Isotope Hydrology

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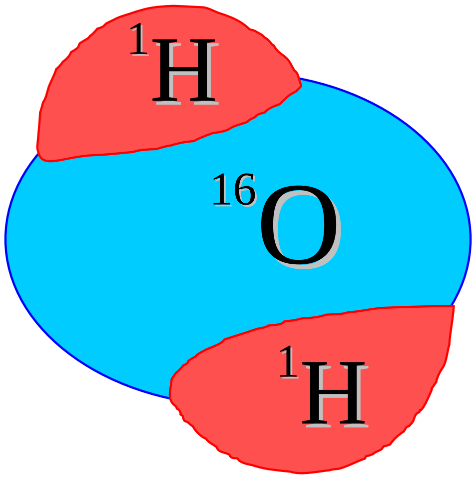
Stable isotopes in water

Element	Isotopes	Abundance (%)
Hydrogen	^{1}H	99.985
	^{2}H	0.015
Carbon	^{12}C	98.89
	^{13}C	1.11
Nitrogen	^{14}N	99.63
	^{15}N	0.37
Oxygen	^{16}O	99.759
	^{17}O	0.037
	^{18}O	0.204

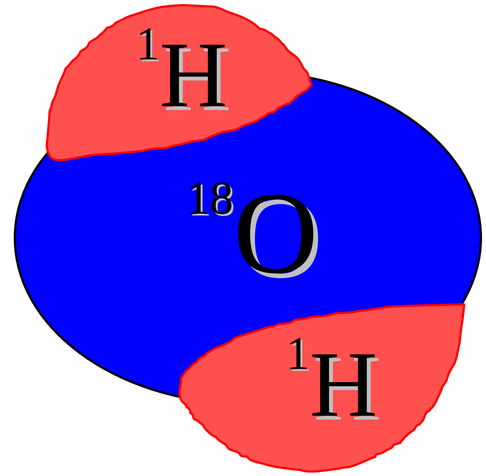
The mass ratio of isotopes in water is large (2:1; 18:16) and the water molecule is light ($H_2O = 18$; $CO_2 = 44$)

➔ Large fractionation effects can be expected

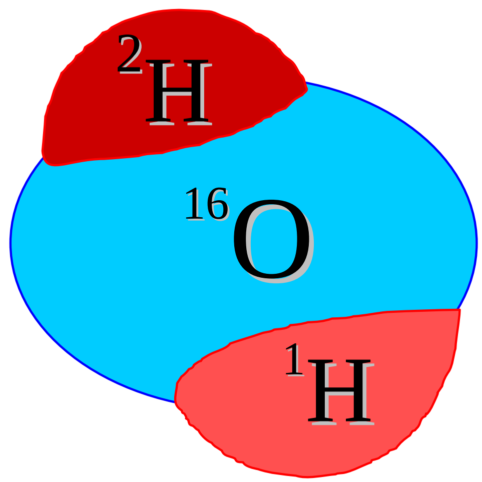
Stable isotopes in water



99.8 %

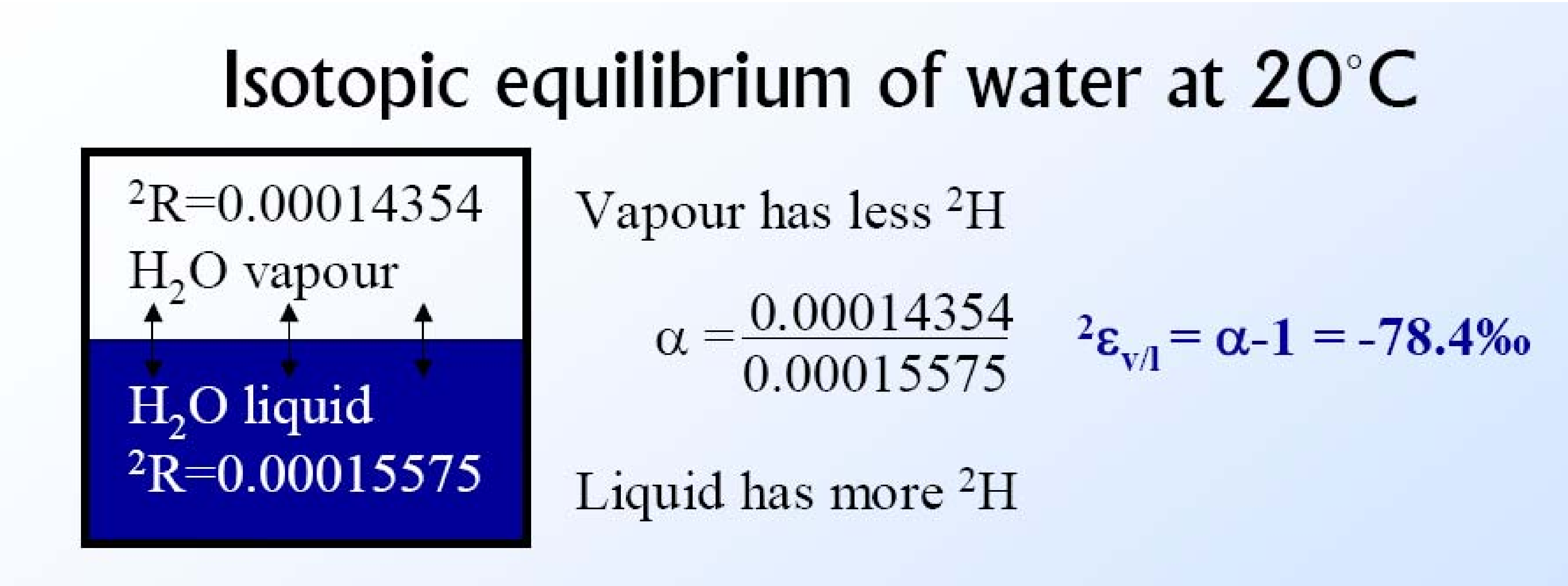


0.2 %



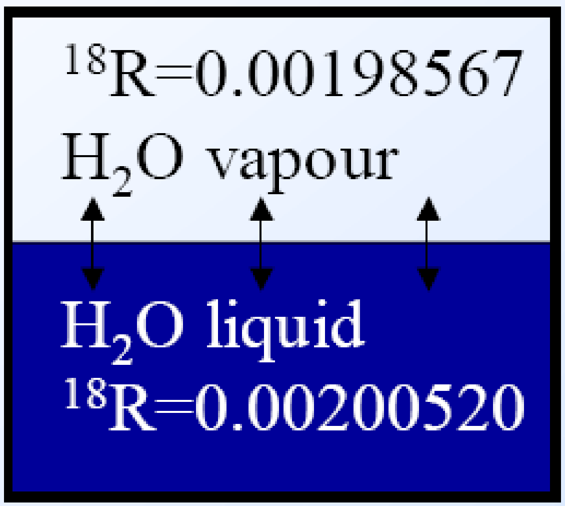
0.015 %

Equilibrium IE



Saturation vapor pressure of "heavy" water is less than saturation vapor pressure of "light" water

Equilibrium IE



Vapour has less ^{18}O

$$\alpha = \frac{0.00198567}{0.00200520}$$

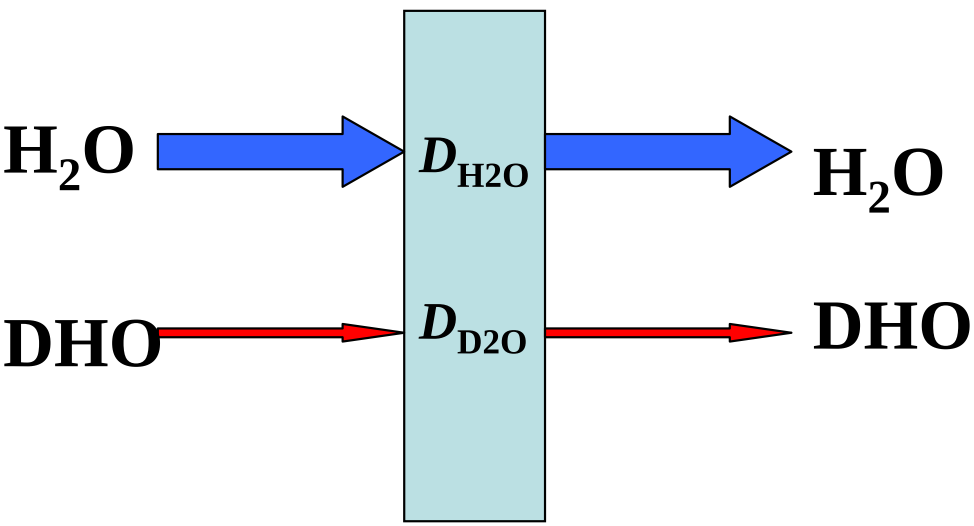
$$^{18}\varepsilon_{v/l} = \alpha - 1 = -9.74‰$$

Liquid has more ^{18}O

At colder temperatures $\varepsilon_{v/l}$ becomes more negative

Kinetic isotope fractionation

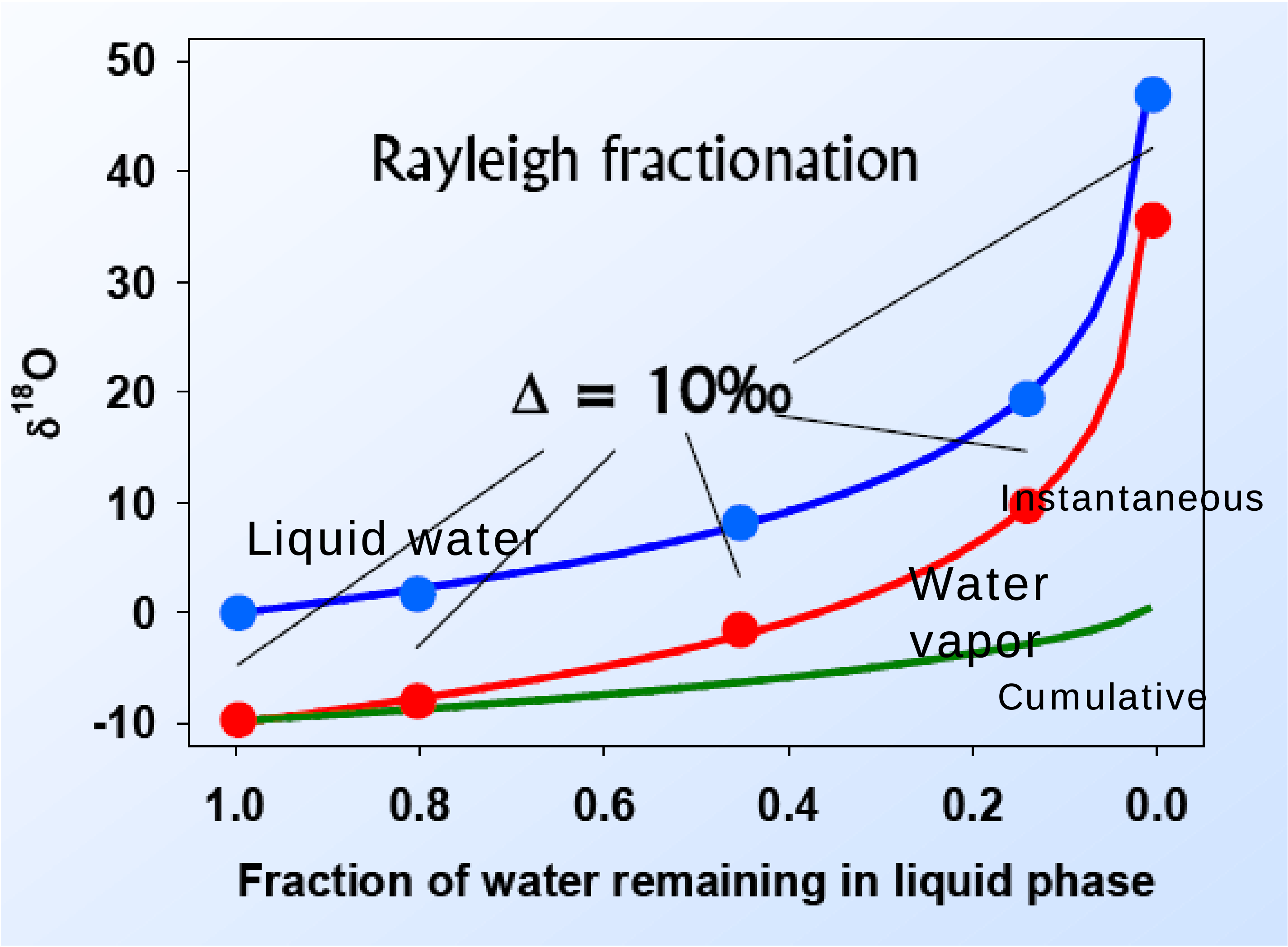
Diffusion is sensitive to molecular mass, isotopically light water diffuses faster than isotopically heavy water; related to evaporation when air humidity is less than 100% or wind



Kinetic fractionation factor

$$\varepsilon_k = \frac{D_{H_2O}}{D_{DHO}} - 1 = 28‰$$

Closed system fractionation

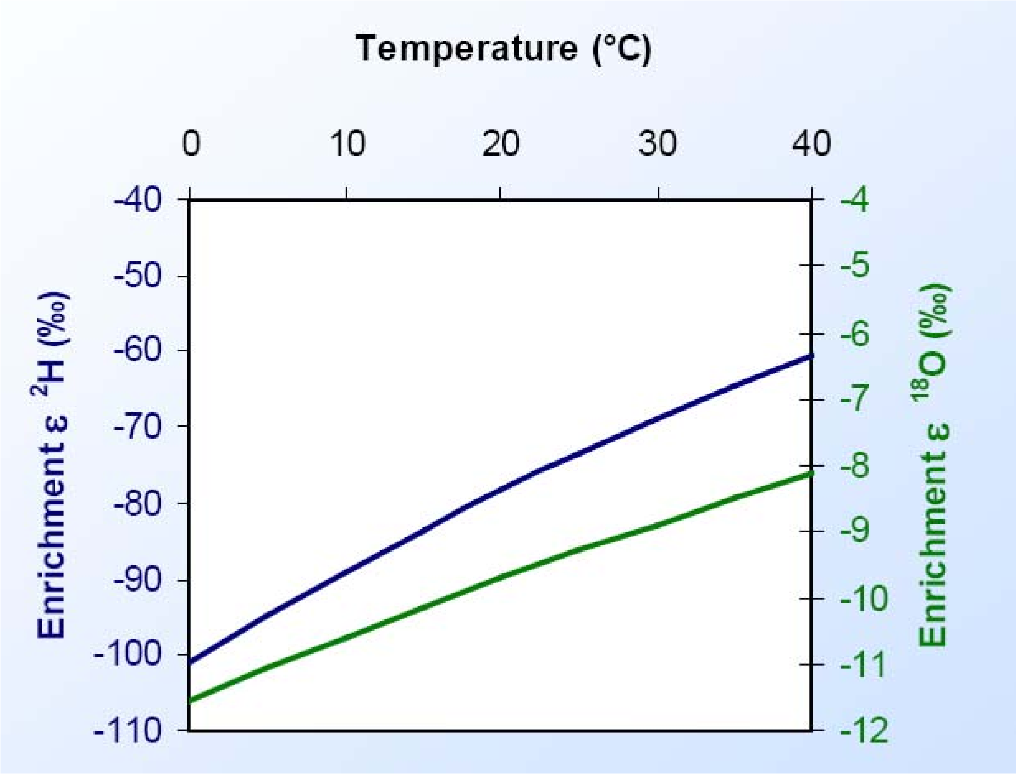


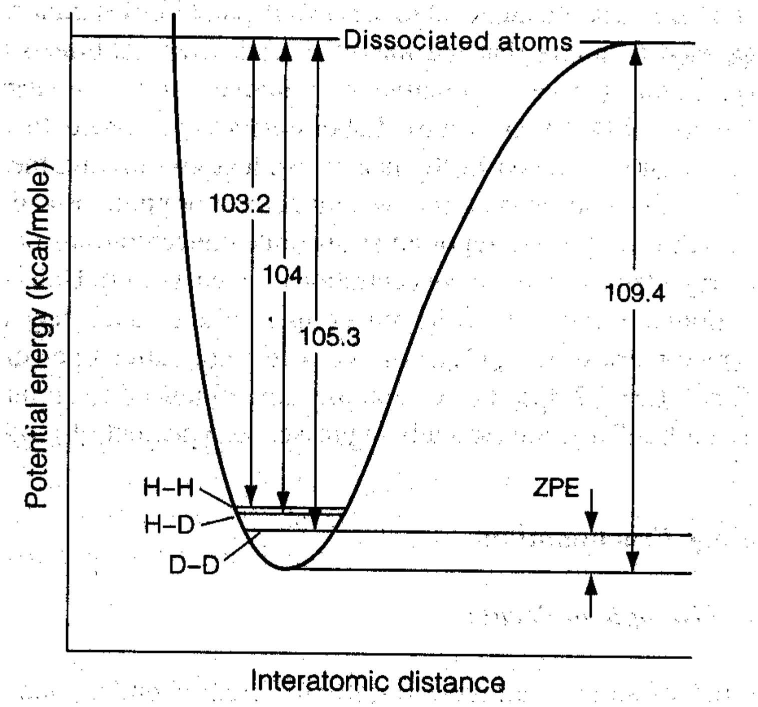
Controls of rainwater $\delta^{18}O$

1. Seasonal effect
2. Continental effect
3. Altitudinal effect
4. Latitudinal effect
5. Amount effect

Controlling factors behind these effects are (i) **temperature** controlling α_{Equ}, and (ii) the **fraction F_v of original water vapor remaining** in the air parcel undergoing precipitation i.e. rainout effect.

Temp.-dependence of Equil. IE



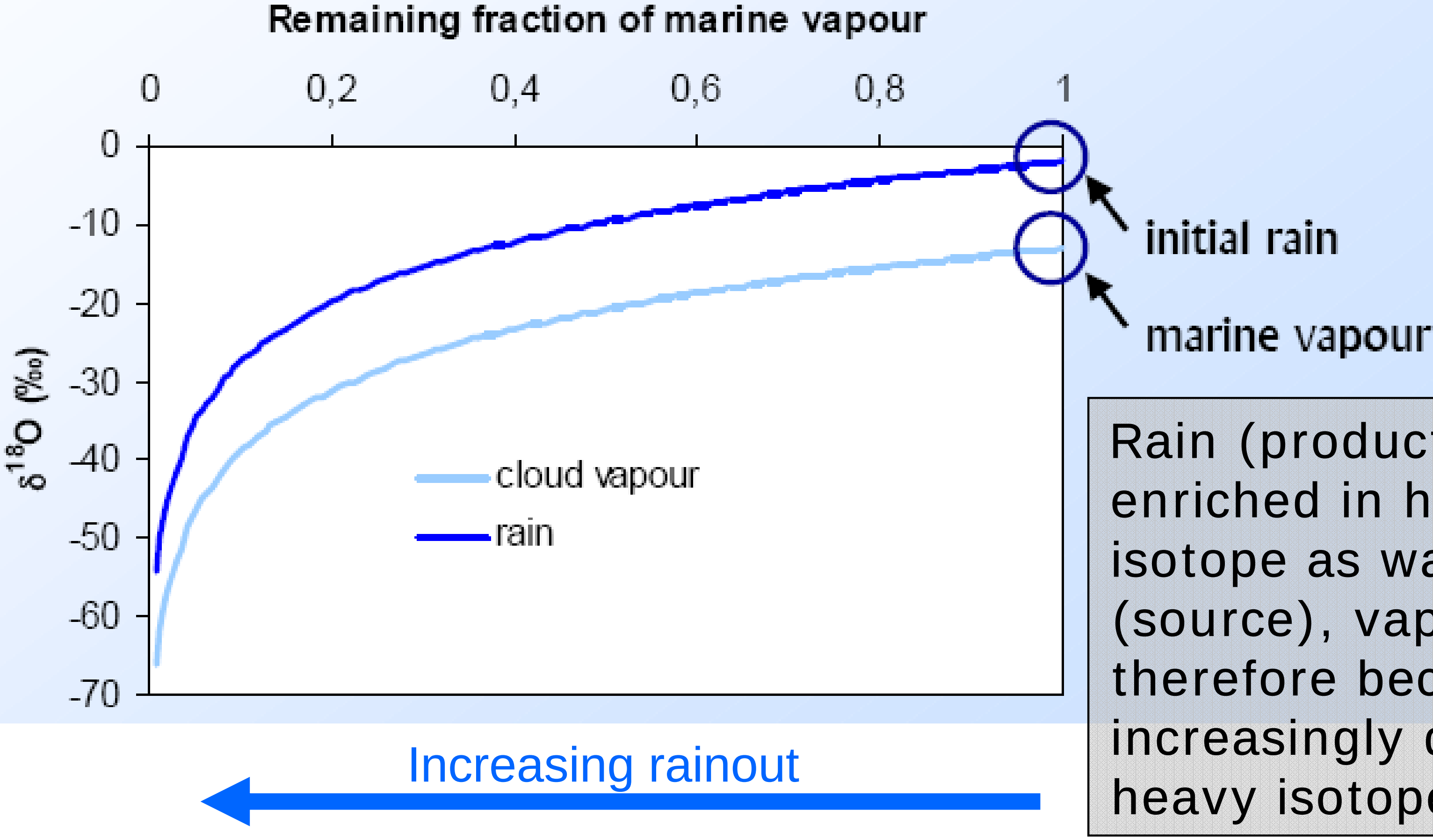


Isotopically heavier molecules are more strongly bonded and have lower zero point energies (ZPE, potential energies) than lighter molecules, due to lower vibrational energy at higher masses; ZPE differences of isotopically different molecules decrease at higher temperatures i.e. α_{EQU} decrease

Rainout processes

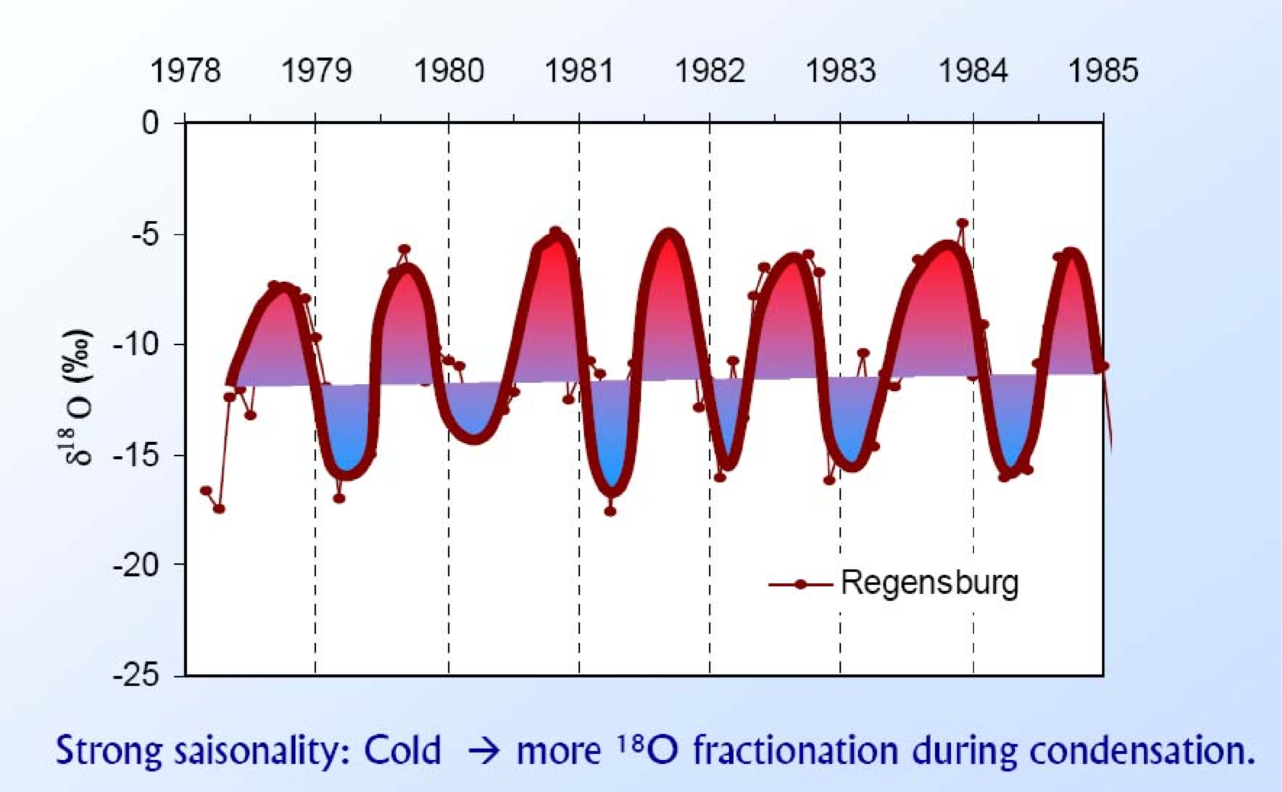
Rayleigh fractionation occurs, when the system is closed regarding the source (= the source is limited)

During rain, the vapour of a cloud is a limited source



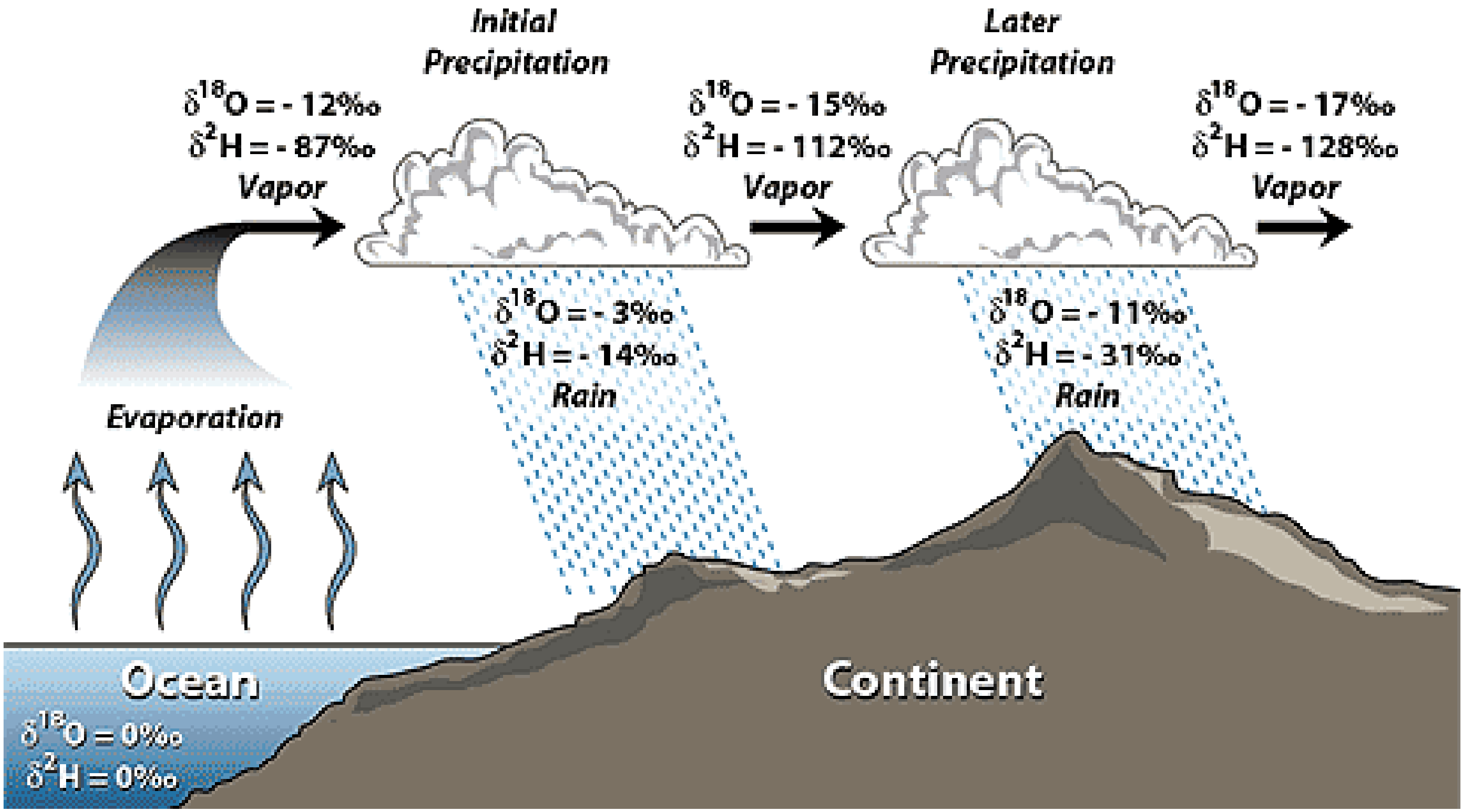
Rain (product) is more enriched in heavy isotope as water vapor (source), vapor therefore becomes increasingly depleted in heavy isotopes

Seasonal effect



Dependent upon the **temperature** of condensation at which rainfall forms, low T/winter – high α_{EQU}, high T/summer – low α_{EQU}. Additonally: *source regions* may differ, *evaporation* during rainfall may enrich rain during summer, and in summer more *recycled water* condensed at higher higher T

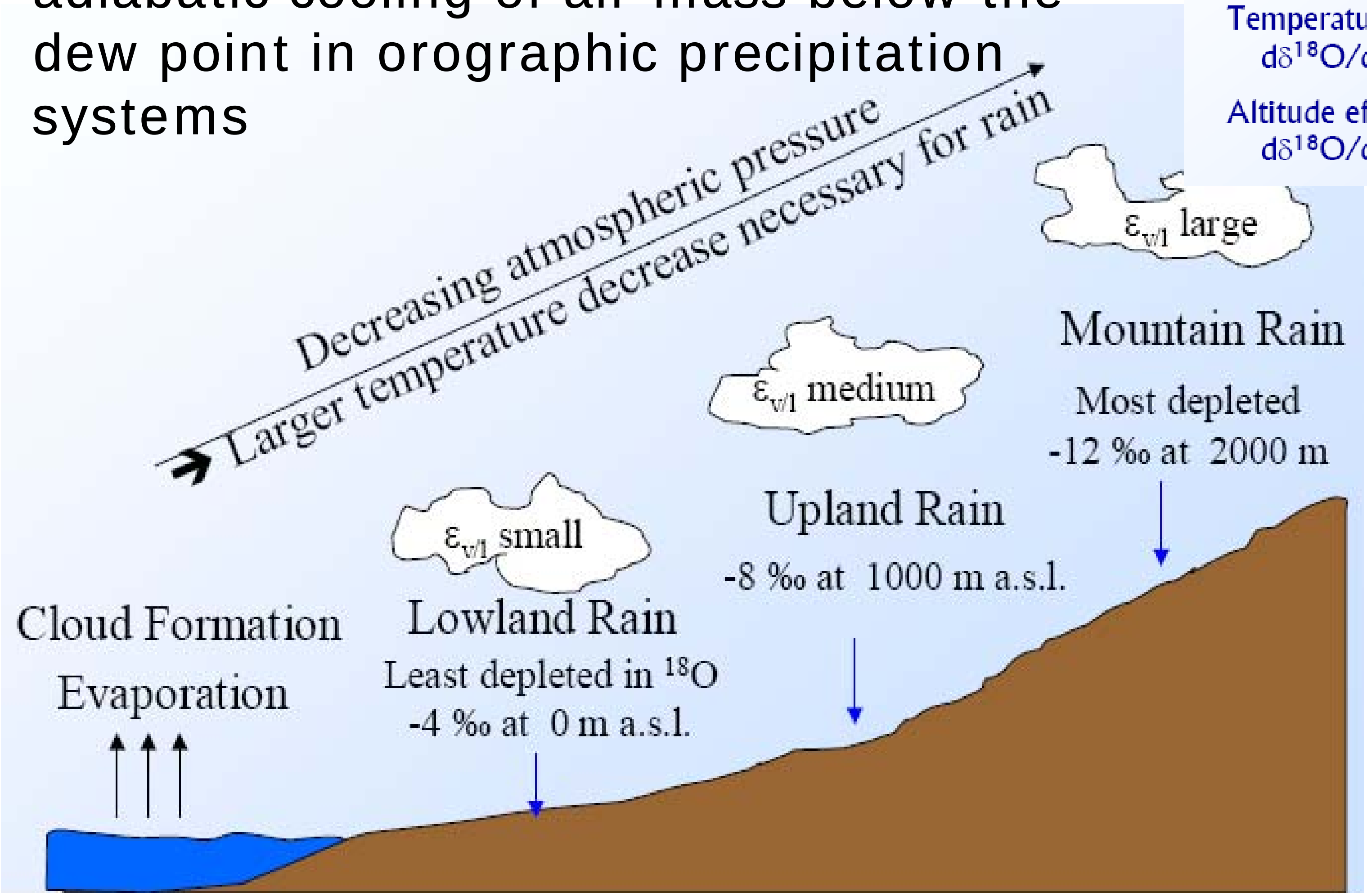
Continental effect



Meteoric water becomes more depleted farther from the source (ocean) of water vapor – rainout (enriched) depletes vapor resource, consecutive rainevents become more depleted. BUT: recycling of evapotranspired vapor e.g. Amazon

Altitudinal effect

Increased rain at higher elevations due to adiabatic cooling of air mass below the dew point in orographic precipitation systems



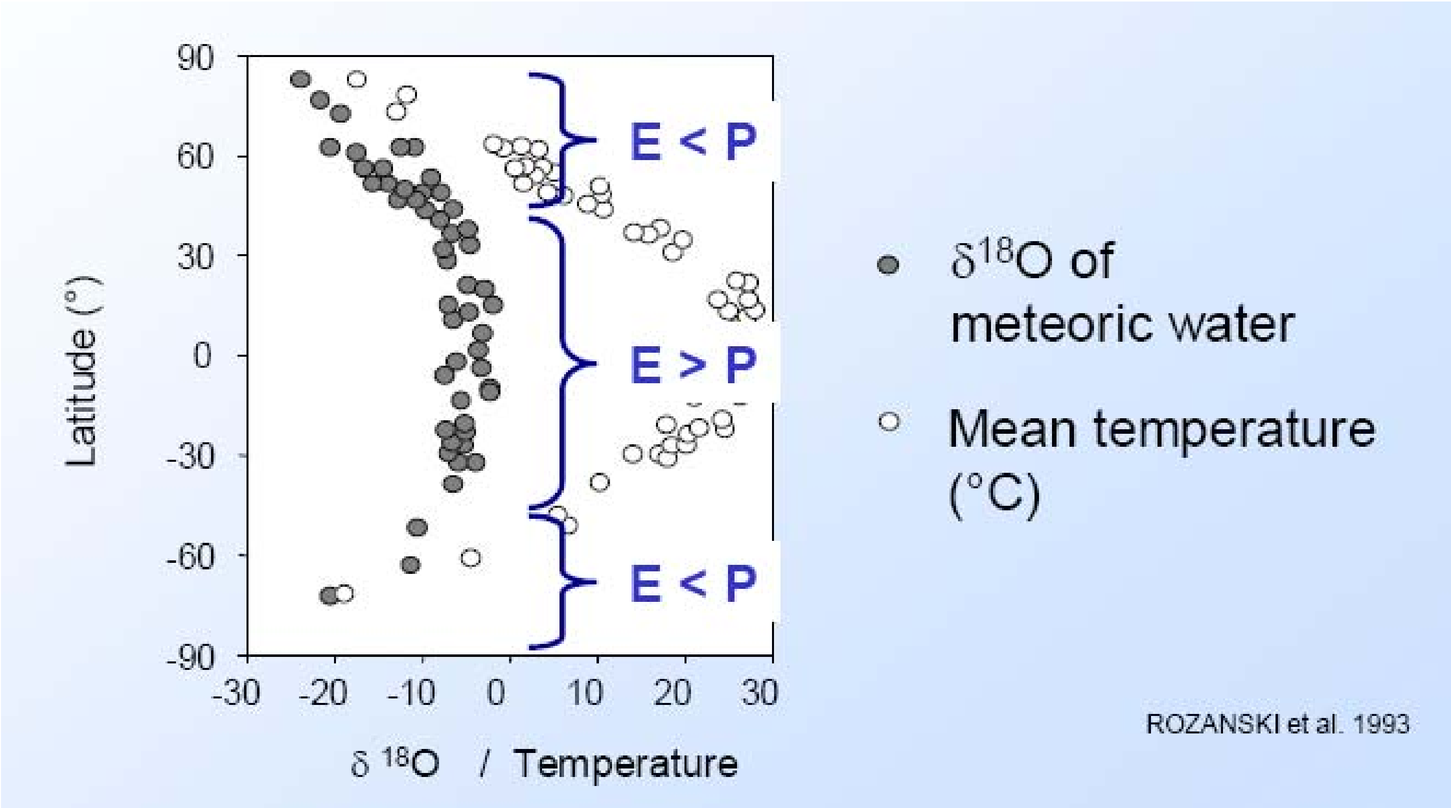
Simple Estimate of Slope:

Moist adiabatic lapse rate:
$dT/dz \sim -0.5$ °C/100 m

Temperature effect:
$d\delta^{18}O/dT \sim 0.6$ ‰/°C

Altitude effect:
$d\delta^{18}O/dz \sim -0.3$ ‰/100 m

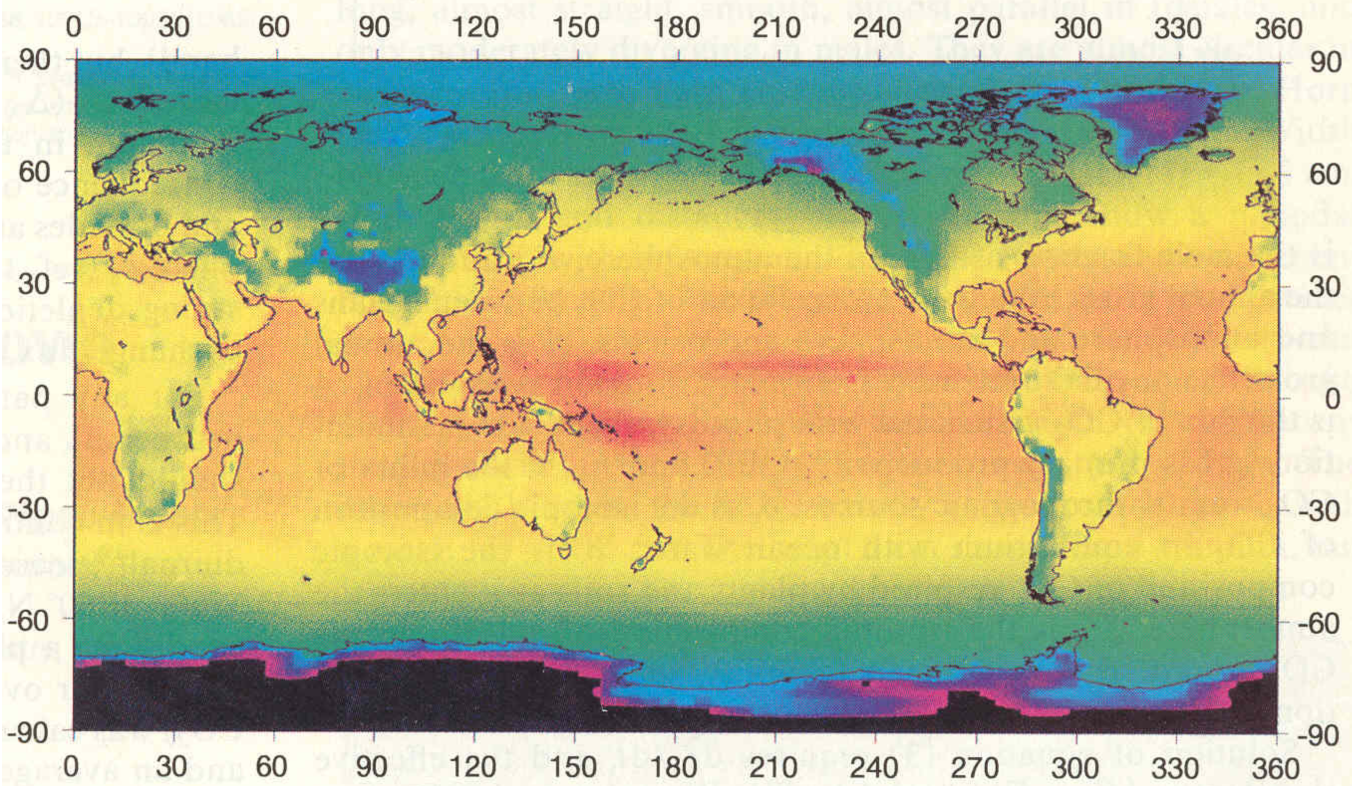
Latitudinal effect



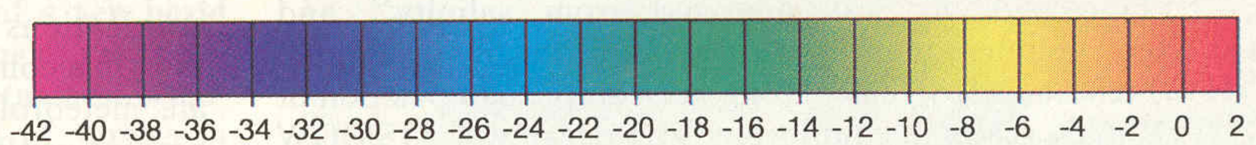
Due to increased rainout and decreased temperatures of condensation at higher latitudes, causing higher α_{EQU}.
T effect: δD_{prec}=5.6 ‰ /°C, $\delta^{18}O_{prec}$=0.6 ‰ /°C

Global extrapolation of latitudinal, altitudinal and continental effects

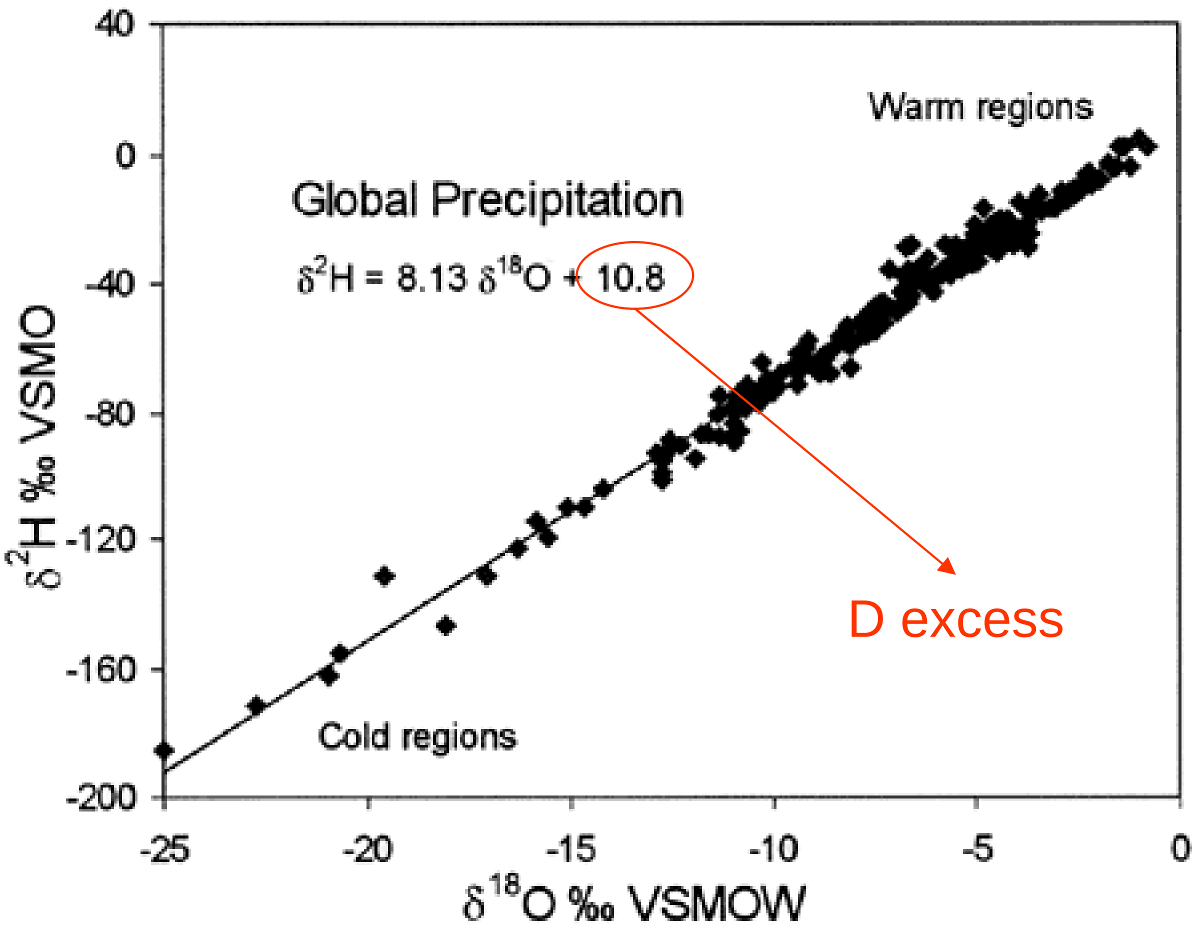
^{18}O signature of precipitation (annual volume weighted)



GNIP - global network of isotopes in precipitation



Global meteoric water line

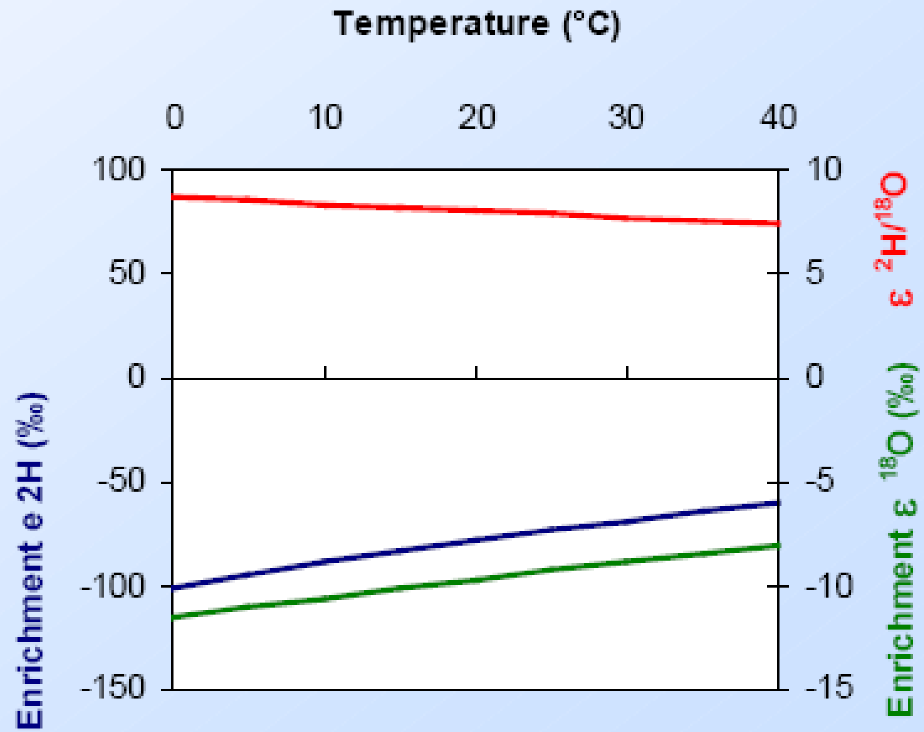


Co-fractionation of D and ^{18}O during evaporation and condensation processes

SMOW - standard mean ocean water - is (i) the reference material against which we measure other waters and (ii) the source of water vapor

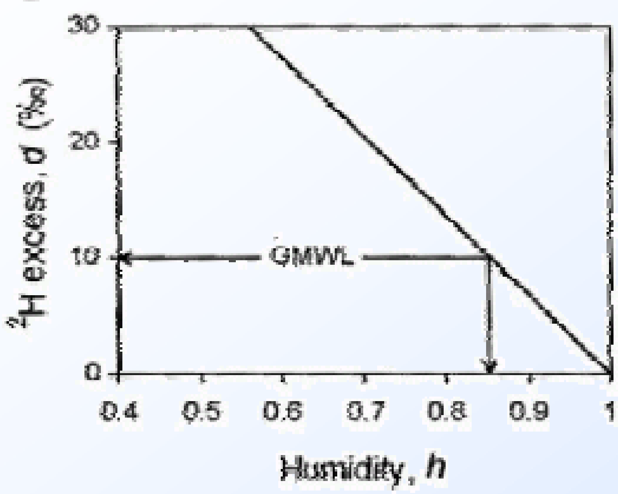
Global meteoric water line

- The source water is the ocean, which has an average equal to 0 ‰ (per definition of SMOW)
- The marine water vapor is lighter than SMOW.
- Slope is determined by the ratio of the equilibrium fractionations of ^{18}O and ^{2}H for the rain condensation process.



D excess

The Craig-Gordon Model of Evaporation



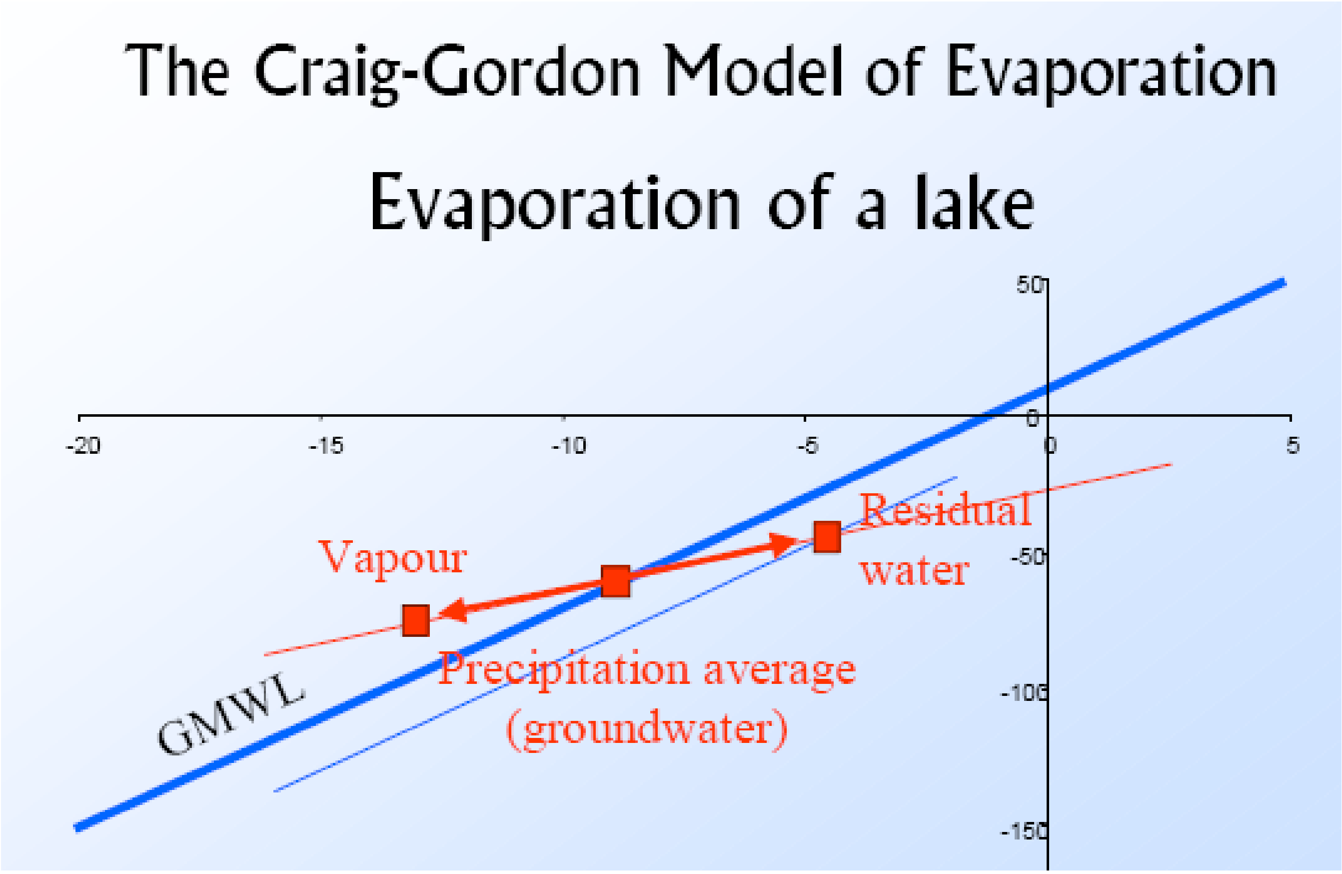
As compared to ^{18}O, ^2H is increasingly enriched by diffusion with decreasing humidity

Explanation of the GMWL

- Slope of ~ 8 due to ~ equilibrium conditions during **condensation** of precipitation in clouds
- Deuterium excess of ~10 ‰ due to a mean humidity of ~85 % during **evaporation** from the ocean

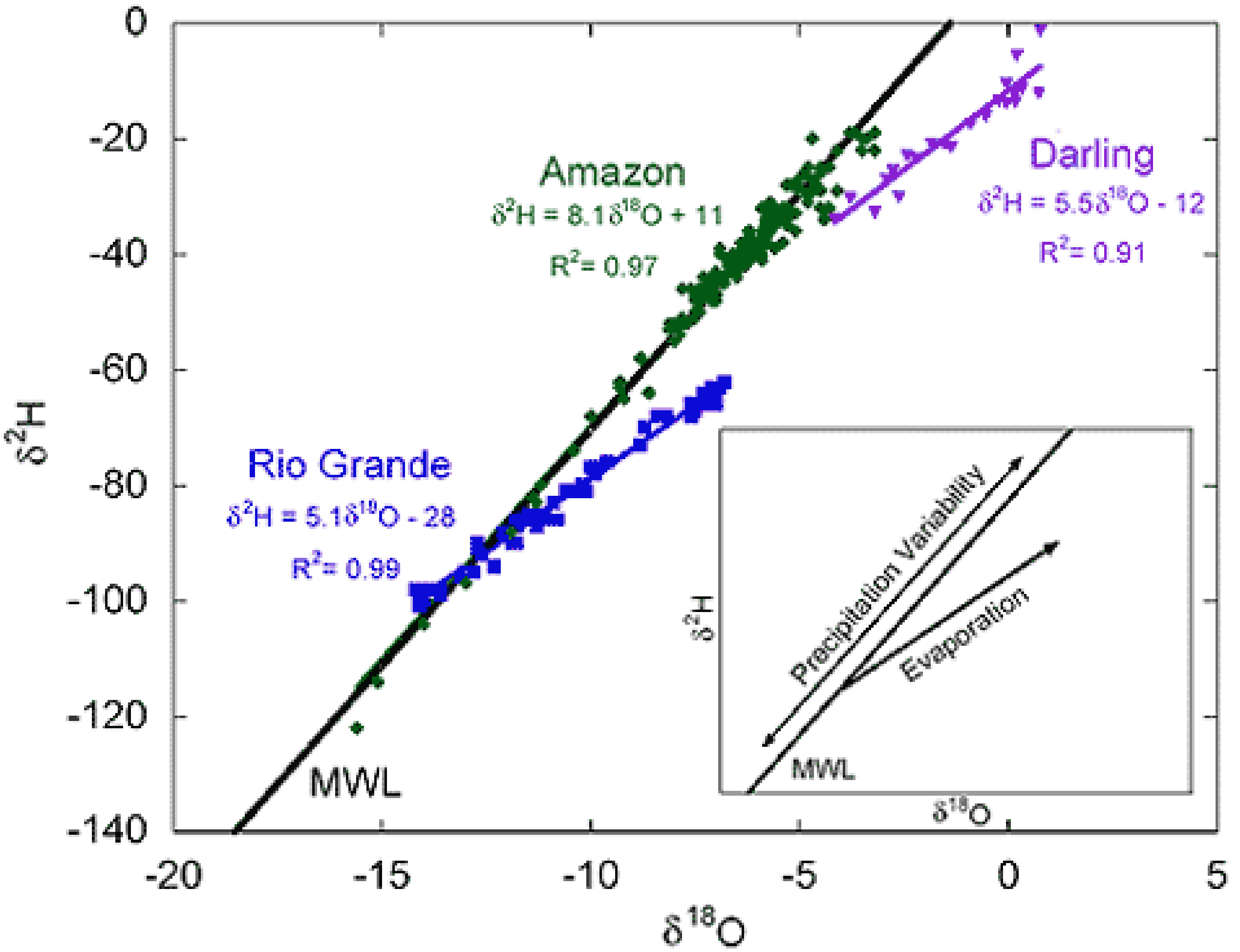
→ D excess is an indicator of the moisture conditions of the source region

Evaporation



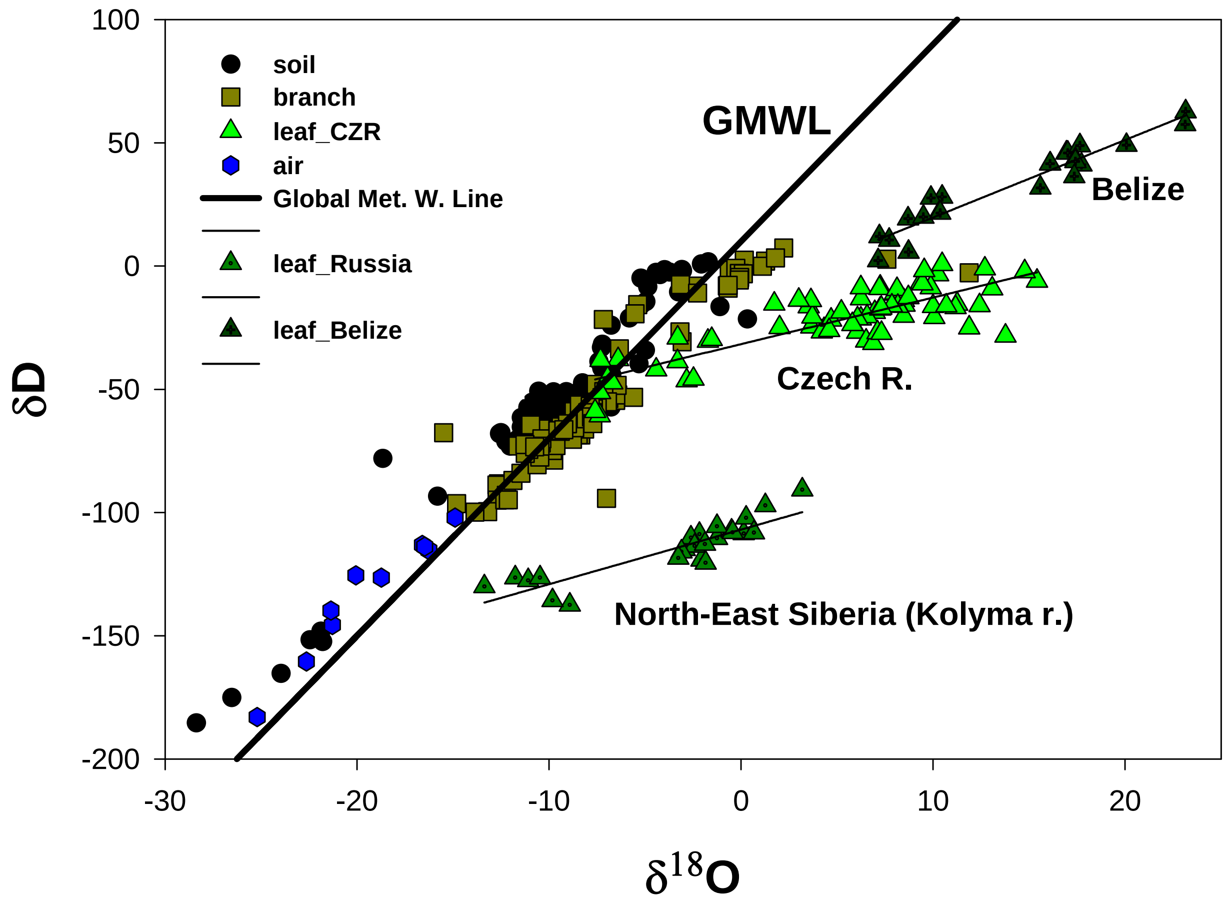
Kinetic isotope fractionation during evaporation is similar for both, δD (25.1 ‰) and $\delta^{18}O$ (28.5 ‰) while equilibrium isotope fractionation differs by a factor of ~8 ‰

Surface waters

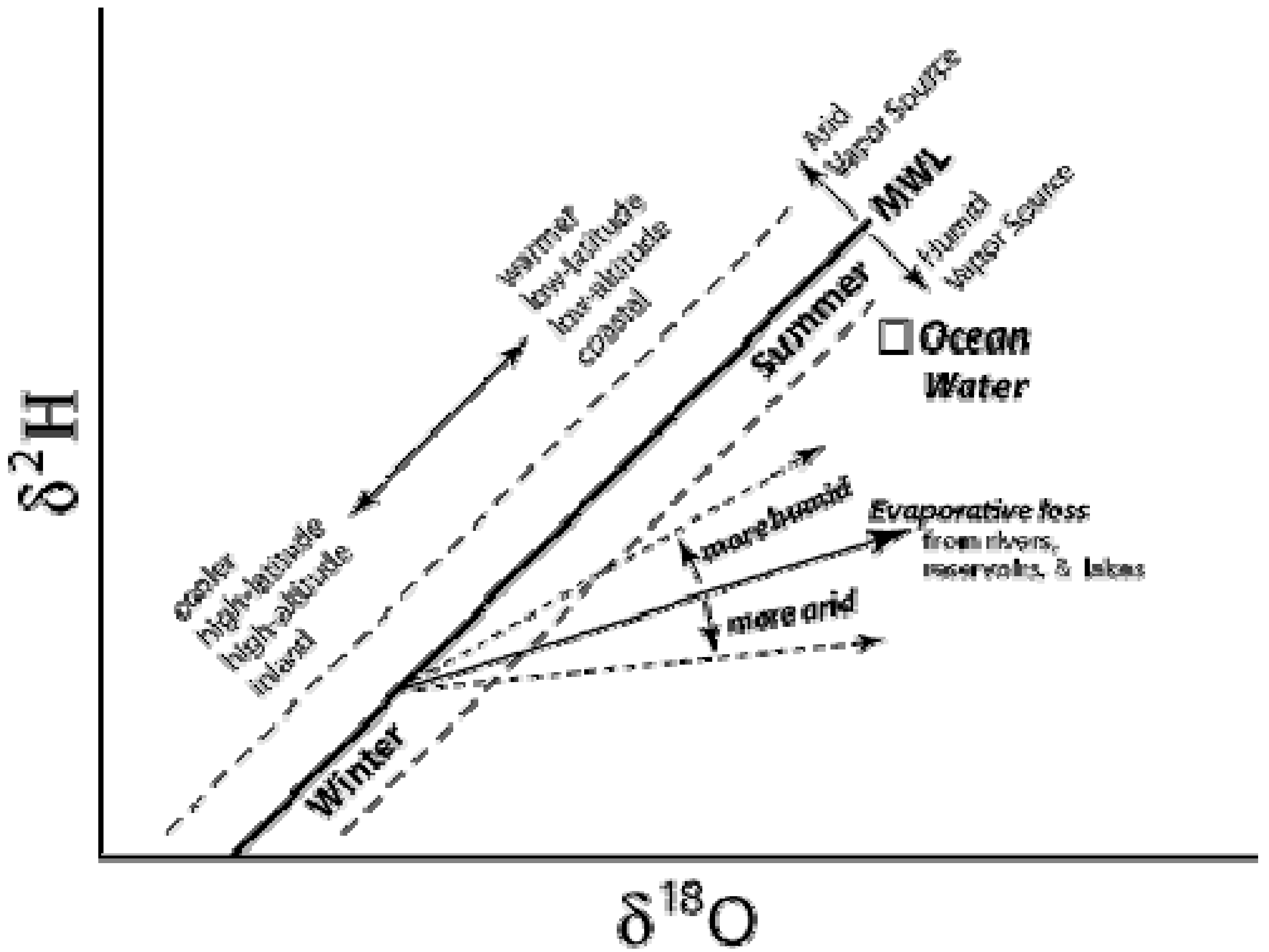


Relative humidity controls the deviation of
The evaporation line from GMWL

Leaf water enrichment



Local meteoric water lines



^{18}O as tracer for

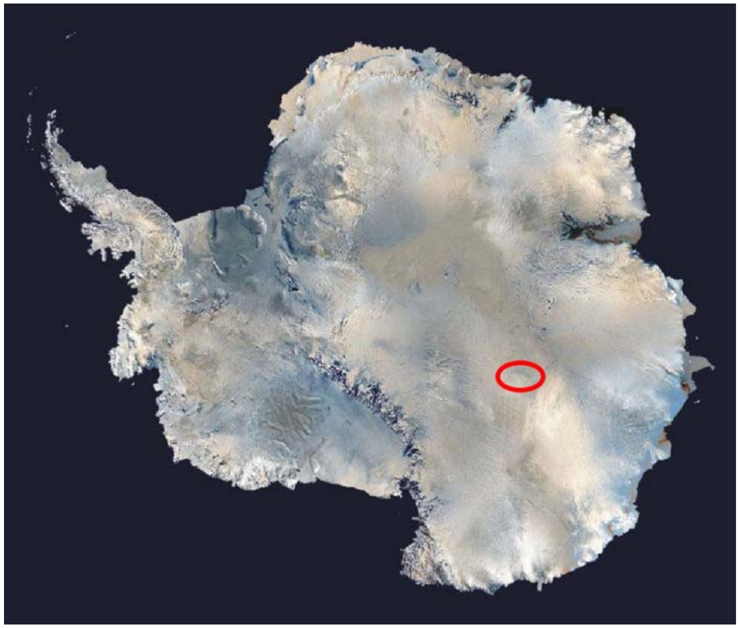
1. Climate (ice cores, wood cores)

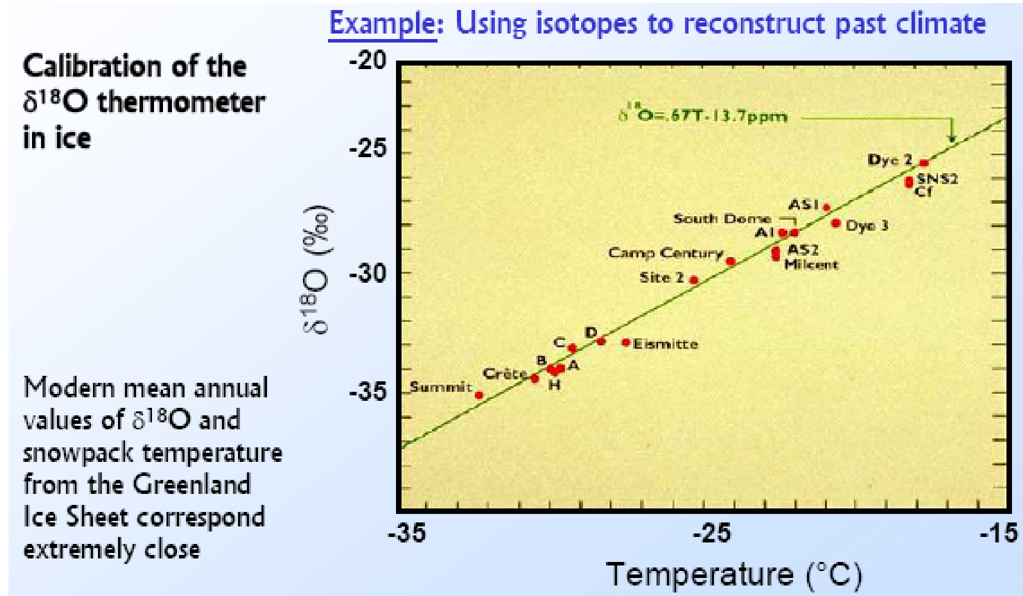
2. Hydrological processes

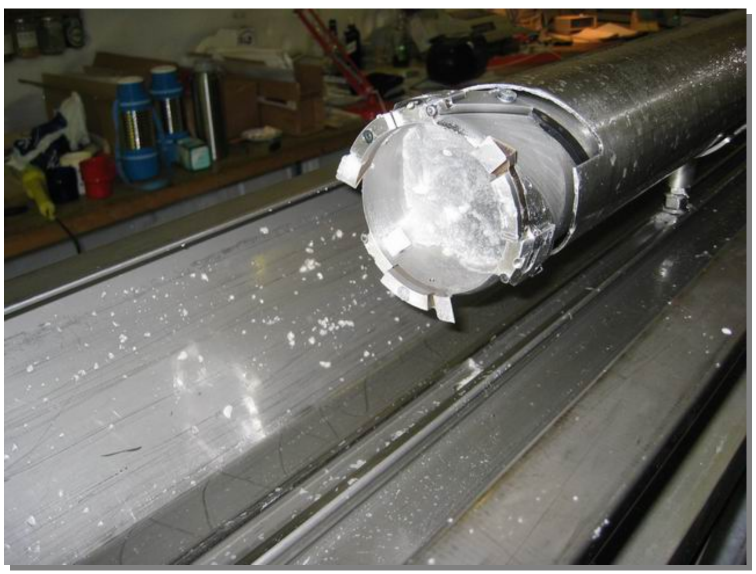
3. Plant water sources

4. Animal origin

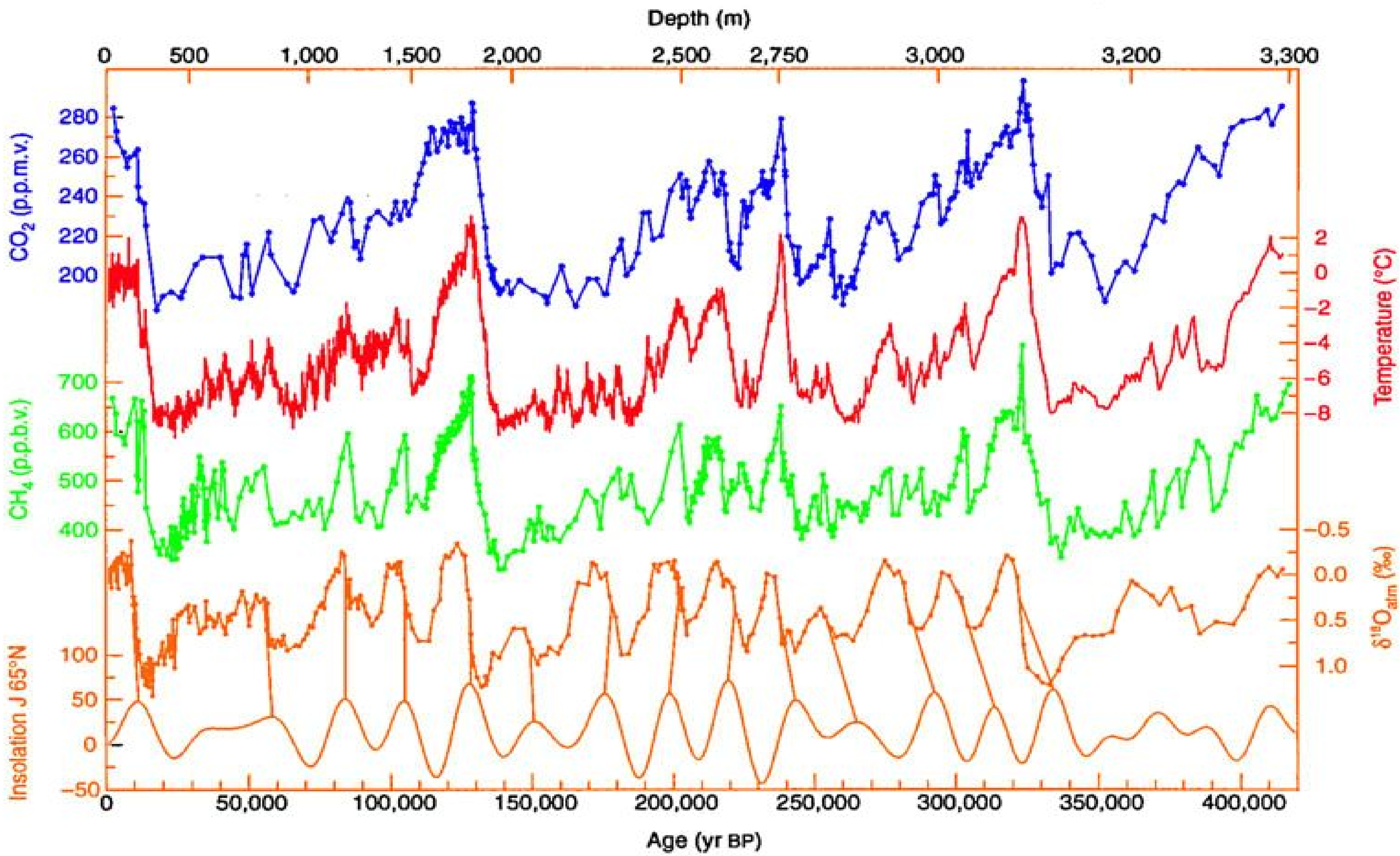
Climate proxies







Vostok ice core



Animal migration and origin

Fig. 2 Geographic patterns of δD values (‰) of wings from field-raised monarch butterflies in eastern North America. All *symbols* indicate wild rearing sites, *circles* indicate sub-sites selected for isotopic analyses (see Table 2). *Dashed line* indicates the approximate breeding limit of eastern North American monarch butterfly

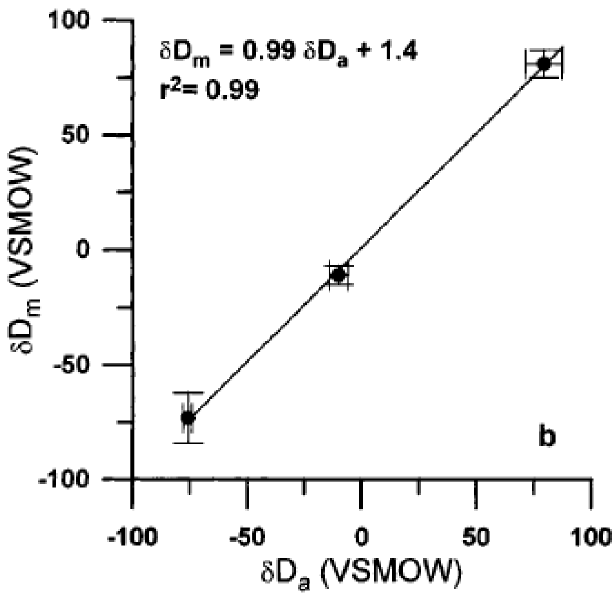
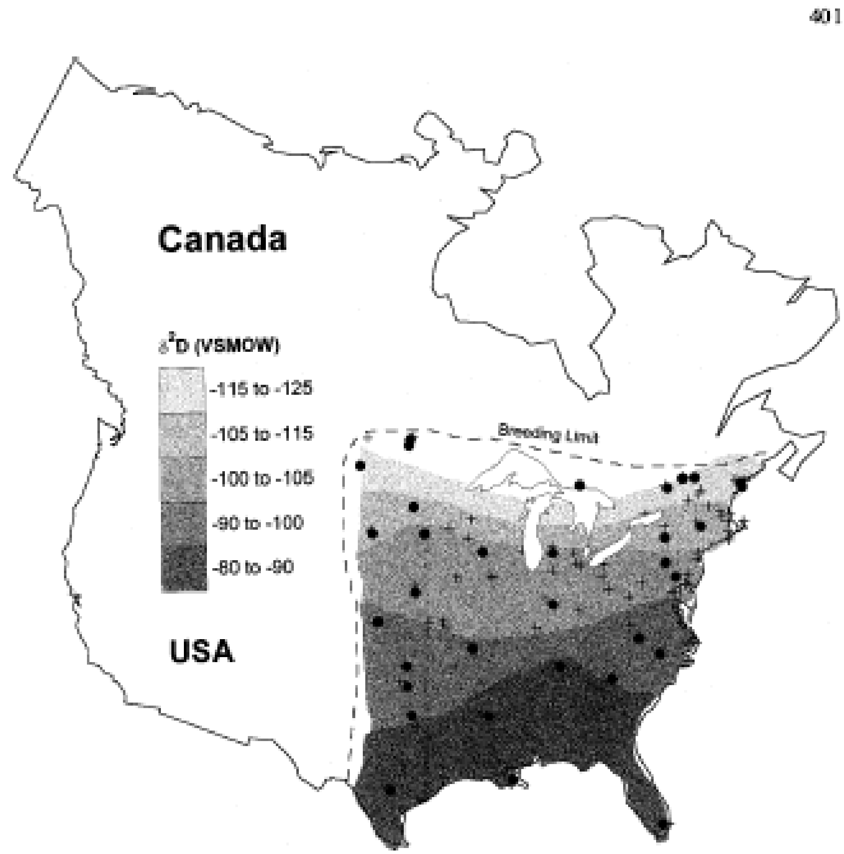


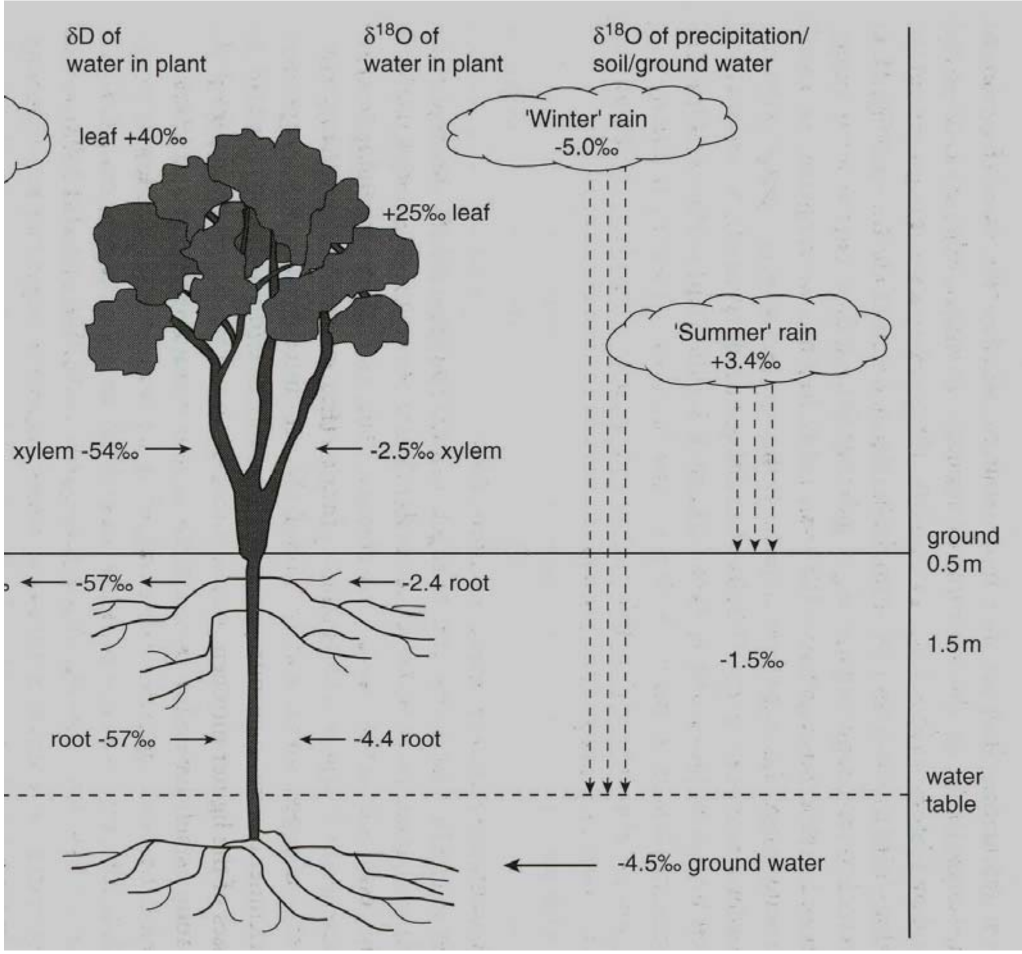
Fig. 1 Relationship between δD values of wings of laboratory-reared monarchs (δD_m) and those of **a** growth water (δD_w) used to raise the larval host plant (*A. curassavica*), and **b** the larval host plant (δD_a). Data from Table 1



Monarch butterflies:
data linked monarch natal origins with wintering colonies; wintering spots in Mexico

Hobson et al. Oecologia (1999) 120:397±404

Plant water sources



1. Different isotope signatures of moisture sources (temperature-dependent)
2. No Δ due to plant water uptake and transport
3. Xylem water = source water
4. Leaf water enrichment, dependent on transpiration, and microclimate
5. ^{18}O incorporation from leaf water into sucrose and later leaf or wood cellulose (^{18}O enrichment by +27 ‰)
6. But ^{18}O exchange reactions during cellulose synthesis