

Geochemical characterization of Ribera de Duero wines: Integrating $^{87}\text{Sr}/^{86}\text{Sr}$ and elemental profiling for origin assessment



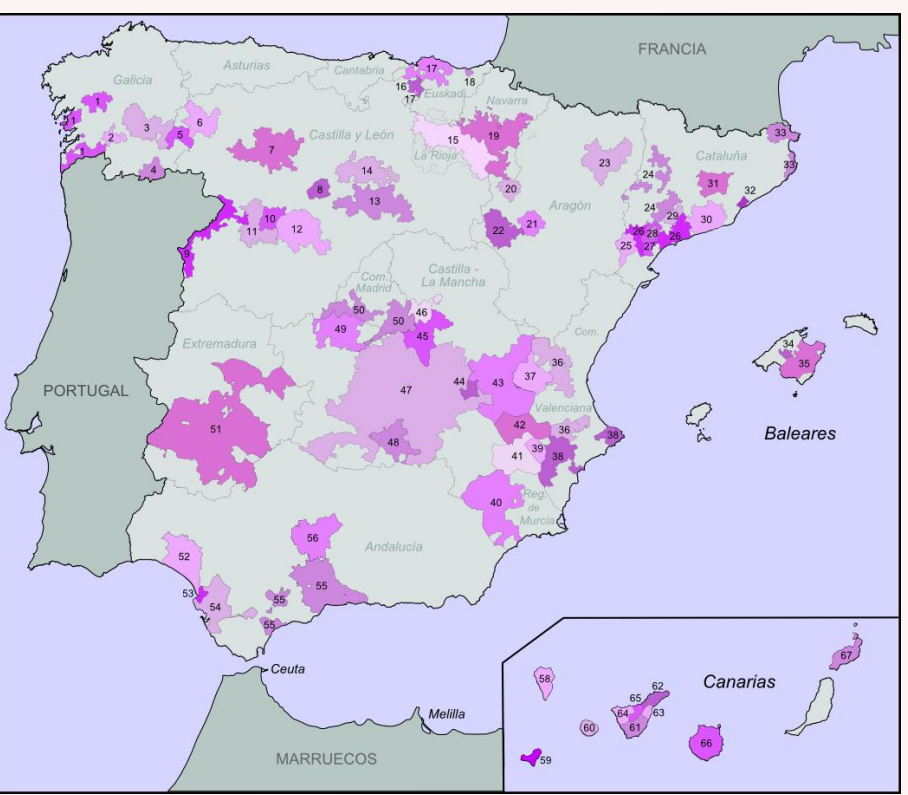
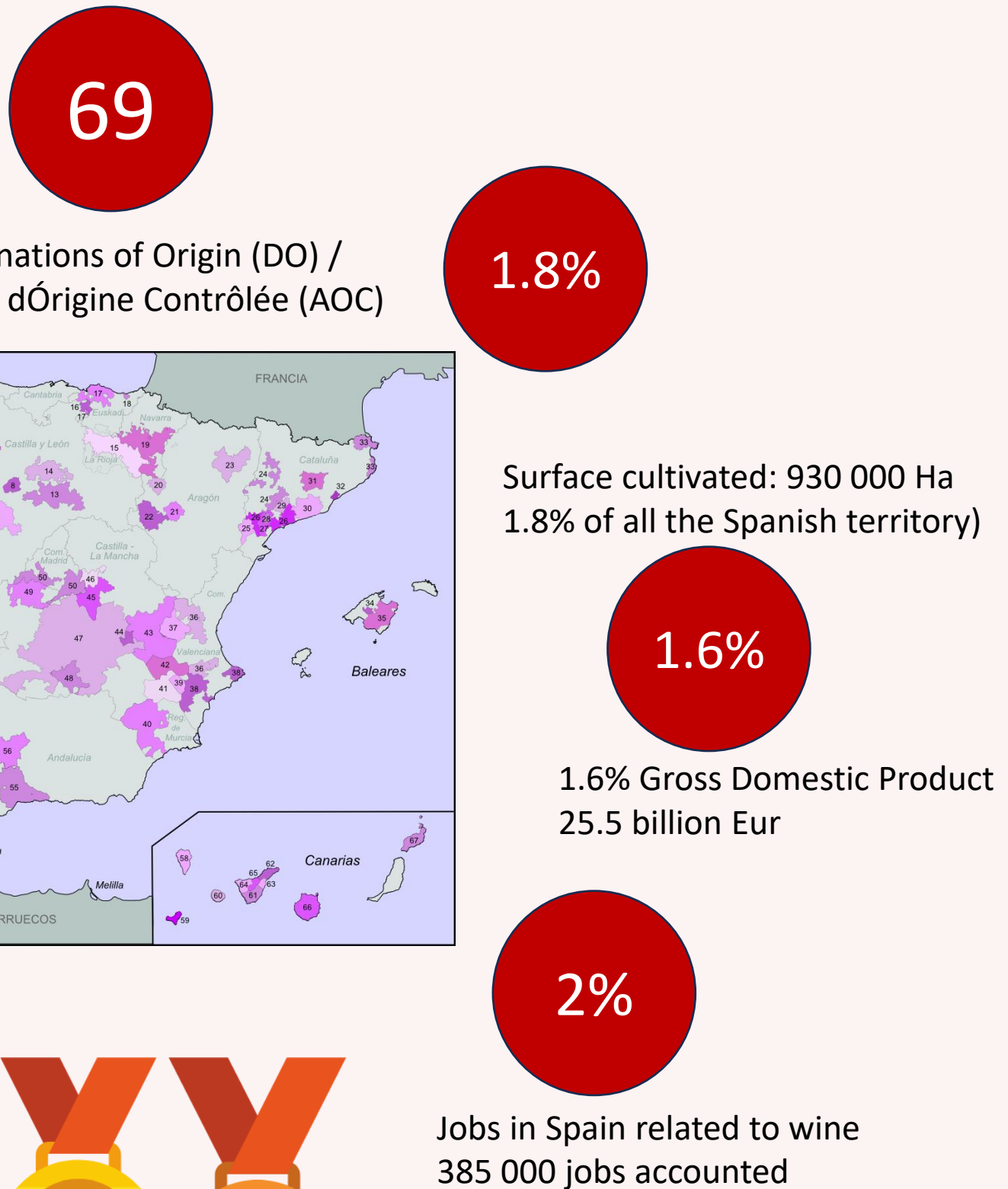
Abstract
In this study, we investigate the combined use of Sr-isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) and multi-elemental composition to assess the geographical traceability of wines from the Ribera del Duero Protected Denomination of Origin (PDO). Several wine samples from different wineries and representative grape varieties from Ribera del Duero were analyzed. Major and selected trace elements were determined by ICP-OES and ICP-MS, while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured using MC-ICP-MS. Multivariate statistical analysis, including Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), were applied to evaluate the discriminating power of the combined geochemical dataset. The results show that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range between 0.7090 and 0.7097, reflecting the regional geological background but providing limited resolution when considered alone. In contrast, the integration of Sr-isotope data with elemental composition significantly improves the differentiation of wine samples according to their geographical origin. Multivariate models reveal coherent groupings that correspond to geological variability within the PDO area.



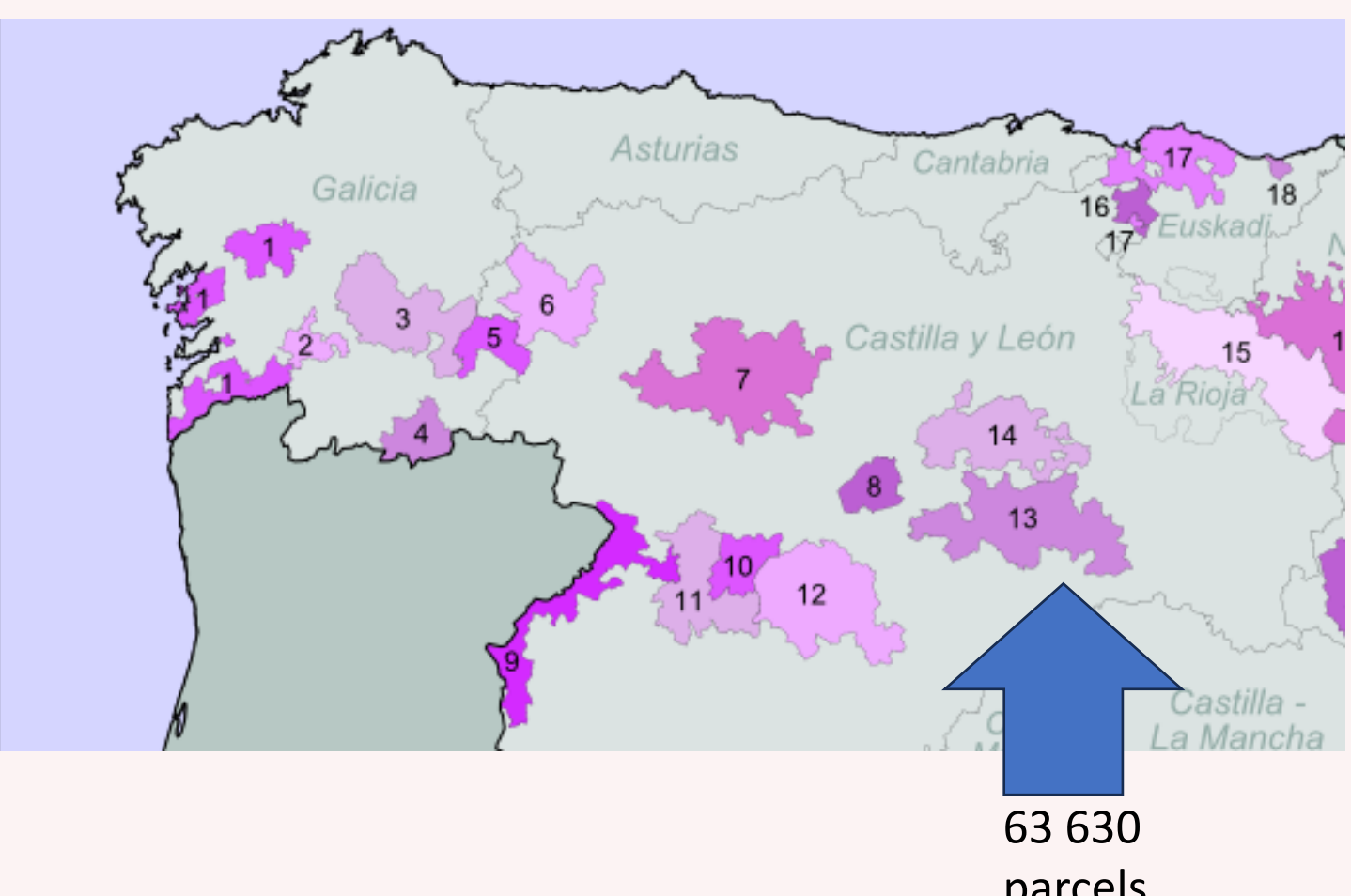
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The Wine in Spain

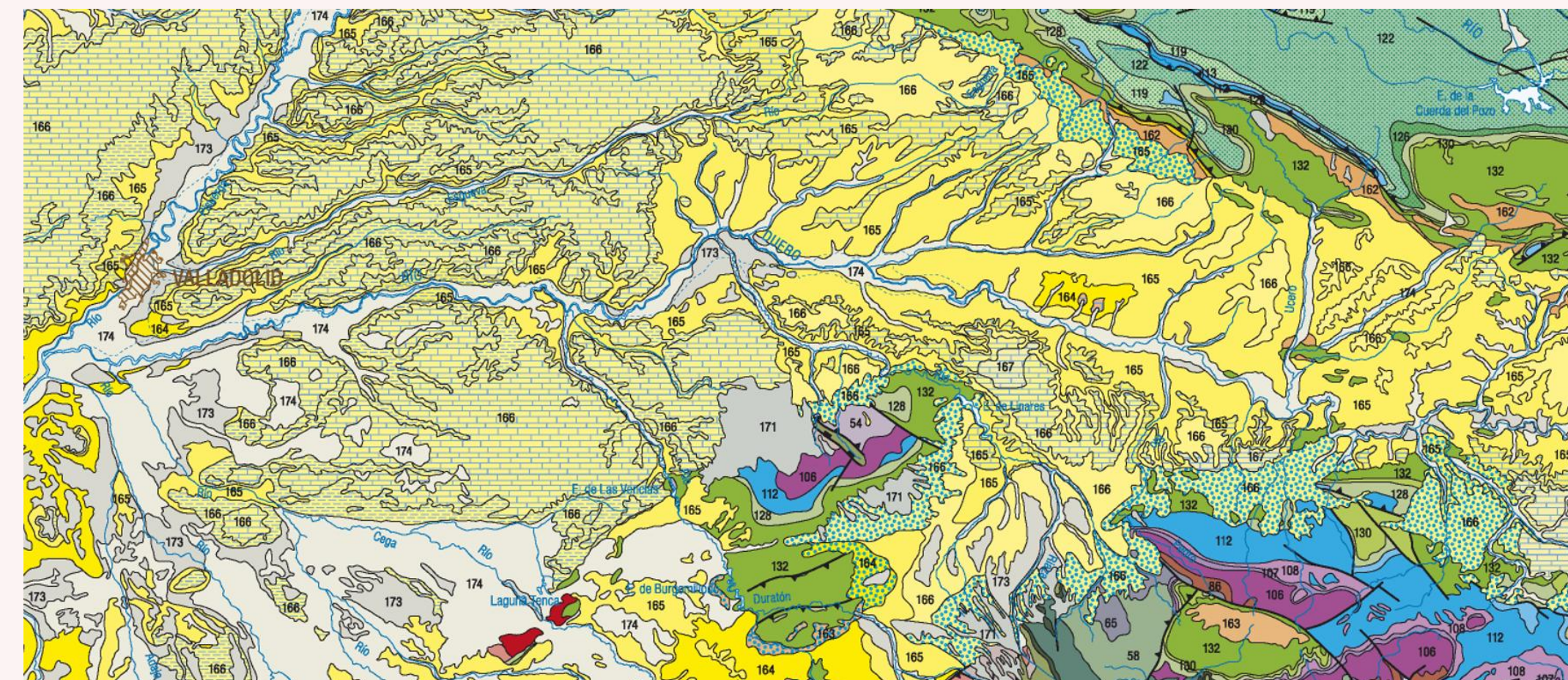


Ribera de Duero DO



Geology of the Ribera del Duero DO

The DO extends stretches for 115 km along the Duero riverbanks. The altitude ranges 720 – 1100 m. Soil layers of silt, sand, clay, limestone and calcareous concretions. The mediterranean / continental climatology dominate the region. Semiarid conditions, low rainfall, extreme temperatures.



- 17x (river); Quaternary deposits
- 164-166 (Miocene sandstone, clasts, lutite, limestone and gypsum)
- 132 (green parts) cretacic limestone and sandstone
- 106-112 Jurassic and triassic formations

Ribera de Duero and Archaeology

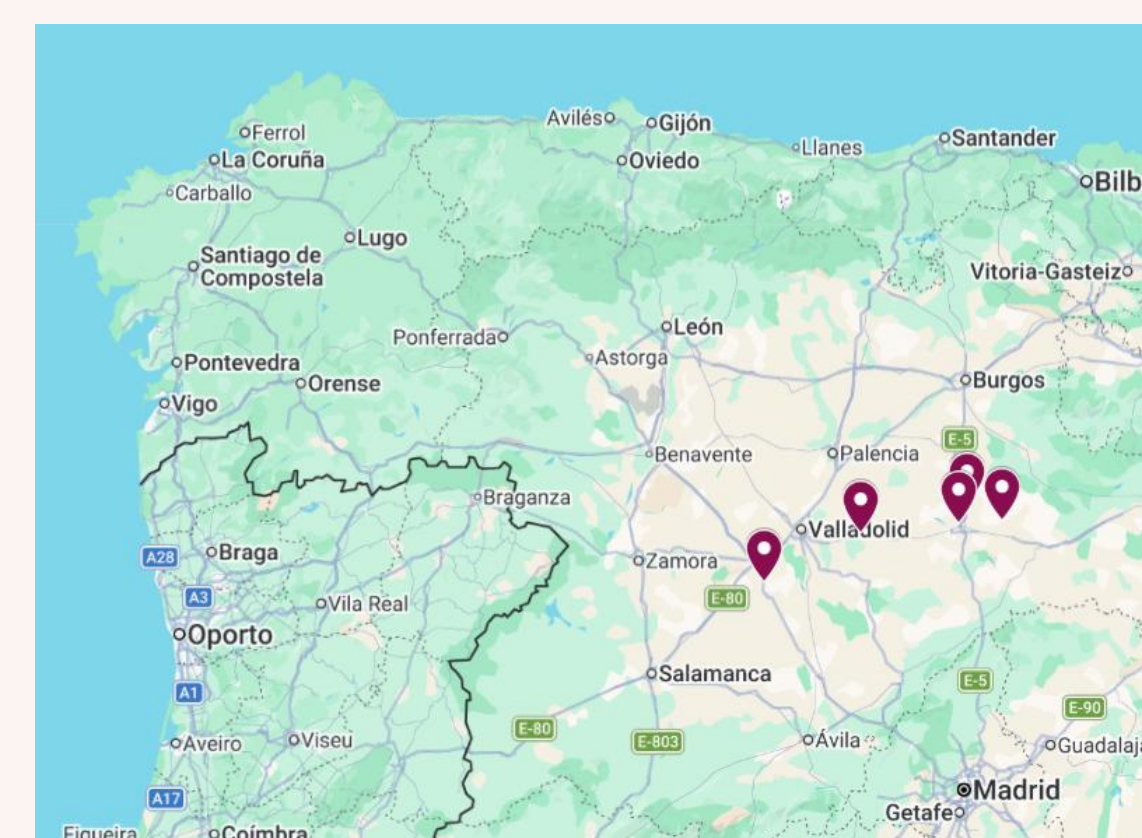


The samples in this Study

We collected several samples directly from the producers. The criteria of eligibility were:

- Wine should be made of grapes collected in only single parcel.
- Organic Culture (no industrial fertilizers).
- All grape varieties are allowed (not controlled variable).

We included one wine from a different DO (Rueda).



The aim

- We want to differentiate wine from different D.O. and different wineries from the same D.O. independently of:
 - The alcohol grade of the wine.
 - The grape variety.
 - The climate conditions (rain) or watering activities.

The tools

- Ethanol determination
- Elemental composition.
- Main anion composition.
- Strontium isotope ratios.

The methods

O Ethanol

CG-FID
0.5 μL injected
Split mode 40%
Isopropanol internal standard
BP40 wax type column

A Ions

Ion Chromatography
Ionic suppression
PVA-quaternary amine
Mobile phase: $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$
buffer pH 9.8
Modifier: CH_3OH

C Elements and isotopes

Digestion
Ultrawave SRC with $\text{HNO}_3/\text{H}_2\text{O}_2$
Sr separation with Sr-resin SPE cartridges

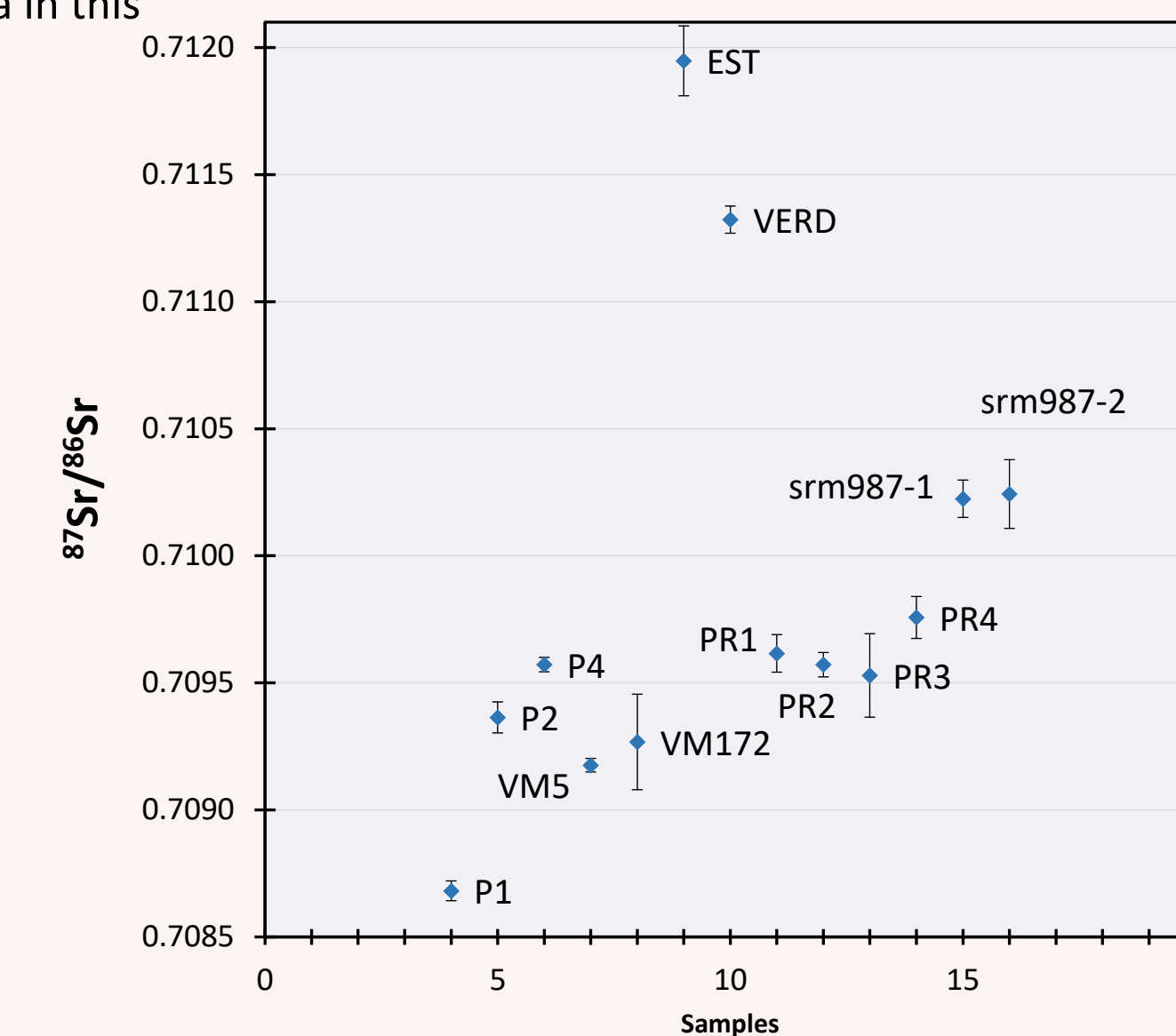
ICP-MS
RF: 1250 W
Micromist PFA neb 100 $\mu\text{L}\cdot\text{min}^{-1}$
Rh internal standard
Variable resolution from R=400 to R=10000

MC ICP-MS
RF: 1200 W
Micromist PFA neb 100 $\mu\text{L}\cdot\text{min}^{-1}$
Static mode ; FC-SEM configuration
10 repetitions
Kr correction
Sample bracketing with NIST SRM 987

Next:

We are looking for partners and researchers to include other regions and D.O. We are increasing the sample population to cover all this D.O. We plan to include the soils in the study

Results & Discussion

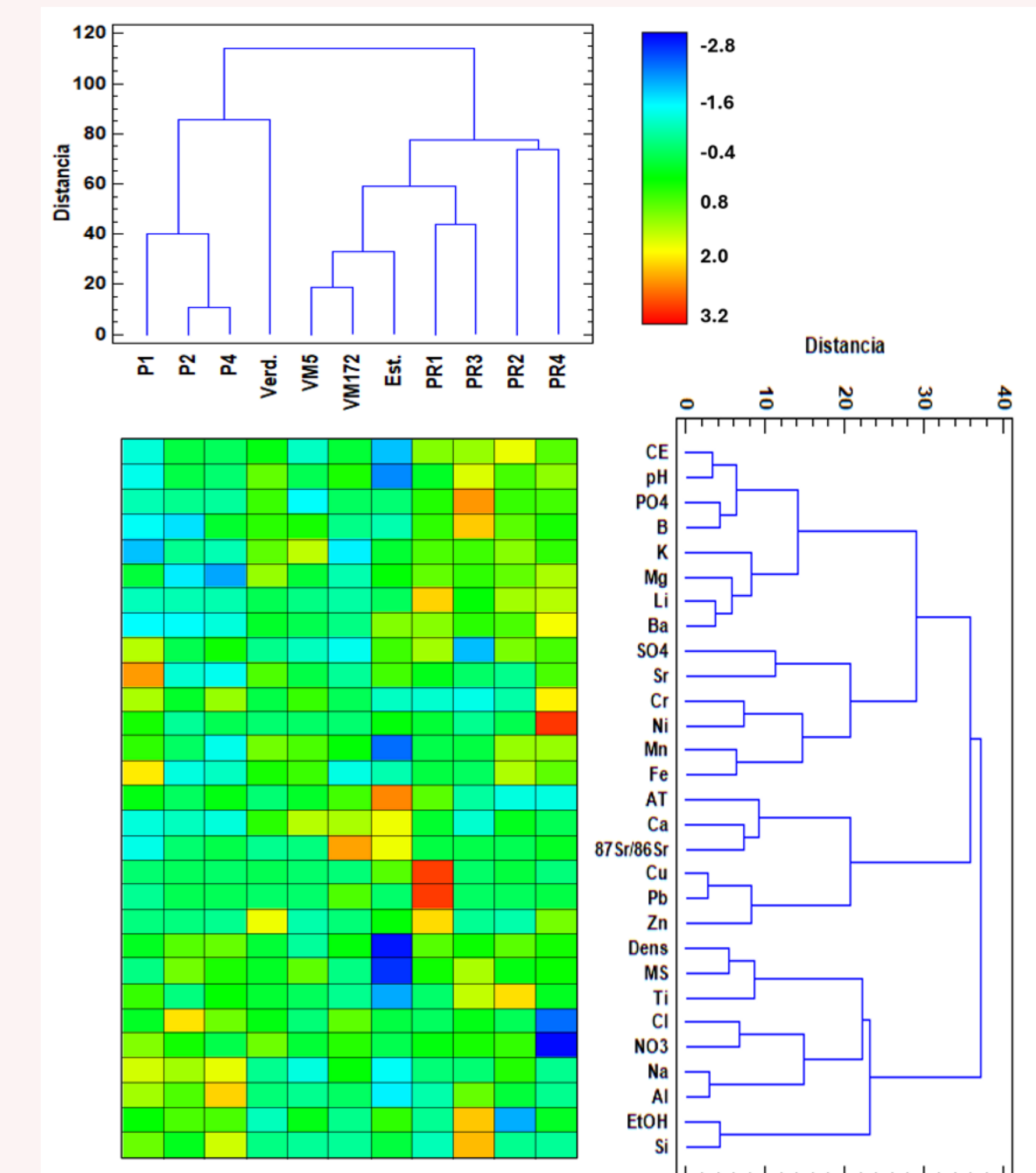


Good differentiation between different regions by $^{87}\text{Sr}/^{86}\text{Sr}$ uniquely

- EST and VERD: Rueda D.O.
- SRM987
- Rest of samples: Ribera de Duero DO

Some trends within the internal uncertainty:

- PR winery show slightly higher values
- Not conclusive yet: population size is too small



Multicomponent approach including the Sr isotope ratios is capable to differentiate different regions and the 3 wineries from the Ribera de Duero D.O.: P; VM and PR

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