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

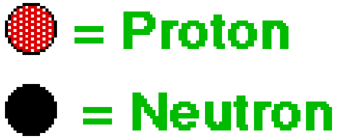
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 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



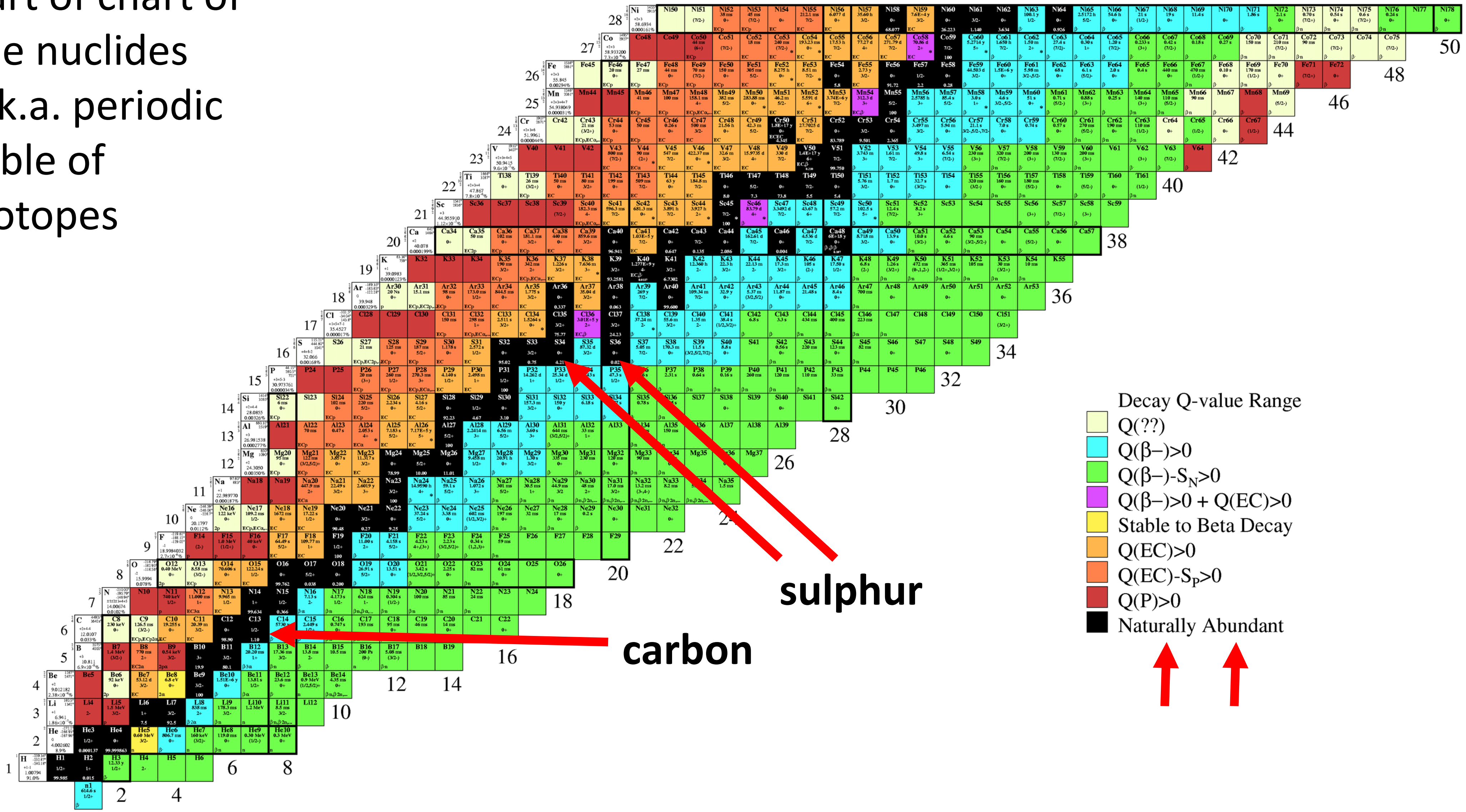
Mass Number
Atomic Number

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

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?

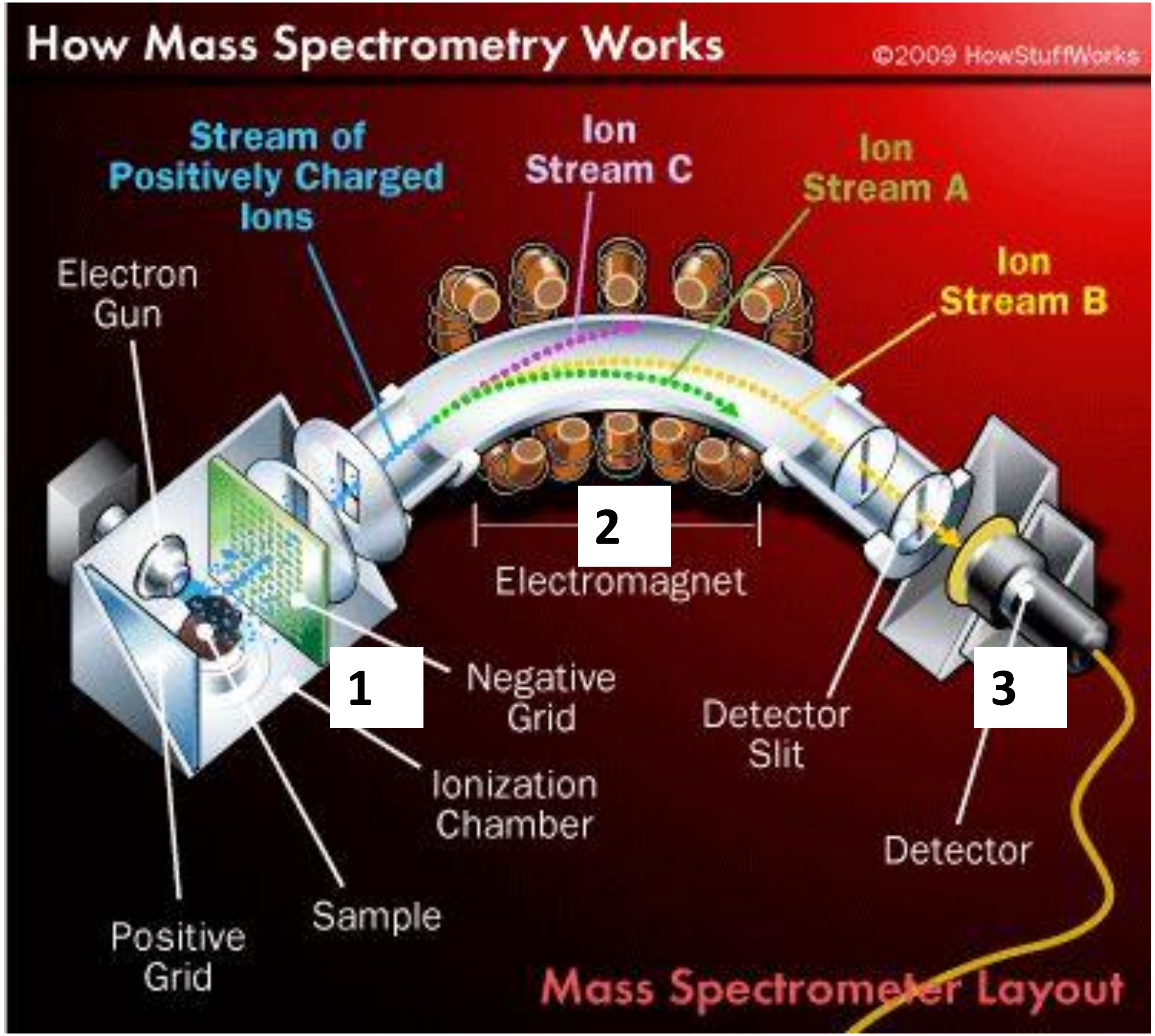
INVENTION OF THE
MASS SPECTROMETER
(J.J. Thomson, 1913)

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

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

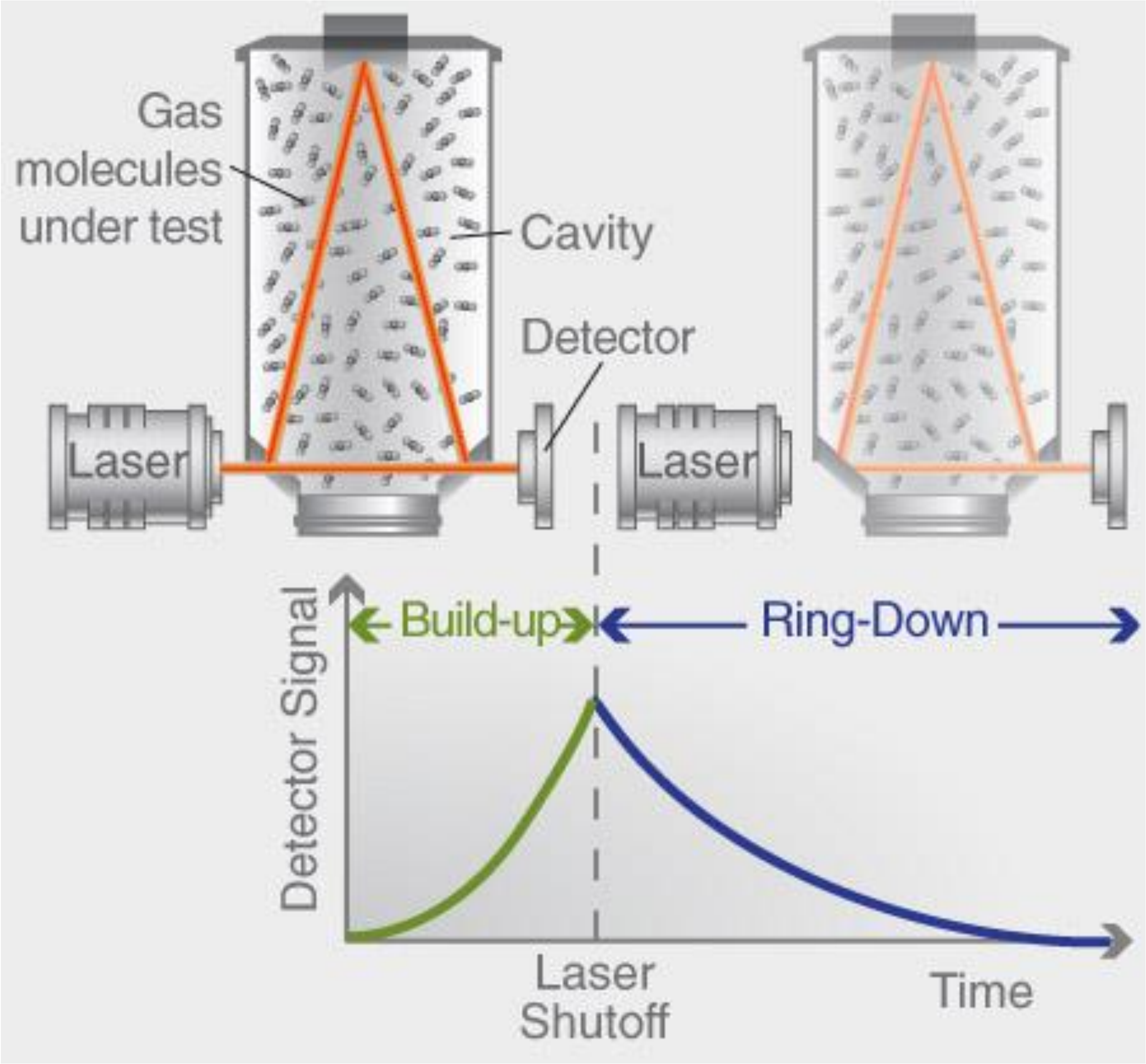
3) **detector:** measures the signal from incoming beams

(under vacuum)



HEAVY vs. light isotopologues
:: BUS vs. car

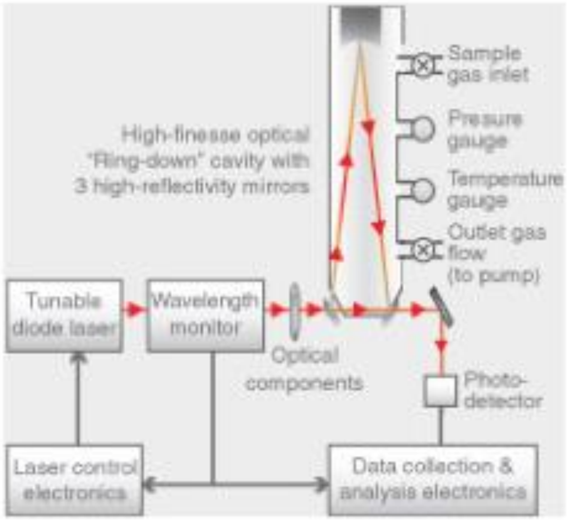
(new instruments) CAVITY RINGDOWN SPECTROSCOPY, CRDS

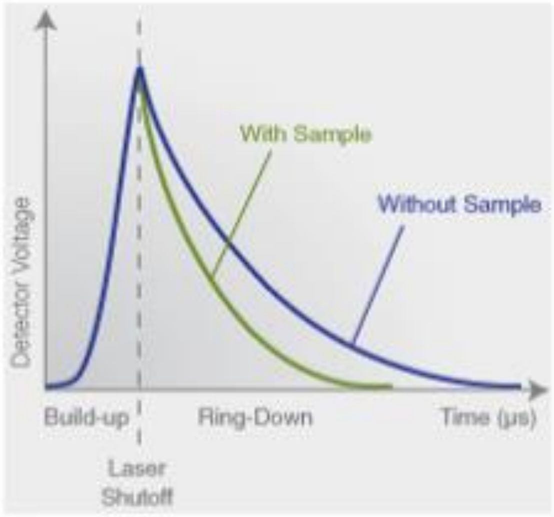


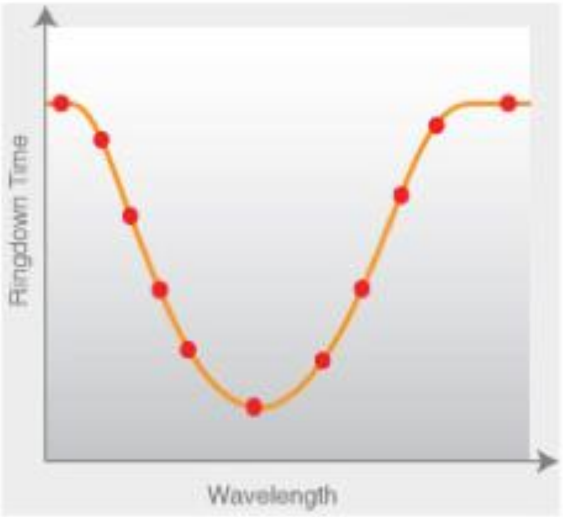
Picarro Wavelength-Scanning Cavity Ringdown Spectroscopic Instrument for Airborne In Situ CO_2 and CH_4 Quantification

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

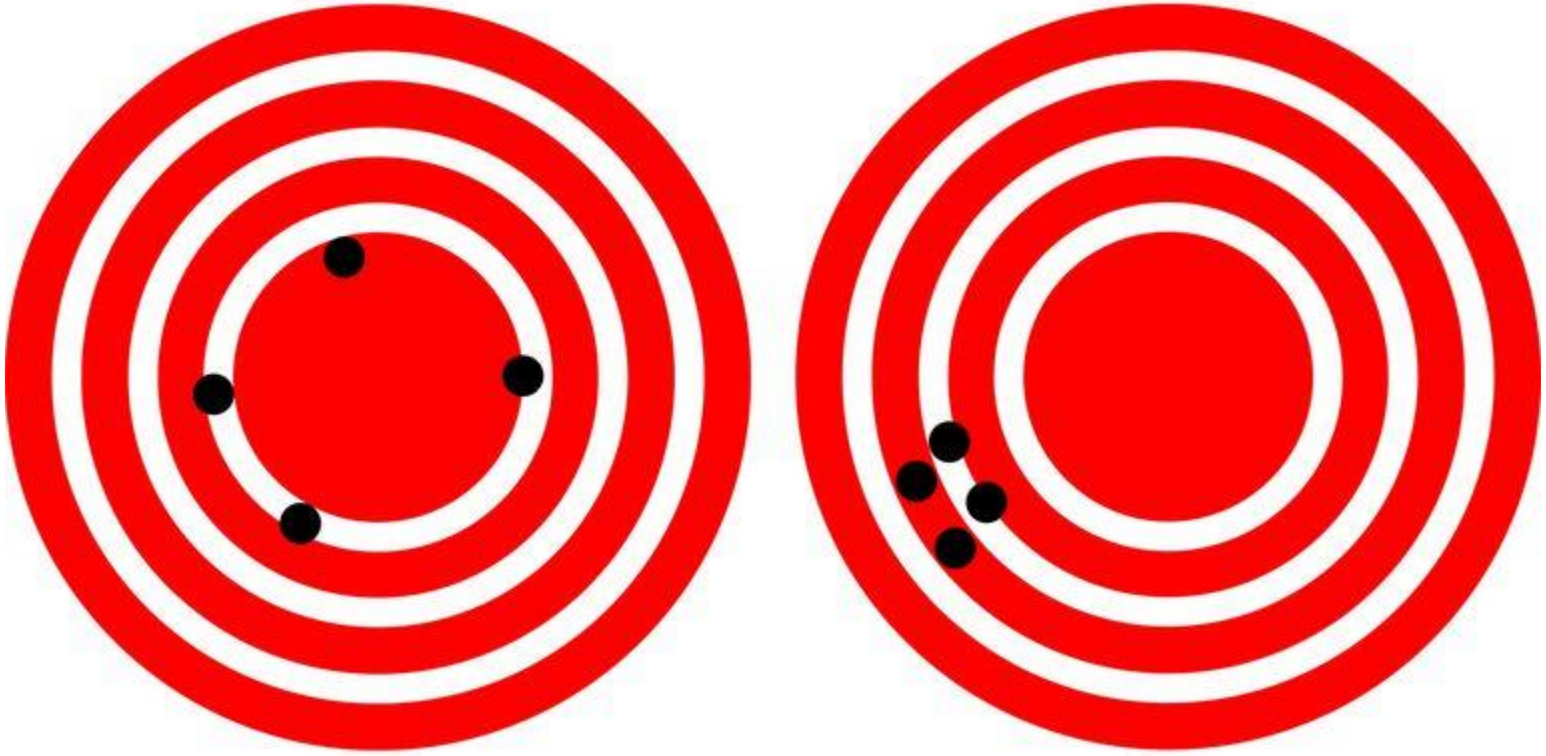






MOST IMPORTANT SLIDE

Accuracy vs. Precision

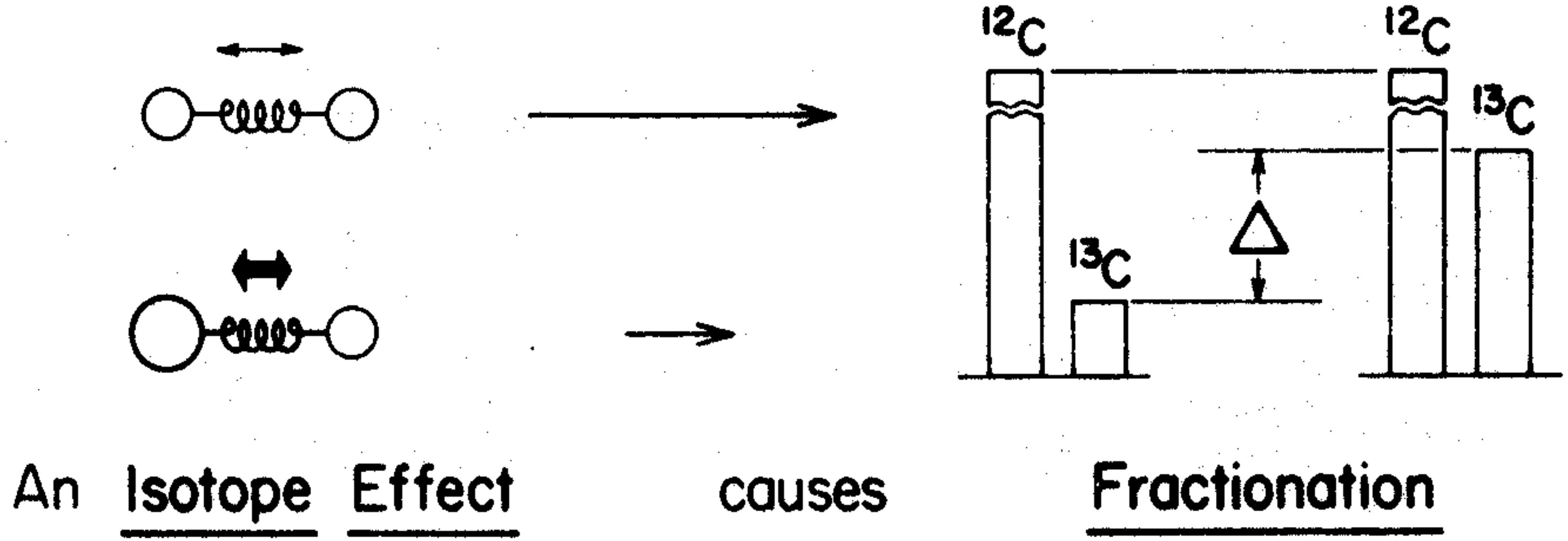


Making Isotopes Useful for Applied Science

- 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

$$\alpha = \frac{R_{reac\tan ts}}{R_{products}}$$

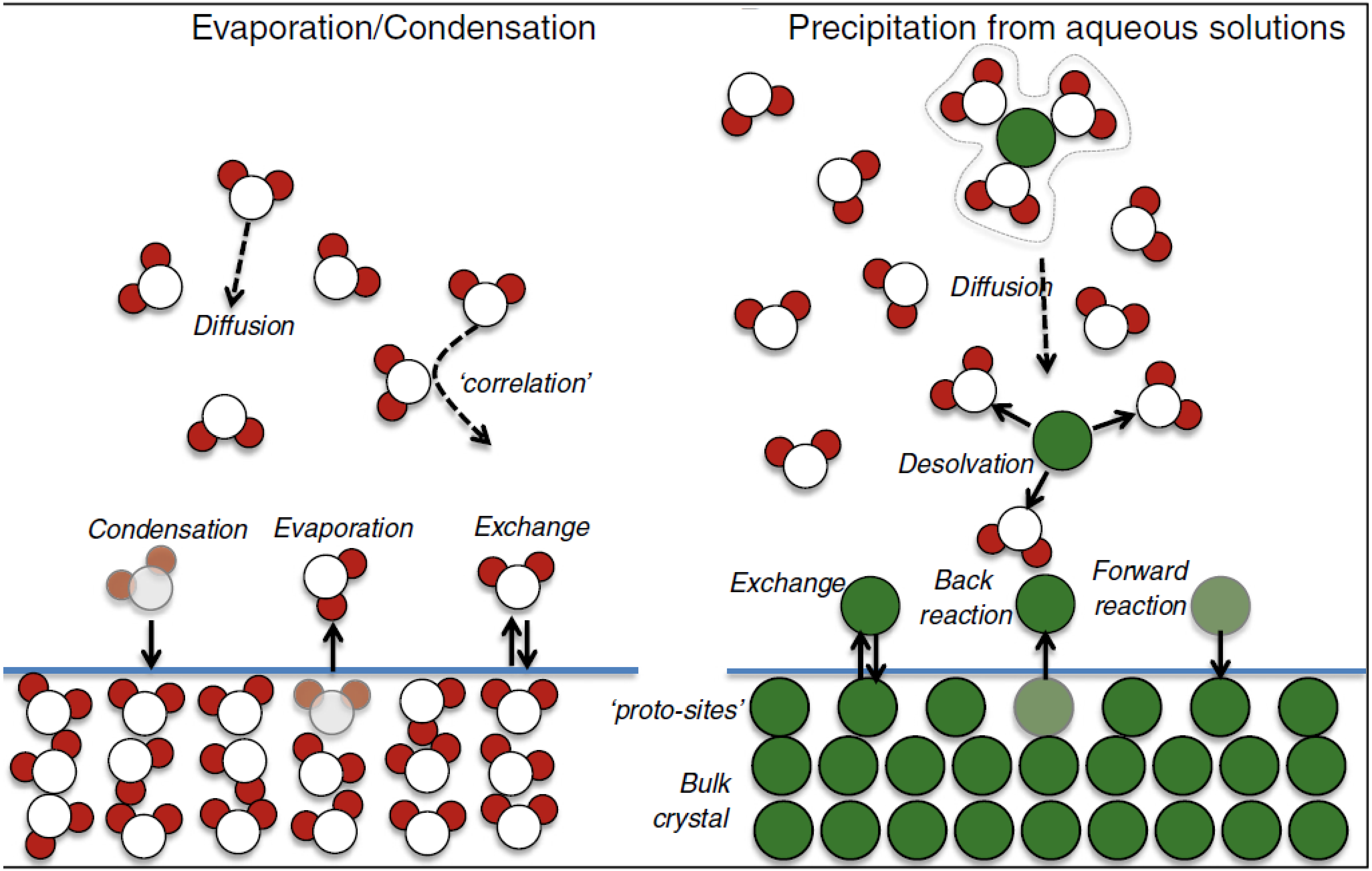
$$H_2O_{water} \longleftrightarrow H_2O_{vapor}$$

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

ISOTOPE FRACTIONATION

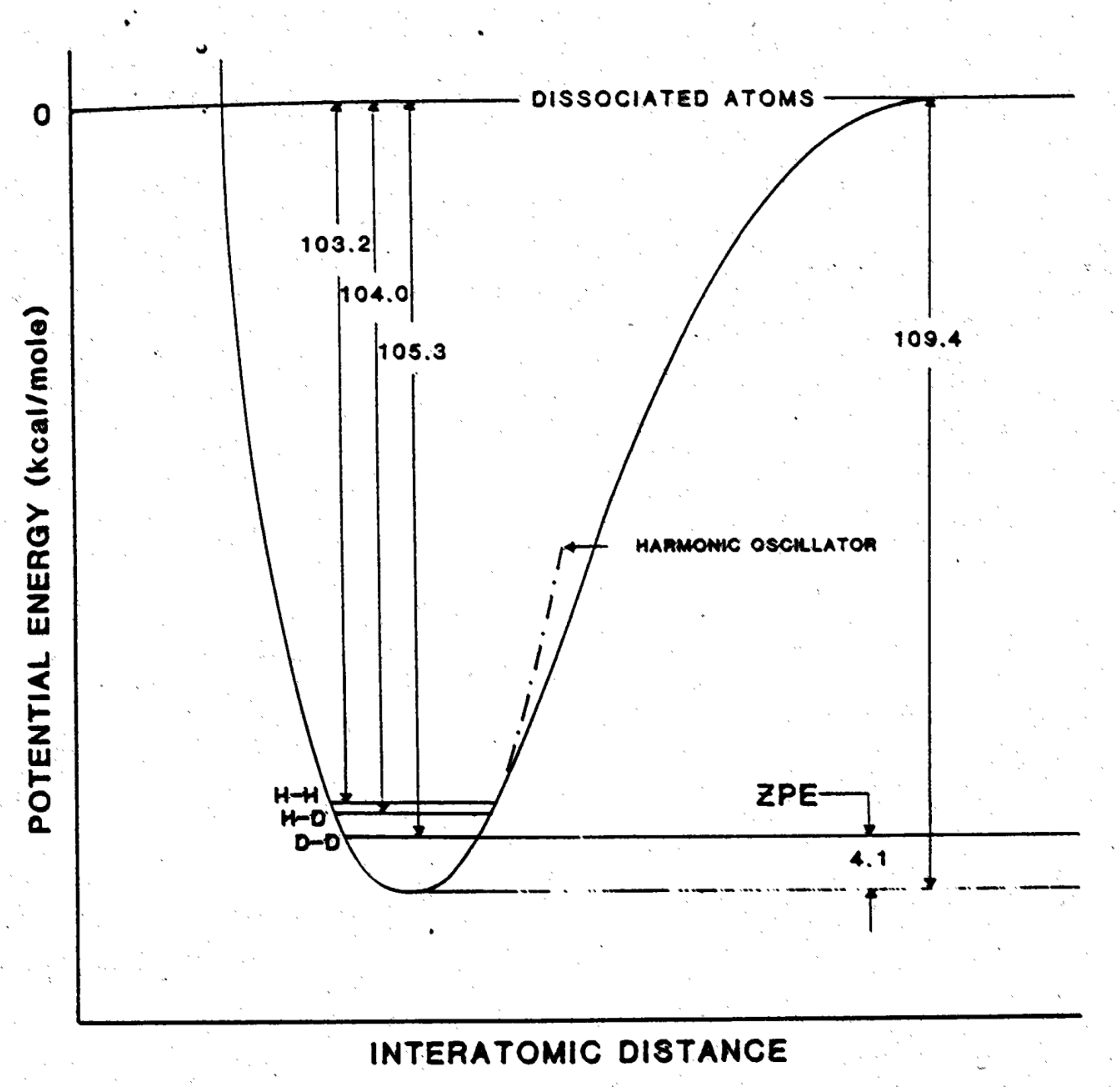
- Natural processes "sort" the isotope composition of matter
- Evaporation, condensation, photosynthesis, respiration, crystallization, etc.
- Two types of fractionation
    - Equilibrium (reversible)
    - Kinetic (unidirectional)
- $\alpha_{A\text{-}B} = R_A \,/\, R_B$
- $\alpha_{A\text{-}B} = (1000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

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?

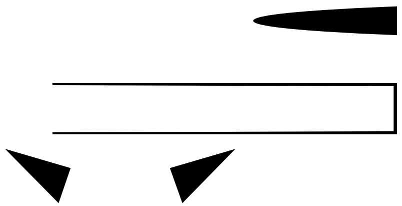
Because ^{18}O forms a stronger covalent bond with C than does ^{16}O.

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:

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

- 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

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

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 $\delta^{13}C_{VPDB}$ = $\left(\frac{\frac{^{13}C}{^{12}C}^{sample}}{\frac{^{13}C}{^{12}C}^{standard}} - 1\right) * 1000$

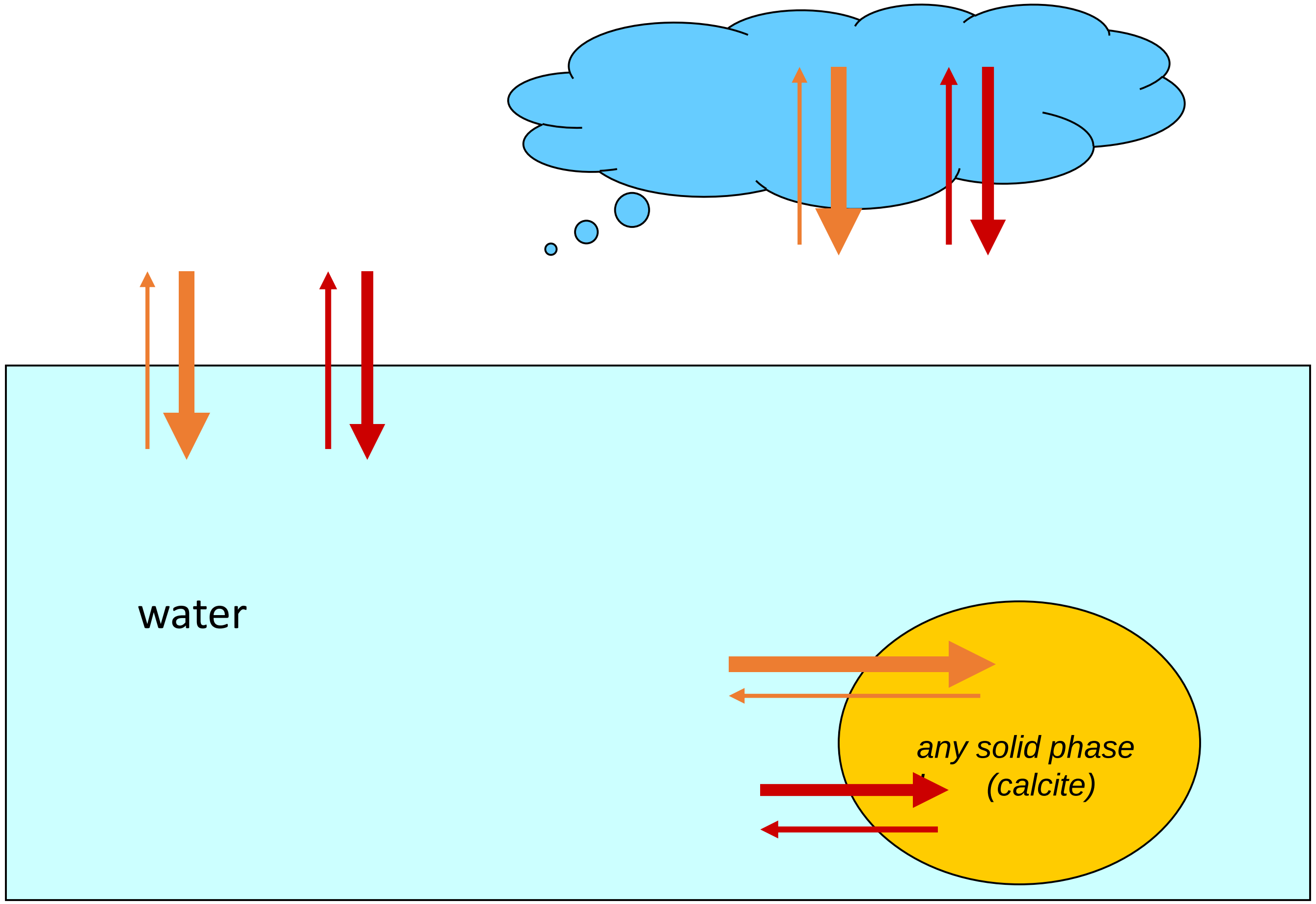
= $\left(\frac{0.0110000}{0.0112372} - 1\right)$ *1000 = **-21.1 ‰**

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

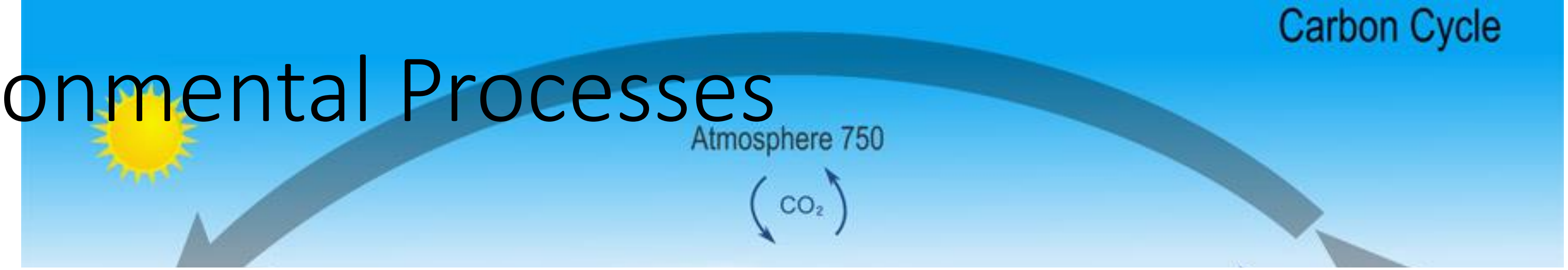
Temperature-dependent fractionation - recap

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

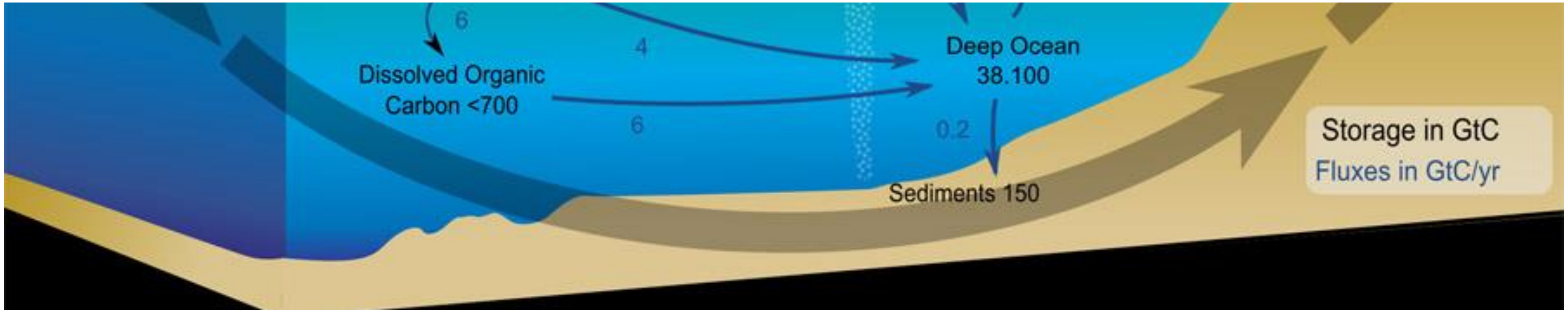


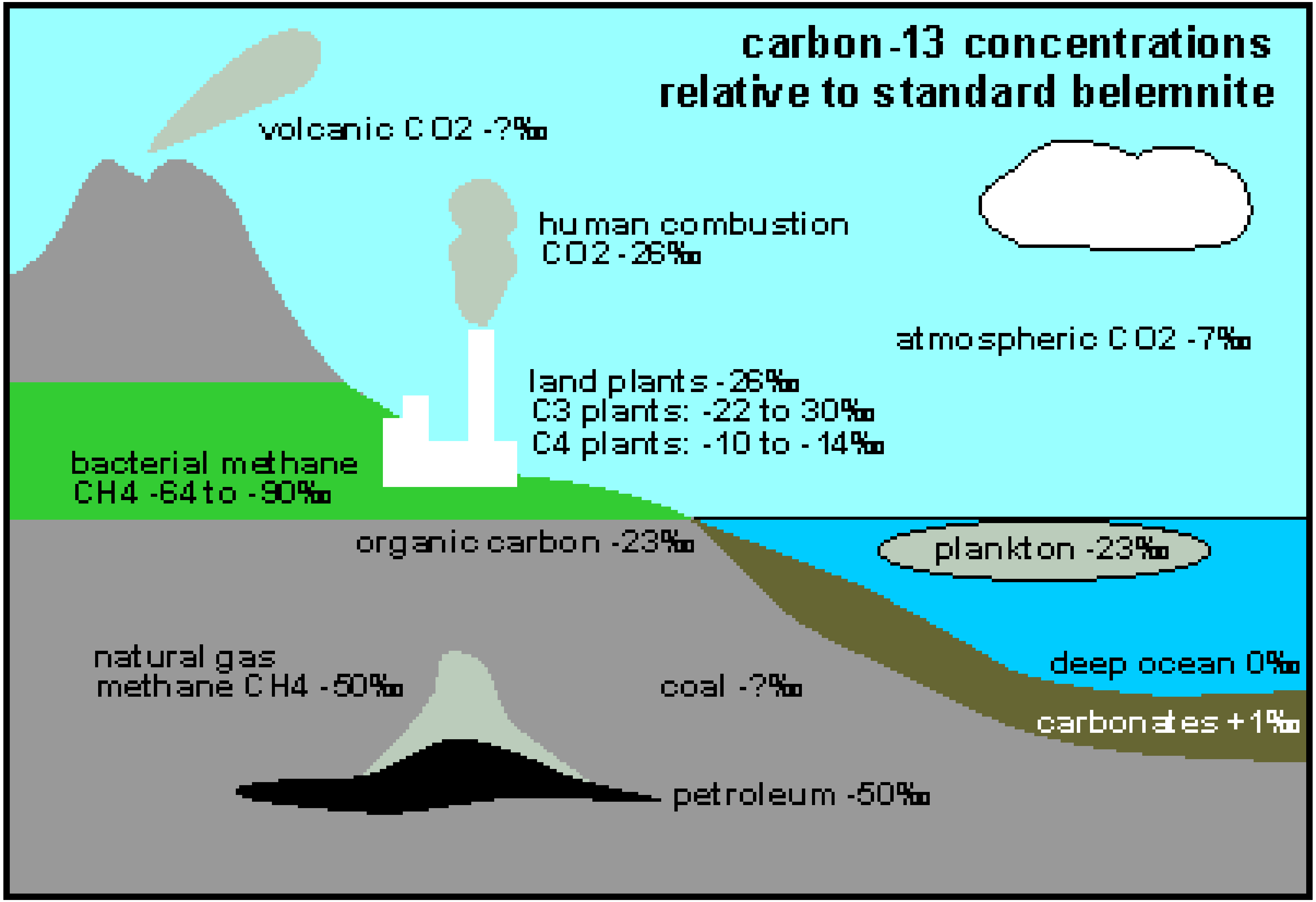
red=warm
blue=cold;
arrows track movement of ^{18}O through phase changes

Environmental Processes

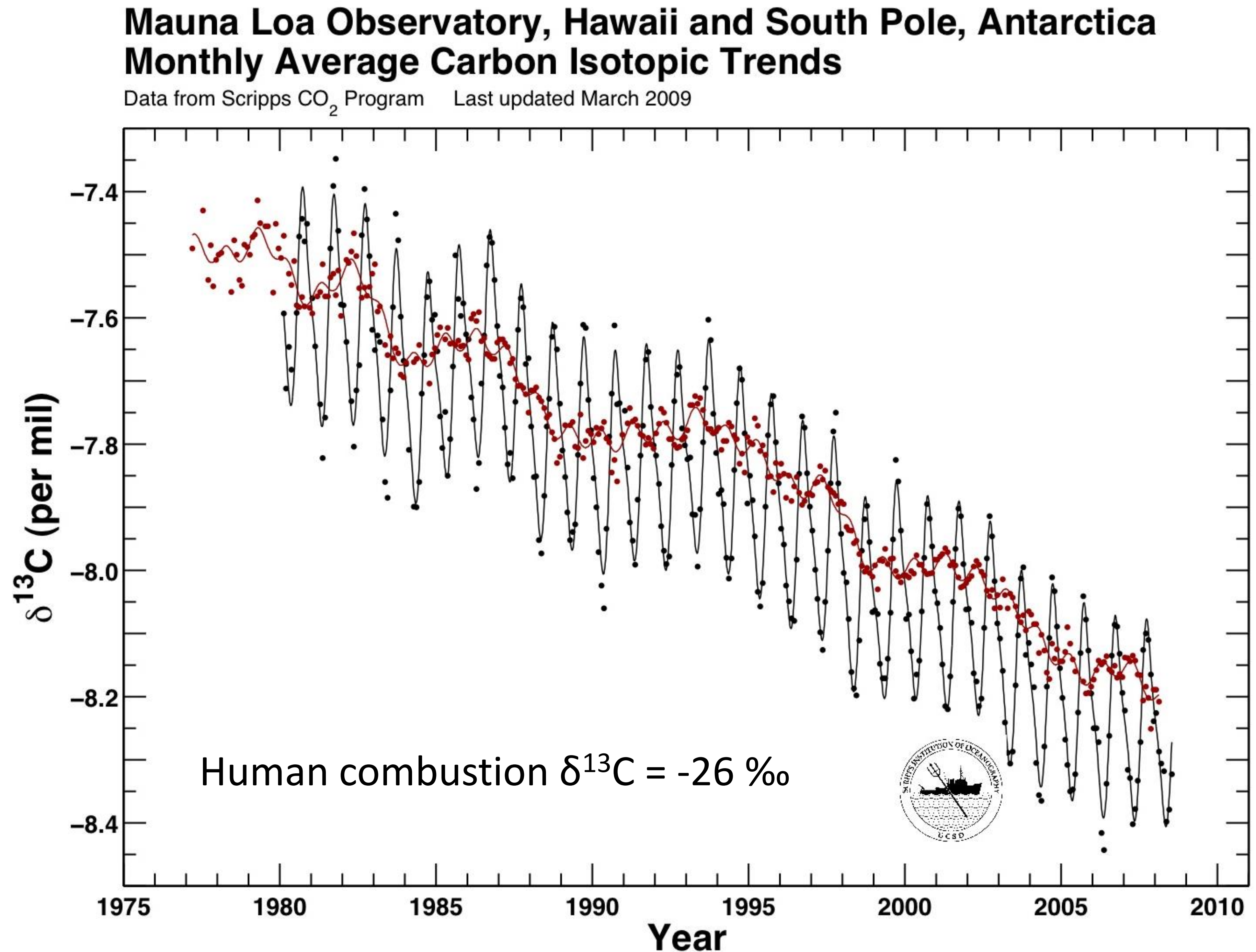


- How do scientists trace these processes? How do we perform "accounting" for the transfers of matter, fluxes in these cycles?
- Isotopes used to corroborate earth science model results
- The water cycle
- Carbon cycle (short term), organic matter, photosynthesis
- Nitrogen cycle
- Sulphur cycle




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

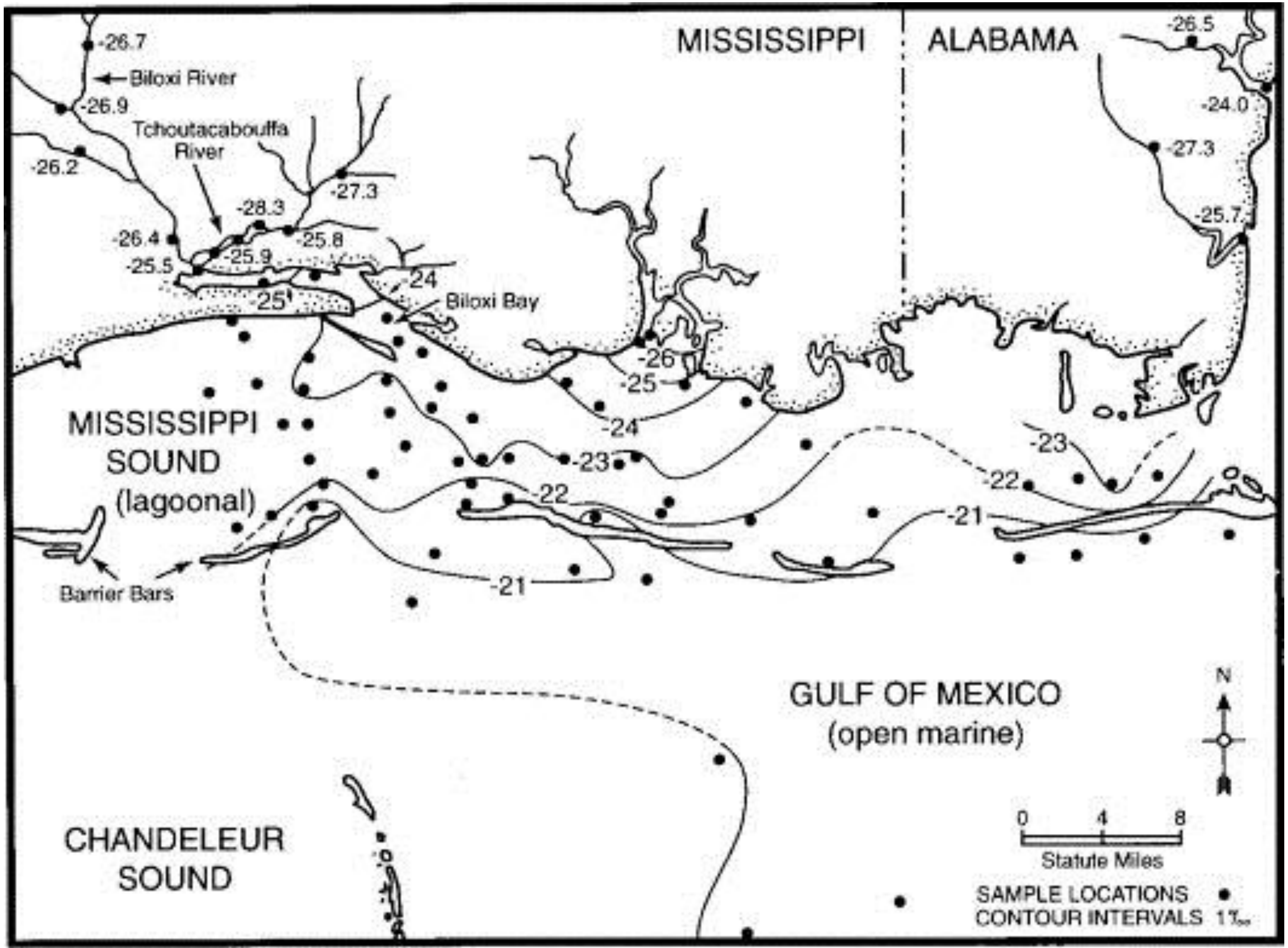


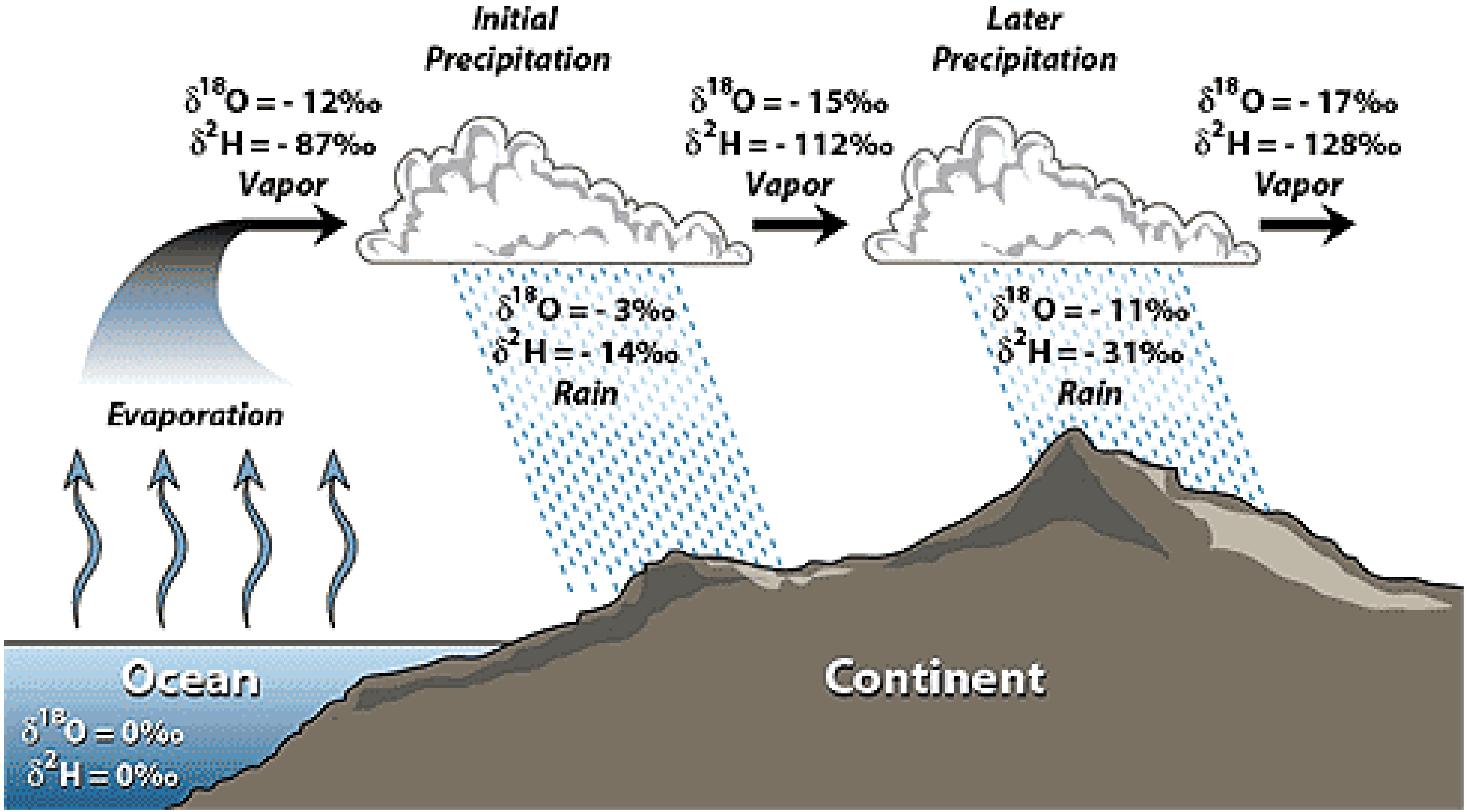
Human combustion $\delta^{13}C$ = -26 ‰

Comparison of C_3, C_4, and CAM plants

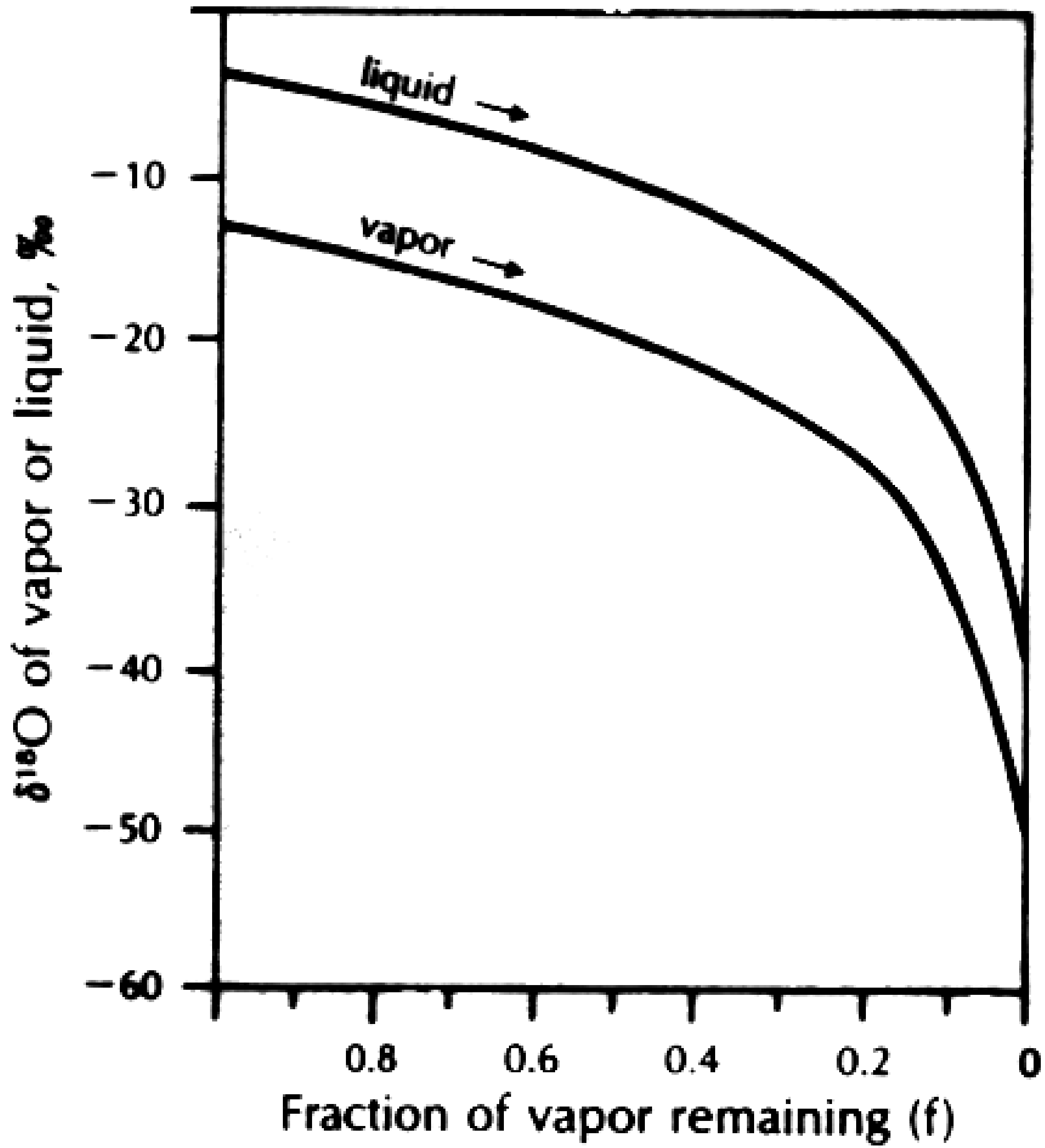
C3 plants	C4 plants	CAM plants
Most plants	Tropical grasses like corn, sugarcane	Succulents, pineapple, agave
Fix carbon in Calvin cycle - attach CO_2 to RuBP	Fix carbon in cytoplasm - attach CO_2 to PEP	Fix carbon at night only, fix it to organic molecules
Enzyme - Rubisco	Enzyme – PEP-ase	Enzyme – 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

Distillation

- 2 varieties, Batch and Rayleigh distillation dependent on if the products stay in contact and re-equilibrate with the reactants
- Batch Distillation:

  $\delta_f = \delta_i - (1 - F)\ 10^3\ln\alpha_{CO2\text{-}Rock}$

  where the isotope of the rock (δ_i) depends on it's initial value (δ_f) and the fractionation factor

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:

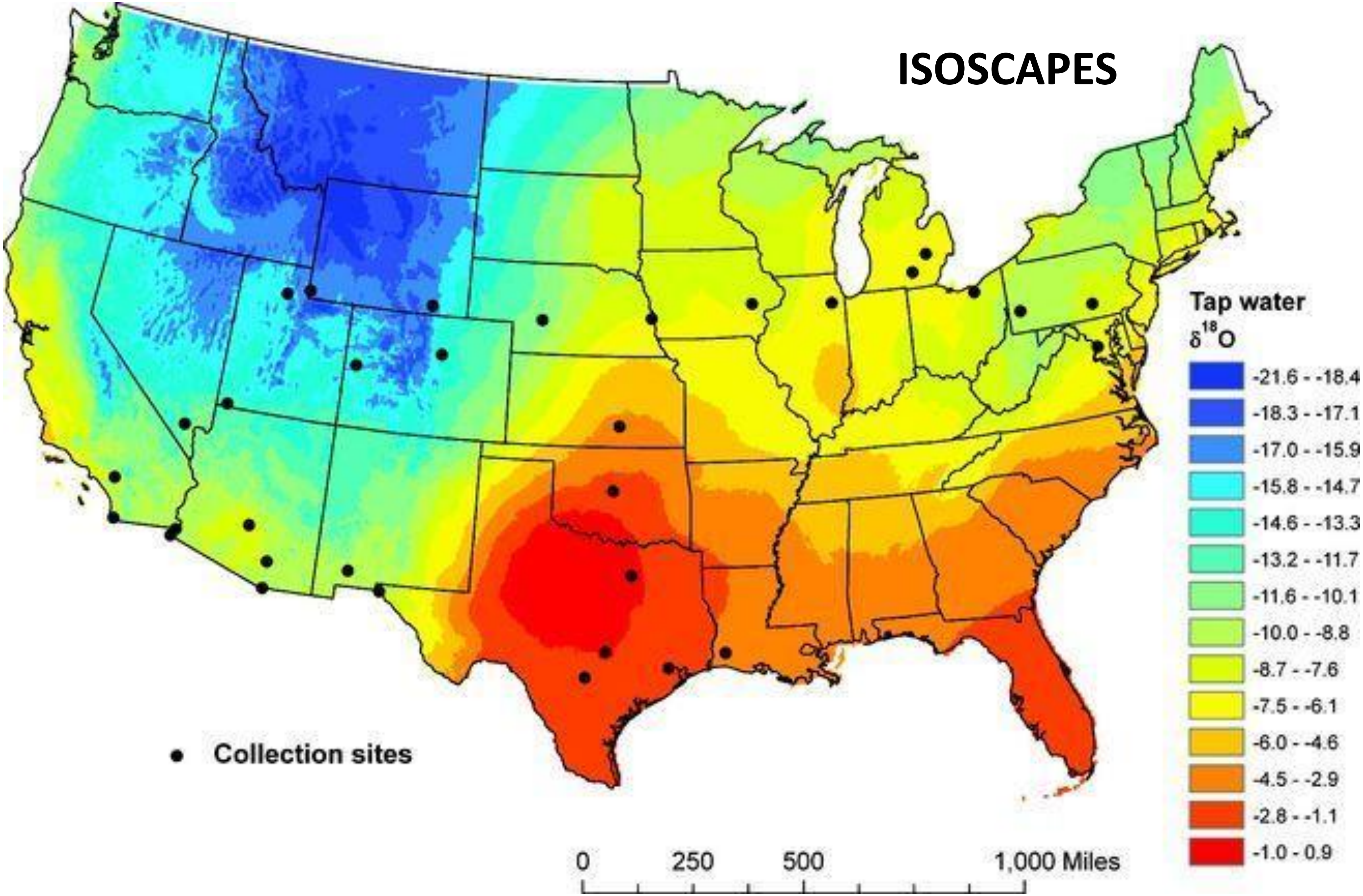
$$R_v = R_v^o f^{\alpha-1}$$

- Rayleigh Distillation

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

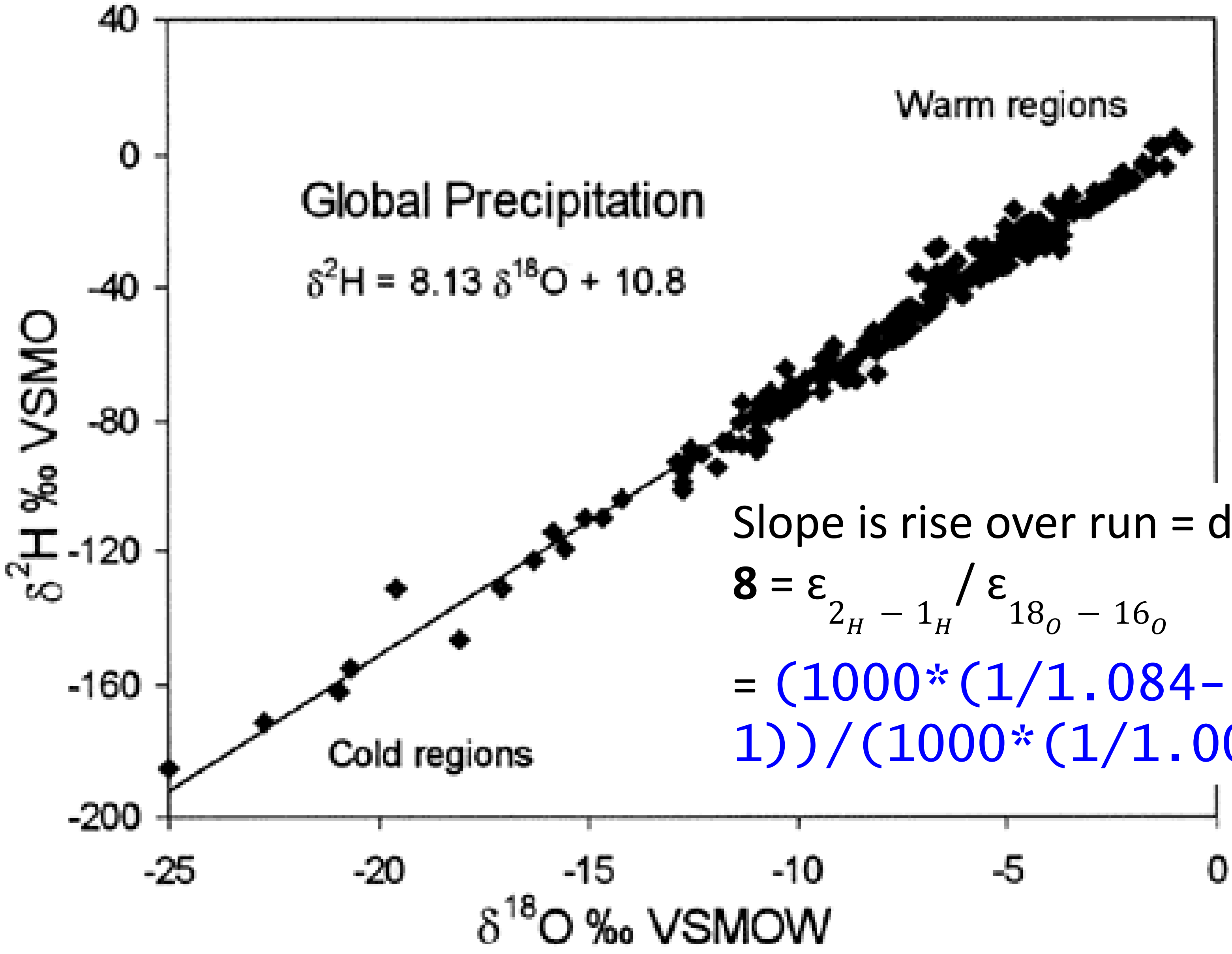
where R_v = isotope ratio of remaining vapor, $R_v°$ = isotope ratio in initial vapor, ƒ = the fraction of vapor remaining and a = the isotopic fractionation factor

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

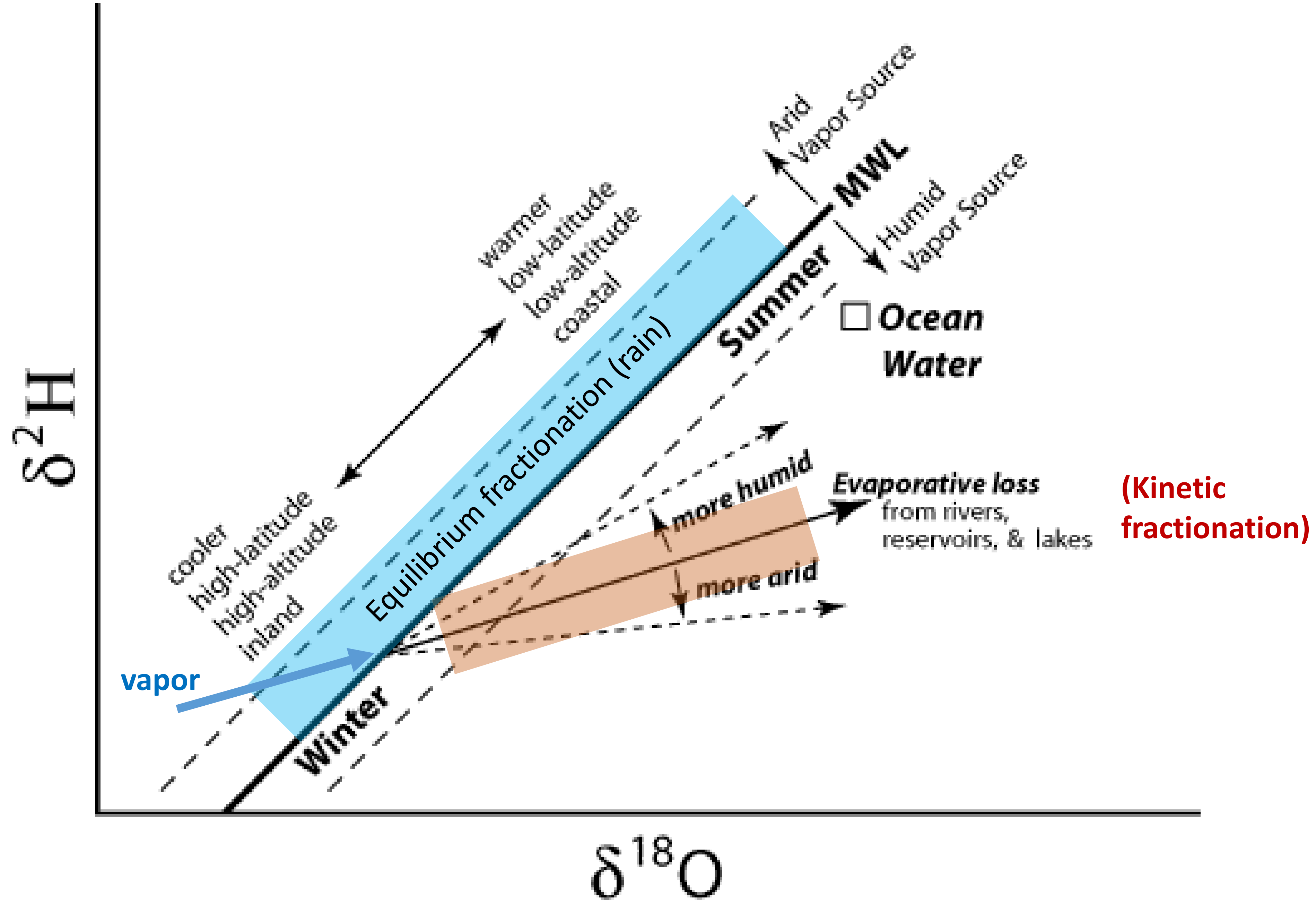
Meteoric Water Line



Slope is rise over run = dy/dx =

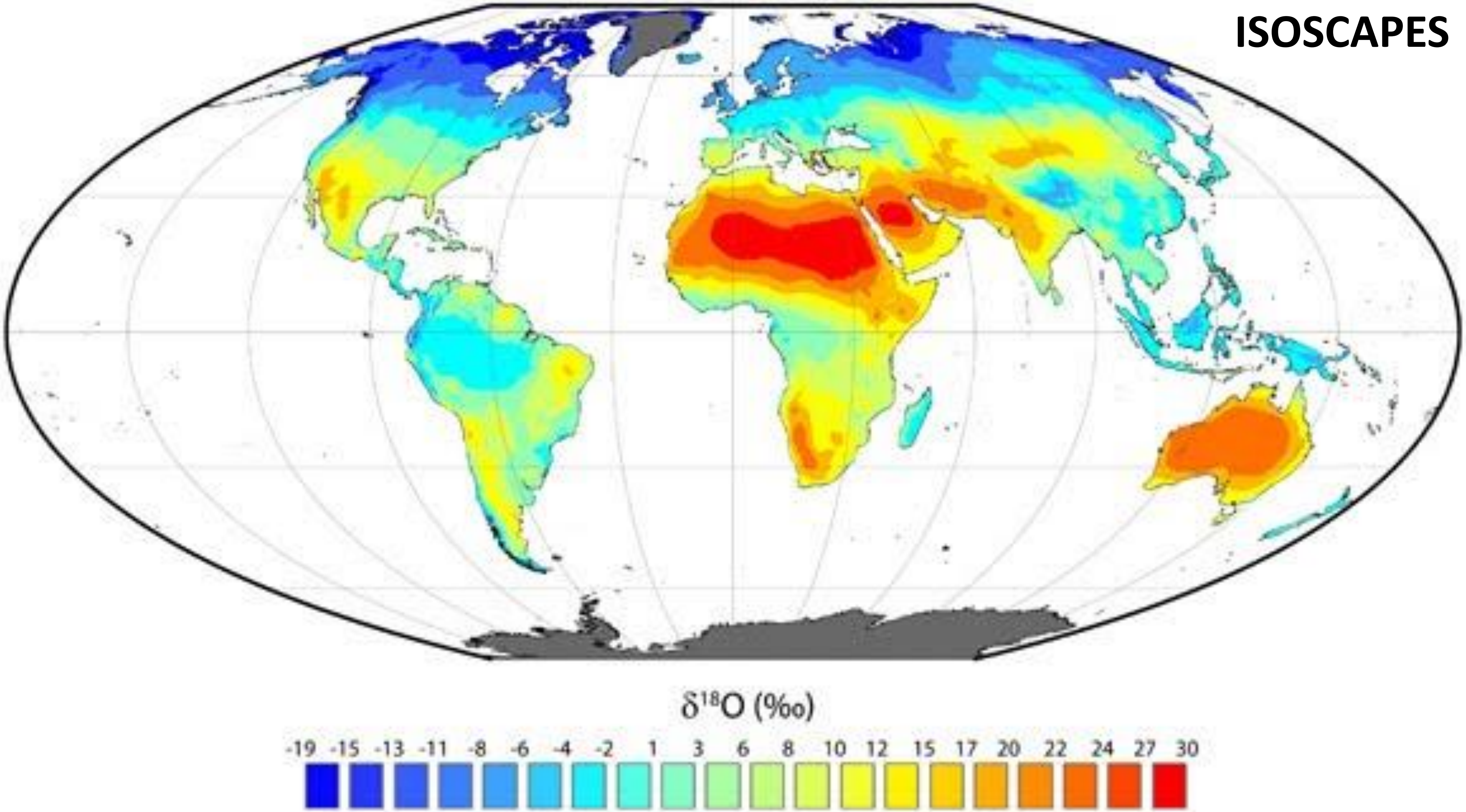
8 = $\varepsilon_{^2H\,-\,^1H} / \varepsilon_{^{18}O\,-\,^{16}O}$

= (1000*(1/1.084-1))/(1000*(1/1.0098-1))

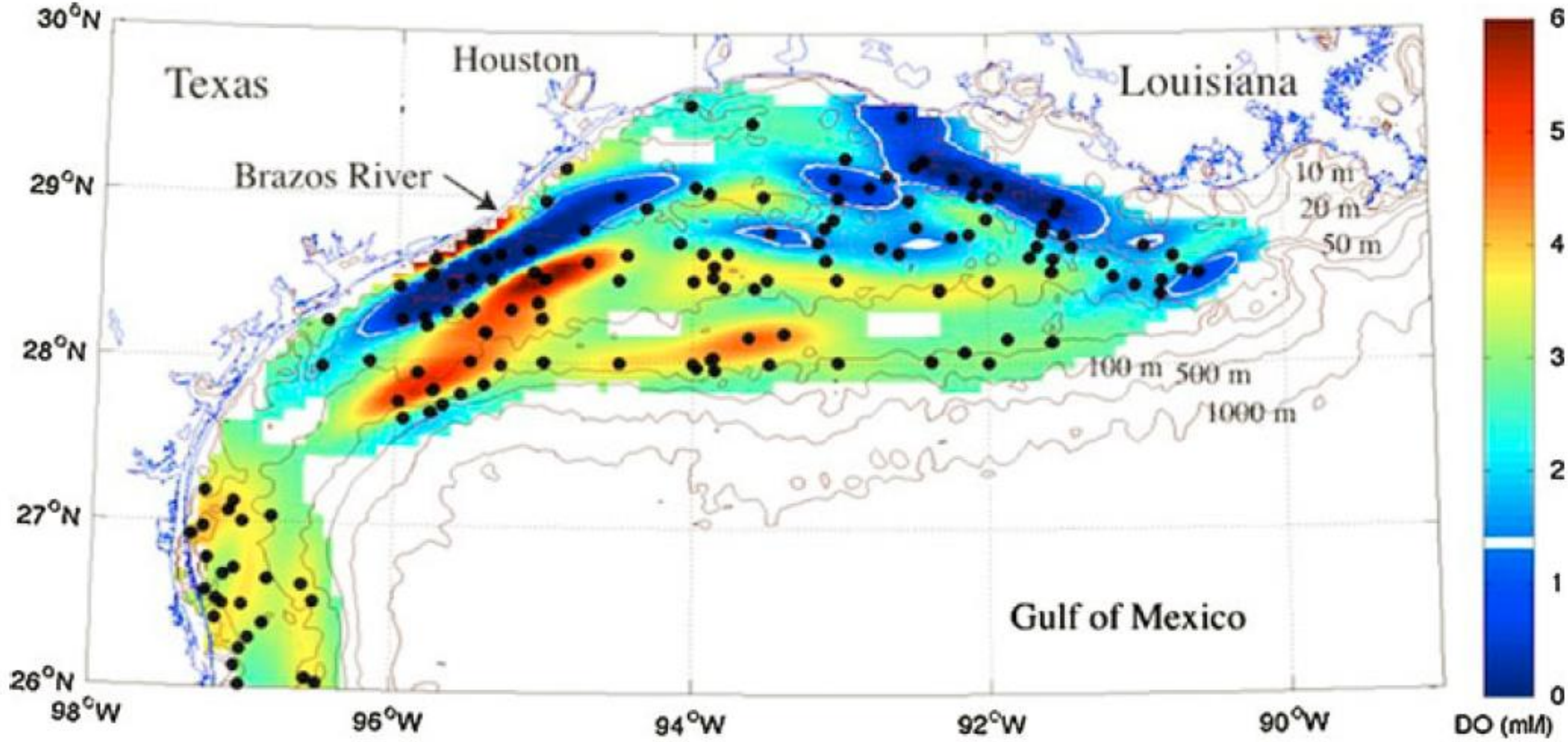


δ²H
δ¹⁸O
Arid
Vapor Source
MWL
Humid
Vapor Source
warmer
low-latitude
low-altitude
coastal
Summer
Ocean
Water
Equilibrium fractionation (rain)
cooler
high-latitude
high-altitude
inland
more humid
Evaporative loss
from rivers,
reservoirs, & lakes
(Kinetic
fractionation)
more arid
vapor
Winter

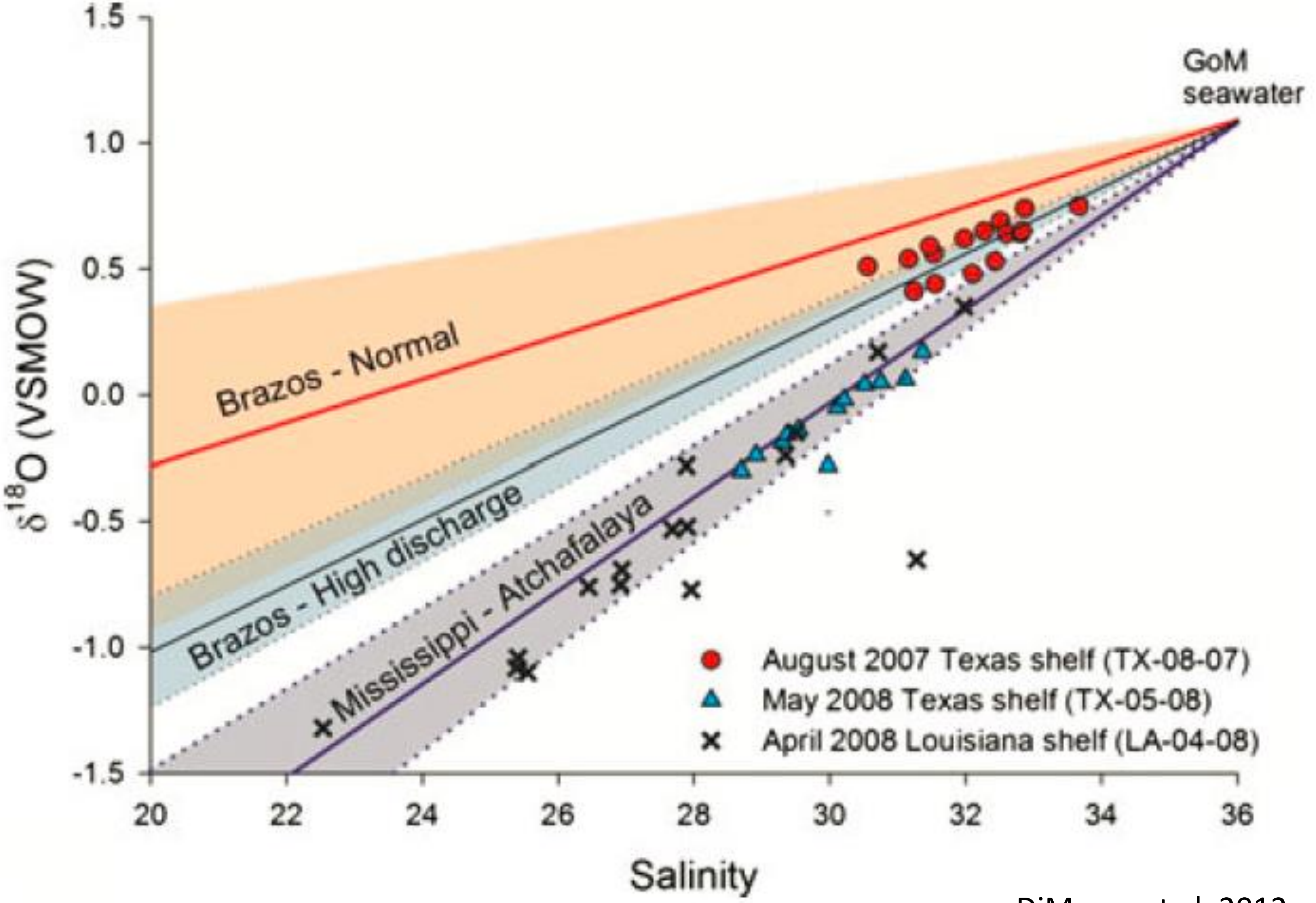
ISOSCAPES



Which rivers are causing dead zones?

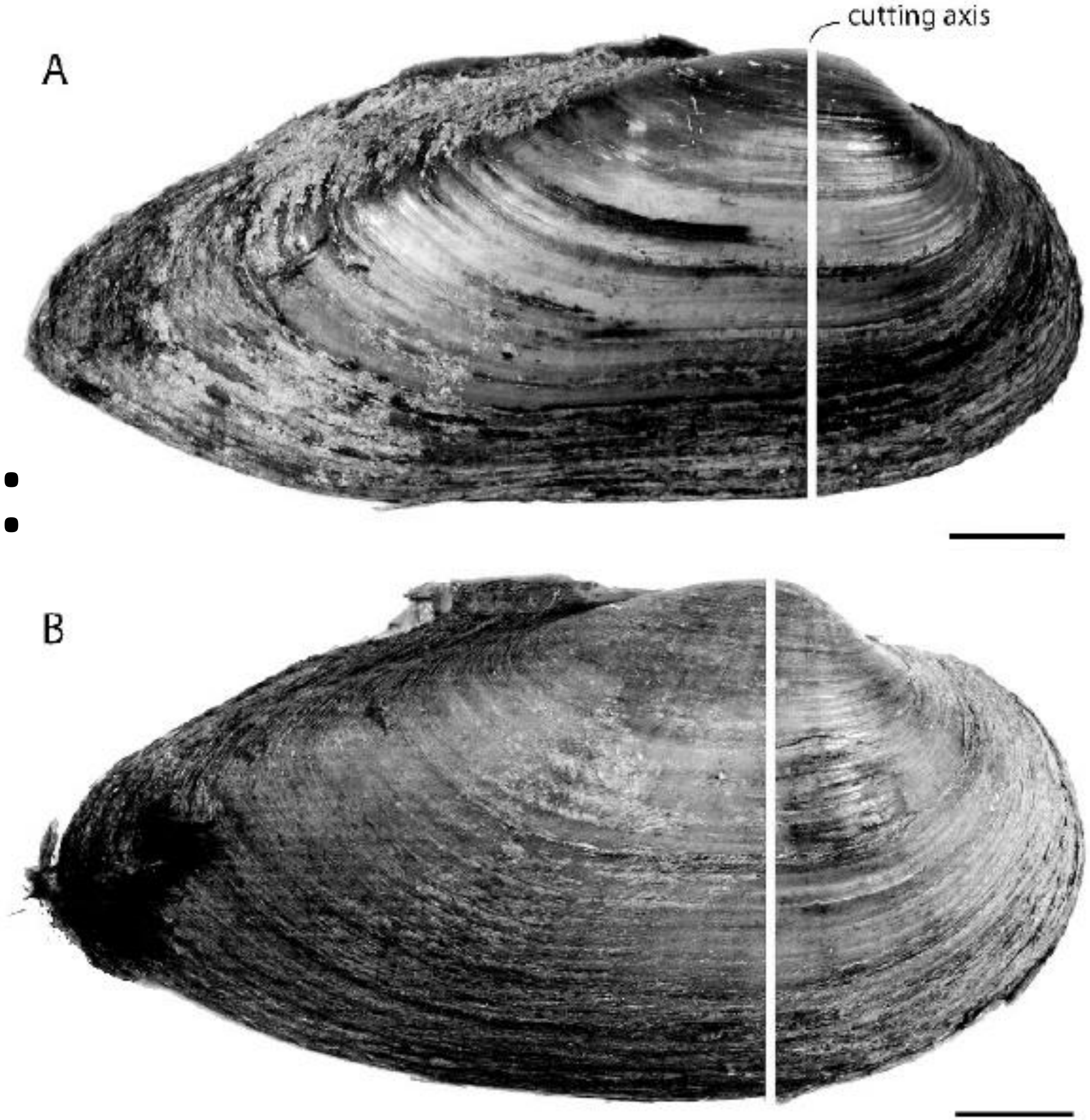


DiMarco et al. (2012)

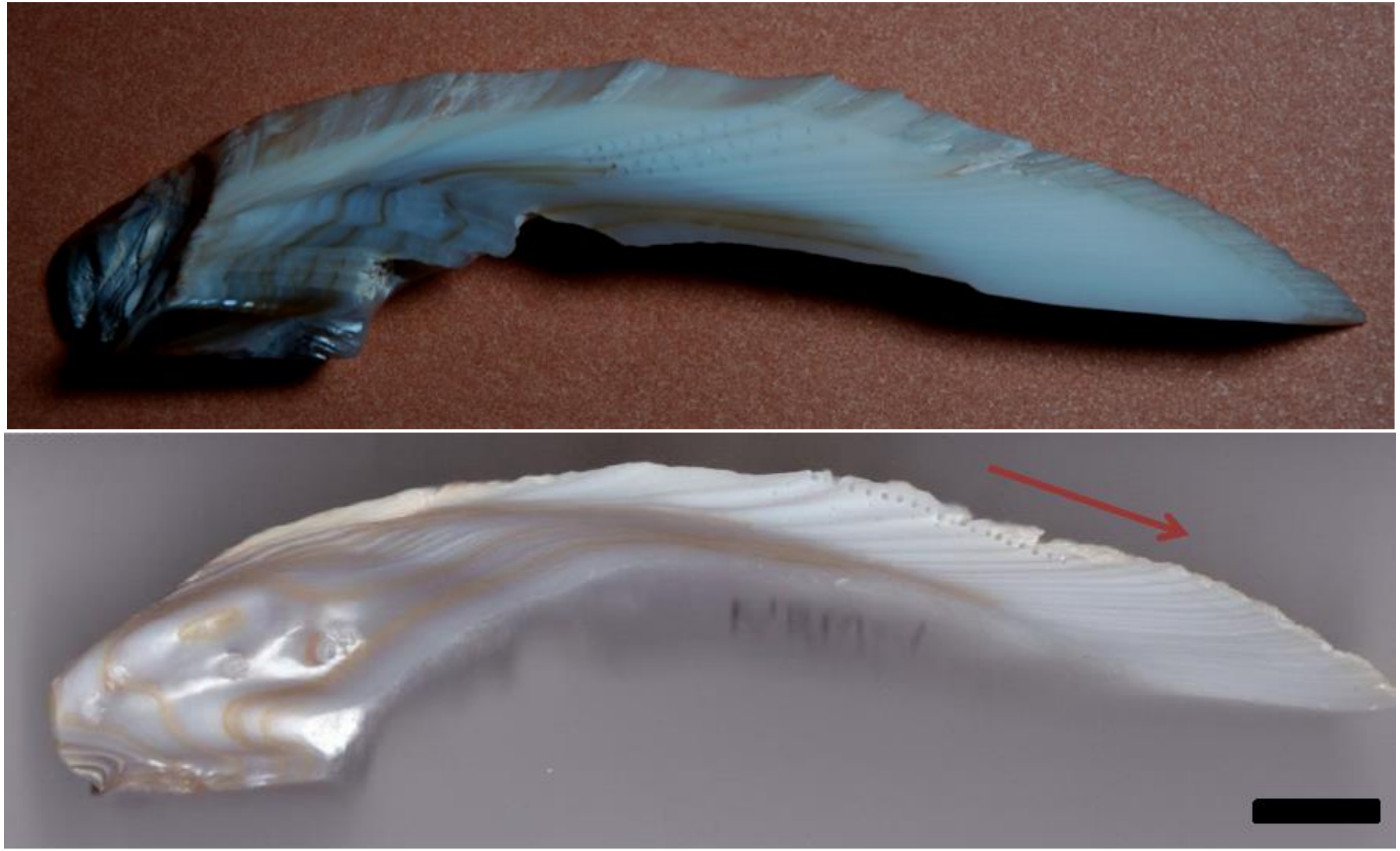


DiMarco et al. 2012

Climate Records: Mussel Shells



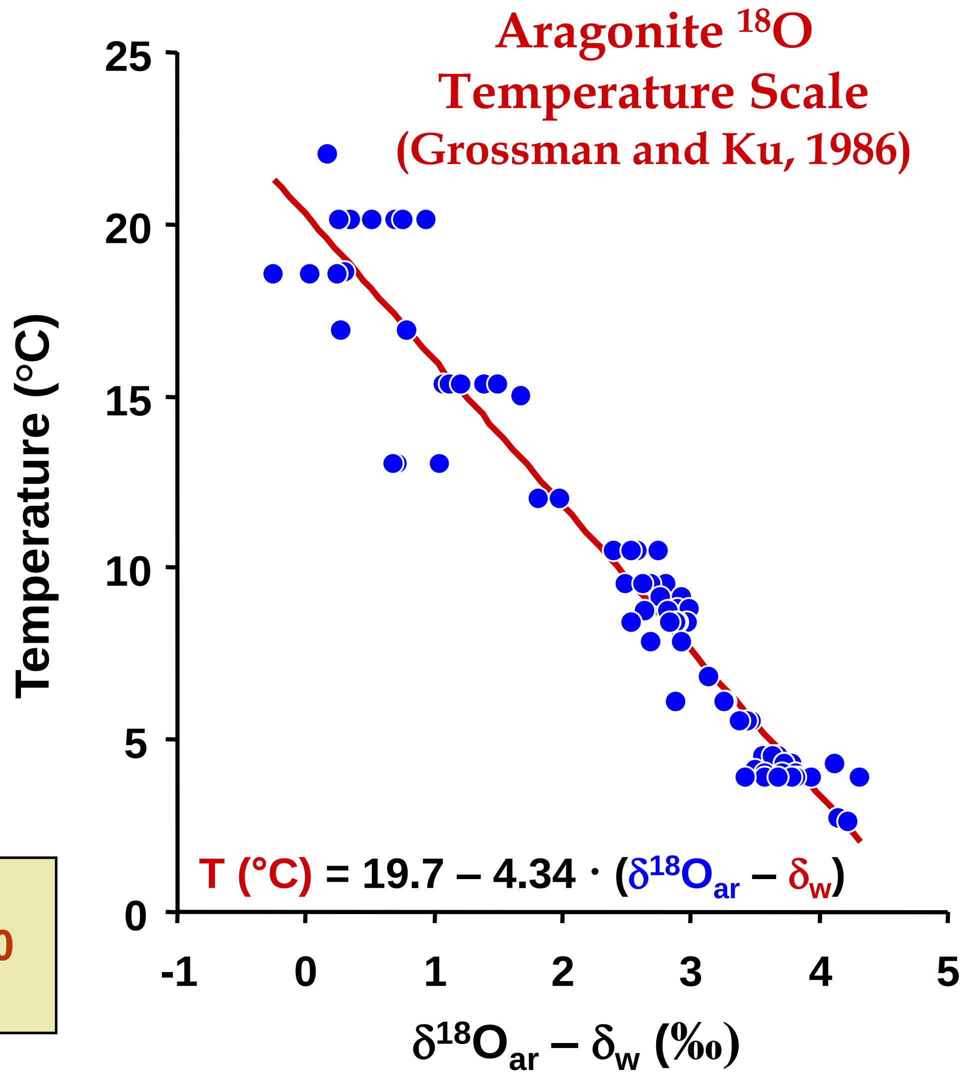
Growth layers, a record like tree rings



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

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



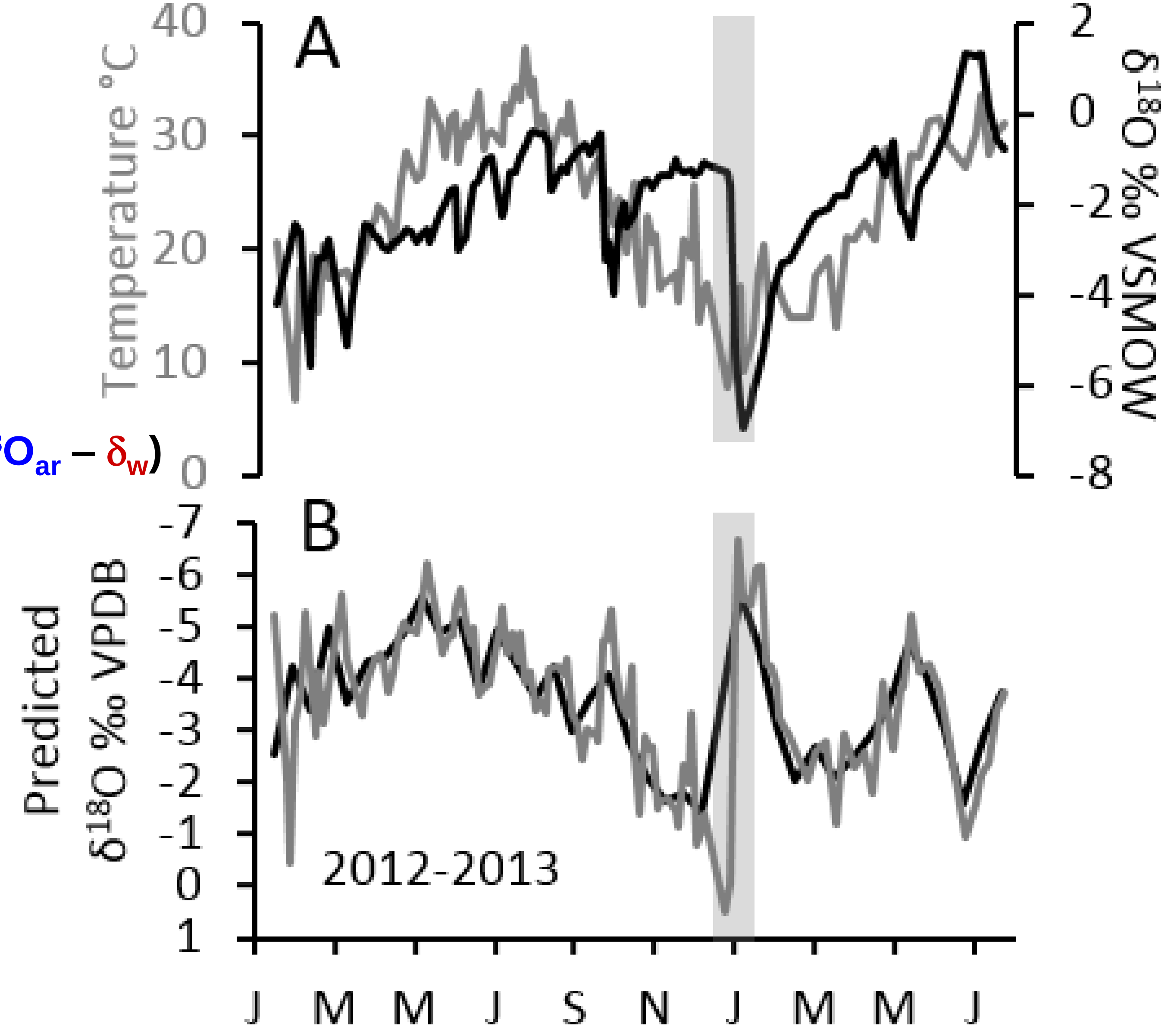
$\delta^{18}O_{ar}$ = $\delta^{18}O$ of aragonite (vs. PDB)

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

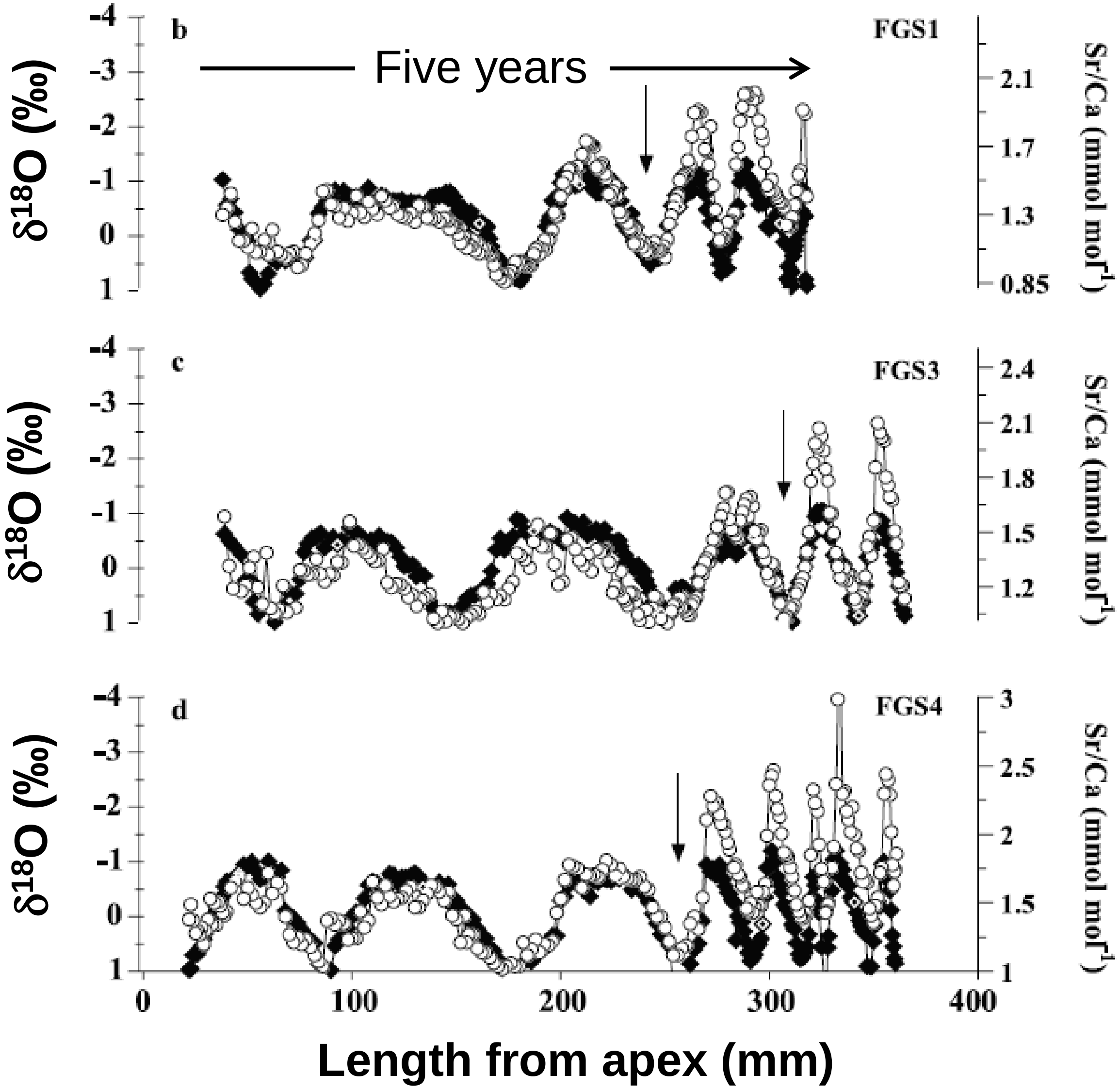
River water observations

$$T\,(°C) = 19.7 - 4.34 \cdot (\delta^{18}O_{ar} - \delta_w)$$

Shell mineral $\delta^{18}O$ predictions

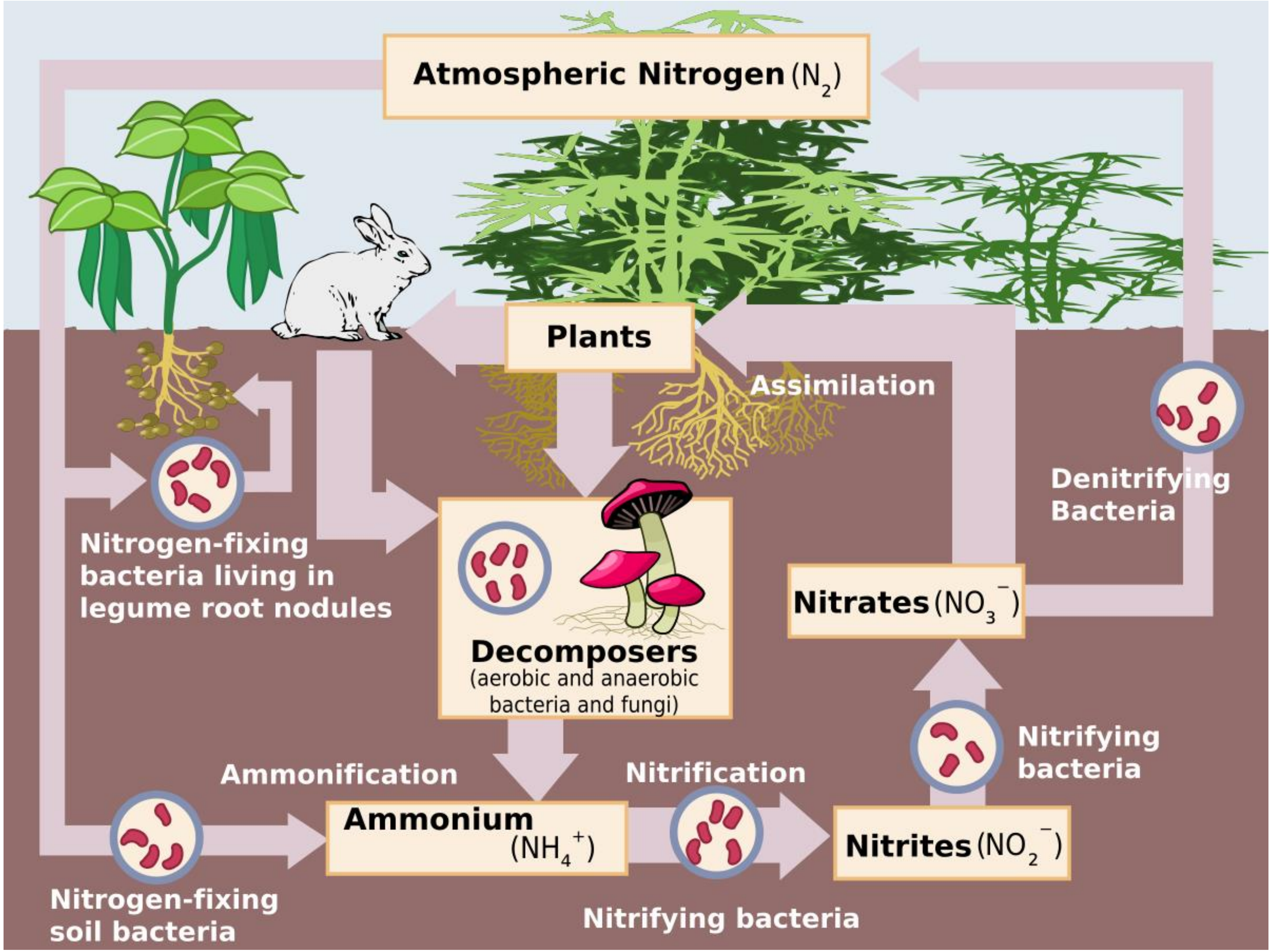


δ^{18}O and Sr/Ca in Modern *Conus* from Stetson Bank, Gulf of Mexico (~24 m)

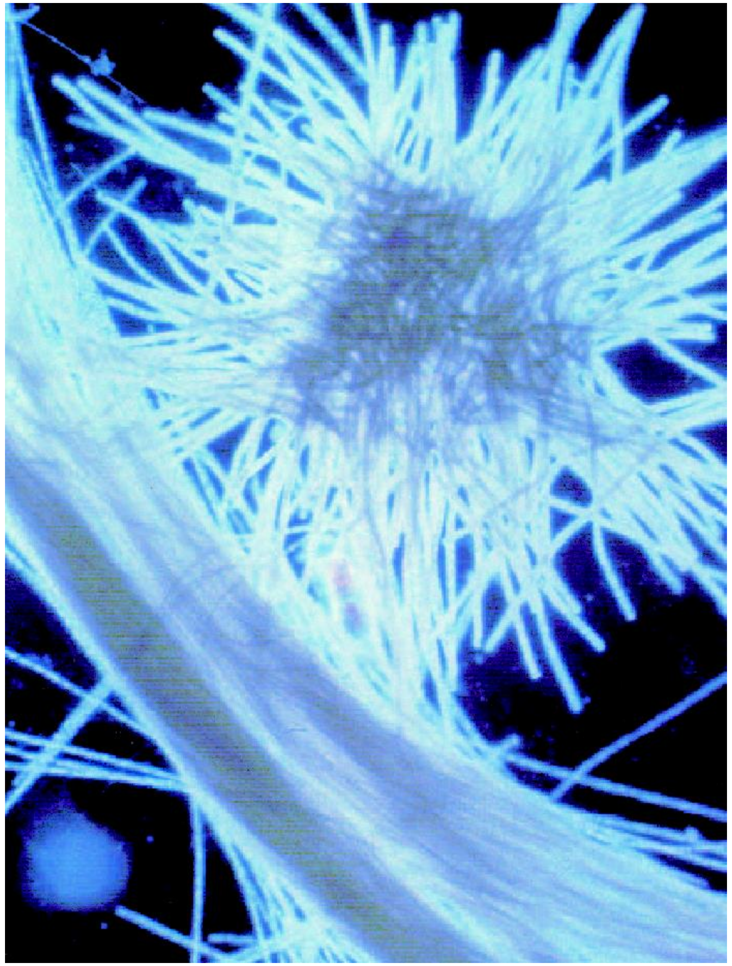


Sosdian et al. (2006)

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


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)

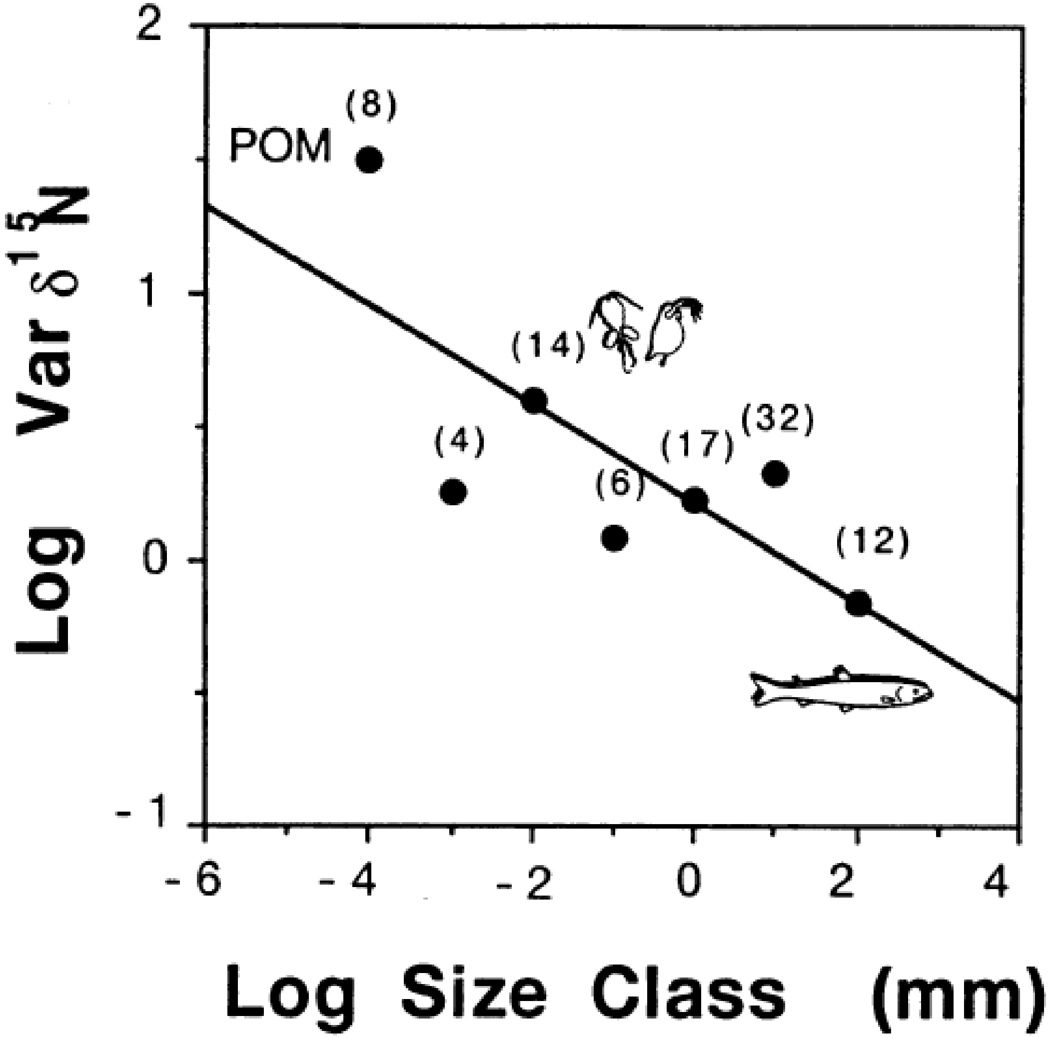
measured as: N_2

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‰)



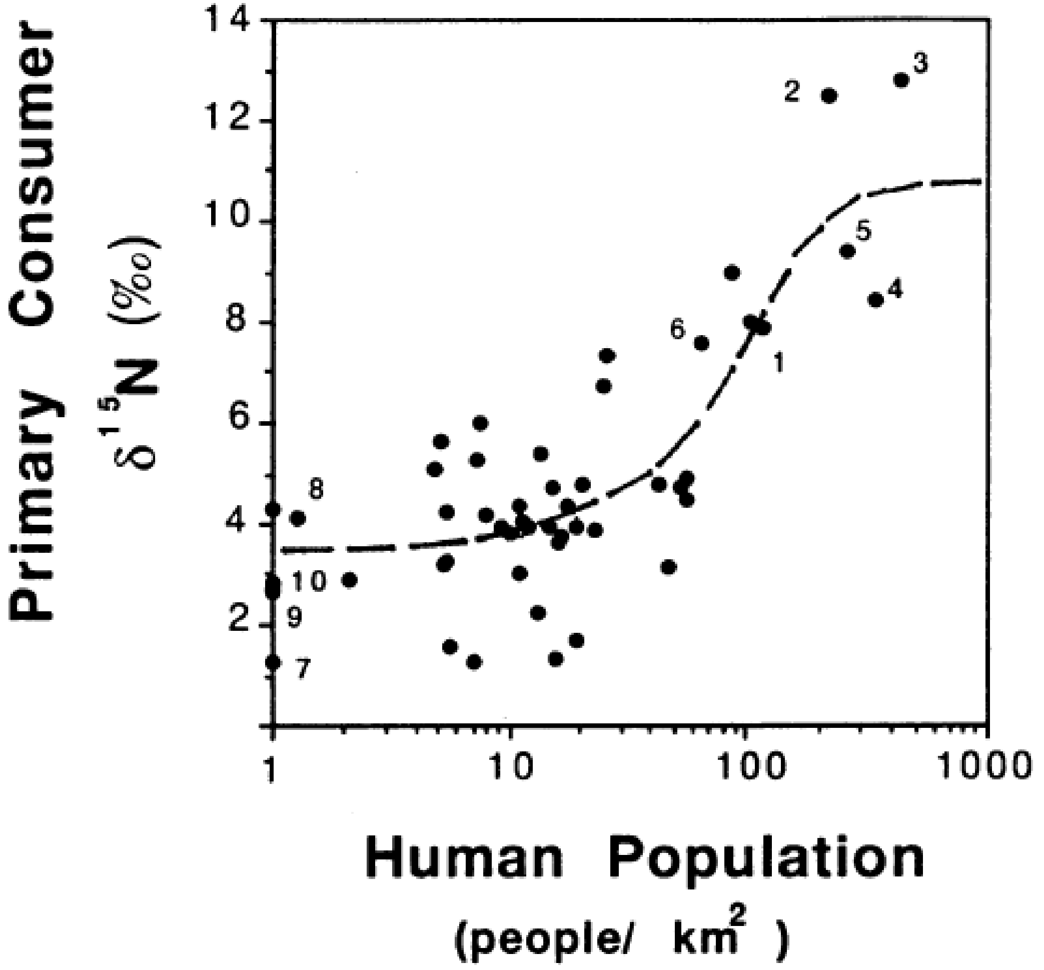
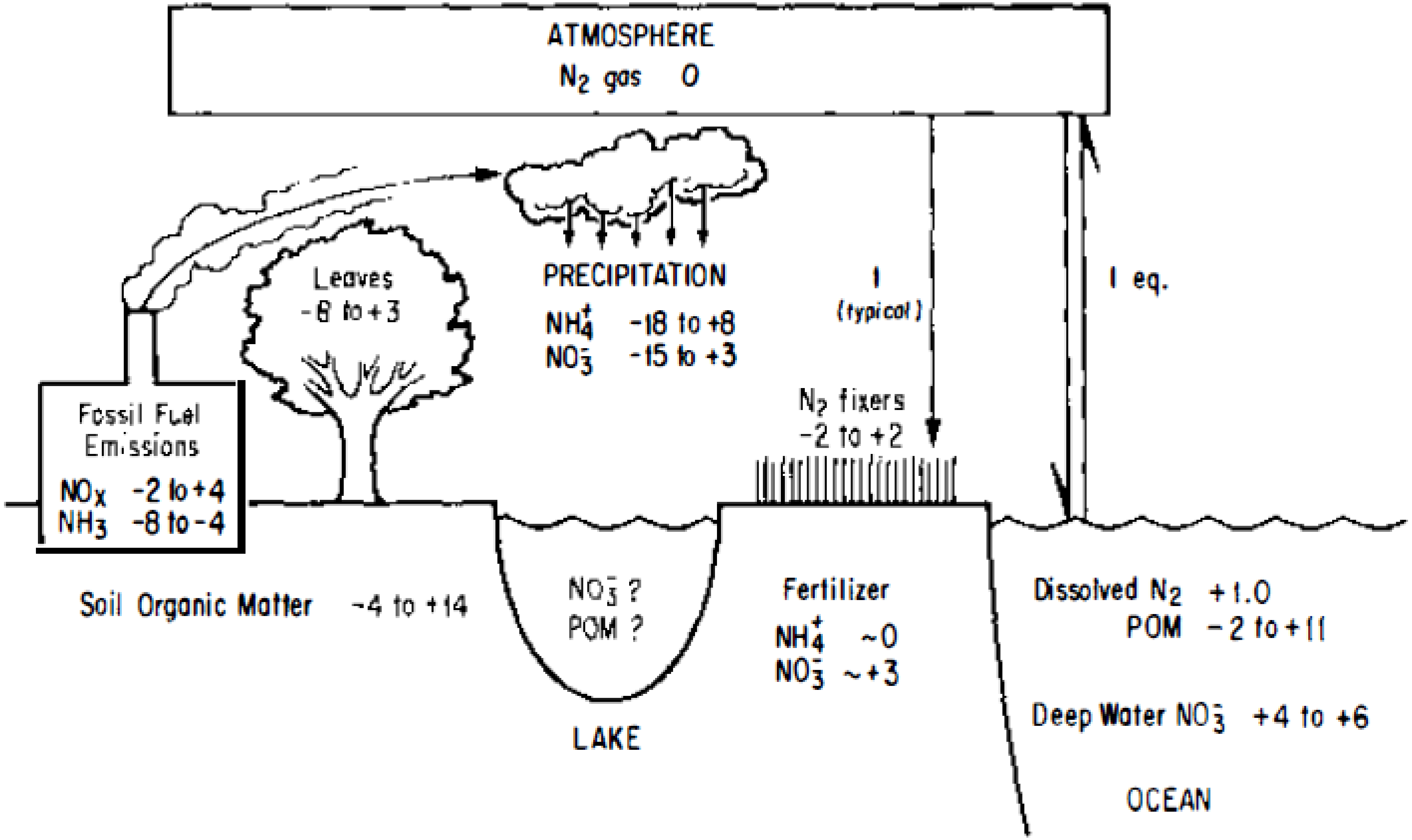
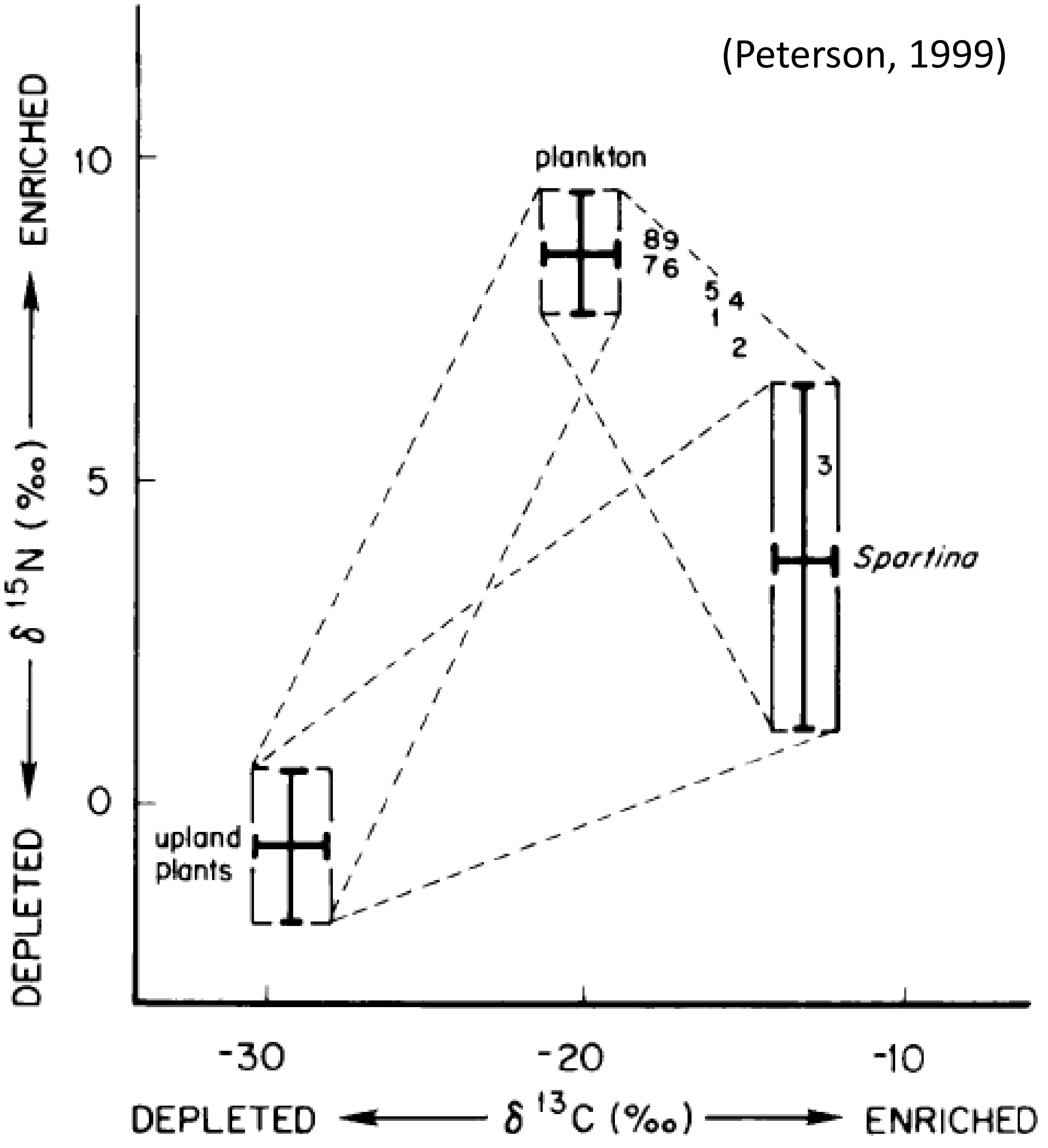
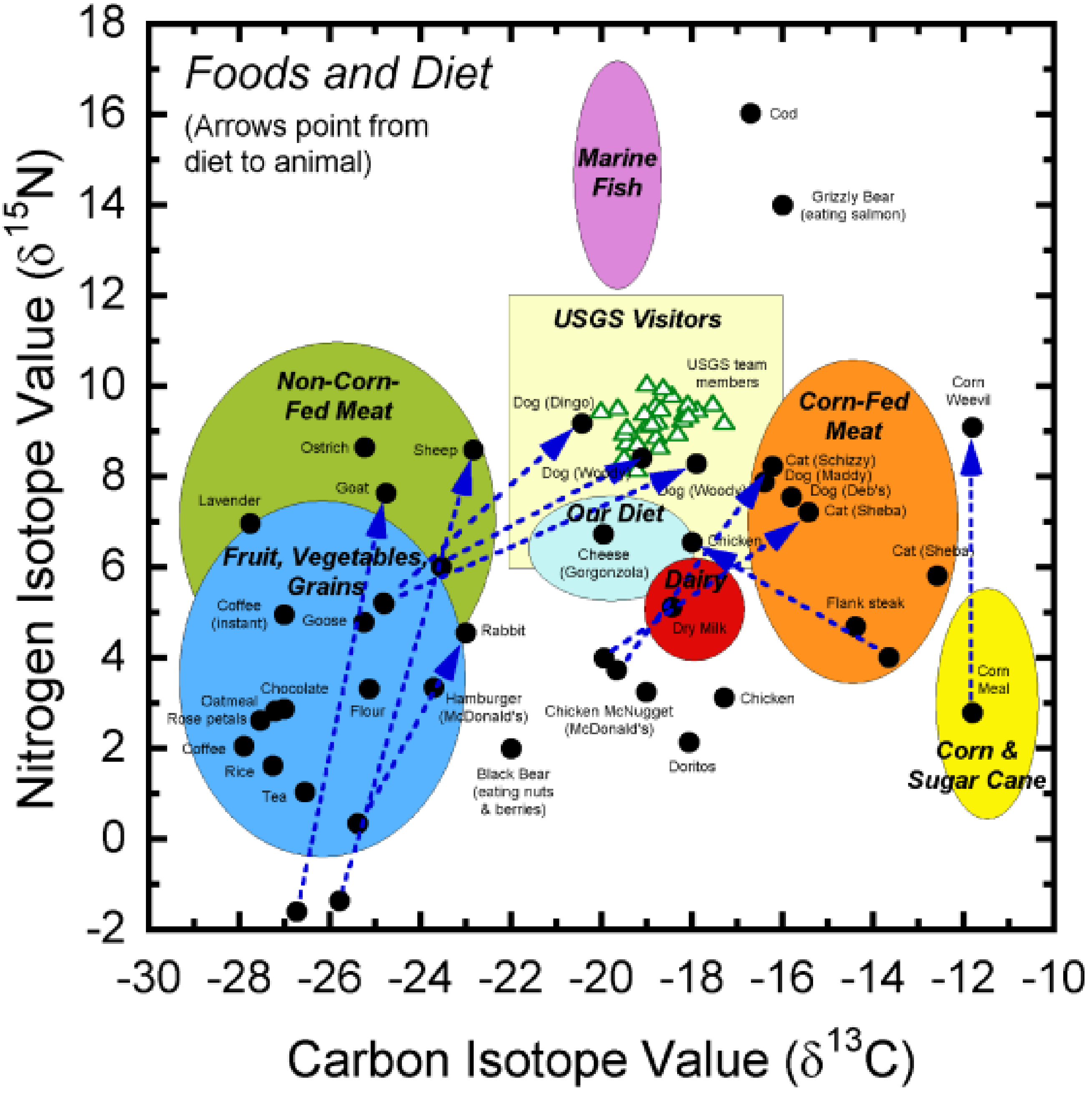


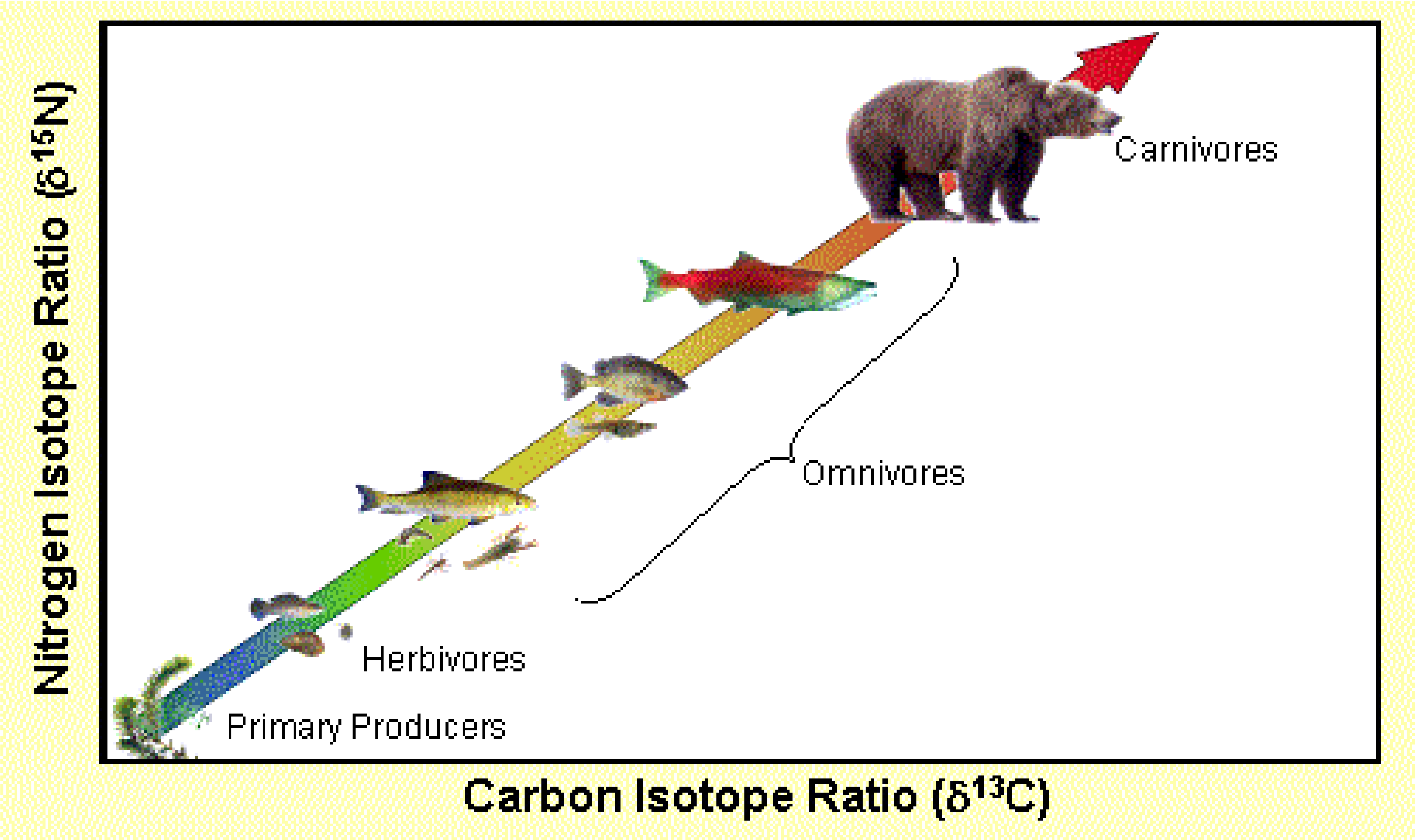
FIG. 2. Variation in the $\delta^{15}N$ signature of primary consumers


ATMOSPHERE
N2 gas 0
Leaves
-8 to +3
PRECIPITATION
NH4+ -18 to +8
NO3- -15 to +3
1
(typical)
1 eq.
Fossil Fuel
Emissions
NOx -2 to +4
NH3 -8 to -4
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 13C (‰) ⟶ ENRICHED
DEPLETED ⟵ δ 15N (‰) ⟶ ENRICHED


Foods and Diet
(Arrows point from diet to animal)
Marine Fish
Cod
Grizzly Bear (eating salmon)
USGS Visitors
USGS team members
Dog (Dingo)
Dog (Woody)
Dog (Woody)
Our Diet
Cheese (Gorgonzola)
Chicken
Dairy
Dry Milk
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)
Chicken McNugget (McDonald's)
Doritos
Chicken
Corn-Fed Meat
Cat (Schizzy)
Dog (Maddy)
Dog (Deb's)
Cat (Sheba)
Cat (Sheba)
Flank steak
Corn Weevil
Corn Meal
Corn & Sugar Cane
Nitrogen Isotope Value ($\delta^{15}N$)
Carbon Isotope Value ($\delta^{13}C$)
18
16
14
12
10
8
6
4
2
0
-2
-30
-28
-26
-24
-22
-20
-18
-16
-14
-12
-10

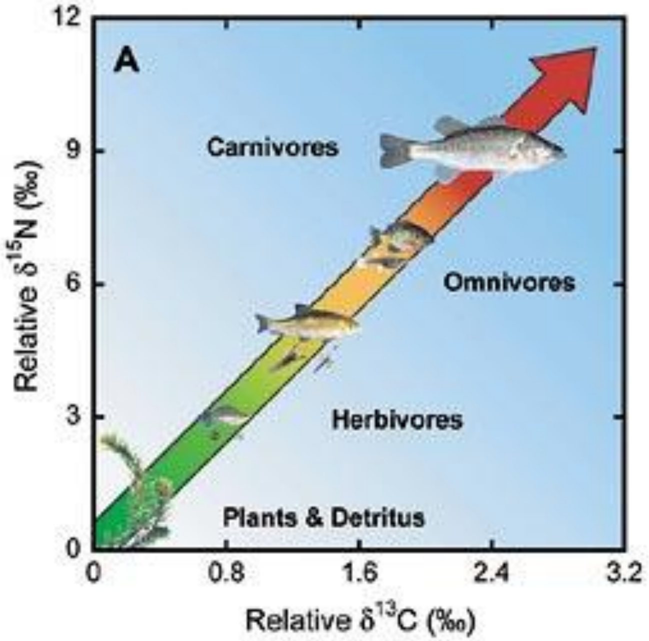

Nitrogen Isotope Ratio ($\delta^{15}N$)
Carnivores
Omnivores
Herbivores
Primary Producers
Carbon Isotope Ratio ($\delta^{13}C$)

Nitrogen isotopes in the food web

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

- -trophic enrichment generally borne out

model:



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

Data: