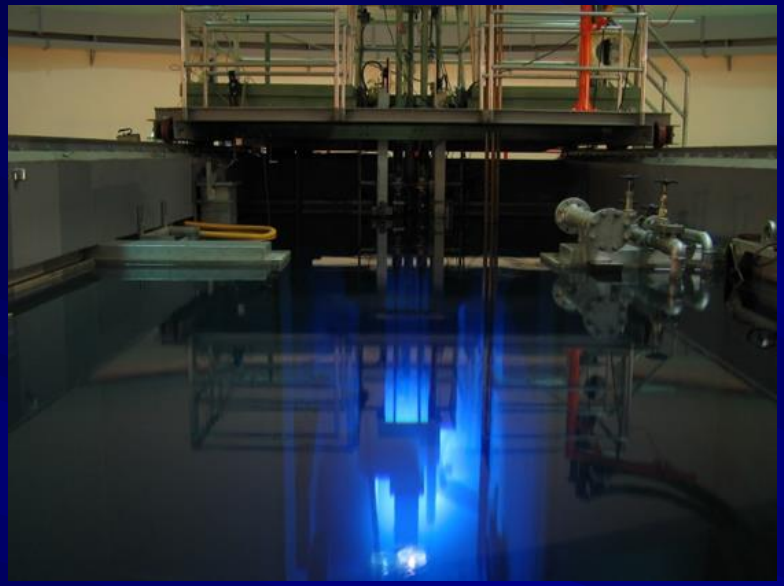
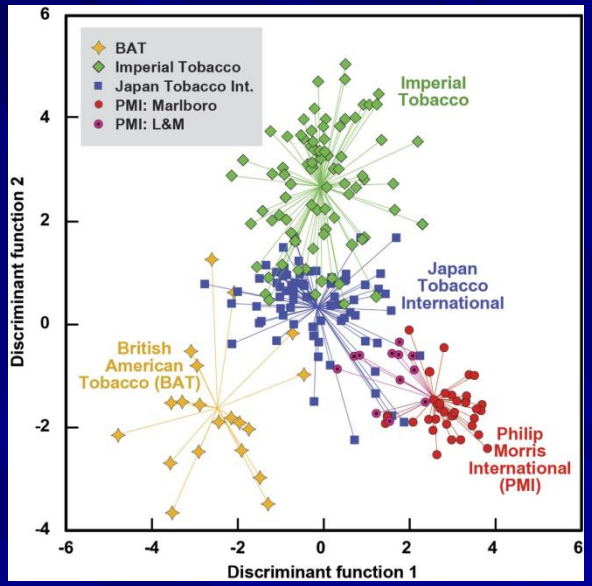
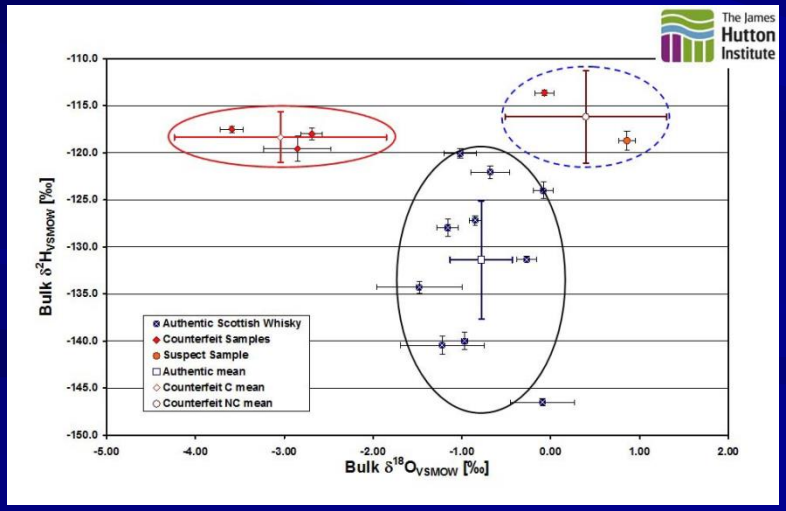
Forensic Geology
Trace Elements and Isotopes





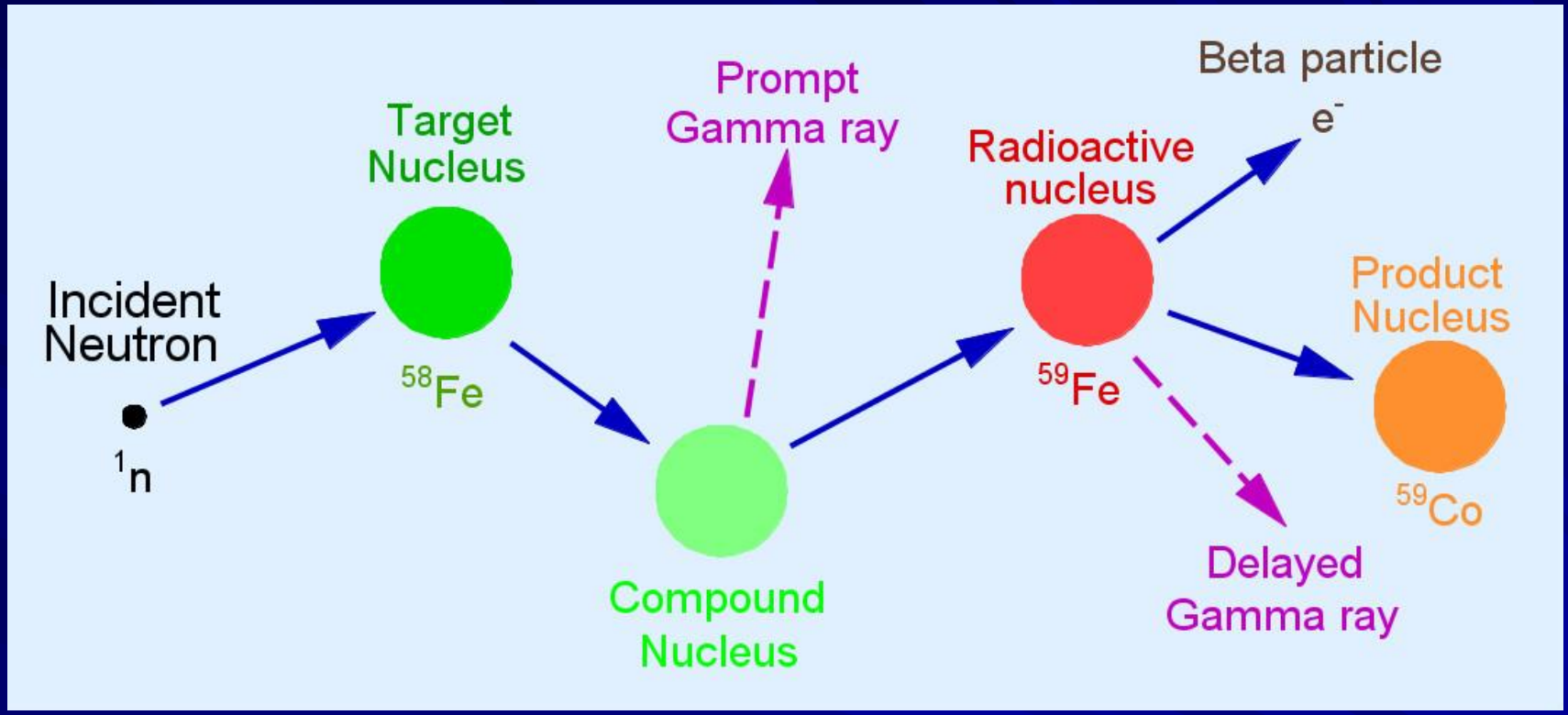


Trace Elements
Instrumental Neutron Activation Analysis (INAA) and X-ray Fluorescence (XRF) Analysis – Forensic Applications

Instrumental Neutron Activation Analysis Laboratory – University of Massachusetts, Lowell, USA

Philips PW2400 Sequential Wavelength Dispersive X-ray Fluorescence Spectrometer – Department of Geological Sciences, University of Canterbury, NZ

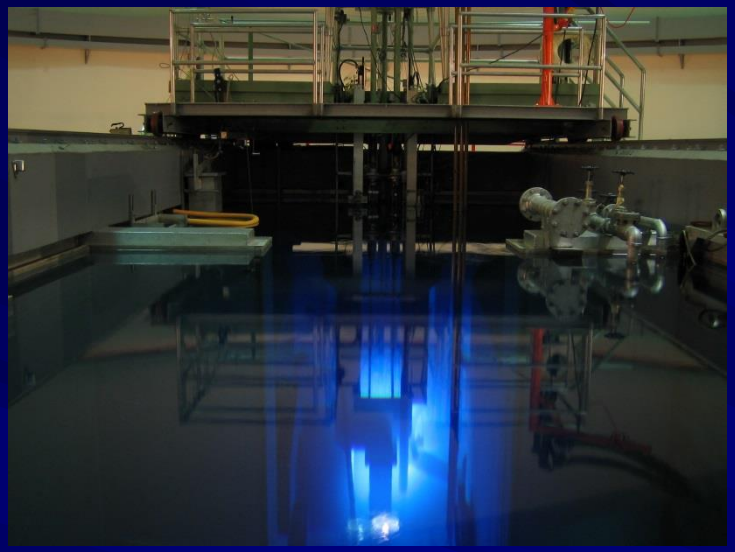
The n–gamma Reaction - The basic reaction for INAA



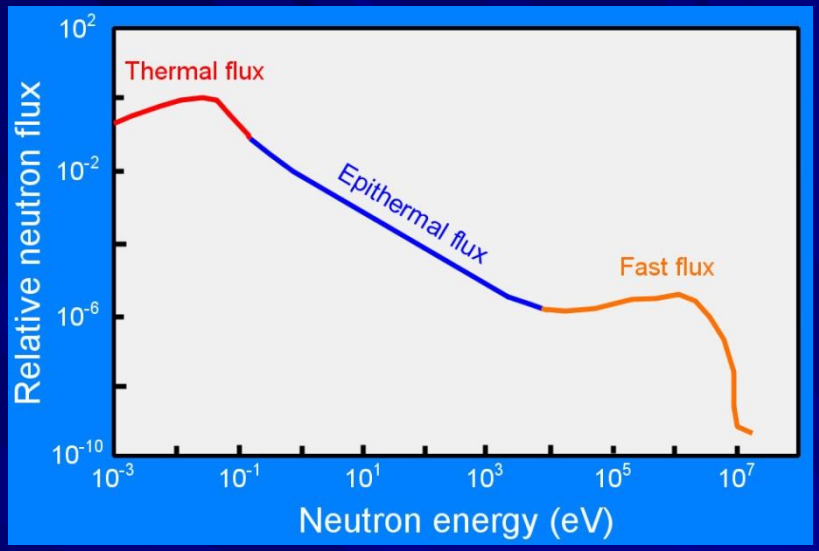
Example: $^{58}Fe + {}^{1}n \longrightarrow {}^{59}Fe + Beta^{-}$ + gamma rays

Gamma ray energies = 142.4, 1099.2, 1291.6 KeV

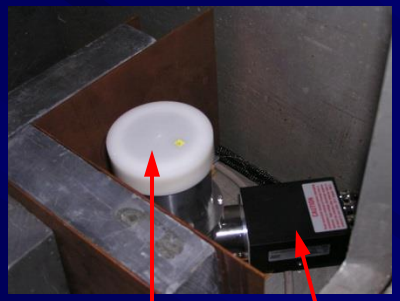
Different neutron energies are used for different types of experiments.



UML 1 Mw Research Reactor



The Neutron Source



Sample detector spacing

Activated sample

Detector

Preamplifier

Amplify signal

Amplifier

Shape signal

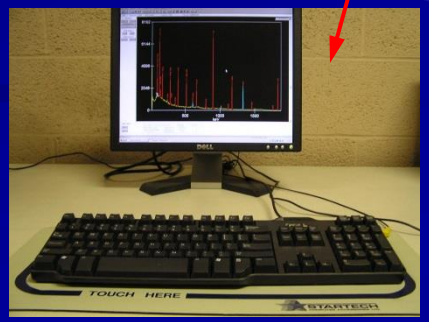
ADC

MCA

Output

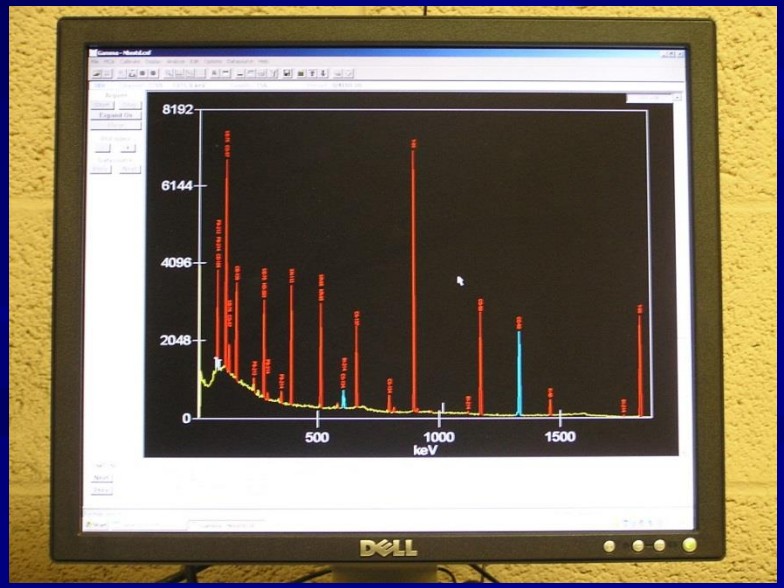
ADC = Analog - Digital Converter

MCA = MultiChannel Analyzer

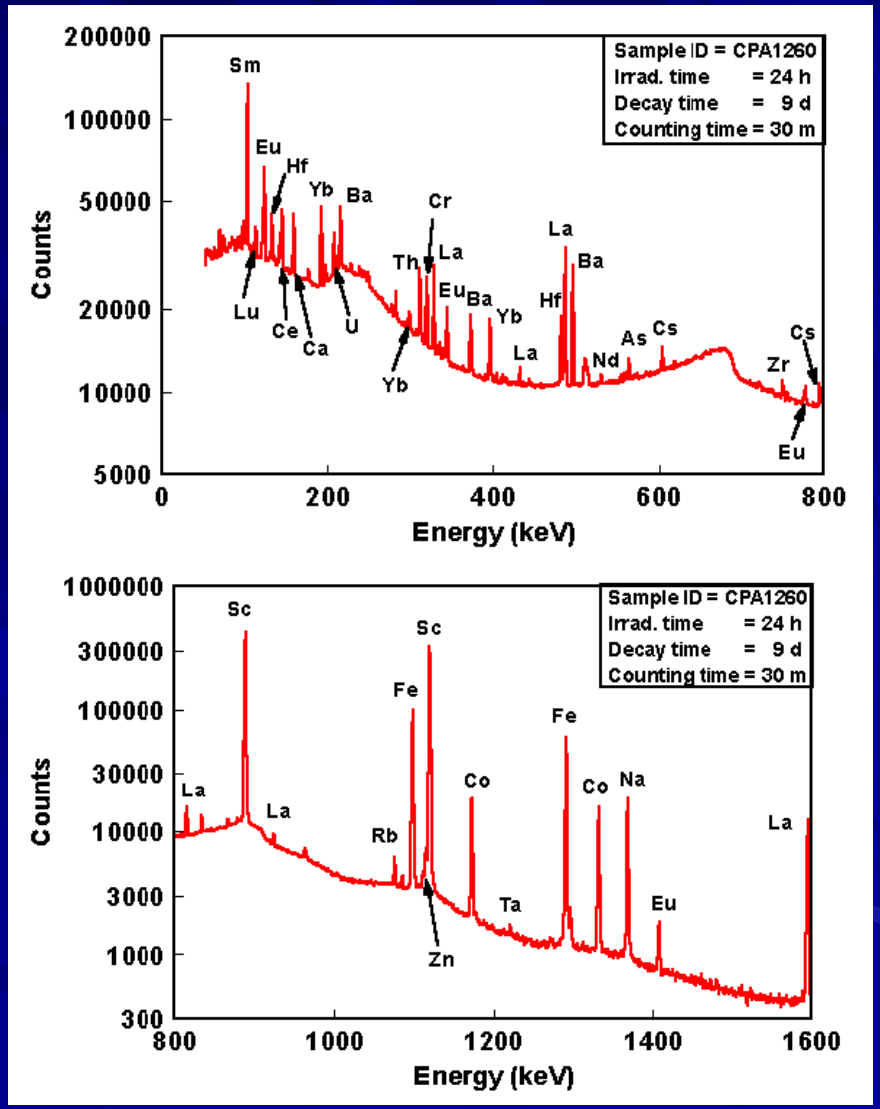


Data acquisition flow sheet

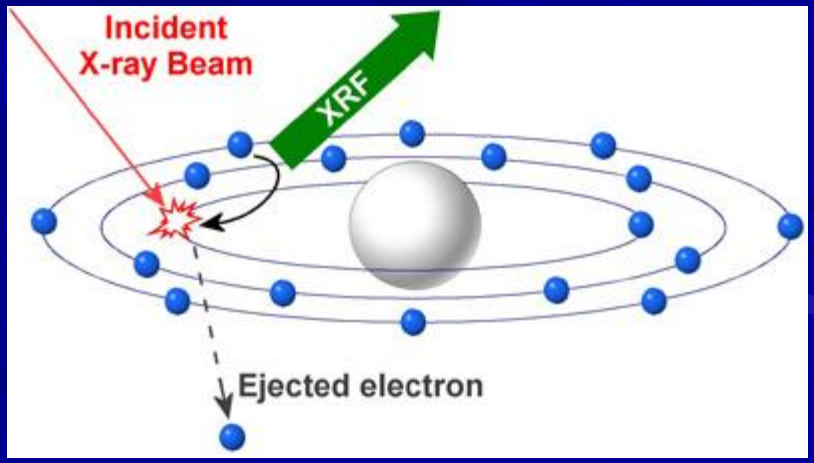
UML INAA Lab



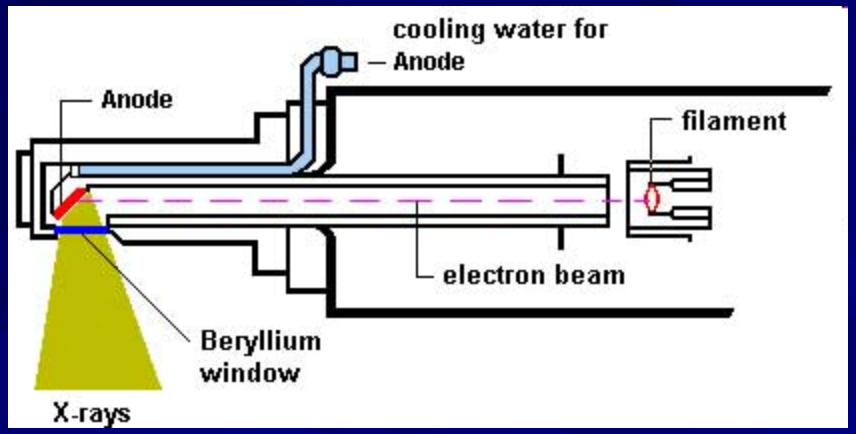
Gamma ray spectrum for a multi element sample



X-ray Fluorescence Analysis (XRF)

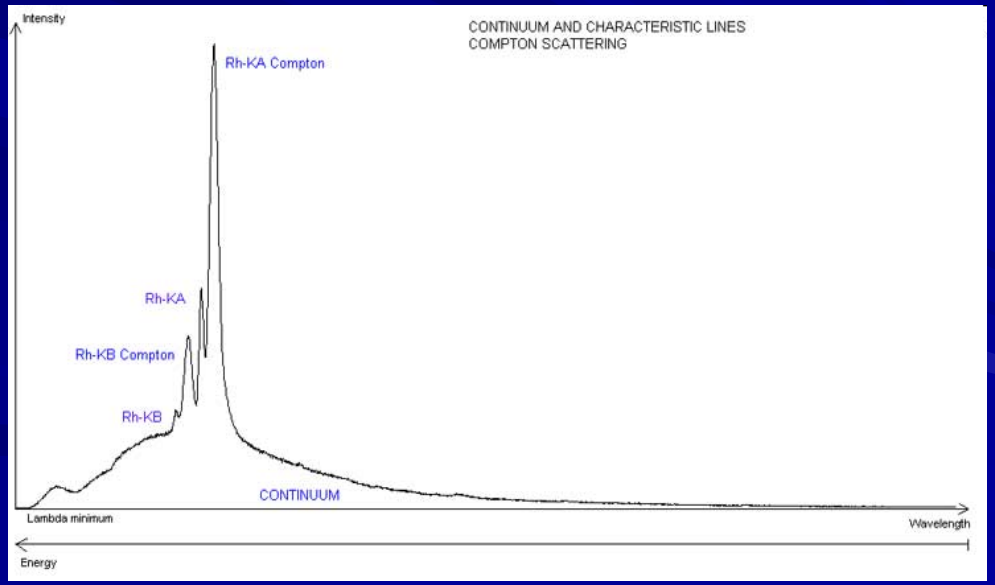


An electron beam impinges on an anode generating X-rays. Rhodium is frequently used for the anode, but other elements are used depending on the type of analysis.

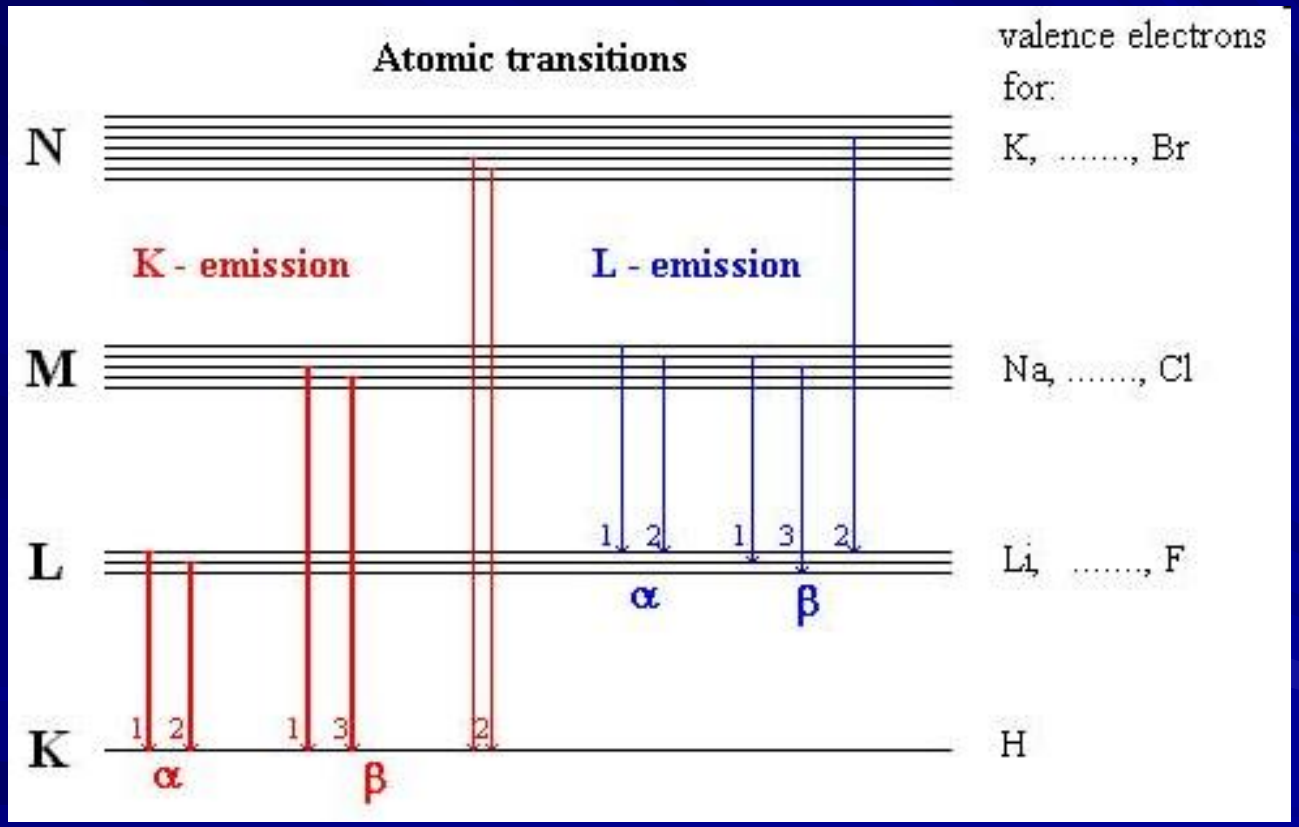


Design of an x-ray tube.

Emitted energy consists of the characteristic X-rays for the anode material plus the continuum.



X-rays from the tube impinge on a sample. The energy is transferred to the sample and electrons are removed from the innermost shells of the atoms. The energy of the resulting x-rays is used to identify the element(s) and the intensity of the emitted x-rays can be used to determine the abundance of the element(s).



Elements analyzed by combined INA-XRF Analysis

INA	XRF	INA	XRF	INA	XRF	INA	XRF	INA	XRF
Na	***Na***	***Cr***	Cr	Rb	***Rb***	***Nd***	Nd	***Ta***	
	Mg	Mn	***Mn***	Sr	***Sr***	***Sm***		***W***	
	Al	***Fe***	***Fe***		***Y***	***Eu***		***Au***	
	Si	***Co***	Co	Zr	***Zr***	***Gd***			***Pb***
	P	***Ni***	***Ni***		***Nb***	***Tb***		***Th***	Th
K	***K***		***Cu***	***Sb***		***Ho***		***U***	
	Ca	***Zn***	***Zn***	***Cs***		***Tm***			
Sc			***Ge***	***Ba***	***Ba***	***Yb***			
	Ti	***As***		***La***	La	***Lu***			
	V	***Se***		***Ce***	Ce	***Hf***			

***Bold Italics – preferred method**

Forensics – Source of the Maple Syrup

Collecting sap the modern way. Plastic barrels and polyethylene tubing.

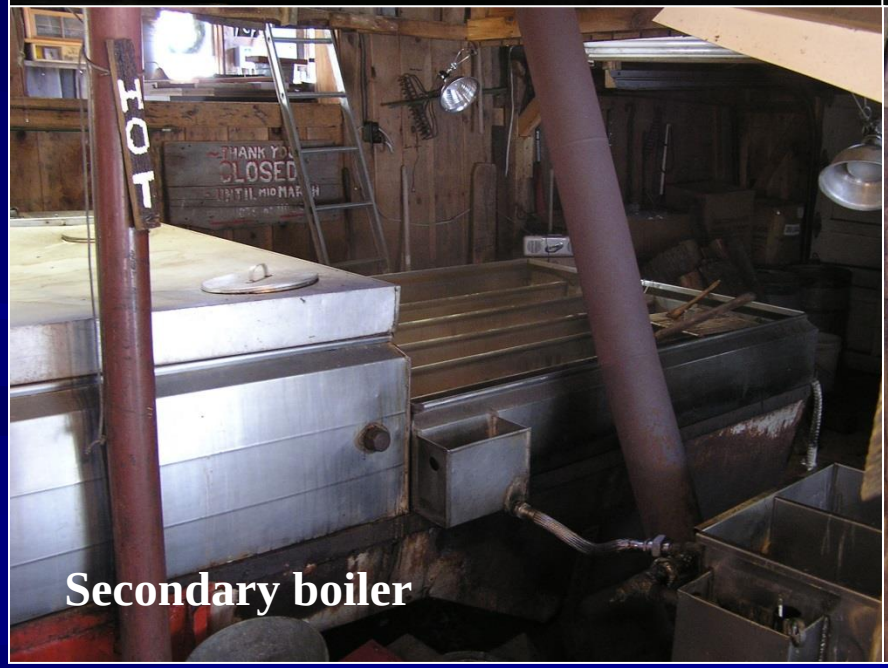
Transferring sap to the sugar house

Sap holding vats

Boiling down the sap


Syrup production line

Main boiler



Secondary boiler


Finish boiler

Final step – filtering the product

During the production of maple syrup there are numerous opportunities for trace constituents to be added to the product.

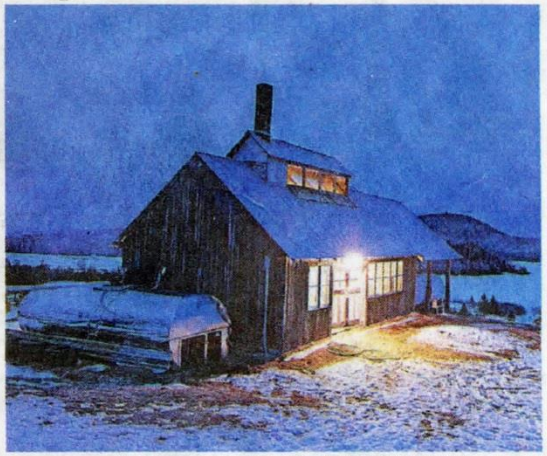
- In the original sap from trace metals in the soil
- During transport
- During boiling of the sap – metals from the evaporators
- During the final filtration

These added constituents can be used to "fingerprint" maple syrups from different sources.

Concentrations (ppm) and ratios of trace metals in Maple Syrup

	Newton	Winsor	Parker A	Parker B	W MA	VT	Quebec
Sc	0.010	0.009	0.004	0.008	0.006	0.002	0.030
Cr	0.67	0.71	0.83	nd	0.87	0.136	1.67
Co	0.094	0.064	0.073	0.046	0.057	0.078	0.119
Zn	9.3	13.1	50.6	19.4	76.3	5.5	19.4
Rb	7.5	3.1	10.2	5.7	15.7	7.5	9.0
Sr	28.6	13.7	10.7	nd	8.3	10.5	17.5
As	0.029	0.014	0.022	nd	0.010	0.016	0.016
Sb	0.018	0.010	0.034	0.004	0.010	0.002	0.009
Se	ppb	nd	nd	nd	nd	nd	8.72
Zn/Cr	13.9	18.5	61	nd	88	40	11.6
Rb/Cs	642	363	433	nd	175	356	419
Ba/Sr	0.59	0.18	0.76	nd	1.29	2.26	0.37
As/Sb	1.59	1.50	0.64	nd	2.24	8	1.91

Tapping into a richly flowing resource in Vt.



PHOTOS BY CALEB KENNA FOR THE BOSTON GLOBE

The sugarhouse for Shadow Lake Maples in Barton, Vt., a syrup operation run by Adam Parke (right) and Todd Scelza.

By Colin Nickerson
GLOBE CORRESPONDENT

GLOVER, Vt. — Cold weather meant a slow start to sap season. And when the taps finally began flowing this month, things only got stickier for a fledgling two-man syrup operation here on three steep knolls by Shadow Lake.

Vacuum pumps hurrying the sap along miles of tubing failed. The new high-tech $28,000 reverse osmosis rig clogged on the initial feed of raw sap. Then, an old tractor skittered into the big red tanker truck.

"Otherwise, it's going great," said Adam Parke, who with business partner Todd Scelza has sunk heart, soul, and nearly a quarter-million dollars — much borrowed from the bank — into the enterprise, called Shadow Lake Maples.

Parke's cheer was genuine. Across the northland, the maple syrup industry is booming as never before. Production has doubled over the past decade to about 880,000 gallons per year, according to federal figures, thanks to swelling domestic and international demand and technological improvements that have boosted yields.

The sugary elixir has even become the target of organized crime.

A 2012 multimillion dollar heist of syrup in Quebec — the French-speaking Canadian province that produces 75 percent of all maple goodies — has

MAPLE SYRUP, Page A7

▶MAPLE SYRUP

Continued from Page A1

played out like an improbable Hollywood caper. Just last month, some of the sticky swag showed up in New England.

More fearsome than thieves to many sugar makers, however, are forecasts of global warming. The industry depends on a fairly predictable stretch of frigid nights and warm days from late February through March – any prolonged break in that pattern could wreak havoc.

Despite such worries, Parke and Scelza — self-starters in a hard-bitten region called the Northeast Kingdom — are betting big they can turn a sweet dream into success.

"We've been talking and plotting for a year or so," said Scelza, 44. "Now we're finally at the doing part."

The two have toiled for months to whip 400 acres of steep, snowbound sugar bush — groomed maple forest — into shape. They've drilled 12,000 taps, hung 80 miles of plastic tubing, and man-handled hulking 4,650-gallon sap collection tanks into place.

"It's a long way from sap drizzling into oldtime pails," Scelza said as he squinted into bright sunlight shafting through stands of graceful 40-year-old sugar maples that — tapped with care — should be gushing pay sap for another 100 years or more. "But it's the same tradition. Vermonters make syrup. We also make profits where you wouldn't expect much. Let's hope we uphold both traditions."

It's a dauntingly rough road leading to smooth syrup.

But stubbornness is first nature to both Scelza — who also runs an excavating business out of Albany, Vt. — and Parke, a seasoned veteran of agriculture who has raised everything from cows to Christmas trees on a high ridge farm in Barton, Vt.

The equipment glitches that accompanied the initial sap flow were briskly sorted out. Spare parts were fetched. Short-circuits were re-circuited. Cursing was kept to a soft minimum.

Forty-eight hours later, the sap was boiling in gleaming oil-fired evaporator pans at Parke's sugarhouse. Steam billowed so thickly that Parke, Scelza, and helper Ozzie Henchel were invisible to each other while laboring only a few yards apart. The sap, which naturally contains about 2 percent sucrose, was transforming fast into the rich amber 66.9-percent sugar solution famed as Vermont Pure.

They made 445 gallons of syrup the first three days. They are still cooking hard."I think we've got the hang of it," said Parke, 56, eyes droopy with fatigue. He'd slept only in two- or three-hour stretches.

In Vermont, one of every four trees is a maple, mainly sugar maple, which holds the sweetest sap. Those trees, plus a unique climate, are why commercial sugar making is confined to the "syrup belt" stretching from Wisconsin to Maine, plus four Canadian provinces.

"It's only in this swath that sap season runs long enough for a money crop," said Jacques Couture, 62, chairman of the Vermont Maple Sugar Makers Association.

CALEB KENNA FOR THE BOSTON GLOBE

Tim Menard (foreground) helped Todd Scelza and Adam Parke run a hose for sap from collecting tanks to a truck bound for the company's sugarhouse in Barton, Vt.

The past decade has seen banner years and bad ones. Overall, however, the industry — once barely more than a cottage craft — is in expansion mode.

"Maple is the rare sector of [Vermont] agriculture that's both increasing production and drawing in new blood," said Henry Marckres, state maple specialist for the Vermont Agency of Agriculture. "It's an all-natural product that suits the tastes of the times."

Timothy Perkins,biologist and director of the University of Vermont's Proctor Maple Research Center, said new technology means that producers can count on a modestly good yield even in so-called bad years, when weather hurts the sap run. "That, coupled with rising demand, means there's more room for boom, less chance for bust," he said.

Vermont is the undisputed king of maple on this side of the border. But it seems a puny princeling when ranked against Quebec's imperial sap flow, which in good years yields at least 7.5 million gallons of syrup or more. Quebec's vast stocked hoards — known as "strategic maple reserves" — give it power to control not only the quantity of precious *sirop d'erable* available to world markets, but also to stabilize prices.

In 2011, a bumper year, Vermont's production was valued at $39.9 million, according to the US Department of Agriculture. In Quebec, the industry is worth more than $300 million in so-so years.

That holds irresistible allure for bad guys.

Last year, thieves targeted a brick warehouse off the Trans-Canadian Highway northeast of Montreal. Their haul: $18 million worth of syrup.

The 545,000 gallons of swag — packed in baby-blue steel drums, each worth 13 times more than the equivalent in crude oil — was spirited away over weeks or months, say Canadian law enforcement officials. It apparently was an inside job.

The barrels were replaced with identical containers filled with water. The loss was discovered accidentally on July 30 by an auditor. Swarms of Canadian and US investigators were soon hot on the trail.

The probe led to criminal charges against 18 alleged "barrel rollers" in Canada. It also led to St. Johnsbury, Vt., where a portion of the booty — equivalent to 12 tanker truckloads — was discovered at Maple Grove Farms, an iconic syrup and maple candy maker whose origins date to 1915. No one at the company has been charged.

In a statement, Maple Grove said it purchased the syrup in good faith with no reason to believe it may have been stolen.

Meanwhile, maple makers in New England — where syrup still possesses a homely aura — are getting used to the notion of their product as an international commodity.

Pauline Couture, who with husband Jacques runs Couture's Maple Shop in Westfield, Vt., was packing an Internet order the other day for shipment to Kuala Lumpur.

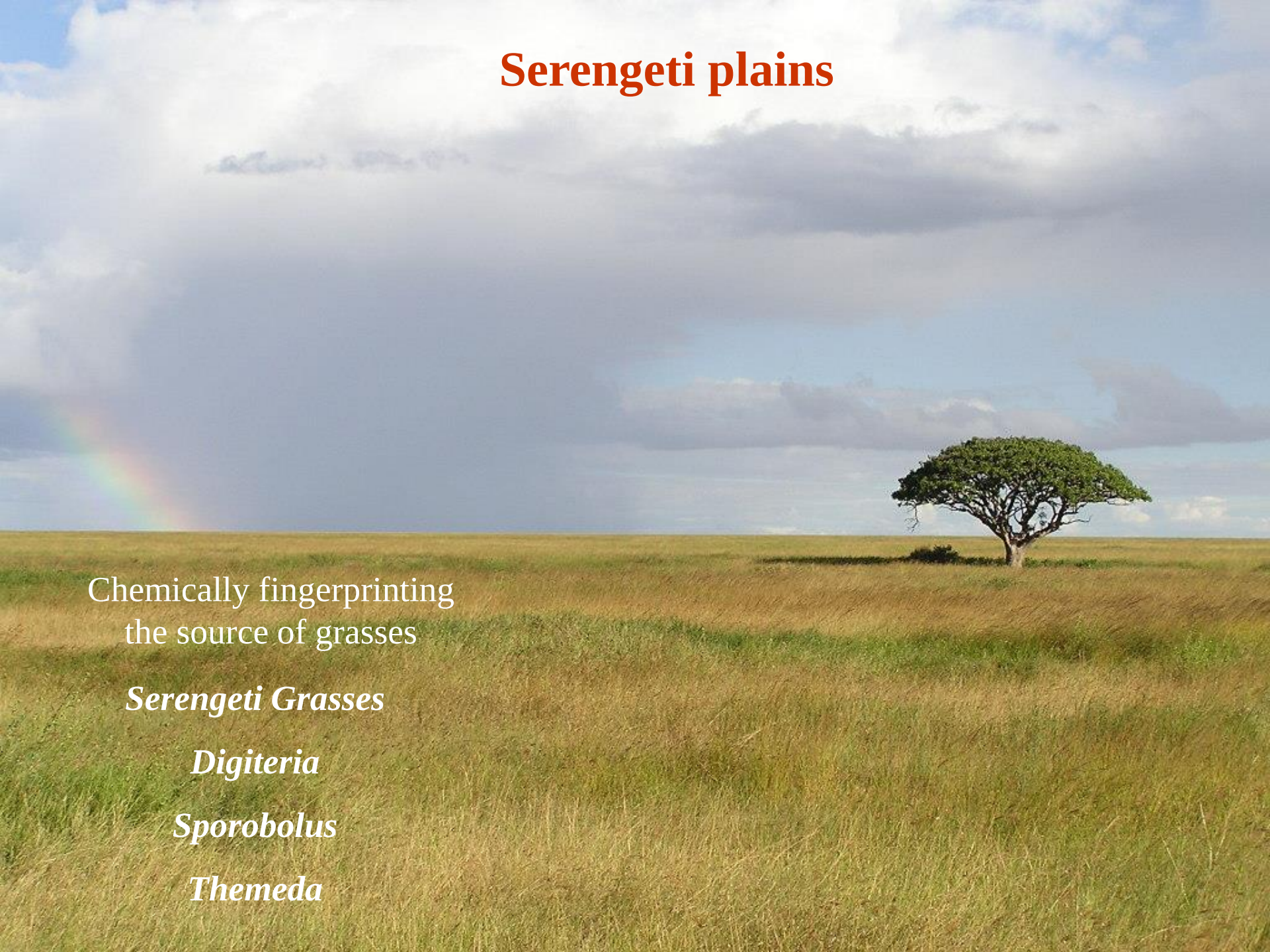
"I can't tell you if Malaysians eat pancakes, but they sure like our syrup," Couture said. "When we started [in 1972], we were selling to tourists or neighbors down the road. Now it's to New York and Nebraska, Japan, and Germany.

"The world is getting smaller," she said. "But maple is getting bigger."

Colin Nickerson can be reached at Nickerson.colin@gmail.com

Location map
for Tanzania
National Parks

Serengeti plains



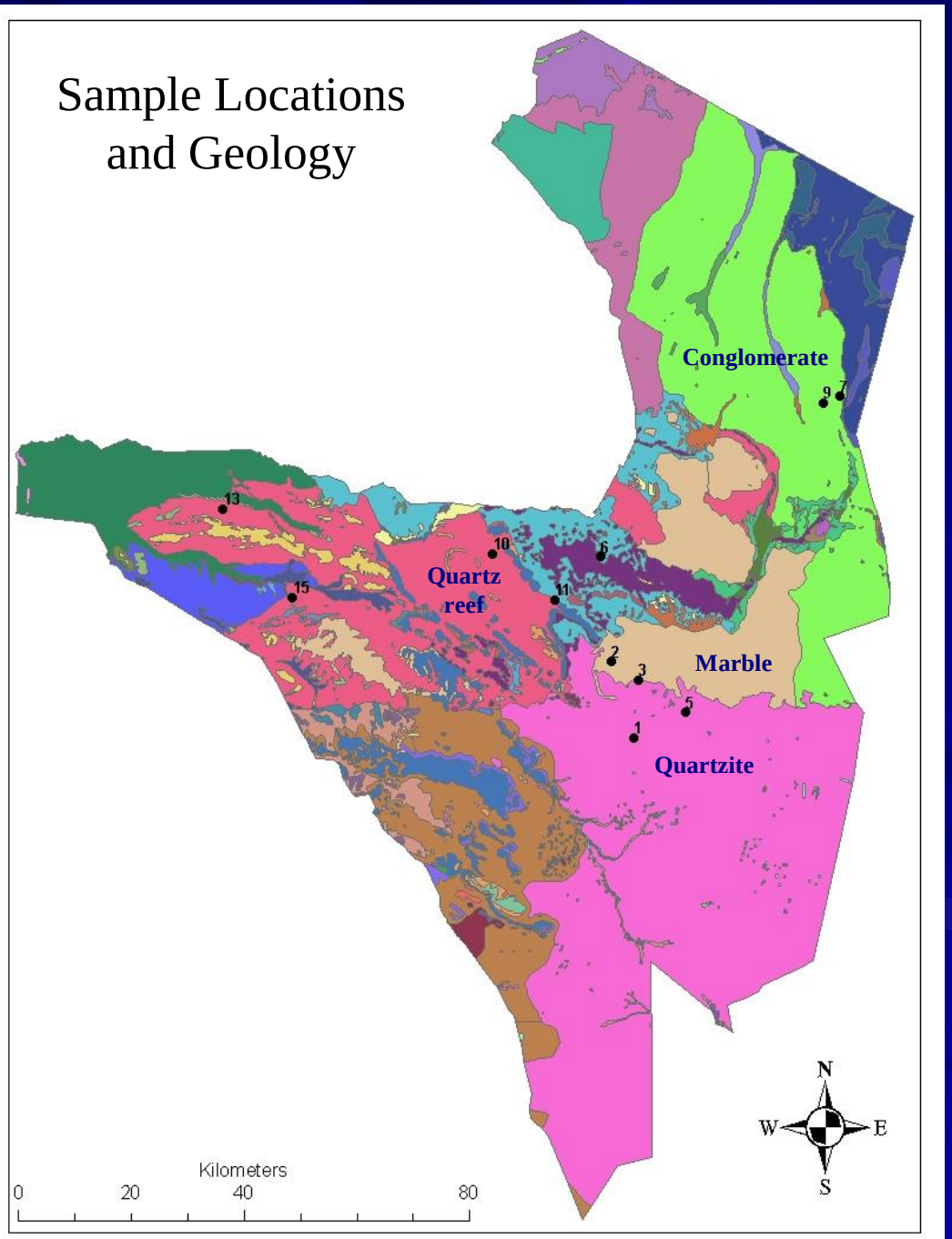
Chemically fingerprinting the source of grasses

Serengeti Grasses

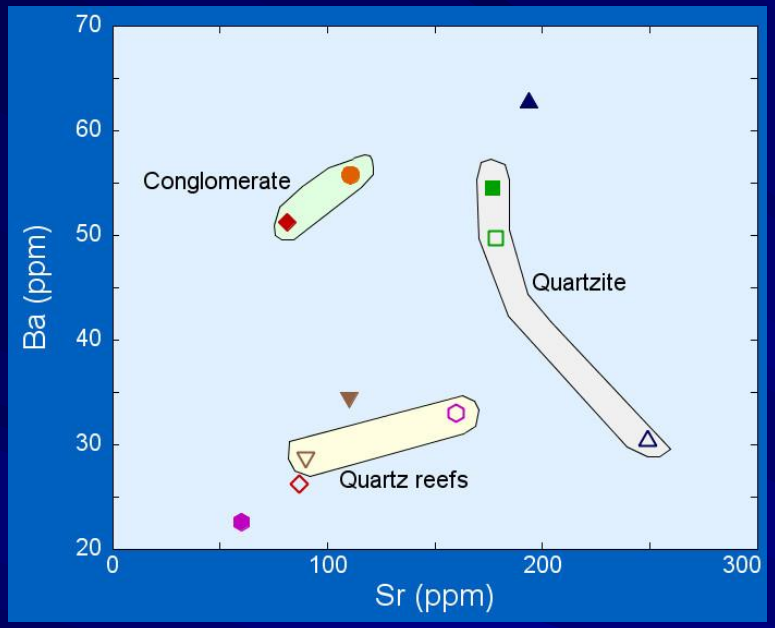
Digiteria

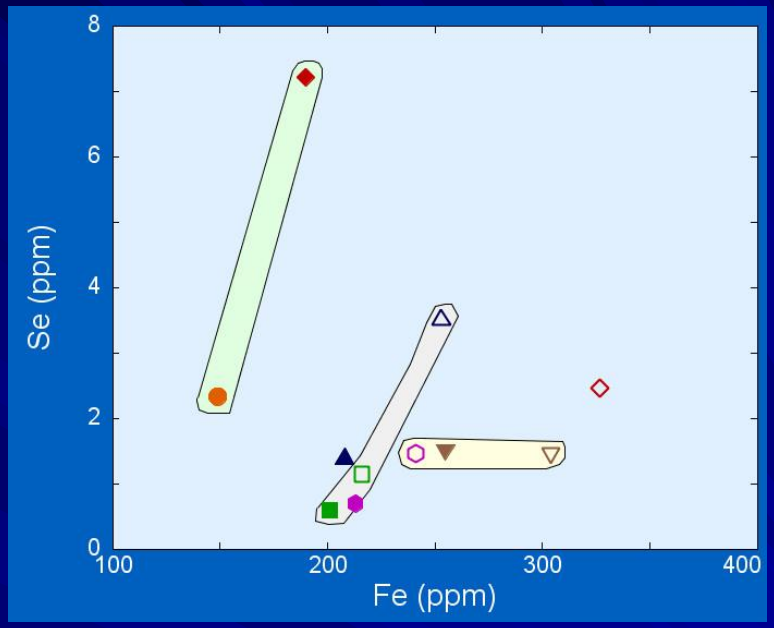
Sporobolus

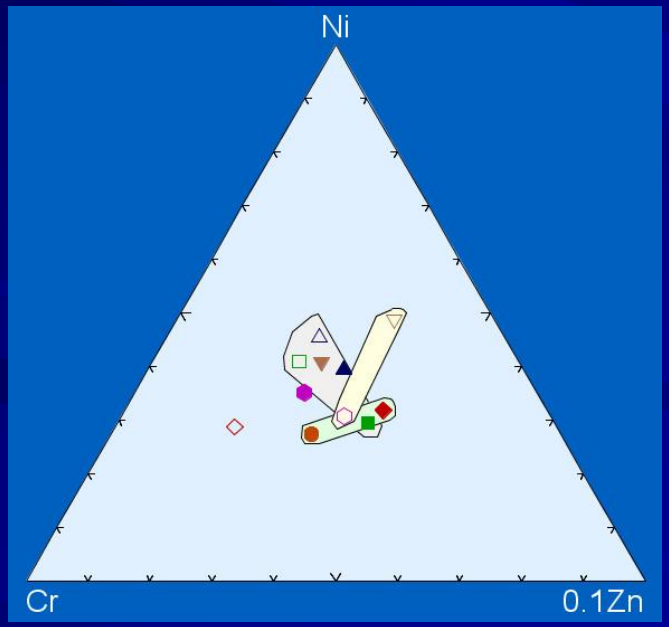
Themeda

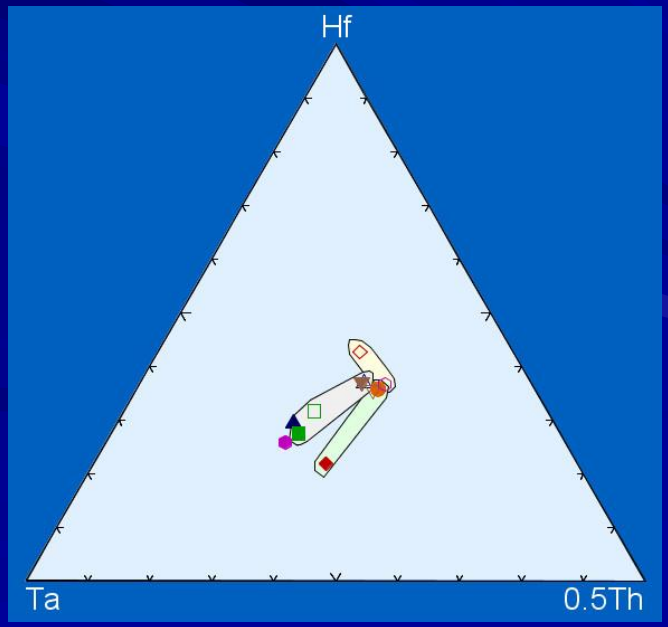

Sample Locations and Geology
Conglomerate
Quartz reef
Marble
Quartzite
13
10
6
15
11
2
3
5
1
9
7
N
W
E
S
Kilometers
0
20
40
80

Trace element distributions for grasses from geographic areas with different bedrock geology.

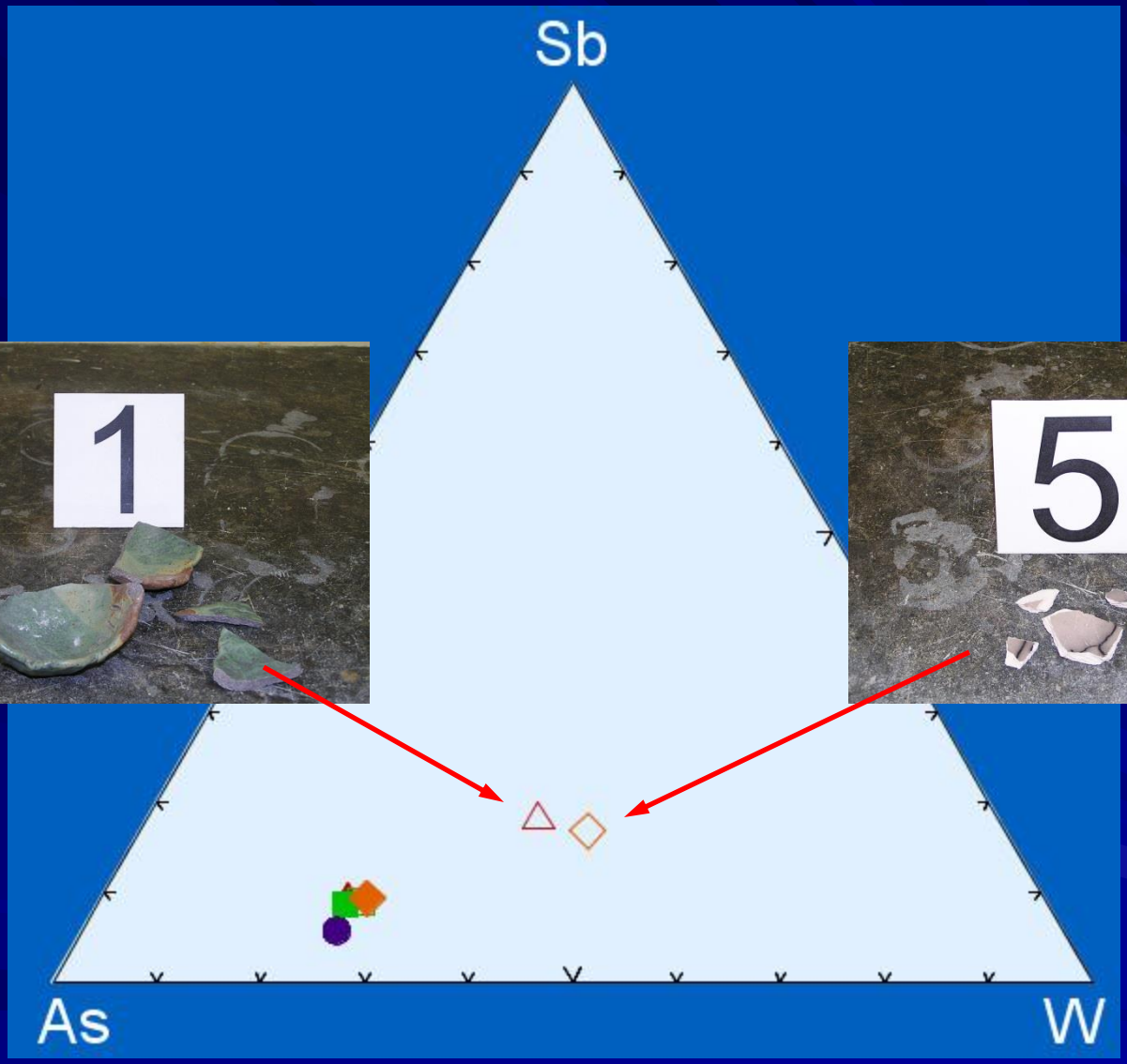








Summary of Materials Used in Glazes	
Material	**Chemistry**
Bentonite	$((Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$
Cryolite	Na_3AlF_6
Dolomite	$CaMg(CO_3)_2$
Epsom salts	$MgSO_4 \cdot 7H_2O$
Fluorspar	CaF_2
Gerstley borate	$2CaO.3B_2O_3.5H_2O$
Kaolin (Kaolinite)	$Al_2Si_2O_5(OH)_4$
Lepidolite	$K(Li,Al)_3(Al,Si)_4O_{10}(F,OH)_2$
Lithium carbonate	$LiCO_3$
Nepheline syenite	Various Na-K-Al silicate minerals
Potash feldspar (K-spar)	$KAlSi_3O_8$
Silica (Quartz)	SiO_2
Soda feldspar (Albite)	$NaAlSi_3O_4$
Whiting (Calcite)	$CaCO_3$
Wollastonite	$CaSiO_3$
Zircopax (Zircon)	$ZrSiO_4$
Colorant Oxides	
Cobalt	Co
Copper carbonate	$CuCO_3$
Hematite	Fe_2O_3
Rutile	TiO_2

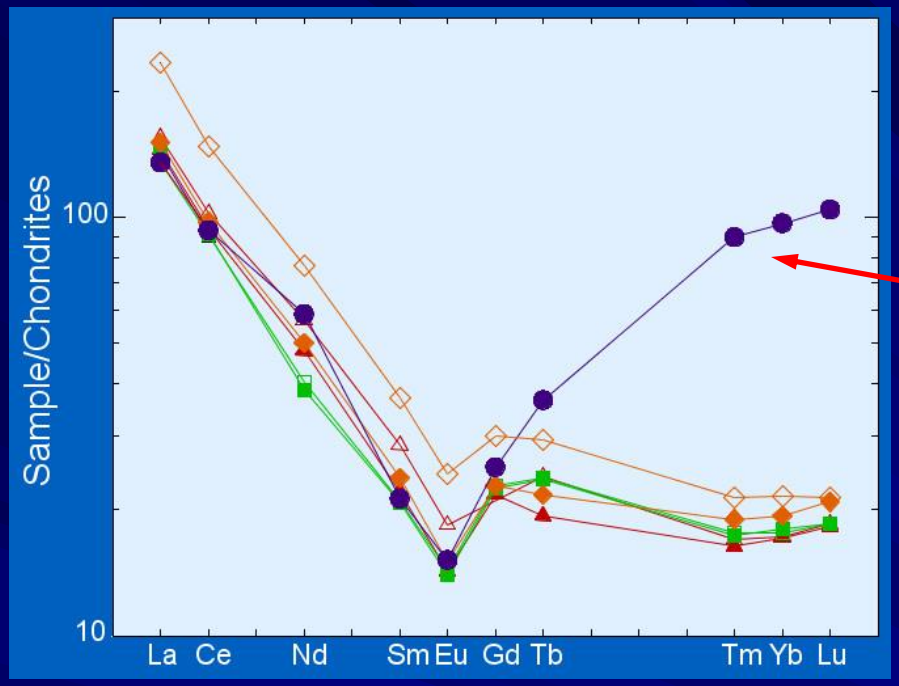

Sb
1
5
As
W


4


3

Co
Cr
Zn

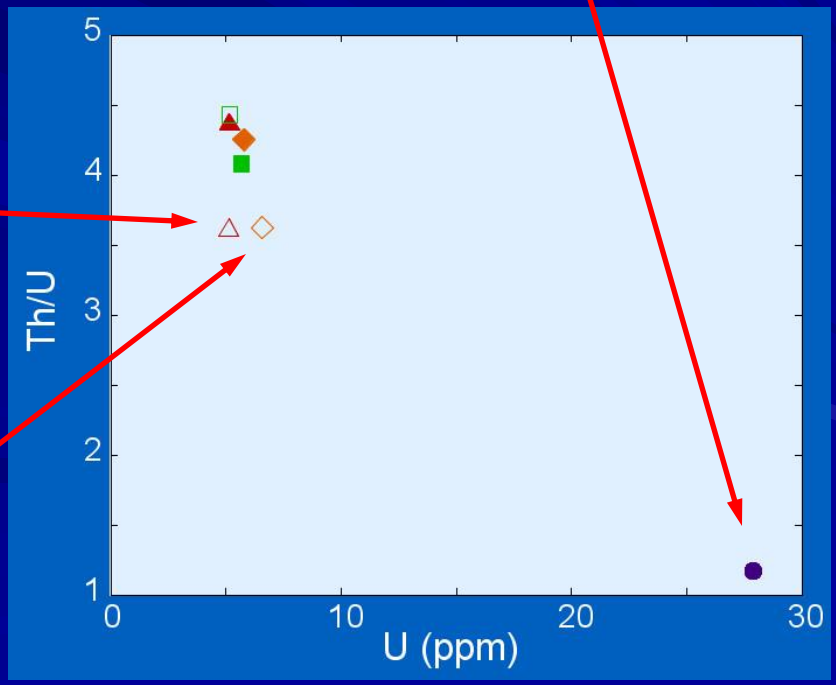

6


Sample/Chondrites
100
10
La Ce Nd Sm Eu Gd Tb Tm Yb Lu


7

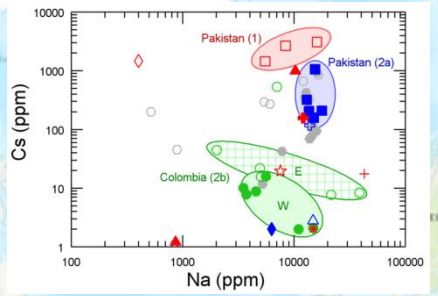

1


5


Th/U
5
4
3
2
1
0
10
20
30
U (ppm)

Fingerprinting Emeralds

Sample Locations



Russia

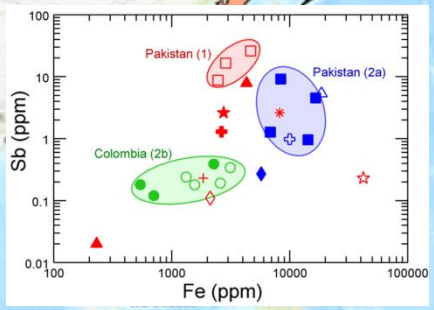
The United States

Colombia

Aghanistan

Pakistan

Egypt



Colombia

Brazil

Zambia

Zimbabwe

Namibia

Australia

Brazil

LEGEND

Location of samples analyzed

Trace elements and Forensic Science

The important point is that for numerous reasons similar materials can have different trace element concentrations. These differences can potentially be used to distinguish between items in a class and either match or eliminate the item.

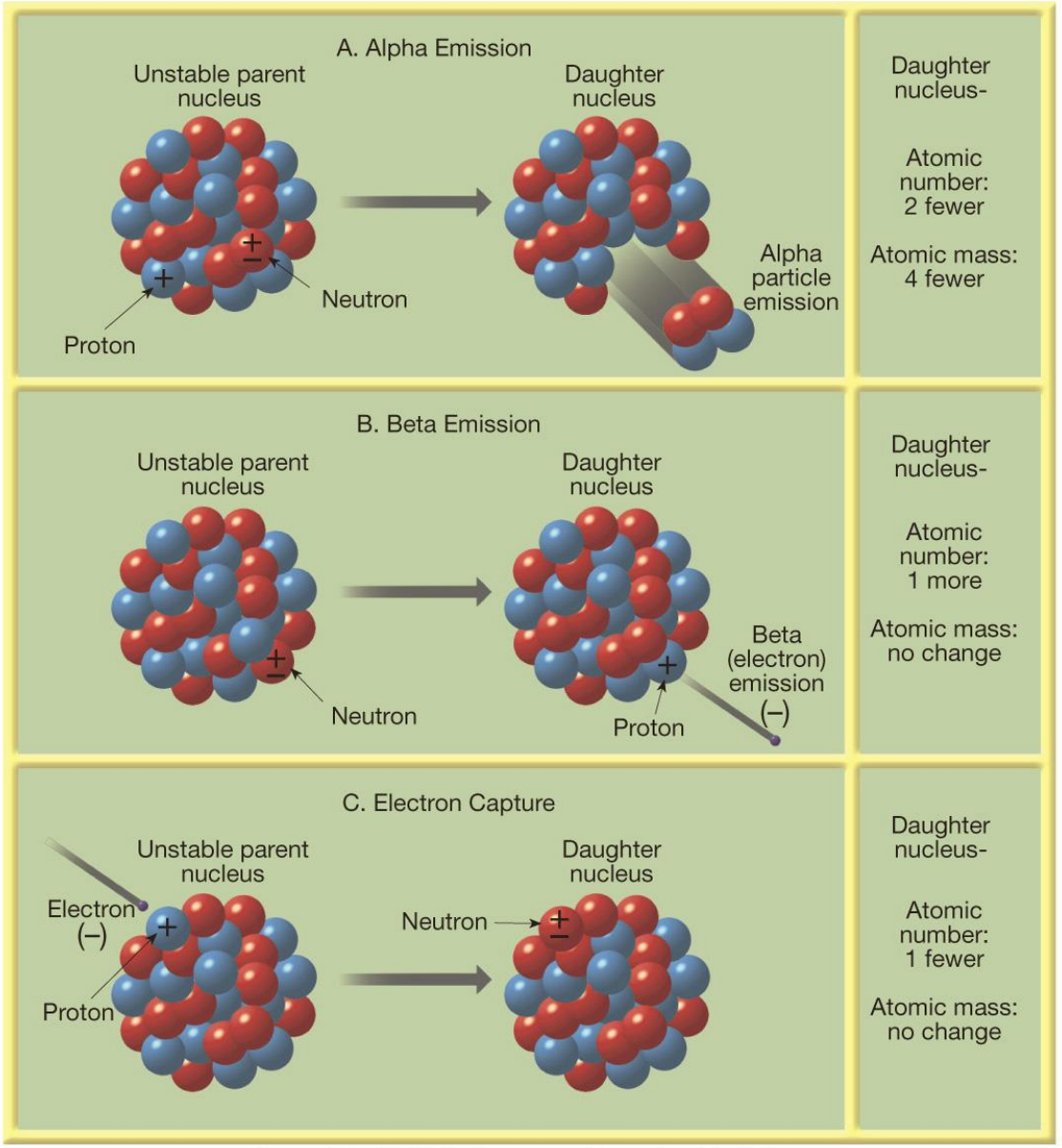
For example: The grass on a suspect's shoe is the same species as that found at a crime scene. But different trace element content for the grass at the crime scene compared to that on the suspect's shoe indicates that the grass on the shoe did not come from the crime scene.

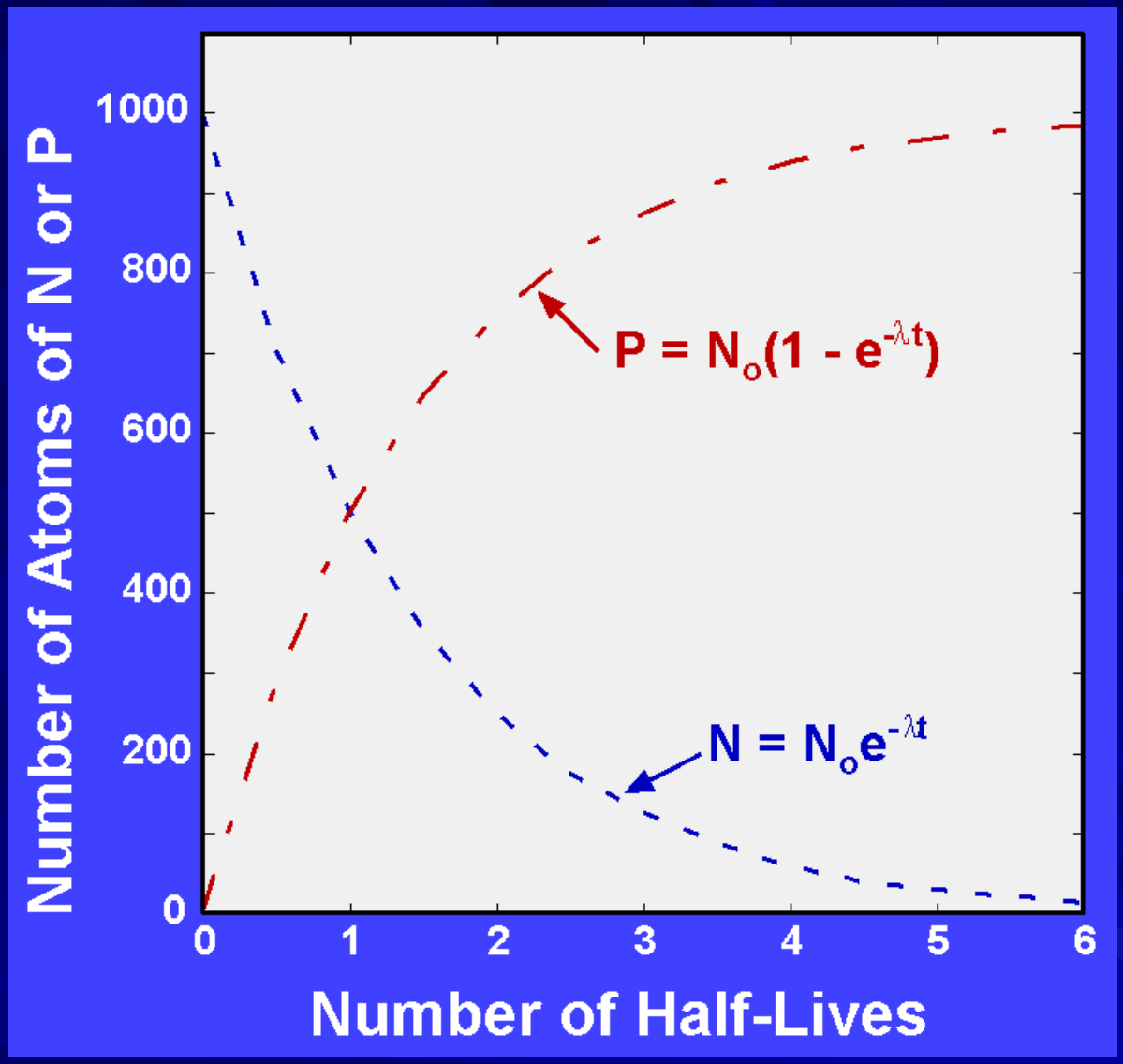
Forensic Geology
Radioactive and Stable Isotopes
Theory and Application to Forensic Investigations

Thermal Ionization Mass Spectrometer (TIMS)
Stanford University, USA

VG Isogas Micromass 602E
Isotope Ratio Mass Spectrometer
University of Queensland, Australia

Radioactive Isotopes – Decay Mechanisms





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

Radioactive isotopes used in the geosciences				
Radioactive parent	Radiogenic progeny	Type of Decay	Half-life (years)	Decay constant (y^{-1})
$^{14}_{6}C$	$^{14}_{7}N$	β^-	5.73×10^3	1.209×10^{-4}
$^{40}_{19}K$	$^{40}_{18}Ar$	ε	1.298×10^9	5.34×10^{-10}
$^{147}_{62}Sm$	$^{143}_{60}Nd$	α	1.06×10^{11}	6.539×10^{-12}
$^{87}_{37}Rb$	$^{87}_{38}Sr$	β^-	4.88×10^{10}	1.42×10^{-11}
$^{232}_{90}Th$	$^{208}_{82}Pb$	α, β^-	1.401×10^{10}	4.948×10^{-11}
$^{235}_{92}U$	$^{207}_{82}Pb$	α, β^-	7.038×10^8	9.849×10^{-10}
$^{238}_{92}U$	$^{206}_{82}Pb$	α, β^-	4.468×10^9	1.551×10^{-10}

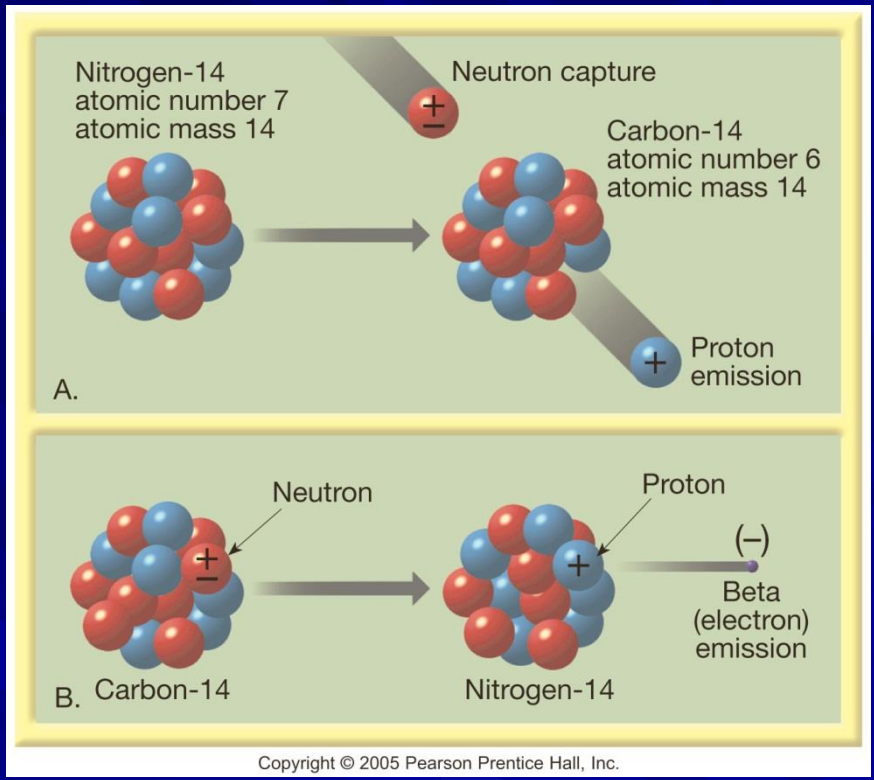
Carbon-14 Dating

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

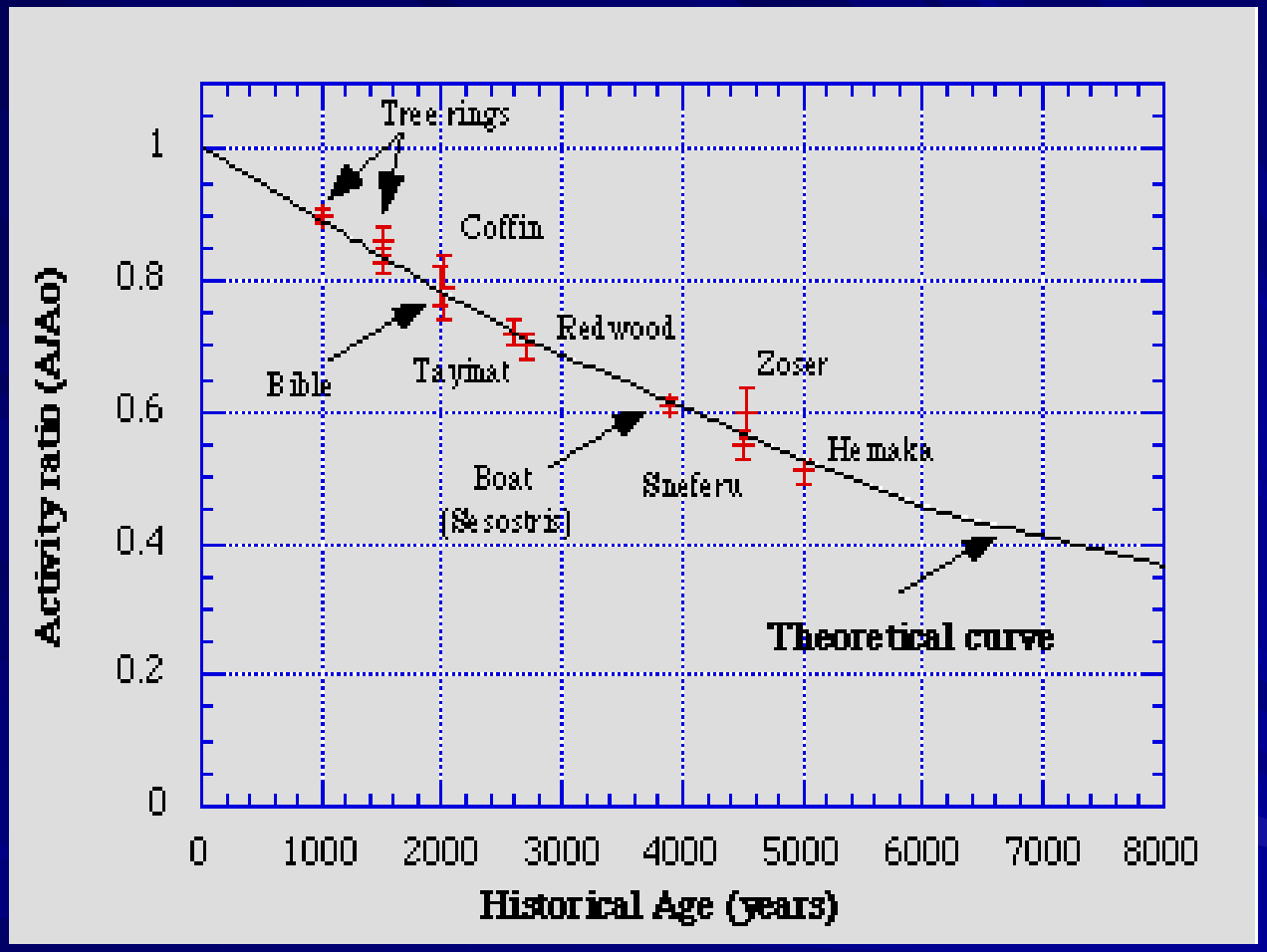
$$^{14}N + n \Rightarrow {}^{14}C + p$$

- ^{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 ^{14}C which disappears as it decays to ^{14}N

$$^{14}C \Rightarrow {}^{14}N + \text{Beta}$$



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



- 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

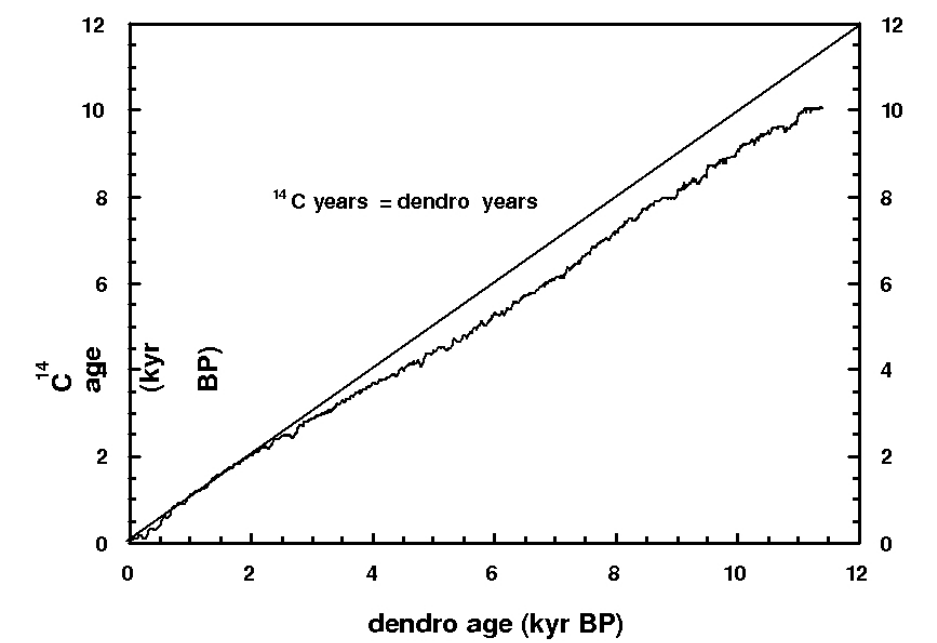


Figure 2. *Radiocarbon calibration curve obtained by dating tree rings (Stuiver and Kra 1986, Kromer and Becker 1993) .*

- For an old sample (>40,000 years) trace contamination by modern carbon results in an incorrect young age
- Testing of nuclear weapons since 1945 has added ^{14}C to the atmosphere

Forensic Carbon-14 Cases

- Dead Sea Scrolls – 150 AD
- Stonehenge – 3100 BC

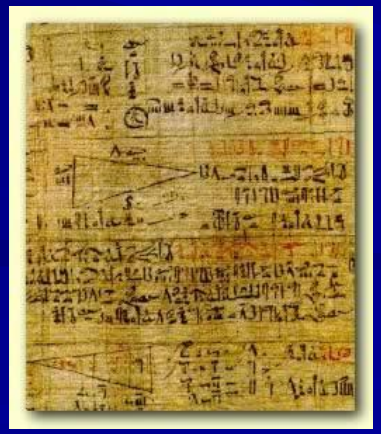
- Hezekiah's Tunnel - 700 BC

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

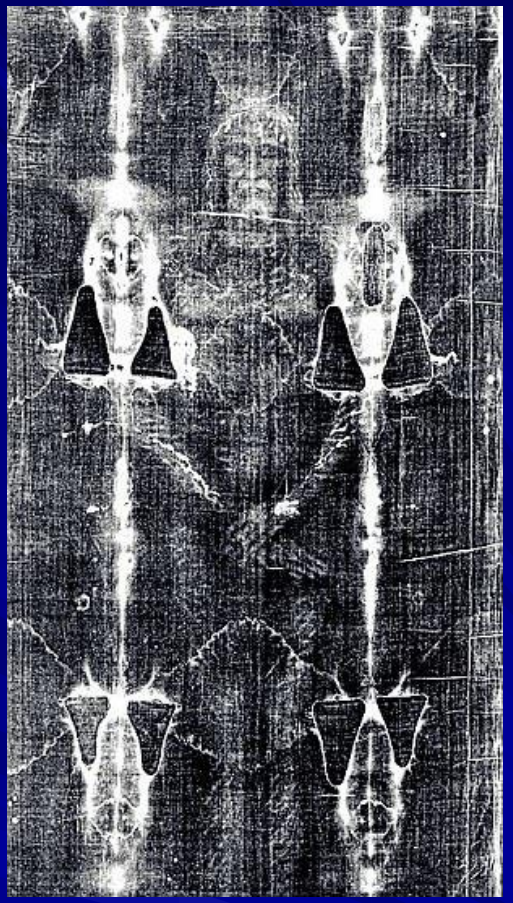
- Cave painting at Lascaux, France

  ^{14}C dated to 14,000 BC

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

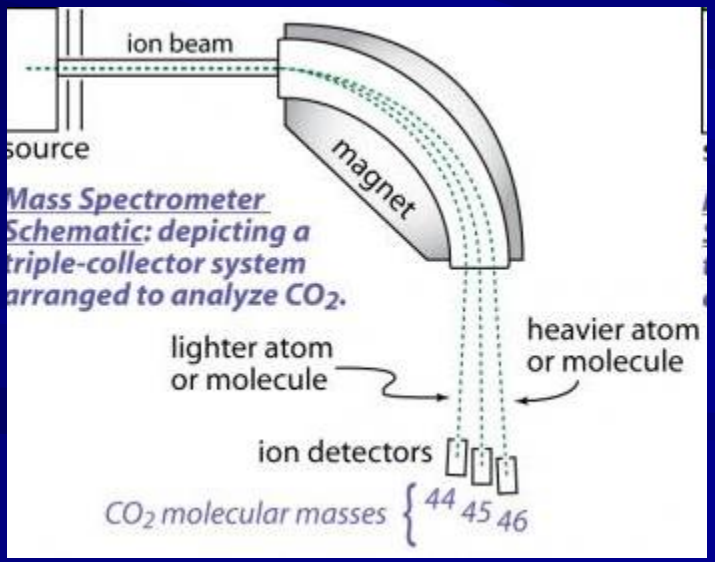


- The Shroud of Turin was ^{14}C dated 1260-1390 AD which suggests that it is a fake
- However, recent evaluation shows that the sample measured was from a medieval patch and/or that it was seriously contaminated with molds, waxes, etc
- New estimates date the shroud from 1300-3000 ybp bases on vanillin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



Stable Isotopes

Laboratory set-up for determining stable isotope abundances



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 (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.

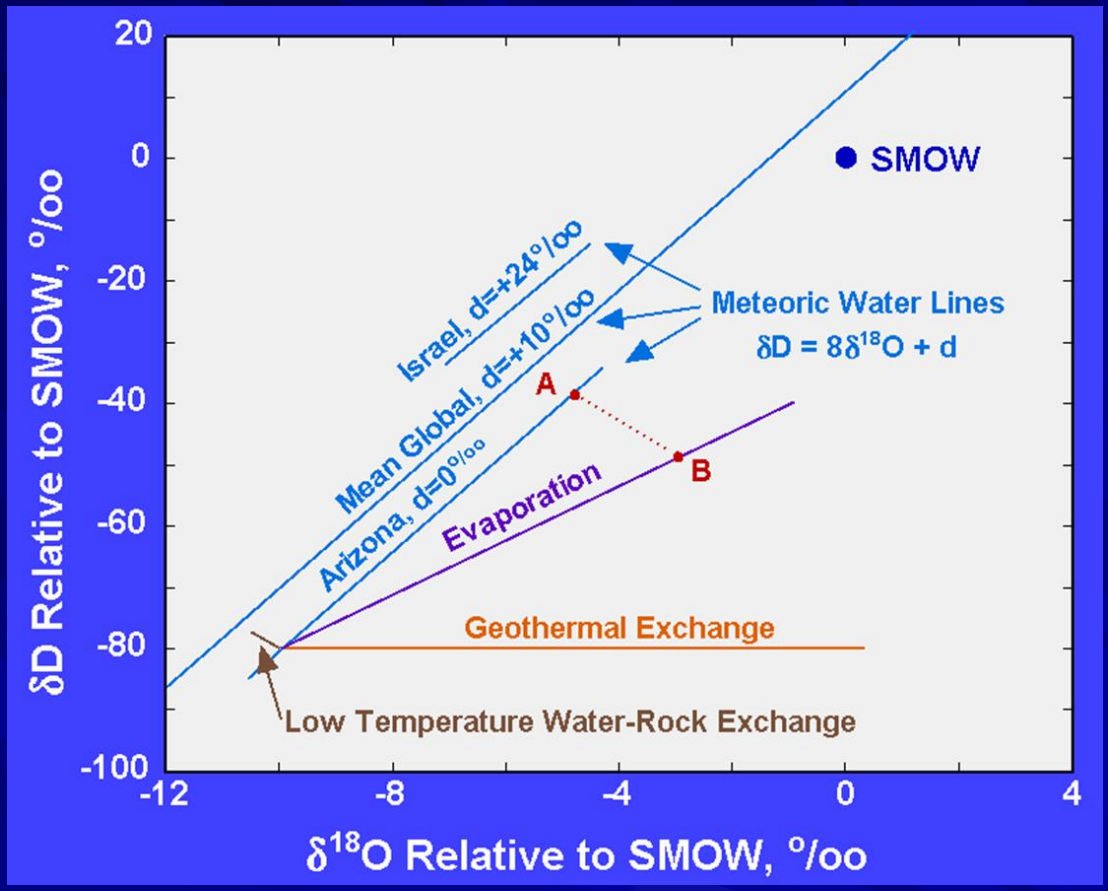
$\delta^{18}O > 0$ Sample **enriched** in heavy isotope (^{18}O) relative to seawater.

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

Stable isotopic fractionation takes place during

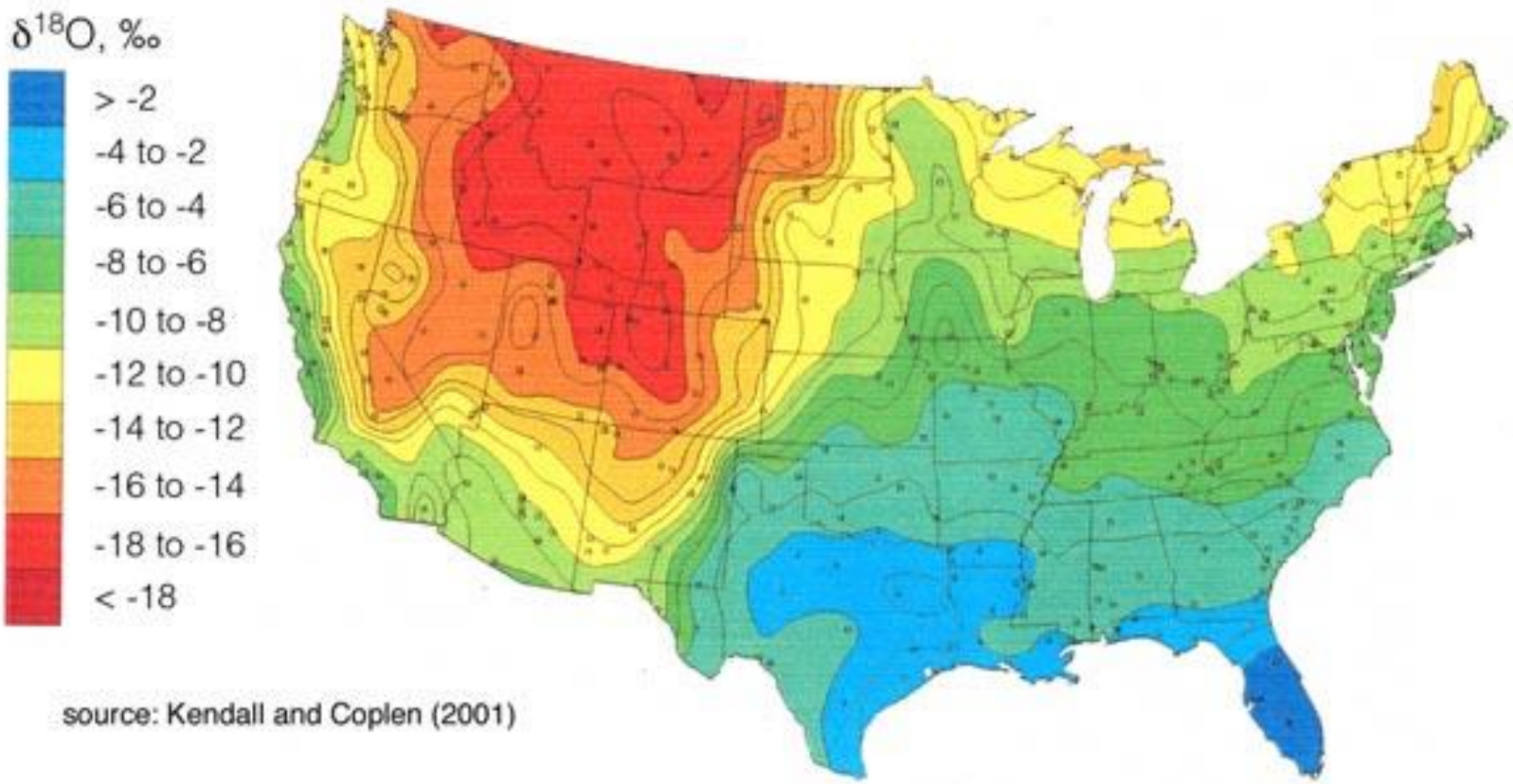
1. Physical,
2. Chemical, and
3. Biological processes

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.



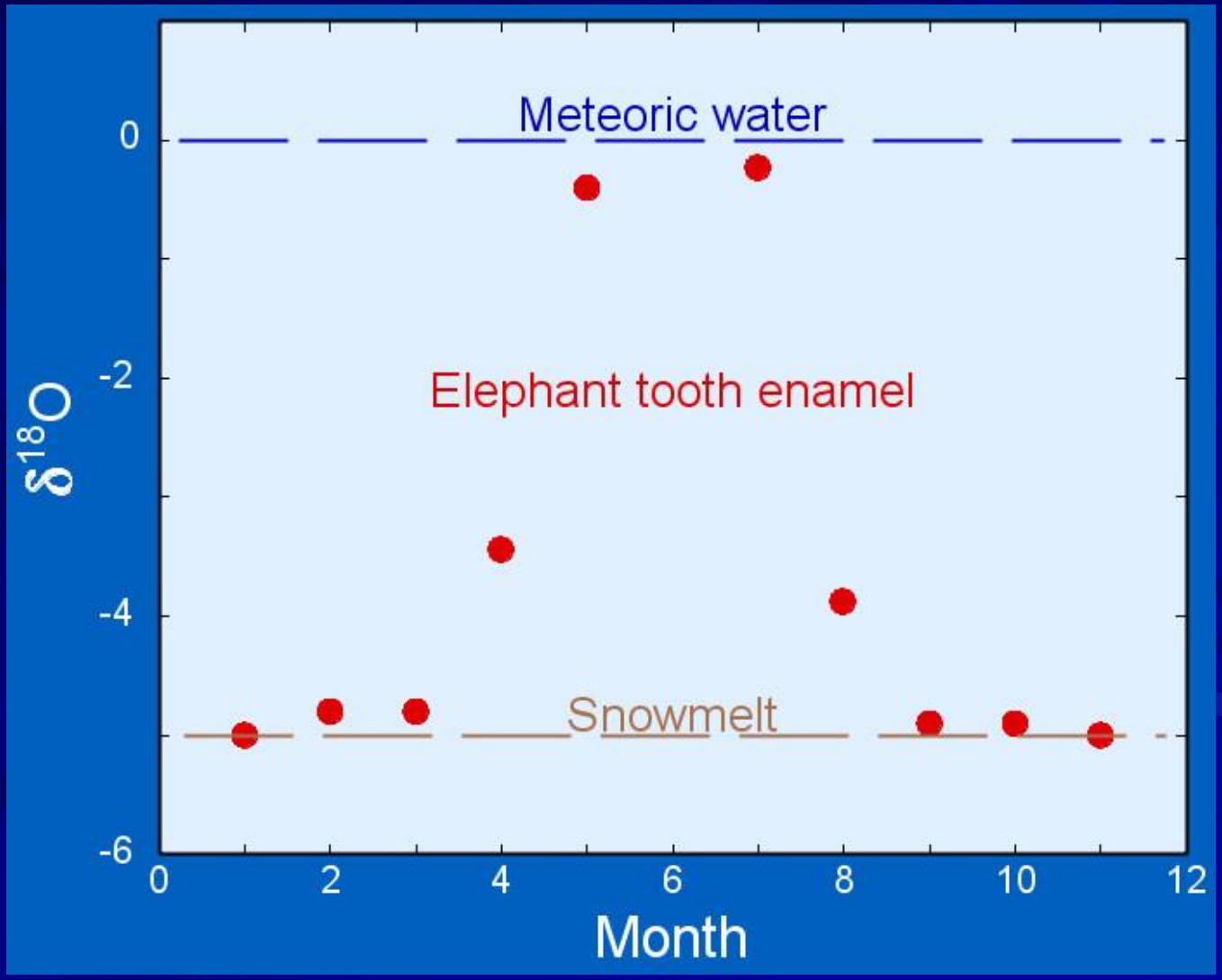
Plot of δD versus $\delta^{18}O$ illustrating the mean global meteoric water line and local meteoric water lines.

Isotopic Composition of Water in the USA

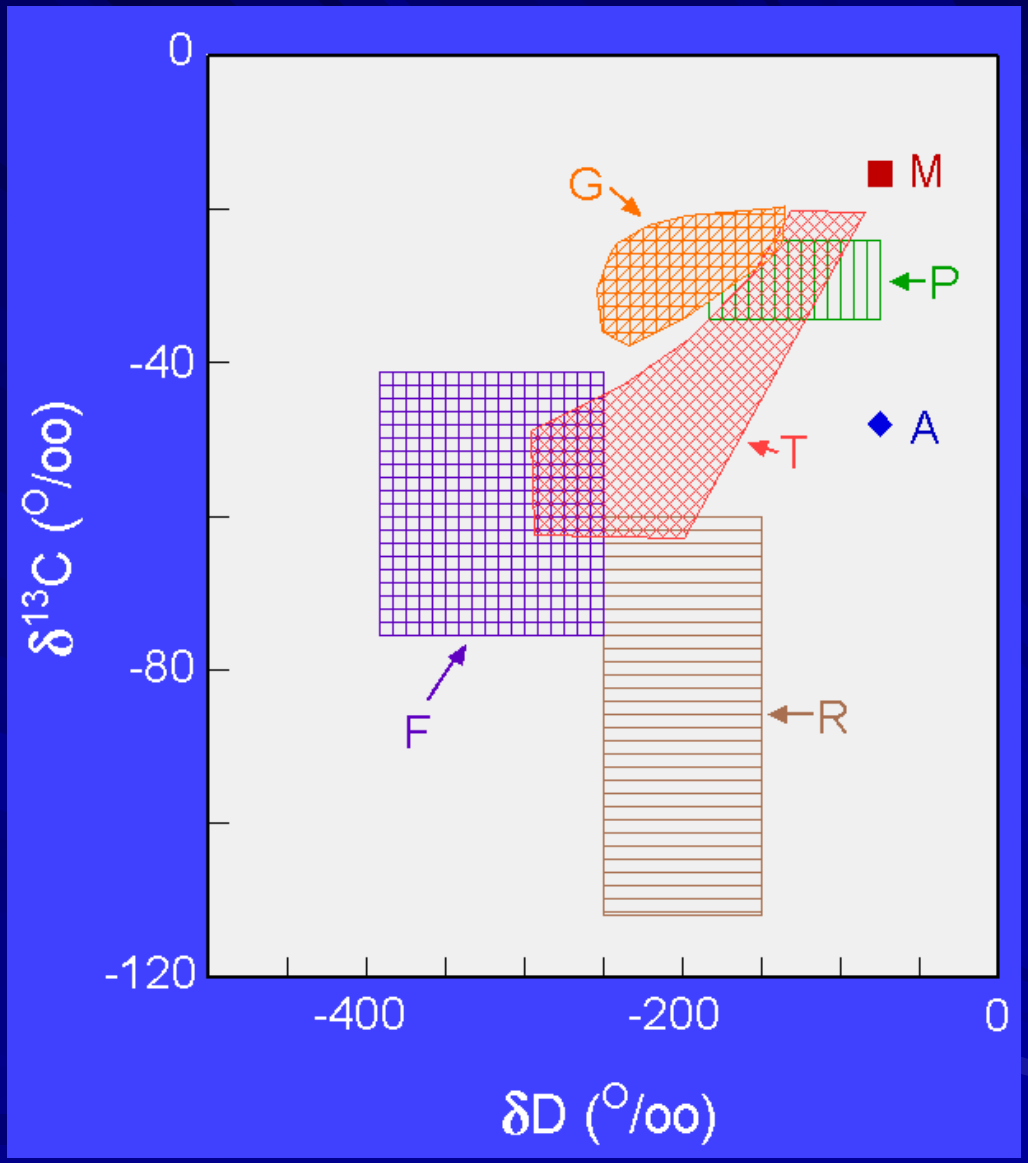


source: Kendall and Coplen (2001)

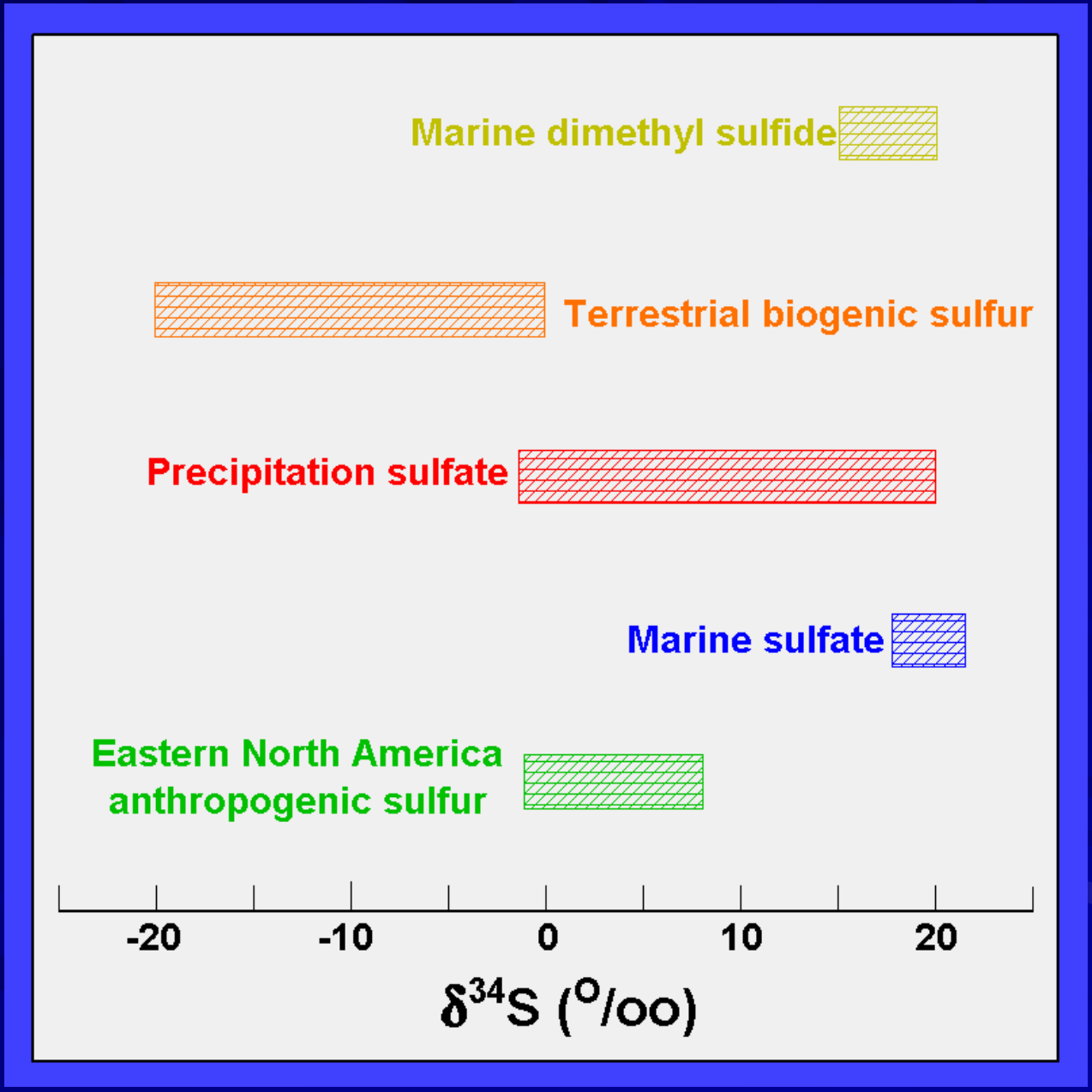
Laser used to analyze enamel layers of an elephant tooth, Amboseli National Park. Drinking water usually comes from snowmelt (Kilimanjaro) but during the rainy season meteoric water is the major source of drinking water.



^{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).



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



Forensic Stable Isotope Case – Large Gasoline Spill

- 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

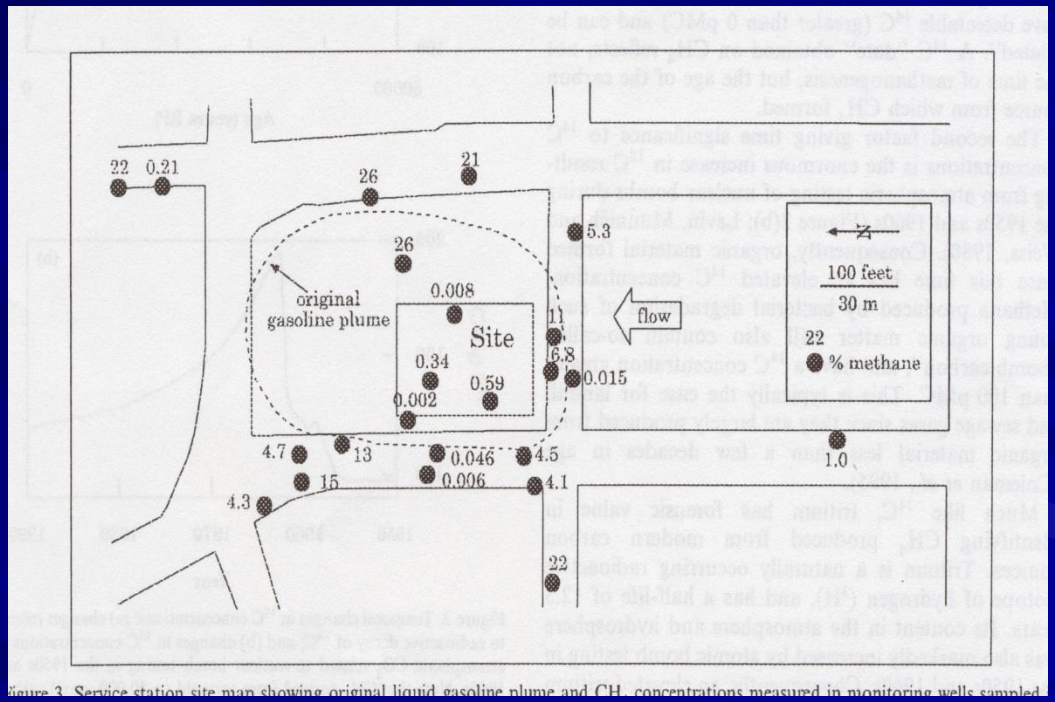
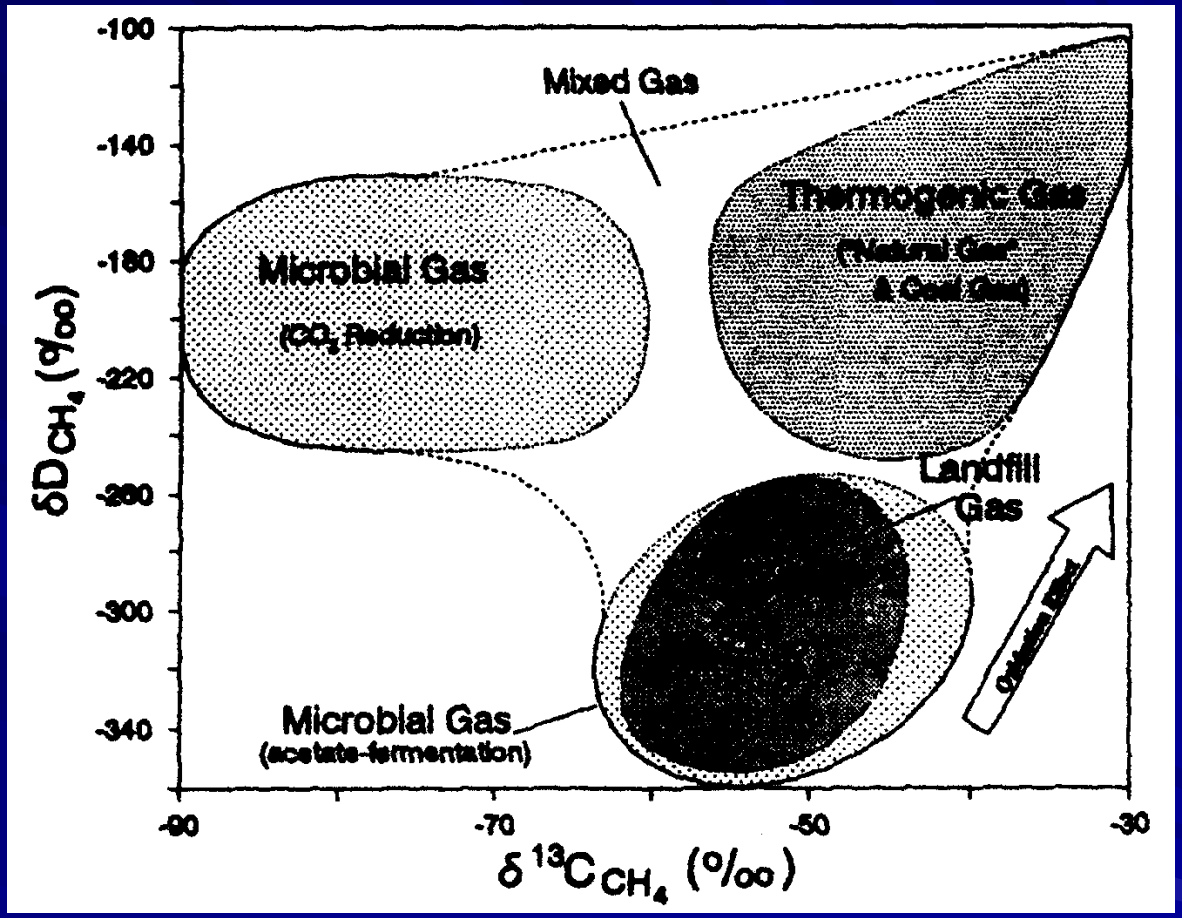


Figure 3. Service station site map showing original liquid gasoline plume and CH_4 concentrations measured in monitoring wells sampled

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

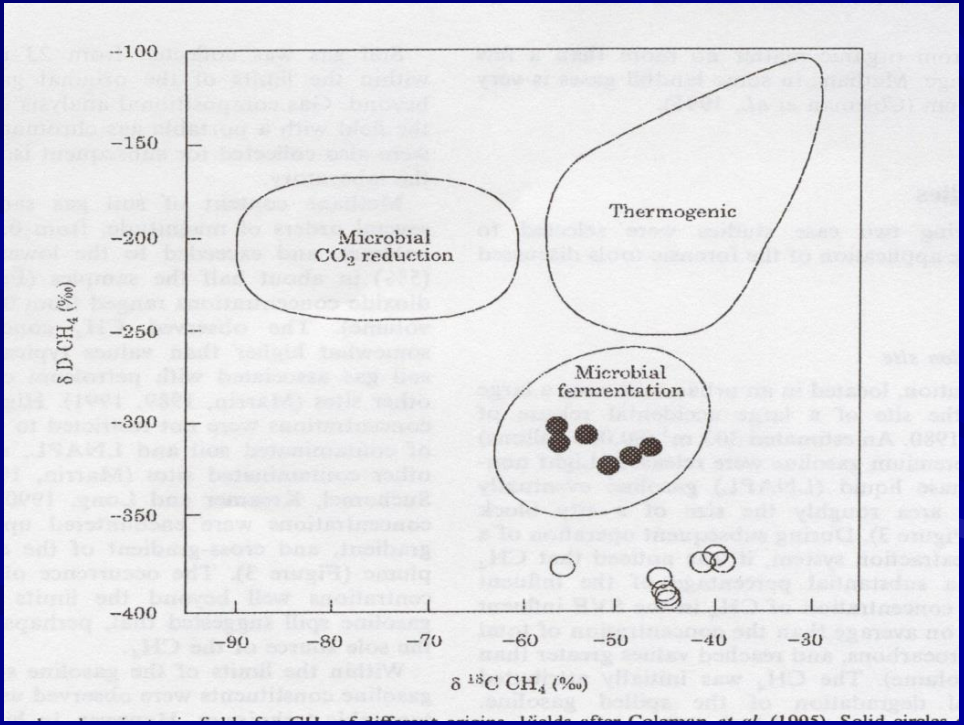
δD versus $\delta^{13}C$ for methane from different sources. Landfill methane plots in the field of acetate-fermentation.



Forensic Stable Isotope Case – Oil Spills

- 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

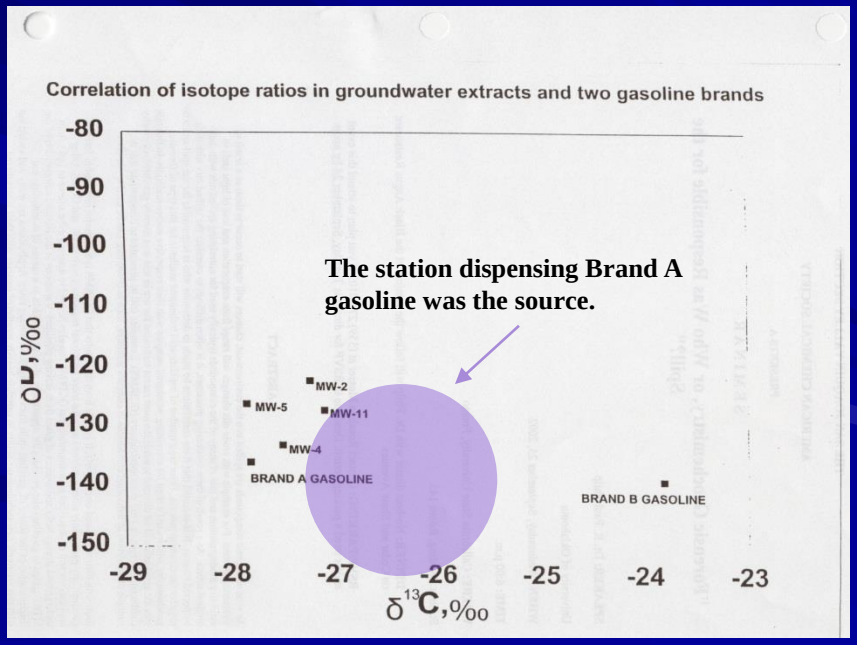


Forensic Stable Isotope Case – Gasoline in Sump Pump

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

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

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

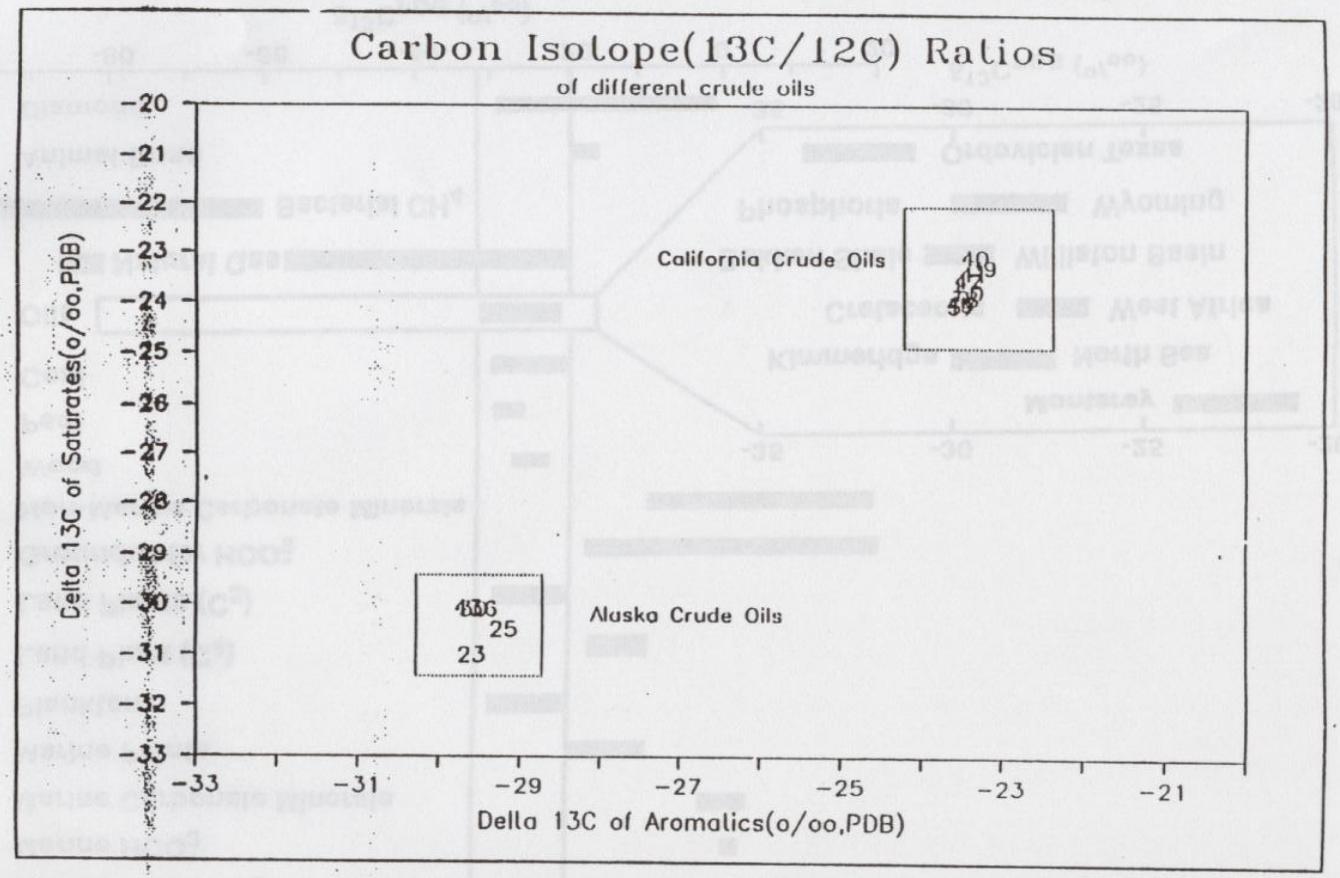
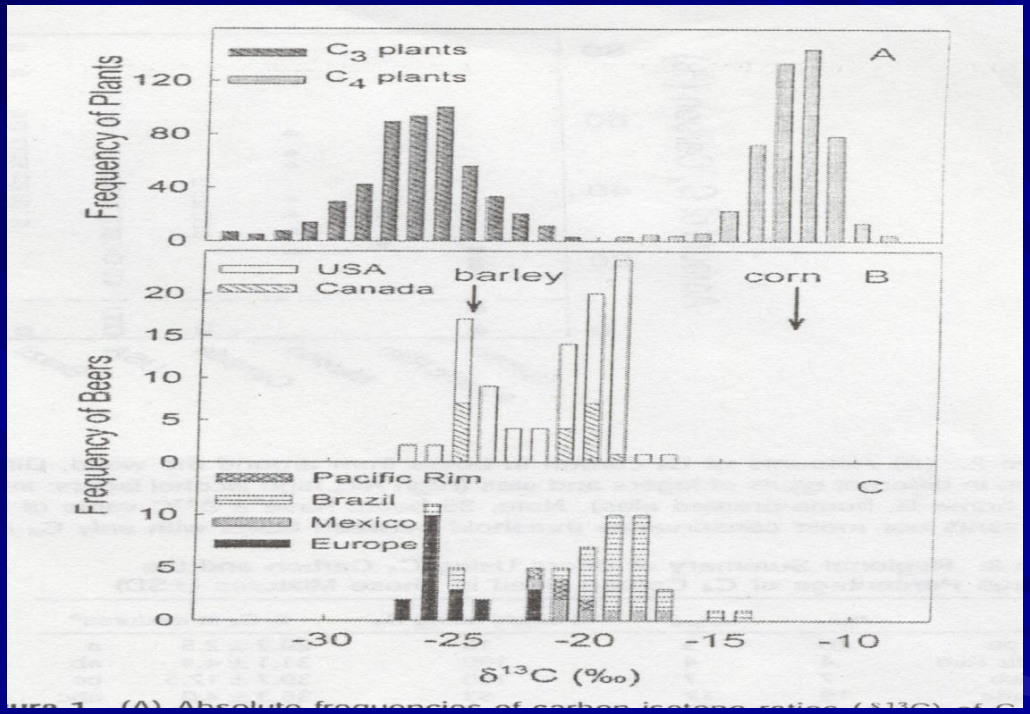


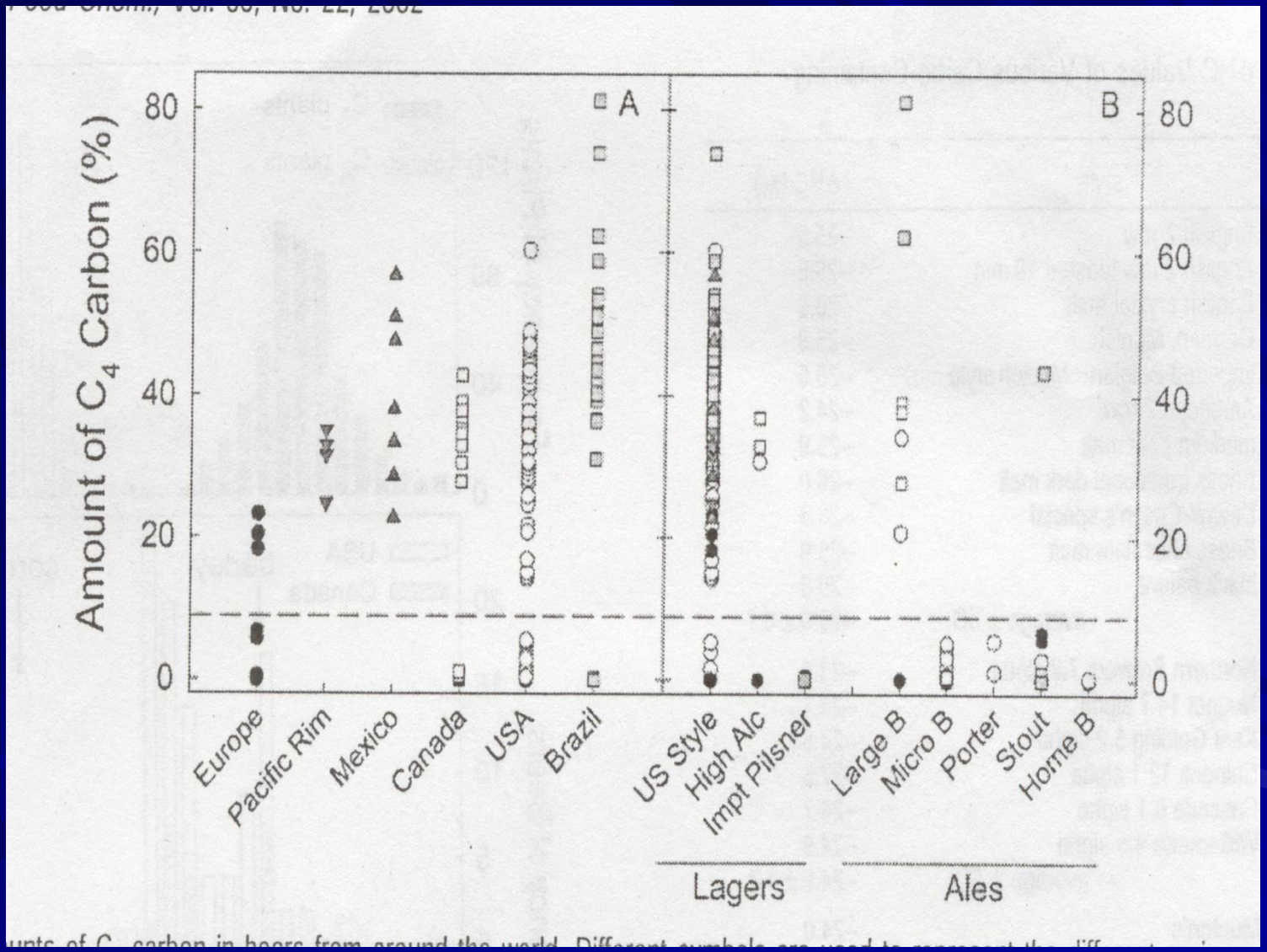
Figure 9.9: BP "American Trader" accident in Huntington Beach, California, February 7, 1990. Correlation among Alaska and California crude oils and beach tar balls on Southern California beaches, based on their carbon isotope ratios.

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

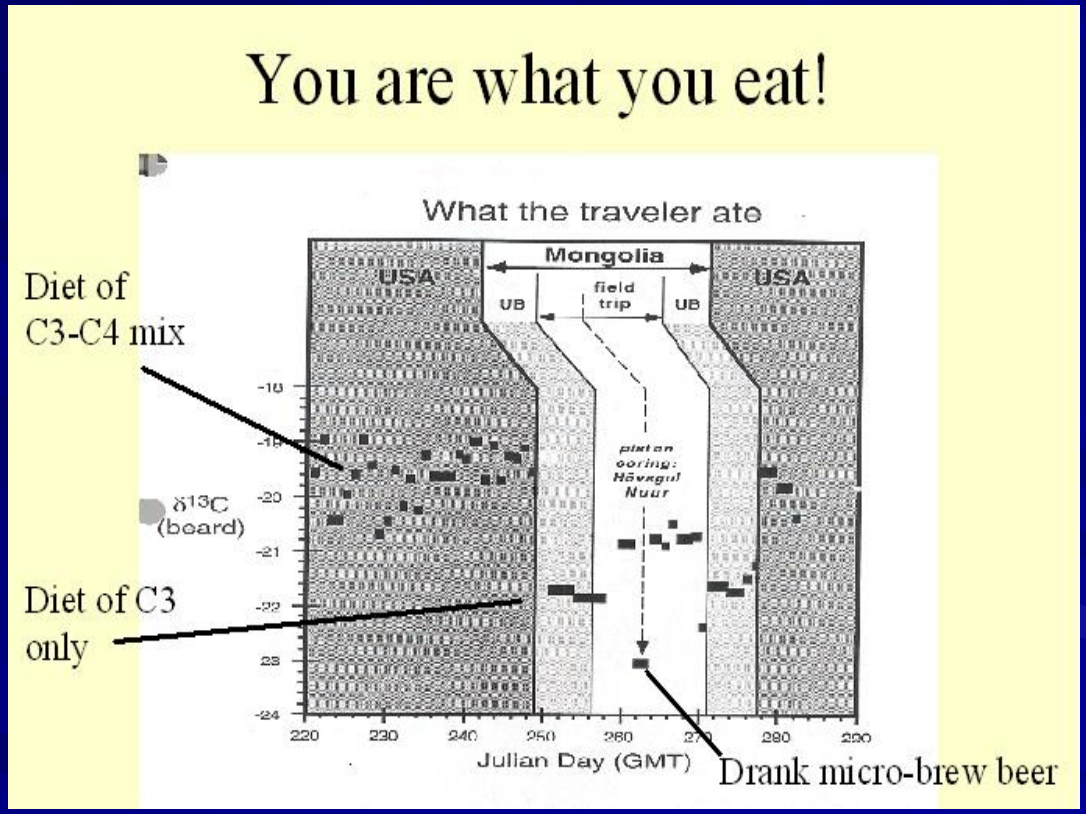


The Delta C-13 value for the beer depends upon the relative amounts of C_3 and C_4 carbon



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



Forensic Geology

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

Ehleringer et al. (1999)