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Radioactive and Stable Isotopes Theory and Application to Forensic Investigations

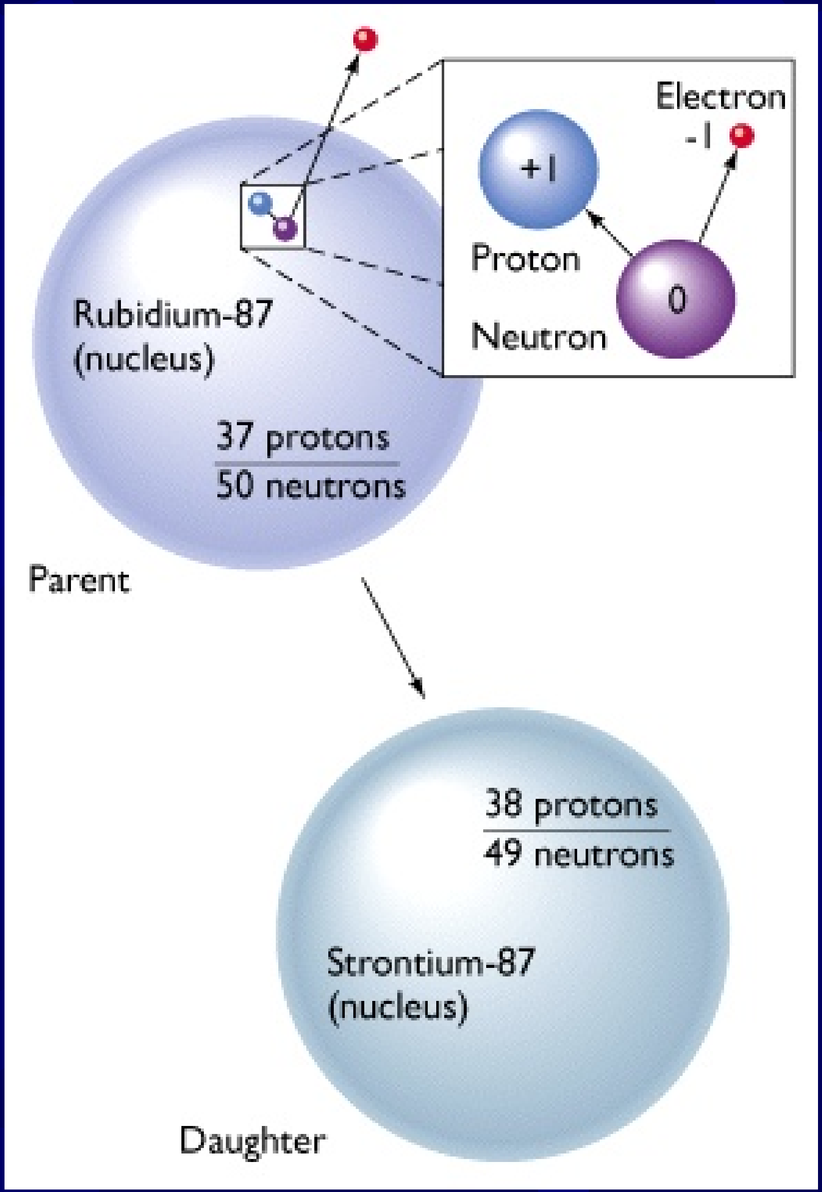
Thermal Ionization Mass Spectrometer (TIMS)

Stanford University, USA

VG Isogas Micromass 602E Isotope Ratio Mass Spectrometer

University of Queensland, Australia

Radioactive Isotopes



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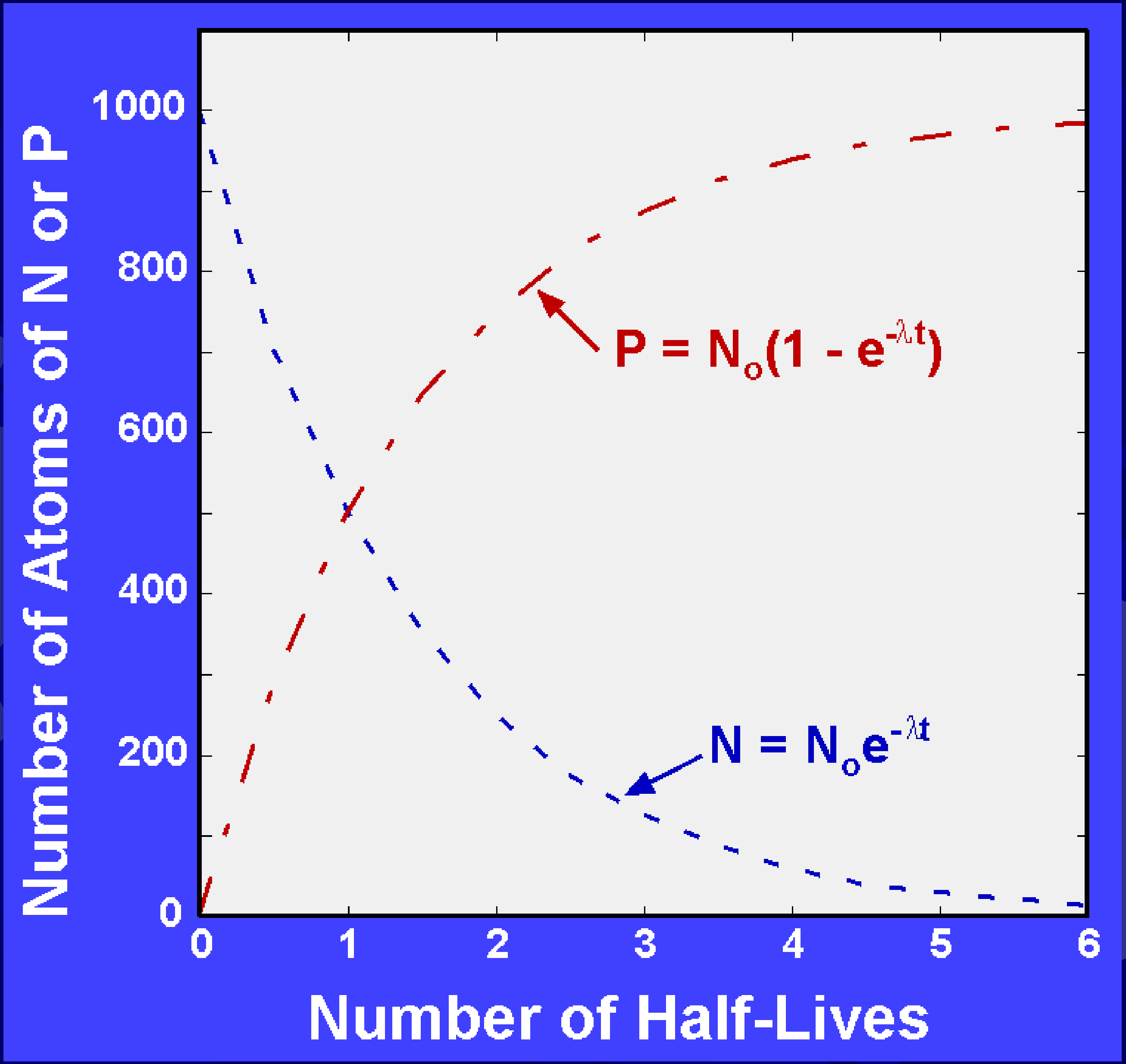
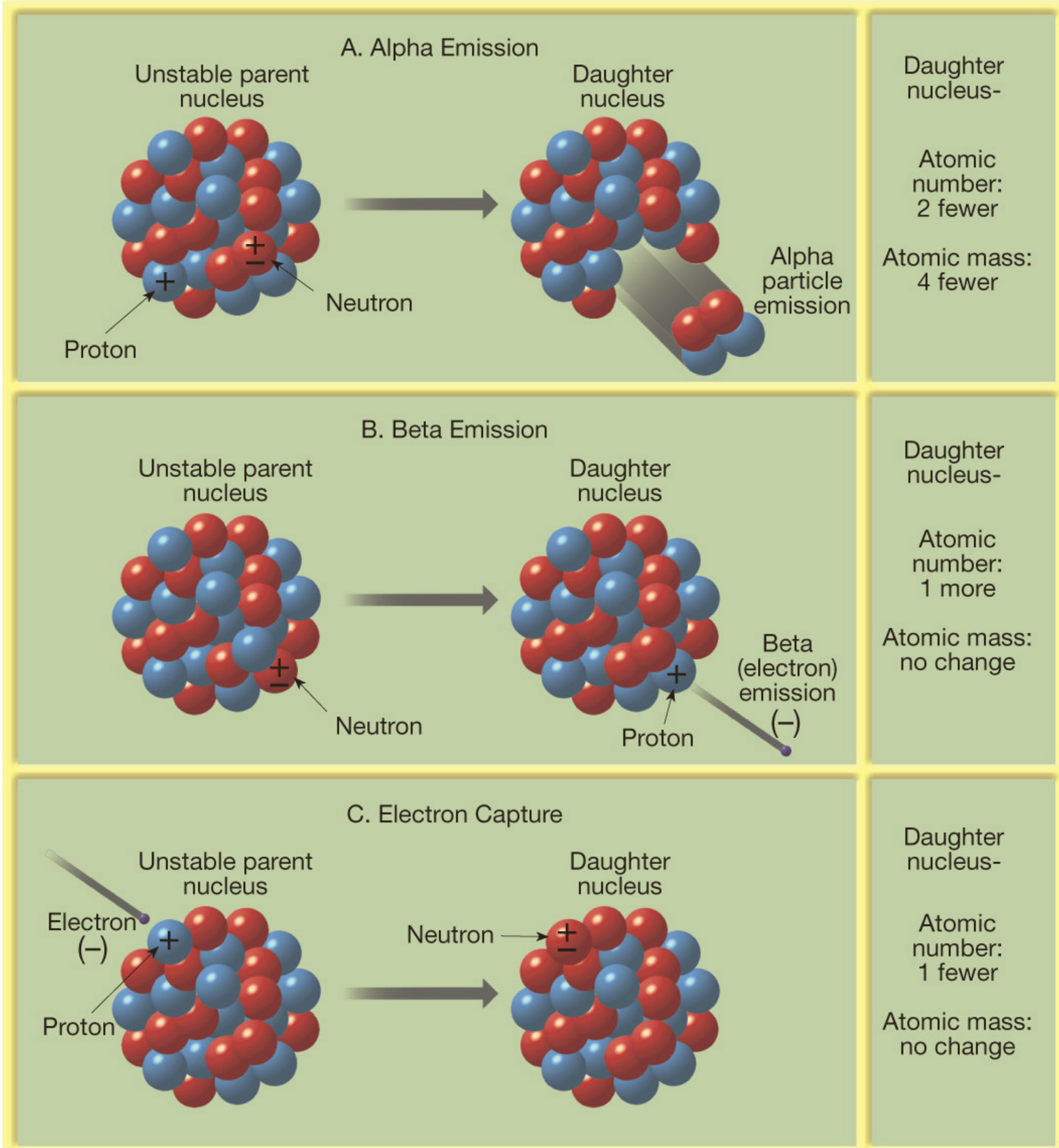


Graphical representation of decay of radioactive parent (N) and growth of radiogenic progeny (P).


A. Alpha Emission
Unstable parent nucleus
Daughter nucleus
Proton
Neutron
Alpha particle emission
Daughter nucleus-
Atomic number: 2 fewer
Atomic mass: 4 fewer
B. Beta Emission
Unstable parent nucleus
Daughter nucleus
Neutron
Proton
Beta (electron) emission (–)
Daughter nucleus-
Atomic number: 1 more
Atomic mass: no change
C. Electron Capture
Unstable parent nucleus
Daughter nucleus
Electron (–)
Proton
Neutron
Daughter nucleus-
Atomic number: 1 fewer
Atomic mass: no change

Geologic Time

- Radioactive Isotopes used in Geologic Dating

Parent	Progeny	half-life (y)
U-238	Lead-206	4.5 billion
U-235	Lead-207	713 million
Thorium 232	Lead 208	14.1 Billion
K-40	Argon-40	1.3 billion
R-87	Sr-87	47 billion
C-14	N-14	5730

- Half-life = time it takes for 1/2 of the parent mass to decay into the daughter mass

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Geologic Time

Carbon 14 Dating

- A cosmic ray neutron (n) collides with an atom of atmospheric Nitrogen (^{14}N) which decays into ^{14}C and hydrogen (p=proton)

  $^{14}N + n \Rightarrow {}^{14}C$ + Hydrogen (proton)

- ^{14}C is rapidly oxidized to $^{14}CO_2$ which is continuously taken up into living organisms
- When the organism dies it stops taking in 14C which disappears as it decays to 14N

  14C => 14N + Beta (beta comes from a neutron going to a proton)

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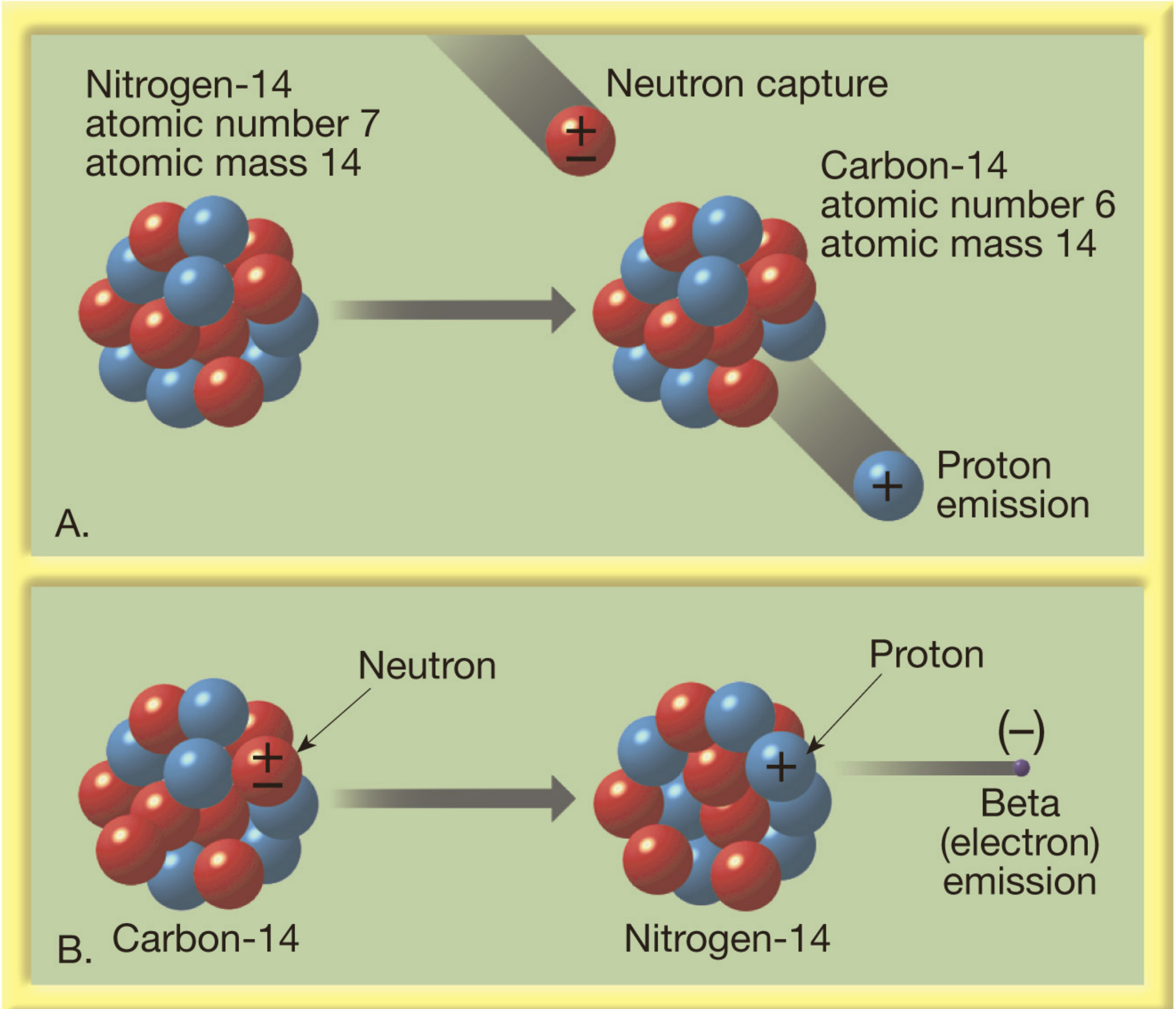
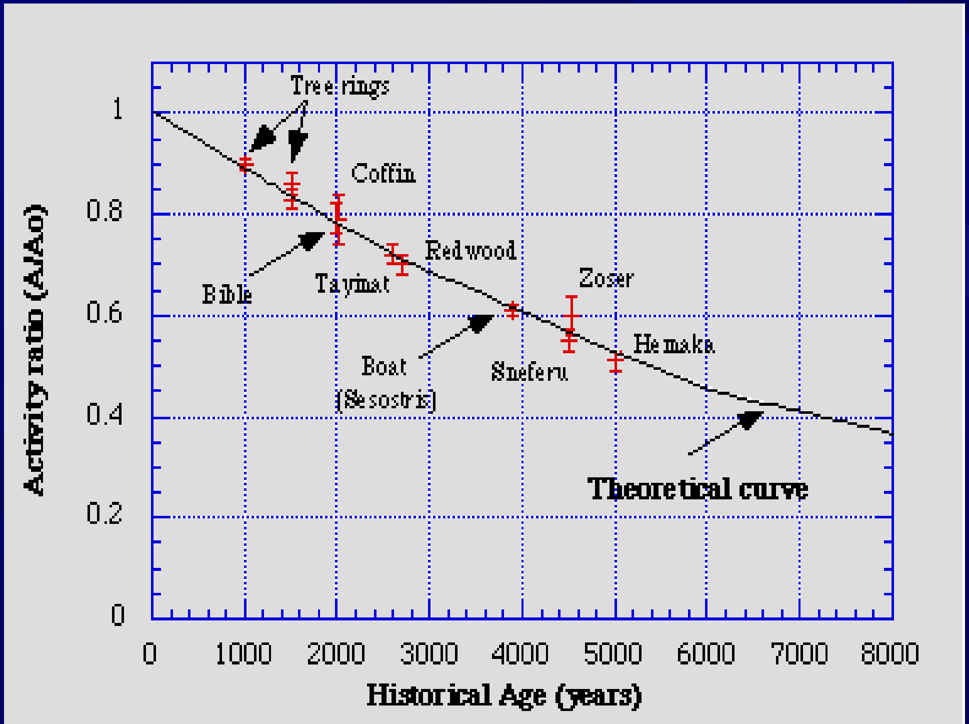

Nitrogen-14
atomic number 7
atomic mass 14
Neutron capture
Carbon-14
atomic number 6
atomic mass 14
Proton
emission
A.
Neutron
Proton
(–)
Beta
(electron)
emission
B.
Carbon-14
Nitrogen-14

Geologic Time

^{14}Carbon Dating

- Dating is accomplished by determining the ratio of ^{14}C to non-radioactive ^{12}C which is constant in living organisms but changes after the organism dies



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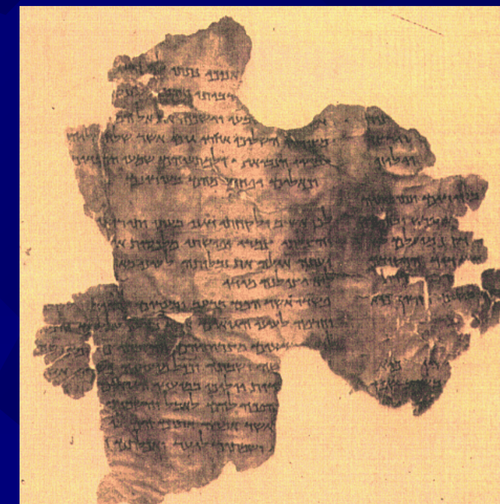
Geologic Time

Carbon 14 Dating

- Because of variations in the cosmic ray flux, the rate of formation of ^{14}C varies with time. This can be corrected by determining ^{14}C activity in samples of know historical age. Bristlecone Pines are often used for this calibration
- For an old sample (>40,000 years) trace contamination by modern carbon results in an incorrect young age
- Testing of nuclear weapons since 1945 have added ^{14}C to the atmosphere

Forensic ^{14}Carbon Cases

- Dead Sea Scrolls – 5-150 AD



- Stonehenge – 3100 BC

- Hezekiah’s Tunnel - 700 BC

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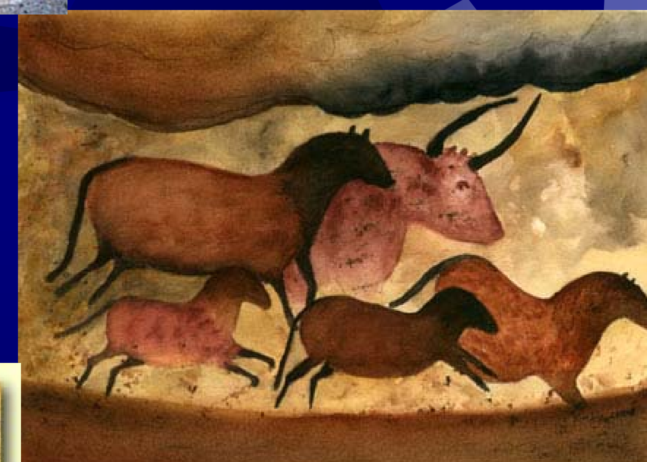
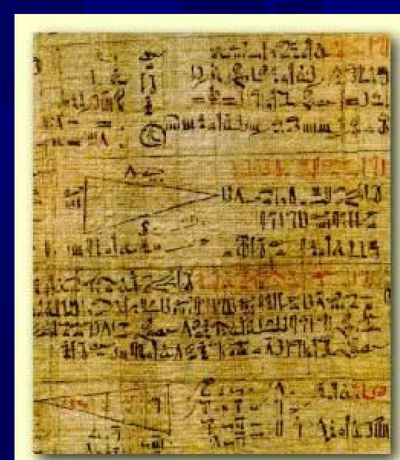
Forensic ^{14}Carbon Cases

- King Arthur's Table in Winchester Castle, England ^{14}C dated to 13th century AD

- Cave painting at Lascaux, France
  ^{14}C dated to 14,000 BC



- Rhind Papyrus on Egyptian math ^{14}C dated to 1850 BC



Forensic ^{14}Carbon Cases

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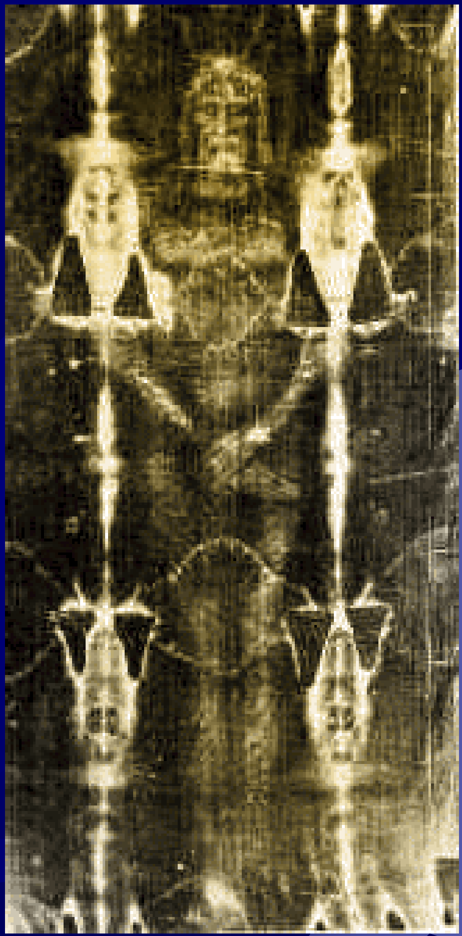
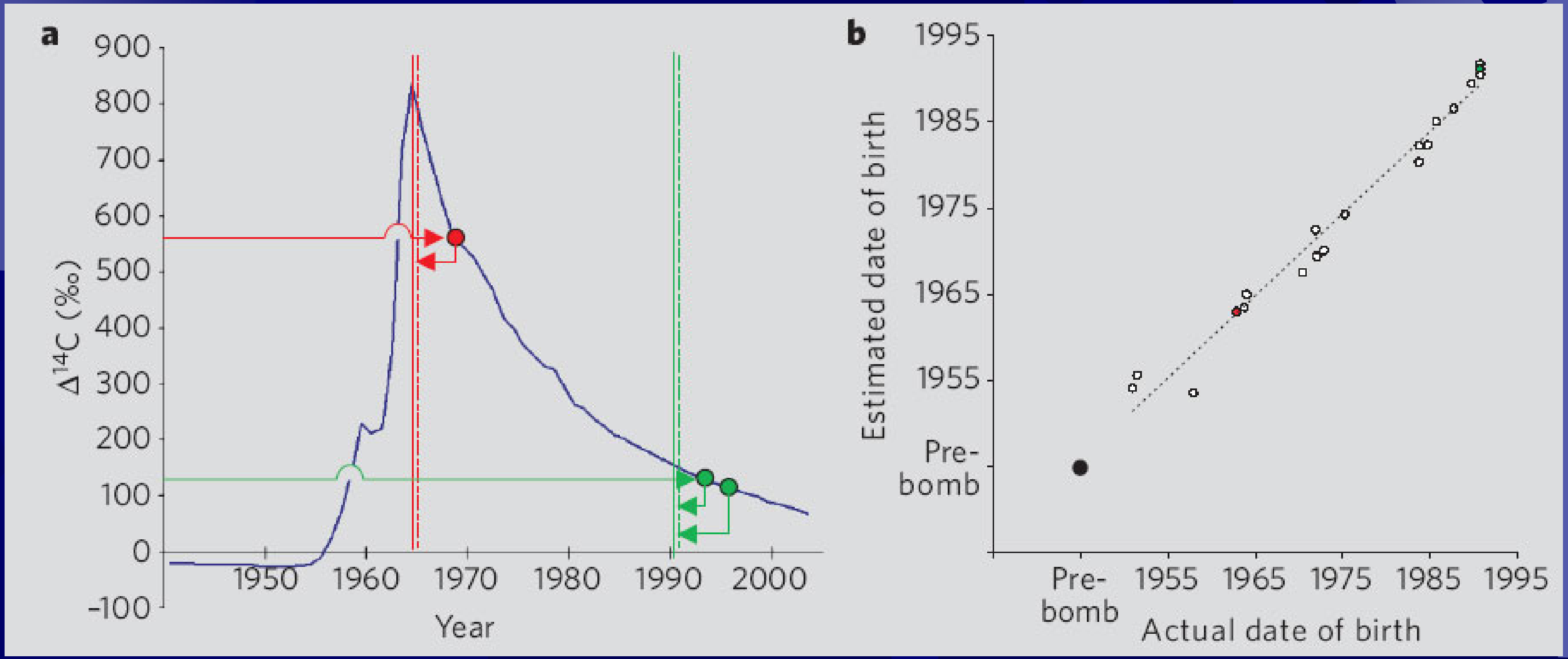
- The Shroud of Turin was ^{14}C dated 1260-1390 AD which suggests that it is a fake
- However, recent evaluation shows that the sample measured was from a medieval patch and/or that it was seriously contaminated with molds, waxes, etc
- New estimates date the shroud from 1300-3000 ybp bases on vanillin retention



Forensic ^{14}Carbon Cases

Above ground nuclear testing during 1955-63 put large amounts of ^{14}C into the atmosphere which was incorporated into the enamel of human teeth. When above ground testing stopped, the ^{14}C input ended and the ^{14}C in the teeth decayed at a fixed rate allowing dating of the teeth



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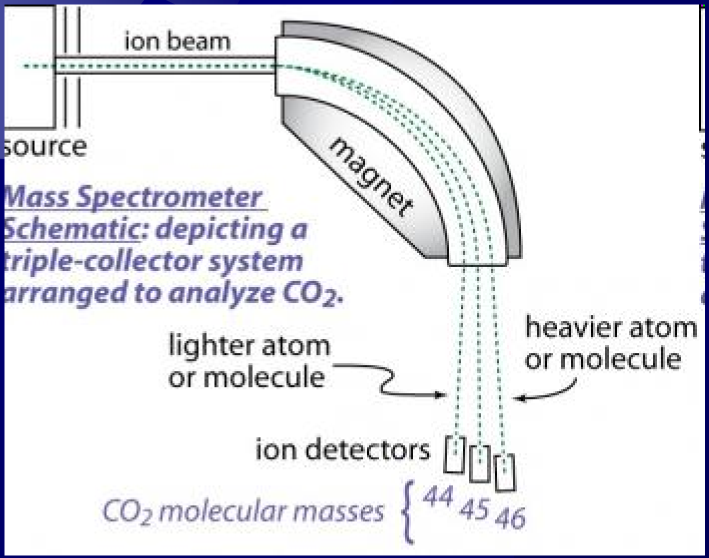
Stable Isotopes

Laboratory set-up for determining stable isotope abundances



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Stable Isotopes Used in Forensic Applications		
Element	Isotope	Atom %
Hydrogen	^{1}H	99.985
	^{2}H	0.015
Carbon	^{12}C	98.9
	^{13}C	1.1
Nitrogen	^{14}N	99.63
	^{15}N	0.37
Oxygen	^{16}O	99.762
	^{17}O	0.038
	^{18}O	0.2

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

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Notation

R: "ratio"

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

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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 δ^{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 δ^{13}C of plant material is always a negative number.

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Stable Isotopes

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

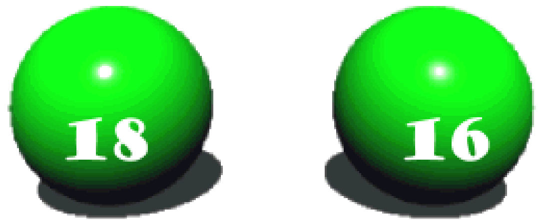
For carbon isotopes:

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.

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Stable isotopic fractionation takes place during

1. Physical,
2. Chemical, and
3. Biological processes

The partitioning of the isotopes is a function of the mass differences and occurs because the isotopically lighter molecule has a greater velocity or a higher vibrational energy.

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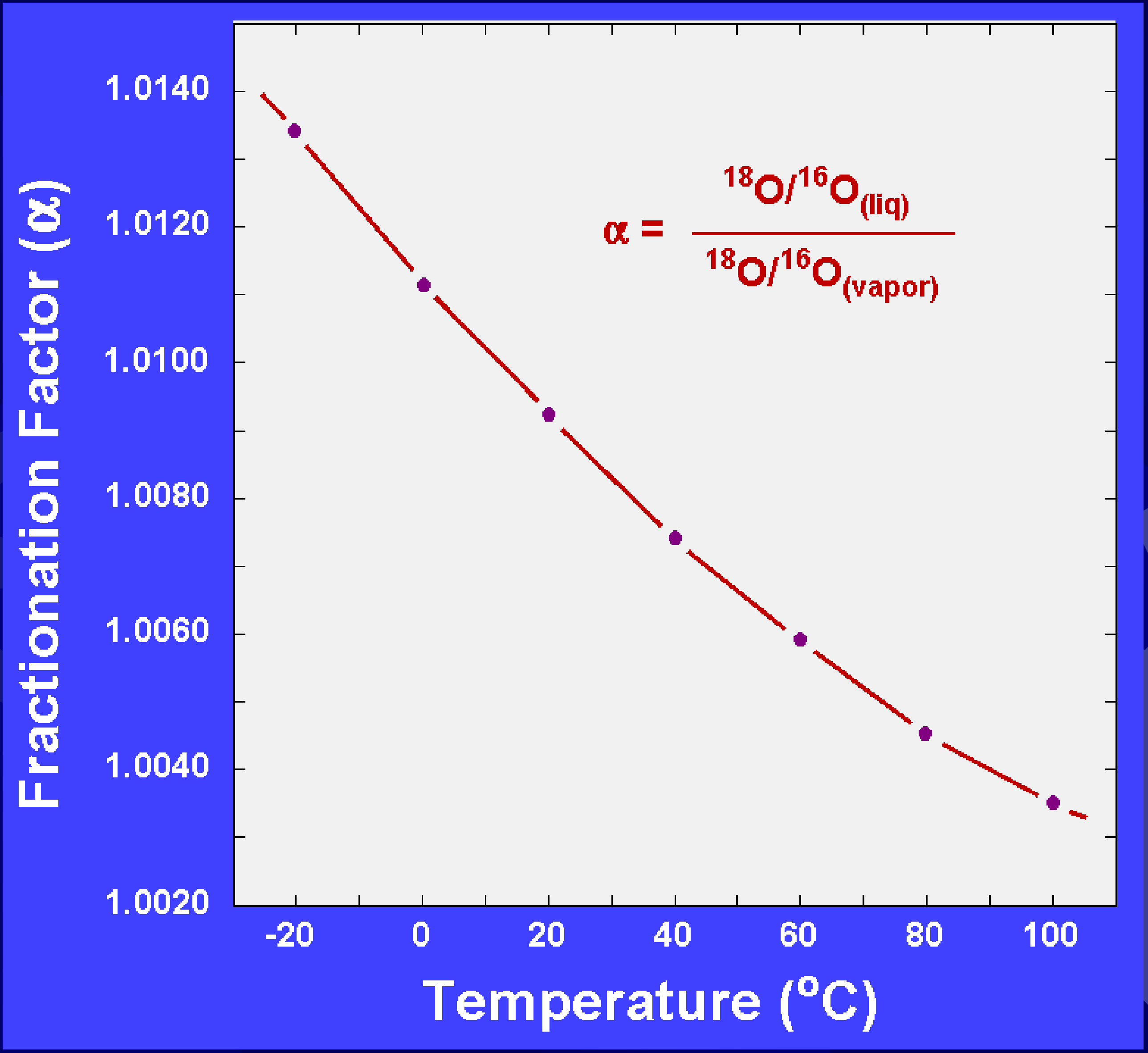
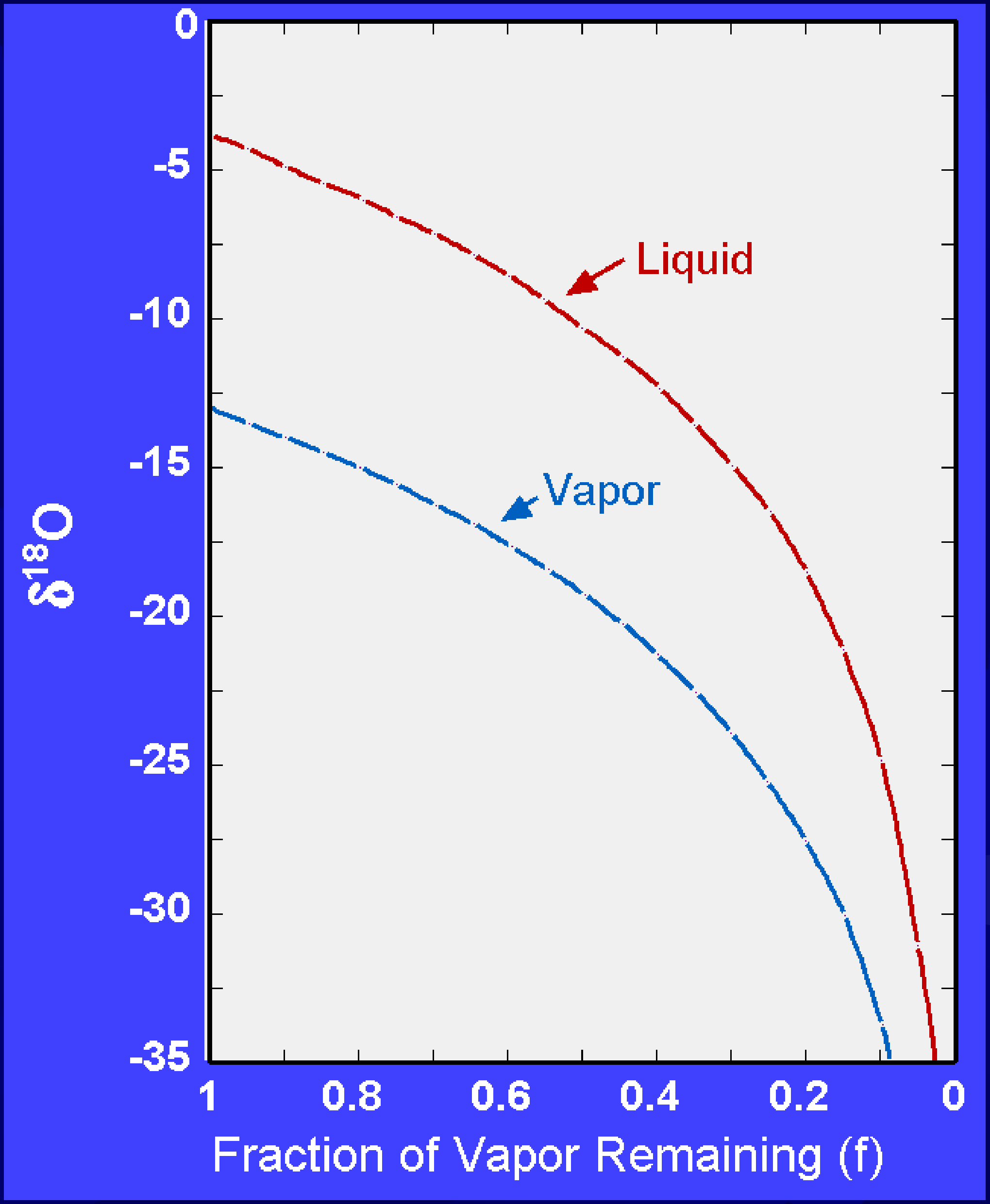


Variation of the isotope fractionation factor for oxygen, as a function of temperature, during the evaporation of water. Note that with increasing temperature the fractionation factor approaches 1.0000. Values from Dansgaard (1964).



Fractionation of oxygen isotopes during Rayleigh distillation of water vapor at 25ºC. The initial $\delta^{18}O$ value of the vapor is –13º/oo.

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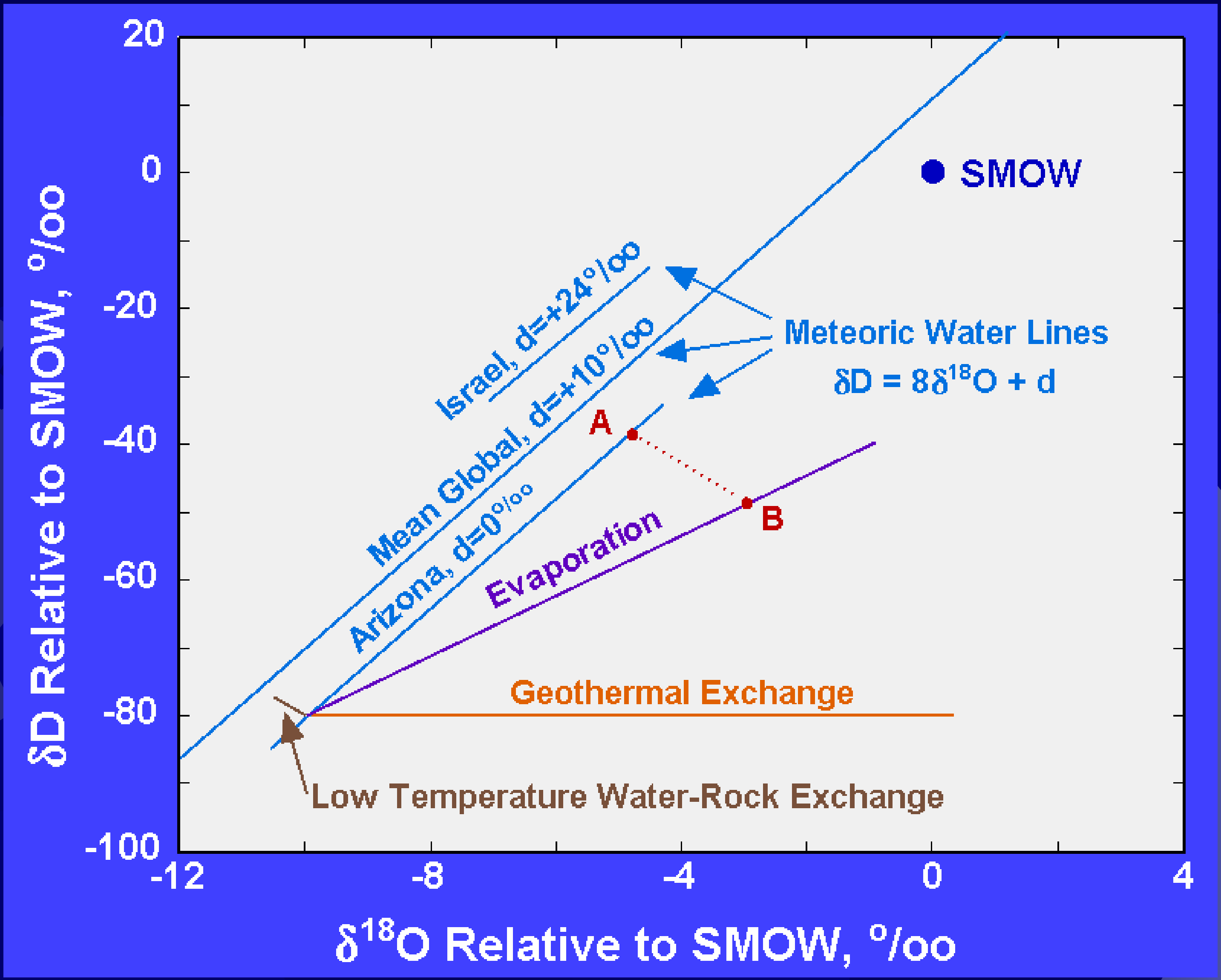
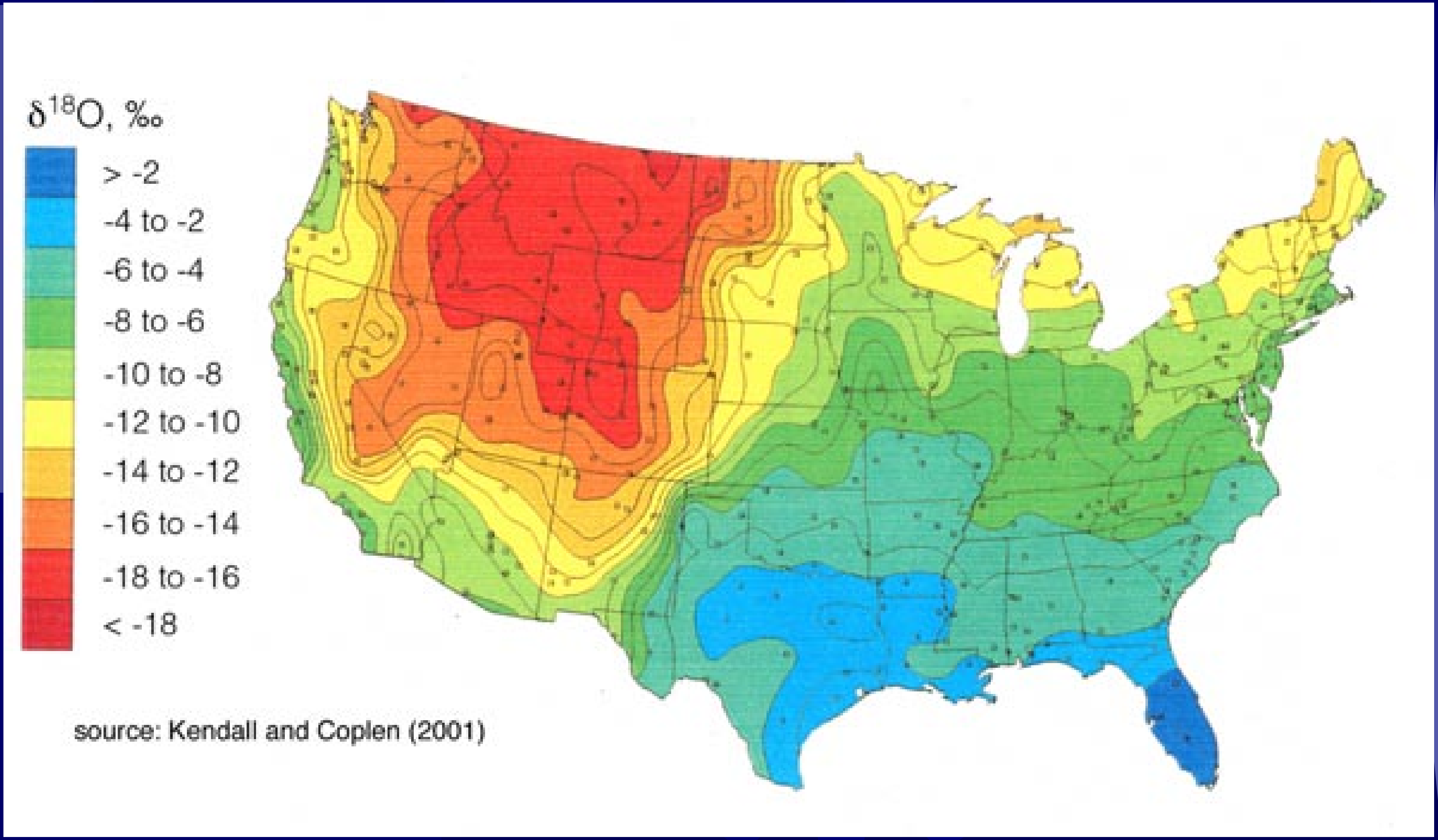


Plot of δD versus $\delta^{18}O$ illustrating the mean global meteoric water line and local meteoric water lines.

Isotopic Composition of Water in the USA



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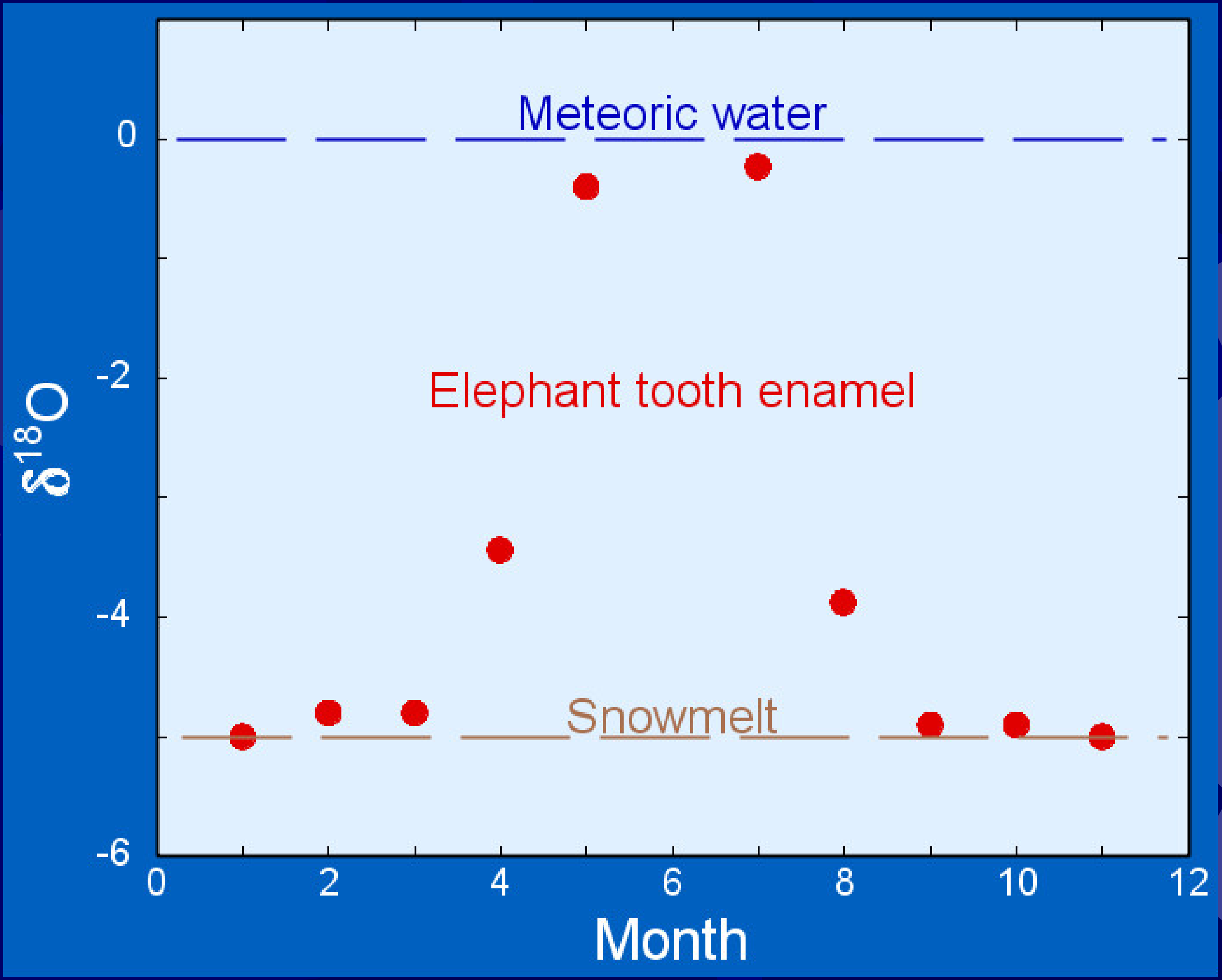
Laser used to analyze enamel layers of an elephant tooth, Amboseli National Park. Drinking water usually comes from snowmelt (Kilimanjaro) but during the rainy season meteoric water is the major source of drinking water.



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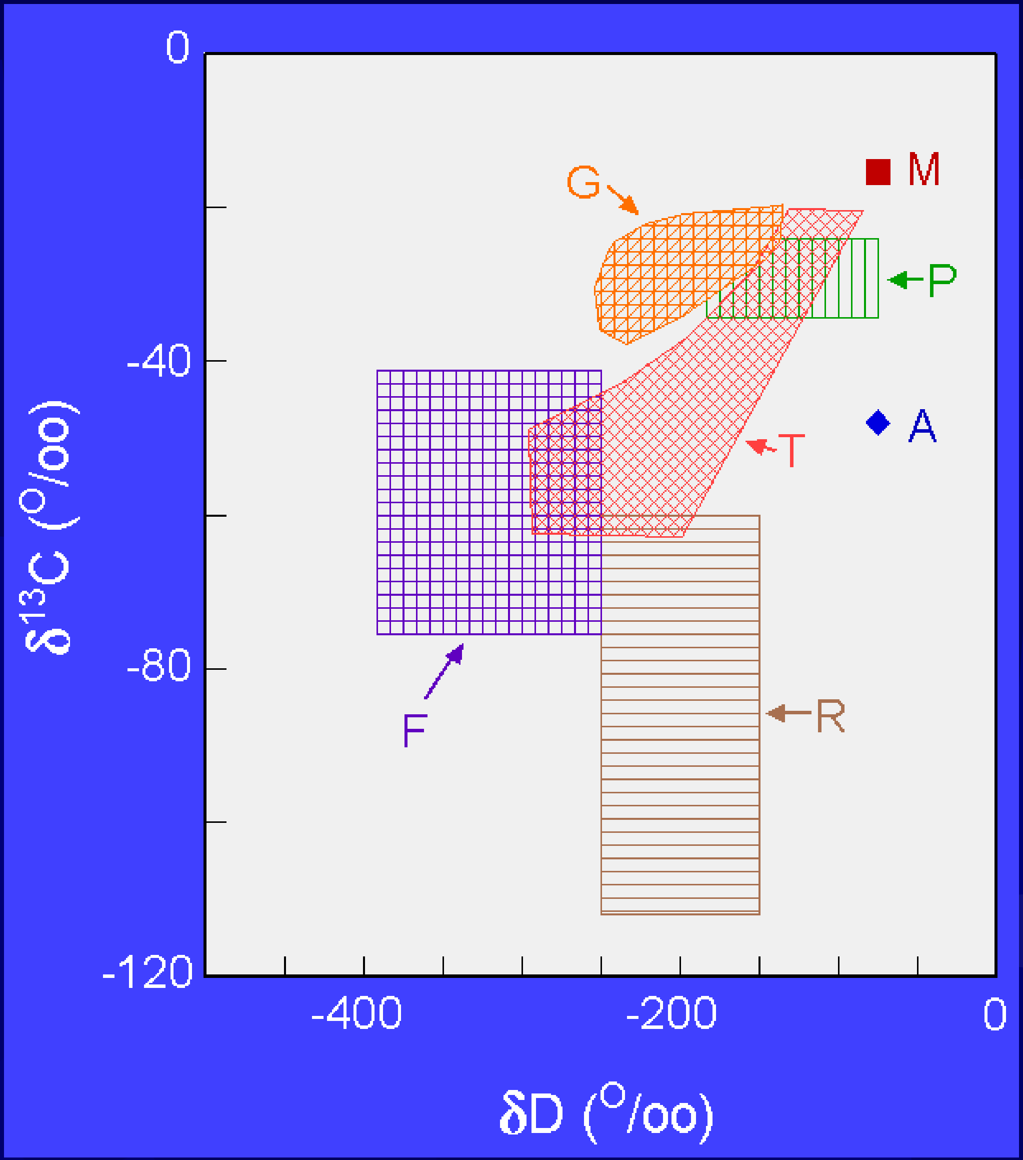

^{13}C and deuterium isotopic values for methane from various sources and reservoirs. P – petroleum, A – atmosphere, G – geothermal (pyrolitic from interaction with magmatic heat), T – thermogenic (from kerogen at elevated temperatures), F – acetate fermentation (bacterial), and R – CO_2 reduction (bacterial). After Schoell (1984, 1988).

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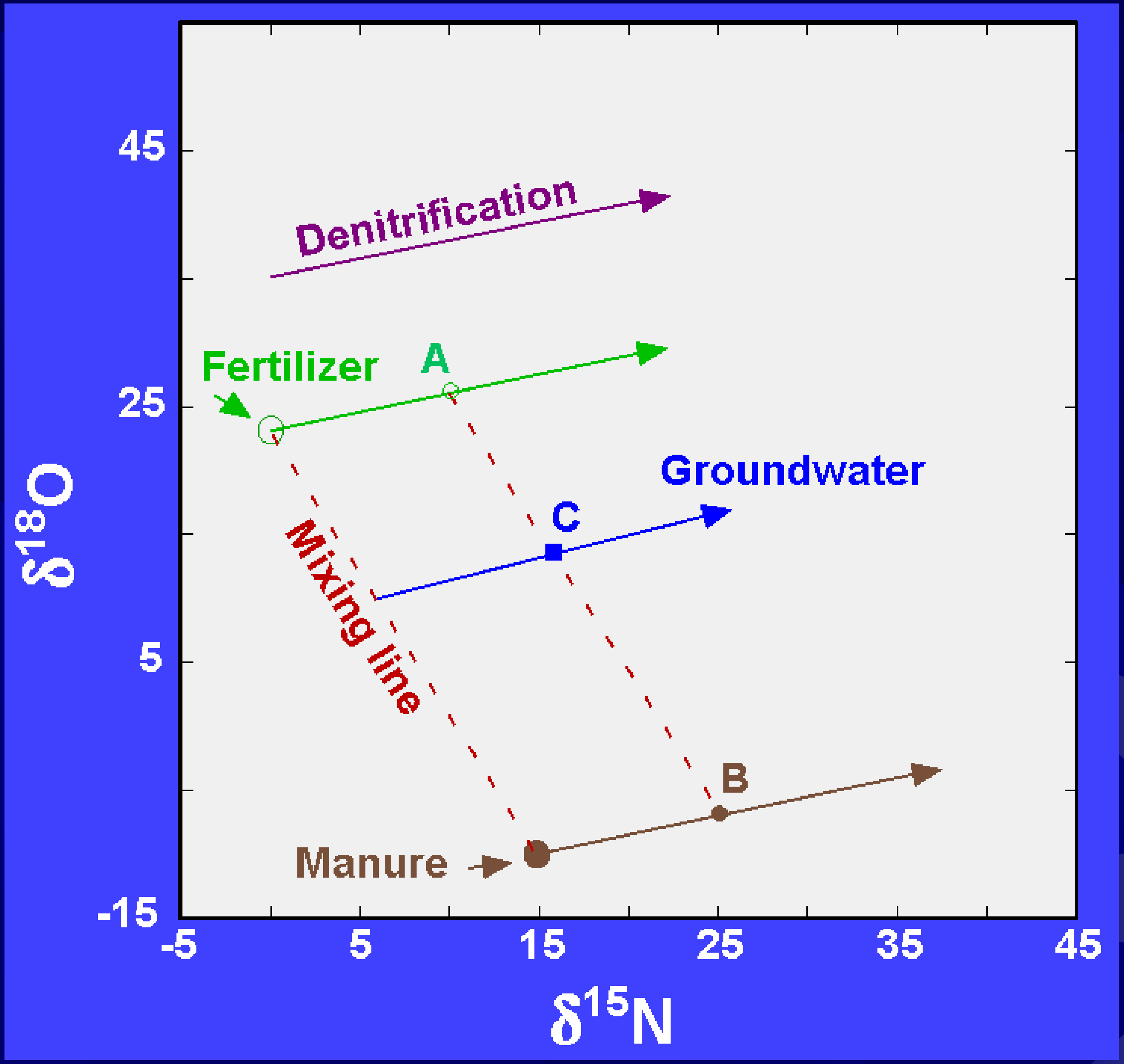

Determination of the relative importance of nitrate sources to a groundwater system. Two sources for nitrates are fertilizer and manure. Both are undergoing denitrification. A and B represent each source at a particular stage in the denitrification process. C is the isotopic composition of the nitrate in the groundwater due to simple mixing. In this example, approximately 60% of the nitrate is contributed by the fertilizer.

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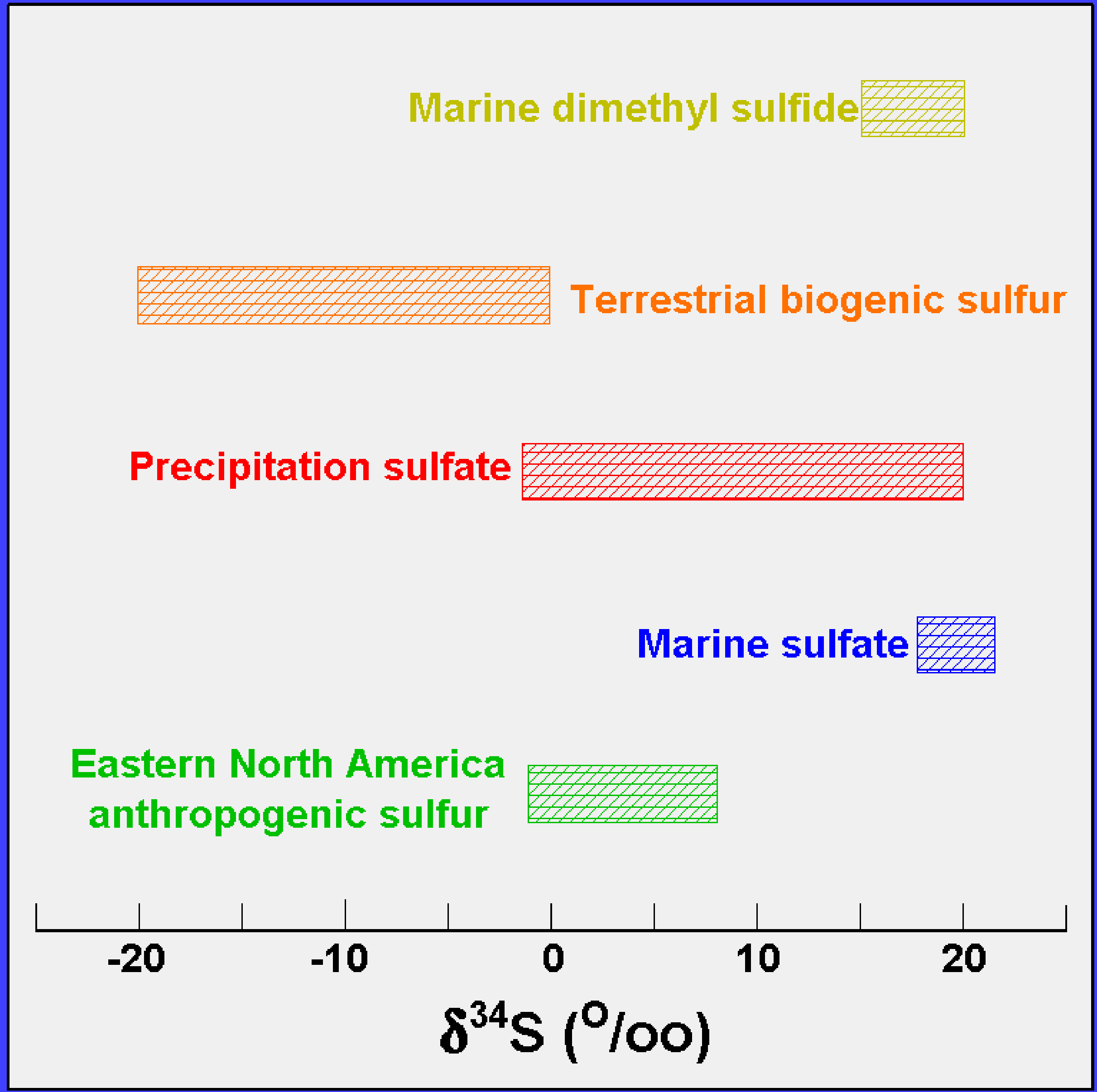

Range of $\delta^{34}S$ values for sulfur sources that contribute to atmospheric sulfur.

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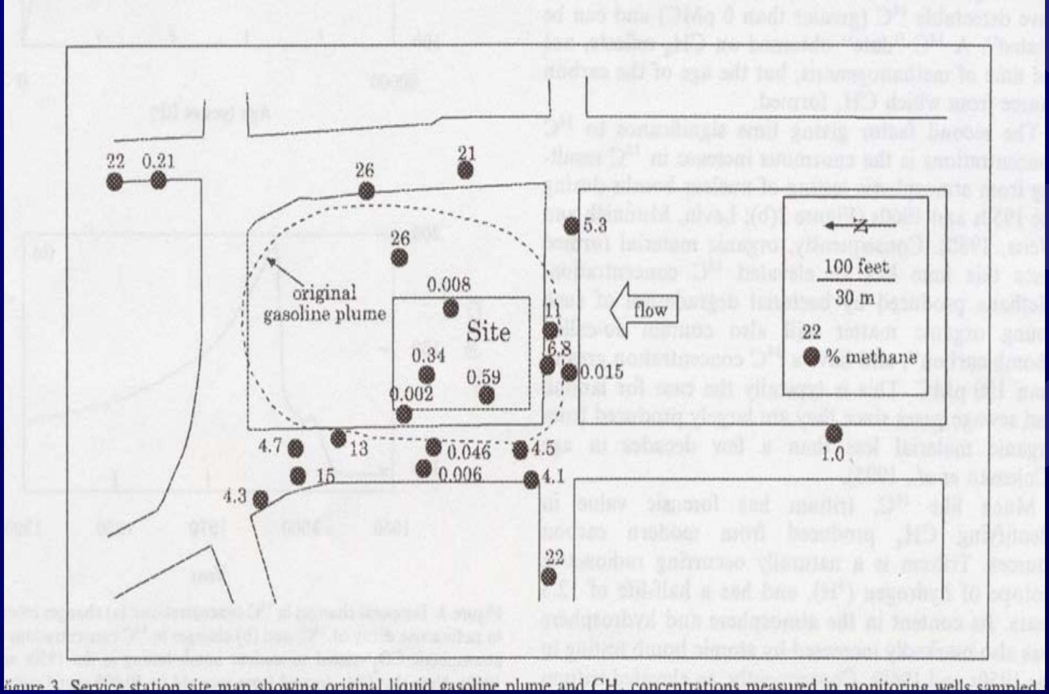
Forensic Stable Isotope Cases

- In 1980 there was a large (80,000gal) gasoline spill from a service station
- Unusual large amounts of methane off gases were found
- Borings showed the area was underlain by lake sediments and sawdust



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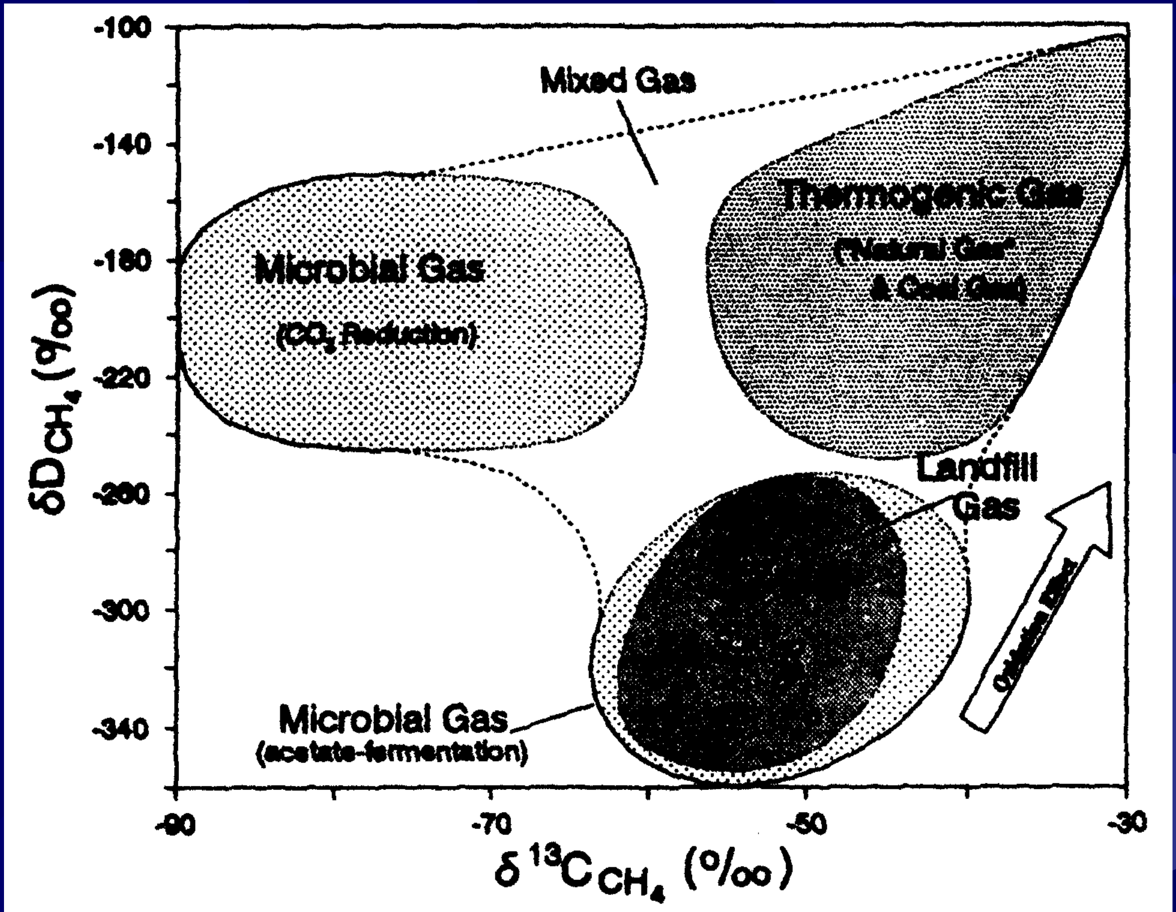
- δD (methane) plotted against $\delta 13C$ showed that the methane was coming from the sawdust and not the gasoline spill



δD versus $\delta^{13}C$ for methane from different sources. Landfill methane plots in the field of acetate-fermentation.

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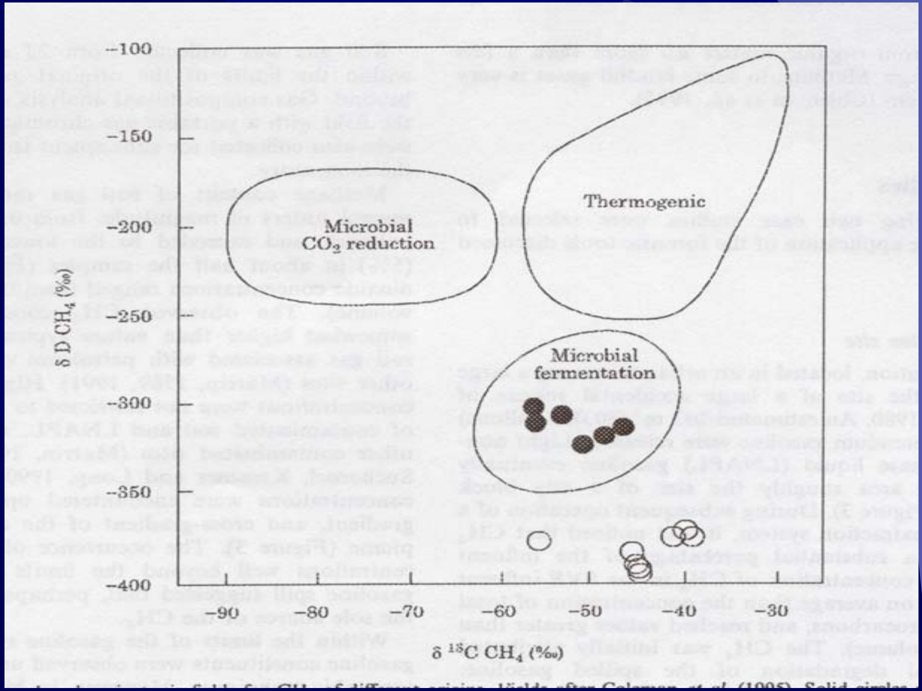
Forensic Stable Isotope Cases

- 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 δ13C (methane) showed that the methane was coming from microbial fermentation



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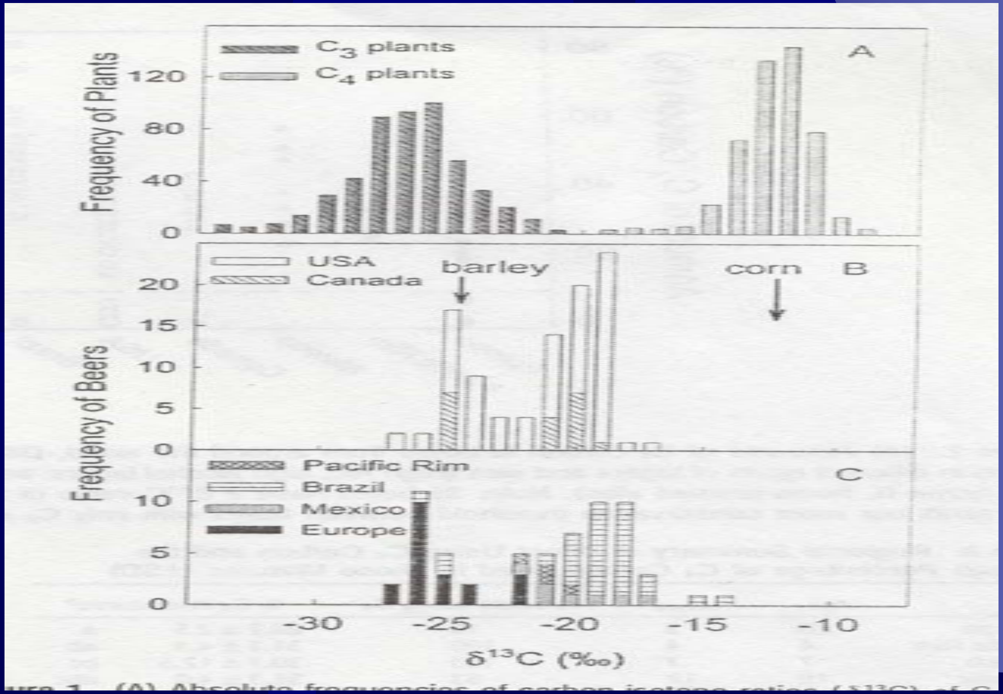
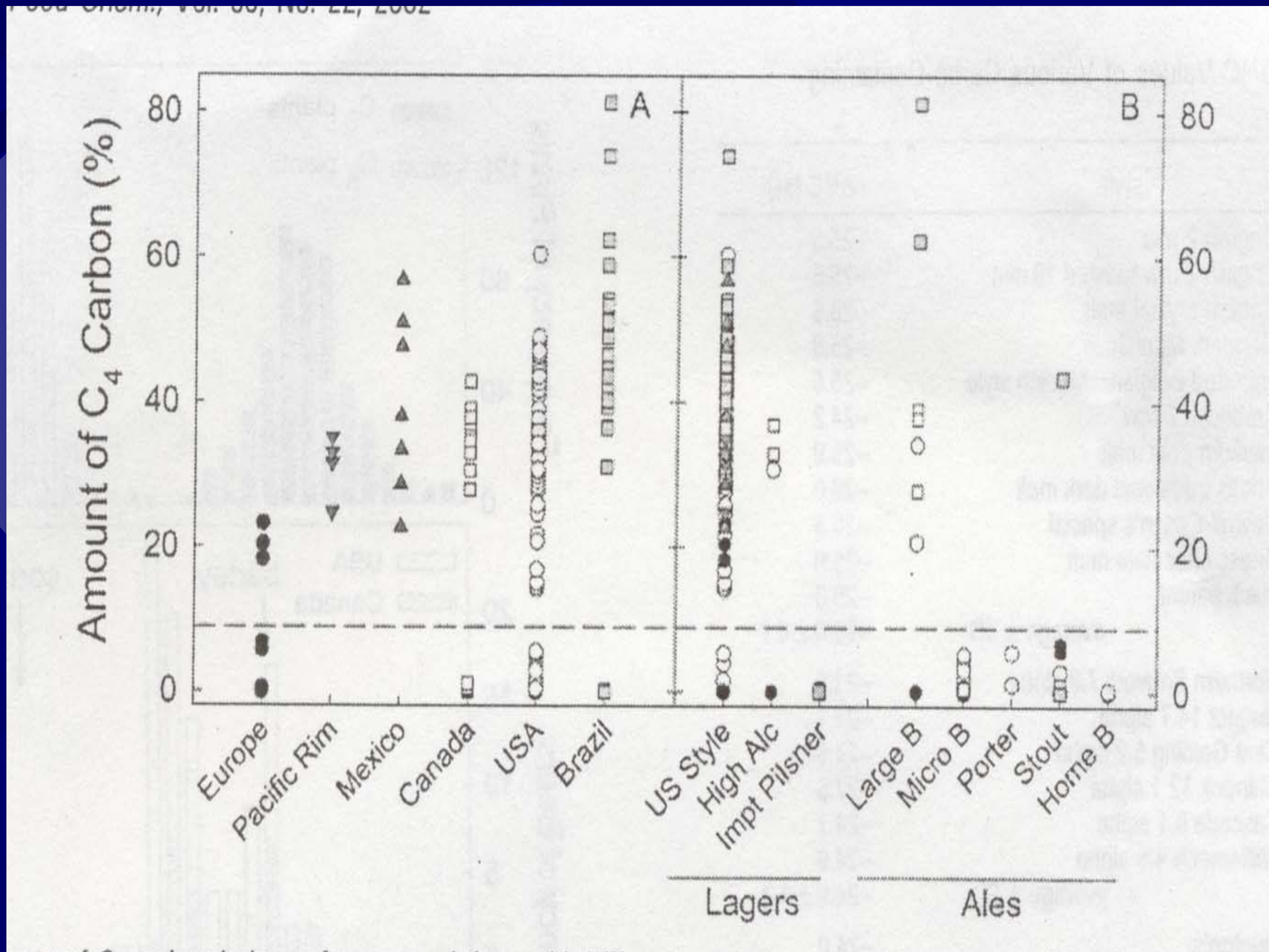
Forensic Stable Isotope Cases

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



The Delta C-13 value for the beer depends upon the relative amounts of C_3 and C_4 carbon



Forensic Stable Isotope Cases

Gasoline Isotopes

- Gasoline from leaky service station tanks is a frequent ground water contaminant
- 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

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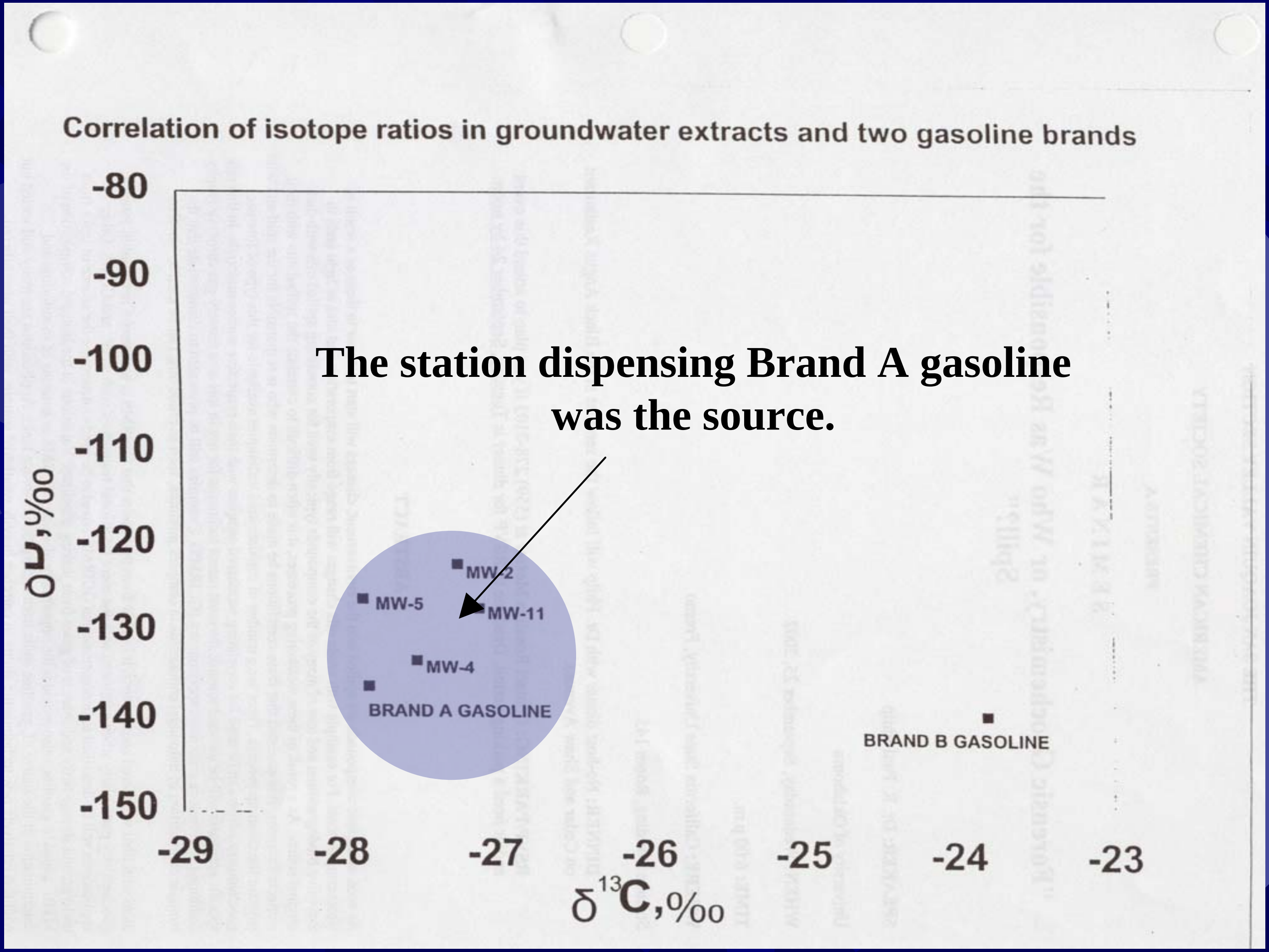
There were two gasoline stations up hill from the professor's house. Which one was the source of the gasoline leaking into the sump pump?



Source of oil found in oil spills

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Distinguish between Alaska and California crude oils on the basis of their C-13 content

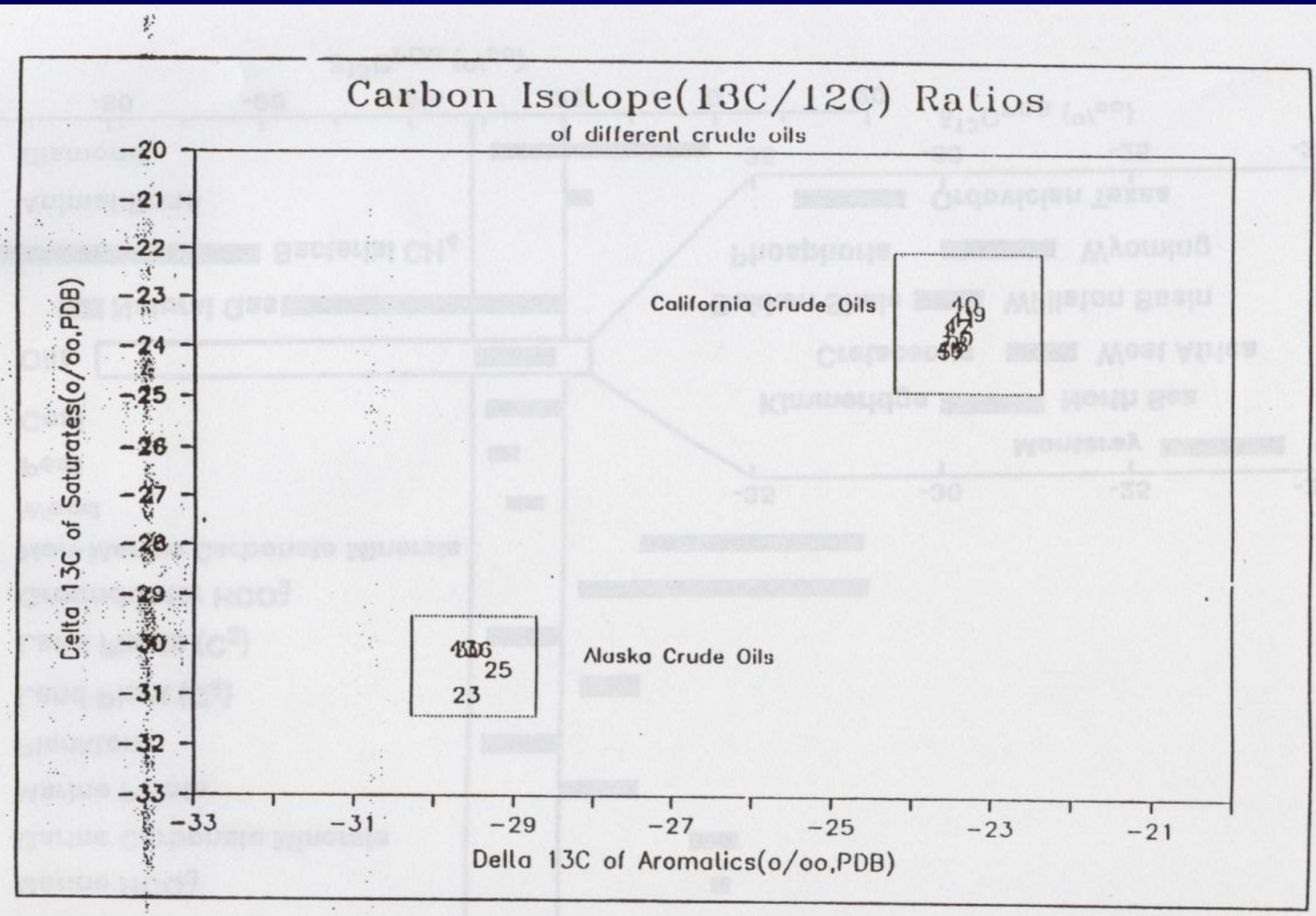

Figure 9.9: BP "American Trader" accident in Huntington Beach, California, February 7, 1990. Correlation among Alaska and California crude oils and beach tar balls on Southern California beaches, based on their carbon isotope ratios.

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

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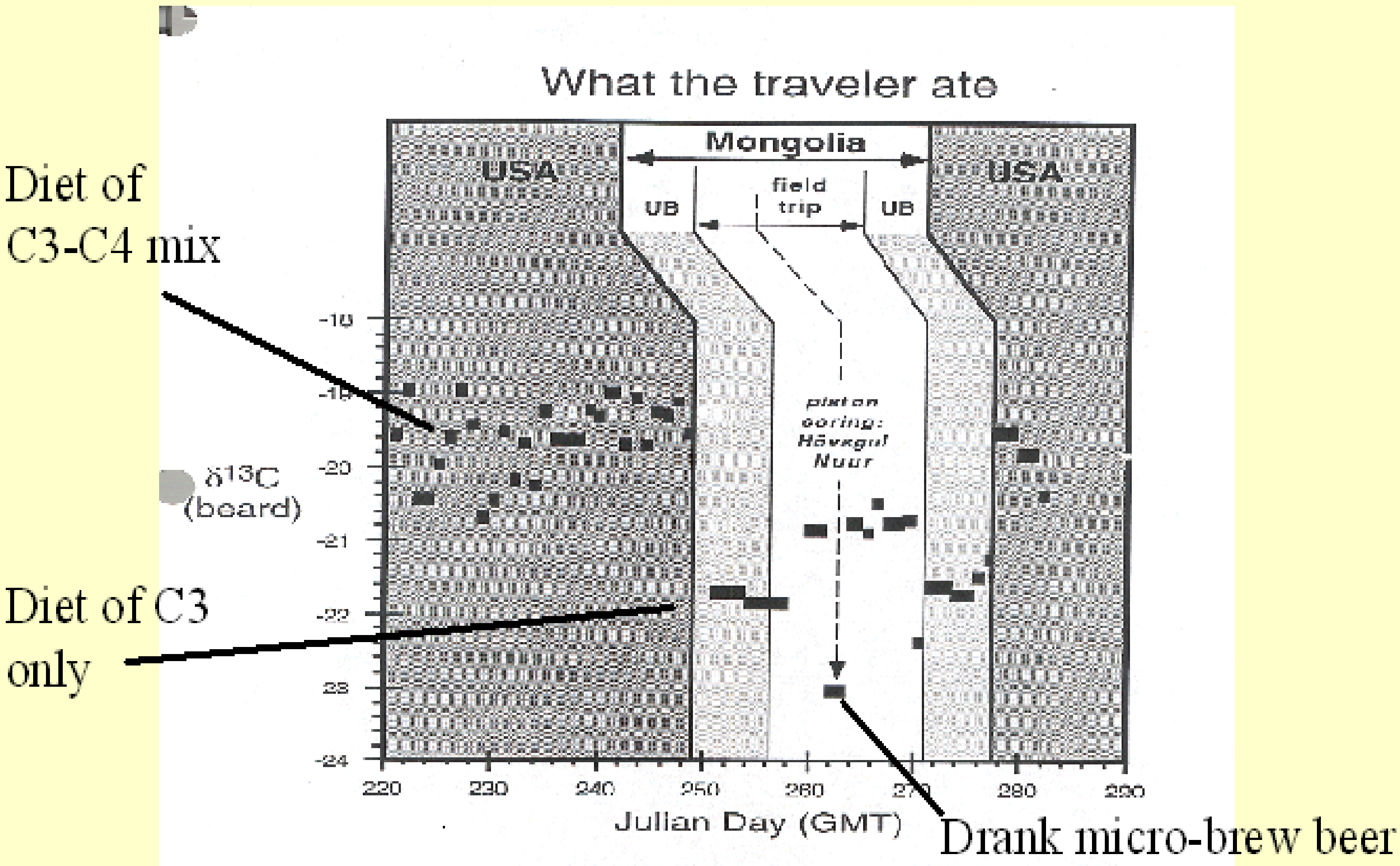
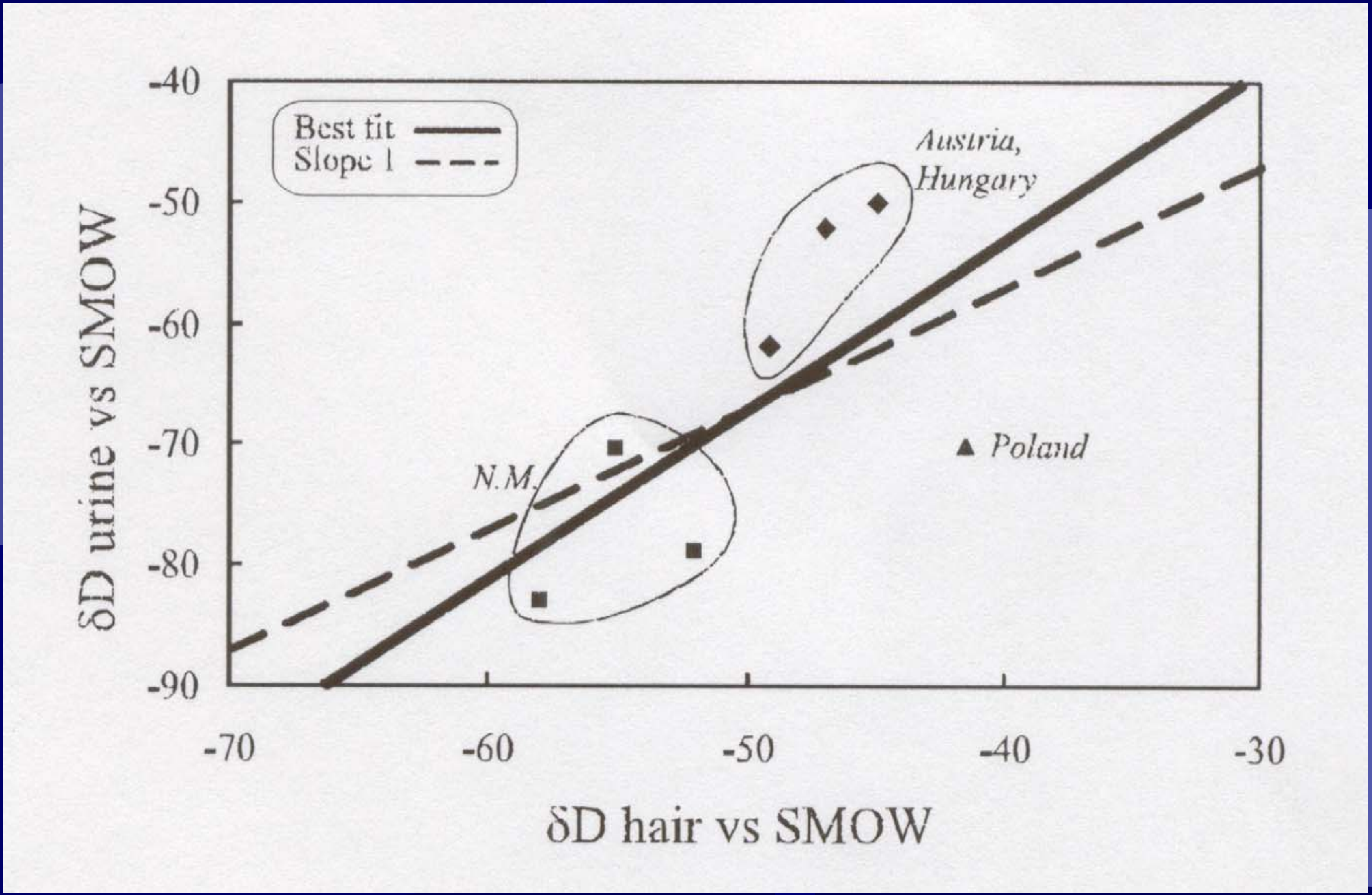
You are what you eat!




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

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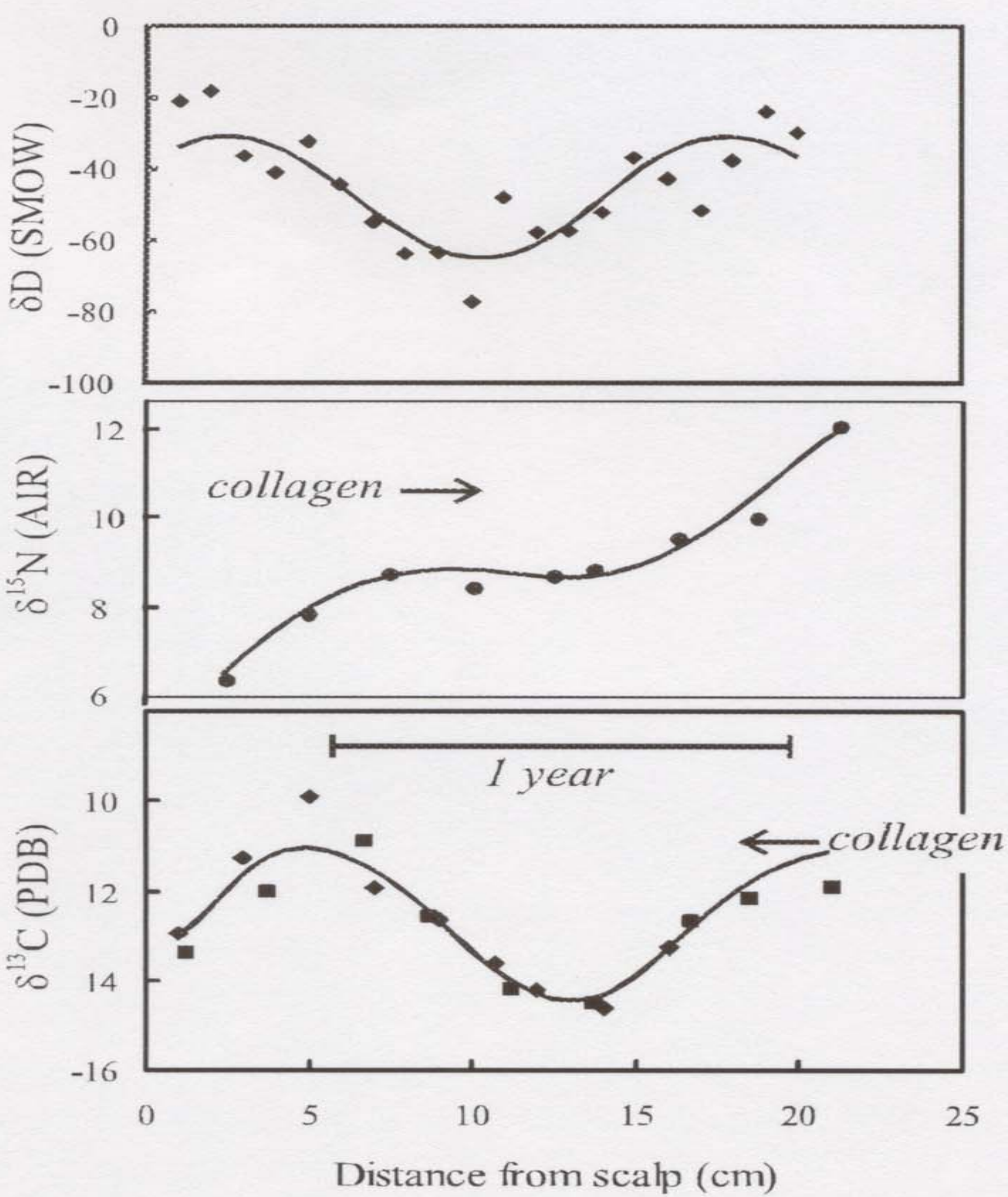
Isotopic values from the hair of an Inca mummy The sinusoidal variations are thought to be related to seasonal variations (more corn in summer, etc.)



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

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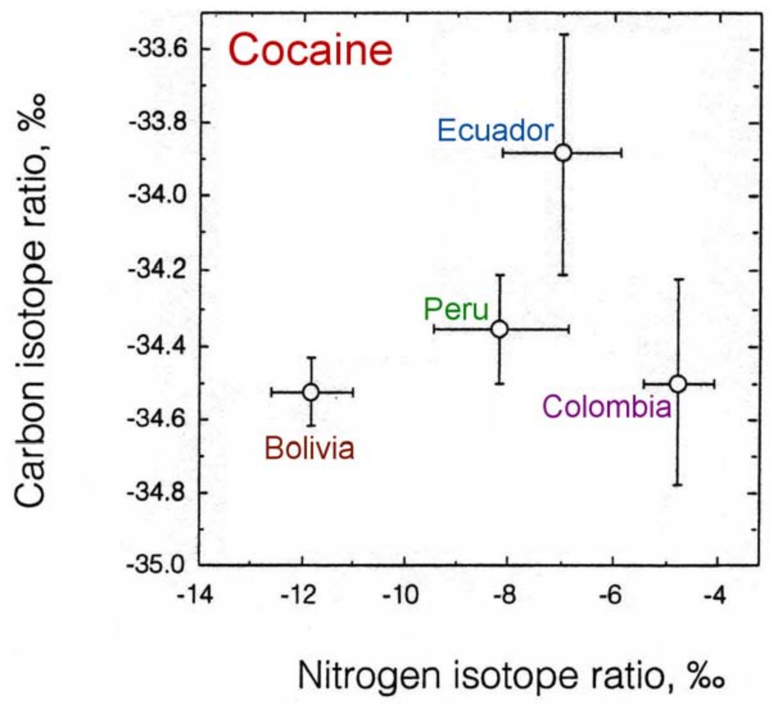
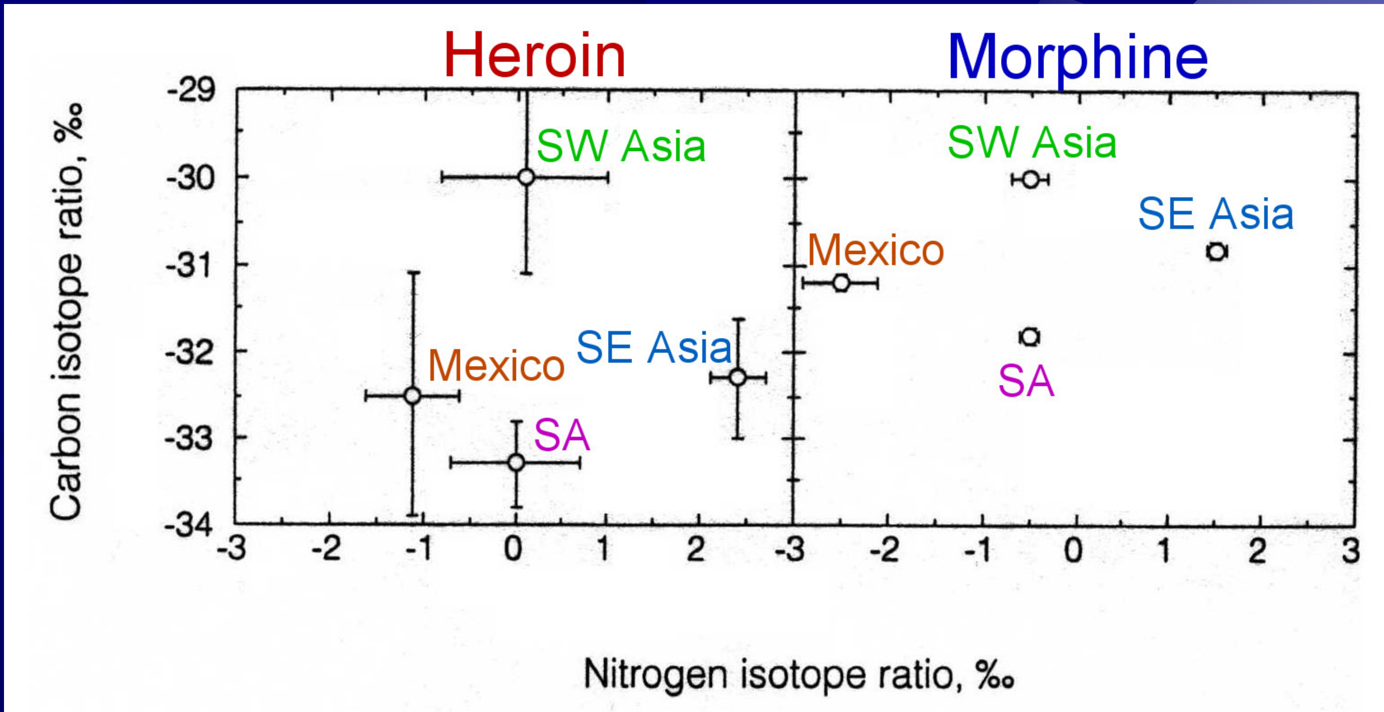
Forensic Geology

Stable isotopes can be used to identify the geo-location of heroin (and morphine) and cocaine.

Ehleringer et al. (1999)





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Concluding Comment

There are many more potential applications using both radioactive and stable isotopes. However, given cost and availability of instrumentation, C-14 dating and carbon, oxygen, and hydrogen stable isotope measurements are most appropriate for forensic investigations. There are a number of commercial laboratories that can provide these measurements if required.

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Acknowledgements

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Other tables and graphics are from:

Eby, G.N. (2004) Principles of Environmental Geochemistry. Thomson.