EVROPSKÁ UNIE
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Analytical hydrogeochemistry

2. Stable isotopes in hydrogeology

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

Outline

- **Isotopes in hydrogeochemistry**
  - Structure of atoms
  - Isotopes
- Radiogenic isotopes
- Cosmogenic isotopes
- Study methods
- Stable isotopes
  - Equilibrium **fractionation**
  - Fractionation coefficient
  - Fractionation with respect to the standard
  - Isotopic enrichment
  - Kinetic fractionation

- Utilization of isotopes in hydrogeochemistry

Repetition

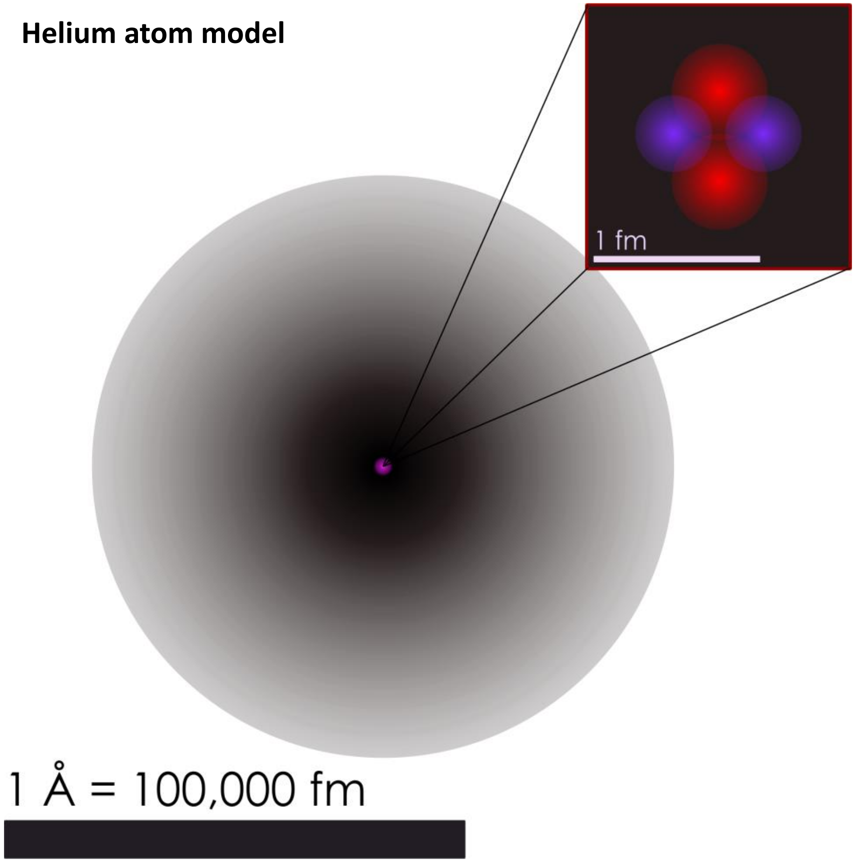
1. What is an isotope? Give an example.
2. What is isotope fractionation? Explain with an example.
3. What physical properties are important in isotope fractionation?
4. What does the value $\delta 2\mathrm{H}$= 2 ‰ tell me about the heavy hydrogen content of ^{2}H in the sample?

STRUCTURE OF ATOMIC NUCLEI

Atomic model

- Core
  - Protons and neutrons.
  - Mass.
- Electron shells
  - The electrons have a particle-wave character and move with a certain probability in the space defined by the *orbitals*.
  - Volume.
- Electroneutral particle
  - Positively charged core.
  - Negatively charged electrons.

Helium atom model



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Atom

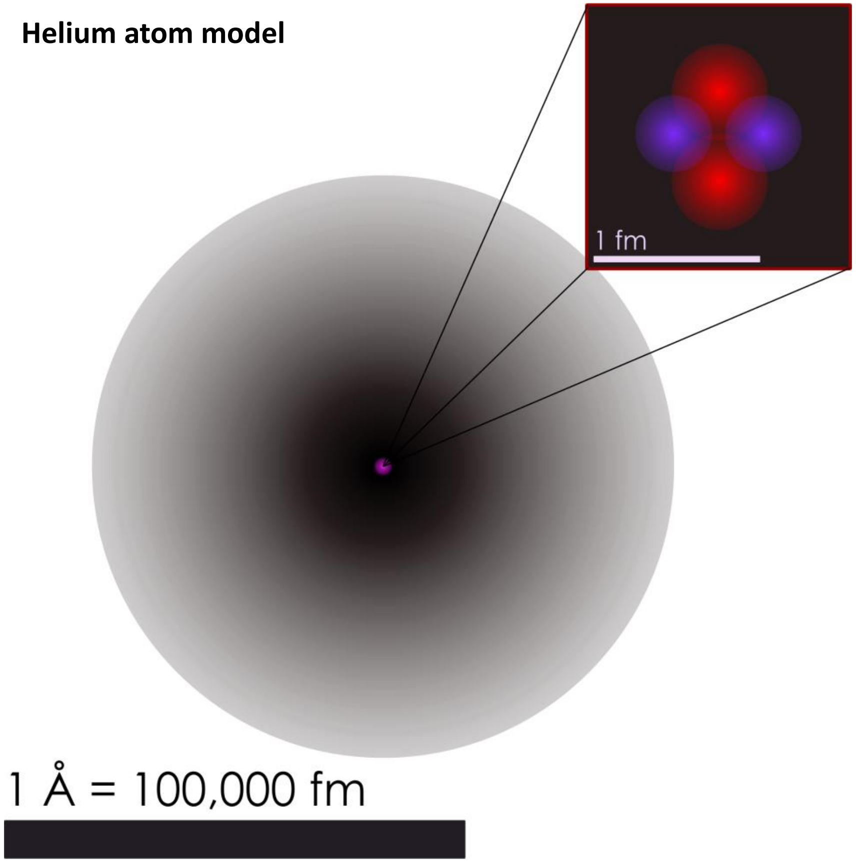
- The properties of an atom are determined by the number of protons in the nucleus.
- Proton number **Z.**
- The proton number also identifies the element to which the atom belongs.
- Neutron number **N.**
- Total number of nucleons (particles in the nucleus) indicates the nucleon (mass) number **A**, which determines which isotope it is:

$$A = Z + N$$

- We then describe the element in general

$$^{A}_{Z}X$$

Helium atom model



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Nuclides and isotopes

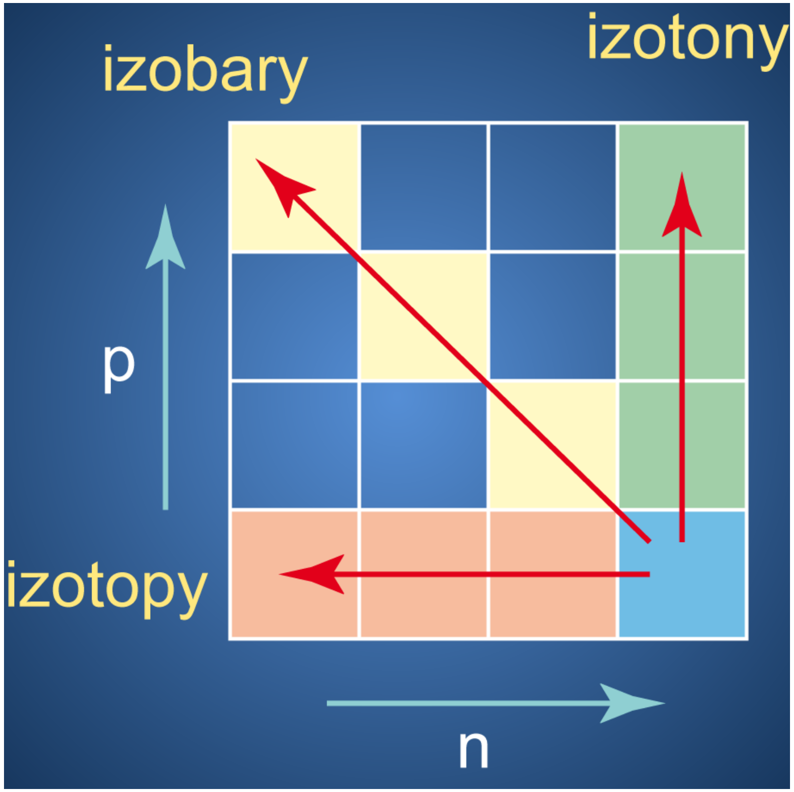
- All atoms of one element have the same proton number, they can differ in the number of neutrons.
- A nuclide is a substance composed of atoms that have the same proton number and nucleon number.

$$^{12}_{6}\mathrm{C},\ ^{18}_{8}\mathrm{O},\ ^{19}_{9}\mathrm{F},\ ^{238}_{92}\mathrm{U}$$

- Isotopes are nuclides that have the same proton number but different nucleon numbers.
- The nuclide is generally used in nuclear physics.
- An isotope is a narrower term used in geochemistry in the context of single element nuclides.

$$^{16}_{8}\mathrm{O},\ ^{17}_{8}\mathrm{O},\ ^{18}_{8}\mathrm{O}$$

Isobars and isotons



- Isobars
  - Atoms with the same number of particles in the nucleus (p + n)
  - E.g.: ^{40}S, ^{40}Cl, ^{40}Ar, ^{40}K, ^{40}Ca
- Isotons
  - Atoms with the same number of neutrons in the nucleus
  - E.g.: ^{36}S, ^{37}Cl, ^{38}Ar, ^{39}K, ^{40}Ca

Nuclear binding energy

proton: 1.007593 daltons = $1.6726231 \times 10^{-27}$ kg

neutron: 1.008982 daltons

electron: 0.000548756 daltons = $9.10093897 \times 10^{-31}$ kg

weight loss δ **= W - M**

W - sum of masses of individual particles

M - mass of combined particles

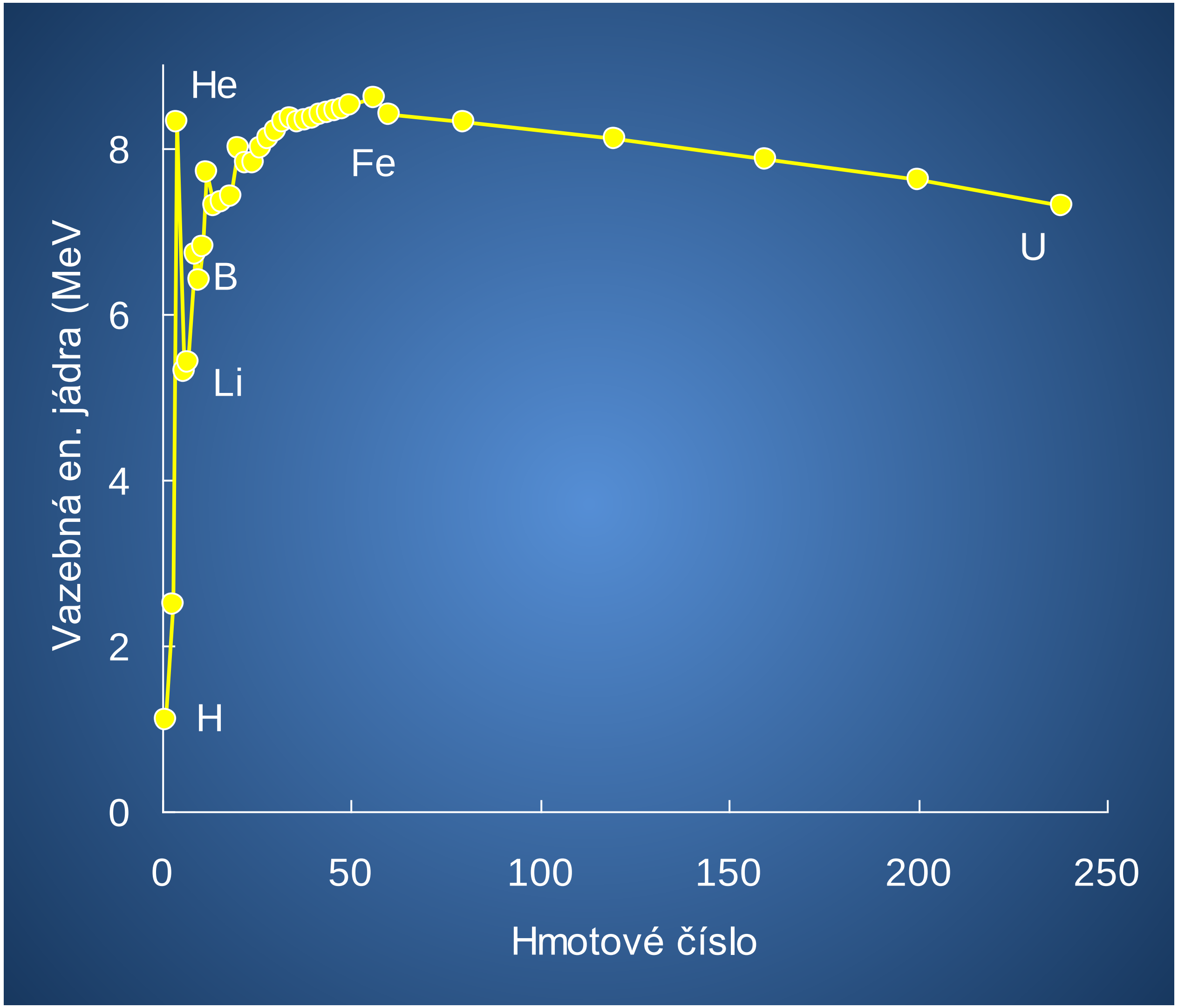
$^{4}He = 2m_p + 2m_n + 2m_e$ = 4.034248 daltons

$m(^{4}He)$ = 4.003873 daltons

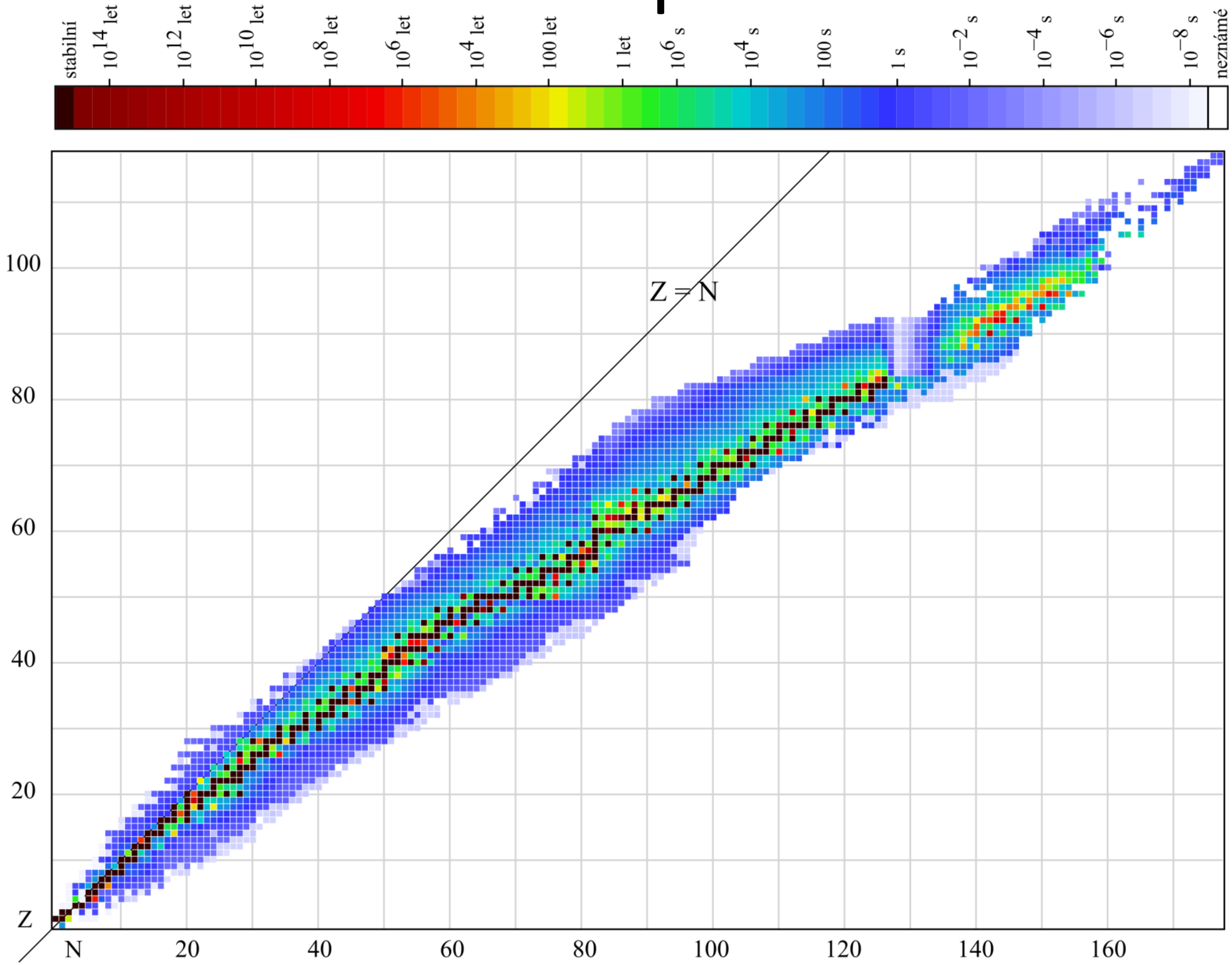
δ = 0.030375 daltons (ie 28.28 MeV -> binding energy)

$$\mathbf{E = mc^2}$$

Nuclear binding energy



Isotopes



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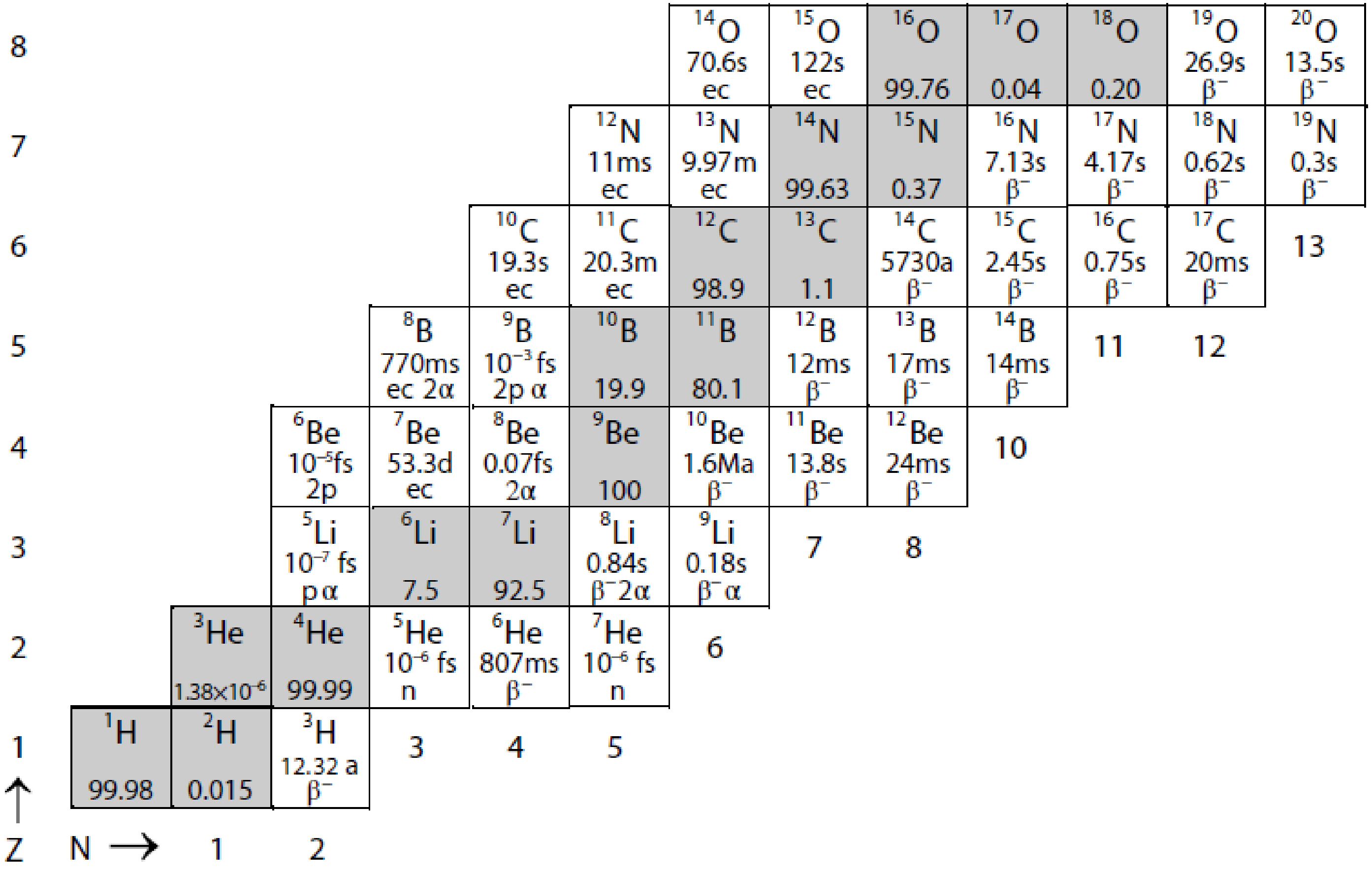
Isotopes



8							^{14}O 70.6s ec	^{15}O 122s ec	^{16}O 99.76	^{17}O 0.04	^{18}O 0.20	^{19}O 26.9s β^-	^{20}O 13.5s β^-
7						^{12}N 11ms ec	^{13}N 9.97m ec	^{14}N 99.63	^{15}N 0.37	^{16}N 7.13s β^-	^{17}N 4.17s β^-	^{18}N 0.62s β^-	^{19}N 0.3s β^-
6					^{10}C 19.3s ec	^{11}C 20.3m ec	^{12}C 98.9	^{13}C 1.1	^{14}C 5730a β^-	^{15}C 2.45s β^-	^{16}C 0.75s β^-	^{17}C 20ms β^-	13
5				^{8}B 770ms ec 2α	^{9}B 10^{-3} fs 2p α	^{10}B 19.9	^{11}B 80.1	^{12}B 12ms β^-	^{13}B 17ms β^-	^{14}B 14ms β^-	11	12	
4			^{6}Be 10^{-5}fs 2p	^{7}Be 53.3d ec	^{8}Be 0.07fs 2α	^{9}Be 100	^{10}Be 1.6Ma β^-	^{11}Be 13.8s β^-	^{12}Be 24ms β^-	10			
3			^{5}Li 10^{-7} fs p α	^{6}Li 7.5	^{7}Li 92.5	^{8}Li 0.84s $\beta^-2\alpha$	^{9}Li 0.18s $\beta^-\alpha$	7	8				
2		^{3}He 1.38×10^{-6}	^{4}He 99.99	^{5}He 10^{-6} fs n	^{6}He 807ms β^-	^{7}He 10^{-6} fs n	6						
1 ↑	^{1}H 99.98	^{2}H 0.015	^{3}H 12.32 a β^-	3	4	5							
Z	N →	1	2										

FIGURE 4.1 Light element isotopes showing percent abundances of the stable isotopes (gray fill) and half-lives of radioisotopes (s, second; m, minute; d, day; a, year) with their principal and secondary decay modes, where α = alpha emission (2p and 2n); ec, electron capture, β^- = electron (beta) emission; n, neutron emission; and p, proton emission. (From *Chart of the Nuclides*, 16th ed., General Electric Co. and KAPL, Inc., 2002.)

Taken from Clark (2015)

Isotopes

- There are at least 3,300 nuclides – naturally occurring or experimentally characterized – the vast majority of which are unstable and rapidly decay. Only the stable and slowly disintegrating isotopes can be found on Earth.
- There are two exceptions:
  1. U and Th decay products,
  2. radionuclides formed by cosmic radiation in the atmosphere.

Isotopes

In terms of use in geology, we can divide isotopes into three categories:

1. **Stable isotope systems**
2. Radiogenic isotope systems
   - The decay of a radioactive isotope produces a radiogenic isotope
3. Cosmogenic isotope systems
   - Formed by bombarding the atmosphere with cosmic rays (^{14}C–^{14}N)

Radiogenic isotopes

- They are formed by the decay of unstable nuclei
  - E.g. ^{87}Rb -> ^{87}Sr
  - End product or decay chain
- During decay, a large amount of energy is released
  - Radioactivity
- The vast majority of existing isotopes are unstable
- Decisive role of half-life
- Use in geochronology, magmatic geochemistry, dating of recent sediments, tritium

Cosmogenic isotopes

- Formed by cosmic rays
  - $^{14}N + n \rightarrow {}^{14}C + p$
- The radiocarbon method
  - Quaternary geology and archeology
  - The content of ^{14}C in an organic sample relative to the content in the atmosphere = age estimate
  - Half-life 5730 years – suitable for dating up to 50000 BP
- Radiogenic ^{3}He

PRINCIPLES OF ISOTOPE FRACTIONATION

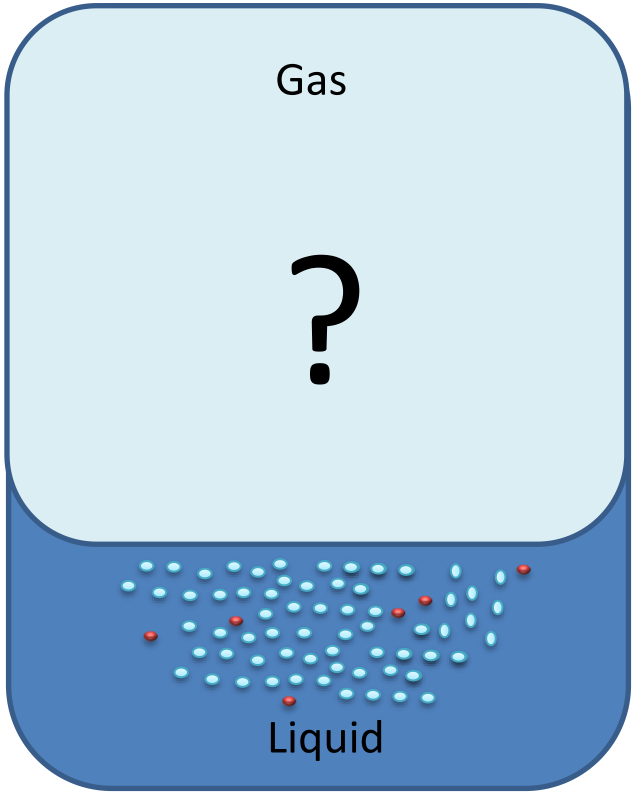
Introductory question

- The container contains liquid water and gas in thermodynamic equilibrium.
- Most water molecules contain the oxygen isotope ^{16}O. Some contain the isotope ^{18}O. The ratio between the amount of ^{16}O and ^{18}O in water is known.
- What will be the isotopic ratio between ^{16}O and ^{18}O in the gas?
  a. The ratio of isotopes in the gas will be the same as in the liquid.
  b. Compared to the liquid, there will be more oxygen ^{16}O in the gas.
  c. Compared to the liquid, there will be more oxygen ^{18}O in the gas.

Liquid water in a closed container

$H - {}^{16}O - H$ ○

$H - {}^{18}O - H$ ●



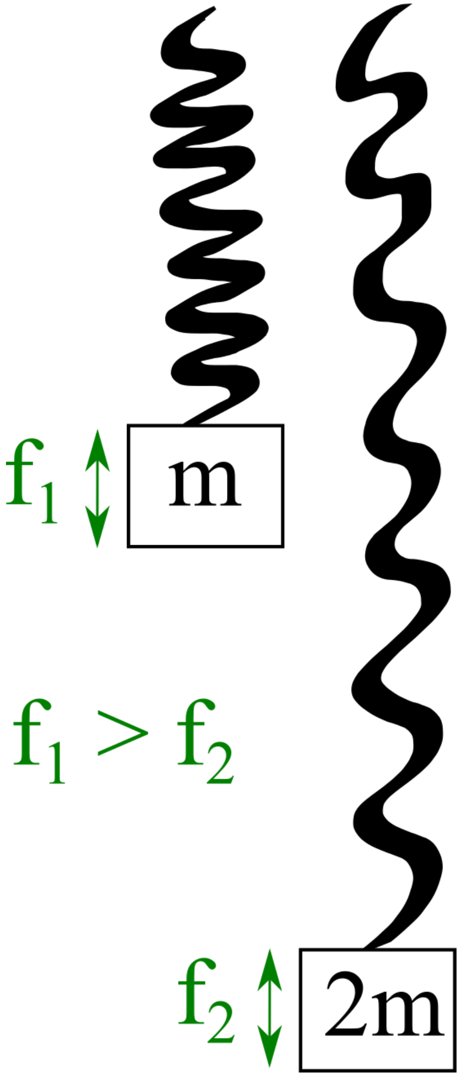
Isotopic fractionation

- Enrichment of one phase by a given isotope compared to another phase.
- The result is a different isotopic composition of sea and rainwater, fossilized shells in different parts of the formation, growth lines in cave sinters, carbon dioxide in the atmosphere and volcanic gases, etc.
- Several types of fractionation mechanisms
  - Equilibrium fractionation
  - Kinetic fractionation
  - Rayleigh distillation
  - …

Physical properties important for fractionation

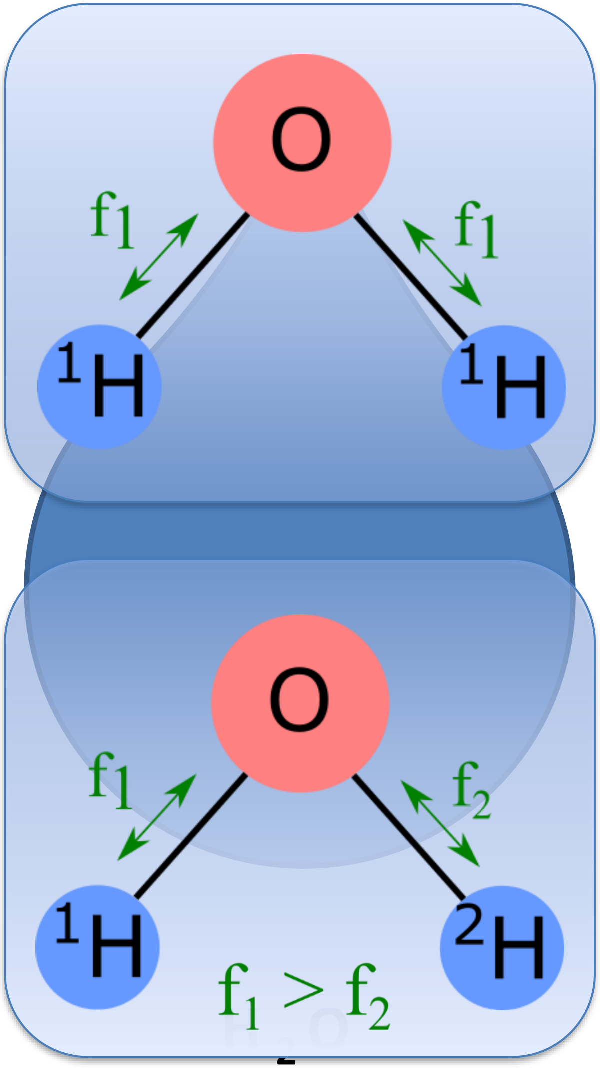
- Low isotope mass and relatively large mass difference between isotopes
  - The difference between ^{87}Sr and ^{86}Sr is 1%
  - The difference between ^{18}O and ^{16}O is 12%
- High degree of covalent bonding – greater effect of energy reduction.
- More oxidation states.
- Relatively high concentration of less represented isotope (at least tenths of %).

Principle of mass fractionation



- If an object hangs on a spring, it will oscillate with higher frequency than a heavier object.

Principle of fractionation



- When replacing a lighter atom with a heavier atom, the frequency (**f**) of the bond vibrations decreases.
- The total bond energy decreases according to

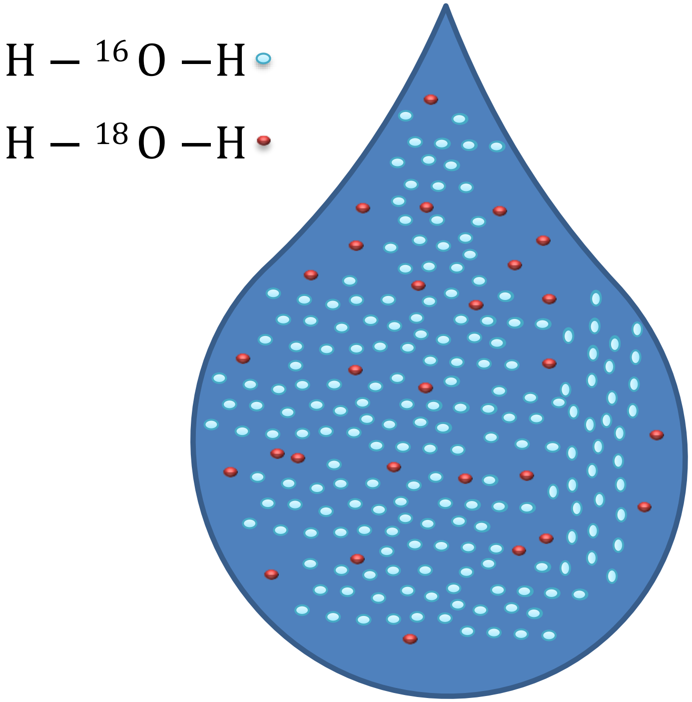
$$\mathbf{E} = h \times \mathbf{f}$$

- The result will be lower internal energy (U).
- The thermodynamic and kinetic properties of the molecule change.

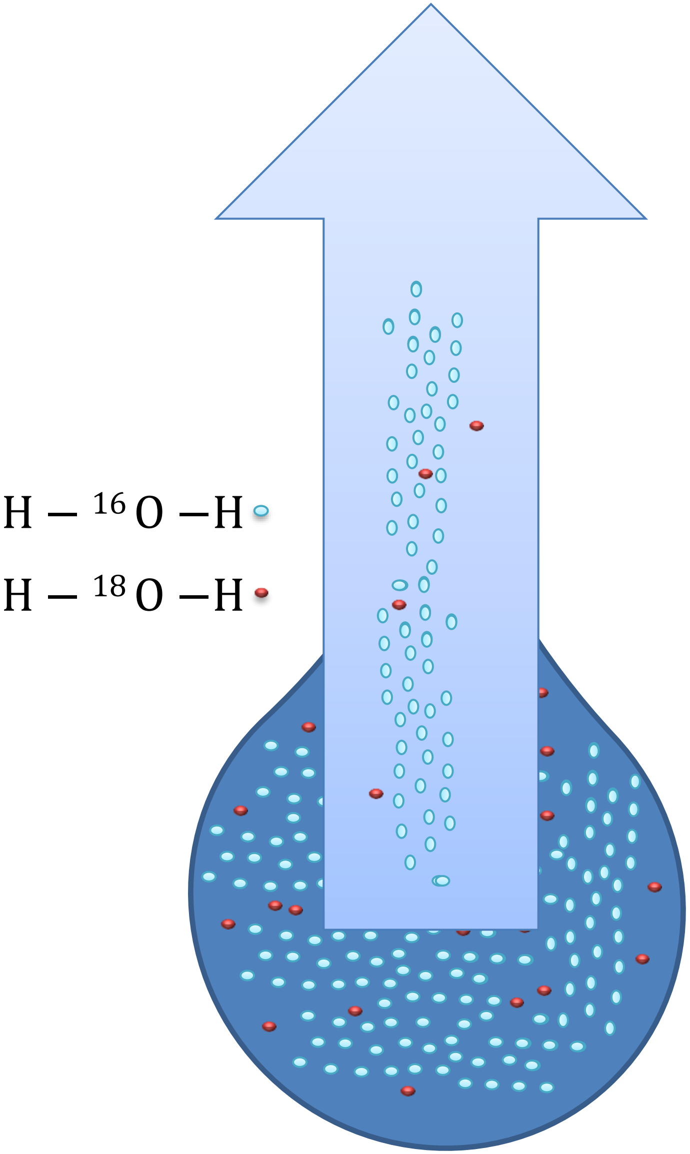
Physical balance

- All molecules of an ideal substance have the same kinetic energy (**E_K**).

$$\mathbf{E_K = ½\,m \times v^2}$$



Physical balance

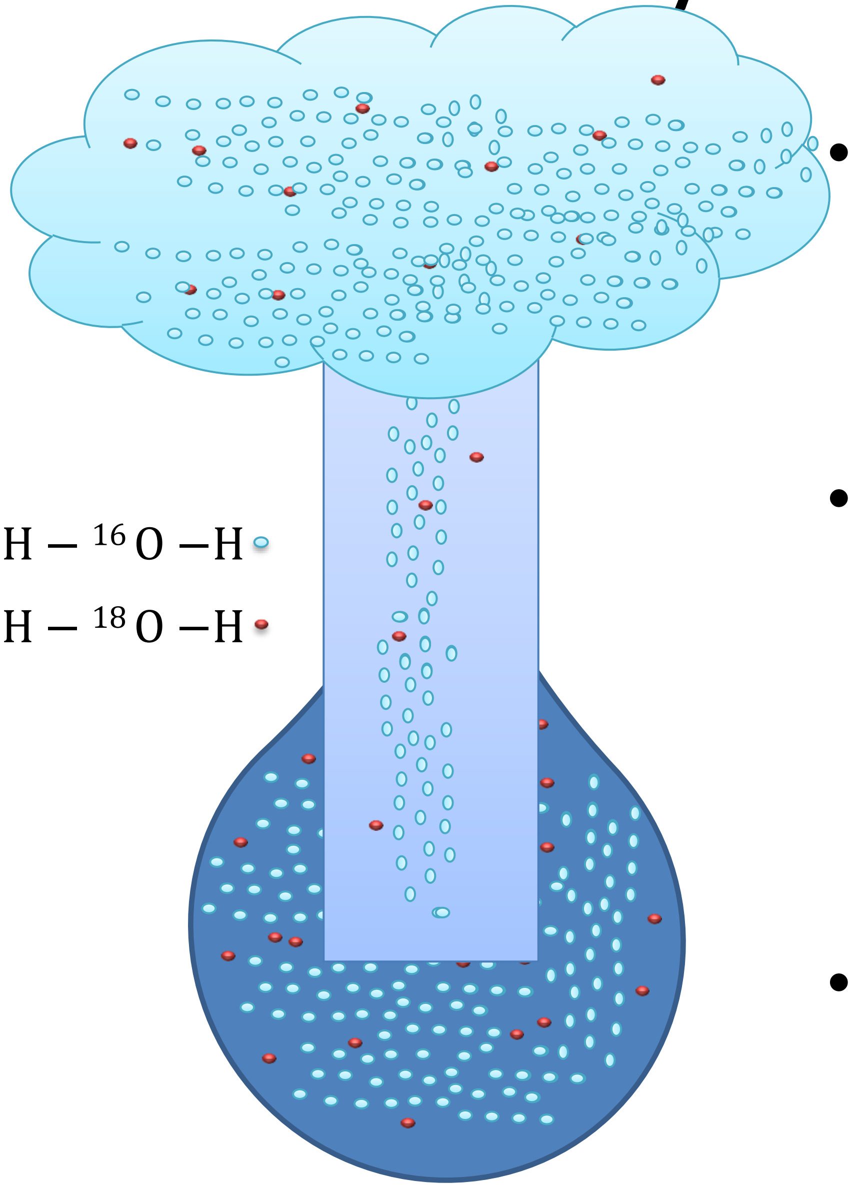


- All molecules of an ideal substance have the same kinetic energy ($\mathbf{E_K}$).

$$\mathbf{E_K = \frac{1}{2}\, m \times v^2}$$

- Heavier water molecules have lower velocity and are less readily released into gas (and conversely, lighter molecules more easily escape from the liquid).

Physical balance



- All molecules of an ideal substance have the same kinetic energy ($\mathbf{E_K}$).

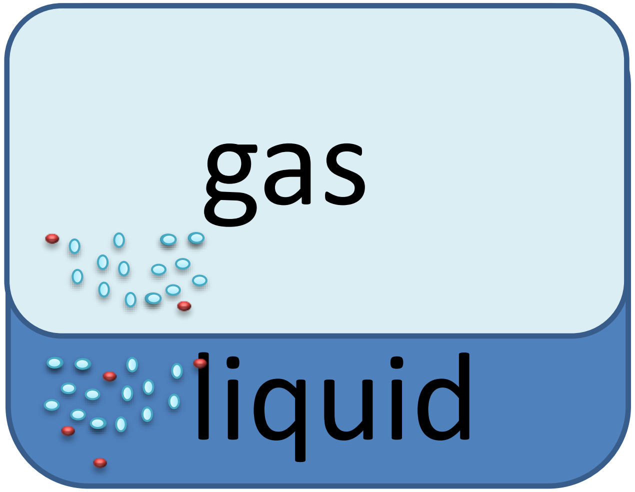
$$\mathbf{E_K = \tfrac{1}{2}\, m \times v^2}$$

- Heavier water molecules have lower velocity and are less readily released into gas (and conversely, lighter molecules more easily escape from the liquid).
- A slight fractionation occurs – the isotope ratio in gas and water will be different.

Fractionation coefficient

$$\alpha_b^a = \frac{R_a}{R_b}$$

- R_a... ratio of the heavier isotope to the lighter isotope in phase a
- R_b... ratio of the heavier isotope to the lighter isotope in phase b



$$\alpha_{gas}^{liquid} = \frac{(^{18}O/^{16}O)_{liquid}}{(^{18}O/^{16}O)_{gas}}$$

$$\alpha_{gas}^{liquid} = 1.0092 \text{ (at 25 °C)}$$

- Specific type of equilibrium constant

Difference with respect to the standard

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 10^3 \text{‰}$$

- Due to the extremely small variations in isotope concentrations, the value is referenced with respect to standards.
- How much the sample differs from the standard:
    - $\delta < 0$ … the sample is depleted of a heavier isotope
    - $\delta > 0$ … the sample is enriched with a heavier isotope

Standards

element	symbol	ratio	standard	abs. ratio
H	δD	$^{2}H/^{1}H$	SMOW	1.557×10^{-4}
If	$\delta^{6}Li$	$^{6}Li/^{7}Li$	NBS L-SVEC	0.08306
B	$\delta^{11}B$	$^{11}B/^{10}B$	NBS 951	4.044
C	$\delta^{13}C$	$^{13}C/^{12}C$	PDB	1.122×10^{-2}
N	$\delta^{15}N$	$^{15}N/^{14}N$	ATM	3.613×10^{-3}
O	$\delta^{18}O$	$^{18}O/^{16}O$	SMOW, PDB	2.0052×10^{-3}
	$\delta^{17}O$	$^{17}O/^{16}O$	SMOW	3.76×10^{-4}
S	$\delta^{34}S$	$^{34}S/^{32}S$	CDT	4.43×10^{-2}

SMOW - Standard Mean Ocean Water (sometimes also VSMOW - Vienna Standard Mean Ocean Water)
PDB - Pee Dee Belemnite (C and O in carbonates, sometimes also VPDB)
ATM - ATMospheric nitrogen
CDT - Canyon Diablo troilite (from meteorite)
NBS - National Bureau of Standards (USA)

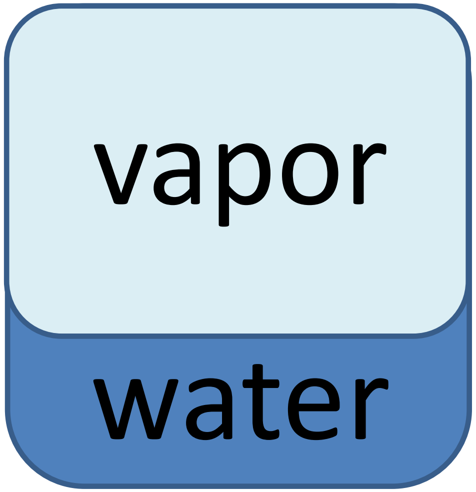
Example 1

- What is the value of δ^{18}O for water vapor above ocean surface (25 °C)?

$$\alpha^{water}_{vapor} = 1.0092 \text{ (at 25 °C)}$$

$$\delta^{18}\text{O}_{ocean} = 0\,‰$$

The ocean is the standard!



vapor

water

$$\delta^{18}\text{O}_{vapor} = \left(\frac{(^{18}\text{O}/^{16}\text{O})_{vapor} - (^{18}\text{O}/^{16}\text{O})_{ocean}}{(^{18}\text{O}/^{16}\text{O})_{ocean}} \right) \times 1000\,‰$$

$$\alpha^{ocean}_{vapor} = \frac{(^{18}\text{O}/^{16}\text{O})_{ocean}}{(^{18}\text{O}/^{16}\text{O})_{vapor}}$$

$$\alpha^{ocean}_{vapor} = \frac{\delta^{18}\text{O}_{ocean} + 1000}{\delta^{18}\text{O}_{vapor} + 1000}$$

Example 1

- What is the value of δ^{18}O for water vapor above ocean surface (25°C)?

$$\alpha_{vapor}^{water} = 1.0092 \text{ (at 25°C)}$$

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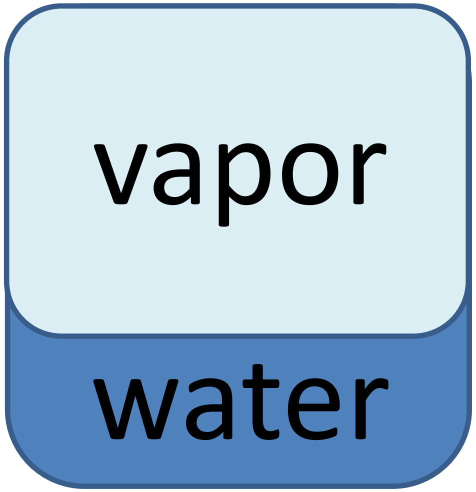


$$\delta^{18}\mathrm{O}_{vapor} = \left(\frac{({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{vapor} - ({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{ocean}}{({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{ocean}}\right) \times 1000\,‰$$

$$\alpha_{vapor}^{ocean} = \frac{({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{ocean}}{({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{vapor}}$$

$$\alpha_{vapor}^{ocean} = \frac{\delta^{18}\mathrm{O}_{ocean} + 1000}{\delta^{18}\mathrm{O}_{vapor} + 1000}$$

$$\delta^{18}\mathrm{O}_{vapor} = \frac{\delta^{18}\mathrm{O}_{ocean} + 1000}{\alpha_{vapor}^{ocean}} - 1000\,‰$$

$$\boldsymbol{\delta^{18}\mathrm{O}_{vapor} = -9.1‰}$$

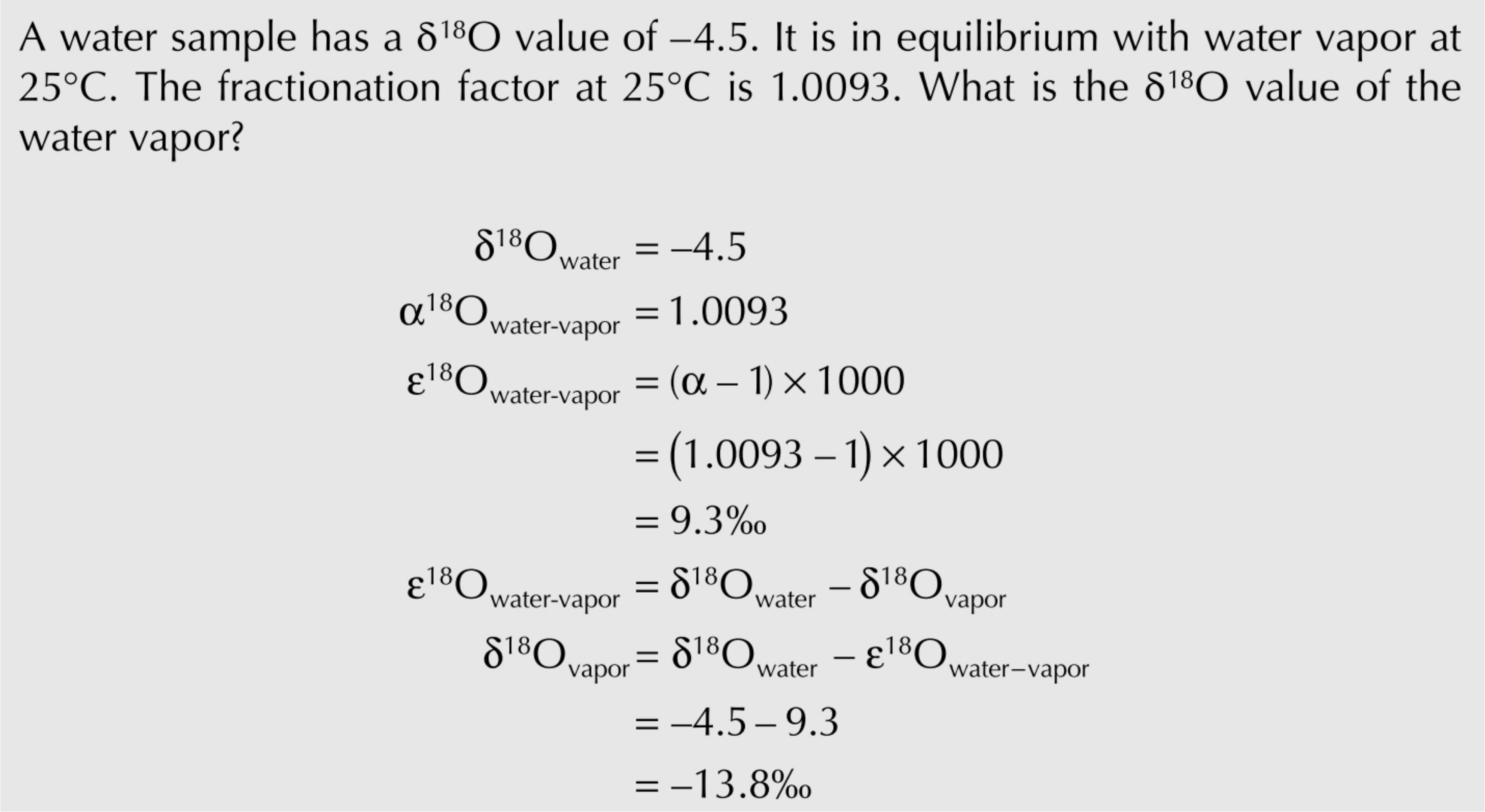
Enrichment factor

$$\delta_a - \delta_b = \Delta_b^a$$

- Sometimes it is advantageous for us to express the difference between the isotope content in two substances
  - E.g. mineral phases crystallized from the melt
- To compare isotope fractionation with δ–‰ values, we can express the fractionation factor α as **the enrichment factor** ε

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

Example



A water sample has a $\delta^{18}O$ value of –4.5. It is in equilibrium with water vapor at 25°C. The fractionation factor at 25°C is 1.0093. What is the $\delta^{18}O$ value of the water vapor?

$$\begin{aligned}
\delta^{18}O_{\text{water}} &= -4.5 \\
\alpha^{18}O_{\text{water-vapor}} &= 1.0093 \\
\varepsilon^{18}O_{\text{water-vapor}} &= (\alpha - 1) \times 1000 \\
&= \left(1.0093 - 1\right) \times 1000 \\
&= 9.3‰ \\
\varepsilon^{18}O_{\text{water-vapor}} &= \delta^{18}O_{\text{water}} - \delta^{18}O_{\text{vapor}} \\
\delta^{18}O_{\text{vapor}} &= \delta^{18}O_{\text{water}} - \varepsilon^{18}O_{\text{water-vapor}} \\
&= -4.5 - 9.3 \\
&= -13.8‰
\end{aligned}$$

Source fractionation

$$\delta_a - \delta_b = \Delta_b^a$$

$$\delta = \left(\frac{R_a - R_b}{R_b}\right) \times 10^3$$

$$R_a = \frac{\delta_a R_b}{10^3} + R_b = \frac{R_b(\delta_a + 10^3)}{10^3}$$

$$\alpha_b^a = \frac{R_a}{R_b}$$

$$\alpha_b^a - 1 = \frac{R_a}{R_b} - 1 = \frac{R_a - R_b}{R_b}$$

$$\alpha_b^a - 1 = \frac{(\delta_a + 10^3) - (\delta_b + 10^3)}{(\delta_b + 10^3)} = \frac{\delta_a - \delta_b}{\delta_b + 10^3}$$

if $\alpha_b^a < 1.010 \; than \; \delta_b + 10^3 \approx 10^3$

$$\alpha_b^a - 1 \approx \frac{\delta_a - \delta_b}{10^3}$$

$$10^3(\alpha_b^a - 1) \approx \delta_a - \delta_b$$

$$10^3(\alpha_b^a - 1) \approx \Delta_b^a$$

Chemical equilibria

- Equations analogous to physical equilibria.
- The stronger covalent bond of heavier atoms results in them preferentially entering compounds where they are more strongly bound.
- As the temperature increases, the value of the equilibrium constant decreases as the significance of the difference in bond strength decreases.
- The difference in bond strength also affects the kinetics of the reactions in which the bonds occur.
  - Weaker bonds lead to a faster reaction of the lighter isotope.
  - Isotopic equilibrium also occurs in chemical equilibrium over time.

Influence of temperature on equilibrium fractionation

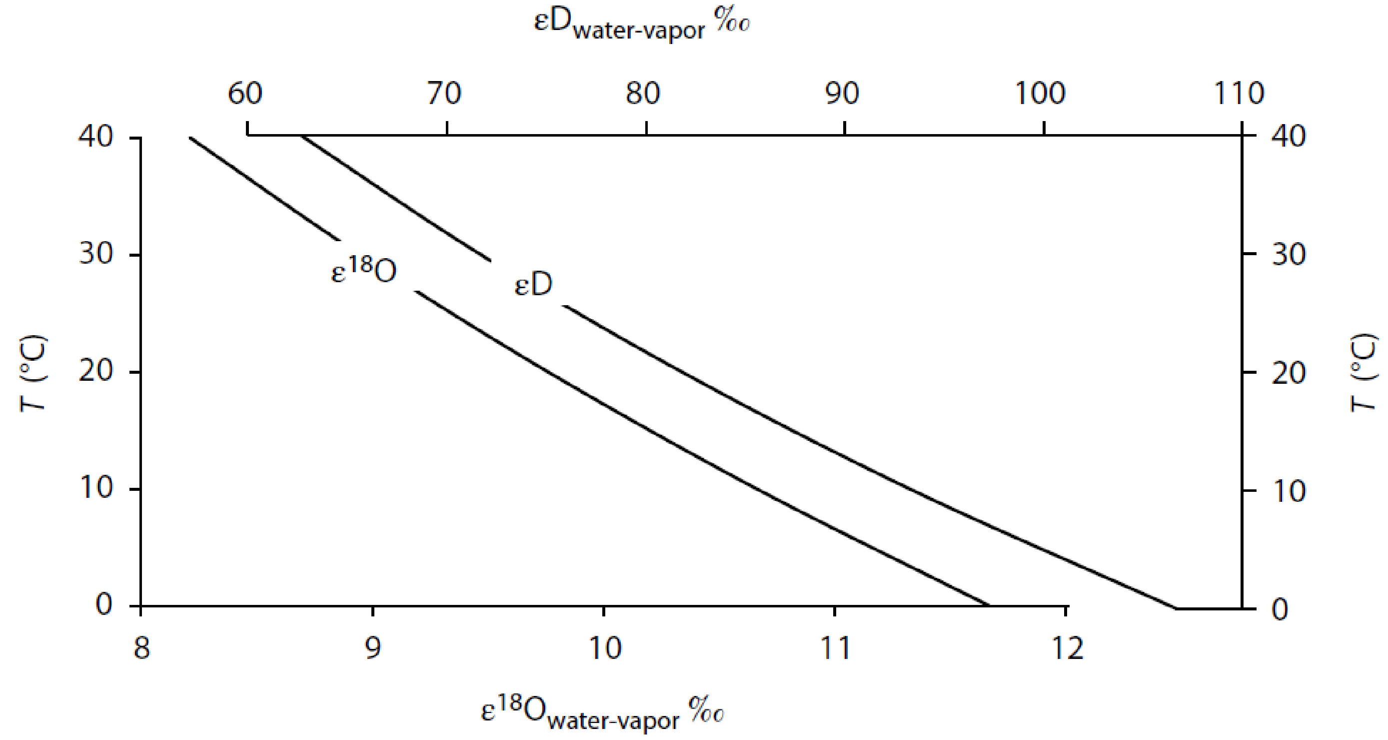


FIGURE 4.2 Temperature effect on fractionation of ^{18}O and D between water and water vapor.

Used from Clark (2015)

- Fractionation is a thermodynamic process – it depends on the temperature
- At high temperatures α is very close to 1
- High values for low temperature processes (surface conditions)

TABLE 4.2

Temperature and Fractionation for Some Common Isotope-Exchange Reactions (*T* in °C)

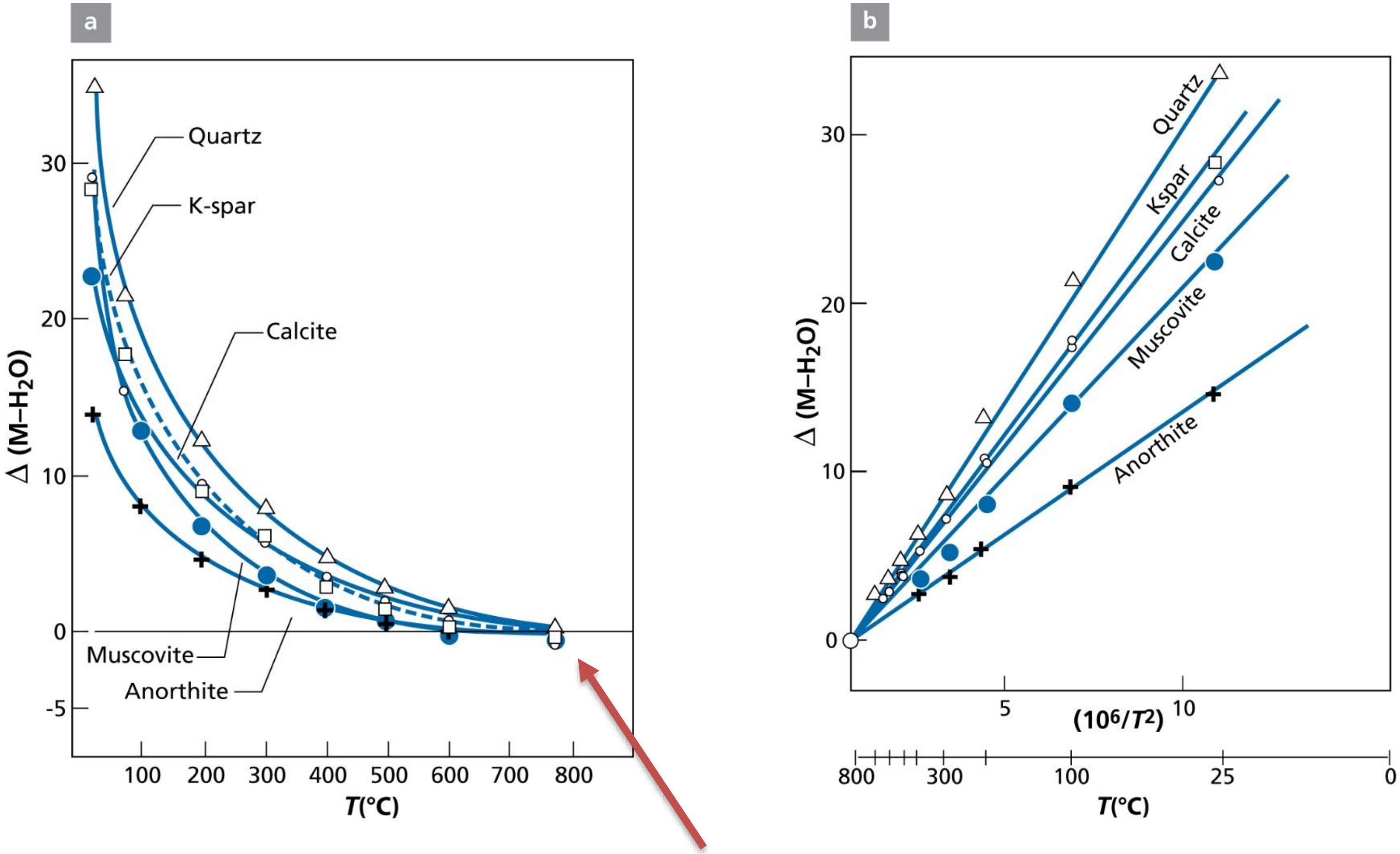
Isotope	Exchange Reaction	Temperature Equation	ε–‰ at 25°C
D	$H_2O—H_2O_{vapor}$	$\varepsilon D_{water-vapor} = 0.0066\ T^2 - 1.36\ T + 106$	76
	$H_2O_{water}—H_2$	$\alpha D_{water-H_2} = 0.00018\ T^2 - 0.034\ T + 4.49$	–1
	$H_2O_{water}—CH_4$	$\varepsilon D_{water-CH_4} = -0.0018\ T^2 + 0.64\ T + 12$	27
	$Gypsum—H_2O$	$\varepsilon D_{water-gypsum} = 0.00008\ T^2 - 0.028\ T - 14$	–15
	$Illite—H_2O$	$\varepsilon D_{water-illite} = -0.0008\ T^2 + 0.4804\ T - 66.904$	–55
	$Kaolinite—H_2O$	$\varepsilon D_{water-kaolinite} = -0.0003\ T^2 + 0.152\ T - 35.368$	–32
^{18}O	$H_2O_{water}—H_2O_{vapor}$	$\varepsilon^{18}O_{water-vapor} = 0.0004\ T^2 - 0.103\ T + 11.64$	9.3
	$CO_2—H_2O$	$\varepsilon^{18}O_{CO_2-water} = 0.0007\ T^2 - 0.240\ T + 45.6$	41.0
	$Calcite—H_2O$	$\varepsilon^{18}O_{CaCO_3-water} = 0.0011\ T^2 - 0.265\ T + 34.3$	28.8
	$Gypsum—H_2O$	$\varepsilon^{18}O_{gypsum-water} = 0.00009\ T^2 - 0.0304\ T + 4.72$	4.0
	$SO_4^{2-}—H_2O$	$\varepsilon^{18}O_{SO_4-water} = 0.0011\ T^2 - 0.275\ T + 34.5$	28.7
	$Illite—H_2O$	$\varepsilon^{18}O_{illite-water} = 0.0004\ T^2 + 0.19\ T + 27.86$	33.1
	$Kaolinite—H_2O$	$\varepsilon^{18}O_{kaolinite-water} = 0.0004\ T^2 + 0.201\ T + 29.12$	34.4
	$SiO_{2(amorph)}—H_2O$	$\varepsilon^{18}O_{SiO_2-water} = 0.0014\ T^2 - 0.336\ T + 42.8$	35.9
^{13}C	$H_2CO_3—CO_{2(g)}$	$\varepsilon^{13}C_{H_2CO_3-CO_2(g)} = -0.000014\ T^2 + 0.0049\ T - 1.18$	–1.1
	$HCO_3^-—CO_{2(g)}$	$\varepsilon^{13}C_{HCO_3-CO_{2(g)}} = 0.00032\ T^2 - 0.124\ T + 10.87$	8.0
	$CO_3^{2-}—CO_{2(g)}$	$\varepsilon^{13}C_{CO_3-CO_{2(g)}} = 0.00033\ T^2 - 0.083\ T + 8.25$	6.4
	$CaCO_3—HCO_3^-$	$\varepsilon^{13}C_{CaCO_3-HCO_{3(g)}} = -0.0002\ T^2 + 0.056\ T - 0.39$	0.9
	$CaCO_3—CO_2$	$\varepsilon^{13}C_{CaCO_3-CO_2} = 0.0009\ T^2 - 0.184\ T + 14.4$	10.3
	$CO_2—CH_4$	$\varepsilon^{13}C_{CO_2-CH_4} = 0.0015\ T^2 - 0.418\ T + 77.7$	70.5
^{34}S	$SO_4^{2-}—H_2S_{(aq)}$	$\varepsilon^{34}S_{SO_4-H_2S} = 0.0019\ T^2 - 0.484\ T + 74.2$	65.4
	$SO_4^{2-}—HS^-_{(aq)}$	$\varepsilon^{34}S_{SO_4-HS} = 0.0017\ T^2 - 0.493\ T + 83.9$	75.4

[1] Epsilon values, ε, for strongly fractionating reactions such as H_2–H_2O cannot be used. Isotope differences should be calculated from α-values using $\alpha_{x-y} = (\delta_x + 1000)/(\delta_y + 1000)$.

Source: From data and references in Clark and Fritz 1997.

Geothermometry

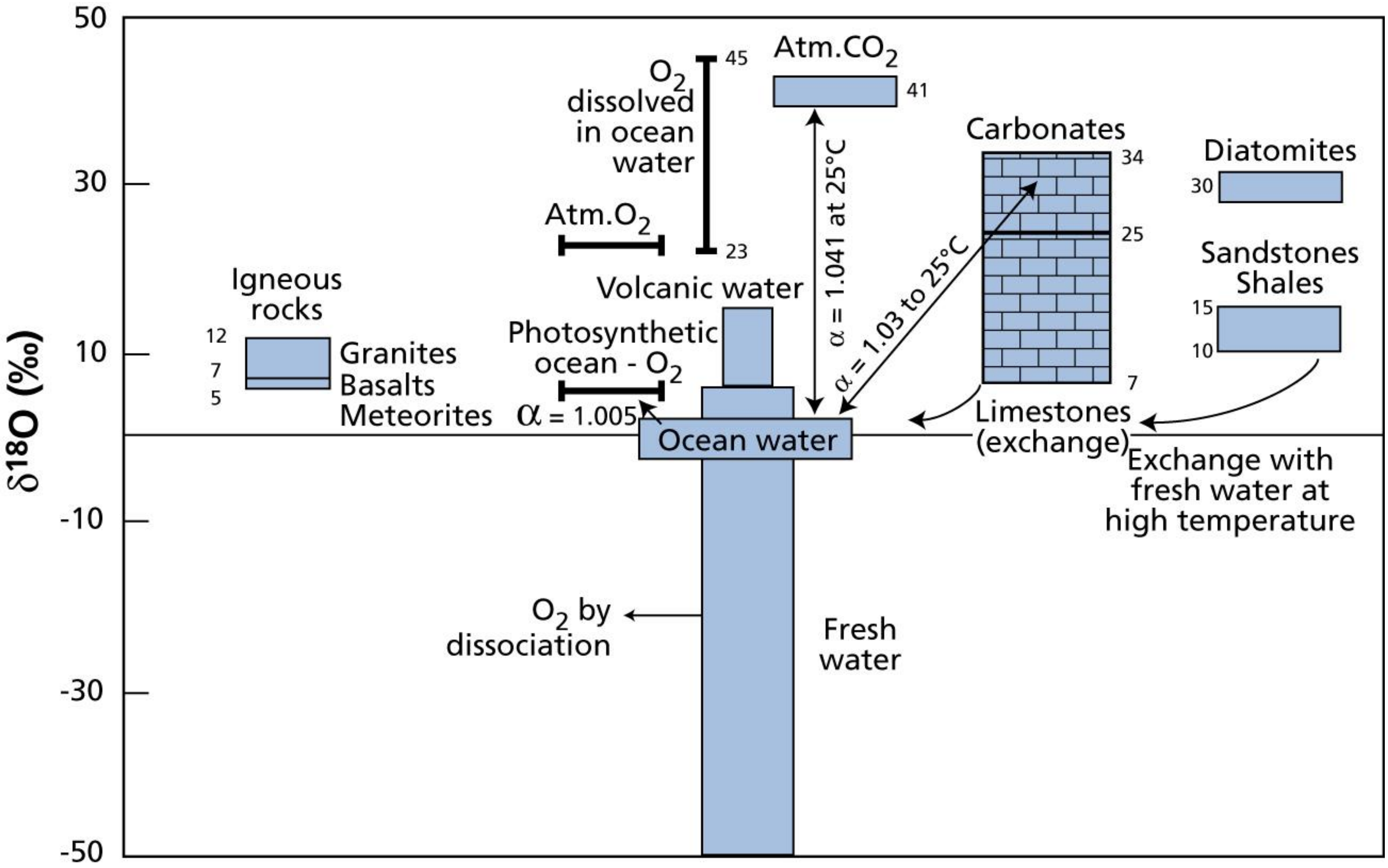
Figure 7.11 Isotope fractionation curves for water and some minerals as a function of temperature (*T*, or $10^6/T^2$). Notice that the curve should theoretically converge to zero. The error is the result of experimental uncertainty. After O'Neil (1986).



Taken from Allègre (2008)

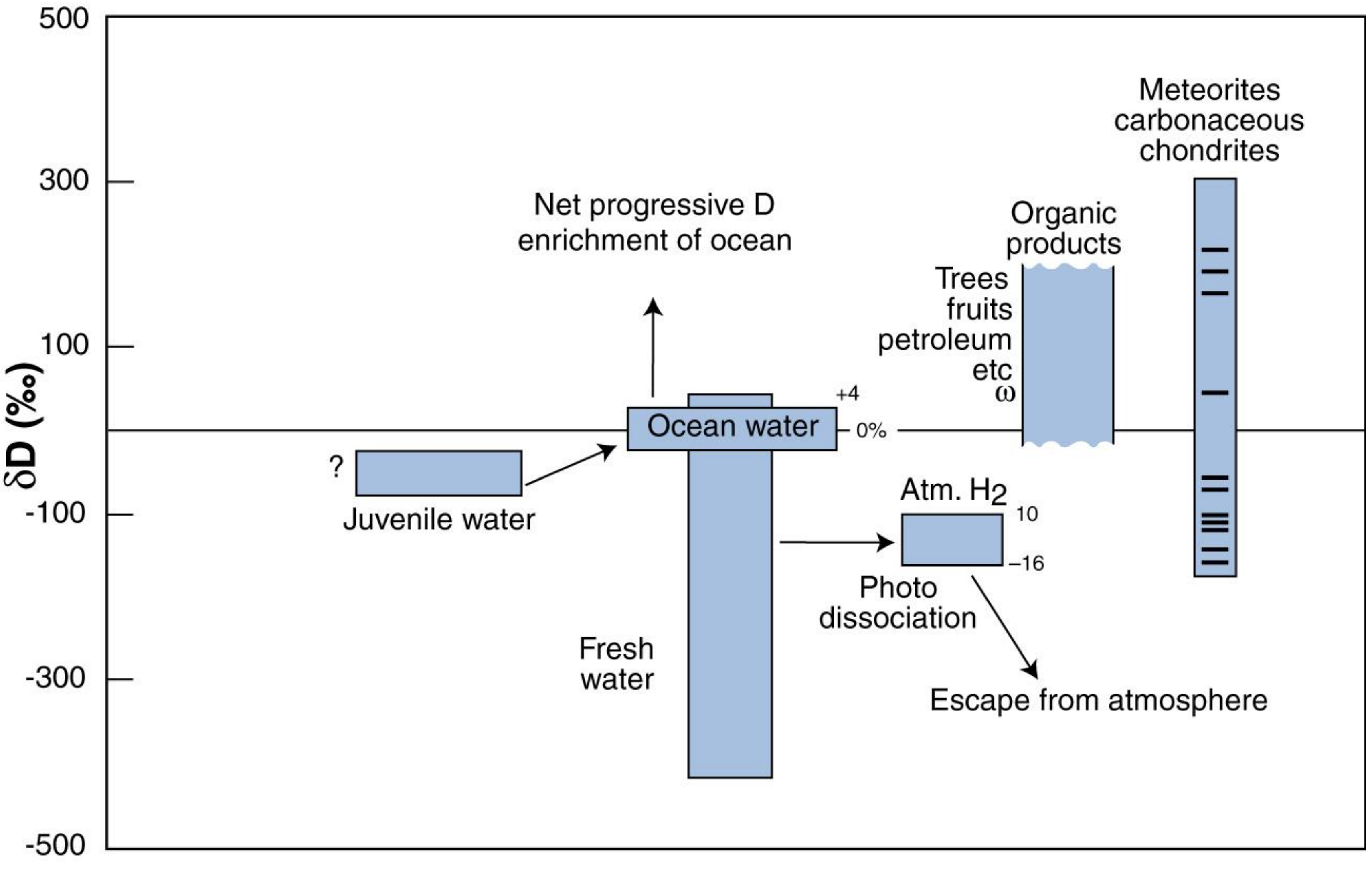
At high temperatures, the fractionation is negligible.

Heavy oxygen $\delta^{18}O$



Taken from Allègre (2008)

Heavy hydrogen δD

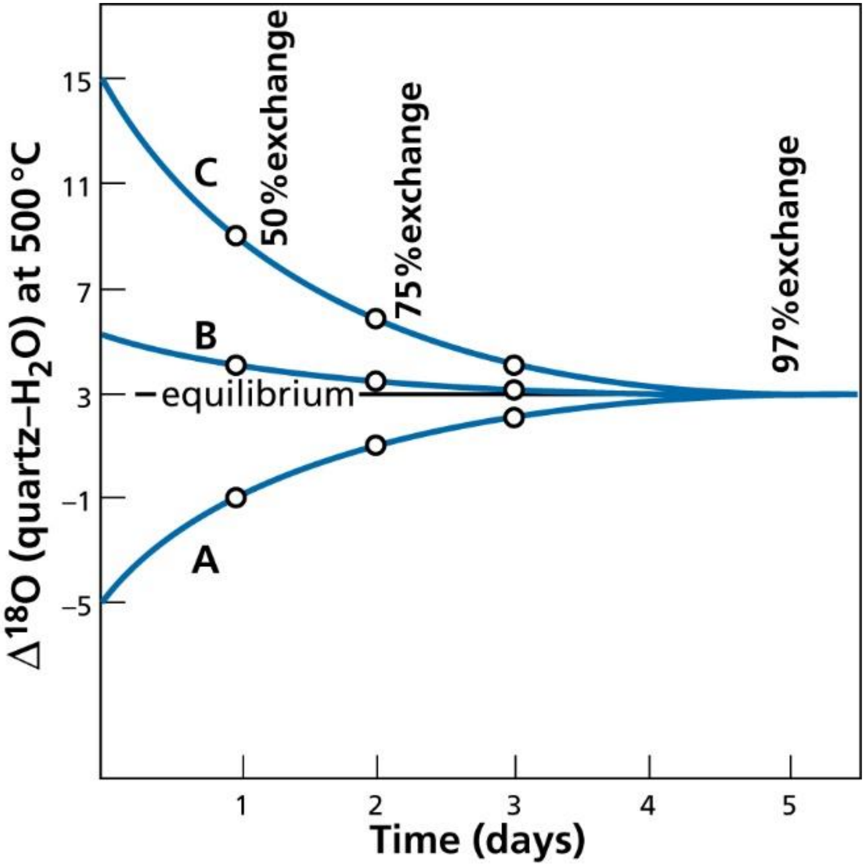


Taken from Allègre (2008)

Kinetic fractionation

- Every process reaches equilibrium after a sufficient time.
- Equilibria disrupted by
  - Chemical reactions
  - Transport of substances
  - Influence of temperature
  - Biological processes
  - And more…
- Out of balance, one direction of reaction significantly prevails.
- If equilibrium is not reached in the process, the process products are enriched in a lighter isotope more than the equilibrium fractionation coefficient would indicate.
- Each process reaches isotopic equilibrium after sufficient time.
- The question is how quickly the system reaches isotopic equilibrium.
- Isotopic exchange is given by:
  - Temperature.
  - It proceeds faster in liquids and gases (due to weak diffusion in solids).
  - Position of a given isotope in the structures of compounds.

Kinetic fractionation

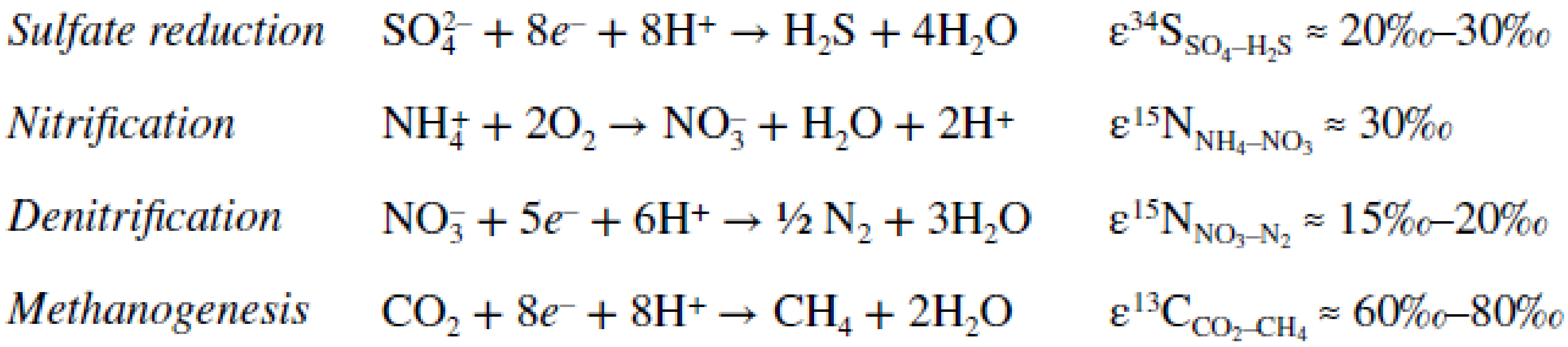


Taken from Allègre (2008)

- Assume that the reaction A -> B takes place and at the same time fractionation takes place.
- If A and B are in contact long enough, isotope exchange will occur until the equilibrium is finally reached.
- In order to maintain the kinetic fractionation, the reactants and products must not be in contact (typically biota effects – removal of reactants away from the cells).
- Temperature accelerates fractionation – kinetic effects at high temperatures are usually not observable.
- The result is "isotopic memory" – the solid phase can carry sealed information about the kinetic fractionation.

Other effects on fractionation

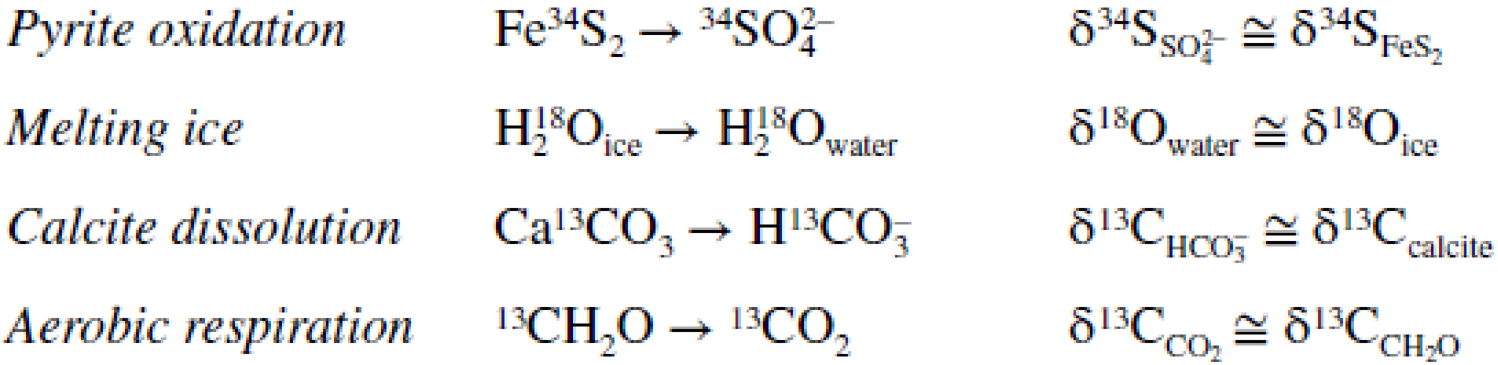
- Diffusion fractionation
  - The difference in velocity of heavier and lighter isotopes
  - It dominates in hydrogeological insulators
- Microbially controlled processes
  - Microorganisms prefer certain isotopes
  - Lighter isotope bonds are more easily broken



Sulfate reduction	$SO_4^{2-} + 8e^- + 8H^+ \rightarrow H_2S + 4H_2O$	$\varepsilon^{34}S_{SO_4-H_2S} \approx 20‰–30‰$
Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	$\varepsilon^{15}N_{NH_4-NO_3} \approx 30‰$
Denitrification	$NO_3^- + 5e^- + 6H^+ \rightarrow \frac{1}{2} N_2 + 3H_2O$	$\varepsilon^{15}N_{NO_3-N_2} \approx 15‰–20‰$
Methanogenesis	$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$	$\varepsilon^{13}C_{CO_2-CH_4} \approx 60‰–80‰$

Quantitative reactions

- Geochemical processes out of equilibrium
  - Redox processes in groundwater
  - Dissolution of minerals with the removal of products
  - Ice melting
- The reaction affects the entire surface (structure) – there is no preference for isotopes



Pyrite oxidation	$Fe^{34}S_2 \rightarrow {}^{34}SO_4^{2-}$	$\delta^{34}S_{SO_4^{2-}} \cong \delta^{34}S_{FeS_2}$
Melting ice	$H_2^{18}O_{ice} \rightarrow H_2^{18}O_{water}$	$\delta^{18}O_{water} \cong \delta^{18}O_{ice}$
Calcite dissolution	$Ca^{13}CO_3 \rightarrow H^{13}CO_3^-$	$\delta^{13}C_{HCO_3^-} \cong \delta^{13}C_{calcite}$
Aerobic respiration	${}^{13}CH_2O \rightarrow {}^{13}CO_2$	$\delta^{13}C_{CO_2} \cong \delta^{13}C_{CH_2O}$

Rayleigh fractionation

- Gradual fractionation of isotopes leads to ever lighter/heavier products
- Evaporation of water from the tank – preferred removal of light isotopes, water is getting heavier

$$R_f = R_o f^{(\alpha-1)}$$

- R_f… Isotopic ratio of the reservoir after the reaction to the residual fraction f
- R_o… initial reservoir isotopic ratio (for f = 1)
- α … fractionation ratio

- Sometimes also *Rayleigh distillation*

Crystallization of magma

- A special case of a closed system – we assume that the crystals are immediately isolated from the rest of the magma.
- Similarly, we can model water condensation and other systems.

$$\mathrm{dA} = k_{\mathrm{A}}\mathrm{A} \quad \mathrm{dB} = k_{\mathrm{B}}\mathrm{B}$$

A and B are representative isotopes

$$\alpha = \frac{k_B}{k_A}$$

fractionation coefficient

$$\ln\frac{B}{B_0} = \alpha \ln\frac{A}{A_0}$$

after integration

$$\frac{B}{B_0} = \left(\frac{A}{A_0}\right)^{\alpha}$$

$$\frac{\dfrac{B}{A}}{\dfrac{B_0}{A_0}} = f^{\alpha-1}$$

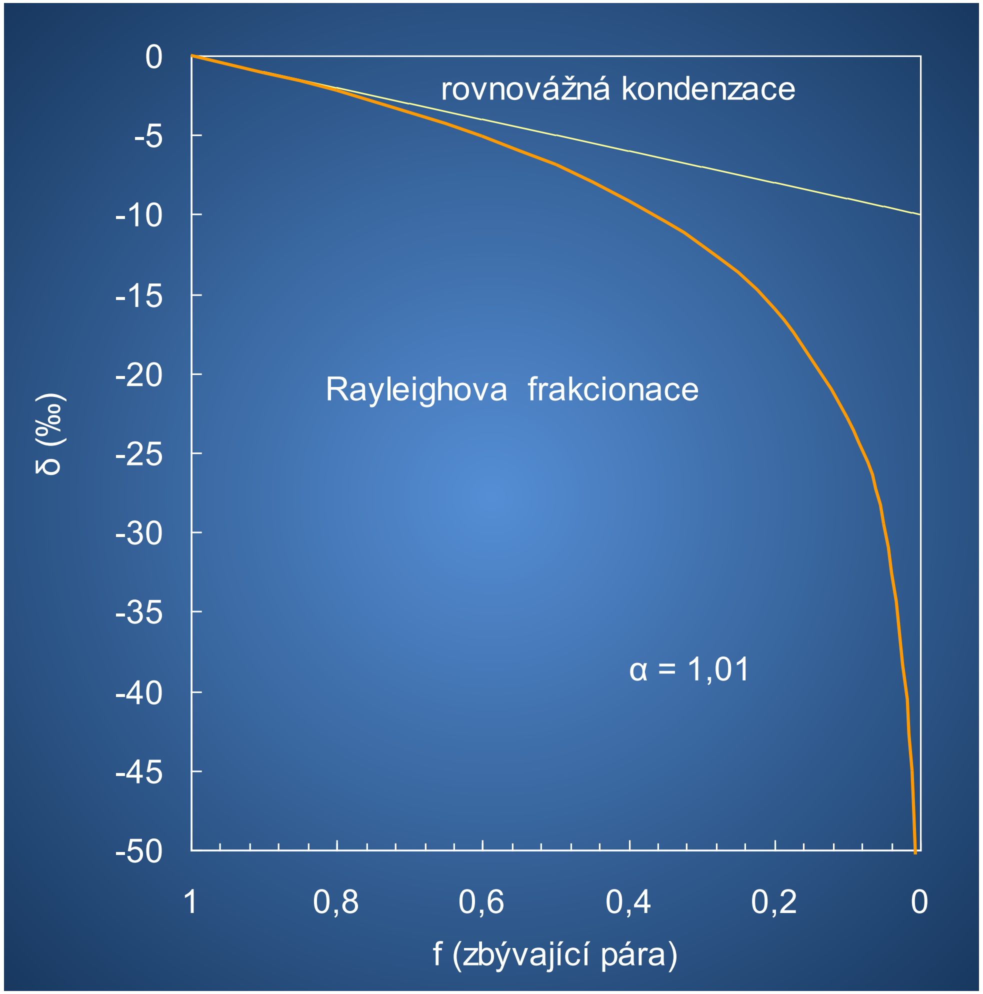
$$\frac{\dfrac{B}{A} - \dfrac{B_0}{A_0}}{\dfrac{B_0}{A_0}} = f^{\alpha-1} - 1$$

$$\delta = 1000\left(f^{\alpha-1} - 1\right)$$

δ is the difference between the original isotopic composition and the isotopic composition after it has condensed (crystallized) part *f*

Fractionation

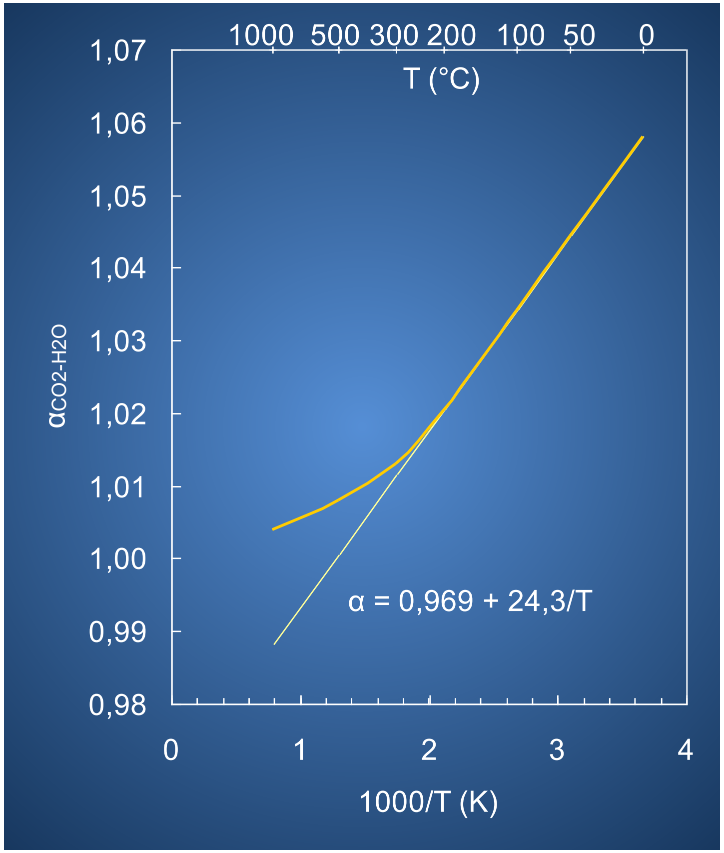
Isotopic composition of the remaining vapor after condensation (*f* − 1) of the amount of water compared to the original isotopic composition of the steam. Non-equilibrium and equilibrium condensation are shown.

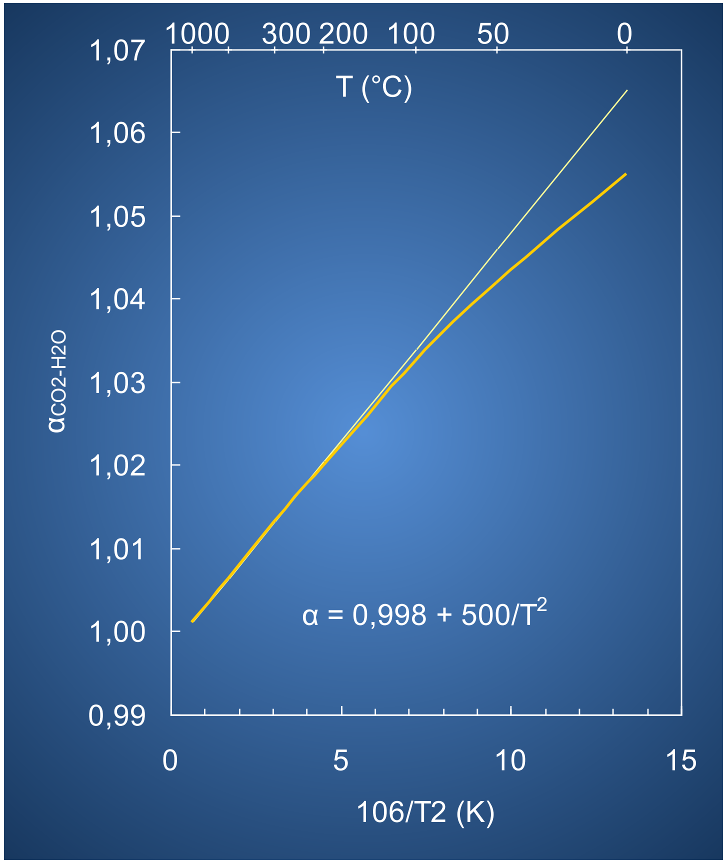


Temperature dependence

The temperature dependence of the fractionation is usually determined experimentally for individual reactions and usually takes the following forms:

$$\alpha = A + \frac{B}{T} \qquad\qquad \alpha = A + \frac{B}{T^2}$$





Dependence on composition and pressure: heavier isotope to a phase with a stronger bond (and covalent) ^{18}O - more in quartz than in magnetite, ^{18}O - more in CO_3^{2-} than in water (30‰); pressure effect negligible: $(\partial G/\partial p) = \Delta V$

UTILIZATION OF STABLE ISOTOPES

Application

- Monitoring of processes in the hydrological cycle resulting in differences in isotopic distribution:
  - Evaporation and formation of atmospheric water
  - Condensation and precipitation with decreasing temperature
  - Re-evaporation on continents
  - Groundwater mixing
  - Water-mineral-gas isotopic exchange (deep water, long retention times)

$\delta^{18}O$ and δD

- General observations
  1. Fresh waters in warm areas are enriched and in cold areas depleted of heavy isotopes
  2. Strong linear correlation between $\delta^{18}O$ and δD in rainwater – slope value 8 and the intersection with the y-axis (D) 10 ‰

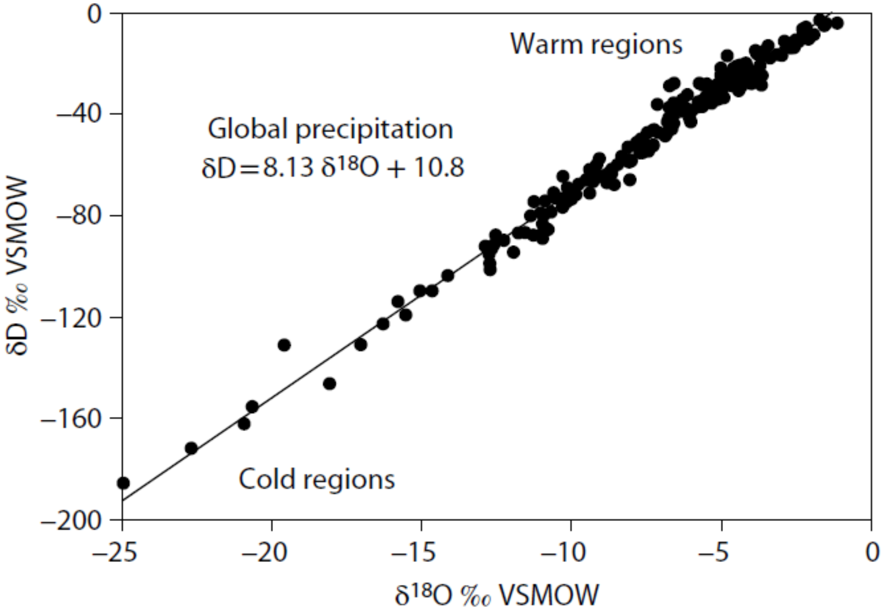


FIGURE 5.2 The $\delta^{18}O$–δD correlation for global precipitation plotted from data on the International Atomic Energy Agency GNIP database (IAEA/WMO 2013). Craig (1961) first observed this correlation in global freshwaters.

Taken from Clark (2015)

Precipitation fractionation

- Rayleigh fractionation

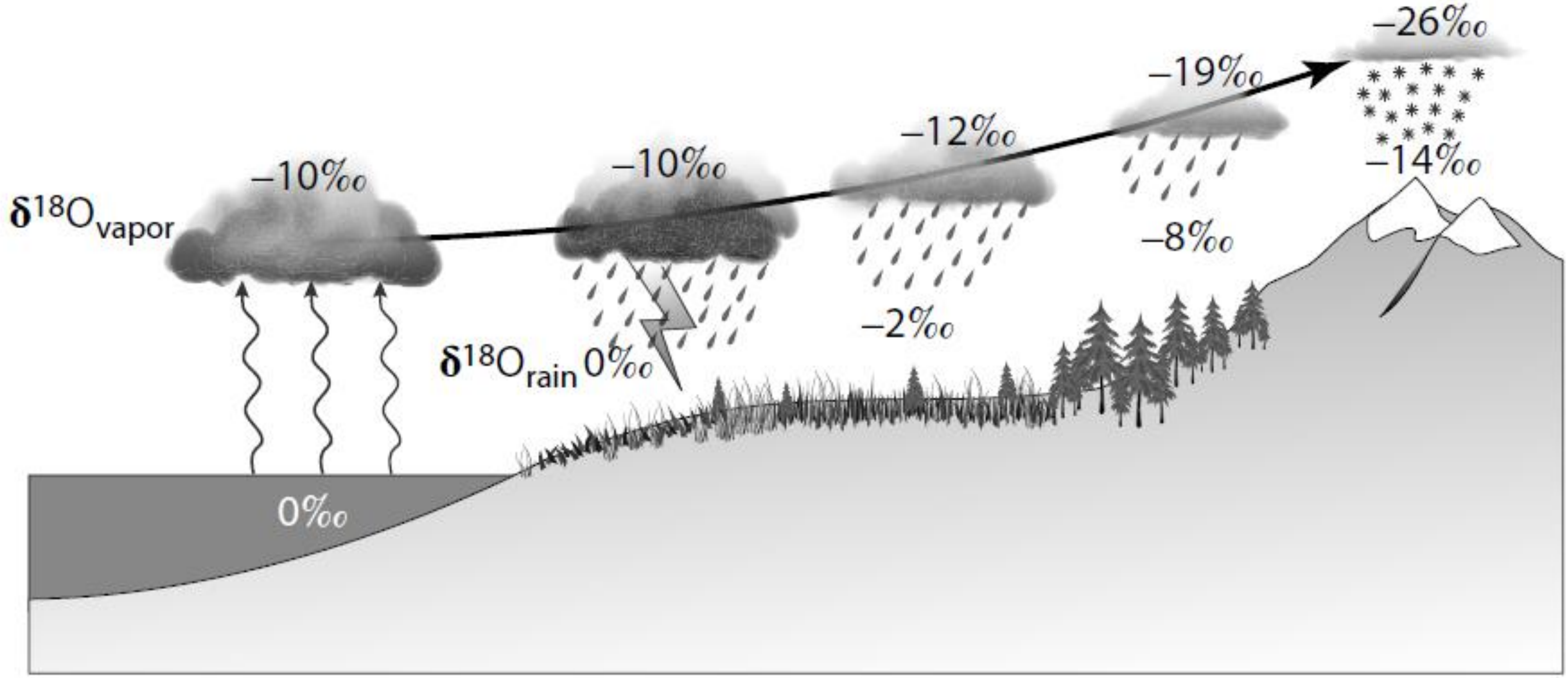
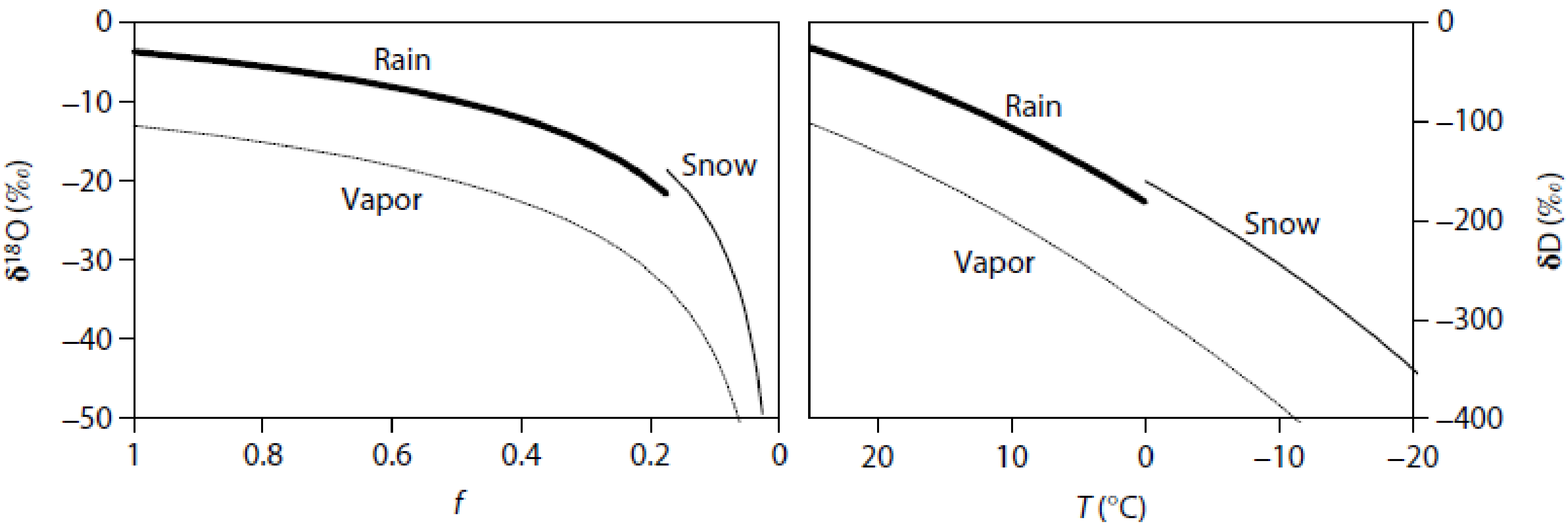


FIGURE 5.4 The evolution in the ^{18}O content of precipitation according to an ideal Rayleigh distillation during rainout. Deuterium follows a similar depletion trend.

Taken from Clark (2015)

Precipitation fractionation

- Ideal development:



(a) (b)

FIGURE 5.5 The evolution of $\delta^{18}O$ and δD in rain and snow during rainout. (a) Plot shows the depletion for both ^{18}O and D as the residual vapor fraction diminishes toward 0. Both isotopes follow the same depletion (but on different scales) with decreasing residual vapor fraction *f*. (b) Plot shows the ideal evolution of $\delta^{18}O$ and δD for a single vapor mass undergoing cooling, showing the co-depletion in ^{18}O and D with decreasing temperature *T*. Note the jump to higher $\delta^{18}O$ and δD at the rain-to-snow transition due to the greater fractionation between vapor and ice versus vapor and water.

Taken from Clark (2015)

Correlation of $\delta^{18}O$ and temperature in precipitation

- Observable in longer-term comparison (annual or monthly averages)

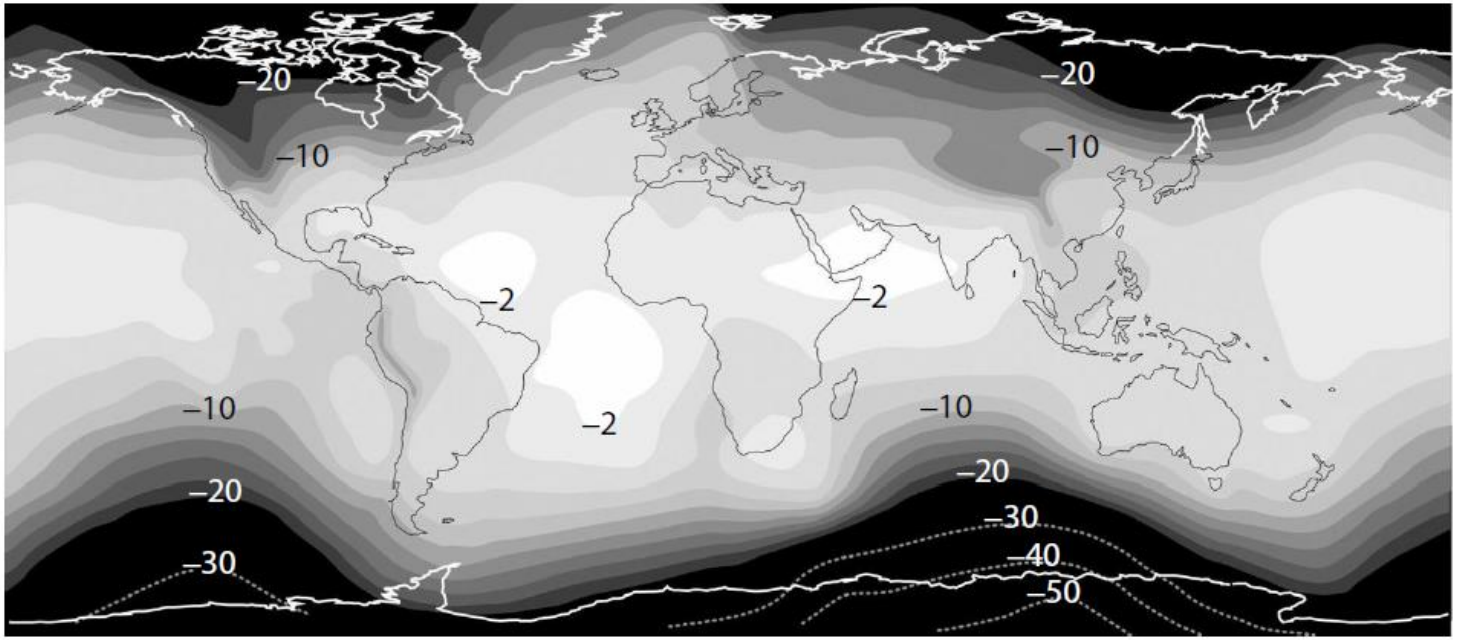


FIGURE 5.6 Global map of $\delta^{18}O$ for precipitation, based on annual averaged data from collected from International Atomic Energy Agency (IAEA) stations over the past 30 years (Rozanski et al. 1993). These long-term data are available at the IAEA Global Network for Isotopes in Precipitation program website.

Taken from Clark (2015)

Correlation of $\delta^{18}O$ and temperature in precipitation

- Correlation indicates little development of rainwater

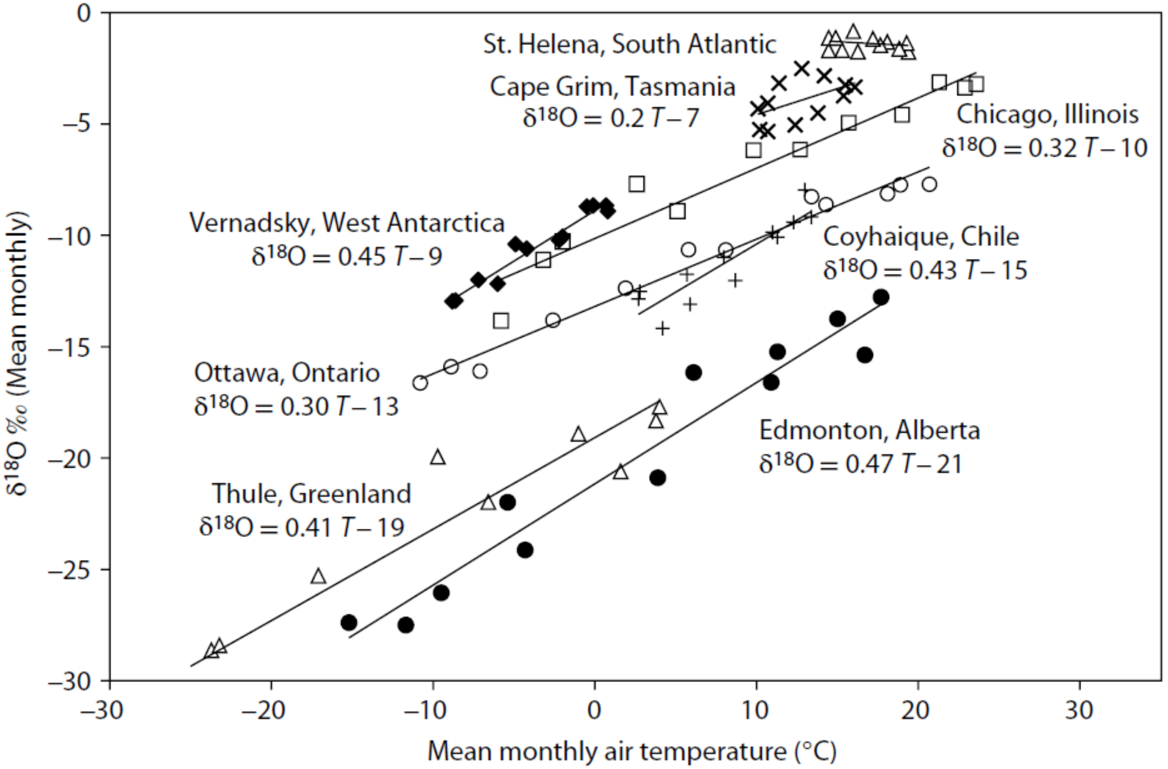


FIGURE 5.7 The correlation between mean monthly air temperature and $\delta^{18}O$ in precipitation at a selection of stations.

Taken from Clark (2015)

Deviations from the ideal

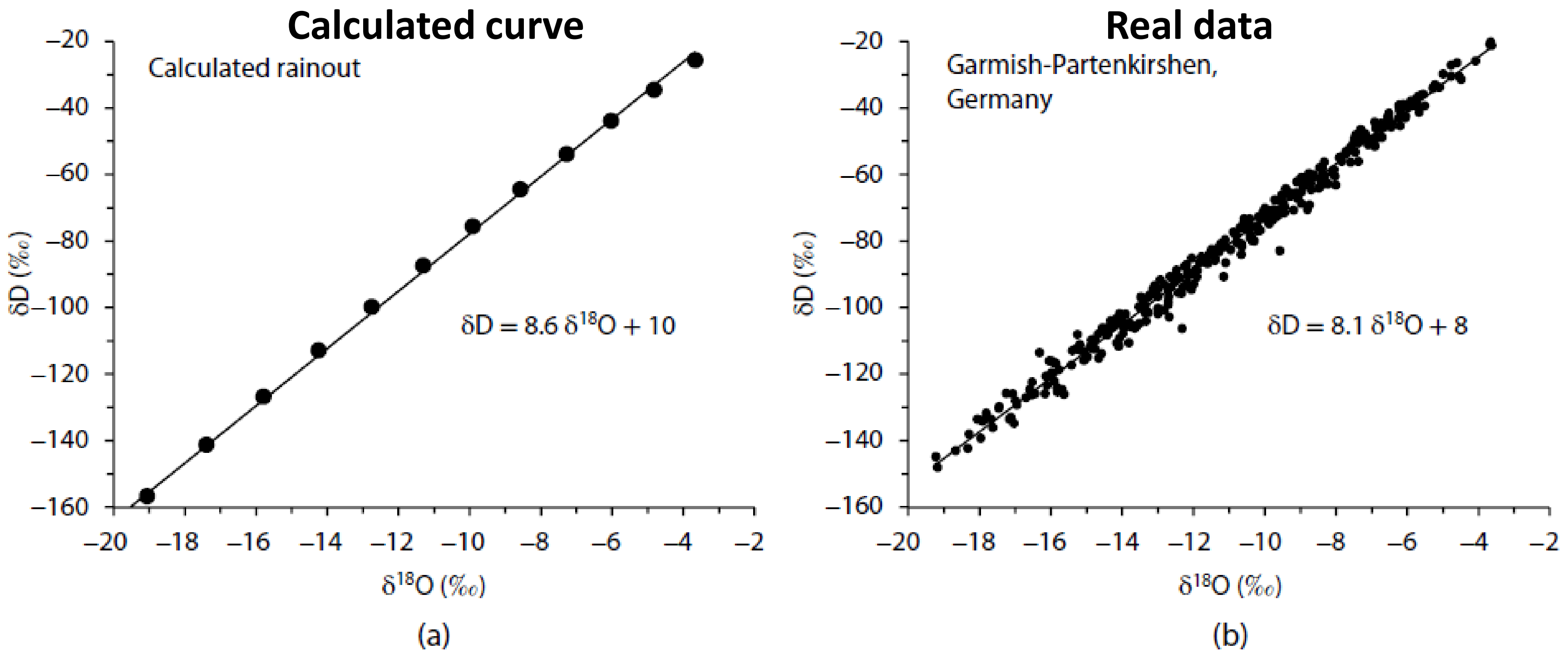
- Problematic correlations of individual events
- Additional water supplied by evaporation from rivers and lakes
  - Mixing of water vapor in the troposphere
  - Precipitation dynamics (vertical gradient of condensation and transport)
- Relationships fit long-term averages well
- Description of empirical relationships

Meteoric water lines

- Global Meteoric Water Line (GMWL)

$$\delta D = 8\ \delta^{18}O + 10‰$$

- Average of many local/regional MWL
  - Various slopes and intersections
- Slope 8 = stronger fractionation of D
  - Increases with lower temperature



(a) (b)

FIGURE 5.8 (a) Meteoric water line for $\delta^{18}O$ and δD in precipitation during rainout calculated using equilibrium fractionation factors, $\varepsilon^{18}O$ and εD, for water–vapor. (b) The meteoric water line for Garmish, Germany, based on precipitation data from 1978 to 2005 (From IAEA/WMO, The GNIP Database, 2013.)

Taken from Clark (2015)

- Observed MWL differs from calculations
- Consequence of non-ideal fractionation

Other influences on the MWL

- Mixing of water vapor of different composition as it moves through the troposphere
- Evapotranspiration from areas of the continent over which the water has passed
- Evaporation after condensation (especially if the air is dry before precipitation)
  - Another enrichment by ^{18}O
  - Necessary to take into account the precipitation intensity – in dry regions significant shifts (extreme effect of evaporation on rain) up to slope 7
  - Weighted averages

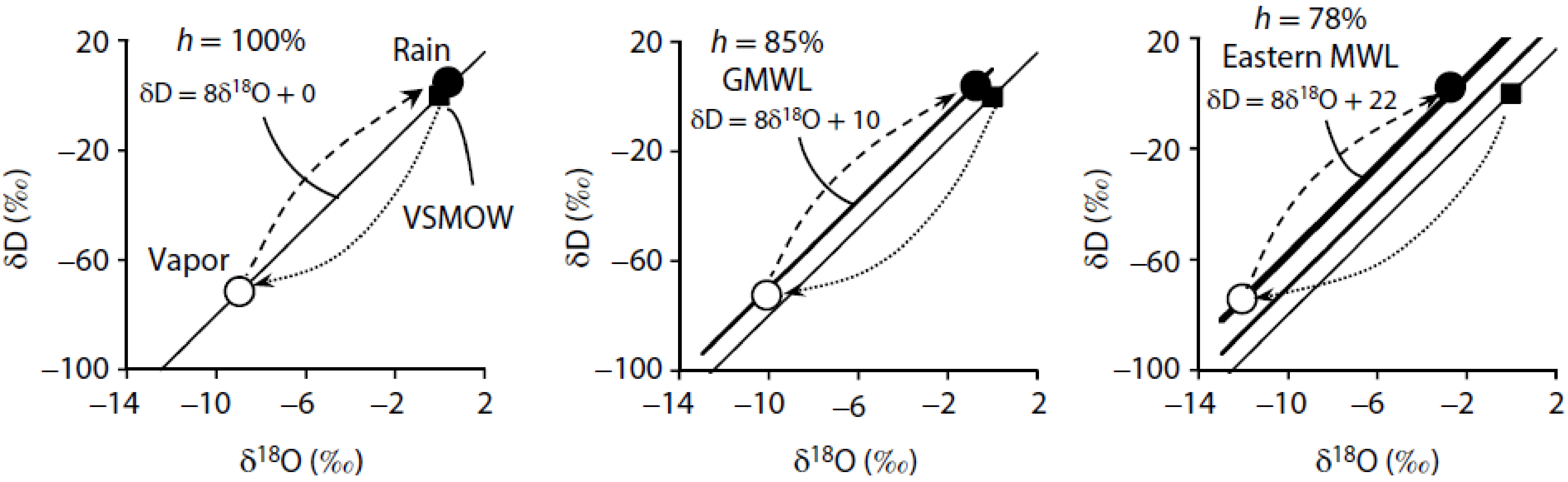
Intersection with D

- MWL does not pass through the SMOW value, at the intersection the D value is +10‰ (deuterium excess)

$$d = \delta D - 8\,\delta^{18}O$$

- It varies regionally in the range from ca. 0 to 20‰
- Influence of kinetic fractionation (nonequilibrium) – faster evaporation than condensation (influence especially on ^{18}O)

Taken from Clark (2015)



Differences in LMWL

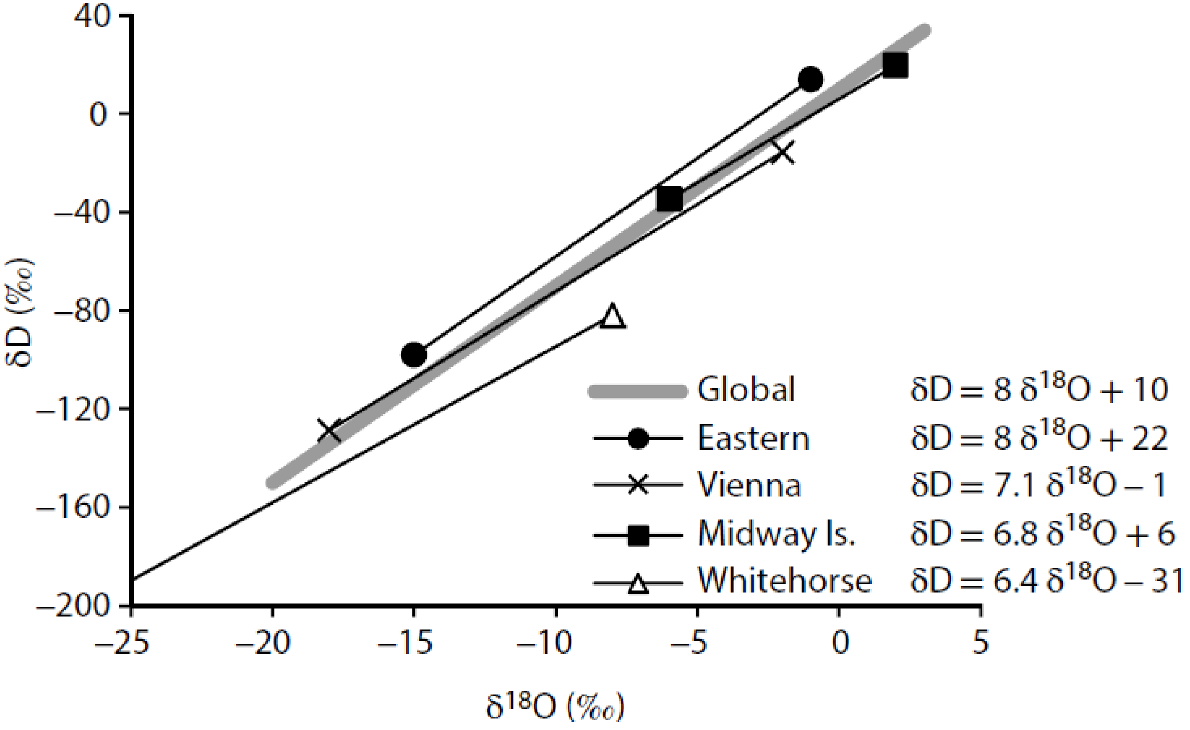


FIGURE 5.11 Local meteoric water lines for selected stations in the International Atomic Energy Agency global network for isotopes in precipitation (GNIP IAEA/WMO 2013).

Taken from Clark (2015)

- Complicates evaluation and comparison

Differences in LMWL

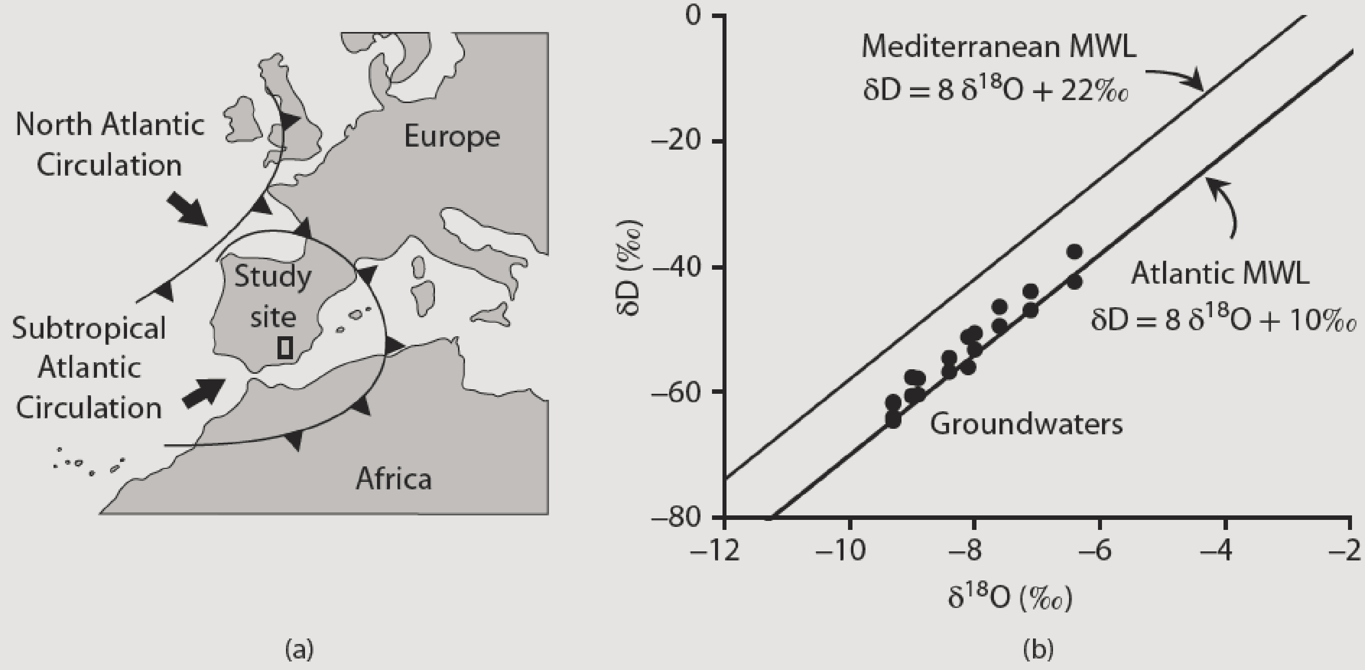


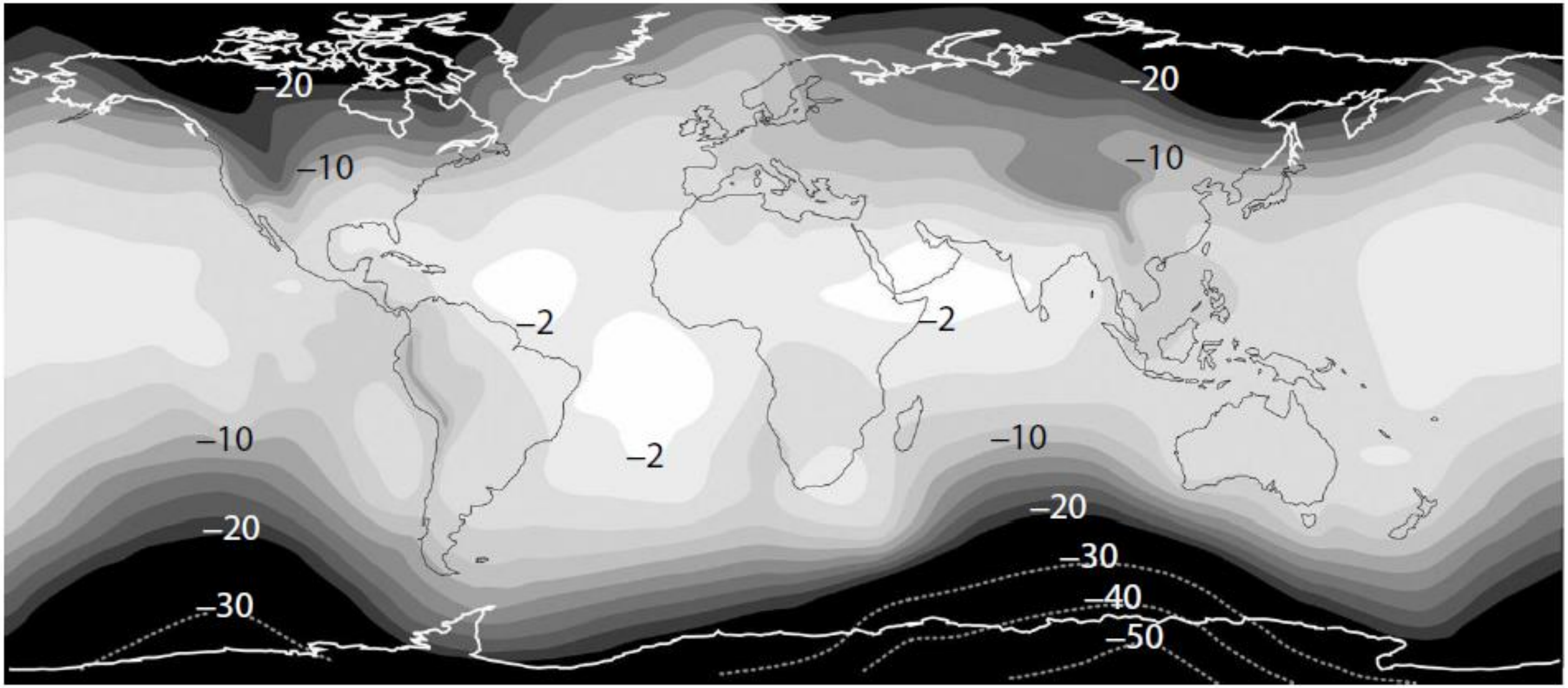
FIGURE 5.12 Source of water vapor for precipitation recharging groundwaters in Mediterranean Spain. (a) Recharge region and the two principal origins of water vapor. (b) Strong deuterium excess in the precipitation from the Mediterranean ($d = 22‰$) and from the Atlantic ($d = 10‰$). Despite proximity to the Mediterranean coast, groundwaters are largely recharged by cyclonic activity in the Atlantic arriving from the northwest (After Cruz-San Julian et al. 1992.)

Taken from Clark (2015)

- Determining origin of water

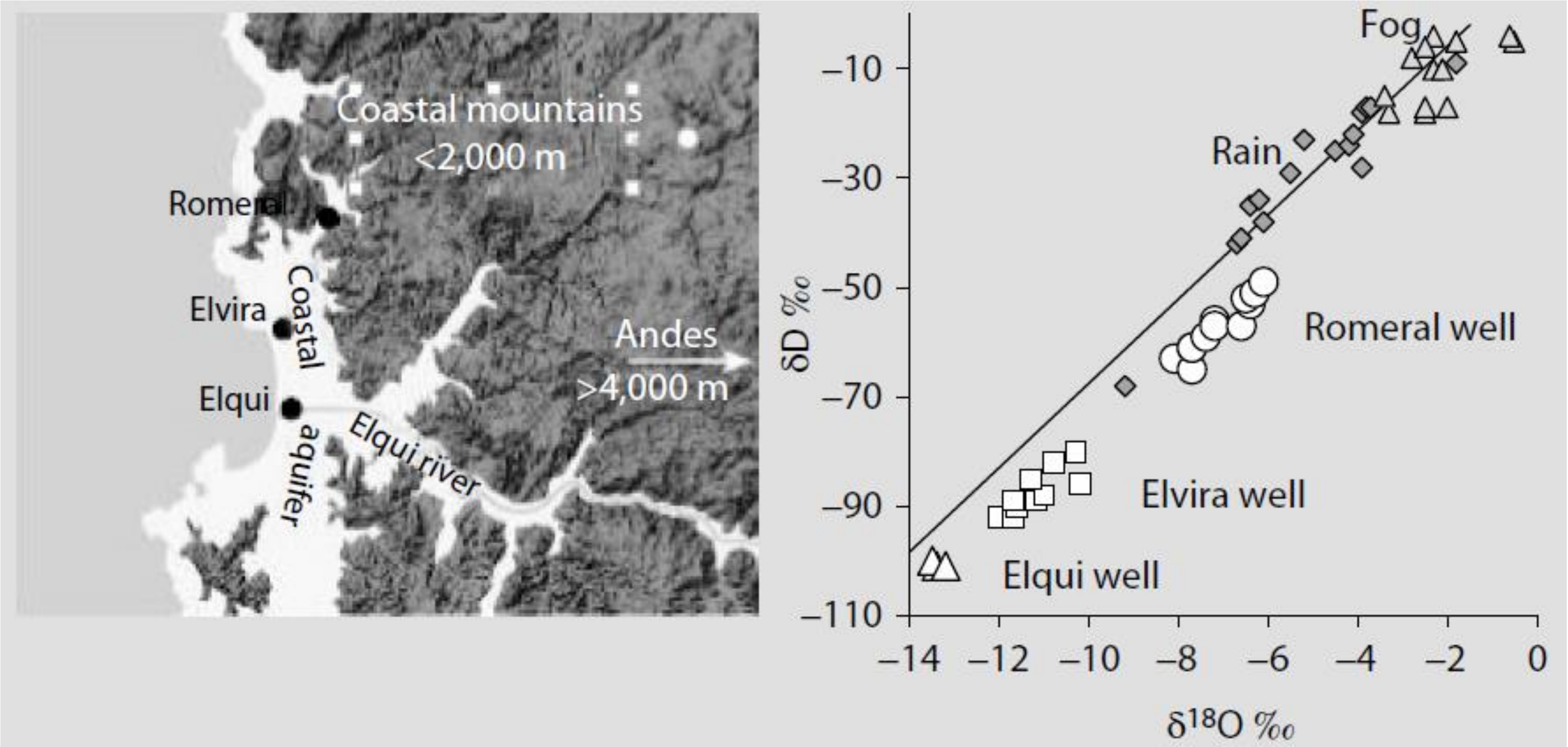
Temperature effects in precipitation

- Distance from the ocean, altitude
- Distinctive origin of groundwater



Taken from Clark (2015)

Example

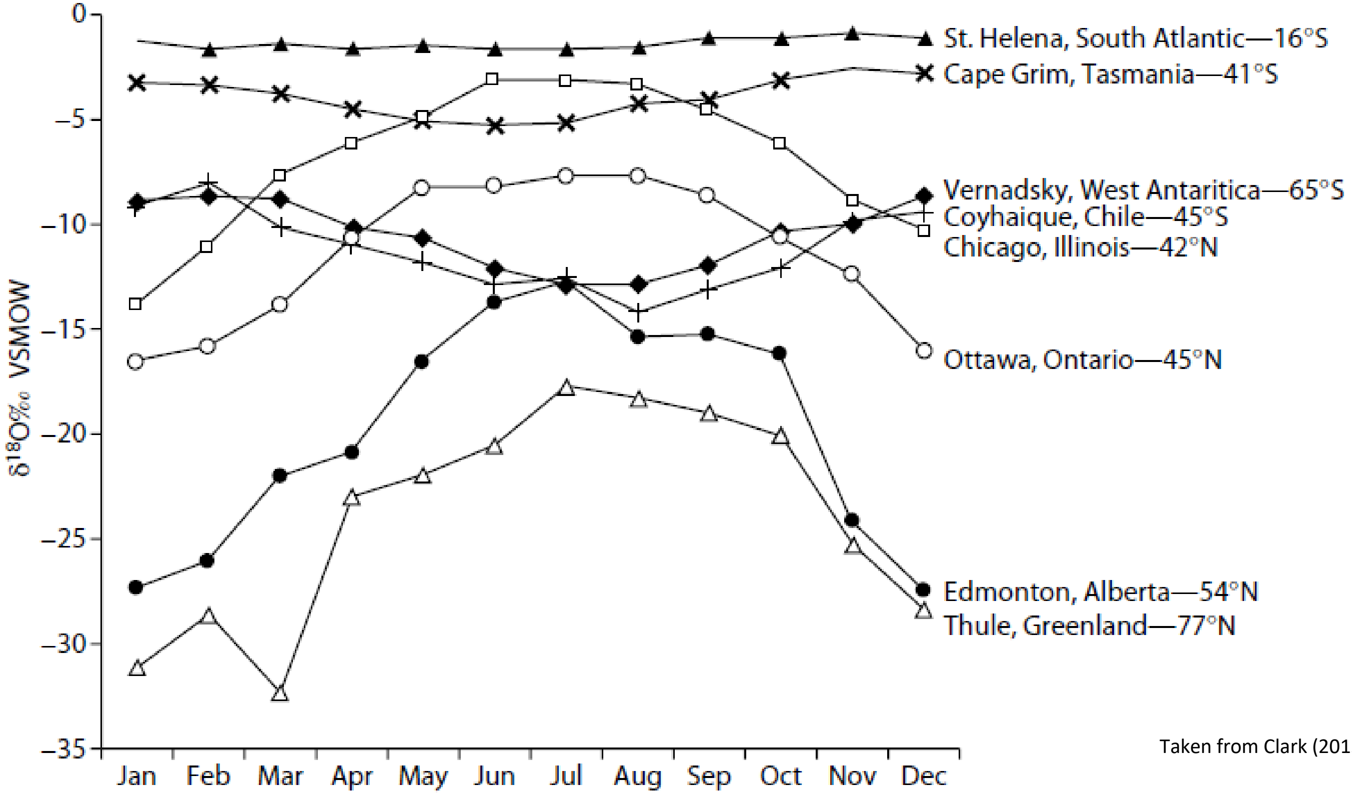


Taken from Clark (2015)

- Coast of Chile – scarce rainfall (100 mm/year)
- What can we say about the origin of waters?

Seasonal effects

- Altitude, distance from the sea and climate zone
- Differences in summer/winter rainfall composition – observable in surface- and ground- water



Taken from Clark (2015)

Example

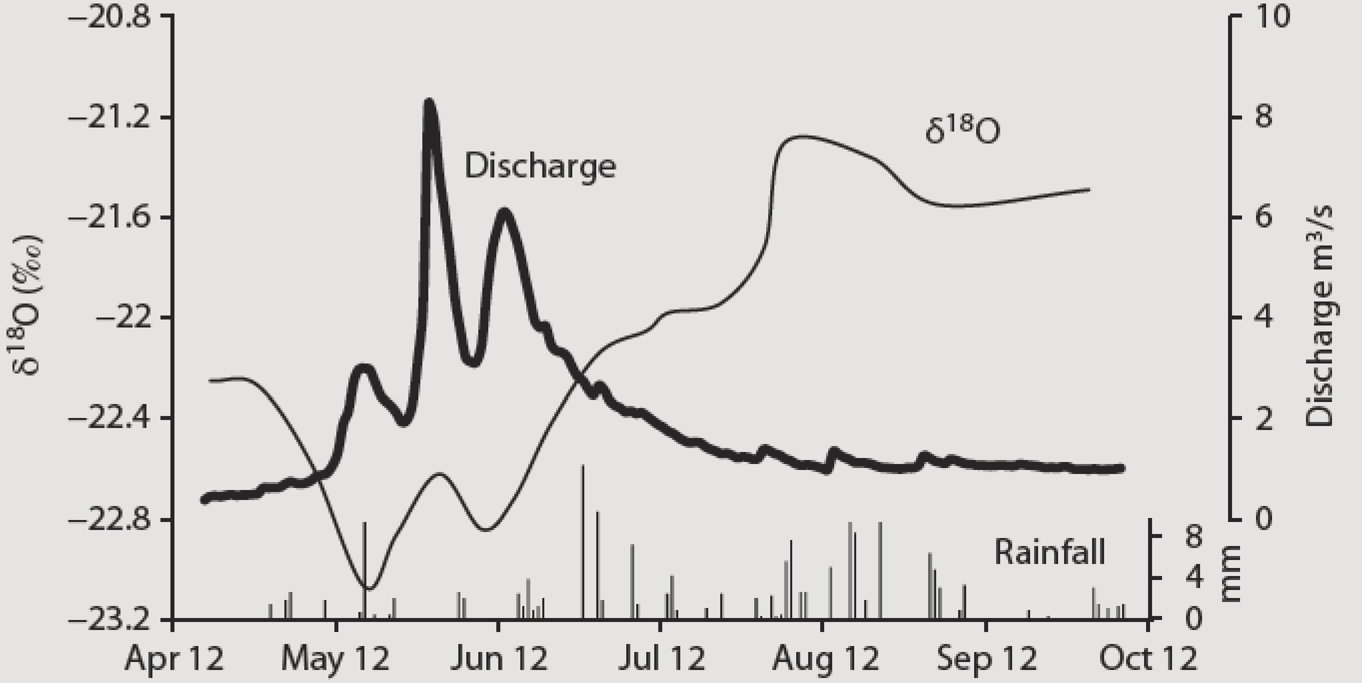


FIGURE 5.16 Flow rate and $\delta^{18}O$ for Wolf Creek basin discharge from spring snowmelt through to the beginning of freeze-up in October 2012. (Data from Li, T. 2013.)

Taken from Clark (2015)

- Alaska – a small catchment area in the permafrost region
- What can we say about the origin of the water in the stream?

Paleoclimatic applications

- Strong correlation of T and $\delta^{18}O$
- Isotopic composition of ice and snow
  - Temperature changes over the last 650,000 years
- Values of $\delta^{18}O$ in calcite precipitated from groundwater (speleothemes)
- Groundwater from the end of the Pleistocene trapped in the aquifers with deep circulation (the high hydraulic gradient of the melting glacier pushed them to a depth from which they wash out extremely slowly).

Paleoclimatic applications

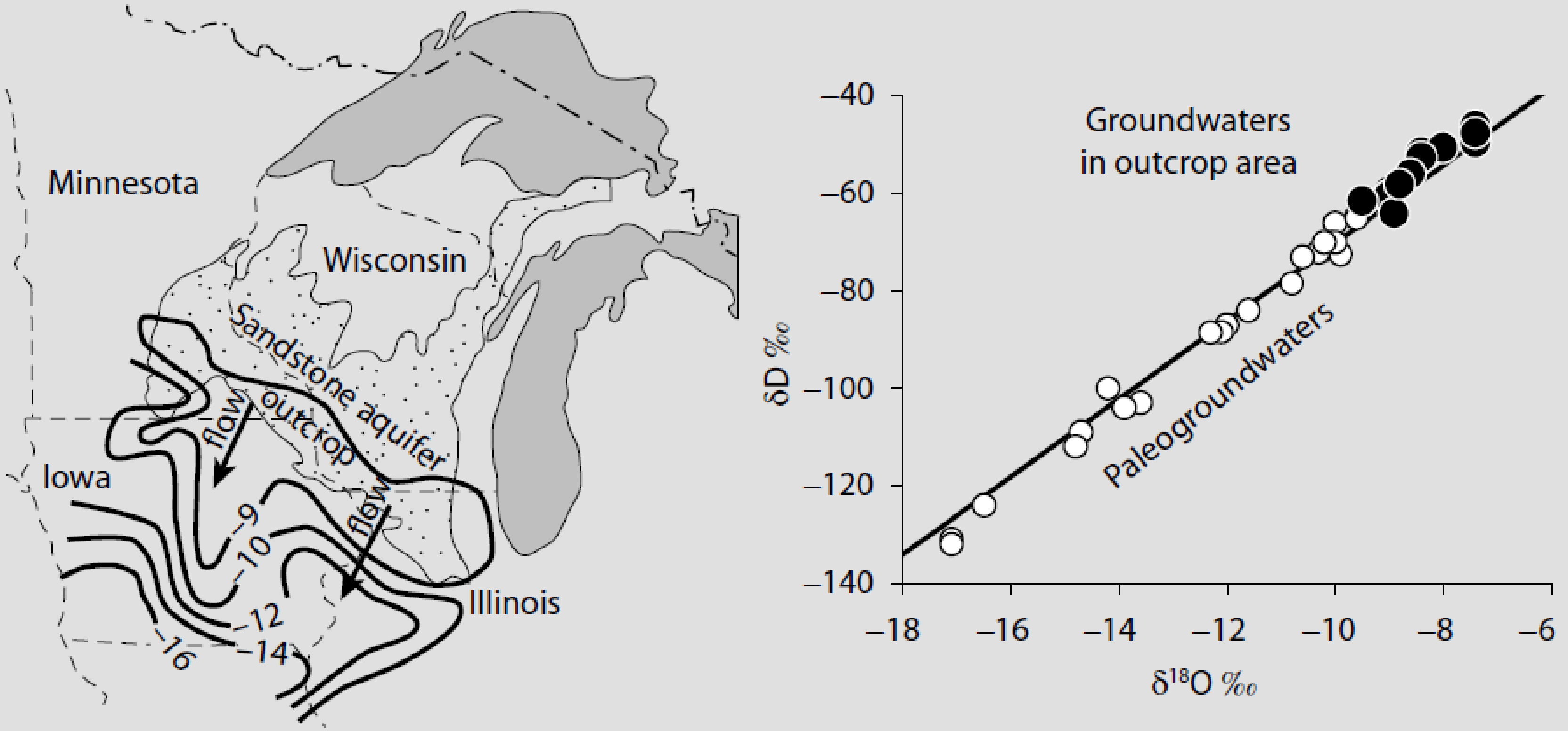


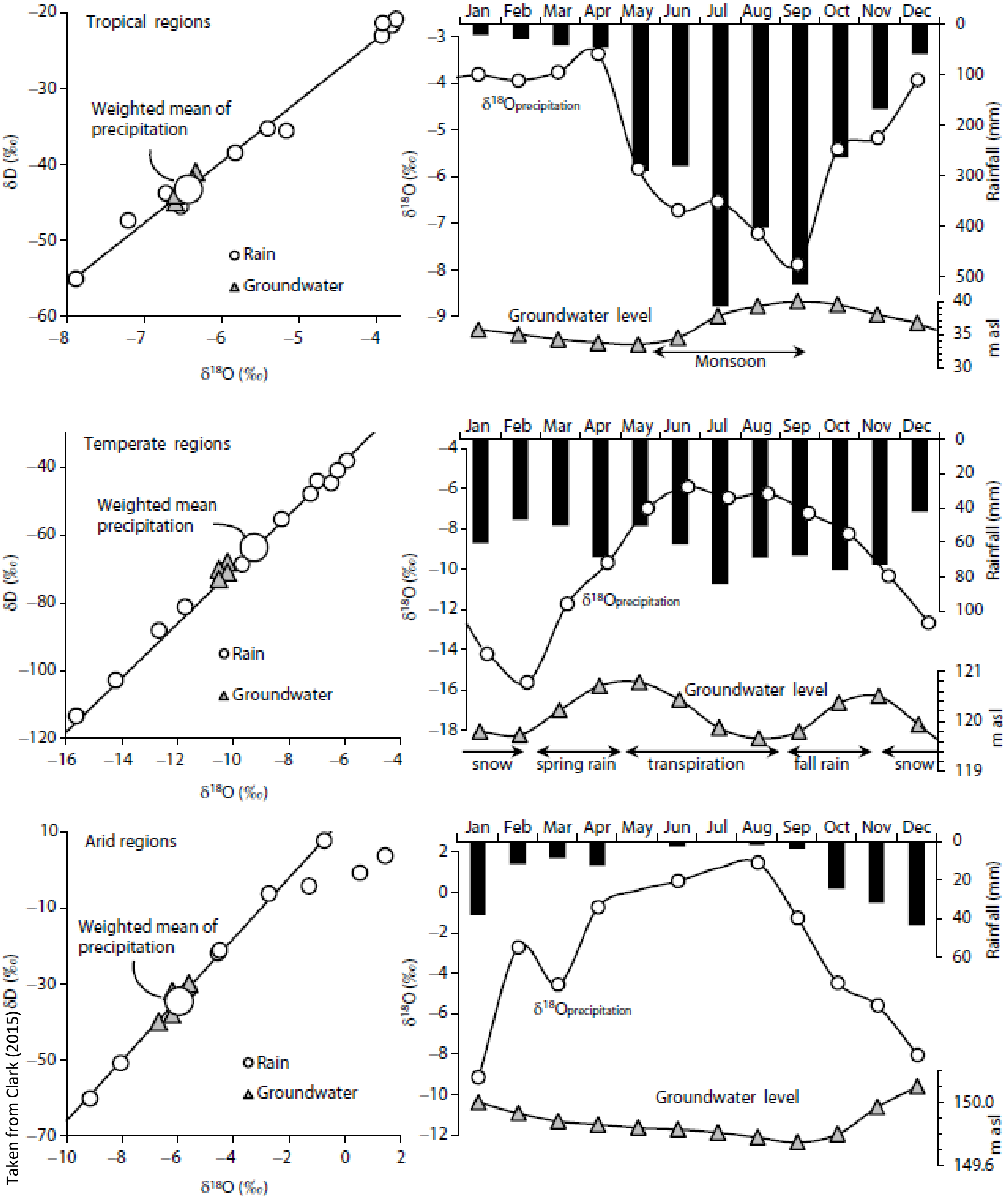
FIGURE 5.19 Glacial meltwater recharged into the Cambrian–Ordovician sandstone aquifer where it outcrops in the northern United States (After Siegel and Mandle 1984). Groundwaters are a mixture of modern precipitation ($\delta^{18}O > -9‰$) and glacial meltwater ($\delta^{18}O$ to −16‰).

Taken from Clark (2015)

- Glacial waters in aquifers.

Groundwater recharge

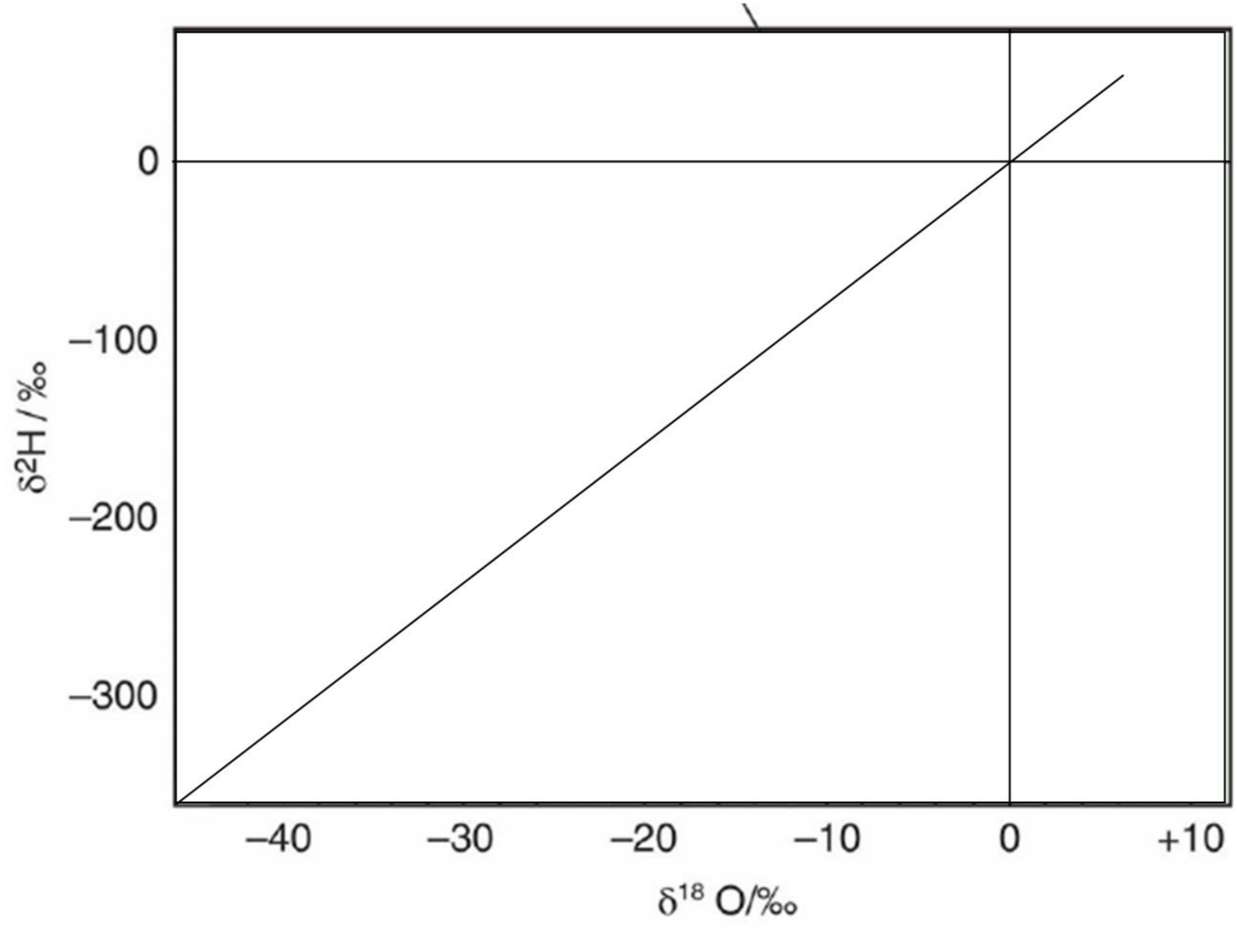
- Infiltration-related processes dampen isotopic variations in groundwater
  - Water mixing, dispersion, evapotranspiration…
- Determination of the average isotopic composition from the monthly averages is problematic
- Weighted averages taking into account precipitation totals
- We can usually simplify the composition of groundwater to the annual weighted average precipitation composition.



Taken from Clark (2015)

- In the tropics, the seasonal precipitation (monsoon) is strongly distorted.
  - The weighted average solves this problem
- In the temperate zone, groundwater is replenished mainly by melting snow and precipitation in spring and autumn.
  - Due to evapotranspiration, decreased summer groundwater recharge
  - The weighted average tends to be heavier than groundwater
- In arid areas, distortion occurs due to the direct evaporation of small precipitation events.
  - Solved by weighted average

Exercises



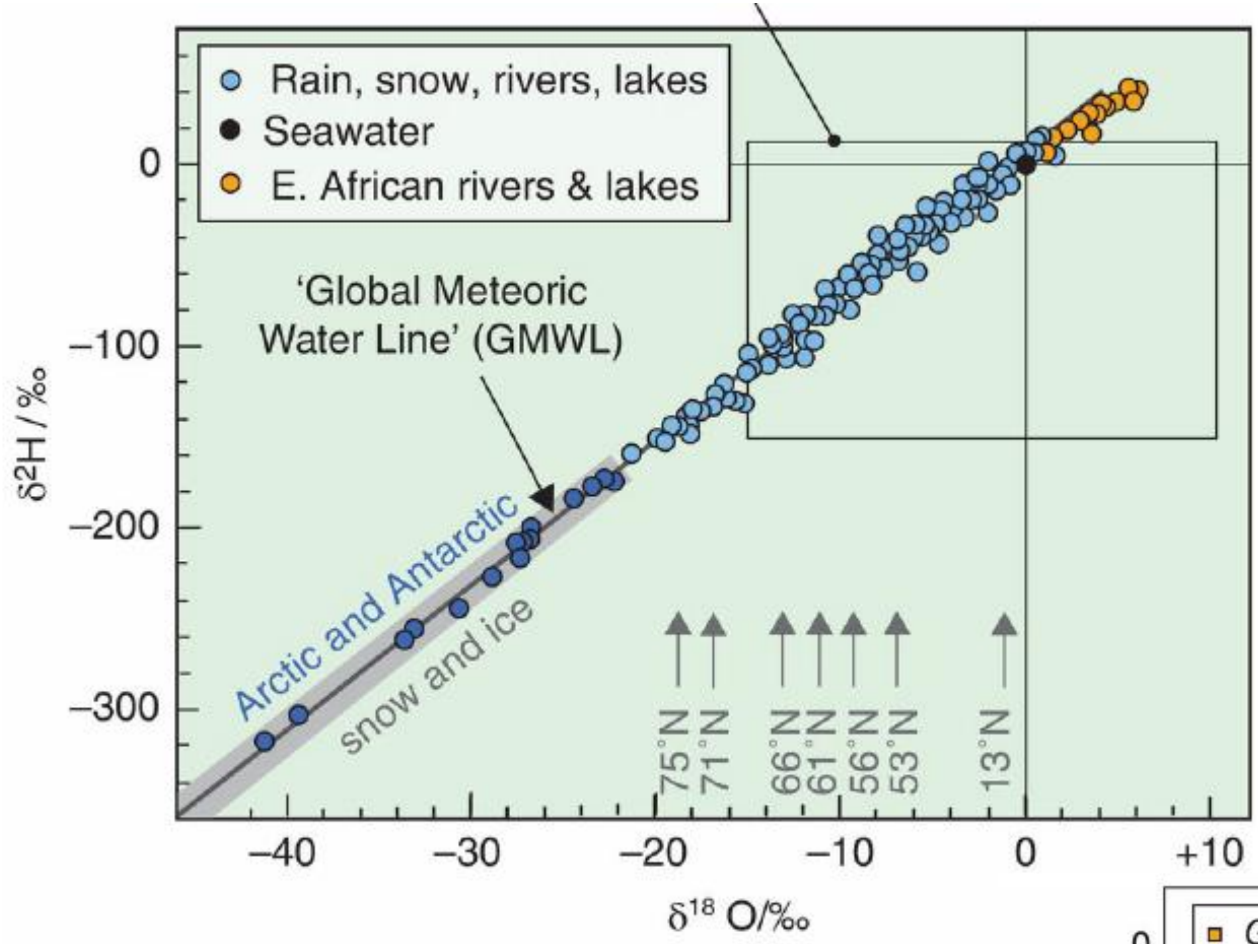
Plot the following points / areas in the H_2O isotopic composition graph:

(a) Average seawater composition (Standard Mean Ocean Water - SMOW)

b) Rainwater

c) Equatorial lakes and rivers with high evaporation

d) Water in polar glaciers



Taken from Gill (2015) by Craig (1961 , 1963) and Taylor (1974)

We can isotopically distinguish three types of water:

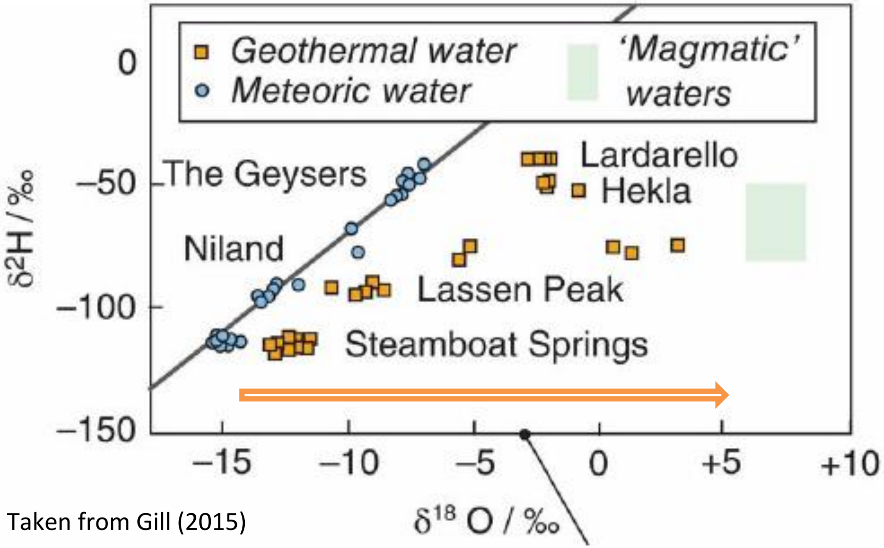
a) Marine

b) Precipitation

c) Geothermal

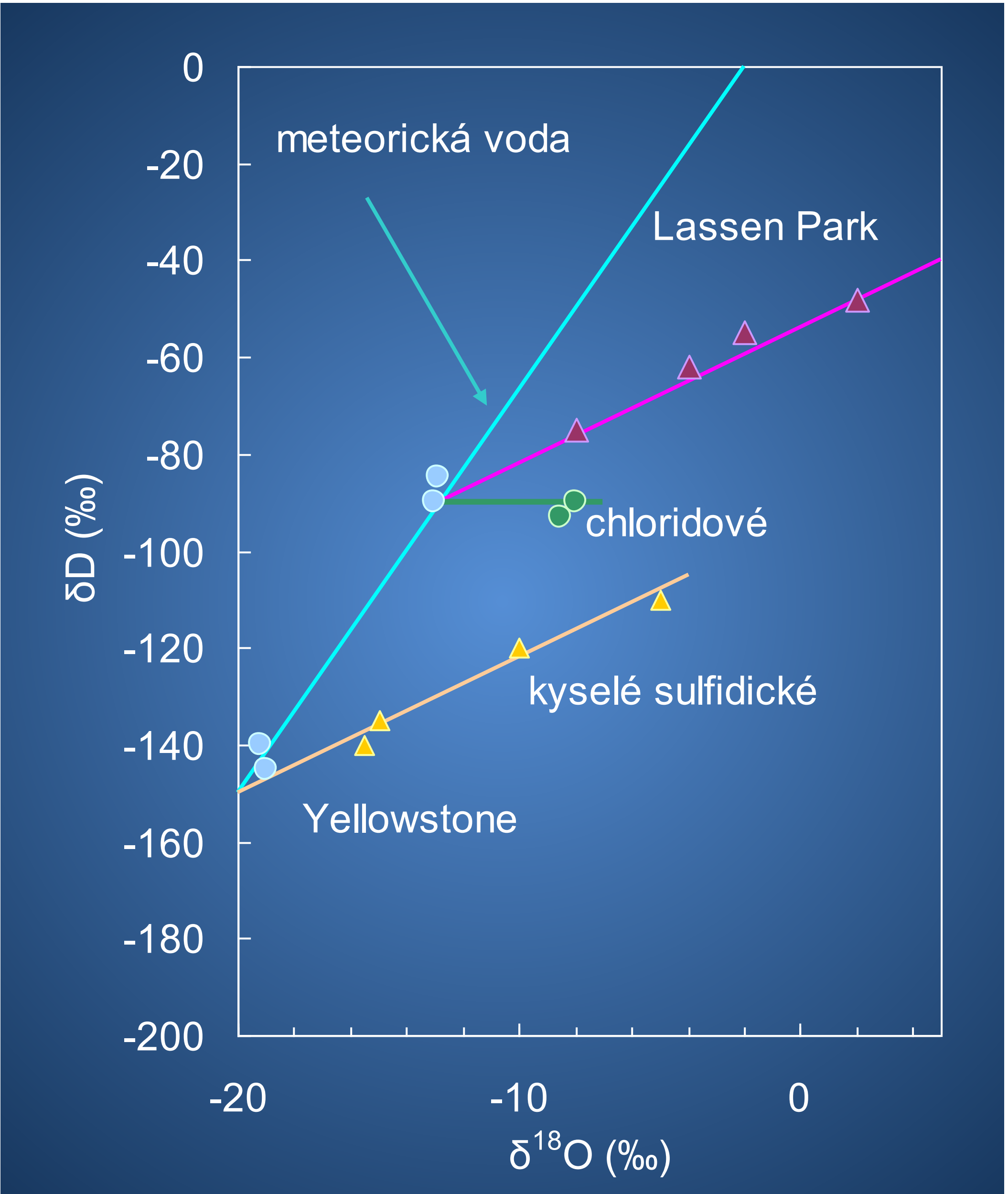
Geothermal waters follow rainwater with respect to δ^2H, but contact with silicate rocks increases δ^{18}O

Large amounts of water interacting with the rock can "imprint" their isotopic composition (ie reveal the origin of the fluid in the processes).



Taken from Gill (2015)

Hydrothermal systems



Fractionation of δD and $\delta^{18}O$

in meteoric hydrothermal systems.

Fractionation occurs due to

heating, boiling and water mixing.

$\delta^{13}C$

	The value of $\delta^{13}C$
Carbonates in sea water	~ 0 ‰
Atmospheric CO_2	−7 ‰
Organic matter	Significantly depleted depending on the mechanism of photosynthesis (C3 and C4)
Plankton – tropics	−20 ‰
Plankton – polar oceans	−25 to −30 ‰
Terrestrial plants	Very variable with a diameter of around −25 ‰
Soil CO_2	−20 ‰
CO_2 in precipitation	Negative, very variable
Carbonates formed in the oceans	Close to zero

$\delta^{13}C$ groundwater

- Determined by the balance of carbon sources and sinks
- Main sources
  - Dissolution of carbonate minerals (relatively heavy carbon)
  - Oxidation of organic matter (relatively light carbon)
  - CO_2 from the soil atmosphere (relatively light carbon)
- Metanogenetic redox processes
  - Methanogenesis produces very light methane and heavy CO_2
  - Oxidation of methane produces light CO_2

Utilization of $\delta^{13}C$

- Carbon origin:
  - Organic (light)
  - Inorganic (heavy)
- Origin of secondary carbonate minerals

Radioactive isotopes

- Tritium, ^{14}C
- Water dating – water with T will be younger than 1950
- Radiocarbon method applicable to organic substances in water
- Problem of water mixing!

^{18}O in carbonates – the key to the paleoclimate

- Calcite in equilibrium with seawater is slightly enriched by ^{18}O.
- The fractionation coefficient is strongly temperature dependent.
- Oxygen ratios in marine carbonates serve as indicators of sea temperature during formation -> paleoclimatic reconstruction.

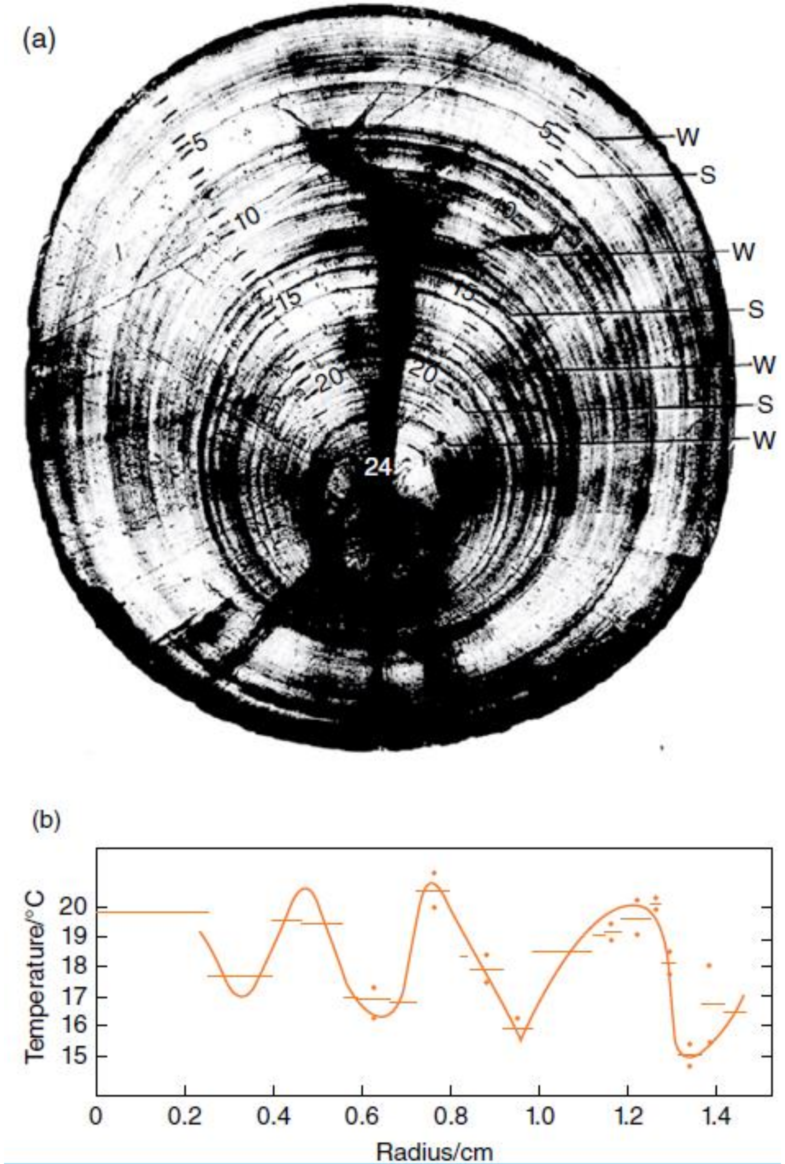
$$\alpha_{water}^{calcite} = \frac{\left({}^{18}\mathrm{O}/{}^{16}\mathrm{O}\right)_{calcite}}{\left({}^{18}\mathrm{O}/{}^{16}\mathrm{O}\right)_{water}}$$

$$\alpha_{water}^{calcite} = 1.0286\ (25°\mathrm{C})$$

$$T[°\mathrm{C}] = 16.5 - 4.3 \times \Delta_{water}^{calcite} + 0.13 \times {\Delta_{water}^{calcite}}^{2}$$

Paleoclimate

- Urey et al. (1951): fractionation of ^{18}O between calcite and water on the example of Jurassic belemnite from the Isle of Skye.
- 4 summer and winter seasons identified.
- Uncertainty is connected with the composition of seawater.



Taken from Gill (2015) according to Urey et al. (1951)

Paleoclimate

$\delta^{18}O$ in the sea is not constant, it changes with temperature due to the deposition of isotopically lighter water in glaciers

Glaciers of Greenland: −30 to −35‰

Antarctic glaciers: −50‰

The total variability of sea water is 1‰

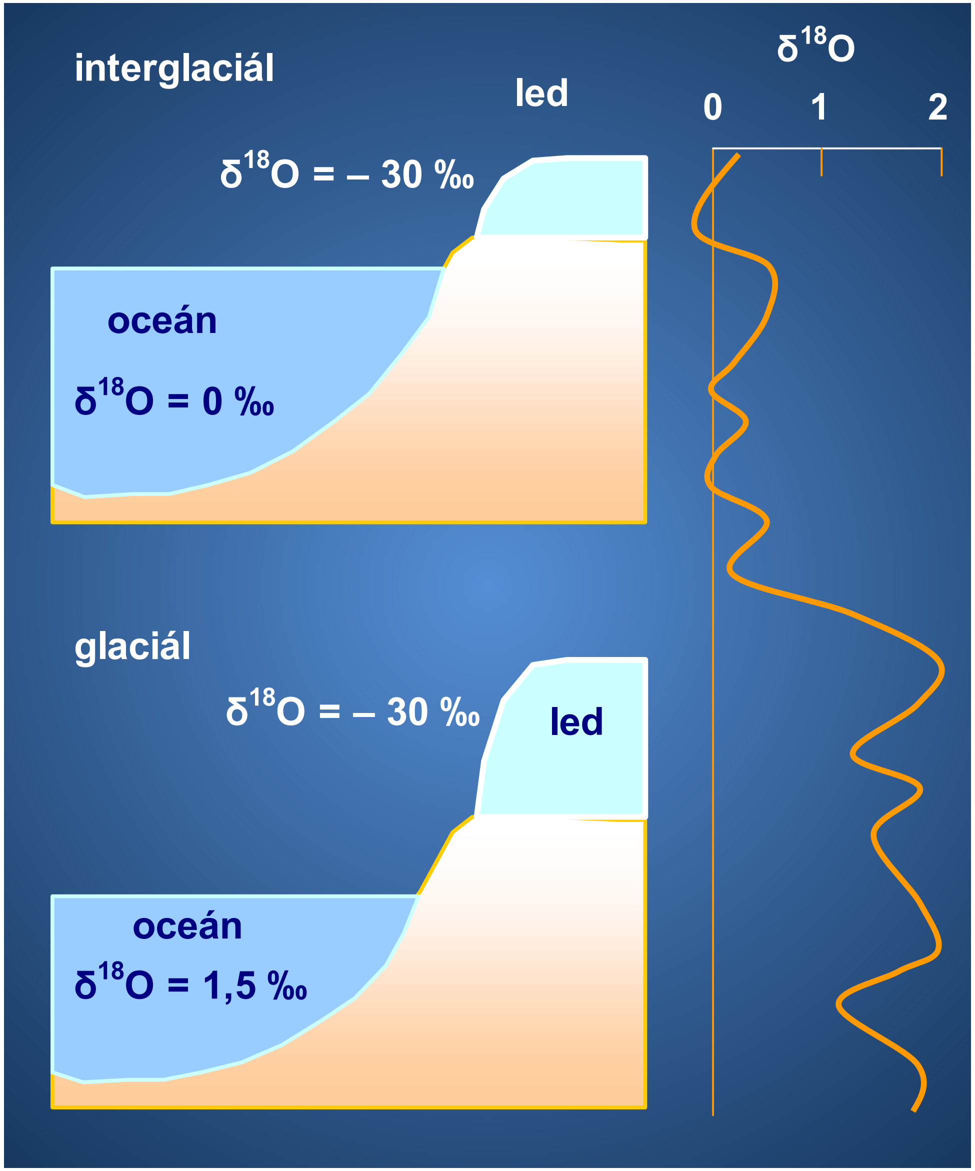
Today's state:

Continental ice: 27.5 million km^3

Water in the oceans: 1350 million km^3

Ice ages: increase in ice by 42 million km^3

level reduction by 125 m



Glaciers

- $\delta^{18}O$ and $\delta^{2}H$ in polar ice changes depending on the temperature during snowfall.
- The Vostok well in East Antarctica provides a dated record for 420,000 years.

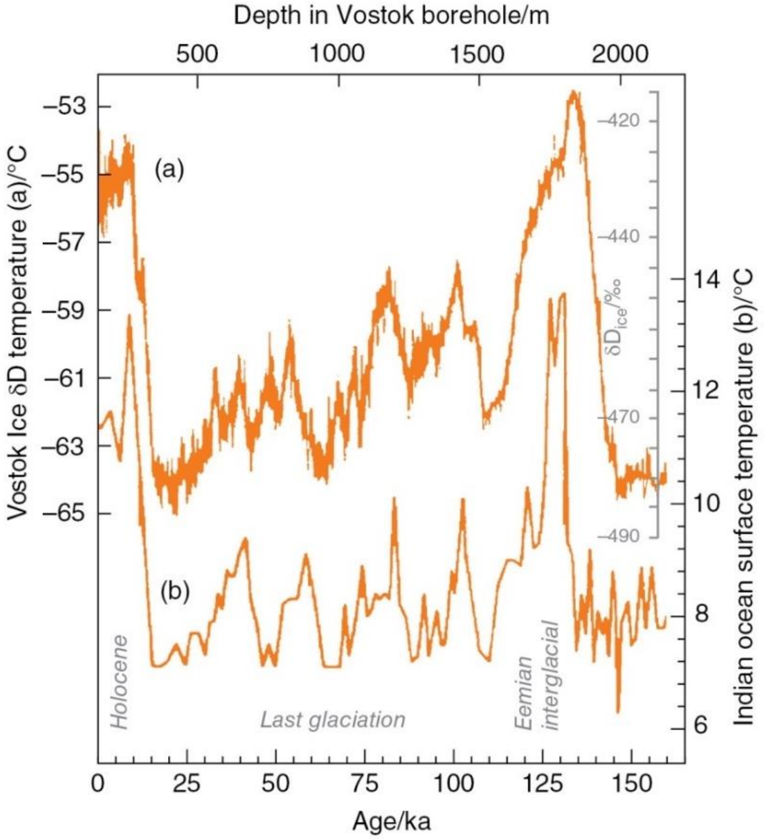
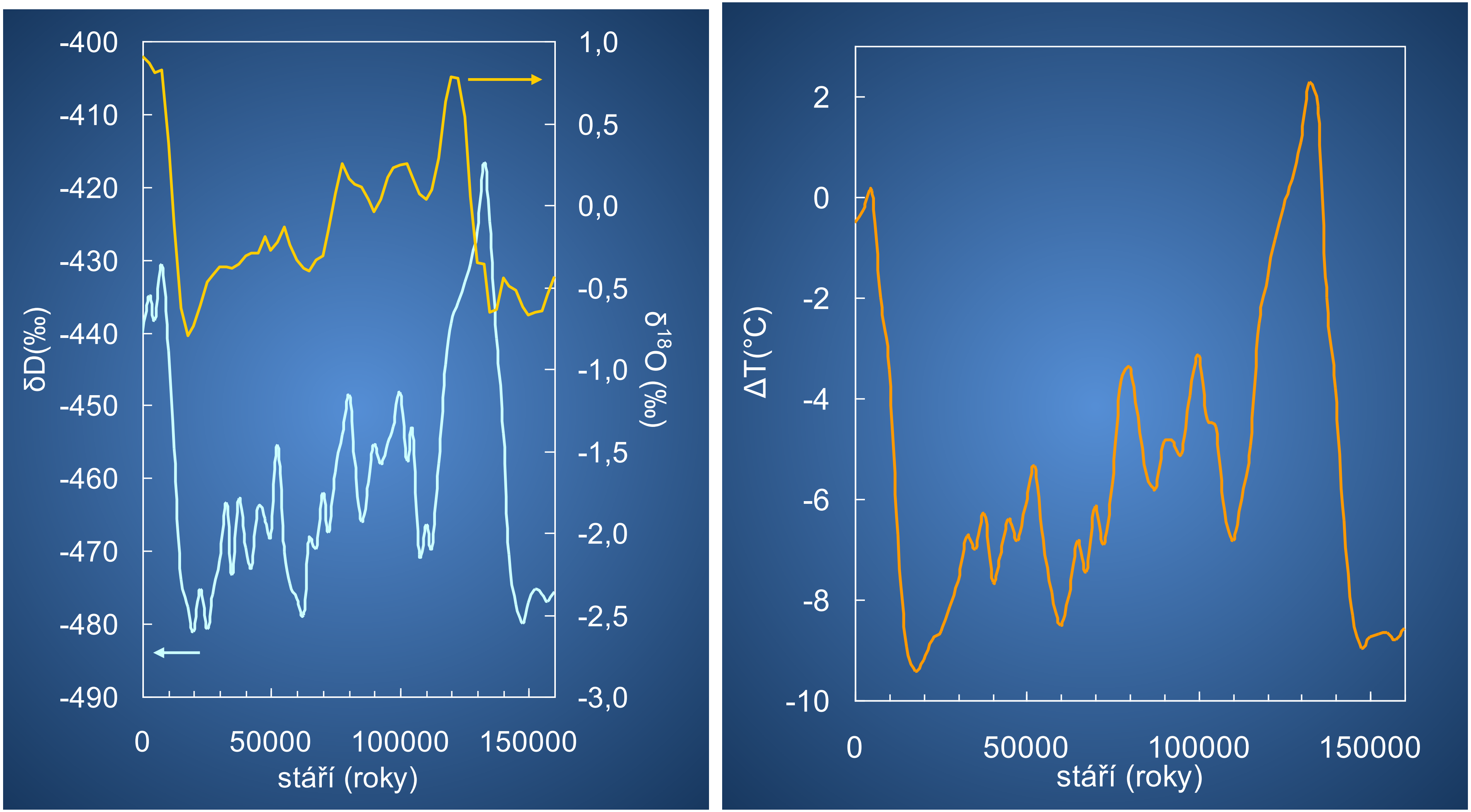


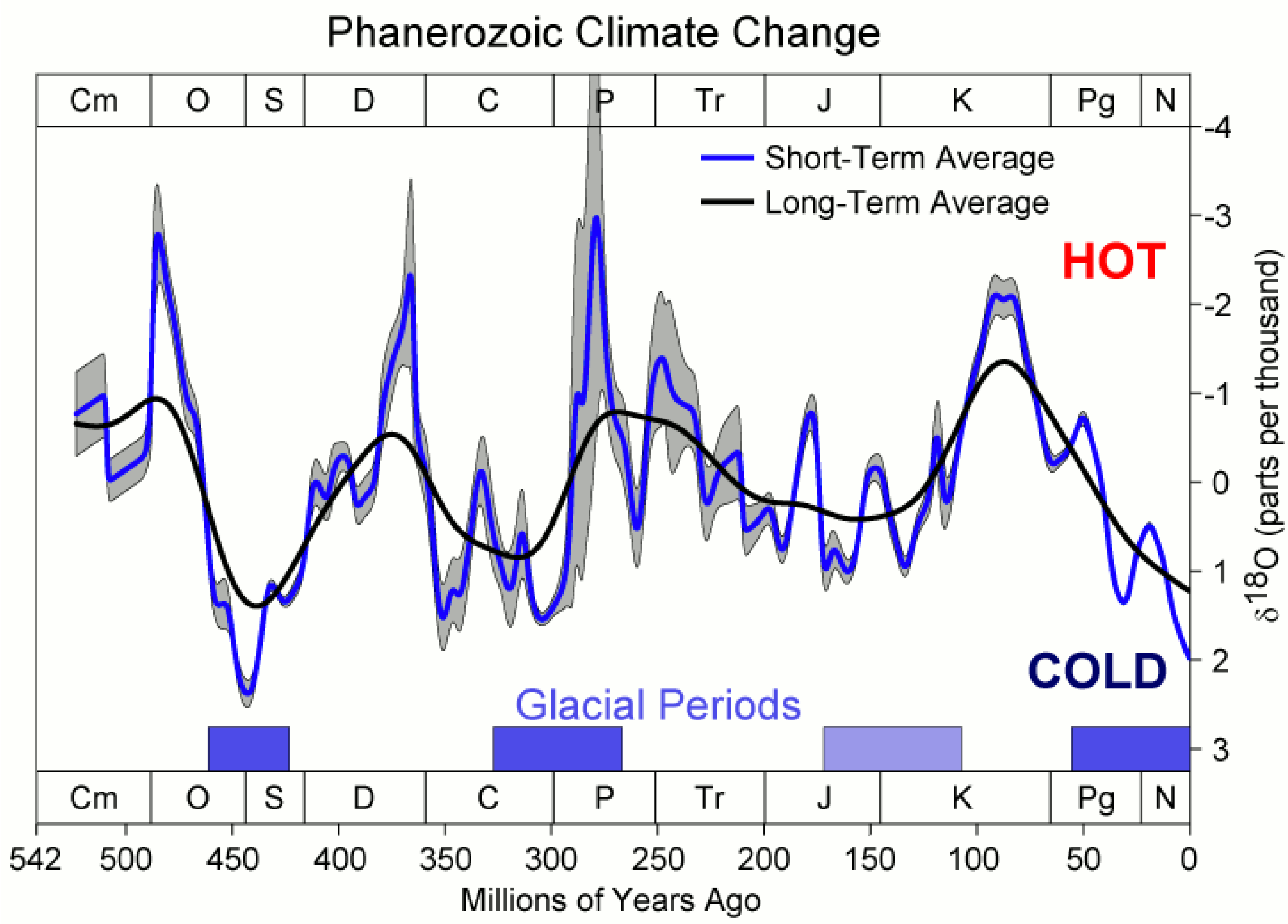
Figure 10.12 (a) Variation in mean annual surface temperature at Vostok Station in East Antarctica over the past 160,000 years (left-hand scale), based on δD measurements on Vostok deep ice cores; the orange scale on the right indicates the corresponding δD values (b) Variation over the same period of summer sea-surface temperature (scale on far right), based on statistical analysis of radiolarian assemblages in borehole RC11-120 in the southern Indian Ocean. (Source: Adapted from Jouzel *et al.*, 1987. Reproduced with permission of Nature Publishing Group; Data from Martinson *et al.*, 1988.)

Fractionation in ice



Reconstruction of paleotemperatures from ice of Vostok well based on δD. The $\delta^{18}O$ curve shows changes in the isotopic composition of the ocean derived from sediment carbonates.

Paleoclimatic data



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Example 3

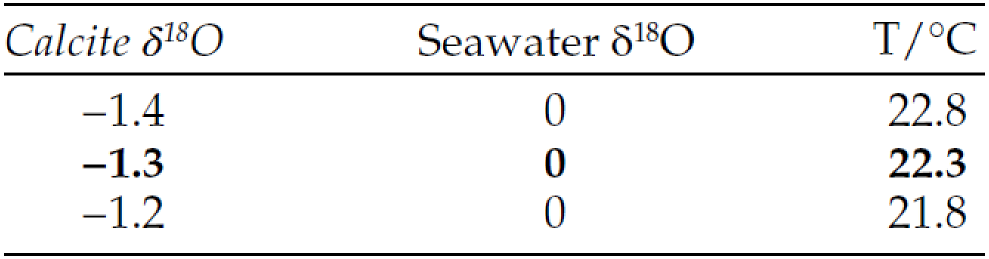
- Analysis of Neogene sea limestone showed a value of $\delta^{18}O = -1.3 \pm 0.1$ ‰.
- Determine the temperature of the seawater in which it was stored. We assume that the isotopic composition of water was the same as today.

$$T[°\mathrm{C}] = 16.5 - 4.3 \times \Delta_{water}^{calcite} + 0.13 \times {\Delta_{water}^{calcite}}^2$$

$$\delta_a - \delta_b = \Delta_b^a$$

Example 3

- Analysis of Neogene sea limestone showed a value of $\delta^{18}O = -1.3 \pm 0.1$ ‰.
- Determine the temperature of the seawater in which it was stored. We assume that the isotopic composition of water was the same as today.



Calcite $\delta^{18}O$	Seawater $\delta^{18}O$	T/°C
−1.4	0	22.8
−1.3	**0**	**22.3**
−1.2	0	21.8

Example 3

- Analysis of Neogene sea limestone showed a value of $\delta^{18}O = -1.3 \pm 0.1$ ‰.
- Determine the temperature of the seawater in which it was stored.
- How do the values change if we assume that the variation in $\delta^{18}O$ for water could be up to 1‰ (ie ± 0.5‰)?

Example 3

- Analysis of Neogene sea limestone showed a value of δ ^{18}O = −1.3 ± 0.1 ‰.
- Determine the temperature of the seawater in which it was stored.
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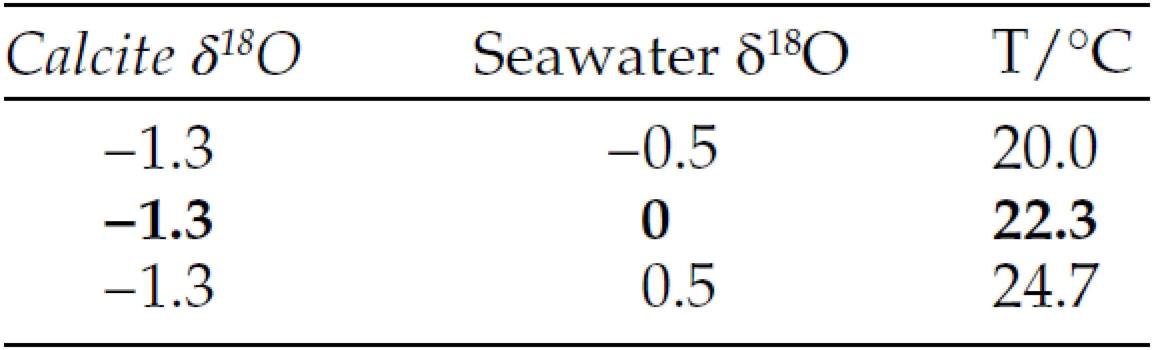


Calcite δ^{18}O	Seawater δ^{18}O	T/°C
–1.3	–0.5	20.0
–1.3	**0**	**22.3**
–1.3	0.5	24.7

The resulting error is 22.3 ± 2.3°C

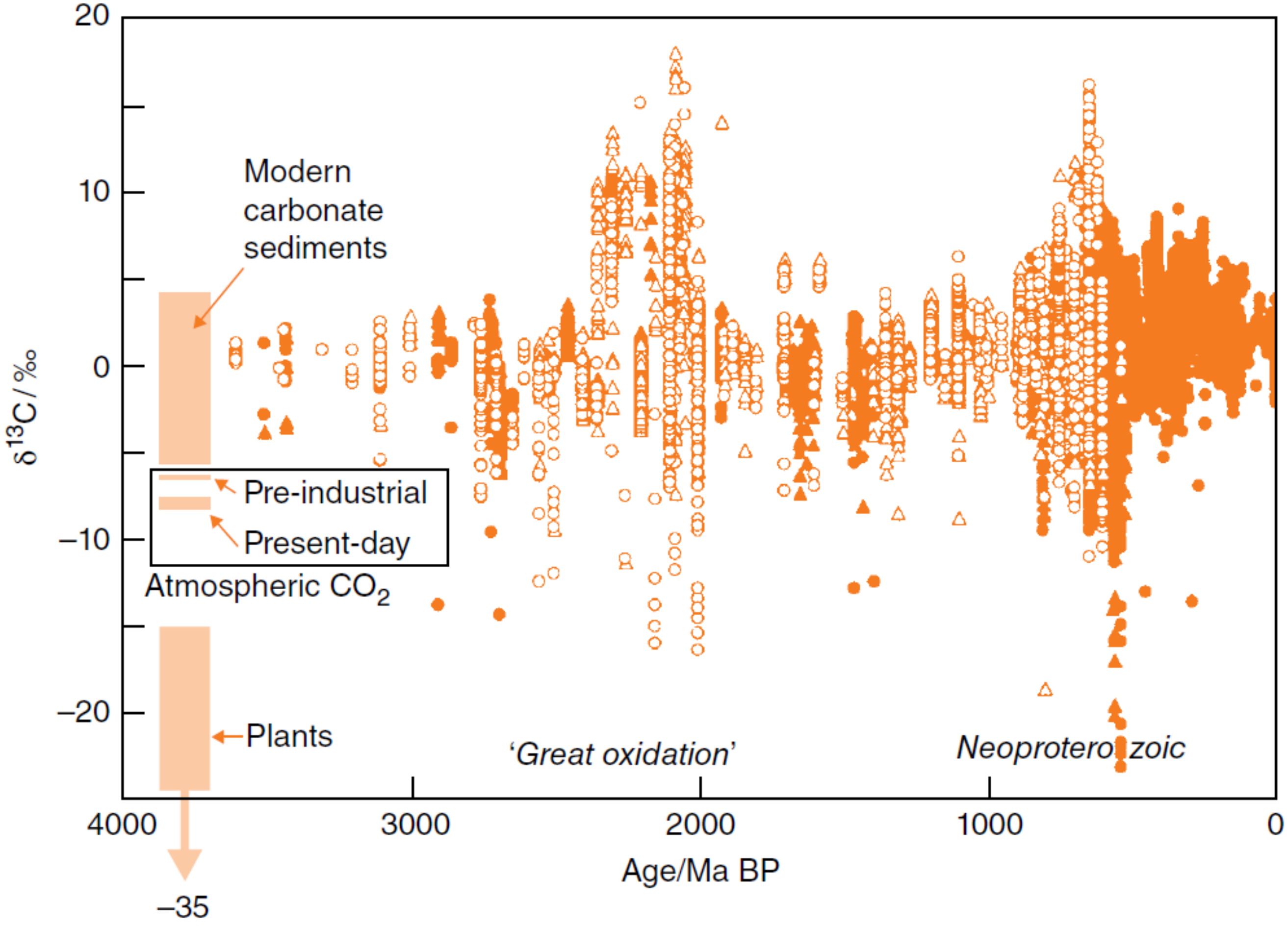
Stable carbon isotopes – the key to history of life

- Seawater and carbonate rocks are enriched in the heavier isotope ^{13}C (~ 5–10‰) compared to the atmosphere.
- Organic matter contains significantly less ^{13}C -> $\delta^{13}C$ ~−20‰.
- Preference of ^{12}C in photosynthesis by the enzyme Rubisco.
- $\delta^{13}C$ is an ideal tracker for monitoring photosynthetic processes.

Forms of carbon occurrence

- Inorganic carbon
  - $\delta^{13}C$ close to zero
- Reduced carbon formed by the decomposition of organic matter
  - $\delta^{13}C$ with significantly negative values

Geochemical traces of the development of life

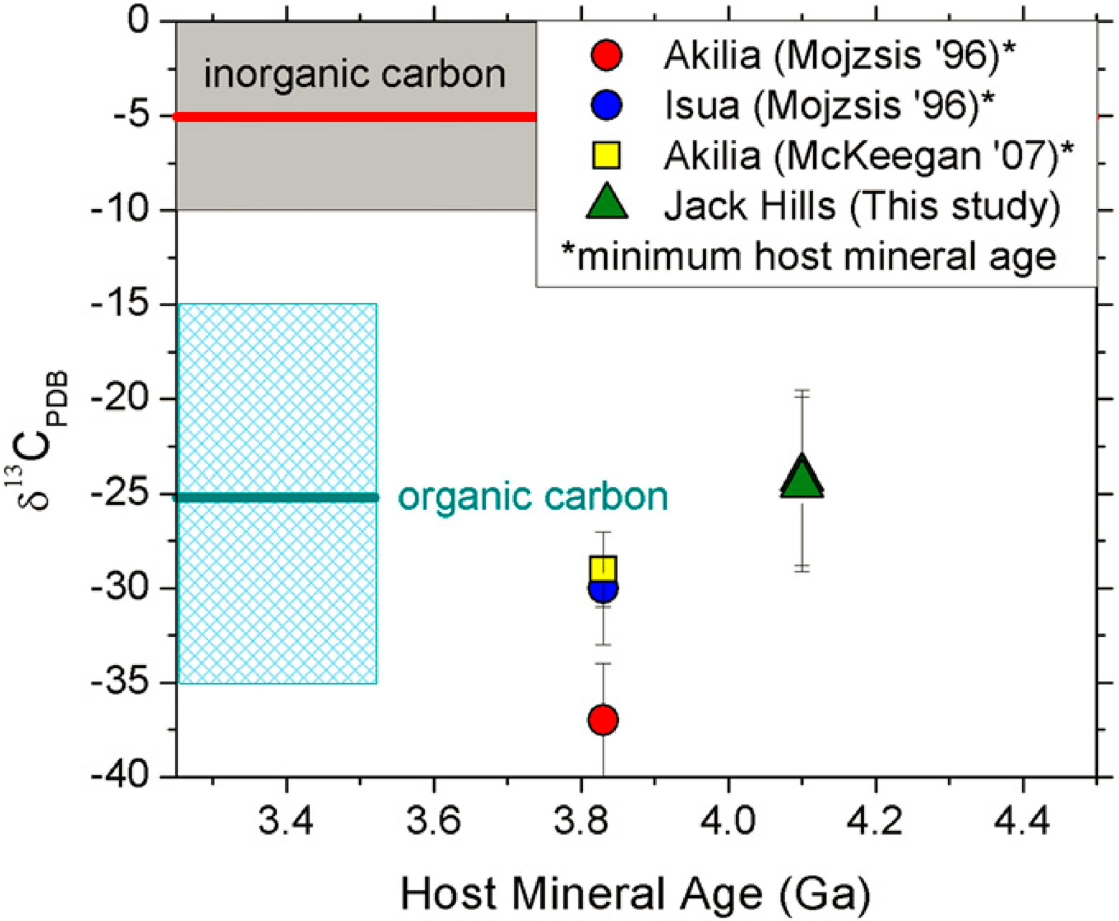


2 disturbances :

1. The first development of photosynthetic organisms associated with the release of oxygen into the atmosphere = CO_2 depletion. Violation of the greenhouse effect.
2. Transition of the first photosynetizing organisms to land = acceleration of O_2 increase.

Taken from Gill (2015) by Shields & Veizer (2002)

The origin of life



Bell et al. 2015 , available at http://www.pnas.org/content/112/47/14518.full.pdf

Archeology – nutrition and origin of people

- Trace elements and isotopes in teeth reflect the isotopic composition of food ingested in childhood.
- This is a reflection of the geology of the area.
- It allows to assess the origin of archaeological finds of human remains.
  - Migration and cultural interactions.
- Nitrogen and carbon isotopes can reveal dietary details.
  - C3 plants: rice, fruits, tubers, nuts, vegetables
  - C4 plants: millet, sugar cane

Tollense Battlefield – dated by ^{14}C to 1250 BC. Evidence of a battle of surprising volume (up to 4000 participants) for the time. Stable isotopes prove their very varied origin.

Archeology - sources of materials

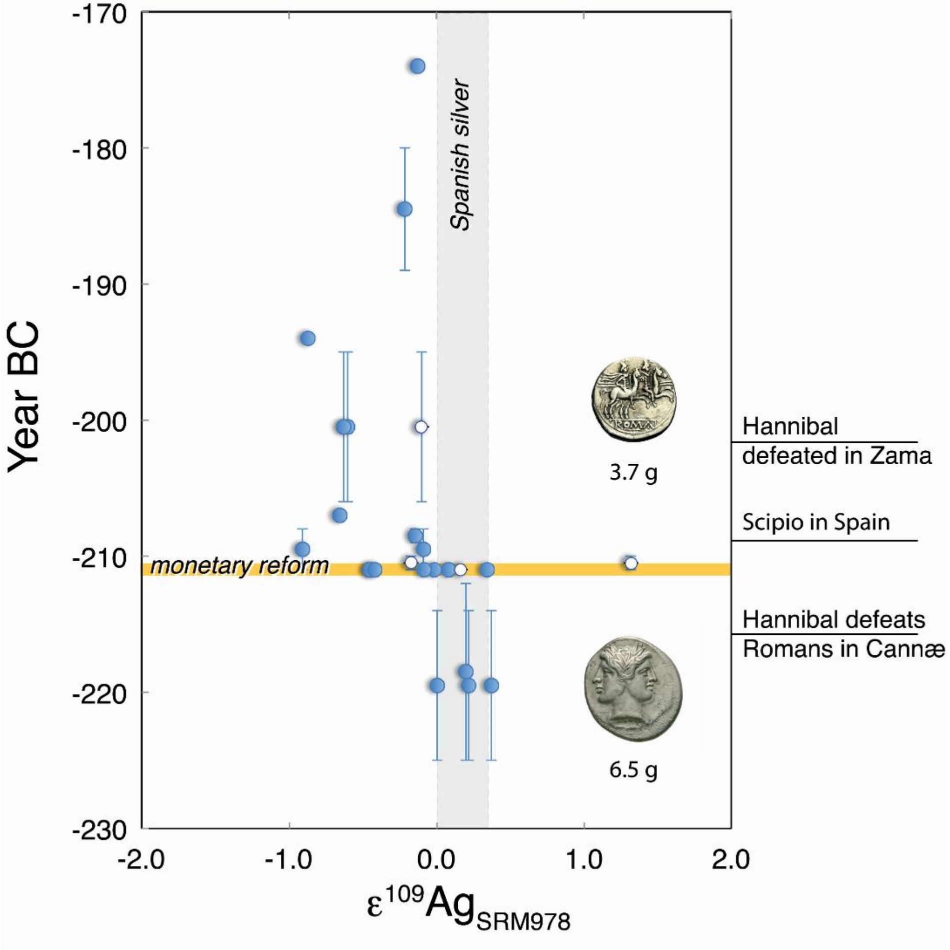
Quadrigatus Cr 29/3

Denarius Cr 60/1

- Origin of stone artifacts (corneas, obsidians, etc.)
- Origin of metals, glasses or pigments.
- Reconstruction of trade routes.

Archeology - sources of materials

Albarède *et al.* (201 6) *Geochem. Persp. Flight.* 2 , 127-137 | doi: 10.7185 / geochemlet.1 613



Silver isotope compositions of Roman silver coins pre- and post-dating the 211 BC monetary reform. Solid symbols: *denarii* (**top**) and *quadrigati* (**bottom**). Open symbols: *victoriati* . Mint ages and uncertainties are from Crawford (1974). Error bars on silver isotope proportions are the same as or smaller than the symbol size. Events listed on the right-hand side are chosen for historical relevance. See Appendix for the range of Spanish values.

EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

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- Unmarked images are author's or taken over with the permission of doc. Zeman and doc. Faimon
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