

***RECONSTRUCTING THE PAST, UNDERSTANDING THE PRESENT
AND PREDICTING THE FUTURE BASED ON
ISOTOPIC ANALYSIS VIA
MULTI-COLLECTOR ICP - MASS SPECTROMETRY***

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Ghent University, Belgium***



MASARYK UNIVERSITY
Czech Republic



ICP – MASS SPECTROMETRY

- **Analytical technique for (ultra)trace element analysis**

- ▶ ° 1983

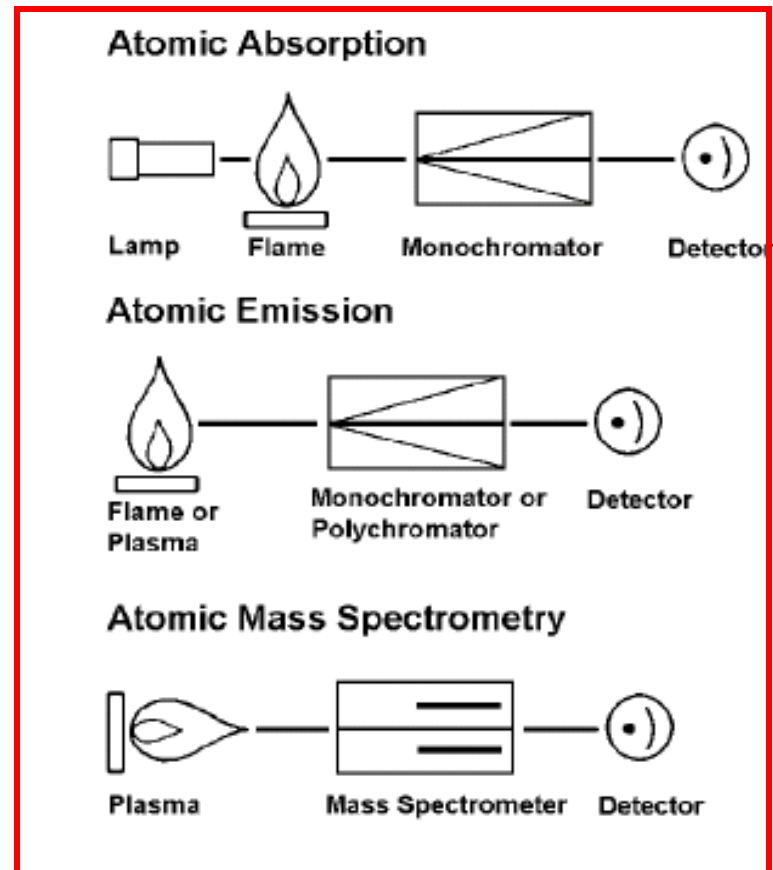
- **Compared to AAS**

- ▶ **Even lower LODs**

- ▶ **Multi-element capabilities**

- **Compared to ICP-OES**

- ▶ **Lower LODs**



ICP – MASS SPECTROMETRY

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- ▶ ° 1983

- **Compared to AAS**

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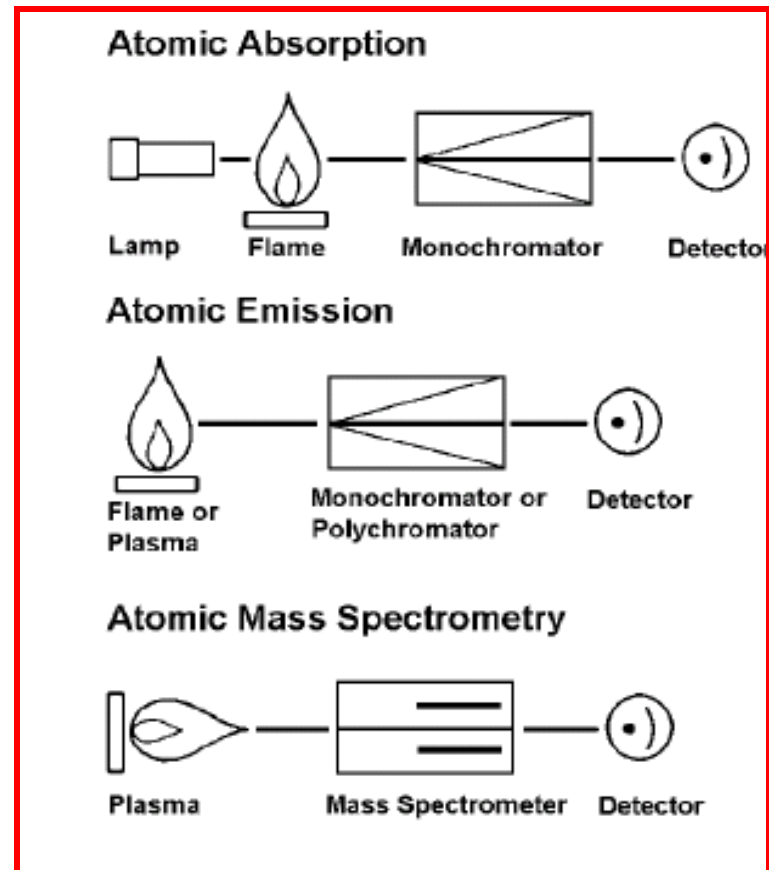
- ▶ **Multi-element capabilities**

- **Compared to ICP-OES**

- ▶ **Lower LODs**

- **Compared to AAS & ICPOES**

- ▶ **Isotopic information !!**



ISOTOPES ?

- **Isotopes of an element M:**

- ▶ **same atomic number A**

- *Same number of protons in their nuclei*
- *Same number of electrons in their shells*

- ⇒ **Identical chemical behaviour**

- *First approximation – statement will be refined later on*

- ▶ **Different mass number Z**

- *Different number of neutrons in their nuclei*

- ⇒ **Different masses**

- **Notation**



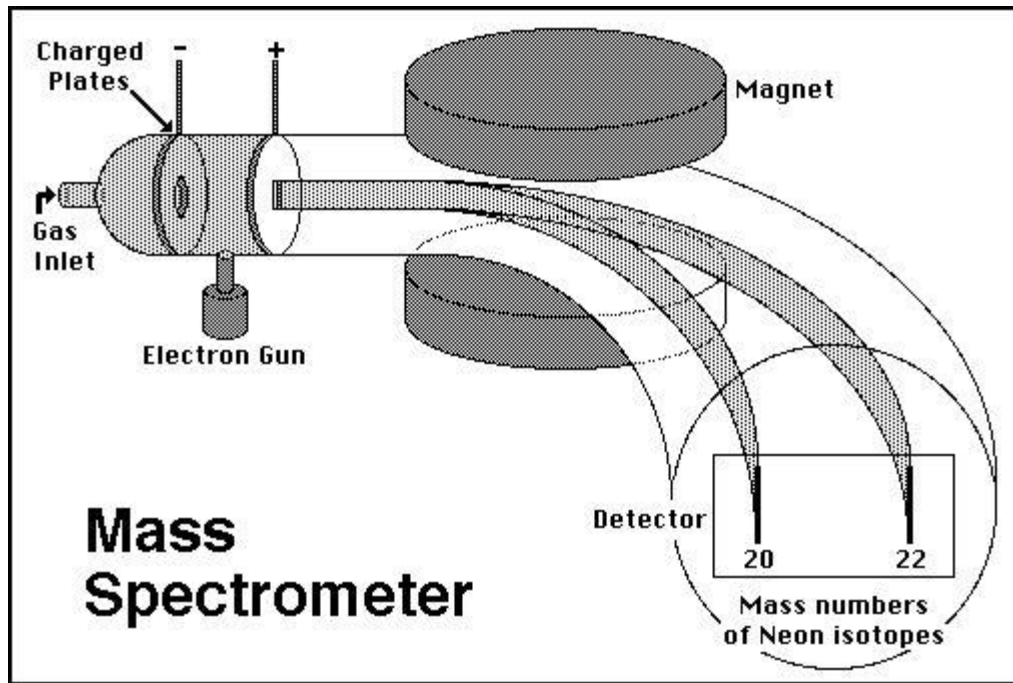
- **Terminology?**

- ▶ **Isotope: same place in PSE**
- ▶ **Todd & Soddy (early 20th century)**



DISCOVERY OF ISOTOPES

- **Separation of isotopes according to their mass in MS**
 - ▶ **Thomson: separation of Ne^+ isotopes in magnetic field**



- ▶ **Later on: Aston → isotopes for a suite of elements**

ISOTOPES ?

Periodic Table of the Elements

1	IA																2	
1	H 1.00794															He 4.0026		
2	IIA												0					
2	Li 6.941	Be 9.01218											B 10.811	C 12.011	N 14.0067	O 16.00	F 18.9984	Ne 20.1797
3	Na 22.989768	Mg 24.305											Al 27.98	Si 28.086	P 30.974	S 32.066	Cl 35.453	Ar 39.948
4	K 39.0983	Ca 40.078	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb 85.4678	Sr 87.62	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs 132.90545	Ba 137.327	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr [223]	Ra [226]	+Ac	Rf	Ha	106	107	108	109	110								



* Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

+ Actinide Series

● Mono-isotopic elements?

▶ ^9Be , ^{19}F , ^{23}Na , ^{27}Al , ^{31}P , ^{45}Sc , ^{55}Mn , ^{59}Co , ^{75}As , ^{89}Y , ^{93}Nb , ^{103}Rh , ^{127}I , ^{133}Cs , ^{141}Pr , ^{159}Tb , ^{165}Ho , ^{169}Tm , ^{197}Au , ^{209}Bi , ^{231}Pa , ^{232}Th

● Other elements?

▶ 2 – 10 isotopes

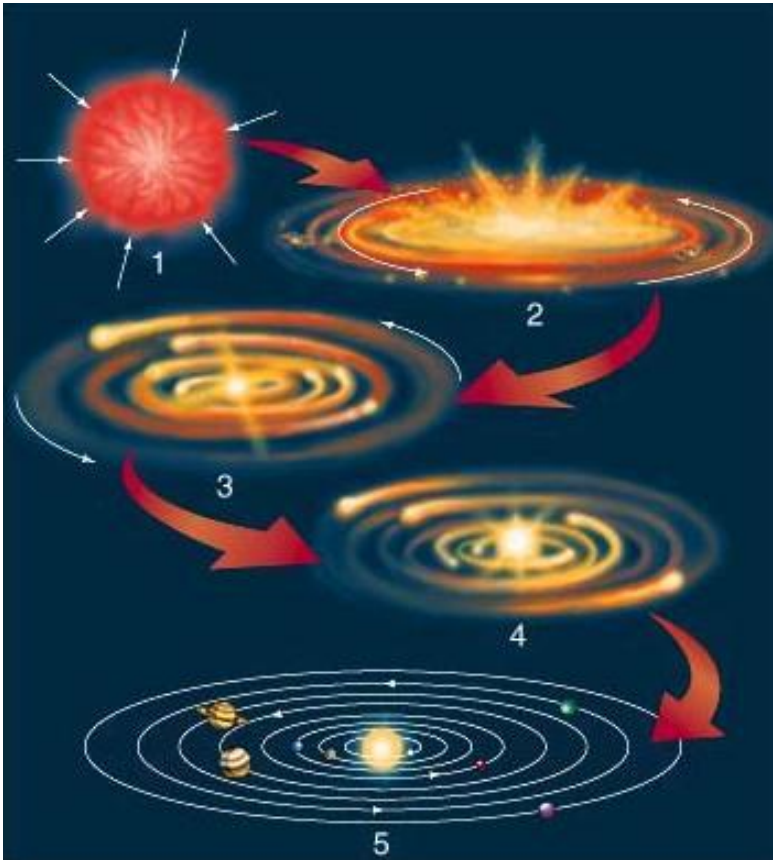
THE ISOTOPIC COMPOSITION OF THE ELEMENTS

- **First approximation:**

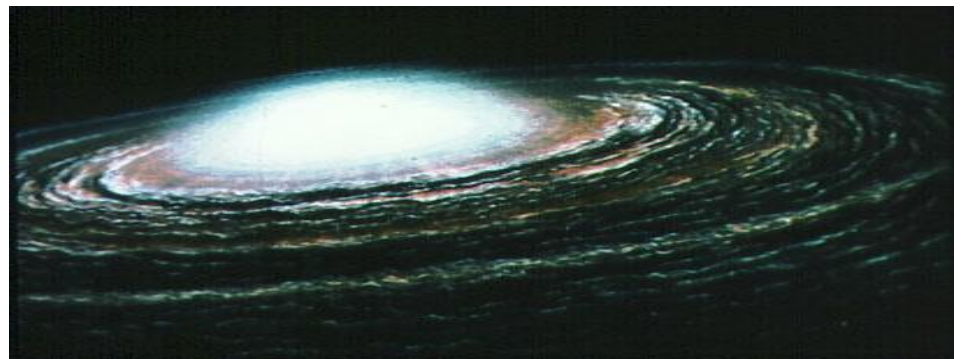
all elements show an isotopic composition that is stable in nature

- **Why ?**

- ▶ ***Thorough mixing during formation of our solar system ($4.6 \cdot 10^9$ years BP)***



The solar system was formed approximately 4.5 billion years ago. The material making up the solar system all came from a single, mostly homogeneous cloud of material (solar nebula). The matter rotated in a flattened plane, splayed out in a disk due to the angular momentum. With time, material not falling to the central sun, would either be thrown out of the system or begin to collect and build up planetesimals. At safe relative distances, planetesimals built up to form the planets.



THE ISOTOPIC COMPOSITION OF THE ELEMENTS

- 1. Decay of naturally occurring, long-lived radionuclides***
- 2. Natural isotope fractionation effects***
- 3. Man-made variations***
- 4. Interaction of cosmic rays with terrestrial matter***
- 5. Variations observed in extra-terrestrial materials***



THE ISOTOPIC COMPOSITION OF THE ELEMENTS

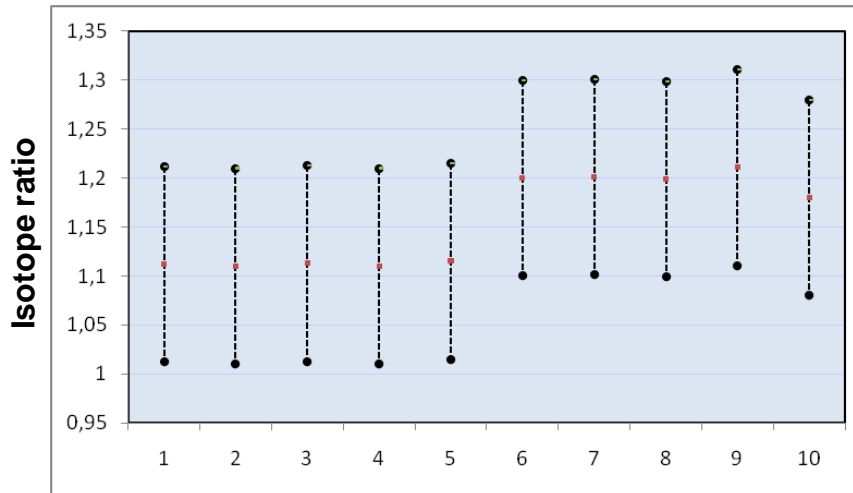
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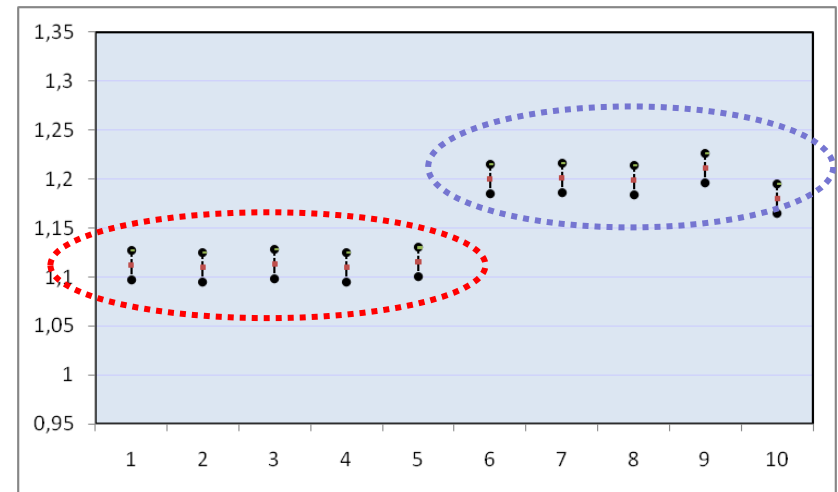
THE ISOTOPIC COMPOSITION OF THE ELEMENTS

1. **Decay of naturally occurring, long-lived radionuclides**
2. **Natural isotope fractionation effects**
3. **Man-made variations**
4. **Interaction of cosmic rays with terrestrial matter**
5. **Variations observed in extra-terrestrial materials**

● Importance of isotope ratio precision?

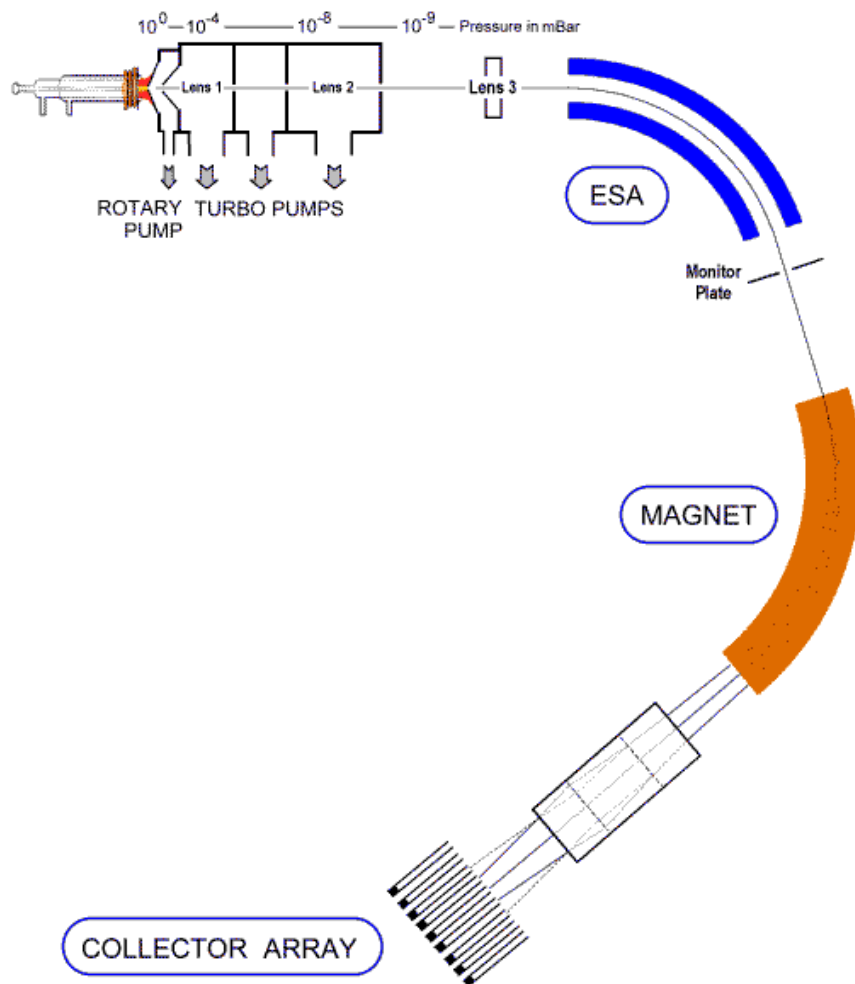


?

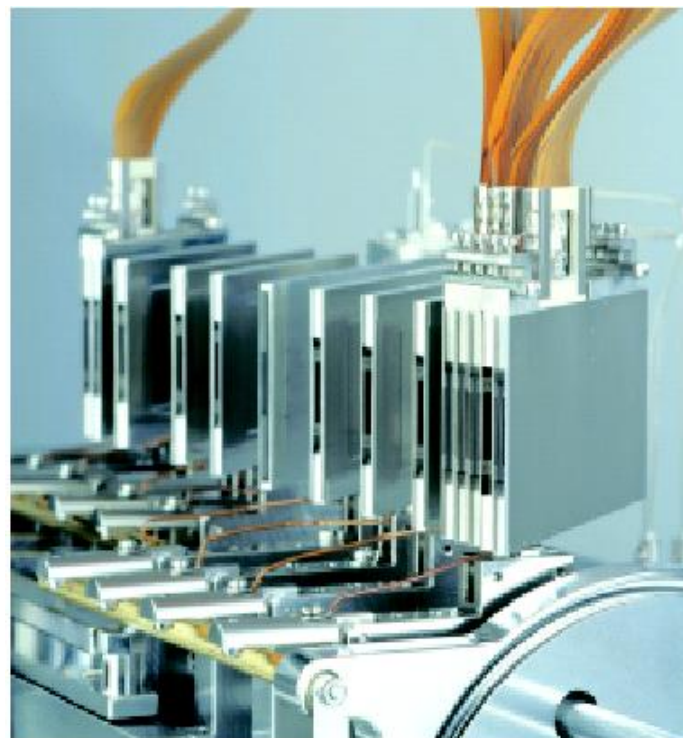


2 different populations \Rightarrow *conclusions!*

MULTI-COLLECTOR ICP – MASS SPECTROMETRY

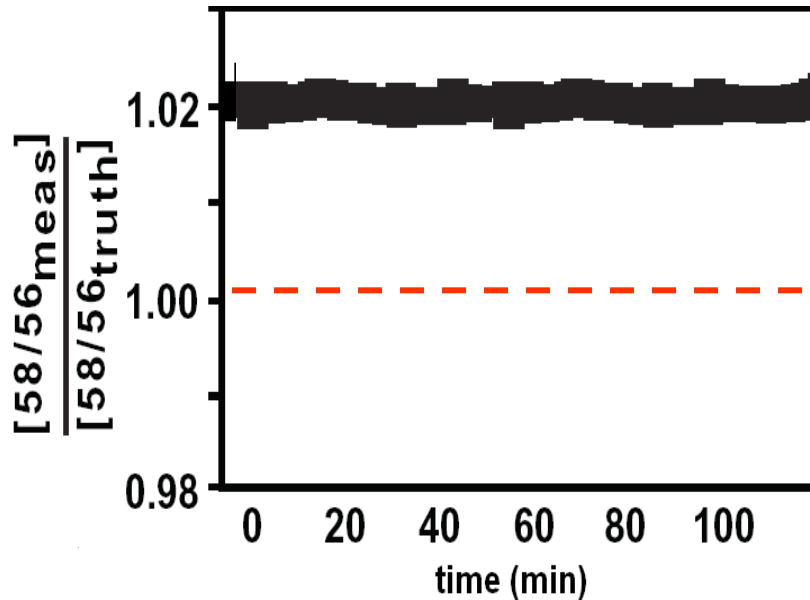


Isotope ratio precision:
down to 0,002 % RSD !



MULTI-COLLECTOR ICP – MASS SPECTROMETRY

INSTRUMENTAL MASS DISCRIMINATION



● Mass discrimination

- ▶ Measured ratio \neq true value
- ▶ Order of magnitude
 - ca. 1% per mass unit @ mid-mass
 - Considerably larger @ low masses
- ▶ Not a systematic $f(\text{time})$

- ▶ ***Caused by space-charge effects***
- ▶ ***Preferential transmission of the heavier isotope***
- ▶ ***Affected by***
 - ***Matrix composition***
 - ***Target element concentration***

Isolation
of target element
required

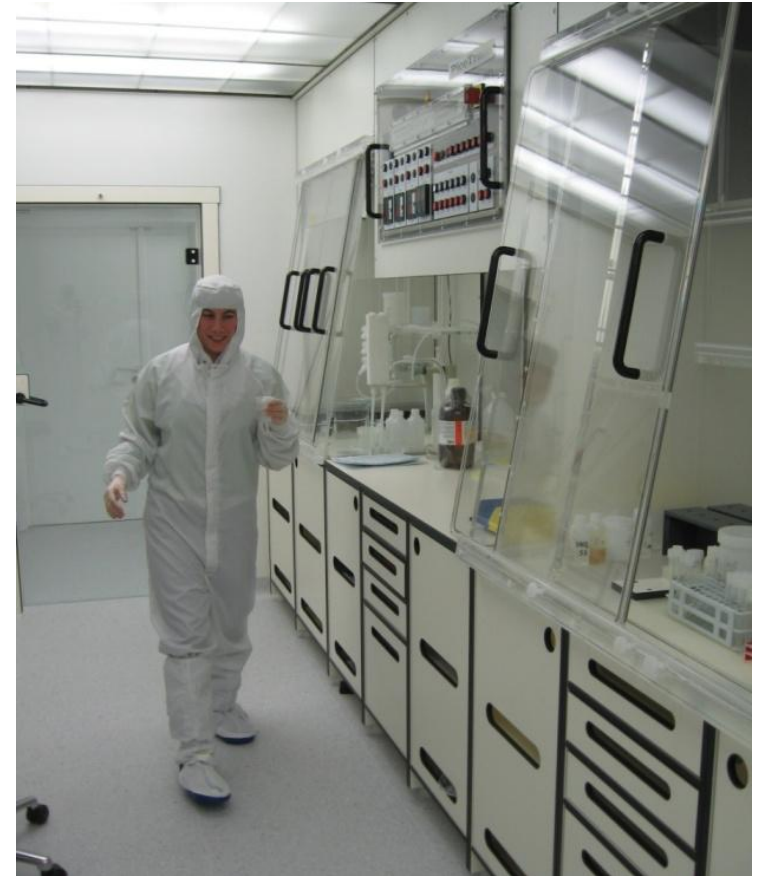
CHROMATOGRAPHIC ISOLATION OF TARGET ELEMENT

- **Class-10 clean lab facilities**

< 10 particles / ft³ @ 0.5 μm vs. millions particles / ft³

Ultrapure water & acids

Discipline!



LECTURE CONTENT ?

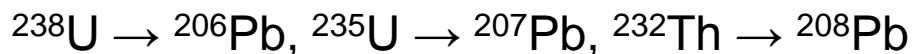
- Real-life applications

- ▶ *Ghent University & international literature*



MEASURING NATURAL VARIATION ELEMENTS WITH RADIOGENIC ISOTOPES

The Classics



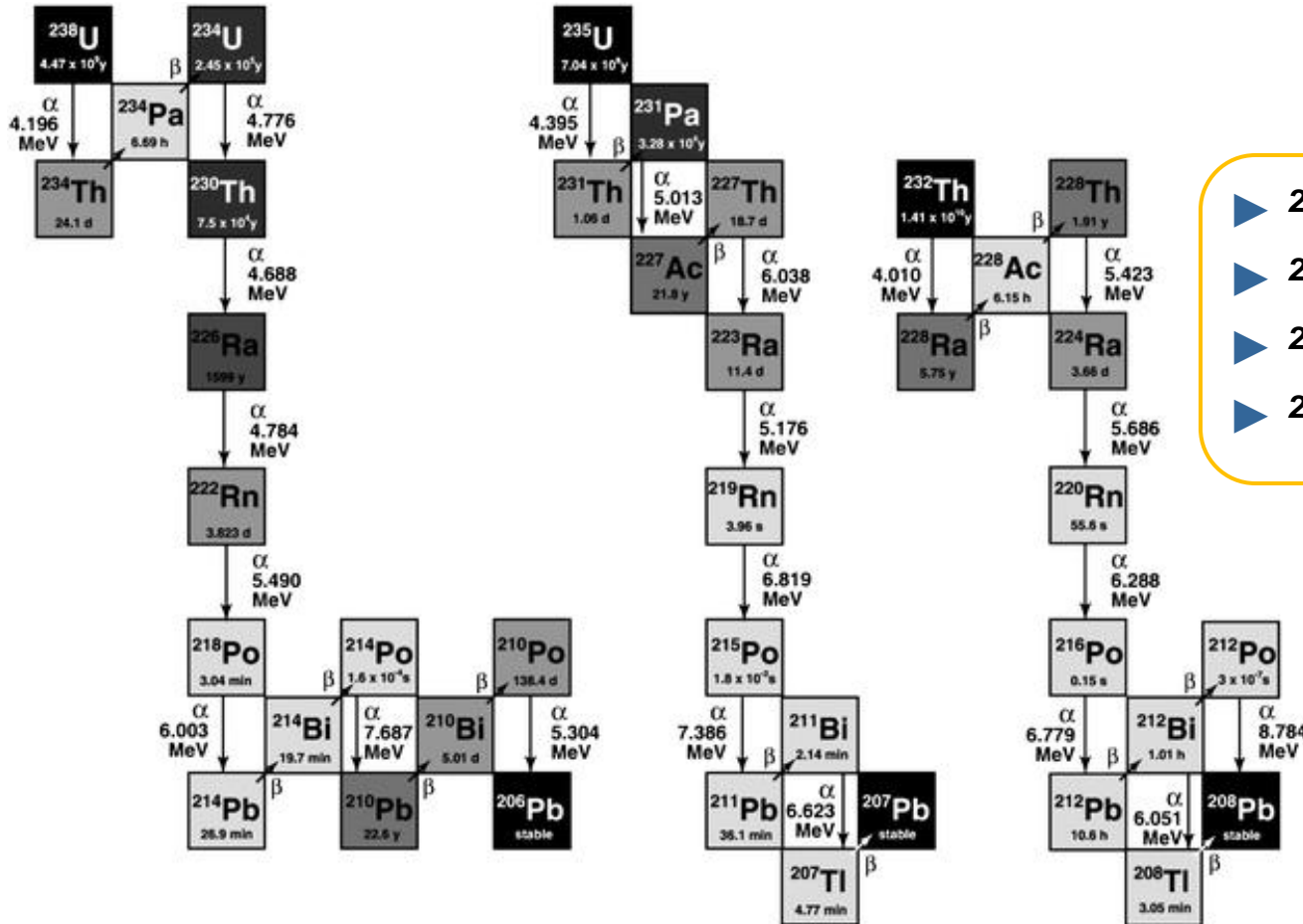
Pb isotope	Natural range of relative isotopic abundance
^{204}Pb	1.04 – 1.65 %
^{206}Pb	20.84 – 27.48 %
^{207}Pb	17.62 – 23.65 %
^{208}Pb	51.28 – 56.21 %
IUPAC, 1997	



Sr isotope	Natural range of relative isotopic abundance
^{84}Sr	0.55 – 0.58 %
^{86}Sr	9.75 – 9.99 %
^{87}Sr	6.94 – 7.14 %
^{88}Sr	82.29 – 82.75 %
IUPAC, 1997	



NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF Pb



- ▶ $^{238}\text{U} \rightarrow ^{206}\text{Pb}$
- ▶ $^{235}\text{U} \rightarrow ^{207}\text{Pb}$
- ▶ $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$
- ▶ ^{204}Pb : not radiogenic



NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF Pb

- **Pronounced variation**

Pb isotope	Natural range of relative isotopic abundance
^{204}Pb	1.04 – 1.65 %
^{206}Pb	20.84 – 27.48 %
^{207}Pb	17.62 – 23.65 %
^{208}Pb	51.28 – 56.21 %

Böhlke et al., J. Phys. Ref. Data, 2005

- **Pb in the earth's crust**

- ▶ Shows isotopic variation, but $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.20$

- **Pb in ores**

- ▶ Shows isotopic variation, but $\ll 1.20$

- Separated from Th & U @ time of ore formation



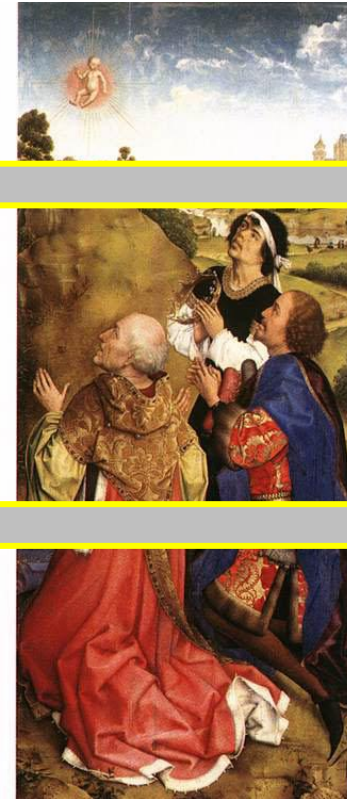
An aerial, isometric-style rendering of a medieval castle. The castle features a central courtyard with a dark blue moat. The buildings are light brown with dark grey roofs and several chimneys. A wooden bridge is visible on the right side of the moat. The surrounding area is green grass.

***PROVENANCE DETERMINATION OF
GLAZED TILES FROM A MEDIAEVAL CASTLE
USING Pb ISOTOPIC ANALYSIS***

PIETER BLADELIN

● Pieter Bladelin

- ▶ **Governor general of all finances of Philip the Good**
 - **Duke of Burgundy & Count of Flanders**
 - **Built a castle in 1448**

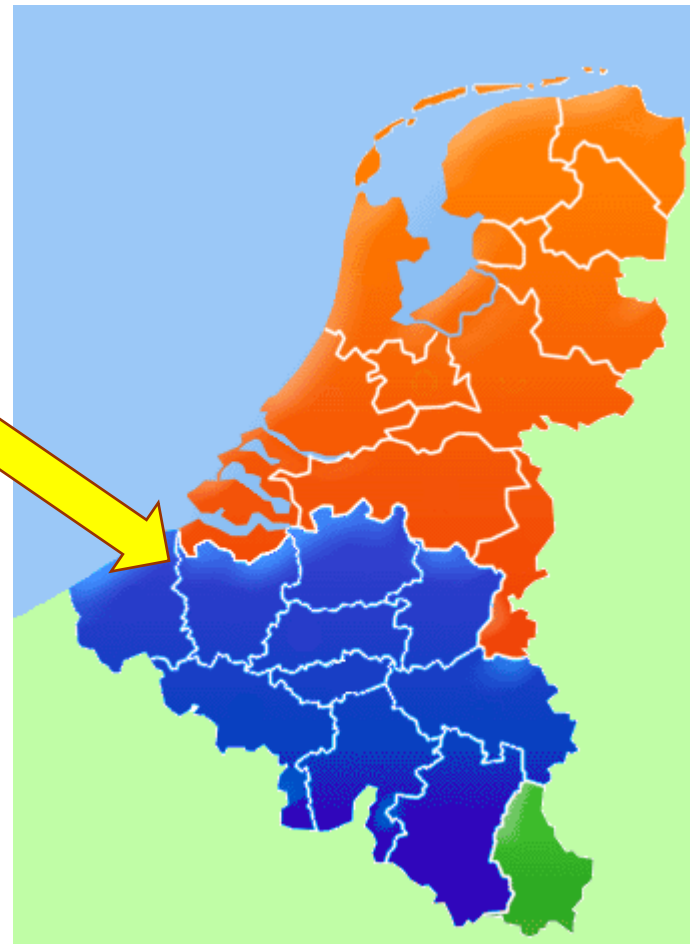
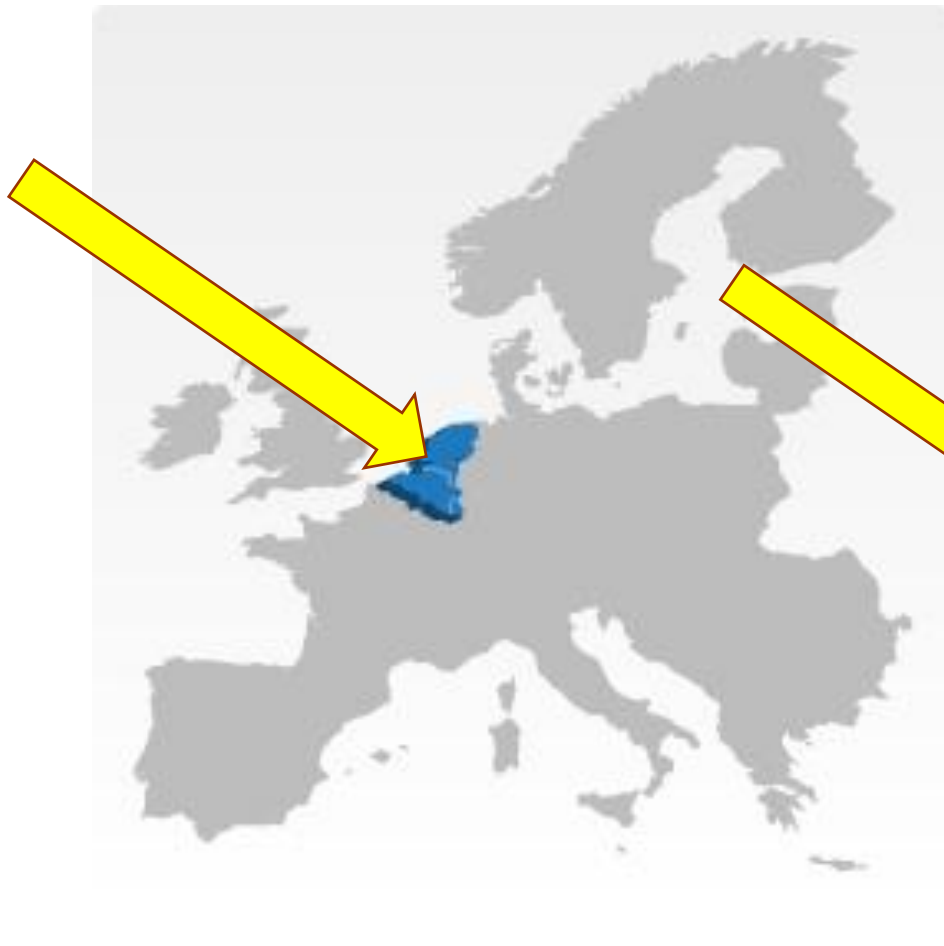


his
castle

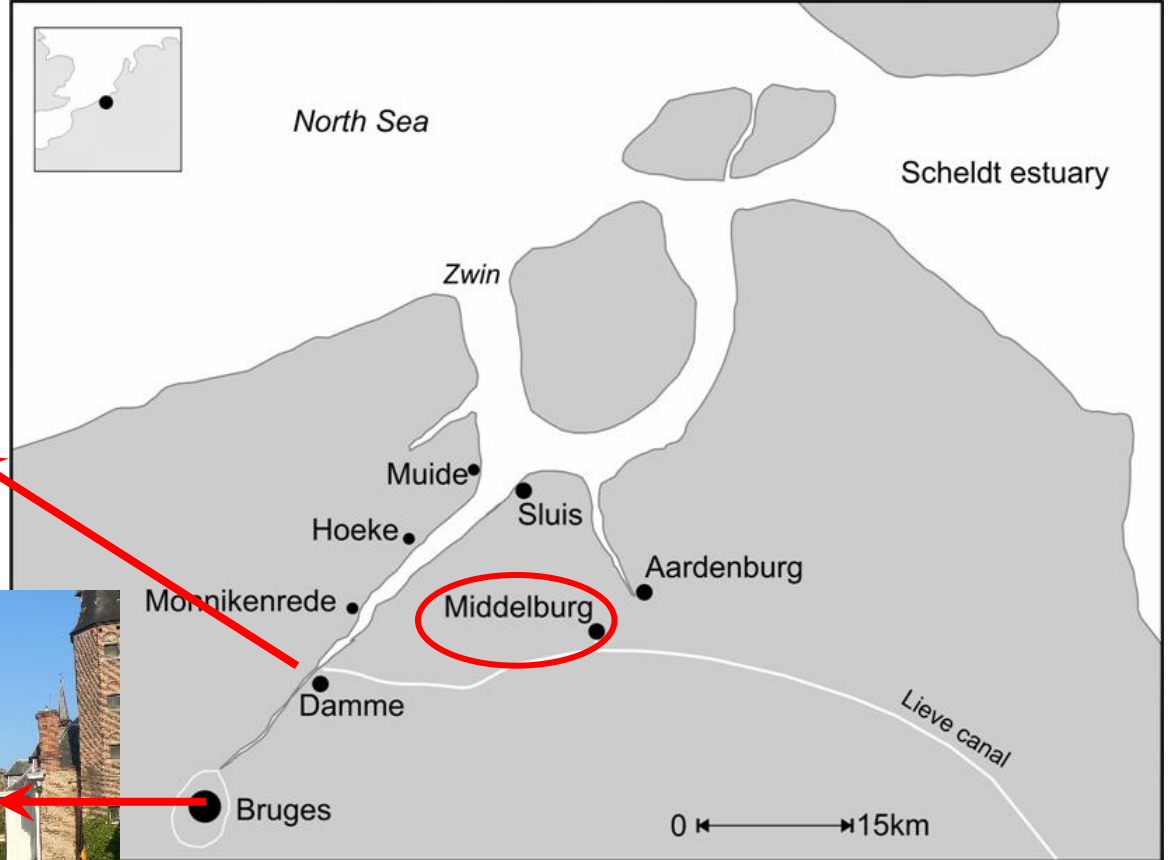
Pieter
Bladelin

Painting by Rogier van der Weyden

CASTLE OF MIDDELBURG NEAR TO BRUGES (BELGIUM)



CASTLE OF MIDDELBURG NEAR TO BRUGES (BELGIUM)



***CASTLE OF MIDDELBURG
NEAR TO BRUGES (BELGIUM)***



TILES FROM CASTLE OF MIDDELBURG NEAR TO BRUGES (BELGIUM)



● Sn-glazed tiles

▶ PB → Pieter Bladelin

▶ Completely different from 15th century local & regional tiles

- Calcareous instead of siliceous & iron-rich
- Tin/lead glaze instead of salt or copper glaze
- Diring technology

▶ Resemblance to Valencian (Spain) tiles?

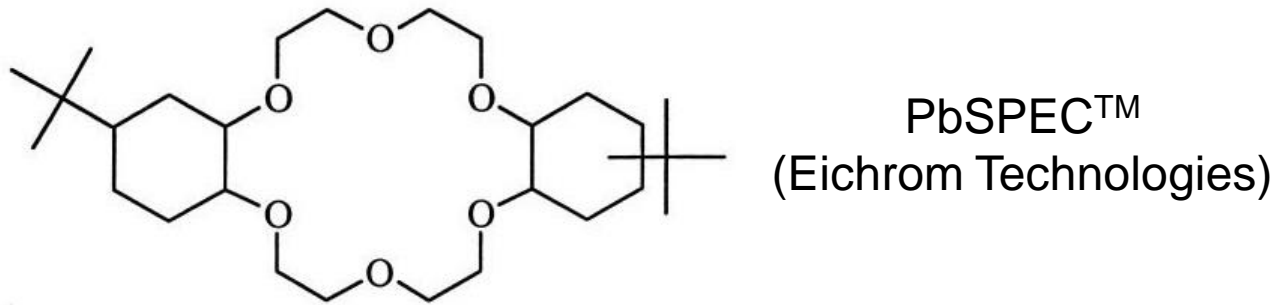
- Floral & islamic designs



ISOTOPIC ANALYSIS OF Pb IN GLAZE

- **Sample preparation**

- ▶ **Extraction of Pb out of glaze using acetic acid**
- ▶ **Isolation of Pb using extraction chromatography**



- ▶ **Appropriate dilution & addition of TI**
 - **Internal standard for correction for mass discrimination**

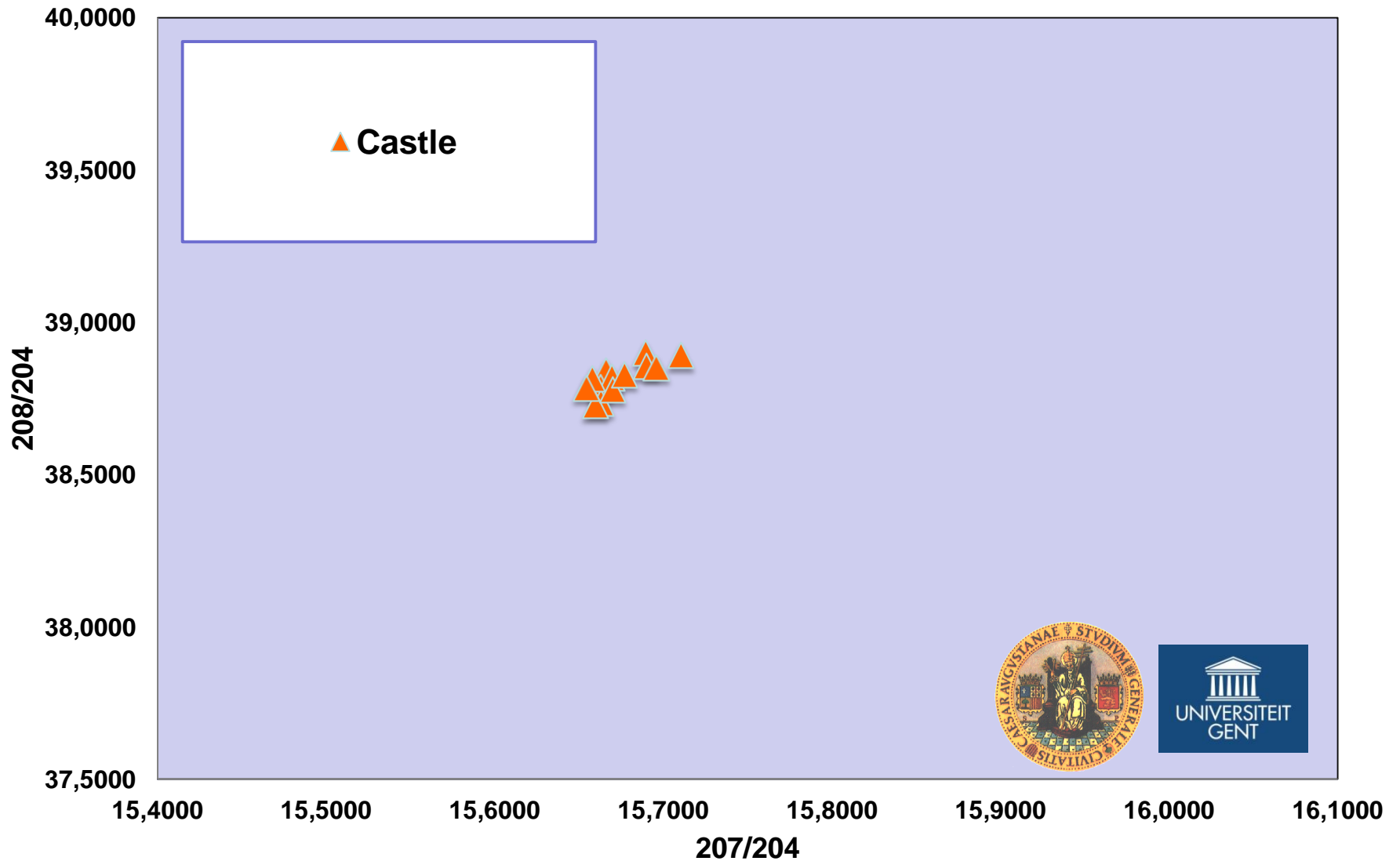
- **Isotopic analysis**

- ▶ **Neptune MC-ICP-MS unit**

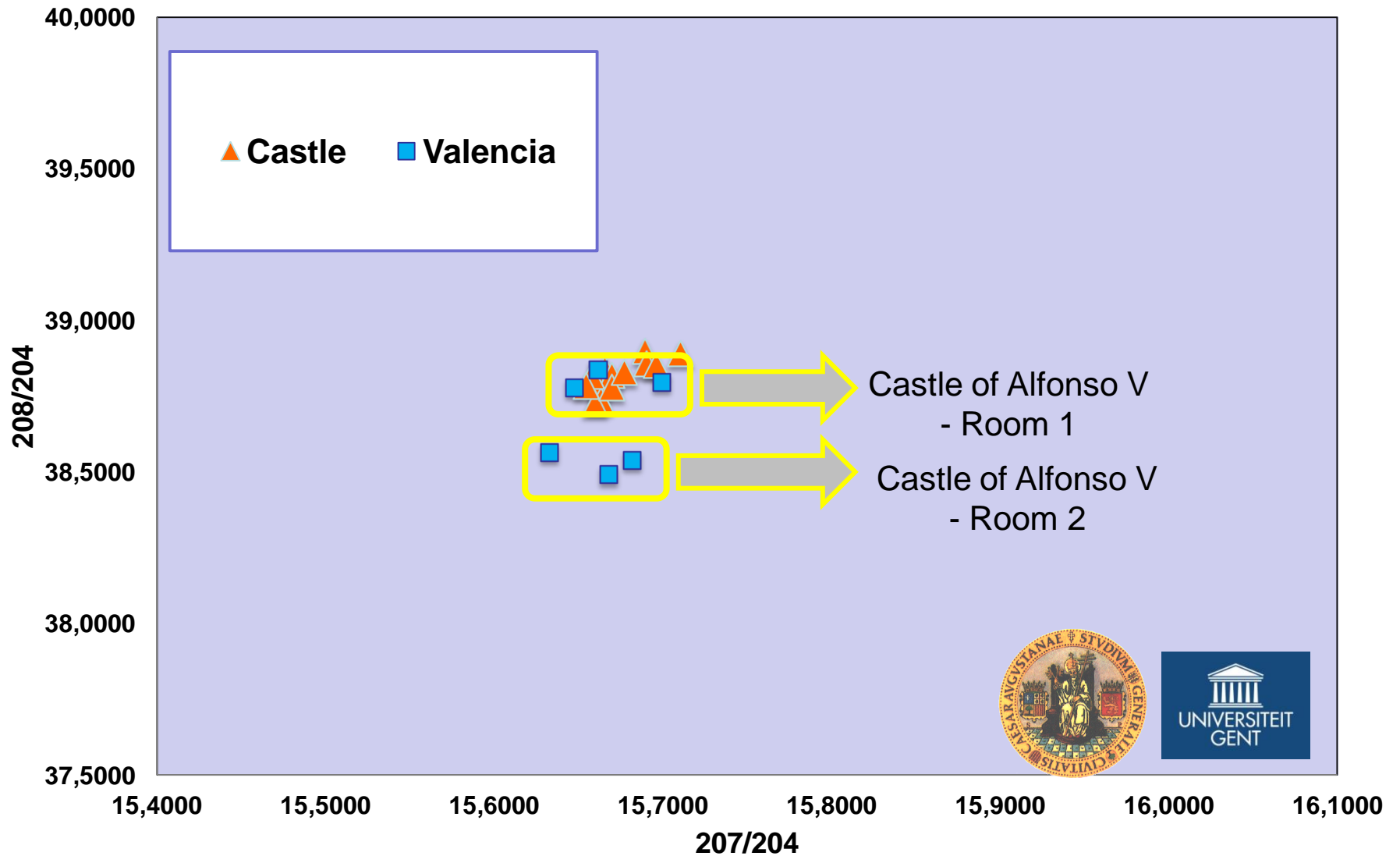
- **Data handling**

- ▶ **Correction for mass discrimination via TI**
- ▶ **Exponential law**

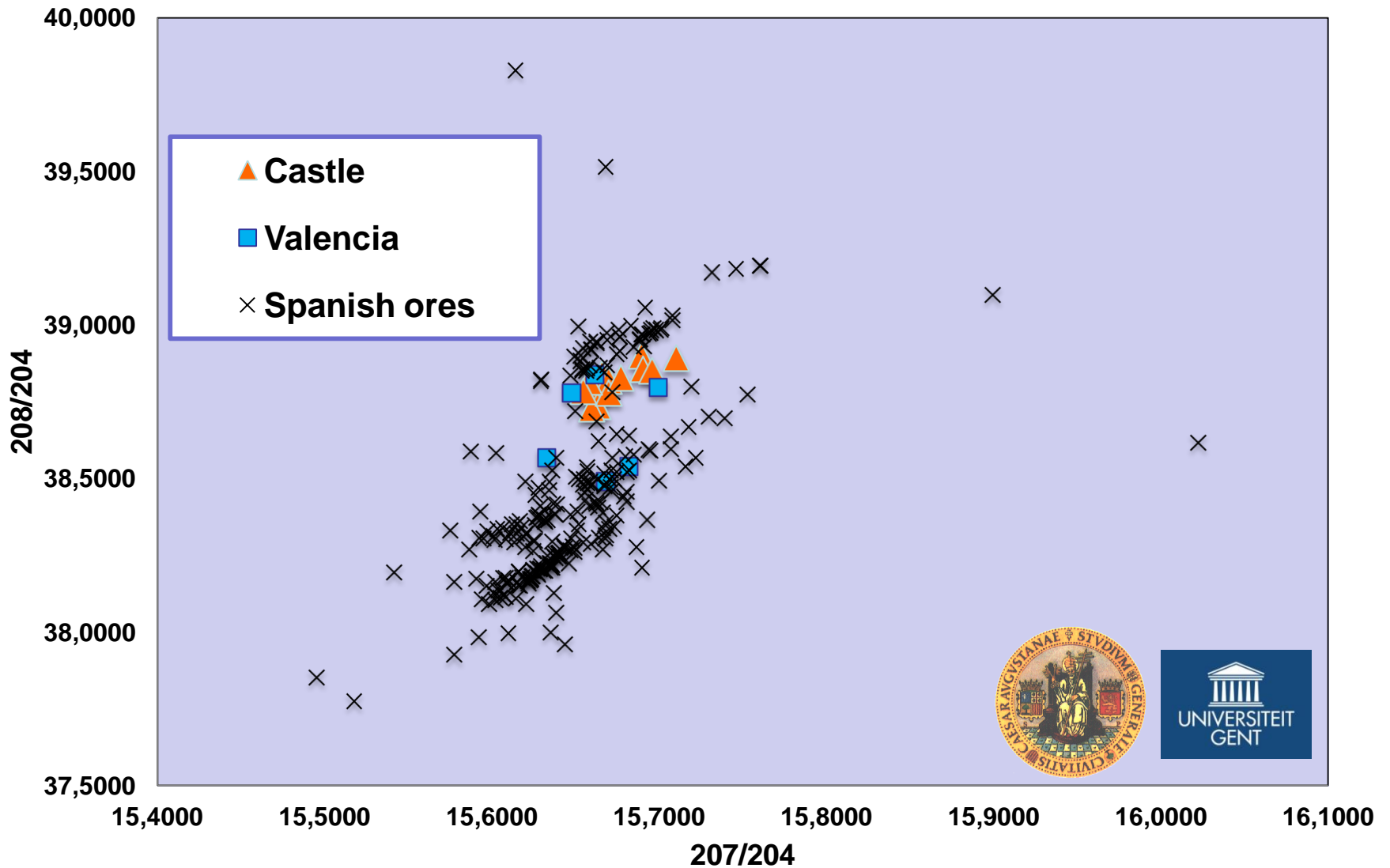
3-ISOTOPE PLOT FOR LEAD



3-ISOTOPE PLOT FOR LEAD

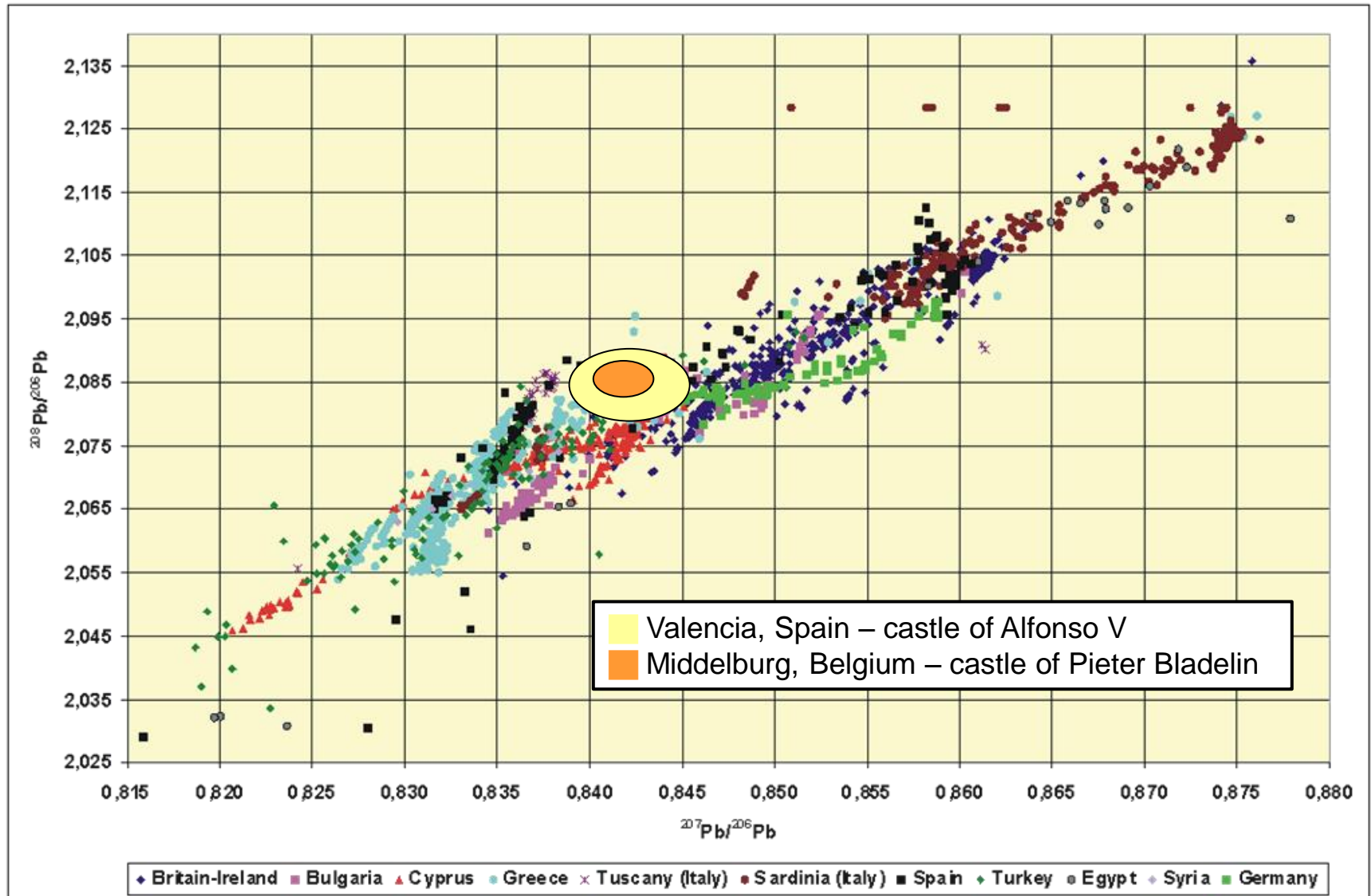


3-ISOTOPE PLOT FOR LEAD



3-ISOTOPE PLOT FOR LEAD

$^{208}\text{Pb}/^{206}\text{Pb}$ VS. $^{207}\text{Pb}/^{206}\text{Pb}$



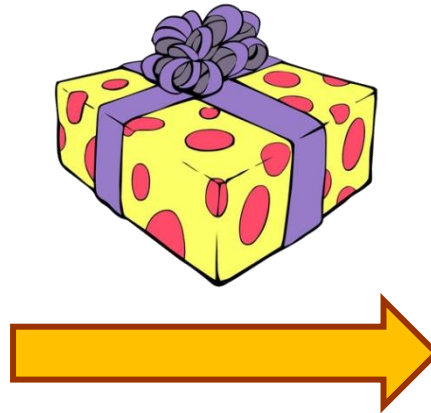
TILES FROM MIDDELBURG CASTLE

ARCHAEOMETRIC INVESTIGATION – CONCLUSIONS

- **Next to Pb isotopic analysis:**
 - ▶ **LA-ICP-MS**
 - ▶ **XRF**
 - ▶ **Raman spectroscopy**
 - ▶ **Thin sections for petrographical assessment**
 - **All results: tiles from**
 - ▶ **Middelburg castle**
 - ▶ **Castle of Alfonso V (Valencia)**
- } common technological context & common origin



TILES FROM MIDDELBURG CASTLE ARCHAEOLOGICAL CONCLUSION



● **Historic sources**

- ▶ **Strong socio-economical and cultural contacts between Philip the Good and Alfonso V between 1444 and 1451**
- ▶ **“Presents” were a well-known practice in the context of 15th century European elites**





***PROVENANCE DETERMINATION OF
SKELETAL REMAINS
USING SR ISOTOPIC ANALYSIS***

VARIATIONS IN THE ISOTOPIC COMPOSITION OF SR

- **Variations in Sr isotopic composition due to:**



- ▶ ***⁸⁷Rb = naturally occurring, long-lived radionuclide***
 - *$T_{1/2} = 48.8 \times 10^9 \text{ y}$*
 - *Isotopic composition of Rb has changed through time*
 - *Isotopic composition of Rb presently equal for all terrestrial materials*
- ▶ ***Isotopic composition of Sr: variable!***
 - *E.g., rocks: dependent on elemental Rb/Sr ratio + age*

Sr isotope	Natural range of relative isotopic abundances
⁸⁴Sr	0.55 – 0.58%
⁸⁶Sr	9.75 – 9.99%
⁸⁷Sr	6.94 – 7.14%
⁸⁸Sr	82.29 – 82.75%

Böhlke et al., J. Phys. Ref. Data, 2005

PROVENANCE DETERMINATION VIA *Sr* ISOTOPIC ANALYSIS

- *Varying geology*
- *Varying Sr isotopic composition*

Quaternary

- Holocene
- Pleistocene

Tertiary

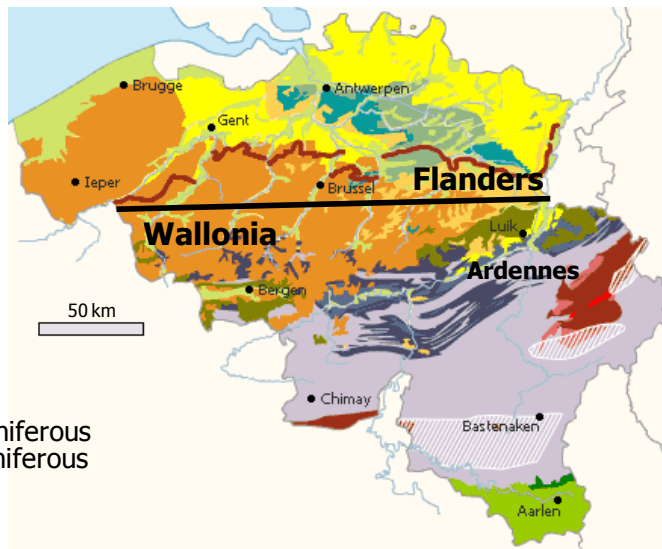
- Pliocene
- Miocene
- Oligocene
- Eocene

Mesozoic

- Cretaceous
- Jurassic
- Triassic
- Permian

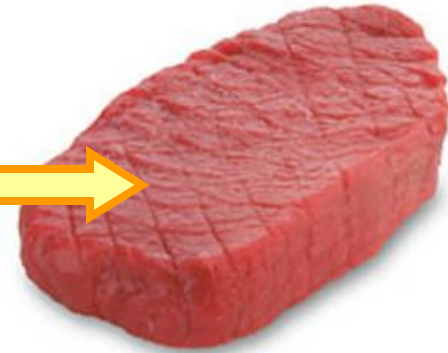
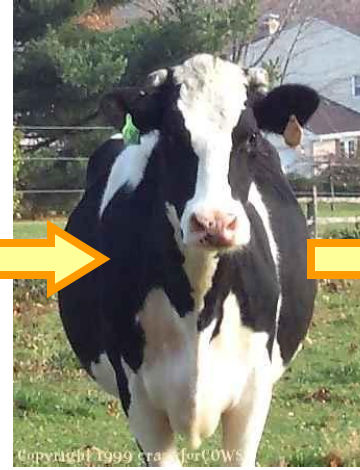
Palaeozoic

- upper-Carboniferous
- lower-Carboniferous
- Devonian
- Silurian
- Cambrian



NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF SR – PROVENANCE DETERMINATION OF AGRICULTURAL PRODUCTS

*Transfer of Sr without
measurable isotopic
fractionation*



NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF SR – PROVENANCE DETERMINATION OF AGRICULTURAL PRODUCTS

● Provenancing agricultural products ?

- ▶ To detect incorrect indication of geographical origin (fraud)

● Which products?

▶ Of plant origin:

- **Wine:** Almeida & Vasconcelos, JAAS, 2001, Barbaste et al., JAAS, 2002
- **Cider:** Garcia-Ruiz et al., ACA, 2007
- **Rice:** Kawasaki et al., Soil Sci Plant Nutr, 2002
- **Ginseng:** Choi et al., Food Chem, 2008
- **Asparagus:** Swoboda et al., ABC, 2008
- ...

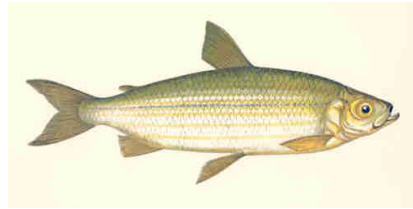
▶ Of animal origin:

- **Cheese:** Fortunato et al., JAAS, 2004
- **Caviar:** Rodushkin et al., ACA, 2008
- ...



AUTHENTICATION OF KALIX (NE SWEDEN) VENDACE CAVIAR

RODUSHKIN ET AL., ACA, 583, 310, 2007



$^{87}\text{Sr}/^{86}\text{Sr}$:
seasonal variation Kalix
< geographical variation
complemented with:
trace element fingerprint
Os isotopic analysis

$^{87}\text{Sr}/^{86}\text{Sr}$

ICP-SFMS

MC-ICP-MS

Day 1 ($n=3$)

Day 2 ($n=3$)

Both days

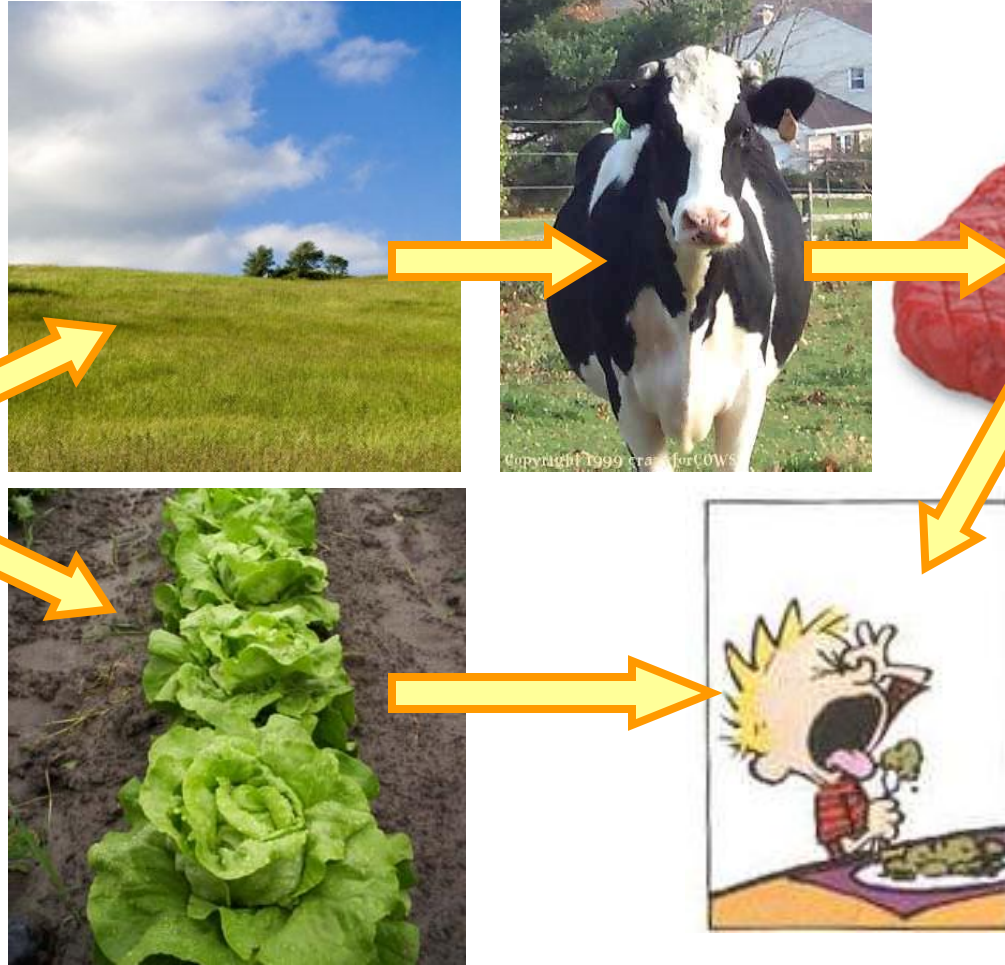
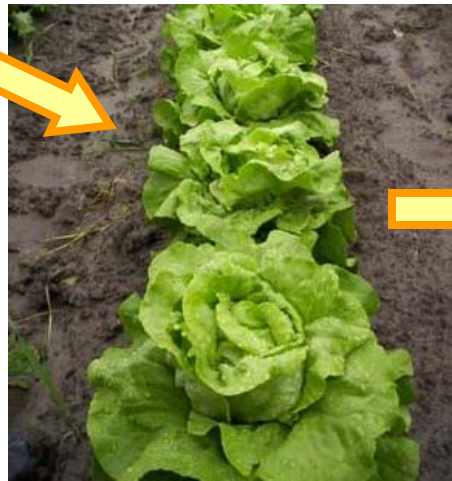
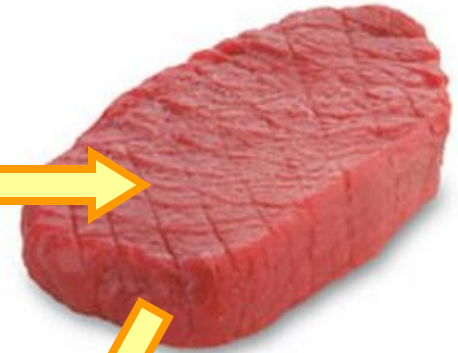
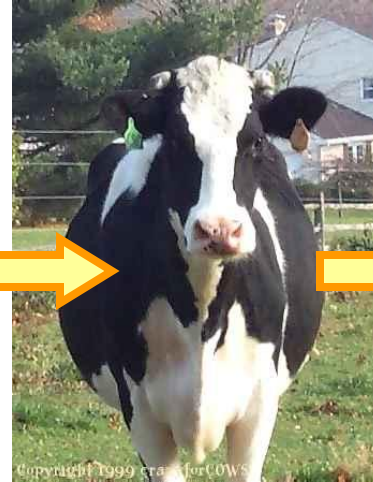
($n=2$)

Kalix, (2005)	0.7102 (17)	0.7102 (14)	0.71017 (4)	0.710646 (6)
Kalix (2004)	0.7106 (10)	0.7102 (10)	0.71040 (48)	0.710700 (12)
Kalix (2003)	0.7110 (10)	0.7108 (12)	0.71087 (29)	0.710990 (18)
Kalix (2003–2005)	0.7106 (8)	0.7104 (6)	0.7105 (8)	0.7108 (4)
Finland	0.7217 (6)	0.7212 (6)	0.72141 (69)	0.721315 (3)
Vänern	0.7224 (14)	0.7222 (22)	0.72231 (19)	0.722270 (10)
USA	0.7185 (10)	0.7181 (12)	0.71834 (54)	0.718257 (36)
Salt	0.7109 (4)	0.7102 (8)	0.71057 (96)	0.710611 (40)
Standard	0.7079 (9)	0.7074 (14)	0.70766 (67)	0.707793 (40)

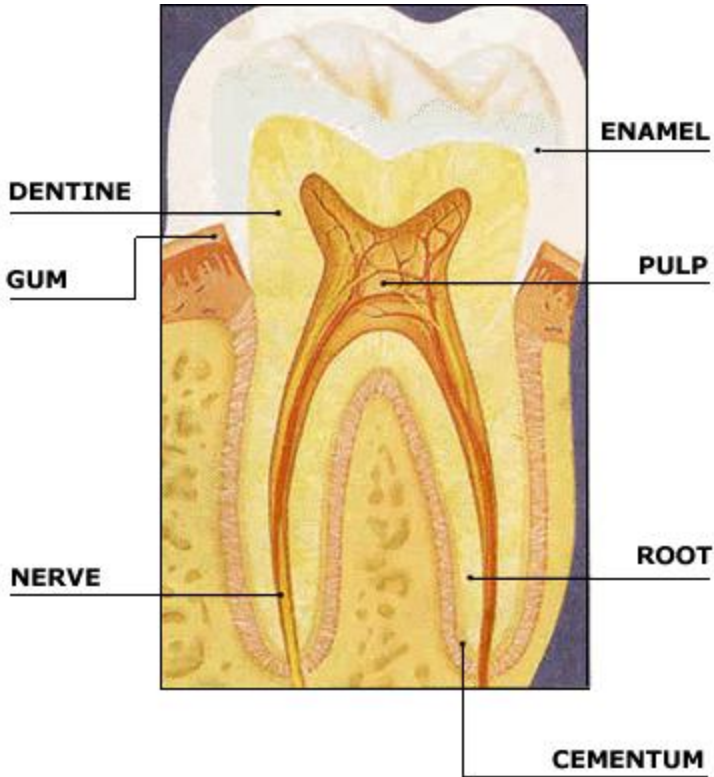


SR ISOTOPIC ANALYSIS FOR PROVENANCE DETERMINATION

*Transfer of Sr without
measurable isotopic
fractionation*



SR ISOTOPIC ANALYSIS FOR PROVENANCE DETERMINATION OF HUMAN REMAINS



- **Enamel**
 - ▶ Formed during early childhood
 - ▶ $^{87}\text{Sr}/^{86}\text{Sr}$ ~ food age 1 – 7
- **Dentine**
 - ▶ Continuously renewed
 - ▶ Faster Sr turnover rate
 - ▶ $^{87}\text{Sr}/^{86}\text{Sr}$ ~ food last years
- **Useful info**
 - ▶ Archaeology



SR ISOTOPIC ANALYSIS FOR PROVENANCE DETERMINATION OF HUMAN REMAINS

● *St-Servatius basilica*

- ▶ *Maastricht, Netherlands*
- ▶ *1600 years of history*
- ▶ *Early christianity in the Maas valley*
- ▶ *Important archaeological excavations*
- ▶ *Analysis of the grave-field population*
 - *Locals and/or immigrants?*

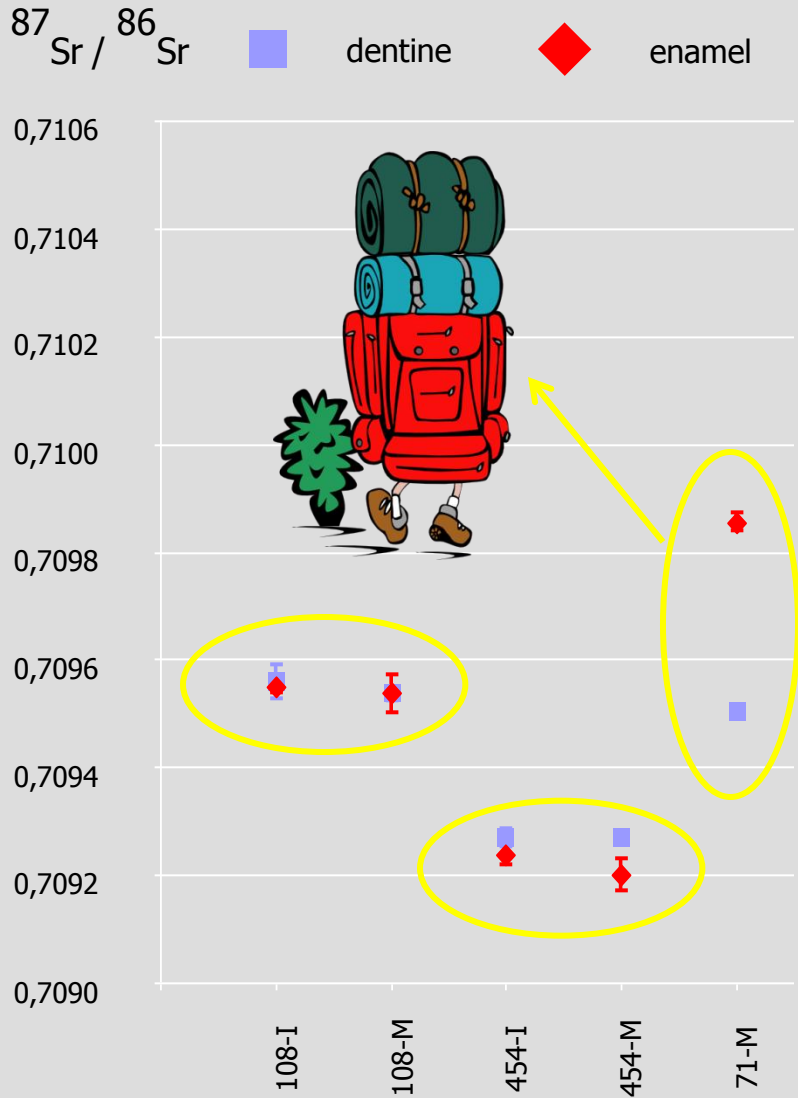


● *Sr isotopic analysis of tooth tissue & soil (UGent & ETH)*

- ▶ *Acid digestion of samples (open beaker – HNO₃ & HCl)*
- ▶ *Isolation of Sr using Sr-spec (Eichrom Technologies)*
- ▶ *Sr isotopic analysis using multi-collector ICP-MS*
 - *Internal correction, based on constant ⁸⁶Sr/⁸⁸Sr*
 - *Russell's equation*



SR ISOTOPIC ANALYSIS FOR PROVENANCE DETERMINATION OF HUMAN REMAINS



← *Pandhof population*
I: incisor, M: molar

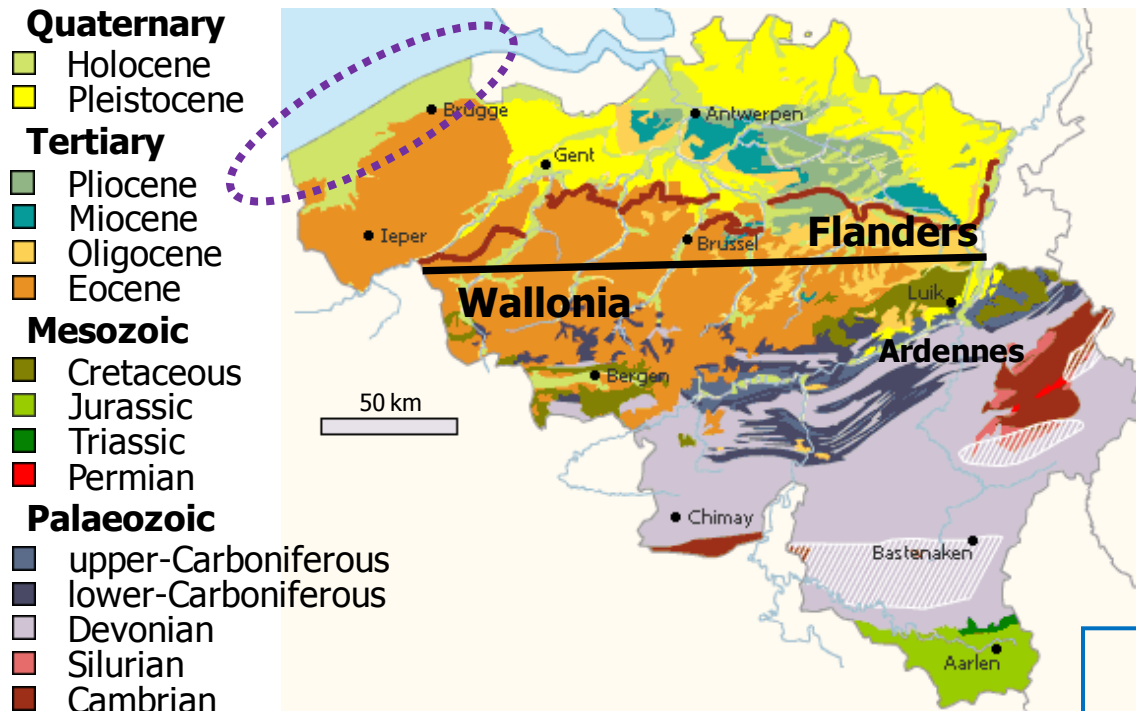
STILL VALID IN A GLOBAL WORLD ?



FROM A GAME TO A REAL-LIFE APPLICATION: FORENSICS

● **Case A: infant killed a few days after birth**

▶ $^{87}\text{Sr}/^{86}\text{Sr}$: if Belgium \Rightarrow coastal region



Degryse et al., *Anal Meth*,
4, 2674-2679, 2012

▶ **Police enquiry**

- \Rightarrow *mother not natively living in that region?*
- *Lived mostly in that region during pregnancy*

FROM A GAME TO A REAL-LIFE APPLICATION: FORENSICS

● Case B

- ▶ $^{87}\text{Sr}/^{86}\text{Sr}$: if Belgium \Rightarrow coastal region
- ▶ No match with missing person from that area
- ▶ Search in other European areas with similar $^{87}\text{Sr}/^{86}\text{Sr}$
- ▶ Possible match found \Rightarrow assumed origin confirmed later

● Case C

- ▶ $^{87}\text{Sr}/^{86}\text{Sr}$: difference between bone & teeth (enamel)
 - Bone: $^{87}\text{Sr}/^{86}\text{Sr}$; if in Belgium \Rightarrow central Flanders
 - Enamel $^{87}\text{Sr}/^{86}\text{Sr}$: outside Benelux
- ▶ Police enquiry
 - Victim came from outside Europe & lived for > 10 years in central Flanders

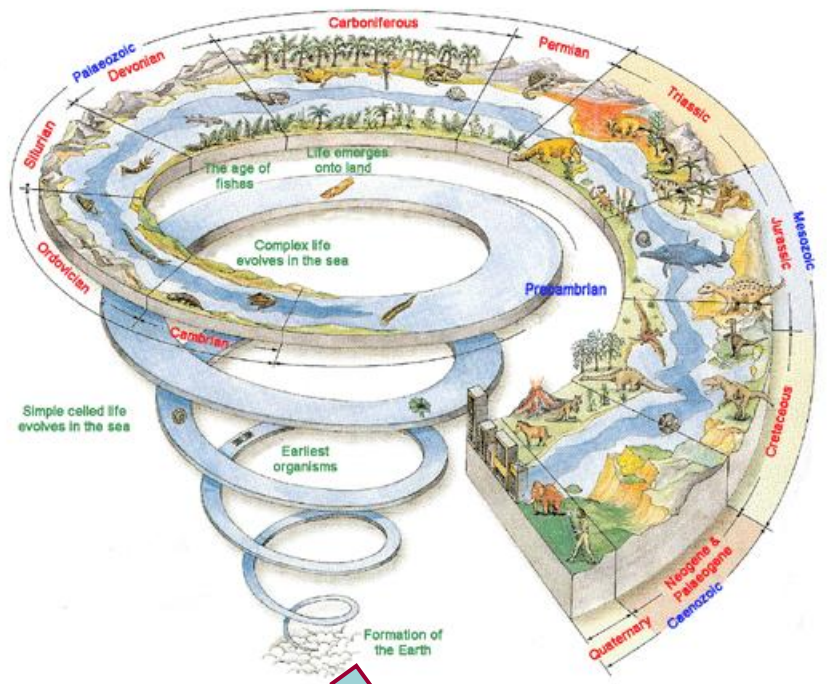
KATHOLIEKE UNIVERSITEIT
LEUVEN

UNIVERSITEIT
GENT

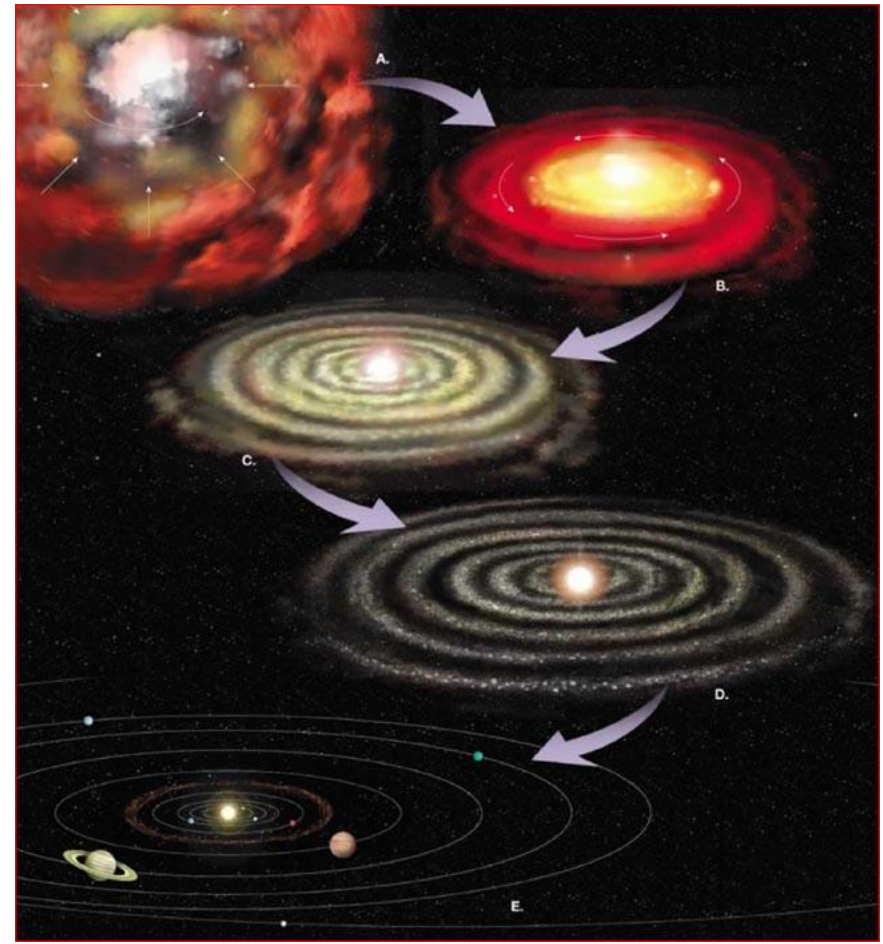


Degryse et al., Anal Meth, 4, 2674-2679, 2012

GOING BACK FURTHER IN TIME ...

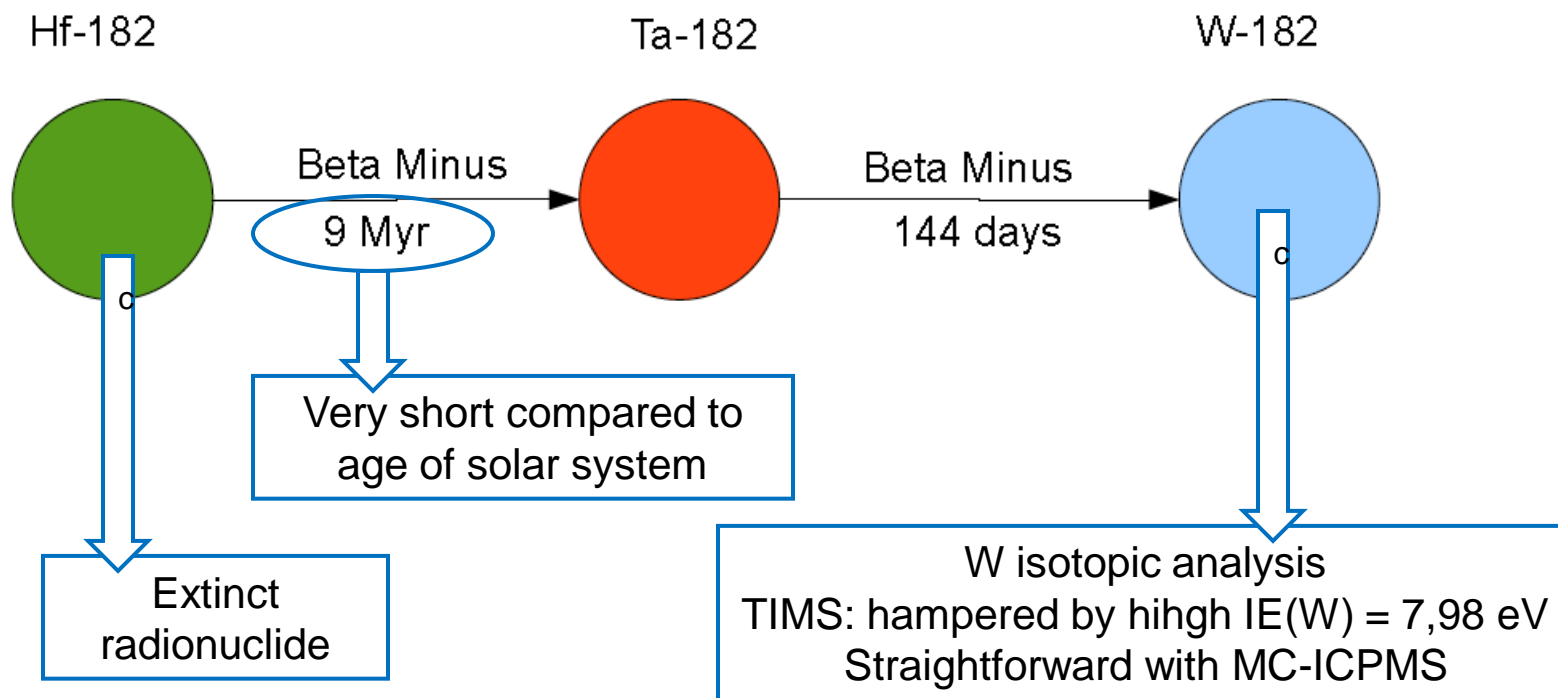


Formation of (our) solar system



THE ^{182}Hf - ^{182}W CHRONOMETER

S.B. JACOBSEN, *EPSL*, **33**, 531, 2005



THE ^{182}Hf - ^{182}W CHRONOMETER

S.B. JACOBSEN, *EPSL*, **33**, 531, 2005

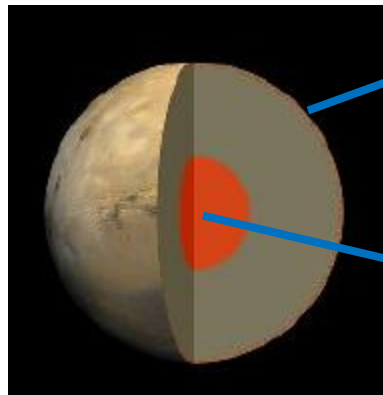
● Formation of a planet ?

▶ Accretion

- Growth of an object by attracting more matter (gravity)

▶ Differentiation

- Core formation



Crust (light)

Iron core (heavy)

Hf = lithophile

⇒

prefers crust

W = siderophile

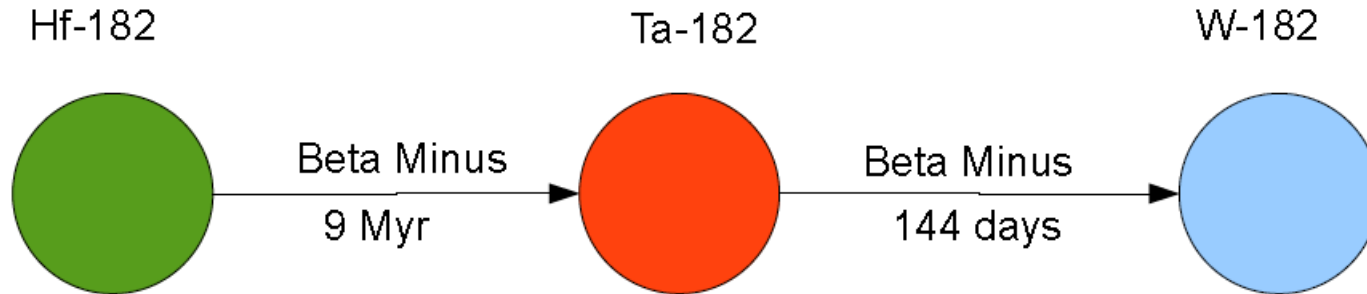
⇒

prefers core



THE ^{182}Hf - ^{182}W CHRONOMETER

S.B. JACOBSEN, *EPSL*, **33**, 531, 2005



- **Effect of planetary differentiation?**

- ▶ **Situation 1: Hf & W only separated after extinction of ^{182}Hf**

- *Hf/W ratio ~ chondritic meteorites (unfractionated reservoir)*

- ▶ **Situation 2: Hf & W were separated while ^{182}Hf was still around**

- *High Hf/W ratio in crust \Rightarrow higher enrichment in ^{182}W*

- **^{182}Hf - ^{182}W chronometer**

- ▶ **Timing of planetary differentiation**

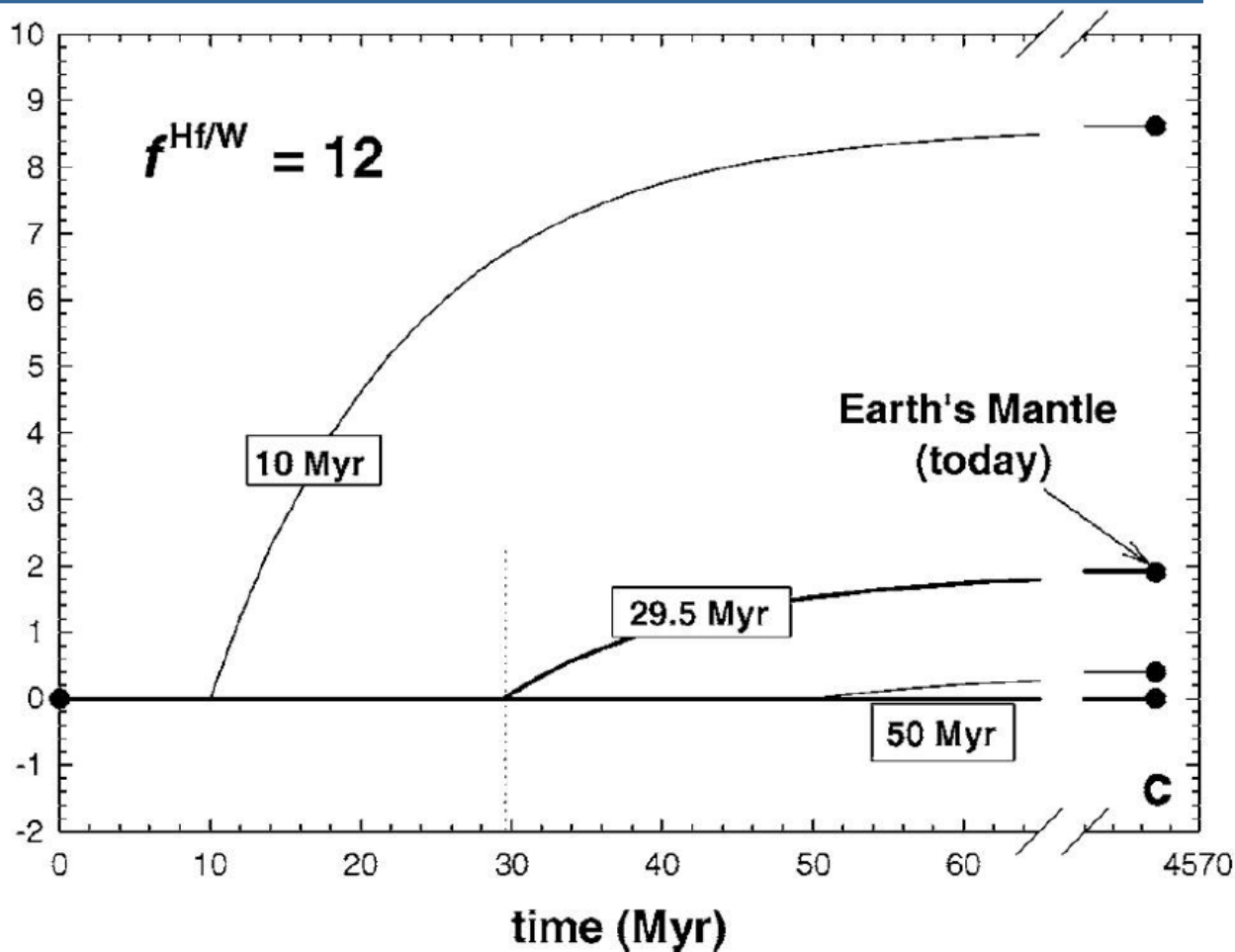


THE ^{182}Hf - ^{182}W CHRONOMETER

S.B. JACOBSEN, *EPSL*, **33**, 531, 2005

Increase in
 $^{182}\text{W}/^{183}\text{W}$
In silicate fraction

$\epsilon_{\text{W(CHUR)}}^*(t)$



MEASURING NATURAL VARIATION ISOTOPE FRACTIONATION EFFECTS

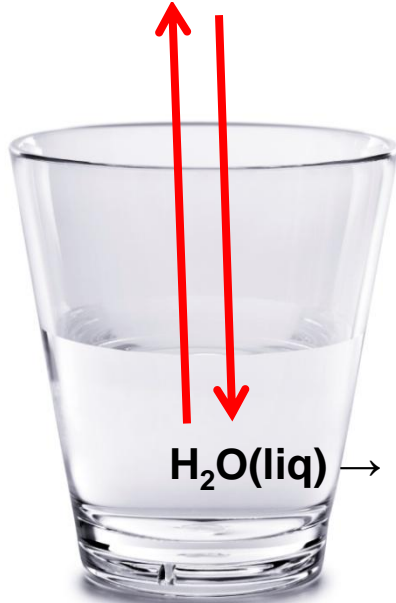
- **Different isotopes of an element**
 - ▶ **Chemically identical**
 - *Determined by number of electrons / protons*
 - ▶ **Different mass**
 - *Different efficiency in participation to*
 - *Chemical reactions*
 - *Physical processes*
- **Magnitude of isotope fractionation?**
 - ▶ **Degree of participation to processes & reactions**
 - ▶ **Relative mass difference between isotopes**
 - *More pronounced for lighter elements*
 - *H, C, N, O, S ⇒ IRMS*
 - *Li, B*
 - *All elements !*
 - ▶ **Thermodynamics & kinetics**



VARIATIONS IN ISOTOPIC COMPOSITION

NATURAL FRACTIONATION EFFECTS

H₂O(gas) → isotopically lighter



H₂O(liq) → isotopically heavier

- **Very small effects**
 - ▶ **Special notation introduced**

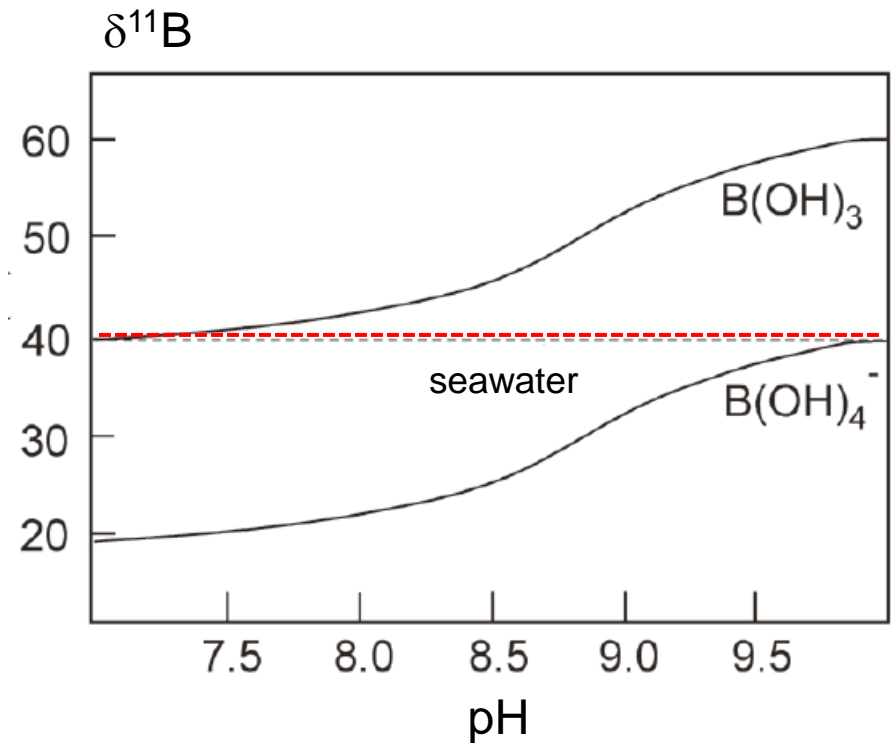
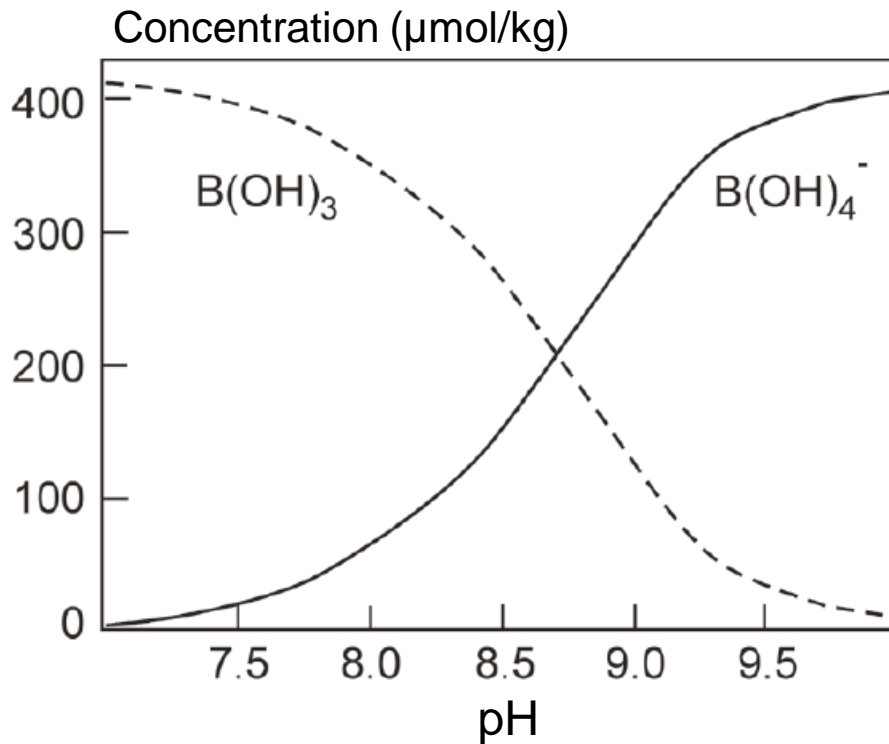
$$\delta^{18}\text{O} \left(\text{‰} \right) = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}} - \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} \cdot 1,000$$



$^{11}\text{B}/^{10}\text{B}$ AS A PALEO PH SEAWATER PROXY

- ***B in seawater:***

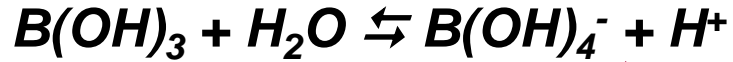
- ▶ ***Present as $\text{B}(\text{OH})_3$ & $\text{B}(\text{OH})_4^-$ / distribution dependent on pH***



- ▶ ***$^{11}\text{B}/^{10}\text{B}$ isotope ratio in the past? \Rightarrow foraminifera & corals***

$^{11}\text{B}/^{10}\text{B}$ AS A PALEO PH SEAWATER PROXY

- In seawater:



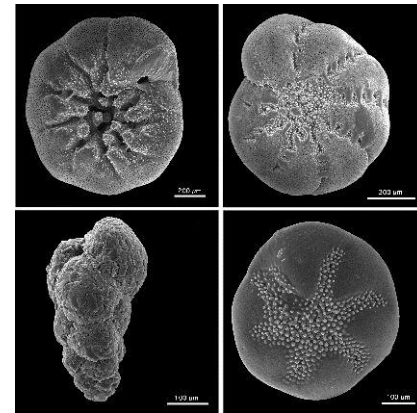
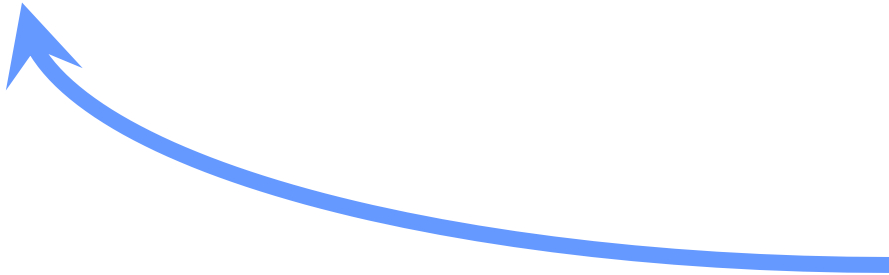
isotopically heavier



isotopically lighter

B(OH)_4^- taken up without isotopic fractionation in corals & foraminifera

pH of seawater as a function(time)



Foraminifera
living or fossil
eukaryotic moncellular
organisms with CaCO_3 skeleton



RELEVANCE OF PH OF SEAWATER ?

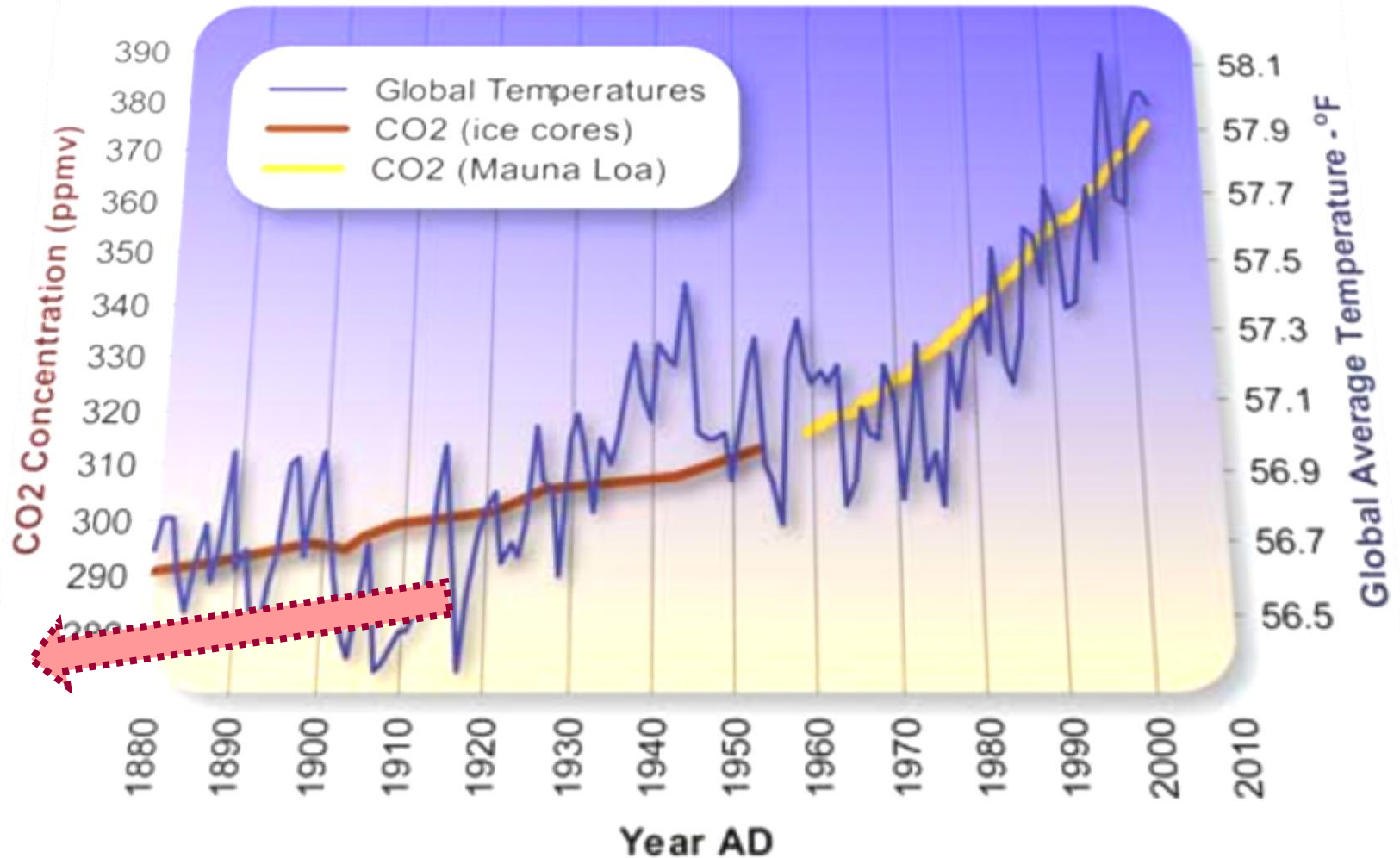
- **Determined by CO_2 concentration in the atmosphere**



- ▶ **Information on CO_2 level over geological times**
- ▶ **Is the current increase in CO_2 level exceptional ?**



RELEVANCE OF PH OF SEAWATER ?



Data Source Temperature: ftp://ftp.ncdc.noaa.gov/pub/data/anomalies/annual_land_and_ocean.ts
Data Source CO2 (Siple Ice Cores): <http://cdiac.esd.ornl.gov/ftp/trends/co2/siple2.013>
Data Source CO2 (Mauna Loa): <http://cdiac.esd.ornl.gov/ftp/trends/co2/maunaloa.co2>

Graphic Design: Michael Ernst, The Woods Hole Research Center



OTHER ISOTOPE RATIOS AS PALEOPROXIES ?

- **Paleoredox proxies: oxic/anoxic conditions in seawater**

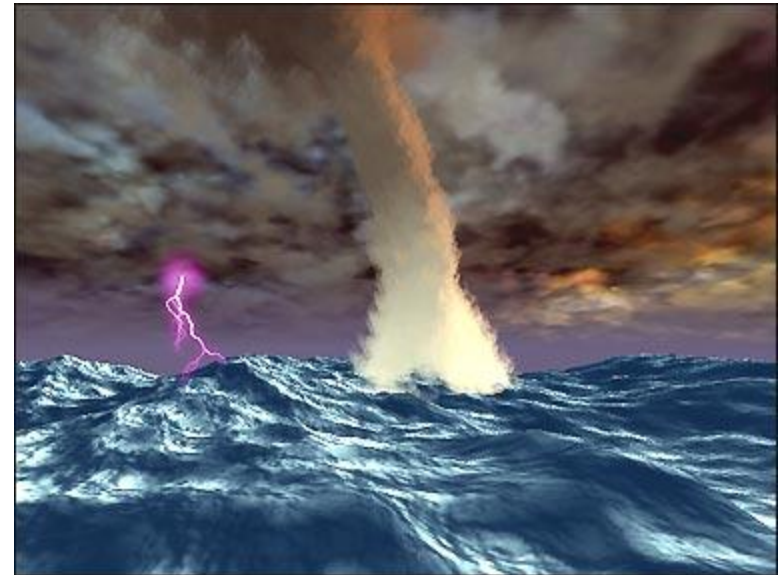
- ▶ *Mo* } e.g., marine sediments
- ▶ *U* }

- **Paleotemperature proxy: seawater**

- ▶ *Ca* } e.g., bivalves

- **Paleoproxy for $p(\text{CO}_2)$**

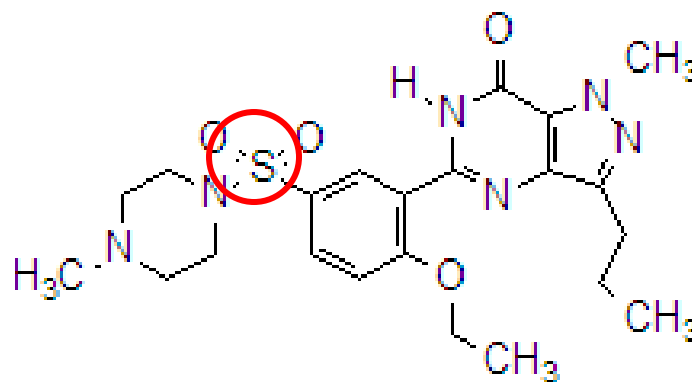
- ▶ *Si* } e.g., diatoms



S ISOTOPIC ANALYSIS FOR TRACING DOWN COUNTERFEIT DRUGS

R. CLOUGH ET AL., ANAL. CHEM., 78, 6126, 2006.

- **Counterfeit drugs**
 - ▶ *violation of intellectual property laws*
 - ▶ *inappropriate quantities of active ingredients*
 - ▶ *may contain ingredients that are not on the label (purity)*
 - ▶ *often inaccurate, incorrect or fake packaging & labeling*
- **“Money making” drugs**



Sildenafil, VIAGRA*



S ISOTOPIC ANALYSIS FOR TRACING DOWN COUNTERFEIT DRUGS

R. CLOUGH ET AL., ANAL. CHEM., 78, 6126, 2006.

- S isotopic analysis in viagra using MC-ICP-MS



$\delta^{34}\text{S}$ relative to Pfizer Viagra

	bulk tablet by laser ablation (‰)	sildenafil citrate by HPLC (‰)
counterfeit Viagra 1	-8.0 ± 0.36	-3.0 ± 0.9
counterfeit Viagra 2	$+10.5 \pm 0.39$	$+5.0 \pm 1.1$

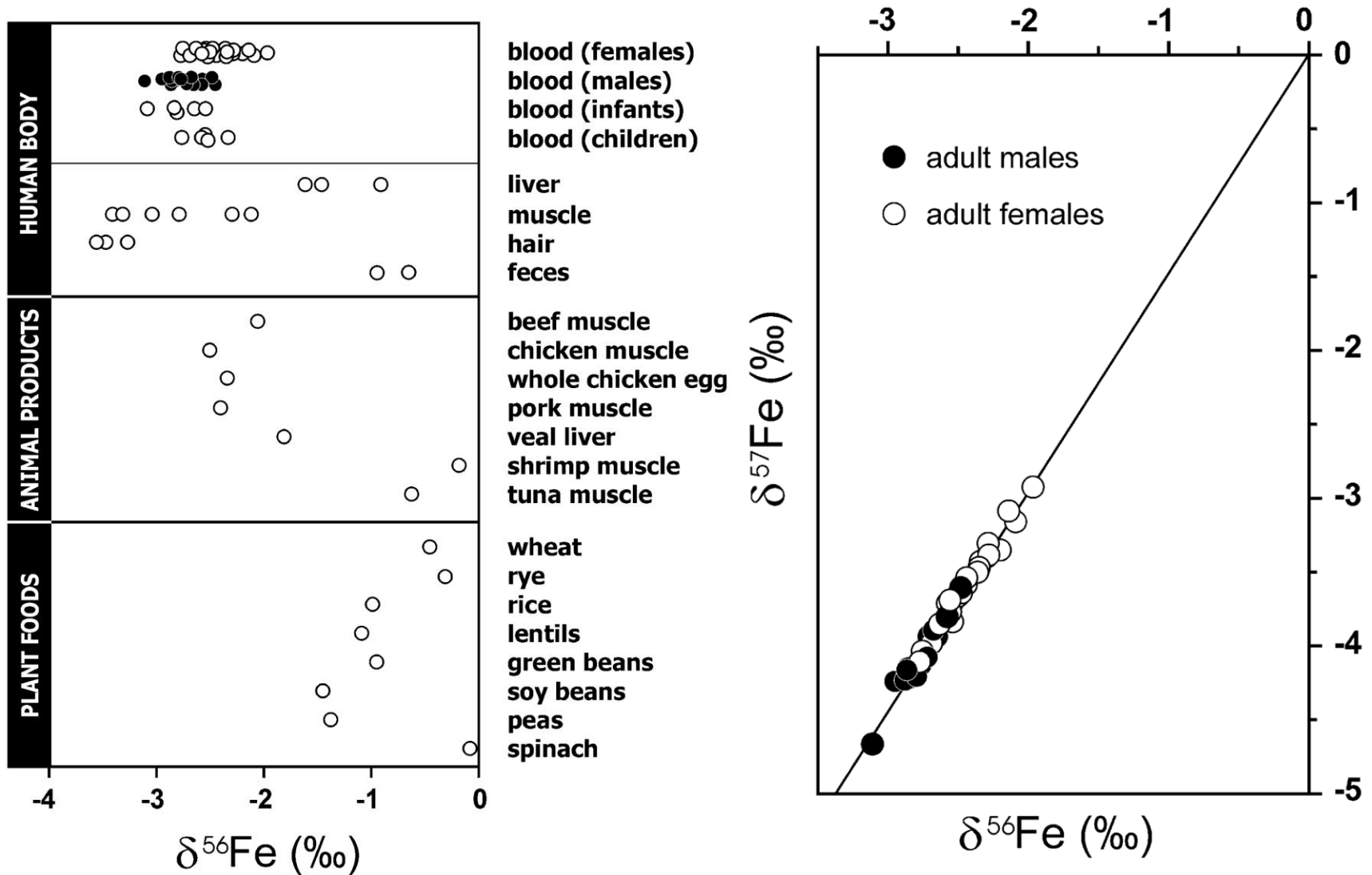


WHAT ABOUT THE FUTURE?



NATURAL ISOTOPE RATIO VARIATIONS IN A BIOMEDICAL CONTEXT

PIONEERING WORK – VON BLANCKENBURG & WALCZYK



***NATURAL ISOTOPE RATIO VARIATIONS IN A BIOMEDICAL CONTEXT
PIONEERING WORK – VON BLANCKENBURG & WALCZYK***

blood

2005 105: 3812-3816
Prepublished online Jan 21, 2005;
doi:10.1182/blood-2004-07-2807

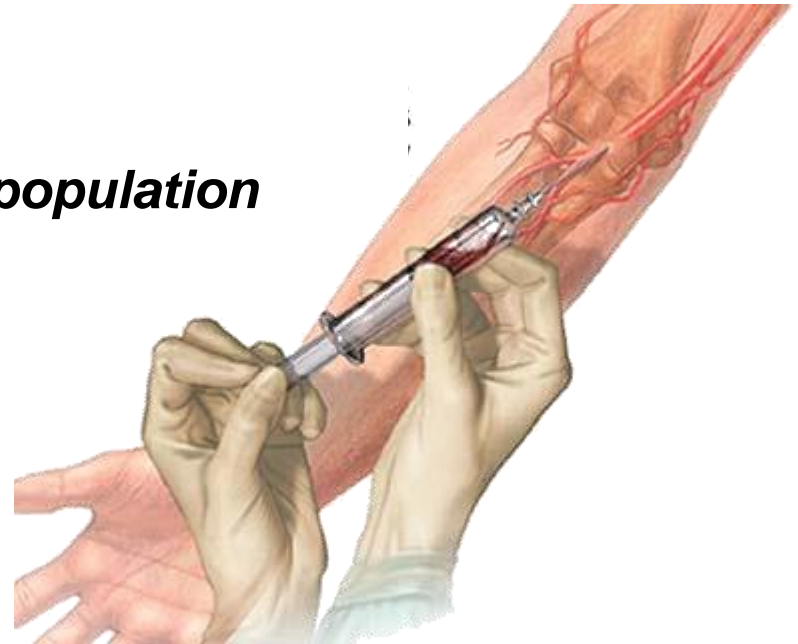
Hereditary hemochromatosis is reflected in the iron isotope composition of blood

Pierre-Alexandre Krayenbuehl, Thomas Walczyk, Ronny Schoenberg, Friedhelm von Blanckenburg and Georg Schulthess



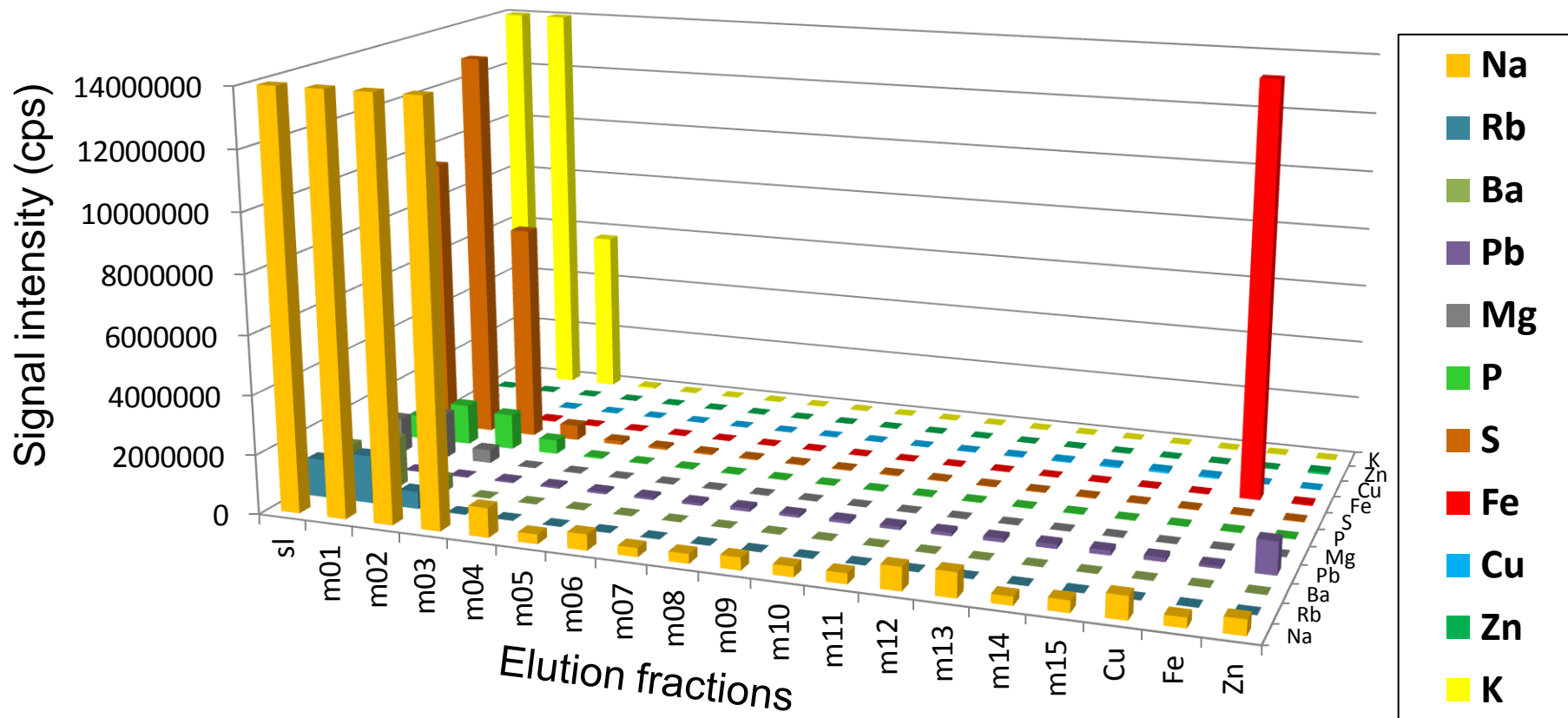
NATURAL ISOTOPE RATIO VARIATIONS IN A BIOMEDICAL CONTEXT RESEARCH PROJECT @ GHENT UNIVERSITY

- ***Other diseases affecting the metabolism of essential elements
⇒ change in isotopic composition in blood ?***
- ***Our study***
 - ▶ ***Fe, Cu & Zn***
 - ▶ ***Step 1: spread in the reference population***
 - ***Determining factors ?***

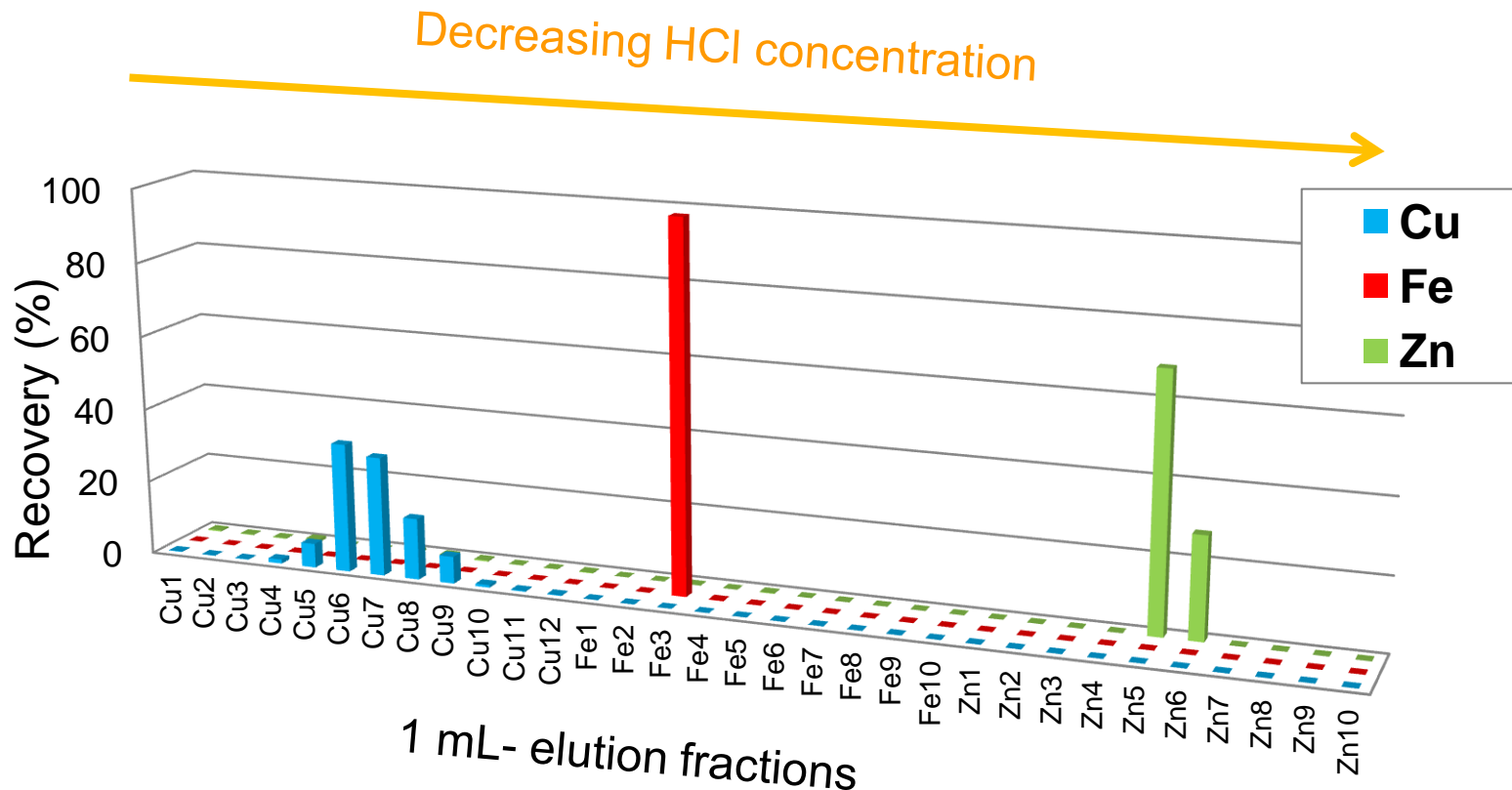


REMOVAL OF MATRIX ELEMENTS

SERONORM TRACE ELEMENTS WHOLE BLOOD



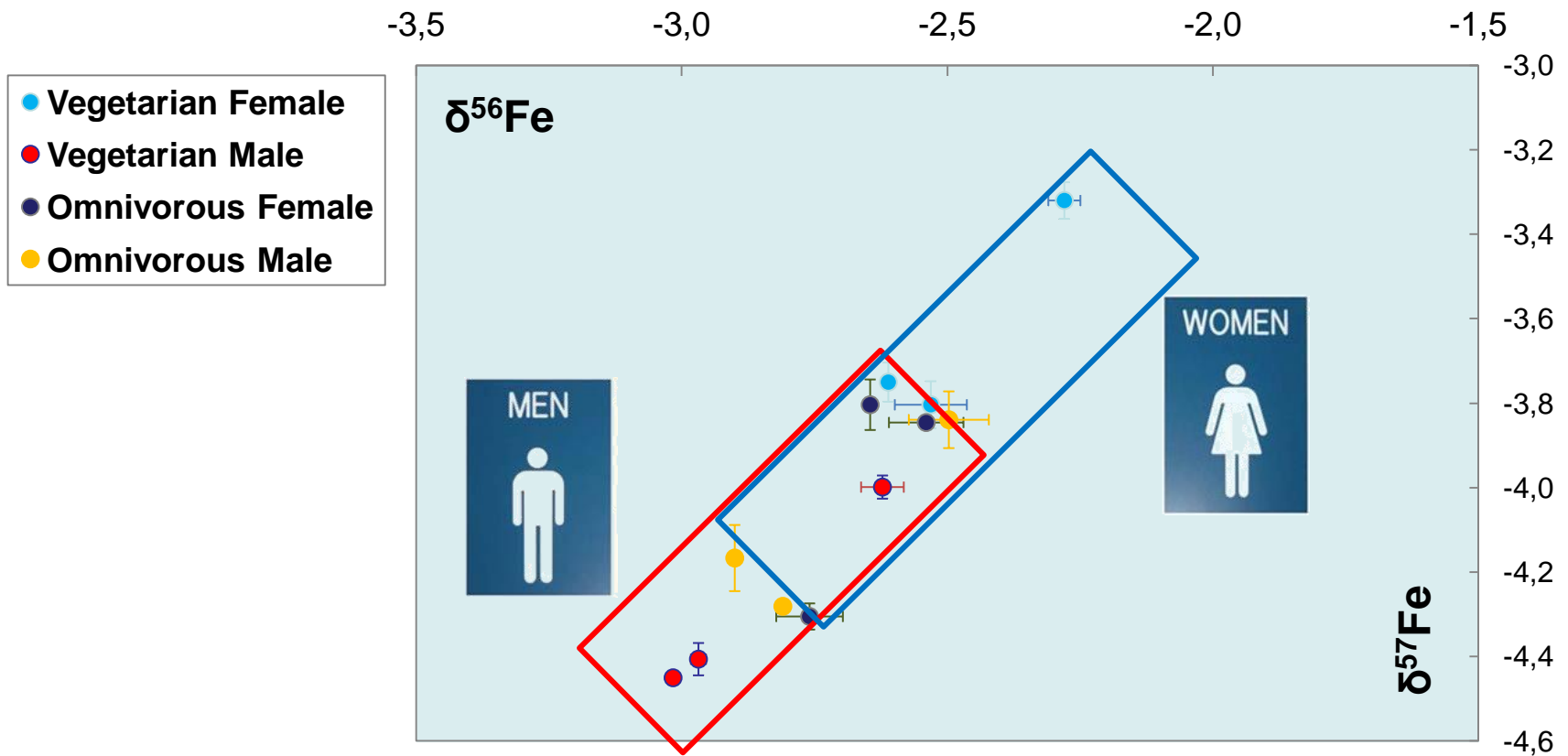
ISOLATION OF CU, FE & ZN SERONORM TRACE ELEMENTS WHOLE BLOOD



100 % target element recovery \Rightarrow no effect of potential on-column fractionation

RESULTS *FE* ISOTOPIC ANALYSIS

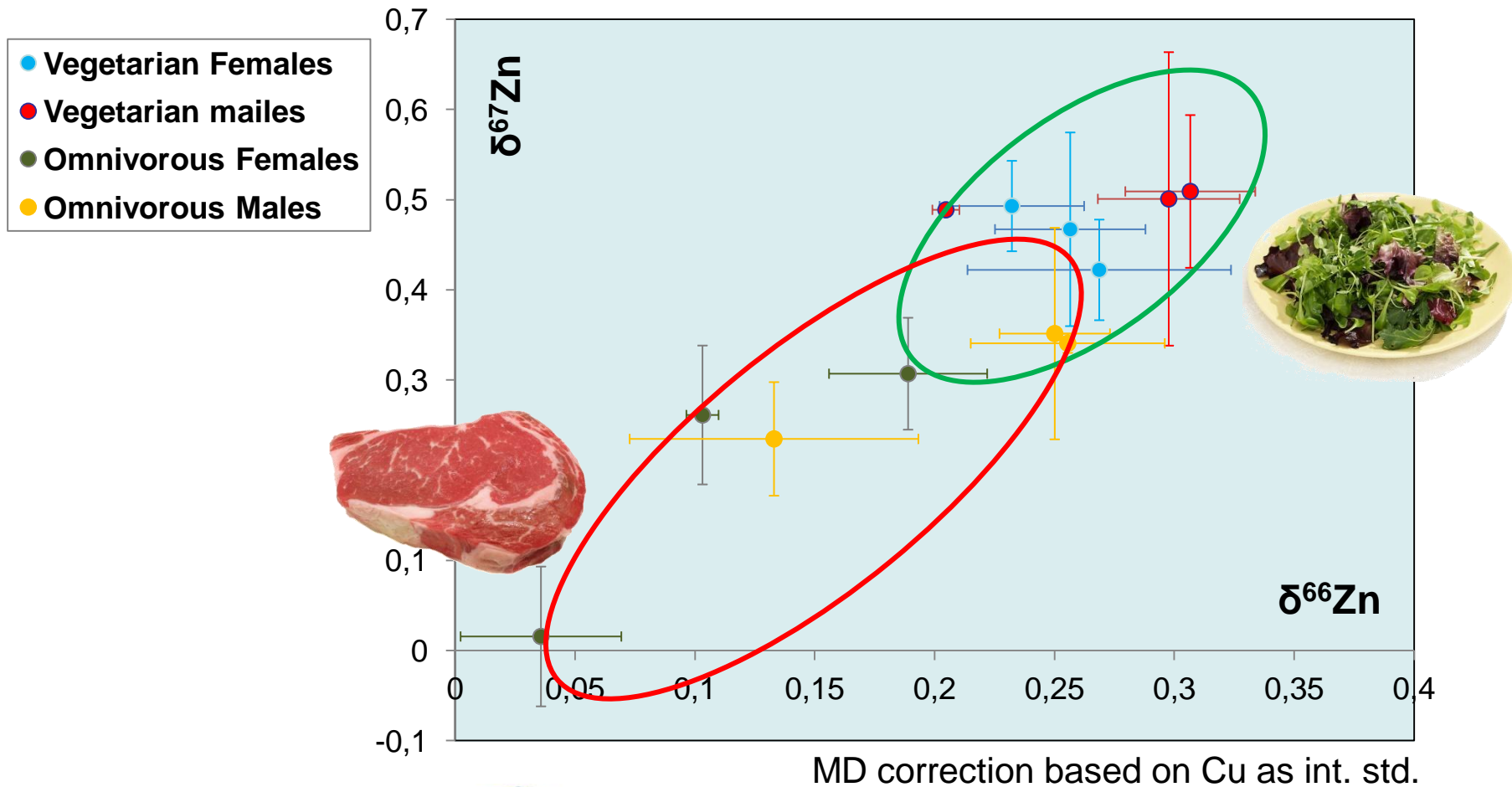
HUMAN BLOOD / REFERENCE POPULATION



MD correction based on Ni as int. std.

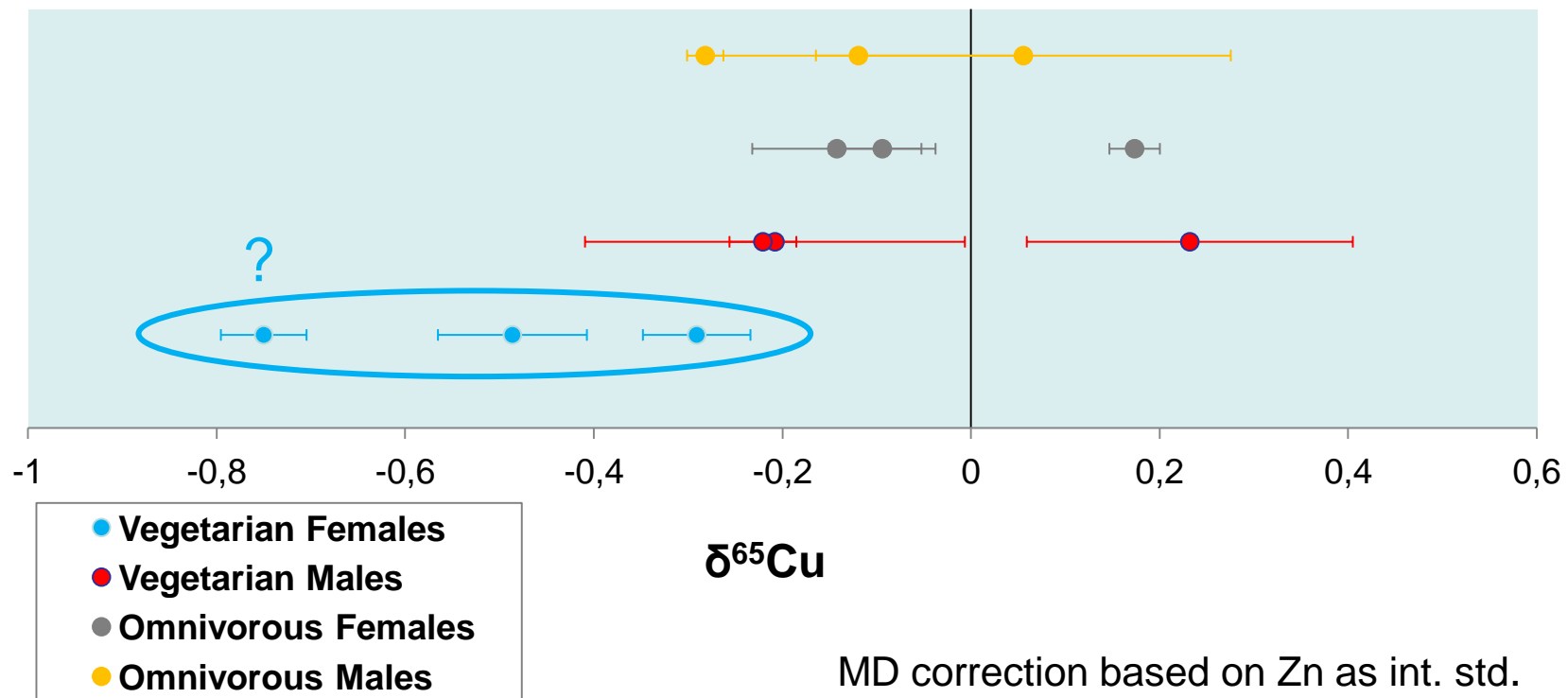
RESULTS ZN ISOTOPIC ANALYSIS

HUMAN BLOOD / REFERENCE POPULATION

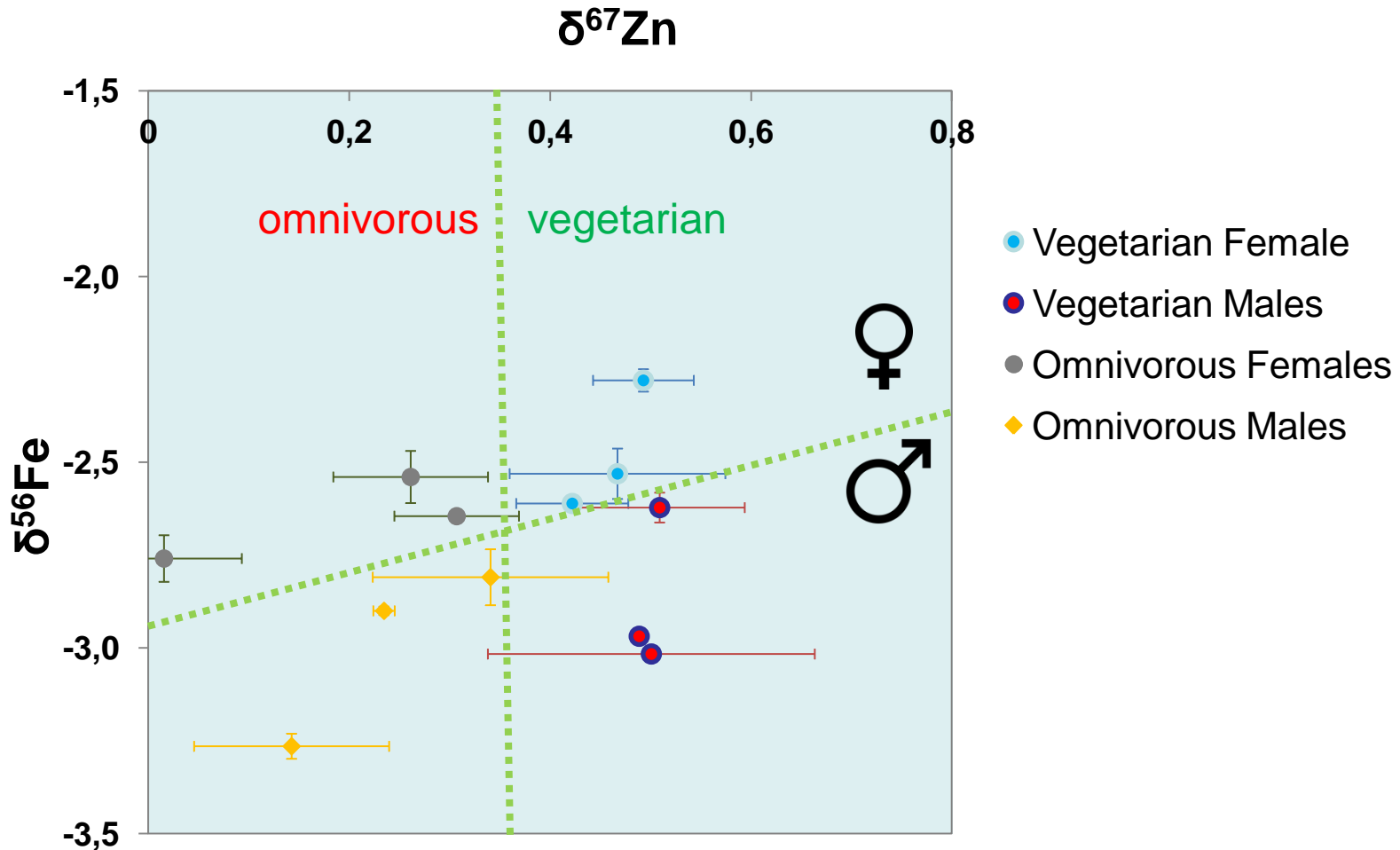


RESULTS *Cu* ISOTOPIC ANALYSIS

HUMAN BLOOD / REFERENCE POPULATION



RESULTS $Fe + Zn$ ISOTOPIC ANALYSIS HUMAN BLOOD / REFERENCE POPULATION



FE, CU, ZN ISOTOPIC ANALYSIS IN HUMAN BLOOD

- ***Factors affecting isotope ratios in reference population***
 - ▶ ***Gender***
 - ▶ ***Feeding habits***
 - ▶ ***...***

- ***Comparison Reference population vs. patient groups***
 - ▶ ***Diseases affecting Fe, Cu and/or Zn metabolism***
 - ▶ ***Diagnostic means?***
 - ***Less invasive***
 - ***Earlier stage of disease ⇒ prediction***

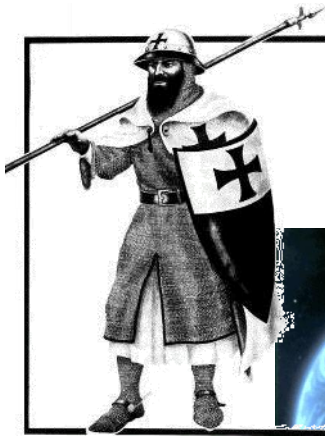
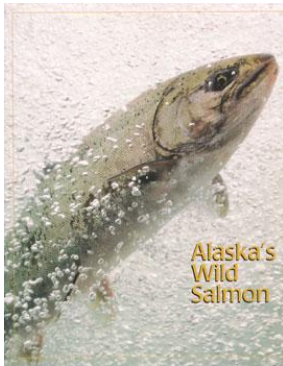
- ***Use in archaeology?***



ISOTOPIC ANALYSIS USING MC-ICP-MS

CONCLUSIONS

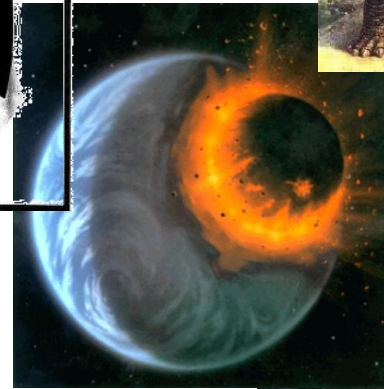
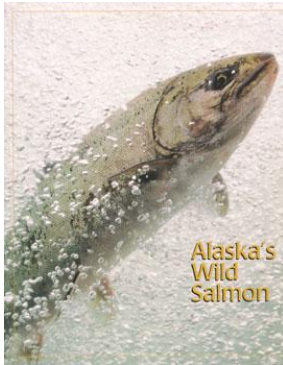
- **Determining (geographical) provenance**
- **Unraveling history**
- **Solving crimes**
- **Diagnosing diseases**



ISOTOPIC ANALYSIS USING MC-ICP-MS

CONCLUSIONS

- **Determining (geographical) provenance**
- **Unraveling history**
- **Solving crimes**
- **Diagnosing diseases**
- **But be careful !**



ISOTOPIC ANALYSIS USING MC-ICP-MS

CONCLUSIONS

- *Determining (geographical) provenance*
- *Unraveling history*
- *Solving crimes*
- *Diagnosing diseases*
- ***But be careful !***

