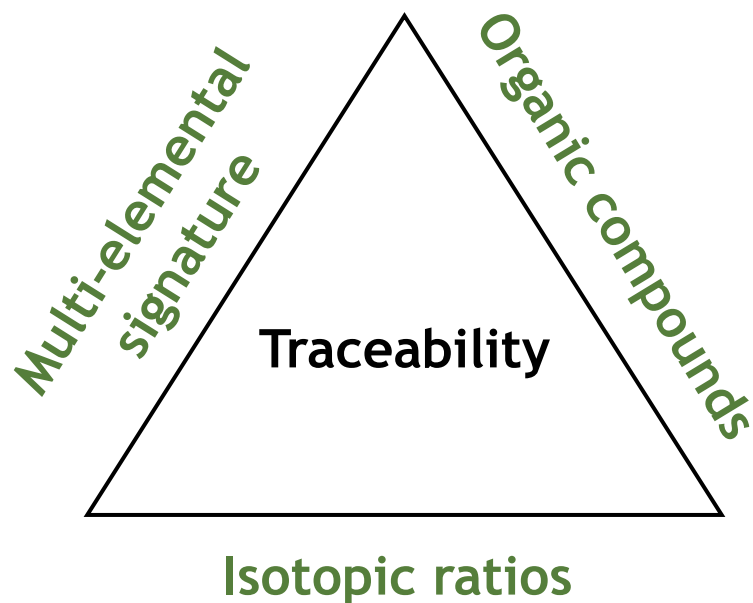


Potential of a new multi-isotope dilution method for the geographical origin discrimination of wines : application to Tunisian wine

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- (3) IPREM, Pau, France
- (4) INRAP, Sidi Thabet, Tunisia

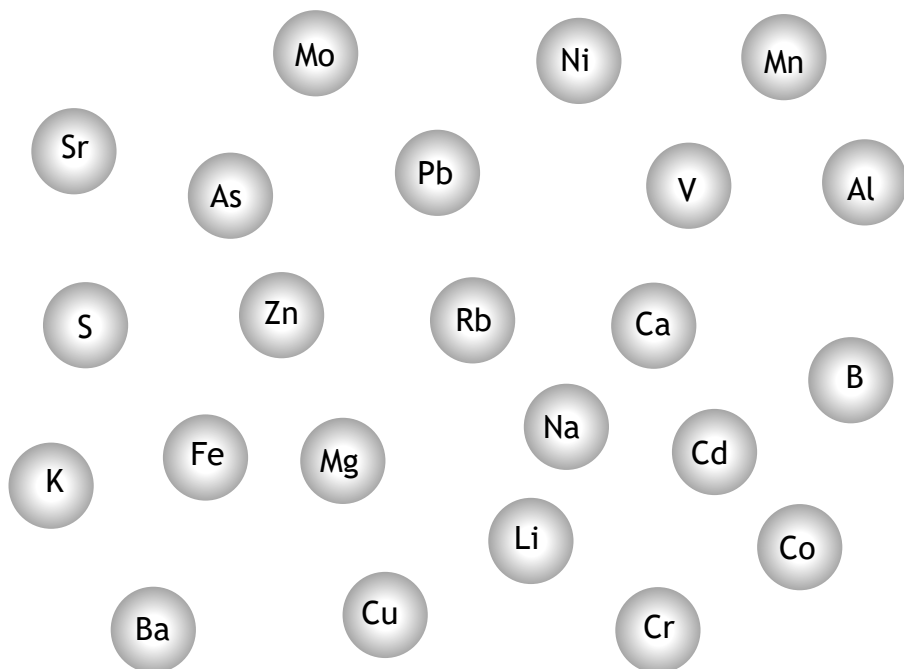
Introduction to traceability



Technique	Element Species	Stability	Cost	Duration	Precision	Discrimination
NMR	++	-	-	+	+	+
MC-ICP-MS (Sr, Pb, B)	-	++	--	--	+++	++
IRMS (C, H, N, O)	+/-	+	+	-	+	+
ICP-MS (23 elements)	++	++	+	+	++	++

Selection of the elements

23 ELEMENTS

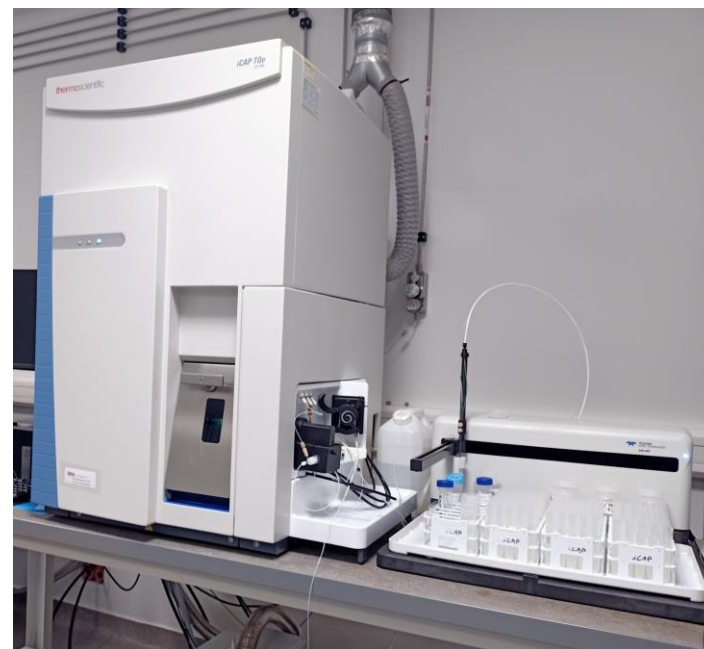


Soil markers

Agricultural practice markers

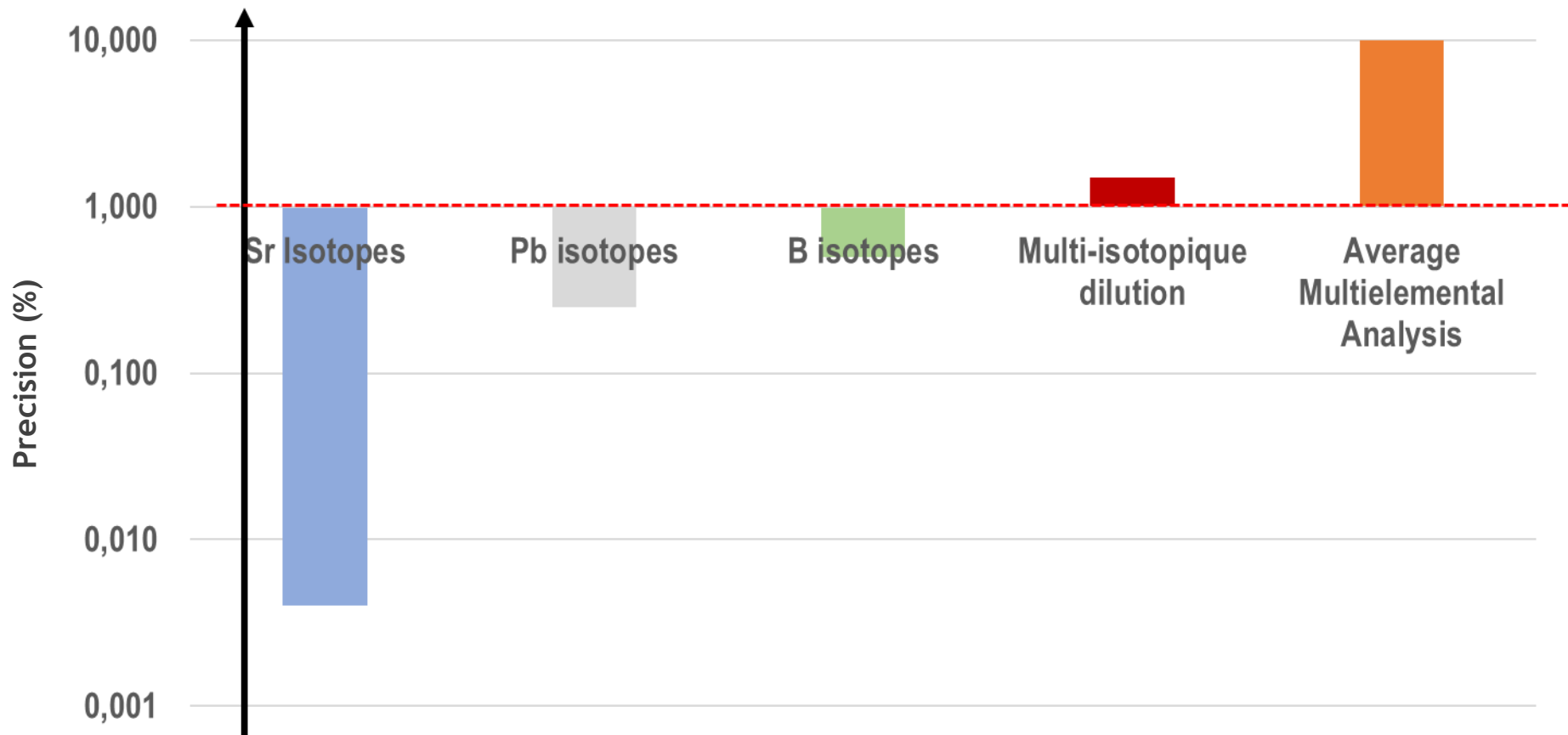
Anthropogenic contamination markers

TRIPLE QUADRUPOLE ICP-MS



Analysis of the elements at the same time

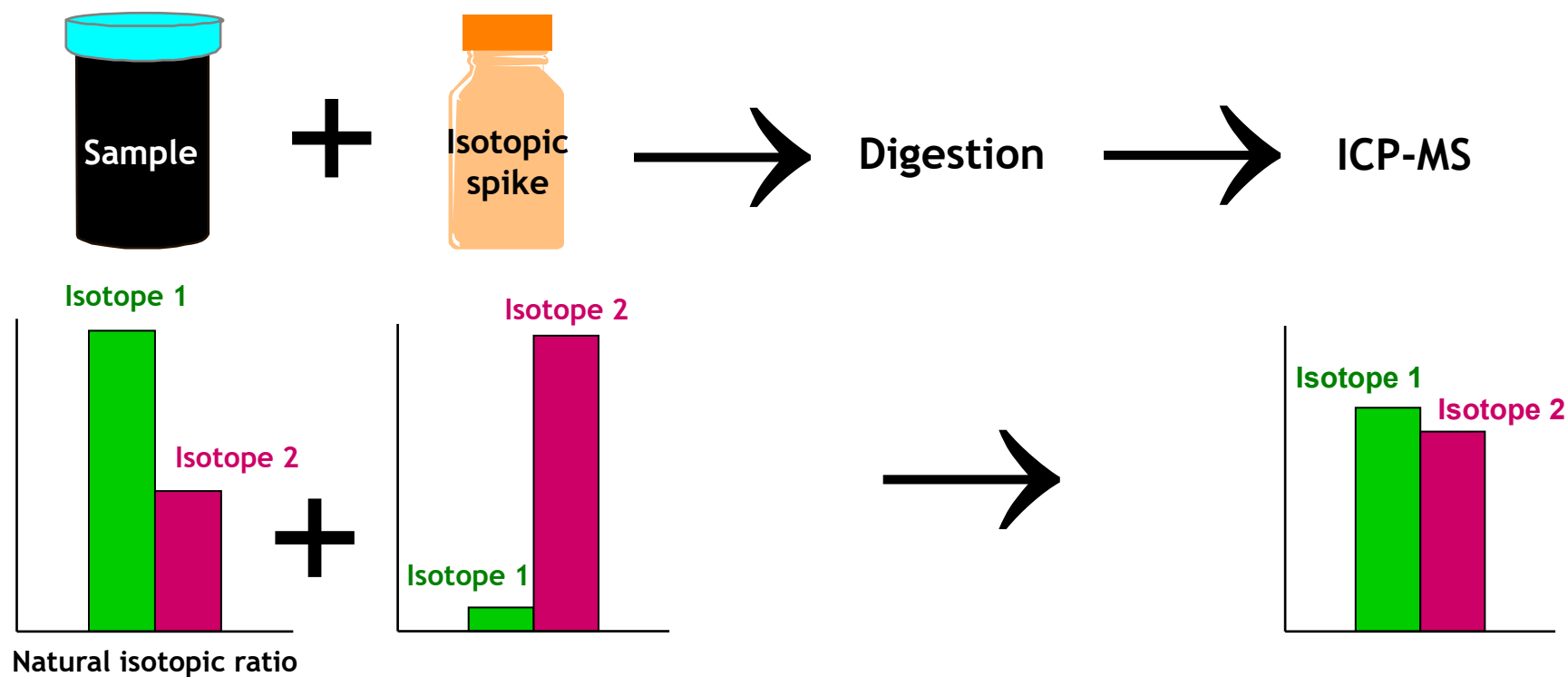
Choice of the analytical strategy for precision optimization



Principle of isotope dilution

A known amount of isotopic spike solution (abnormal isotopic distribution) is added to a known amount of sample. The element concentration in the sample is calculated from the measured isotopic ratio.

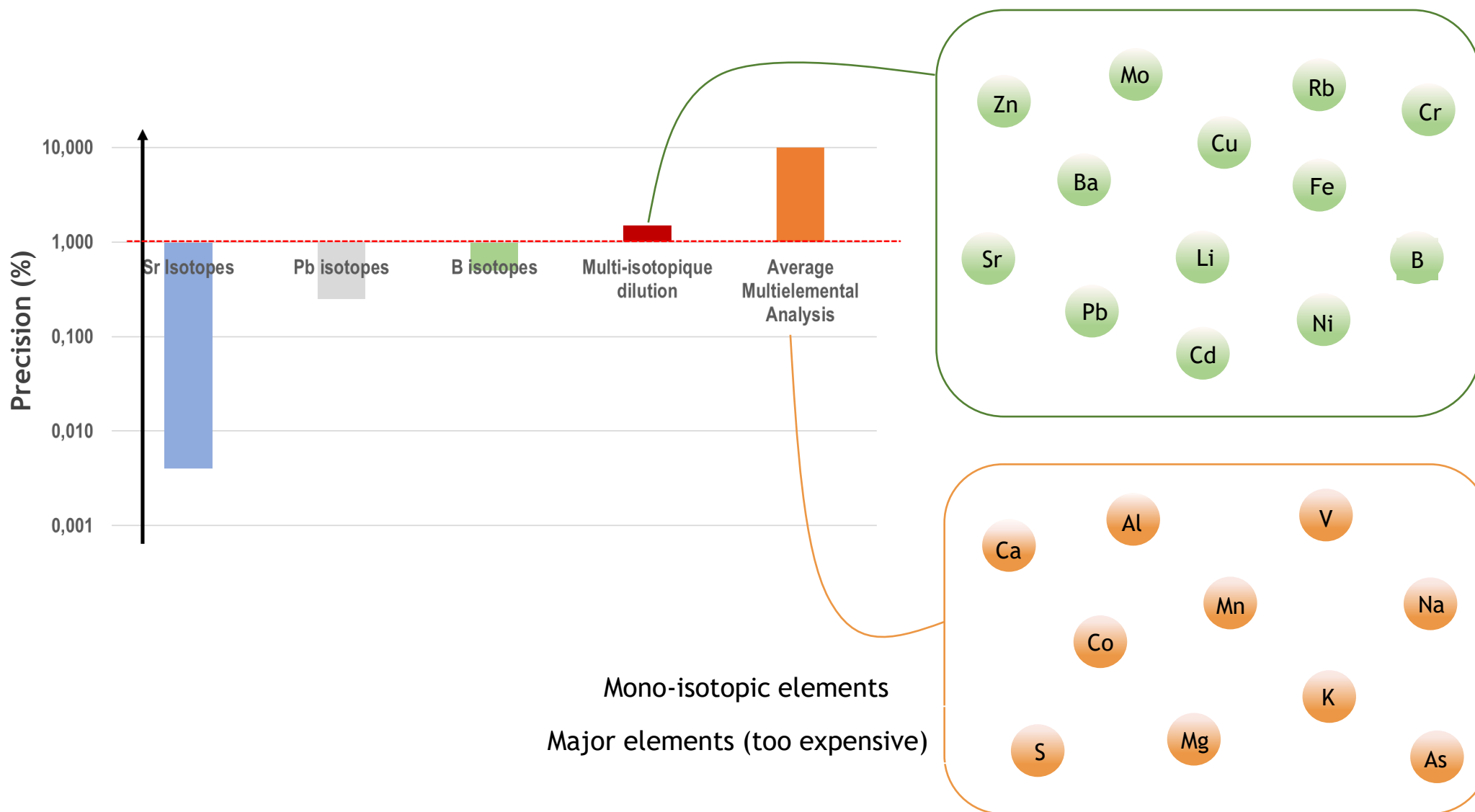
Isotopic spike is like a perfect internal standard



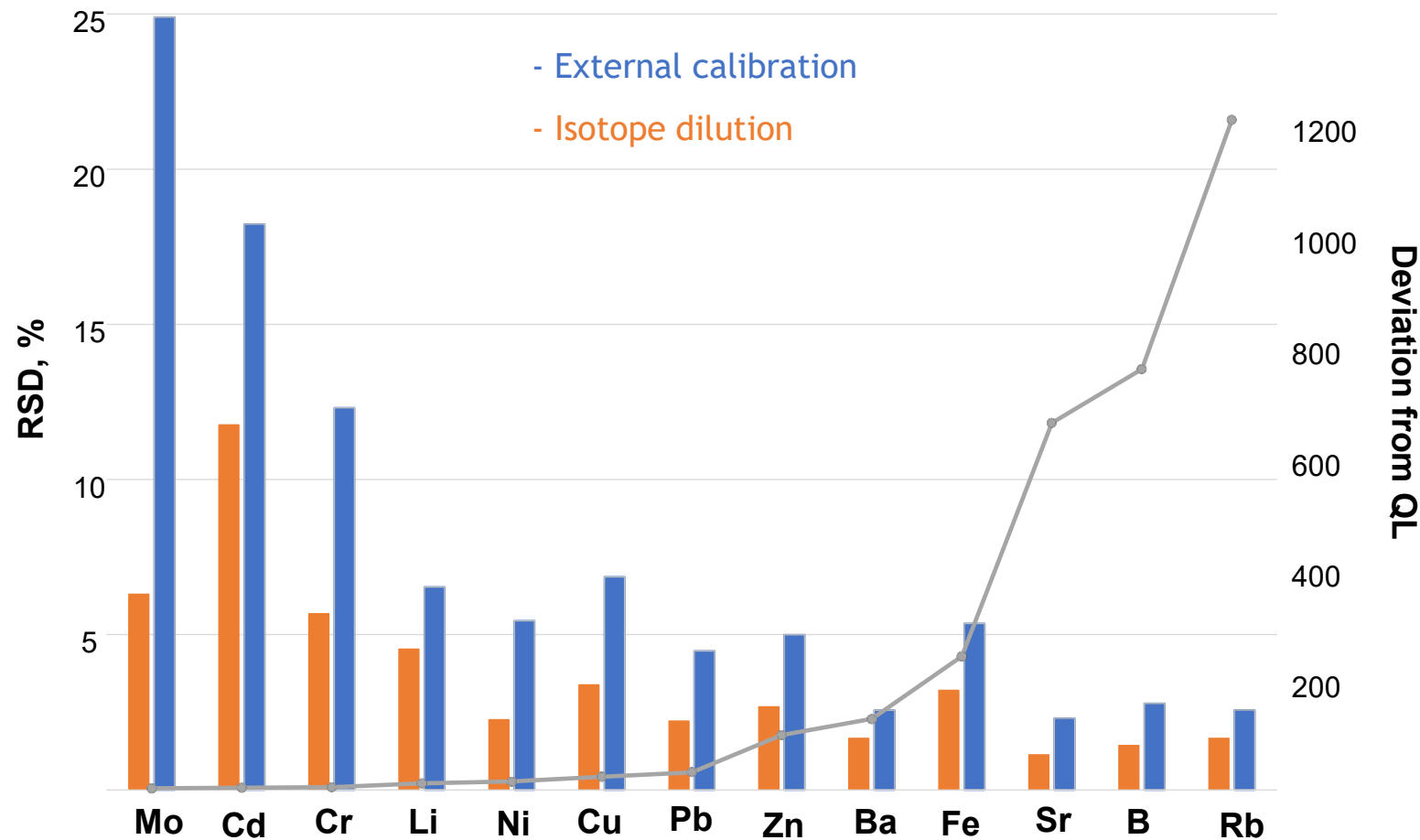
👍 Correction of digestion efficiency

👍 Correction of matrix effects and ICP-MS stability

Choice of the analytical strategy for precision optimization



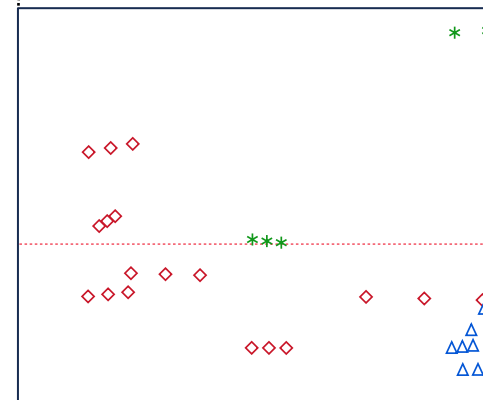
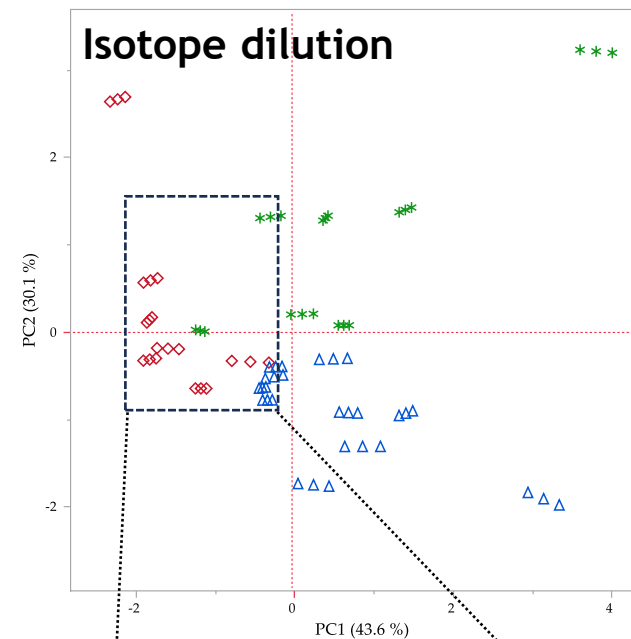
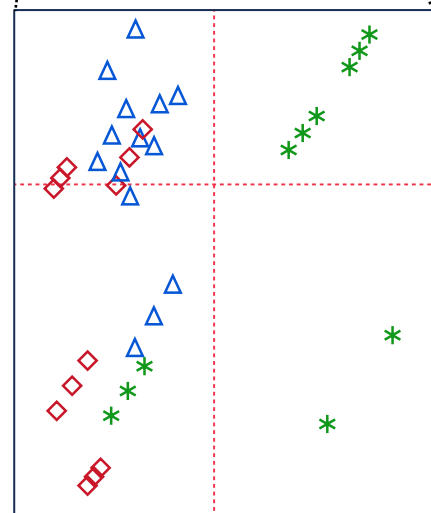
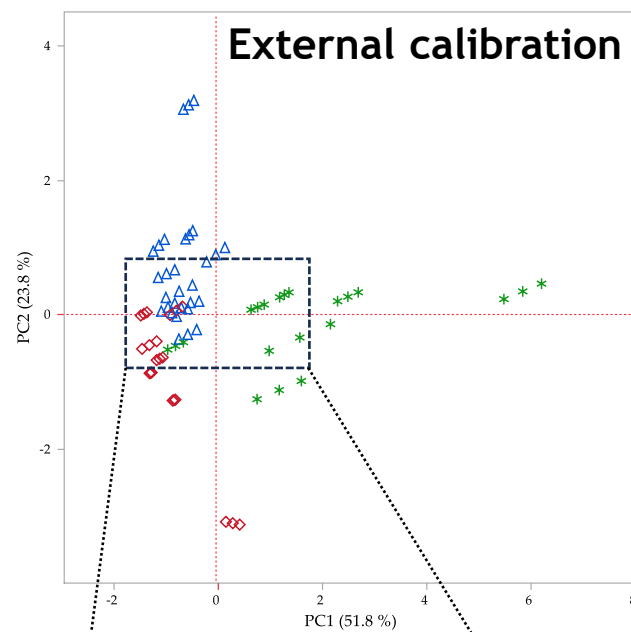
Improvement of the precision thanks to isotope dilution



- Improvement of the precision up to a factor 5
- QL effect
- Possibility to reach precision of about 1%

Improvement of the discrimination thanks to improvement of the precision

(Δ) Italy
(*) Tunisia
($\diamond$) Spain



Figures of merit of the method

Validation protocol

- 2 spike levels: **spike 1** (approximately double the natural concentration)
spike 2 = 2 x spike 1
- n = 6 replicates
- on 3 different days

Accuracy

88,3 - 114,6%

Both external calibration and
isotopic dilution

Precision inter-days

1,5 - 13,0%

Precision intra-day

0,8 - 14,3%

Sensitivity (µg/L)

Element	QL	Element	QL	Element	QL
Li	2	Cd	0,05	Mn	5
B	10	Ba	1	Co	0,02
Cr	5	Pb	0,5	As	0,05
Fe	10	Na	200	Mo	2
Ni	2	Al	50	V	0,5
Cu	5	S	500	Sr	2
Zn	5	Mg	20	Ca	200
Rb	2	K	200		

Flow chart of the analytical process

1. SAMPLE PREPARATION



2. SAMPLE ANALYSIS by ICP-QQQ-MS

3. DATA TREATMENT FOR EACH INDIVIDUAL ELEMENT/WINE ORIGIN

Descriptive statistic : box-plots → SELECTION OF DISCRIMINANT ELEMENTS

4. MULTIVARIATE STATISTICAL ANALYSIS

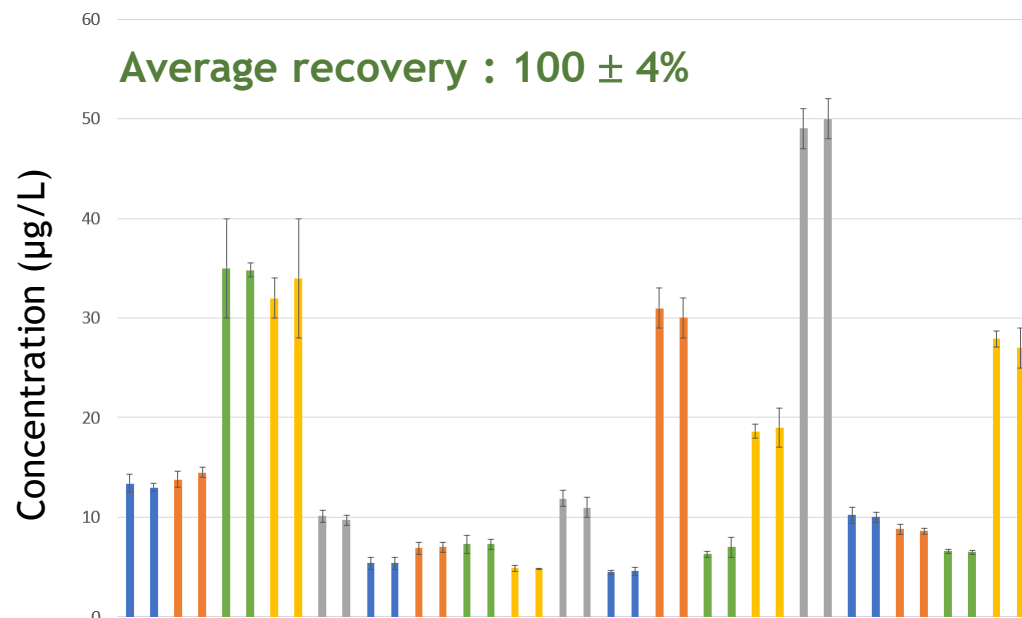
Principal Component Analysis (discriminant elements) → DISCRIMINATION OF WINE ORIGIN

Sampled bottle effect

Analysis of 2 different bottles of the
same wine

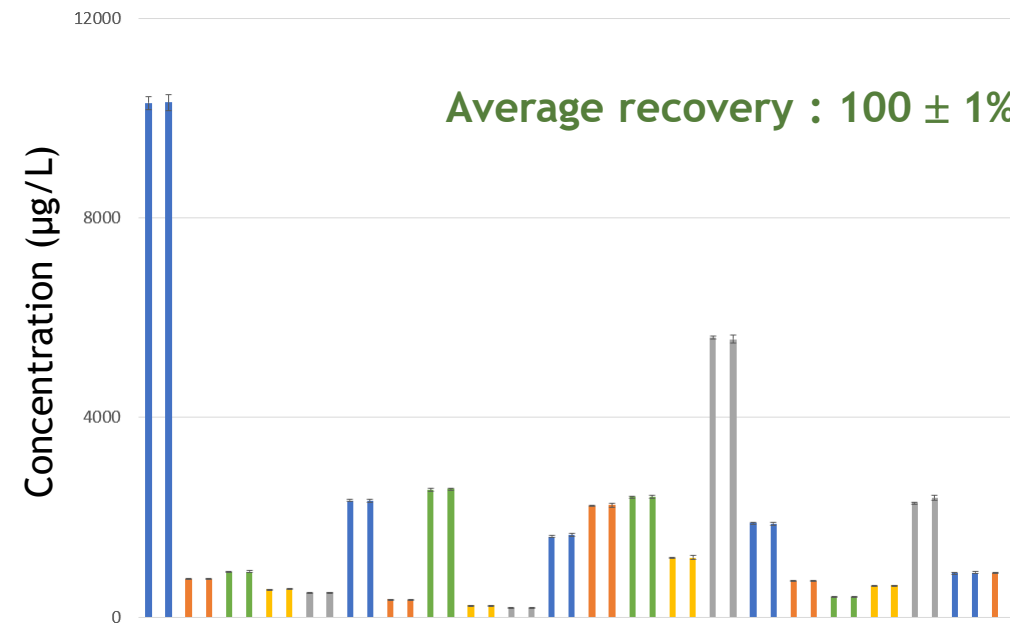
LITHIUM

Average recovery : $100 \pm 4\%$



STRONTIUM

Average recovery : $100 \pm 1\%$

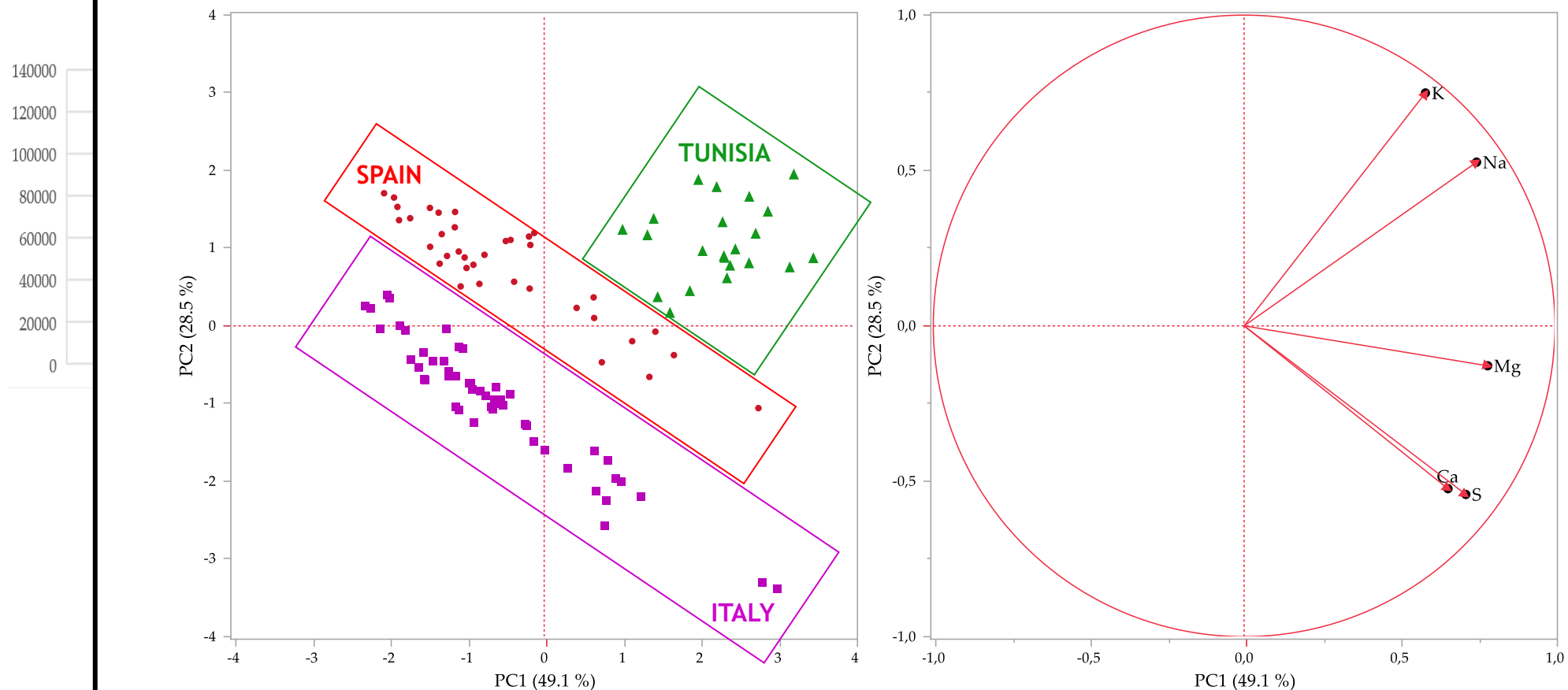


Map of the samples at the national level



Discrimination at the national level

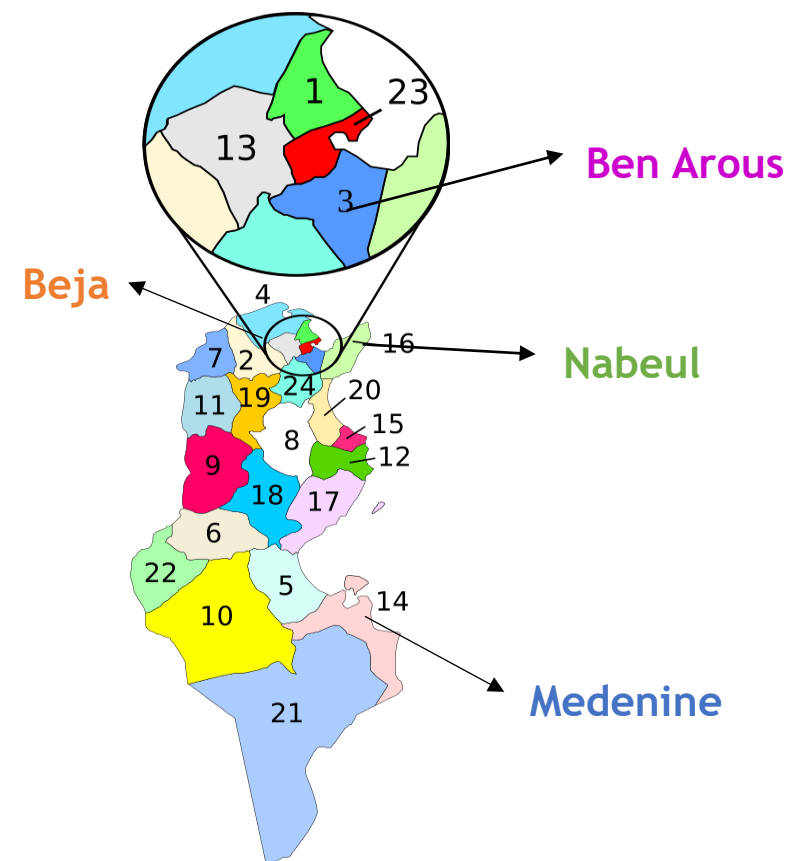
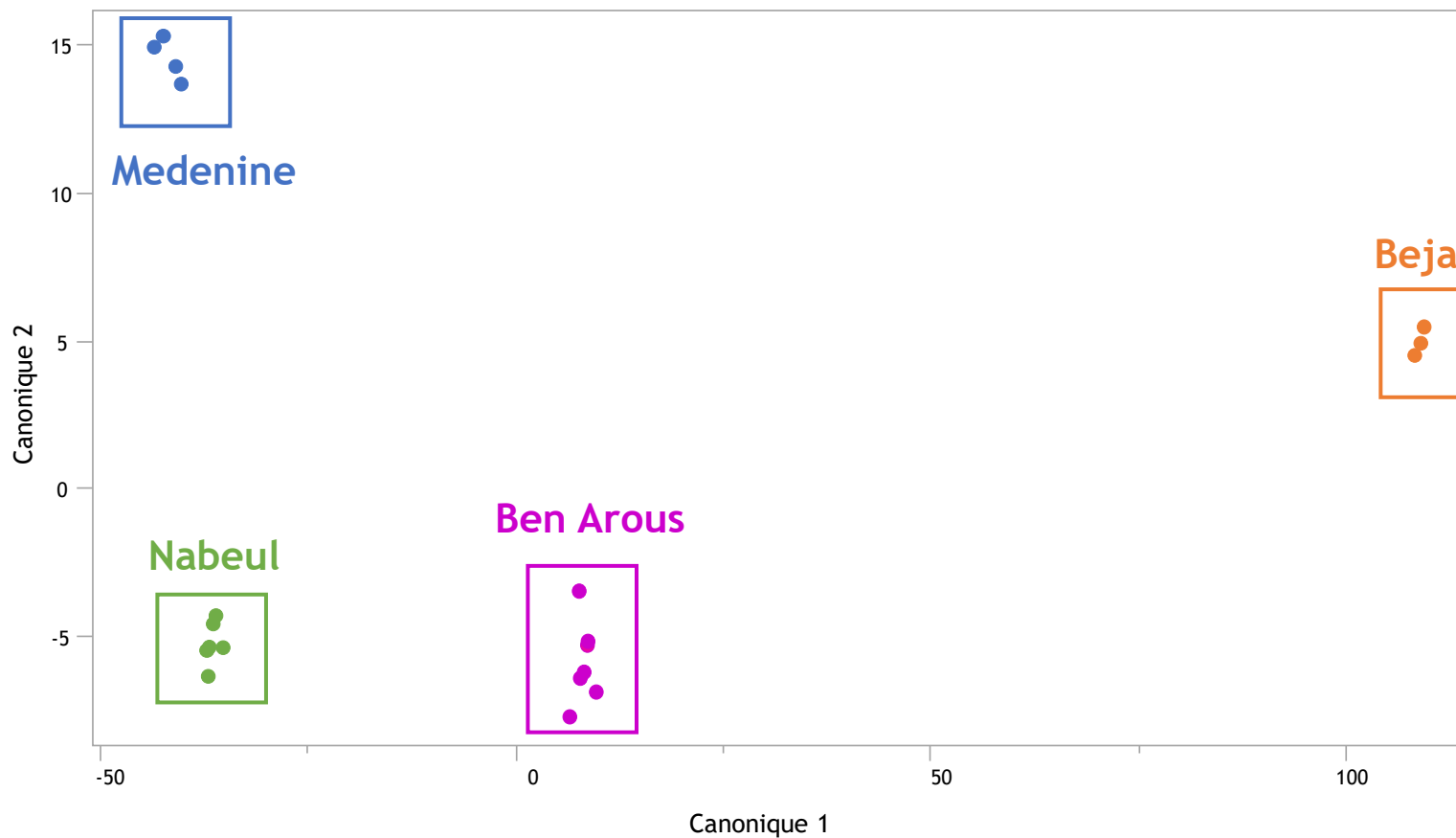
PCA performed on the content of **K**, **Na**, **Mg**, **Ca**, and **S**.



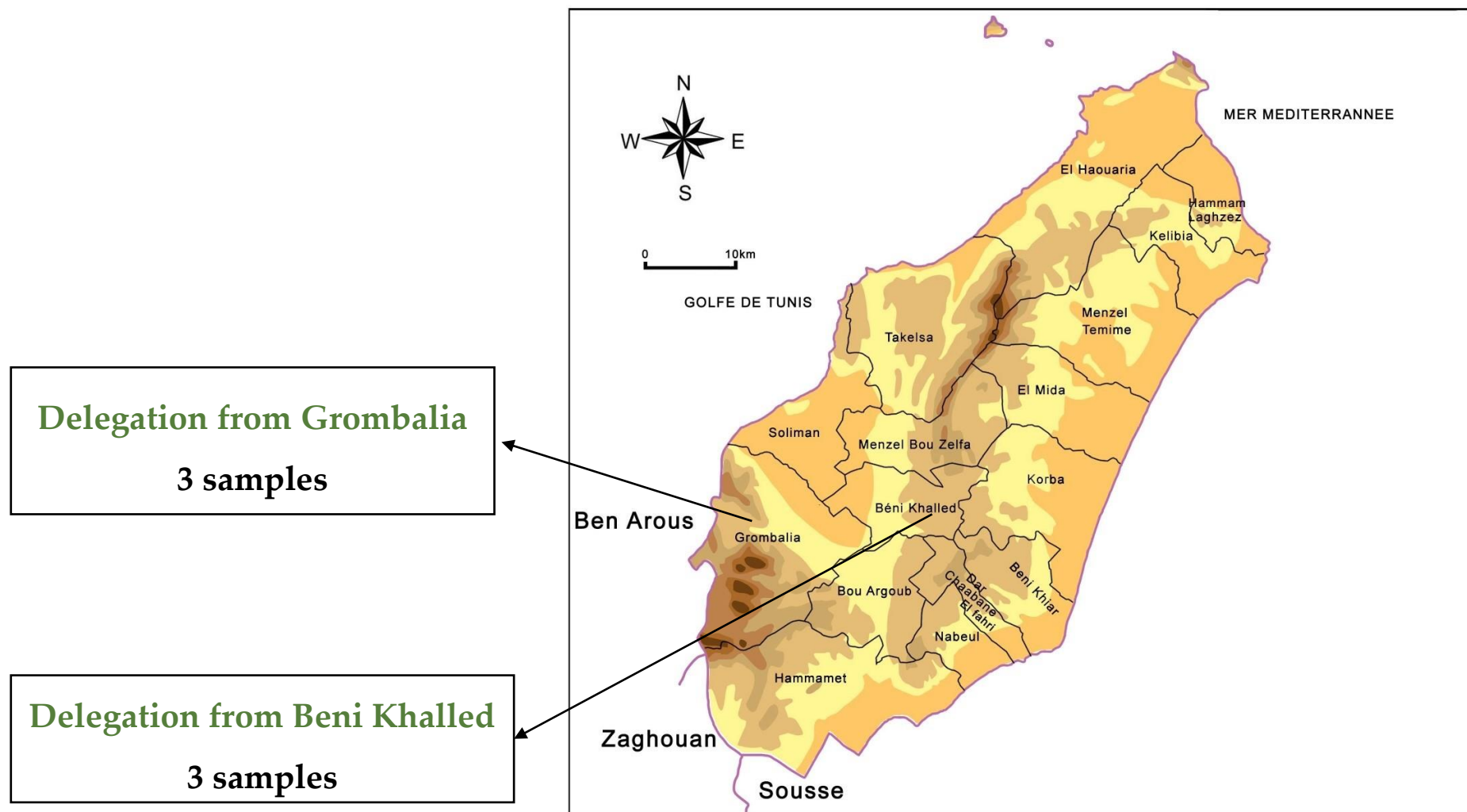
Ca

Discrimination at the regional level

LDA performed on the content of the 23 elements



Map of the samples at the delegation level (gouvernorate from Nabeul)

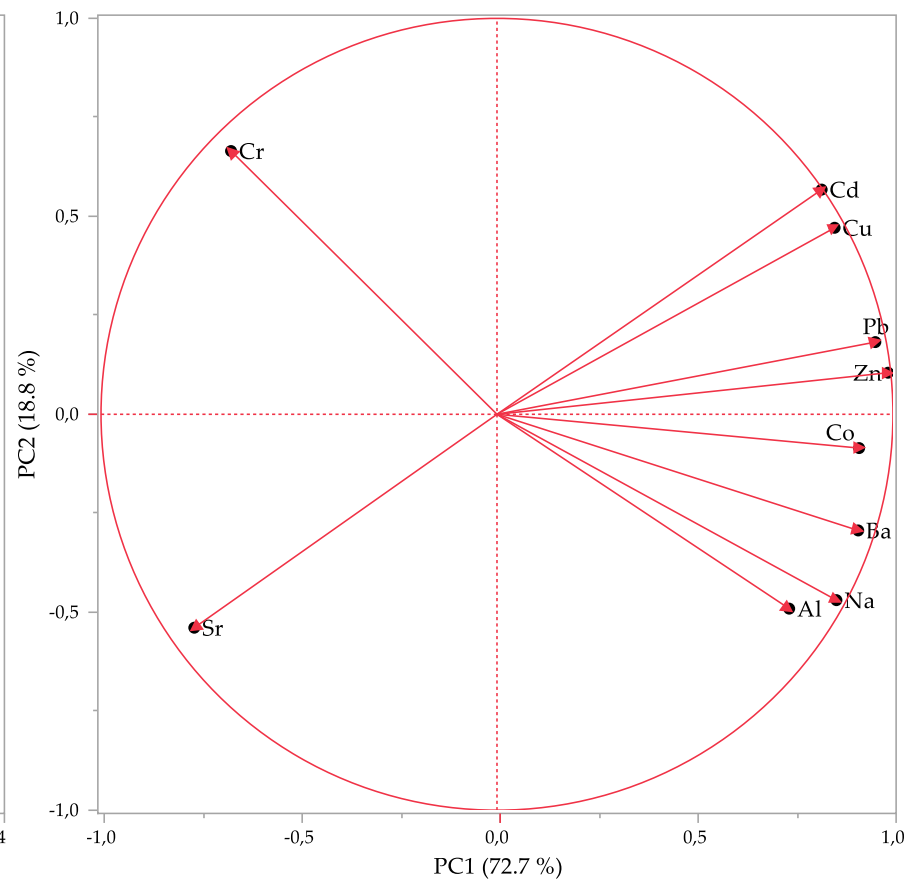
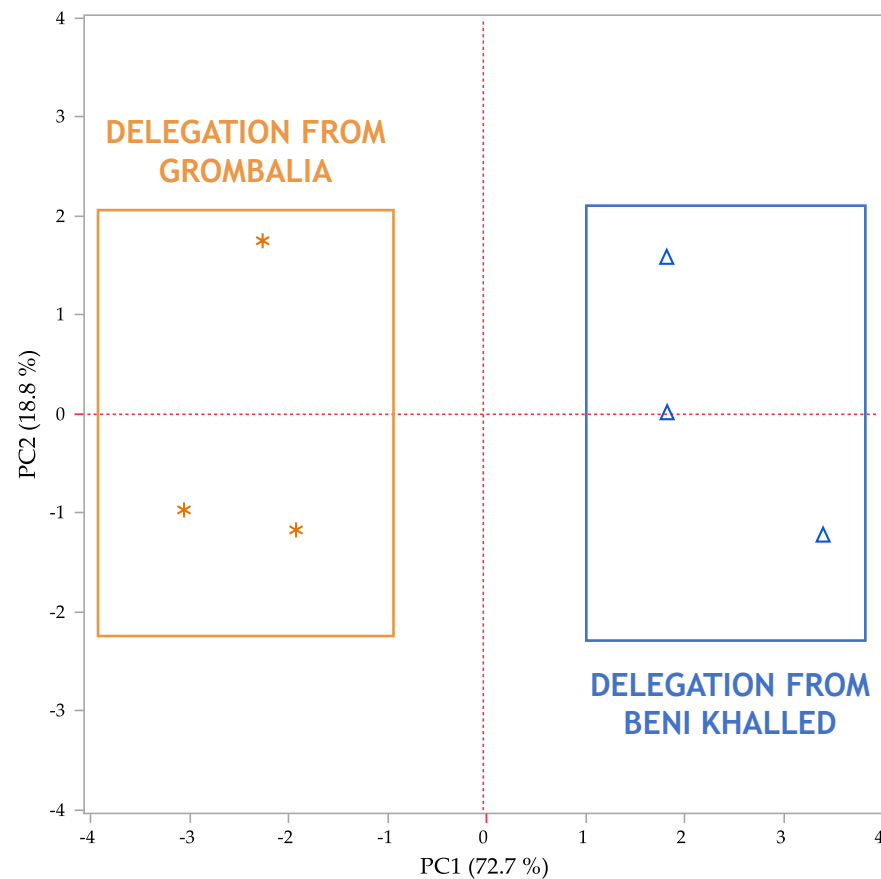


Discrimination at the delegation level

PCA performed on the content of **Cr, Sr, Cu, Zn, Rb, Cd, Ba, Pb, Al, Co, and Na**

Cr and

35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
2500,0
2000,0
1500,0
1000,0
500,0
0,0



Rb

Pb

Na

Conclusions

- Development and validation of a multi-isotope dilution method for the determination of 23 elements in wine with a **good precision**
- **Selection of the elements of interest** depending on the application to perform
- Possibility to **discriminate wines origin at different geographical level** (country, region, almost "farm")
- Other applications possible : **organic/non organic, other matrices...**

Acknowledgements

Fundings



AND YOU FOR YOUR ATTENTION

