STABLE ISOTOPES IN ENVIRONMENTAL SCIENCE

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Contents

- Basics of applied isotope science
  - What are isotopes?
  - What are the methods of stable isotope science?
  - What are the applications?
    - Oxygen and hydrogen isotopes and the water cycle
    - Carbon isotopes and food webs
    - Nitrogen isotopes and food webs

Periodic Table of the Elements

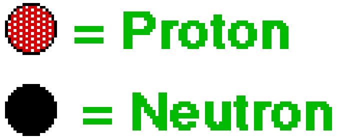
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.38	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.631	33 **As** Arsenic 74.922	34 **Se** Selenium 78.972	35 **Br** Bromine 79.904	36 **Kr** Krypton 84.798
37 **Rb** Rubidium 85.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molybdenum 95.95	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.711	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.294
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.328	57-71	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.085	79 **Au** Gold 196.967	80 **Hg** Mercury 200.592	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [269]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicium [277]	113 **Nh** Nihonium unknown	114 **Fl** Flerovium [289]	115 **Mc** Moscovium unknown	116 **Lv** Livermorium [298]	117 **Ts** Tennessine unknown	118 **Og** Oganesson unknown

57 **La** Lanthanum 138.905	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.242	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.055	71 **Lu** Lutetium 174.967
89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide

WHAT IS AN ISOTOPE?

An atom of an element that has a specific number of neutrons



Mass Number A

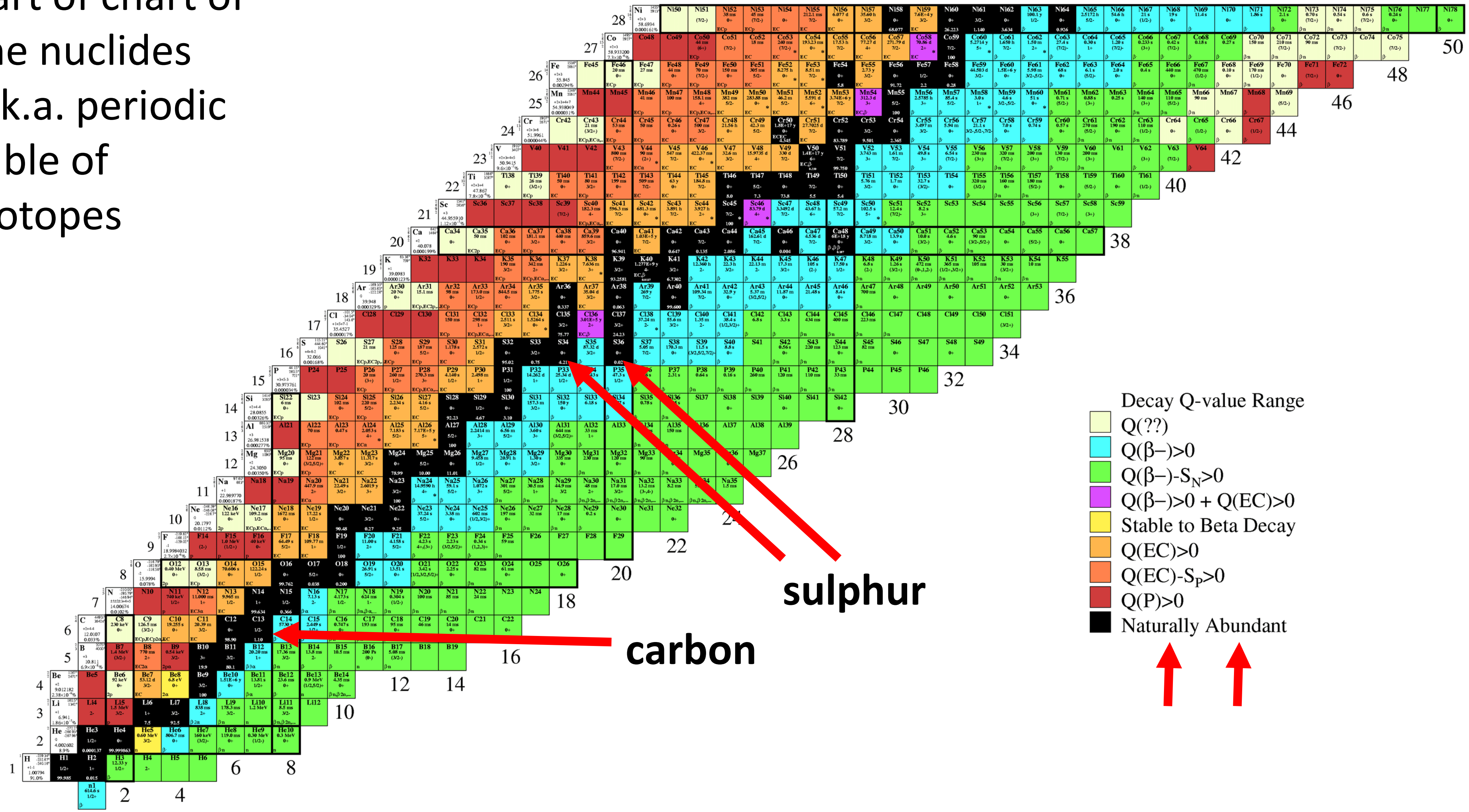
Atomic Number Z

$${}^{A}_{Z}C$$

Z = Protons
A = Mass Number
A = Protons + Neutrons

CHART OF THE NUCLIDES

Part of chart of the nuclides a.k.a. periodic table of isotopes



Isotopes

- Isotopes have different # of neutrons, and thus a different mass
- Effect on reactions in small, but real, and provides another measurement of reactions – affected by similar physicochemical parameters!
- Also a critical tracer – the isotopes can be used to track molecules in a reaction!

<u>Isotopologues</u>: molecules that differ in isotopic composition.

WHERE DOES ISOTOPE SCIENCE COME FROM?

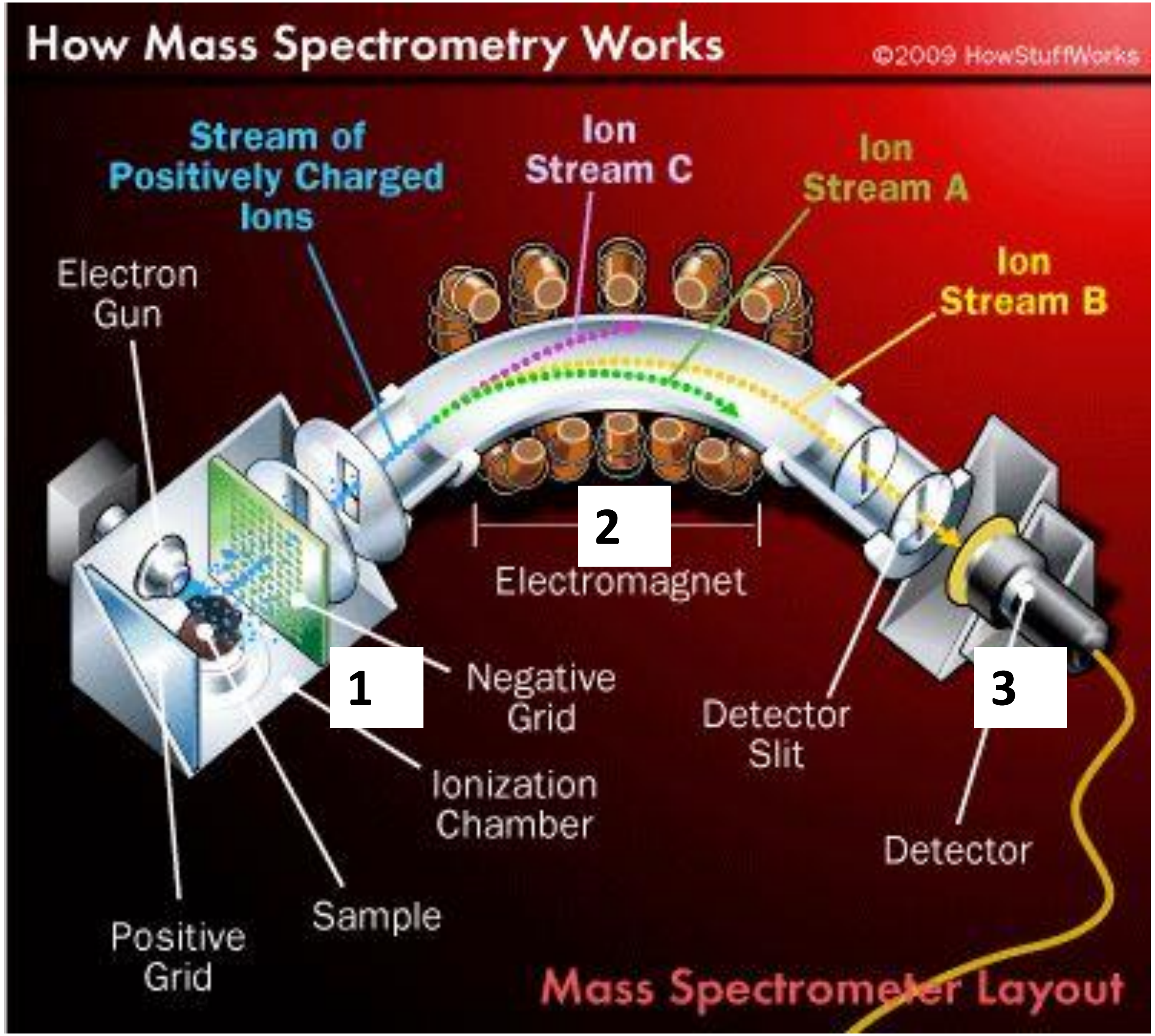
INVENTION OF THE
MASS SPECTROMETER
(J.J. Thomson, 1913)

1) **source**: sends ions
down the flight tube

2) **magnet**: separates the
beam into different
mass/charge ratios,
the "mass analyzer"

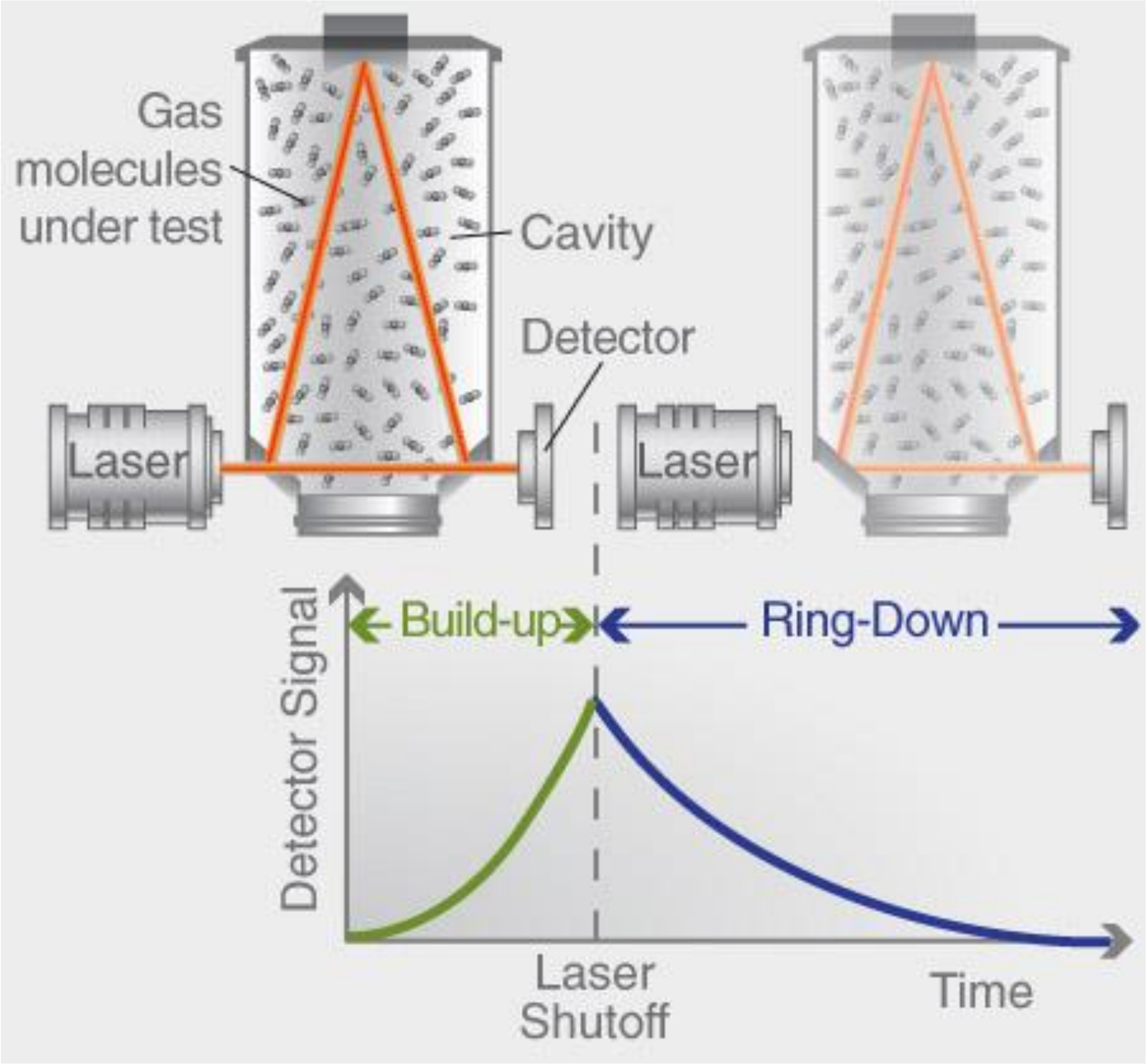
3) **detector:** measures the
signal from incoming beams

(under vacuum)



HEAVY vs. light isotopologues
:: BUS vs. car

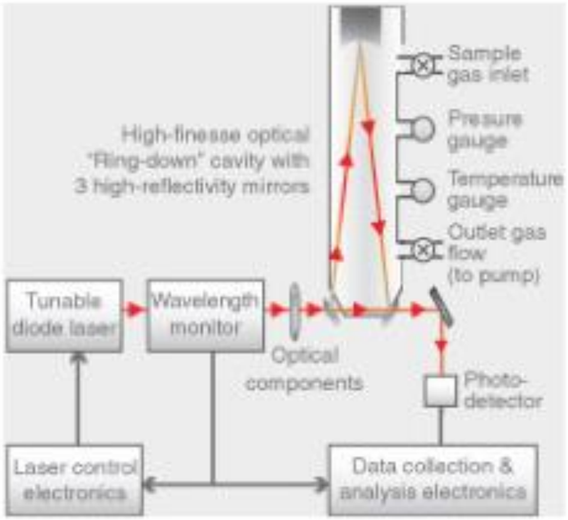
(new instruments) CAVITY RINGDOWN SPECTROSCOPY, CRDS

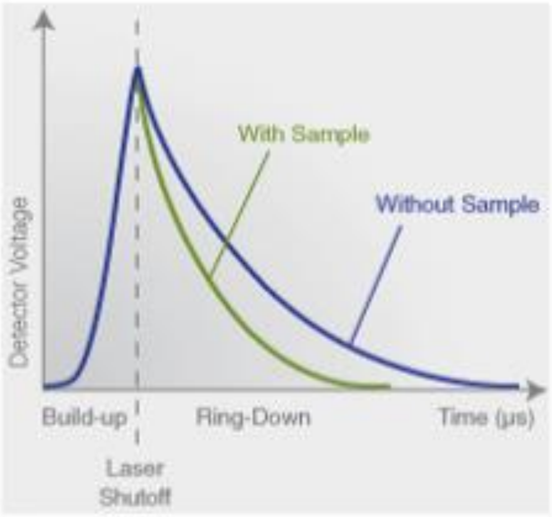


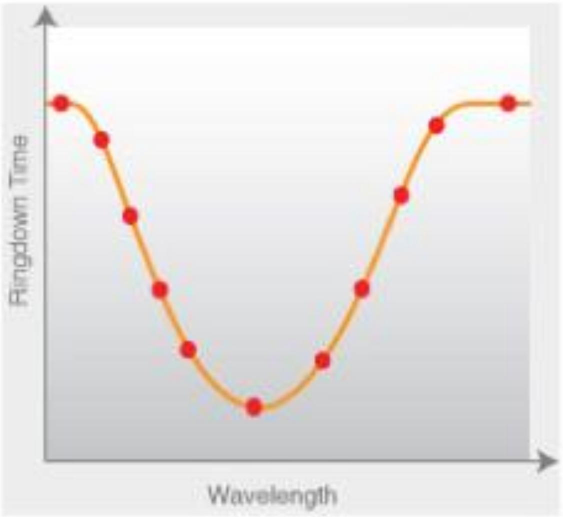
Picarro Wavelength-Scanning Cavity Ringdown Spectroscopic Instrument for Airborne In Situ CO_2 and CH_4 Quantification

Instrument Leads: Teresa Campos and Frank Flocke

- Fast-response commercial instrument (Picarro)
- Precision (0.2-s averaging time):
  - 250 ppbv CO_2
  - 3 ppbv CH_4
- Vendor specified 5-Hz frequency response
  - actual response not yet verified in field setting

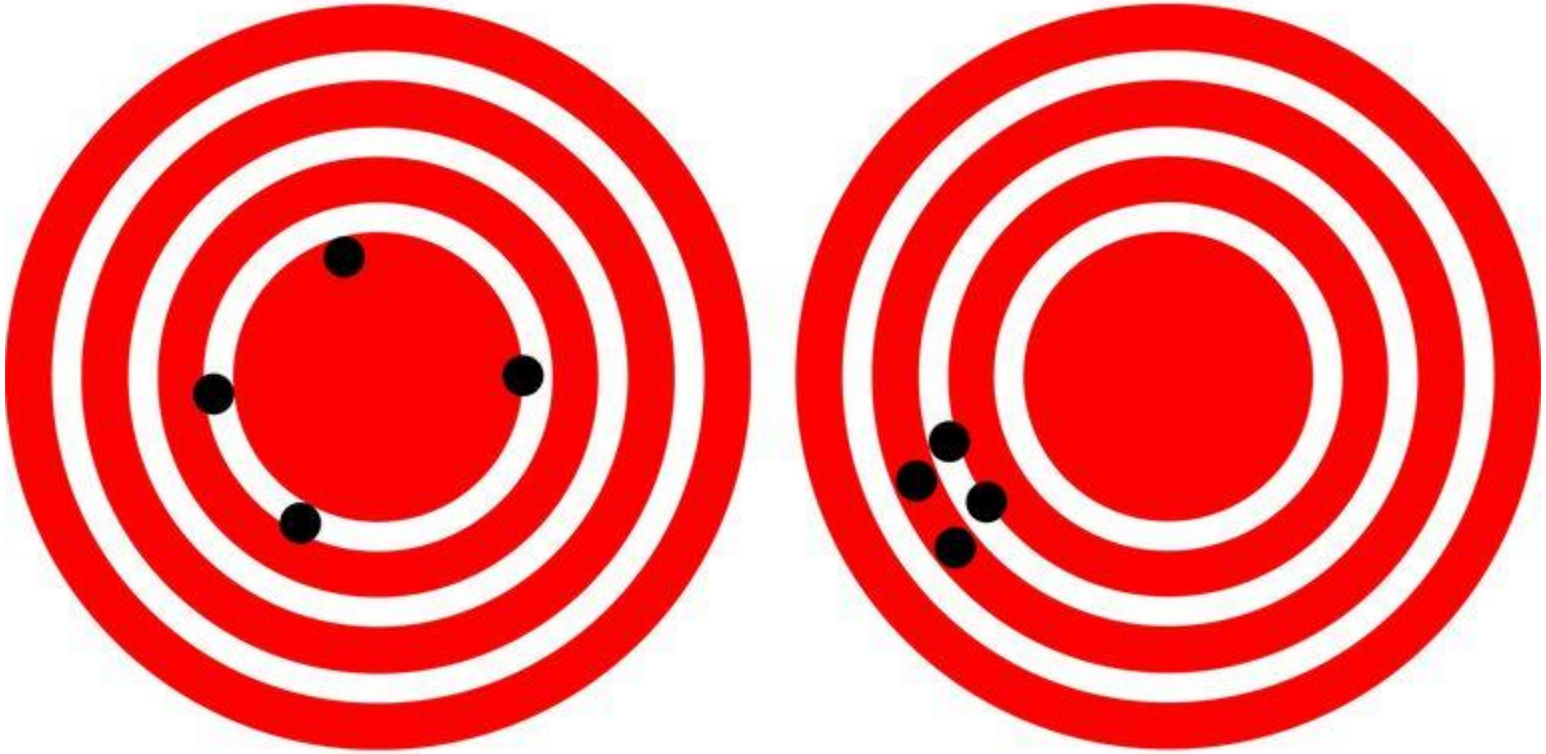






MOST IMPORTANT SLIDE

Accuracy vs. Precision

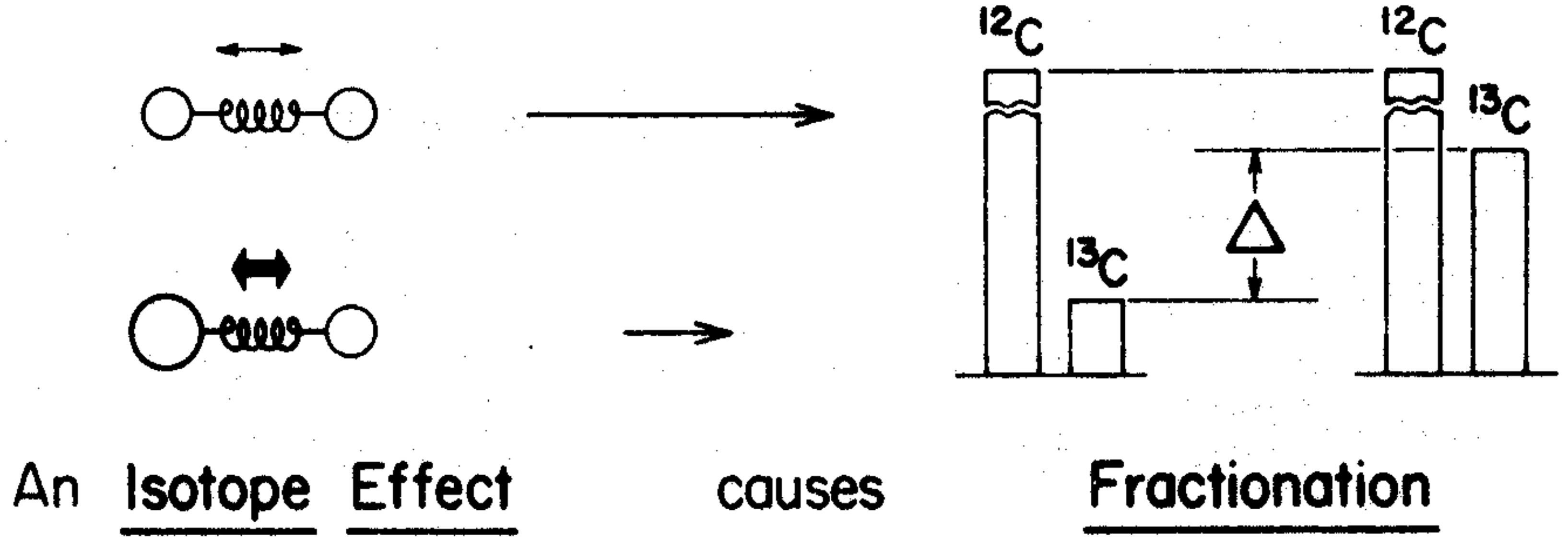


Making Isotopes Useful for Applied Science

- 1916: Invention of mass spectrometer by J.J. Thomson
- 1934: Harold Urey discovers isotopes of hydrogen
- **1953: Discovery of the oxygen isotope "paleothermometer"**
  - Sam Epstein (student of Harold Urey)
  - Calcite ($CaCO_3$) $^{18}O/^{16}O$ varies with temperature of crystallization
- 1961: Harmon Craig standardized data reporting, delta notation, per mil scale, common isotope standards (SMOW)
- 1964-1990s: Willi Dansgaard traced components of the water cycle, Vostok Ice Core (high resolution record of ice ages)

Fractionation

- A reaction or process which selects for one of the stable isotopes of a particular element
- If the process selects for the heavier isotope, the reaction product is ‘heavy’, the reactant remaining is ‘light’
- Isotope fractionation occurs for isotopic exchange



Fractionation

- Fractionation is a reaction, but one in which the free energy differences are on the order of 1000x smaller than other types of chemical reactions
- Just like other chemical reactions, we can describe the proportion of reactants and products as an equilibrium or as a kinetic function

Fractionation Factor, α

- R is the ratio of heavy to light isotopes
- α, or fractionation factor, is the ratio between reactant and product

$$\alpha = \frac{R_{reactants}}{R_{products}}$$

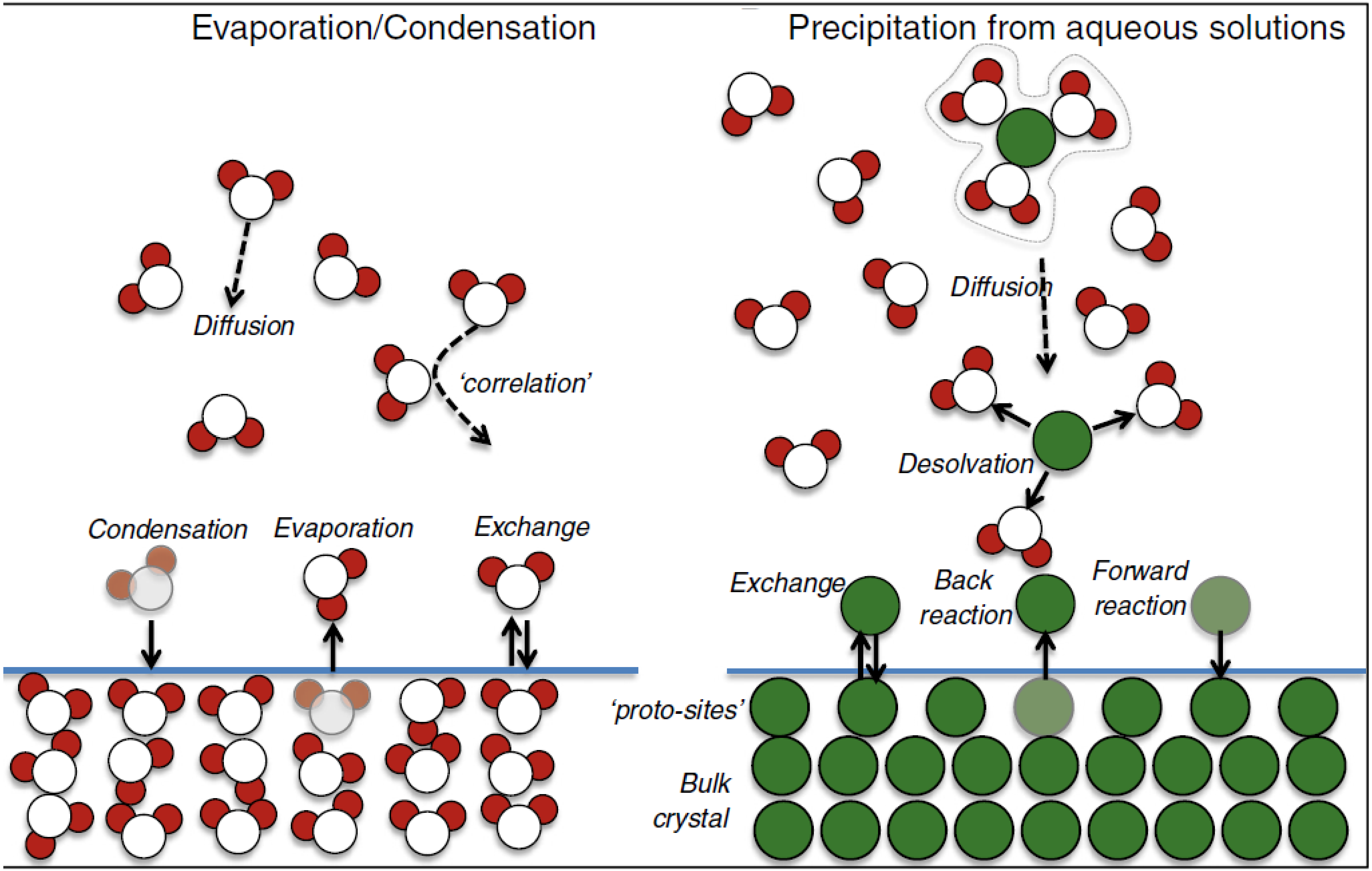
$$H_2O_{water} \longleftrightarrow H_2O_{vapor}$$

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

ISOTOPE FRACTIONATION

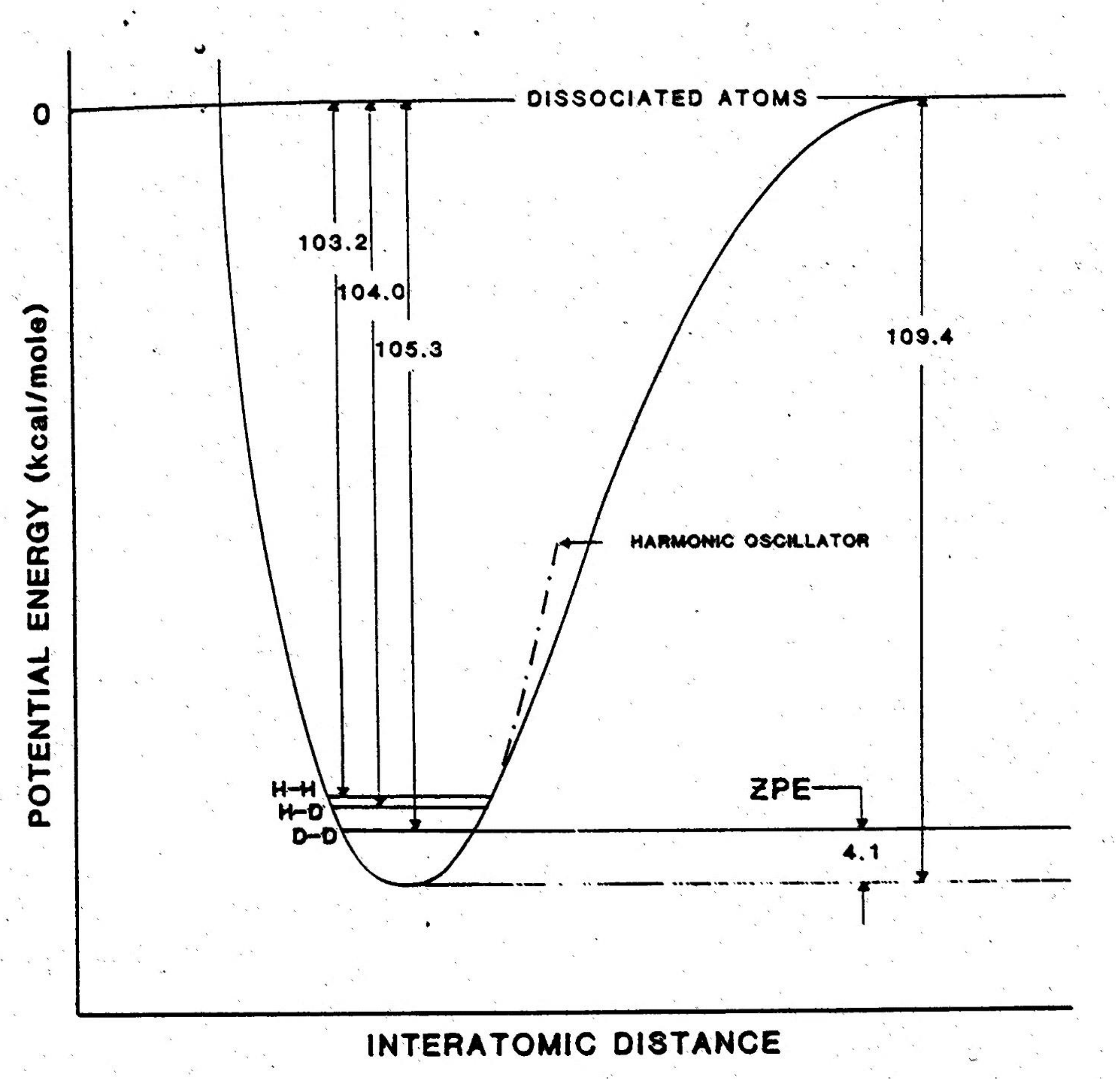
- Natural processes “sort” the isotope composition of matter
- Evaporation, condensation, photosynthesis, respiration, crystallization, etc.
- Two types of fractionation
  - Equilibrium (reversible)
  - Kinetic (unidirectional)
- $\alpha_{A\text{-}B} = R_A / R_B$
- $\alpha_{A\text{-}B} = (1000 + \delta_A) / (1000 + \delta_B)$
- $\alpha^* = 1/\alpha = \alpha_{B\text{-}A} = R_B / R_A$
- $\varepsilon_{A\text{-}B} = (\alpha_{A\text{-}B} - 1) \cdot 1000$
- $\varepsilon_{A\text{-}B} \sim \delta_A - \delta_B \sim 1000 \ln \alpha_{A\text{-}B}$

https://wwwrcamnl.wr.usgs.gov/isoig/isopubs/itchch2.html



Evaporation/Condensation
Precipitation from aqueous solutions
Diffusion
'correlation'
Condensation
Evaporation
Exchange
Diffusion
Desolvation
Exchange
Back reaction
Forward reaction
'proto-sites'
Bulk crystal

- The heavy isotope forms a lower energy bond; it does not vibrate as violently. Therefore, it forms a stronger bond in the compound.
- The Rule of Bigeleisen (1965) - The heavy isotope goes preferentially into the compound with the strongest bonds.



Kinetic fractionation: e.g., evaporation, diffusion

Because the kinetic energy for heavy and light isotopes is the same, we can write:

$$\frac{v_L}{v_H} = \sqrt{\frac{m_H}{m_L}}$$

In the case of $^{12}C^{16}O$ and $^{13}C^{16}O$ we have:

$$\frac{v_L}{v_H} = \sqrt{\frac{28.99827}{27.994915}} = 1.0177$$

Regardless of the temperature, the velocity of $^{12}C^{16}O$ is 1.0177 times that of $^{13}C^{16}O$, so the lighter molecule will diffuse faster and evaporate faster.

FRACTIONATION DURING PHYSICAL PROCESSES

- Mass differences also give rise to fractionation during physical processes (diffusion, evaporation, freezing, etc.).
- Fractionation during physical process is a result of differences in the velocities of isotopic molecules of the same compound.
- Consider molecules in a gas. All molecules have the same average kinetic energy, which is a function of temperature.

$$E_{kinetic} = \tfrac{1}{2} m v^2$$

WHY IS K DIFFERENT FROM 1.0?

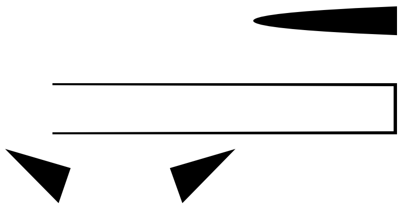
Because ^{18}O forms a stronger covalent bond with C than does ^{16}O.

The vibrational energy of a molecule is given by the equations:

$$\boxed{E_{vibrational} = \tfrac{1}{2} h\nu}$$

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}}$$

$$\boxed{F = -kx}$$



Thus, the frequency of vibration depends on the mass of the atoms, so the energy of a molecule depends on its mass.

Equilibrium Fractionation

- For an exchange reaction:

$$\tfrac{1}{2}\, C^{16}O_2 + H_2{}^{18}O \leftrightarrow \tfrac{1}{2}\, C^{18}O_2 + H_2{}^{16}O$$

- Write the equilibrium:

$$K = \frac{(C^{18}O_2)^{\frac{1}{2}}(H^{16}O_2)}{(C^{16}O_2)^{\frac{1}{2}}(H^{18}O_2)}$$

-
- Where activity coefficients effectively cancel out
- For isotope reactions, K is always small, usually 1.0xx (this K is 1.047 for example)

Equilibrium fractionation:
Temperature effects on fractionation

- The fractionation factors, α, are affected by T (recall that this affects E_A) and defined empirically:

- Then, $$10^3 \ln \alpha_b^a = \frac{A \times 10^6}{T^2} + B$$

Where A and B are constants determined for particular reactions and T is temp. in Kelvins

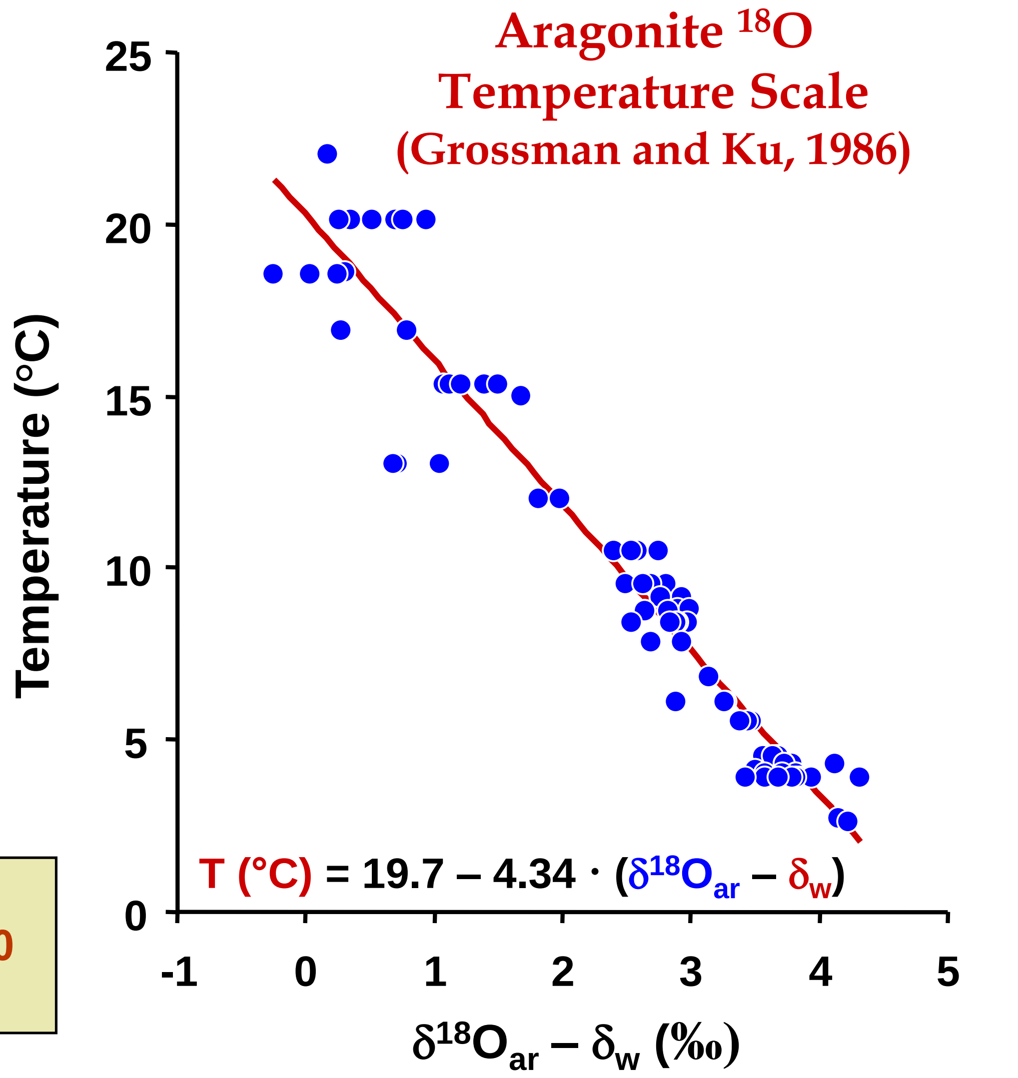
- As T increases, Δ decreases – at high T Δ goes to zero

$$\boxed{10^3 \ln \alpha_b^a \approx \delta_a - \delta_b = \Delta_b^a}$$

Oxygen Isotopes in Mollusk Shells

- $CaCO_3$ δ^{18}O depends on T and δ^{18}O of water (δ_w)
- -0.2‰ per °C (at 25°C)
- Analytical precision ±0.1‰ ≈ ±0.5°C

$$\delta^{18}\mathrm{O}\ (‰) = \frac{(^{18}\mathrm{O}/^{16}\mathrm{O})_x - (^{18}\mathrm{O}/^{16}\mathrm{O})_{std}}{(^{18}\mathrm{O}/^{16}\mathrm{O})_{std}} \times 1000$$

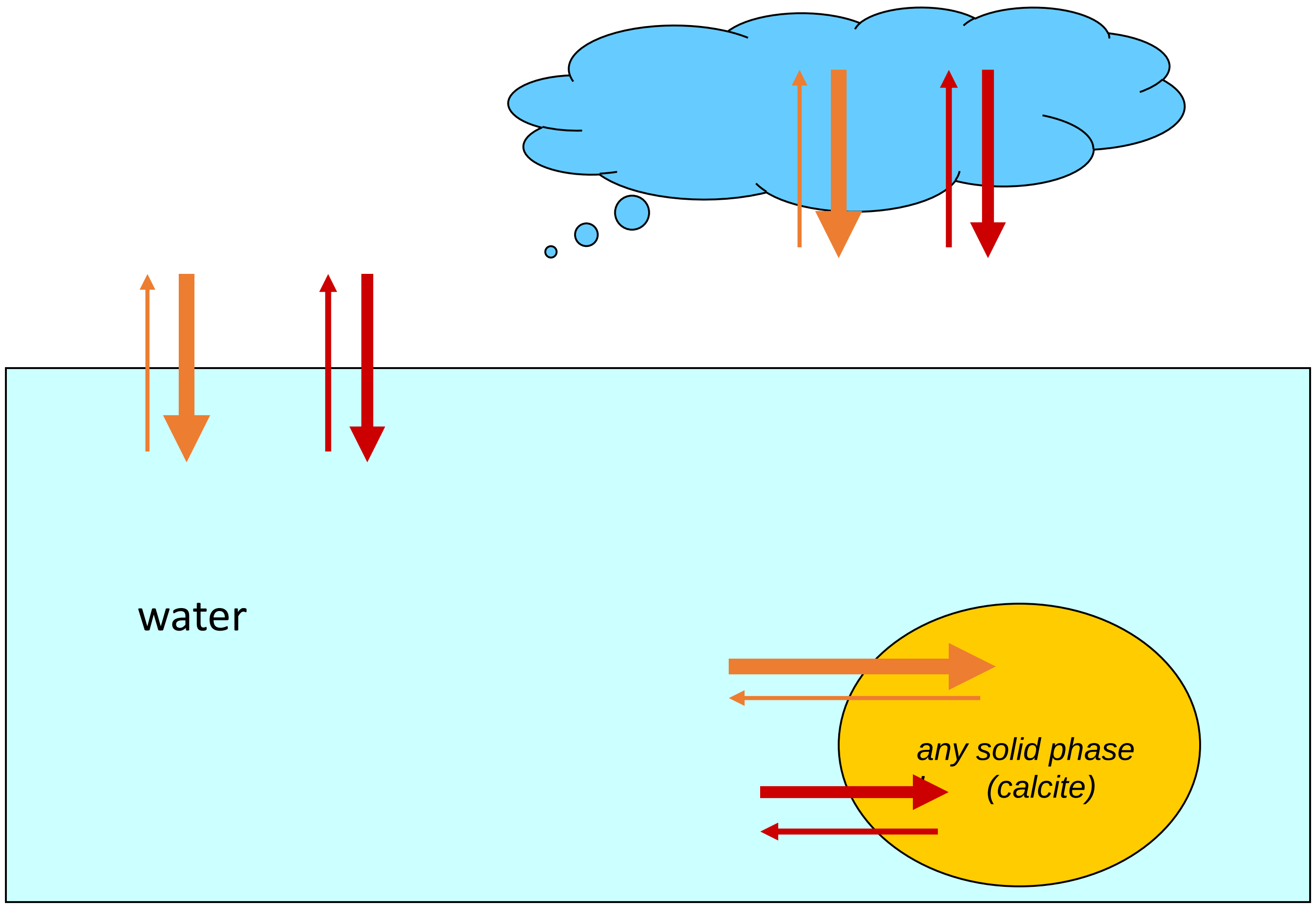


$\delta^{18}O_{ar}$ = δ^{18}O of aragonite (vs. PDB)

δ_w = δ^{18}O of water (vs. SMOW)

Temperature-dependent fractionation - recap

Equilibrium fractionation is temperature-dependent, **always**.



red=warm
blue=cold;
arrows track movement of ^{18}*O through phase changes*

Per mil scale (‰) and "delta" **δ notation**

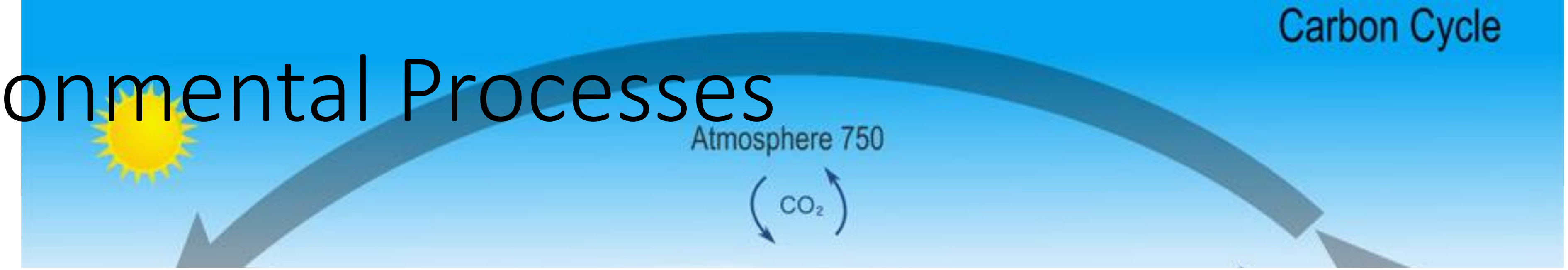
- R is the ratio of the abundance of the heavy isotope to the light isotope ($^{18}O/^{16}O$ or $^{13}C/^{12}C$, for example)
- $\left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) * 1000$ = ‰ value = $\left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000$
- Can be positive or negative or zero
- Leaf sample $\delta^{13}C_{VPDB}$ = $\left(\frac{\frac{^{13}C}{^{12}C}^{sample}}{\frac{^{13}C}{^{12}C}^{standard}} - 1\right) * 1000$

= $\left(\frac{0.0110000}{0.0112372} - 1\right)$ *1000 = **-21.1 ‰**

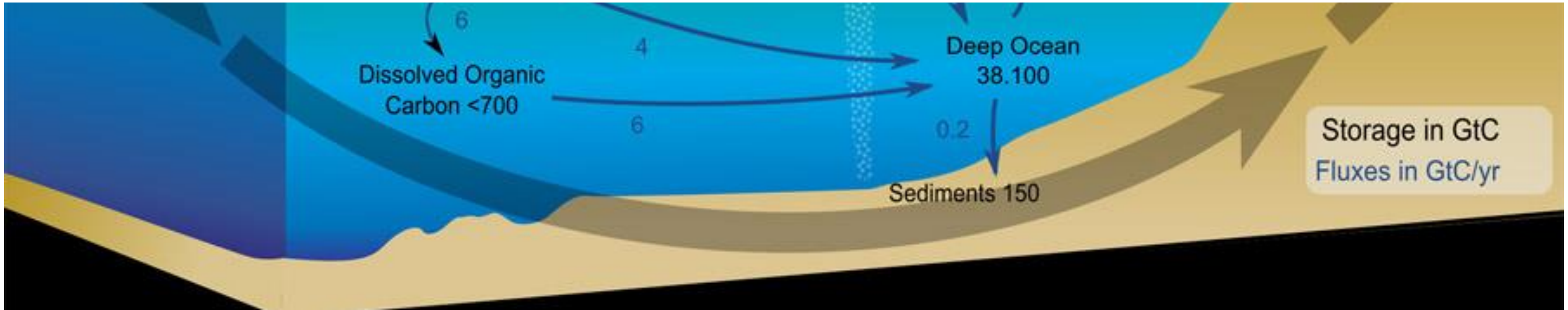
Isotope Standards

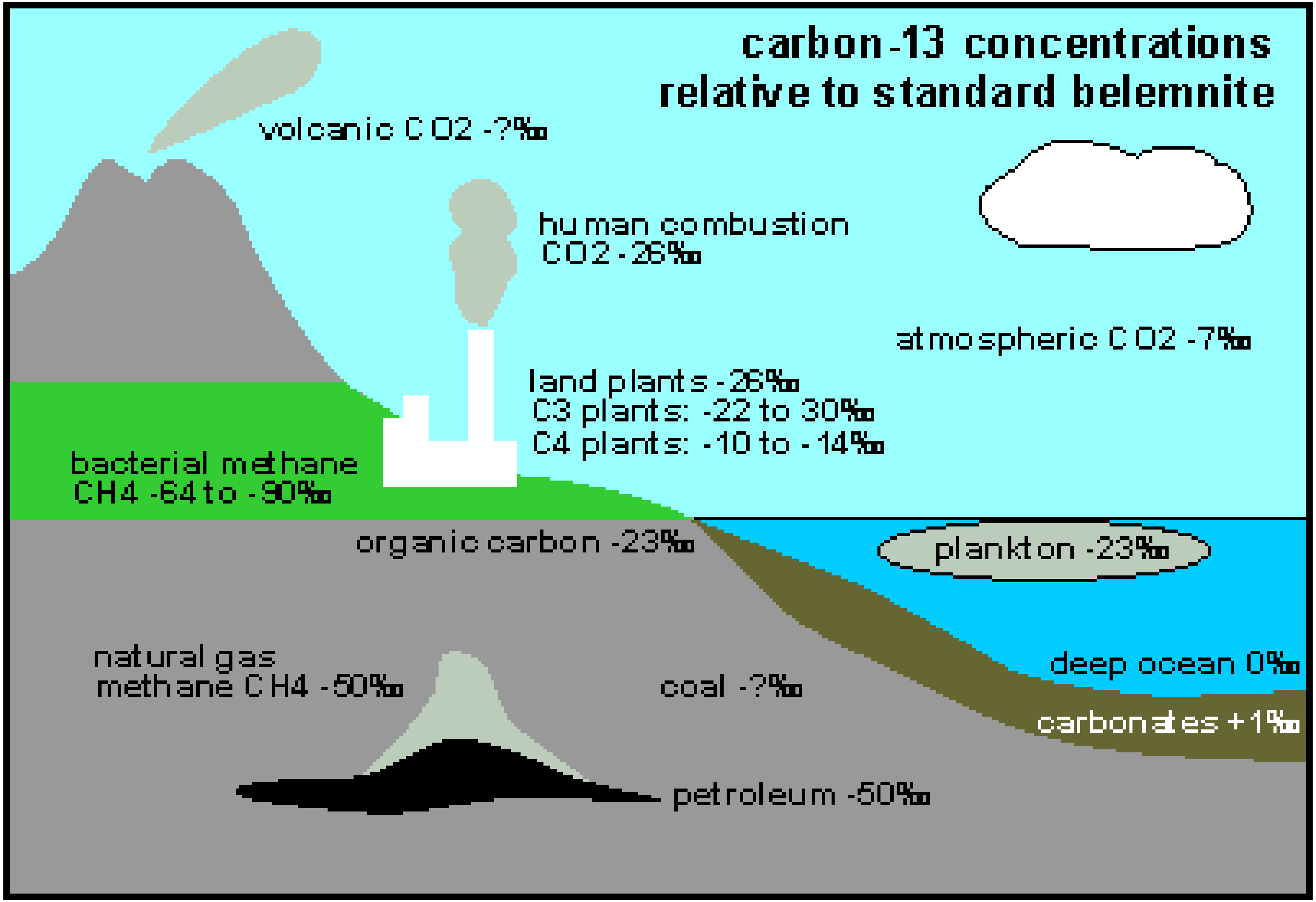
- VSMOW – Vienna Standard Mean Ocean Water – bunch of ocean water kept in Austria – O and H standard
- PDB – Pee Dee Belemnite – fossil of a belemnite from the Pee Dee formation in Canada – C and O
- CDT – Canyon Diablo Troilite –meteorite fragment from meteor crater in Arizona, contains FeS mineral Troilite – S
- AIR – Atmospheric air - N

Environmental Processes

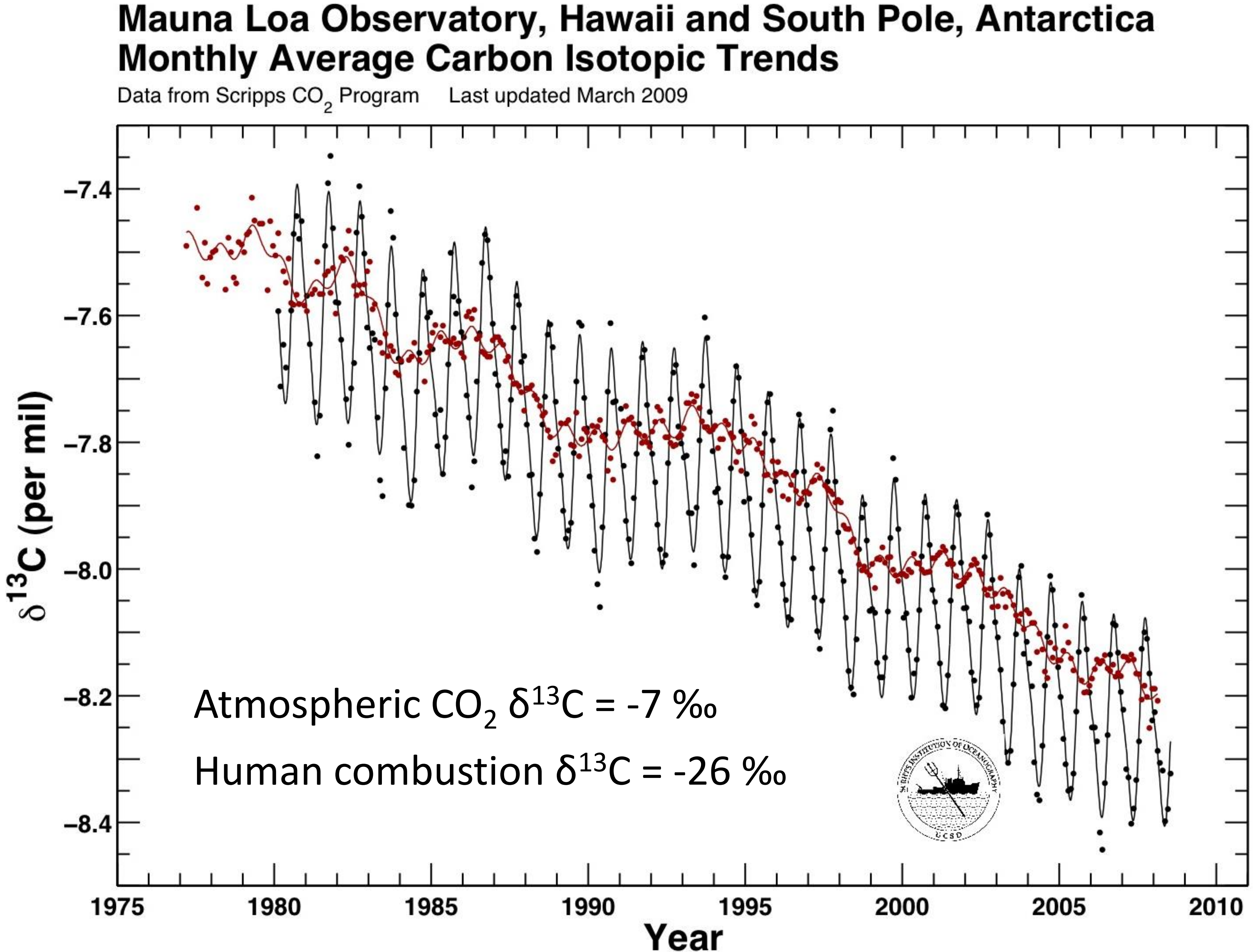


- How do scientists trace these processes? How do we perform "accounting" for the transfers of matter, fluxes in these cycles?
- Isotopes used to corroborate earth science model results
- The water cycle
- Carbon cycle (short term), organic matter, photosynthesis
- Nitrogen cycle
- Sulphur cycle




carbon-13 concentrations
relative to standard belemnite
volcanic CO2 -?‰
human combustion
CO2 -26‰
atmospheric CO2 -7‰
land plants -26‰
C3 plants: -22 to 30‰
C4 plants: -10 to -14‰
bacterial methane
CH4 -64 to -90‰
organic carbon -23‰
plankton -23‰
natural gas
methane CH4 -50‰
coal -?‰
deep ocean 0‰
carbonates +1‰
petroleum -50‰

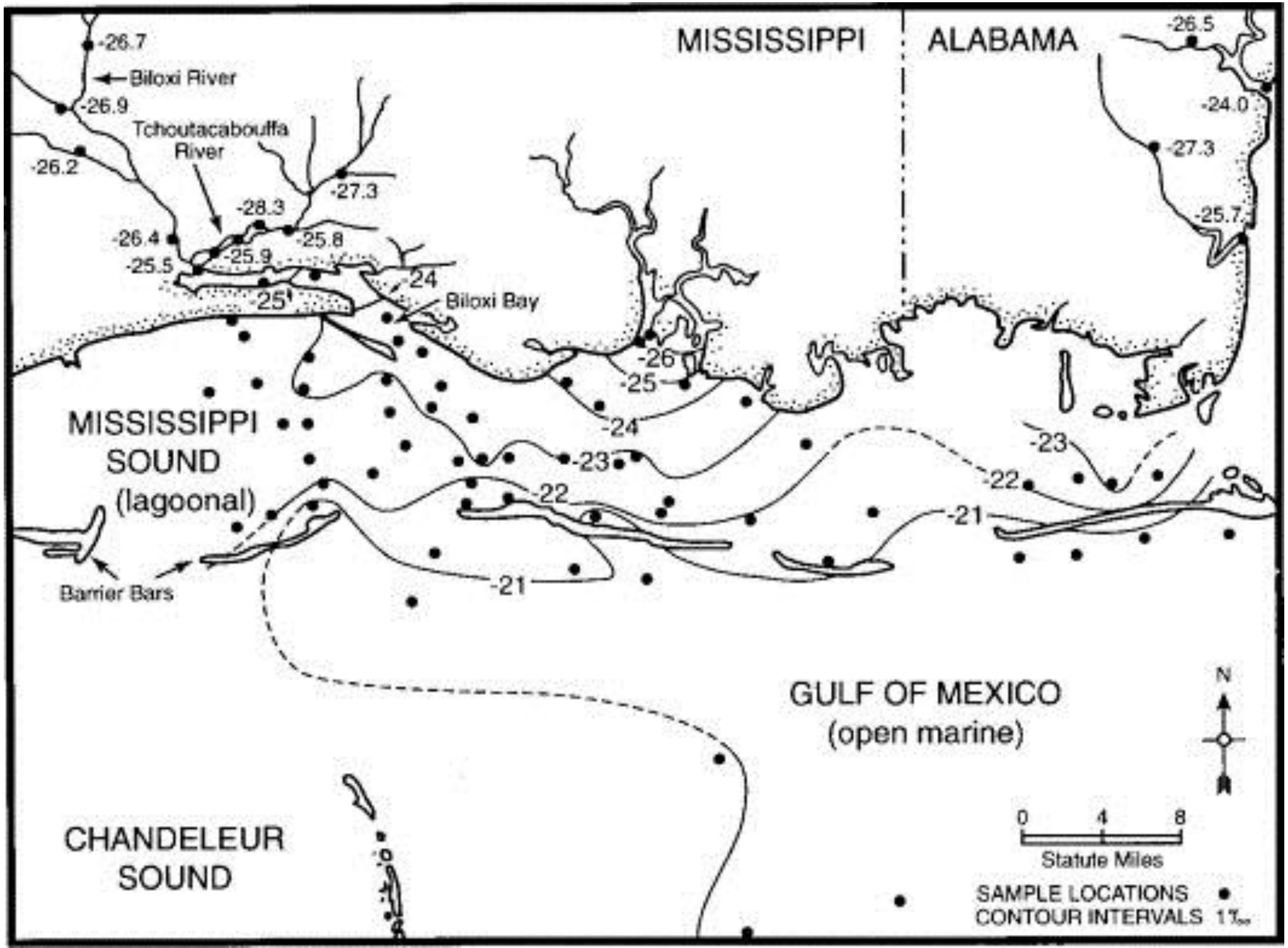
Mauna Loa monthly mean CO_2 concentration 1958-2015

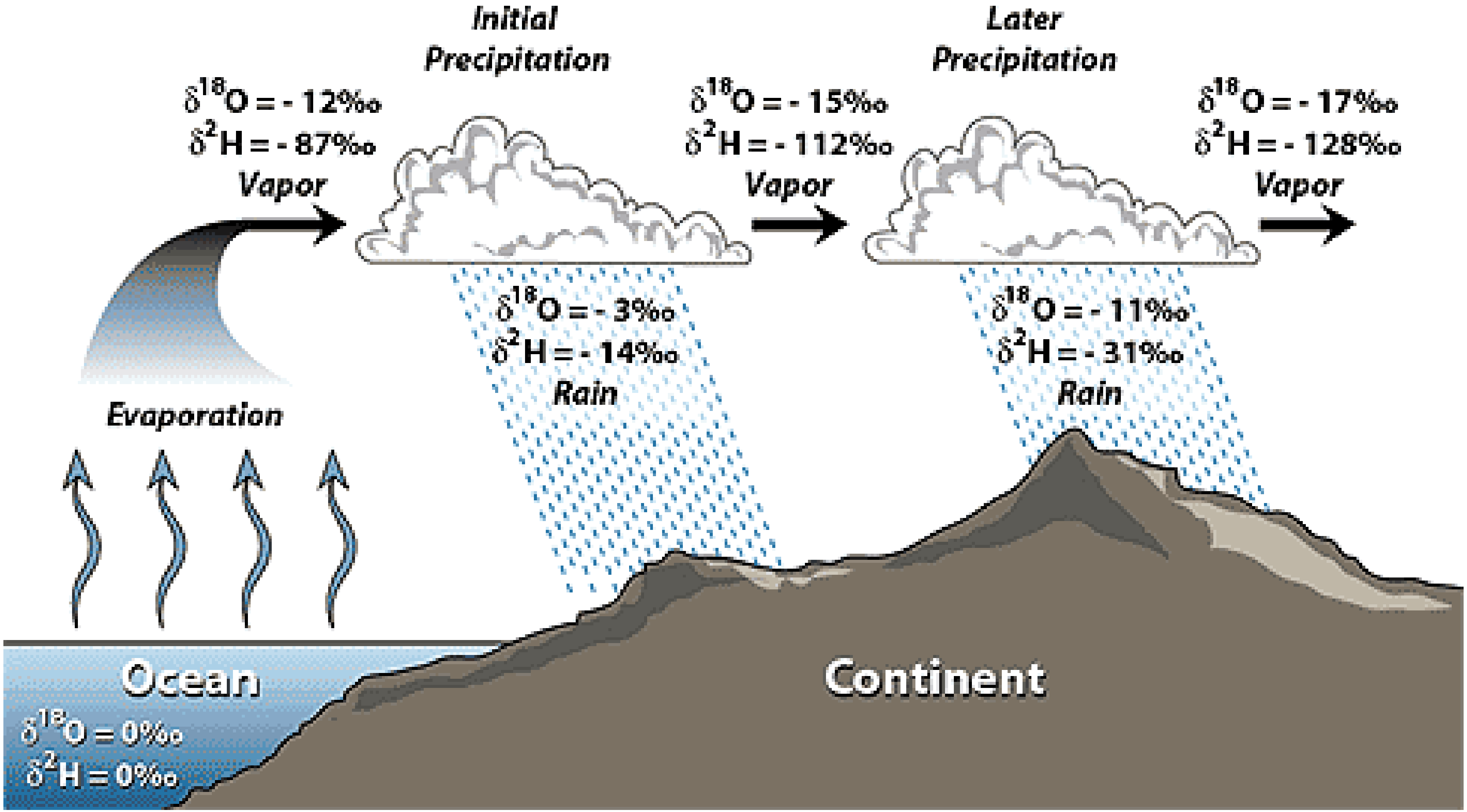


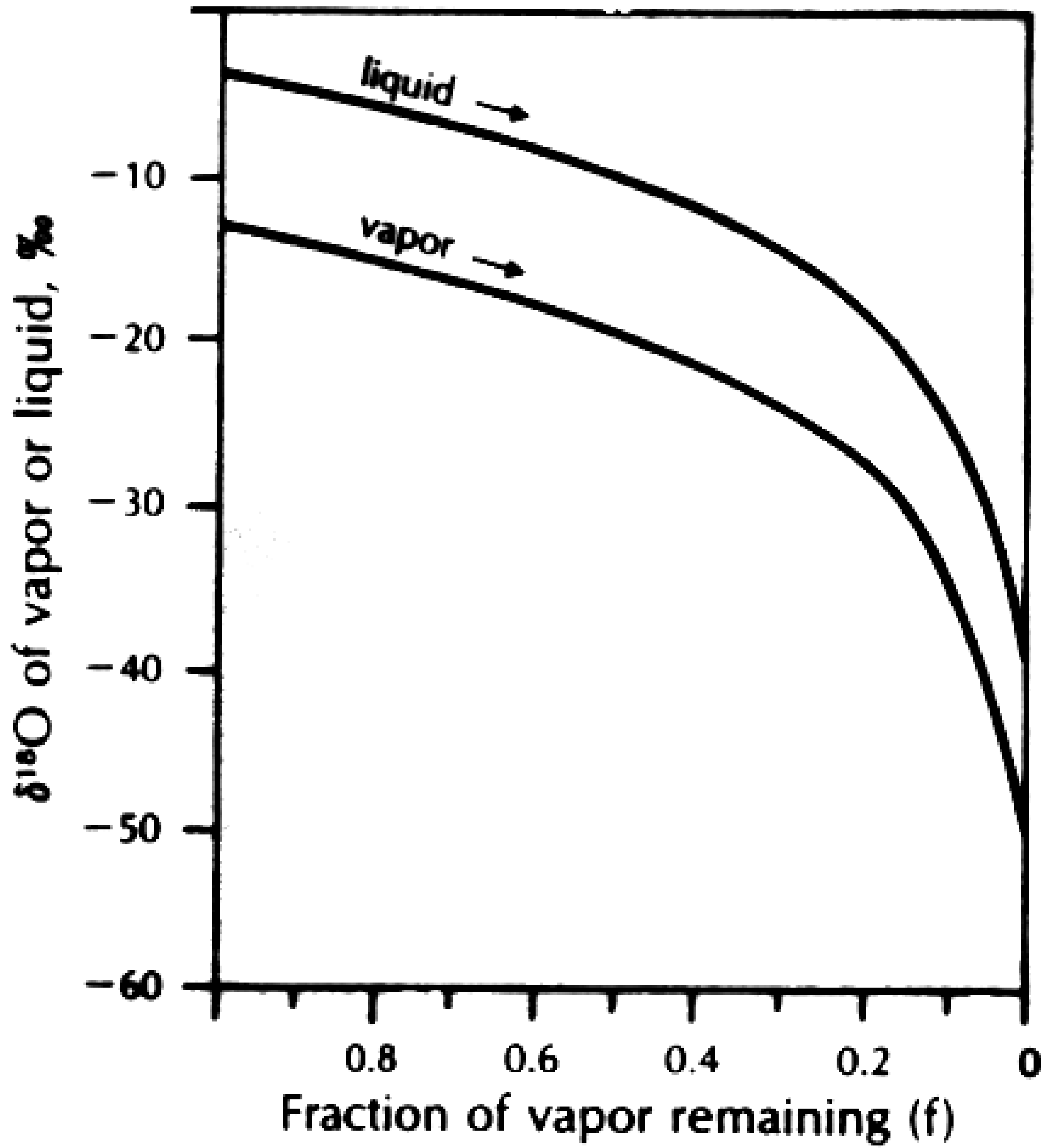
Comparison of C_3, C_4, and CAM plants

C3 plants	C4 plants	CAM plants
Most plants	Tropical grasses like corn, sugarcane	Succulents, pineapple, agave
Fix carbon in Calvin cycle - attach CO_2 to RuBP	Fix carbon in cytoplasm - attach CO_2 to PEP	Fix carbon at night only, fix it to organic molecules
Enzyme - Rubisco	Enzyme – PEP-ase	Enzyme – PEP-ase
Most energy efficient method	1/2 way between these two	Best water conservation
Loses water through photorespiration	Loses less water	Loses least water

Terrestrial (-26‰) to marine (< -23‰) $\delta^{13}C$ gradient (Peterson, 1999)




Initial Precipitation
Later Precipitation
δ18O = - 12‰
δ2H = - 87‰
Vapor
δ18O = - 15‰
δ2H = - 112‰
Vapor
δ18O = - 17‰
δ2H = - 128‰
Vapor
δ18O = - 3‰
δ2H = - 14‰
Rain
δ18O = - 11‰
δ2H = - 31‰
Rain
Evaporation
Ocean
δ18O = 0‰
δ2H = 0‰
Continent



Effect of Rayleigh distillation on the $\delta^{18}O$ value of water vapor remaining in the air mass and of meteoric precipitation falling from it at a constant temperature of 25°C.

Complications:

1) Re-evaporation
2) Temperature dependency of α

RAYLEIGH DISTILLATION

Isotopic fractionation that occurs during condensation in a moist air mass can be described by Rayleigh Distillation. The equation governing this process is:

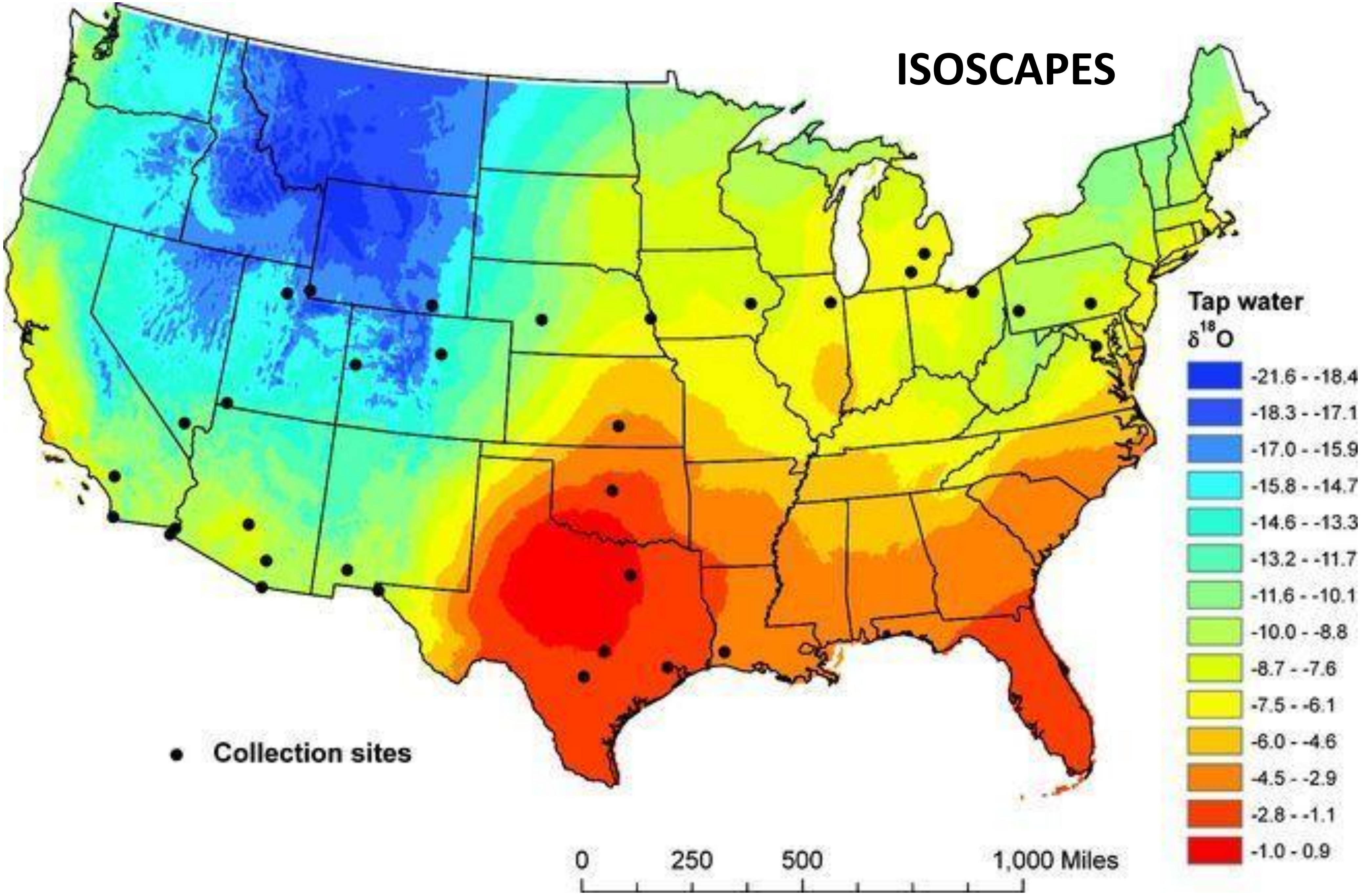
$$R_v = R_v^o f^{\alpha-1}$$

- Rayleigh Distillation

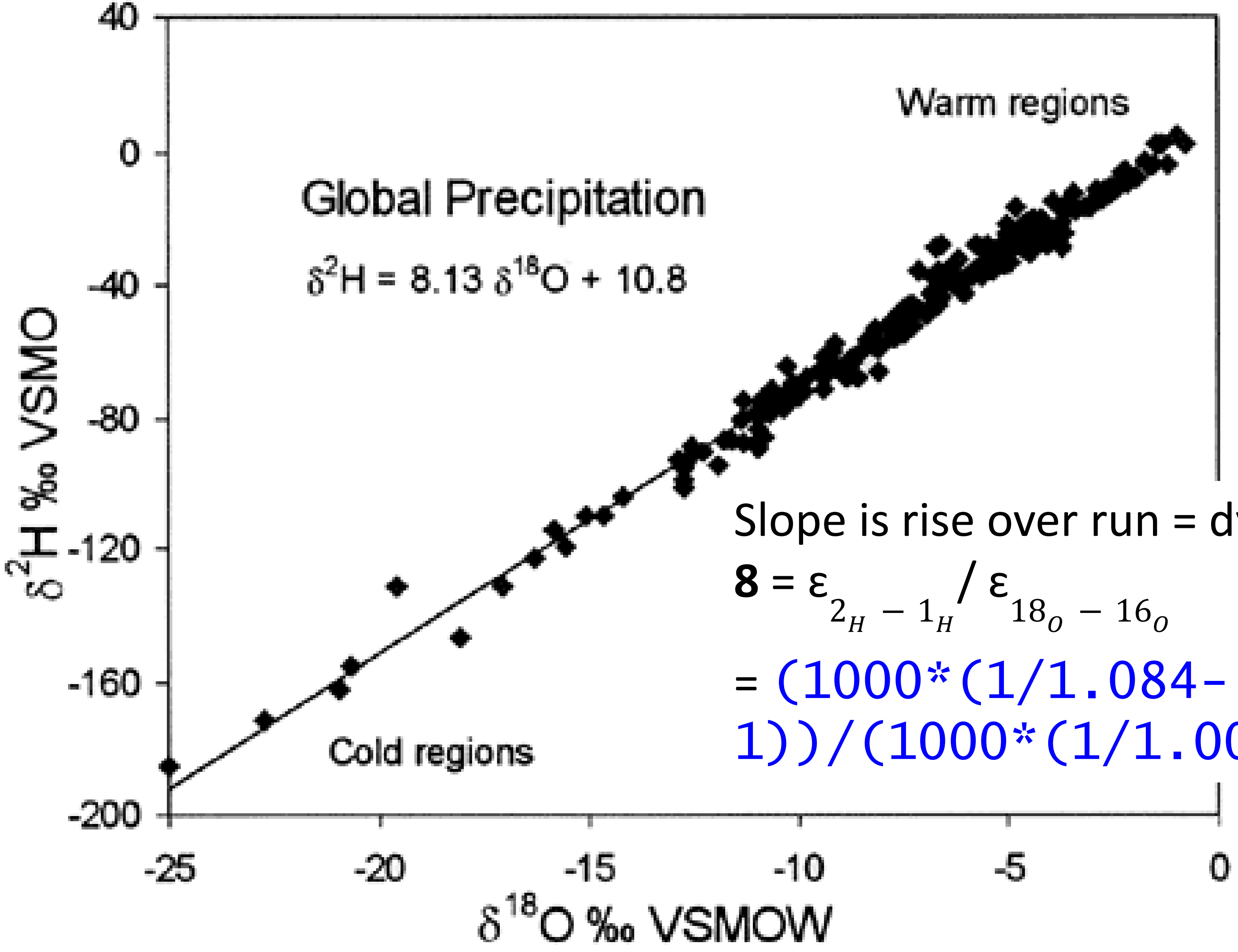
  $\delta_f - \delta_i = 10^3(F^{(\alpha-1)} - 1)$

where R_v = isotope ratio of remaining vapor, $R_v°$ = isotope ratio in initial vapor, ƒ = the fraction of vapor remaining and a = the isotopic fractionation factor

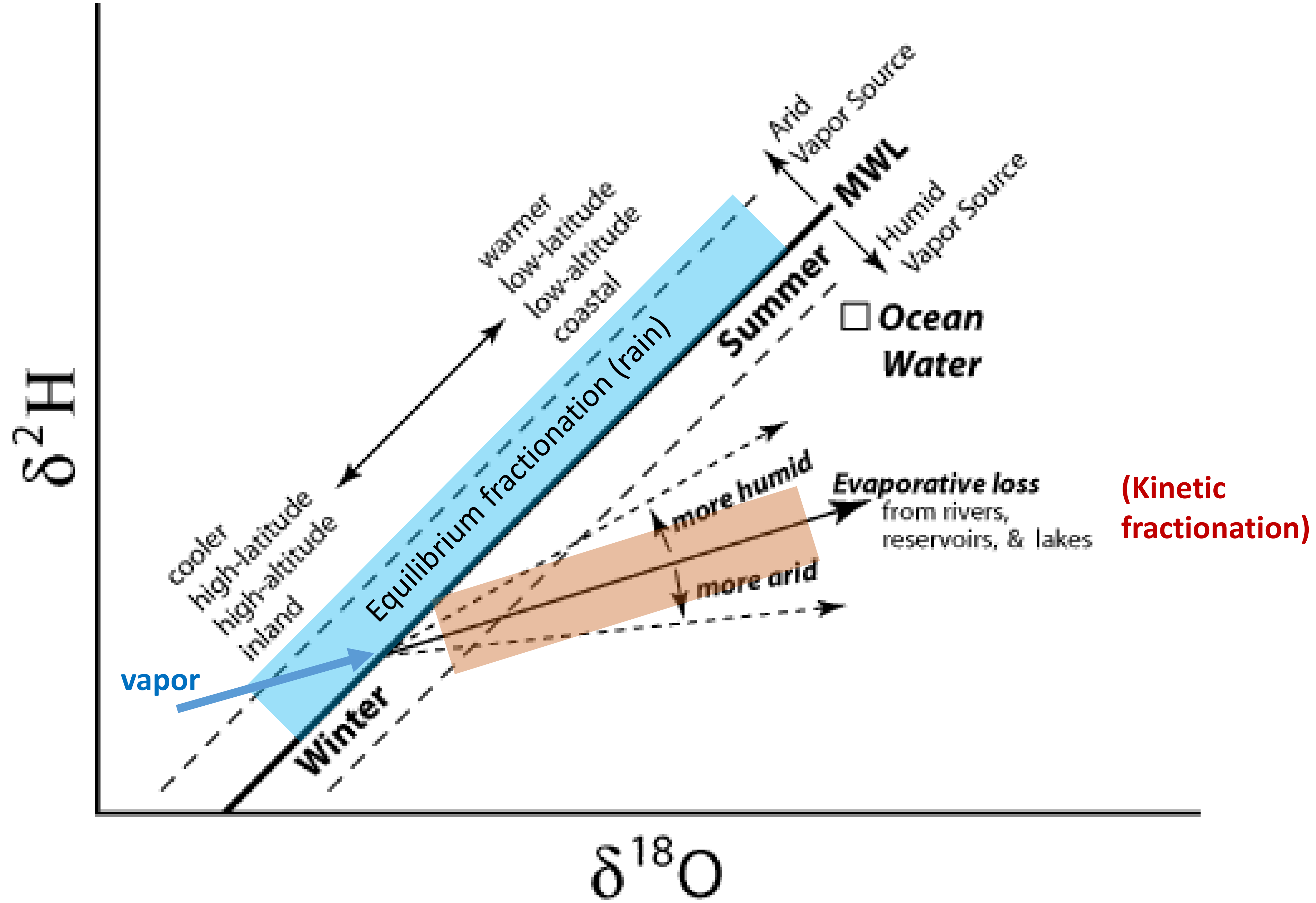
ISOSCAPES


Tap water
δ18O
-21.6 - -18.4
-18.3 - -17.1
-17.0 - -15.9
-15.8 - -14.7
-14.6 - -13.3
-13.2 - -11.7
-11.6 - -10.1
-10.0 - -8.8
-8.7 - -7.6
-7.5 - -6.1
-6.0 - -4.6
-4.5 - -2.9
-2.8 - -1.1
-1.0 - 0.9
Collection sites
0
250
500
1,000 Miles

MWL
Meteoric Water Line

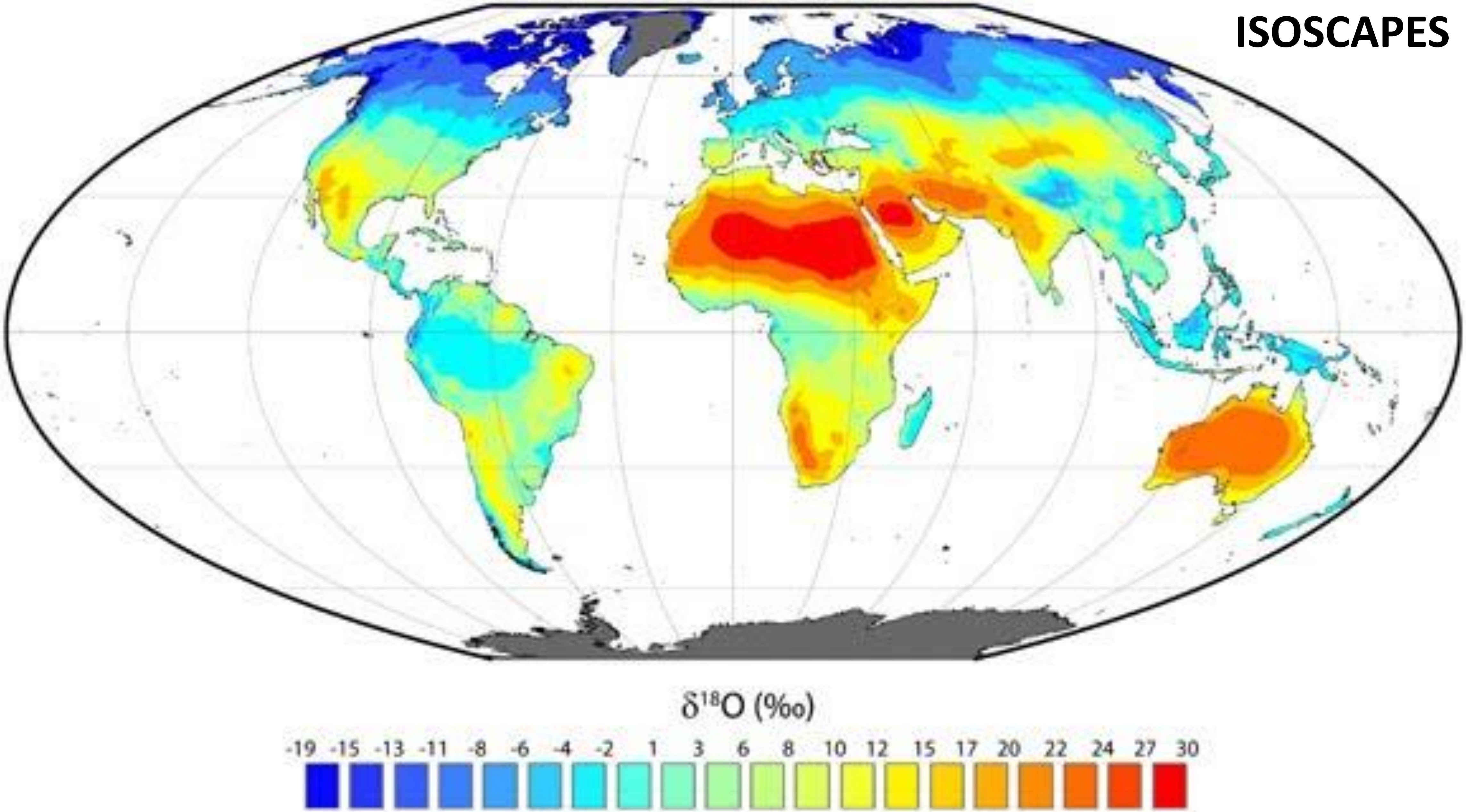


Slope is rise over run = dy/dx =
8 = $\varepsilon_{^2H\,-\,^1H} / \varepsilon_{^{18}O\,-\,^{16}O}$
= (1000*(1/1.084-1))/(1000*(1/1.0098-1))

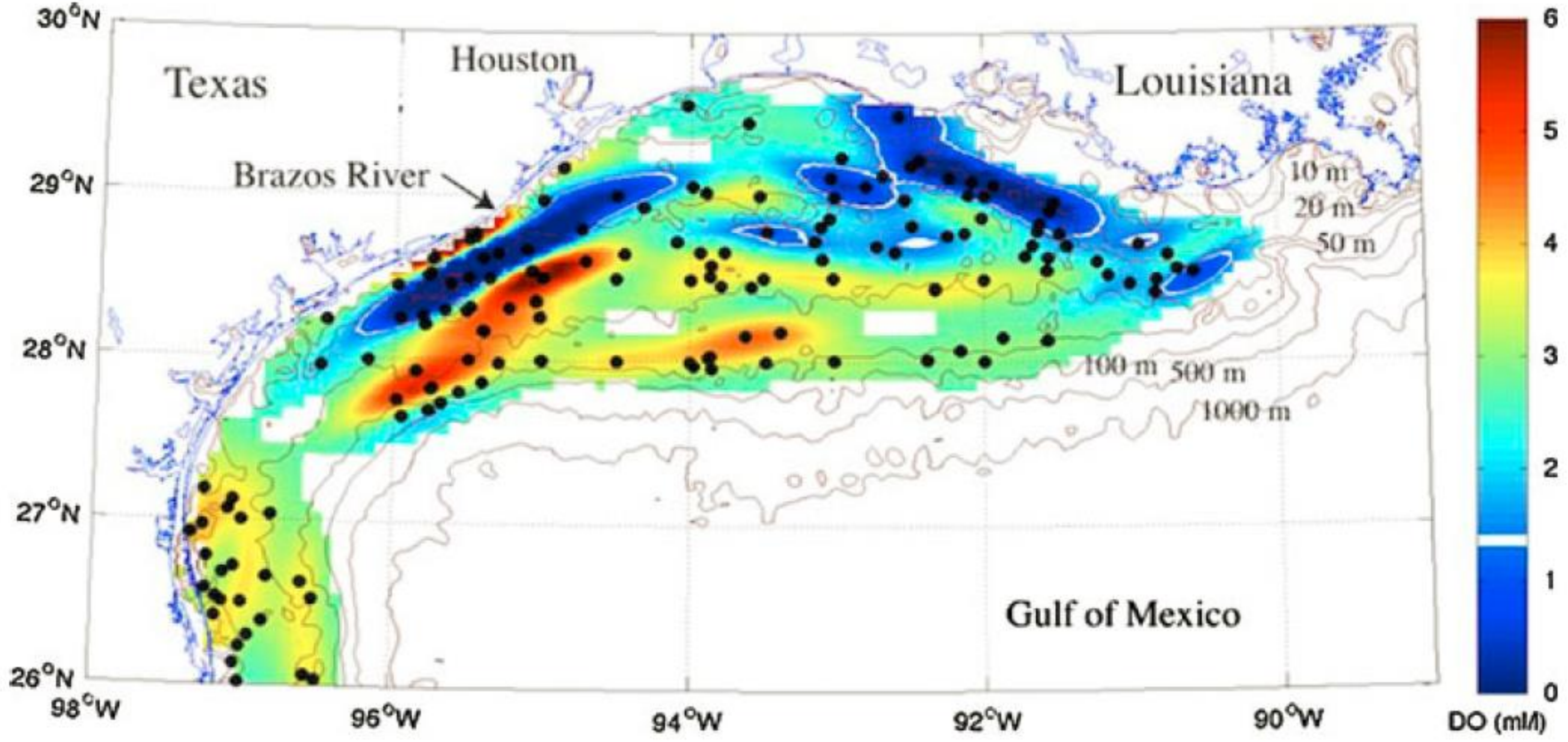


δ^2H
$\delta^{18}O$
Arid Vapor Source
MWL
Humid Vapor Source
Ocean Water
warmer
low-latitude
low-altitude
coastal
cooler
high-latitude
high-altitude
inland
Equilibrium fractionation (rain)
Summer
Winter
vapor
more humid
more arid
Evaporative loss
from rivers,
reservoirs, & lakes
(Kinetic fractionation)

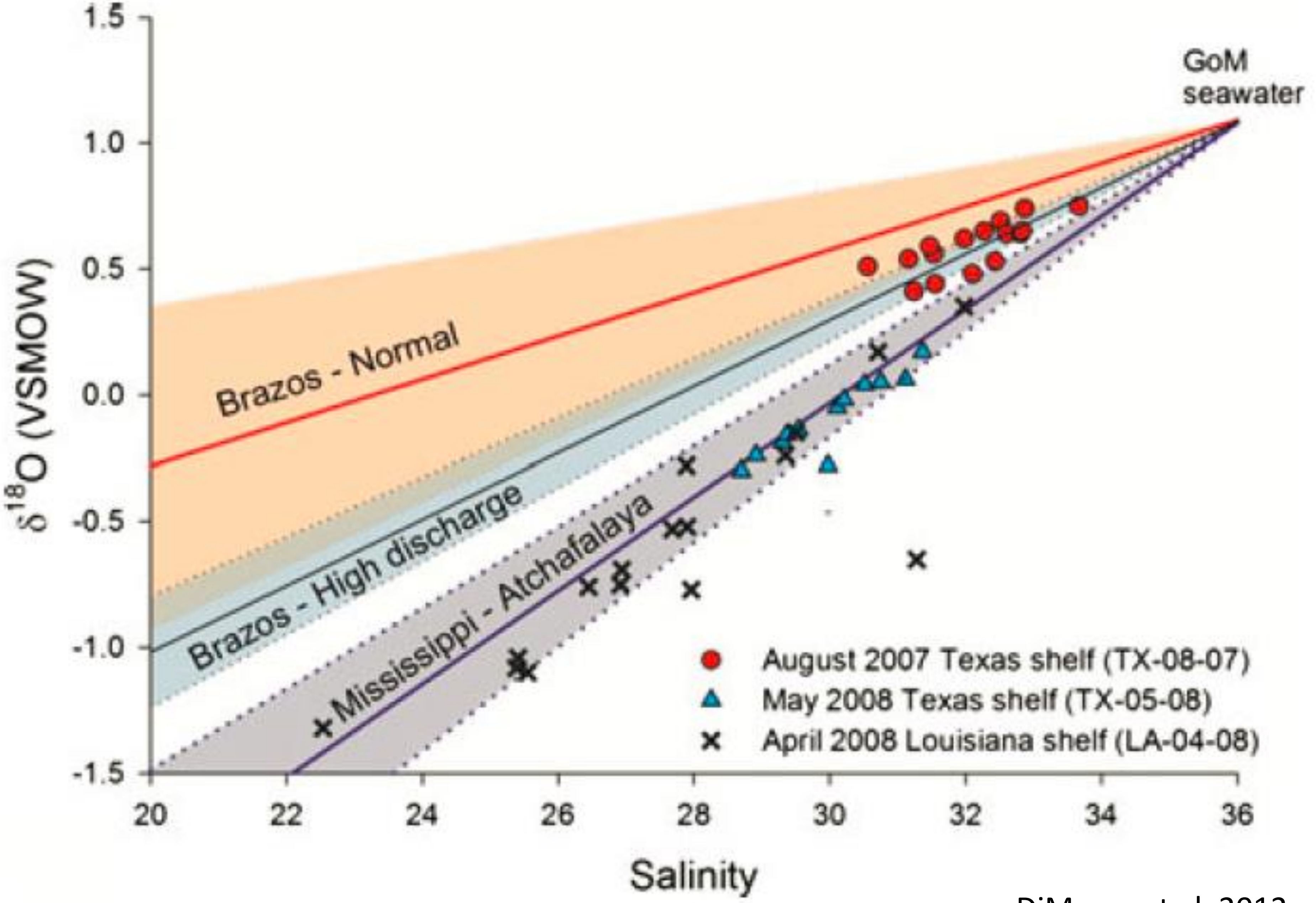
ISOSCAPES



Which rivers are causing dead zones?

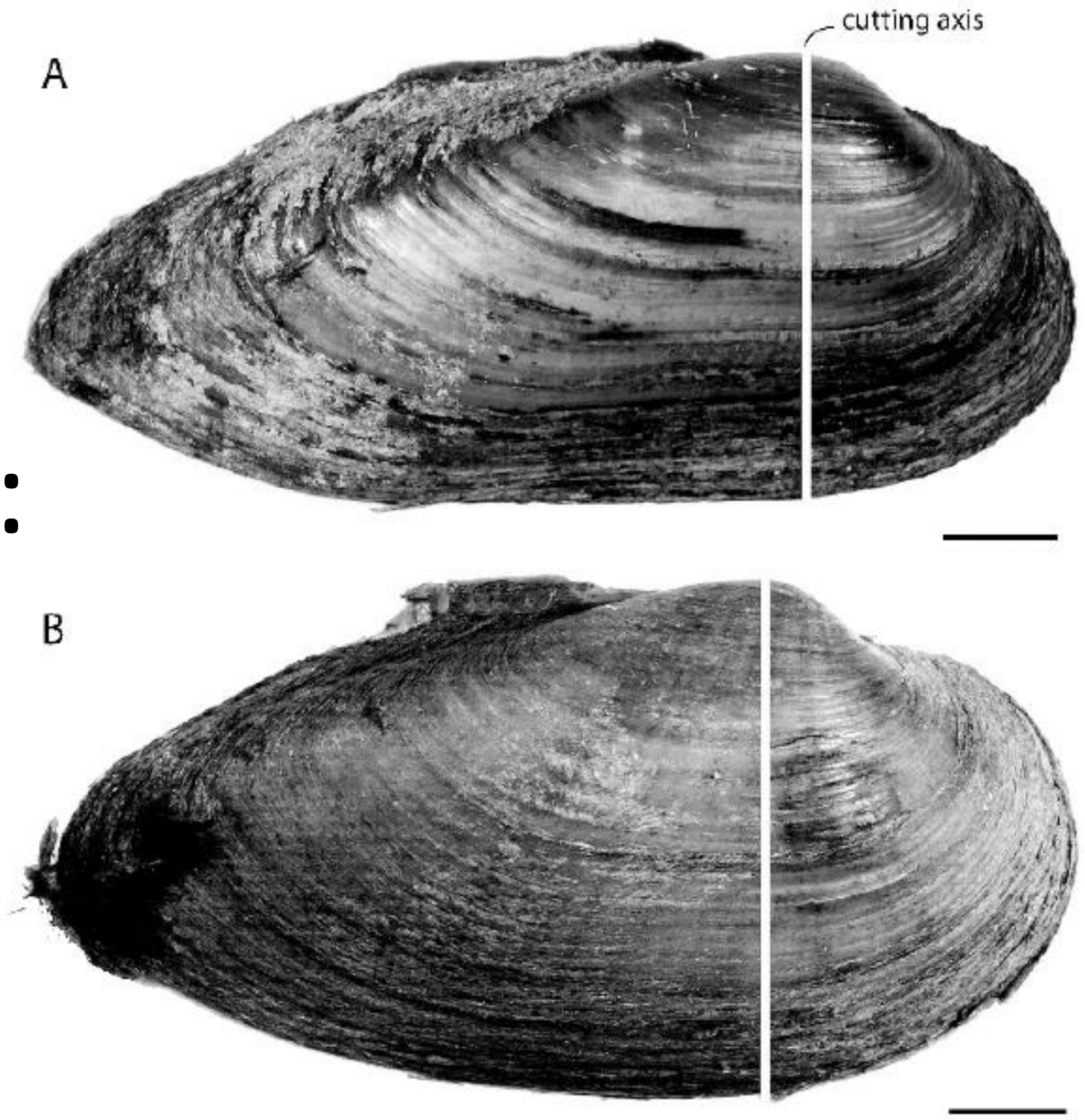


DiMarco et al. (2012)

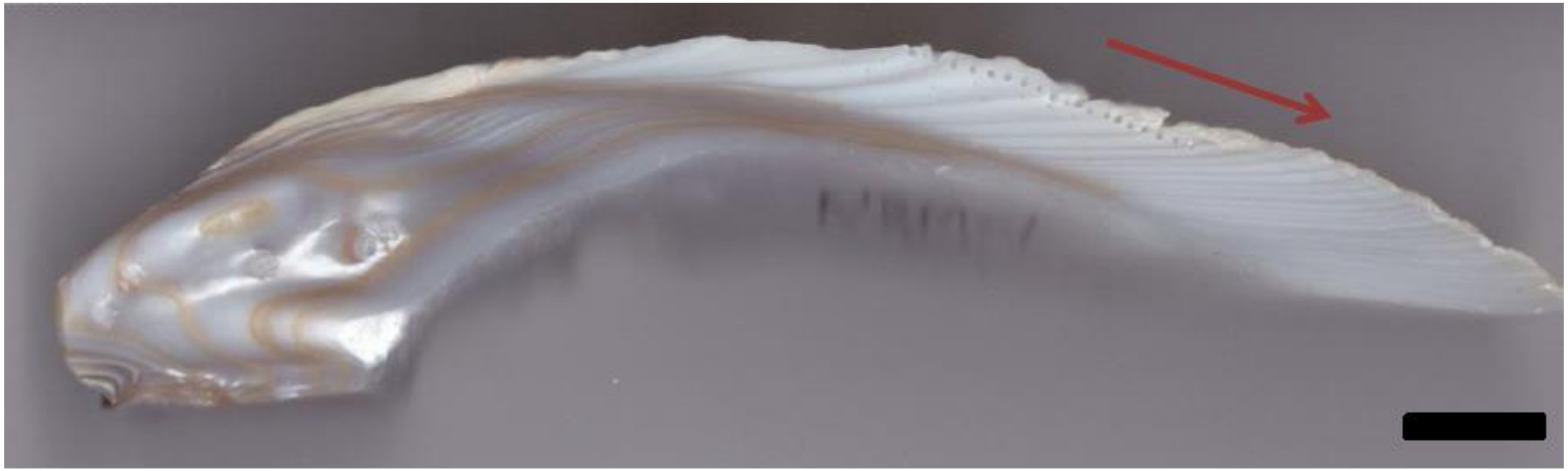


DiMarco et al. 2012

Climate Records: Mussel Shells



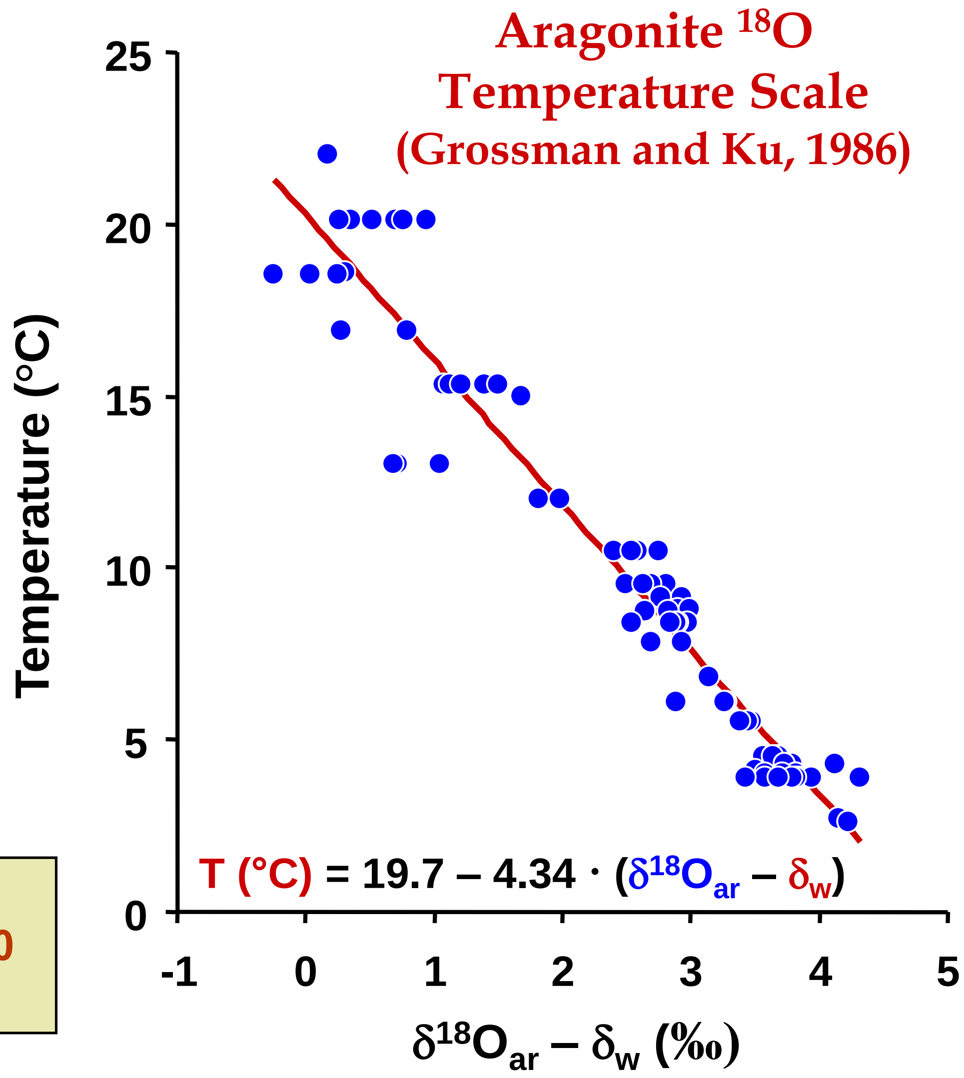
Growth layers, a record like tree rings



Oxygen Isotopes in Mollusk Shells

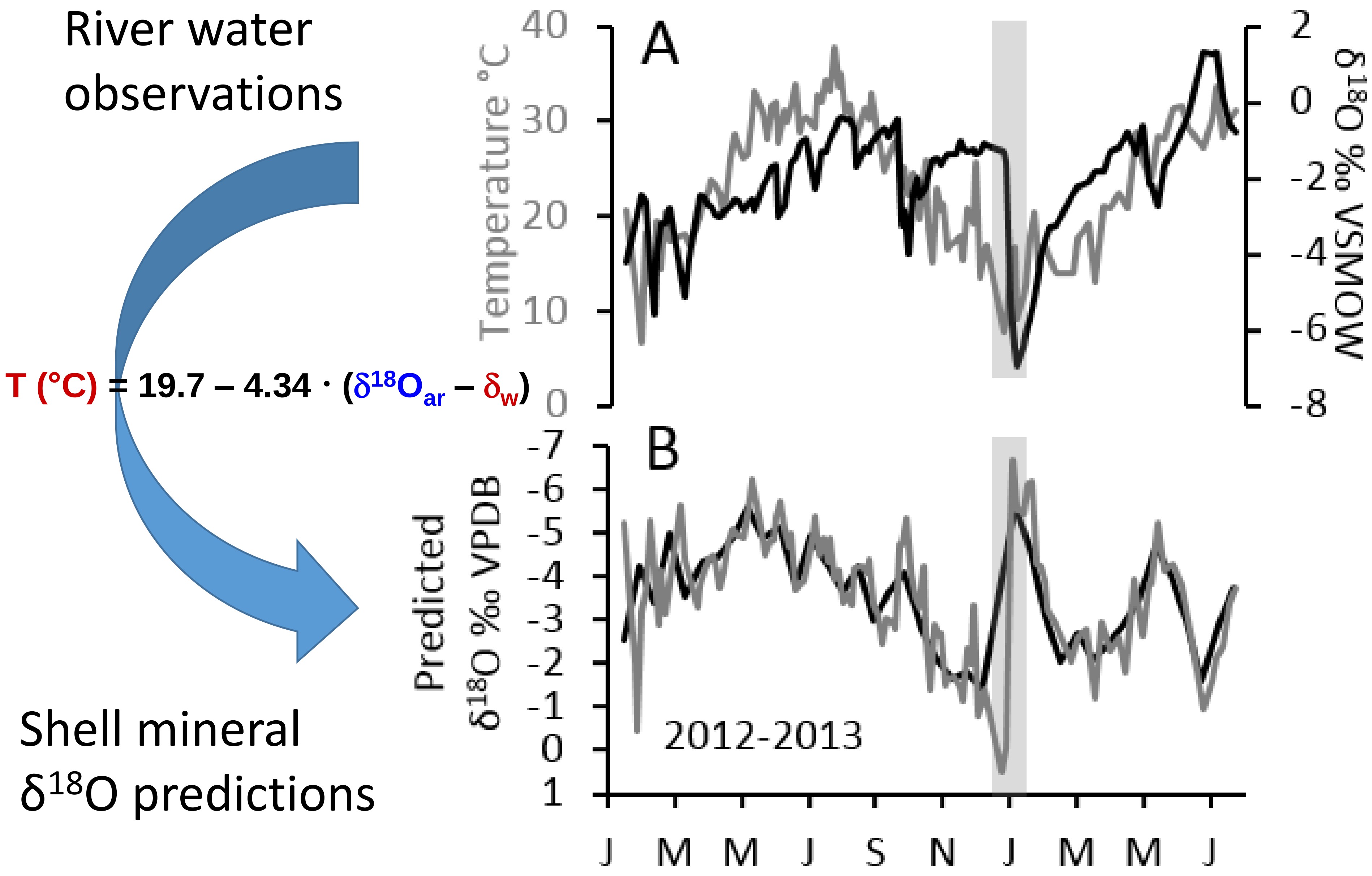
- $CaCO_3$ $\delta^{18}O$ depends on T and $\delta^{18}O$ of water (δ_w)
- -0.2‰ per °C (at 25°C)
- Analytical precision ±0.1‰ ≈ ±0.5°C

$$\delta^{18}O\ (‰) = \frac{(^{18}O/^{16}O)_x - (^{18}O/^{16}O)_{std}}{(^{18}O/^{16}O)_{std}} \times 1000$$

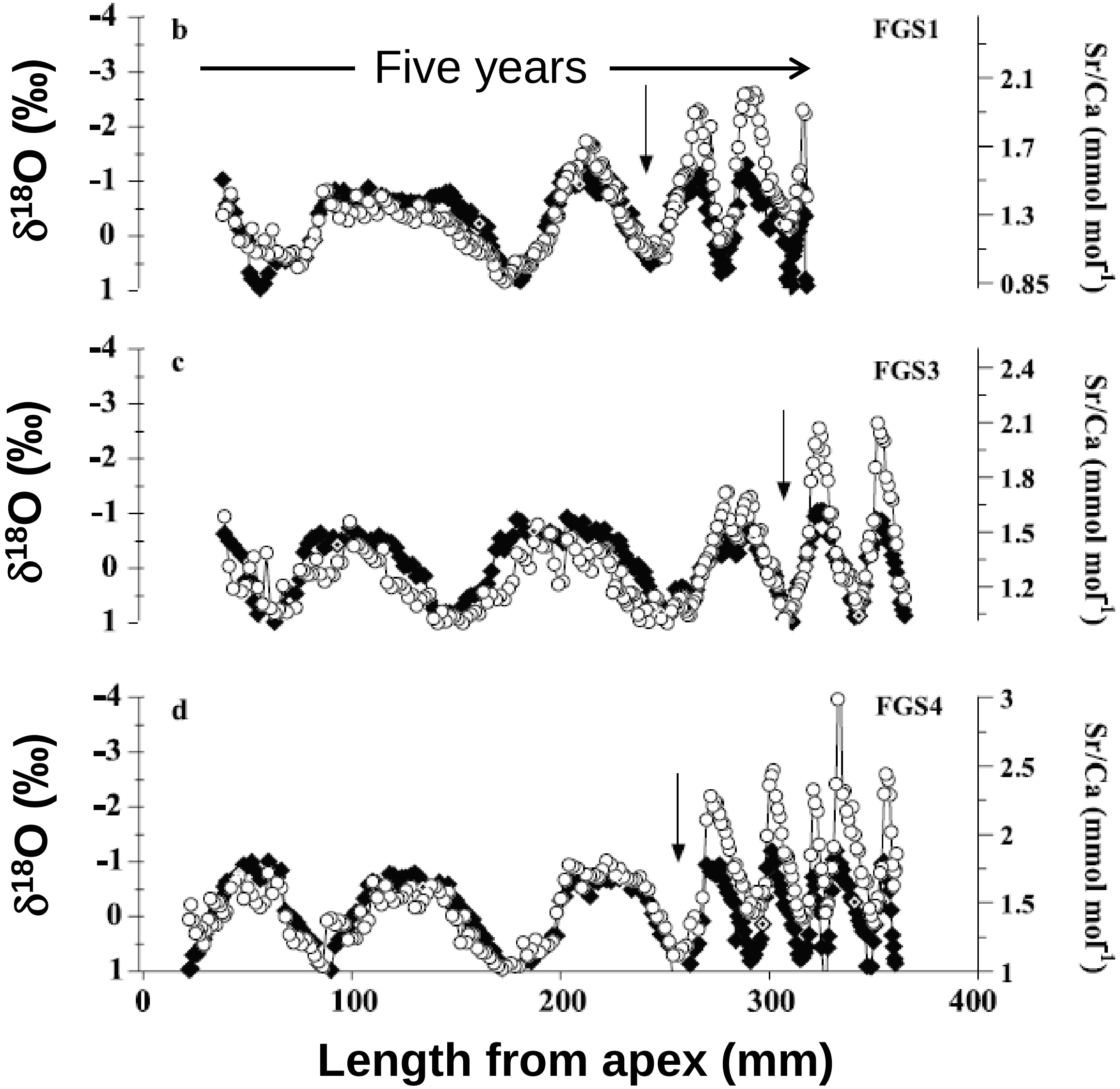


$\delta^{18}O_{ar}$ = $\delta^{18}O$ of aragonite (vs. PDB)

δ_w = $\delta^{18}O$ of water (vs. SMOW)

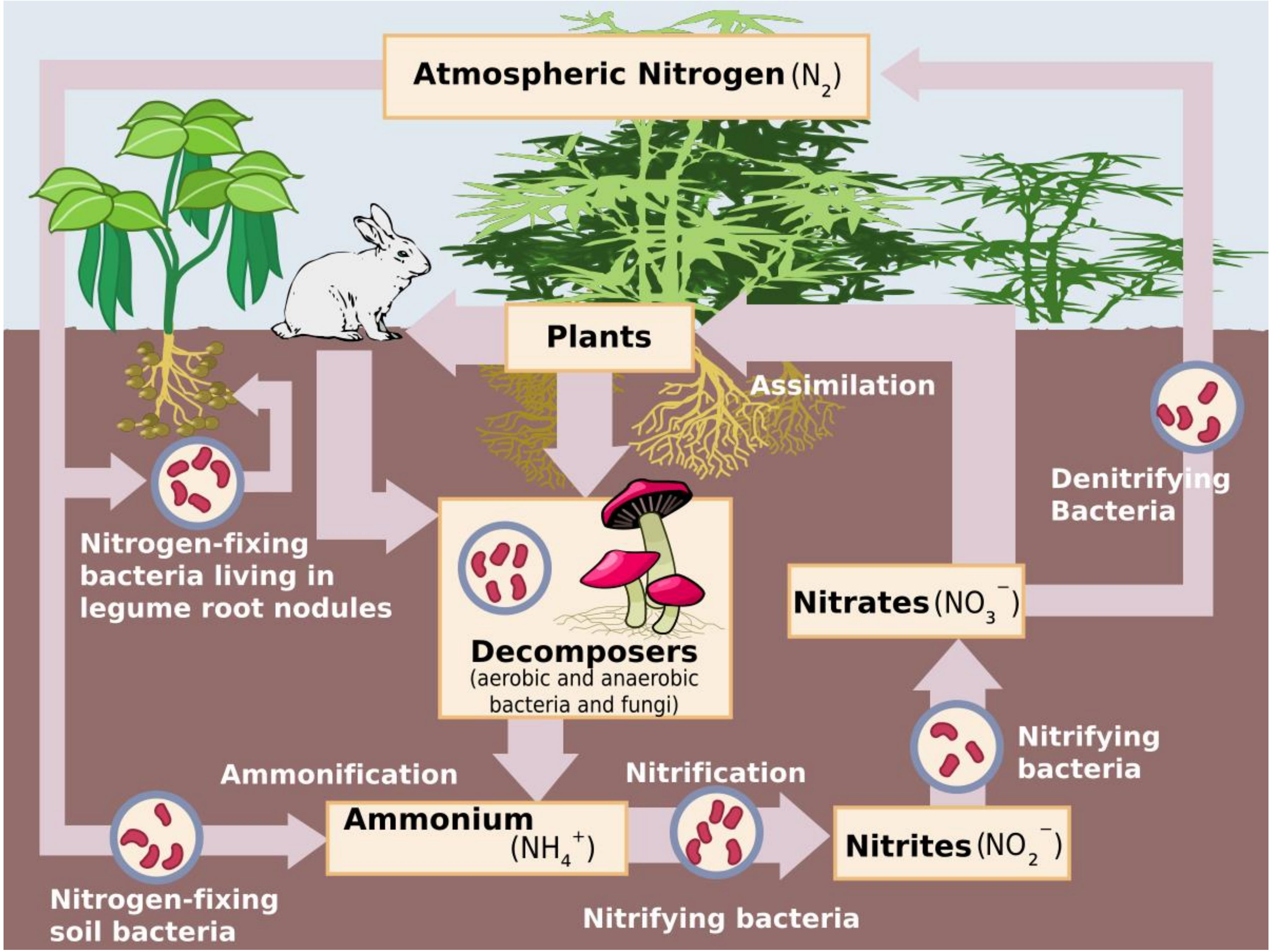

River water observations
T (°C) = 19.7 – 4.34 · (δ18Oar – δw)
Shell mineral δ18O predictions
A
B
Temperature °C
40
30
20
10
0
δ18O ‰ VSMOW
2
0
-2
-4
-6
-8
Predicted δ18O ‰ VPDB
-7
-6
-5
-4
-3
-2
-1
0
1
2012-2013
J
M
M
J
S
N
J
M
M
J

δ^{18}O and Sr/Ca in Modern *Conus* from Stetson Bank, Gulf of Mexico (~24 m)



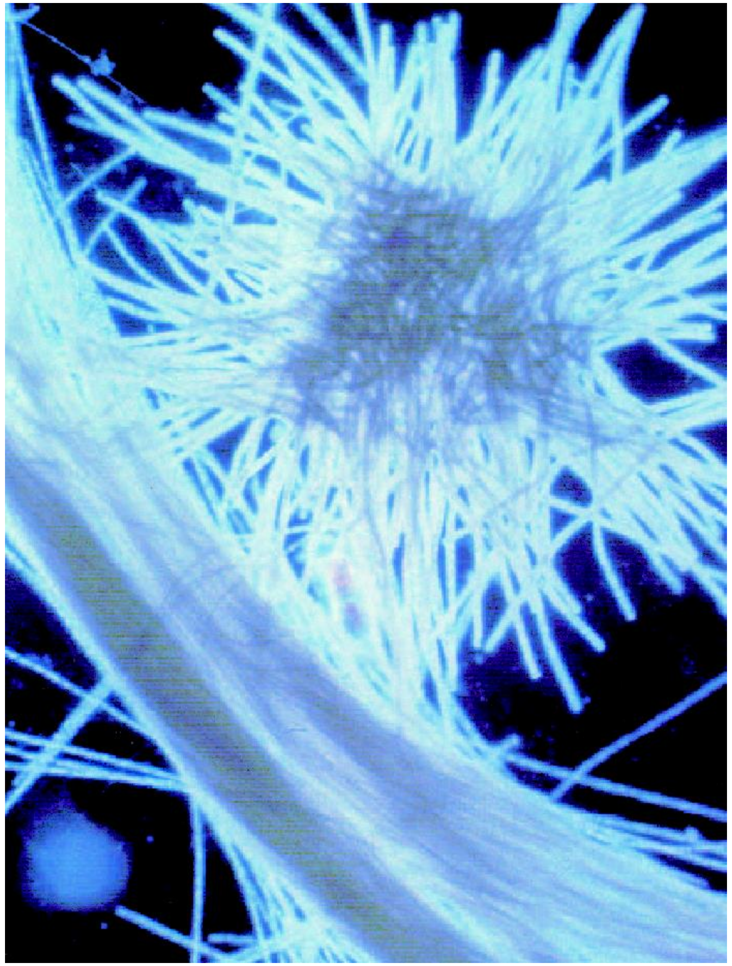
- Seasonal temperature variation and growth recorded in δ^{18}O (◆) and Sr/Ca (○)
- Specimen ages 5, 5.5, and 8 years

Sosdian et al. (2006)



Atmospheric Nitrogen (N_2)
Plants
Assimilation
Denitrifying Bacteria
Nitrogen-fixing bacteria living in legume root nodules
Decomposers
(aerobic and anaerobic bacteria and fungi)
Nitrates (NO_3^-)
Nitrifying bacteria
Ammonification
Nitrification
Ammonium (NH_4^+)
Nitrites (NO_2^-)
Nitrogen-fixing soil bacteria
Nitrifying bacteria

Nitrogen isotope basics



two stable isotopes:
^{14}N: 99.64%
^{15}N: 0.36%

standard = N_2 in air ($^{15}N/^{14}N$ = 0.00368)

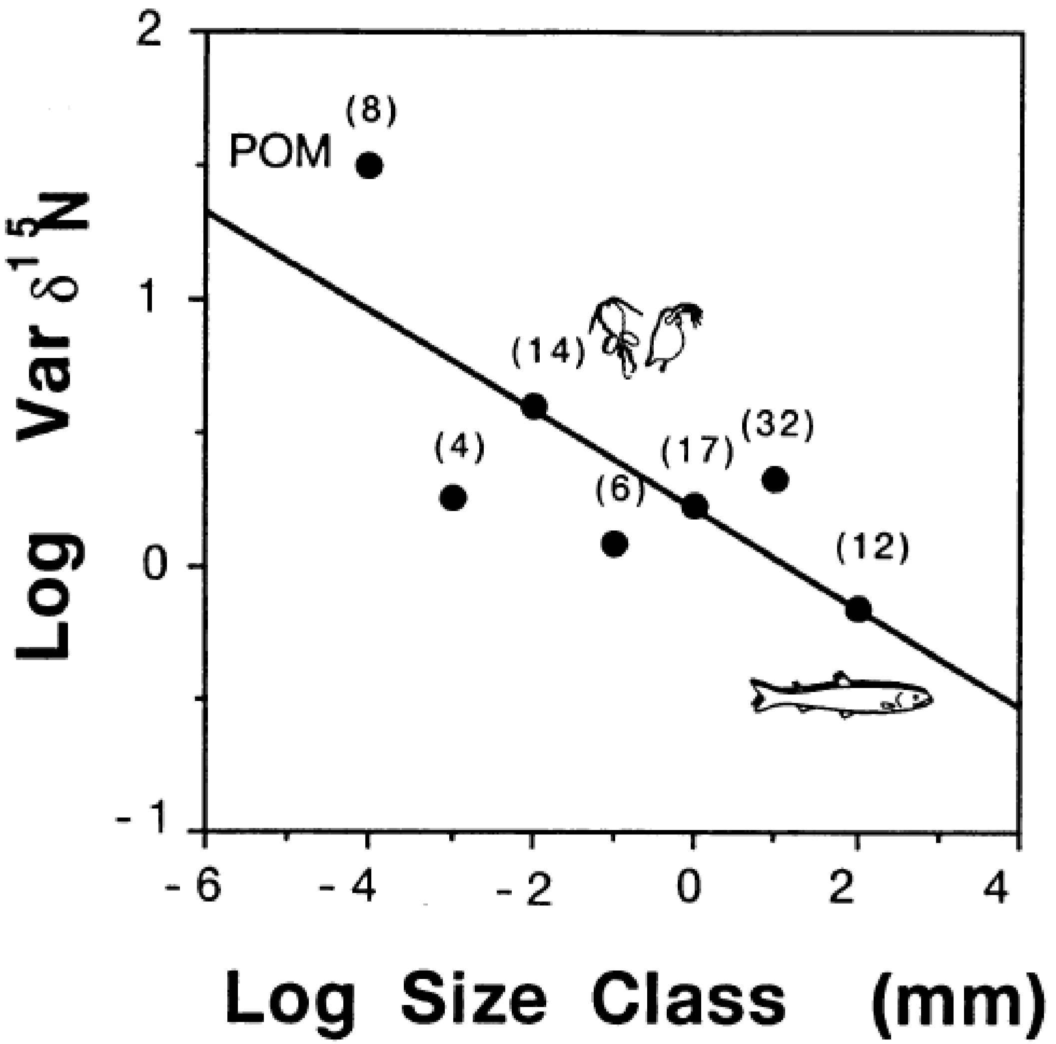
measured as: N_2

Isotopic composition of environmental sources of N:
Nitrate, rain: -13 to +2
Organic N, soil: 0 to +9
Fertilizer: -5 to +5
Animal waste: +8 to +22

N Reactions and Fractionations:

1.	nitrogen fixation	$N_2 \rightarrow NO_3$ (subtropical oceans)	-2 to 0‰ NO_3(aq)
2.	nitrification	$NH_3 \rightarrow NO_3$ (soils)	-20‰
3.	denitrification	$NO_3 \rightarrow NO_2 \rightarrow N_2$	-30‰
4.	primary production	$NO_3 \rightarrow$ particulate organic matter	-2 to -5

Seawater ™^{15}N depends on sources of water (deep = 5‰, surface gyre = 0‰)



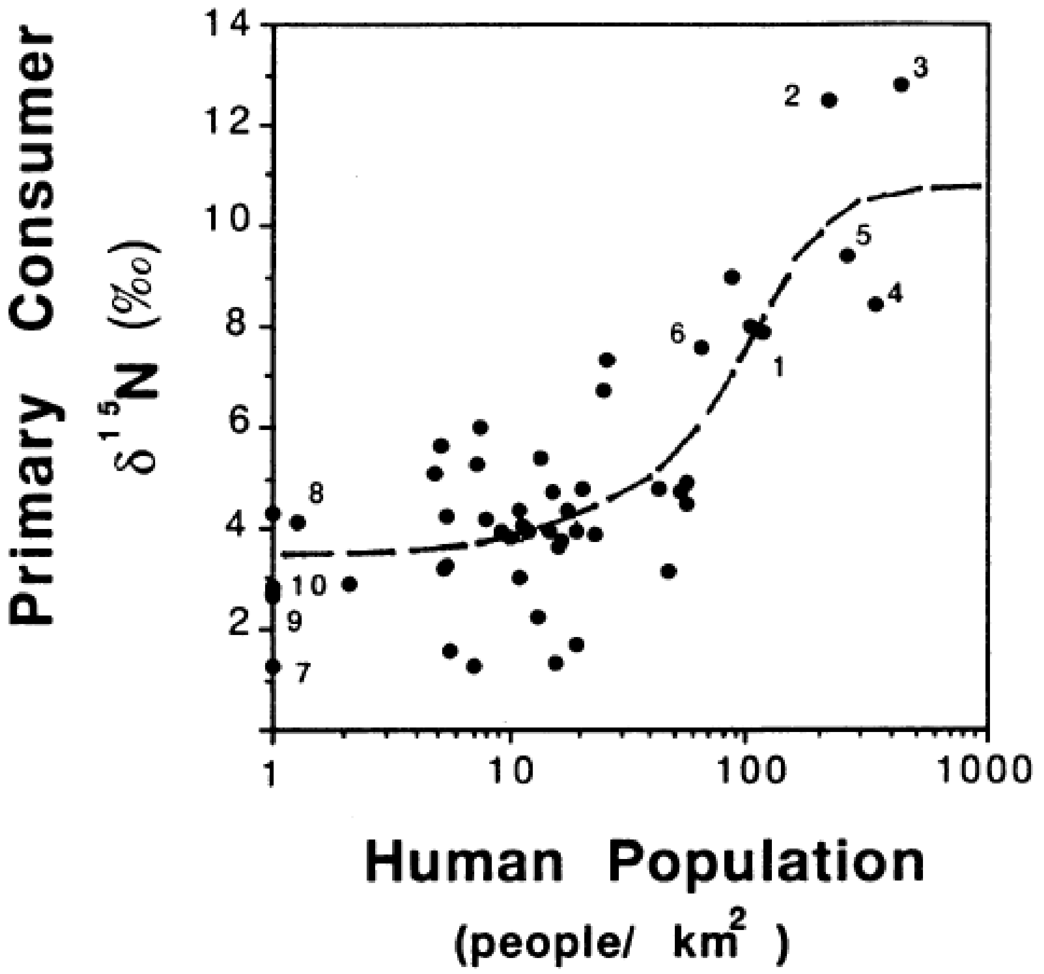
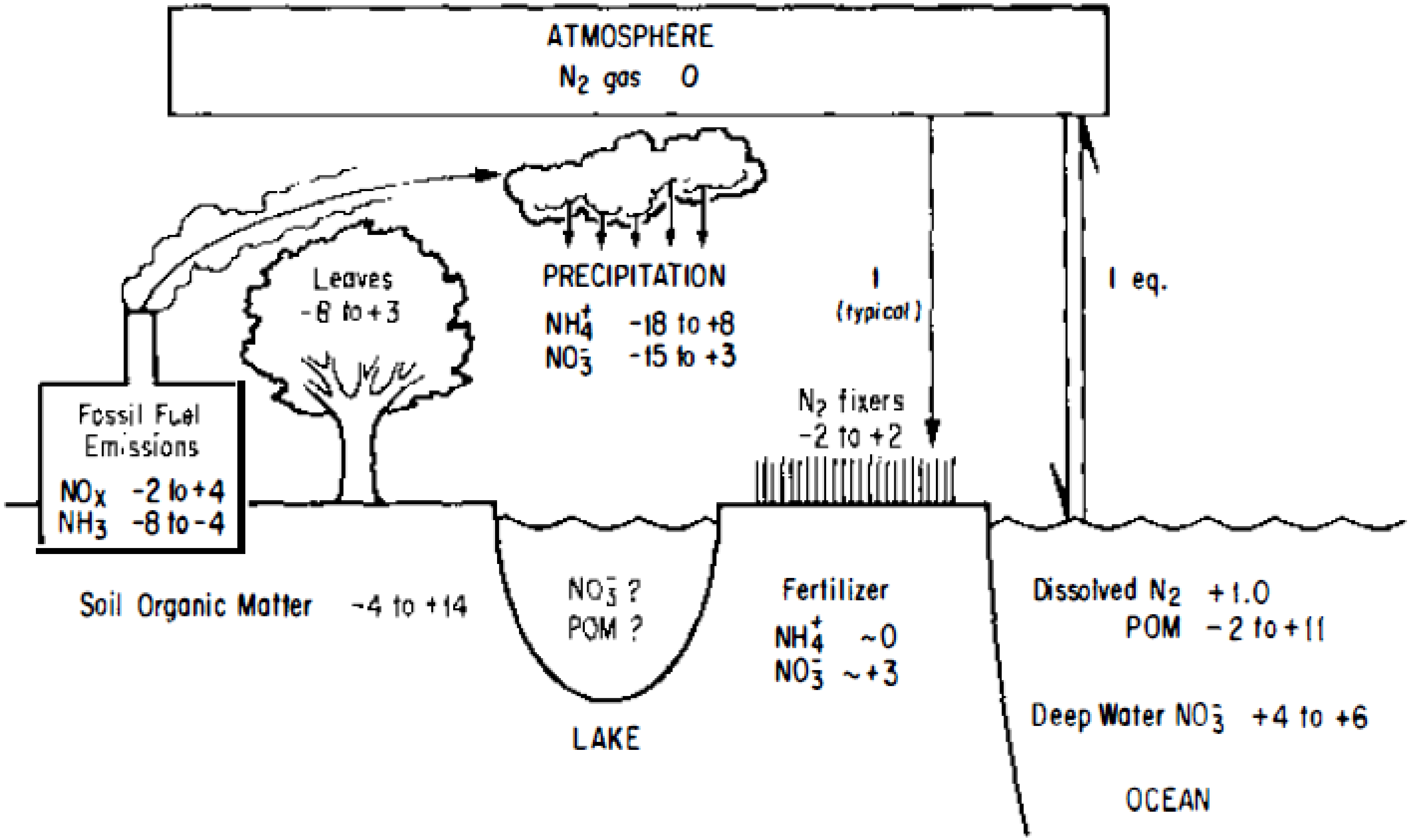
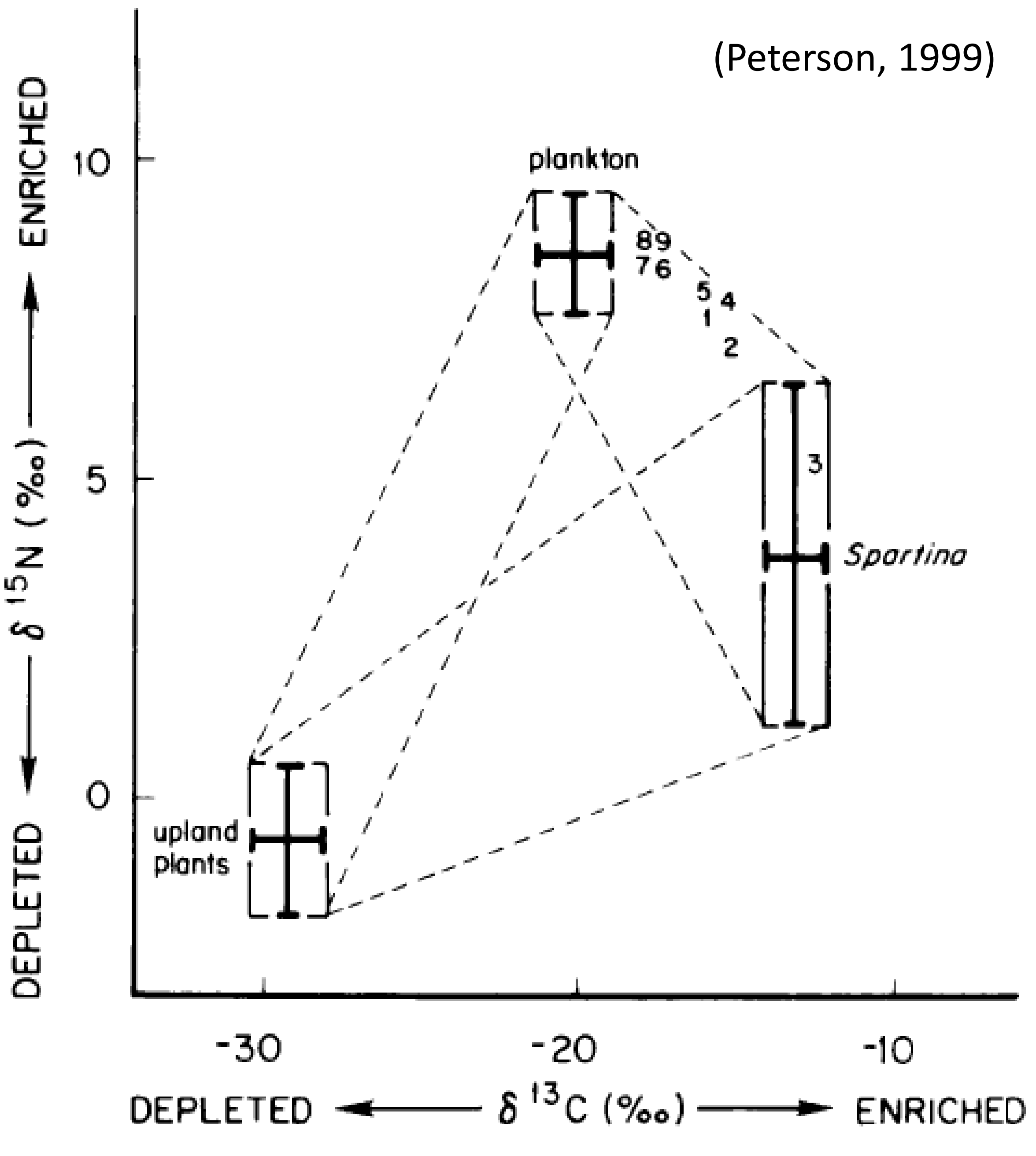
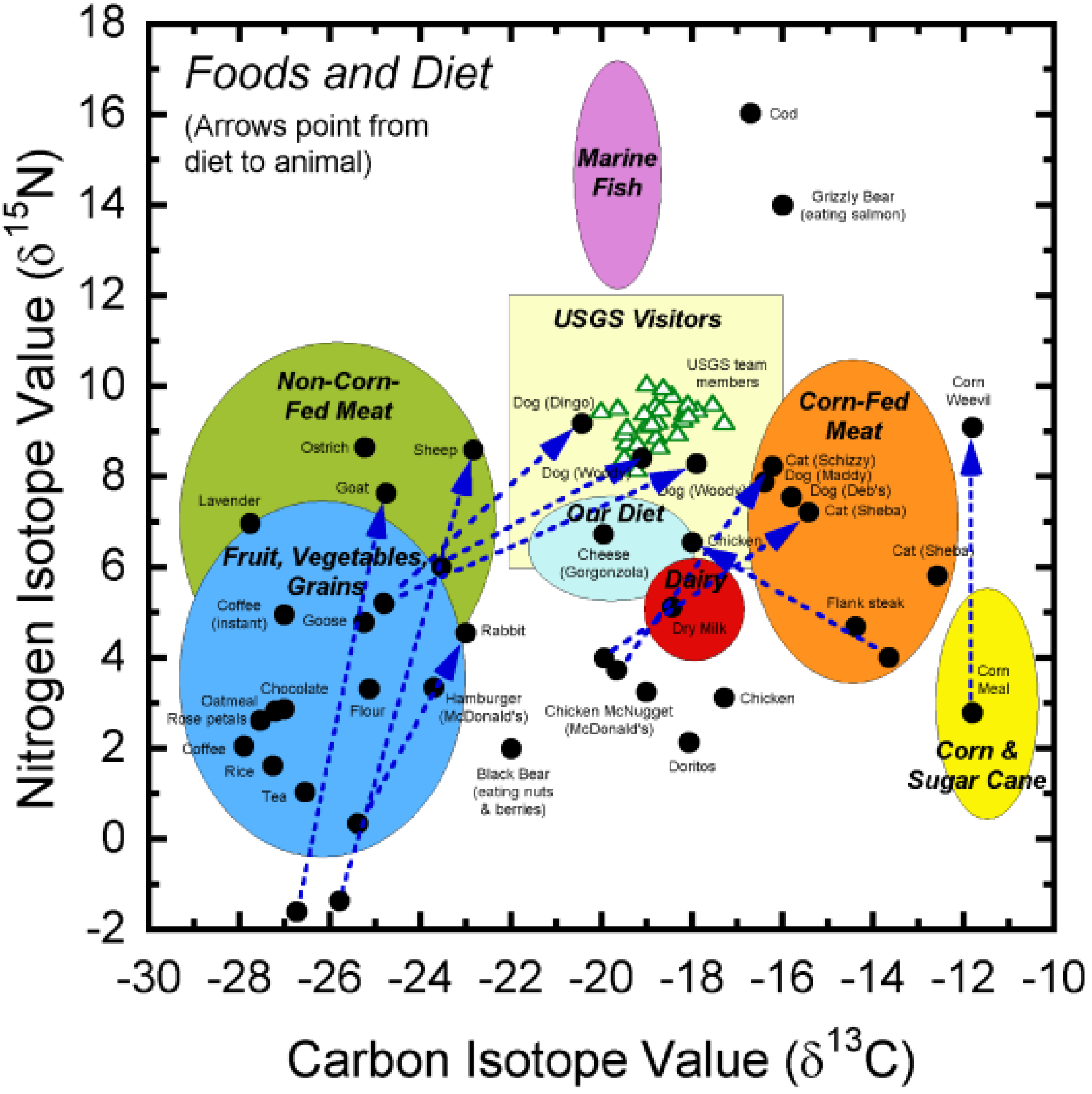
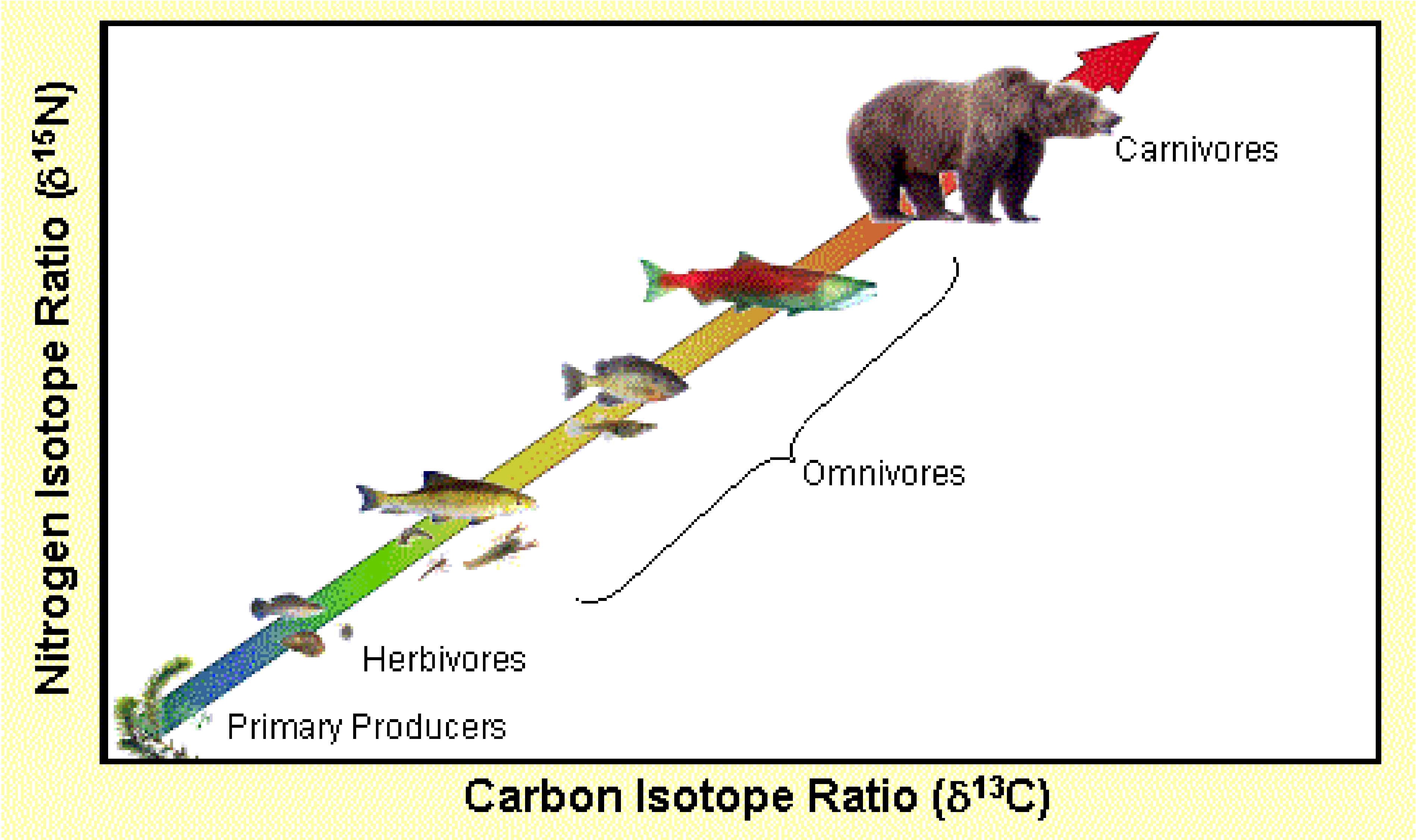


FIG. 2. Variation in the $\delta^{15}N$ signature of primary consumers


ATMOSPHERE
N2 gas 0
PRECIPITATION
NH4+ -18 to +8
NO3- -15 to +3
Leaves
-8 to +3
Fossil Fuel
Emissions
NOx -2 to +4
NH3 -8 to -4
1
(typical)
1 eq.
N2 fixers
-2 to +2
Soil Organic Matter -4 to +14
NO3- ?
POM ?
LAKE
Fertilizer
NH4+ ~0
NO3- ~+3
Dissolved N2 +1.0
POM -2 to +11
Deep Water NO3- +4 to +6
OCEAN


(Peterson, 1999)
plankton
89
76
5 4
1
2
3
Spartina
upland plants
10
5
0
-30
-20
-10
DEPLETED ⟵ δ 15N (‰) ⟶ ENRICHED
DEPLETED ⟵ δ 13C (‰) ⟶ ENRICHED


Foods and Diet
(Arrows point from diet to animal)
Marine Fish
Cod
Grizzly Bear (eating salmon)
USGS Visitors
USGS team members
Dog (Dingo)
Non-Corn-Fed Meat
Ostrich
Sheep
Goat
Lavender
Fruit, Vegetables, Grains
Coffee (instant)
Goose
Rabbit
Chocolate
Oatmeal
Rose petals
Coffee
Rice
Tea
Flour
Hamburger (McDonald's)
Black Bear (eating nuts & berries)
Our Diet
Cheese (Gorgonzola)
Dairy
Dry Milk
Chicken McNugget (McDonald's)
Doritos
Chicken
Corn-Fed Meat
Cat (Schizzy)
Dog (Maddy)
Dog (Deb's)
Cat (Sheba)
Flank steak
Corn Weevil
Corn Meal
Corn & Sugar Cane
Nitrogen Isotope Value (δ^{15}N)
Carbon Isotope Value (δ^{13}C)



Nitrogen Isotope Ratio ($\delta^{15}N$)
Carnivores
Omnivores
Herbivores
Primary Producers
Carbon Isotope Ratio ($\delta^{13}C$)

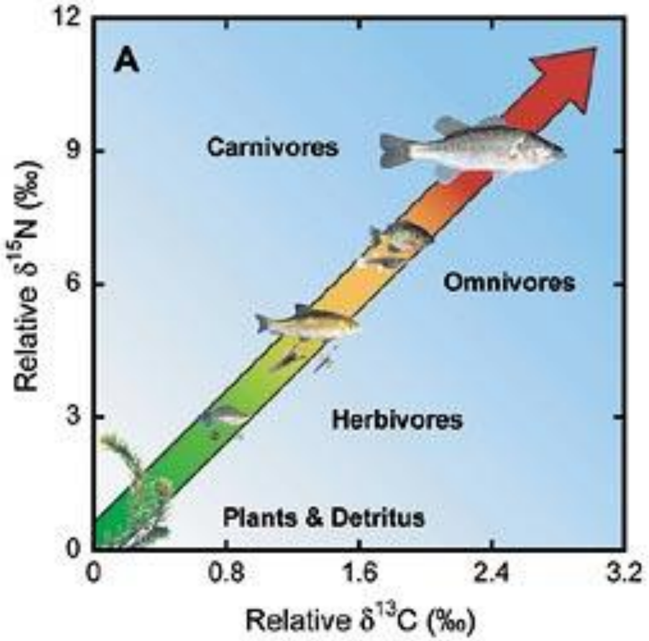
Nitrogen isotopes in the food web

Data:

- -1st order control : you are what you eat

- -trophic enrichment generally borne out

model:



Minigawa & Wada, 1984; McCutchan et al., 2003