Stable Isotopes and Snow Monitoring

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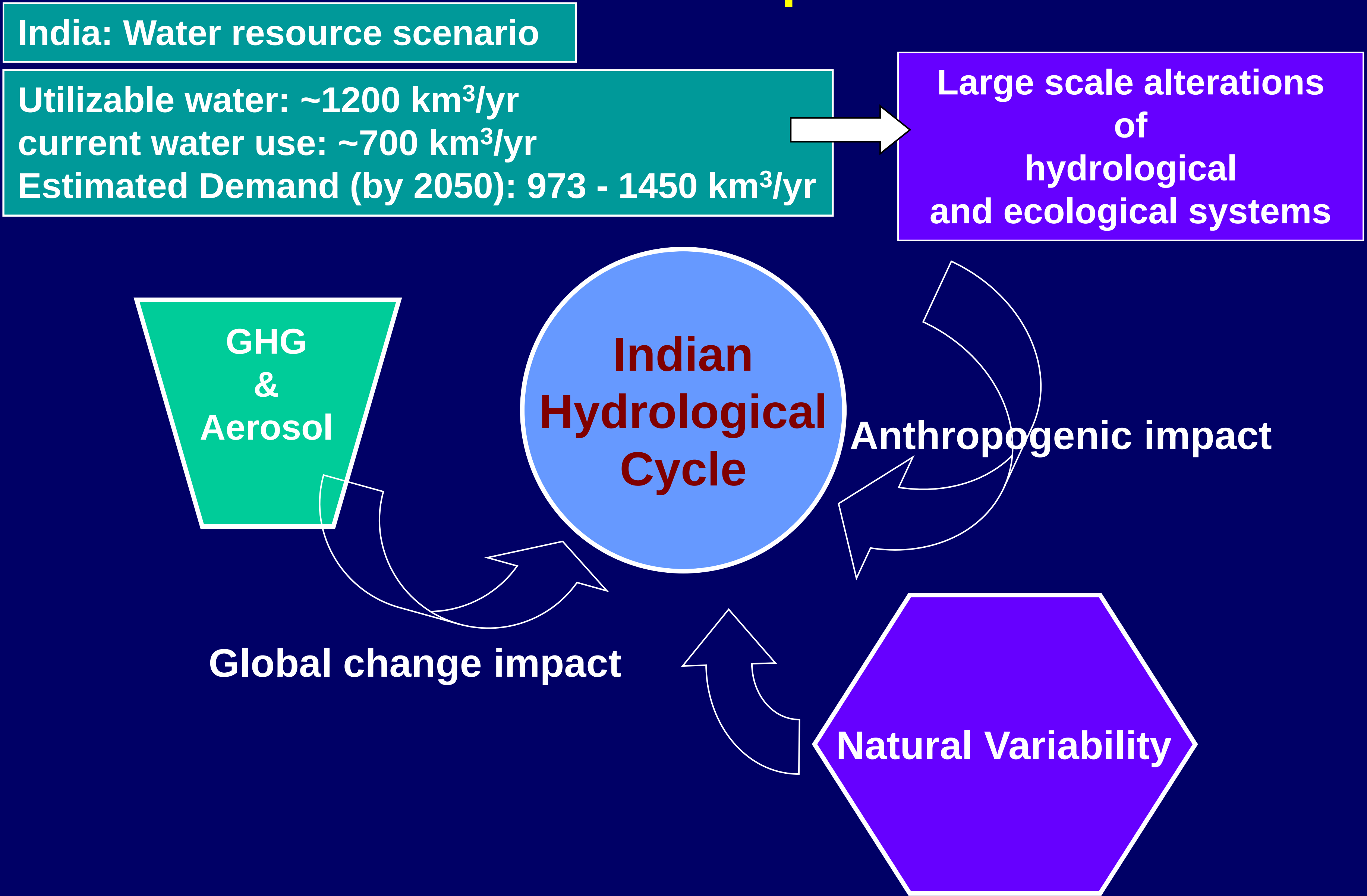
Backdrop



India: Water resource scenario

Utilizable water: ~1200 km^3/yr
current water use: ~700 km^3/yr
Estimated Demand (by 2050): 973 - 1450 km^3/yr

Large scale alterations
of
hydrological
and ecological systems

GHG
&
Aerosol

Indian
Hydrological
Cycle

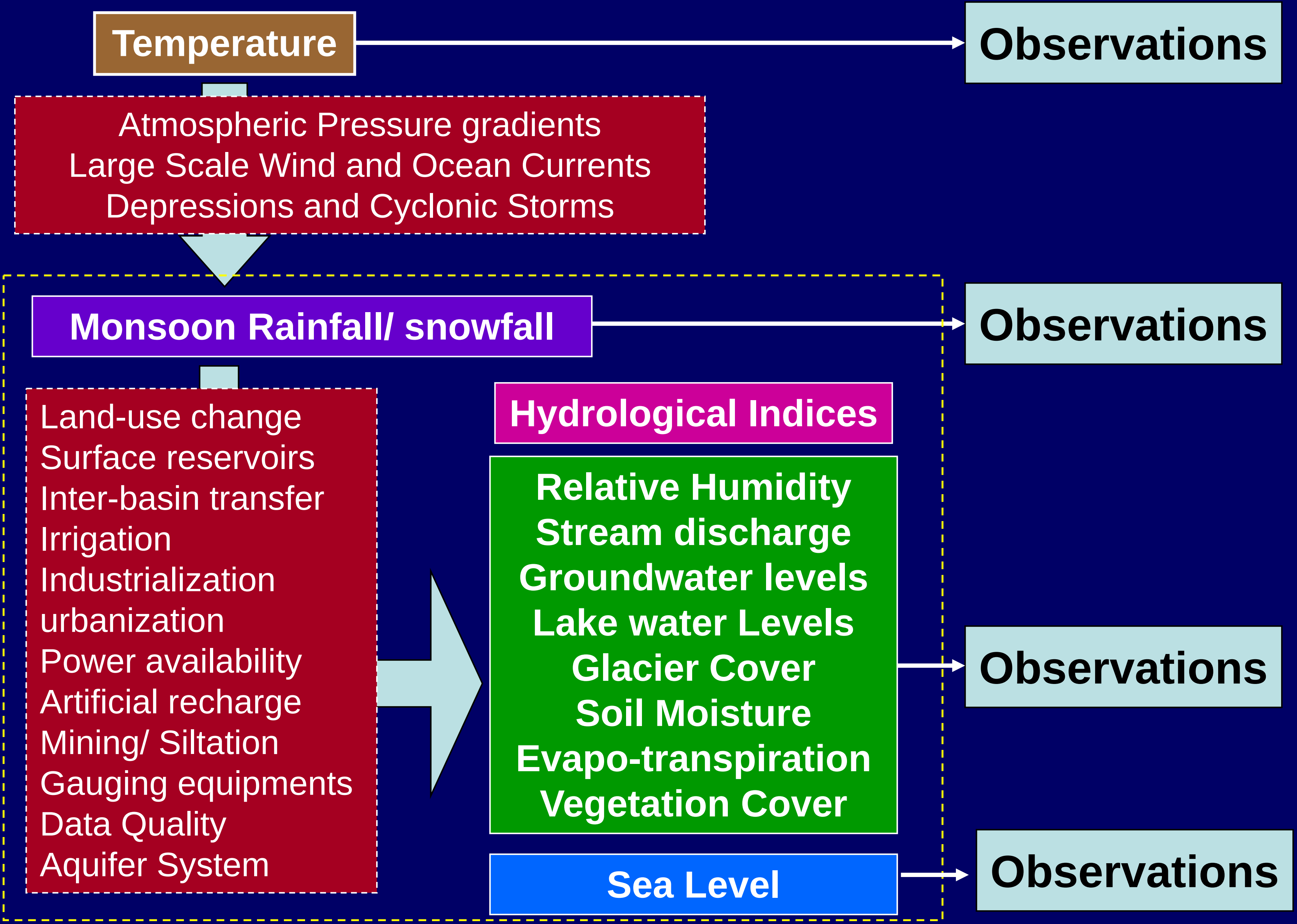
Anthropogenic impact

Global change impact

Natural Variability

Isotope tracing can strengthen Hydrometric approach

Divergence in Regional Observational Systems



Temperature

Observations

Atmospheric Pressure gradients
Large Scale Wind and Ocean Currents
Depressions and Cyclonic Storms

Monsoon Rainfall/ snowfall

Observations

Land-use change
Surface reservoirs
Inter-basin transfer
Irrigation
Industrialization
urbanization
Power availability
Artificial recharge
Mining/ Siltation
Gauging equipments
Data Quality
Aquifer System

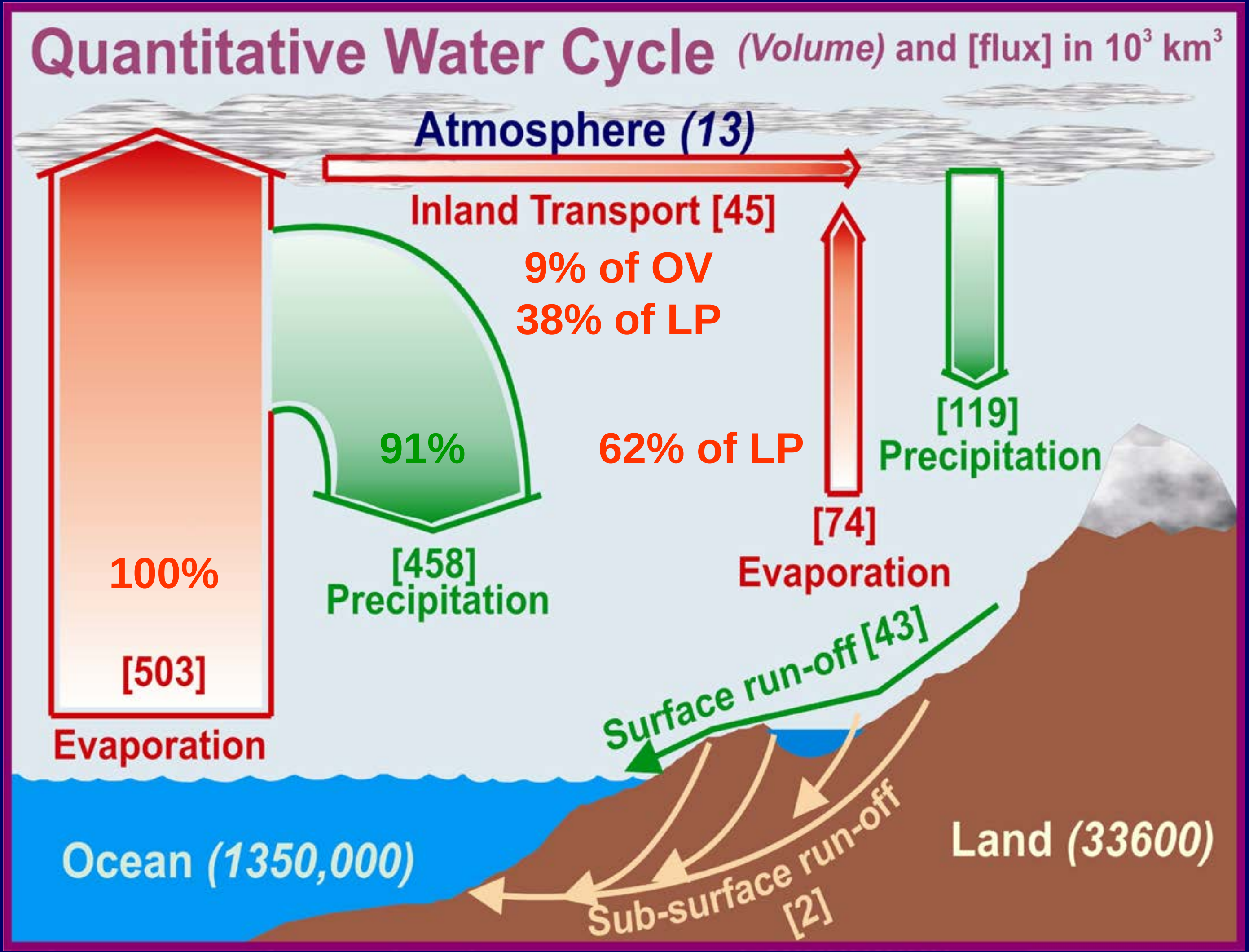
Hydrological Indices

Relative Humidity
Stream discharge
Groundwater levels
Lake water Levels
Glacier Cover
Soil Moisture
Evapo-transpiration
Vegetation Cover

Observations

Sea Level

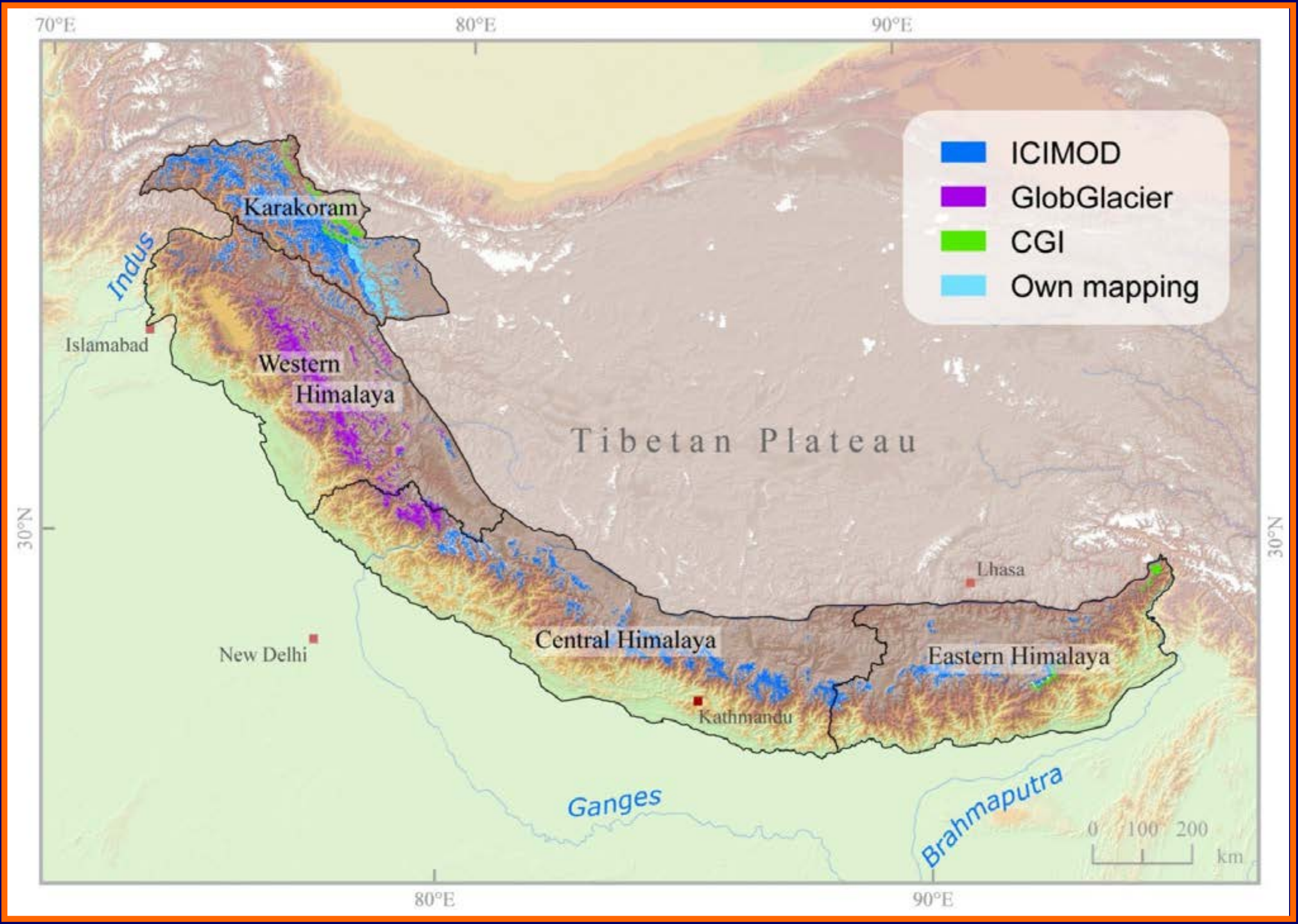
Observations



- Quantitative information on components/ processes, their controls and fluxes across hydrological boundaries can help analyse, predict and minimise adverse impacts to our natural, agricultural and urban environments.
- Baseline data on characteristics features is essential for future comparison.

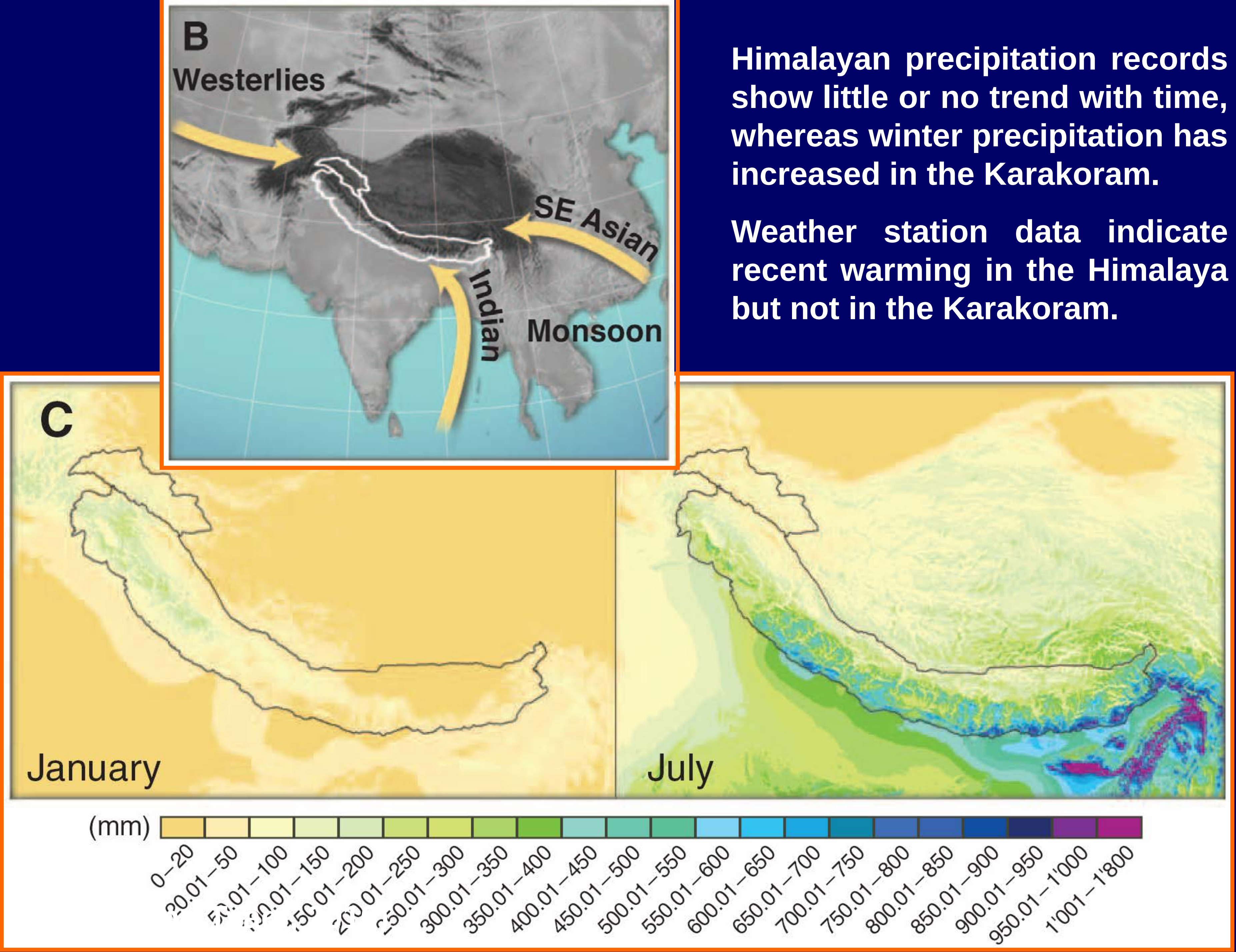
Himalayan and Karakoram Glacier

Bolch et al., 2012 (Science)



Area: ~40,800 km^2
Volume: 2300 km^3

- **Annual amounts of ice and snow melt along with its seasonal and spatial variability, as well as the contributions of precipitation to discharge, are all uncertain**
- **Dependency of ~800 million people for water in non-rainy period**
- **Hydropower, irrigataion, ecology and groundwater recharge**



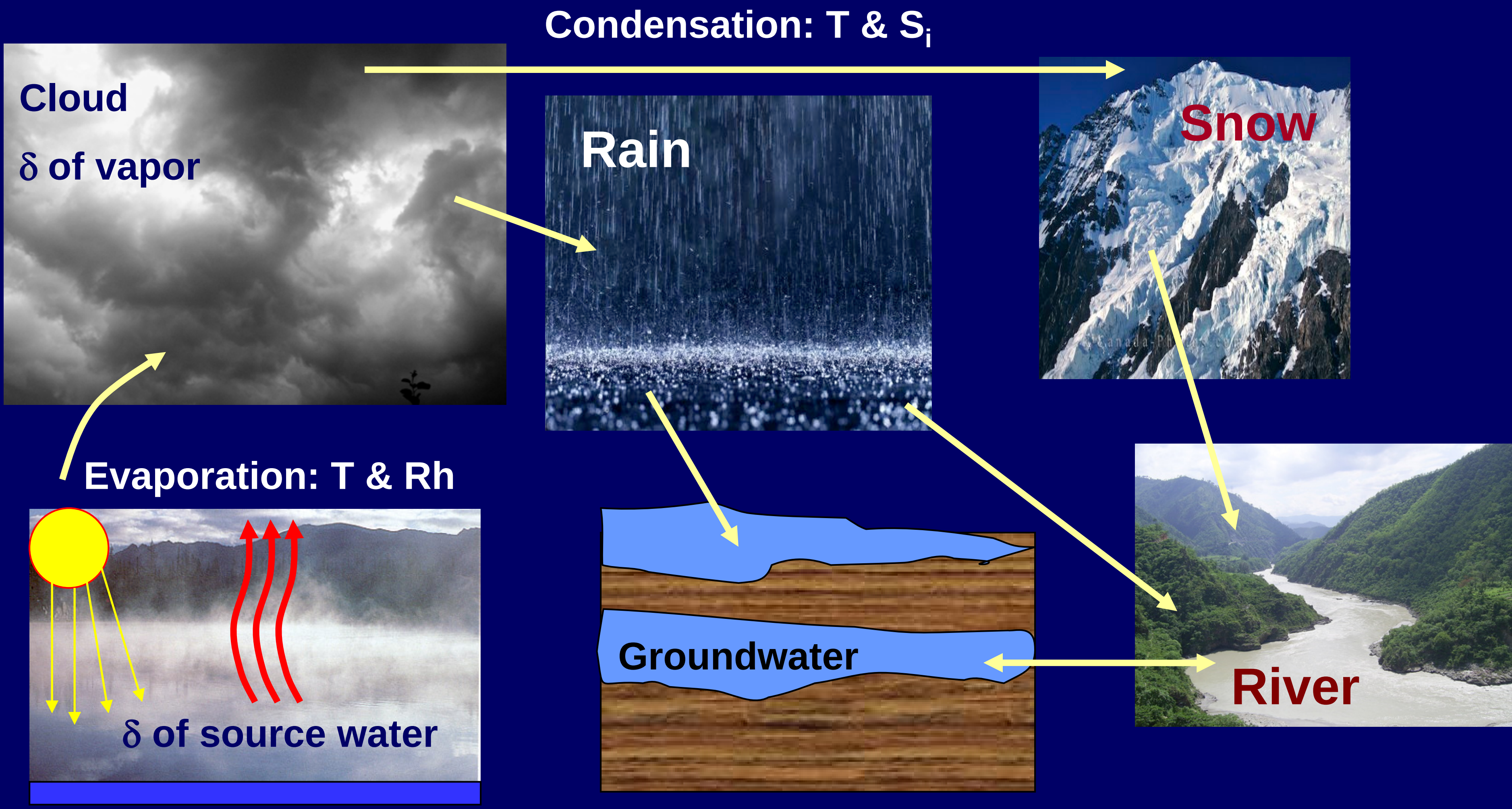
Himalayan precipitation records show little or no trend with time, whereas winter precipitation has increased in the Karakoram.

Weather station data indicate recent warming in the Himalaya but not in the Karakoram.

Specific Questions concerning Himalayan Glaciers

- Are all glacier-basins responding identically to climate change?
  - (Is climate change identical in all basins?)
- Can we classify the Himalayan glacier-basins into diminishing, sustaining or growing types
- What are the principal causes of diminishing sustainability of various basins?
  - Precipitation amount
  - Snow-rain relative proportion
  - Increased melting
  - Increased sublimation
- What is the *altitude-wise* glacial *ice*-melt and *snow*-melt contribution to stream discharge in each glacier basin?
- What is the magnitude of *regionally variable* relative contribution of SW Summer Monsoon, Western disturbances and local recycling?
- Are atmospheric tele-connections of greater relevance than currently believed?

Water molecules record the information about their origin and path in their isotopic composition



Condensation: T & S_i

Cloud

δ of vapor

Rain

Snow

Evaporation: T & Rh

δ of source water

Groundwater

River

Oxygen and Hydrogen Isotopes !!

Oxygen 15.9994(3) g·mol^{-1}

Isotopes	**Natural Abundance**	**Atomic mass**
^{16}O (8p+8n)	99.762%	15.9949146 u
^{17}O (8p+9n)	0.038%	16.9991315 u
^{18}O (8p+10n)	0.200%	17.999160 u

Abundance Ratio ^{18}O / ^{16}O = 0.002004171 = 2004.17× 10^{-6}

One ^{18}O atom per 499 atoms of ^{16}O

Hydrogen 1.00794(7) g·mol^{-1}

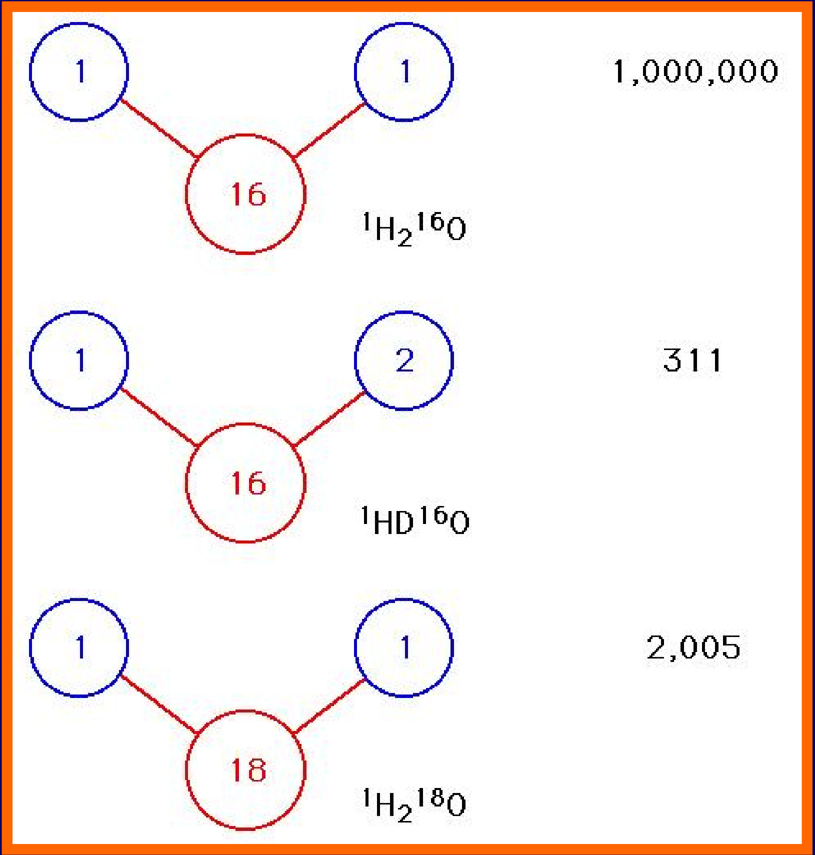
Isotopes	**Natural Abundance**	**Atomic mass**
^{1}H (1p + 0n)	99.985%	1.00782503 u
^{2}H (1p + 1n)	0.015%	2.01410177 u

Abundance Ratio ^{2}H / ^{1}H = 0.0001500225 = 150 × 10^{-6}

One ^{2}H atom per 6666 atoms of ^{1}H

Isotopic Molecular Species
(*isotopologues*)

1. $H_2{}^{16}O$
2. $H_2{}^{17}O$
3. $H_2{}^{18}O$
4. $HD^{16}O$
5. $HD^{17}O$
6. $HD^{18}O$
7. $DD^{16}O$
8. $DD^{17}O$
9. $DD^{18}O$



Relative abundance of isotopic water				
$H_2{}^{16}O$	**$H_2{}^{18}O$**	**$H_2{}^{17}O$**	**$HD^{16}O$**	**$D_2{}^{16}O$**
99.78%	0.20%	0.03%	0.0149%	0.022 ppm
18	20	19	19	20

How Isotopic Composition is expressed and why it is done this way?

$$\delta(\text{in ‰}) = \left[\frac{R_{\text{Sample}}}{R_{\text{Standard}}} - 1\right] \times 1000$$

$$\delta = \left(\frac{R_{\text{Sample}} - R_{\text{Standard}}}{R_{\text{Standard}}}\right) \quad \text{or} \quad \delta = \left(\frac{R_{\text{Sample}}}{R_{\text{Standard}}} - 1\right)$$

Why ratio of sample to standard ?

Why multiply by 1000 ?

Expressing the Isotopic Composition

1. Absolute abundance of heavier isotopic molecular species of water is very small in any natural water sample.

   ~2000 $H_2{}^{18}O$ and ~150 $HD^{16}O$ in 1000000 $H_2{}^{16}O$

2. Variation in absolute abundance of heavier isotopic molecular species is even smaller

2005 atoms of ^{18}O
per million atoms of ^{16}O

$^{18}O/^{16}O = 0.002005$

2025 atoms of ^{18}O
per million atoms of ^{16}O

$^{18}O/^{16}O = 0.002025$

Expressing the Isotopic Composition

$$\delta\,(‰) = \left(\frac{\left[\dfrac{\text{Abundance of less abundant (heavier) isotope}}{\text{Abundance of more abundant (lighter) isotope}} \right]_{\text{Sample}}}{\left[\dfrac{\text{Abundance of less abundant (heavier) isotope}}{\text{Abundance of more abundant (lighter) isotope}} \right]_{\text{Standard}}} - 1 \right) \text{x } 1000$$

Example

$$\delta\,(‰) = \left(\frac{[0.0020253]_{\text{Sample}}}{[0.0020052]_{\text{Standard}}} - 1 \right) \text{x } 1000$$

$$\delta\,(‰) = (1.010000 - 1) \text{ x } 1000 = 10\,‰$$

A $\delta^{18}O$ value of +10 ‰ signifies that sample has 10‰ (i.e. 1%) more ^{18}O than the standard. VSMOW Standard: 2005.2 atoms of ^{18}O /1000000 atoms of ^{16}O (1% =20.052 atoms of ^{18}O)

+10‰ ⟶ Sample has 2025.252 atoms of ^{18}O /1000000 atoms of ^{16}O

-10‰ ⟶ Sample has 1985.148 atoms of ^{18}O /1000000 atoms of ^{16}O

International Standard Reference materials for expressing isotopic composition of water

SMOW, VSMOW, SLAP and GISP

$$\boxed{\left(\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}}\right)_{\mathrm{VSMOW}} = (2005.2 \pm 0.5) \times 10^{-6}}$$

$$\boxed{\left(\frac{^{2}\mathrm{H}}{^{1}\mathrm{H}}\right)_{\mathrm{VSMOW}} = (155.75 \pm 0.45) \times 10^{-6}}$$

Standard Light Antarctic Precipitation (SLAP)

- $\delta^{18}\mathrm{O}_{\mathrm{SLAP}}$ = -55.50‰ VSMOW; $\delta\mathrm{D}_{\mathrm{SLAP}}$ = -428.0‰ VSMOW

Greenland Ice Sheet Precipitation (GISP)

- $\delta^{18}\mathrm{O}_{\mathrm{GISP}}$ = -24.76‰ VSMOW: $\delta\mathrm{D}_{\mathrm{GISP}}$ = -189.5‰ VSMOW

Isotope Systematics

Isotope Fractionation

- Differential partitioning of isotopes between the two compounds or between the two phases of a compound in a physicochemical reaction.
- Differential partitioning of one isotope over another on one side of the thermodynamic reaction.
- Differential partitioning of isotopes due to molecular diffusion.

Causal factors for Fractionation

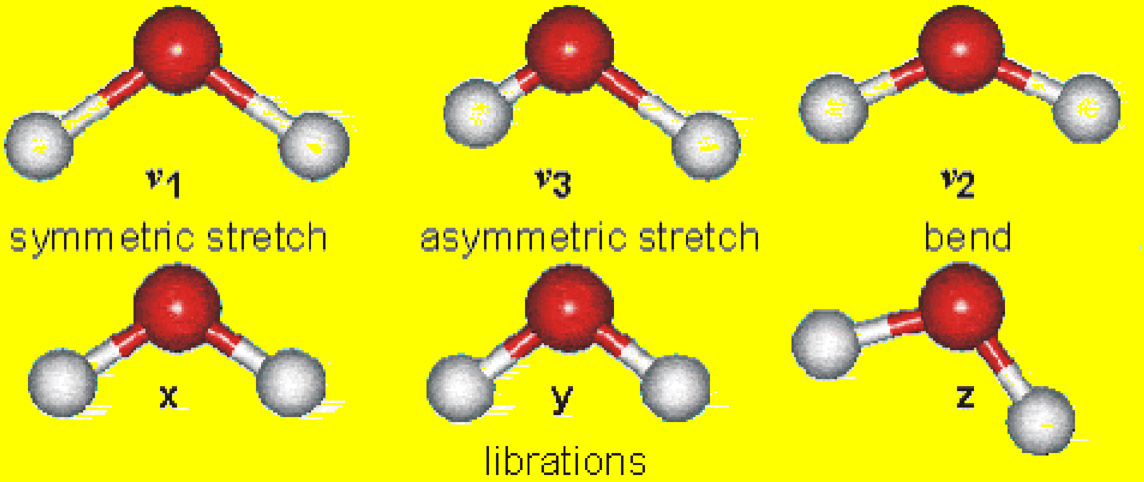
1. Chemical properties of water isotopologues are identical but physical properties (bond strength, rotational, vibrational and translational frequencies, density, vapour pressure, collision frequency, diffusive velocities etc) are different due to their mass differences.
2. Differences between above properties of isotopologues are affected by temperature.
3. kinetic energy = kT = $\frac{1}{2}mv^2$

$$\frac{1}{2}{\Huge m}v^2 = \frac{1}{2}m{\Huge V}^2$$

4. Lower velocities → smaller collision frequency →slower rate of reaction
5. Heavier molecules have greater binding energies and requires more energy to break the bonds. Therefore, heavier isotopes form stronger bonds

Let us watch a dance before understanding partition function

Vibrations of water molecule



Three different ways of isotope fractionation

1. **Fractionation during physicochemical reactions under equilibrium condition.**
    a. Phase Change
    b. Chemical Transformation
    c. Isotope Exchange
    d. Mineral Solution
    e. Gas Solution

2. **Fractionation during physicochemical reactions under non-equilibrium (kinetic) conditions.**
    a. Sudden Temperature change
    b. Addition or removal of reactant or product

3. **Fractionation during molecular diffusion.**
    a. Diffusion or atoms or molecules across concentration gradient

Fractionation Factor

The isotope fractionation is mathematically expressed by the ratio of abundance ratios of the heavy / light isotope between reactant and product and is referred to as the fractionation factor (α).

$$\alpha = \frac{\left[\frac{\text{Heavier isotope}}{\text{Lighter isotope}}\right]_{\text{Reactant}}}{\left[\frac{\text{Heavier isotope}}{\text{Lighter isotope}}\right]_{\text{Product}}} = \frac{R_{\text{Reactant}}}{R_{\text{Product}}}$$

$$^{18}\alpha\ (\text{Water} - \text{Vapour}) = \frac{\left[\frac{^{18}O}{^{16}O}\right]_{\text{Water}}}{\left[\frac{^{18}O}{^{16}O}\right]_{\text{Vapour}}}$$

$$^{18}\alpha\ (\mathit{Vapour} - \mathit{Water}) = \frac{\left[\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}}\right]_{\mathit{Vapour}}}{\left[\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}}\right]_{\mathit{Water}}}$$

$^{18}\alpha$ (water-vapor) = 1.00937 at 25° C

$^{18}\alpha$ (vapor-water) = 0.990717 at 25° C

$[\alpha^* > 1$ and $\alpha^+ < 1$ such that $\alpha^* = 1/\alpha^+]$

Equilibrium Enrichment

$$\varepsilon_{x-y} = (\alpha - 1).10^3 = \left(\frac{R_x}{R_y} - 1 \right).10^3$$

$$\delta\ (‰) = \left(\frac{[R]_{\text{Sample}}}{[R]_{\text{Standard}}} - 1 \right) \text{x } 1000$$

$$\alpha_{X-Y} = \frac{1 + \frac{\delta_X}{1000}}{1 + \frac{\delta_Y}{1000}} = \frac{1000 + \delta_X}{1000 + \delta_Y}$$

$$10^3 \ln \alpha$$

Determination of Equilibrium Fractionation Factor

- In principal, the equilibrium fractionation factor can be theoretically calculated from ratios of partition functions between the two phases.
- Fractionation factors have also been estimated experimentally, by several workers for different equilibrium systems and at different absolute temperatures.

$$\boxed{10^3 \ln \alpha_{(l-v)}(^{18}O) = 6.7123\left(\frac{10^3}{T}\right) - 1.6664\left(\frac{10^6}{T^2}\right) - 7.685 + 0.35041\left(\frac{10^9}{T^3}\right)}$$

$$\boxed{10^3 \ln \alpha_{(l-v)}(D) = 1158.8\left(\frac{T^3}{10^9}\right) - 1620.1\left(\frac{T^2}{10^6}\right) + 794.84\left(\frac{T}{10^3}\right) - 161.04 + 2.9992\left(\frac{10^9}{T^3}\right)}$$

Horita and Wesolowski (1994)

$$\boxed{10^3 \ln \alpha}$$

Fractionation factors Based on Equations by Horita and Wesolowski (1994)

Temp. °C	$10^3\ln\alpha^{18}$	$^{18}\alpha$	$^{18}\varepsilon$	$10^3\ln\alpha^2$	α^2	ε^2	$\left(\frac{10^3\ln\alpha^2}{10^3\ln\alpha^{18}}\right)$
0	11.75	1.0118	11.82	105.96	1.1118	111.78	9.0
5	11.19	1.0113	11.25	99.00	1.1041	104.06	8.8
10	10.67	1.0107	10.73	92.54	1.0970	96.96	8.7
15	10.18	1.0102	10.24	86.55	1.0904	90.40	8.5
20	9.73	1.0098	9.78	80.97	1.0843	84.34	8.3
25	9.30	1.0093	9.35	75.79	1.0787	78.74	8.1
30	8.90	1.0089	8.94	70.96	1.0735	73.54	8.0
40	8.17	1.0082	8.20	62.24	1.0642	64.21	7.6
50	7.51	1.0075	7.54	54.61	1.0561	56.13	7.3
60	6.93	1.0069	6.95	47.90	1.0491	49.07	6.9
70	6.40	1.0064	6.42	41.98	1.0429	42.88	6.6
80	5.92	1.0059	5.93	36.74	1.0374	37.42	6.2
90	5.48	1.0055	5.49	32.07	1.0326	32.59	5.9
100	5.08	1.0051	5.09	27.90	1.0283	28.29	5.5

Determination of Kinetic Fractionation Factor

$$\alpha = \text{Diffusive Fractionation} = \frac{v^*}{v} = \frac{\sqrt{\dfrac{kT}{2\pi m^*}}}{\sqrt{\dfrac{kT}{2\pi m}}} = \sqrt{\frac{\mu}{\mu^*}}$$

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

(m: $H_2{}^{18}O$ = 20; $HD^{16}O$ =19; $H_2{}^{16}O$ =18) (M: 28.8 for 79% N_2 + 21% O_2)

$$\frac{1}{\mu_{16}} = \frac{1}{18} + \frac{1}{28.8}$$

$$\frac{1}{\mu_{18}} = \frac{1}{20} + \frac{1}{28.8}$$

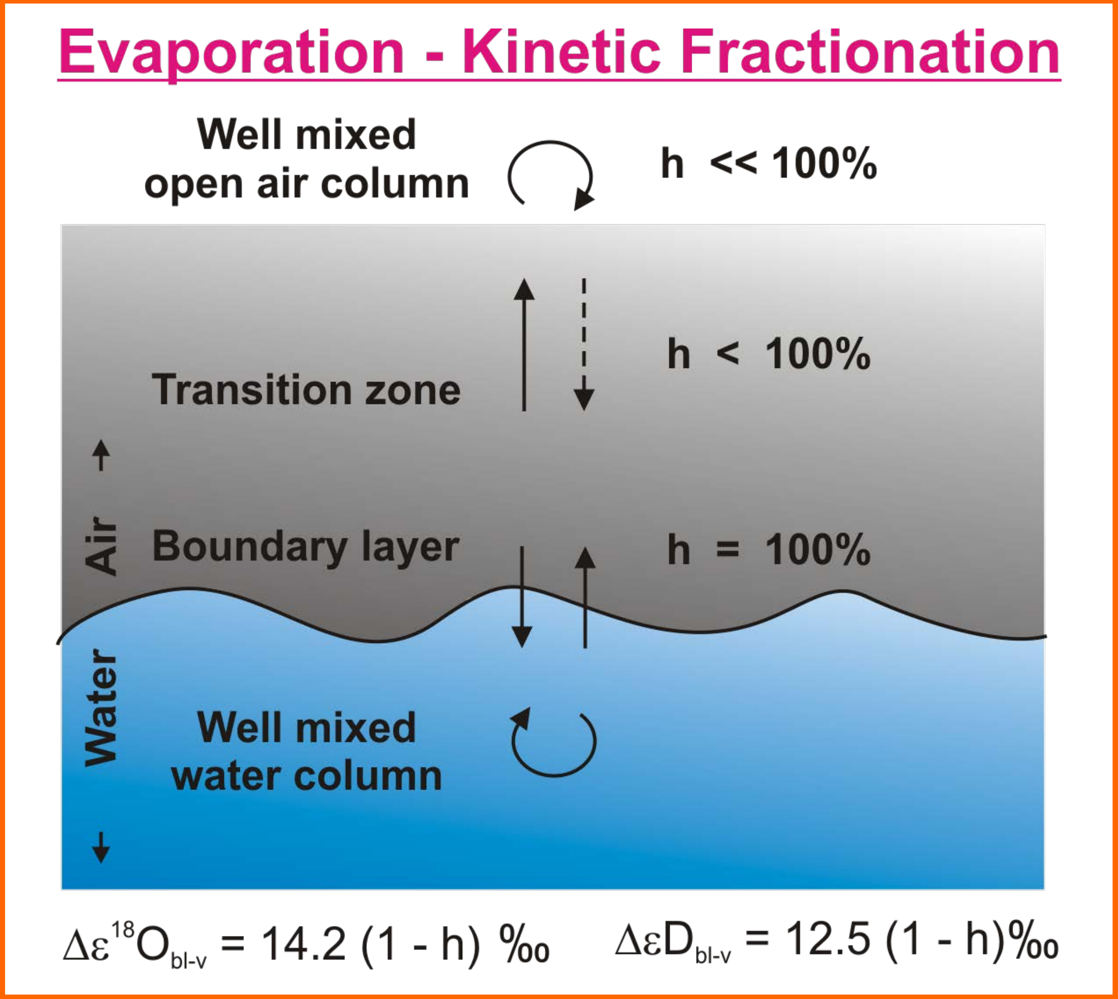
$$\frac{1}{\mu_2} = \frac{1}{19} + \frac{1}{28.8}$$

$$\Delta\varepsilon^{18} = 31‰$$

$$\Delta\varepsilon^{2} = 16‰$$

This magnitude of fractionation is never observed in nature.

Diffusive Fractionation



$\Delta\varepsilon^{18}O_{bl\text{-}v} = 14.2\,(1 - h)$ ‰ $\Delta\varepsilon D_{bl\text{-}v} = 12.5\,(1 - h)$‰

Total Fractionation

$$\varepsilon^{18}_{(l-bl)} + \Delta\varepsilon^{18}_{(bl-v)}$$

Magnitude of kinetic fractionation for Oxygen > that for Hydrogen ⟶ $[\Delta\varepsilon^{2}/\Delta\varepsilon^{18} = 0.88]$ @ Rh

Magnitude of equilibrium fractionation for Oxygen < that for Hydrogen ⟶ $[\varepsilon^{2}/\varepsilon^{18} = \sim 8]$ @ T

Rayleigh Distillation

Rayleigh Distillation

The general form of a Rayleigh distillation equation states that the isotope ratio (R) in a diminishing reservoir of the reactant is a function of its initial isotopic ratio (R_o), the remaining fraction of that reservoir (*f*) and the equilibrium fractionation factor for the reaction ($\alpha_{\text{product-reactant}}$):

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

$$\boxed{\delta \cong \delta_0 + \varepsilon \,.\ln f}$$

$$\boxed{\delta\ {}^{18}O_{v(f)} \cong \delta_0\ {}^{18}O_v + \varepsilon\, {}^{18}O_{l-v} \,.\ln f}$$

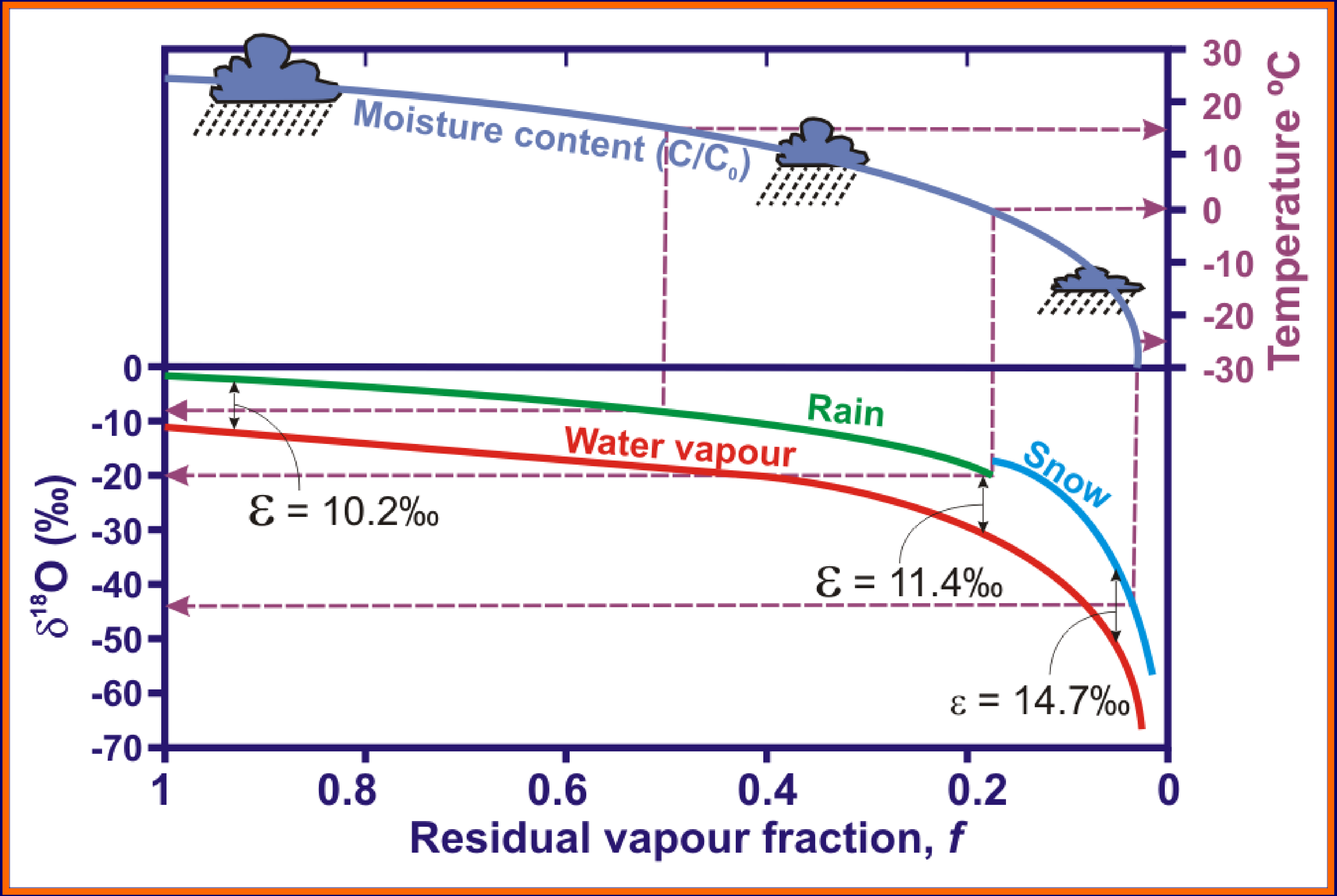
$$\boxed{\delta\ {}^{18}O_{Rain(f)} = \delta\ {}^{18}O_{v(f)} + \varepsilon\, {}^{18}O_{l-v(T)}}$$

How these equations are derived?

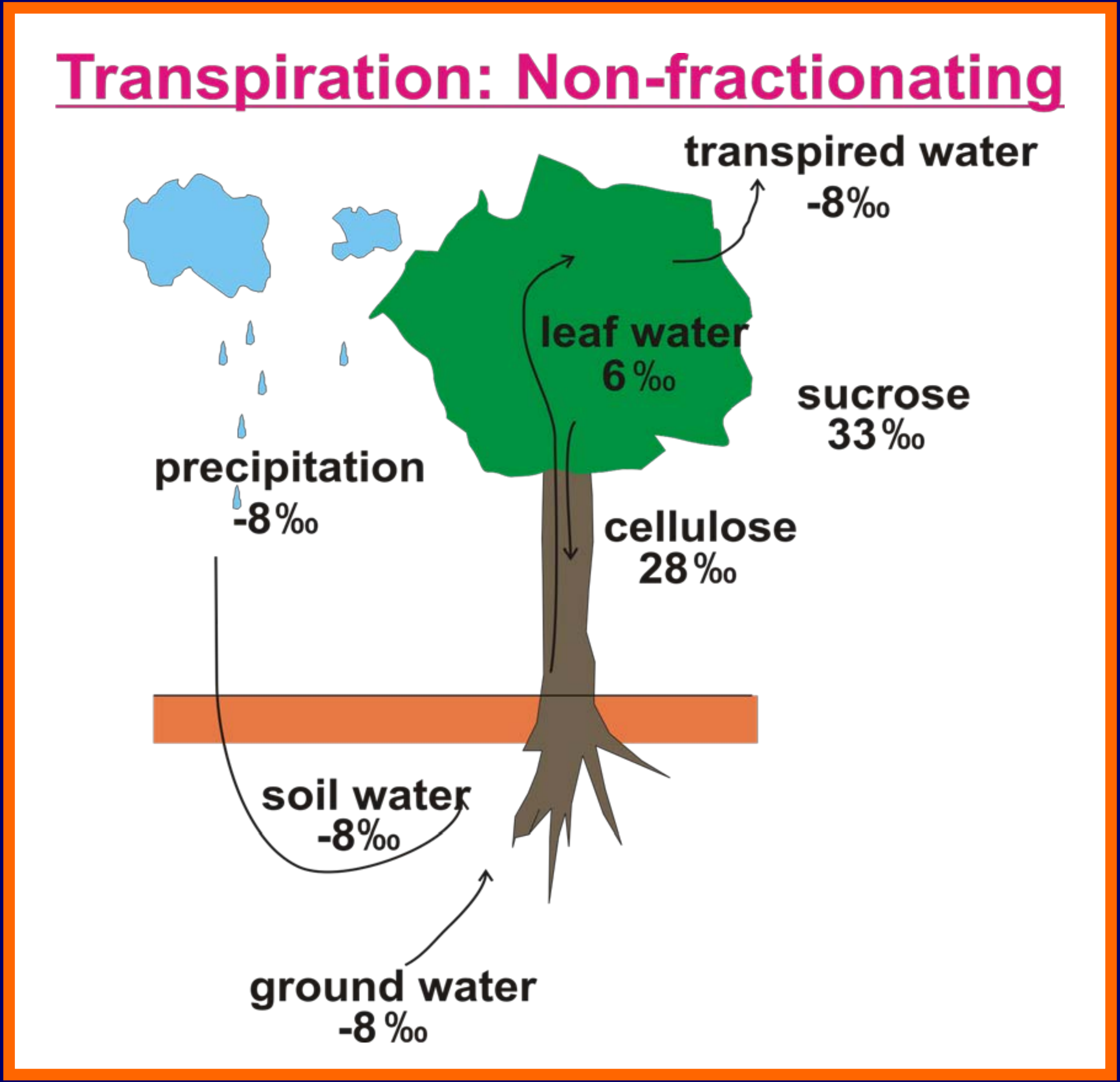
Essential Conditions for applicability of Rayleigh Equation

1. Both reactant and product reservoirs are well mixed.
2. Reactant and product remain in intimate contact for interaction.
3. Forward and backward rate of reactions are equal i.e. thermodynamic equilibrium is established.
4. Product is removed only after equilibrium established.
5. Reactant or product is neither removed nor added suddenly into system.
6. There is no sudden temperature change which disturbs thermodynamic equilibrium

Rayleigh Distillation Schematic



$$\delta \cong \delta_0 + \varepsilon . \ln f$$



Transpiration is a non-fractionating process but transpired vapour can cause isotopic change in the atmospheric vapour reservoir due to significant addition of vapour.

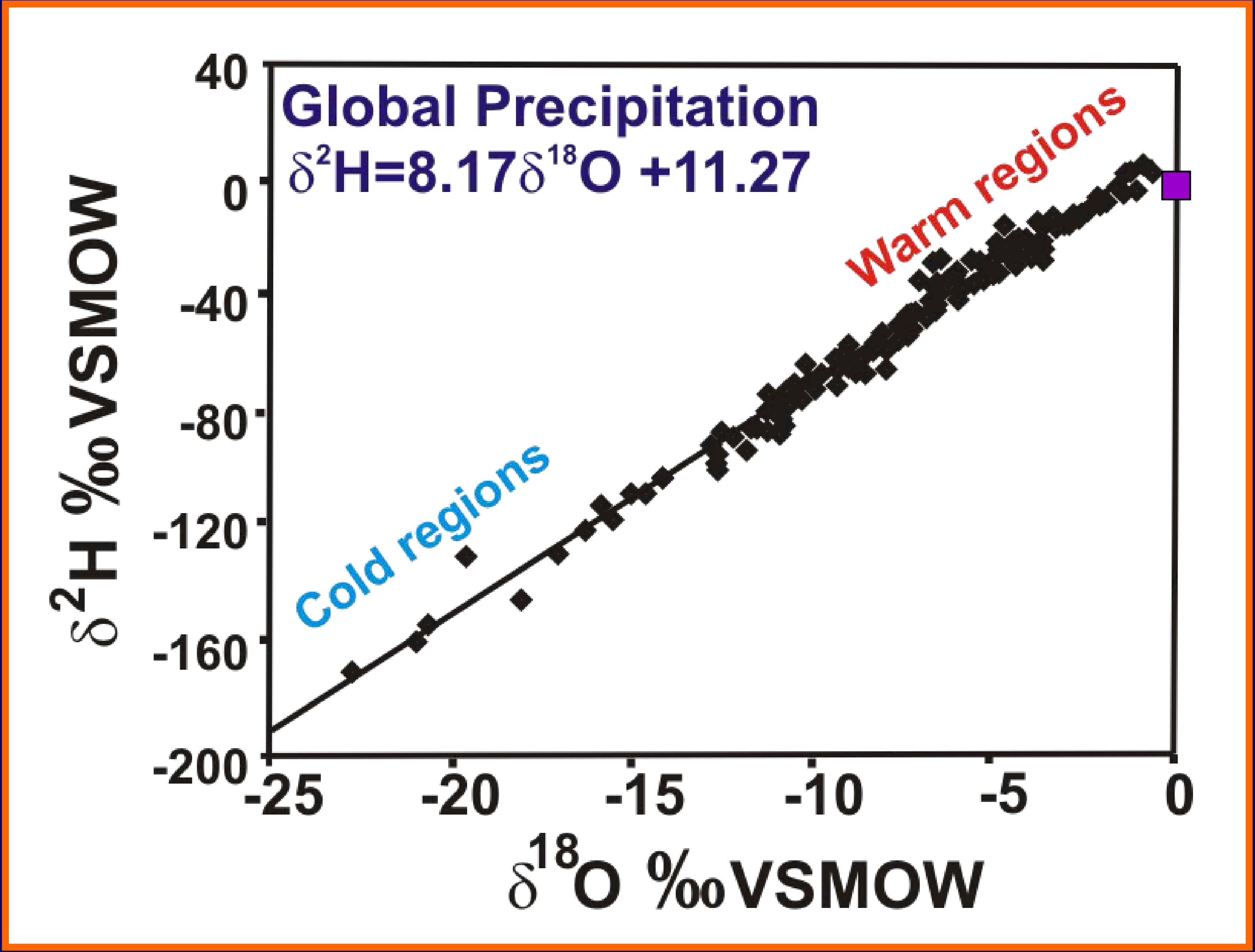
Relationship between $\delta^{18}O$ and δD

Craig’s Meteoric Water Line

- In spite of the great complexity in different components of the hydrological cycle, $\delta^{18}O$ and δD in fresh surface waters (representing precipitation) correlate on a global scale.

$$\boxed{\delta D = 8 \times \delta^{18}O + 10 \quad (\text{‰ SMOW})}$$

Global Meteoric Water Line (GMWL)



Slope ~8 and intercept non-zero (i.e. GMWL does not pass through Ocean water)

Significance of slope and intercept

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

$$\delta \cong \delta_0 + \varepsilon \, . \ln f$$

$$\delta^{18}\mathrm{O} = \delta^{18}\mathrm{O}_0 + \left({}^{18}\varepsilon \times \ln f \right)$$

$$\delta\mathrm{D} = \delta\mathrm{D}_0 + \left({}^{2}\varepsilon \times \ln f \right)$$

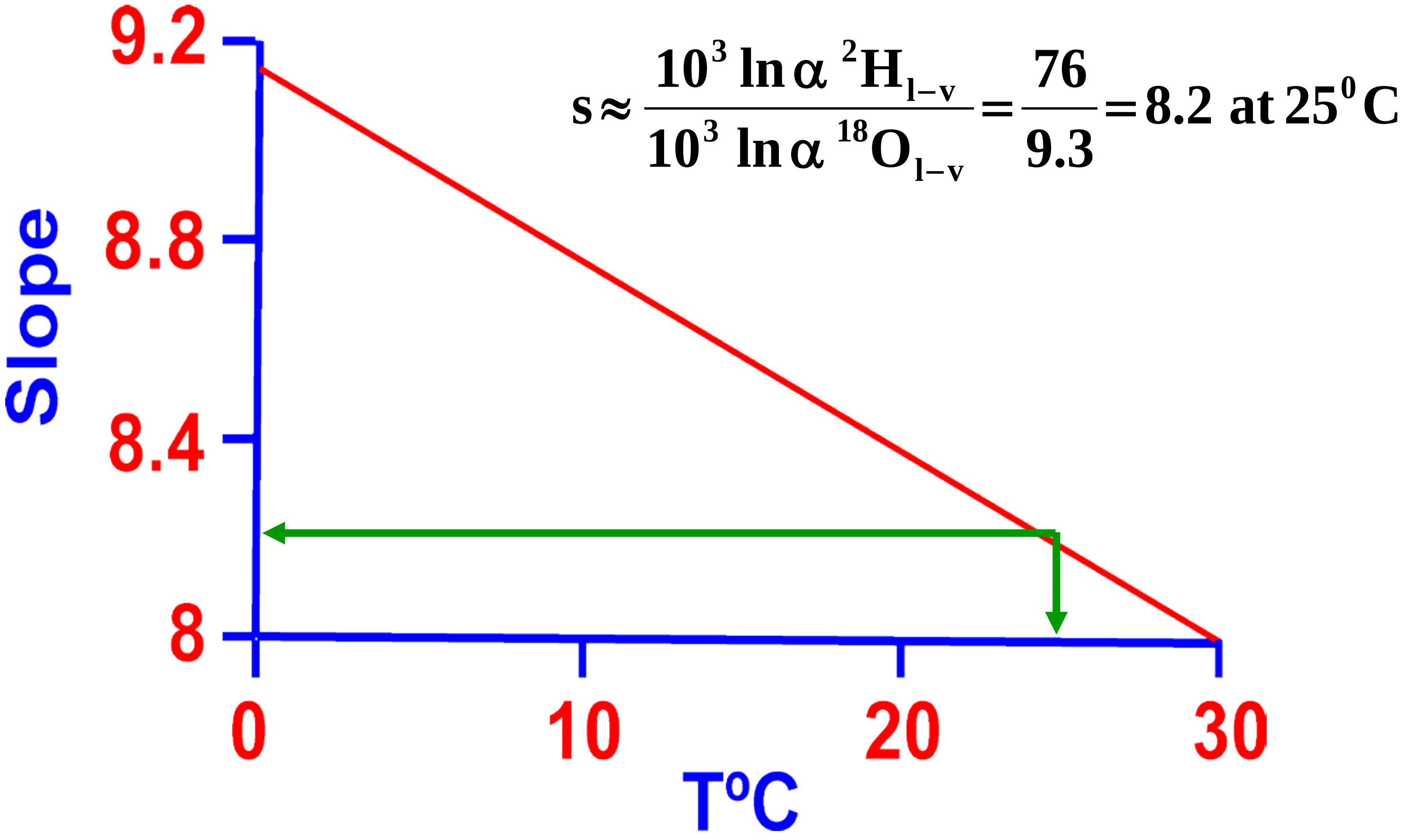
$$\delta\mathrm{D} = \delta^{18}\mathrm{O} \times \left(\frac{{}^{2}\varepsilon}{{}^{18}\varepsilon} \right) + \left[\delta\mathrm{D}_0 - \delta^{18}\mathrm{O}_0 \times \left(\frac{{}^{2}\varepsilon}{{}^{18}\varepsilon} \right) \right]$$

How?

$$y = x \times m + c$$

Slope of $\delta^{18}O$-δD regression line

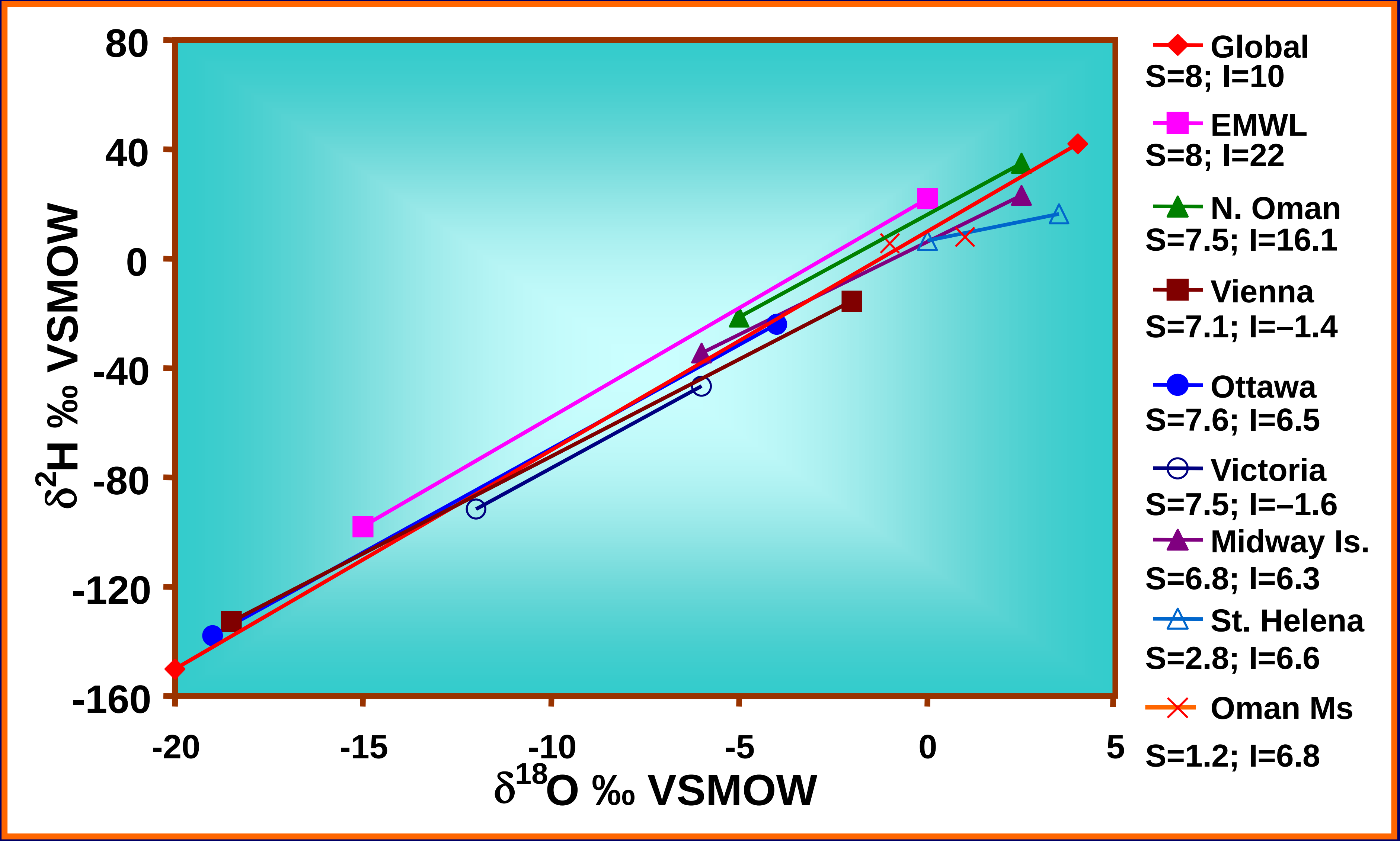
Why is the slope of GMWL around 8?



$$s \approx \frac{10^3 \ln \alpha\ {}^2H_{l-v}}{10^3 \ln \alpha\ {}^{18}O_{l-v}} = \frac{76}{9.3} = 8.2 \text{ at } 25^0 C$$

Slope of GMWL signifies the ratio of fractionation factor for hydrogen and oxygen. The slope of LMWL can be affected by the evaporation from the falling raindrops

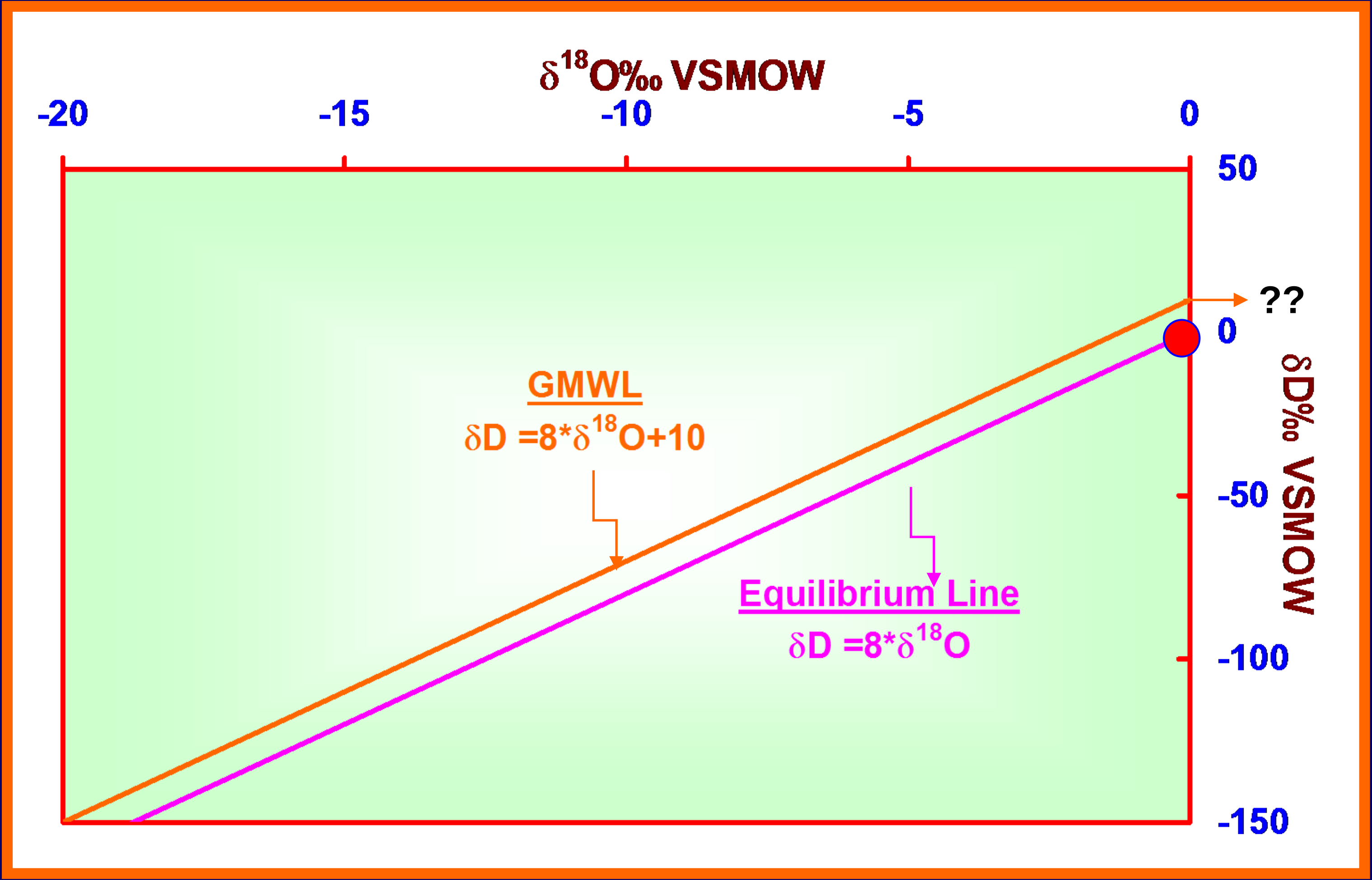
Local Meteoric Water Lines



What is the interpretative significance of slope and intercept values ?

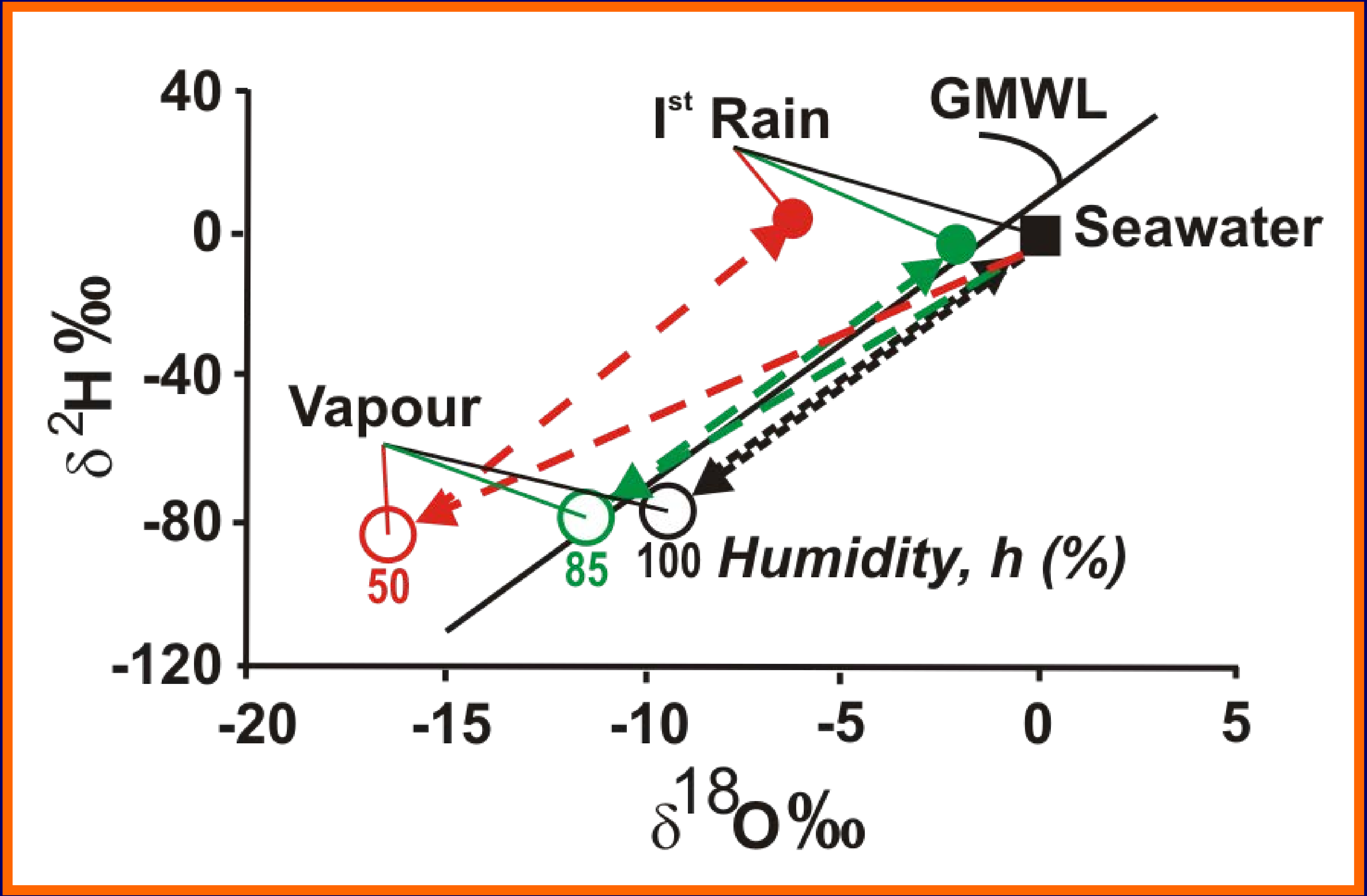
Intercept of $\delta^{18}O$-δD regression line

Why is the D-intercept of GMWL around 10 ?



Intercept = 10 in GMWL signifies condensation from vapour formed under Rh = 85%
Intercept > 10 for MWL signifies condensation from vapour formed under Rh < 85%

Humidity in the Oceanic Source Region



Why GMWL does not pass through isotopic composition value of sea water ?

Deuterium excess (*d*-excess)

$$\boxed{d\text{-excess} = \delta D - 8 \times \delta^{18}O\,(‰)}$$

The observed intercept of the GMWL was advantageously used by Dansgaard, to define a parameter (*d*-excess), which can be calculated for individual pair of $\delta^{18}O$ and δD using following equation.

The basic premise behind defining such a parameter is that whenever kinetic fractionation is involved, the net ratio of fractionation for deuterium to oxygen is different from 8.

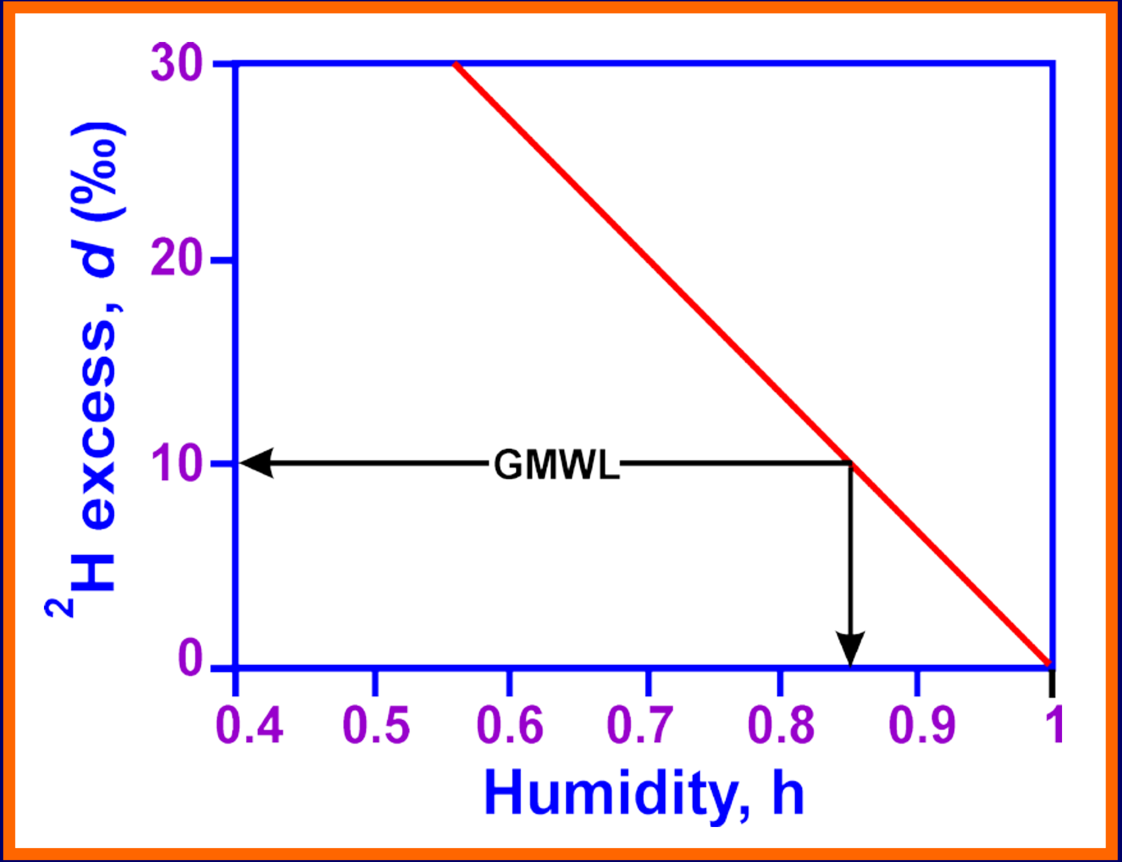
$$\boxed{\delta D = 8 \times \delta^{18}O + \text{Excess Deuterium}}$$

$$\boxed{\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}}\right) = \frac{{}^2\varepsilon}{{}^{18}\varepsilon} = \sim 8}$$

$$\boxed{\left[\frac{\Delta\varepsilon^2 H_{(bl\text{-}v)}}{\Delta\varepsilon^{18} O_{(bl\text{-}v)}} \approx 0.88\right]}$$

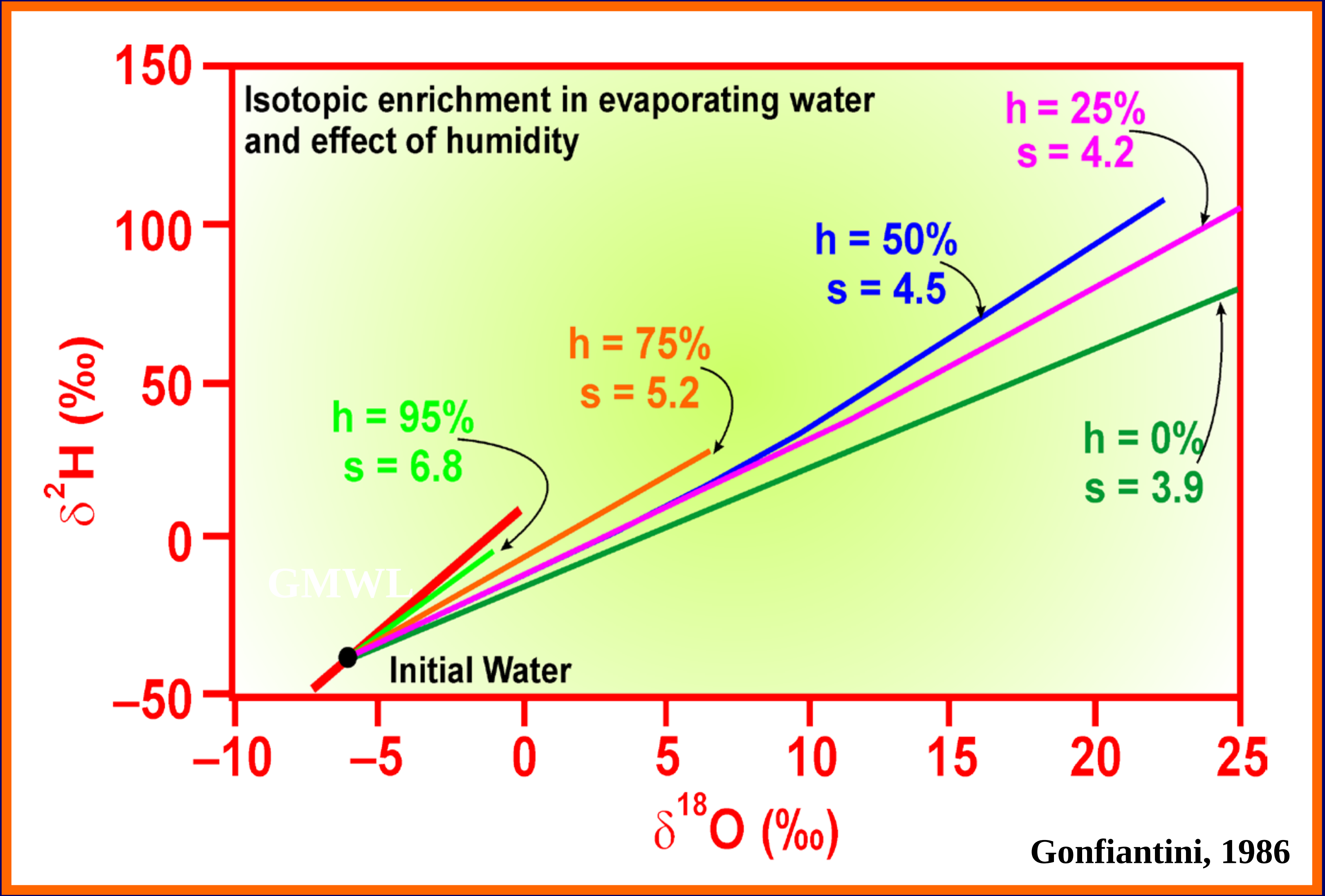
d-excess in vapour and Humidity

What does d-excess (= δD – 8*δ^{18}O) signify?



d-excess can be calculated for individual δ^{18}O-δD pair and it signifies the kinetic fractionation due to evaporation. On evaporation, *d*-excess of the residual water decreases and consequent vapour has correspondingly higher *d*-excess. The rain formed from such a vapour also has high *d*-excess.

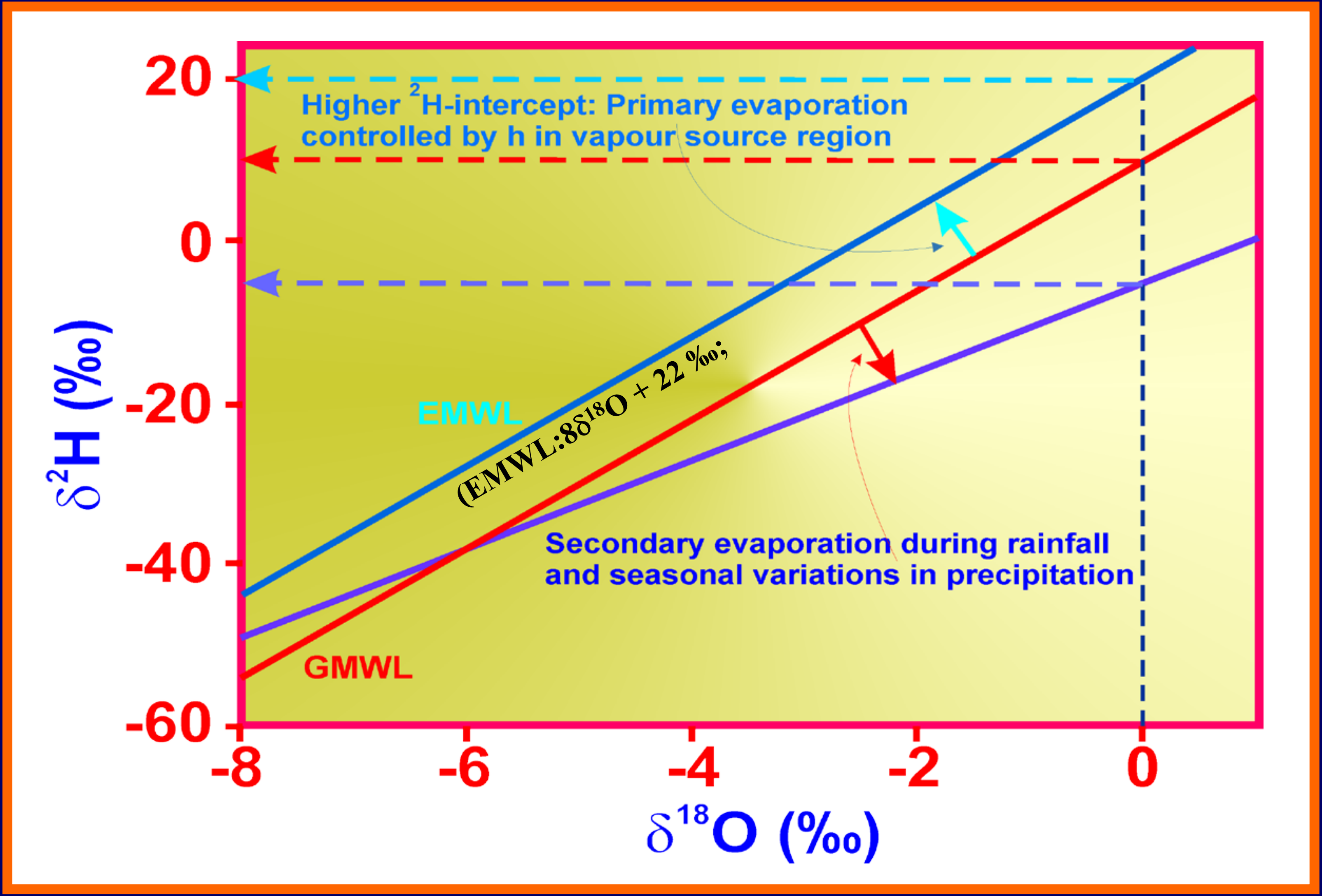
Isotopic evolution of water on evaporation



Gonfiantini, 1986

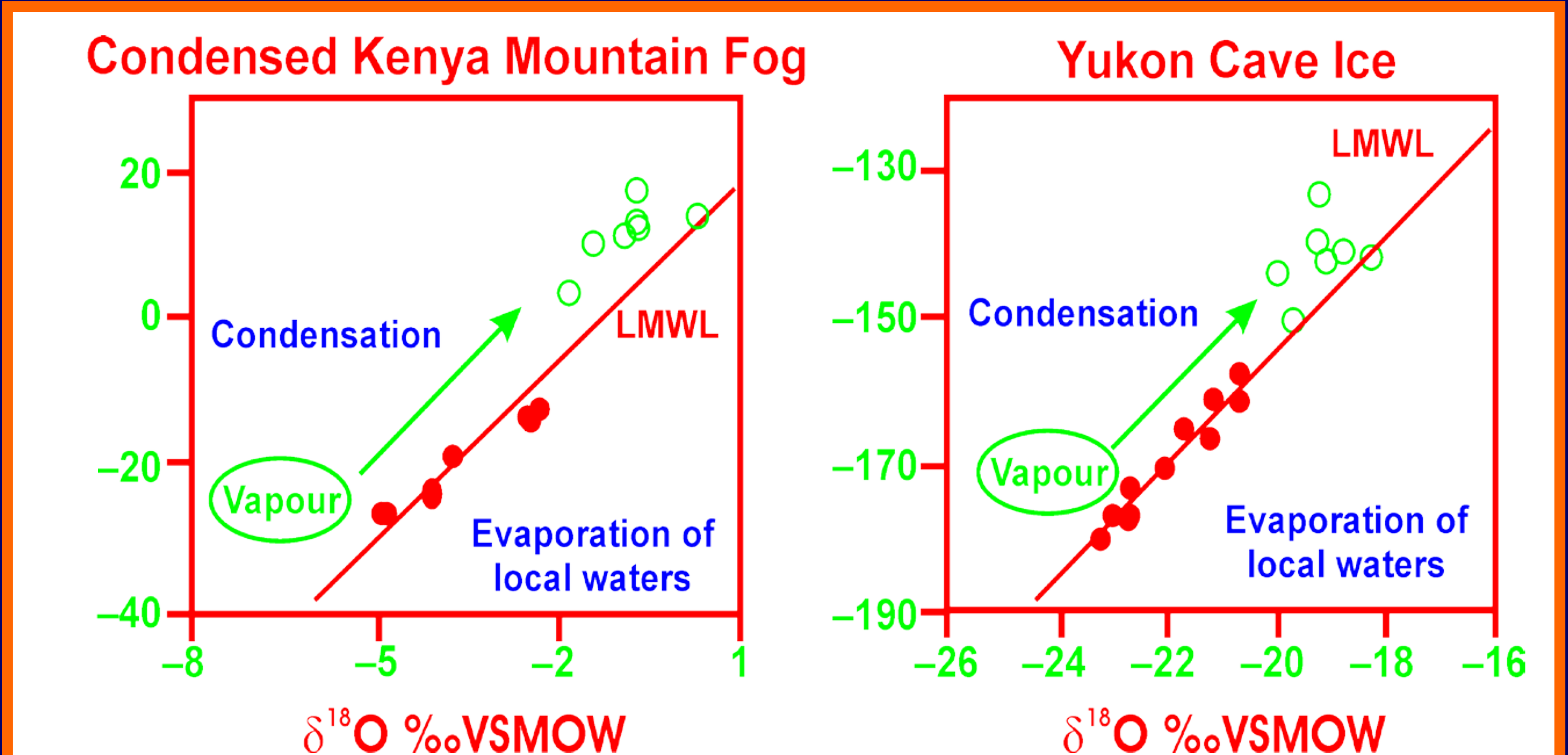
Lower Rh → lower slope along which evaporating water will evolve isotopically

Vapor from Mediterranean



Why does EMWL has same slope as GMWL but much higher D-intercept?

Recycling of vapor



Ingraham and Matthews, 1988

Why do mountain fog and cave ice samples fall above LMWL?

Isotope Effects

Isotope Effects - 1

1. Temperature Effect (δ-T Relationship)
   - Decreasing δ values with decreasing T
2. Latitude Effect
   - Decreasing δ values with increasing Latitude
3. Continental Effect
   - Decreasing δ values with increasing inland distance
4. Amount Effect
   - Increasing δ values with decreasing amount of rain
5. Altitude Effect
   - Decreasing δ values with increasing altitude
6. Seasonal Effect
   - Greater seasonal extremes in T generate strong seasonal variations

Isotope Effects - 2

δ-T Relationship

Dansgaard (1964) established a linear relationship between surface air temperatures and δ values for mean annual precipitation on a global basis.

$$\delta^{18}O = 0.695\ T_{annual} - 13.6‰\ SMOW$$

$$\delta^{2}H = 5.6\ T_{annual} - 100‰\ SMOW$$

Based on monthly average temperatures the global relationship is:

$$\delta^{18}O = (0.338 \pm 0.028)\ T_{monthly} - 11.99\ ‰\ SMOW$$

On average, a 1‰ decrease in average annual $\delta^{18}O$ corresponds to a decrease of about 1.1 to 1.7 ºC in the average annual temperature.

Departure from global relationship occurs at the regional to local scale due to physiographic variation.

Isotope Effects - 3

Latitude Effect

Basis:

1. From the δ-T relationship, polar regions should have lower δ values.
2. Polar regions are situated at the end of Rayleigh rainout process therefore, $\delta^{18}O$ gradient is expected to be steeper.

- -0.6‰ for $\delta^{18}O$ per º latitude for continental stations of the North America
- -2‰ for $\delta^{18}O$ per º latitude for the colder Antarctic Stations.
- Very low gradients in the low latitudes where over 60% of atmospheric vapour originates

Isotope Effects - 4

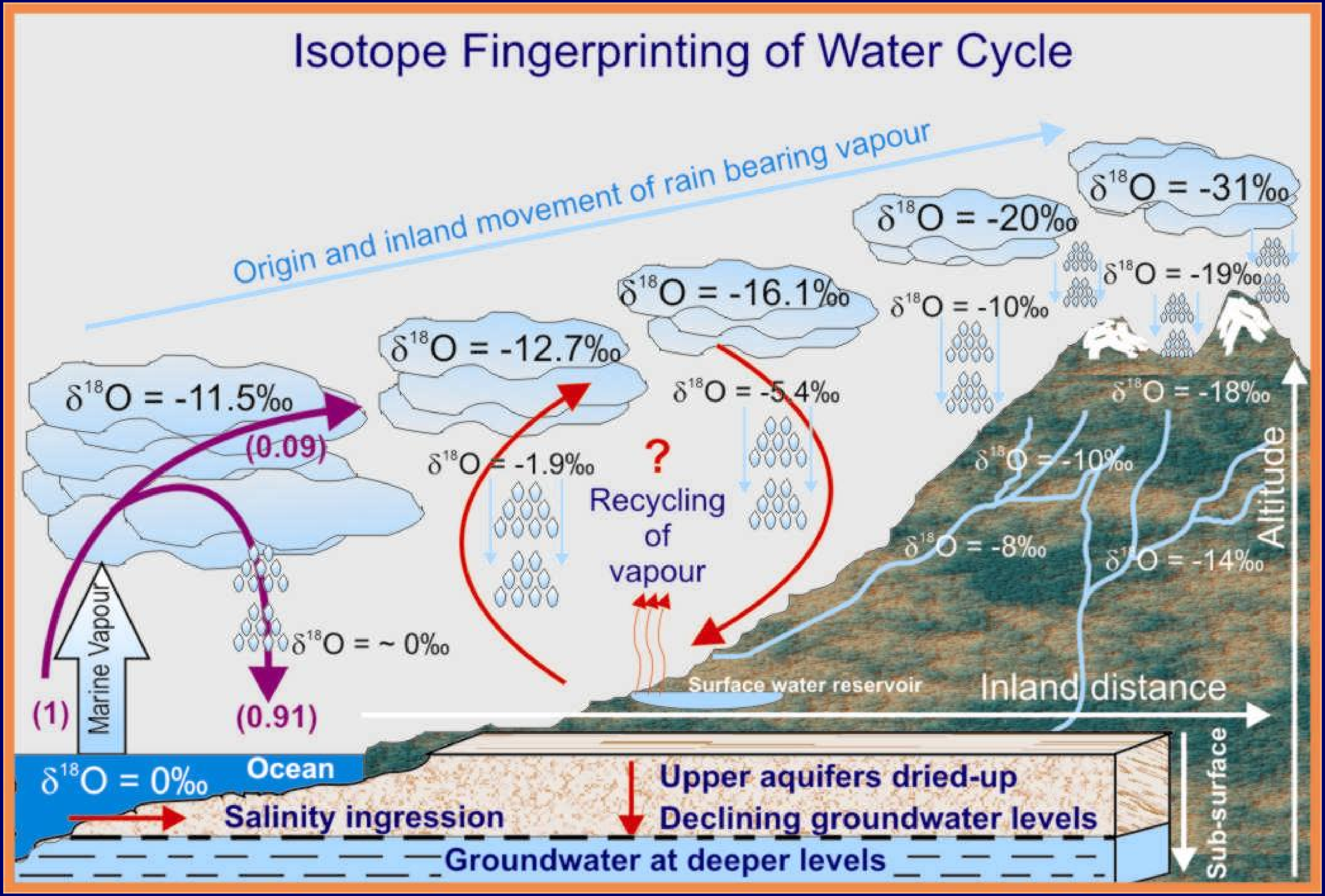
Altitude Effect (Alpine or Elevation effect)

Basis

1. Orographic precipitation occurs as a vapour mass rises over the landscape and cools adiabatically (by expansion) causing rainout.
2. At higher altitudes where the average temperatures are lower, precipitation will be isotopically depleted.

$\delta^{18}O$: -0.15 to -0.5 ‰ per 100 m rise in elevation

δD: -1 to -4 ‰ per 100 m rise in elevation



Vapor source region, advancement of vapor front, recycled component, groundwater and snow melt contribution to river etc. can be studied

Interpretative Significance

Interpretative Significance

$\delta^{18}O$-δD Regression line slope

1. If the slope of $\delta^{18}O$-δD regression line for a set of samples is less than that of GMWL it is an indication that the water under consideration has undergone certain degree of evaporation.
2. The intersection point of LMWL and GMWL is indicative of the average isotopic composition of precipitation at that location.
3. Intersection point of LMWL and $\delta^{18}O$-δD regression line for groundwater is indicative of the average isotopic composition of the surface water from which the groundwater is recharged.
4. If the $\delta^{18}O$-δD regression line slope for groundwater is less than that for LMWL, considerable evaporation before recharge can be suggested.

$\delta^{18}O$-δD Regression line Intercept

1. If the slope of LMWL is ~8 and intercept is >10‰ it is an indication that precipitation is derived from vapour which is produced by kinetic evaporation under considerably lower relative humidity.

Interpretative Significance

$\delta^{18}O$ and δD values

1. Depending on the geographical location of the station, lower (isotopically depleted) values of both $\delta^{18}O$ and δD could be associated with: either higher altitude, greater distance from vapour origin region, considerable rainout or rainfall during NE winter precipitation.
2. Higher (isotopically enriched) values of both $\delta^{18}O$ and δD could be associated with evaporation from falling raindrops in small rain events, proximity to vapour source region,

d-excess values

1. Lower than average *d*-excess of a particular rainwater sample could be due to evaporation from falling raindrops or it could as well signify considerable rainout from original marine vapour parcel.
2. Higher (than average) *d*-excess in a particular rainwater sample signifies either formation of marine vapour parcel under lower (than average) relative humidity (for e.g. from Mediterranean Sea) or contribution of recycled vapour from continental areas for that particular event.

It seems as if we know about the nature only little more than they know ! !
Scientific quest must continue for our safe and peaceful existence

Thanks for your patience.

-Deshpande

N* = Number of heavy isotopes and N = Number of light isotopes at time t

$$R_v = \frac{N^*}{N} \quad \text{and} \quad R_l = \frac{dN^*}{dN}$$

$$\alpha = \frac{R_l}{R_v} > 1$$

$$\alpha . R_v = R_l$$

$$dR_v = \frac{1}{N}.dN^* - N^*.\frac{dN}{N^2}$$

$$dR_v = \frac{dN}{N}.\frac{dN^*}{dN} - \frac{N^*}{N}.\frac{dN}{N}$$

$$dR_v = \frac{dN}{N}.R_l - R_v.\frac{dN}{N}$$

$$dR_v = \frac{dN}{N}.\alpha R_v - R_v.\frac{dN}{N}$$

$$dR_v = \frac{dN}{N}.R_v(\alpha - 1)$$

$$\frac{dR_v}{R_v} = \frac{dN}{N}.(\alpha - 1)$$

$$\ln R_v = (\alpha - 1)\ln N + K$$

Initializing at t =0, $N = N_0$ and $R_v = R_{v0}$

$$\ln R_{v0} = (\alpha - 1)\ln N_0 + K$$

$$K = \ln R_{v0} - (\alpha - 1)\ln N_0$$

$$\ln R_v = (\alpha - 1)\ln N + \ln R_{v0} - (\alpha - 1)\ln N_0$$

$$\ln R_v - \ln R_{v0} = (\alpha - 1)\ln N - (\alpha - 1)\ln N_0$$

$$\ln\left(\frac{R_v}{R_{v0}}\right) = (\alpha - 1)\ln\left(\frac{N}{N_0}\right)$$

$$\left(\frac{R_v}{R_{v0}}\right) = \left(\frac{N}{N_0}\right)^{(\alpha - 1)}$$

$$\left(\frac{R_v}{R_{v0}}\right) = f^{(\alpha - 1)}$$

$$\left(\frac{R_v}{R_{v0}}\right) = f^{(\alpha - 1)}$$

$$\left(\frac{\left(10^{-3}\delta_v + 1\right)R_{std}}{\left(10^{-3}\delta_{v0} + 1\right)R_{std}}\right) = f^{(\alpha - 1)}$$

$$\ln\left(10^{-3}\delta_v + 1\right) - \ln\left(10^{-3}\delta_{v0} + 1\right) = (\alpha - 1).\ln f$$

If x<<1; ln(x+1) ≈ x

$$10^{-3}\delta_v - 10^{-3}\delta_{v0} = (\alpha - 1).\ln f$$

$$10^{-3}\delta_v = 10^{-3}\delta_{v0} + (\alpha - 1).\ln f$$

$$\delta_v = \delta_{v0} + (\alpha - 1)10^3.\ln f$$

$$\delta_v = \delta_{v0} + \varepsilon.\ln f$$

$$\delta_l = \delta_v + \varepsilon_{(l-v)}$$

$$\delta = \left(\frac{R_{Sam}}{R_{Std}} - 1\right) x\, 10^3$$

$$(10^{-3}\delta + 1)R_{Std} = R_{Sam}$$

$$\varepsilon = (\alpha - 1).10^3$$

Go to Rayleigh Distillation

$$\delta D = \delta D_0 + \varepsilon_D . \ln f$$

$$\delta^{18}O = \delta^{18}O_0 + \varepsilon_{18} . \ln f$$

$$\ln f = \frac{\delta D - \delta D_0}{\varepsilon_D}$$

$$\delta^{18}O = \delta^{18}O_0 + \varepsilon_{18} \cdot \left(\frac{\delta D - \delta D_0}{\varepsilon_D} \right)$$

$$\left(\delta^{18}O - \delta^{18}O_0 \right) . \left(\frac{\varepsilon_D}{\varepsilon_{18}} \right) = \delta D - \delta D_0$$

$$\delta D = \delta^{18}O . \left(\frac{\varepsilon_D}{\varepsilon_{18}} \right) + \left[\delta D_0 - \delta^{18}O_0 . \left(\frac{\varepsilon_D}{\varepsilon_{18}} \right) \right]$$

ε_D at 25 °C	78.74	ε_{18} at 25 °C	9.35
$\Delta\varepsilon_D$ at 85% Rh	1.88	$\Delta\varepsilon_{18}$ at 85% Rh	2.13
$\Delta\varepsilon_D + \varepsilon_D$	80.62	$\Delta\varepsilon_{18} + \varepsilon_{18}$	11.48
δD of Ocean water	0	$\delta^{18}O$ of Ocean water	0
δD_0 of vapor in open air above Ocean	–80.62	$\delta^{18}O_0$ of vapor in open air above Ocean	-11.48

$$\text{Intercept} = \delta D_0 - \delta^{18}O_0 \cdot \left(\frac{\varepsilon_D}{\varepsilon_{18}}\right)$$

Considering slope = $\varepsilon_D / \varepsilon_{18} \approx 8$

$$\text{Intercept} = -80.62 - (-11.48) \times (8) = 11.2$$

Return to significance of slope and intercept