FOOD PROVENANCE BY ELEMENTAL AND ISOTOPIC FINGERPRINT METHODS

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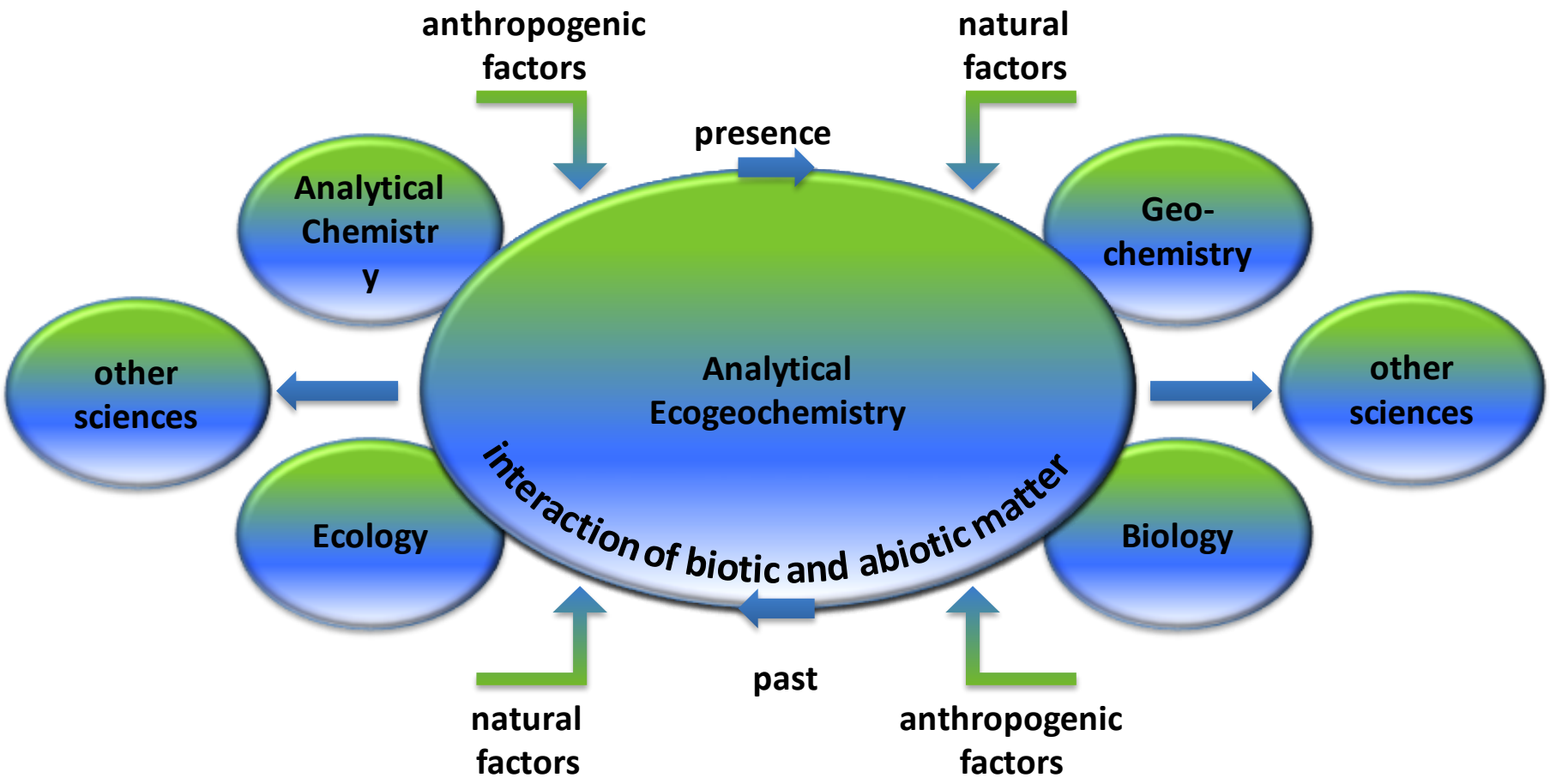
Research focus: bioresources, renewable resources, biologically based technologies
Construction: 2009 - 2011
Lab relocation: April-2011
Opening ceremonies: Sep-2011

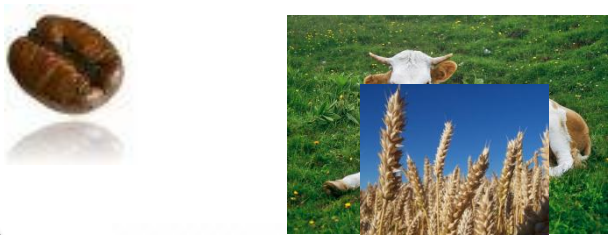
Analytical Ecogeochemistry



Rationals

Thuna, made in Austria

Global food trade



provenance

maldeclaration

authenticity

...how to control???

adulateration

quality

low quality

Food Authenticity/Food Provenance

Rationals

- Consumer protection:
  - Food safety
  - Genuineness (‚You get what you pay for')
- Producer protection
  - Competition
  - Proof of provenance (consumer confidence)
- Protection of regionality
  - Diverstiy of production
  - Specific production processes

EU regulation

New framework for Quality schemes in agriculture enters into force

03/01/2013

Guaranteeing **quality to consumers** and a **fair price for farmers** are the twin aims of the new Quality Regulation that enters into force today.

Based on the proposal tabled by the Commission in 2010 the text is a very balanced compromise between the Council, the Parliament and the Commission.

It encourages the diversification of agricultural production, protect product names from misuse and imitation and help consumers providing information on product characteristics and farming attributes.

http://ec.europa.eu/agriculture/quality/

EU regulation

The new Regulation on quality schemes for agricultural products and foodstuffs achieves a **simplified regime for several quality schemes** by putting them under one single legal instrument.

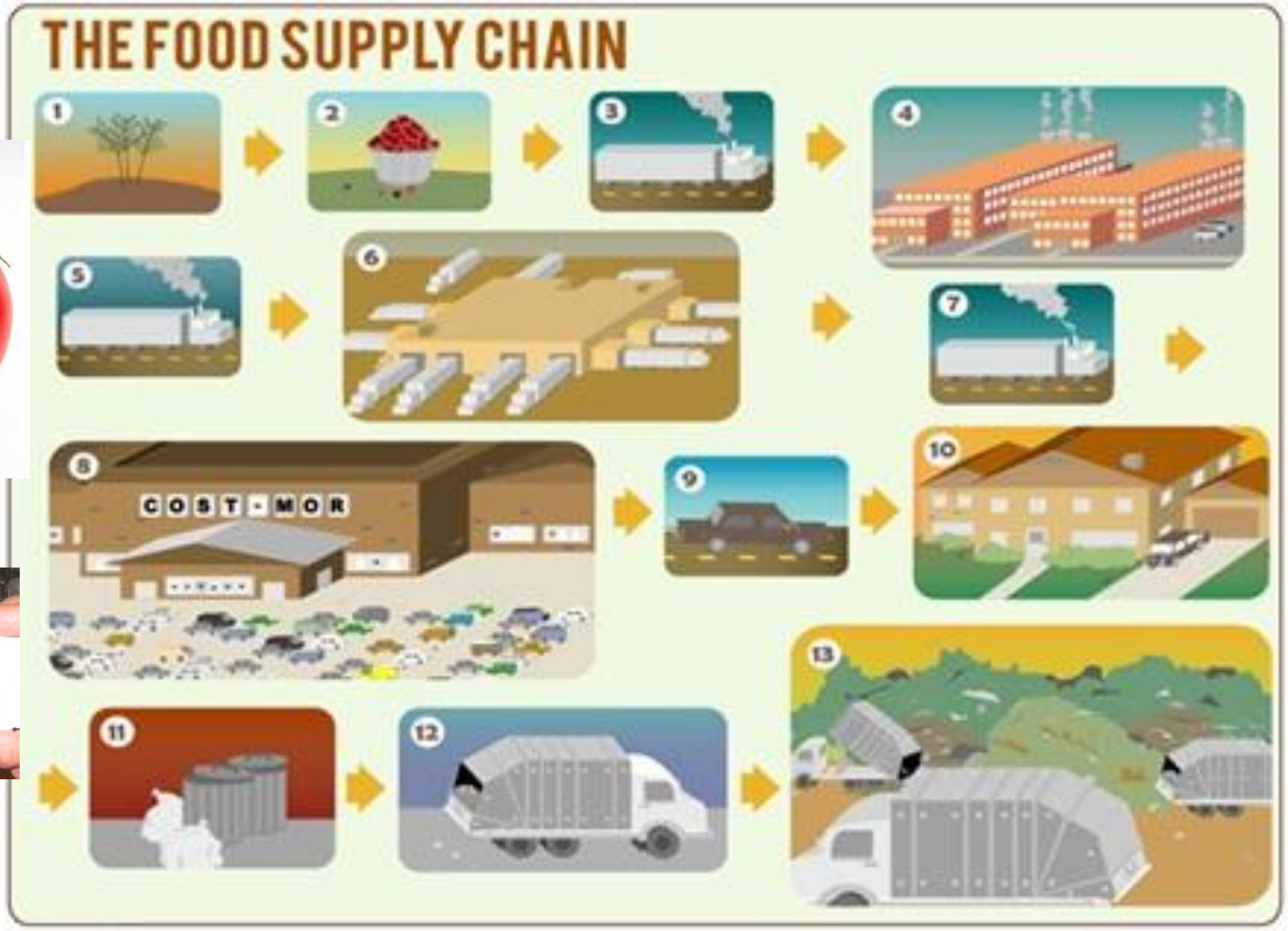
Furthermore, it creates a more **robust framework for the protection and promotion of quality agricultural products**.

The key elements of the new Regulation include:

- more coherence and clarity to the EU quality schemes,
- a reinforcement of the existing scheme for protected designations of origin and geographical indications (PDOs and PGIs),
- overhauling the traditional specialities guaranteed scheme (TSGs),
- laying down a new framework for the development of optional quality terms to provide consumers with further information, it creates and protects the optional quality term "mountain product".

http://ec.europa.eu/agriculture/quality/

Traceability solutions



Traceability solutions

Traceability by

- Software solution
- Databases
- www-information platforms

Marking by

- RFID-tags
- Code systems
- Animal passports
- Animal tattoos

....added systems are not fraud-resistent

Independent solutions

- Information is an intrinsic food property and does not have to be added
- Information is unique for the food commodity
- Information can be identified (simple and cheap)
- Information is fraud resistant

Analytical methods (1)

- Molecular-biological methods
  - DNA (e.g. DNA marker in olive ois)
  - ELISA technique (cultivation of specific antibodies for the determination of defined proteins)
  - Amplified Fragment Length Polymorphism (AFLP) markers (fish, seafood)
  - Genetic fingerprint analysis (e.g. cereals)
- Identification of specific chemical and physical parameter

  (e.g. honey: water content, ash content, sugar content, pH, differential scanning calorimetry; rheology)
- Sensory analysis (electronic nose)

  (e.g. wine: colour, taste, aroma....)

Analytical methods (2)

- Identification of specific components and evaluation using multivariate statistics
  - IR spectroscopy (e.g. fruits, wine, sugar addition to honey)
  - Raman spectroscopy (e.g. adulteration of oils)
  - Front Face Fluorescence Spectroscopy (measurements of fluorophores e.g. aromatic amino acids; vitamine A and B2, chlorophyll)
  - Chromatographic methods (HPLC; GC) (e.g. beta-lactoglobuline in milk, organic acids in fruit juices; adulteration of olive oil)
  - Organic mass spectrometry (non targeted fingerprint)

Analytical methods (3)

- Identification of elemental and isotopic fingerprints
  - specific isotope ratios (isotopic fingerprints)
    - NMR; SNIF-NMR (H,C)
    - IR-MS (GSMS) (H,C,N,O,S)
    - TIMS (Sr,Pb)
    - ICP-MS (Sr,Pb,U,Ca,S,B)
  - Identification of specific elements and evaluation using multivariate statistics (multielement fingerprints)
    - AAS
    - ICP-AES
    - ICP-MS

Elemental and isotopic fingerprinting

elemental fingerprint

isotopic fingerprint

natural variation
locally specific signal

<< intrinsic marking >>

Elemental and isotopic fingerprinting

elemental fingerprint

isotopic fingerprint

natural variation
locally specific signal

<< intrinsic marking >>

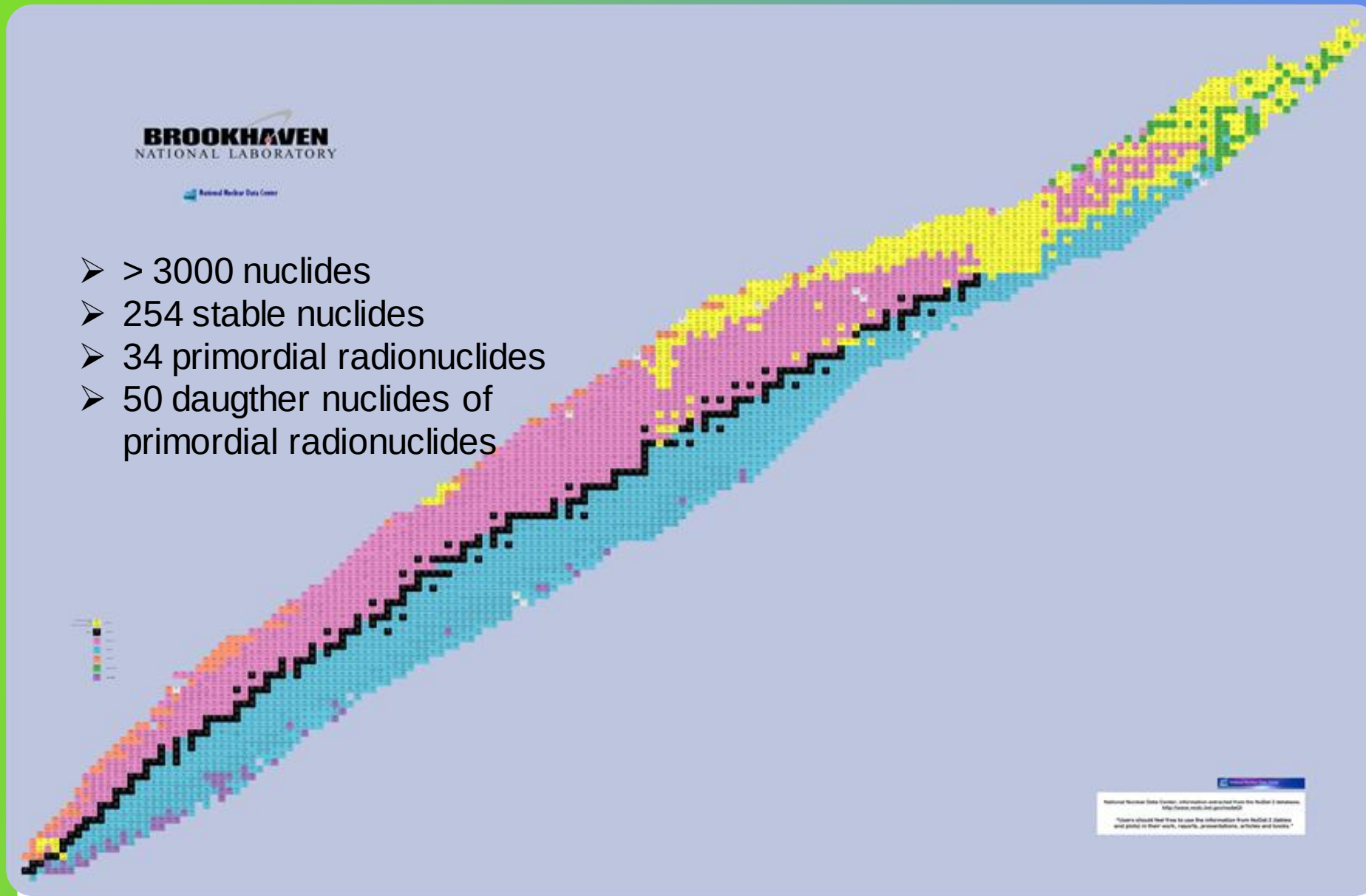
(multi)-elemental spikes

enriched stable isotopes

marking via elemental spikes or enriched isotopes

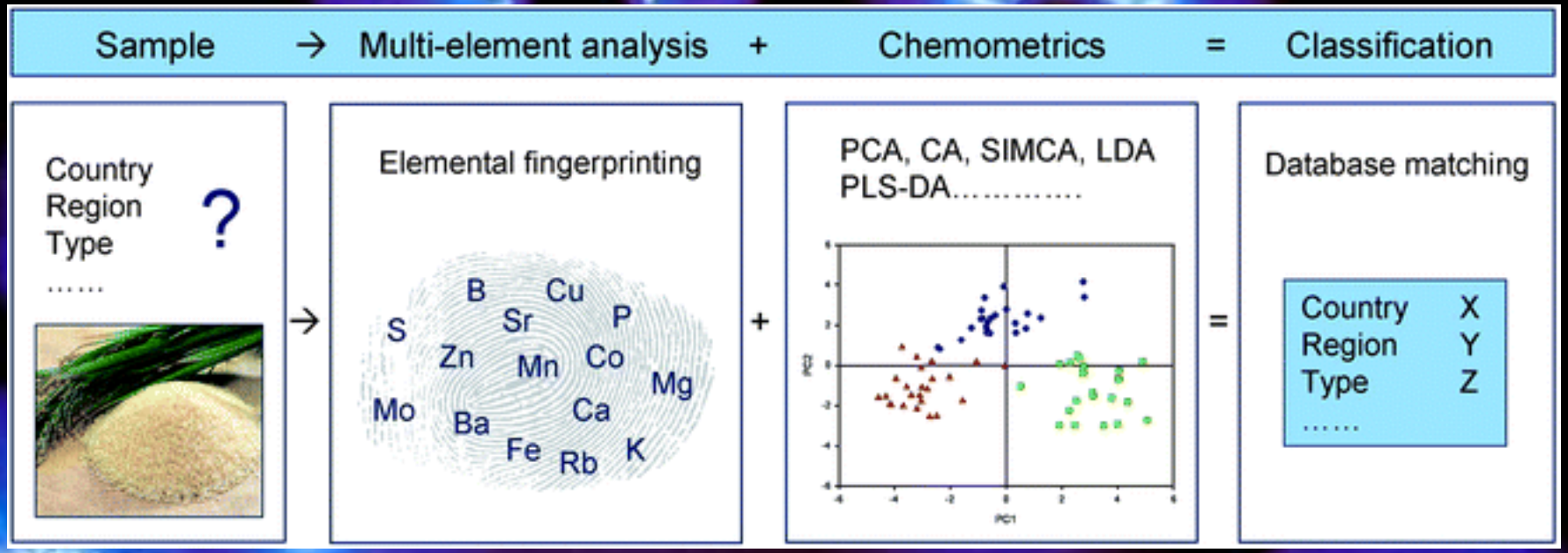
<< extrinsic marking >>

Nuclide map



- > 3000 nuclides
- 254 stable nuclides
- 34 primordial radionuclides
- 50 daugther nuclides of primordial radionuclides

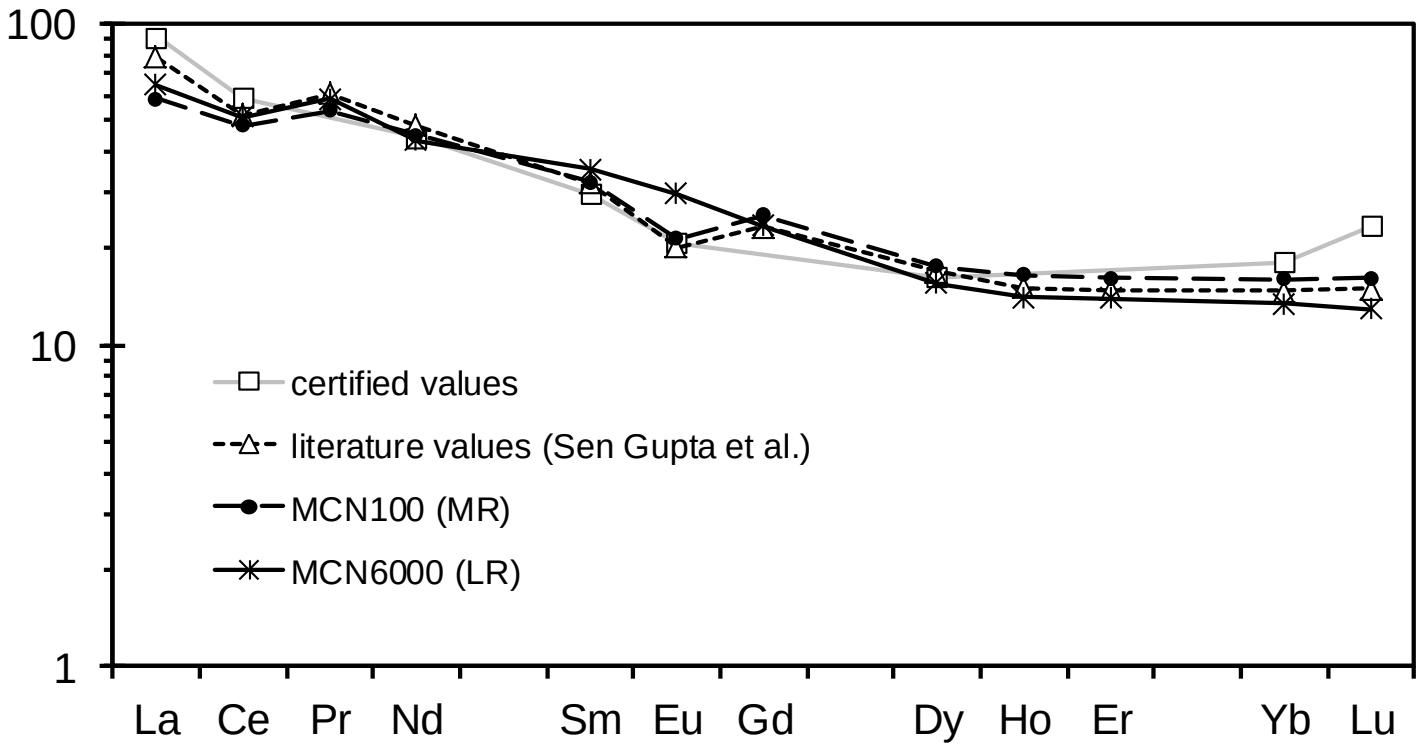
Elemental and isotopic fingerprint



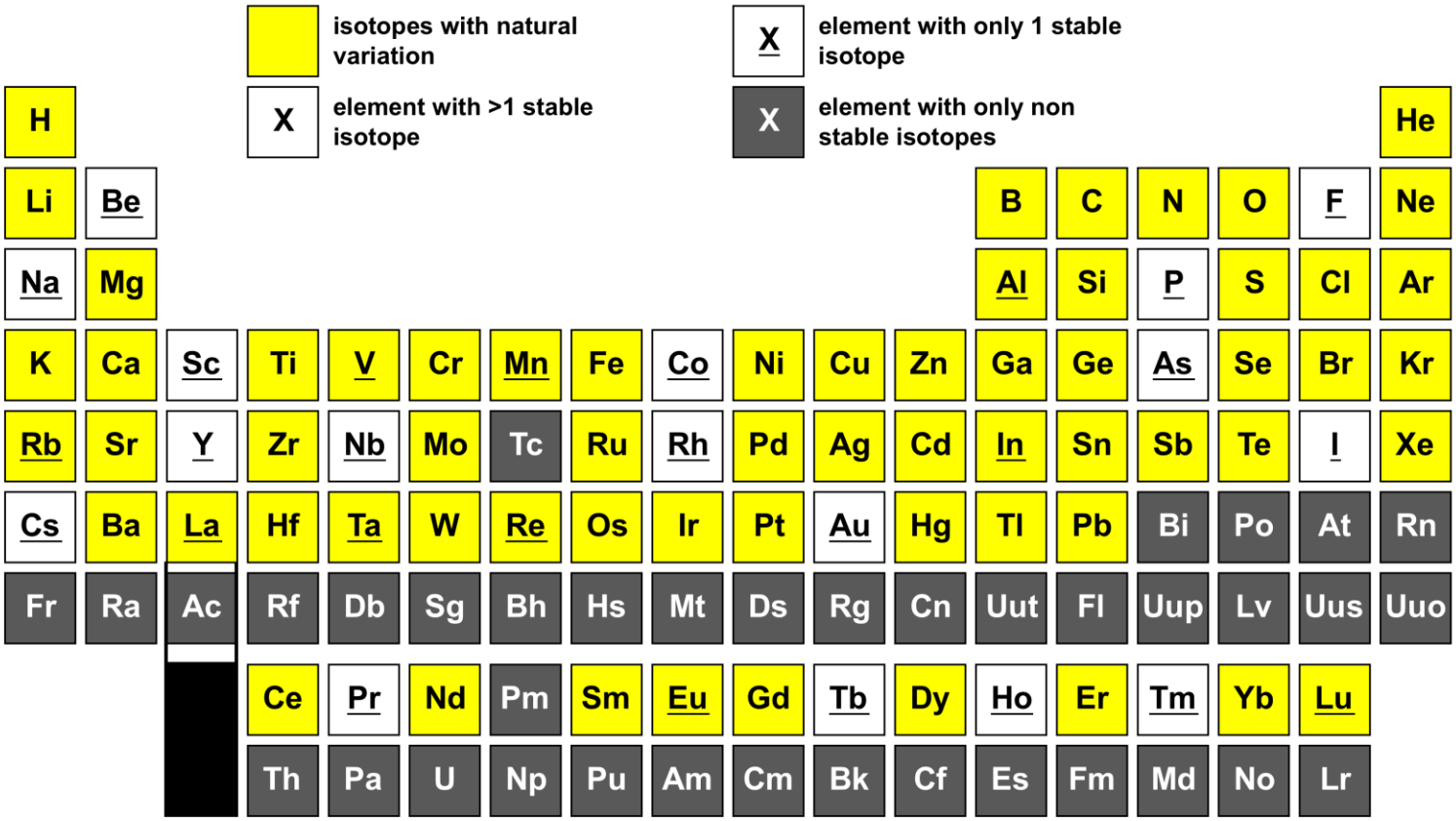
Source: Husted et al. J. Anal. Atom. Spectrom. 2011, 26, 52-79

Elemental fingerprint of REE for proof of authenticity / origin

- Determination of elemental fingerprints (e.g. rare earth elements)

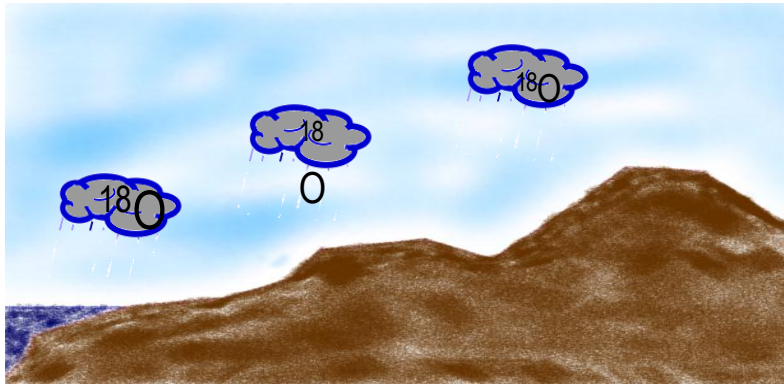


Natural variation of isotopic systems

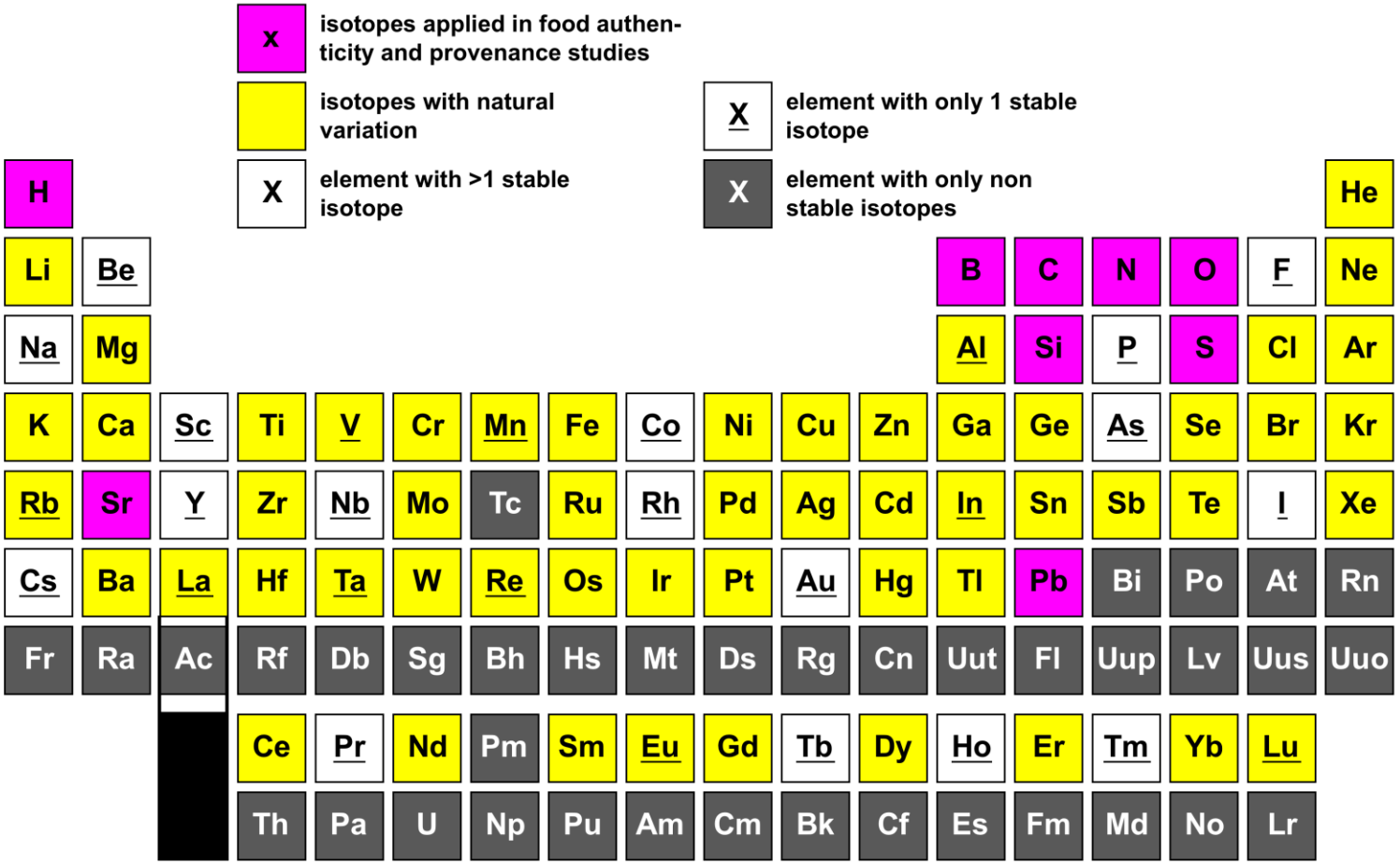


Natural variation of isotopic systems

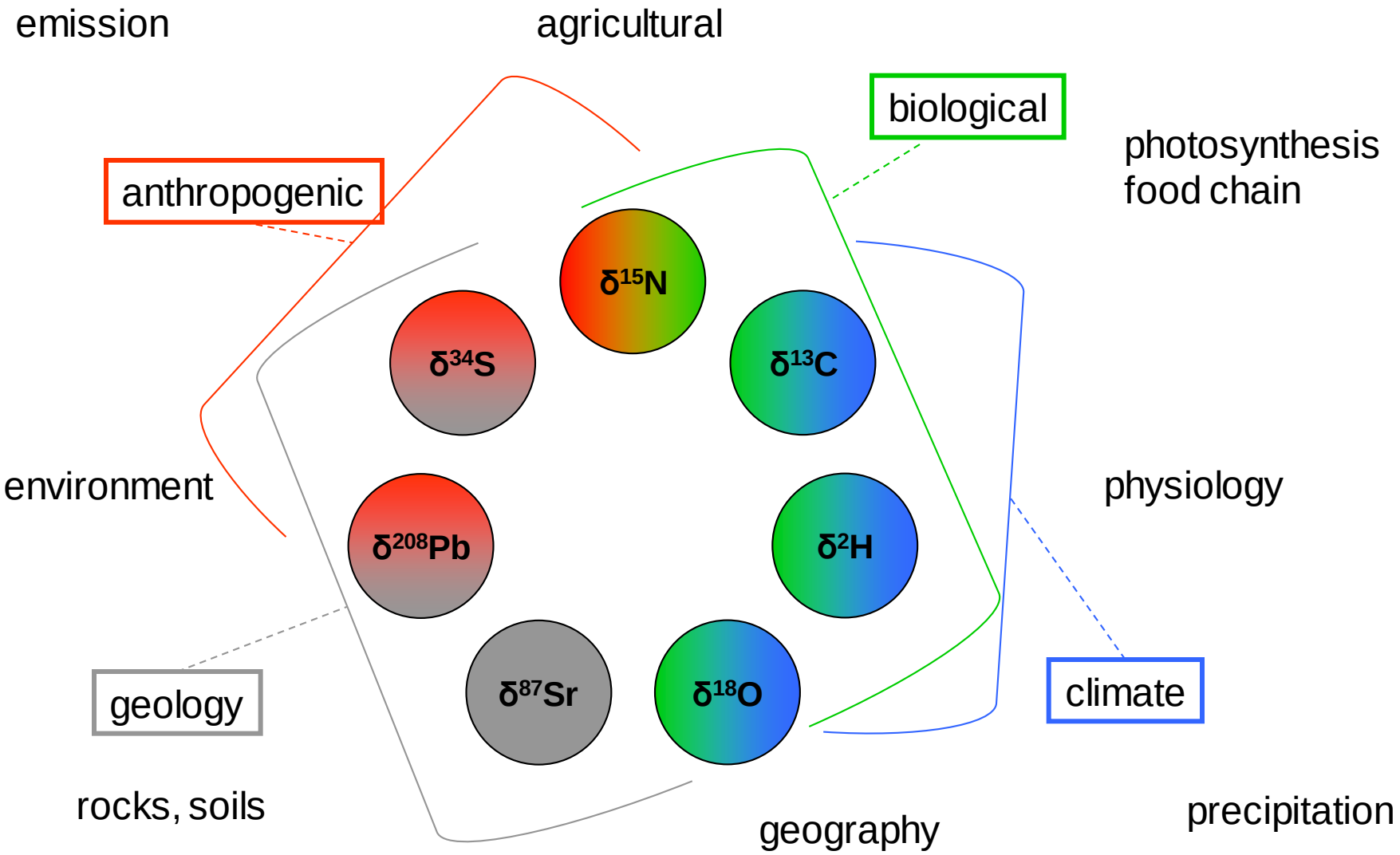
- Natural chemical processes
  - Radioactive decay (e.g. U, Pb)
  - Redox reactions (e.g. Fe)
  - Photoreactions (e.g. Hg)
  - pH dependent reactions (e.g. B)
- Natural physical processes
  - Diffusion (e.g. C, H, O)
  - Precipitation (e.g. H, O)
- Natural biochemical processes
  - Microbial activities (e.g. S, N)
  - Plant activities (e.g. C, Si)



Isotopic Systems
Used in Food Provenance Studies



The ‚big 7‘


emission
agricultural
biological
photosynthesis
food chain
anthropogenic
δ15N
δ34S
δ13C
environment
physiology
δ208Pb
δ2H
δ87Sr
δ18O
geology
climate
rocks, soils
geography
precipitation

Pb Isotopic Variation

Pb ^{204}Pb; ^{206}Pb; ^{207}Pb ; ^{208}Pb

Radioactive decay:

^{238}U ---- ^{206}Pb

^{235}U ---- ^{207}Pb

$^{244}Pu/^{232}Th$ ---- ^{208}Pb

^{204}Pb – ^{200}Hg

only 1 stable

only non
es

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

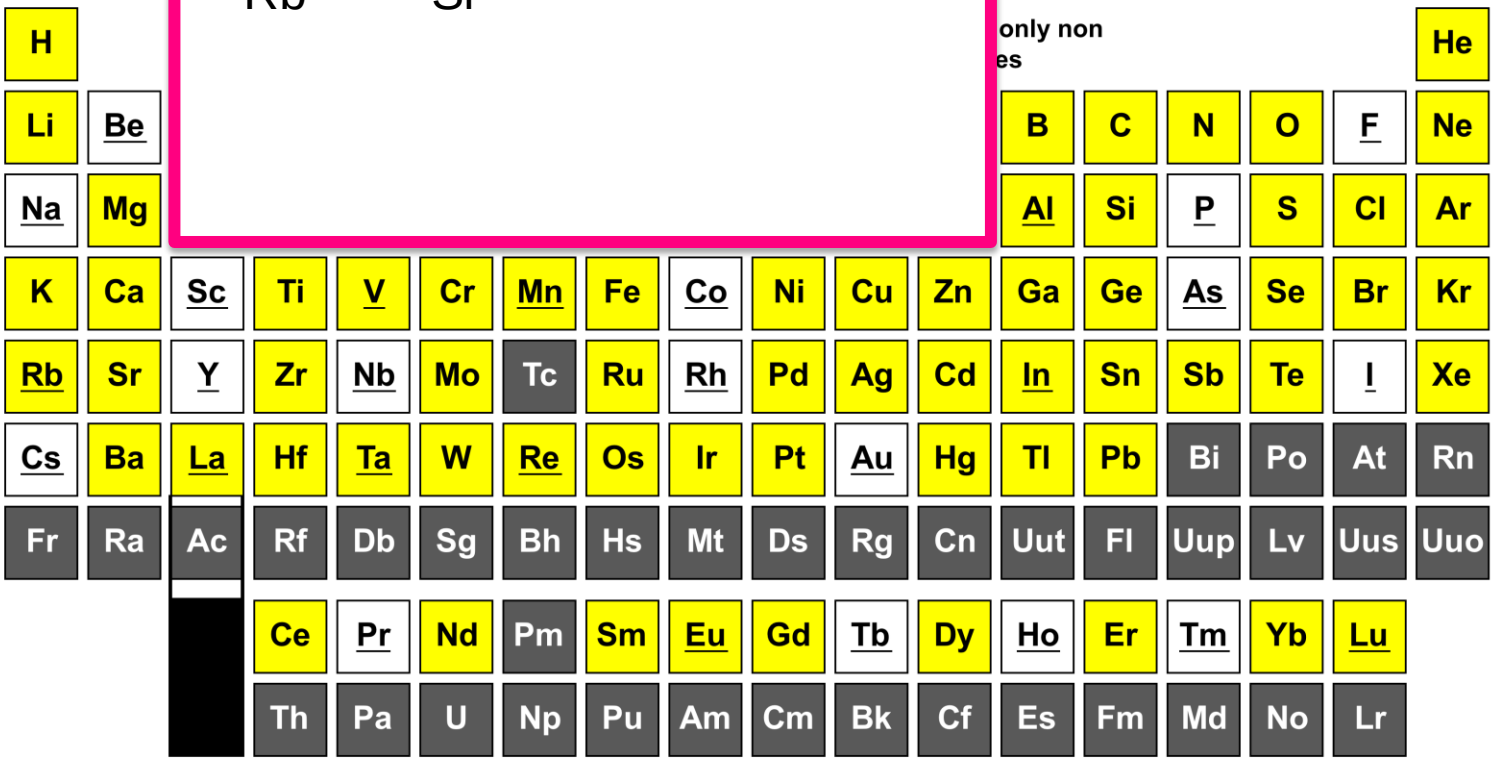
Sr Isotopic Variation

Sr ^{84}Sr; ^{86}Sr; ^{87}Sr; ^{88}Sr

Radioactive decay:
^{87}Rb ---- ^{87}Sr

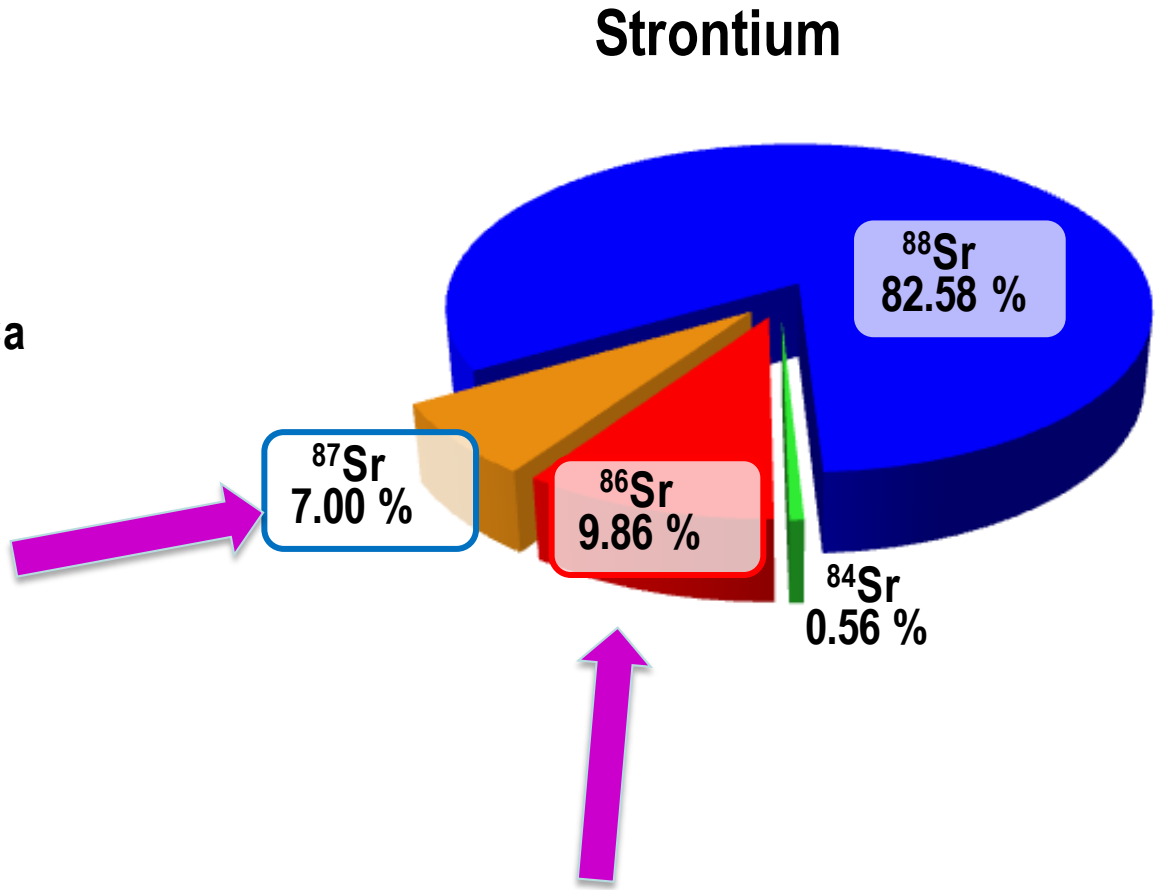
only 1 stable

only non
es

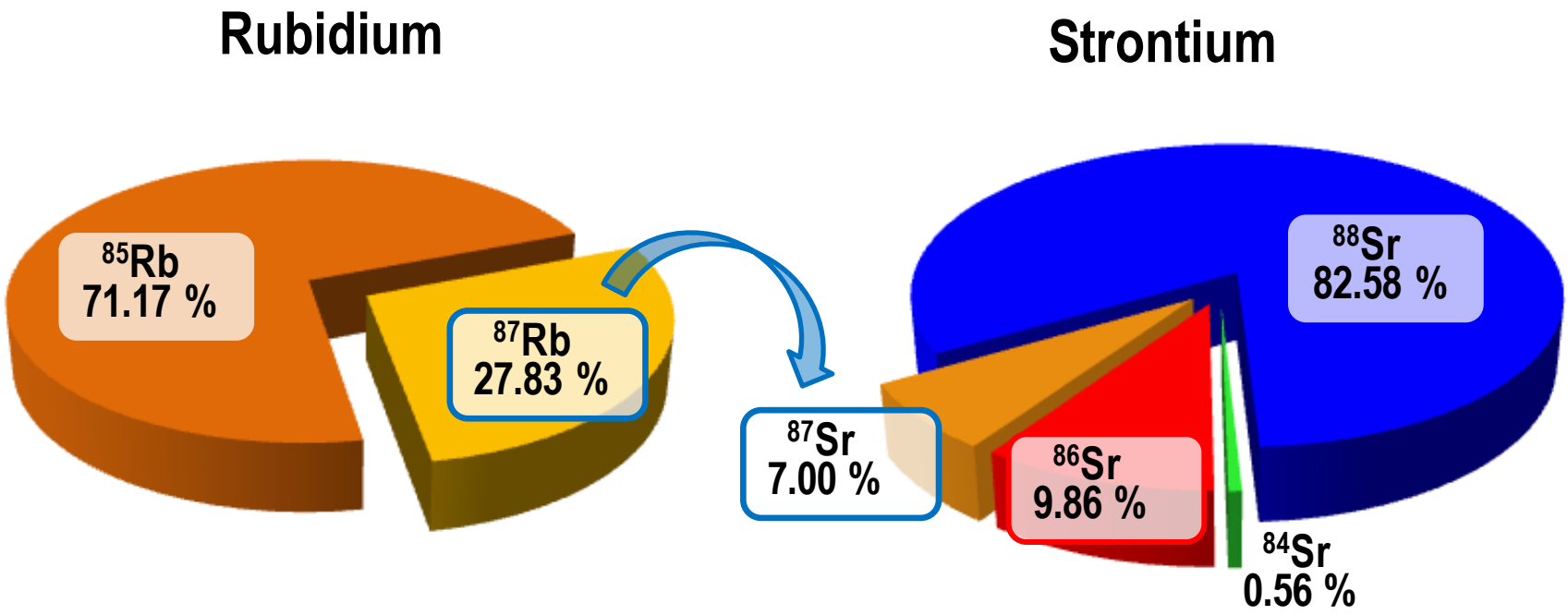


Sr isotopic system

- ubiquitous
- chemical similarity to Ca



Sr/Rb isotopic system



$$^{87}Rb \longrightarrow {}^{87}Sr + \beta^- + \nu + Q$$

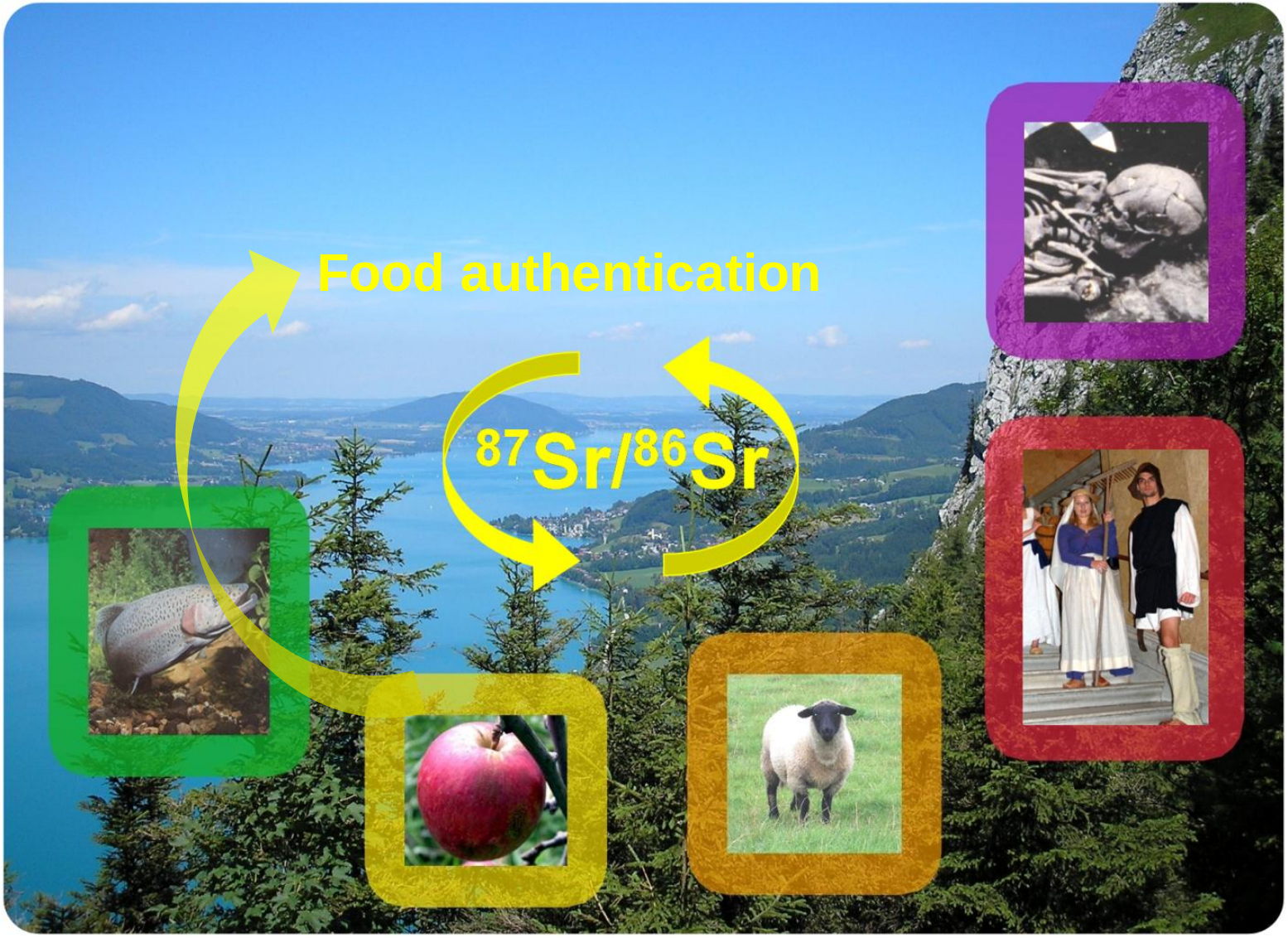
$T_{1/2}$ … half life($T_{1/2} = 48.8*10^9$ a)

λ … decay constant($\lambda = 1.42*10^{-11}$ a^{-1})

variation of $^{87}Sr/^{86}Sr$ with geological provenance

- geochemical composition
- geological age

Sr cycle



Provenancing of strawberry raw products using elemental and isotopic fingerprints – a pilot study

Sample preparation

1

Cutting, freeze drying and homogenization

(replicate analysis n=5)

2

Microwave assisted acid digestion

3

Measurement of the elemental pattern with ICP- Quadrupol MS ‘Nexion 300D’

4

Sr/matrix separation with a specific resin (elimination of Rb interference)

Sample preparation

5

Concentration screening with ICP-Quadrupol MS ‘Nexion 300D’

6

Measurement of the isotope ratio $^{87}Sr/^{86}Sr$ with Multicollector-ICP-MS ’Nu Plasma HR’

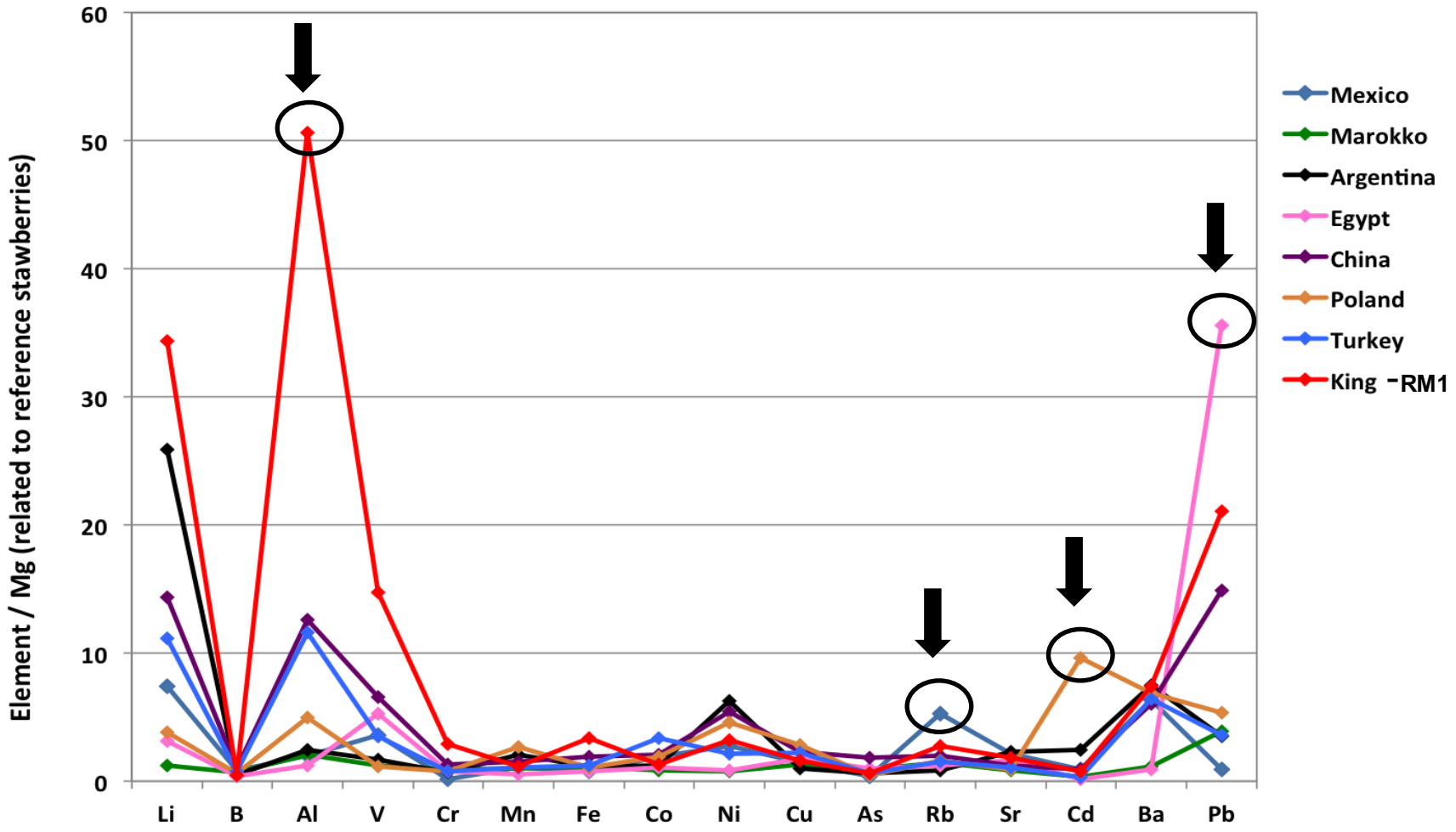
7

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{corr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_{meas} \times \left(\frac{m_{87}}{m_{86}}\right)^{f}$$

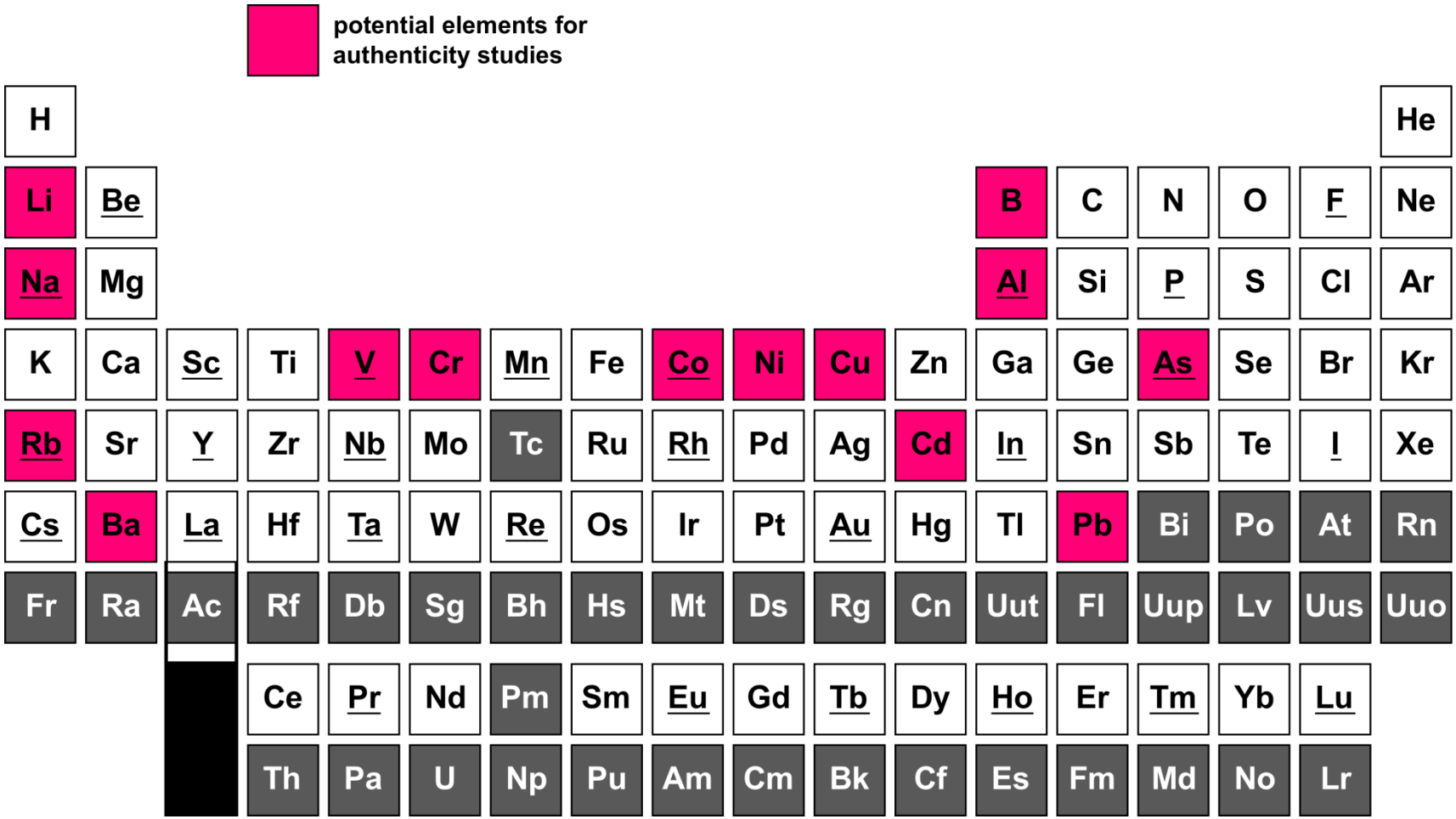
Data evaluation

Blank, Rb, Instrumental Isotopic fractionation

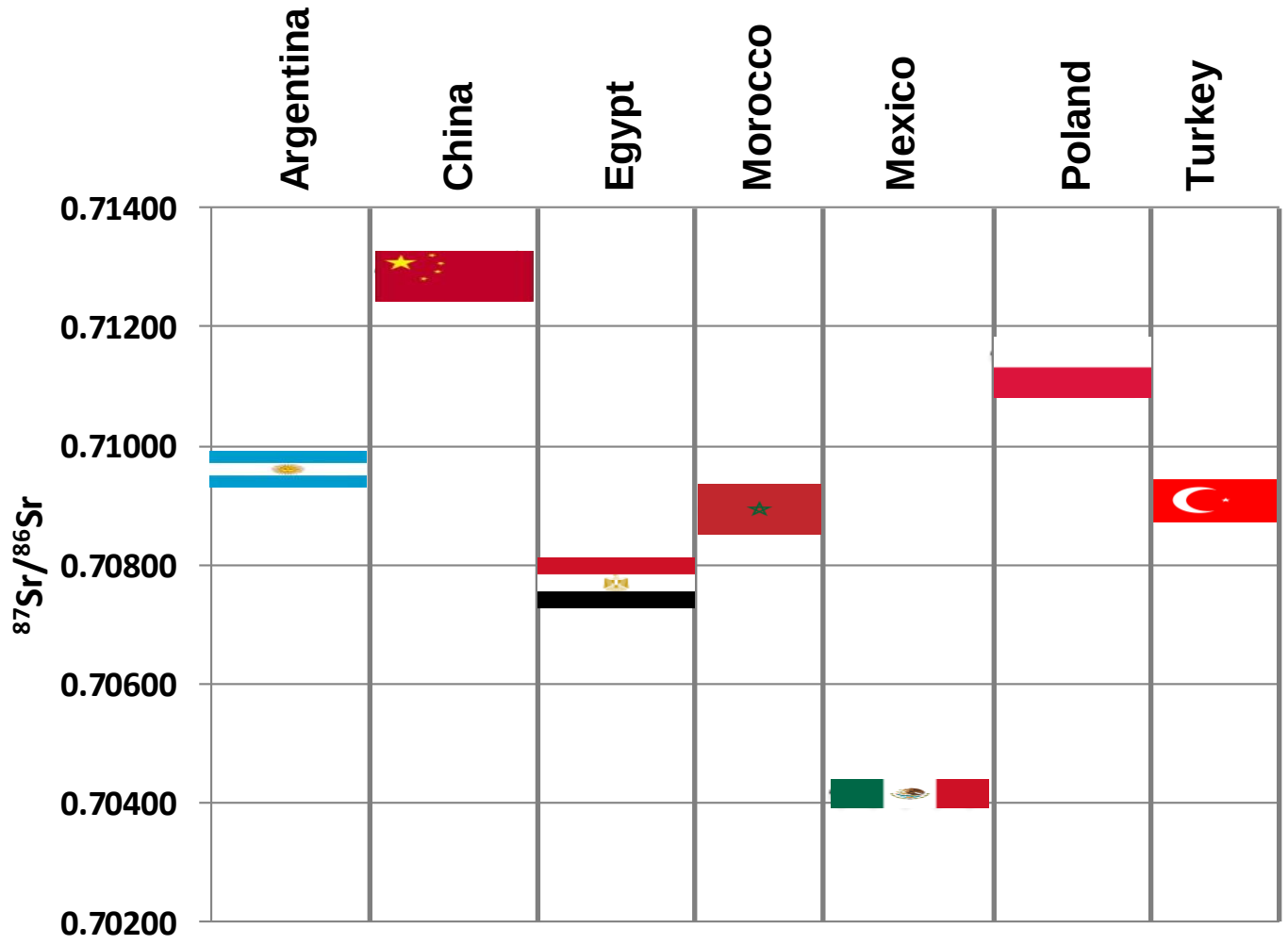
Results – elemental pattern



Results – Elemental Pattern



Sr isotopic data



Sr isotopic fingerprinting

Applicability of Sr isotope ratios

- Regional signal can be determined via bioavailable fraction from soil
- Direct link from soil to plant
- Annual and seasonal stability

Parameters to be considered

- Change of irrigation
- Influence of fertilizer
- Regional heterogeneity of the soil

Sr isotopic fingerprinting

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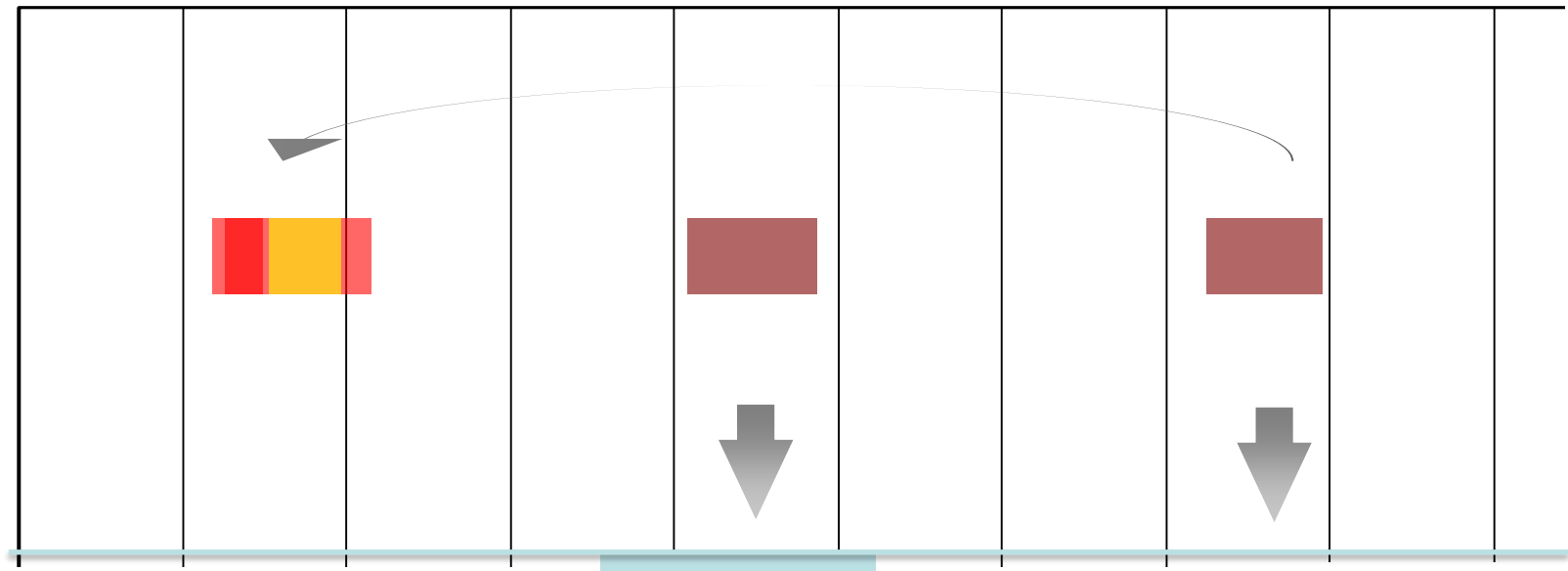
Marchfeld asparagus

Marchfeld: Sr range and source

harvest 2005: n = 20
harvest 2006: n= 35

Soil sample
(7 locations)

Soil sample
(1 location)



0.7050

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

0.7210

Soil extracts
1M NH_4NO_3

- Sr range is stable on an annual basis
- Sr source: leachable Sr in soil
- Sr signal in extract different to total soil

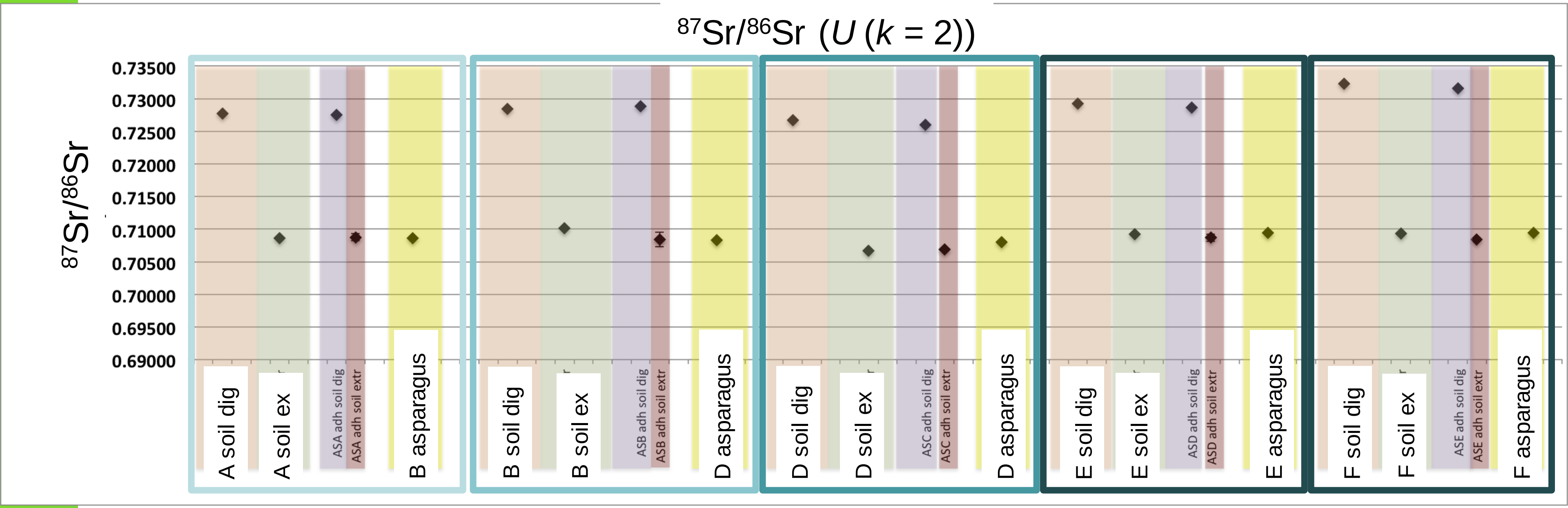
Sr sources

Sr isotopic composition

- Maternal rock
- Wet and dry deposition

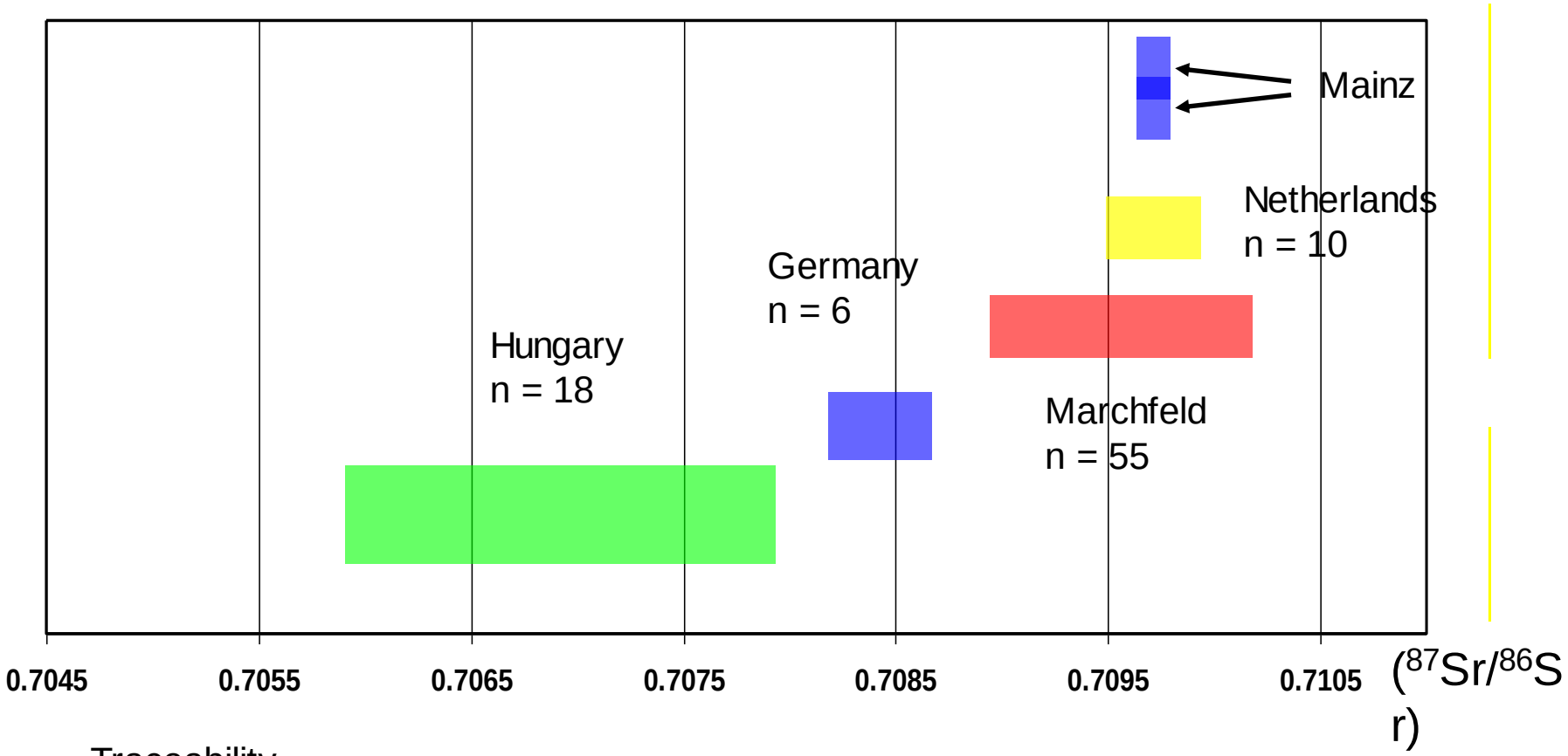
- 20 % weathering
- 80 % recycled Sr

*Miller EK, Blum JD and Friedland AJ, Nature **362**, 1993, 438-441*



$^{87}Sr/^{86}Sr$ (U (k = 2))
$^{87}Sr/^{86}Sr$
0.73500
0.73000
0.72500
0.72000
0.71500
0.71000
0.70500
0.70000
0.69500
0.69000
A soil dig
A soil ex
ASA adh soil dig
ASA adh soil extr
B asparagus
B soil dig
B soil ex
ASB adh soil dig
ASB adh soil extr
D asparagus
D soil dig
D soil ex
ASC adh soil dig
ASC adh soil extr
D asparagus
E soil dig
E soil ex
ASD adh soil dig
ASD adh soil extr
E asparagus
F soil dig
F soil ex
ASE adh soil dig
ASE adh soil extr
F asparagus

Marchfeld: Sr range and source



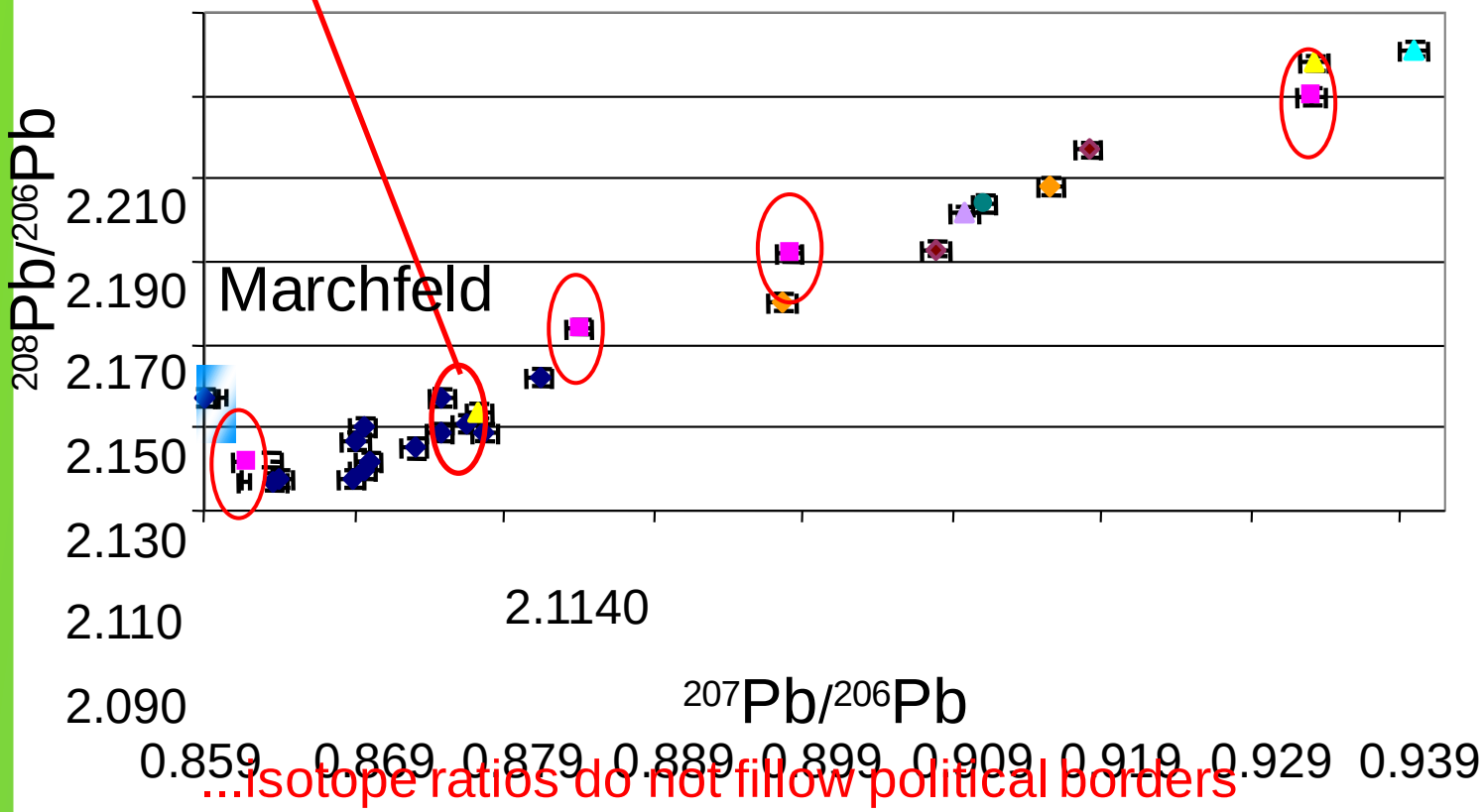
Traceability

- Marchfeld: hand picked by lab staff (traceable)
- other regions: purchased at the market (not traceable)

- include other signatures
- multivariate statistics

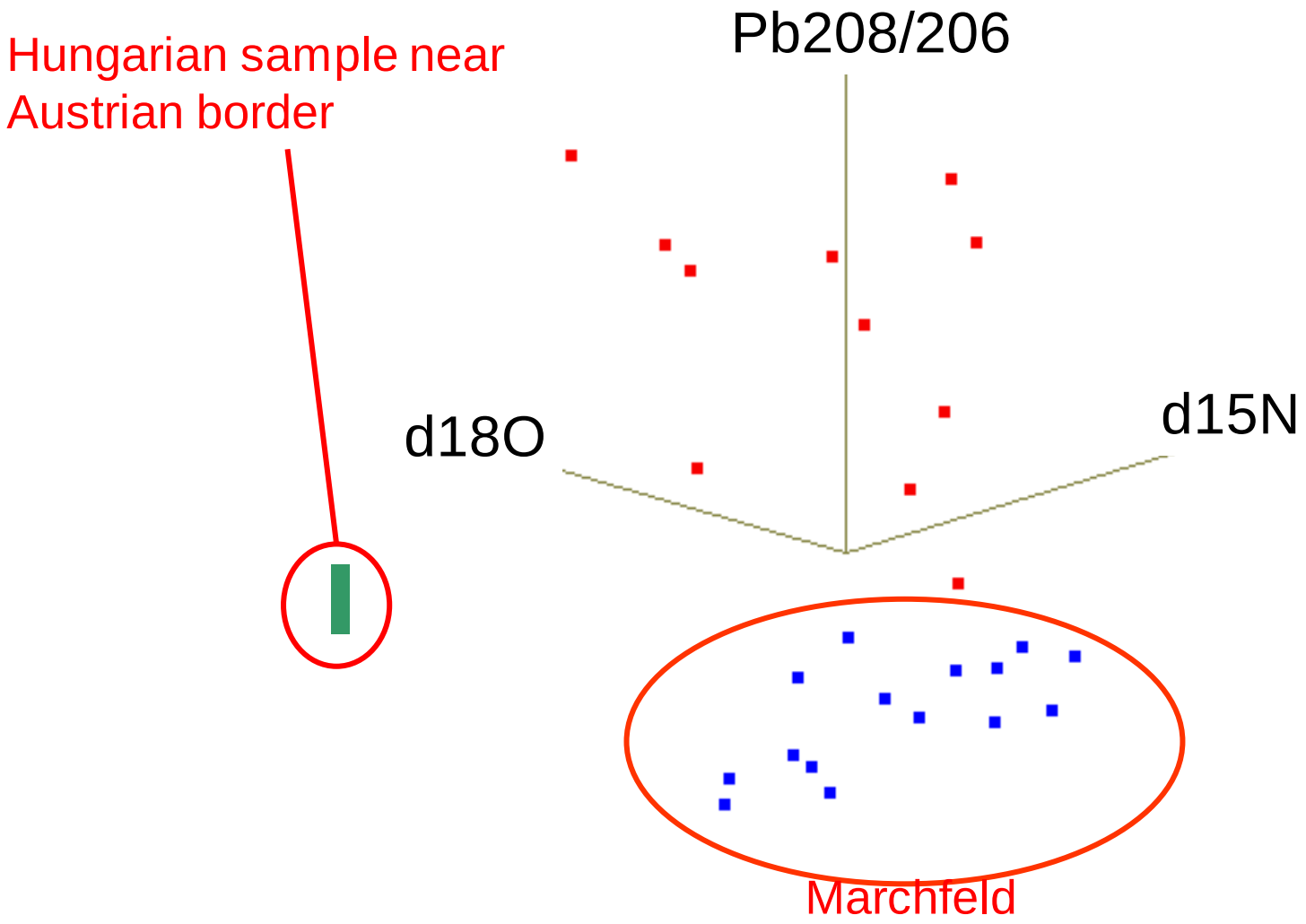
Marchfeld asparagus

Hungarian sample near Austrian border



...isotope ratios do not follow political borders

3D main component analysis



Predicting Provenance

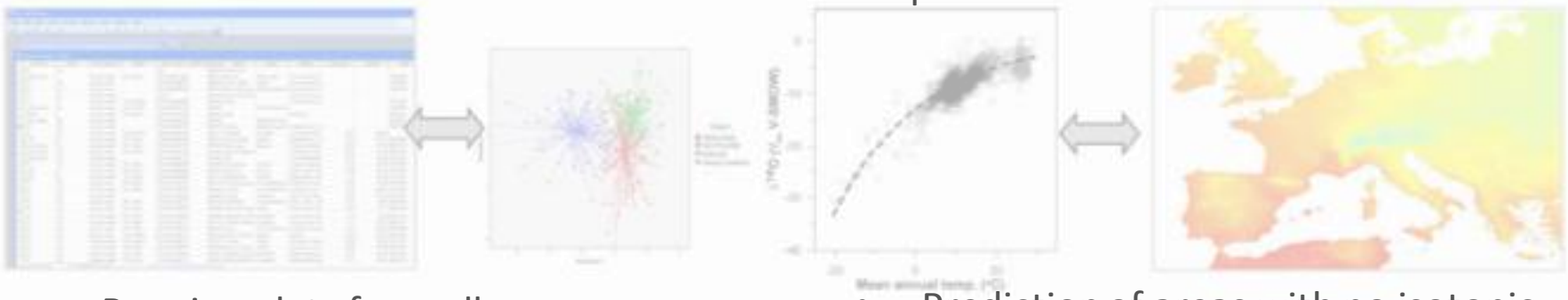
Complementary approaches for the verification of food provenance

Databases

Origin is determined by comparison to data wihtin a database

Isoscapes

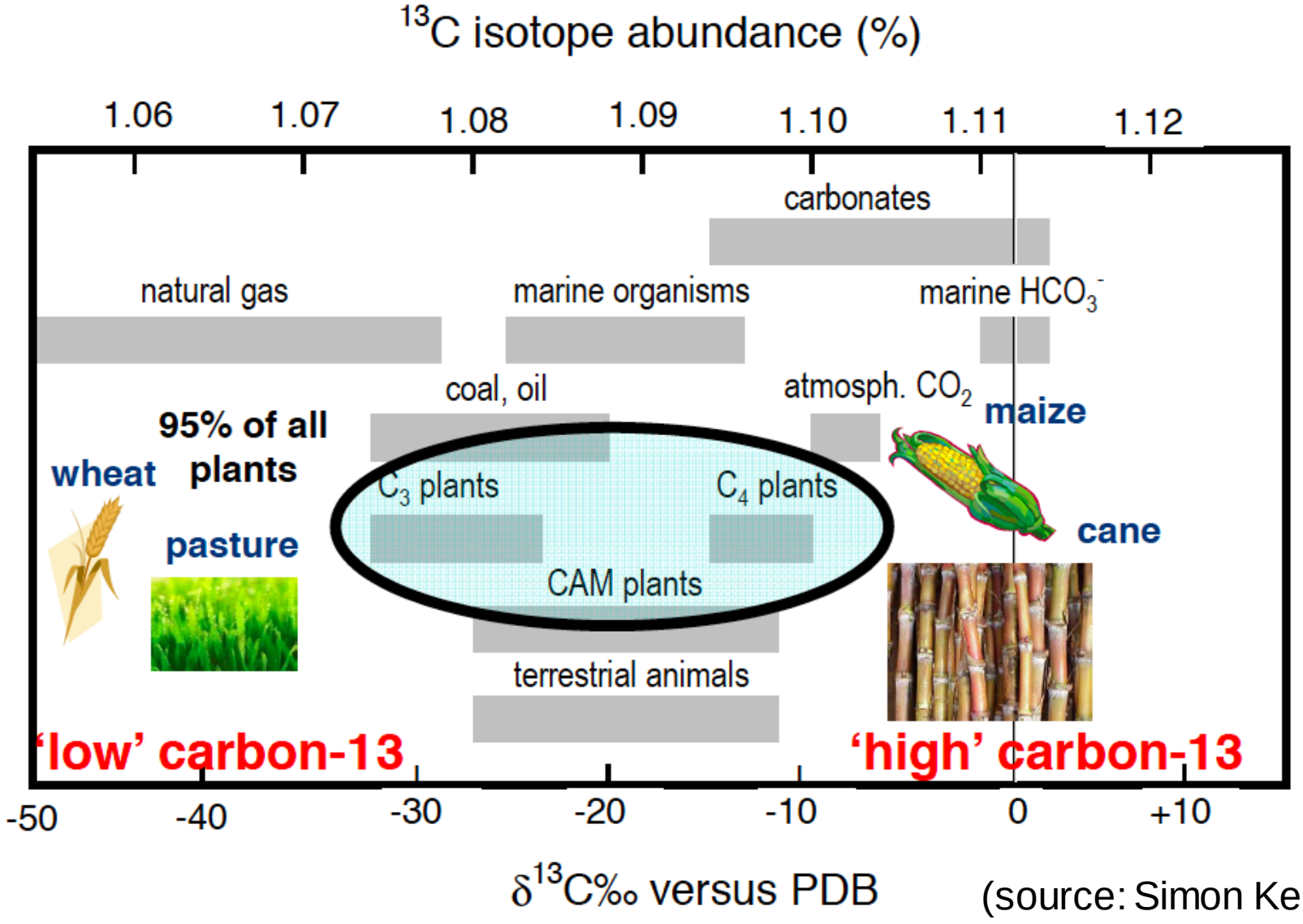
Origin is detemrined by comparing the data within a food to interpolated geo-climatic factors depicted in an isotopic map



- Requires data from all provenances (authentic samples)
- Expensive (large number of datas)
- Stability has to be proven (regular update)

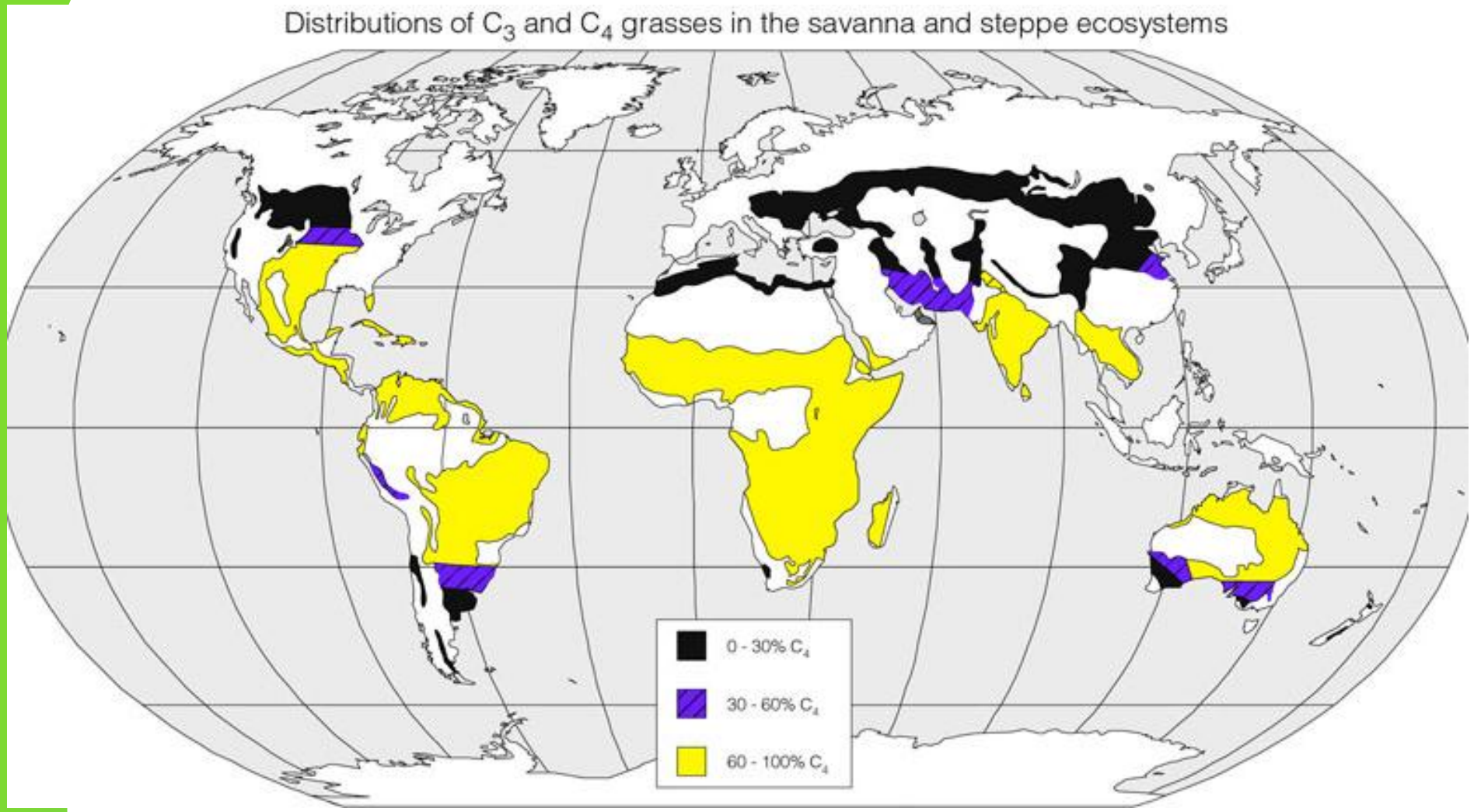
- Prediction of areas with no isotopic data
- Large scale data might overlook regionality
- Annual/seasonal stability has to be proven

$\delta^{18}O$ in plants

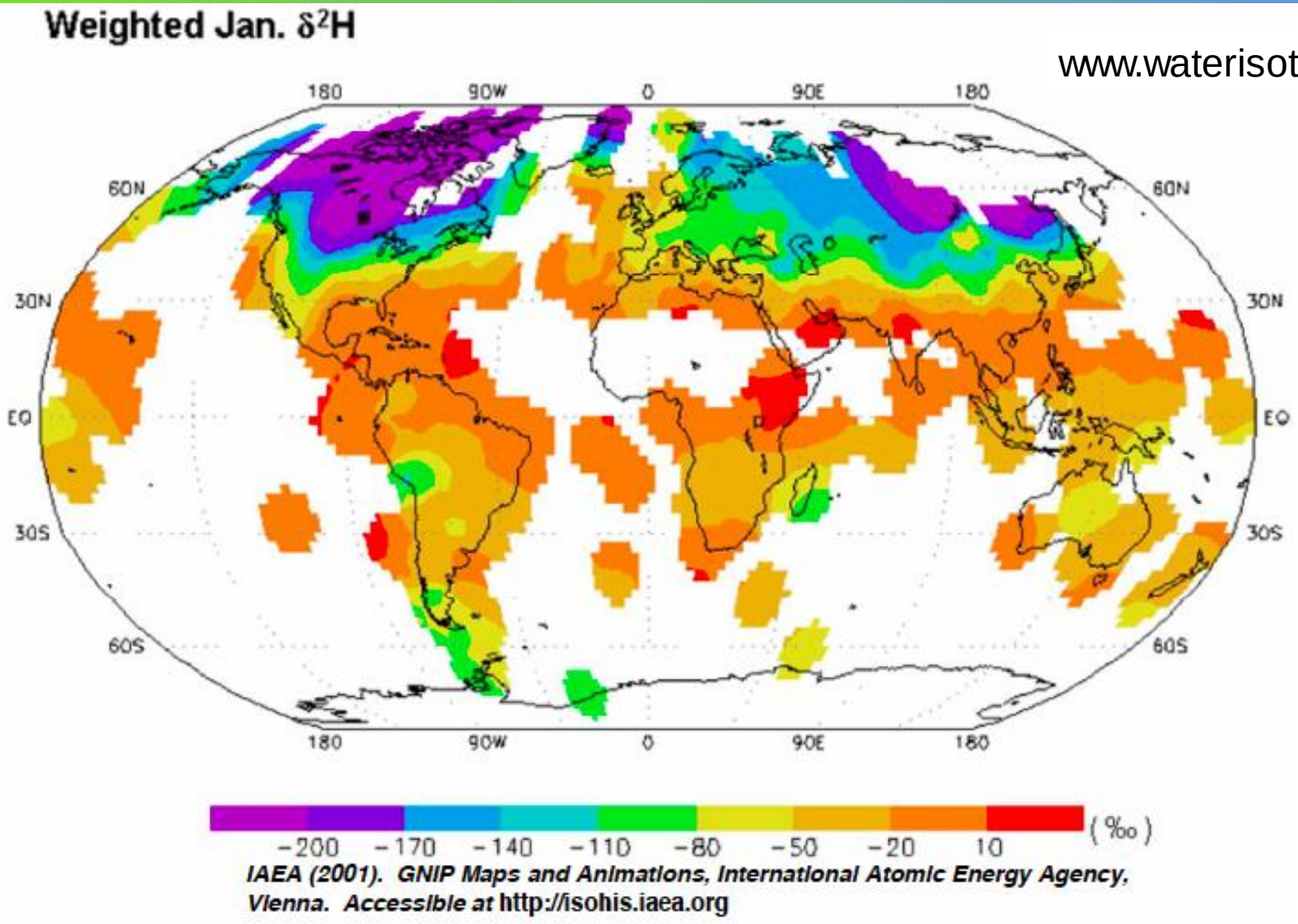


(source: Simon Kelly)

Distribution of C3 and C4 plants

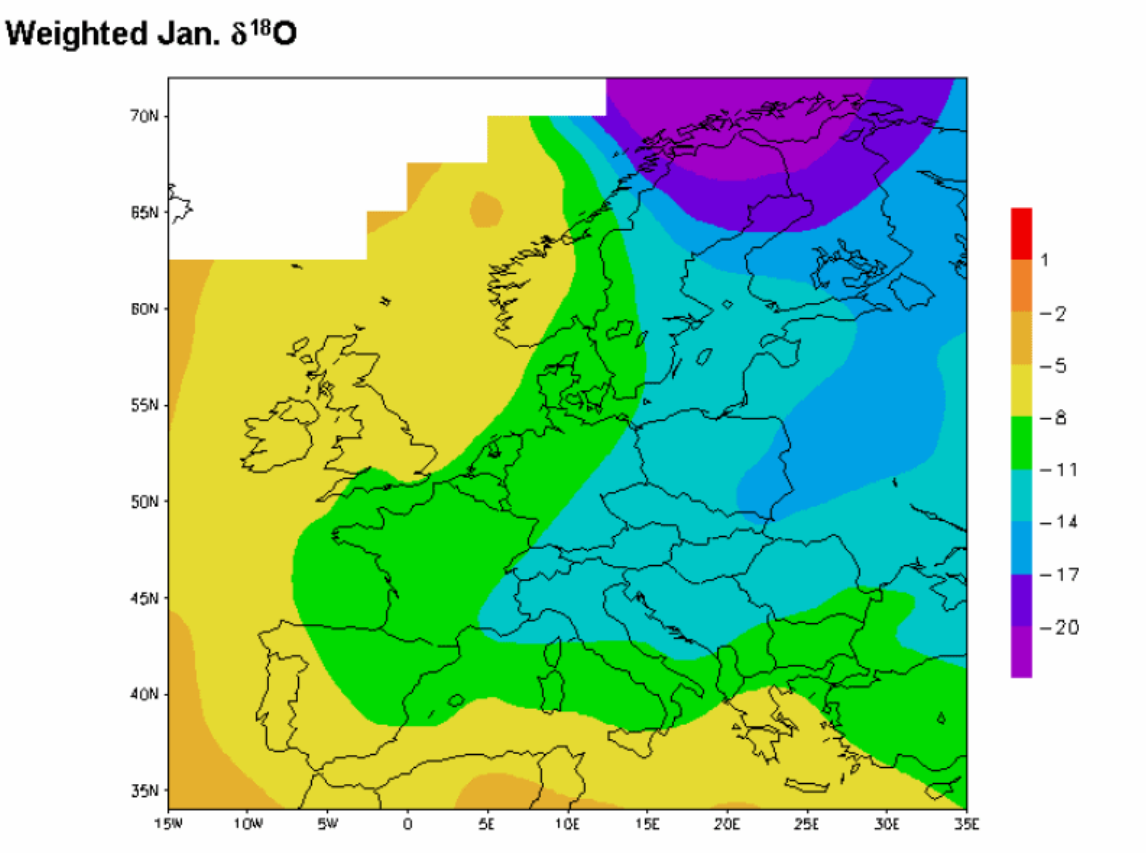


H and O isoscapes



Assessment of ‚isoscapes‘

- Continuous maps of isotope ratios for authenticity, migration and more

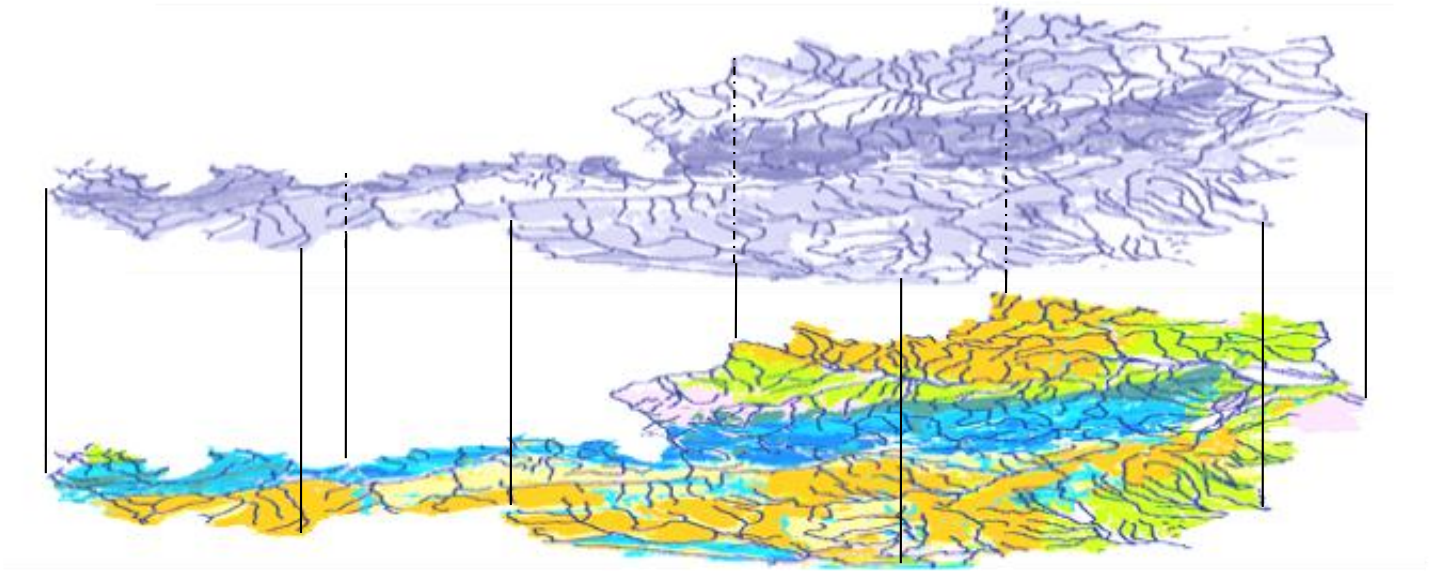


Sr isoscapes

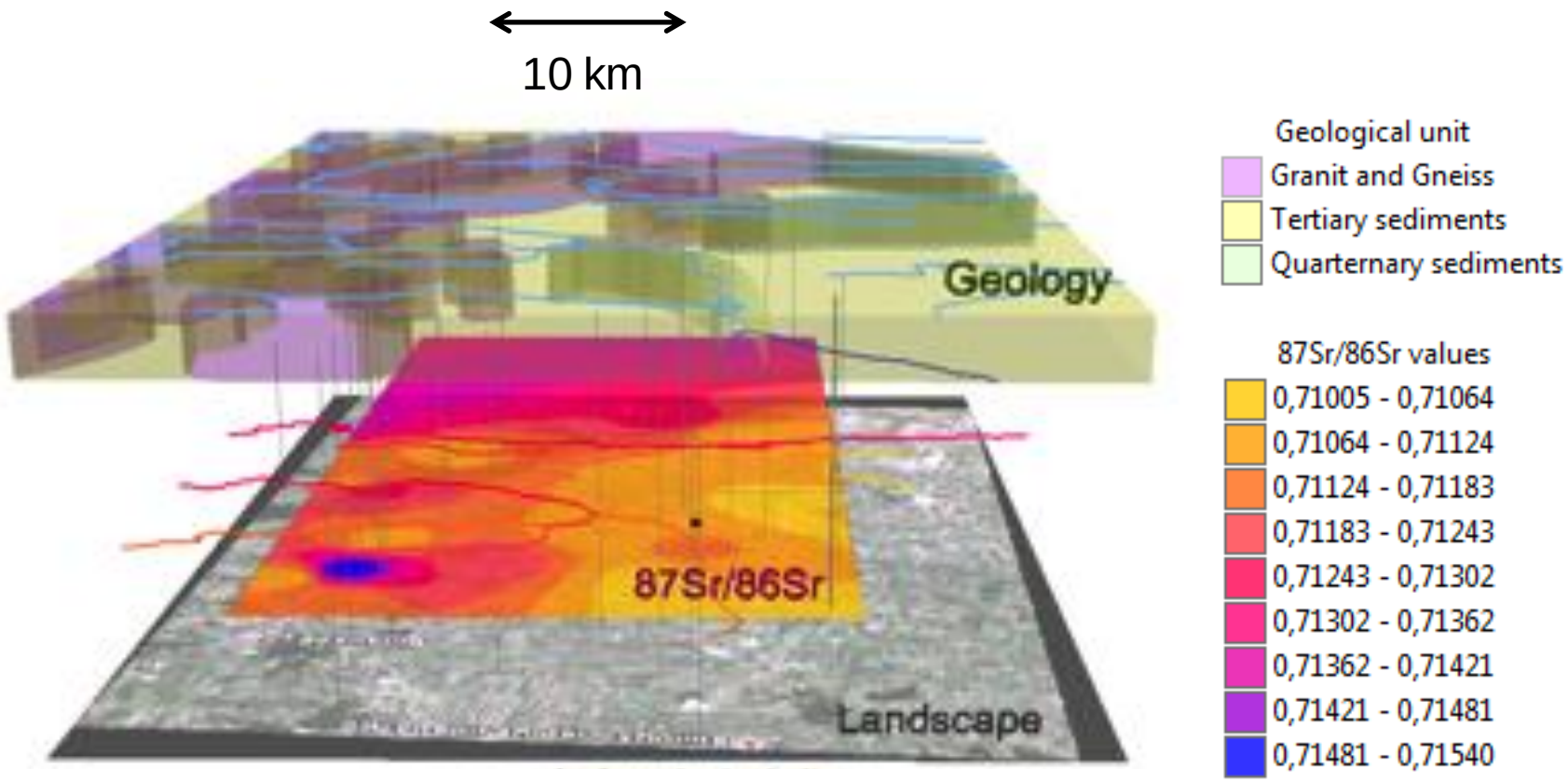
- Isoscapes for
  - Bioavailable $^{87}Sr/^{86}Sr$ in soils
  - $^{87}Sr/^{86}Sr$ in rivers and lakes

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

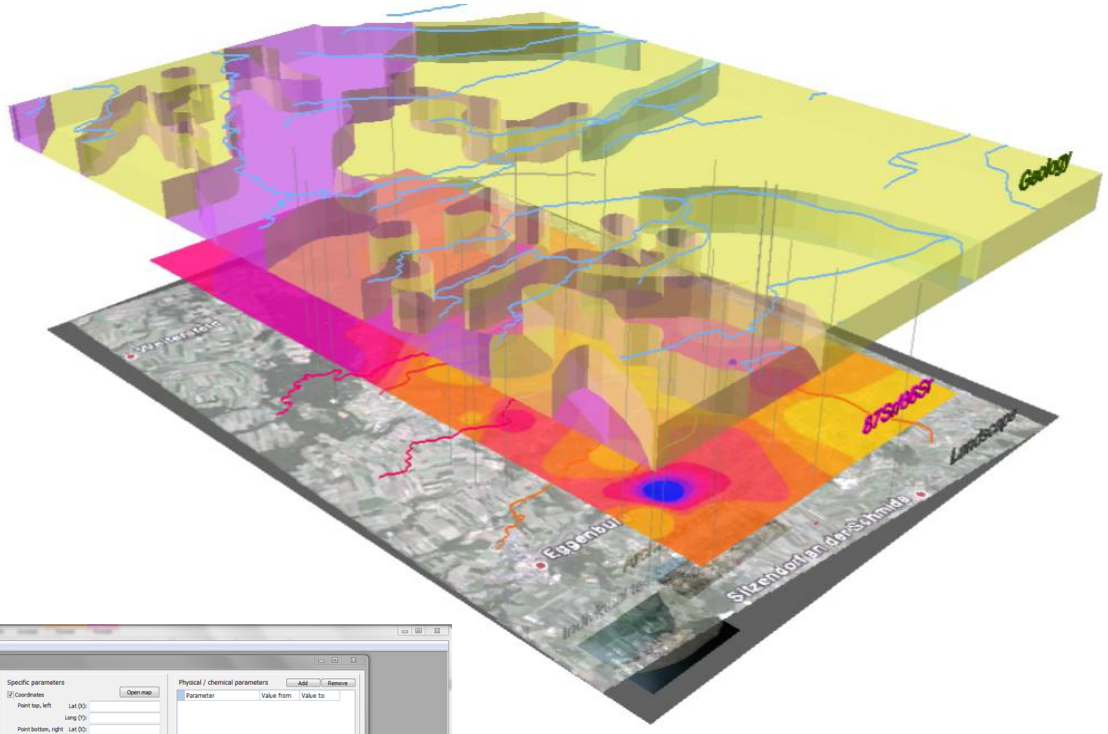
geology



Sr – isoscape – definition of a region by the bioavailable Sr

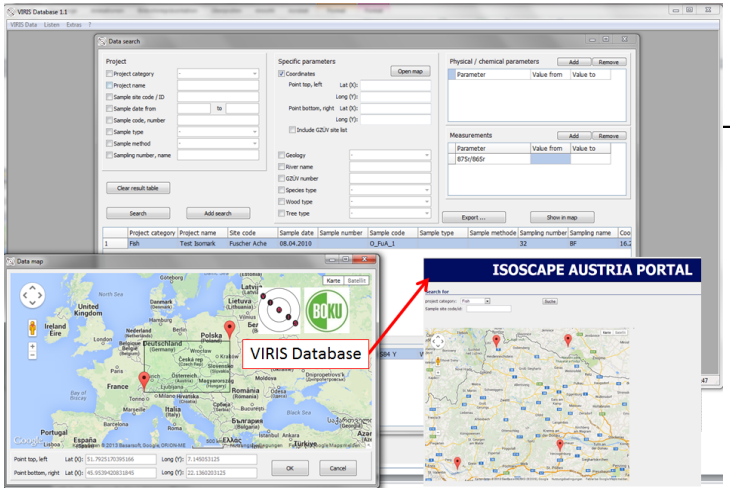


Sr – isoscape – definition of a region by the bioavailable Sr



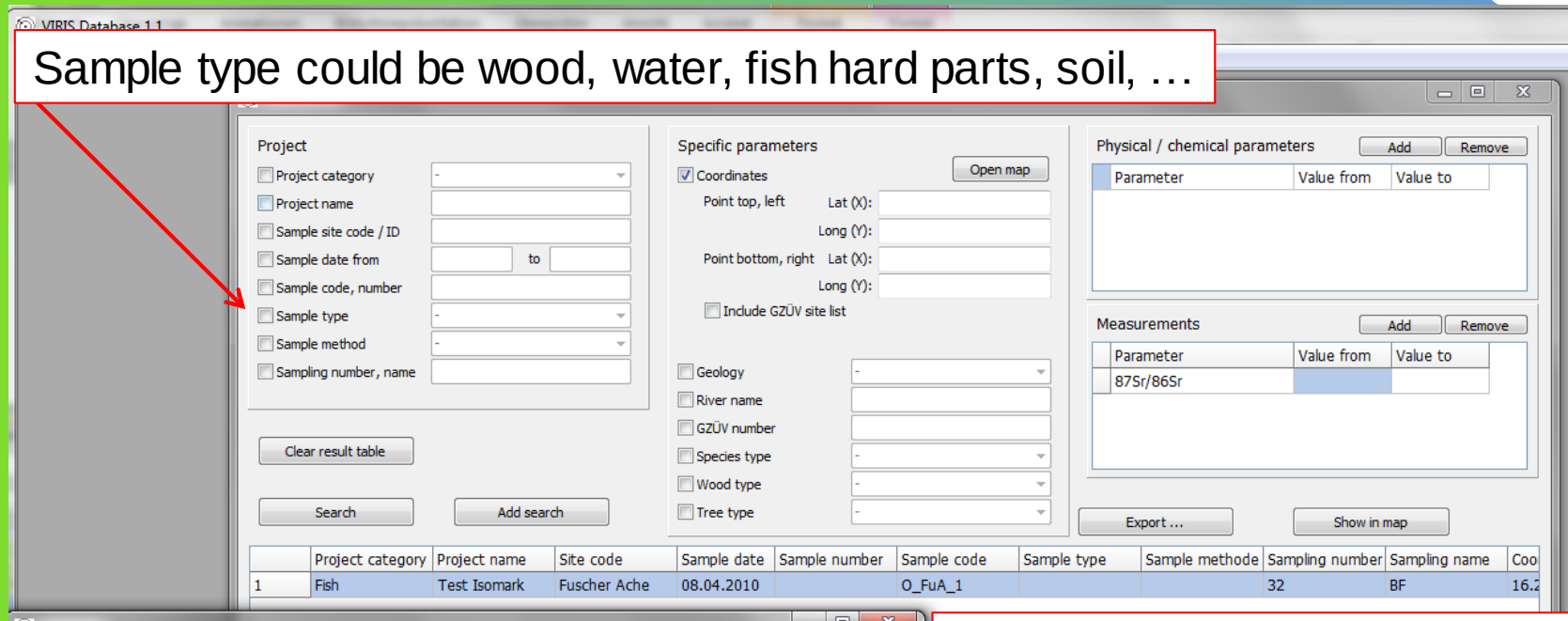
Geological unit
- Granit and Gneiss
- Tertiary sediments
- Quarternary sediments

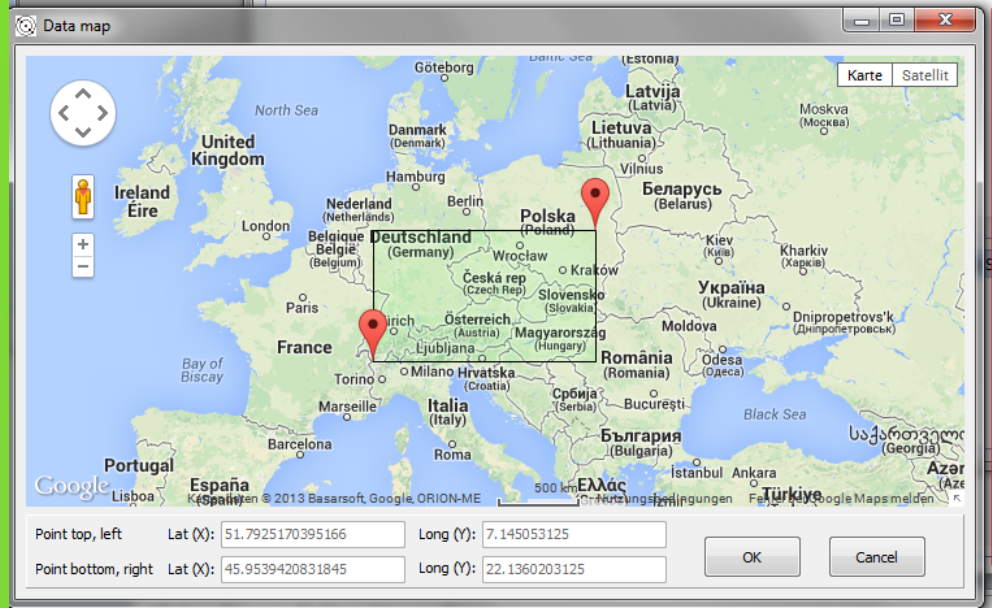
87Sr/86Sr values
- 0,71005 - 0,71064
- 0,71064 - 0,71124
- 0,71124 - 0,71183
- 0,71183 - 0,71243
- 0,71243 - 0,71302
- 0,71302 - 0,71362
- 0,71362 - 0,71421
- 0,71421 - 0,71481
- 0,71481 - 0,71540



Sr isoscape work - VIRIS database

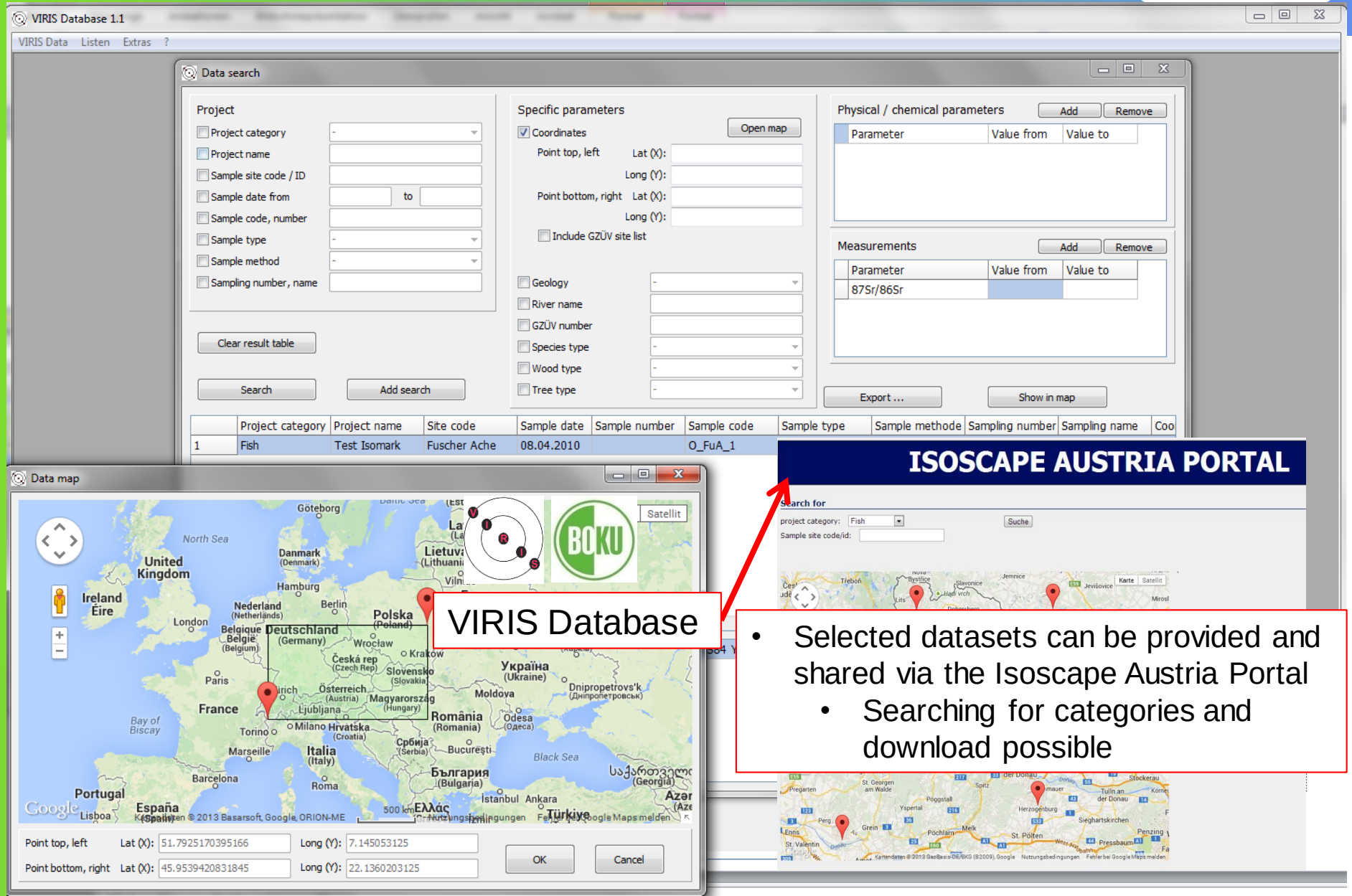
Sample type could be wood, water, fish hard parts, soil, …



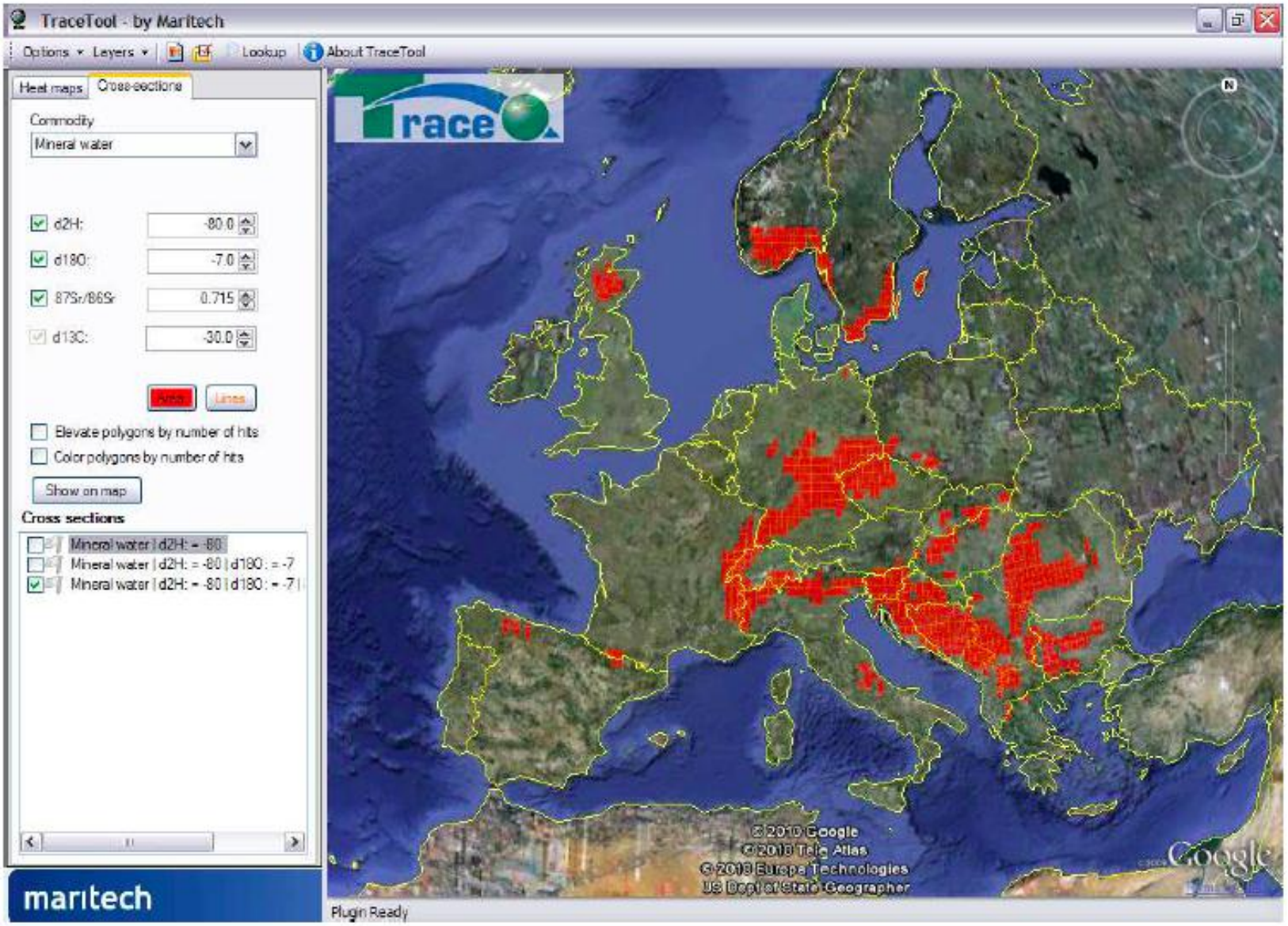


- Input via Excel spread sheets in different categories of projects and samples, including quality judgement, instrumental settings, pictures, links to original data, citation etc.
- Searching data possible
  - by a wide variety of requests, including the measured parameter (e.g. $^{87}Sr/^{86}Sr$)
  - by a geographical window that can be opened from the database and that allows to select a geographical area

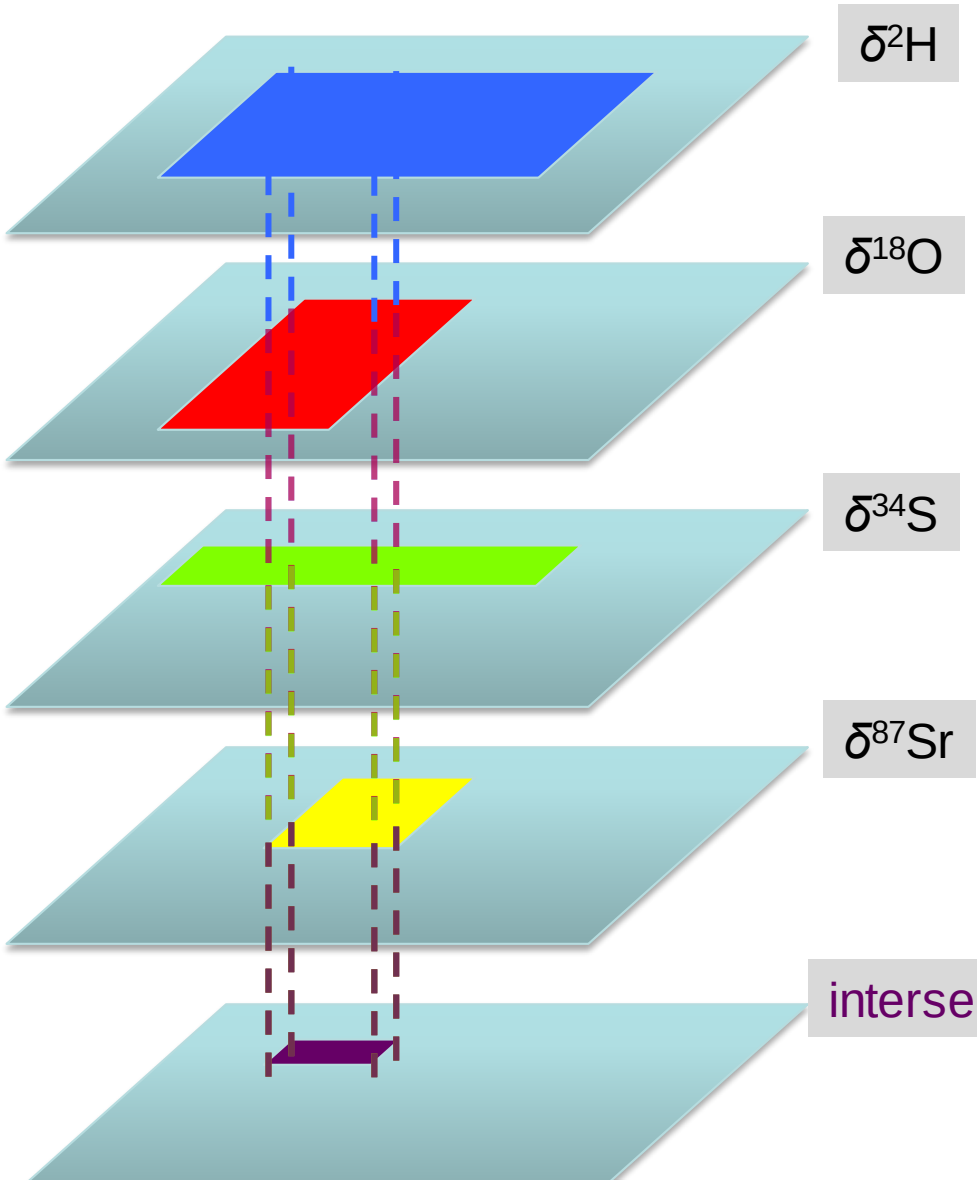
Sr isoscape work - Isoscape Austria Portal



TRACE project (trace.eu.org)



Combining areas of origin



Combination of isotopic and elemental information: Determination of the origin of green coffee beans

Standard protocol ICP-MS

Microwave digestion

Sr/matrix separation

Multielement analysis

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

ICP-SFMS

Element 2

ICP-QMS

Elan DRCe

MC-ICP-SFMS

Nu Plasma HR

Standard protocol IRMS

grinding

drying

Elemental analyser(EuroEA)

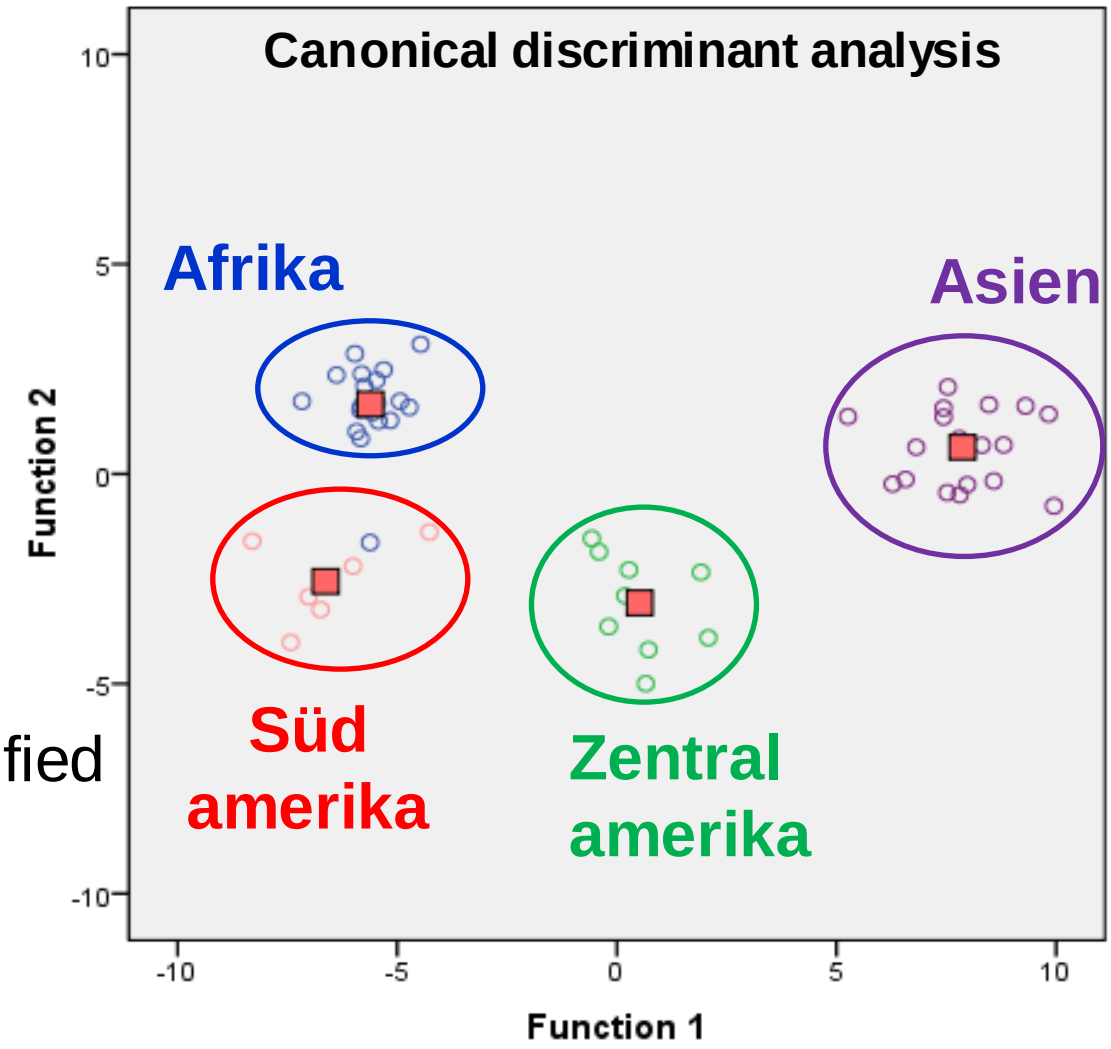
$\delta^{13}C$ $\delta^{34}S$ $\delta^{18}O$

$\delta^{15}N$ $\delta^{2}H$

IRMS (Sira II; Isoprime)

Continental origin

- Multielement analysis
- $^{87}Sr/^{86}Sr$

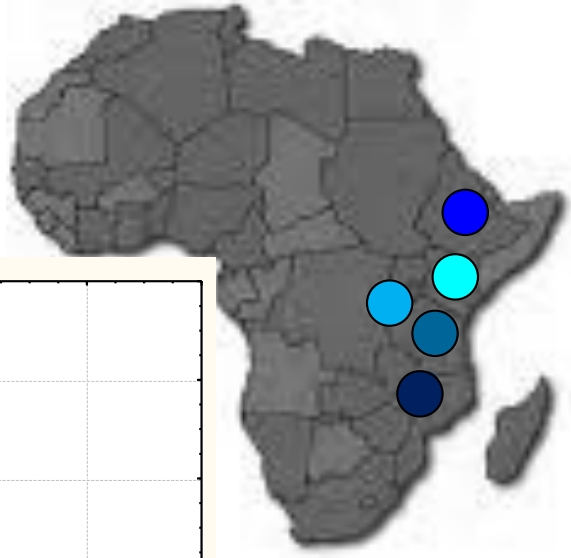


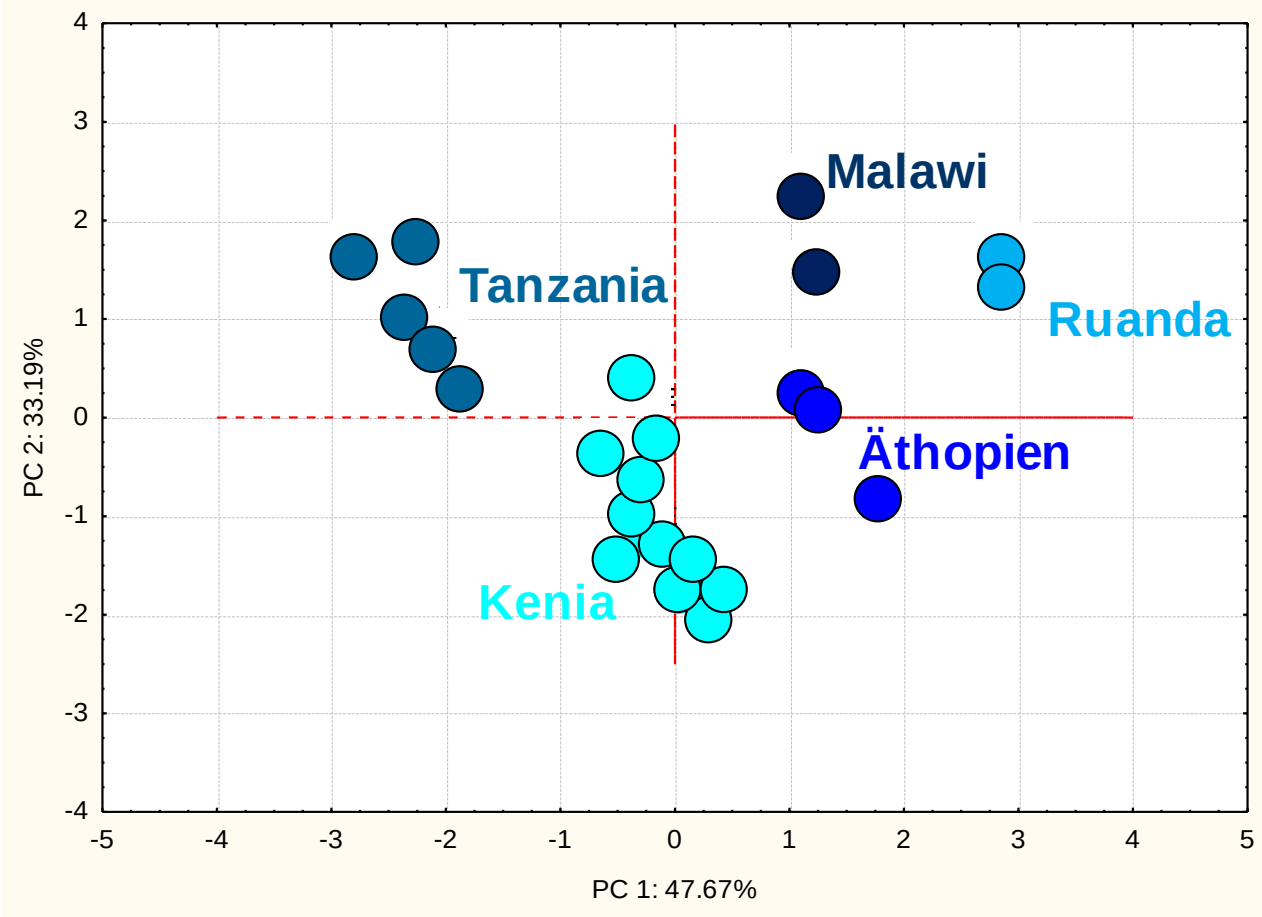
98.1 % classified

Regional origin

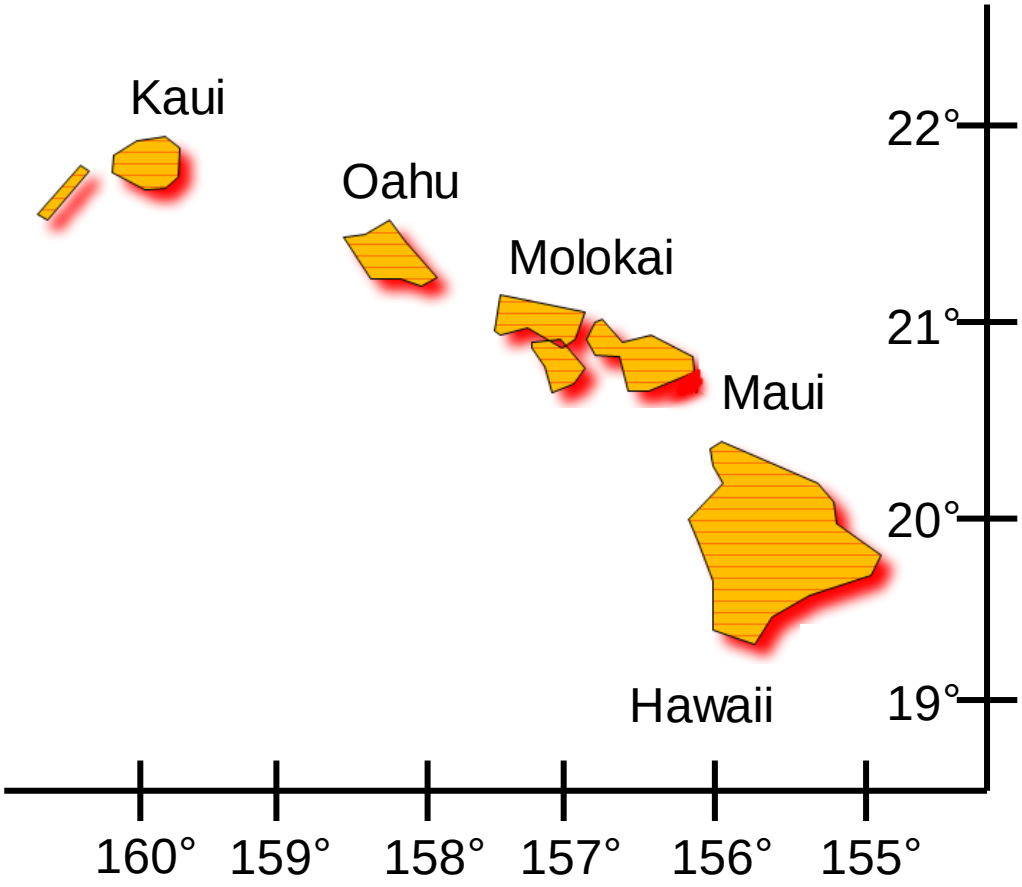
(Rodrigues et al., European Food Research and Technology)

- $^{87}Sr/^{86}Sr$
- $\delta\,^{18}O$



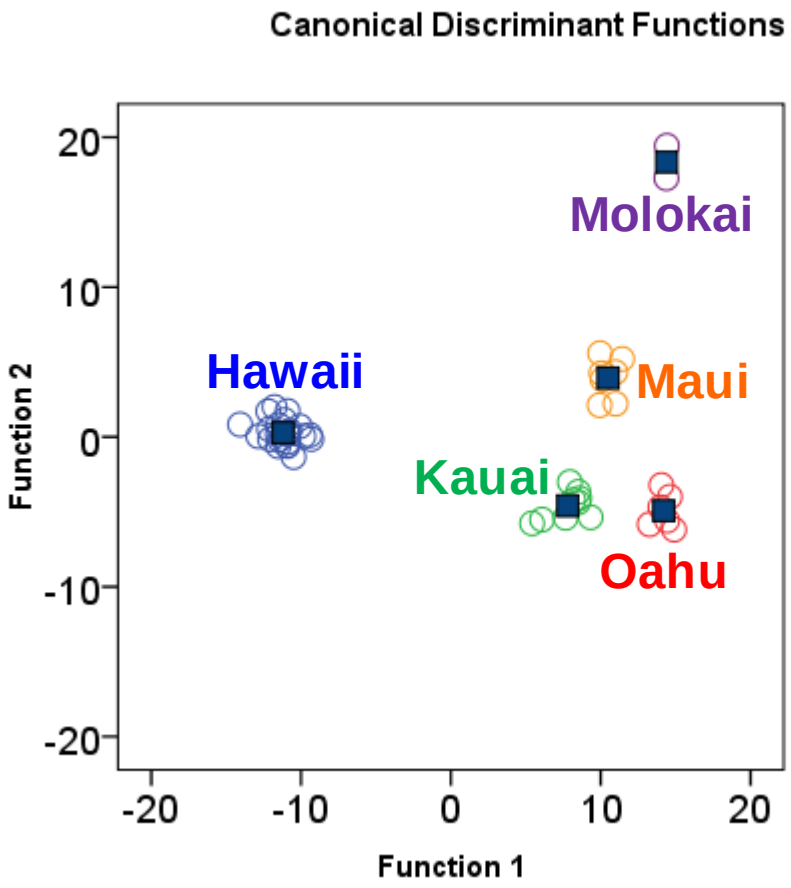


Case study: Hawaii



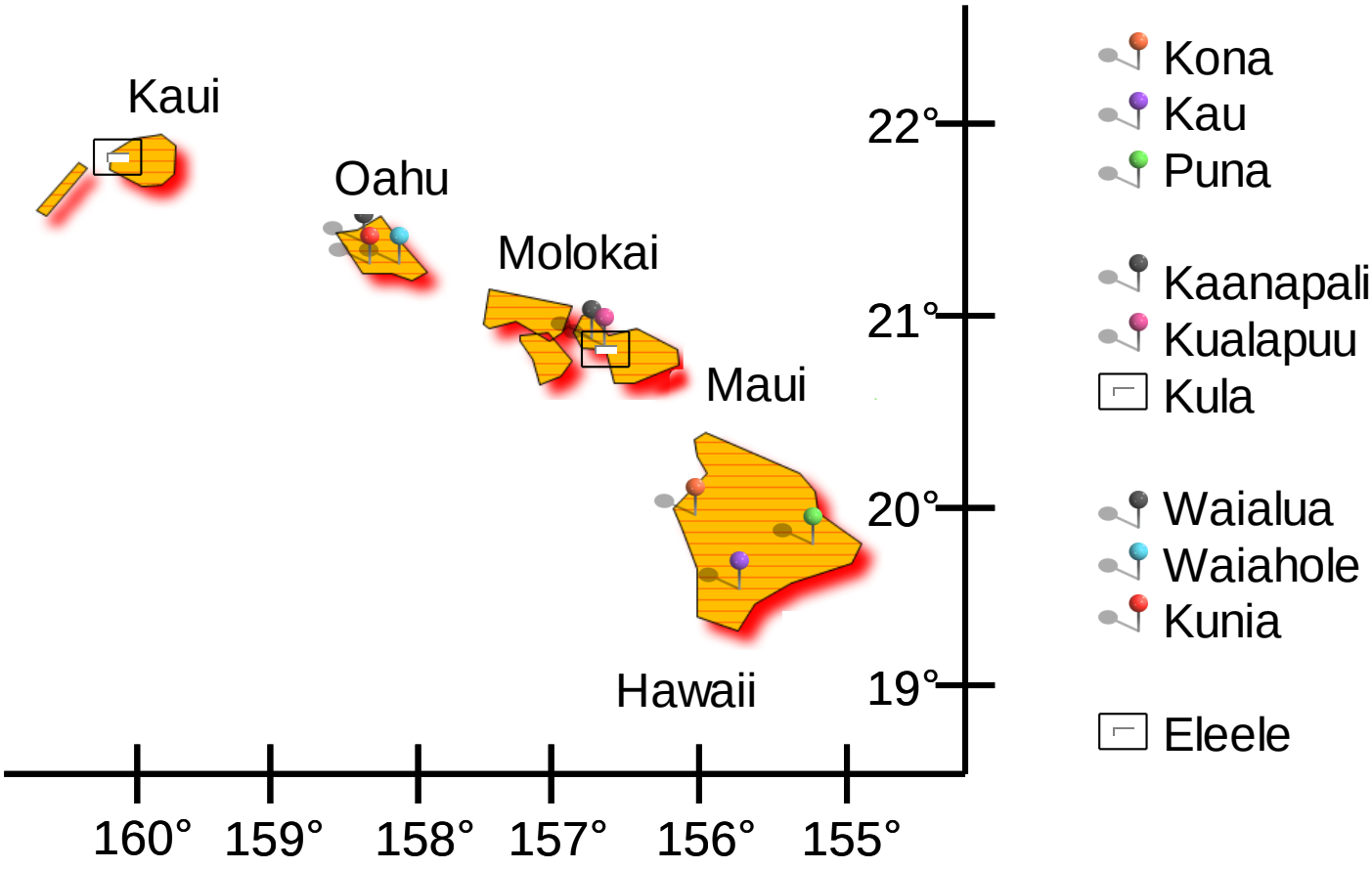
- $^{87}Sr/^{86}Sr$
- $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{34}S$
- Lanthanide, B, Na, Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Mo, Ba, Pb and Bi

Hawaii – origin of islands

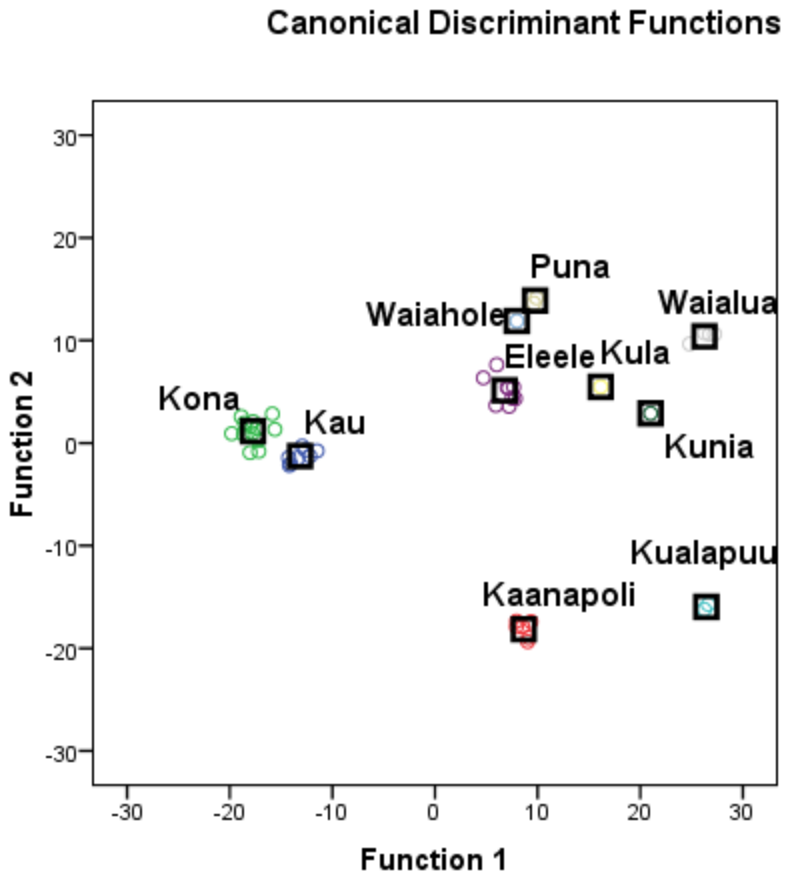


- $\delta^{34}S$
- Lanthanide, B, Al, Fe, Ni, Cu, Rb, Sr, Mo, Ba

Hawaii – regions within islands



Hawaii – regions within islands

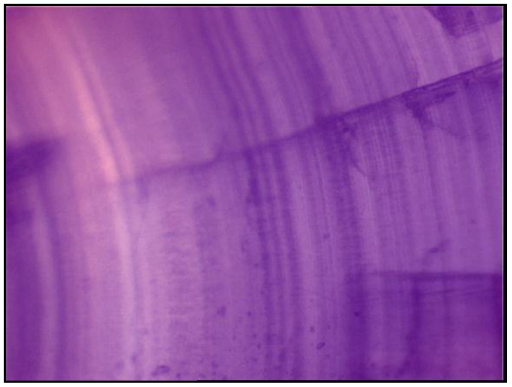


- $\delta^{34}S$
- $\delta^{18}O$
- Y, La, Ce, Sm, B, Al, Fe, Ni, Cu, Rb, Sr, Mo, Ba

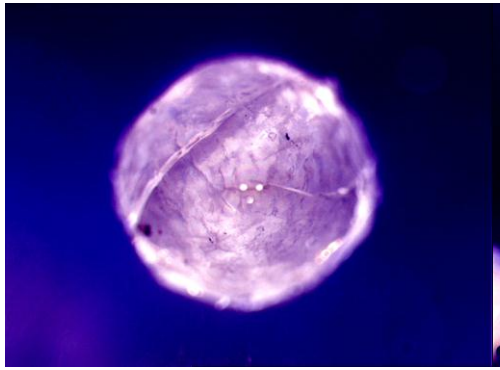
Provenance of Fish

Fish Hard Parts

Otoliths

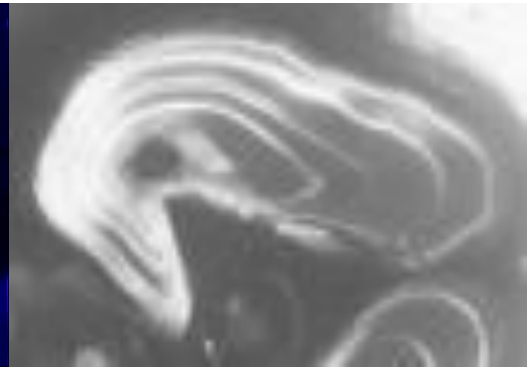


Back bone



Eye lenses

Scales



Fin rays

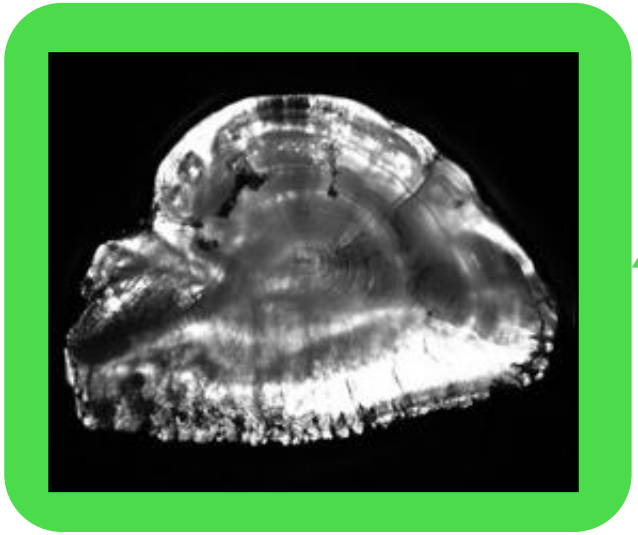
Non lethal strategy

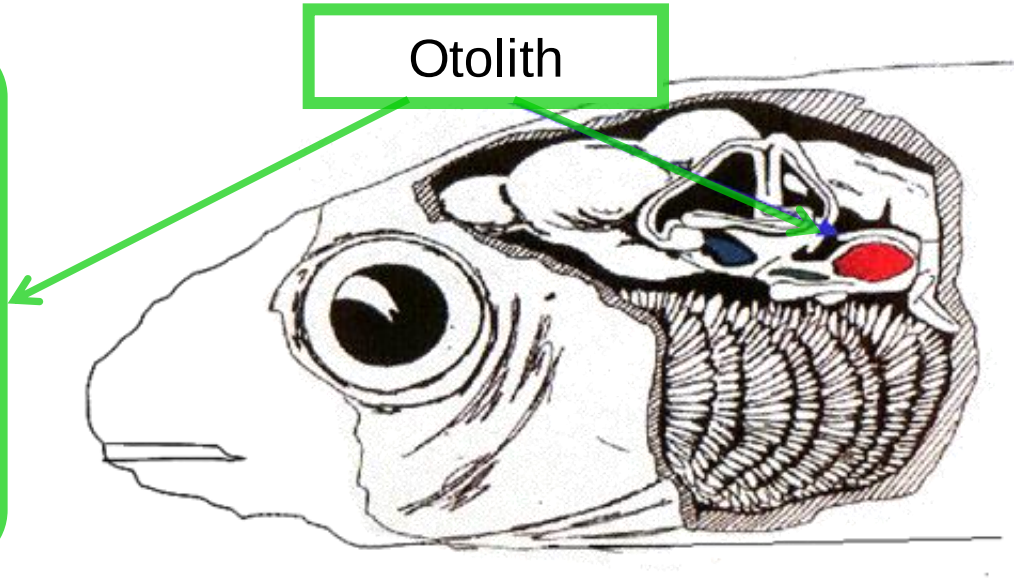
Sr Isotopes in Fish Otoliths

- **Otolith** = ear stone of the fish

  → function: balance, orientation, hearing

  - metabolically inert
  - Grows in discrete layers
  - Ca ↔ Sr
  - Analysis by LA-ICP-MS



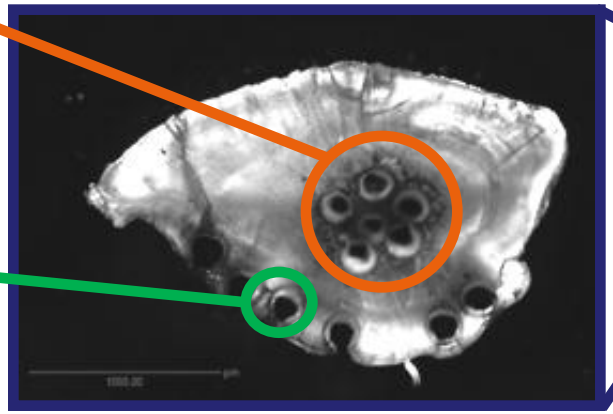


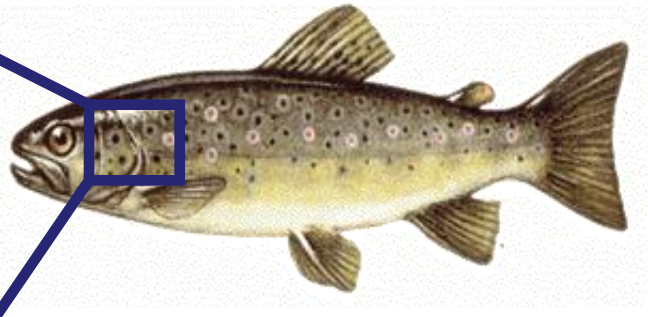
http://www.marine.maine.edu (07-07-03)

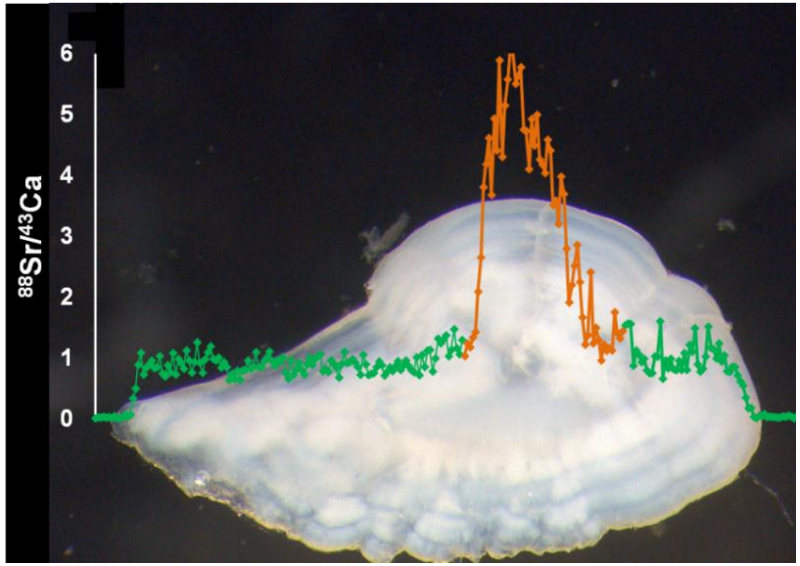
Different Areas of the Otolith Represent different age times

Otolith – core:
Sr-signature of the juvenile habitat

Otolith – rim:
Sr –signature of the adult habitat



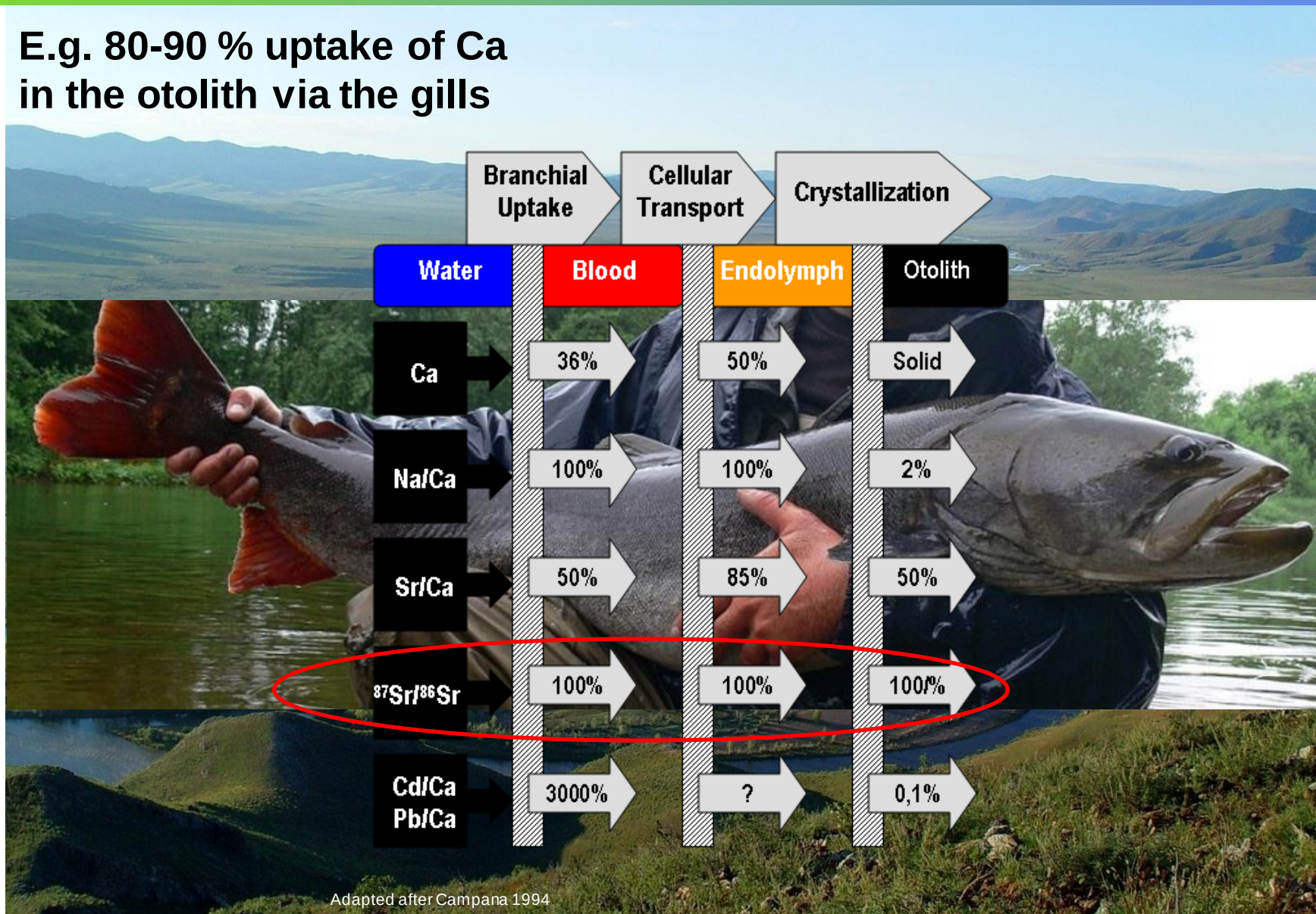




- Migration pattern
- Fish provenance
- Fish stock management
- Population identification
- Population dispersion
- Age determination
- Biomonitor
  - Temperature
  - Salinity
  - contaminationgen

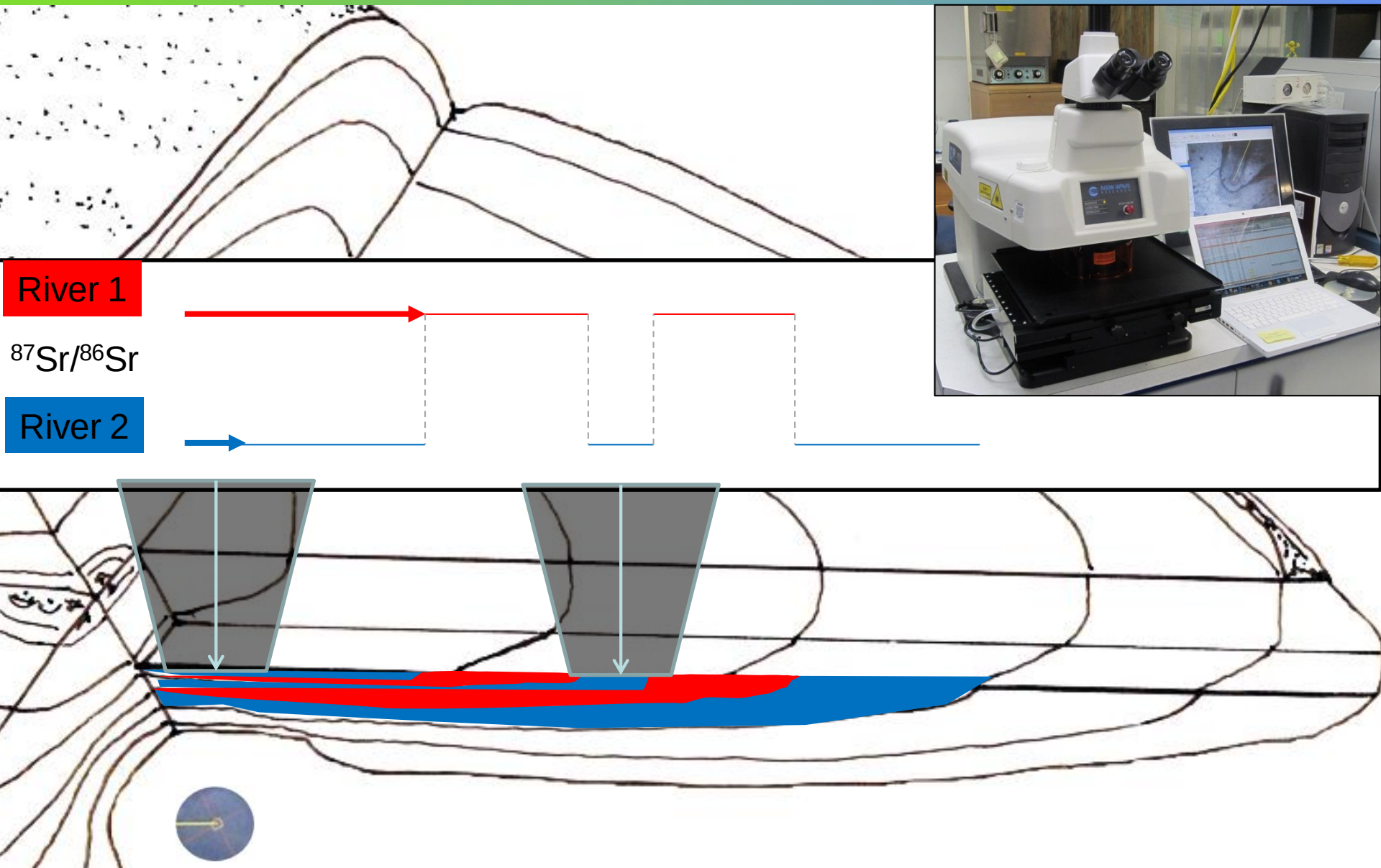
Elemental uptake in the different fish hard parts

E.g. 80-90 % uptake of Ca in the otolith via the gills



Adapted after Campana 1994

Time resolved analysis using LA-ICP-MS



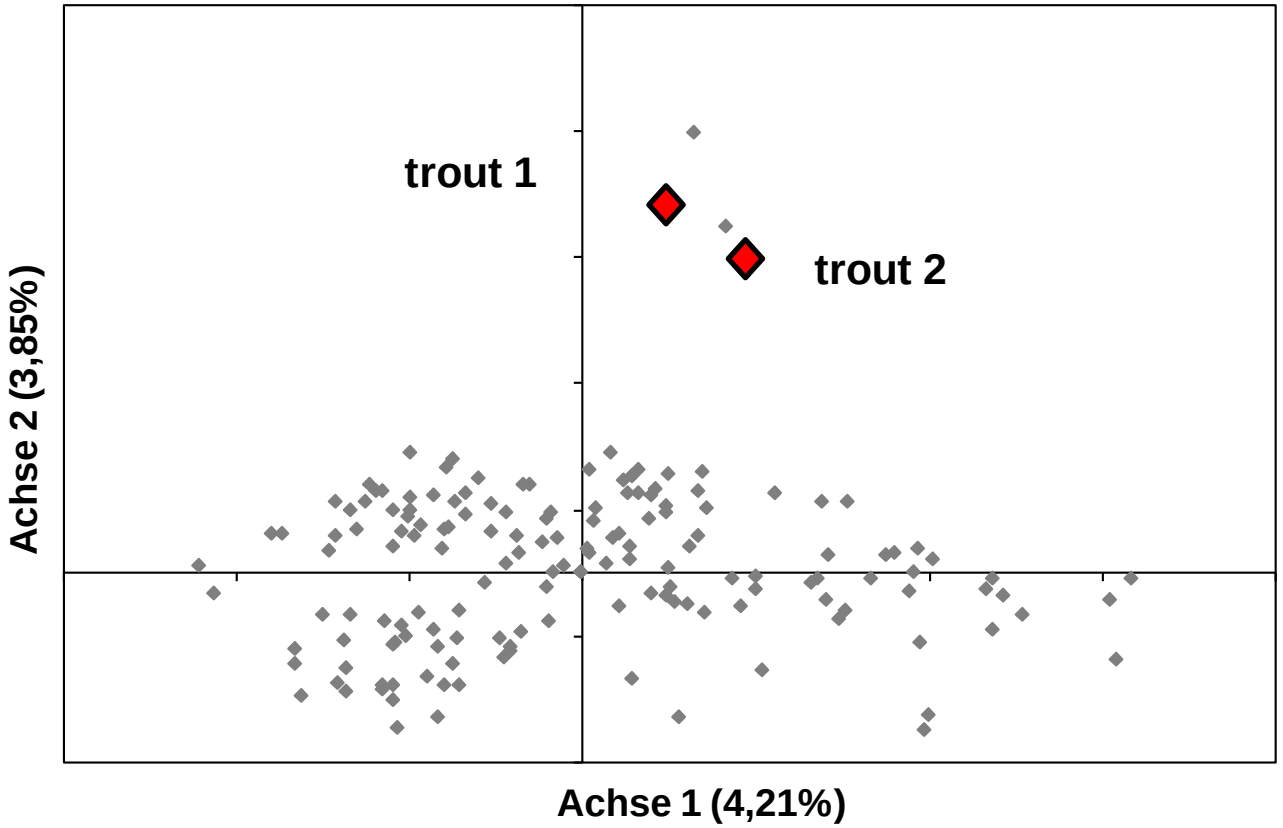
Example: change of habitat (trout)

Windbach (Gneiss)

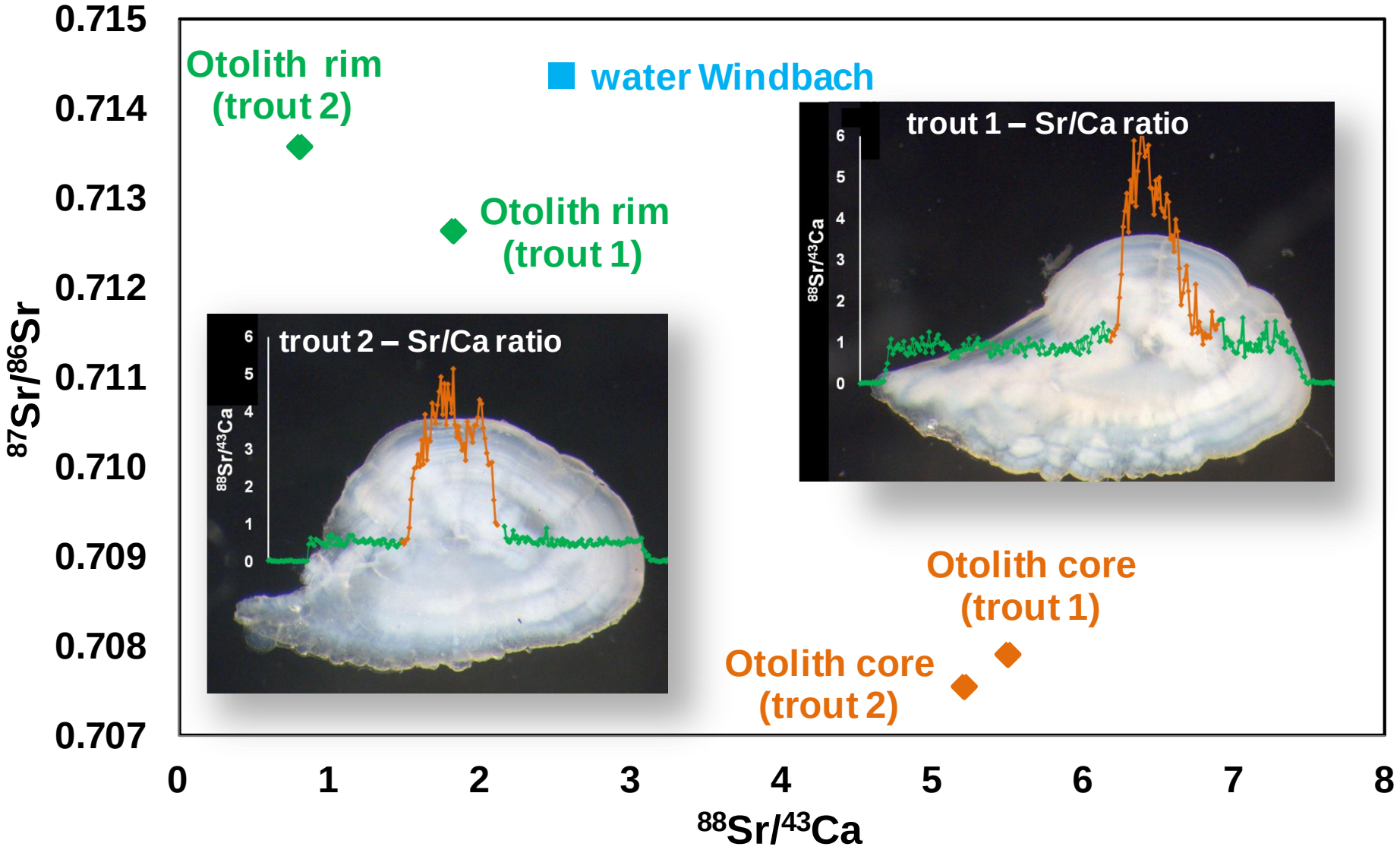
Anras (Dolomit)

Genetical fingerprint

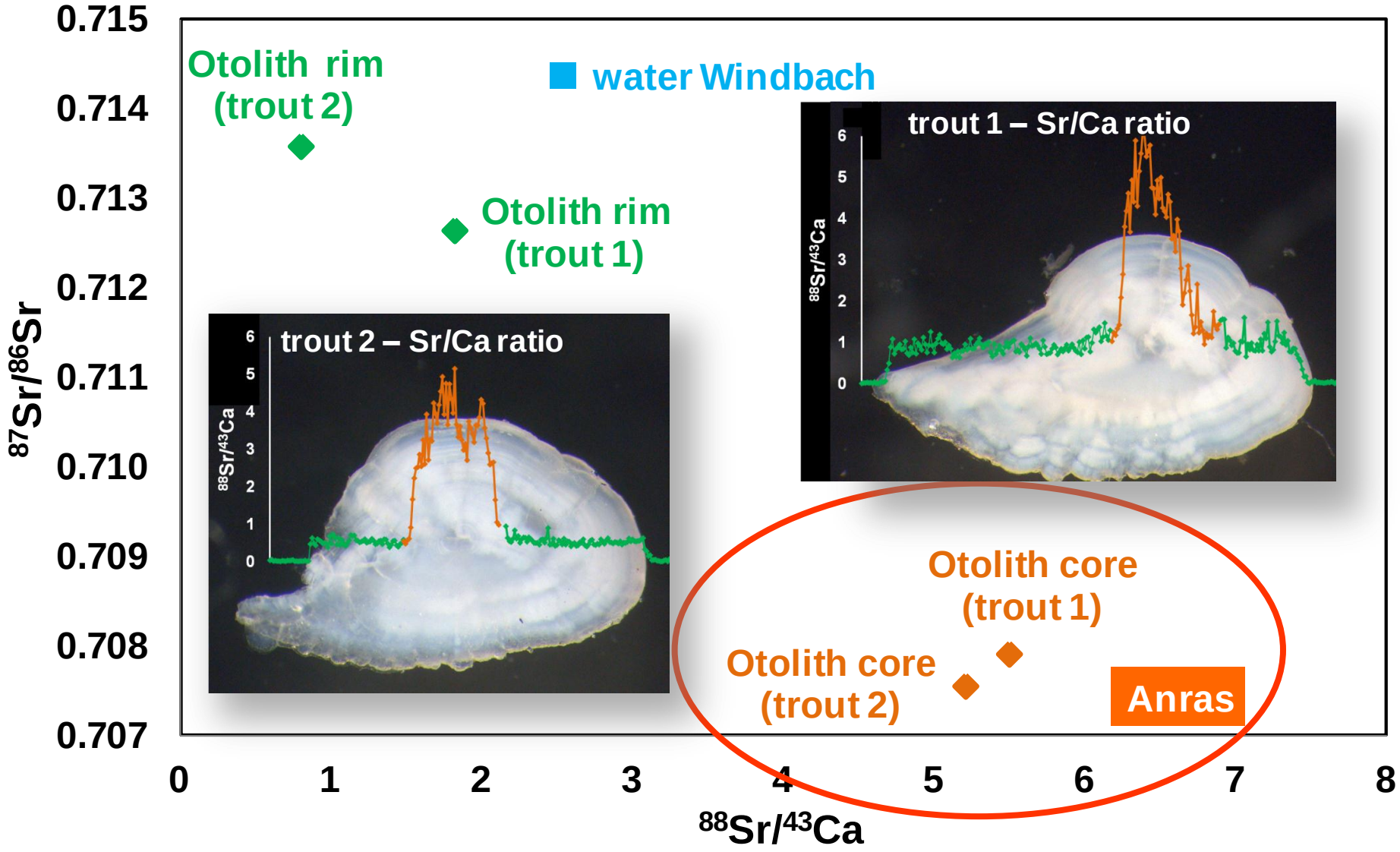
genetics (factorial correspondence analysis)



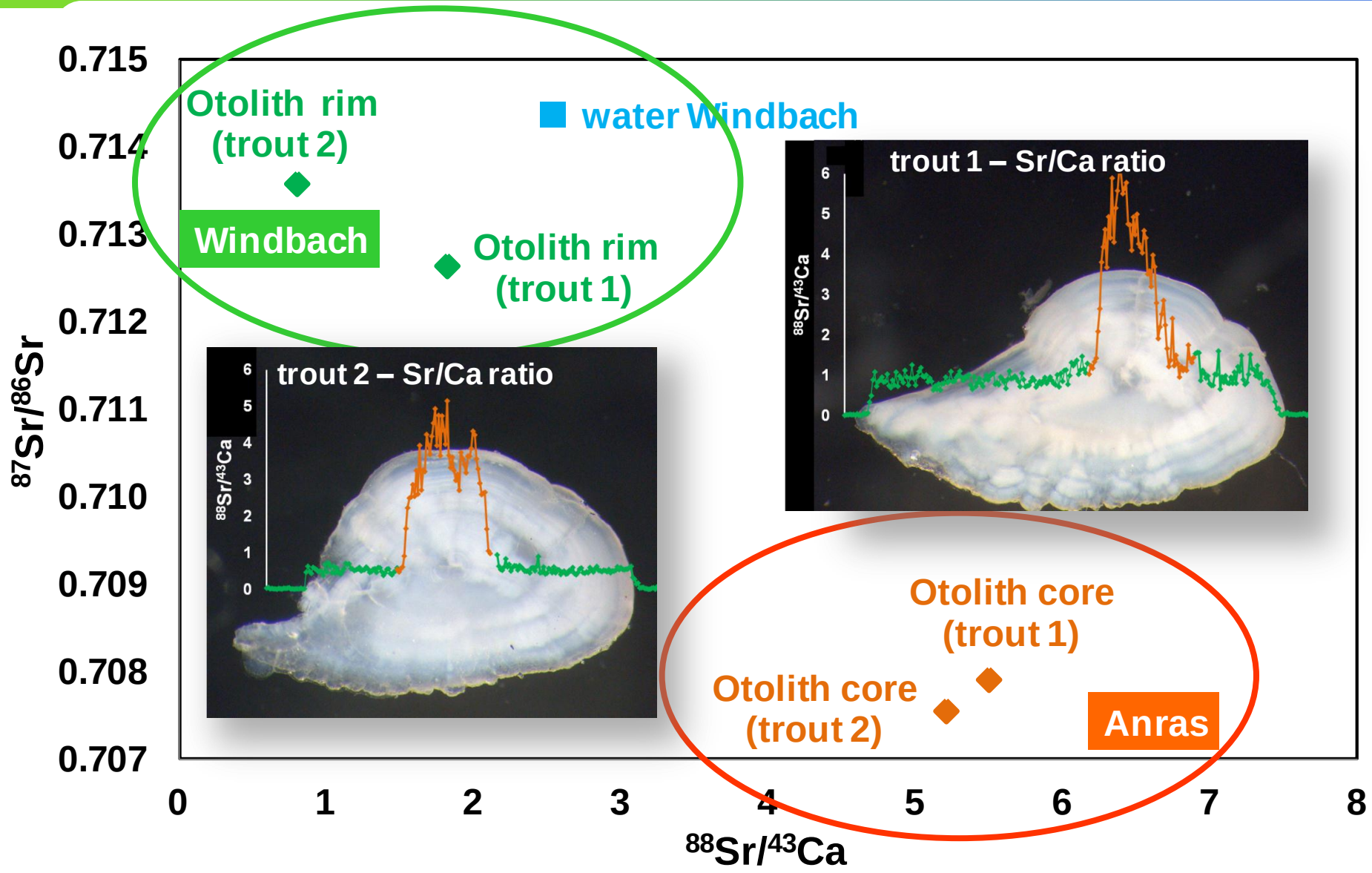
Element- and isotopic analysis



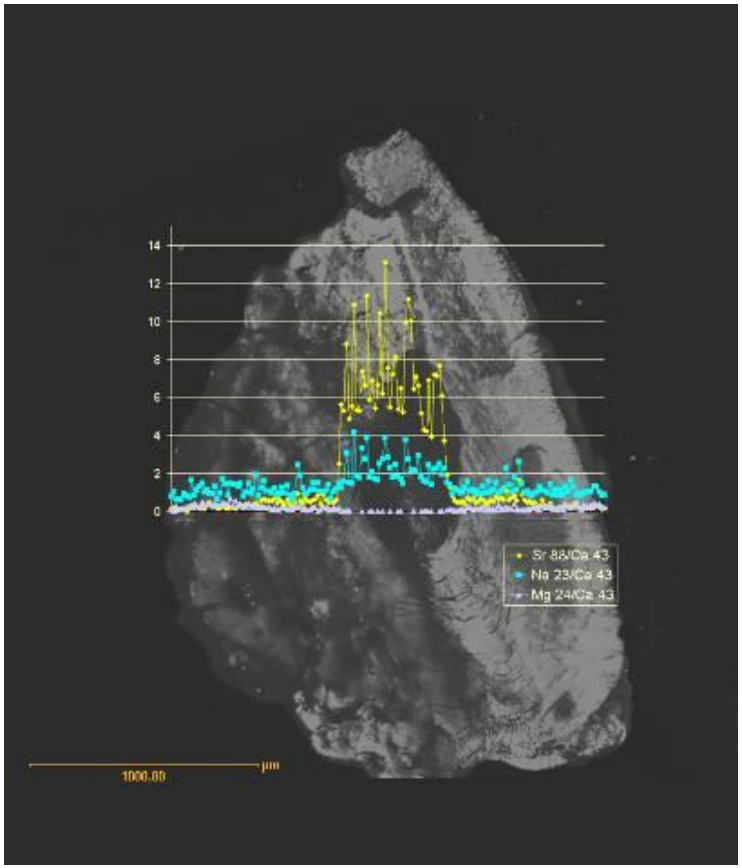
Element- and isotopic analysis



Element- and isotopic analysis

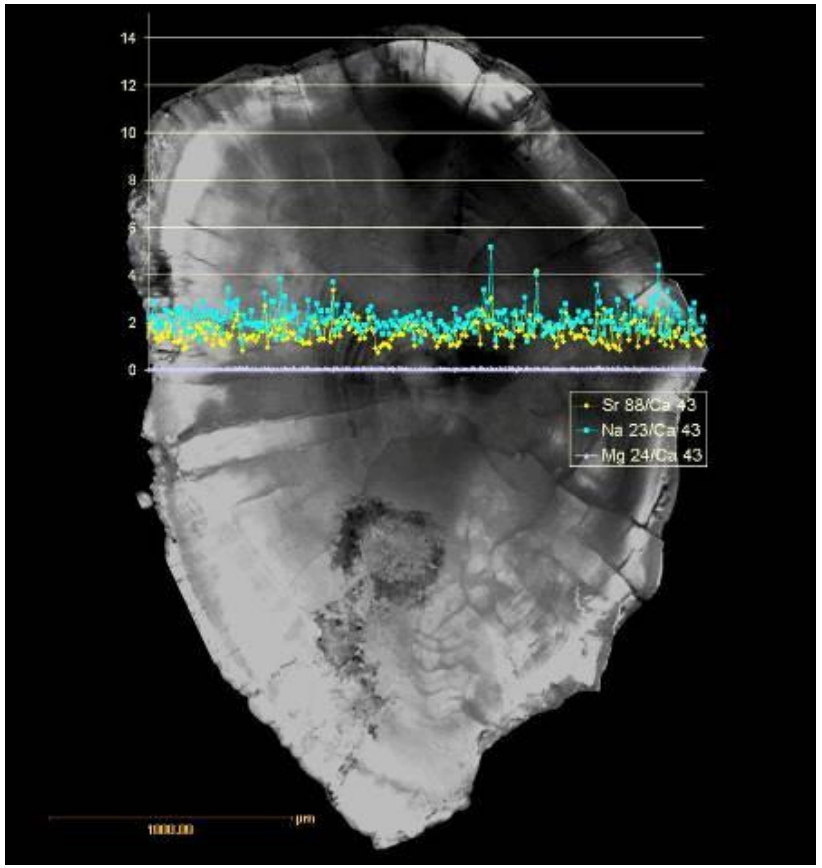


Comparison of fish otoliths of rainbow trout from different fish farms



Juvenile phase: groundwater

Adult phase: surface water



Juvenile and adult phase in the same water

Habitat identification
fish ponds in different geological regions

Otolithen:

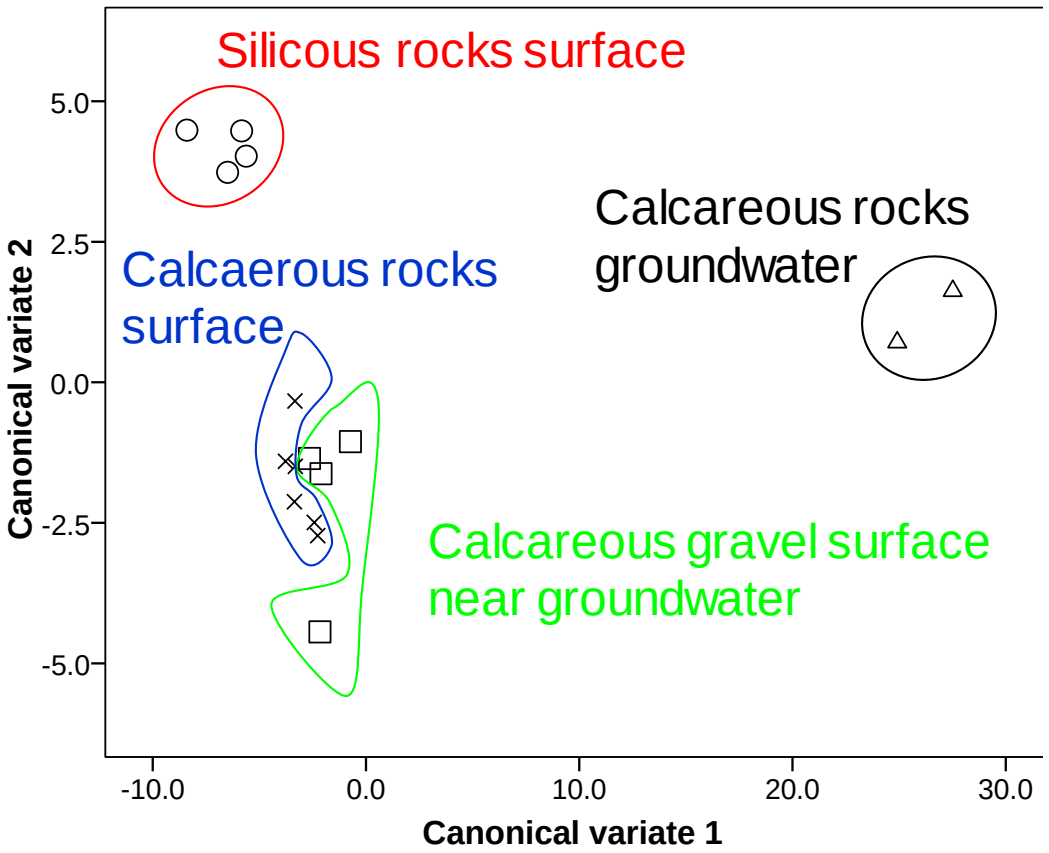
100% identification of the habitat clusters

via

$^{23}Na/^{43}Ca$, $^{88}Sr/^{43}Ca$ and $^{87}Sr/^{86}Sr$

(Discriminant analysis)

Water sample clusters:



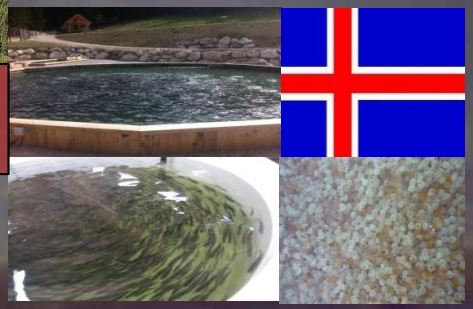
Zitek, A., M. Sturm, H. Waidbacher and T. Prohaska (2010). *Fisheries Management and Ecology, 17, 435-445*

Salmonide: chemical life history (age: 12 months)

Eismeersaibling

~4 Mon. Laser spot = 50 µm

120 µm

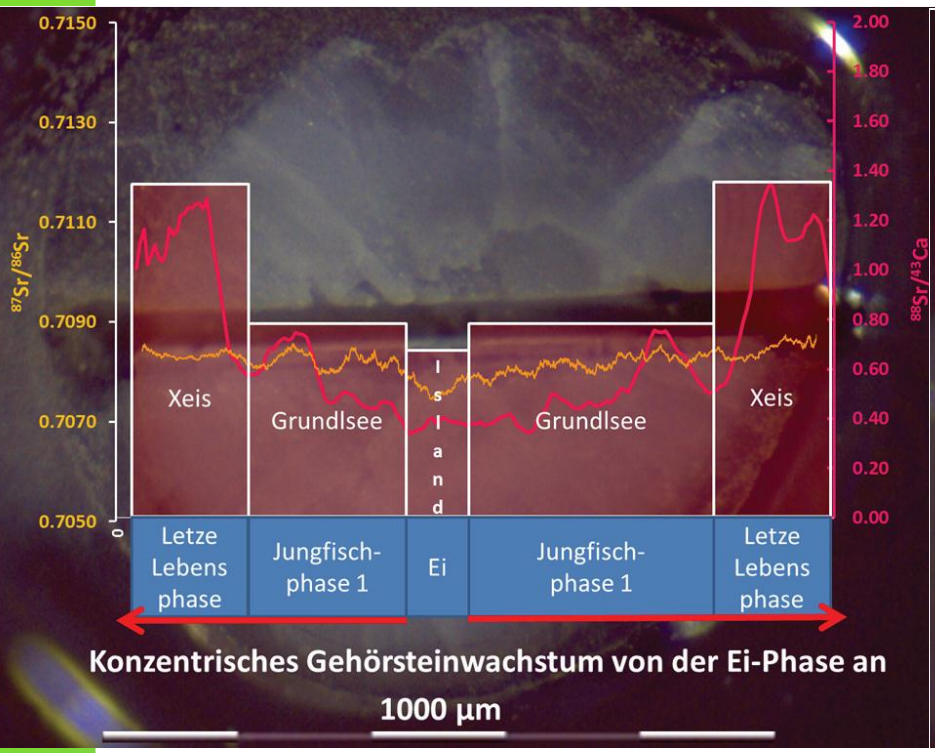


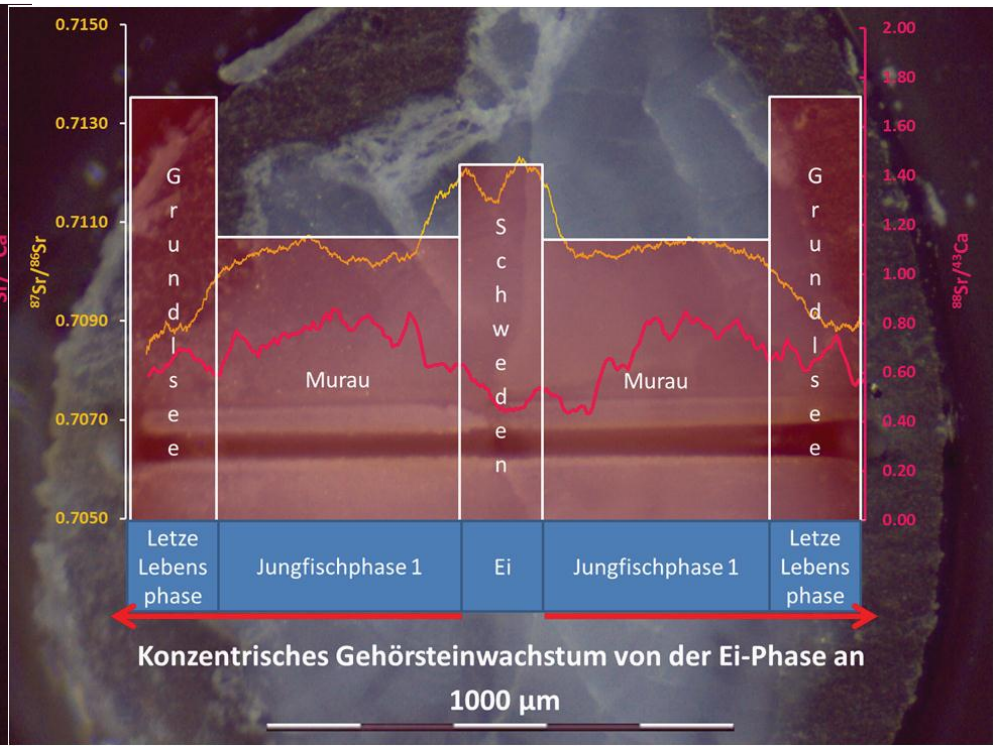
1000 µm

otolith growths

Comparison of life histories

- Individual ‚chemical curriculum' of fish ($^{87}Sr/^{86}Sr$, Sr/Ca)
- Time resolved analysis from the egg to the last months
- Significant difference in the life histories





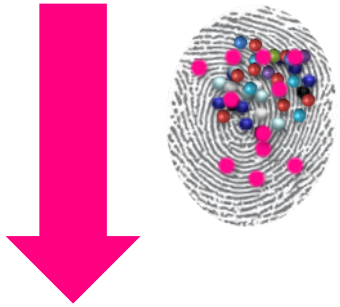
Elemental and isotopic fingerprinting

elemental fingerprint

isotopic fingerprint

natural variation
locally specific signal

<< intrinsic marking >>



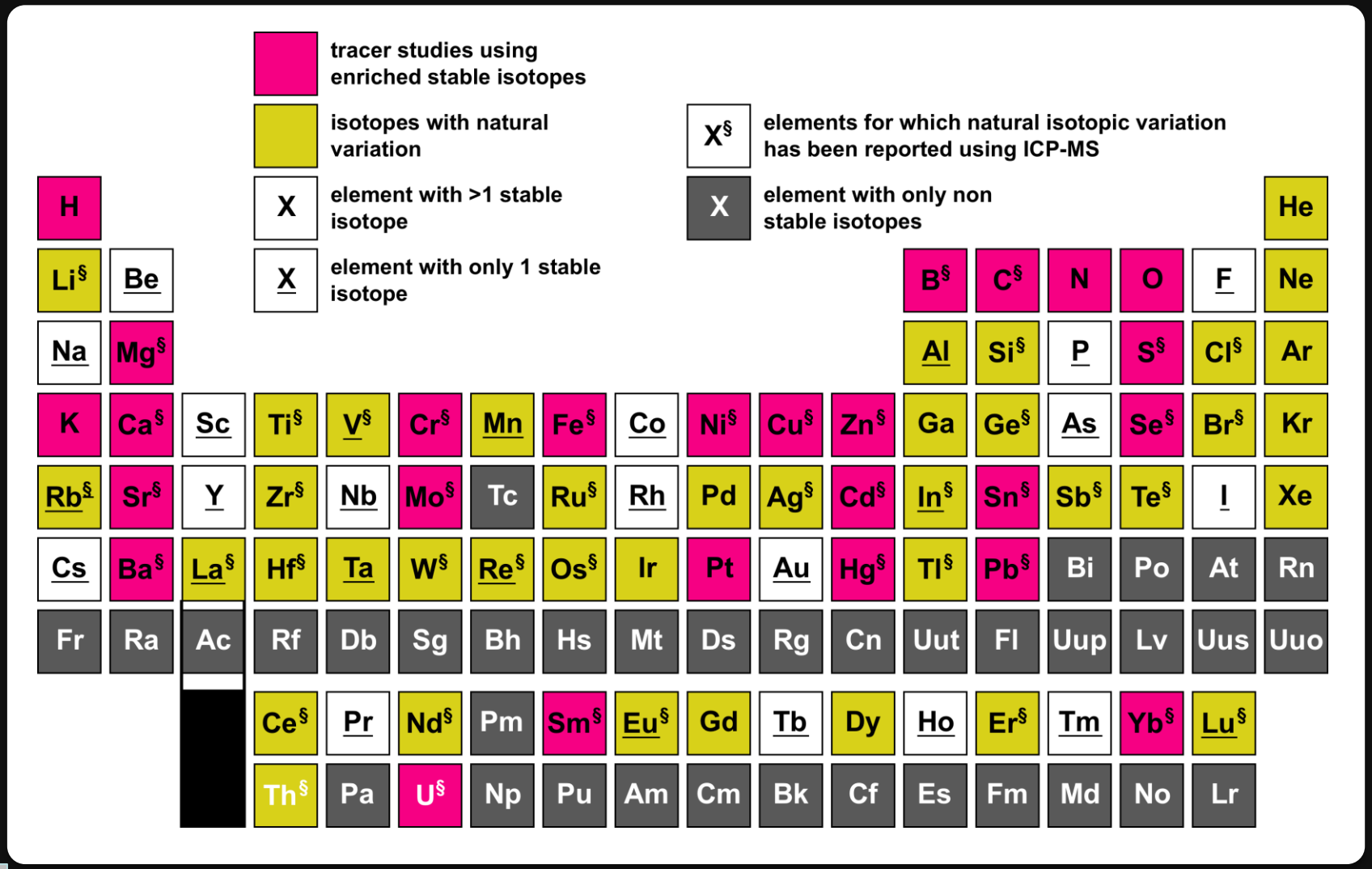
(multi)-elemental spikes

enriched stable isotopes

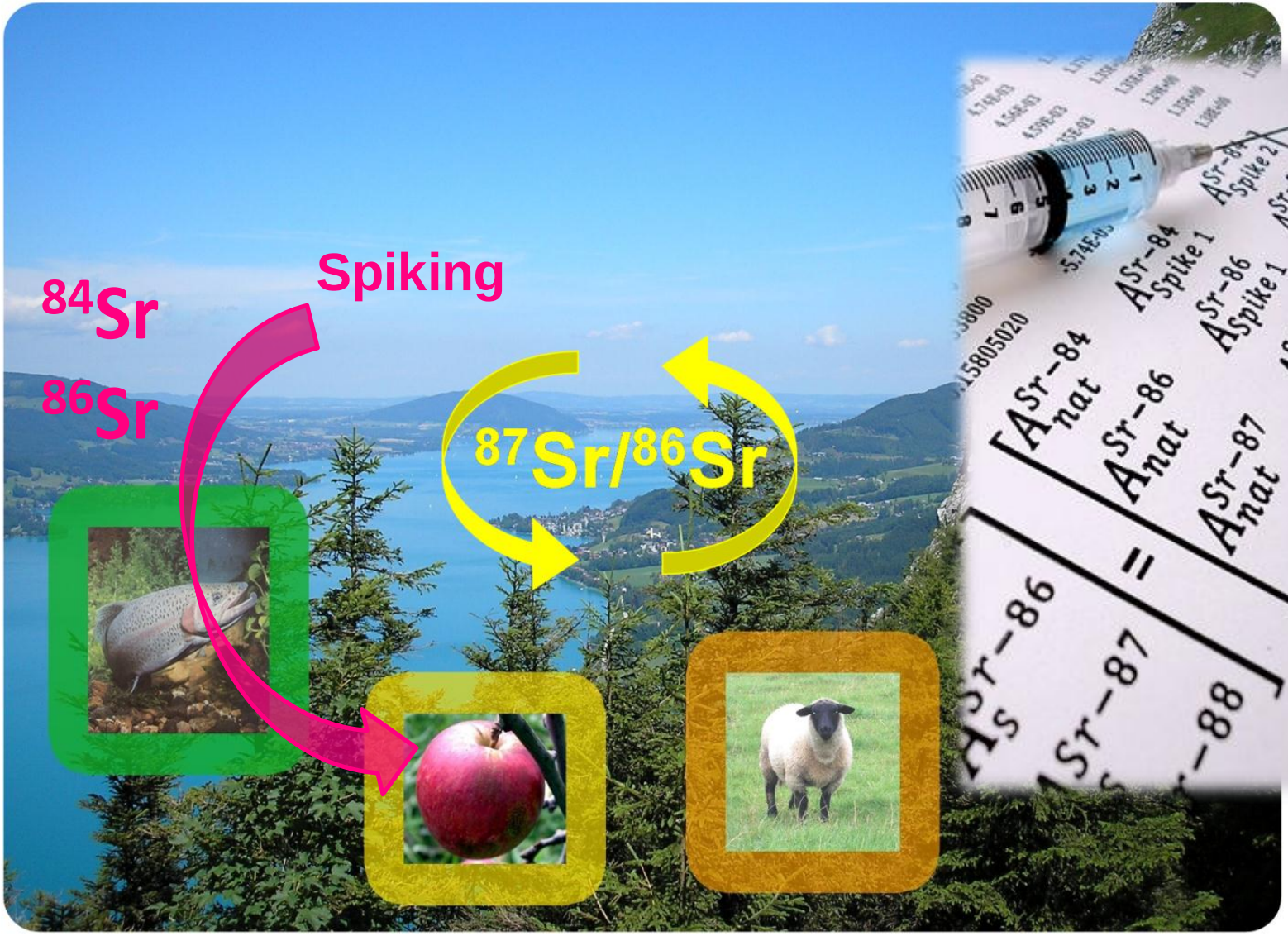
marking via elemental spikes or enriched isotopes

<< extrinsic marking >>

Enriched stable isotope tracer studies



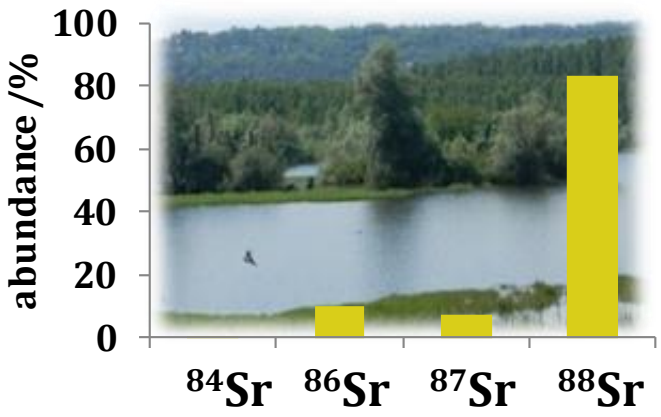
Sr Spiking

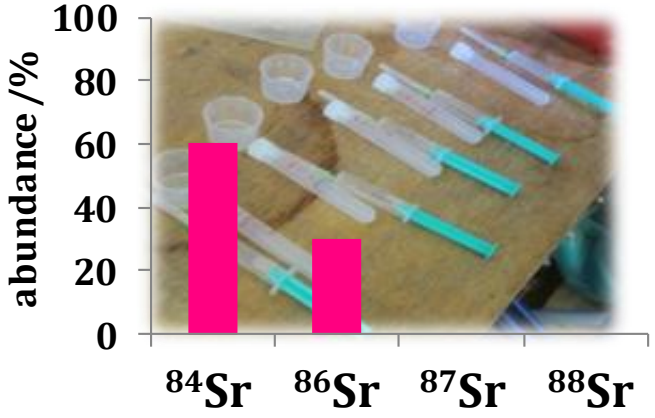


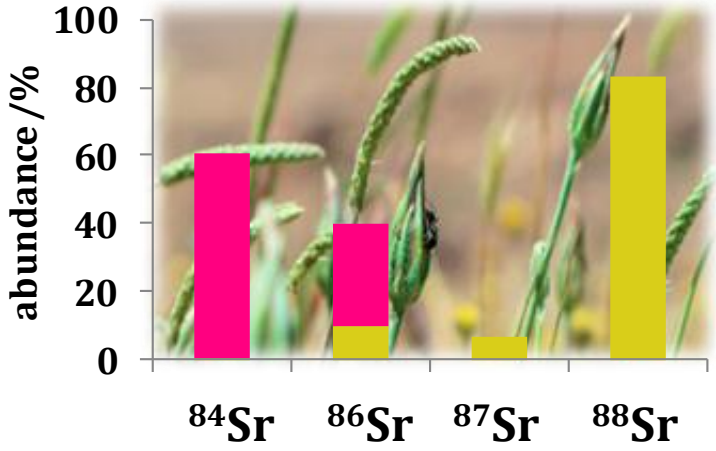
Enriched stable isotopic spikes

AIM: Inducing a significant change of the natural

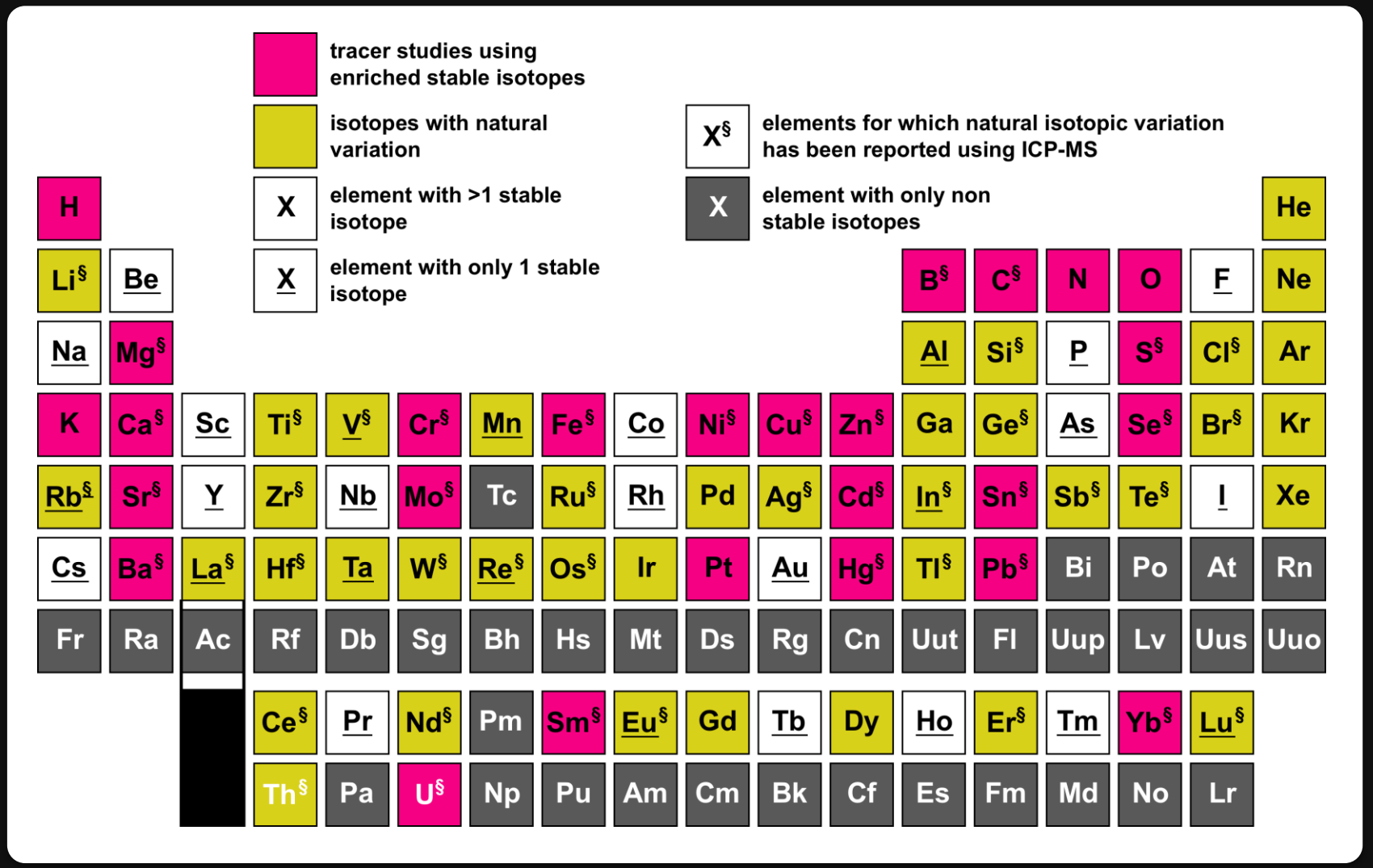
Enriched stable isotope tracer studies
Basic principle



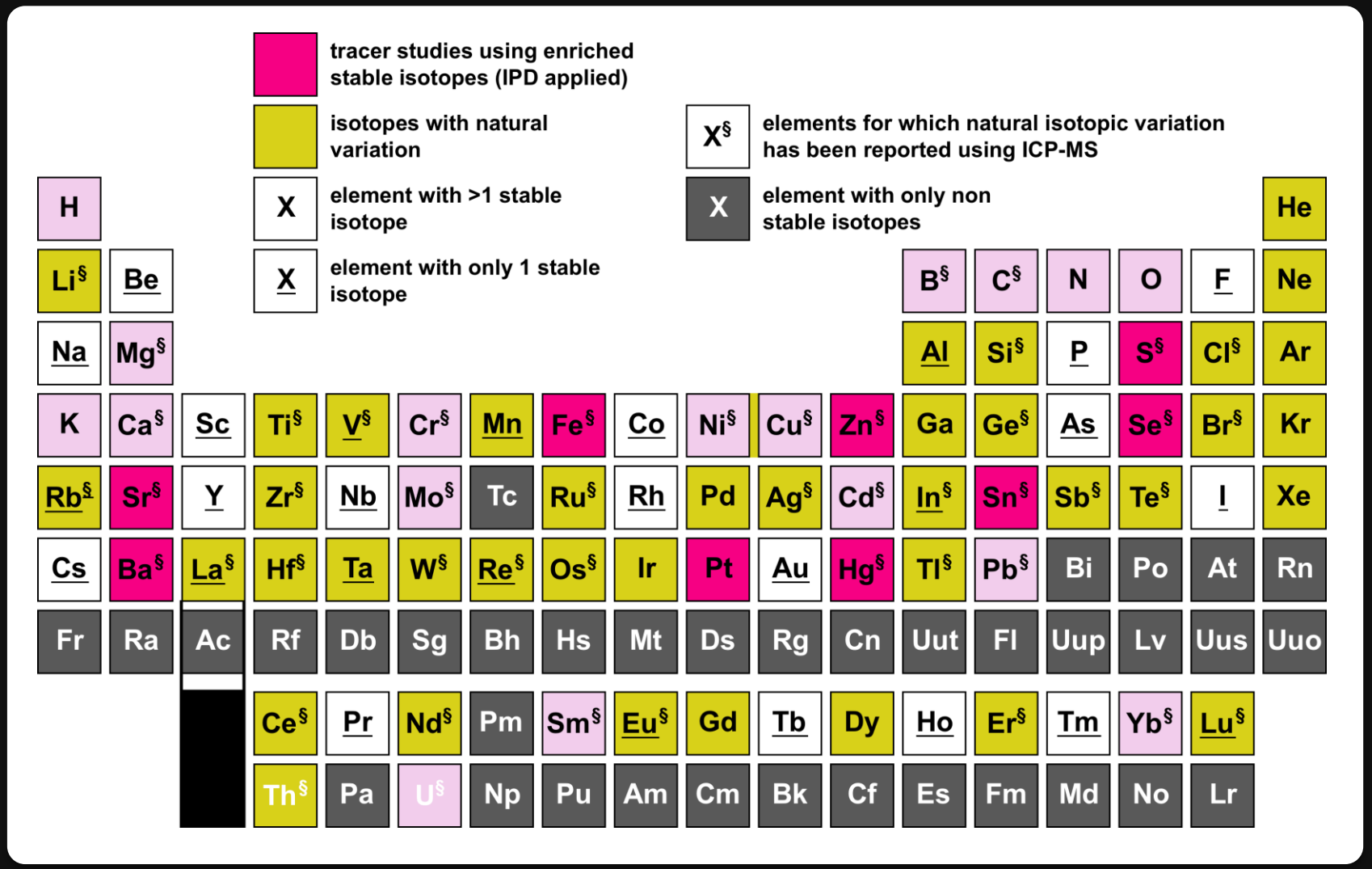




Enriched stable isotope tracer studies



Enriched stable isotope tracer studies
Isotope pattern deconvolution (IPD)

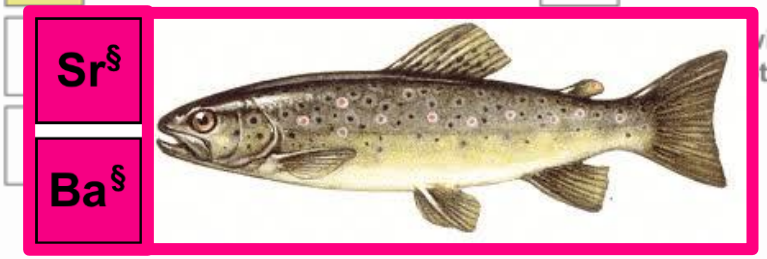


Enriched stable isotope tracer studies
Isotope pattern deconvolution (IPD)

tracer studies using enriched stable isotopes (IPD applied)

isotopes with natural variation

X§ elements for which natural isotopic variation has been reported using ICP-MS



H, He
Li§, Be, Ne
Na, Mg§, Ar
K, Ca§, Sc, Co, Ni§, Cu§, Zn§, Ga, Ge§, As, Se§, Br§, Kr
Rb§, Sr§, Y, Rh, Pd, Ag§, Cd§, In§, Xe
Cs, Ba§, La§, Rn
Fr, Ra, Ac, Uuo
Th§, Pa, U§, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr

Enriched stable isotope tracer studies
Isotope pattern deconvolution (IPD)

tracer studies using enriched stable isotopes (IPD applied)

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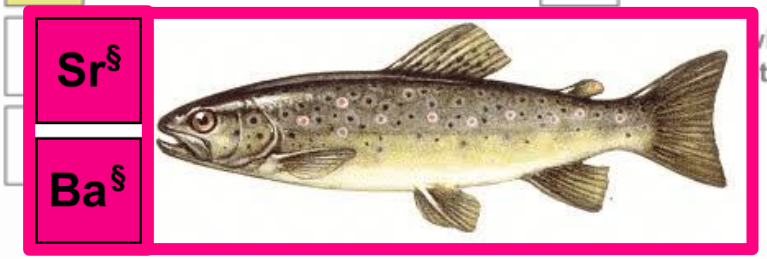
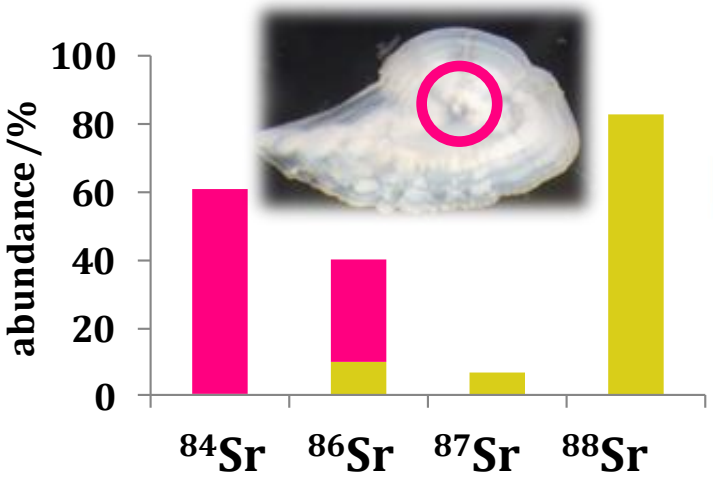
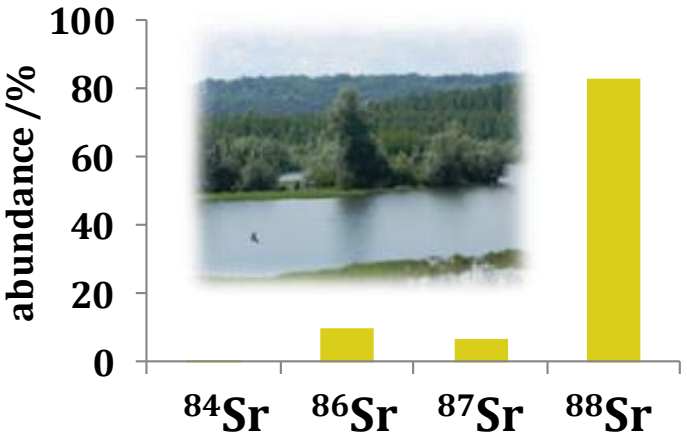


H, He
Li§, Be, Ne
Na, Mg§, Ar
K, Ca§, Sc, Co, Ni§, Cu§, Zn§, Ga, Ge§, As, Se§, Br§, Kr
Rb§, Sr§, Y, Rh, Pd, Ag§, Cd§, In§, Xe
Cs, Ba§, La§, Rn
Fr, Ra, Ac, Uuo
Th§, Pa, U§, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr

Evaluation of the double isotope tracer Isotope pattern deconvolution



$$\begin{bmatrix} A_1^{84} \\ A_2^{86} \\ A_3^{87} \\ A_4^{88} \end{bmatrix} = \begin{bmatrix} A_{Sr-nat}^{84} & A_{Sp-84}^{84} & A_{Sp-86}^{84} & A_{Rb-nat}^{84} \\ A_{Sr-nat}^{86} & A_{Sp-84}^{86} & A_{Sp-86}^{86} & A_{Rb-nat}^{86} \\ A_{Sr-nat}^{87} & A_{Sp-84}^{87} & A_{Sp-86}^{87} & A_{Rb-nat}^{87} \\ A_{Sr-nat}^{88} & A_{Sp-84}^{88} & A_{Sp-86}^{88} & A_{Rb-nat}^{88} \end{bmatrix} \times \begin{bmatrix} x_{Sr-nat} \\ x_{Sp-84} \\ x_{Sp-86} \\ x_{Rb-nat} \end{bmatrix}$$



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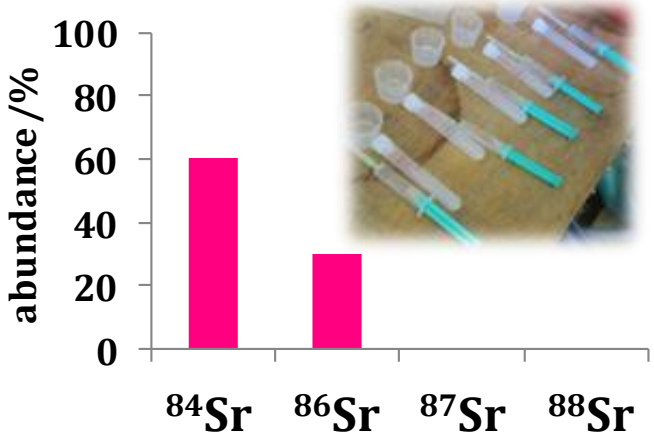
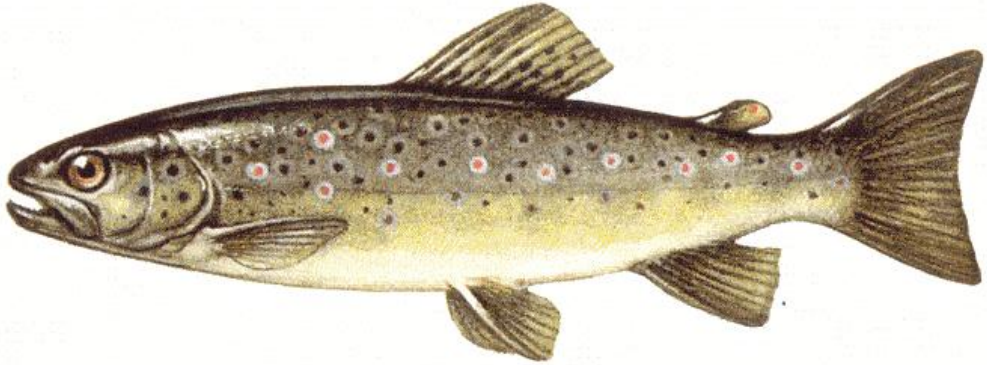


molar fraction ratio of x_{Sp1}/x_{Sp2} of double spike in central otolith region

J. Irrgeher, A. Zitek, M. Cervicek, T. Prohaska; *J. Anal. At. Spectrom.*, 2014,29, 193-200

APPLICATION:
Transgenerational marking of fish

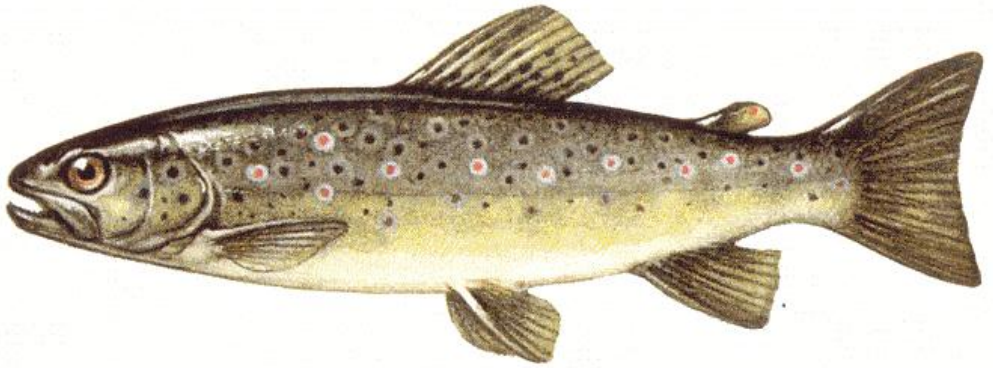


- **Ecological application**
  Mass marking of larvae without interfering with natural spawning, dispersal

- **Aquaculture** (affordable marking method)
  Quality management (authenticity and origin)

Transgenerational marking of fish

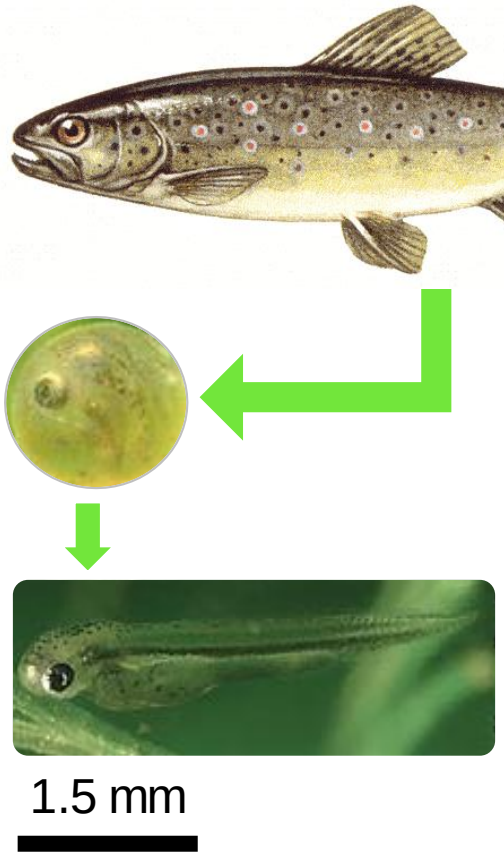
- **Maternal transfer** of **elements** to **eggs**
- **Otolith:**
  - **first hard part** developing (within the egg)
  - stores **maternal information**
- After hatching, uptake of **environmental information**

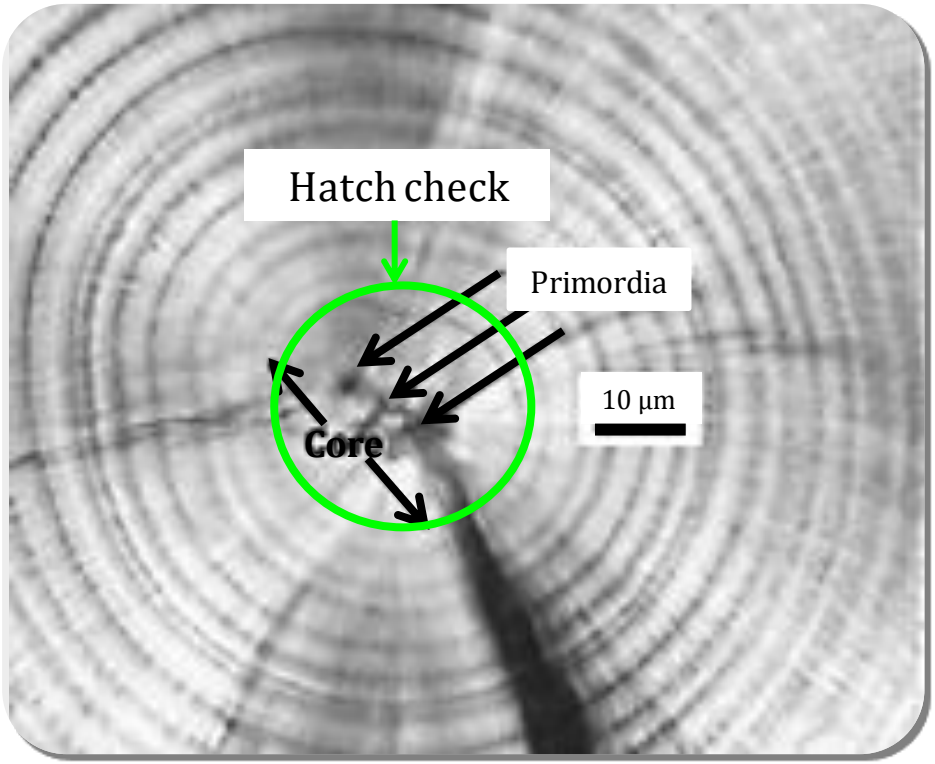


Maternally derived area of fish otolith

The **center of the otolith** is **created within the egg**;
contains the maternal information

- **Hatch check:** visual clue for the area, where **maternal information** can be expected

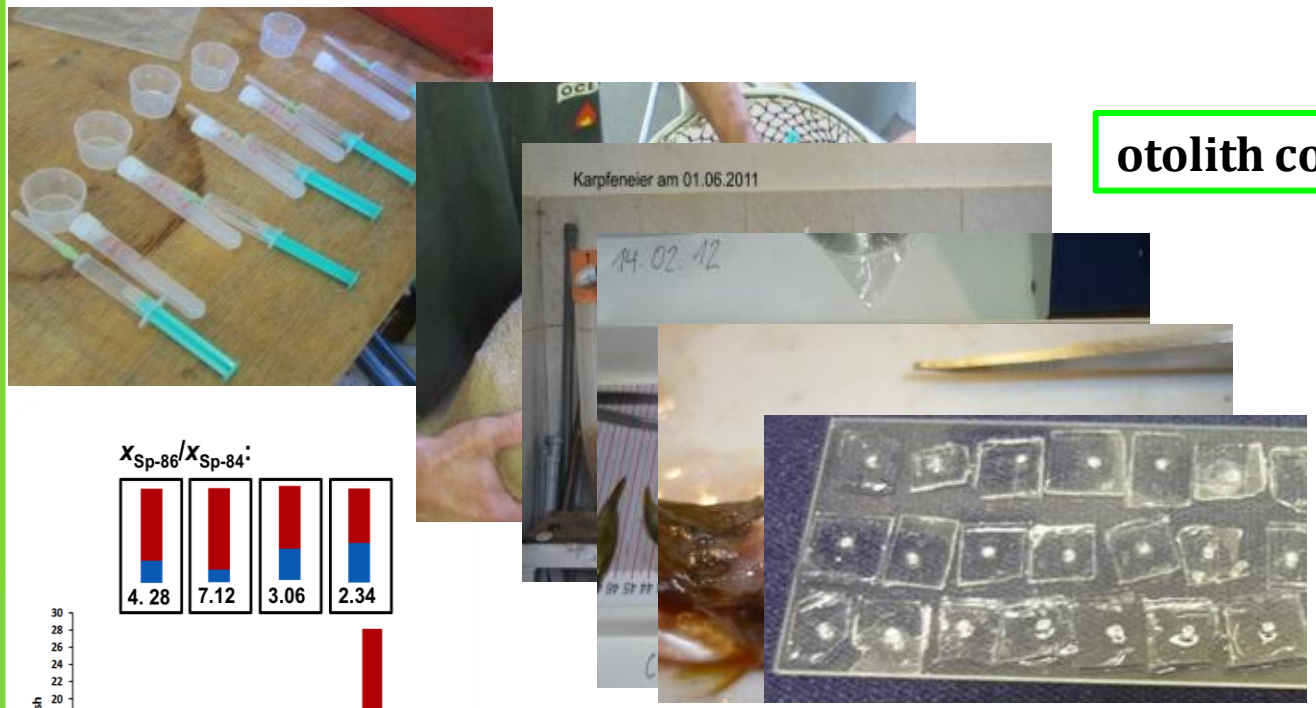


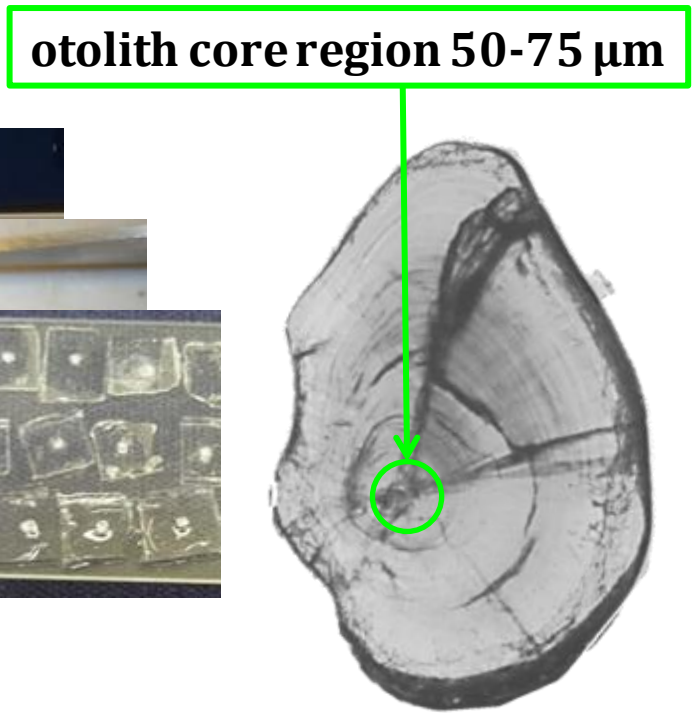


Transgenerational isotopic marking of freshwater fish using a $^{86}Sr/^{84}Sr$ double spike

- **Model species:**
  - Carp: cyprinids (100.000-300.000 eggs/kg body weight)
  - Brown trout: salmonids (1.500-2.000 eggs/kg body weight)

Fischzucht Kreuzstein





A. Zitek, J. Irrgeher, M. Cervicek, M. Horsky, M. Kletztl, T. Weismann, T. Prohaska
(*Marine and Freshwater research, in press*)

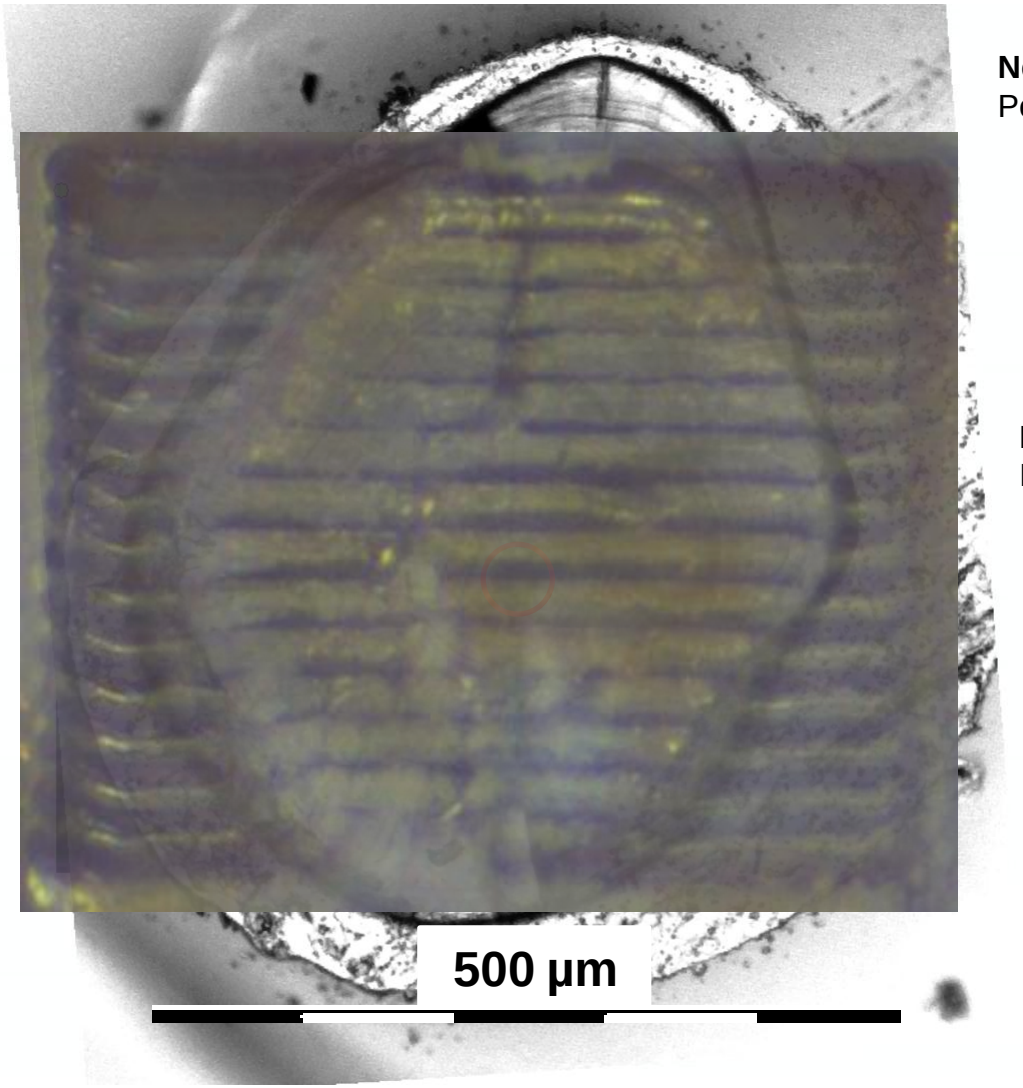
LA-ICP-Q-MS of a single carp otolith (ca. 4440 µg ^{86}Sr kg^{-1} fish)

$^{86}Sr/^{88}Sr$

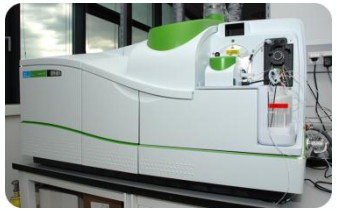
- 0.0
- 0.10-0.12
- 0.12-0.13
- 0.13-0.14

$^{86}Sr/^{88}Sr$ natural ~0.12

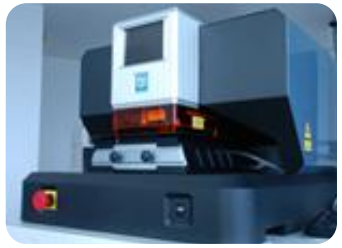
He carrier gas
Spot size: 35 µm
Scan speed: 2 µm s^{-1}
Rep. rate: 20 Hz



Nexion 300D (ICP-Q-MS)
Perkin Elmer



NWR193
Laser Ablation System



$^{86}Sr/^{88}Sr$

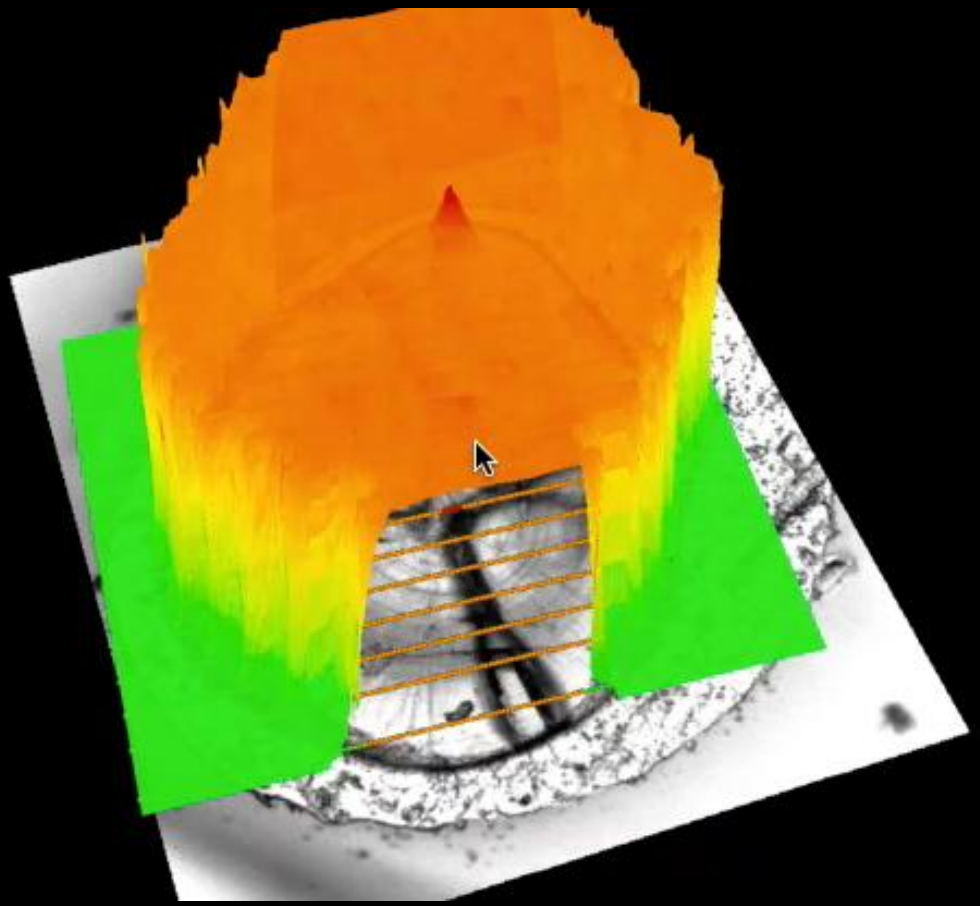
0.0

0.10-0.12

0.12-0.13

0.13-0.14

$^{86}Sr/^{88}Sr$ natural ~0.12



Nexion 300D (ICP-Q-MS)
Perkin Elmer

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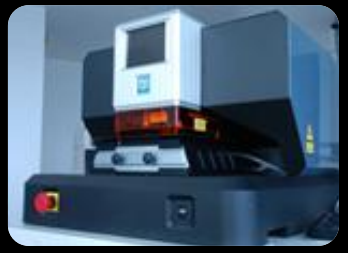
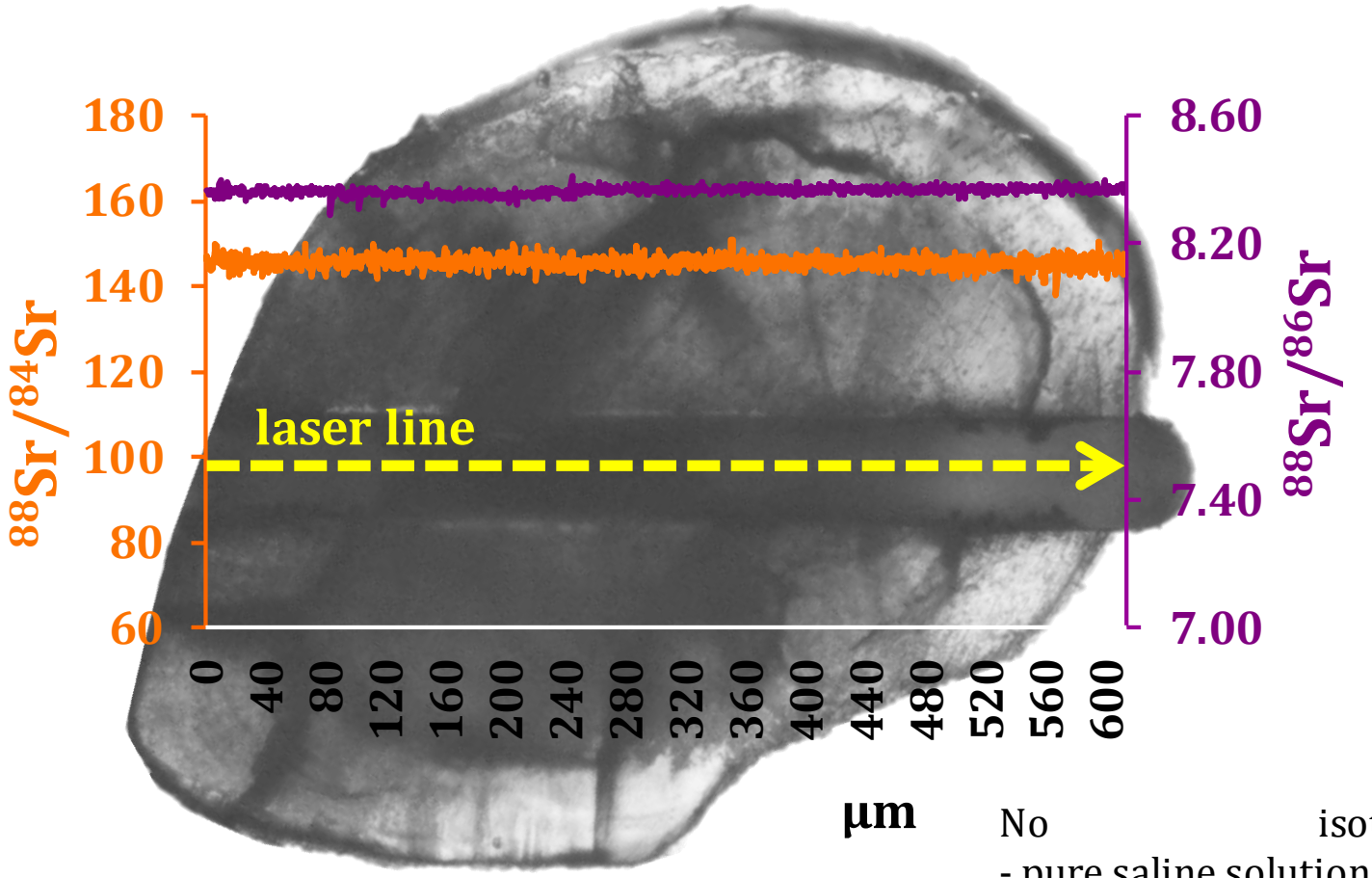
Laser Ablation System



Absolute $^{88}Sr/^{84}Sr$ and $^{88}Sr/^{86}Sr$ ratios – Control fish

- **No change of natural Sr isotopic signature**



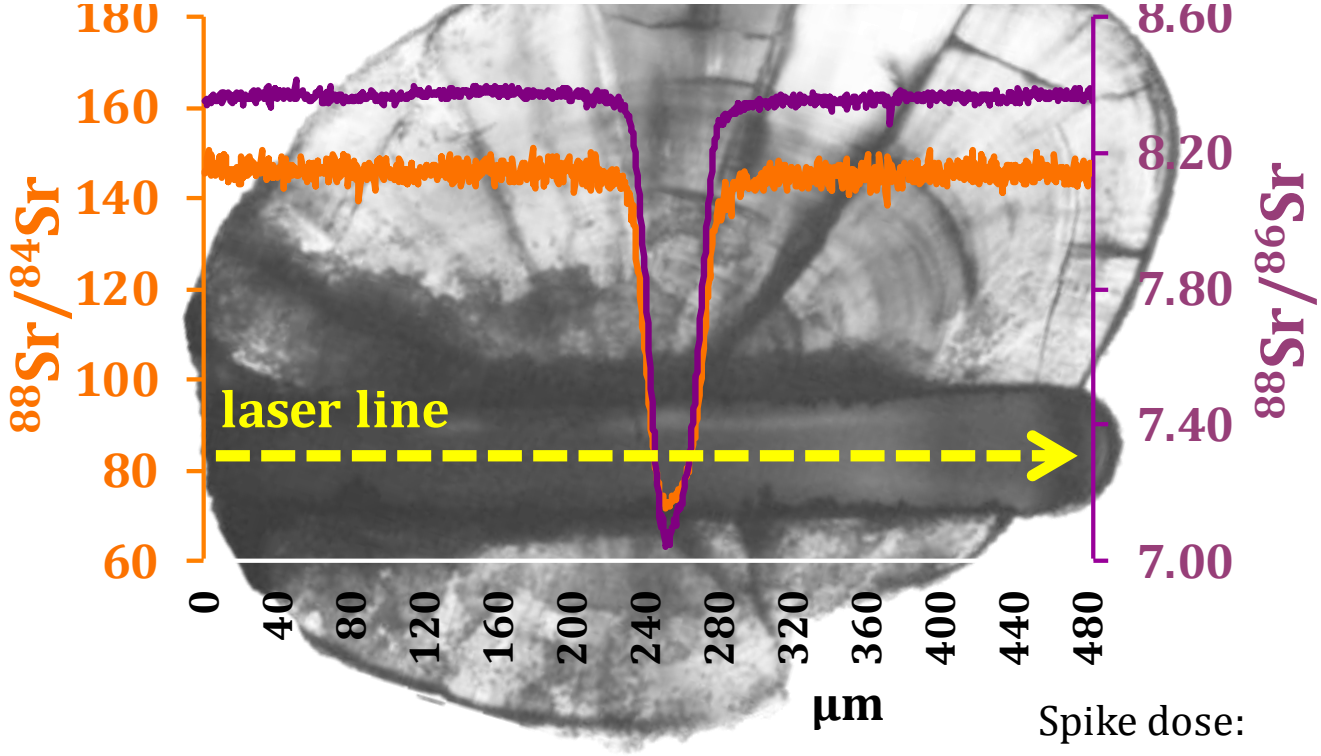
No isotope - pure saline solution injected

A. Zitek, J. Irrgeher, M. Cervicek, M. Horsky, M. Kletztl, T. Weismann, T. Prohaska (*Marine and Freshwater research, in press*)

Absolute $^{88}Sr/^{84}Sr$ and $^{88}Sr/^{86}Sr$ ratios – Spiked fish

- **Significant change of natural Sr isotopic signature in the core region of otoliths:**

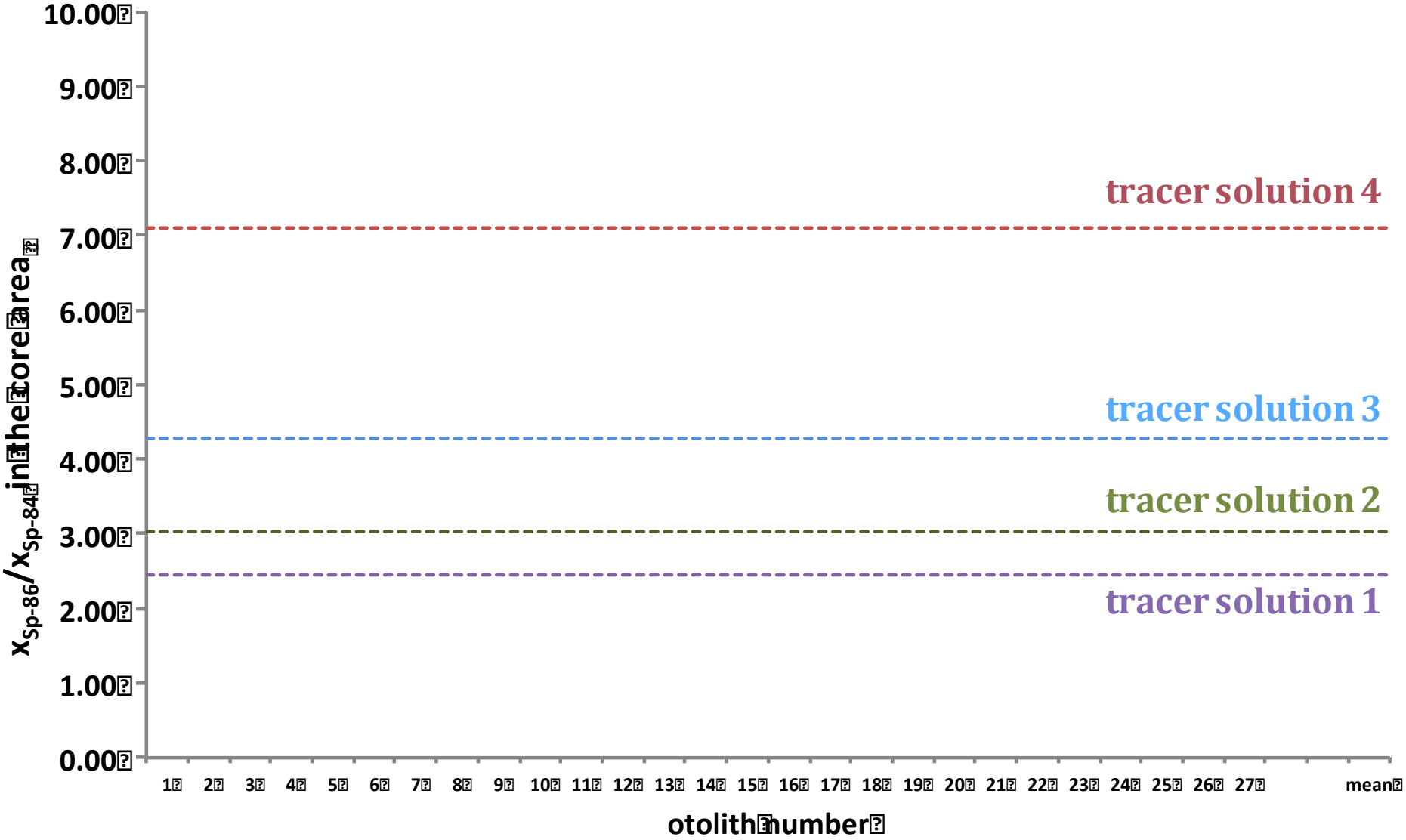
  Sr tracer: 0.1 – 3.5 %



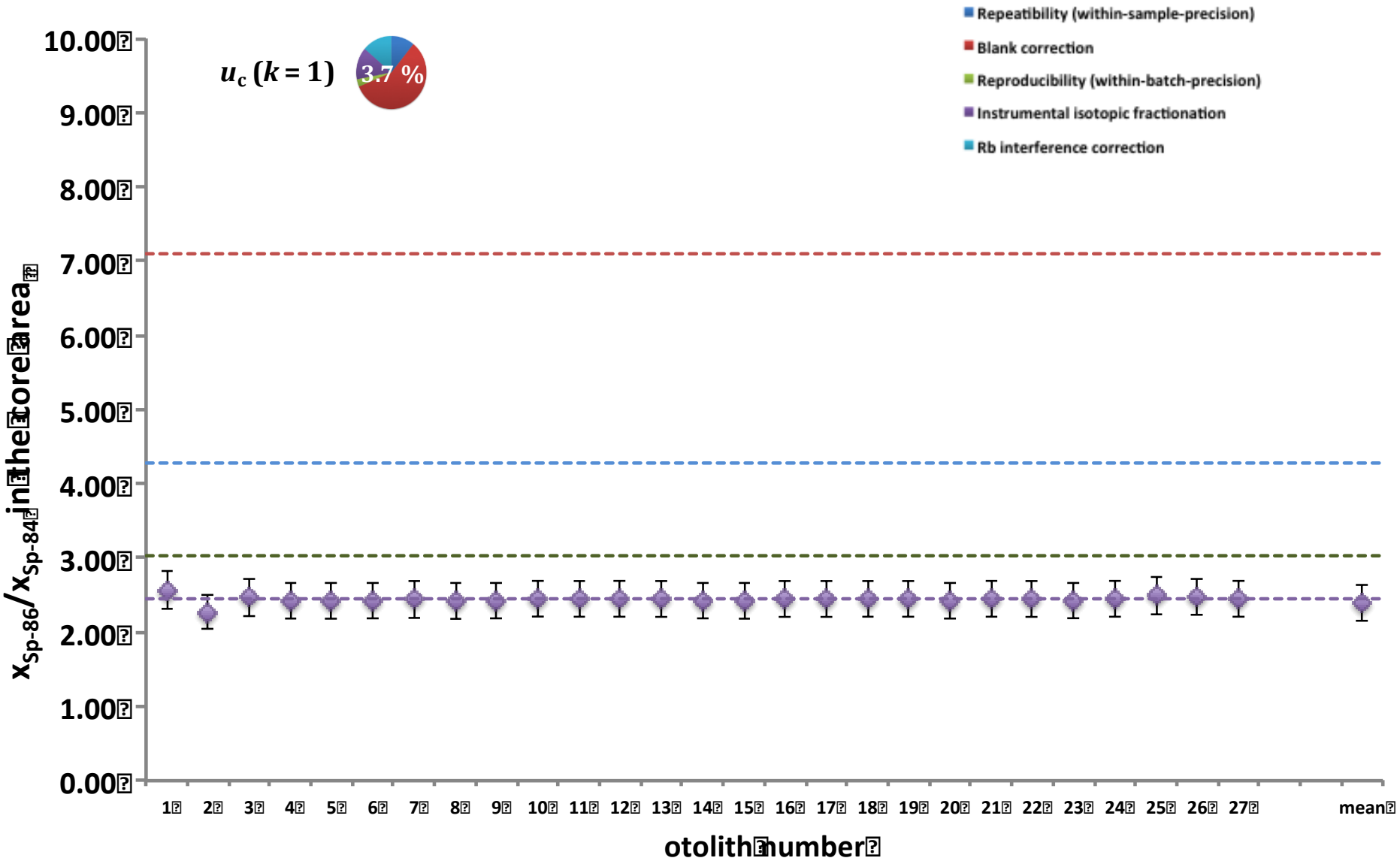
Spike dose:
1.3 mg ^{84}Sr
5.5 mg ^{86}Sr/kg fish

A. Zitek, J. Irrgeher, M. Cervicek, M. Horsky, M. Kletztl, T. Weismann, T. Prohaska
(*Marine and Freshwater research, in press*)

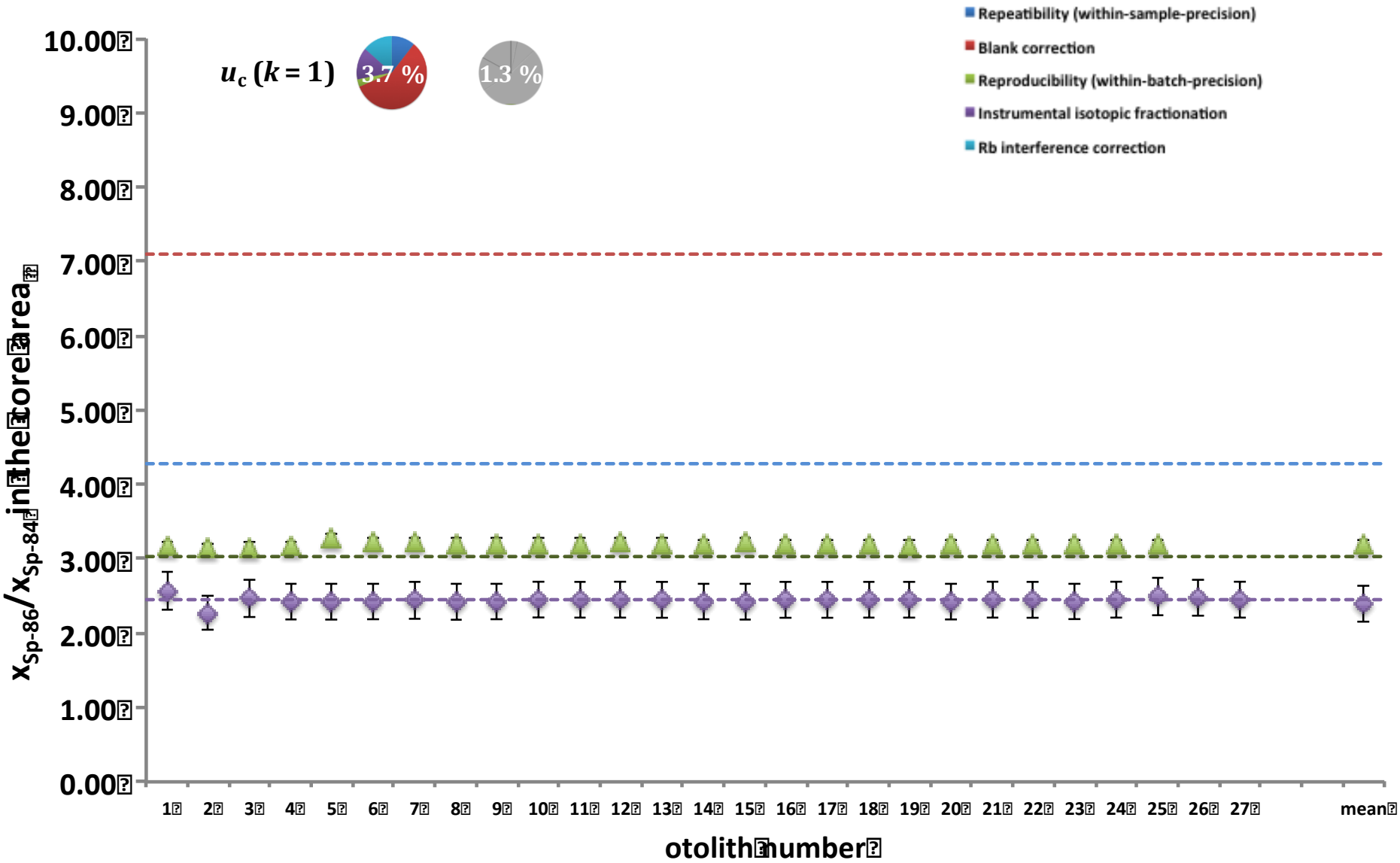
Deconvolved molar fraction ratio of the double spike ($x_{Sp\text{-}86}/x_{Sp\text{-}84}$)



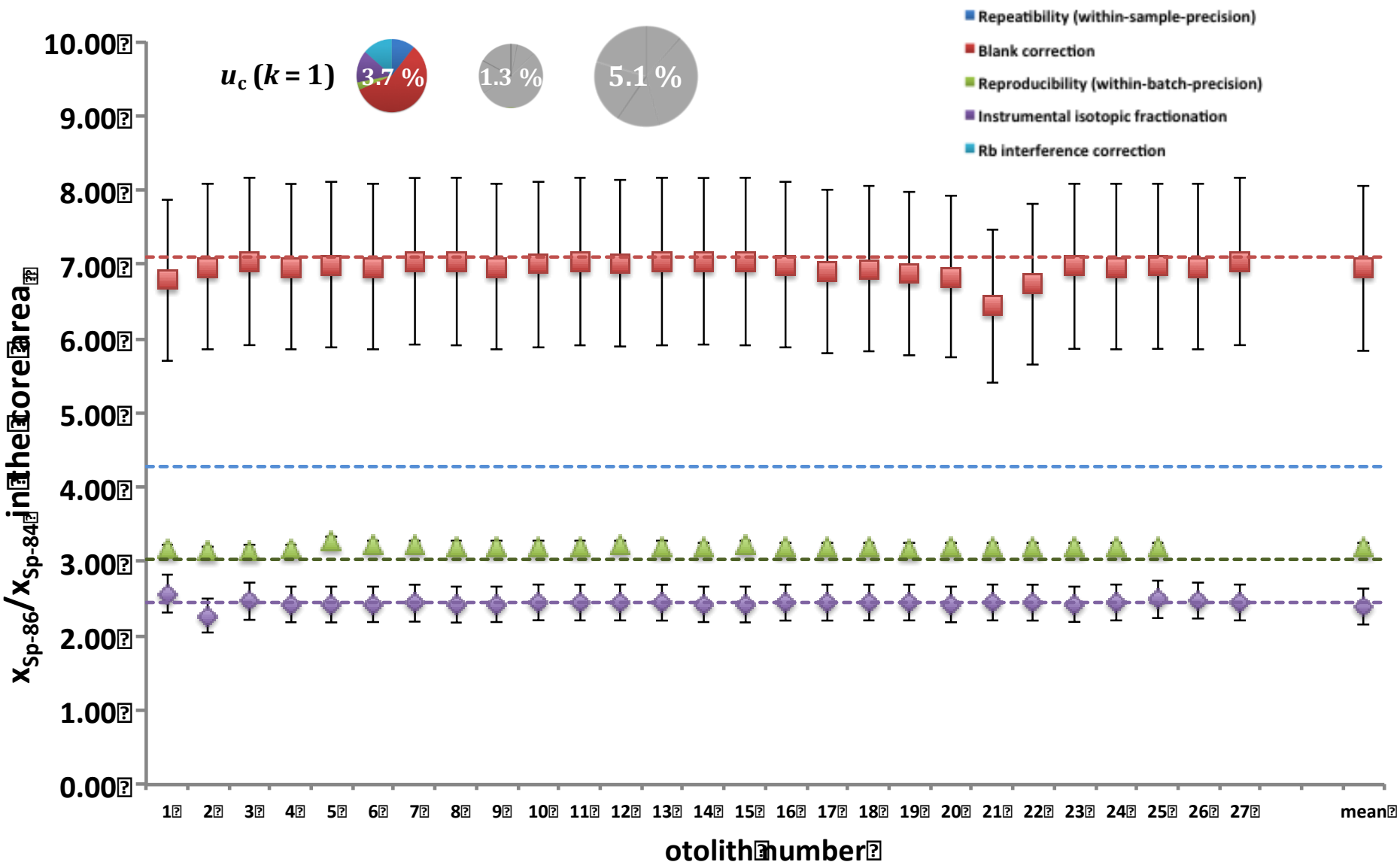
Deconvolved molar fraction ratio of the double spike ($x_{Sp\text{-}86}/x_{Sp\text{-}84}$)



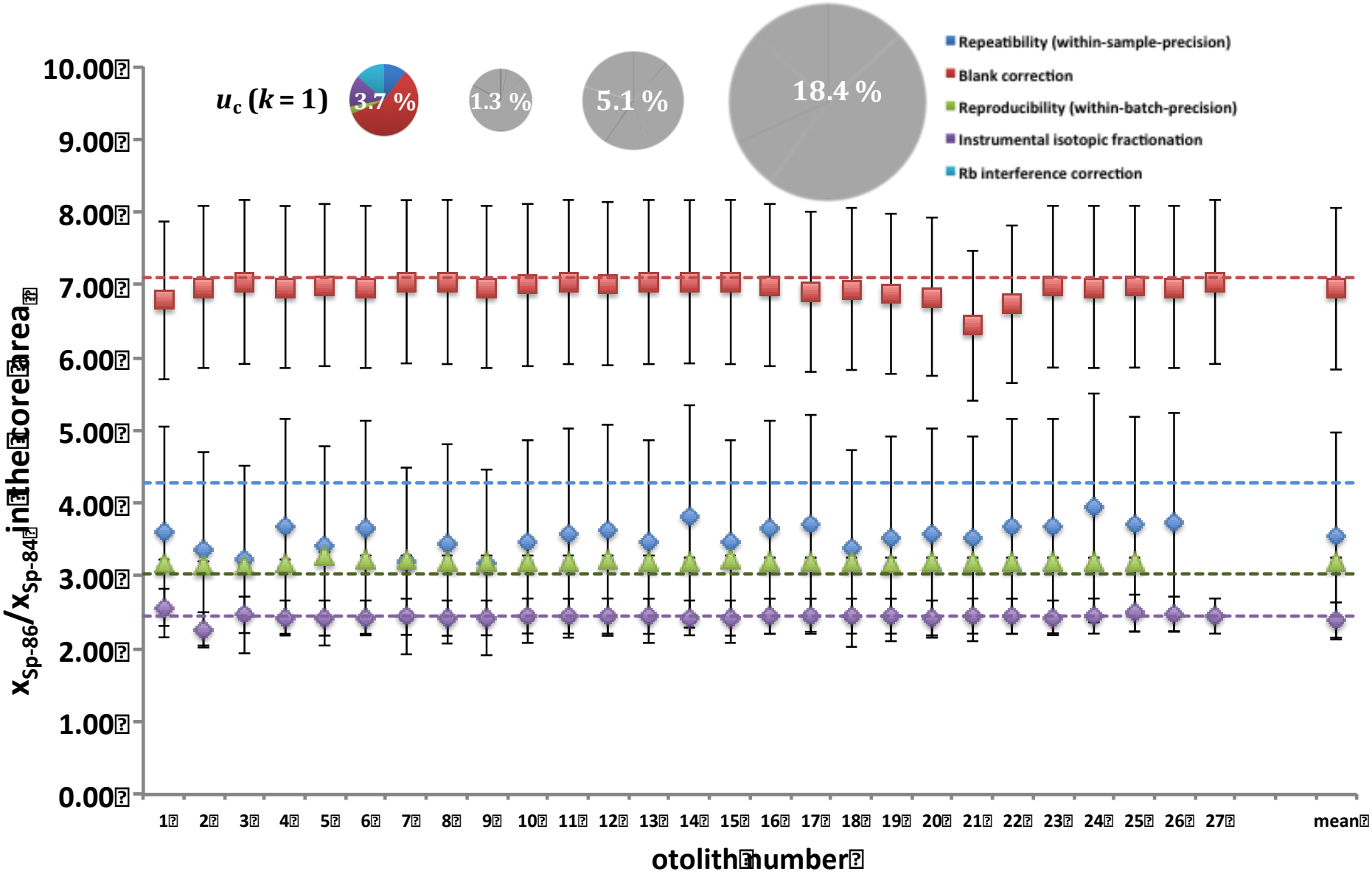
Deconvolved molar fraction ratio of the double spike ($x_{Sp\text{-}86}/x_{Sp\text{-}84}$)



Deconvolved molar fraction ratio of the double spike ($x_{Sp\text{-}86}/x_{Sp\text{-}84}$)



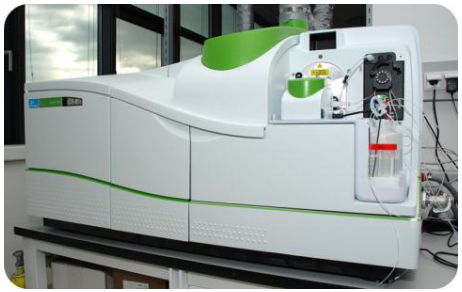
Deconvolved molar fraction ratio of the double spike ($x_{Sp\text{-}86}/x_{Sp\text{-}84}$)

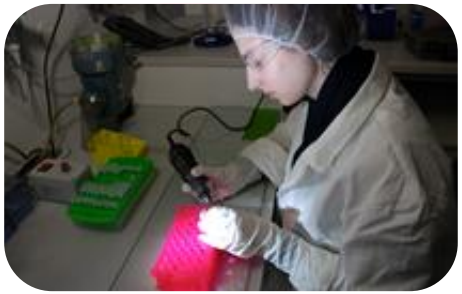


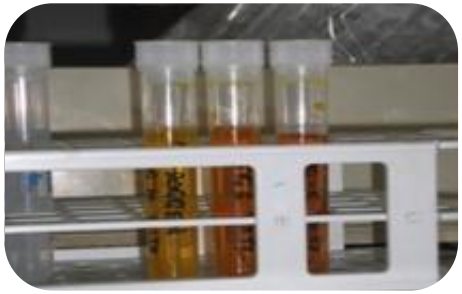
Requirements

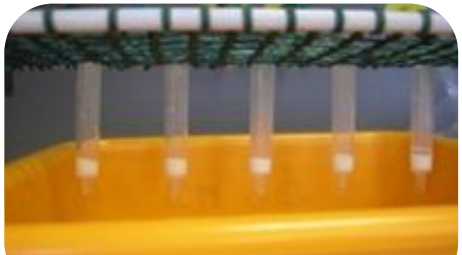
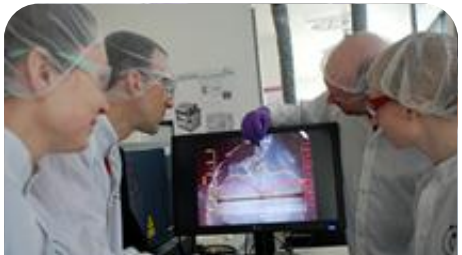
Requirements elementsl/isotopic fingerprint

- Instrumentation
- Infrastructure
- Personell
- Consumables








Requirements elementsl/isotopic fingerprint

- Instrumentation (multi-elemental fingerprinting)
  - ICP-AES (30.000 – 8.000 U$) / 5000 – 10000U$/year
  - ICP-QMS (70.000-40.0000 U$)/ 10000 – 15000 U$/Year

- Instrumentation (isotope ratio analysis)
  - *(ICP-QMS (70.000-40.0000 U$)/ 10000 – 15000 U$/Year)*
  - *(ICP-SFMS (300.000 – 500.000 U$/ 10.000 – 15.000 U$/year)*
  - TIMS (250.000 – 500.000 U$/ 10.000 – 15.000 U$/year)
  - MC-ICP-SFMS (500.000-800.0000 U$)/ 15.000 – 20.000 U$/Year

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  - TIMS (250.000 – 500.000 U$/ 10.000 – 15.000 U$/year)
  - MC-ICP-SFMS (500.000 – 800.0000 U$)/ 15.000 – 20.000 U$/Year

Requirements elementsl/isotopic fingerprint

- Infrastructure / consumables

- Cleaning and chemicals (100.000 – 200.000) / 10.000 U$/year
- Sample preparation (100.000 – 300.000 U$) / 20.000U$/year
- Analytical laboratory (500.000 – 1.000.000 U$) / 10.000U$/year

Requirements elementsl/isotopic fingerprint

- Collaboration

- Isotopic measurements (light stable isotopes)
  50 – 200 U$ / sample

- Isotopic measurements (heavy stable isotopes)
  50 – 200 U$ / sample

- Elemental fingerprint (multielement)
  50 – 250 U$ / sample

Acknowledgements

START Projekt 267N11 'VIRIS'
P21404-B17 'IsoMark'