Lecture 13: Proxies of Paleoclimate II

Heavy-Water Ice

Today's Learning Outcomes

1. Be able to define what an isotope is

2. Be able to explain what isotope fractionation is

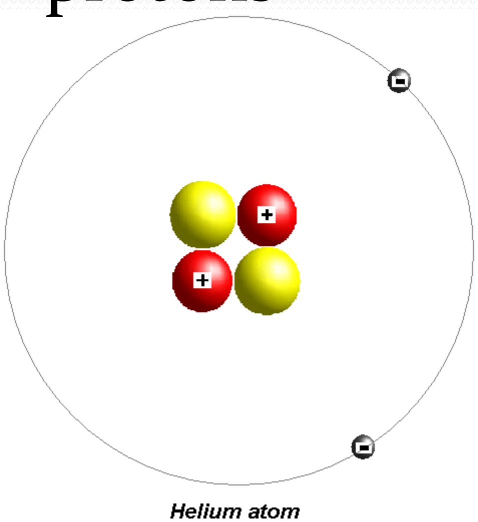
3. Be able to explain delta notation

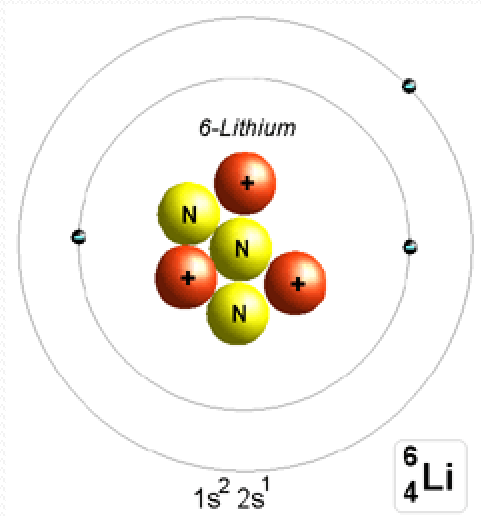
4. Know how temperature correlates with oxygen isotopes when measured from land sources versus when measured from ocean sources

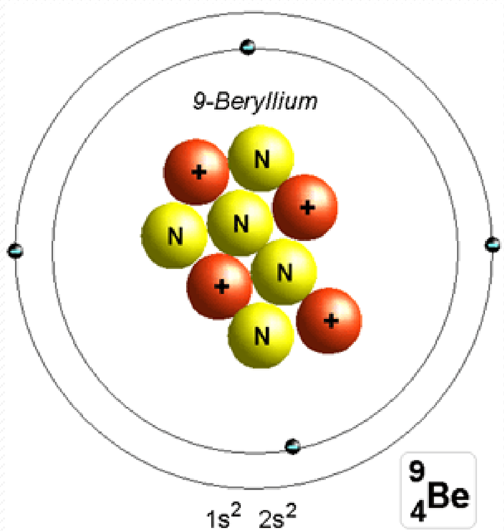
5. Be able to explain why the negative atmospheric carbon isotope excursion over the past 100 years can be explained by fossil fuels use

Atom Structure & Isotopes

- Elements are defined by the number of protons in a nucleus
  - Carbon (6 protons); Lead (82 protons)
- Atomic weight is (effectively) number of neutrons + protons

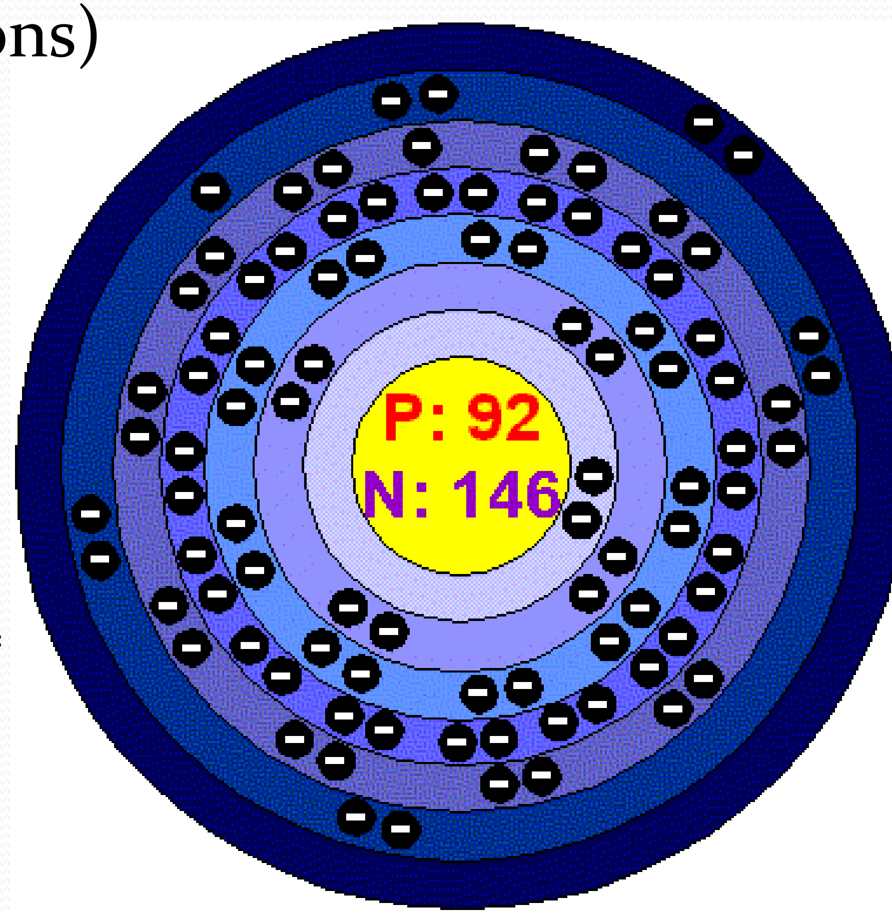






Isotopes

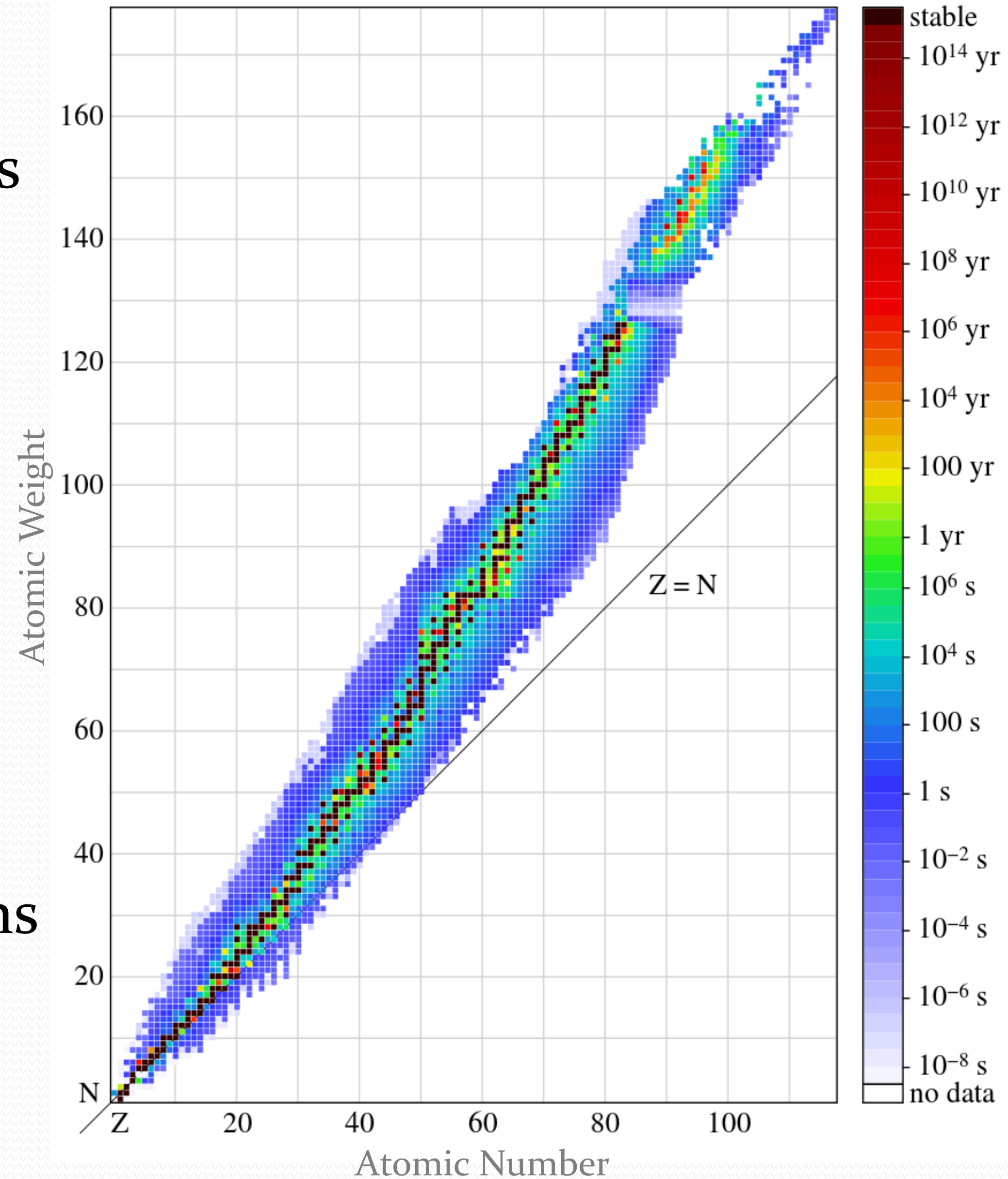
- Some elements have forms with differing weights (different number of neutrons)
  - These different forms are known as <u>isotopes</u>
  - ^{238}Uranium/^{235}Uranium



Atomic Number (Z) = number of protons

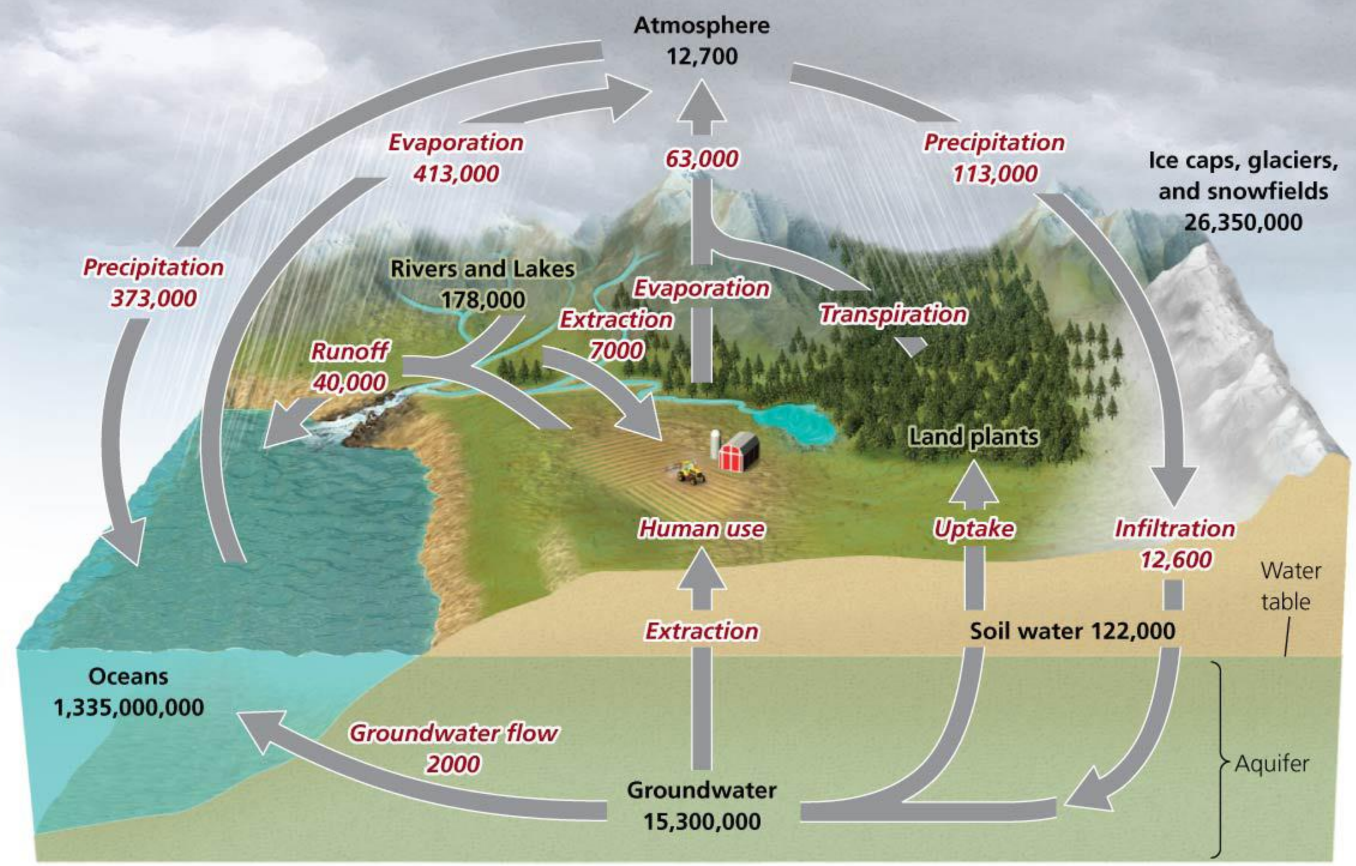
Atomic Weight (A) =
number of protons
+
number of neutrons

- Generic term for atomic configurations are nuclides
  - ~1700 known
  - ~430 occur naturally
  - ~200 stable
- ~230 unstable naturally occurring nuclides
- Large discrepancies between number of protons and neutrons usually unstable



Isotope Fractionation

- Differences in the relative abundance of different isotopes of an element between two reservoirs



Cause of Isotope Fractionation

- Preferential movement of heavy versus light isotopes dependent largely on chemical bonding and <u>mass</u>

- At a given temperature (= average energy) lighter isotopes have more kinetic energy than heavy isotopes
  - Easier for lighter isotopes to escape system (ex. evaporate, cross membrane)
  - Easier for heavy isotopes to be captured in a crystalline solid (ex. mineral formation)

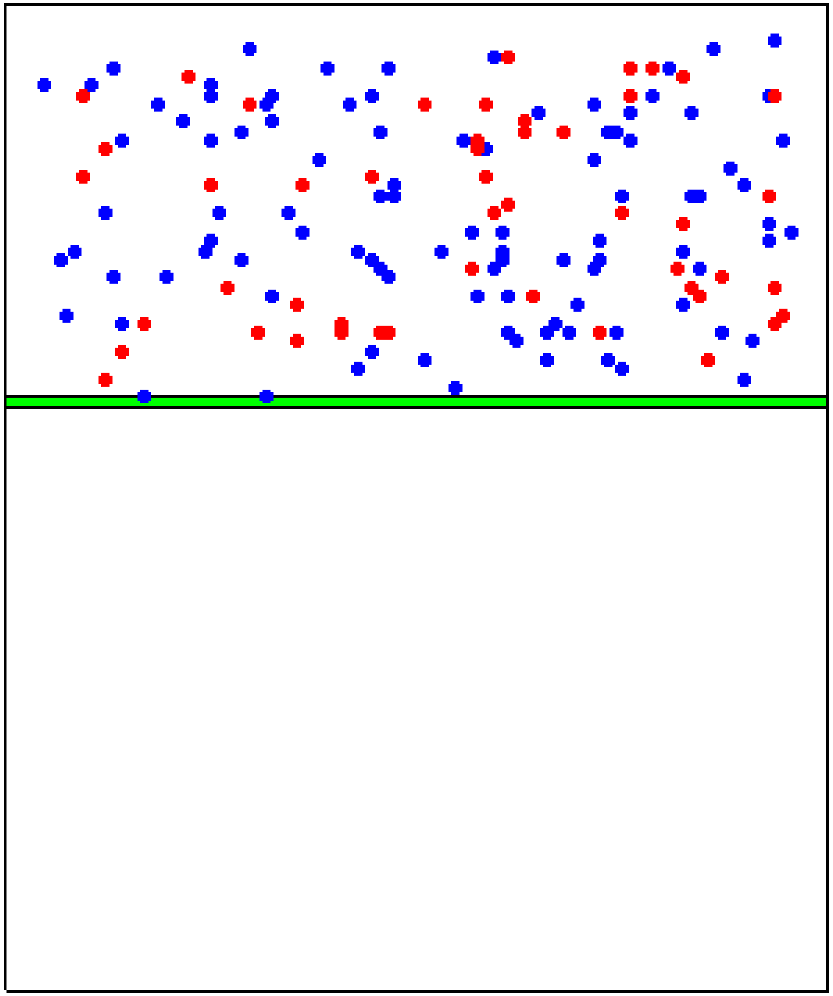
Isotope Fractionation

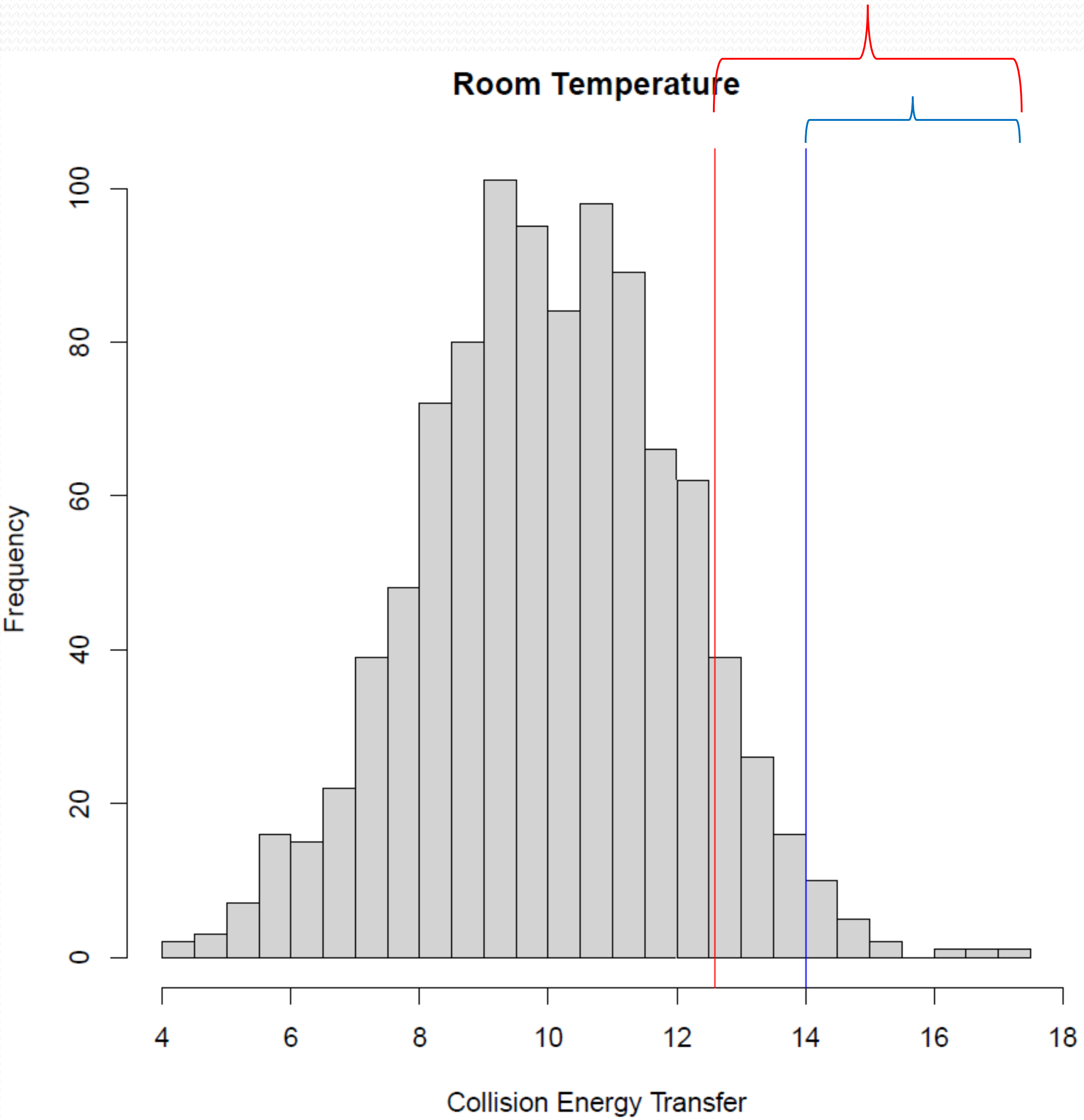
Blue isotope = heavy

Red isotope = light

Light isotope easier to keep moving as a gas

Heavy isotope harder to keep moving, more likely to settle into solid form and leave the atmosphere





Red line: energy required for light isotope to evaporate

Blue line: energy required for heavy isotope to evaporate

Light isotope threshold will be surpassed far more often and be overrepresented in the resulting gas

Percent Fractionation

- Fractionation is often mass-dependent

- Larger proportional difference in mass = larger fractionation

- ^{238}U vs ^{235}U is a 1.3% mass difference ← heavy isotopes

- ^{18}O vs ^{16}O is a 12.5% mass difference
- ^{14}C vs ^{12}C is a 16.7% mass difference
- ^{2}H vs ^{1}H is a 100% mass difference

light isotope

Stable Isotope Fractionation

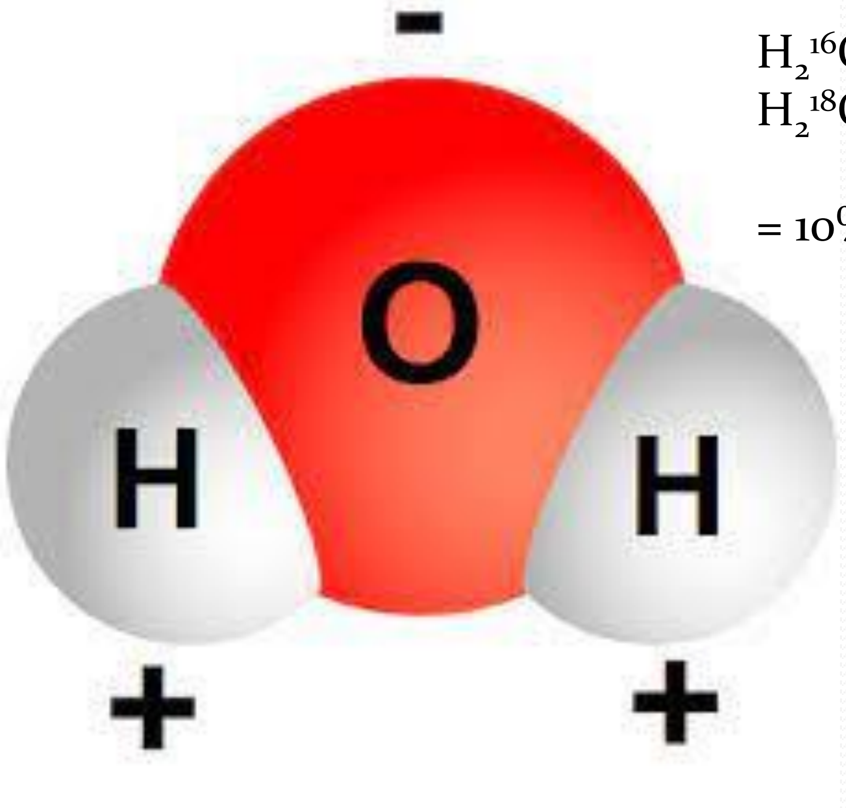
- Traditionally uses light elements (H, C, N, O, & S)
  - Large mass percent differences between isotopes
  - Less common than stable isotope still abundant enough to measure very accurately
  - These elements make up majority of biological and mineral objects

- Useful for reconstructing environmental change, biological pathways, and many other histories

Element	Isotope	Relative Abundance (%)
Hydrogen	^{1}H	99.9844
	^{2}H	0.0156
Carbon	^{12}C	98.89
	^{13}C	1.11
Nitrogen	^{14}N	99.63
	^{15}N	0.36
Oxygen	^{16}O	99.763
	^{17}O	0.0375
	^{18}O	0.1995
Sulfur	^{32}S	95.02
	^{33}S	0.75
	^{34}S	4.21
	^{36}S	0.02

Water Isotopes

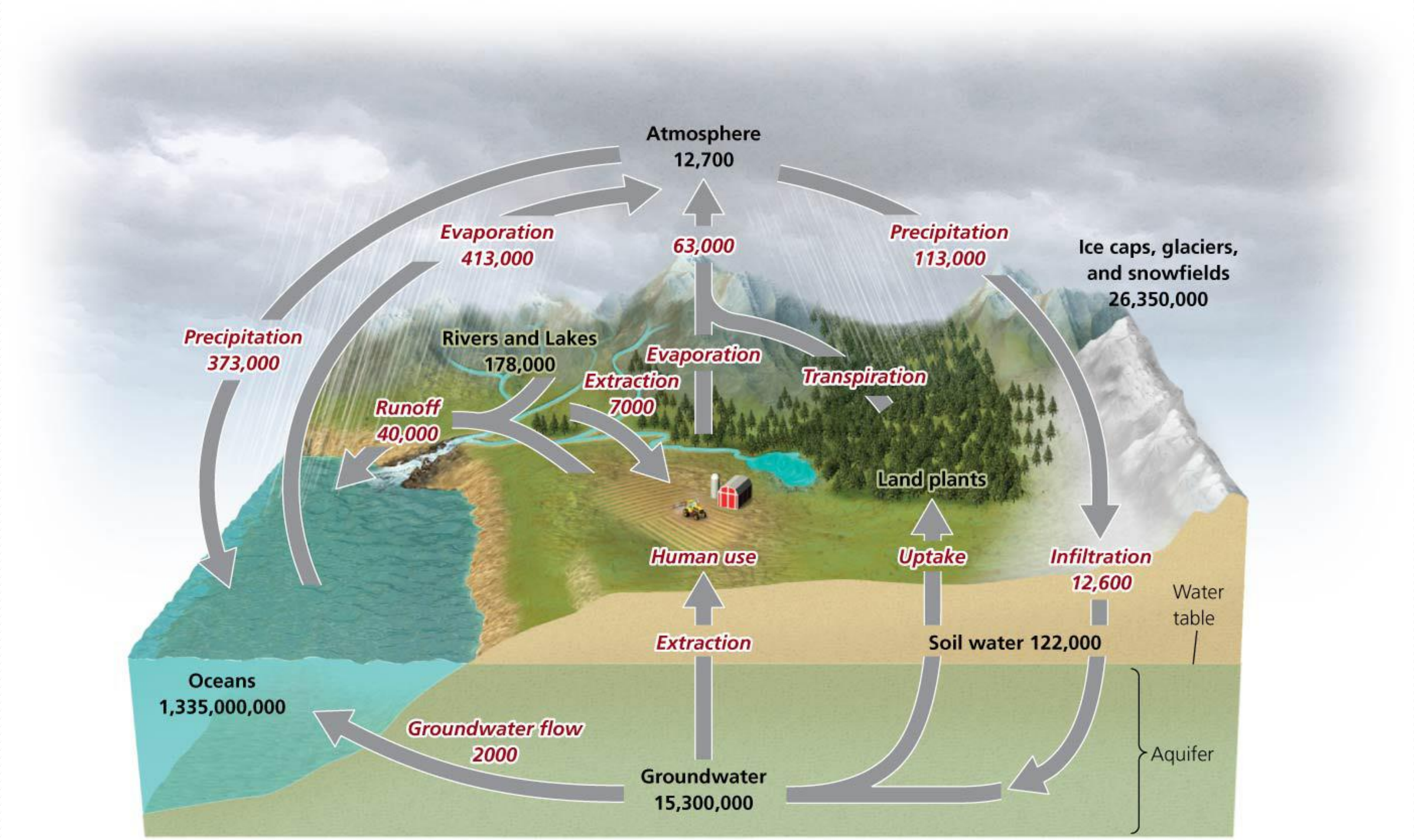
- Water contain oxygen with different isotopes
  - Mostly ^{16}O



$H_2{}^{16}O$ atomic mass = 18
$H_2{}^{18}O$ atomic mas = 20

= 10% difference in mass

Water is constantly cycling on Earth



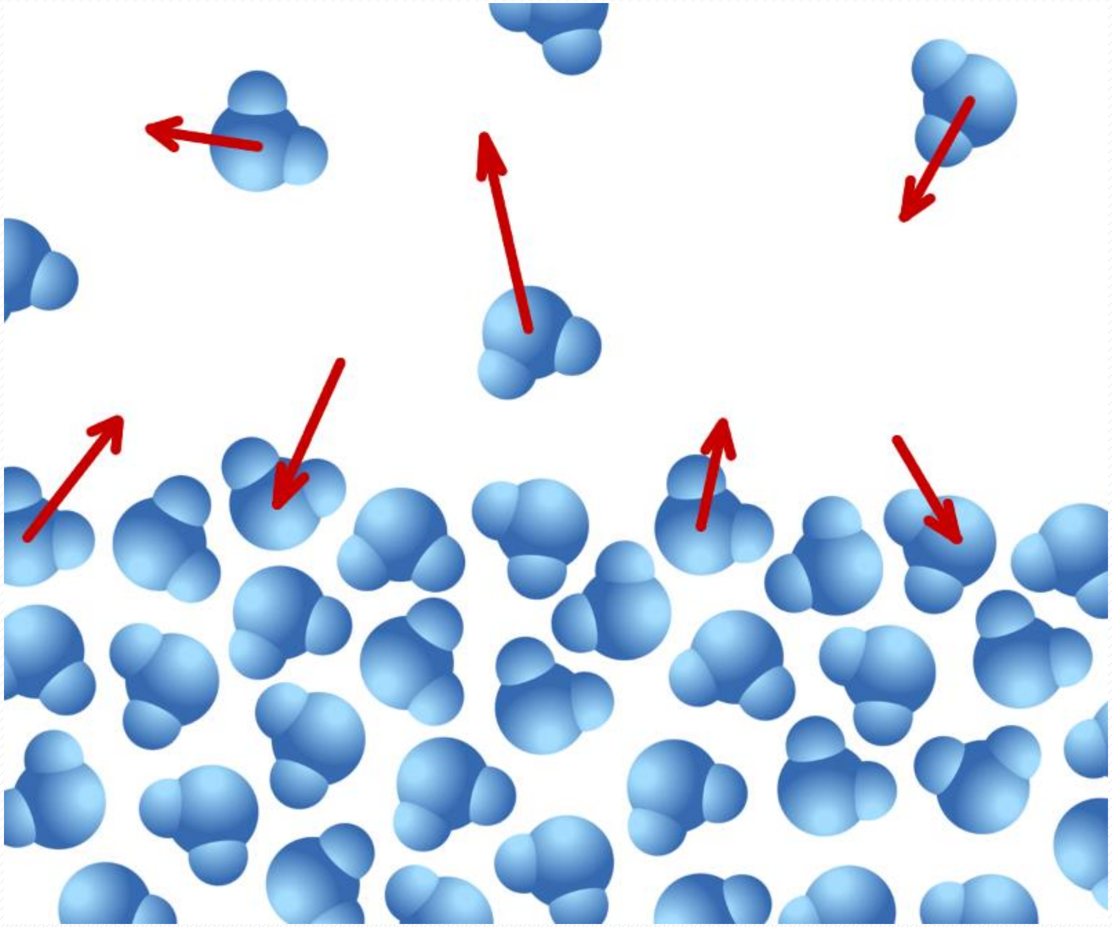
Water-Vapor Transitions

<u>**Evaporation**</u> is the change of a liquid to a gas

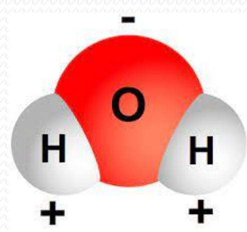
- light isotope favored

<u>**Condensation**</u> is the change of a gas to a liquid

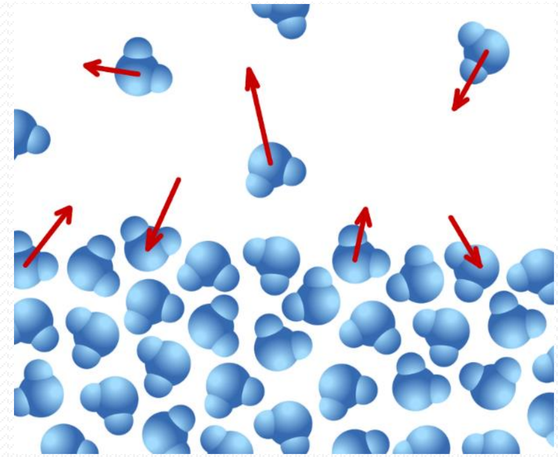
- heavy isotope favored



Water molecules are moving around at different speeds (= amounts of kinetic energy) in a glass, and transfer energy to one another by colliding.



Water molecules are attracted to one another; they have cohesion, due to having magnetic poles.

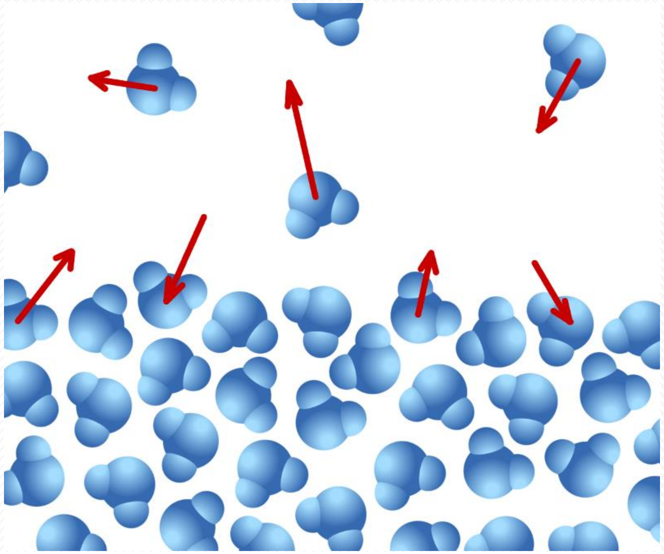


<u>High-velocity</u> molecules on the surface can escape the attractive forces of other water molecules, becoming a gas (a.k.a. evaporation)

Mass-dependent Fractionation

It takes **more kinetic energy transfer** to increase the velocity of something heavy compared to something light

When a random collision occurs between water molecules, it is <u>more likely</u> that a light water molecule will receive enough energy to reach "escape velocity" and evaporate, compared to a heavier molecule.



$H_2{}^{16}O$ evaporates more easily than $H_2{}^{18}O$

More $H_2{}^{16}O$ will be in the air than in the water it evaporated from

How much more easily does $H_2{}^{16}O$ evaporate?

It depends on temperature!

Temperature-Dependent Fractionation

- As temperature drops so does average kinetic energy meaning that it gets less and less likely that a collision has enough energy to get a heavy isotope to escape velocity
  - At high temperature very high average kinetic energy

Much easier for the light isotope

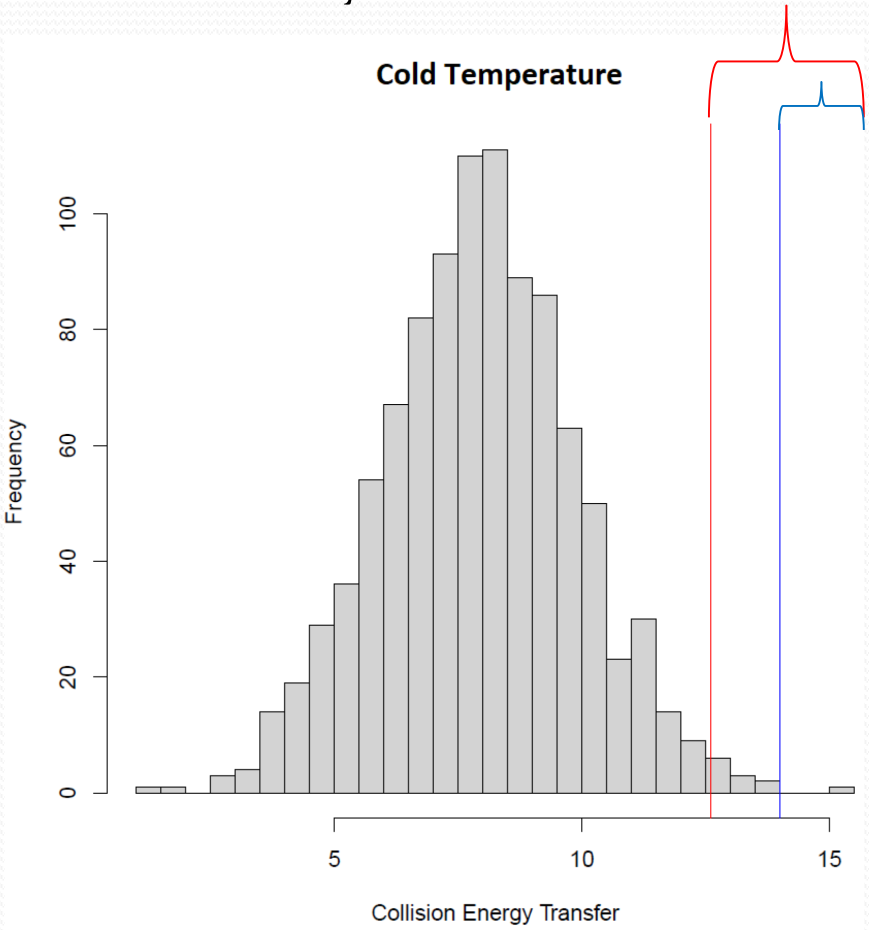
Equally easy for both isotopes.

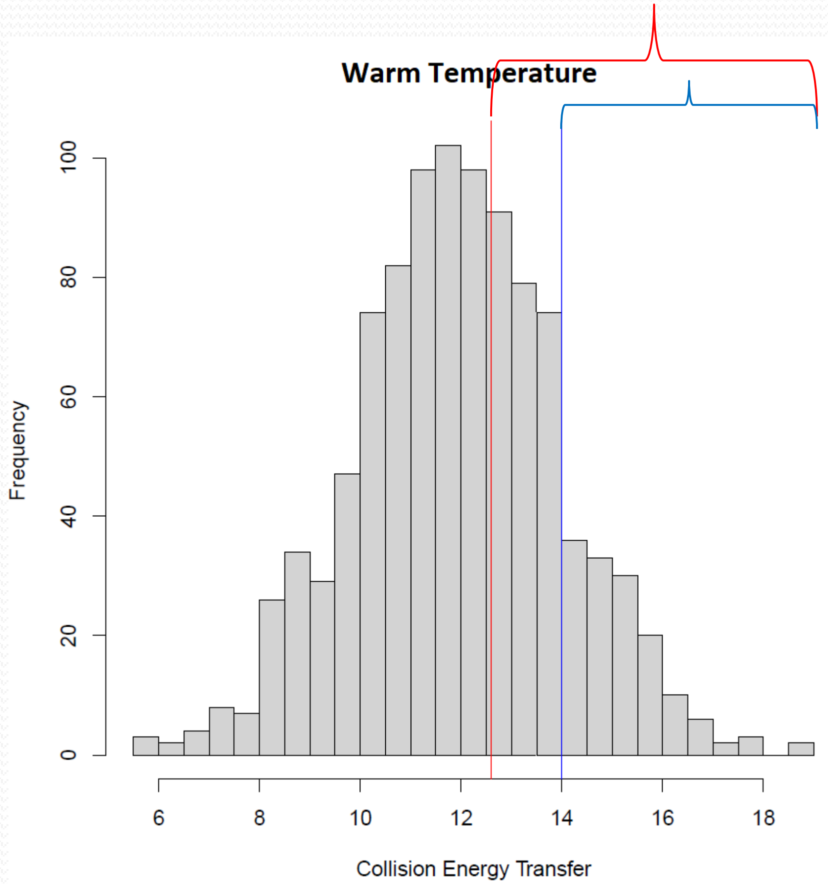
Red line: energy required for light isotope to evaporate

Blue line: energy required for heavy isotope to evaporate

Cold temperature make it very hard to reach threshold for heavy isotope

*Actually even harder than shown because real distribution is not normal



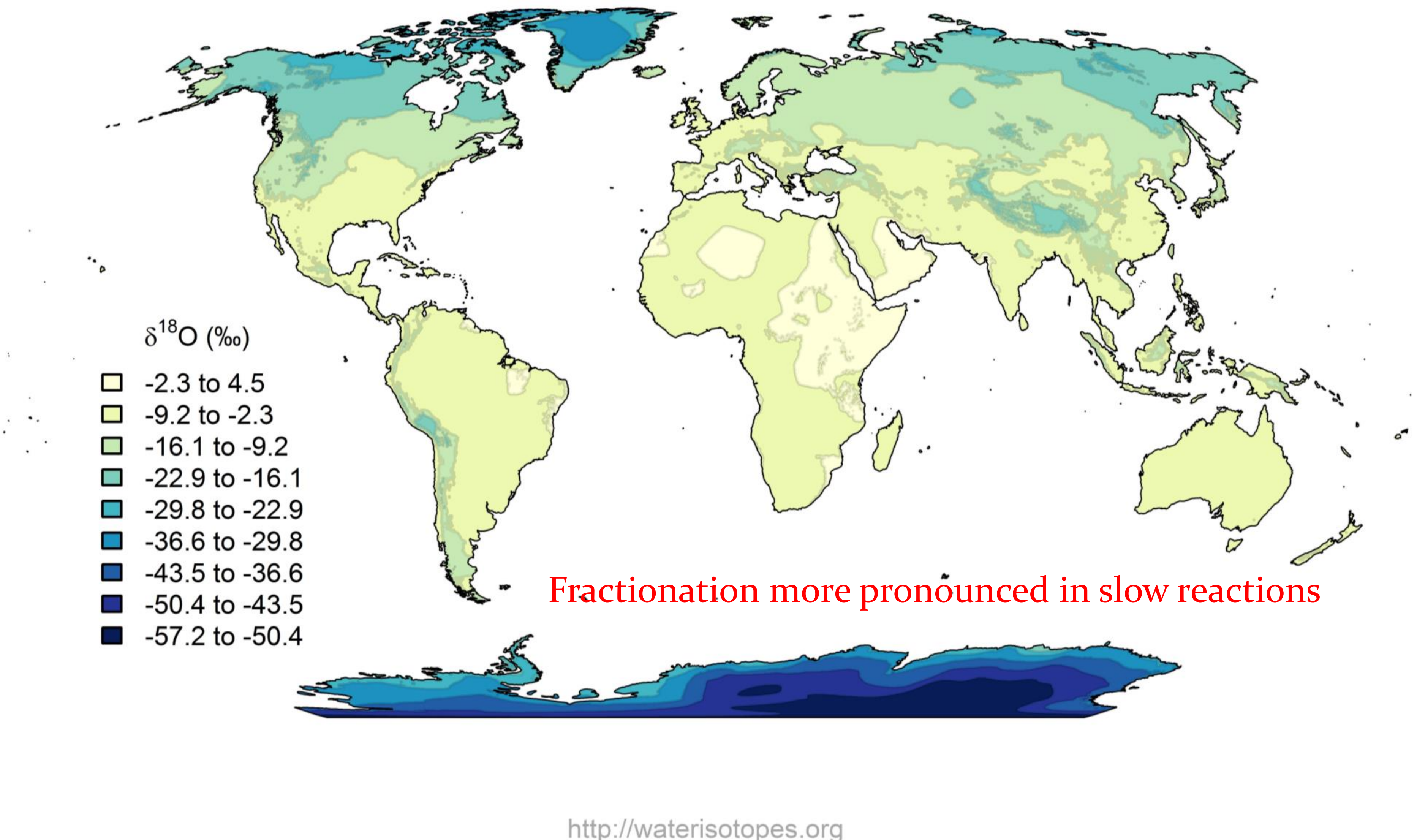


Oxygen as temperature paleoproxy

- If we have oxygen records captured in the rock record we can work backwards to estimate ancient temperatures!

…and glaciers are a chronological record of precipitation

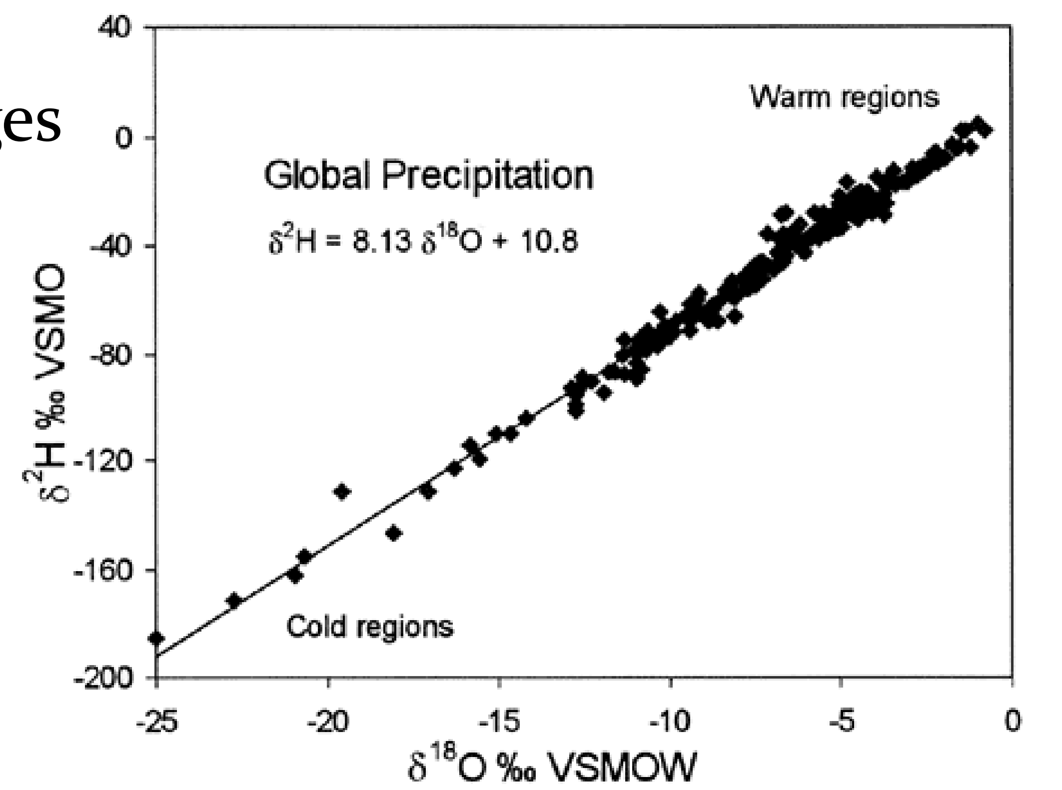
Fractionation Is Temperature Dependent



Global Meteoric Water Line

- Because precipitation is largely sourced from the same reservoir (oceans)

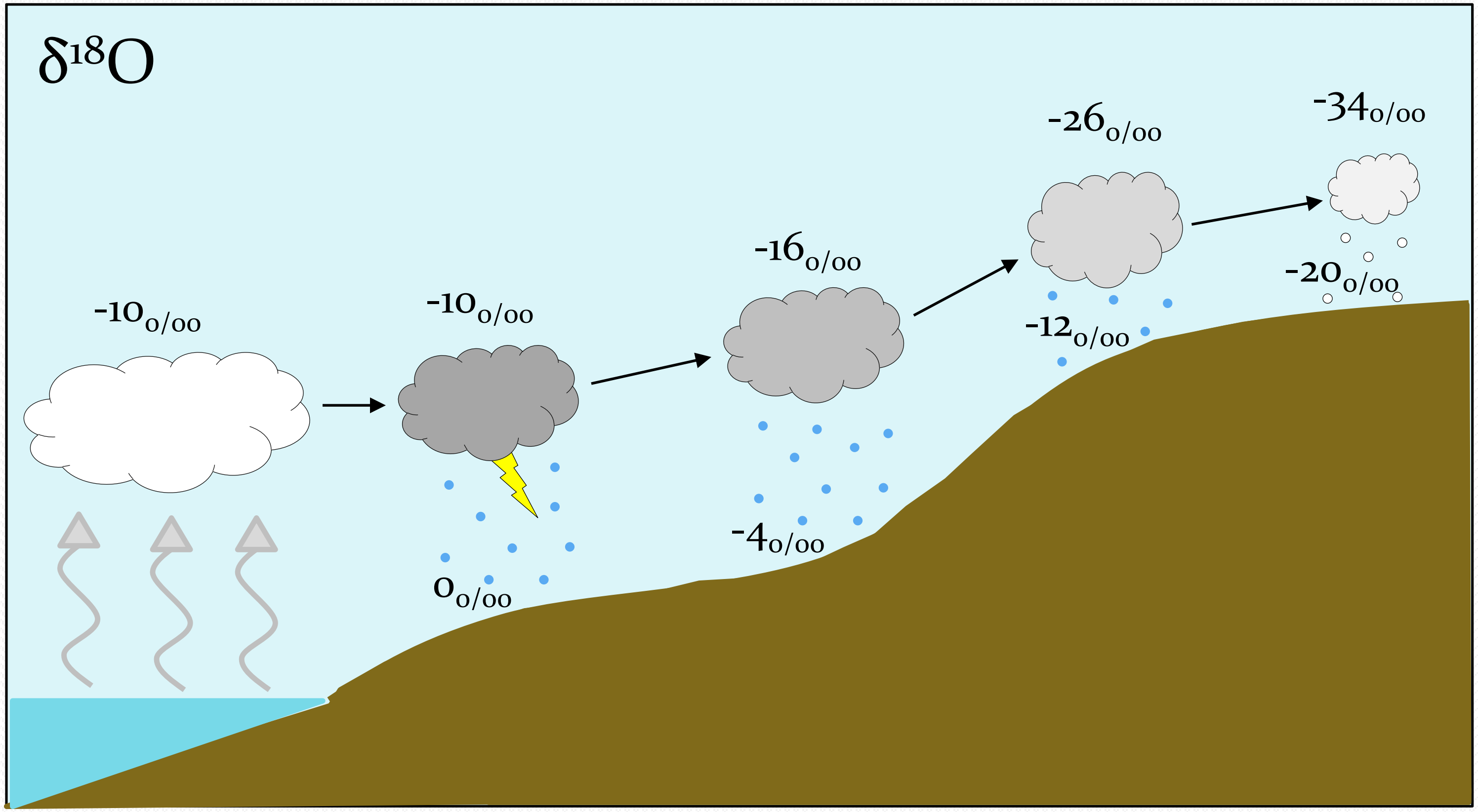
there are linear changes in δO and δH across the Earth



Clark & Fritz 1997; Rozanski et al. 1993

Altitude/Temperature Trend

- As water travels inland the water remaining in clouds is increasingly light (as is the resulting precipitation)



Delta(δ) Notation

delta

$$\delta X_{sample} = \{(R_{sample} - R_{standard}) / R_{standard}\} * 1000$$

"R" stands for ratio of your isotopes of interest

- Units of parts per thousands (also known as parts per mil)
  - Abbreviated as $_{o/oo}$ in many cases

- % is parts per hundred
- o/oo is parts per thousand
- ppm is parts per million
- ppb is parts per billion

Delta Notation Example

$\delta^{18}O$ is the proxy being worked with

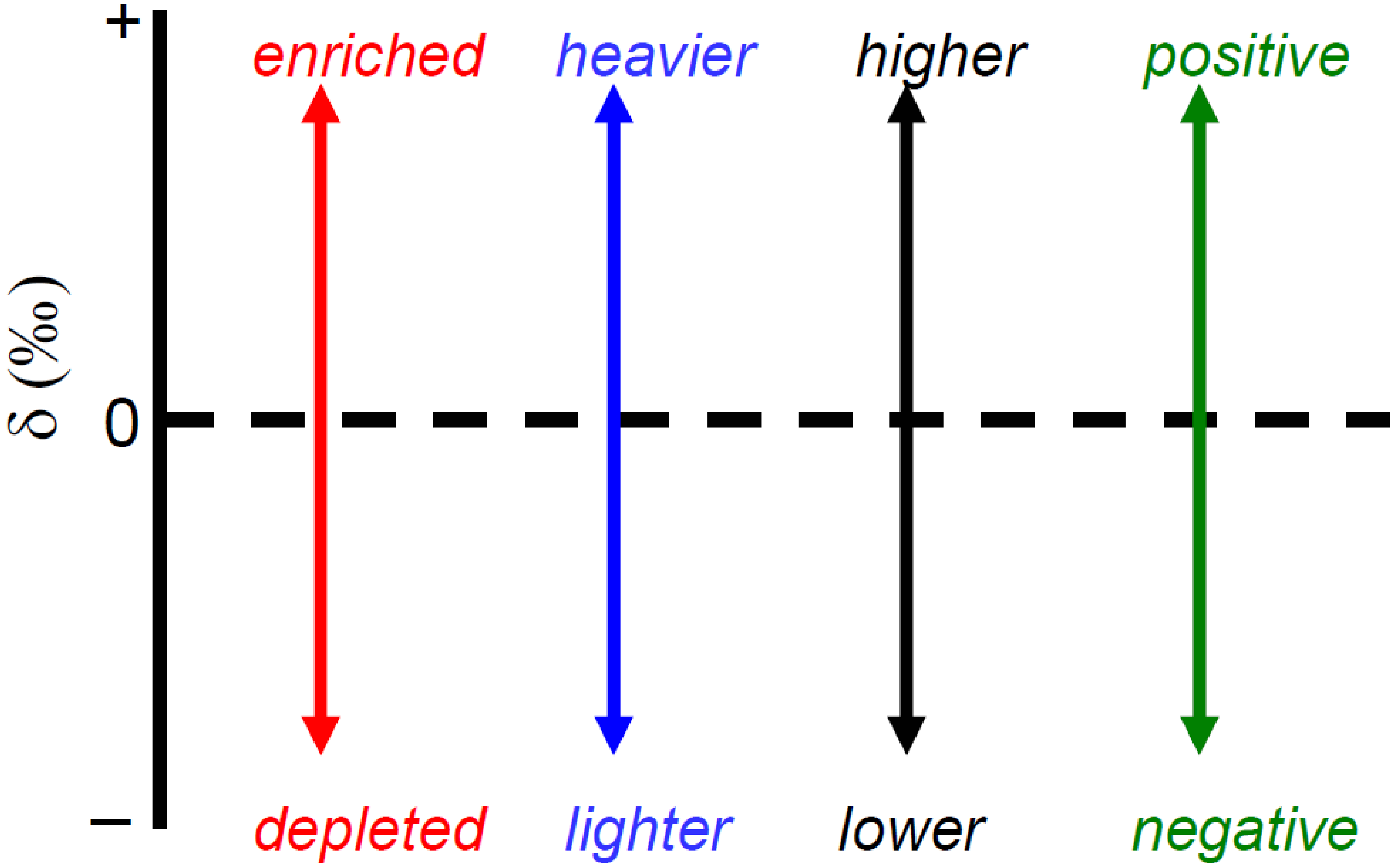
The "sample" is what you are analyzing

The "standard" is a control to compare your sample to. For oxygen it's a sample of modern ocean water

$$\underset{\text{(in ‰)}}{\delta^{18}O} = \frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{standard}}}{(^{18}O/^{16}O)_{\text{standard}}} \times 1000$$

Lower $\delta^{18}O$ = less of the heavy isotope = colder = "depleted"
Higher $\delta^{18}O$ = more of the heavy isotope = warmer = "enriched"

Isotope Terminology



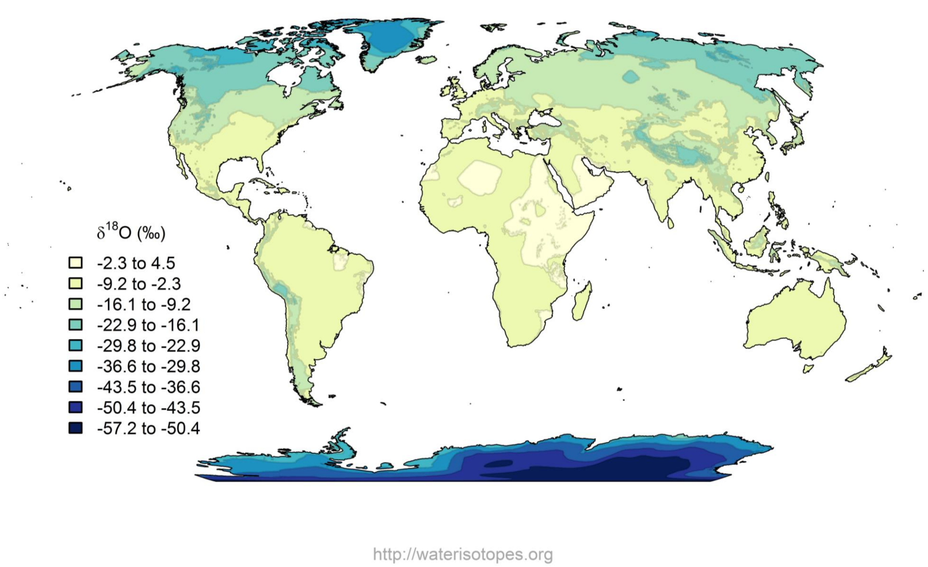
Why Use Delta Notation At All?

- Isotope ratios at any one time/location are local but we often want to compare between locations or through time
  - More useful to look at changes over time or some gradient in location (ex. latitude) with some baseline of comparison (= standard)

- Analogy: the weather in a specific location doesn’t tell us much about climate but if lots of locations are increasing in temperature over time that is a measure of climate

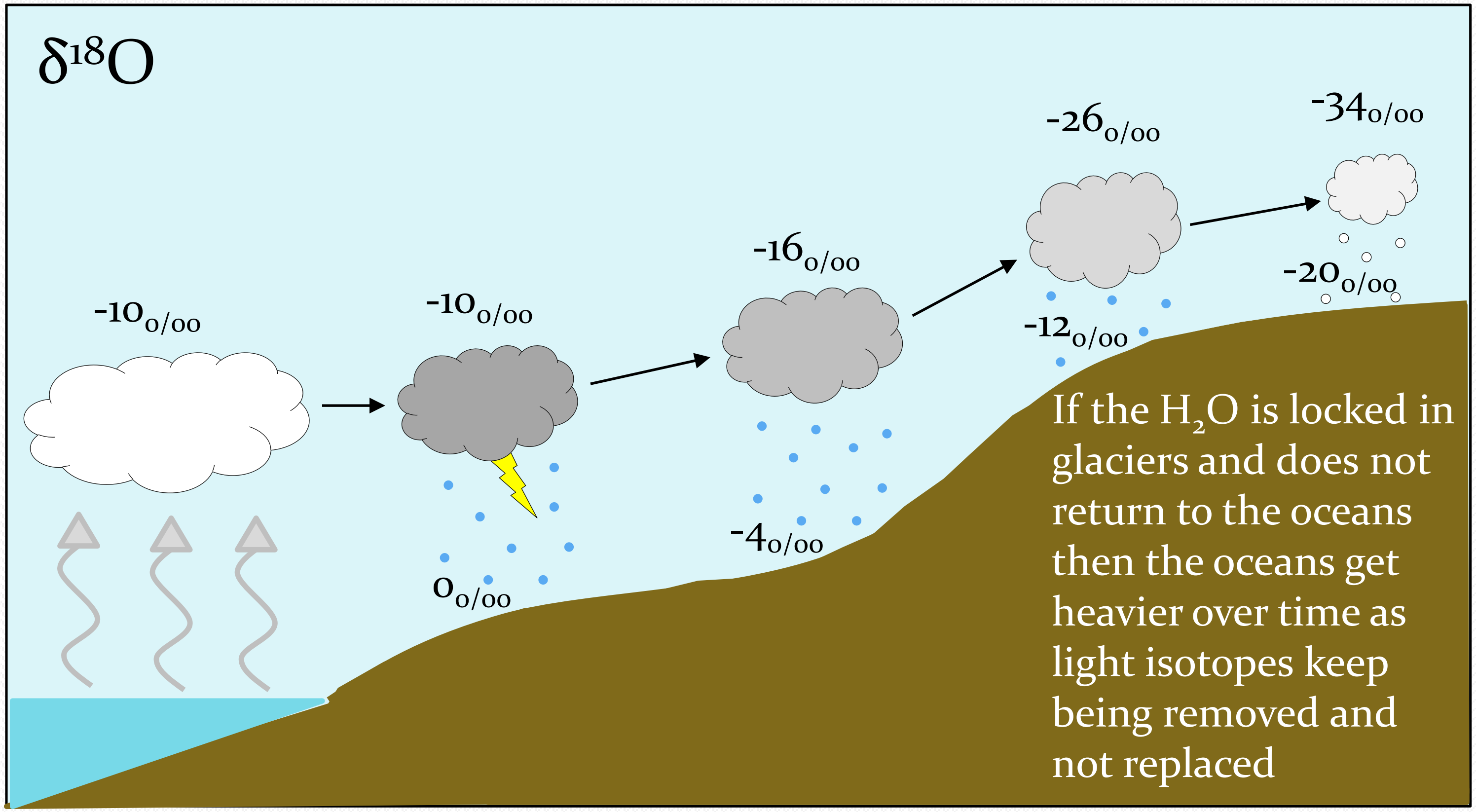
Oxygen Isotopes as Temperature Proxies

- In the present oxygen isotopes measured from $\mathbf{H_2O}$ are strongly correlated to temperature
  - Surplus of light oxygen (^{16}O) compared to the standard = negative/light/depleted $\delta^{18}O$
  - More and more difficult for heavy isotopes to evaporate from oceans and move to land the colder it is



Altitude/Temperature Trend

- As water travels inland the water remaining in clouds is increasingly light (as is the resulting precipitation)



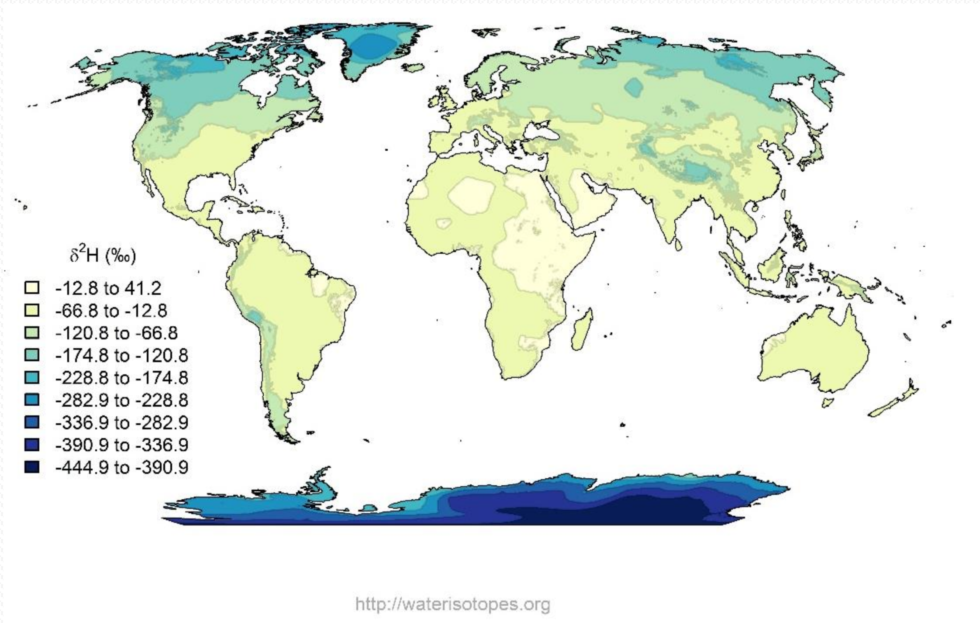
Ancient H_2O Records

- Glaciers preserve both H_2O and trapped bubbles of atmosphere laid down in annual bands
- Ice cores give the best continuous records
  - Greenland (0-130,000 years ago)
  - Antarctica (0-800,000 years ago)

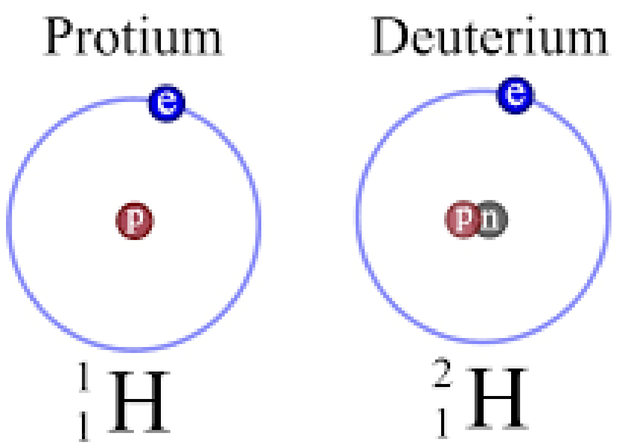
- Article in 2019 reported snapshots of preserved atmosphere in 2.7 Ma ice in Antarctica

Hydrogen Isotopes & Temperature

- Hydrogen isotopes in H_2O fractionate the same way that oxygen does and can also be used to track temperature

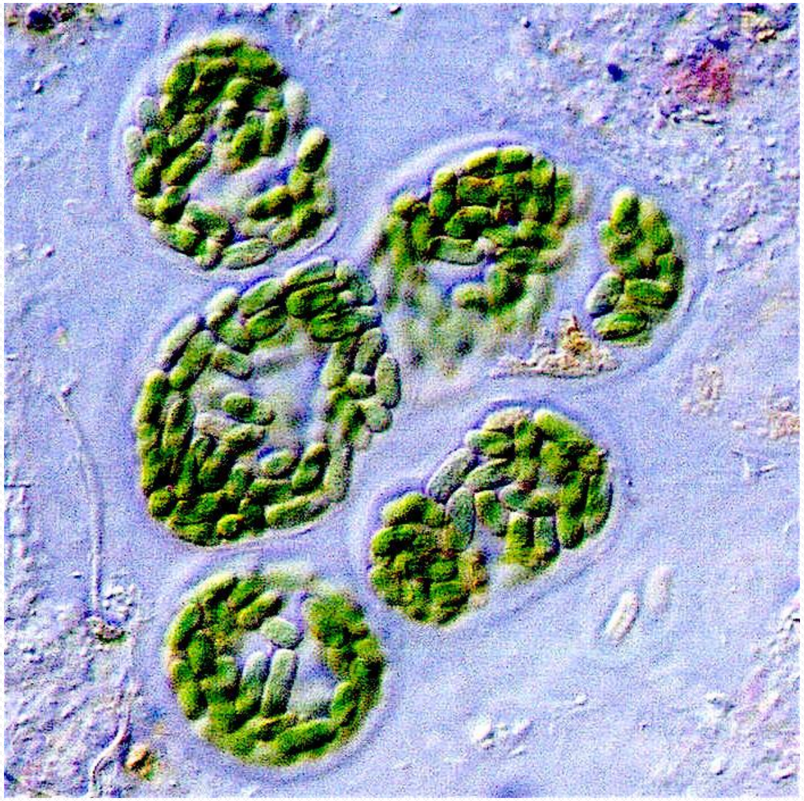


Colder snow is more depleted in deuterium than warmer rain is



Hydrogen Isotopes in Plant Tissues

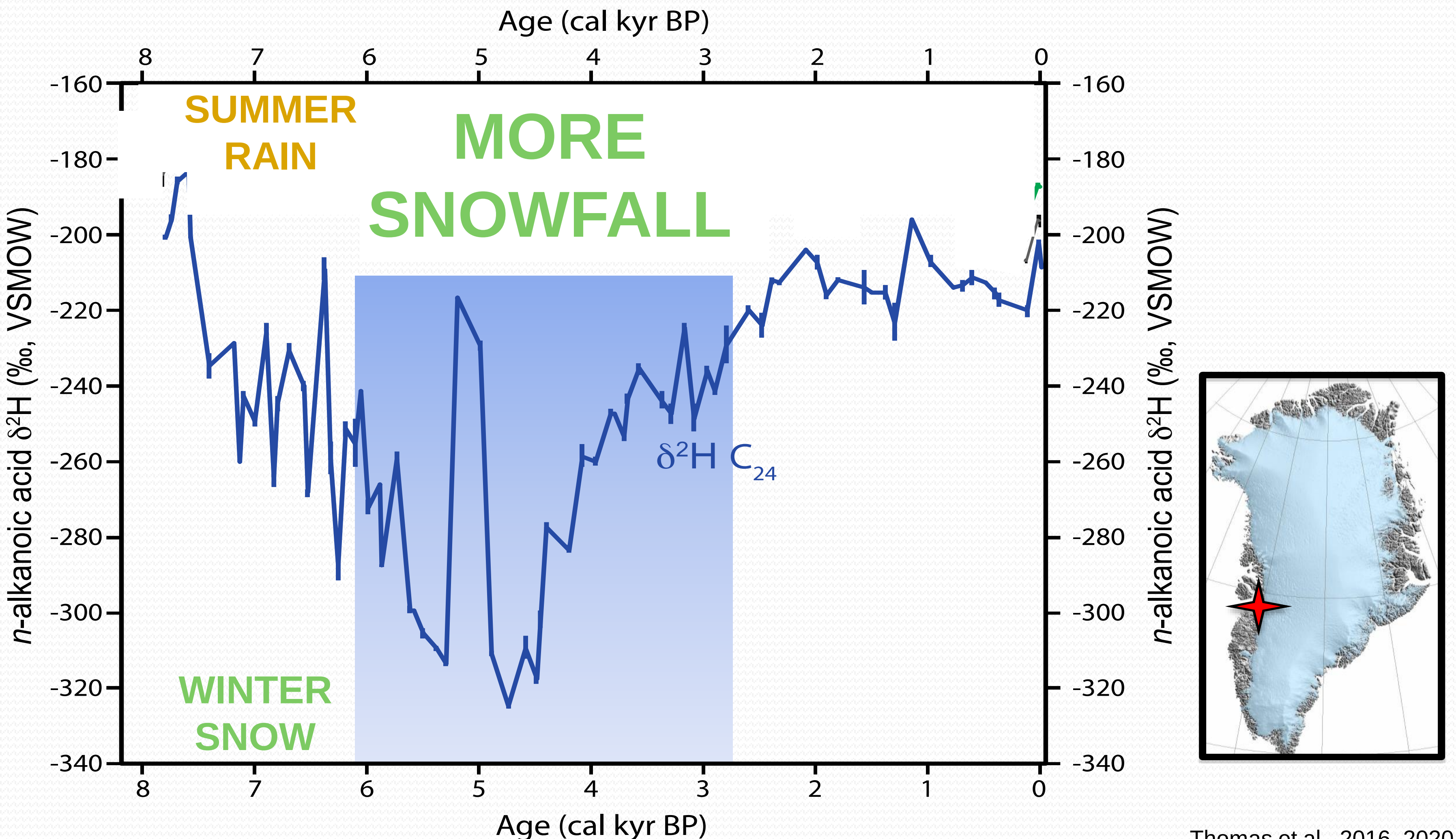
- Because photosynthesis converts water to organic tissue hydrogen isotopes of plants reflect the local temperature as well
  - Oxygen in the tissues represents a mix of atmosphere and water sources complicated interpretations



Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

Hydrogen Isotopes in Plant Tissues

- Geology department's own Professor Elizabeth Thomas measures H isotopes from plant tissues of ancient lake deposits

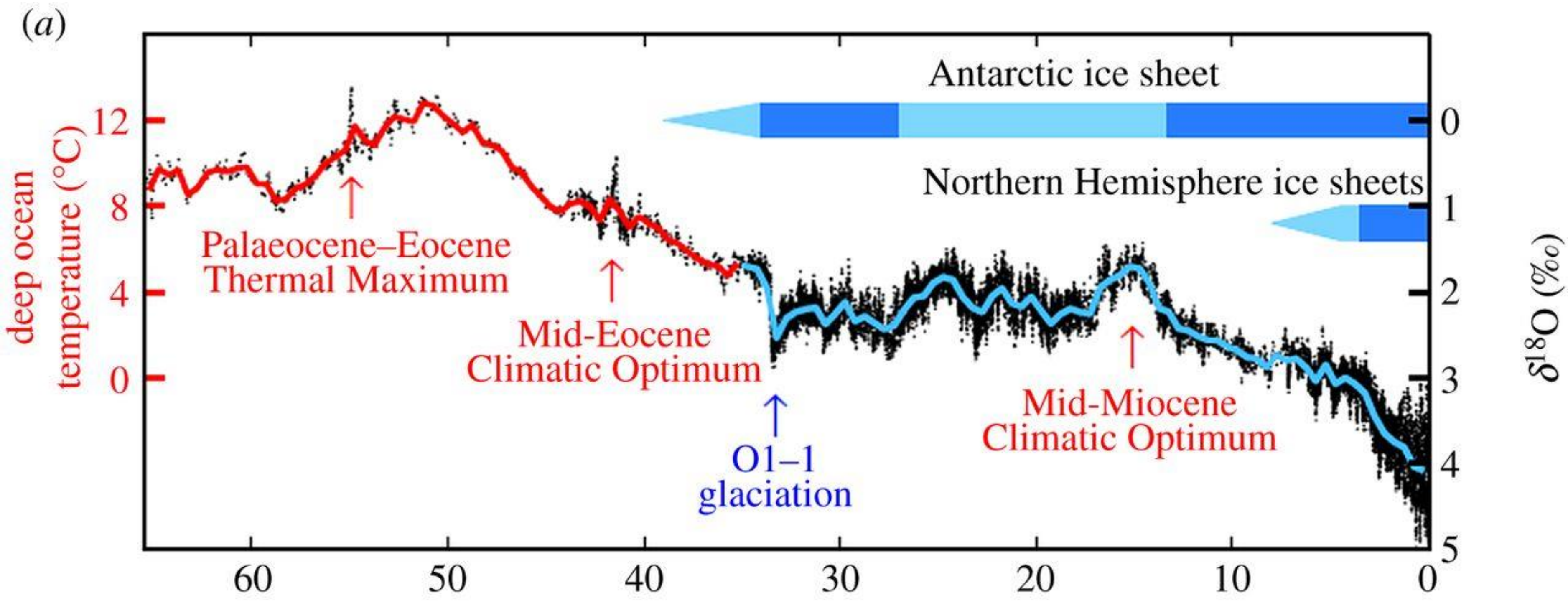


Thomas et al., 2016, 2020

Figure S6

Temperature Records

- Ice cores are only continuous back to <1 Ma so we need another source of oxygen isotopes to reconstruct temperature for the rest of Earth's history



Organic Carbonate ($CaCO_3$)

- Marine organisms use the oxygen from the water to build their shells ($CaCO_3$) and thus reflect changes in the ocean reservoir

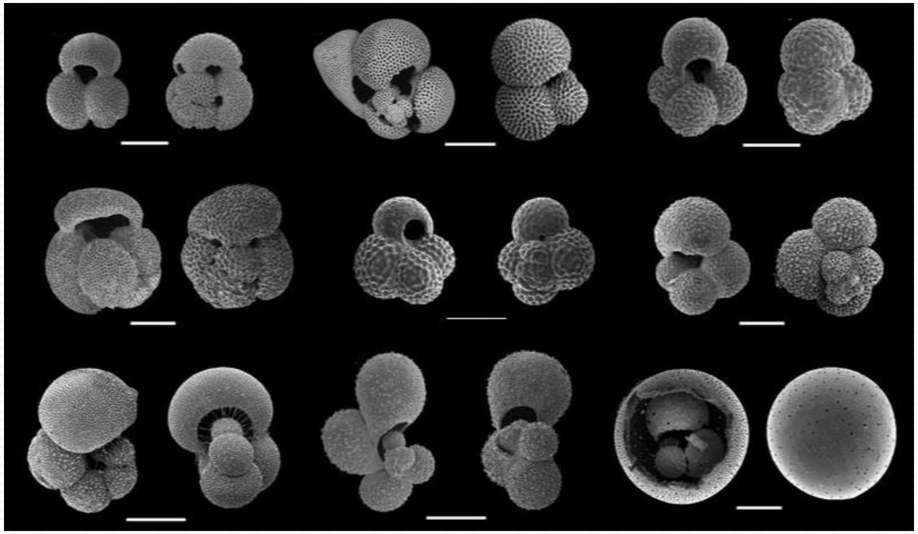
$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3$$

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3$$

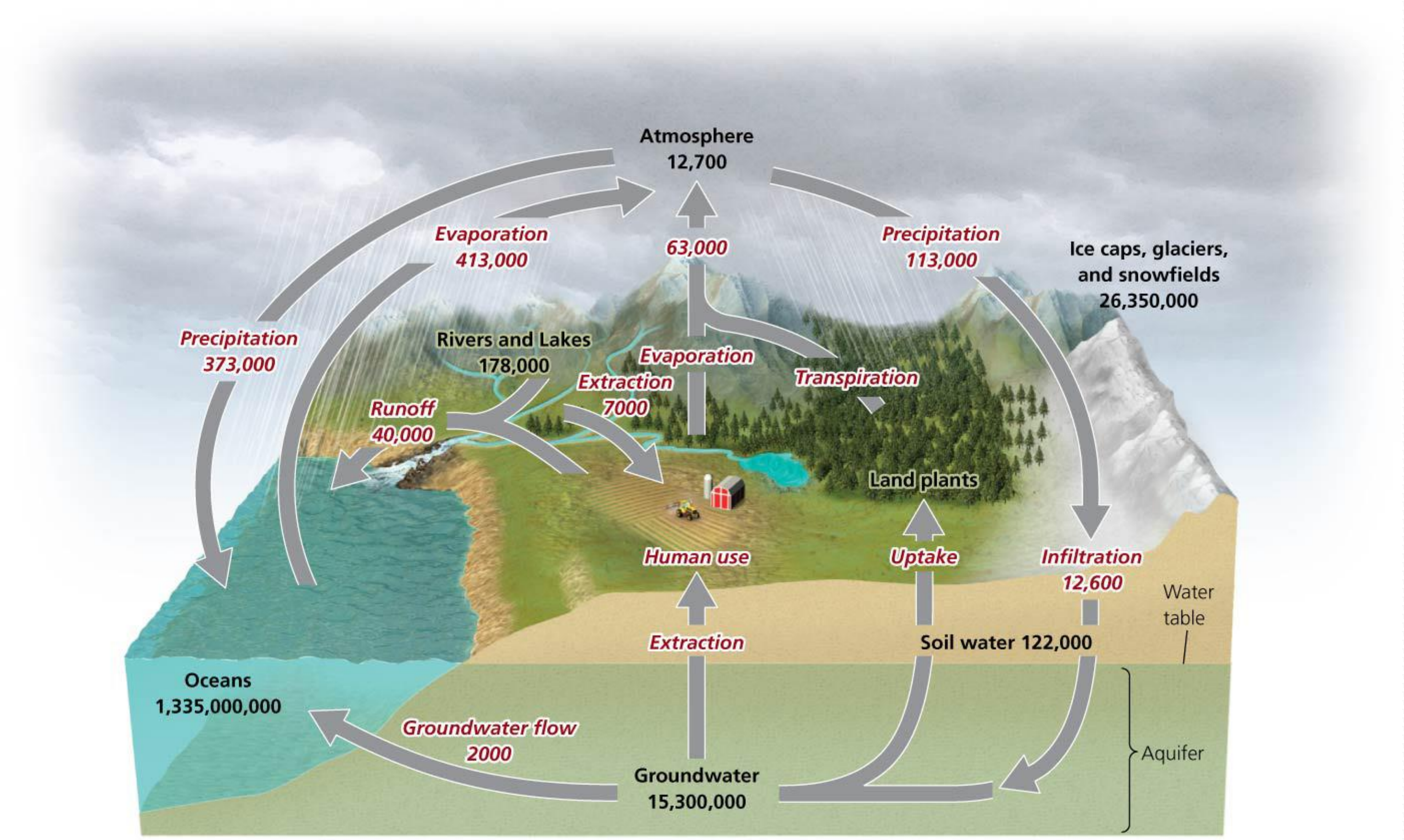
$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

$$CO_2 + H_2O + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

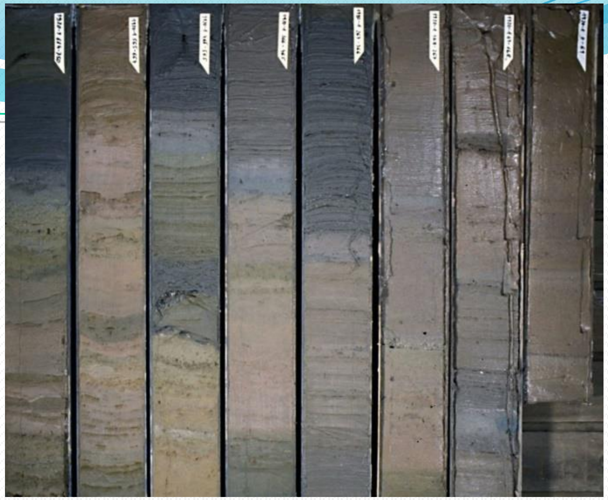


Foraminifera make shells from carbonate

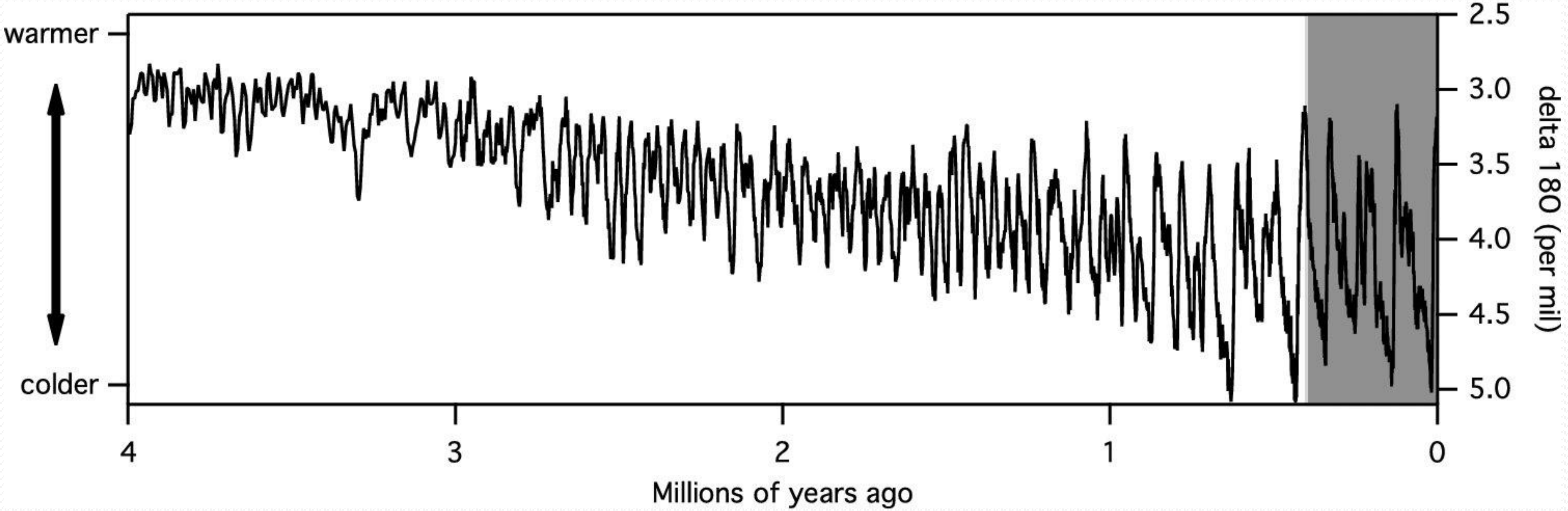
When more water is in glaciers, the remaining water in oceans is <u>***enriched***</u> in the heavy isotope



Oxygen isotopes in ocean fossil sediments are a proxy of how much ice is in glaciers, thus global temperature



- **When looking at oxygen isotopes from the ocean reservoir (i.e. $CaCO_3$) an enriched $\delta^{18}O$ indicates cooling** **[opposite of ice or plant-based signature]**

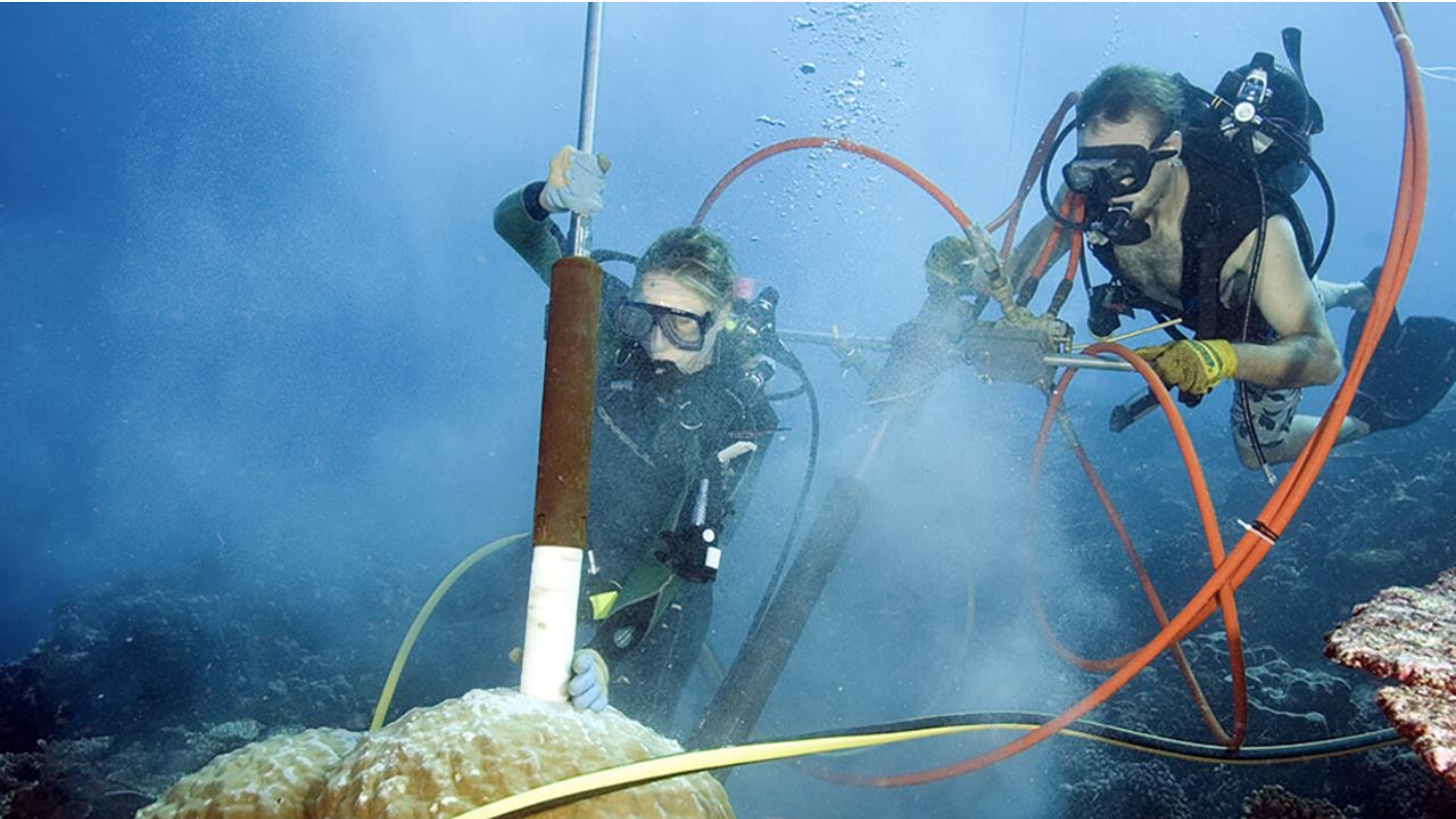


^{18}O Record Source?

- Corals
  - Many different groups claimed this niche in Earth history
  - Aragonite & calcite
- Conodonts
  - Extinct eel-like vertebrates
  - Few cm to m scale
  - Apatite 'teeth'
- Foraminifera (aka forams)
  - Single celled organisms with a calcite shell
  - Typically <1 mm in size (but up to 20cm)
  - Benthic and planktic forms

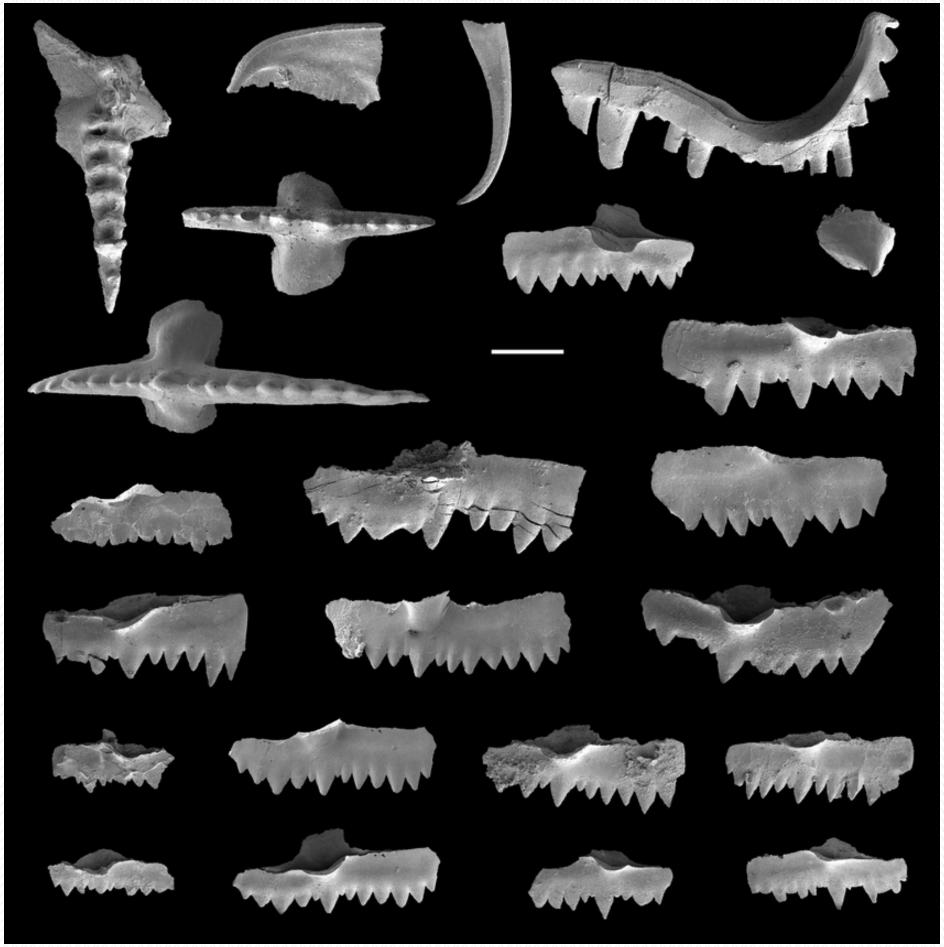
Rudist bivalve (Cretaceous reef-building organisms)

Coral (being cored by paleoclimatologist and stable isotope geochemist, Kim Cobb, prof @ Georgia Tech)



Conodonts

- "Close" relative to us



Benthic Forams

Biological Effects

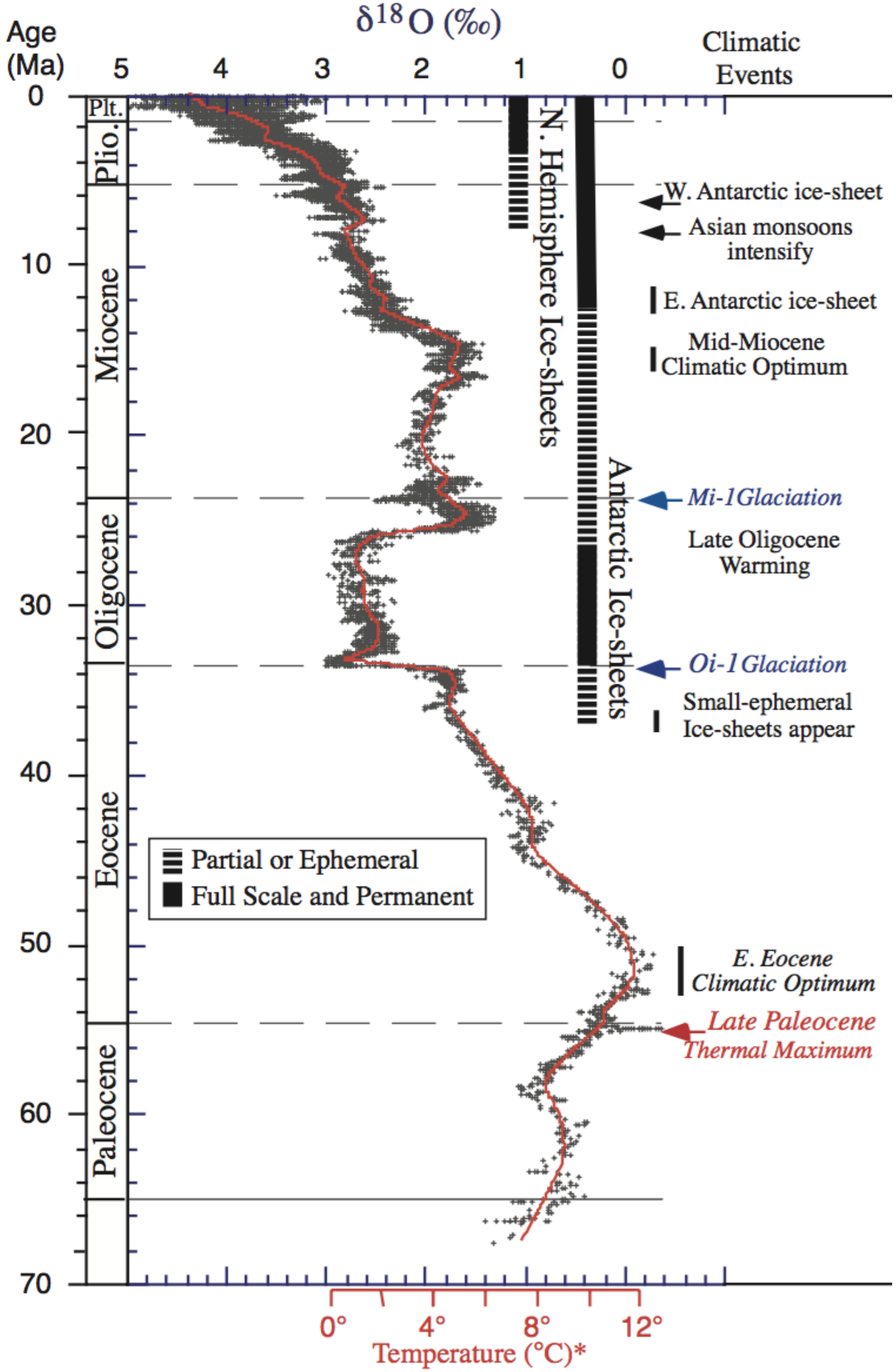
- Different species of the same group live in different environments
  - Sea-bottom [cold] versus open-ocean [warmish] species

- Within species individuals in the modern day migrate often [temperature-change over life-cycle]

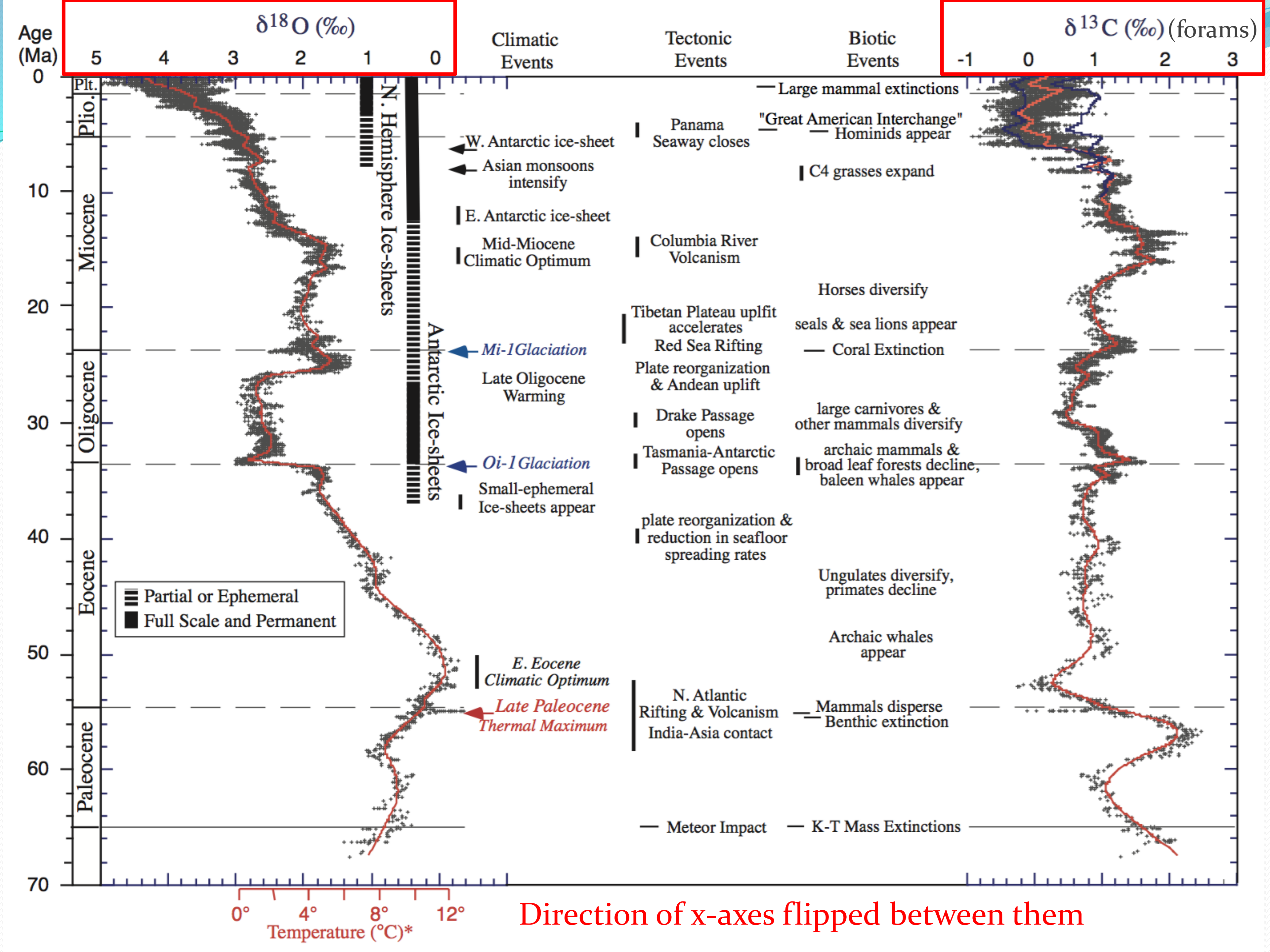
- Changes in environment over the course of life
  - Move from inshore nursery to offshore

Why Forams?

- Planktic forams can be found over entire ocean not just nearshore
- Huge numbers of individuals to test and cross-validate results across
- Living or closely related species to study fractionation and account for species-specific biases
- Potentially could use anything with $CaCO_3$



Zachos et al. 2001

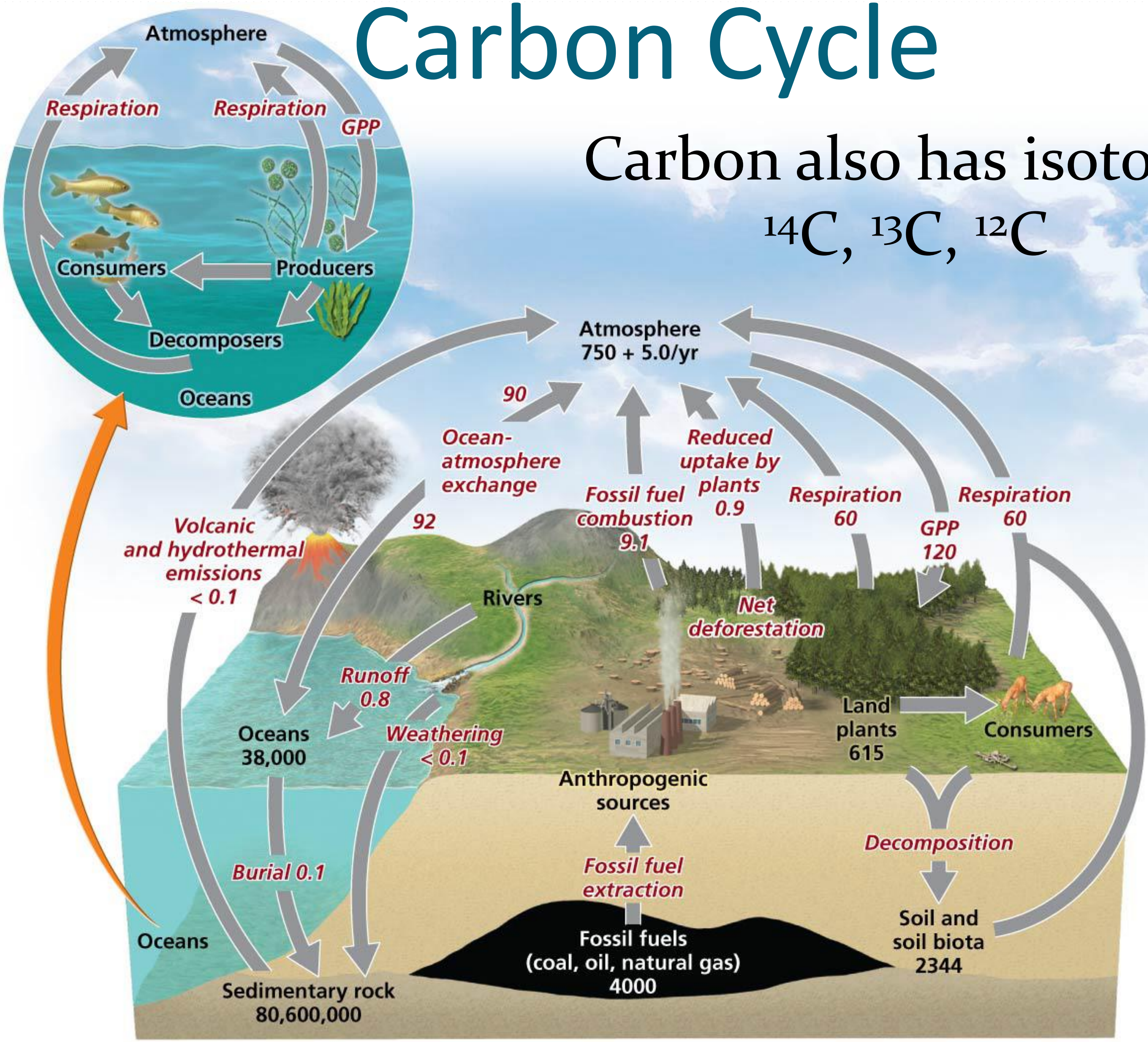


Age (Ma)
δ18O (‰)
5 4 3 2 1 0
Climatic Events
Tectonic Events
Biotic Events
δ13C (‰) (forams)
-1 0 1 2 3
0
10
20
30
40
50
60
70
Plt.
Plio.
Miocene
Oligocene
Eocene
Paleocene
N. Hemisphere Ice-sheets
Antarctic Ice-sheets
W. Antarctic ice-sheet
Asian monsoons intensify
E. Antarctic ice-sheet
Mid-Miocene Climatic Optimum
Mi-1 Glaciation
Late Oligocene Warming
Oi-1 Glaciation
Small-ephemeral Ice-sheets appear
E. Eocene Climatic Optimum
Late Paleocene Thermal Maximum
Panama Seaway closes
Columbia River Volcanism
Tibetan Plateau uplift accelerates
Red Sea Rifting
Plate reorganization & Andean uplift
Drake Passage opens
Tasmania-Antarctic Passage opens
plate reorganization & reduction in seafloor spreading rates
N. Atlantic Rifting & Volcanism
India-Asia contact
Meteor Impact
Large mammal extinctions
"Great American Interchange"
Hominids appear
C4 grasses expand
Horses diversify
seals & sea lions appear
Coral Extinction
large carnivores & other mammals diversify
archaic mammals & broad leaf forests decline, baleen whales appear
Ungulates diversify, primates decline
Archaic whales appear
Mammals disperse
Benthic extinction
K-T Mass Extinctions
Partial or Ephemeral
Full Scale and Permanent
0° 4° 8° 12°
Temperature (°C)*
Direction of x-axes flipped between them

Carbon Cycle

Carbon also has isotopes

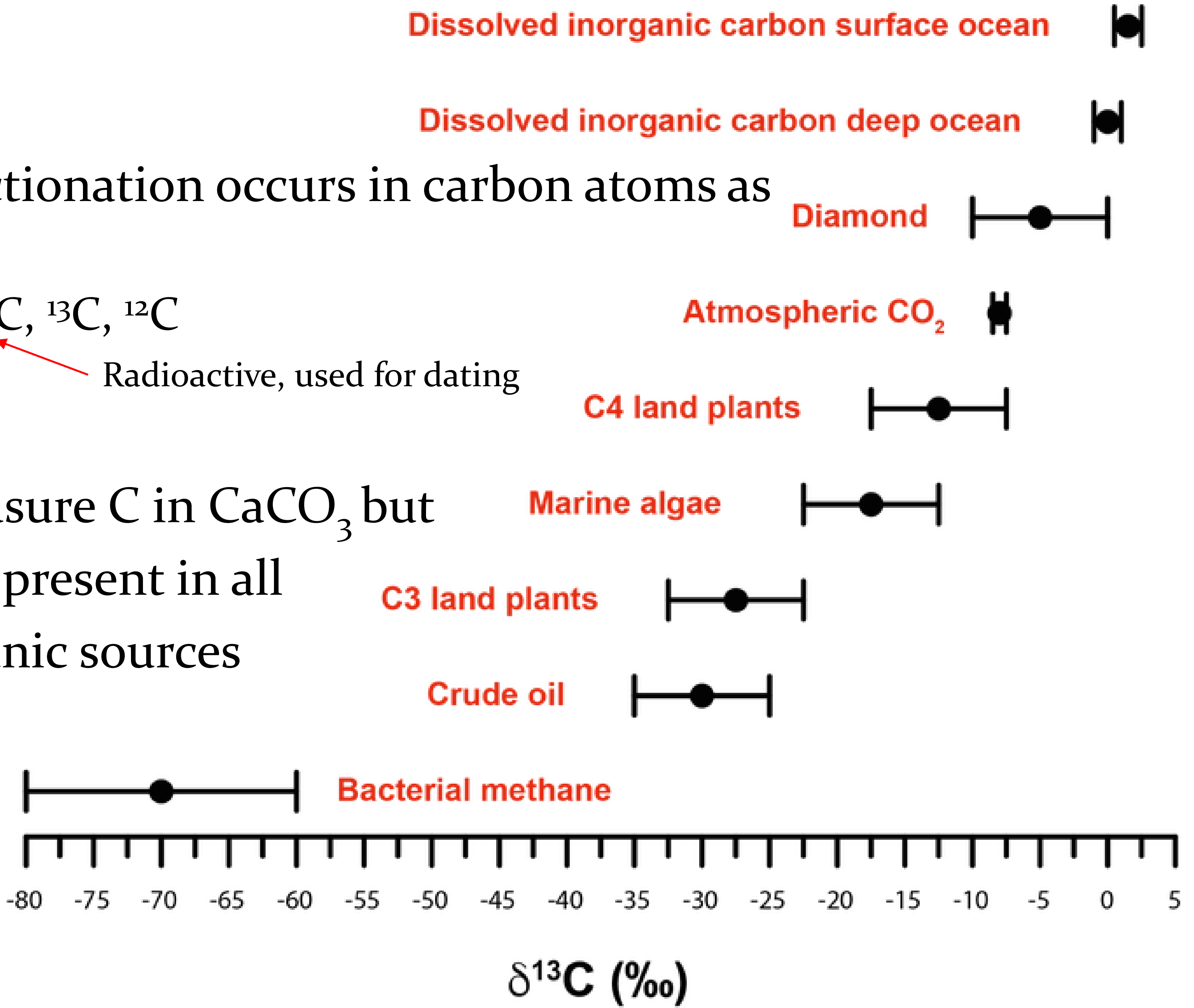
^{14}C, ^{13}C, ^{12}C



- Fractionation occurs in carbon atoms as well
  - ^{14}C, ^{13}C, ^{12}C

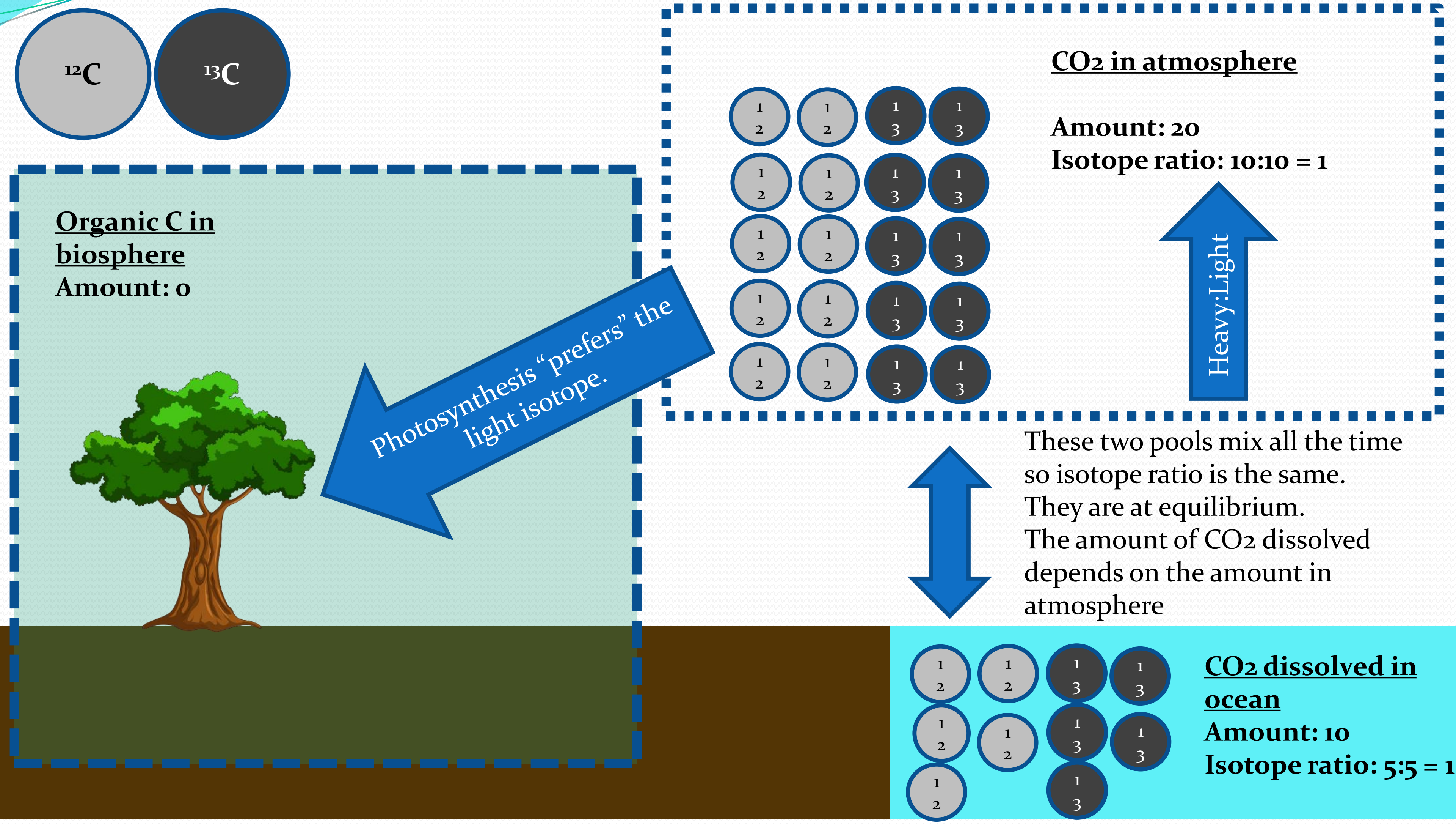
Radioactive, used for dating

- Measure C in $CaCO_3$ but also present in all organic sources

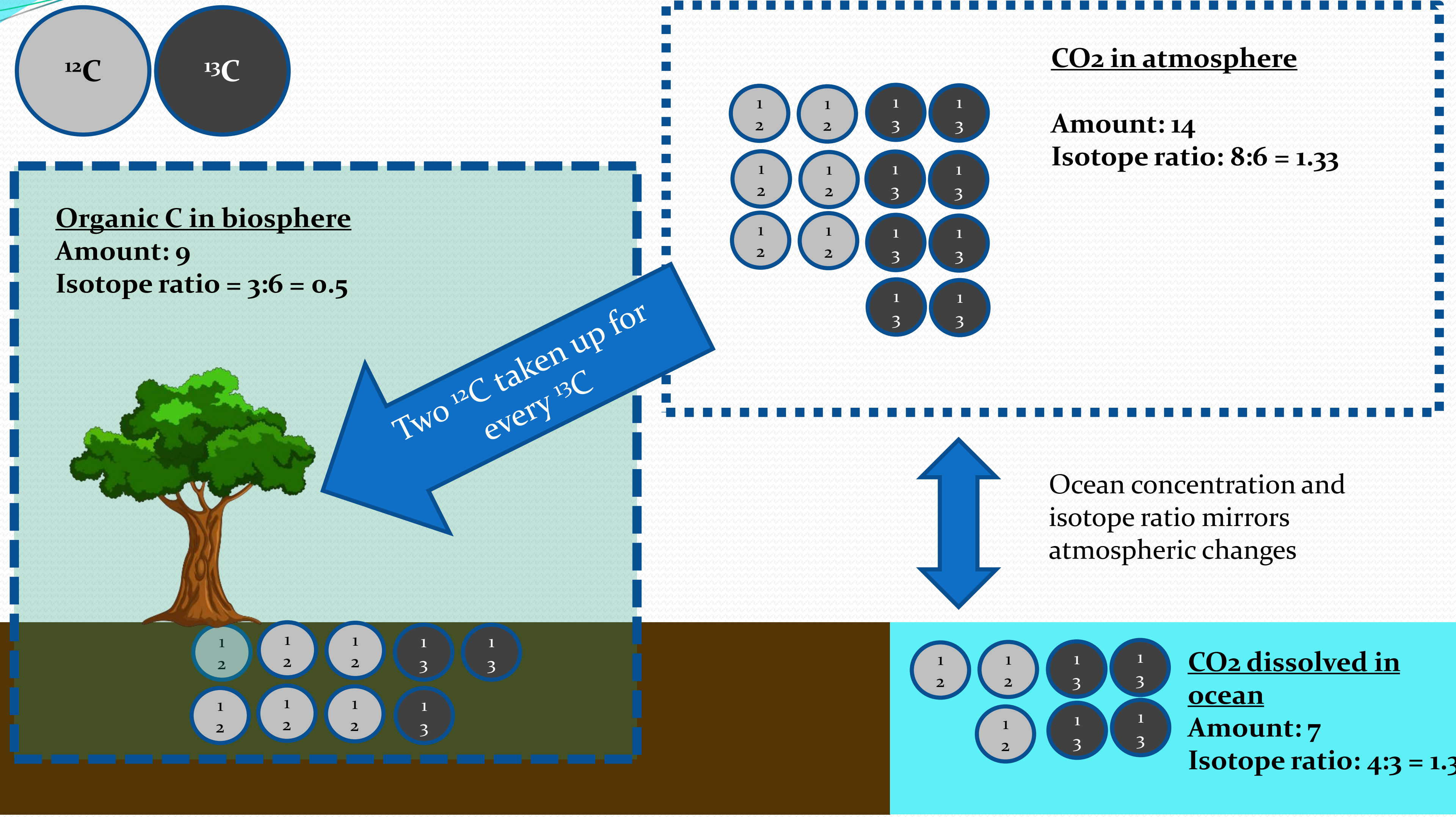


Carbon Isotope Excursions

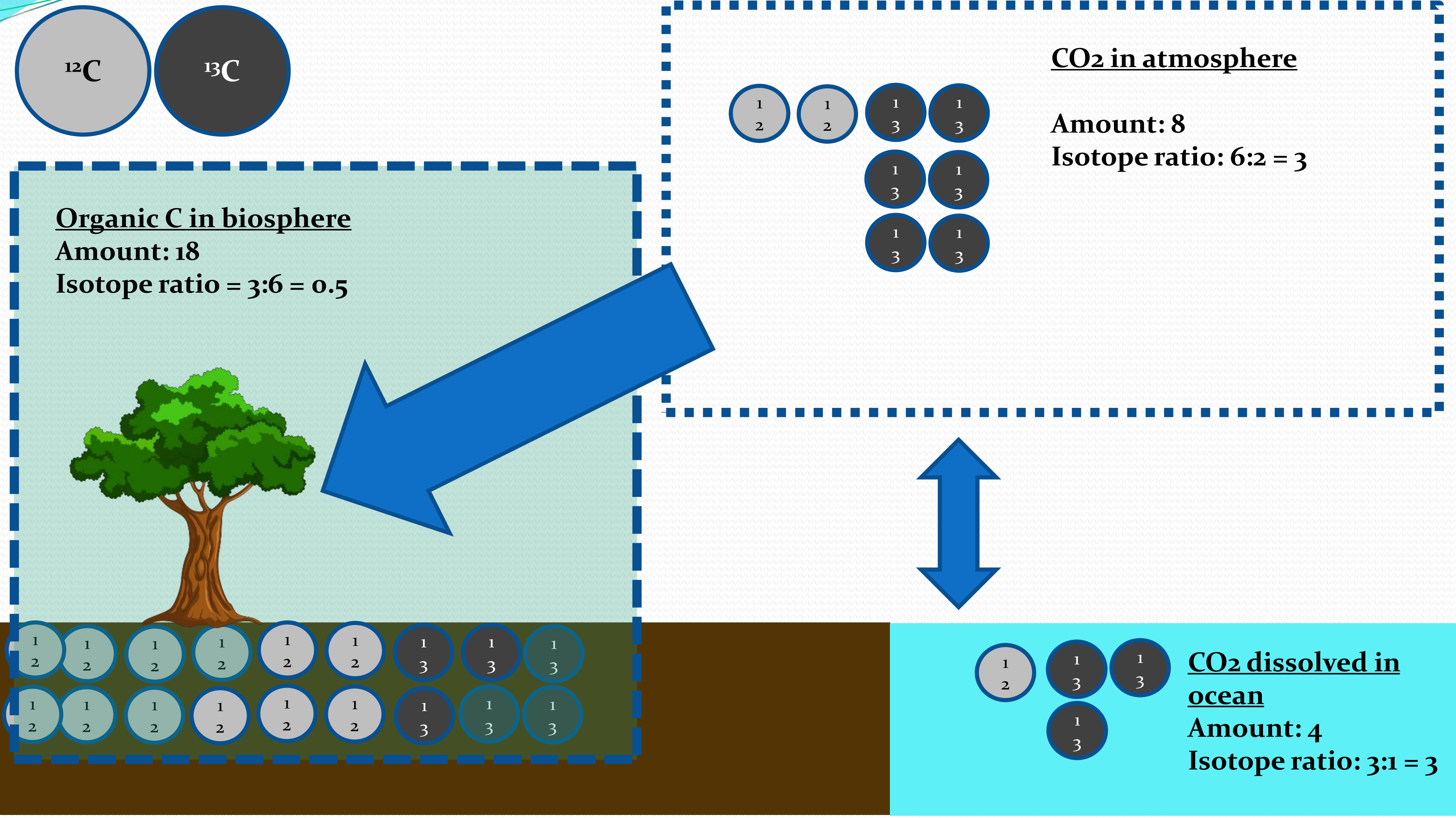
- Earth's carbon system relatively robust to changes in $\delta^{13}C$ (narrow band of values overall)
  - $\pm 2_{0/00}$ considered significant over 100,000 years
- Changes in the $\delta^{13}C$ can tell us about shifts in the balance of the carbon cycle through time
- Correlations between temperature and carbon are more complicated than oxygen though
  - Large excursions, in any direction, are often associated with major environmental changes and extinction events though

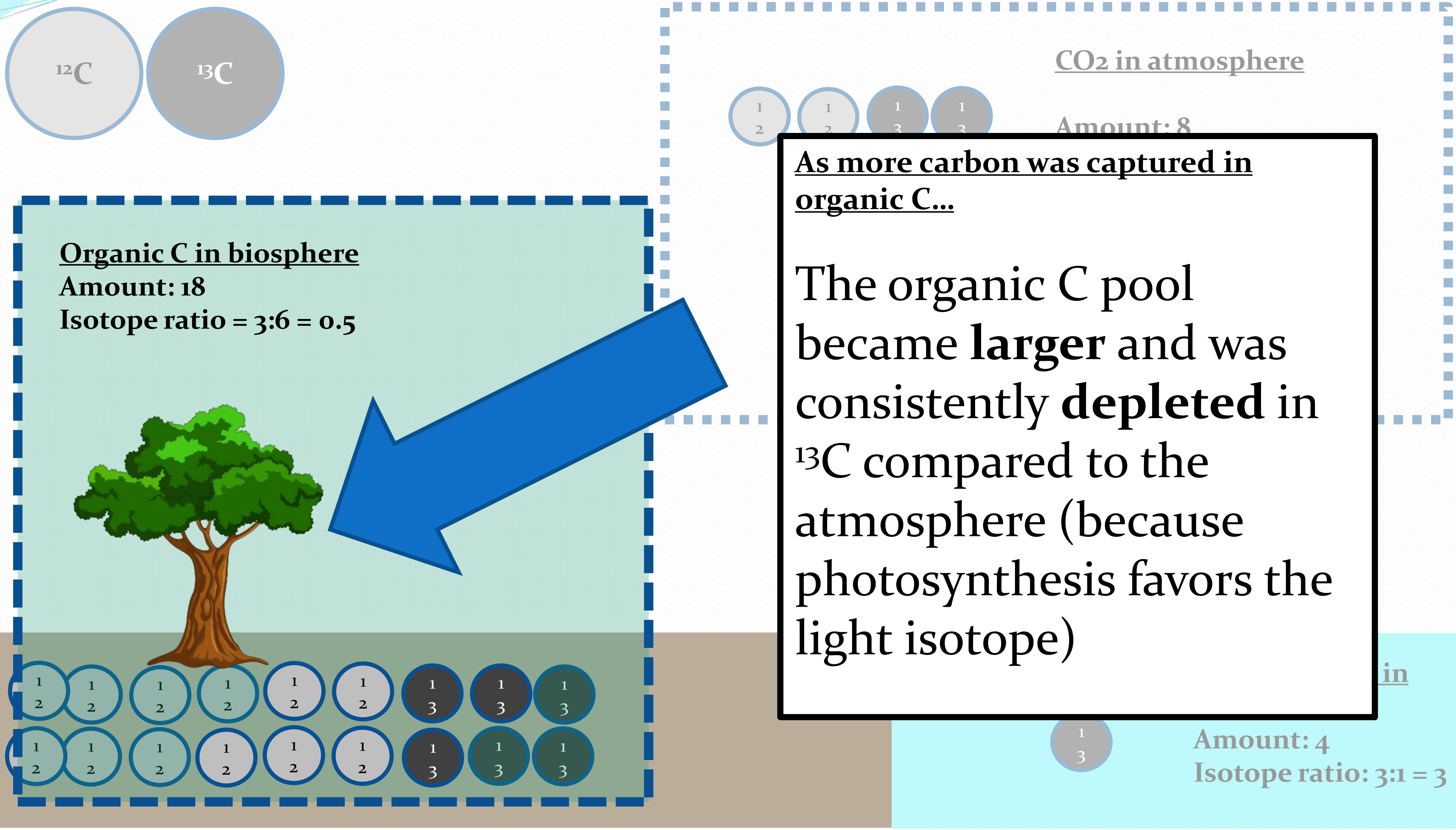


^{12}C
^{13}C
CO2 in atmosphere
Amount: 20
Isotope ratio: 10:10 = 1
Heavy:Light
Organic C in biosphere
Amount: 0
Photosynthesis “prefers” the light isotope.
These two pools mix all the time so isotope ratio is the same. They are at equilibrium. The amount of CO2 dissolved depends on the amount in atmosphere
CO2 dissolved in ocean
Amount: 10
Isotope ratio: 5:5 = 1



^{12}C
^{13}C
CO2 in atmosphere
Amount: 14
Isotope ratio: 8:6 = 1.33
Organic C in biosphere
Amount: 9
Isotope ratio = 3:6 = 0.5
Two ^{12}C taken up for every ^{13}C
Ocean concentration and isotope ratio mirrors atmospheric changes
CO2 dissolved in ocean
Amount: 7
Isotope ratio: 4:3 = 1.3


^{12}C
^{13}C
CO2 in atmosphere
Amount: 8
Isotope ratio: 6:2 = 3
Organic C in biosphere
Amount: 18
Isotope ratio = 3:6 = 0.5
CO2 dissolved in ocean
Amount: 4
Isotope ratio: 3:1 = 3



As more carbon was captured in organic C...

The organic C pool became **larger** and was consistently **depleted** in ^{13}C compared to the atmosphere (because photosynthesis favors the light isotope)

^{12}C ^{13}C

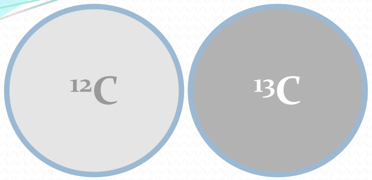
CO2 in atmosphere

Amount: 8
Isotope ratio: 6:2 = 3

As more carbon was captured in organic C…

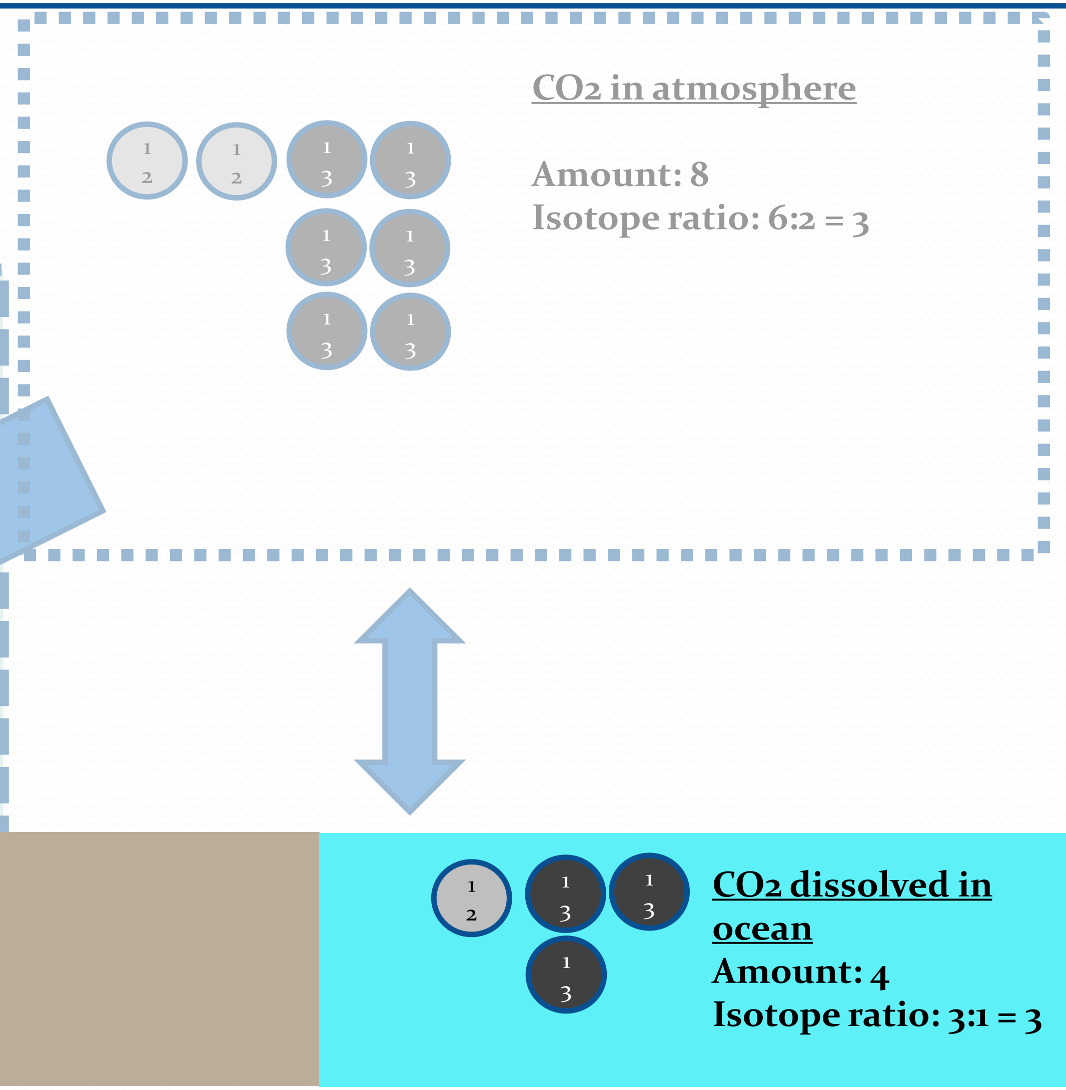
The atmospheric pool became **smaller** and, also importantly, **enriched** in ^{13}C compared to its original composition

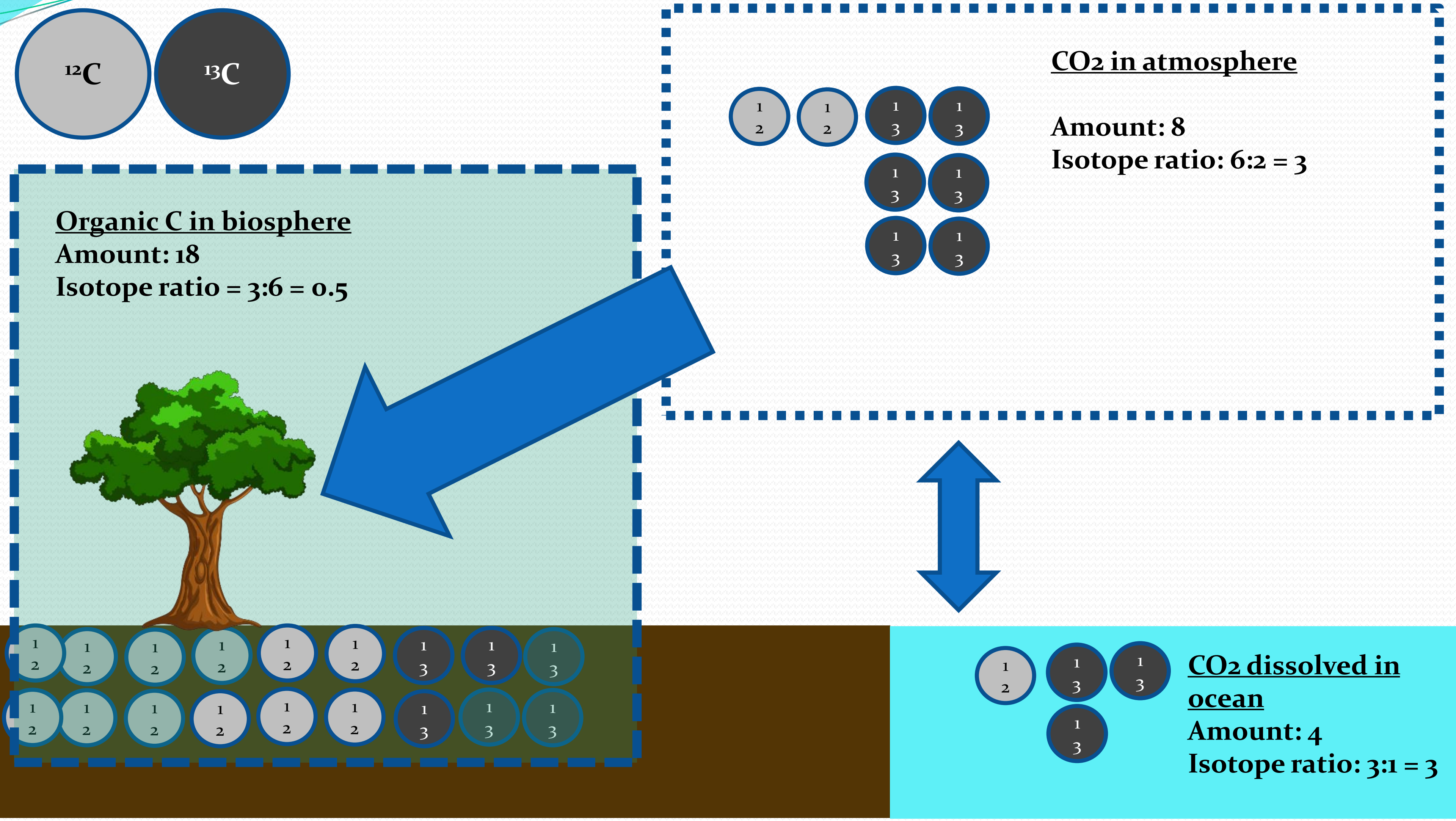
CO2 dissolved in ocean
Amount: 4
Isotope ratio: 3:1 = 3

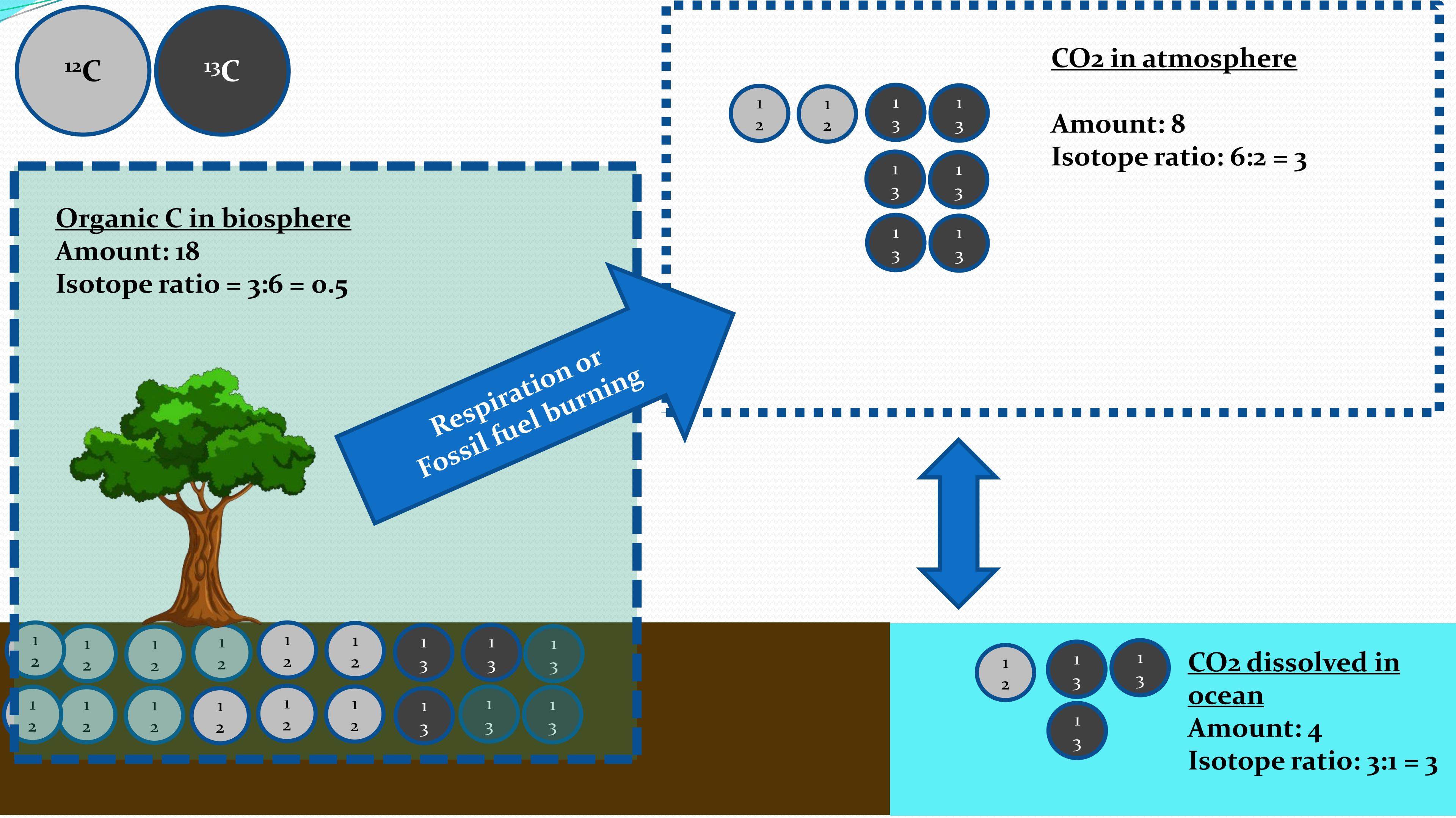


As more carbon was captured in organic C...

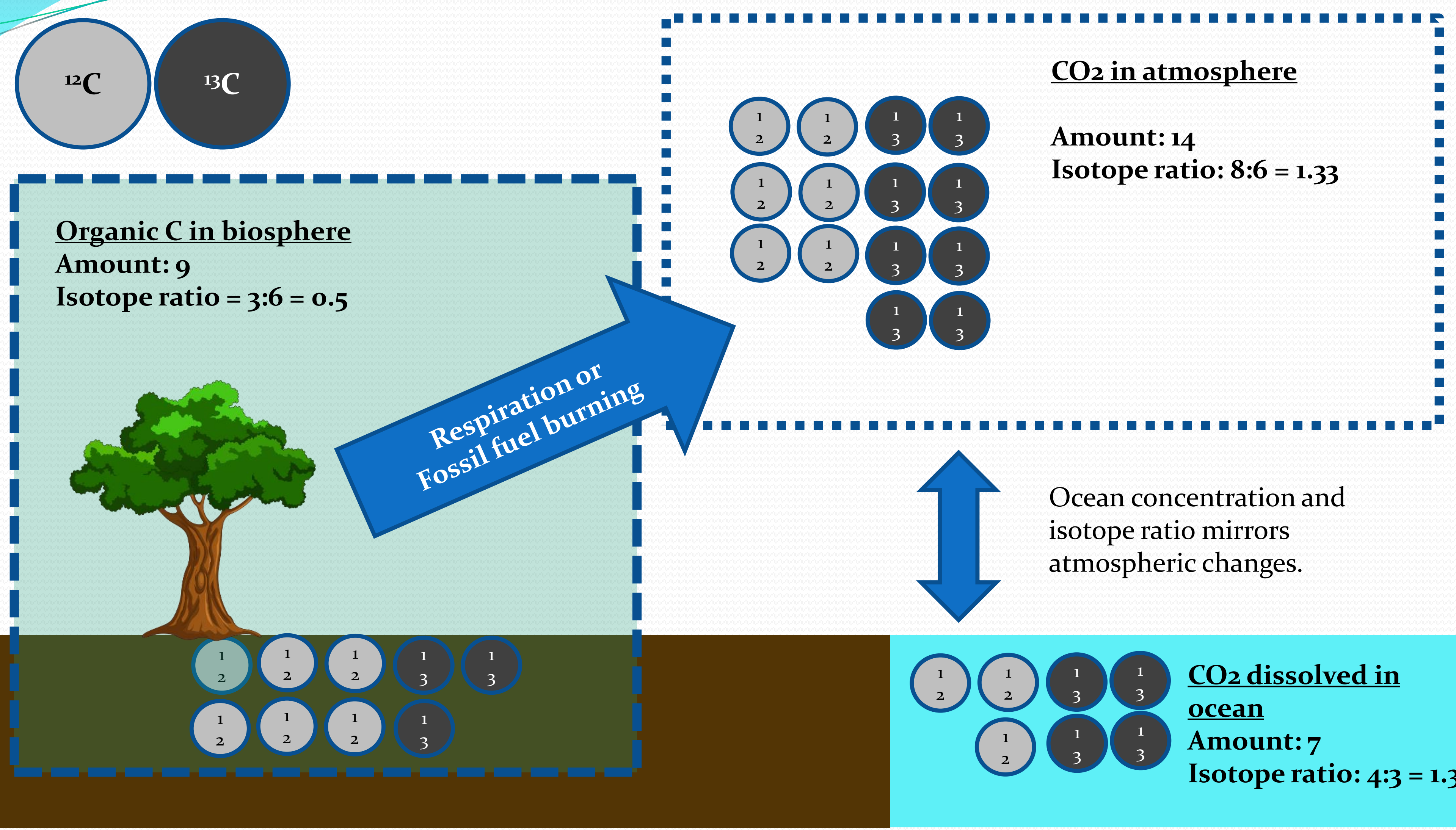
The dissolved CO_2 pool tracked the changes in the atmosphere, becoming **smaller** and also more **enriched** in ^{13}C




^{12}C
^{13}C
CO2 in atmosphere
Amount: 8
Isotope ratio: 6:2 = 3
Organic C in biosphere
Amount: 18
Isotope ratio = 3:6 = 0.5
CO2 dissolved in ocean
Amount: 4
Isotope ratio: 3:1 = 3



¹²C
¹³C
CO2 in atmosphere
Amount: 8
Isotope ratio: 6:2 = 3
Organic C in biosphere
Amount: 18
Isotope ratio = 3:6 = 0.5
Respiration or Fossil fuel burning
CO2 dissolved in ocean
Amount: 4
Isotope ratio: 3:1 = 3



¹²C
¹³C
CO2 in atmosphere
Amount: 14
Isotope ratio: 8:6 = 1.33
Organic C in biosphere
Amount: 9
Isotope ratio = 3:6 = 0.5
Respiration or
Fossil fuel burning
Ocean concentration and
isotope ratio mirrors
atmospheric changes.
CO2 dissolved in
ocean
Amount: 7
Isotope ratio: 4:3 = 1.3

- **When atmospheric CO_2 concentrations are low**, enrichment of the heavy isotope in that pool (expressed as **$\delta^{13}C$) is high**

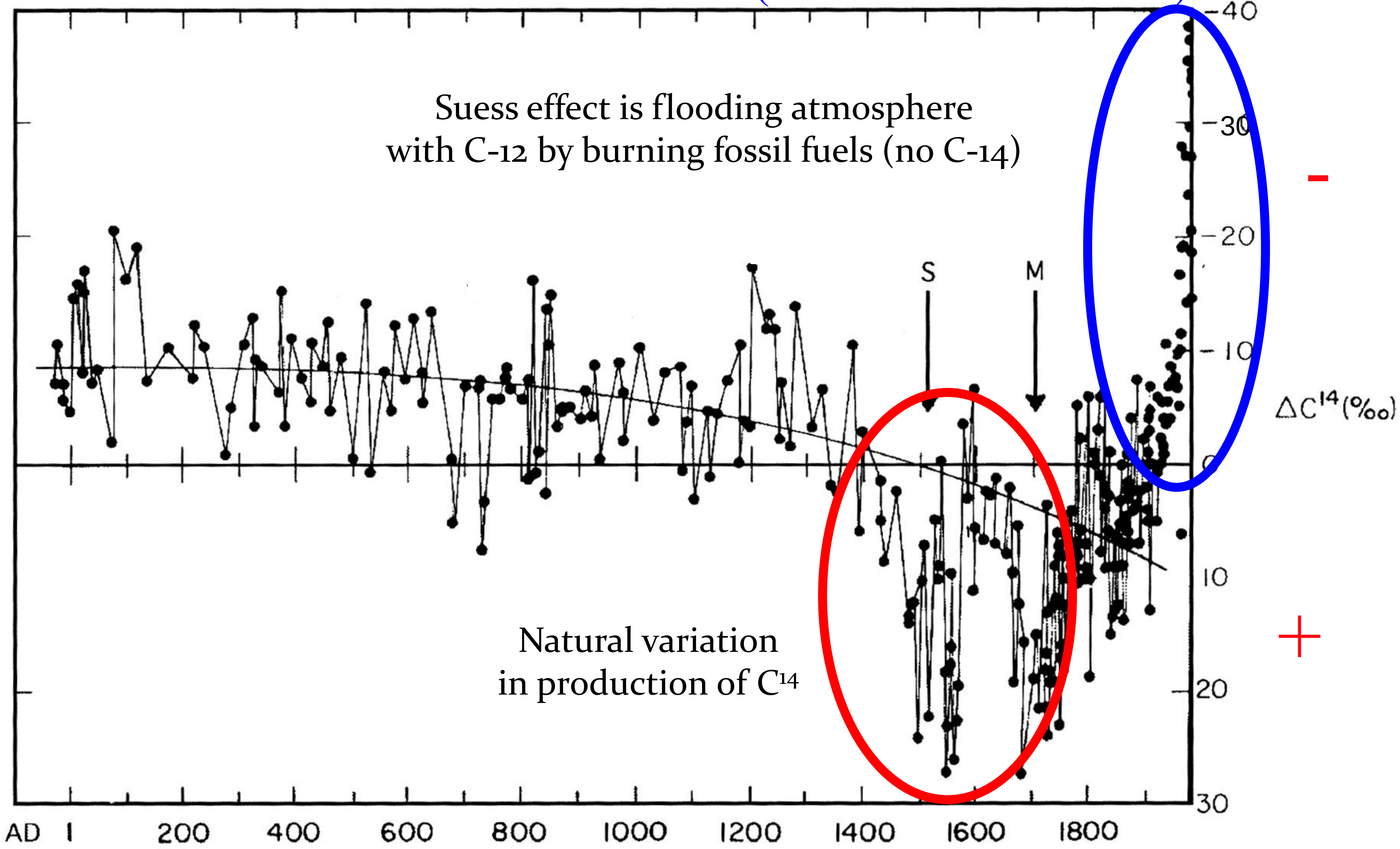
- **When atmospheric CO_2 concentrations are high**, enrichment of the heavy isotope in that pool (expressed as **$\delta^{13}C$) is low**

- Same is true for ocean water

Fossil Fuel Carbon Isotopes

- Fossil fuels are composed of organic matter
  - Coal = land plants
  - Oil & gas = plankton
- Biological tissues "prefers" light isotopes of carbon so fossil fuels are a depleted reservoir
  - The C_{14} that was present has also decayed long ago
- Burning them releases all that super-light carbon into the atmosphere and is measurable

Suess Effect (Industrial Revolution)



Isotope Takeaways

- The correlation between value and temperature is dependent on the reservoir you are measuring for O & H
  - ^{2}H and ^{18}O has a positive correlation with temperature when measuring isotopes from land sources
  - ^{2}H $_{and}$ ^{18}O has a negative correlation with temperature when measuring isotopes from ocean sources

- The strong negative carbon excursion recently in the atmosphere is only explainable by burning fossil fuels

Today's Learning Outcomes

1. Be able to define what an isotope is
2. Be able to explain what isotope fractionation is
3. Be able to explain delta notation
4. Know how temperature correlates with oxygen isotopes when measured from land sources versus when measured from ocean sources
5. Be able to explain why the negative atmospheric carbon isotope excursion over the past 100 years can be explained by fossil fuels use