



Optimization of extraction
chromatographic procedures for the
isolation of Pb and Sr using Eichrom
resins for isotope ratio analysis of
archaeological artefacts

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presentation outline

- I. archaeological projects
 - Roman Bone – project
 - Saint Servatius – project
- II. analytical methodology
 - sample digestion
 - Pb & Sr isotope ratio analysis
 - Pb & Sr isolation from its sample matrix
- III. isotopic data for the Roman Bone – project
 - single collector – ICP – MS results
 - multi-collector – ICP – MS results
- IV. conclusions
- V. acknowledgement

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III. isotopic data for the Roman Bone – project

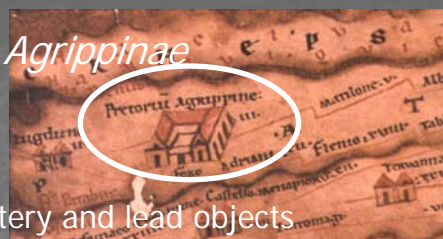
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Roman Bone – project

- ❑ cemetery of Roman settlement, *Pretoria Agrippinae*
 - 1st – 3rd century A.D.
 - Valkenburg, The Netherlands
 - infant bone tissue, soil, garum, amphorae, pottery and lead objects
- ❑ preliminary AAS studies : Pb concentration in bone tissue very high as compared to :
 - Pb concentrations in 'modern' bone (teenagers : 4 $\mu\text{g g}^{-1}$)
 - Pb concentrations in surrounding soil
- ❑ Roman Era : significant Pb exposure
 - plumbing systems, Pb salts as food additives and for conservation of wine
- ❑ Pb
 - toxic, possibly carcinogenic, negative effects on many body functions



Roman Bone – project

At what age did Pb exposure commence ?

pre – or post natal ?



Is diagenesis (**post mortem Pb exchange between bone and soil**)
the main source for 'bone Pb' ?

Pb isotopic analysis using
inductively coupled plasma – mass spectrometry (ICP – MS)
of infant bone tissue, soil, garum, amphorae, pottery and
lead objects

Saint Servatius – project

□ basilica of Saint Servatius

- early Christendom in Maas valley, 1600 years rich history
- Maastricht, The Netherlands
- in honor of Saint Servatius, bishop of Tongeren: 4th century A.D.
- important attraction and cultural inheritance



□ investigation of the buried population at the cemetery around the basilica of Saint Servatius

- skeletal material : bone tissue and tooth tissue
- heterogeneity of the buried population, local people or immigrants ?

□ Sr isotopic analysis

- tooth enamel's composition reflects the place of birth
- tooth dentine's and bone's composition reflects place of decease
- soil and animal tooth and bone tissue for local Sr signature

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analytical methodology

I. sample digestion

- ✓ complete dissolution of all sample types
- ✓ quantitative recovery for target element (Pb or Sr)
- ⇒ limiting (detectable) isotopic fractionation

II. isolation of target element from its matrix

- ✓ pure Pb or Sr fraction only
- ✓ quantitative recovery for target elements
- ⇒ minimising matrix effects on measured isotope ratio
- ⇒ permitting a more accurate correction for mass discrimination

III. isotope ratio measurements

- ✓ single collector – ICP – dynamic reaction cell – MS (Ghent)
- ✓ multi-collector – ICP – sector field – MS (Zürich)

digestion procedures

- ❑ quantitative recovery for target elements required
 - avoiding (detectable) isotopic fractionation
(*e.g.*, 1 isotope is preferably incorporated at the outer side of a bone, others at the inner side, causing different isotope ratios in different parts of the bone)
- ❑ optimization using Certified Reference Materials
 - enamel, dentine, bone tissue & garum : NIST SRM 1400 Bone Ash
 - soil : BCR 141 Calcareous Loam Soil & BCR 142 Light Sandy Soil
 - Pb objects : Pb foil
 - amphorae & pottery : no reference material available
⇒ based on visual observation

digestion procedures

□ tooth tissues (enamel & dentine)

- $\pm 0,2$ g enamel or dentine in beaker
- 8 mL 14 M HNO_3 , hot plate until one drop left
- 5 mL 12 M HCl , hot plate until evaporation
- uptake in 14 M HNO_3 under ultrasonic agitation



□ Pb tools

- $\pm 0,1$ g turnings in beaker
- 20 mL 1,4 M HNO_3 , hot plate
- soft heating until totally dissolved

□ soil, bone, garum, amphorae, pottery

- microwave-assisted acid digestion
- transfer to beaker and evaporation to gel
- redissolution in 14 M HNO_3 and dilution to ± 1 M HNO_3

microwave-assisted acid digestion

soil ($\pm 0,2$ g)

acids	microwave settings
5 mL HNO ₃ + 2 mL HCl + 2 mL HF cool down, + 1 mL HClO ₄	20 min 250 W, 8 min 600 W, 15 min 250 W 20 min 250 W, 8 min 400 W, 15 min 250 W
beaker contains digest + 2 mL HNO ₃ + 2 mL HF + 2 mL HClO ₄	

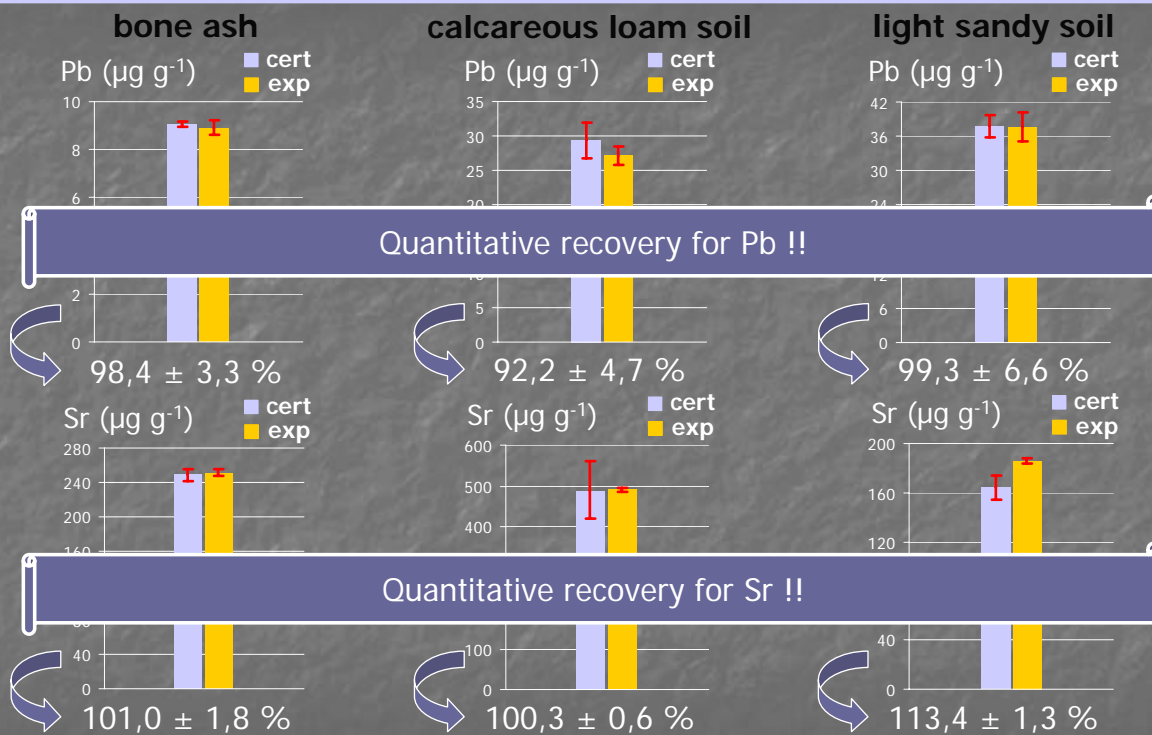
bone & garum ($\pm 0,2$ g)

acids	microwave settings
6 mL HNO ₃ + 1,5 mL HCl	5 min 250 W, 5 min 400 W, 5 min 250 W

amphorae & pottery ($\pm 0,2$ g)

acids	microwave settings
3 mL HNO ₃ + 1 mL HCl + 5 mL HF	10 min 250 W, 10 min 600 W, 10 min 250 W

recoveries for digestion procedures



Pb & Sr isotope ratio analysis

□ Pb

- 4 stable isotopes : ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb
- ^{206}Pb , ^{207}Pb and ^{208}Pb formed by alpha-decay of ^{238}U , ^{235}U and ^{232}Th
- ^{204}Pb not radiogenic
- ICP – MS : no spectral interferences for Pb

□ Sr

- 4 stable isotopes : ^{84}Sr , ^{86}Sr , ^{87}Sr , ^{88}Sr
- only ^{87}Sr is radiogenic
- beta-decay of ^{87}Rb to ^{87}Sr \Rightarrow co-present in *e.g.*, rocks
- $\text{mass}(^{87}\text{Rb isotope}) = 86,909184$; $\text{mass}(^{87}\text{Sr isotope}) = 86,908890$
- required resolution $\sim 300\,000$, impossible
- preliminary Rb/Sr separation is necessary !

Pb & Sr isotope ratio analysis

inductively coupled plasma – mass spectrometry (ICP – MS)

single collector ICP – MS
PE SCIEX Elan 6100 DRC_{plus}
quadrupole mass filter



1 electron multiplier

⇒ **sequential detection**
of different isotopes

isotope ratio precision (with Ne
as collision gas in DRC) :
~ 0,1 % RSD

multi-collector ICP – MS
Nu Plasma HR & Nu Plasma 1700
sector field mass spectrometer



12 fixed Faraday cups
+ 3 electron multipliers



10 fixed & 6 movable
Faraday cups + 3
electron multipliers

⇒ **simultaneous detection**
of different isotopes

isotope ratio precision :
~ 0,001 % RSD



Pb & Sr isolation from its sample matrix

□ why ?

- minimizing **matrix effects** on measured isotope ratio
signal decrease or increase for the same initial amount of ions, due to the matrix
- permitting a more accurate correction for **mass discrimination**
bias between the experimentally determined isotope ratio and the corresponding "true" isotope ratio
- required for MC – ICP – MS (superior precision), beneficial for SC – ICP – MS

□ requirements ?

- quantitative : avoiding (detectable) **isotopic fractionation**
e.g., 1 isotope is preferably incorporated at the outer side of a bone, others in the inner side, causing different isotope ratios in different parts of the bone
- selective : only 'interested' in the pure Pb or Sr fraction

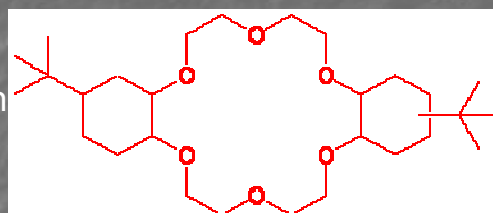


Pb & Sr isolation from its sample matrix



Pb specTM & Sr specTM, Eichrom Technologies Inc.

extraction chromatographic separation by means of a column containing 4,4'(5')-di-*tert*-butylcyclohexano-18-crown-6



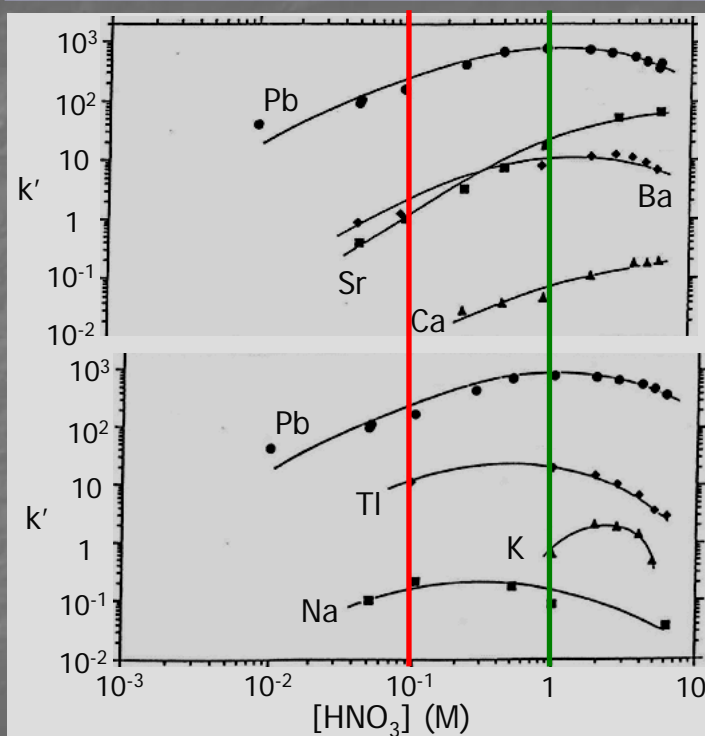
□ Sr : Sr specTM (C. Pin *et al.*, *Anal. Chim. Acta*, 269, 249-255, 1992)

- 1,0 M 4,4'(5')-di-*tert*-butylcyclohexano-18-crown-6
- solvent : 1-octanol
- 40 weight% of organic solution loaded on inert chromatographic support

□ Pb : Pb specTM (E.P. Horwitz *et al.*, *Anal. Chim. Acta*, 292, 263-273, 1994)

- 0,75 M 4,4'(5')-di-*tert*-butylcyclohexano-18-crown-6
 - solvent : isodecanol
- ⇒ lower 18-crown-6 concentration and longer chain alcohol for Pb selectivity

binding properties of Pb on Pb specTM



- focus on :
 - Pb (target)
 - Sr, Ca (bone)
 - Ba (soil)
- $k'_{Na,K,Ca}$ low
- 1 M HNO_3 :
 - highest k'_{Pb} ($\sim 10^3$)
 - $k'_{Sr} \sim 20$, $k'_{Ba} \sim 10$
- 0,1 M HNO_3 :
 - $k'_{Pb} \sim 3 \cdot 10^2$
 - $k'_{Sr} \sim 1$, $k'_{Ba} \sim 2$

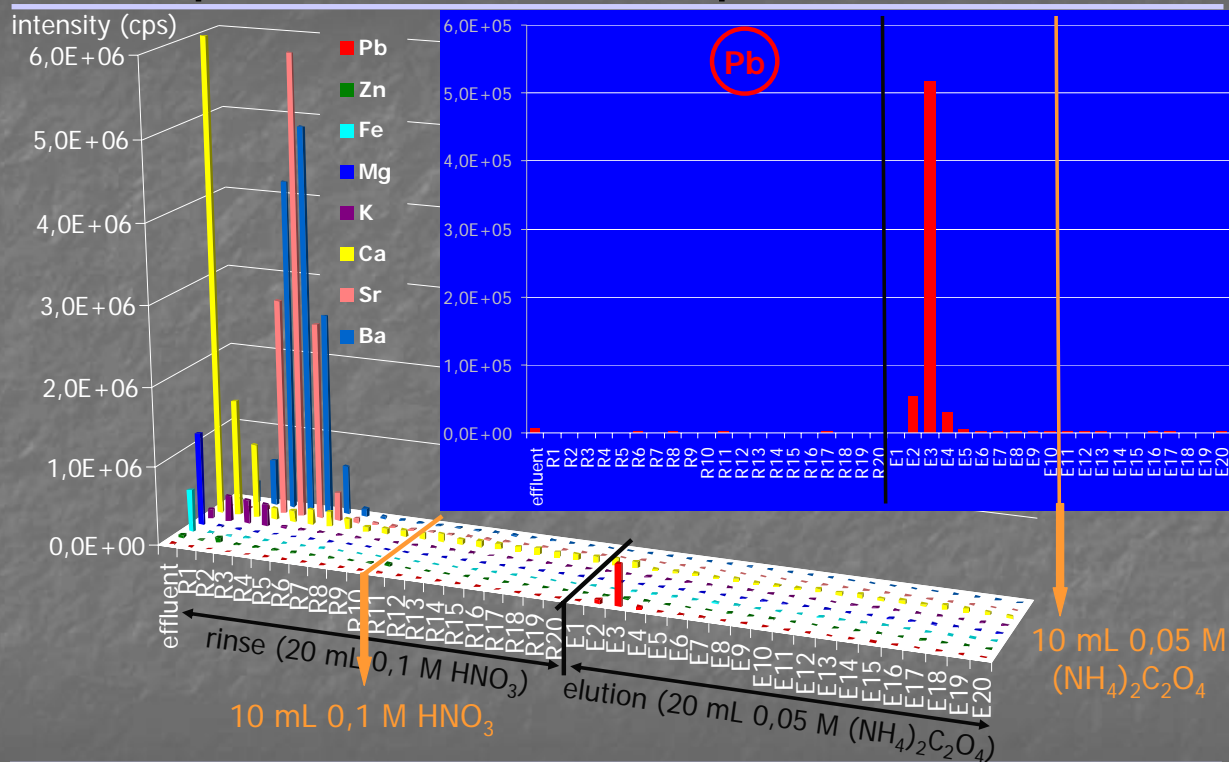
- load sample in 1 M HNO_3
- rinse with 0,1 M HNO_3
(= matrix removal)
- elution of Pb fraction ?

elution of Pb from Pb specTM

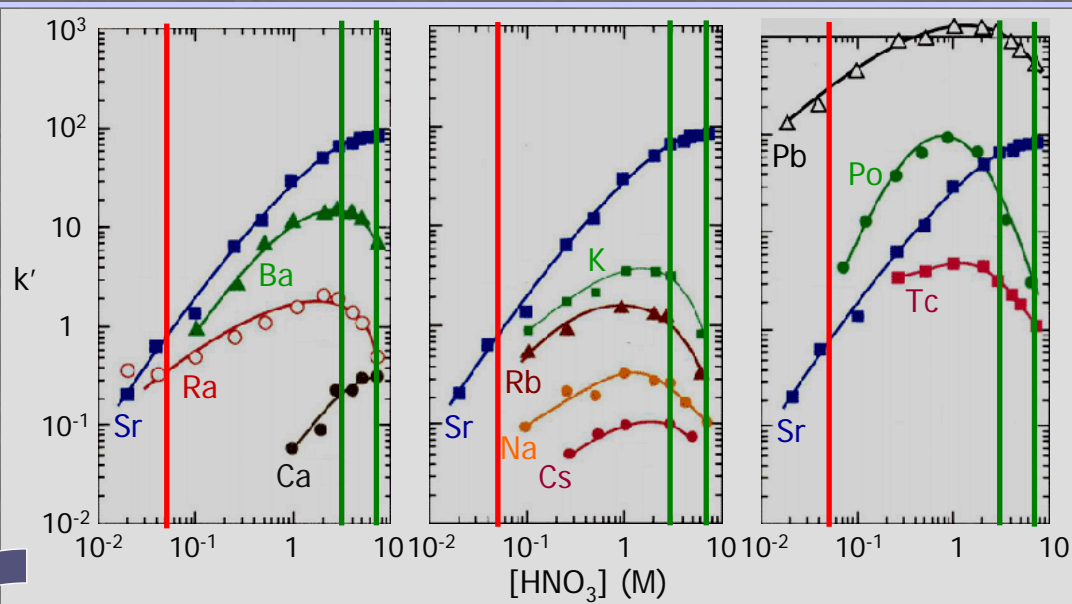
- ❑ amount of Pb (standard solution) loaded onto column : 10 µg
- ❑ rinse with 40 mL 0,1 M HNO₃
- ❑ elution with 20 mL H₂O
 - Pb recovery : 38 ng = 0,38 %
- ❑ elution with 20 mL 0,1 M Na₄EDTA solution, pH 7,5
 - EDTA blank values : 93 ng Pb + many other impurities
 - EDTA causes strong signal suppression (~ 40 % for Pb)
 - Pb recovery : 6,1 µg = 61 % (real value is higher)
- ❑ elution with 20 mL 0,05 M (NH₄)₂C₂O₄ solution
 - (NH₄)₂C₂O₄ blank values : 5 ng Pb + low levels of other impurities
 - (NH₄)₂C₂O₄ causes light signal enhancement (~ 2 %)
 - Pb recovery : 10,5 µg = 105 % (1 experiment)



optimization of Pb specTM for soil



binding properties of Sr on Sr specTM



- Sr (target), Rb (isobaric interference), Ca (bone), Ba (soil), Pb (similar)
- loading + rinsing : 3 – 7 M HNO₃ : highest k'_{Sr} ($\sim 10^2$) + k'_{matrix} low
- elution : 0,05 M HNO₃ : $k'_{Sr} \sim 0,8$

Rb/Sr separation using Sr specTM

- amount of Sr (standard solution) loaded onto column : 10 μg
- Sr/Rb ratio 0,1; 1 and 10 in order to evaluate the separation of the isobars ^{87}Sr and ^{87}Rb
- standard solution in 3 M HNO_3 , rinse with 20 mL 3 M HNO_3 and elution with 20 mL 0,05 M HNO_3 :



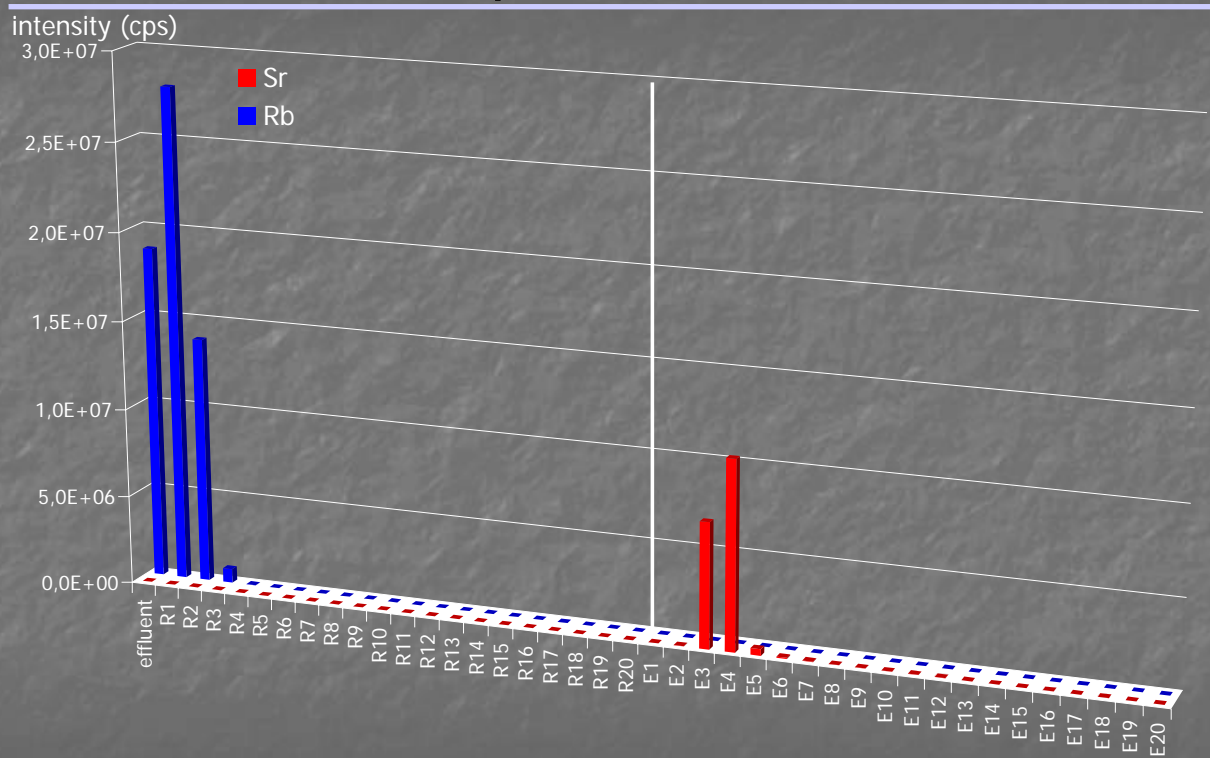
- 3 M : $k'_{\text{Sr}} = 70$, $k'_{\text{Rb}} = 1$
- Rb in eluent < 0,4 ng for all ratios
- Sr in eluent ~ 1 μg for all ratios = 10 %

- standard solution in 7 M HNO_3 , rinse with 20 mL 7 M HNO_3 and elution with 20 mL 0,05 M HNO_3 :

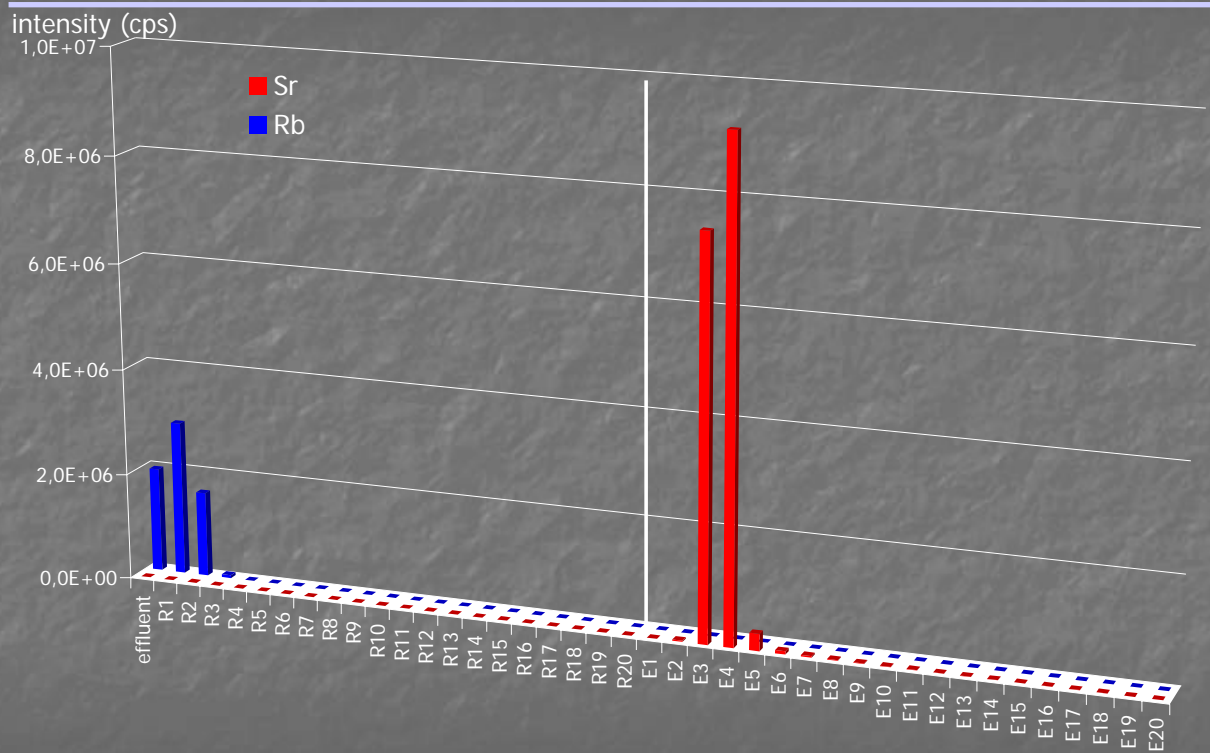


- 7 M : $k'_{\text{Sr}} = 90$, $k'_{\text{Rb}} = 0,3$
- Rb in eluent < 0,4 g for all ratios
- Sr in eluent for all ratios : 100,0 % ! (1 experiment)

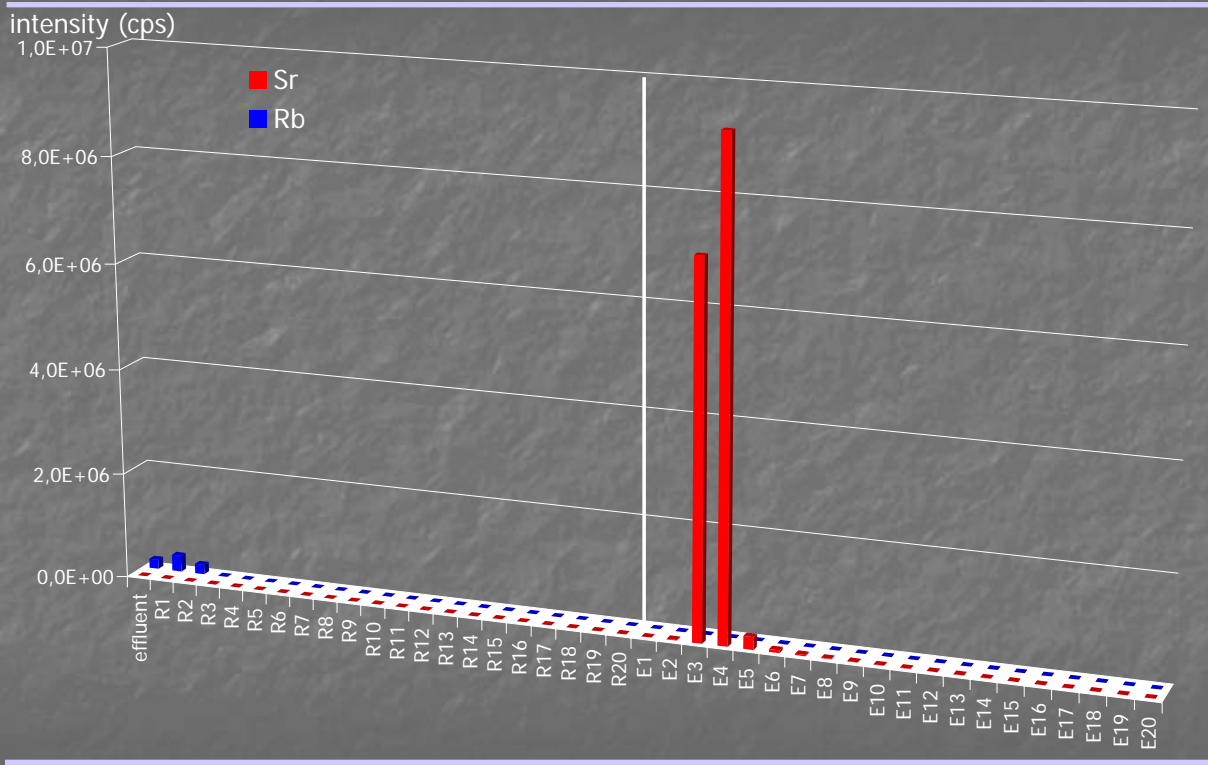
Rb/Sr separation ratio 0,1



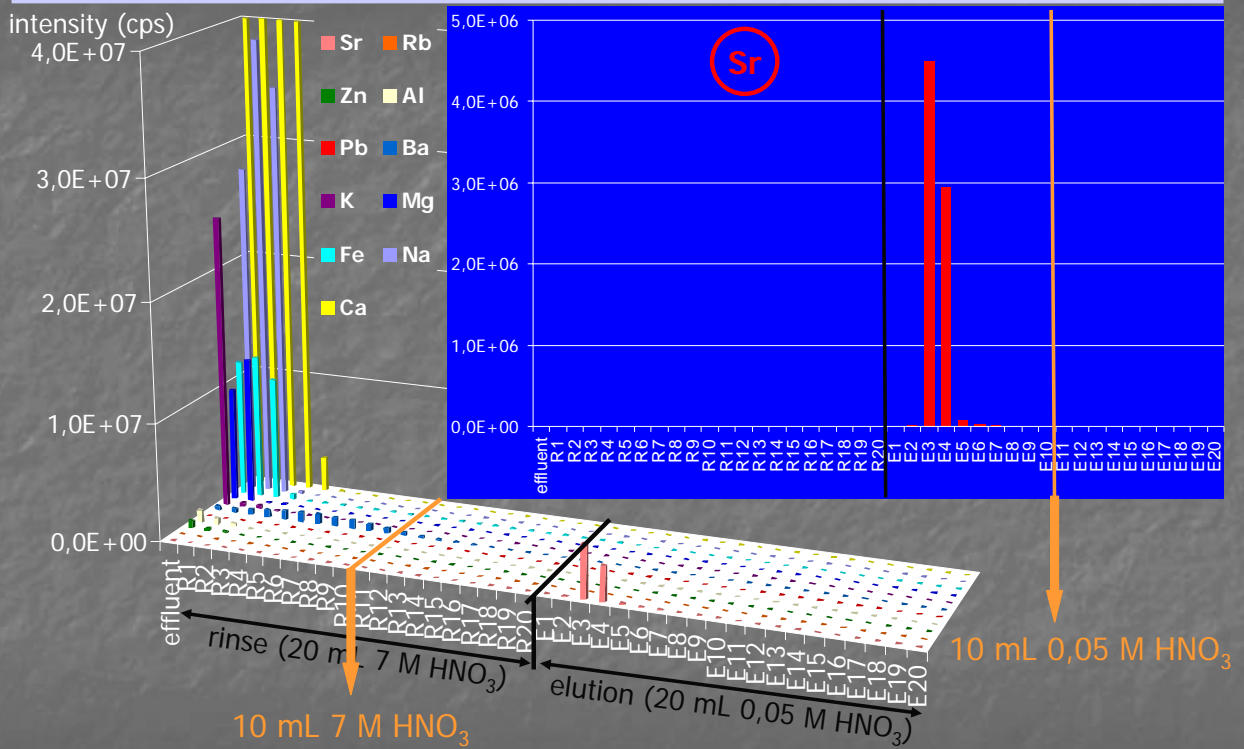
Rb/Sr separation ratio 1



Rb/Sr separation ratio 10



optimization of Sr specTM for bone



experimental recoveries for Pb & Sr

□ Pb (uncertainties given as 95 % confidence intervals)

- bone : $99,8 \pm 5,1$ %
- soil : $100,3 \pm 1,5$ %

□ Sr (uncertainties given as 95 % confidence intervals)

- Rb/Sr separation is successful for every ratio !
- bone : $100,0 \pm 3,1$ %
- soil : $99,5 \pm 2,3$ %
- tooth tissue : $97,8 \pm 4,4$ %

isotopic behaviour on Pb & Sr specTM

□ recoveries are quantitative

⇒ no isotopic fractionation expected

□ check using multi-collector – ICP – MS

□ Pb : NIST SRM 981

- experimental $^{207}\text{Pb}/^{206}\text{Pb}$ ratio before column : $0,9146820 \pm 0,0000107$
- experimental $^{207}\text{Pb}/^{206}\text{Pb}$ ratio after column : $0,9146850 \pm 0,0000062$
- certified : $0,914750$; bias due to mass discrimination

□ Sr : NIST SRM 987

- experimental $^{87}\text{Sr}/^{86}\text{Sr}$ ratio before column : $0,7101452 \pm 0,0000078$
- experimental $^{87}\text{Sr}/^{86}\text{Sr}$ ratio after column : $0,7101435 \pm 0,0000062$
- certified : $0,710248$; bias due to mass discrimination



no (detectable) isotopic fractionation on Pb specTM & Sr specTM



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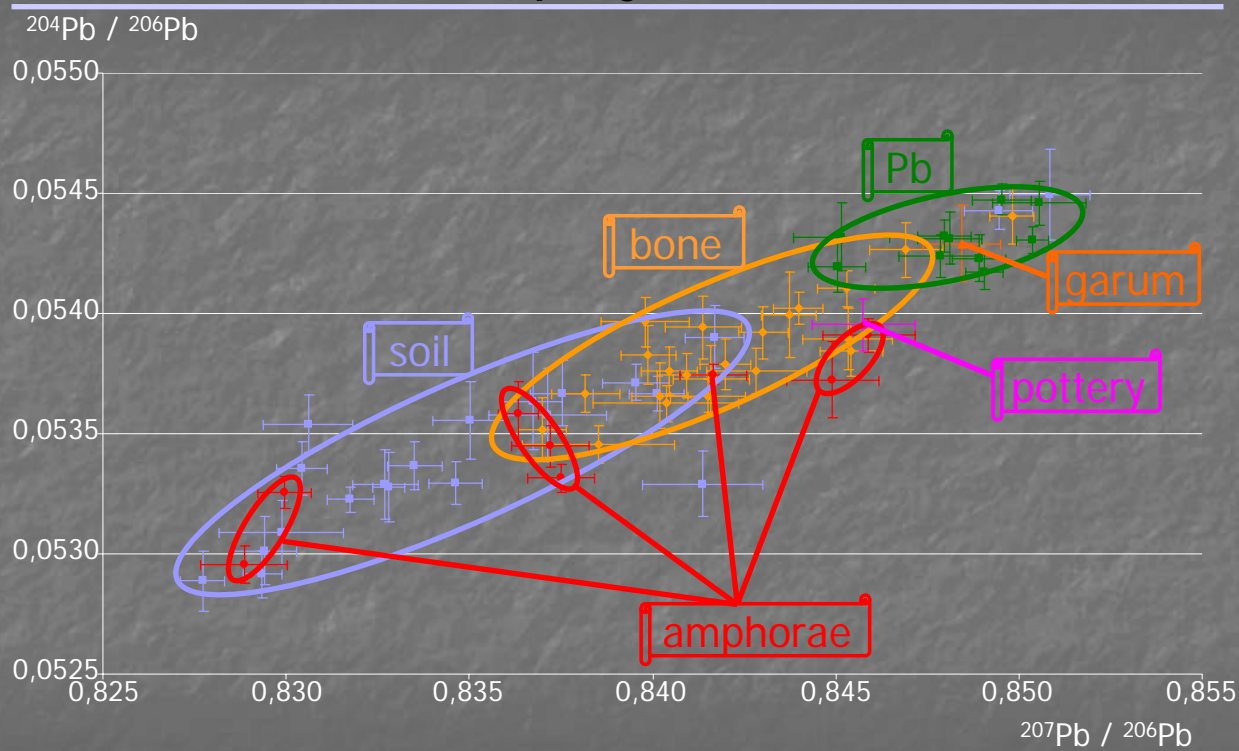
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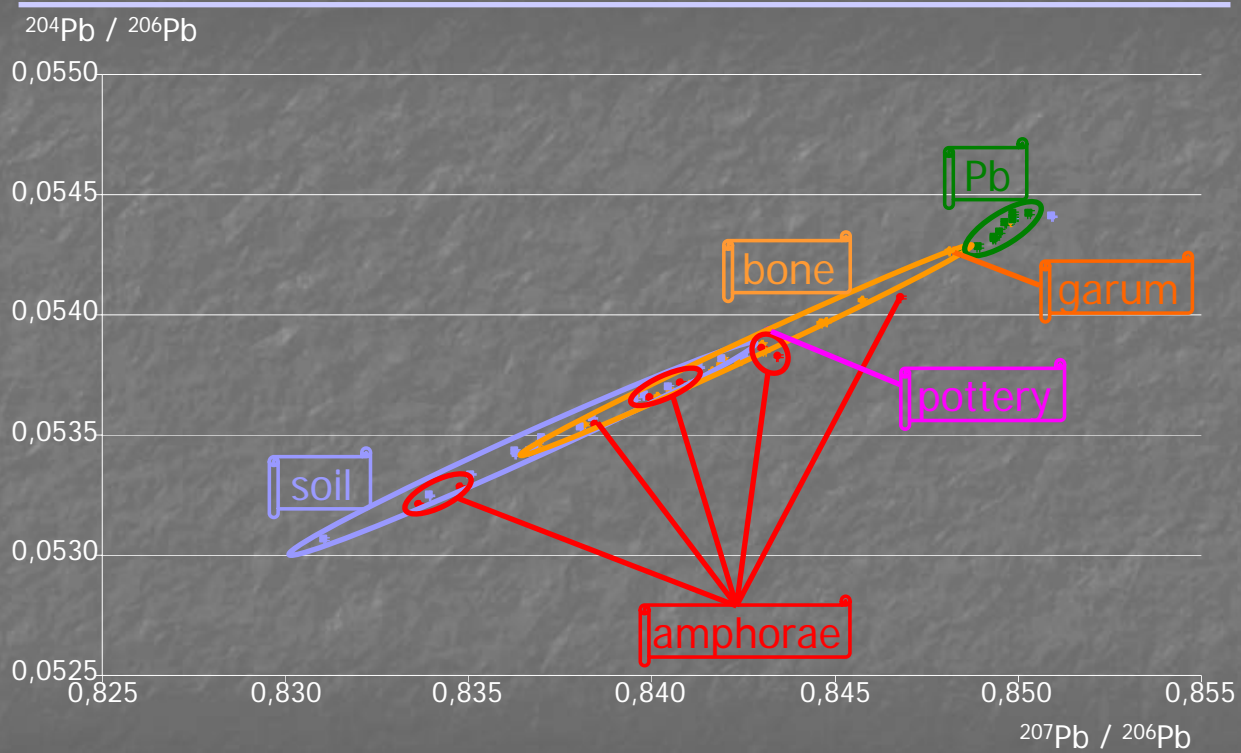
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Roman Bone project – SC results



Roman Bone project – MC results



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conclusions

□ Pb specTM & Sr specTM

- can be used for isolation of Pb & Sr from heavy matrices
(*e.g.*, bone and tooth tissue, soil,...)
- fast process
- selective
- pure Pb & Sr fraction
- quantitative
- no isotopic fractionation occurs on the column



**ultimately suited for isolation of a target element
from its matrix preceding isotopic analysis using
single collector – and multi-collector – ICP –
mass spectrometry**

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acknowledgement

- ❑ MSc Karen Van Hoecke – Pb isolation
- ❑ MSc Gonzalo Huelga Suárez – Sr isolation
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- ❑ Dr Felix Oberli (ETH Zürich) – multi-collector measurements
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- ❑ Dr Freek de Wolff (Leiden University Medical Center) – sample delivery

**thank you for
your attention !**

