Study of the distribution of Rare Earth Elements in soil and in Vitis Vinifera L.cv Cannonau in two different regions

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Introduction

Vitis vinifera L. cultivar "Cannonau" (Magnoliopsida Vitaceae) has been grown for years in the Italian regions to produce a fine wine, with Controlled Designation of Origin (DOC) and Denomination of Controlled and Guaranteed Origin (DOCG). From a geological point of view, the "terroir" has been defined as the geochemistry of soil, surface and ground water. Recent studies, regarding vitis vinifera, based on geochemical characterization have clearly shown the connection among geological origin, vineyard soil and grape berries (Marchionni et al., 2013; Pepi and Vaccaro, 2018).

Materials and Methods

The sampling areas were three different vineyards, two located in the valleys Pardu and Pelau in Sardinia (Italy) and one in Susegana in the Veneto Region (Northern Italy)(Fig. 1 and 2). 10 soil samples (Sardinia) and 6 samples (Veneto) were collected at the depth of 40 cm along the vineyard line, at intervals of 1m and at 50 cm of distance: each samples was collected in triplicate. At harvest time, grape clusters were freshly picked form grapevines and stored in polyethylene bags.
The grape berries were centrifuged to separate the juice residue (JR) from solid residue (SR). The soil and grape berries (JR and SR) samples were prepared by acid digestion on an open hot plate following the procedure by Pepi et al., 2019.
The concentrations of REE in samples of soil and juice or solid residues of grape berries were determined by inductively coupled plasma mass spectrometry (ICP-MS). The data were elaborated with multivariate statistics analysis (Linear Discrimination Analysis).

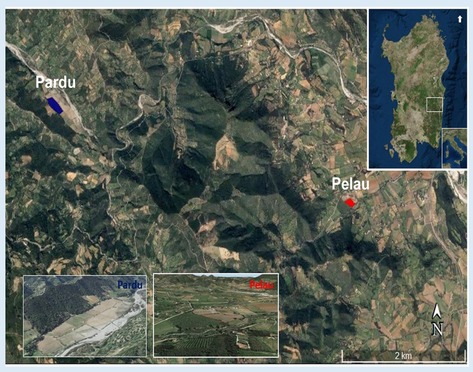


Fig.1.- Geographical map of the Sardinia region, showing the location of the two vineyards studied, Pardu and Pelau.

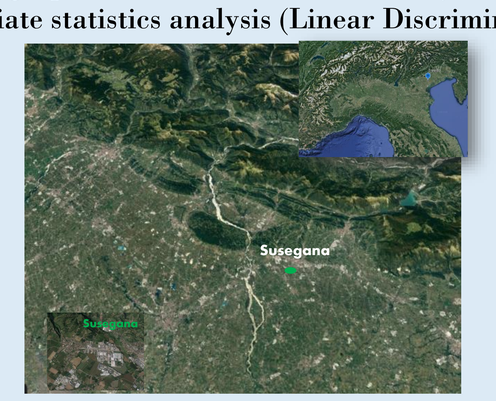
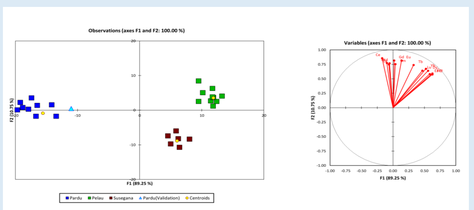


Fig.2.- Geographical map of the Veneto region, showing the location of the vineyard studied, Susegana.

Statistical results

To establish the geochemical differences due to geographical origin, Principal Component Analysis (PCA) was applied to all data in soils and grape samples from the three vineyards (Fig. 6, 7 and 8). From PCA analysis it was observed that the samples are not randomly grouped, but rather depending on the vineyard they come from.

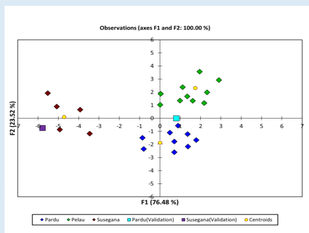


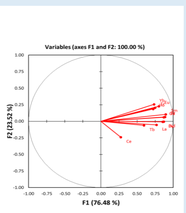
In soil samples data the PCA analysis explained 100% of total variance. The correlation-loading plot of soil data showed that the variables REE were strongly correlated with PC1, explaining 89,25% of variance.

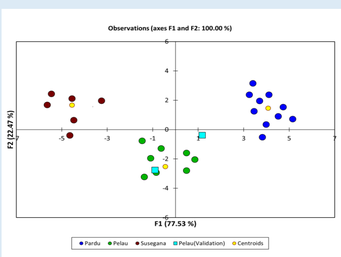
Fig. 6.- PCA in the soil samples. The red points show the Pelau vineyard, the green ones show the Susegana vineyard and the blue ones show the Pardu vineyard.

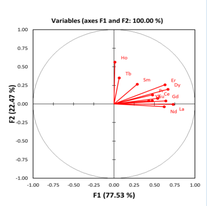
In SR samples data the PCA analysis explained 100% of total variance. The correlation-loading plot of SR data showed that the variables REE were strongly correlated with PC1, explaining 76.48% of variance, while the Ce, La, Dy, Nd and Tb are correlated with the PC2, explaining 23.52% of variance.

Fig. 7.- PCA in the SR samples. The red points show the Pelau vineyard, the green ones show the Susegana vineyard and the blue ones show the Pardu vineyard.









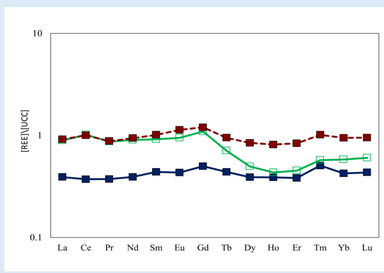
In JR samples data the PCA analysis explained 100% of total variance. The correlation-loading plot of JR data showed that the variables REE were strongly correlated with PC1, explaining 77,53% of variance, while the Ha, Sm are correlated with the PC2, explaining 22,47% of variance.

Fig. 8.- PCA in the JR samples. The red points show the Pelau vineyard, the green ones show the Susegana vineyard and the blue ones show the Pardu vineyard.

The geochemical and statistical analysis allowed to discriminate the vineyard soils and grape berries according to geolithological characteristics of each area and to identify possible geochemical markers for the cultivar "Cannonau".

Geochemical results

In the figures below are shown the REEs in the samples of soil (Fig. 3), SR (Fig. 4) and JR (Fig. 5). REEs contents have been normalized to the Upper Continental Crust (UCC, Rudnick and Gao 2003).

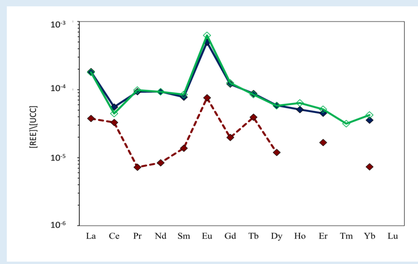


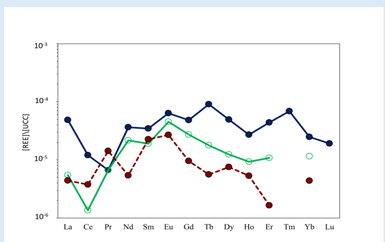
The normalized patterns of the soil of the two vineyards plot from Sardinia very close, exhibiting the same REEs distribution pattern probably due to the similar genetic processes for the soils. The soil from Pelau showed REEs values higher than the Pardu ones. The soil from Susegana revealed higher values of Light REEs (LREE) than Heavy REEs (HREE). Each vineyard soil was identified on the base of the different REE concentrations.

Fig. 3.- REEs pattern in the soil samples. The red line shows the Pelau vineyard, the green one shows the Susegana vineyard and the blue one shows the Pardu vineyard.

The normalized patterns of SR samples from Pardu and Susegana vineyards plot the same trend. SR samples showed in both areas an Eu pronounced positive anomaly and a Ce negative one; SR samples from Pelau showed lower values, with Eu pronounced positive anomaly, La and Ce slight positive anomalies and Pr slight negative anomaly.
The positive anomaly of Eu could be due to the interchangeability of Eu3+ with Ca2+ during physiological processes of plant growth occurring in soil (Zeng et al. 2003; Pepi et al. 2016)

Fig. 4.- REEs pattern in the SR samples. The red line shows the Pelau vineyard, the green one shows the Susegana vineyard and the blue one shows the Pardu vineyard.





The normalized patterns of JR samples from Pelau showed a Pr, Sm and Eu slight positive anomalies. The Pardu samples revealed a Pr pronounced negative anomaly.
Finally JR samples from Susegana showed a Ce very pronounces negative anomaly and Eu slight postive one.
The negative anomaly of Ce in Susegana samples suggests a depletion in absorption and translocation, probably due to the lower availability and mobility of Ce4+ (Wen et al. 2002; Pepi et al., 2016), whereas negative anomalies could be due a different agronomic practises.

Fig. 5.- REEs pattern in the JR samples. The red line shows the Pelau vineyard, the green one shows the Susegana vineyard and the blue one shows the Pardu vineyard.

Conclusions

The concentration of rare earth elements (Rees) was evaluated by ICP-MS in soil and grape beriies of Vitis Vinifera L. cultivar Cannonau, from two different localities in region Sardinia and Veneto. Each vineyard soil was geologically characterized on the base of different REE concentration.
Juice and soild residues of grape berries (Cannonau) supported the identification of each vineyard based on REE concentration.
The work aimed to determine a valid method to identify the terroir, it means a relation between vineyard soil and grape berries. REEs can be used to this aim of geographic designation of origin, also allowing a tool against the counterfeit of wines.
At last the same method also should be valid with other label agriculture product closely related to geographic designation.

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