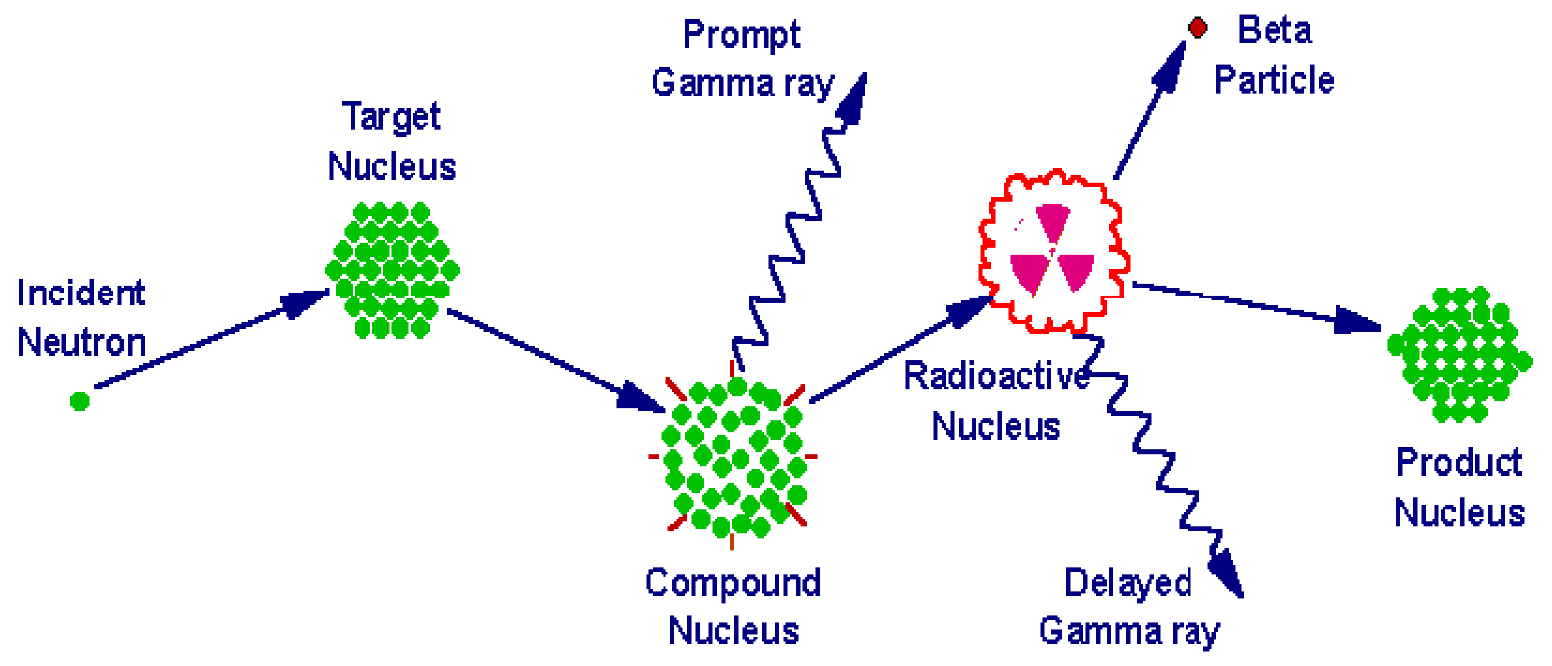
Environmental and Forensic Applications of Instrumental Neutron Activation Analysis (INAA)

Department Environmental, Earth, & Atmospheric Sciences

The n–gamma Reaction

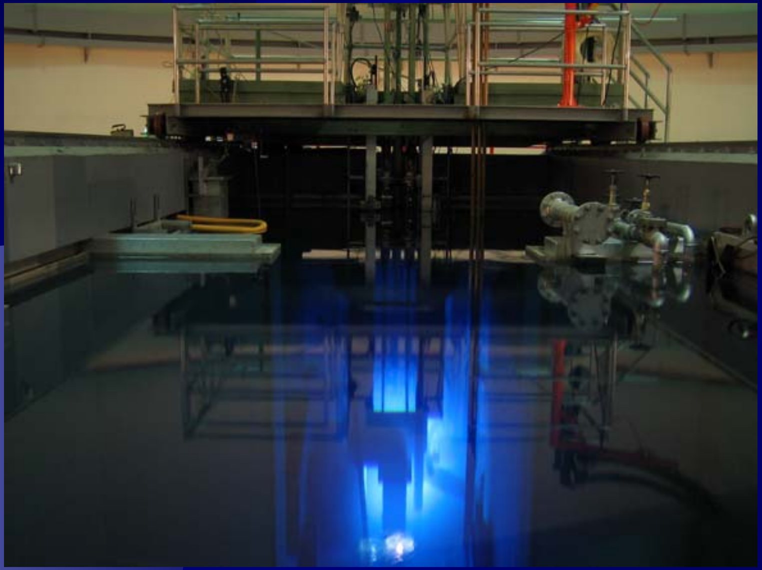
The basic reaction for INAA

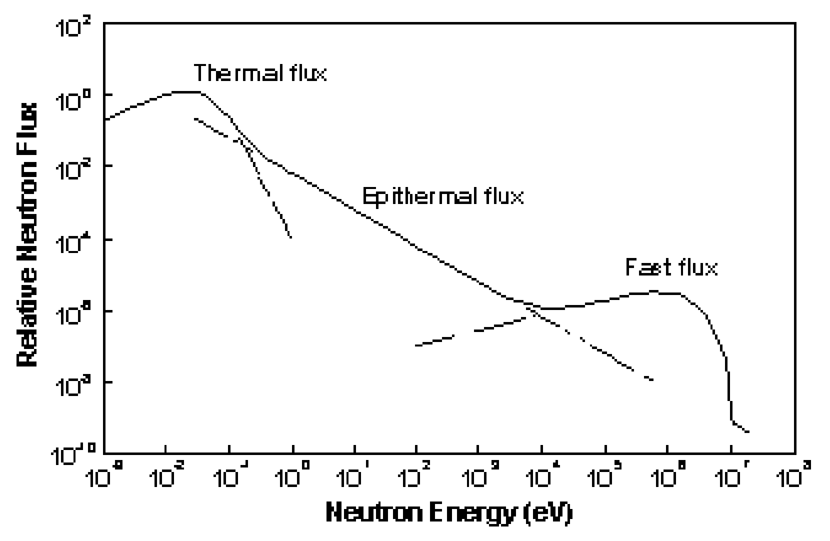


Example: $^{58}\text{Fe} + {}^{1}\text{n} \longrightarrow {}^{59}\text{Fe} + \text{Beta}^{-} + \text{gamma rays}$

Gamma ray energies = 142.4, 1099.2, 1291.6 KeV

Different neutron energies are used for different types of experiments.

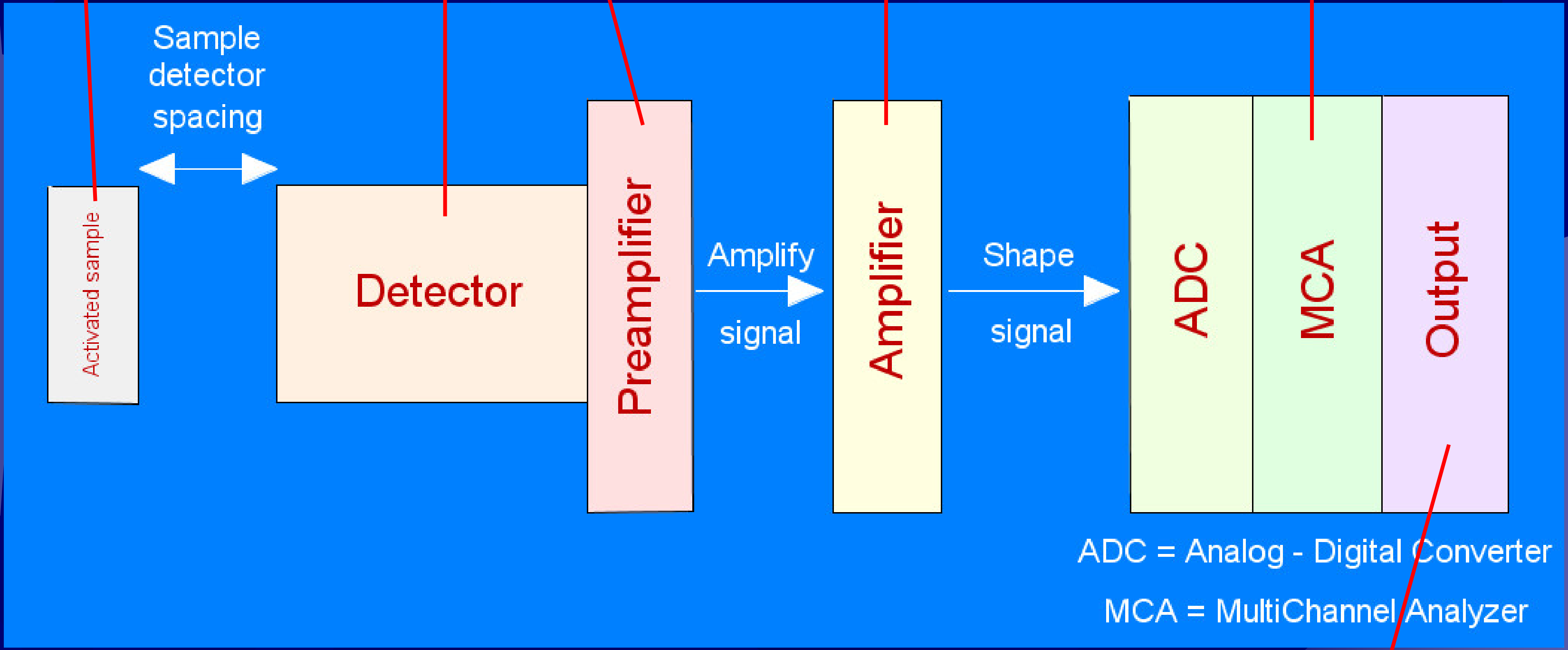




UML 1 Mw Research Reactor

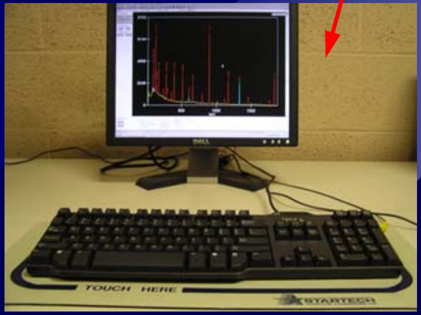
The Neutron Source

Data acquisition flow sheet



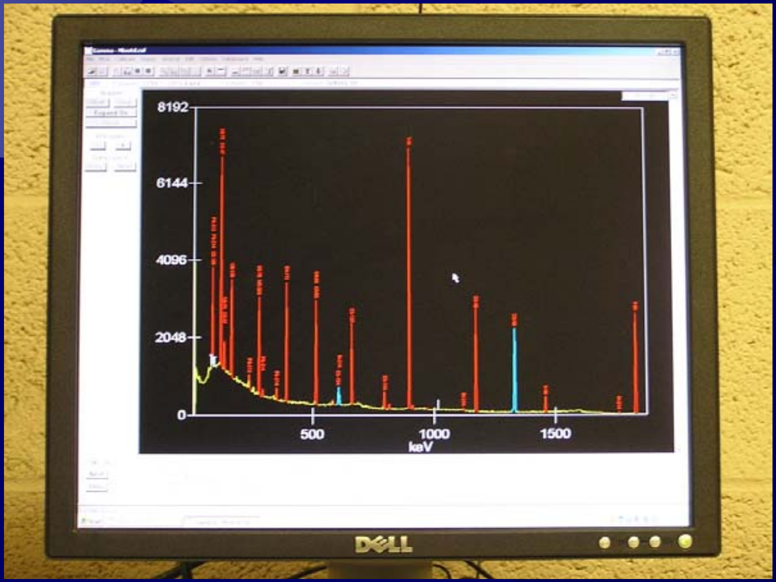
ADC = Analog - Digital Converter

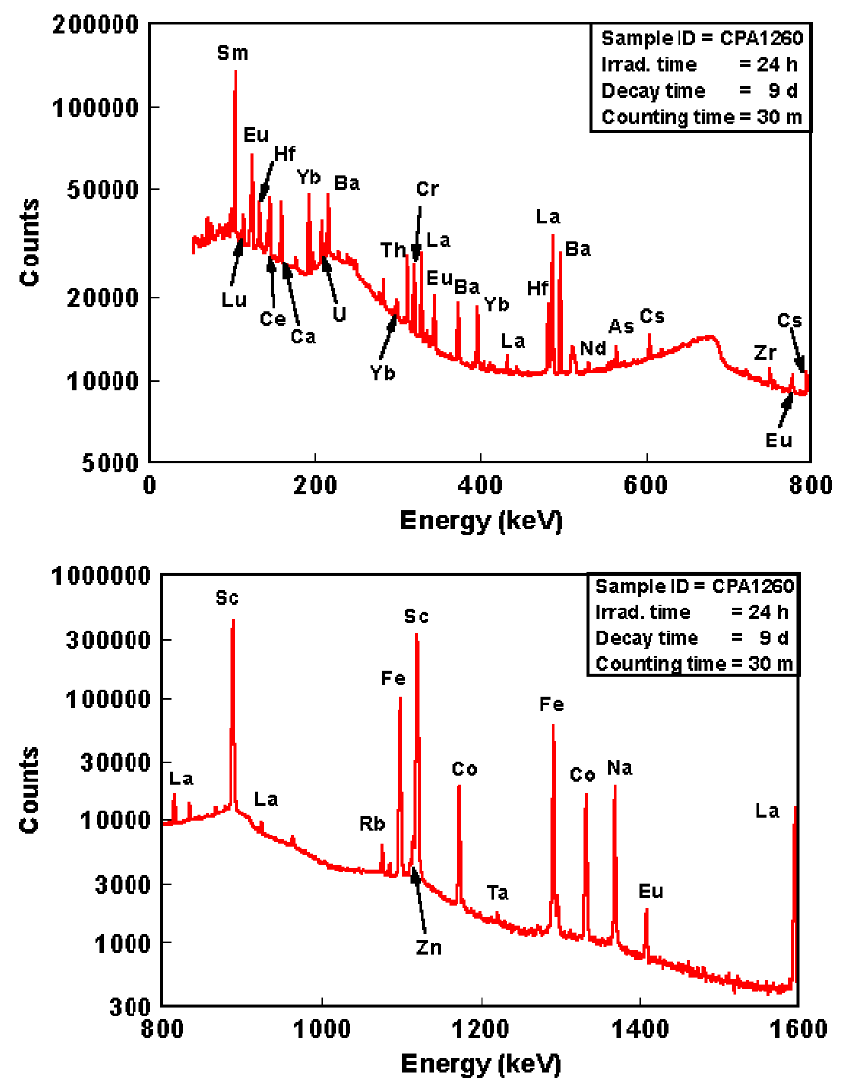
MCA = MultiChannel Analyzer

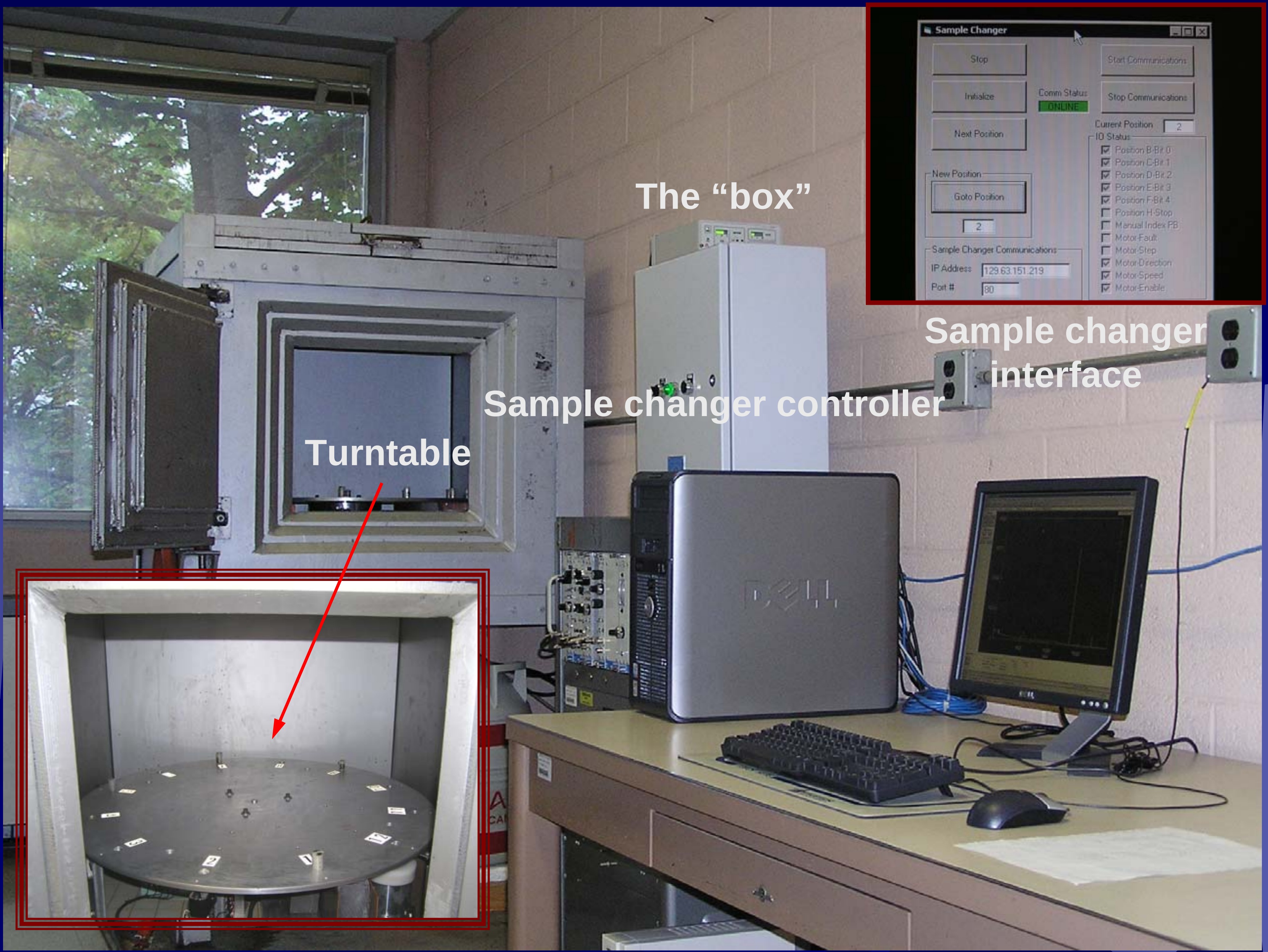


Gamma ray spectrum for a multi element sample

UML INAA Lab







Comm Status: ONLINE

Current Position: 2

New Position: 2

Sample Changer Communications

IP Address: 129.63.151.219

Port #: 80

IO Status
- ☑ Position B-Bit 0
- ☑ Position C-Bit 1
- ☑ Position D-Bit 2
- ☑ Position E-Bit 3
- ☑ Position F-Bit 4
- ☐ Position H-Stop
- ☐ Manual Index PB
- ☐ Motor-Fault
- ☐ Motor-Step
- ☑ Motor-Direction
- ☑ Motor-Speed
- ☑ Motor-Enable

The “box” combines all the spectroscopy and MCA functions – HV to detector, spectroscopy amplifier, ADC, MCA.

Factors to be considered in INAA

- Corrections for inter-element interferences
- Flux monitoring
- Decay corrections to some initial time *t* and for decay during counting
- Fission product corrections if the sample contains significant U
- Selection of appropriate standards
- Selection of optimum decay times prior to counting. Function of half-lives of elements of interest
- Geometry considerations

INAA Analysis Scheme

- Irradiate sample (thermal neutrons)
- Count sample 5 to 10 days after irradiation to determine short-lived isotopes
- Count sample 4 to 8 weeks after irradiation to determine long-lived isotopes
- Calculate concentrations after applying decay, interference, fluence, and fission-product corrections.

Detection limits (DL) for elements that can be determined by INAA	
DL (nanograms)	Elements
0.01-0.1	Au, Eu, Ho, Ir, Sm, Lu
0.1-1	Ag, As, Co, Cs, Hf, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, W, Yb
1-10	Ba, Br, Ce, Cr, Gd, Mo, Na, Nd, Ni, Rb, Sr, Zn, Zr
10-100	K
100-1000	Fe

Advantages of INAA

- Can analyze a large number of elements simultaneously
- Very low detection limits for many elements
- Small sample sizes (1 – 200 mg)
- No chemical preparation
- Nondestructive. The material is available for other analytical techniques
- Relatively low entry cost (~$60,000) compared to other high sensitivity analytical methods

Applications of INAA at UML

- Trace element analysis - rocks and minerals
- Sediment and soil compositions
- Partitioning of metals between phases in coal
- Origin of archaeological artifacts
- Tephra correlation for archaeological studies
- Trace metals in nanotech materials
- Forensics
- Chemistry of atmospheric aerosols
- Distribution of metals in tree rings
- Chemistry of grasses

Chemistry of Atmospheric Aerosols

Deposition of Aerosols Onto Mass Bays

Co-Investigators

D. Golomb, UML

D. Ryan, UML

J. Underhill, UML

S. Zemba, Cambridge Environmental, Inc.

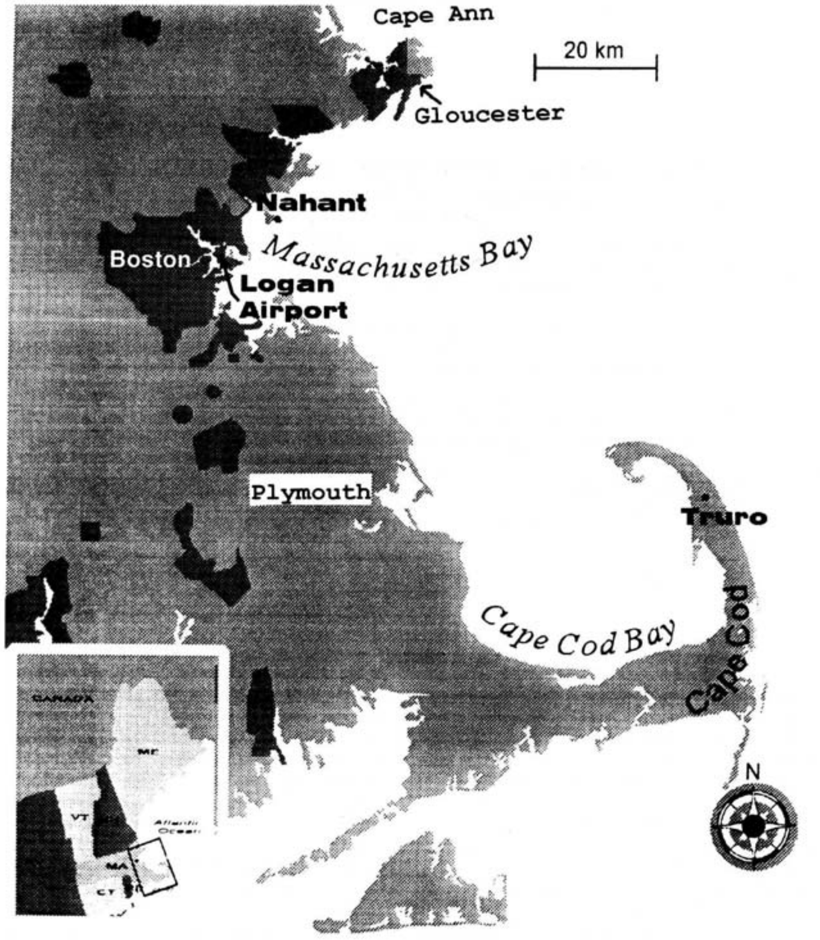


Fig. 1 Map of Massachusetts Bay. Nahant and Truro field sites are indicated. Shaded areas indicate population centers greater than 20,000 people.

Location of aerosol sampling sites – Nahant and Truro

Aerosol Sampling Location, Truro

Field site

Wet & Dry
Collectors

(Photographs courtesy
of Dr. David Ryan, UML)

Dichot sampler

Dry and wet total deposition amounts were calculated for both sites. Atmospheric aerosols were major contributors of Fe, Mn, Zn, and Cd to Mass Bays. For most metals dry deposition was greater at Nahant presumably because of the close proximity of the site to Metropolitan Boston. Factor analysis was used to identify and apportion the sources of the aerosols.

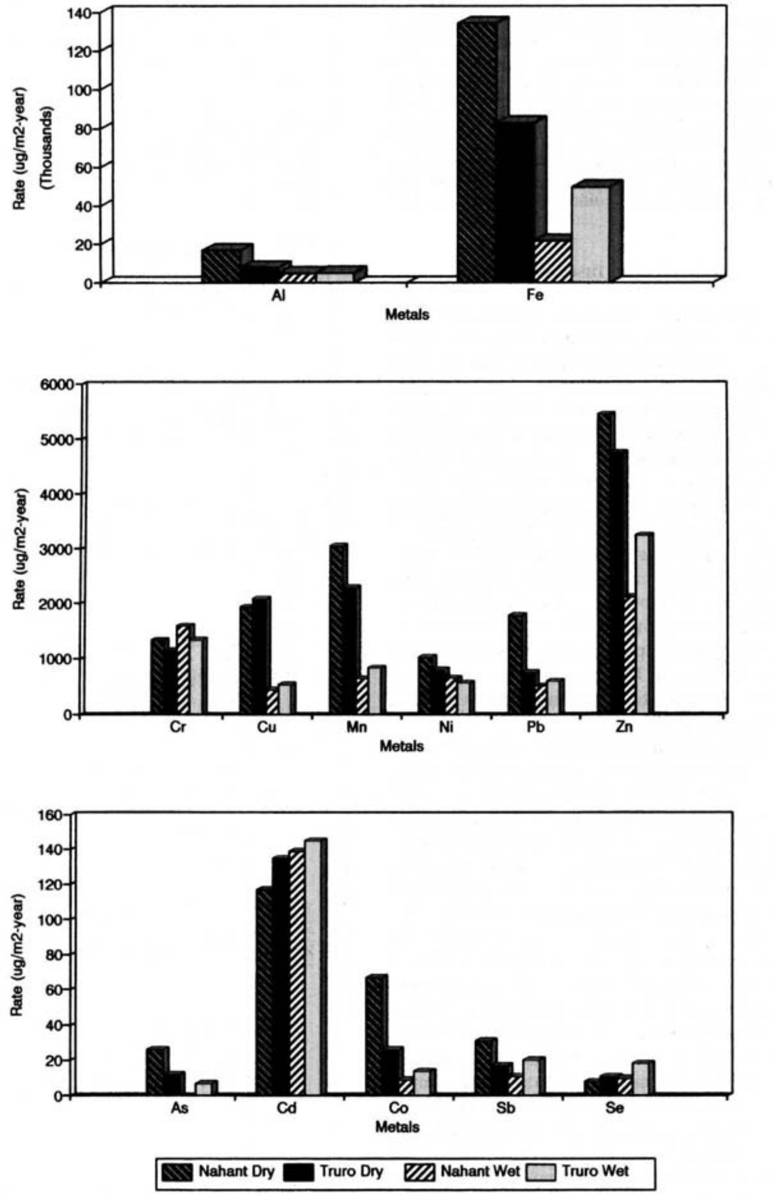


Fig. 3. Bar chart of annual deposition rates of metals ($\mu g\, m^{-2}\, yr^{-1}$). Note that not all metals were analyzed in all three fractions.

Rotated Factor Loadings for Nahant Dry Deposition

Element	**F1**	F2	F3	F4	Communality
As	**0.84**				75.3
Ce	**0.91**				87.8
Fe	**0.88**				89.1
La	**0.86**				86.9
Sc	**0.94**				93.9
Sm	**0.96**				94.7
Cd		0.83			80.5
Co		0.80			70.0
Cr		0.82			86.2
Cu		0.76			72.4
Ni		0.50	0.49		51.5
Al			0.60		46.3
Mn			0.46		46.8
Pb			0.72		52.1
Sb				0.70	71.3
Se				0.66	46.9
Zn				0.40	44.7
%Variance	**46.6**	18.9	11.0	6.1	82.7

F1 – automotive & crustal, F2 – oil combustion, F3 – soil, F4 – coal combustion & incineration.

Can we tell if F1 represents a crustal or automotive source?

Yes! The value of REE geochemistry

- Chondrite-normalized patterns are distinctive for different sources
- We use chondrite (a meteorite type representative of the composition of the earth's mantle) normalization to remove the variability in elemental abundances (Oddo-Harkins rule)

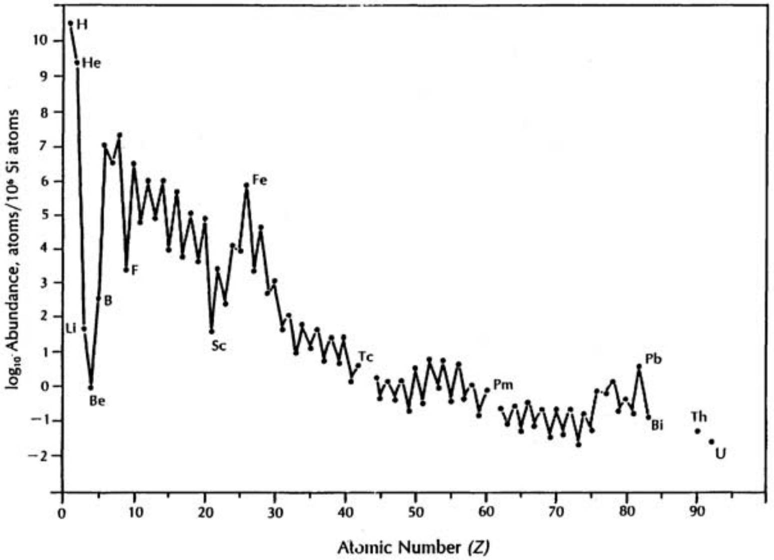
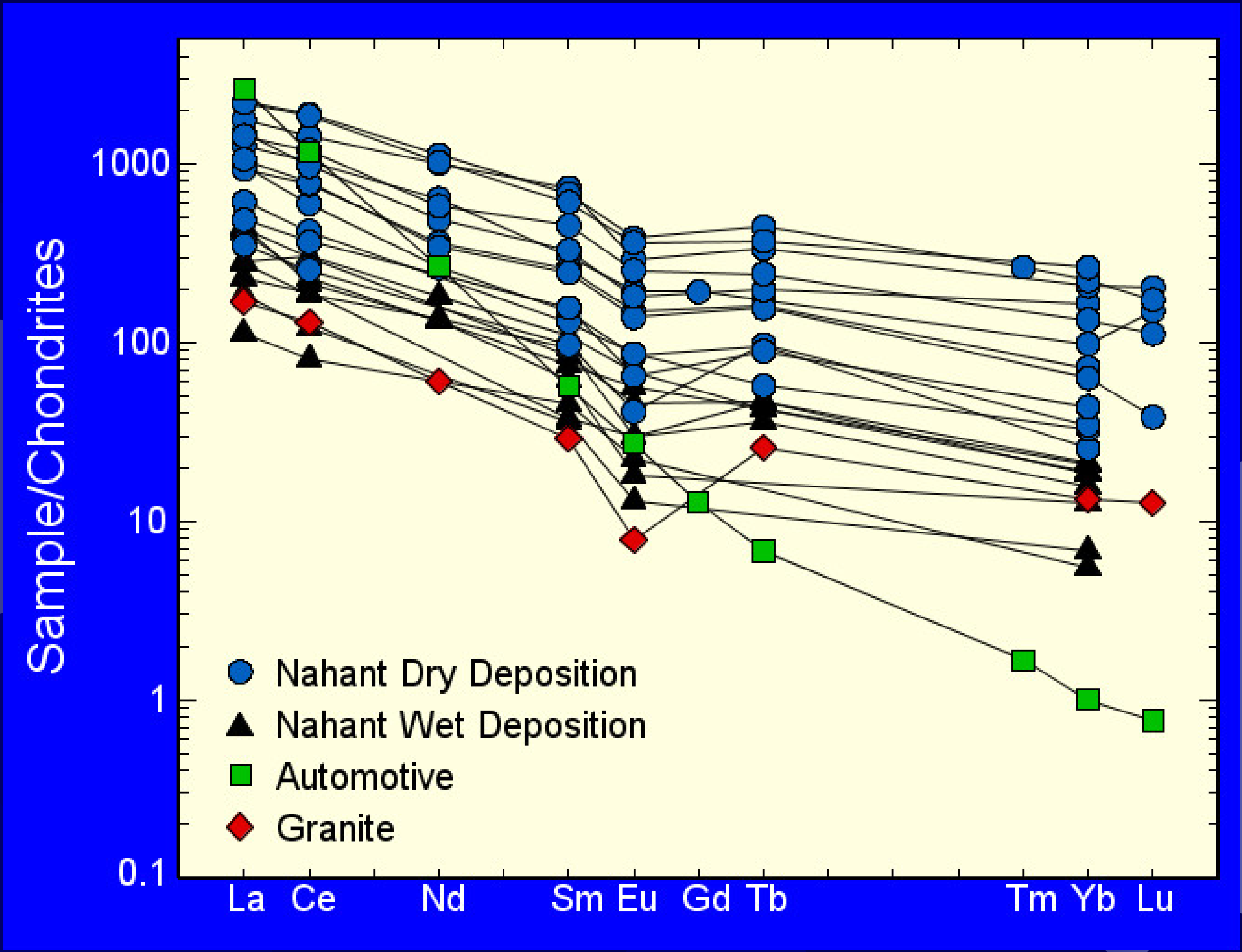
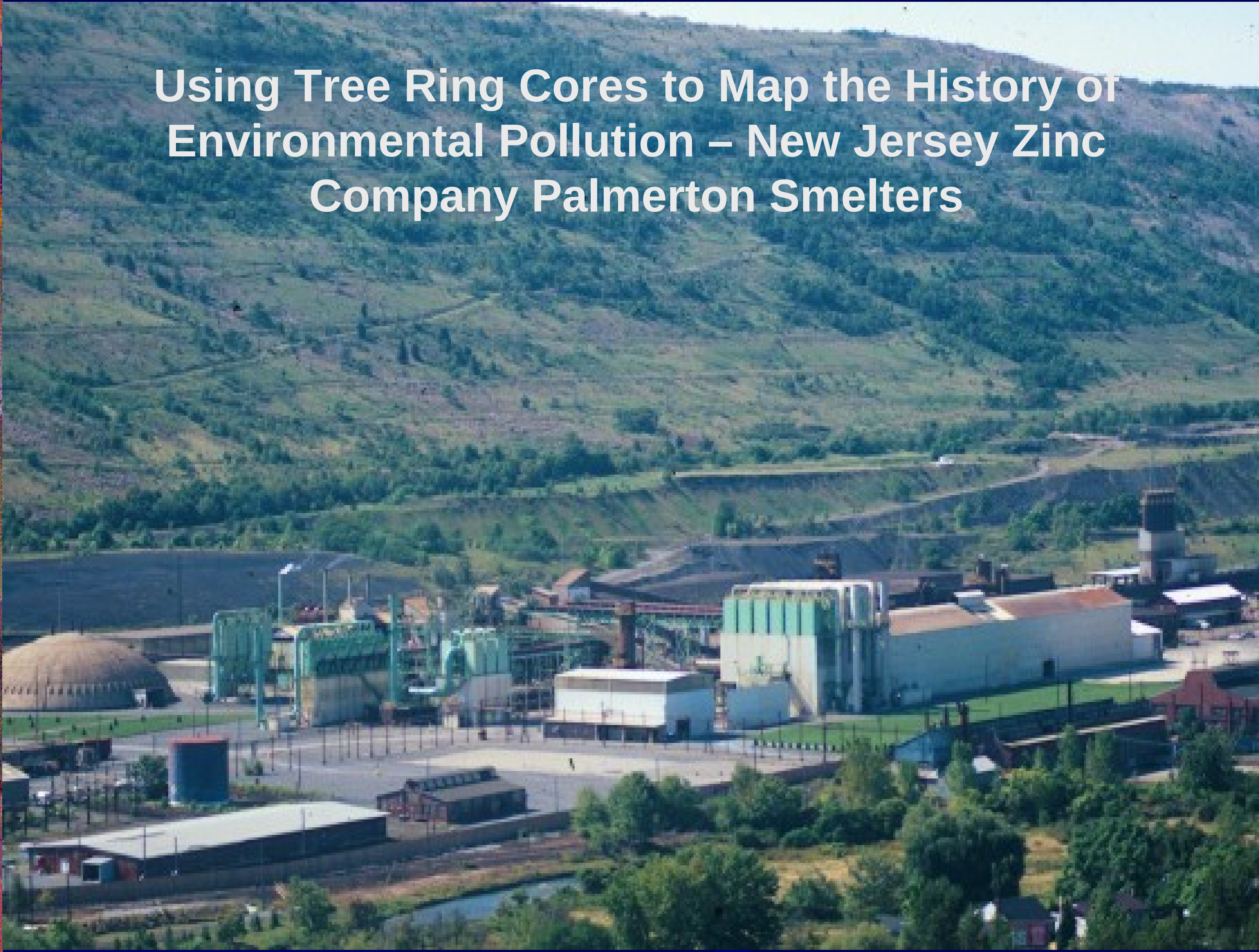


Figure 2.2 Abundances of the chemical elements in the solar system in terms of atoms per 10^6 atoms of Si. The data were derived primarily by analysis of carbonaceous chondrite meteorites and by optical spectroscopy of light from the Sun and nearby stars (Anders and Ebihara, 1982).

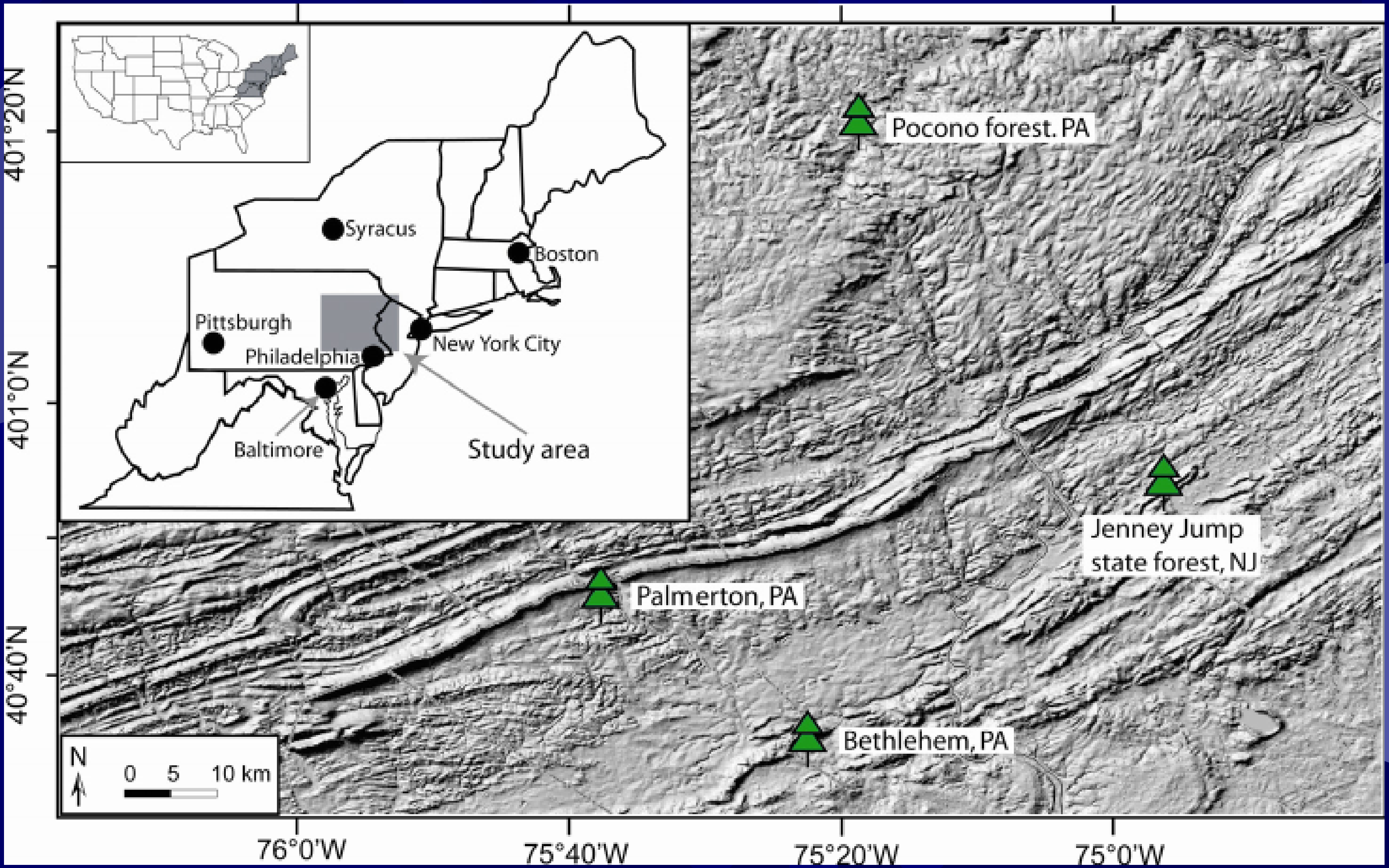


F1 is a crustal, not an automotive source

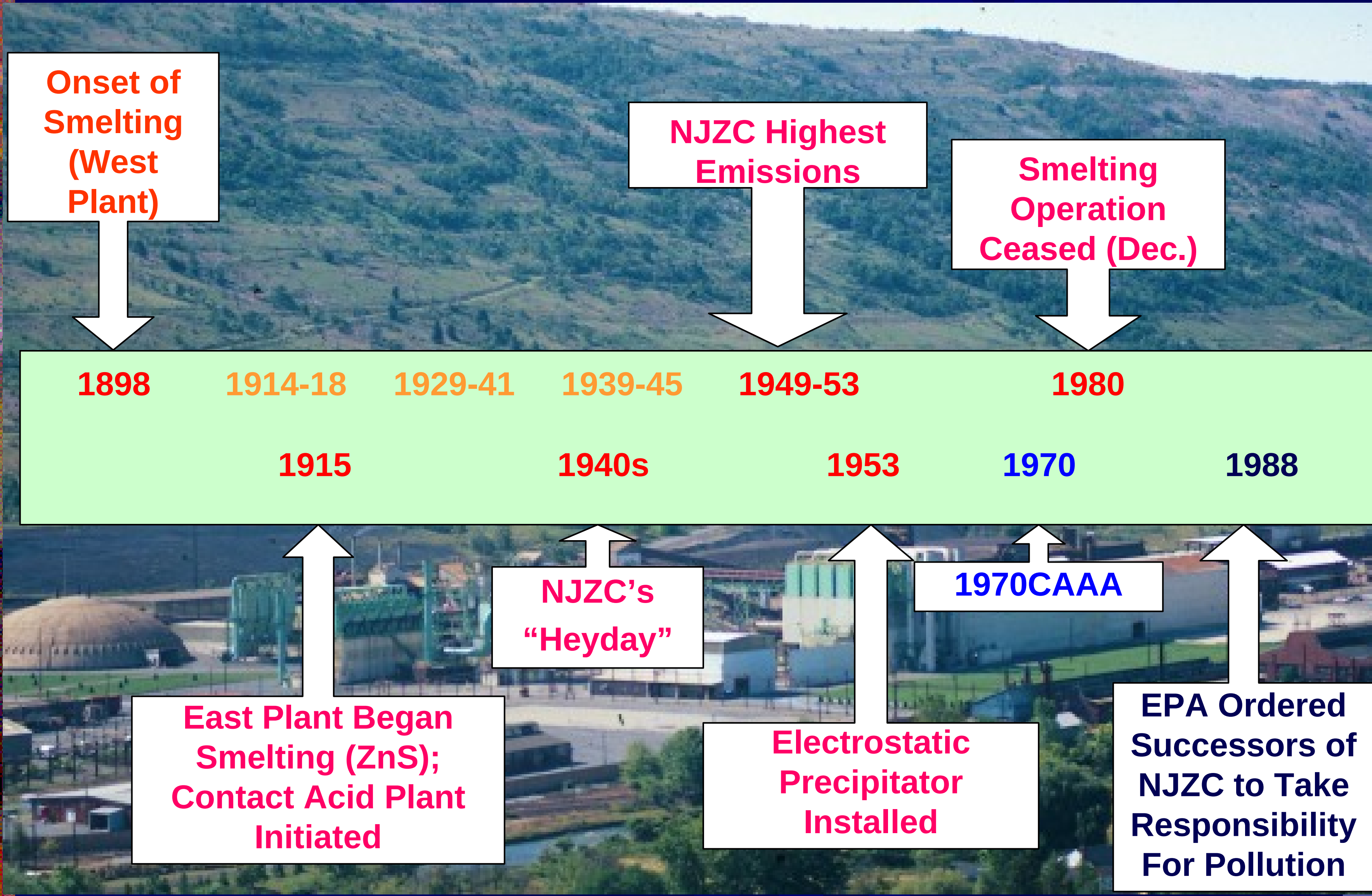
Using Tree Ring Cores to Map the History of Environmental Pollution – New Jersey Zinc Company Palmerton Smelters



Between 1898 and 1980 New Jersey Zinc had several operating smelters at Palmerton, PA. Electrostatic precipitators were installed in 1953.



Smelter Operations at Palmerton, PA



Onset of Smelting (West Plant)

NJZC Highest Emissions

Smelting Operation Ceased (Dec.)

1898 1914-18 1929-41 1939-45 1949-53 1980

1915 1940s 1953 1970 1988

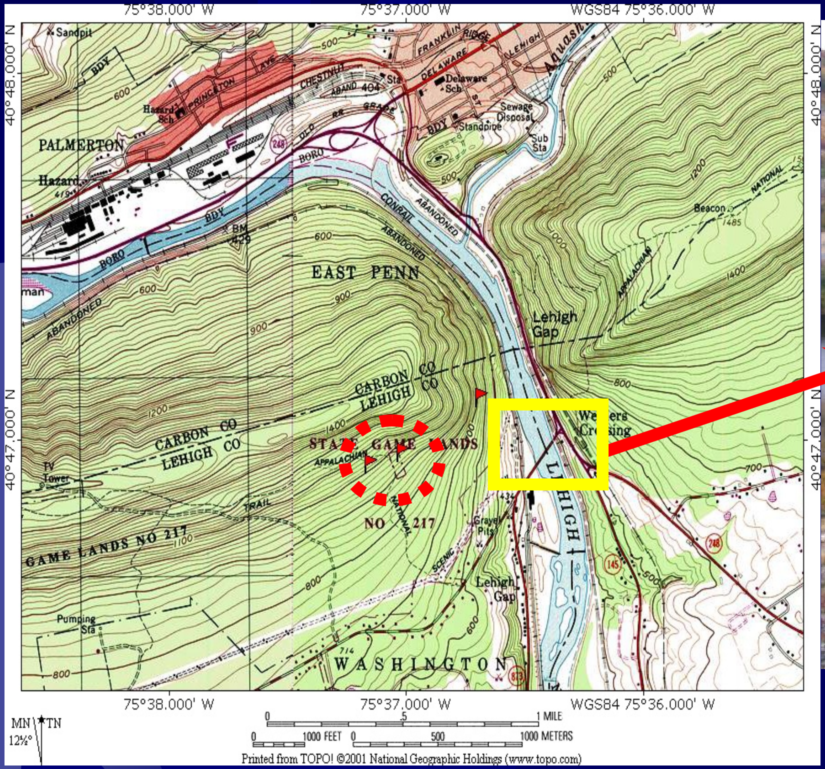
East Plant Began Smelting (ZnS); Contact Acid Plant Initiated

NJZC's "Heyday"

Electrostatic Precipitator Installed

1970CAAA

EPA Ordered Successors of NJZC to Take Responsibility For Pollution



Sampling: Kittatinny Ridge; adjacent to West Plant

West Plant → Northern bank of Lehigh River

East Plant → Southern bank of Aquashicola Creek

Surrounding Landscape → Severely damaged (multiple causes)

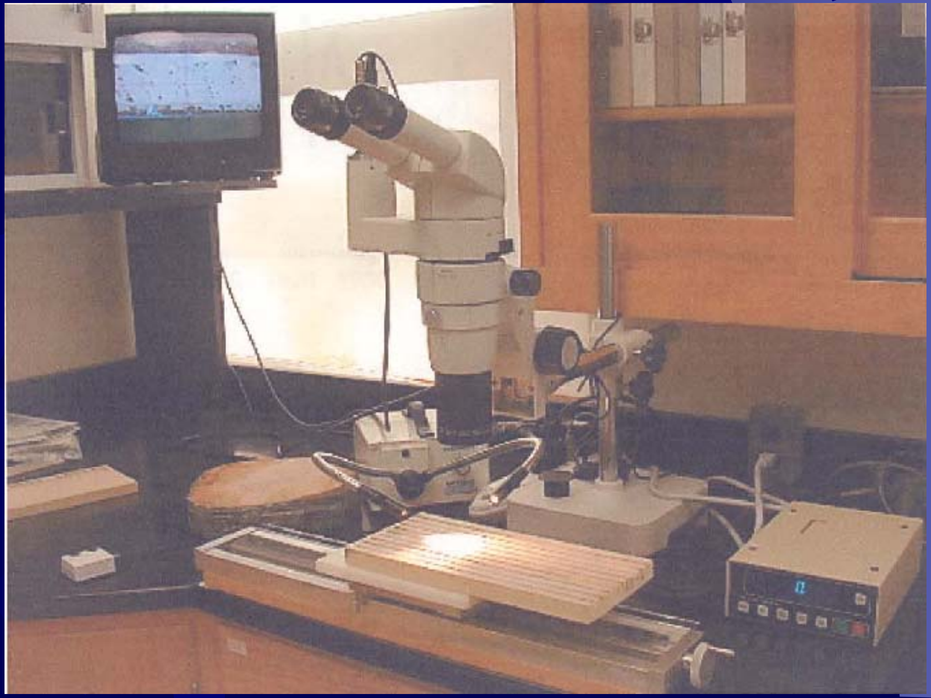
Tree Coring and Ring Width Measurements

→ **Increment borers**

17 Red Oak trees

8 Chestnut Oak trees

2 cores/tree



Metals released during smelter operation can be delivered to trees by

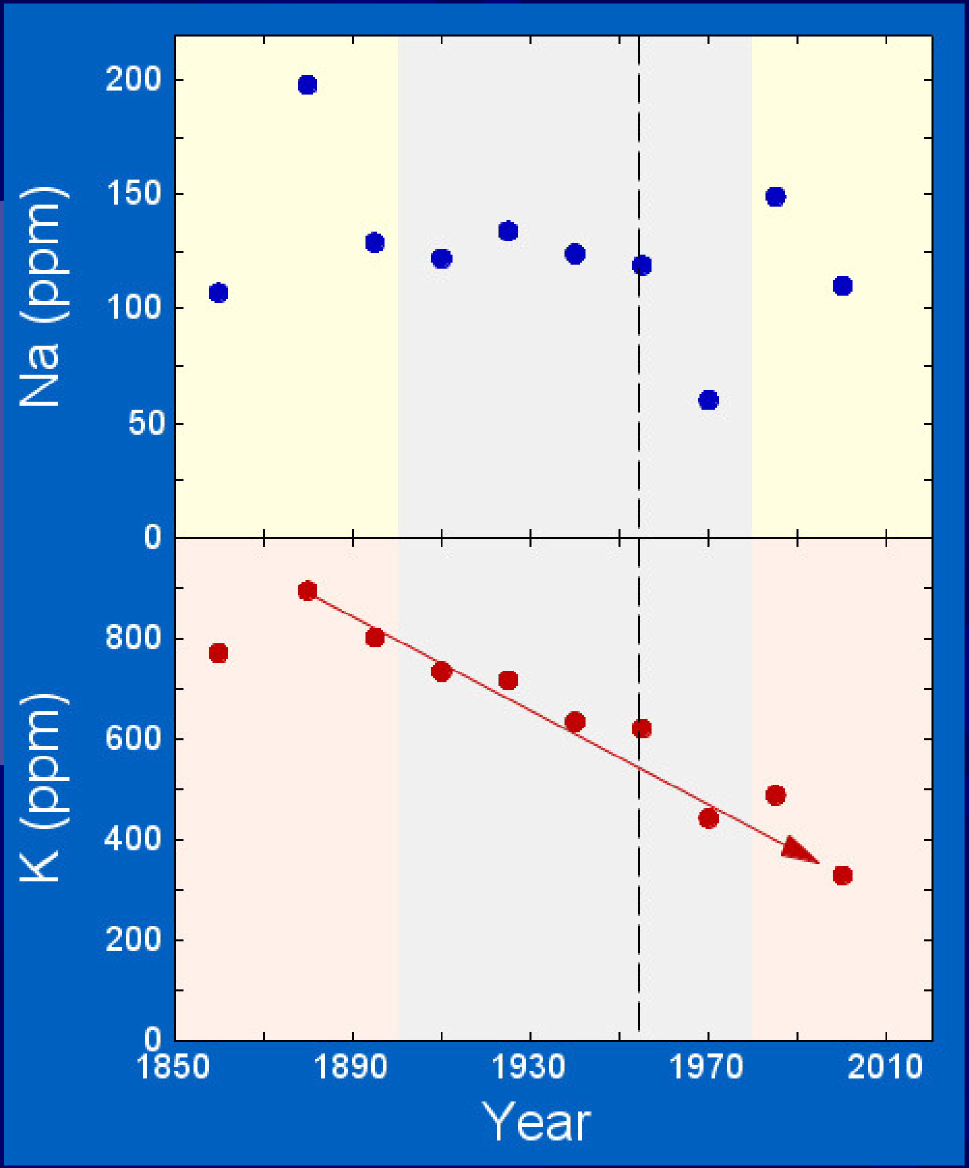
1. Direct deposition on leaves.
2. Through the soil-root interface.

Trace Elements in tree ring core samples were analyzed by INAA

10 selected subsamples

5-yr incrementally pooled samples from a *Chestnut Oak were analyzed by INAA.*

Na and K versus Time

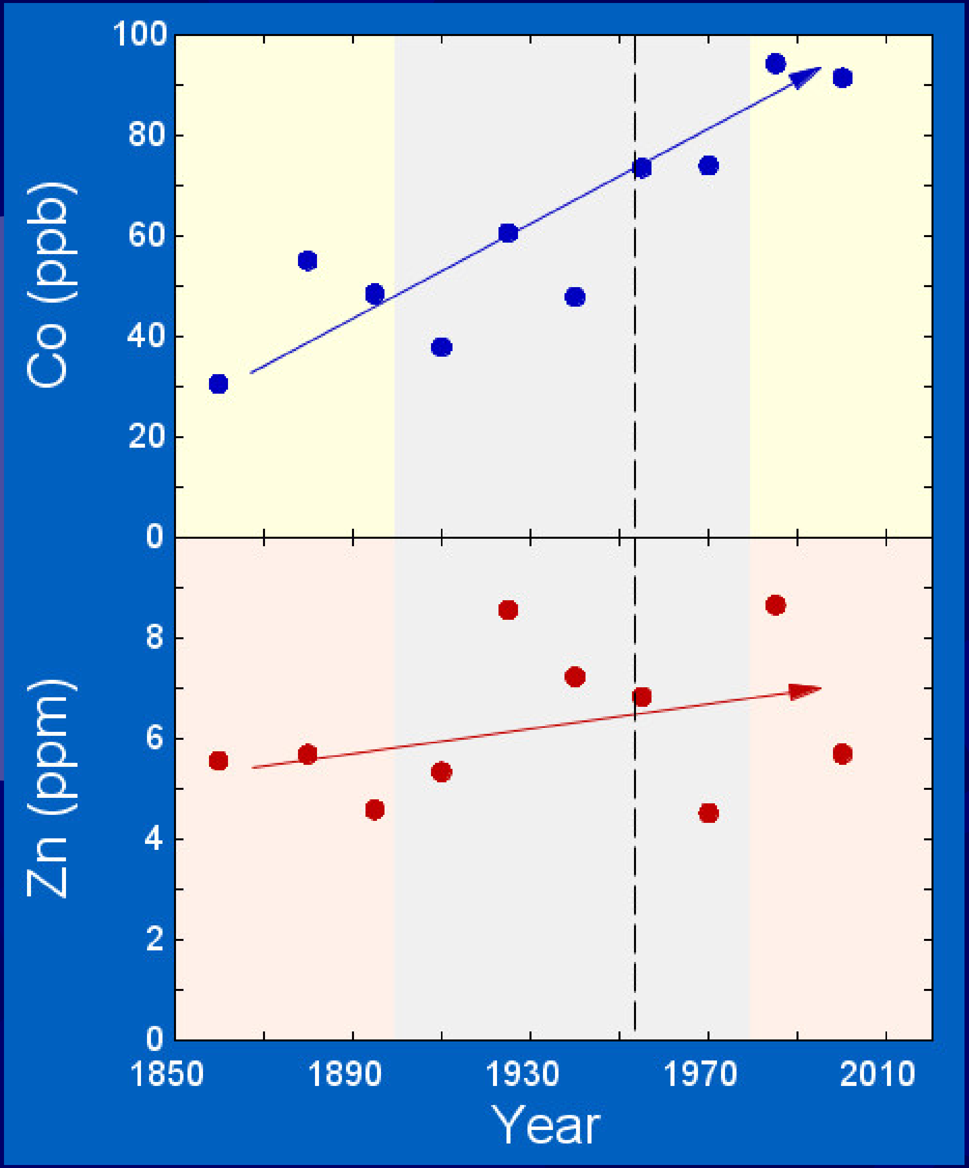


Area shaded gray represents the time during which the smelters were active.

Dashed line denotes the year in which precipitators were installed and the Franklin mine closed. Franklin Furnace ores were no longer smelted in Palmerton

Na shows no trend, but during the time smelting was done at Palmerton **K** declined. This decline continued after smelting ceased. **K** is a nutrient element and the data suggest that this element was depleted with time. Such a depletion would lead to stress on the tree. Stable isotope and tree ring widths also indicate that the tree was under stress during the time of smelter operation.

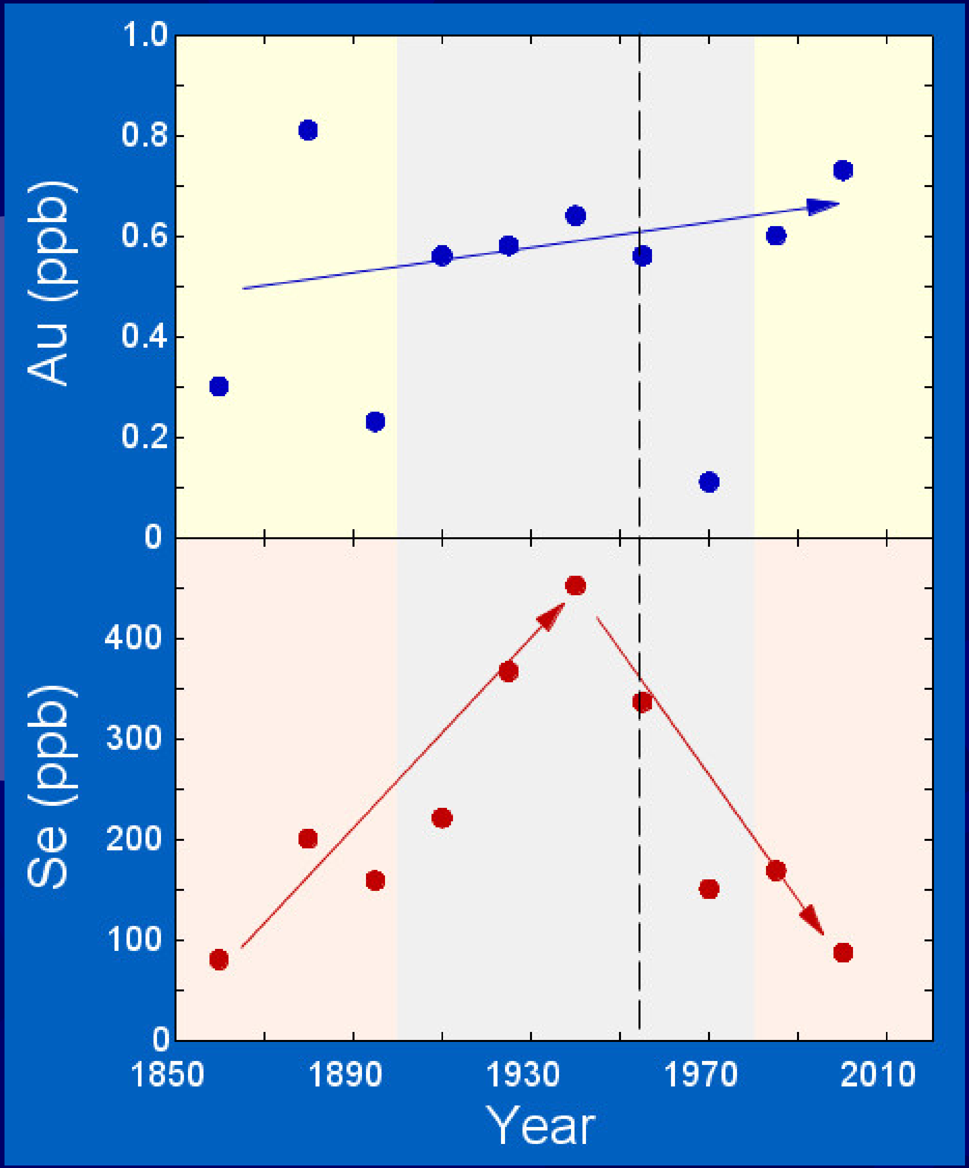
Co and Zn versus Time



Co increases throughout the time of smelter operation and the increase continues after cessation of smelting.

Zn, which was the major metal emission, shows an irregular pattern but general increase with time. The most recent tree ring increment indicates that **Zn** uptake is decreasing.

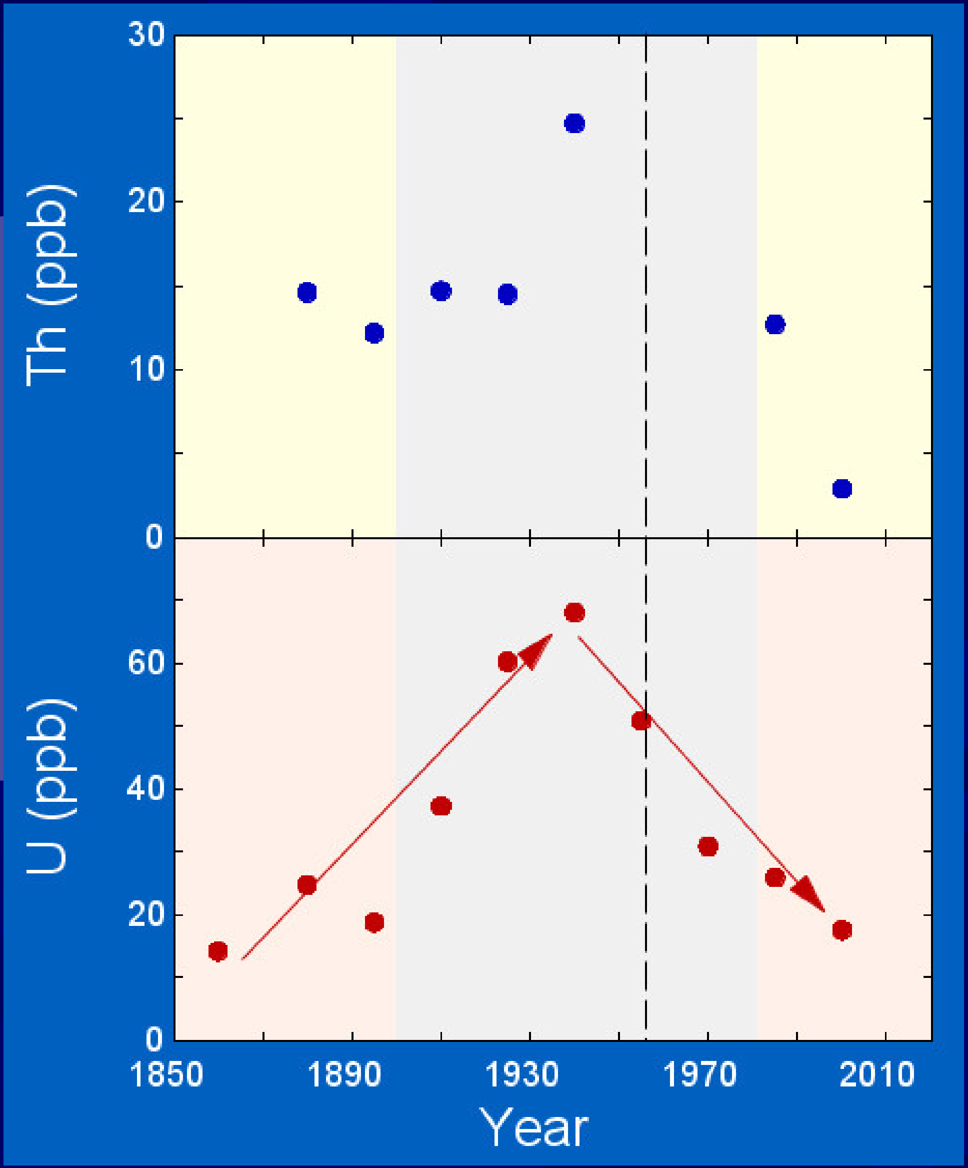
Au and Se versus Time



Au generally increases during the period of smelter operation.

Se, as do a number of other metals (subsequent slides) initially shows an increase and then a decrease. The change in behavior roughly corresponds to the time when (1) precipitators were installed and (2) ores from Franklin Furnace were no longer smelted at Palmerton. After cessation of smelter operation **Se** returns to pre-smelter levels.

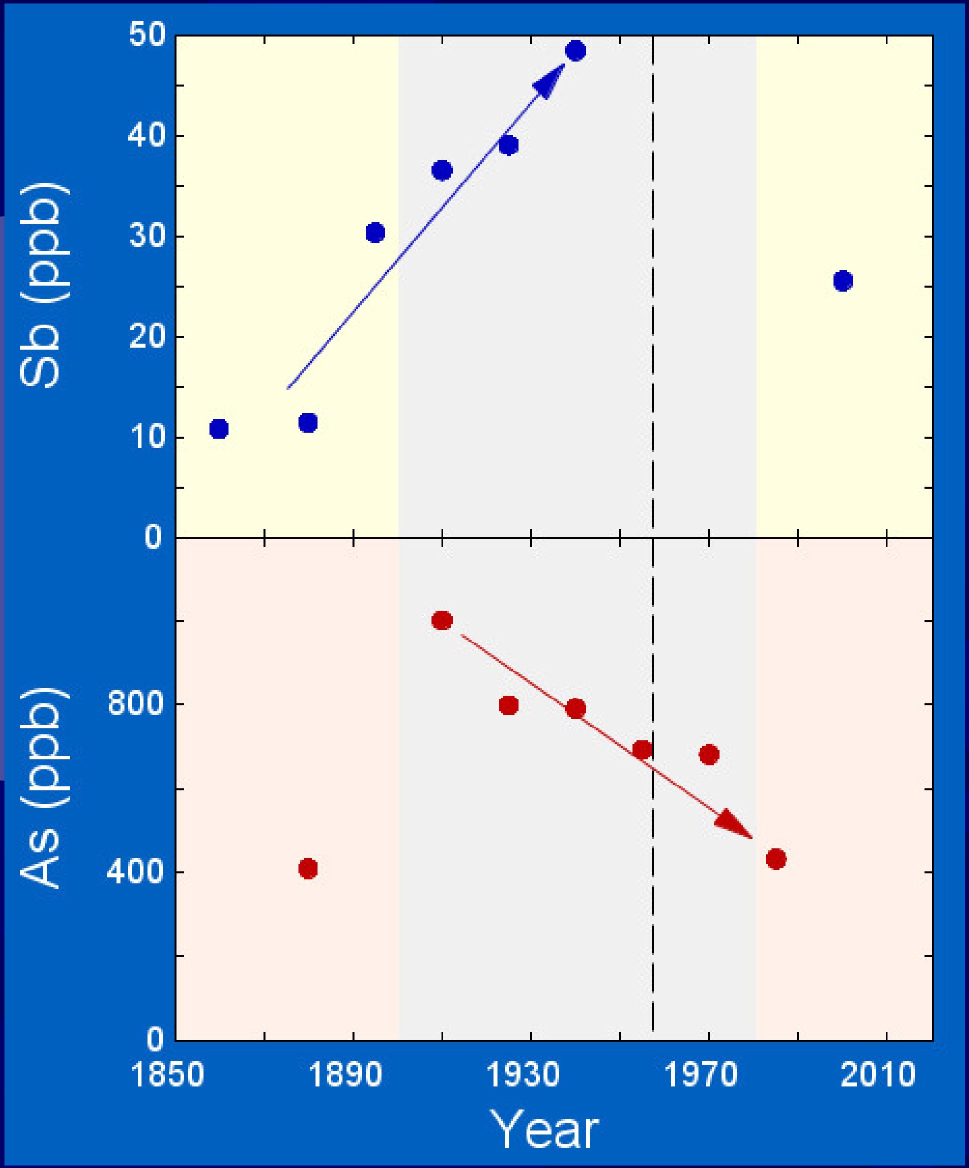
Th and U versus Time



Th variations with time are erratic.

U initially shows an increase and then a decrease. A similar pattern to that shown by **Se**. After cessation of smelter operation, **U** returns to pre-smelter levels.

Sb and As versus Time



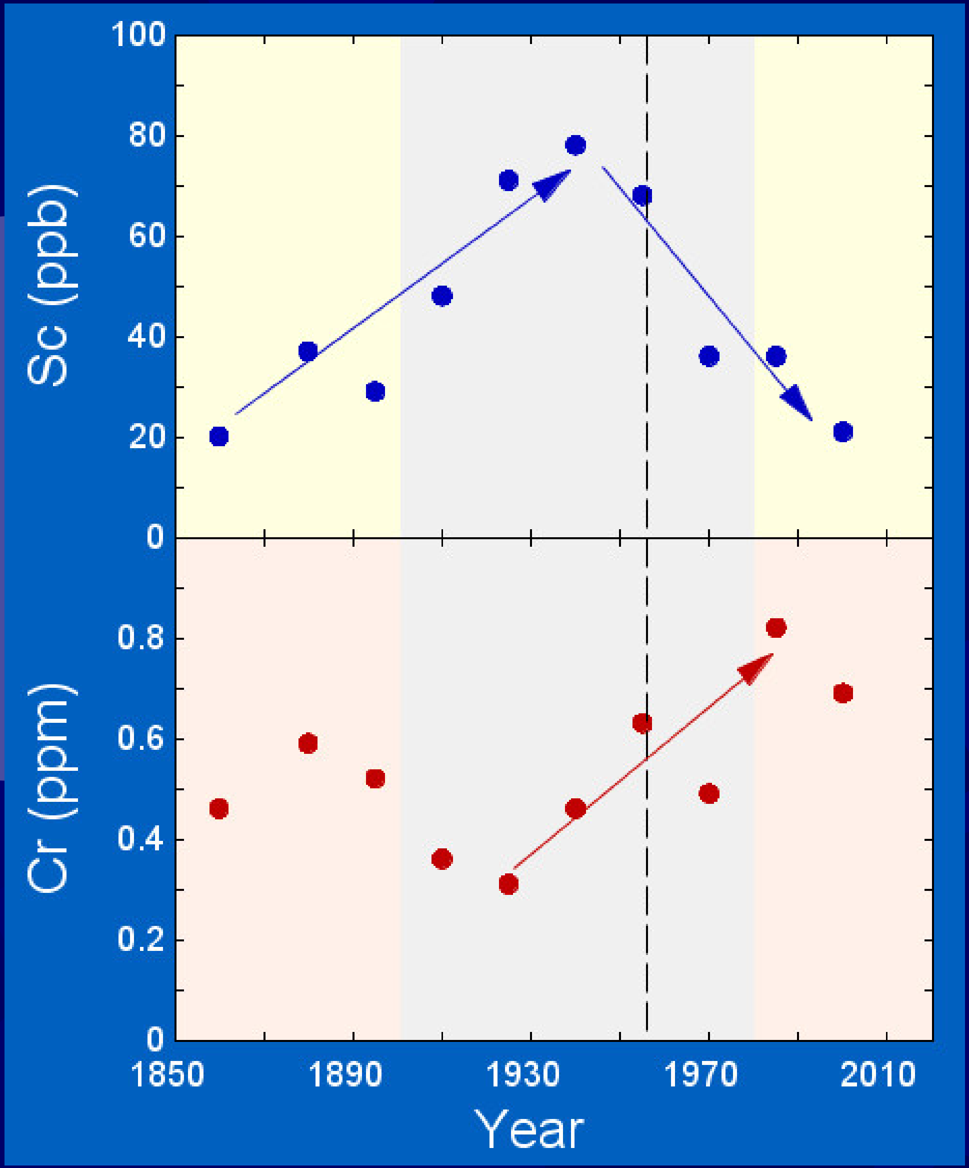
Sb and **As** show antithetical behavior with time.

Sb gradually increases over the time of smelter operation, although we do not have data for the later time periods.

As shows a sharp increase at the start of smelter operation and then decreases with time. This may reflect rapid removal of **As** from the soil.

After cessation of smelter operation, both elements return to near pre-smelter levels.

Sc and Cr versus Time



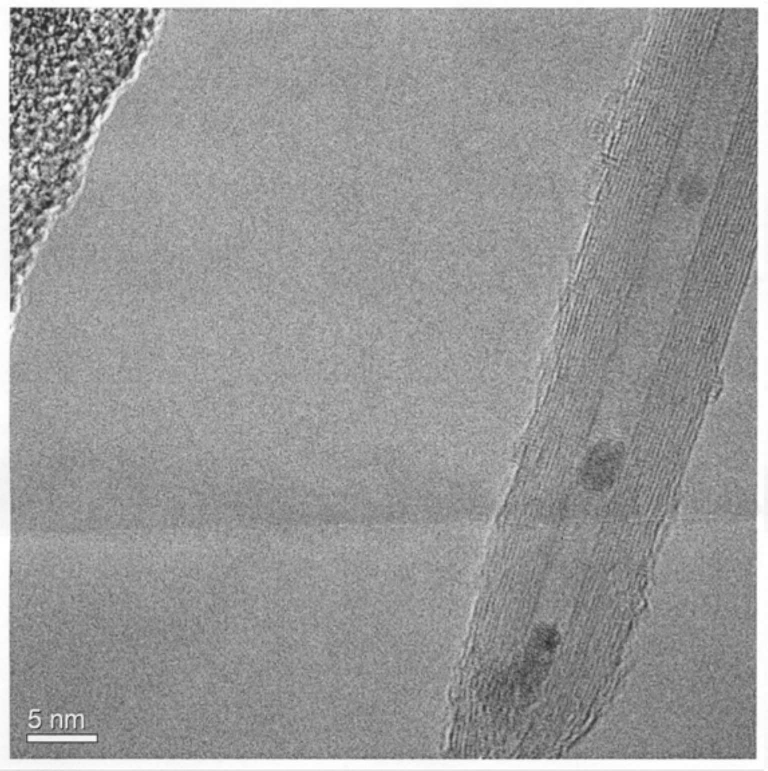
Sc initially increases and then decreases to pre-smelter operation concentrations.

Cr initially shows irregular variation with time and then increases towards the present.

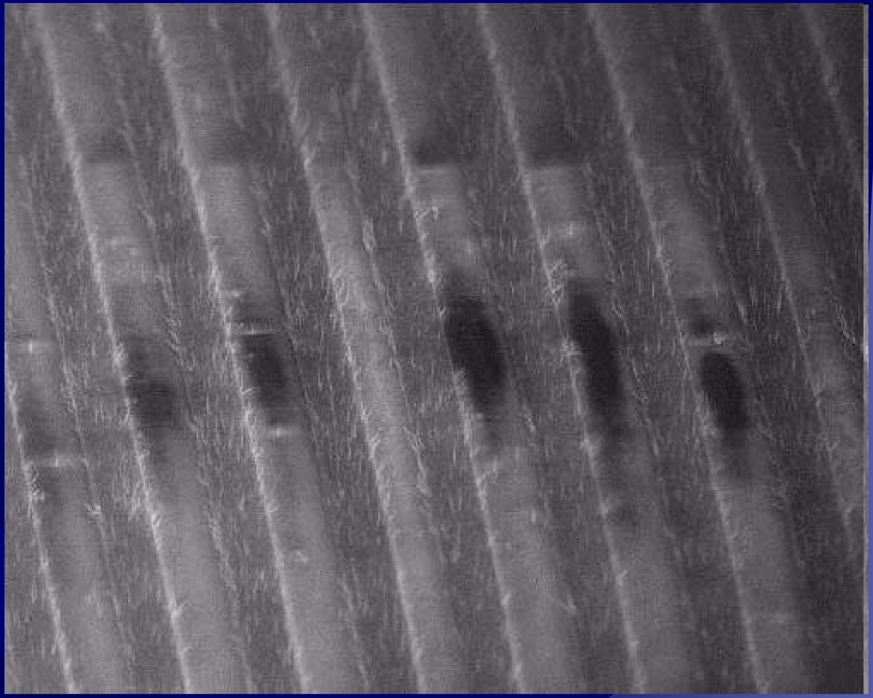
Summary

- Variations in trace metal concentrations in tree rings reflect anthropogenic inputs. These variations can be complex.
- Decrease in K during the entire time of smelter operation most likely represents leaching of K from the soil. Large amounts of sulfur dioxide were emitted during smelter operation which led to local acid rain.
- Se, U, and Sc show a complex behavior initially increasing and then later in the tree ring record decreasing in abundance. This change in behavior roughly corresponds with the installation of precipitators and the cessation of smelting of Franklin Furnace ores. If these trace metals largely enter the tree by deposition on leaves the installation of the precipitators may account for the decrease in metal concentration.
- Co, Cr, and Zn generally increase throughout the period of smelter operation.
- In the 20+ years since the cessation of smelter operation, As, Sc, Se, U, and Zn have returned to pre-smelter concentrations. The other trace metals are still found at elevated levels in the tree rings.

Chemistry of carbon nanotubes



This image is a 12 nanometer carbon nanotube, filled with several 3-4 nm cobalt nanoparticles.



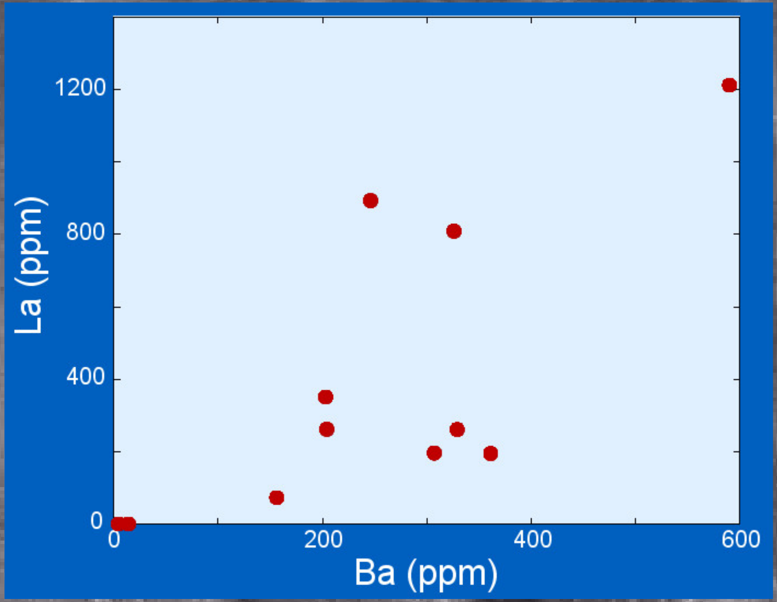
Aligned carbon nanotubes (10 microns long) on Chromium lines (~10 micron wide) at site density about 5x106/cm2. The whole structure was fabricated on a glass substrate.

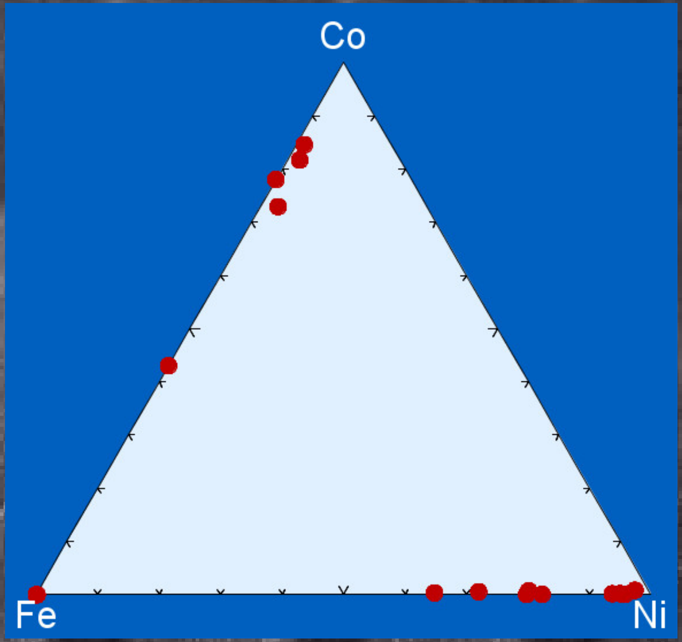
Chemistry of a variety of carbon nanotubes. Note the distinctive chemical compositions which reflect the catalysts/substrates used to manufacture the nanotube and the added components.

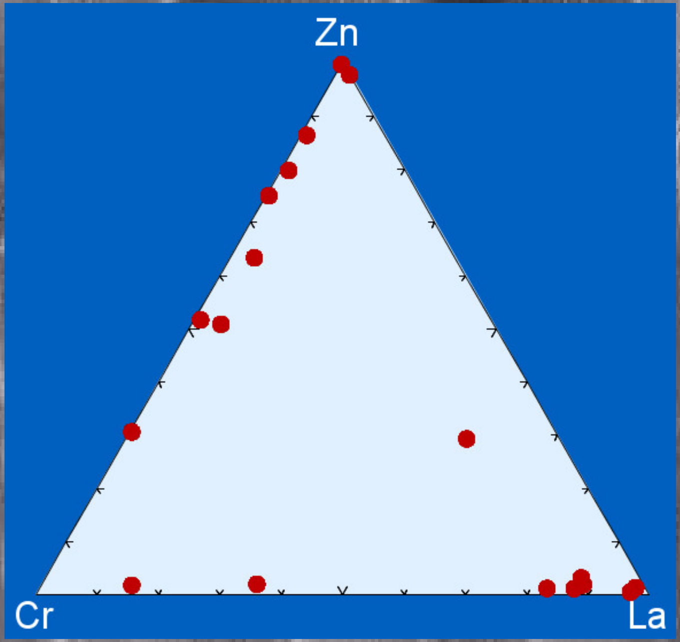
Samp	Fe	Cr	Co	Ni	Zn	Ba	La	Ce	Nd	U	As	Sb	W	Ag	Au
NT1	715	57	3585	89	240	nd	4.1	nd	nd	0.18	0.11	0.11	nd	nd	0.47
NT2	1207	19.2	45	4938	17.6	590	1212	0.21	nd	nd	nd	0.06	nd	20.8	nd
NT3	3293	38	8	12992	3	307	196	0.24	nd	nd	0.65	0.24	2.13	0.13	nd
NT4	6080	53	63	11219	103	361	195	0.15	nd	0.08	0.83	0.1	nd	17.5	nd
NT5	1133	414	34.5	17077	9.4	156	73	0.22	nd	0.04	0.02	0.06	0.53	nd	1.44
NT6	660	44	3952	63	299	nd	3.3	nd	0.1	0.2	nd	0.19	nd	2.47	nd
NT7	408	39	18.4	7816	7.7	203	351	1.7	nd	nd	nd	0.13	nd	3.53	nd
NT8	5124	471	102	13238	15.3	204	262	0.98	nd	nd	nd	0.32	0.3	nd	nd
NT9	909	23.7	2	4220	5	326	809	5.3	nd	nd	1.48	0.13	nd	nd	nd
NT10	1099	35	14.5	24833	3.7	329	261	0.77	nd	nd	nd	0.17	0.15	5.97	nd
NT11	308	97	116	13737	33	246	893	0.19	nd	nd	nd	0.07	0.25	0.57	nd
NT12	24496	5.4	2.3	31	5.9	14	0.12	0.3	20.5	nd	0.02	0.07	1.05	0.38	5.73
NT13	25229	8	1	nd	2073	nd	0.63	nd	9.1	nd	0.05	0.08	1.47	nd	12.7
NT14	899	114	2710	107	221	nd	13.8	nd	8.7	0.41	0.2	0.58	5.2	nd	2.19
NT15	841	180	2982	nd	206	nd	19.2	nd	nd	0.14	0.15	0.12	0.26	nd	nd
NT16	90760	48	1.7	22.5	21.3	4.4	0.24	0.46	nd	nd	0.15	2.38	0.14	3.18	4.14
NT18	82171	3.4	0.9	10.5	10.4	nd	0.07	0.19	nd	nd	0.1	0.06	nd	0.79	12.5
NT19	187	nd	141	nd	5.9	nd	0.14	0.27	0.2	nd	nd	0.03	0.25	3.27	1.22
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb

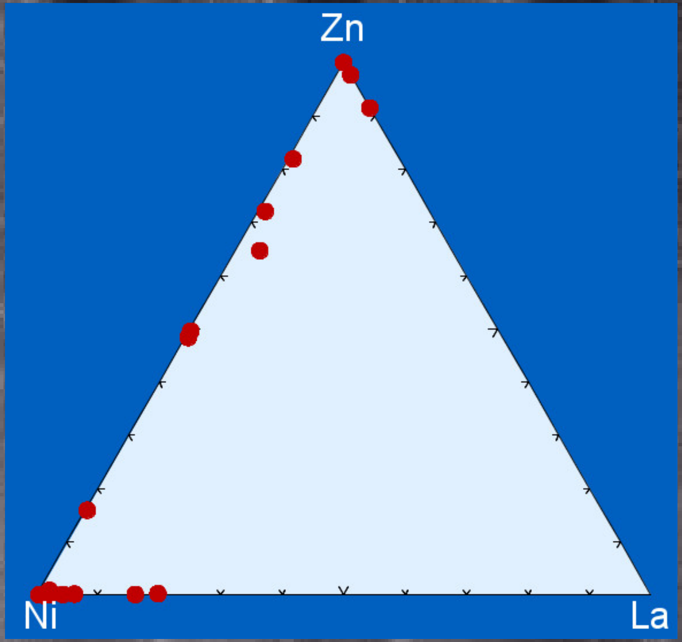
Department Environmental, Earth, & Atmospheric Sciences

Chemical data for carbon nanotubes









Forensics – Source of the Maple Syrup

Collecting sap the old fashioned way

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

Transferring sap to the sugar house

Sap holding vats

Boiling down the sap

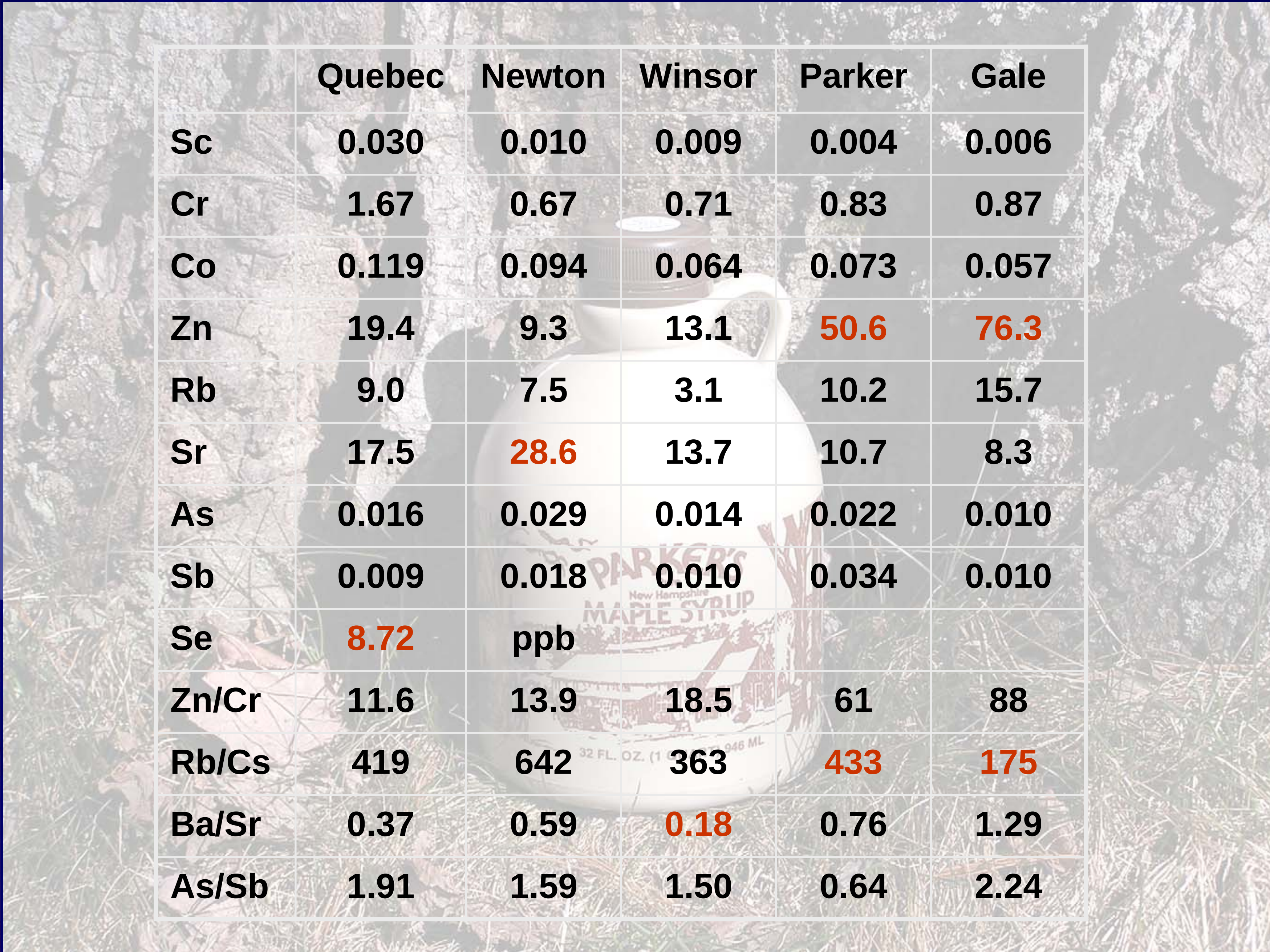
Syrup production line

Main boiler

Secondary boiler

Finish boiler

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



	Quebec	Newton	Winsor	Parker	Gale
Sc	0.030	0.010	0.009	0.004	0.006
Cr	1.67	0.67	0.71	0.83	0.87
Co	0.119	0.094	0.064	0.073	0.057
Zn	19.4	9.3	13.1	50.6	76.3
Rb	9.0	7.5	3.1	10.2	15.7
Sr	17.5	28.6	13.7	10.7	8.3
As	0.016	0.029	0.014	0.022	0.010
Sb	0.009	0.018	0.010	0.034	0.010
Se	8.72	ppb			
Zn/Cr	11.6	13.9	18.5	61	88
Rb/Cs	419	642	363	433	175
Ba/Sr	0.37	0.59	0.18	0.76	1.29
As/Sb	1.91	1.59	1.50	0.64	2.24

Serengeti burning and animal behavior – chemistry of grasses

Collaborative project with **S. Eby, Syracuse University**

Location map for Tanzania National Parks

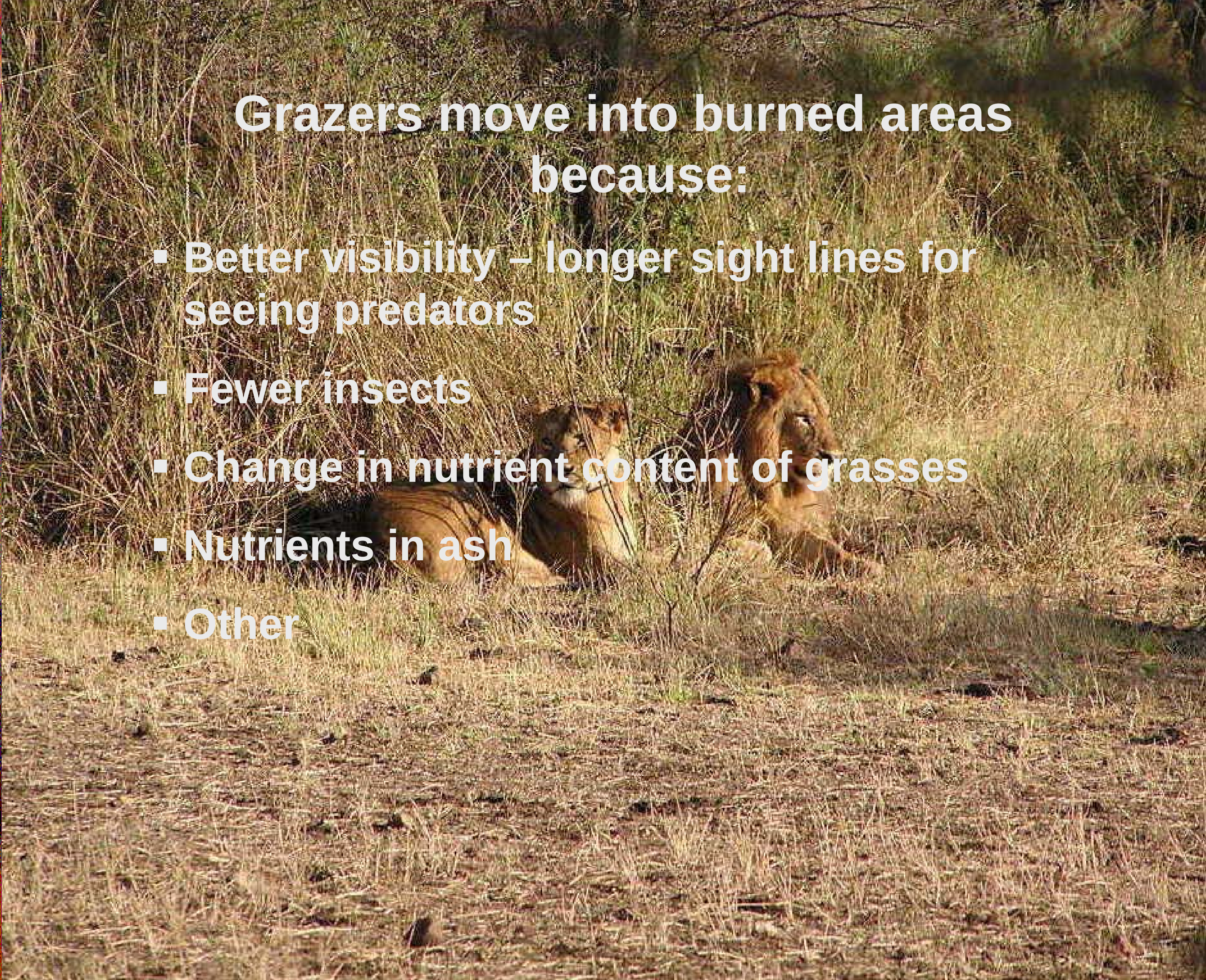
Prey

Predators

Fire management plan – controlled burning

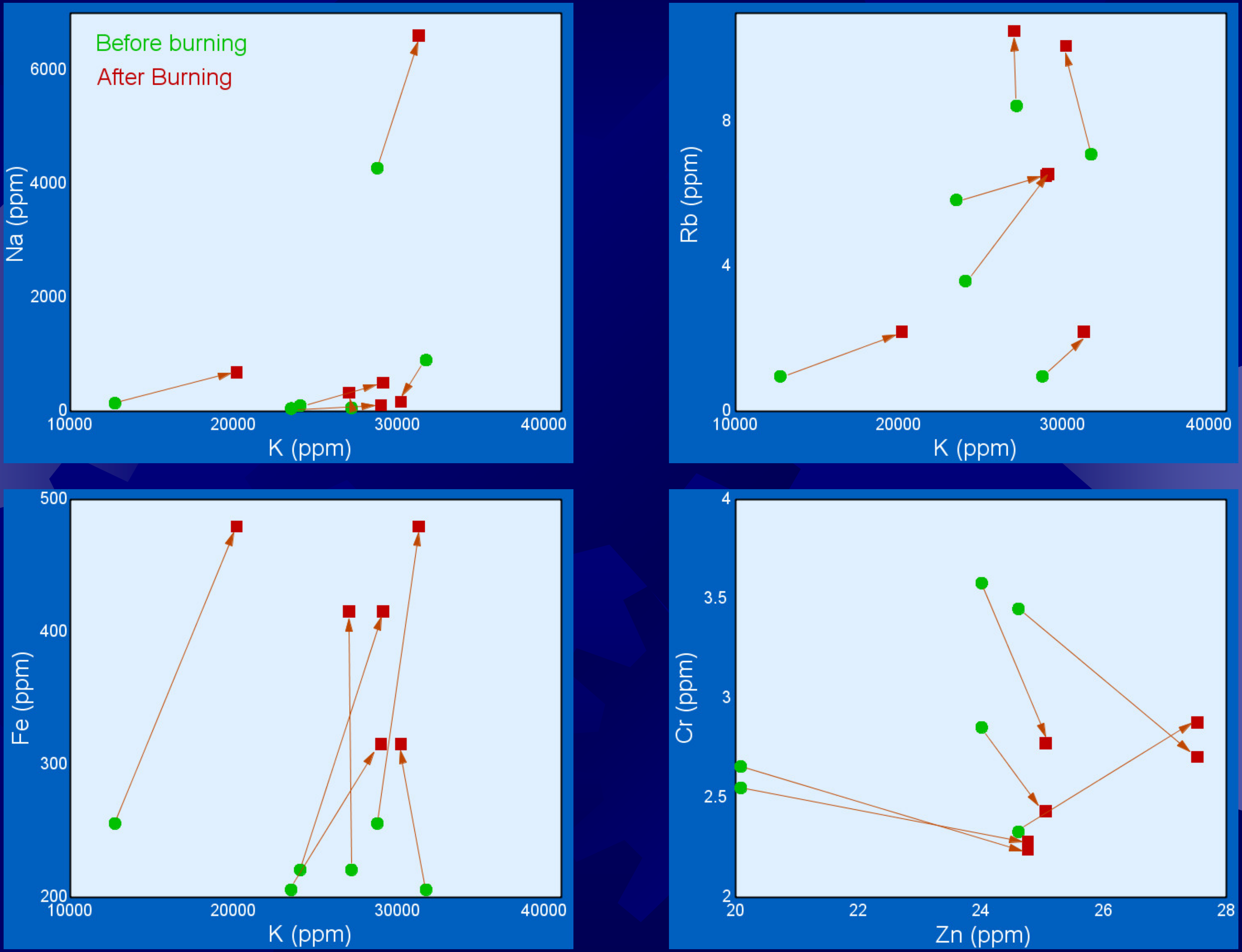
Animals rapidly move to burned areas – why?

Grazers move into burned areas because:

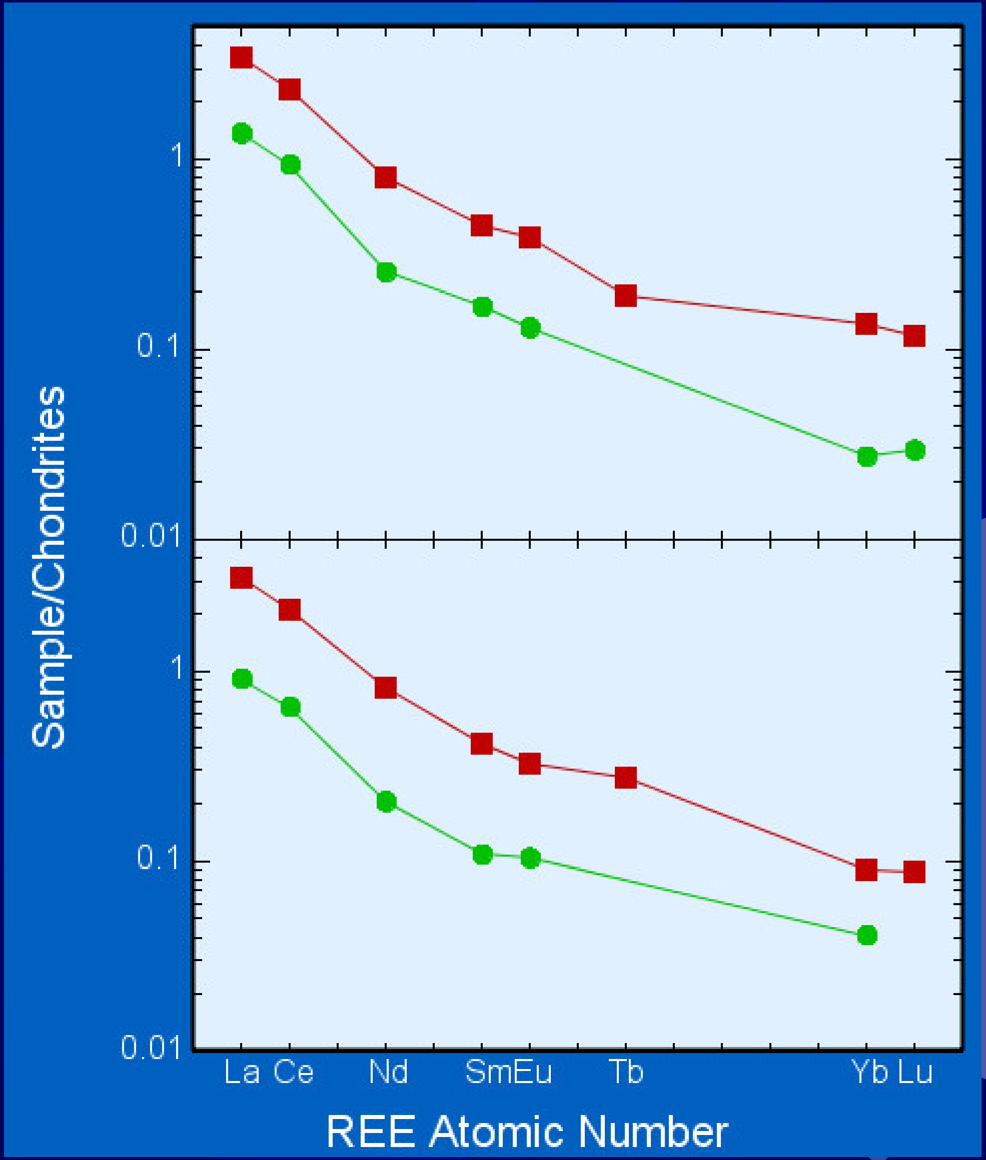


- Better visibility – longer sight lines for seeing predators
- Fewer insects
- Change in nutrient content of grasses
- Nutrients in ash
- Other

Change in elemental concentrations in grasses before and after an area is burned. In most cases elemental concentrations increase after burning. The notable exception is Cr.

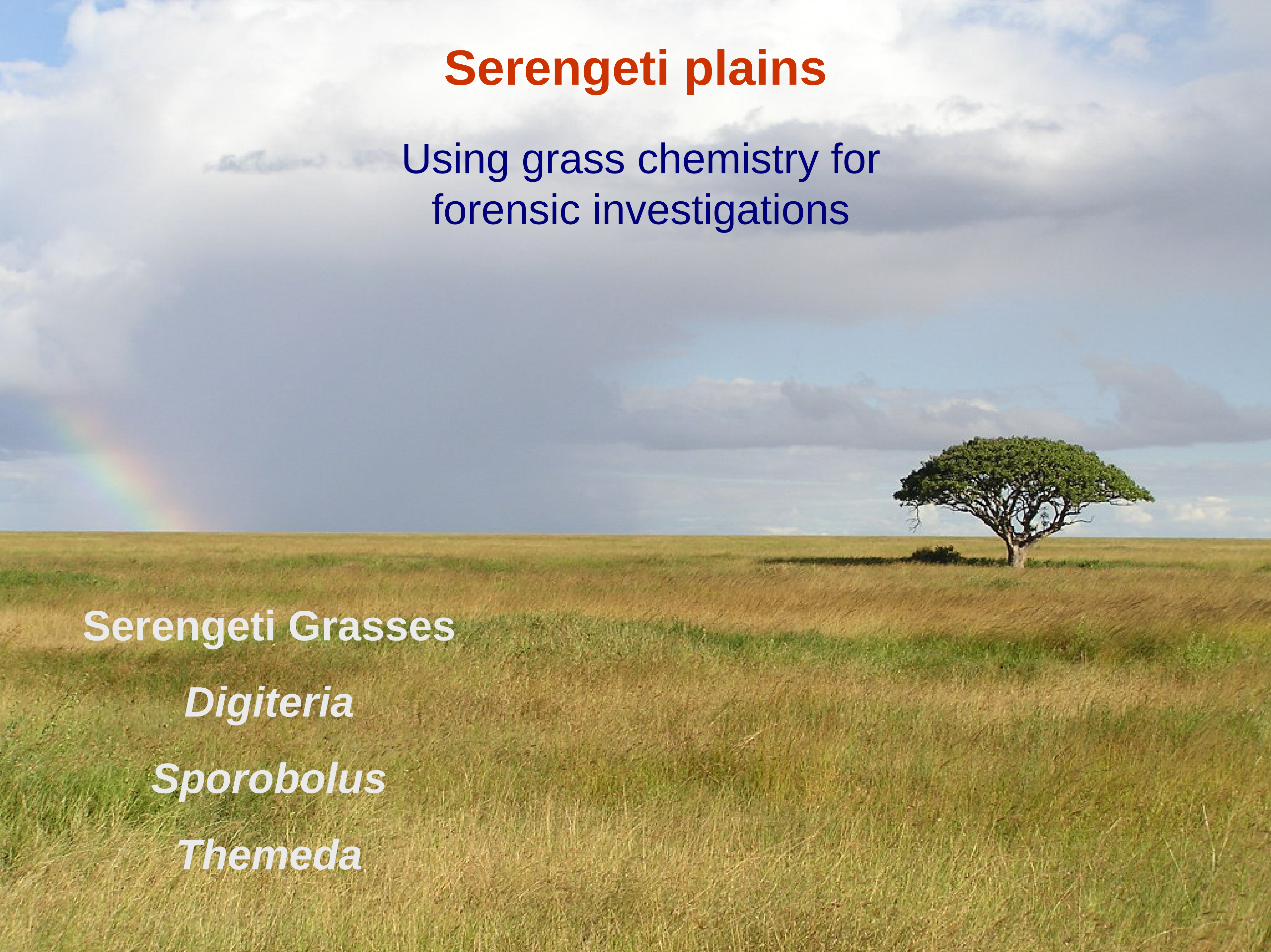


First ever REE concentrations determined for Serengeti grasses. Concentrations are in the range 1000 to 10 nanograms. REE patterns reflect REE concentrations of the underlying weathered volcanic ash.



Serengeti plains

Using grass chemistry for forensic investigations



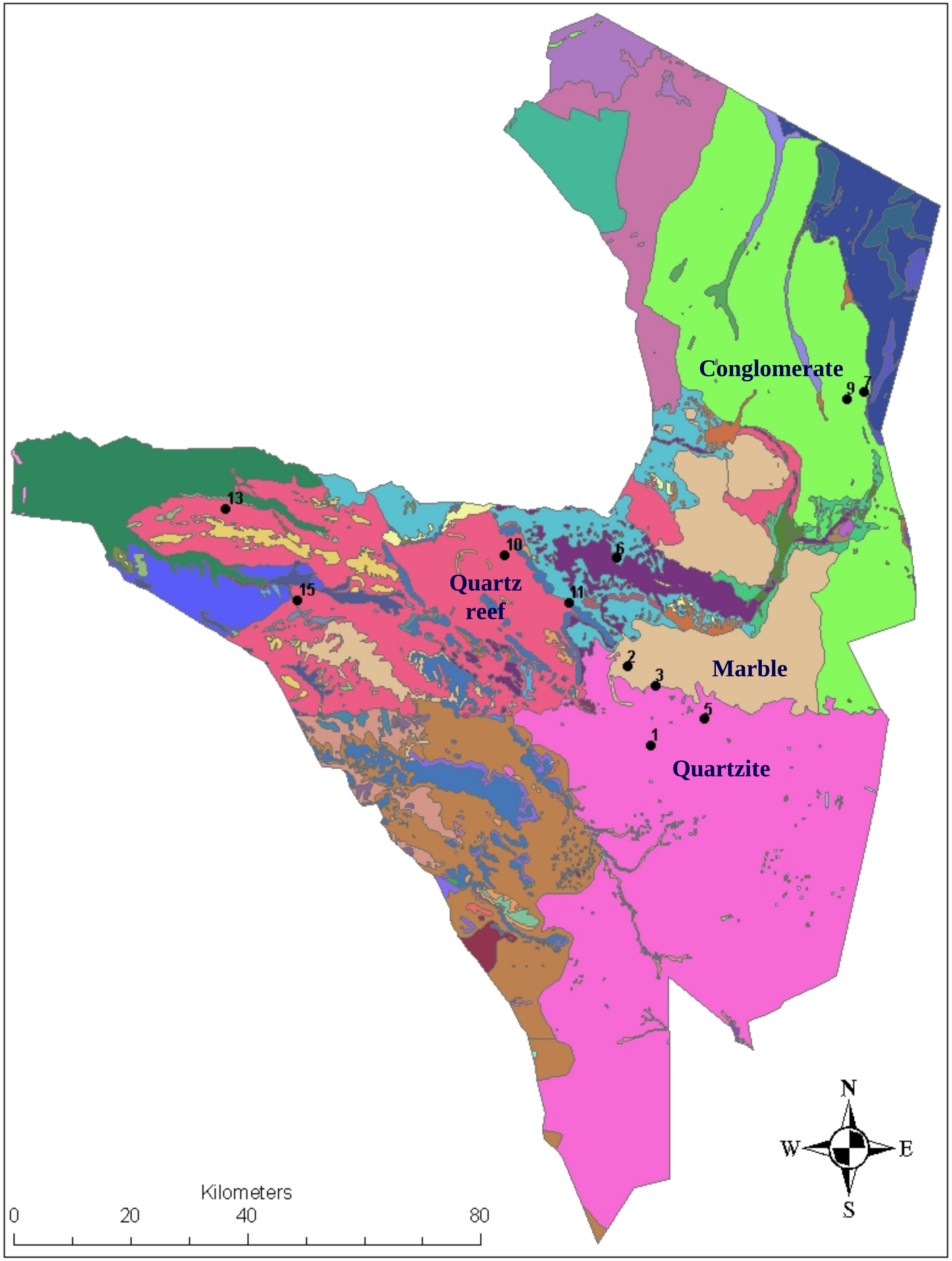
Serengeti Grasses

Digiteria

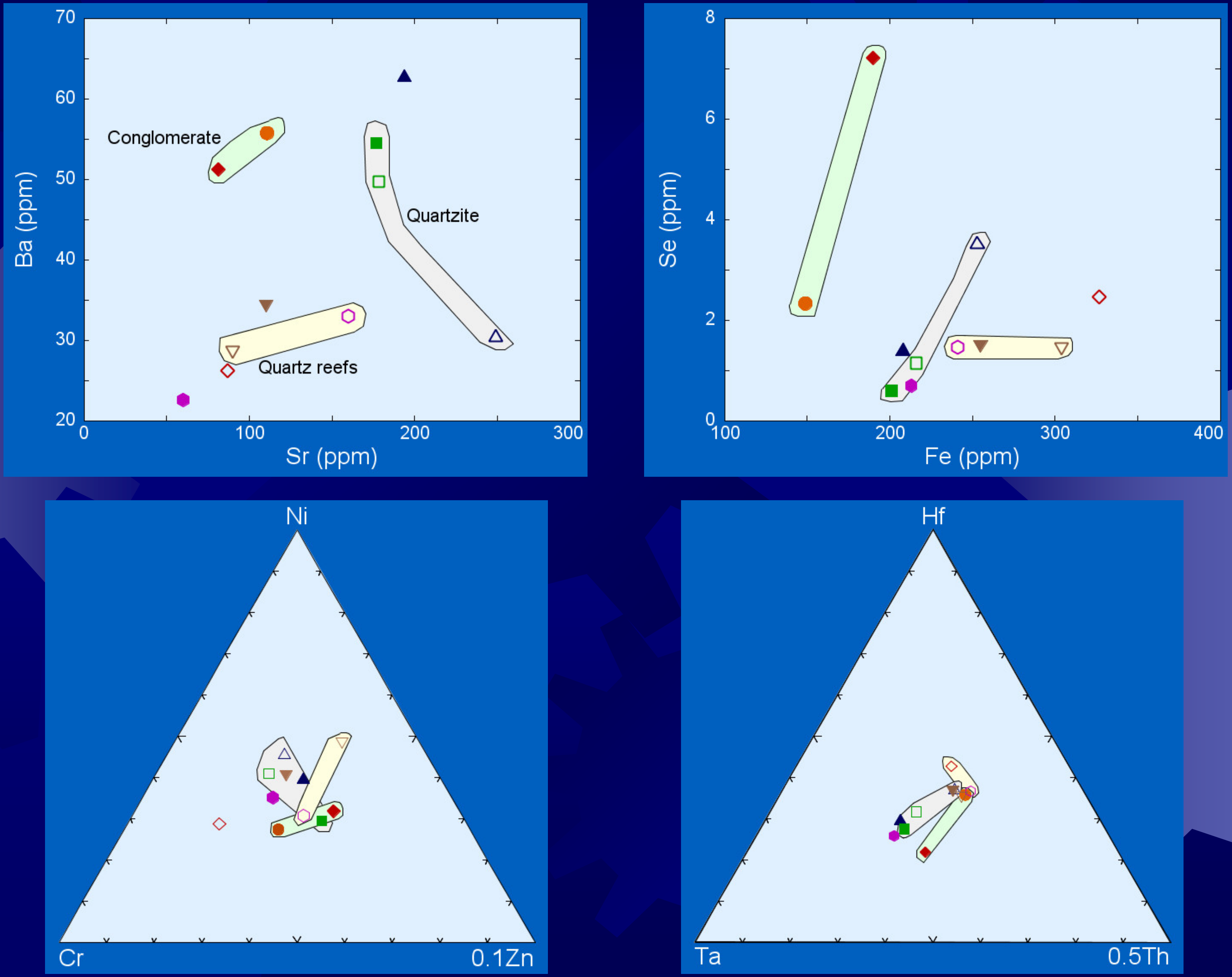
Sporobolus

Themeda

Sample Locations and Geology



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



Department Environmental, Earth, & Atmospheric Sciences

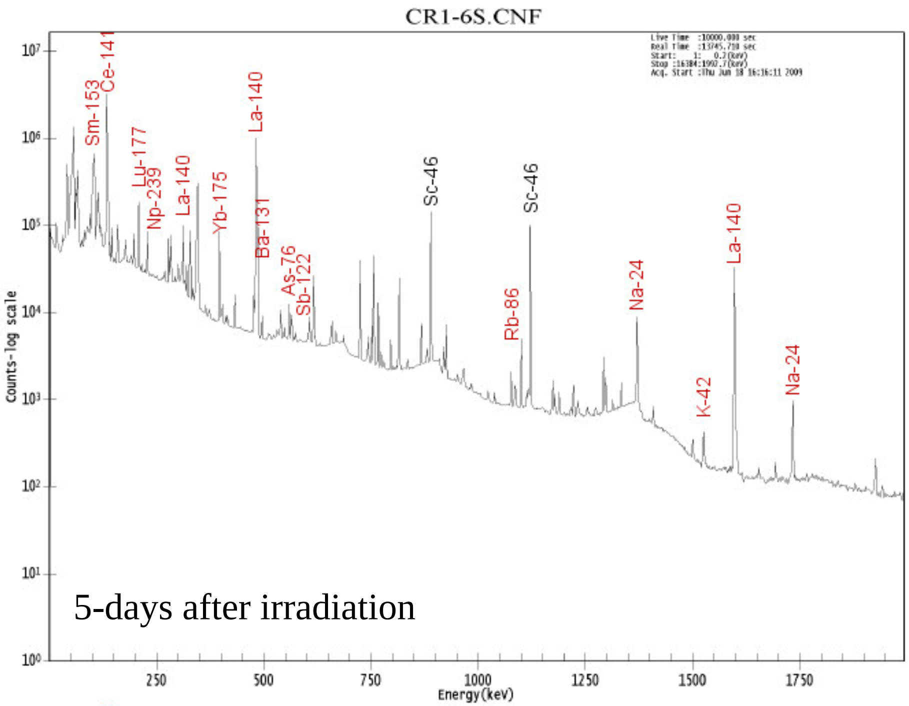
Using trace elements to Identify pottery fragments

Department Environmental, Earth, & Atmospheric Sciences

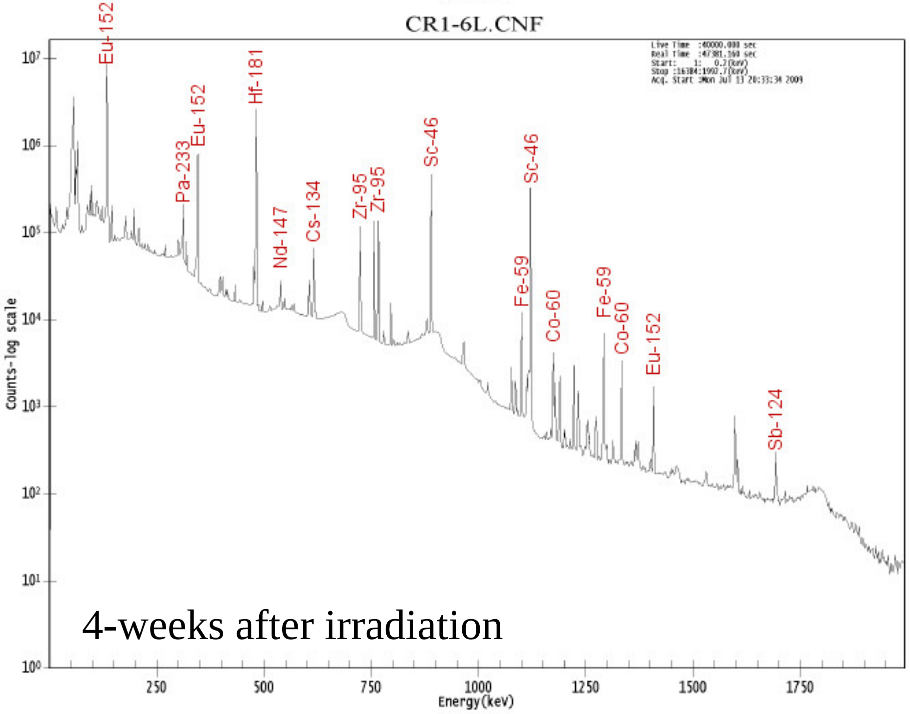
Summary of Materials Used in Glazes

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

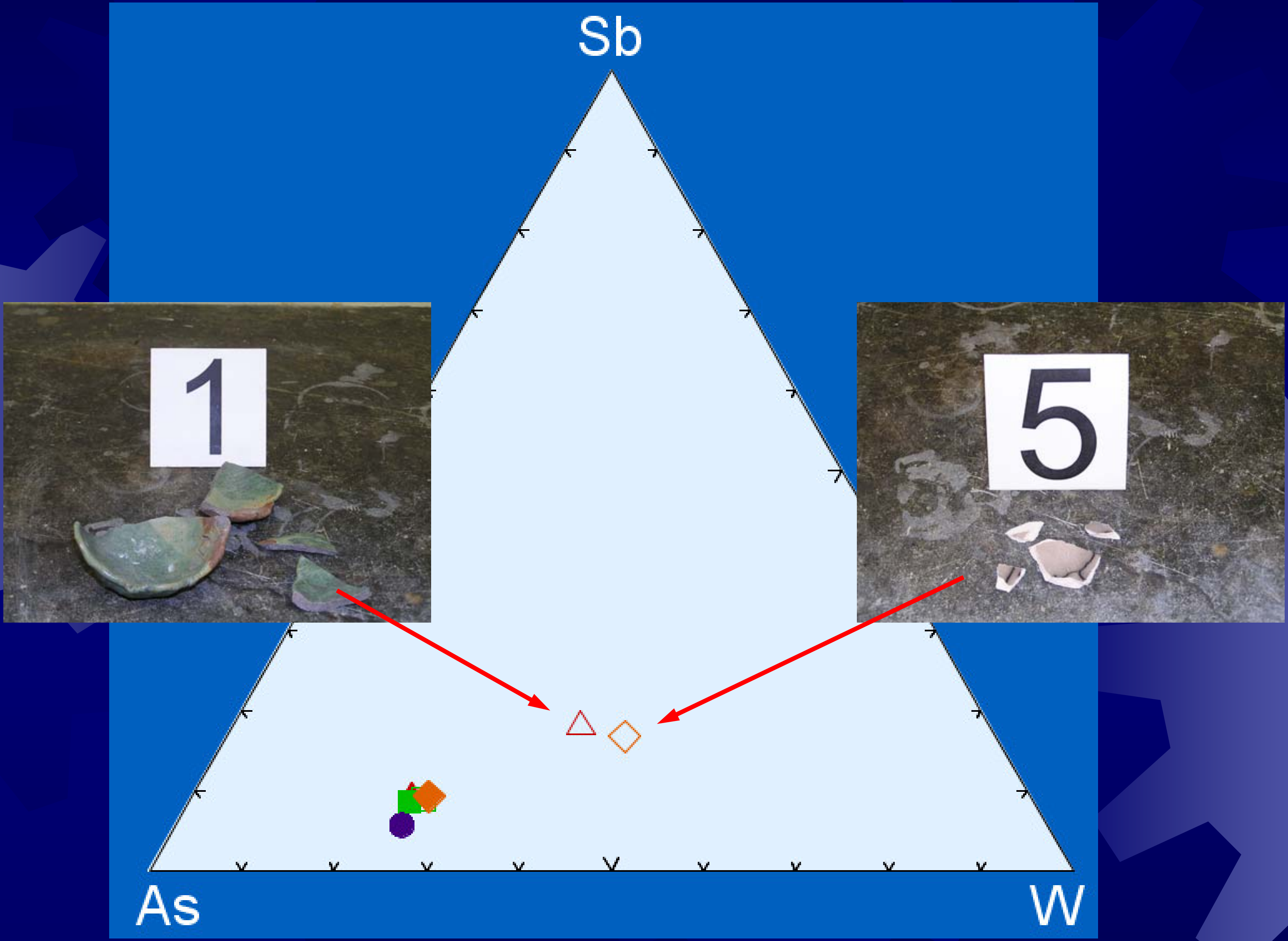
Gamma ray spectrum for Ceramic 6

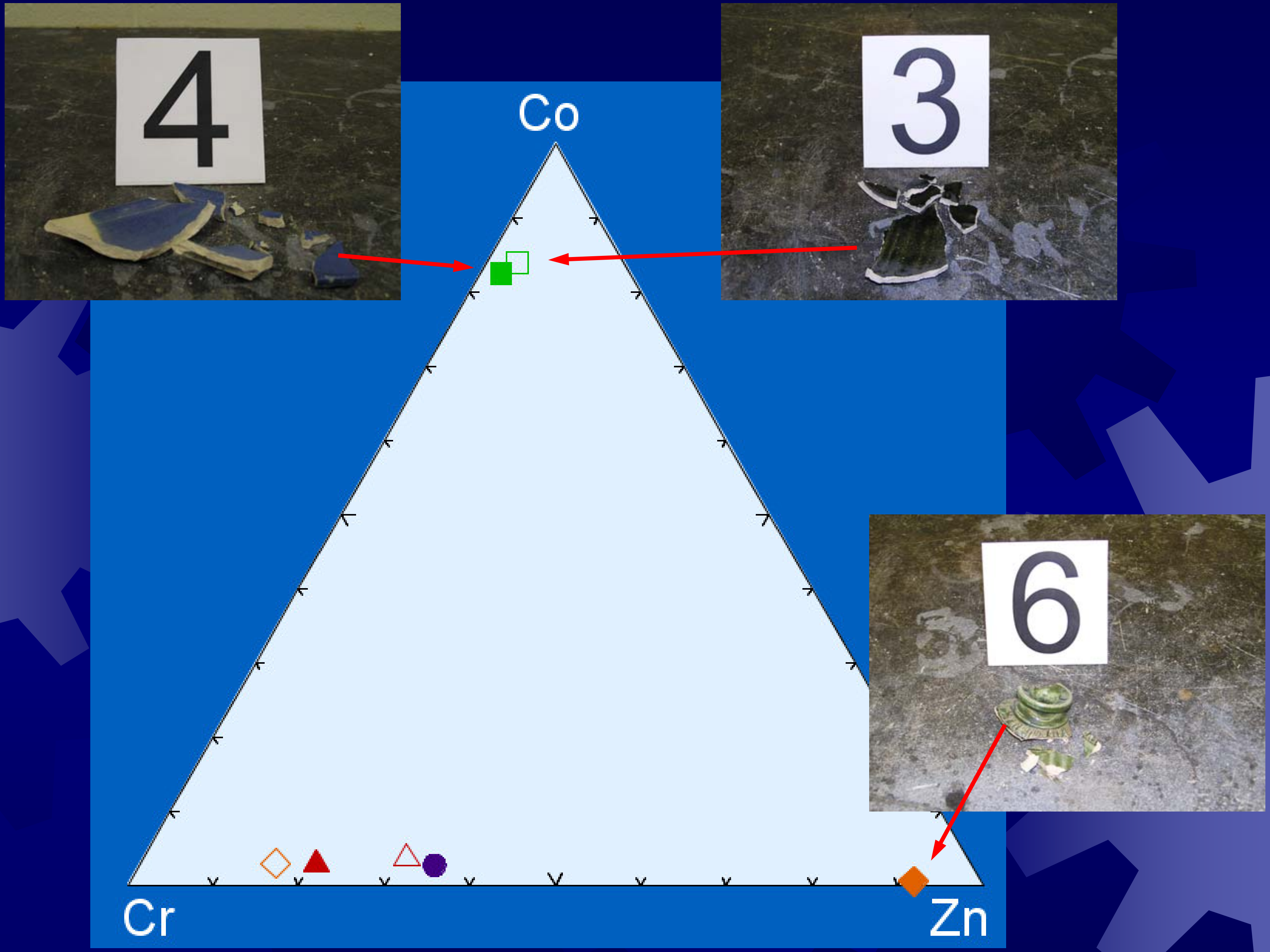


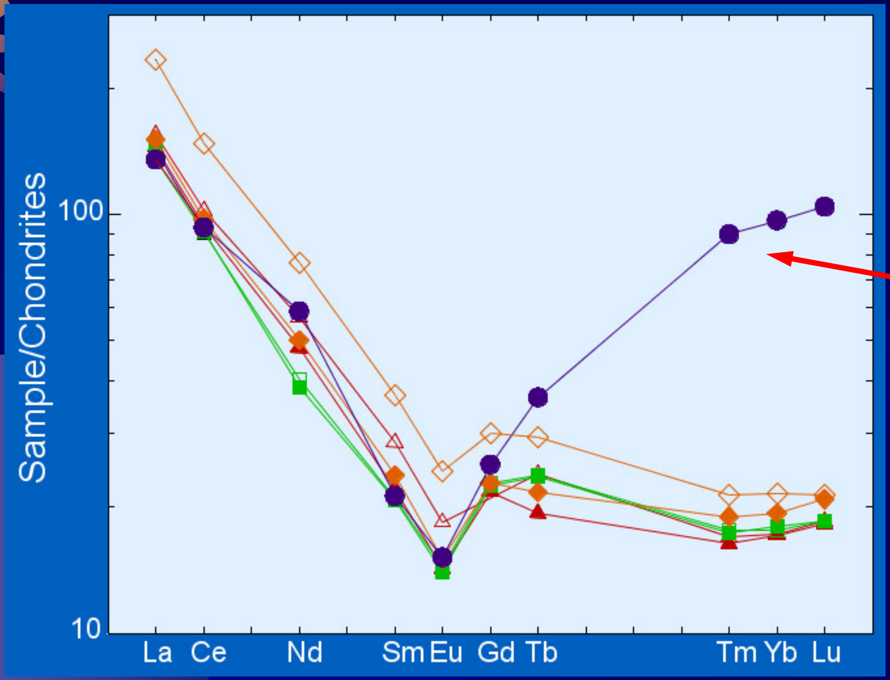
5-days after irradiation



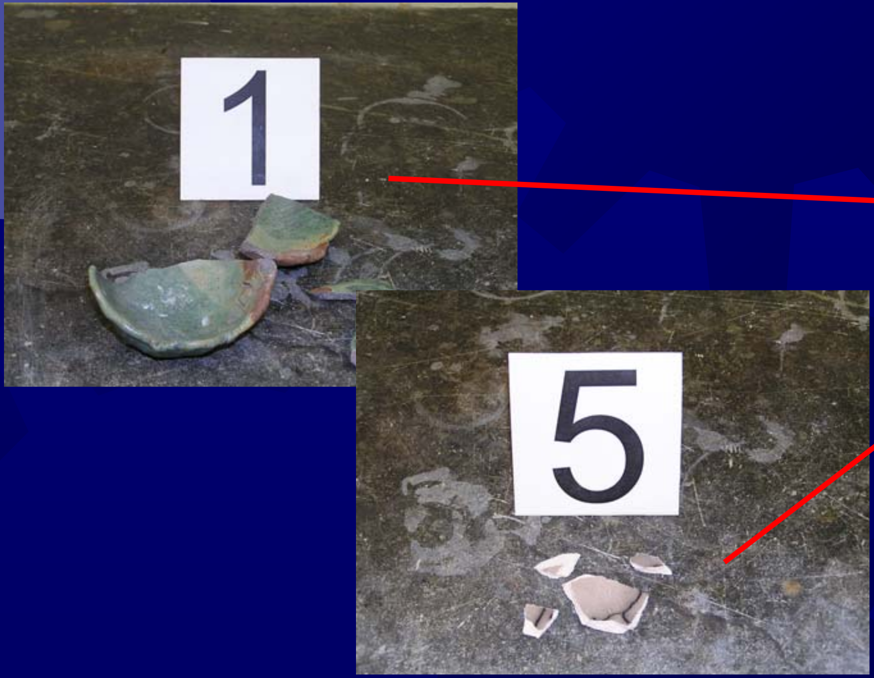
4-weeks after irradiation

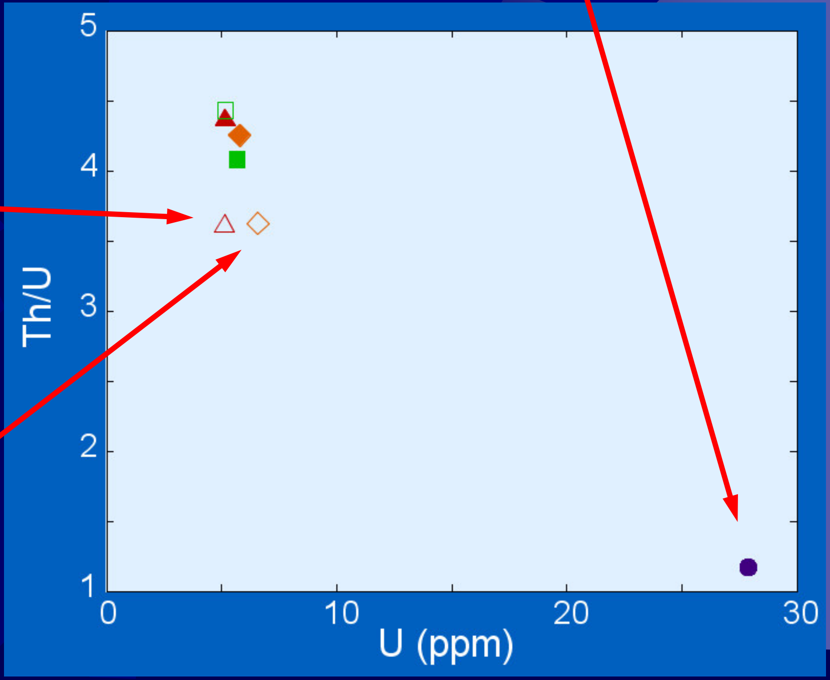

Sb
1
5
As
W


4
3
Co
6
Cr
Zn

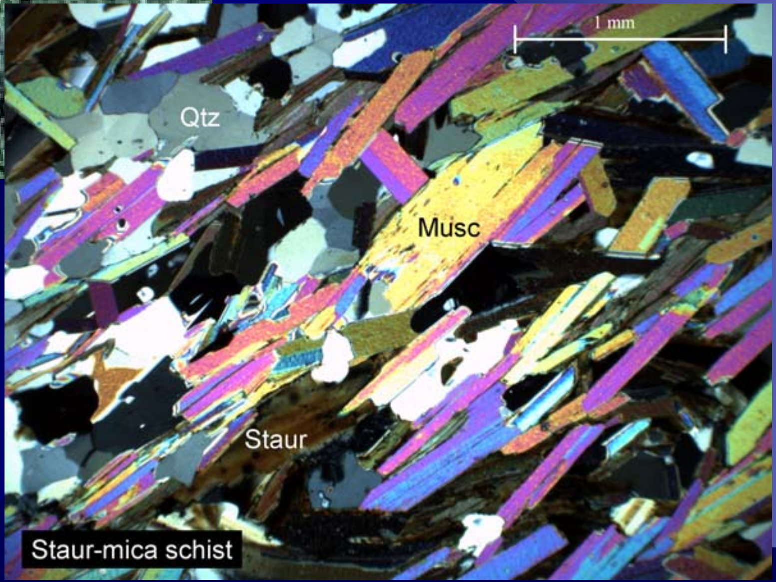

Sample/Chondrites
100
10
La
Ce
Nd
Sm
Eu
Gd
Tb
Tm
Yb
Lu


7
G-1


1
5


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

That's All Folks!



Staur-mica schist