SHORT COURSE
ISOTOPIC ANALYSIS USING ICP – MASS SPECTROMETRY

Frank Vanhaecke

Ghent University, Belgium

MASARYK UNIVERSITY
Czech Republic

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WHERE EXACTLY IS BELGIUM?

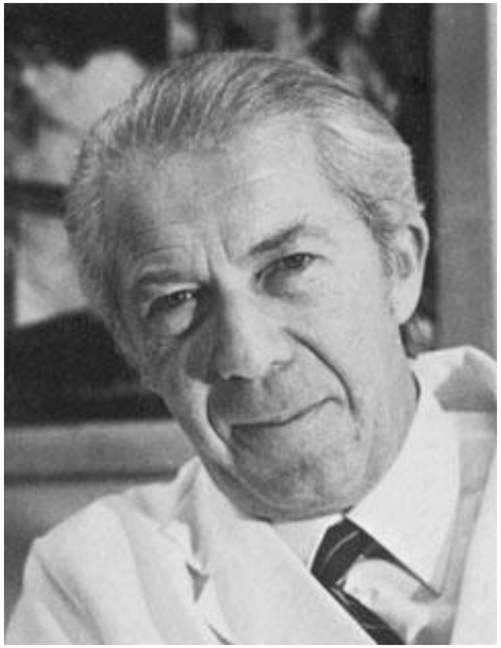
- **Facts**
  - Area: 30,528 km²
  - Population ~ 11,000,000
  - Inhabitation density: 360 /km²
  - Capital: Brussels
    - European Parliament
    - NATO headquarters
  - Northern part: Flanders (Dutch)
  - Southern part: Wallonia (French)

WHERE SHOULD I KNOW BELGIUM FROM?

Belgium map © bugbog.com

PERHAPS … WHO KNOWS?

Leo Baekeland?
Chemist, inventor
“Father of plastics”
Bakelite
phenol-formaldehyde resin



Christian de Duve?
Biochemist
Nobel Prize for Medicine in 1974
Discovered lysosomes and peroxisomes
as cell organelles

PERHAPS … WHO KNOWS?

***Eddy Merckx*?**

1960-70s,

5 times winner of Tour de France

World Champion

World hour record holder

"The cannibal"

***Kim Clijsters*?**

Recently "retired"

3 times US open, 1 time Australian open

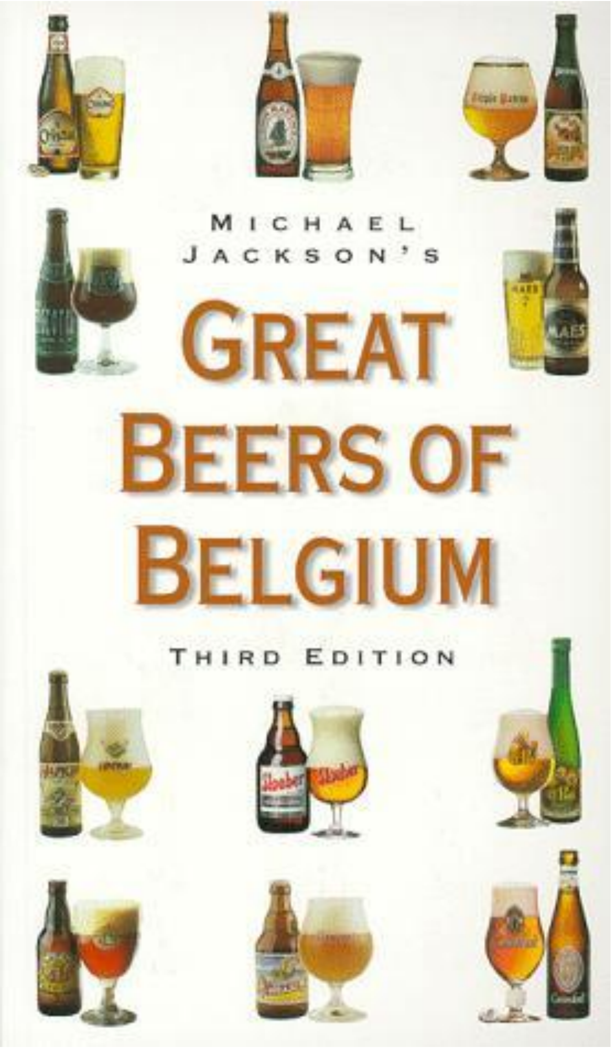
Achieved nr. 1 world ranking

PERHAPS … WHO KNOWS?

Tintin

The smurfs

WHERE SHOULD YOU KNOW BELGIUM FROM?



MICHAEL JACKSON'S

GREAT BEERS OF BELGIUM

THIRD EDITION

Trappist beers – alcohol content: 6 – 12%

WHERE SHOULD YOU KNOW BELGIUM FROM?

WHAT ABOUT GHENT?

- ***Wikipedia?***
  - ***Ghent started as a settlement at the confluence of the Rivers Scheldt and Lys and became in the Middle Ages one of the largest and richest cities of northern Europe. Today it is a busy city with a port and a university.***

THE MIDDLE AGES IN GHENT
GRAVENSTEEN CASTLE (1180)

THE MIDDLE AGES IN GHENT
FRIDAY'S MARKET SINCE 1199 !

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THE MIDDLE AGES IN GHENT
GRASLEI – MEDIAEVAL PORT

THE MIDDLE AGES IN GHENT
THE BELFRY & GOTHIC CHURCHES

GHENT UNIVERSITY
°1817 - ~38,000 STUDENTS & ~7,000 STAFF MEMBERS

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DEPARTMENT OF ANALYTICAL CHEMISTRY

ATOMIC & MASS SPECTROMETRY RESEARCH GROUP
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THE ISOTOPIC COMPOSITION OF THE ELEMENTS

ISOTOPES ?

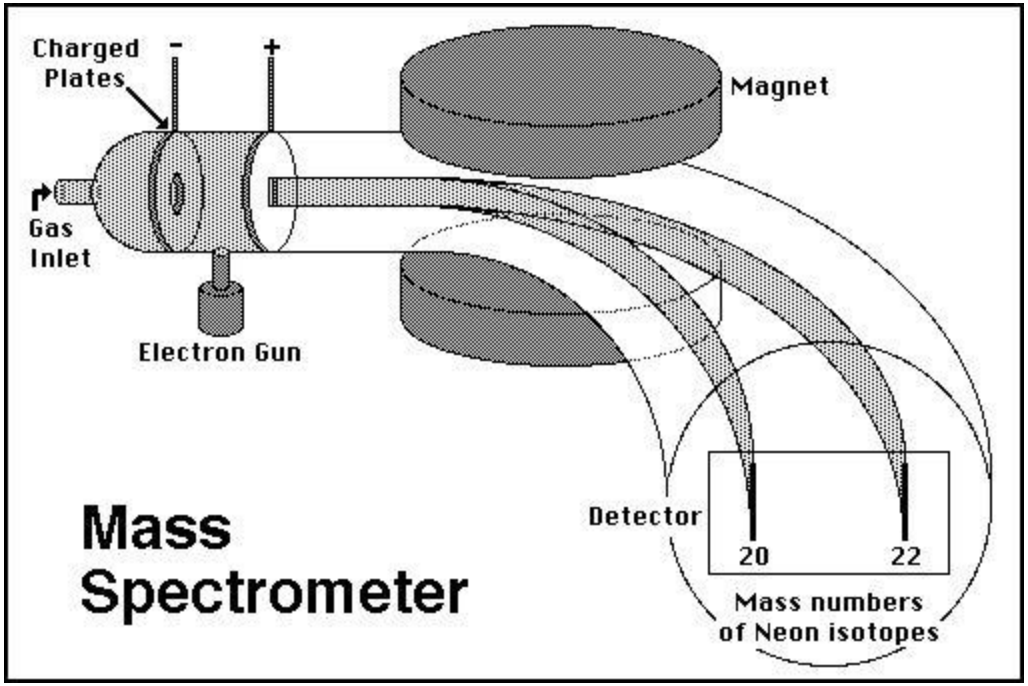
- *Isotopes of an element M:*
  - *same atomic number A*
    - *Same number of protons in their nuclei*
    - *Same number of electrons in their shells*
  - ⇒ *Identical chemical behaviour*
    - *First approximation – statement will be refined later on*
  - *Different mass number Z*
    - *Different number of neutrons in their nuclei*
  - ⇒ *Different masses*
- *Notation*

$^{A}_{Z}X$ *or* ^{A}X

- *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***

http://www.hibbing.edu/chem/abomb/page_id_64208.html

ISOTOPES?

- *Mono-isotopic elements?*
  - ***^{9}Be, ^{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*
  - *Relative abundances define fraction of element M as nuclide ^{n}M*

$$\theta(^{1}M) = \frac{N(^{1}M)}{\sum_{i=1}^{i=m} N(^{i}M)} = \frac{n(^{1}M)}{\sum_{i=1}^{i=m} n(^{i}M)}$$

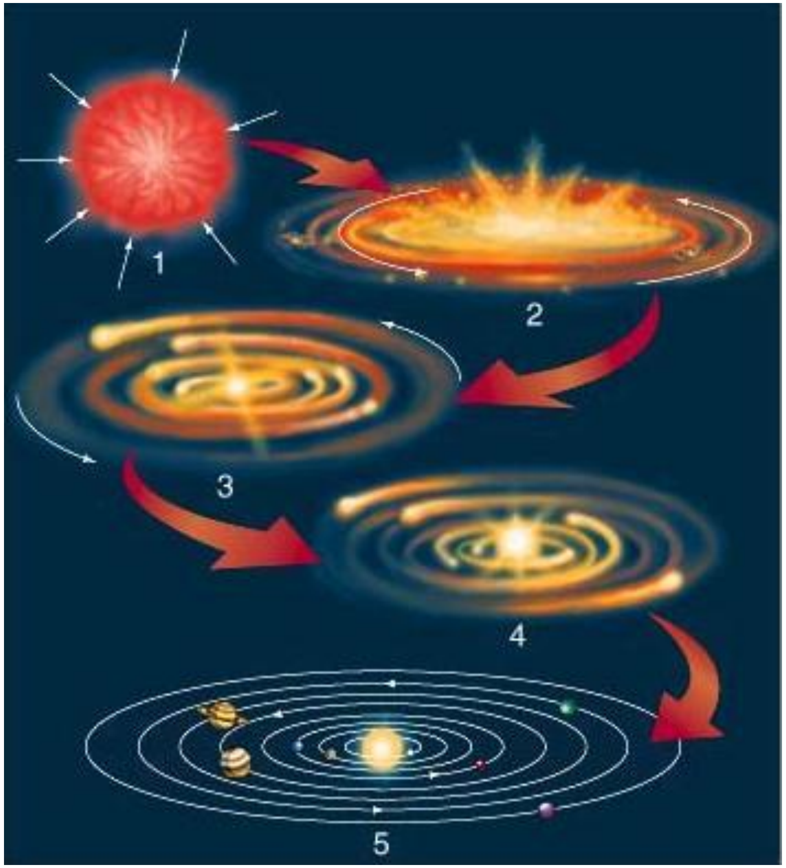
- *N: number of atoms*
- *N: number of moles*

THE ISOTOPIC COMPOSITION OF THE ELEMENTS

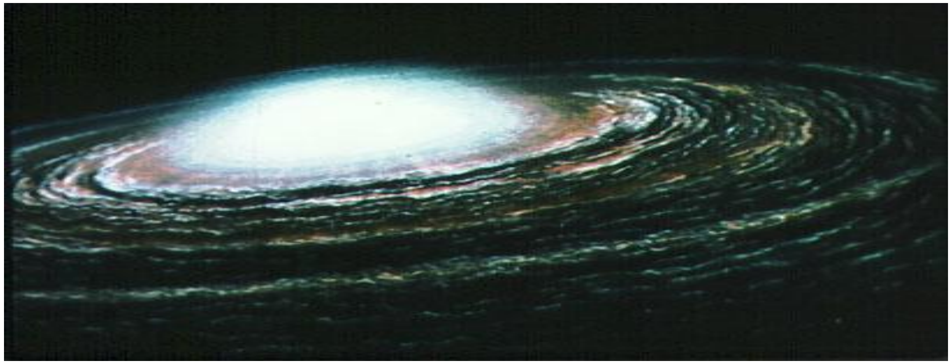
- ***First approximation:***

  all elements show an isotopic composition that is stable in nature

- ***Why ?***
  - ***Thorough mixing during formation of our solar system (4.6 . 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.



VARIATIONS IN THE ISOTOPIC COMPOSITION OF THE ELEMENTS

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

RADIOACTIVE DECAY

- ***Radioactive nuclide: undergoes spontaneous radioactive decay***
  - ***α-decay:***

    $${}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}\alpha$$

    - ***Predominantly for heavy nuclides with m > 200***
  - ***β –decay***

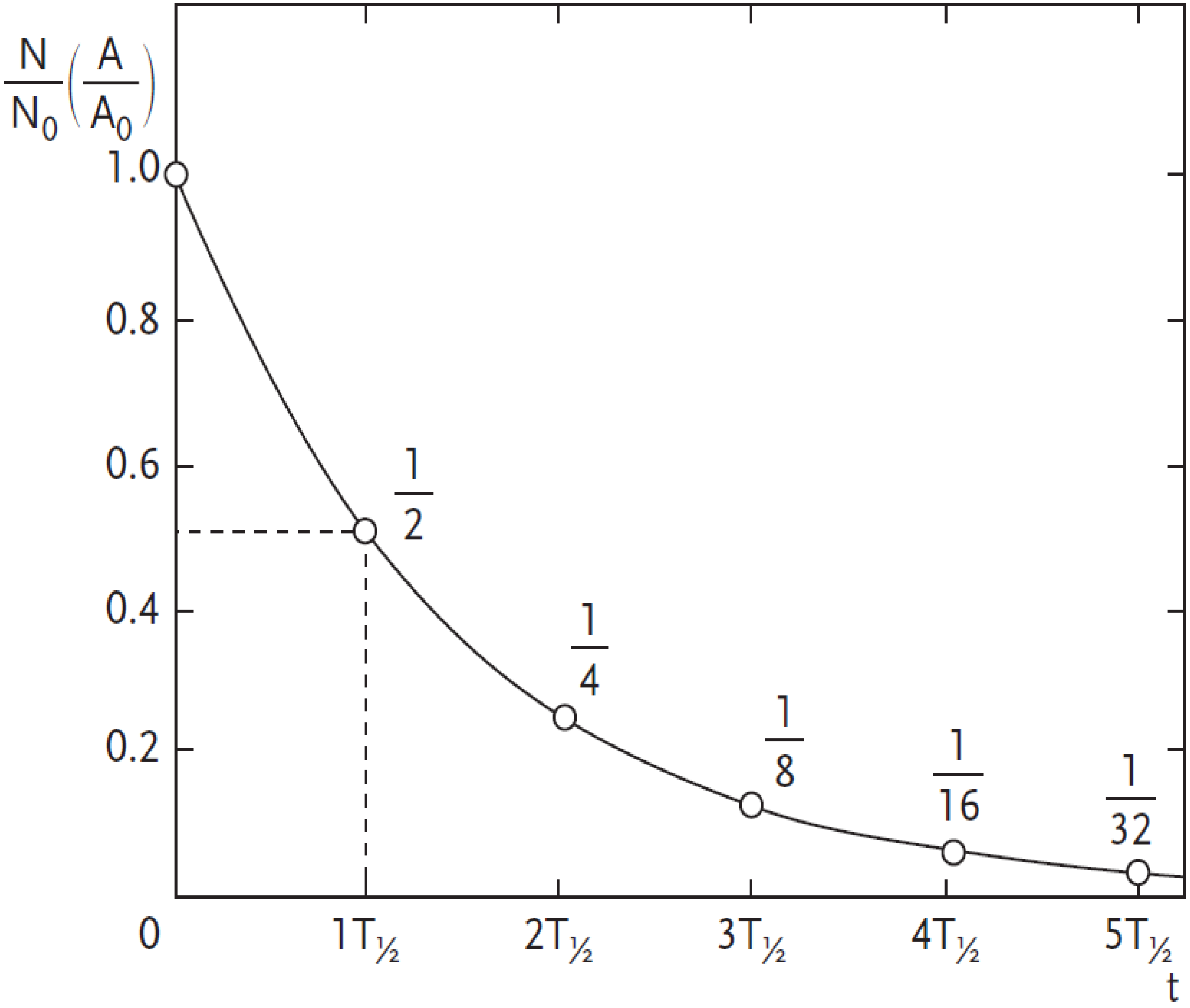
    β^- decay: ${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + {}^{0}_{-1}\beta^- + \bar{\nu}$ **[n → p and β^-]**

    β^+ decay: ${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + {}^{0}_{1}\beta^+ + \nu$ **[p → n and β^+]**

    electron capture: ${}^{A}_{Z}X + {}^{0}_{-1}e^- \rightarrow {}^{A}_{Z-1}Y + \nu$ **[p → n and e^-capture from K shell]**

    - ***E distributed over β-particle & (anti)neutrino***
    - ***β-particles show continuous E-distribution***
  - ***γ-radiation***
    - ***Emitted by nucleus in excited state (upon relaxation)***

RADIOACTIVE DECAY



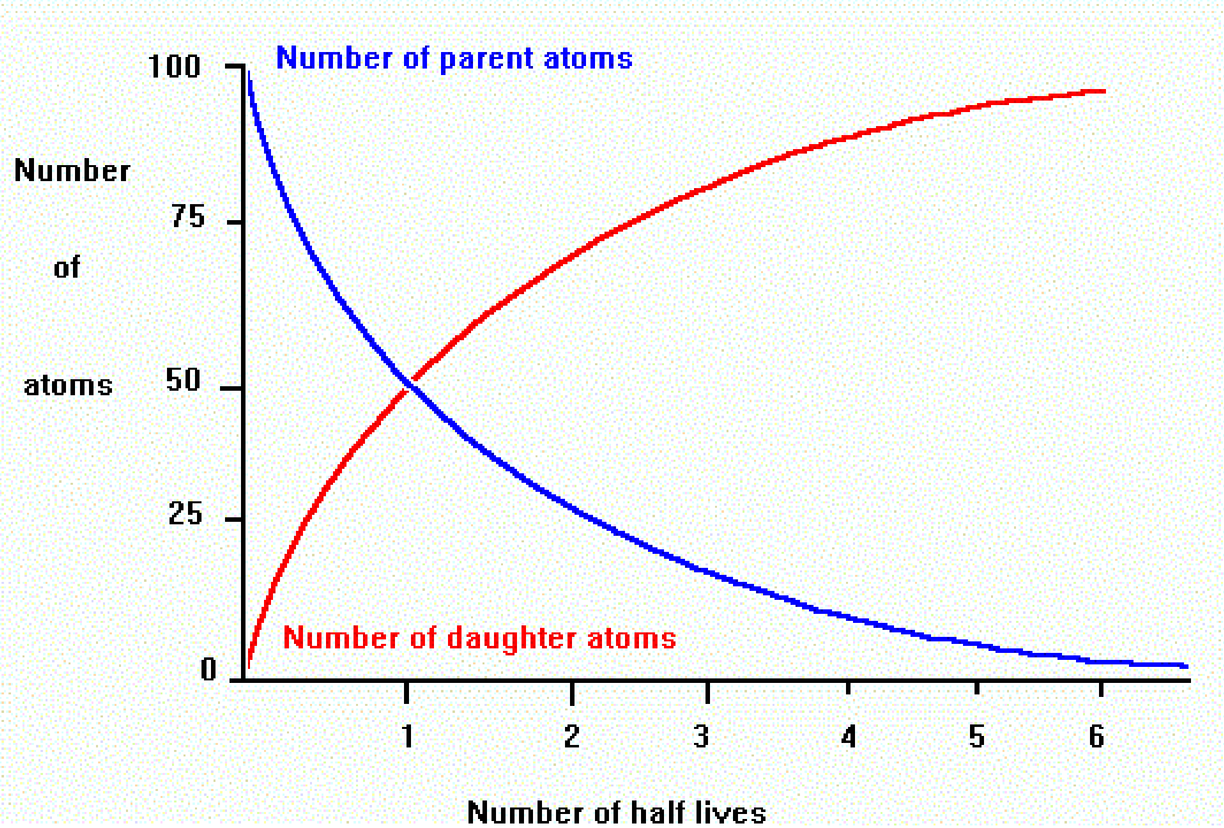
Characteristic $T_{1/2}$

$$\lambda = \frac{\ln 2}{T_{1/2}}$$

$$N_t = N_0 \cdot e^{-\lambda t}$$

RADIOACTIVE DECAY

- ***Production of daughter nuclide***



graph courtesy of www.gpc.peachnet.edu/%7Epgore/geology/geo102/radio.htm

http://www.earlham.edu/~smithal/radiometric-origins.htm

VARIATIONS IN ISOTOPIC COMPOSITION - DECAY OF NATURALLY OCCURRING, LONG-LIVED RADIONUCLIDES

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

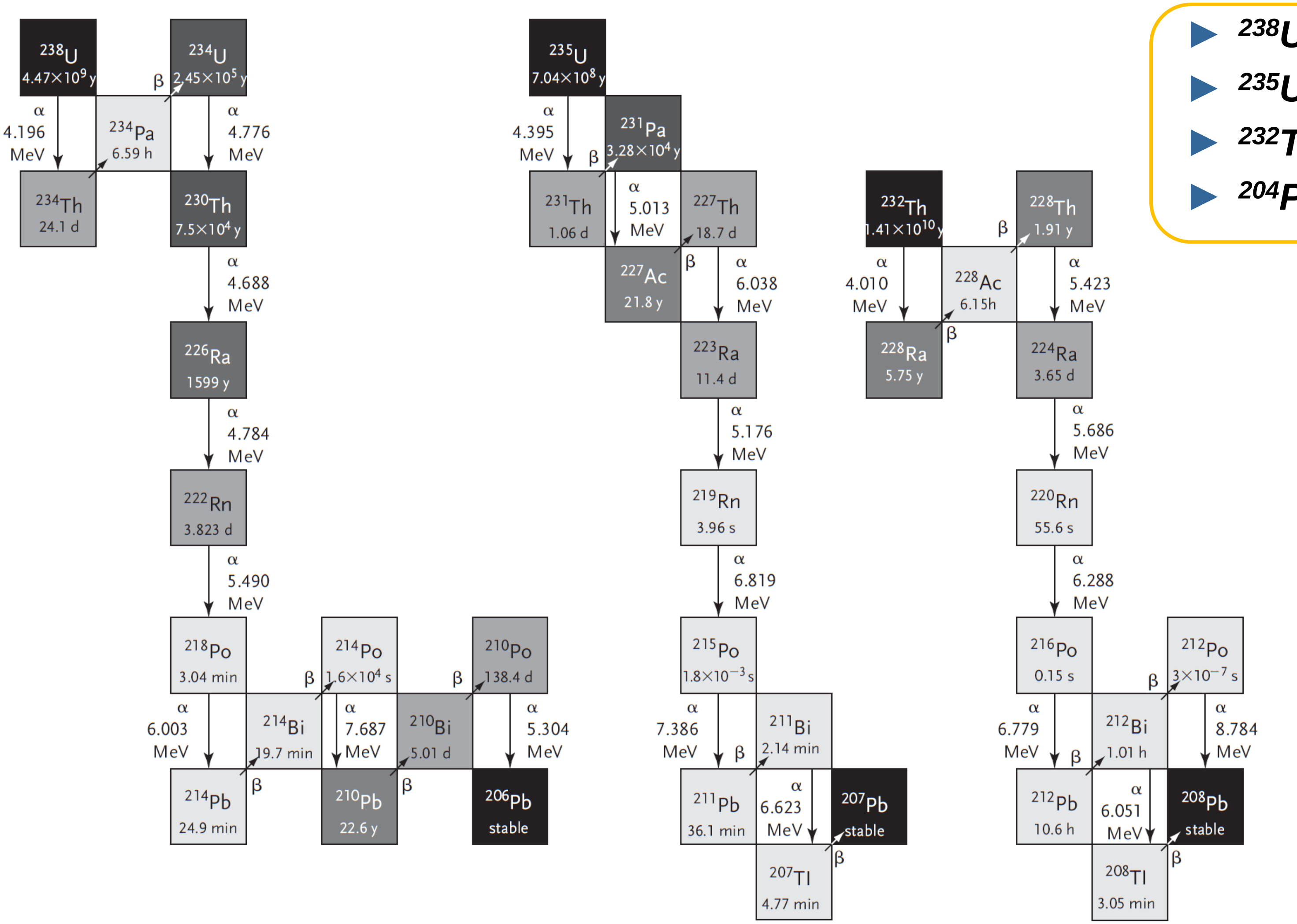
$$^{87}\mathrm{Rb} \rightarrow {}^{87}\mathrm{Sr} + \beta^{-} + \bar{\nu}$$

  - ***^{87}Rb = naturally occurring, long-lived radionuclide***
    - ***$T_{1/2} = 48.8 \times 10^{9}$ 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 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

VARIATIONS IN ISOTOPIC COMPOSITION - DECAY OF NATURALLY OCCURRING, LONG-LIVED RADIONUCLIDES



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

B. Bourdon *et al*, Rev. Miner. Geochem, 52, 1-19, 2003.

VARIATIONS IN ISOTOPIC COMPOSITION - DECAY OF NATURALLY OCCURRING, LONG-LIVED RADIONUCLIDES

- ***Variations in the isotopic composition of Pb***
  - $^{238}U \rightarrow {}^{206}Pb$; ^{238}U: $T_{1/2} = 4.5 \times 10^{9}$ y
  - $^{235}U \rightarrow {}^{207}Pb$; ^{235}U: $T_{1/2} = 7.1 \times 10^{8}$ y
  - $^{232}Th \rightarrow {}^{208}Pb$; ^{232}Th: $T_{1/2} = 1.4 \times 10^{10}$ y
  - ^{204}Pb = not radiogenic
- ***Consequences ?***
  - *Isotopic comp. Pb in the presence of U and/or Th changes as f(time)*
    - *Extremely slowly, cf.* $T_{1/2}$
  - *Isotopic comp. Pb in rocks, dependent on*
    - *Pb/U and Pb/Th elemental ratios*
    - *Time during which elements have "spent together"*
  - *Isotopic comp. Pb varies as a f(place), f(ore deposit), …*

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

VARIATIONS IN ISOTOPIC COMPOSITION - DECAY OF NATURALLY OCCURRING, LONG-LIVED RADIONUCLIDES

Element containing radiogenic nuclide(s)	Isotopes (isotopic abundance as mole fraction) with radiogenic nuclides indicated by the arrow	Parent radionuclide ($T_{1/2}$)	Radioactive decay
Nd	^{142}Nd (0.2680-0.2730) $\Rightarrow$ ^{143}Nd (0.1212-0.1232) ^{144}Nd (0.2379-0.2397) ^{145}Nd (0.0823-0.0835) ^{146}Nd (0.1706-0.1735) ^{148}Nd (0.0566—0.0678) ^{150}Nd (0.0553-0.0569)	^{147}Sm ($1.06\ 10^{11}$ yrs)	$^{147}\text{Sm} \rightarrow {}^{143}\text{Nd} + \alpha$

VARIATIONS IN ISOTOPIC COMPOSITION - DECAY OF NATURALLY OCCURRING, LONG-LIVED RADIONUCLIDES

Element containing radiogenic nuclide(s)	Isotopes (isotopic abundance as mole fraction) with radiogenic nuclides indicated by the arrow	Parent radionuclide ($T_{1/2}$)	Radioactive decay
Hf	^{174}Hf (0.001619-0.001621) $\Rightarrow$ ^{176}Hf (0.05206-0.05271) ^{177}Hf (0.18593-0.18606) ^{178}Hf (0.27278-0.27297) ^{179}Hf (0.13619-0.13630) ^{180}Hf (0.35076-0.35100)	^{176}Lu (3.57 . 10^{10} yrs)	$^{176}Lu \rightarrow {}^{176}Hf + \beta^- + \overline{\upsilon}$

there is also a small fraction (3%) of ^{176}Lu that decays to ^{176}Yb via electron capture

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VARIATIONS IN ISOTOPIC COMPOSITION - DECAY OF NATURALLY OCCURRING, LONG-LIVED RADIONUCLIDES

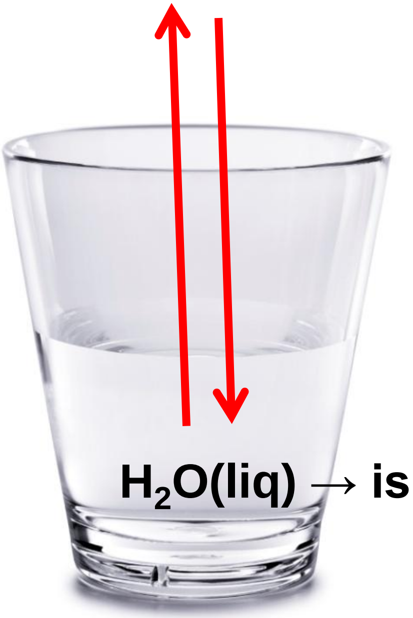
Element containing radiogenic nuclide(s)	Isotopes (isotopic abundance as mole fraction) with radiogenic nuclides indicated by the arrow	Parent radionuclide ($T_{1/2}$)	Radioactive decay
Os	^{184}Os (†) ^{186}Os $\Rightarrow$ ^{187}Os ^{188}Os ^{189}Os ^{190}Os ^{192}Os	^{187}Re (4.161 . 10^{10} yrs)	$^{187}\mathrm{Re} \rightarrow {}^{187}\mathrm{Os} + \beta^{-} + \bar{\upsilon}$

VARIATIONS IN ISOTOPIC COMPOSITION
NATURAL ISOTOPE FRACTIONATION EFFECTS

- ***Isotope fractionation?***
  - ***Due to their relative difference in mass, different isotopes of the same element may take part with a (slightly !!) different efficiency in physical processes or in (bio)chemical reactions.***
  - ***Both differences in reaction rate (kinetics) and in equilibrium state (thermodynamics) have been described.***

ISOTOPE FRACTIONATION DURING A PHYSICAL PROCESS – EVAPORATION OF WATER

H_2O(gas) → isotopically lighter



H_2O(liq) → isotopically heavier

Rayleigh equation

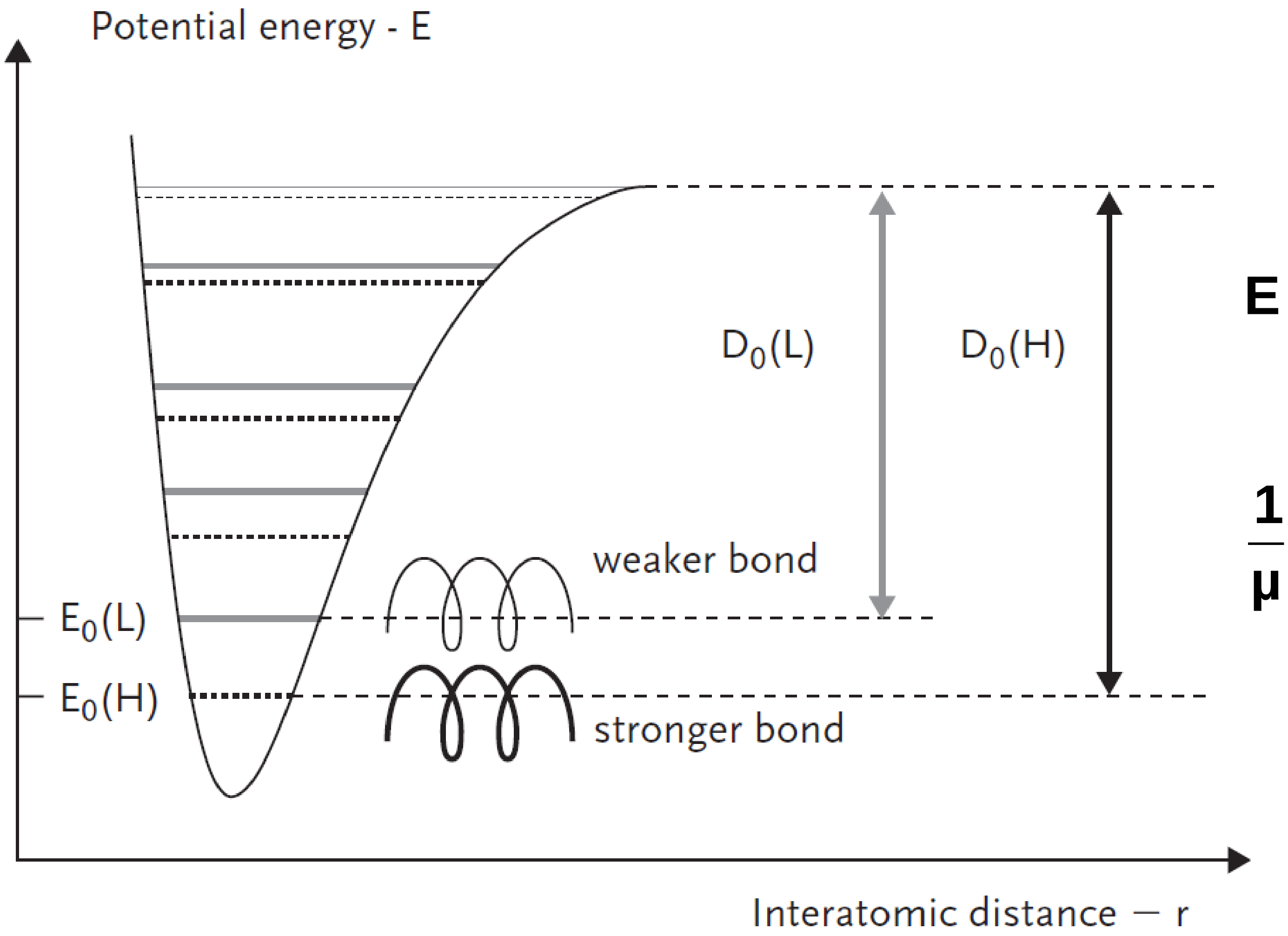
$$R_t = R_0 f_t^{(\alpha-1)}$$

- ***R = $^{18}O/^{16}O$***
- ***f_t fraction of water(liq) remaining***
- ***Fractionation factor α***

$$\alpha = \sqrt{\frac{\left({}^{18}O/{}^{16}O\right)_{vapor}}{\left({}^{18}O/{}^{16}O\right)_{liquid}}}$$

- ***α approaches 1 at high T***

THERMODYNAMIC ISOTOPE FRACTIONATION EFFECT
DISSOCIATION OF A DIATOMIC MOLECULE

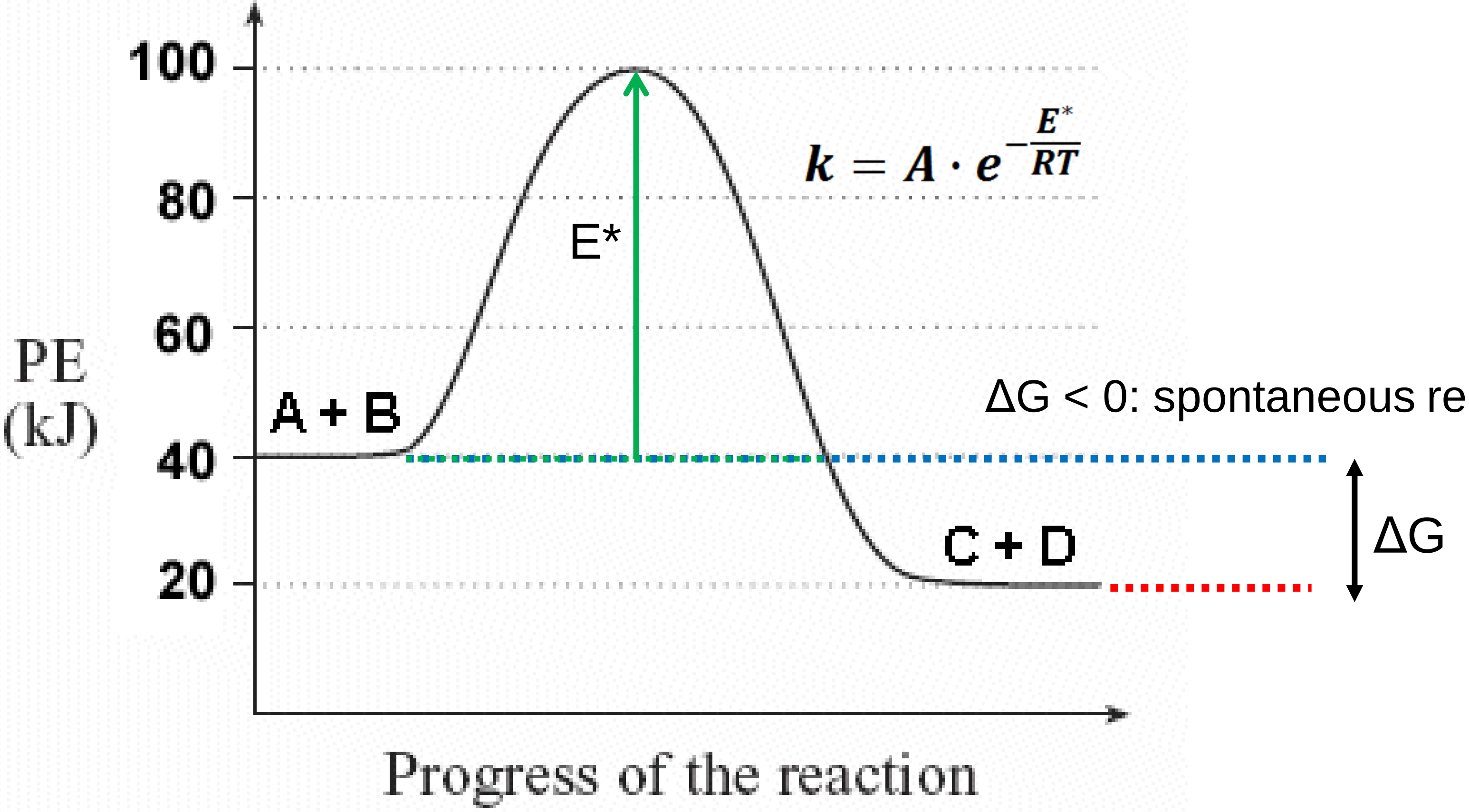


$$E = \left(n + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

F. Vanhaecke *et al*, JAAS, 24, 863-886, 2009.

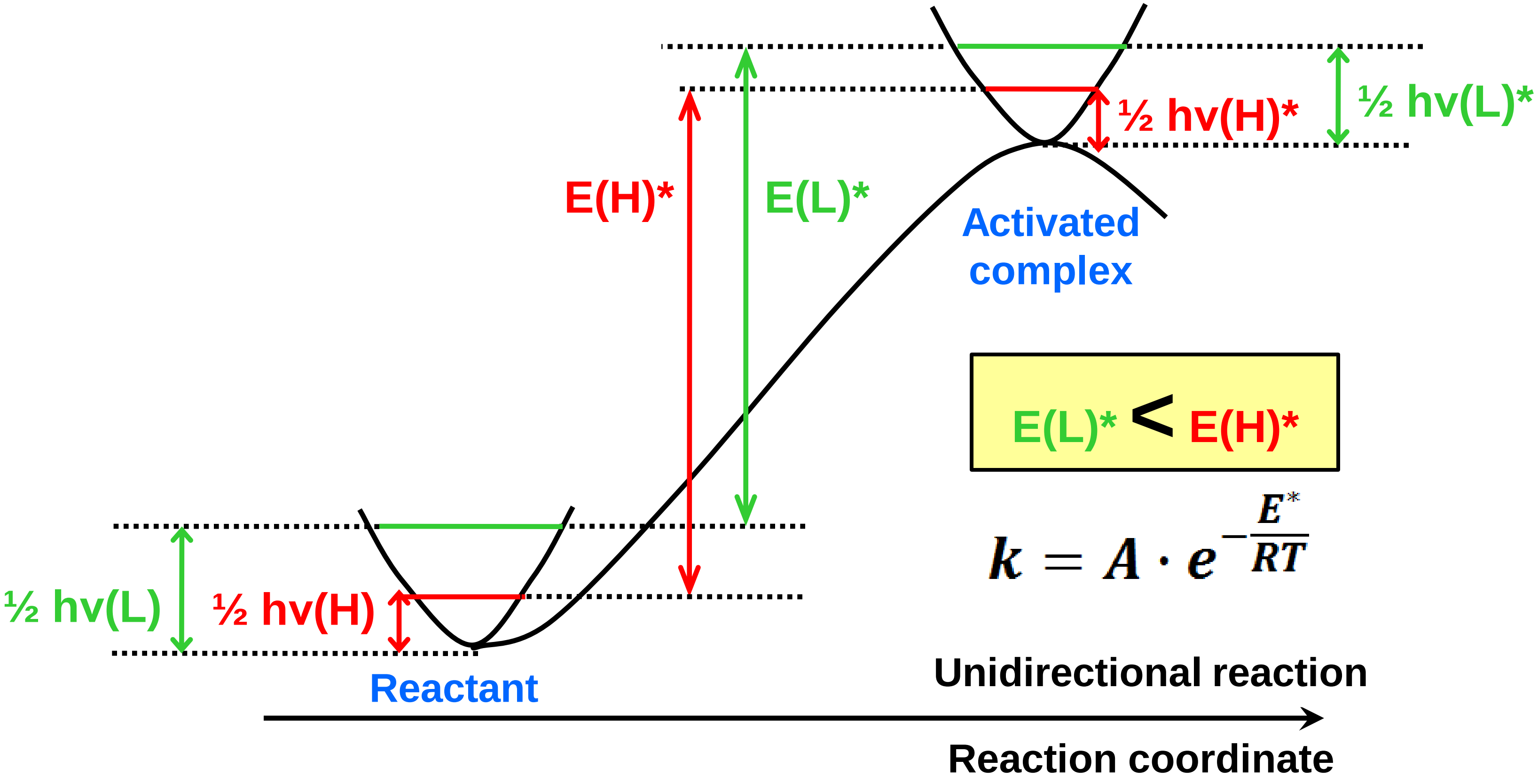
POTENTIAL ENERGY DIAGRAM – CHEMICAL REACTION



$$k = A \cdot e^{-\frac{E^*}{RT}}$$

ΔG < 0: spontaneous reaction

KINETIC ISOTOPE FRACTIONATION EFFECT
CHEMICAL REACTION – ROLE OF ACTIVATION ENERGY



½ hν(L)*

½ hν(H)*

E(H)*

E(L)*

Activated complex

½ hν(L)

½ hν(H)

Reactant

E(L)* < E(H)*

$$k = A \cdot e^{-\frac{E^{*}}{RT}}$$

Unidirectional reaction

Reaction coordinate

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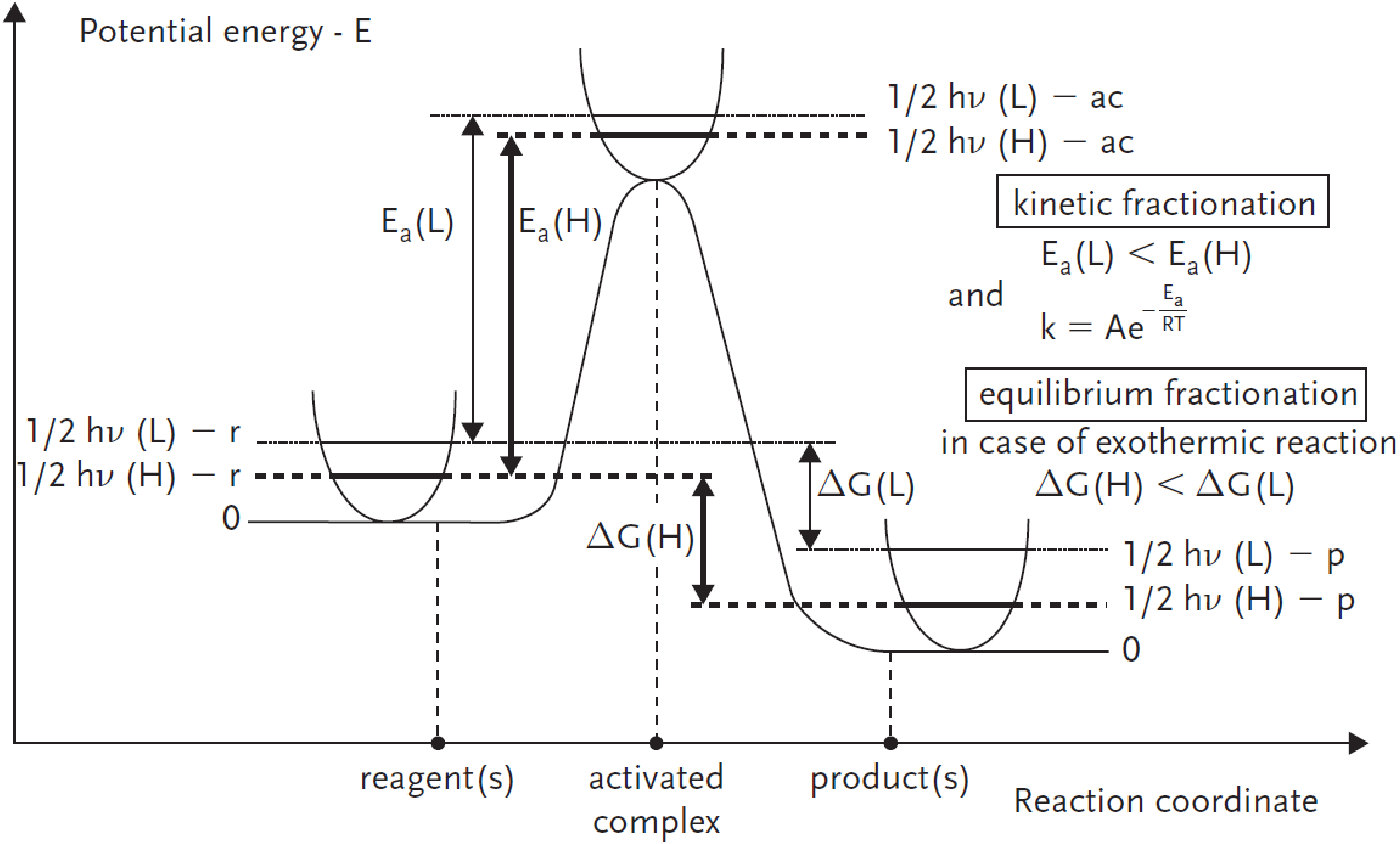
F. Vanhaecke *et al*, JAAS, 24, 863-886, 2009.

ISOTOPE FRACTIONATION EFFECT
CHEMICAL REACTION



kinetic fractionation

$E_a(L) < E_a(H)$

and

$k = Ae^{-\frac{E_a}{RT}}$

equilibrium fractionation

in case of exothermic reaction

$\Delta G(H) < \Delta G(L)$

Note: assuming $\Delta G = \Delta H + T\Delta S \approx \Delta H$

VARIATIONS IN ISOTOPIC COMPOSITION
NATURAL ISOTOPE FRACTIONATION EFFECTS

- Extent of isotope fractionation?
  - ~ Relative difference between the masses of the isotopes
    - More pronounced for light isotopes
    - But, discovered for more and more elements owing to higher precision in MS
  - ~ Extent to which element takes part in processes
    - Physical processes
      - Evaporation, condensation
      - Diffusion
      - …
    - (Bio)chemical reactions
- Also mass-independent isotope fractionation (rare)
  - Difference in size between nuclei of isotopes
    - Not always linear relation with mass
  - Hyperfine coupling between nuclear spin & electron cloud

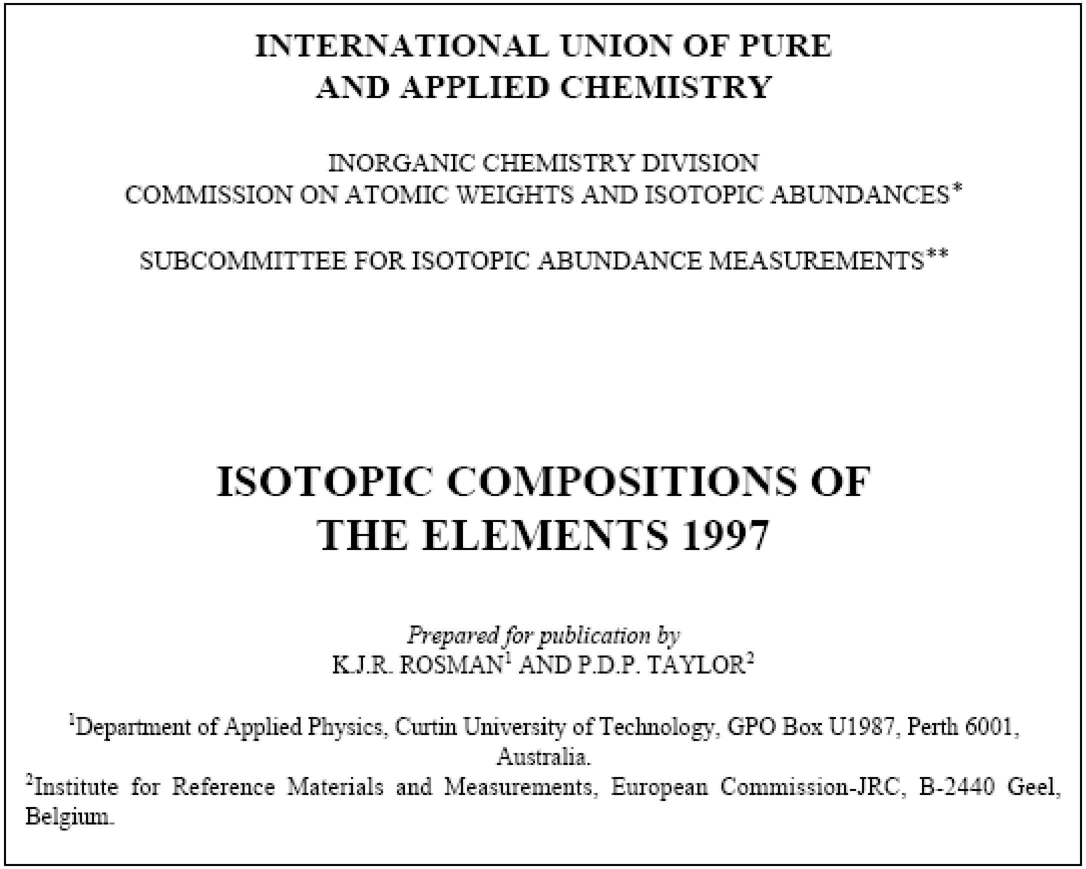
VARIATIONS IN ISOTOPIC COMPOSITION
NATURAL FRACTIONATION EFFECTS

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

$$\delta^{18}O\left(\,^{0}\!/_{00}\right) = \frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}} - \left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}} \cdot 1{,}000$$

$$\varepsilon^{18}O = \frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}} - \left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}} \cdot 10{,}000$$

VARIATIONS IN ISOTOPIC COMPOSITION
NATURAL FRACTIONATION EFFECTS



INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION
COMMISSION ON ATOMIC WEIGHTS AND ISOTOPIC ABUNDANCES*

SUBCOMMITTEE FOR ISOTOPIC ABUNDANCE MEASUREMENTS**

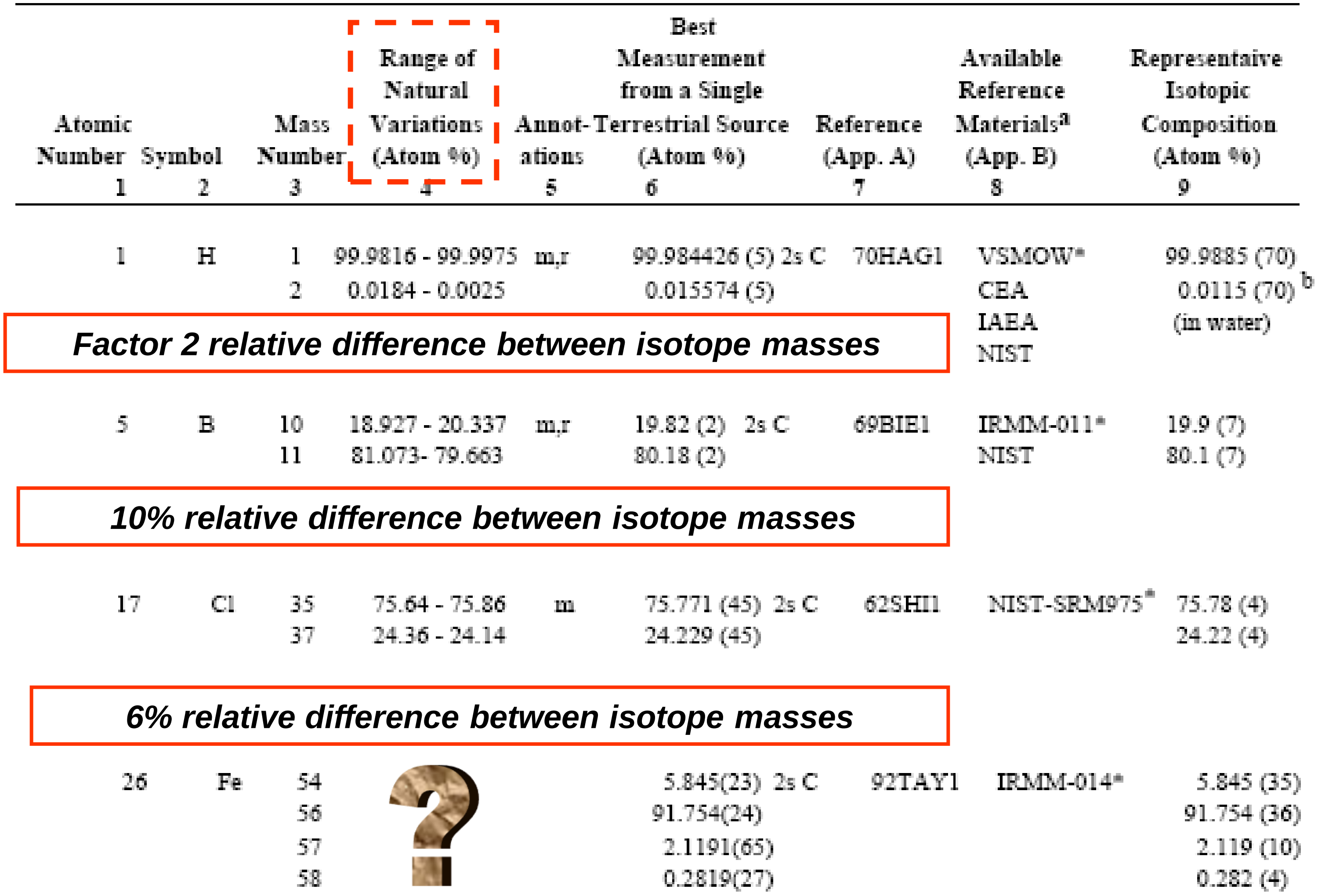
ISOTOPIC COMPOSITIONS OF THE ELEMENTS 1997

Prepared for publication by
K.J.R. ROSMAN[1] AND P.D.P. TAYLOR[2]

[1]Department of Applied Physics, Curtin University of Technology, GPO Box U1987, Perth 6001, Australia.

[2]Institute for Reference Materials and Measurements, European Commission-JRC, B-2440 Geel, Belgium.

VARIATIONS IN ISOTOPIC COMPOSITION
NATURAL FRACTIONATION EFFECTS



Atomic Number 1	Symbol 2	Mass Number 3	Range of Natural Variations (Atom %) 4	Annotations 5	Best Measurement from a Single Terrestrial Source (Atom %) 6	Reference (App. A) 7	Available Reference Materials[a] (App. B) 8	Representaive Isotopic Composition (Atom %) 9
1	H	1	99.9816 - 99.9975	m,r	99.984426 (5) 2s C	70HAG1	VSMOW*	99.9885 (70)
		2	0.0184 - 0.0025		0.015574 (5)		CEA	0.0115 (70)[b]
							IAEA	(in water)
							NIST	
5	B	10	18.927 - 20.337	m,r	19.82 (2) 2s C	69BIE1	IRMM-011*	19.9 (7)
		11	81.073- 79.663		80.18 (2)		NIST	80.1 (7)
17	Cl	35	75.64 - 75.86	m	75.771 (45) 2s C	62SHI1	NIST-SRM975*	75.78 (4)
		37	24.36 - 24.14		24.229 (45)			24.22 (4)
26	Fe	54			5.845(23) 2s C	92TAY1	IRMM-014*	5.845 (35)
		56			91.754(24)			91.754 (36)
		57			2.1191(65)			2.119 (10)
		58			0.2819(27)			0.282 (4)

Factor 2 relative difference between isotope masses

10% relative difference between isotope masses

6% relative difference between isotope masses

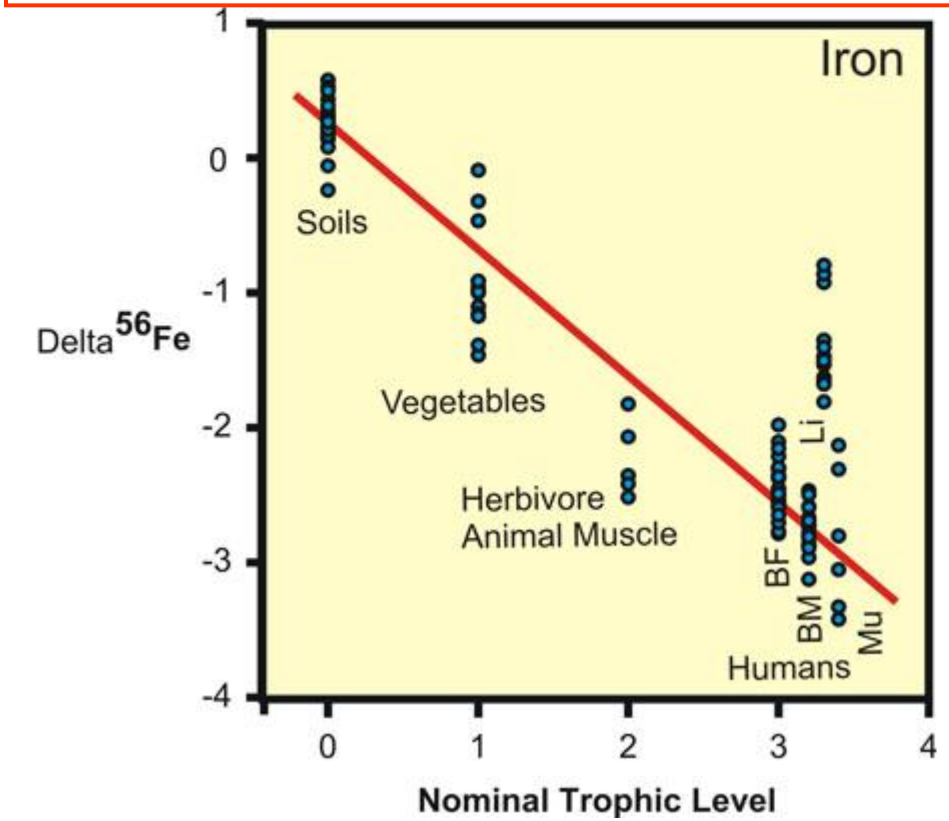
Difference too small for measurable isotope fractionation ?

VARIATIONS IN ISOTOPIC COMPOSITION
NATURAL FRACTIONATION EFFECTS

26	Fe	54	5.845(23) 2s C	92TAY1	IRMM-014*	5.845 (35)
		56	91.754(24)			91.754 (36)
		57	2.1191(65)			2.119 (10)
		58	0.2819(27)			0.282 (4)

?

Difference too small for measurable isotope fractionation ?



No !

von Blanckenburg *et al.*

Fractionation reported for increasing number of (heavier) elements: improved MS precision

VARIATIONS IN ISOTOPIC COMPOSITION
MAN-MADE VARIATIONS

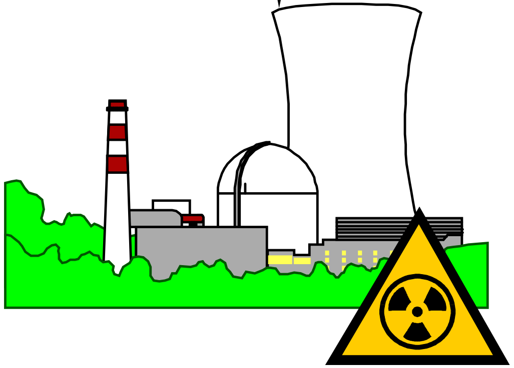
mined uranium

0.715% ^{235}U and 99.28% ^{238}U

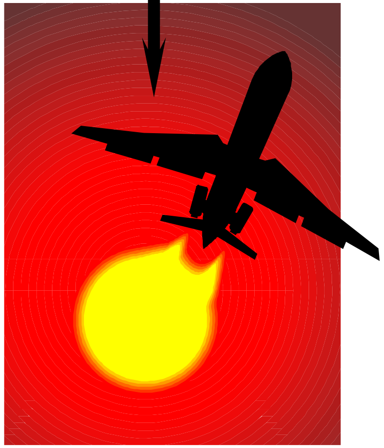
isotopic enrichment

waste =
depleted U (DU)
depleted in ^{235}U
very high density !

ammunition & projectiles penetrating armored steel



fission reactor
fuel enriched in ^{235}U



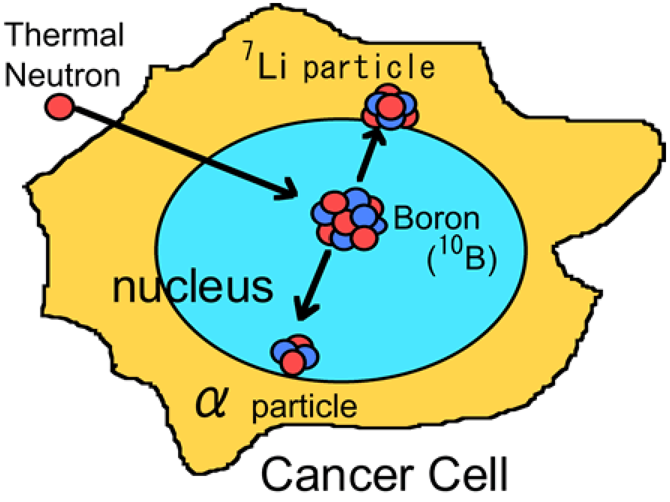
counterweights in airplanes

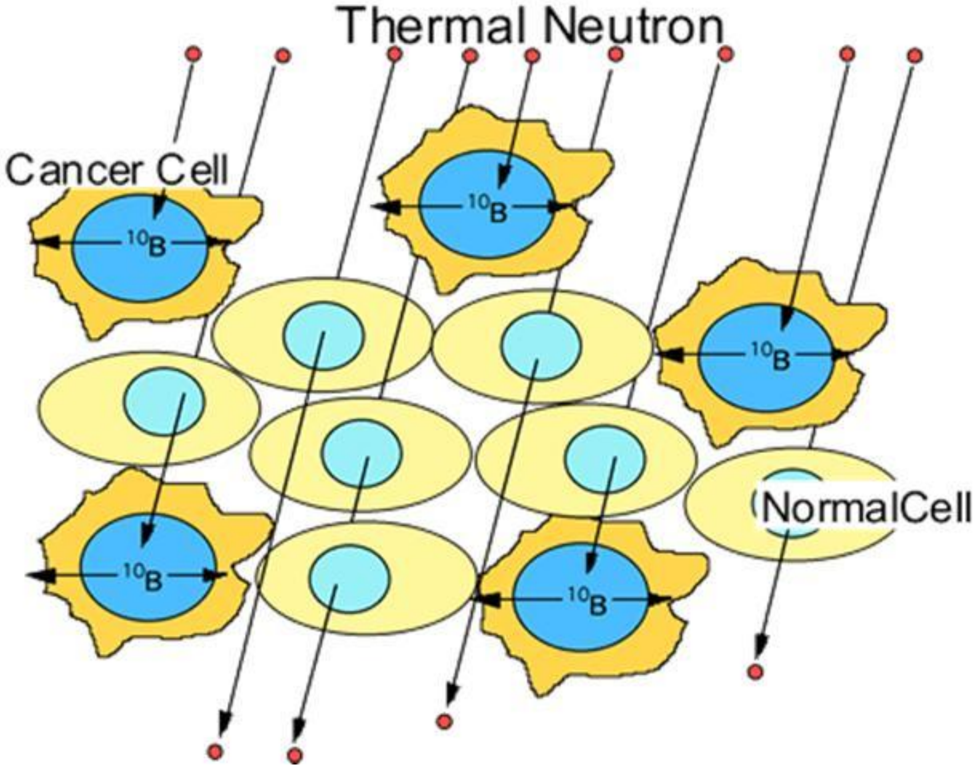
VARIATIONS IN ISOTOPIC COMPOSITION
MAN-MADE VARIATIONS

- ***Enrichment of B in ^{10}B:***
  - ***^{10}B thermal neutron cross-section 6 x higher than that of ^{11}B***
    - ***Control of chain reaction in nuclear fission reactor***
    - ***Boron neutron capture theory (BNCT)***

- ***BNCT: experimental anti-cancer therapy***
  - ***Administration of ^{10}B-containing drug***
    - ***Selective accumulation in tumoral (neoplastic) tissue***
  - ***Irradiation with thermal neutrons***
    - ***^{10}B undergoes (n,α) reaction and is converted into ^{7}Li***
  - ***α-particle only travels distance ≈ one cell***
    - ***Damage limited to cell wherein process takes place***

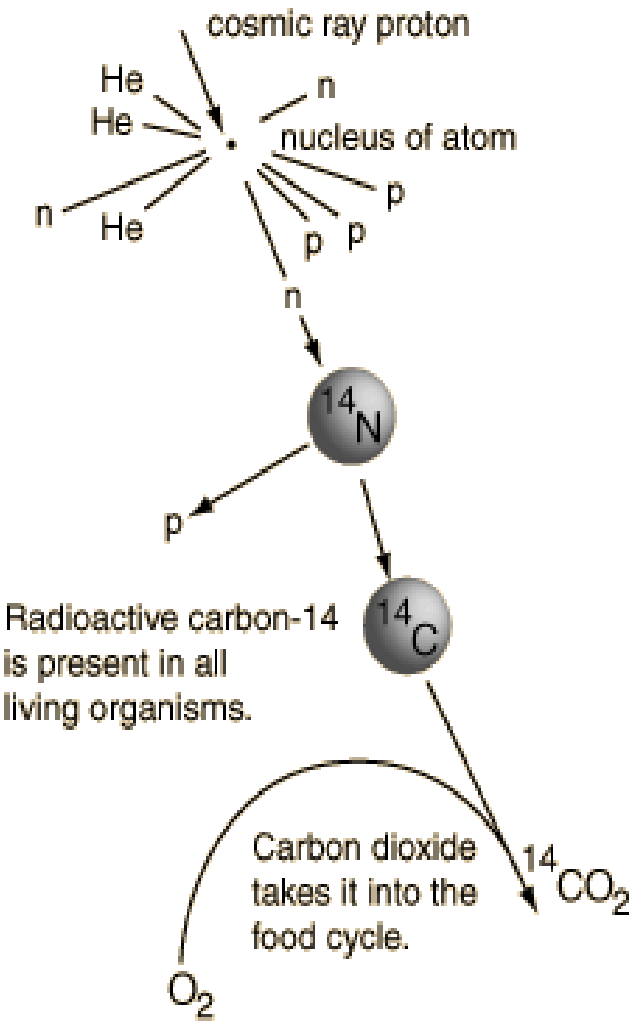
MAN-MADE VARIATIONS IN ISOTOPIC COMPOSITION
BORON NEUTRON CAPTURE THERAPY





- ***Less damage to healthy than to neoplastic tissue***

VARIATIONS IN ISOTOPIC COMPOSITION
INTERACTION OF COSMIC RAYS WITH TERRESTRIAL MATTER



- *Formation of ^{14}C in the atmosphere*
  - *Cosmic rays*
  - *Spallation*
  - *Production of neutron*
  - $^{14}N + n \rightarrow {}^{14}C + p$
- ^{14}C
  - *Radionuclide*
  - $T_{1/2} = 5730\ y$
  - *Production & decay in dynamic equilibrium*
  - *Constant abundance of ^{14}C, next to ^{12}C & ^{13}C*
- *Also other “cosmogenic” nuclides formed*
  - *Stable nuclides & radionuclides*
  - *Extremely low concentrations*
  - *In the atmosphere*
  - *On the earth’s surface (to a lesser extent)*

VARIATIONS IN ISOTOPIC COMPOSITION – VARIATIONS OBSERVED IN EXTRA-TERRESTRIAL MATERIALS

In extraterrestrial materials, some elements show
an isotopic composition not known in terrestrial materials

- ***Extraterrestrial materials ?***

Many iron meteorites display an enrichment in ^{107}Ag unseen in any terrestrial silver. It is now widely accepted that the ^{107}Ag enrichment is a result of the decay of the now extinct radionuclide ^{107}Pd ($T_{1/2}$ = 6.5 x 10^6 y). Since Pd is more siderophile than Ag, “core” formation results in high Pd/Ag elemental ratios, as displayed in iron meteorites (these meteorites are often considered a good “model” for the planetesimals). Terrestrial material that is accessible on the other hand (the silicate fraction) is characterized by much lower Pd/Ag elemental ratios. Therefore, in all terrestrial material, the ^{107}Ag/^{109}Ag isotope ratio is (very close to) 1.081. In some iron meteorites however, the ^{107}Ag/^{109}Ag isotope ratio can substantially deviate from this value (values up to 9 has been reported!).

Iron meteorite (5% of meteorites)

Hoba meteorite, Namibia (50 ton)

HOW TO MEASURE ISOTOPE RATIOS – SINGLE-COLLECTOR ICP-MS INSTRUMENTS

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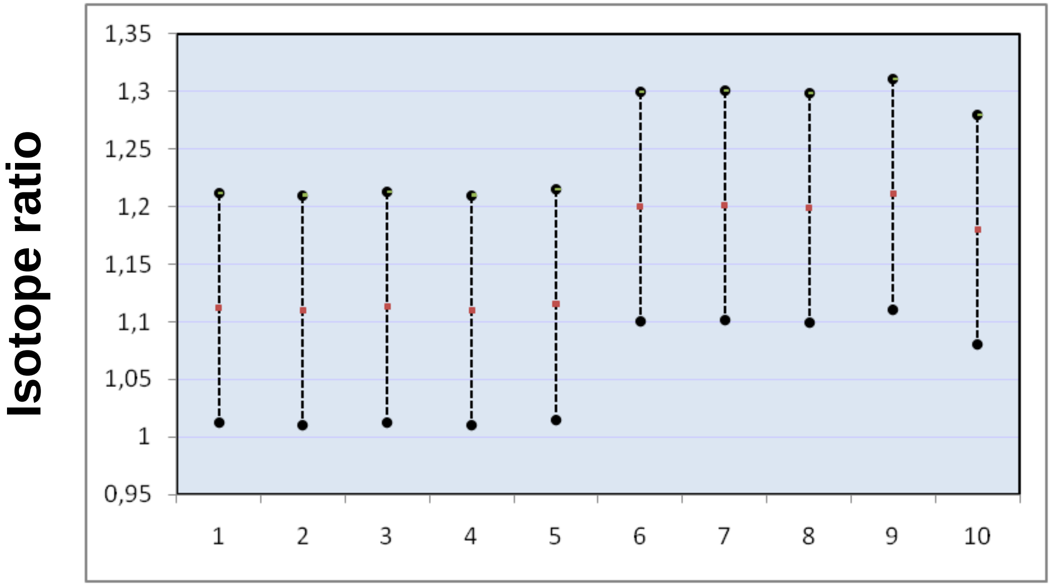
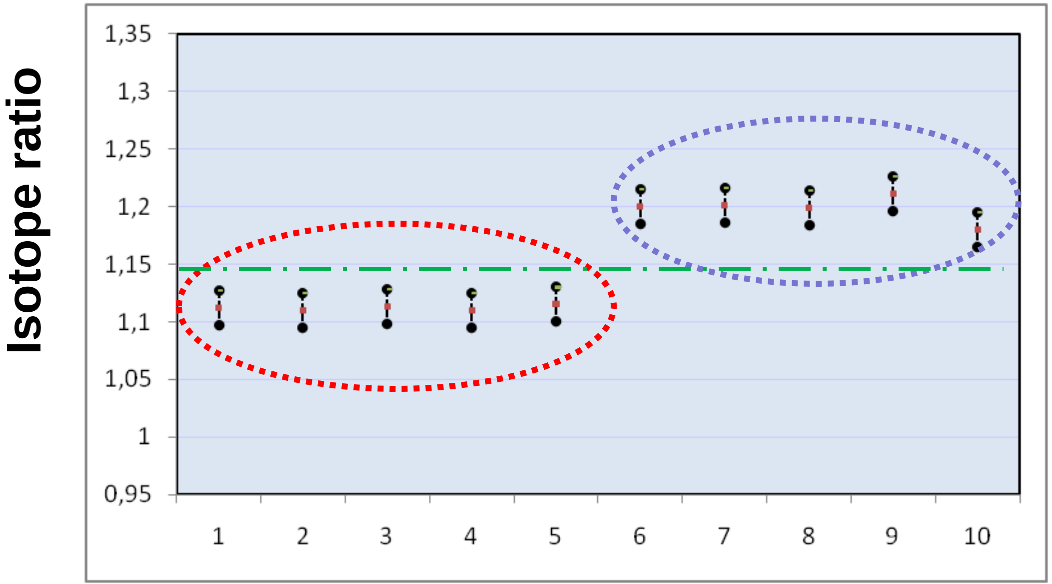
IMPORTANCE OF ISOTOPE RATIO PRECISION



?



2 different populations
⇒
***conclusions*!**
…

WHAT CAN WE EXPECT IN TERMS OF ISOTOPE RATIO PRECISION ?

- *Ultimate limit set by counting statistics*
- *Poisson counting statistics*
  - *Valid if variation in arrival of ions @ detector = statistically governed*
  - *Then* $st.dev(N) = \sqrt{N}$
    - *N = total # counts (not count rate!)*

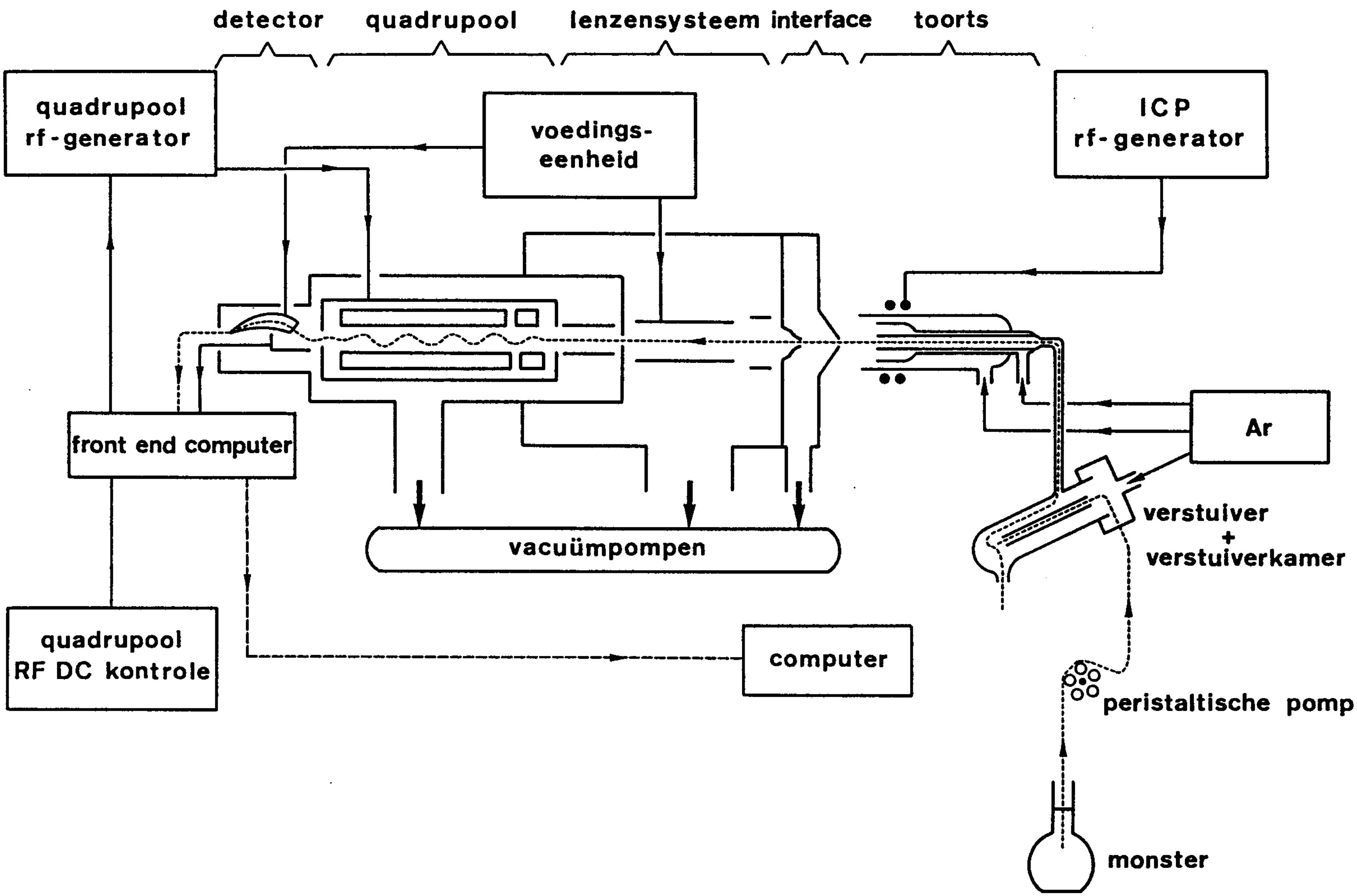
$$RSD\% = \frac{st.dev(N)}{N}\,.100\% = \frac{1}{\sqrt{N}}\,.100\%$$

- *Ultimate limit?*

$$\boxed{RSD\% = \sqrt{\frac{1}{N_1} + \frac{1}{N_2}}\,.100\%}$$

  - *Importance of acquiring a high number of counts*
    - *Sufficiently high signal intensities*
    - *Sufficiently long measurement times*

"TRADITIONAL" QUADRUPOLE-BASED ICP-MS



HOW TO GET THE BEST ISOTOPE RATIO PRECISION? "TRADITIONAL" QUADRUPOLE-BASED ICP-MS

- *Optimum conditions?*
  - *Sufficiently high signal intensities*
    - *Cf. detector dead time*
  - *Sufficiently long measurement time*
  - *Isotope ratio close to 1*

- *Problem?*
  - *ICP = noisy source*

- *Warning*
  - *Do not compare apples & pears*
  - *St. dev (mean) = st. dev. /* $\sqrt{N}$ *= st. error*

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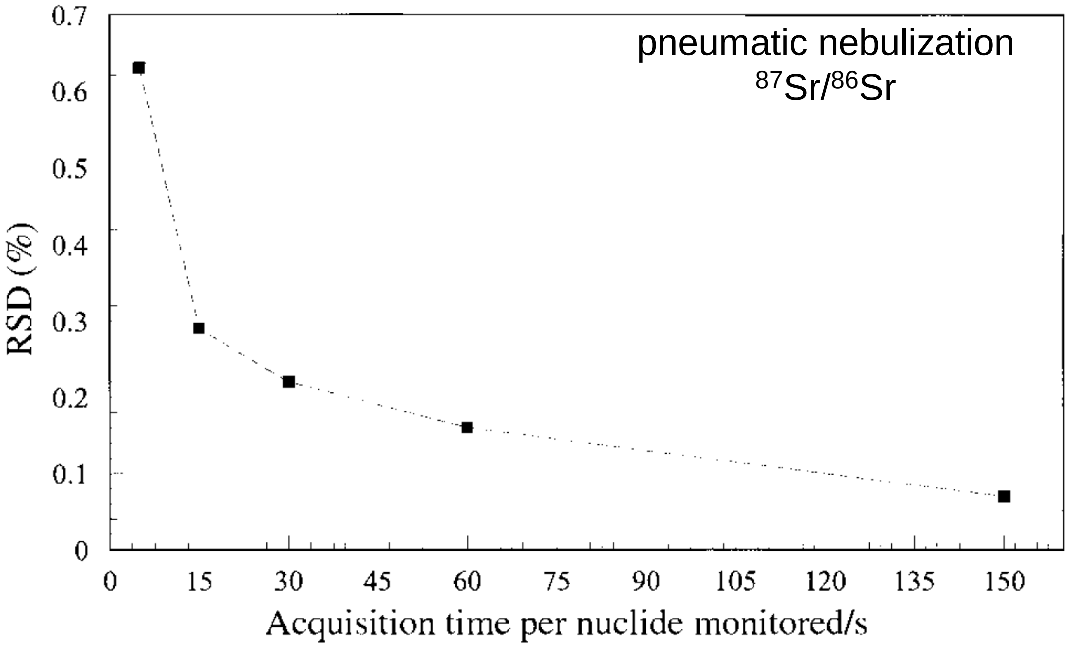
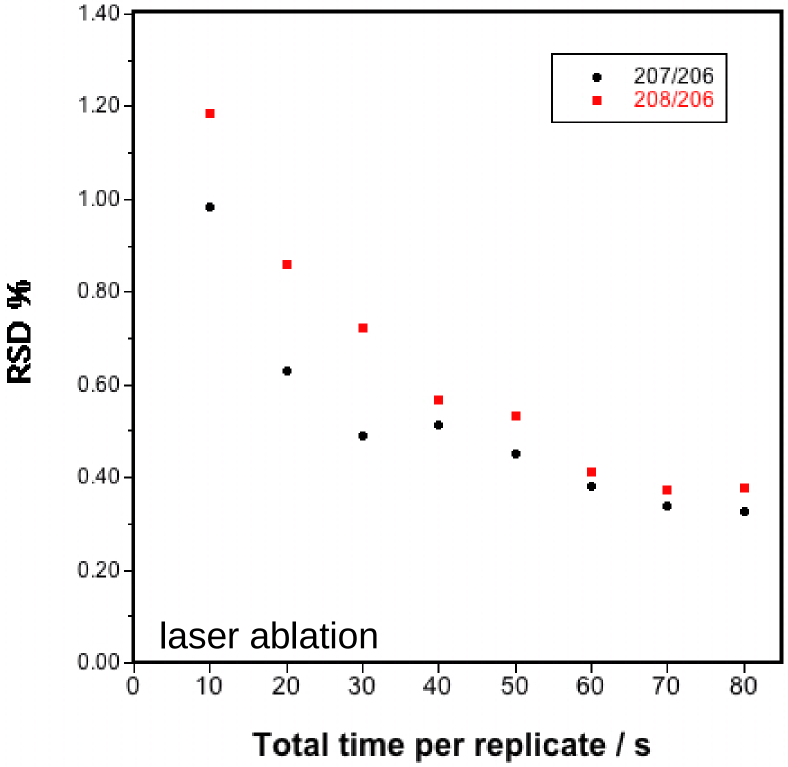
HOW TO GET THE BEST ISOTOPE RATIO PRECISION? "TRADITIONAL" QUADRUPOLE-BASED ICP-MS

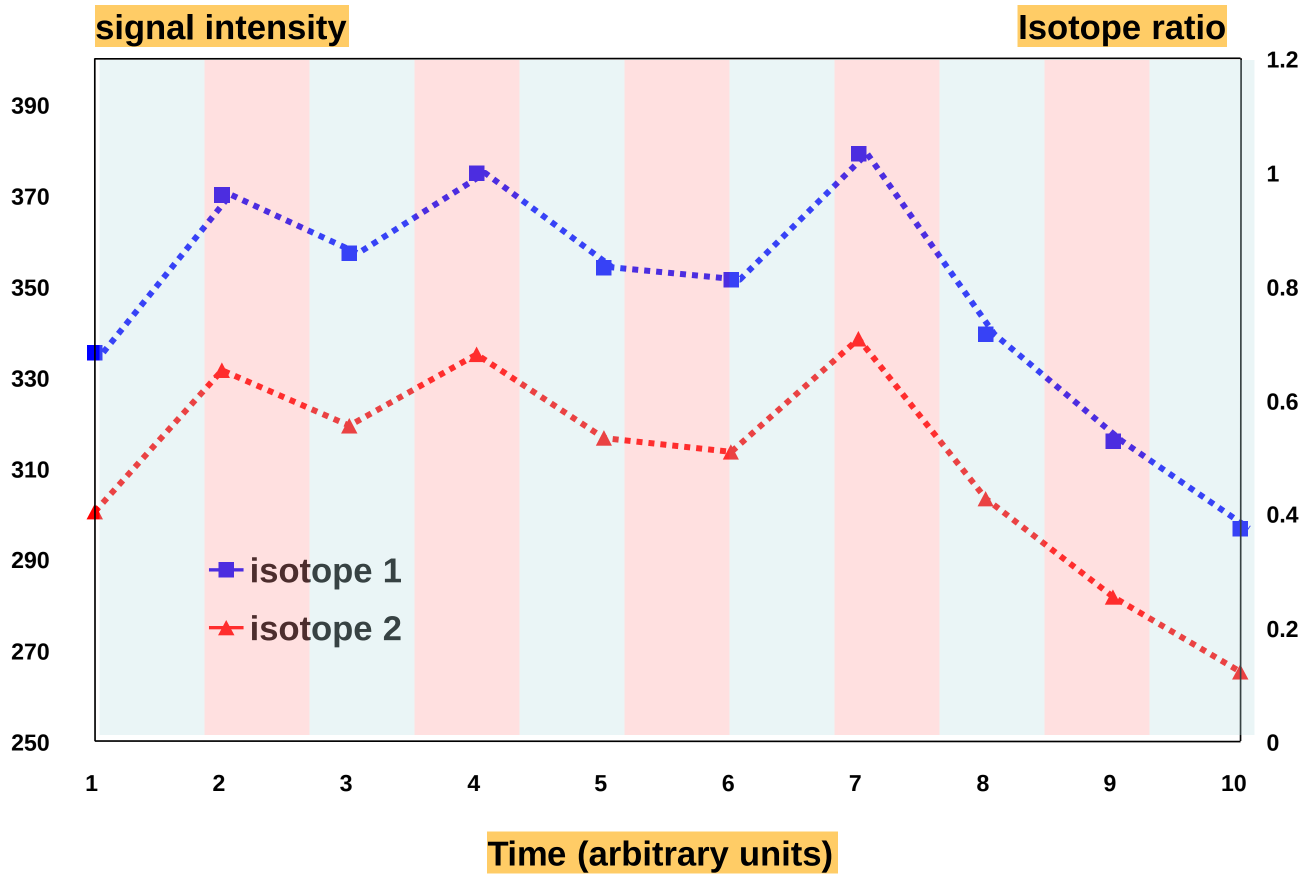




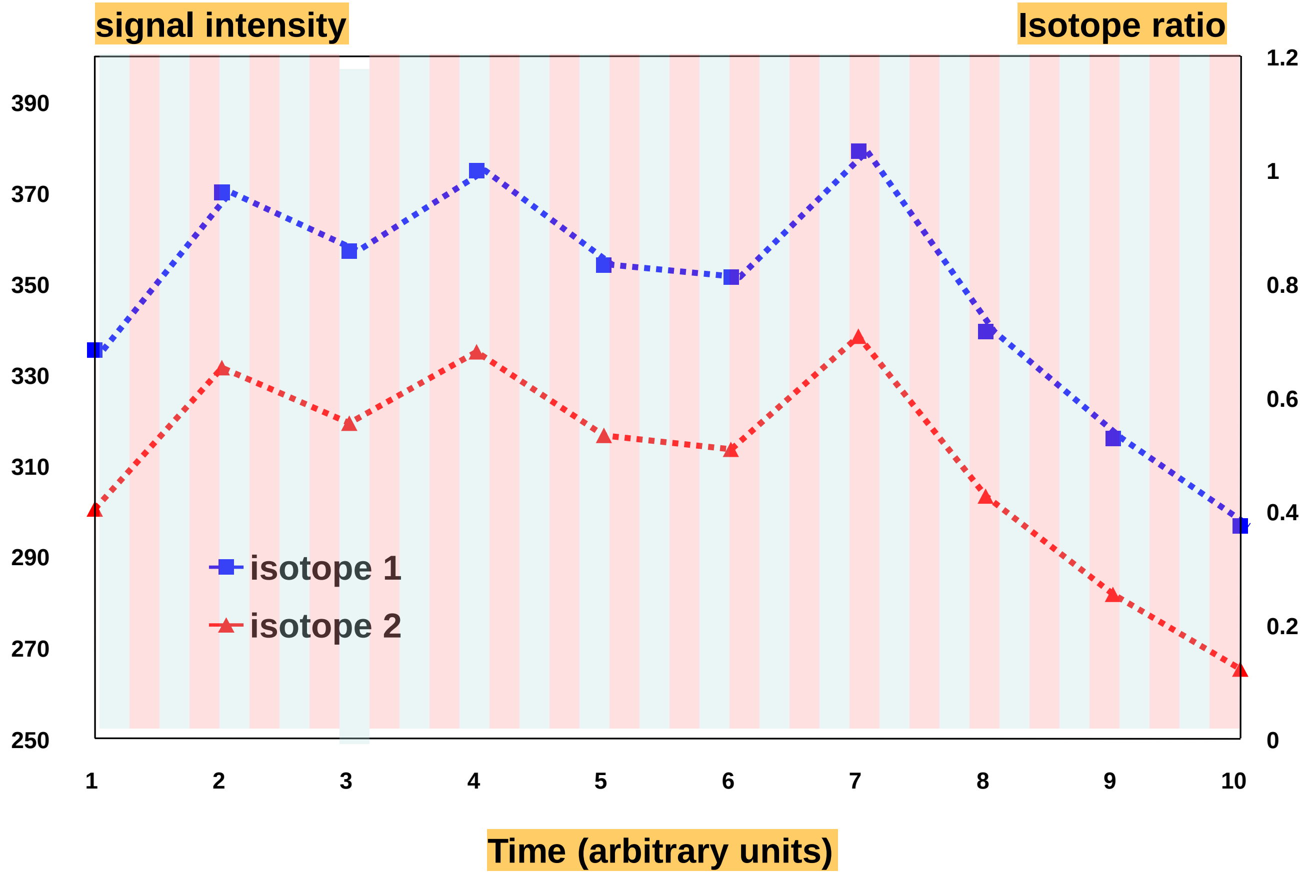
sufficiently high total acquisition time
cf. Poisson counting statistics

F. Vanhaecke *et al*, JAAS, 14, 1691-1696, 1999.
M. Resano *et al*, JAAS, 23, 1182-1191, 2008.

HOW TO GET THE BEST ISOTOPE RATIO PRECISION? "TRADITIONAL" QUADRUPOLE-BASED ICP-MS



HOW TO GET THE BEST ISOTOPE RATIO PRECISION? "TRADITIONAL" QUADRUPOLE-BASED ICP-MS



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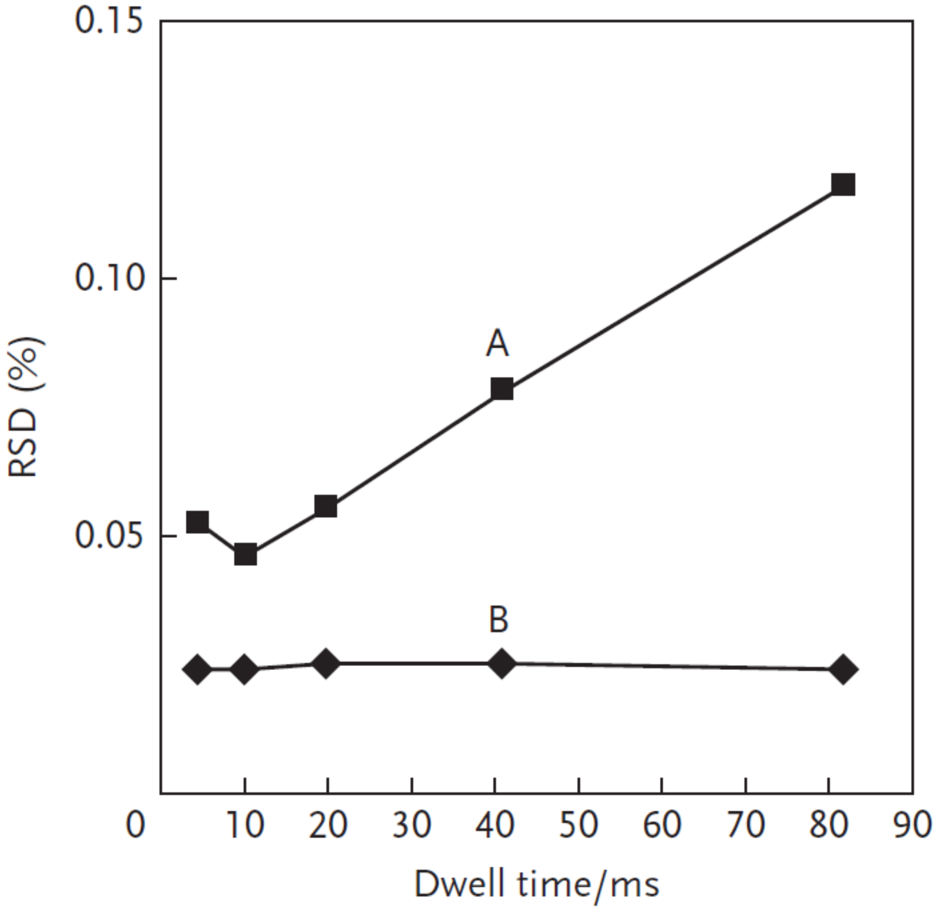
HOW TO GET THE BEST ISOTOPE RATIO PRECISION? "TRADITIONAL" QUADRUPOLE-BASED ICP-MS



- ***Residence time / acquisition point***
  - ***Sufficiently low***
  - ***Too low values?***
    - ***Large fraction of time lost***
    - ***Settling time***

28 Begley, I.S. and Sharp, B.L. (1994) Occurrence and reduction of noise in inductively-coupled plasma mass spectrometry for enhanced precision in isotope ratio measurement. *J. Anal. At. Spectrom.*, **9**, 171–176.

Figure 2.23 ^{107}Ag/^{109}Ag isotope ratio precision (RSD for 10 replicate measurements) as a function of the acquisition time per nuclide: (a) predicted on the basis of Poisson counting statistics; (b) observed experimentally. Reproduced with permission of the Royal Society of Chemistry from [28].

HOW TO GET THE BEST ISOTOPE RATIO PRECISION? "TRADITIONAL" QUADRUPOLE-BASED ICP-MS

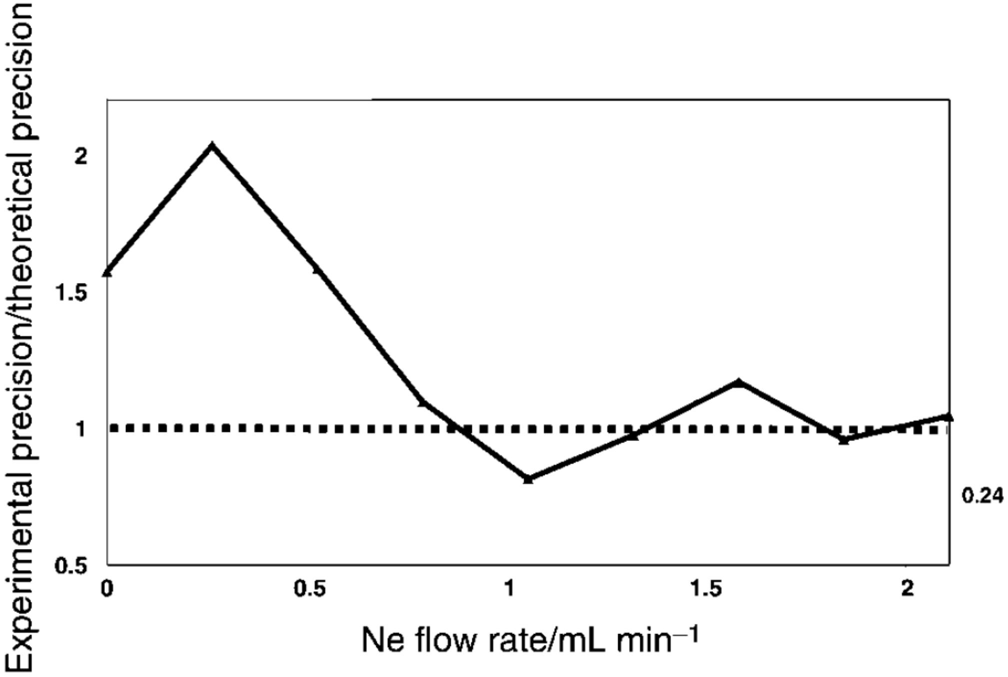
- *An example of data acquisition conditions:*
  - *Scanning mode*
    - *Peak hopping/jumping*
  - *Dwell time / acquisition point (per sweep)*
    - *10 ms*
  - *Number of acquisition points / spectral peak*
    - *1*
  - *Number of sweeps per replicate measurement*
    - *3250*
  - *Total acquisition time per replicate measurement*
    - *~3 min*
  - *Number of replicate measurements*
    - *10*
- *Optimum measurement precision? ~0.1 % RSD*

DIFFERENT ACQUISITION TIMES FOR DIFFERENT ISOTOPES ?

- ***Sometimes used***
  - ***Higher # of counts accumulated for low-abundant isotope***
    - ***Cf. Poisson counting statistics***
  - ***Lower scan speed***
    - ***Cf. noisy source***
  - ***Compromise conditions***

QUADRUPOLE-BASED ICP-MS
IMPROVEMENT WITH A COLLISION/REACTION CELL

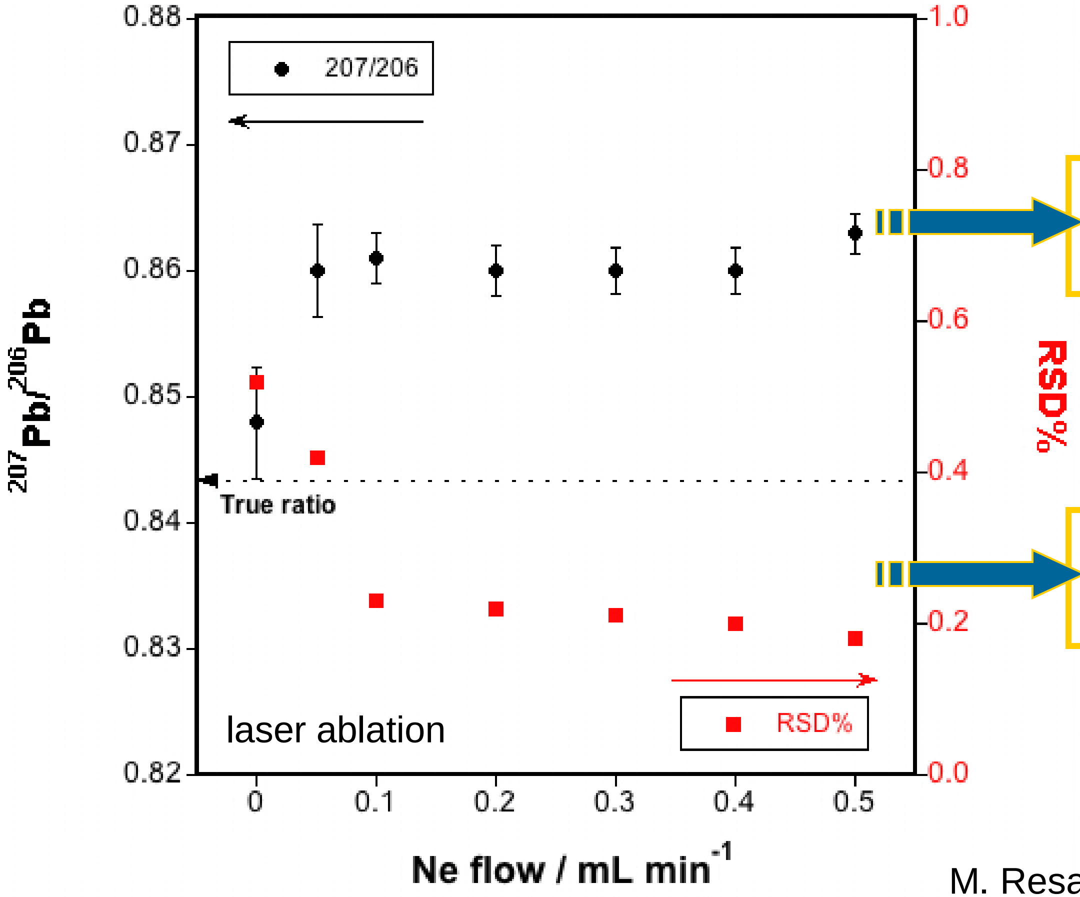
- ***Use of Ne as non-reactive collision gas in DRC***
  - ***Mixing of ions sampled at slightly different moments in time***
  - ***Collisional damping ⇒ improved isotope ratio precision***



L. Moens *et al, JAAS,* 16, 991–994, 2001.

QUADRUPOLE-BASED ICP-MS
IMPROVEMENT WITH A COLLISION/REACTION CELL

- ***Use of Ne as non-reactive collision gas in DRC***
  - ▶ ***Mixing of ions sampled at slightly different moments in time***
  - ▶ ***Collisional damping ⇒ improved isotope ratio precision***



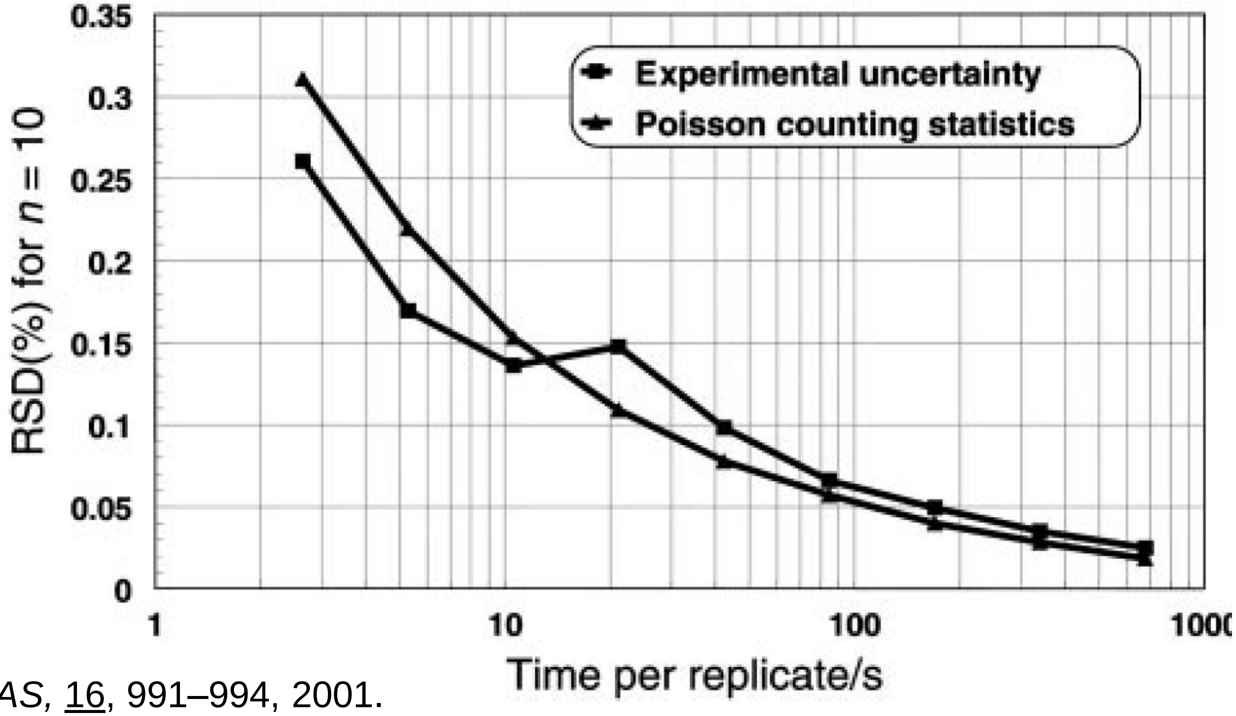
Increased mass discrimination

Improved isotope ratio precision

M. Resano *et al*, JAAS, 23, 1182-1191, 2008.

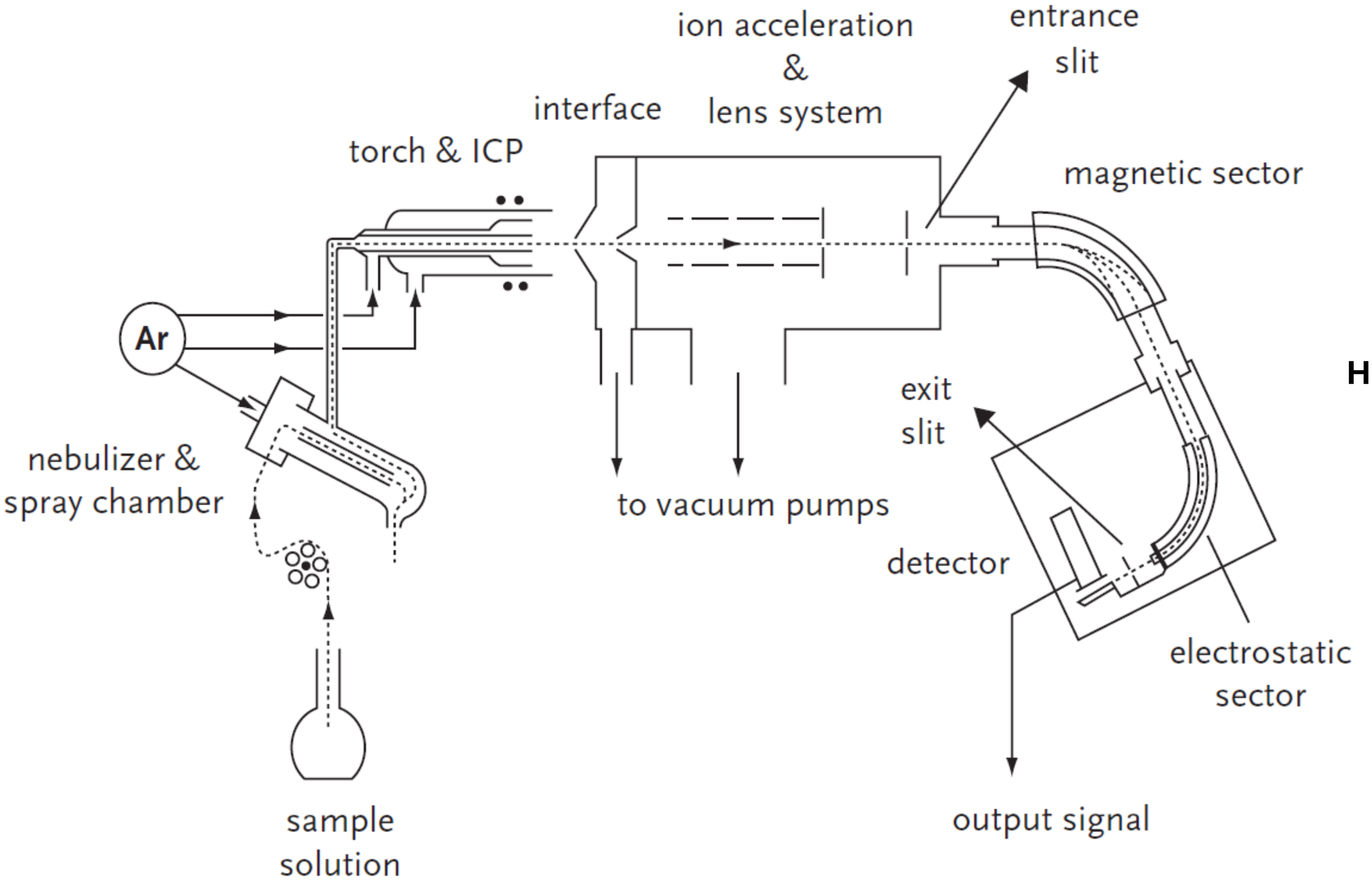
QUADRUPOLE-BASED ICP-MS EQUIPPED WITH A COLLISION/REACTION CELL

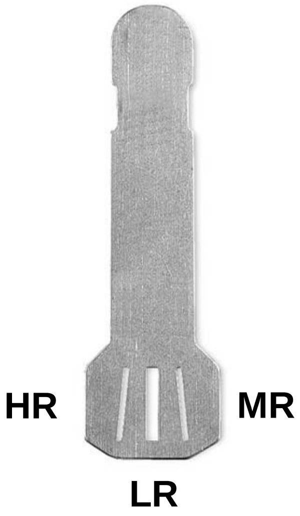
- ***Other guidelines are still valid***
  - ***Low dwell time / acquisition point***
  - ***1 acquisition point / spectral peak***
  - ***Acquiring a sufficiently high # of pulses***
    - ***Sufficiently high target element concentration***
    - ***Sufficiently long measurement time per replicate***



L. Moens *et al*, *JAAS*, 16, 991–994, 2001.

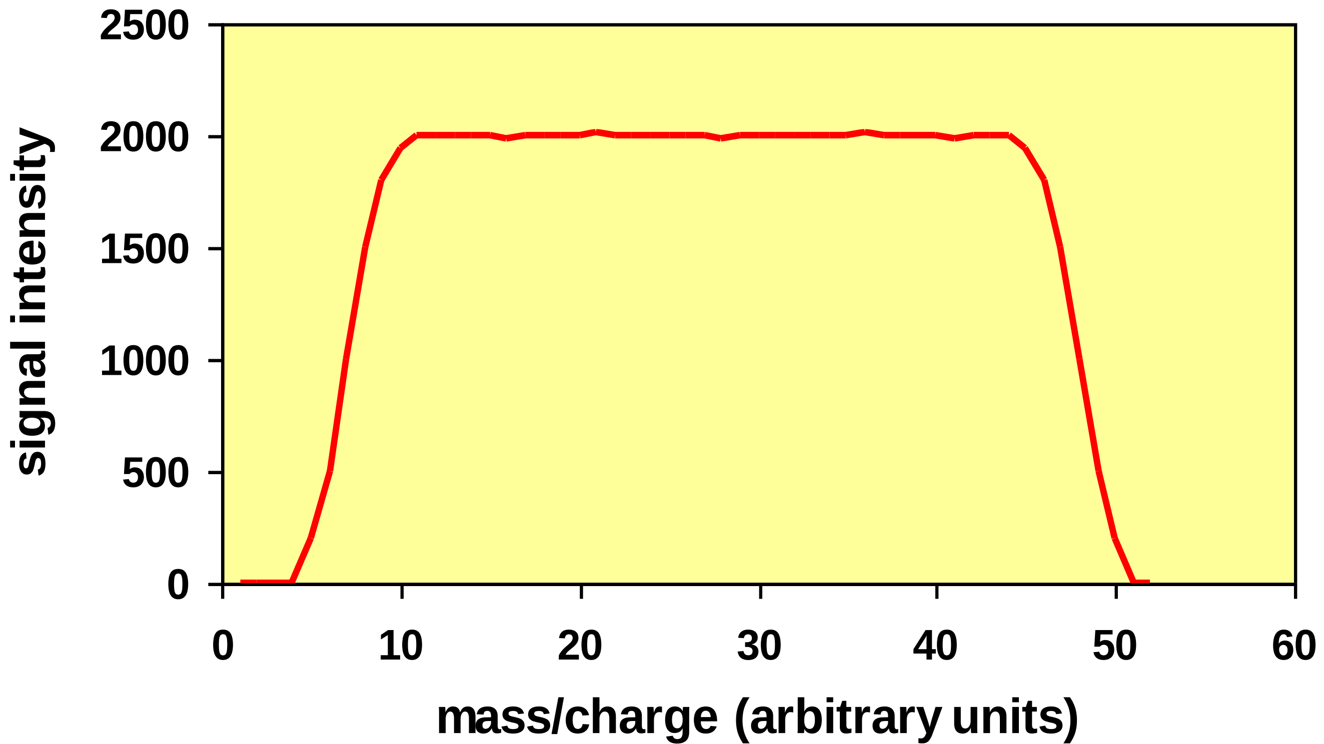
SECTOR FIELD ICP – MASS SPECTROMETRY





Selection of resolution setting R = 300, 4000 or 10000

SECTOR FIELD ICP – MASS SPECTROMETRY
IMPROVED ISOTOPE RATIO PRECISION AT LOW R



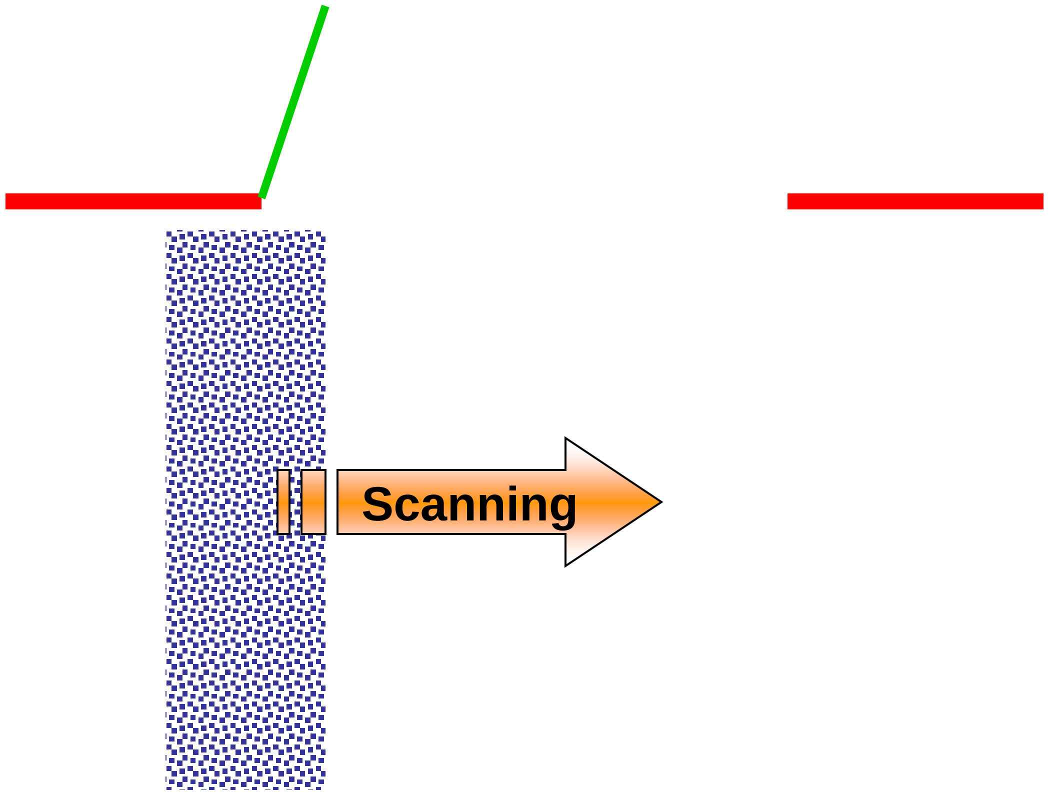
- ***Optimum measurement precision? ~0.025 – 0.05% RSD***

HOW ARE FLAT-TOPPED PEAKS OBTAINED ?

Width of ion beam

<

Exit slit width



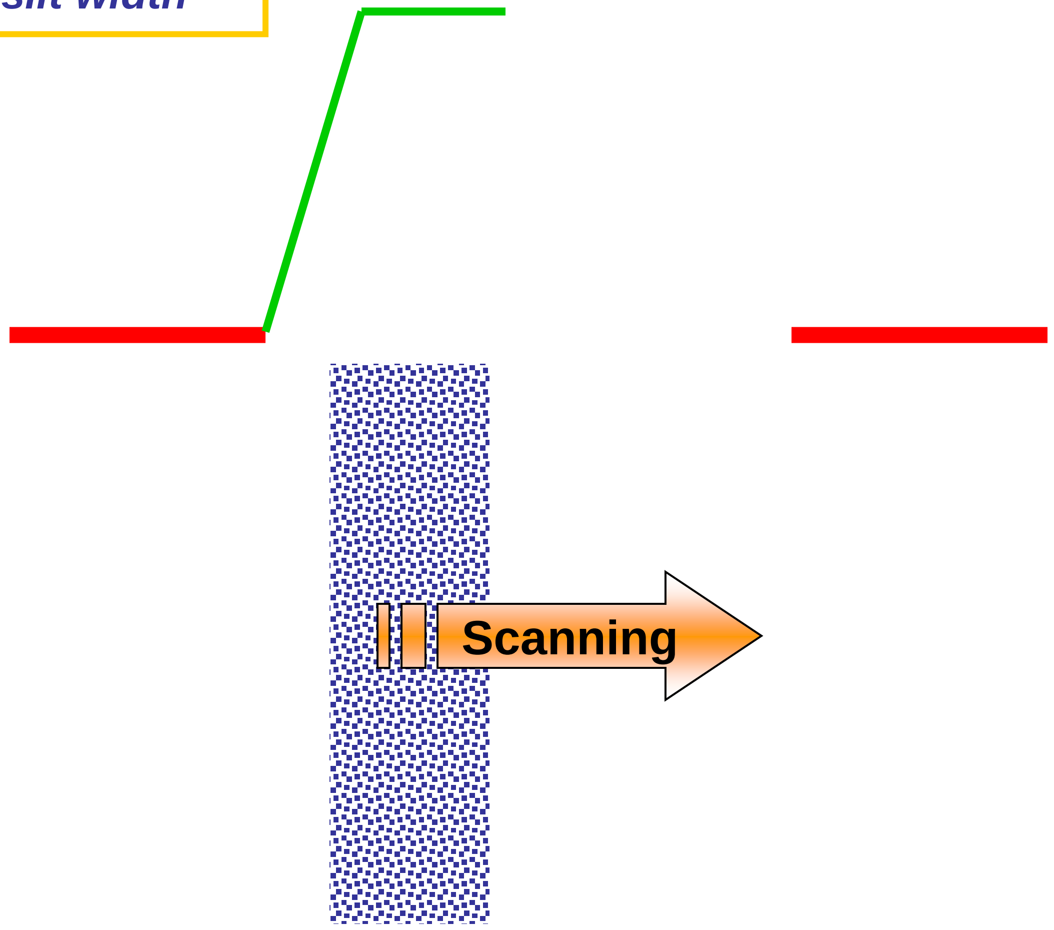
Wide exit slit

HOW ARE FLAT-TOPPED PEAKS OBTAINED ?

Width of ion beam

<

Exit slit width



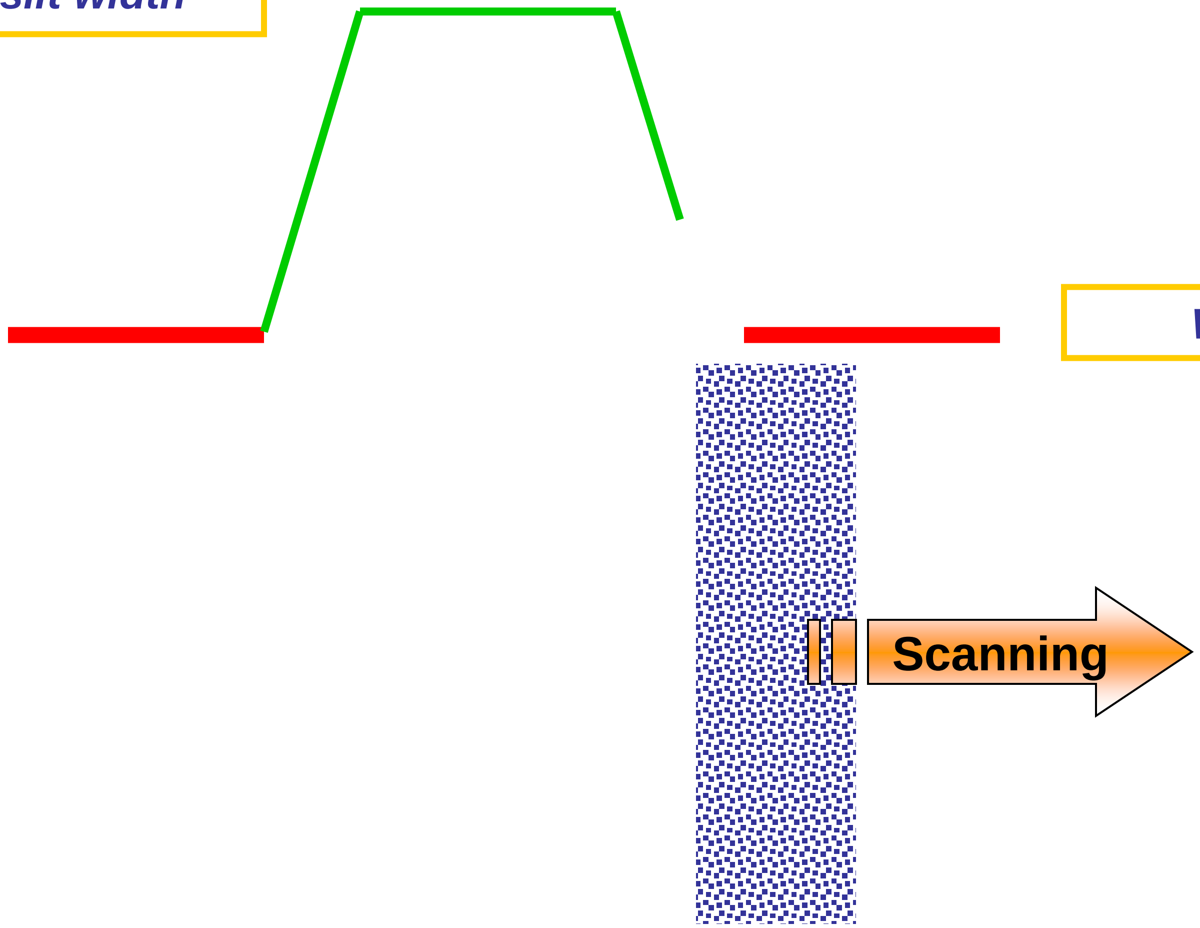
Wide exit slit

HOW ARE FLAT-TOPPED PEAKS OBTAINED ?

Width of ion beam

<

Exit slit width



Wide exit slit

SECTOR FIELD ICP – MASS SPECTROMETRY
IMPROVED ISOTOPE RATIO PRECISION AT LOW R

- ***Vanhaecke et al., Anal. Chem., 567-569, 68, 1996***

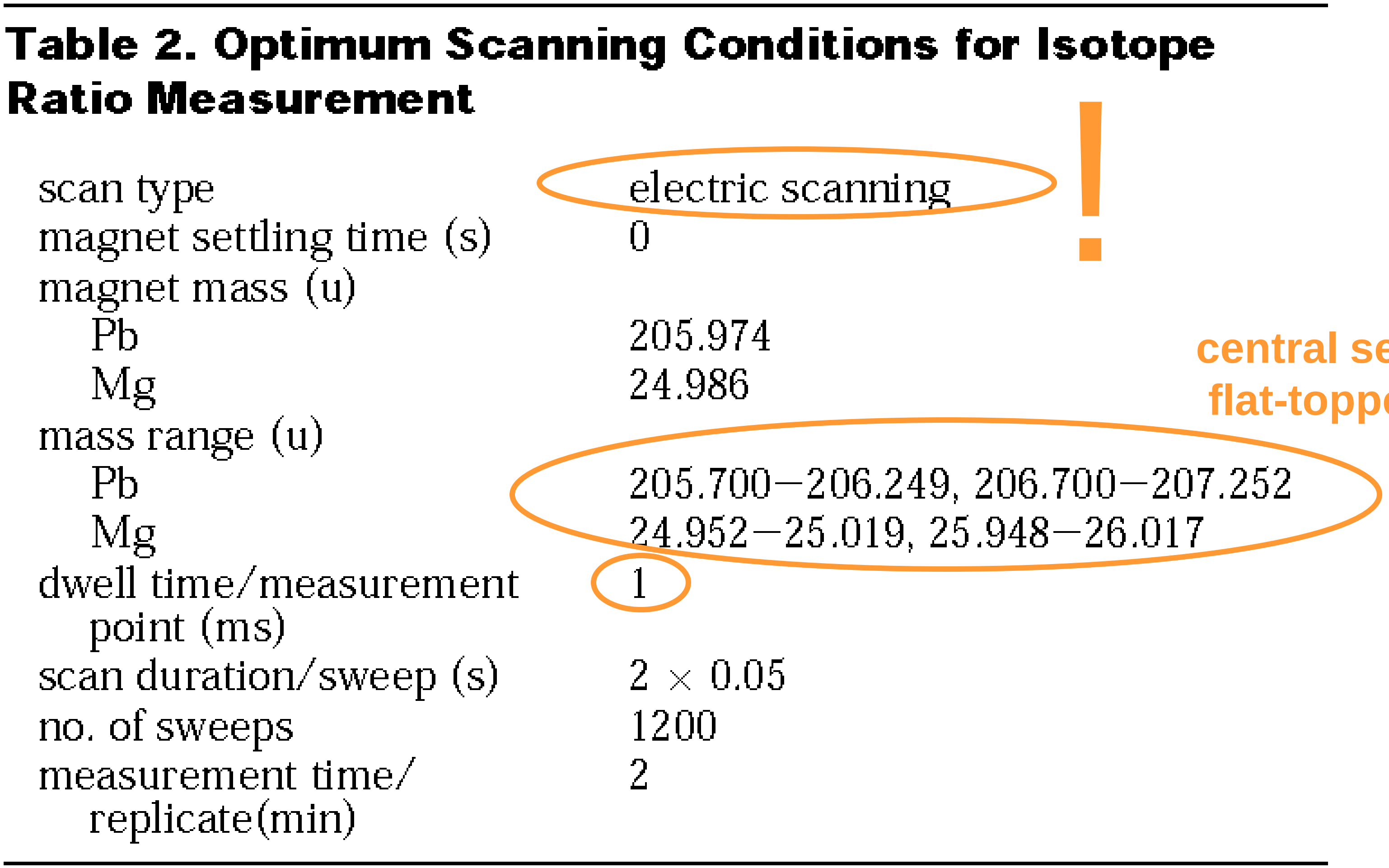


Table 2. Optimum Scanning Conditions for Isotope Ratio Measurement

scan type	electric scanning
magnet settling time (s)	0
magnet mass (u)	
Pb	205.974
Mg	24.986
mass range (u)	
Pb	205.700–206.249, 206.700–207.252
Mg	24.952–25.019, 25.948–26.017
dwell time/measurement point (ms)	1
scan duration/sweep (s)	2 × 0.05
no. of sweeps	1200
measurement time/replicate(min)	2

!

central section of flat-topped peak

SECTOR FIELD ICP – MASS SPECTROMETRY
IMPROVED ISOTOPE RATIO PRECISION AT LOW R

- *Vanhaecke et al., Anal. Chem., 567-569, 68, 1996*

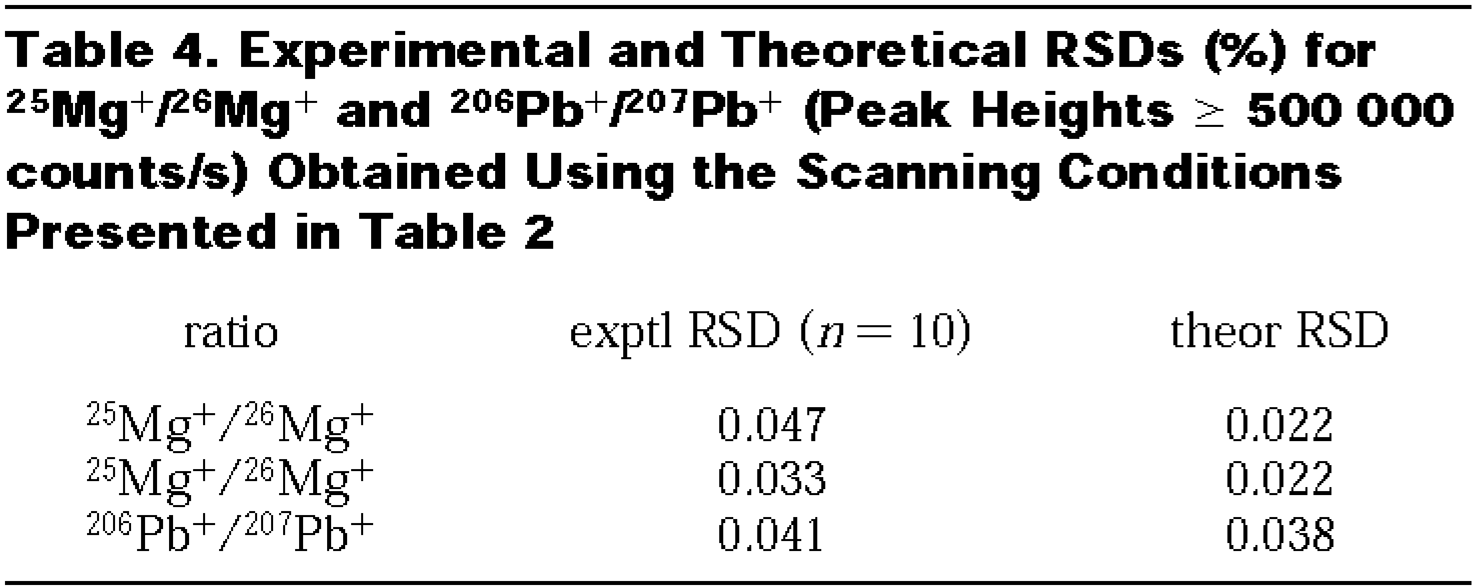
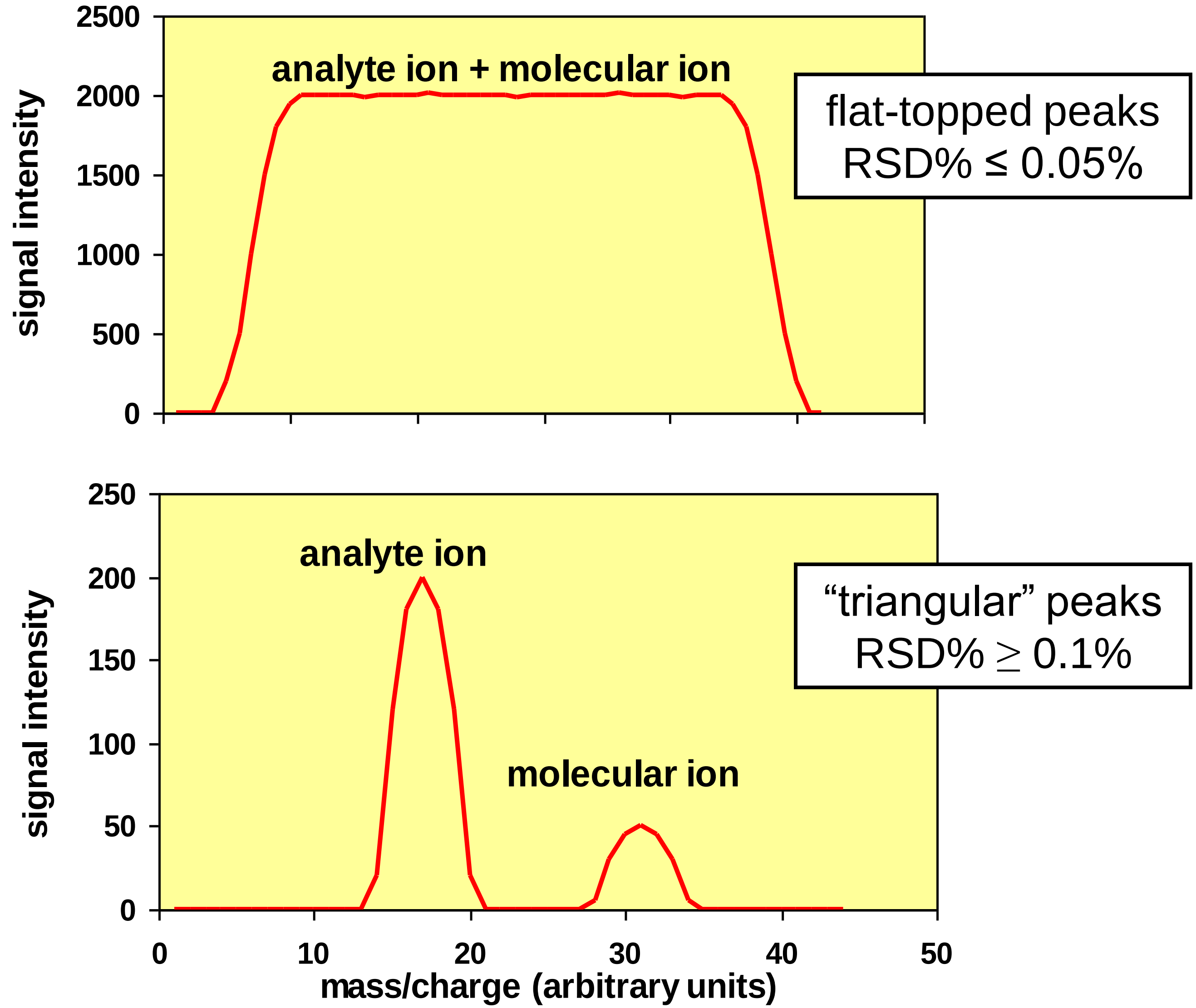


Table 4. Experimental and Theoretical RSDs (%) for $^{25}Mg^+/^{26}Mg^+$ and $^{206}Pb^+/^{207}Pb^+$ (Peak Heights ≥ 500 000 counts/s) Obtained Using the Scanning Conditions Presented in Table 2

ratio	exptl RSD ($n = 10$)	theor RSD
$^{25}Mg^+/^{26}Mg^+$	0.047	0.022
$^{25}Mg^+/^{26}Mg^+$	0.033	0.022
$^{206}Pb^+/^{207}Pb^+$	0.041	0.038

SECTOR FIELD ICP – MASS SPECTROMETRY
ISOTOPE RATIO PRECISION AT MEDIUM R ?



flat-topped peaks
RSD% ≤ 0.05%

“triangular” peaks
RSD% ≥ 0.1%

SECTOR FIELD ICP – MASS SPECTROMETRY
ISOTOPE RATIO PRECISION AT MEDIUM R ?

- *Vanhaecke et al., Anal. Chem., 268-273, 69, 1997*

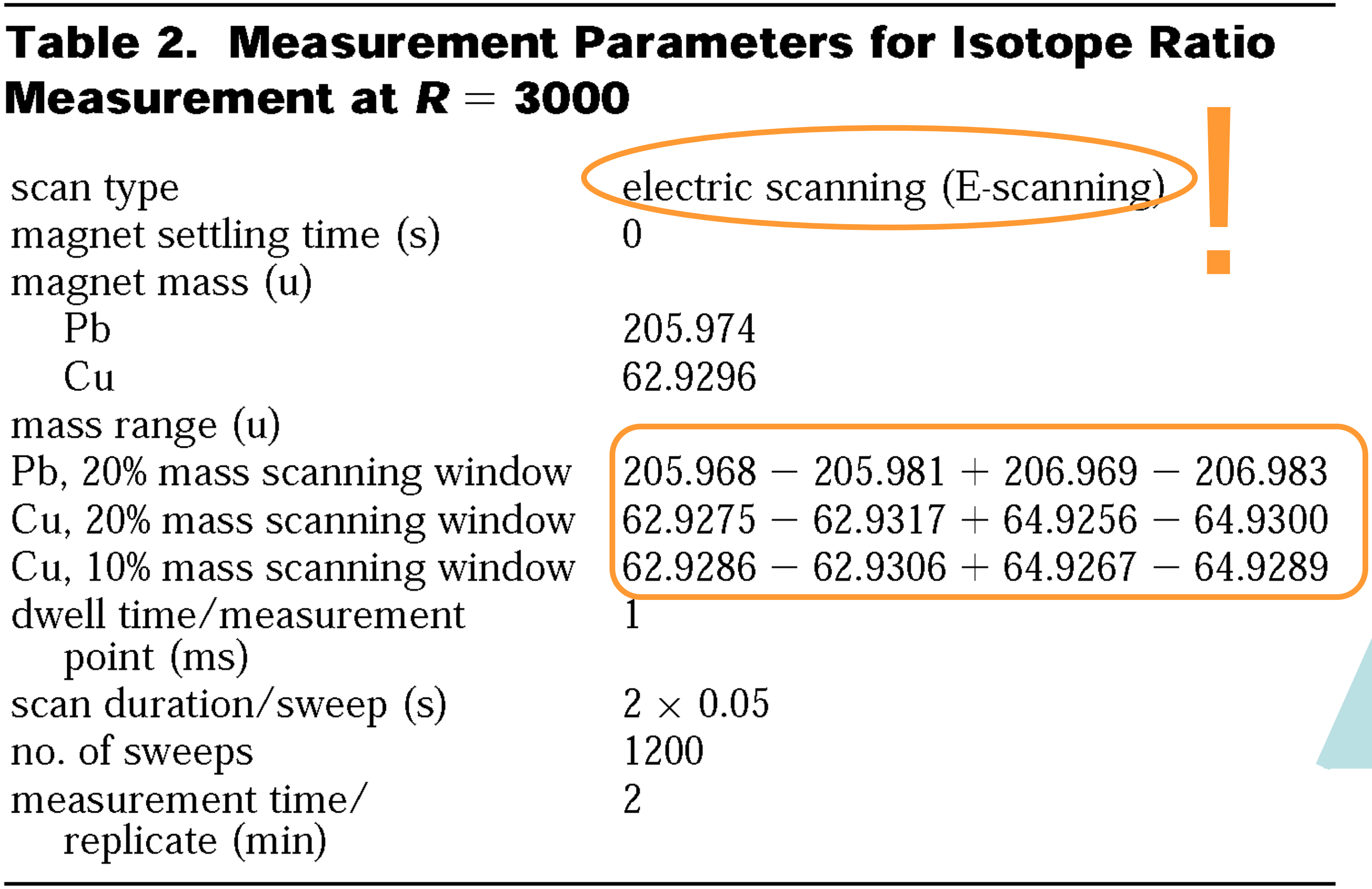
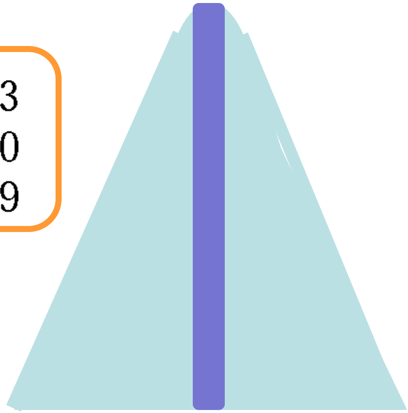


Table 2. Measurement Parameters for Isotope Ratio Measurement at *R* = 3000

scan type	electric scanning (E-scanning)
magnet settling time (s)	0
magnet mass (u)	
Pb	205.974
Cu	62.9296
mass range (u)	
Pb, 20% mass scanning window	205.968 − 205.981 + 206.969 − 206.983
Cu, 20% mass scanning window	62.9275 − 62.9317 + 64.9256 − 64.9300
Cu, 10% mass scanning window	62.9286 − 62.9306 + 64.9267 − 64.9289
dwell time/measurement point (ms)	1
scan duration/sweep (s)	2 × 0.05
no. of sweeps	1200
measurement time/replicate (min)	2

!



SECTOR FIELD ICP – MASS SPECTROMETRY
ISOTOPE RATIO PRECISION AT MEDIUM R ?

- *Vanhaecke et al., Anal. Chem., 268-273, 69, 1997*

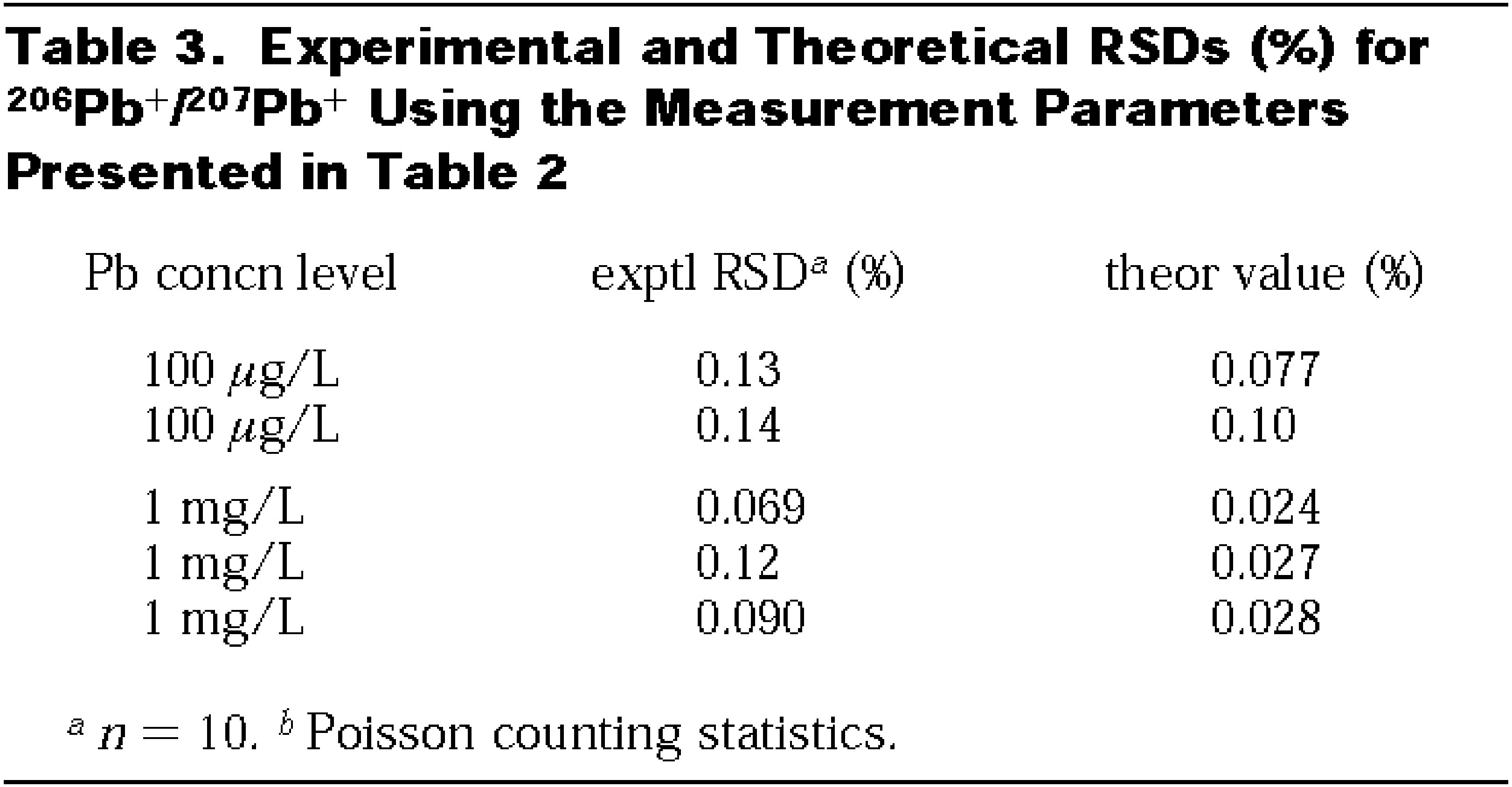


Table 3. Experimental and Theoretical RSDs (%) for $^{206}Pb^+/^{207}Pb^+$ Using the Measurement Parameters Presented in Table 2

Pb concn level	exptl RSD[a] (%)	theor value (%)
100 μg/L	0.13	0.077
100 μg/L	0.14	0.10
1 mg/L	0.069	0.024
1 mg/L	0.12	0.027
1 mg/L	0.090	0.028

[a] $n = 10$. [b] Poisson counting statistics.

SECTOR FIELD ICP – MASS SPECTROMETRY
ISOTOPE RATIO PRECISION AT MEDIUM R ?

- *Vanhaecke et al., Anal. Chem., 268-273, 69, 1997*

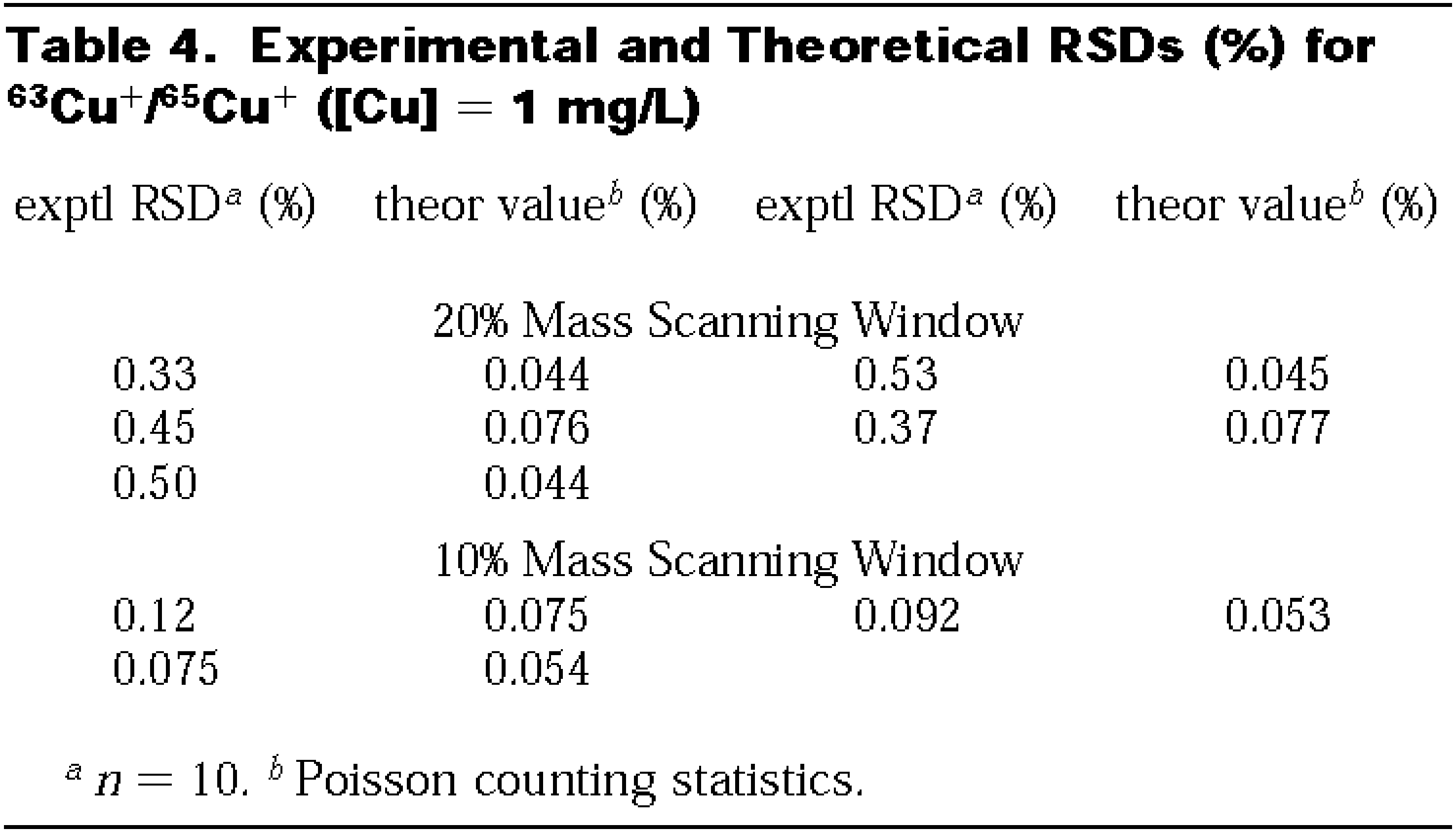
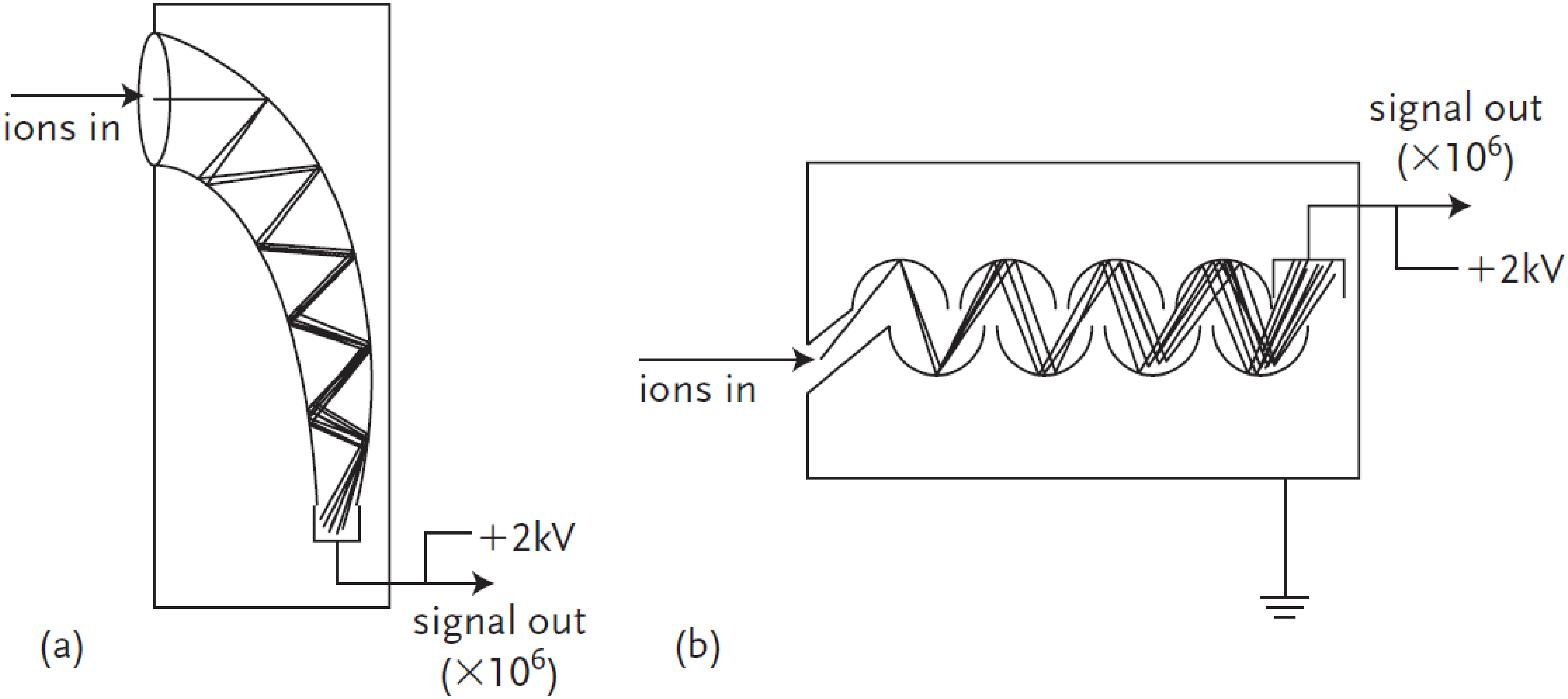


Table 4. Experimental and Theoretical RSDs (%) for $^{63}Cu^+/^{65}Cu^+$ ([Cu] = 1 mg/L)

exptl RSD[a] (%)	theor value[b] (%)	exptl RSD[a] (%)	theor value[b] (%)
	20% Mass Scanning Window		
0.33	0.044	0.53	0.045
0.45	0.076	0.37	0.077
0.50	0.044		
	10% Mass Scanning Window		
0.12	0.075	0.092	0.053
0.075	0.054		

[a] $n = 10$. [b] Poisson counting statistics.

ION DETECTION VIA ELECTRON MULTIPLIER



multiplication factor: 10^7 – 10^8 / pulse counting mode vs. analog mode

DETECTOR DEAD TIME
EM OPERATED IN PULSE COUNTING MODE

- *Handling of one ion ⇒ no possibility to detect another one*
  - *10 – 100 ns*
- *More pronounced effects at higher count rates*
- *Accurate isotope ratio (≠ 1) determination requires correction*
- *Correction for non-paralyzable detector:*

$$\boxed{\frac{1}{\text{observed count rate}} = \frac{1}{\text{actual count rate}} + \text{dead time (in s)}}$$

- *Experimental determination of dead time (τ) required*
  - *Various methods for determination*
    - *Do not forget to set $\tau = 0$ in software prior to experimental determination*
  - *Detector dead time → instrument software for automatic correction*

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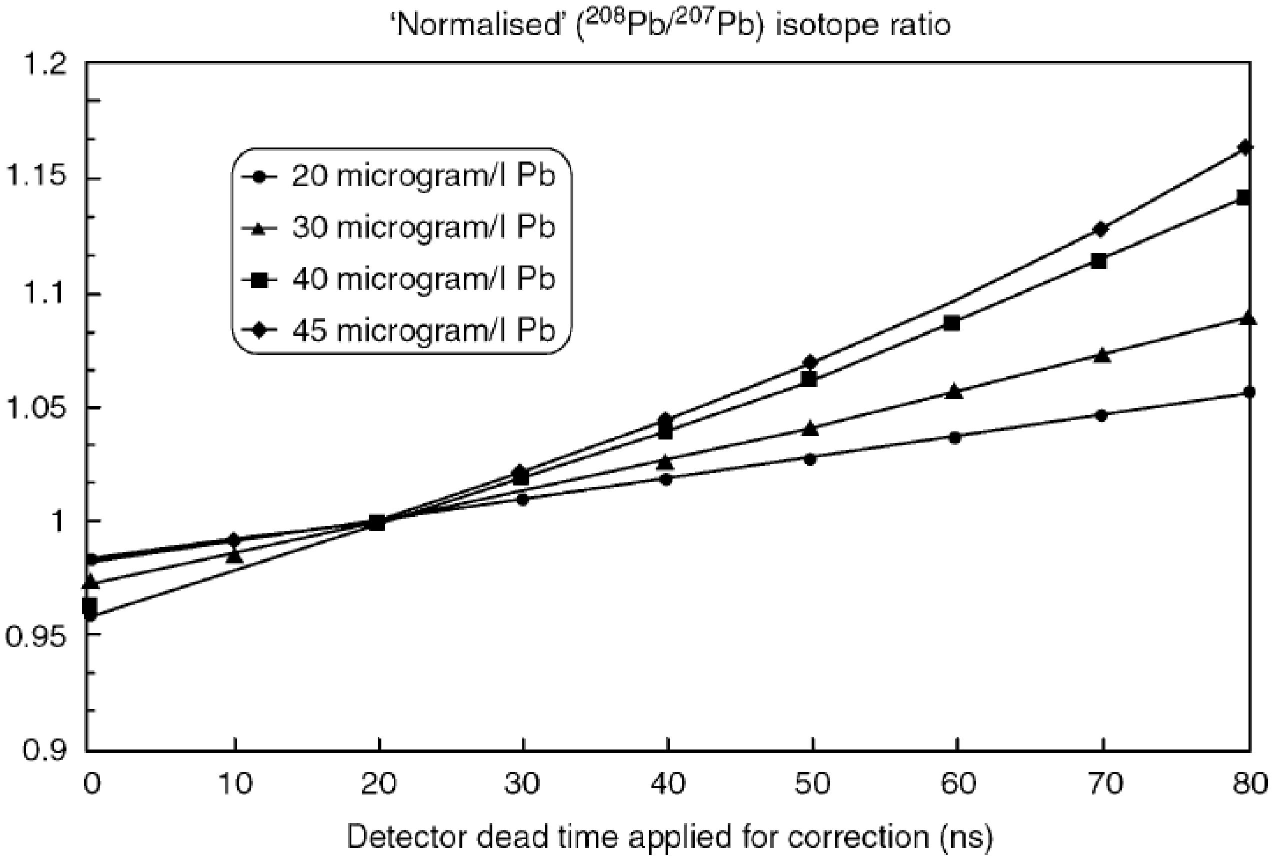
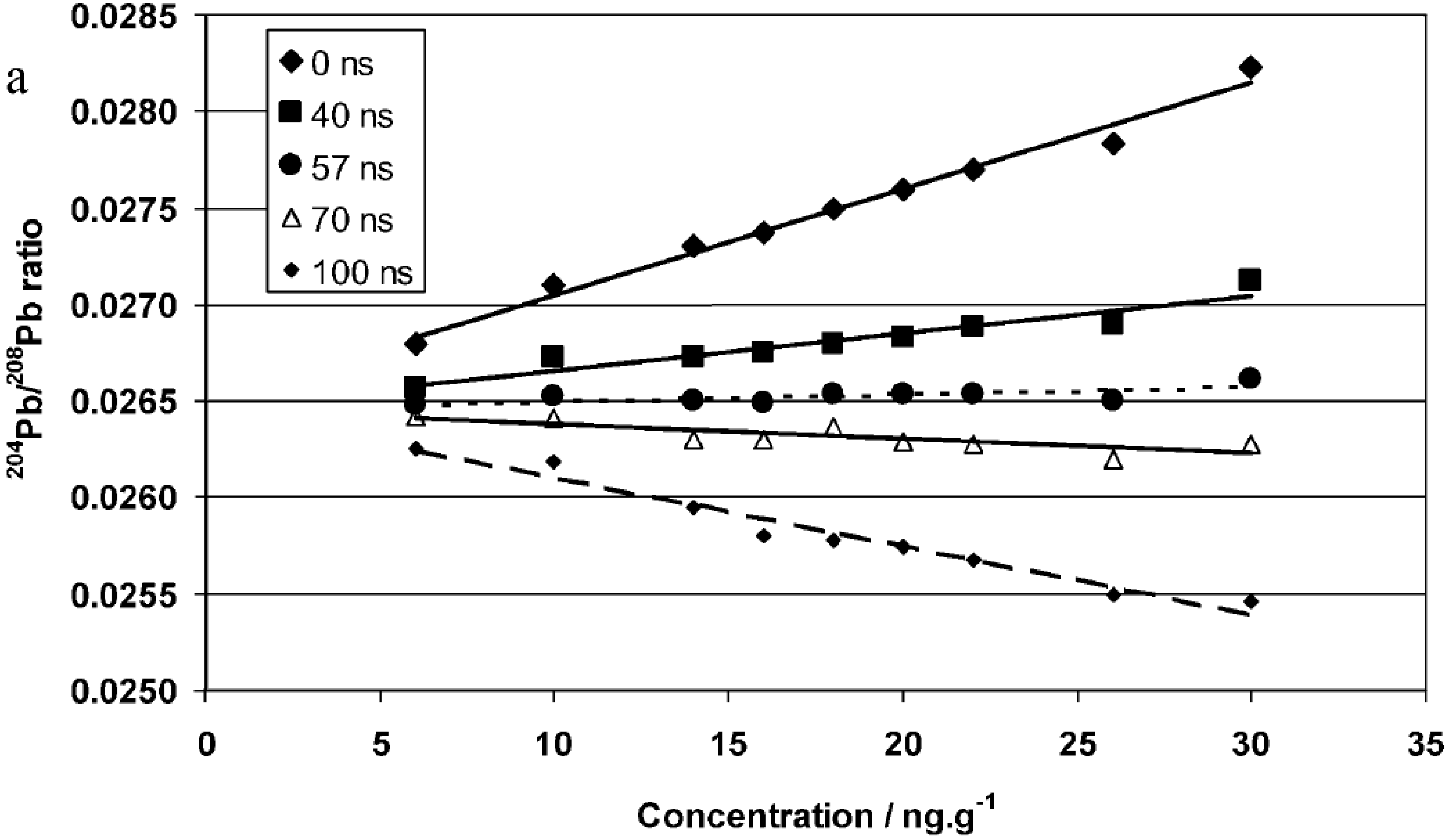
DETERMINATION OF DETECTOR DEAD TIME



Normalized $^{208}Pb/^{207}Pb$ isotope ratio (= $(^{208}Pb/^{207}Pb)_{measured}/(^{208}Pb/^{207}Pb)_{true\ value}$) plotted as a function of the value applied for dead time correction of the 'raw' results obtained for solutions with a Pb concentration ranging from 20 to 45 µg/L. In this particular case, the dead time of the detection system was observed to be ± 20 ns.

F. Vanhaecke et al, JAAS, 13, 567–571, 1998.

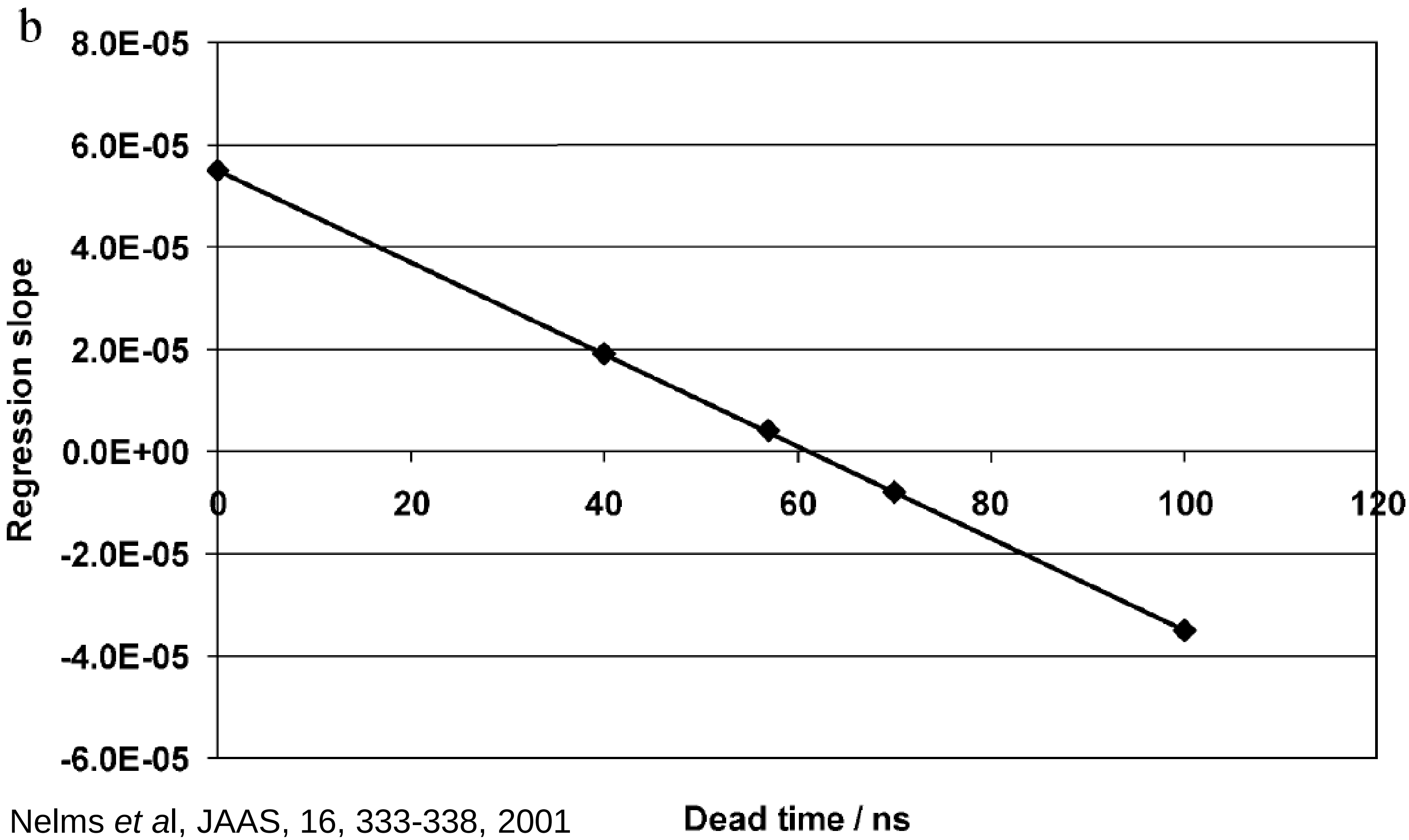
DETERMINATION OF DETECTOR DEAD TIME



Variation of the $^{204}Pb/^{208}Pb$ isotope ratio
as a function of the Pb concentration
for various assumed values of detector dead time.

S. M. Nelms *et al*, JAAS, 16, 333-338, 2001.

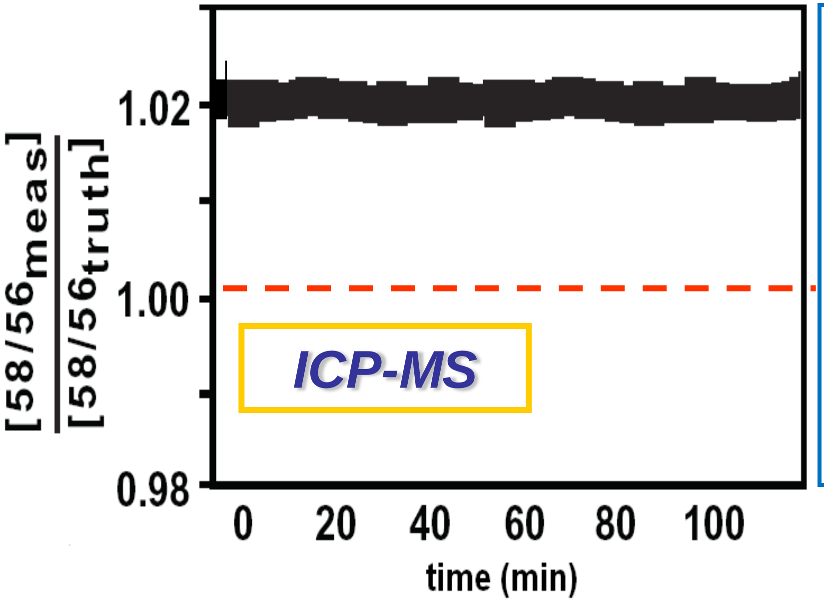
DETERMINATION OF DETECTOR DEAD TIME



S. M. Nelms *et al*, JAAS, 16, 333-338, 2001

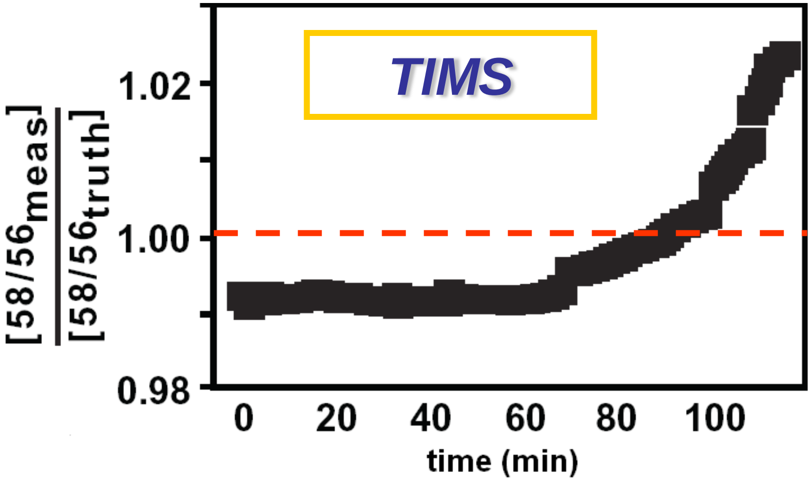
Slope of the curve obtained on plotting the ^{204}Pb/^{208}Pb isotope ratio vs. the Pb concentration as a function of the assumed value for the detector dead time. The intersection of the line thus obtained with the x-axis provides the actual dead time.

PRECISION, PRECISION, WHAT ABOUT ACCURACY ?
MASS DISCRIMINATION IN ICP-MS



- ***Mass discrimination***
  - ***Measured ratio ≠ true value***
  - ***Order of magnitude***
    - ***ca. 1% per mass unit @ mid-mass***
    - ***Considerably larger @ low masses***
  - ***Not a systematic f(time)***

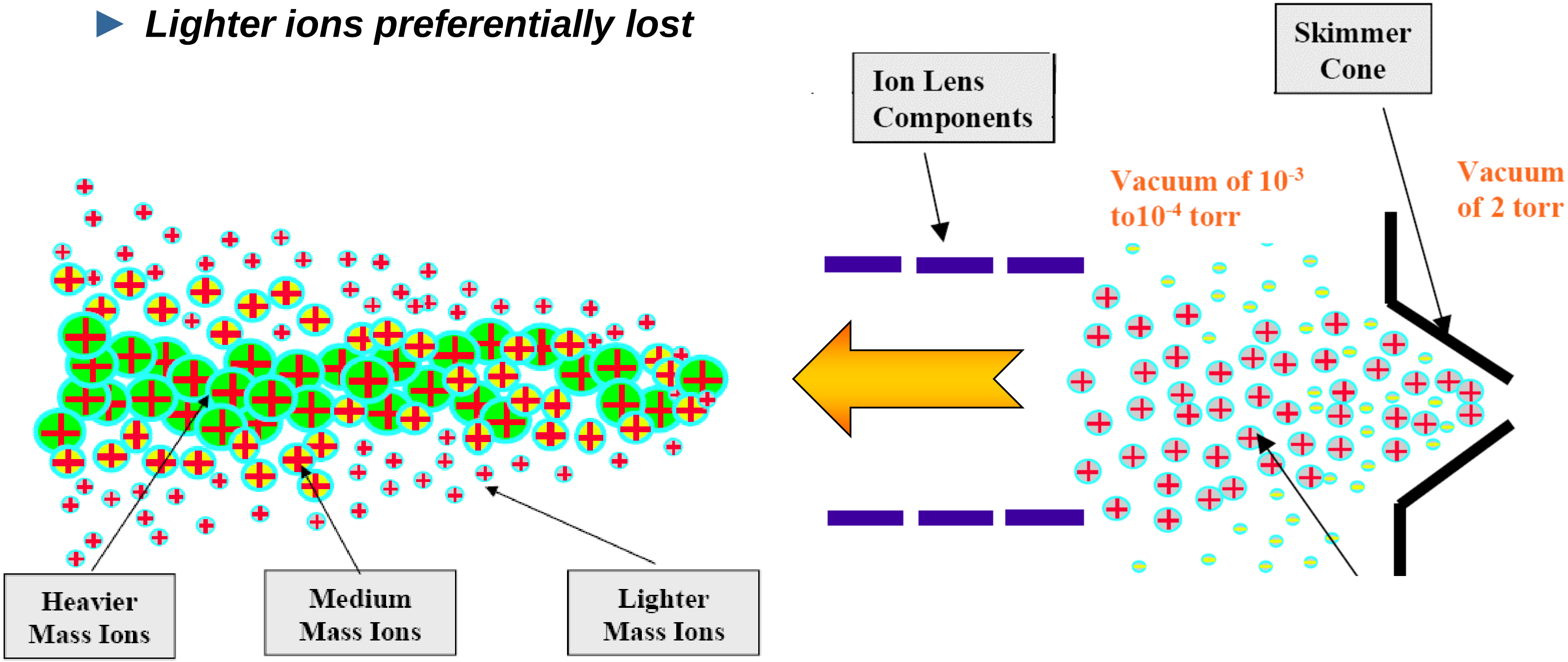
- ***NOT = mass fractionation !***
  - ***TIMS***
  - ***First***
    - ***measurement result < true value***
  - ***Later on:***
    - ***measurement result > true value***



F. Albarede and B. Beard, Rev. Miner. Geochem., 55, 113–150, 2004.

SPACE-CHARGE EFFECTS IN THE ICP-MS INTERFACE

- *All ions forced to move with v_{Ar} (collisions)*
  - *$E_{kin} = ½ mv^2$ and hence, $f(m_{ion})$*
- *Electrostatic repulsion between positively charged ions*
  - *Defocusing of ion beam*
  - *Lighter ions preferentially lost*

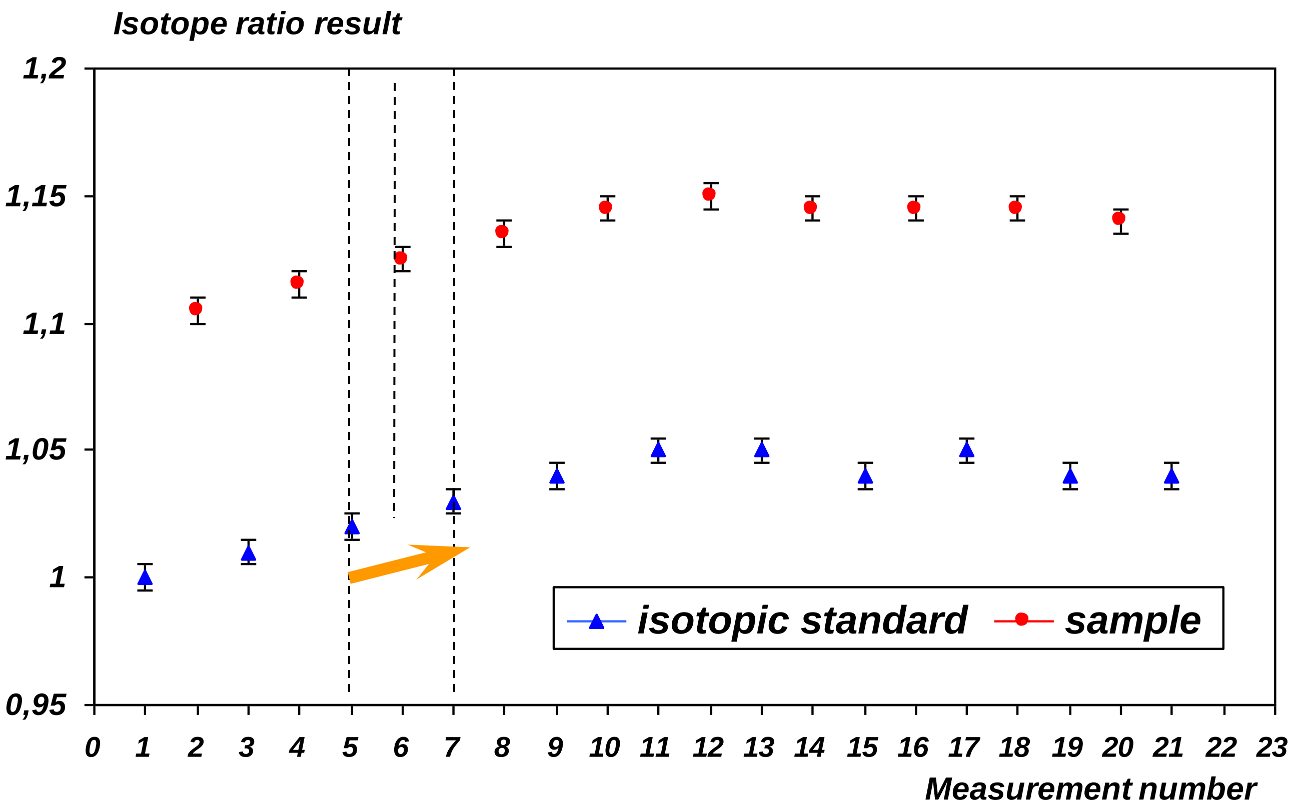


MASS DISCRIMINATION CORRECTION IN SINGLE-COLLECTOR ICP-MS

External correction

Based on comparison of experimental result and certified value for isoropic reference material

Preferably via bracketing (std – sample – std – sample – …)



MASS DISCRIMINATION CORRECTION IN SINGLE-COLLECTOR ICP-MS

Internal correction – type I

If at least one isotope ratio of the target element is constant in nature

E.g., Sr: isotopic composition displays natural variation, but $^{86}Sr/^{88}Sr$ = constant

Comparison of experimental result and certified value for $^{86}Sr/^{88}Sr$

Calculation of correction factor ε or β, to be used for further correction

$$K = \frac{R_{true}}{R_{obs}} = \left(1 + \varepsilon_{linear} \cdot \Delta m\right)$$

$$K = \frac{R_{true}}{R_{obs}} = \left(\frac{m_1}{m_2}\right)^{\beta}$$

$$K = \frac{R_{true}}{R_{obs}} = \left(1 + \varepsilon_{power}\right)^{\Delta m}$$

$$K = \frac{R_{true}}{R_{obs}} = e^{\left(\varepsilon_{exponential} \cdot \Delta m\right)}$$

Various approaches lead to similar results

(no significant differences)

MASS DISCRIMINATION CORRECTION IN SINGLE-COLLECTOR ICP-MS

<u>Internal correction – type II</u>

Using an element, close in mass number, added to the sample

E.g., Tl added to sample solutions intended for Pb isotopic analysis

Comparison of experimental result and certified value for ^{203}Tl/^{205}Tl

Calculation of correction factor ε or β, to be used for further correction

$$K = \frac{R_{true}}{R_{obs}} = \left(1 + \varepsilon_{linear} \cdot \Delta m\right)$$

$$K = \frac{R_{true}}{R_{obs}} = \left(\frac{m_1}{m_2}\right)^{\beta}$$

$$K = \frac{R_{true}}{R_{obs}} = \left(1 + \varepsilon_{power}\right)^{\Delta m}$$

$$K = \frac{R_{true}}{R_{obs}} = e^{\left(\varepsilon_{exponential} \cdot \Delta m\right)}$$

Various approaches lead to similar results

(no significant differences)

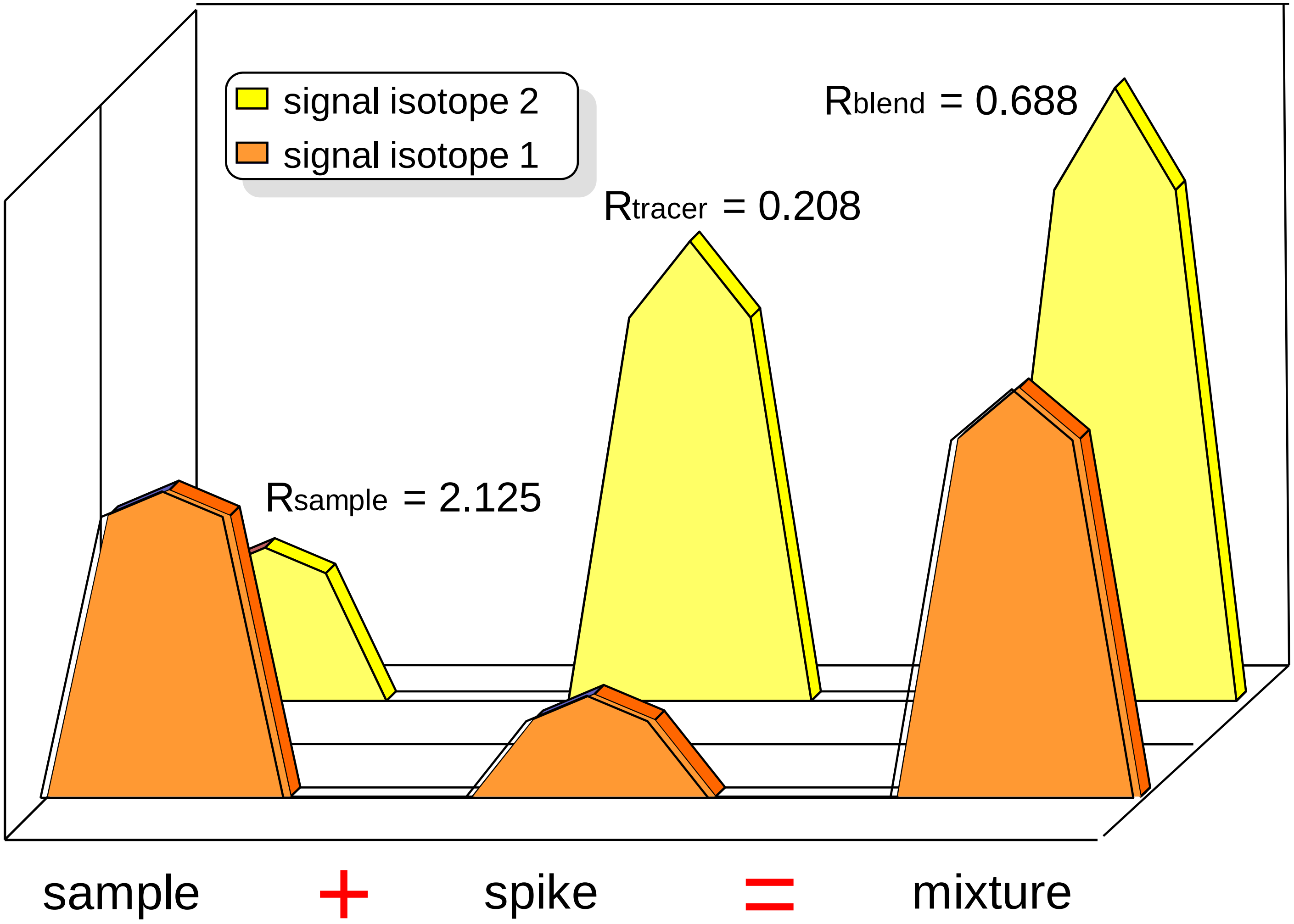
ISOTOPE RATIO PRECISION WITH ICP-MS (OPTIMUM VALUES)

Type of ICPMS instrument	Internal isotope ratio precision (RSD)
Traditional quadrupole-based ICPMS	≥ 0.1%
Quadrupole-based ICPMS with pressurized collision/reaction cell	≥ 0.025%
Single-collector sector field ICPMS	≥ 0.025% at LR and ≥ 0.1% at MR
Multi-collector ICPMS	≥ 0.002% at LR and ≥ 0.005% at MR

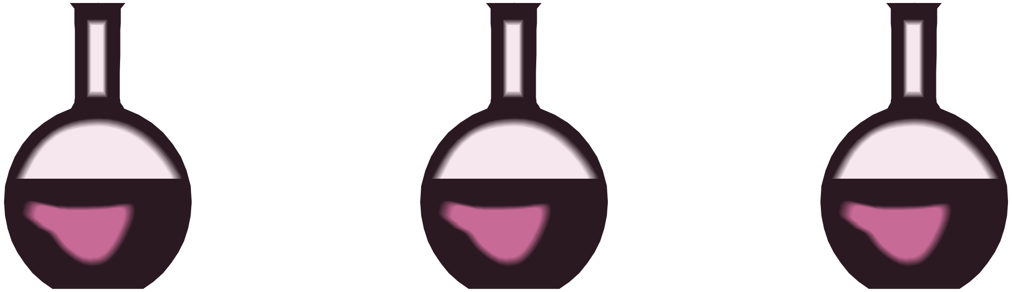
- ***Applications***
  - ***Induced variations ⇒ single-collector***
  - ***Natural variations due to radiogenic nuclide***
    - ***Geochronological dating ⇒ multi-collector***
    - ***Provenance determination ⇒ single- & multi-collector***
  - ***Natural variations due to fractionation ⇒ multi-collector***
  - ***Natural variations due to extinct radionuclides ⇒ multi-collector***

INDUCED VARIATON
ELEMENTAL ASSAY VIA ISOTOPE DILUTION

PRINCIPLE OF ISOTOPE DILUTION (ID)



PRINCIPLE OF ISOTOPE DILUTION (ID)



sample **spike** **mixture**

***mixture* = known amount of sample + known amount of spike**

***spike* : different isotopic composition**

determination of ratio (enriched isotope / reference isotope) in:

- ***sample***
- ***spike***
- ***mixture***

Isotope ratios:much more more "robust" than signal intensities !

ELEMENTAL ASSAY USING ISOTOPE DILUTION

$$R_{sample} = \frac{{}^{1}n_{sample}}{{}^{2}n_{sample}} \quad R_{spike} = \frac{{}^{1}n_{spike}}{{}^{2}n_{spike}} \quad R_{mixture} = \frac{{}^{1}n_{sample} + {}^{1}n_{spike}}{{}^{2}n_{sample} + {}^{2}n_{spike}}$$

<u>spike enriched in ^{1}n</u>

$$R_{mixture} = \frac{{}^{1}n_{sample} + {}^{1}n_{spike}}{\dfrac{{}^{1}n_{sample}}{R_{sample}} + \dfrac{{}^{1}n_{spike}}{R_{spike}}}$$

$${}^{1}n_{sample} = \frac{R_{sample}}{R_{spike}} \cdot \left(\frac{R_{spike} - R_{mixture}}{R_{mixture} - R_{sample}} \right) \cdot {}^{1}n_{spike}$$

$${}^{1}n_{spike} = \theta_{spike}(1) \,.\, n_{spike}$$

$$n_{sample} = \frac{{}^{1}n_{sample}}{\theta_{sample}(1)}$$

ELEMENTAL ASSAY USING ISOTOPE DILUTION

$$R_{sample} = \frac{{}^{1}n_{sample}}{{}^{2}n_{sample}} \quad R_{spike} = \frac{{}^{1}n_{spike}}{{}^{2}n_{spike}} \quad R_{mixture} = \frac{{}^{1}n_{sample}+{}^{1}n_{spike}}{{}^{2}n_{sample}+{}^{2}n_{spike}}$$

$\underline{\text{spike enriched in } {}^{1}n}$

$$ {}^{1}n_{samp} = \frac{R_{sample}}{R_{spike}} \cdot \left(\frac{R_{spike} - R_{mixture}}{R_{mixture} - R_{sample}}\right) \cdot {}^{1}n_{spike}$$

$$ {}^{1}n_{spike} = \theta(1) \,.\, n_{spike}$$

$\underline{\text{spike enriched in } {}^{2}n}$

$$ {}^{2}n_{sample} = \left(\frac{R_{spike} - R_{mixture}}{R_{mixture} - R_{sample}}\right) \cdot {}^{2}n_{spike}$$

$$ {}^{2}n_{spike} = \theta_{spike}(2) \,.\, n_{spike} \qquad \text{and} \qquad n_{sample} = \frac{{}^{2}n_{sample}}{\theta_{sample}(2)}$$

optimum $R_{mixture} = \sqrt{R_{sample} \cdot R_{spike}}$

ELEMENTAL ASSAY USING ISOTOPE DILUTION

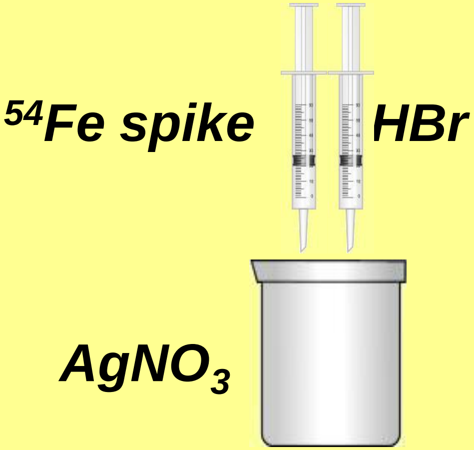
- ***Advantages***
  - ***After isotopic equilibration: analyte losses do no affect result***
  - ***Isotope ratios barely affected by changes in sensitivity (matrix effects)***
  - ***Most reliable calibration method***
    - ***High accuracy***
    - ***High precision***
- ***Disadvantages***
  - ***Not suited for mono-isotopic elements***
    - ***Be, Na, Al, P, K, Sc, Mn, Co, As, Y, Nb, Rh, I, Cs, Pr, Ho, Tm, Au, Bi, Th***
      - ***Sometimes : use of long-lived radionuclide (e.g., ^{129}I)***
  - ***High purchase price of spikes***
    - ***≥1000 € / 100 mg***
      - ***Isotopic enrichment & nuclide (natural isotopic abundance)***
  - ***Analyte concentration has to be approximately known***
- ***Use of IDMS ?***
  - ***Reference measurements***
  - ***Analyte losses to be expected***

DETERMINATION OF ULTRA-TRACE AMOUNTS OF FE IN AGNO$_3$ SOLUTIONS

- ***Goal?***
  - ***Determination of Fe in $AgNO_3$ solutions***
    - ***Ag-matrix: ~ 600 $g.L^{-1}$ Ag***
    - ***memory effects & signal suppression***
  - ***ICP-MS: max. ~ 100 $mg.L^{-1}$ Ag***
    - ***dilution of the samples (external calibration)***
    - ***LOD = 1200 $ng.g^{-1}$***
  - ***precipitation of Ag as AgBr***
    - ***co-precipitation of Fe?***
    - ***isotope dilution as a calibration method***

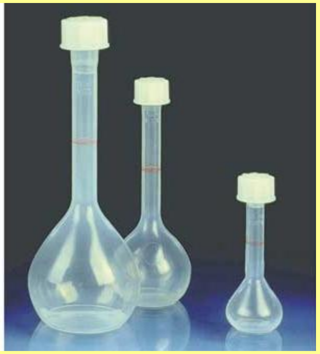
L; Balcaen *et al*, ABC, 377, 1020-1025, 2003..

DETERMINATION OF FE IN AGNO$_3$ SOLUTIONS
PRECIPITATION OF AG$^+$ AS AGBR + ID



precipitation of Ag

Filtration



Dilution (50x)

⇨ **Ag-content: ± 1 mg.L-1**

!! CONTAMINATION !!

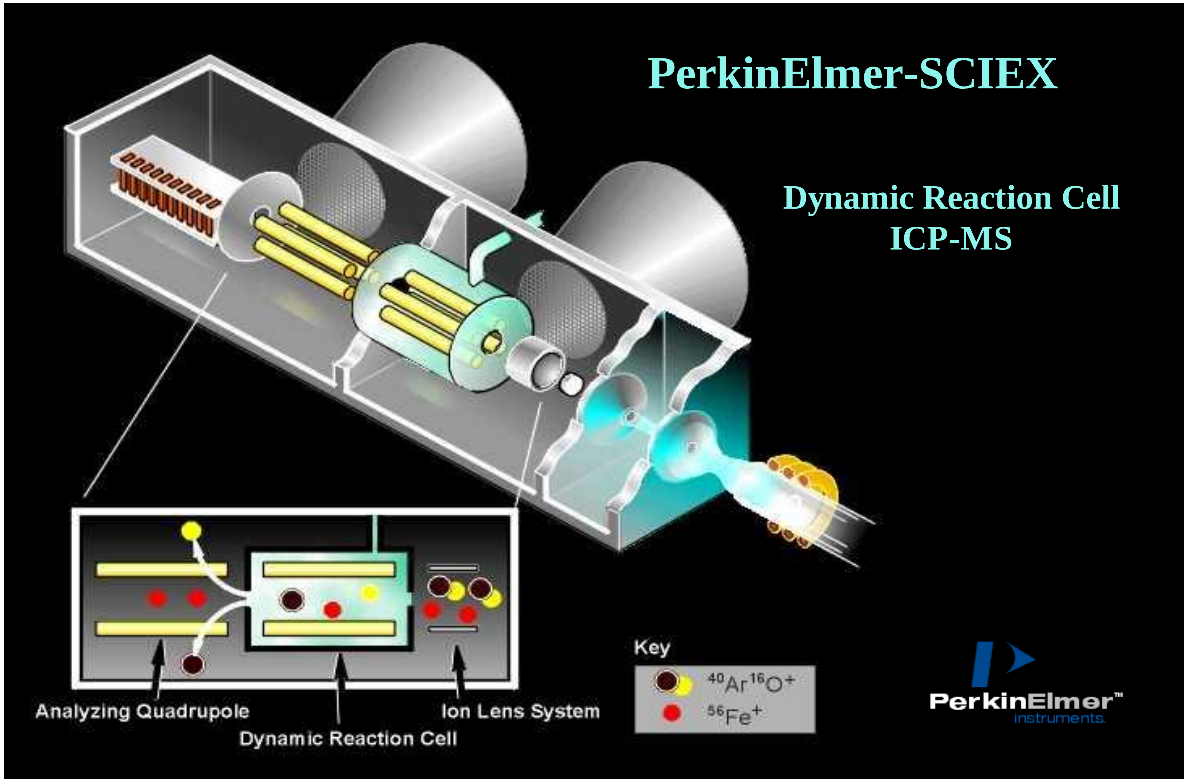
L; Balcaen *et al*, ABC, 377, 1020-1025, 2003..

Determination of Fe in AgNO$_3$ solutions
Spectral interferences

	^{54}Fe (5,85 %)	^{56}Fe (91,8 %)	^{57}Fe (2,12 %)	^{58}Fe (0,28 %)
Isobaric nuclide	$^{54}Cr^+$			$^{58}Ni^+$
Ar-containing molecular ion	$^{40}Ar^{14}N^+$ $^{38}Ar^{16}O^+$ $^{36}Ar^{18}O^+$	$^{40}Ar^{16}O^+$	$^{40}Ar^{16}OH^+$ $^{38}Ar^{18}OH^+$	$^{40}Ar^{18}O^+$
Ca-containing molecular ion		$^{40}Ca^{16}O^+$	$^{40}Ca^{16}OH^+$	$^{40}Ca^{18}O^+$ $^{42}Ca^{16}O^+$
Cl-containing molecular ion	$^{37}Cl^{16}OH^+$			$^{23}Na^{35}Cl^+$

L; Balcaen *et al*, ABC, 377, 1020-1025, 2003..

Determination of Fe in AgNO$_3$ solutions
Overcoming spectral overlap via chemical resolution



Use of NH$_3$ to induce selective ion-molecule reactions allowing spectral overlap to be overcome at m/z = 54 & 56

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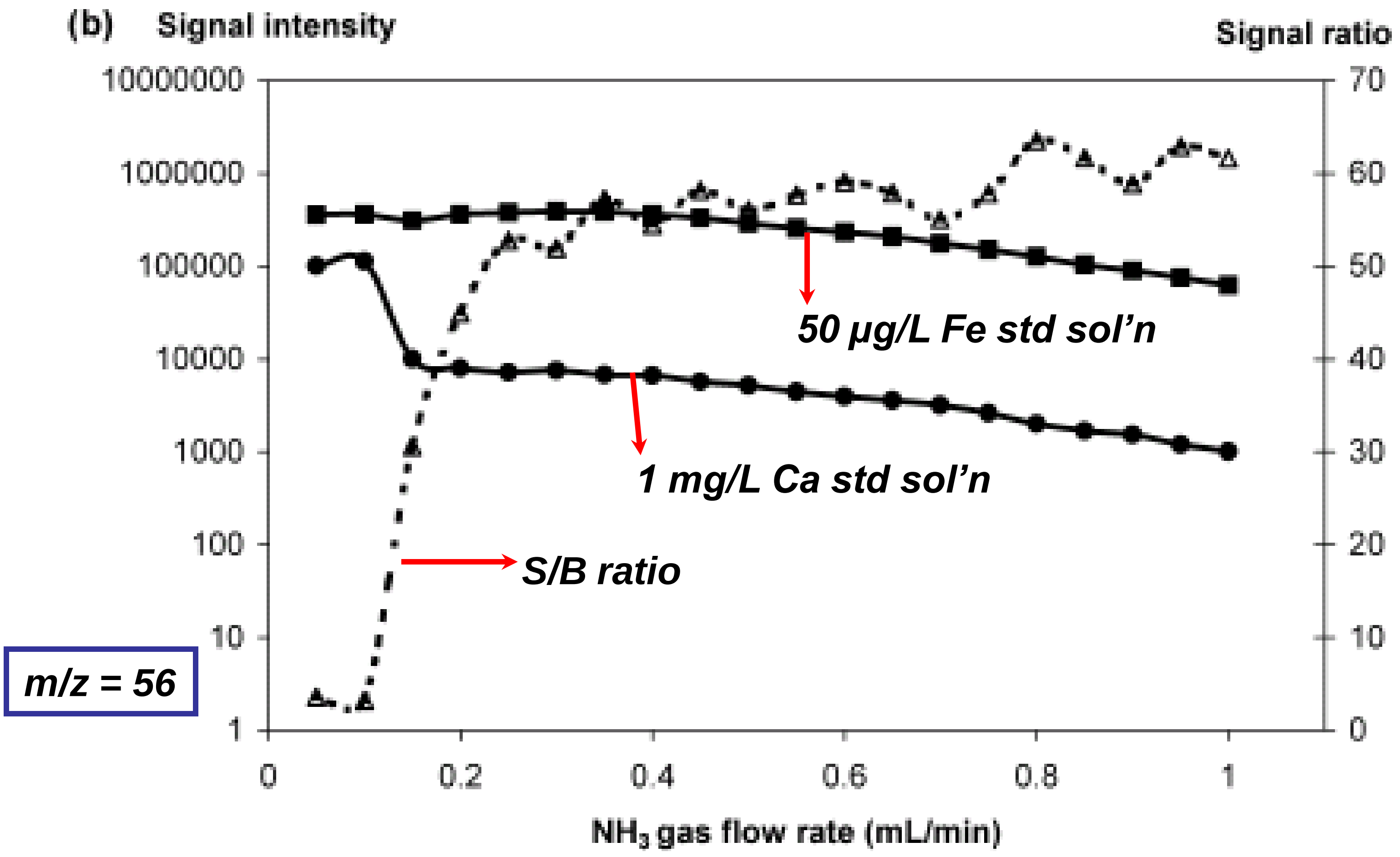
L; Balcaen *et al*, ABC, 377, 1020-1025, 2003..

DETERMINATION OF FE IN $AGNO_3$ SOLUTIONS
OVERCOMING SPECTRAL OVERLAP VIA CHEMICAL RESOLUTION



50 µg/L Fe std sol'n

1 mg/L Ca std sol'n

S/B ratio

m/z = 56

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L; Balcaen *et al*, ABC, 377, 1020-1025, 2003..

DETERMINATION OF ULTRA-TRACE AMOUNTS OF FE IN $AgNO_3$ SOLUTIONS

	Sample 1 (µg g^{-1})	Sample 2 (µg g^{-1})	Sample 3 (µg g^{-1})
	0.997	17.92	0.075
	0.947	18.22	0.091
	0.954	18.38	
Average	**0.966**	**18.17**	**0.083**
Standard deviation	0.027	0.23	0.012
RSD%	3	1	14

- ***Comparison of LODs***
  - ***Dilution of sample solution → 1200 ng/g***
  - ***AgBr precipitation + ID → 10 ng/g***

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L; Balcaen *et al*, ABC, 377, 1020-1025, 2003..

ISOTOPE DILUTION IN ELEMENTAL SPECIATION ANALYSIS?

- *Speciation analysis?*
  - ***Separation, identification, quantification of the different chemical forms (oxidation state, molecule) in which the target element occurs***
    - ***Examples***
      - ***Cr(III) vs. Cr(VI)***
      - ***Different toxic & non-toxic As-containing compounds***
      - ***Inorganic Hg vs. MeHgX***
      - ***…***
  - ***Combination of separation technique with ICP-MS***
    - ***Separation technique***
      - ***Liquid chromatography – HPLC***
      - ***Gas chromatography – GC***
      - ***Field flow fractionation – FFF***
      - ***Capillary electrophoresis – CE***
    - ***ICP-MS as element-selective & sensitive detector***

ISOTOPE DILUTION IN ELEMENTAL SPECIATION ANALYSIS
SPECIES-SPECIFIC ISOTOPE DILUTION

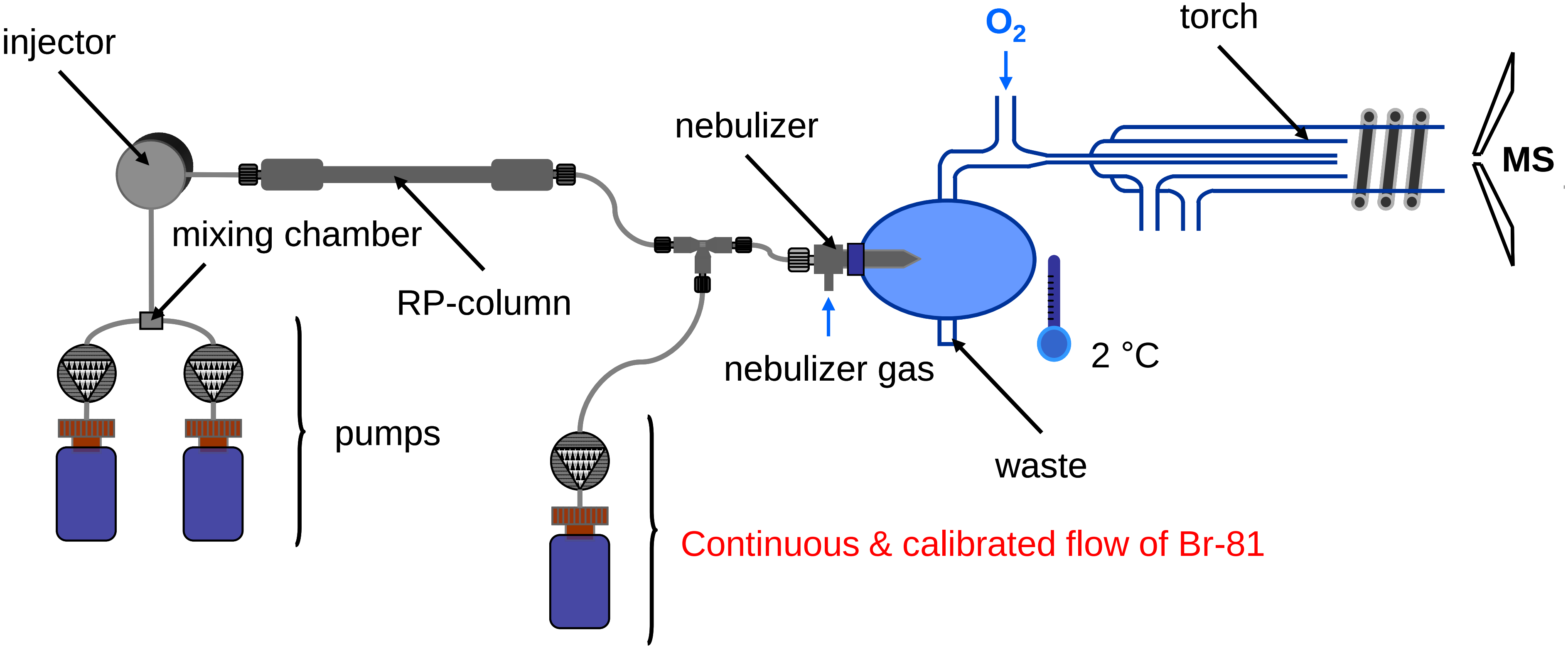
- ***What?***
  - ***Synthesis of specific compound with non-natural isotopic composition***
  - ***Addition of this compound to sample***
    - ***As early as possible in the analysis process***
- ***Advantages ?***
  - ***Automatic correction for:***
    - ***Non-quantitative derivatization (if relevant, e.g., GC-ICP-MS)***
    - ***Non-quantitative extraction (if relevant, e.g., SPME)***
    - ***Non-quantitative column recovery***
    - ***Variations in ICP-MS sensitivity due to***
      - ***Matrix effects***
      - ***Gradient elution***
      - ***Signal drift***
      - ***Instrument instability***
      - ***…***
  - ***Important remark***
    - ***No correction for non-quantitative recovery out of solid matrix***

ISOTOPE DILUTION IN ELEMENTAL SPECIATION ANALYSIS
SPECIES-UNSPECIFIC ISOTOPE DILUTION

- ***When ?***
  - ***No standards available***
    - ***Identity of species not known***
    - ***Too many species to synthesize them all***
    - ***Species too complicated to synthesize***
    - ***Synthesis of standards too labour-intensive and/or time-consuming***

- ***Advantages ?***
  - ***Automatic correction for changes in ICP-MS sensitivity***
    - ***Gradient elution***
    - ***Matrix changes as f(time)***
    - ***Signal instability & drift***

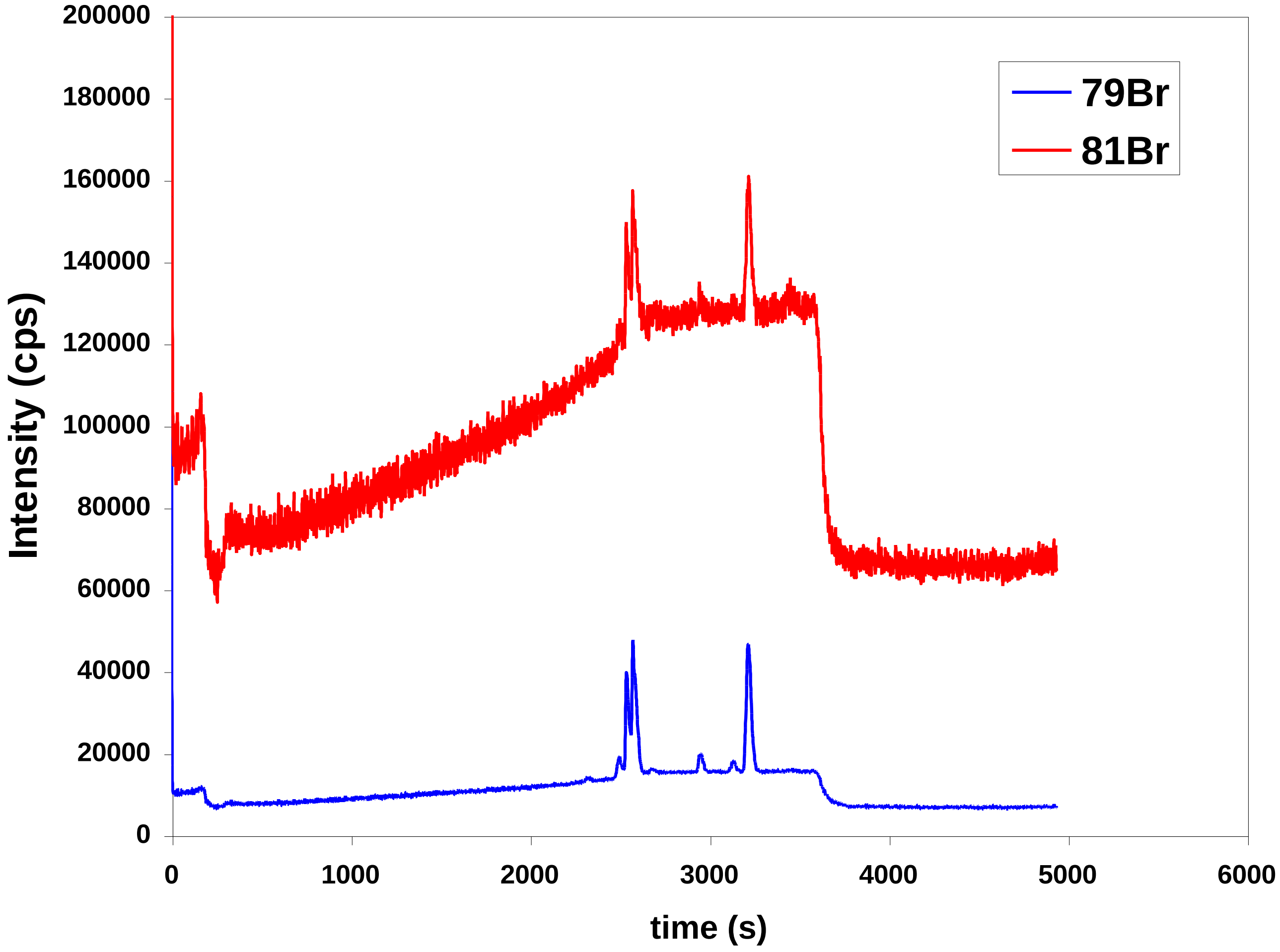
ISOTOPE DILUTION IN ELEMENTAL SPECIATION ANALYSIS
SPECIES-UNSPECIFIC ISOTOPE DILUTION



Continuous & calibrated flow of Br-81

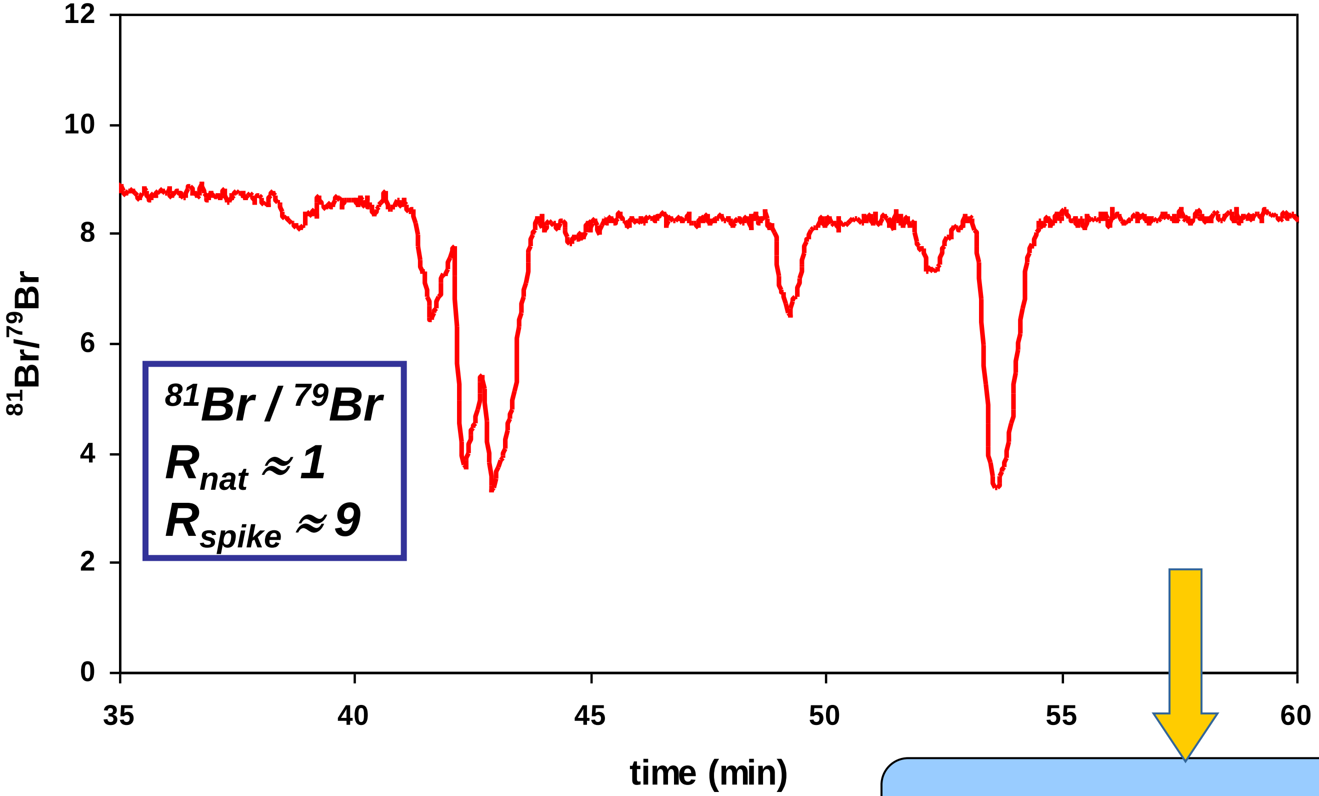
Meermann *et al. ABC,* 402, 439-448, 2012

BR-CONTAINING DRUG: HPLC-ICP-MS METABOLITE PROFILING QUANTIFICATION VIA SPECIES UNSPECIFIC ISOTOPE DILUTION



F. Cuyckens *et al*, ABC 390, 1717–1729, 2008.

BR-CONTAINING DRUG: HPLC-ICP-MS METABOLITE PROFILING QUANTIFICATION VIA SPECIES UNSPECIFIC ISOTOPE DILUTION



^{81}Br / ^{79}Br

$R_{nat} \approx 1$

$R_{spike} \approx 9$

Via ID formula ⇒ mass flow chromatogram

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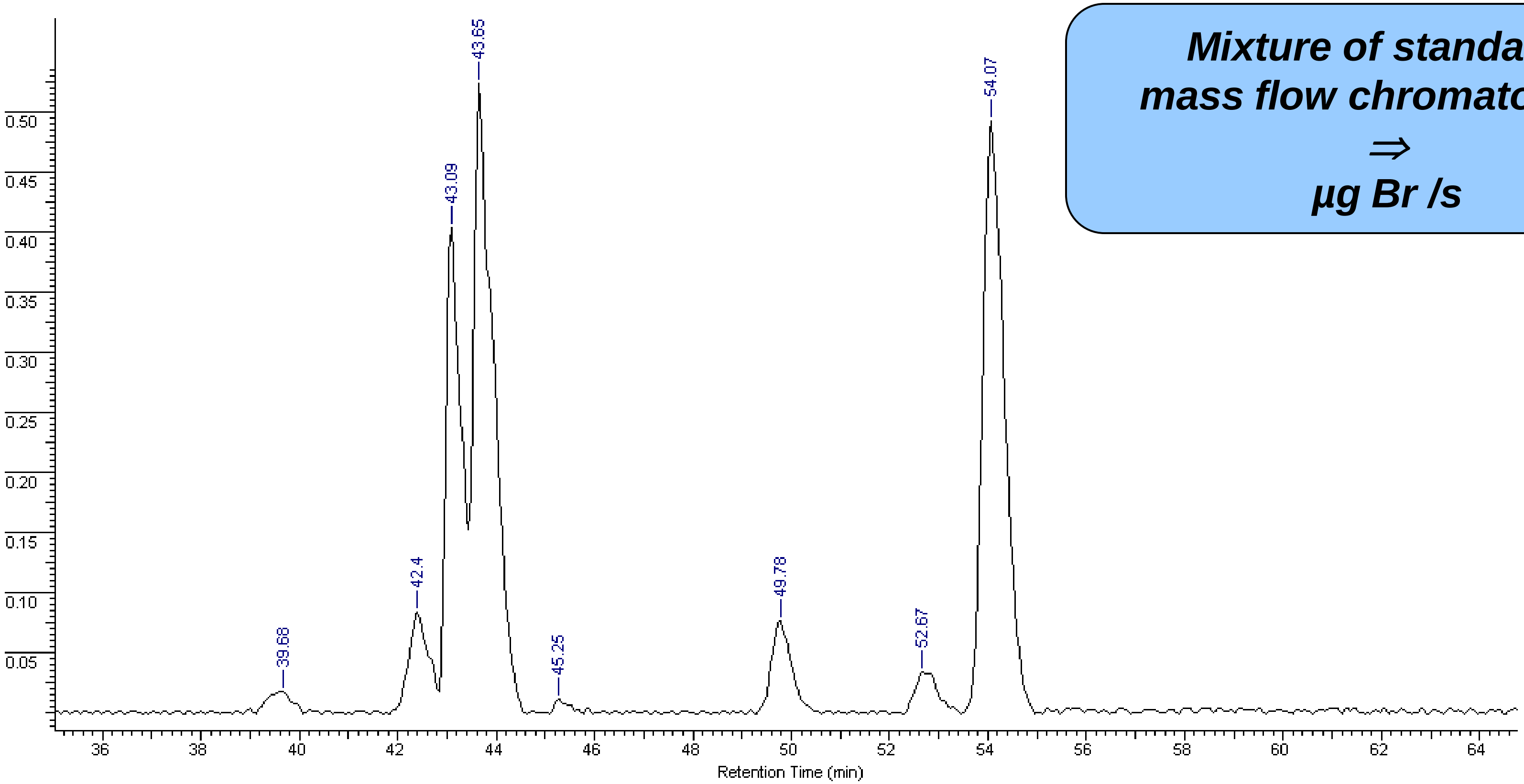
F. Cuyckens *et al*, ABC 390, 1717–1729, 2008.

BR-CONTAINING DRUG: HPLC-ICP-MS METABOLITE PROFILING QUANTIFICATION VIA SPECIES UNSPECIFIC ISOTOPE DILUTION



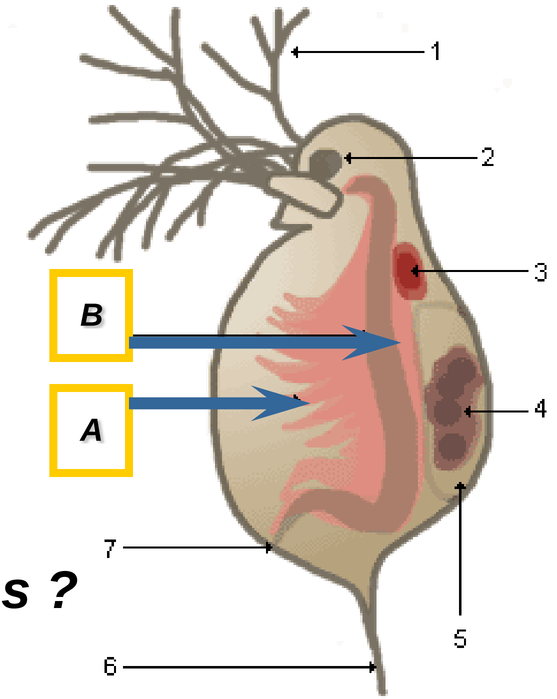
Mixture of standards
mass flow chromatogram
⇒
µg Br /s

F. Cuyckens *et al*, ABC 390, 1717–1729, 2008.

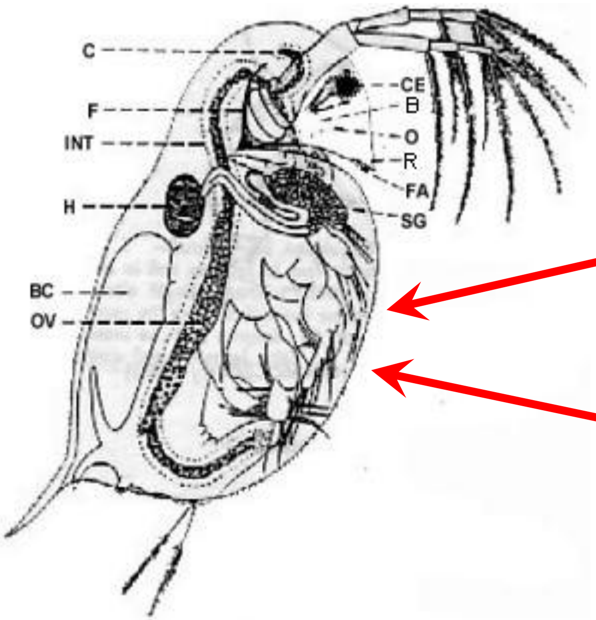
INDUCED VARIATION
TRACER EXPERIMENTS WITH STABLE ISOTOPES

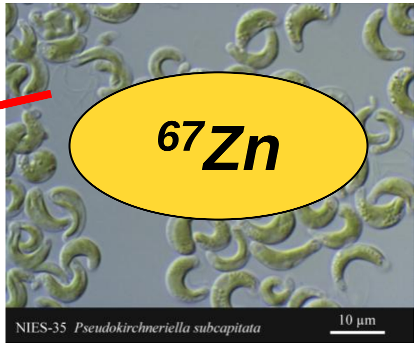
TRACER EXPERIMENTS FOR STUDYING THE UPTAKE OF ZN BY DAPHNIA MAGNA

- ***Usual assumption:***
  - ***Toxicity caused by waterborne metal only***
    - ***Uptake via gills (A)***
  - ***Effect of dietary metals ignored***
    - ***Uptake via alimentary channel (B)***
- ***Our study:***
  - ***Effects of dietary Zn ?***
    - ***Exposure experiment (total Zn / ICP-MS)***
    - ***Reprocductive toxicity***
  - ***Relative importance of both exposure routes ?***
    - ***Stable isotopic tracer experiment (ICP-MS)***



TRACER EXPERIMENTS FOR STUDYING THE UPTAKE OF ZN BY DAPHNIA MAGNA





^{67}Zn

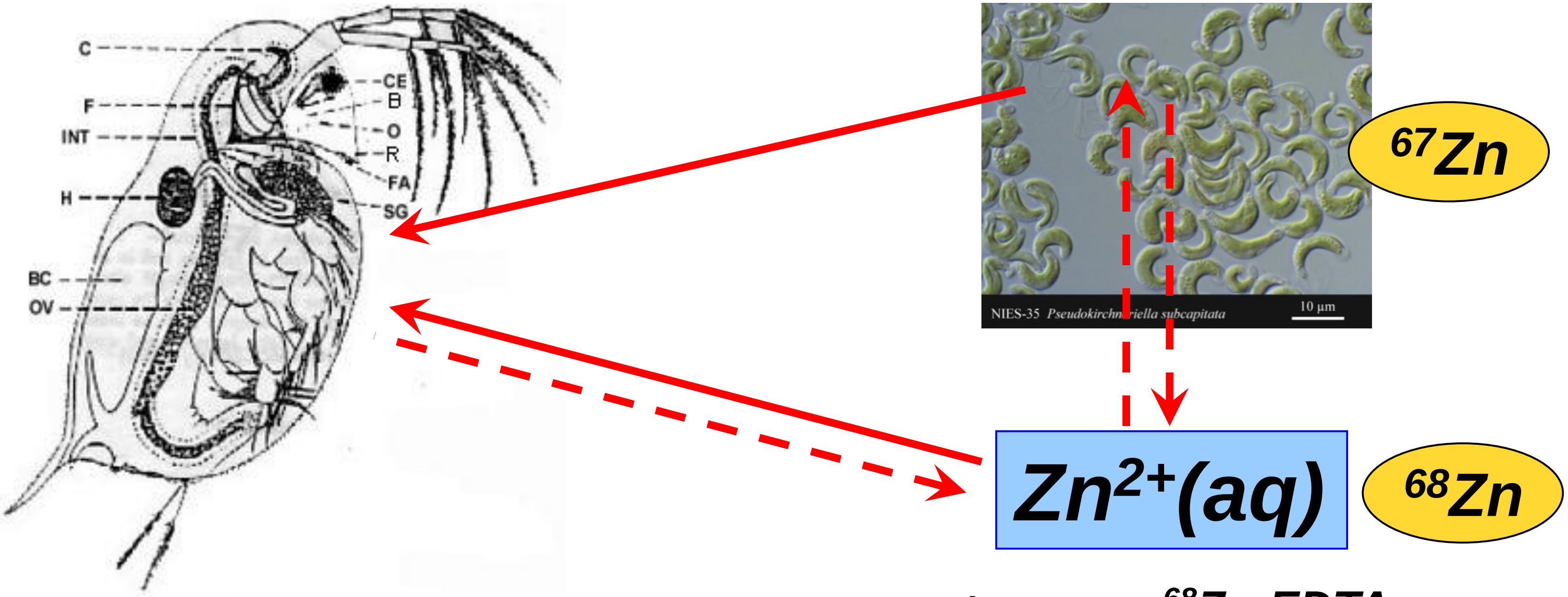
$Zn^{2+}(aq)$

^{68}Zn

Zn isotopic analysis
using sector field ICP-MS
At R = 4000

L. Balcaen *et al*, ABC, 390, 555–569, 2008.

TRACER EXPERIMENTS FOR STUDYING THE UPTAKE OF ZN BY DAPHNIA MAGNA



^{67}Zn

Zn^{2+}(aq)

^{68}Zn

+ excess ^{68}Zn-EDTA
to minimize effect of ^{67}Zn leaching
from algae

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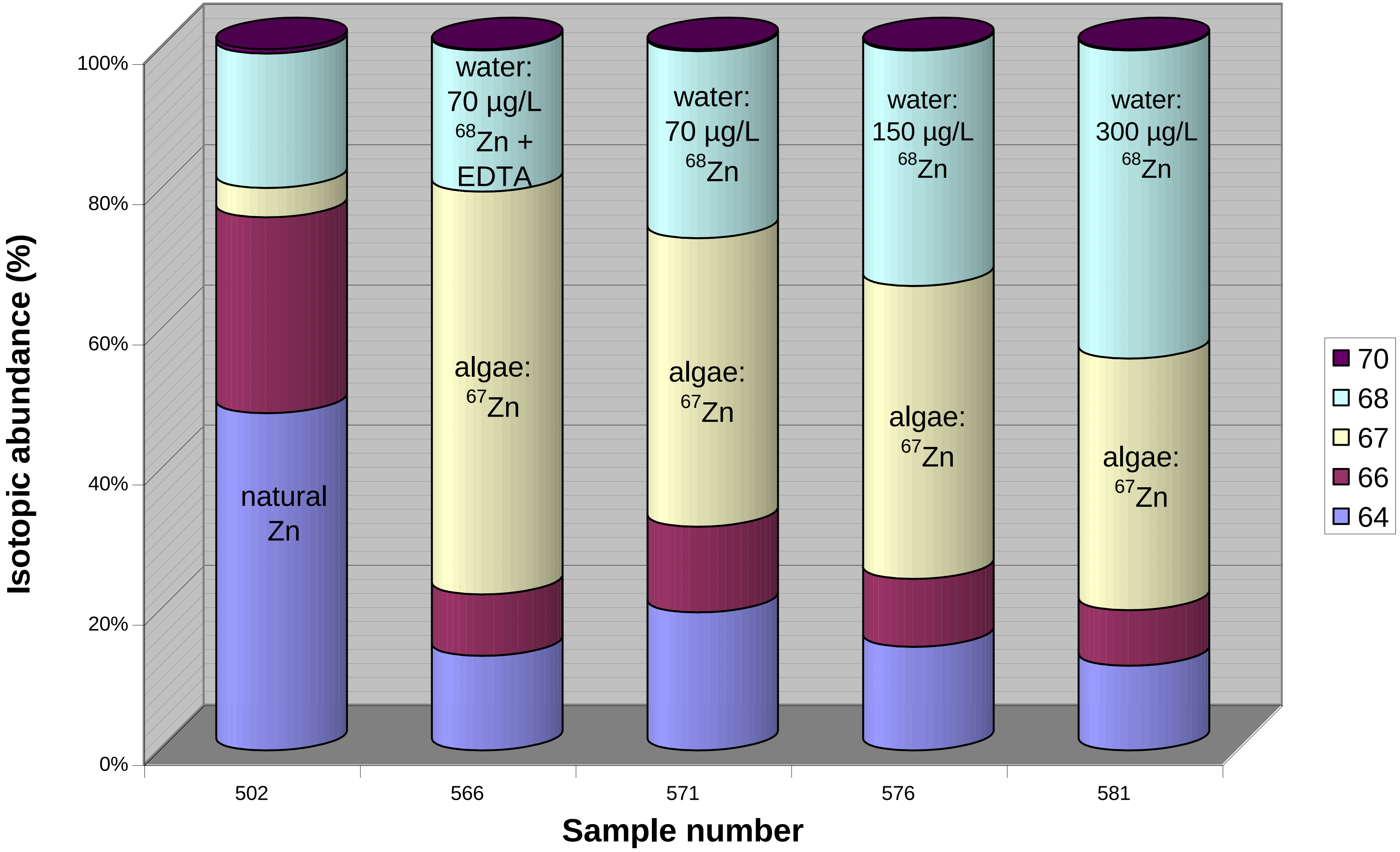
L. Balcaen *et al*, ABC, 390, 555–569, 2008.

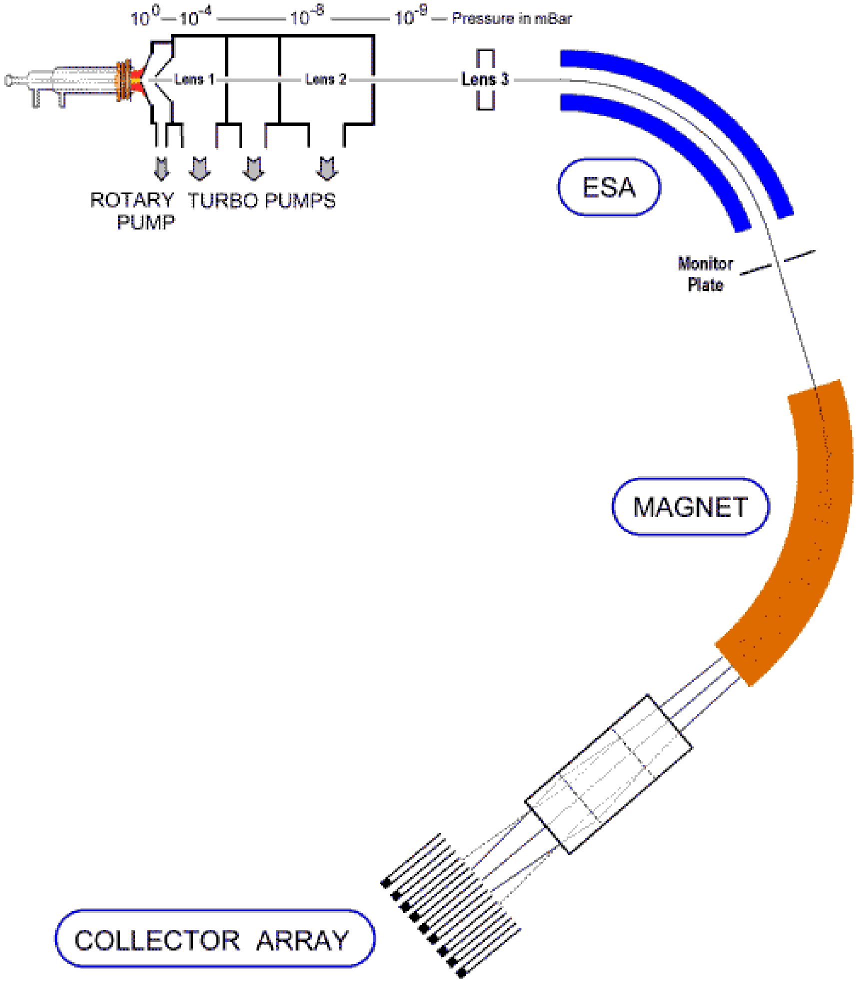
TRACER EXPERIMENTS FOR STUDYING THE UPTAKE OF ZN BY DAPHNIA MAGNA



L. Balcaen *et al*, ABC, 390, 555–569, 2008.

NATURAL VARIATION

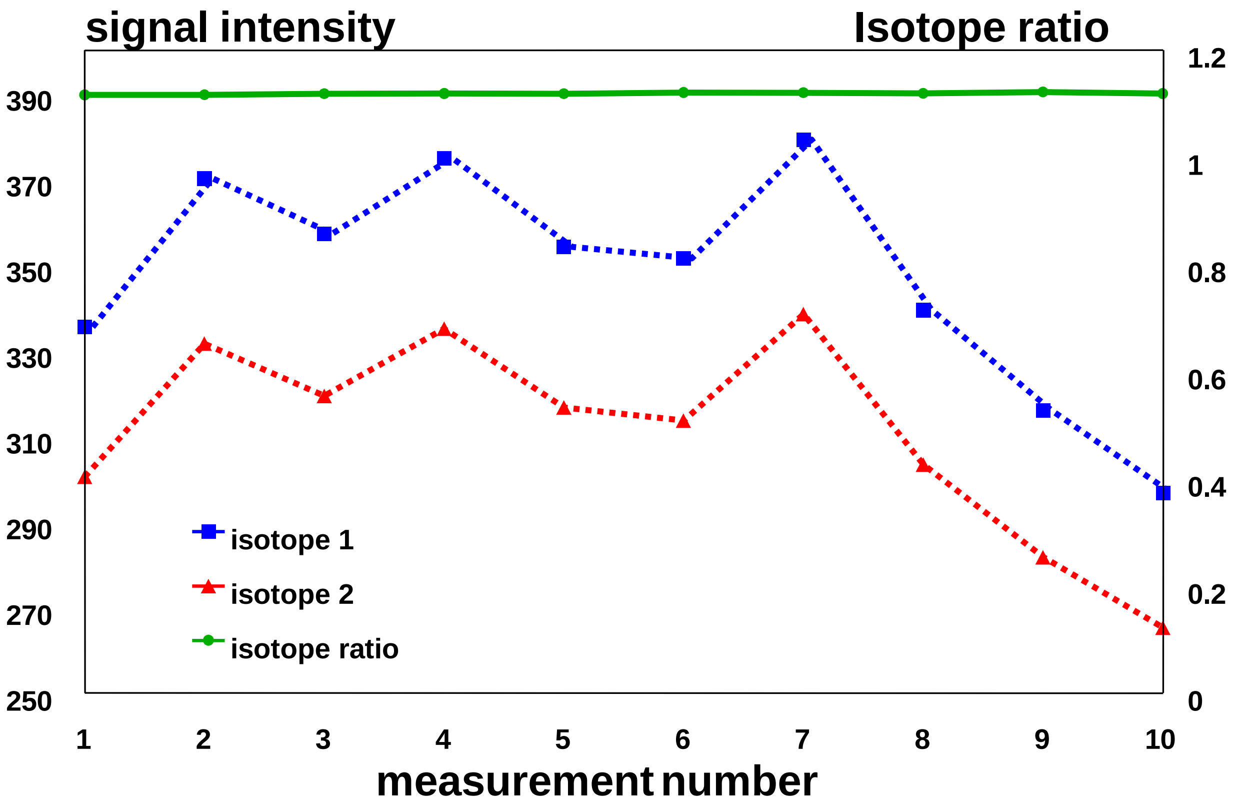
MULTI-COLLECTOR ICP – MASS SPECTROMETRY



Isotope ratio precision:

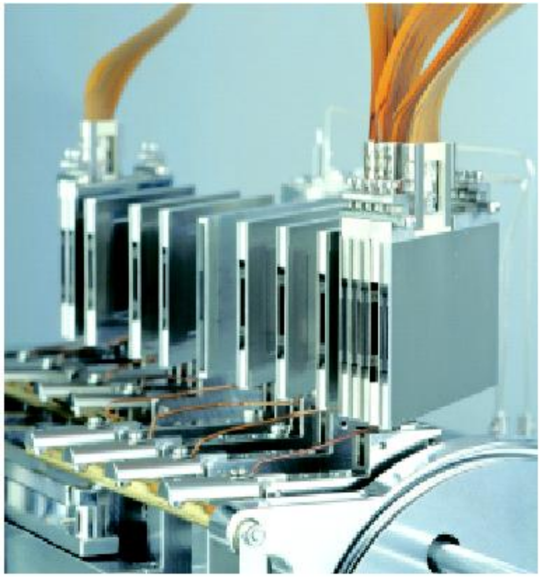
down to 0,002 % RSD !

ARRAY OF FARADAY COLLECTORS:
SIMULTANEOUS MONITORING OF ION SIGNAL INTENSITIES



Isotope ratio precision:

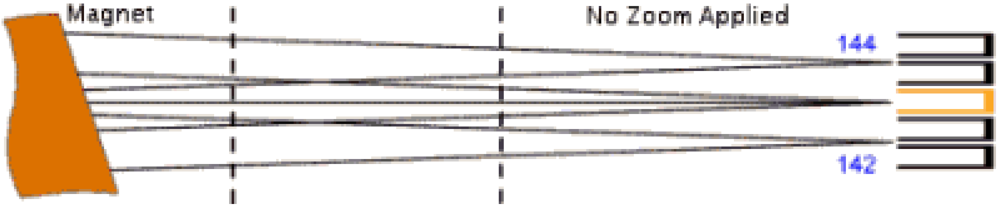
down to 0,002 % RSD !



- ***Simultaneous monitoring:***
  - ▶ ***Automatic correction for signal instability & signal drift***
  - ▶ ***Higher isotope ratio precision***
- ***With ICP-MS instrument equipped with only one detector:***
  - ▶ ***Mimicked by fast 'hopping'***

ION BEAMS → FARADAY COLLECTORS ?

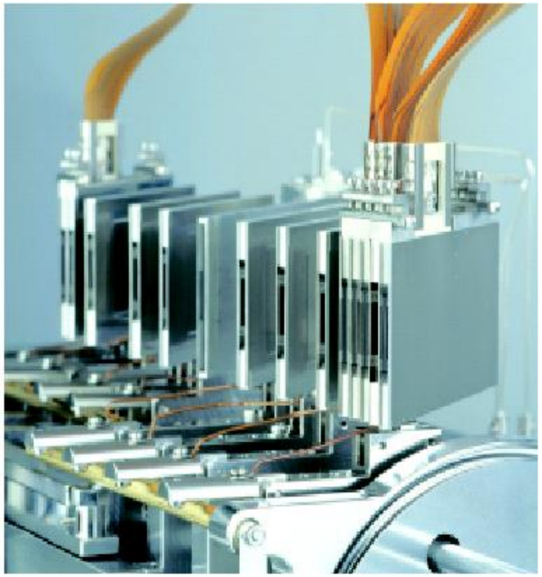
Zoom optics



The ion beams are steered into the appropriate collectors by applying suitable voltages on the zoom "optics" (= electrostatic lenses).

Moveable detectors

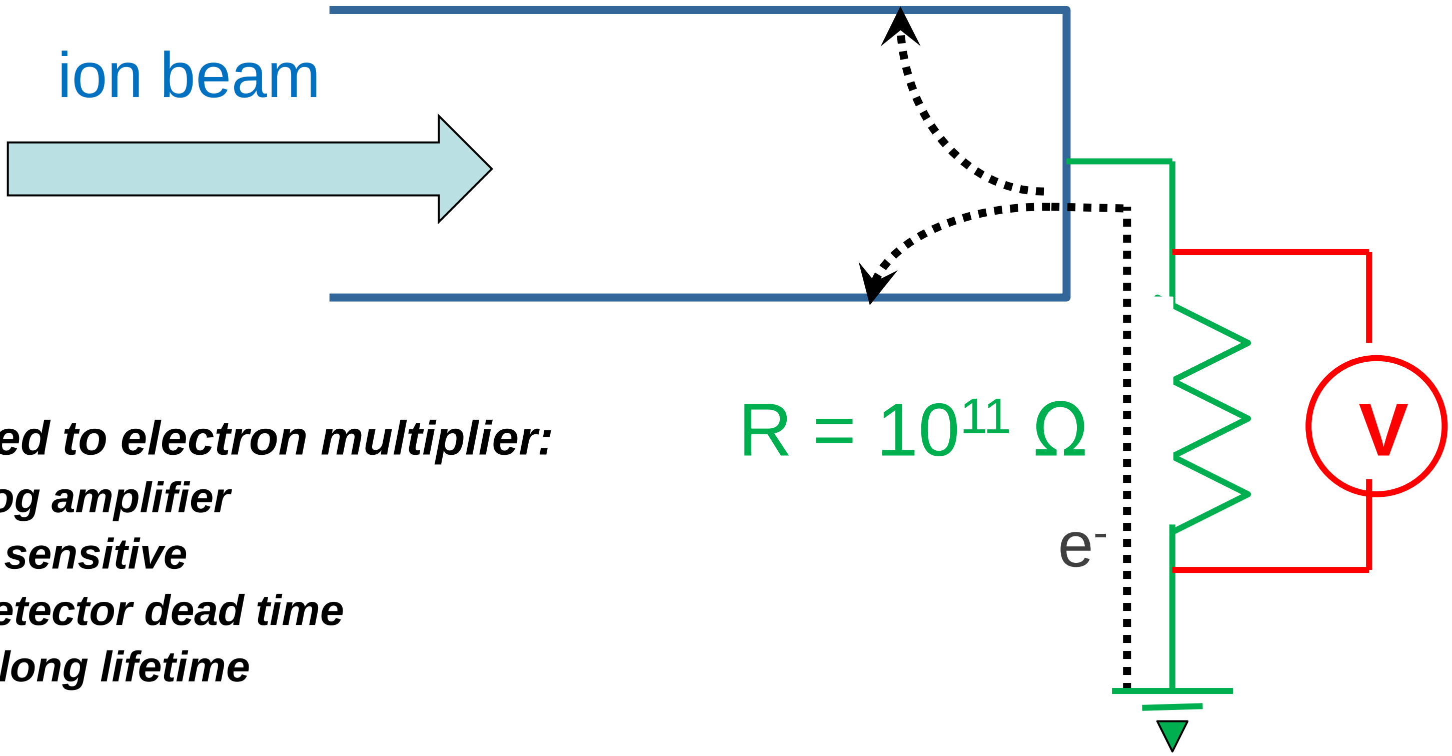
(motorized)



The position of the Faraday collectors can be optimised with respect to the respective ion beams

Or a combination of both …

FARADAY COLLECTOR – OPERATING PRINCIPLE



- ***Compared to electron multiplier:***
  - ***Analog amplifier***
  - ***Less sensitive***
  - ***No detector dead time***
  - ***Very long lifetime***

MULTI-COLLECTOR ICP – MASS SPECTROMETRY

- ***Dedicated tool for highly precise isotopic analysis***

- ***Competitor for thermal ionization mass spectrometry – TIMS***

- ***Advantages compared to TIMS ?***
  - ***Ion source operated at atmospheric pressure***
    - ***Straightforward sample introduction***
      - ***Contnuous pneumatic nebulization***
      - ***Laser ablation (bulk & spatially resolved analysis of solid samples)***
  - ***High ionization efficiency***
      - ***TIMS: formation of M^+ ions limited to elemnts with IE < 7.5 eV***
  - ***Higher sample throughput***
  - ***Isolation of target element not required ??***

MASS DISCRIMINATION IN MULTI-COLLECTOR ICP – MASS SPECTROMETRY

- ***Same phenomenon as in single-collector ICP-MS***

- ***Due to high precision:***
  - ***Matrix exerts measurable influence on mass discrimination***

    ⇒ <u>isolation</u> of analyte element
  - ***Analyte concentration exerts influence on mass discrimination***

    ⇒ <u>Matching</u> of target element concentrations within ± 30%

MASS DISCRIMINATION CORRECTION IN MULTI-COLLECTOR ICP-MS

If high precision & accuracy is required:

Isolation of target element – pure & quantitative

Matching of element concentration in samples & standards within ± 30%

External correction

Based on comparison of experimental result and certified value for isoropic reference material

Bracketing (std – sample – std – sample – …)

Internal correction – type I

If at least one isotope ratio of the target element is constant in nature

E.g., Sr: isotopic composition displays natural variation, but $^{86}Sr/^{88}Sr$ = constant

Comparison of experimental result and certified value for $^{86}Sr/^{88}Sr$

Calculation of correction factor ε or β, to be used for further correction

Internal correction – type II

Using an element, close in mass number, added to the sample

E.g., Tl added to sample solutions intended for Pb isotopic analysis

Comparison of experimental result and certified value for $^{203}Tl/^{205}Tl$

Calculation of correction factor ε or β, to be used for further correction

MASS DISCRIMINATION CORRECTION IN MULTI-COLLECTOR ICP-MS

Linear law model

$$K = \frac{R_{true}}{R_{obs}} = \left(1 + \varepsilon_{linear} \cdot \Delta m\right)$$

Power law model

$$K = \frac{R_{true}}{R_{obs}} = \left(1 + \varepsilon_{power}\right)^{\Delta m}$$

Exponential law model

$$K = \frac{R_{true}}{R_{obs}} = e^{\left(\varepsilon_{exponential} \cdot \Delta m\right)}$$

Russell's equation

$$K = \frac{R_{true}}{R_{obs}} = \left(\frac{m_1}{m_2}\right)^{\beta}$$

Significant differences !!

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INTERNAL MASS DISCRIMINATION CORRECTION IN MULTI-COLLECTOR ICP-MS

	110/111 R_{exp}/R_{true}	110/112 R_{exp}/R_{true}	110/113 R_{exp}/R_{true}	110/114 R_{exp}/R_{true}	110/116 R_{exp}/R_{true}
No MD	1	1	1	1	1
MD according to linear law ($\varepsilon_{lin} = 0.01$)	0.99010	0.98039	0.97087	0.96154	0.94340
MD according to power law ($\varepsilon_{power} = 0.01$)	0.99010	0.98030	0.97059	0.96098	0.94205
MD according to expontial law ($\varepsilon_{exp} = 0.01$)	0.99005	0.98020	0.97045	0.96079	0.94176
MD according to Russell's equation ($\beta = -1.11053$)	0.99000	0.98019	0.97056	0.96111	0.94272

- ***Application of various correction methods***
  - ***Will result in relatively small differences***
  - ***Significant threat in precise isotope ratio work***
  - ***Still issue of discussion between specialists***

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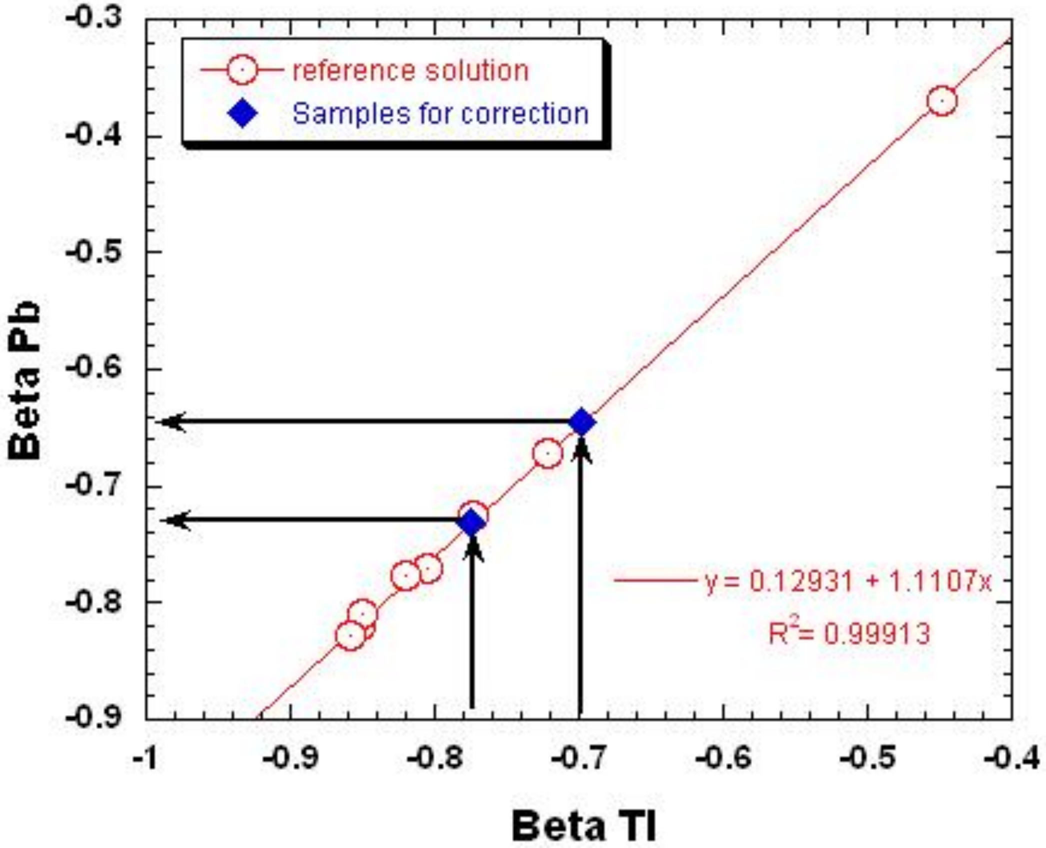
INTERNAL MASS DISCRIMINATION CORRECTION IN MULTI-COLLECTOR ICP-MS



Internal correction – type II

Tl added to sample solutions intended for Pb isotopic analysis

Further refinement: deduction of correction factor β(Pb) via β(Tl)

Linear relationship between β(Pb) and β(Tl) defined via reference solutions

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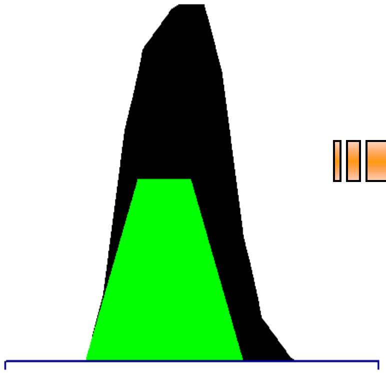
SPECTRAL INTERFERENCES IN MULTI-COLLECTOR ICP – MASS SPECTROMETRY?

- Usually: target element isolated from matrix
  - Clean-up of spectrum
  - No analyte isolation in case of laser ablation for sample introduction
- Ar introduced @ 20 L/min in ICP
  - Ar^+
  - Ar^{2+}
  - Ar-containing molecular ions – ArH^+, ArN^+, ArO^+, ArOH^+, …
- Isotope ratio determination
  - At least two nuclides free from spectral overlap
- High precision
  - Down to 0.002% RSD
  - Limited contribution of interfering ion, already dramatic !
    - In contrast to situation for element determination …

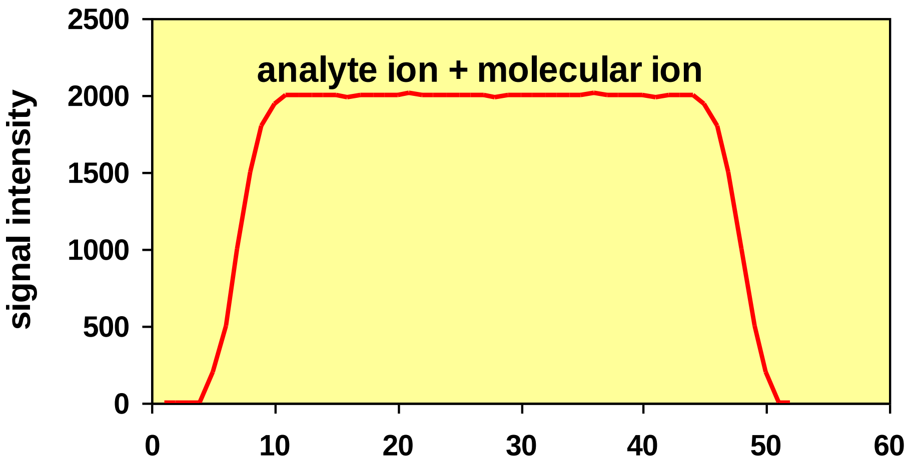
FULL HIGH RESOLUTION IN MULTI-COLLECTOR ICP-MS?

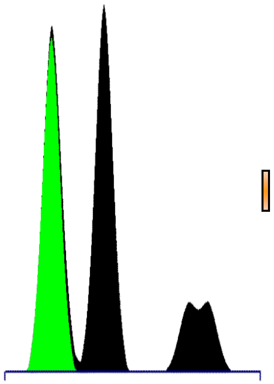
Single-collector ICP-MS

Multi-collector ICP-MS

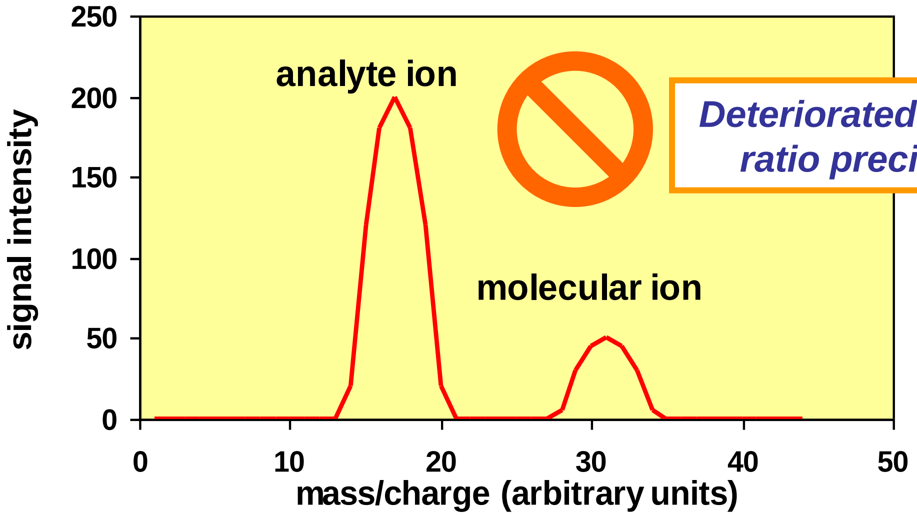


Low R



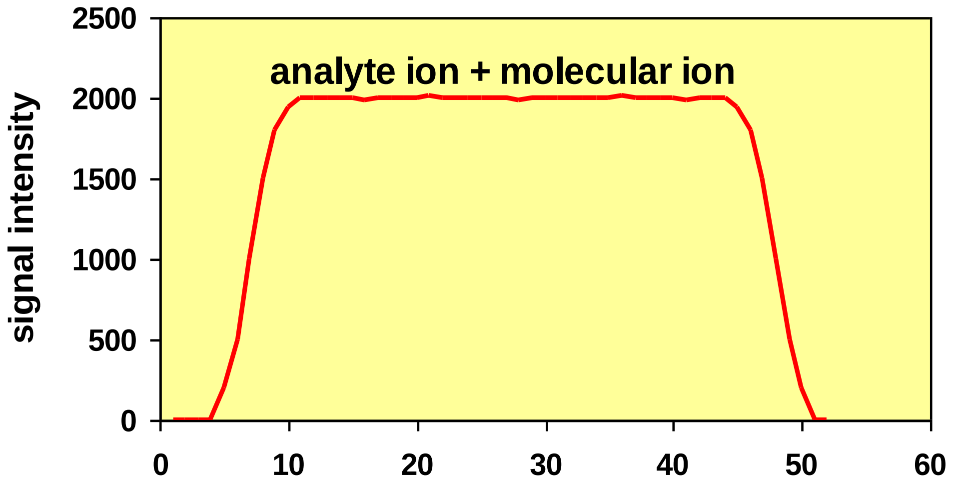


High R



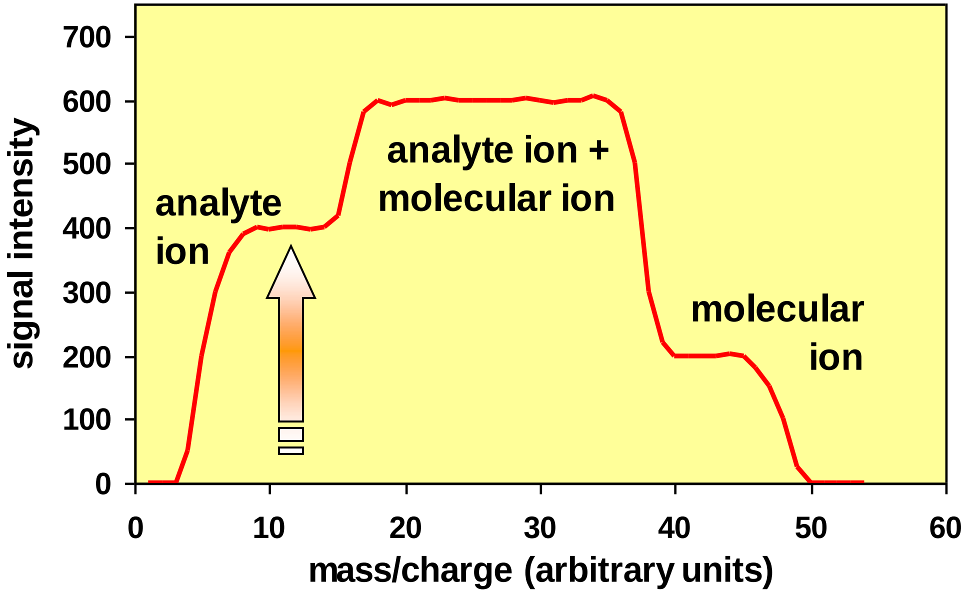
Deteriorated isotope ratio precision !

PSEUDO-HIGH RESOLUTION IN MULTI-COLLECTOR ICP-MS
THE BEST OF TWO WORLDS



Low mass R

down to 0.002% RSD



Pseudo high mass R

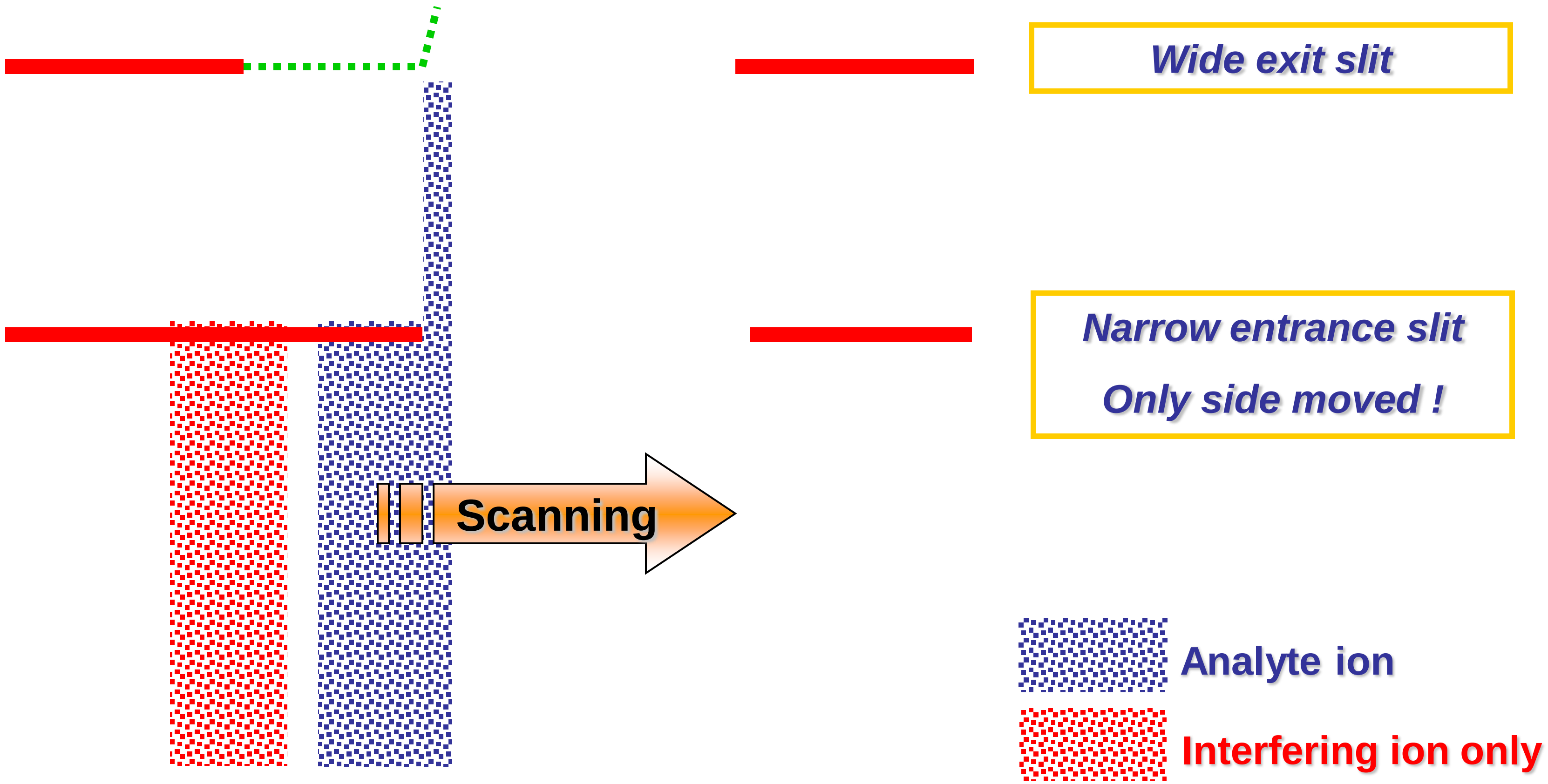
reduced entrance slit width

exit slit width not changed

Interference-free measurement

down to 0.005% RSD

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

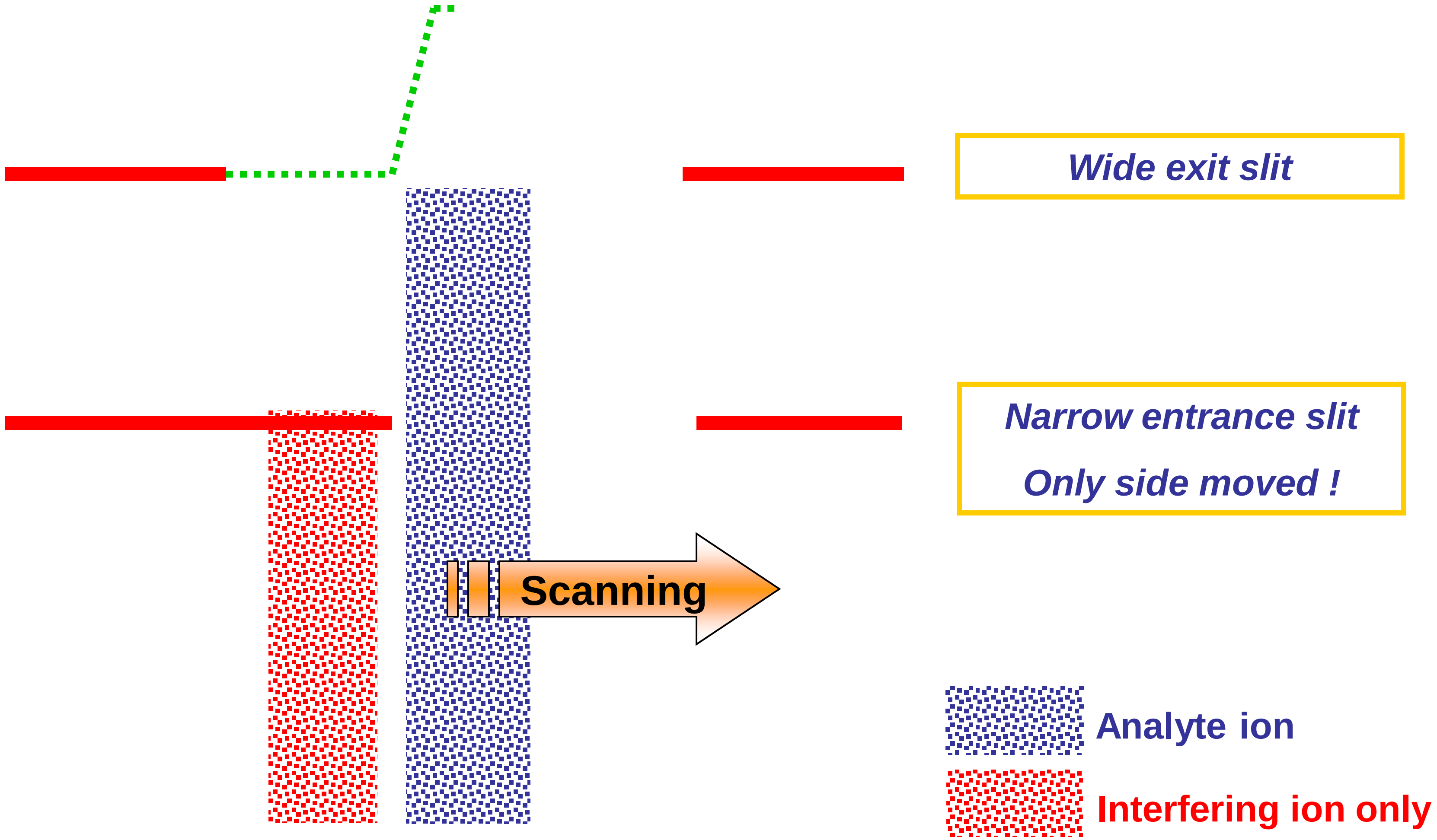
Narrow entrance slit

Only side moved !

▨ Analyte ion

▨ Interfering ion only

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

Narrow entrance slit

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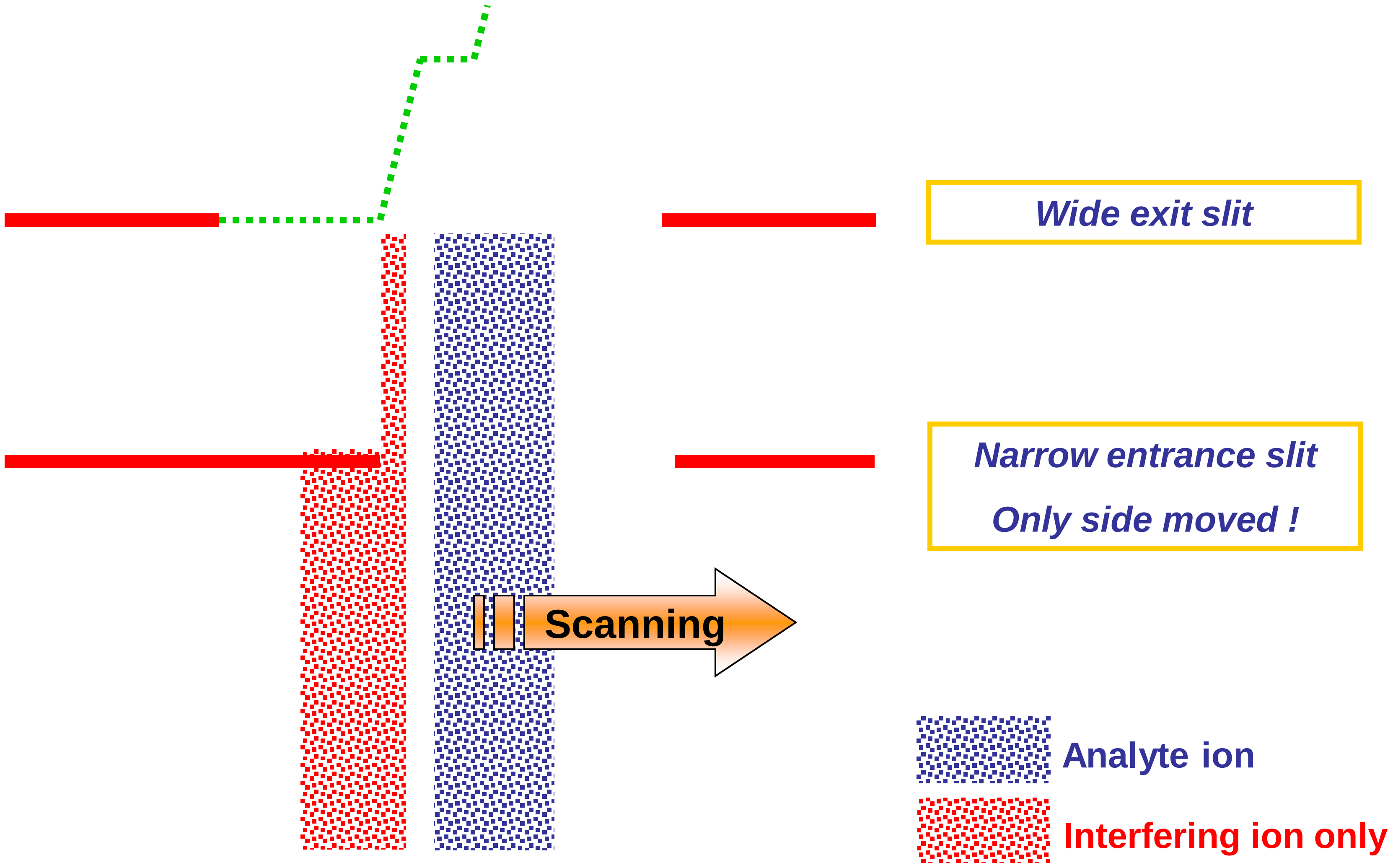
Interfering ion only

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

Narrow entrance slit

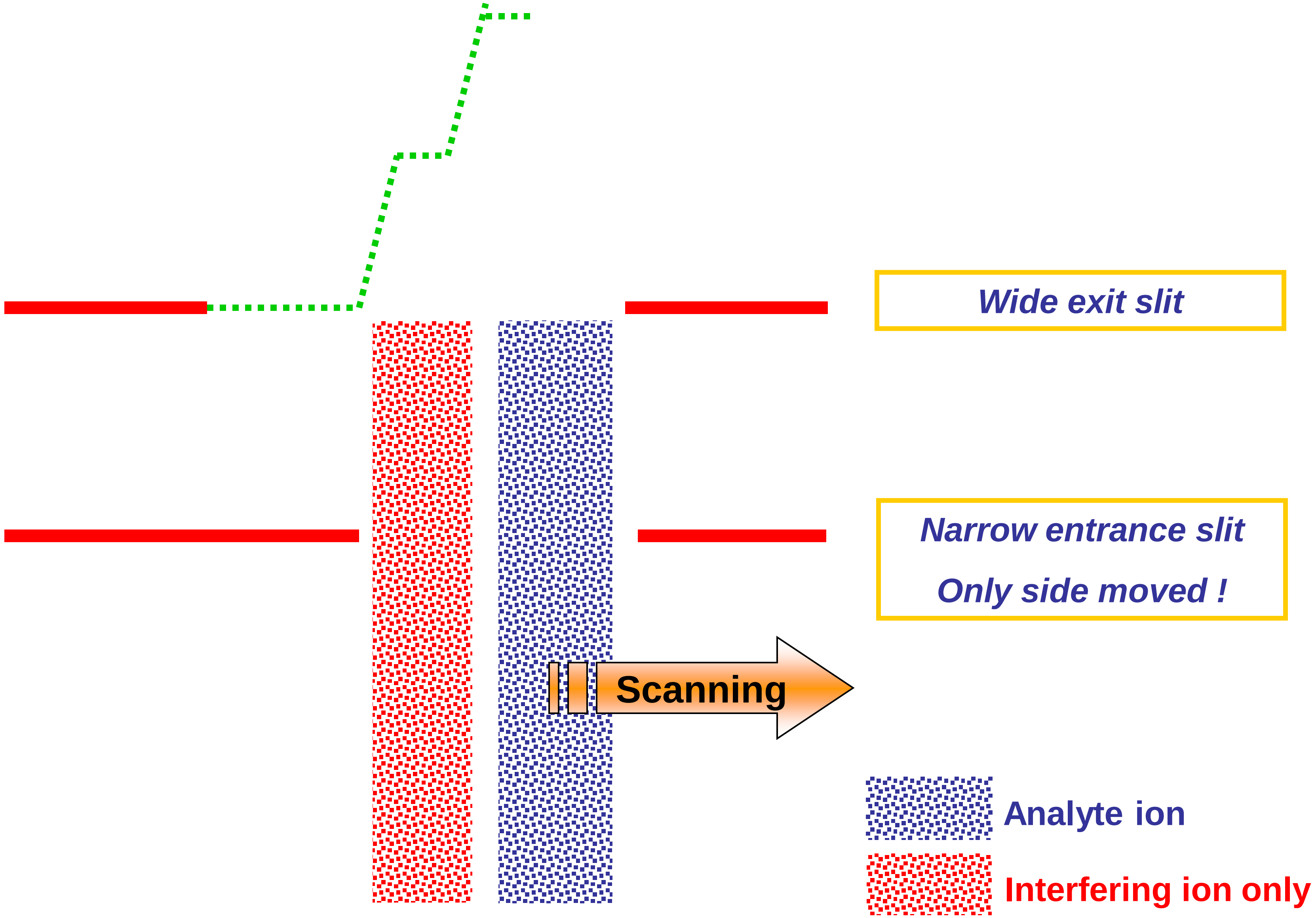
Only side moved !

Scanning

Analyte ion

Interfering ion only

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

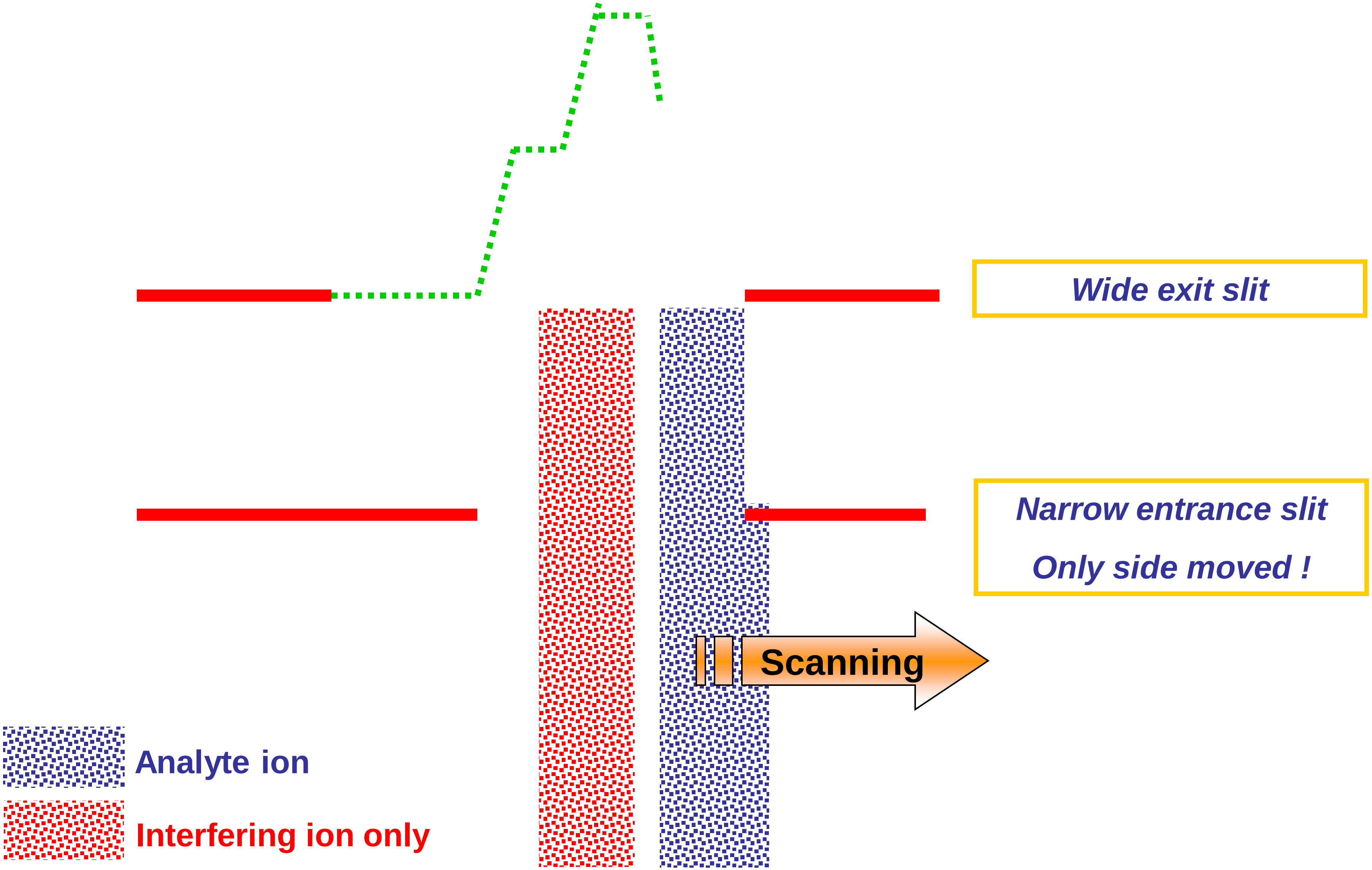
Narrow entrance slit

Only side moved !

Analyte ion

Interfering ion only

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

Narrow entrance slit

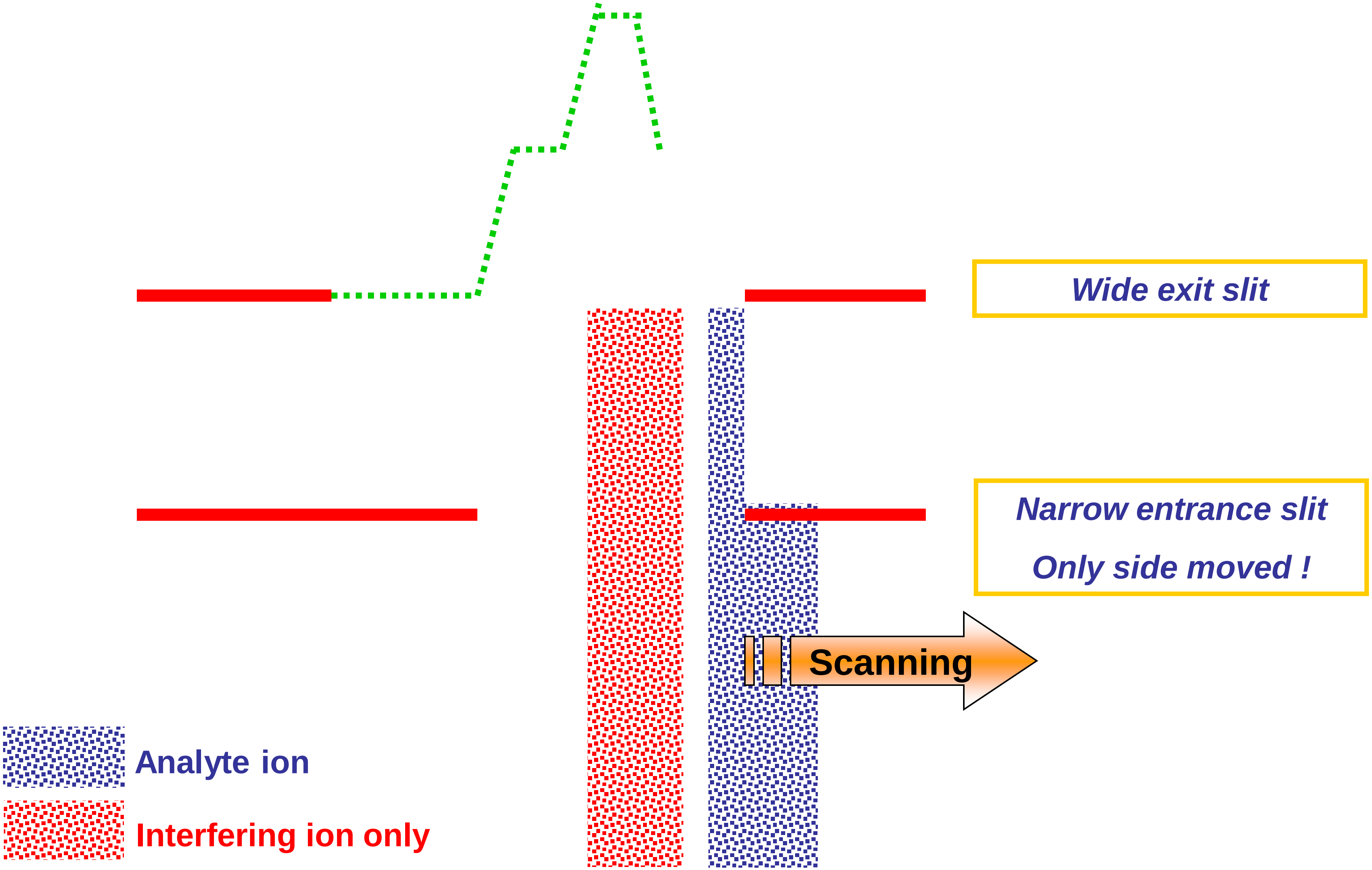
Only side moved !

Scanning

▨ **Analyte ion**

▨ **Interfering ion only**

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

Narrow entrance slit

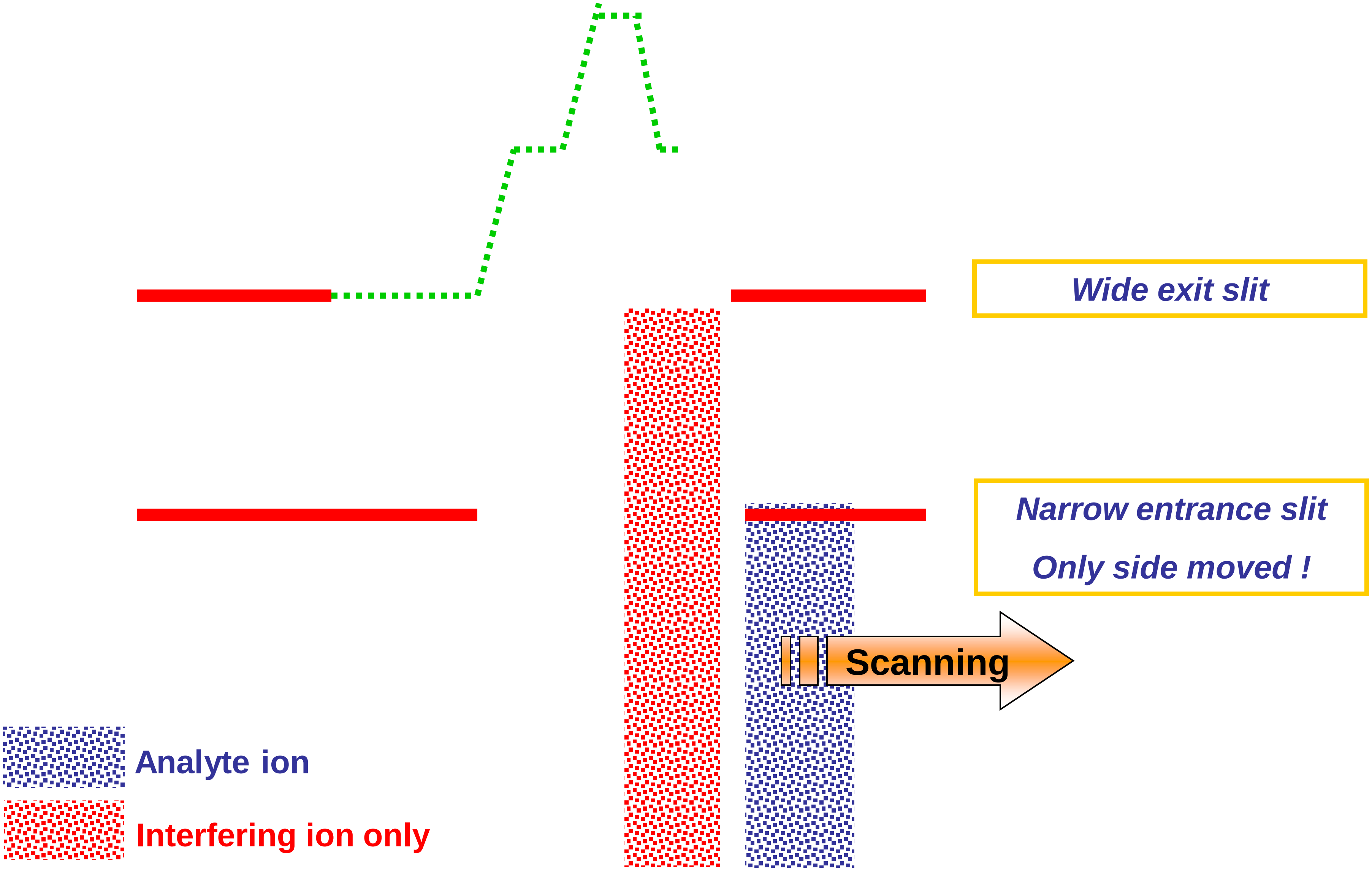
Only side moved !

Scanning

▨ **Analyte ion**

▨ **Interfering ion only**

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

Narrow entrance slit

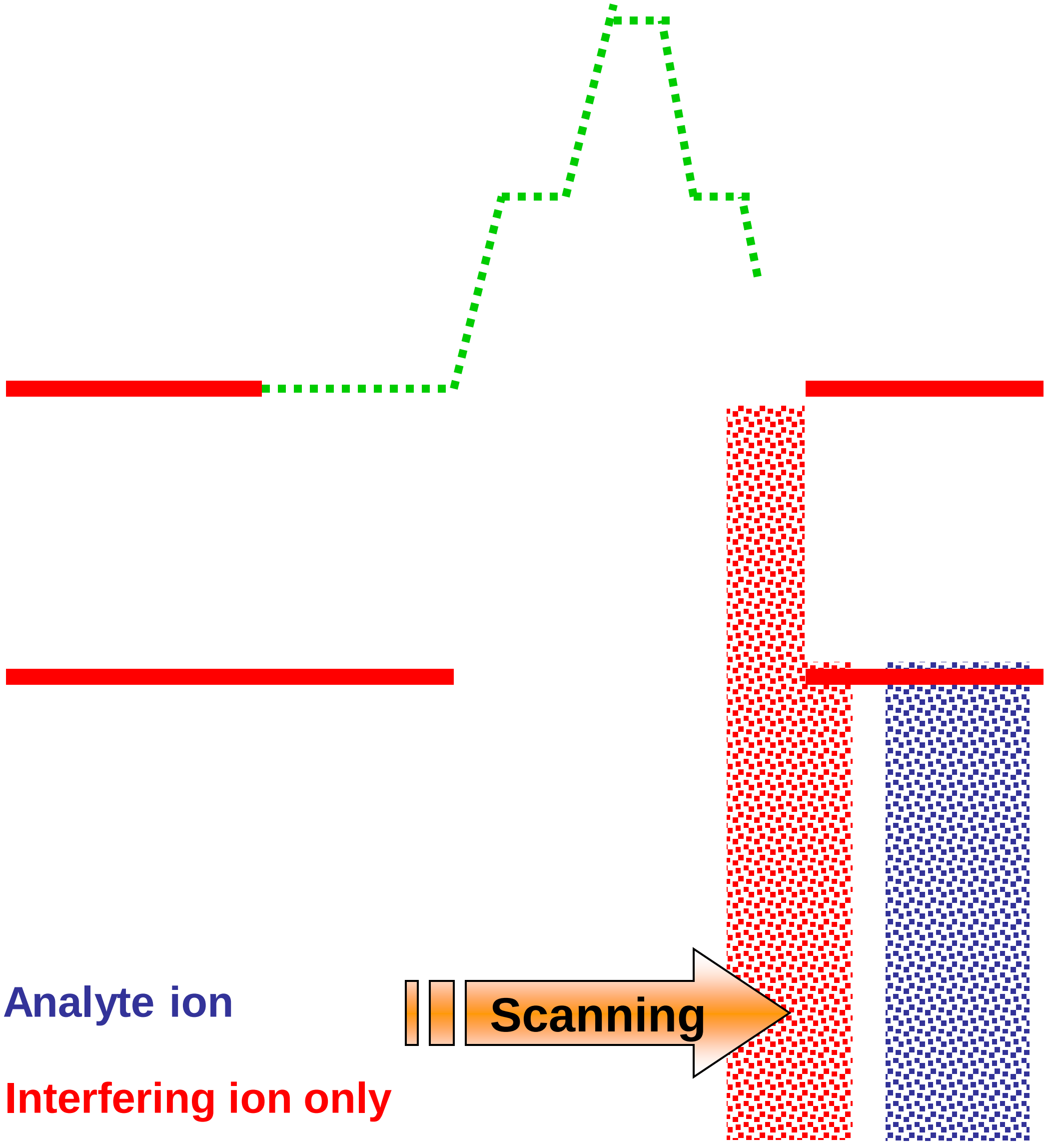
Only side moved !

Scanning

▨ **Analyte ion**

▨ **Interfering ion only**

MASS SPECTRAL PEAK SHAPE
PSEUDO-HIGH MASS RESOLUTION



Wide exit slit

Narrow entrance slit

Only side moved !

Scanning

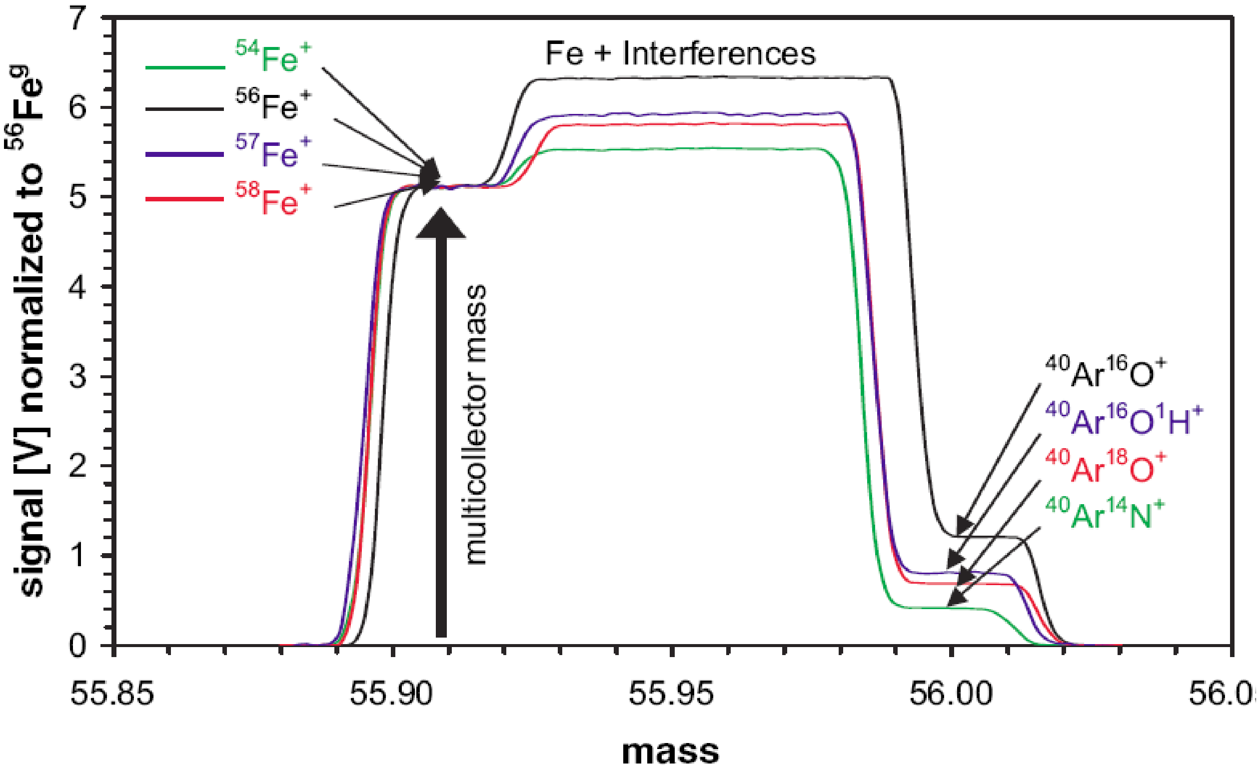
▨ **Analyte ion**

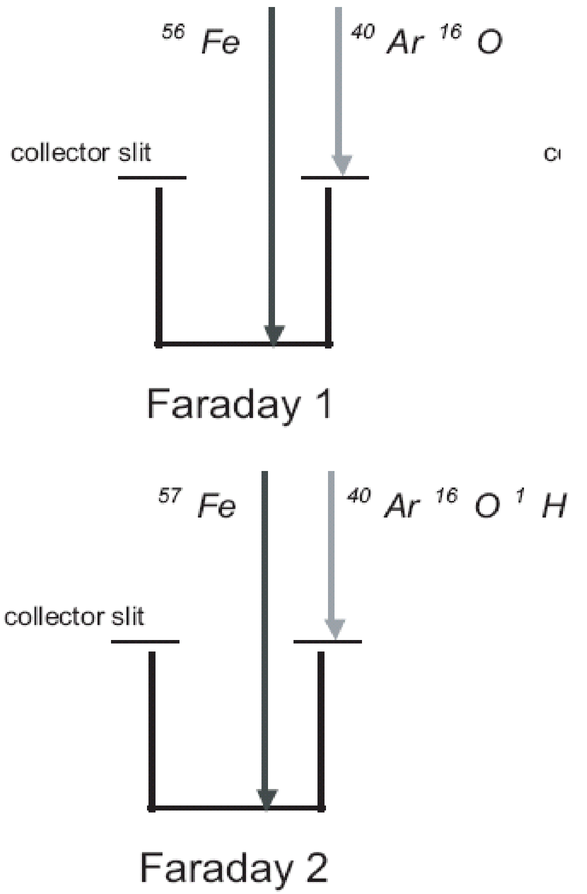
▨ **Interfering ion only**

PSEUDO-HIGH RESOLUTION IN MULTI-COLLECTOR ICP-MS
EXAMPLE: MEASUREMENT OF FE ISOTOPE RATIOS

Spectral scan

Static collection





Interference-free measurement of Fe isotope ratios

Static multi-collection at m/z values where only analyte ions contributes to signal intensity

S. Weyer, & J.B. Schwieters, Int. J. Mass Spectrom., <u>226</u>, 355–368, 2003

NATURAL VARIATION

APPLICATIONS BASED ON RADIOGENIC NUCLIDES

NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF SR

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

$$^{87}\mathrm{Rb} \rightarrow {}^{87}\mathrm{Sr} + \beta^{-} + \bar{\nu}$$

- ***^{87}Rb = naturally occurring, long-lived radionuclide***
  - ***$T_{1/2}$ = 48.8 x 10^9 y***
  - ***Isotopic composition of Rb has changed through time***
  - ***Isotopic composition odf 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 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

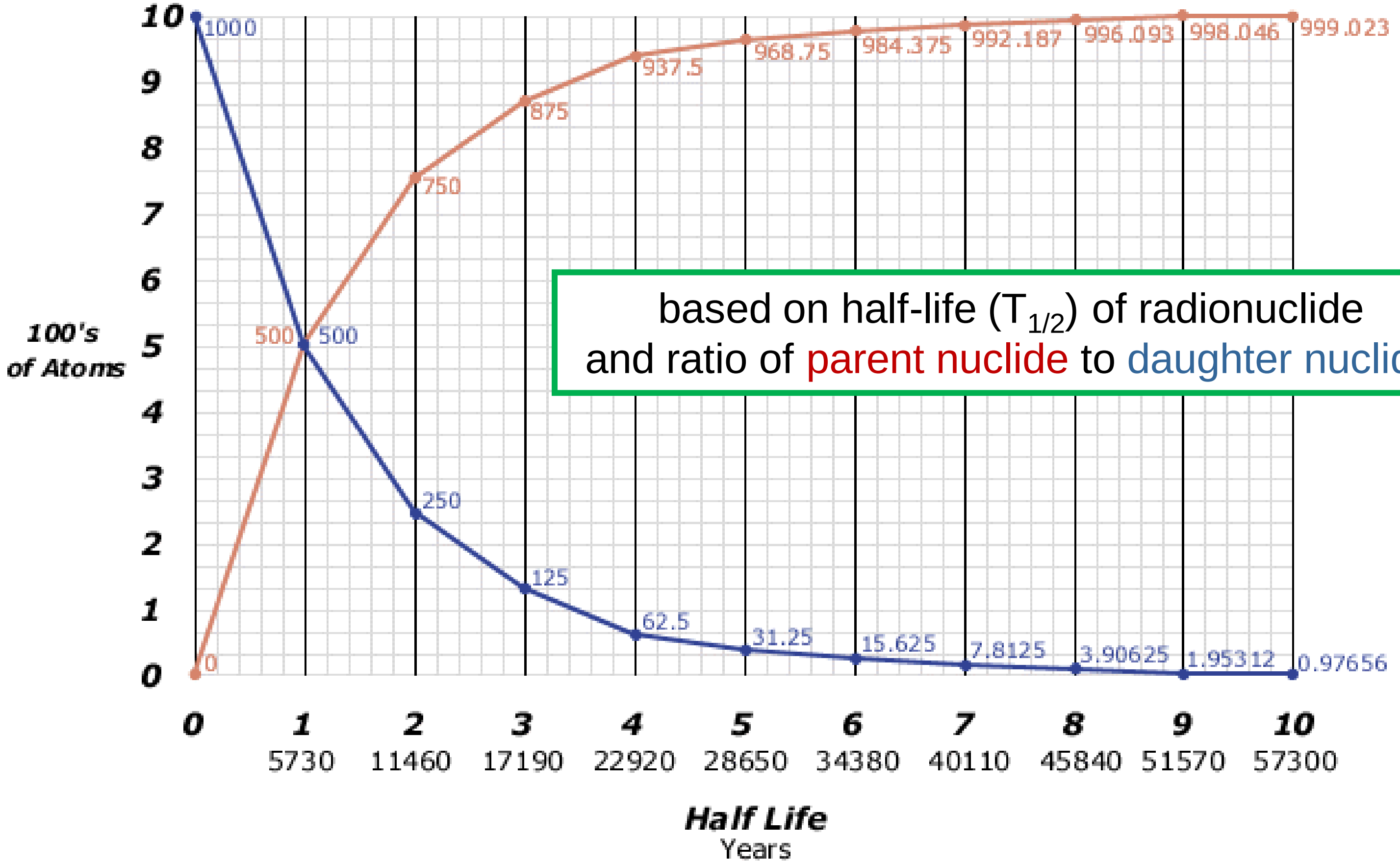
NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF SR

- ***Pronounced variation!***
  - ***Measurable by***
    - ***TIMS***
    - ***MC-ICP-MS***
    - ***Single-collector ICP-MS***
- ***Sr isotopic analysis useful for:***
  - ***Provenance determination***
    - ***Agricultural products***
      - ***Wine, cheese, …***
    - ***Human remains***
      - ***Archeological findings***
      - ***Forensics***
    - ***…***
  - ***Geological dating - Rb-Sr dating***

quite often with single-collector ICP-MS

very seldom with single-collector ICP-MS

RADIOMETRIC DATING



based on half-life ($T_{1/2}$) of radionuclide
and ratio of parent nuclide to daughter nuclide

UNIVERSITEIT
GENT

RB-SR DATING

$$^{87}Rb \rightarrow {}^{87}Sr + \beta^{-} + \bar{v}, \text{ with } T_{1/2} = 48.8 \cdot 10^{9}\, y, \text{ or } \lambda = \frac{\ln 2}{T_{1/2}} = 1.42 \cdot 10^{-11}$$

- **Possibilty for dating (t-determination)**
  - **Igneous & metamorphic rocks, via**
    - **Rb-rich minerals they contain**
    - **whole rock dating**
  - **Production of ^{87}Sr as function(t):** $^{87}Sr = \left(^{87}Sr\right)_i + {}^{87}Rb \cdot (e^{\lambda t} - 1)$
  - **Absolute isotope amounts are difficult to determine accurately**
  - **Divide left & right side by ^{86}Sr**
    - **Note: ^{86}Sr does not vary as function(t)**

$$\frac{^{87}Sr}{^{86}Sr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_i + \frac{^{87}Rb}{^{86}Sr} \cdot (e^{\lambda t} - 1)$$

  - **Resolve equation for t:**

$$t = \left(\frac{1}{\lambda}\right) \cdot \ln\left(1 + \frac{^{86}Sr}{^{87}Rb} \cdot \left[\left(\frac{^{87}Sr}{^{86}Sr}\right) - \left(\frac{^{87}Sr}{^{86}Sr}\right)_i\right]\right)$$

RB-SR DATING

- **Based on:**

$$t = \left(\frac{1}{\lambda}\right) \cdot \ln\left(1 + \frac{^{86}Sr}{^{87}Rb} \cdot \left[\left(\frac{^{87}Sr}{^{86}Sr}\right) - \left(\frac{^{87}Sr}{^{86}Sr}\right)_i\right]\right)$$

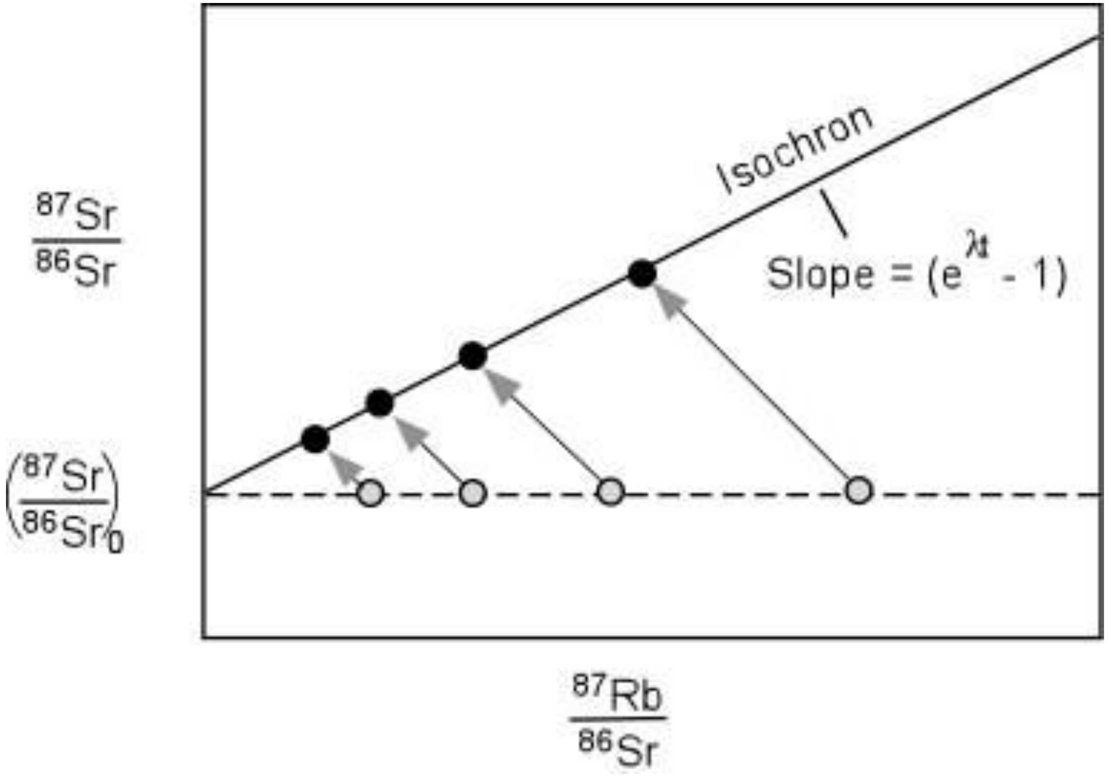
- **Needed?**
  - Rb/Sr elemental ratio
    - Traditionally determined via IDMS (accuracy & precision)
  - $^{87}Sr/^{86}Sr$ isotope ratio
    - TIMS, MC-ICP-MS, ICP-MS
  - $(^{87}Sr/^{86}Sr)_{initial}$
- **Condition?**
  - System has always been closed with respect to Rb & Sr
- **In practice?**
  - Isochron dating

RB-SR ISOCHRON DATING

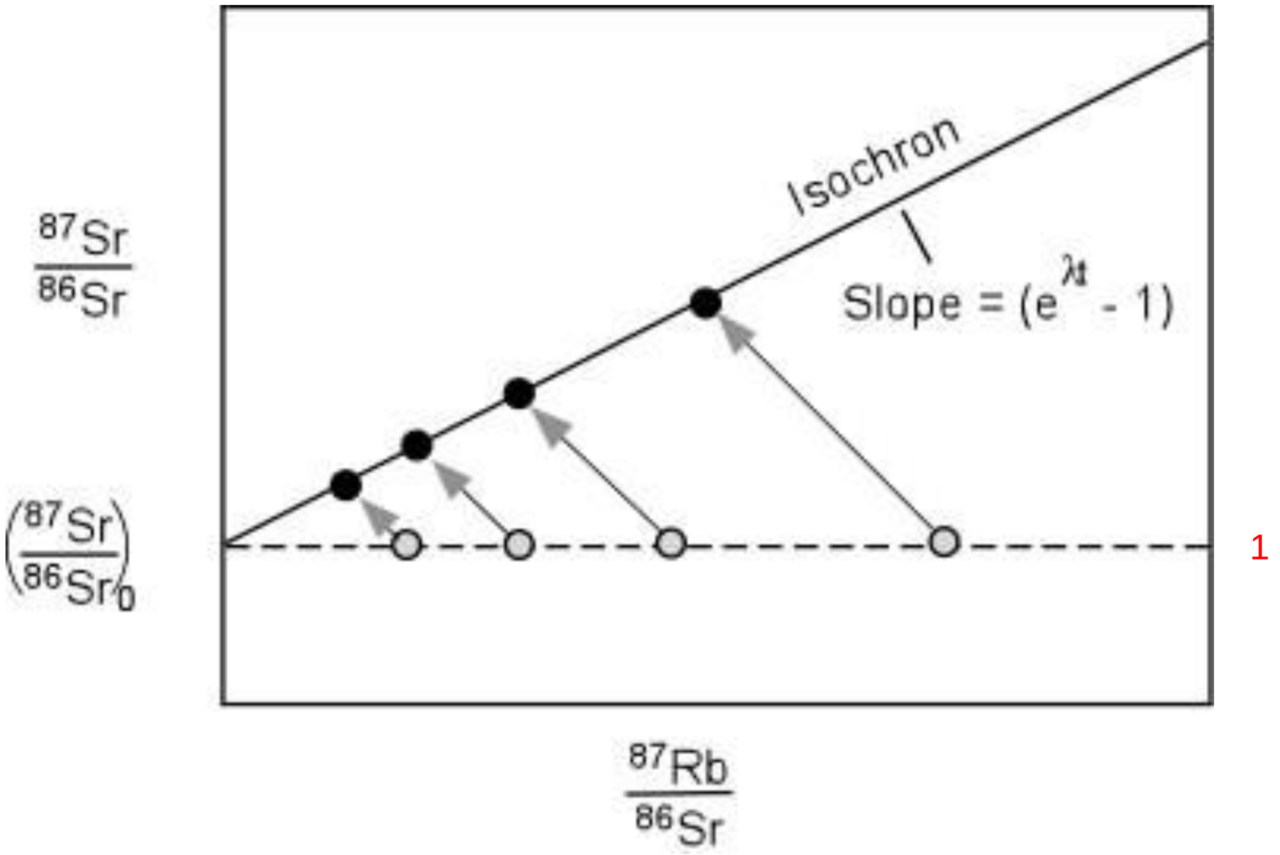
$$\frac{{}^{87}Sr}{{}^{86}Sr} = \left(\frac{{}^{87}Sr}{{}^{86}Sr}\right)_i + \frac{{}^{87}Rb}{{}^{86}Sr} \cdot (e^{\lambda t} - 1)$$

- ***Is equation for straight line: y = a + bx***
  - ***With y = ^{87}Sr/^{86}Sr and x = ^{87}Rb/^{86}Sr***

isochron

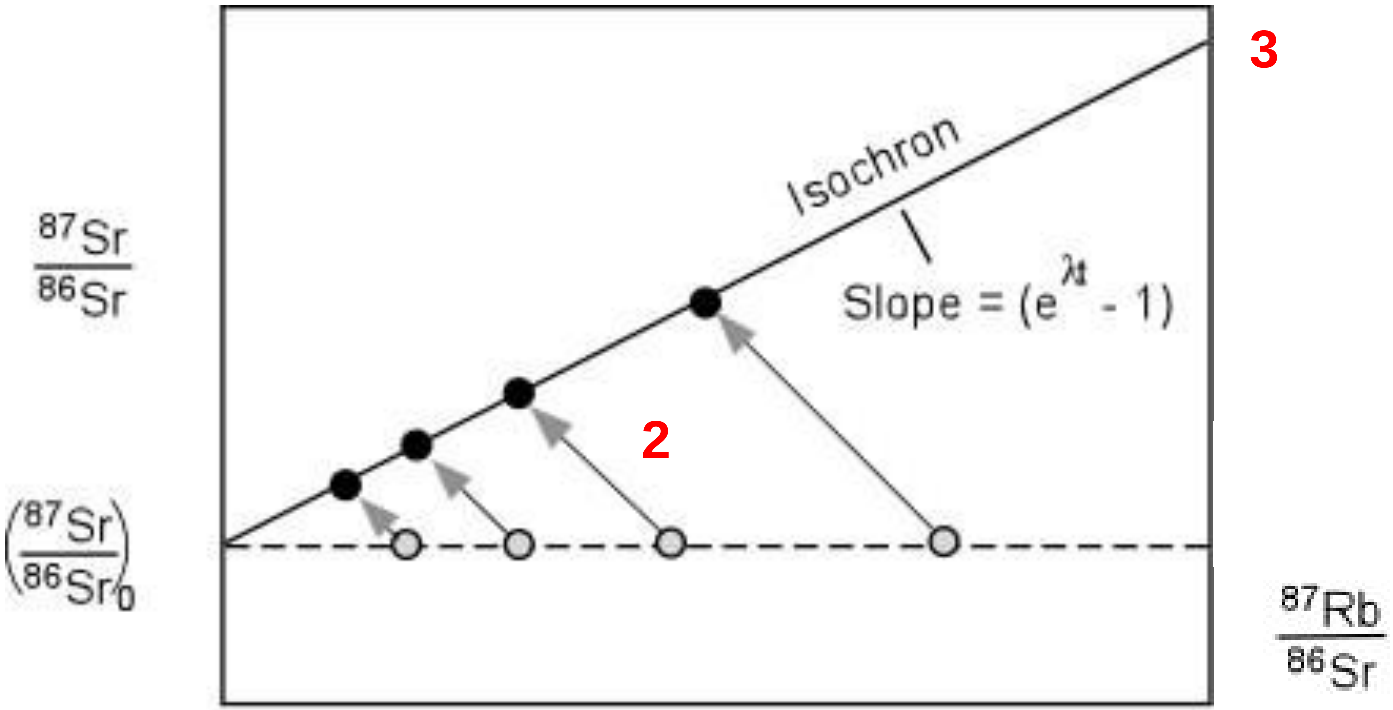


RB-SR ISOCHRON DATING



***1**: at the time of the genesis of the rock, all of its minerals display the same ^{87}Sr/^{86}Sr isotope ratio*

RB-SR ISOCHRON DATING



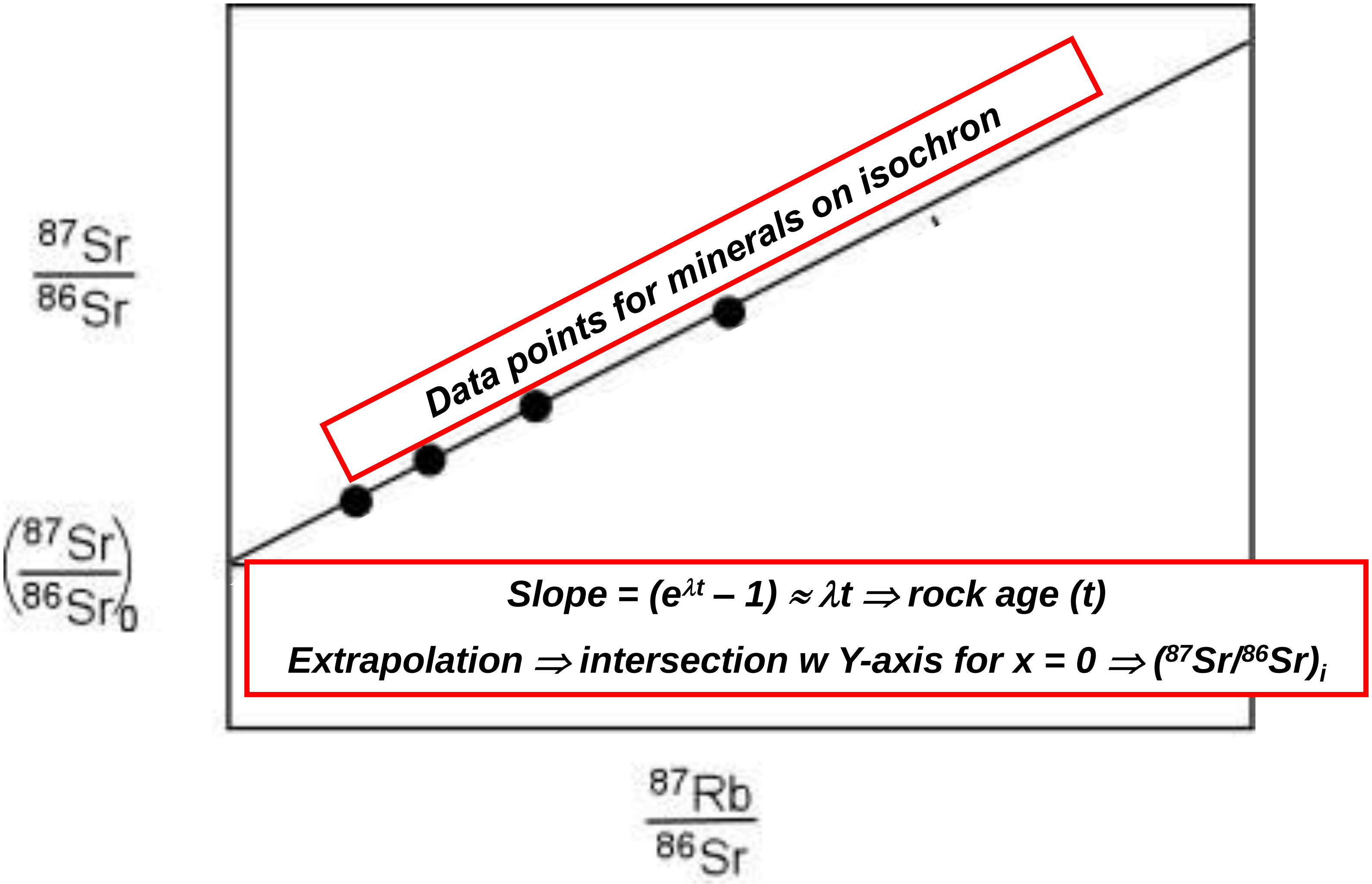
2: as the rock ages, ^{87}Rb decays into ^{87}Sr $\Rightarrow$

the Rb concentration decreases & the Sr concentration increases

the ^{87}Sr/^{86}Sr isotope ratio increases

Data points for all minerals remain on one straight line = isochron (3)

RB-SR ISOCHRON DATING IN PRACTICE



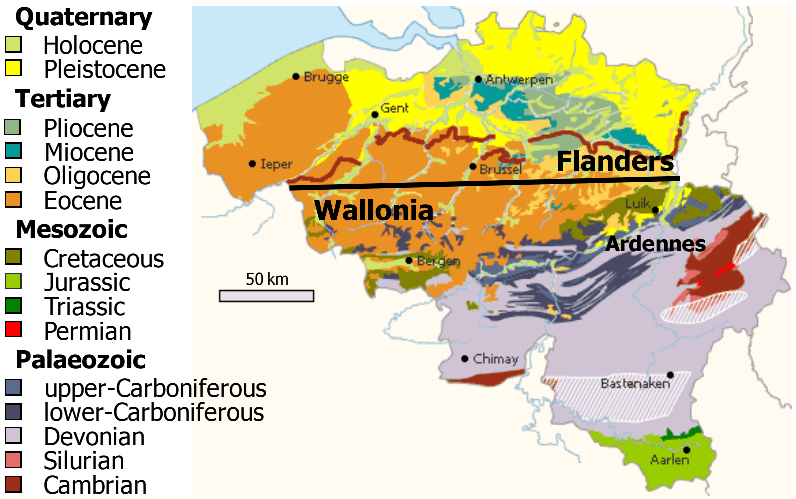
Data points for minerals on isochron

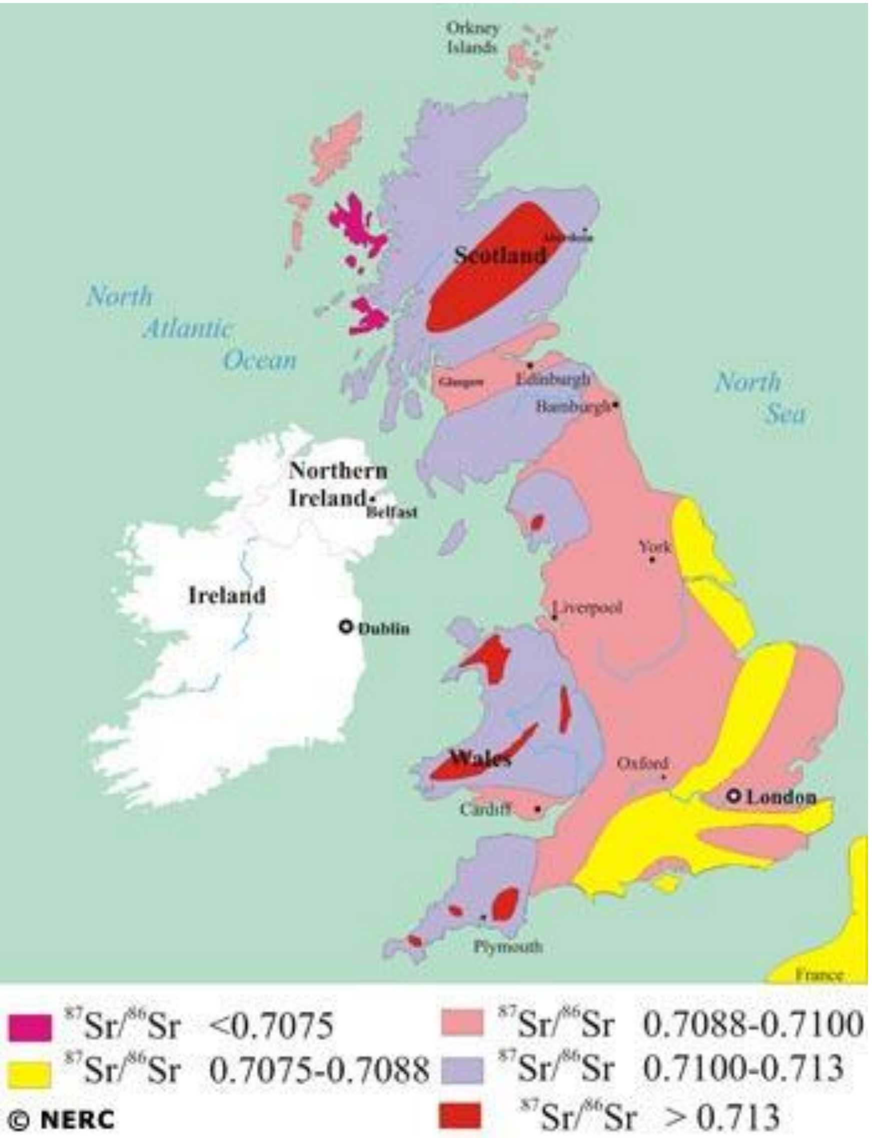
Slope = $(e^{\lambda t} - 1) \approx \lambda t \Rightarrow$ rock age (t)

Extrapolation $\Rightarrow$ intersection w Y-axis for x = 0 $\Rightarrow (^{87}Sr/^{86}Sr)_i$

PROVENANCE DETERMINATION VIA SR ISOTOPIC ANALYSIS

- ***Varying geology***
- ***Varying Sr isotopic composition***
- ***Sr isotopic composition, same for:***
  - ***Rocks***
  - ***Soil***
  - ***Vegetation***
  - ***Cattle***
  - ***….***



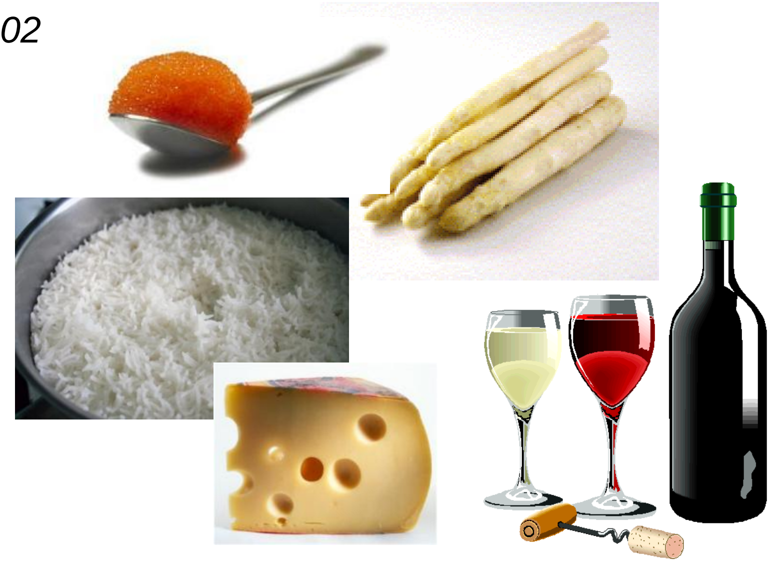


NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF SR – PROVENANCE DETERMINATION OF AGRICULTURAL PRODUCTS

Transfer of Sr without measurable isotopic fractionation

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

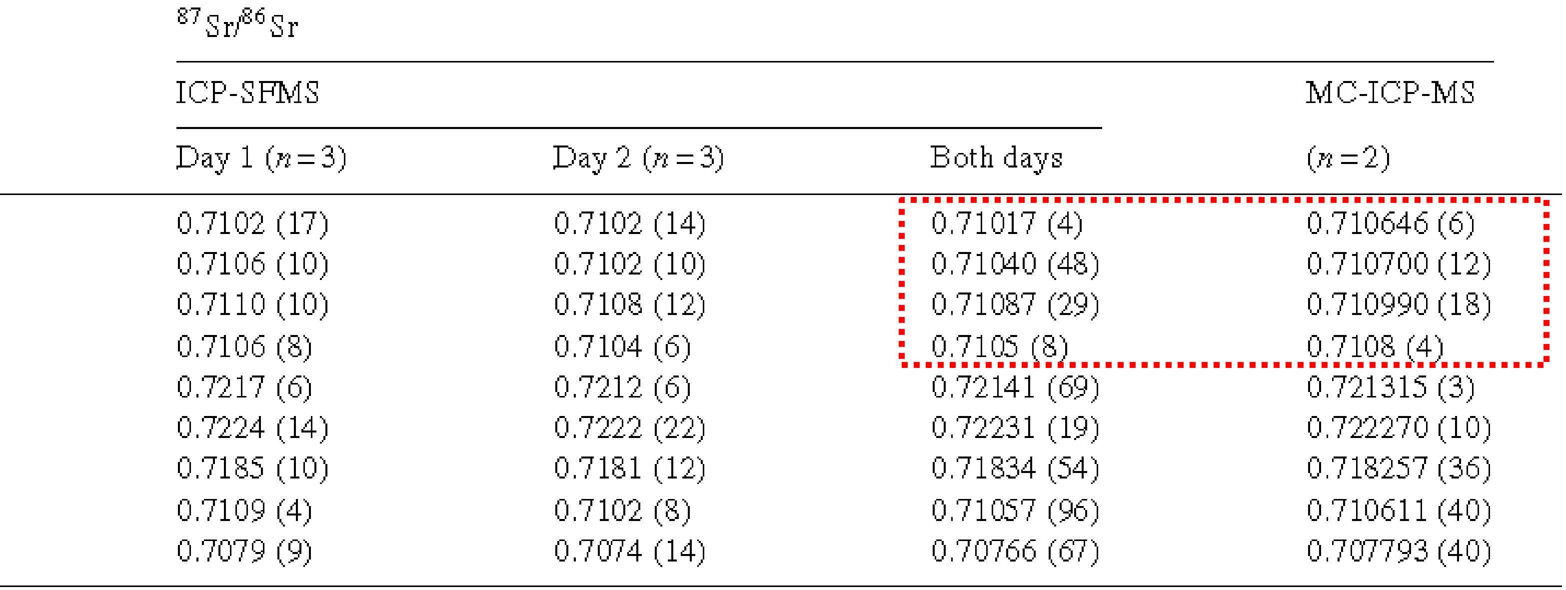
- ***Provenancing agricultural products ?***
  - ***To detect incorrect indication of geographical origin (fraud)***
- ***Which products?***
  - ***Of plant origin:***
    - ***Wine:*** *Almeida & Vasconselos, JAAS, 2001, Barbaste et al., JAAS, 2002*
    - ***Cider:*** *Garcia-Ruiz et al., ACA, 2007*
    - ***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

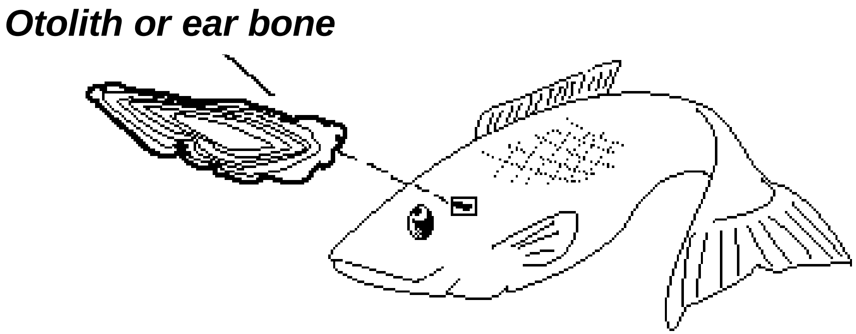
RODUSHKIN ET AL., ACA, 583, 310, 2007

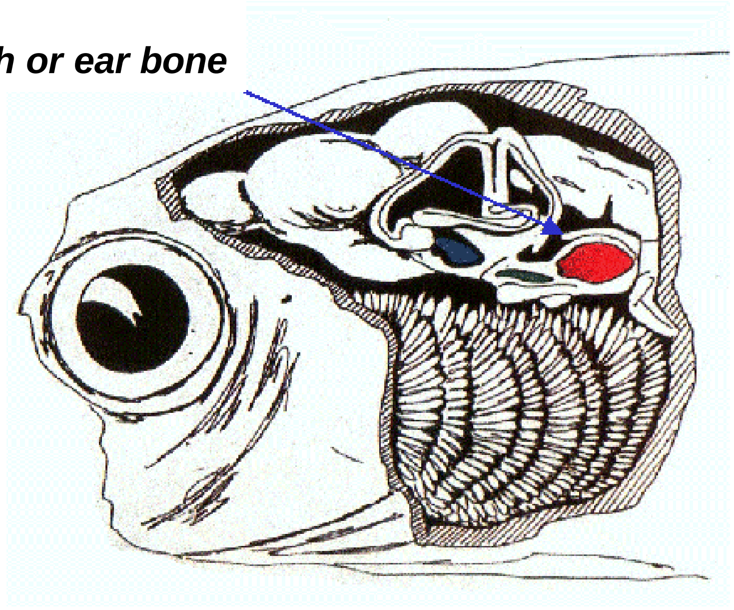
$^{87}Sr/^{86}Sr$:
seasonal variation Kalix
< geographical variation
complemented with:
trace element fingerprint
Os isotopic analysis



	$^{87}Sr/^{86}Sr$			
	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)

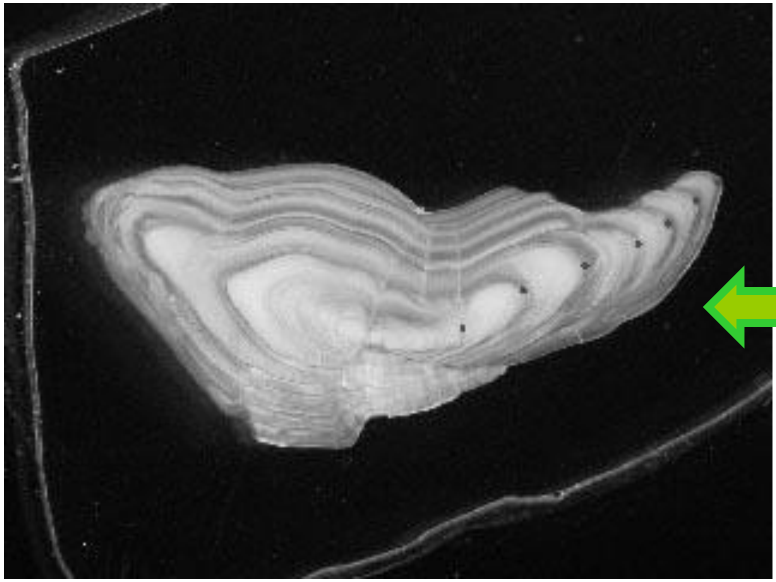
SR ISOTOPIC ANALYSIS OF FISH OTOLITHS FOR DISCOVERING FISH MIGRATION PATHS



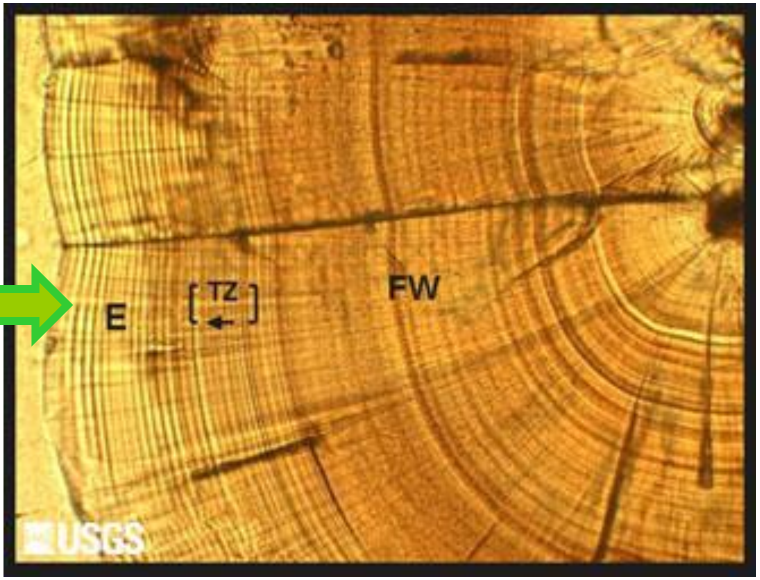


- ***Otoliths or "ear bones" consist of three pairs of small carbonate bodies that are found in the head of teleost (bony) fish. Otoliths are primarily associated with balance, orientation and sound detection, and function similarly to incus, malleus and stapes in the inner ear of mammals***
- ***An otolith's ring structure can provide information about an individual's age, growth rate, and environment. In some cases, these patterns are a natural record; in other cases they are induced by man.***

SR ISOTOPIC ANALYSIS OF FISH OTOLITHS FOR DISCOVERING FISH MIGRATION PATHS



Fish otolith with growth rings



Tree rings

Occurrence of growth rings ⇒ Chronological archive

⇒

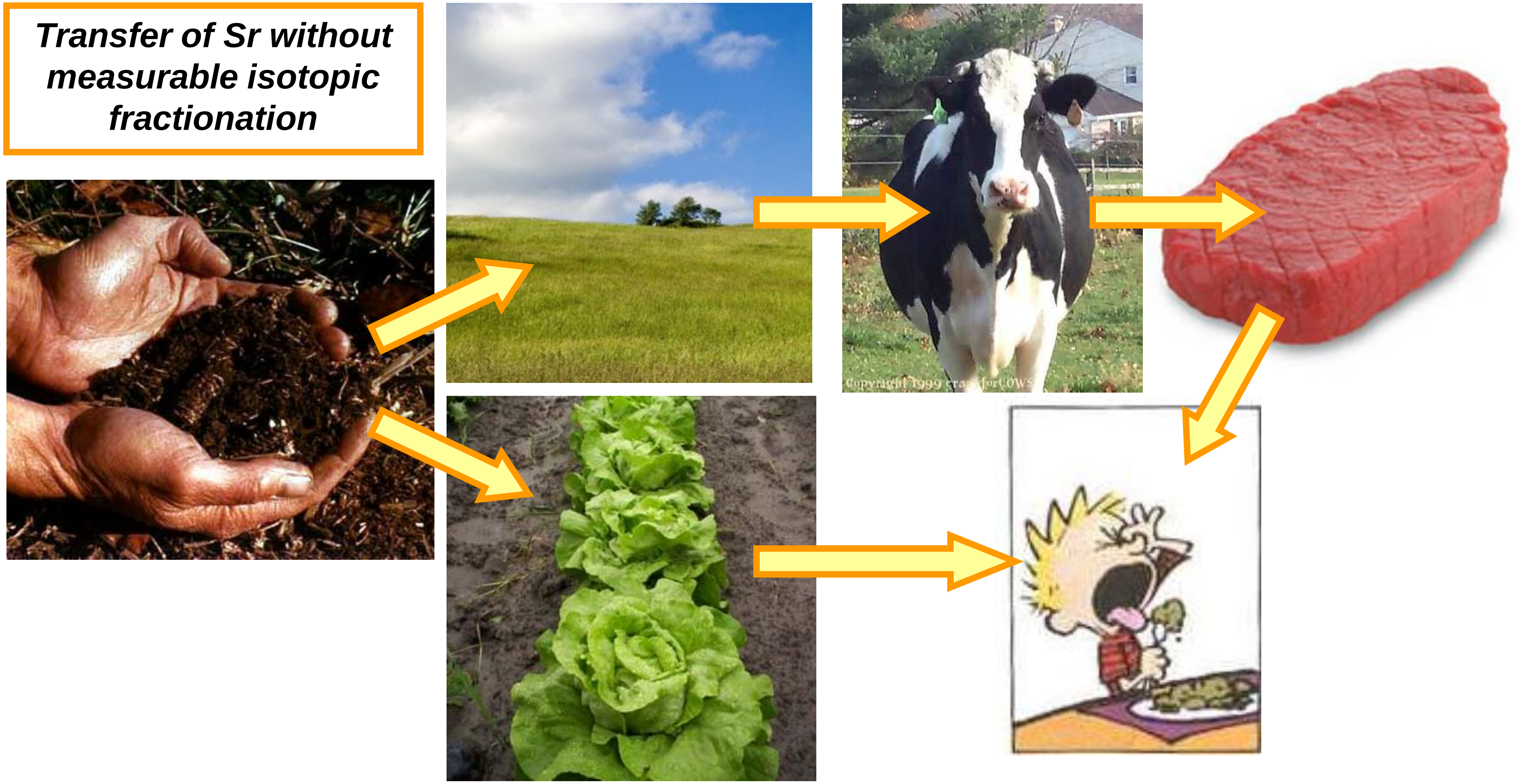
Spatially resolved Sr isotopic analysis via laser ablation MC-ICP-MS

⇒

Reveals migration pathways with sub-annual resolution

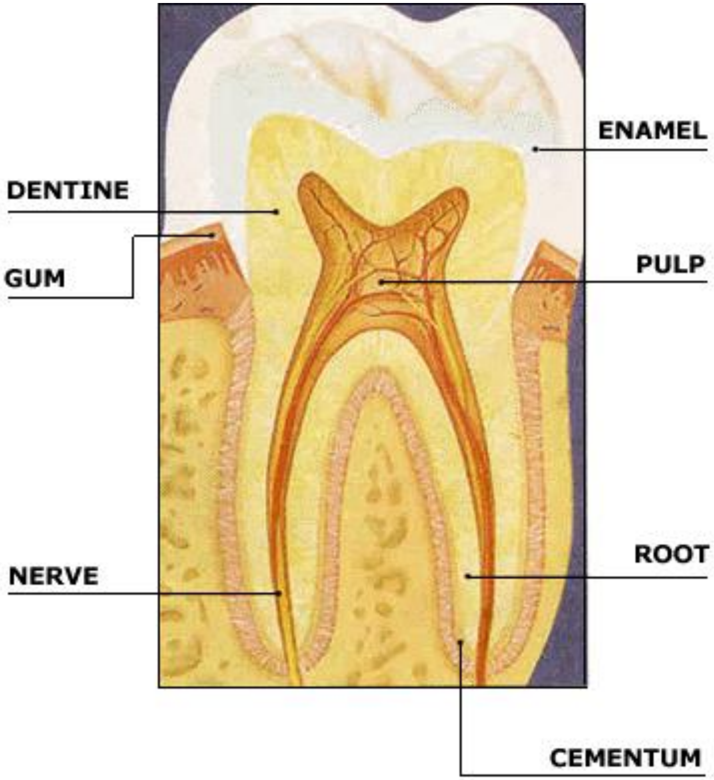
Outridge et al., Environ. Geol., 2002, 42, 891-899

Natural variations in the isotopic composition of Sr – Provenance determination of agricultural products



Transfer of Sr without measurable isotopic fractionation

SR ISOTOPIC ANALYSIS FOR PROVENANCE DETERMINATION OF HUMAN REMAINS



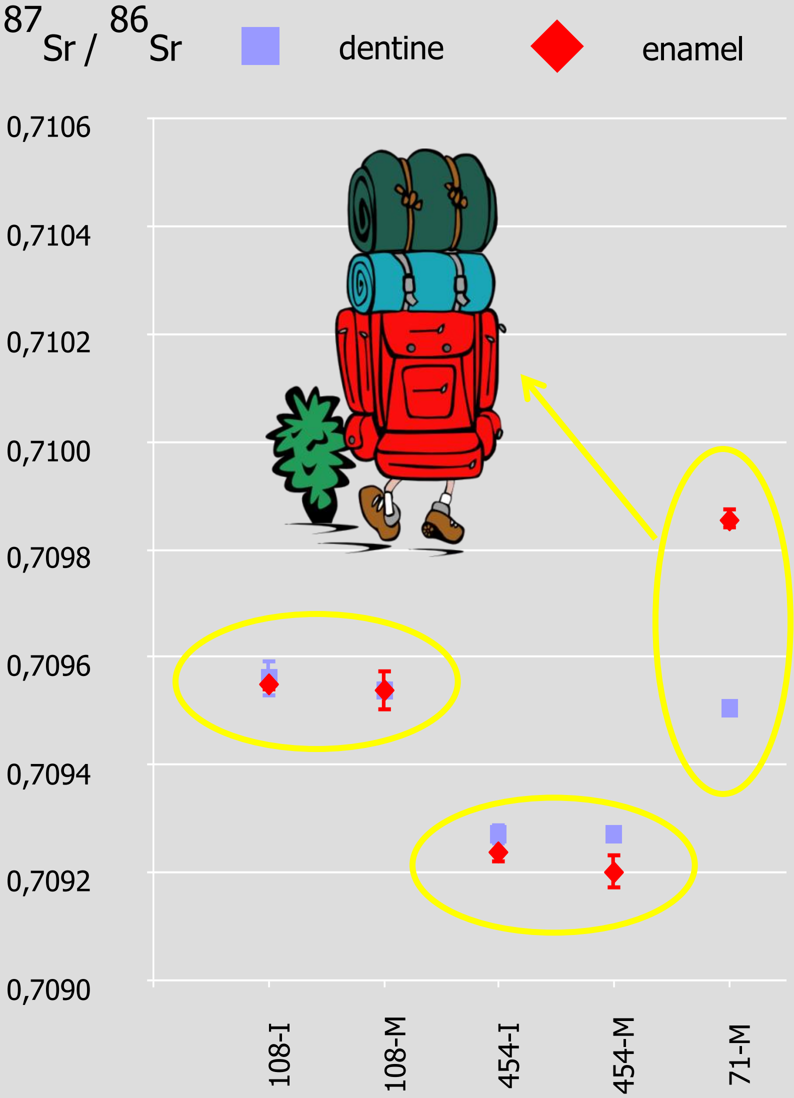
- ***Enamel***
  - ***Formed during early childhood***
  - ***$^{87}Sr/^{86}Sr$ ~ food age 1 – 10***
- ***Dentine***
  - ***Continuously renewed***
  - ***Faster Sr turnover rate***
  - ***$^{87}Sr/^{86}Sr$ ~ food last years***
- ***Useful info***
  - ***Archaeology***
  - ***Forensics***

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 – HNO_3 & HCl)***
  - ***Isolation of Sr using Sr-spec (Eichrom Technologies)***
  - ***Sr isotopic analysis using multi-collector ICP-MS***

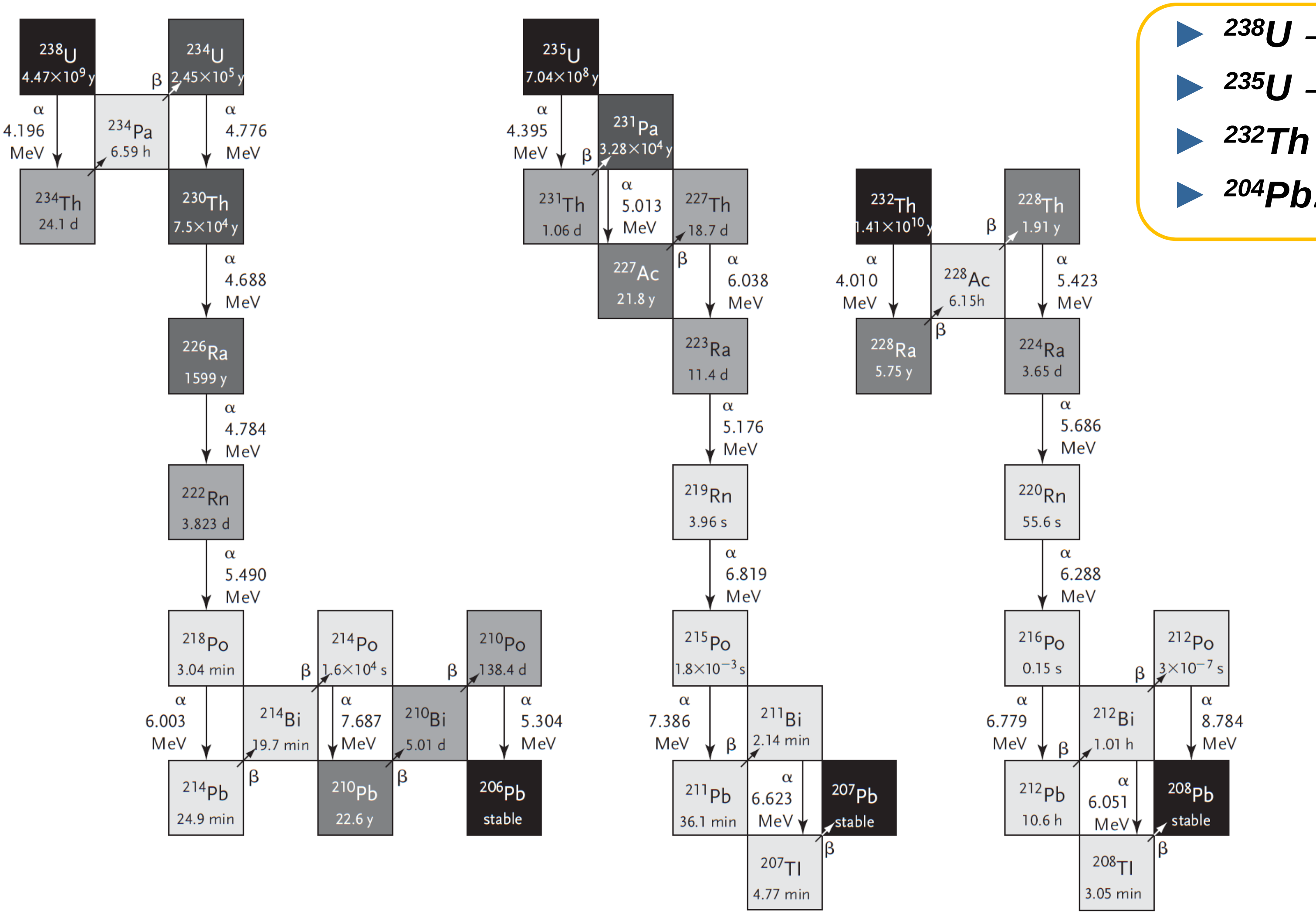
SR ISOTOPIC ANALYSIS FOR PROVENANCE DETERMINATION OF HUMAN REMAINS



←*Pandhof population*

I: incisor, M: molar

NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF PB

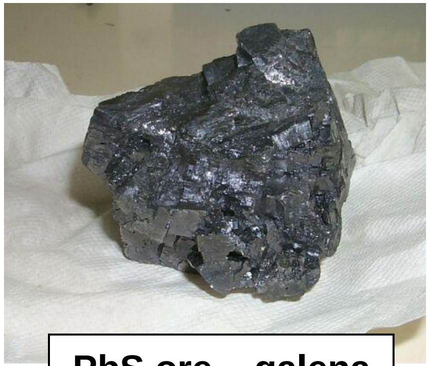


- ***^{238}U → ^{206}Pb***
- ***^{235}U → ^{207}Pb***
- ***^{232}Th → ^{208}Pb***
- ***^{204}Pb: not radiogenic***

B. Bourdon *et al*, Rev. Miner. Geochem, 52, 1-19, 2003.

NATURAL VARIATIONS IN THE ISOTOPIC COMPOSITION OF PB

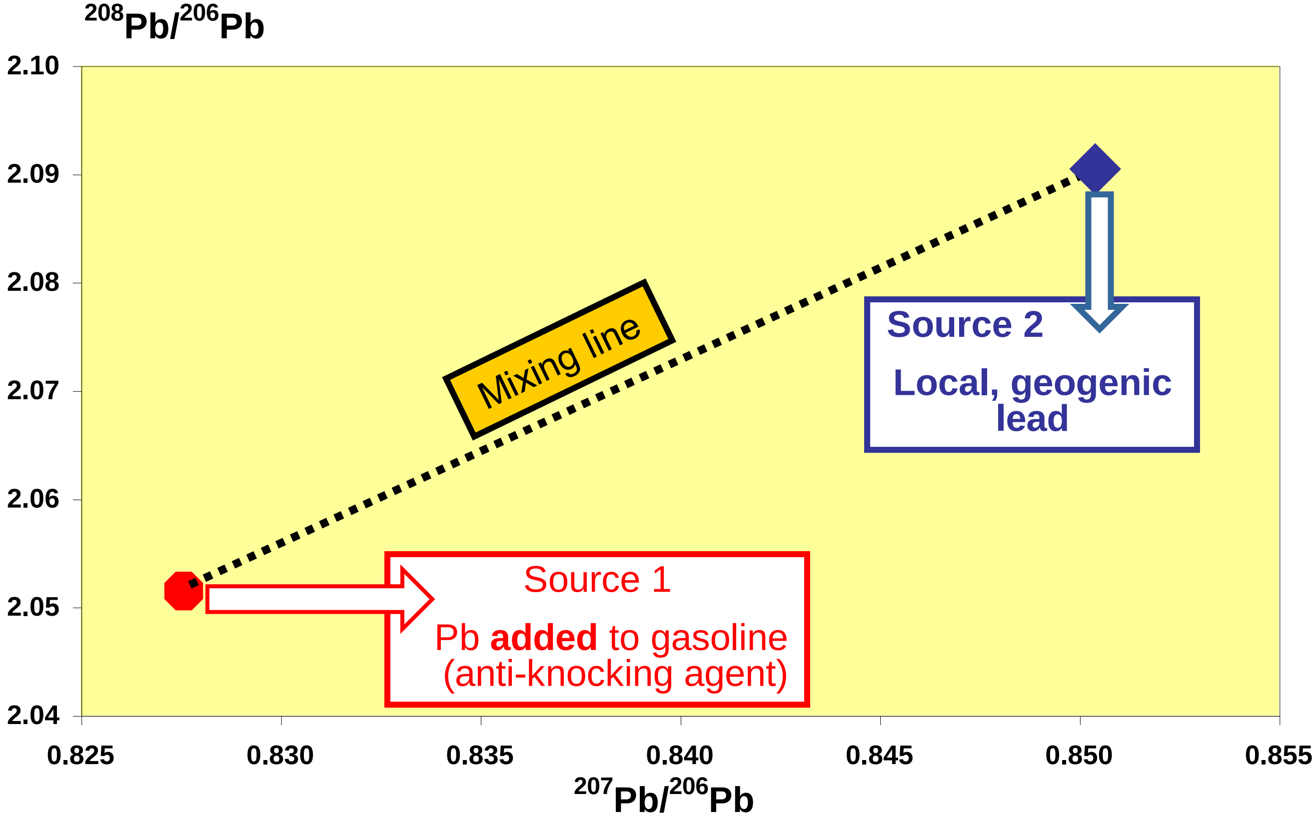
- *Pronounced variation!*
  - *Measurable by TIMS, MC-ICP-MS, single-collector ICP-MS*
- *Pb in the earth's crust*
  - *Shows isotopic variation*
  - $^{206}Pb/^{207}Pb \sim 1.20$
- *Pb in ores*
  - *Ore formation ⇒ separation of Pb from Th & Pb*
    - *Isotopic compostion of Pb "frozen"*
  - *≠ mines show ≠ Pb isotopic composition:*
    - *Time of ore deposit formation*
    - *U/Pb, Th/Pb ratio in parent material*
- *Isotope ratio applications ?*
  - *Distinction between crustal Pb & ore-Pb*
  - *Distinction between Pb (ores) of different provenance*



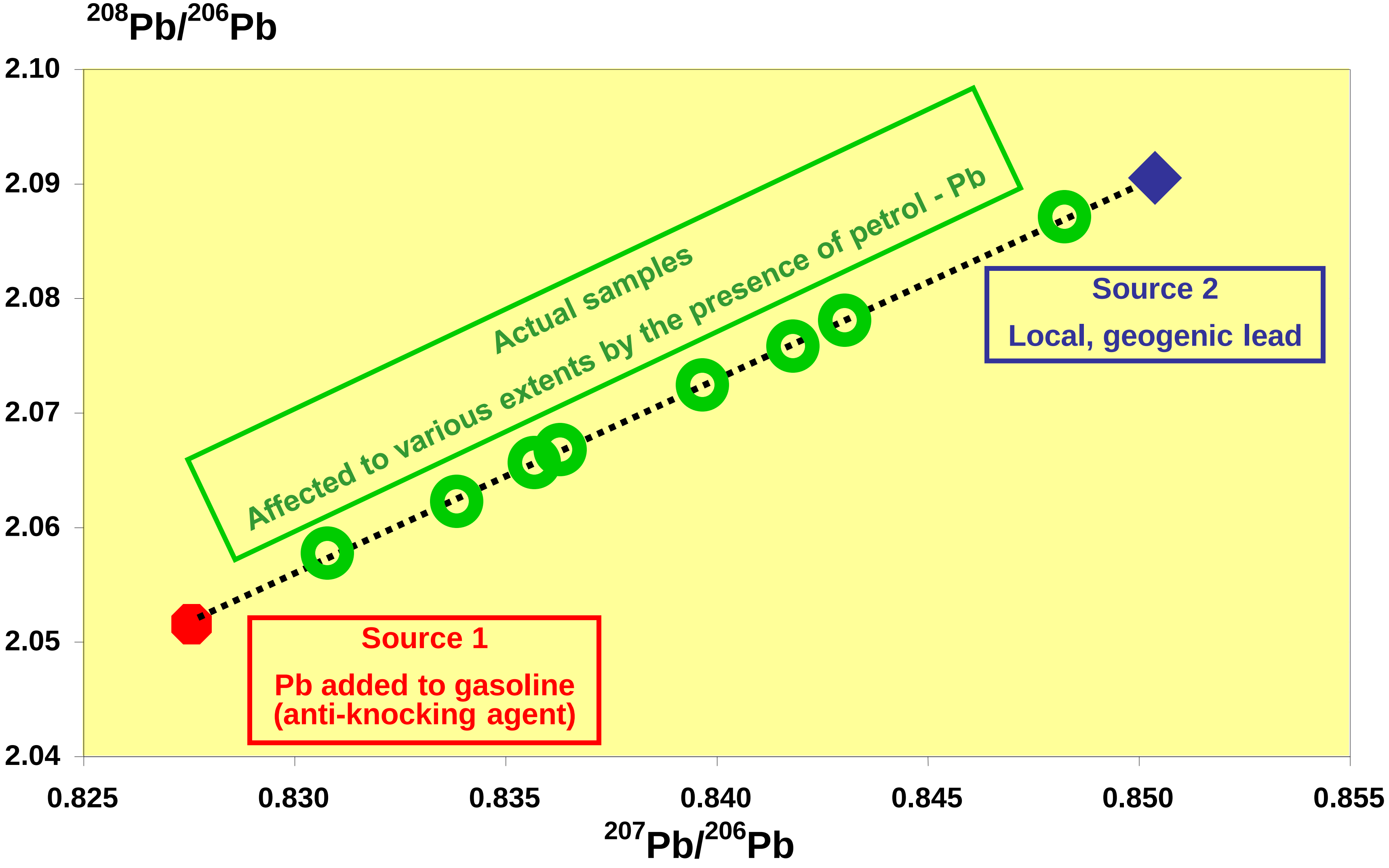
PbS ore – galena

PB – ENVIRONMENTAL POLLUTION

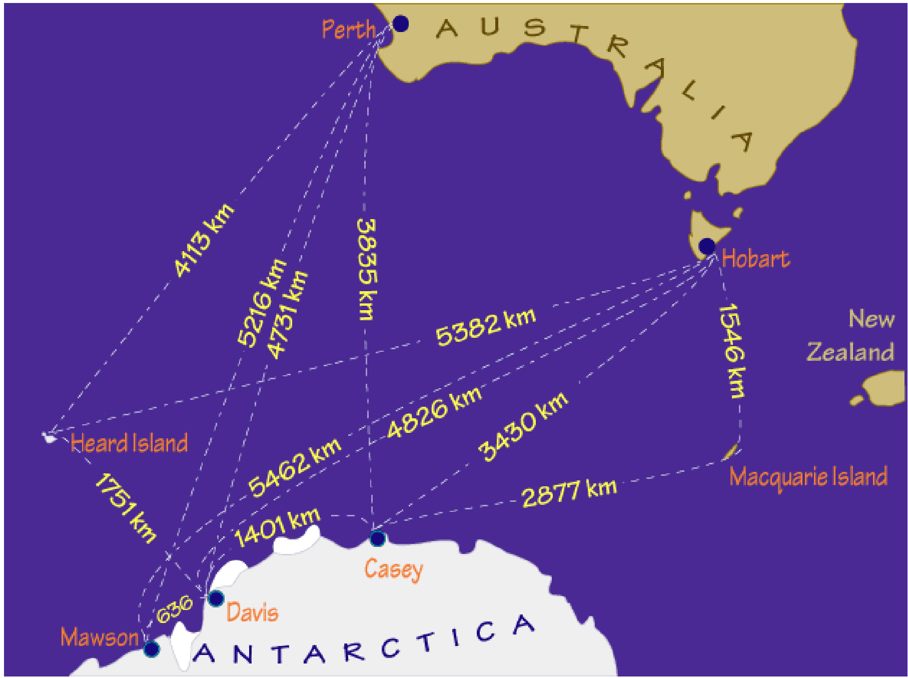
- *Pb in the atmosphere*
  - *Geogenic background: crustal “signature”*
  - *Pollution: “ore signature”*
  - *⇒ possibility to calculate relative contributions*

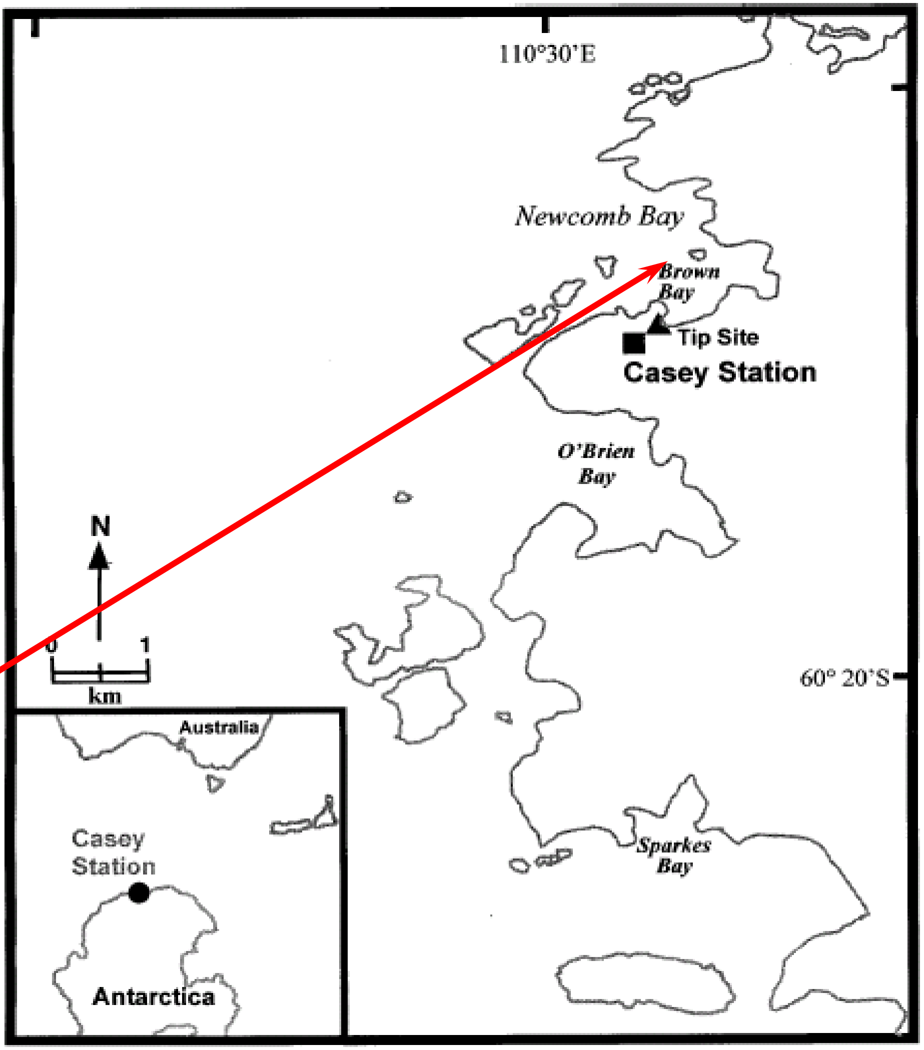


PB – ENVIRONMENTAL POLLUTION
CALCULATION OF RELATIVE CONTRIBUTIONS



CASE STUDY – PB POLLUTION IN MARINE SEDIMENTS NEAR CASEY STATION, ANTARCTICA





Pollution established @ Brown Bay

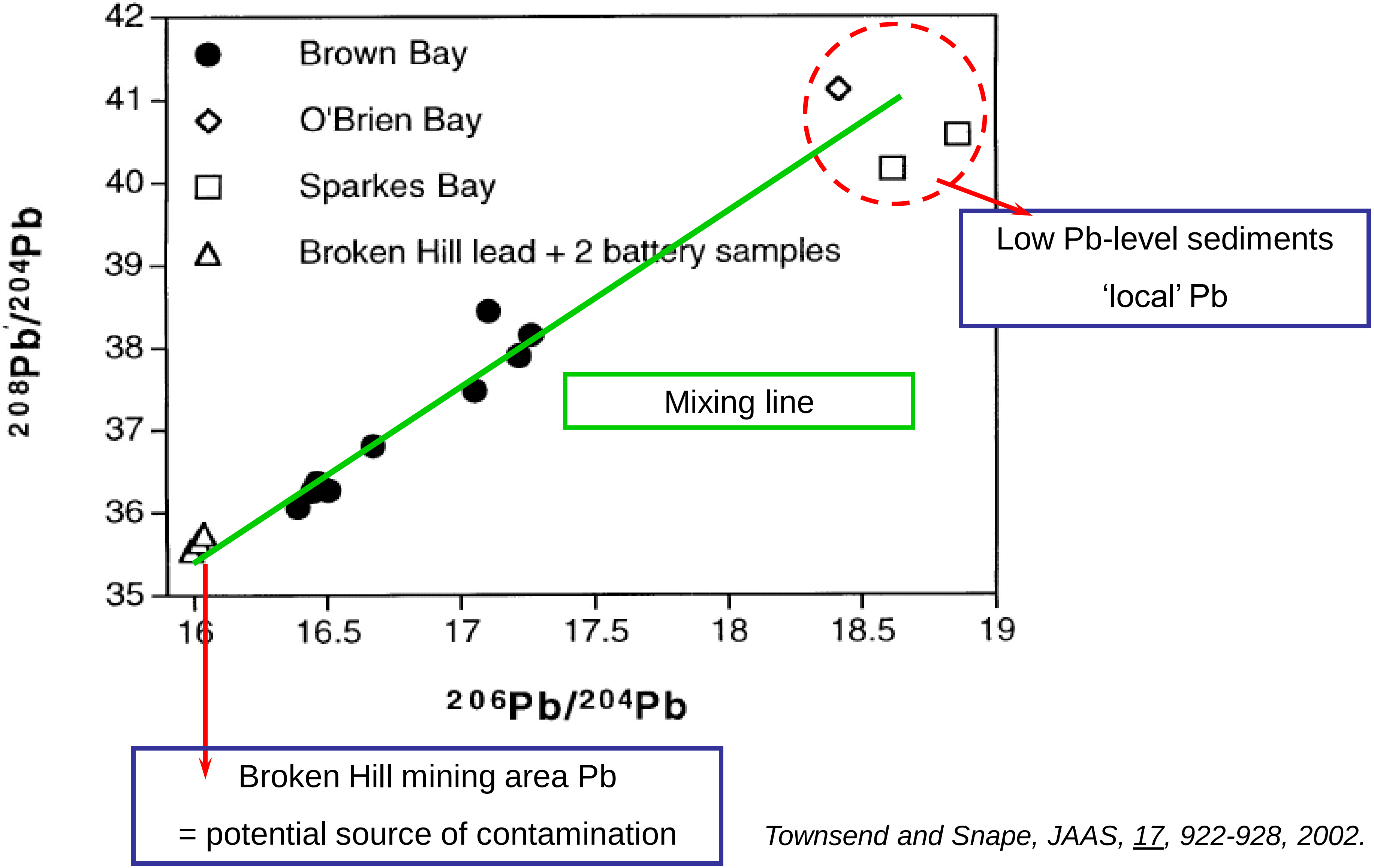
Townsend and Snape, JAAS, 17, 922-928, 2002.

Case study – Pb pollution in marine sediments near Casey station, Antarctica

- *Samples*
  - *Grab samples + core samples*
- *Sample preparation*
  - *Stored frozen*
  - *Dried at 105°C*
  - *Sieved to <2mm grain size*
  - *Total digestion using concentrated mineral acids, including HF*
- *Measurement of Pb isotope ratios*
  - *Single-collector sector field ICP-MS*
    - *1200 scans in ~2 min*
    - ^{201}*Hg monitored to correct for potential isobaric interference on* ^{204}*Pb*
    - *Correction for mass discrimination corrected using NIST SRM 981*
      - *Isotopic reference material*
      - *Bracketing approach*

Townsend and Snape, JAAS, 17, 922-928, 2002.

CASE STUDY – PB POLLUTION IN MARINE SEDIMENTS NEAR CASEY STATION, ANTARCTICA



Low Pb-level sediments

'local' Pb

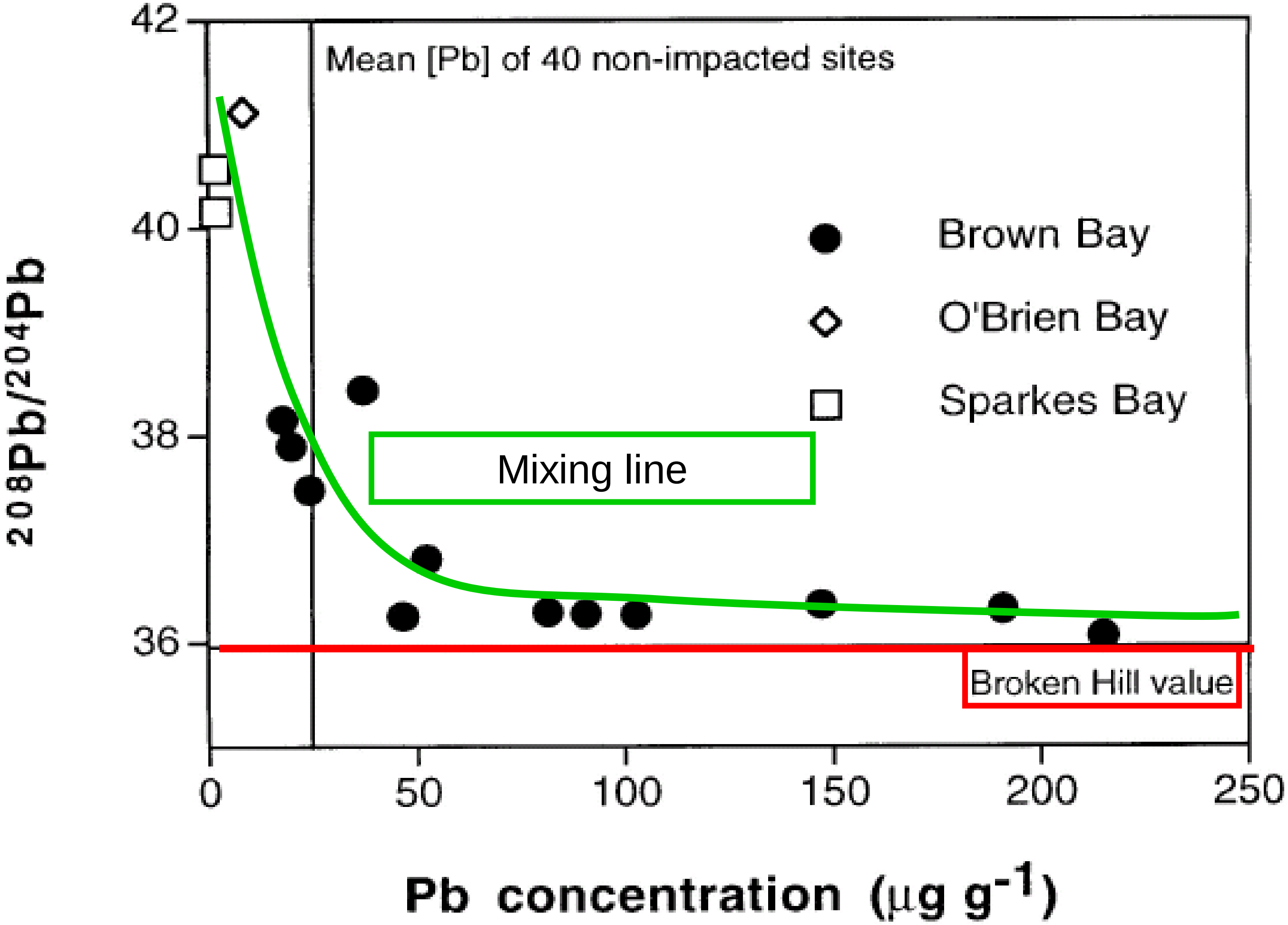
Mixing line

Broken Hill mining area Pb

= potential source of contamination

Townsend and Snape, JAAS, 17, 922-928, 2002.

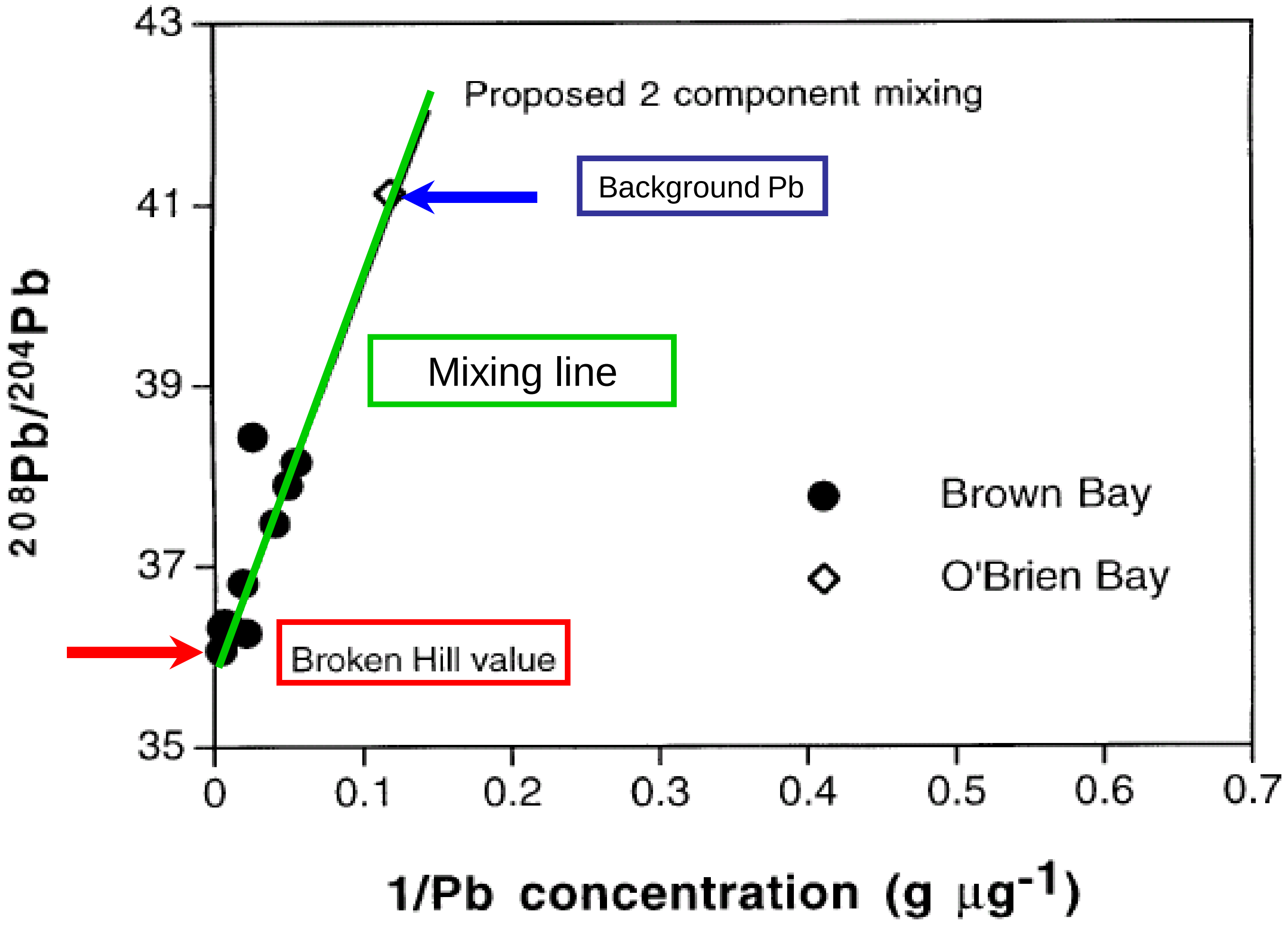
CASE STUDY – PB POLLUTION IN MARINE SEDIMENTS NEAR CASEY STATION, ANTARCTICA



The higher the Pb concentration, the closer the $^{208}Pb/^{204}Pb$ ratio to the Broken Hill value

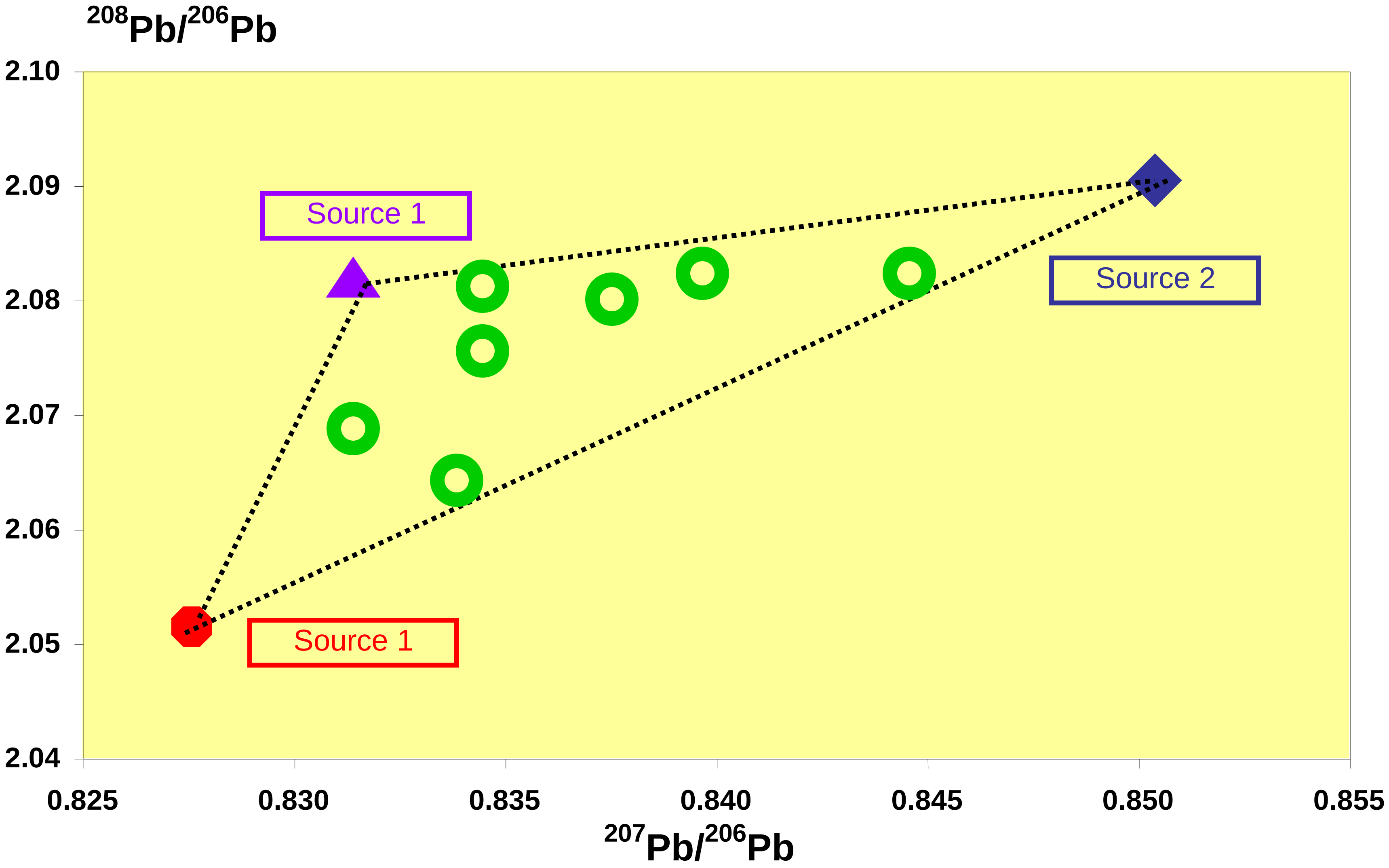
Straight lines are preferred ⇒ use 1/Pb instead

CASE STUDY – PB POLLUTION IN MARINE SEDIMENTS NEAR CASEY STATION, ANTARCTICA



Townsend and Snape, JAAS, 17, 922-928, 2002.

PB – ENVIRONMENTAL POLLUTION
MORE THAN TWO SOURCES…



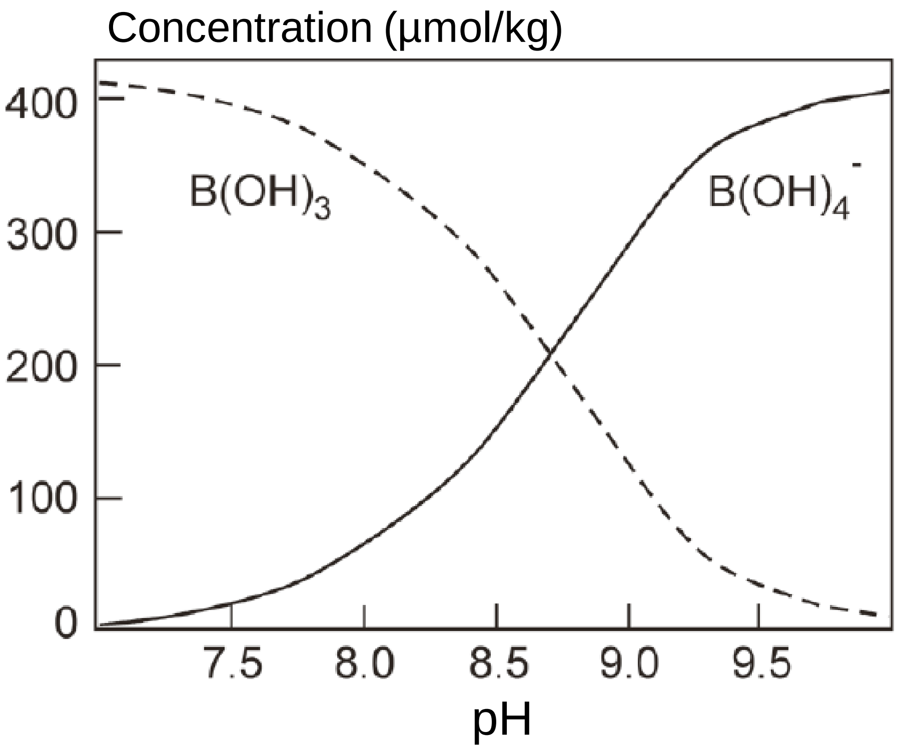
F. Vanhaecke *et al*, JAAS, 24, 863-886, 2009.

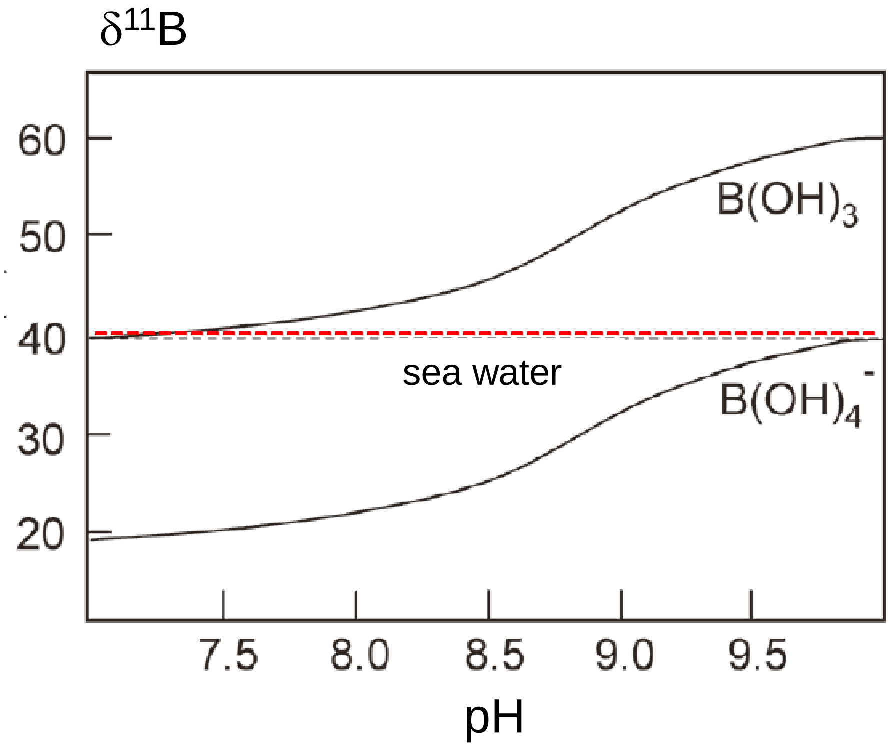
NATURAL VARIATION APPLICATIONS BASED ON ISOTOPE FRACTIONATION

MC-ICP-MS only …

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

- ***B in seawater:***
  - ***Present as $B(OH)_3$ & $B(OH)_4^-$ / distribution dependent on pH***





  - ***^{11}B/^{10}B isotope ratio in the past? ⇒ foraminifera & corals***

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

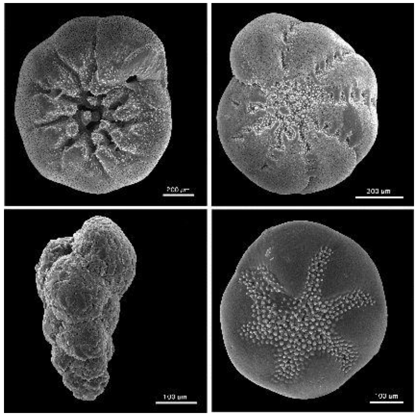
- ***In seawater:***

$$B(OH)_3 + H_2O \leftrightharpoons B(OH)_4^- + H^+$$

isotopically
heavier

isotopically
lighter

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



Foraminifera
living or fossil
eukaryotic monocellular
organisms with $CaCO_3$ skeleton

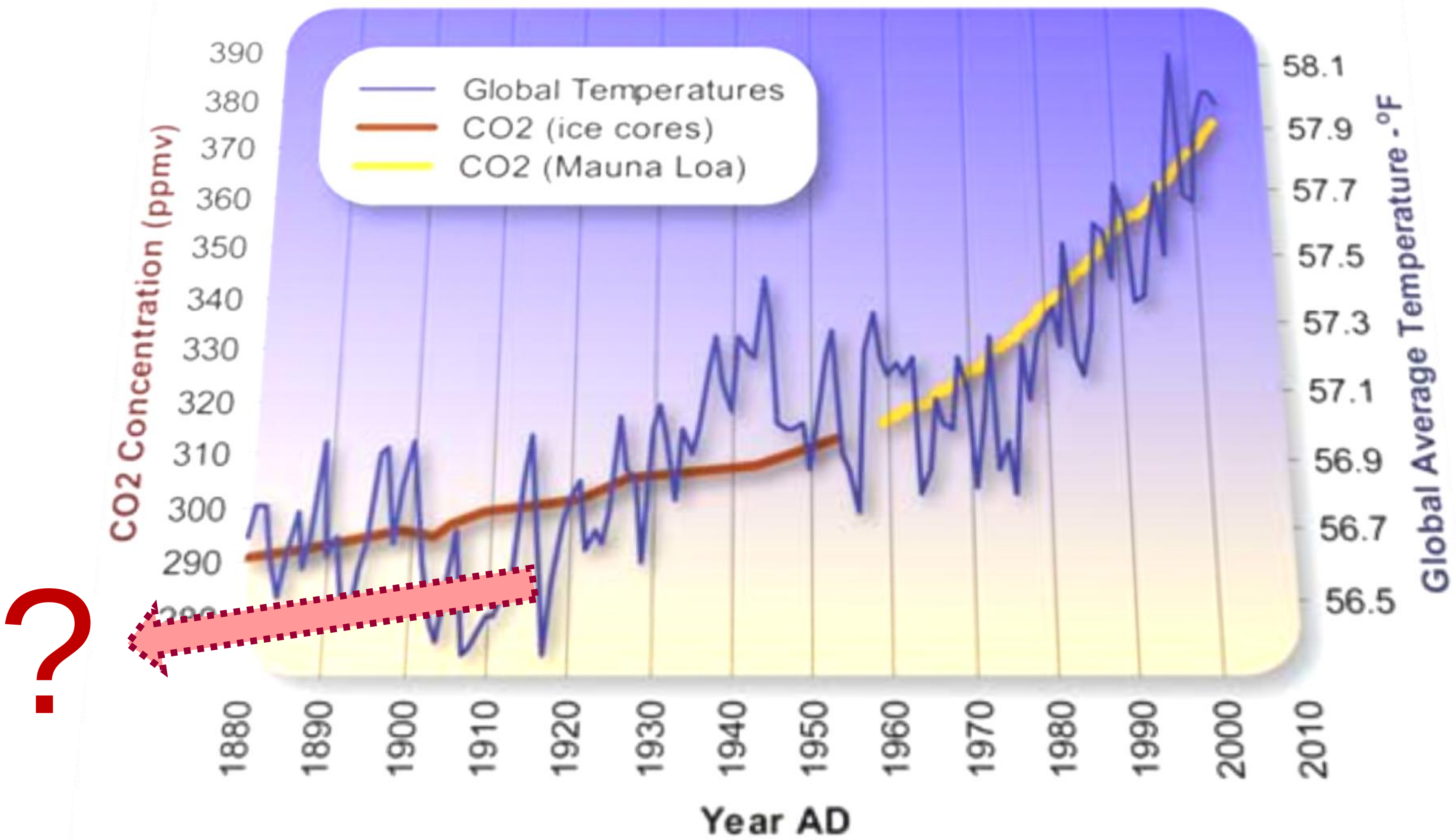
pH of seawater as a
function(time)

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 ?



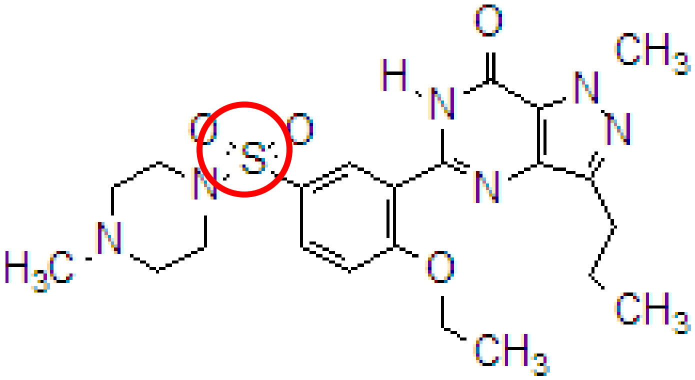
Data Source Temperature: ftp://ftp.ncdc.noaa.gov/pub/data/anomalies/annual_land.and.ocean.ts
Data Source CO2 (Siple Ice Cores): http://cdiac.esd.ornl.gov/ftp/trends/co2/siple2.013
Data Source CO2 (Mauna Loa): http://cdiac.esd.ornl.gov/ftp/trends/co2/maunaloa.co2

Graphic Design: Michael Ernst, The Woods Hole Research Center

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*

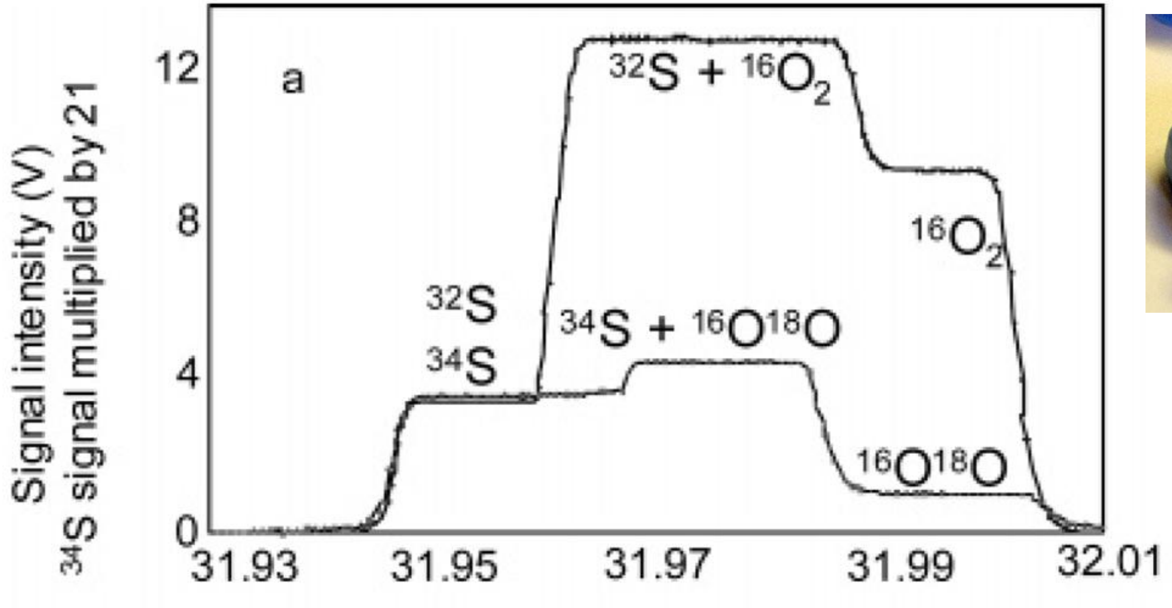


Sildenafil, VIAGRA*

S ISOTOPIC ANALYSIS FOR TRACING DOWN COUNTERFEIT DRUGS

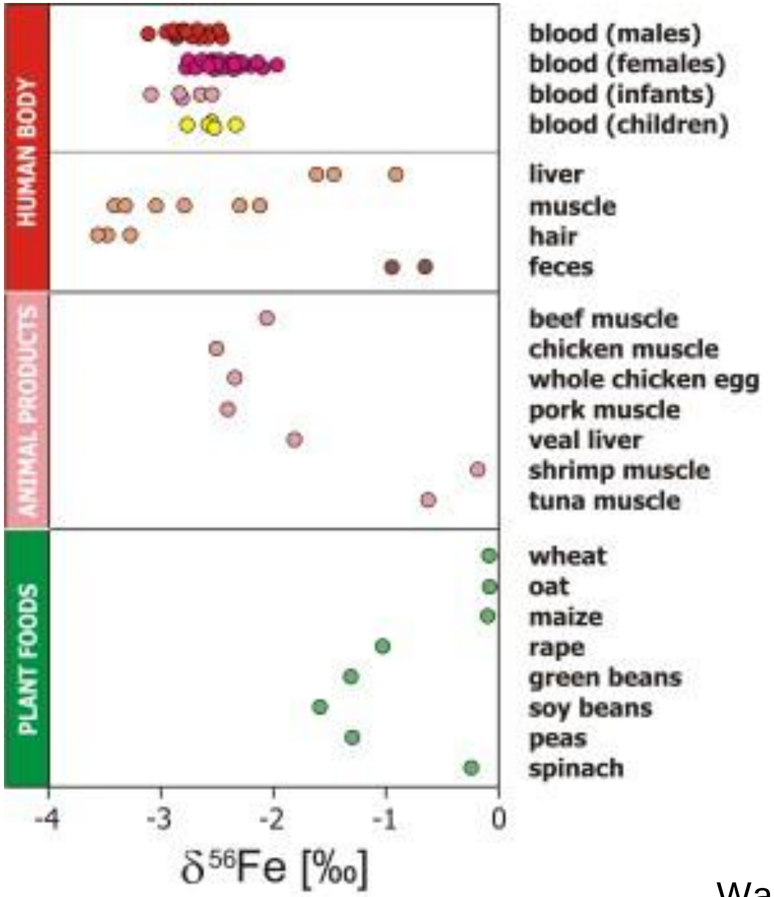
R. CLOUGH ET AL., ANAL. CHEM., 78, 6126, 2006.

- ***S isotopic analysis in viagra using LA-MC-ICP-MS***
  - ***Higher mass resolution***



	δ^{34}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 ± 0.39	+5.0 ± 1.1

STUDY OF ISOTOPE FRACTIONATION IN THE CONTEXT OF BIOMEDICAL APPLICATIONS

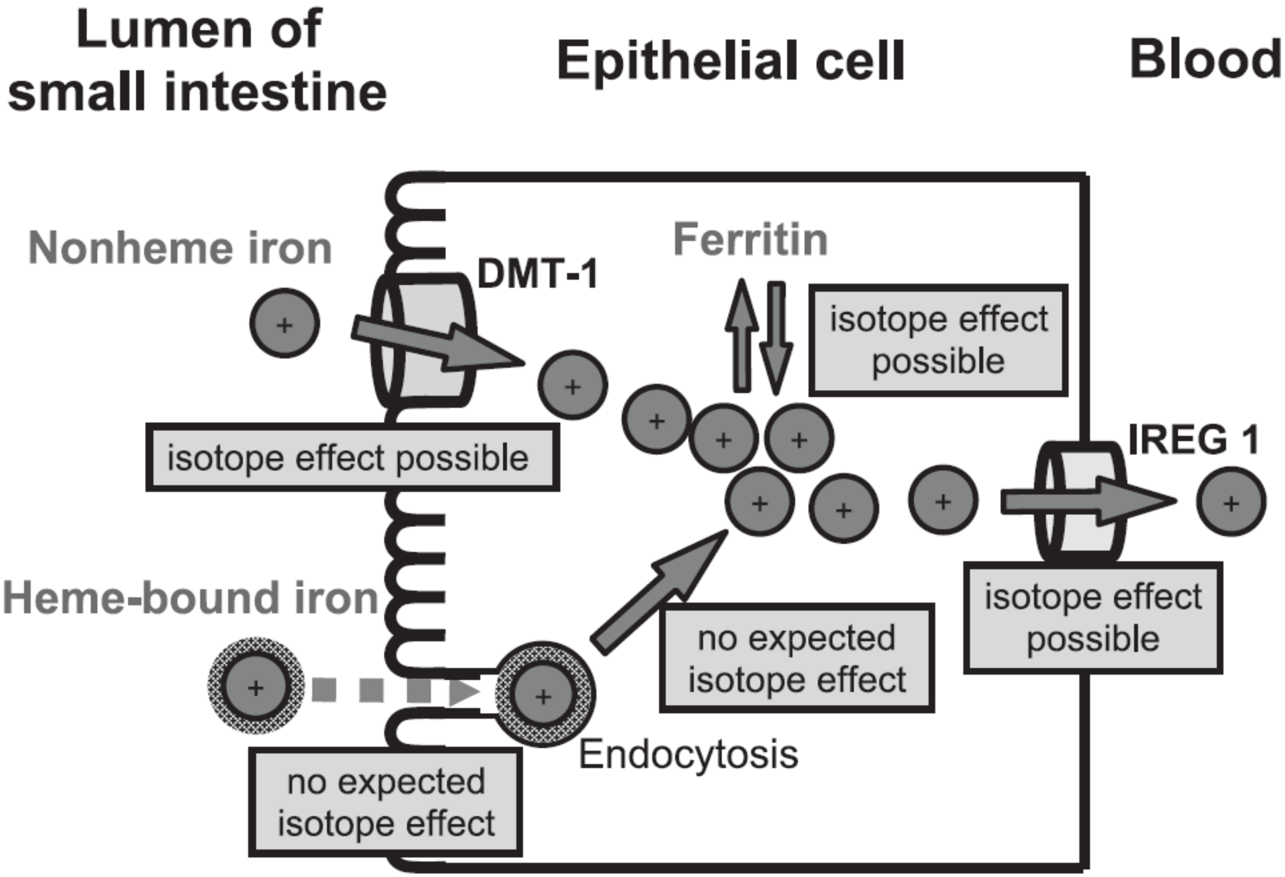


As Fe proceeds through the food chain, $\delta(^{56}Fe/^{54}Fe)$ is reduced by approx 1 ‰ with each trophic level.

Thorough investigation should provide information on uptake & transfer of Fe.

Walczyk and von Blanckenburg, Science, 295, 2065- 2066, 2002.

UPTAKE OF FE IN THE SMALL INTESTINE



Fe isotopic analysis ⇒ tool for efficiency of (non-heme) iron absorption

Tool for diagosing hereditary chromatosis

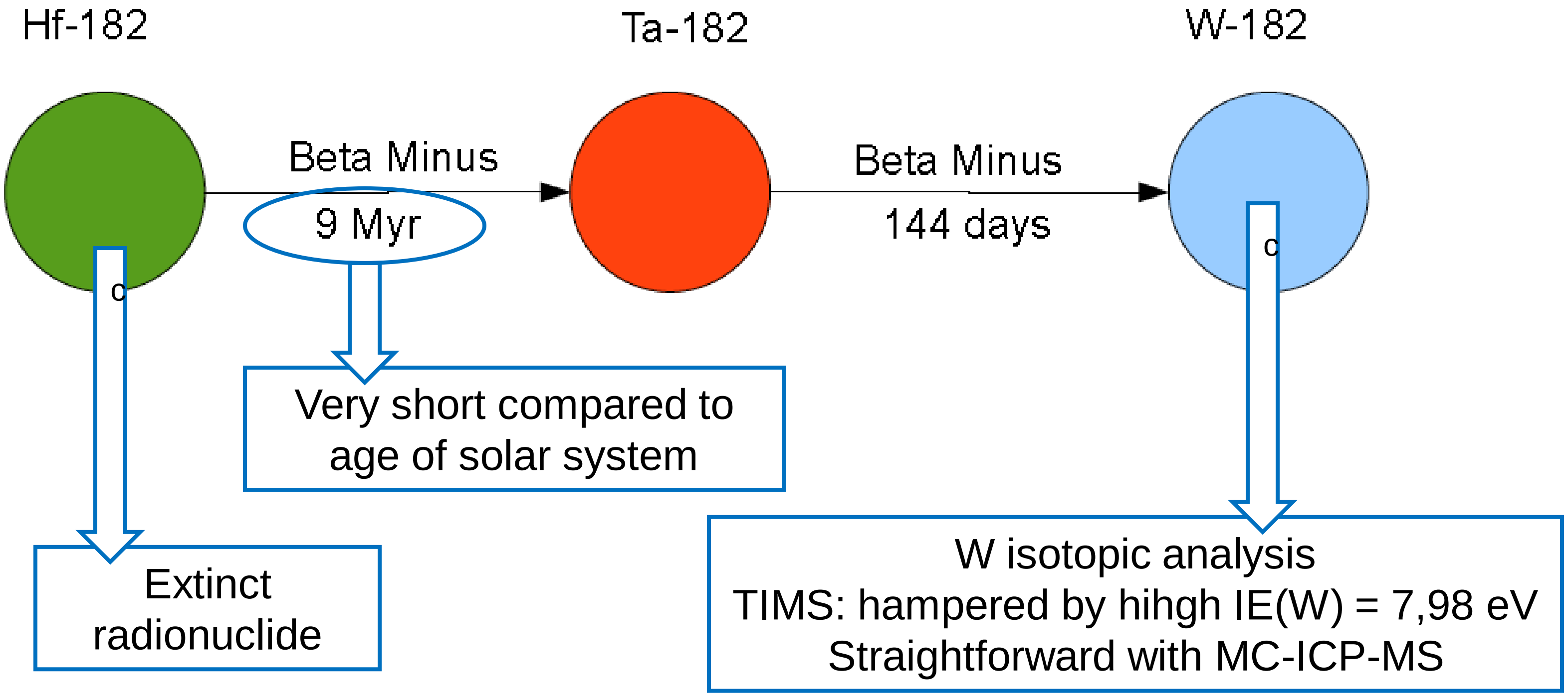
Krayenbuehl *et al*, Blood, 105, 3812-3816, 2005.

NATURAL VARIATION APPLICATIONS BASED ON EXTINCT RADIONUCLIDES

MC-ICP-MS only …

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

S.B. JACOBSEN, EPSL, 33, 531-570 2005.



Very short compared to age of solar system

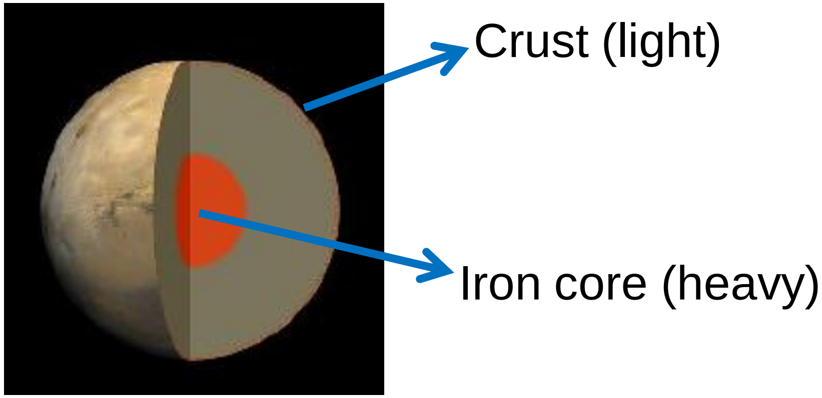
Extinct radionuclide

W isotopic analysis
TIMS: hampered by hihgh IE(W) = 7,98 eV
Straightforward with MC-ICP-MS

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

S.B. JACOBSEN, EPSL, 33, 531-570, 2005.

- ***Formation of a planet ?***
  - ***Accretion***
    - ***Growth of an object by attracting more matter (gravity)***
  - ***Differentiation***
    - ***Core formation***

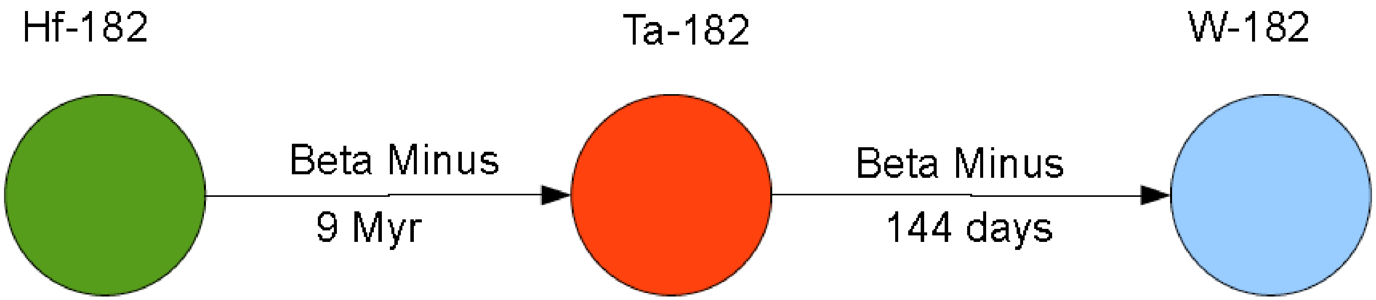


Hf = lithophile
$\Rightarrow$
prefers crust

W = siderophile
$\Rightarrow$
prefers core

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

S.B. JACOBSEN, EPSL, 33, 531-570 2005



Hf-182

Ta-182

W-182

Beta Minus

9 Myr

Beta Minus

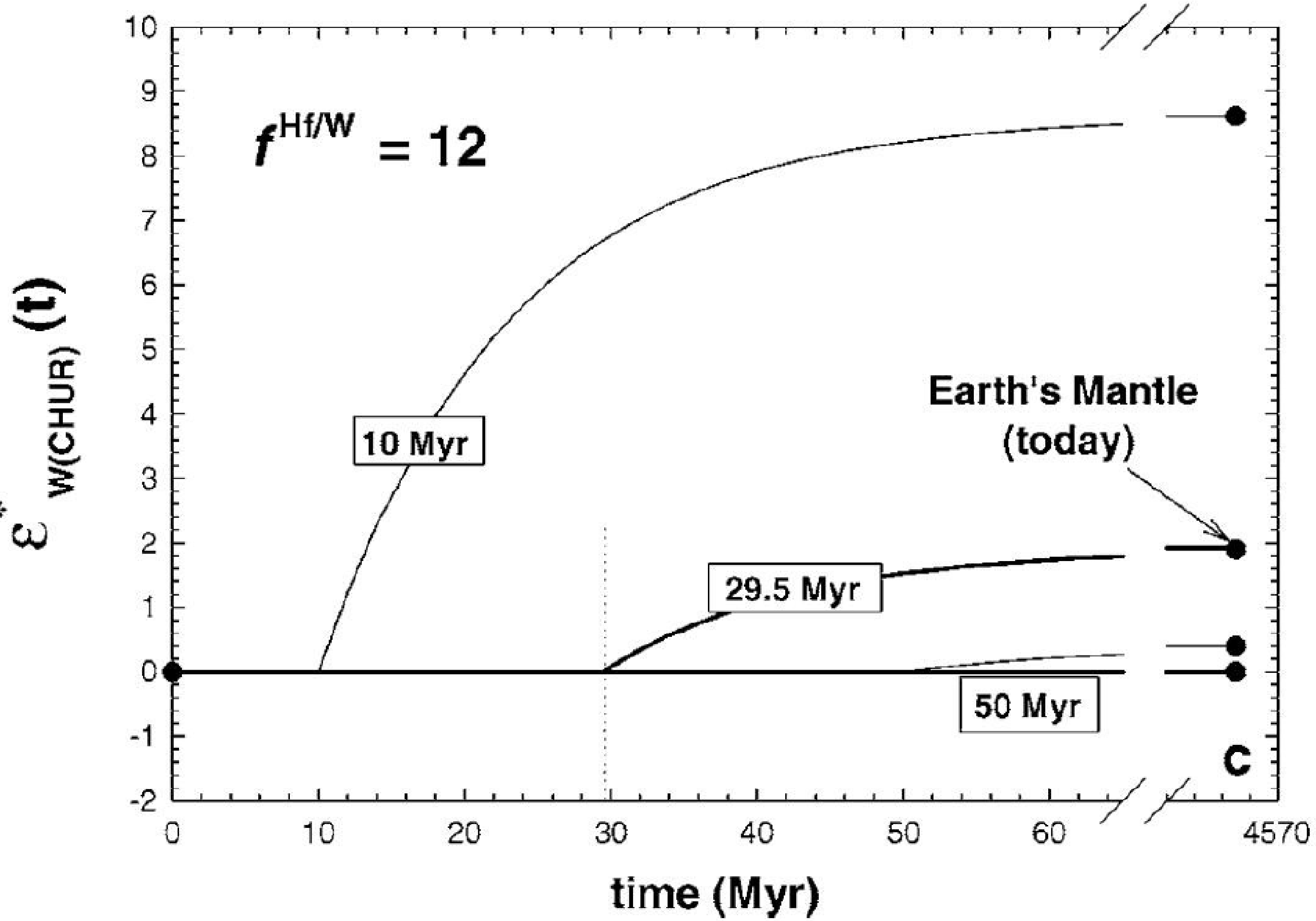
144 days

- ***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 ⇒ 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, 531-570 2005

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



THE END …