Periodic Table of the Elements

Main groups

Main groups

Transition metals

1 1A																	18 8A
1 **H** 1.00794	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 **He** 4.00260
3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.81	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.998403	10 **Ne** 20.1797
11 **Na** 22.98977	12 **Mg** 24.305	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 **Al** 26.98154	14 **Si** 28.0855	15 **P** 30.97376	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.996	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.710	51 **Sb** 121.757	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.29
55 **Cs** 132.9054	56 **Ba** 137.33	57 ***La** 138.9055	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.9665	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0254	89 **†Ac** 227.0278	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (269)	109 **Mt** (268)	110 (271)	111 (272)	112 (277)		114 (289)		116 (289)		118 (293)

*Lanthanide series	58 **Ce** 140.12	59 **Pr** 140.9077	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.50	67 **Ho** 164.9304	68 **Er** 167.26	69 **Tm** 168.9342	70 **Yb** 173.04	71 **Lu** 174.967
†Actinide series	90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	93 **Np** 237.048	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Naturally Occurring Isotopes in Water

Blue shaded squares are stable and the unshaded squares are unstable (radioactive) nuclides.
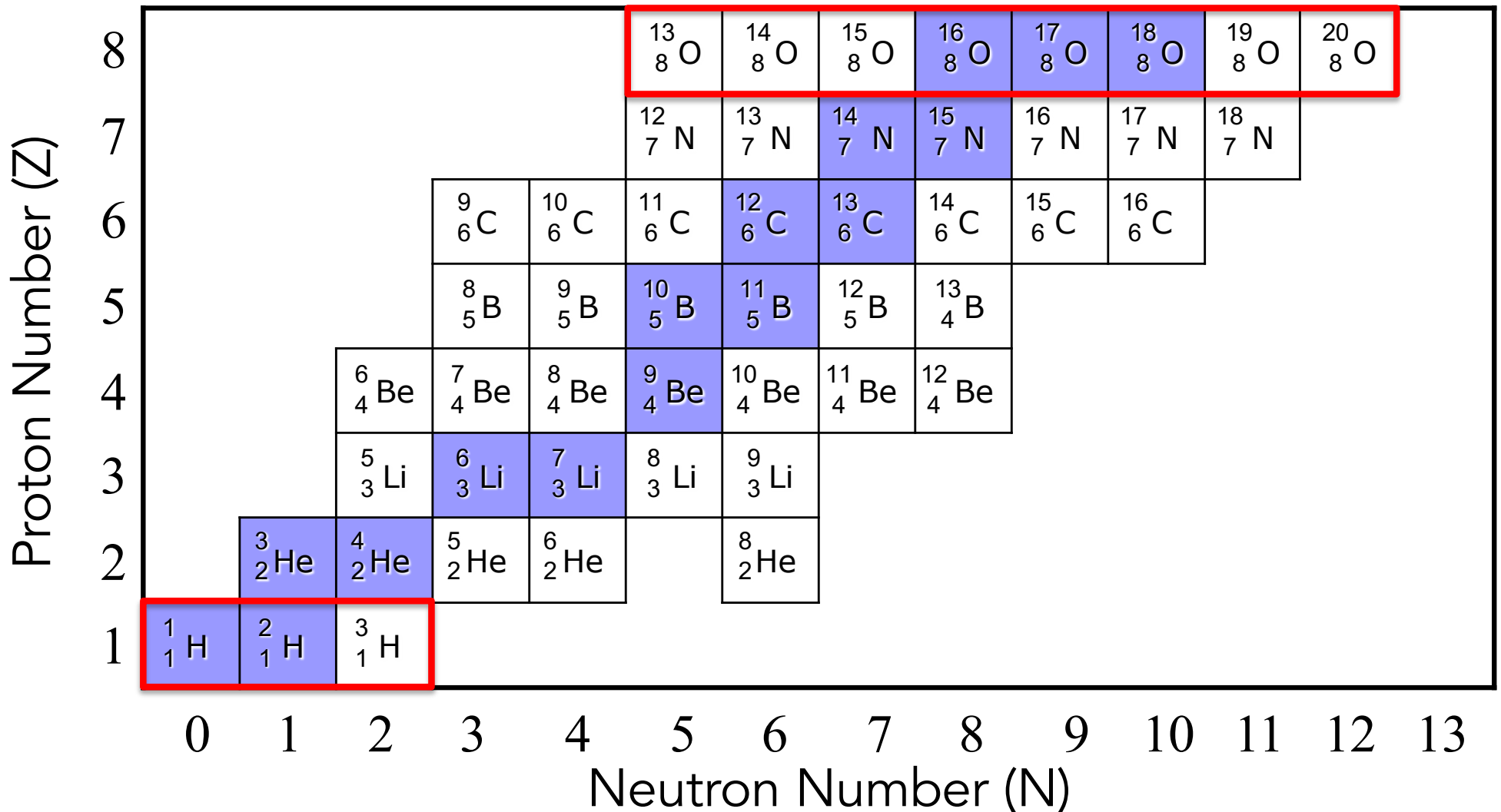
Isotope Natural Abundances

Hydrogen Isotopes: 2 stable, 1 unstable (radioactive):

^{1}H, Protium (H)	99.984%
^{2}H, Deuterium (D)	0.0159%
^{3}H, Tritium (T)	5×10^{-6}%

Oxygen Isotopes: 3 stable, 5 unstable (radioactive):

^{16}O	99.630%
^{17}O	0.0375%
^{18}O	0.1995%

Isotope Natural Abundances

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

$^1H^1H^{16}O$ - most common (highest vapor pressure)
$^1H^1H^{18}O$ - less common
$^1H^2H^{16}O$ - least common
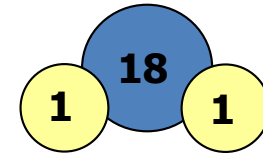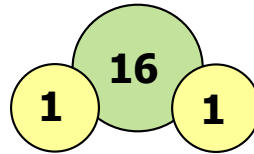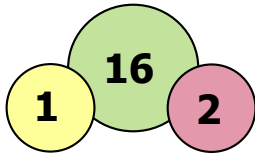
Isotopologues = identical compounds that differ in isotope composition.
($^1H^1H^{16}O$ vs. $^1H^1H^{18}O$ vs. $^1H^2H^{16}O$)

Hydrologic Cycle

Water Links
Earth + Atmosphere

rain clouds

precipitation

cloud formation

evaporation

from vegetation

from streams

from soil

from ocean

transpiration

lake storage

surface runoff

infiltration

soil

percolation
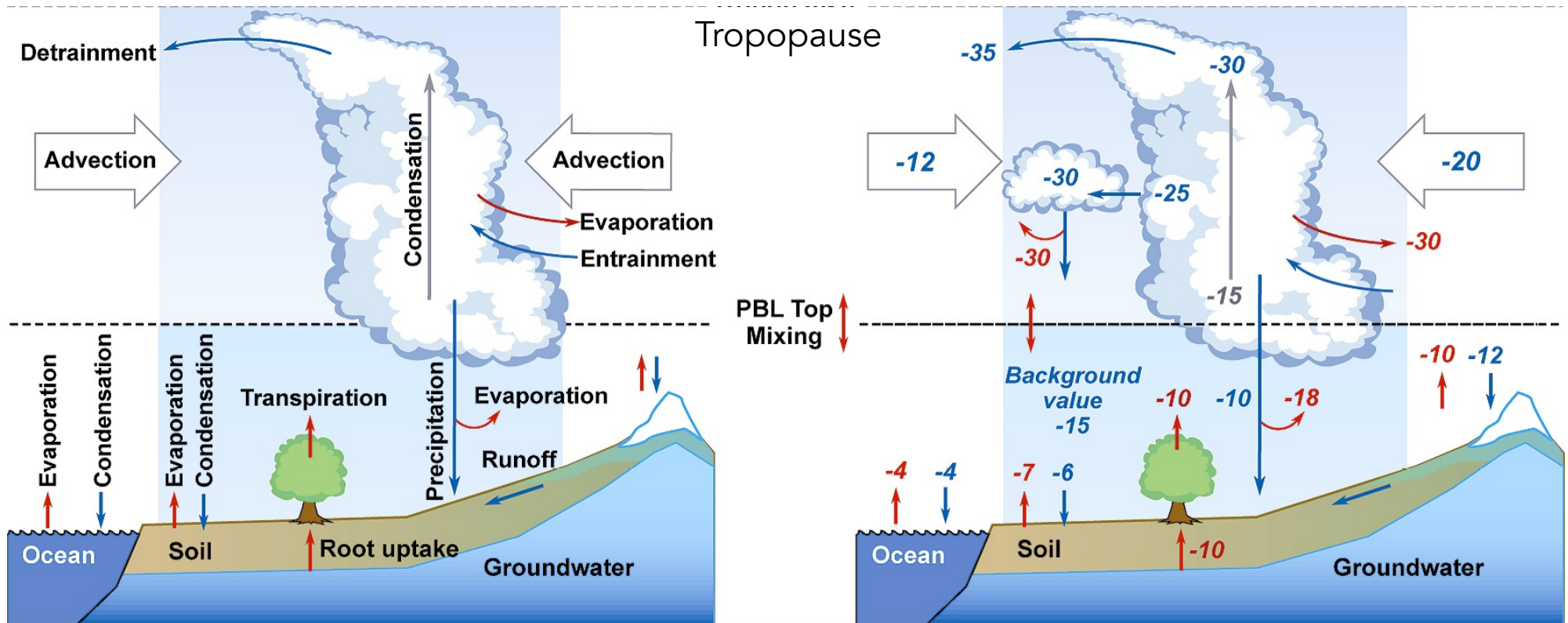
rock

deep percolation

ground water

ocean
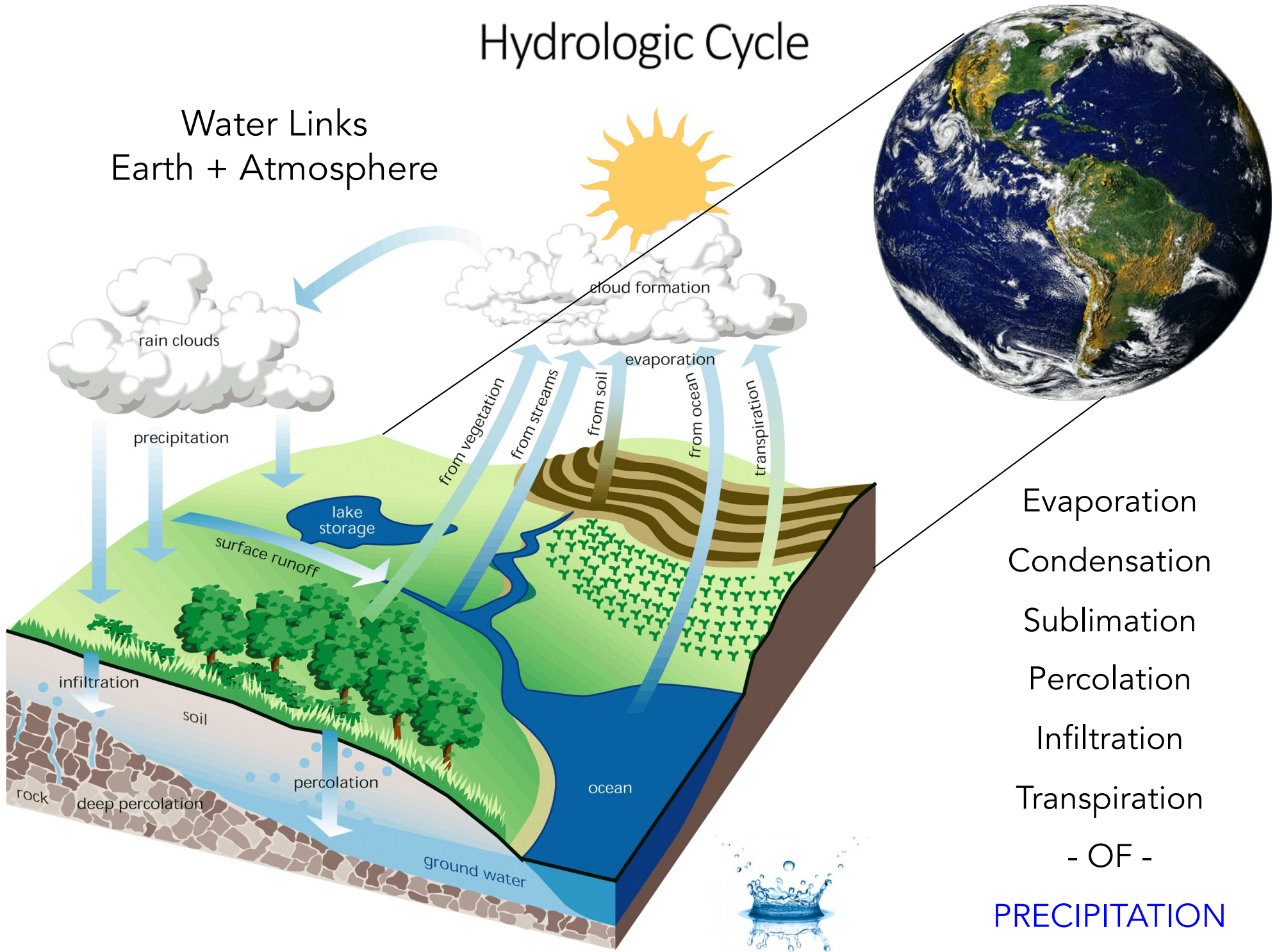
Evaporation

Condensation

Sublimation

Percolation

Infiltration

Transpiration

- OF -

PRECIPITATION

Water Isotope Partitioning by Hydrologic Pools & Fluxes
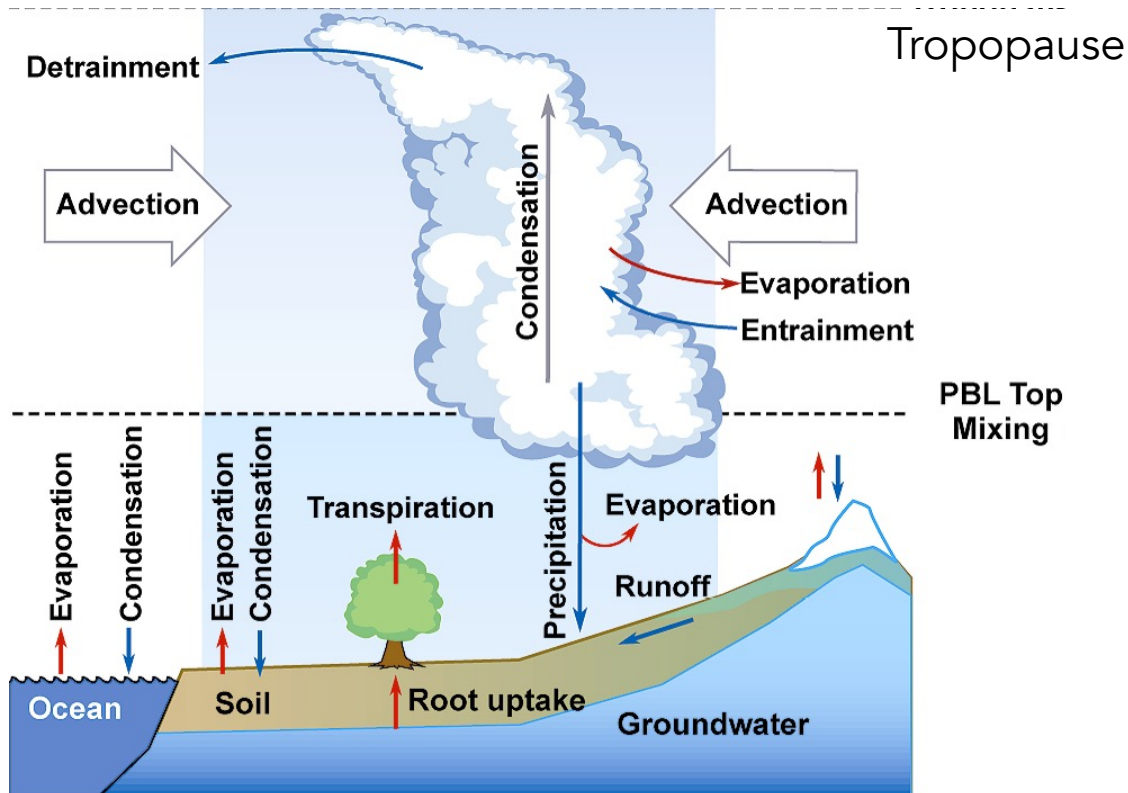
Water Isotope Partitioning by Hydrologic Pools & Fluxes

Values are $\delta^{18}O$

What about MAGNITUDE, MIXING, and MEASUREMENT?

5 Water World Rules to Remember

Expect fractionation during phase changes (liquid ⟷ vapor)

Temperature will impact isotopic composition
(lower temps = larger isotopic effects)

The isotopic composition of any water is a result
of fractionation, mixing, or both.

Always anticipate that both equilibrium and kinetic
fractionation effects may be at play.

Biology can influence isotope values of water too.

Stable Isotope Expression: Delta (δ) Notation

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

R = isotope ratio of RARE / COMMON.
$^2H/^1H$ or $^{18}O/^{16}O$
(very small number)

$[(R_{sample} / R_{standard}) - 1]$ is a small number.
multiplying value by 1000 allows us to express the value in **per mil.**
(parts per thousand or $\permil$)

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 $R_{sample}/R_{standard} = 1$ or $\delta R = 0\permil$.
International Atomic Energy Association (IAEA) maintains these reference standards.

International Reference Standards

Isotope System	Ratio	IAEA Reference Standard	Reference Standard Abundance Ratio
^2H	$^2H/^1H$	**V-SMOW:** (Vienna-Standard Mean Ocean Water)	155.76×10^{-6}
^{18}O	$^{18}O/^{16}O$	**V-SMOW:** (Vienna-Standard Mean Ocean Water)	2005.2×10^{-6}

Reference standard was originally called SMOW but is now called V-SMOW.

Measurements are calibrated to other international standards
that span a wide range of values.

Other International Standards

Abbreviation	Standard Name	δ^2H_{VSMOW}	$\delta^{18}O_{VSMOW}$
V-SMOW	Standard Mean Ocean Water	0‰	0‰
SLAP	Standard Light Antarctic Precipitation	-428.0‰	-55.5‰
GISP	Greenland Ice Sheet Precipitation	-189.7‰	-24.8‰
NBS-1	National Bureau of Standards (NBS) 1	-47.1‰	-7.9‰
NBS-1A	National Bureau of Standards (NBS) 1A	-183.2‰	-24.3‰

For the most part, this course is concerned with TWO main processes that have isotope effects:

Fractionation
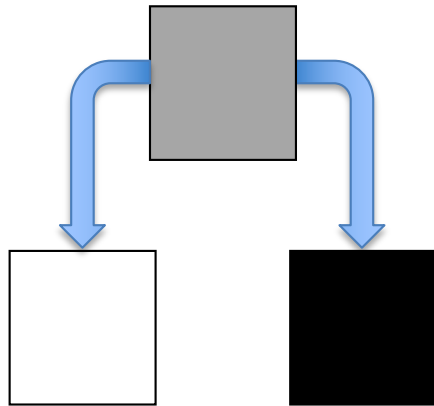
Mixing
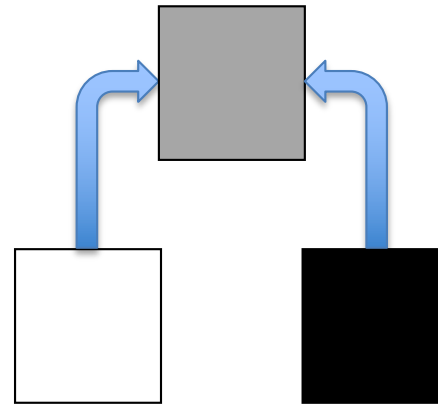
Questions?

Mixing

A process that combines different substrates into a product
(the making of a homogeneous whole – e.g., baking)

Fractionation

A process that occurs during chemical reactions when the
abundances of the heavy isotopes in the substrate are different
than the abundances of the heavy isotopes in the product(s)

Isotope Fractionation Factor: $\alpha_{A-B} = R_A/R_B$
(A and B are substrate and product respectively)

Isotope Enrichment Factor: $\varepsilon_{A-B} = (\alpha - 1) \bullet 1000 ‰$

Types of Fractionation

Exchange or Equilibrium

– Complete back-reactions occur

– Product and reactant offset by constant fractionation factor (α)

Kinetic (Non-Equilibrium)

– Incomplete back-reactions or none occur

– Product and reactant δ values can evolve in concert (closed system),
or reactant composition determines product composition (open system)

Transport or Diffusive (Non-Equilibrium)

– Can be thought of as a special case of kinetic fractionation
along a flux/concentration gradient

– Incomplete back-flux is a necessary condition

Examples of Fractionation Types

Exchange or Equilibrium

– Liquid droplet formation from vapor in clouds (rain!)

– Evaporation at the boundary layer (100% RH) of water body (ocean/lake)

Kinetic

– Mineral precipitation out of magma

– Evaporation of waters (<100% RH)

– Biosynthesis of compounds (enzyme-mediated)

Transport or Diffusive

– Diffusion through boundary layer over water, out of leaves, through soils

During any fractionation event these are NOT mutually exclusive.

For water, it is very common to have both equilibrium and kinetic fractionation occur as water cycles and moves.

Rayleigh Fractionation (Distillation)

What is this Process?

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

Assumptions

- Material is continuously removed from a mixed system containing molecules of two or more isotope species (e.g., H2O with ^{18}O and ^{16}O).
- Fractionation accompanies the removal process and at any instance is described by the fractionation factor alpha (α).
- Alpha (α) does not change during the process.

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

Rayleigh Fractionation in Action: Monsoon!
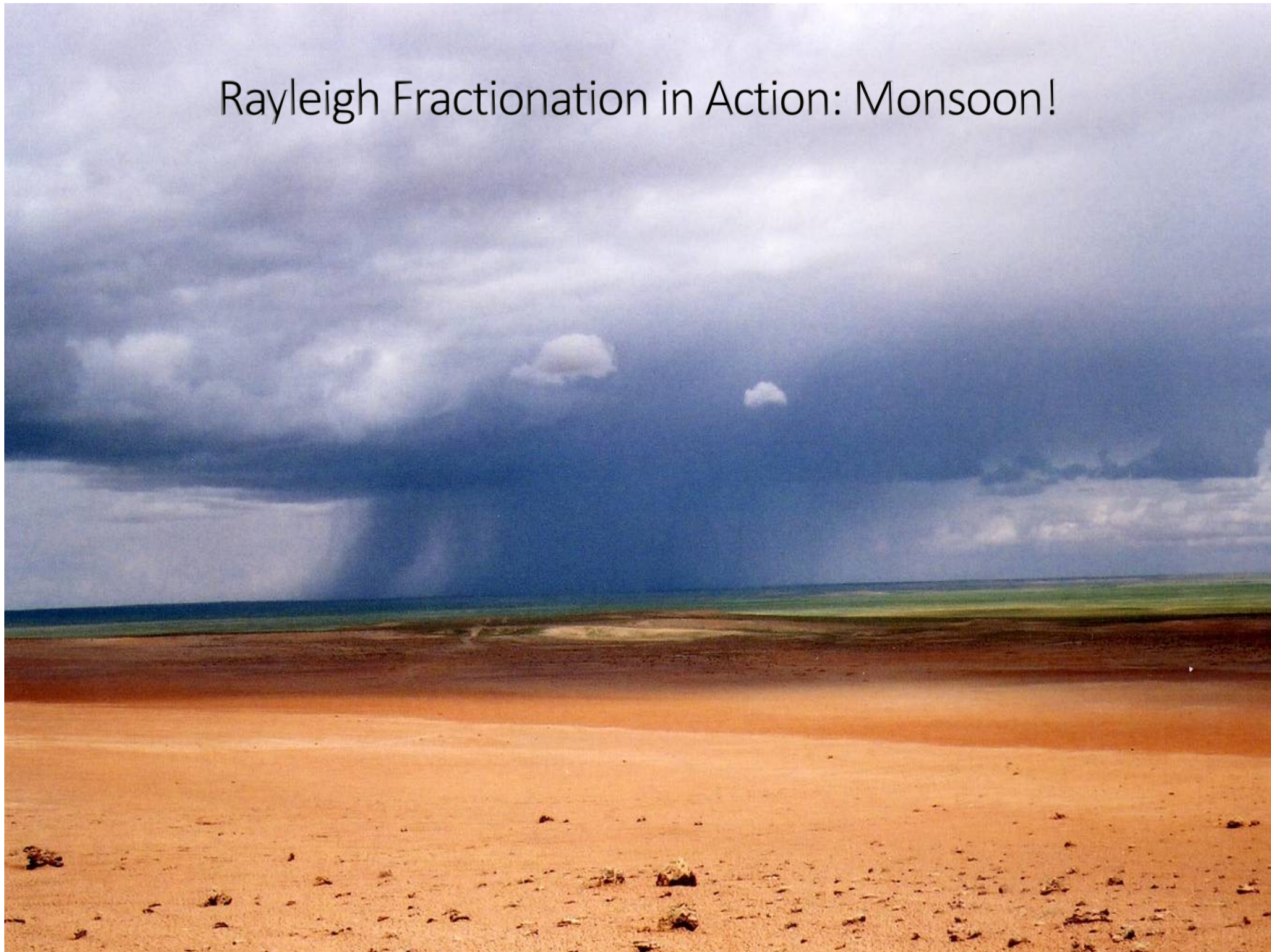
Rayleigh Fractionation in Action: Monsoon!

Accumulation of Light Isotopes
$^1H^1H^{16}O$
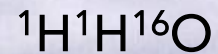
Liquid <-> Vapor
(equilibrium mixture)

Liquid

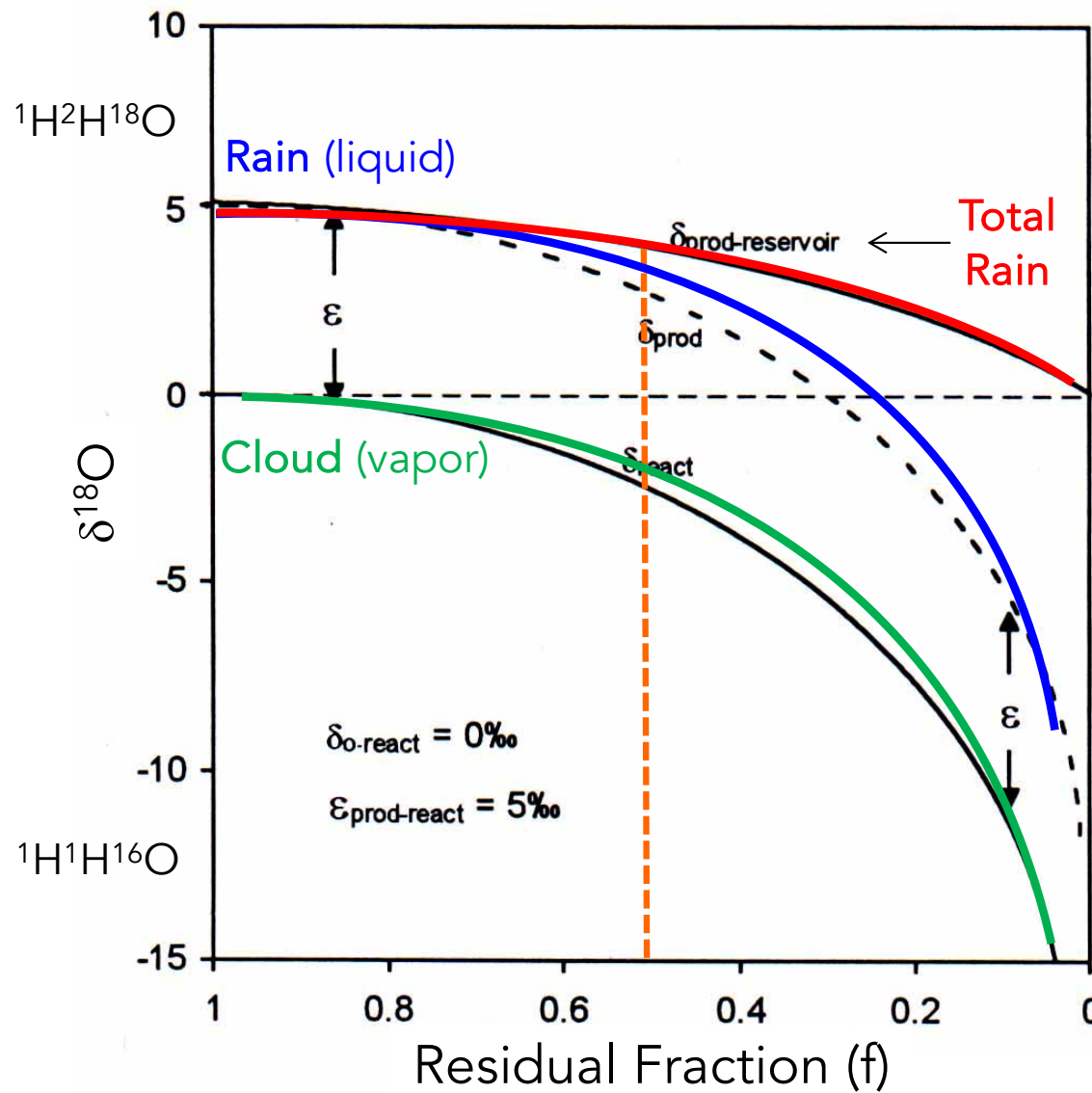$^1H^2H^{18}O$
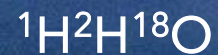
Accumulation of Heavy Isotopes
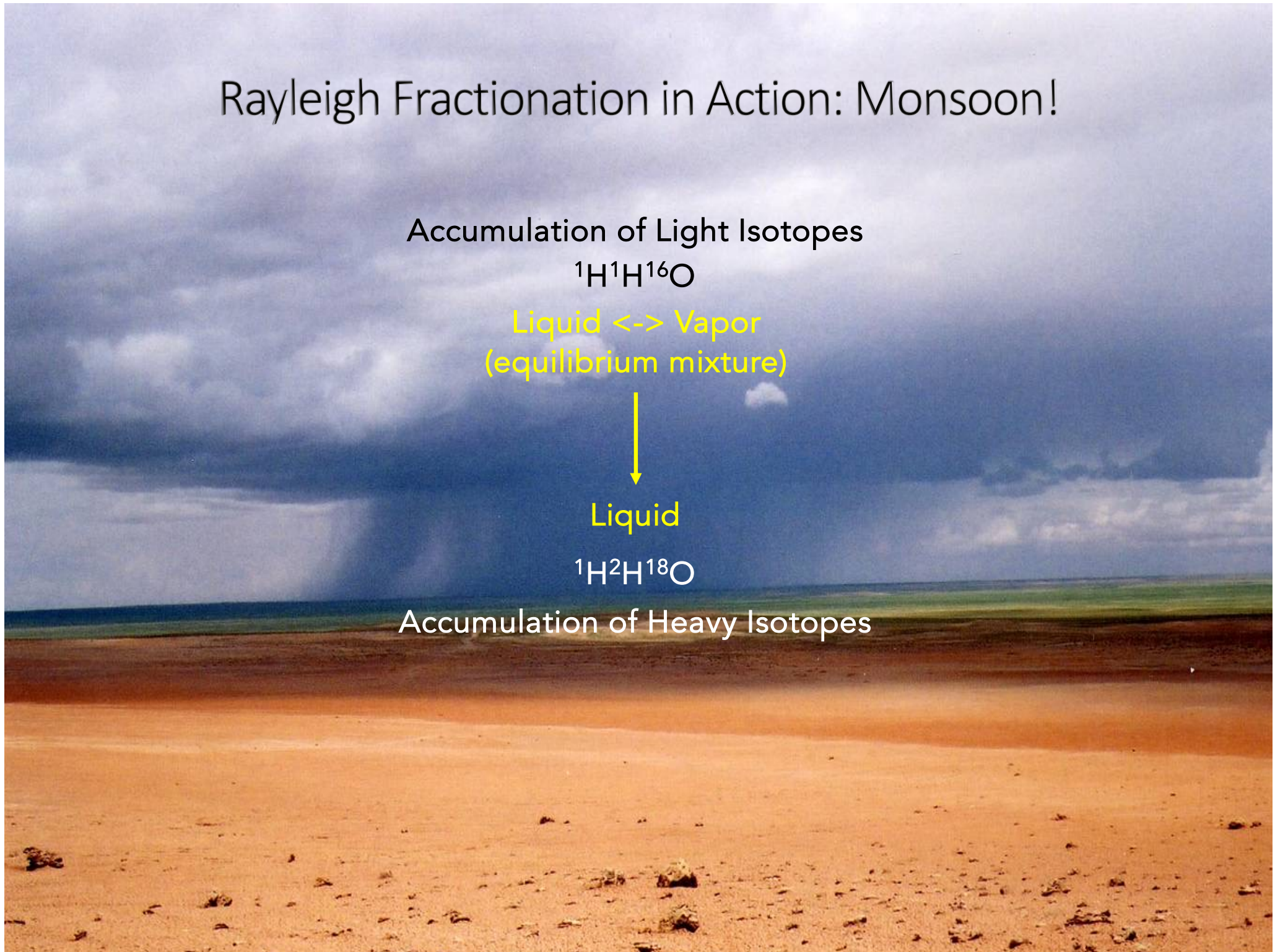
Rayleigh Fractionation (Distillation)

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

R_t and R_0 are the ratios at time "t" and zero (initial)
f is the fraction remaining at t
α is the fractionation factor between water and vapor

Rayleigh Fractionation from Rainfall (Condensation)

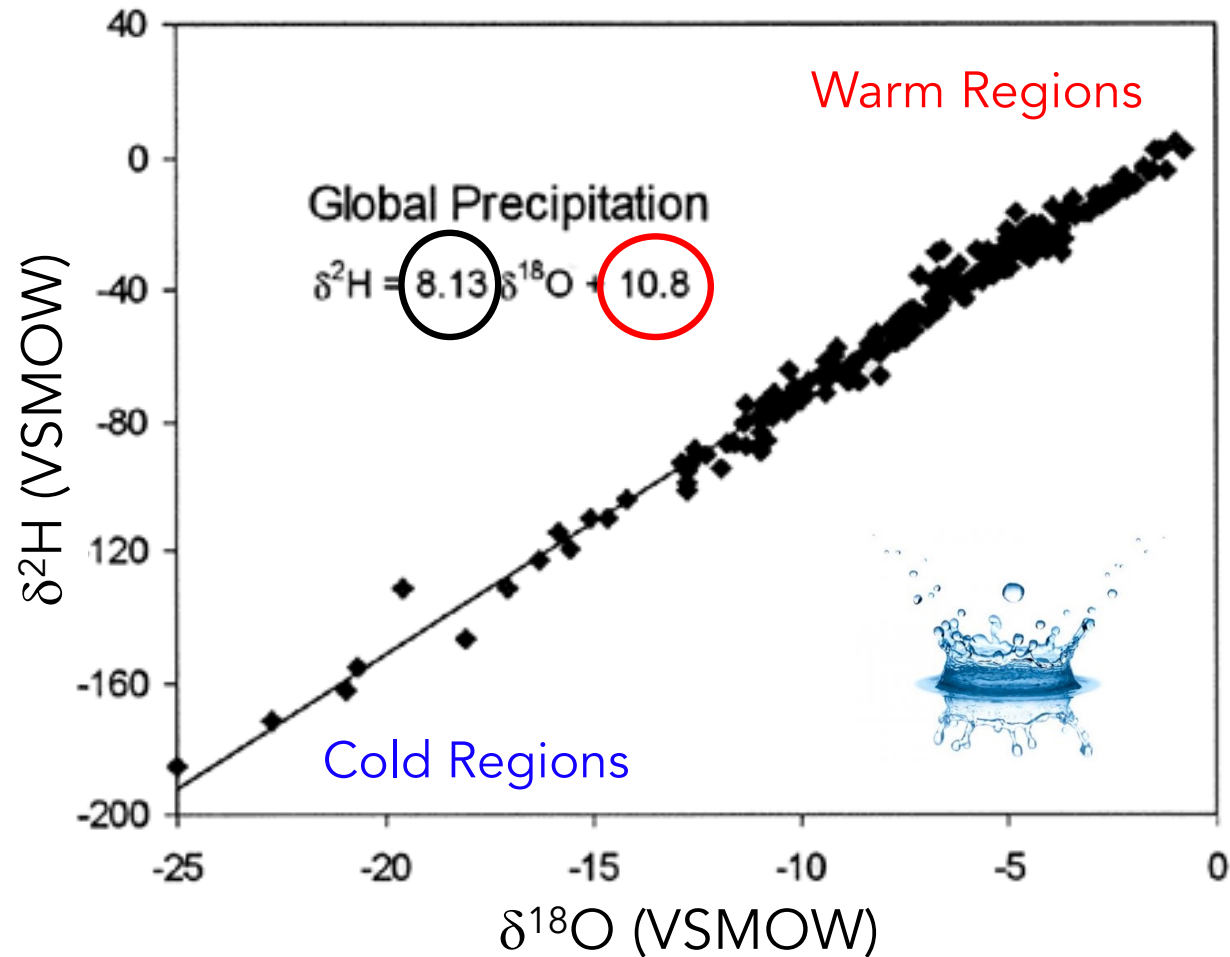BOTH δ_{prod} and δ_{react} become progressively lower as "f" changes.

Clark and Fritz 1997

Questions?

Equilibrium Fractionation Factors for Water Isotopes (Vapor to Liquid)

- @ 20°C
  - $\varepsilon^2 H_{v-l} = 74‰$
  - $\varepsilon^{18} O_{v-l} = 9.2‰$
  - $\varepsilon^2 H / \varepsilon^{18} O =$ 8.0
- @ 80°C
  - $\varepsilon^2 H_{v-l} = 38‰$
  - $\varepsilon^{18} O_{v-l} = 4.5‰$
  - $\varepsilon^2 H / \varepsilon^{18} O =$ 8.4
- **Mass Differences**
  - $(^2H - {}^1H) / {}^1H = 1$
  - $(^{18}O - {}^{16}O) / {}^{16}O = 0.125$
  - $1 / 0.125 =$ 8.0

Equilibrium fractionation factors for hydrogen isotopes are ~8x those for oxygen isotopes

Global Meteoric Water Line (GMWL)

Warm Regions

Global Precipitation

$\delta^2 H = 8.13 \, \delta^{18}O + 10.8$

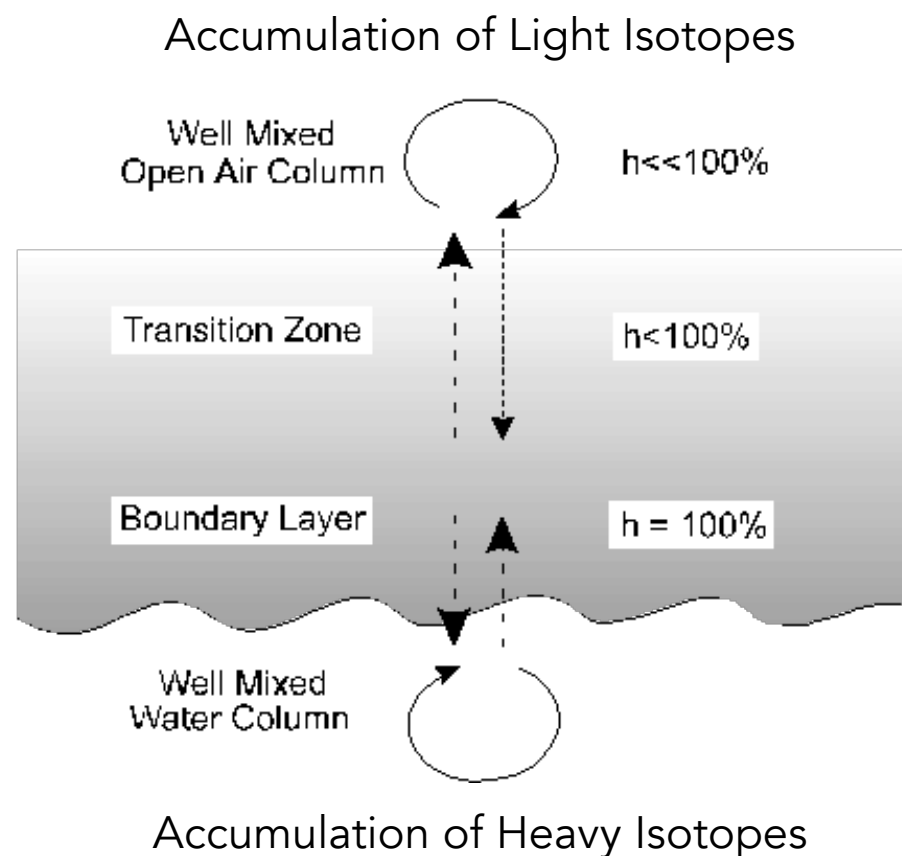$\delta^2 H$ (VSMOW)

$\delta^{18}O$ (VSMOW)

Cold Regions

Condensation in the real world is an *equilibrium* process!
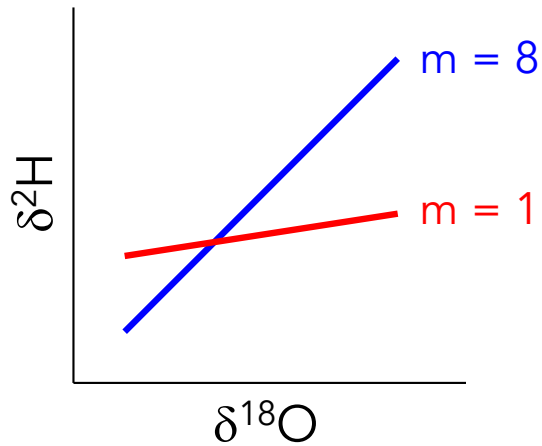
Intercept of **+10‰**?

Looking at Equilibrium and Kinetic Fractionation Together

- Open Air
  - Large and Well-Mixed
  - RH<<100%

- Transition Zone (TZ)
  - Turbulently Mixed <100% RH
  - Decreasing Humidity Upwards

- Boundary Layer (BL)
  - Thin and Well-Mixed (100% RH)

- Liquid
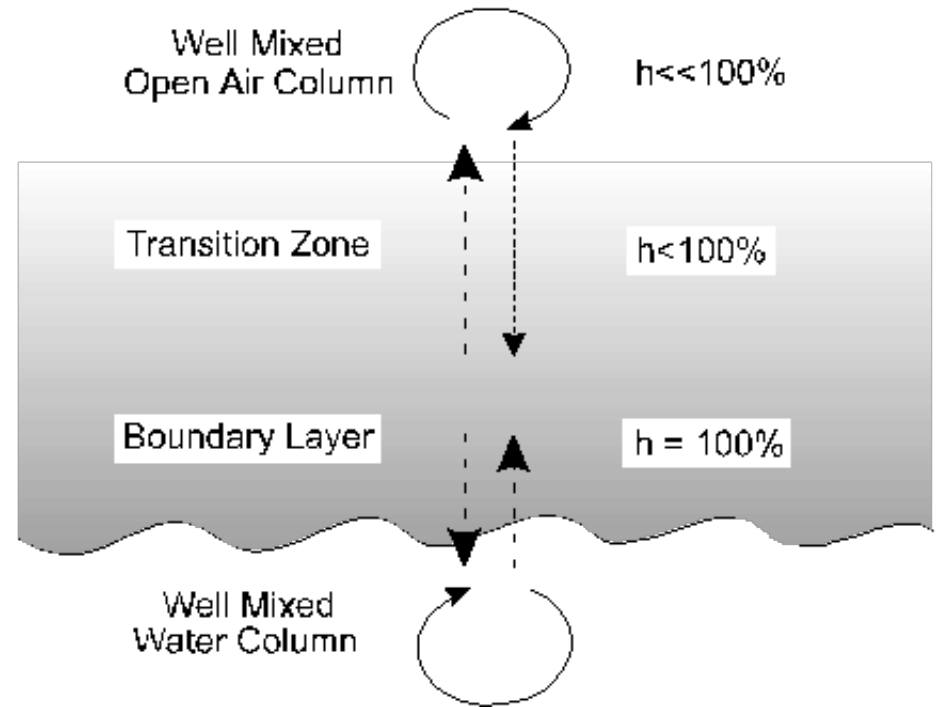 - Large (ocean) or Small (droplet)
  - Mixed or Stratified

Accumulation of Light Isotopes

Well Mixed Open Air Column   h<<100%

Transition Zone   h<100%

Boundary Layer   h = 100%

Well Mixed Water Column

Accumulation of Heavy Isotopes

Gat 1996

Looking at Equilibrium and Kinetic Fractionation Together

δ^2H (y-axis)

$\delta^{18}O$ (x-axis)

m = 8

m = 1

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

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

Well Mixed
Open Air Column   h<<100%

Transition Zone   h<100%

Boundary Layer   h = 100%

Well Mixed
Water Column

Gat 1996

Why Doesn't GMWL Intercept 0?

The *d*-excess of precip-2 > precip-1

$\delta^2H = +15$

$\delta^2H = +10$

$\delta^{18}O$

SMOW

δ_{precip}
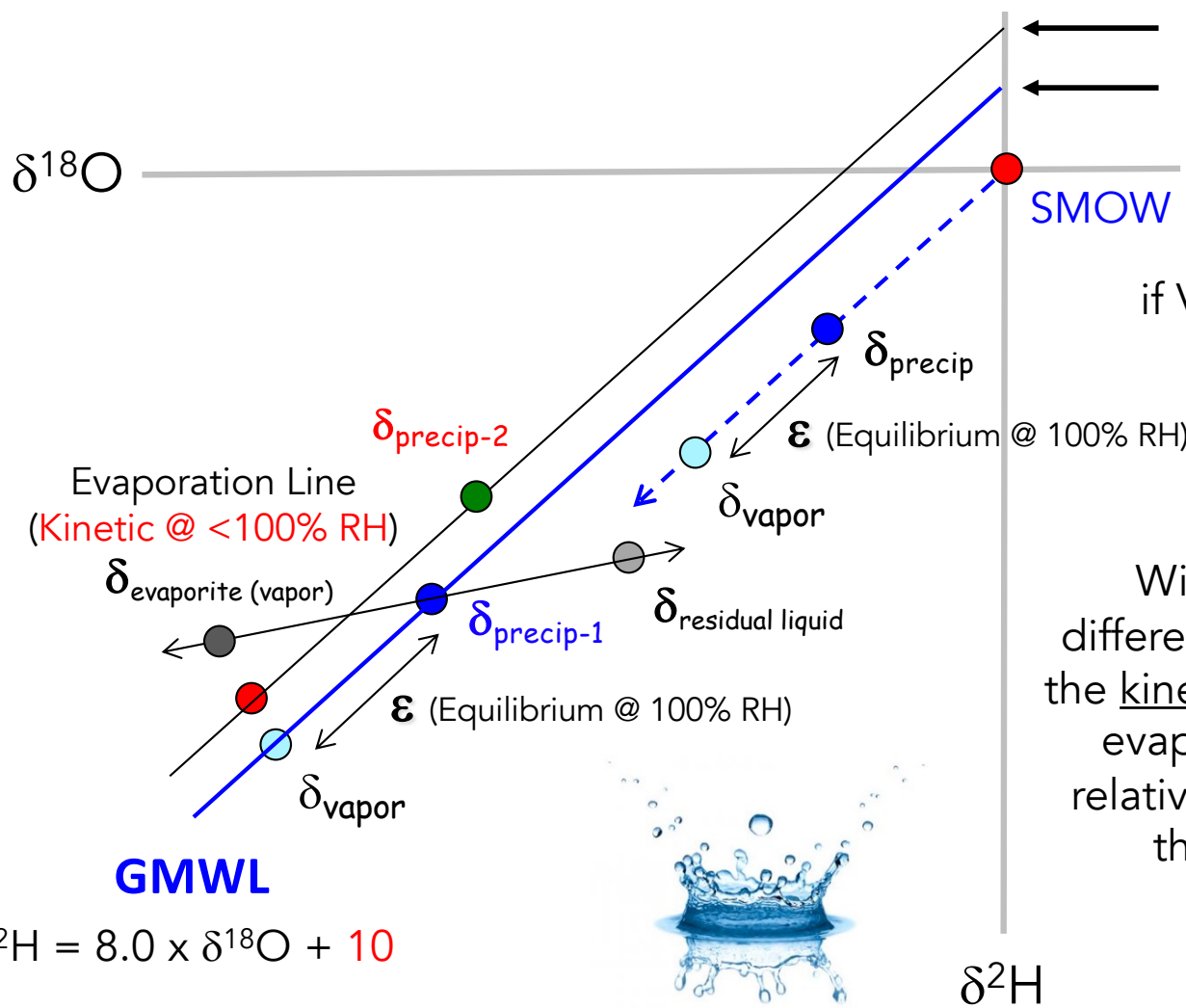
$\delta^2H = 8.0 \times \delta^{18}O$
if V-L are in isotopic equilibrium
(no kinetic fractionation)

ε (Equilibrium @ 100% RH)

$\delta_{precip-2}$

Evaporation Line
(Kinetic @ <100% RH)

δ_{vapor}

$\delta_{evaporite\ (vapor)}$

$\delta_{precip-1}$

$\delta_{residual\ liquid}$

ε (Equilibrium @ 100% RH)

δ_{vapor}

With the greater mass and mass
difference of O isotopes, when you add
the <u>kinetic (non-equilibrium)</u> effect during
evaporation it has a disproportional
relative impact on O more than H such
that water vapor falls "off" the
GMWL on the O-side.

GMWL

$\delta^2H = 8.0 \times \delta^{18}O + 10$

δ^2H

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

Deuterium Excess (*d*)

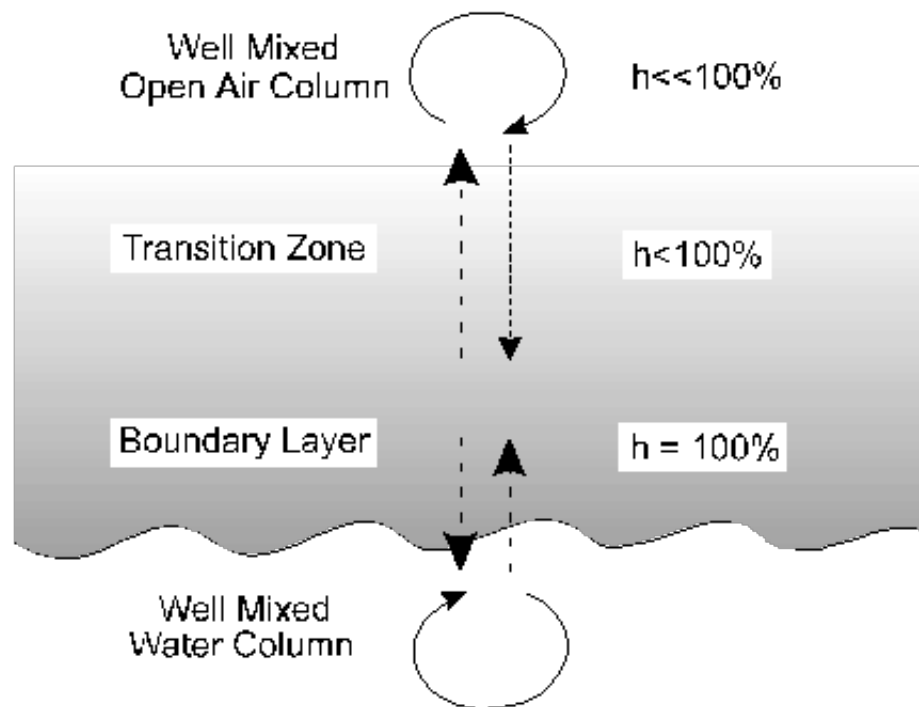$$d = \delta^2H - 8 \times \delta^{18}O$$

Clark and Fritz 1997
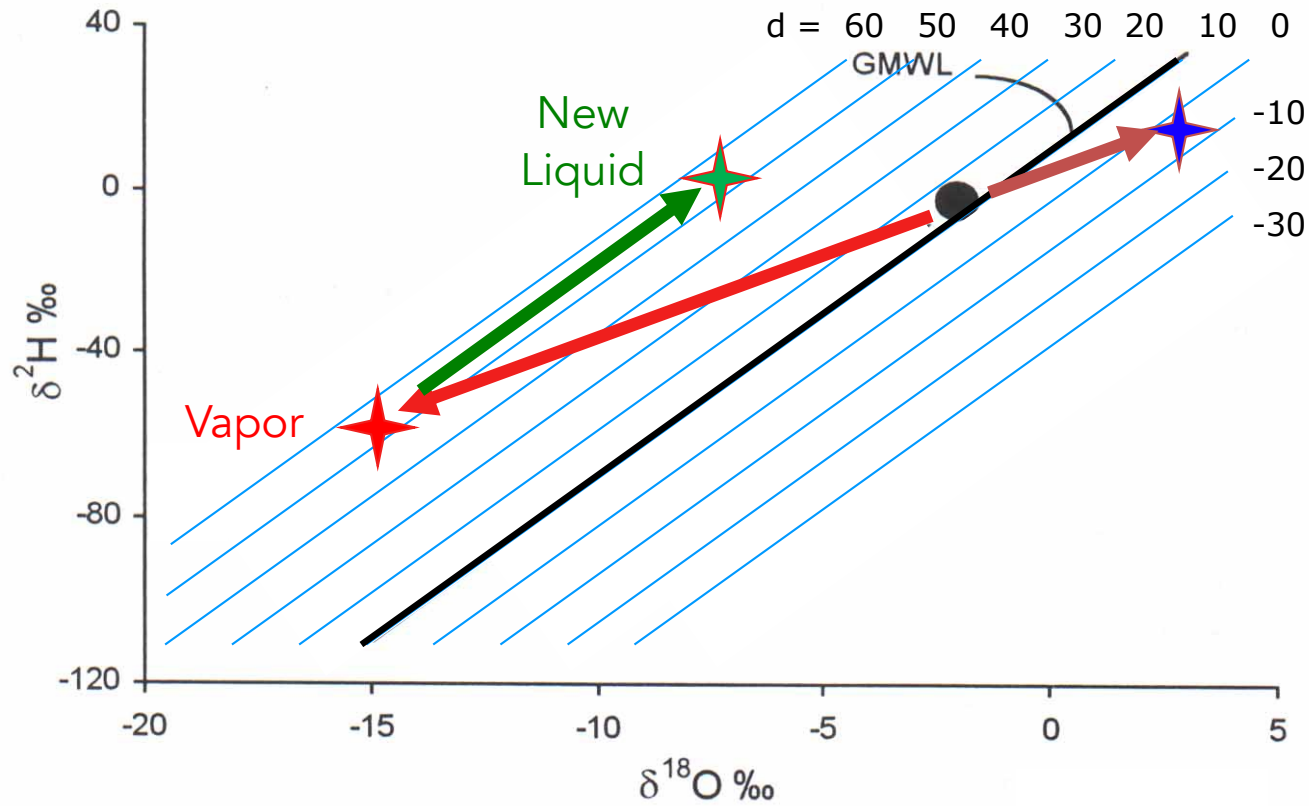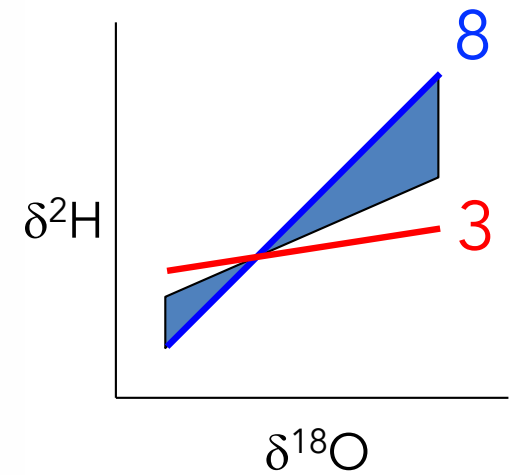
Looking at Equilibrium and Kinetic Fractionation Together

The net ratio of ^{2}H and ^{18}O isotope effects is a blend of the equilibrium and kinetic slopes, typically between 3 and 8.

Larger deuterium excess = higher or lower humidity?

The coupled ^{2}H and ^{18}O system gives us a "proxy" for kinetic fractionation, **deuterium excess,** which is driven by humidity.
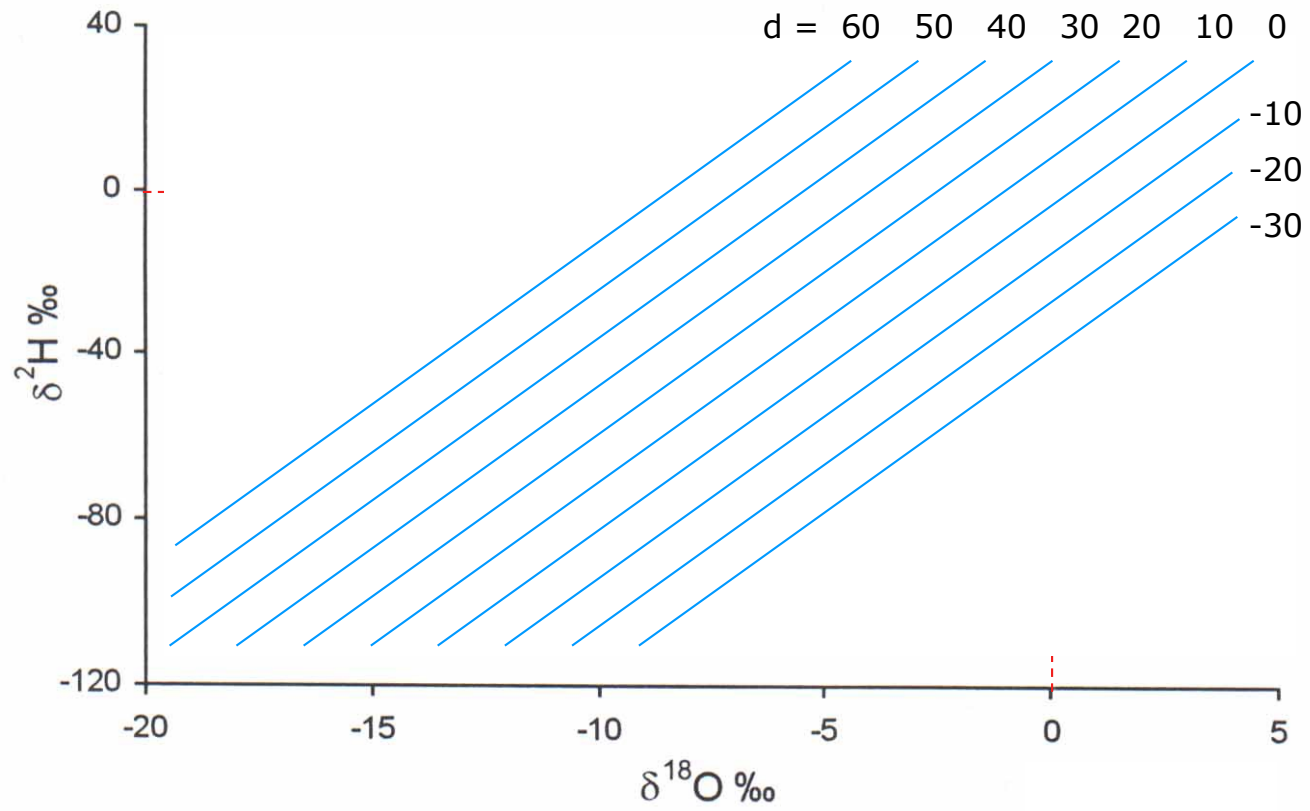

Well Mixed
Open Air Column   h<<100%

Transition Zone   h<100%

Boundary Layer   h = 100%

Well Mixed
Water Column

Gat 1996

Deuterium Excess (*d*)

d of seawater (SMOW) is 0 – 8 x 0 = 0‰

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

Clark and Fritz 1997

Precipitation Deuterium Excess and Relative Humidity

Bowen and Revenaugh 2003
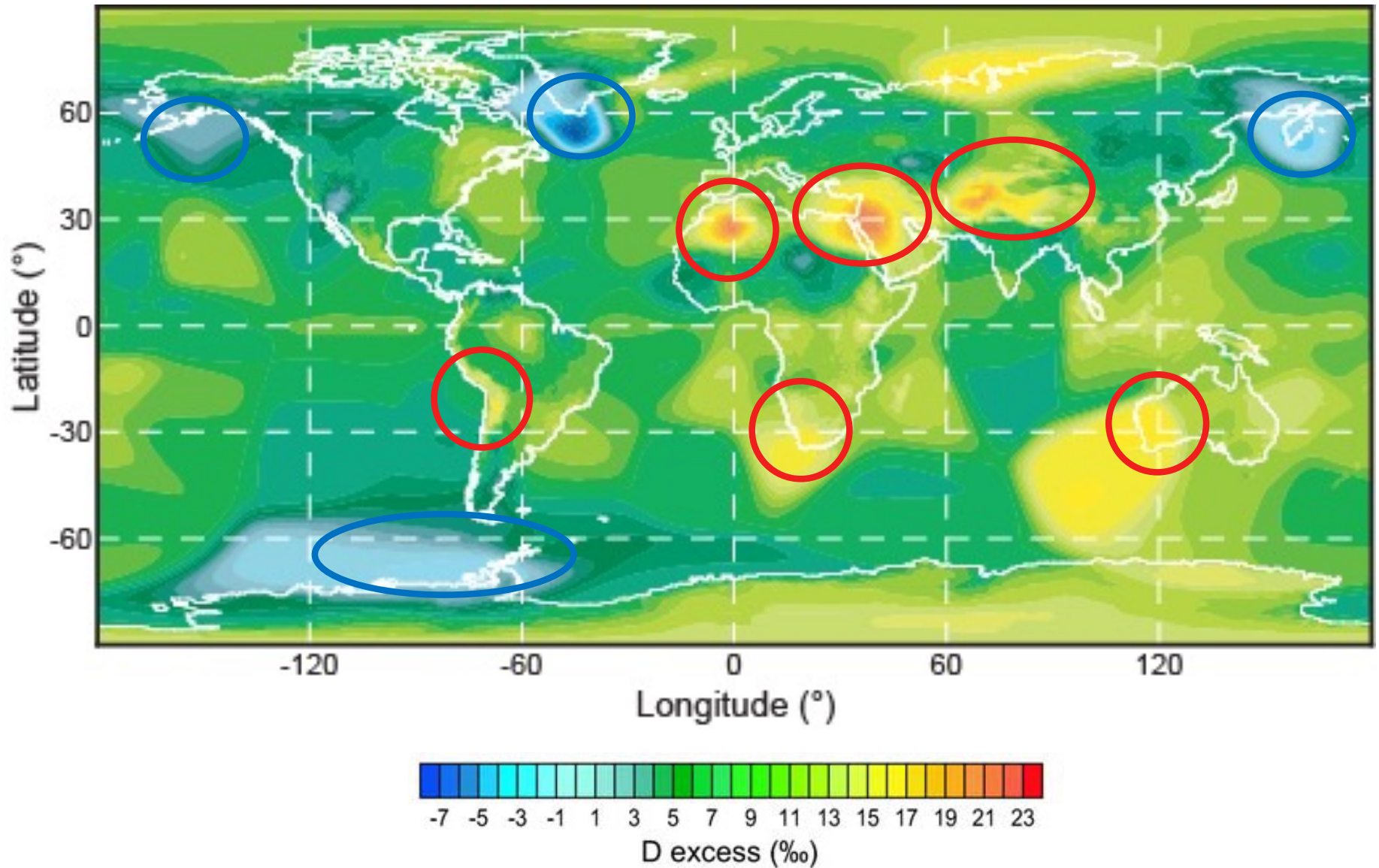
Craig–Gordon Model

Brings both equilibrium and kinetic effects together to show isotope evolution during phase changes of H_2O:

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

α_{eq} equilibrium fractionation factor (1.009)
α_k kinetic fractionation factor (1.0285)
h_{air} humidity [vapor pressure of water] in air
δ_{awv} molar ratio of $^{18}O/^{16}O$ (or $^2H/H$) of atmospheric water vapor

Craig and Gordon 1965, Dongmann et al. 1974, Flanagan et al. 1991

Questions?

Spatial Variability of Oxygen Isotopes in Hydrologic Fluxes

-30‰

-25‰

rain
-10

-20‰

water vapor
-15‰

rain
-5‰

evaporation

river
-8‰

VSMOW = 0‰

Values are $\delta^{18}O$‰
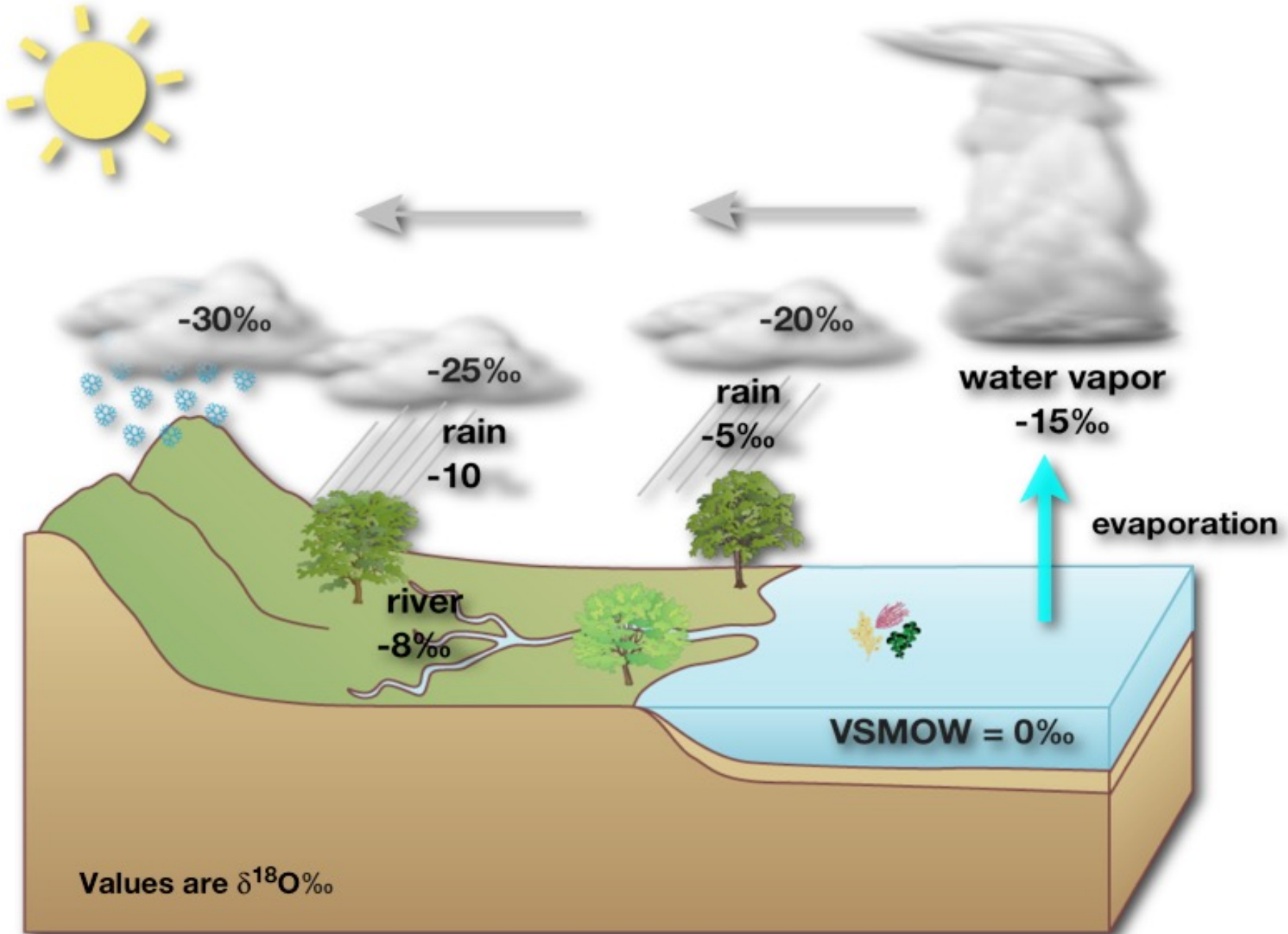
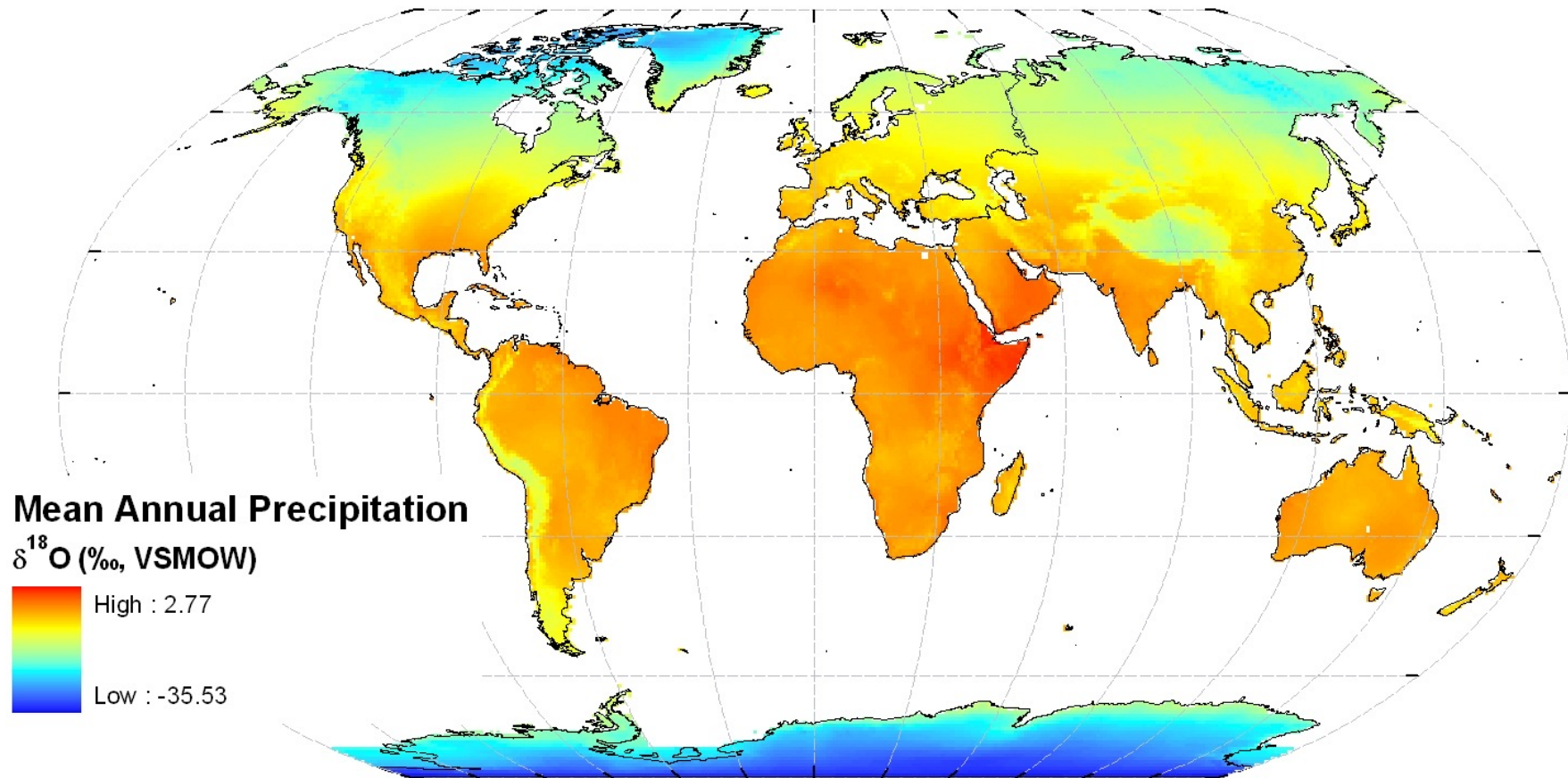# GNIP: Global Network for Isotopes in Precipitation

http://isohis.iaea.org
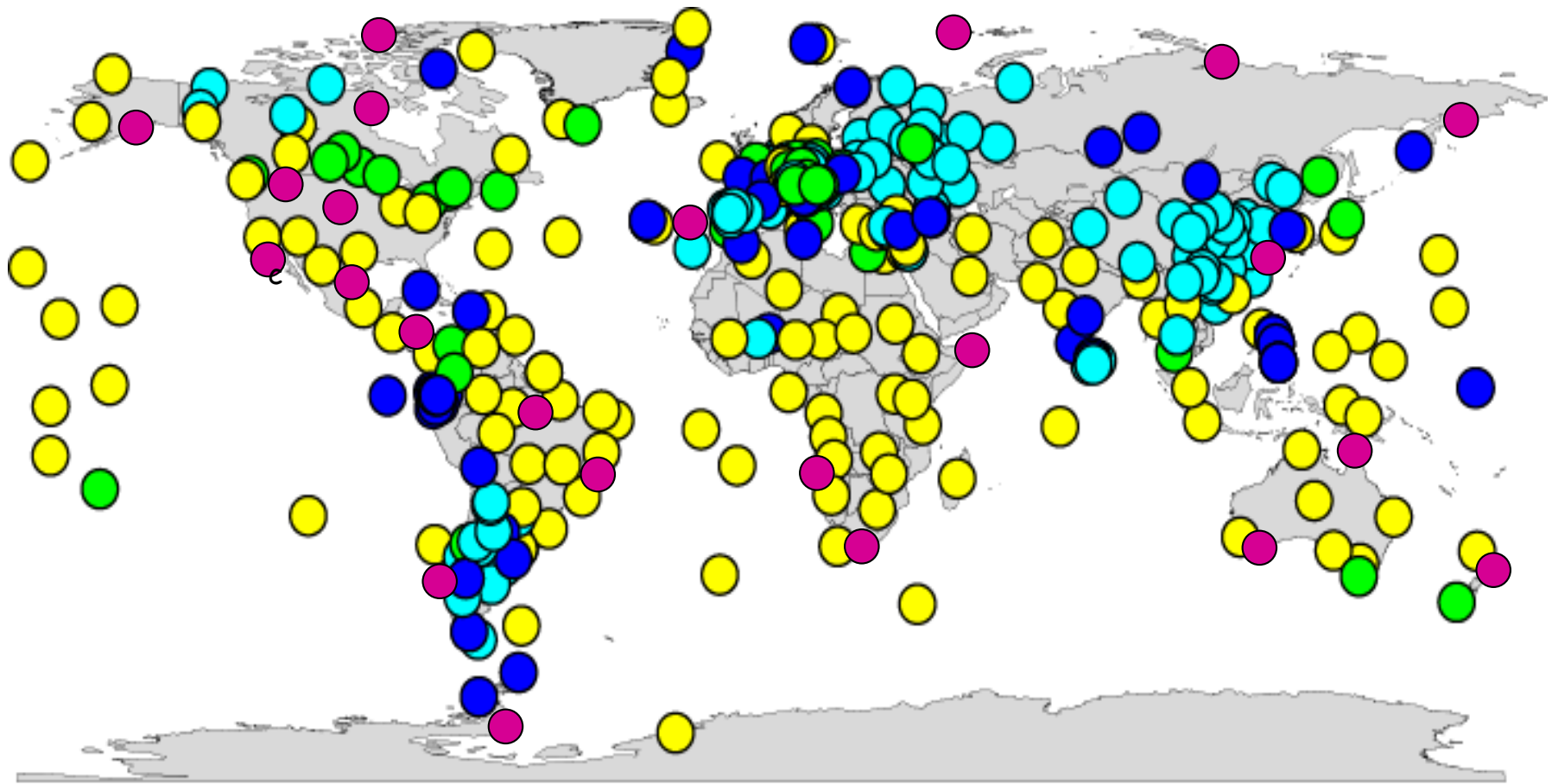
First Year of $\delta^{18}O$ Observation

⬤ 1960-69 (n = 134) ⬤ 1970-79 (n = 47) ⬤ 1980-89 (n = 101) ⬤ 1990-00 (n = 66) ⬤ 2007-20 (n = 23)

Stable Isotopes in Precipitation
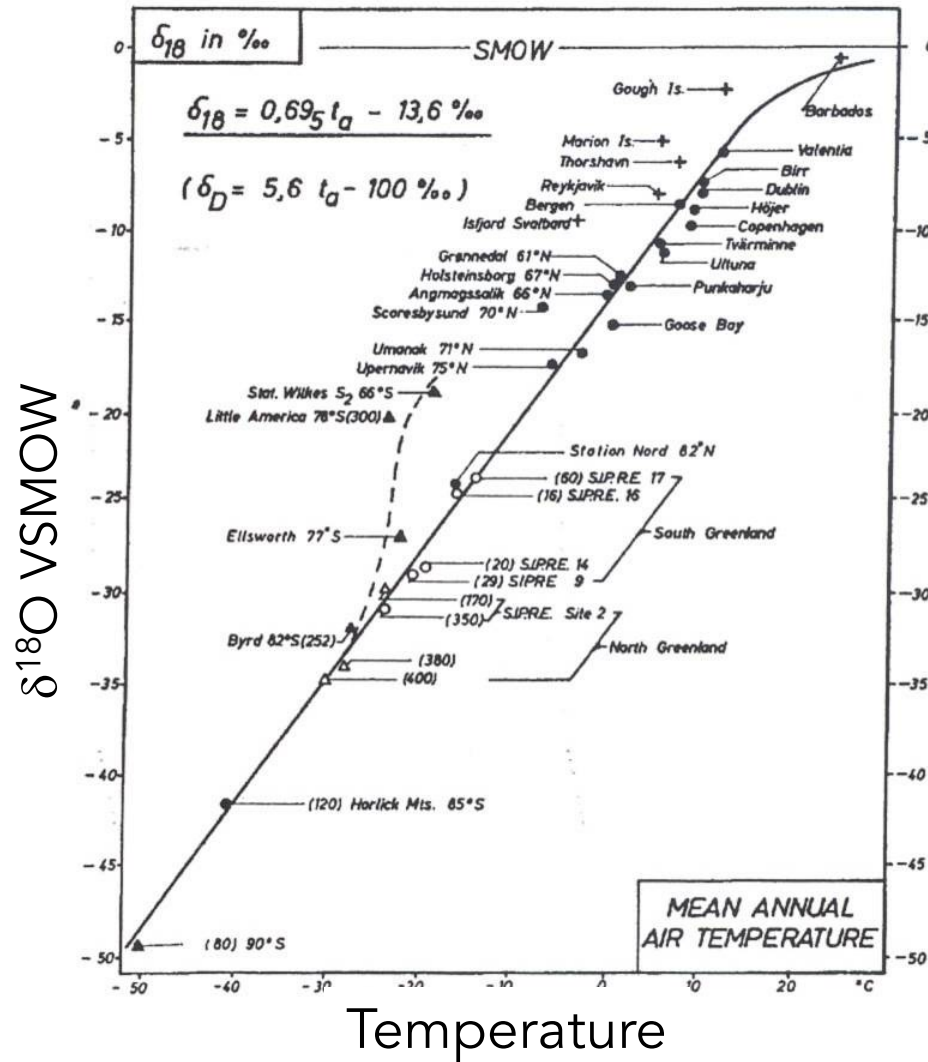

Mean Annual Precipitation
$\delta^{18}O$ (‰, VSMOW)

High : 2.77

Low : -35.53

www.waterisotopes.org

Processes Behind Patterns?

Temperature Effects

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

$$\delta^2H = (5.6)T_{average} - 100‰$$
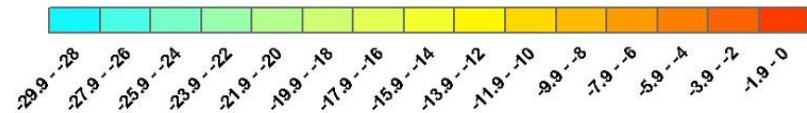
Dansgaard 1964, Rozanski et al. 1993

The Continental Effect

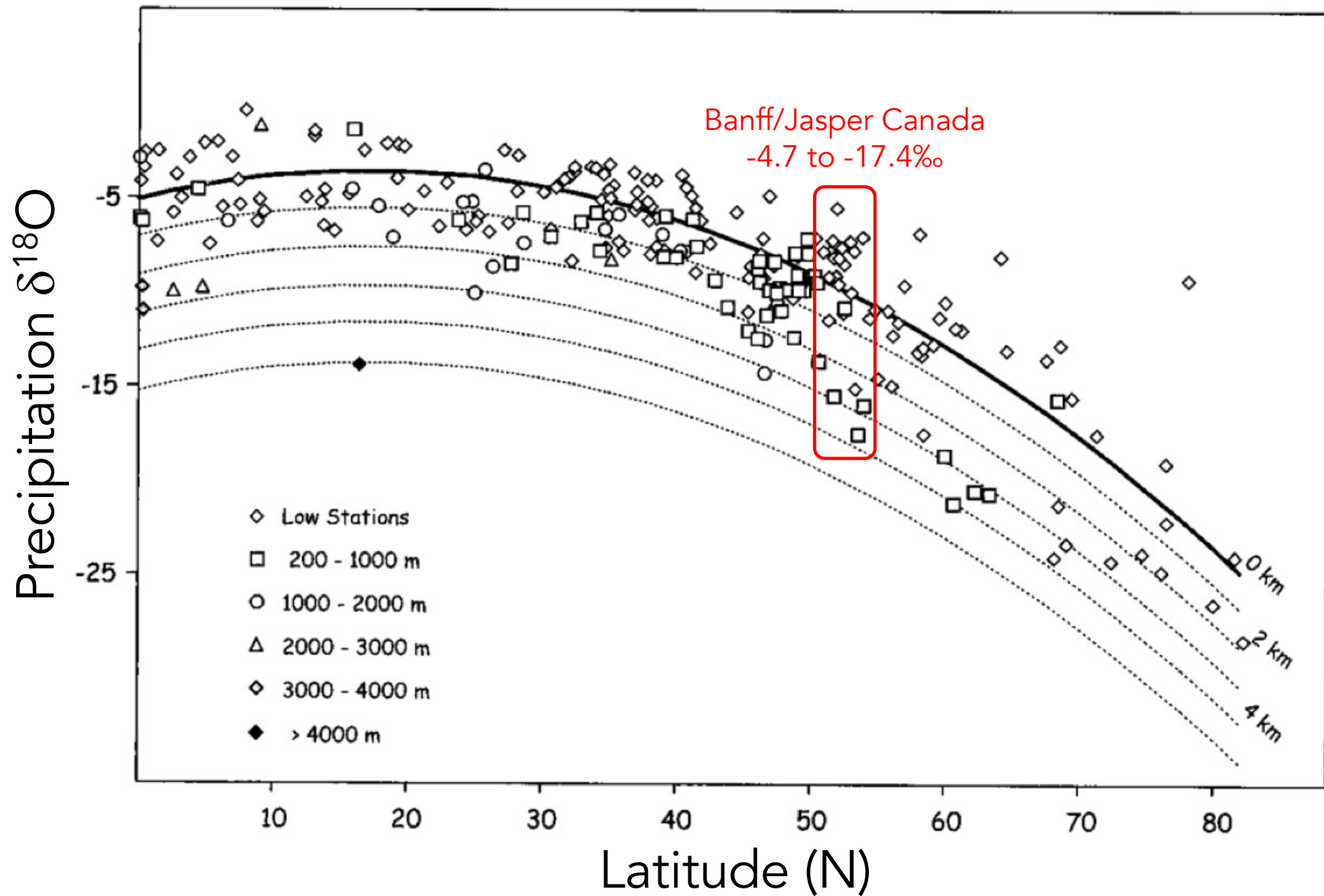Precipitation isotope δ values decrease towards continental interior.

Reflects the fact that vapor is sourced from the oceans, rains out over the continents, plus winter precipitation (snow) is formed at colder temperatures.
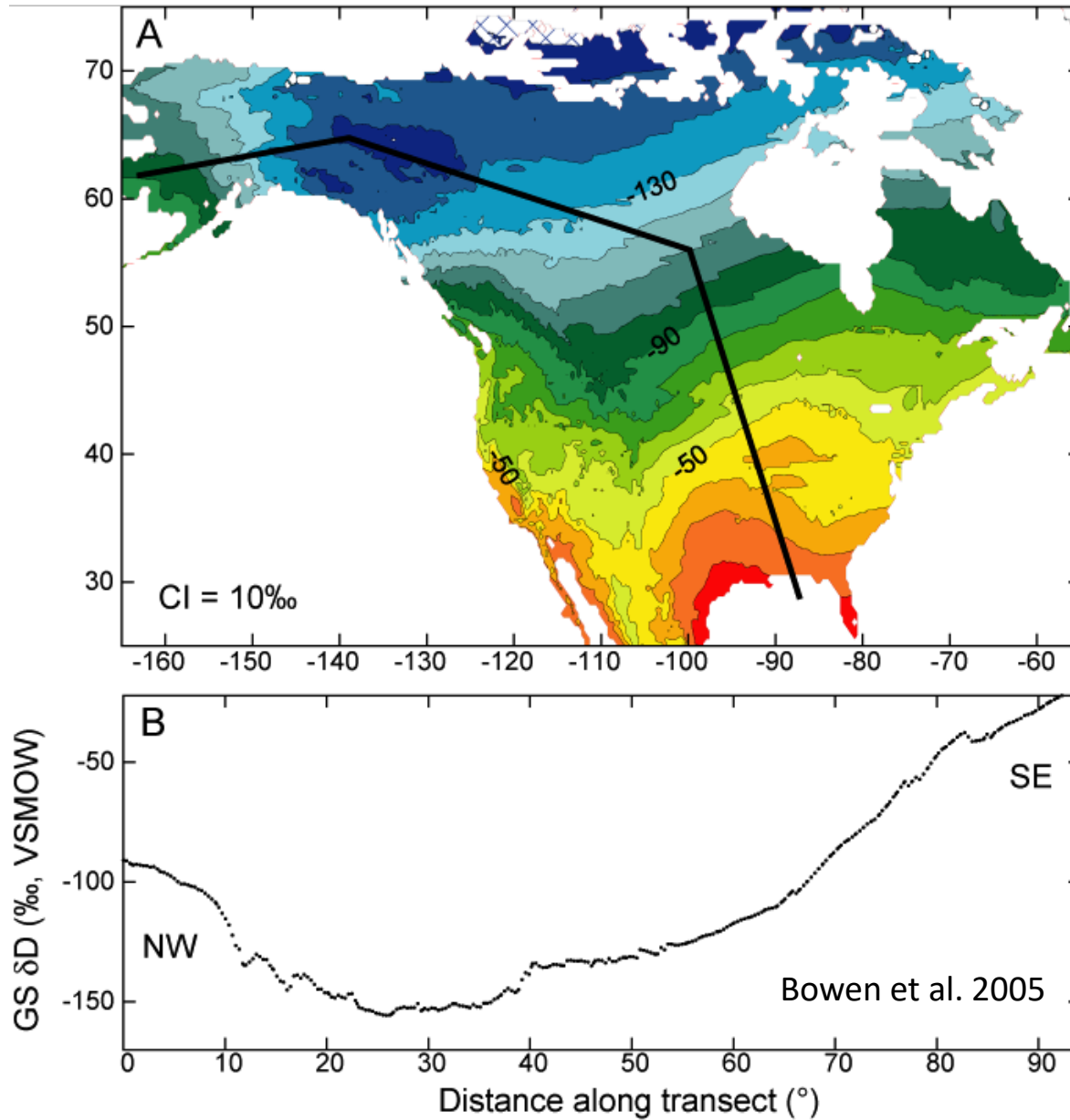

$\delta^{18}O$ of Annual Precipitation

-29.9 - -28 | -27.9 - -26 | -25.9 - -24 | -23.9 - -22 | -21.9 - -20 | -19.9 - -18 | -17.9 - -16 | -15.9 - -14 | -13.9 - -12 | -11.9 - -10 | -9.9 - -8 | -7.9 - -6 | -5.9 - -4 | -3.9 - -2 | -1.9 - 0
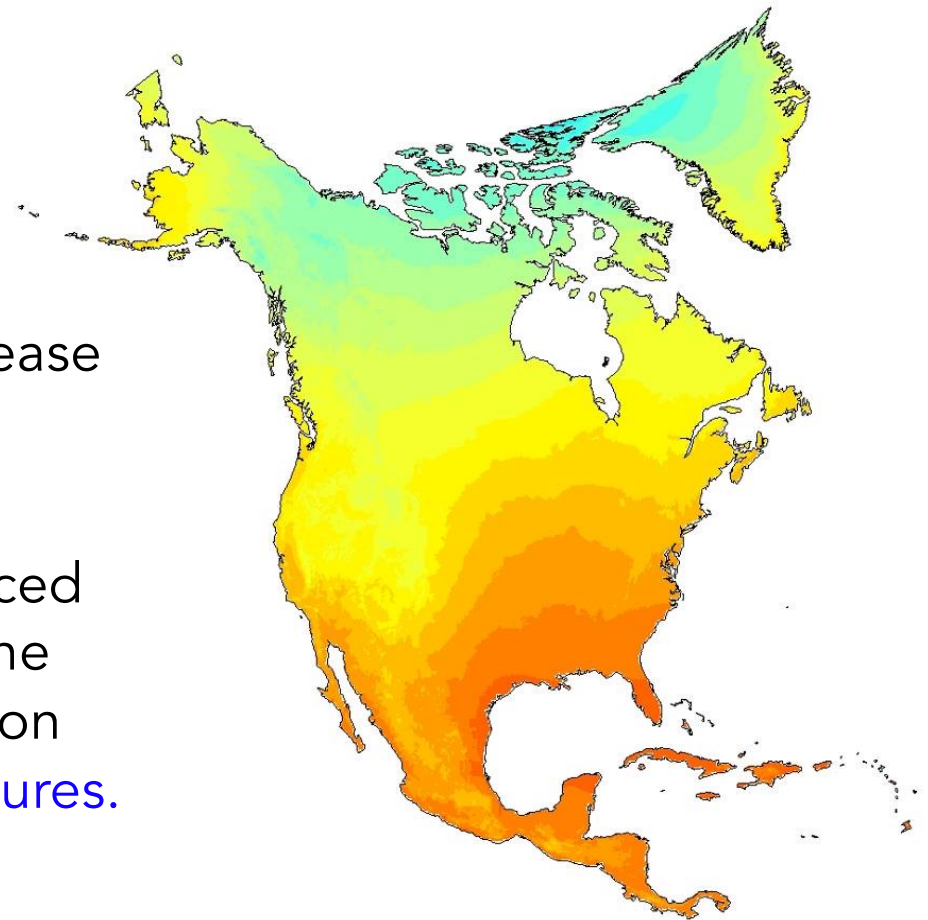
Continental Effect: Latitude and Altitude

Banff/Jasper Canada
-4.7 to -17.4‰

Bowen and Wilkinson 2002

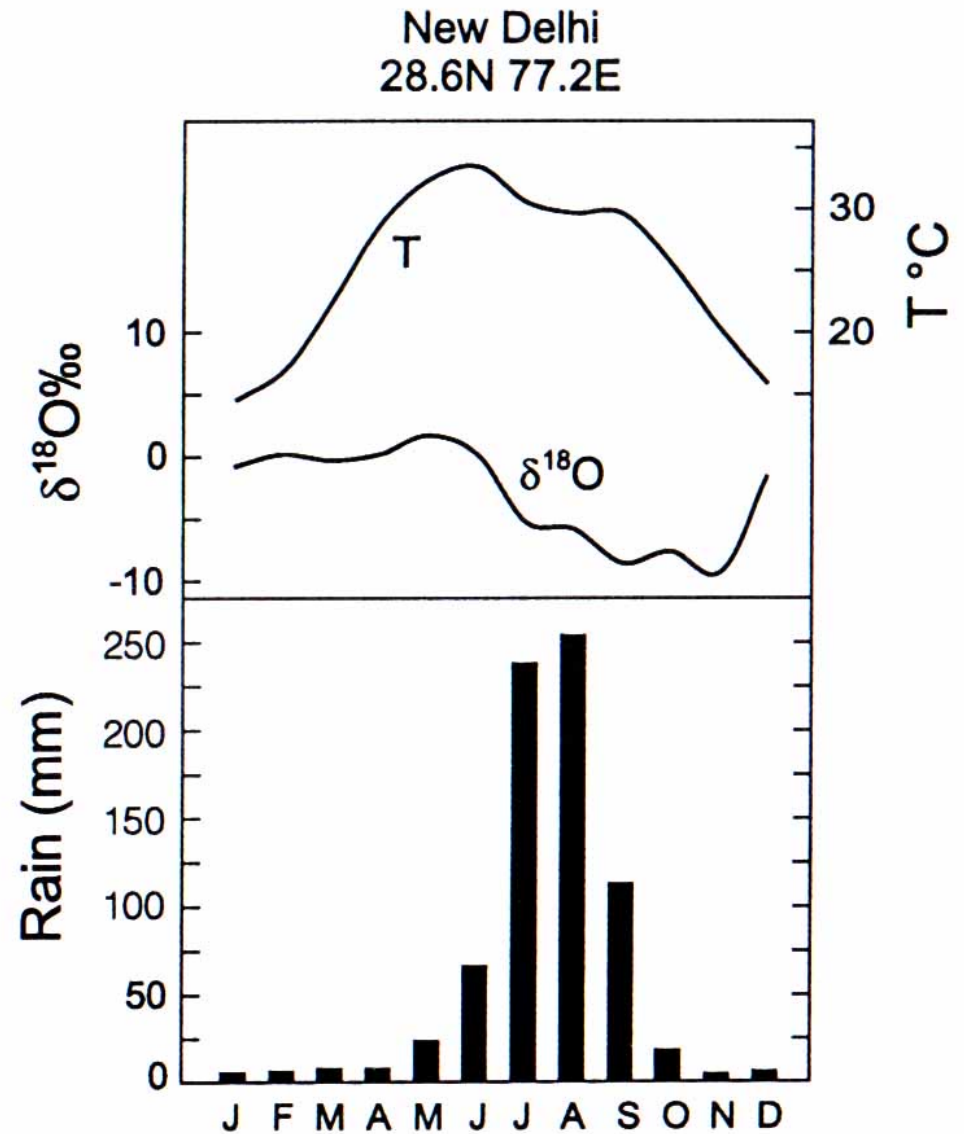# North American δ²H Isoscape

Distillation in Action

Latitude Effect

Altitude Effect

Continentality

Bowen et al. 2005

The Amount Effect

Precipitation isotope δ values decrease with increasing amounts of rainfall (rain out).

Generally follows the predictions of a Rayleigh model forced by lapse rate of cooling airmass.

Rozanski et al. 1993

Source Areas

Atmospheric Circulation – North America

Variability in moisture source needs to be considered as another effect governing local precipitation isotope values

Example:
North American Monsoon

Amundson et al. 1996