# Traceability of Food and Agricultural Products in the Danube Region


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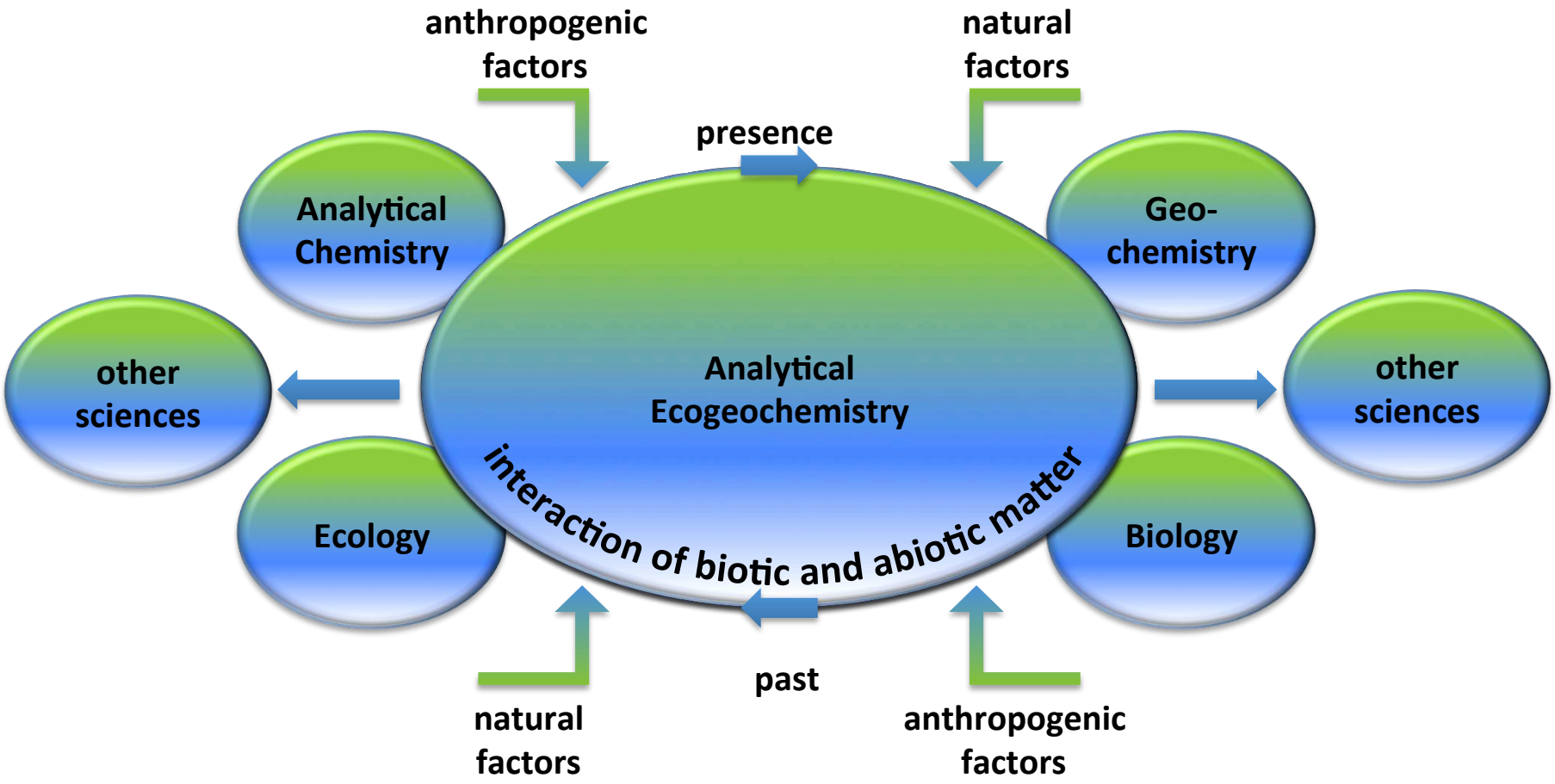
# BOKU
# University and Research Center - Tulln

Research focus: bioresources, renewable resources, biologically based technologies
Construction: 2009 - 2011
Opening: 2011

# Analytical Ecogeochemistry



# Global food trade

# 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/

# FAO: Quality and Origin

Español | Français | English

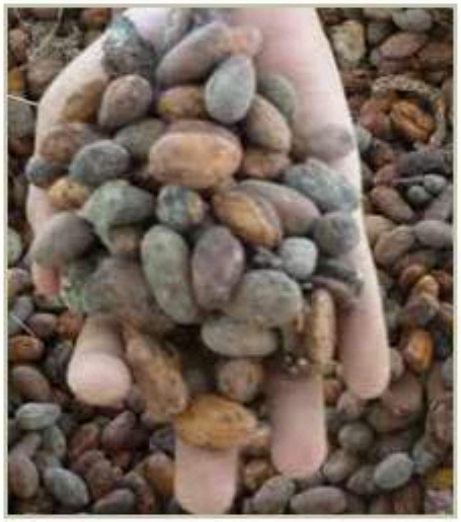
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS


Quality&Origin

- Home
- What is it?
- The programme
- Webtool
- Training
- Events
- Resource
- Technical Assistance
- Links
- Partners
- Contacts
- Quality&Origin Europe

## Quality linked to geographical origin: product, people and place

Some agricultural and food products are distinguished from one another by certain characteristics, qualities or reputations resulting essentially from their geographical origin. This differentiation can be attributed to the unique local features of the product, its history or its distinctive character linked to natural or human factors such as soil, climate, local know-how and traditions (all covered by the term "terroir").



**FAO is implementing a programme to support the development of procedures focusing on origin-linked specific quality that will contribute to rural development.**

These products of origin-linked quality can increase food security, inasmuch as they contribute to rural development and the preservation of food diversity, while also offering consumers a wider choice. Indeed,

# FAO: Quality and Origin

Russian

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS


**Quality&Origin in Europe and Central Asia - Traditional Agricultural and Food Products**

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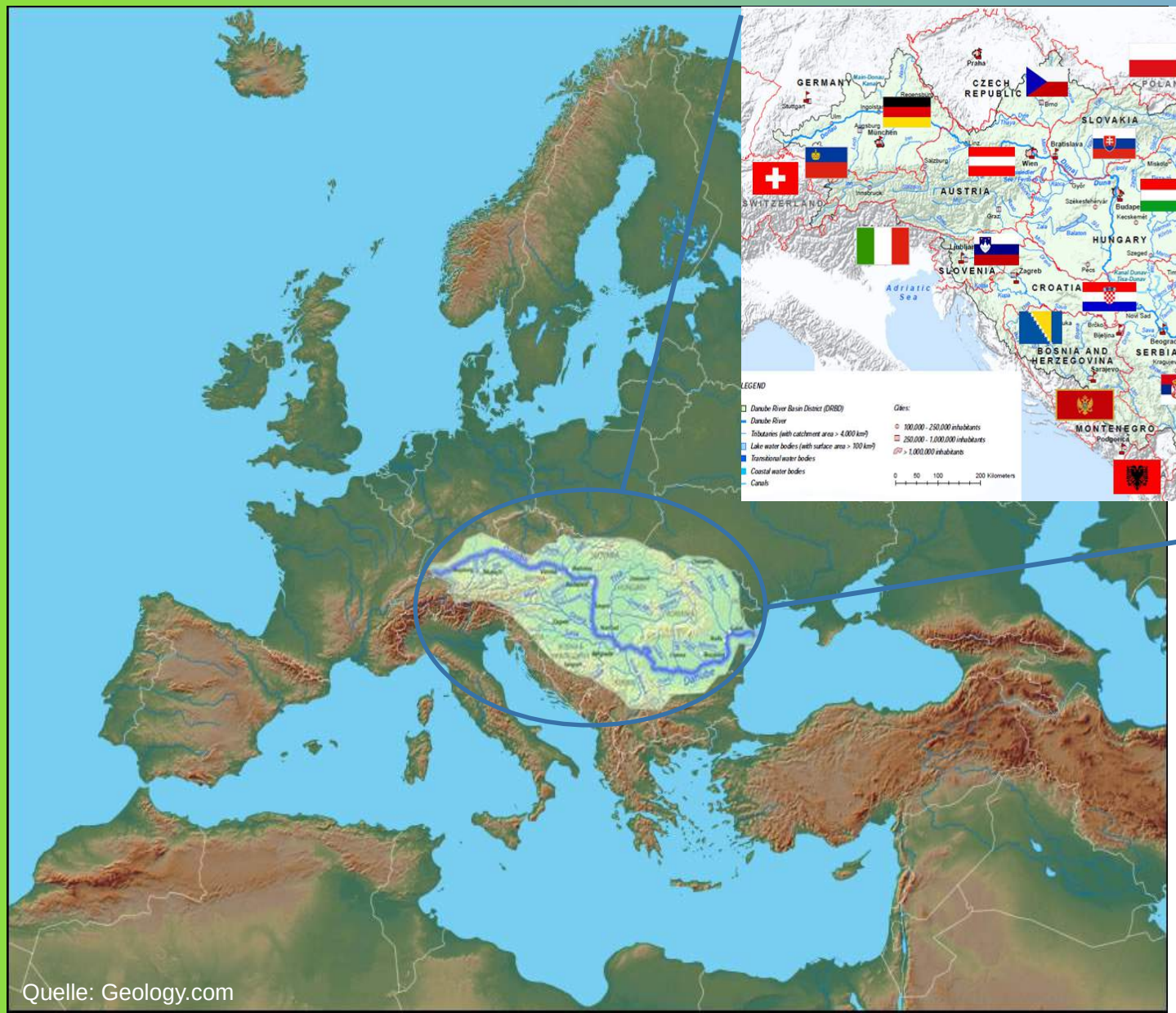
## HOMEPAGE

Sustainable rural development is a key contributor to food security and is essential for improving nutrition and life quality. The demand for traditional agricultural and food products is increasing both from the people in the region and from visitors. That is an indicator of consumer's preferences for authentic and quality food linked to a particular region or country and creates the potential for development of niche markets for promoting rural economy, increasing farmers' income and creating opportunities to maintain the population in less favored or remote areas.

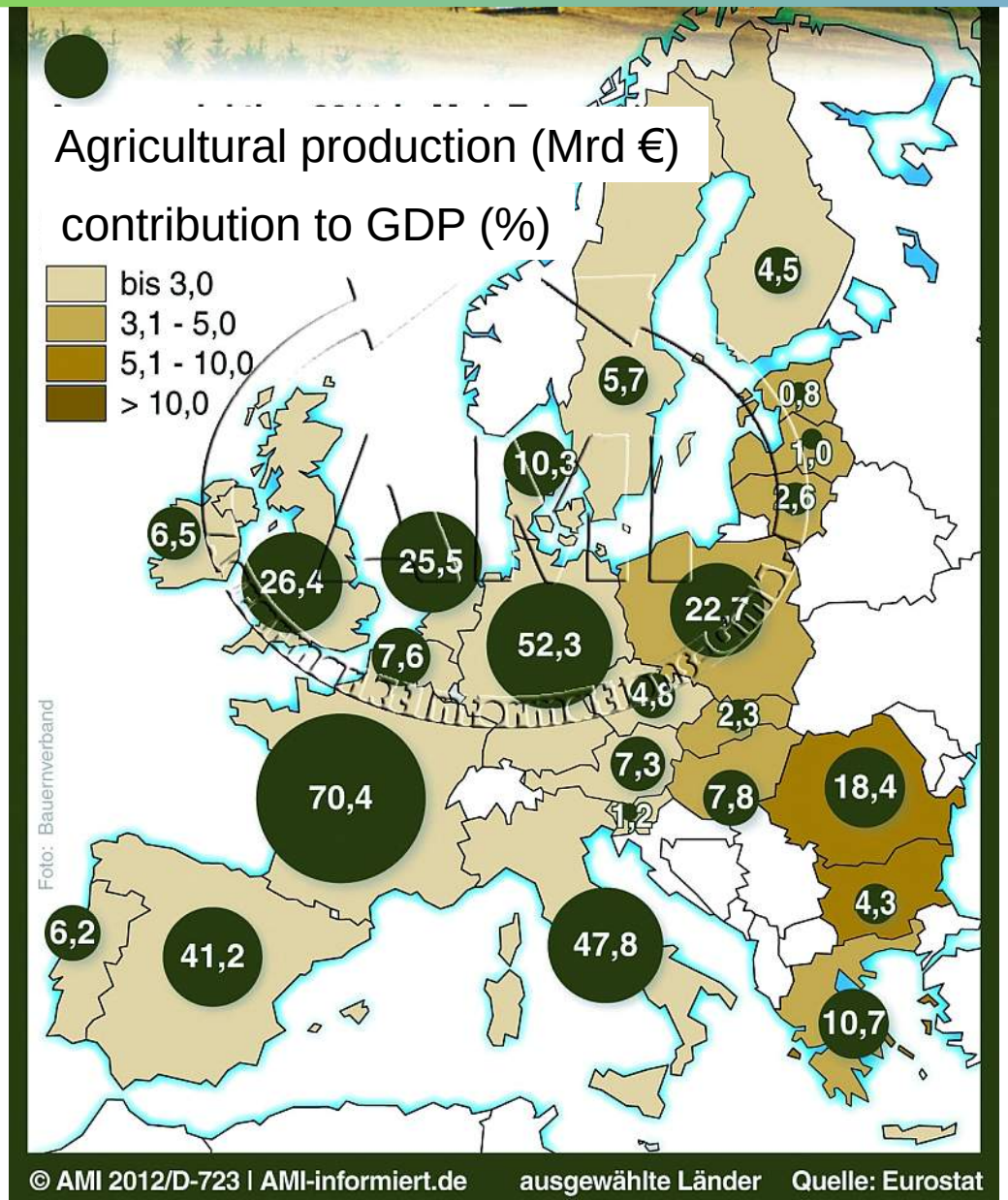
With the multiple aim to provide guidance for the development and implementation of new origin-based quality schemes, such as geographical indications, to promote and support the production and preservation of traditional agricultural and food products, to contribute to rural development and to diversify the available food, FAO launched in 2007 the Programme on Quality Linked to Geographical Origin (www.foodquality-origin.org).

**Traditional regional agricultural and food products – perspective policy for rural development, nutrition improvement and food security sustainability**

# regional importance of the Danube catchment



# Agricultural Production EU 27 (2011)



# 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....)

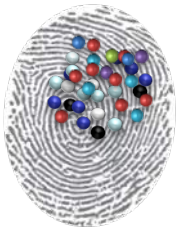
# Analytical methods (2)

- 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
  - Identification of specific elements and evaluation using multivariate statistics (multielement fingerprints)
    - AAS
    - ICP-AES
    - ICP-MS
  - 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)

# Elemental and isotopic fingerprinting



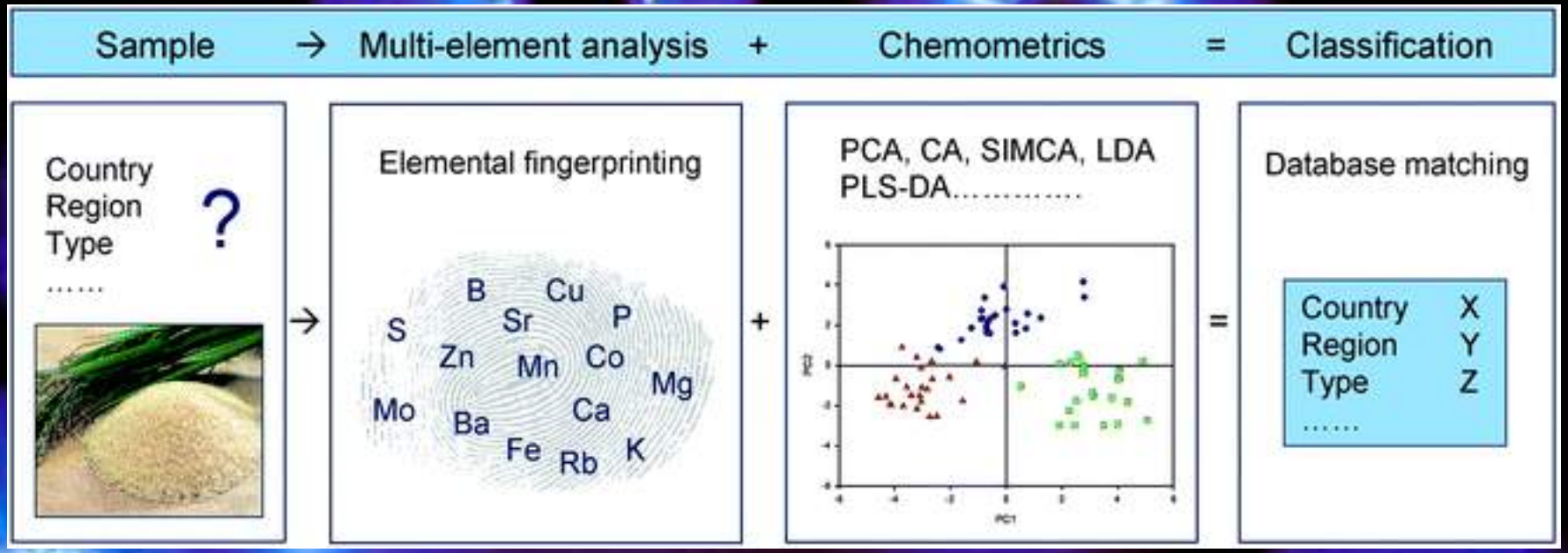
**elemental fingerprint**

**isotopic fingerprint**

**natural variation**
**locally specific signal**

**<< intrinsic marking >>**

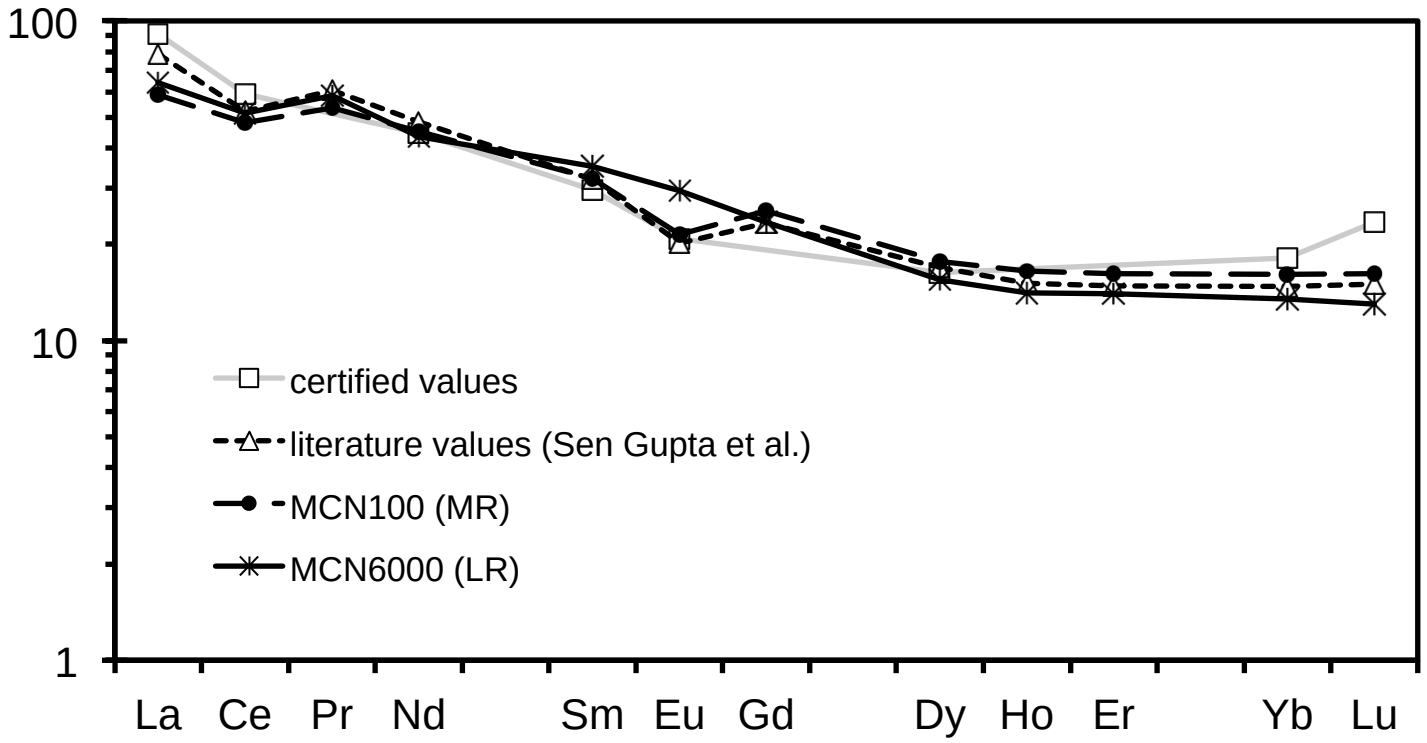
# Elemental and isotopic fingerprint



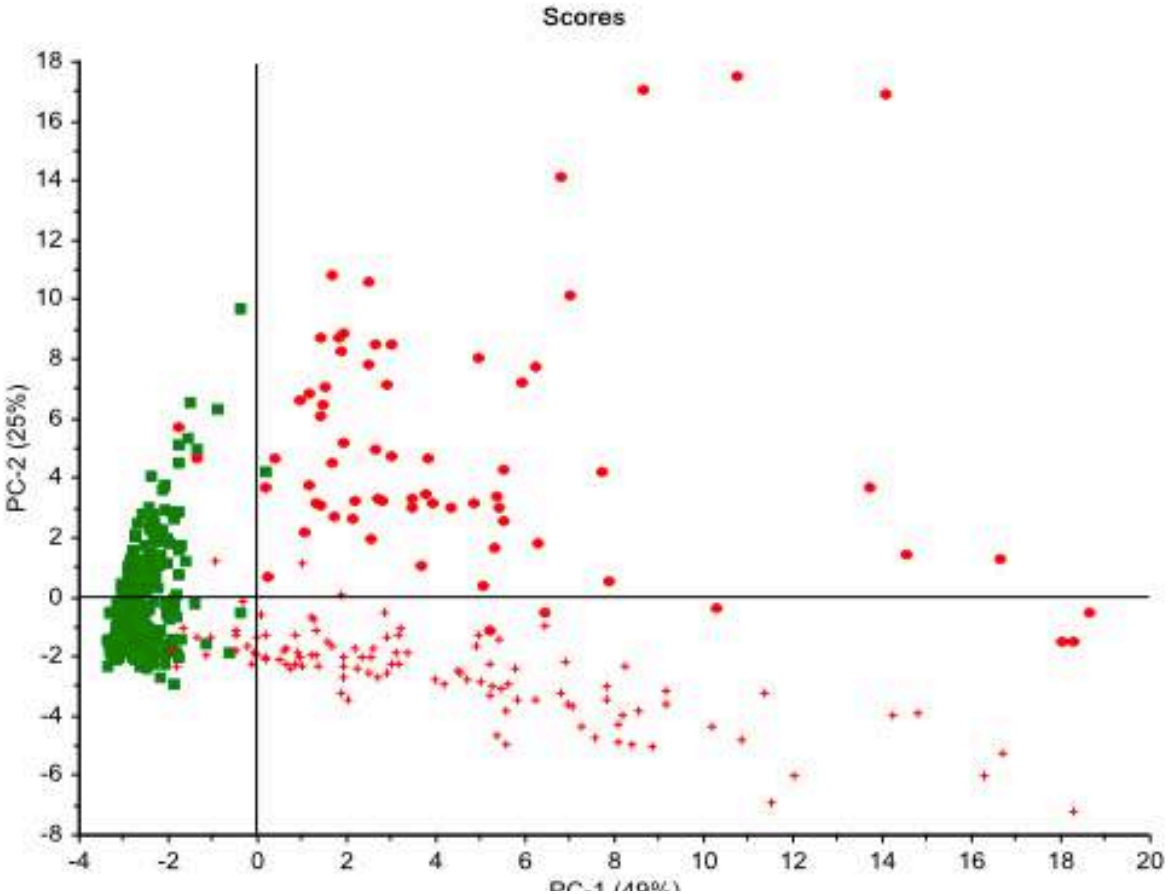

Source: Husted et al. J. Anal. Atom. Spectrom. 2011, 26, 52-79

# Elemental fingerprint of REE for proof of authenticity / origin

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



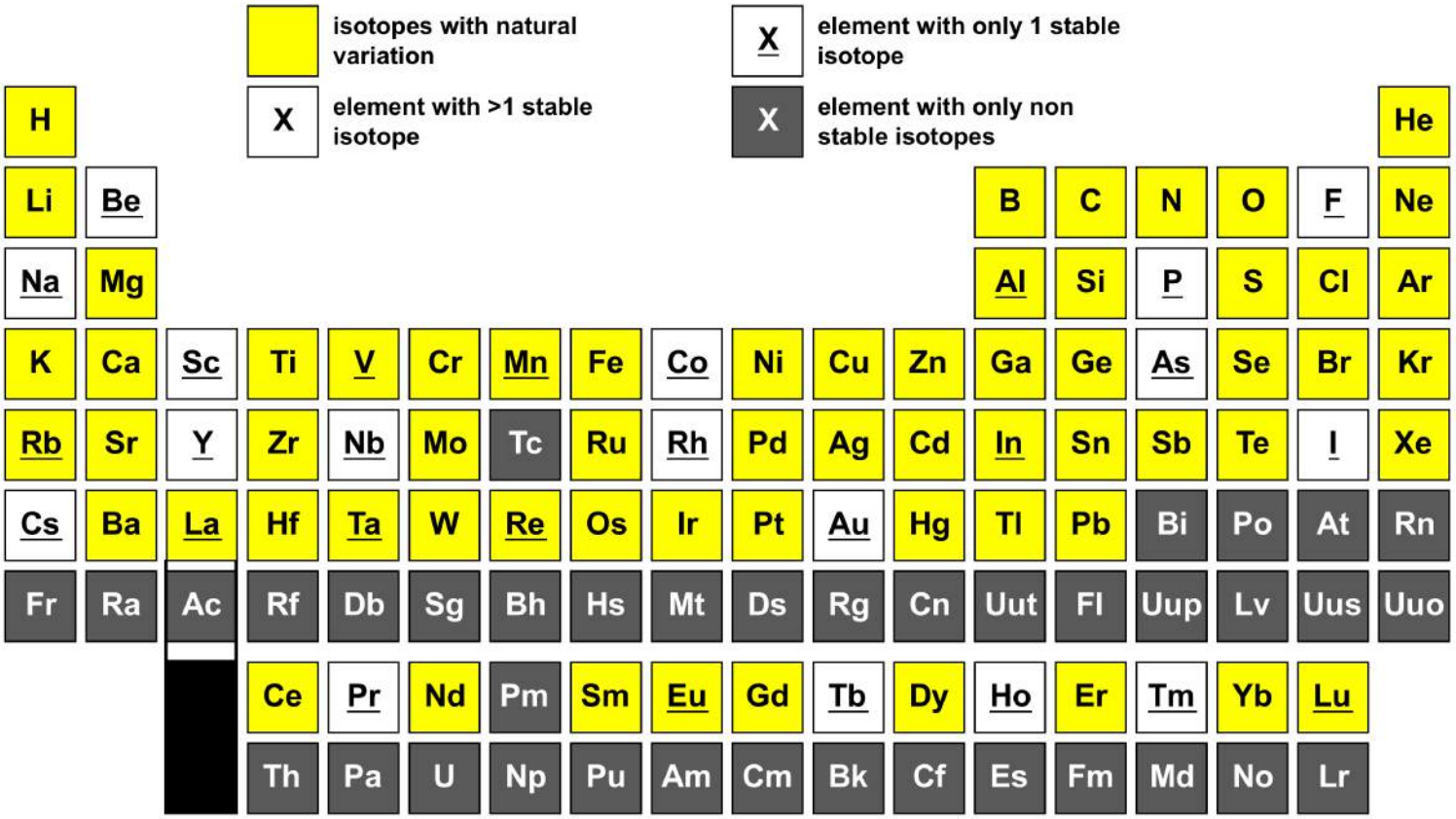
# REE pattern for the provenance of pumpkin seed




score plot PCA (Austria ■ China ● Russia ✚)

*(source: Daniela Zettl, PhD thesis, Montanistic University Leoben, 2013)*

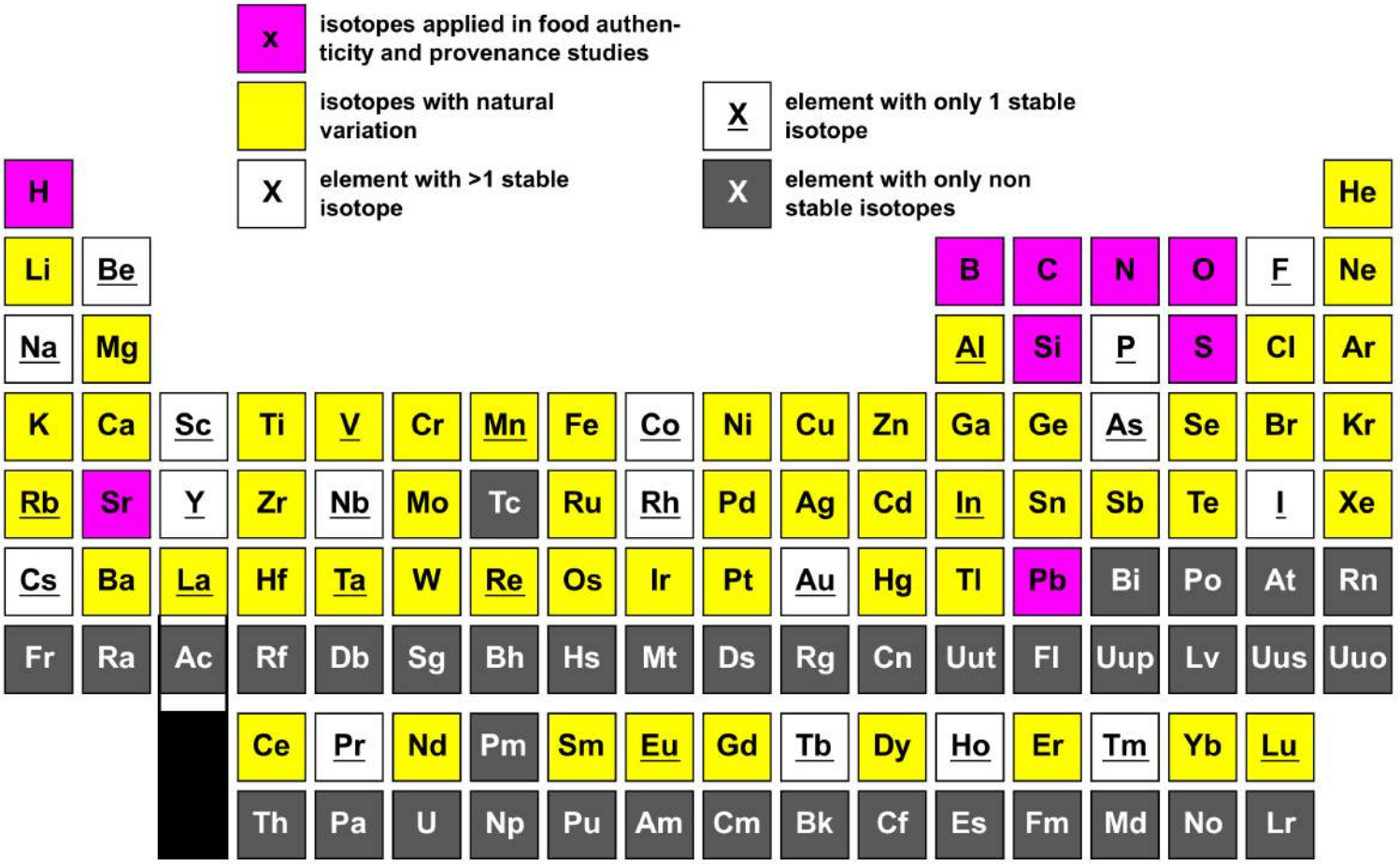
# Natural variation of isotopic systems



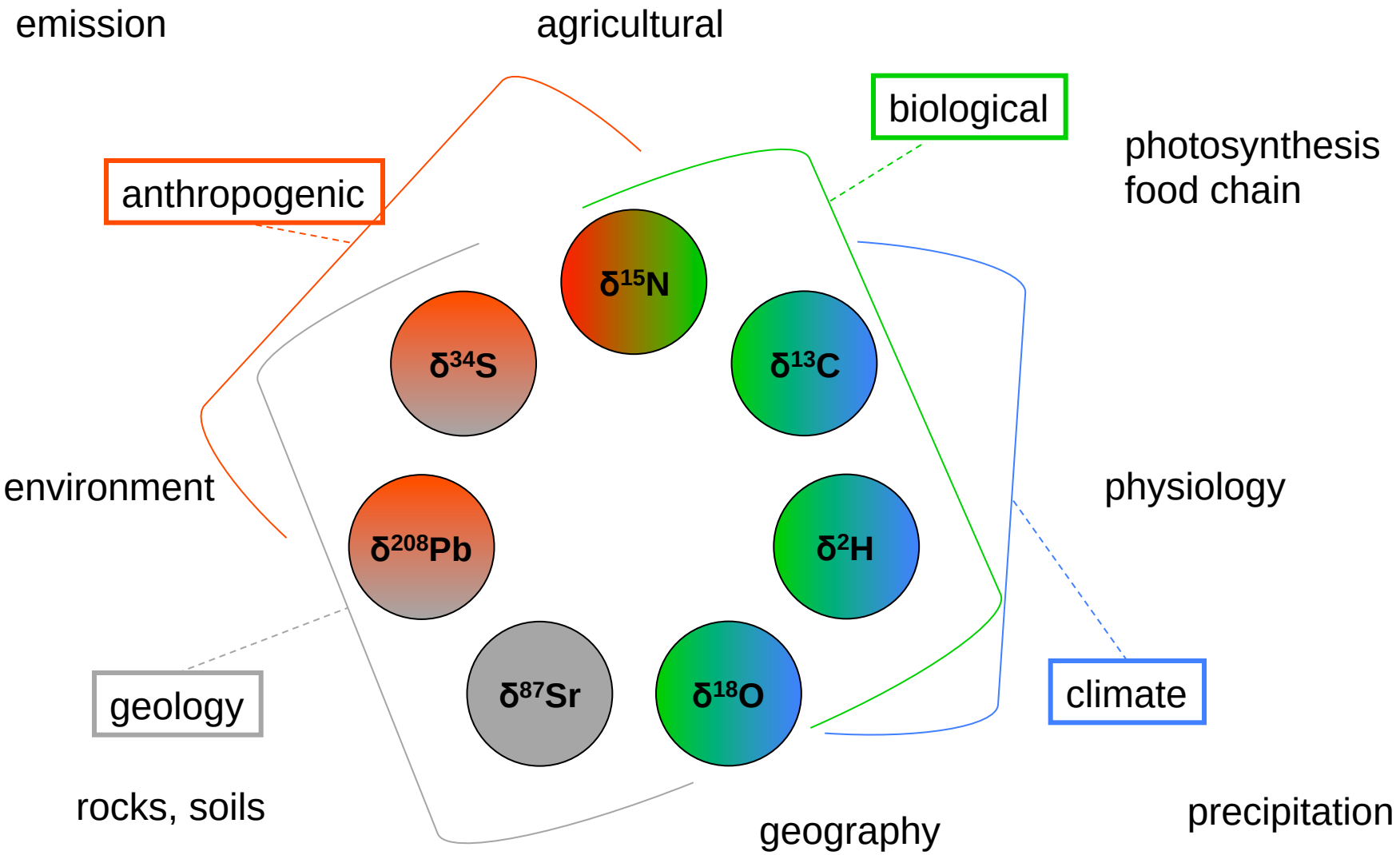
# Natural variation of isotopic systems

- 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



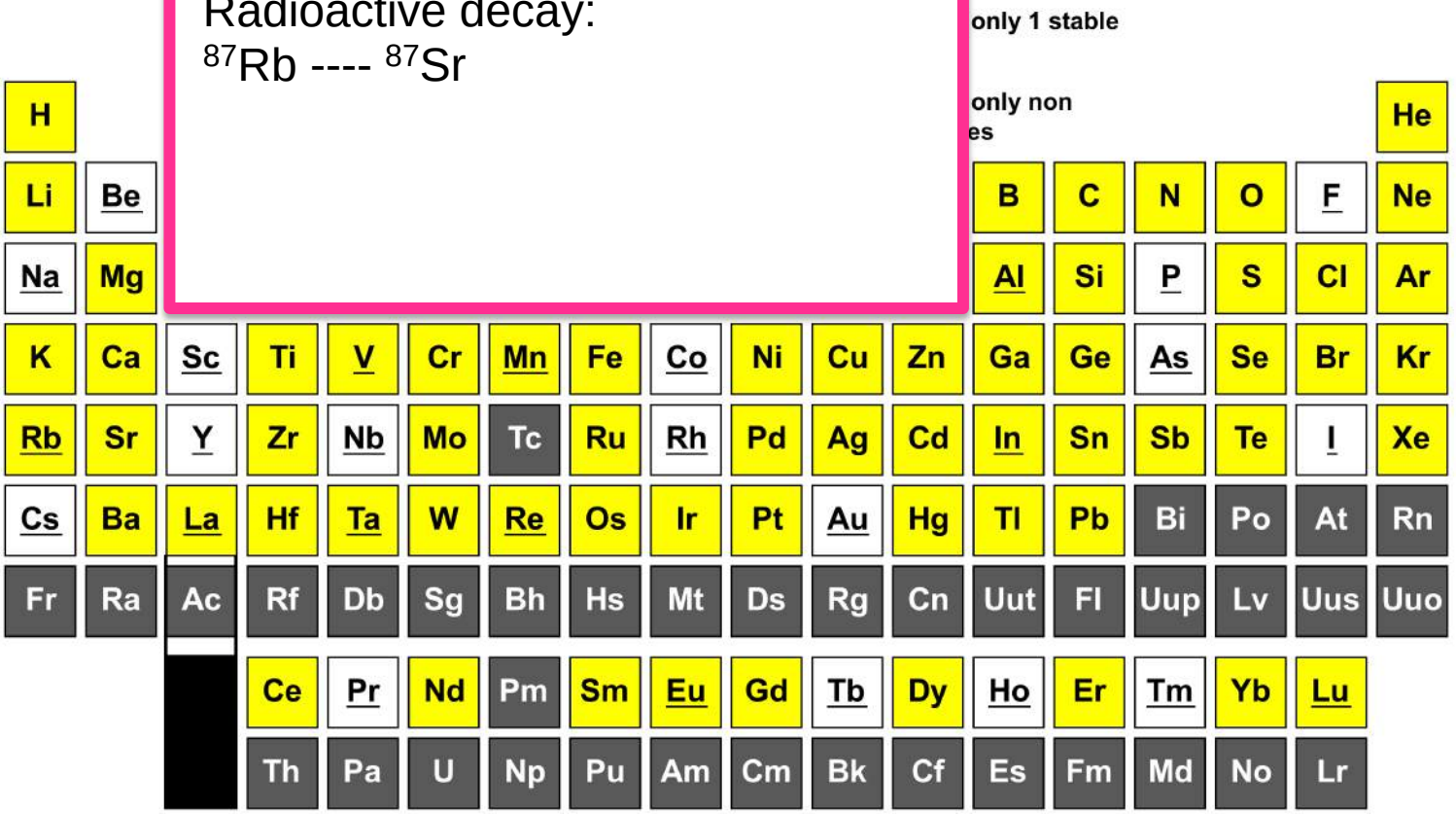
# The ‚big 7‘


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

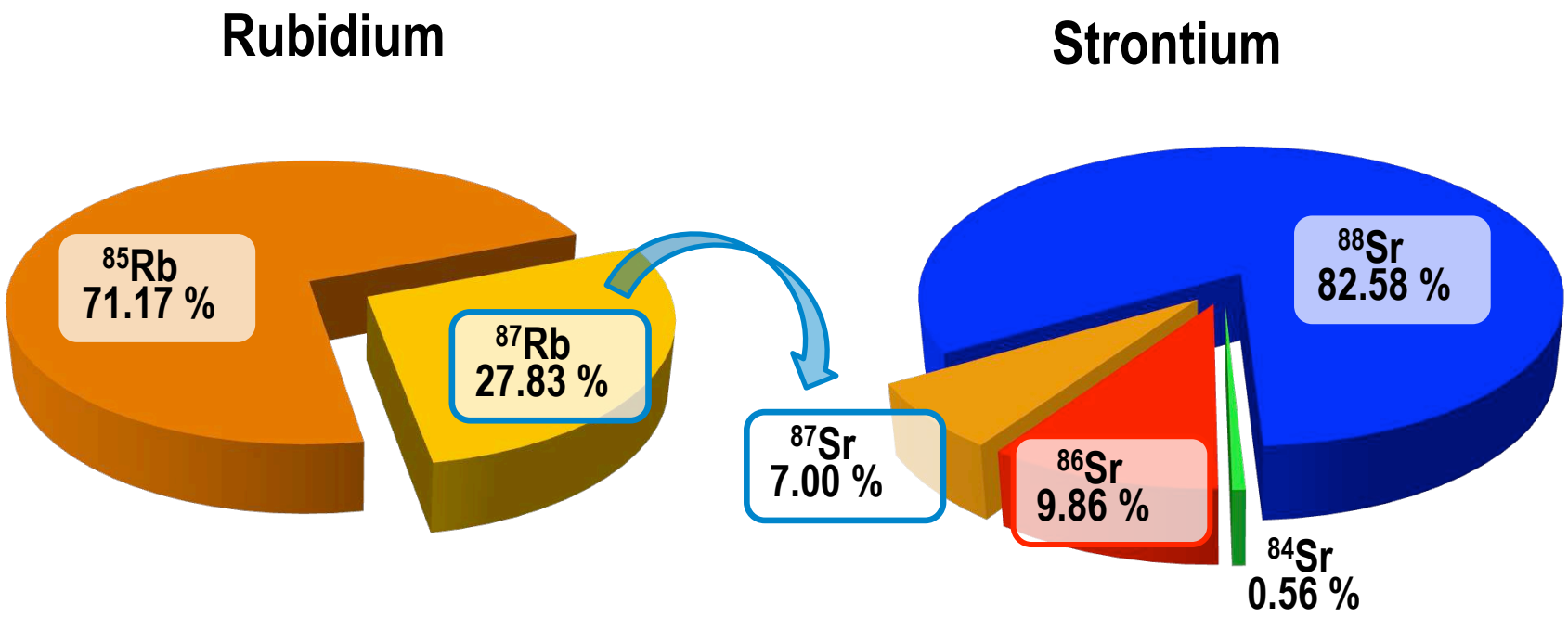
# Sr Isotopic Variation

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

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



# 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)

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

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

- geochemical composition
- geological age

# Sr Sources

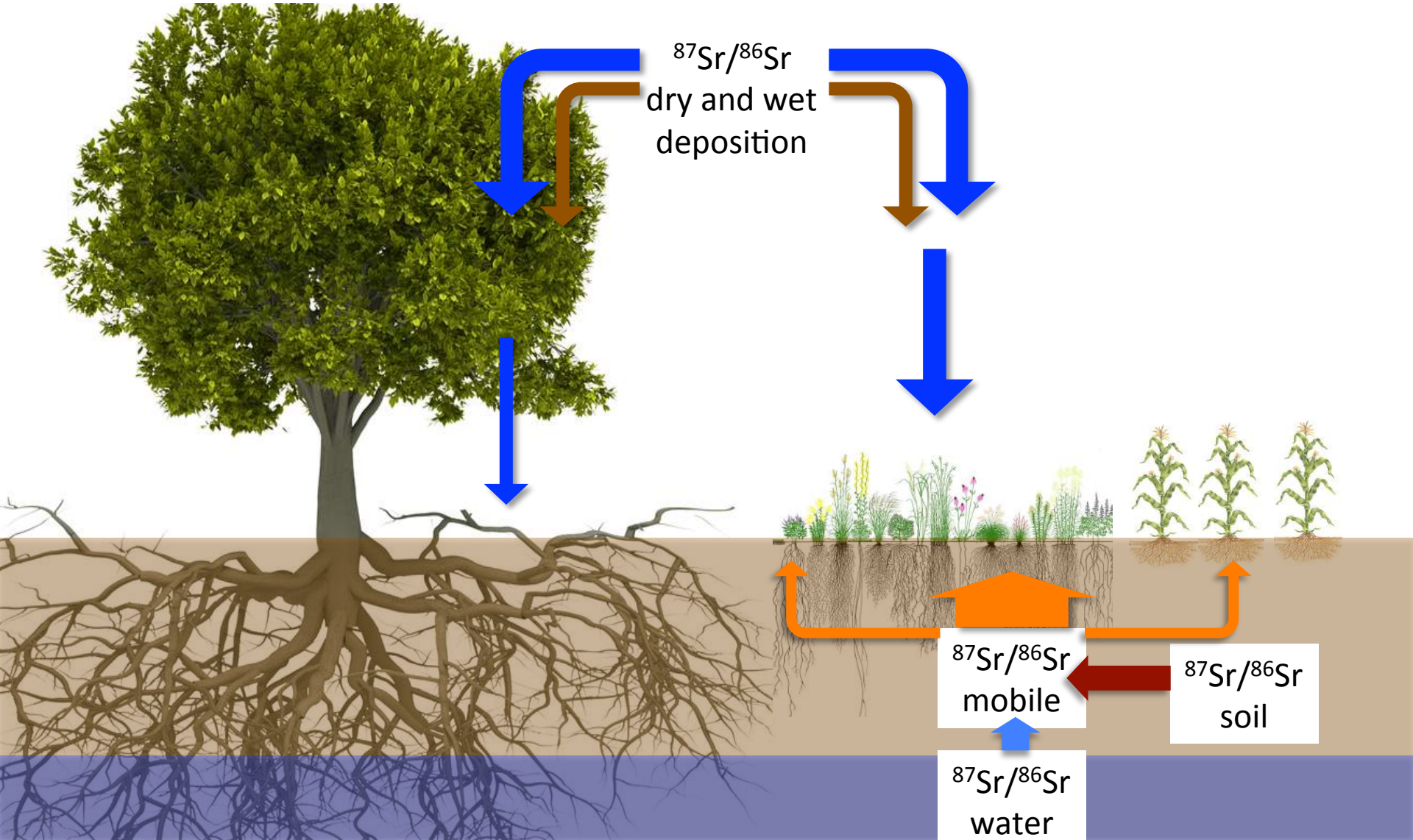
Sr isotopic composition

- maternal rock
- wet and dry deposition

- 20 % weathering
- 80 % recycled Sr

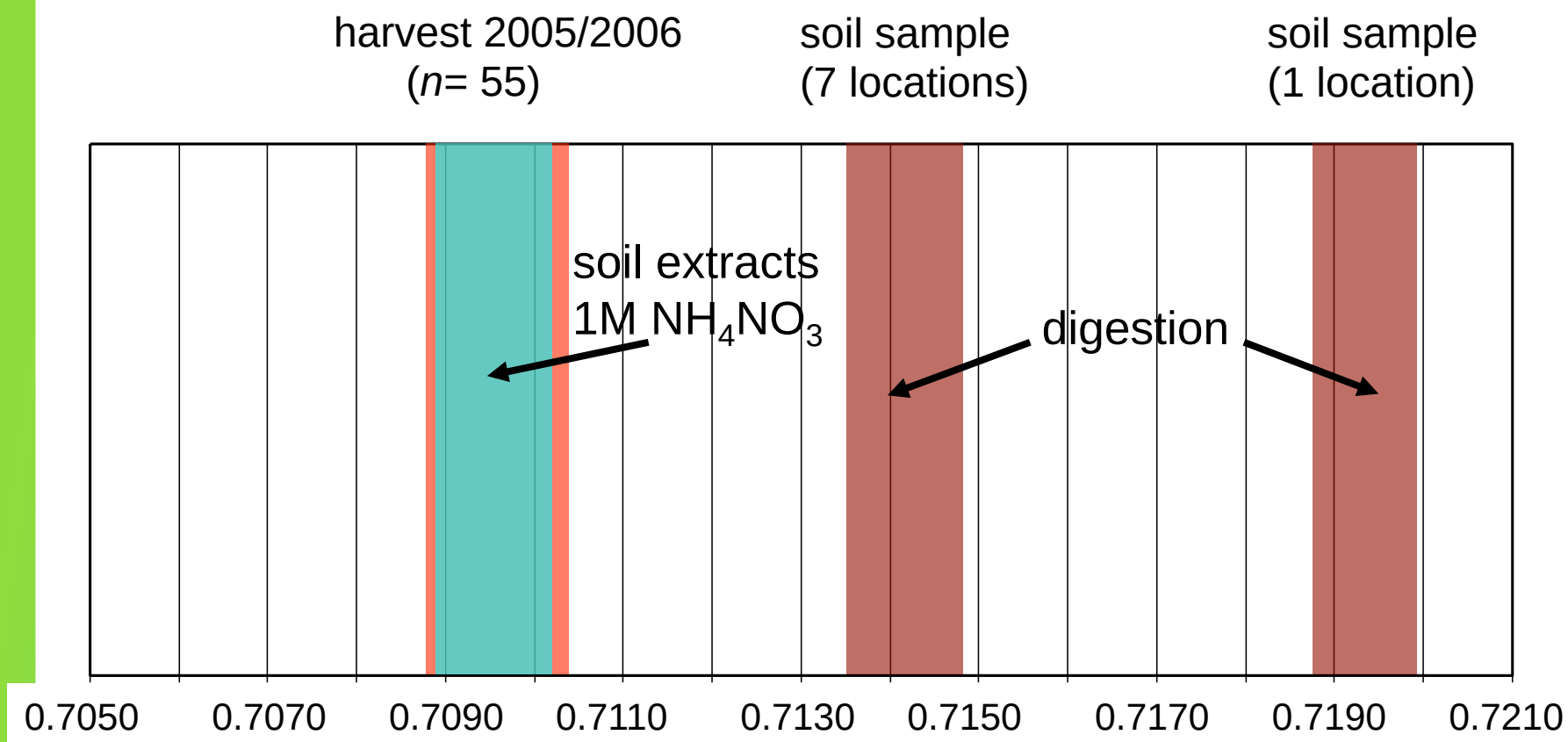
*Miller EK, Blum JD and Friedland AJ, Nature **362**, 1993, 438-441*

# herbaceous (shallow, fibrous root system)
# woody (deeper, coarse root system) plants



# Bioavalable Sr in soils as proxy for plant Sr

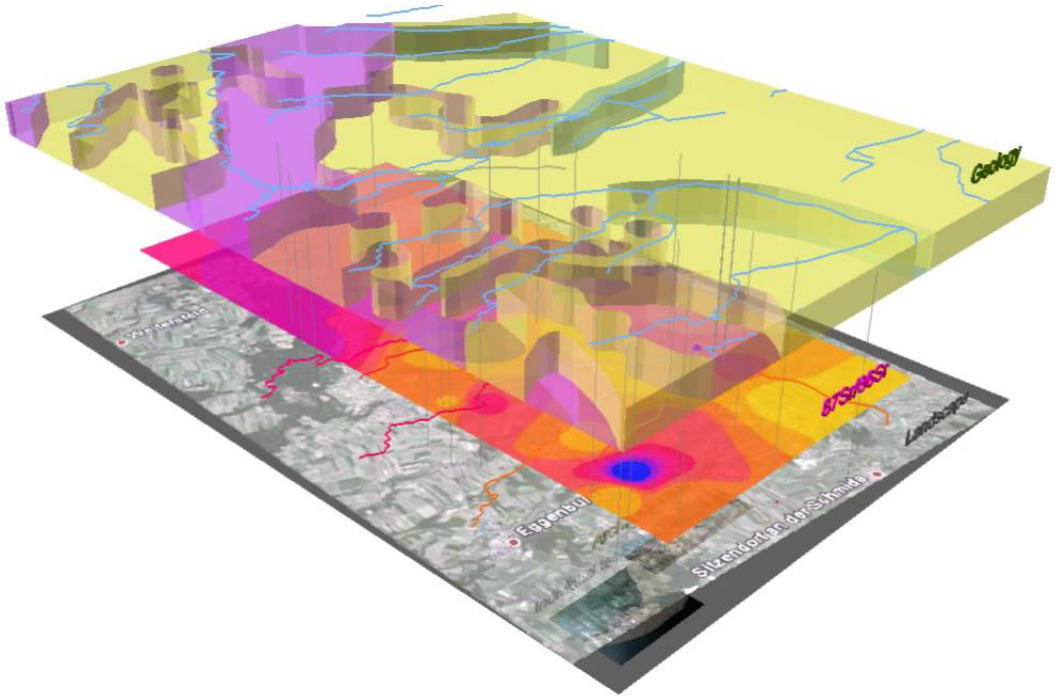
## example: asparagus from Marchfeld/Austria




S. Swoboda, M. Brunner, S. Boulyga, P. Galler, M. Horacek, G. Stingeder and T. Prohaska - J Anal Bioanal Chem. 390. 487- 494, 2008

# Provenancing of food via the assessment of isoscapes of bioavalable Sr in the Danube catchment

- bioavailable Sr in soil
  - accessible via $NH_4NO_3$ extract
  - different to total soil $^{87}Sr/^{86}Sr$
  - good proxy for plant Sr




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

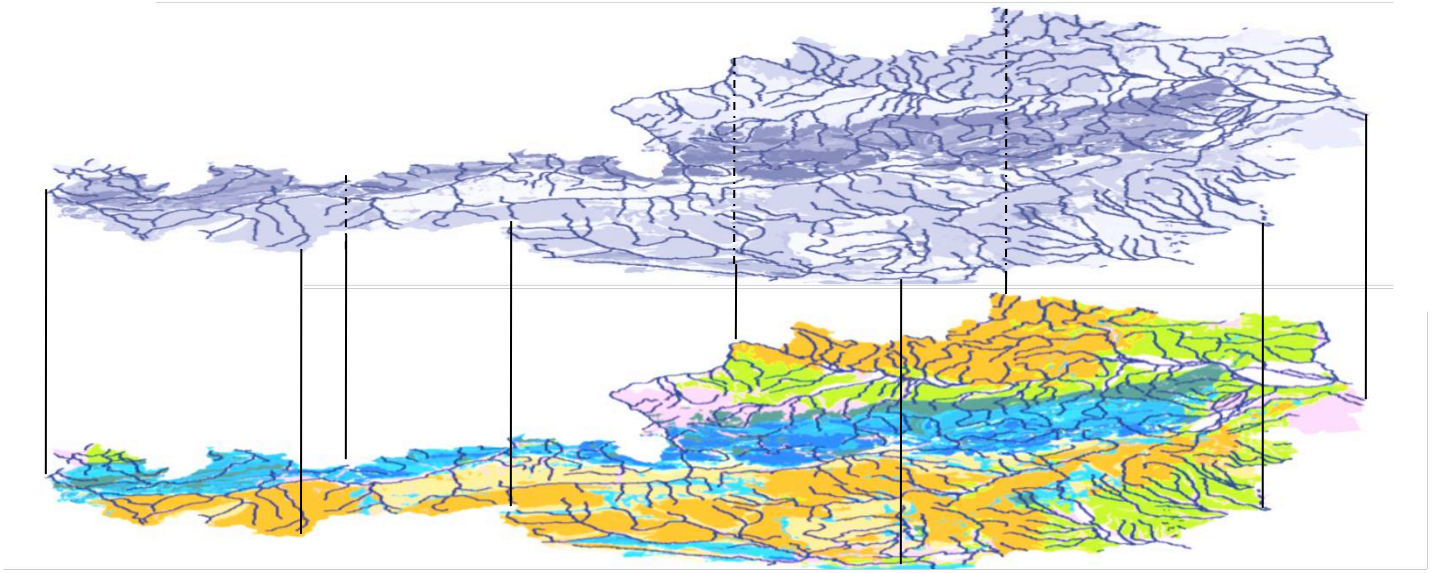
87Sr/86Sr values
- 0,71005 - 0,71064
- 0,71064 - 0,71124
- 0,71124 - 0,71183
- 0,71183 - 0,71243
- 0,71243 - 0,71302
- 0,71302 - 0,71362
- 0,71362 - 0,71421
- 0,71421 - 0,71481
- 0,71481 - 0,71540

# Sr isoscapes

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

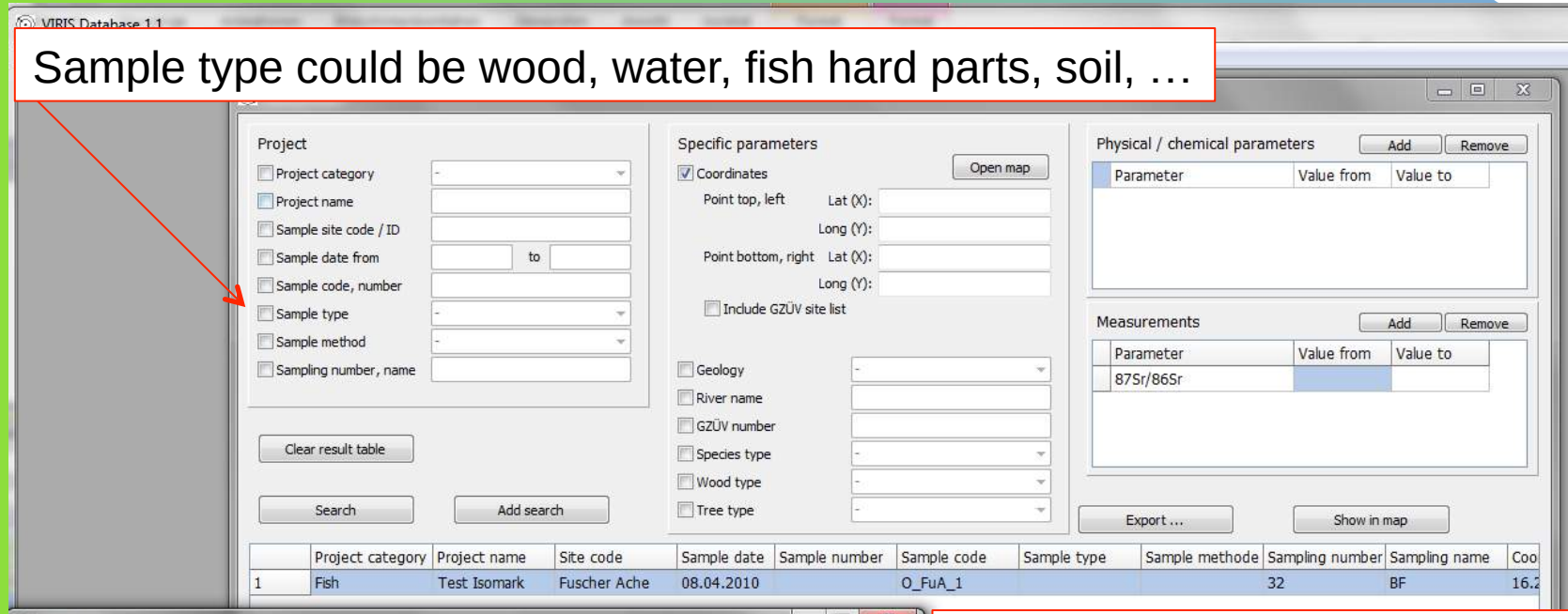
$^{87}Sr/^{86}Sr$

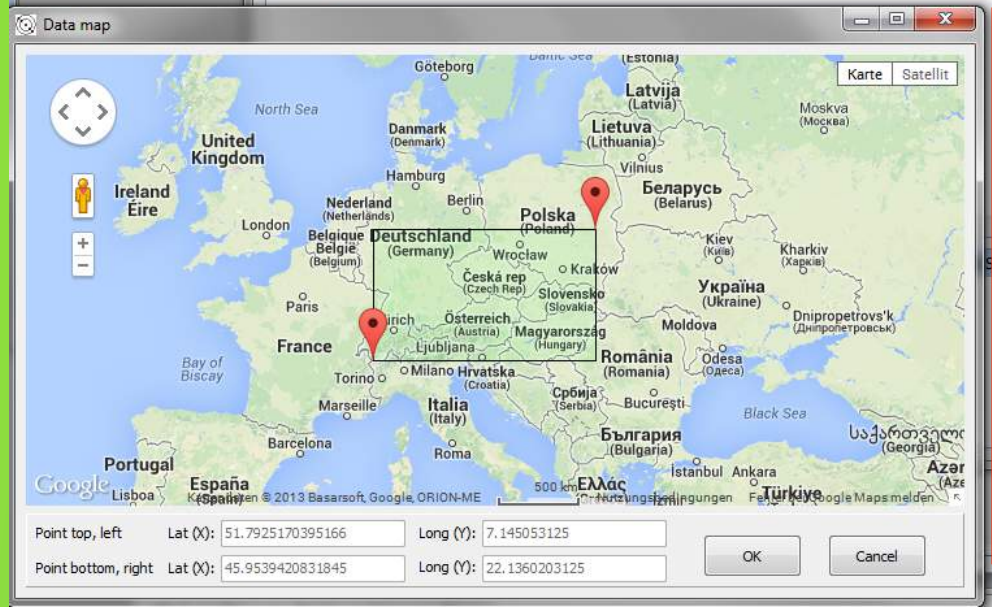
geology



# Sr isoscape work - VIRIS database

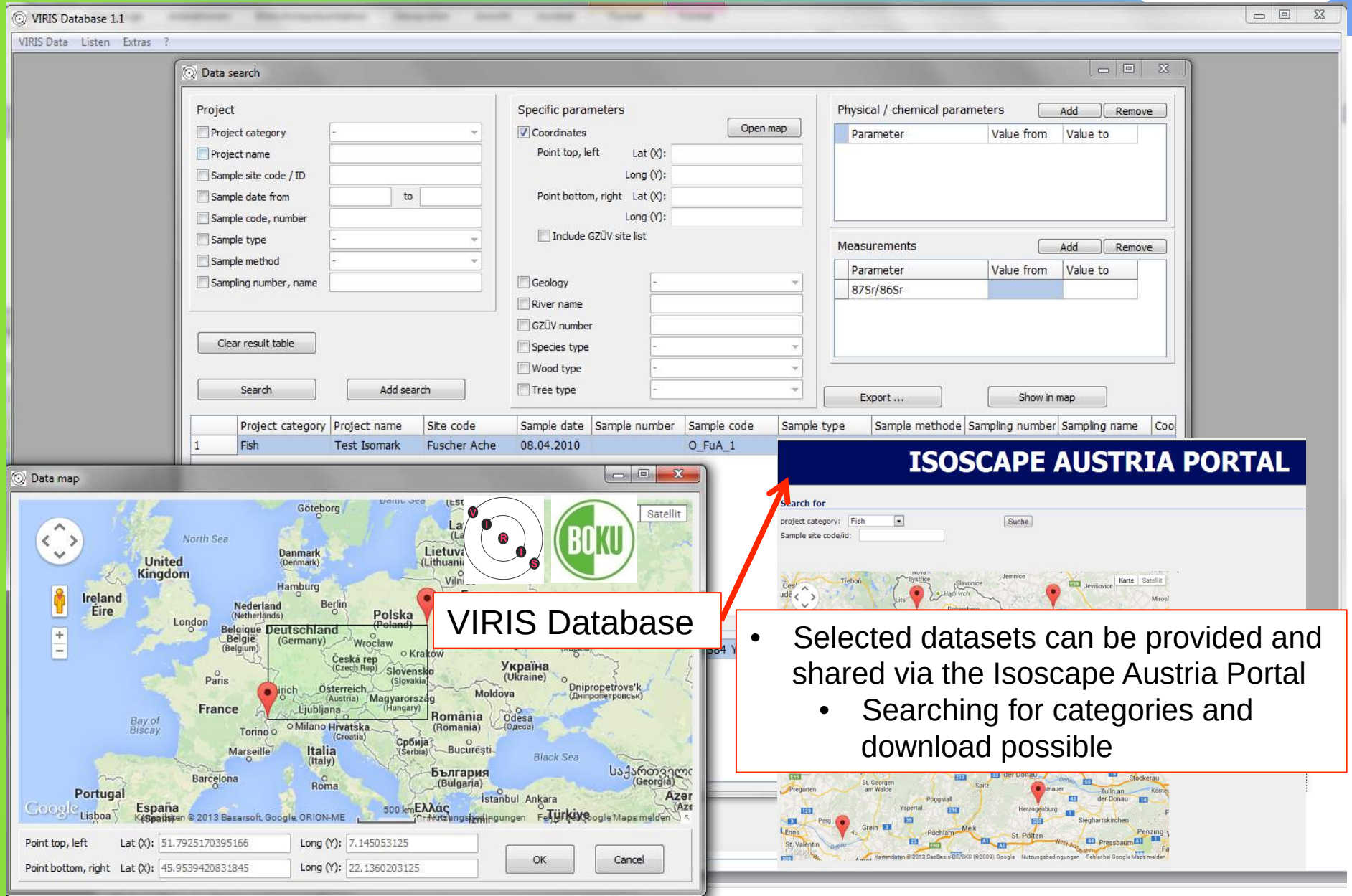
Sample type could be wood, water, fish hard parts, soil, …



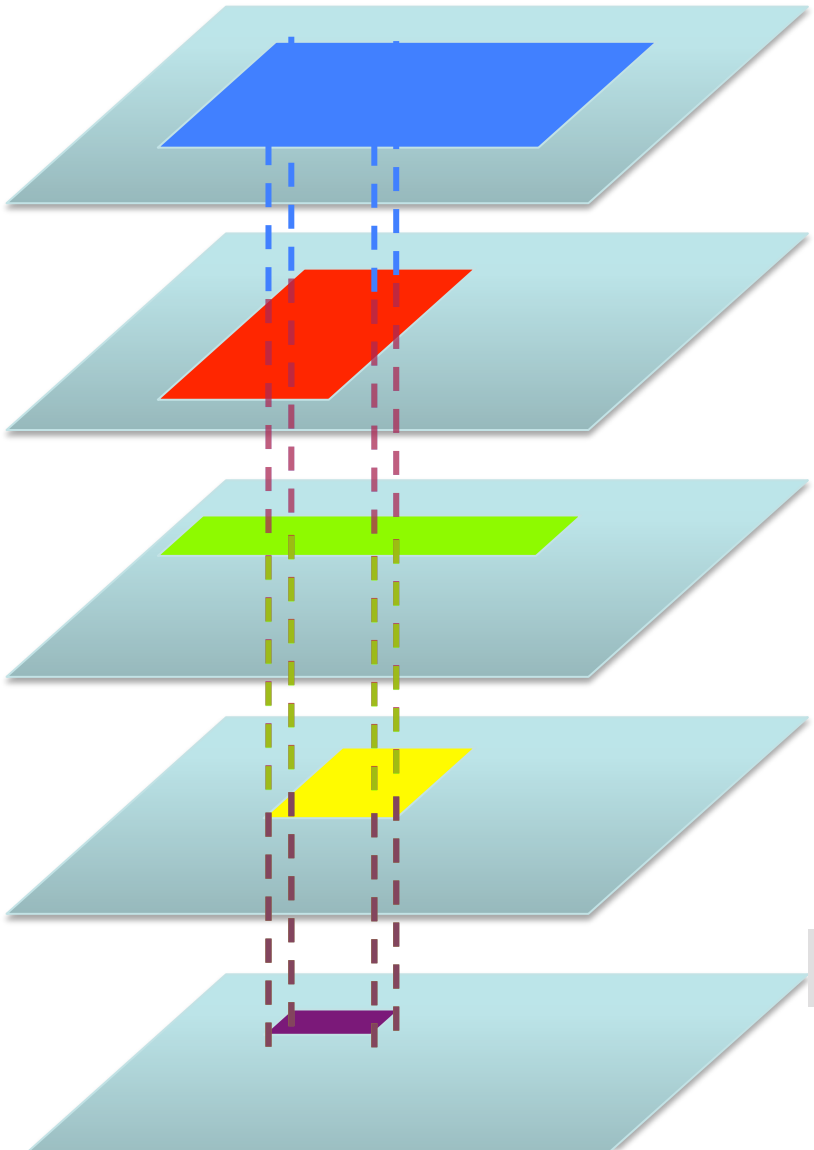




- Input via Excel spread sheets in different categories of projects and samples, including quality judgement, instrumental settings, pictures, links to original data, citation etc.
- Searching data possible
  - by a wide variety of requests, including the measured parameter (e.g. $^{87}Sr/^{86}Sr$)
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



# Combining isotopic information of areas of origin



$\delta^{2}H$

$\delta^{18}O$

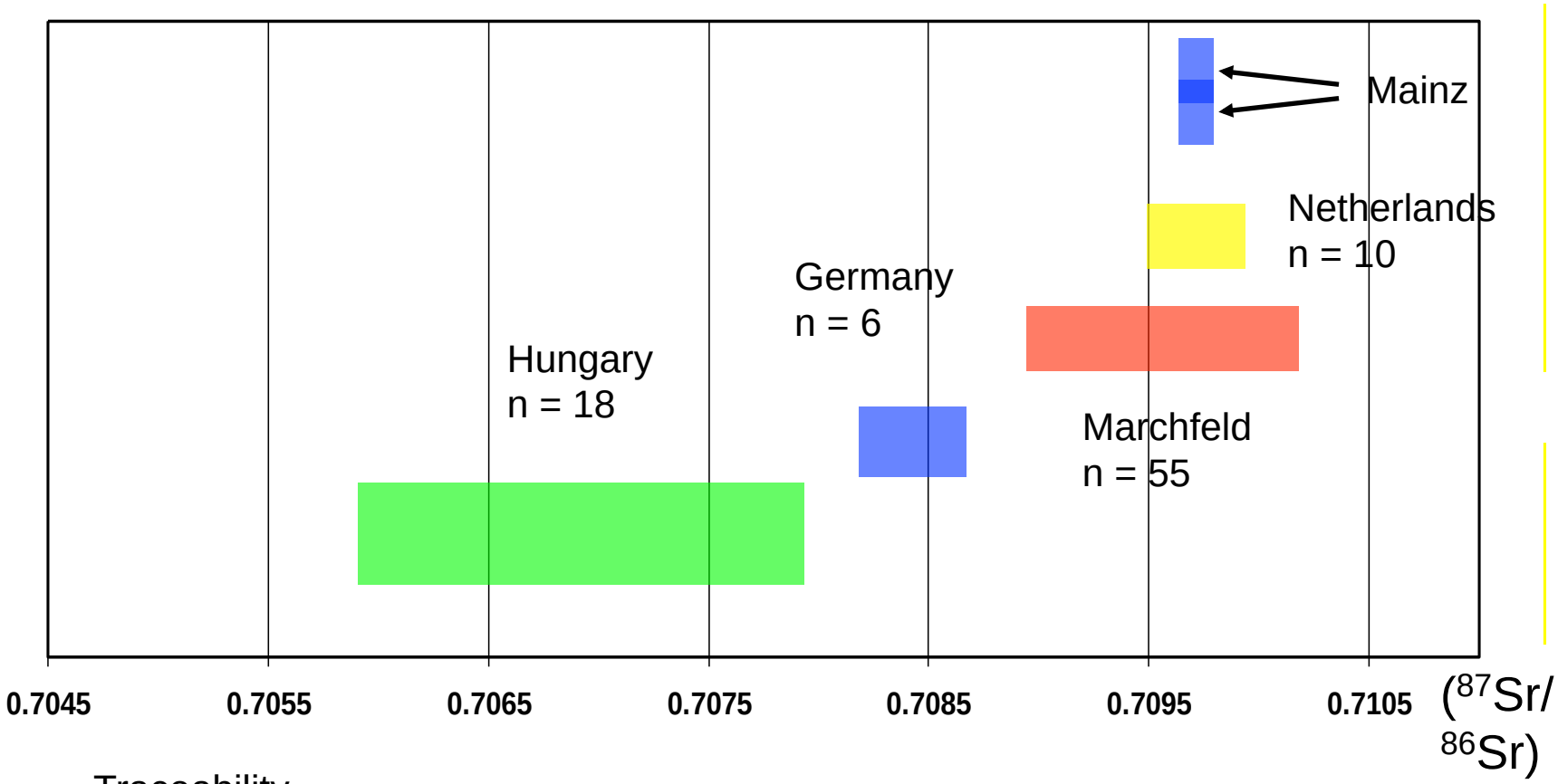
$\delta^{34}S$

$\delta^{87}Sr$

intersection – area of provenance

# Marchfeld asparagus

# Marchfeld: Sr range and source



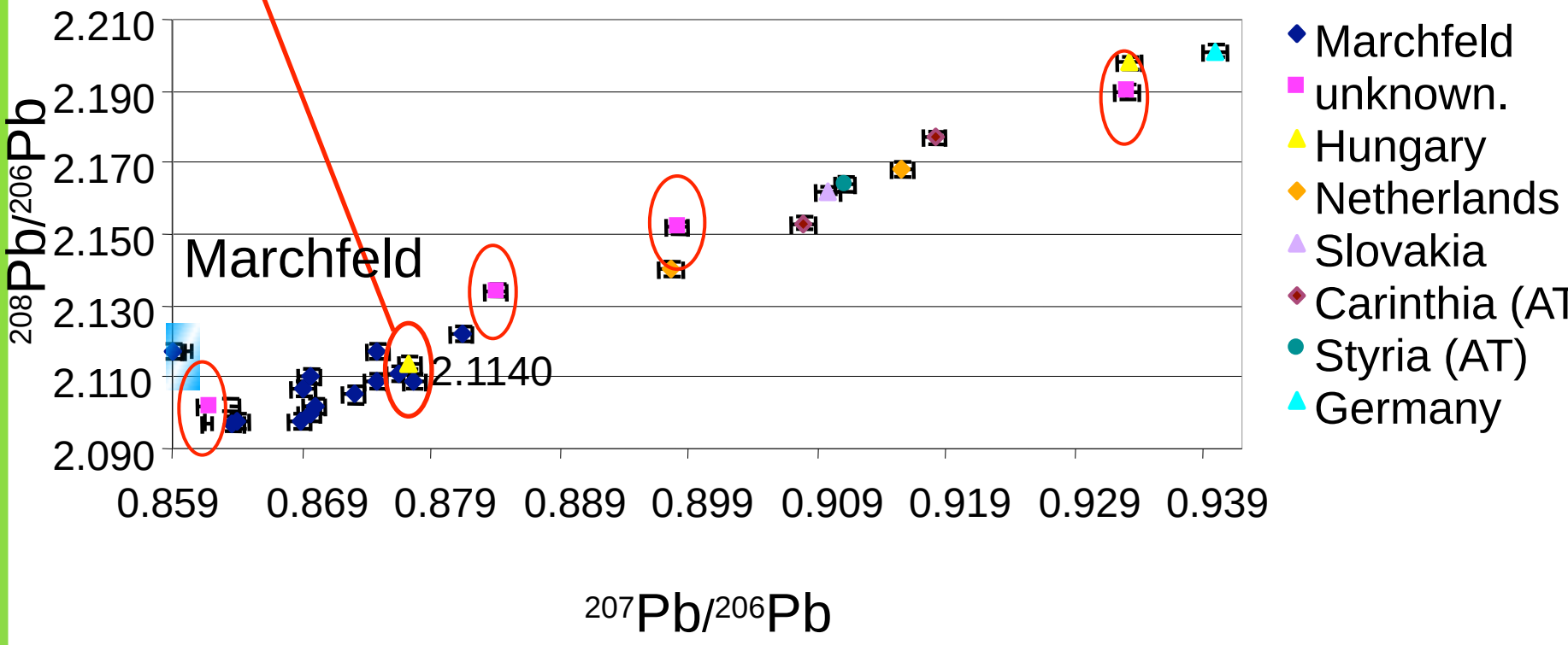

Traceability

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

- include other signatures
- multivariate statistics

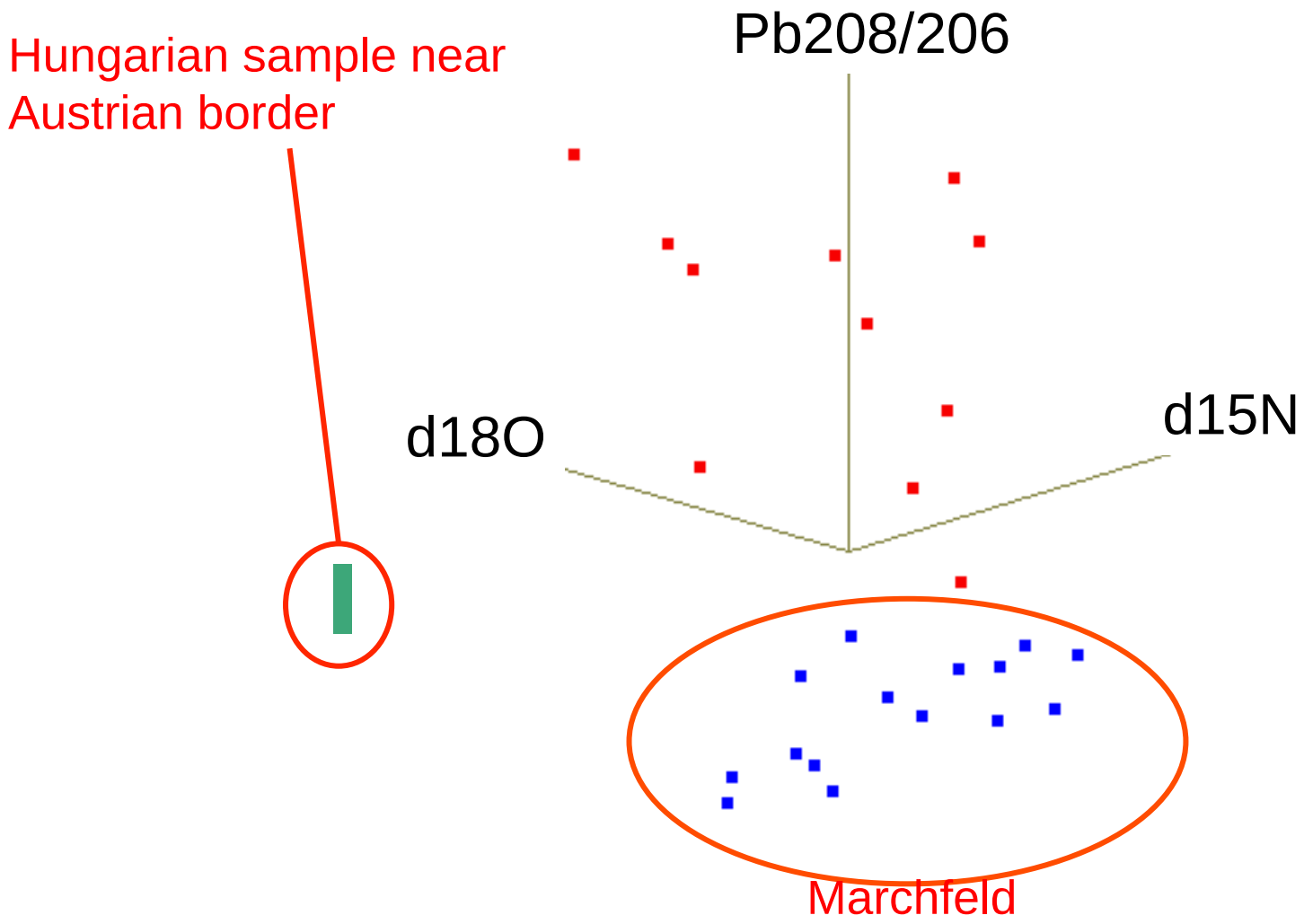
# Marchfeld asparagus

Hungarian sample near Austrian border

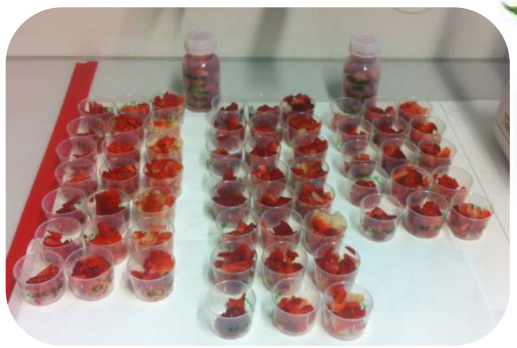


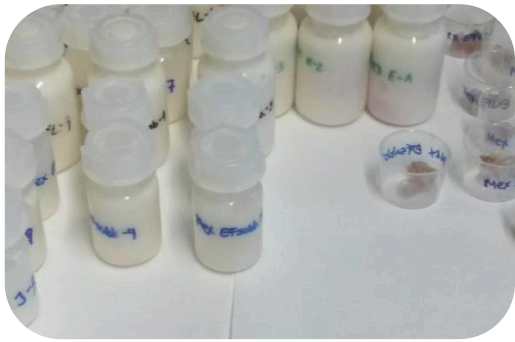

...isotope ratios do not follow political borders

# 3D main component analysis

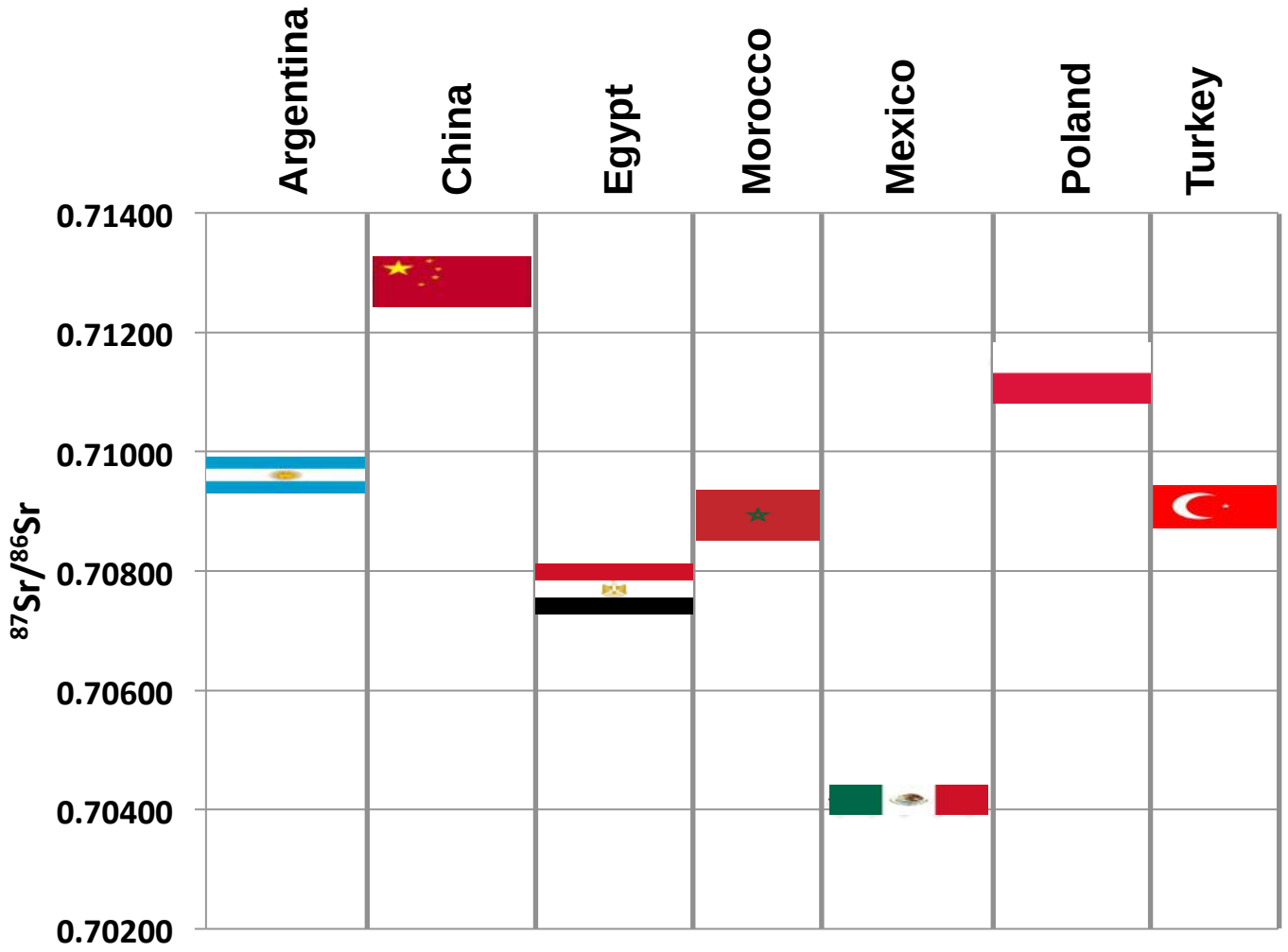


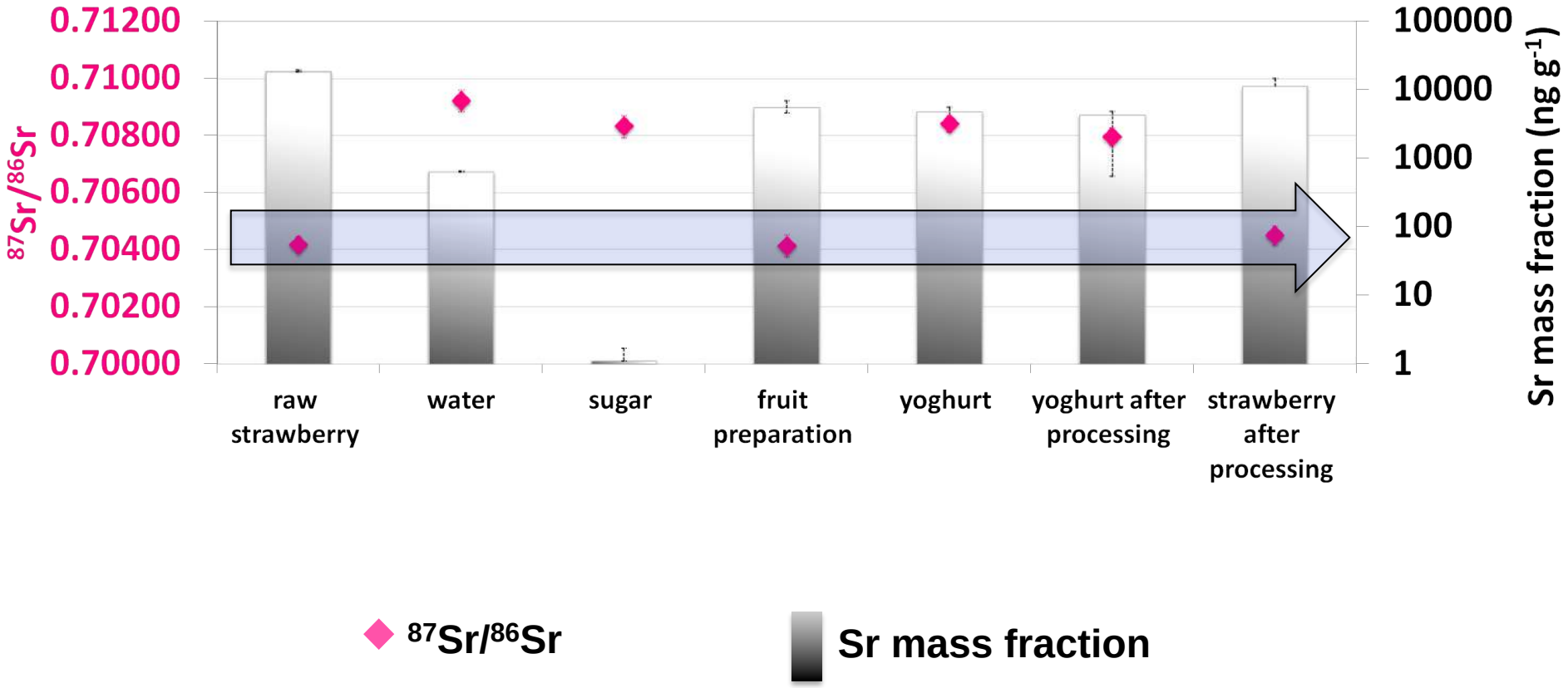
# Provenancing of strawberry raw products using elemental and isotopic fingerprints – a pilot study





# Sr isotopic data




0.71200
0.71000
0.70800
0.70600
0.70400
0.70200
0.70000
87Sr/86Sr
100000
10000
1000
100
10
1
Sr mass fraction (ng g-1)
raw strawberry
water
sugar
fruit preparation
yoghurt
yoghurt after processing
strawberry after processing
87Sr/86Sr
Sr mass fraction

# 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**

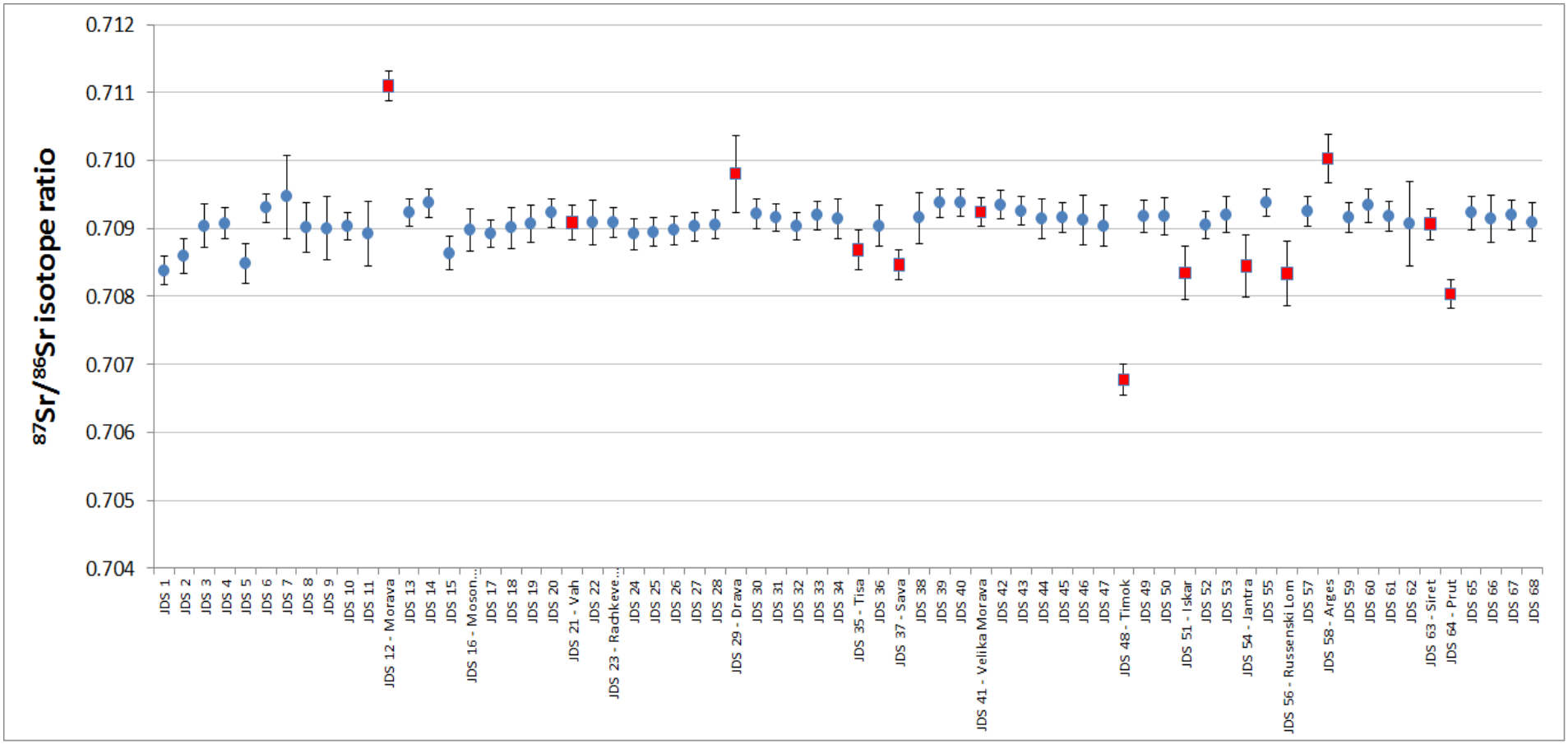
- Change of irrigation
- Influence of fertilizer
- Regional heterogeneity of the soil
- Influence of processing

# Danube isoscape

- **Joint Danube Survey 3**


# Sr isoscape along the danube

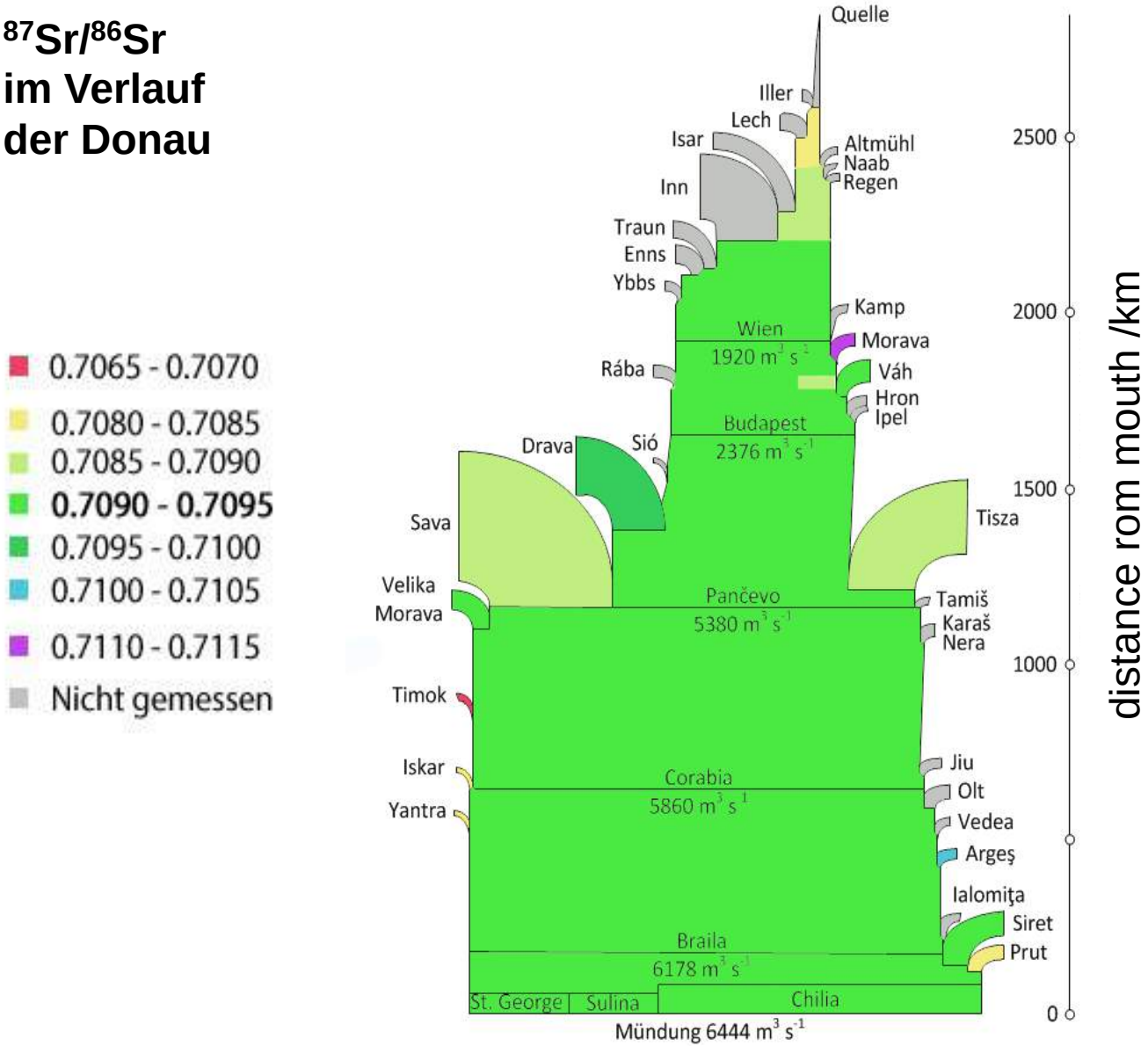
## $^{87}Sr/^{86}Sr$ isotope ratio



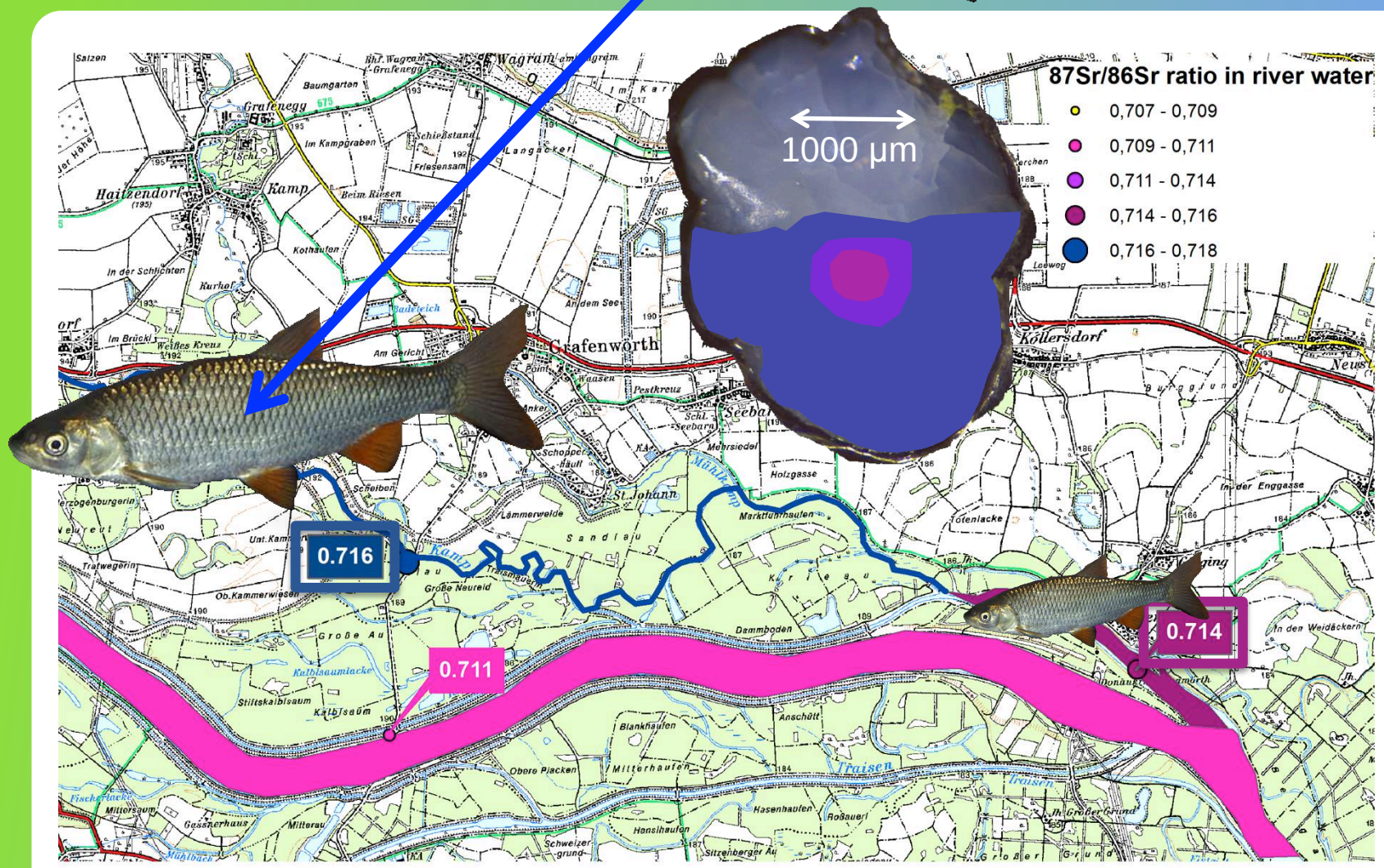

$n$=3, error bars $u_c$ ($k$=1)

# Sr isoscape along the danube

**$^{87}Sr/^{86}Sr$ im Verlauf der Donau**



# Migration between isozones



# Advanced analytical methods for caviar provenancing

## Using Sr isotopes, elemental patterns and genetics


**Anastassiya Tchaikovsky, Andreas Zitek, Leo Congiu, Thomas Prohaska**

*University of Natural Resources and Life Sciences Vienna, BOKU-UFT, VIRIS*
*University of Padova, Department of Biology*

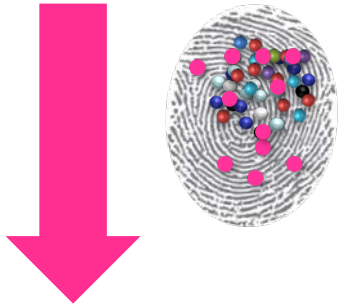
# Elemental and isotopic fingerprinting

elemental fingerprint

isotopic fingerprint

natural variation
locally specific signal

<< intrinsic marking >>



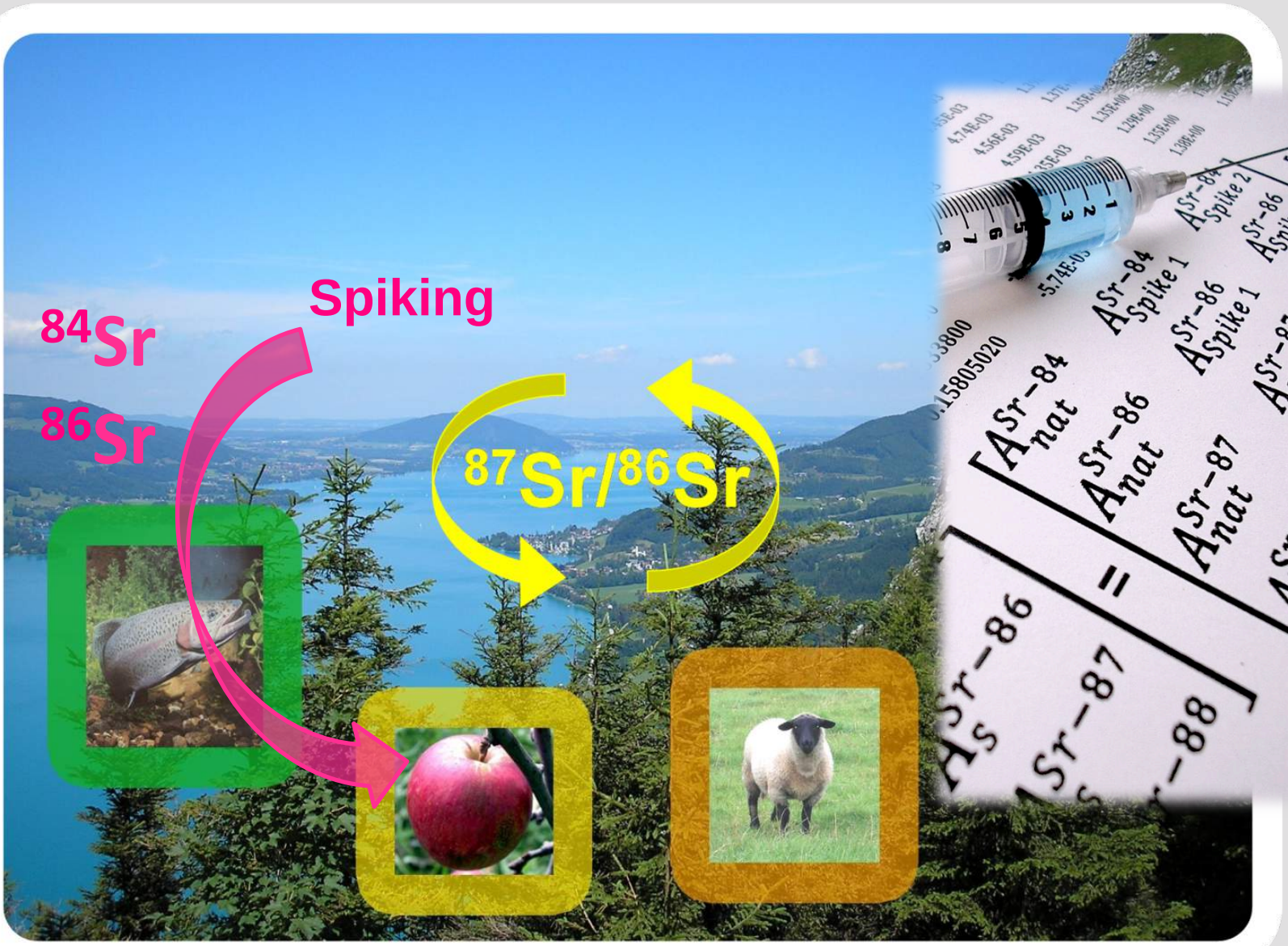
**(multi)-elemental spikes**

**enriched stable isotopes**

**marking via elemental spikes or enriched isotopes**

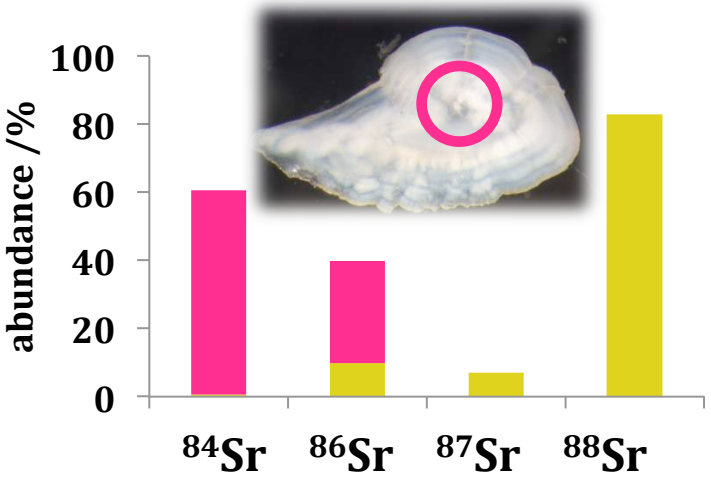
**<< extrinsic marking >>**

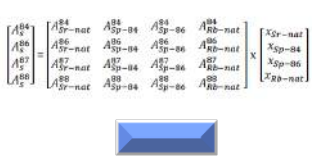
# Sr Spiking

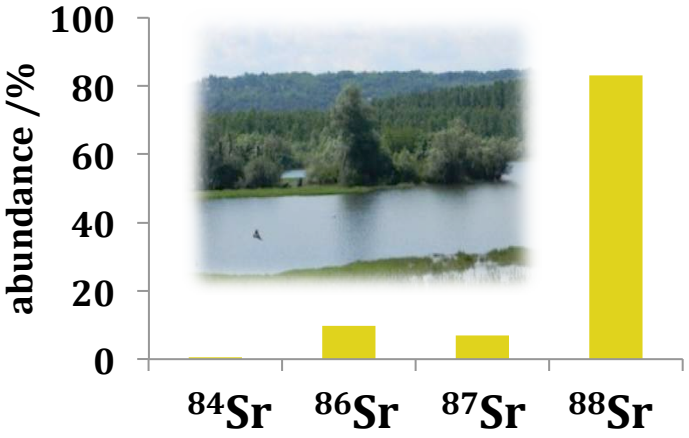


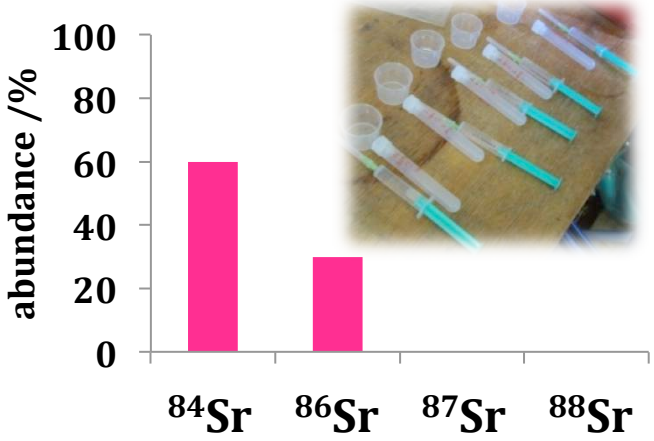

• To trace element fluxes in an ecosystem
• To identify sources and sinks
• To mark a specific abiotic or biotic matter in an ecosystem
• To monitor metabolic fluxes of an element
Enriched stable isotopic spikes
AIM: Inducing a significant change of the natural

# Evaluation of the double isotope tracer
# Isotope pattern deconvolution



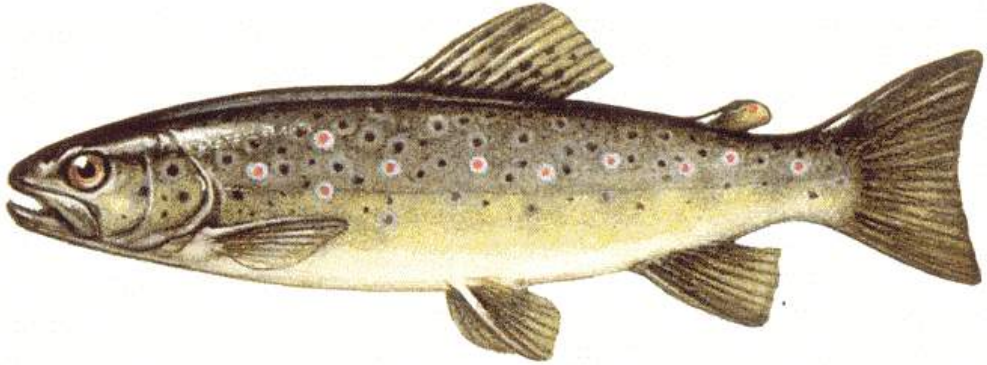



**molar fraction ratio of $x_{Sp1}/x_{Sp2}$ of double spike in central otolith region**

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

# APPLICATION:
# Transgenerational marking of fish



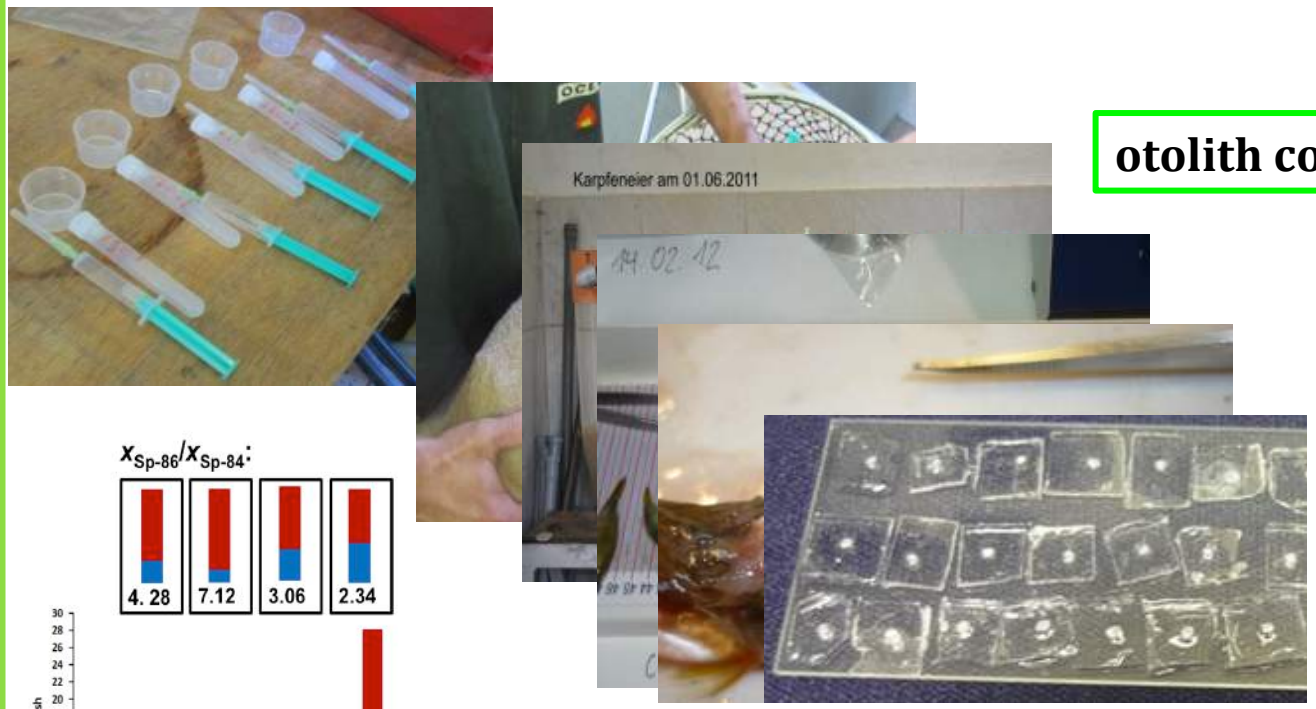
- **Ecological application**
  Mass marking of larvae without interfering with natural spawning, dispersal

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

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

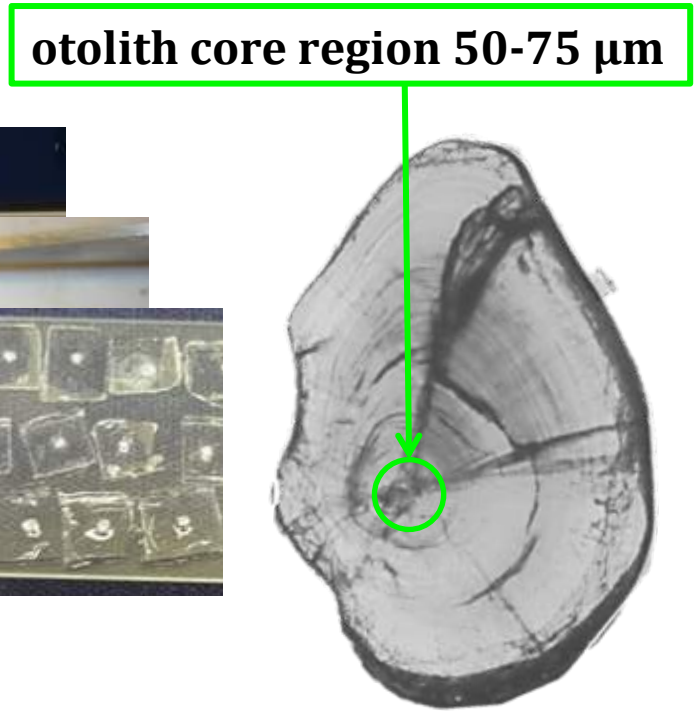
- **Model species:**
  - Carp: cyprinids (100.000-300.000 eggs/kg body weight)
  - Brown trout: salmonids (1.500-2.000 eggs/kg body weight)

Fischzucht Kreuzstein










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

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

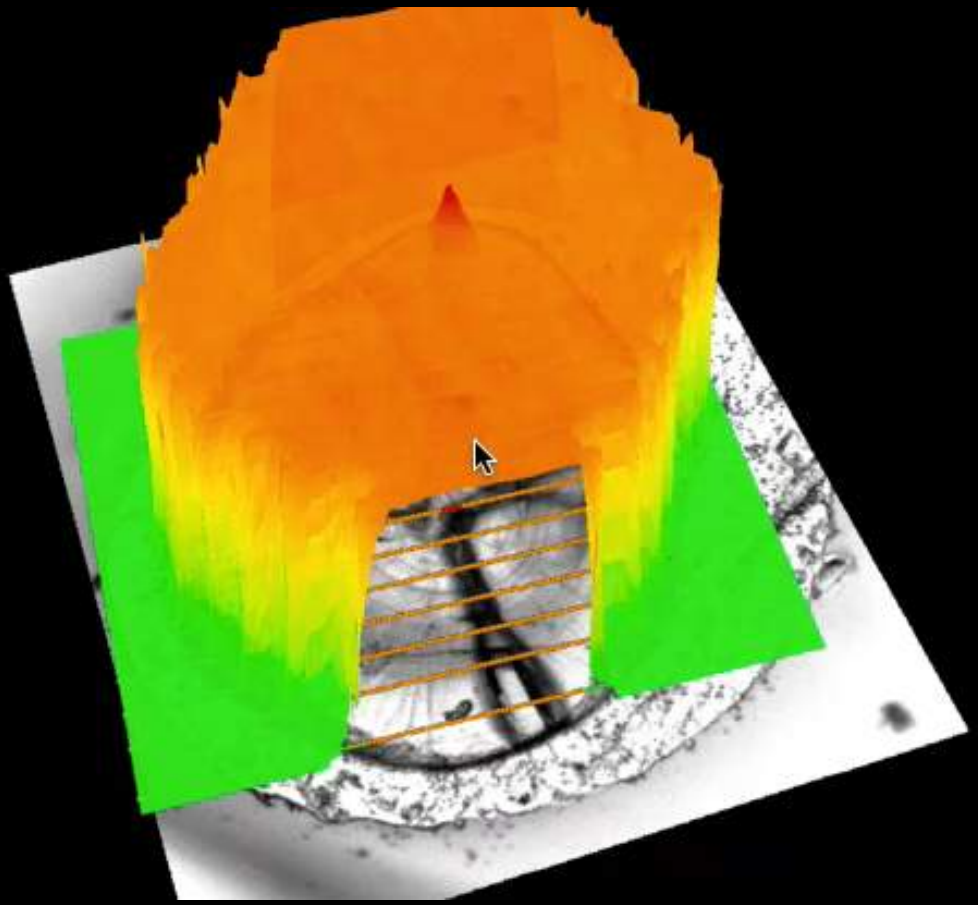
0.0

0.10-0.12

0.12-0.13

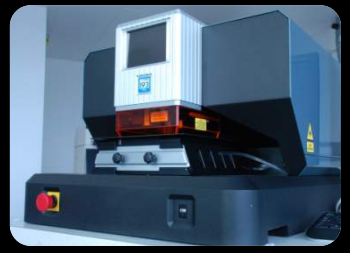
0.13-0.14

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

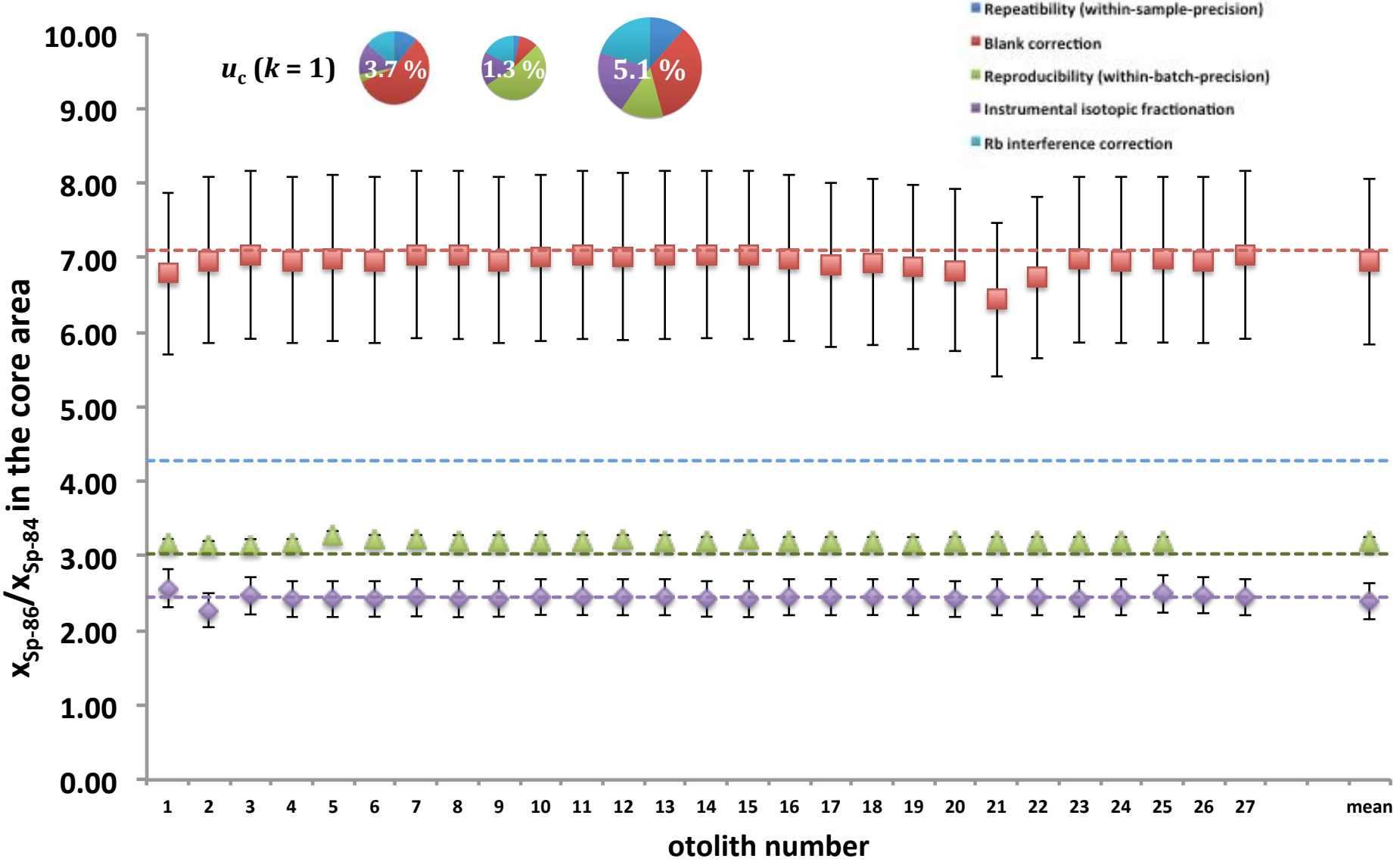


**Nexion 300D** (ICP-Q-MS)
Perkin Elmer

**NWR193**
Laser Ablation System



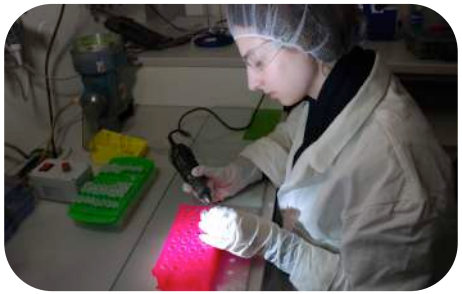
# Deconvolved molar fraction ratio of the double spike ($x_{Sp\text{-}86}/x_{Sp\text{-}84}$)



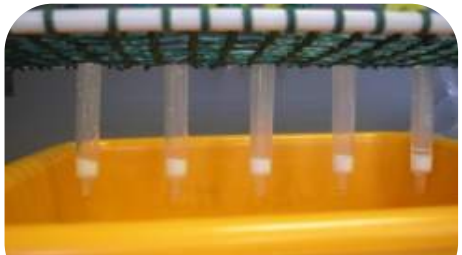
# Requirements elemental/isotopic fingerprint

- Instrumentation
- Infrastructure
- Personell
- Consumables







# Requirements elemental/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

# Requirements elemental/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 elemental/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’