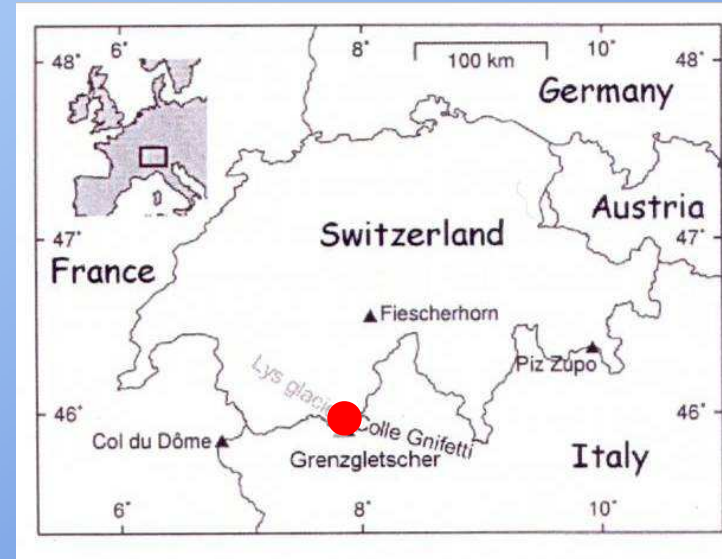




**Trace elements and Polycyclic
Aromatic Hydrocarbons (PAHs)
in snow and ice sampled at
Colle Gnifetti, Monte Rosa (4450 m),
during the last 10,000 years:
Environmental and climatic implications**

The Colle Gnifetti drilling site



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Venezia, November 28th 2008

The Colle Gnifetti core

What we have done in Villigen (PSI)

Storage, visual stratigraphy, density calculations, log, first processing

Discontinuous analysis

Major ions

Stable H, O isotopes

Dating

Volcanoes

Saharan dust depositions

Annual Layer Counting

^3H , Pu , ^{210}Pb (core2)

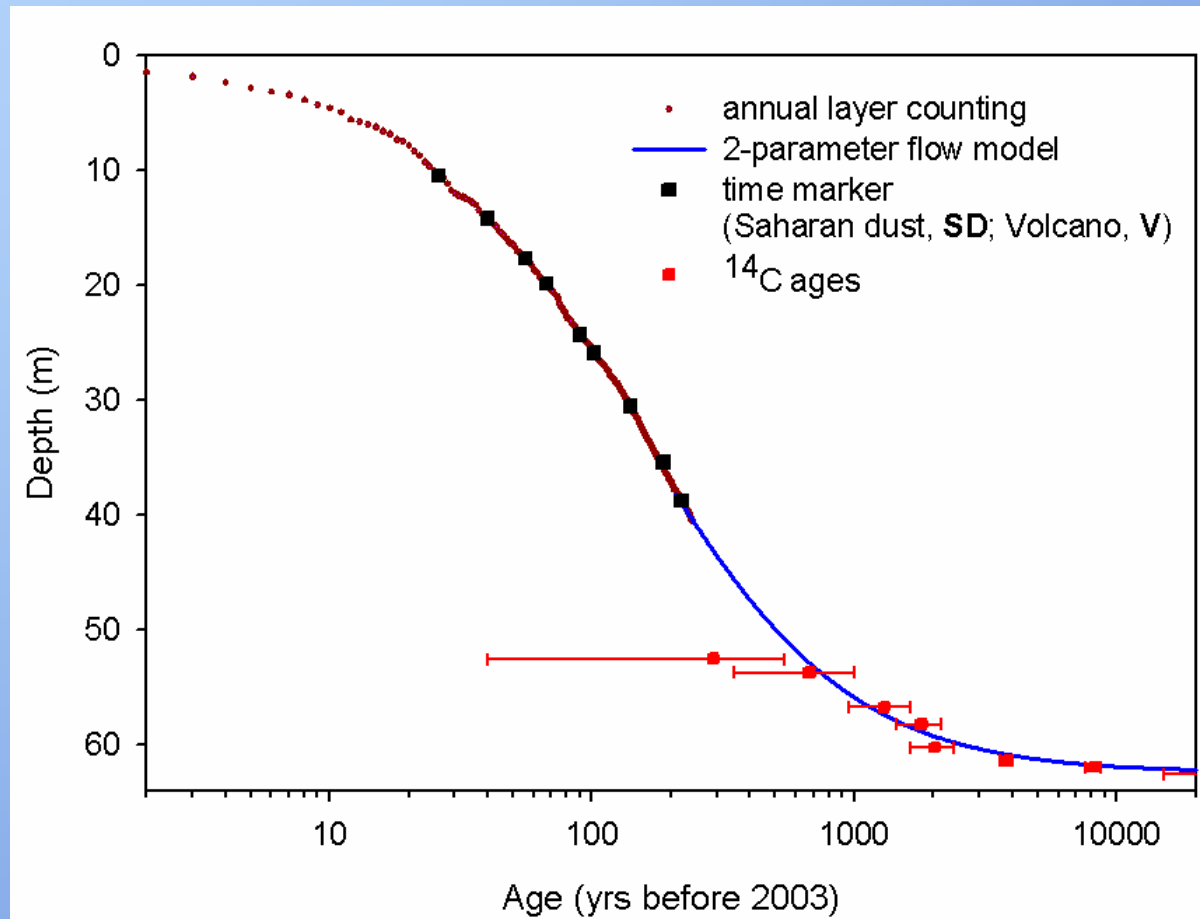
^{14}C



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Analysis carried out at PSI

What we have done in Villigen (PSI): dating



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CG dating

What we have done in Venezia

Designing, building and testing of a new melting system for continuous decontamination and on-line analysis of alpine ice/firn core

On-line continuous analysis

Trace elements by ICP-QMS
Conductivity

On-line solid-phase extraction for semi-continuous PAHs analysis

Discontinuous analysis

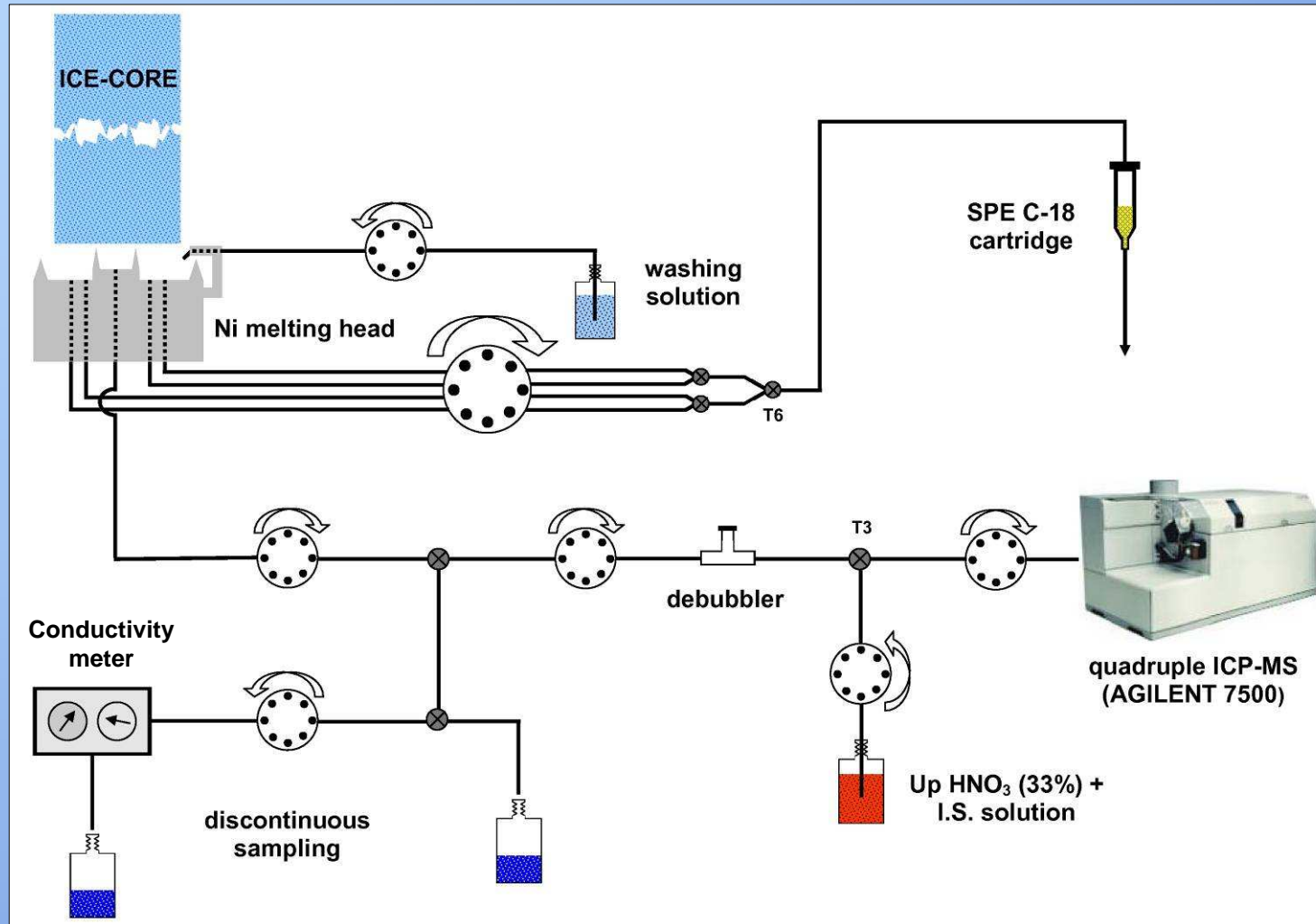
Trace elements by ICP-SFMS
Trace elements by ICP-OES
Pb isotopes
 ^{239}Pu



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Analysis carried out in Venezia

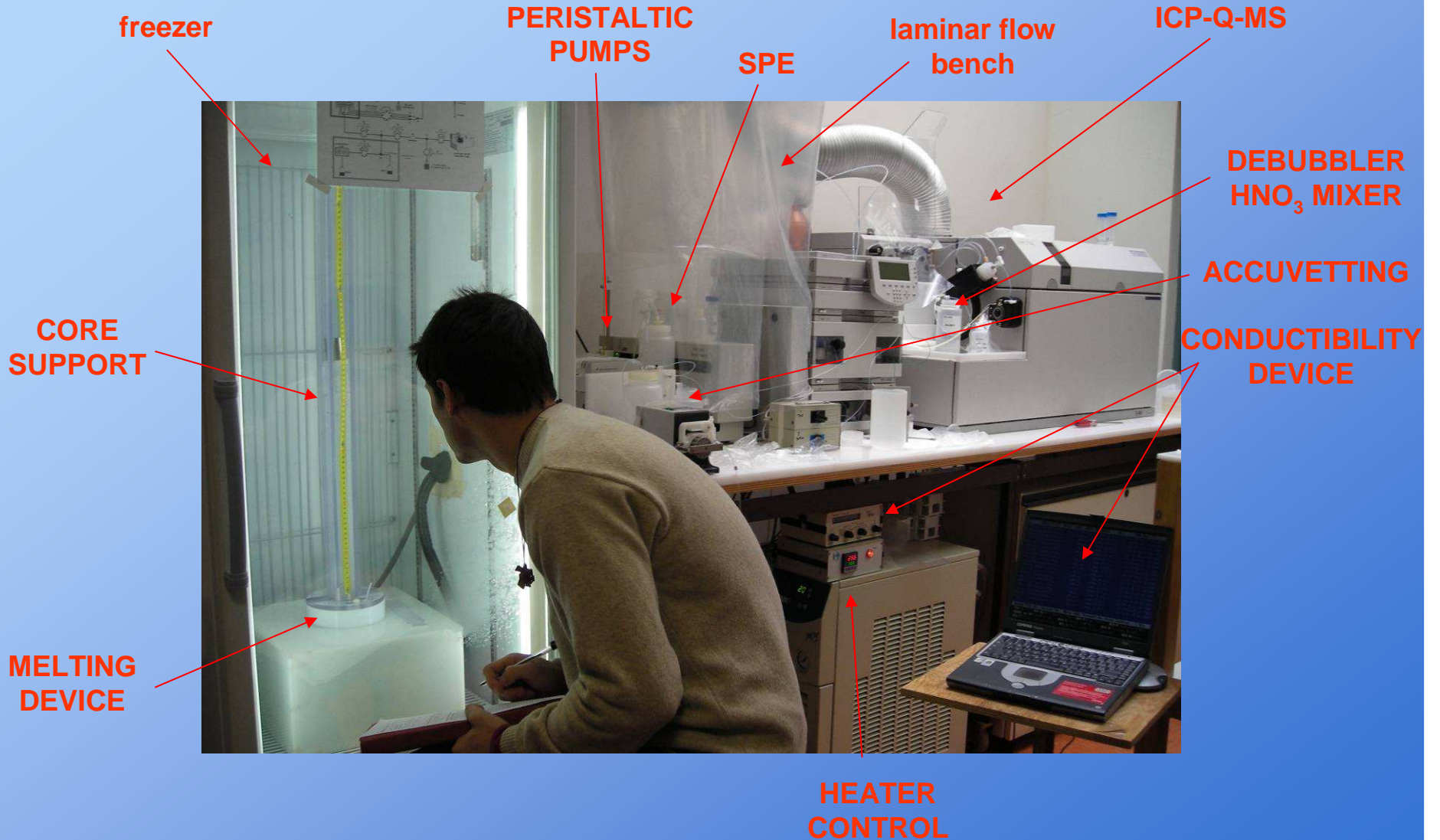
The "Venetian" melting system draft



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The melting system

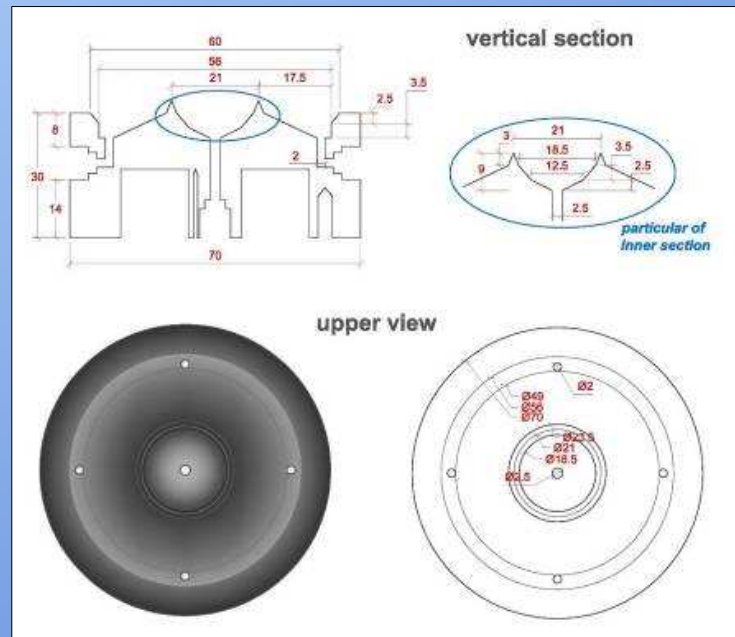
The "Venetian" melting system picture



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The Colle Gnifetti core

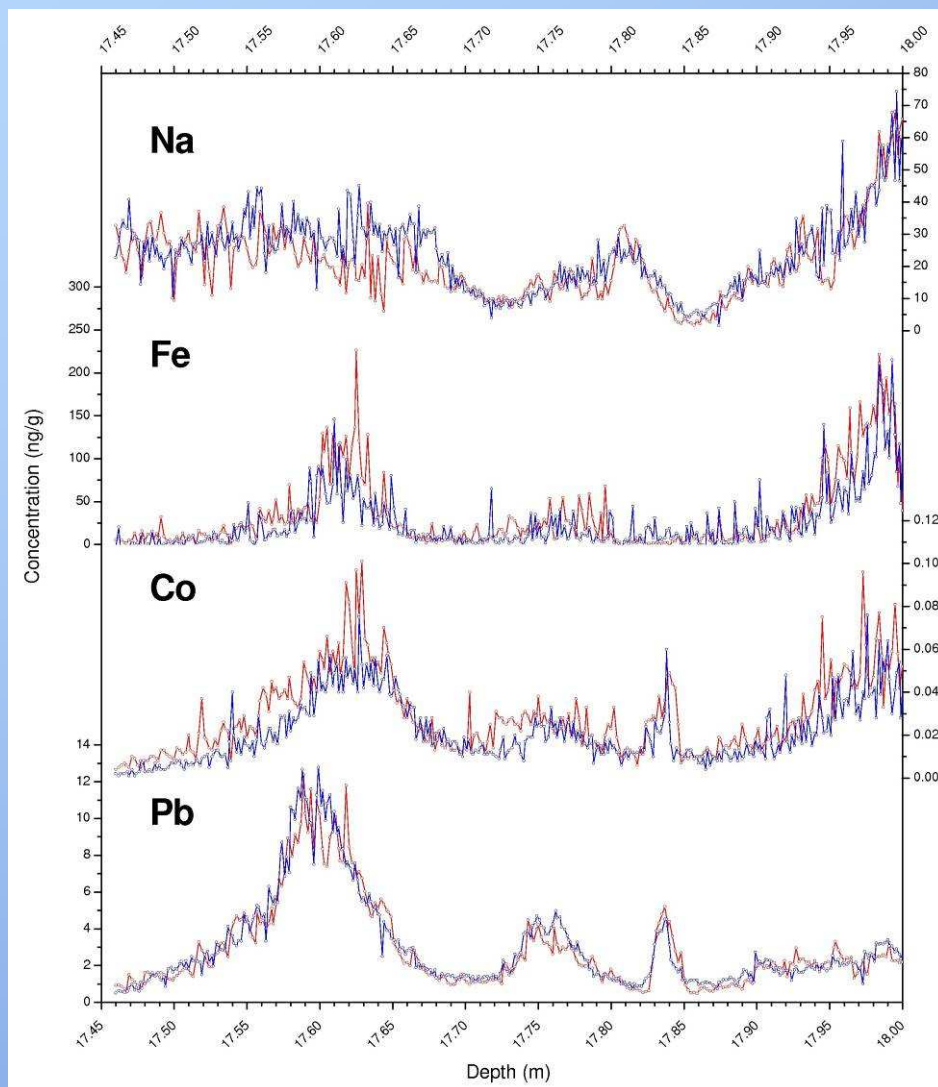
The "Venetian" melting heads



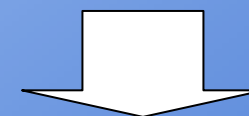
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The melting system

Continuous ICP-QMS analysis: reproducibility test



Analysis of parallel ice and firn sections during different analytical sessions



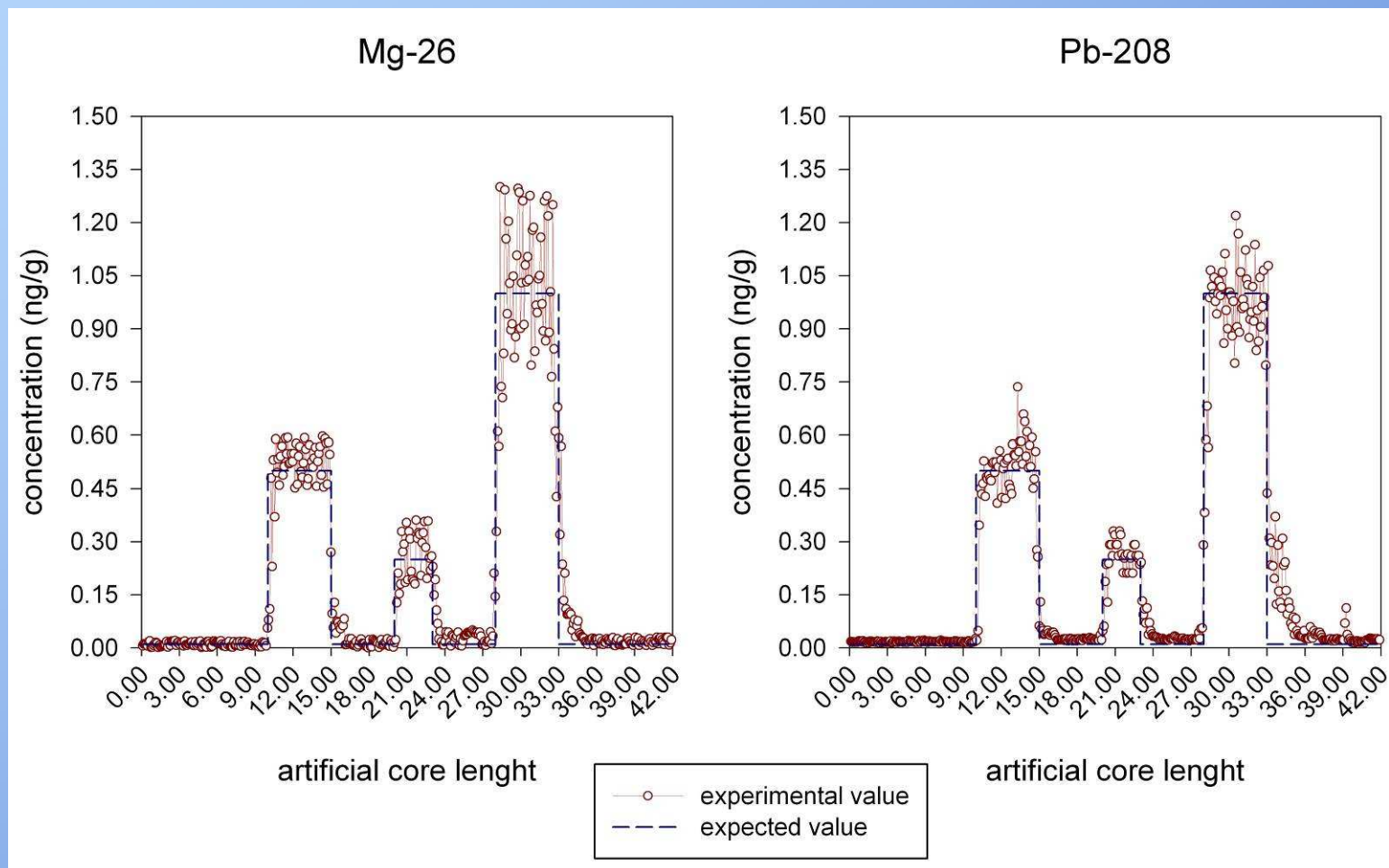
Very good fitting except for Zn which is strongly affected by external contaminations



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Validation

Continuous ICP-QMS analysis: recovery test



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Validation



Tofana di Rozes - Dolomites

Continuous and discontinuous trace elements analysis

21 elements by continuous ICP-QMS

42,000 measurements
900,000 concentration data

Resolution 0.9 – 2.5 mm (interpolation 10 mm)

22 isotopes by ICP-SFMS

6 elements by ICP-OES (Ca, Mg, Na, K, Fe, Al)

214 measurements

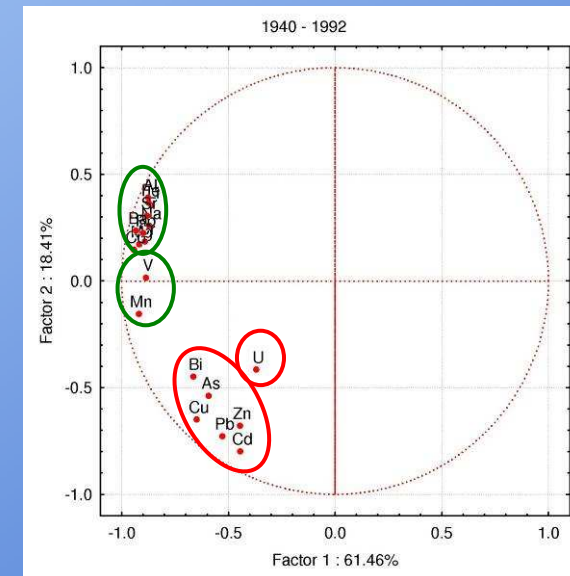
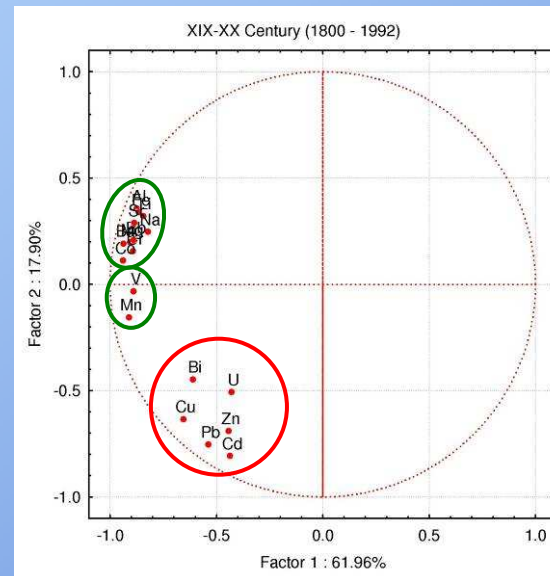
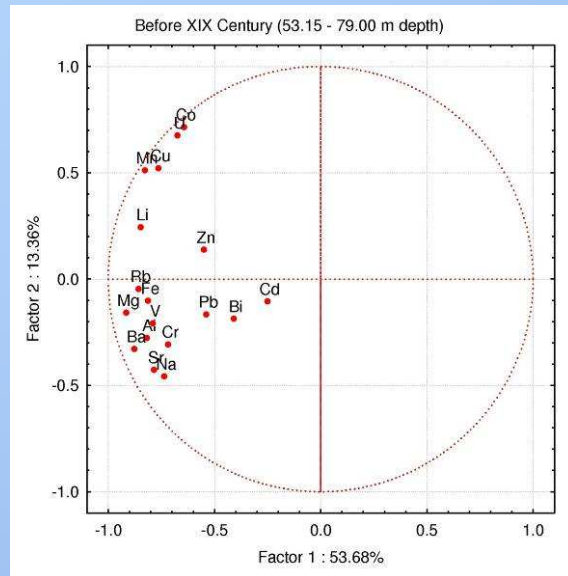
Resolution 20 - 30 cm



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Trace elements determination

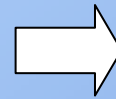
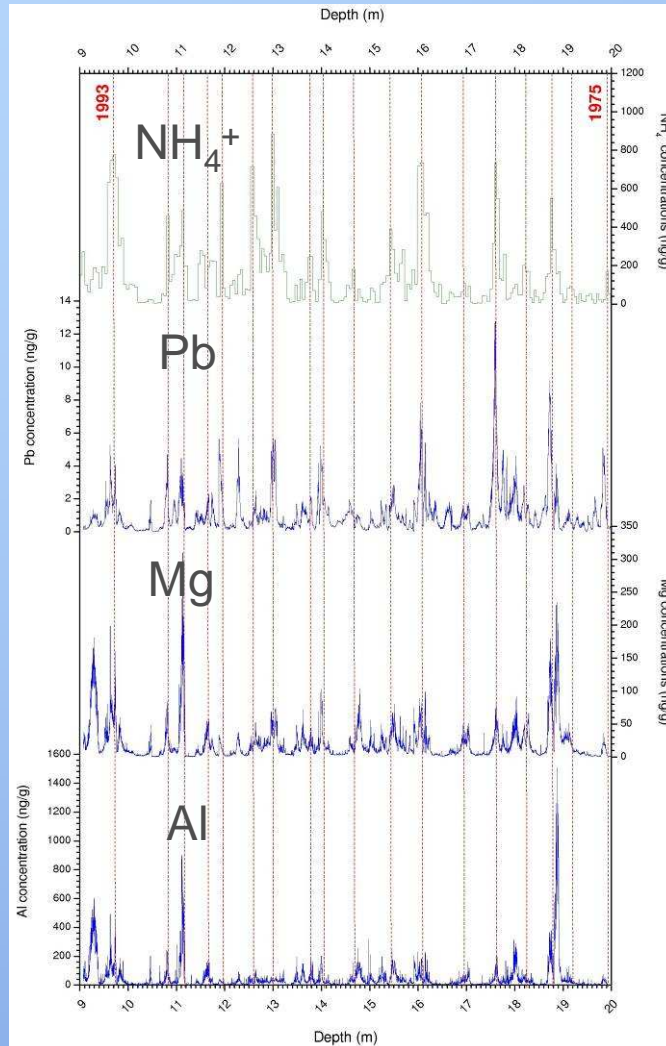
Principal component analysis



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Multivariate statistics

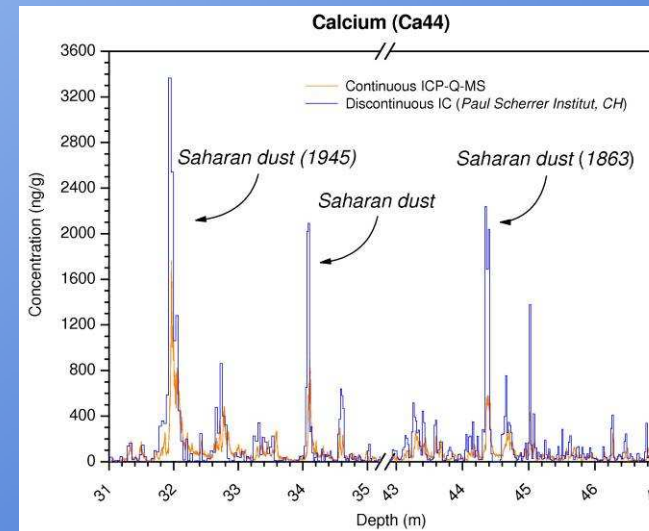
Short-term variations



ALC from 1200 (~) to 2003 AD

Not consistent with ¹⁴C dating

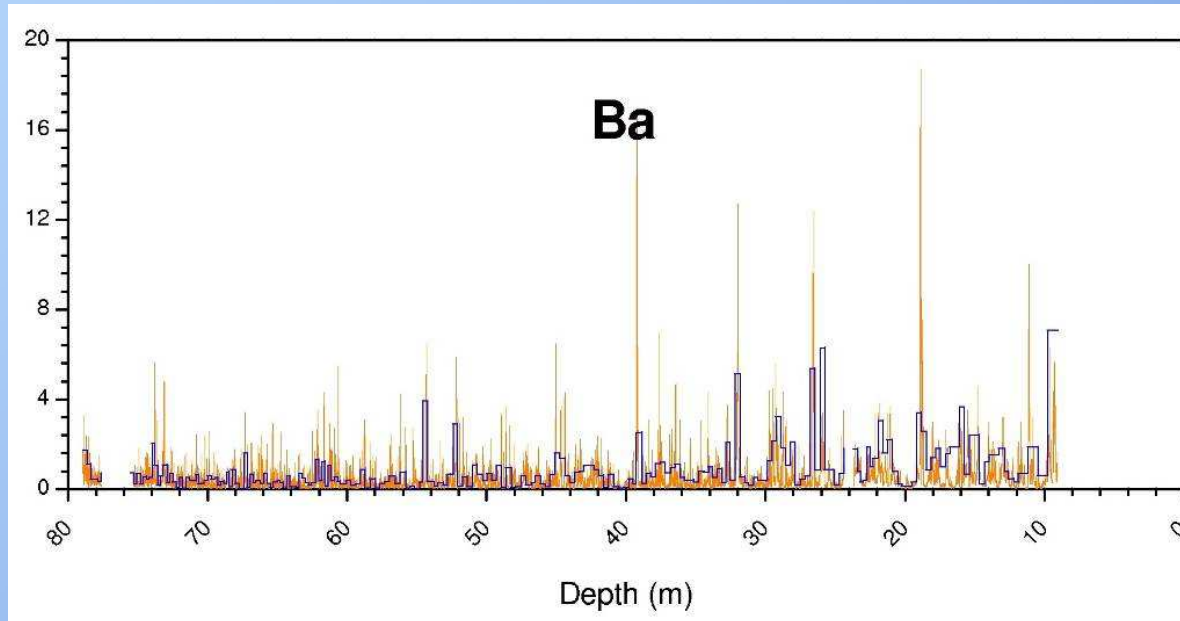
1200 AD { 66.45 m (ALC)
71.10 m (¹⁴C)



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Trace elements profiles

Long-term variations: crustal elements



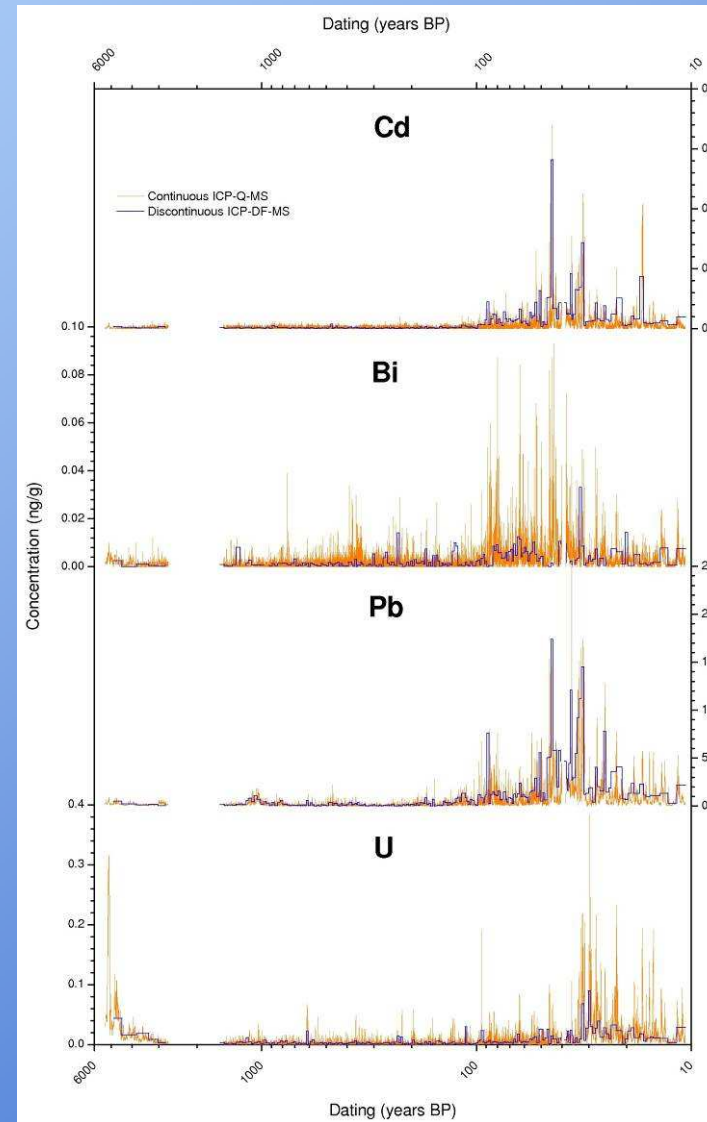
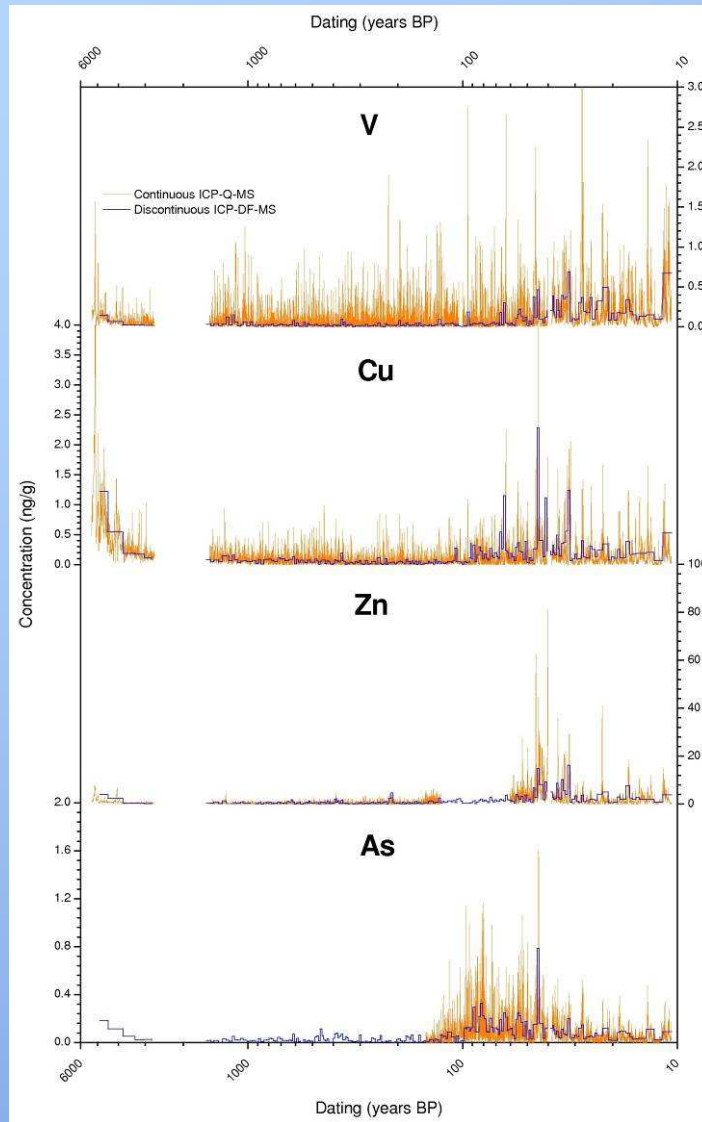
	XX Century			Pre-XX Century			Increase factor
	mean	median	max	mean	median	max	
Li	0.045	0.018	1.6	0.034	0.015	1.3	1.2
Na	28	17	725	24	12	477	1.4
Mg	19	10	236	16	10	266	1.0
Al	38	15	1258	28	11	682	1.4
Sc	0.015	0.011	0.098	0.0098	0.0085	0.052	1.3
Ti	0.20	0.10	1.6	0.094	0.067	0.70	1.4
Cr	0.085	0.040	2.2	0.060	0.038	0.92	1.1
Mn	1.3	0.70	17	0.79	0.50	35	1.4
Fe	26	9.7	807	24	13	479	0.7
Co	0.029	0.021	0.42	0.016	0.013	0.179	1.5
Pb	0.089	0.041	2.8	0.064	0.034	0.97	1.2
Sr	0.75	0.34	17	0.56	0.35	11	1.0
Ba	0.59	0.28	15	0.36	0.21	5.3	1.3



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Trace elements profiles

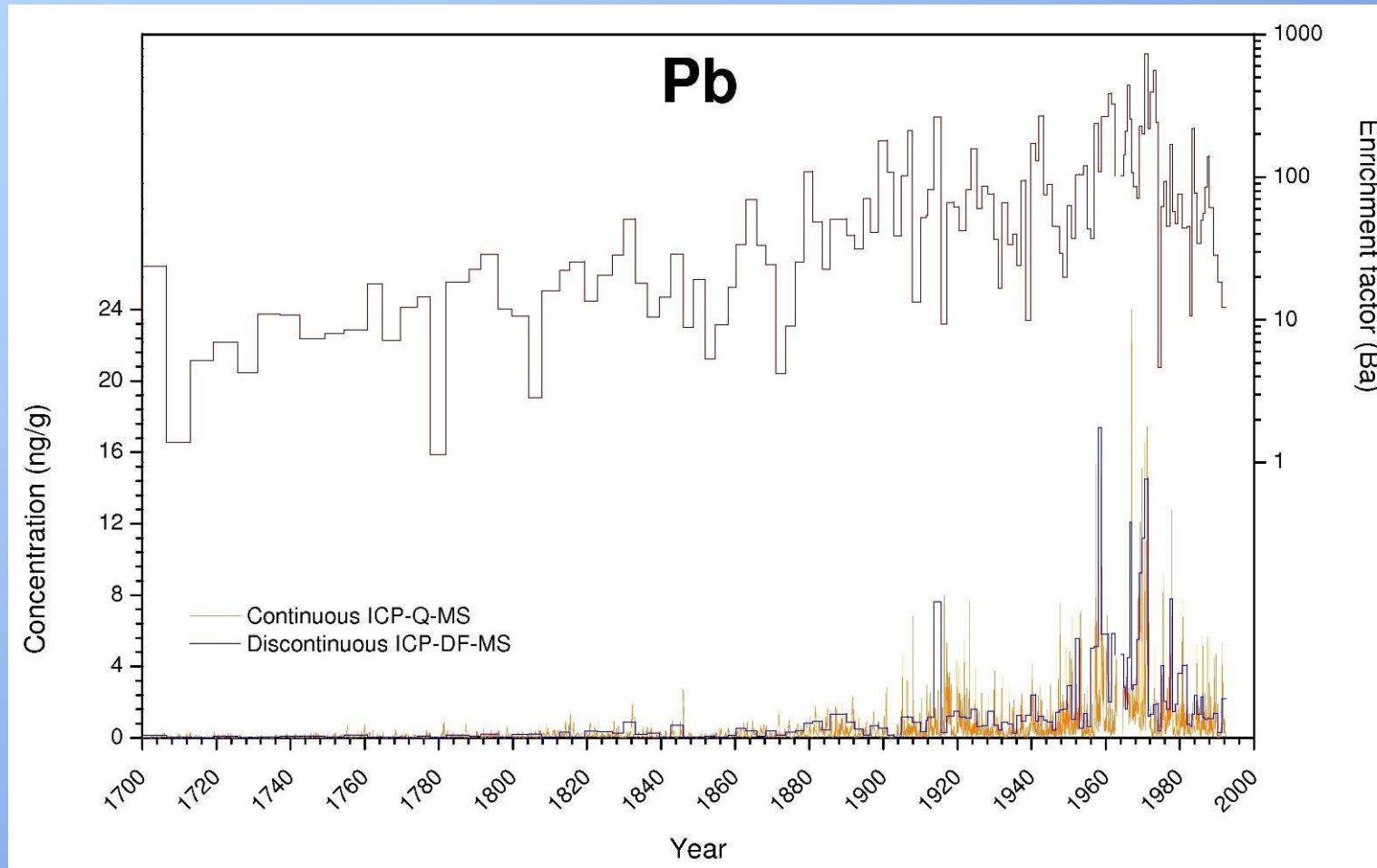
Long-term variations: anthropogenic elements



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Trace elements profiles

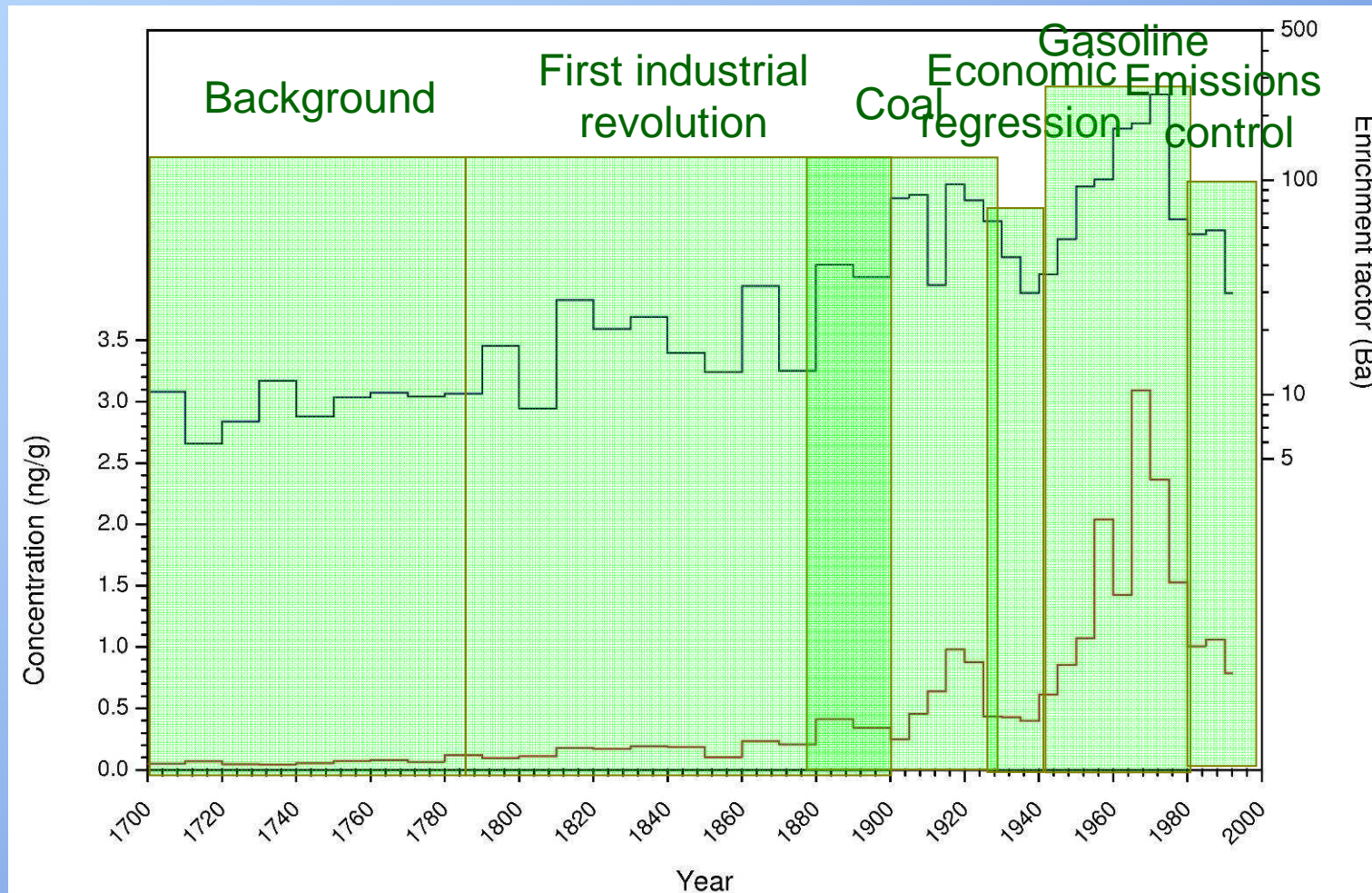
Anthropogenic metals: Pb



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Trace elements profiles

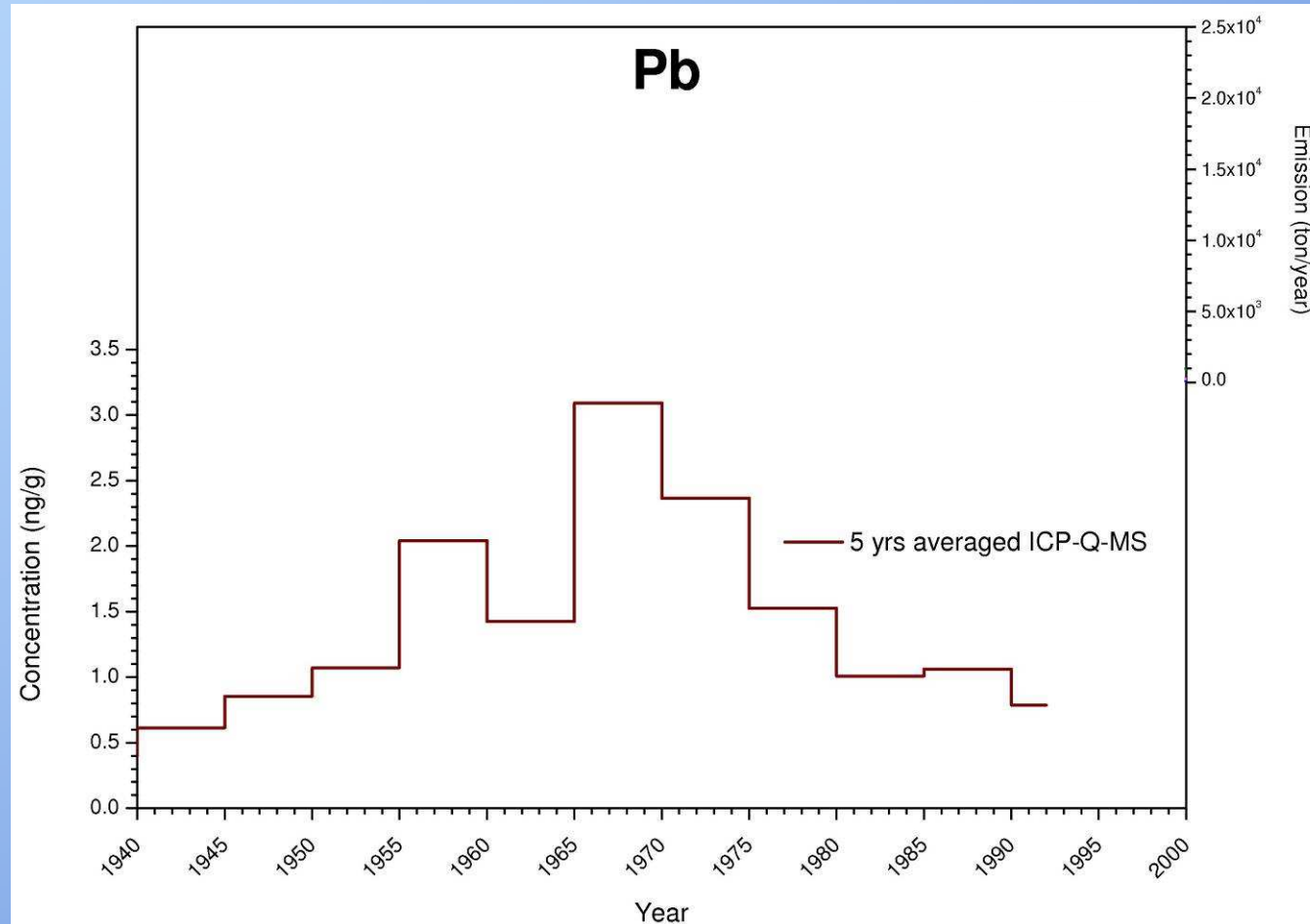
Anthropogenic metals: Pb



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Trace elements profiles

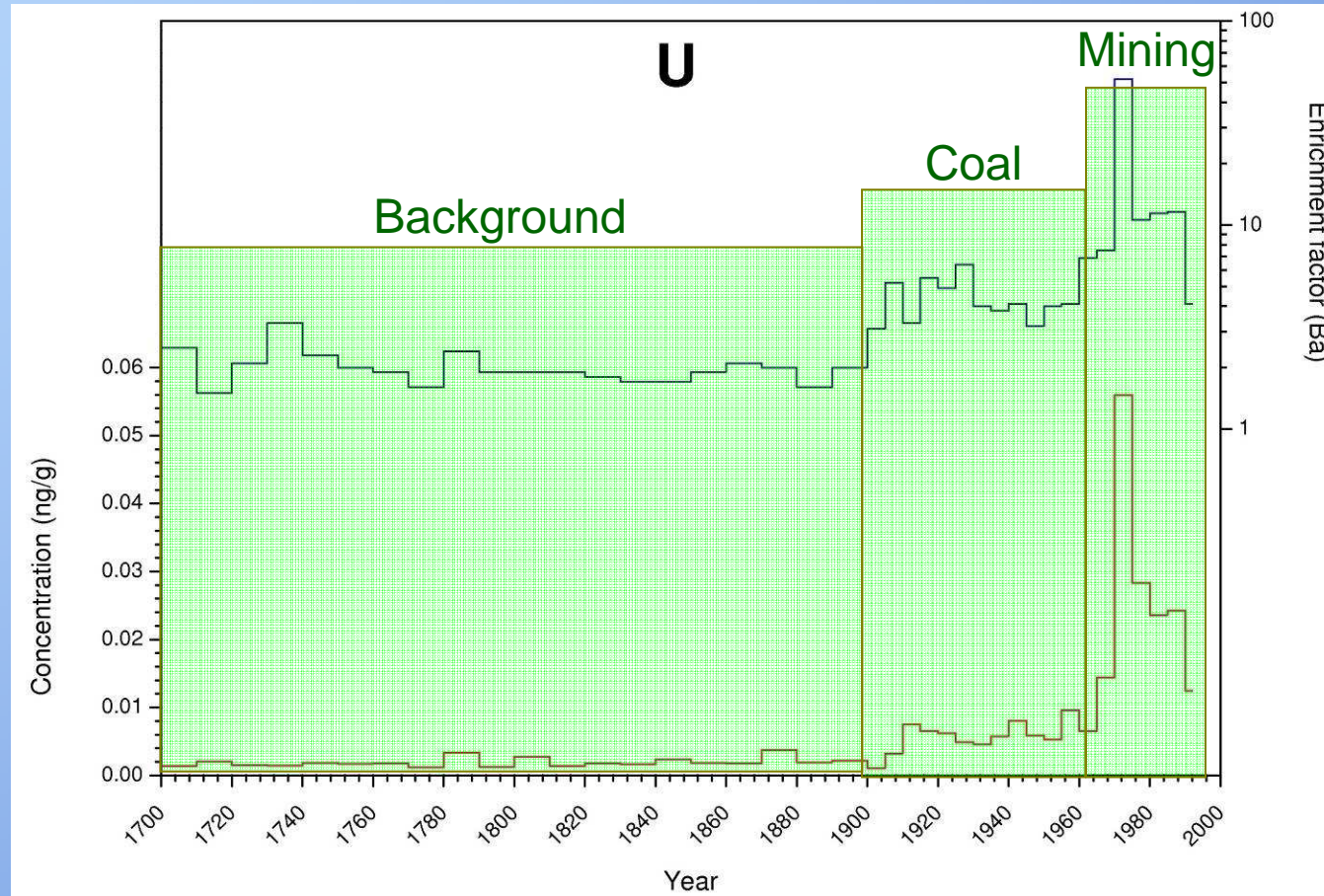
Anthropogenic metals: Pb



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Trace elements profiles

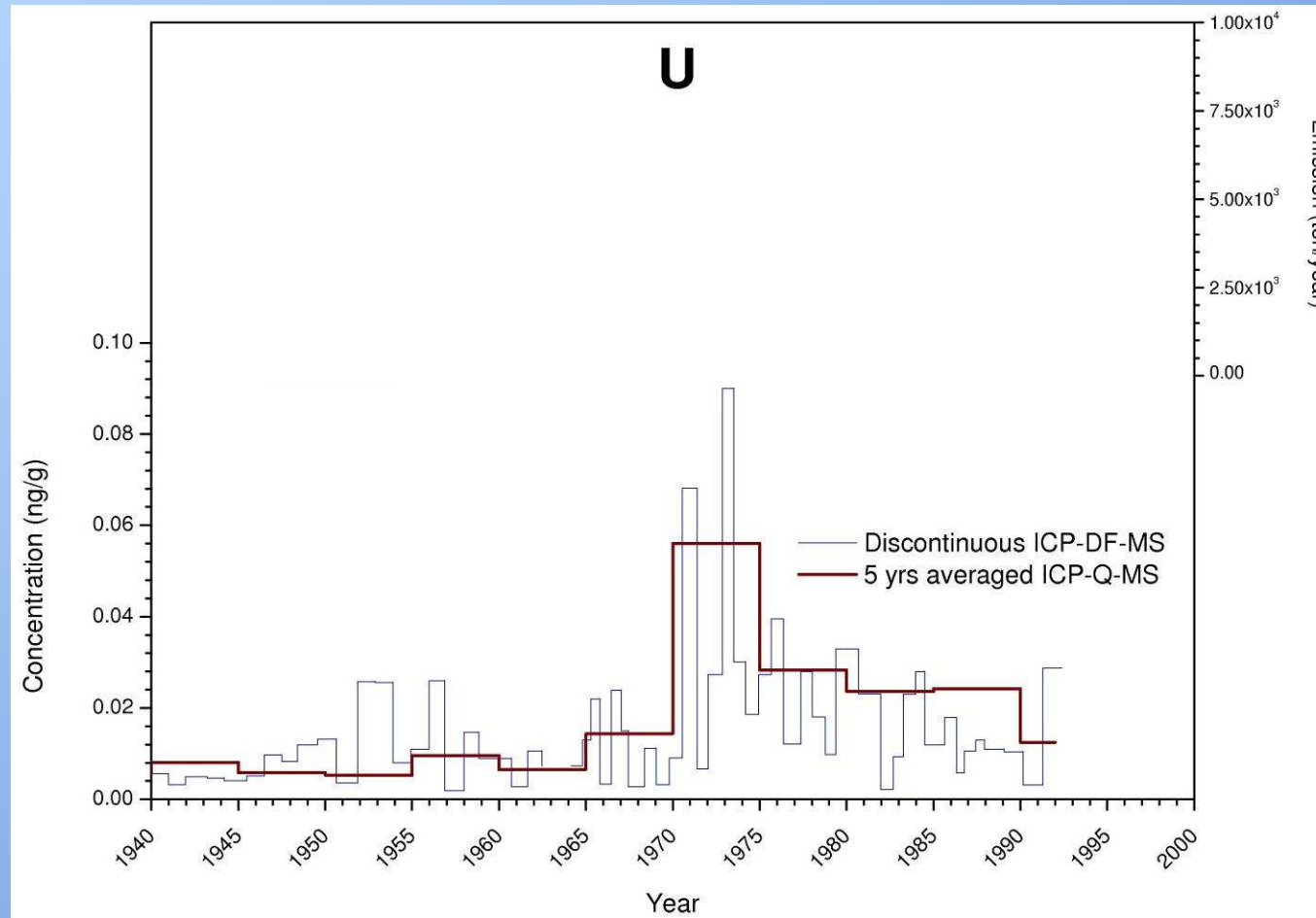
Anthropogenic metals: U



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Trace elements profiles

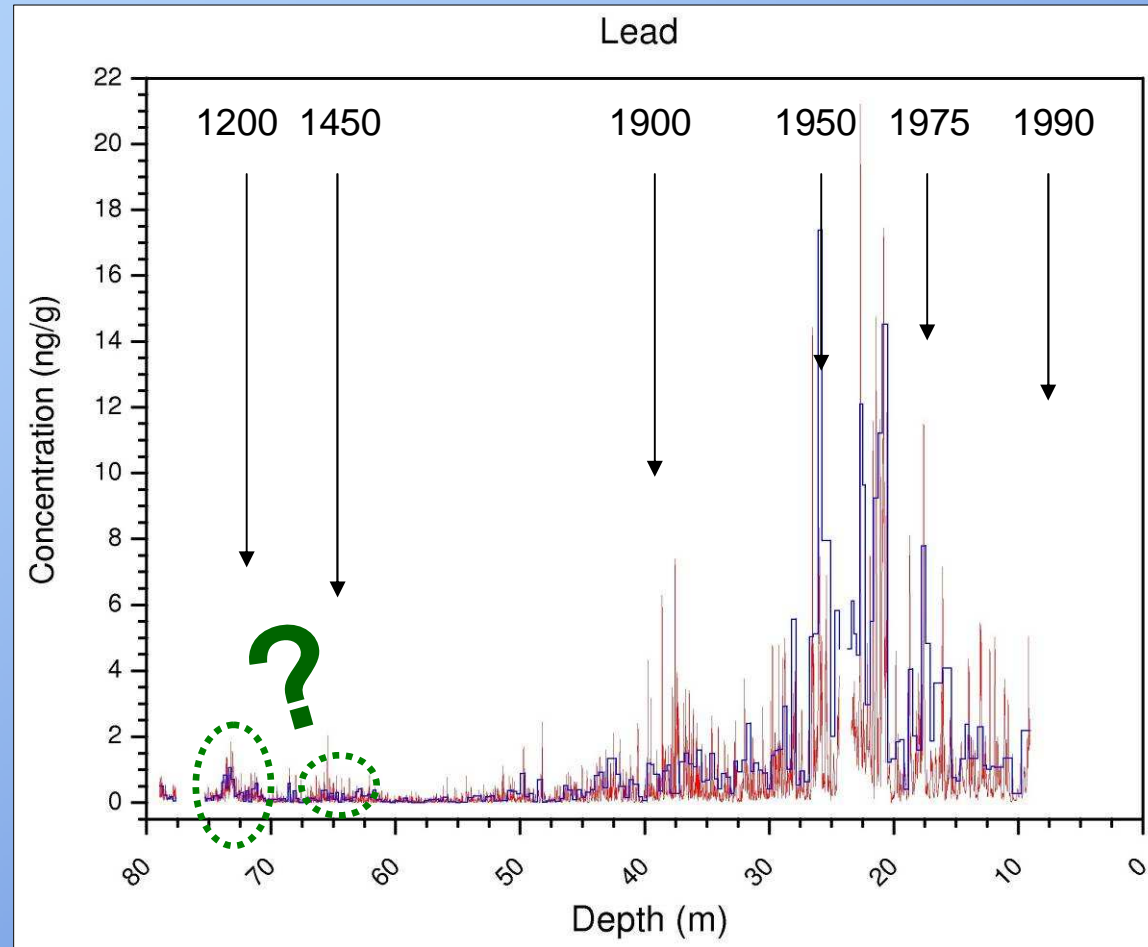
Anthropogenic metals: U



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Trace elements profiles

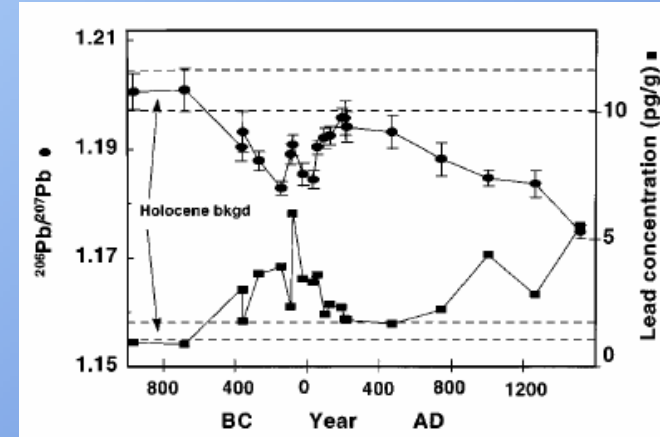
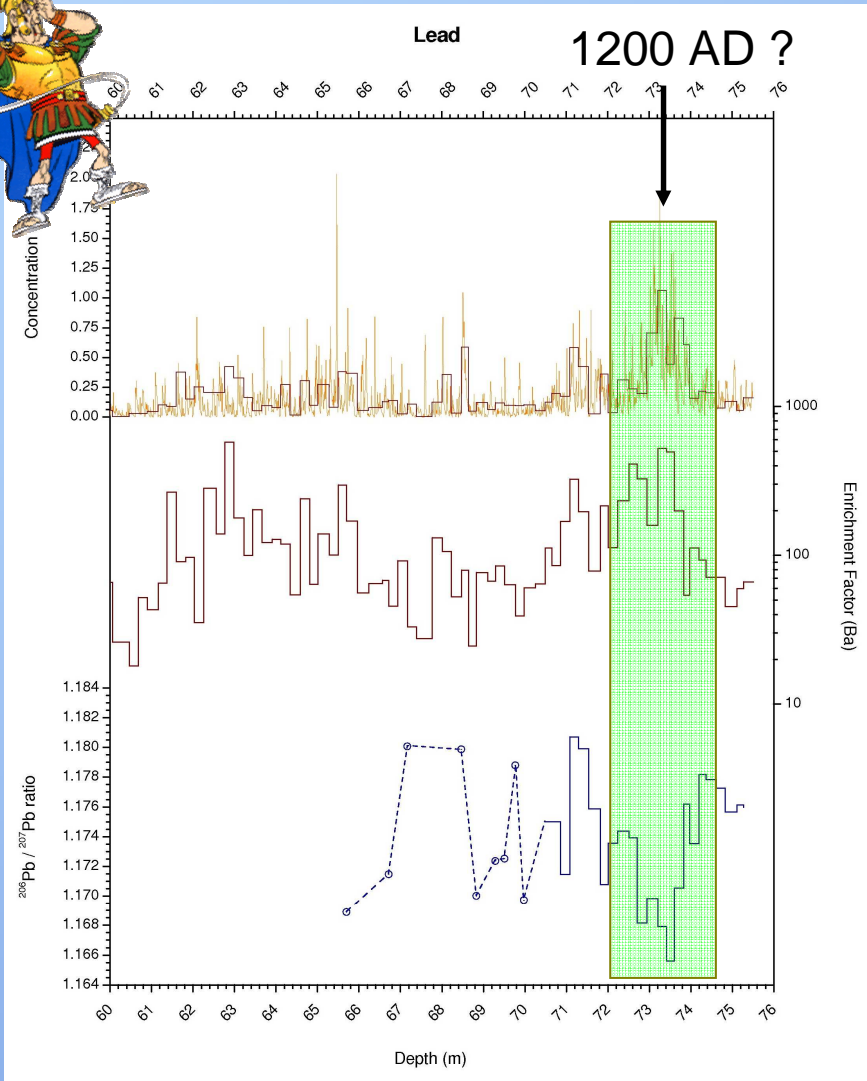
Pb: a useful tool for dating validation?



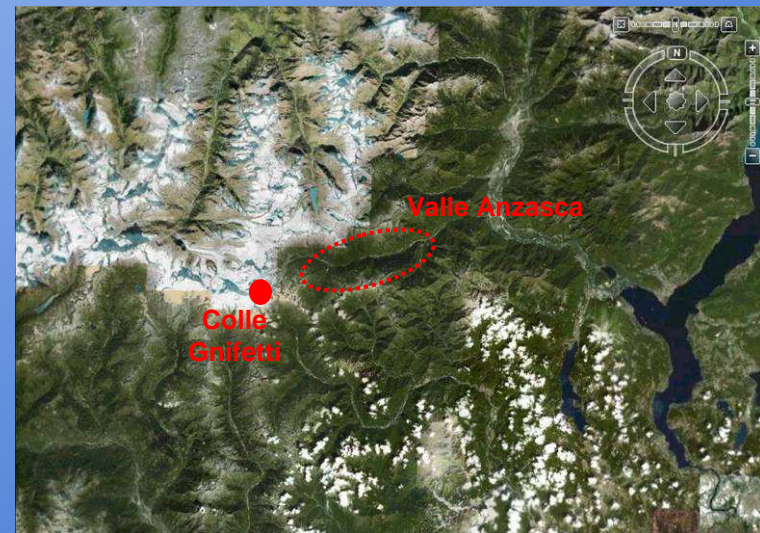
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Trace elements profiles

Pb profile: a tool in dating validation?



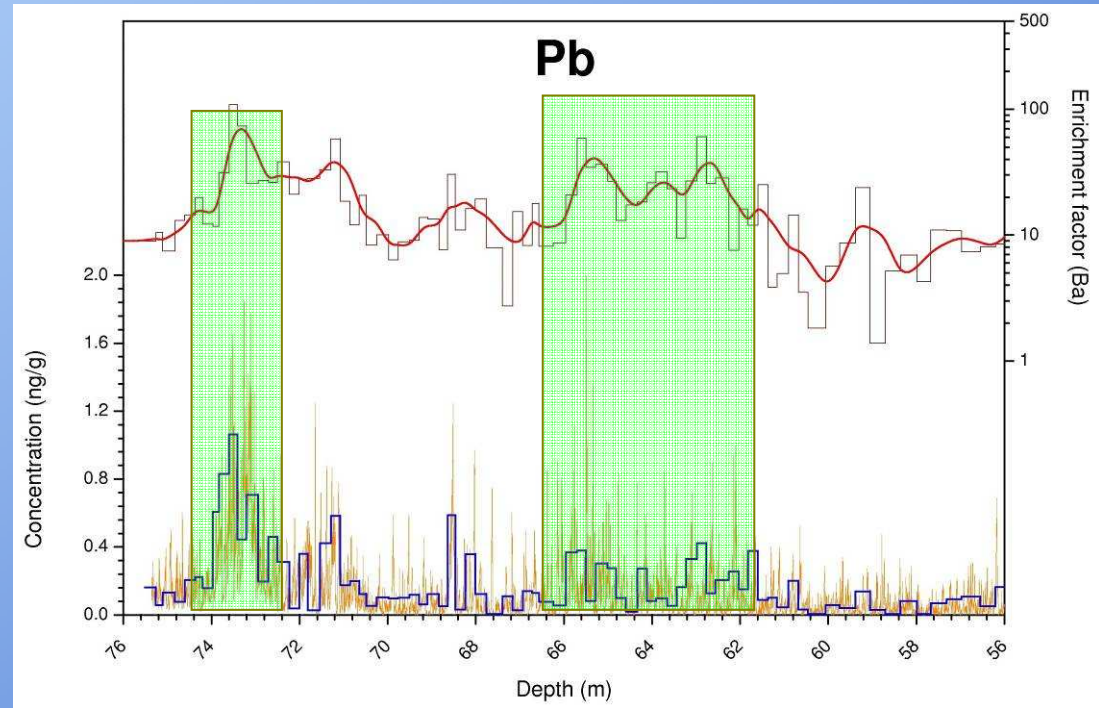
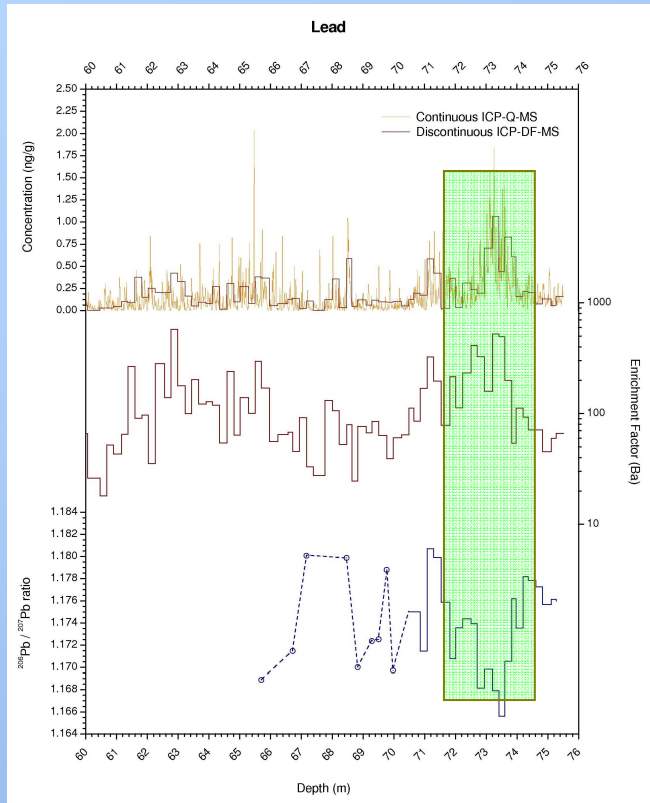
Rosman, 1997



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Trace elements profiles

Pb: a useful tool for dating validation?



Roman
Empire

Middle Ages

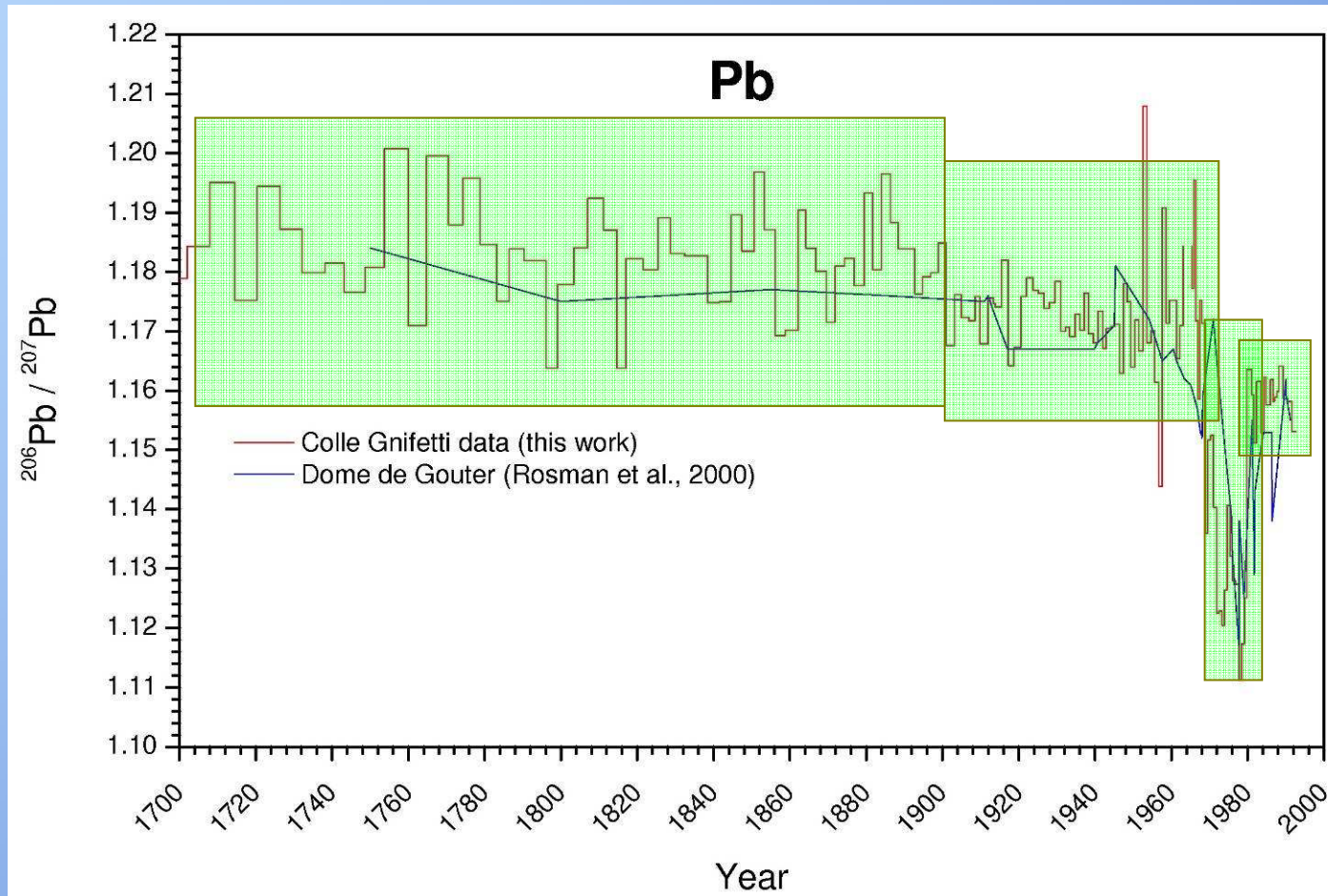
(ALC 1200 AD at 66.5m)



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Trace elements profiles

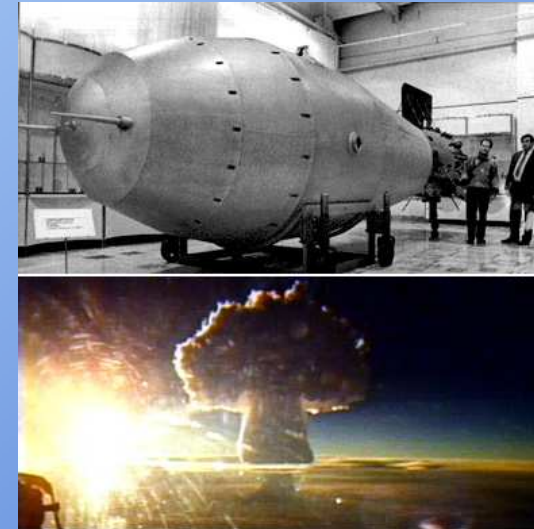
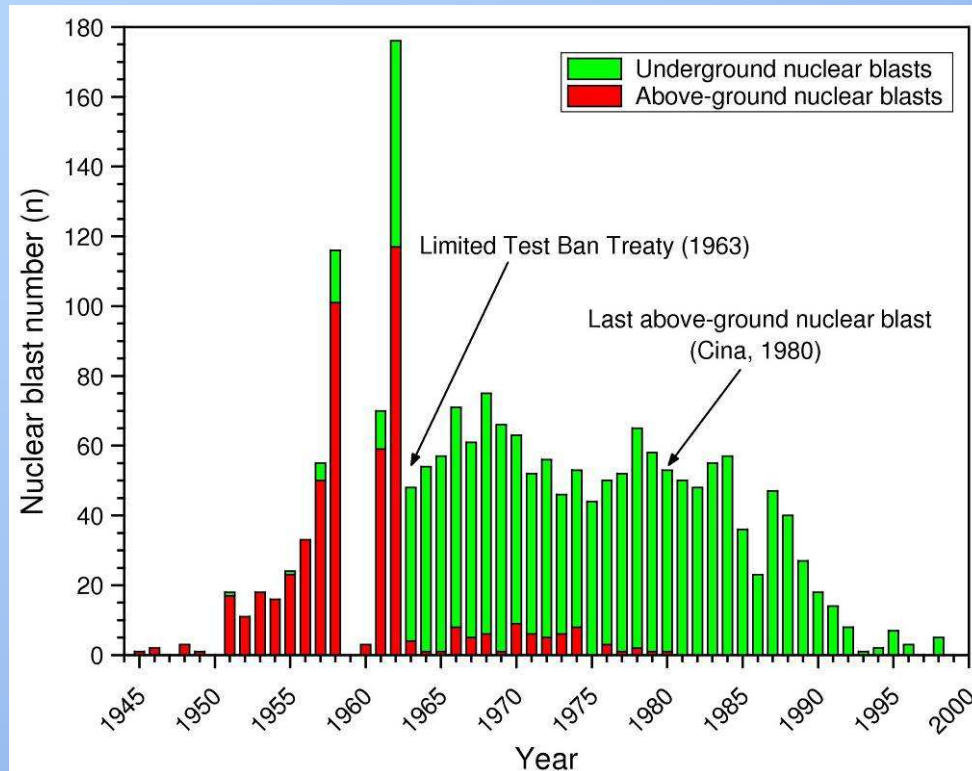
Lead isotopes in industrial period



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Pb isotopic ratio profile

Pu: a worldwide "cold war" pollutant



Tsar bomb, Arctic Siberia; 30 October 1961

57 Mton (more than 5 times the total amount of traditional explosives during 2°World War)

Blast at 4000 m a.s.l.; nuclear mushroom cloud high about 60 km



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Pu determination

Pu profile in CG firn core

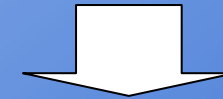
Semi-quantitative determination



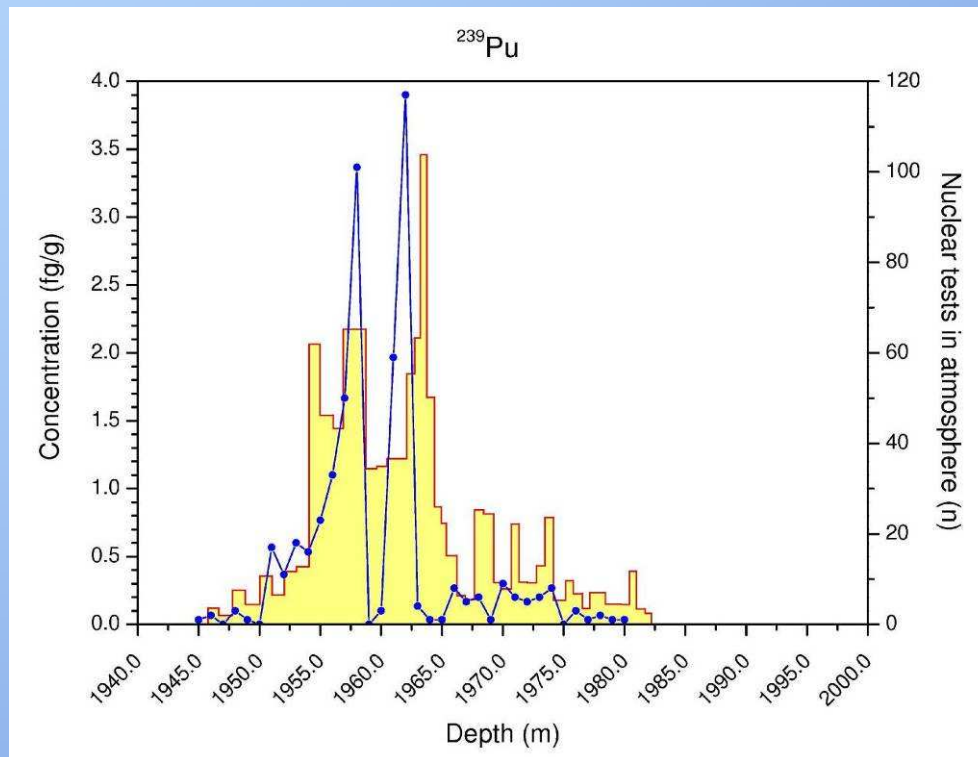
Without external calibration and/or IS spiking (^{241}Pu) only semi-quantitative analysis

Calibration using ^{238}U linear regression parameters

UH^+ interference doesn't affect the method for $[\text{U}] < 50 \text{ pg/g}$



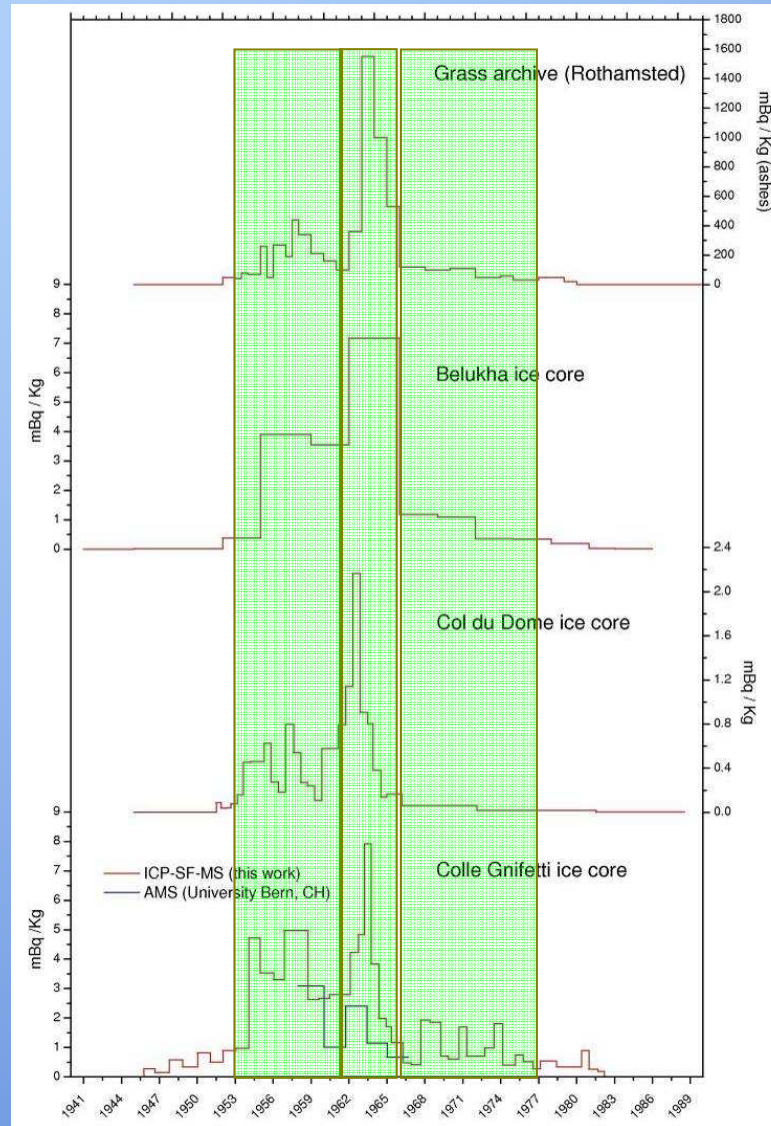
Fast screening method for “clean” matrix analysis; not appropriate for complex samples (soil, sediments, biological) without a purification step



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Pu determination

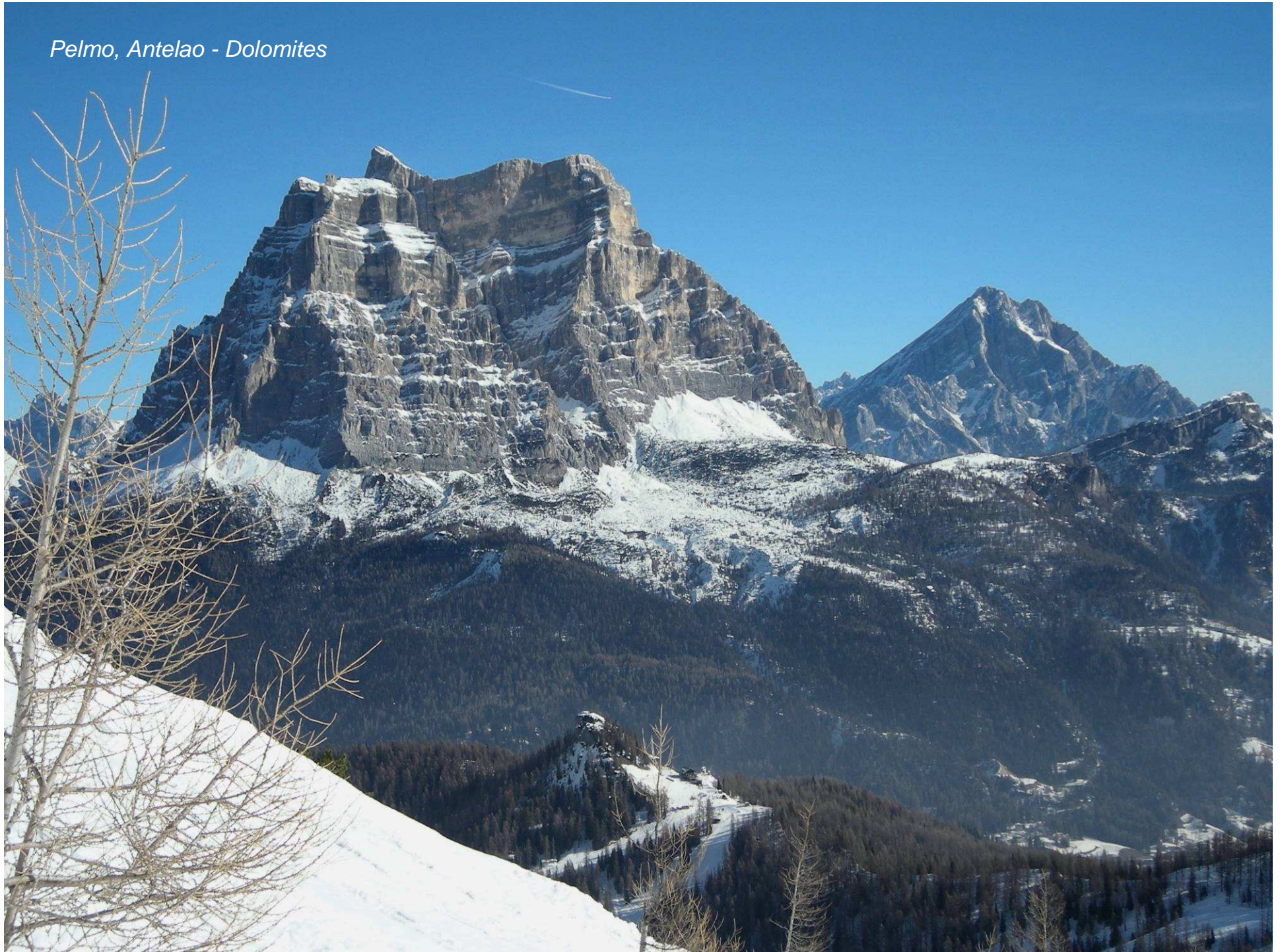
Pu profile in CG firn core



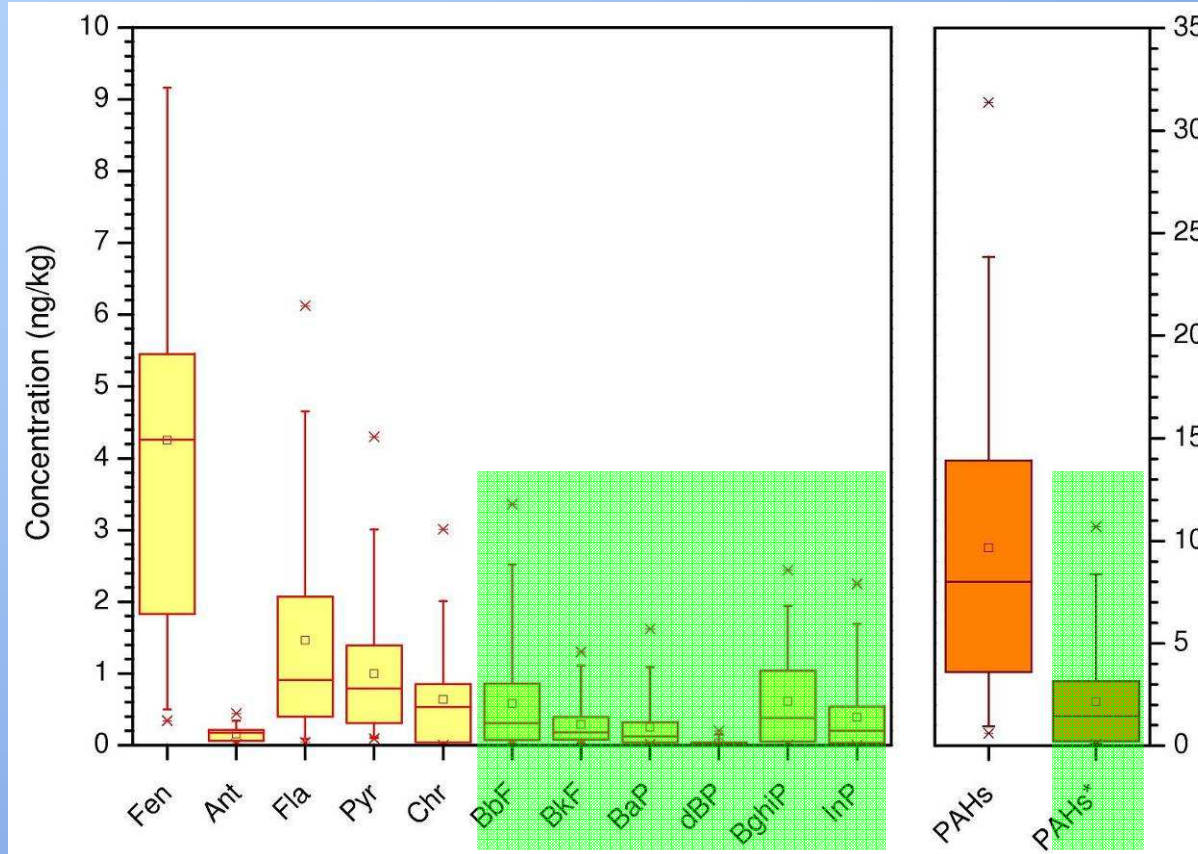
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Pu determination

Pelmo, Antelao - Dolomites



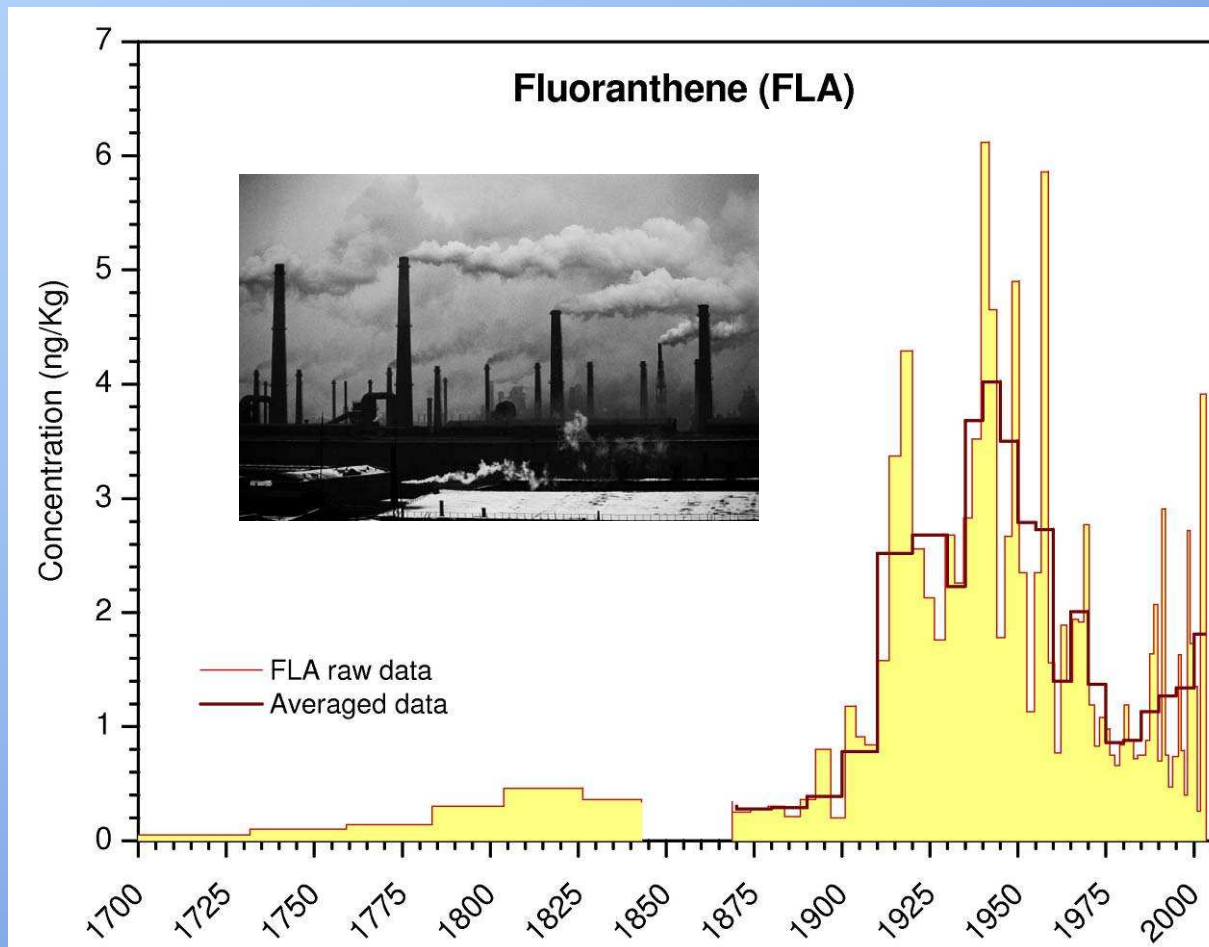
PAHs pattern



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Polycyclic Aromatic Hydrocarbons

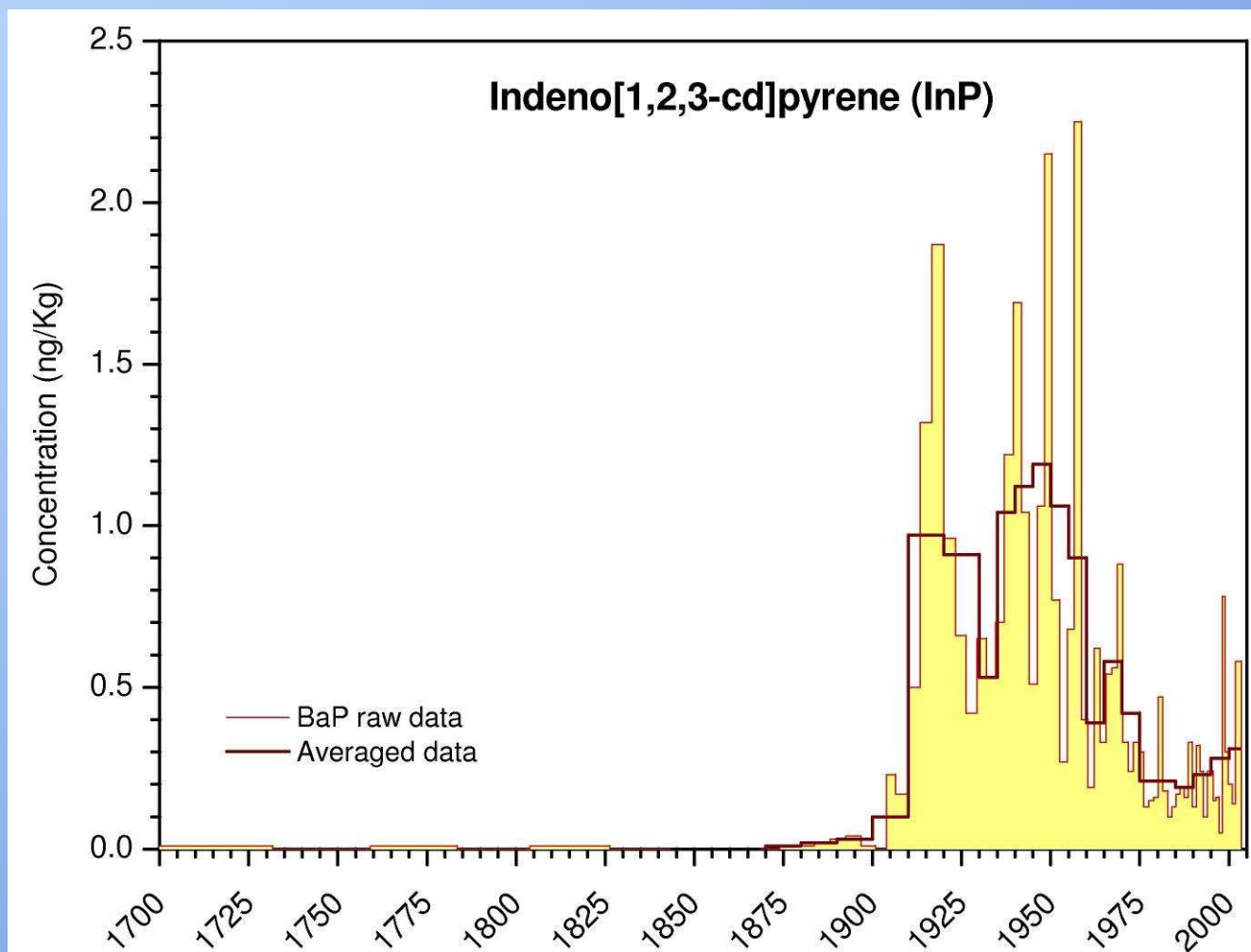
Fluoranthene



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Polycyclic Aromatic Hydrocarbons

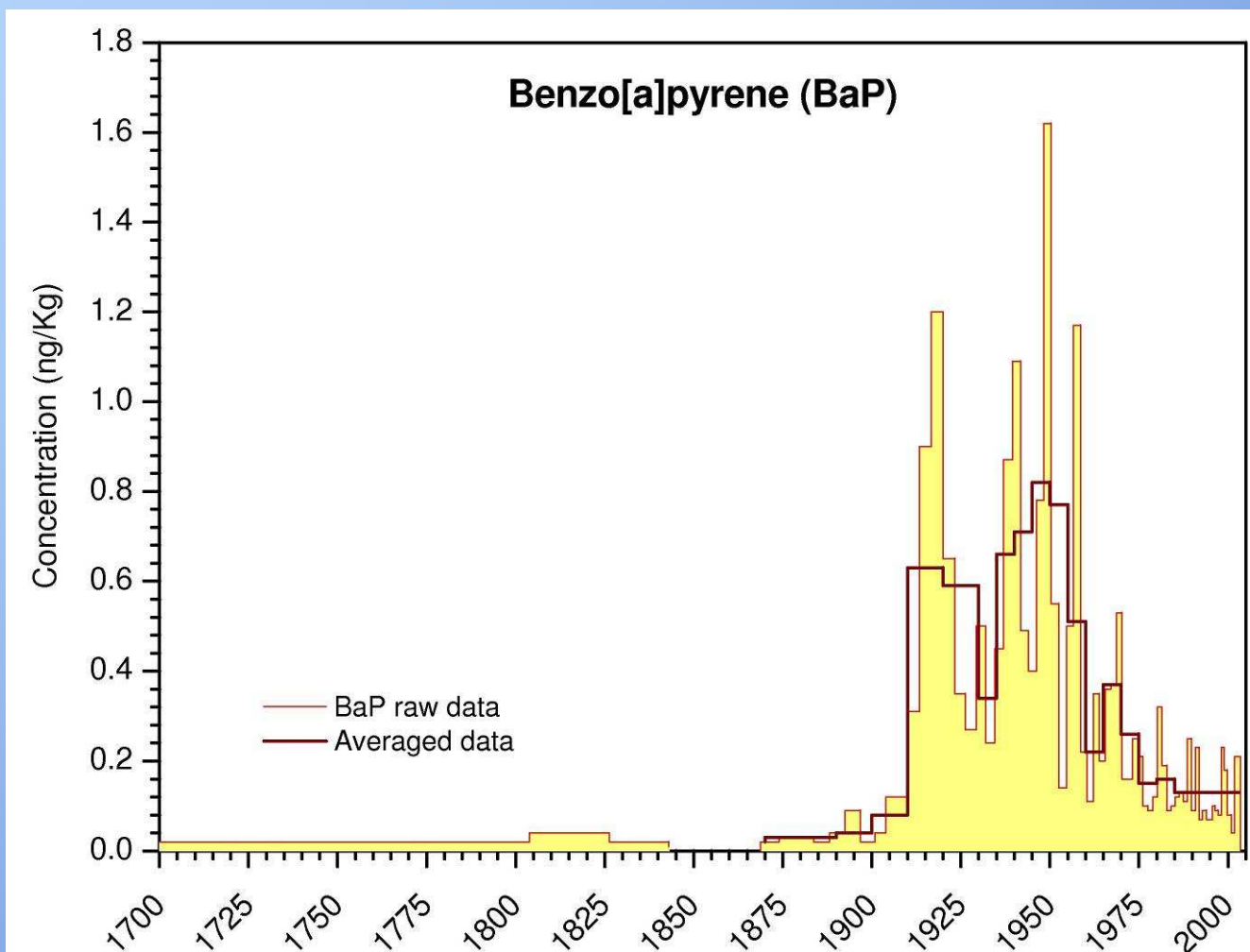
Indeno[1,2,3-cd]pyrene



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Polycyclic Aromatic Hydrocarbons

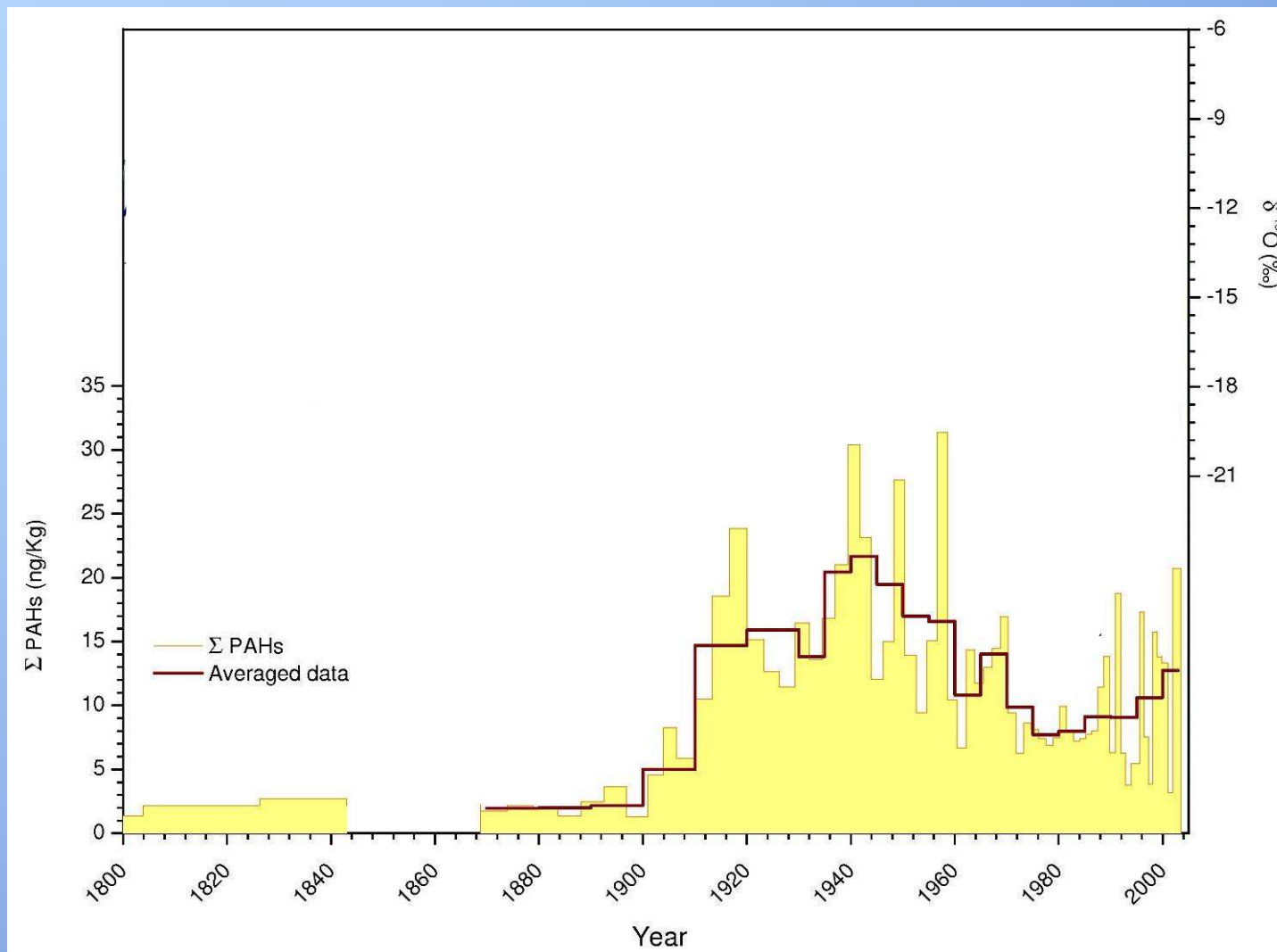
Benzo[a]pyrene



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Polycyclic Aromatic Hydrocarbons

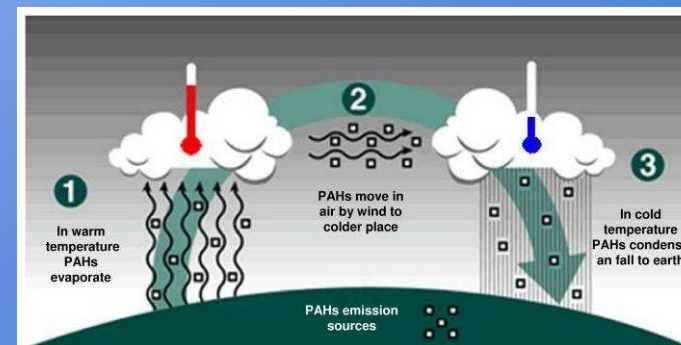
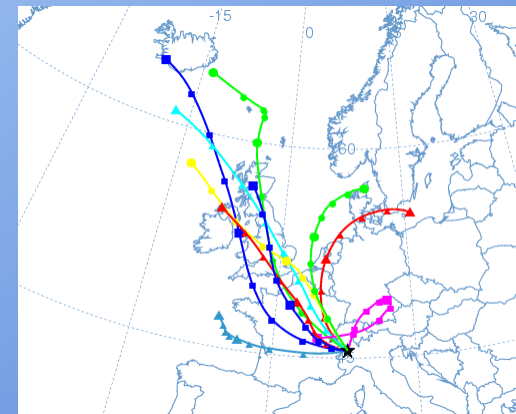
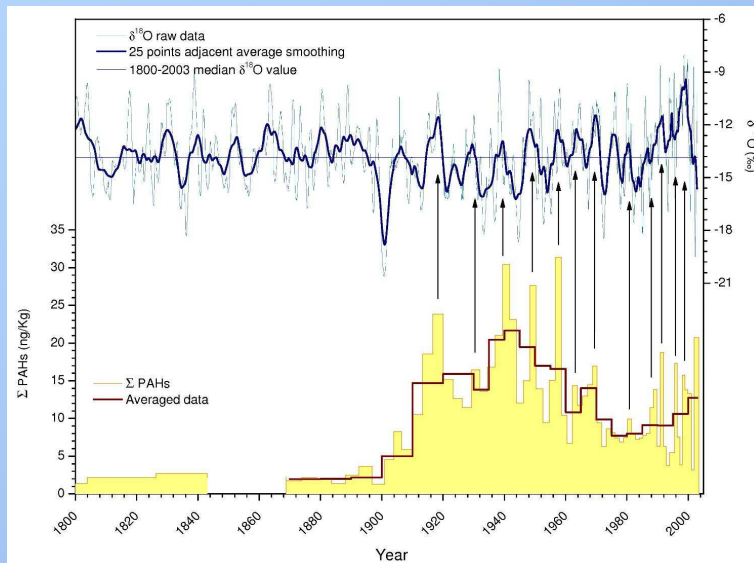
PAHs short-term variation and temperature



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Polycyclic Aromatic Hydrocarbons

PAHs short-term variation and temperature



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Polycyclic Aromatic Hydrocarbons

Marmolada, South Face - Dolomites



Conclusions

Designing, building and testing of a new melting system for continuous decontamination and on-line analysis of alpine ice/firn core

Continuous trace elements (ICP-QMS) and conductivity determination; semi-continuous solid phase extraction (SPE)

Discrete sampling and discontinuous analysis of trace elements, Pb isotopes and ^{239}Pu (ICP-SFMS)

Trace elements profiles

Short-term variations due to boundary layer and air masses trajectories seasonal changes; ALC implications

Increase of crustal TE concentrations during warm periods

Variations of anthropogenic TE concentrations during industrial revolution consistent with emission inventories in Europe

Conclusions

Polycyclic Aromatic Hydrocarbons profiles

First high-resolution PAHs record in ice and firn core

Long-term depositions influenced by anthropogenic emissions

Short-term PAHs profiles as function of climatic conditions: higher concentrations in warm periods

^{239}Pu profile reflects main periods of nuclear testing in atmosphere

High resolution profile

Validation of a rapid semi-quantitative method

Pb isotopes profile

High resolution profile

Evidences of "Turin isotopic experiment"

Prospectives

Searching for new evidences to support or reject current dating

Analyzing chips sections for TE and dust

Analyzing deepest sections of this ice core

High resolution POPs analysis (PAHs, PCBs, ...) and TE on a new shallow firn core drilled on Colle Gnifetti

Comparing CG data with other archives (lake sediments, peat-bogs) collected in the Alps

Acknowledgments



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Dr. Paolo Gabrielli
Dr. Paul Vallelonga



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Dr. Fabio Decet
Dr. Roberto Fiabane



Prof. Heinz Gaggler
Dr. Margit Schwikowski
Dr. Michael Sigl
Dr. Theo Jenk



Dr. Barbara Delmonte



A dramatic mountain landscape at dawn or dusk. The scene is filled with mist and low-hanging clouds. Sunlight breaks through the clouds from the left, creating a series of rays that illuminate the scene. The mountains are dark and silhouetted against the lighter sky. The overall mood is serene and majestic.

thanks for your attention!