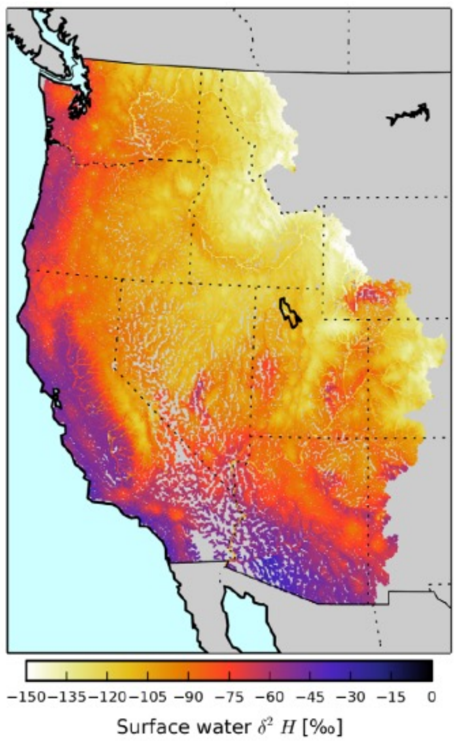
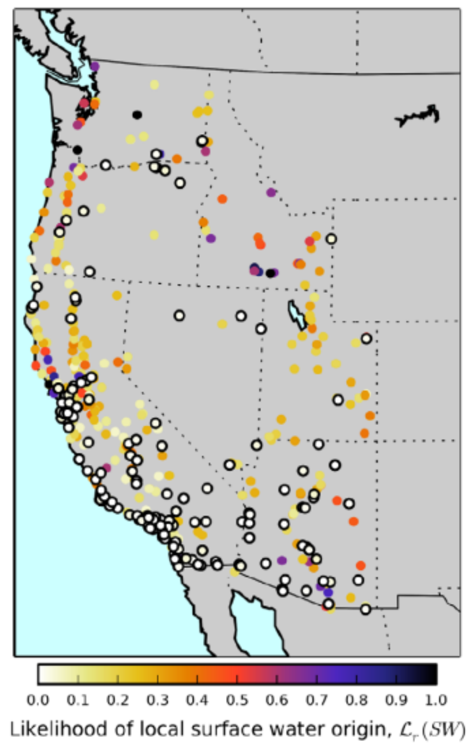
IsoCamp

SIRFER @ Utah

2017

stableisotopes.utah.edu





Water Isotopes and Isoscapes

Gabe Bowen

University of Utah

The Plan

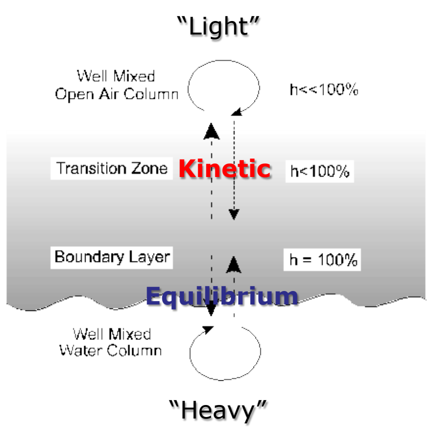
- Review and expand on **Principles** underlying isotopic variation in the water cycle
- Explore **Case Studies** showing how these principles can be integrated to understand water isotope variation across systems and scales
  - Atmosphere/precipitation
  - Surface (river) water
  - Tap water

Refresher: Important processes

1. Phase change reaction
   a. Equilibrium & kinetic effects
   b. 2 elements, 4(5) isotopes, 3(4) parameters (δ^2H, $\delta^{18}O$, D-excess…$\Delta^{17}O$)
2. Mixing
   a. Spatial
   b. Temporal

Phase change rxn: Craig-Gordon

- Open air
  - Well-mixed
  - Large
- Transition zone (TZ)
  - Turbulently mixed
  - Decreasing humidity upwards
- Boundary layer (BL)
  - Thin, well-mixed layer
  - 100% RH
- Liquid
  - Large (ocean) or small (droplet) body of water
  - Mixed or stratified



Gat, 1996

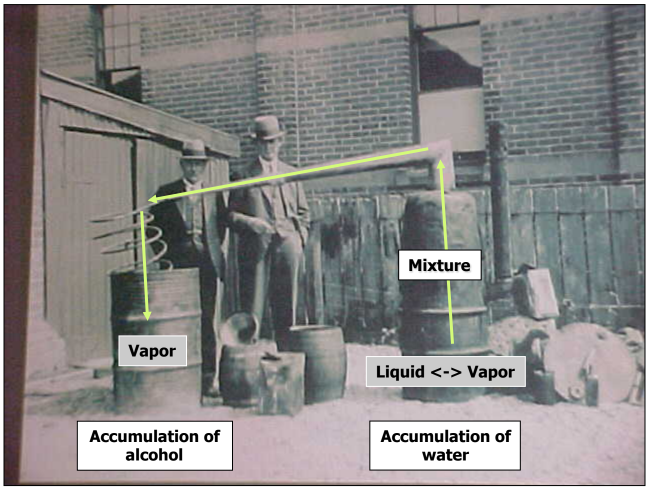
Rayleigh Distillation

- A processes by which fractionation (of isotopes, elements, molecules, elephants) leads to a change in 2-component reactant mixture
- Is it Rayleigh Distillation?
  - Open system
    - No addition of material
    - Rapidly and continuous removal of product
  - Product is fractionated relative to the reactant
- The Rayleigh equation describes the composition of the reactant pool as a function of reaction progress:

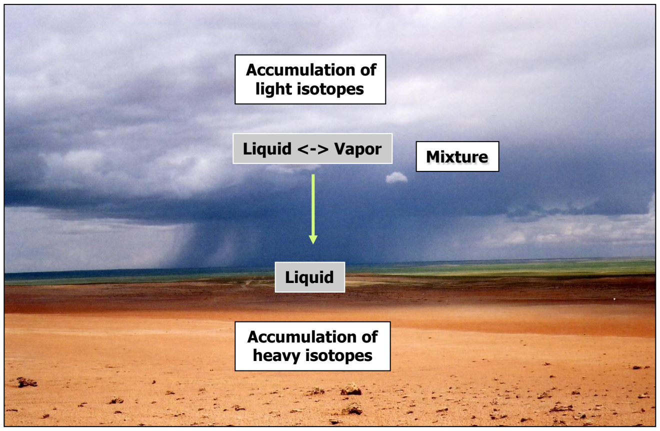
$$R = R_0 f^{(\alpha - 1)}$$

R and R_0 are current and initial isotope ratios
f is fraction of reactant remaining

Rayleigh Distillation

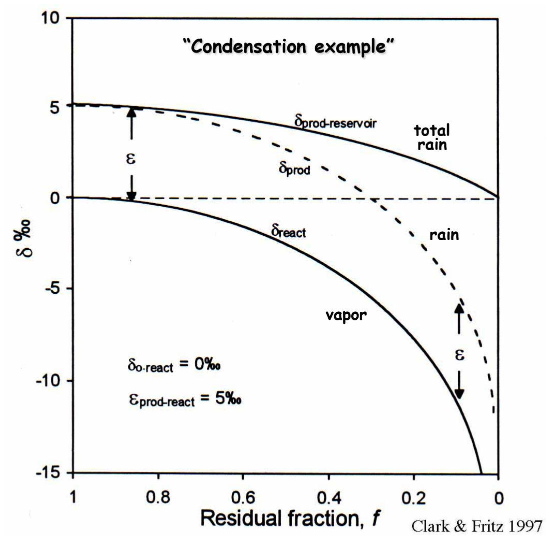


Rayleigh Distillation



Rayleigh Distillation and Precipitation

- Precipitation formed from condensation of cloud vapor
- Equilibrium process (free atmosphere RH ≈ 100%)
- **But one element of complexity…**



Q: What causes precipitation?

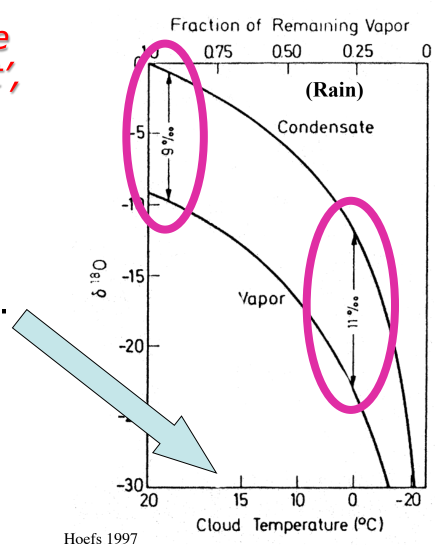
Q: How does this change our Rayleigh Distillation model?

Rayleigh Distillation and Precipitation

!!! This does not cause the 'temperature effect', but it contributes (slightly) to it !!!

As condensation proceeds, the temperature of the remaining cloud decreases.

Thus, α increases, resulting in a greater difference between cloud and rain H_2O



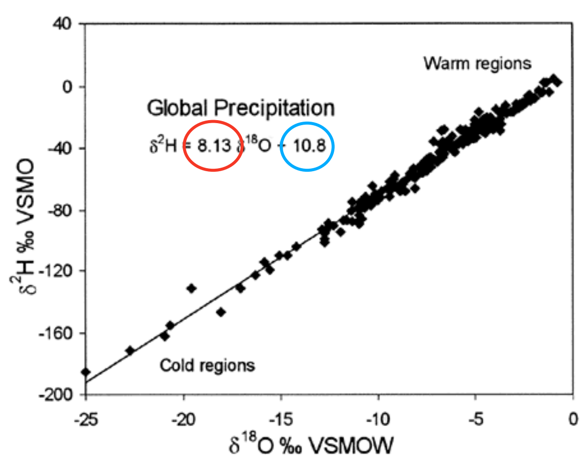
Hoefs 1997

A note on the equilibrium fractionation factors for water isotopes

- at 20° C
  - ε^2H = 74‰
  - $\varepsilon^{18}O$ = 9.2‰
  - $\varepsilon^2H / \varepsilon^{18}O$ = 8.0
- at 80° C
  - ε^2H = 38‰
  - $\varepsilon^{18}O$ = 4.5‰
  - $\varepsilon^2H / \varepsilon^{18}O$ = 8.4

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

The Global Meteoric Water Line



Condensation is an equilibrium process

so

Most precipitation δ values lie along a Global Meteoric Water Line (GMWL) of slope 8

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

The intercept of the GMWL is +10‰

Clark and Fritz, 1997; GMWL defined by Craig, 1961

The Evaporative Flux

- The isotopic composition of the evaporating flux depends on
  - the isotopic composition of the liquid
  - the combination of equilibrium and kinetic (diffusion) fractionation factors
- This flux is 'added' to the atmosphere, affecting vapor δ values
- Its isotopic composition is lighter than that of the liquid water

$$\varepsilon_t = \varepsilon_e + \Delta\varepsilon\ (1 - h)$$

ε_t = total enrichment
ε_e = equilibrium enrichment
$\Delta\varepsilon$ = kinetic enrichment
h = open air humidity

Let's look at equilibrium and kinetic enrichment factors

Q: What was the relationship between $\varepsilon_e{}^2H$ and $\varepsilon_e{}^{18}O$?

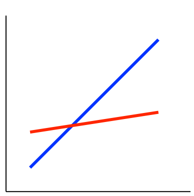
A: $\varepsilon_e{}^2H / \varepsilon_e{}^{18}O = 8$

$\Delta\varepsilon^2H$ and $\Delta\varepsilon^{18}O$ give us a different relationship

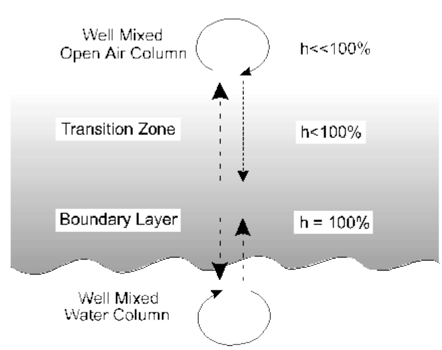
Kinetic
$\alpha^2H \approx \alpha^{18}O$

Equilibrium
$\alpha^2H = 8*\alpha^{18}O$

δ^2H



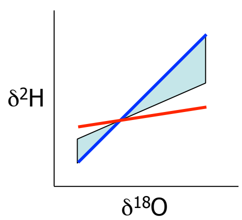
$\delta^{18}O$

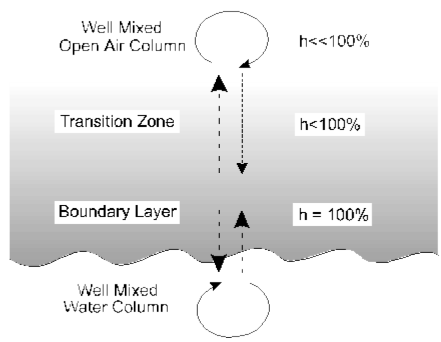


Gat, 1996

Let's look at equilibrium and kinetic enrichment factors

- The net ratio of ^2H and ^{18}O isotope effects is a blend of the Equilibrium and Kinetic ratios, typically between 3 and 8
- The coupled $^2H/^{18}O$ system gives us a "proxy" for kinetic fractionation… **deuterium excess**

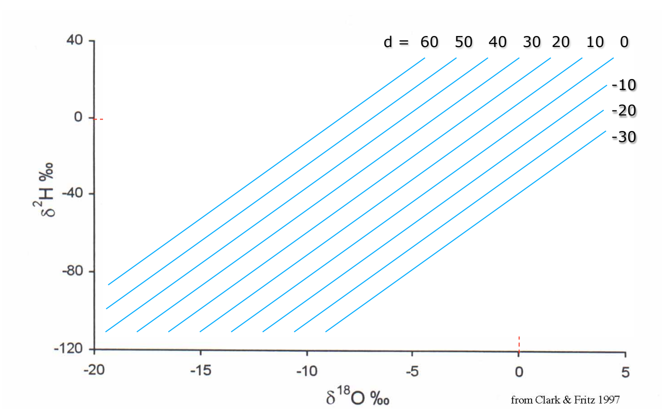




Gat, 1996

Deuterium Excess (d)

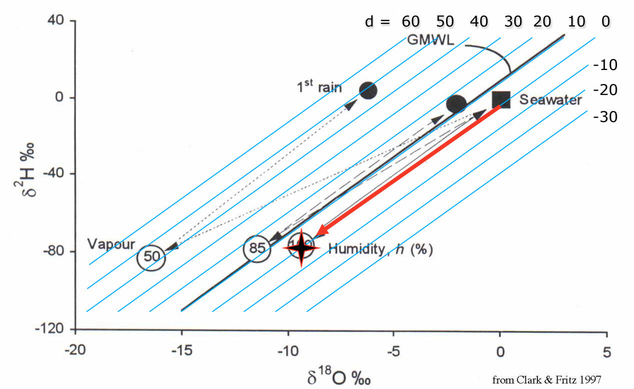
- d of seawater is 0 – 8 x 0 = 0‰



$d = \delta^2H - 8 \times \delta^{18}O$

Deuterium Excess (d)

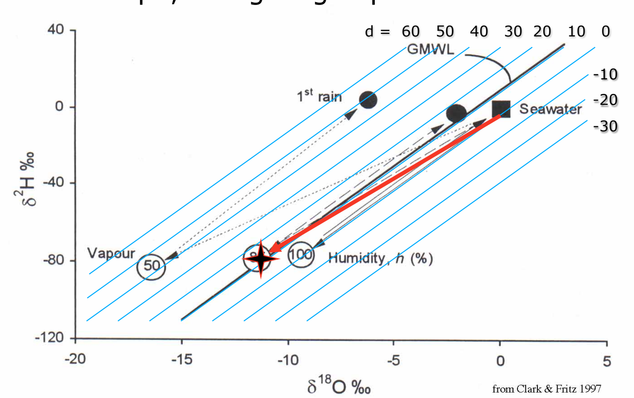
- If sea water evaporated at 100% RH (equilibrium process) it would produce vapor with d = 0‰



$d = \delta^2H - 8 \times \delta^{18}O$

Deuterium Excess (d)

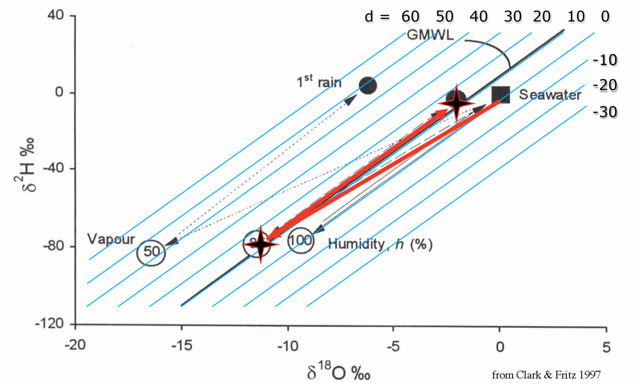
- The atmospheric humidity over the oceans is ~80%
- The kinetic isotope effect is expressed, reducing the evaporation slope, and giving vapor with d = +10‰



$d = \delta^2H - 8 \times \delta^{18}O$

Deuterium Excess (d)

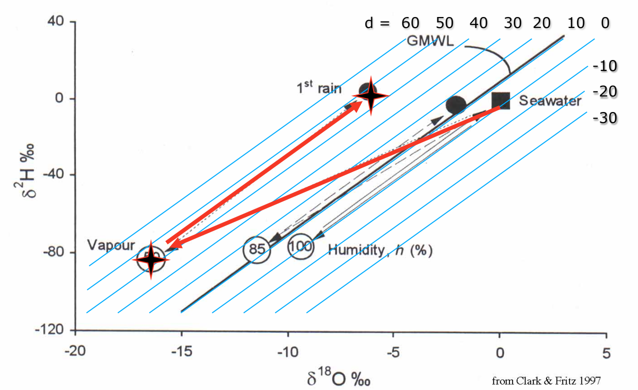
- The precipitation condensing from this vapor (equilibrium process) preserves the d value of +10‰
- This gives us the intercept of the GMWL



$d = \delta^2H - 8 \times \delta^{18}O$

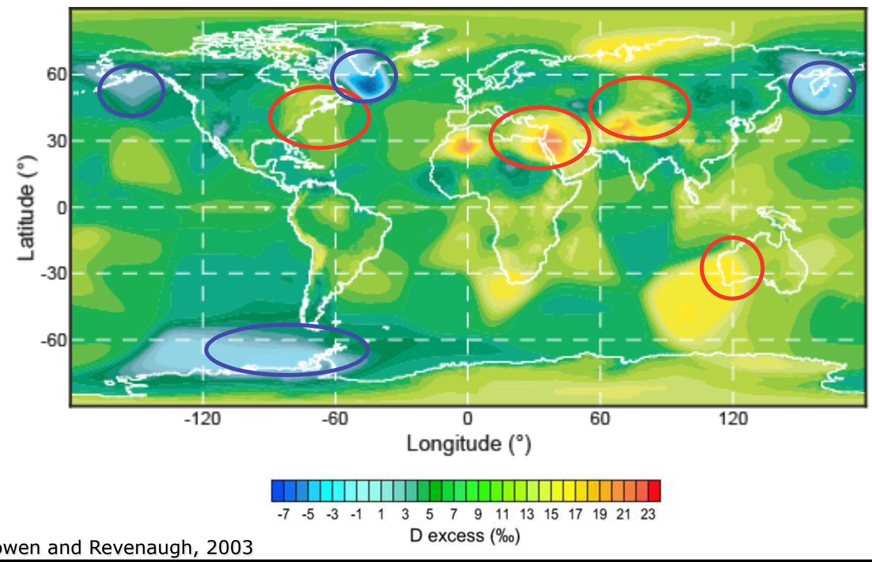
Deuterium Excess (d)

- At lower RH, evaporation lines have lower slopes (<<8)
- The resulting vapor (and precipitation) has higher d values



$d = \delta^2H - 8 \times \delta^{18}O$

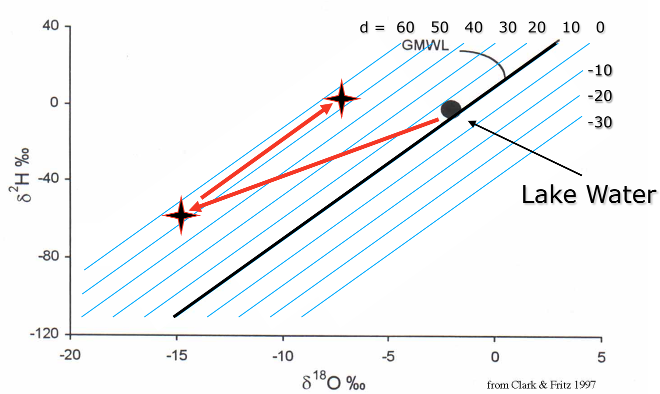
Precipitation Deuterium Excess and RH



Bowen and Revenaugh, 2003

Deuterium Excess (d)

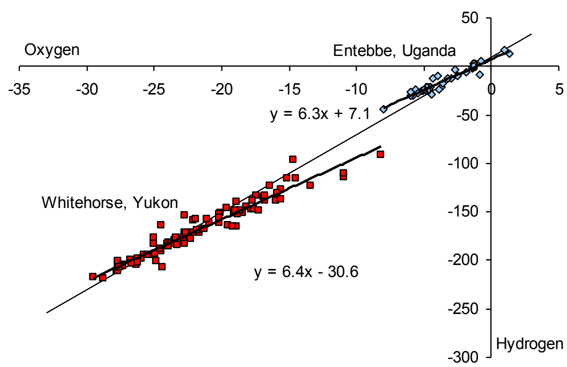
- The same principle applies to re-evaporation of surface water from the continents, which can occur at very low RH (slope as low as ~3)



$d = \delta^2H - 8 \times \delta^{18}O$

Local Meteoric Water Lines

- Isotopic variability in local precipitation often does not follow the GMWL
- What kinds of processes could the Local Meteoric Water Lines shown here reflect?



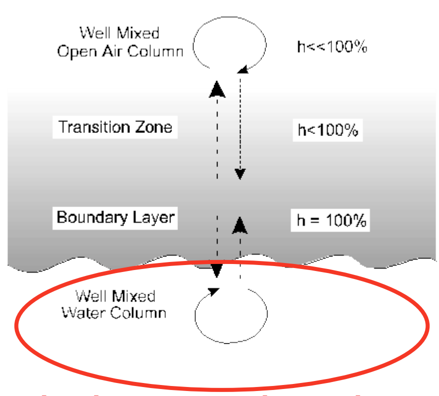
Data: GNIP

The Other Side of Evaporation: Evapoconcentration

Isotope effects related to the model layers

- Open air
  - Vapor flux diffusing downward carries atmospheric signal
- Transition zone
  - Kinetic fractionation during diffusion
- Boundary layer
  - Equilibrium fractionation between vapor and liquid
- Liquid
  - Liquid δ value labels the upward flux of vapor

Evaporation removes vapor with a different isotopic composition than the liquid.



What happens to the δ values of the remaining liquid?

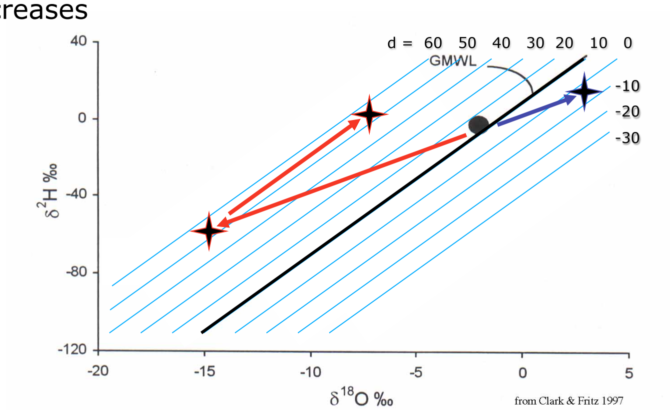
Gat, 1996

The Residual Water

- If a significant fraction of the liquid water is evaporated, the δ values of the remaining water will increase (remember 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
  - The back-flux of water from the atmosphere (relative size, rate, and isotopic composition)
- Depending on the system, this last factor can be insignificant (the ocean) or the most important factor (leaf water)

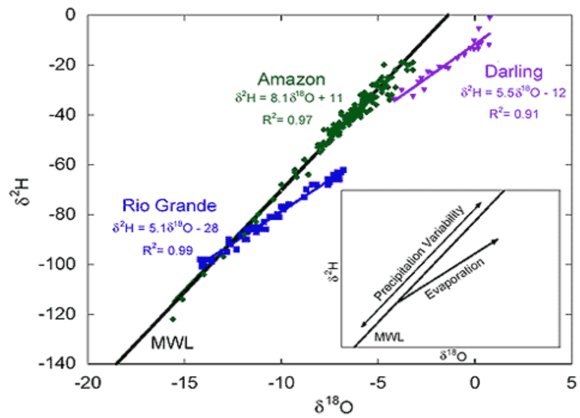
Deuterium Excess (d)

- For large bodies of water, the evaporation line can be extended to show the change in residual water δ values and d
- As evapoconcentration proceeds, δ values increase and d decreases



$d = \delta^2H - 8 \times \delta^{18}O$

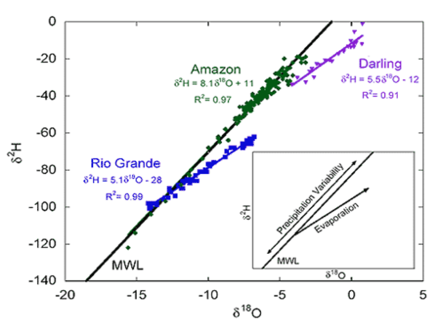
Evaporation Lines for Rivers

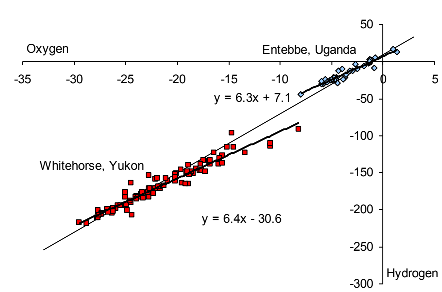


Q: Why do these evaporation lines have different slopes?

Evaporation Lines vs. LMWLs

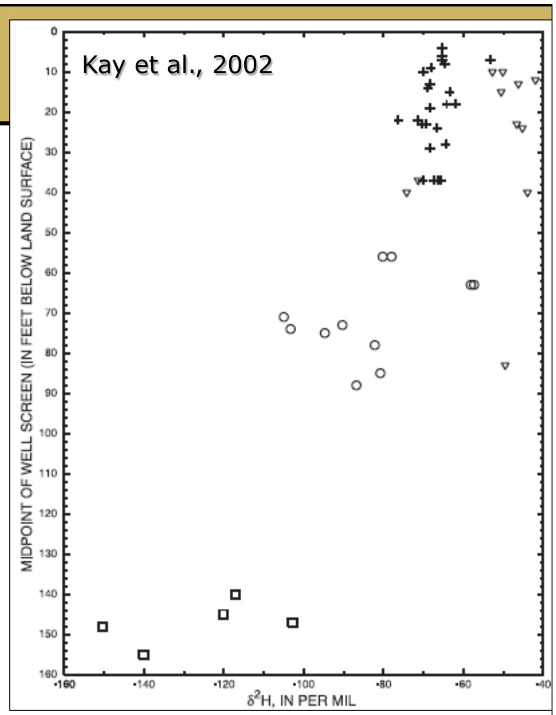
- A note of caution
  - LMWLs are sometimes defined using surface waters
  - This can be a useful practice, providing a 'reference line' for other water samples, but
  - Precipitation and surface-water defined LMWLs can reflect different processes and should not be confused



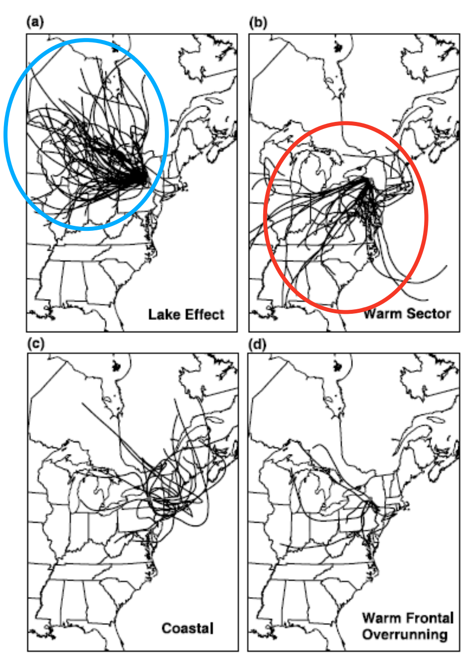


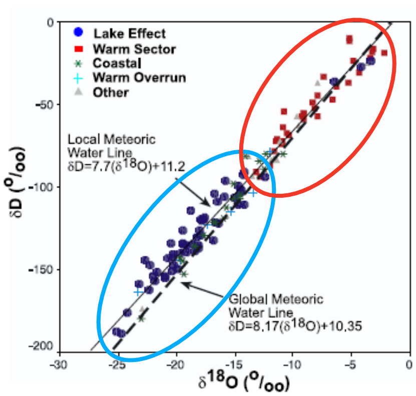
Mixing

- Linear mixing of endmembers
- Natural and human-influenced processes
- Sources signals arise from separation in space or time



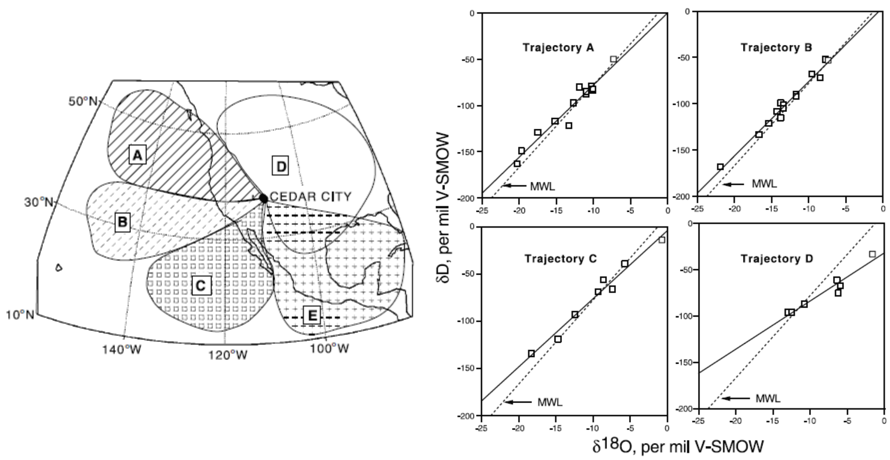
Mixing in the Atmosphere





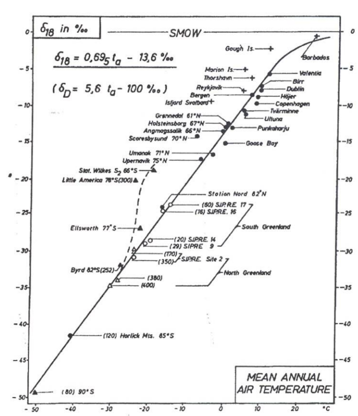
Burnett et al., 2004

Another Example…



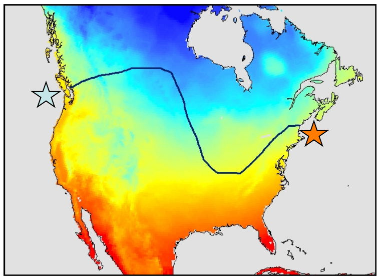
Friedman et al., 2002, *JGR*

Precipitation Isotope Ratios and Temperature

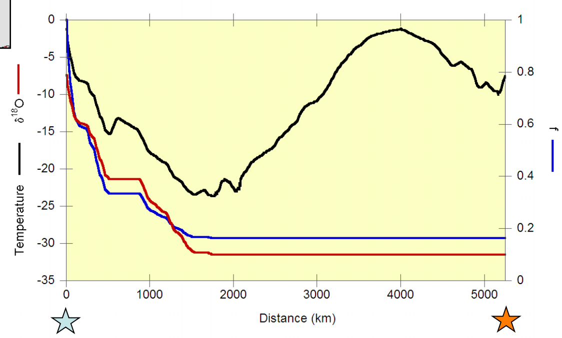


Dansgaard, 1964

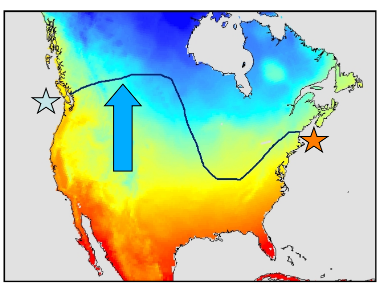
Transport and Distillation



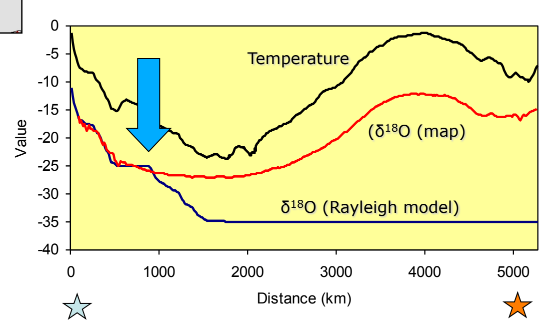
- According to Rayleigh, air mass isotopic composition is determined by:
  - initial temperature and δ value, and
  - **lowest** temperature encountered (extent of rainout)



Transport and Distillation



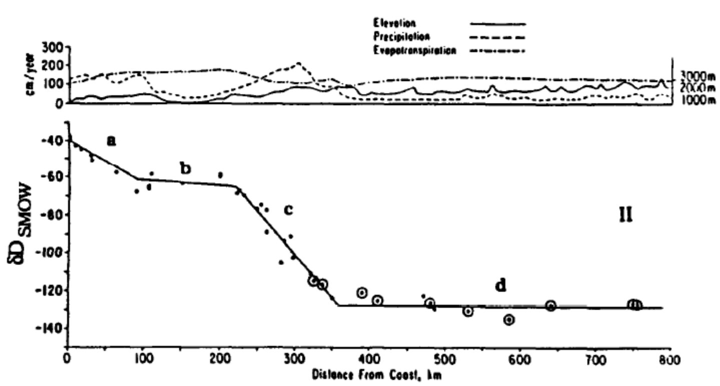
Rayleigh works well in the absence of mixing



Mixing

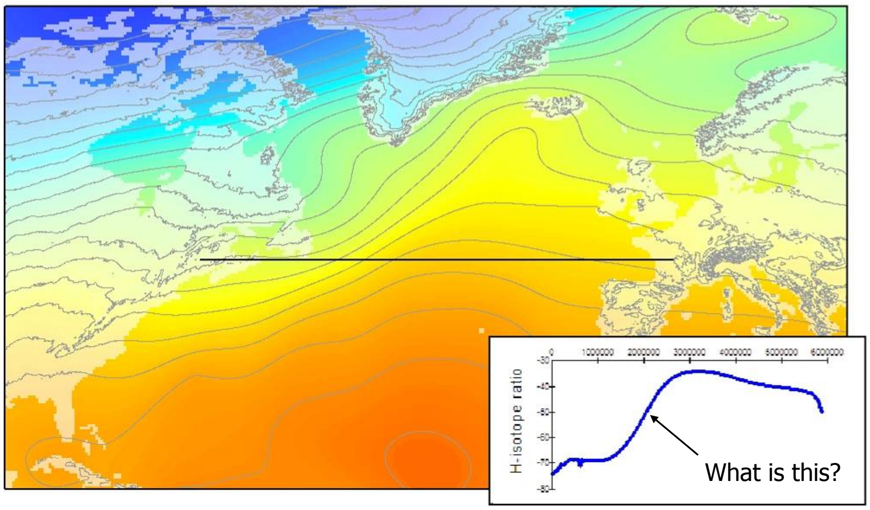
- Addition of water along transport path
  - Evapotranspiration (recycling)
  - Eddy diffusion
  - Groundwater recharge/discharge
  - Merging tributaries
  - Urban runoff/effluent

An Example: California/Nevada Transect



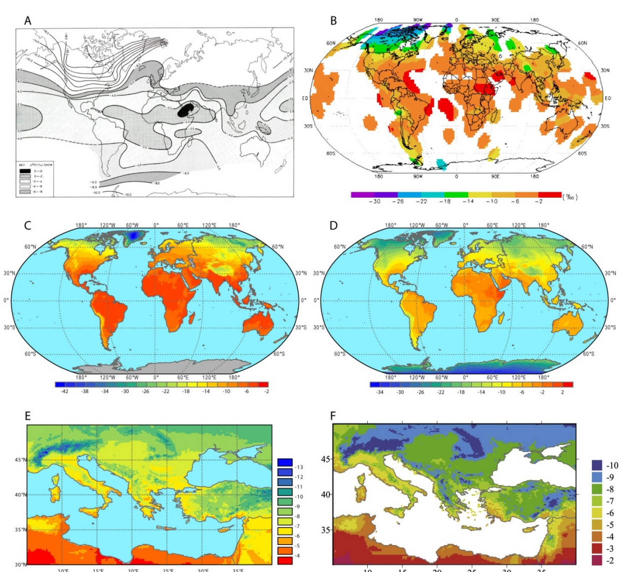
Ingraham and Taylor, 1991, *WRR*

North Atlantic Precipitation Isotopes



Data: GNIP

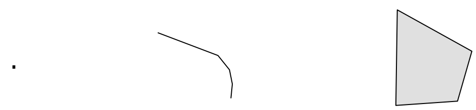
'Isoscapes': Isotopic landscapes



Bowen, 2010, *Isoscapes*
www.WaterIsotopes.org

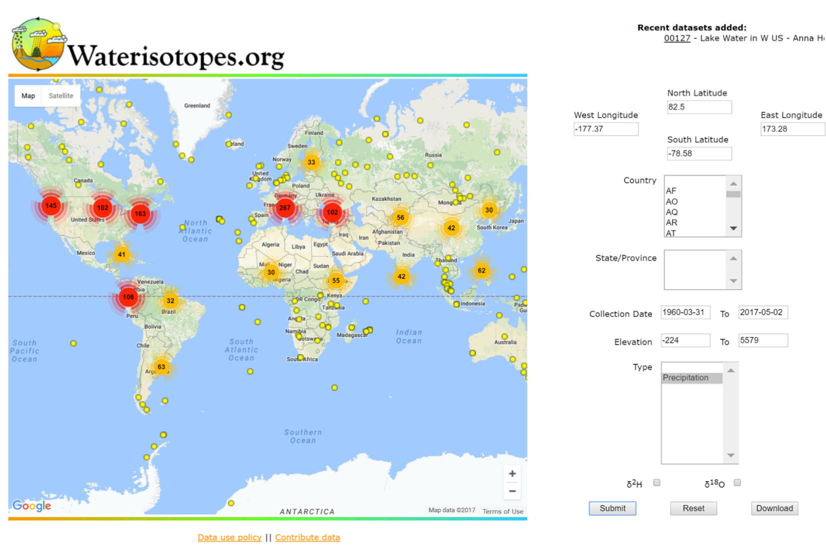
Spatial Data Structures

- Vector (discrete)
  - Shapes composed of discrete georeferenced nodes linked in sequence
  - Each shape possesses attributes (think of columns in a spreadsheet)

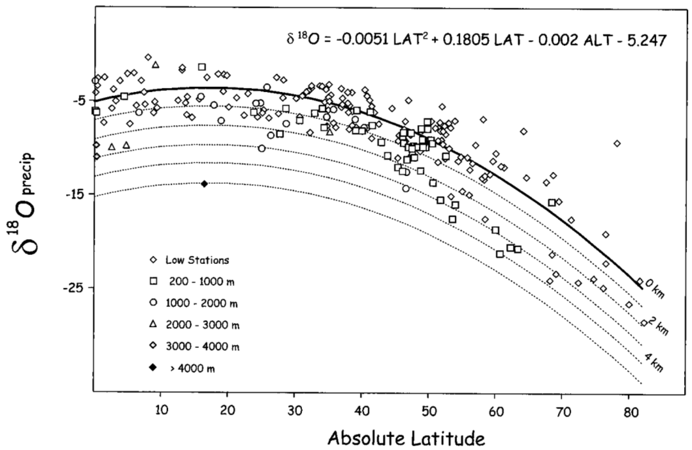


- Raster (pseudo-continuous)
  - Regular rectangular grid of pixels
  - Each pixel has 1 or more attributes (bands)

A Precipitation Isoscape



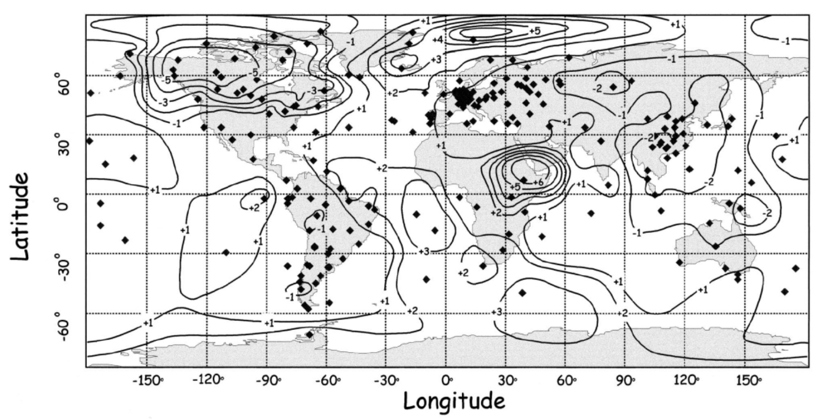
A Precipitation Isoscape



Q: What processes are we representing here?

Bowen and Wilkinson, 2002, *Geology*

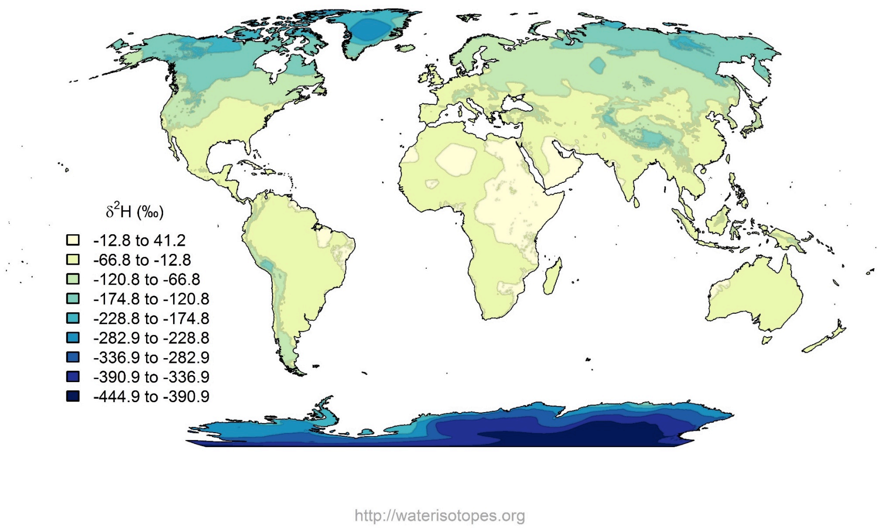
A Precipitation Isoscape



Q: What processes are we representing here?

Bowen and Wilkinson, 2002, *Geology*

A Precipitation Isoscape

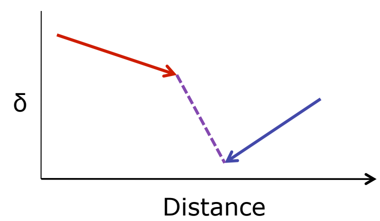


What can we do with an Isoscape?

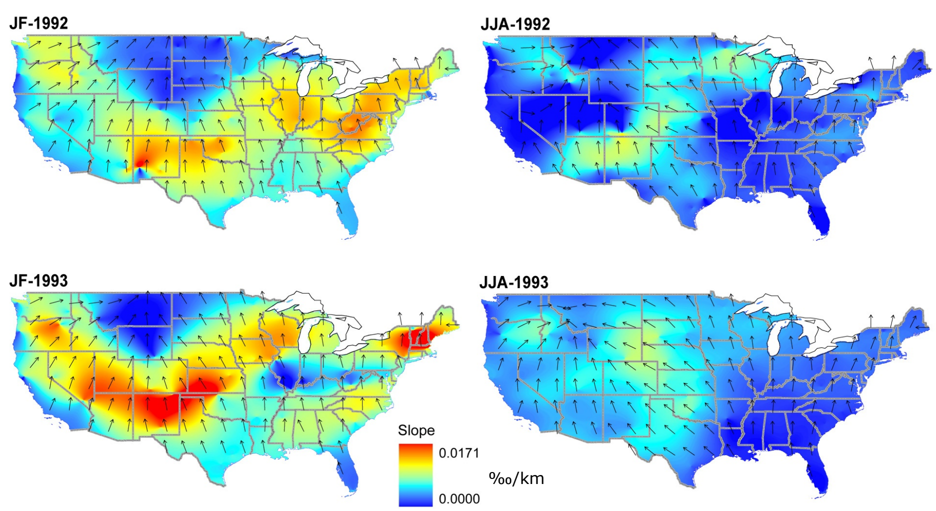
- Analyzing isoscape surfaces
- Comparing isoscapes
- Aggregating information over areas

Analyzing Surfaces: Isoscape Gradient

- Isotope gradient anomalies can reflect:
  - Non-random precipitation distribution
  - Juxtaposition of air masses

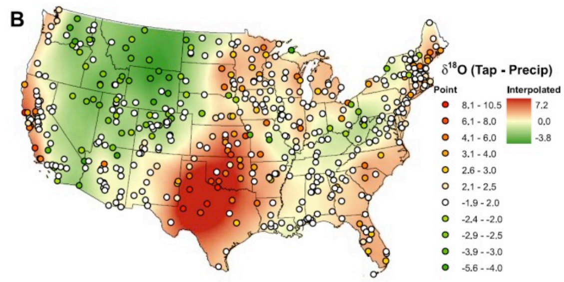


Precipitation δ¹⁸O Gradient, USA



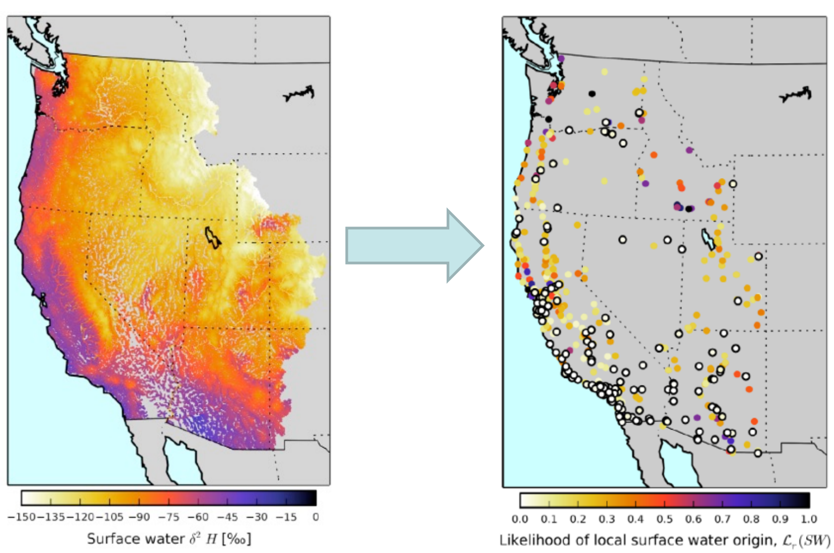
Liu et al., 2010, *JGR*

Comparing: US Surface Waters



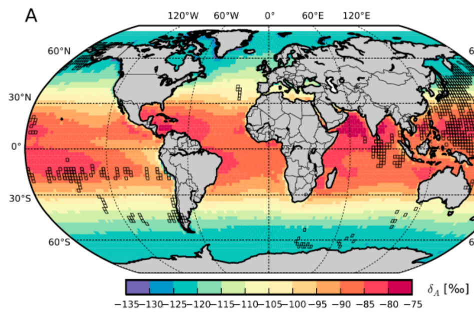
Bowen et al., 2007, *WRR*

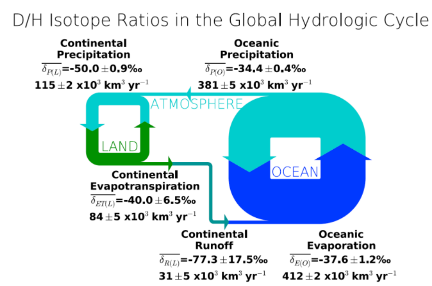
Aggregating: Tap Water Sources



Good et al., 2014, *WRR*

Aggregating: Global Water Isotope Budgets





Good et al., 2015, *GRL*