ABSORPTION OF RARE EARTH ELEMENTS IN GRAPEVINE RAISED IN VOLCANIC AND CARBONATE SOILS

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INTRODUCTION

In the age of food industry globalization, there is a brand-new problem related to the knowledge on food origin. The recent awareness of consumers has brought to the development of research for the determination of the geographic origin of food products in order to avoid any fraud. Over the last few years, there has been a significant growth in wine demand by new markets, like Asia and South America, and the growth of the request caused the conversion of big agricultural areas to vineyard. However, due to the soil quality and the local climatic conditions of the different geographical areas, the new vineyards might not be able to guarantee a high-level quality production. Therefore, it is fundamental to preserve the quality of the wine product and to define markers and parameters to help ensure consumers; for this reasons, many studies have been carried out to find a way to preserve the wine identity through the designation of origin.

As it is known, the chemical composition of wine is influenced by many factors such as grape variety, soil, climate, agricultural practices, wine making practices, transport, and storage (Marengo & Aceto, 2003; Spercovà & Suchànez, 2005). Provided that the factors influencing the wine features are multiple and difficult to analyze altogether, in this work we focused on the basic product of the wine, namely the grapevine, looking for the criteria useful for grape varieties identification. It has been shown, that the Rare Earth Elements (REEs) retain their distribution in the transition from soil to plants and can therefore be used as geographical markers in the food industry (Brown *et al.*, 1990; Tyler, 2004). Although the concentration of trace elements and REEs in plant is very low, they play a fundamental role as a source of information. The plants absorb the REEs in a selective way: some parts of the plant such as the roots and the leaves absorb most of the REEs, whereas the absorption in the stem is minor, and it even decreases in the fruits (Censi *et al*., 2014).

Recent study showed the REEs importance for wine identification, to prevent fraud, and to counterfeit labels by identifying the geographical origin of the wines. Extensive studies have been carried out on wines from all over the world (Rossano *et al.*, 2007; Gonzàlvez *et al.*, 2009; Martin *et al.*, 2012; Aceto *et al.*, 2013).

In the frame of the present research, we chose two areas located in Sicily, and in particular in the Hyblean Plateau (SE Sicily) and at the Mt. Etna (Eastern Sicily). We selected three wineries: Avide, Cos, and Don Saro, respectively. These agricultural companies sit on different soils, since Avide and Cos vineries occur on carbonate soil, whereas Don Saro on volcanic soil.

Related to the rock that crops out, the content of REEs in soils is very different; besides, the different climatic conditions affect the absorption of these elements by the vine plants.

In this work, we highlighted how different cultivars can absorb REEs in different amounts and how to use REEs as a discriminating tool; at the same time, our aim was to investigate how the climatic factors and soil can affect the REEs absorption.

RARE EARTH ELEMENTS (REES)

The content of REEs in soil is linked to the origin of the parent rocks and reflects their mineral composition. Usually, low concentrations are found in sandy soils, whereas there are relatively high concentrations in clay-rich soils. Trace element concentrations significantly differ among the soil groups and geographic regions (Sumner, 2000).

Usually, acid soils contain lesser amount of lanthanides than alkaline soil presumably for the easy removal of soluble hydroxide complexes. LREEs are usually more abundant than HREEs in soils, as reported in many studies (*e.g.*, Zhu *et al.*, 1997). However, the mobility of REEs is not equal in all the soils, due to several factors such as, in particular, the weathering processes; in fact, loss of surface layer can be observed in wet climates due of the effects of leaching and alteration (Tyler, 2004). Another factor affecting the mobility of REEs is the pH of the soil as described in Censi *et al.* (2005) and Tyler & Olsson (2001).

Until the last decades, poor attention was paid to the content of REEs in plants and to their physiological functions. One of the first studies done by Robinson *et al.* (1958), linked the REEs concentrations in the leaves of hickory trees and in the soil. Laul *et al.* (1979) evidenced that the relative REEs abundances in plants and soils are strictly correlated and that the absorption of REEs by plants depends also by the plant species.

SAMPLING AREAS

The areas selected for the present study, are located in eastern Sicily. The first area is located at the feet of Mt. Etna, whereas the second area sits in the Hyblean Plateau, a carbonate platform located in the southeastern Sicily. In the first area, the choice fell on the vineyard of Don Saro, located in Linguaglossa, in the eastern flank of Mt. Etna. In the second area two vineyards were selected, few kilometers away from each other: the Avide wineries and the COS vineyard, both located in the municipality of Comiso (Ragusa).

Mount Etna

The Mount Etna, located in eastern Sicily, is the largest and most active volcano in Europe. It covers an area of 1200 km^2 and rises to an altitude of 3350 m a.s.l. Mt. Etna is a layer-alkaline volcano, which developed on a continental crust formed by Mesozoic clastic and carbonate deposits (Lentini, 1982). The composition of its magma ranges from alkali basalt to trachyte, although most of its lavas have hawaiitic composition (Tanguy *et al.*, 1997). The studied vineyard is located in the municipality of Linguaglossa, at the feet of Mount Etna, on a lava flow dating back to the period between the 122 BC and 1669 AD (Branca *et al.*, 2011). The soils of Mt. Etna area originate from the disintegration of volcanic rocks of basaltic and andesitic composition. They are skeleton-rich soils and the profile thickness is generally quite exiguous. They are loose and very permeable and the color the color is dark-brown to almost black. The Mt. Etna soils are poor in nitrogen content but, despite this, have a considerable degree of fertility, due to the presence of nutrients, particularly phosphates and potassium salts, which come from the alteration of apatite, plagioclase and ash (Giovannini *et al.*, 1963; Principi, 1961).

In Linguaglossa area (Mt. Etna) the average annual temperature rose from 18 °C at sea level until 1 °C at an altitude of 2900 m. Above 1000 meters, the temperature gradient seems constant (5.8 °C/km) for the entire volcanic edifice. In municipality of Linguaglossa the rainfall is abundant amounting to 1100 mm per year, significantly higher than the 650 mm per year in the region of Sicily. Precipitation is concentrated from October to January and very low contributions occur from June to August.

Hyblean Plateau

The Hyblean Plateau is located in the southeastern corner of Sicily. The Plateau is considered the northernmost portion of the non-deformed Pelagian Block, subducted beneath the European plate (Burollet *et al.*, 1978); the emergence of the block is due to the clash between the African plate and the Peloritani-Calabrian Orogen, that began in the Tertiary, (Lentini *et al.*, 1996; Catalano *et al.*, 2000; Scarascia *et al.*, 2000). The Plateau consists of a thick carbonate succession mainly deposited as platform facies with age ranging between Mesozoic-Cenozoic and Quaternary. The stratigraphic sequence is intercalated by volcanites from three different ages, *i.e.*, Cretaceous, Late Miocene, and Pliocene Pleistocene (Bianchi *et al.*, 1987).

The study area, sit on Middle Pleistocene yellowish and poorly stratified calcarenites. The base of the Formation consists of several meters of sand, gravel and conglomerates with carbonate elements and reddish sandy matrix containing few fossils (mollusks and calcareous algae). Soils of the Hyblean Plateau are calciumrich soil with substrates formed by sands of early Pleistocene age. The calcareous rocks in the area of the Hyblean Plateau, undergo strong weathering and are subject to dissolution processes.

In the Comiso area, the monitoring of temperature and rainfall was made by the Hydrographic Service of Civil Engineering for the period of time ranging from 1966 to 1990. The area has semi-arid climatic conditions, with average temperatures ranging from 16 to19 °C. The annual rainfall is lower than the previous area, ranging between 400-450 mm per year; and they are mainly concentrated from September to March with almost no rain during the summer.

Grape Types

We have chosen 4 white grape (Carricante, Grecanico, Ansonica, and Moscato) and 6 red grape cultivars (Cabernet, Sauvignon, Frappato, Merlot, Nerello Cappuccio, Nerello Mascalese, and Nero d'Avola).

The analyzed cultivars include both autochthonous and allochthonous grape varieties. The autochthonous varieties are Inzolia, Carricante, Grecanico, Moscato, Frappato, Nerello Cappuccio, Nerello Mascalese, and Nero d'Avola, whereas the selected autochthonous grape varieties are Cabernet Sauvignon and Merlot, both of French origin and characterized by high adaptability to different climatic and lithological conditions.

SAMPLING AND ANALYTICAL METHODS

In the two studied areas, samples of soils, rocks and plants were collected in the years 2013 and 2014.

Soil and rock sampling

31 soil samples were collected on May 2013 and their positions were accurately georeferenced using a GPS device. Among these samples, 11 were sampled in the vineyard of Don Saro (Mt. Etna), 9 in the Avide vineyard, and 11 in the COS vineyard (Hyblean Plateau). The first 10 cm of the soil were excised and the sample (500 g) was collected, at a depth between 10 and 20 cm and then stored in a refrigerator in signed and sealed plastic bags.

17 rock samples were collected in the two areas; 7 were representative of rocks outcropping in Don Saro winery whereas 10 of those outcropping in the areas of the Avide and COS wineries (between Acate and Chiaramonte towns).

Plant Sampling

The plant samples were collected during the harvest period; in the Etnean area the harvest usually takes place between late September and early October, whereas for the area of the Hyblean Plateau the harvest period takes places earlier, from late August through the end of September. The samples of grapes were manually collected by clippers, placed into sterile bags and then frozen. The breakdown of samples was done in the geochemistry laboratory of the Department of Biology, Geology and Environment at the University of Catania. The thawed grape was subjected to washing with MilliQ water. The samples obtained for each year were treated according two different methods that were then compared. For the samples collected in 2013, the berries were divided into juice and residues by centrifugation. For the samples collected in 2014, skins and seeds were separated before obtaining the juice by centrifugation. Moreover, in 2014, samples of grapevine leaves were also collected at the beginning of May *i.e.*, before the leaves were subjected to any type of treatment. Leaves sample were detached from the branches, weighed and washed with MilliQ water. The leaves were placed in a stove at 70 °C for 48 hours according to the Zhang & Shan (2001) procedure and, once dried, they were milled in an agate mortar.

Sample analyses

X-ray fluorescence (XRF) was used for the determination of major, minor and trace elements of rocks and soils, whereas Mass-Inductively Coupled Plasma Spectrometry (ICP-MS) was used either for inorganic and organic samples (juices, residues, skins, seeds and leaves) to determine trace and ultra-trace elements. For XRF analyses, samples were prepared into tablets of pressed powder, whereas for ICP-MS analyses, samples were prepared as described in the following chapters.

ICP-MS analyses were carried out with the spectrometer X series, Thermo Electron Corporation, equipped with CCT® (Collisional Cell Tecnology) at the department of Physics and Earth Sciences of the University of Ferrara. The inorganic and organic samples were dissolved with a mixture of strong acids and/or oxidants according to the method of "wet digestion" (also known as "acid digestion") described in Chao & Sanzalone (1992). The dissolution procedure for juice samples is described in Pepi *et al.* (2016), which was modified for skin, seeds, and leaves samples using different amount of sample and acid.

RESULTS

In the present work, the REEs functionality was investigated in order to assess whether they can be used as territorial markers also to prevent counterfeiting of a wine and its territorial brand.

According to the results achieved, the chemical composition of a wine is influenced by many factors (*i.e.*, grape variety, soil climate, agricultural practices, wine making practices, transport and storage); since it is difficult to analyze the overall factors, this study was focused on the grapevine.

The ICP-MS results, obtained from soil and rock samples, were normalized to the average Upper Crust composition (Rudnick & Gao, 2003), whereas the organic samples were normalized to the average concentration of their related soils.

Soil and rock

As expected the soils of the two study areas evidenced extremely different compositions. The soil from Mount Etna is characterized by lower SiO_2 content than soil of Hyblean Plateau area. As regards TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, Na_2O, and P_2O_5 contents, soils in the Etnean area have higher values than soils of the Hyblean Plateau.

Mt. Etna soils are andosols, derived from volcanic parent rocks and resulted richer in REEs, especially LREEs. The normalized patterns of REEs evidenced a positive europium anomaly, which is of primary derivation due to plagioclase content of the parent rock.

The Hyblean Plateau soils are carbonate soils with a terrigenous component; the REEs content was lower than the values measured in the Etna soils and a clear fractionation between LREE, HREE, and MREE was not evident. The positive europium anomaly is due to the terrigenous component, whereas the negative anomaly of cerium is typical of carbonate rocks.

Organic matter

The measured concentrations of REEs in the organic component of grapevine plants were different depending on the part of the plant considered. Indeed leaves showed higher REEs contents, followed by juices, residues, skins, and lastly by seeds.

The climatic conditions affected the absorption of REEs by plants; indeed, by relating the average REEs absorbed by the plant to the average REEs concentration of soil, it was clear that the plants growing in arid climatic conditions of the Hyblean Plateau absorb the REEs from the soil at a greater extent compared to plants raised in the temperate climate of the Mt. Etna wineries.

When comparing the plants grown in the same winery, it was been noticed that the absorption varied slightly according to the type of grape, since some types of grapevine varieties facilitate the absorption of certain elements than others, especially as regards the LREEs.

The next step was to compare the same type of cultivars, raised in different environments; this comparison showed very significant differences on the absorption of REEs. As showed in Fig. 1, where the concentrations of REE of the Juice of two types of cultivars (Merlot and Inzolia) are compared, plants grown in the Hyblean carbonate soil (COS winery) showed higher concentrations in REEs than those grown in the Etnean volcanic soil (Don Saro winery). The comparison of Fig. 1 showed that, depending on the REEs content, it is possible to distinguish the provenance area.

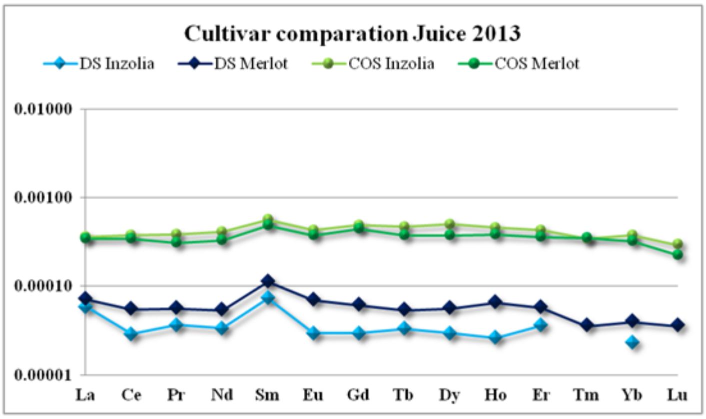

Fig. 1 - Comparison between juice from two different cultivar (Inzolia and Merlot). Cos is a winery in a carbonate soil and DS is a winery in a volcanic soil.

A statistical approach was carried out for further discrimination. The approaches used are Box Plots, Principal Component Analysis (PCA), and Linear Discriminant Analysis (LDA; Fig. 2). The statistical approaches either confirmed the previous statement and added some new information. In fact, for the organic samples (*i.e.*, leaves, juice, residues, skins, and seeds) the soil type resulted clearly distinguishable on the basis of LREEs contents.

The PCA, allowed to better distinguish between the two types of soils, whereas the LDA allowed to distinguish the vineyard provenance of the organic grapevine samples. Among the organic samples, the best discrimination resulted from leaves and juices, which had the highest REEs content. The differences among the various cultivars were also highlighted, discerning among cultivars grown in different environments.

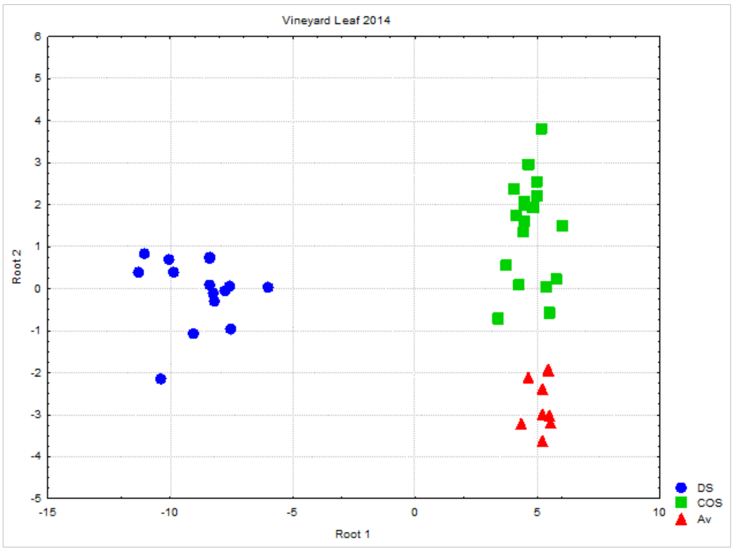

Fig. 2 - Linear Discriminant Analysis on leaves sample of the three vineyards (Don Saro, COS, and Avide).

CONCLUSION

The main results can be summarized as follows:

i) the various parts of the plant uptake the REEs differently; the higher concentrations resulted in leaves followed by juice, skins, residues and, finally, in seeds;

ii) the uptake of REEs is higher in plants growing in an arid climate conditions than those growing in a temperate climate;

iii) the plants growing in the same environment show slight differences in the uptake of some elements, according to the type of grape;

iv) the same grape growing in different soil types shows differences in the uptake of REEs allowing to identify their provenance.

The results of this research should be extended to other types of terrain and vineyards in other regions to observe differences due to the climate as well as to the soil type; moreover, a database should be created and used to establish a unique geographical territoriality of food products.

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