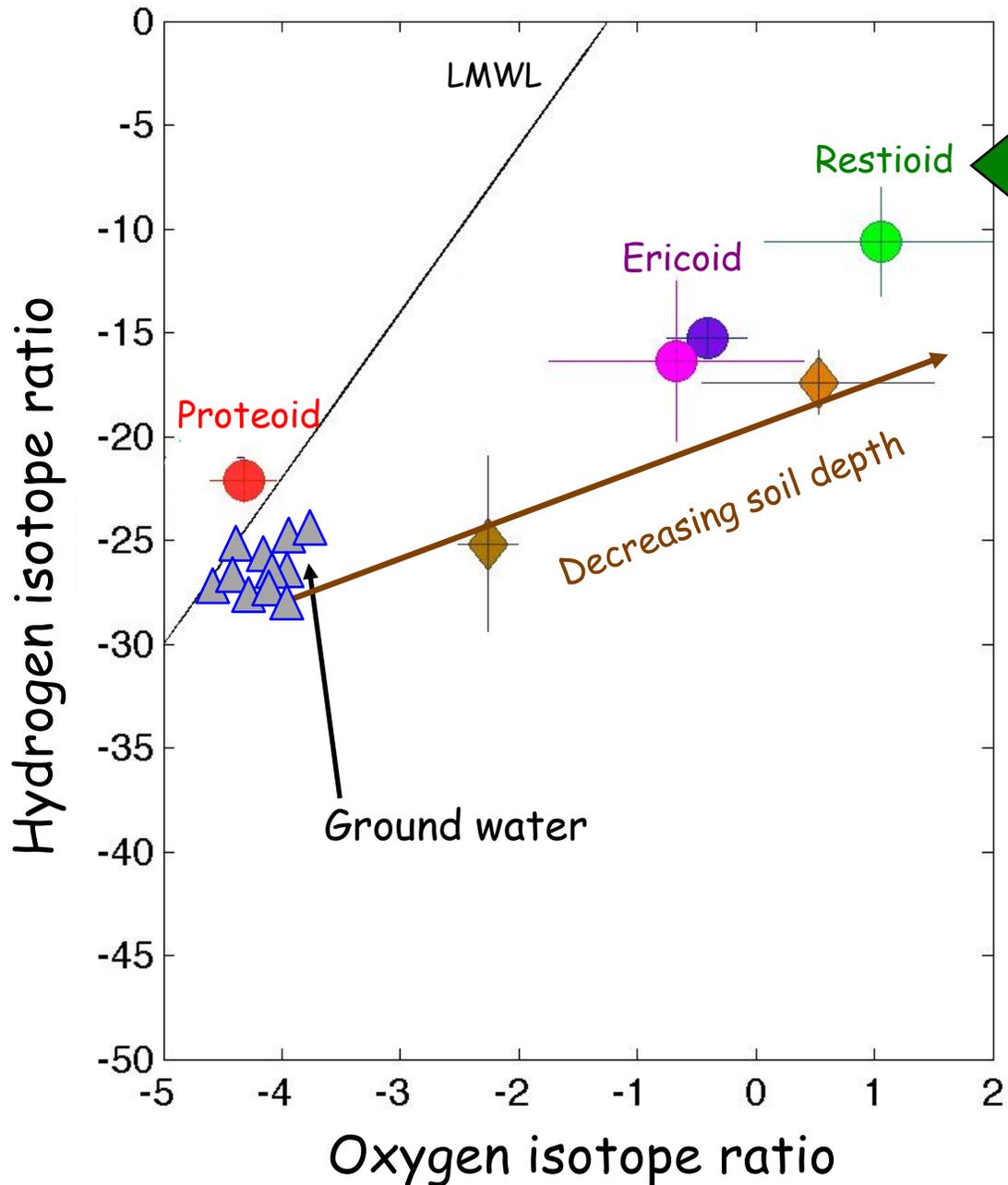


Control  
Treatment

West et al. 2012

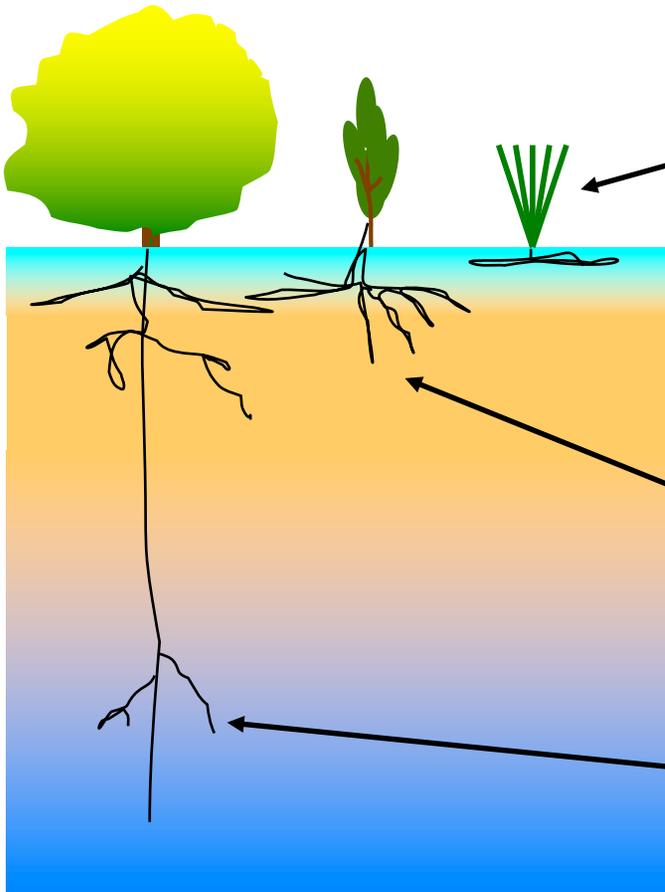
# Isotopic evidence for different rooting depths

West et al. 2012



# What water source(s) do restios use? [or what protects them from drought stress?]

Proteoid  
Ericoid  
Restioid



Is it cloud moisture?

Shallow water uptake in  
ericoids and a few restioids

Deep water uptake in the  
proteiods



Interspaces

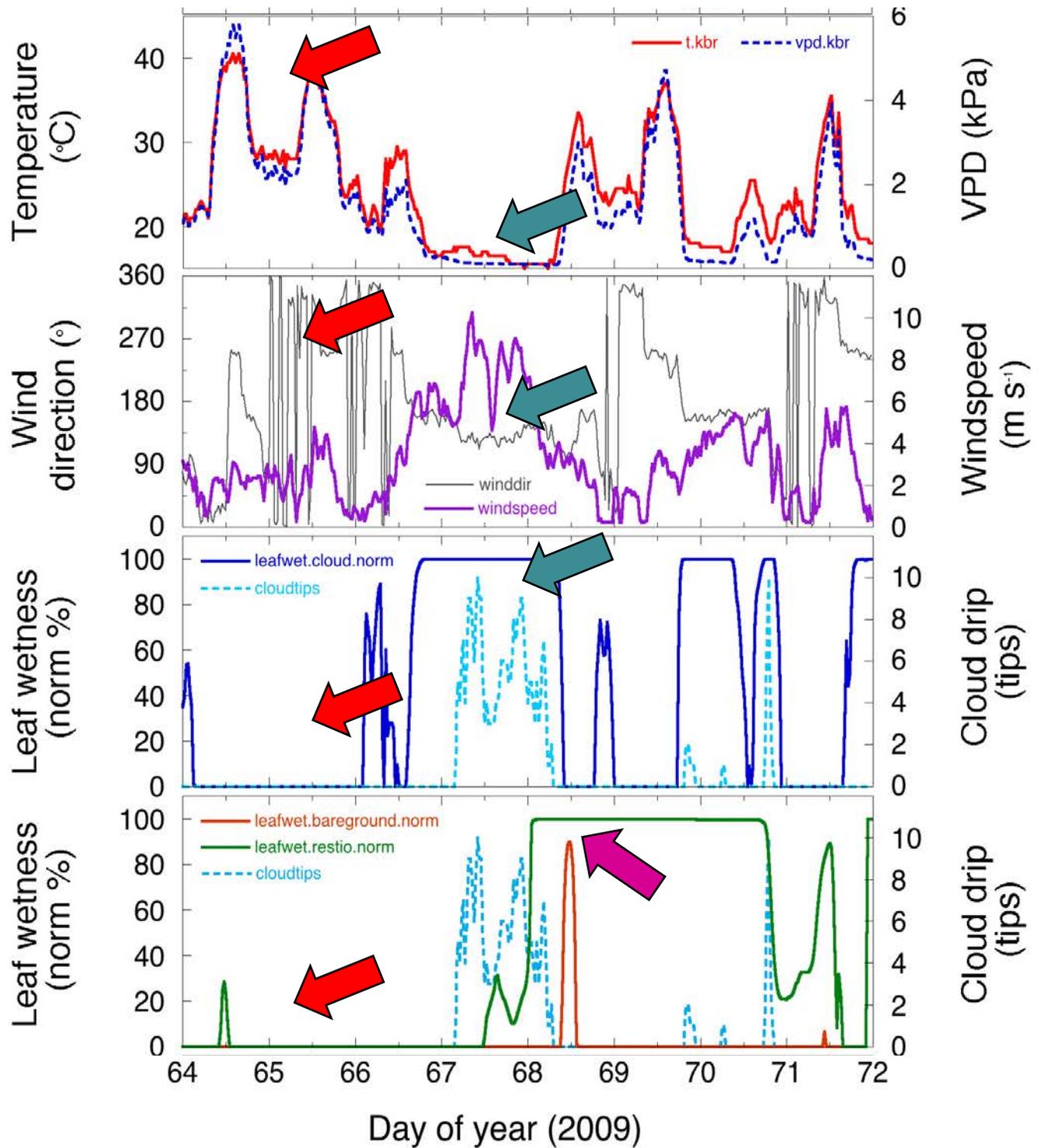
Under Plants



Interspaces  
[bareground]

Under Plants

S-easter cloud  
breaks the  
summer drought  
for Restios

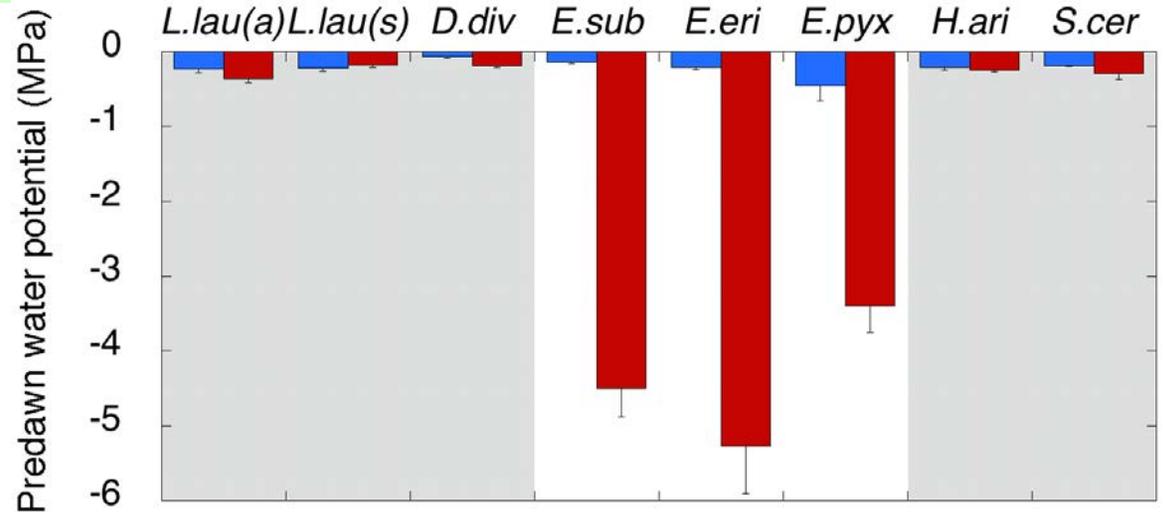
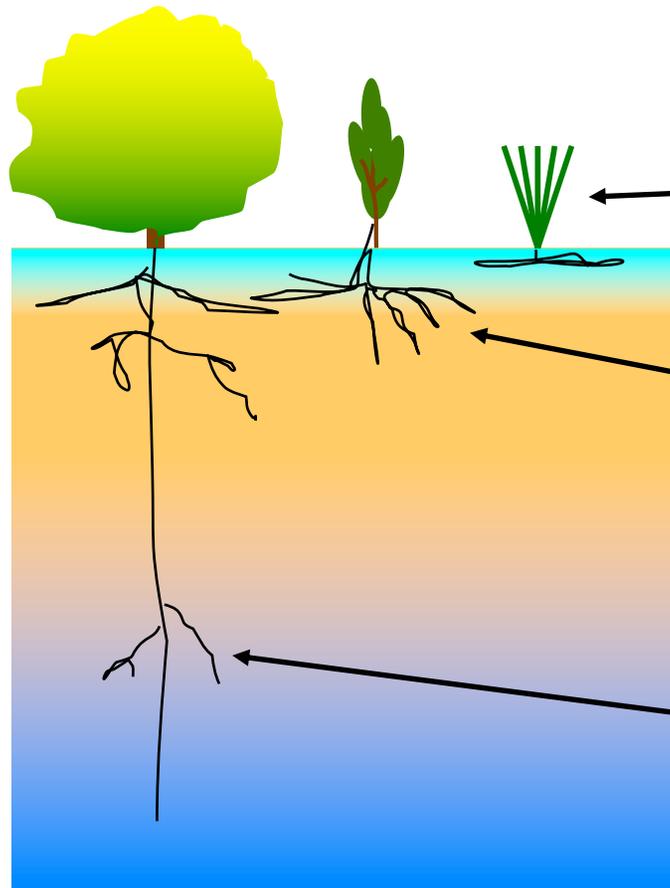


# Patterns and mechanisms of drought stress in functional groups

Proteoid

Ericoid

Restioid

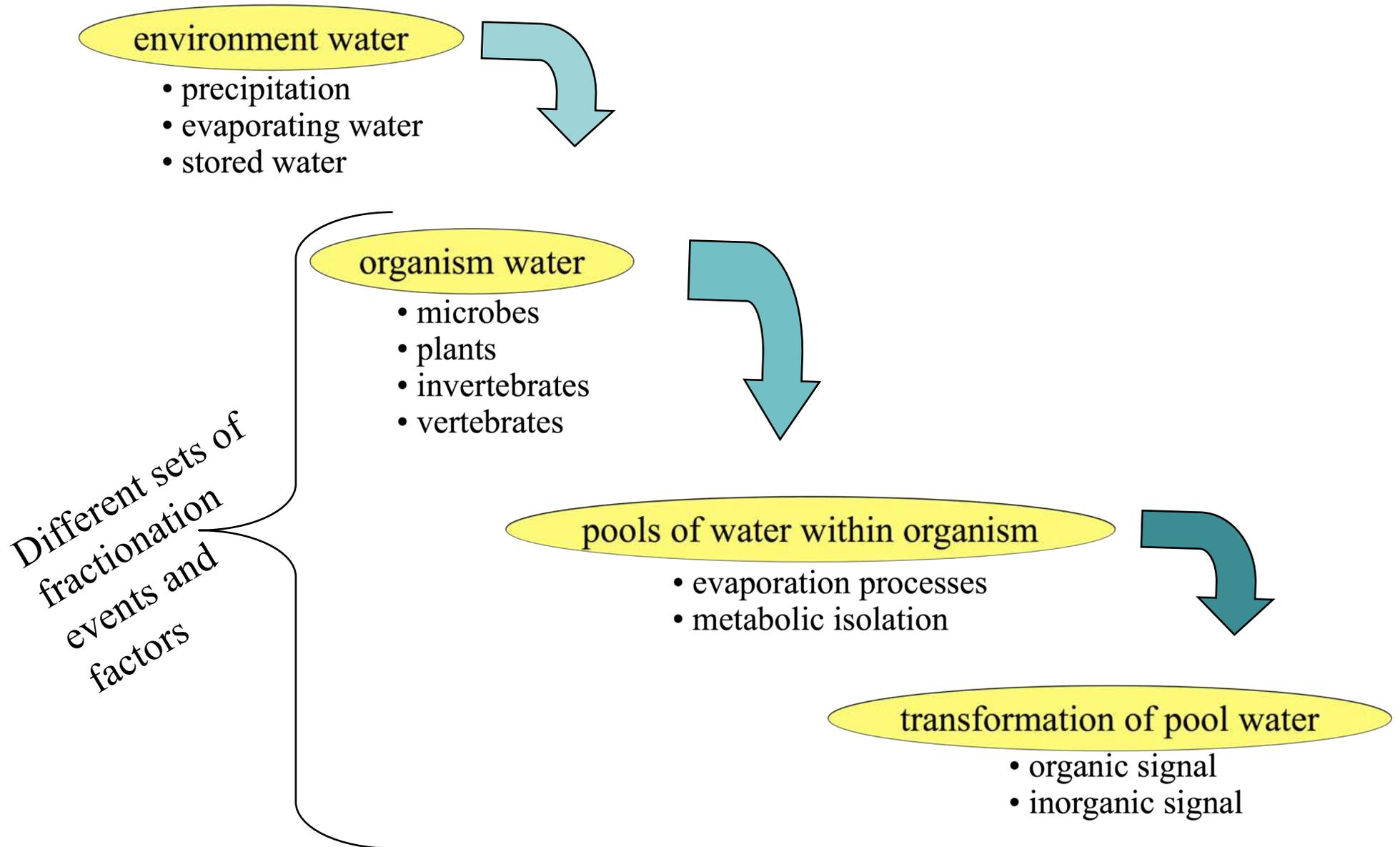


- very shallowly rooted
- drought "avoider"
- mild water stress (cloud moisture)

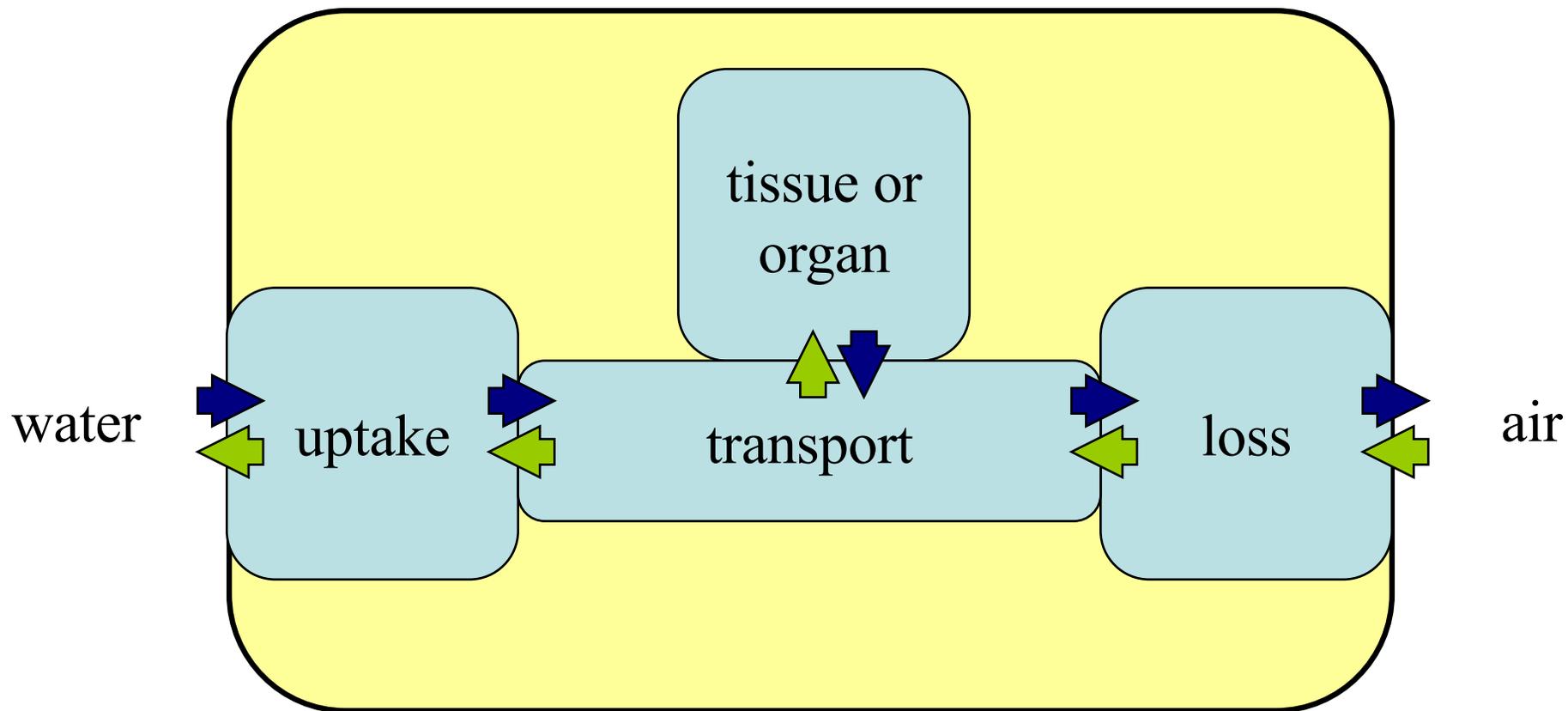
- shallow rooted
- drought "tolerator"
- experiences severe water stress

- deeply rooted
- drought "avoider"
- mild water stress (deep water)

# Conceptual Framework

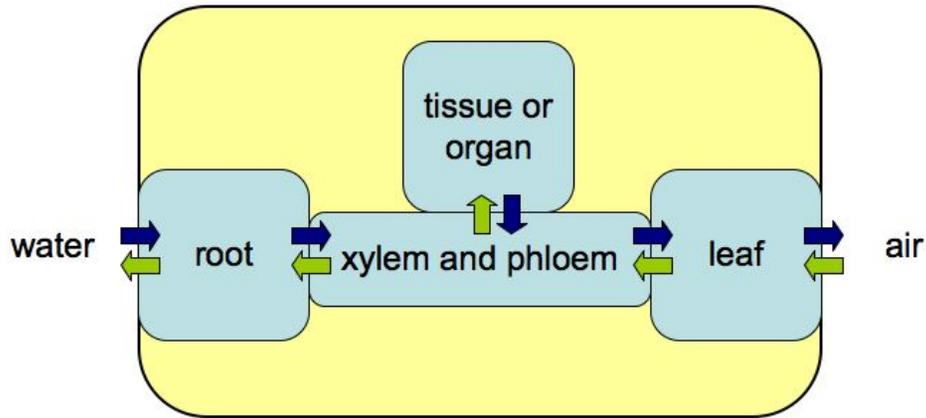


# General Model

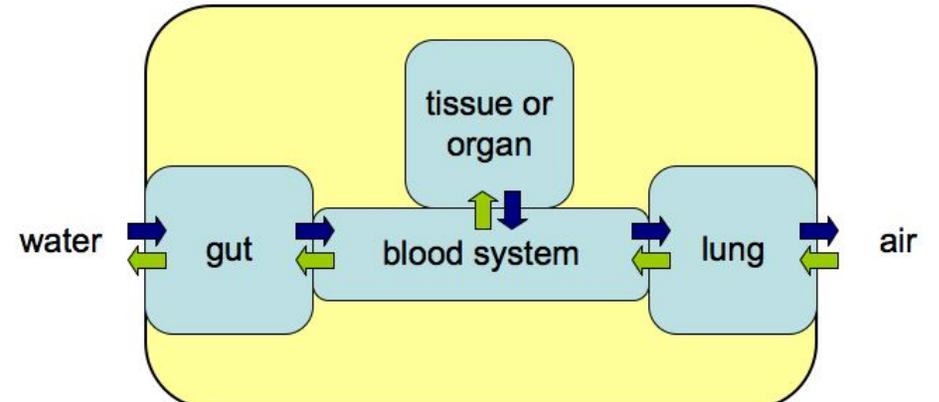


# Specific Models

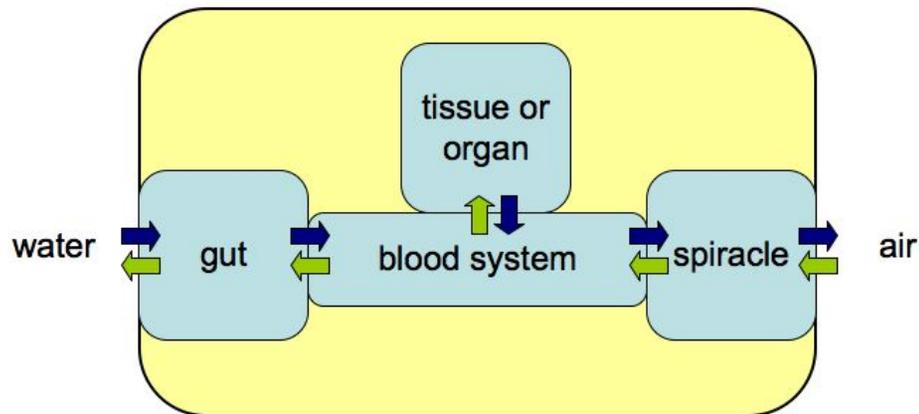
Plant



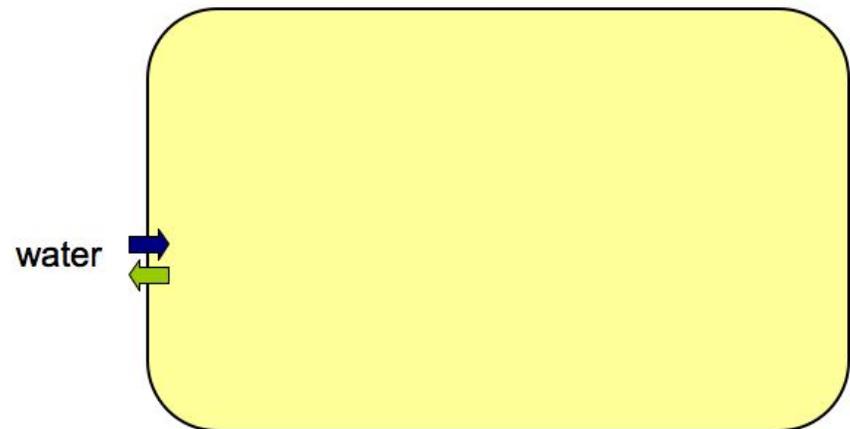
Vertebrate



Insect



Microbe



## ***Quantitative models:***

These have been developed to understand pools of water

### ***Evaporation models:***

for plants, animals, and bodies of waters all are inherently related to Craig-Gordon model (even string-of-lakes)

### ***Body water models:***

for animals, all models incorporate metabolism and evaporation (incl. Kohn, Gretebeck, and Podlesak models)

pools of water within organism

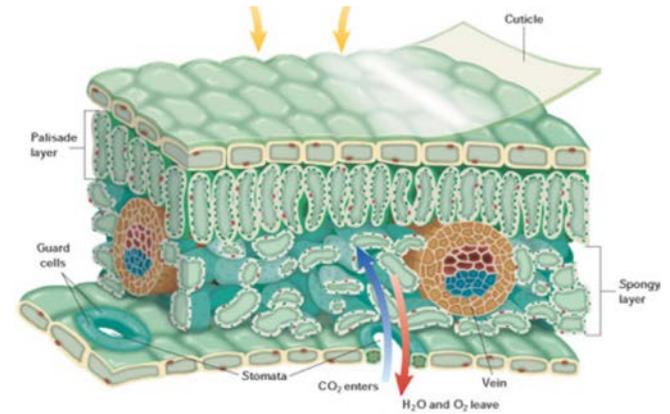
- evaporation processes
- metabolic isolation

### ***Intracellular processes:***

isotope gradients can exist across membranes in biological systems (Kreuzer et al. model)

# What happens to leaf water?

Craig Gordon (1965), Dongmann et al. (1974), Farquhar and Lloyd (1993) have shown:



$$\Delta^{18}\text{O}_e = \varepsilon^+ + \varepsilon_k + (\Delta^{18}\text{O}_v - \varepsilon_k) \frac{e_a}{e_i}$$

$\Delta^{18}\text{O}_e$  enrichment of leaf water ( $\Delta$  = enrichment above the source)

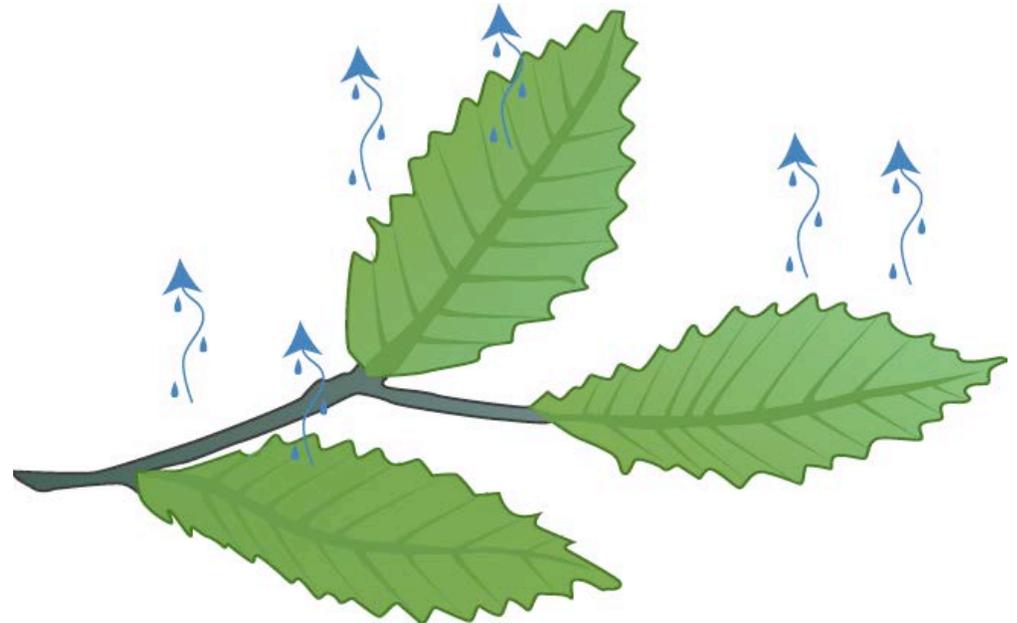
$\Delta^{18}\text{O}_v$  Water vapor

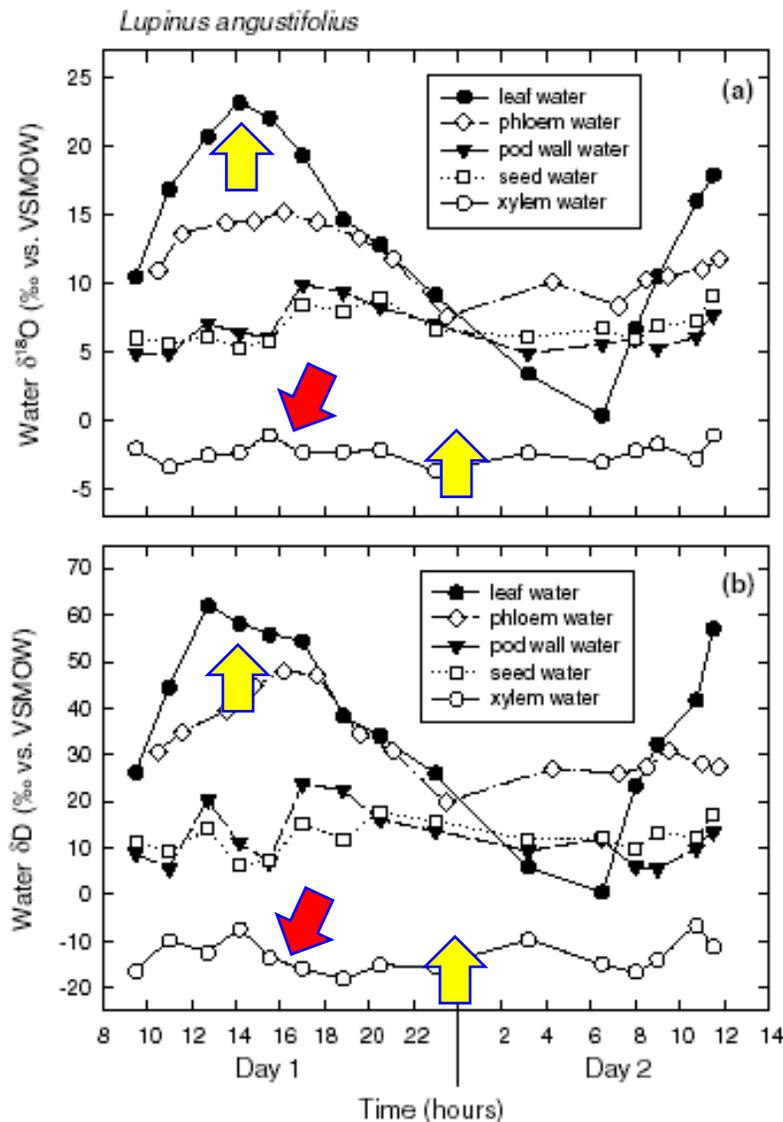
$e_a/e_i$  Atmosphere - leaf vapor gradient

$\varepsilon^+$  Equilibrium fractionation

$\varepsilon_k$  Kinetic fractionation

$$\varepsilon_k = \frac{3r_s + 2r_b}{r_s + r_b}$$



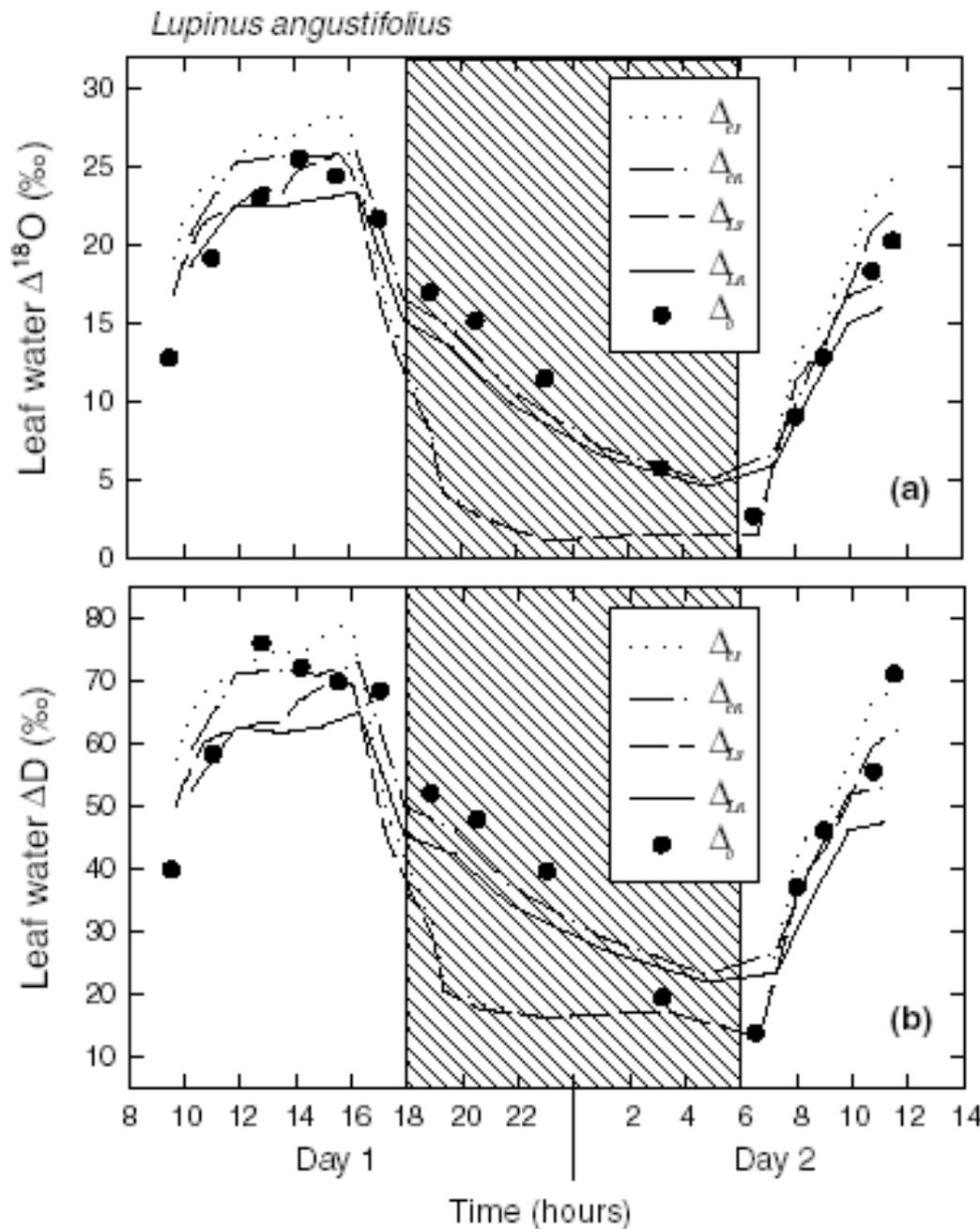


**Figure 6.** Diurnal variation in (a) oxygen and (b) hydrogen isotope ratios of various water components in *Lupinus angustifolius*. Leaf water samples were collected in bulk from 10 leaflets; pod-wall and seed water samples were collected in bulk from four to six fruits. Xylem and phloem water were also collected in bulk from several individuals at each sampling time. Samples were collected on 1 and 2 November 2000.

BUT . . .

The steady-state Craig-Gordon model rarely works (e.g. midday for 1+ hour, “maybe” at night or under water deficit conditions)

MUCH more data is needed + modeling, validation and case studies (vapor is a critical ‘unmeasured’ variable; Dawson, *in press*)



Non-steady state models require:

- Leaf anatomical properties
- Total leaf water concentration
- Leaf conductance
- Amount of atm.-vapor in leaf intercellular space

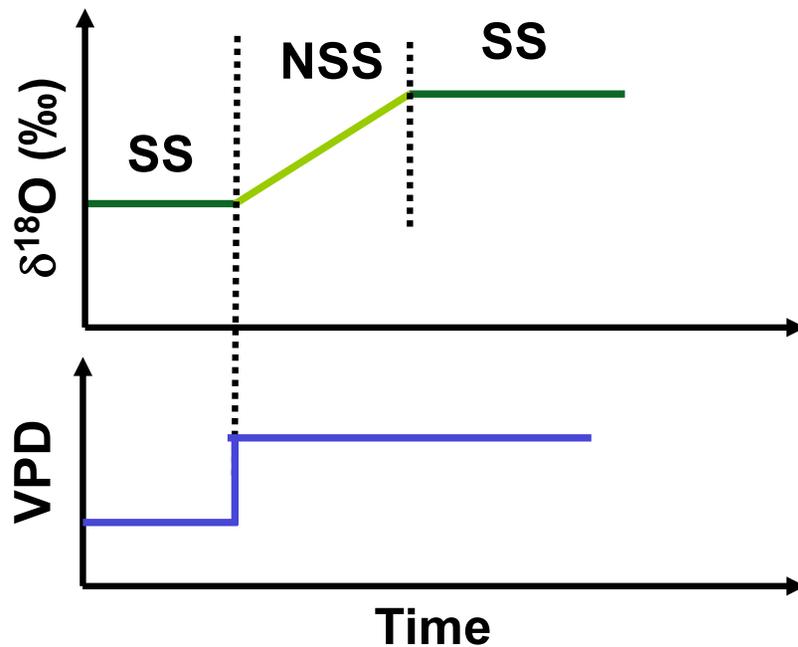
**Figure 8.** Comparison of modelled and observed (a) oxygen and (b) hydrogen isotope enrichment in leaf water of *Lupinus angustifolius*. Night-time hours are shaded. Symbols are as follows: predicted steady-state evaporative site enrichment ( $\Delta_{es}$ ); predicted non-steady-state evaporative site enrichment ( $\Delta_{en}$ ); predicted steady-state average leaf water enrichment ( $\Delta_{Ls}$ ); predicted non-steady-state average leaf water enrichment ( $\Delta_{Ln}$ ); and observed enrichment ( $\Delta_0$ ).

# Non Steady State Model (NSS) leaf water model

$$\Delta^{18}\text{O}_{LN} = \underbrace{\Delta^{18}\text{O}_L}_{\text{Steady State Model (SS)}} - \frac{\alpha_k \alpha^+}{g_i e_i} * \frac{1 - e^{-\rho}}{\rho} * \frac{d(W\Delta_L)}{dt}$$

Steady State Model (SS)

Non Steady State Model (NSS)



$$\alpha_k = 1 + \epsilon_k$$

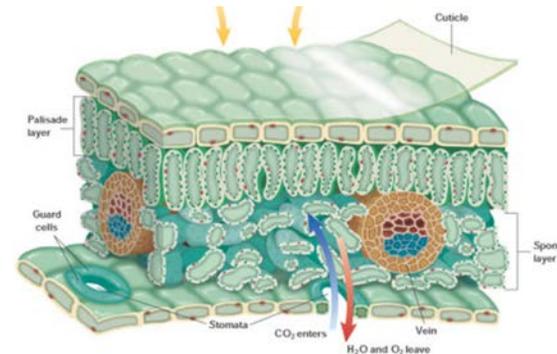
$$\alpha^+ = 1 + \epsilon^+$$

$\rho$  Péclet number

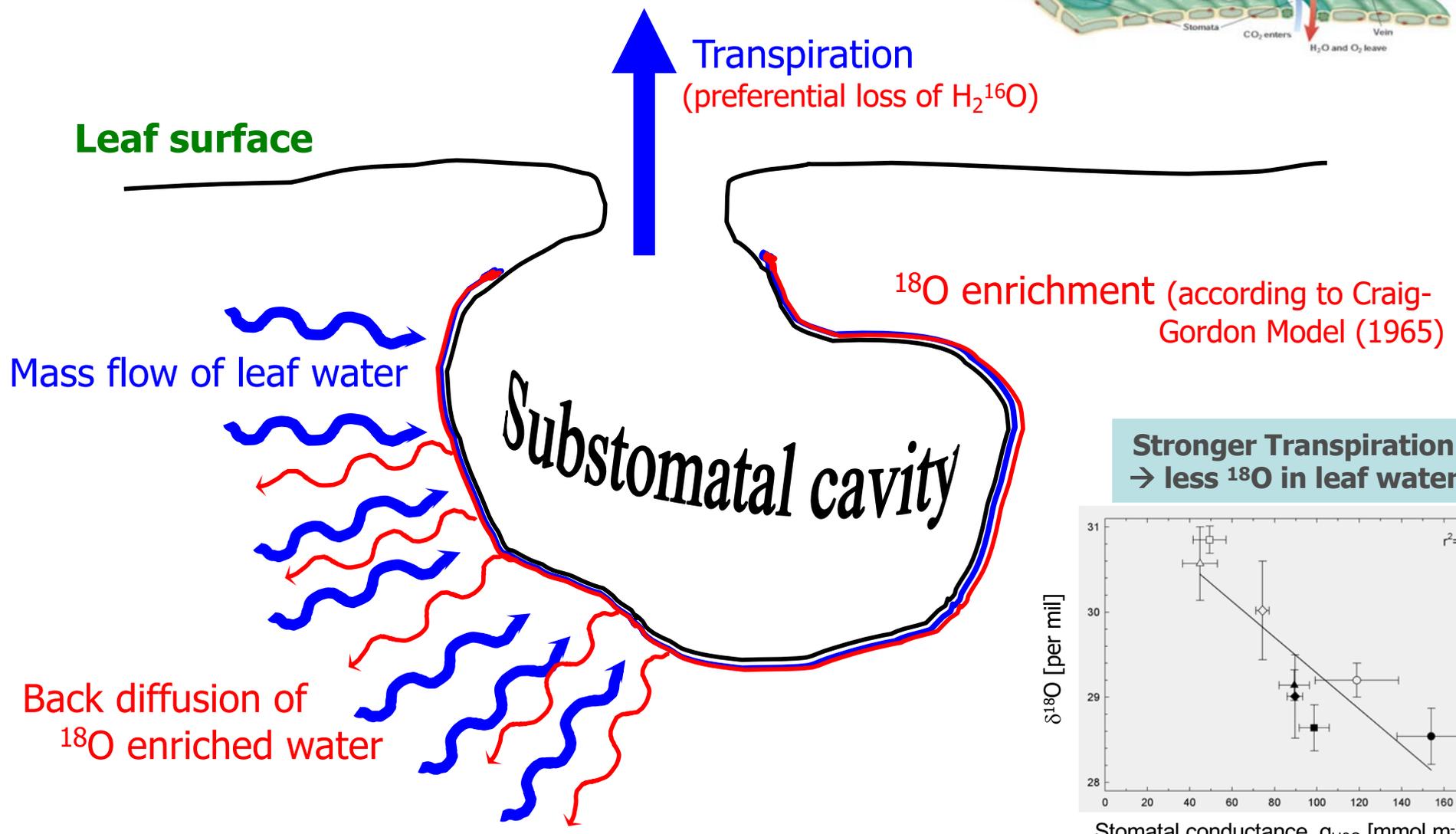
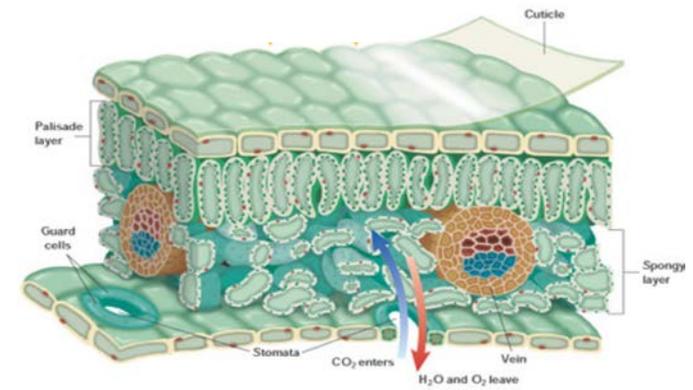
$g_i$  Total Conductance

$e_i$  Vapor Pressure inside Leaf

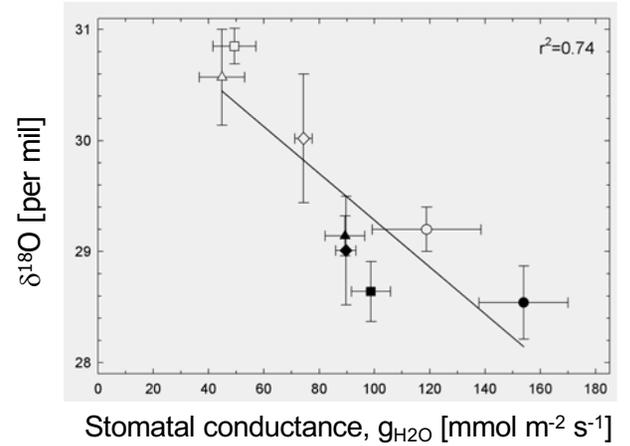
$W$  Leaf Water Concentration



# Péclet Effect



**Stronger Transpiration  
→ less <sup>18</sup>O in leaf water**

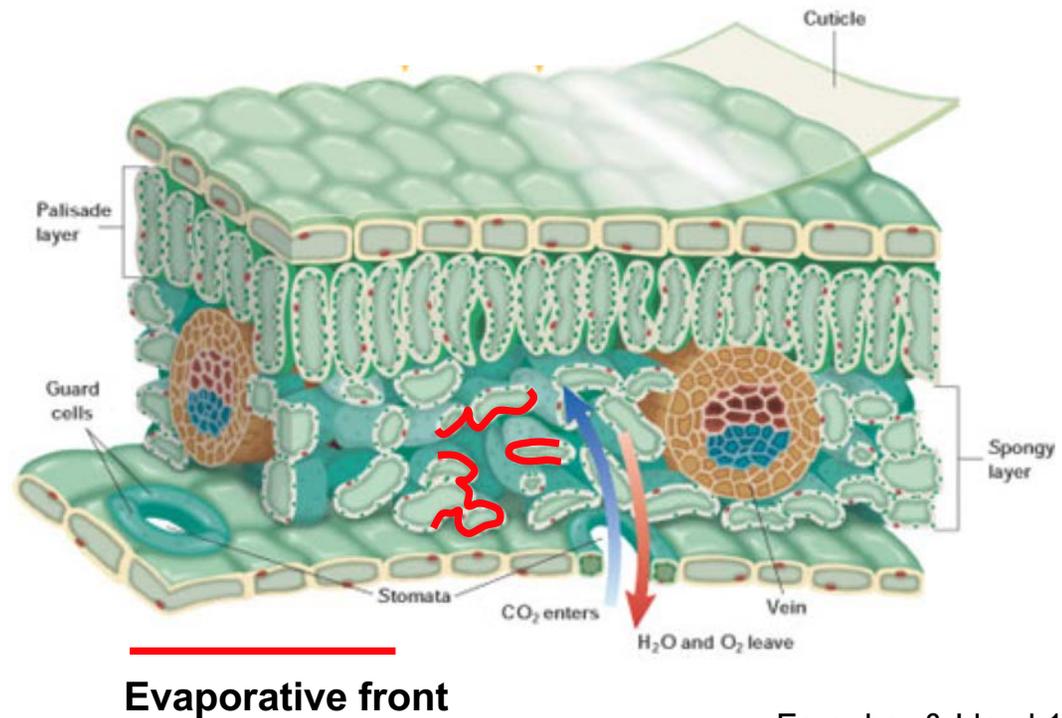


# Péclet Effect

$$\Delta^{18}O_L = \frac{\Delta^{18}O_e(1 - e^{-\rho})}{\rho}$$

$$\rho = \frac{LE}{CD}$$

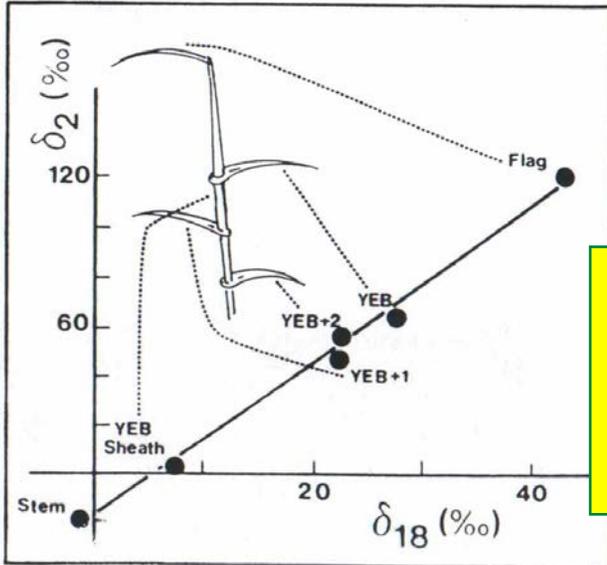
- L Effective path length
- E Transpiration
- C Molar density of Water
- D Diffusivity of Water



Farquhar & Lloyd 1993

# Leaf-Water Enrichment . . next steps . .

Barley Leaves

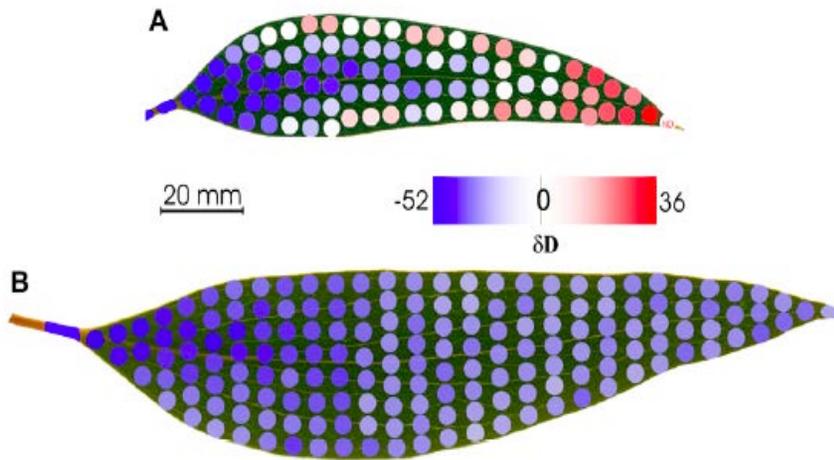


Walker & Lance 1991

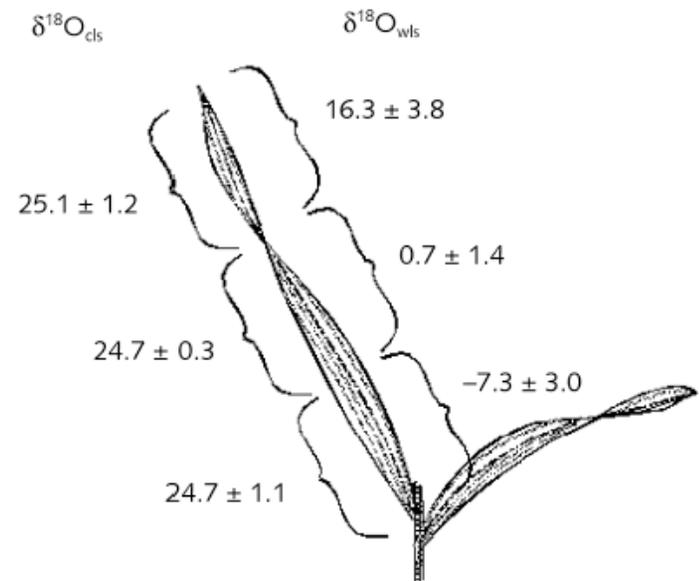
Leaf water becomes highly enriched during transpiration

Water vapor leaving the leaf via transpiration will be depleted and re-enter the air surround the leaf

Can we use this leaf water isotope information to better understand what "sets" the  $\delta^{18}\text{O}$  of cellulose or n-alkanes and also to partition evaporation from transpiration?



Santrucek et al. 2007; Plant Phys



Helliker & Ehleringer 2002; New Phyt

# Leaf Water Model

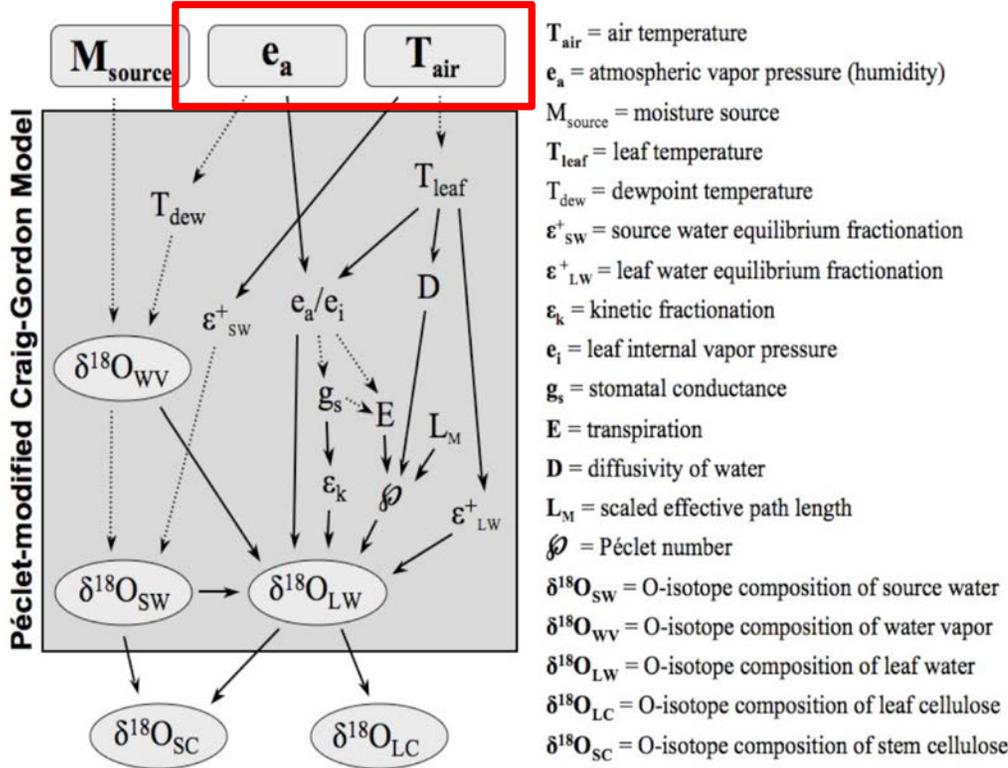
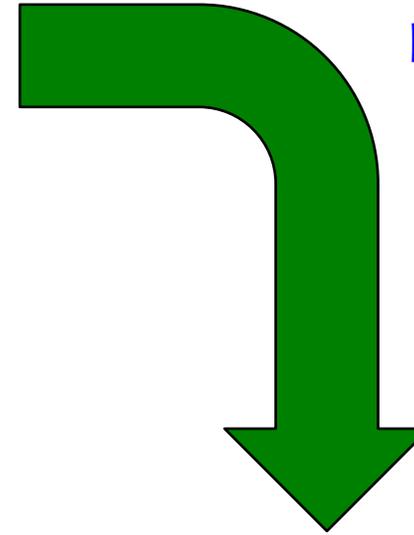


Fig. 1. Schematic illustration showing the functional relationships between the primary model variable (rounded squares) and secondary model variables (symbols within the shaded box) that influence leaf cellulose  $\delta^{18}\text{O}$  and stem cellulose  $\delta^{18}\text{O}$  in the Péclet-modified Craig-Gordon (PMCG) model. All variables containing isotope values (secondary variables as well as model outputs) are highlighted in ovals. Solid lines represent functions contained in the original PMCG model, and dotted lines indicate the functional relationships that we added to the model so that the effects of  $e_a$ ,  $T_{air}$ , and  $M_{source}$  on  $\delta^{18}\text{O}_{LC}$  and  $\delta^{18}\text{O}_{SC}$  could be tested.



## Findings

Modeled vs.  
Measured  
 $\delta^{18}\text{O}_{LC}$   $R^2 = 0.97$   
 $\delta^{18}\text{O}_{SC}$   $R^2 = 0.91$

**Key Driver = VPD**

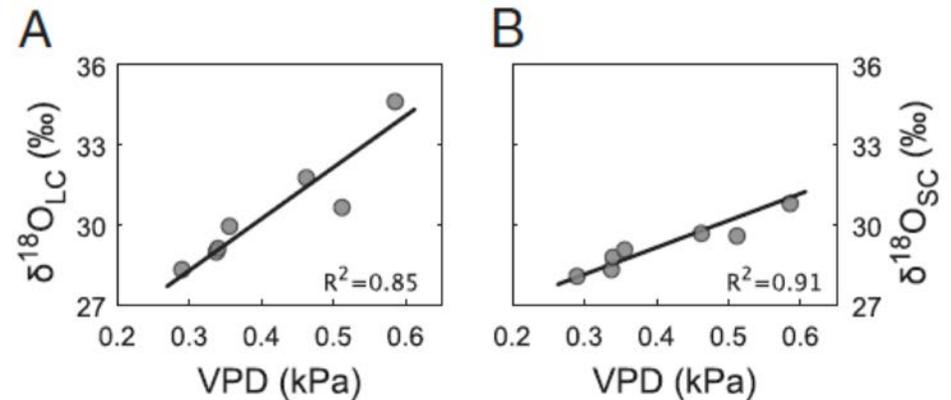
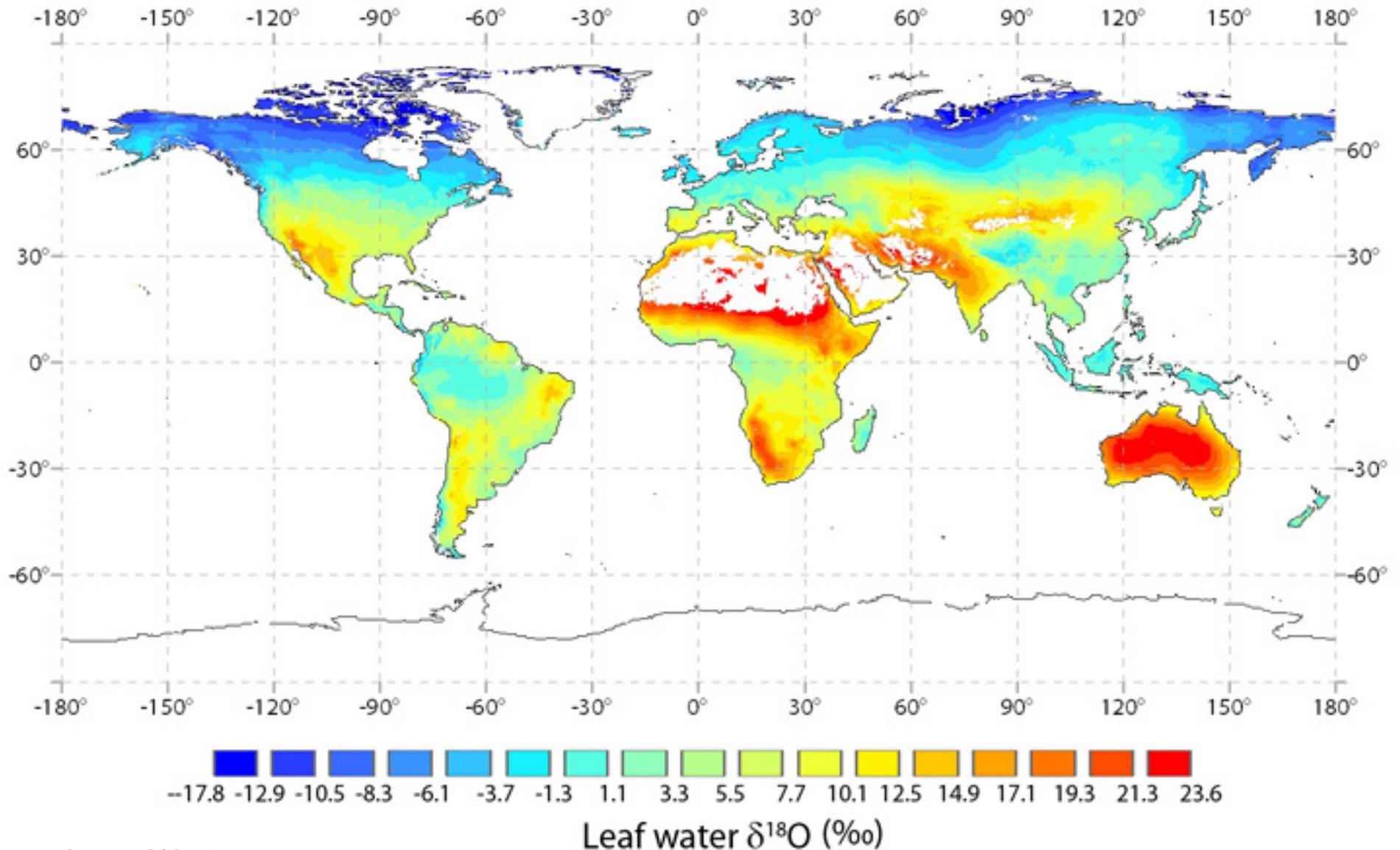


Fig. 4. The relationship between mean annual leaf-to-air vapor pressure difference (VPD) and  $\delta^{18}\text{O}$  values in (A) leaf and (B) stem cellulose for measured values across the seven sites along the Mauna Loa gradient.



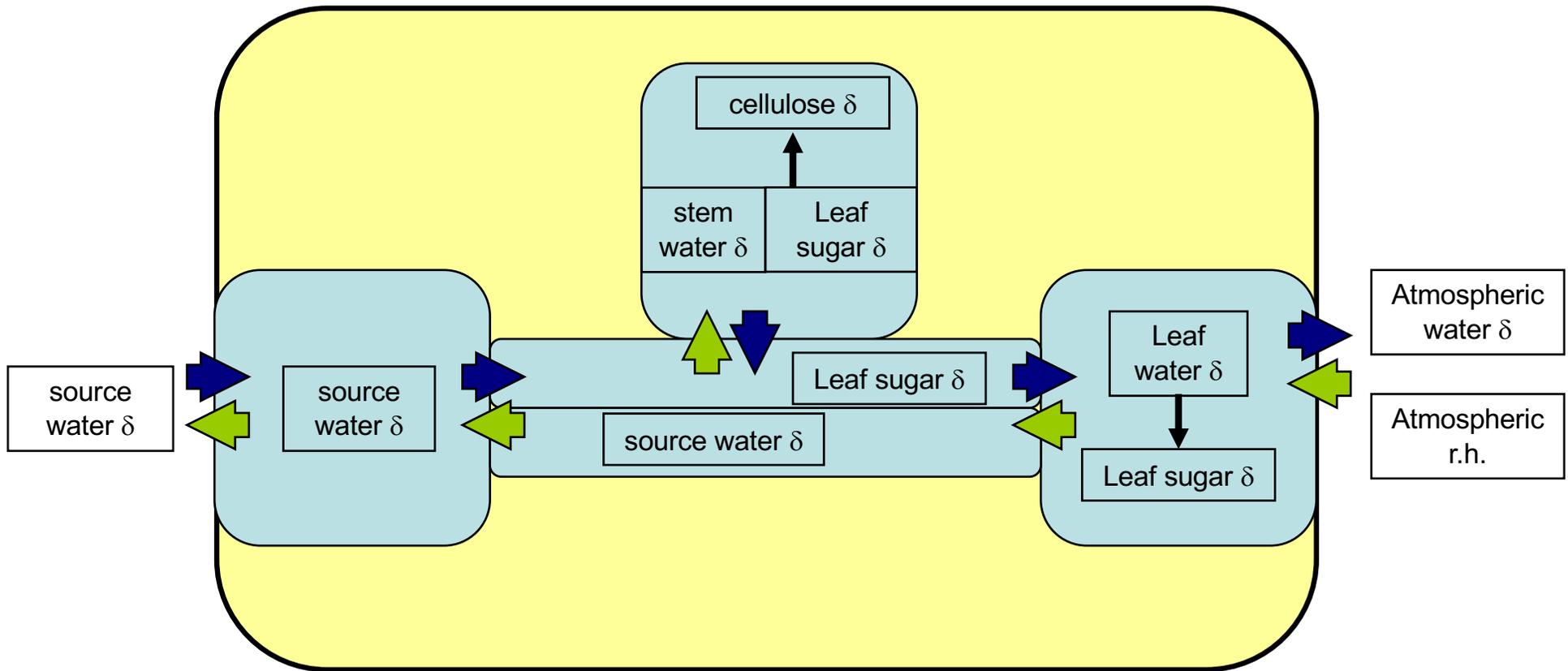
From Jason West

Model of plant  
 $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ :  
 Linking to secondary  
 metabolism and  
 GIS integration

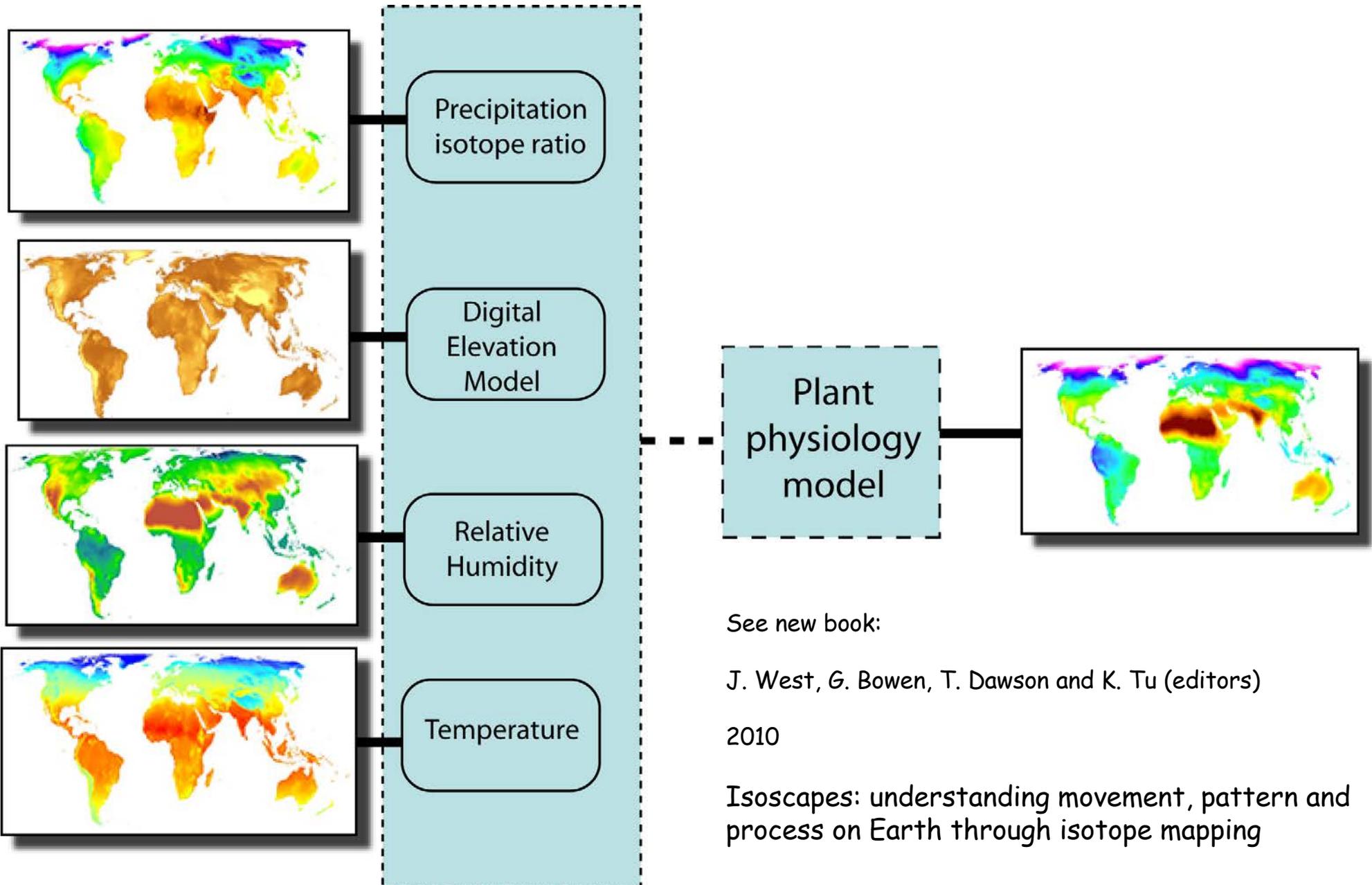
$$R_{wl} = \alpha^* \left[ \alpha_k R_{wx} \left( \frac{e_i - e_s}{e_i} \right) + \alpha_{kb} R_{wx} \left( \frac{e_s - e_a}{e_i} \right) + R_a \left( \frac{e_a}{e_i} \right) \right]$$

$$\delta_s = \delta_{wl} + \epsilon$$

$$\delta_{cb} = f_o(\delta_{wb} + \epsilon_{bc}) + (1 - f_o)(\delta_s)$$



# Building an "Isoscape" of 18-O in leaf cellulose (after J. West)



See new book:

J. West, G. Bowen, T. Dawson and K. Tu (editors)

2010

Isoscapes: understanding movement, pattern and process on Earth through isotope mapping