The Use of Isotope Geochemistry in Forensic Geology

Stable Isotopes

Modified from a PowerPoint presentation prepared by J. Crelling, Southern Illinois University

Isotopes

Two Categories

- Unstable – isotopes that continuously and spontaneously break down/decay in other lower atomic weight isotopes
- Stable – isotopes that do not naturally decay but can exist in natural materials in differing proportions

Stable Isotopes

- The absolute values of isotope concentrations are usually too small to measure and compare accurately
- So the convention is to compare isotope ratios of any given element to a standard value for that element

Stable Isotopes

- Elements can exist in both stable and unstable (radioactive) forms. Most elements of biological interest (including C, H, O, N, and S) have two or more stable isotopes, with the lightest of these present in much greater abundance than the others.

Isotopes of Major Elements of Interest in Plant Physiology and Ecology

Element	Isotope	Abundance (%)
Hydrogen	1H	99.985
	2H	0.015
Carbon	12C	98.89
	13C	1.11
Nitrogen	14N	99.63
	15N	0.37
Oxygen	16O	99.759
	18O	0.204
Sulfur	32S	95.00
	33S	0.76
	34S	4.22
	36S	0.014

Stable Isotopes

Notation

R: "ratio"

R = $^{heavy}Element/^{light}Element$ for carbon: $^{13}C/^{12}C$

Stable Isotopes

More Notation

δ: "del"

δ^{heavy}Element = [(R_{sample}/$R_{standard}$)-1]1000 (‰, per thousand, also called per mil)

For carbon this becomes $\delta^{13}C$ (termed "del 13 C")

For carbon, $R_{standard}$ comes from "Pee Dee Belemnite", or "PDB" a limestone rock from South Carolina.

Plant carbon always has less of the heavy isotope compared with this standard, so the $\delta^{13}C$ of plant material is always a negative number.

Stable Isotopes

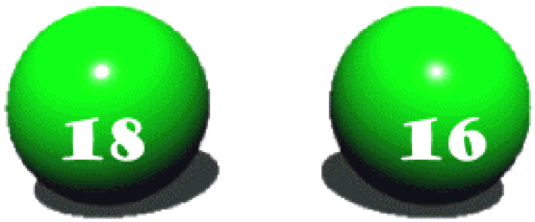
As the value of δ for a sample increases, the relative abundance of the rare (heavy) also isotope increases.

For carbon isotopes:

As the value of $\delta^{13}C$ increases i.e., "becomes more positive"	There is *enrichment* in ^{13}C
As the value of $\delta^{13}C$ decreases i.e., "becomes more negative"	There is *depletion* in ^{13}C

Stable Isotopes (Oxygen as an Example)

Same element with two different atomic masses:



Changes in $^{18}O/^{16}O$ ratios are TOO small to directly measure.

$$\delta^{18}O = \left[\frac{^{18}O/^{16}O_{(sample)} - {}^{18}O/^{16}O_{(SMOW)}}{^{18}O/^{16}O_{(SMOW)}} \right] \times 1000$$

Sample is compared to a standard; in the case of oxygen, the standard is seawater:

SMOW = Standard Mean Ocean Water

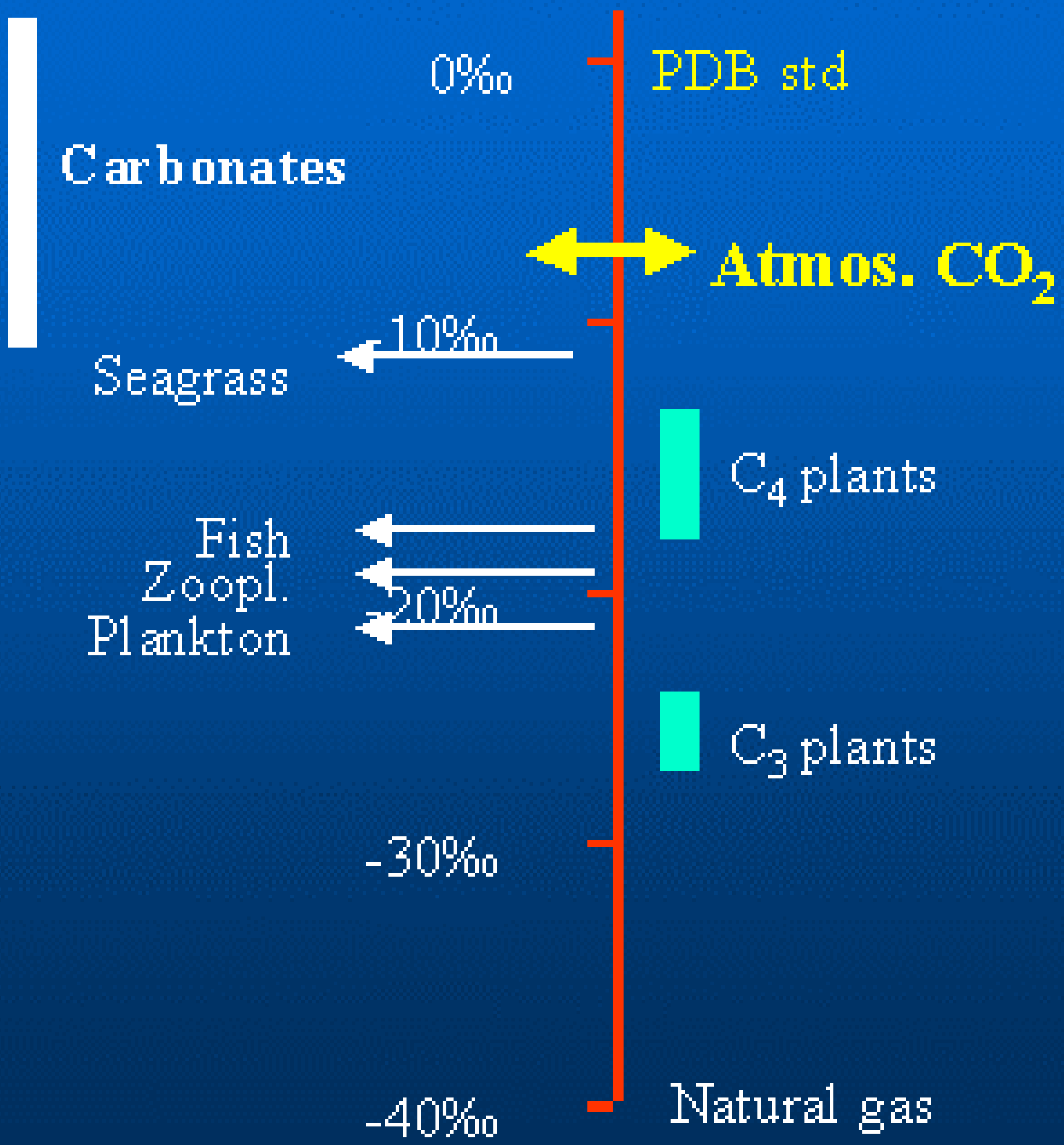
$\delta^{18}O$ in units of per thousand, called 'per mil' and denoted as ‰ .

$\delta^{18}O = 0$ Sample has same ratio as that in seawater.

$\delta^{18}O > 0$ Sample **enriched** in heavy isotope (^{18}O) relative to seawater.

$\delta^{18}O < 0$ Sample **depleted** in heavy isotope (^{18}O) relative to seawater.

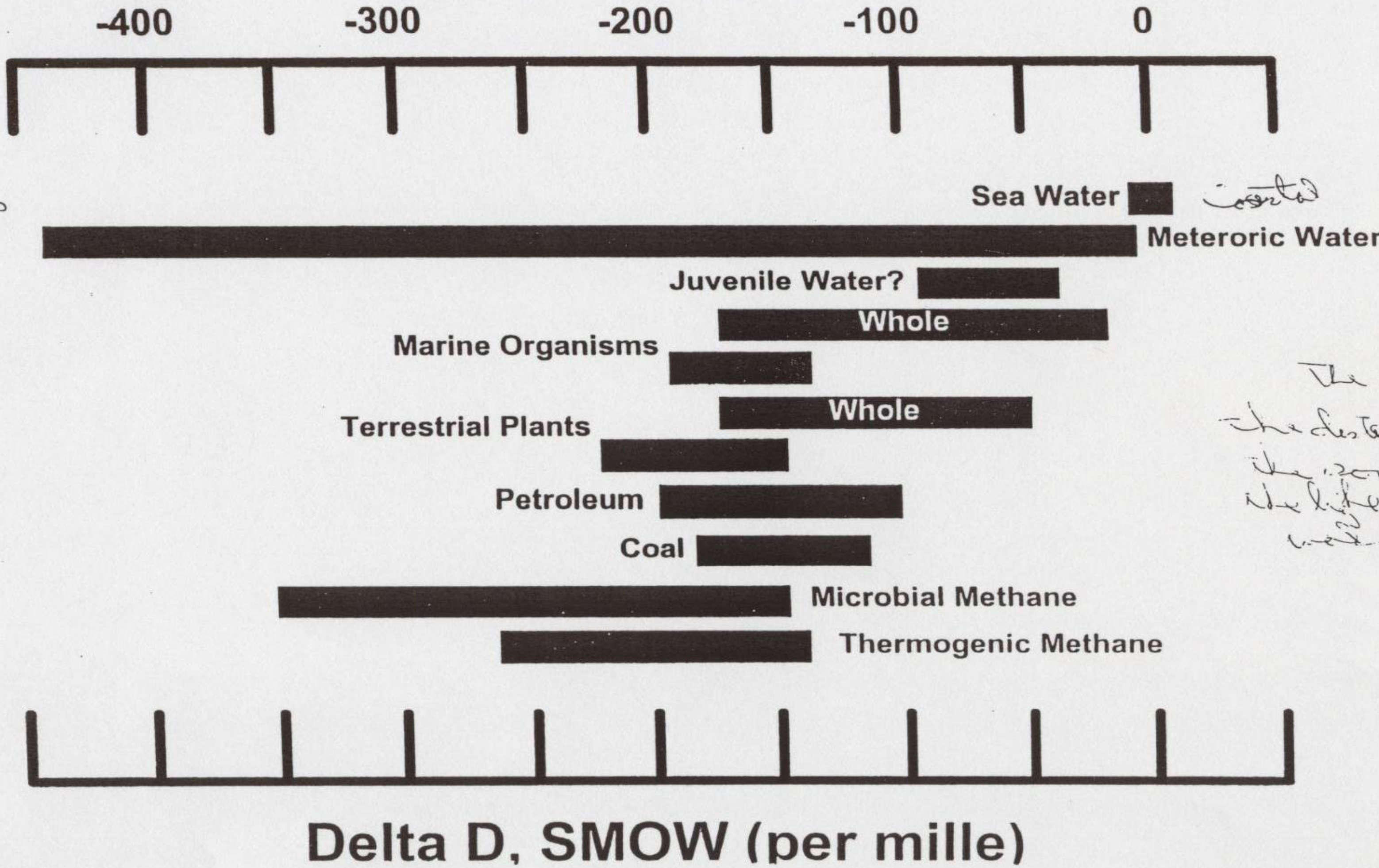
Range of carbon isotopes



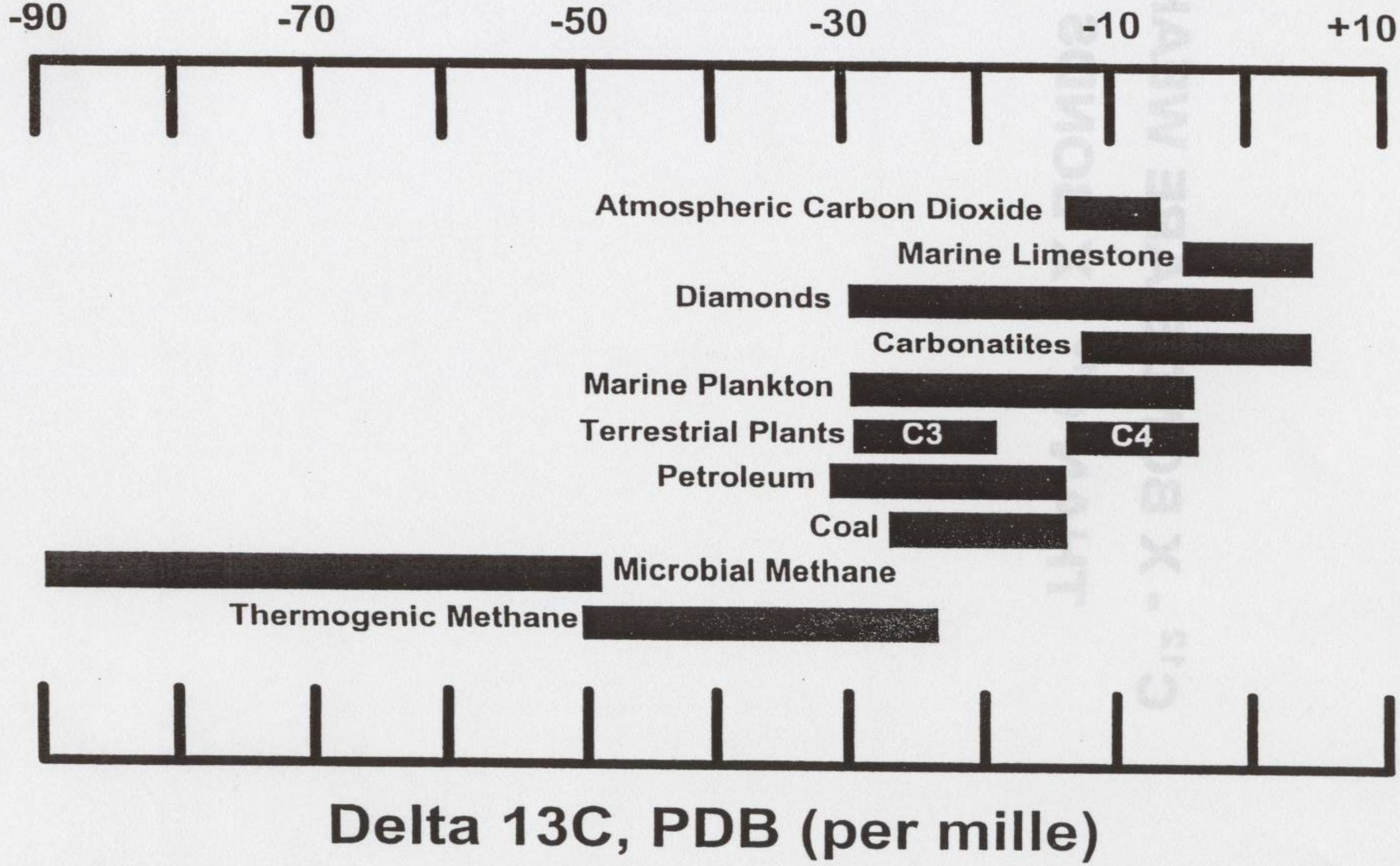
^{13}C enriched = HEAVY

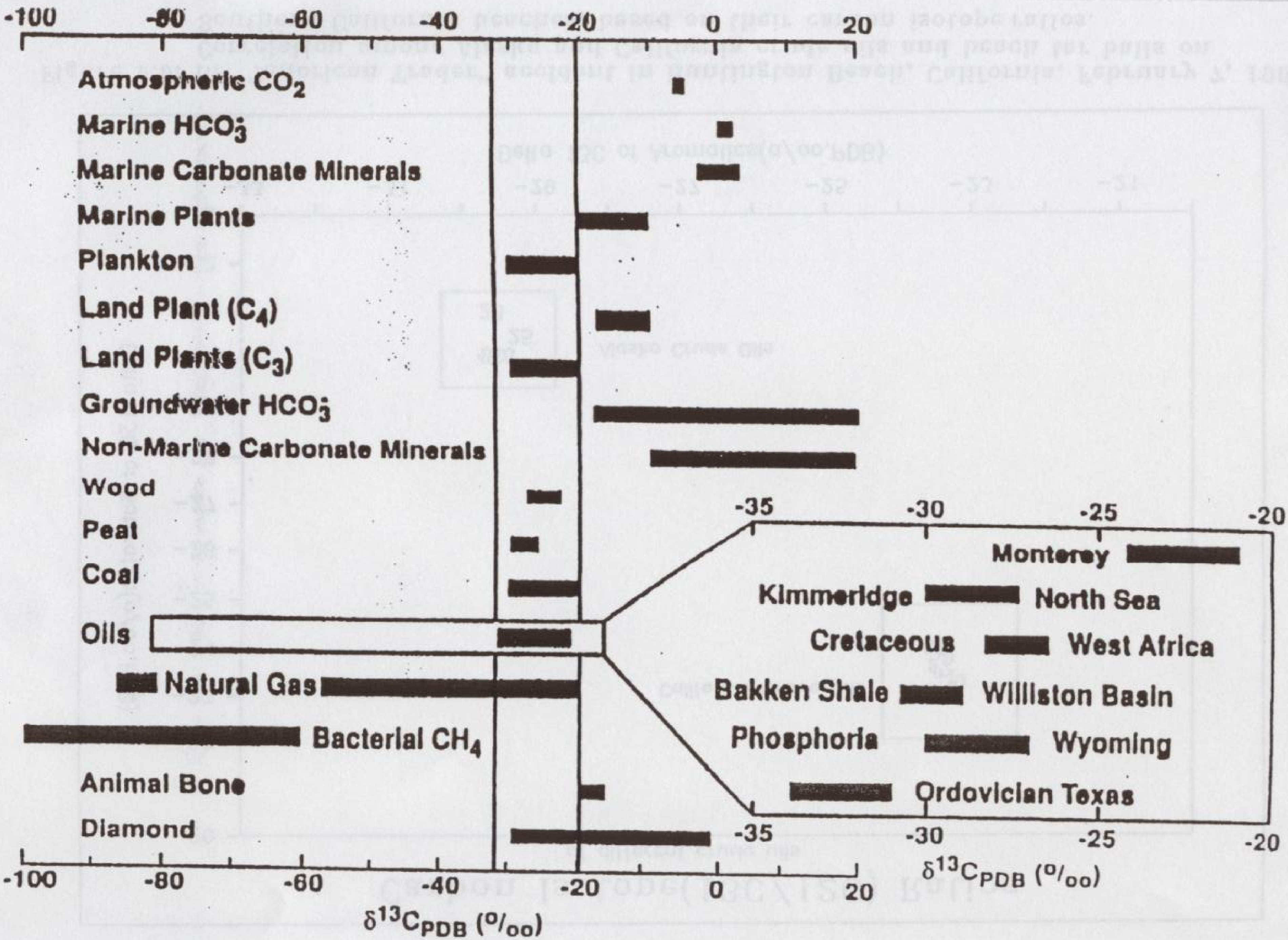
^{13}C depleted = LIGHT

Delta D Values of Selected Materials



Delta 13C Values of Selected Materials





-100
-80
-60
-40
-20
0
20
Atmospheric CO_2
Marine HCO_3^-
Marine Carbonate Minerals
Marine Plants
Plankton
Land Plant (C_4)
Land Plants (C_3)
Groundwater HCO_3^-
Non-Marine Carbonate Minerals
Wood
Peat
Coal
Oils
Natural Gas
Bacterial CH_4
Animal Bone
Diamond
$\delta^{13}C_{PDB}$ (‰)
-35
-30
-25
-20
Monterey
Kimmeridge
North Sea
Cretaceous
West Africa
Bakken Shale
Williston Basin
Phosphoria
Wyoming
Ordovician Texas
$\delta^{13}C_{PDB}$ (‰)

What accounts for the range of stable isotope composition?

- *Molecules react at different rates depending on their isotopic composition*

- *All biological and chemical reaction could fractionate isotopes*

- *Electron structure determines chemical properties*
- *Nucleus determines physical properties*

Stable Isotopes

Stable isotopes are useful as:

1. Tracers (for example, identifying food sources)

2. Indicators of physical or biological processes. (This is because fractionation can occur during many physical and biological processes).

Stable Isotopes

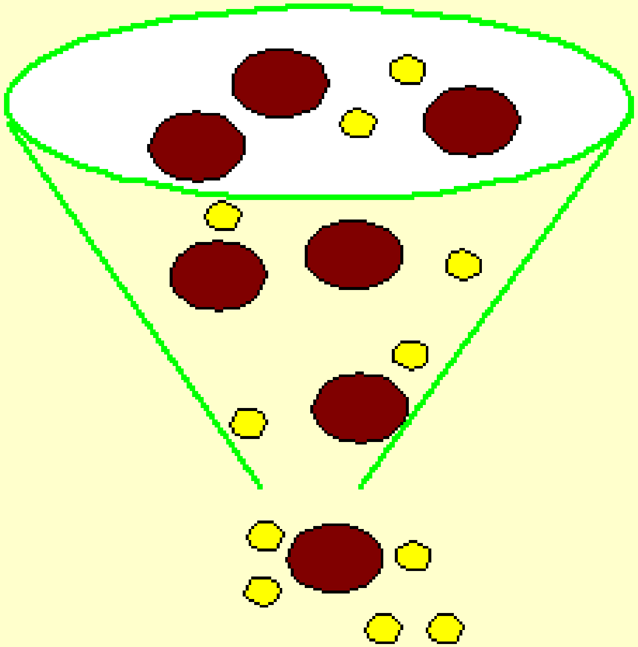
Because ^{12}C bonds are weaker than ^{13}C bonds all natural processes will tend to fractionate one or the other resulting in enrichment or depletion

Stable Isotopes

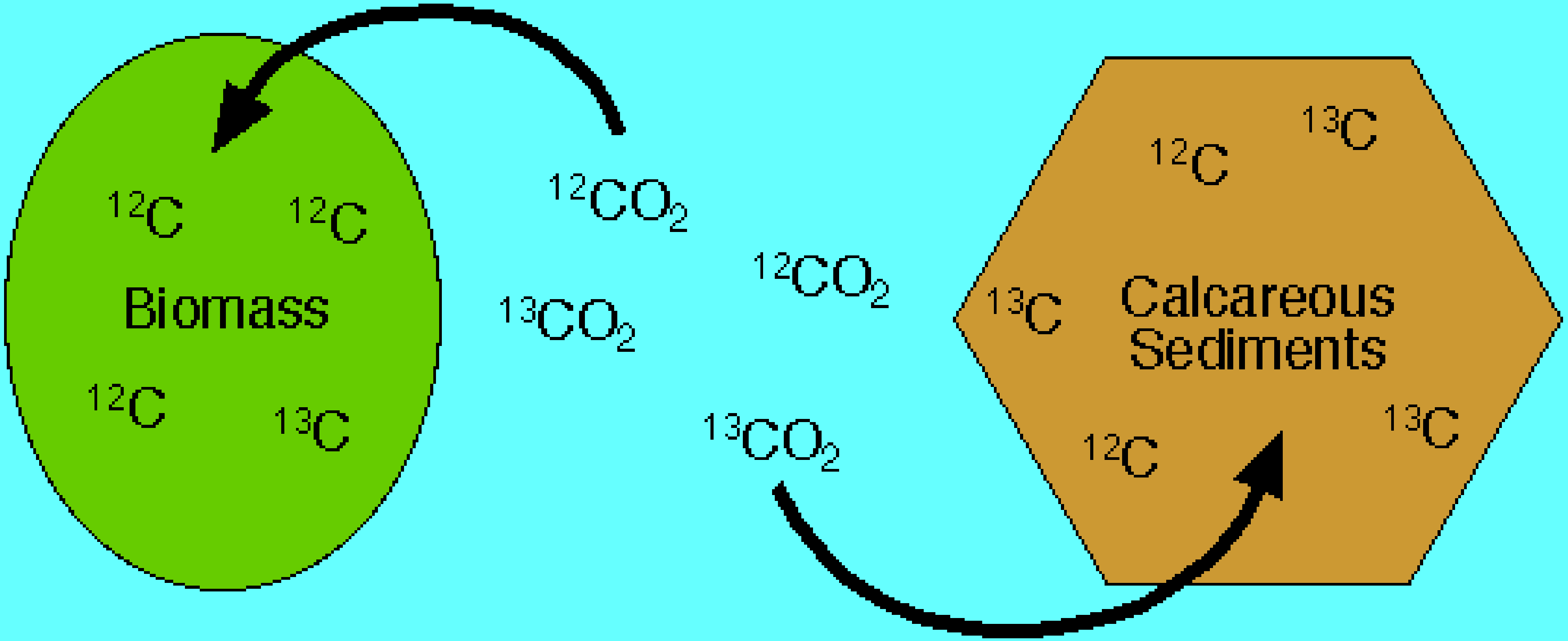
More Notation

α = Isotope fractionation = $R_{source}/R_{product}$

Fractionation is change in R that occurs during a physical or biological transformation

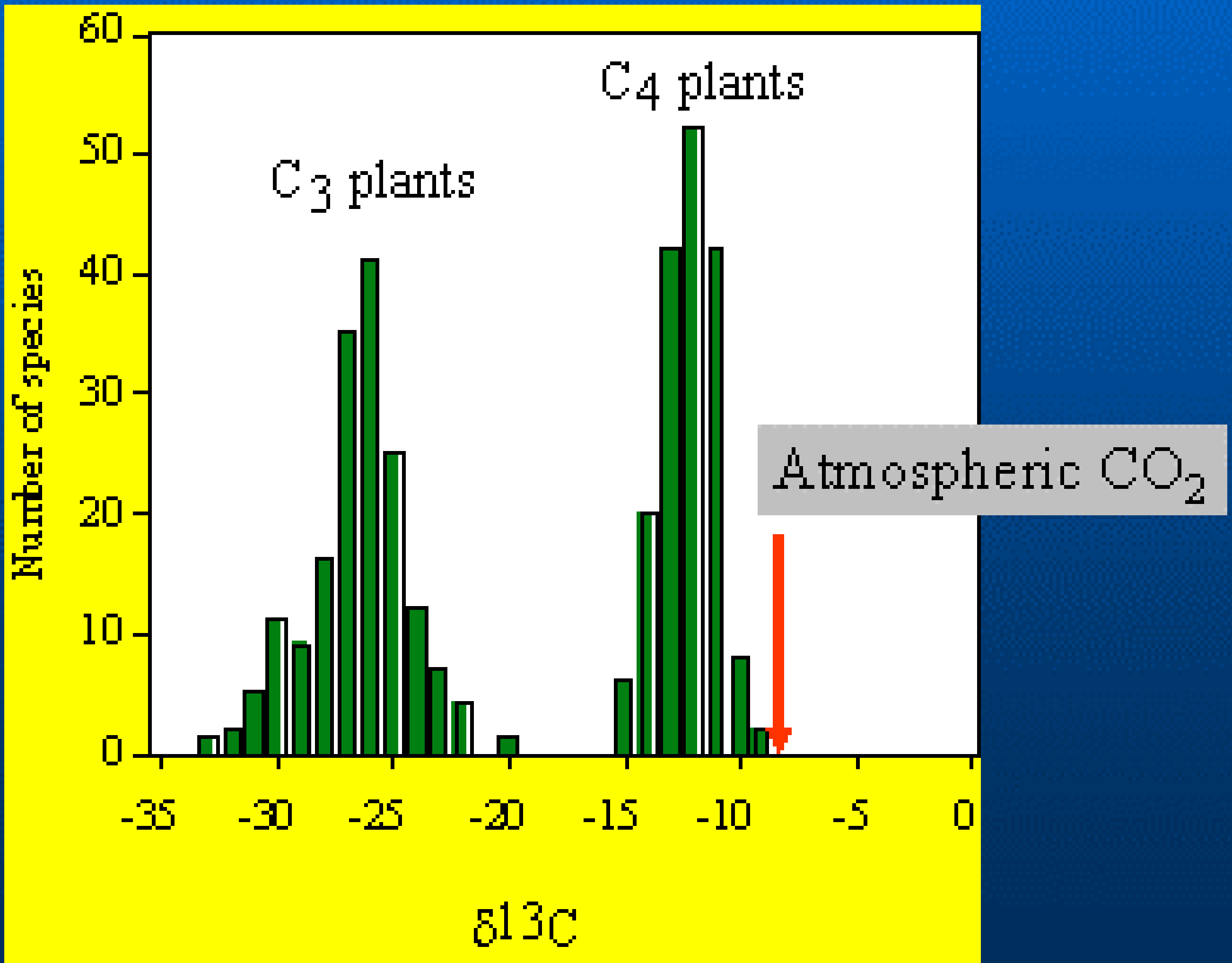


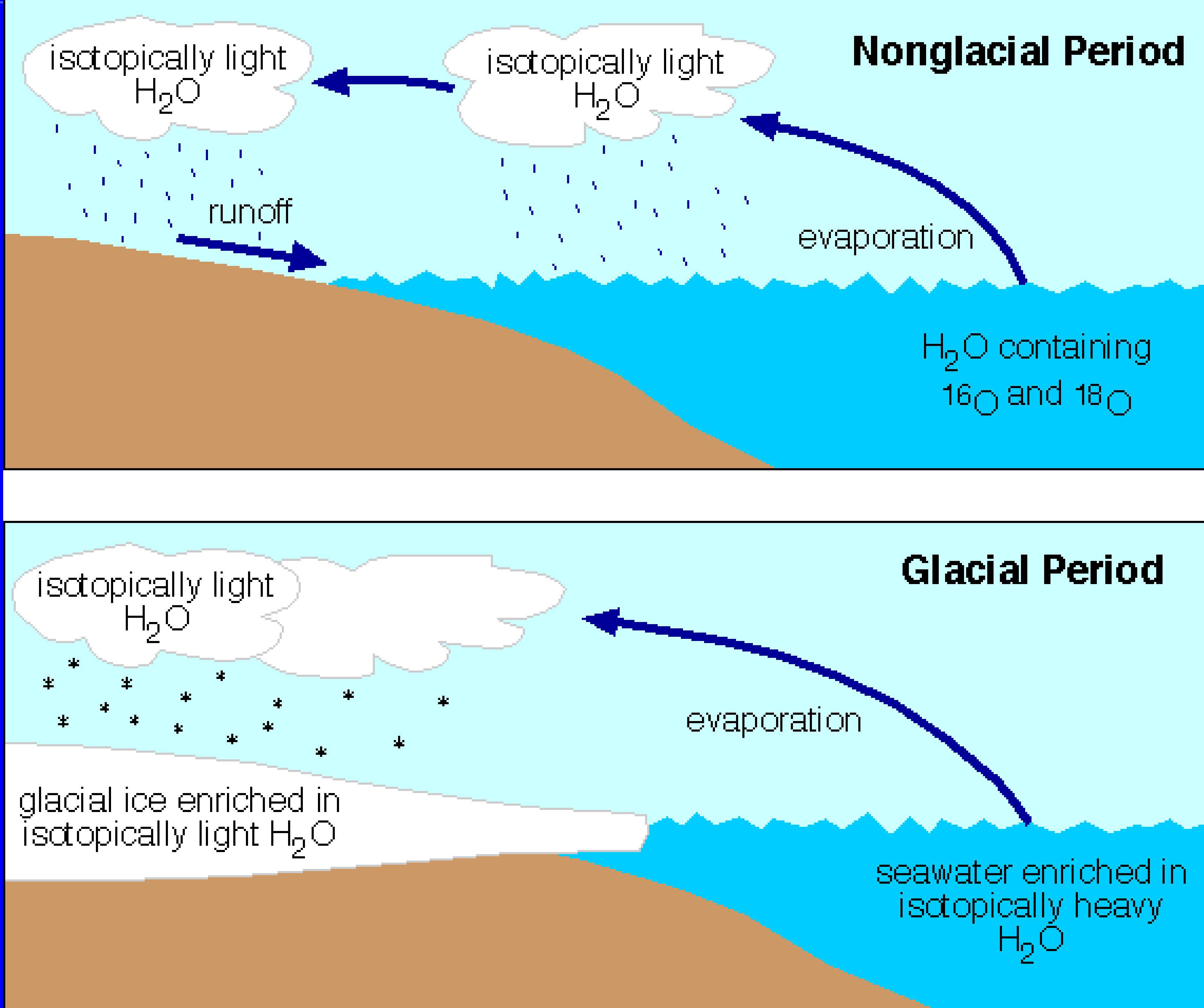
photosynthesis fixes preferentially more $^{12}CO_2$

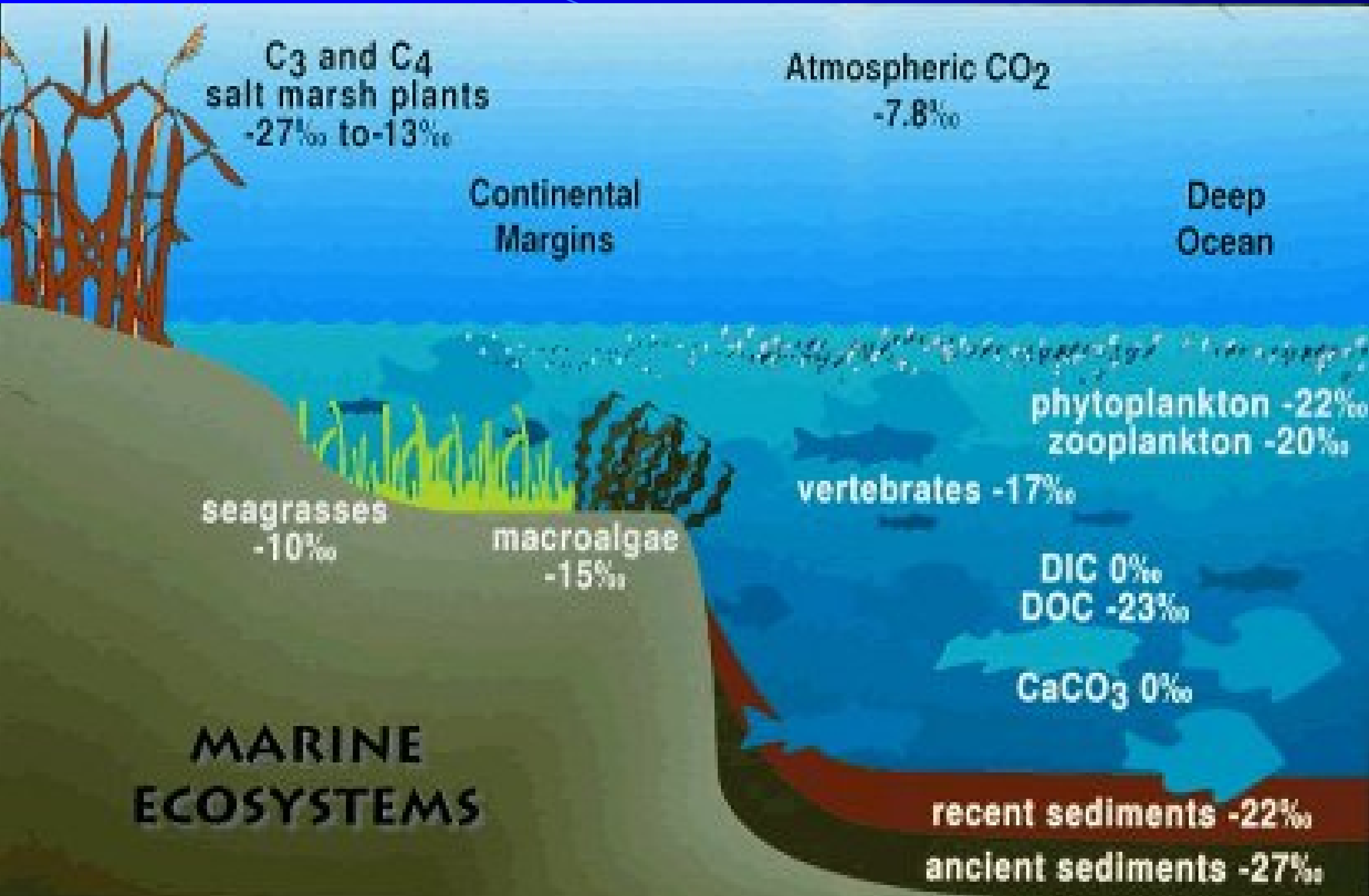


leaving an increased abundance of $^{13}CO_2$ to form calcareous skeletal materials

$\delta^{13}C$ depends on enzyme pathway



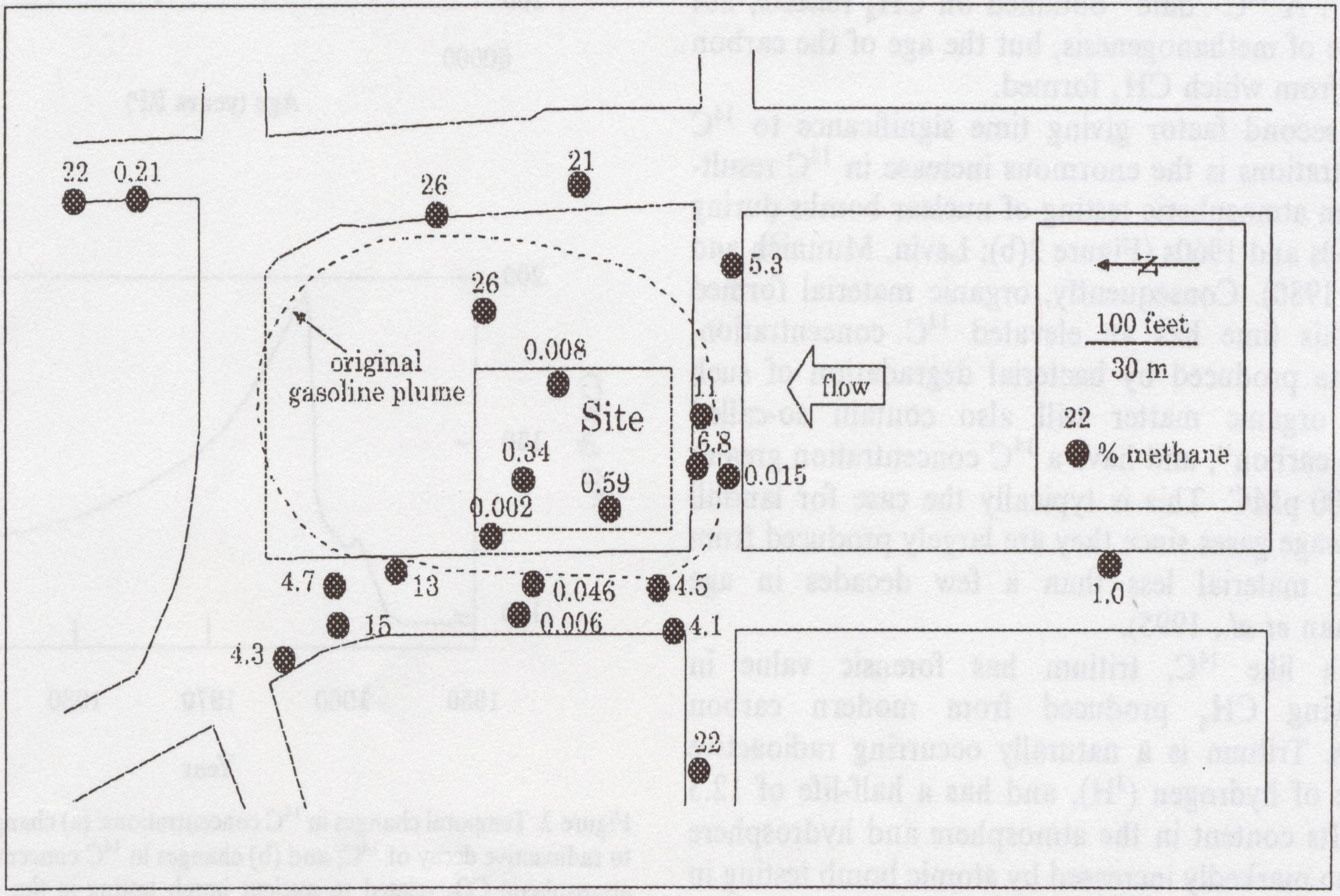

Nonglacial Period
isotopically light
H_2O
isotopically light
H_2O
runoff
evaporation
H_2O containing
^{16}O and ^{18}O
Glacial Period
isotopically light
H_2O
evaporation
glacial ice enriched in
isotopically light H_2O
seawater enriched in
isotopically heavy
H_2O



C_3 and C_4 salt marsh plants -27‰ to -13‰
Atmospheric CO_2 -7.8‰
Continental Margins
Deep Ocean
phytoplankton -22‰
zooplankton -20‰
vertebrates -17‰
seagrasses -10‰
macroalgae -15‰
DIC 0‰
DOC -23‰
$CaCO_3$ 0‰
MARINE ECOSYSTEMS
recent sediments -22‰
ancient sediments -27‰

Forensic Stable Isotope Cases

- In 1980 there was a large (80,000gal) gasoline spill from a service station
- Unusual large amounts of methane off gasses were found
- Borings showed the area was underlain by lake sediments and sawdust
- δD (methane) plotted against $\delta^{13}C$ showed that the methane was coming from the sawdust and not the methane



igure 3. Service station site map showing original liquid gasoline plume and CH_4 concentrations measured in monitoring wells sample

Areas showing $\delta^{13}C$ and δD for methane generated by biological CO_2 reduction, biological fermentation and thermogenic processes

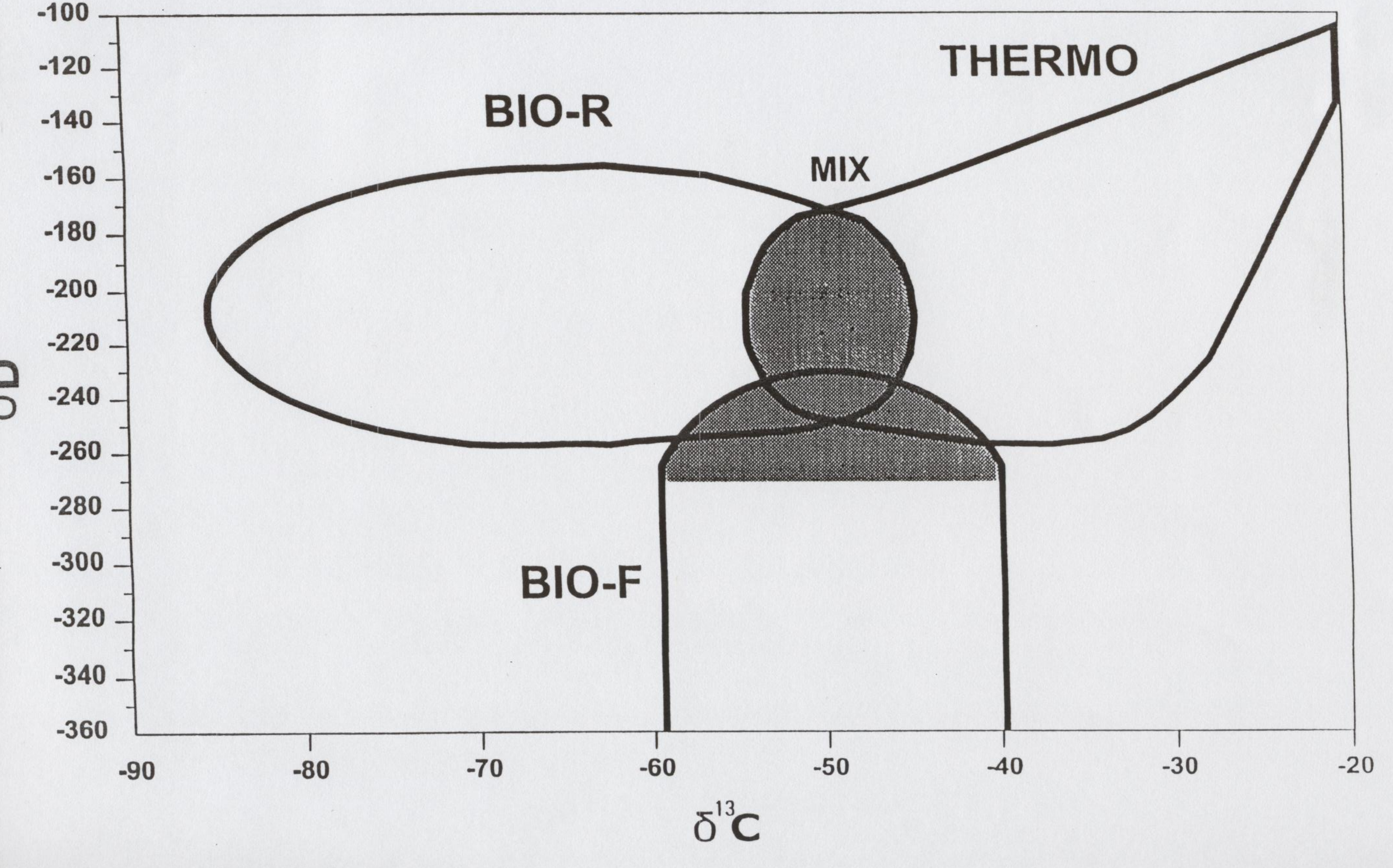
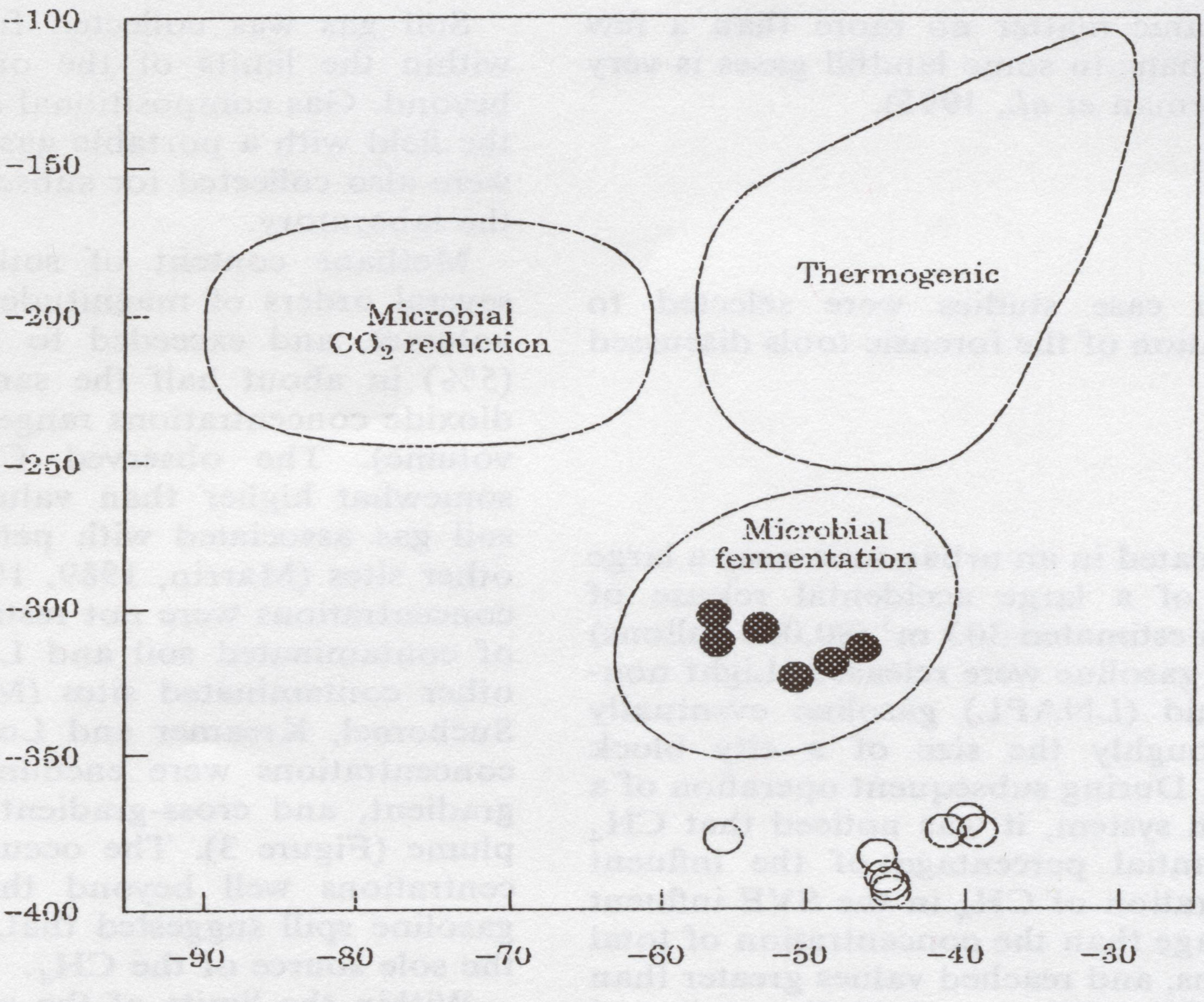


Table 9
Range of carbon and deuterium isotope ratios for methane derived from different origins

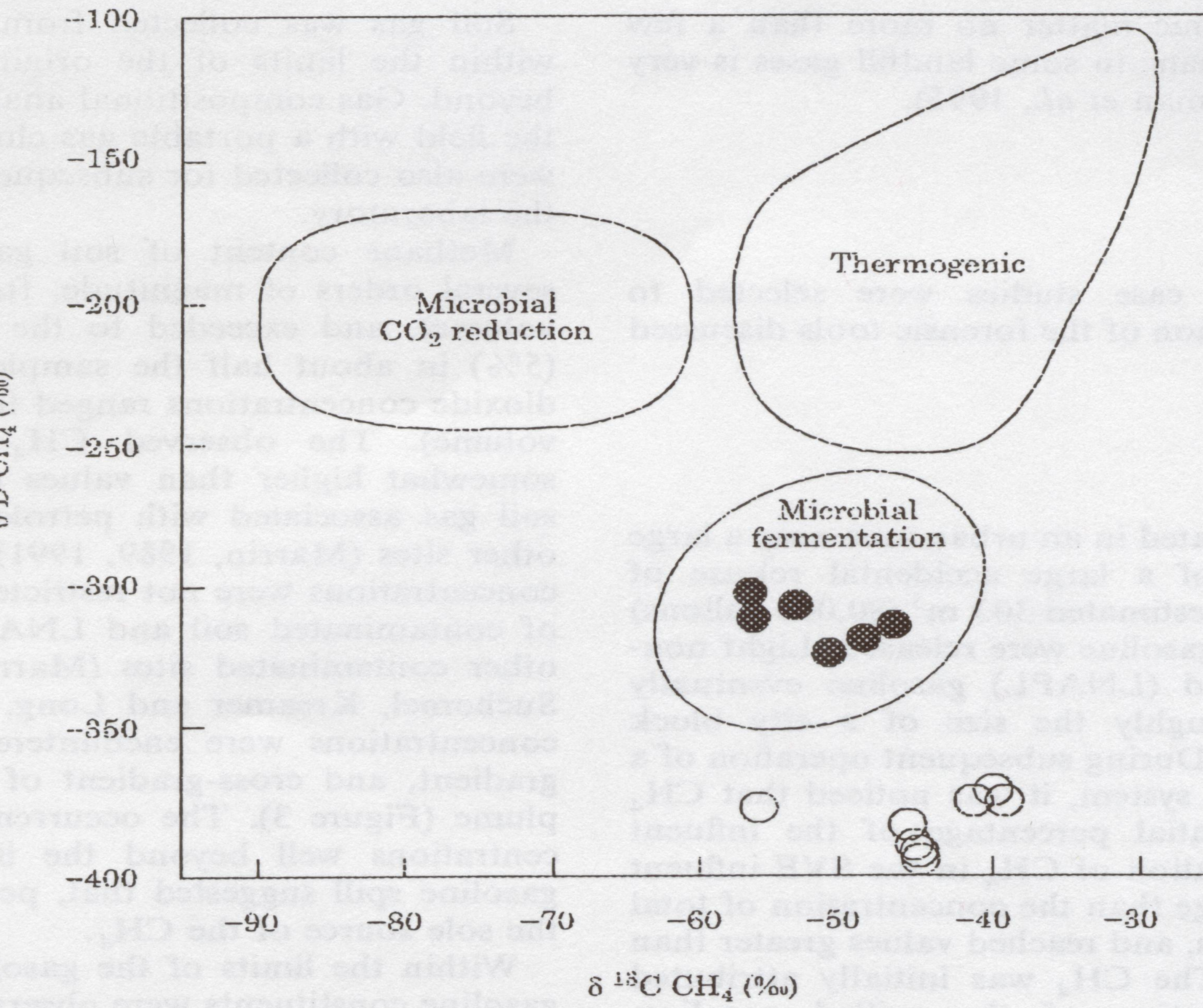
		$\delta^{13}C$	δD
Biogenic	CO_2 reduction Organic acid decomposition	-100 to -60 -60 to -50	-150 to -250 -250 to -350
Thermogenic	Early maturity Optimum maturity Late maturity	-50 to -40 -40 to -30 -30 to -15	-300 to -220 -220 to -160 -160 to -90



...fields for CH_4 of different origins. Fields after Coleman et al. (1995). Solid circles

Forensic Stable Isotope Cases

- Oil spills were found at an industrial facility where crude oil was stored
- Natural seeps of oil and gas were also present as well as numerous pipelines
- Large amounts of hydrocarbons, CO_2, CH_4, H_2 were present in the soil
- δD (methane) plotted against $\delta^{13}C$ (methane) showed that the methane was coming from microbial fermentation

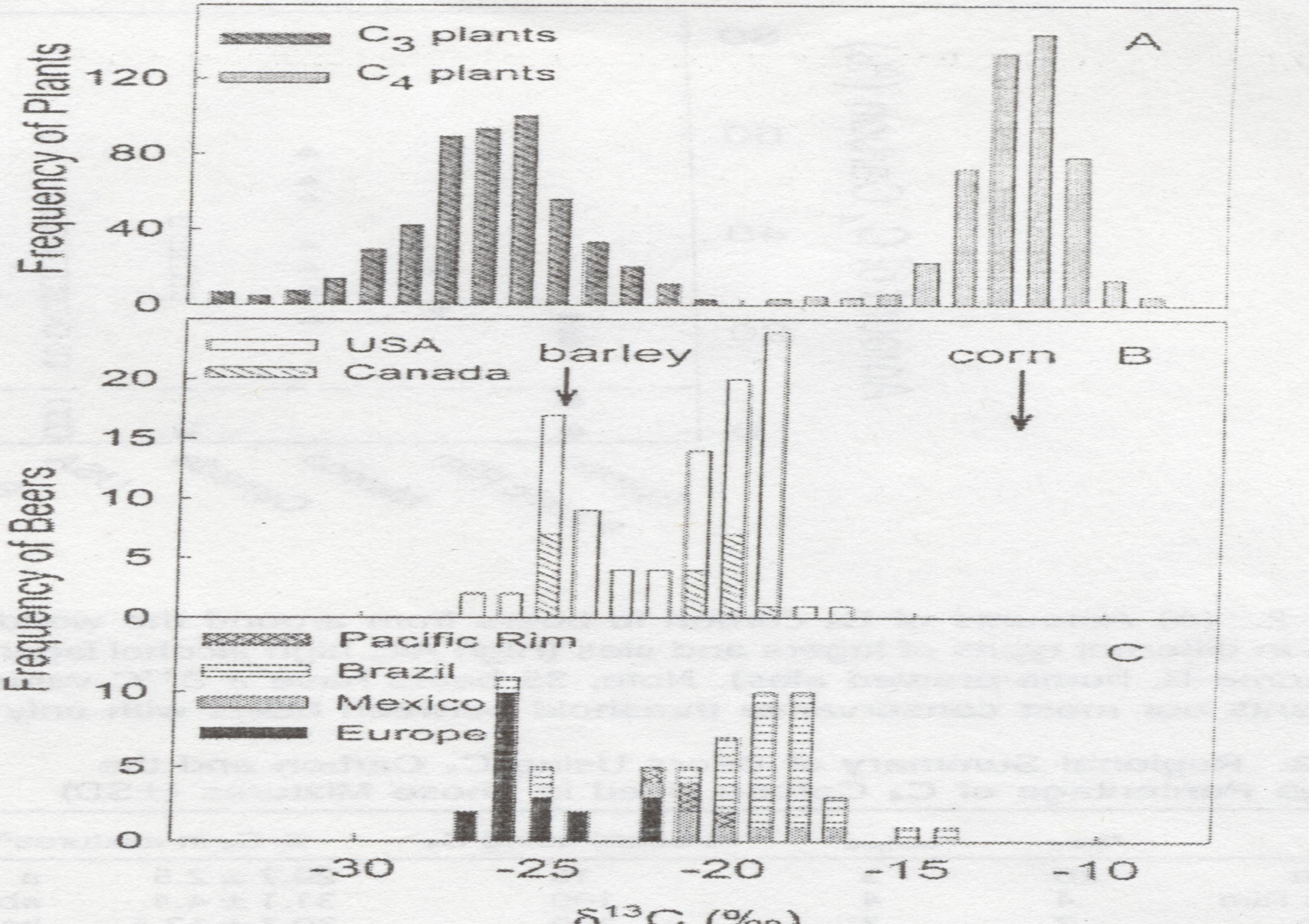


isotopic fields for CH_4 of different origins. Fields after Coleman *et al.* (1995). Solid circles

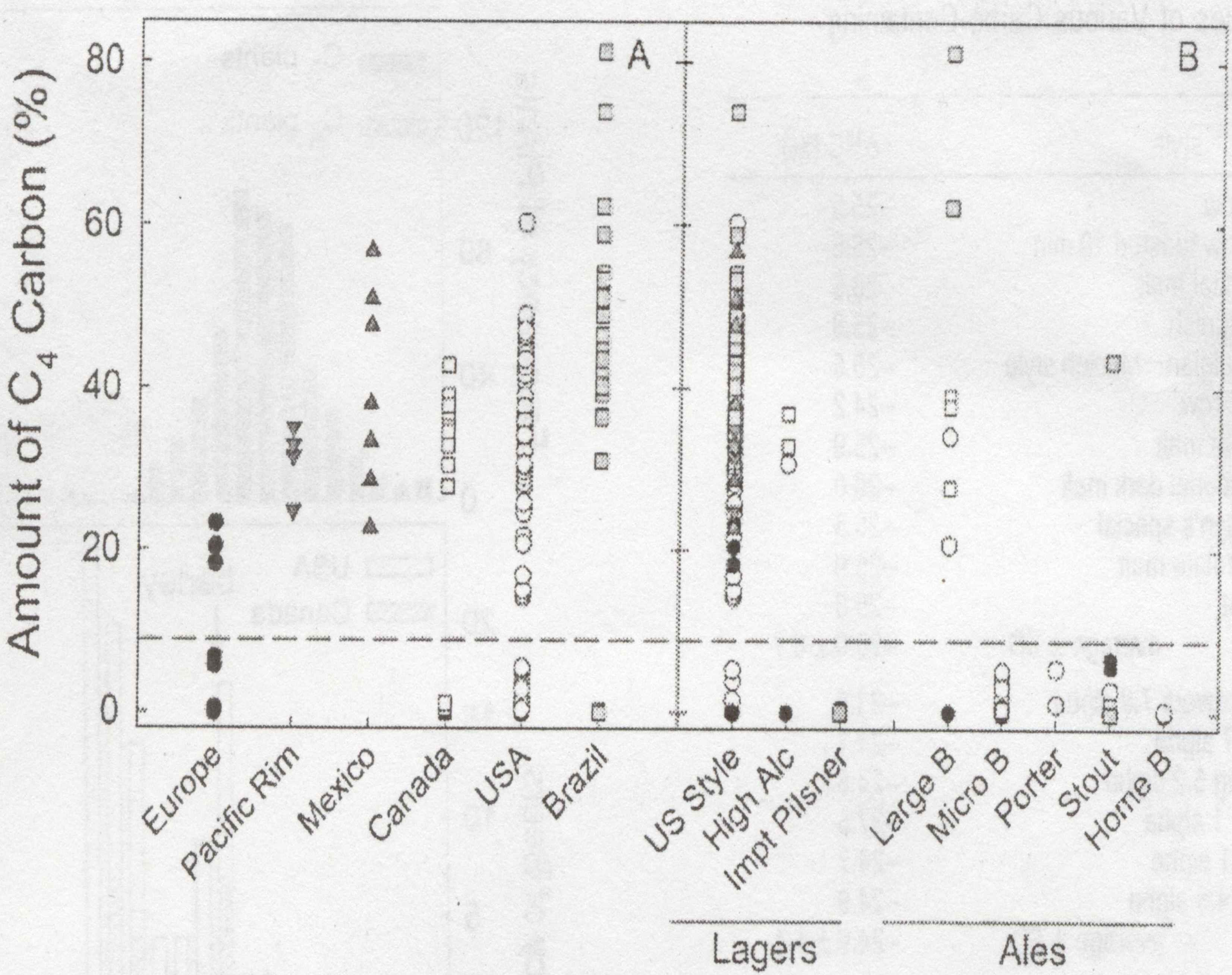
Forensic Stable Isotope Cases

Isotope Geochemistry of Beer

- When plants convert CO_2 into sugars by photosynthesis They use two different processes yielding sugars with 3 carbon atoms (C3 plants) and 4 carbon atoms (C4) plants
- C3 plants are barley, rice, etc.
- C4 plants are corn, cane sugar, etc.
- Each plant leaves its isotopic signatures in the resulting beer



ure 1. (A) Absolute frequencies of carbon isotope ratios ($\delta^{13}C$)



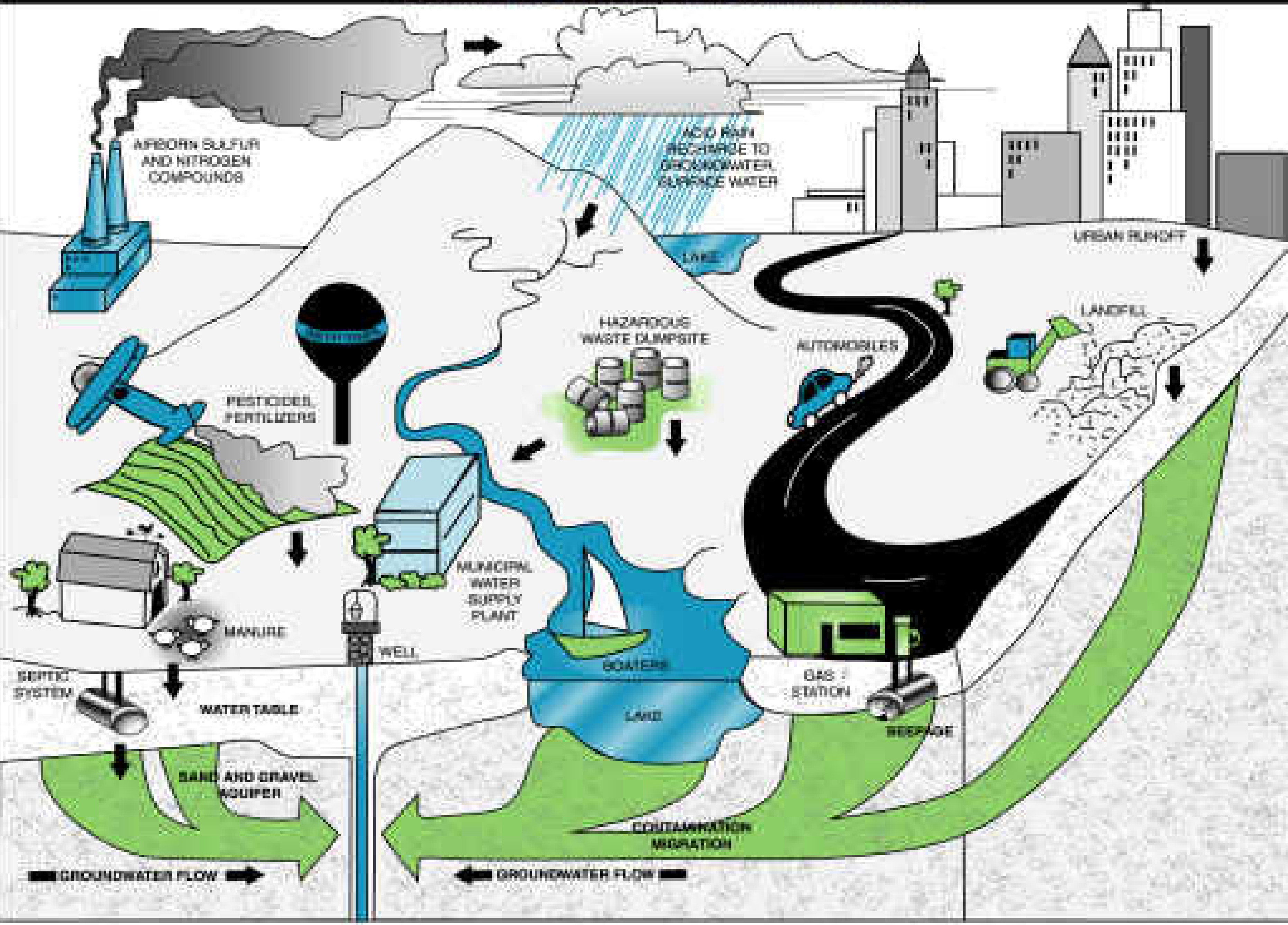
...unts of C_4 carbon in beers from around the world. Different symbols are used to represent the different ...

Forensic Stable Isotope Cases

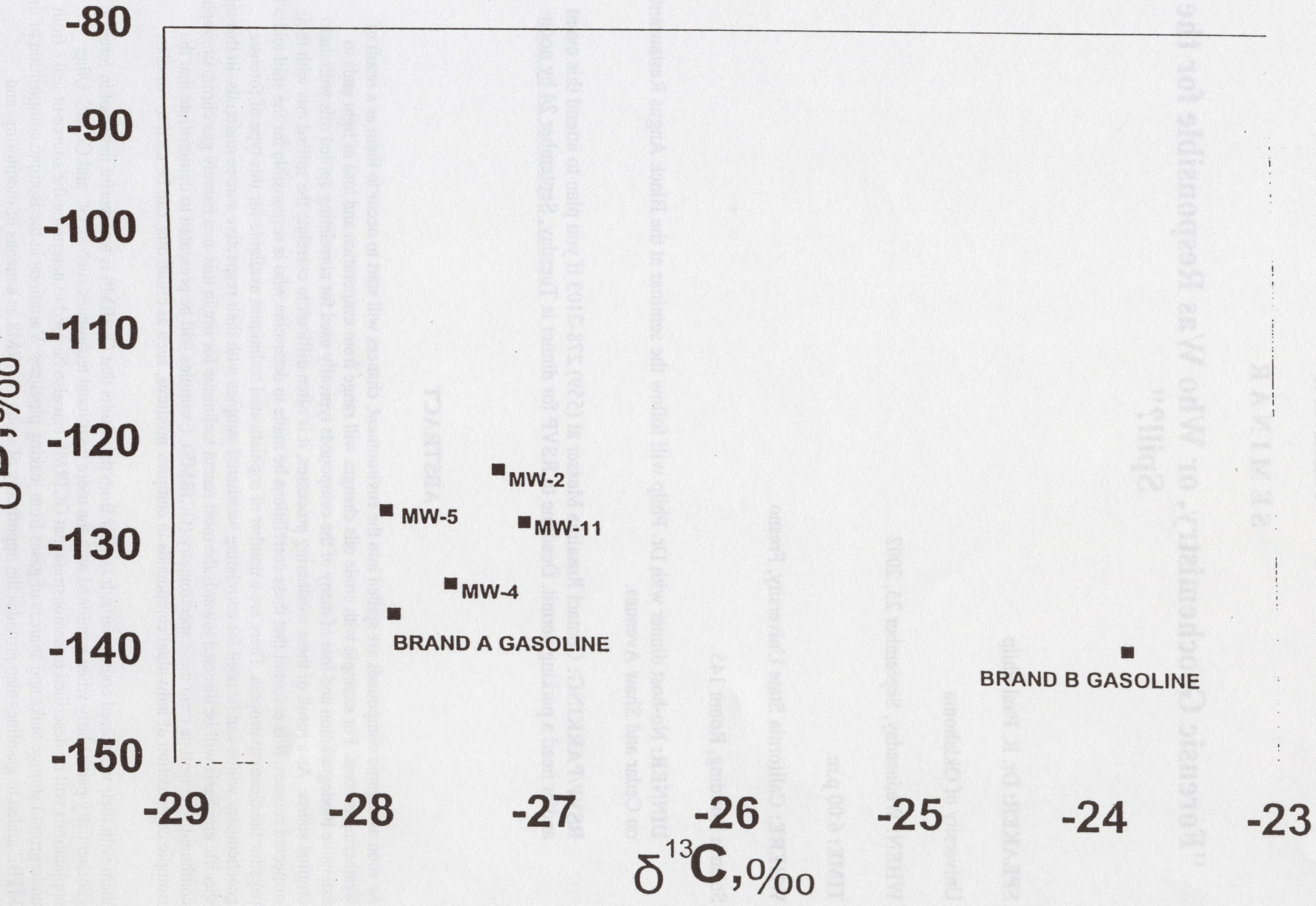
Gasoline Isotopes

- Gasoline from leaky service station tanks is a frequent ground water contaminant
- I had a professor at Penn State who woke up one night to a popping sound in his basement
- It turned out to be gasoline leaking into his sump pump from a leaky gas station up the hill from his house
- The gasoline was exploding every time the pump came on

SOURCES OF GROUNDWATER CONTAMINATION



Correlation of isotope ratios in groundwater extracts and two gasoline brands



Where Did the Oil Come From

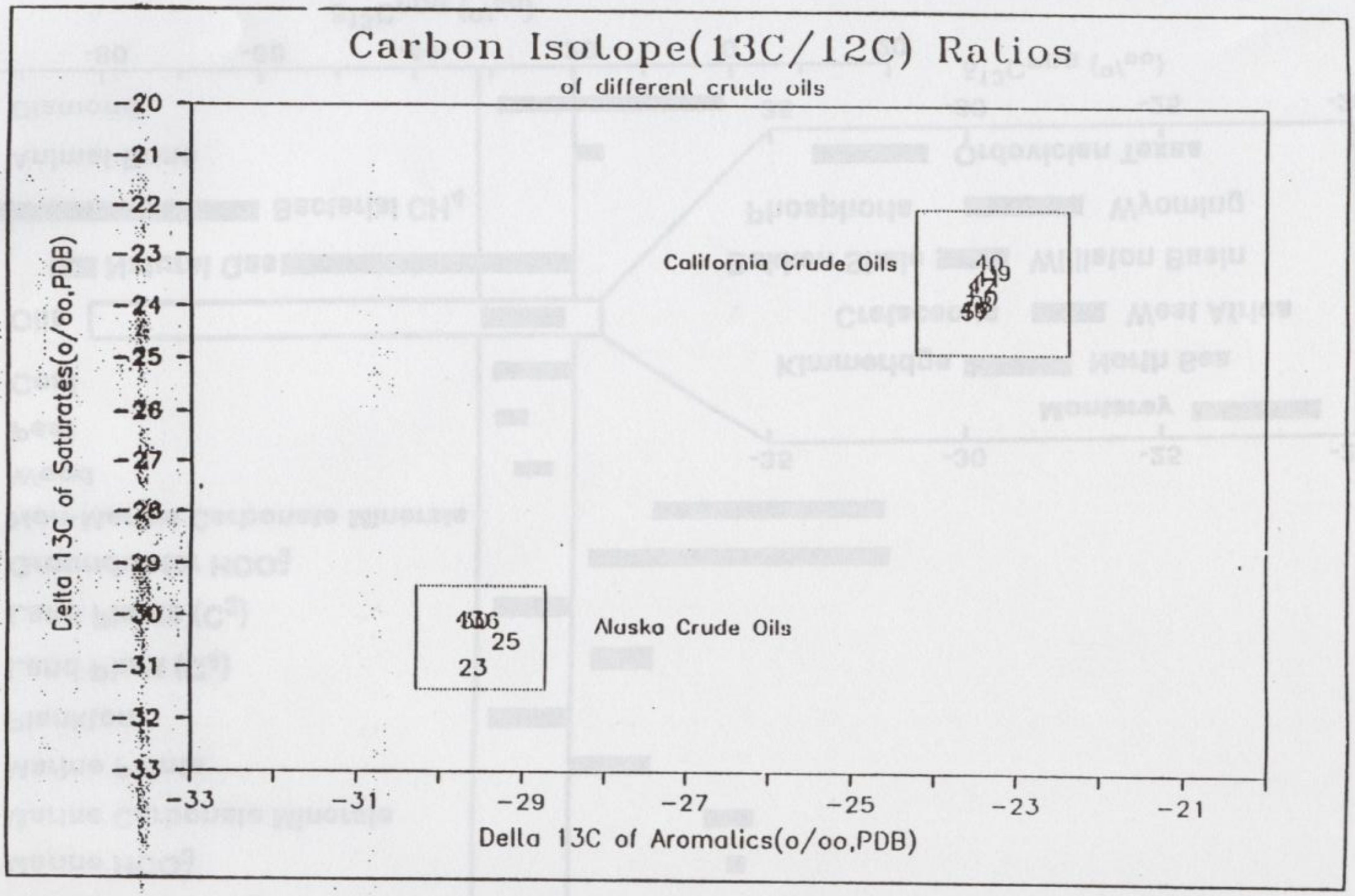
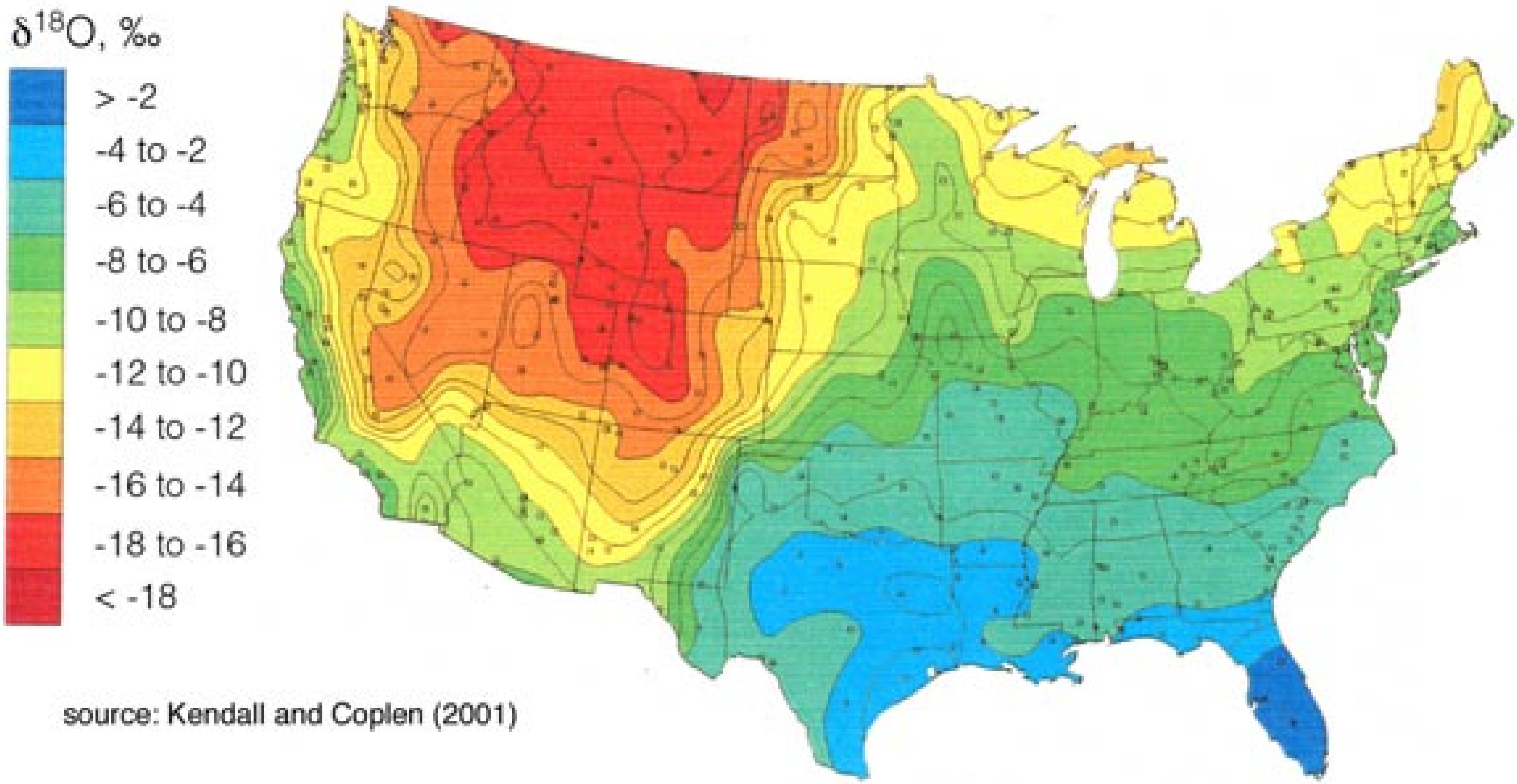


Figure 9.9: BP "American Trader" accident in Huntington Beach, California, February 7, 1990. Correlation among Alaska and California crude oils and beach tar balls on Southern California beaches, based on their carbon isotope ratios.

You Are What You Eat & Drink

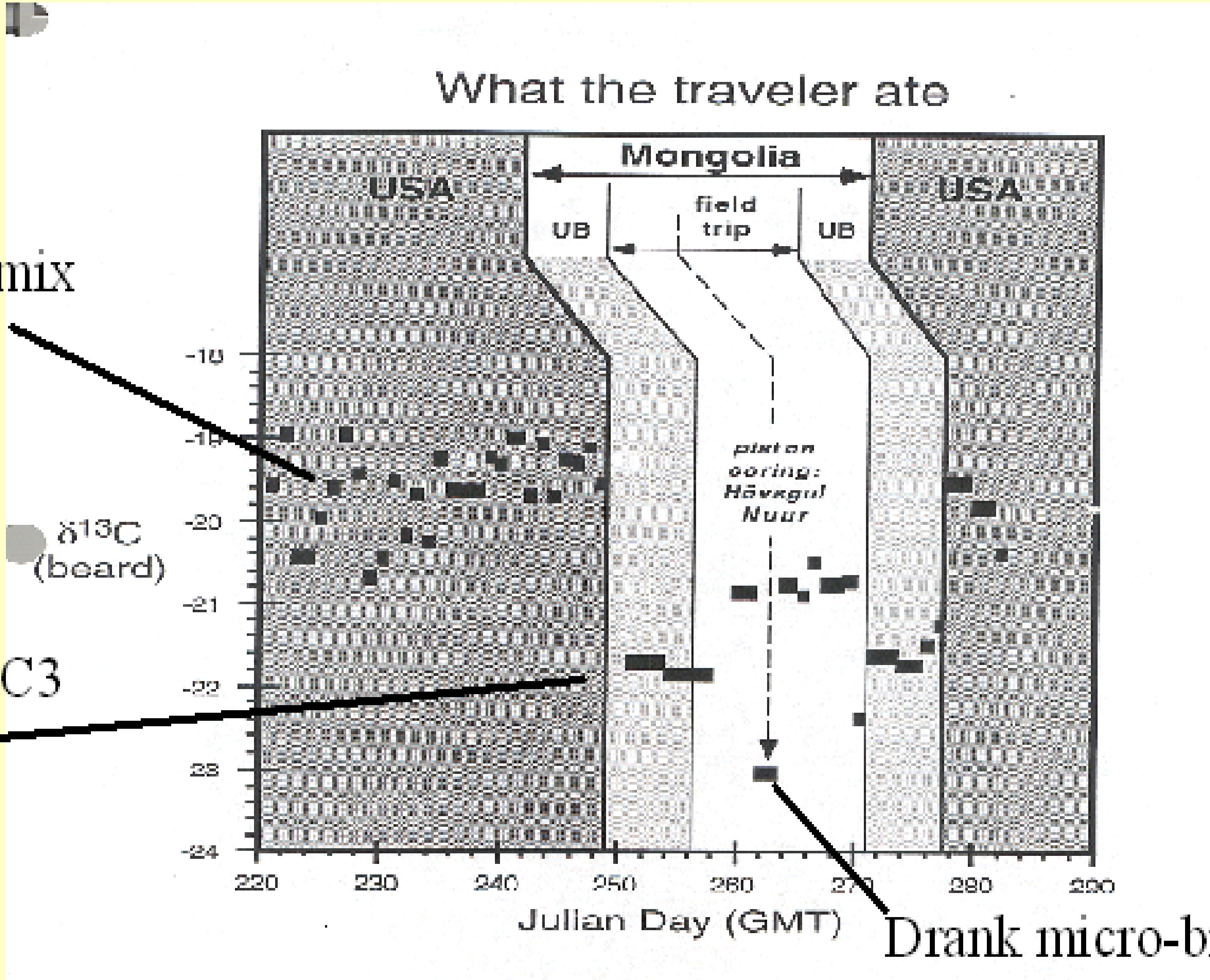
- The isotopic content of both food and water vary from place to place
- People and animals eating and drinking in different places take on the isotopic signatures of their environment
- Your travel history is in your hair, teeth, bones, etc

Isotopic Composition of Water in the USA



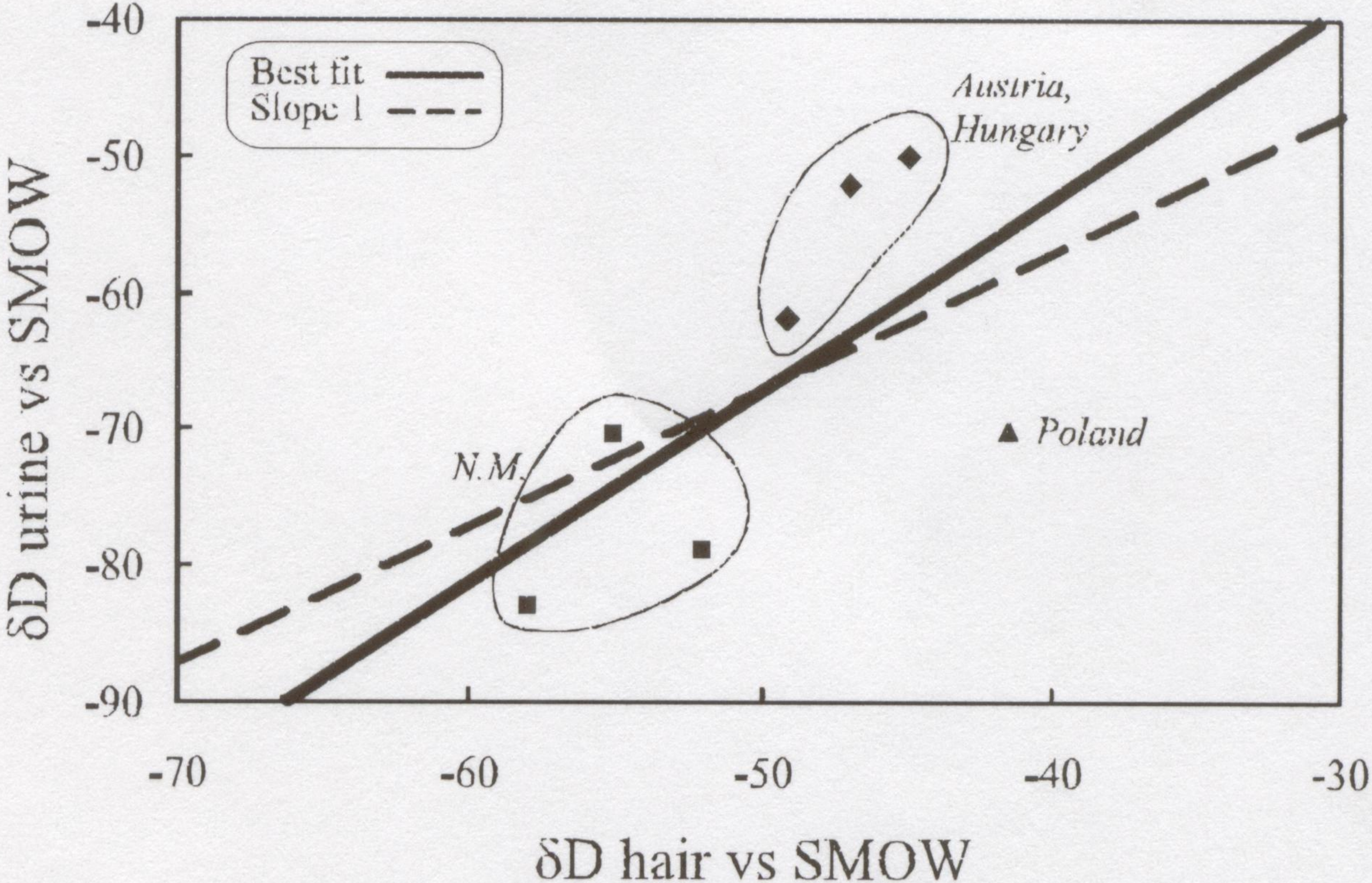
You are what you eat!

Diet of C3-C4 mix



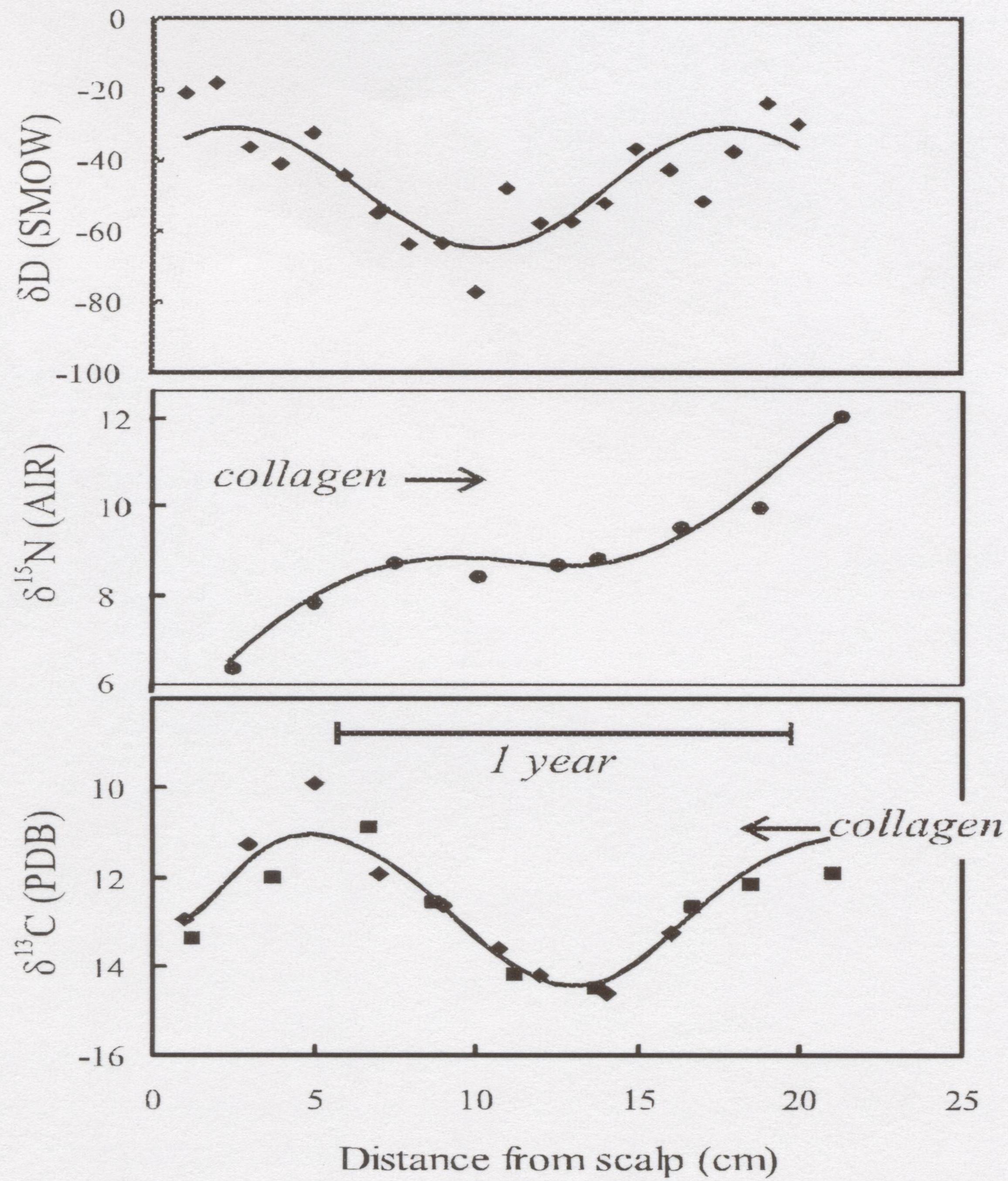
Diet of C3 only

Drank micro-brew beer



Best fit
Slope 1
Austria,
Hungary
N.M.
Poland
-40
-50
-60
-70
-80
-90
-70
-60
-50
-40
-30
δD urine vs SMOW
δD hair vs SMOW

Isotopic values from the hair of an Inca mummy The sinusoidal variations are thought to be related to seasonal variations (more corn in summer, etc.)



Forensic Stable Isotope Cases

From where did the Ice Man Commeth?

Research reported in Science (31 Oct 2003) compared Sr, Pb, O, and Ar isotopes from the iceman to the local geology and concluded that he originated within ~60 miles of where he was found and that he migrated through a number of local valleys