TERROIR AND CV. GLERA (*Vitis Vinifera L.*): IDENTIFICATION OF GEOGRAPHICAL ORIGIN BY MEANS OF GEOCHEMICAL ANALYSIS

SALVATORE PEPI
Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Via Saragat 1, 44121 Ferrara

INTRODUCTION

During the 20th century, the increasing demand of wine in the international commerce has required more controls in order to avoid falsifications and the incorrect use of denomination labels. Recent studies have aimed at the importance of the connection between quality of Prosecco and the territory (Boatto *et al*., 2013). The study belongs to a research project with title "The characterization, valorisation and development of the DOC area Prosecco" in order to safeguard the quality and traceability of the "Made in Italy" products.

The traceability geographical system assure the provenance of food products, in order to verify the origin declared on the denomination labels and to avoid that unsafe products reaching the consumers. The geographical origin assessment of Prosecco wine is essential, being one of the most important factors that determine its commercial value. The geographical origin, in fact is based on the relationship between the characteristic of the wine and the concept of *Terroir*. The *Terroir* describes a particular grape variety with specific organoleptic characteristics, linked to a precise climate area, a geologic setting, and a particular wine district or wine region (Haynes, 1999; Van Leeuwen & Seguin, 2006; Costantini & Bucelli, 2008). Moreover, the word *Terroir* includes the specific characteristics of the soil, topography, climate, geology, geomorphology, landscape, and biodiversity: a concept, which refers to the physical and biological environment identifiable, that make the Prosecco unique. Geology is one of the disciplines that is considered essential to explain the concept of *Terroir*.

Reynolds (2010) established that the grapevine produce good wine on different geological outcrops, such as: schists (Porto, Mosel), limestone, gypsum, and marl (Champagne, Bourgueil, Chinon, Chablis, Barbaresco, Chianti, Marsala, Barolo, Roja), clay (Sauternes, Prosecco). Other studies have showed, instead, that the geology does not affect the quality of wine but it could condition its characteristics, for example: the best Nebbiolo and the Chardonnay wine are produced on the marls, while the Gamay wine on the schists (Wilson & Beazley, 1998; Reynolds, 2010). The researches on geographical territoriality in wine are based on the idea that the chemical elements of the grapevine reflect those of the soil and they could affect the finished product. Some authors showed as the pattern of wine reflects the geochemistry of soil, climate, treatment, etc. (Jakubowski, *et al.*, 1999; Almeida & Vasconcelos, 2003).

The interest for the wine-producing protection has affected different study and research aimed to this topic. The main purpose of this study is to determine the correspondence among geo-lithological features of the area, geochemistry of vineyard soil, and chemical composition of grape (juice and solid residue). This research allowed to identify the characteristic territorial markers of Glera cultivar. In addition, this study developed: *i*) methods of treatment and analysis of the samples of grapes divided into two types (juice and residual solid); *ii*) description and identification of the trace elements contents in the soil; *iii*) characterization of the grape juice (juice and solid residue) and the product wine, in order to verify the correlation of the elements in different parts; *iv*) chemometric approaches on soil samples and grapes for the definition of territorial markers.

MATERIALS AND METHODS

Sampling and Treatment

The analysed vineyards belong to ten distinct wineries, which are located in the alluvial plain of the Veneto-Friuli Region and included in the DOC (Controlled Designation of Origin) area of Prosecco wine.

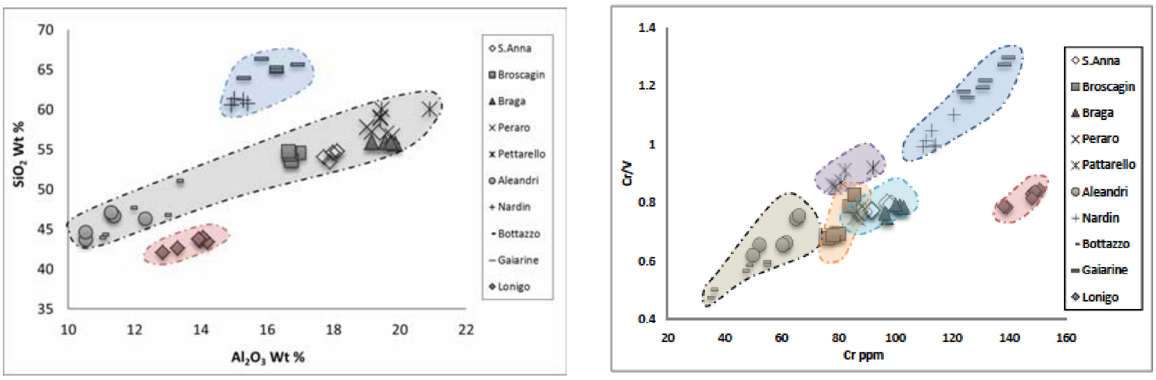
Moreover, sampling areas belong to the basins of the following rivers: Agno-Guà (Lonigo), Brenta (Pattarello), Livenza-Tagliamento (Aleandri, Nardin), Piave (Bottazzo-Gaiarine), Adige (S. Anna, Broscagin, Braga, Peraro).

The analysis of major and trace elements contents in soil were carried out by means of XRF (X-Ray Fluorescence spectroscopy), whereas the soil, grape and wine samples were analysed by means of ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

As regards grape's samples, they were divided into two parts by means of centrifuge: the juice and solid residue (skin, seed, flesh). The division of the grape into the two parts allowed to experiment a further methodology of study for the territoriality geographic, in accordance with the established existing methods (Bertoldi *et al.*, 2009, 2011; Rogiers, *et al.*, 2006). Moreover, juice and solid residue analysis could be considered more representative to detect useful values for the purposes of the traceability rather than the single grape sample.

RESULTS AND DISCUSSIONS

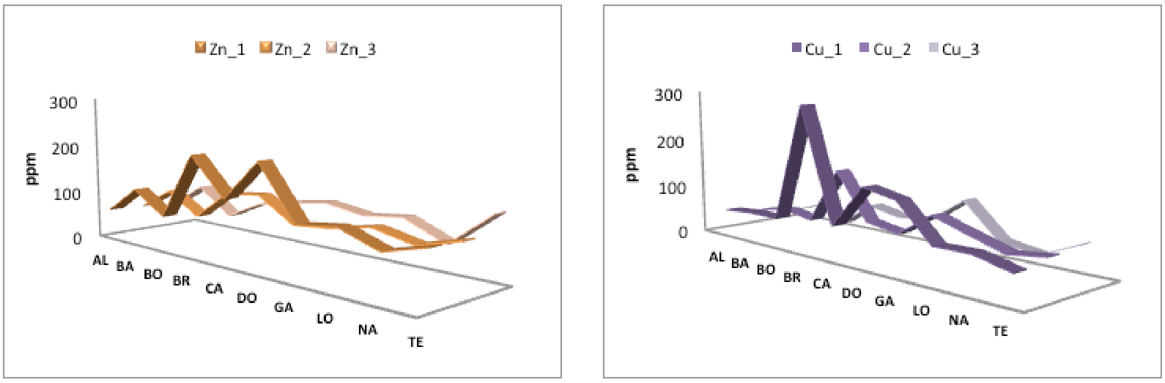
XRF analysis on the soil samples highlighted compositional variations depending on geographical origin. It can be observed (Fig. 1) that the soil of Gaiarine and Nardin show high values of SiO_2 due to the presence of mineral of sedimentary origin (especially quartz). Likewise, the positive correlation among Al_2O3 *vs.* SiO_2 (wt.%; Fig. 1a) in both groups of soil evidenced the presence of aluminosilicates and clays minerals (Pattarello). By contrast, soils from Aleandri and Bottazzo are linked to a higher presence of carbonate minerals and dolomite (Petrini *et al*., 2014). The Al_2O_3% *vs.* Fe_2O_3% relationships indicates the presence in the fine fraction of clay minerals and probably of oxides/hydroxides in the samples, except for the samples from Lonigo that evidence the presence of femic minerals. Application of the Cr/V *vs.* Cr diagram to soil samples reveals a marked shift in Cr concentrations, reflecting sediment composition from five rivers basins. Moreover, the diagram in Fig. 1b allows to discriminate the soil in relation to geographic origin and proves to be a good origin marker for the subject area.



(a) (b)

Fig. 1 - Relationships between a) Al_2O_3 and SiO_2 (wt.%); b) Cr (ppm) and Cr/V for soils.

Heavy metal content in soil and grape was determined to evaluate a possible anthropic source, such as the use of pesticide. The results highlighted that heavy metal (Co, Cr, Ni, V, Pb, Zn, and Cu) are accumulated in the top 20 cm of soils, probably due to the use of fertilizer and organic matter (Van der Perk *et al*., 2004). The distribution of Cu and Zn at different depth is reported in Fig. 2; it can be observed that Cu and Zn are strictly correlated and associated to the anthropic activity, in particular to the use of pesticide. The quality of the soil and of the agricultural products allowed to compare the elements concentration (Co, Cr, Ni, V, Pb, Zn, and Cu) with the tabled requirements of Law Decree 152/06 and subsequent amendments. This comparison evidence that the samples of Lonigo have the highest concentrations of Co and Pb respect to the threshold values, likewise the samples of Broscagin for the Cu.



(a) (b)

Fig. 2 - Heavy metals Cu (a) and Zn (b) distribution at the three different depths (0-20, 20-40, 40-60 cm); AL (Aleandri), BA (S.Anna), BO (Bottazzo), BR (Broscagin), CA (Braga), DO (Pattarello), GA (Gaiarine), LO (Lonigo), NA (Nardin), TE (Peraro).

Considering the high concentrations of metals in the soil, it was deemed appropriate to verify if they could cause problem of assimilation in the grape. For this reason, the heavy metal content (As, Pb, Ag, Cd, and Zn) was compared with ministerial decree 29 December 1986, European regulation 2006/1881 CE, and International Organisation of Vine and Wine (OIV). The results highlighted that As, Pb, Ag, Cd, and Zn are within the limits indicated by law, with the exception of Cu.

For each vineyard, in addition, the assimilation coefficients were calculated in order to assess the uptake of metals in the grape (juice and solid residue) and in the wine, as fingerprints of their own specific content in soil.

Assimilation coefficients K_s, K_r, and K_v are given respectively by the ratio among the concentration of an element in the juice, in the solid residue, and in the wine and the concentration of same element in the soil (Faccia *et al*., 2010a, b):

$$K_s=C_{juice}/C_{soil}, \quad Kr=C_{sol.res}/C_{soil} \text{ and } Kv= C_{wine}/C_{soil}.$$

Fig. 3 show that the patterns follow the same trend for all the coefficients but, in general, the elements are assimilated in high concentration in the solid residue compared to juice and wine. This behaviour could be linked to correct ripening process (Fregoni, 2013), for which these elements would be further moved from solid residue to juice; instead, the pattern of wine doesn't follow solid residue and juice for the most part of the elements, probably due to vinification process.

Considering Lonigo's winery as an example, the soil is characterized by high concentration of Mg, Ca, Mn, Sr and Fe, whereas in juice, solid residue, and wine evidenced low concentration of these elements. By contrast Pattarello and Gaiarine winery showed a low concentration in soil compared to grape and wine. This suggests that elements are linked to more stable mineral phases compared to others area. Thus, results of assimilation coefficient are different from one winery to another suggesting that the uptake of the chemical elements does not depend only by the plant but also by soil, climate and another variable (Elgawhary *et al.*, 1972).

Analyses of the data by means of software XLSTAT (Version 2015.5.02) were carried out to assess the possible geochemical marker. PCA (Principal Component Analysis), Test U of Mann-Whitney and LDA (Linear Discrimination Analysis) were performed.

Through geochemical analysis and statistical approaches (LDA, PCA), the vineyard soils were discriminated according to the geo-lithological characteristic of the area and to the trace elements found in the grape. Processing results by means of scatter-graph and LDA allowed to discriminate the soil according to their origins. As for grape samples, it was observed a high variability of data linked to different factors (irrigation, micro-clima, anthropic activity, etc).

Therefore, in order to minimize the variability due to the differences above discussed, the wineries were allocated to different groups. Principal component analysis (PCA) resulted a valid tool to discriminate the test areas. The Geochemical markers that allowed to discriminate the ten Prosecco winery resulted: Ba, Cr, Zr, Ni, Sr, and Rb.

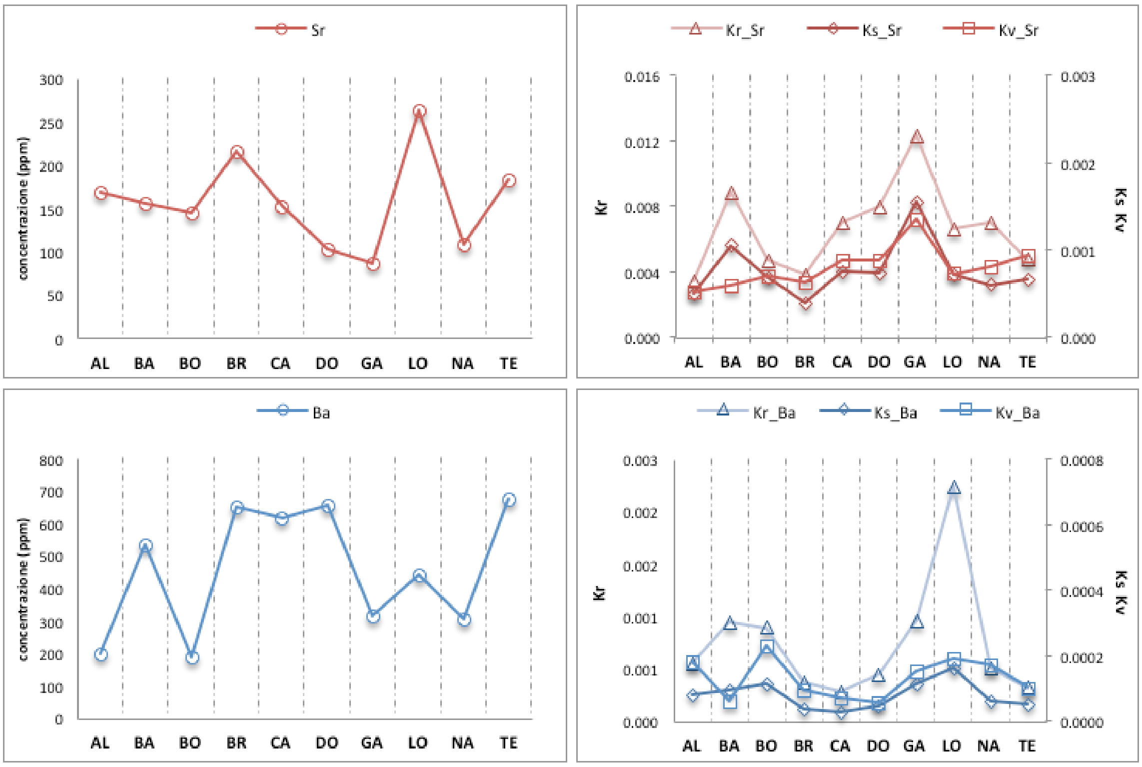


Fig. 3 - Assimilation coefficients for the ten Procecco winery: AL (Aleandri), BA (S. Anna), BO (Bottazzo), BR (Broscagin), CA (Braga), DO (Pattarello), GA (Gaiarine), LO (Lonigo), NA (Nardin), TE (Peraro).

CONCLUSIONS

In this study, it was evaluated the trace and ultra-trace elements composition of soils, juice and wine for the definition of geographical marker useful to define the territoriality of the Made in Italy. The analysed grape variety was *cv. Glera*, which is famous for the production of Prosecco, an Italian high quality wine considered worldwide as an excellence.

Soil characterization by XRF analyses and statistical processing (LDA) allowed to discriminate the test areas according to geographical origin. However, soil contaminations by heavy metals (Pb, Cu, and Zn) suggest a possible contamination related to human activity.

The division of the grape in two parts, juice and solid residue, allowed to introduce a further methodology. The adopted treatment highlights that the components of the grape show a different macro- and micro-element concentration in the juice and solid residue, confirming a fractionation process in the grape.

Furthermore, the metals found in the grape reflect the mobility of elements from soil to grape, and the effect of human activity and vinification process.

PCA and LDA statistical analysis particularly resulted valid tools to discriminate geochemical marker. Moreover, the comparison of the results obtained for the grapes were useful to confirm the origin of *cv. Glera*.

Finally, the results of this research are useful to identify the correct relationship between the winery district and the Glera cultivar, demonstrating as some trace and ultra-trace elements could be considered as possible marker for geographical origin.

REFERENCES

Almeida, M.C.R & Vasconcelos, M.T.S.D (2003): Multielement composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin. *J. Agr. Food Chem.*, **51**, 4788-4798.

Bertoldi, D., Larcher, R., Nicolini, G., Bertamini, M., Concheri, G. (2009): Distribution of rare earth elements in Vitis vinifera L. 'Chardonnay' berries. *Vitis*, **48**, 49-51.

Bertoldi, D., Larcher, R., Bertamini, M., Otto, S., Concheri, G., Nicolini, G. (2011): Accumulation and distribution pattern of macro- and microelements and trace elements in Vitis vinifera L. cv. Chardonnay Berries. *J. Agr. Food Chem.*, **59**, 7224-7236.

Boatto, V., Galletto, L., Barisann, L., Bianchin, F. (2013): The development of wine tourism in the Conegliano Valdobbiadene area. *Wine Econ. Pol.*, **2**, 93-101.

Costantini, E.A.C & Bucelli, P. (2008): Suolo, vite ed altre colture di qualità: l'introduzione e la pratica dei concetti "terroir" e "zonazione". *Ital. J. Agron.*, **3**, 23-33.

Elgawhary, S.M., Malzer, G.L., Barber, S. (1972): Calcium and strontium transport to plant roots. *Soil Sci. Soc. Am. Pro.*, **36**, 749-799.

Faccia, F., Vaccaro, C., Marrocchino, E., Tassinari, R. (2010a): Trace and ultratrace elements in grapes: possible application for geographical traceability. 89^{th} Simp Meeting "L'evoluzione del sistema Terra dagli atomi ai vulcani" Ferrara, 307.

Faccia, F., Vaccaro, C., Sansone, L., Marocchino, E., Tassinari, R. (2010b): Elementi in traccia e ultra-traccia nell'uva: possibili applicazioni ai fini della tracciabilità geografica. VIII International terroir congress. Soave, 76-81.

Fregoni, M. (2013): Viticoltura di Qualità - Trattato dell'eccellenza da terroir. Tecniche nuove, Milano, 960 p.

Haynes, S.J. (1999): Geology and wine 1. Concept of terroir and role of geology. *Geosci. Can.*, **26**, 190-194.

Jakubowski, N.R., Brandt, D., Stuewer, H., Eschnauer, R., Goertges, S. (1999): Analysis of wines by ICP-MS: Is the pattern of the rare earth elements a reliable fingerprint for the provenance?. *J. Anal. Chem.*, **364**, 424-428.

Petrini, R., Sansone, L., Slejko, F.F., Marcuzzo, P., Tomasi, D. (2014): The $^{87}Sr/^{86}Sr$ strontium isotopic systematics applied to Glera vineyards: A tracer for the geographical origin of the Prosecco. *Food Chem.*, **170**, 138-144.

Reynolds, A. (2010): Terroir: the effect of physical environment on vine growth, grape ripening and wine sensory attributes. *In*: "Managig Wine Quality Viticulture and Wine Quality", A.G. Reynolds ed., Woodhead Publishing Limited, 606 p.

Rogiers, S.Y, Greer, D.H., Hatfield, J.M., Orchard, B.A, Keller, M. (2006): Mineral sinks within ripening berries (Vitis vinifera. *L. Vitis*, **45**, 115-123.

Van der Perk, M., Jetten, V., Heskes, E., Segers, M., Wijntjens, I. (2004): Transport and retention of copper fungicides in vineyards. *Int. Ass. Hydrol. Sci.*, **288**, 437-443.

Van Leeuwen, C. & Seguin, G. (2006): The concept of terroir in viticulture. *J. Wine*, **17**, 1-10.

Wilson, J.A. & Beazley, M. (1998): Terroir: The role of Geology, climate and culture in the making of French Wines. Wine Appreciation Guild, Wine Wheels, 336 p.