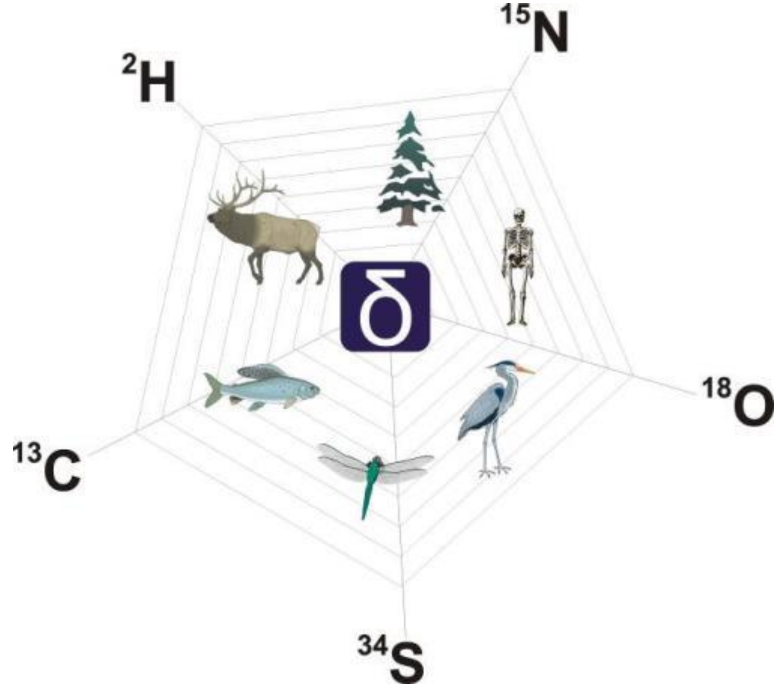
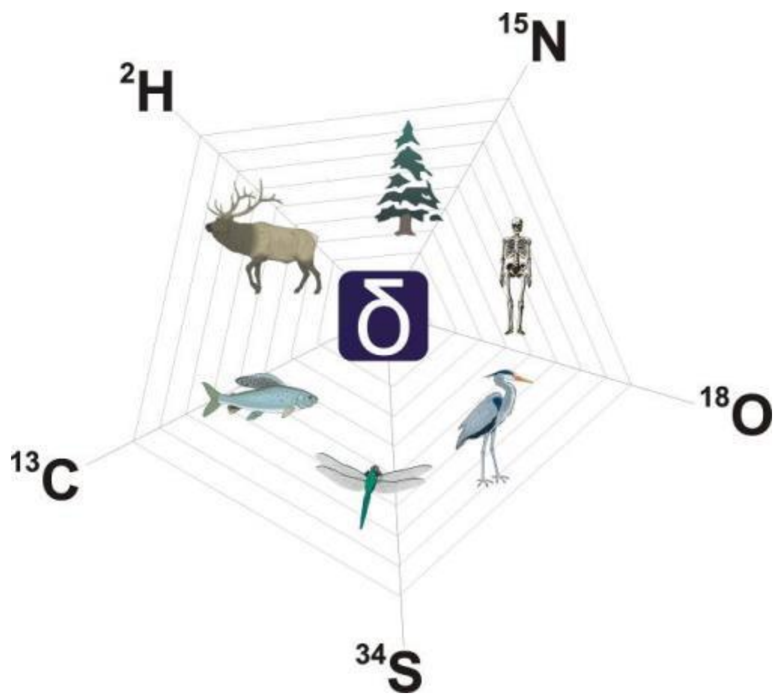
An overview of stable isotope applications to ecological and environmental studies (HOBSON)

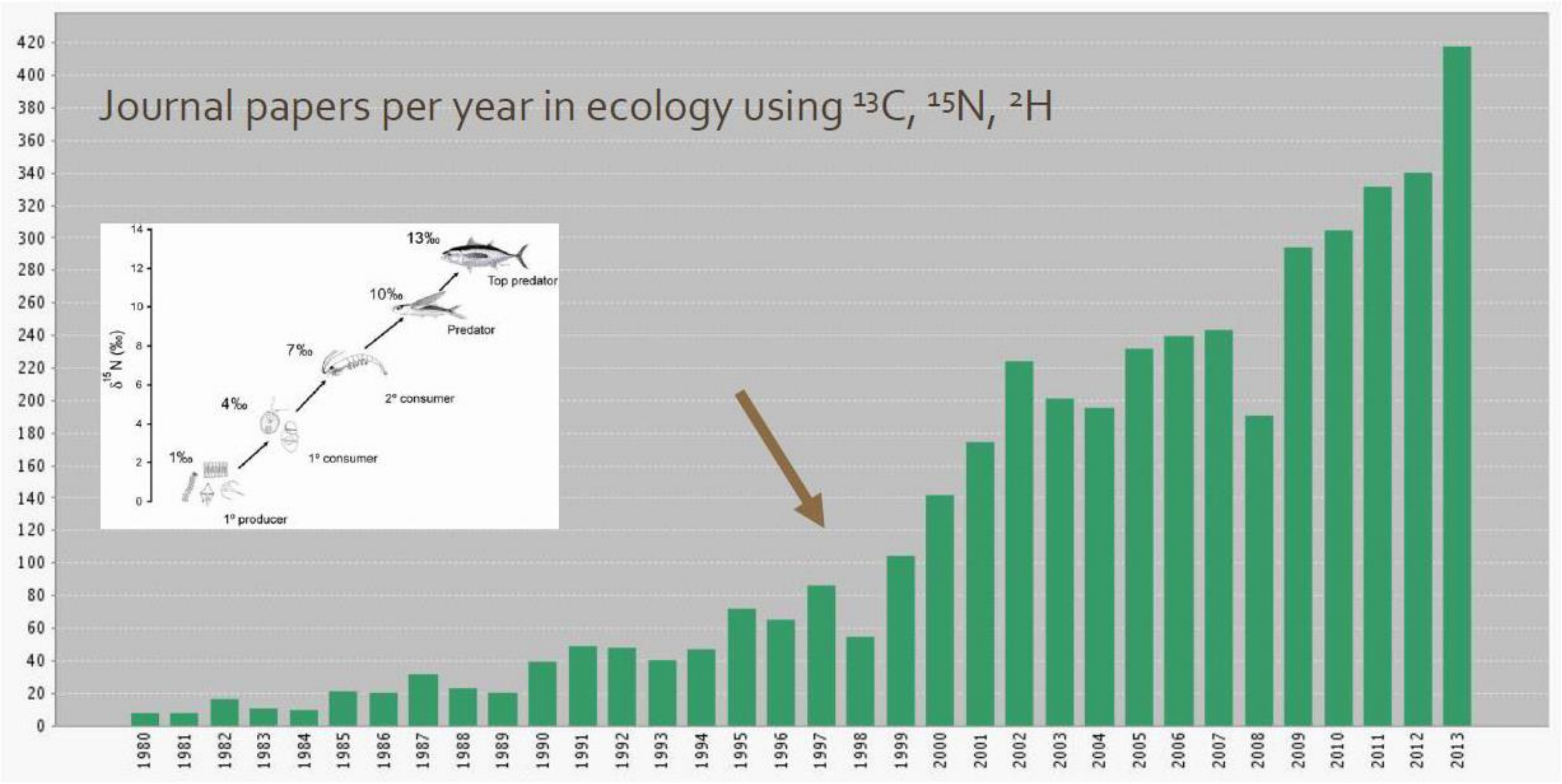


Overview
Hobson-1(Monday)

- What are stable isotopes?
- How are they measured?
- CNOHS
- Foodwebs
- Hydrology
- Migration



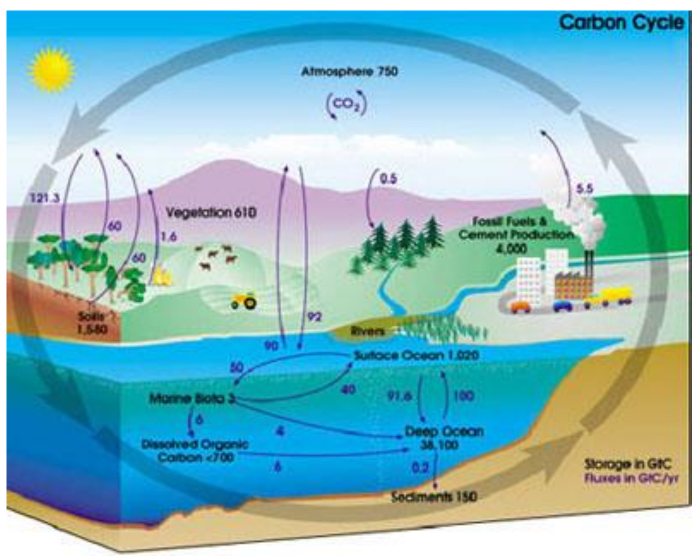
Why are we here?

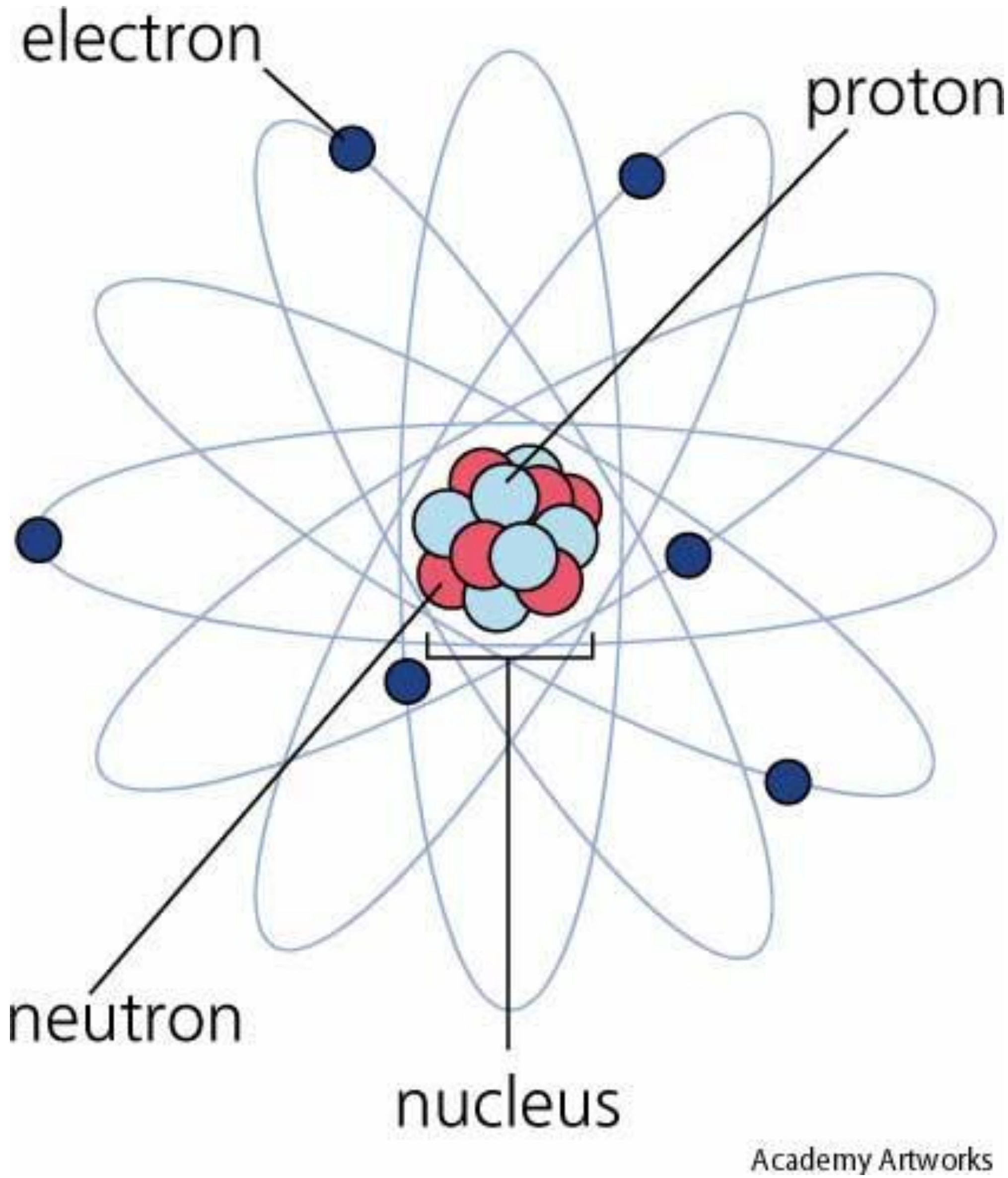


1980-2013: L. Wassenaar

Advantages:

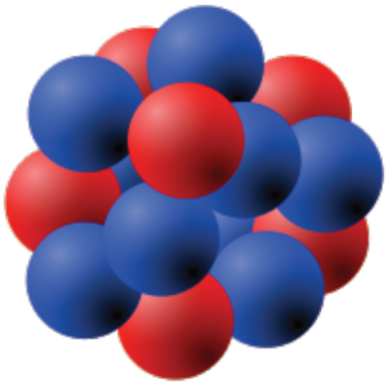
- Direct linkage between lithosphere, biosphere and atmosphere ….
- Principles are scale independent ….
- One of the few retrospective tools available..




electron
proton
neutron
nucleus
Academy Artworks

Atomic structure

A nucleus with
Z protons
N neutrons



Isotopes:

Nuclides of the same element (same Z) but different number of neutrons (N, and thus A=N+Z) are called **isotopes**.

Example: **carbon isotopes** (Z = 6, X = C):

Full notation: $^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$

Short notation: ^{12}C, ^{13}C, ^{14}C

Origins of elements and isotopes

- Hydrogen burning FUSION: $E = mc^2$
  - $^{1}H + {}^{1}H = {}^{2}H + \beta^{+} + \nu$ + 0.422 MeV
  - $^{2}H + {}^{1}H = {}^{3}He + \gamma$ + 5.493 MeV
  - $^{3}He + {}^{3}He = {}^{4}He + {}^{1}H + {}^{1}H$ + 12.859 MeV
- Helium burning
  - $^{4}He + {}^{4}He + {}^{4}He = {}^{12}C$

- CNO cycle
  - $^{12}C + {}^{1}H = {}^{13}N + \gamma$
  - $^{13}N = {}^{13}C + \beta^{+} + \nu$
  - $^{13}C + {}^{1}H = {}^{14}N$
  - $^{14}N + {}^{1}H = {}^{15}O$
  - $^{15}O = {}^{15}N + \beta^{+} + \nu$
  - $^{15}N + {}^{1}H = {}^{12}C + {}^{4}He$
- Carbon burning
  - $^{12}C + {}^{4}He = {}^{16}O$
- Oxygen burning
  - $^{16}O + {}^{4}He = {}^{20}Ne$
- Neon burning
  - $^{20}Ne + {}^{4}He = {}^{24}Mg$

Isotopologues

- Identical compounds having different isotopic species distributed among them.

Water (H_2O)

$H_2{}^{16}O$ (mass 18), $HD^{16}O$ (mass 19) and $H_2{}^{18}O$ (mass 20)

Carbon Dioxide (CO_2)

Mass 44 = $^{12}C^{16}O^{16}O$

Mass 45 = $^{13}C^{16}O^{16}O$, $^{12}C^{17}O^{16}O$, $^{12}C^{16}O^{17}O$

Mass 46 = $^{12}C^{18}O^{16}O$, $^{12}C^{16}O^{18}O$, $^{13}C^{17}O^{16}O$, $^{13}C^{16}O^{17}O$, $^{12}C^{17}O^{17}O$

Natural abundance of common light elements

Element	Isotope	Abundance	δ Range in ‰
Hydrogen	^{1}H	99.9844 %	D/ H = 700 ‰
	^{2}H (D)	0. 0156 %	
Oxygen	^{16}O	99.763 %	$^{18}O/^{16}O$ = 100 ‰
	^{17}O	0. 0375 %	
	^{18}O	0. 1995 %	
Carbon	^{12}C	98.89%	$^{13}C/^{12}C$ = 100
	^{13}C	1. 11%	
Nitrogen	^{14}N	99.64%	$^{15}N/^{14}N$=50
	^{15}N	0. 36%	
Sulfur	^{32}S	95.02%	$^{34}S/^{32}S$ = 100
	^{33}S	0.75%	
	^{34}S	4.21%	
	^{36}S	0.02%	

Some key characteristics

- Isotopologues generally have equal chemical properties.
- BUT their mass differences confer different physical properties.
  - Heavier isotopic molecules have lower mobility
  - Stronger binding energy
  - Fewer collisions
  - Lower diffusion energy

Measurement

Stable Isotope analysis

- Sample preparation
  - Chemically convert sample material (ie rocks, water, biological materials) into gas
  - Quantitative

- Measurement of isotope ratios
  - Mass spectroscopy
  - Laser cavity molecular spectroscopy

- Normalization of results
  - Laboratory references
  - International standards

$$\delta_{sample/V-SMOW/SLAP} = \frac{\delta_{sample/ws} - \delta_{V-SMOW/ws}}{\delta_{SLAP/ws} - \delta_{V-SMOW}} \times \delta_{SLAP}$$

Stable Isotope mass specs are gas-source

D/H	→	H_2
$^{18}O/^{16}O$	→	CO_2, CO, O_2
$^{13}C/^{12}C$	→	CO_2, CO
$^{15}N/^{14}N$	→	N_2
$^{34}S/^{32}S$	→	SO_2, SO, SF_6
$^{37}Cl/^{35}Cl$	→	CH_3Cl

Combust:

$$(C_6H_{10}O_5)_n + O_2 \longrightarrow CO_2 + H_2 0$$

$$(C_6H_{10}O_5)_n + C \longrightarrow CO + H_2$$

Reduce:

$$H_2 0 + Zn \longrightarrow H_2 + ZnO$$

React:

$$SiO_2 + BrF_5 \longrightarrow O_2 + SiF_2$$

$$O_2 + C \longrightarrow CO_2$$

Equilibrate:

$$C^{16}O_2 + 2H_2{}^{18}O \longrightarrow C^{16}O^{18}O + 2H_2{}^{16}O^{18}O$$

Purification

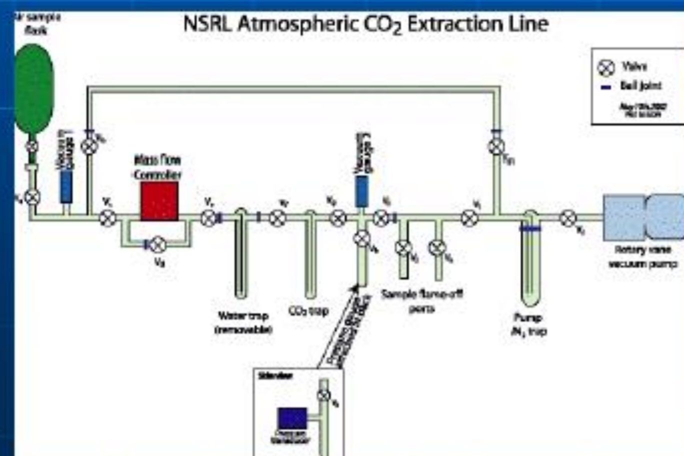
Vacuum lines

Cryogenic (LN2) traps for separation of gasses

Reaction vessels for chemical reactions in vacuum

Usually used in conjunction with "off-line" isotope analysis

Necessary for some analyses ie silicate analyses



Gas Chromatography

Uses a GC column to separate gasses

He

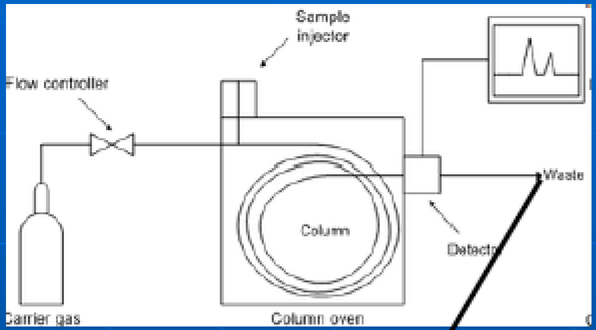
TCD detectors

usually in a singe instrument as a preparatory inlet to a mass spectrometer

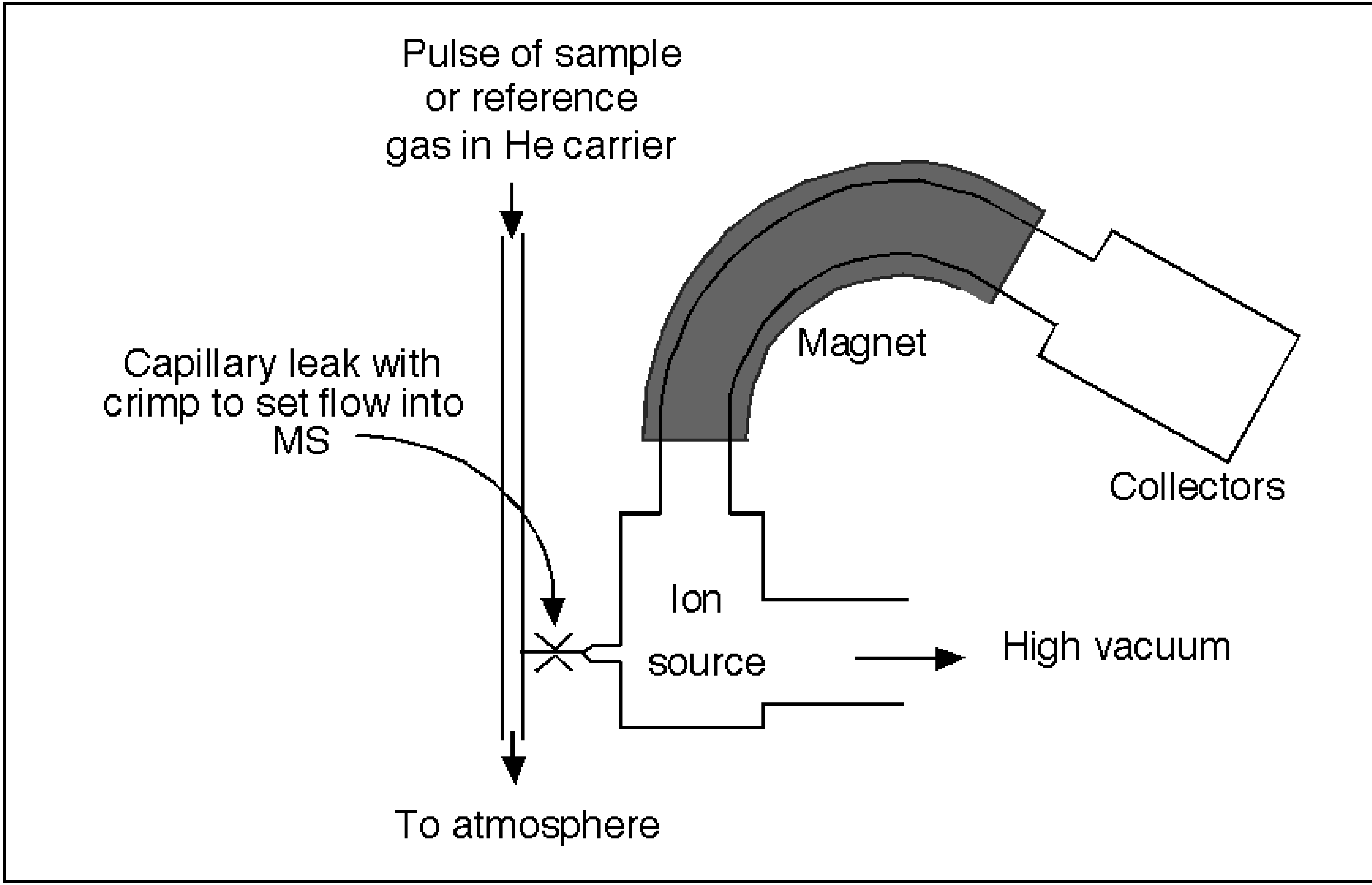
Combustion/Reduction

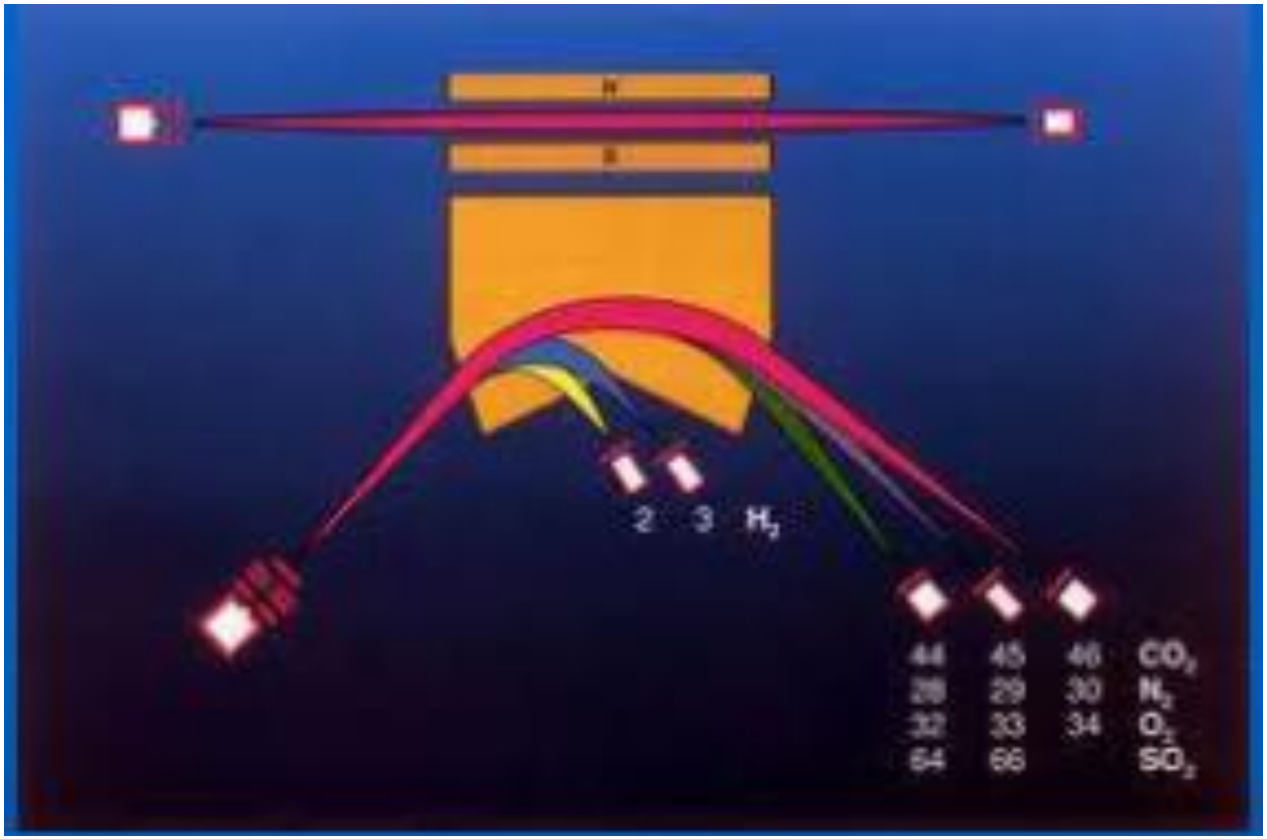
Automation

"On-Line"



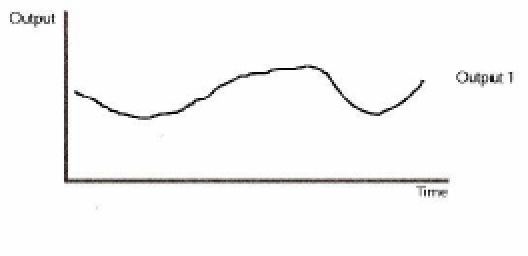
Mass
Spec

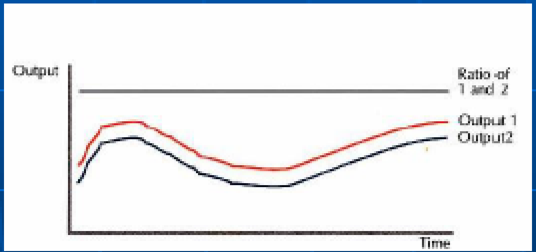

Pulse of sample
or reference
gas in He carrier
Capillary leak with
crimp to set flow into
MS
Magnet
Collectors
Ion
source
High vacuum
To atmosphere


2 3 H2
44 45 46 CO2
28 29 30 N2
32 33 34 O2
64 66 SO2

How do we get the highest accuracy and precision?

(1) Ratio measurement: measuring ratios makes life easier

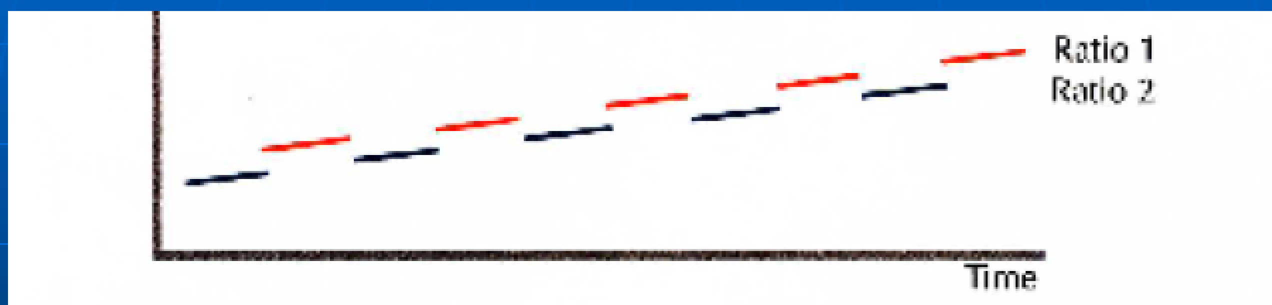




Isotope 1 and isotope 2 being measured at the same time, precision and accuracy of the ratios are independent of the signal stability.

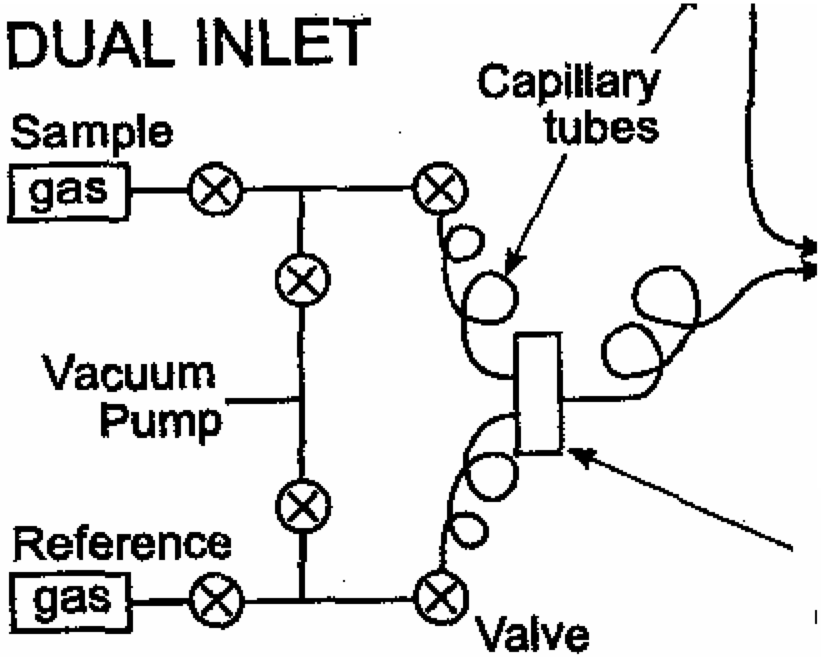
How do we get the highest accuracy and precision?

(2) Difference measurement:
measuring the difference between sample and reference makes life easier

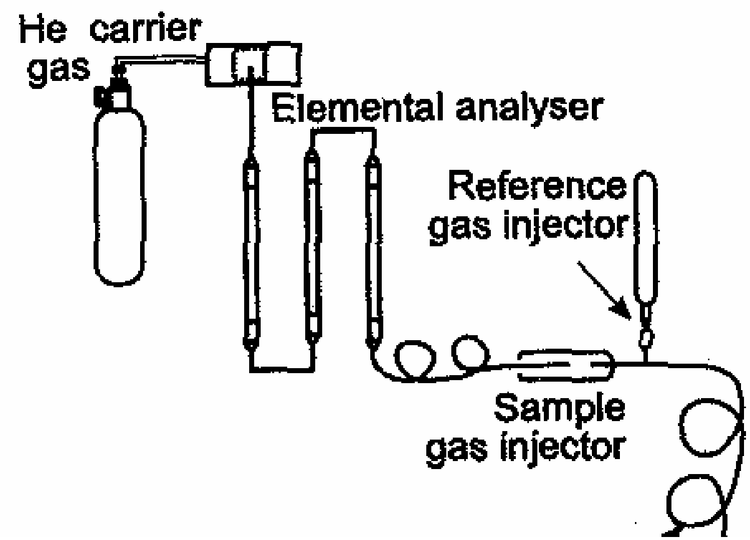


By measuring relative differences, the highest precision can be achieved

DUAL INLET



CONTINUOUS FLOW
INLET



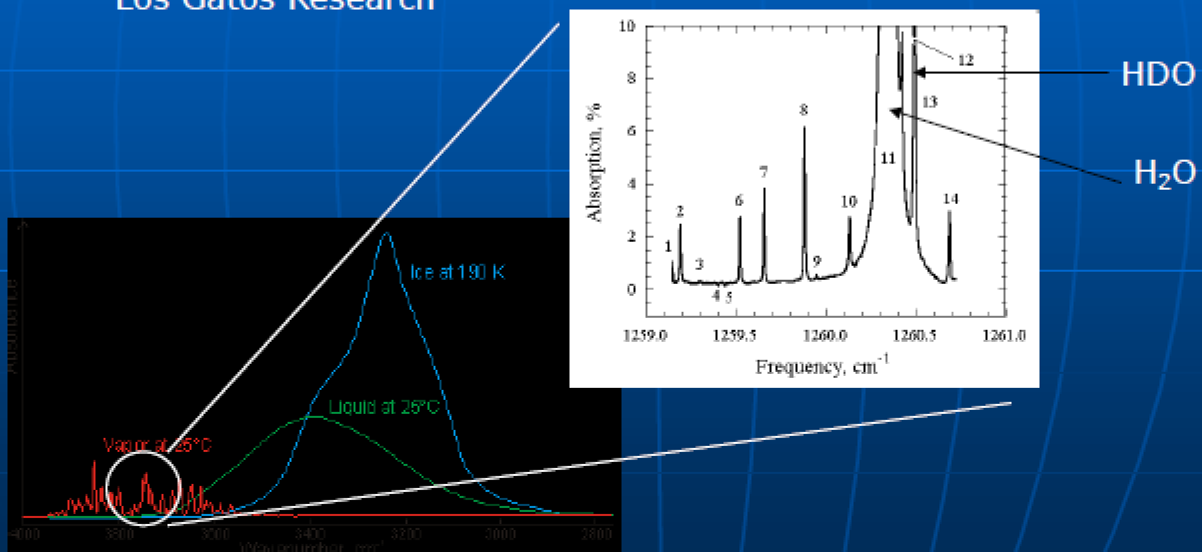
Dual Inlet vs Continuous Flow

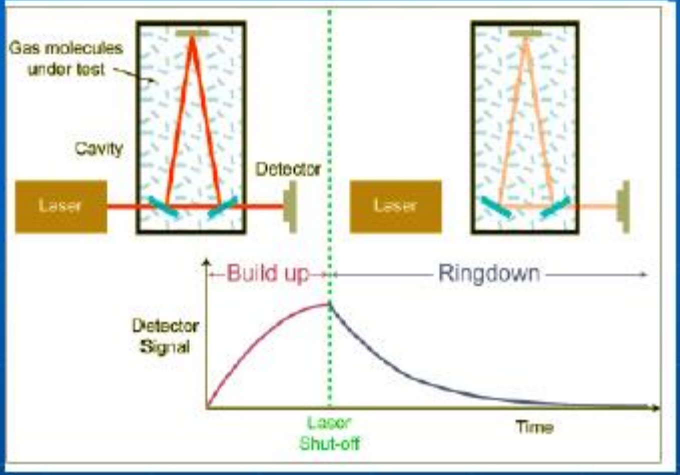
- Dual Inlet
  - Compares reference gas to sample gas many times (say n=8)
  - Precision high
  - Sample size requirements high
  - Throughput is slow
  - Offline preparation of sample needed
- Continuous flow
  - Compares reference to sample ONCE
  - Lower precision
  - Low sample size
  - Throughput high
  - No offline prep.

Optical Methods

Two Competing technologies:

1. Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS)
   Picarro Inc
2. Off-axis integrated cavity output spectroscopy (OA-ICOS)
   Los Gatos Research





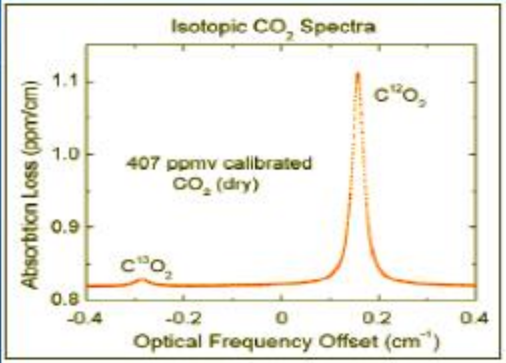
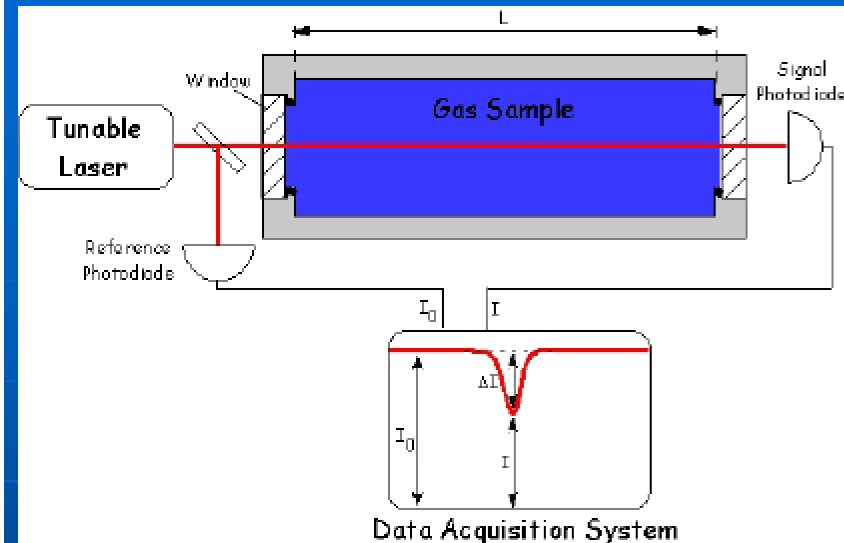
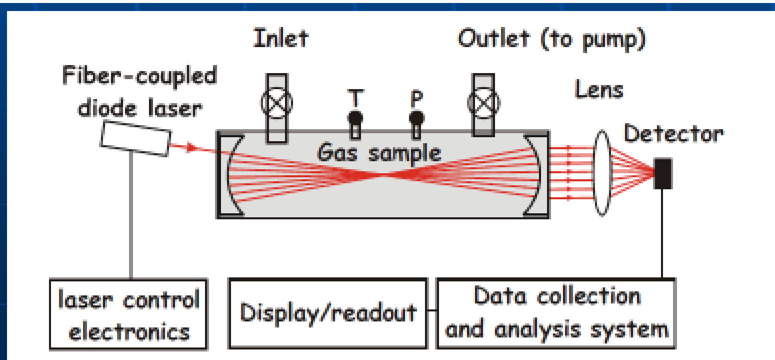


Figure 4. High resolution infrared absorption spectrum of CO_2 isotopes, recorded by a WS-CRDS instrument.



Beers Law: $\Delta I/I_o = 1\text{-}\exp(-\alpha L)$



- Absorption spectrometry is a direct measure of concentration
- Very selective - C2H2 absorbs light between 1510 - 1545 nm
- Fast – laser can be reproducibly swept at > 100 Hz
- For a 1 meter sample containing 100 torr of 1 ppm acetylene, ΔI/I0 ~ 10-5
- Increase pathlength by (1-R)-1 ~ 10,000 times, giving several kilometers of effective path
- Single-pass ΔI/I0 ~ 10-5 □ Multipass ΔI/I0 ~ 10-1 (a considerable absorption)

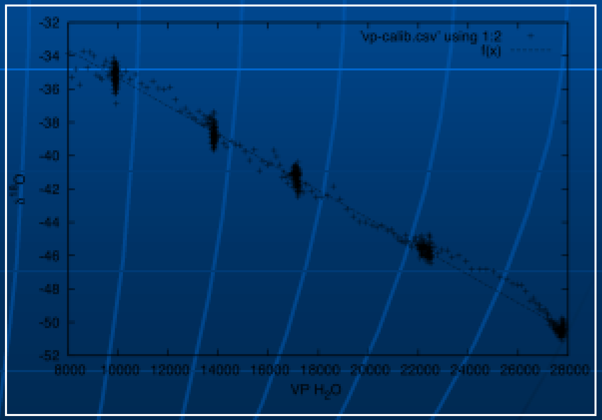
Pros - cons

Pros

- Do one thing really well – eg H2O
- No compressed gasses
- No moving parts
- Cheap
- Simple mechanically

Cons

- Do one thing
- Difficult to calibrate
- Like IRMS – instrumental effects



Stable isotope measurements

1950's

1960's

1970's

1990's

2000's

Isotope notation and fractionation

- δ notation (in "parts per thousand" or "permil")

$$\delta^{H}X = [(R_{sample}/R_{standard} - 1)] * 1000$$

Where H = heavy isotope mass, X = element,
R = ratio of heavy to light isotope of the element

Natural ranges in isotope ratios:
ca. 600‰ for $\delta^{2}H$
ca. 100‰ for $\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$
ca. 30‰ for $\delta^{15}N$

Further notes on δ notation

- Values can be positive or negative.
- Linearly related to percent (%) abundance of the heavier isotope.
- Convenient (i.e. 1% change in abundance is 10‰).
- δ notation is not "exact" in all mathematical applications and isotopic ranges and Atom Percent (^{H}AP), Fractional (F) and Ratio (R) nomenclature is typically used (see Fry chapter).
- However, as Biologists, δ-notation will cover all your needs unless you delve into "spiking" experiments!

Stable Isotope Standards

Standards by definition have a 0‰ value of the δ-scale.

Internal lab standards must be corrected to International reference standards.

International reference materials are distributed by

US National Institute of Standards and Technology (NIST) and

International Atomic Energy Agency (IAEA).

NIST: <www.nist.gov>

IAEA: <www.iaea.or.at >

Primary Reference Materials

VSMOW/2 - Vienna Standard Mean Ocean Water	$D/H = 155.76 \times 10^{-6}$
VSMOW/2 - Vienna Standard Mean Ocean Water	$^{18}O/^{16}O = 12005.2 \times 10^{-6}$
PDB - Pee Dee Belemnite (exhausted, now calculated using $\delta^{18}O_{VSMOW}$=30.91 ‰	$^{18}O/^{16}O = 2067.2 \times 10^{-6}$
PDB - Pee Dee Belemnite	$^{13}C/^{12}C = 1123.75 \times 10^{-5}$
Air / (NBS- 14)	$^{15}N/^{14}N = 367.6 \times 10^{-5}$
CDT - Canyon Diablo Troilite	$^{34}S/^{32}S = 449.94 \times 10^{-4}$

Isotope fractionation factor (α)

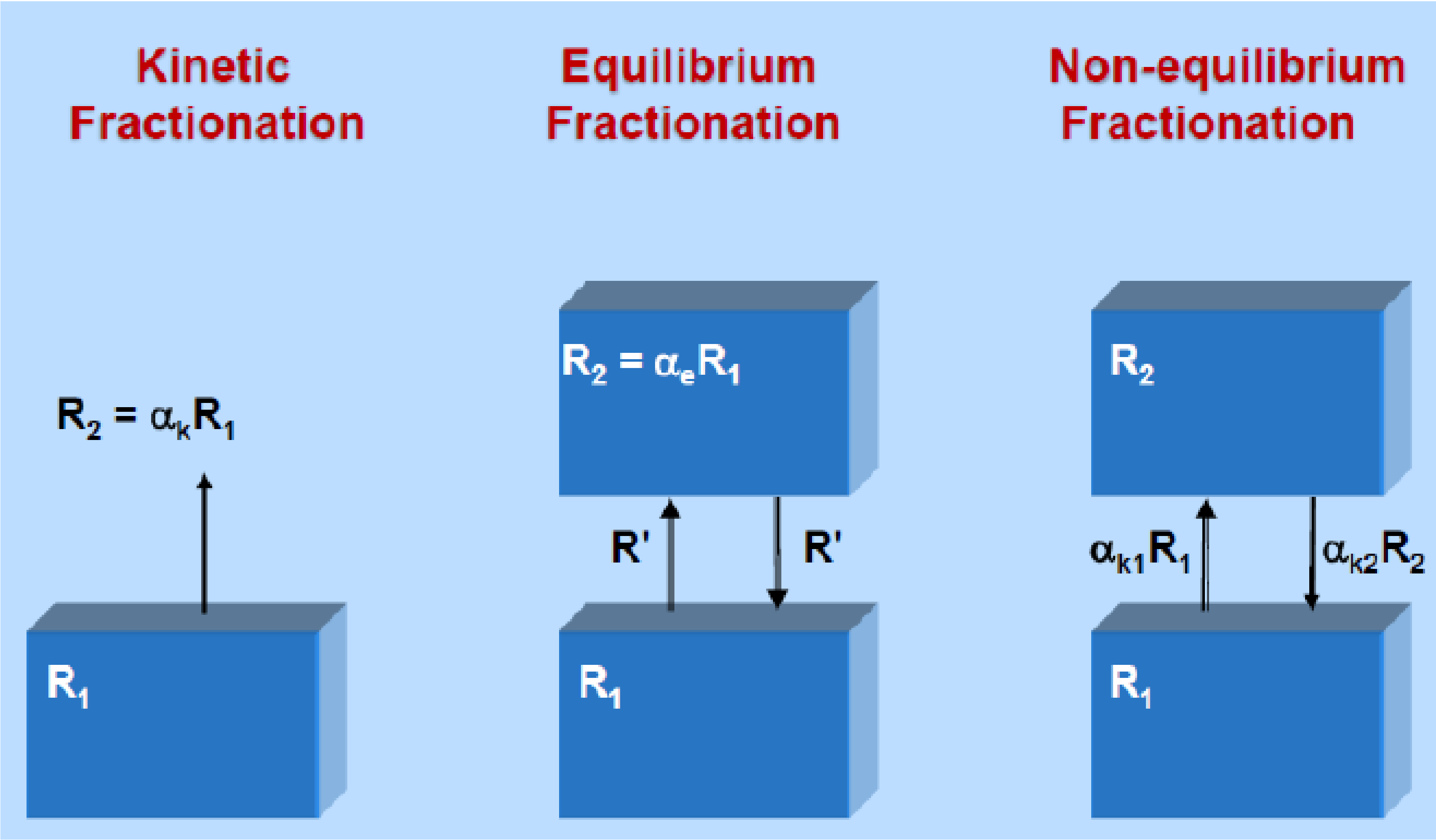
- A term to describe the partitioning of isotopes.
- Due to difference in rates of reaction for different molecular species.

$$\alpha = R_{reactant} / R_{product}$$

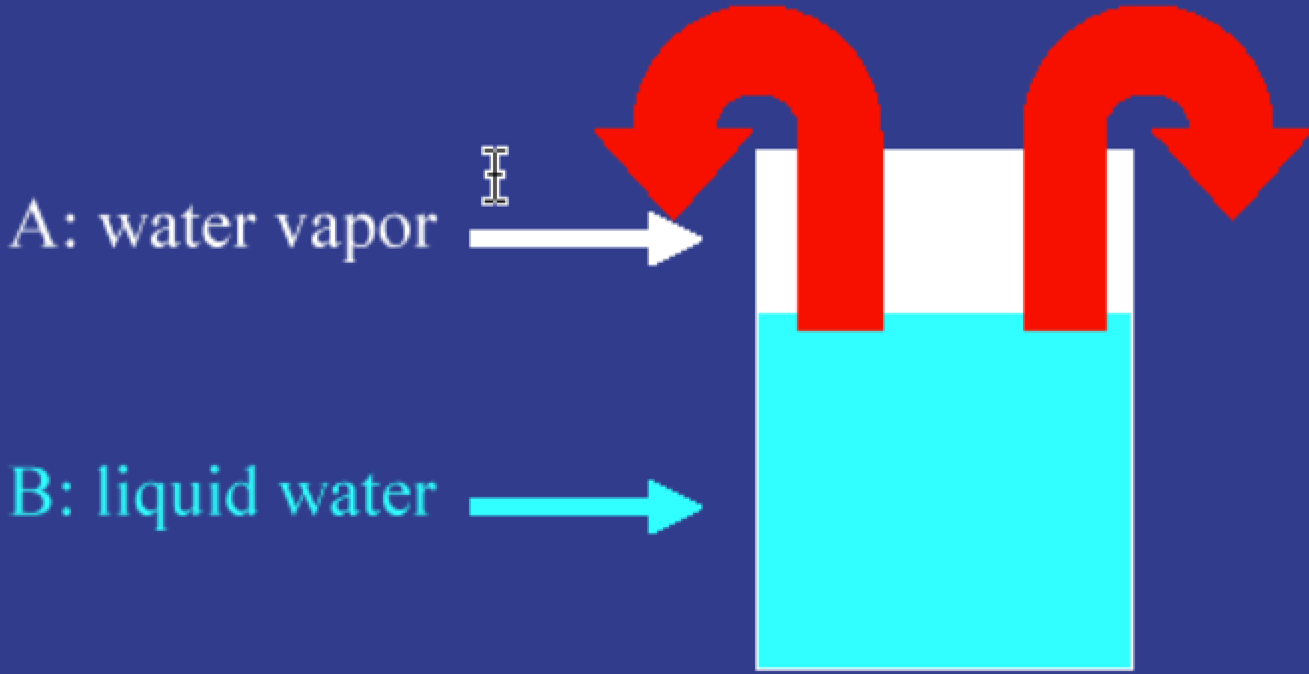
$$\alpha^{18}O_{water\text{-}vapor} = (^{18}O/^{16}O_{water} / \ ^{18}O/^{16}O_{vapor})$$

Sources of fractionation

- Kinetic or non-equilibrium
  - Diffusion: “lighter is faster”
  - Evaporation: “lighter is preferred”
  - Kinetic effects: “lighter bonds break first”
  - Metabolic effects: e.g. respiration, photosynthesis.
- Equilibrium
  - Ratios can differ among several equilibrium phases (e.g. water-vapor).

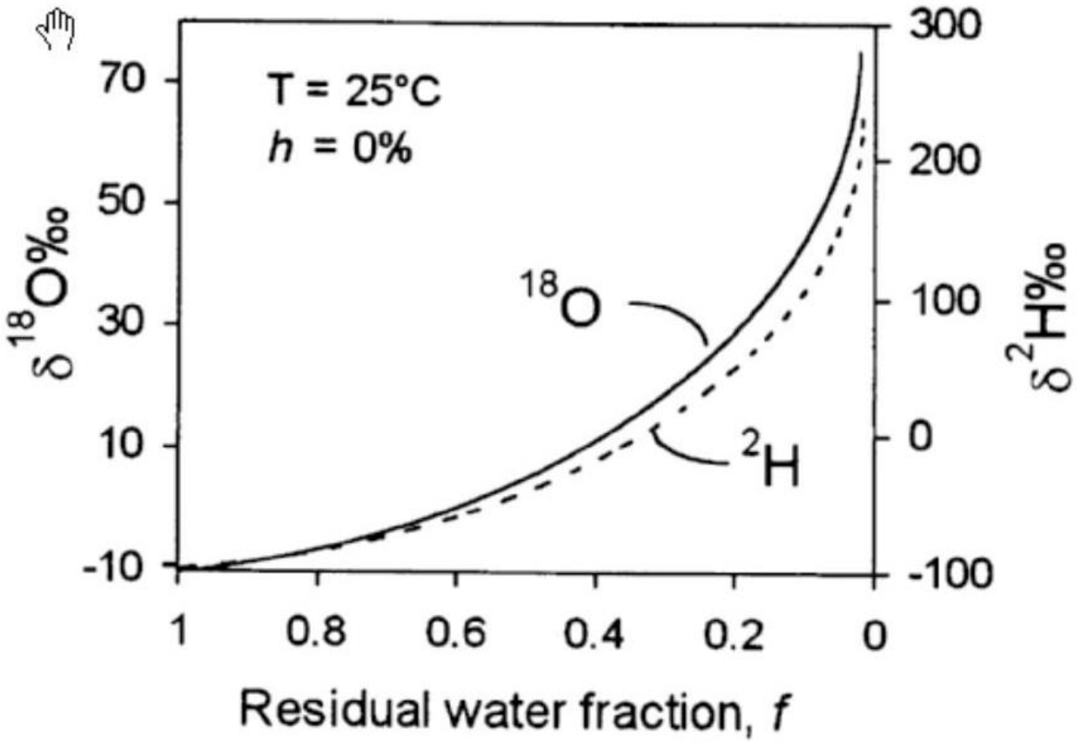


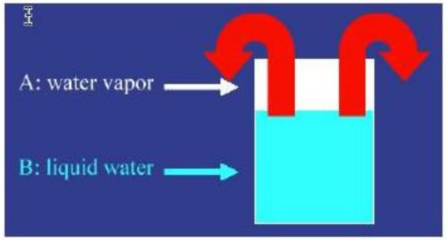
Kinetic Fractionation
Equilibrium Fractionation
Non-equilibrium Fractionation
$R_2 = \alpha_k R_1$
R_1
$R_2 = \alpha_e R_1$
R'
R'
R_1
R_2
$\alpha_{k1} R_1$
$\alpha_{k2} R_2$
R_1



$$\alpha_{A-B} = R_A / R_B = \overbrace{{}^{2}H / {}^{1}H_a}^{\text{vapor}} \Big/ \underbrace{{}^{2}H / {}^{1}H_b}_{\text{liquid}}$$

Rayleigh Distillation

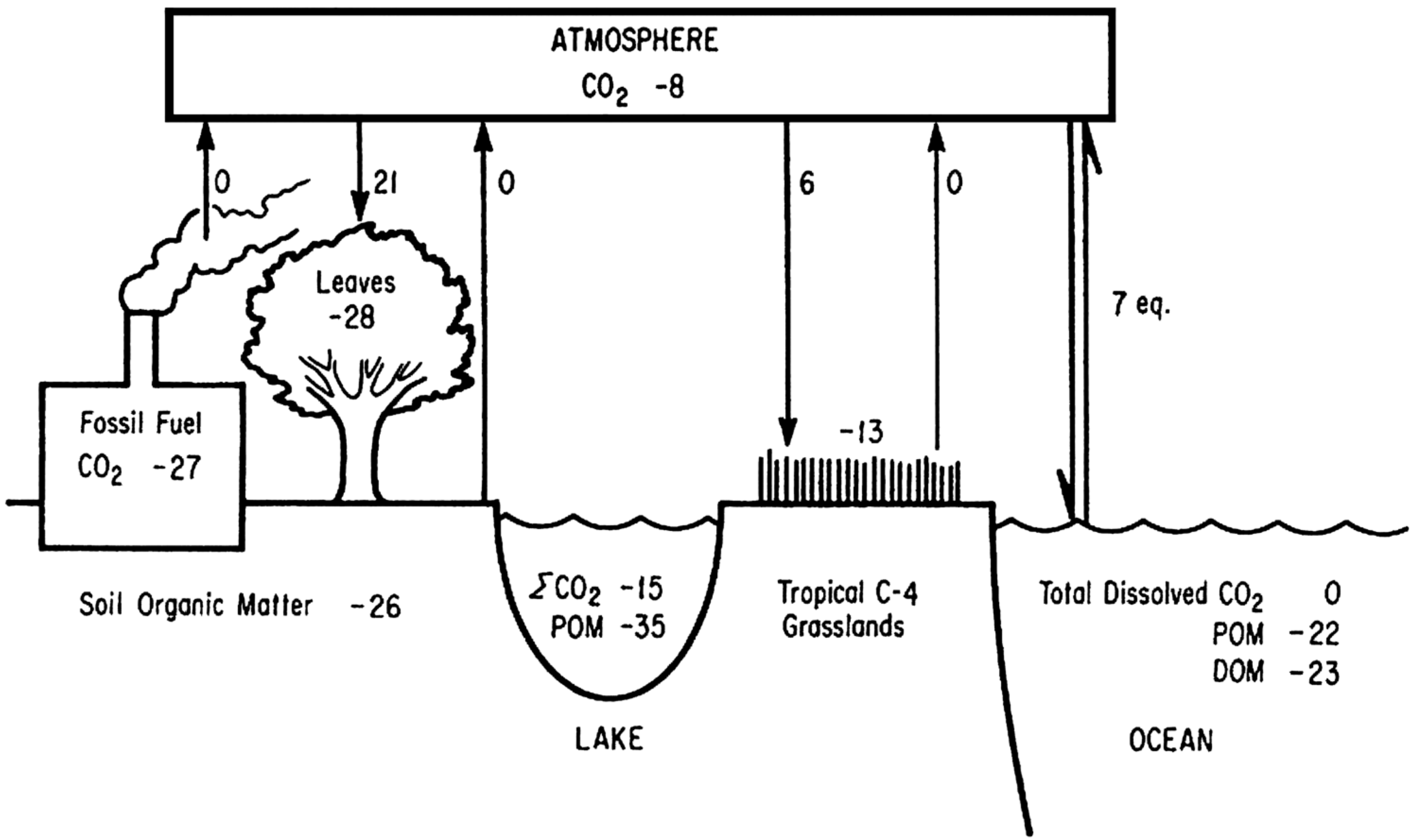




Some examples of isotopic fractionations in the Biosphere

- Elements and isotopes circulate in the atmosphere and *fractionation* and *mixing* bring about characteristic isotope distributions.
- Large (well buffered) pools provide points of "stability"
  - E.g. Ocean (H,O,S,C), atmosphere (N).
- Fractionation is the agent of change.
- Plants, microbes fix nutrients and change isotope distributions for C,N,S.

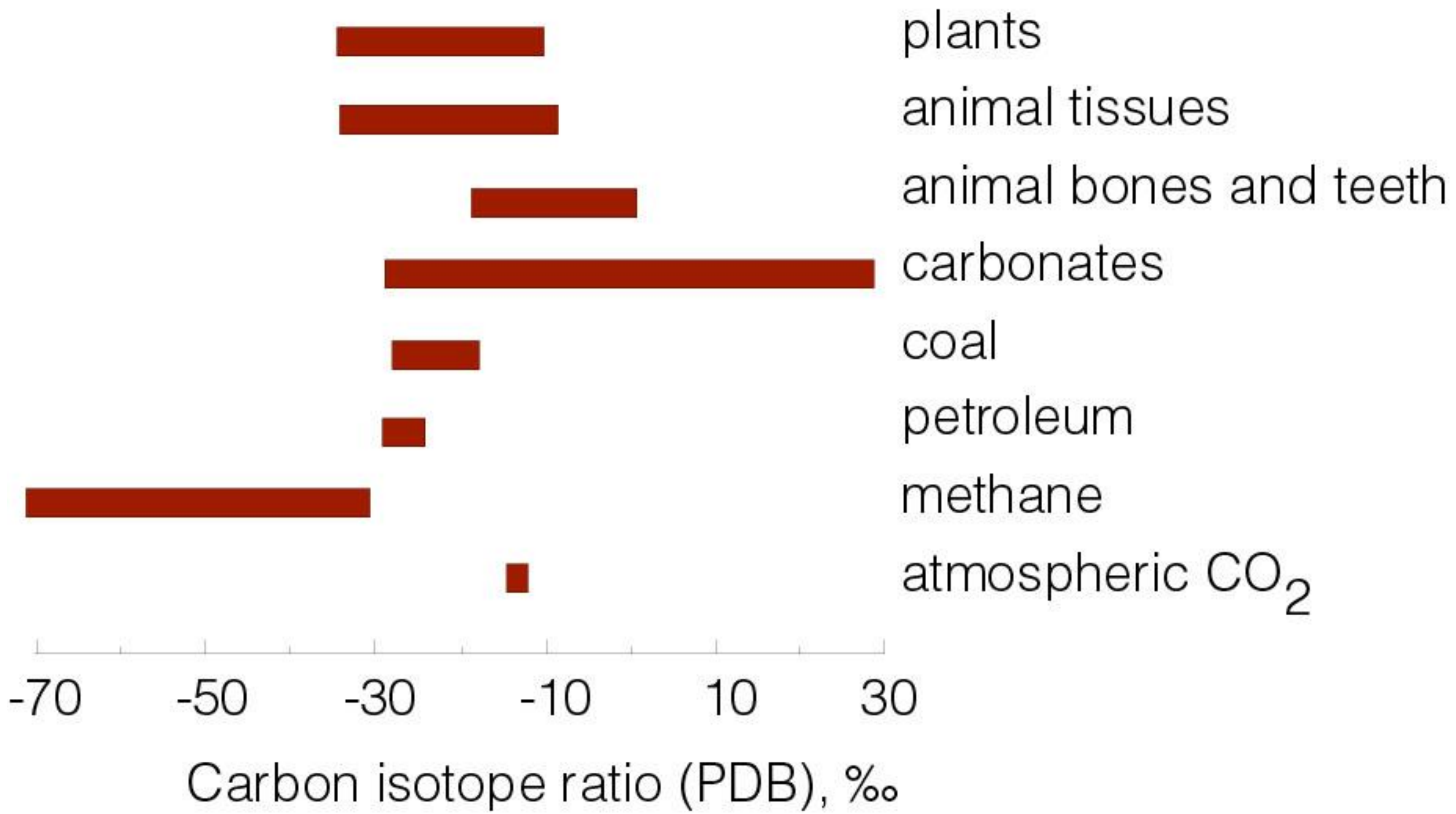
Carbon


ATMOSPHERE
CO_2 -8
0
21
0
6
0
7 eq.
Leaves
-28
Fossil Fuel
CO_2 -27
-13
Soil Organic Matter -26
ΣCO_2 -15
POM -35
Tropical C-4
Grasslands
Total Dissolved CO_2 0
POM -22
DOM -23
LAKE
OCEAN

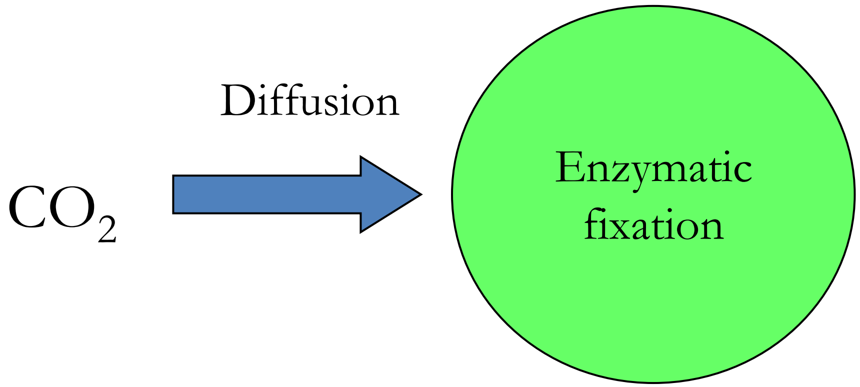
Carbon cycle

- Active exchanges between atmosphere, terrestrial ecosystems, sea surface.
- Atmospheric CO_2 (~-8 $^{o}/_{oo}$)
- C3 Photosynthesis ~-20 $^{o}/_{oo}$ fractionation (-28 $^{o}/_{oo}$ plant tissue).
- C4, CAM Photosynthesis ~-5 $^{o}/_{oo}$(-13 $^{o}/_{oo}$).
- Ocean: dissolved CO_2 ~ +8 $^{o}/_{oo}$, bicarbonate production ~ 0 to +1 $^{o}/_{oo}$.
- Planktonic photosynthesis ~-20 $^{o}/_{oo}$.

What is the typical range of δ values?



Plant C fixation



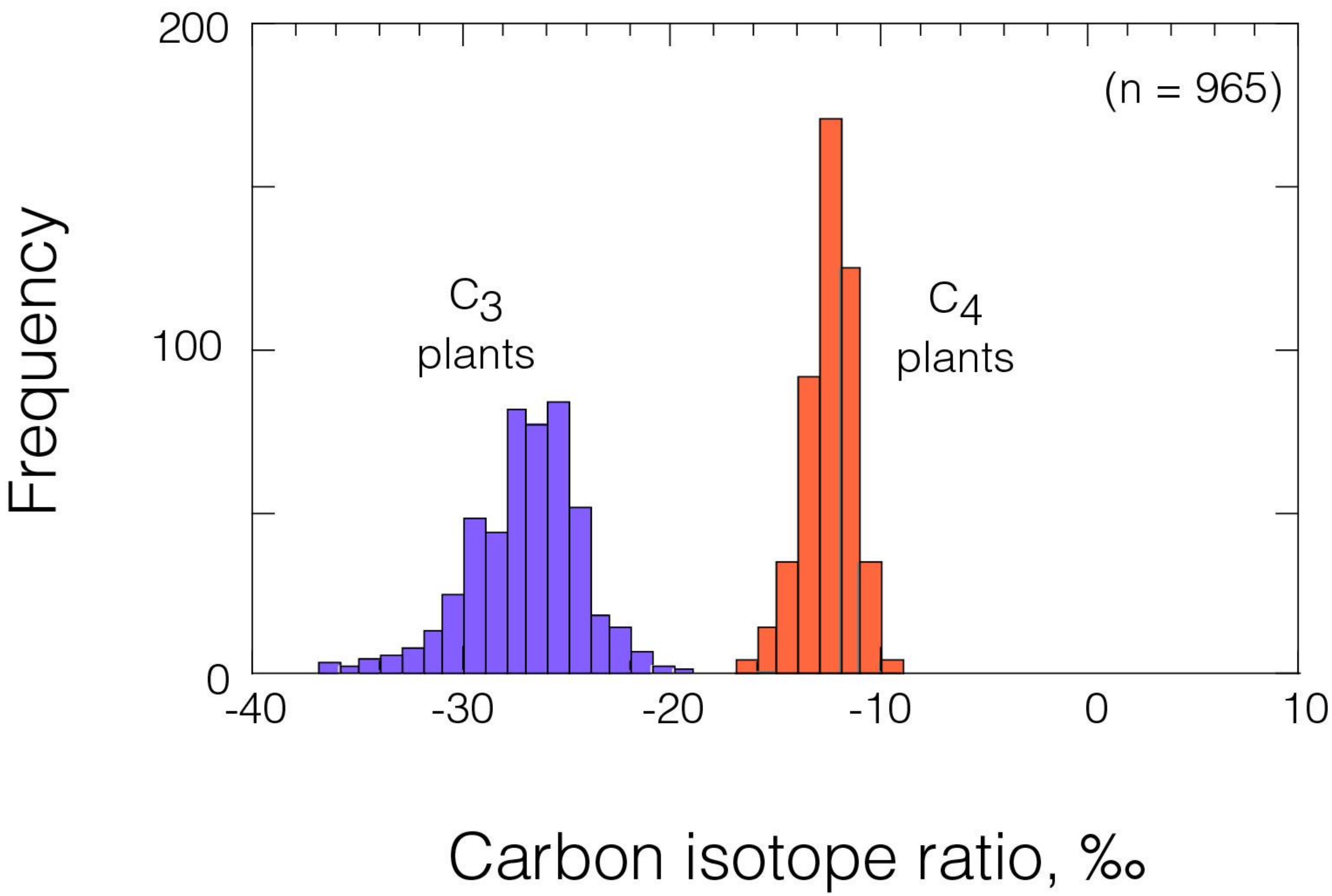
C3: Calvin cycle, RUBISCO
ribulose biphosphate carboxylase

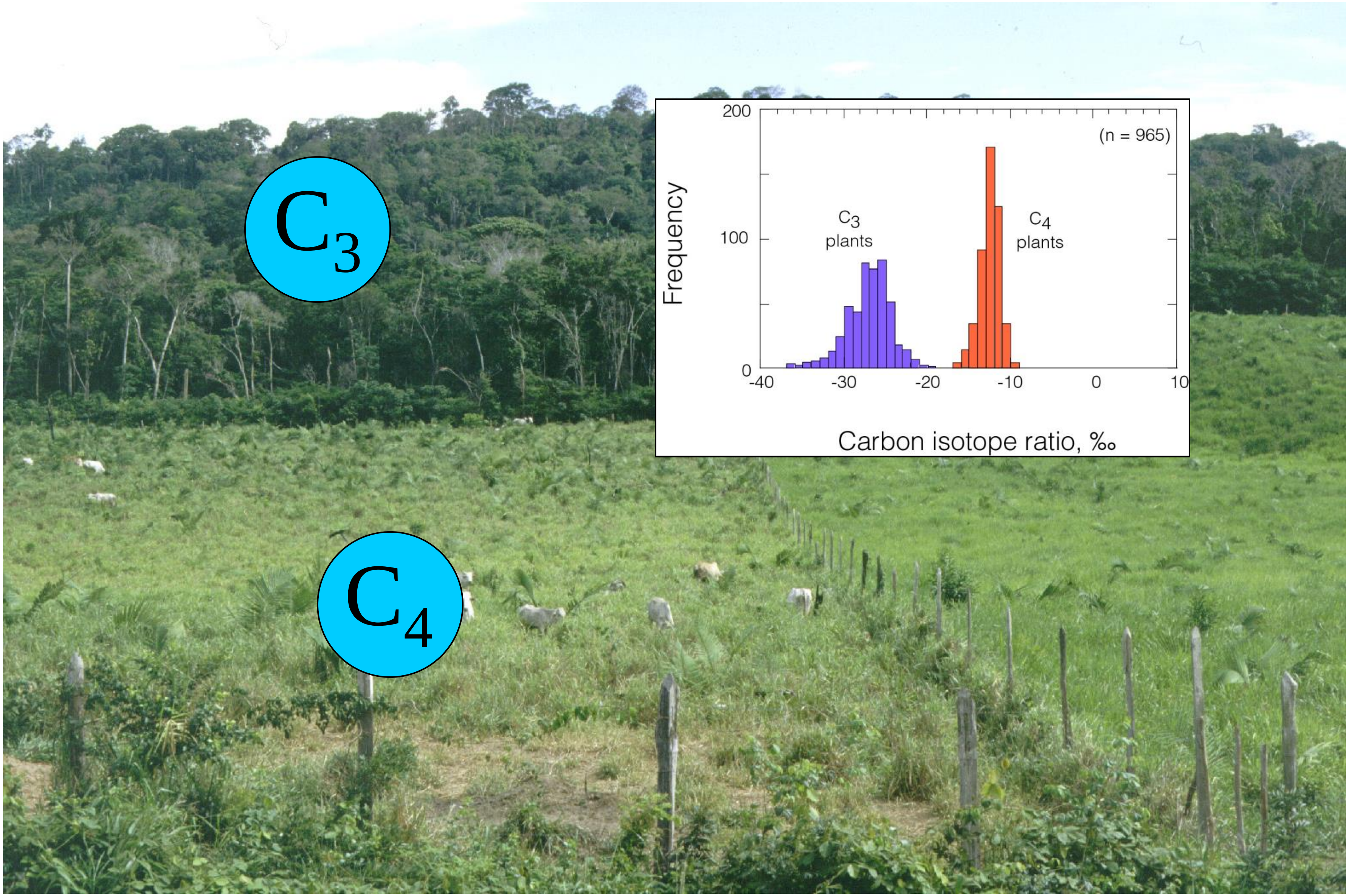
Diffusion $\Delta\delta$ = ~-4 $^{o}/_{oo}$
Rubisco $\Delta\delta$ = ~-29 $^{o}/_{oo}$

C4: Hatch-Slack cycle, PEP
Phosphoenolpyruvate carboxylase

Diffusion $\Delta\delta$ = ~4 $^{o}/_{oo}$
Rubisco $\Delta\delta$ = ~6 $^{o}/_{oo}$

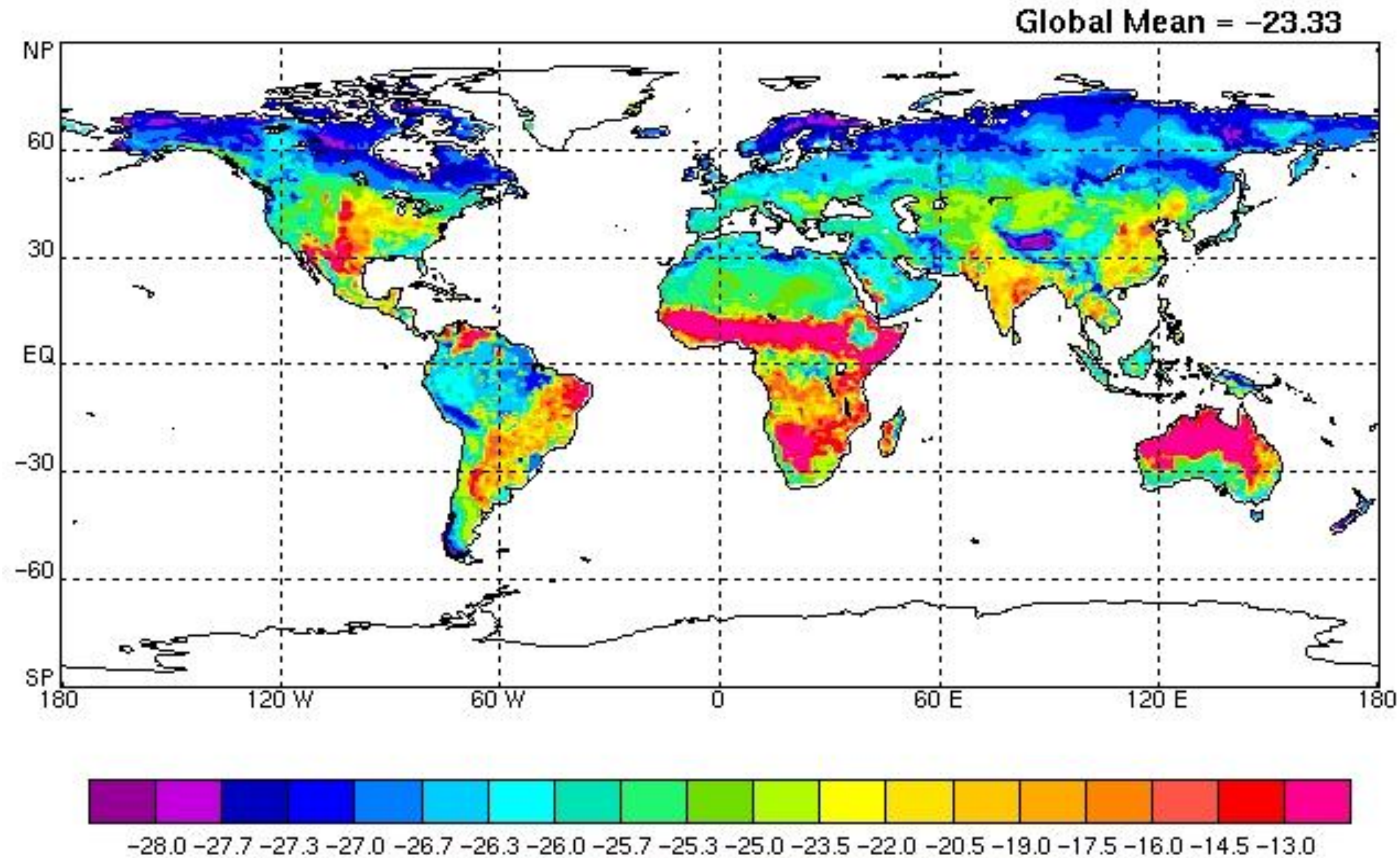
CAM: Crassulacean acid metabolism, PEP into C4 acids at night, refixed by Rubisco during day


200
100
0
-40
-30
-20
-10
0
10
(n = 965)
C3
plants
C4
plants
Frequency
Carbon isotope ratio, ‰



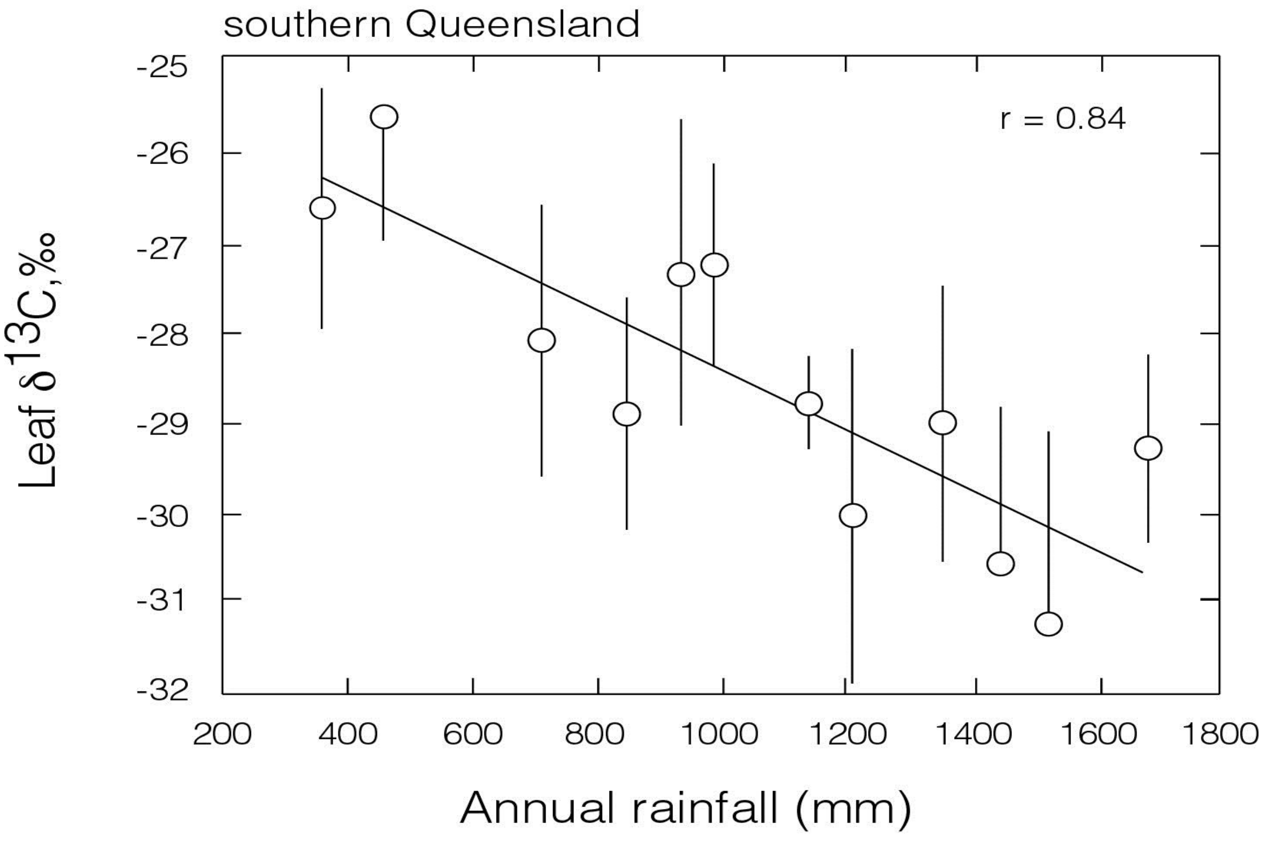
C_3
C_4
200
100
0
Frequency
(n = 965)
C_3 plants
C_4 plants
-40
-30
-20
-10
0
10
Carbon isotope ratio, ‰

Model estimates of plant organic $\delta^{13}C$



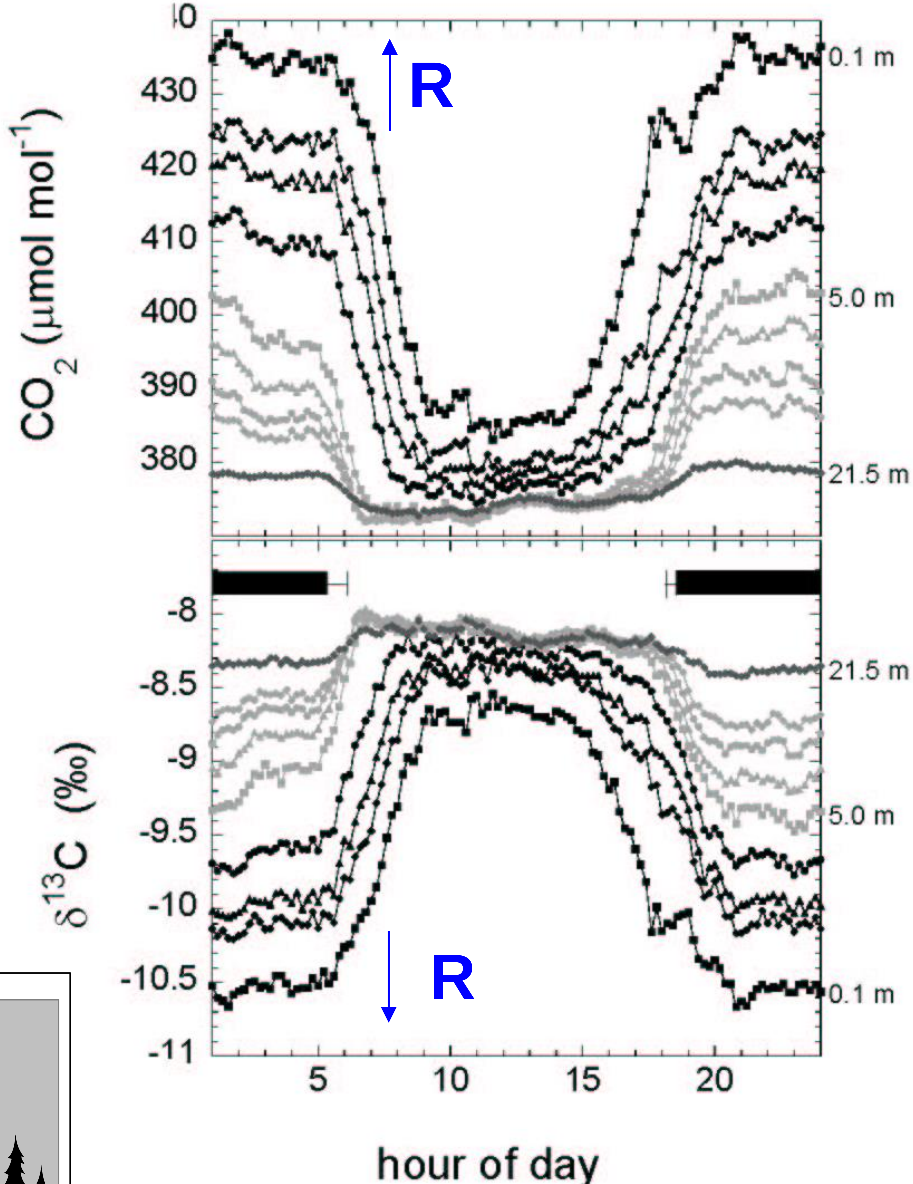
Suits et al. (2005)

But, water stress affects isotopic discrimination …

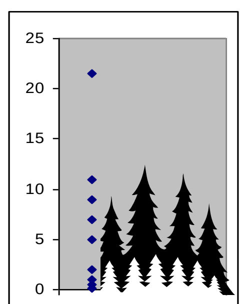


Stewart et al. (1995)

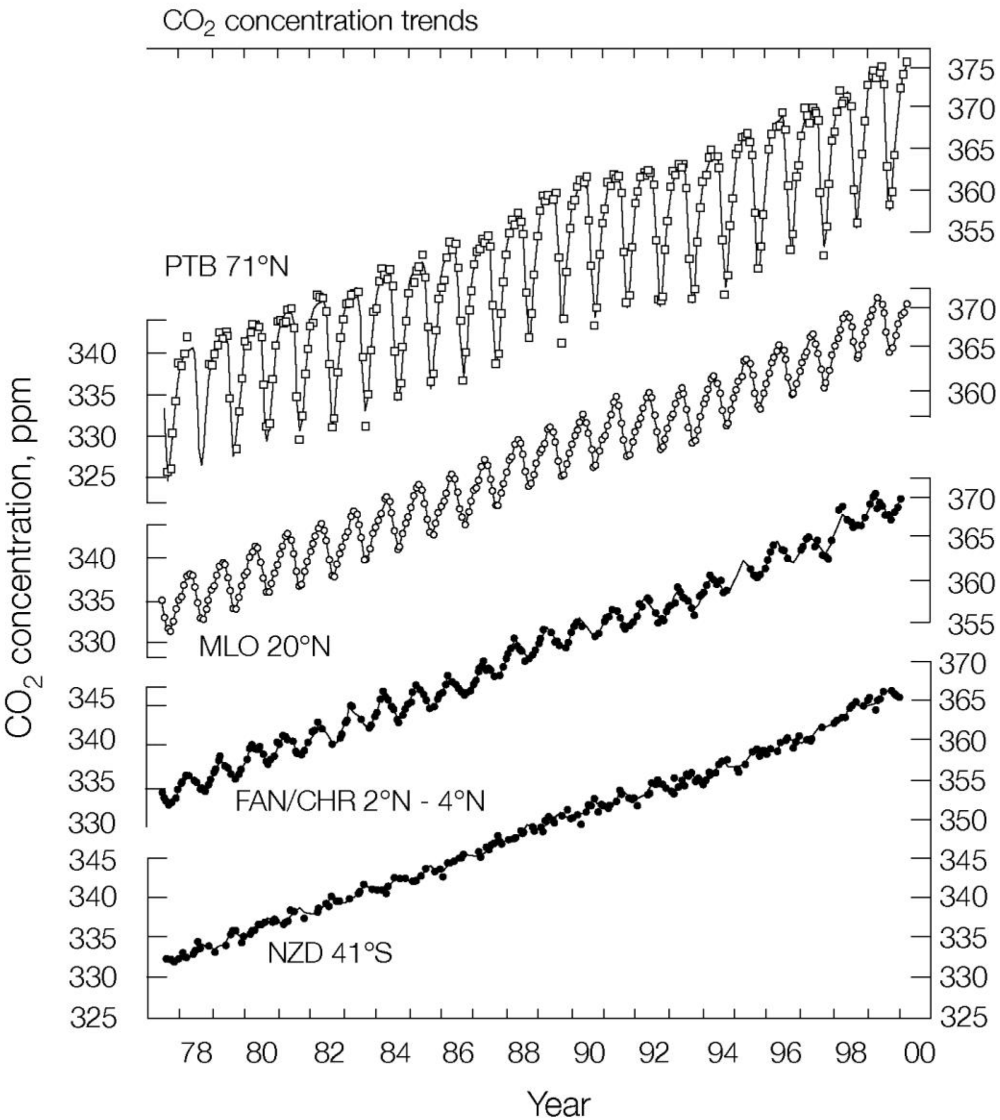
Isotopic patterns in a subalpine forest: 3-month averages

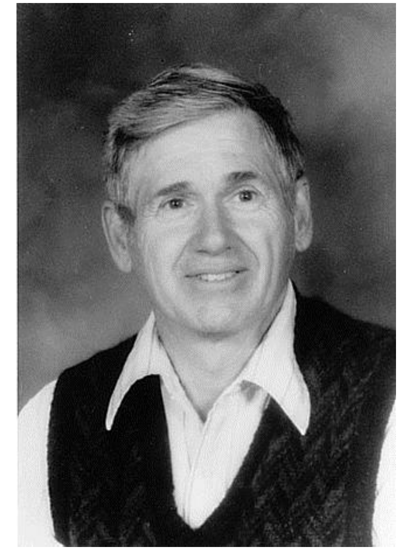


R: respiration

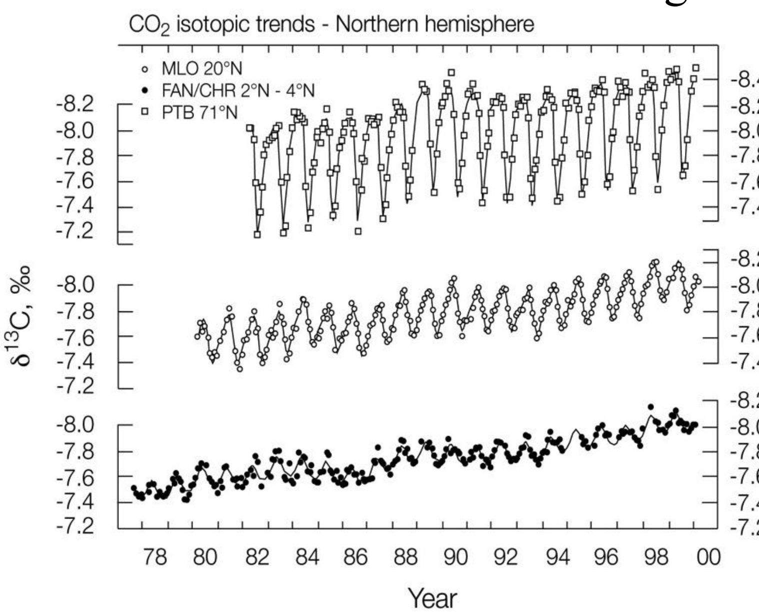


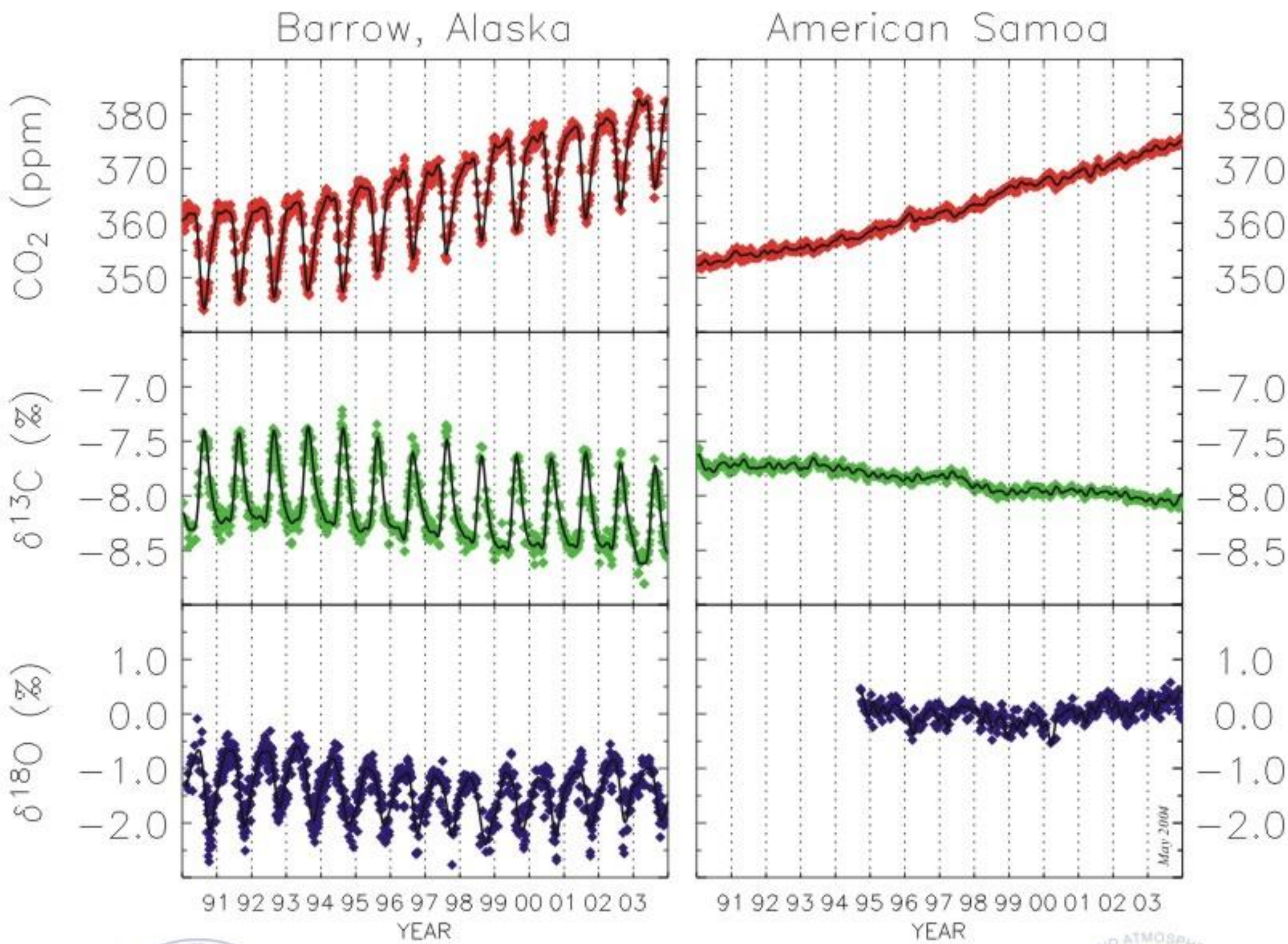
Bowling et al. (2005)





Dave Keeling

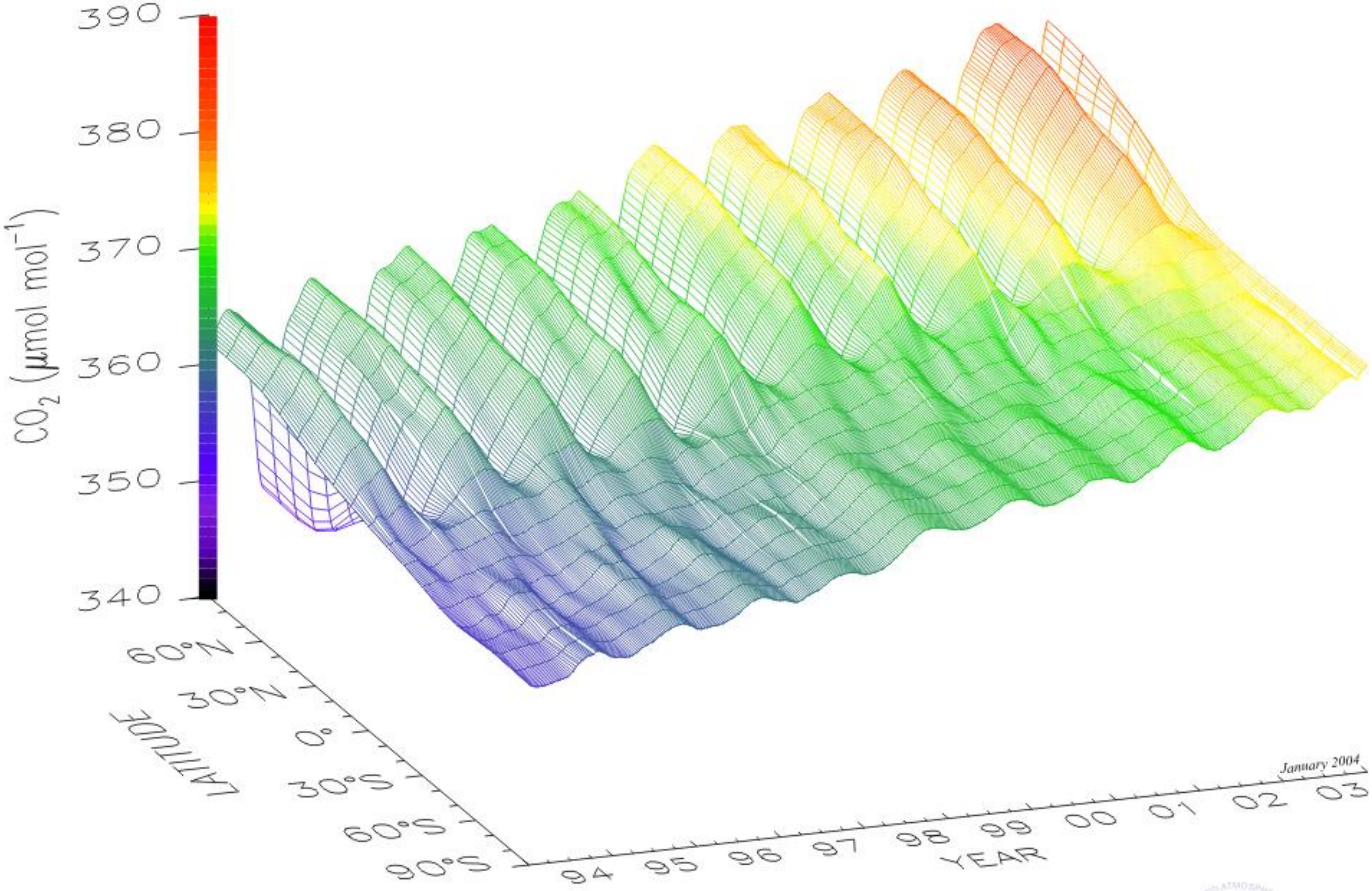




Time series showing the relationships between atmospheric carbon dioxide (upper panel), carbon-13 (middle panel) and oxygen-18 (lower panel) isotopic composition in the marine boundary layer. The measurements were made at NOAA CMDL and the University of Colorado INSTAAR using samples provided by the NOAA CMDL cooperative air sampling network. Data are shown for Barrow and Samoa, revealing the greater seasonal variations at high northern latitudes driven by the terrestrial biosphere. The isotope data are expressed as deviations of the carbon-13/carbon-12 ratio in carbon dioxide from the VPDB-CO_2 standard, in per mil (parts per thousand) Contact: Dr. Jim White, CU INSTAAR, Boulder, Colorado, (303) 492-5494. James.white@colorado.edu.

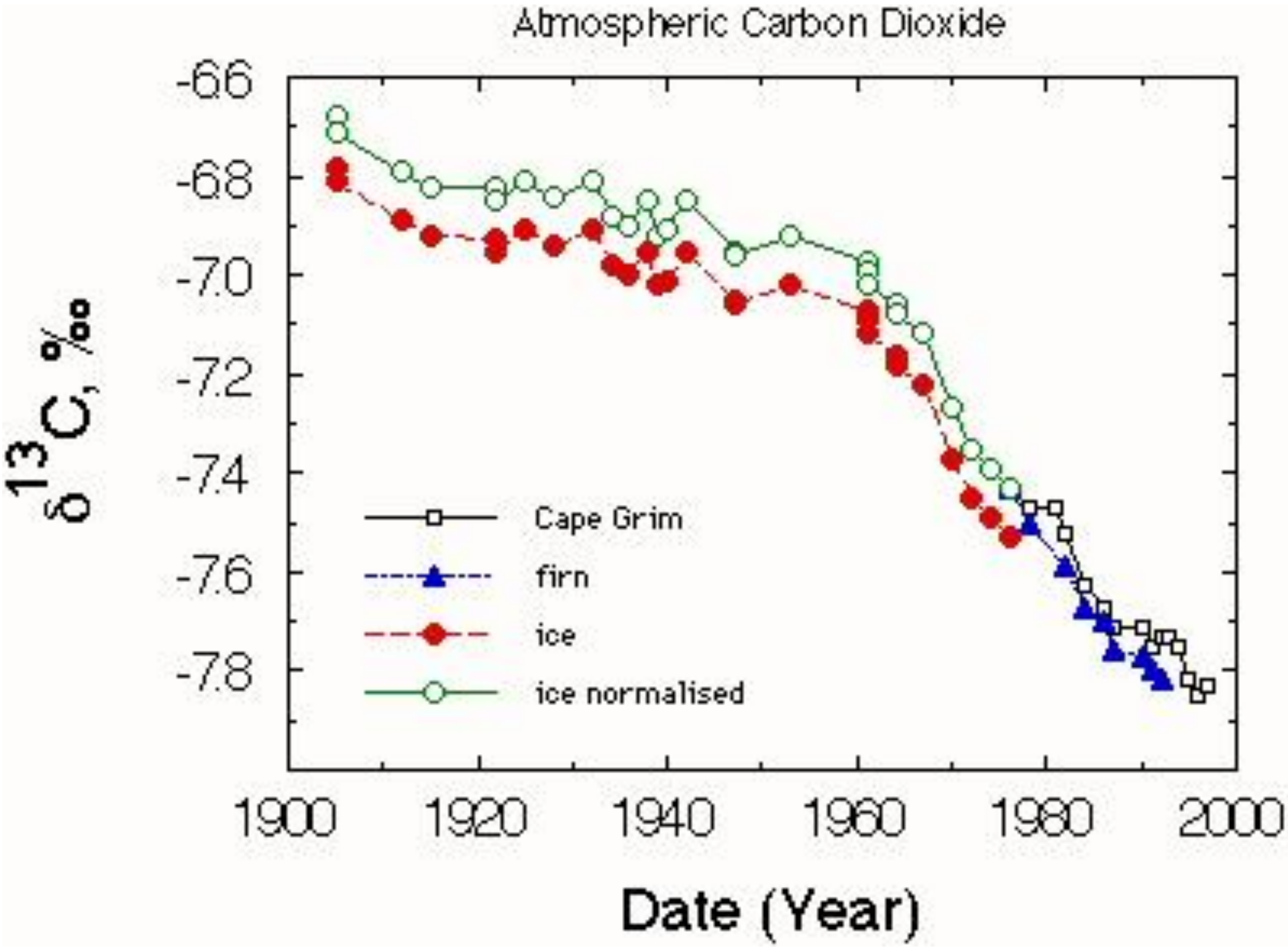
Global Distribution of Atmospheric Carbon Dioxide

NOAA CMDL Carbon Cycle Greenhouse Gases

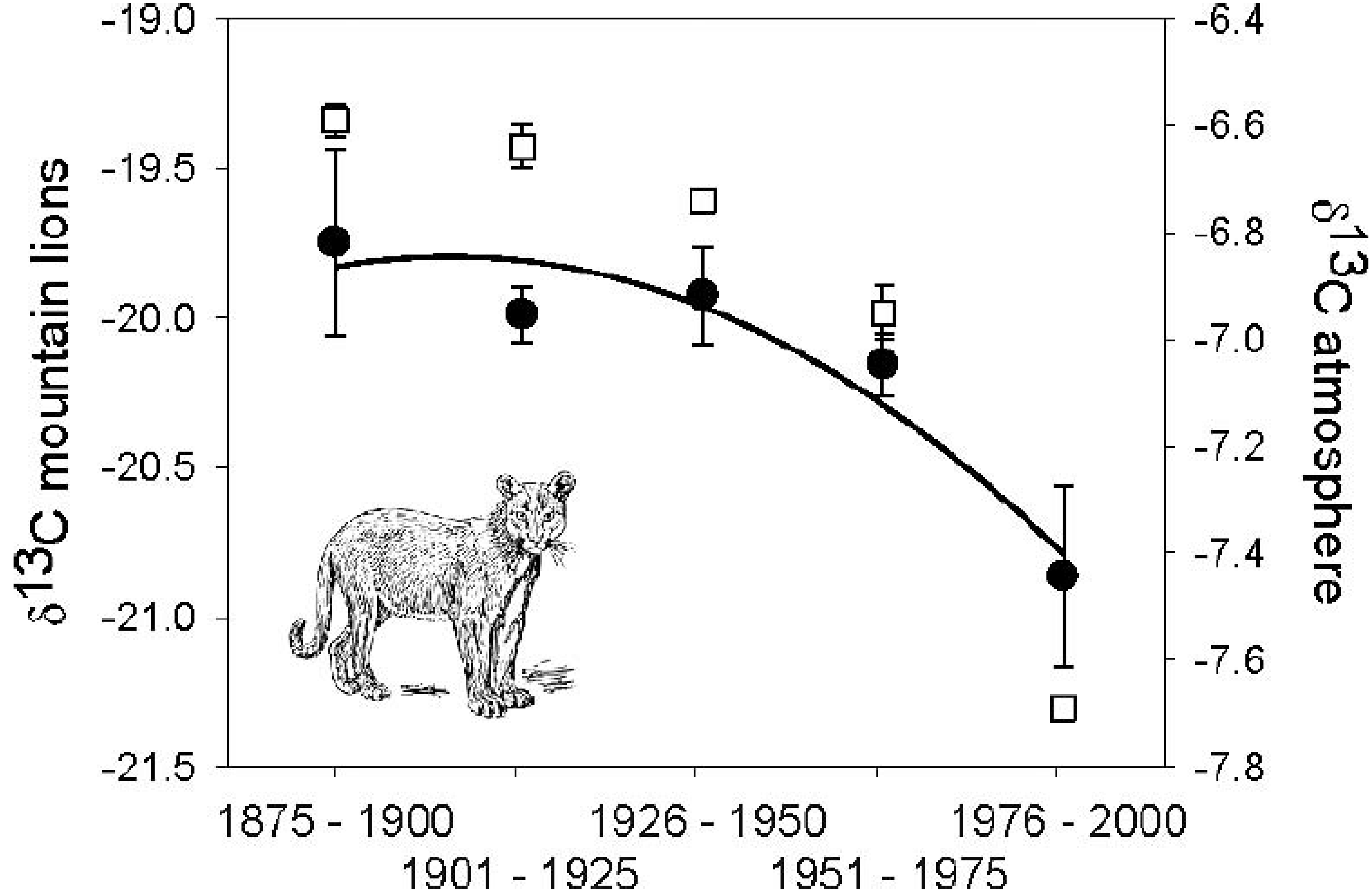


Three dimensional representation of the latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer. Data from the NOAA CMDL cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Principal investigators: Pieter Tans and Thomas Conway, NOAA CMDL Carbon Cycle Greenhouse Gases, Boulder, Colorado, (303) 497-6678 (pieter.tans@noaa.gov, http://www.cmdl.noaa.gov/ccgg).

$\delta^{13}C$ of the atmosphere is changing

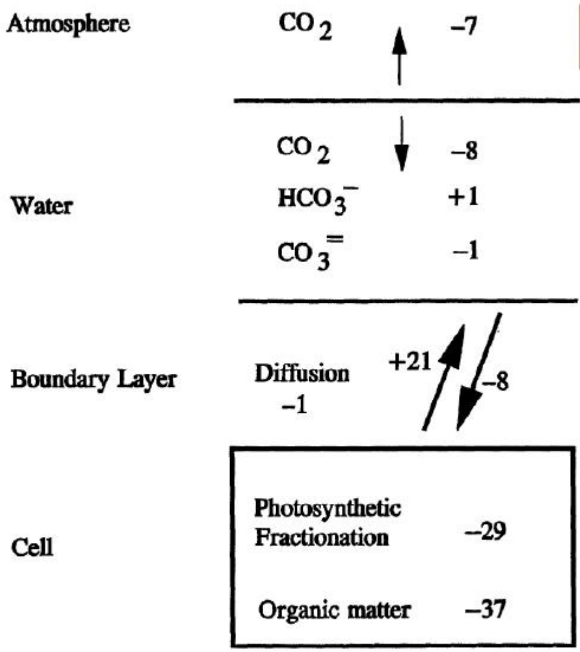


Francey et al. (1999)

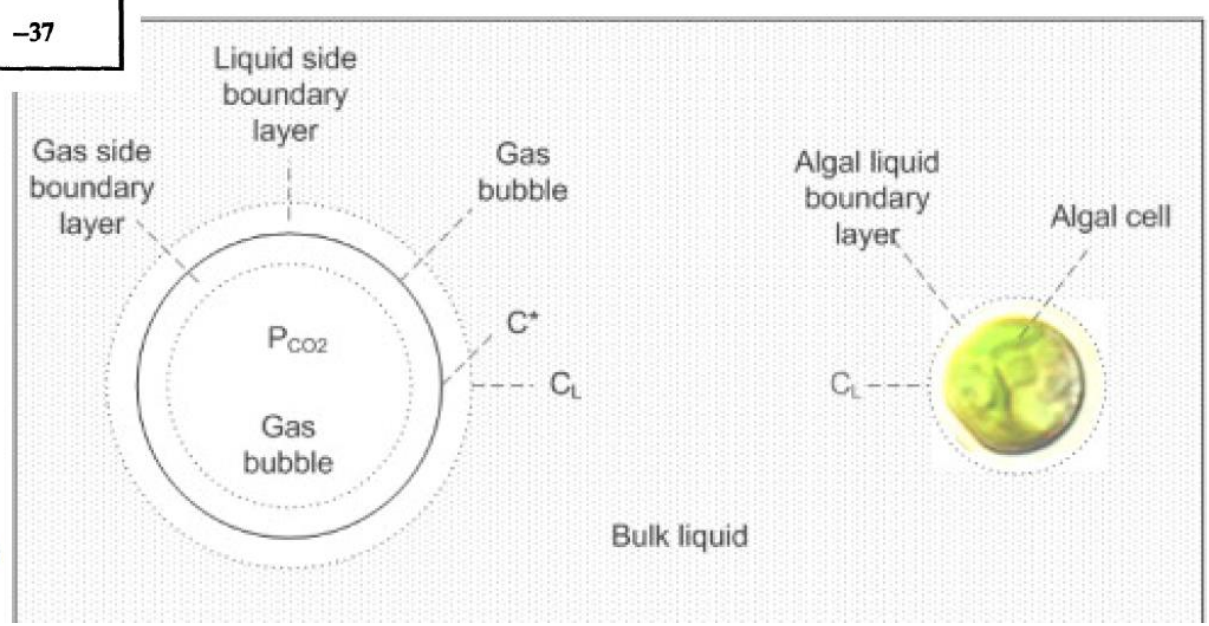


Ben-David & Flaherty (2012)

Boundary layer diffusion



CO_2 limitation causes reduced fractionation



Hecky and Hesslein 1995

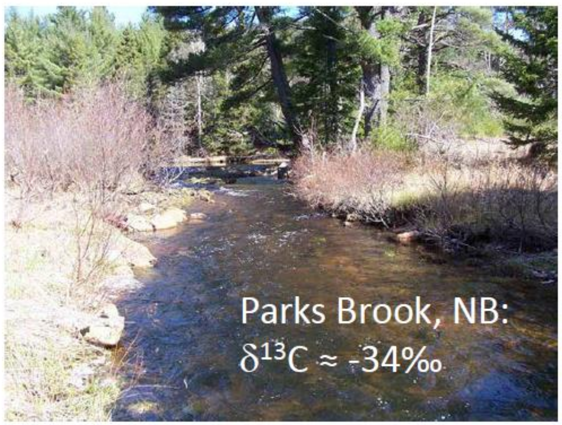
Aerated, turbulent, flowing, suspended

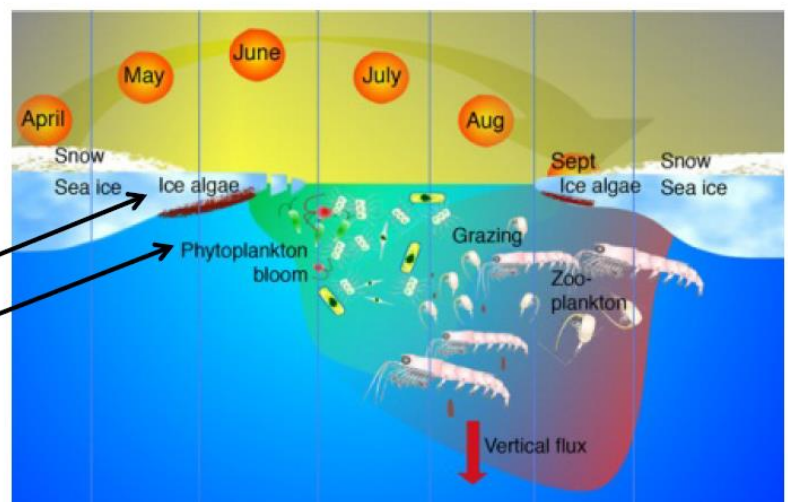
Low $\delta^{13}C$ in algae

Stagnant, overgrown, attached

High $\delta^{13}C$ in algae

Surprise Creek, QLD; $\delta^{13}C \approx -22‰$



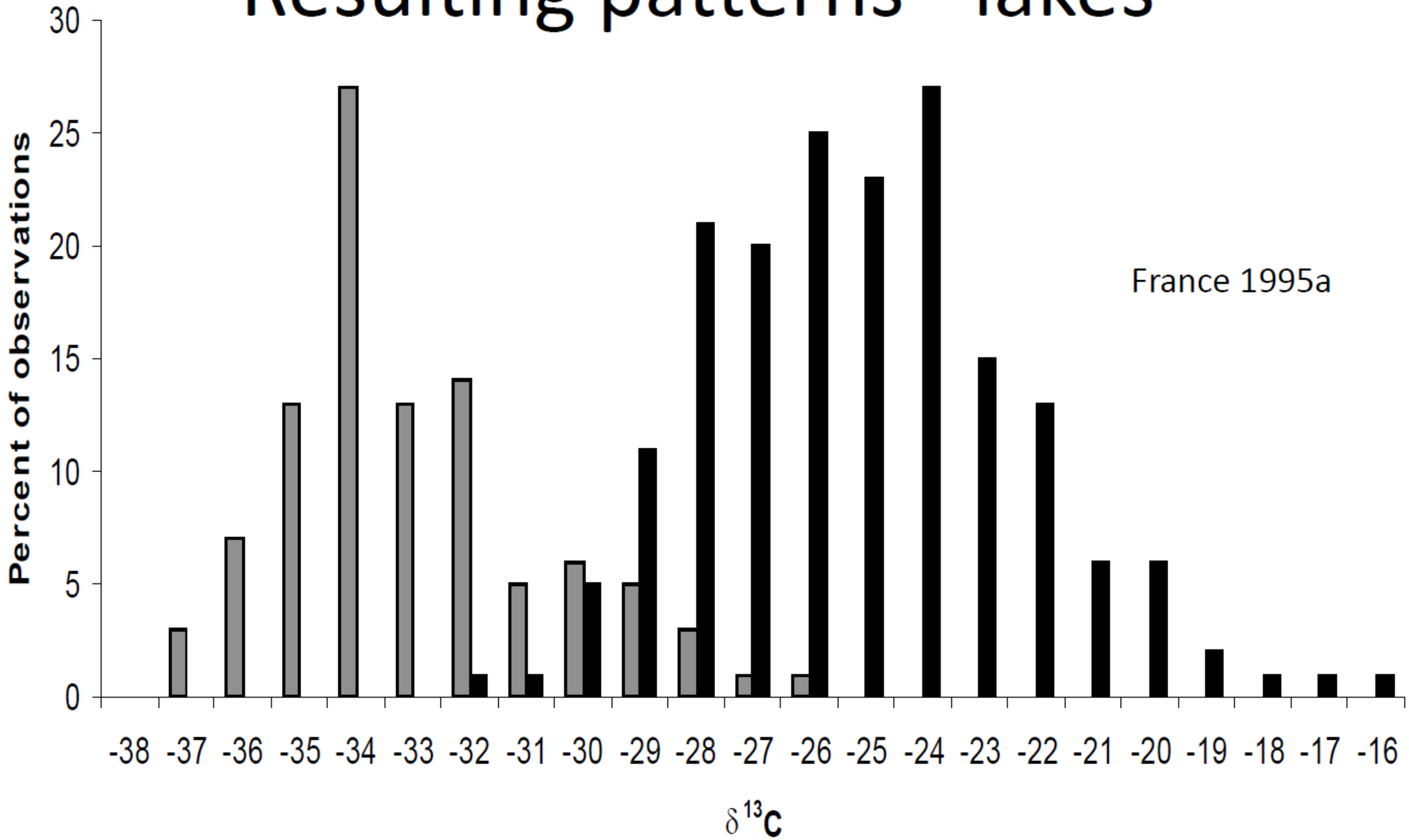


-18‰

-28‰

Hobson et al. 1995

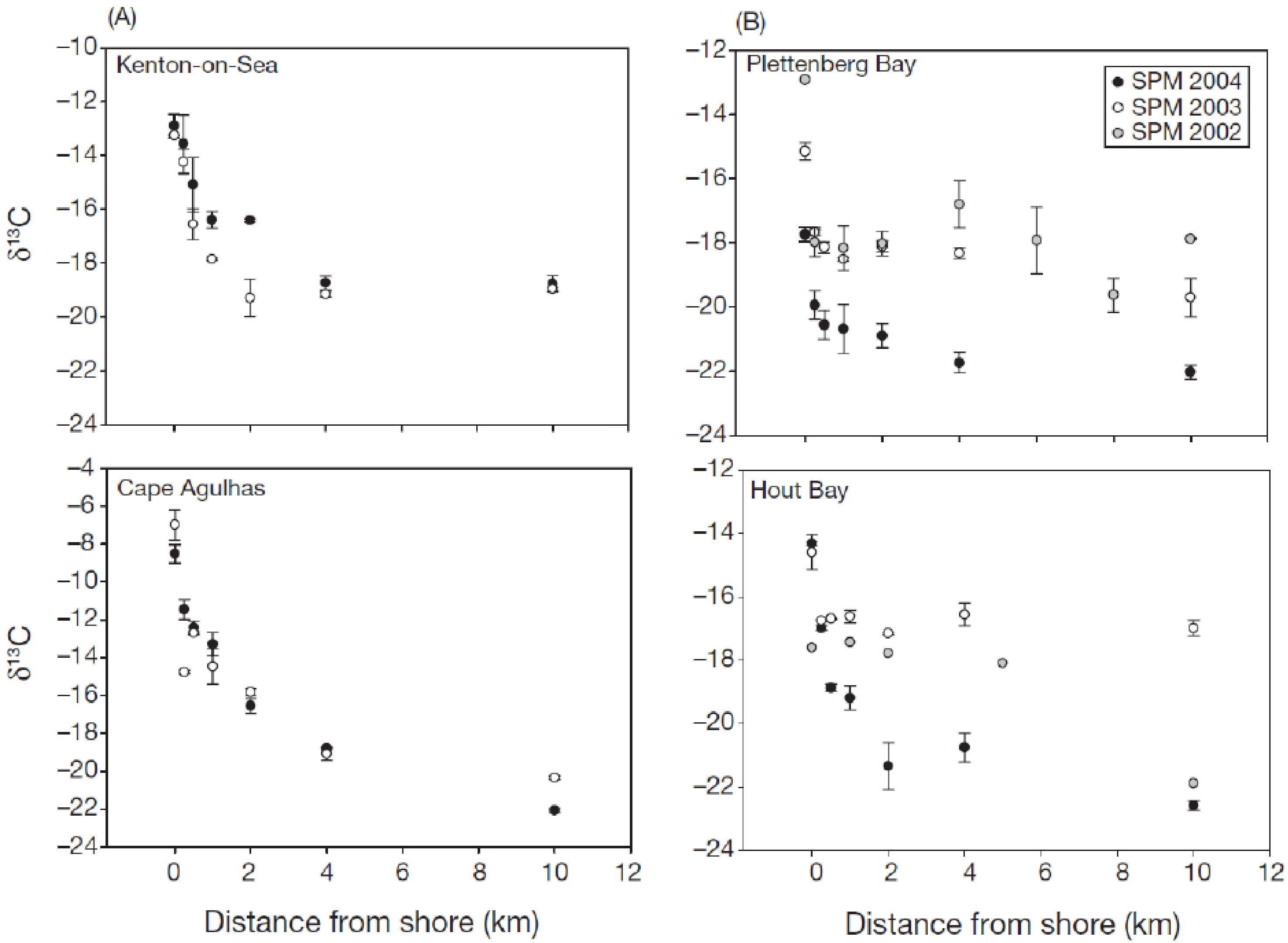
Resulting patterns - lakes



Base of food web is phytoplankton

Base of food web is periphyton

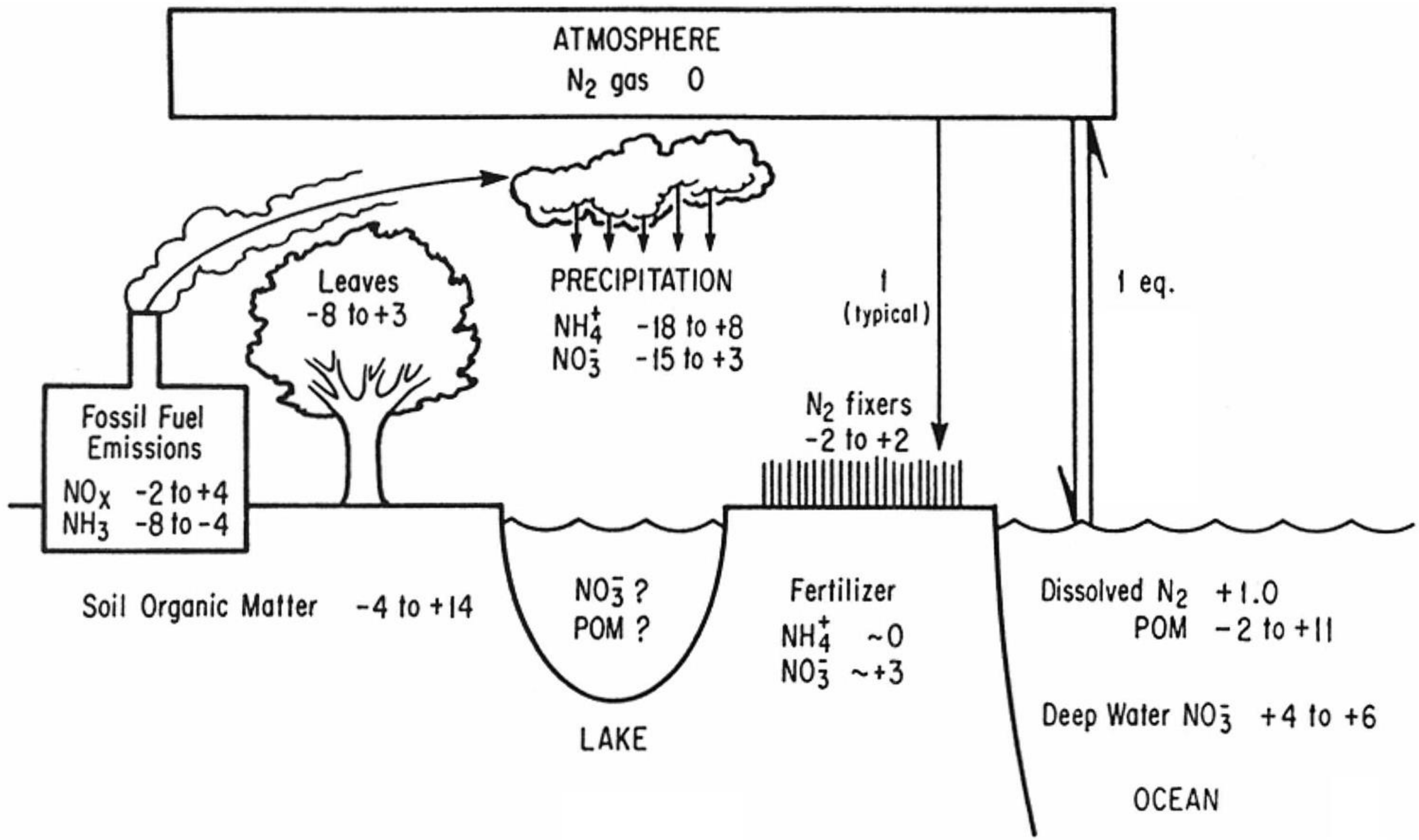
Resulting patterns - oceans



C Summary

- Tracer of plant photosynthetic pathway (C3, C4, CAM) and water-use efficiency.
- Marine vs. freshwater/terrestrial C sources.
- Spatial Indicator of aquatic primary production (benthic/inshore vs pelagic/offshore).
- Tracer of C source and mechanisms related to atmospheric and global change.

Nitrogen



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

Nitrogen Cycling

- Atmospheric reservoir of 0‰
- Because N is limiting, fractionation is generally low.
- Faster loss of ^{14}N than ^{15}N in particulate N decomposition leads to increase in ^{15}N with depth in oceans and soil.
- So, plants that rely on soil N tend to be more enriched than those depending on atmospheric N.
- Nitrification and denitrification are the key sources of fractionation.
- Phytoplankton use N_2 gas, ammonia and nitrate.

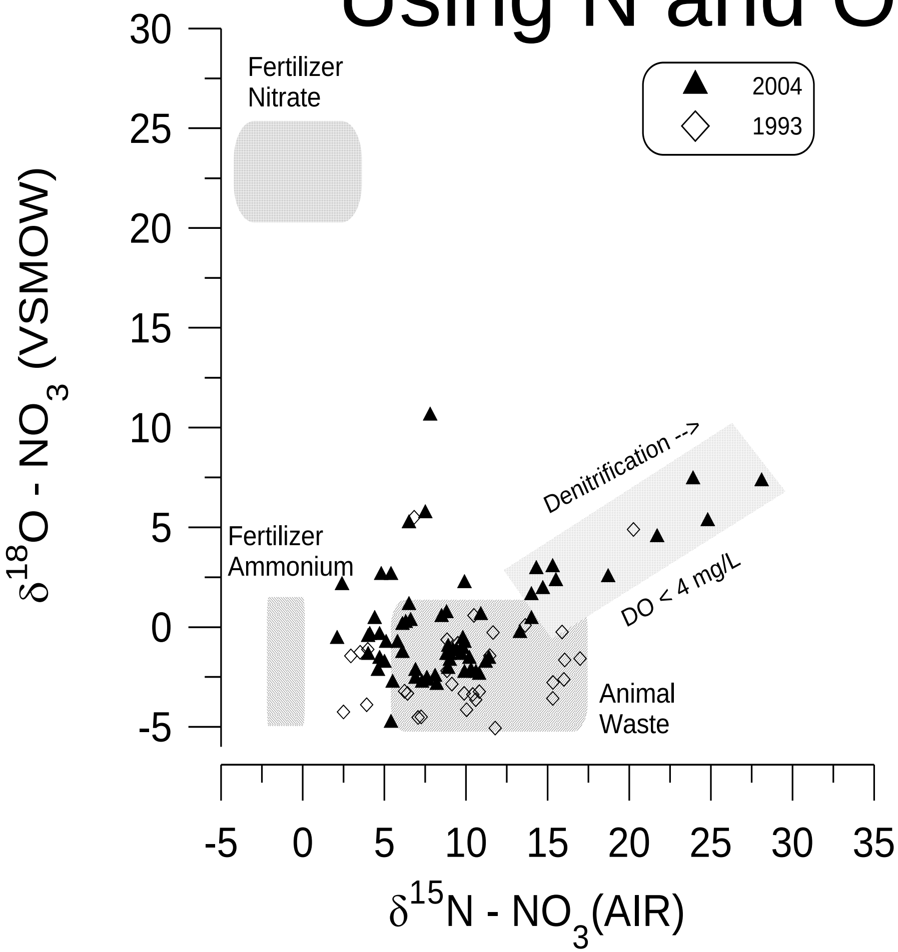
Nitrogen Processes

- *Nitrification* - conversion of NH_4^+ to NO_3^- by oxidation
- *Ammonification* - conversion of organic N to NH_4^+
- *Denitrification* - NO_3^- reduced to N_2O or N_2

Utility of Nitrogen Isotopes

- Identify *sources* of nitrate to aquatic systems.
- Geochemical *processes* and chemical reactions such as nitrification or denitrification
- N sourcing to plants ..
- Terrestrial vs marine inputs to foodwebs
- Foodweb trophic level indicator

Using N and O isotopes together…

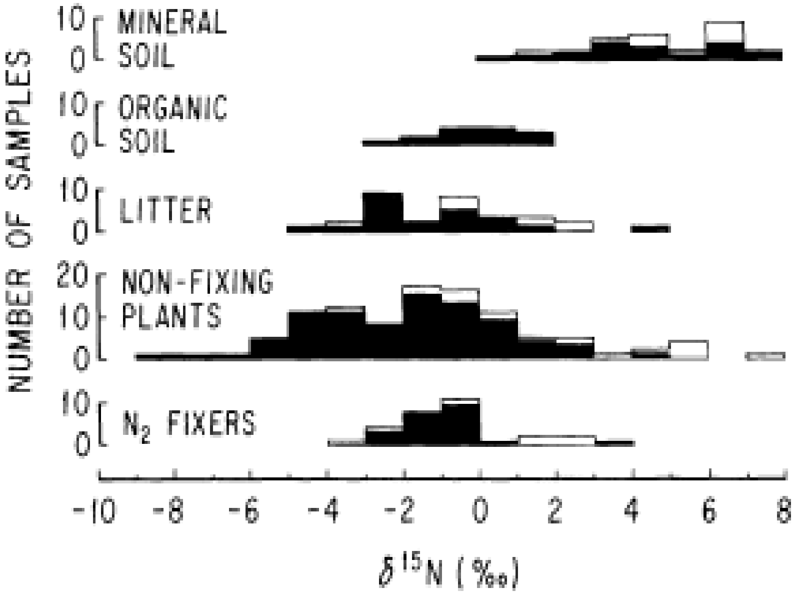


•Significant shift in ^{15}N to lower values (switch to inorganic fertilizer use from manure – BMP)

•Denitrification – limited to suboxic riparian zones and deep (>30yr) groundwater

**L. Wassenaar

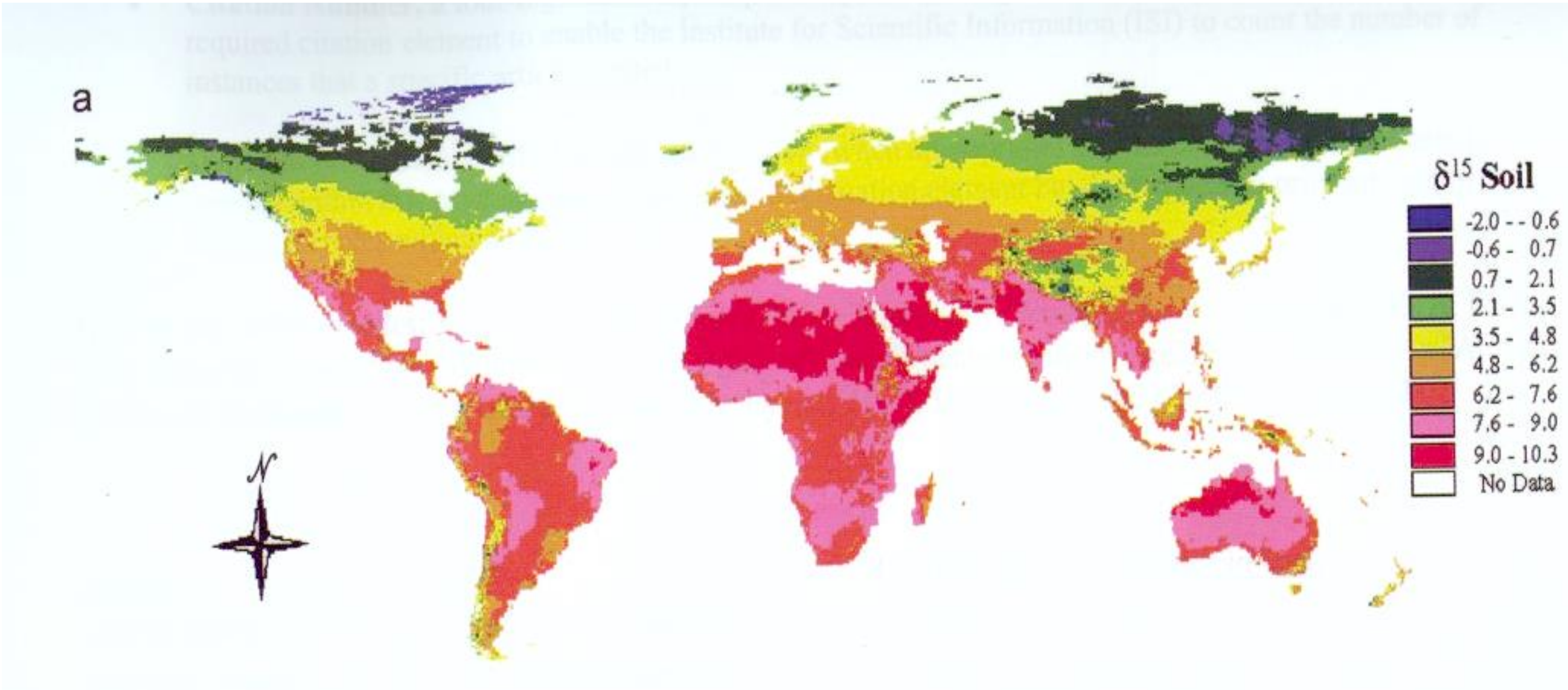
Variation in Soil and Plants



Observations from Fry (1991)

1. Large variation
2. No correlation with precipitation
3. Soils more enriched than plants
4. N_2-fixers near 0 ‰

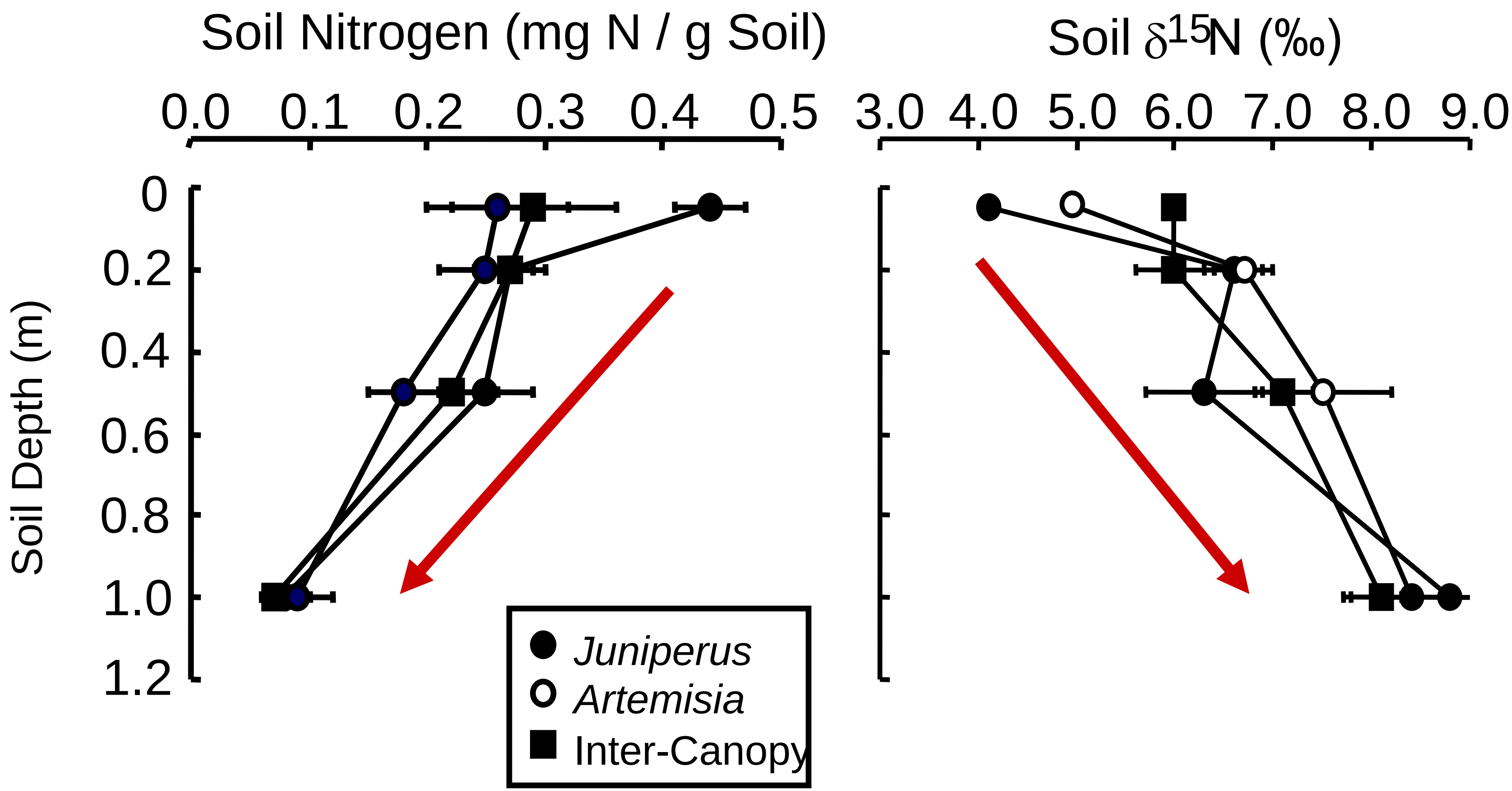
General Trends in Soil δ^{15}N



Amundson et al. (2003)

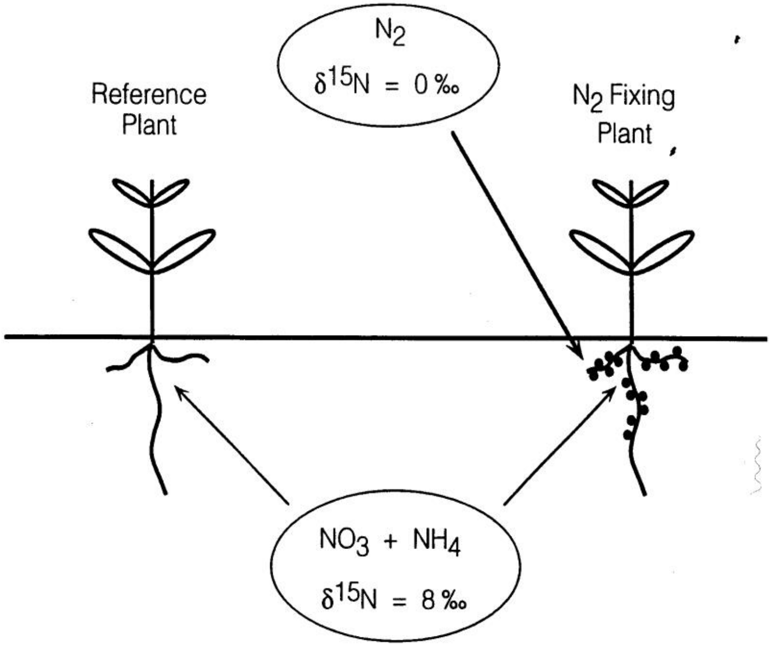
Values are usually positive (but there are exceptions)

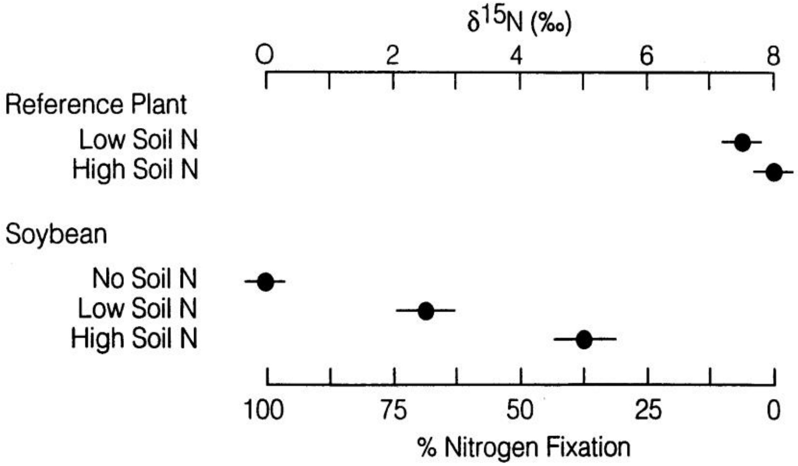
General Trends in Soil $\delta^{15}N$



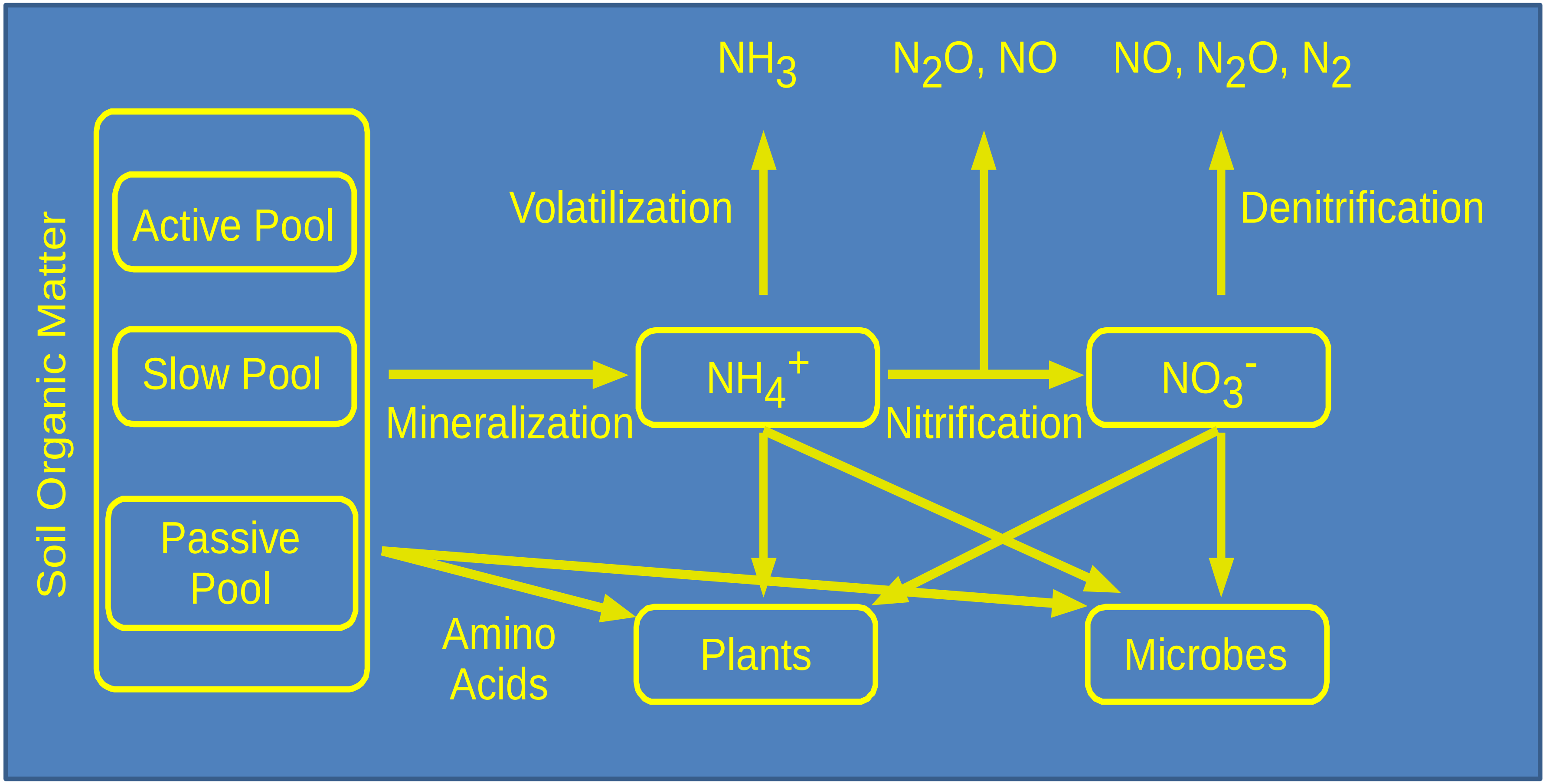
From: Evans and Ehleringer (1993)

What Controls Plant $\delta^{15}N$?



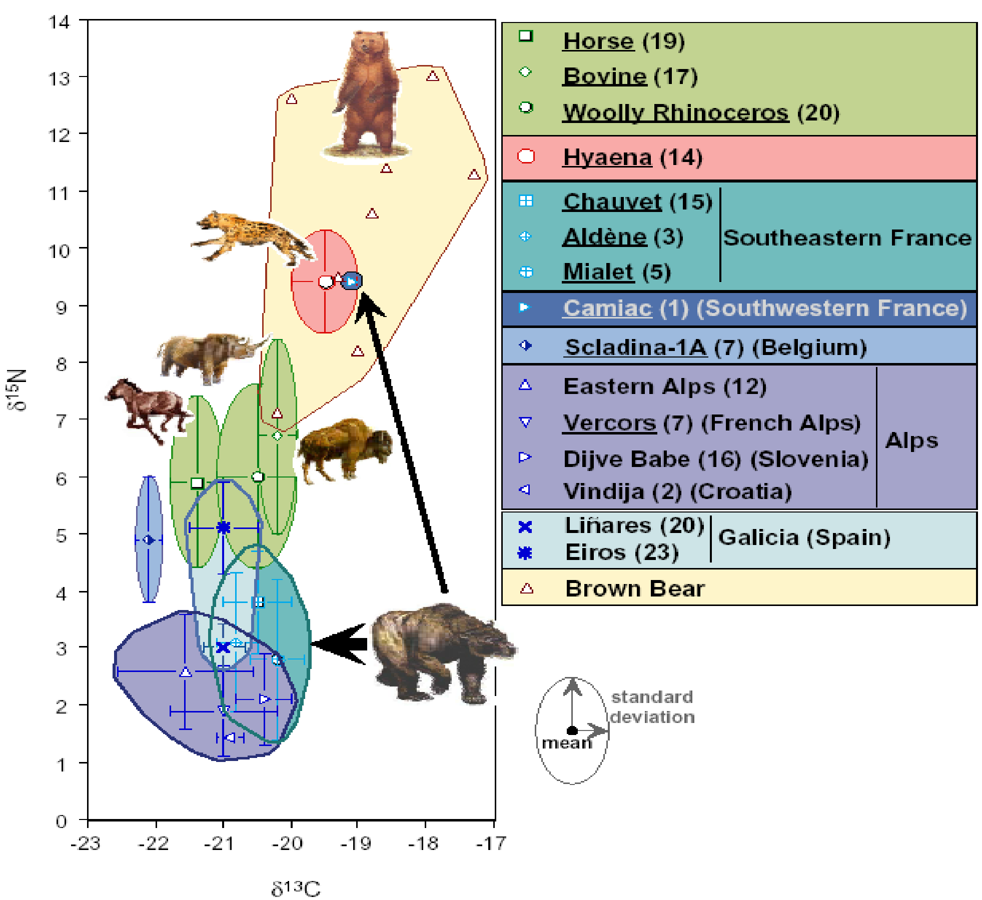


Soil Nitrogen Transformations



Högberg (1997)
Shearer and Kohl (1990)

δ[15]N as a trophic indicator



REVIEW OF CARBON AND NITROGEN COLLAGEN ISOTOPIC COMPOSITIONS IN CAVE BEARS AND BROWN BEARS FROM WESTERN EUROPE DURING MARINE OXYGEN ISOTOPIC STAGE 3 (~50,000 - 25,000 BP)

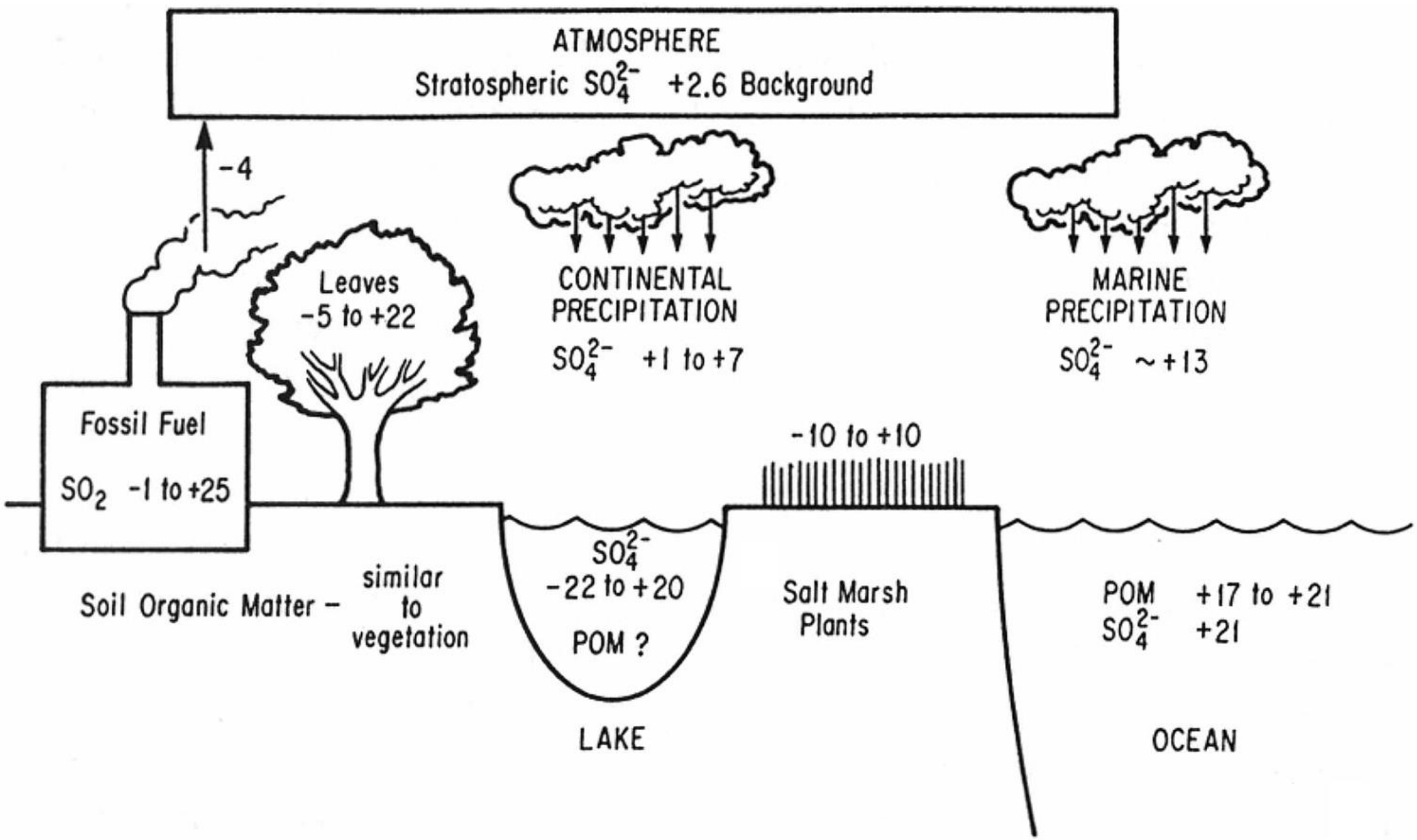
Values are from Bocherens *et al.*, 1994, 1995, 1997, unpublished; Fernandez-Mosquera *et al.*, 2001; Nelson *et al.*, 1998; Richards, 2000; Richards *et al.*, 2000

Review by Bocherens, 3rd International Conference on Applications of Stable isotope Techniques to Ecological Studies,

Summary N

- Tracer of N nutrients and contaminants. Especially powerful with $\partial^{18}O$
- N fixing vs. non-fixing plants.
- Atmospheric NOx tracing.
- Soils
- Foodweb trophic-level and source (marine vs terrestrial) indicator.

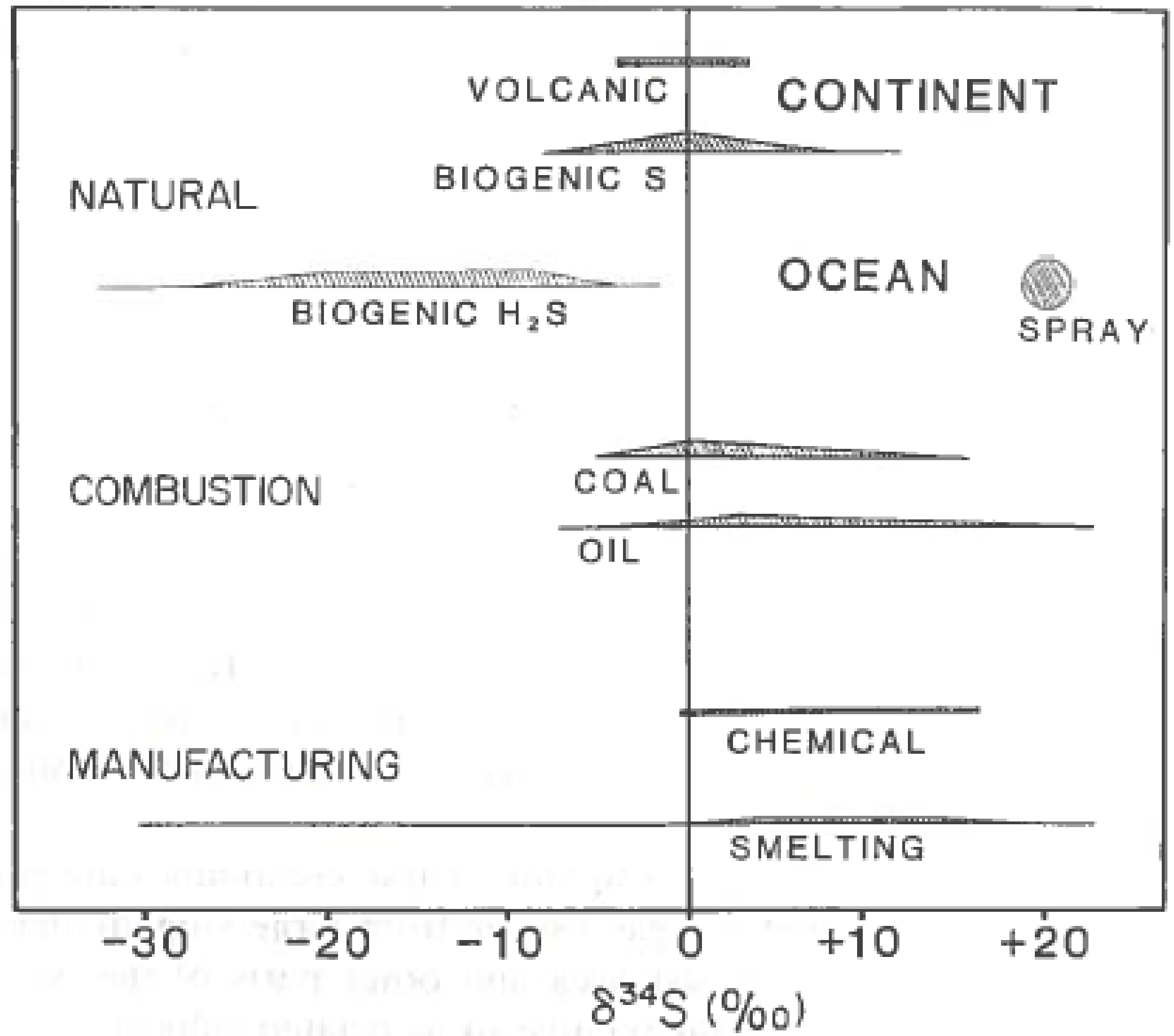
Sulfur



ATMOSPHERE
Stratospheric SO_4^{2-} +2.6 Background
−4
Leaves
−5 to +22
CONTINENTAL
PRECIPITATION
SO_4^{2-} +1 to +7
MARINE
PRECIPITATION
SO_4^{2-} ~+13
Fossil Fuel
SO_2 -1 to +25
−10 to +10
Soil Organic Matter − similar to vegetation
SO_4^{2-}
−22 to +20
POM ?
LAKE
Salt Marsh
Plants
POM +17 to +21
SO_4^{2-} +21
OCEAN

Sulfur Forms in Environment

Sulfur Valence	*Inorganic*	*Organic*
+6	$SO_4^{=}$, HSO_4^{-}	sulfatides
+4	SO_3^{2-}, SO_2	sulfolipids
0	elemental S	
-1	pyrite FeS_2	dimethyl disulfide
-2	H_2S, HS^{-}, S^{2-}	amino acids, etc

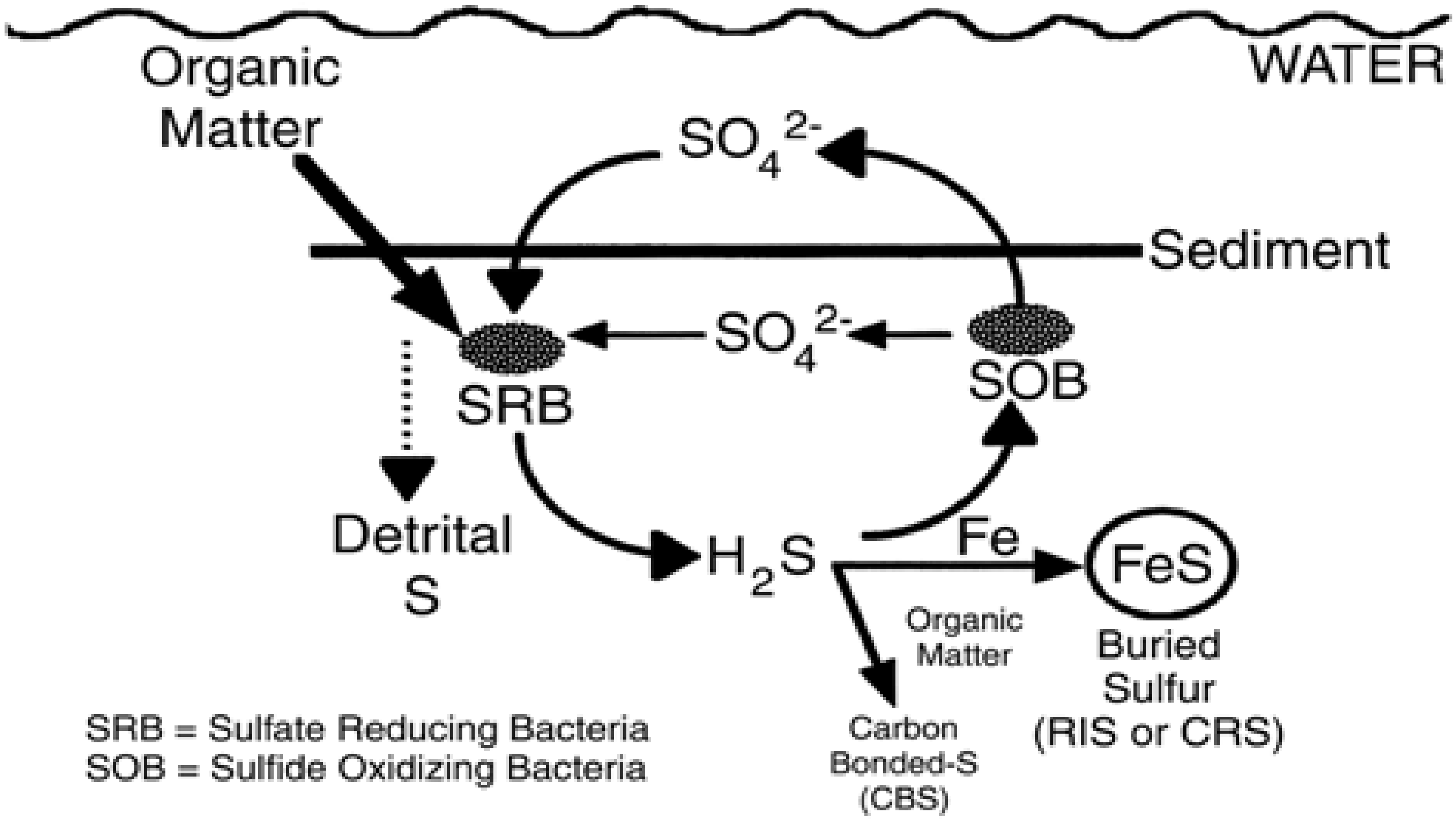

VOLCANIC
CONTINENT
BIOGENIC S
NATURAL
OCEAN
BIOGENIC H2S
SPRAY
COMBUSTION
COAL
OIL
CHEMICAL
MANUFACTURING
SMELTING
−30
−20
−10
0
+10
+20
δ34S (‰)

Sulfur Cycle

- Sulfate in the ocean is the primary reservoir that is $21^{o}/_{oo}$ heavier than primordial sulfur (e.g. Canyon Diablo Troilite).
- Fixation by plants has a small isotope effect but reduction in sediments and anaerobic conditions has a large effect ($30\text{-}70^{o}/_{oo}$).
- Continental vegetation ($+2$ to $+6^{o}/_{oo}$) vs marine plants ($+17$ to $+21^{o}/_{oo}$).

Sources of Sulfate

- dissolution of evaporites (gypsum, anhydrite)
- oxidation of pyrite
- atmospheric precipitation (minor)
- volcanic emissions
- hydrogen sulfide from bogs, fossil fuel combustion



WATER
Organic Matter
SO_4^{2-}
Sediment
SO_4^{2-}
SRB
SOB
Detrital S
H_2S
Fe
FeS
Organic Matter
Buried Sulfur (RIS or CRS)
Carbon Bonded-S (CBS)
SRB = Sulfate Reducing Bacteria
SOB = Sulfide Oxidizing Bacteria

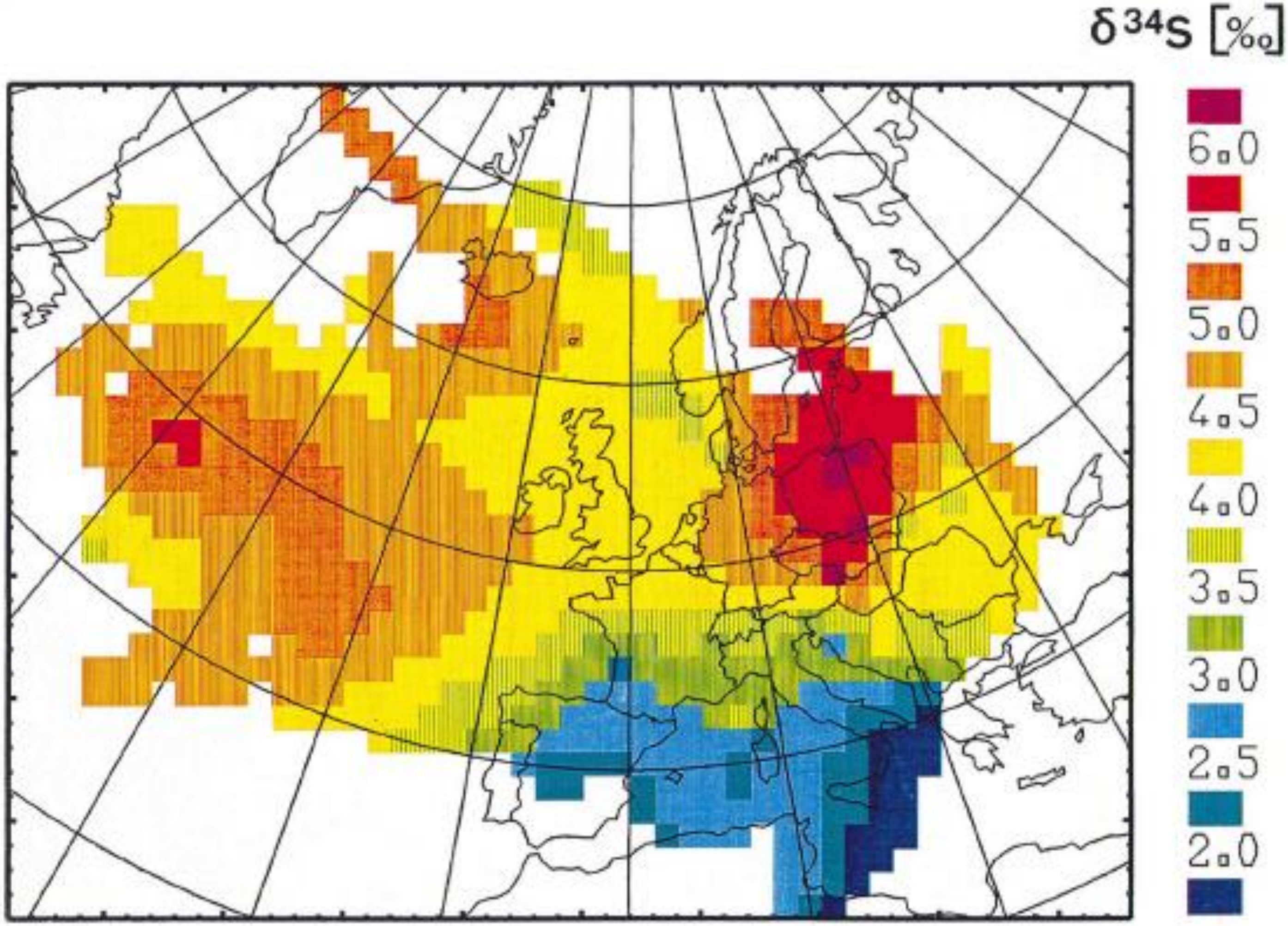


Fig. 8. Mean δ^{34}S-values at Sonnblick associated with back trajectories passing through grid elements (indicated on the axes).

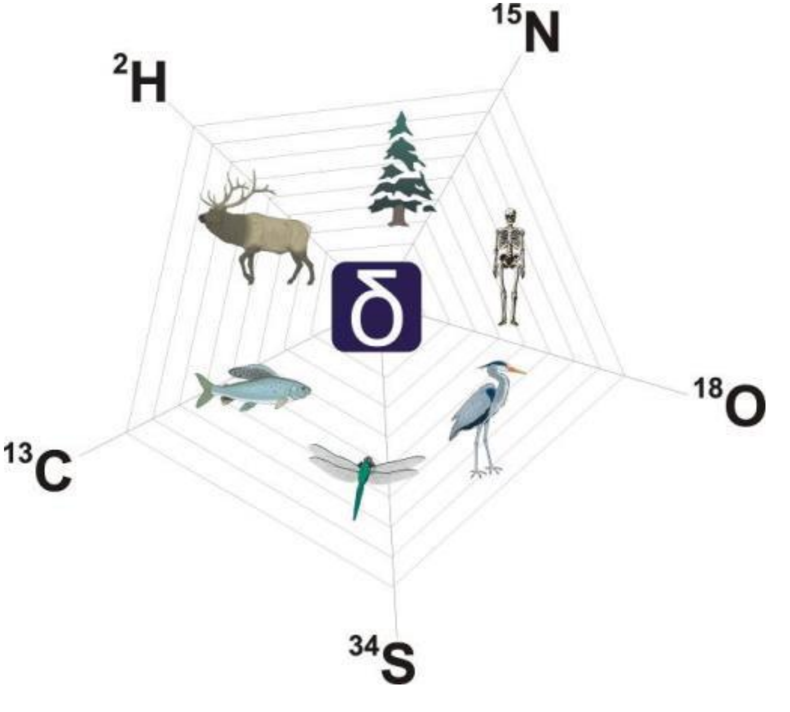
Pichlmayer et al. (1998)

Summary S

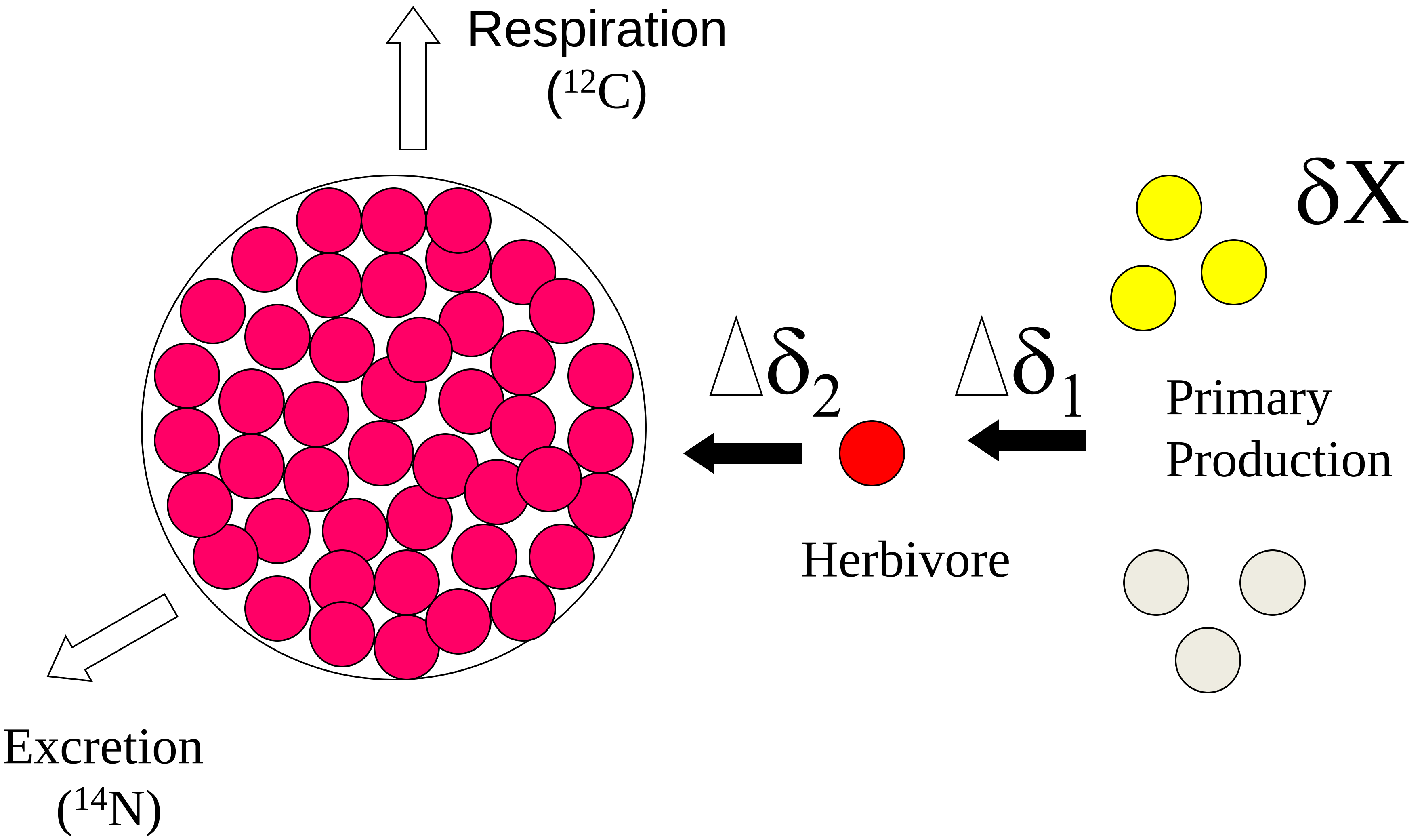
- S isotope ratios are frequently used to identify sources of dissolved species
- isotope ratios give information about geochemical processes and chemical reactions
- for $SO_4^{=}$ - isotopes of S and O can be used
- Animal studies: marine vs. terrestrial, estuaries, marshes; S-amino acids …..

Applications (CNS)

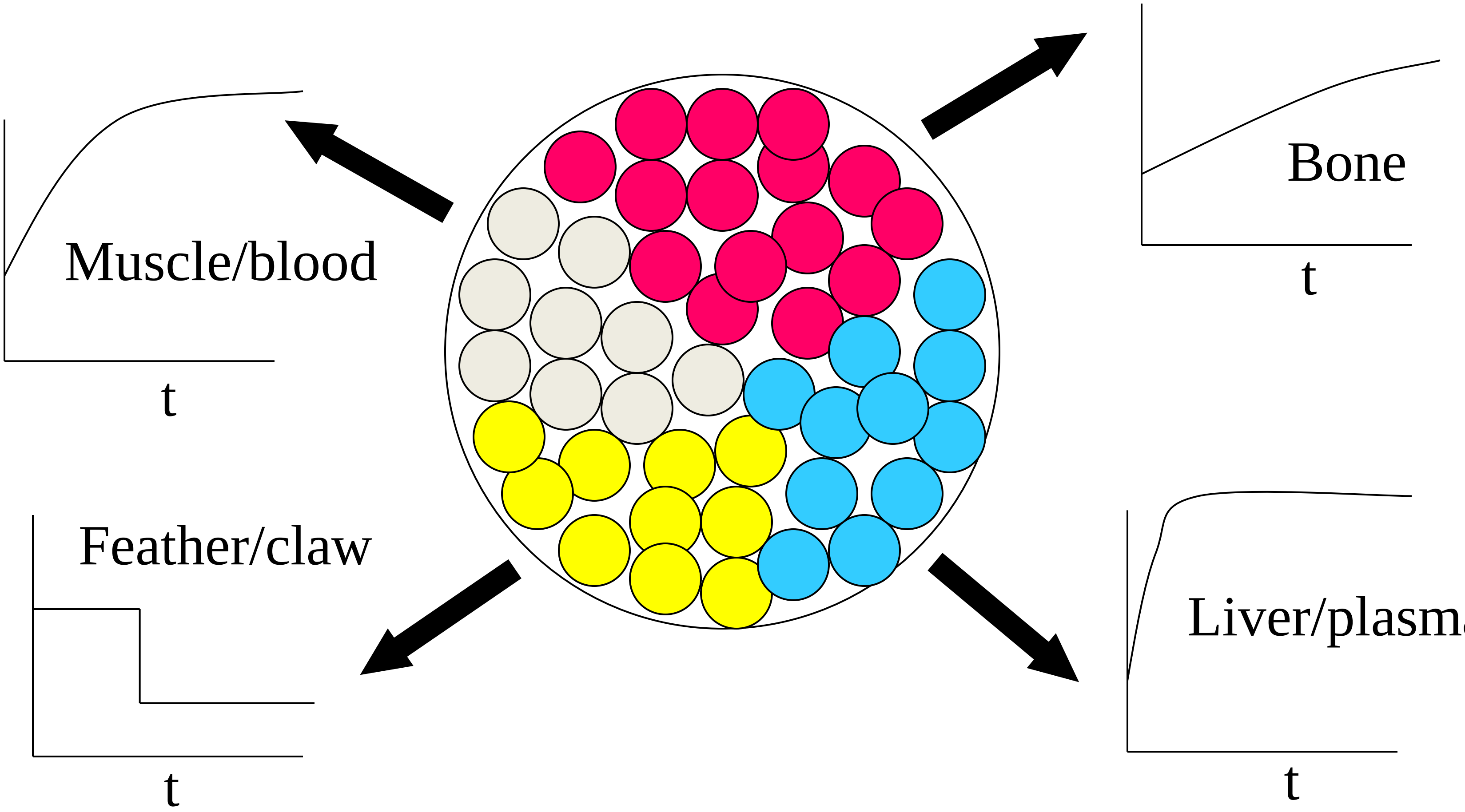
- Foodwebs …..

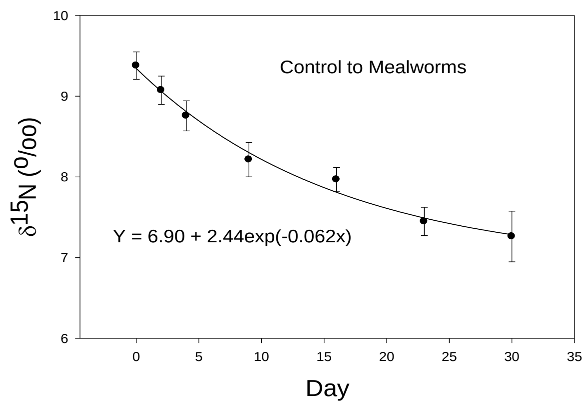


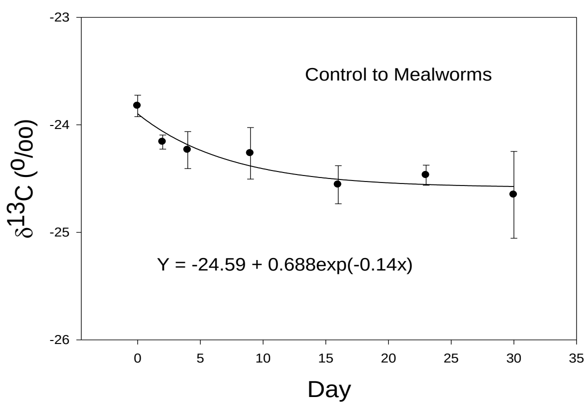
The basic principles of trophic level and source determinations

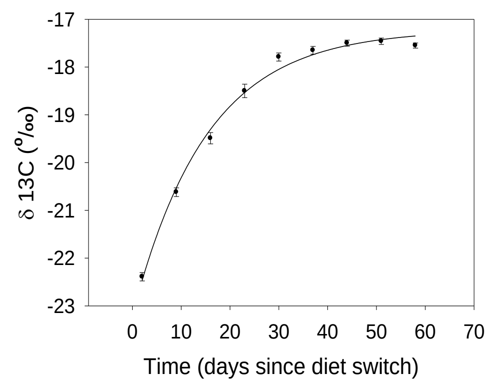


Choice of tissue .....



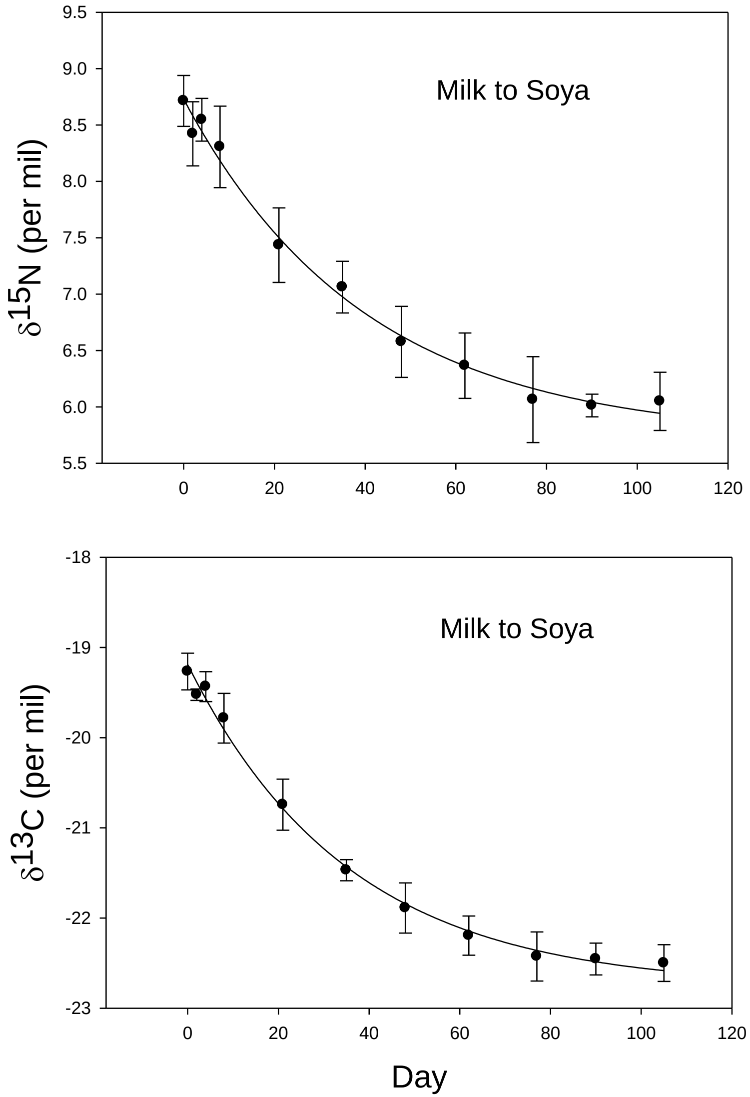






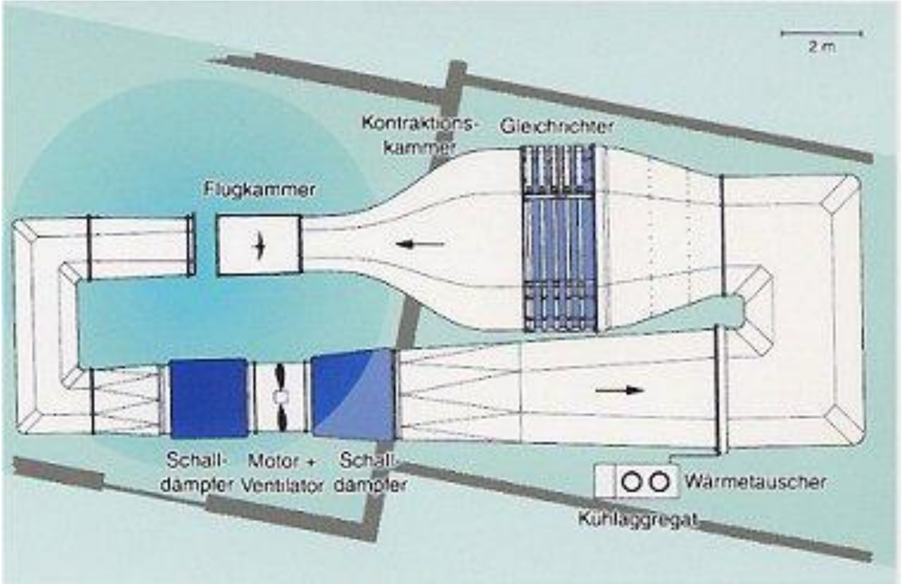
Hobson and Bairlein *CJZ81:1630-1635*

Evans-Ogden et al *Auk* . 121:170-177



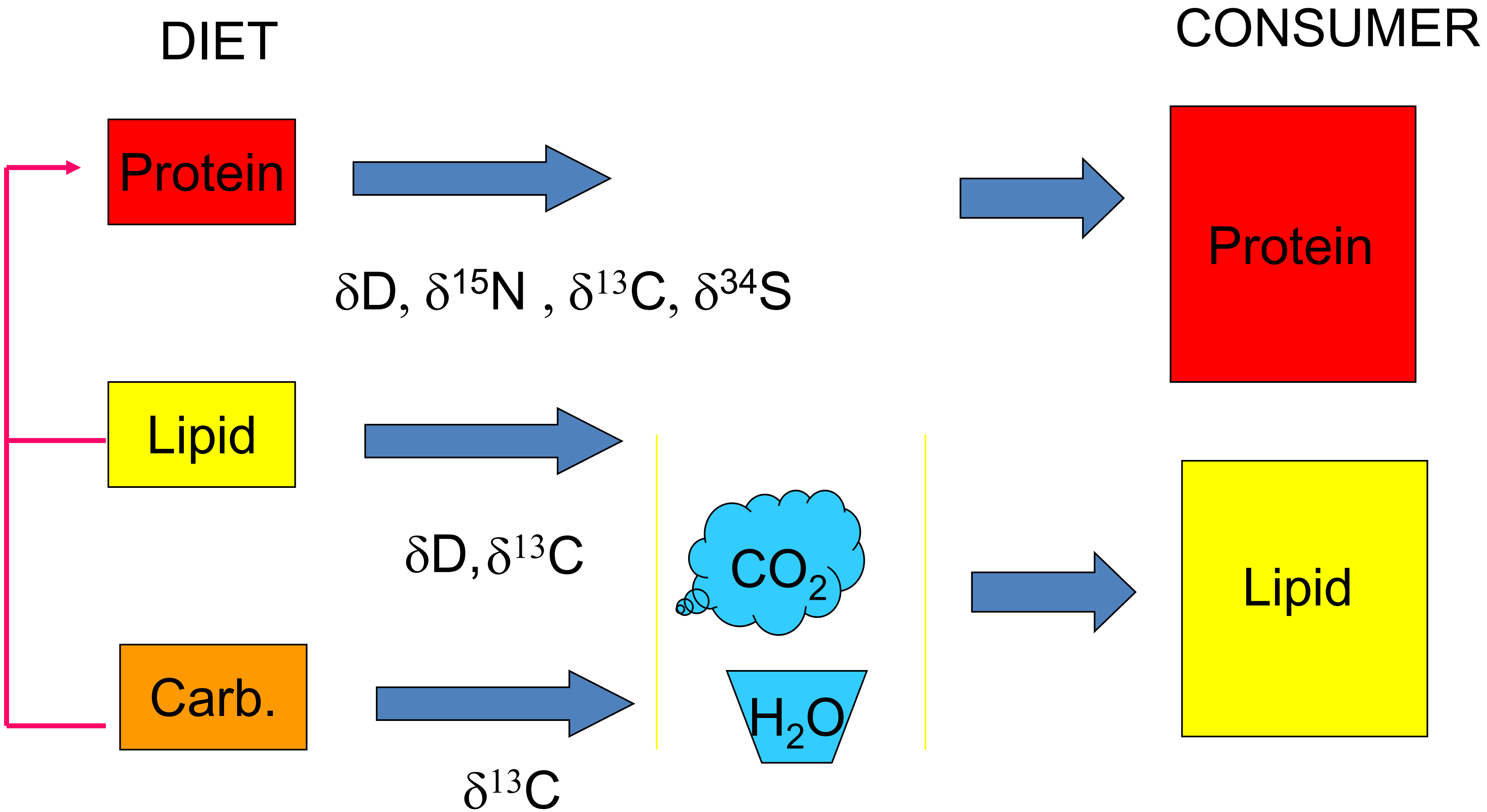
Mirón et al. 2006 J. Exp. Biol

Using a wind tunnel and isotopic dietary shifts to mimic migration



Max Planck Institute for Ornithology

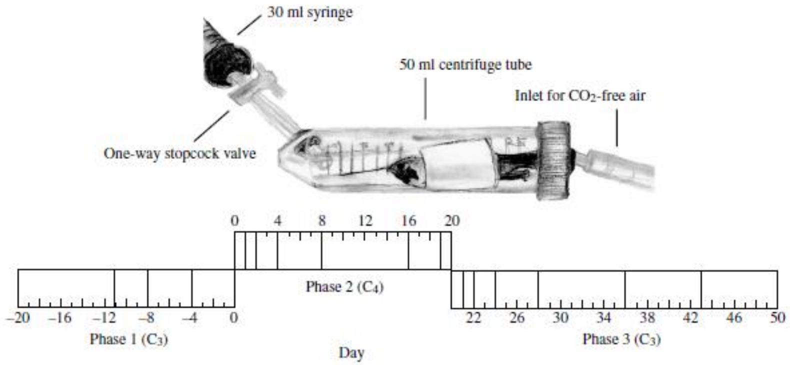
Metabolic routing: "differential allocation of isotopically distinct dietary components to different tissues (Schwarcz 1991)".

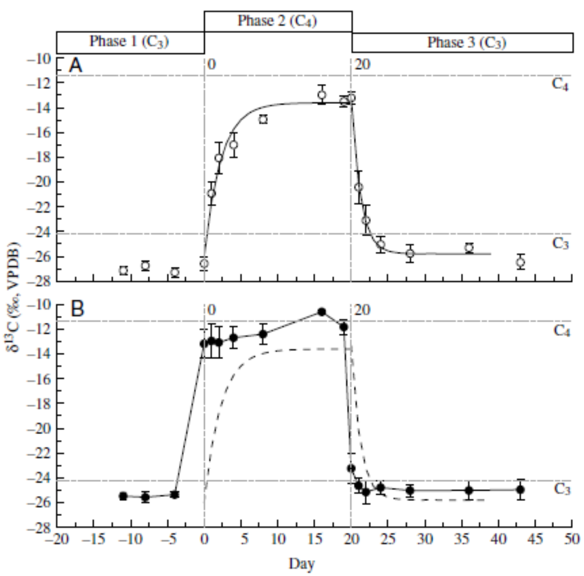


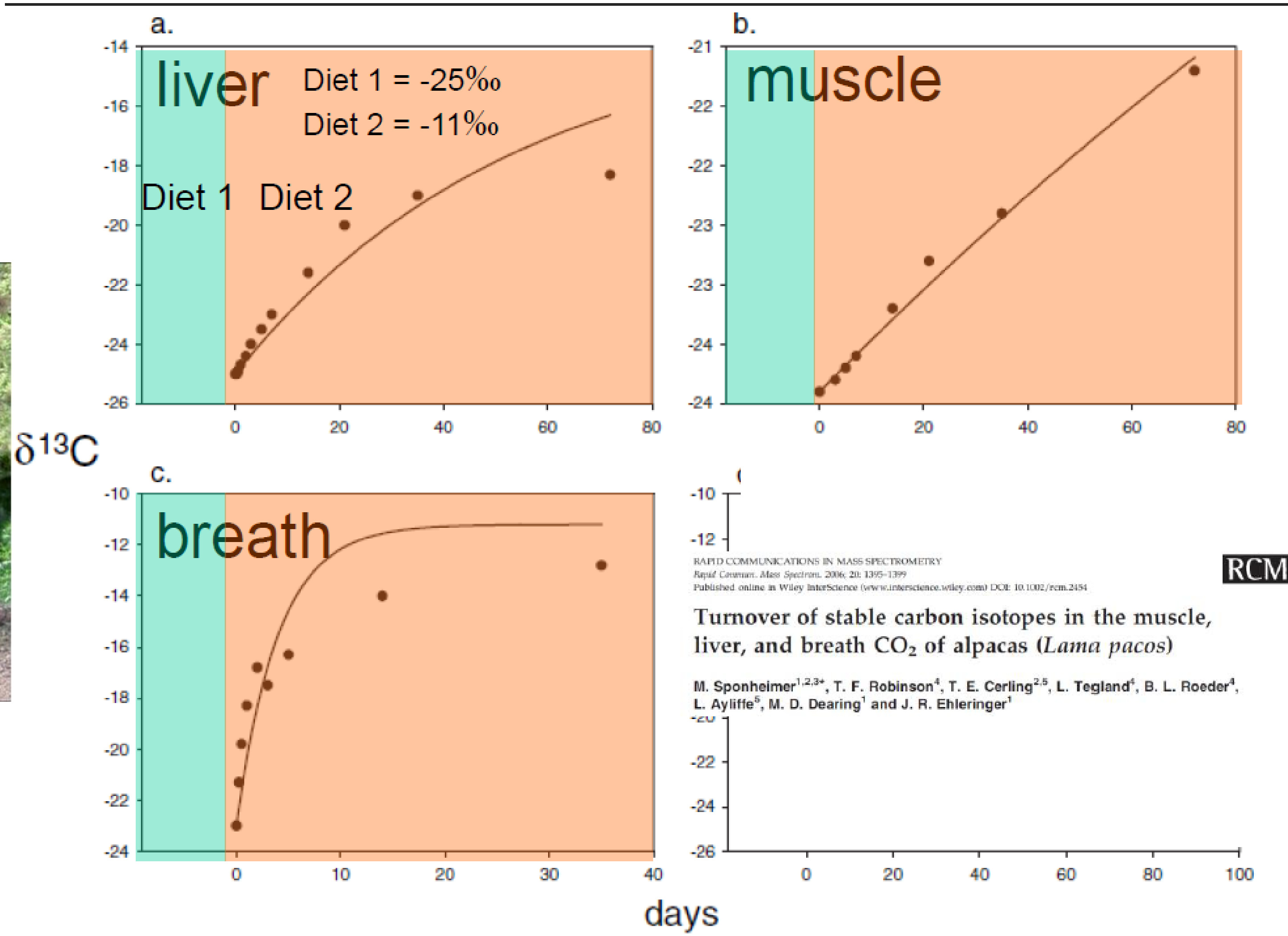
The Journal of Experimental Biology 209, 2622-2627
Published by The Company of Biologists 2006
doi:10.1242/jeb.02293

Metabolic substrate use and the turnover of endogenous energy reserves in broad-tailed hummingbirds (*Selasphorus platycercus*)

Scott A. Carleton*, Bradley Hartman Bakken and Carlos Martínez del Rio
Department of Zoology and Physiology, University of Wyoming, Laramie, WY 82071, USA
*Author for correspondence (e-mail: scarlet@uwyo.edu)







RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2006; 20: 1395–1399
Published online in Wiley InterScience (www.interscience.wiley.com) DOI: 10.1002/rcm.2454

RCM

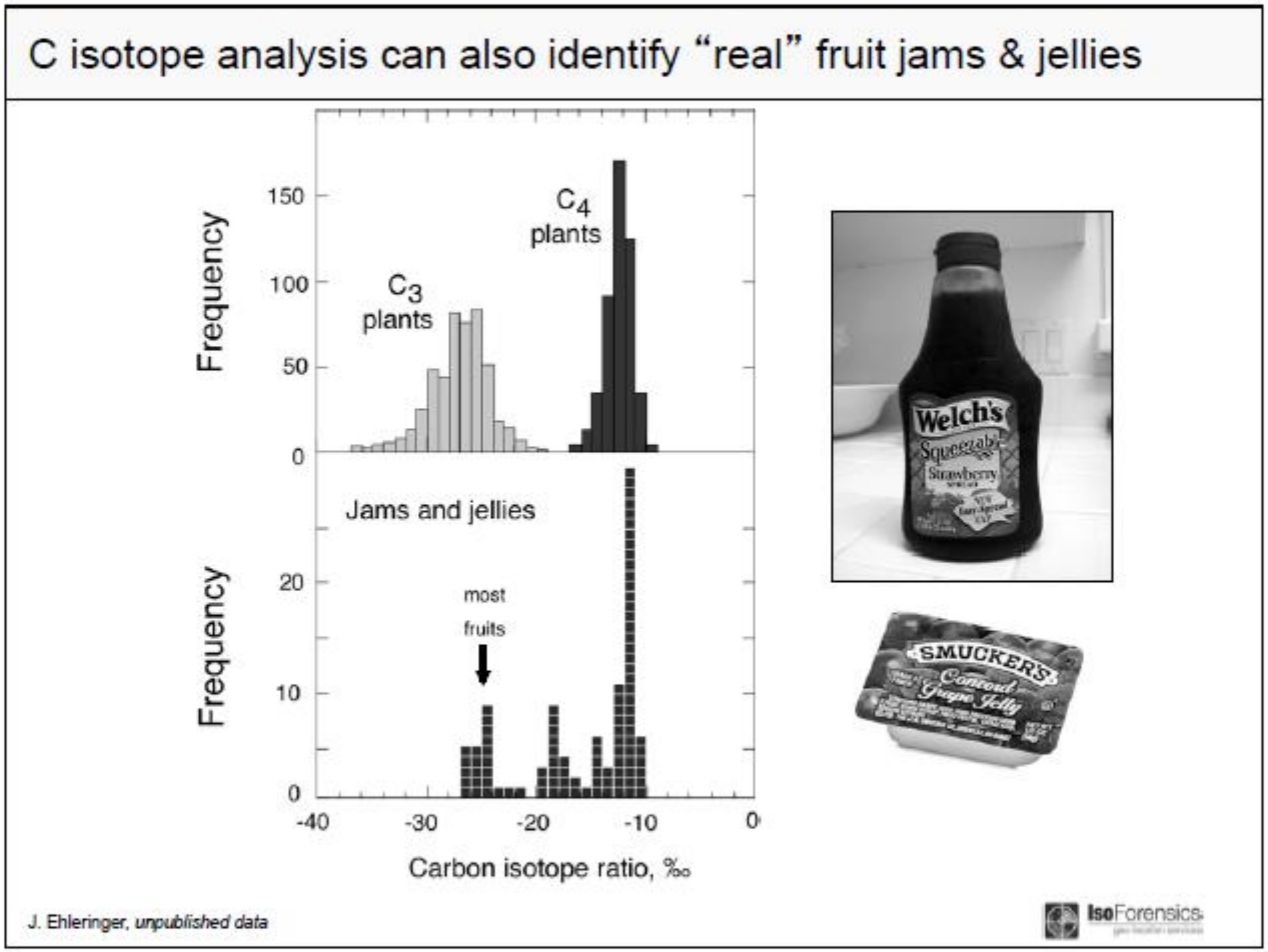
Turnover of stable carbon isotopes in the muscle, liver, and breath CO_2 of alpacas (*Lama pacos*)

M. Sponheimer[1,2,3*], T. F. Robinson[4], T. E. Cerling[2,5], L. Tegland[4], B. L. Roeder[4], L. Ayliffe[5], M. D. Dearing[1] and J. R. Ehleringer[1]

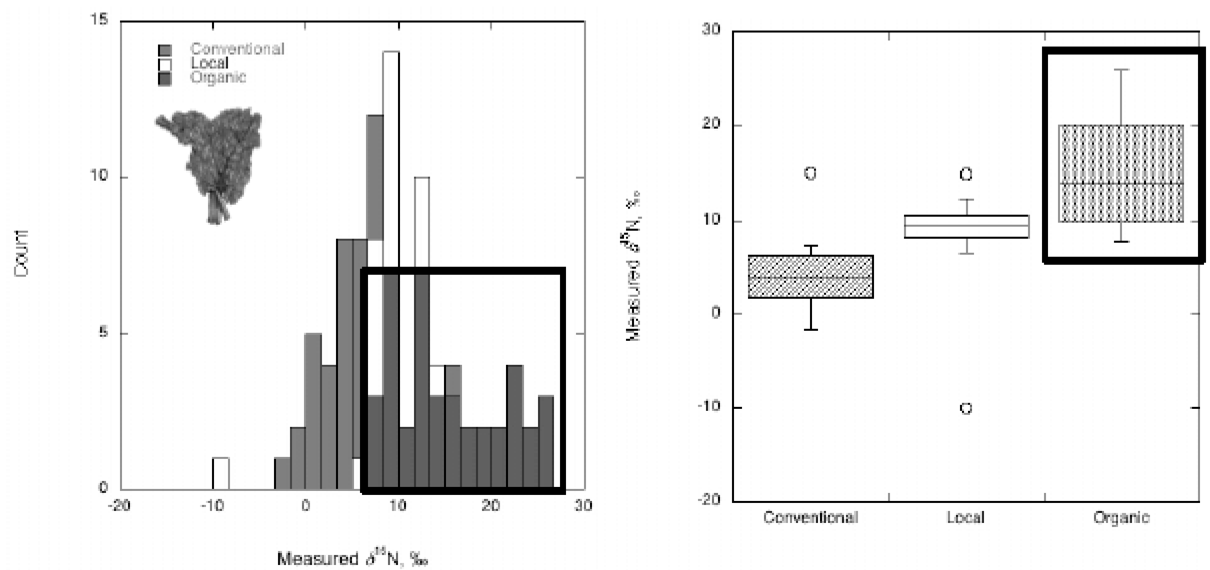
Advantages of the SI approach

- Time integrated (depending on tissue)
- Can trace macromolecules (proteins, lipids, carbohydrates).
- Can trace individual amino acids and fatty acids (compound-specific).
- Can investigate current or historical/paleo diets.

Food adulteration studies



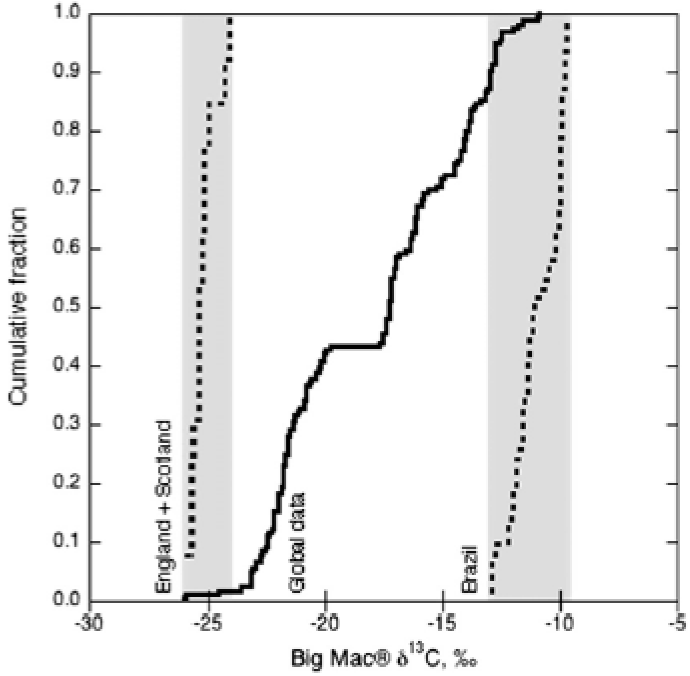
N isotope ratios of organic & conventional leafy greens differ



L. Chesson & J. Ruff, *unpublished data*

IsoForensics

Carbon isotope ratios reveal both C_3 and C_4 feed for beef cattle



- Big Mac® sandwiches purchased from across the globe
- Pure C_3 diet = England & Scotland (−25 ‰)
- Pure C_4 diet = Brazil (−11 ‰)

Martinelli et al. 2011 *Food Chemistry*

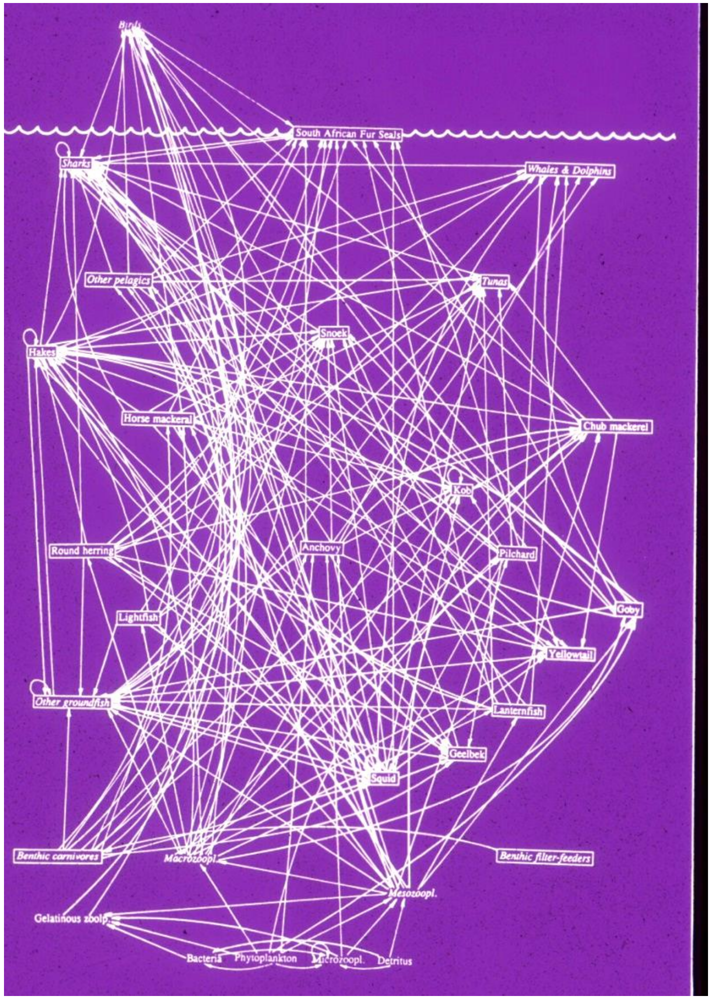
IsoForensics

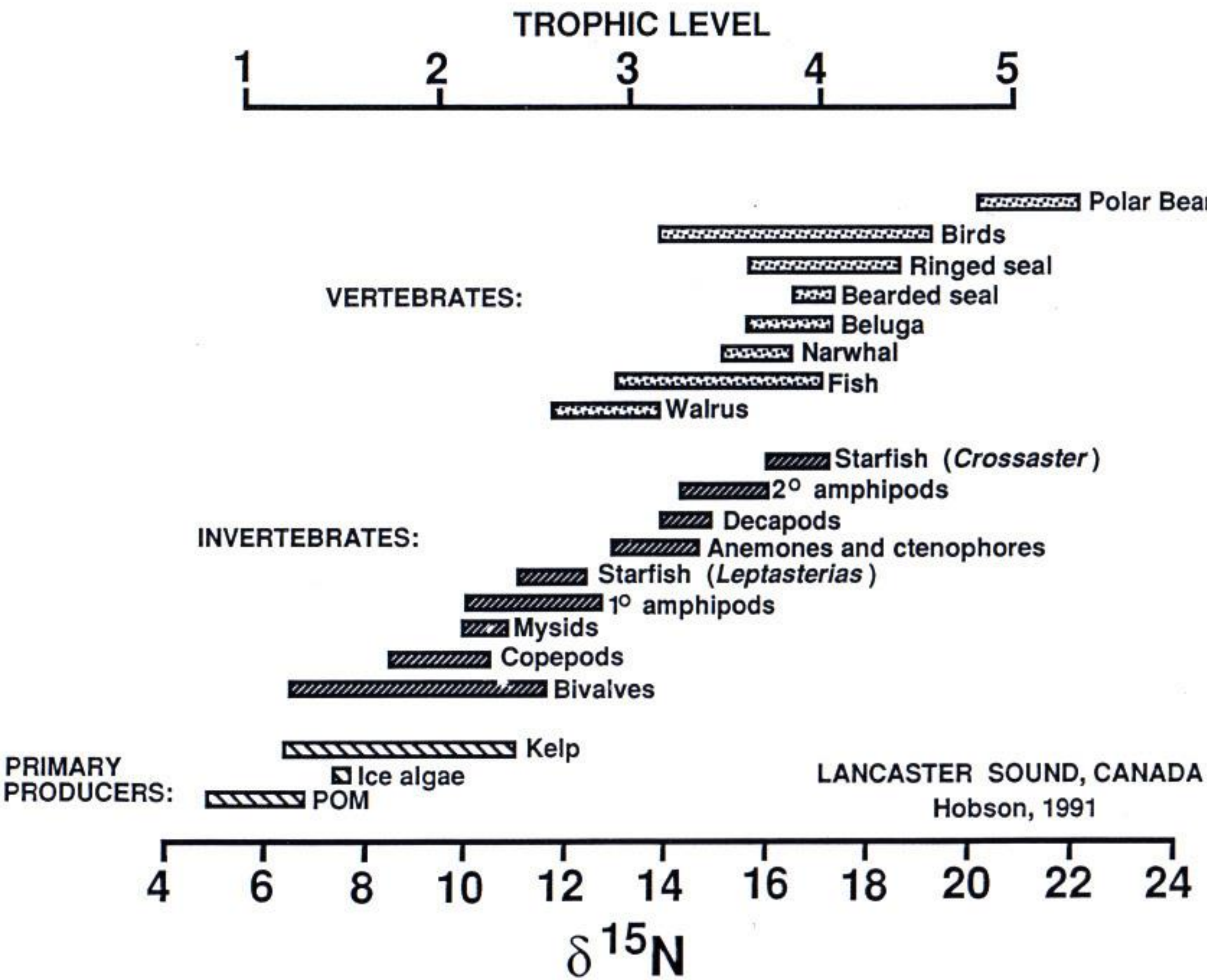
Some real-world examples …

$\delta^{15}N$

Previous conventional approaches:

Foodweb theory has greatly outpaced empirical support ….

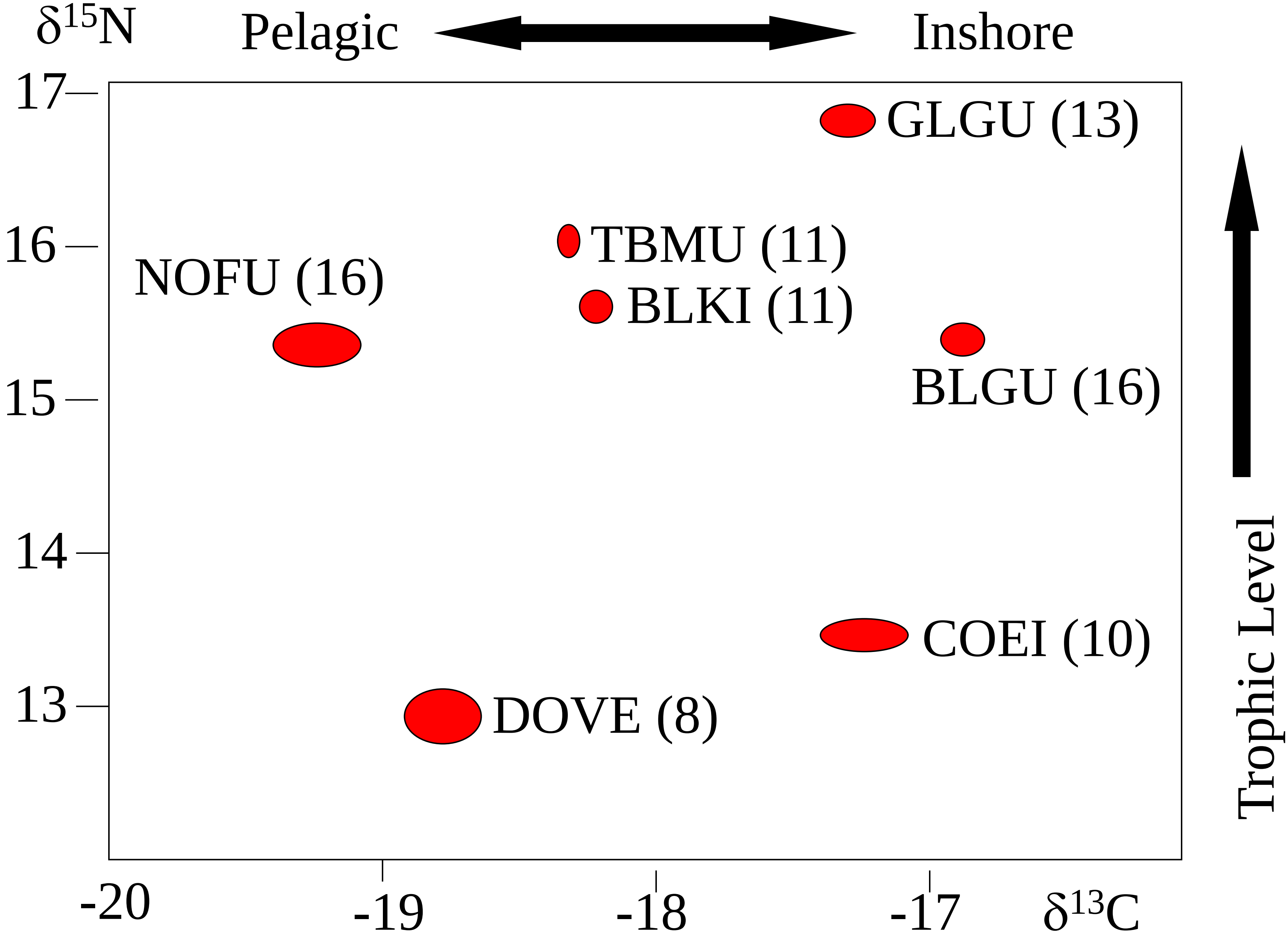




TROPHIC LEVEL
1
2
3
4
5
Polar Bear
Birds
Ringed seal
VERTEBRATES:
Bearded seal
Beluga
Narwhal
Fish
Walrus
Starfish (Crossaster)
2° amphipods
Decapods
INVERTEBRATES:
Anemones and ctenophores
Starfish (Leptasterias)
1° amphipods
Mysids
Copepods
Bivalves
Kelp
PRIMARY PRODUCERS:
Ice algae
POM
LANCASTER SOUND, CANADA
Hobson, 1991
4
6
8
10
12
14
16
18
20
22
24
δ15N

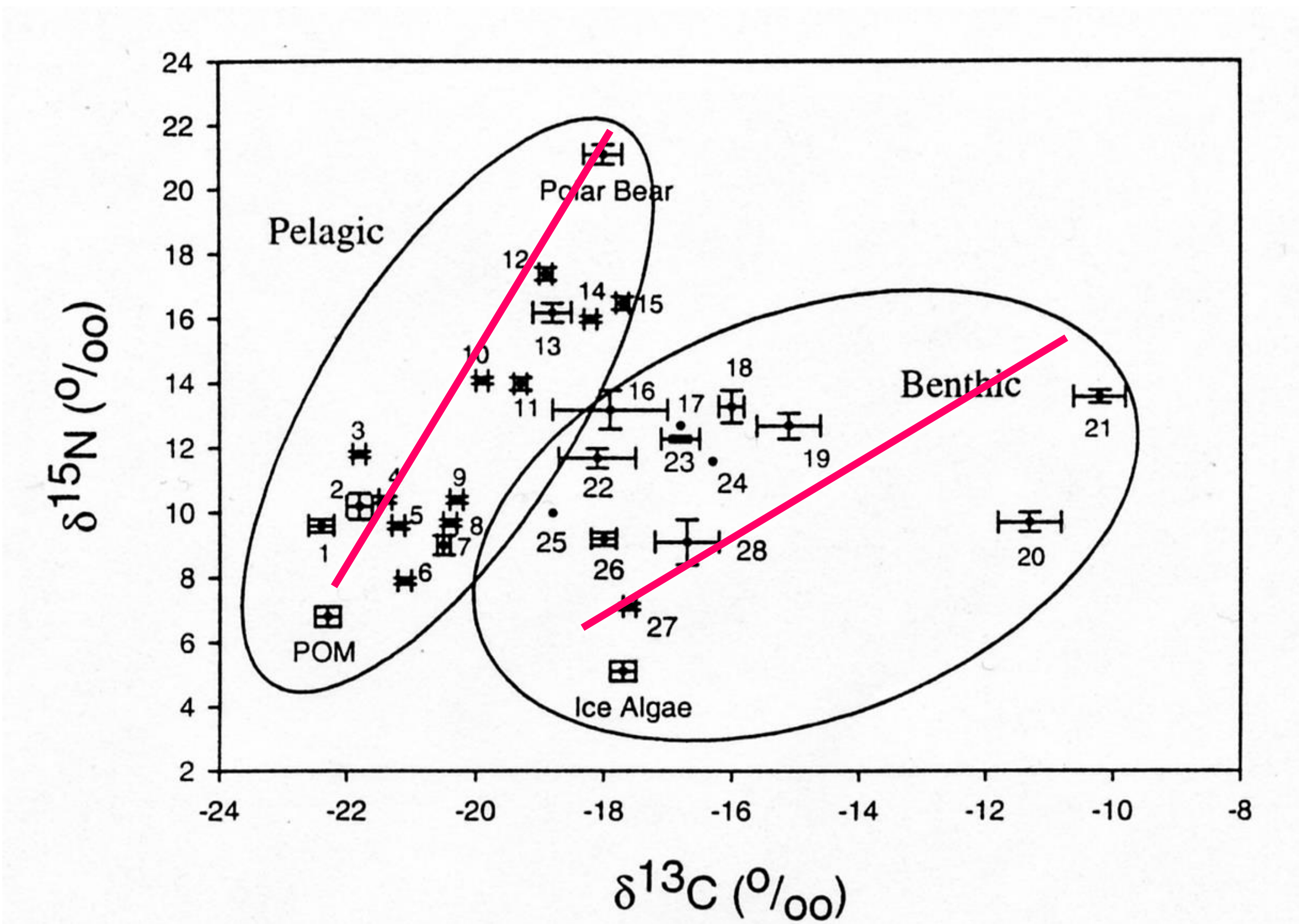
$$TL = 1 + (\delta^{15}Nc - \delta^{15}Nbase)/\Delta\delta^{15}N$$

$$TL = 2 + (\delta^{15}Nc - \delta^{15}N_{TL2})/\Delta\delta^{15}N$$



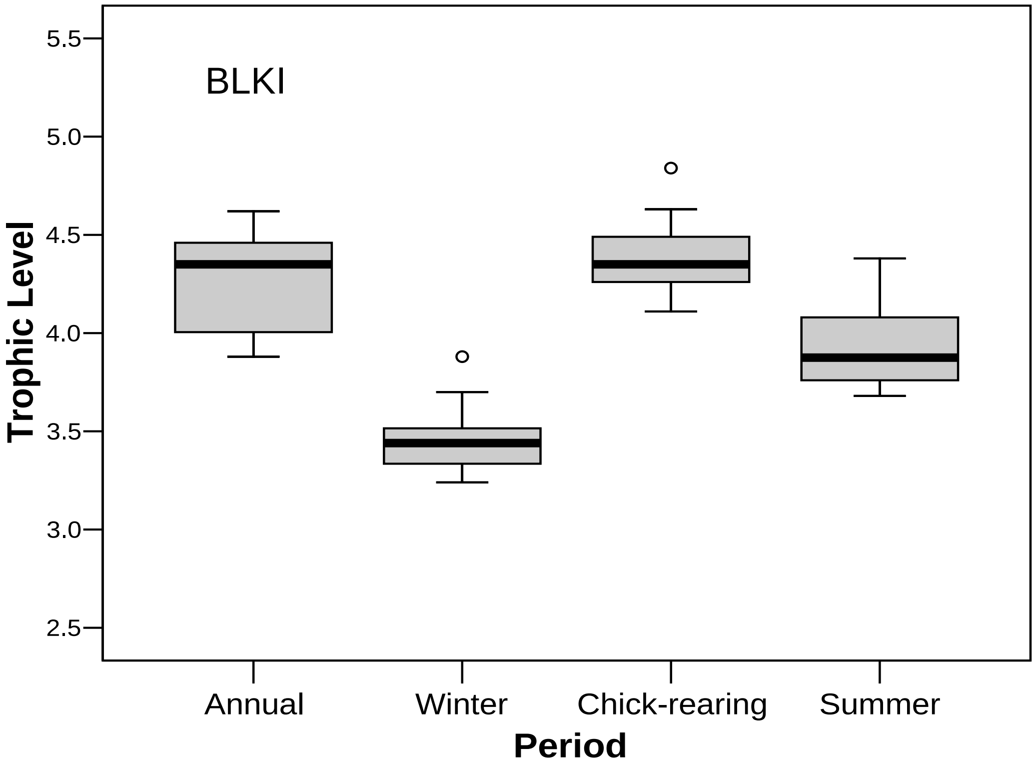
δ15N
Pelagic
Inshore
17
16
15
14
13
GLGU (13)
TBMU (11)
NOFU (16)
BLKI (11)
BLGU (16)
COEI (10)
DOVE (8)
Trophic Level
-20
-19
-18
-17
δ13C

See a benthic vs. pelagic effect in marine systems ….

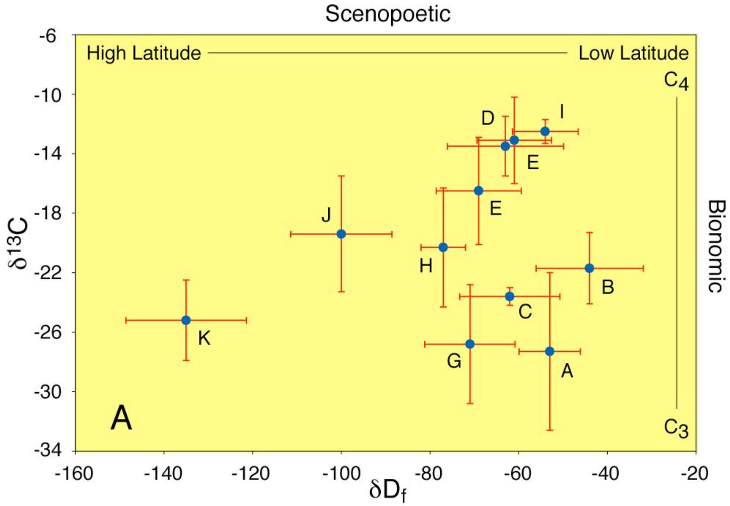


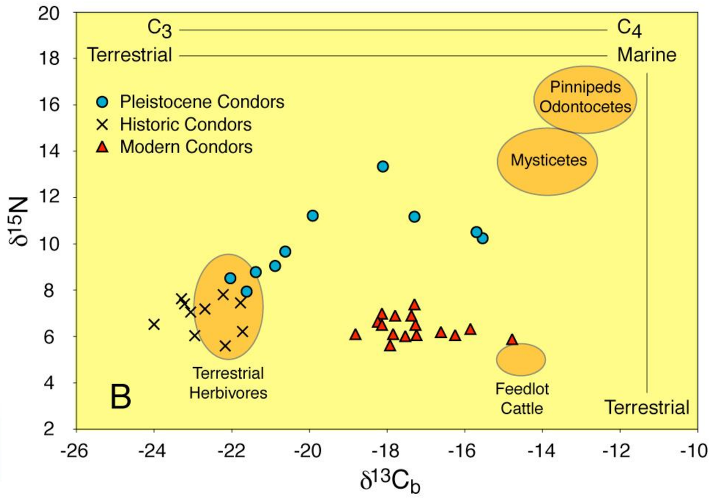
Hobson et al. 2002

Using multiple tissues …

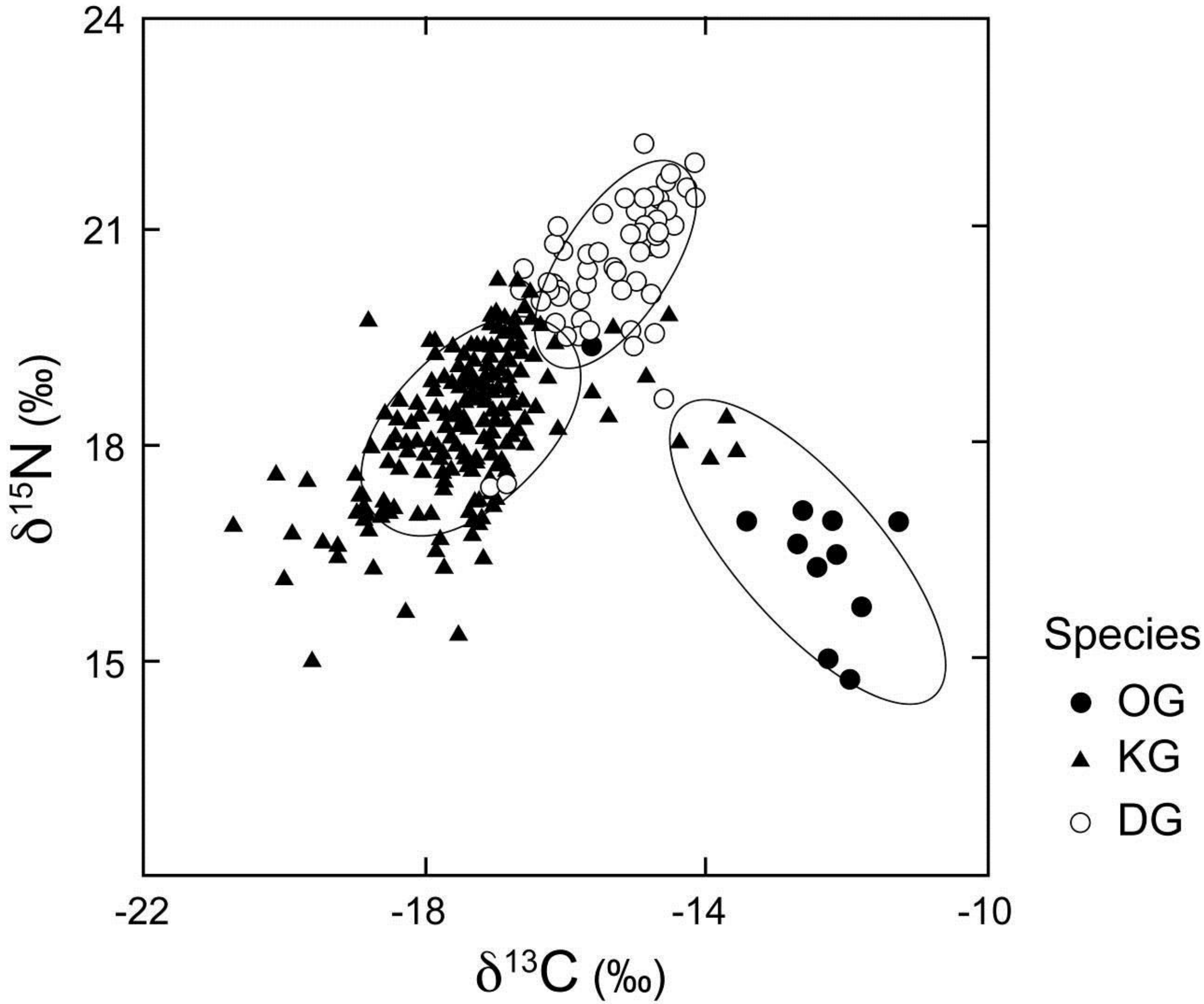


Further examples of the benefits of a dual-isotope approach

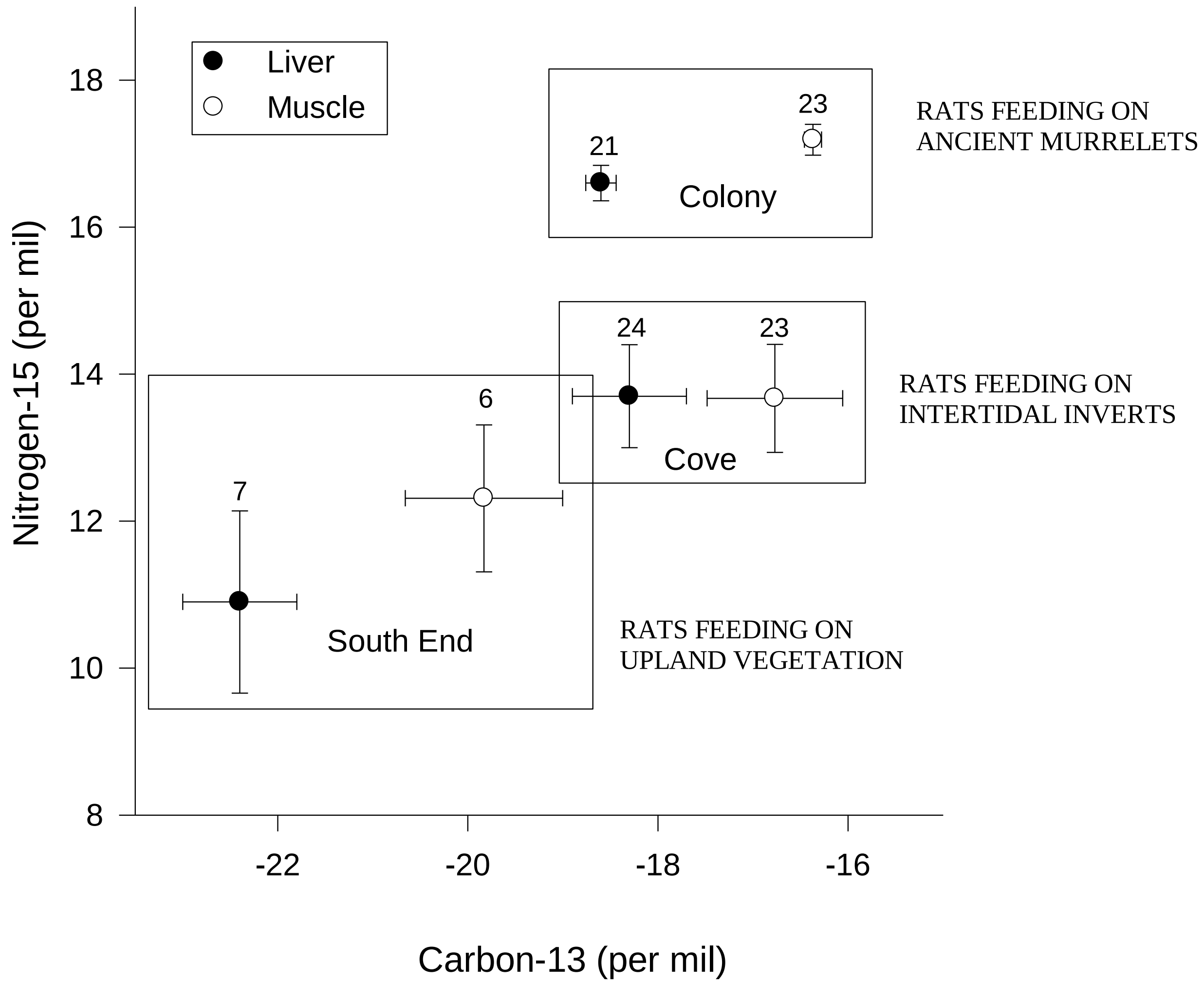




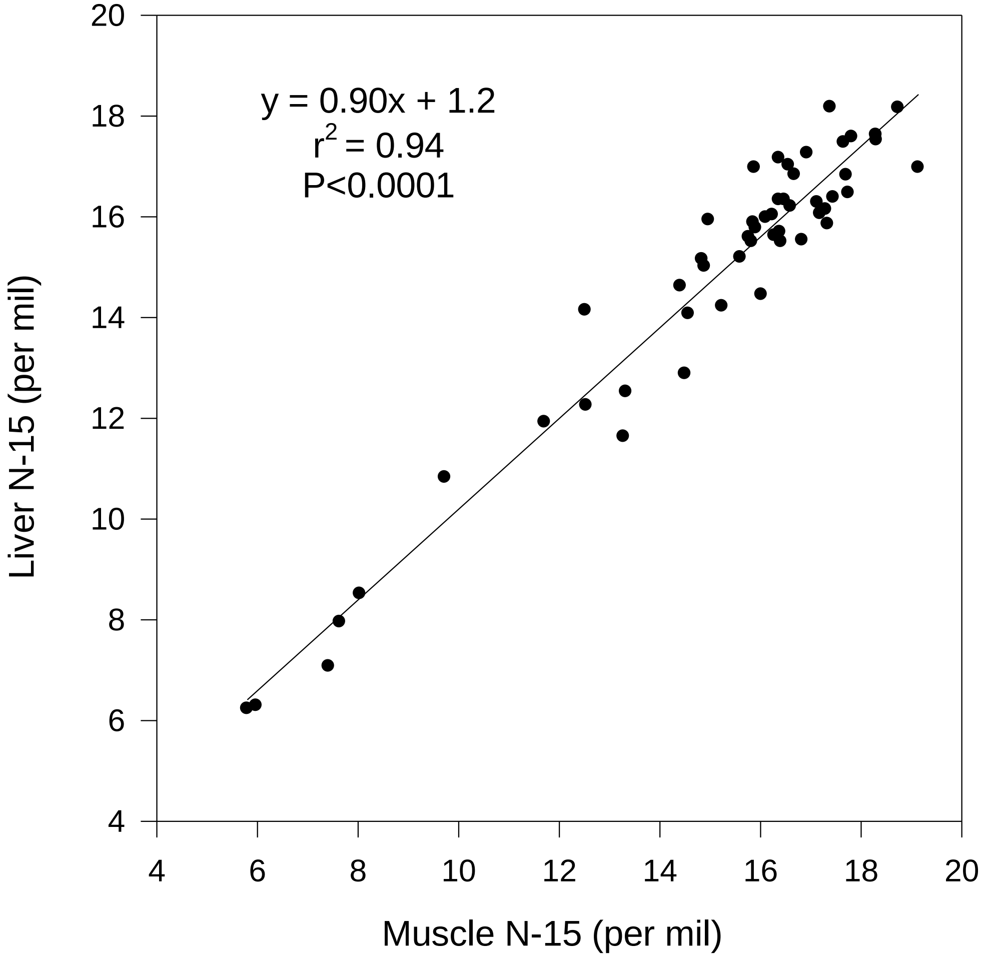
Niche segregation ….



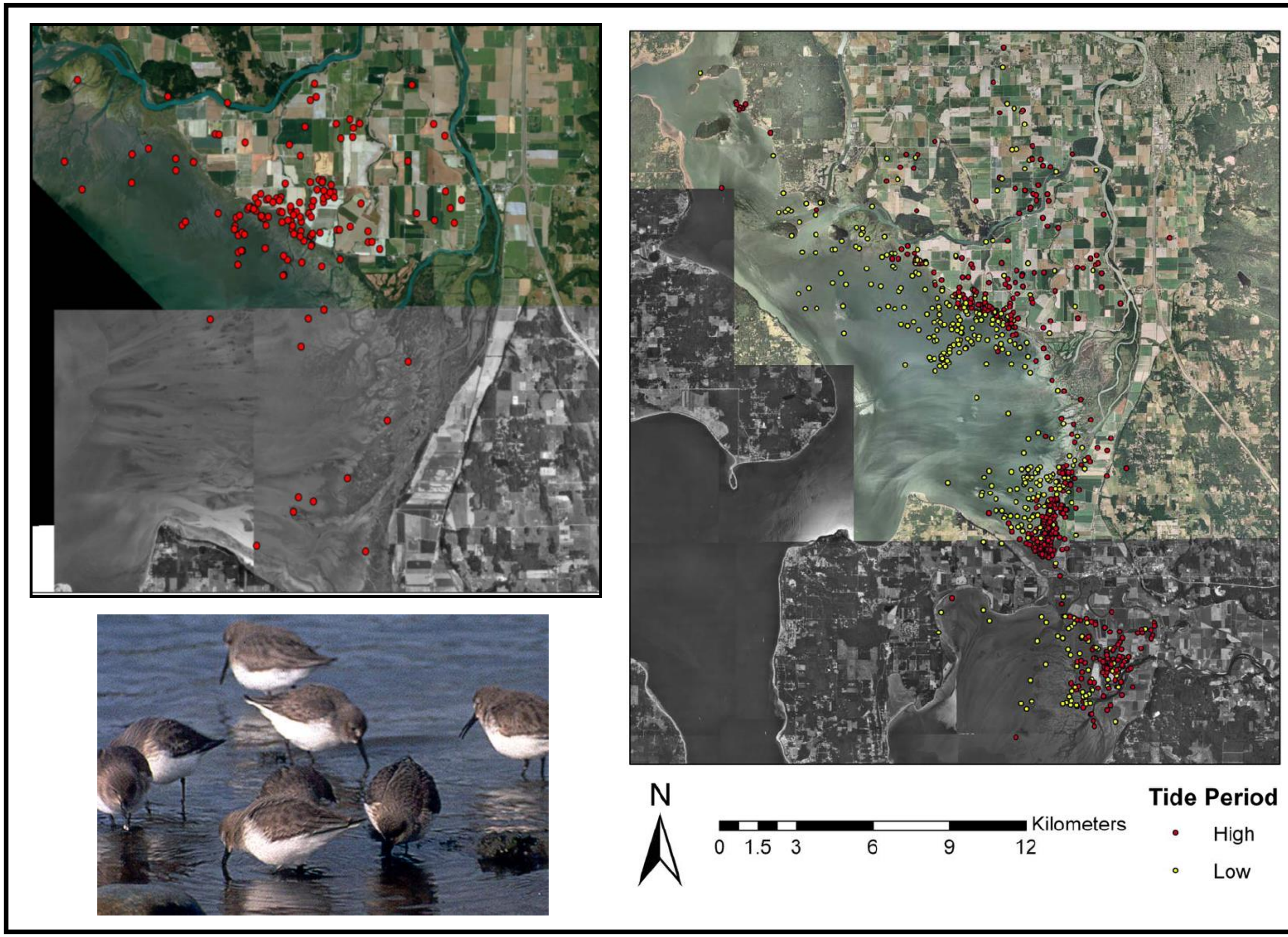
Rats on seabird islands …..

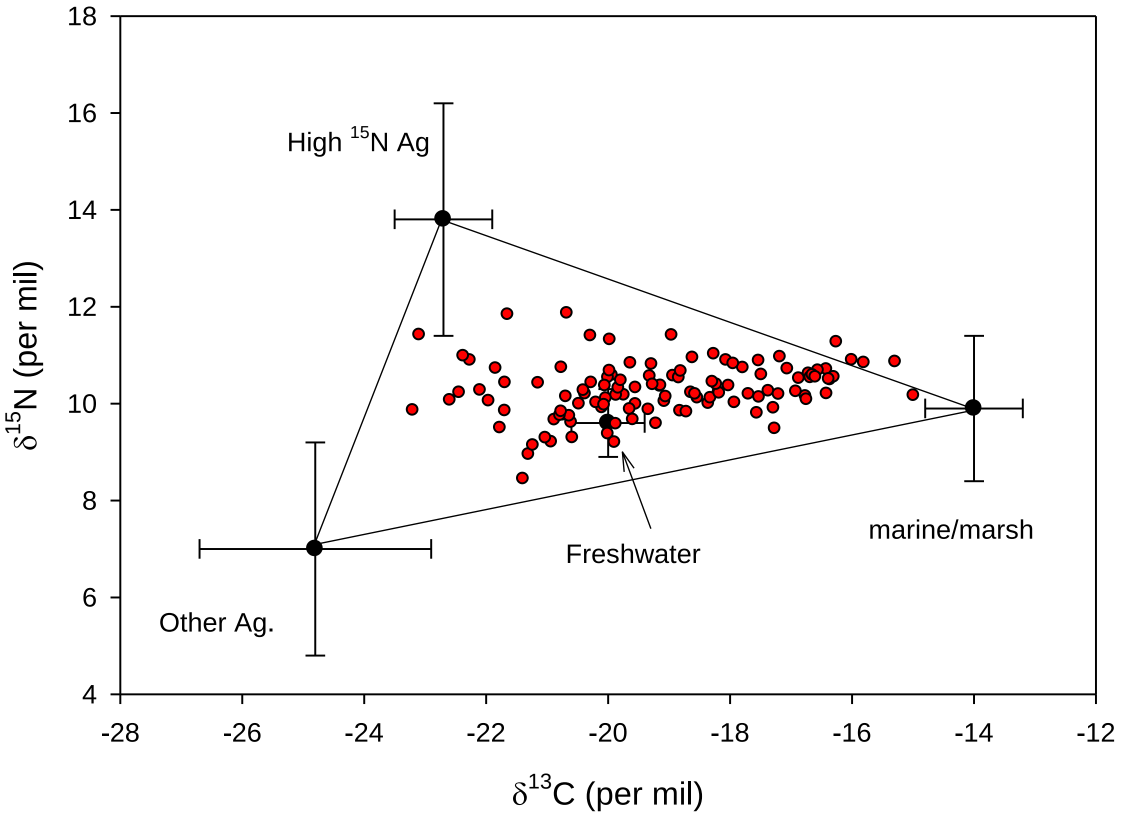


Hobson et al. *J. Wildlife Manage.*63:14-25.

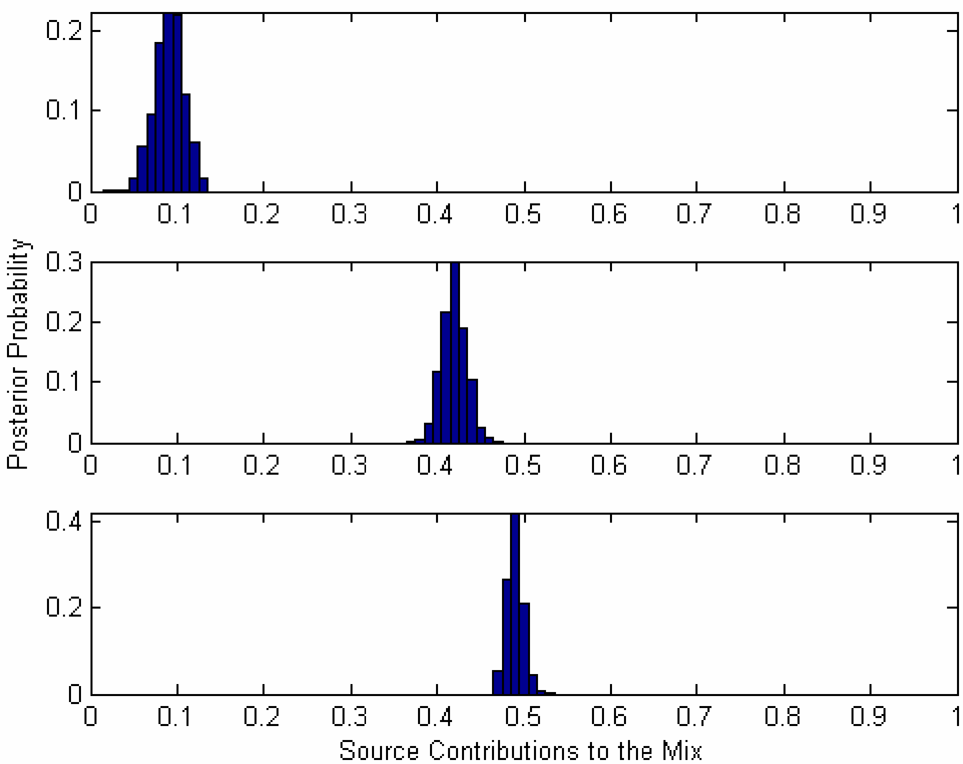


Hobson et al. *J. Wildlife Manage.*63:14-25.


N
Kilometers
0 1.5 3 6 9 12
Tide Period
High
Low



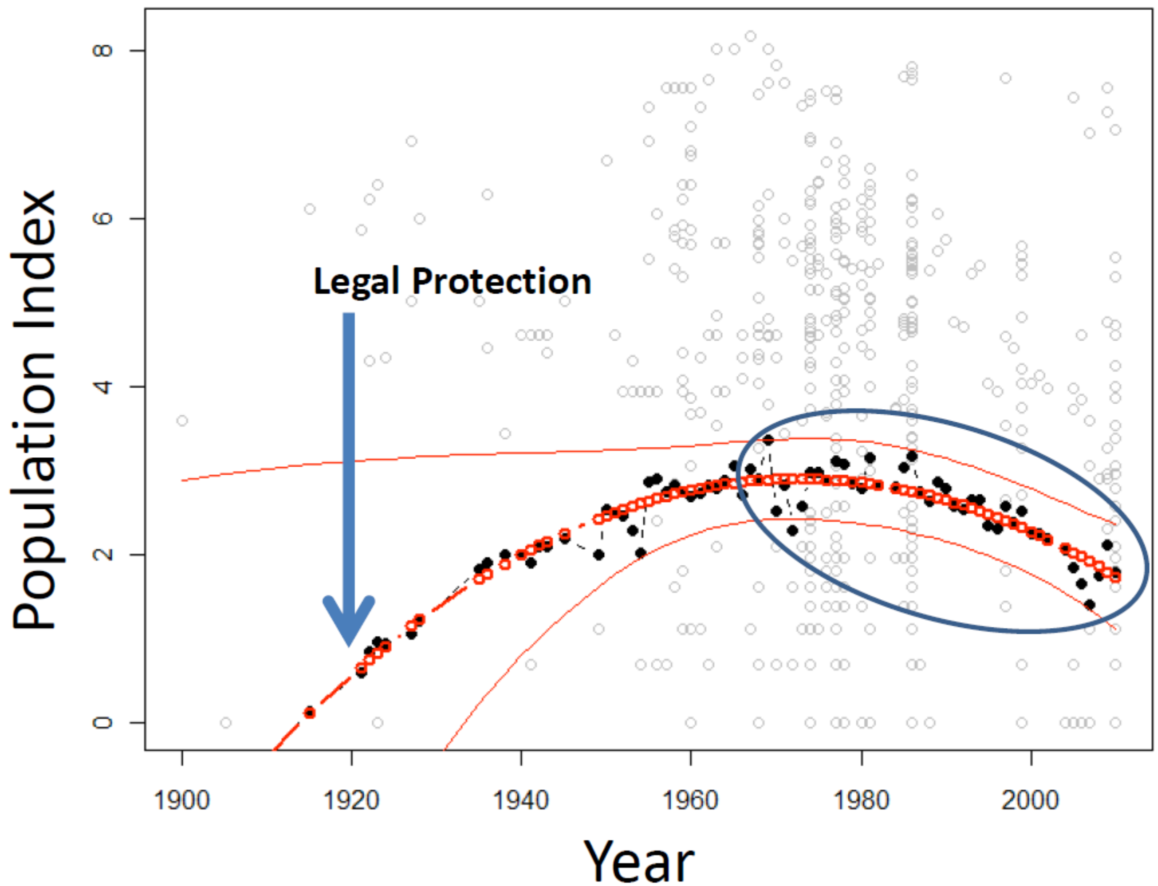
18
16
14
12
10
8
6
4
-28
-26
-24
-22
-20
-18
-16
-14
-12
δ15N (per mil)
δ13C (per mil)
High 15N Ag
Other Ag.
Freshwater
marine/marsh

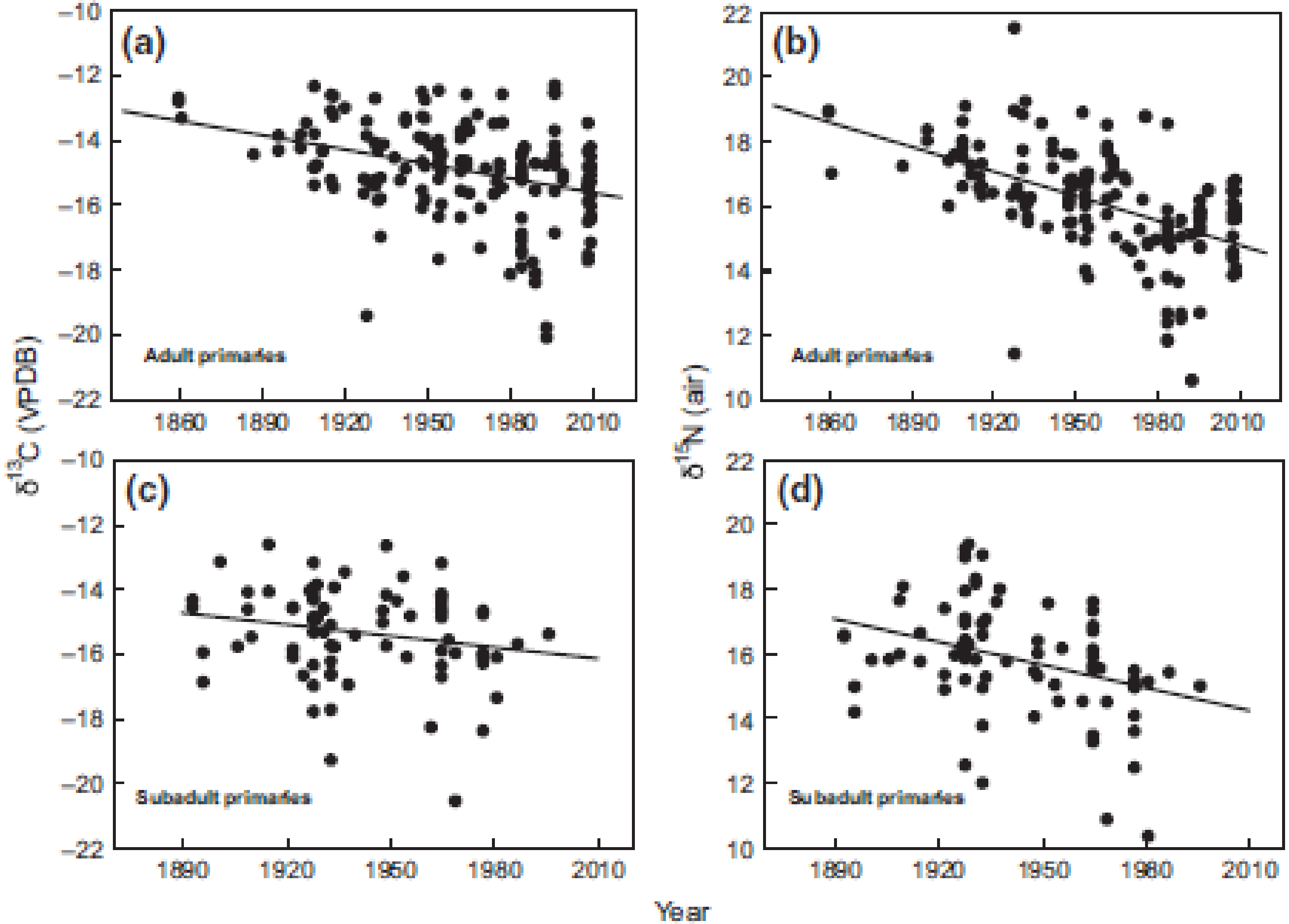


Source	Mean Percent	95% CI
High ^{15}N Ag.	8.2	6.8 to 10.5
Other Ag.	42.2	40.1 to 44.2
Freshwater Plume	0.1	0 to 0.9
Marine/Marsh	49.2	46.9 to 50.0

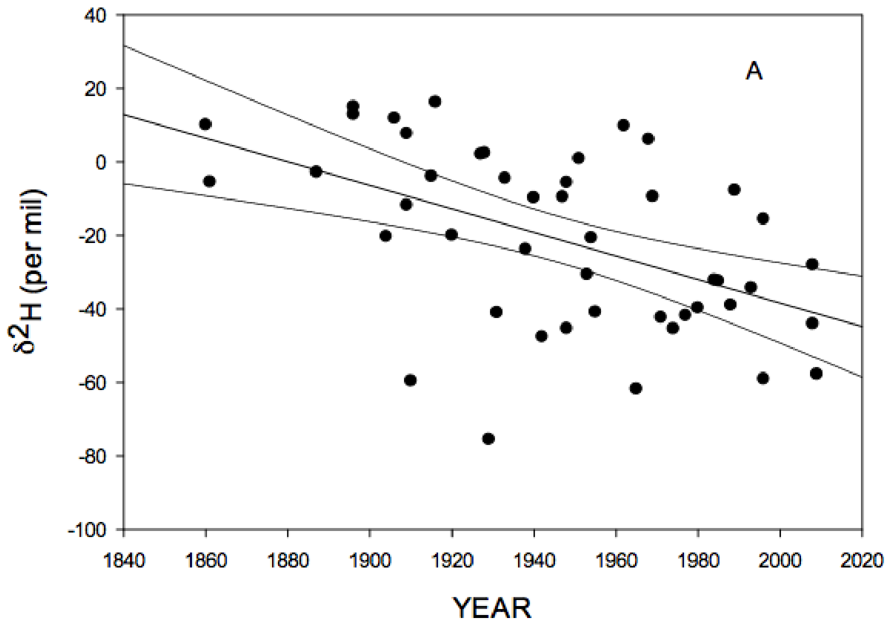
GLAUCOUS-WINGED GULLS *LARUS GLAUCESCENS* AS SENTINELS FOR A CENTURY OF ECOSYSTEM CHANGE

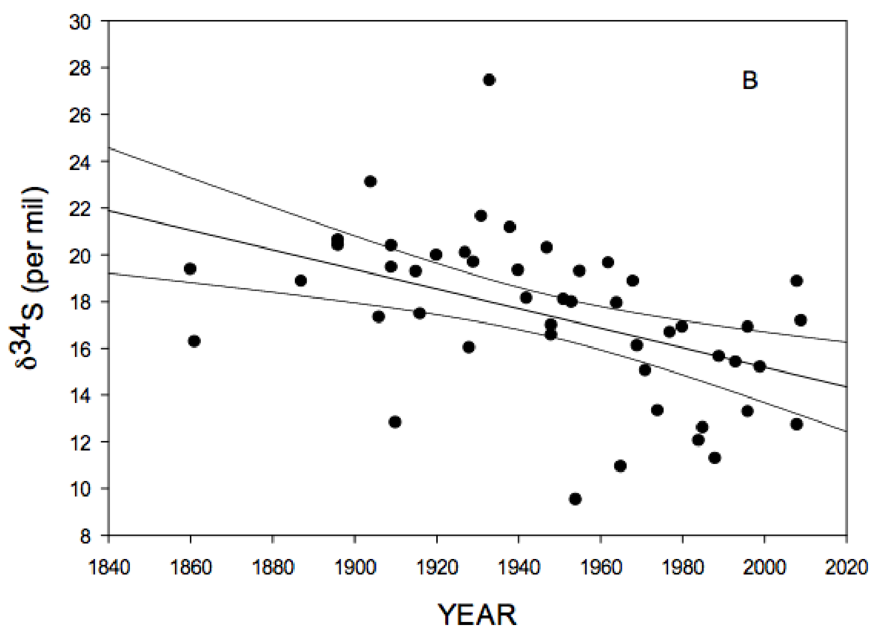
Blight, L.K. 2012 PhD



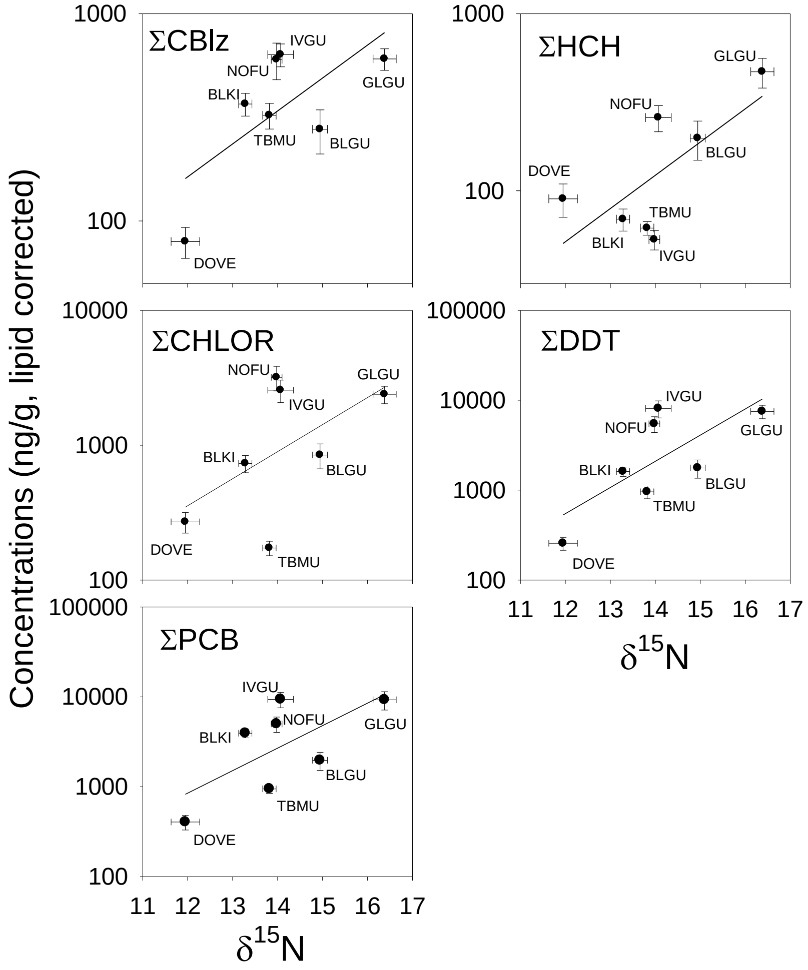


Shift to terrestrial/freshwater prey or lower TL marine prey?


A
δ2H (per mil)
40
20
0
-20
-40
-60
-80
-100
1840
1860
1880
1900
1920
1940
1960
1980
2000
2020
YEAR

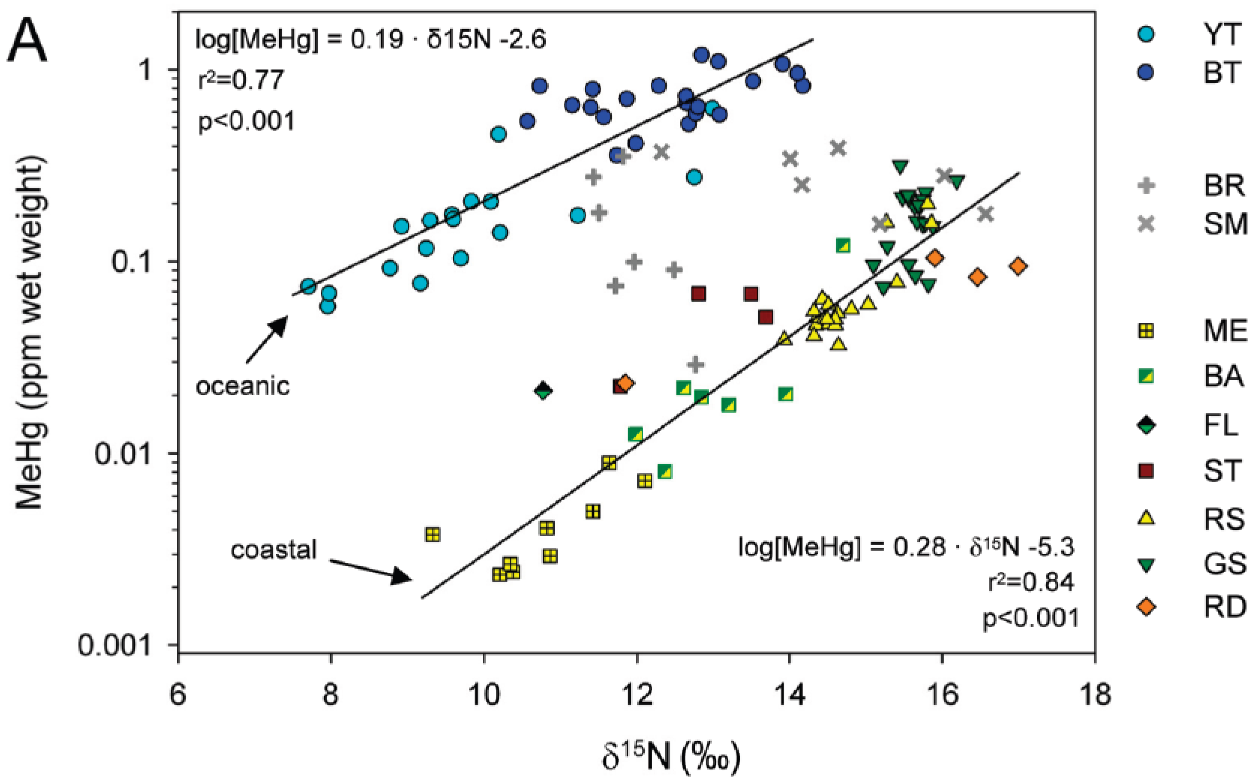

B
δ34S (per mil)
30
28
26
24
22
20
18
16
14
12
10
8
1840
1860
1880
1900
1920
1940
1960
1980
2000
2020
YEAR

Contaminants (OCs) and trophic level….



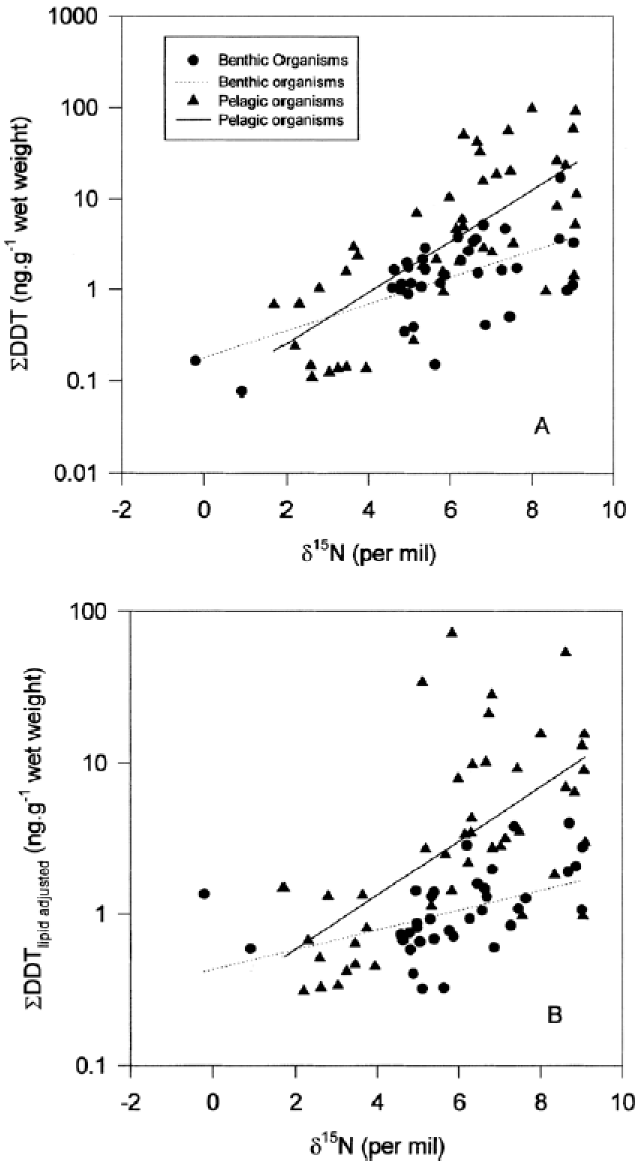
Fisk et al. *Environmental Pollution* 113:225-238

Clearly different food chains with different Hg characteristics



Senn et al. 2010

Biomagnification differences



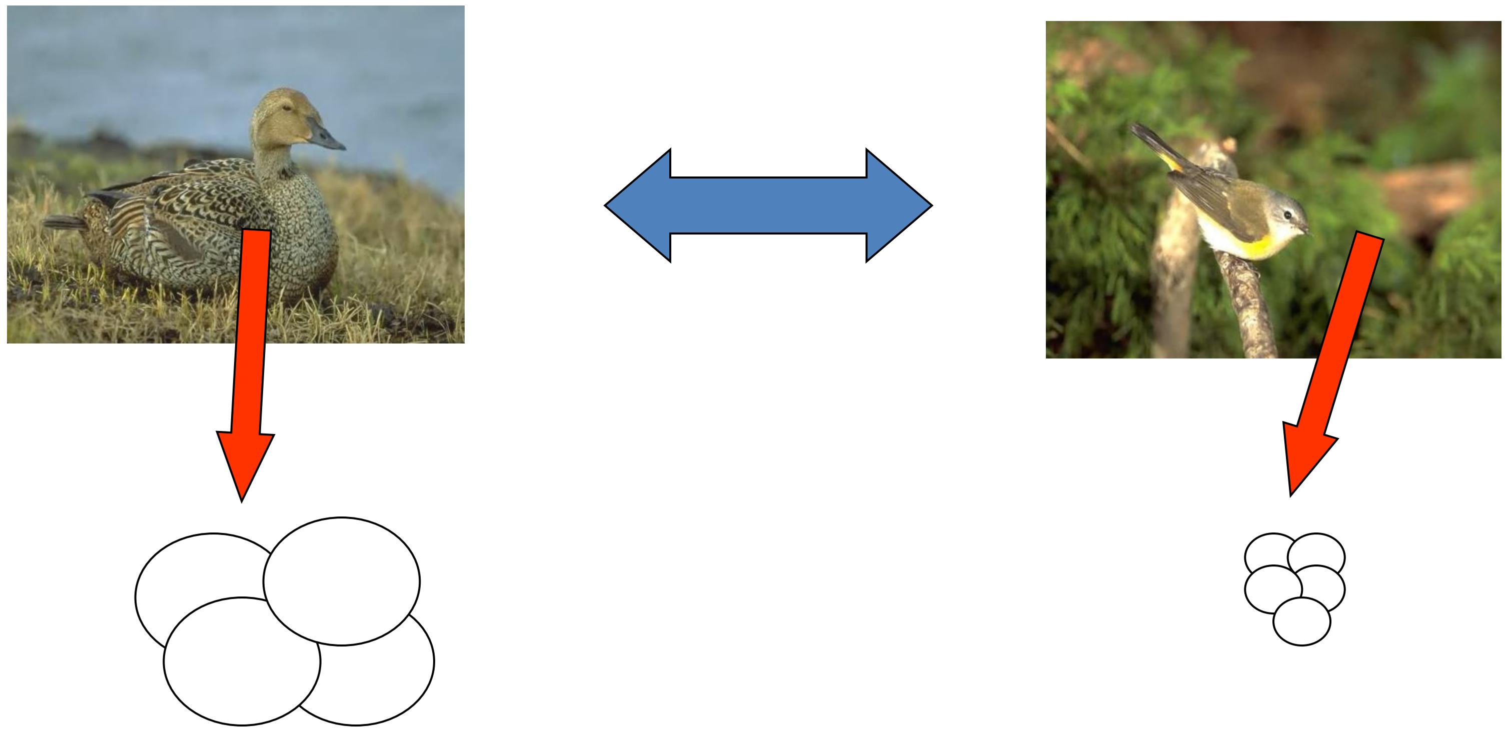
Organisms separated into benthic and pelagic food chains (based on δ^{13}C)

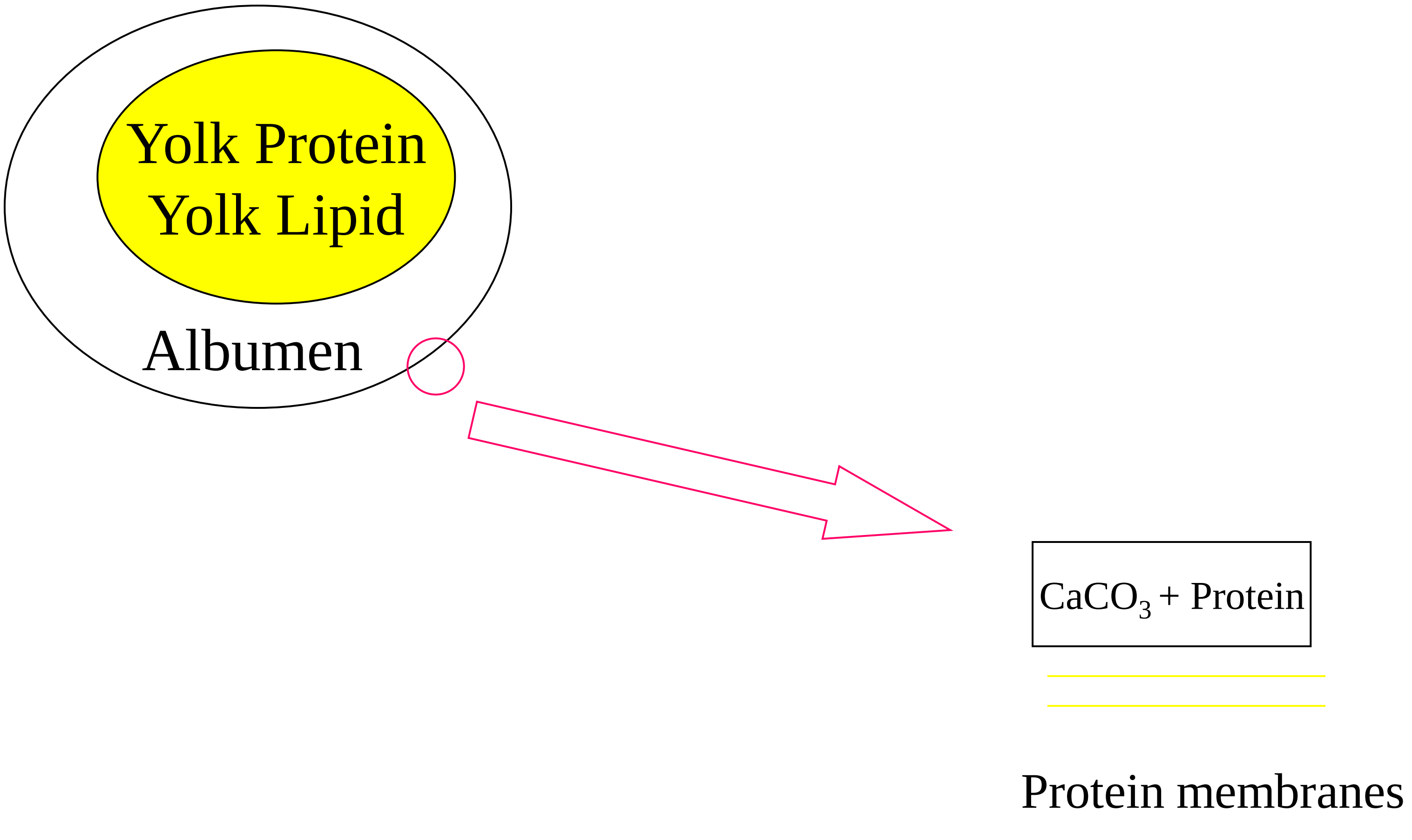
Slope of DDT-δ^{15}N regression higher for pelagic food chain

Kidd et al. 2001

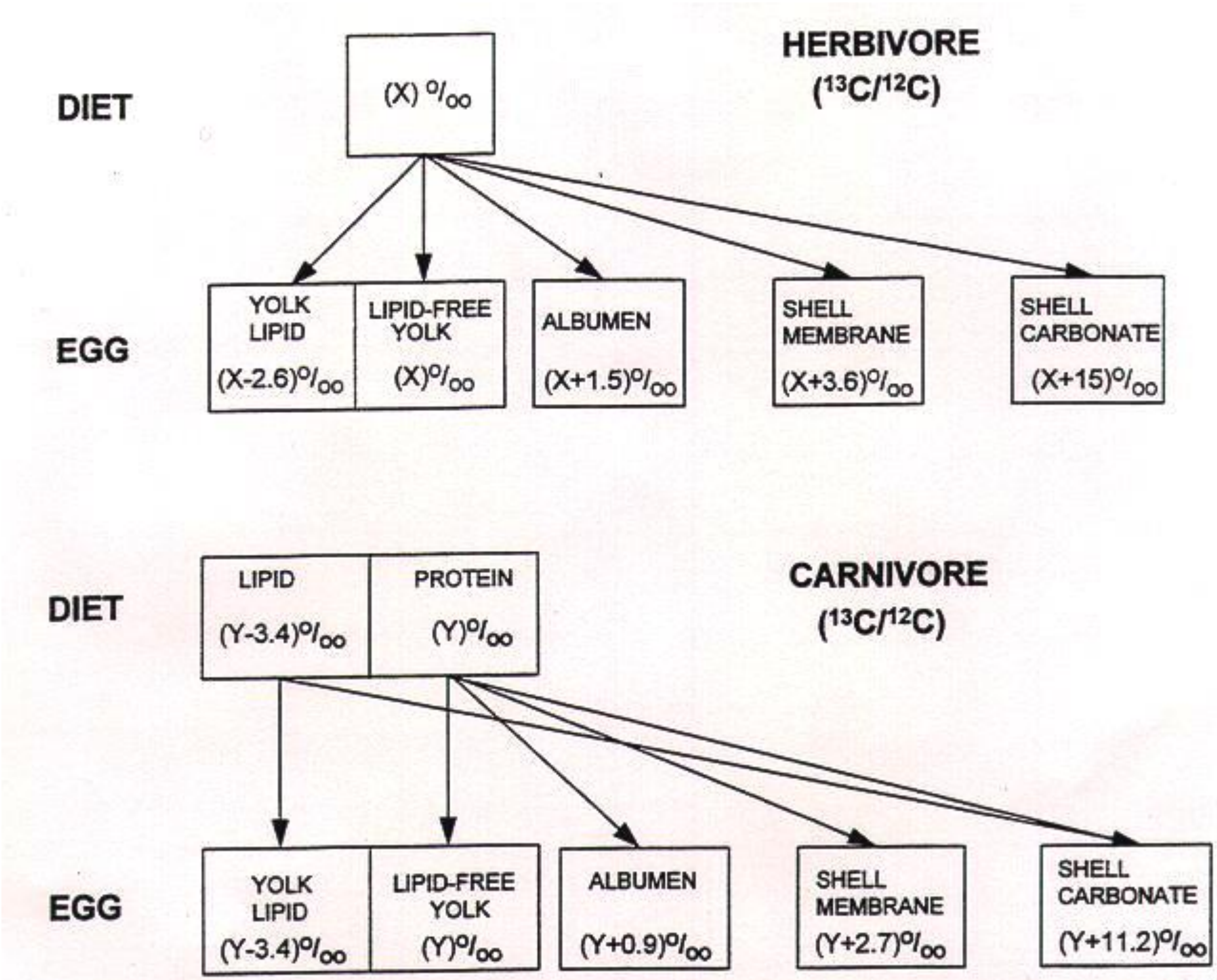
Understanding nutrient allocations to reproduction

Capital vs Income Dichotomy
Drent and Daan (1980)

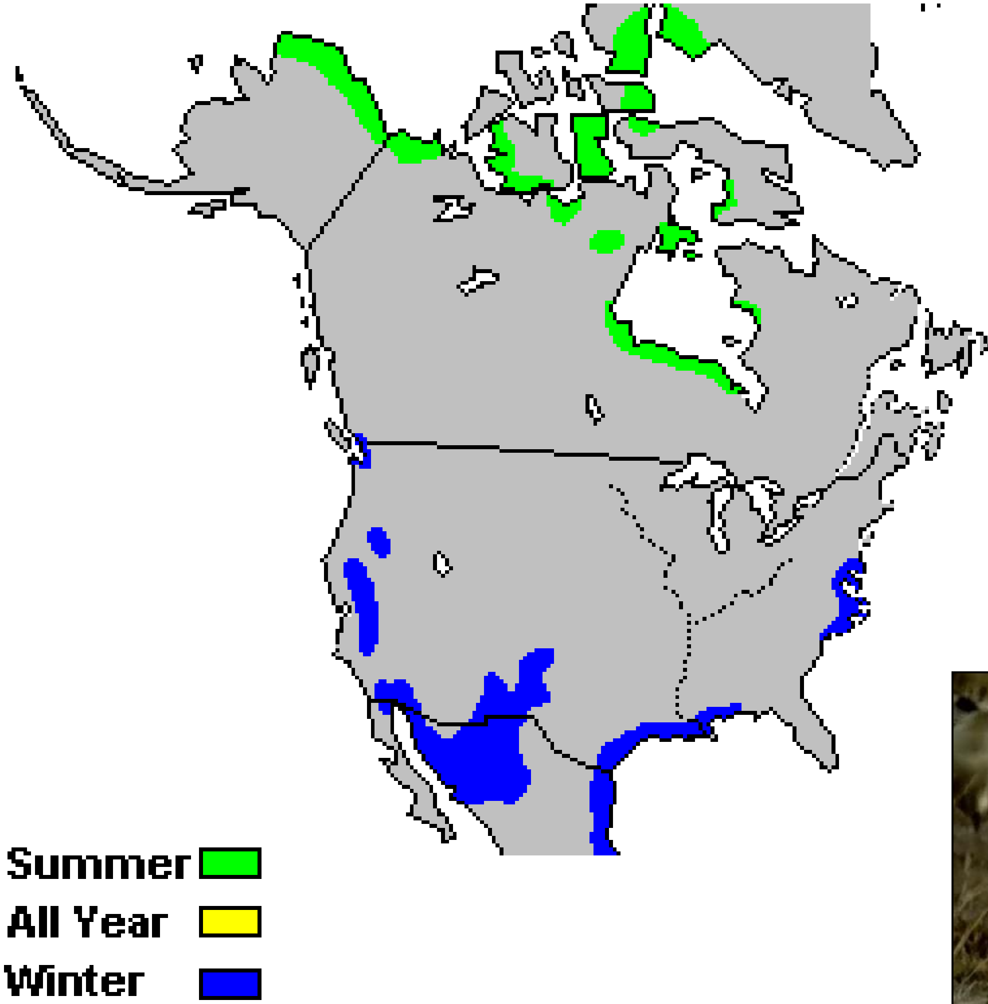


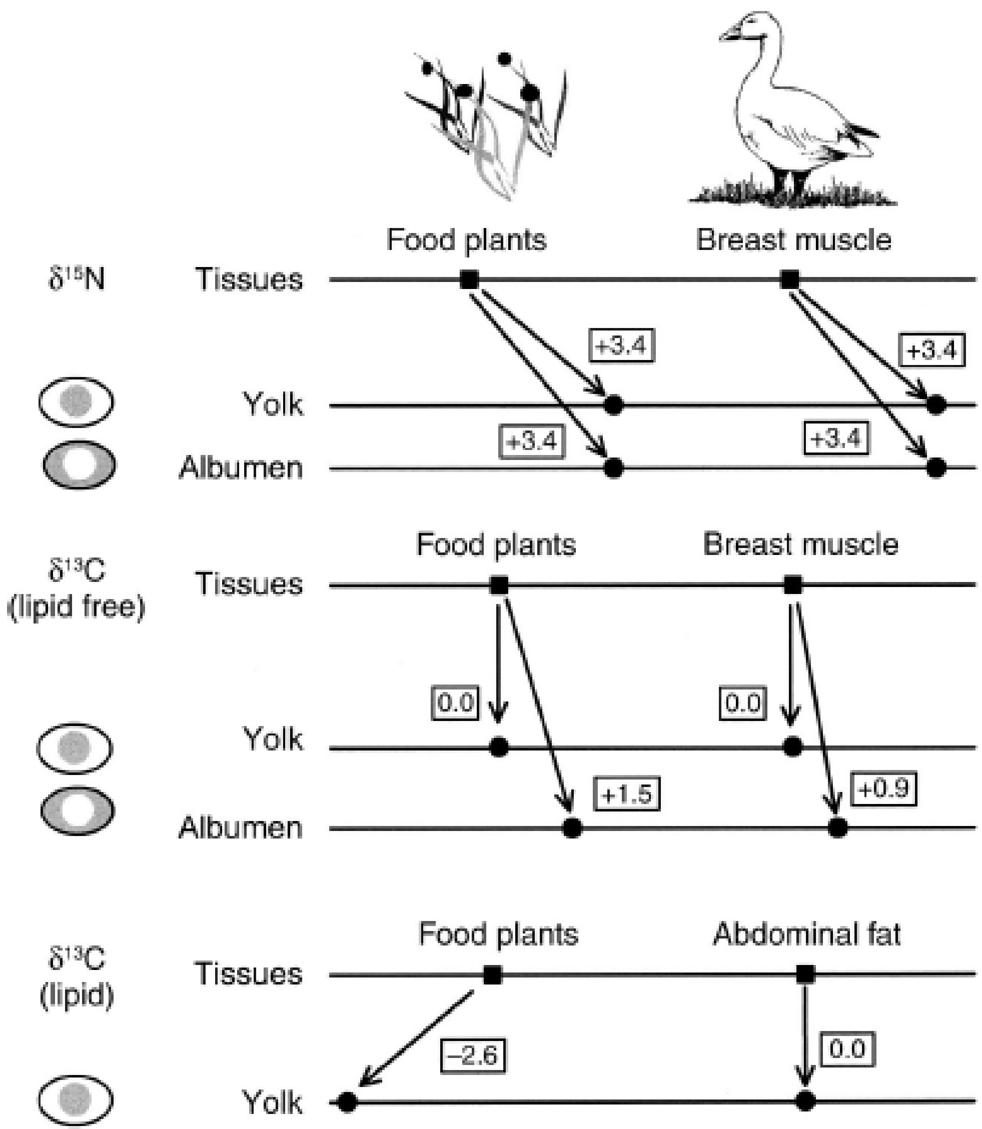

Yolk Protein
Yolk Lipid
Albumen
$CaCO_3$ + Protein
Protein membranes

Exogenous egg fractionation experiment



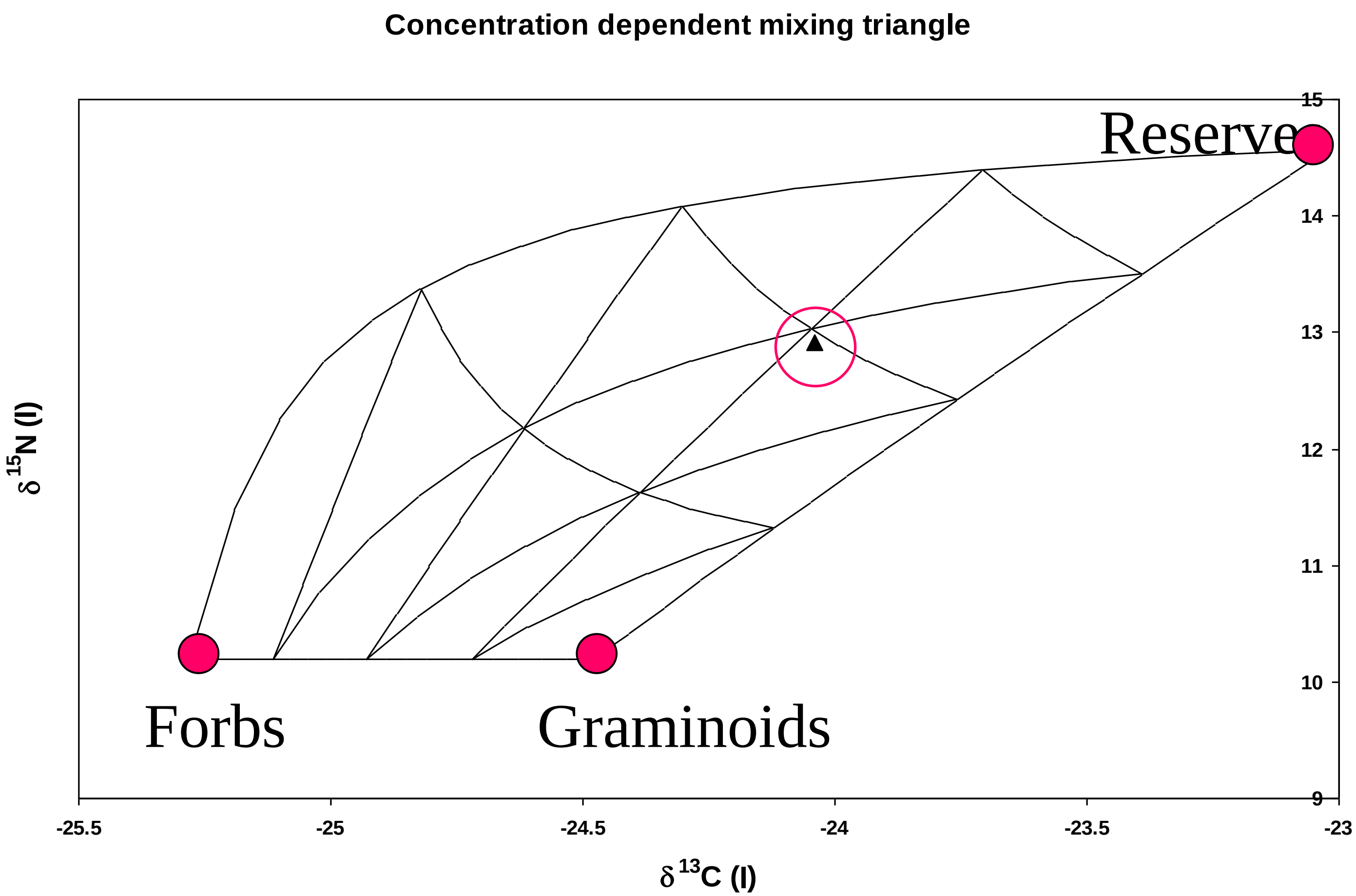
Hobson *Condor* 97:752-762.


Summer
All Year
Winter



Gauthier et al. (2003) Ecology 84:3250-3264

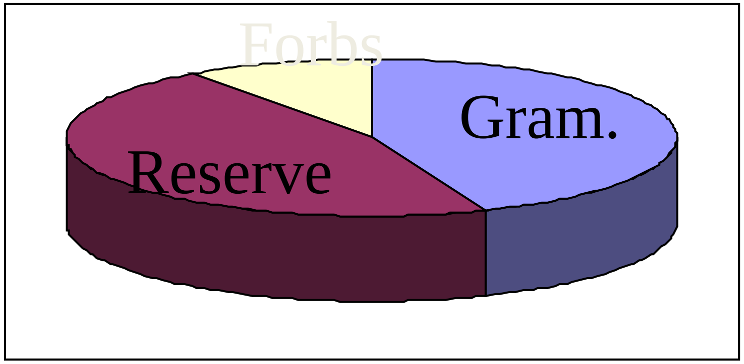
Snow Goose mixing model



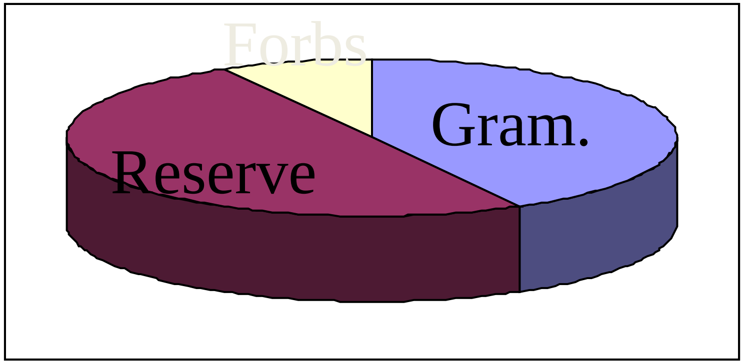
Gauhtier et al. *Ecology* **84:3250-3264**

Contributions to eggs ….

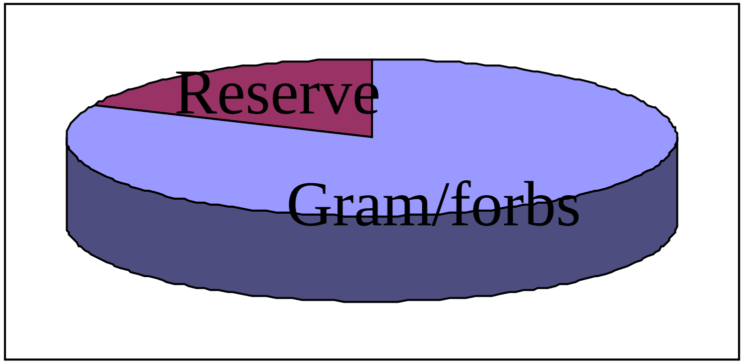
Yolk Protein



Albumen



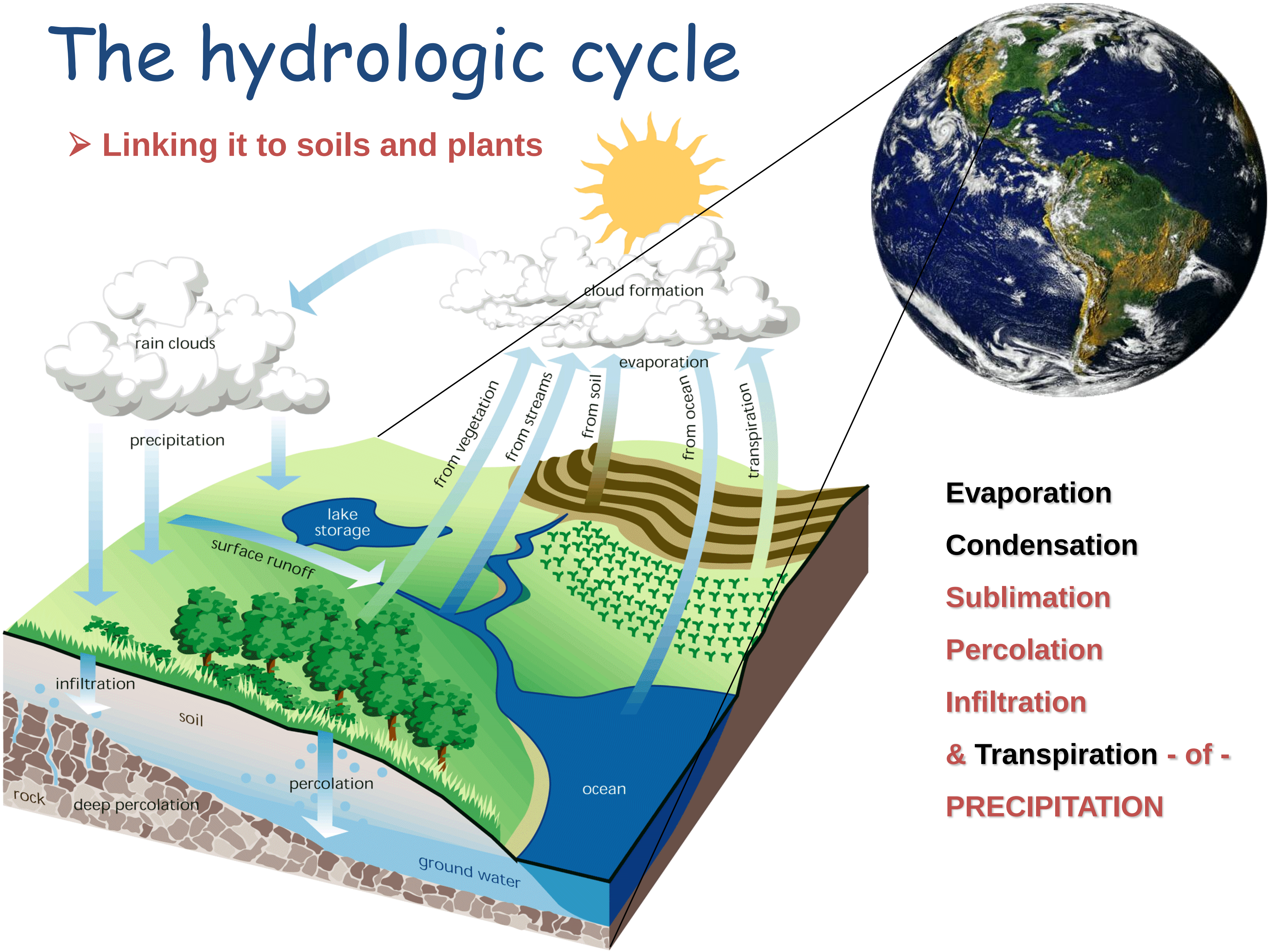
Egg lipid



Gauhtier et al.

The hydrologic cycle

- **Linking it to soils and plants**



Evaporation

Condensation

Sublimation

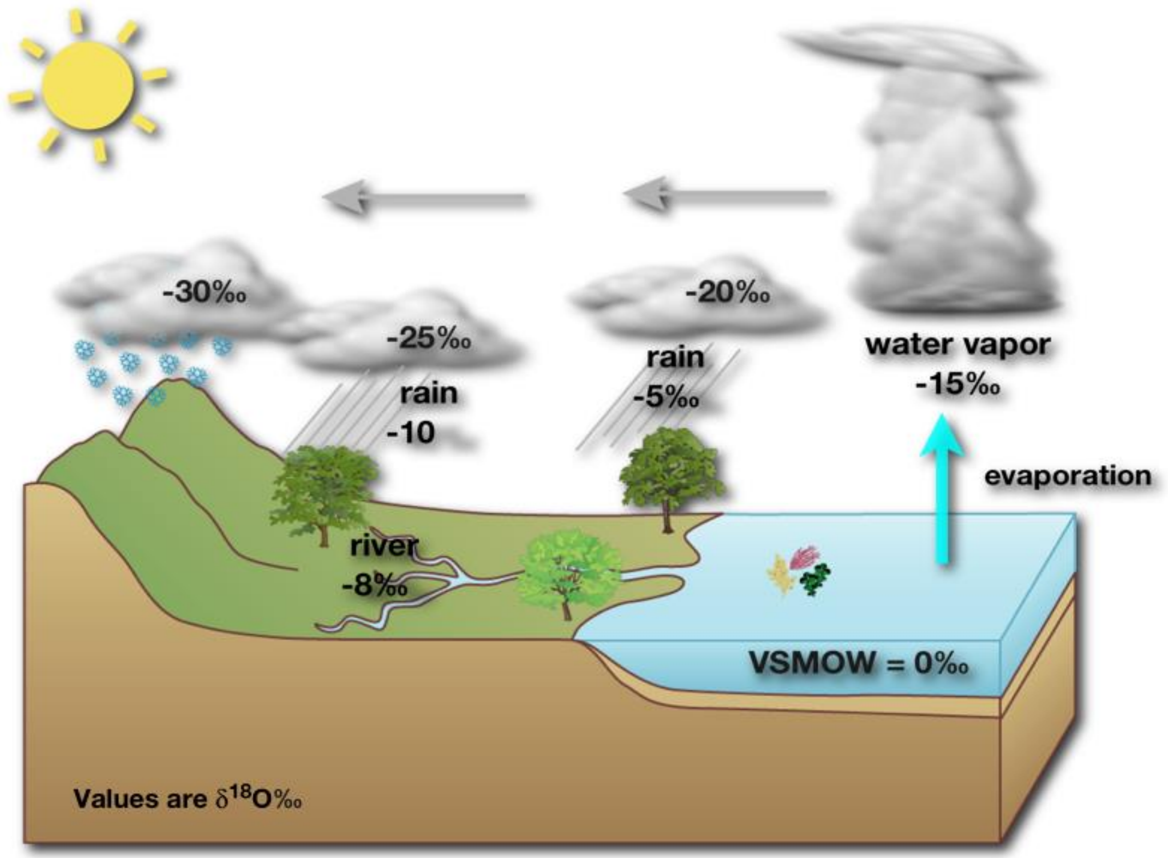
Percolation

Infiltration

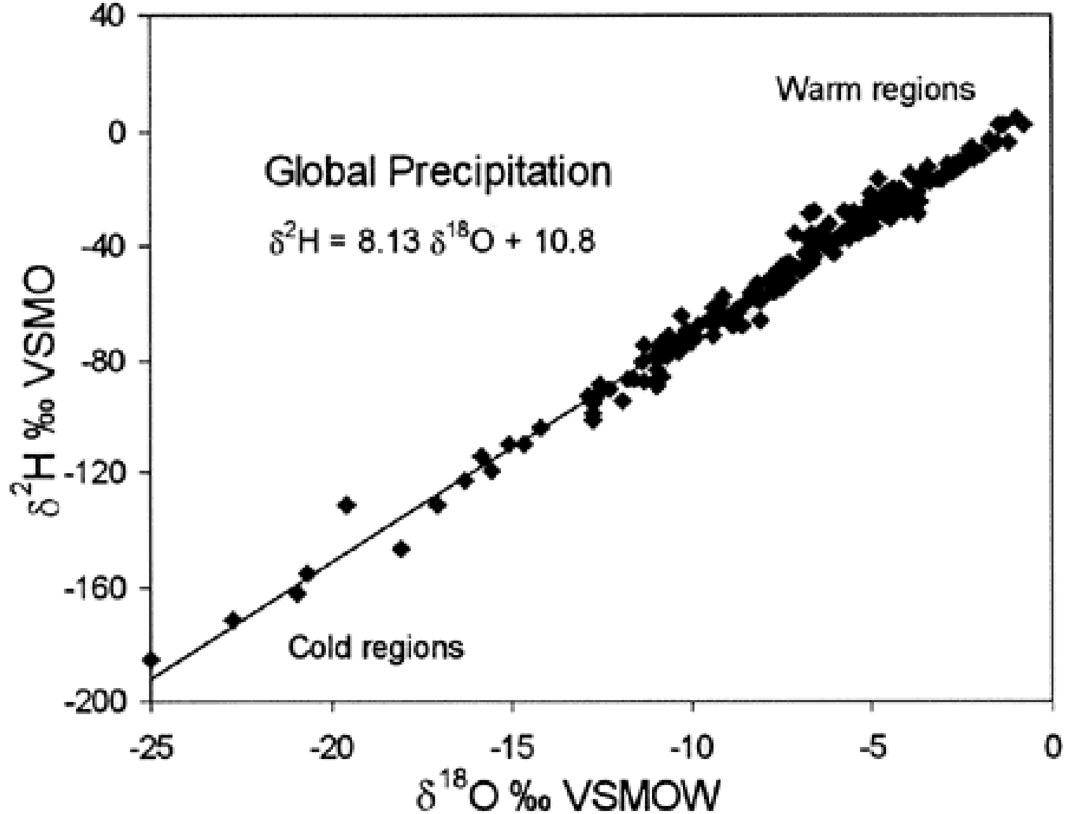
& Transpiration - of -

PRECIPITATION

In preparation for the Hydrospehere



The Global Meteoric Water Line, GMWL



Condensation
is an equilibrium process

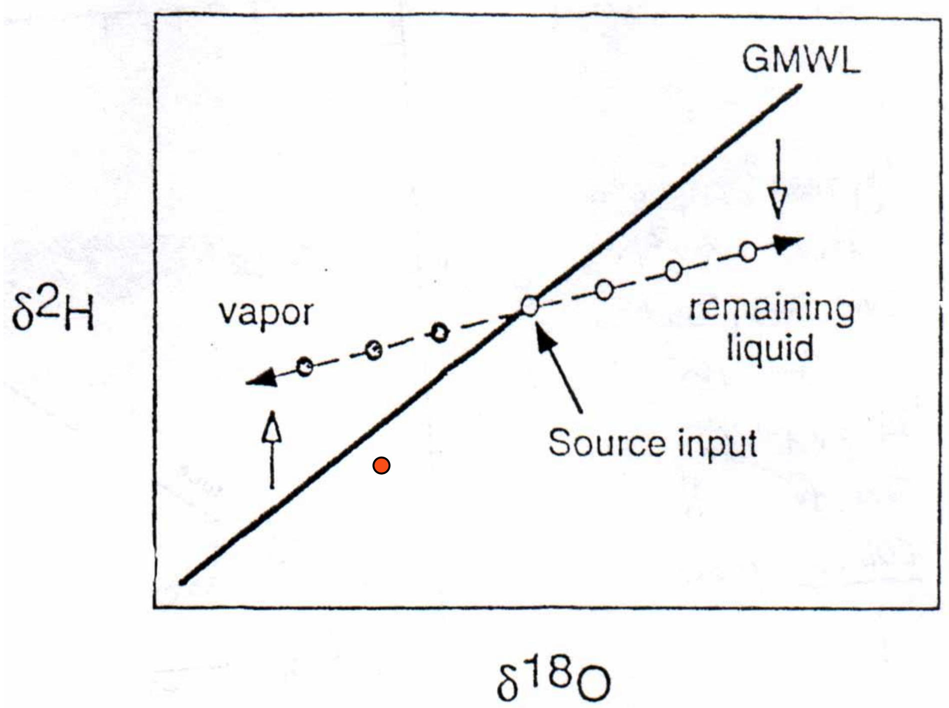
so

Most precipitation δ values lie along a Global Meteoric Water Line (GMWL) of slope ~8

$(\varepsilon^2H / \varepsilon^{18}O = 8)$

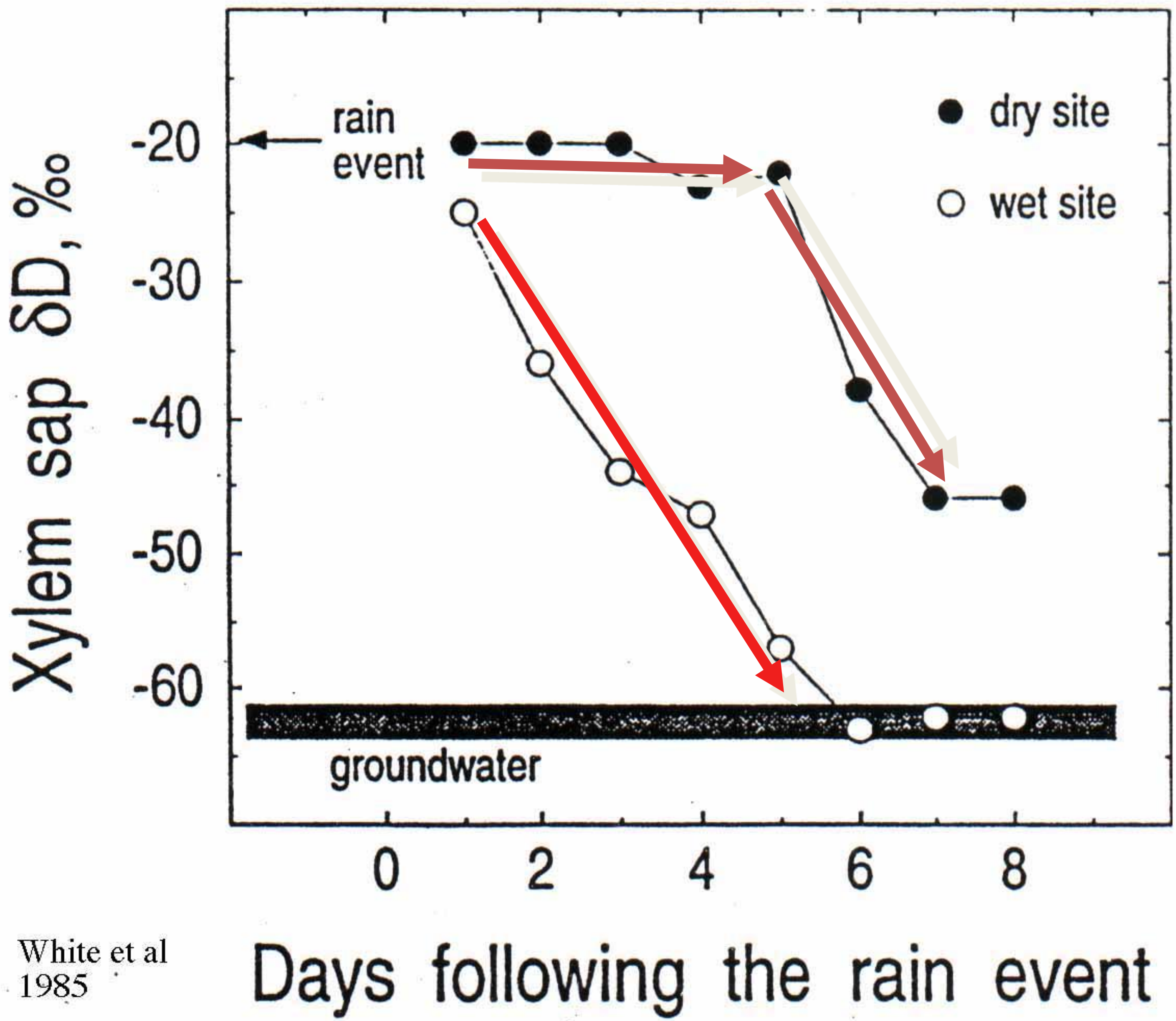
After Clark and Fritz, 1997; GMWL defined by Craig, 1961

d-excess & the Global Meteoric Water Line



The "see-saw" affect of evporative (kinetic) isotope fractionation (after Gat 1996)

Isotopes Reflect Soil Water Use Patterns



White et al
1985

The Thinking: Land plants will always have higher δD than aquatic plants because of evaporative enrichment

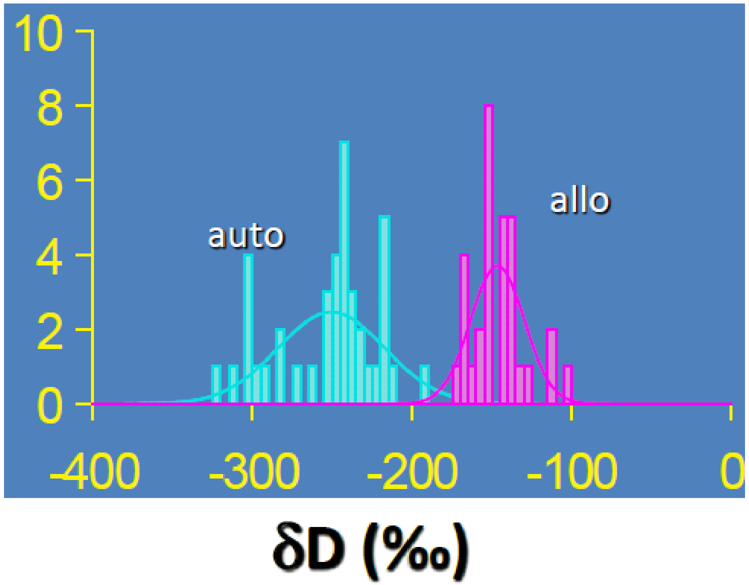
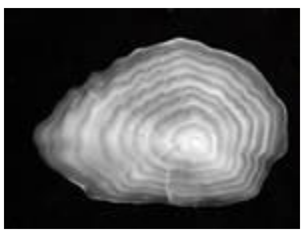


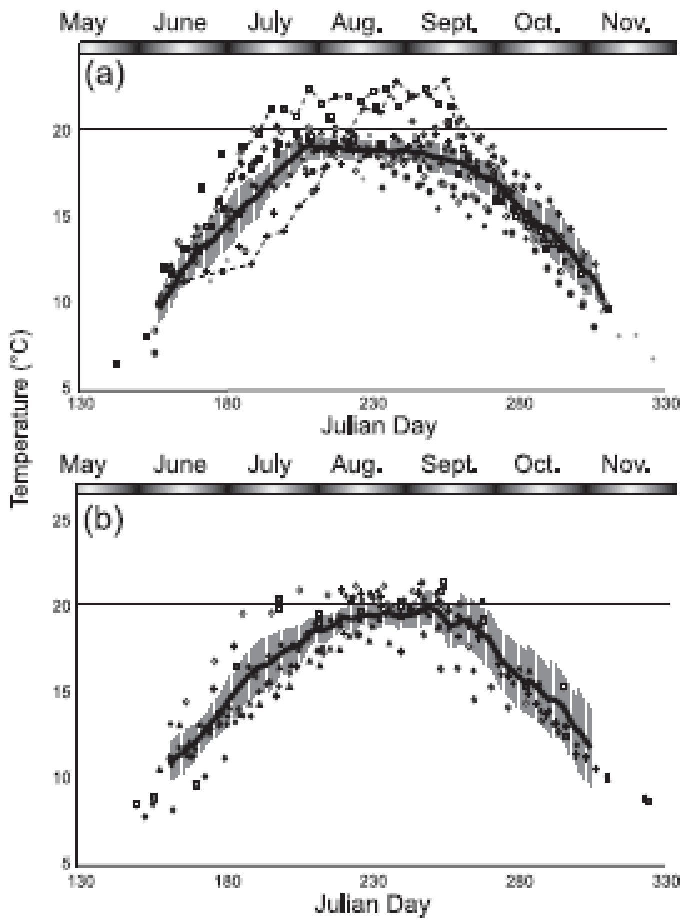
TABLE 3. Agreement between energy source partitioning using $\delta^{13}C$ and δD in Fossil Creek.

	$\delta^{13}C$			δD		
Source	Mean ± SE (‰)	CI	*n*	Mean ± SE (‰)	CI	*n*
Algae	−35.1 ± 0.6		15	−264.3 ± 11.5		10
Terrestrial	−27.8 ± 0.7		6	−151.3 ± 7.3		5
Fish	−30.3 ± 0.8		5	−181.6 ± 5.9		9
Algae	33.9 ± 11.1	7.7–60.1		26.9 ± 5.7	14.2–39.5	
Terrestrial	66.1 ± 11.1	39.9–92.3		73.1 ± 5.7	60.5–85.8	

Doucett et al. 2007

O isotopes can be used to infer ambient temperatures …

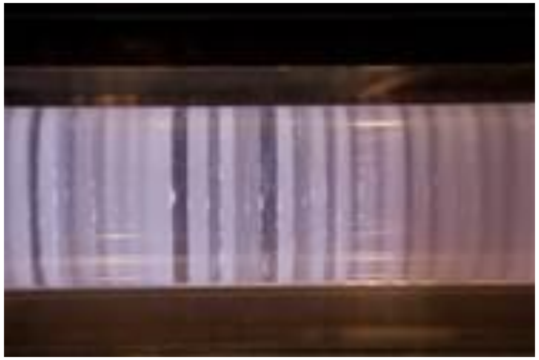


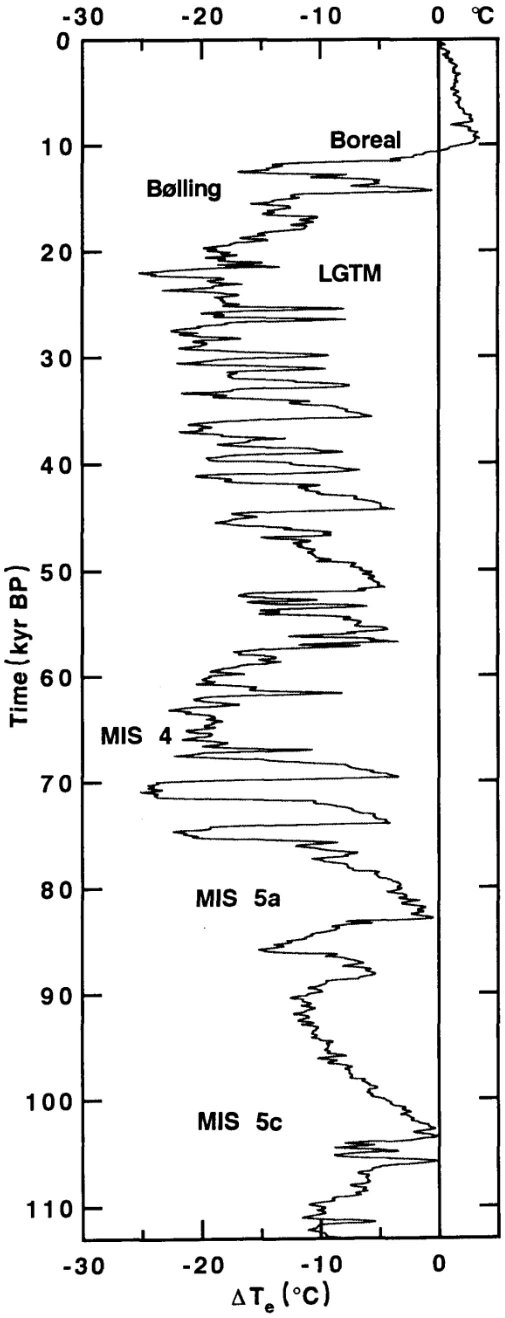


Chinook Salmon otolit T based on δ18O increments In otolith aragonite

Wurster et al. 2005 (CJFAS)

Paleotemp based on $\delta^{18}O$ of Greenland ice.





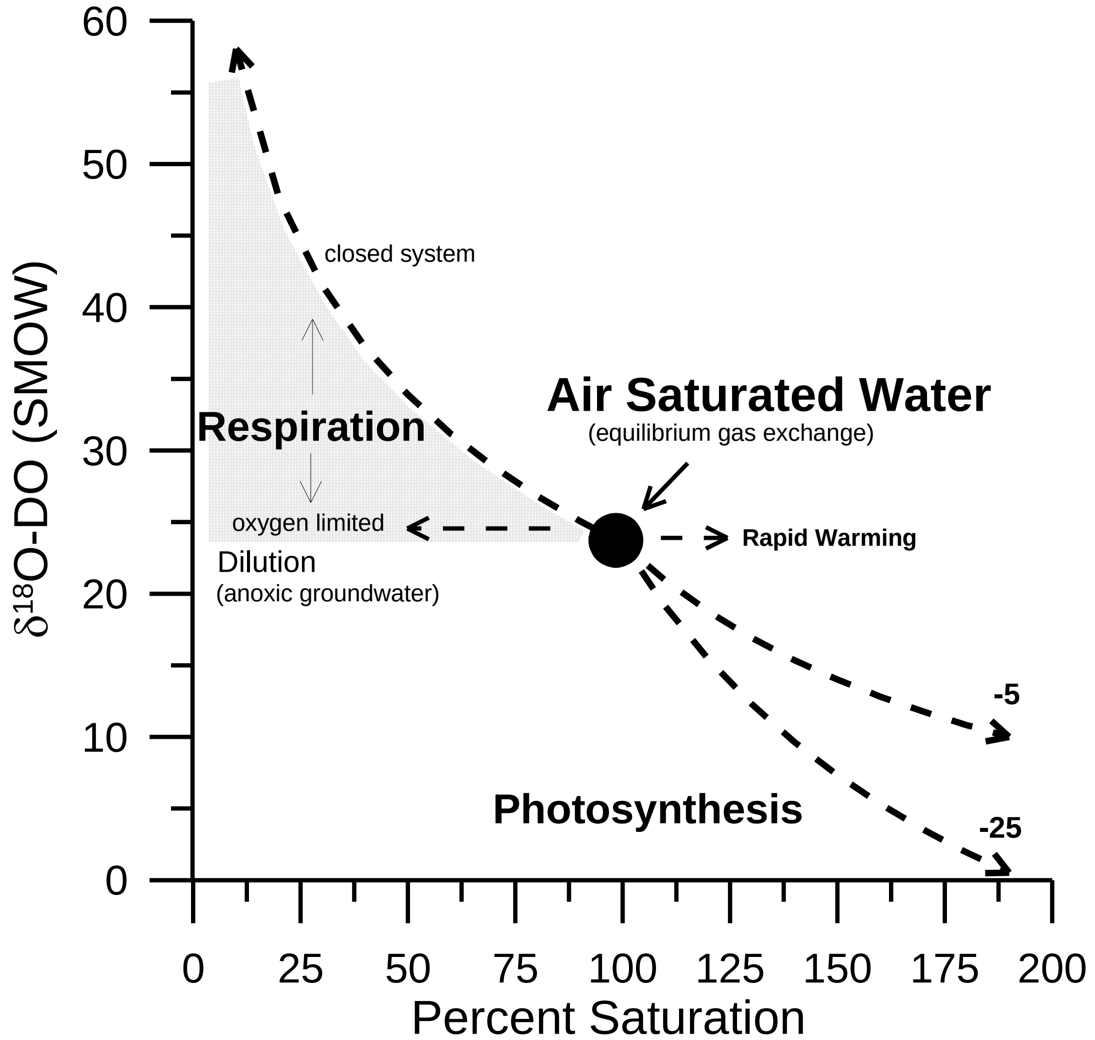
Johnsen et al (2002) Tellus.

Stable Isotope Tracer of O_2

- O_2 Sources
  - Air - globally constant $\delta^{18}O_2$ = +23.5 ‰
  - Photosynthesis (biotic inputs) $\delta^{18}O_2$ = water (0 ‰ to -25 ‰)
- And Biogeochemical/Physical Processes
  - Water column and benthic respiration– O_2 consumption
  - Photosynthesis (algae) – O_2 input
  - Dilution (groundwater) – decrease in O_2 saturation

- ^{18}O provides an additional tracer concerning DO source and process that concentration data cannot provide

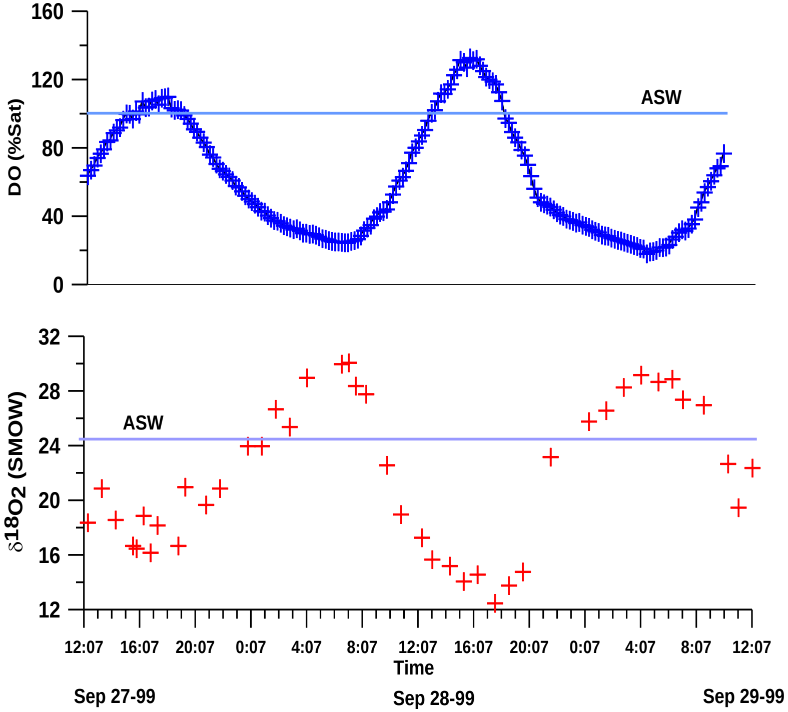
Isotopic DO Trends



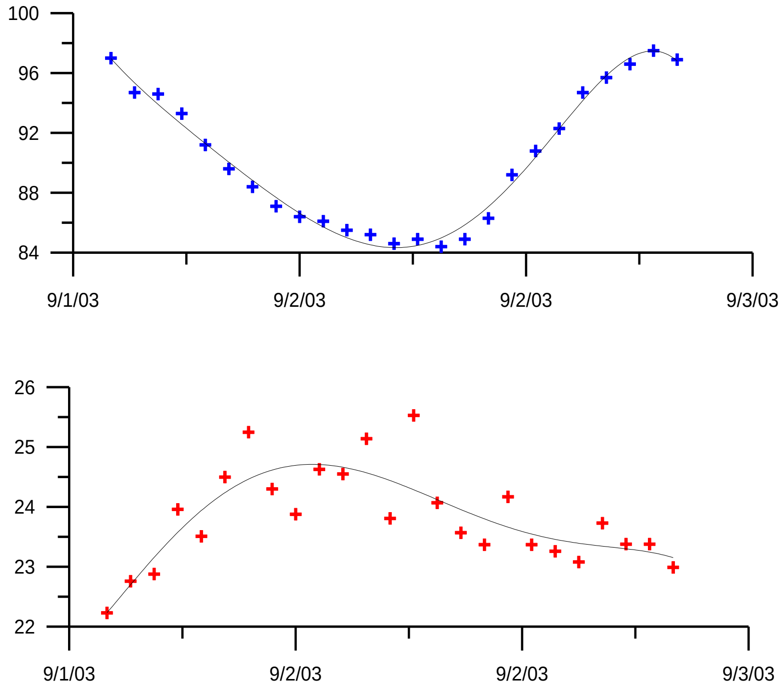
L. Wassenaar

Diel Cycles – A Prevalent Transient Process

Wetland



River



**L.Wassenaar

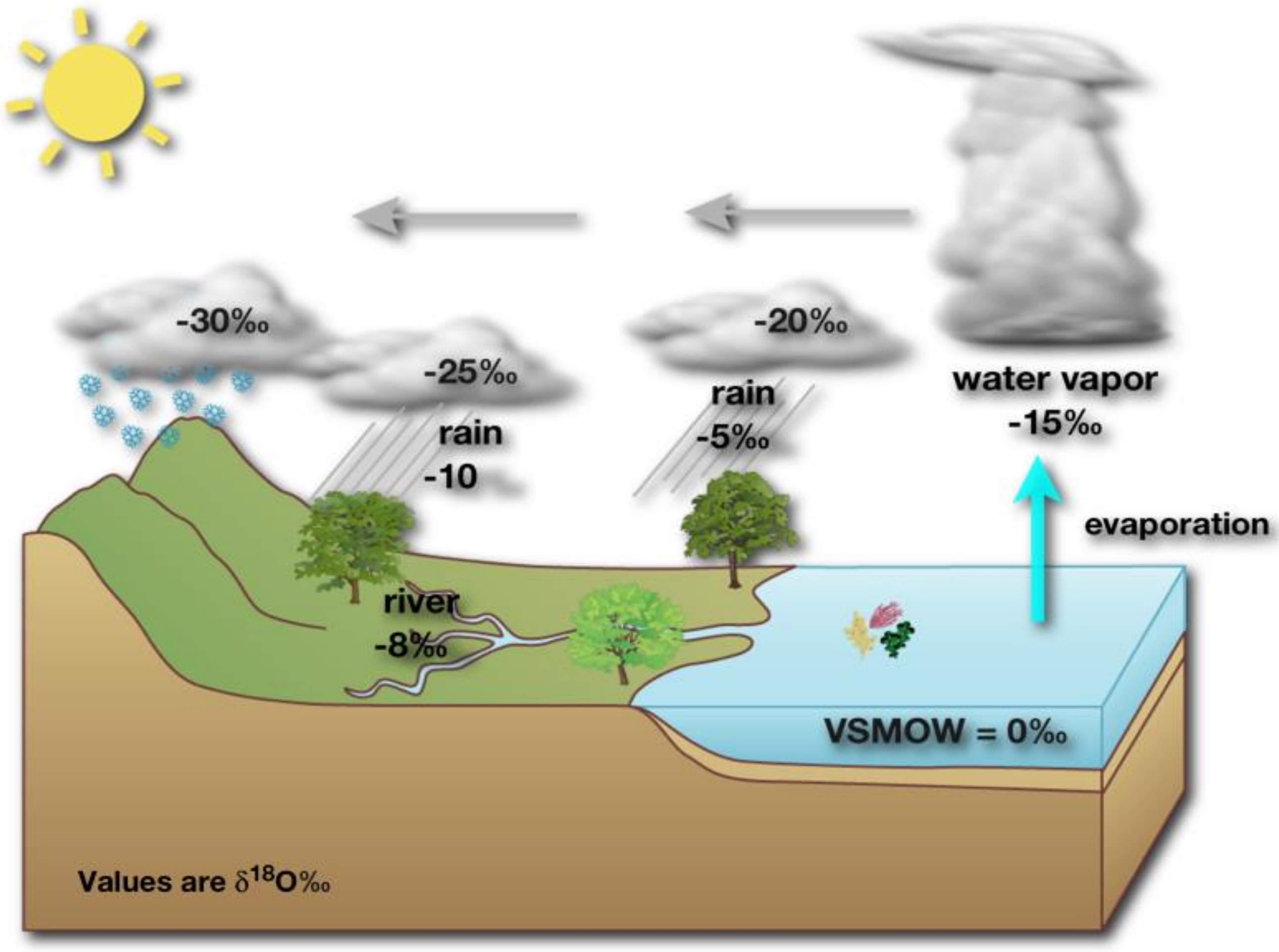
Summary H,O

- Tracers of the Hydrologic cycle (H,O).
- Water sources and evaporative mechanisms (H,O).
- Paleo recorder of past T esp. through ice cores and carbonates… (H, O)
- Precipitation-based isoscapes for animal tracking and forensics (mostly H).
- Metabolism of aquatic systems (dissolved O).
- Use of $\delta^{18}O$ to trace NO_3, PO_4, SO_4 .. (O)

Applications (H,O)

- Migration tracking using the water isotopes.
- Food web applications to come later in the week!

Migratory tracking breakthrough with water isotopes



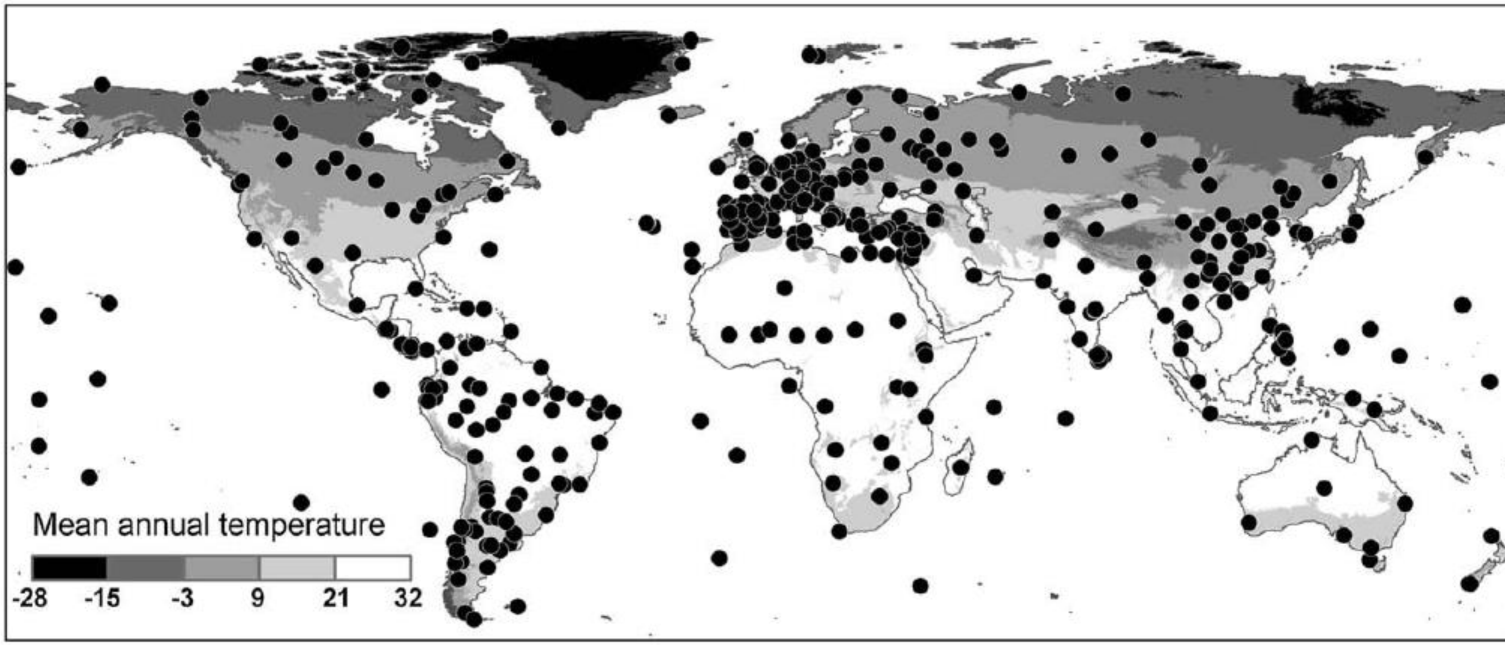
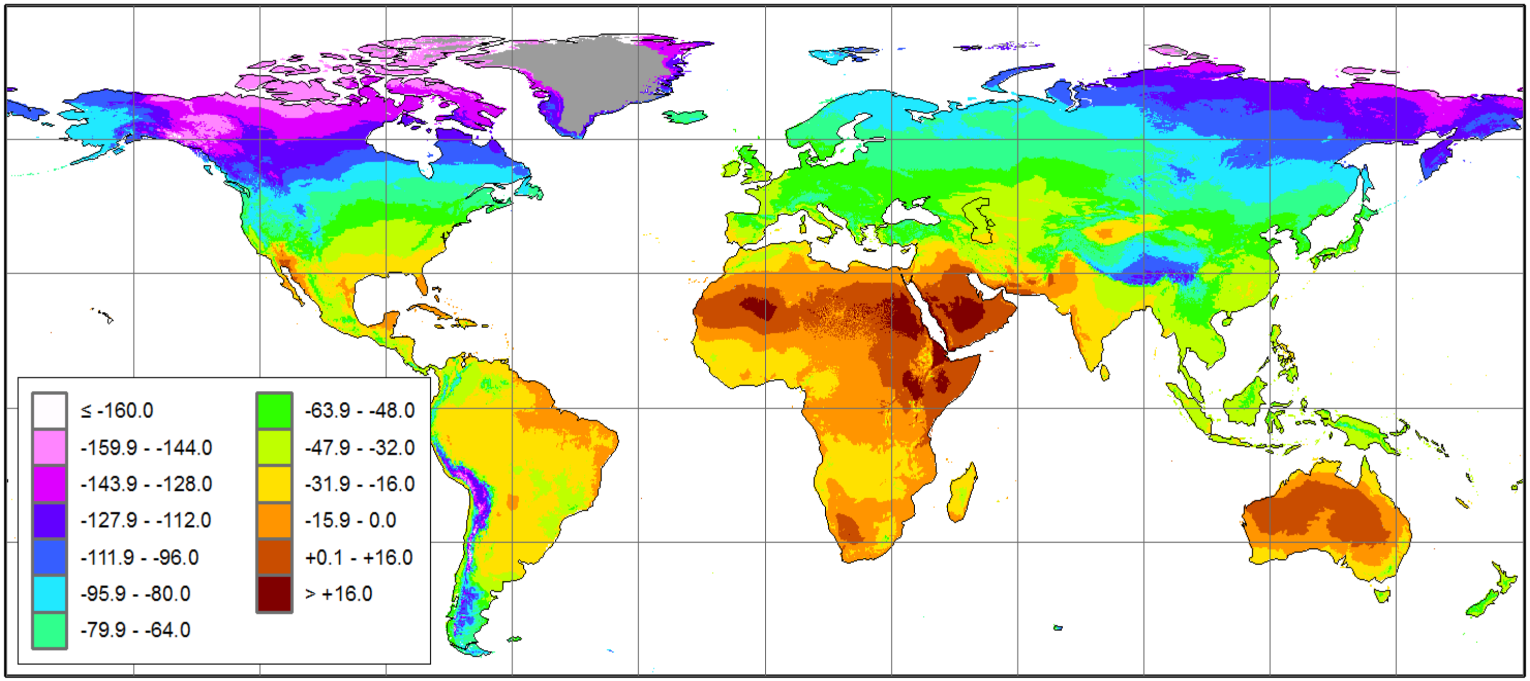
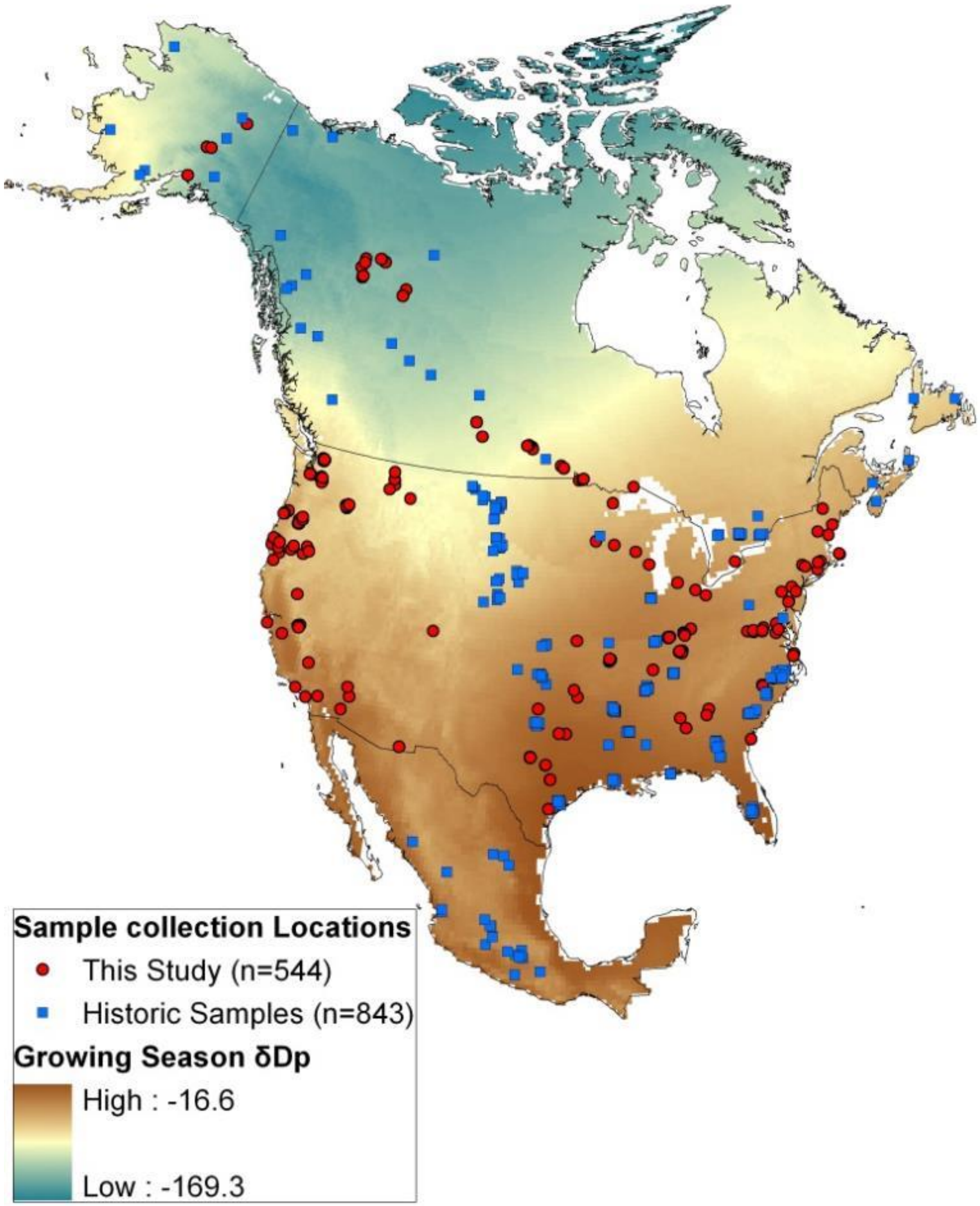


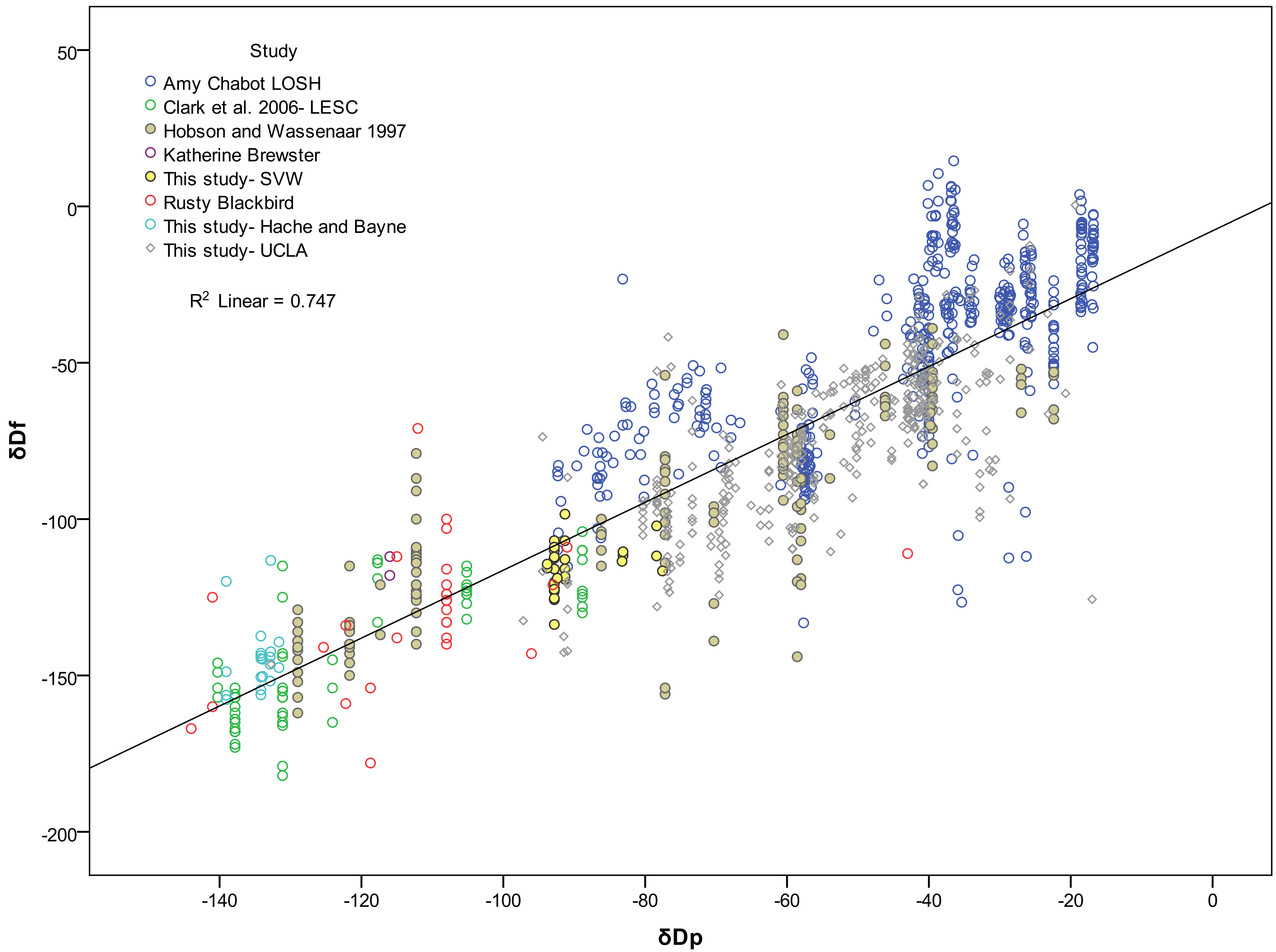
Fig. 1. Map showing the individual GNIP stations that measured the (weighted) annual mean δ^2H and δ^{18}O composition of precipitation for at least 1 year during 1960–2001 ($N = 467$). Background map shows the annual mean temperature (WorldClim data; see Hijmans et al., 2005).

Latest growing-season δ^2Hp

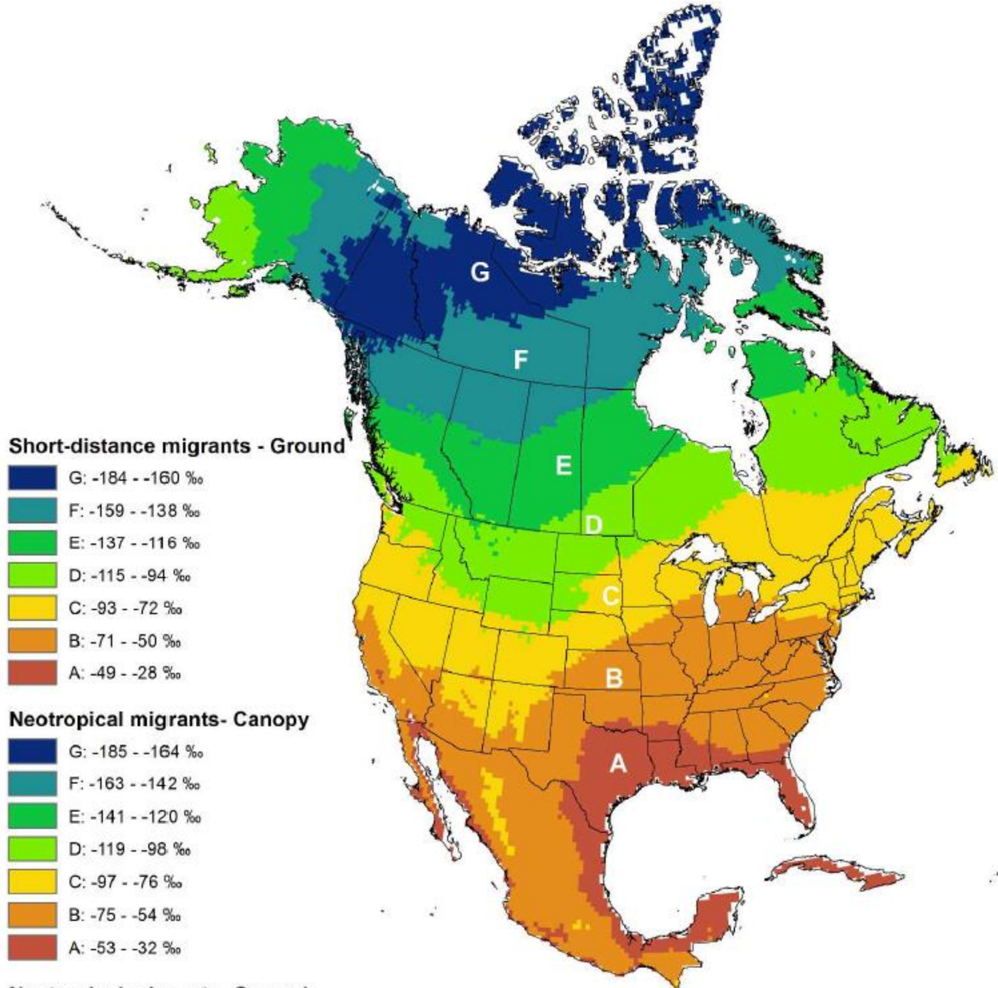


Wassenaar, IAEA.

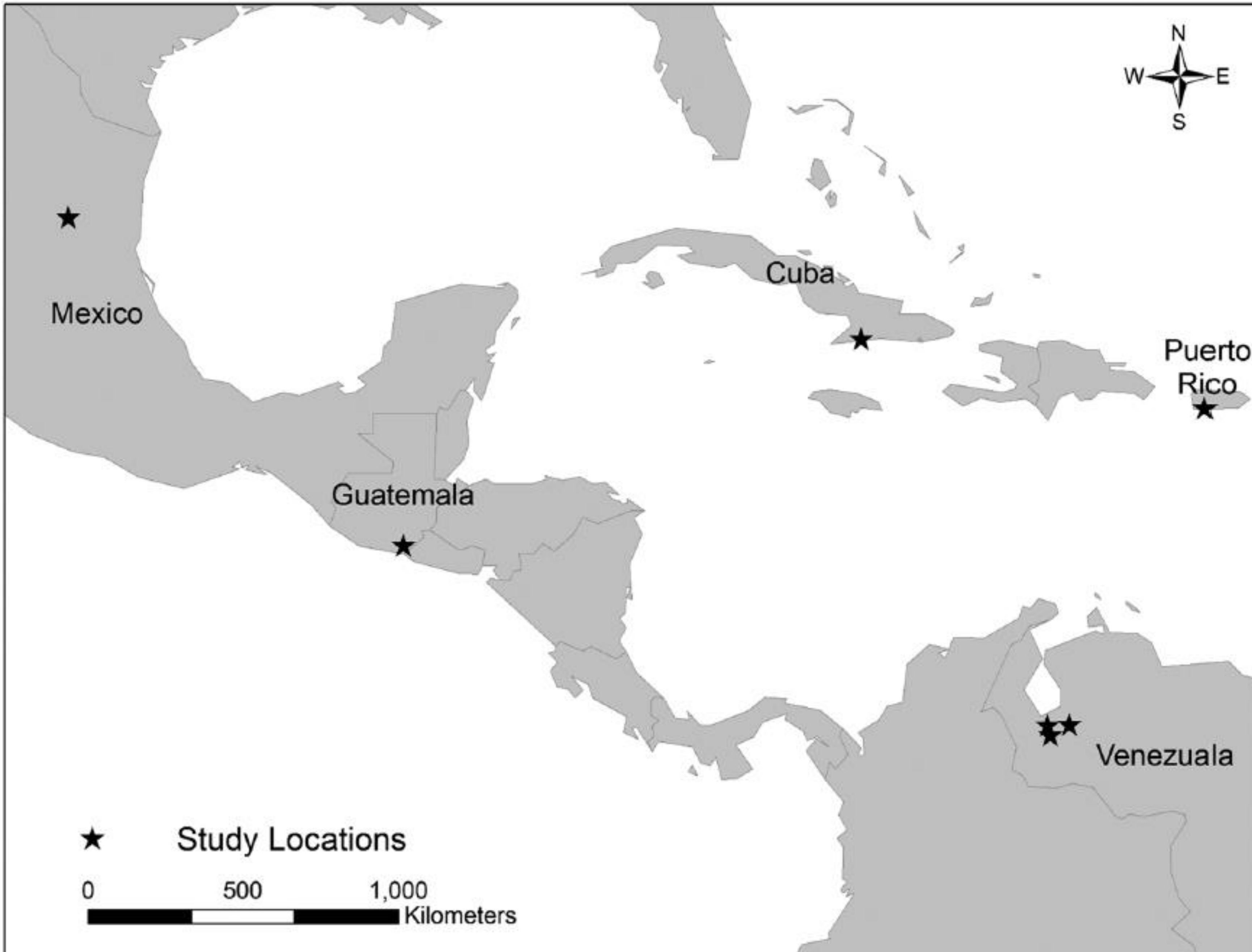

Sample collection Locations
This Study (n=544)
Historic Samples (n=843)
Growing Season δDp
High : -16.6
Low : -169.3

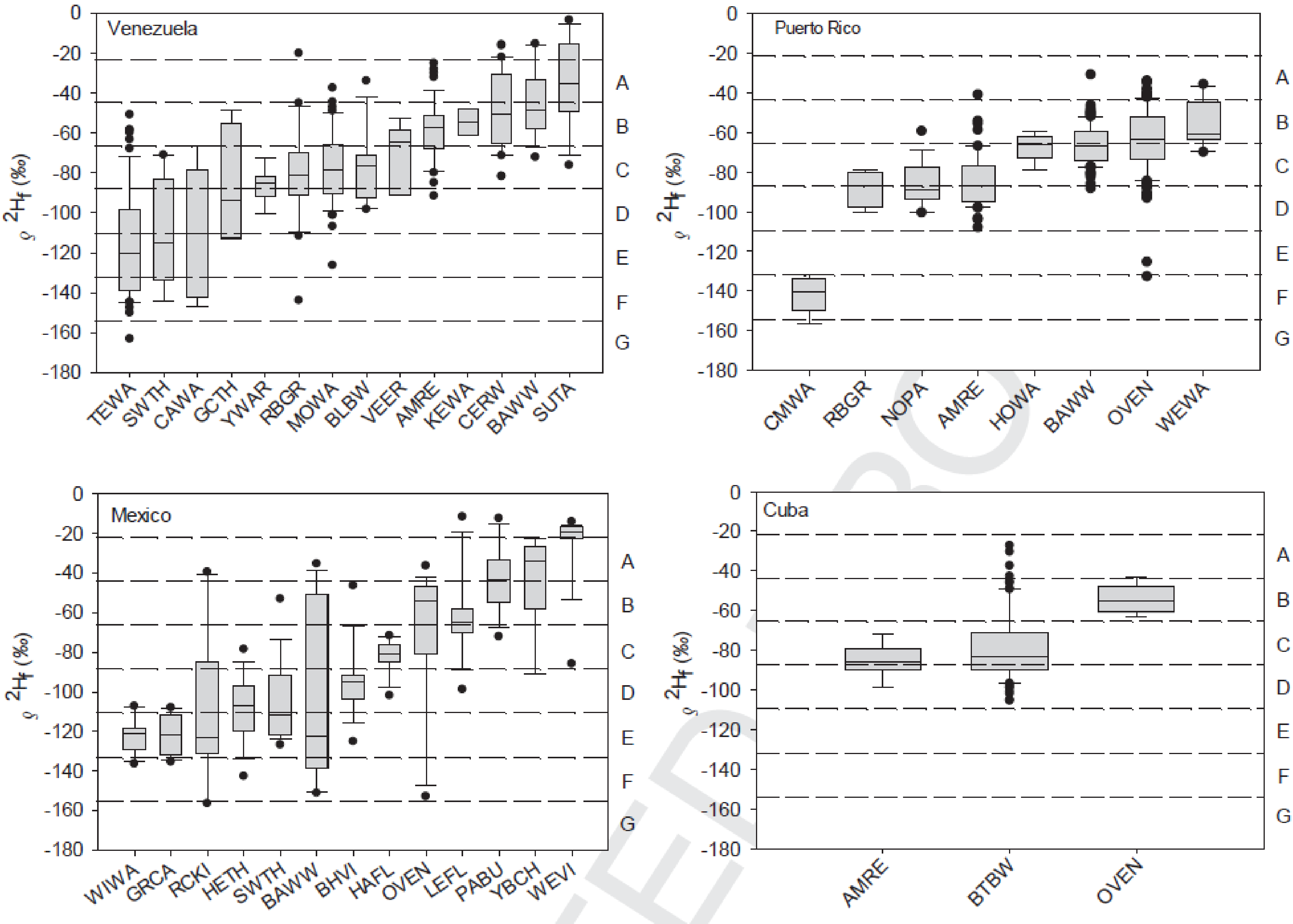


Hobson et al. *PLoS ONE* (2012)

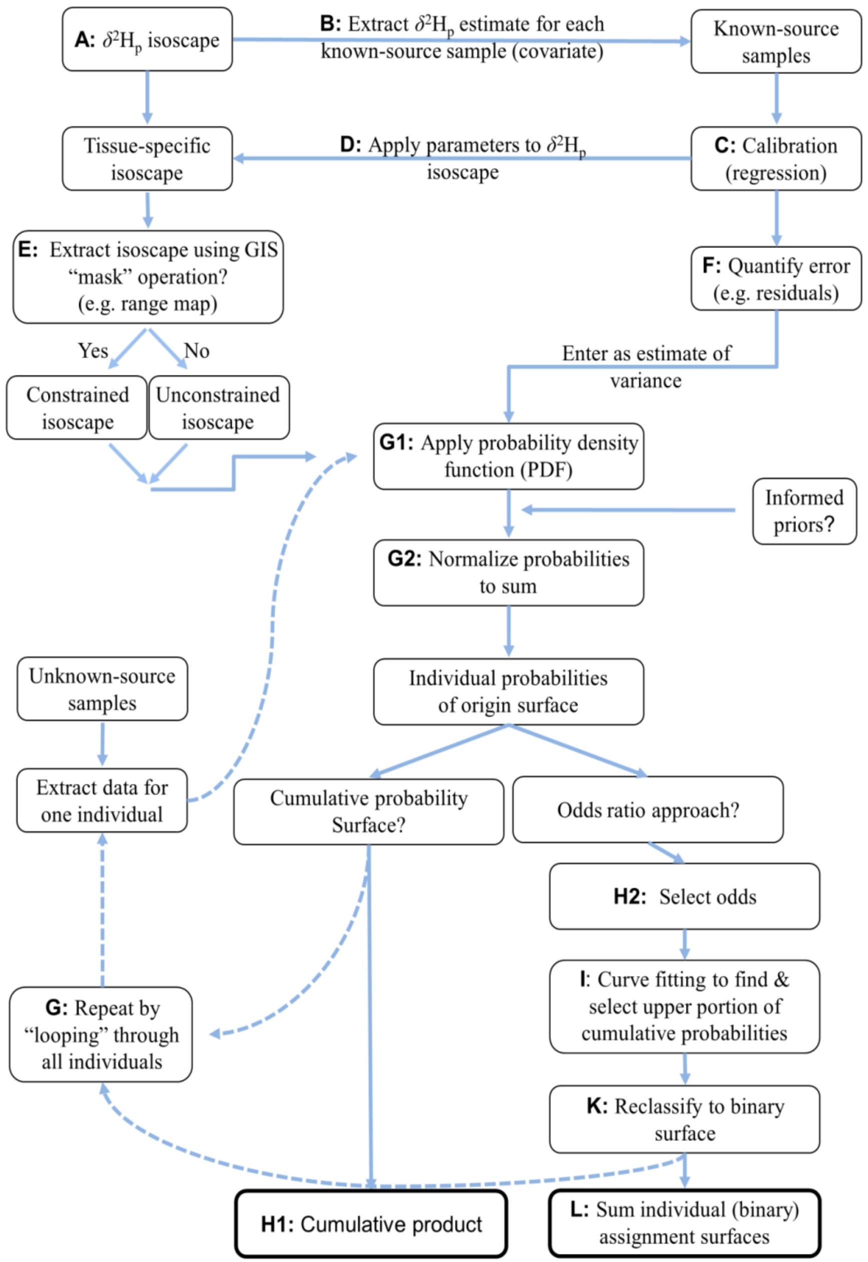


Hobson et al. *JFO* (2014)

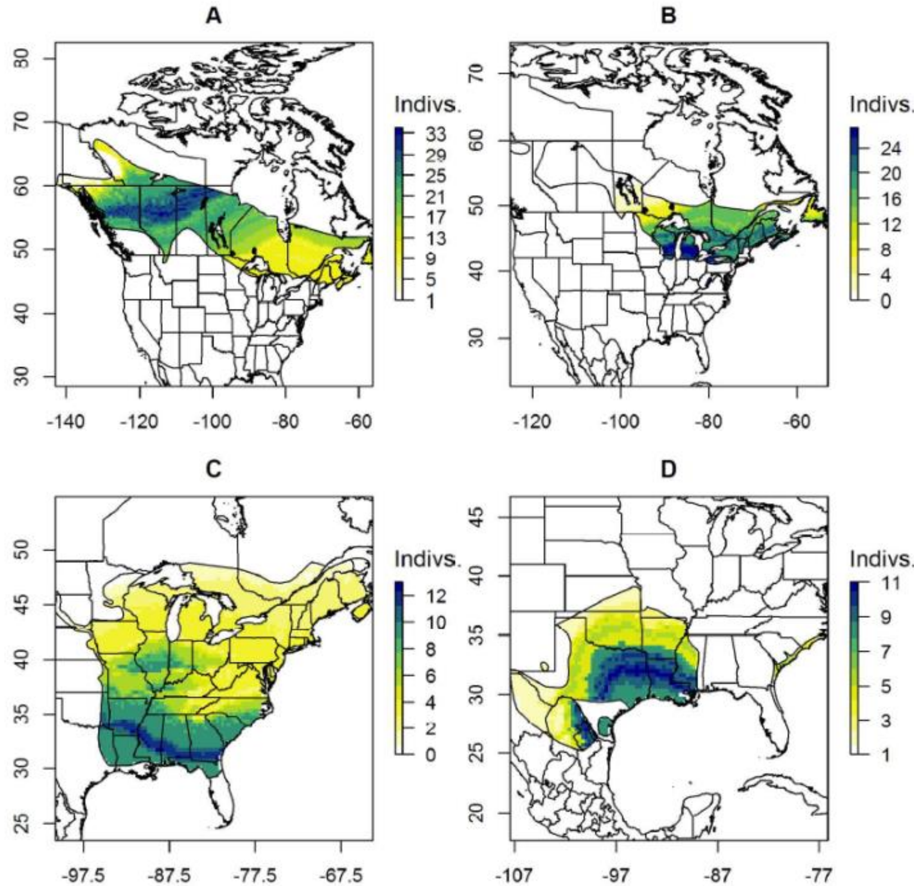

N
W
E
S
Mexico
Cuba
Puerto
Rico
Guatemala
Venezuala
Study Locations
0
500
1,000
Kilometers



Hobson et al. *JFO* (2014)

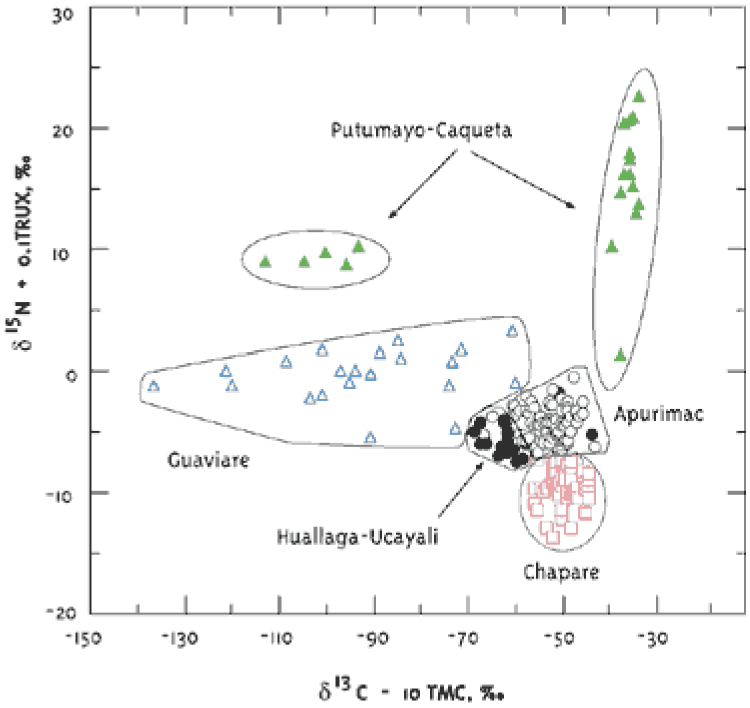


Mike Wunder Univ. Colorado (Denver)



Hobson et al. *JFO* (2014)

Forensic applications are broad:



Murder investigation …

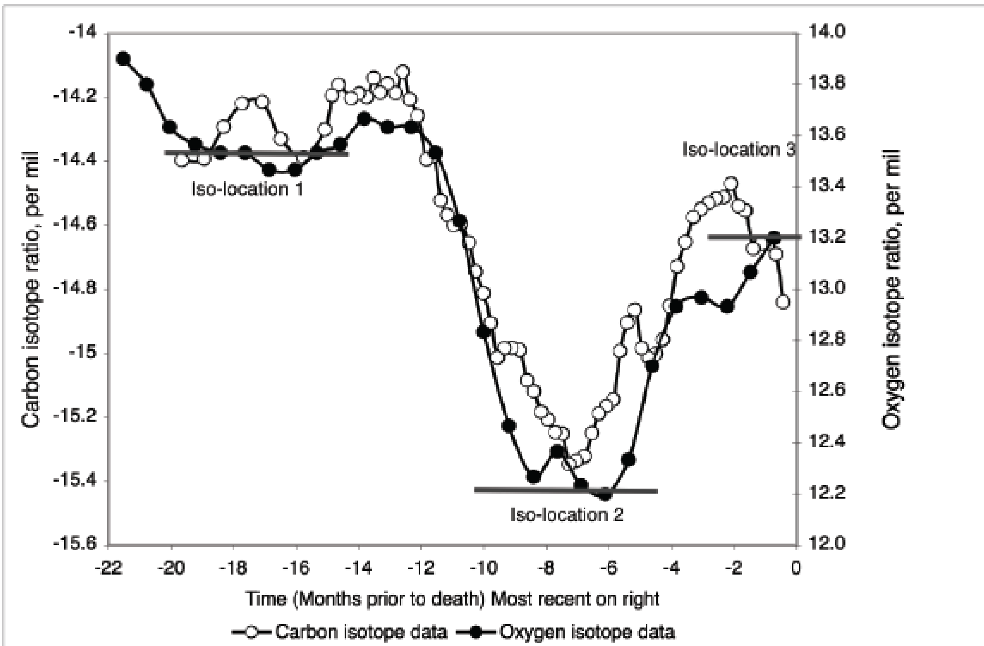
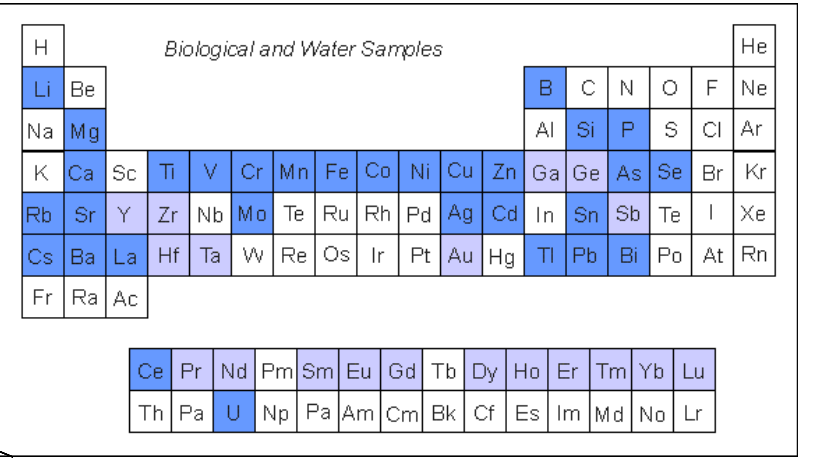
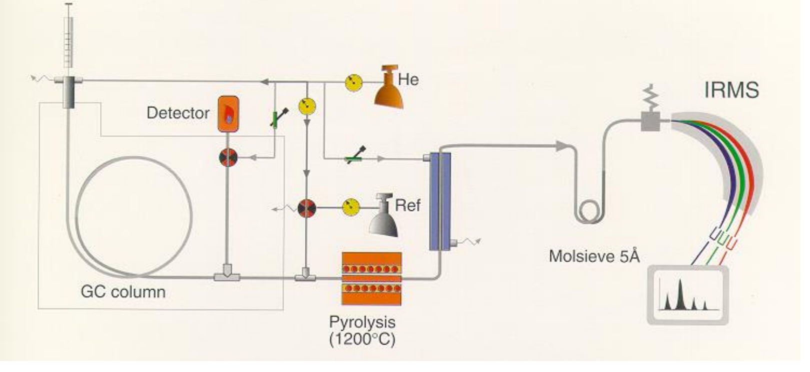


Figure 10. A plot of the carbon and oxygen isotope data measured from hair from the Sierra Nevada murder victim as a function of time prior to the victim's death with three iso-locations marked Time was calculated based on an average growth rate of 0.4 mm/day. Data are 3-point running means. Iso-locations are those regions where it is suggested that the victim had resided for a period of time.

Future?

Trace element/heavy isotope





Compound specific Mass spectrometry