Environmental and Geological Applications of Instrumental Neutron Activation Analysis

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“Instrumental Neutron Activation Analysis is an obsolete analytical technique.”

NSF program director

Yes, No, Maybe?

Principles of Instrumental Neutron Activation Analysis

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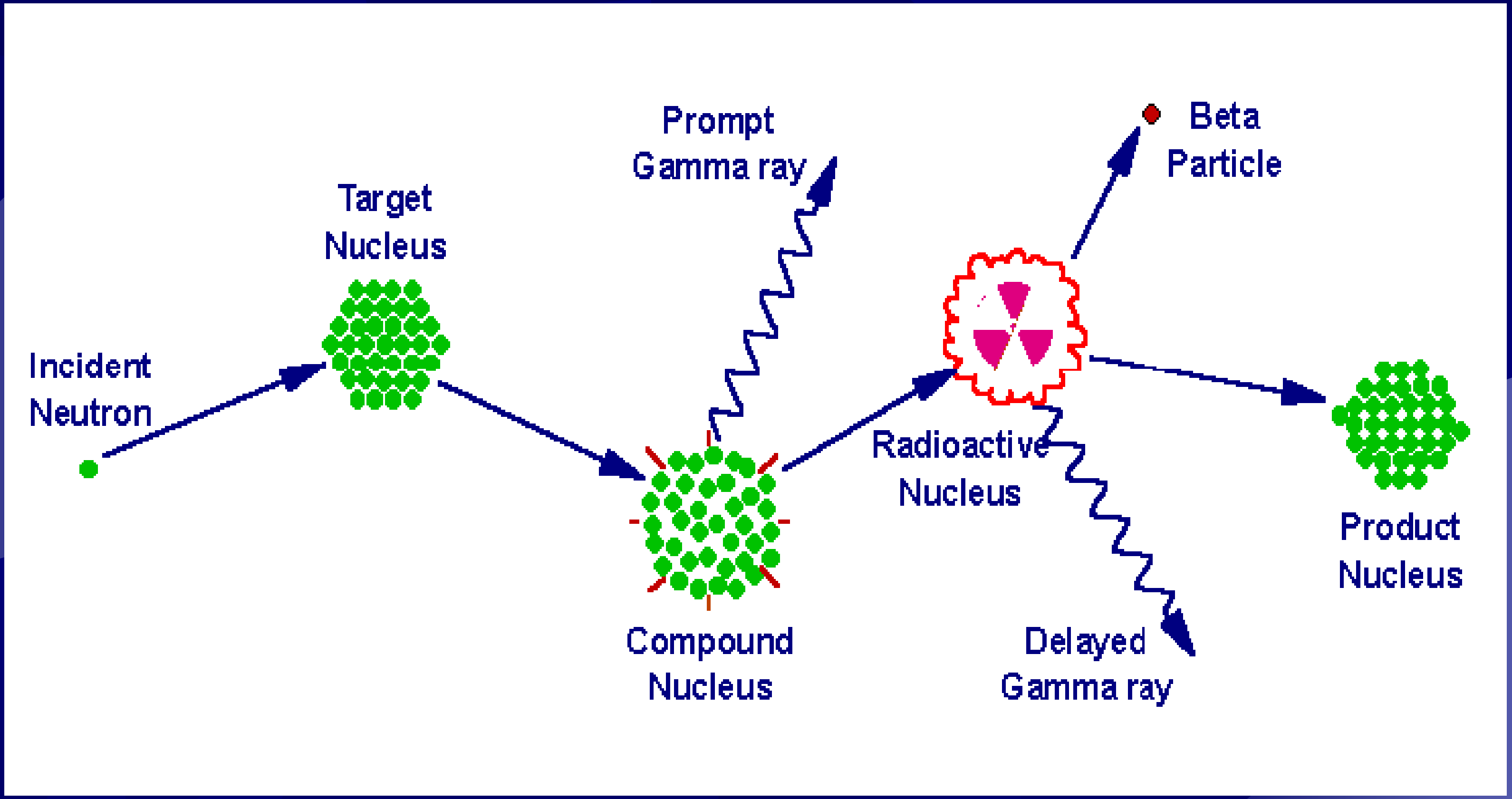
The n–gamma Reaction

The basic reaction for INAA



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

Gamma ray energies = 142.4, 1099.2, 1291.6 KeV

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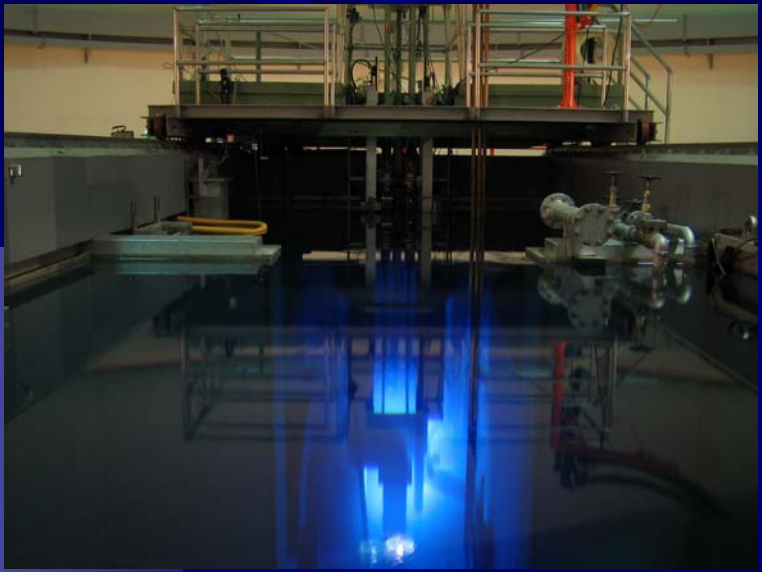
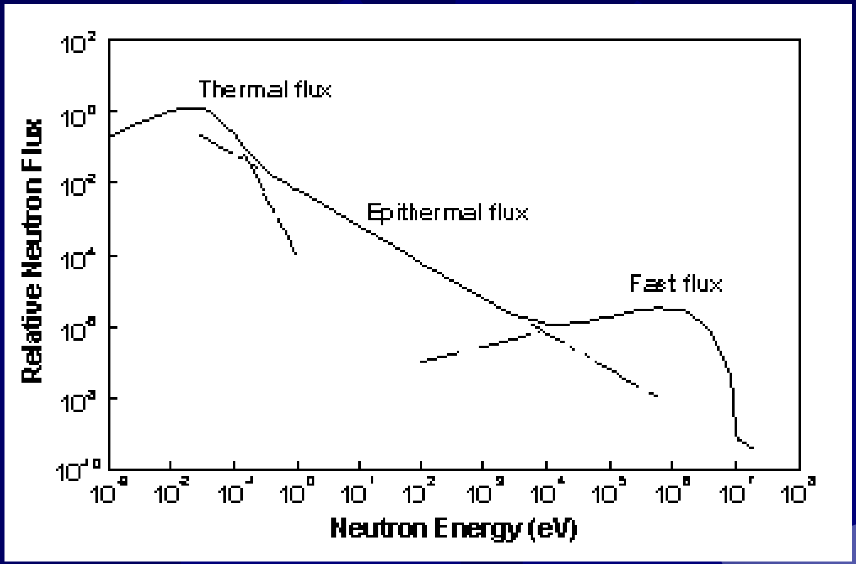
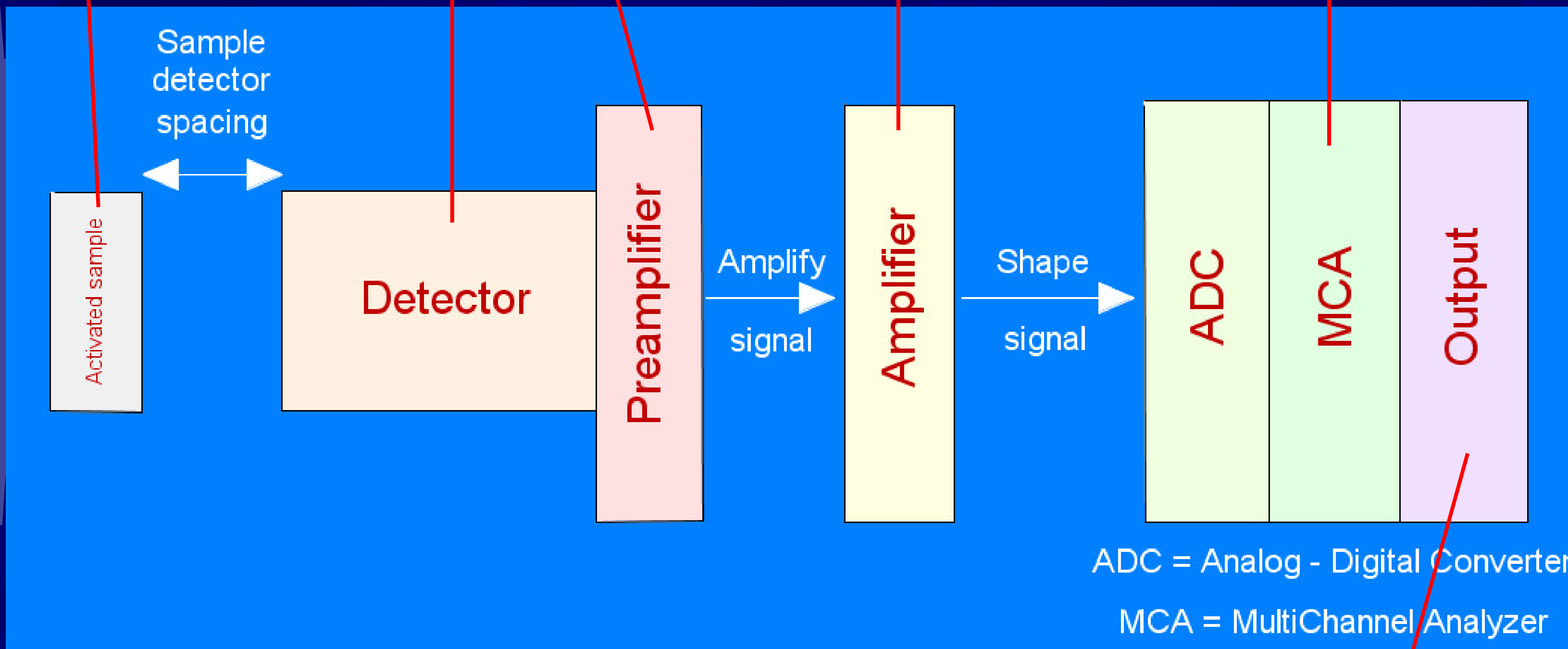
Different neutron energies are used for different types of experiments.

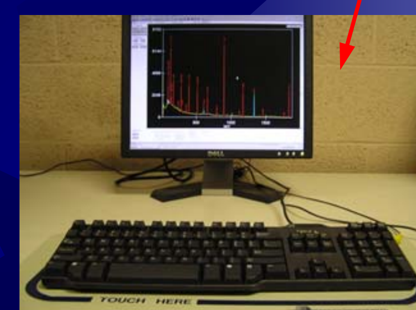




UML 1 Mw Research Reactor

The Neutron Source

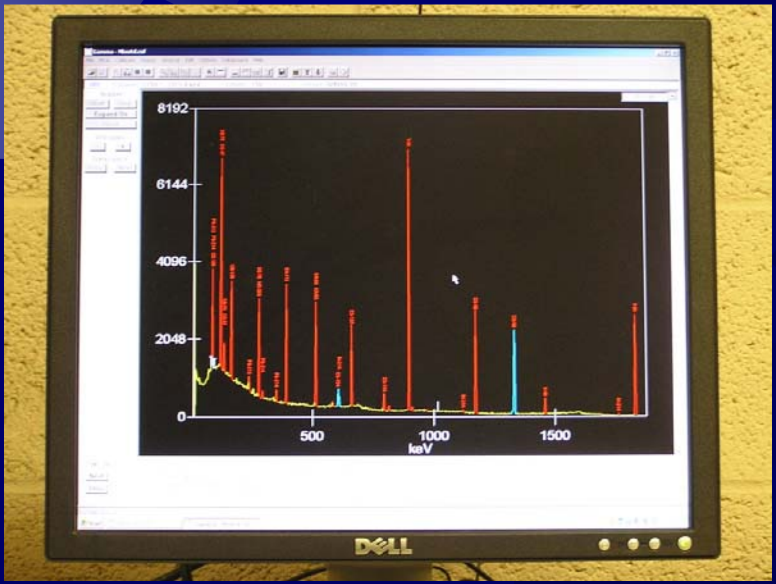


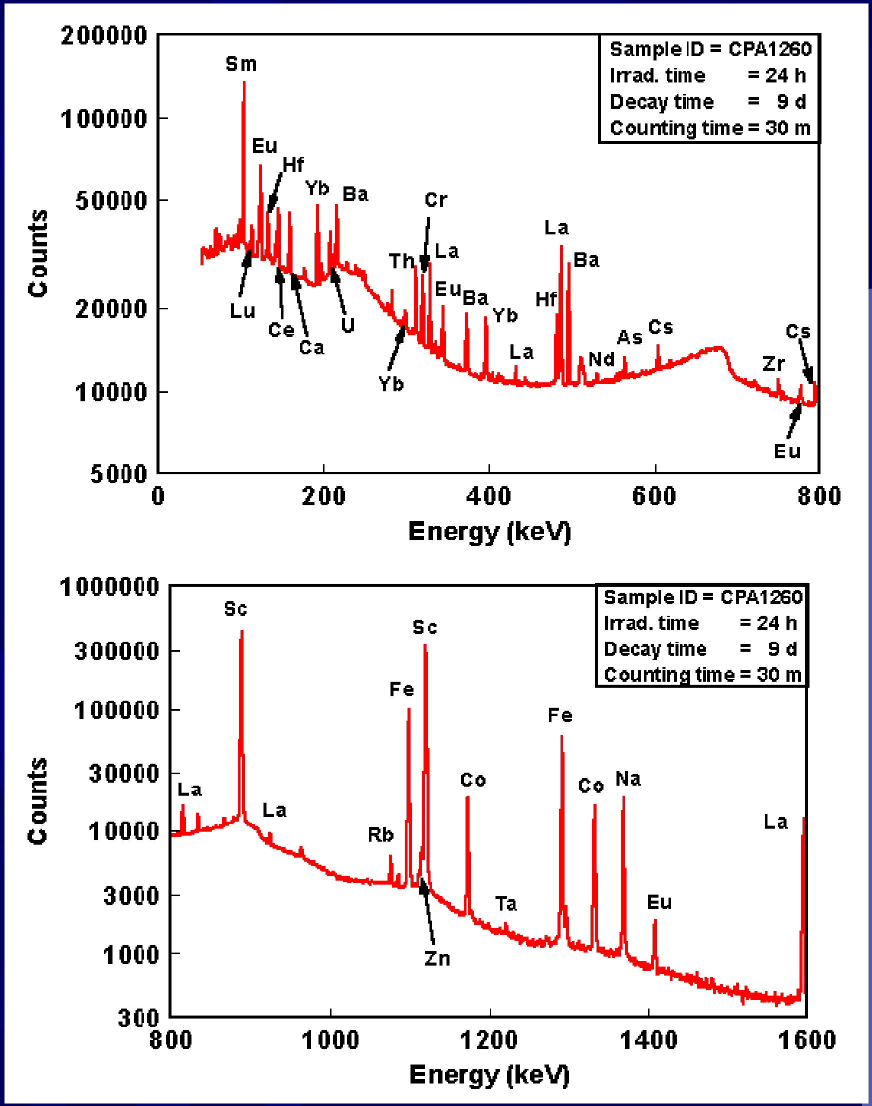


Data acquisition flow sheet

Gamma ray spectrum for a multi element sample

UML INAA Lab





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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.

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Sensitivity (pg)	Elements
1	Dy, **Eu**
1-10	In, **Lu**, **Mn**
10-100	**Au**, Ho, **Ir**, Re, **Sm**, **Lu**
100-1E3	**Ag**, Ar, **As**, Br, Cl, **Co**, **Cs**, Cu, Er, Ga, **Hf**, I, **La**, **Sb**, **Sc**, **Se**, **Ta**, **Tb**, **Th**, **Tm**, **U**, **W**, **Yb**
1E3-1E4	Al, **Ba**, **Cd**, **Ce**, **Cr**, **Hg**, Kr, **Gd**, Ge, Mo, **Na**, **Nd**, **Ni**, Os, Pd, **Rb**, Rh, Ru, **Sr**, Te, **Zn**, **Zr**
1E4-1E5	Bi, Ca, **K**, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
1E5-1E6	F, **Fe**, Nb, Ne
1E7	Pb, S

Elements routinely analyzed in environmental and geological samples at UML.

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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

Major Disadvantage of INAA compared to ICP-MS

Can't analyze for all elements of interest. Partner with X-ray fluorescence spectrometry (XRF)

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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***

So, Is INAA Obsolete?

"I am a little concerned about the quality of some of the trace element data but this is a general criticism of the way geochemists are doing ICP-MS. Personally, I don't think REE data at +/- 5-10% are "fit to purpose" but this is what many ICP-MS labs are producing. ***Certainly such data are of inferior quality to the ID and INAA REE data we laboured long and hard to produce 20 years ago.*** One can do 1-2% RSD on REE by ICP-MS but you need to understand, monitor and correct all the potential pitfalls."

Comments from a *Lithos* review.

No!

For many applications it is the method of choice or is a competitive choice with respect to ICP-MS.

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.

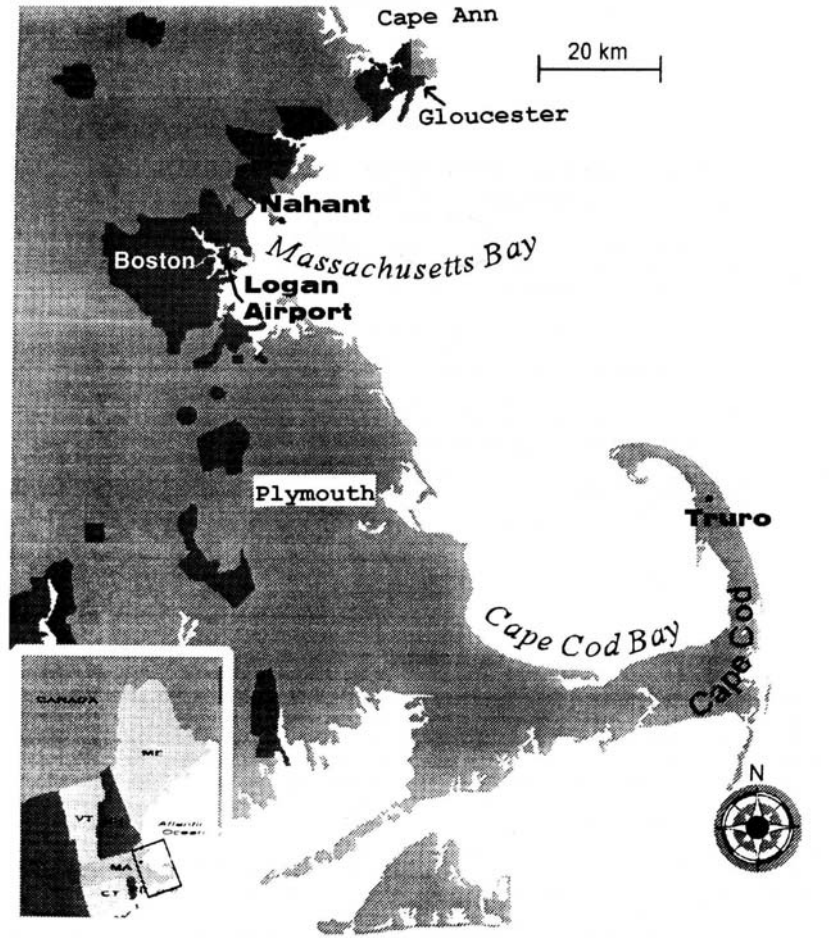

Fig. 1 Map of Massachusetts Bay. Nahant and Truro field sites are indicated. Shaded areas indicate population centers greater than 20,000 people.

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

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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.

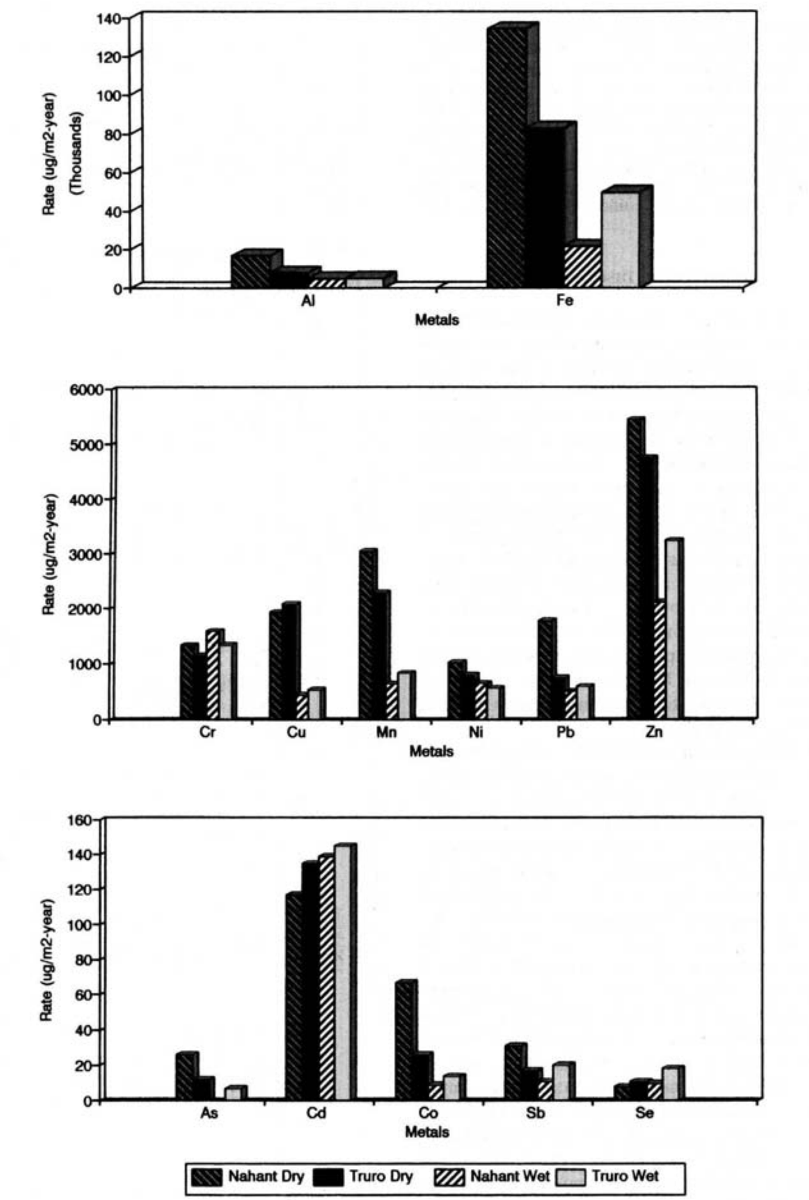

Fig. 3. Bar chart of annual deposition rates of metals ($\mu g\,m^{-2}\,yr^{-1}$). Note that not all metals were analyzed in all three fractions.

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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.

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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)

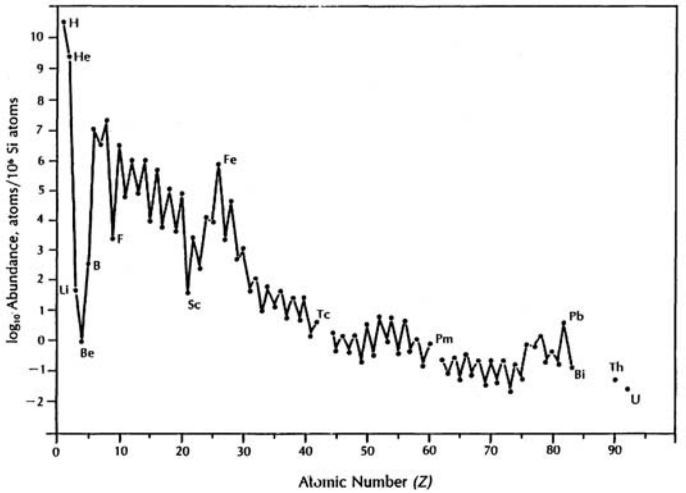

Figure 2.2 Abundances of the chemical elements in the solar system in terms of atoms per 10^6 atoms of Si. The data were derived primarily by analysis of carbonaceous chondrite meteorites and by optical spectroscopy of light from the Sun and nearby stars (Anders and Ebihara, 1982).

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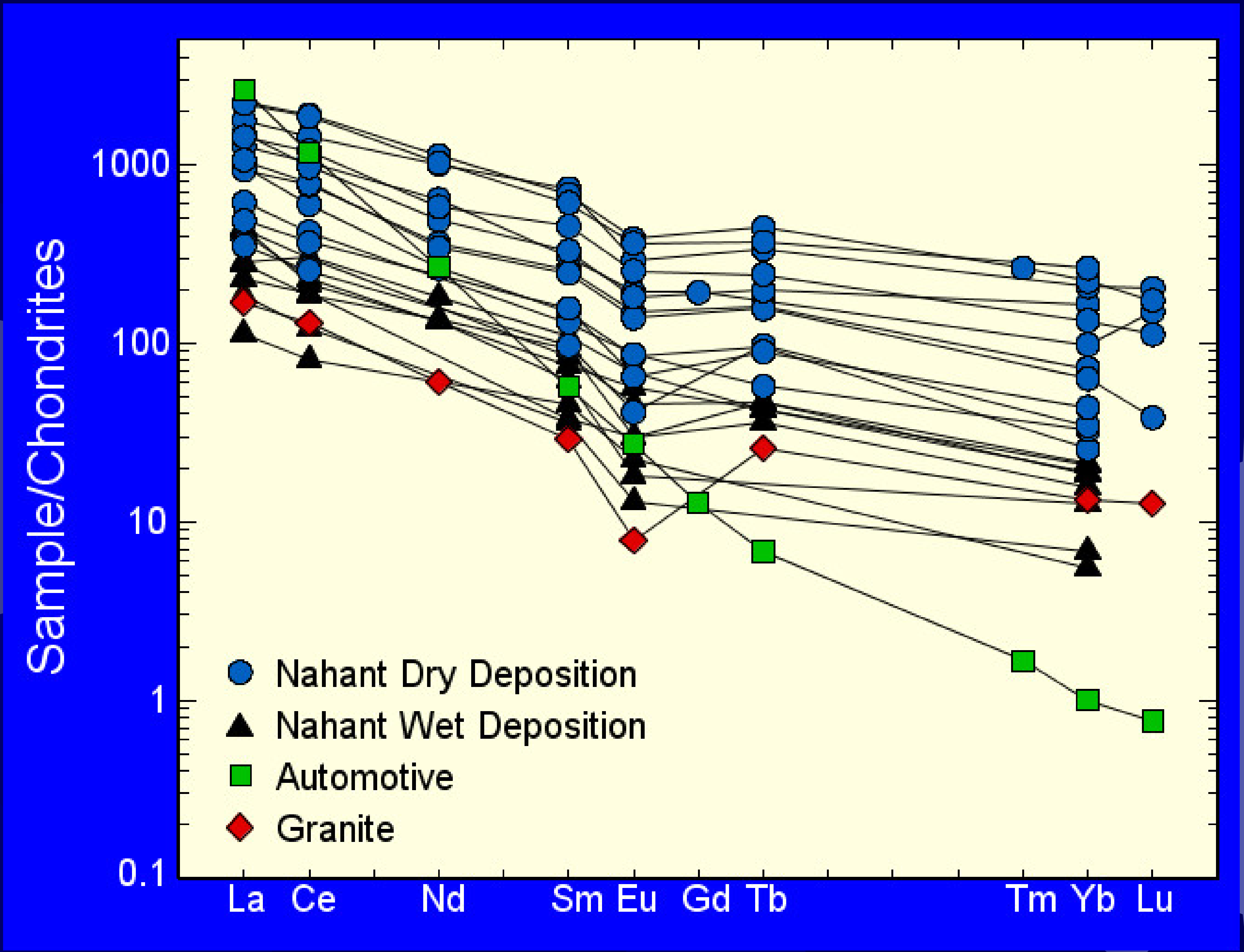

F1 is a crustal, not an automotive source

Tree-ring width and isotopic records showing industrially induced physiological stress and recovery of trees in the northeastern USA: Carbon-cycle implications

Co-Investigators

Long Li, Zicheng Yu, Gray Bebout, T. Stretton, Andrew Allen, Peter Passaris

Lehigh University

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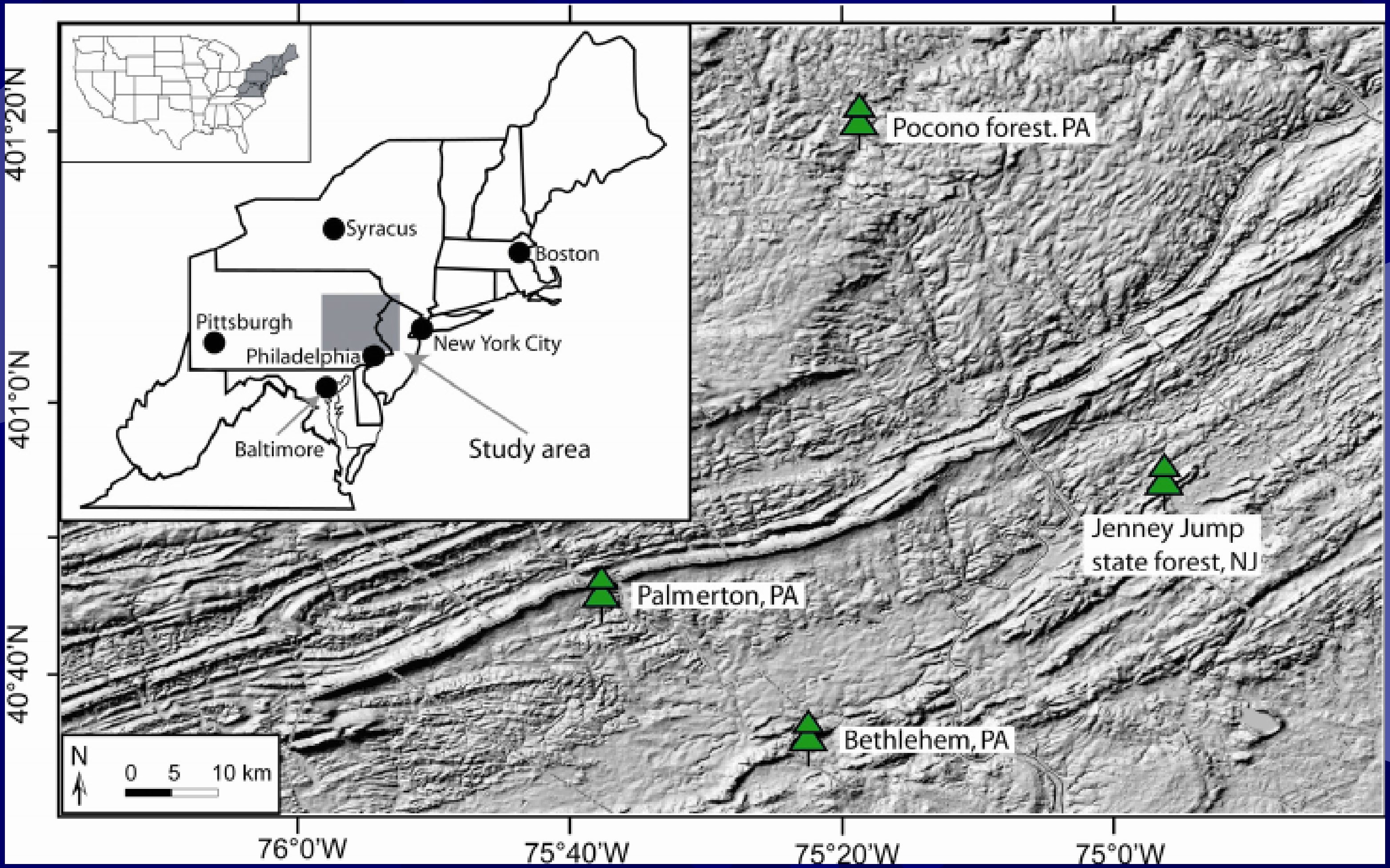
Between 1898 and 1980 New Jersey Zinc had several operating smelters at Palmerton, PA.

Electrostatic precipitators were installed in 1953.



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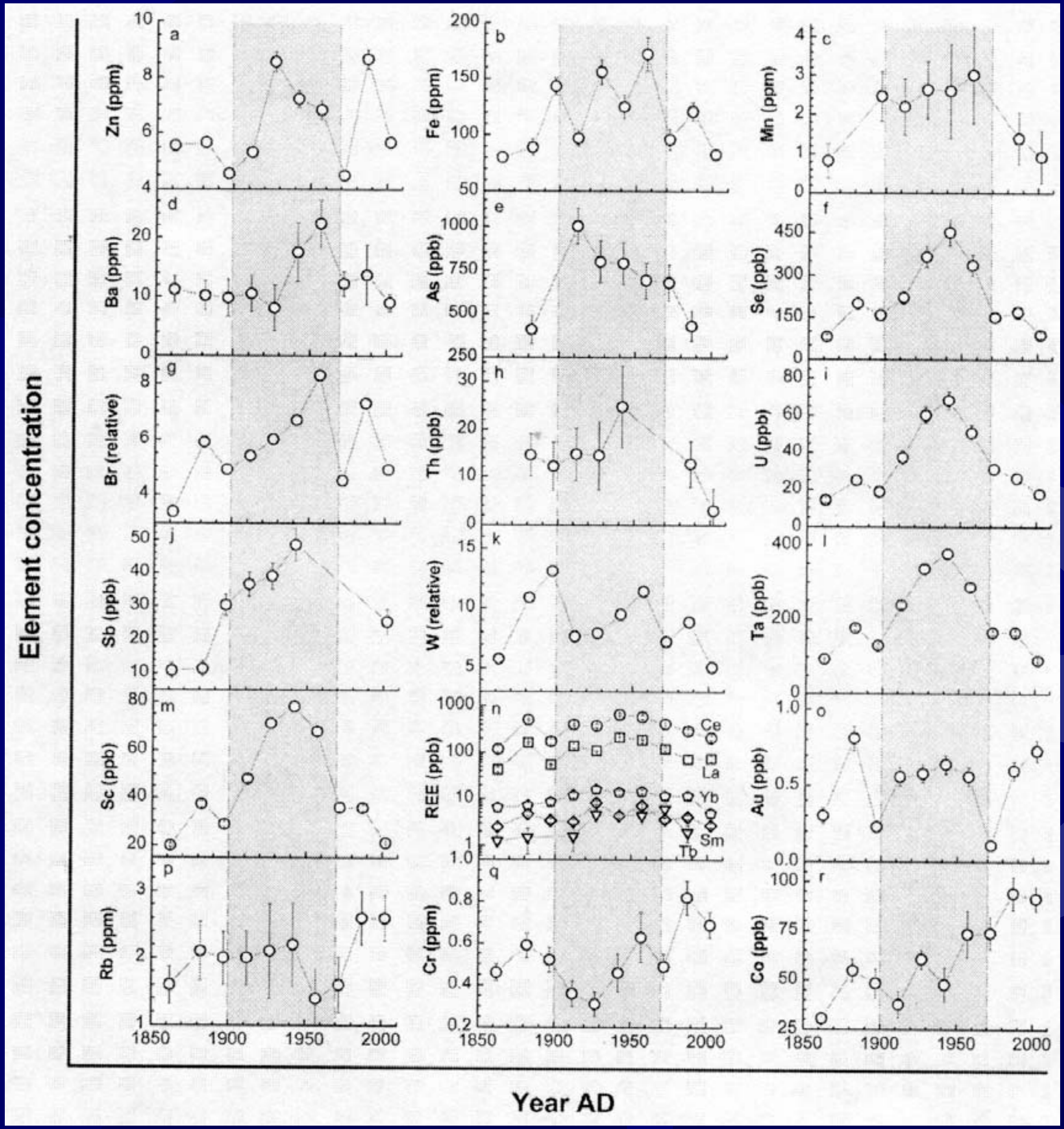
Metal variations in tree-ring cores



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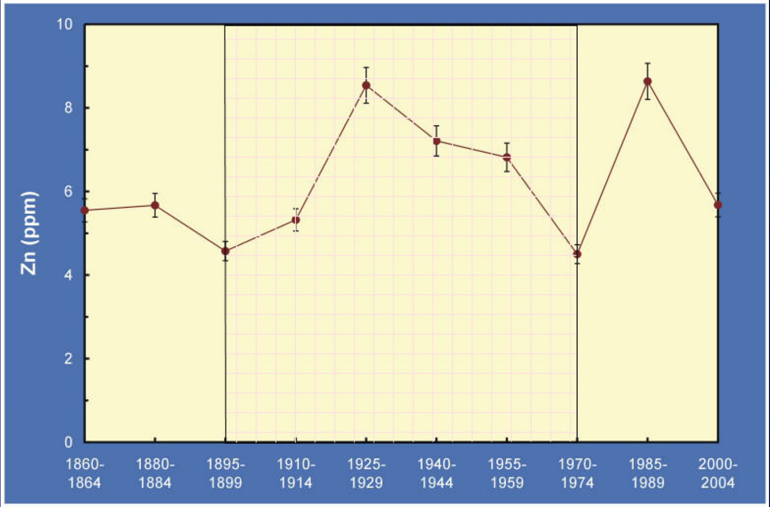
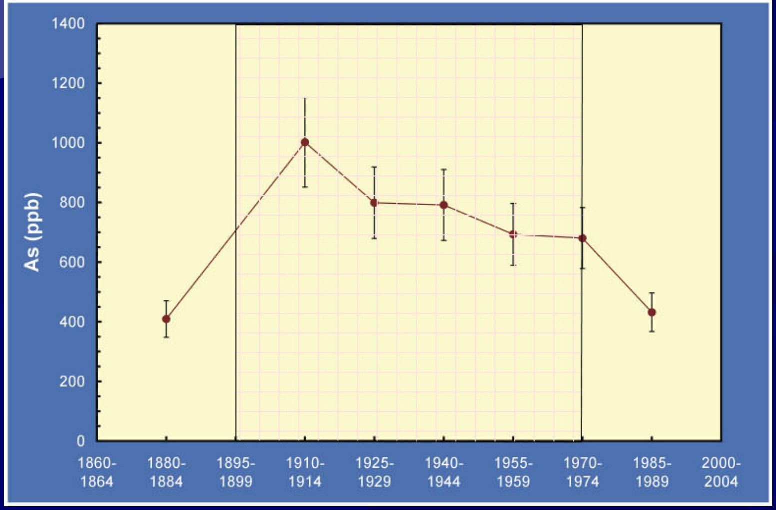
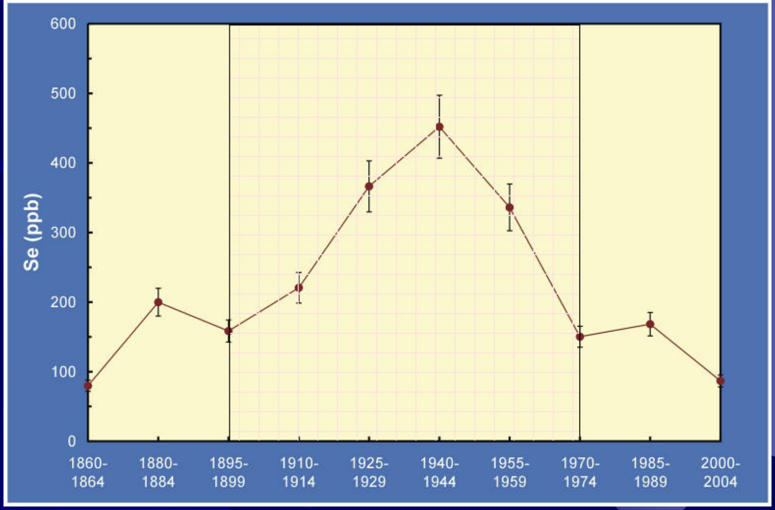
Time – concentration plots for As, Se, and Zn showing sensitivity and error associated with INAA measurements.







Forensics – Source of the Maple Syrup

Collecting sap the old fashioned way

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

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Transferring sap to the sugar house

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Sap holding vats

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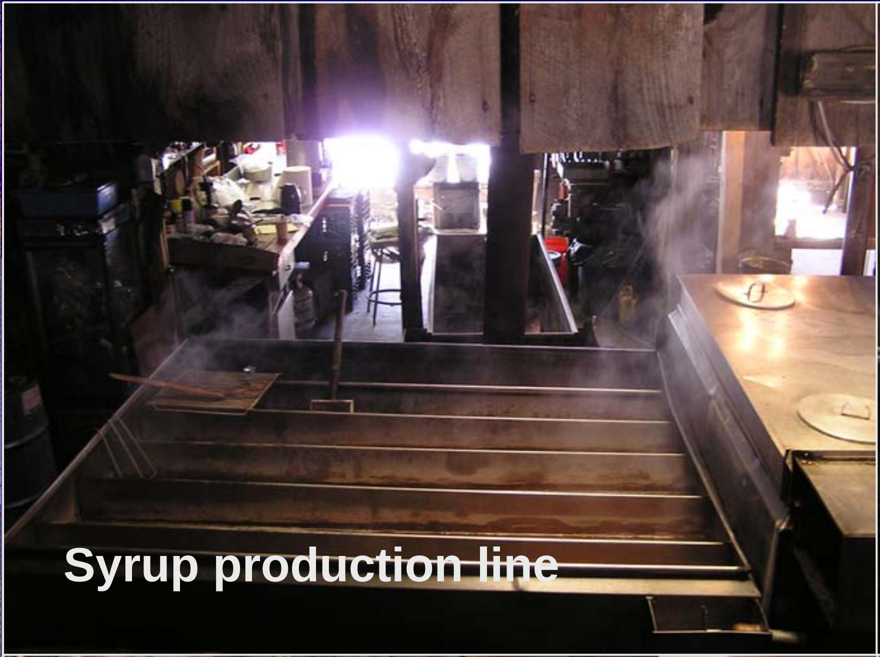
Boiling down the sap


Syrup production line

Main boiler

Secondary boiler


Finish boiler

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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

Trace metals in nanotech materials – Respirable particles

Element	Carbon Black	Fullerene	Nano TiO_2	CNT	Silica	Nano alumina	
Fe	25.9	11.7	24.1	**2441**	**450**	18.6	ppm
Sc	0.002	0.003	**4.88**	nd	0.200	0.028	ppm
Cr	0.303	0.099	2.18	**536**	1.68	0.714	ppm
Co	0.015	0.024	0.43	**19582**	0.30	0.030	ppm
Ni	0.3	0.4	nd	**317**	**64**	0.2	ppm
Zn	8.26	4.15	32.8	**1202**	6.45	37.5	ppm
Ba	nd	0.89	**52.4**	nd	14.8	nd	ppm
Sr	6.0	nd	nd	nd	9.7	nd	ppm
Ce	4.79	3.91	1.56	nd	4.60	3.36	ppm
Zr	nd	nd	**13743**	**1305**	32.2	**134**	ppm
Ta	0.010	0.017	**61.9**	nd	0.048	0.008	ppm
As	0.050	0.010	**16.3**	0.58	0.212	0.022	ppm
Mo	nd	nd	1.6	**415**	nd	nd	ppm
Sb	0.020	0.002	**321**	**16.27**	0.089	1.23	ppm
W	0.030	0.004	**11.96**	0.46	0.034	**27.9**	ppm
Au	**47.5**	0.03	**99.7**	1.29	nd	nd	ppb
Se	nd	0.66	nd	nd	**9.5**	**23.5**	ppb

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Serengeti burning and animal behavior – chemistry of grasses

Collaborative project with S. Eby, Syracuse University

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Location map for Tanzania National Parks


Prey

Predators

Fire management plan – controlled burning

Animals rapidly move to burned areas – why?

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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

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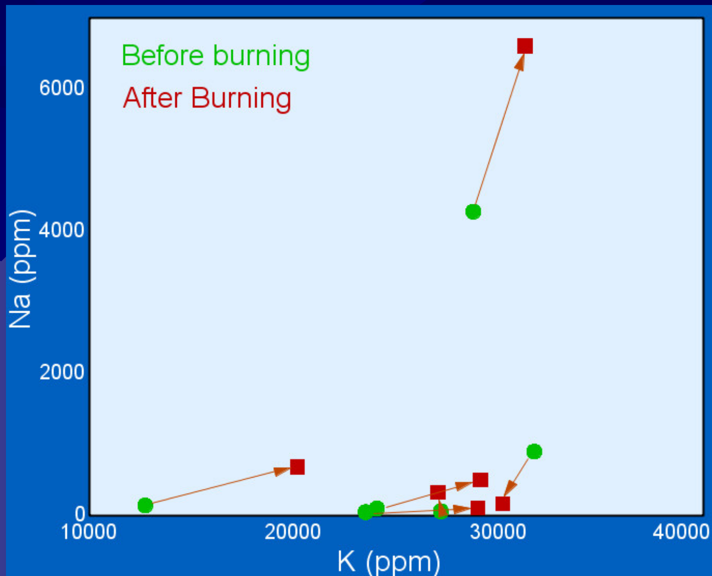
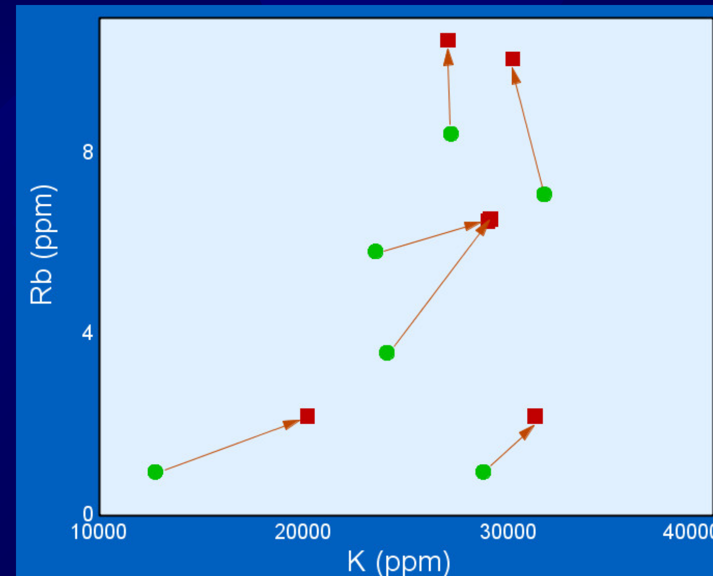
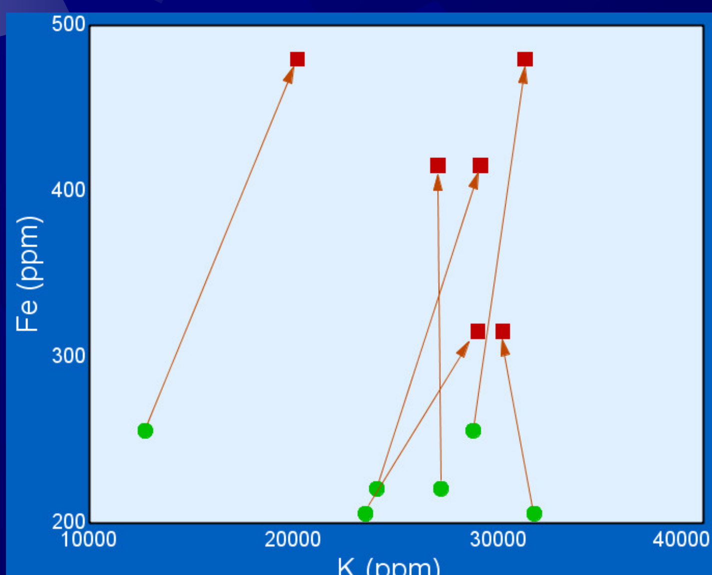
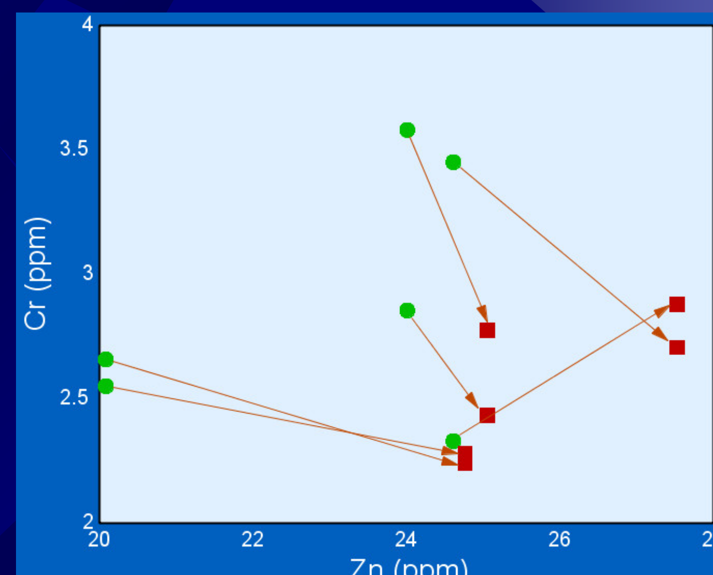
Change in elemental concentrations in grasses before and after an area is burned. In most cases elemental concentrations increase after burning. The notable exception is Cr.









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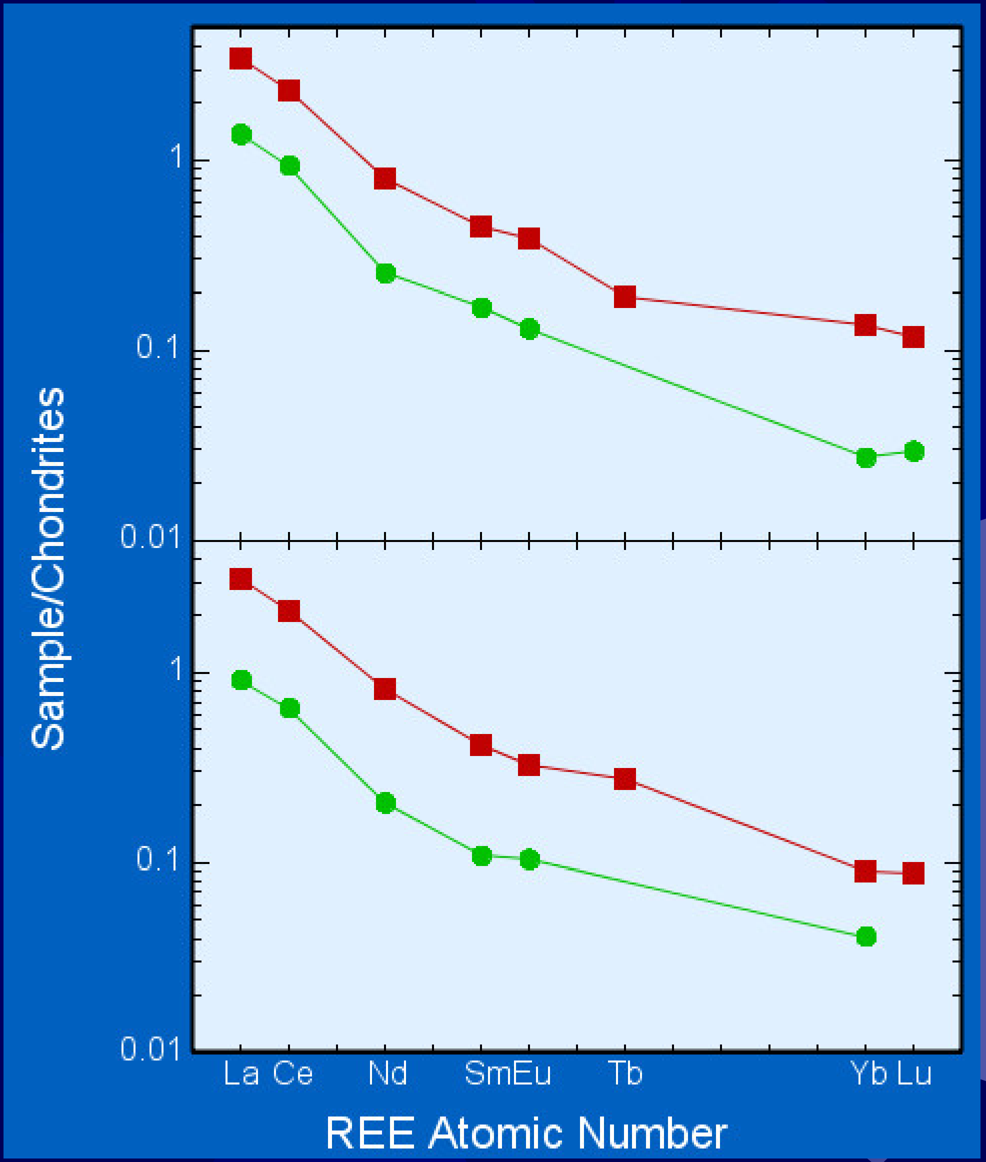
First ever REE concentrations determined for Serengeti grasses. Concentrations are in the range 1000 to 10 nanograms. REE patterns reflect REE concentrations of the underlying weathered volcanic ash.



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That's All Folks!