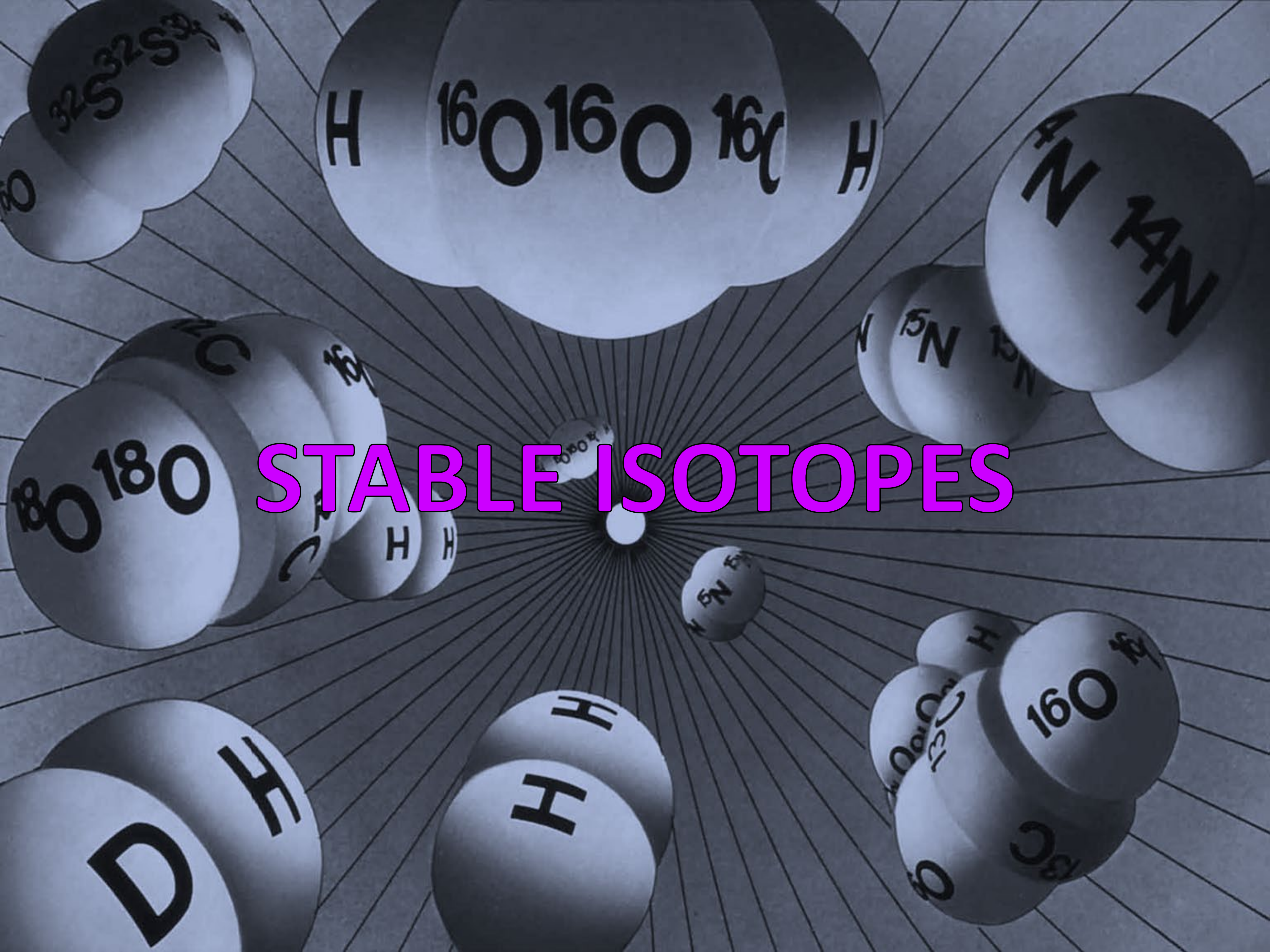


STABLE ISOTOPES

STABLE ISOTOPES

SUMMARY:

- Definition of Geochemistry and Geochemistry of stable isotopes. Definition of isotope and stable isotope
- The most used light stable isotopes: H, B, **O, C**, N, S
- How isotope concentrations are measured: mass spectrometers
- How isotope concentrations are expressed: the δ notation
- Equilibrium and kinetic isotope fractionation

STABLE ISOTOPES GEOCHEMISTRY

GEOCHEMISTRY studies **Earth's chemistry**, using chemical techniques to explore its processes and history.

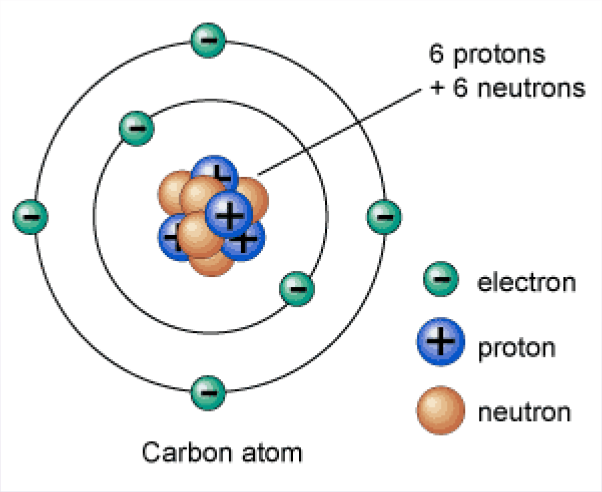
STABLE ISOTOPE GEOCHEMISTRY, a branch of geochemistry, uses **non-radioactive isotopes** to investigate similar issues.

Certain elements with atomic weights below 40 show significant isotope abundance variations in different compounds due to inorganic and biological processes.

Key elements in Earth Sciences—Hydrogen (H), Carbon (C), Nitrogen (N), Oxygen (O), and Sulfur (S)—are crucial in rock formation, mineral deposits, the hydrological cycle, and life processes.

BASICS OF CHEMISTRY

- ✓ Atoms consist of a nucleus and orbiting electrons.
- ✓ The nucleus, with a positive charge, holds most of the atom's mass. Electrons have minimal mass and a negative charge, orbiting the nucleus.
- ✓ Atoms are neutral, with equal numbers of **protons** (positive) and **electrons** (negative).



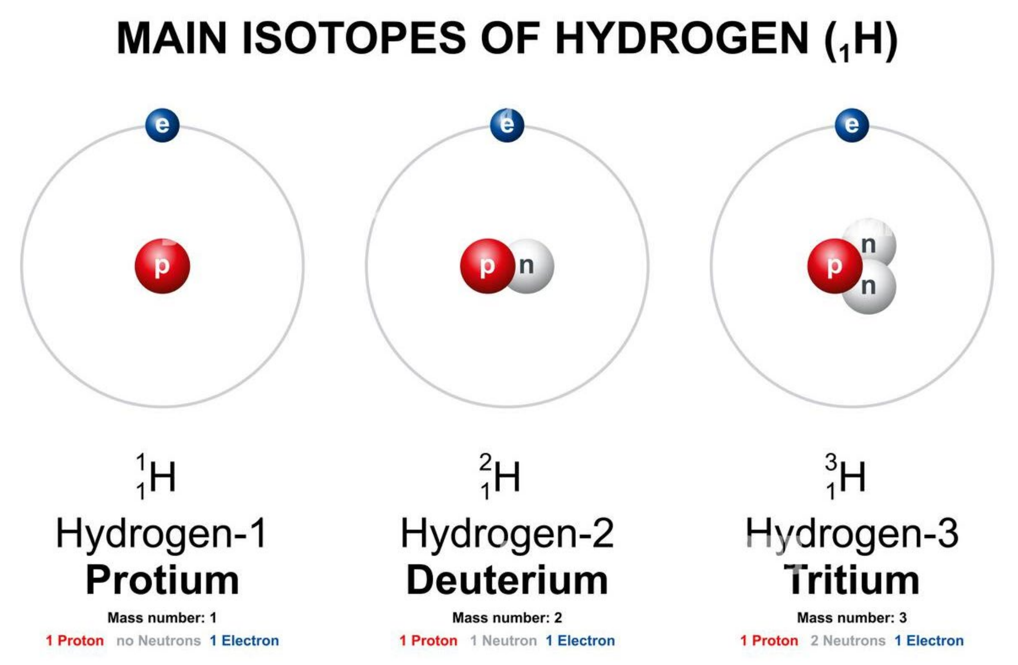
- ✓ Each element’s atom has a specific number of electrons, determining its chemical behavior (valence level).
- ✓ Protons set the **atomic number** (e.g., carbon, Z = 6).
- ✓ The nucleus also contains neutrons, with no charge and the same mass as protons.
- ✓ **The mass number** (A) is the sum of protons and neutrons.

STABLE ISOTOPES

The term **isotope** comes from Greek, meaning "equal place," as isotopes share the same spot in the periodic table.

Isotopes have the **same number of protons** (same atomic number Z) but **different numbers of neutrons**, resulting in varying mass numbers (A).

Since isotopes have the same number of electrons, they show **nearly** identical behavior in chemical reactions and physical processes.



ISOTOPES IN NATURE

In nature, there are approximately 300 stable isotopes and approximately 1200 unstable (radioactive) isotopes.

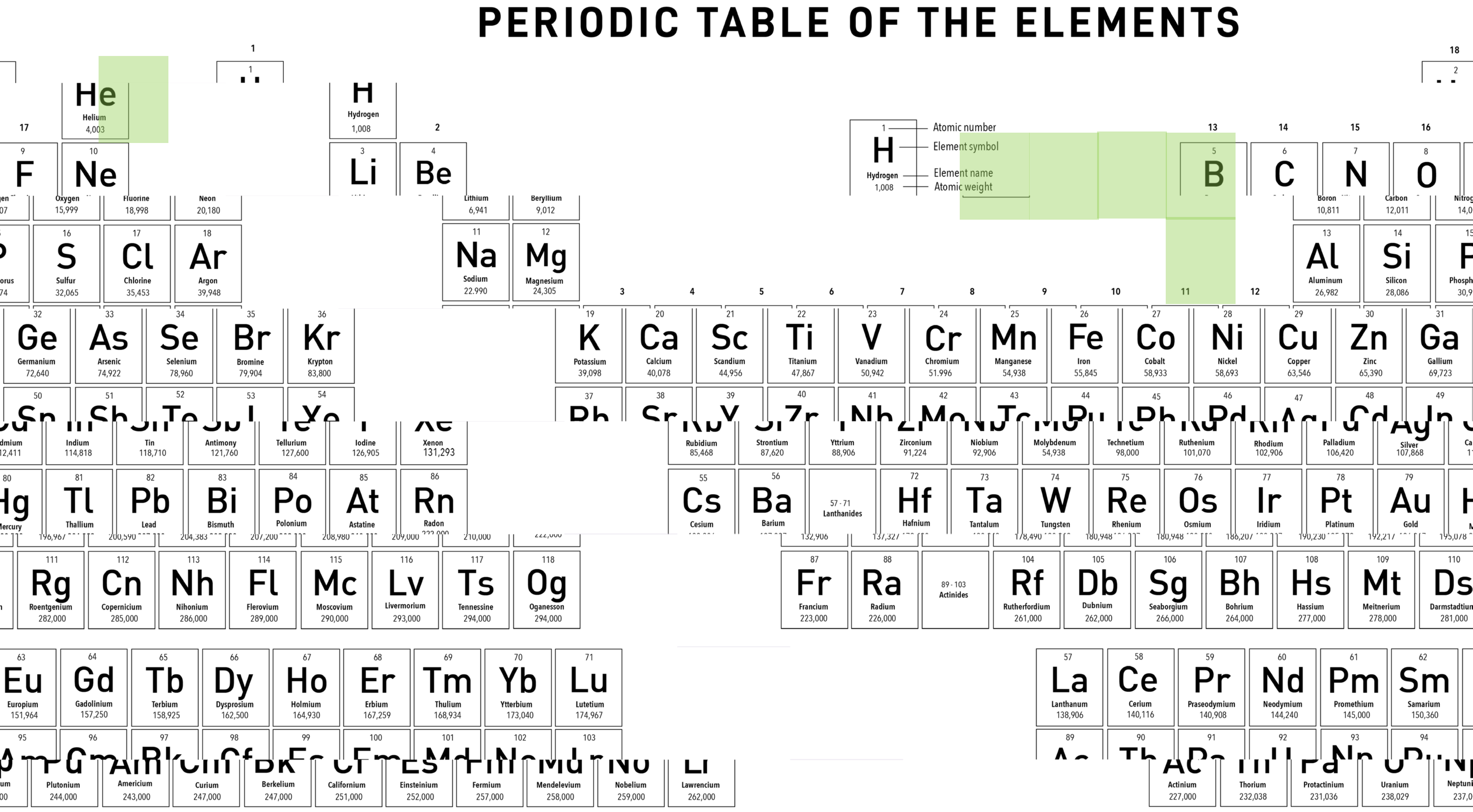
Typically, in various elements, one particular isotope predominates, such as ^{16}O for oxygen.

In the field of geosciences, radioactive isotopes have played and continue to play a crucial role in the determination of "absolute" geological time through radiometric dating.

Stable isotopes have significant applications in environmental, paleoenvironmental, and paleobiological studies. Notably, the light stable isotopes of the following elements are of great importance:

HYDROGEN
BORON
NITROGEN
OXYGEN
CARBON
SULFUR

LIGHT STABLE ISOTOPES



www.periodictable.co.za | Designed by Mia Viljoen

THE MOST STUDIED

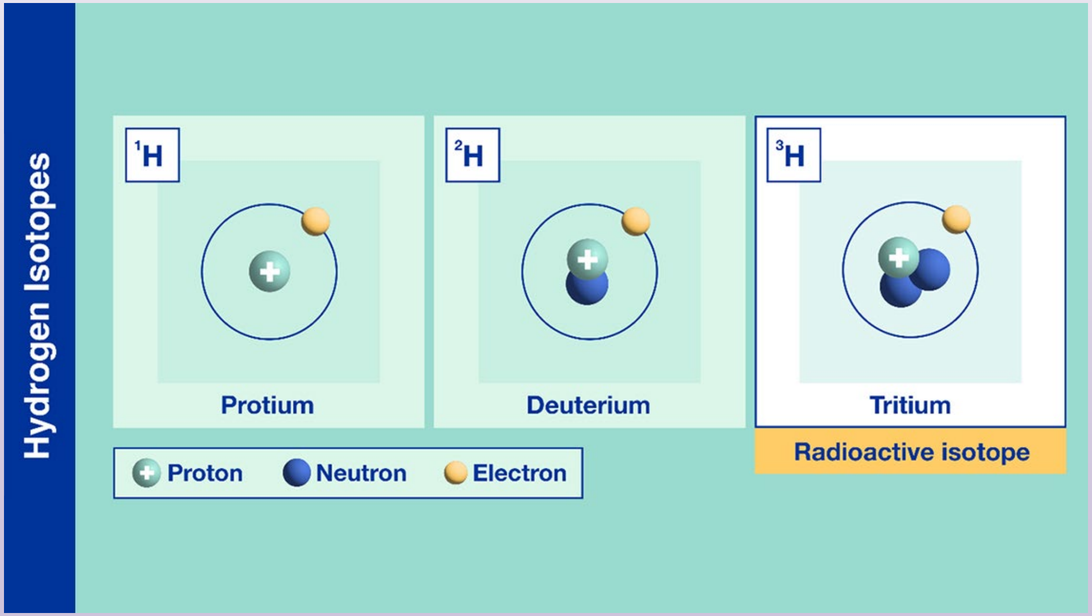
Carbon	^{12}C	98,8922%	**Boron**	^{10}B	19,82%	**Nitrogen**	^{14}N	99,6349%
	^{13}C	1,1078%		^{11}B	80,18%		^{15}N	0,3669%
Hydrogen	^{1}H	99,984426%	**Oxygen**	^{16}O	99,7628%	**Sulfur**	^{32}S	95,00%
	^{2}H, D	0,015574%		^{17}O	0,0372%		^{33}S	0,76%
				^{18}O	0,2004%		^{34}S	4,22%
							^{36}S	0,014%

WE WILL FOCUS ON **CARBON, OXYGEN** and HYDROGEN

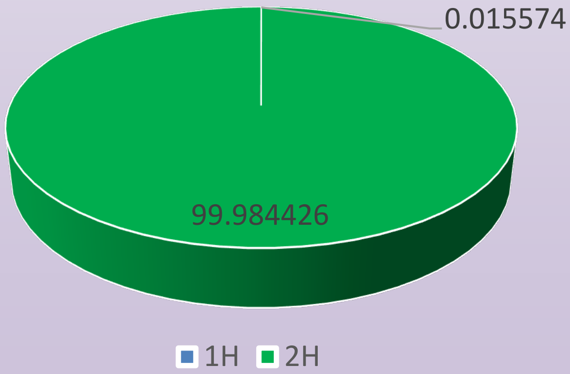
HYDROGEN ISOTOPES

Hydrogen has **two stable isotopes**: the most common, ^{1}H, with one proton, and Deuterium (^{2}H or D), with one proton and one neutron.

There is also a **radioactive isotope**, Tritium (^{3}H or T), with one proton and two neutrons.



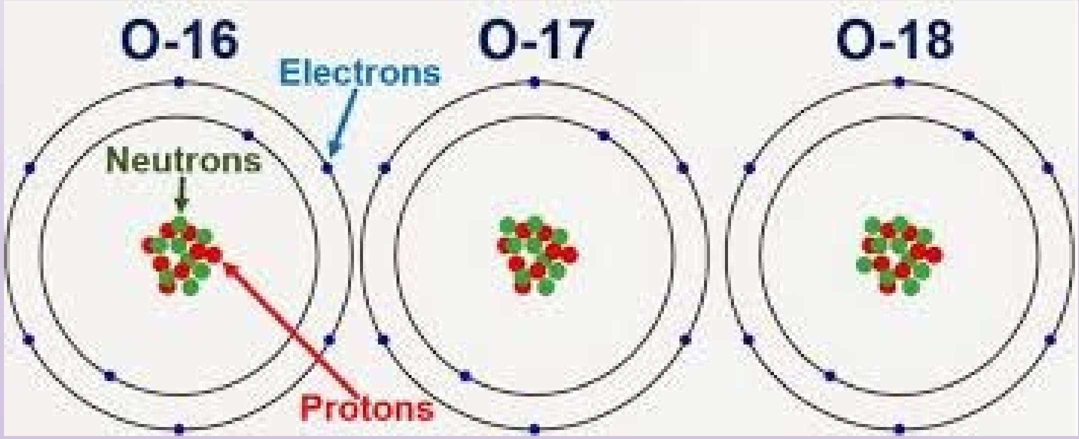
Hydrogen	
^{1}H	99,984426%
^{2}H D	0,015574%



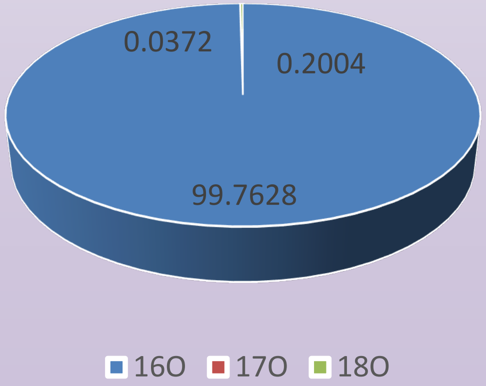
OXYGEN ISOTOPES

Oxygen has three stable isotopes: **^{16}O**, **^{17}O**, and **^{18}O**, along with ten radioactive ones

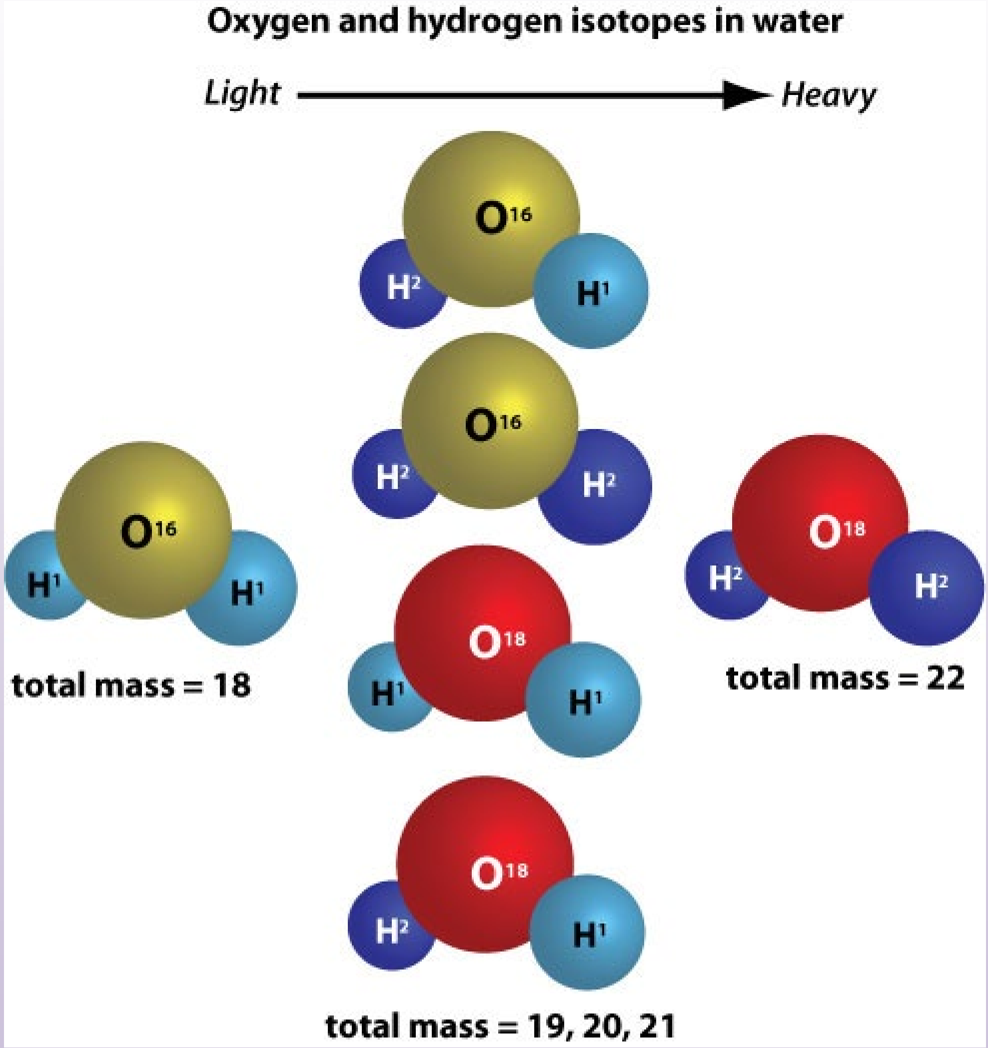
The most common is **^{16}O** ("light oxygen"), while **^{18}O** is known as "heavy oxygen." Due to its rarity, **^{17}O** is not typically covered in this course.



Oxygen	^{16}O	99,7628%
	^{17}O	0,0372%
	^{18}O	0,2004%



WATER MOLECULE – H_2O



Consider previous isotopic abundance

Consider that molecules with more than one rare isotope are very rare in nature.

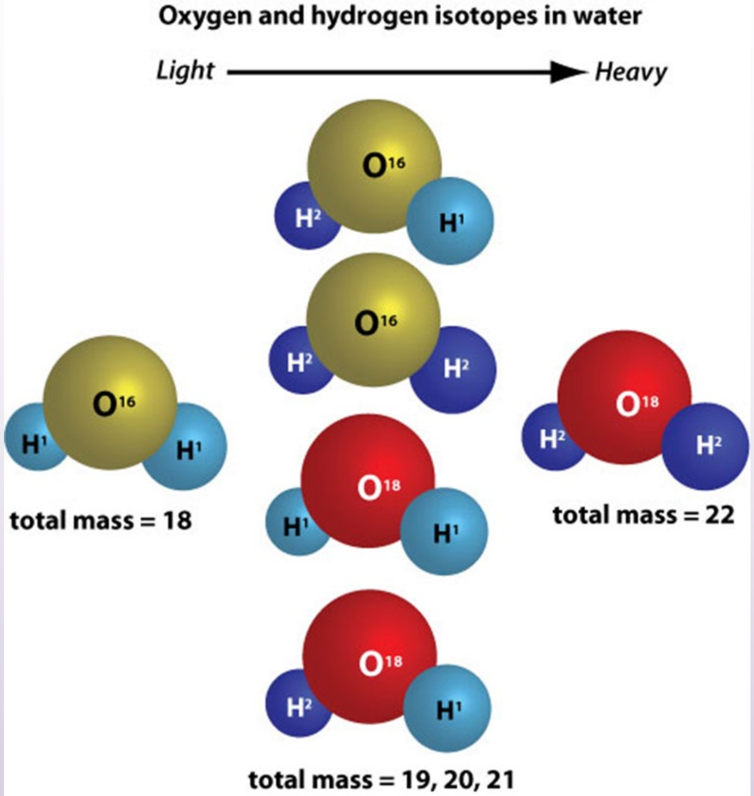
Which is the most common water molecule?

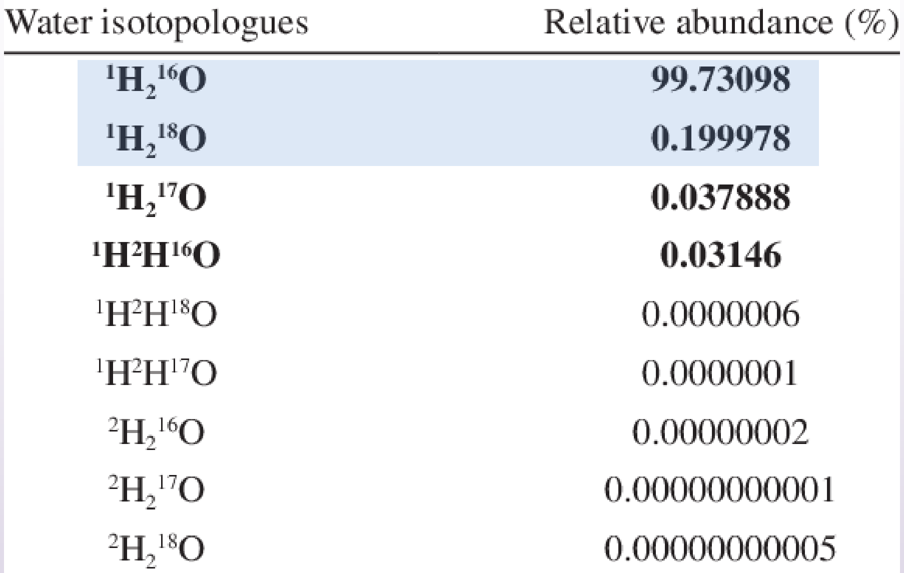
Which the most common water molecule?

1. 1H2 17O — 0% 0
2. 1H2 16O — 0% 0
3. HD 16O — 0% 0
4. H2 18O — 0% 0
5. D2 18O — 0% 0

https://app.wooclap.com/events/PCCM24/0

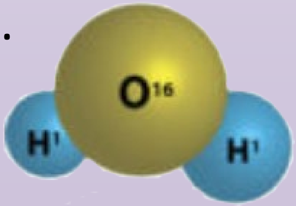
WATER MOLECULE (H_2O) - 1





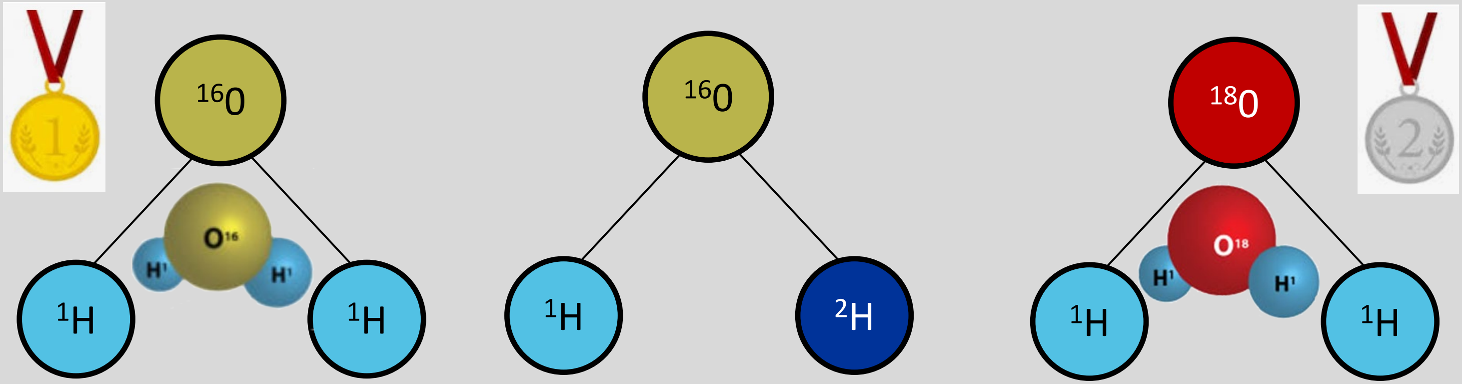
Water isotopologues	Relative abundance (%)
$^{1}H_2{}^{16}O$	99.73098
$^{1}H_2{}^{18}O$	0.199978
$^{1}H_2{}^{17}O$	0.037888
$^{1}H^{2}H^{16}O$	0.03146
$^{1}H^{2}H^{18}O$	0.0000006
$^{1}H^{2}H^{17}O$	0.0000001
$^{2}H_2{}^{16}O$	0.00000002
$^{2}H_2{}^{17}O$	0.00000000001
$^{2}H_2{}^{18}O$	0.00000000005

Based on previous abundances, the most common water molecule is **$^{1}H_2{}^{16}O$**, but there are also different molecules $^{1}H_2{}^{17}O$, $HD^{16}O$, $H_2{}^{18}O$ and $D^{18}O$.



Molecules with more than one rare isotope are very rare in nature.

WATER MOLECULE (H_2O) - 2



$^1H_2{}^{16}O$

MW= 18

$^1H_2{}^{17}O$ -$^1HD^{16}O$

MW= 19

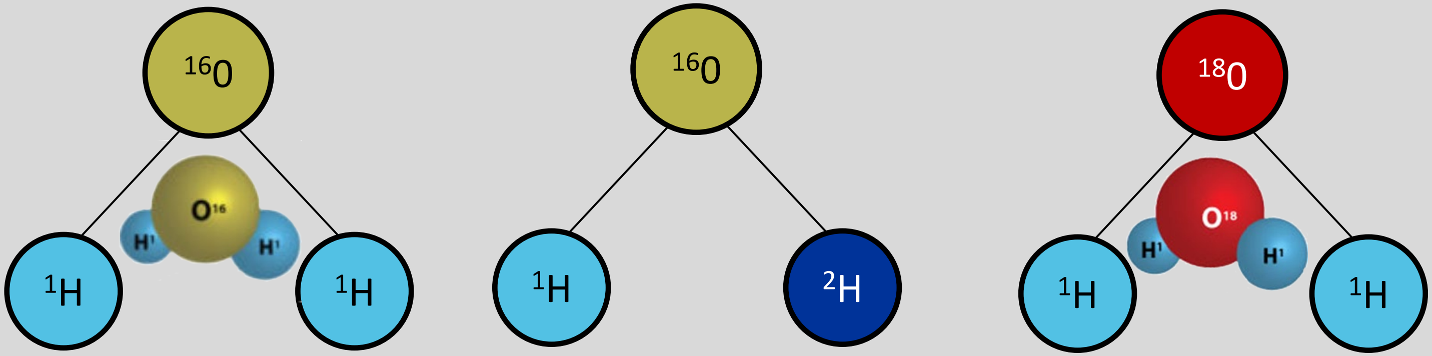
$^1H_2{}^{18}O$

MW=20

Water can consist of different isotope combinations of H (^1H; D) and O (^{16}O; ^{18}O). Deuterium (D or ^2H) nearly doubles the mass of ^1H.

- H_2O molecule containing the most common isotopes (^1H and ^{16}O) has a molecular weight (MW) = 1 + 1 + 16 = 18.
- H_2O molecule containing one D (^2H) or ^{17}O has a molecular weight (MW) = 2 + 1 + 16 = 19, a 5% increase.
- H_2O molecule containing one ^{18}O (heavy oxygen) has a molecular weight (MW) = 1 + 1 + 18 = 20, a 10% increase.

WATER MOLECULE (H_2O) - 3



$^1H_2{}^{16}O$

MW= 18

$^1H_2{}^{17}O$ - $^1HD^{16}O$

MW= 19

$^1H_2{}^{18}O$

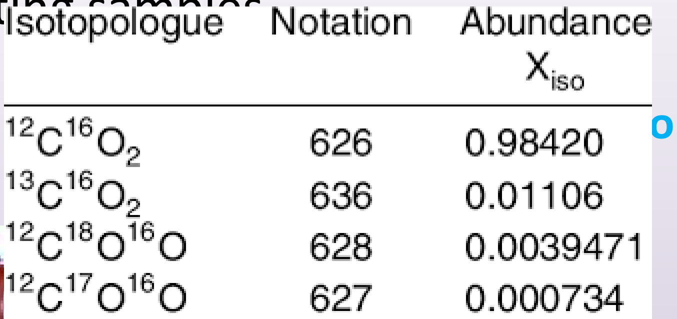
MW=20

The energy needed to vaporize the heavier water molecules is higher, so during the evaporation process a fractionation takes place:
the heavier isotopes will tend to remain in the liquid state while the lighter isotopes will statistically tend to pass to the vapor state.
A standard seawater sample (Vienna Standard Mean Ocean Water, or **VSMOW**) will have a different isotope ratio than a sample of Arctic snow (Standard Light Arctic Precipitation, or **SLAP**).

CARBON ISOTOPES

Carbon (C) has 3 natural isotopes: ^{12}C, ^{13}C and ^{14}C. ^{12}C, ^{13}C are stable, ^{14}C is radioactive.

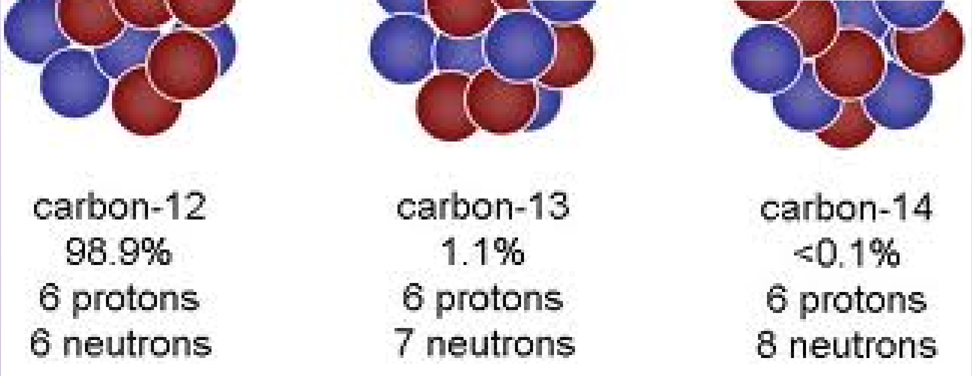
^{13}C and ^{12}C are isotopes used to study the structure of carbon-containing compounds. ^{14}C, produced by nitrogen bombardment, has a half-life of 5.760 years and is used for dating samples.



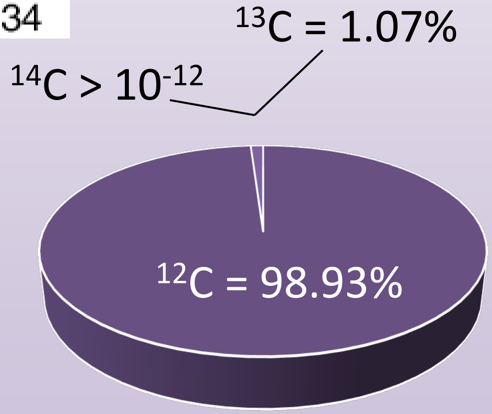
Isotopologue	Notation	Abundance X_{iso}
$^{12}C^{16}O_2$	626	0.98420
$^{13}C^{16}O_2$	636	0.01106
$^{12}C^{18}O^{16}O$	628	0.0039471
$^{12}C^{17}O^{16}O$	627	0.000734

on

^{12}C	98,8922%
^{13}C	1.1078%

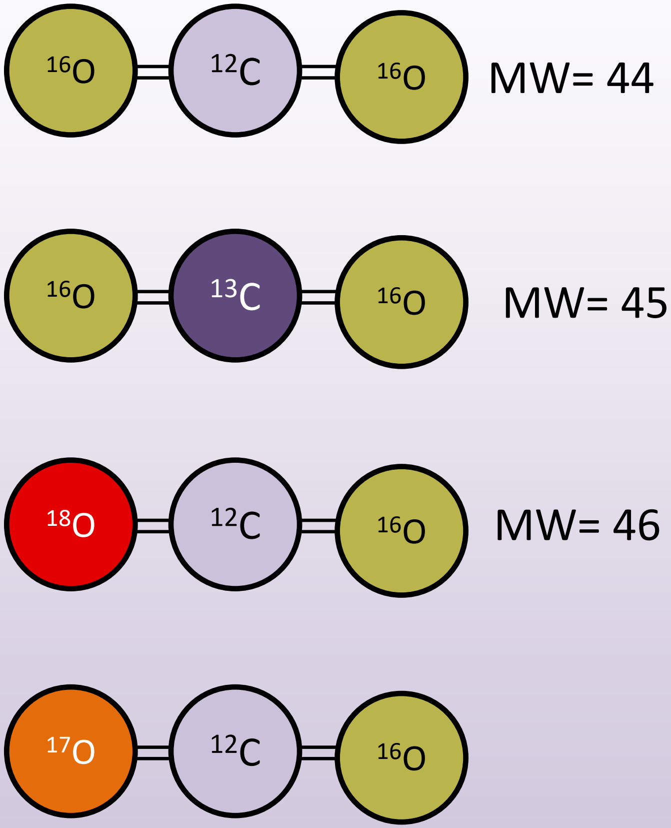


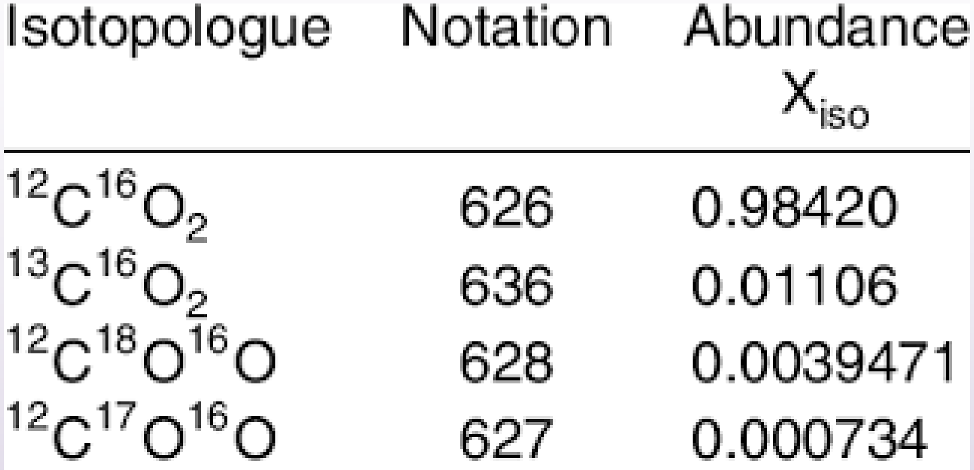
Atomic structure of ^{12}C, ^{13}C e ^{14}C



Abundance (%) di ^{12}C, ^{13}C e ^{14}C

CARBON DIOXIDE MOLECULE (CO_2)





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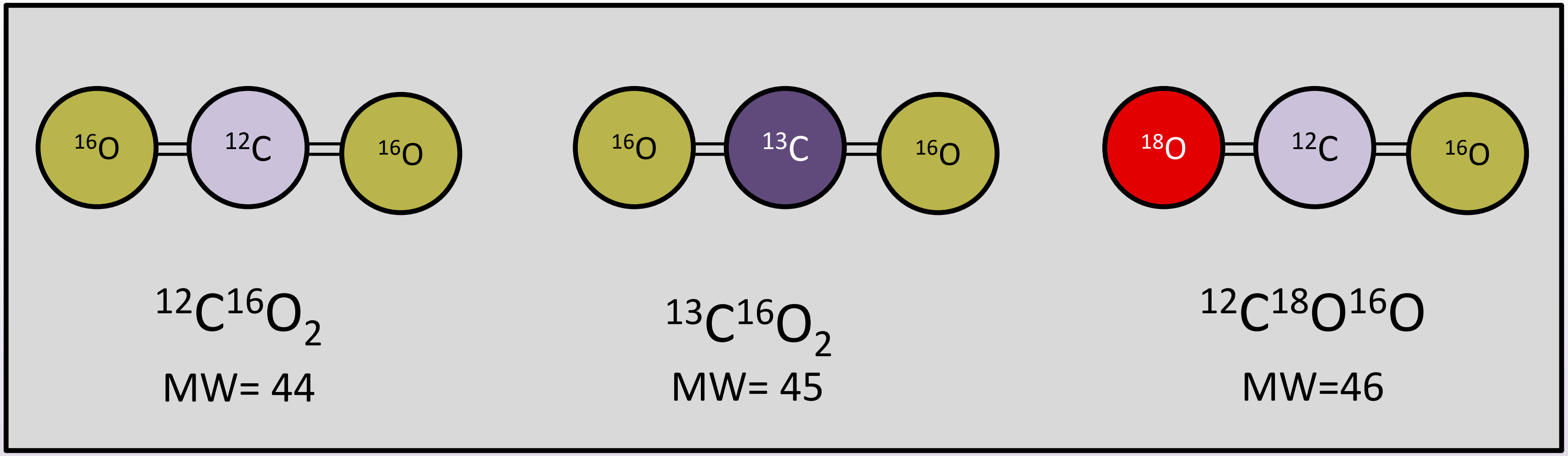
$^{12}C^{18}O^{16}O$	628	0.0039471
$^{12}C^{17}O^{16}O$	627	0.000734

Based on previous abundances, the most common carbon dioxide molecule is $^{12}C^{16}O_2$, but there are also different molecules $^{13}C^{16}O_2$, $^{12}C^{18}O^{16}O$ and $^{13}C^{18}O^{16}O$.

Molecules with more than one rare isotope are very rare in nature.

9842 : 110 : 39 : 7

CARBON DIOXIDE MOLECULE (CO_2)



$^{12}C^{16}O_2$

MW= 44

$^{13}C^{16}O_2$

MW= 45

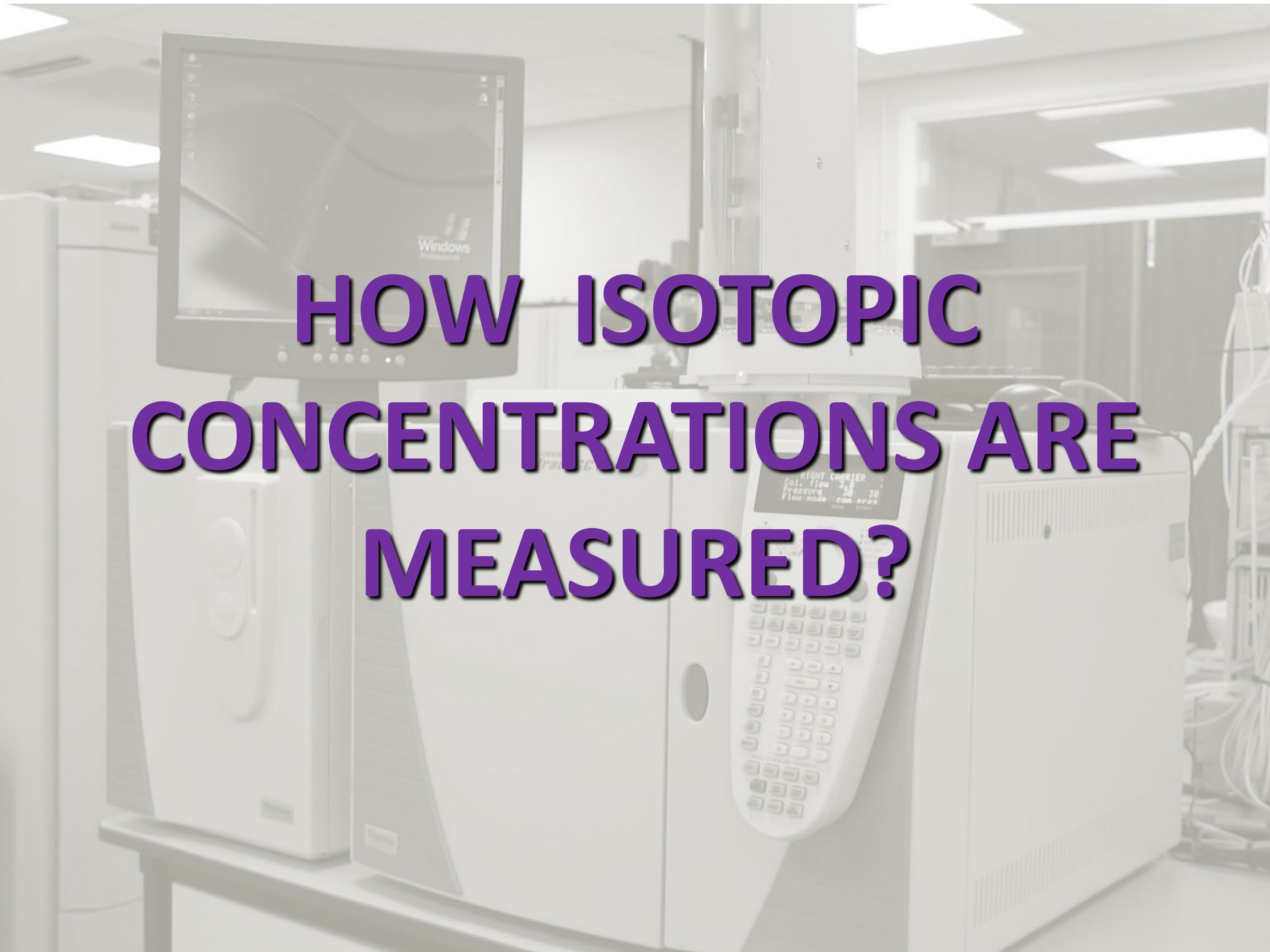
$^{12}C^{18}O^{16}O$

MW=46

$^{12}C+^{16}O+^{16}O$ → molecular weight → 12+16+16 = 44

$^{13}C+^{16}O+^{16}O$ → molecular weight → 13+16+16 = 45 +1%

$^{12}C+^{18}O+^{16}O$ → molecular weight → 12+18+16 = 46 +1%



HOW ISOTOPIC CONCENTRATIONS ARE MEASURED?

MASS SPECTROSCOPY

The fundamental principle of mass spectrometry is **separating ions by their mass-to-charge ratio**, typically using magnetic fields.

Ionization occurs by passing the molecules of the sample through an electron beam with known energy.

How to procede?

ISOTOPE-RATIO MASS SPECTROMETRY

Isotope-ratio mass spectrometry (IRMS) is a subfield within mass spectrometry**.**

It is used to measure **relative isotopic abundances** in a sample with high accuracy.

IRMS finds applications in both Earth and Environmental Sciences.

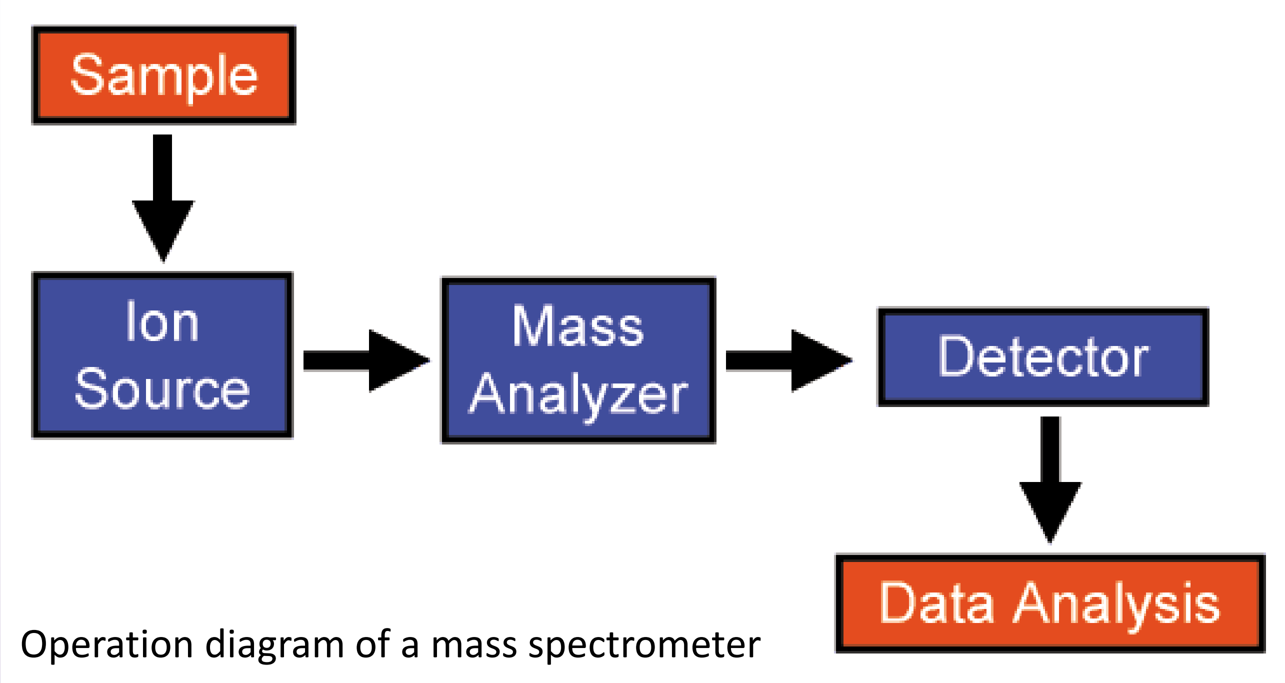
Isotope Ratio Mass Spectrometer Isotope and Processing Devices

⬇

-Isotopic analyses examine natural isotopic composition due to mass-based fractionation.

-Radiogenic isotopic analyses measure radiogenic products to determine chronological data

MASS SPECTROMETER- 1

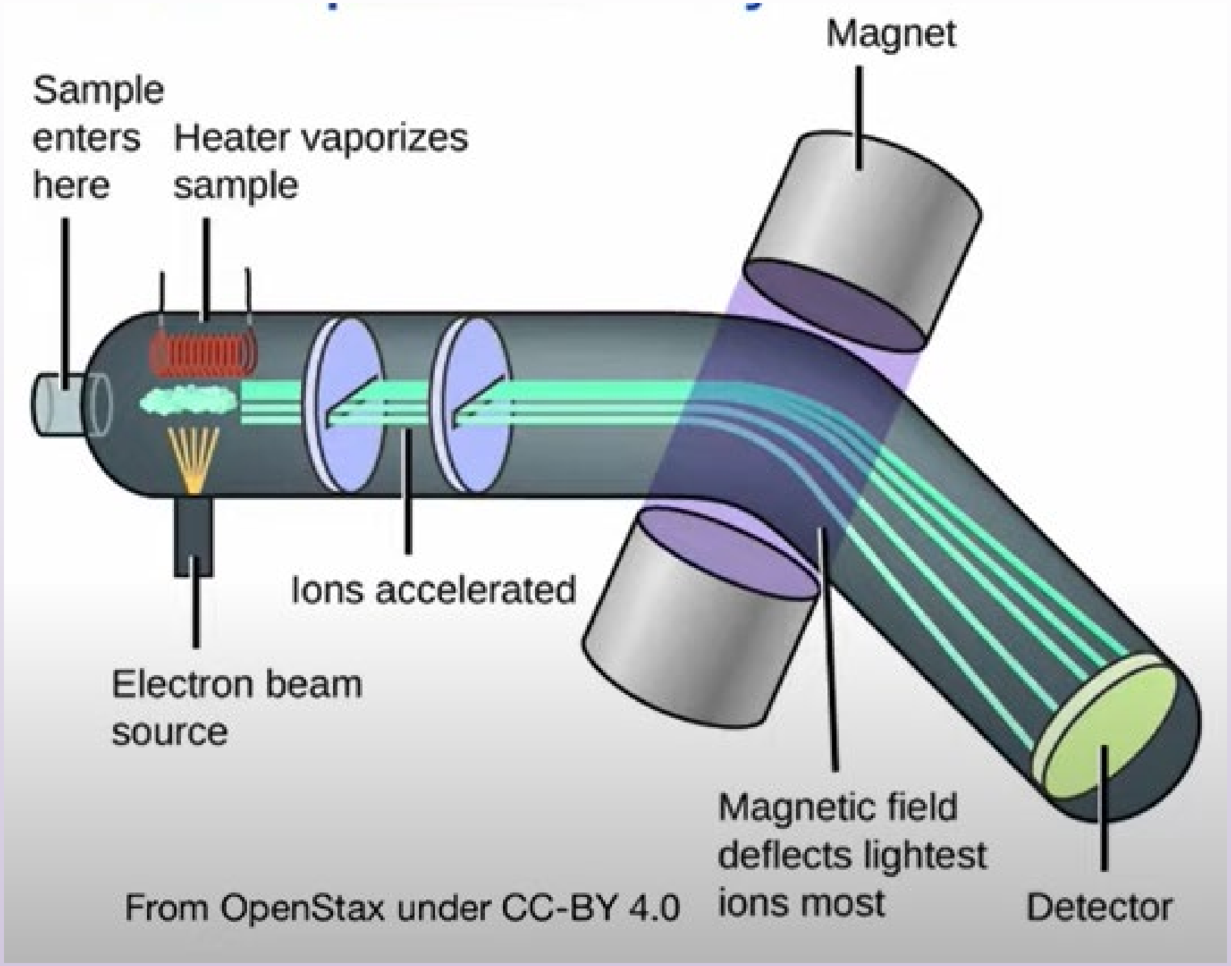


Operation diagram of a mass spectrometer

The mass difference in lighter isotopes (atomic weight <40) leads to **observable variations in chemical, physical, and biological processes**, reflected in measurable changes in isotopic in samples.

MASS SPECTROMETER- 2

CO_2 →



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Note: To measure isotope concentrations of an element (e.g., O or C) in a substance (e.g., $CaCO_3$), it must first be converted into a gas (e.g., CO_2).

Mass spectrometers are used to quantify isotope concentrations of elements like O or C. IRMS separates gas molecules by their mass.

HOW TO MEASURE O AND C ISOTOPES

To determine O and C isotope concentrations (e.g., in foraminifera or other fossils), carbon dioxide (CO_2) is used. CO_2 is produced by reacting with orthophosphoric acid (H_3PO_4), as shown in the following reaction

$$3CaCO_3 + 2H_3PO_4 \rightleftharpoons 3CO_2 + 3H_2O + Ca_3(PO_4)_2$$

$CaCO_3$: Calcium carbonate
H_3PO_4: Phosphoric acid
CO_2: Carbon dioxide
H_2O: Water
$Ca_3(PO_4)_2$: Tricalcium phosphate

The reaction shows the interaction between calcium carbonate ($CaCO_3$) and phosphoric acid (H_3PO_4), resulting in the formation of carbon dioxide (CO_2), water (H_2O), and calcium phosphate($Ca_3(PO_4)_2$). The double arrow ($\rightleftharpoons$) indicates that this reaction is reversible.

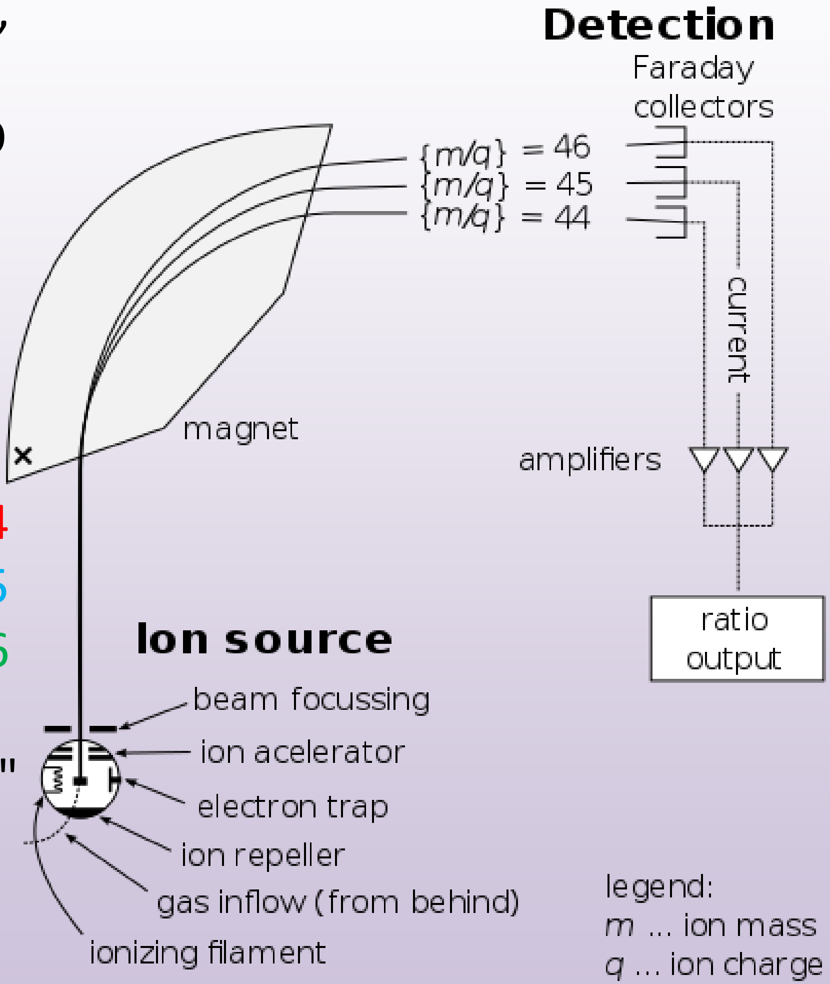
HOW TO MEASURE O AND C ISOTOPES

The molecular weight of a CO_2 molecule, measured in the mass spectrometer, varies based on the isotopic species of O and C it contains.

The most common CO_2 configurations are:

$^{12}C + {}^{16}O + {}^{16}O \rightarrow MW = 12 + 16 + 16 = 44$
$^{13}C + {}^{16}O + {}^{16}O \rightarrow MW = 13 + 16 + 16 = 45$
$^{12}C + {}^{18}O + {}^{16}O \rightarrow MW = 12 + 18 + 16 = 46$

These molecules have at most one "rare" isotope, while those with two "rare" isotopes are extremely rare.



DELTA NOTATION

ISOTOPIC CONCENTRATION: δ NOTATION

The delta (δ) notation is a way to express the results of comparative measurements between a sample and a standard in isotope ratio analysis.

CONVENTIONS

$\delta_{notation}$ represents the difference between the measurements of the sample (R_{sample})and the standard (R_{std}).

The isotope ratio is always expressed as the ratio between the "heavy" and the "light" isotope. For example: ^{18}O / ^{16}O or ^{13}C / ^{12}C.

For both oxygen and carbon delta values (δ) are expressed in parts per thousand (‰), instead of per cent (%).

$$\delta_{notation} = \left(\frac{R_{\ sample} - R_{\ standard}}{R_{\ standard}} \right) x\ 1000 \left(\frac{R_{\ sample}}{R_{\ standard}} - 1 \right) x\ 1000$$

R_{sample} = sample isotopic ratio ($^{18}O/^{16}O_{sample}$; $^{13}C/^{12}C_{sample}$)
R_{stand} = standard isotopic ratio ($^{18}O/^{16}O_{std}$; $^{13}C/^{12}C_{std}$)

δ NOTATION

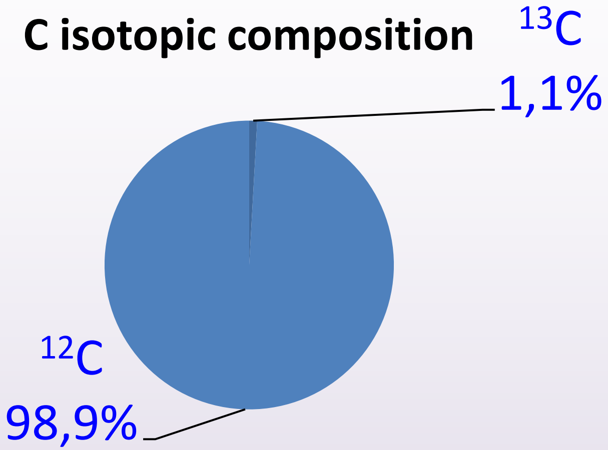
$$\delta_{\ notation} = \left(\frac{R_{\ sample} - R_{\ standard}}{R_{\ standard}} \right) x\ 1000$$

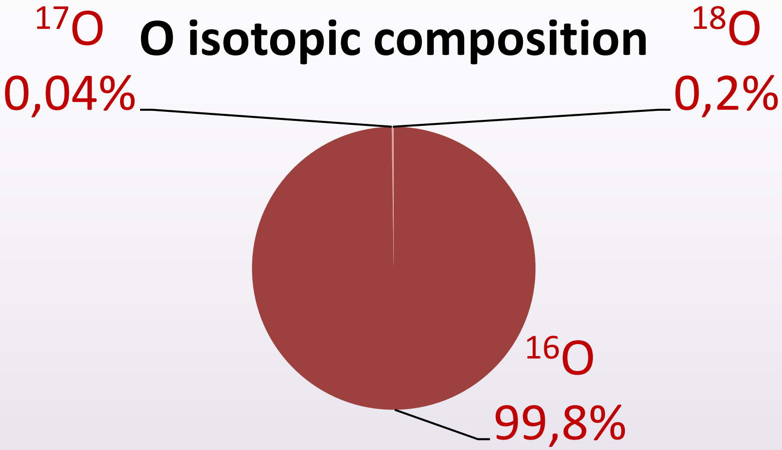
$$\delta_{\ notation} = \left(\frac{R_{\ sample}}{R_{\ standard}} - 1 \right) x\ 1000$$

δ is the delta value (usually expressed in per mil, ‰)
$\mathbf{R}_{\text{sample}}$ is the isotopic ratio (e.g., $^{13}C/^{12}C$ or $^{18}O/^{16}O$) of the sample
$\mathbf{R}_{\text{standard}}$ is the isotopic ratio of the reference standard

The δ notation offers two key advantages: first, since the abundances of heavy isotopes are low and result in decimal values, the δ notation multiplies these values by 1,000 for more practical usage; second, introducing a standard enables comparability of data across different laboratories.

RARE HEAVY ISOTOPES : R_{sample}


C isotopic composition


O isotopic composition

$$\delta = \left(\frac{R\ sample - R\ standard}{R\ standard}\right)\ x\ 1000 \left(\frac{R\ sample}{R\ standard} - 1\right)\ x\ 1000 = \left(\frac{\frac{^{18}O}{^{16}O} sample}{\frac{^{18}O}{^{16}O} standard} - 1\right) \text{x } 1000$$

The concentrations of heavy isotopes, like ^{18}O and ^{13}C, are very low, leading to R_{sample} ratios with many decimals. Instead of reporting individual isotope ratios,

~~$R_{sample} = {}^{18}O/\ {}^{16}O$~~
~~$R_{sample} = {}^{13}C/\ {}^{12}C$~~

$Rx = {}^{18}O/\ {}^{16}O$ x1000
$Rx = {}^{13}C/\ {}^{12}C$ x1000

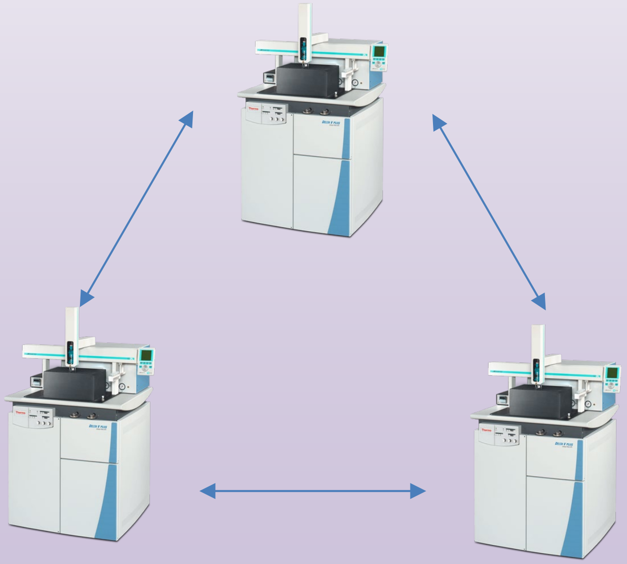
$[(R_x - R_{std})/R_{std})]$ x 1000

INTER-LABORATORY REPRODUCIBILITY : R_{stand}

R_{sample} is compared to a standard (R_{std}). This approach improves reproducibility and enables easy comparison of results across different laboratories.

$$\delta\ notation = \left(\frac{R\ sample}{R\ standard} - 1\right) x\ 1000 = \left(\frac{\frac{^{18}O}{^{16}O} sample}{\frac{^{18}O}{^{16}O} standard} - 1\right) \text{x } 1000$$

Inter-laboratory reproducibility is often controlled or verified through the use of a **standard**. A standard is a reference material that is used to ensure consistency and accuracy across different laboratories. By using the same standard, laboratories can compare their results to a common baseline, helping to identify discrepancies and ensuring that the variation in results is due to experimental conditions and not errors or inconsistencies in the methods or equipment used.



INTERNATIONAL REFERENCE STANDARDS

Laboratories often use internal standards, but results are adjusted to international reference standards. In isotope geochemistry, 4 standards are used for the five main elements (H, C, N, O, S):

H,O	**VSMOW (Vienna Standard Mean Ocean Water)**	water
C,O	**PDB (Pee Dee Belemnite)**	carbonates
N	**AIR (Ambient Inhalable Reservoir)**	atmospheric air
S	**CDT (Canyon Diablo Troilite, meteorite)**	



The **PDB** standard, used for measuring O and C isotopes in $CaCO_3$, reflects the isotopic composition of ***Belemnitella americana*** from the PeeDee Formation (Upper Cretaceous - South Carolina).

The **SMOW** standard, for H and O isotopes in H_2O, represents the average global ocean isotopic composition. These standards are maintained by the International Atomic Energy Agency (IAEA) in Vienna.

CONVERSIONS: PDB -VSMOW scales

To convert oxygen isotope values between the PDB (Pee Dee Belemnite) and VSMOW (Vienna Standard Mean Ocean Water) scales, you can use the following equations:

From δ18O (PDB) to δ18O(VSMOW):

$\delta^{18}O_{\text{VSMOW}} = 1.03091 \times \delta^{18}O_{\text{PDB}} + 30.91$

From δ18O (VSMOW) to δ18O (PDB):

$\delta^{18}O_{\text{PDB}} = (\delta^{18}\text{O}_{\text{VSMOW}} - 30.91) / 1.03091$

These conversion formulas account for the small difference in the isotope ratios between the two standards. VSMOW is typically used for water and PDB for carbonate-based materials like shells and corals.

If a δ^{18}O value is 1 ‰ in PDB, what is the correct value in VSMOW using the conversion formula?

Go to **wooclap.com** and use the code **PCCM24**

Question: If a δ^{18}O value is 1 ‰ in PDB, what is the correct value in VSMOW using the conversion formula?

1. 29.91 ‰
2. 31.94 ‰
3. 28.50 ‰
4. 33.01 ‰

https://app.wooclap.com/events/PCCM24/0

CONVERSIONS: PDB -VSMOW scales

Explanation for students (if needed): The conversion between PDB and VSMOW is done using the formula:

$$\delta^{18}O_{\text{VSMOW}} = 1.03091 \times \delta^{18}O_{\text{PDB}} + 30.91$$

By substituting $\delta^{18}O$ (PDB) = 1 ‰, we get:

$$\delta^{18}O_{\text{VSMOW}} = 1.03091 \times 1 + 30.91 = 31.94091\ ‰$$

Therefore, a $\delta^{18}O$ (PDB) value of 1 ‰ corresponds to approximately 31.94 ‰ in $\delta^{18}O$ (VSMOW).

δ NOTATION VALUES

$$\delta_{isotope} = [(R_{sample} - R_{std})/R_{std}] \times 1000$$

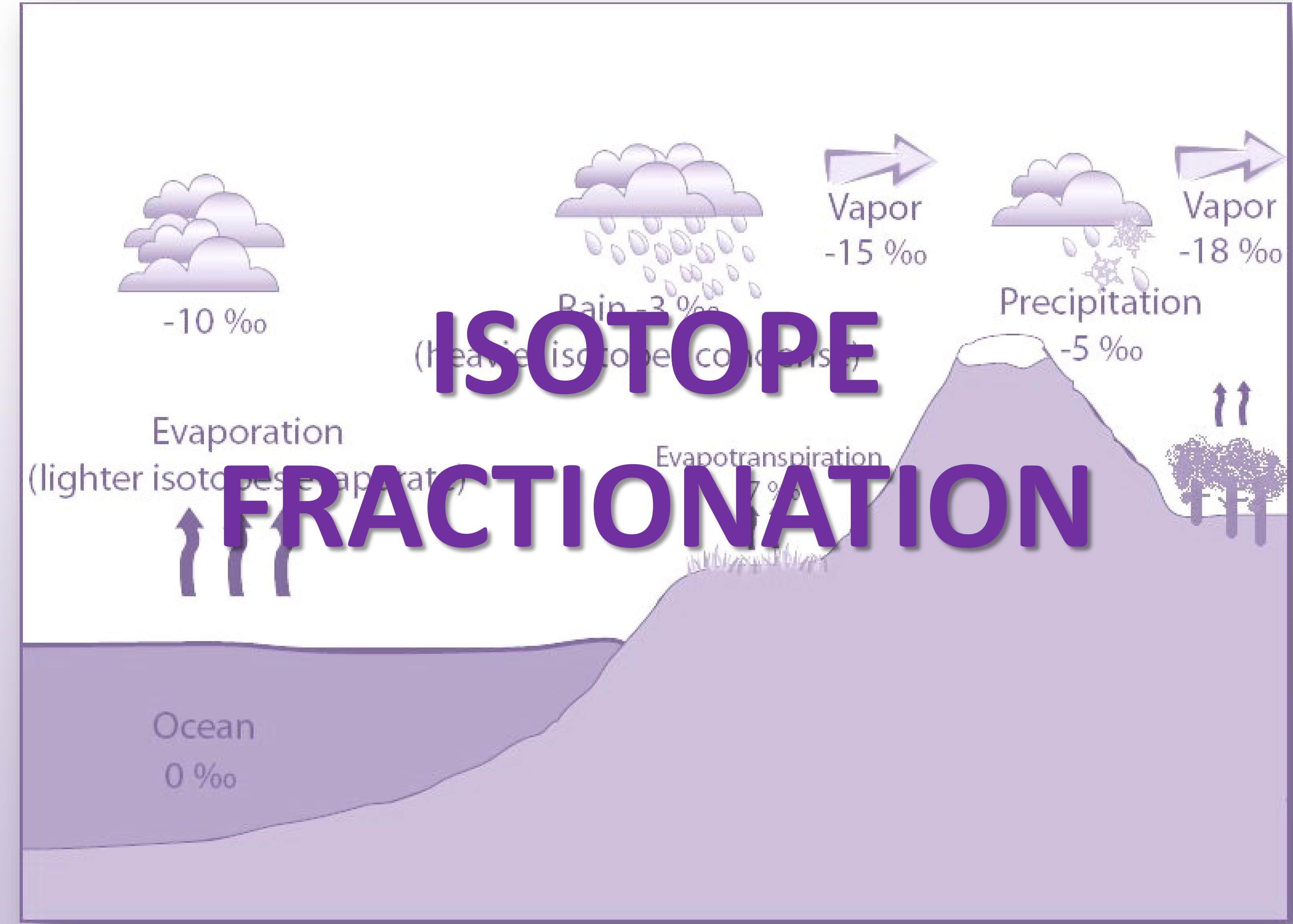
$$\delta^{18}O = \frac{{}^{18}O/{}^{16}O_{sample} - {}^{18}O/{}^{16}O_{standard}}{{}^{18}O/{}^{16}O_{standard}} \times 1000$$

-The $\delta_{isotope}$ will be positive if $R_{sample} > R_{std}$
→ the sample is enriched in heavy isotopes compared to the standard (for example if $^{18}O\ R_{sample} > {}^{18}O\ R_{std}$)

-The $\delta_{isotope}$ will be negative if $R_{sample} < R_{std}$
→ the sample is depleted in heavy isotopes compared to the standard (for example if $^{18}O\ R_{sample} < {}^{18}O\ R_{std}$)

-If $\delta^{18}O$ = 2 ‰, it means the CO_2 in the sample (e.g., from a foraminifer shell) is enriched by 2 parts per thousand in the heavy isotope ^{18}O compared to the CO_2 in the standard, as measured by the mass spectrometer.

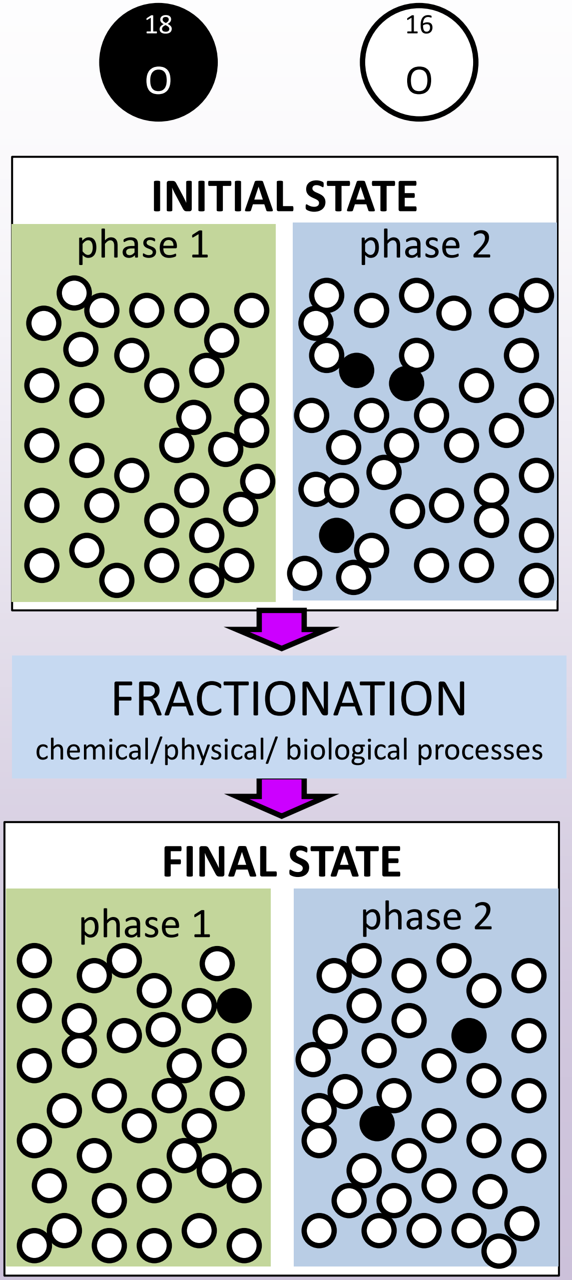
ISOTOPE FRACTIONATION



ISOTOPE FRACTIONATION: DEFINITION

The properties of isotopes of the same element are very similar as they depend on the atom's electronic configuration. However, they are not identical, and isotopes like ^{16}O and ^{18}O show different behaviors in various natural processes.

ISOTOPE FRACTIONATION is the process by which isotopes of the same element are unevenly distributed between different substances or phases in a natural system.
This occurs because lighter and heavier isotopes react or transfer differently during chemical (e.g., calcite precipitation), physical (e.g., evaporation), and biological (e.g., photosynthesis) processes.
Isotopic fractionation is essential in studying environmental and geochemical processes, as it provides valuable insights into climate and geological history.



INITIAL STATE

phase 1

phase 2

FRACTIONATION

chemical/physical/ biological processes

FINAL STATE

phase 1

phase 2

ISOTOPE FRACTIONATION: : WHY

Isotopic fractionation occurs because isotopes of an element have different masses (due to variations in the number of neutrons), **and these mass differences (vibrational energy) affect the thermodynamic properties of the compounds/phases they form**. There are two main types of isotopic fractionation.

EQUILIBRIUM ISOTOPE FRACTIONATION

refers to the selective separation of isotopes between substances/phases in chemical equilibrium. This fractionation arises from the reduced vibrational energy when a heavier isotope (e.g., ^{18}O) replaces a lighter one (e.g., ^{16}O). It occurs in reversible reactions.

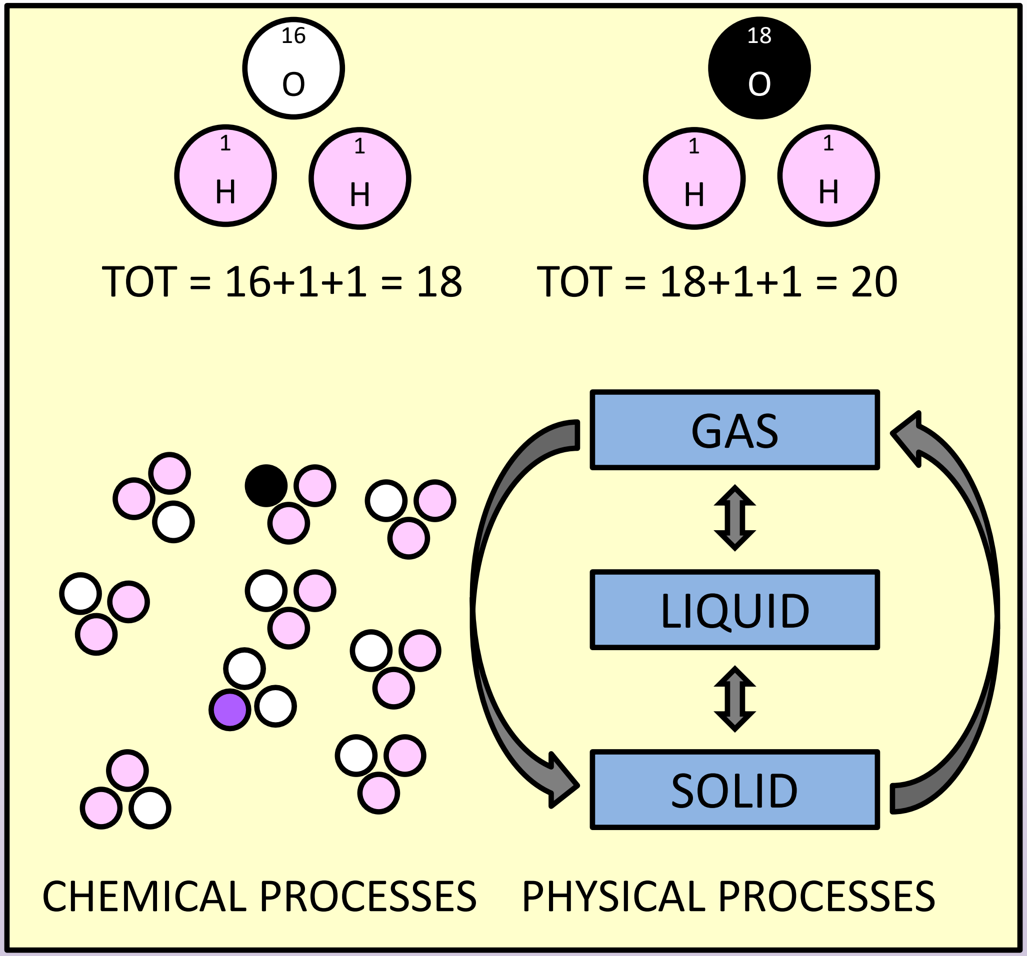
KINETIC FRACTIONATION

is isotopic separation based on mass that occurs during one-way processes, like photosynthesis and evaporation. In biological processes, which are typically kinetic, organisms preferentially use lighter isotopes due to the lower "energy costs" associated with them.

ISOTOPE FRACTIONATION -1

Molecules like H_2O with different isotopes (H and O) form chemical bonds of varying strength due to atomic mass differences.

H_2O molecules with different isotopic compositions show slight variations in behavior during chemical reactions and physical processes like evaporation and condensation in closed systems.



TOT = 16+1+1 = 18

TOT = 18+1+1 = 20

GAS

LIQUID

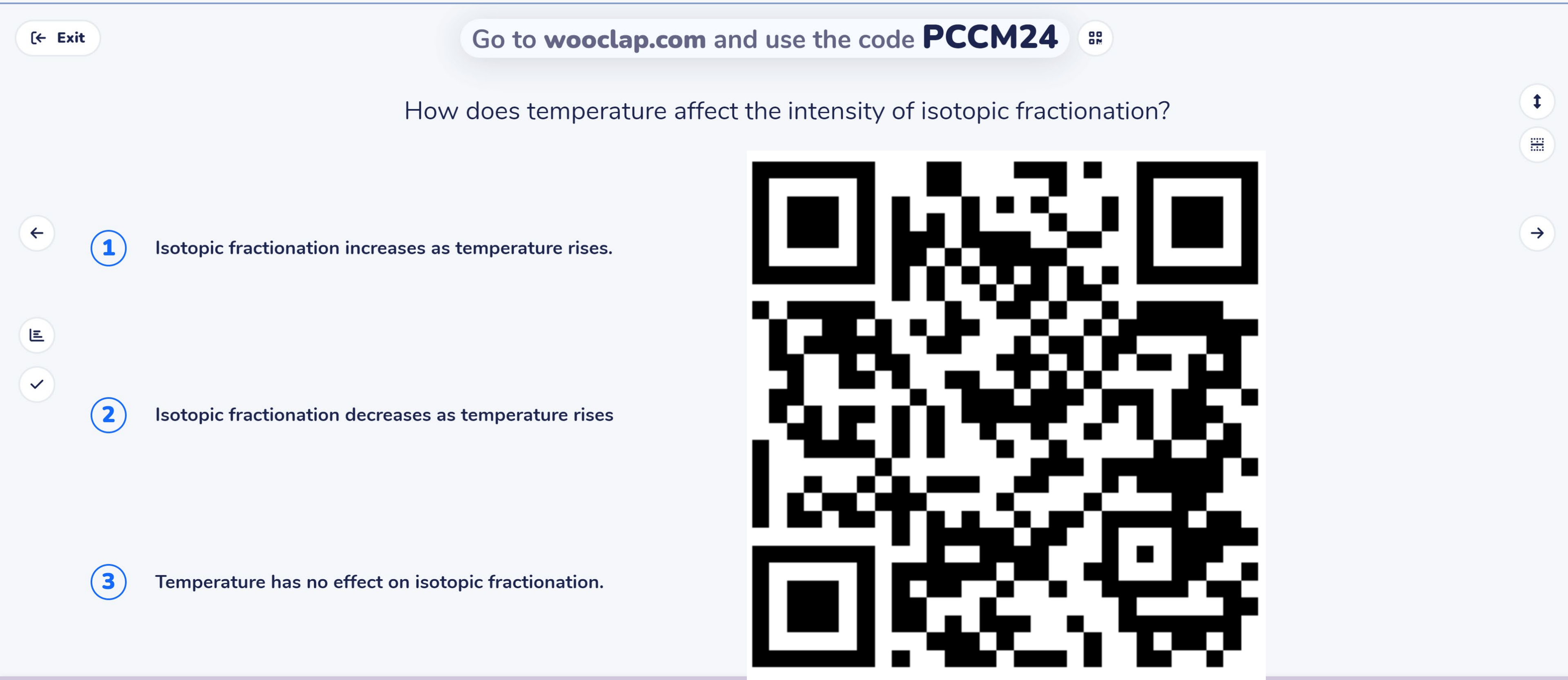
SOLID

CHEMICAL PROCESSES

PHYSICAL PROCESSES

In a chemical reaction, atoms exchange "partners" and form new bonds, while in physical processes, only their state (gas, liquid, solid) changes. **Bonds with lighter isotopes break more easily than those with heavier isotopes.**

How does temperature affect the intensity of isotopic fractionation?



Go to **wooclap.com** and use the code **PCCM24**

How does temperature affect the intensity of isotopic fractionation?

1. Isotopic fractionation increases as temperature rises.
2. Isotopic fractionation decreases as temperature rises
3. Temperature has no effect on isotopic fractionation.

https://app.wooclap.com/events/PCCM24/0

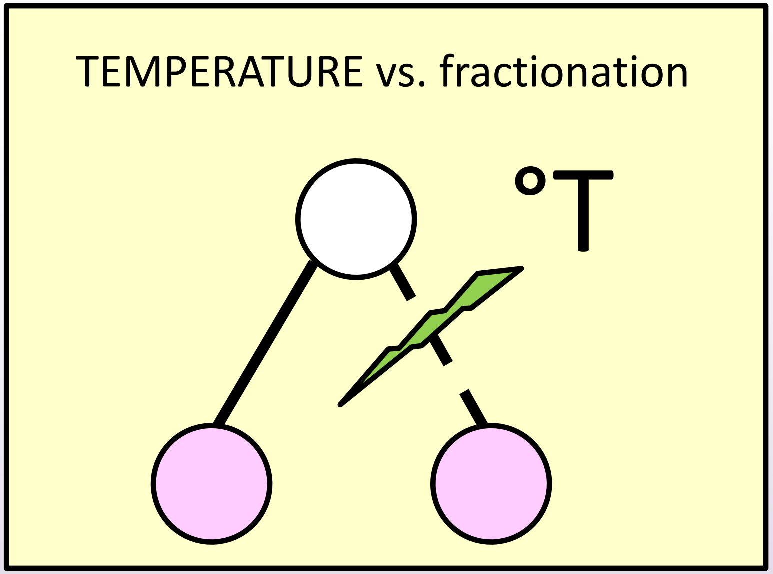
ISOTOPE FRACTIONATION -2

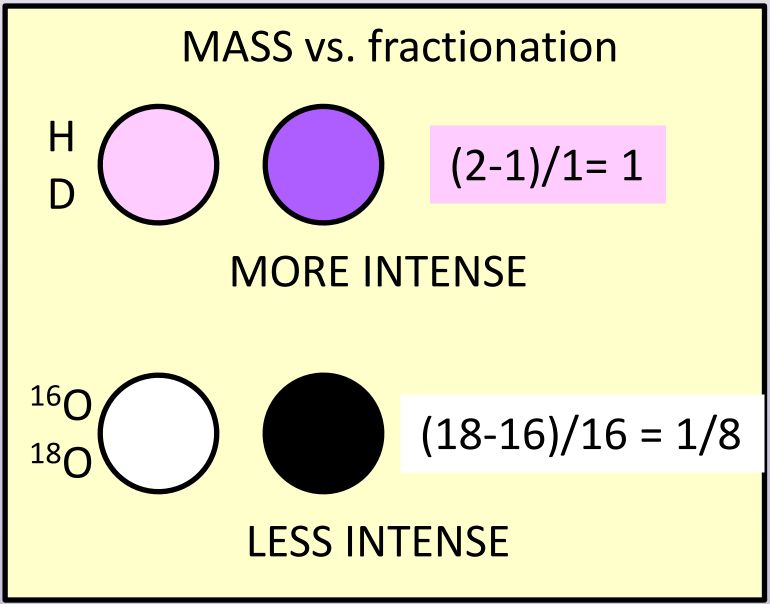
The TEMPERATURE factor

Isotope fractionation varies with temperature, **being more pronounced at lower temperatures** when the differences in isotope behavior are most significant, but it decreases as temperatures rise.

The MASS factor

The degree of fractionation is influenced by temperature and the specific atoms involved. **Fractionation is more pronounced for isotopes with significant relative mass differences**. For instance, the fractionation between hydrogen and deuterium (which is twice as heavy as hydrogen) is much more intense than in the case of oxygen, where the mass difference is smaller: (18-16) / 16 = 1/8.


TEMPERATURE vs. fractionation


MASS vs. fractionation

ISOTOPE FRACTIONATION -3

EQUILIBRIUM FRACTIONATION characterizes exchange reactions between isotopes taking place in two distinct phases of the same compound, occurring at a rate that sustains equilibrium, as seen in **the transformation of water vapor into liquid water**. Even though the process is at equilibrium, the rate of exchange differs, resulting in an enrichment of one of the two isotopes. This type of reaction can be described as follows:

$$^{16}O_{vapor} + {}^{18}O_{liquid} \leftrightarrow {}^{18}O_{vapor} + {}^{16}O_{liquid}$$

$$^{1}A + {}^{2}B \leftrightarrow {}^{2}A + {}^{1}B$$

reactants products

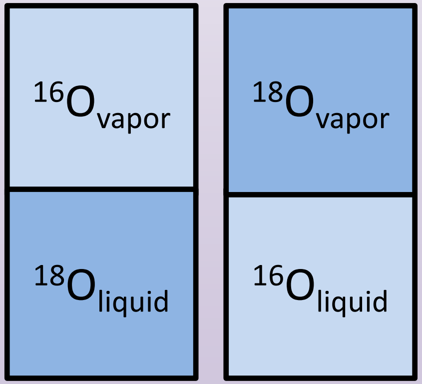
where
A and B are the phases (vapor and liquid)
Indexes 1 and 2 are the isotopes (^{16}O and ^{18}O)

The Equilibrium constant (K) of the reaction is:

$$K = \frac{[^{1}B]\,[^{2}A]}{[^{2}B]\,[^{1}A]}$$

products

reactants


$^{16}O_{vapor}$
$^{18}O_{vapor}$
$^{18}O_{liquid}$
$^{16}O_{liquid}$

..which can expressed as the isotope ratio in each phase:

$$R_{A(vap)} = \frac{[^{2}A]}{[^{1}A]} \qquad R_{B(liq)} = \frac{[^{2}B]}{[^{1}B]}$$

and

$$K = \frac{[R_A]}{[R_B]} = \alpha_{A\text{-}B}$$

ISOTOPE FRACTIONATION -4

$$R_{A(vap)} = \frac{[^{2}A]}{[^{1}A]} \qquad R_{B(liq)} = \frac{[^{2}B]}{[^{1}B]} \qquad K = \frac{[R_A]}{[R_B]}$$

The value of the K indicates the position of the equilibrium:
$K>1$: Products are favored, and the equilibrium shifts to the right.
$K<1$: Reactants are favored, and the equilibrium shifts to the left.

The isotopic chemical fractionation factor
is the ratio of the relative abundances of an element's isotopes ($^{18}O/^{16}O$) in two different substances or phases, resulting from a chemical or physical process.
This factor measures the degree of separation between lighter and heavier isotopes during a chemical reaction or phase transition, such as condensation or evaporation. The fractionation factor is usually expressed as:

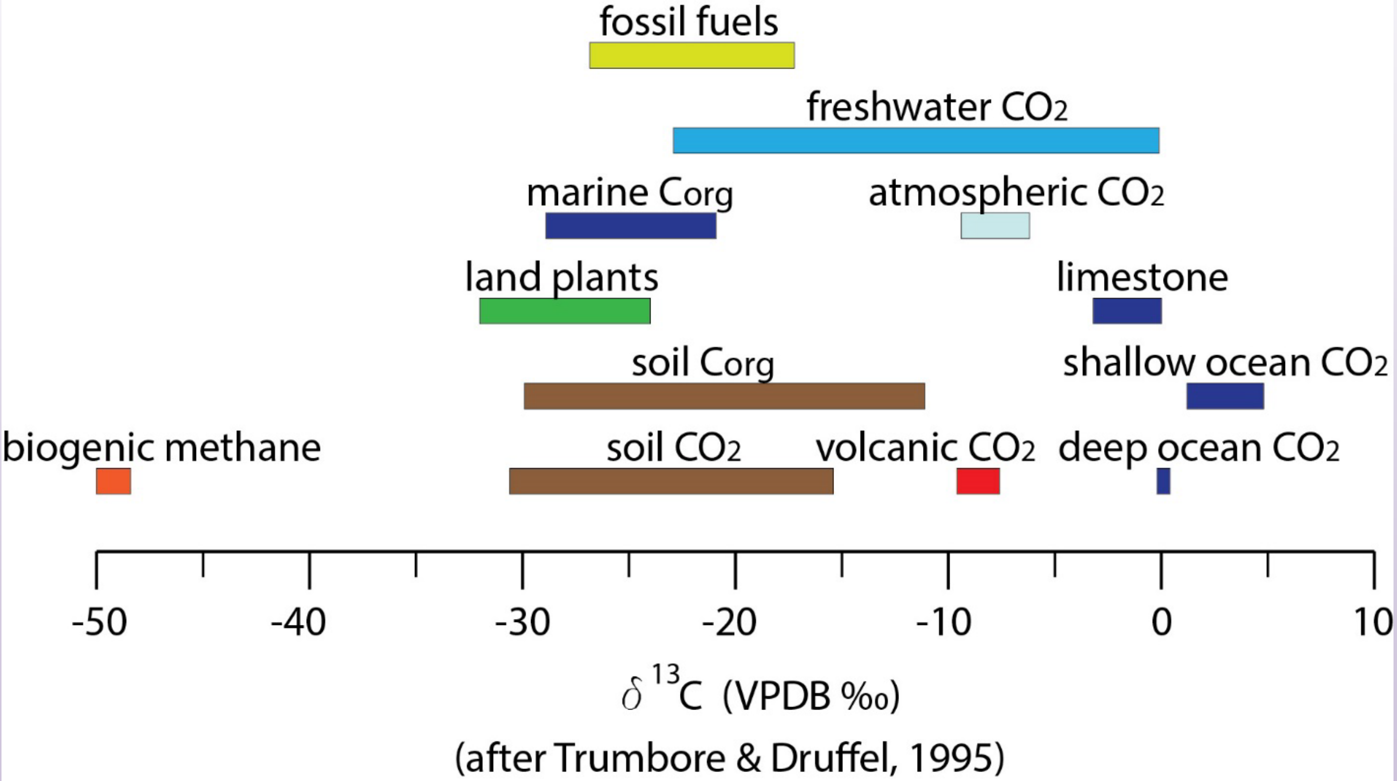
$$\alpha_{\mathrm{A-B}} = \mathrm{K} = \frac{[RA]}{[RB]}$$

where R is the ratio of the heavy to light isotope ($^{18}O/^{16}O$) in each phase

ISOTOPIC VARIABILITY IN NATURE

Isotopic fractionation causes significant variation in the carbon (C) and oxygen (O) isotopic composition in biological and geological materials, including water and air.

VARIABILITY OF $\delta^{13}C$ IN NATURE



(after Trumbore & Druffel, 1995)

The $\delta^{13}C$ of natural carbon compounds varies widely, ranging from ~0 to ~-110 ‰ relative to the VPDB standard.

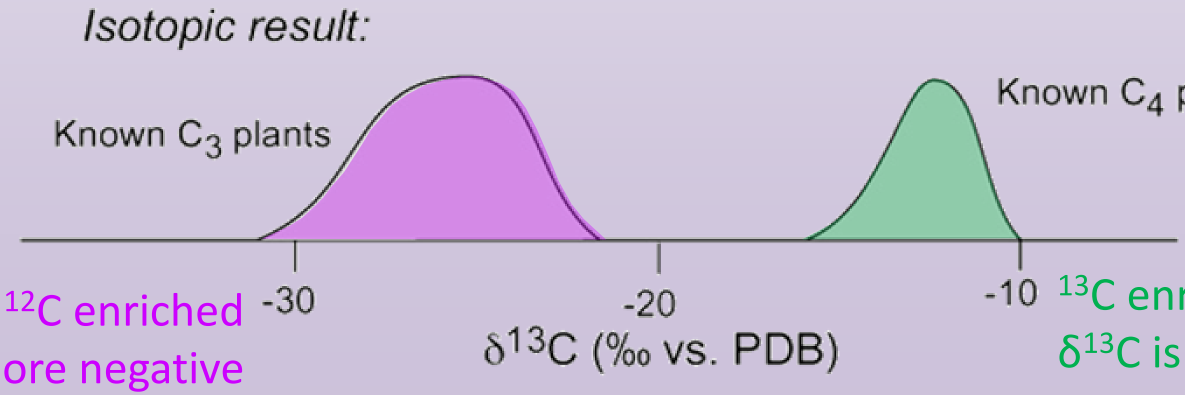
CARBON E PHOTOSYNTHESIS

This variation occurs because, during photosynthesis, **plants prefer the lighter isotope, ^{12}C, absorbing less ^{13}C (and ^{14}C) from CO_2 in the atmosphere or water.**

Different photosynthetic mechanisms show varying fractionation patterns.

Algae differ from terrestrial plants.

C3 plants (e.g., angiosperms, trees, shrubs, and temperate herbaceous plants - Calvin-Benson cycle) discriminate more against ^{13}C than **C4 plants** (e.g., corn in arid regions), which use the Hatch-Slack pathway

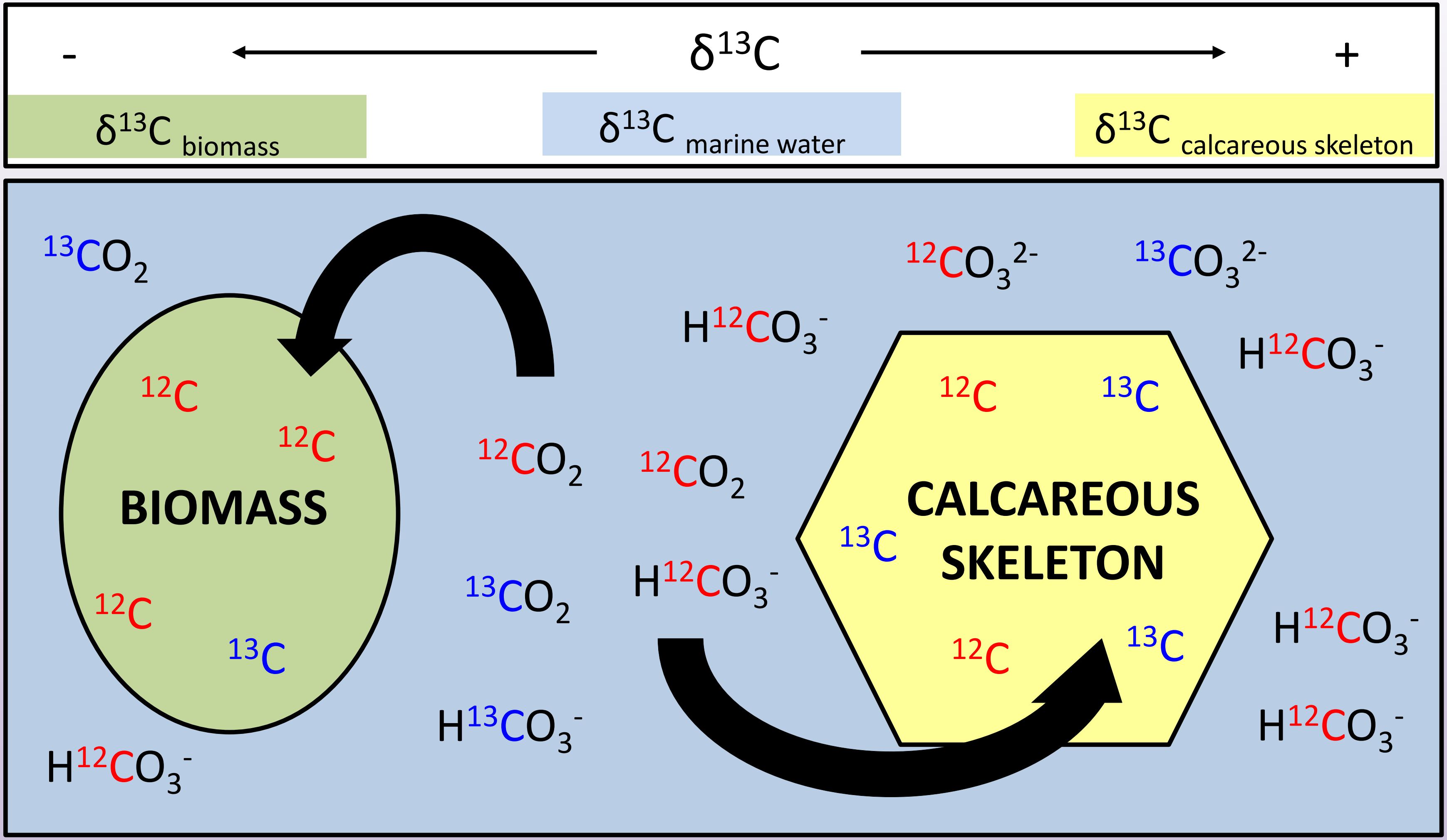


^{12}C enriched
$\delta^{13}C$ is more negative

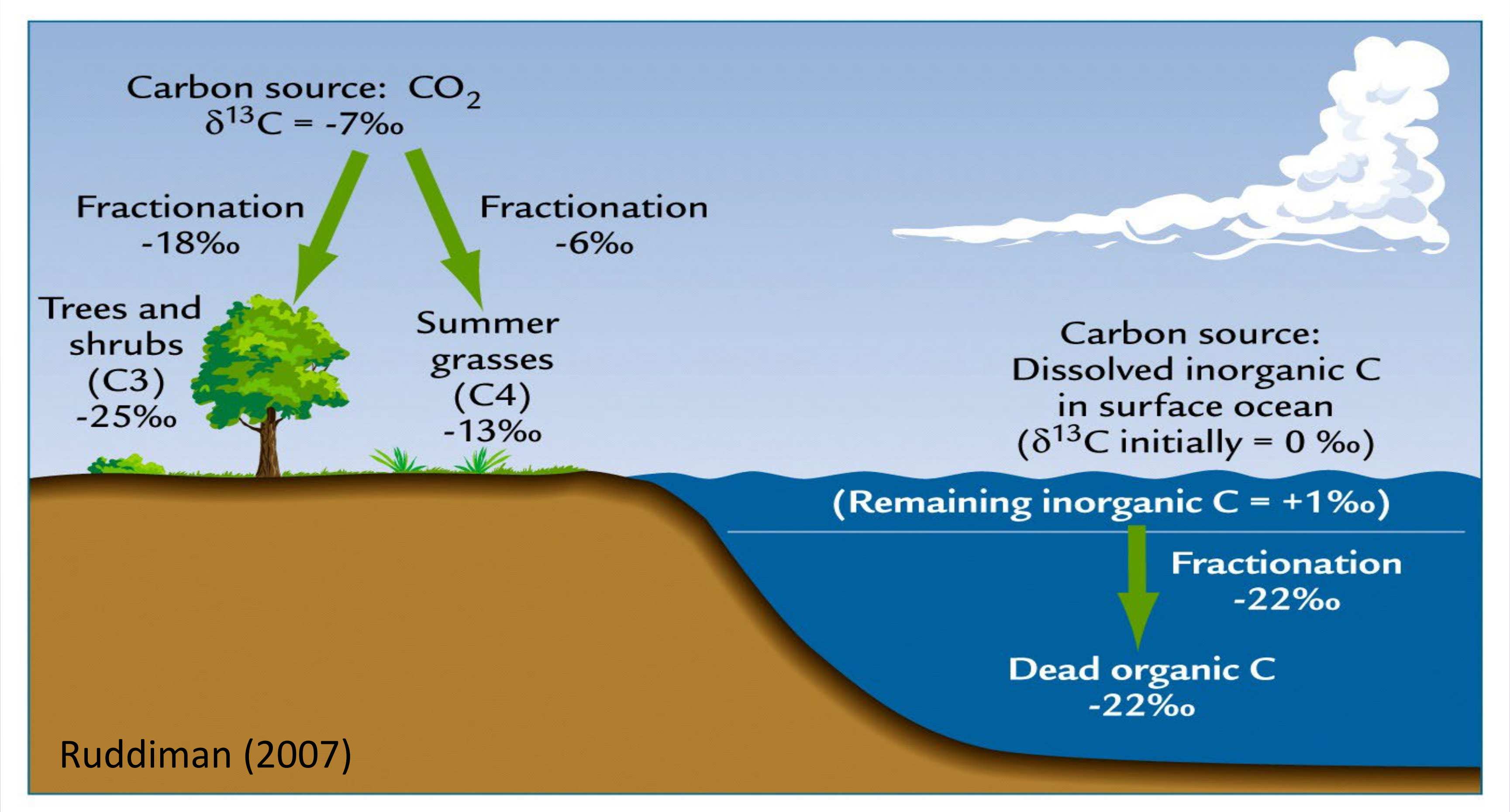
^{13}C enriched
$\delta^{13}C$ is less negative

MARINE PHOTIC ZONE

Photosynthesis preferentially fixes $^{12}CO_2$ (light Dissolved Inorganic Carbon - DIC), leaving a greater abundance of heavy DIC available to form calcareous skeletons.



$\delta\ ^{13}C$ and PHOTOSYNTESIS: A SUMMARY



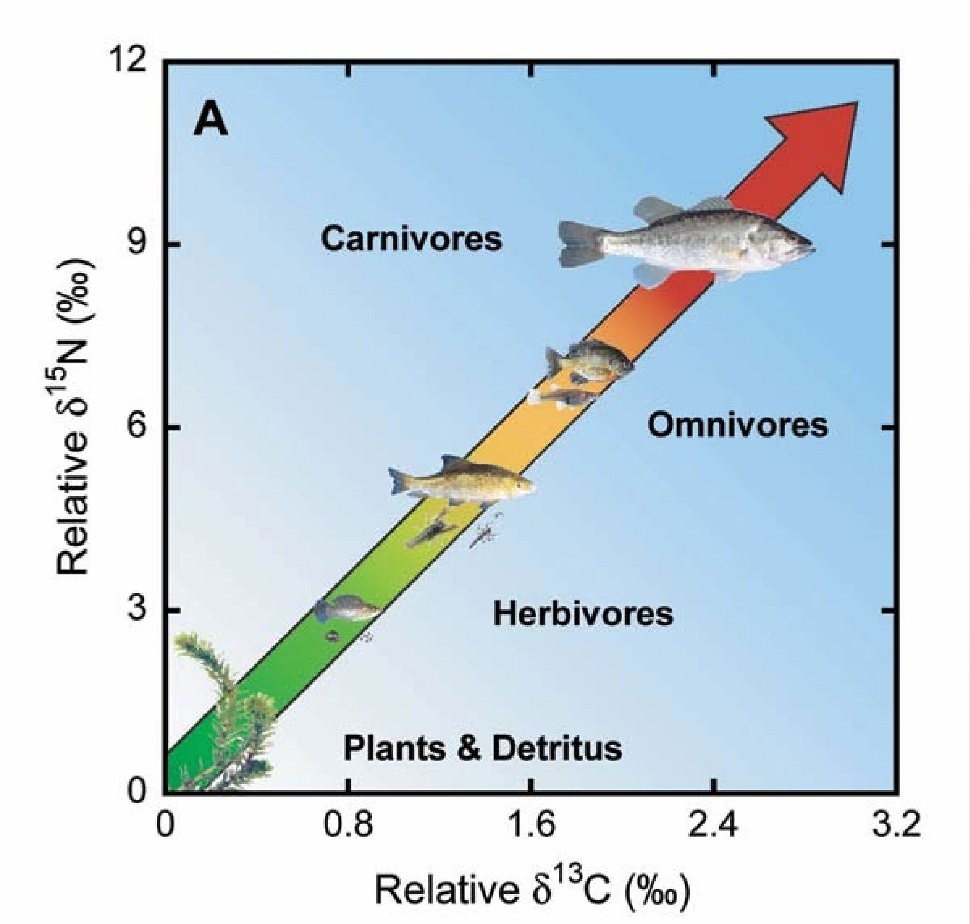
Ruddiman (2007)

CARBON ISOTOPES AND THE FOOD CHAIN

The isotopic composition of plants is passed through the food chain via fractionation, affecting herbivores and their predators.

Herbivores that consume primarily C3 plants will have a different carbon isotopic composition than those eating C4 plants.

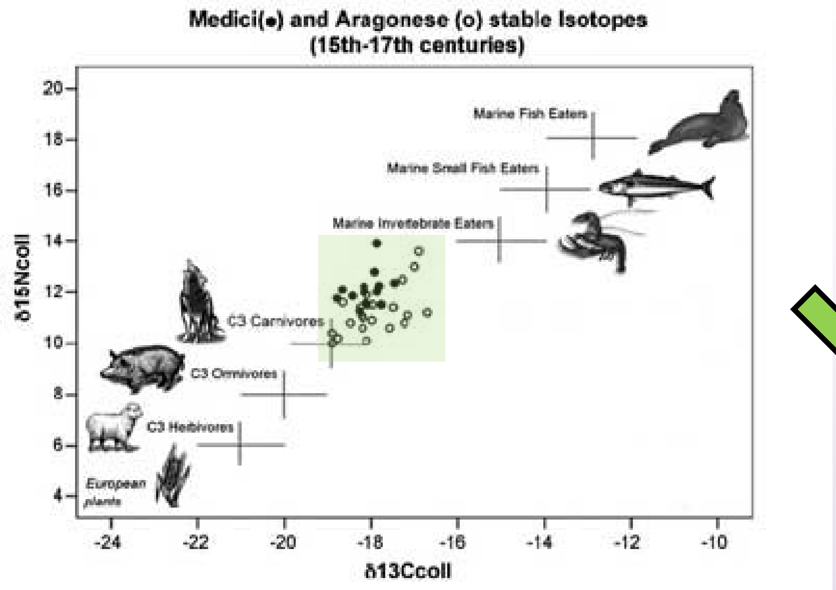
This helps paleoecologists determine the diets of ancient animals.



Isotopic views of food webs in the Everglades (McCutchan et al., 2003)

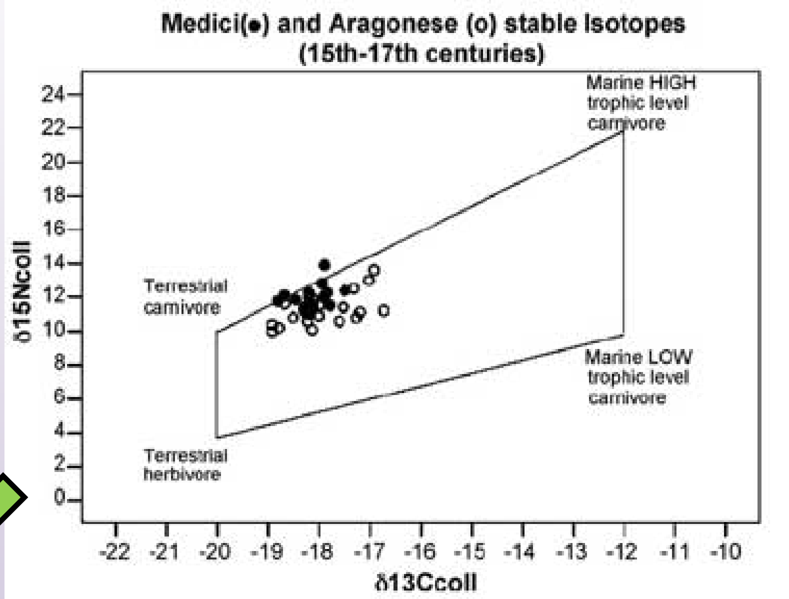
The **isotopic composition** of N and C in animal tissues reflects their **diet** and helps determine their **position in the food chain**.

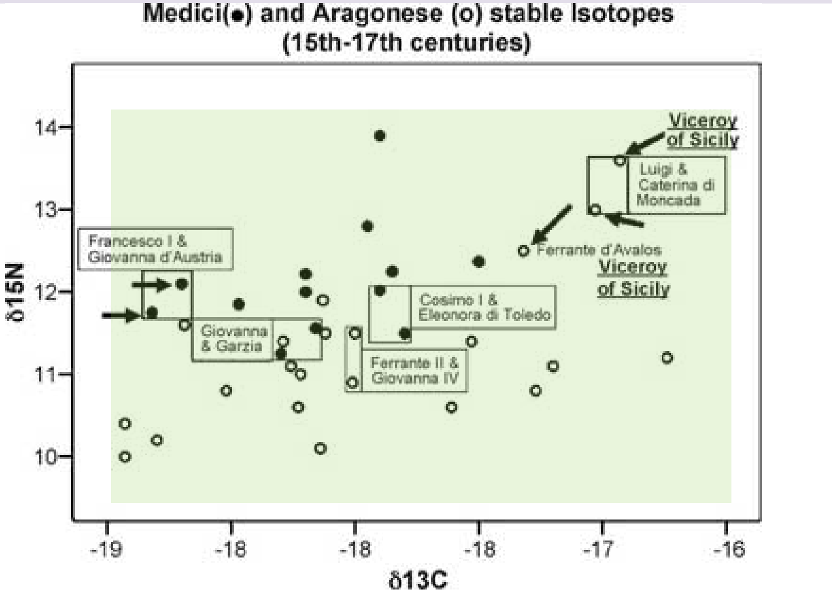
CARBON ISOTOPES AND HUMAN PALEODIETS



Diet of Medici (FI) and of Aragonese (NA)

+2–4 ‰ in nitrogen
+0.5–1 ‰ in carbon



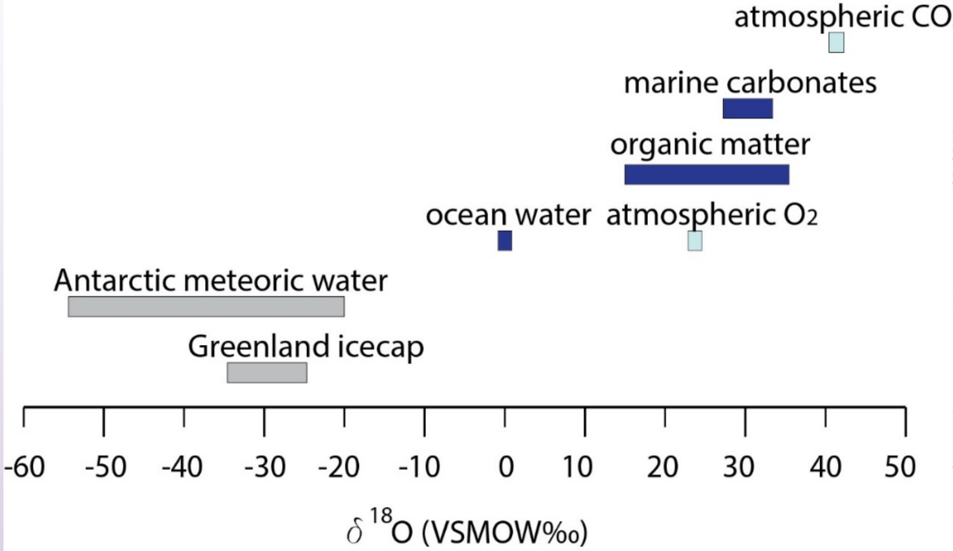


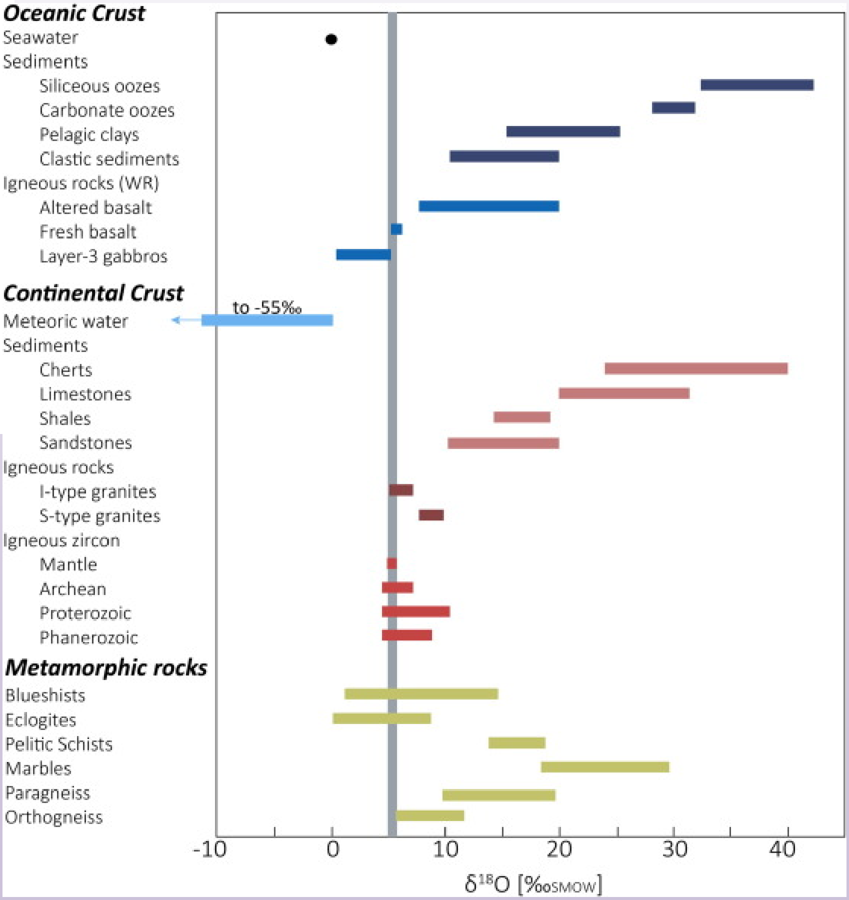
Linear interpolation with the bone collagen δ^{13}C values, estimating a fish integration of the diet at 14–30 % for the Medici (black circles) and at 12–40 % for the Aragonese (white circles).

GOUT: Replacement disease characterized by the deposition of uric acid in the joints, which become swollen and painful.

VARIABILITY OF δ^{18}O IN NATURE

Isotopic fractionation causes significant variation in oxygen (O) isotopic composition in biological and geological materials, including water and air.





VARIABILITY OF OXYGEN ISOTOPES

RAINFALL OXYGEN ISOTOPIC VARIABILITY

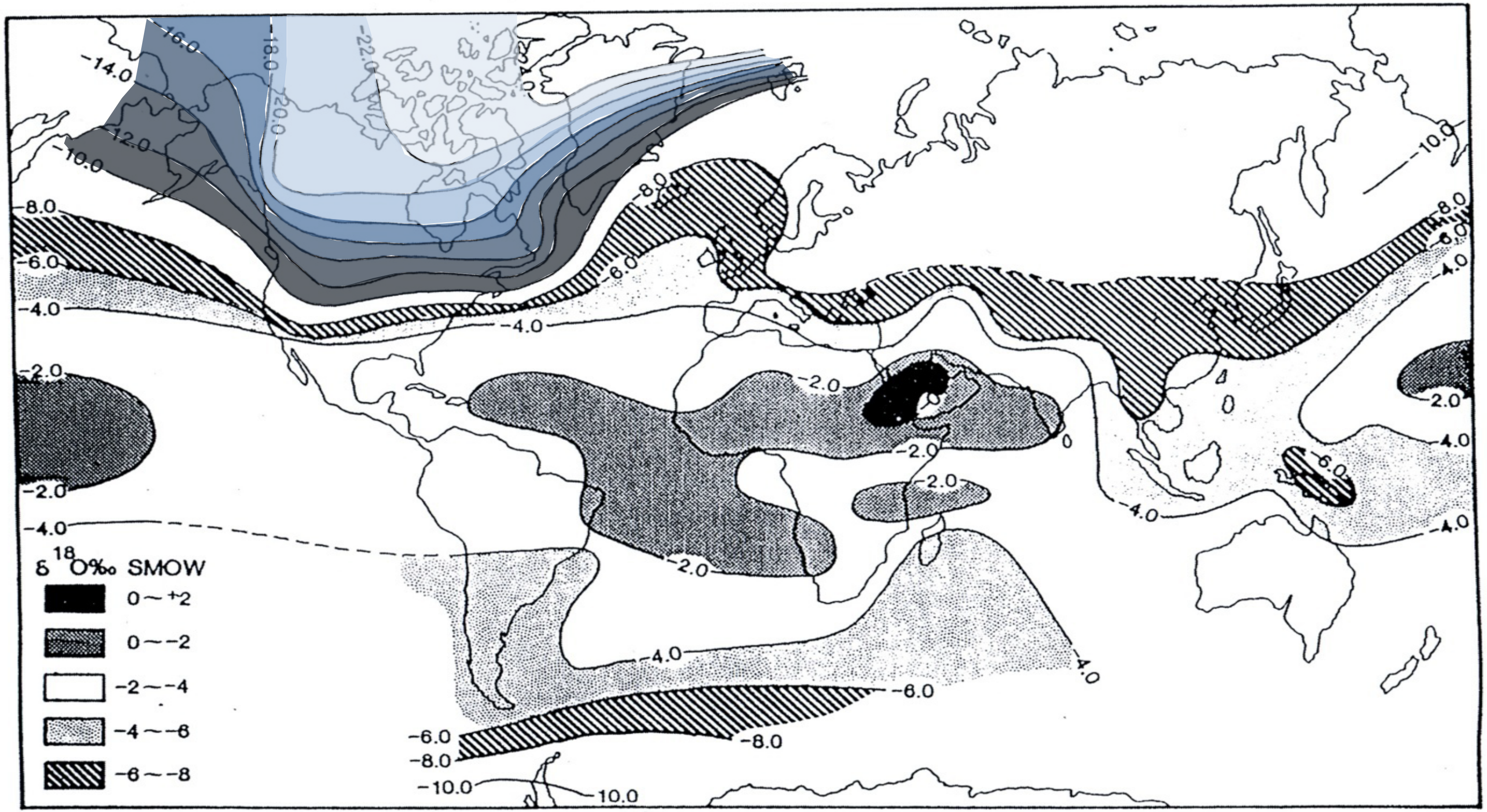
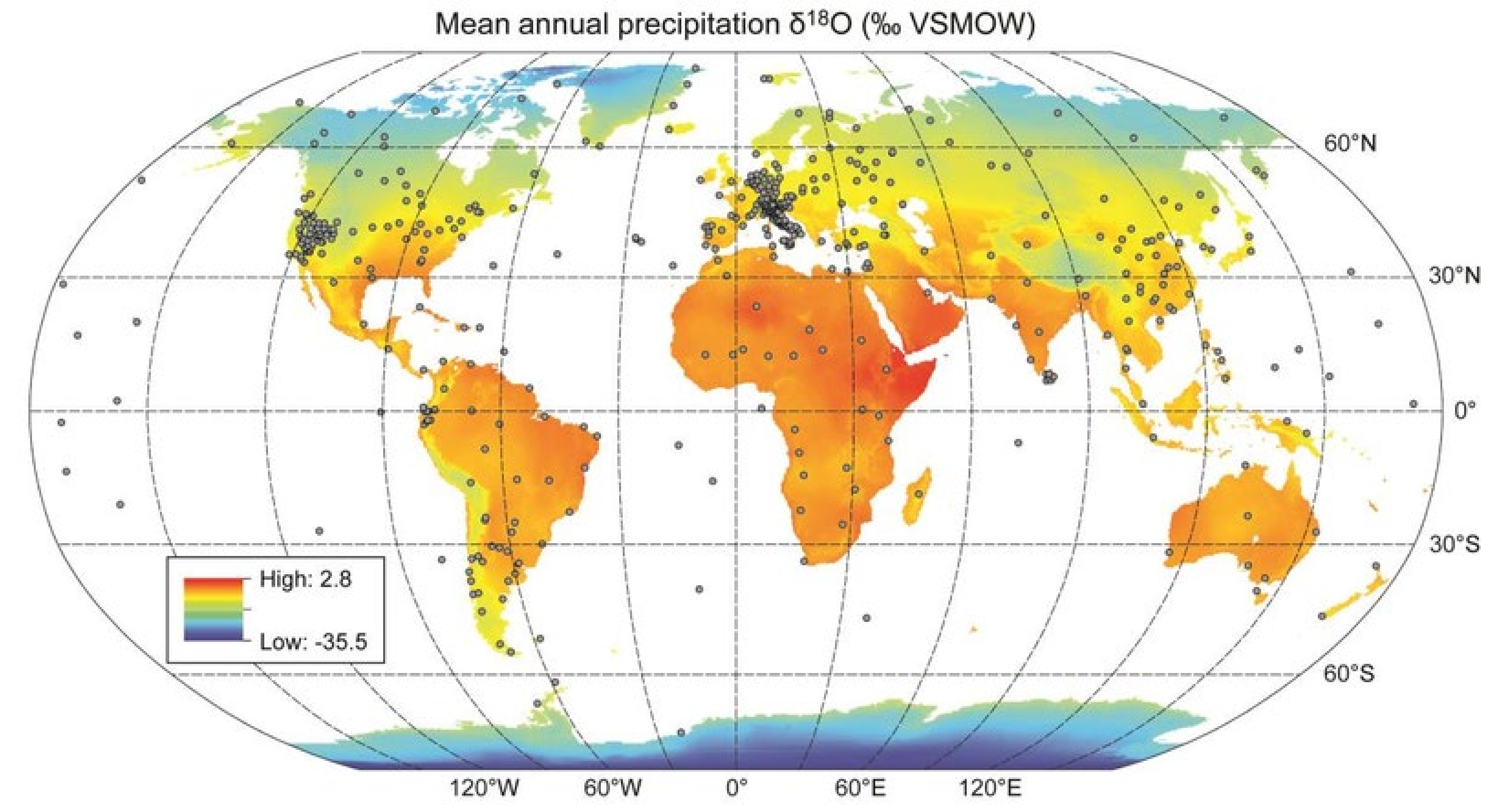


Figure 1-12. Mean annual $\delta^{18}O$ values of precipitation from the IAEA network stations (Yurtsever, 1975).

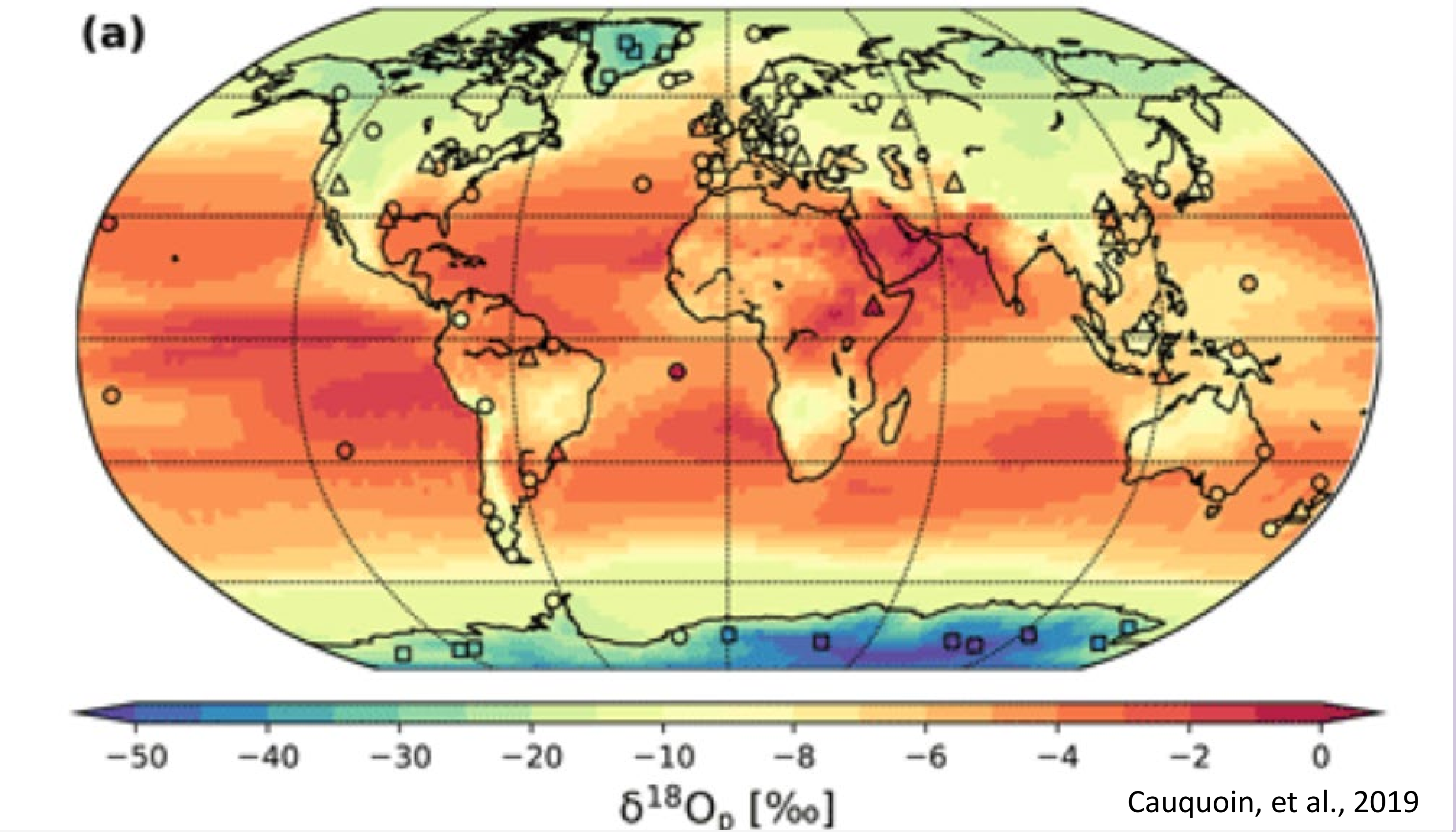
The $\delta^{18}O$ in nature is highly variable. The isotopic composition of precipitation, $\delta^{18}O$, ranges from -2 to -22 ‰, primarily due to the hydrological cycle.

GLOBAL DISTRIBUTION OF ANNUAL $\delta^{18}O$ IN PRECIPITATION



Baker, 2014

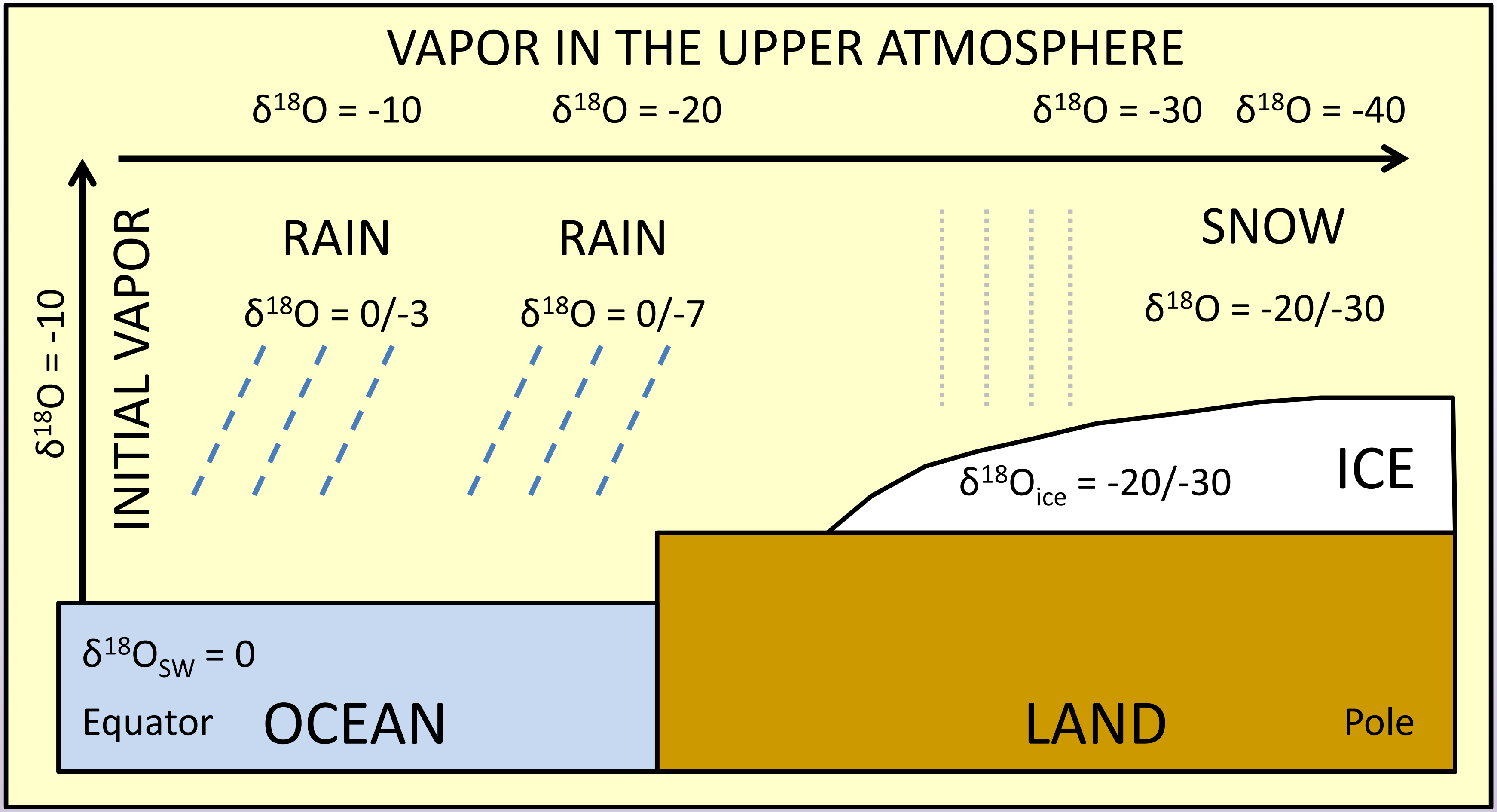
GLOBAL DISTRIBUTION OF ANNUAL $\delta^{18}O$ IN PRECIPITATION



Cauquoin, et al., 2019

Figure 1 **(a)** Global distribution of simulated (background pattern) and observed (colored markers; see text for details) annual mean $\delta^{18}O_p$ values in precipitation under PI conditions. The data consist of 70 GNIP stations (circles), 15 ice core records (squares; Table 1) and 33 speleothem records (triangles). **(b)** Modeled vs. observed annual mean $\delta^{18}O_p$ at the different GNIP,

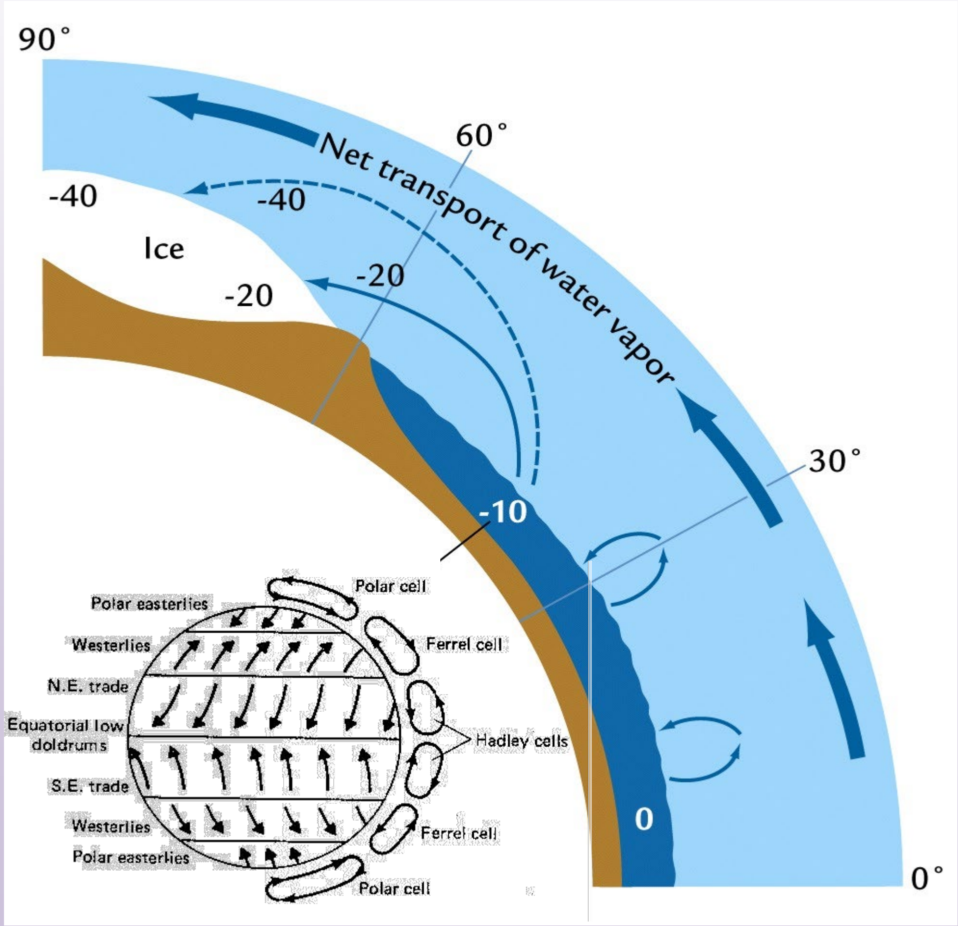
LARGE SCALE δ ^{18}O VARIABILITY



Oxygen isotope concentrations vary across the hydrosphere, atmosphere, and oceans. On average, oceans have δ^{18}O = 0.0 ‰, while ice caps range from -20 ‰ to -30 ‰, with all values subject to variation.

OXYGEN AND HYDROLOGICAL CYCLE

The Earth functions like a multistage distillation column, where isotopic fractionation from the hydrological cycle is known as "**RAYLEIGH FRACTIONATION**" or "**DISTILLATION** .

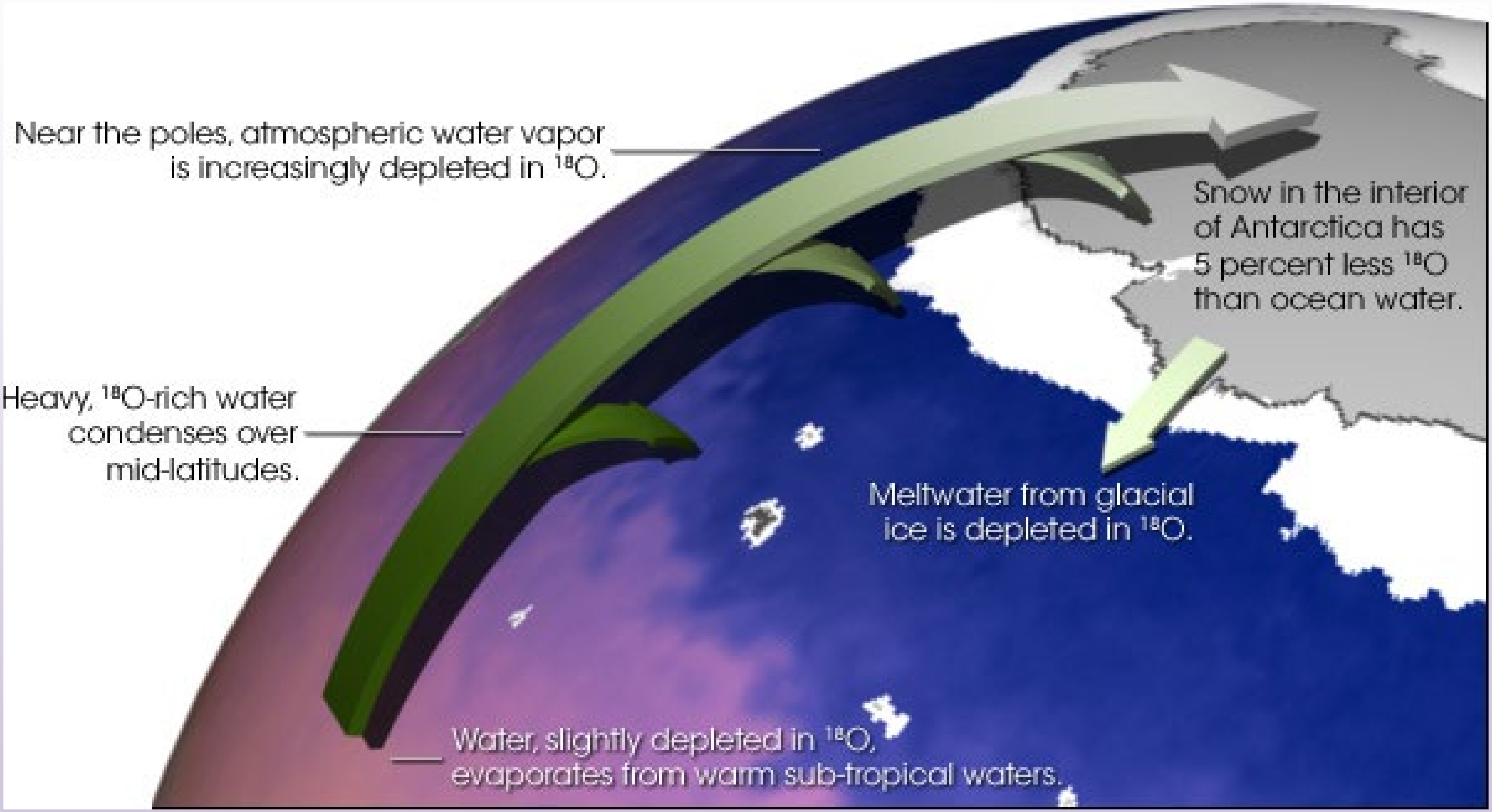


Water (H_2O) evaporating at the equator becomes lighter (enriched in ^{16}O) compared to the water left in the ocean, known as the "**rain out effect**."

As this H_2O moves toward higher latitudes, it condenses and precipitates as "heavy" water. The clouds become isotopically lighter, a process called the "**latitude effect**."

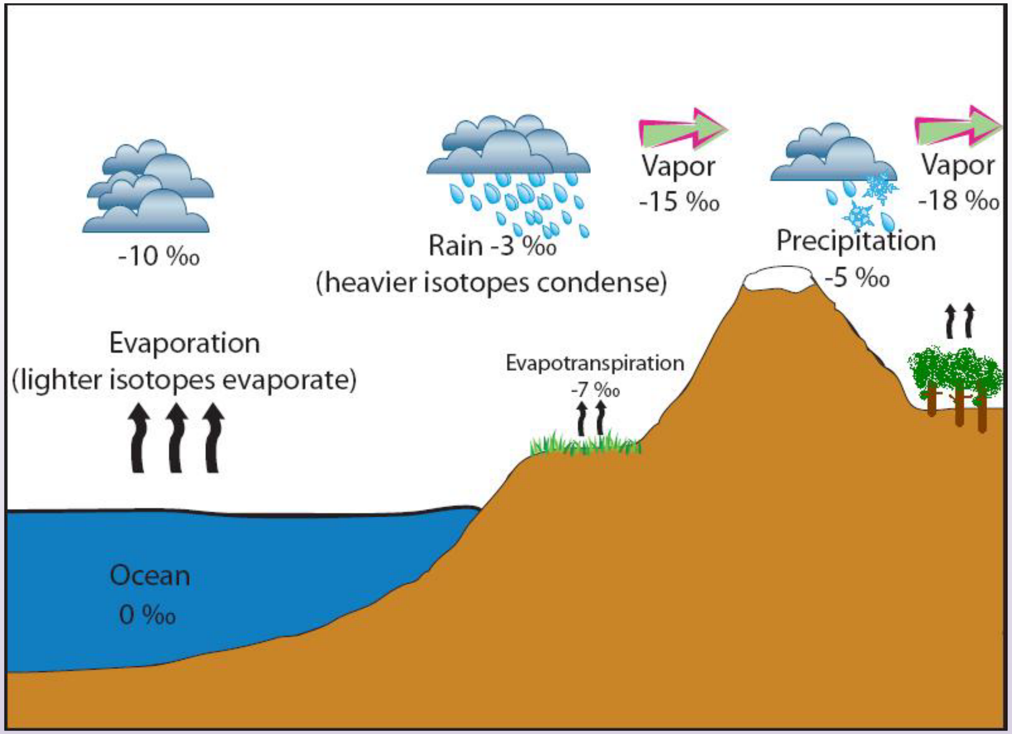
At higher latitudes, precipitation, including polar snowfall, is increasingly enriched in ^{16}O.

LATITUDE EFFECT



As you move to higher latitudes, precipitation comes from progressively "lighter" clouds, enriched in ^{16}O.

δ^{18}O, EVAPORATION AND PRECIPITATIONS



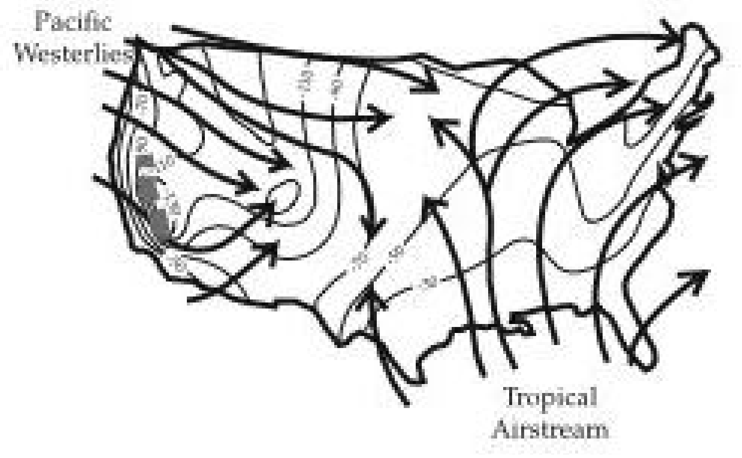
When water evaporates, $H_2^{16}O$ molecules evaporate more easily, making the vapor enriched in light isotopes ($\delta^{18}O$ = -10 ‰).

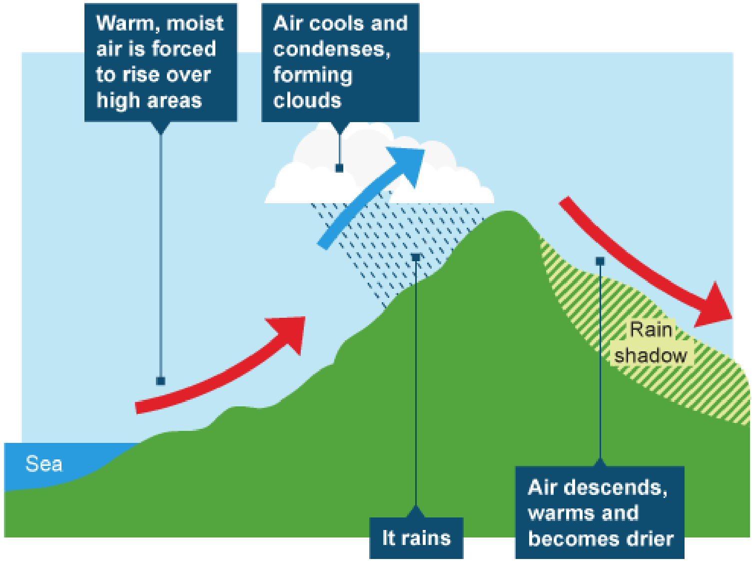
$H_2^{16}O$ vapor is lighter than $H_2^{18}O$ due to its higher vapor pressure, favoring its transition to the gas phase.

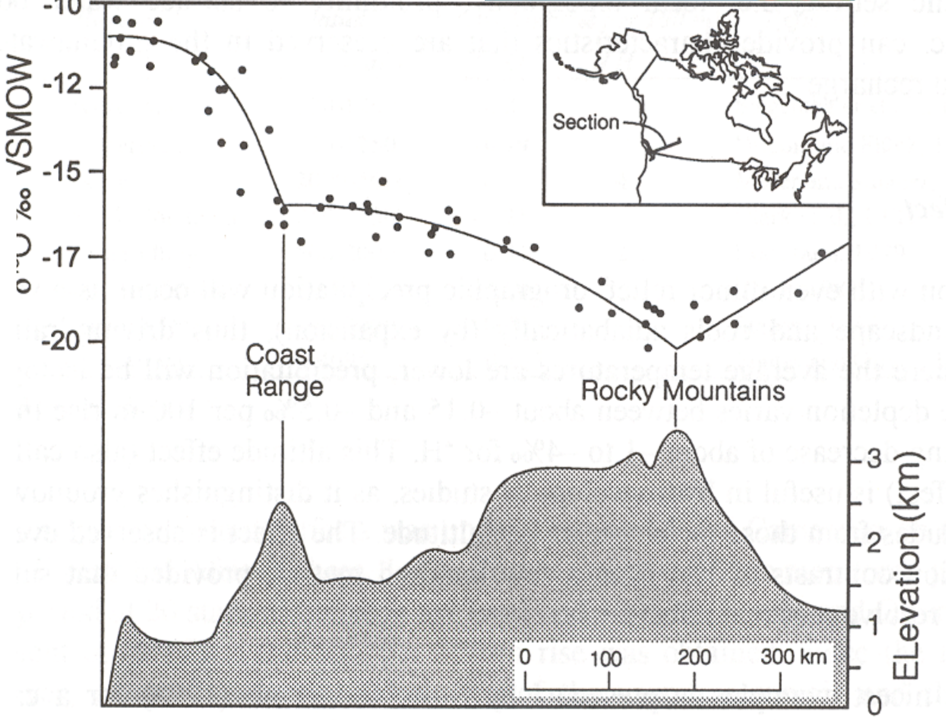
When water vapor condenses, it becomes enriched in heavier molecules ($H_2^{18}O$).

Vapor pressure, in simple terms, is the pressure exerted by the vapor (gaseous form) of a substance when it's in equilibrium with its liquid or solid form at a given temperature. It represents the tendency of molecules in the liquid or solid phase to escape into the gas phase. The higher the vapor pressure, the more readily a substance will evaporate.

δ ^{18}O: ALTITUDE EFFECT



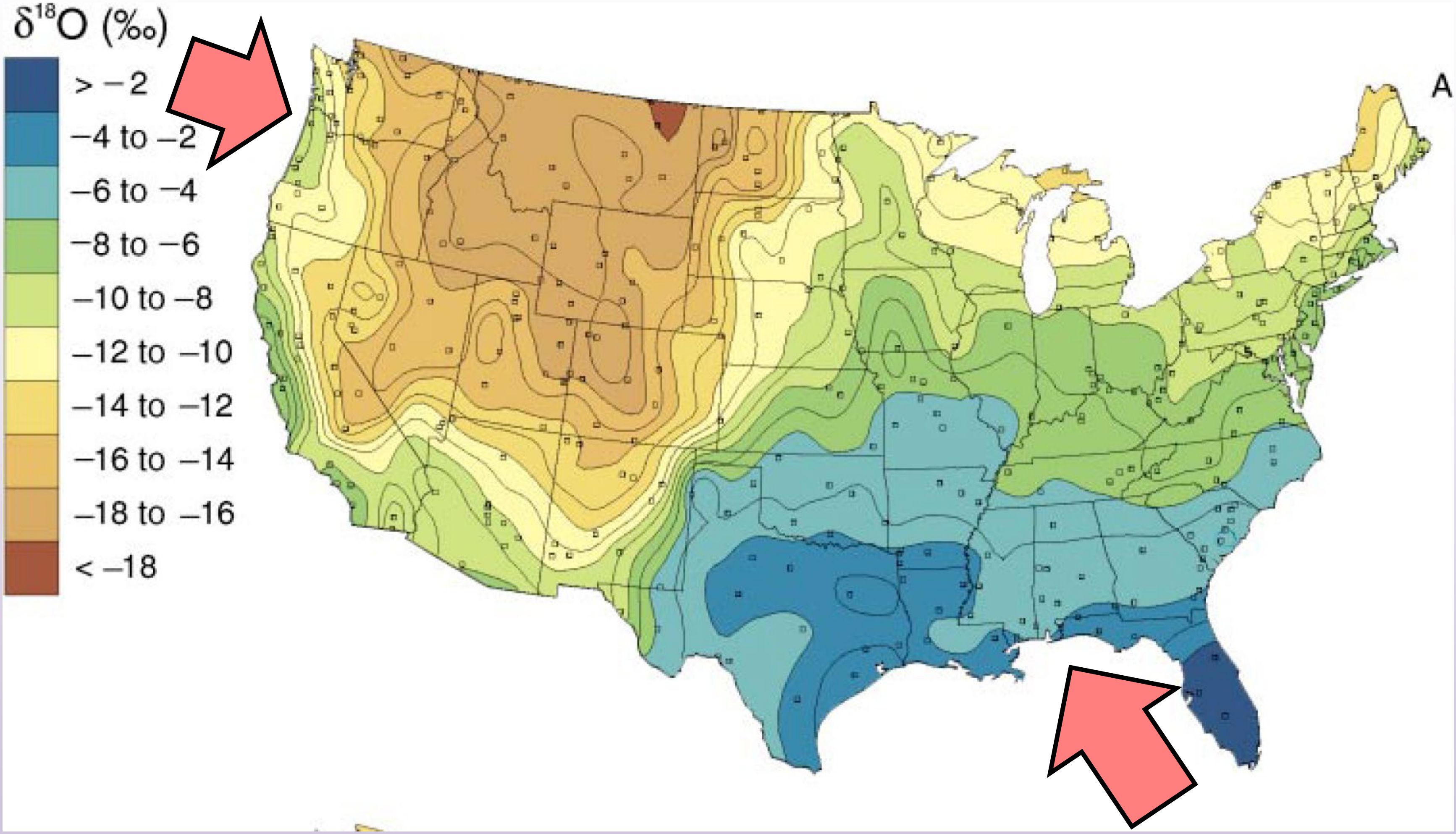




Moist masses of air carried by the prevailing winds. Masses of air are forced to rise. Condensation and precipitation.

Progressive decrease in the values of δ^{18}O along a section (North Pacific coast – USA)

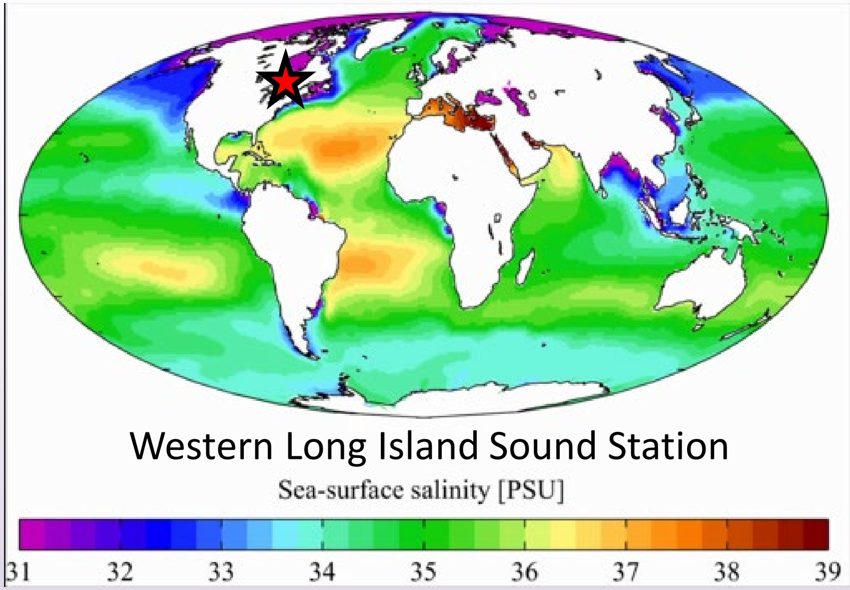
δ ^{18}O: CONTINENTALITY



The δ^{18}O value decreases as air masses move inland from oceans, due to progressive rainout of heavier isotopes (^{18}O). This phenomenon, known as "continentality," results in lighter δ^{18}O values in precipitation as distance from the coast increases.

δ^{18}O AND SALINITY

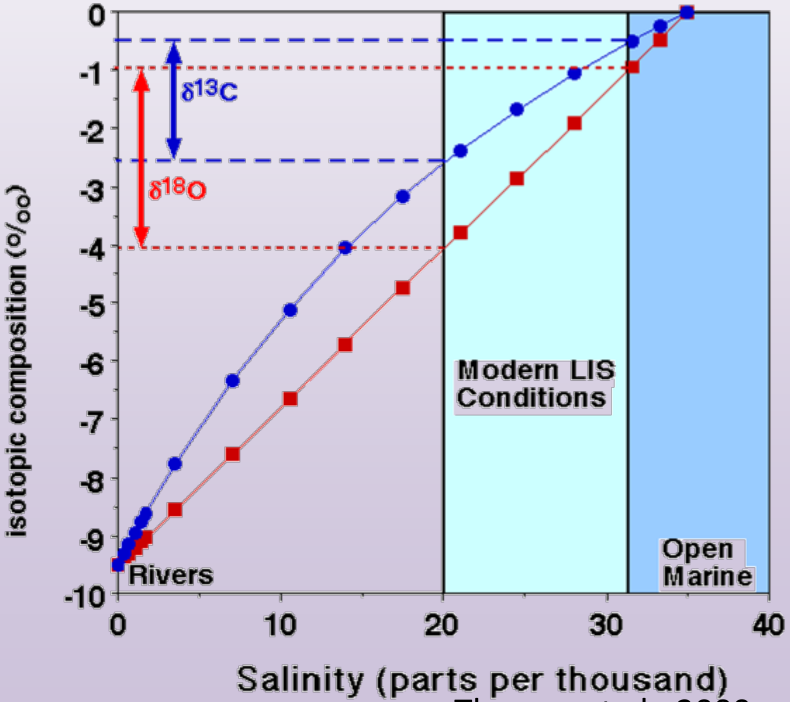
World Ocean Atlas 2009



Western Long Island Sound Station

The δ^{18}O of seawater reflects evaporation and freshwater input, while salinity indicates evaporation and freshwater supply conditions.

The covariance between salinity and δ^{18}O is common in marine environments, as both are influenced by similar oceanographic and climatic processes (evaporation and precipitation).



Thomas et al., 2000

Why salinity and $\delta^{18}O$ often covary?

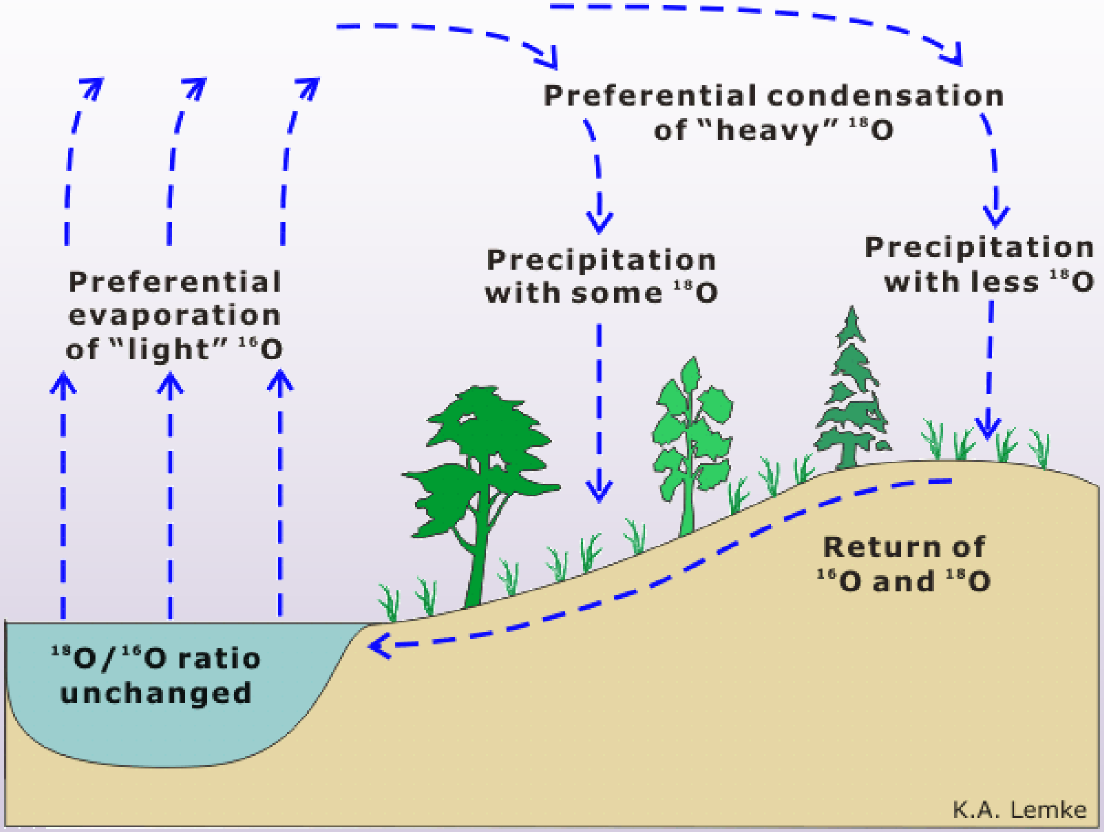
Evaporation: In regions with high evaporation rates, water evaporates, leaving behind salts, thus increasing salinity. Simultaneously, the preferential evaporation of light water molecules containing ^{16}O results in an increase in the $^{18}O/^{16}O$ ratio (δ ^{18}O) in the remaining water. Consequently, in these regions, both salinity and delta ^{18}O increase, leading to a positive covariance between the two variables.

Precipitation: Regions with heavy precipitation often receive moist air with lower salt concentrations and a lighter isotopic composition in terms of delta ^{18}O. When this air condenses to form clouds and precipitation, salinity decreases, and delta ^{18}O decreases, creating a negative covariance between the two variables.

In summary, the covariance between salinity and delta ^{18}O in marine environments is the result of evaporation and precipitation processes that affect both variables in similar ways. These data are frequently used in oceanography and climatology to understand environmental and climatic changes in the oceans.

THE OCEAN ISOTOPIC MIXING

Despite regional variations, the ocean is thought to maintain isotopic equilibrium over long periods.
While equatorial waters are enriched in ^{18}O due to evaporation, this is balanced by lighter precipitation at higher latitudes, with ocean circulation ensuring overall stability in the global average $\delta^{18}O$.



The mixing time of ocean waters is approximately a thousand years, which is the time needed to achieve global homogenization of water in terms of isotopic composition and other tracers.

On a geological time scale, the oxygen isotopic composition of ocean waters cannot be assumed to have remained constant.

SUMMARY: $\delta\,^{18}O_{SEAWATER}$ VARIATIONS

The isotopic composition of seawater oxygen ($\delta^{18}O_{\text{SEAWATER}}$) may have changed gradually over geological time due to various mechanisms.

Our focus is on understanding variations in the isotopic concentrations of both contemporary and ancient marine waters.

Oxygen isotopic fractionation during the hydrological cycle (e.g., evaporation, precipitation, runoff) **shows that $\delta^{18}O_{\text{SEAWATER}}$ is influenced by**:

- **Latitude** (latitude effect, evaporation + precipitation)
- **Salinity**
- **Ice cap volume** (polar ice is isotopically very light).

On a geological time scale, the oxygen isotopic composition of ocean waters cannot be assumed to have remained constant.