



2nd ISO-FOOD Symposium
Portorož, Slovenia



Oral Communication

GEOGRAPHICAL ORIGIN DISCRIMINATION OF WINES BY A NEW MULTI-ISOTOPIC DILUTION METHOD

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April 24 – 26, 2023



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Wine traceability and authenticity

Wine is one of the oldest alcoholic beverages

Wine **traceability** and **authenticity** are important factors for consumers' and producers' protection

Wine **chemical composition** is related to the **origin**, as it is affected by:

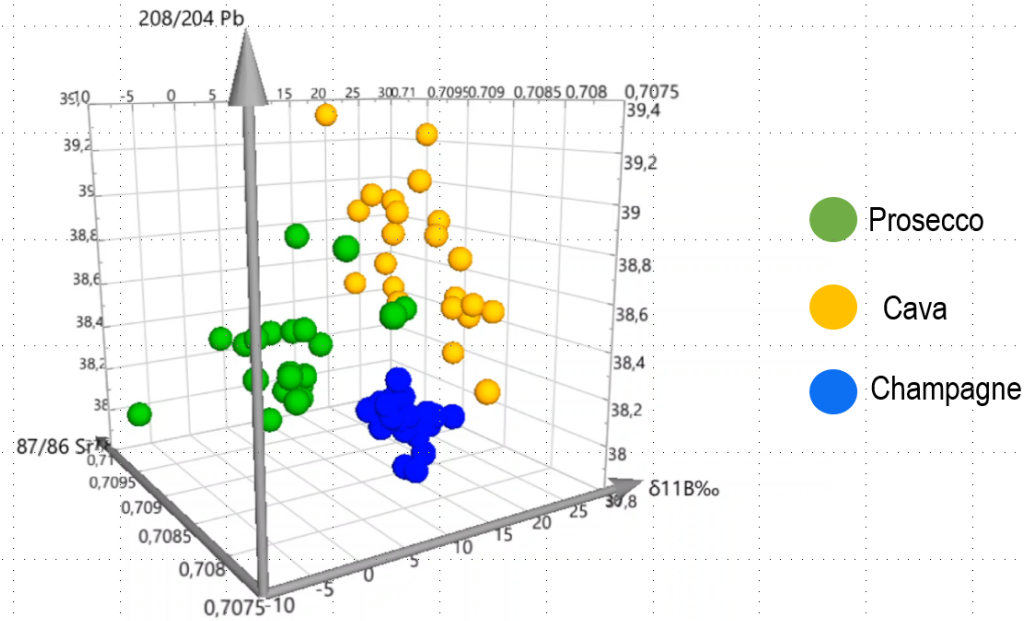
- **geochemistry of the soil**
- **anthropogenic contaminations**
- **agricultural practices**

Wine traceability can be achieved through **organic and inorganic compounds (concentrations and/or isotopes ratios)**
⇒ **Inorganic elements are more stable**



Wine traceability through non-traditional elements isotopic ratios measurements

3D Plot



PROS

- Powerful for the excellent precision

CONS

- Sophisticated analytical instruments (multi-collector ICP-MS)
- Long sample preparation and analyte purification

LONG AND EXPENSIVE

DEVELOP A NEW METHOD ABLE TO ACHIEVE **GOOD PERFORMANCE** BUT **FASTER** AND AT A **LOWER COST**

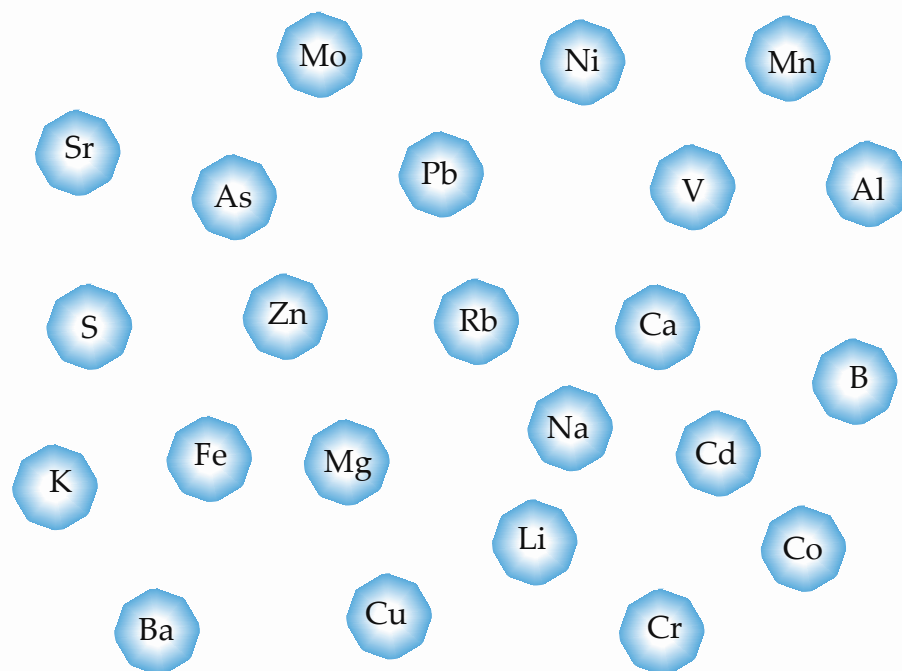
$^{87}\text{Sr}/^{86}\text{Sr}$: Sr isotope ratio as **tracer** of the **type** and **age** of the soil

$^{208}\text{Pb}/^{204}\text{Pb}$: Pb isotope ratio as **tracer** of the **local atmosphere**

$\delta^{11}\text{B}\text{‰}$: B isotope ratio as a **tracer** of the **soil pH** and the **agricultural practices**

Introduction of the new method: Selection of the elements

23 ELEMENTS

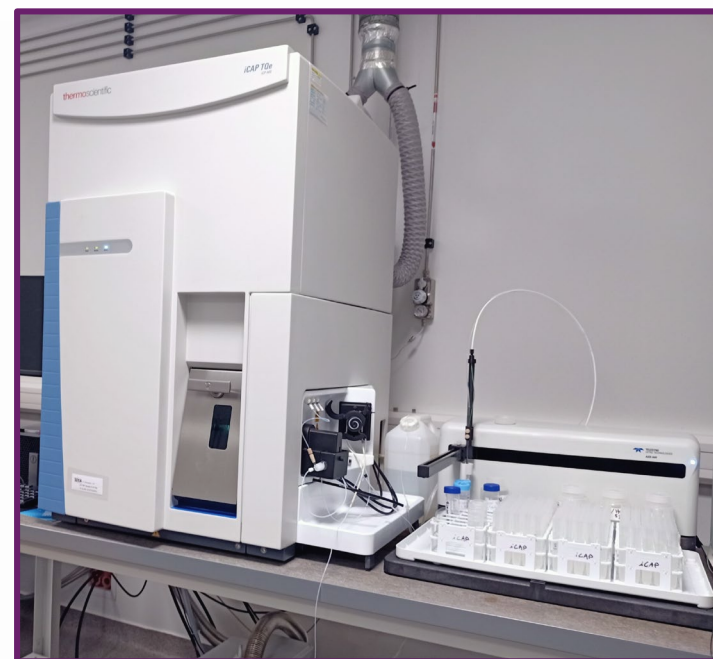


Soil markers

Agricultural practice markers

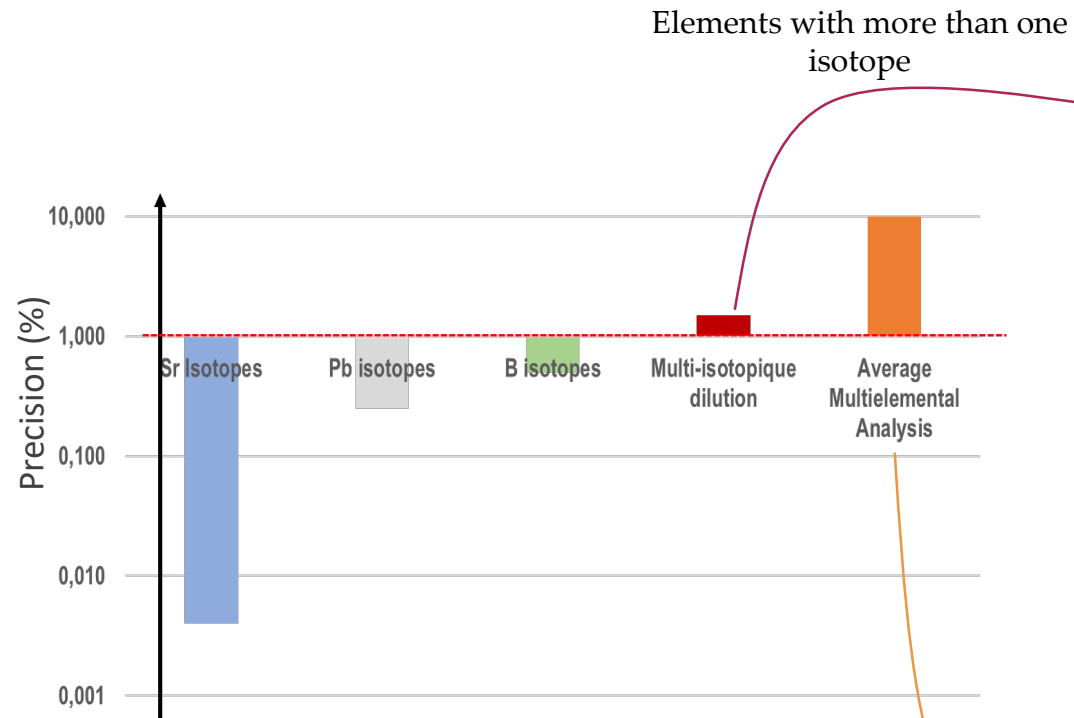
Anthropogenic contamination markers

TRIPLE QUADRUPOLE ICP-MS

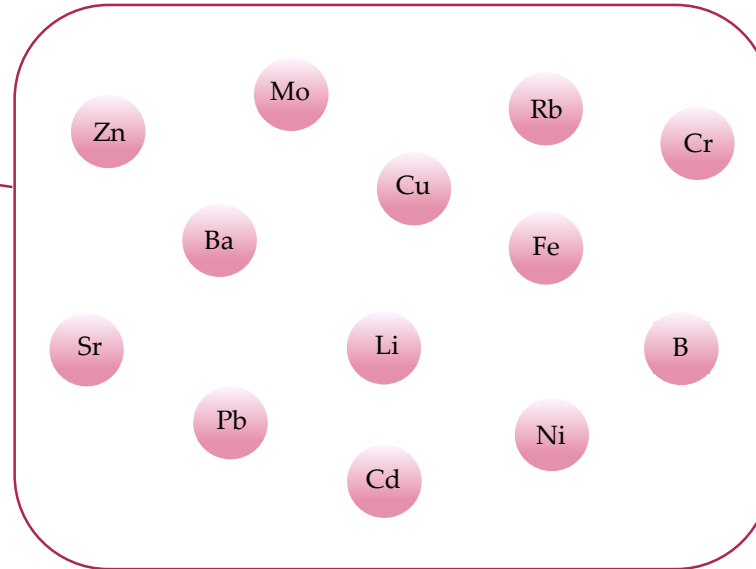


Analysis of the elements at the same time
Removal of the interferences

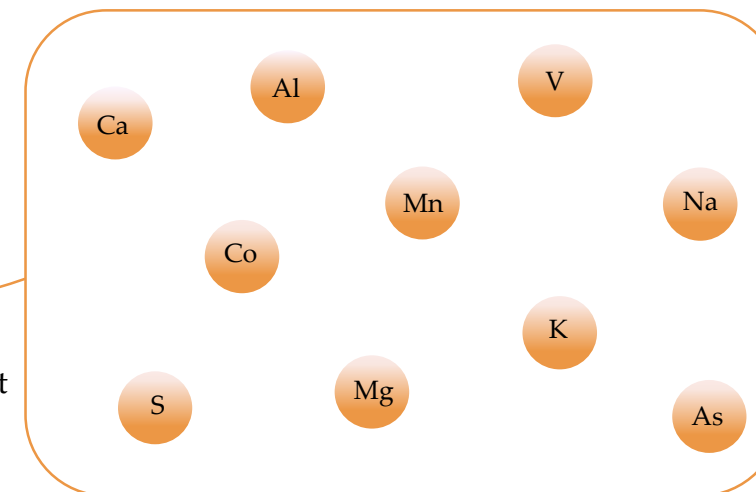
Introduction of the new method: Analytical approach



Elements with more than one isotope

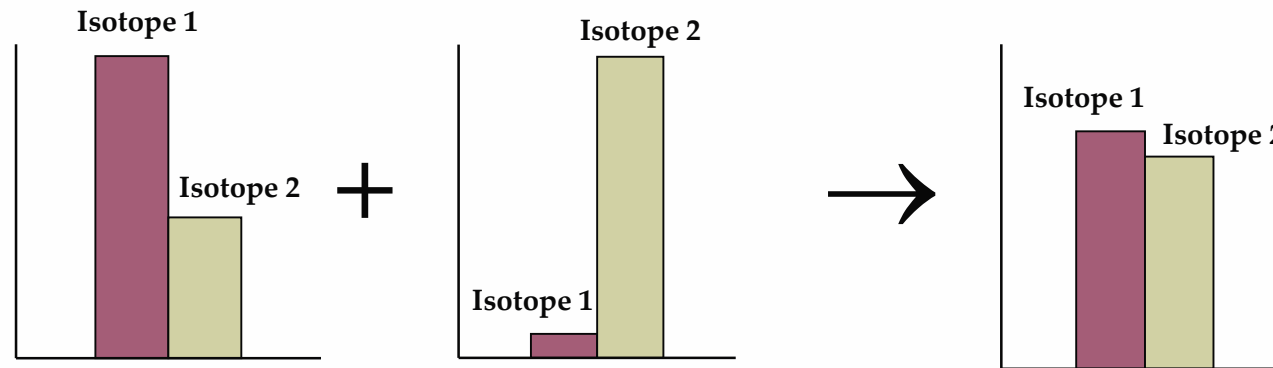


Mono-isotope elements
Elements too much abundant
(too expensive)



Isotopic Dilution Method

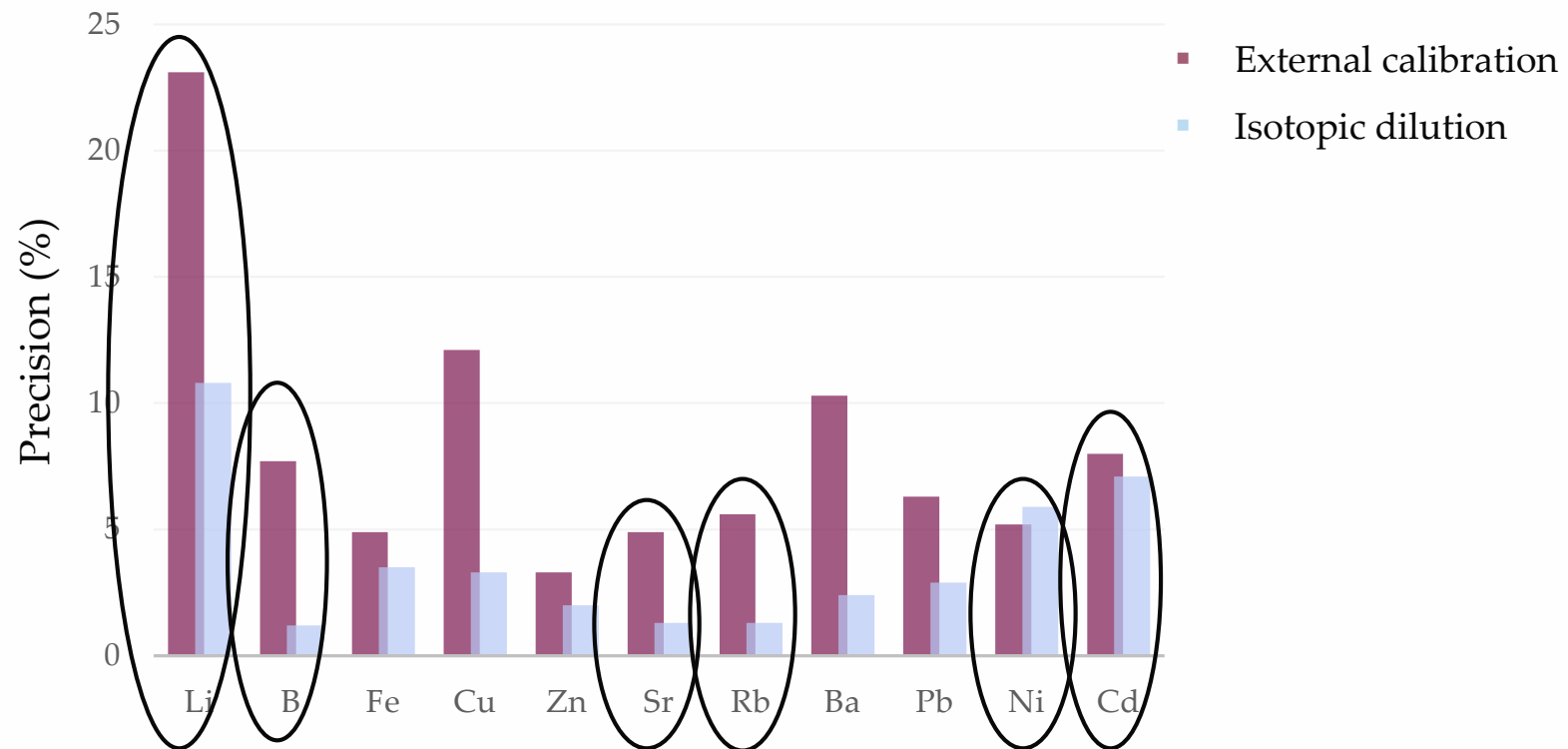
A known amount of isotopic spike solution (abnormal isotopic distribution) is added to a known amount of sample.
The element concentration in the sample is calculated from the measured isotopic ratio.



The **isotopic spike solution** works as a **perfect internal standard**

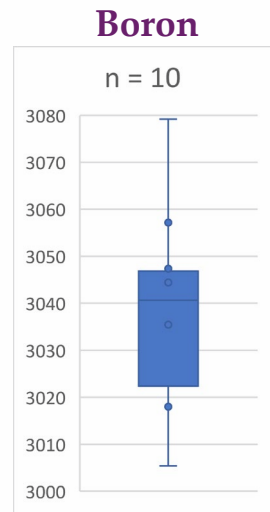
Correction of the sample preparation efficiency
Correction of the matrix effects and the stability of the ICP-MS signal

Improvements brought by the isotopic dilution method

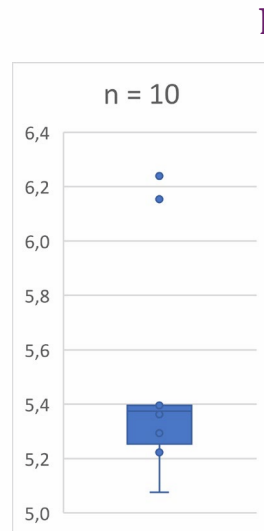


- Improvement of the precision up to six times
- Effect of Quantification Limit (QL)
- Possibility to reach a precision of about 1%

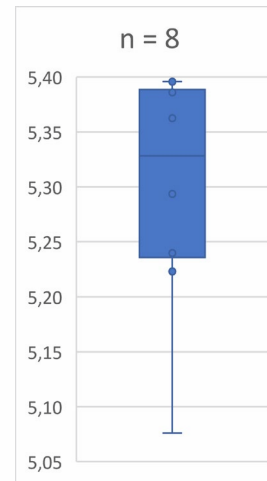
Introduction of the new method: Number of replicates



**3035 ± 55 ppb
(1,8 %)**



**5,5 ± 0,8 ppb
(14,5 %)**



**5,3 ± 0,2 ppb
(3,8 %)**

n = 10
Statistically representative
Elimination of outliers
Long preparation

n = 6
Still statistically representative
Elimination of outliers
Good compromise

Method Validation

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 intra-day

0,8 - 14,3%

Precision inter-days

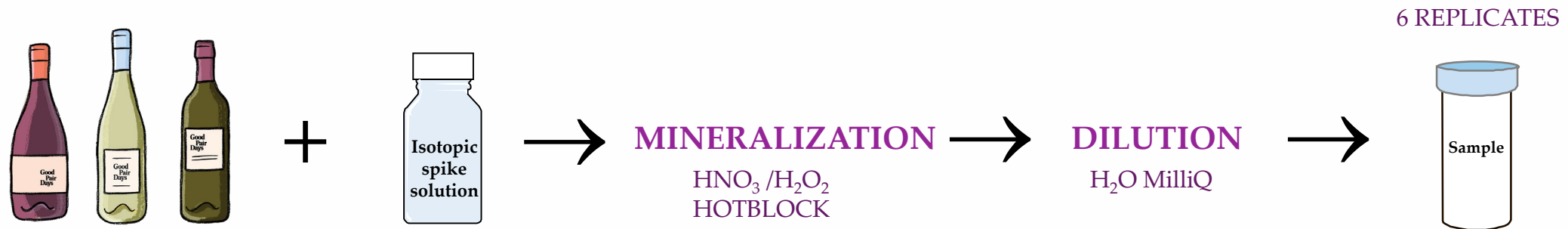
1,5 - 13,0%

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		

ANALYTICAL PROCEDURE FOR WINE TRACEABILITY

1. SAMPLE PREPARATION



2. SAMPLE ANALYSIS by ICP-QQQ-MS

3. DATA TREATMENT FOR EACH INDIVIDUAL SAMPLE/ELEMENT

Descriptive statistic: box-plots → **ELIMINATION OF OUTLIERS**

4. DATA TREATMENT FOR EACH ELEMENTS/WINE ORIGIN

Descriptive statistic: box-plots → **SELECTION OF DISCRIMINANT ELEMENTS**

5. MULTIVARIATE STATISTICAL ANALYSIS

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

**APPLICATION OF THE
NEW METHOD TO WINE
TRACEABILITY AT
DIFFERENT
GEOGRAPHICAL LEVELS**



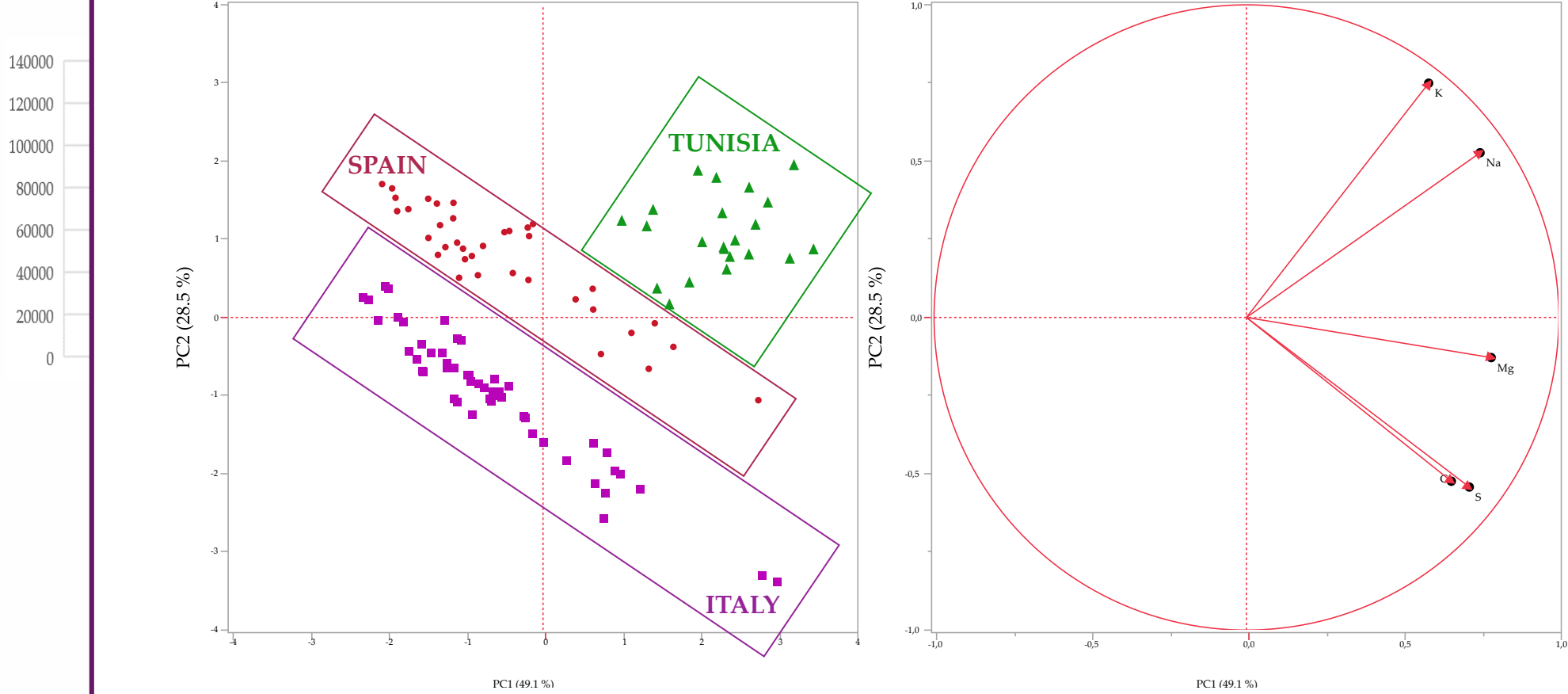
Discrimination of geographical origin

NATION LEVEL DISCRIMINATION



NATION LEVEL DISCRIMINATION

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

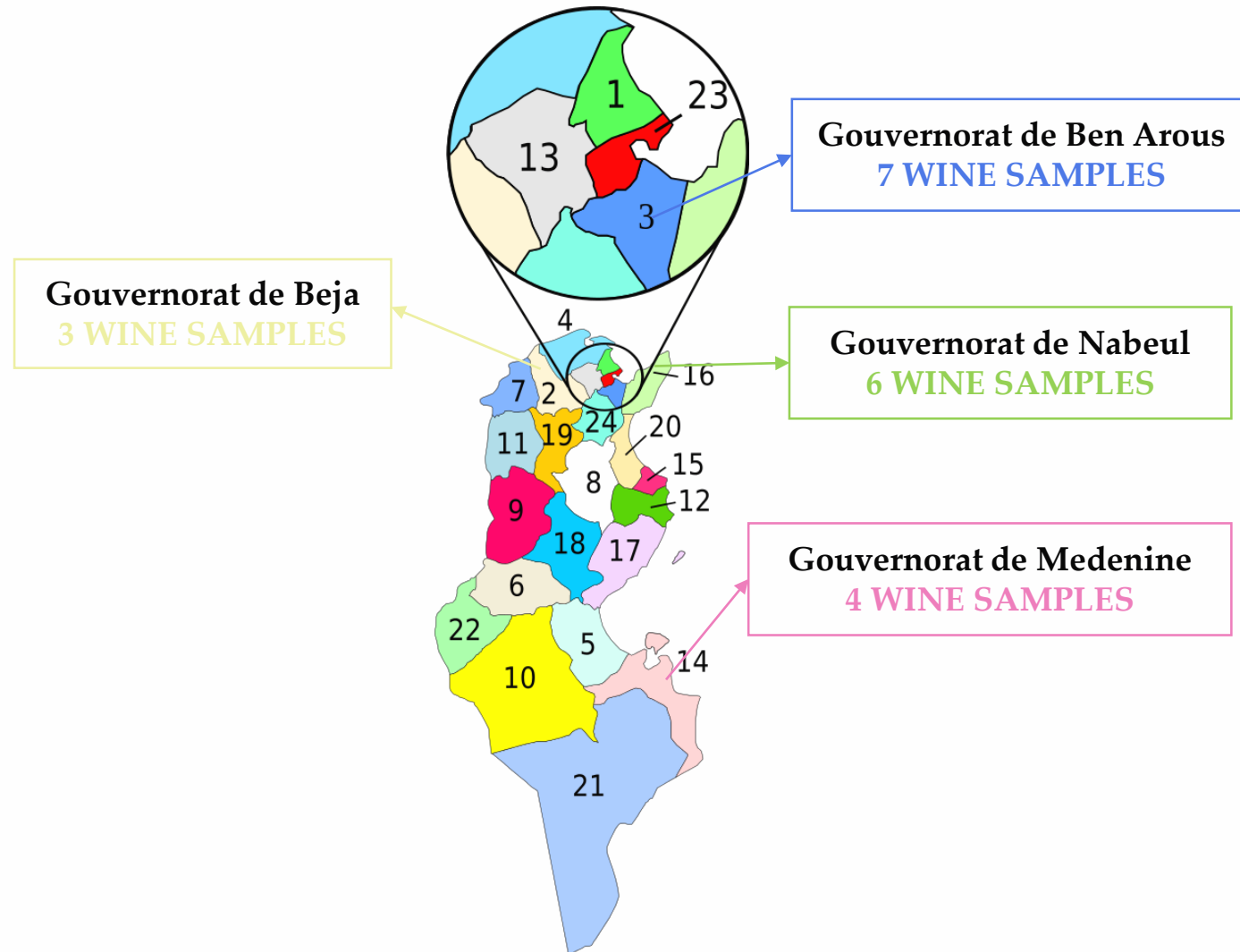


DISCRIMINATION OF THE WINES COMING FROM THE DIFFERENT NATIONS

Ca

Discrimination of geographical origin Tunisian wines

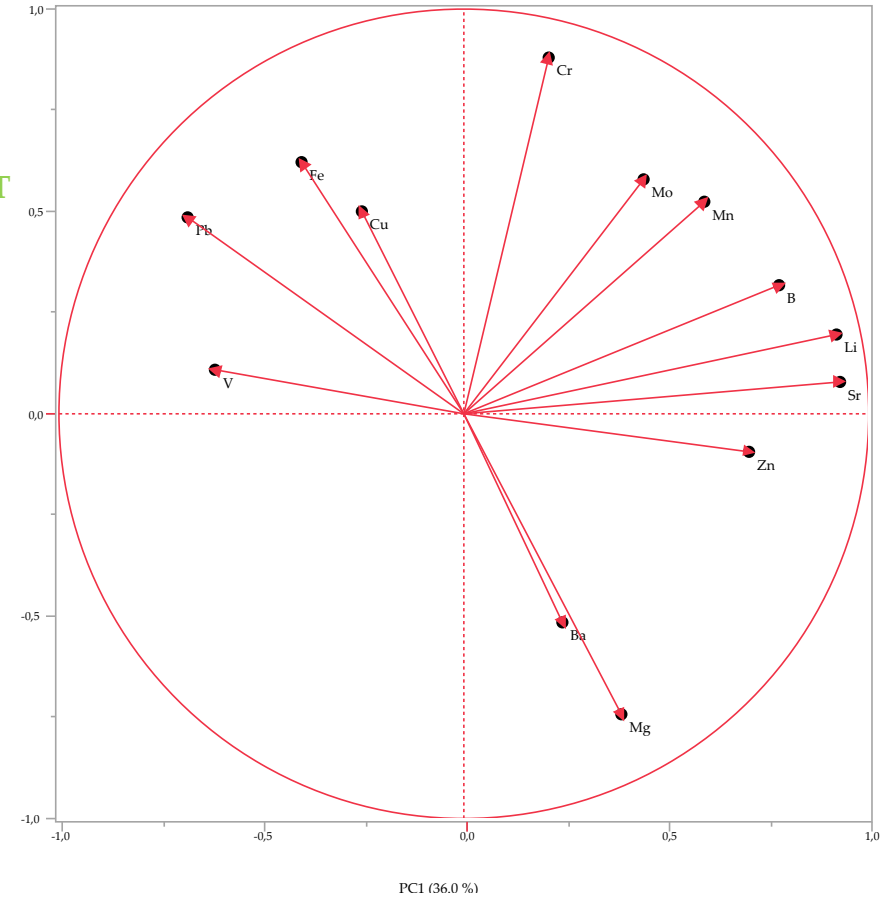
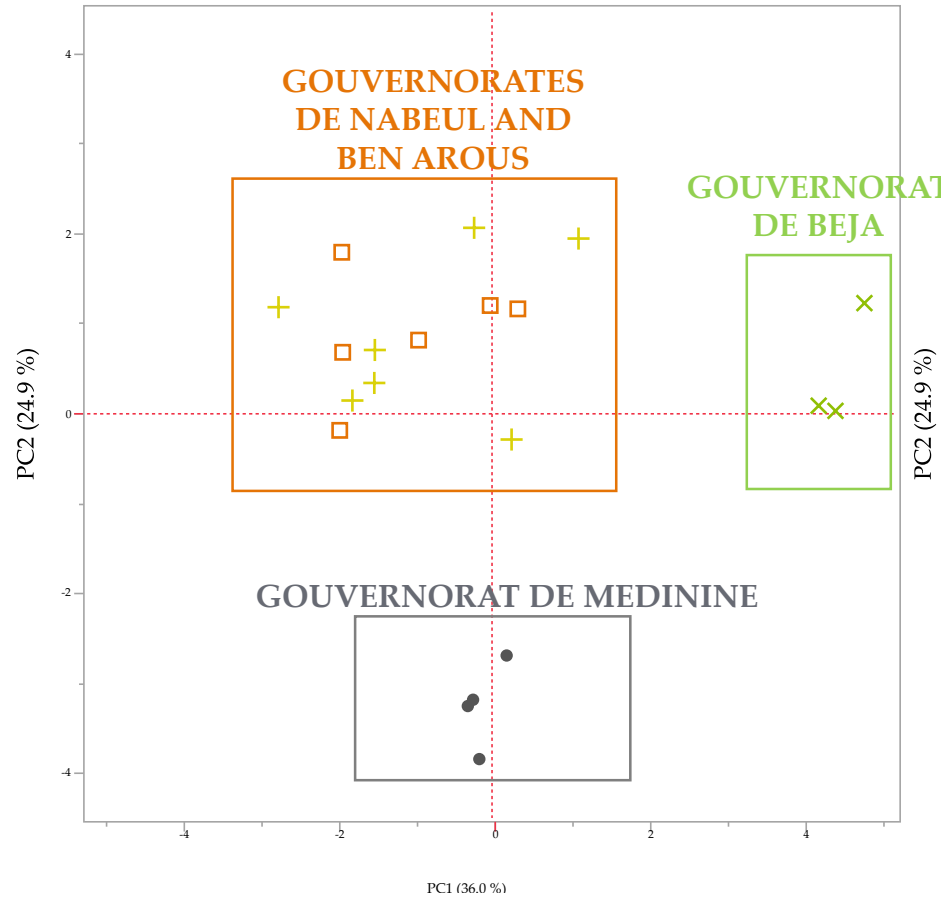
GOVERNORATE LEVEL DISCRIMINATION



GOUVERNORATE LEVEL DISCRIMINATION

PCA performed on the content of Cr, Fe, Cu, Mo, Pb, V, Ba, Mn, Mg, Li, B, Zn, and Sr

DE BEJA



DISCRIMINATION OF THE WINES COMING FROM BOTH THE
GOUVERNORATES DE BEJA AND DE MEDININE

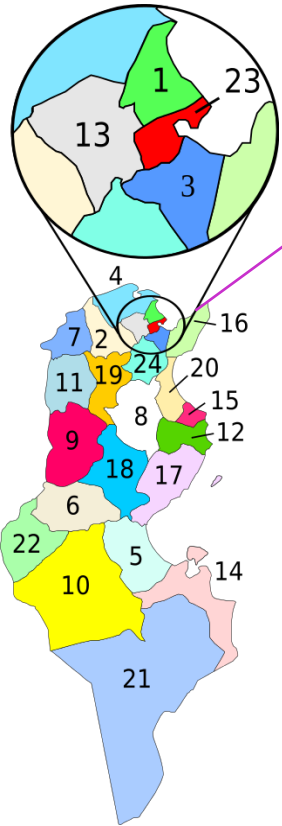
Ben Arous Medinine Nabeul Béja

FIGURE 11 GOUVERNORAT DE MEDININE

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Discrimination of geographical origin Tunisian wines

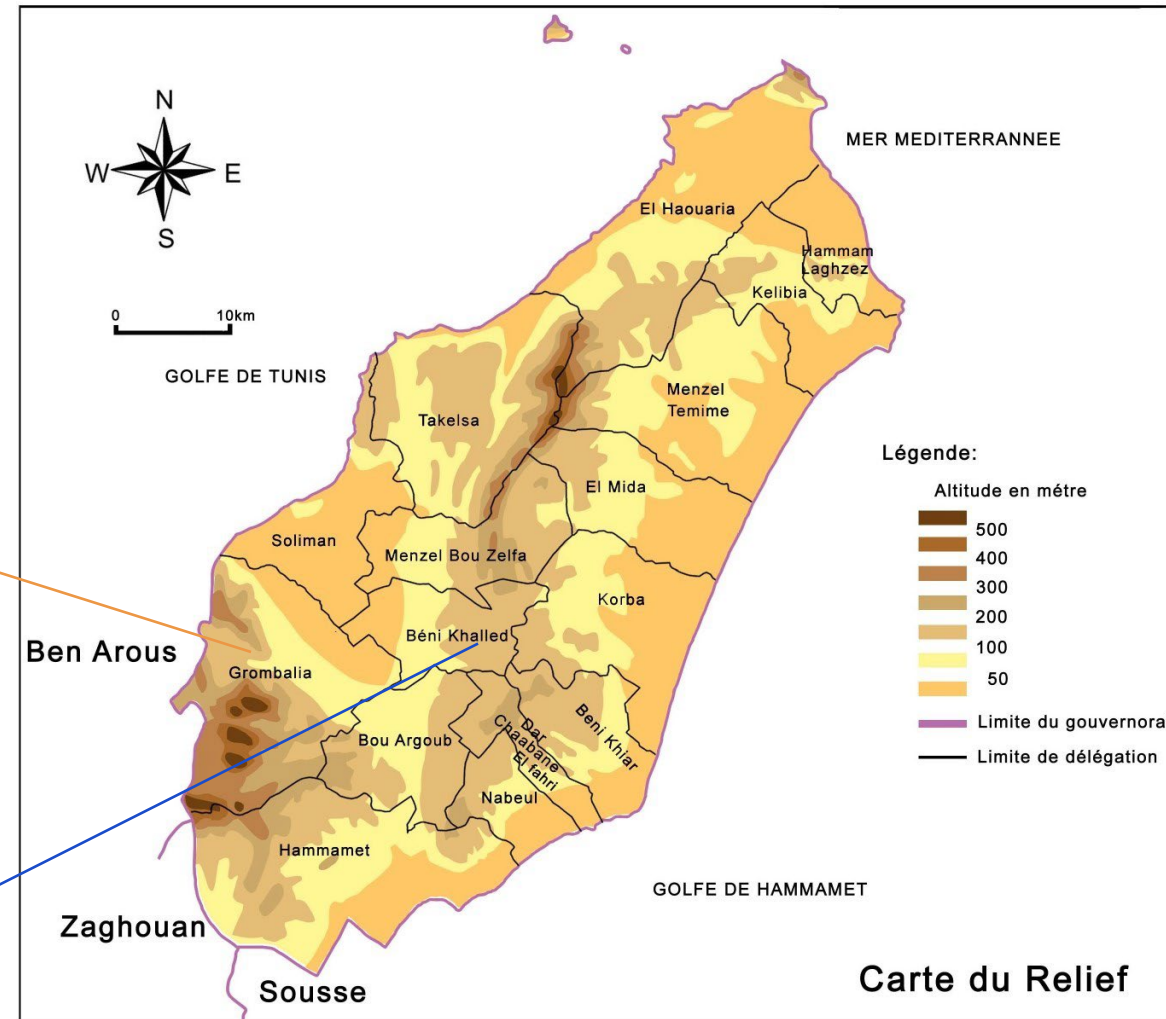
DELEGATION LEVEL DISCRIMINATION



Gouvernorat de Nabeul

Delegation de Grombalia
3 WINE SAMPLES

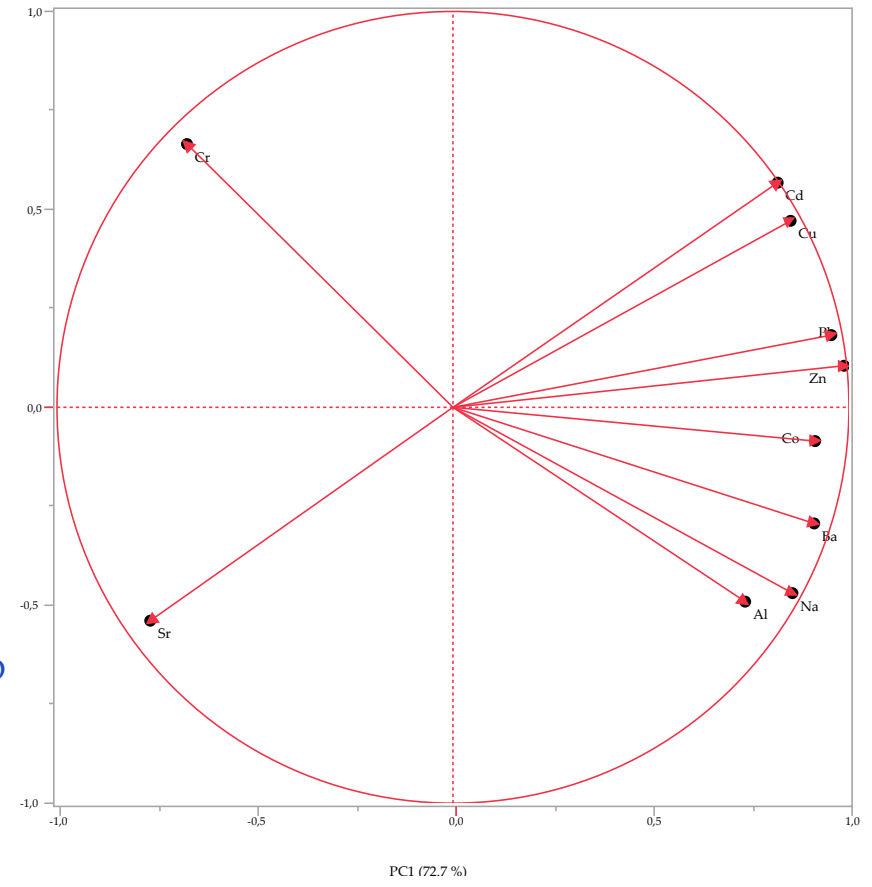
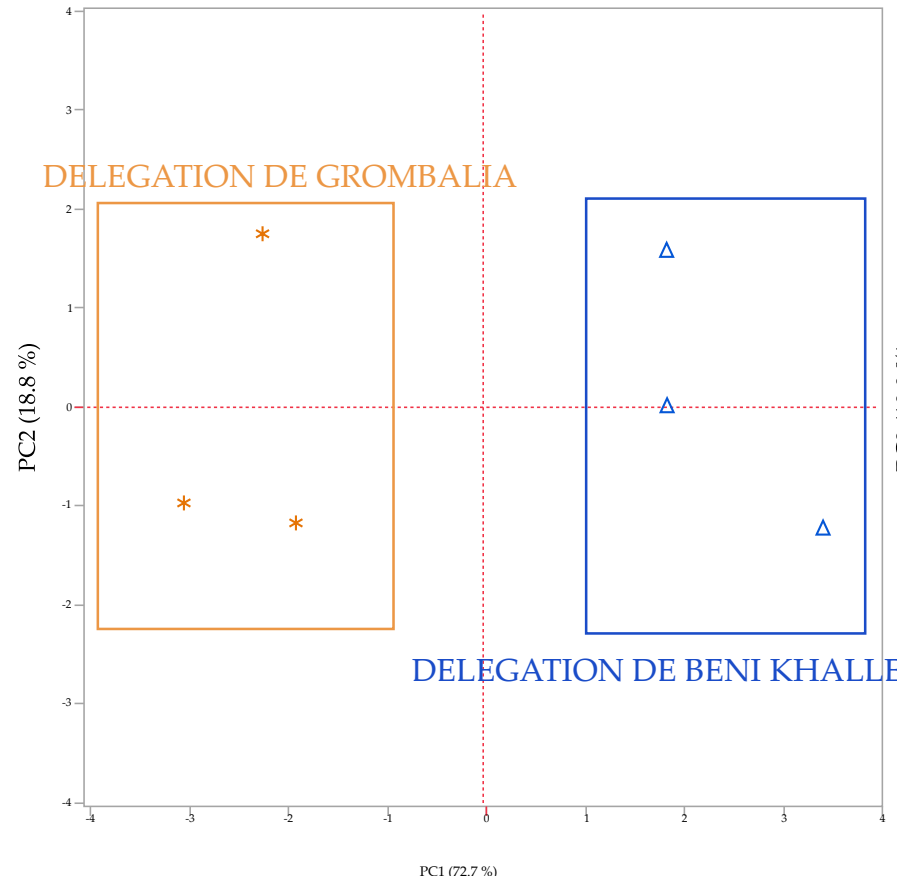
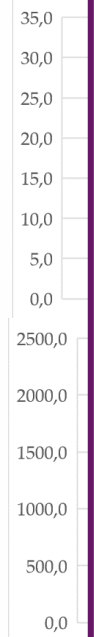
Delegation de Beni Khalled
3 WINE SAMPLES



DELEGATION LEVEL DISCRIMINATION

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

Cr and



Rb

Pb

Na

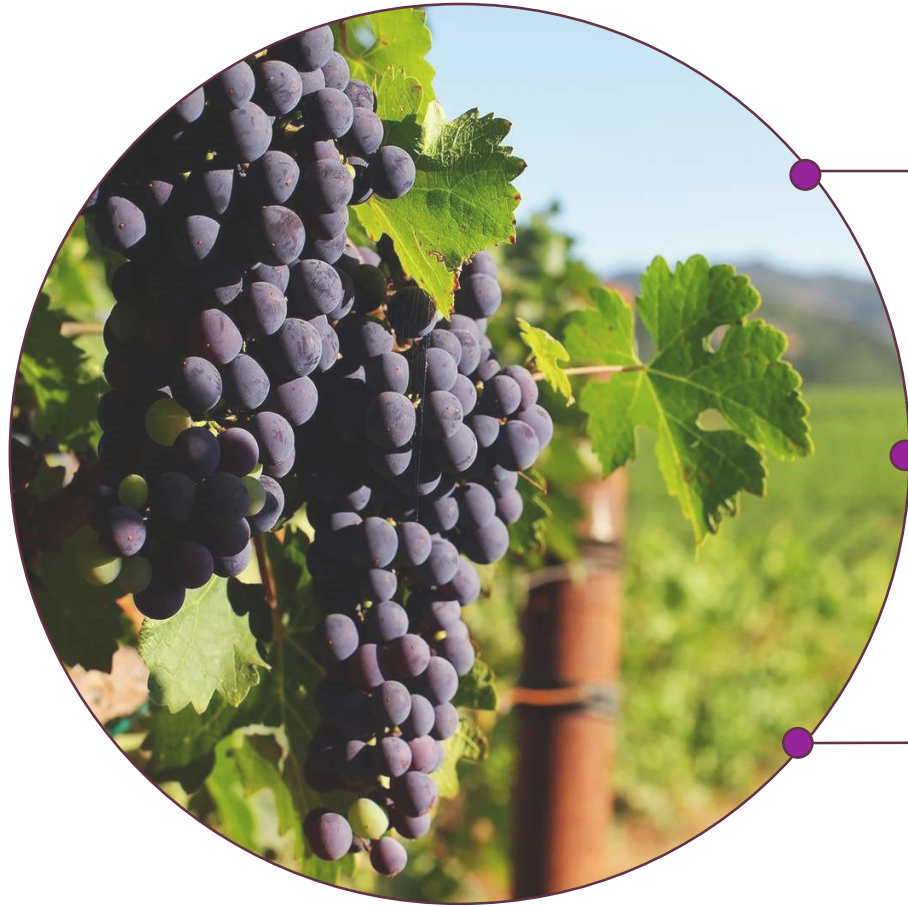
DISCRIMINATION OF THE WINES COMING FROM THE TWO DELEGATIONS OF NABEUL

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CONCLUSIONS



The developed method achieve good **accuracy and precision**

Good preliminary results for **wine traceability**

Ability to discriminate **wine origins** at different **geographical levels** (**nations, gouvernorates, delegations**) selecting only some of the analysed elements



Acknowledgements

Fundings



TunTwin Project



TRACE WINDU

Tracewindu Project

Affiliations



Ultra Traces Analyses Aquitaine





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THANK YOU FOR YOUR KIND ATTENTION!



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