Olivier F.X. Donard

IPREM
Institut des sciences analytiques et de physico-chimie pour l'environnement et les matériaux

Analytical strategies using combined isotopic signatures or multi - isotopic - dilution methods to ascertain the origin of wines and foods.

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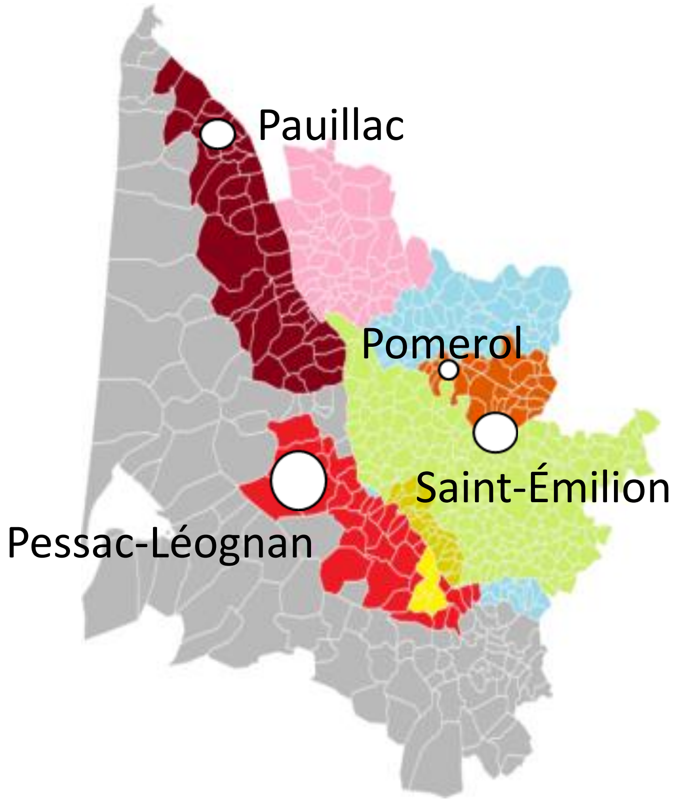
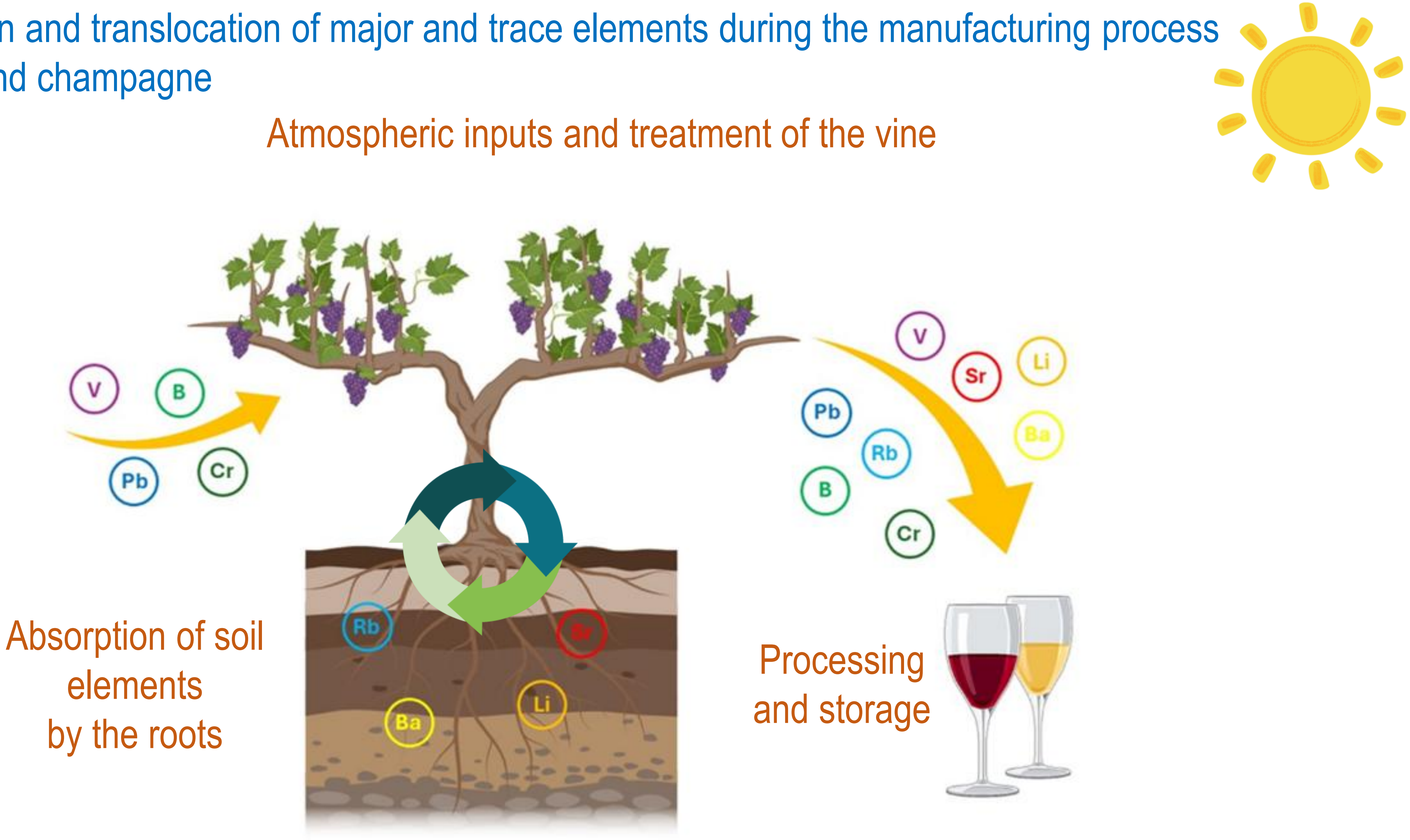
« True » Bordeaux Wines : 44 wines



- 11 Pomerol (Red Wine)
- 4 Saint-Emilion (Red Wine)
- 16 Pessac-Léognan (Red Wine)
- 9 Pessac-Léognan (Red Wine)
- 4 Pauillac (Red Wine)

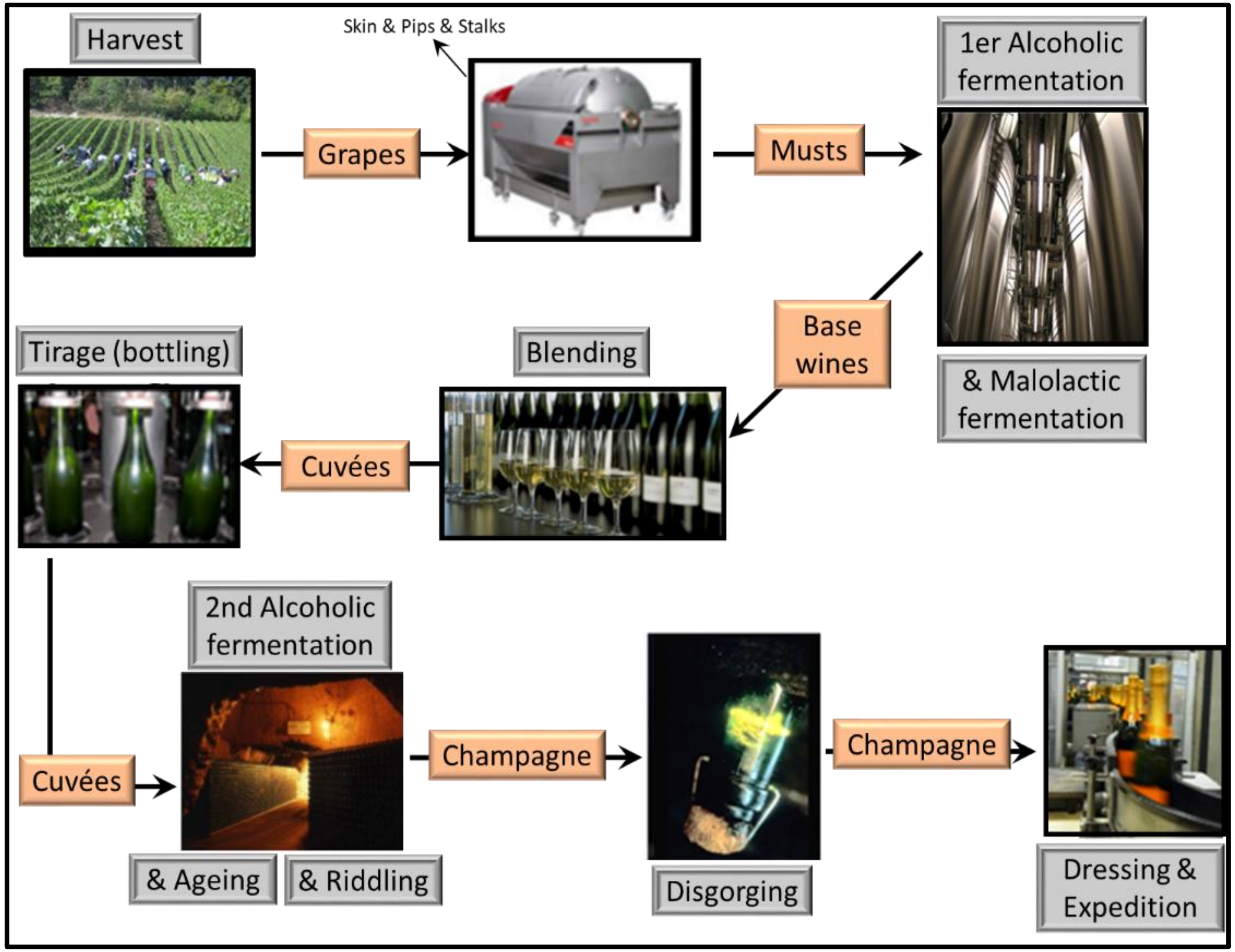
Chinese wines: 3 red wines

Absorption and translocation of major and trace elements during the manufacturing process of wine and champagne



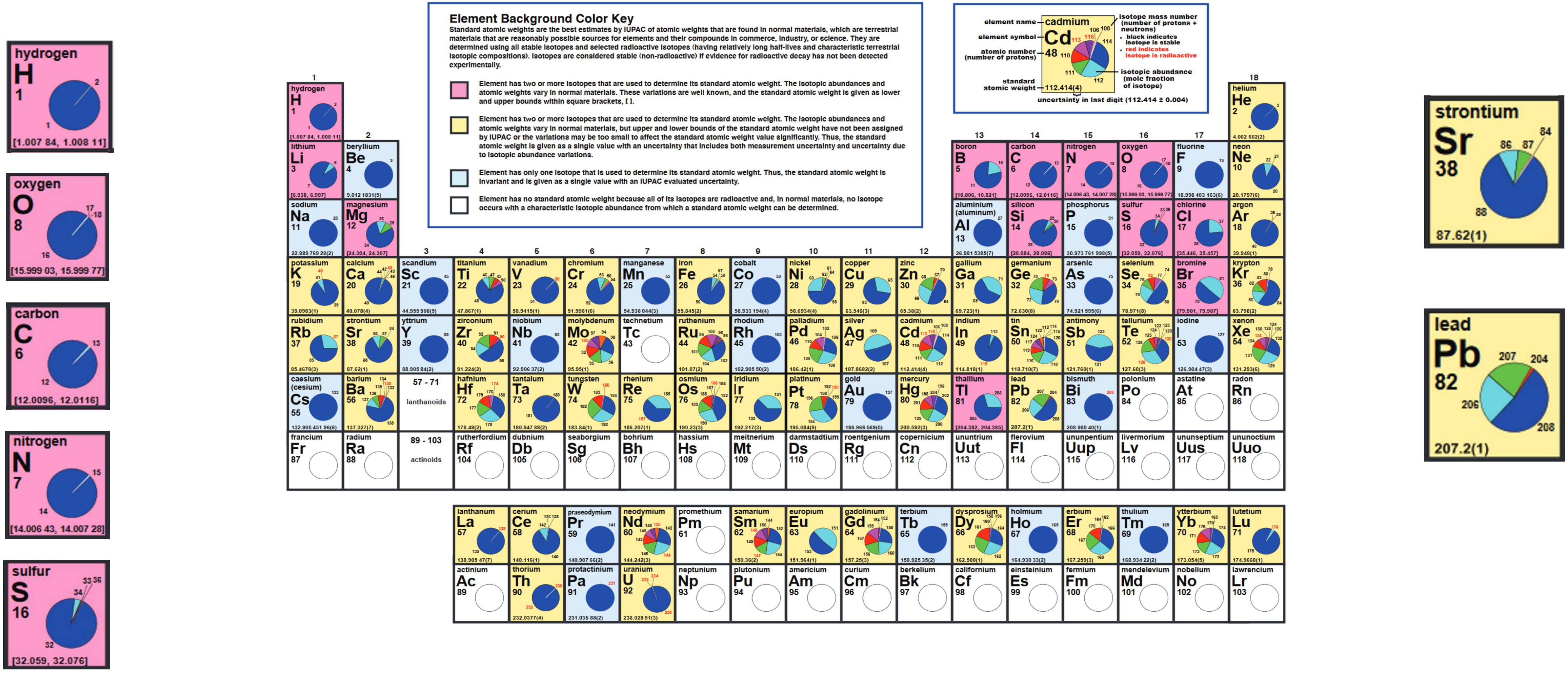
Origins of trace elements and inorganic isotopic signatures in wines

Elemental and isotopic signatures from the soil up-take



Process & storage

IUPAC Periodic Table of the Isotopes



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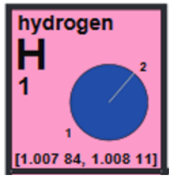
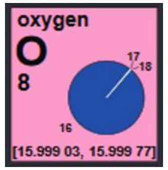
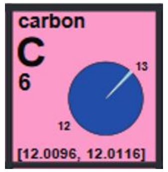
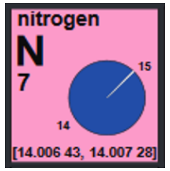
Traditional isotopic systems



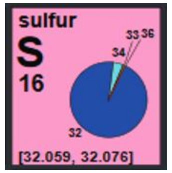


Water





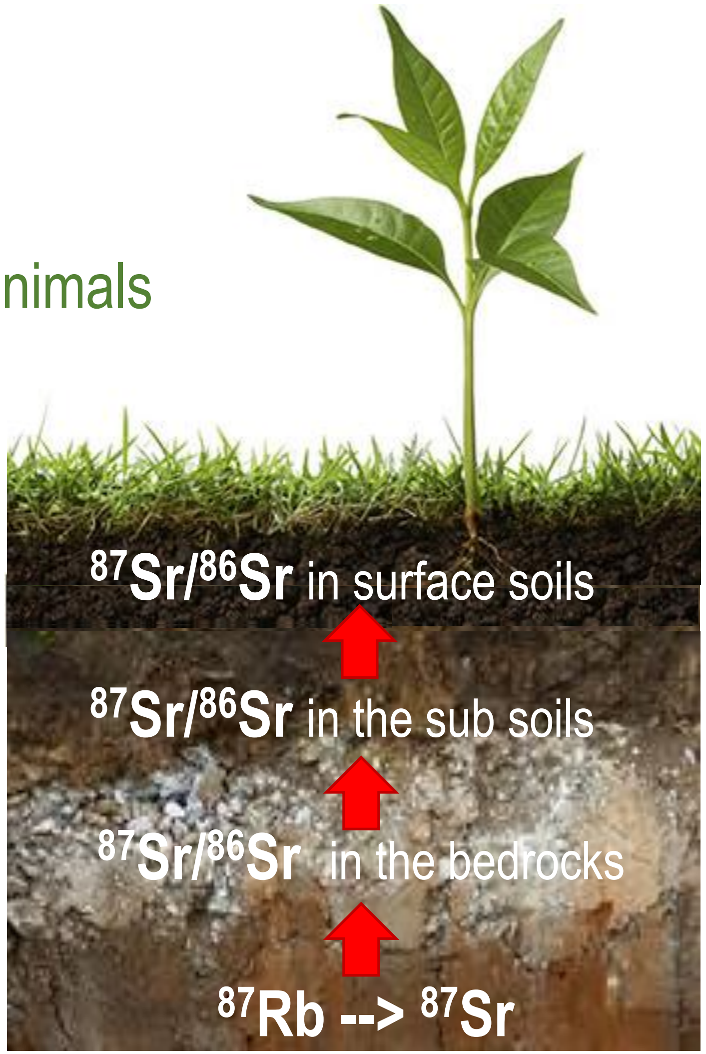
Climat, Agriculture

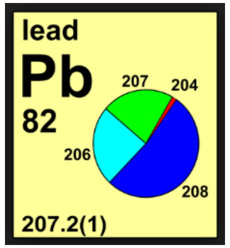


Geology, Volcanoes

Non traditional isotopic systems

$^{87}Sr/^{86}Sr$ in soils, plants, animals





Atmospheric inputs

$^{208}Pb/^{206}Pb$

$^{207}Pb/^{206}Pb$

Geogeni signature

$^{208}Pb/^{204}Pb$

$^{206}Pb/^{204}Pb$

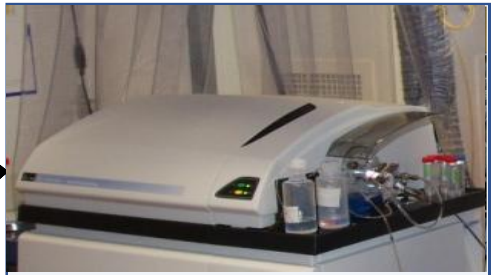
Echantillons

V ~ 10- 20mL

Mineralisation:

HNO_3 + H_2O_2

1



Q-ICP-MS / DRCII

Analyses:

Li, Be, B, Al, Mg, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba, Pb

Isotopes du B

2

Purification

- **<u>Sr</u>: Eichrom Sr-B50-S**
- **<u>Pb</u>: Dowex AG1-X8**
- **<u>B</u> : Amberlite IRA 743**

Multicollecteur ICP-MS

Isotopic Analysis:

Isotope Sr

(150 ppb)

Isotope Pb

(10 ppb)

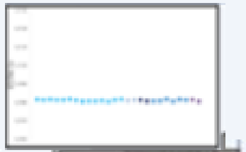
Isotopes B

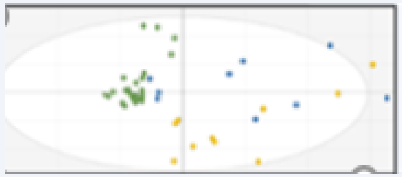
(400 ppb)

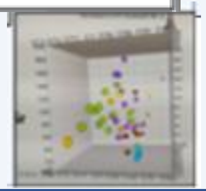
3

3

Traitement des données

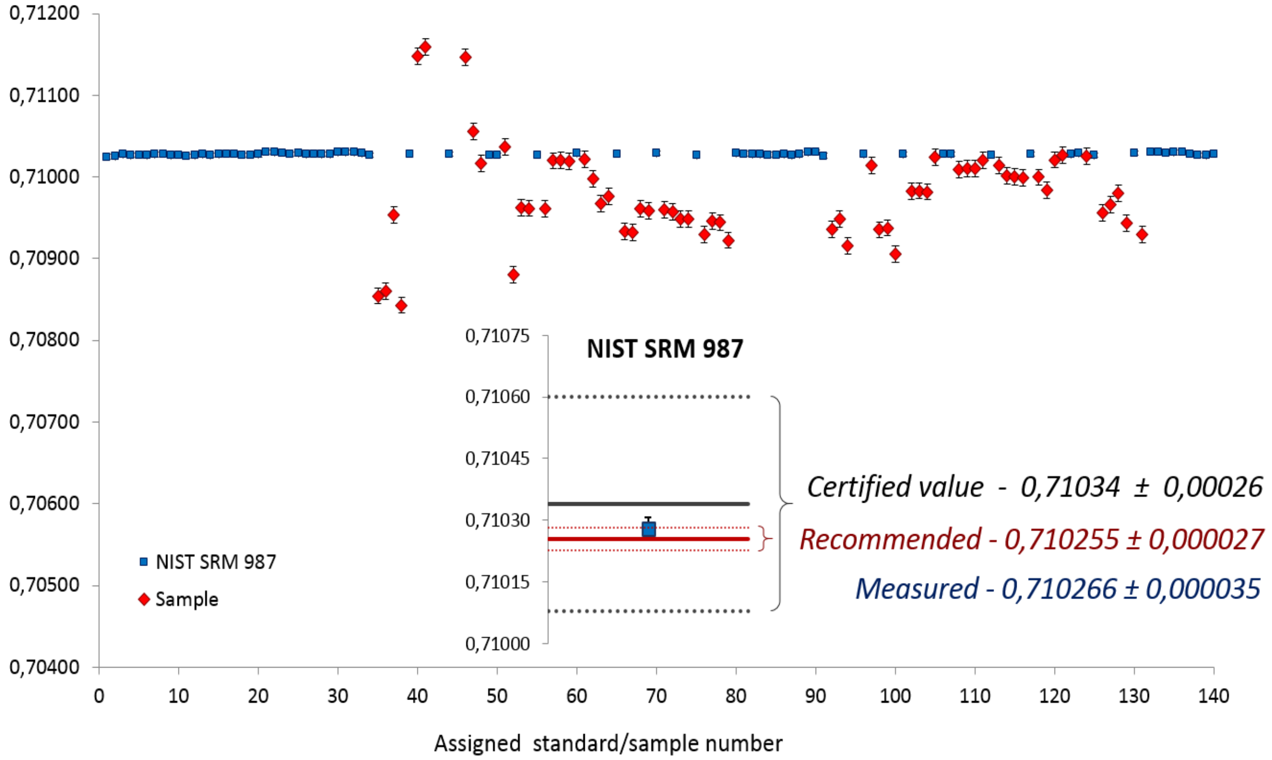




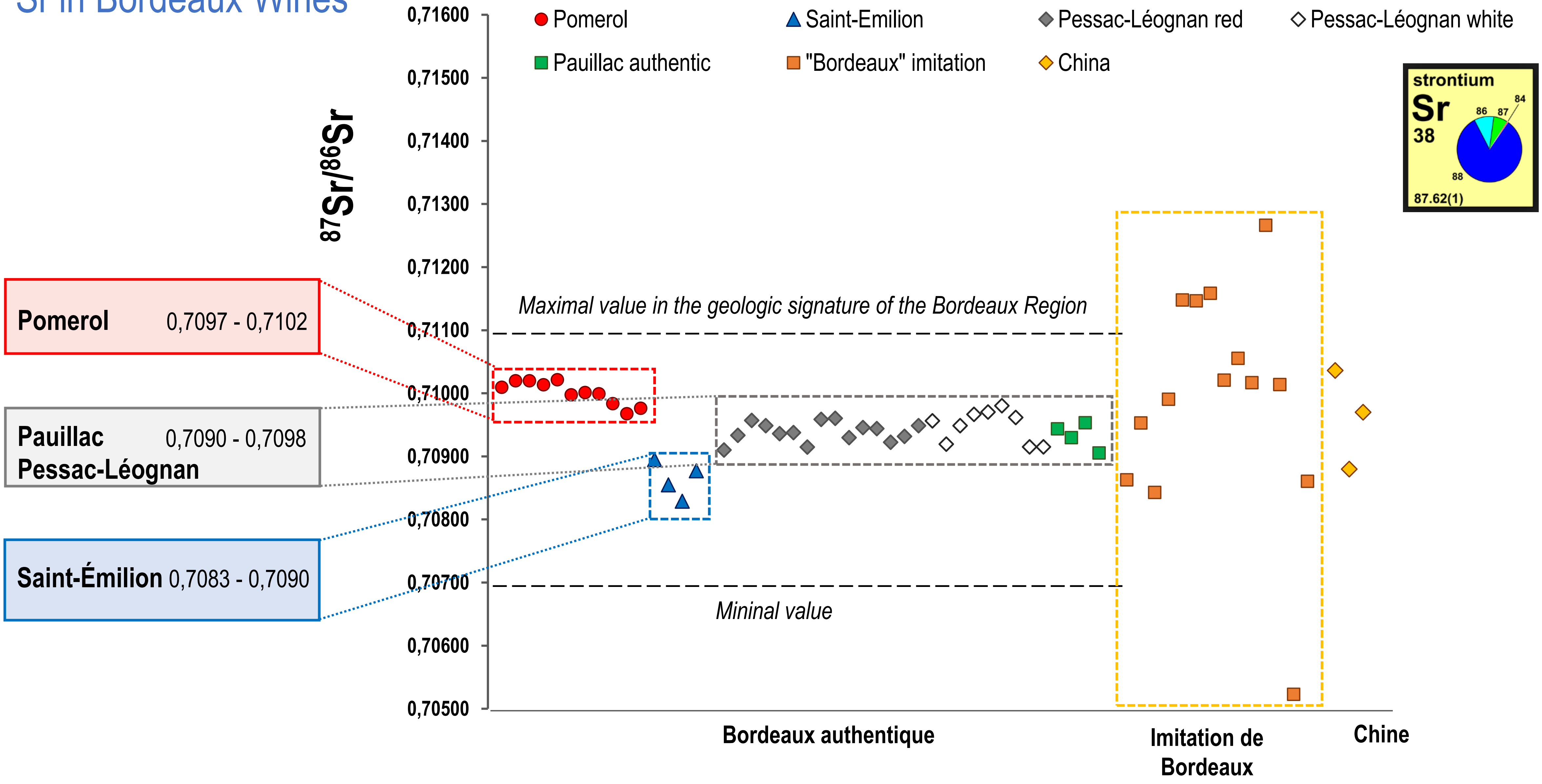


Nu Plasma HR (Nu Instruments)

Nu 1700 (Nu Instruments)



$^{87}Sr/^{86}Sr$ in Bordeaux Wines



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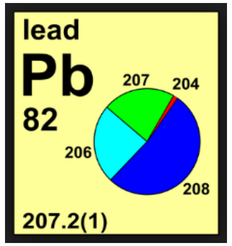
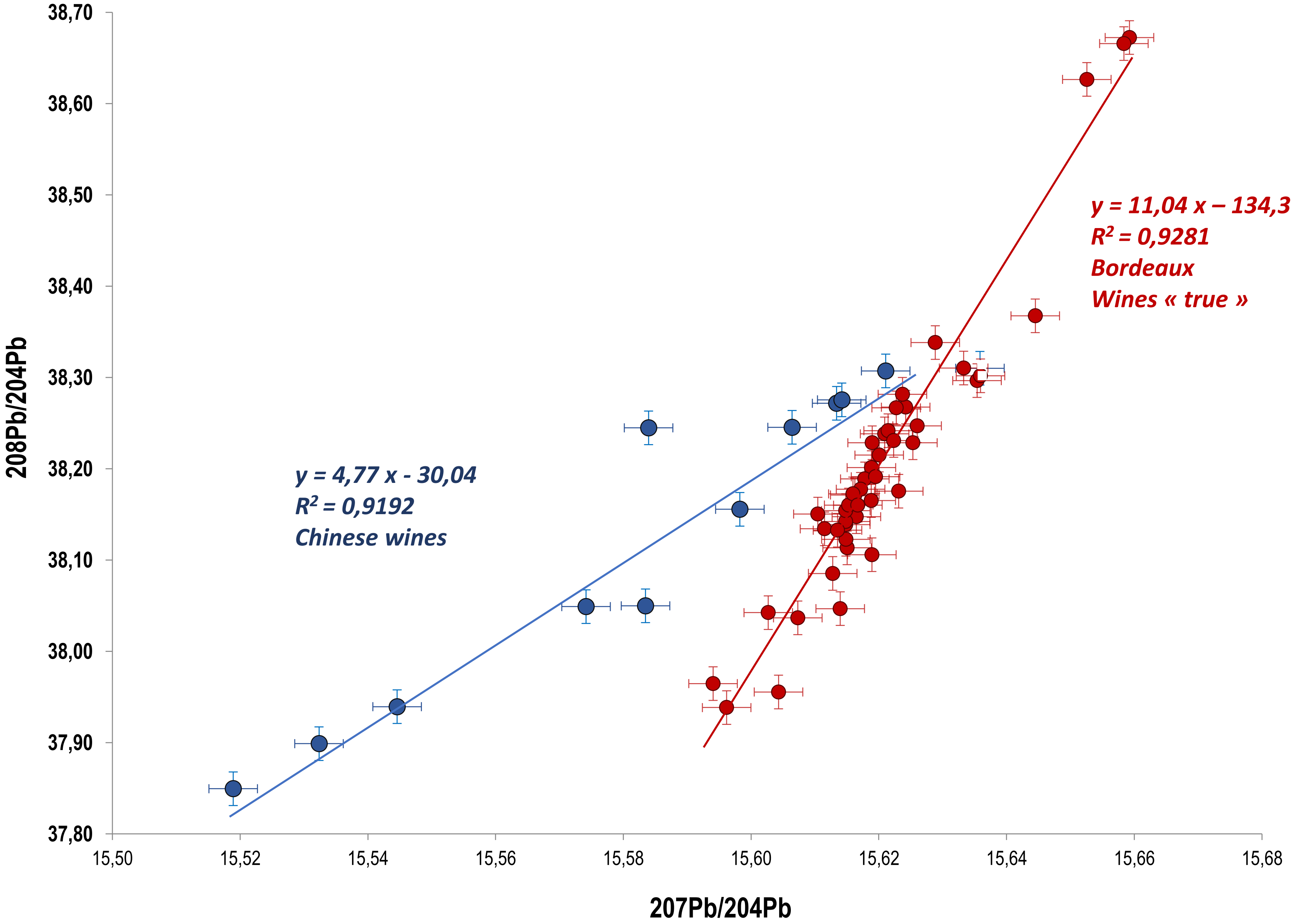
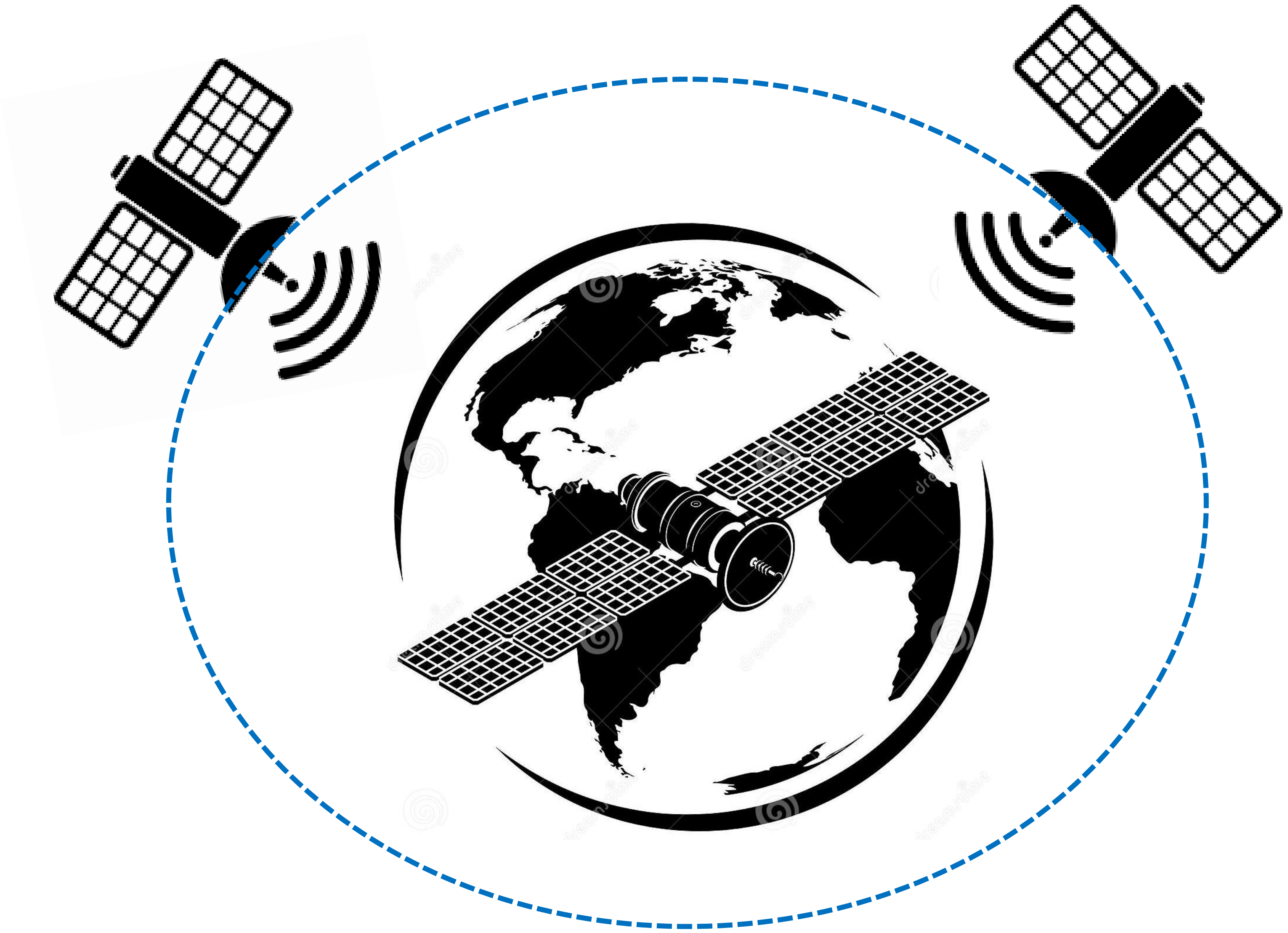


France / China: Discrimation of origine



E. Polekh Epova et al.



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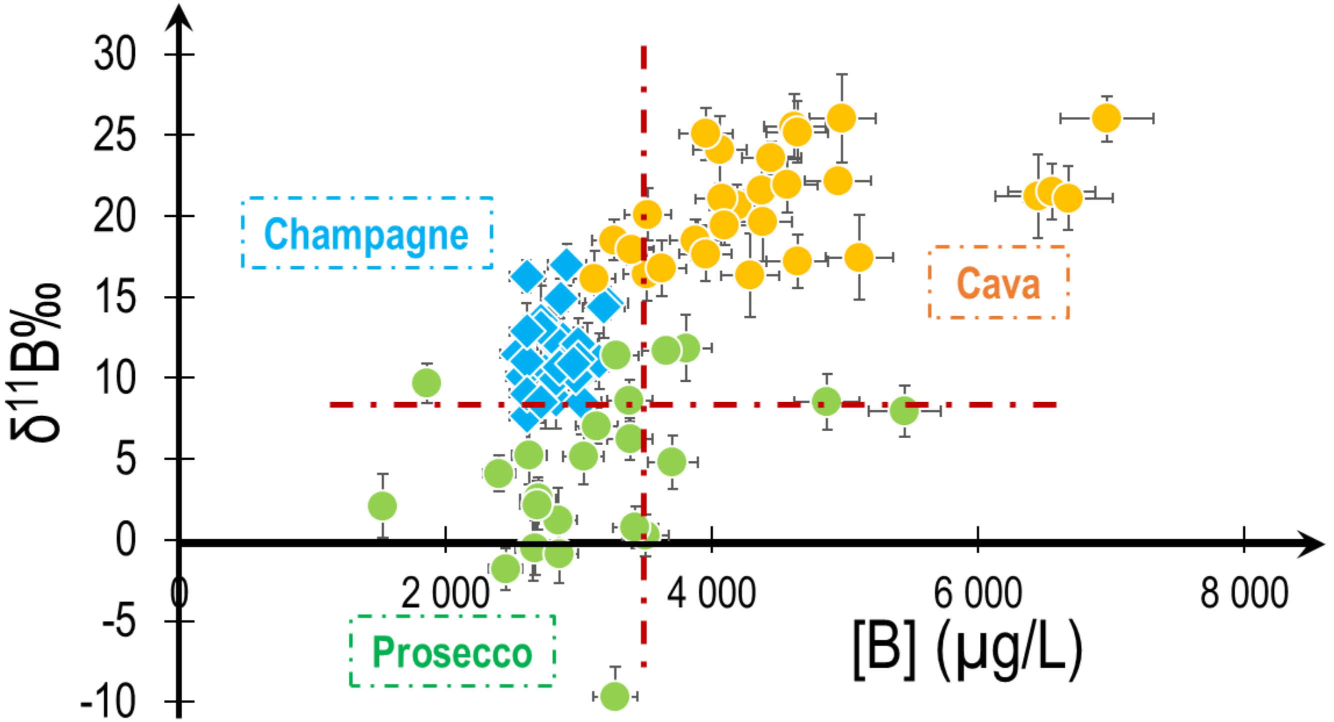
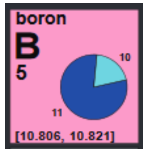
Cava, Champagne & Prosecco





Several possible explanations..

- the pH of the soil:

Cava: Acaline soils (pH : 7,2 - 8,5) → Boric acid (enrichissement in ^{11}B) → $\delta^{11}B$ ↑

Prosecco: Acidic soils (pH : 4,2 - 6,5) → Boric acid (no enrichissement en ^{11}B) → $\delta^{11}B$ ↓

Champagne: Alaclines solis(pH : 7,8 - 8,5) → Boric acid (enrichissement in ^{11}B) → $\delta^{11}B$ ↑

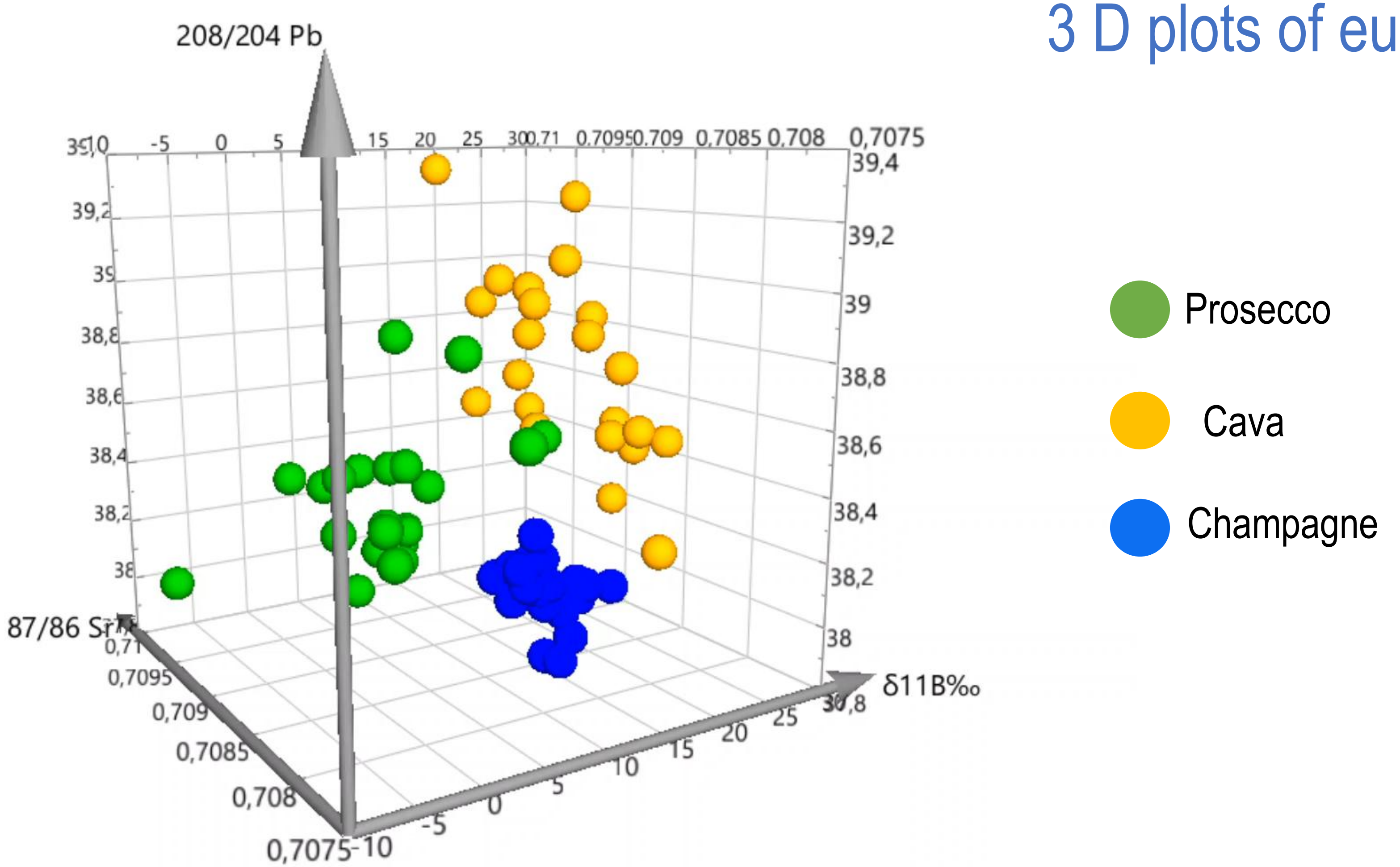
➢ ***Fertilization & Irrigation:***

Champagne: Irrigation forbiden

Cava: [B] ↑ → Fertilization & Irrigation

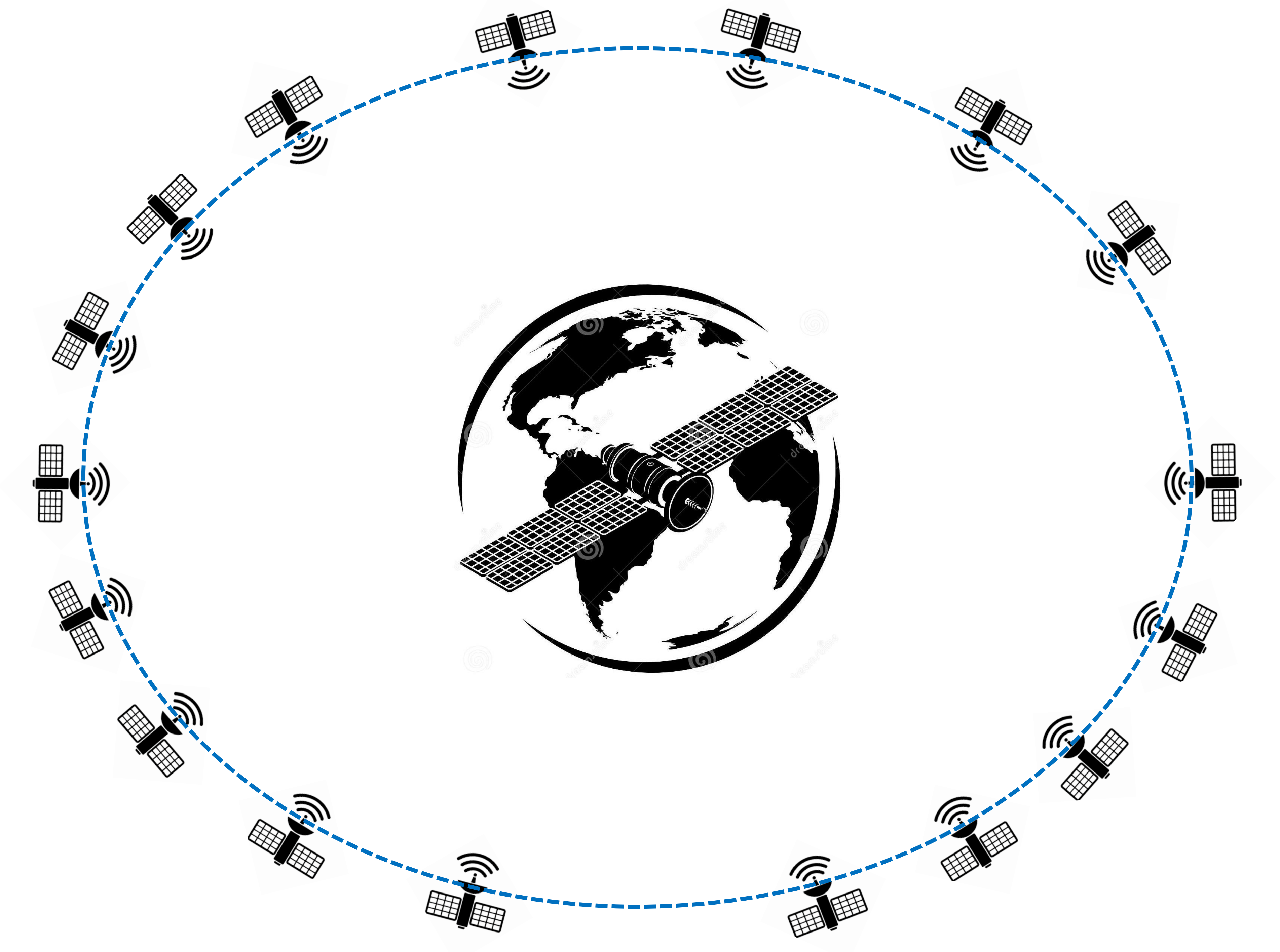
F. Abo et al.,1984 – Influence du bore et du manganèse sur la nutrition, le développement et la production du blé sur le sols de régions tempérée et aride

3 D plots of european sparkling wines



1. $^{87}Sr/^{86}Sr$ **:** Soil signature
2. **$^{208}Pb/^{204}Pb$: Mainly atmospheric inputs**
3. **δ^{11}B‰ :** Reflecting the pH of the soil and the agricultural practices.

R. Cellier et al.



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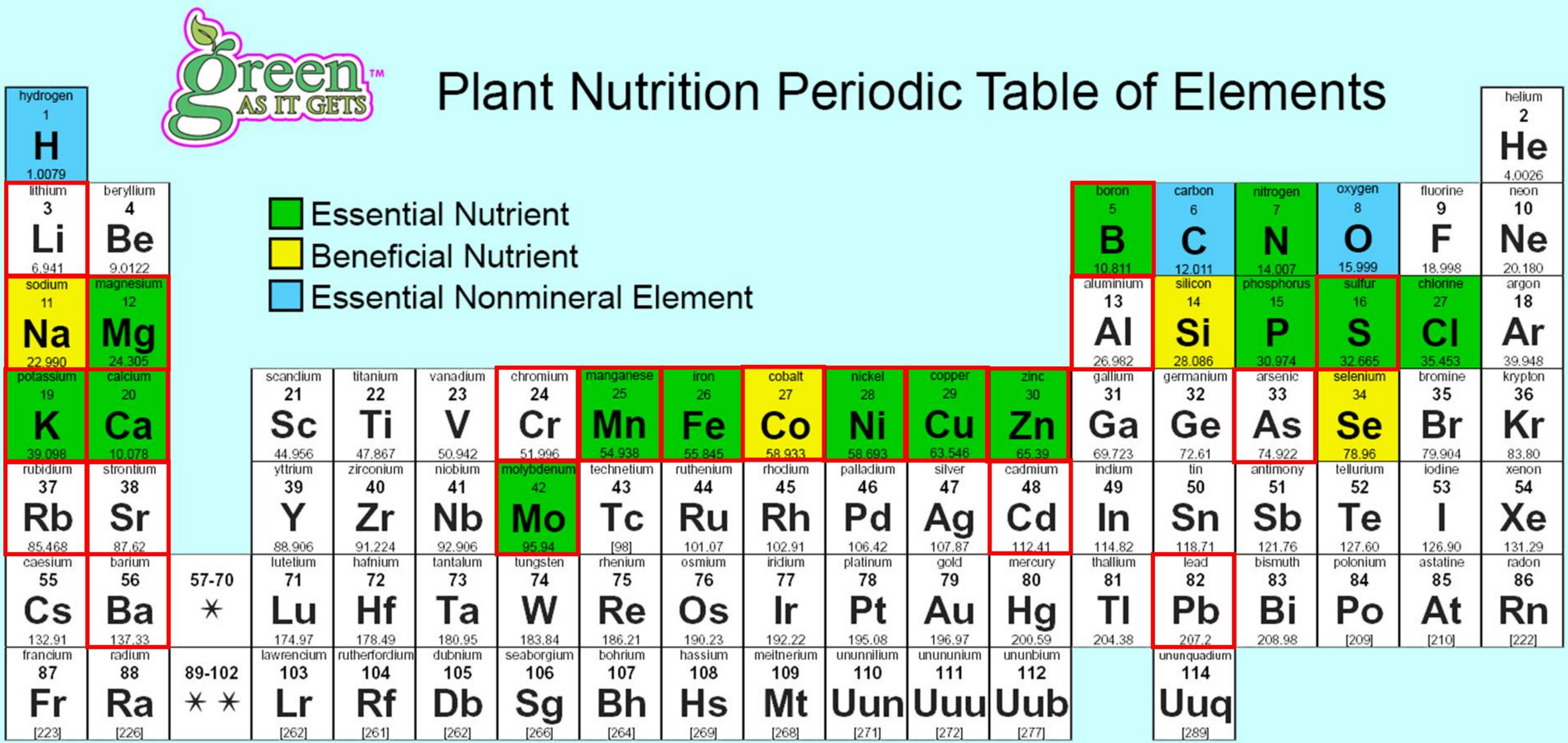
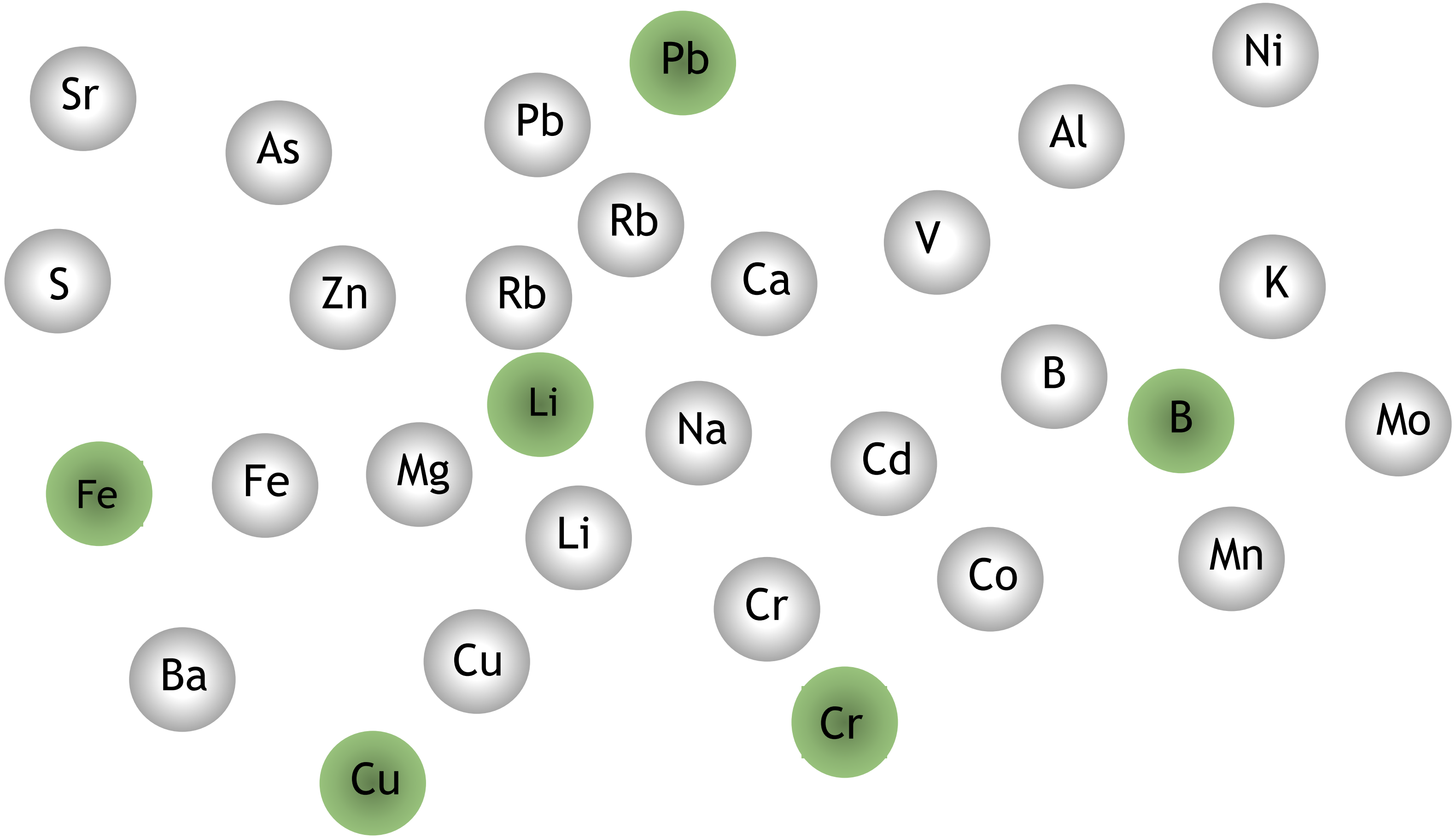
Elements of Interest



Using multi-isotopic dilution for high resolution geographical traceability : 23 isotopic spikes



Isotope	µg/g
10B	30 000
57Fe	15 000
67Zn	7 500
86Sr	2 500
87Rb	2 000
137Ba	500
65Cu	400
53Cr	200
61Ni	120
207Pb	100
95Mo	70
6Li	35
11Cd	1

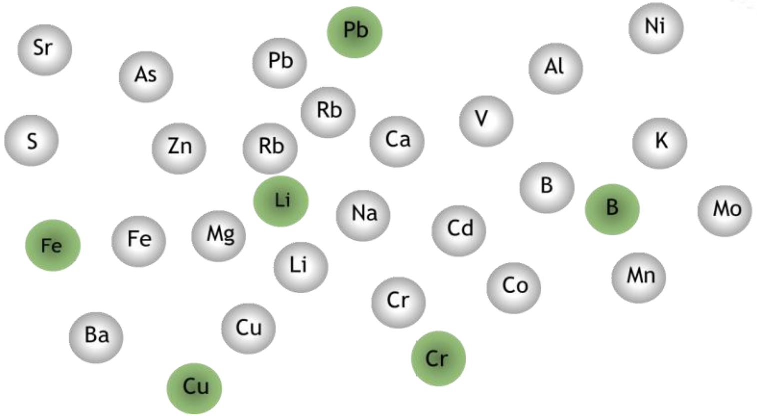
Analytical strategies

ICP-QQQ-MS Simultaneous multi-isotopic-dilution by ICP/MS

- Soil markers
- Agricultural practice markers
- Anthropogenic contamination markers

$$C_s = C_{sp}\,\frac{m_{sp}}{m_s}\,\frac{M_s}{M_{sp}}\,\frac{R_m A^b_{sp} - A^a_{sp}}{A^a_s - R_m A^b_s}$$

Equation for isotopic dilution



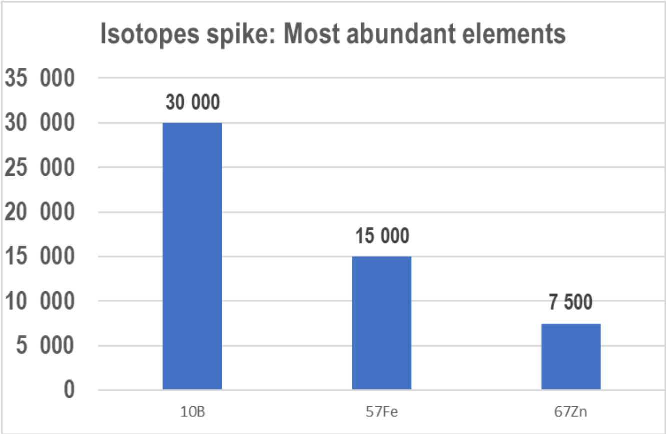
Typical precision: **< 2 %**

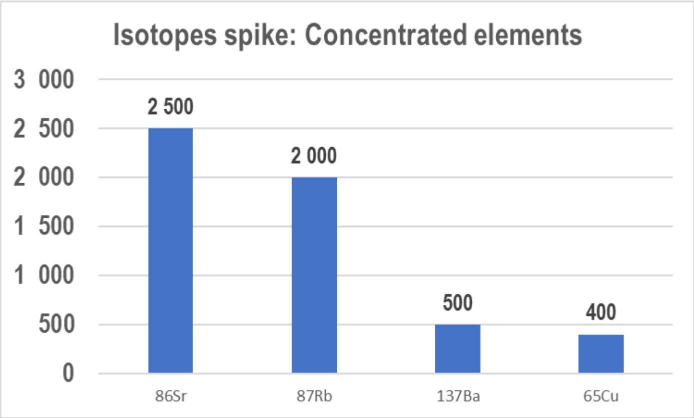
- Very high precision
- Multi-elemental information
- High samples through-put (200/day)
- = Reduced cost of analysis
- Important potential of improvment
- Applicability to other food matrices

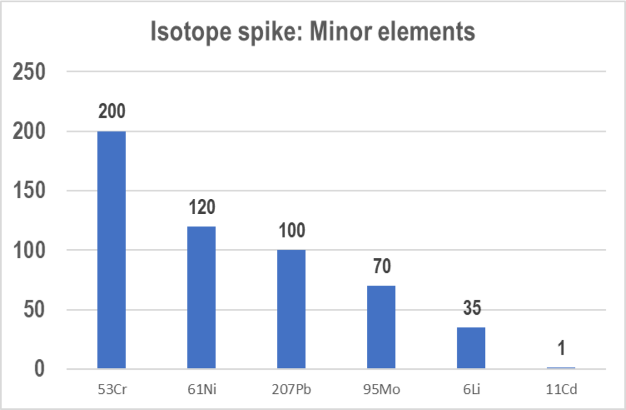
$$C_s = C_{sp} \frac{m_{sp}}{m_s} \frac{M_s}{M_{sp}} \frac{R_m A_{sp}^b - A_{sp}^a}{A_s^a - R_m A_s^b}$$

Typical equation for isotopic dilution

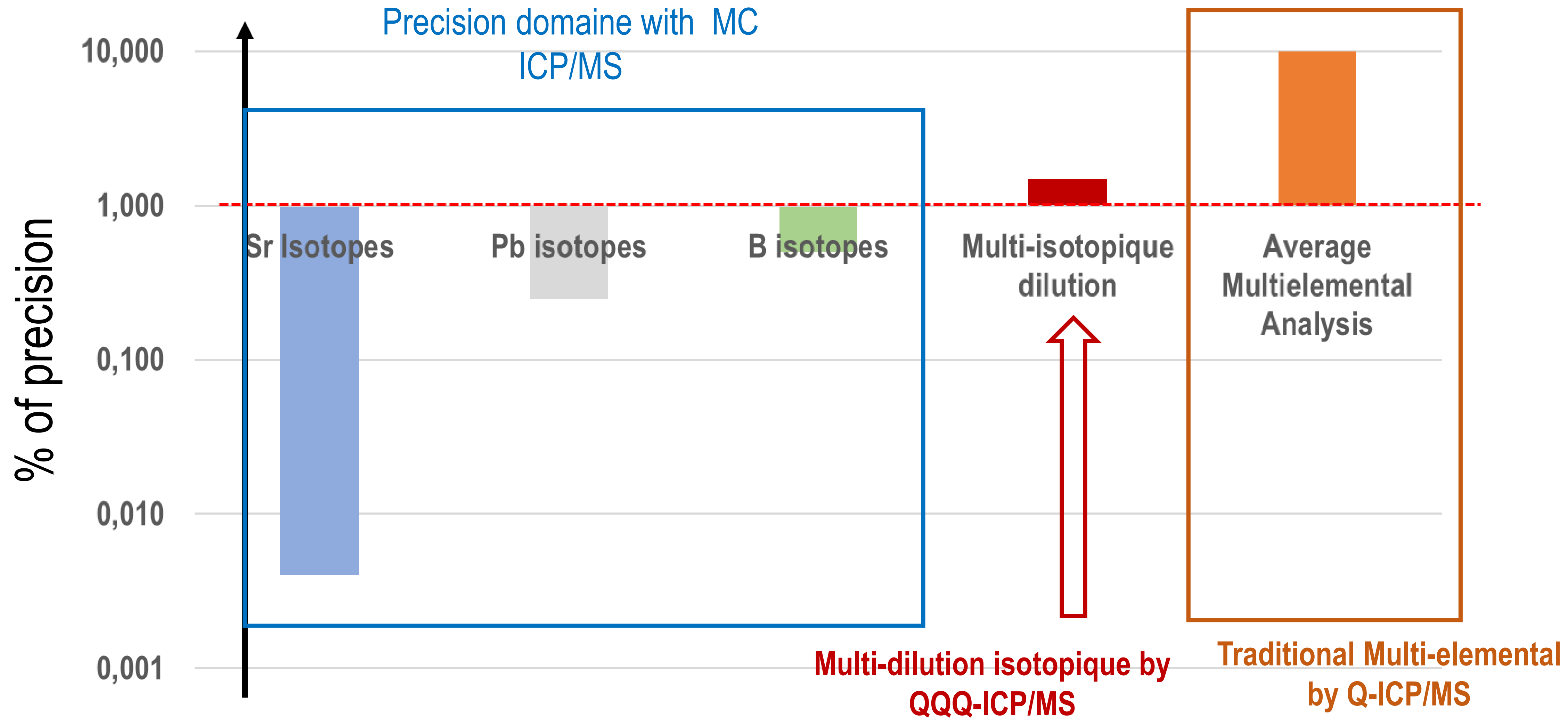
μg/g







Selected primary spike concentrations



Precision domaine with MC ICP/MS
10,000
1,000
0,100
0,010
0,001
% of precision
Sr Isotopes
Pb isotopes
B isotopes
Multi-isotopique dilution
Average Multielemental Analysis
Multi-dilution isotopique by QQQ-ICP/MS
Traditional Multi-elemental by Q-ICP/MS

The Wine in Blue project

Questions

- Terroir signature
- Traceability , fraud
- Wine quality over time
- Bio or not Bio
- Impact of Climat Change
- Stability of environmental conditions

Data Generation

Quality of the data: Inorganic and isotopic

High precision isotopic signatures
Multi-elemental
Isotopic range
Light isotops signatures.

Geographical localisation
Region description
GPS

Climatic conditions

Other data

Data Storage

Microsoft
Cloud Solution Provider

Data Processing by AI

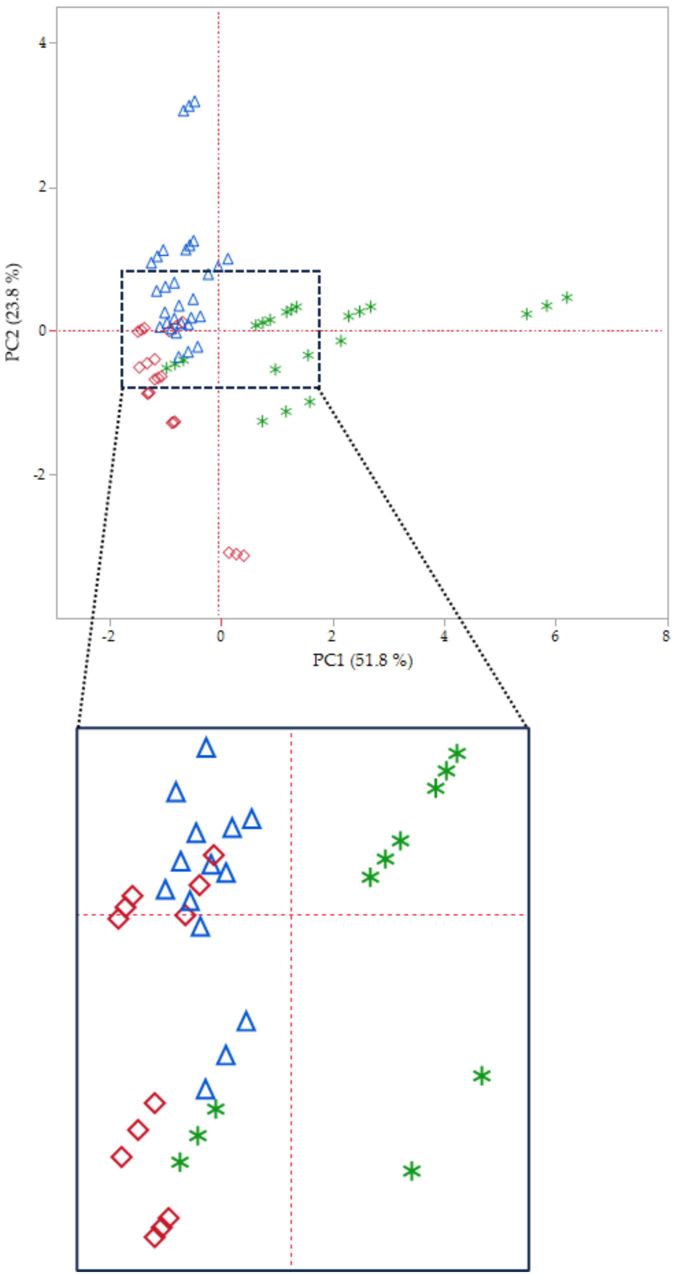
- Importance of Data preparation

Data sorting

Decision on most discriminating factors

Answer
Operators comparison,
Different Algorithms

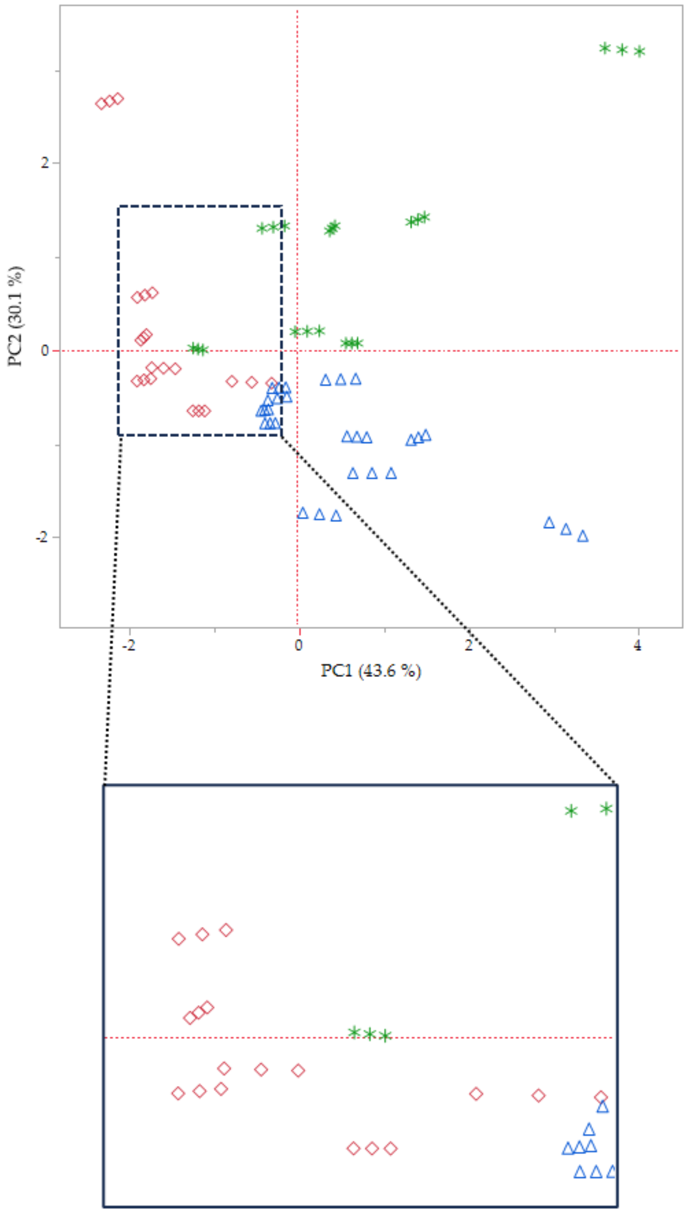
Improved discrimination potential using traditional statistics on pole of wines coming from diffrent origines



Traditional multielemental analysis by QQQS ICP/MS

Routine mutielemental traditional precision

< 10 %

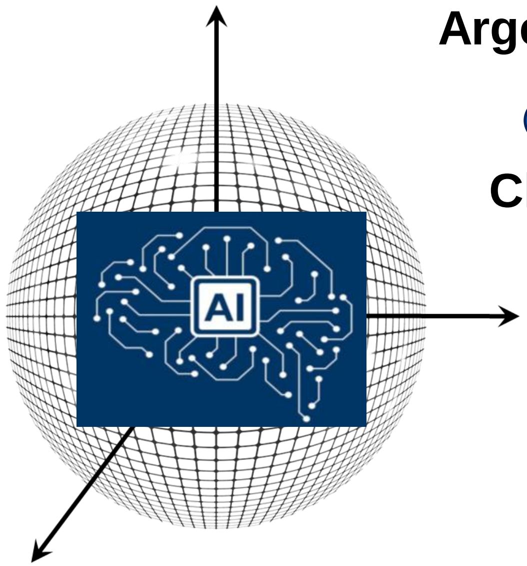


Traditional multielemental analysis using multisotopic dilution by QQQS ICP/MS

Routine mutielemental traditional precision

< 2 %

Multi-isotopic dilution : Reference Data Basis powered by AI



Argentina

Chili

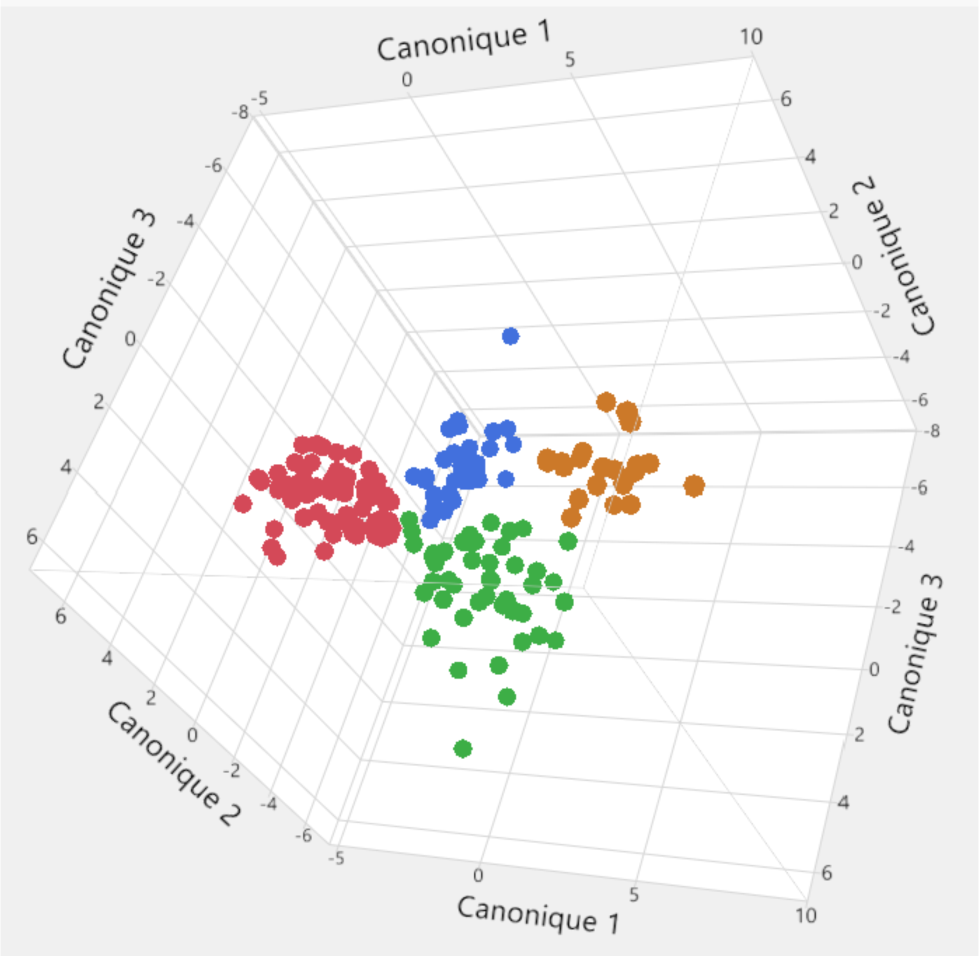
Existing

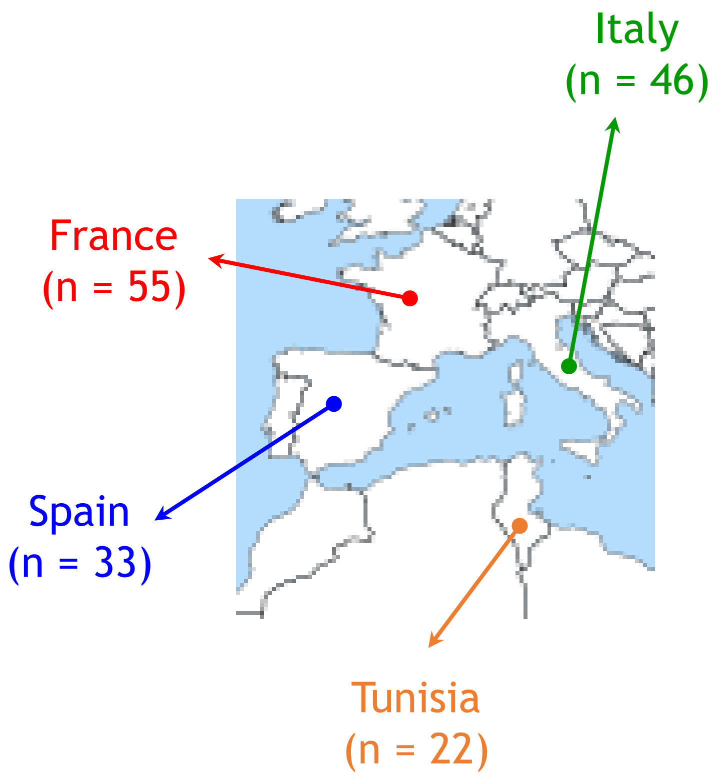
TRACE WINDU

Application of traditional chemometrics

- Discrimination at the national level

LDA applied to the 23 elements on 4 countries

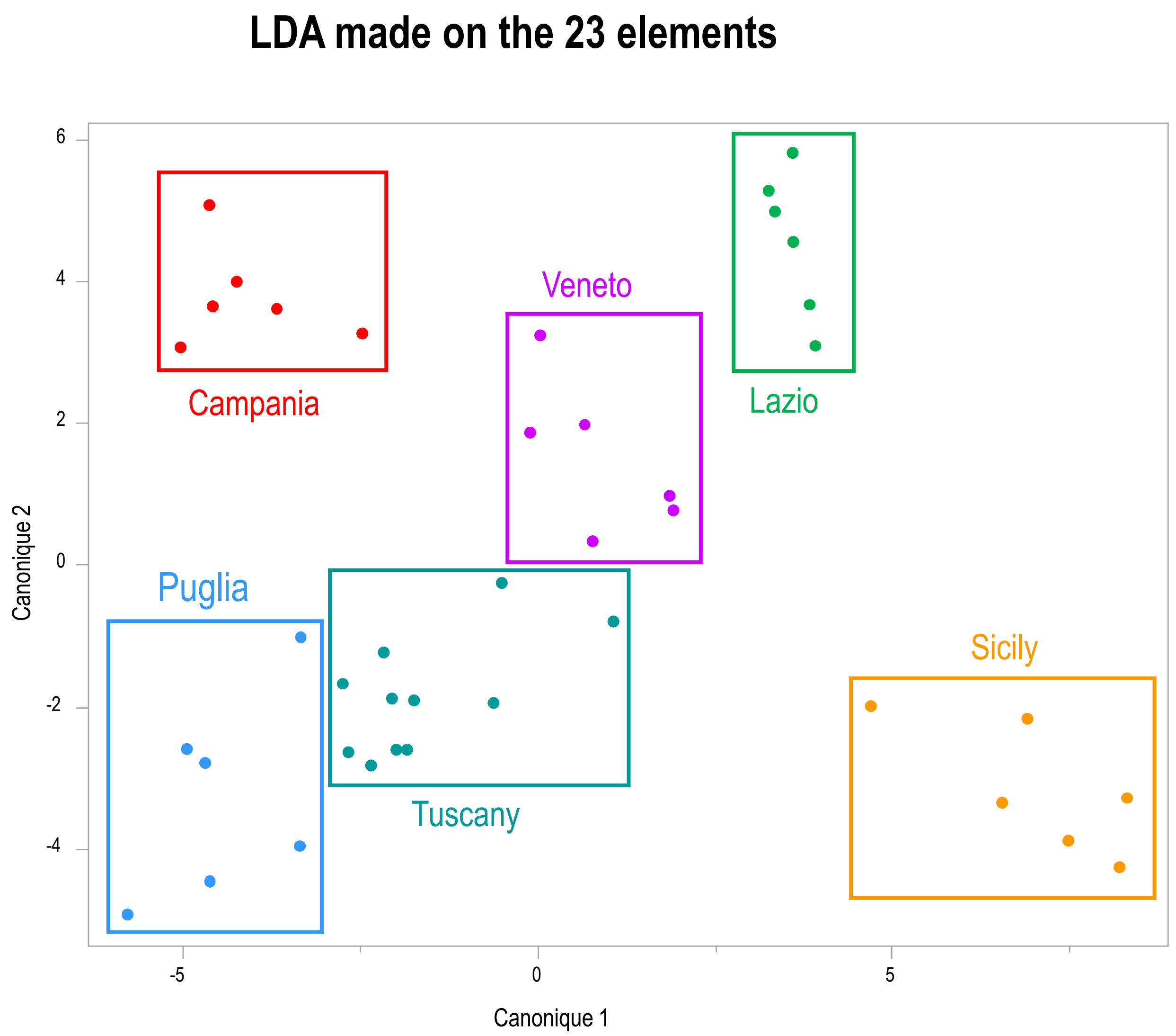


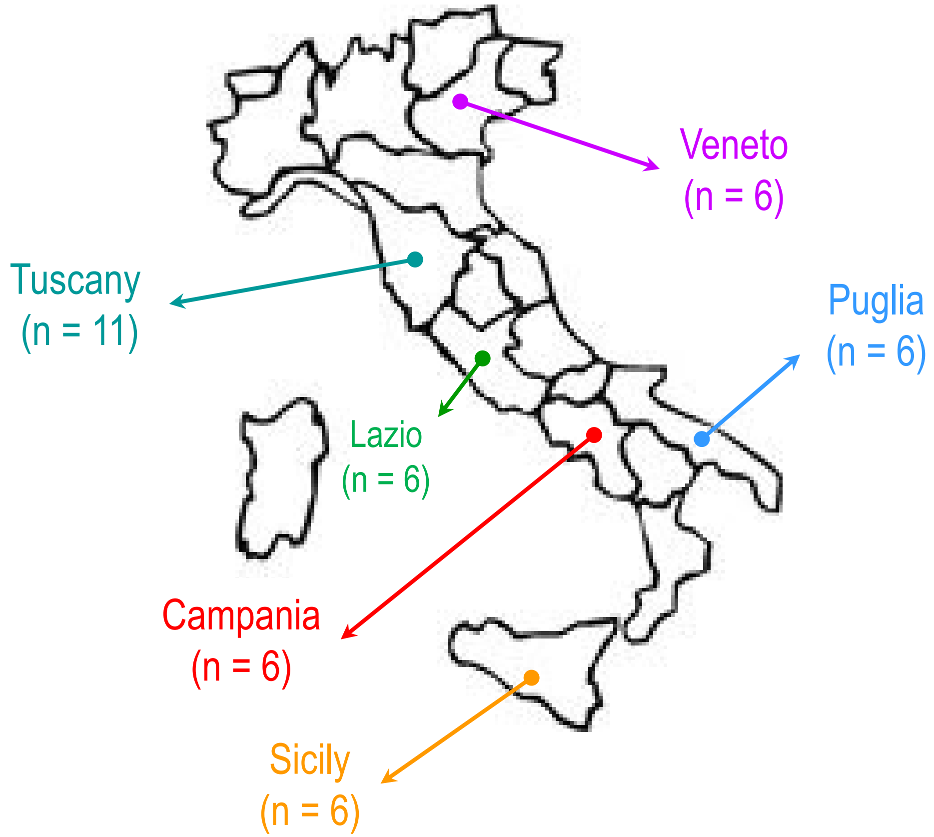


Lambda of Wilk : < 0,0001 (< 0,005)

R^2 = 0,9654 (> 0,9)

Application at the regional level in Italy





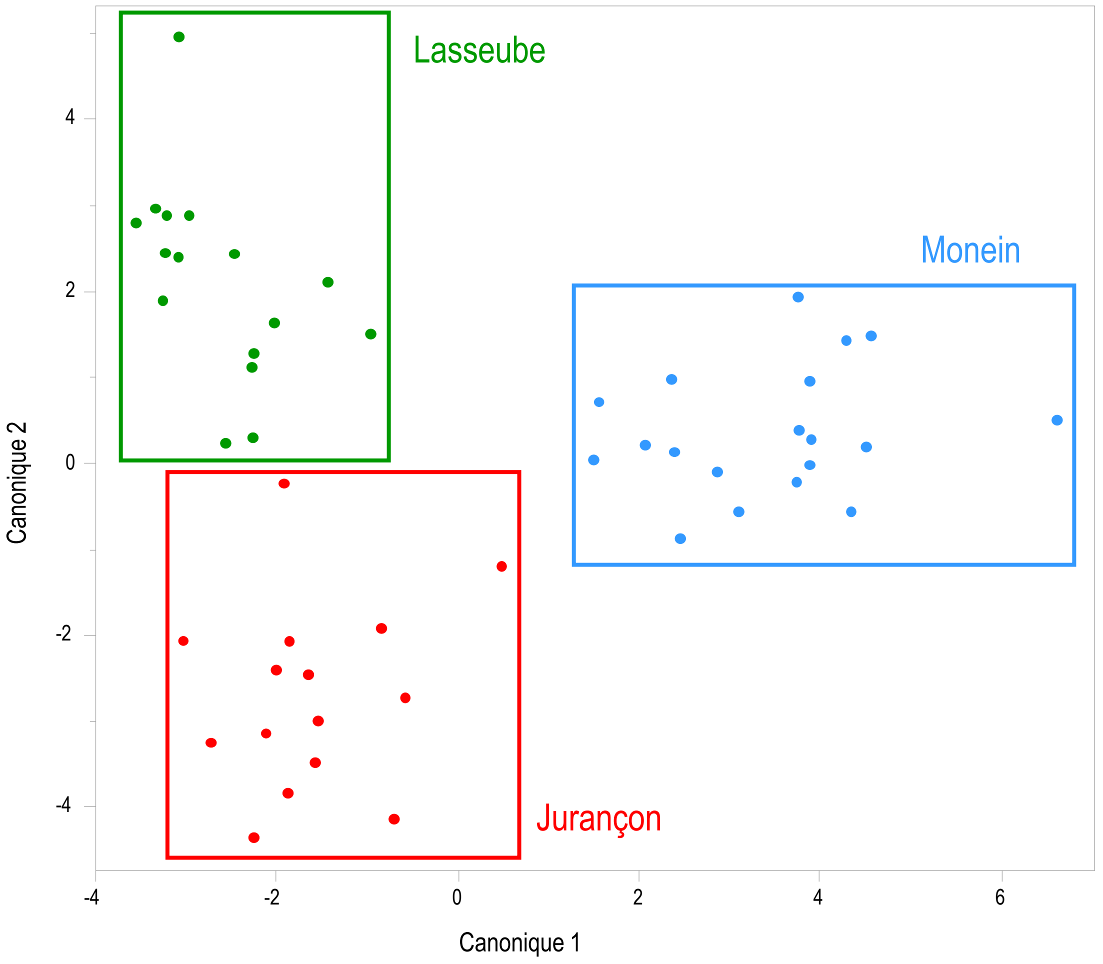
Lambda of Wilk : < 0,0001 (< 0,005)

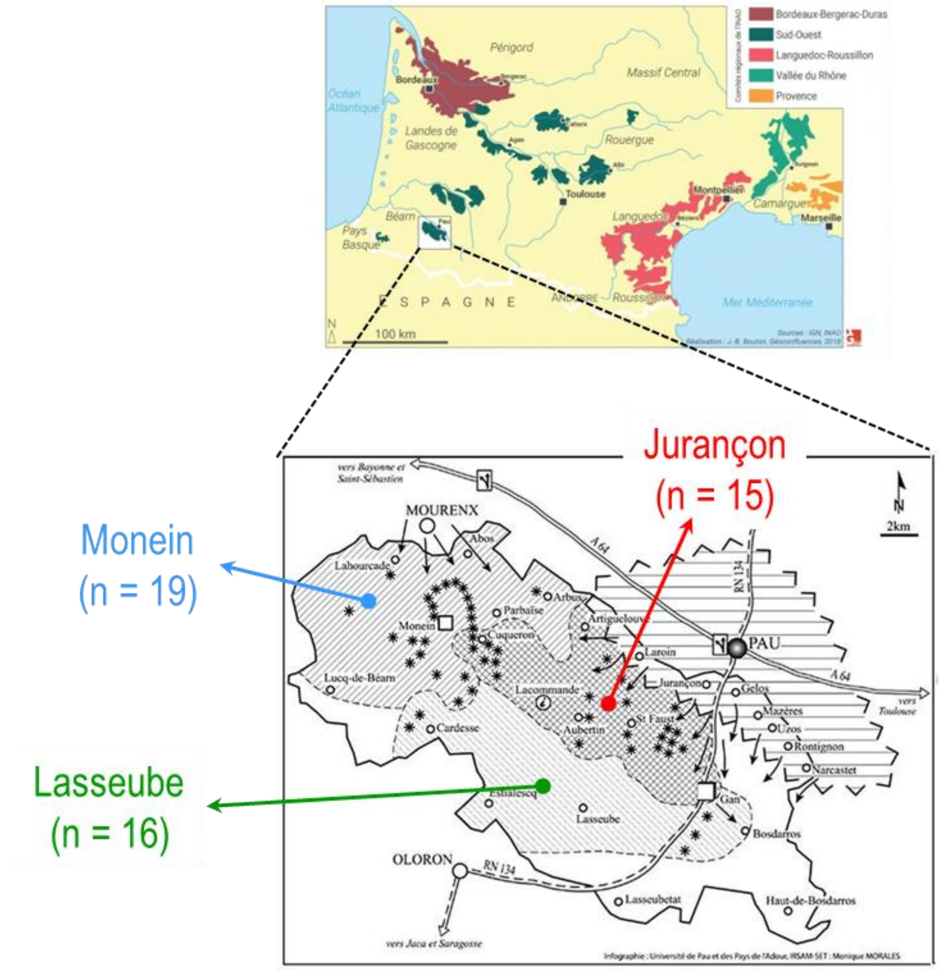
R^2 = 0,9953 (> 0,9)

Application of traditional chemometrics

- Discrimination at the « Vineyard» level : Coteaux de Jurançon

LDA applied to the 23 elements on the 3 "Coteaux de Jurançon"



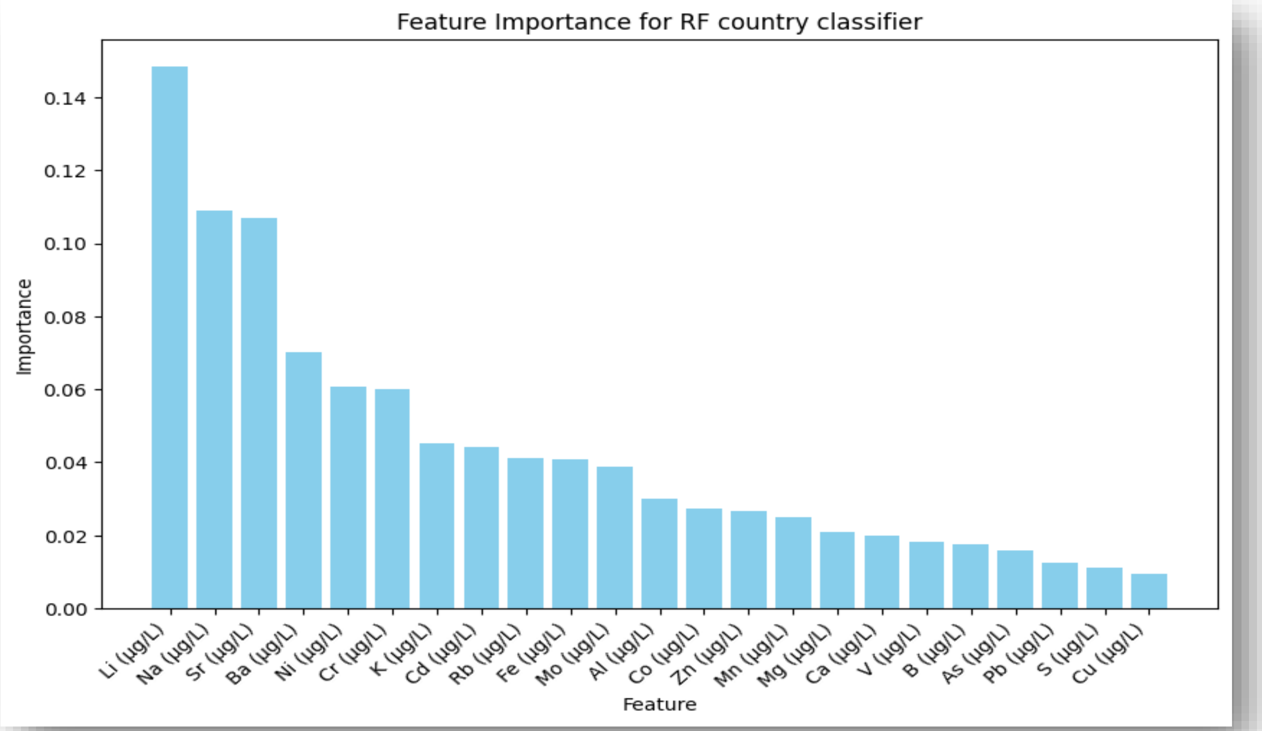


Lambda of Wilk : < 0,0001 (< 0,005)

R^2 = 0,9833 (> 0,9)

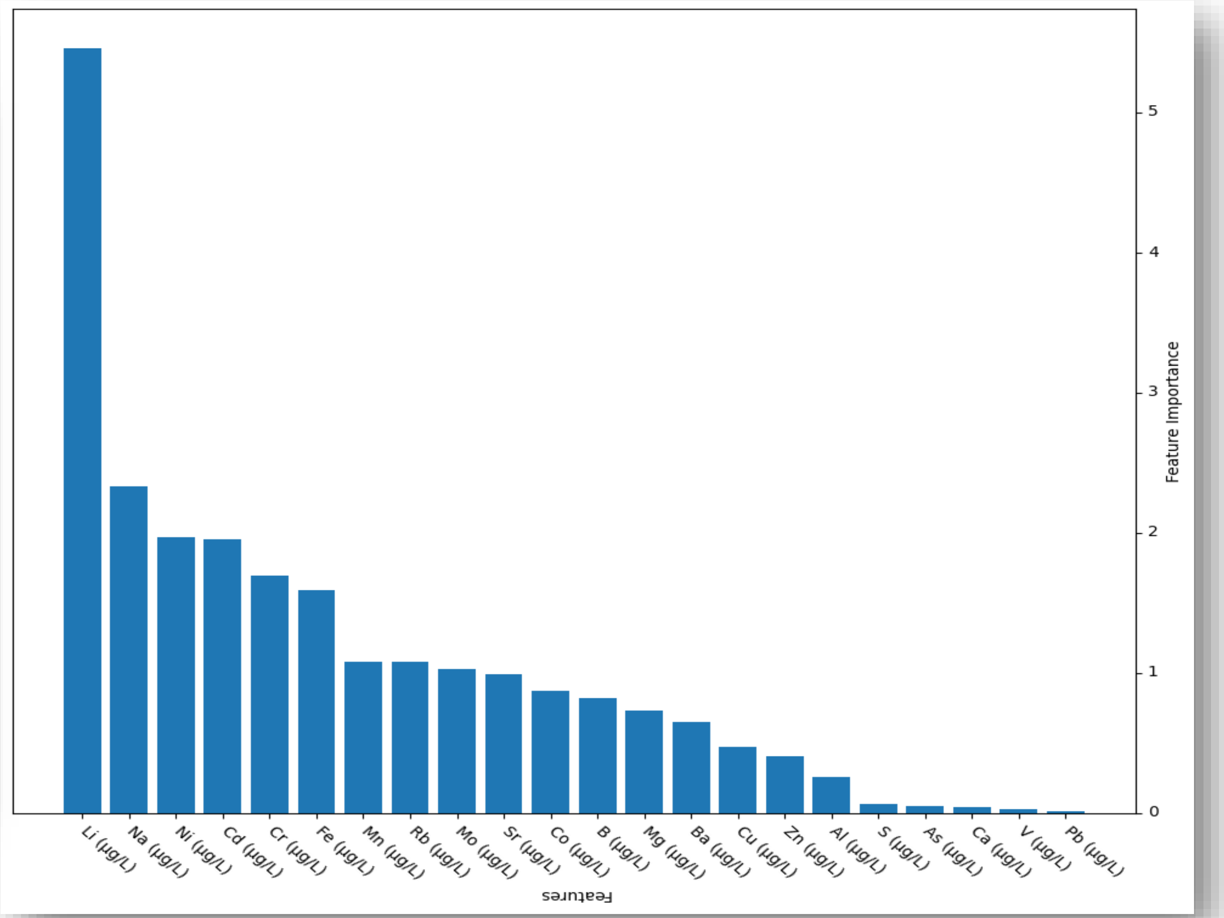
Best classification strategies based on AI and performed on the total European and Magrebin Data Basis

Decision Tree and Random Forest



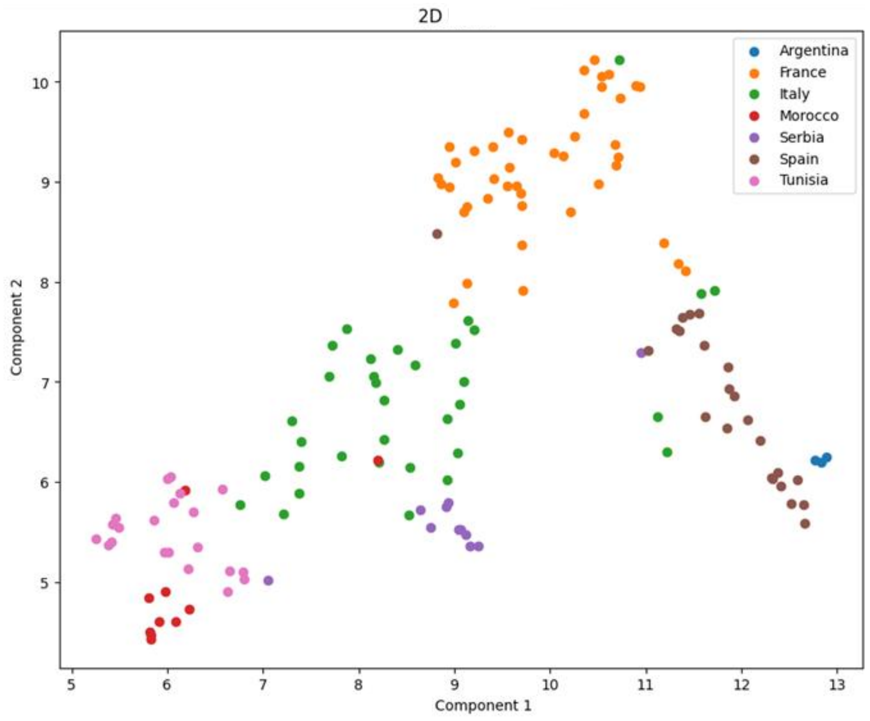
RF model showed 0.9 accuracy in classifying wines by its country of orgin

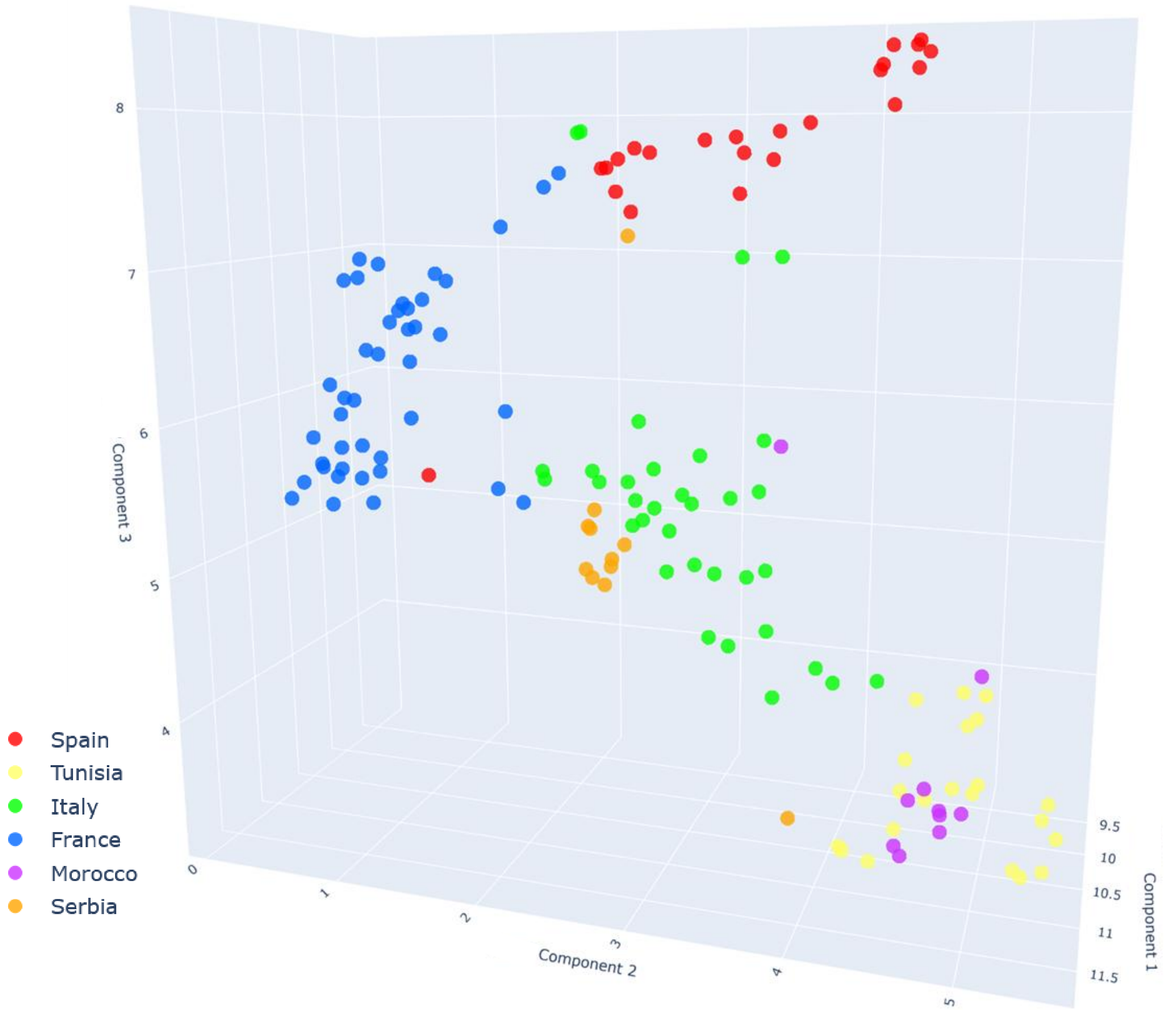
Gradient Boosting Trees



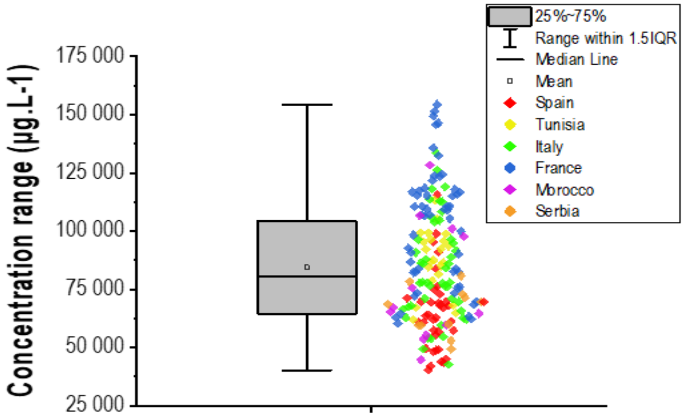
Between XGBoost, LightGBM, and CatBoost, XGBoost model performed best with 0.93 accuracy.

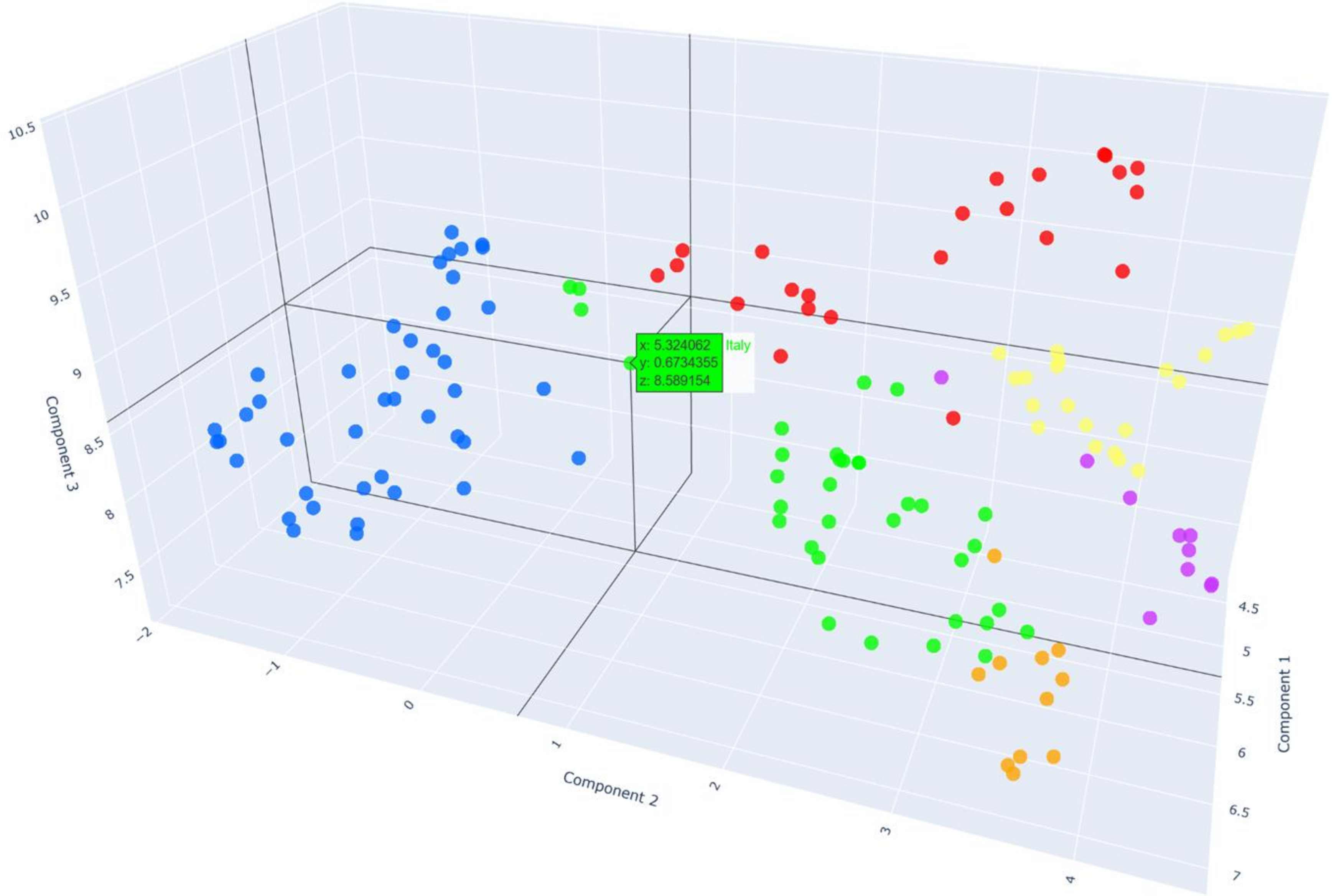
2D and 3D Spatial distribution of the Data Basis

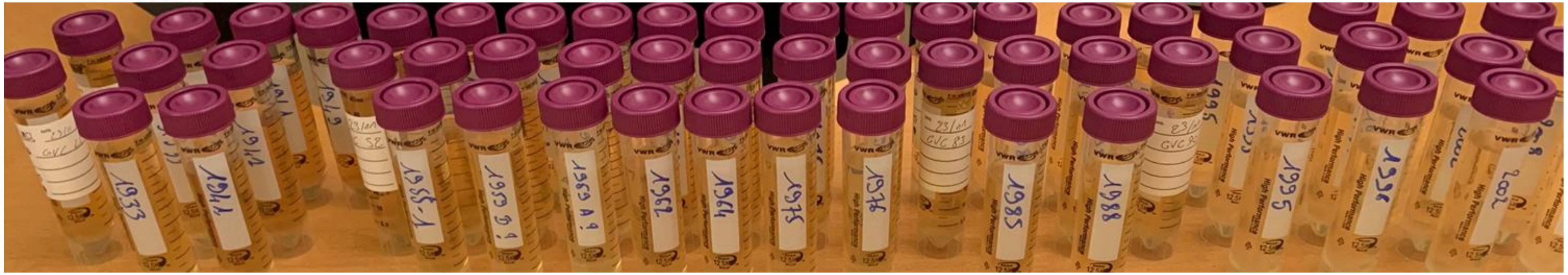




Best 2D and 3D Spatial distribution of the Data Basis after appropriate mathematical operation with agronomical and geogenic relevance : *Evaluation of the spreading performance by specific AI tests*





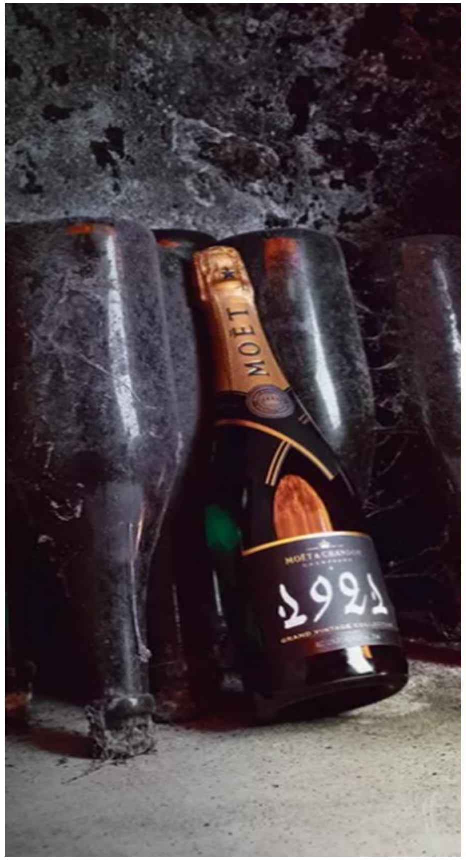


1921-2021: A CENTURY OF GRAND VINTAGES

CHAMPAGNE TASTING IN THE GALERIE IMPERIALE

The samples:

Moët & Chandon Grand Vintage



GRAND VINTAGE COLLECTION **2008** MAGNUM À LA VOLÉE
GRAND VINTAGE COLLECTION **2002** MAGNUM À LA VOLÉE

GRAND VINTAGE COLLECTION **1996** MAGNUM À LA VOLÉE
GRAND VINTAGE COLLECTION **1995** MAGNUM À LA VOLÉE

GRAND VINTAGE COLLECTION **1988** MAGNUM DOSÉ
GRAND VINTAGE COLLECTION **1985** MAGNUM DOSÉ

GRAND VINTAGE COLLECTION **1976** MAGNUM DOSÉ
GRAND VINTAGE COLLECTION **1975** MAGNUM DOSÉ

GRAND VINTAGE COLLECTION **1964** MAGNUM DOSÉ
GRAND VINTAGE COLLECTION **1962** MAGNUM À LA VOLÉE

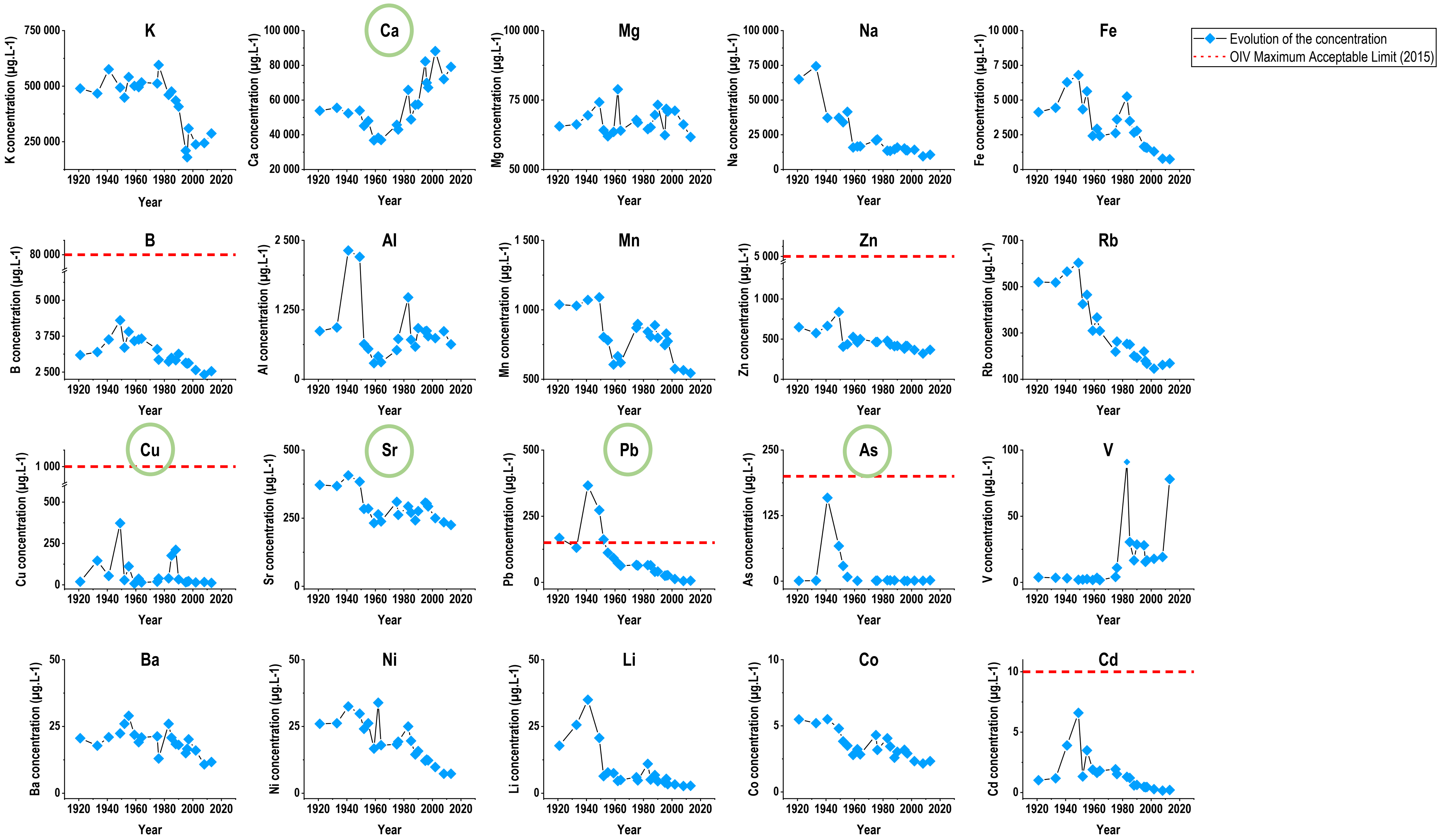
GRAND VINTAGE COLLECTION **1959** MAGNUM À LA VOLÉE
GRAND VINTAGE COLLECTION **1955** BOUTEILLE À LA VOLÉE

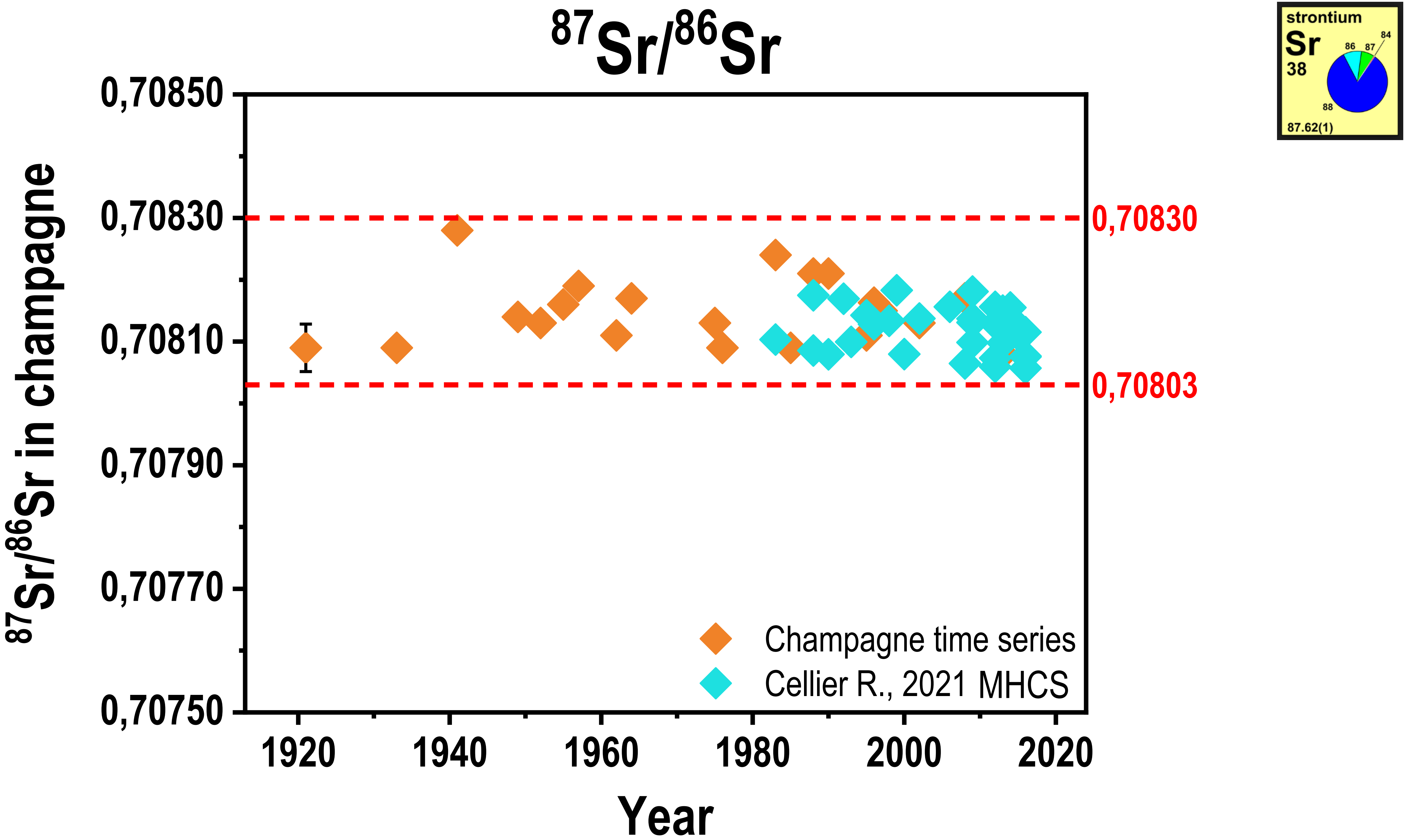
GRAND VINTAGE COLLECTION **1949** BOUTEILLE À LA VOLÉE
GRAND VINTAGE COLLECTION **1941** BOUTEILLE À LA VOLÉE

GRAND VINTAGE COLLECTION **1933** BOUTEILLE À LA VOLÉE

GRAND VINTAGE COLLECTION **1921** BOUTEILLE À LA VOLÉE

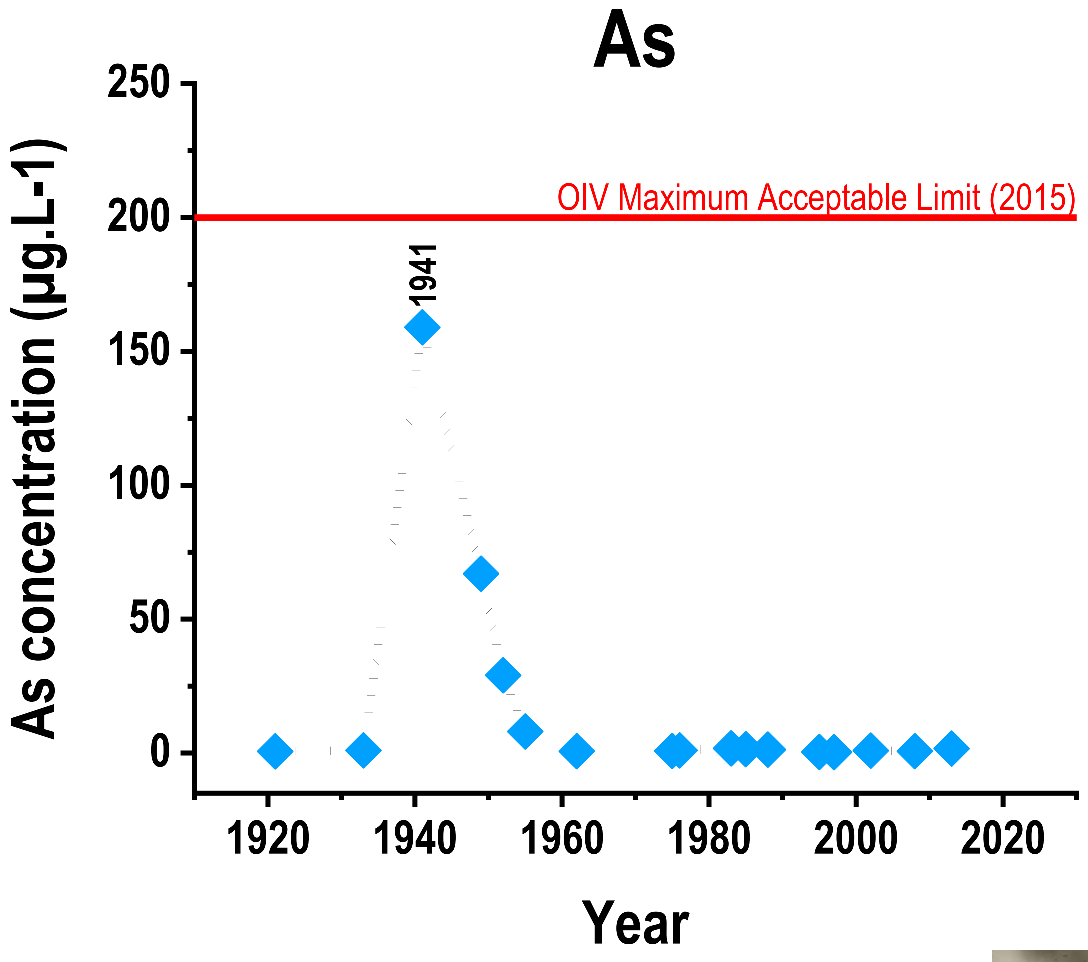
Evolution of elements in Champagne over a century

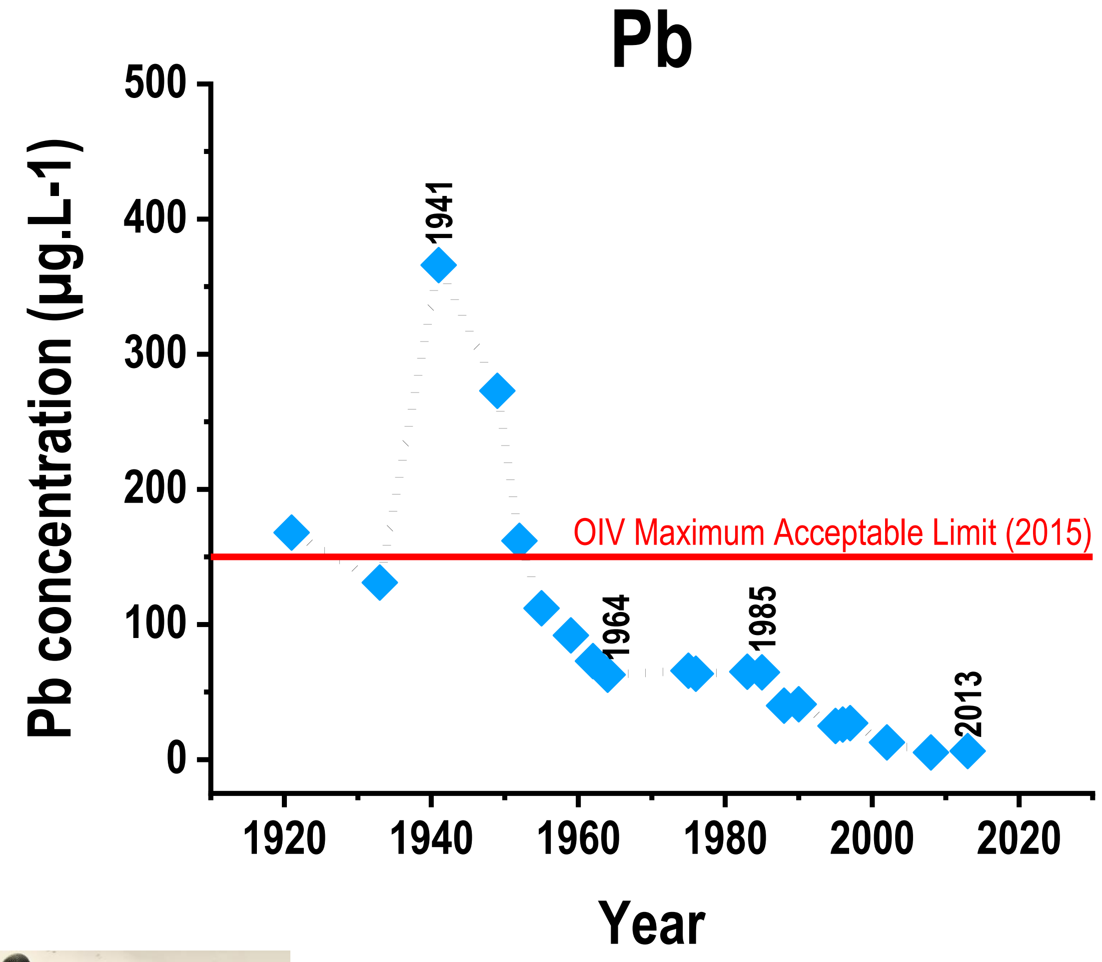




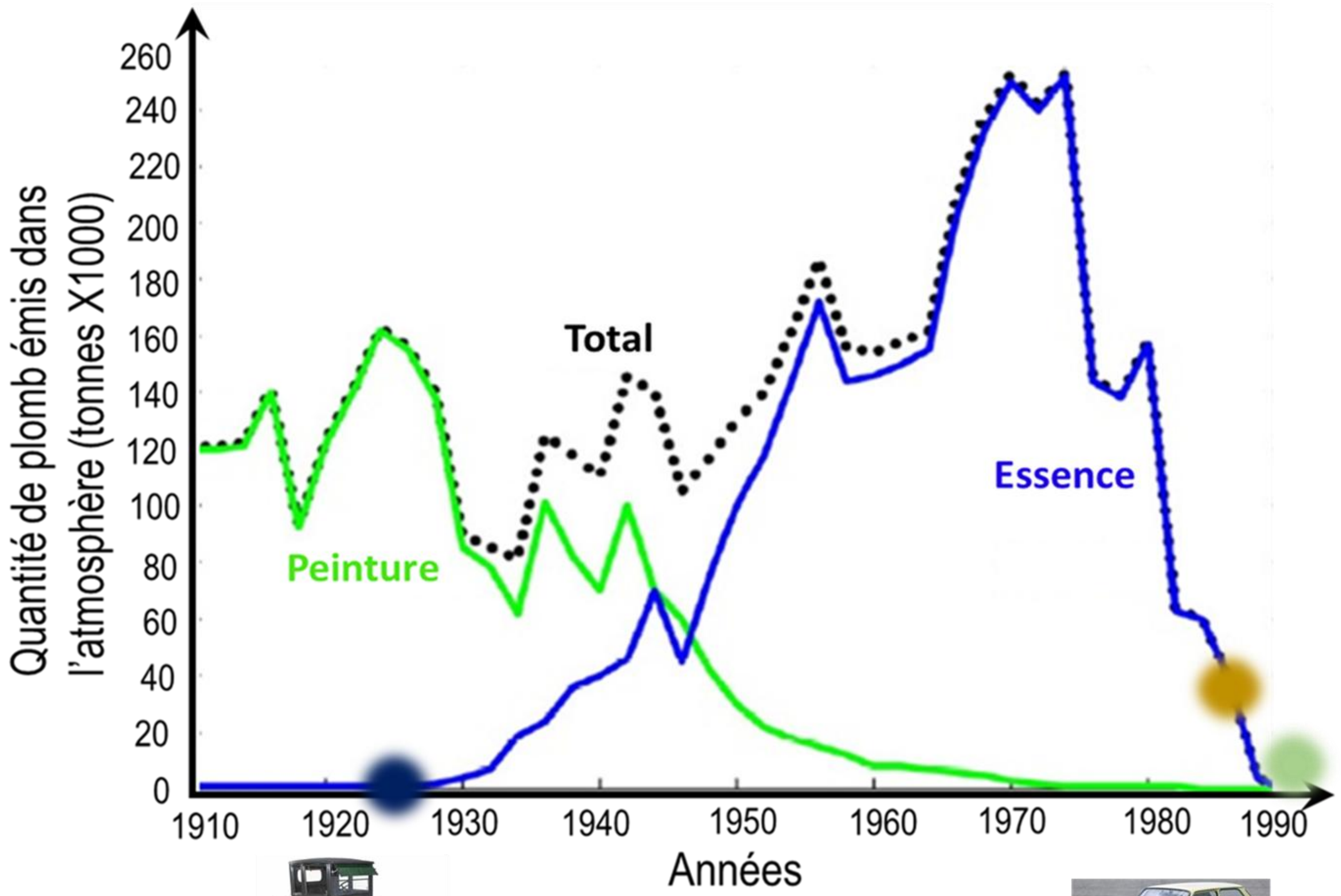
$^{87}Sr/^{86}Sr$
$^{87}Sr/^{86}Sr$ in champagne
0,70850
0,70830
0,70810
0,70790
0,70770
0,70750
0,70830
0,70803
1920
1940
1960
1980
2000
2020
Year
Champagne time series
Cellier R., 2021 MHCS
strontium
Sr
38
86
87
84
88
87.62(1)

As & Pb concentrations in Champagne during 1940 to 1945

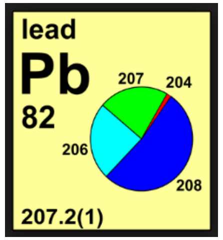


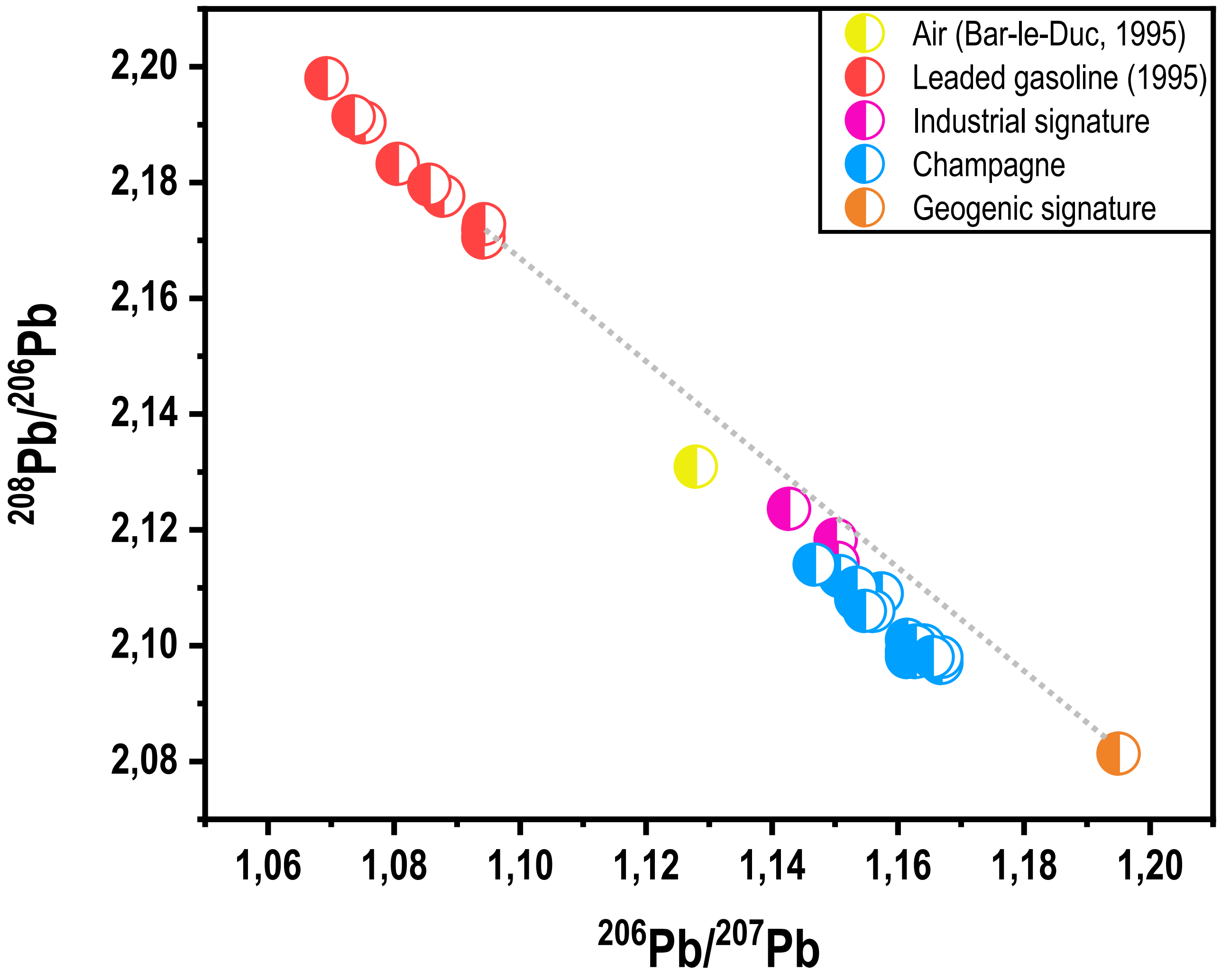


Historical evolution of Pb emissions in the atmosphere



Pb isotopic signatures in Champagne: tracing the sources

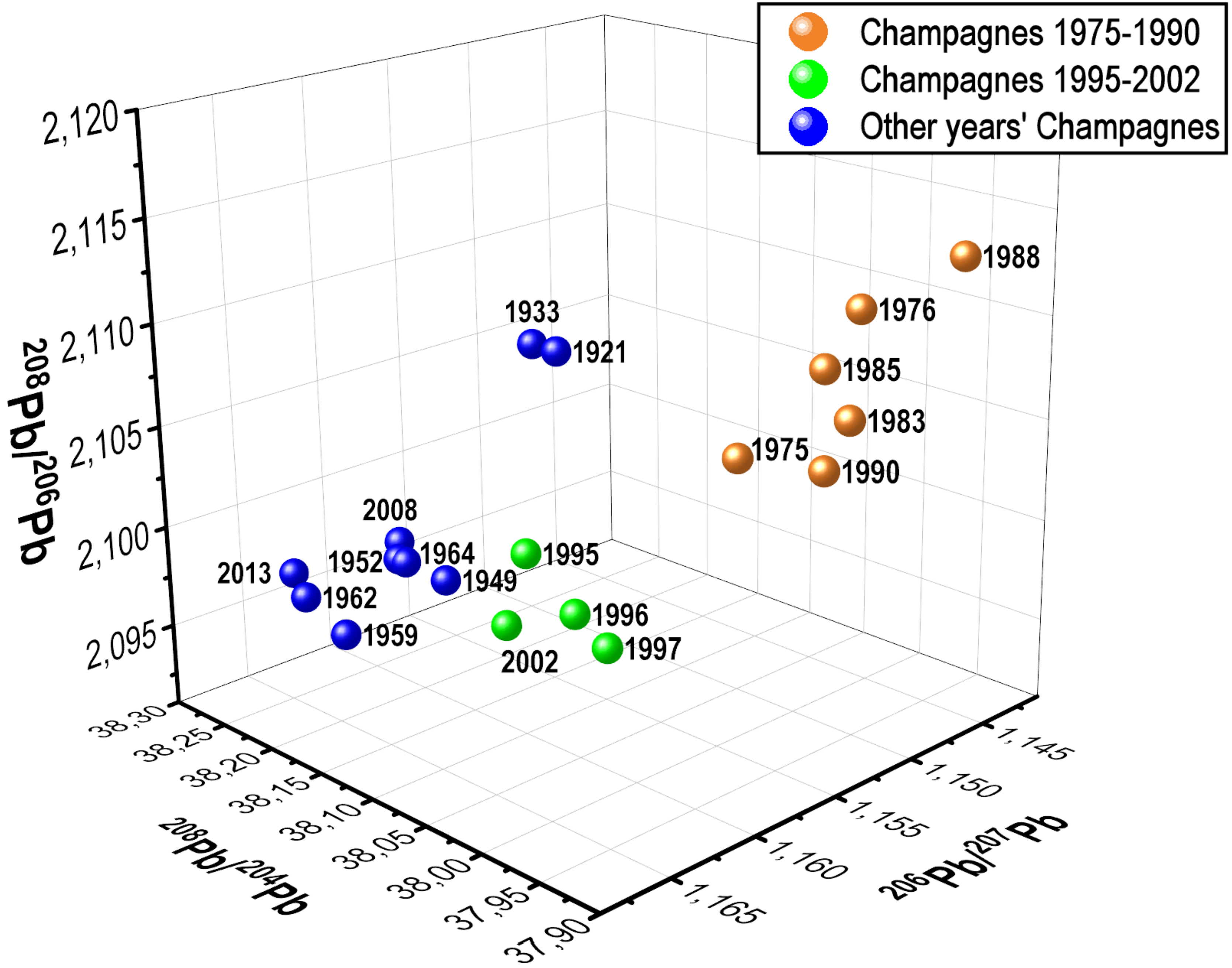


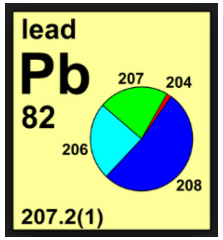


Potential of lead elemental and isotopic signatures for authenticity and geographical origin of Bordeaux wines Epova, E.N., Bérail, S., Séby, F., Barre, J.P.G., Vacchina, V., Médina, B., Sarthou, L., Donard, O.F.X. (2020) Food Chemistry, 303, art. no. 125277

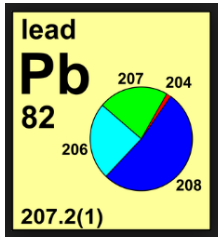
Multi-element and multi-isotopic profiles of Port and Douro wines as tracers for authenticity Coelho, I., Matos, A.S., Epova, E.N., Barre, J., Cellier, R., Ogrinc, N., Castanheira, I., Bordado, J., Donard, O.F.X.(2023) Journal of Food Composition and Analysis, 115, art. no. 104988, .

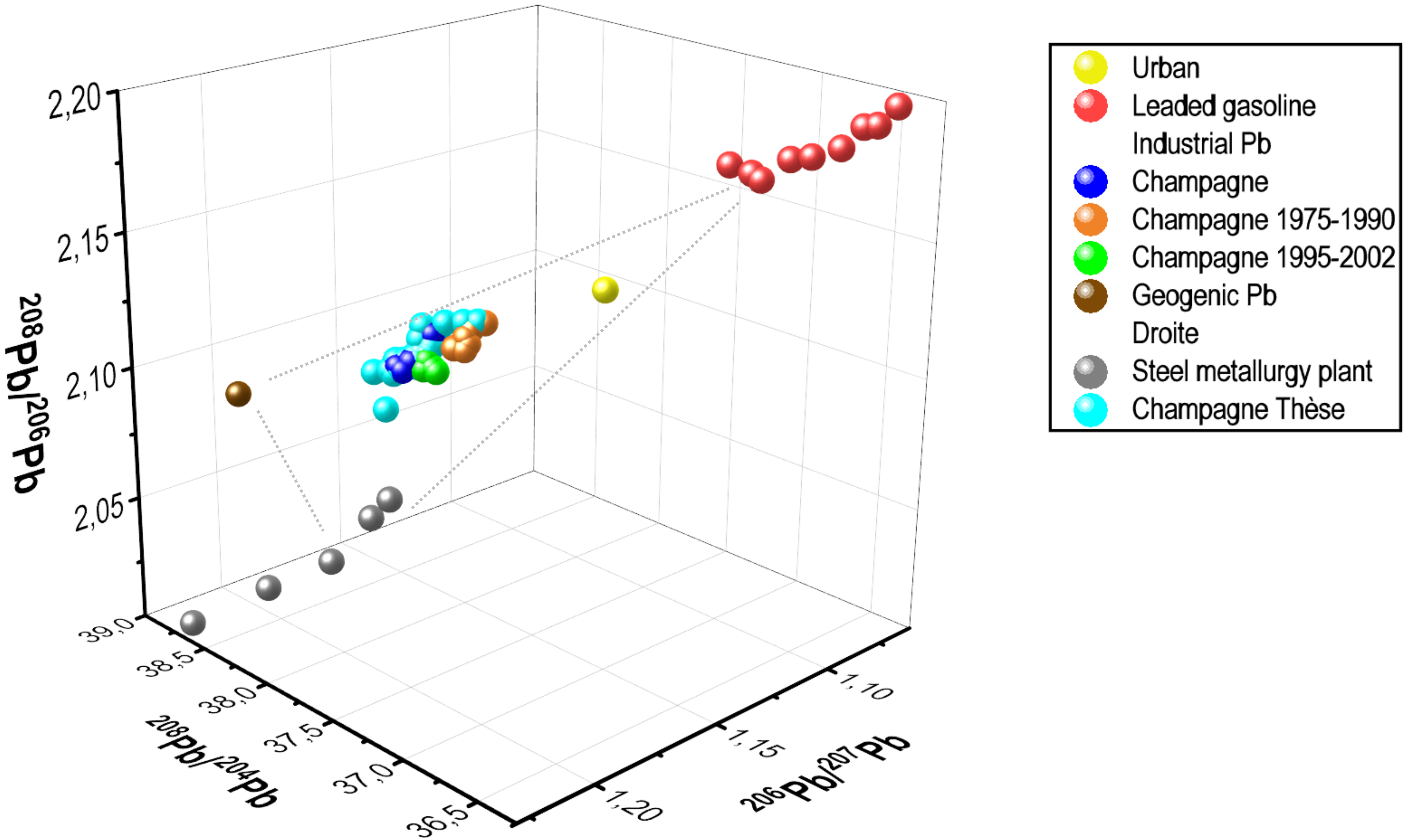
Pb isotopic signatures in Champagne and in time: tracing the sources



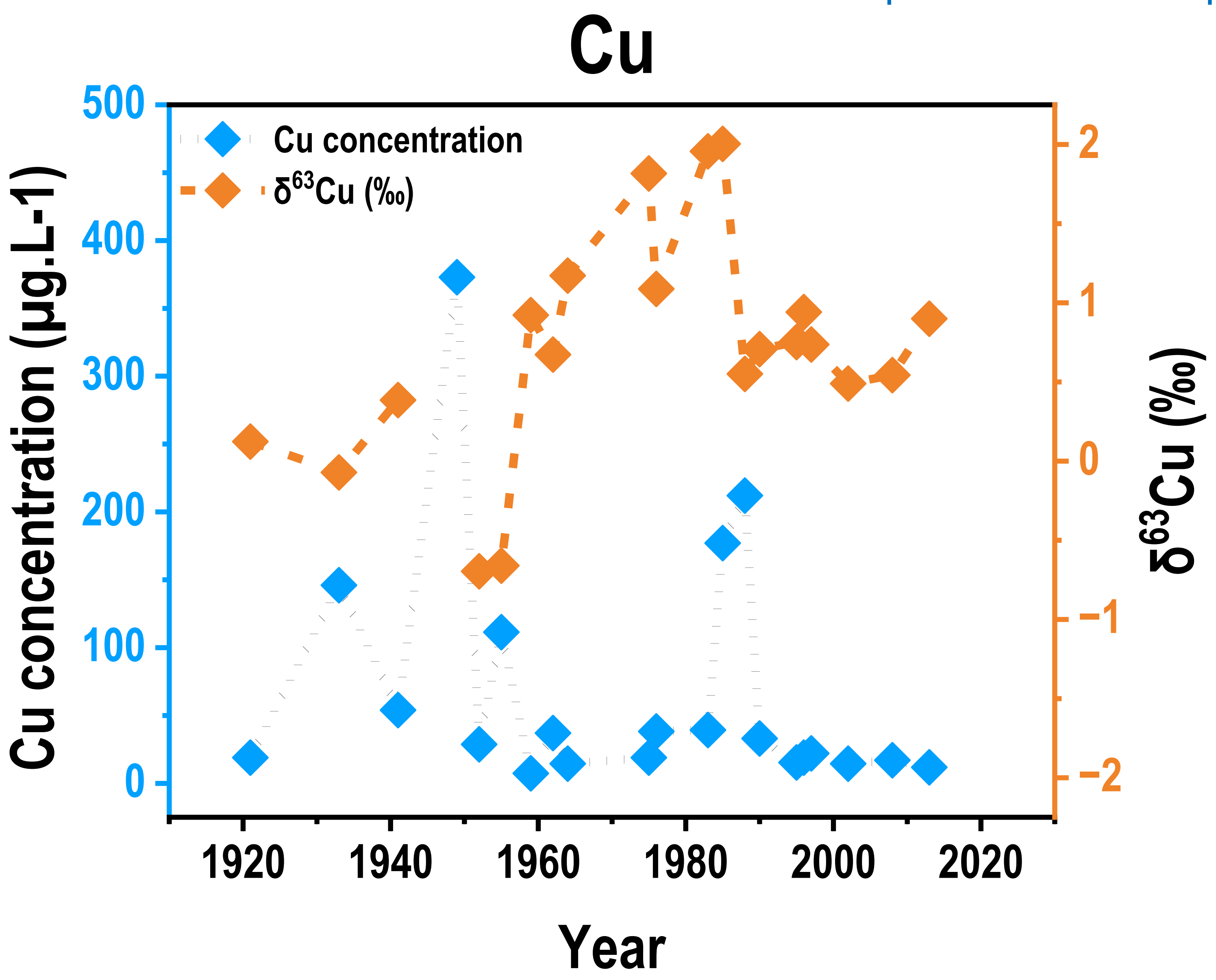


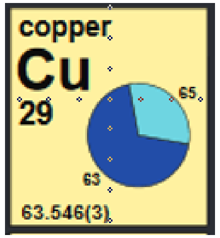
Unravelling the sources of Pb in Champagne over the century



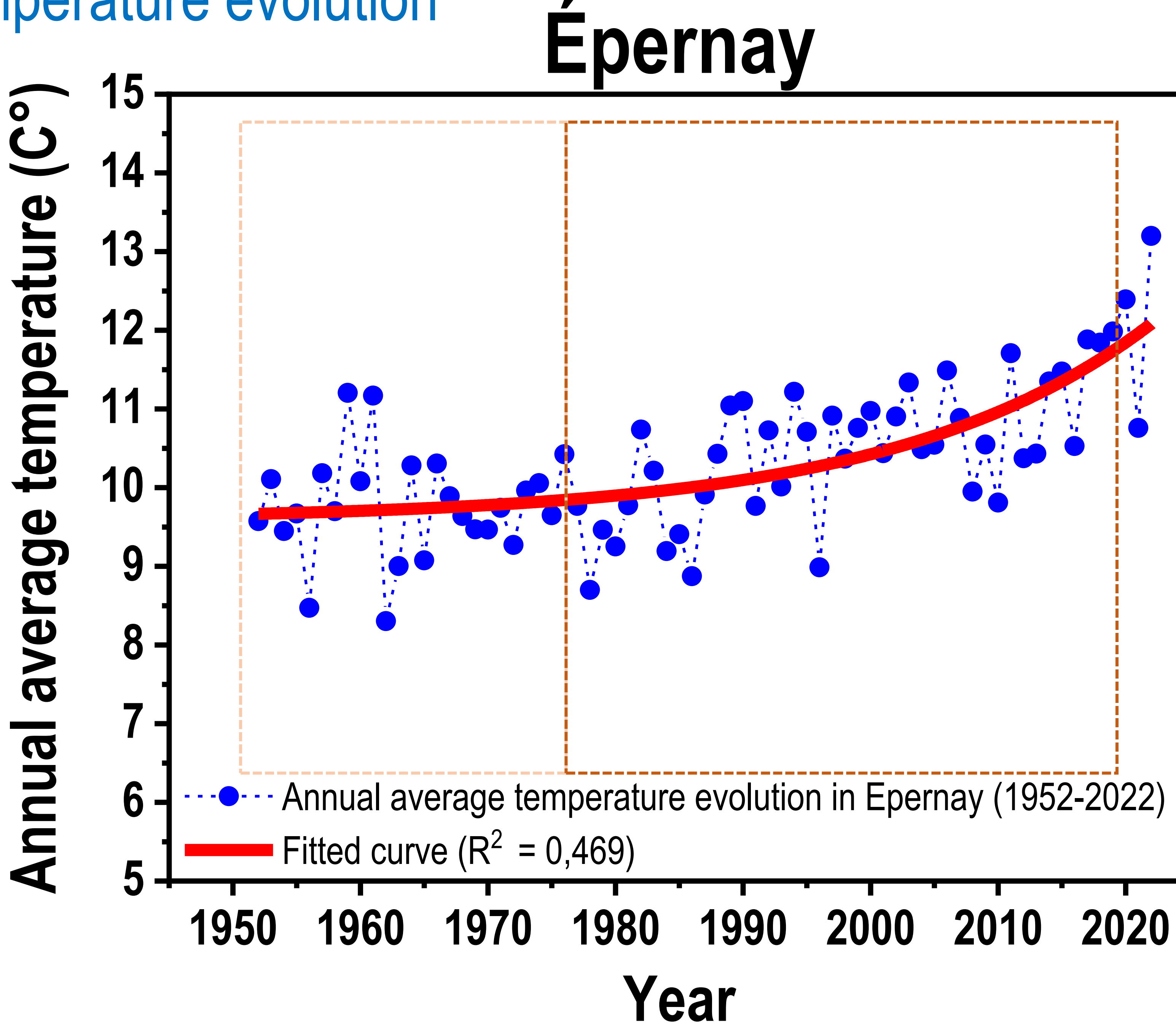


Evolution of the Cu sources and wine treatment process in Champagne over the century



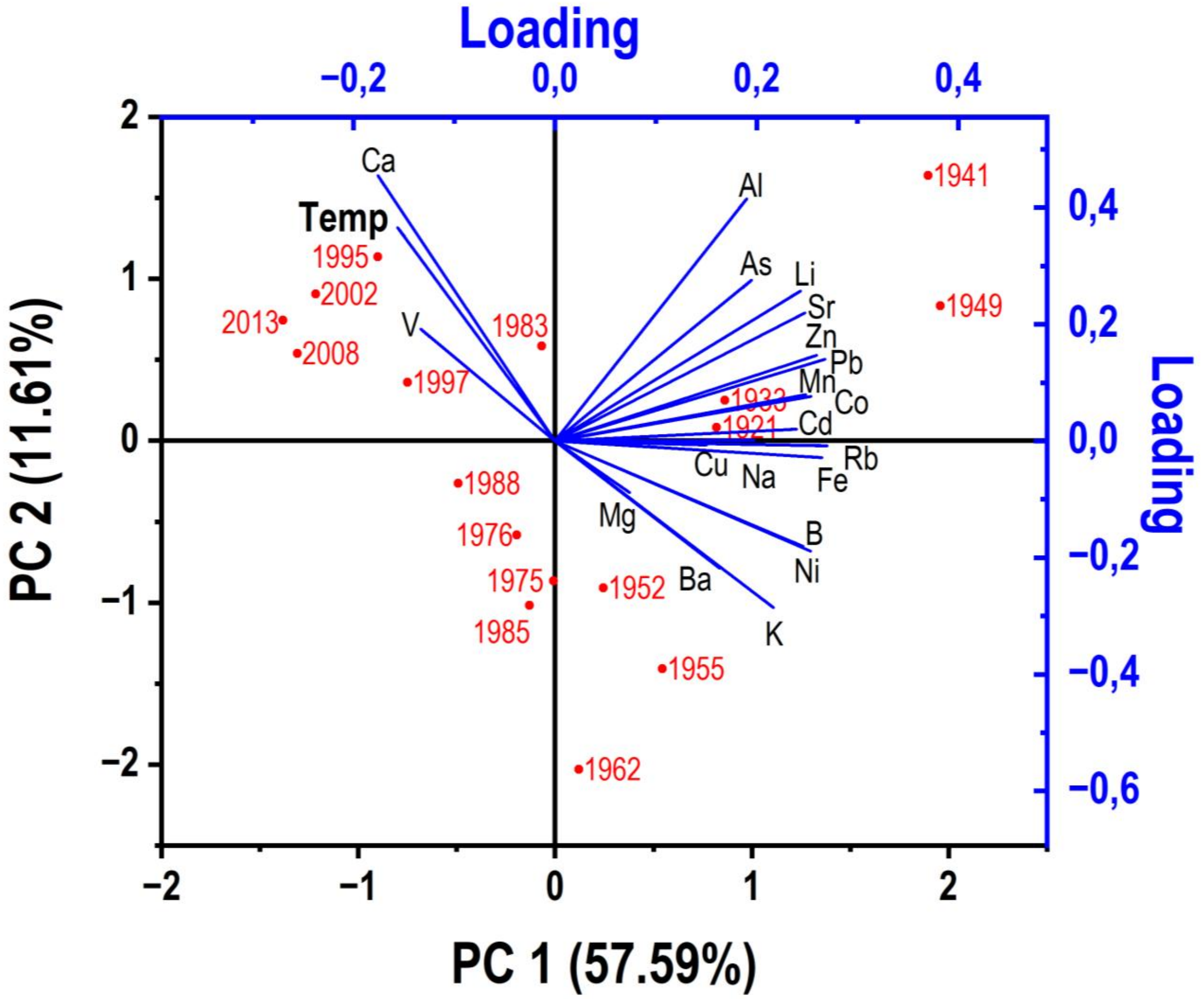


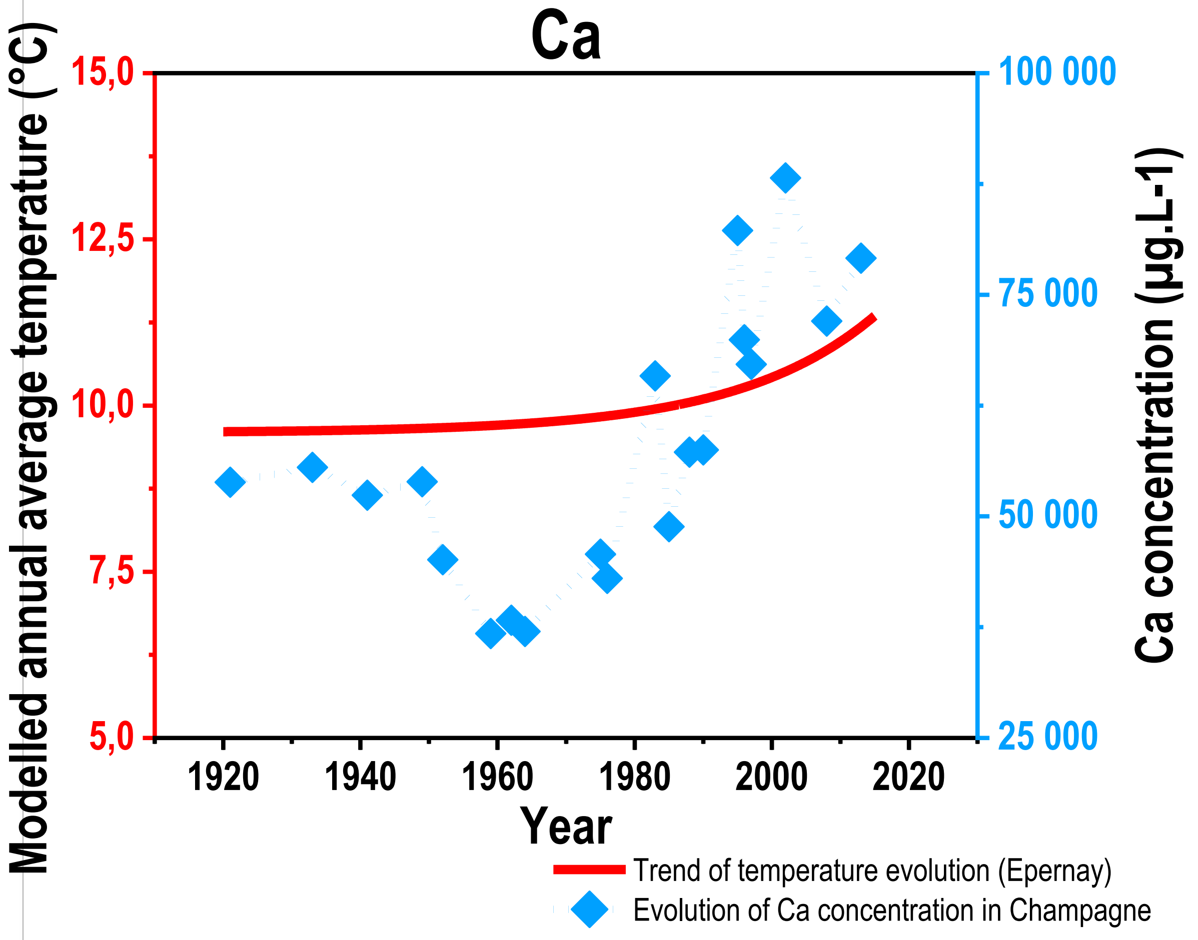
Climate: temperature evolution



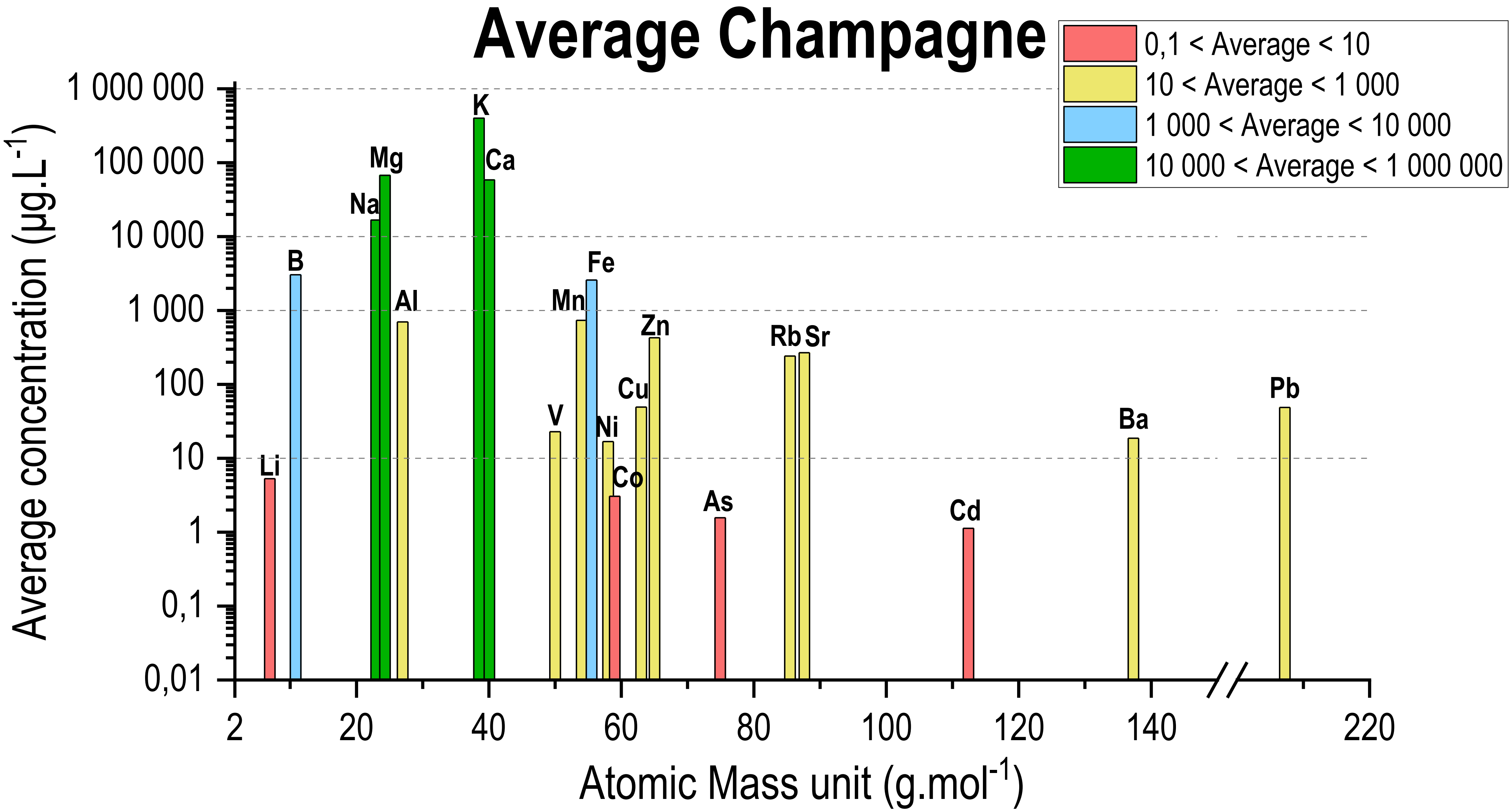
Annual temperatures were extracted from ERA5-Land data (from 1952 to present)

Role of temperature

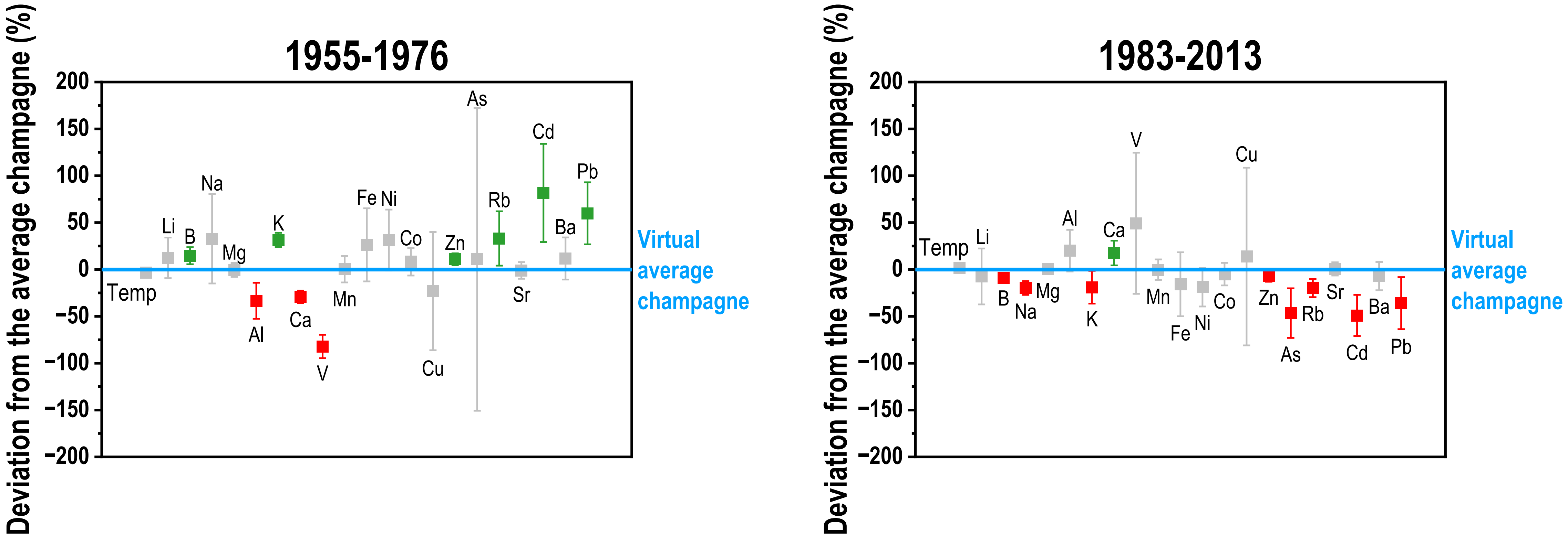




Typical average concentrations of elements between 1955 up to 2013 in Champagne



Possible impact of climate change on the elements partitioning in Champagne



Significantly **higher** than average champagne concentration (95%)
Not significantly different from average champagne (95%)
Significantly **lower** than average champagne concentration (95%)

UAB
Universitat Autònoma de Barcelona

VITEC
CENTRO TECNOLÓGICO DEL VINO

UNIVERSITÀ DI PISA

INNOLABS

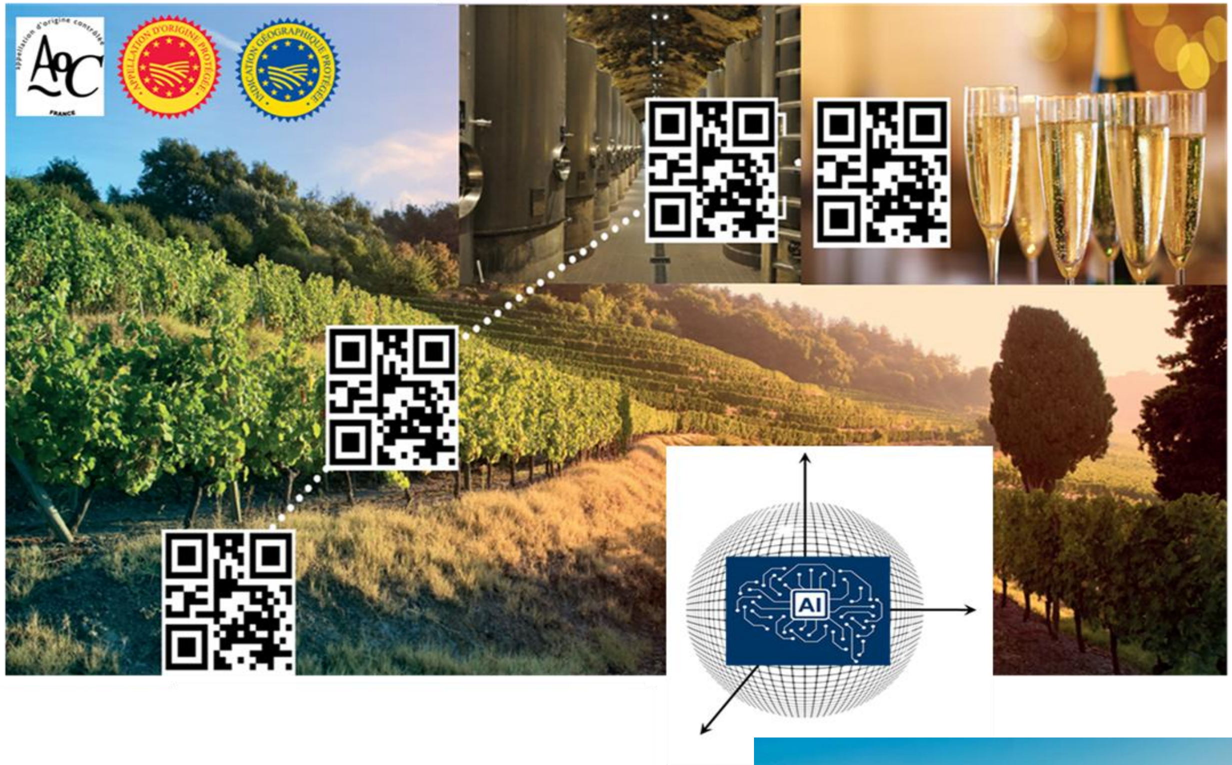
Plantaže

INTI

UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

UT2A
Ultra Traces Analyses Aquitaine

DUNAV NET



TRACE WINDU

Commission européenne

Relevance

In supermarkets worldwide, at least 10% of the
products have been adulterated.
Studies estimate that food fraud costs
the global food industry between

US $10 billion and US $ 50 billion
a year.





Source: https://illicittrade.com/infographics

Quality Policy regarding food geographical origin

Protected Designation of Origin
PDO

Protected Geographical Indication
PGI

Traditional Speciality Guaranteed
TSG

Geographical Indications of food products

Appellation d'Origine Contrôlée (Since 1919)

Wines
over 300 wines

Liquors and alcohols
25 products

Olives, Olive oil
13 products

Honey
Corse, Vosges

Cheese
45 French cheeses

Beef and Lamb
7 products

Poultry
4 products

Milk, Butter, Cream
52 products

Lentils
de Le Puy-en-Velay

Sea food
Mont Saint-Michel

Fruits
7 products

Lavender
Essentielle oil

appellation d'origine contrôlée
AOC
FRANCE

APPELLATION D'ORIGINE PROTÉGÉE