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Absorption of Rare Earth Elements in grapevine of volcanic and carbonate soil

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1.**Introduction**

In the age of food industry globalization, there is a brand-new problem of fundamental importance related: to the knowledge about the origin of the food. Recently the awareness of consumers, has been stimulating towards solving problems of origin identification.

The reasons for the growing consumer's interest are: specific culinary and organoleptic qualities associated with the growing region, health, patriotism toward their region, decline in consumer confidence in products grown outside, growing media attention to quality of food, attention to the well-being of both animals and the environment and the production methods used (Gilg, 1998) (Ilbery, 1998) (Kelly, 2003). All of these factors mean that consumers prefer to spend on product quality than quantity.

The recent awareness of consumers has brought to the development of much research for the determination of the geographic origin of food products in order to avoid fraud. The European Union (EU) has identified specific patterns of quality to be respected for the cultivation and production of foodstuffs: Protected Designation of Origin (PDO or even ODP); Protected Geographical Indication (PGI) and Traditional Specialities Guaranteed (TSG). PDO regards those specific agricultural products that are produced and prepared in a given geographical area, PGI regards agricultural products and foodstuffs which are closely related to the geographical restricted and TSG regards traditional character in composition or means of production (European Commission 2007) (Drivelos, 2012).

Besides the European denominations, there are denominations, of Italian origin, which relate only to wines: Designation of Origin DOC and Designation of Origin Controlled and Guaranteed DOCG.

The DOC designation certifies the area of origin, delineating the areas of harvest, which can be used for the production of wine, marked with the certification. The characteristics of these wines are related to the natural environment. The wines are subjected, during the phase of production, to a preliminary chemical-physical analysis and an organoleptic test.

The DOCG designation indicating the geographical origin of a wine. The wines, in possession of the label must meet certain characteristics: to be recognized as DOC for at least five years; be particularly valuable wines, in relation to the characteristics inherent quality, compared to the average of similar wines classified.

In the production phase, the wines are analyzed chime-physics and an examination organoleptic, or certifying accordance with the requirements. The examination will be repeated again even in the bottling stage. Finally there is also an examination of sensory.

Over the last few years there has been a significant growth in wine demand by new markets like Asia and Sud America. The growth of the request caused the conversion in vineyard of big agricultural areas formerly planted with cereals. However, the soil quality and different climatic conditions in the new vineyards cannot be able to give a quality production. So it is fundamental to preserve the quality of the wine product, and to define markers and parameters to help ensure consumers: for this reason, many studies have been carried out to find a way to preserve the wine identity through the designation of origin.

Italy is one of the main wine producers in the world, with 42 million of hectoliters for year (2011date ISTAT), is a dead heat with France the largest producer of European wine. The first four Italian regions for wine production are: Veneto, Emilia-Romagna, Puglia and Sicily, which produce 60% of the national production of wine. In the present work we have chosen Sicily, whose wine area is the largest in Italy with its 107,000 hectares, despite the Sicilian territory is 60% hilly, 25% mountainous and only 15% of it is flat.

The chemical composition of wine is influenced by many factors, grape variety, soil, climate, agricultural practices, wine making practices, transport and storage (Marengo E., 2003) (Spercovà J., 2005). Provided that the factors influencing the wine features are multiple and difficult to analyze all together, in this work we focused on the basic product of the wine, namely the grapevine, looking for the criteria useful for grape varieties identification.

Authentication and traceability of a product are not the same thing. Authentication discriminate between foods of the same type, but different in their geographical origin, botany, variety or different technological processes used. The traceability instead has the purpose of connecting a food with the soil from which the raw materials have been produced, it is more difficult to find markers useful for the traceability with respect to authenticity.

It has been shown, by some scientific works, that the REEs retain their distribution in the transition from soil to plants and can therefore be used as markers geographical in the food industry (Brown P.H., 1990) (Tyler, 2004).

The research conducted so far, in this field, seem to prove the theory, food treated are very different: tomatoes and related products (Bettinelli, 2005), Piedmont hazelnuts (Oddone, 2009) and Hungarian paprika (Brunner, 2010). The method seems to work for not very large production chains, such as fruit and vegetables, the product becomes more complex and more discrimination will be difficult, with the increase of the processes involved.

Although the concentrations of trace elements and of Rare Earth Elements, in plants, are very low, they play a fundamental role as a source of a lot of information, in particular as regards the Rare

Earth Elements. There are many works that have studied the distribution of REEs from the perspective mineralogical and geochemical (Liu, 1993) (Scott, 1990) (Wronkiewicz, 1990).

Only since the late 90's increased attention on the environmental effects of REE, especially their accumulation in plants (Ichihashi, 1992), in soil (Zhang, 2001) (Wyttenbach A., 1998), in sediments (Zhu J, 1997) and in biological samples (Tu, 1994).

Attention focused on the Rare Earth Elements, which are absorbed from the various parts of the plant during growth, by considering either the soil on which the grapes grow and the climatic conditions

Rare Earth Elements, are not as rare as their name can make believe, especially as regards the Light Rare Earth Elements, while the Heavy Rare Earth Elements have smaller quantities. The production of REEs is concentrated in a few countries, in order of production they are: China, Australia, Russia, USA, India, Canada and Vietnam. The demand for REE in the last 30 years has undergone constant changes in the years 50-60 of this century was the most requested europium, necessary for the production of cathode ray tubes. From the 80s to the early 90s, the question focused on cerium, used for TVs and monitors. Today there is greater demand for neodymium, praseodymium and dysprosium aimed at producing magnets.

In China, due to the presence of both the deposits of REEs that mineral extraction, the need arose to check what effects environmental and toxicological have the REEs, on crops. Many studies have been conducted in this respect, even if most of these are in the original language making it difficult for the divulging in the worldwide field, while others are partly available in reviews (Brown, 1990) (Hu, 2004) (Tyler, 2004). It appears that at low concentrations of REEs, both favored the growth and the production of some cultures (Guo, 1985) (Hu, 2004) (Ning, 1985).

Favorable results have meant that Chinese agriculture began to make extensive use of fertilizers containing REEs also since the 70s and 80s, production of the first commercial fertilizer nitrate of La, Ce, Pr and Nd , called “Changle-REEs” (Wu, 1995) (Yu, 1995). Over time have created new fertilizer, to be used in more and more areas and on different types of crops, also the practice began to spread outside of China, also expanding in some areas of the US and in the UK (Hu, 2004).

It is expected that the use of fertilizers based on REE, will continue to grow in the coming decades (Volokh, 1990).

Many studies have been conducted on the absorption of REE by plants, most of which was conducted in China, where 80% of the world's REE production is gathered (Brown, 1990); there, Rare Earth-containing fertilizers are widely used together with N fertilizers (Xu, 1997) (Wen HY., 2000).

The Rare Earth are absorbed by plants in different ways, depending on the species of the plant, the soil on which the plant is grown and the climatic conditions to which the plant is subjected, (G., 1977) (Ichihashi, 1992) (Miekeley N., 1994) (Wyttenbach A., 1998).

The plants absorb the REE in a selective way: some parts of the plant such as the roots and the leaves absorb most of the Rare Earths Elements: whereas the absorption in the stem is minor, and it decreases even in the fruits. The absorption is most in the roots and leaves because through them nutrients are absorbed by the plant (Nakashiki TM, 1997) (Xingkai X., 2002) (Xu, 1997) (Zhang ZY., 2002).

Recent study show the REE importance for identification of food origin (e. g. pumpkin seed oil), to improve quality control, to detect falsifications and protect the local economy (Bandoniene D., 2013) (Joebstl D., 2010). The same chemical analyses were also carried out on wine, to prevent fraud to counterfeit labels by identifying the geographical origin of the wines. Extensive studies have been carried out on wines from all over the world (Aceto M., 2013) (Gonzàlvez A., 2009) (Martin AE., 2012) (Rossano EC., 2007).

The areas chosen for the analysis are located in Sicily, and consist on the Hyblean Plateau and on the Mt. Etna. We selected three wineries Avide, Cos and Don Saro, respectively. This agricultural companies sit on in different soils, being Avide and Cos, carbonate soil, while Don Saro is a winery on volcanic soil.

Related to the rock that crop 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 study we want to highlight how different cultivars can absorb REEs in different amounts and, if it is the case, to use REEs as a discriminating tool; at the same time, we want to investigate how the climatic factors and soil can affect their absorption.

Viticulture in Sicily

The vine (Vitis vinifera) is a plant of very ancient origins, found in fossils from the Miocene, is native to the Mediterranean region, particularly in the Middle East. The vine was cultivated since ancient times, the first pictorial evidence of wine dates back to 7500 years ago (Ryan, 1999).

Viticulture in Sicily has ancient origins. Paleobotanical findings of Vitis show that grape has been eaten by the native populations since the Protohistoric Age (Collesano, 1998). Macroremains grapevine were found in provincial Agrigento, Trapani and Enna (Costantini, 1989) (Leighton, 1993) (Leighton, 1999).

According to the literature, Phoenicians introduced culture of the vine in the island and spread this knowledge throughout the Mediterranean and introduce the “Fiano” grape variety.

In the island, the grapevine was already present in wild form, as evidenced by the discovery of grape plants called "ampellidi" at the slopes of Mt. Etna and in the area of Agrigento.

Subsequently, the Greeks, who starting from the VIII century b. C. remained on the island for 500 years, developed viticulture in the fertile soils of the island, as well as the Romans did later in 264 b. C.. These two cultures are creators of accommodation of grapevine as “*alberello*” [cultivation form of the grapevine with reduced expansion, ideal for environments characterized by particular environmental conditions, the plant is grown under conditions reduced and closer to the ground, are located such types of cultivation in Val d'Aosta, due to the low temperatures, and in Sicily because of limited rainfall (Fregoni, 2013)].

In pre-Roman, southern Italy it was called "*Enotria*", it mean "*land of wine*" by” oinos” meaning wine and “*enotros*” that was the wooden pole that holds grapevine.

Each culture that succeeded in the course of time in the island has left an indelible mark of it, even in the cultivation of grapevine, especially during the Aragonese domination and the following Spanish domination, the agriculture and the culture of grapevine made enormous progress.

Sicilian wine production recorded its first boom in 1773, with the large-scale commercialization of the wines of Marsala thanks to the English Woodhouse.

In 1880-81, the grapevines Sicilian suffered a frightening epidemic, due to phylloxera, the vineyard area decreased from 320,000 to 175,000 hectares. The epidemic and the two world wars caused a setback in the production of Sicilian wines.

The recovery from these events was only in the 80-90th of the last century, in recent years there has been a restructuring of wine production, with improvement of cultivation techniques with the use of mechanization and a careful retraining of Sicilian wine, conducted by the Regional Institute of grapevine and wine. This picture is called “Miracle Siciliano”; Sicilian wines are not used anymore only to bring warmth and body to the wines of northern Italy, but are used for producing wines that express the “*terroir”* of Sicily.

Today Sicily is the largest wine producer region in Italy, its soils have an incredible variety of territories, spanning from sedimentary sandy soils located a few meters above the sea level, to vineyards grown in volcanic soils of Mt. Etna, the largest active volcano in Europe.

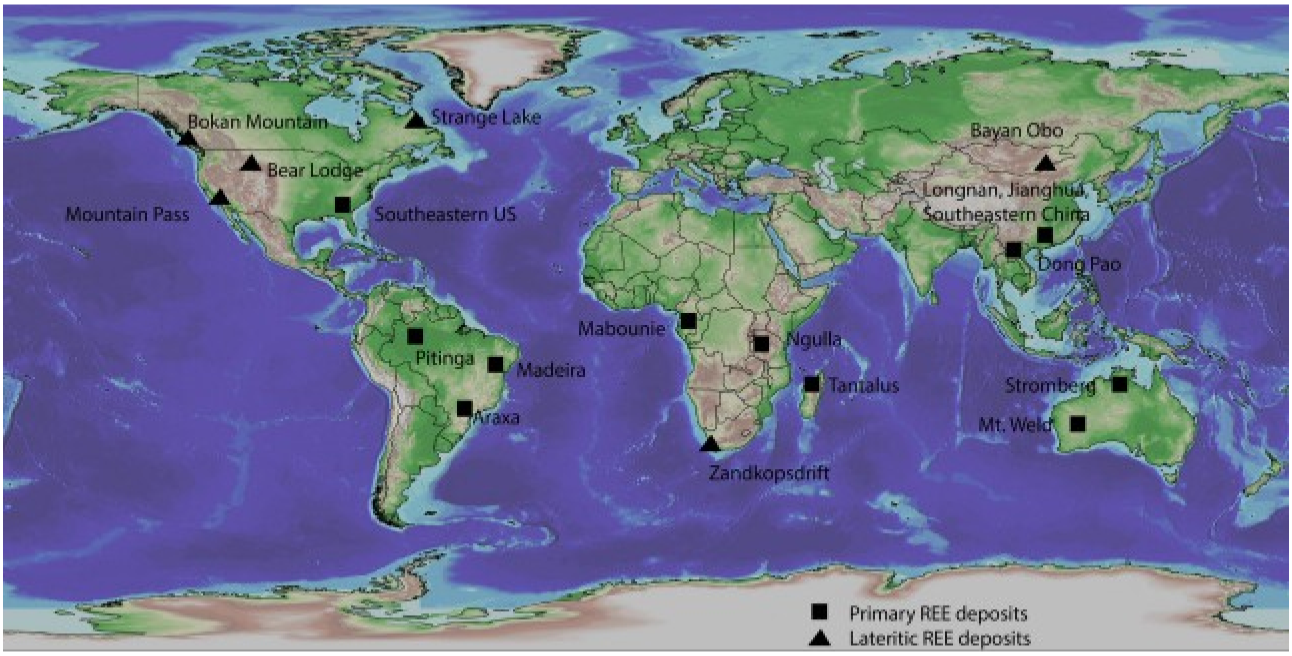
The main production areas are located in the administrative province of Trapani (western Sicily), the territories of Mt. Etna and the vineyards of the province of Syracuse.

Sicily is the Italian region with the most important wine heritage of Italy, followed by Puglia and Veneto regions. Most of the land dedicated to grapevine breeding is gathered in the hills 65%, 30% in the plains and only 5% in the mountains, the latter almost exclusively in the area of Mt. Etna.

According to 2008 year data the area occupied by vineyards, is of 119.893 hectares, of which an area of approximately 76.900 hectares is dedicated to white grapes, a percentage of 64.1%, while in the remaining areas, amounting about 42.839ha, red grape varieties are bred (Salvia, 2008).

According to data of the Land Registry Bourbon dating 1844, viticulture at Mt. Etna, was carried out on over 50% of the agricultural area, for a total of 25,600ha . Today this area is dramatically reduced because of the high costs of accommodation and plant cultivation of grapes in the mountains compared to cultivation in the plain, and the area cultivated with grapevine has been reduced to a few thousand hectares. Despite this, viticulture at the Etna is the most important mountain of the region, not only for the historical and socio-economic aspects, but primarily for the uniqueness of the wines that are obtained from local vines. Here, DOC dates back to 1968, one of the oldest in Italy. The vineyards cover an altitude between 300 and 900 meters above the sea level, reaching even 1,100 meters in some cases (Sparacio, 2010).

2.Rare Earth Elements



Picture 1 Primary and lateric Rare Earth Elements deposits in the world (Cocker, 2012).

The International Union of Pure and Applied Chemistry (IUPAC) defines as Rare Earth Element a series of seventeen chemical elements in the periodic table, Scandium (Sc), Yttrium (Y) and the series of lanthanides Lanthanum (La), Cerium (Ce) Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu). Among these elements only the promethium, which it is a radioactive element with a half-life of 2.62 years, is found in nature in concentrations practically irrelevant, whereas the other elements occur in nature. Scandium and Yttrium are considered part of the group of the Rare Earths, as they are located in the same mineral deposits of the lanthanides and exhibit similar chemical properties. In the present thesis with the title of "Rare Earth Element" (REEs), we will refer to the series of lanthanides, excluding promethium.

The terrestrial distribution of REEs follows the rule of Oddo-Harkins, who says: elements with even atomic number are much more common in the universe than those with odd atomic number. This rule is valid for all of the elements in the universe**,** and particular evident in the Lanthanides**.** The REEs, can be divided according to their atomic number into 2 groups: Lights Rare Earth Elements (LREEs), this group includes elements ranging from La to Gd which are relatively more soluble and more basic:, in the second group we find the Heavy Rare Earth Elements (HREEs), element enclosed in this group the least mobile elements ranging from Tb to Lu. Some authors also distinguish a third group of elements Medium Rare Earths Elements (MREEs), which includes elements from Sm to Ho (Xu, 2002). During the processes of weathering fractionation of REEs occurs, especially LREEs that will enrich the weathered material.

The Lanthanide series consists of element characterized as having ground state electronic configurations with at least one electron in the 4f electronic orbital. The REEs are usually +3 oxidative state. But the Ce, can be also +4 in some oxidizing environments and Eu can be also +2 in reducing conditions.

Properties of Lanthanide Elements (Natural)

Element	Atomic Number	Atomic Mass	Ionic Radius (pm)	Oxidation Status	Density (g/cm3)
La	57	138,9	117	+3	6,15
Ce	58	140,2	115	**+3**,+4	6,77
Pr	59	140,9	113	**+3**,+4	6,77
Nd	60	144,2	143	+2,+3,+5	7,00
Sm	62	150,4	135	**+3**,+2	7,52
Eu	63	151,9	131	**+3**,+2	5,24
Gd	64	157,3	108	+**3**,+2,+1	5,90
Tb	65	158,9	106	**+3**,+4	8,23
Dy	66	162,5	121	+2,+3,+4	8,55
Ho	67	164,9	104	+3	8,79
Er	68	167,3	103	+3	9,06
Tm	69	168,9	117	**+3**,+2	9,32
Yb	70	173,0	116	**+3**,+2	6,97
Lu	71	174,9	100	+3	9,84

Valence values in bold are for the main oxidation states

Table 1 Properties of Lanthanide Elements (Natural) (Kabata-Pendias, 2011).

The REEs, having affinity with silicate phases, are mostly concentrated in the silicate portions of the Earth, namely in the crust and in the mantle. These elements are abundant in igneous rocks, especially in those types of acid and clay sediments. They are embedded in many common minerals, of which are stoichometric constituents such as: monazite (monacite), (La, Ce, Th)PO_4; bastnasite, (CeF)CO_3; cheralite, (Ce, La, Y, Th)PO_4; and xenotime, YPO_4.The organic component has an important role in the distribution of REEs causing an increased concentration in humus horizons of soils in forest-soil litter.

Global production of REEs in recent decades has grown remarkably in the production. The two major sources of REEs, especially Ce, are monazite and bastnasite. In particular monazite, is associated with granite and gneiss rocks, and is very resistant to weathering, this means that thanks to the sedimentary processes focus in the sands of the beaches. China currently holds 80% of World production of these elements (Brown P.H., 1990).

The use of REEs in the field of the industrial sector is very diverse, ranging from the glass production (especially as colorants), to sophisticated electronic devices, metal alloys, catalytic converters, radar, rechargeable batteries etc. Cerium is added to the diesel fuel to lower the ignition temperature and slightly also as a filter (Ulrich, 2003).

Abundance of lanthanides in the environment (mg/kg)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Earth's Crust	30	60	8,2	28	4,7	1,2	5,4	0,6	3,7	0,8	2,8	0,5	2,2	0,3
Igneous Rocks														
Mafic	2-70	4-60	1-15	2-30	0,1-1,7	0,01-4	0,1-8	0,1-1,2	0,05-7	0,1-1,5	0,1-1	0,1-0,6	0,1-3,5	0,1-0,6
Acid	30-150	20-250	6-30	18-80	6-11	1-2	4-10	1-2,5	5-8	1,3-2	3,4-4,7	0,3-0,7	3-45	0,5-1,2
Sedimentary Rocks														
Argillaceus	30-90	3-90	6-10	18-35	5-7	1-2	5-7,5	0,9-1,1	4-6	1-1,8	2,5-4	0,2-0,6	2,2-4	0,2-0,7
Sandstones	17-40	25-80	4-9	16-48	4-10	0,7-2	3-10	1,6-2	2,6-7,2	0,05-2	1,5-6	0,3-0,7	1,2-4,4	0,8-1,2
Calcareus	4-10	7-20	1-2,5	5-9	1-2	0,2-0,4	1,3-2,7	0,2-0,4	0,8-2	0,2-0,3	0,4-0,7	0,03-0,2	0,3-1,6	0,003-0,2
Soils														
Arenosols (sandy)	0,9-3,5	8,4-21	1,4	3,6-7	0,7-3,5	0,2-0,6	0,7-5	0,2-0,5	0,8-5	0,2-1,1	0,3-1,7	0,4-0,5	0,4-1,5	0.05-0,3
Podzols (medium loarry)	5-21	44-56	5,5-6,2	18,7-26	3,5-6,3	1,3-1,5	4-5,9	1,0-1,2	3,6-5	1,1-2	2,1-2,3	0,4-0,6	2,3-2,8	0.4-0,5
Cambisols (heavy loarry)	20-36	32-64	13-15	18,2-31	3,4-5,9	0,6-1,7	6-15	0,7-1,4	7-11	1-2	1,7-4,8	0,5-0,8	1,3-3,3	0,2-0,5
Calcisols (calcareus)	_	_	_	_	_	_	_	_	_	_	0,5-0,8	_	_	_
Histosols (organic)	1,4-9,2	2-42	7,7	1-1,2	0,3-5,7	0,03-1,9	3,6-4,7	0,04-0,9	4,7	0,8	2,05	_	0,1-2,0	0,01-0,29

Soil group are given in according to the WB

Table 2 Abundance of lanthanides in the environment (mg/kg) (Kabata-Pendias, 2011)

REEs in soil

The content of REEs in soil is linked to the origin of the source rocks from which the soil derive, reflecting the mineral composition of these rocks. Usually, lower concentrations are found in sandy soils, whereas there are major concentrations in soils of clay type.

Trace element concentrations significantly differ among both soil groups and geographic regions (Sumner, 2000).

Humic acids play a very important role in the fractionation of Rare Earth Elements during weathering and transport on the Earth's surface, the binding activity of them being influenced by the pH conditions (Sonke J.E., 2006). Usually, acid soils contain less amount of lanthanides than alkaline soils, a possible cause may be due to the easy removal of soluble hydroxide complexes.

(Chojnicki J., 2000) noted a strong positive correlation between some LREEs (mainly La, Ce**,** Pr**,** Nd**,** Sm**)** and the fraction of fine-grained soil**.** LREEs are usually more abundant than HREEs in soils, as reported in many studies e.g. (Zhu J, 1997) conducted a study on the soil of China.

In many soils REEs are concentrated in the amorphous Fe-oxide- bound fraction (Hu, 2006).

In Andosols, Ferrasols and Leptosols REEs accumulate in the residual fraction, associated with carbonates, oxides, silicates and phosphates.

They define "Andosols" dark soils, often black, characterized by outcrops of volcanic ash, formed by complexes of allophane minerals and humus. They are also found on igneous rocks consolidated to glassy or finely crystalline phases, provided that the alteration has taken place quickly and that has released amorphous phases susceptible to fix the organic substance.

“Ferrosols” are soils usually formed from basalt materials. They are characterized by a low contrast between surface (A) horizon and the upper subsoil (B21) horizon. They have high levels of iron oxide shipping, usually greater than 5%.

According to the database of world's soil resources FAO, "Leptosol" soils are very superficial set of hard rock or highly calcareous soils or extremely gravelly and / or stony. They are mostly found in mountain areas, or where erosion keeps pace soil formation or removes the top layer of soil.

Moreover, REEs with odd atomic number accumulate in exchangeable fraction and soluble in water (Hu, 2006).

It has been proven by various authors that microorganisms affect the behavior of REEs in soils, especially as regards the interaction with organic ligands (Censi, 2010) (Ozaki T, 2006) (Perelomov L V, 2008).

The mobility of REEs in soil is considered to be low (Gaillardet J, 2003); nevertheless recent studies show that REEs are mobile during weathering in warm, humid conditions (Balashov, 1964) (Fleet, 1984) especially for the weathering of igneous rocks in warm climates (Banfield, 1989) (Mongelli, 1993) (Price, 1991).

It was also observed an extraction slightly greater with respect to certain elements (Sm, Eu Tb and Nd). The mobility of REEs however, is not equal in all of the soils, since there are factors that affect it, such as weathering, which is the factor that most affects their mobility; in fact in wet weather conditions, loss of surface layer can be observed due of the effects of leaching and alteration (Tyler, 2004). Another factor that affects the mobility of REEs is the pH of the soil as seen in the work by (Censi, 2005) (Tyler G., 2001).

The extensive use of REEs that was done in the industrial sector over the last decades has brought changes in their contents in soils. High concentrations in sludge and emissions of volatile industries have led to an accumulation of these elements in the soil even in areas far from heavily populated zones. High concentrations of La, Ce, Sm, Eu and Tb have been found in urban and industrial areas, probably due to release into the natural environment from coal combustion and from processes of energetic materials and nuclear activity. Other sources of pollution from REEs is due to anthropogenic factors are derived from petrochemical industries (Cenzi, 2004) (Kulkarni P., 2006) and urban pollution, as was seen in Warsaw in comparison with suburban areas (Zimny H., 1996).

In addition to industry another important source of REEs is from agriculture. Indeed, in 1980 China started making wide use of REEs enriched fertilizers (Ding, 2006). Fertilizers are a mixture obtained by extracting nitrates from minerals containing REEs through the use of nitric acid (Xu, 2002), only in 2001 it was calculated in China, according to data collected by the China Rare Earth Center, the application of about 3400 tons of REEs on millions of hectares of cultivated land. Many studies have been conducted in Chinese soils in order to assess the effects caused by this excess of REEs, both in soils and in food grown in them. (Xu X., 2001) contends that a application of REEs less than 230 g / ha per year does not influence the processes of oxidation and mineralization of soil. Less than 95% of REEs added to the soils are absorbed by these and seen their poor solubility is going to accumulate in soils (Hu, 2006).

REEs in Plants

Until the last decades poor attention was paid to the content of REEs in plants and physiological functions that these could cause. One of the first studies was done by (Robinson, 1958), who developed a work on hickory trees, considering the similarity between the REEs contained in the leaves of these trees and in soil. (Laul, 1979) studied the relative REEs abundances in plants and in the soil and found that the concentration found in plants is a direct consequence of the land on which the plants home. The content of REEs in plants decreases with increasing atomic number. Studies conducted also found that the absorption of REEs by plants is not the same, some species are relatively prone to REEs absorption. It seems that the woody plants have a great capacity for absorption, in particular the trees of hickory studied by (Robinson, 1958). Even mosses, lichens and bryophytes absorb high concentration of these elements as has been seen in various articles (Ruhling, 1987) (Djingova, 2003). As earlier reported, China does extensive use of REEs enriched fertilizers.

Despite that their use incentives some processes of plants as seed germination, root growth, nodulation and the production of chlorophyll, it seems that they are not essential elements for the growth of plants (Hu, 2004) (Liu, 1988) (Nakamaru, 2006). These improvements are made at low REEs concentrations, while at high doses, various studies have shown that the effects on plants are harmful, even leading to the death of plants. The addition of a concentration of 0.01mg / l nutrient solution to the plants disturbs the mineral balance in the tissues of plants (Shtangeeva, 2007) and (Zhu, 1999) have shown, the inhibition of the germination of the seeds in concentrations La above 200 mg / l.

Some of the Authors, who found positive effects on the part of the plants subjected to concentrations of REEs, however, did not specify in their articles the compounds of REEs used in their experiments nor discussed their function in the plant metabolism (Liu, 1988) (Xijie, 1986).

From an experiment conducted by (Xu, 2002), on corn plants treated with fertilizer enriched with REEs, also comparing various doses of fertilizers, it was observed that the accumulation of REEs in plants is not uniform, the plant accumulates in a selective way the elements. The accumulation will take place especially in the roots and leaves, whereas it is lower in the stem and even less of the fruits. The roots and leaves are the preferential ways of absorption, since in these parts of the plant the accumulation is greater. The same study noted that there is a greater accumulation of LREE (especially La and Ce) than the HREE. The results obtained from this work, have been confirmed on various species of plants by various authors (Ding, 2006) (De Boulois, 2008).

(Wyttenbach, 1997) studied the leaves of six different plant species grown in the same site, the concentrations of REEs, found in the leaves, despite the ground is the same for all, exhibit differences that are controlled by the species.

The study of concentrations of REEs in plants has gained increasing importance, in particular as regards foodstuffs (Goering, 2004) (Linag, 2005) (Liu, 1988). The use made of these elements as fertilizer, and the low solubility of REEs in the soils, means, a large accumulation in soils and therefore in foods derived from crops. There is clear evidence of toxic effects of the accumulation of REEs in plants such as, alterations on cell membranes of the plants and on the metabolism of microorganisms. What is certain is that an overdose has inhibitory effects on living organisms (Qiu, 2005). The effects on humans are not well known yet, even though studies carried out on (Cenzi, 2004). Currently concentration limits for human consumption have not been established by law yet.

Lanthanum (La)

Approximately 0.0018% of the Earth's crust is made up of La. The lanthanum is a lithophile element; it is located within monazite (Ce, La, Th, Nd, Y) PO_4 ,which may contain up to 25% of lanthanum, and also in a uncommon mineral like Cerite $(Ce,La)_9(Mg, Fe)Si_7(O,OH,F)_{28}$. La may be found in trace amounts in some rock-forming minerals like biotite, apatite, pyroxene and feldspar. It has a strong affinity for felsic igneous and a lower affinity of ultramafic rock. It has two natural isotopes ^{138} La and ^{139} La, the last representing 99% of total occurring lanthanum.

Its average concentration in the Earth's crust is $3.9 * 10^1$ milligrams per kilogram, while the oceanic average concentration amounts to 3.4×10^{-6} milligrams per liter. Lanthanum was discovered in 1839 by Carl Gustaf Mosander, a Swedish chemist. The discovery was accidental, the scientist was searching for impurities in some cerium bearing samples. While trying to isolate the impurities treated the nitrate cerium Ce (NO_3) with dilute nitric acid HNO_3, he noted that despite most of his sample was insoluble, part of it was soluble and concluded that it was the oxide of a new element, initially popularized the discovery because he was studying what he believed a second new mineral from the same experiment however proved to be an mixture. In the same year, a student called Axel Erdmann discovered lanthanum in a new mineral from the island Laven, located in a Norwegian fjord.

Today lanthanum is mainly obtained from the sand of monazite $(La, Ce, Nd, Pr)PO_4$ through an ion exchange process. World production of titanium oxide is around 12,000 tons per year, while the reserve notes are about 6 million tons.

This element is used in the film industry for the production of carbon arc lamps, used for the illumination of the studies and for the projectors. It is also used for the production of 25% of the Misch metal, which is a material that is used for the realization of the stones ignition of cigarette lighters. The lanthana La_2O_3 is used for the production of camera lenses and other types of special lenses.

Soil

The data about the contents of REEs in soil are very scarce. The average concentration of REEs usually corresponds to their content in sedimentary rocks, with the exception of the calcareous rocks, in this case in fact, the soils are richer than REEs in the parent rocks. The REEs are usually concentrated in alkaline soils than that in acid soils, the probable cause is the easy removal of their hydroxide complexes (Kabata-Pendias, 2001).

The average concentration of lanthanum content in subsoil is 25.6 mg Kg^{-1} and 23.5 mg Kg^{-1} in topsoil with range ranging respectively from 0.78 to 155 mg Kg^{-1} in subsoil and from 1.1 to 143 mg Kg^{-1} in topsoil. The average concentration of topsoil and subsoil is 0.905 mg Kg^{-1}.

Low concentrations of lanthanum in subsoil (less than 17 mg Kg^{-1}) are located in central and northern Finland, central Nordway and Sweden, in glacial drift covered mainland Europe (from Netherlands to Poland), in central Hungary and in parts of southern and eastern Spain. High levels of lanthanum in the subsoil (major to 36 mg Kg^{-1}) have in the north of Portugal, the Galicia (northern Spain) due to the crystalline basement of the Iberian Massif, and in Italy in alkaline igneous provinces, in the Massif Central, in Brittany, in karst soils of Croatia and Slovenia, in loess/paleoplacer that stretches from northern France to Germany, in the southeastern part of Norway and in the northwestern part of Sweden (Salpeteur, 2005).

Areas where there are abnormalities of lanthanum are in western Greece in soils of clay, the anomalies are associated with Phosphorite and Gypsum.

In topsoil concentrations of lanthanum they are low in Scandinavia, for the rest follow the same pattern of subsoil. You may find abnormalities in granites of Northern Ireland. The lanthanum into the soil shows strong correlations, including in a range from 0,70 to 0,98, with the other REEs.

Plant

The plants usually contain low concentrations of REES (Horovitz, 1974) (Markert, 1987) which depend from the soil and plant species.

The data concerning the content of REEs in plants, dealing mainly the LREEs. In particular, the absorption of REEs on plants subjected to concentrations gradually higher, to observe the behavior of the plants and at what concentrations they can have damaging effects for plants and therefore also for humans (Asher, 1990) (Asher, 1991) (Brown, 1990) (Hu, 2004) (Tyler, 2004) (Von Wiren, 1995). Studies have been performed on corn (Zea mays) and mungbean (Vigna radiata), through the use of solution cultures, to observe the plant reaction (Diatloff, 1995a). (Diatloff, 1995 b) (Diatloff, 1995c), there were toxic effects on root elongation, decrease the growth of corn and mungbean with concentrations greater than 0,2 µM in soil solution, with lower concentrations there were positive effects on plant growth. Corn accumulates significantly lower concentrations of La, compared the mungbean (Diatloff, 2008)

Cerium (Ce)

Cerium is the most abundant REE and represents approximately 0.0046% of the Earth's crust. It has four natural isotopes: ^{136}Ce, ^{138}Ce ^{140}Ce and ^{142}Ce; the last of them includes 88.5% of the total mass of cerium present in nature. Even cerium, such as lanthanum, is mainly found in monazite and also in Perovskite, a titanium ore, and in allanite. Its average concentration in the Earth's crust is 6.65×10^{1}milligrams per kilogram, while the oceanic average concentration amounts to 1.2×10^{-6} milligrams per liter**.**

Granites, with 230 mg kg -1tend to have a higher cerium content than the mafic volcanic rocks, which have an average content of 30 mg kg -1 (Manson, 1966) (Manson, 1982).

The discovery of cerium is due to Jöns Jacob Berzelius and Wilhelm von Hisinger matter, a Swedish and a German chemist, respectively. The discovery took place simultaneously in 1803.

Cerium is a malleable, ductile and soft, gray - iron, it is slightly harder than lead. This metal is very reactive, it tarnishes easily in the air, it oxidizes slowly in cold water and rapidly in hot water. It can be dissolved by acids.

Cerium is mainly obtained from the monazite-bearing sand through an ion exchange process; the world production amounts to 23,000 tons for year .

Cerium is used as a catalyst in petroleum refineries and as the binding agent to make special metals. Other uses are the realization of the Misch that is used in cigarette lighters and even the lamps used in the film industry. The cerium oxide Ce_2O_3 and CeO_2 is a component used in the production of self-cleaning ovens and of incandescent lantern mantles, it is also used for polishing glass surfaces. sulfate cerium $Ce(SO_4)_2$ is instead used in some types of chemical analyses. In the glass industry uses other compounds of cerium, mainly for the production of certain types of glass and for the removal of color from the glass.

Soil

The abundance of cerium in soil varies from 15.8 to 97 mg kg $^{-1}$, quoted with a mean of 48 mg kg $^{-1}$. The highest amounts, as for all of REEs, are found in alkaline and acidic soils because of their easy removal of hydroxide complexes. Soils carbonate, resulting from carbonate rocks show a significant enrichment in REEs (Kabata-Pendias, 2001).

The average concentration in subsoil is 54 mg kg -1 and 48.2 mg kg -1 in the topsoil, these averages are included in a range from 4.1 to 379 mg kg -1 for the subsoil and from 2.45 to 267 mg kg $^{-1}$ in the topsoil. With an average ratio of topsoil and subsoil of 0.899.

Low values of Ce, in subsoil, of less than 35 mg kg $^{-1}$, are especially measured in Finland, in the glacial drift which covers the northern part of continental Europe, which includes mainly from Netherlands to Poland, in West Hungary central, in the basin of Paris in France and the south east of Spain. In contrast, high values above 75 mg kg $^{-1}$ are located in metamorphic and granite rocks of northern Portugal, and in the north west of Spain, in the Massif Central and Brittany in France, in Italy, so high concentrations are located in the alkaline provinces containing strong anomalies, in karst of Croatia and Slovenia, close to Austria, in the sedimentary deposits loess/paleoplacer that stretches from France to Germany and finally in Sweden (Salpeteur, 2005).

The lowest concentration amount soft cerium is in Scandinavia, with topsoil values only slightly higher than in Slovakia. By contrast, the highest higher concentrations are distributed in a large area in western Spain near Almeria, characterized by clastic rocks, schist and orthogneiss, in Variscan Extreadura, in the Pyrenees Central and Western and the island of Gran Canaria, where the concentration is high connected to the basic alkaline volcanism.

Cerium shows good correlations, between 0.6 and 0.8 with the other REEs, both in the subsoil and in topsoil. The correlations are higher with LREEs (La, Pr, Nd, Sm) because they have similar atomic weight and ionic radius.

Plant

Research was conducted to observe the effects of the absorption of cerium by plants on corn and mungbean, proving toxic effect on root elongation and decrease the growth of mungbean and corn with greater concentration 0,2 µM in soil solution, and positive effects with lower concentrations. Moreover it is seen that at the same concentration of solution the plants absorb the element in a different way, with a greater absorption by the corn compared to mugbean (Diatloff, 1995a) (Diatloff, 1995 b) (Diatloff, 1995c) (Diatloff, 2008).

Praseodymium (Pr)

Praseodymium is mainly found in monazite (Ce, La, Th, Nd, Y) PO_4 which is very rich in Rare Earth Elements. Its average concentration in the Earth's crust is 9.2 milligrams per kilogram, while the oceanic average concentration amounts to 6.4×10^{-7} milligrams per liter.

Praseodymium is the discover of Carl F. Auer von Welsbach, a German chemist, who, separated him from a material known as didymium which is a mixture of praseodymium and neodymium. Today it is achieved through an ion exchange process from monazite-bearing sand.

The major use of praseodymium is in the metallurgical industry as the binding agent for the production of high-strength metals used for the production of aircraft engines. Even praseodymium is part of the elements that constitute the Misch metal,(5%), the metal is used for the production of flint stones into the lighters. In the film industry it is used as a core for the production of carbon arc lamps. In fiber optic cable the praseodymium using it as a doping agent where is used as a signal amplifier. Another field where it is used is in the glass industry, for the production of didymium glass, which is used to produce welding goggles and glass blower. Praseodymium salts are used as coloring agents to give the yellow color to glasses and enamels.

Soil

The average content of Pr in subsoil is 6.04 mg kg $^{-1}$, in a range from 0.14 to 32.9 mg kg^{-1} and 5.60 mg kg^{-1} in the topsoil, with a range from 0.29 to 31.6 mg kg $^{-1}$ .The average ratio topsoil / subsoil is 0.897 mg kg $^{-1}$.

Regarding the subsoil, there are low values of less than 4 mg kg $^{-1}$. Praseodymium mainly occurs in Finland, in the glacial drift that goes from the Netherlands to Poland, in central Hungary, in the Paris basin in France and in the south east of Spain (Salpeteur, 2005). High concentrations in excess of 9 mg kg $^{-1}$ are found in northern Portugal and northwestern Spain, located in Variescan granites and metamorphic rocks, so high concentrations can also be found in the Massif Central and Brittany in France, in the Italian alkaline provinces, containing strong anomalies in Karst of Croatia, Slovenia and Austria, in the southwest of Norway and Sweden and in the north-east with loess / paleoplacer extending from northern France to Germany (Salpeteur, 2005). In Europe, are in Slovakia, whereas the lowest in Finland. Huge concentrations are found in Spain in clastic rocks, shale and gneiss in the garden in the area of Almeria, and the Canary Islands are also found high values associated with basic alkaline volcanic rocks. The models that we have for the topsoil are similar to those of the subsoil.

The praseodymium is strongly correlated with the other REEs, especially with LREEs, La, Ce, Nd and Sm which are similar to atomic weight, both ionic radius.

Plant

Until now it has not been recognized to praseodymium no specific role from biological viewpoint. The element has a low toxicity, but until now no specific studies have been conducted.

The content of praseodymium in plants varies both according to the condition of the environment (content of praseodymium in the soil, climate) to the species to which the plant it belongs.

Neodymium (Nd)

Neodymium is very abundant in nature, it is quite as abundant as copper. Neodymium, as many REEs, is located in monazite e bastnaesite. Its average concentration in the Earth's crust is 4.15×10^{1} milligrams per kilogram, while the oceanic average concentration amounts to 2.8×10^{-6} milligrams per liter.

Neodymium was discovered by Carl F. Auer von Welsbach, a German chemist, in 1885, he separated the neodymium, and praseodymium from a material known as didymium. Now a days it is obtained through a process of ion exchange, from monazite-bearing sand.

Neodymium is yellow silver colored metal, it is very reactive, it tarnishes rapidly in air and reacts with cold water and rapidly with hot water.

Neodymium has different uses, it constitutes 18% of Mish metal, used in power stones lighters. It is also used together with praseodymium as a component of didymium glass, which is used for making glasses and glass blower from welder. Another use, always in the glass and to remove the color from green glass, color is due to contaminants of iron, or it is added to color glass in shades of purple, red or gray. Other uses are in the glass industry for the creation of glass used by astronomers to the calibration of the spectrometers. It is also used for the laser and for the creation of artificial rubies. Neodymium salts are used as colorants but always for coloring glazes.

The main areas of neodymium extractionare located in Brazil, China, USA, India, Sri Lanka and Australia. World reserves are estimated at around 8 million tons, the production of neodymium oxide worldwide is about 7,000 tons for year.

Soil

The average content of neodymium in subsoil is 22.4 mg kg^{-1}, within a range that ranges from 0.46 to 111 mg kg^{-1} in the topsoil content is slightly lower, with an average concentration of 20.8 mg kg^{-1} with a range from 1.14 to 132 mg kg^{-1}. The average topsoil / subsoil ratio is 0.896.

Low Concentrations of neodymium less than 15 mg kg^{-1} have been detected in the subsoil of Finland, in the glacial drift That goes from Netherlands to Poland, in the Paris Basin, France, Hungary central and south-eastern Spain. Conversely, the European locations where concentrations of neodymium are highest than 32 mg kg $^{-1}$ are in granite and metamorphic rocks above the Variscan belt located between northern Portugal and northwestern Spain, in the Massif Central and in Brittany in France, in the Italia alkaline provinces, in karst of Slovenia, Croatia and Austria, in loess / paleoplacer ranging from Germany to northern France, in southwestern Norway, and the north west of Sweden (Salpeteur, 2005).

Low concentrations of topsoil are in Scandinavia and in Slovakia. The highest concentrations of the topsoil in Europe are in western Spain, in the area of Almeria, where clastic rocks, schist and orthogneiss crop out; high values are also in the central and western part of the Pyrenees, and in Gran Canaria, in the latter area high concentrations are due to the alkaline mafic volcanism. The pattern between Topsoil and subsoil remains the same throughout Europe.

Neodymium has strong correlations > 0.6 and very strong > 0.8 with other REEs, both in topsoil than in subsoil. The correlations are greater with LREEs, La, Ce, Pr, Sm whose ionic radius and atomic weight are very similar to each other.

Plant

Neodymium has no role recognized by the biological viewpoint because of the scarcity of work on this element. Nevertheless, he is paid a moderate toxicity.

The content of neodymium in plants depends on the environmental conditions and the species of plant.

Promethium (Pm)

Promethium is obtained by-products of uranium fission. Another way to get it is through the bombardment of neodymium ^{146} with neutrons. Promethium does not occur in nature. Its most stable isotope is the promethium ^{145}, this isotope has a half-life of 17.7 years old, downhill fast neodymium ^{145}.

Several groups of scientists have claimed for the element discovery, but were unable to confirm this discovery ever because of the extreme difficulty of separating promethium from other elements. Evidence of its effective existence came in 1944, thanks to Jacob A. Marinsky, Lawrence E. Glendenin and Charles D. Coryell. Scientists do not divulged the discovery until 1946 because of World War II; they discovered the new element, while analyzing the byproducts of uranium fission products in a nuclear reactor.

Given the extreme rarity of the item and the huge costs that you would meet to produce it there are currently no practical uses of promethium. Nevertheless its possible theoretical use could be for the realization of a nuclear-powered battery that would be able to provide energy for 5 years. Other possible uses theorists promethium are: Portable X-ray source, in radioisotope thermoelectric generators can provide electricity to satellites and space probes, and finally in the military field for communication with submerged submarines.

Soil and Plants

Promethium is not present in the nature environment.

Samarium (Sm)

Samarium is the fifth most abundant Rare Earths Element, it is a silvery-white metal, relatively stable at ambient temperature in dry air, but it ignites when heated to a temperature above 150° C and forms an oxide coating in moist air. It was never found in free form in nature, but it is contained in many minerals, including monazite, bastnasite and samarskite. Its average concentration in the Earth's crust is 7.05 milligrams per kilogram, whereas the oceanic average concentration amounts to 4.5×10^{-7} milligrams per liter.

1853 is the year in which the first spectroscopic observation of samarium was done by Jean Charles de Marignac Galissard, a Swiss chemist; the scientist looked at it in a material known as dydimia. In 1879 the element was isolated from the mineral samarskite $(Y, Ce , U, Fe)_3 (Nb, Ta, Ti)_5O_{16})$, by a French chemist , Paul-Émile Lecoq de Boisbaudran.

Currently, samarium is obtained by ion exchange process from the sand of monazite (Ce, La, Th, Nd, Y) PO_4 which contains up to 2.8% of samarium.

Its uses are multiple: realization of arc lamps carbon used in the film field, it also constitutes 1% of Mish metal used to make the flints into the lighters. The samarium oxide

Sm_2O_3 in the glass industry, is used for the realization of glasses that absorb infrared radiation. This oxide also acts as a catalyst, for dehydration and dehydrogenation of ethanol C_2H_6O. Also samarium form a compound with cobalt $SmCo_5$, forming a strong permanent magnet capable to resist demagnetization of each material.

The main areas of extraction of samarium are in the United States, China, Brazil, India, Australia and Sri Lanka. World production of samarium oxide is about 700 tons per annum and world reserves are estimated at 2 million tons.

Soil

We divide the average content of samarium between subsoil and topsoil. For the subsoil is the average concentration of 4.38 mg kg^{-1}, comprised in a range that goes from 0.1 to 18.2 mg kg^{-1}, while for the topsoil is the average concentration of 3.96 mg kg^{-1} comprised in a range that goes from 0.23 to 30 mg Kg^{-1}, with an average ratio between topsoil and subsoil of 0.88.

Lower concentrations in the subsoil, according to (Salpeteur, 2005) at concentrations less than 2.87 mg kg^{-1} are located in Finland, in the glacial rift that covers the northern part of Europe, that goes from Poland to Netherlands , in central Hungary, in the Paris Basin in France and Spain in the south east.

High concentrations of samarium in the subsoil, greater than 6.61 mg kg^{-1} are located in granitic rocks and Metamorphic outcrops found between Portugal and eastern Spain, in the Massif Central in France, in the Italian alkaline province, in Croatia, Austria and Slovenia, in part of the loess / paleoplacer area of northern France to Germany, in the southwest of Norway and in northeastern Sweden (Salpeteur, 2005).

The lowest concentration of samarium in the topsoil occurs in Scandinavia and in Slovakia, but in the latter with slightly higher concentrations. High concentrations of samarium in topsoil found in the Iberian Massif located in western Spain, as well as in central and eastern Pyrenees, and in the island Gran Canaria is characterized by an alkaline mafic volcanism. As for the other REEs, as described above, the trends of subsoil and topsoil are very similar. Samarium shows strong correlations with the other LREEs.

Plant

Samarium is characterized by low toxicity. Also for this element, there are many studies about it; from the biological viewpoint and he has not been given until now no role in the biological field. The content of samarium in plants, depends on the environment in which the plants grow and the plant species examined.

Europium (Eu)

Europium is the most reactive REE. It rapidly tarnishes in air at ambient temperature, burns at about 150 °C to 180 °C and rapidly reacts with water. It is a silvery and soft metal, rare and expensive, it is one of the least abundant of REEs. It is never found in nature as a free element, since is located in the mineral monazite (Ce, La, Th, Nd, Y) PO_4. Its average concentration in the Earth's crust is 2.0 milligrams per kilogram, while the oceanic average concentration amounts to 1.3×10^{-7} milligrams per liter.

The discovery of europium dates back to 1896, thanks to a French chemist Eugène-Antole Demarçay. The scientist suspected that the samples of an item, which had been recently discovered, the samarium, were contaminated with an unknown element, which was europium.

Now a days, europium is obtained through an ion exchange process from the sand of monazite (Ce, La, Th, Nd, Y) PO_4, although since 1901 he was already able to produce this element with a degree reasonably pure. The main mining areas are China and the United States. World reserves are estimated at 150,000 tons, and world production is 100 tons per year.

Currently, there are no commercial applications for europium, since it is a good absorber of neutrons, it is being studied for use in nuclear reactors. However, as regards its compounds, europium oxide Eu_2O_3 is widely used in the electronics industry as red phosphorus in televisions and as an activator of the yttrium-based phosphors.

Soil

The average content of europium in the subsoil is of 0.84 mg kg^{-1}, included in a range that goes from 0.05 to 4.66 mg kg^{-1}, that of the topsoil is slightly lower, as for the other REEs, has an average concentration of 0.77 mg kg^{-1} in a range from 0.05 to 6.99 mg kg^{-1}. The average ratio of topsoil/subsoil is 0.884.

With regard to the subsoil, in Europe the lower concentrations, less than 0.59 mg kg^{-1} are found in Sweden and Finland Central, in glacial drift in Northern Europe that goes from Poland to Netherlands, in central Hungary, in France in the Paris basin and the south east of Spain. The greatest concentrations in Europe of europium in the subsoil, greater than 1.18 mg kg^{-1} are found in igneous and metamorphic rocks of the Variscan basement in Portugal and Northern Spain, Galicia and Extremadura, in the granitoid rocks of the central Pyrenees, in the Italian magmatic provinces containing alkaline strong anomalies, in Brittany in France, Croatia and Slovenia in the loess / paleoplacer area of northen France to Germany, in eastern Slovakia, Hungary, in the southwest of Norway and in the northeast of Sweden (Salpeteur, 2005).

In Europe, high amounts of europium are detected located in Central Macedonia and Thrace in Greece, these values are due to the felsic rock and mineralization, while the anomaly in Western Greece is associated with clay soils and phoshorite mineralization.

In topsoil, the low concentrations of europium are located in Scandinavia and slightly higher in the Eastern Pyrenees, in the Variscan basement of Spain, in metamorphic rocks Nevado Filàbride in south-eastern Spain, in the alkaline mafic volcanic rocks of Gran Canaria, in northeast Italy. Although for most of the cases the pattern of concentrations of europium in topsoil reflect those of Subsoil. The average ratio of topsoil / subsoil is 0.88.

Plant

The European is characterized by low toxicity. So far he has not been recognized any role from biological viewpoint because of the scarcity of studies. Its content in plants varies according to several factors: the concentration of the element in the soil on which the plant grows, the weather conditions and plant species.

Gadolinium (Gd)

Gadolinium is a silvery metal, shiny, mobile, and versatile, It is one of the most abundant REEs. It is never found in nature but is contained in many rare minerals and it is mainly found within monazite and bastnasite. Its average concentration in the Earth's crust is 6.2 milligrams per kilogram, while the oceanic average concentration amounts to 7×10^{-7} milligrams per liter. The main mining areas are China, USA, Brazil, Sri Lanka, India and Australia with reserves that are believed to exceed a million tons. World production is of about 400 tons per annum.

In 1880 there was the first spectroscopic evidence of the existence of gadolinium by the Swiss chemist Jean Charles Galissard de Marignac, in the minerals didymia and gadolinite (Ce, La, Nd, Y) $_2FeBe_2Si_2O_{10}$.

Gadolinium has a great ability to capture thermal neutrons. This ability makes it suitable to be used for the realization of control rods for nuclear reactors. Although the isotopes of gadolinium more suited to this function (gadolinium ^{155} and gadolinium ^{157}) are present only in minimal amounts, causing the control rods rapidly lose their effectiveness. There are also other uses of this element, in combination with the yttrium, form garnets that are used in microwave technology; bonded with iron, chromium and other metals improves strength at high temperatures and oxidation resistance and improves the workability. Furthermore compounds of gadolinium are used for the realization of phosphors used in color television.

Soil

The average concentration of gadolinium in the subsoil is of 4.24 mg kg^{-1}, and for the topsoil is 3.85 mg kg^{-1}. The range in which is included the concentration in the subsoil is between 0.1 and 16 mg kg $^{-1}$, topsoil is instead between 0.20 and 36 mg kg^{-1}, with an average ratio between topsoil and subsoil is 0.897.

Low concentrations of gadolinium, of less than 2.86 mg kg^{-1}, in the subsoil of Europe, are concentrated in the center and north-eastern Finland, in the glacial drift that goes from Netherlands to Poland, in France in the Paris basin , in central Hungary and in southern and eastern Spain. Concentrations higher than 6 mg kg^{-1} are in the crystalline basement of the Iberian Massif located between northern Portugal and northwestern Spain, in the central and eastern Pyrenees, the Massif Central in France, in alkaline igneous provinces of northern Greece and Italy (Plant, 2005), in karst soils of Slovenia and Croatia, Hungary and southern Austria, in the loess / paleoplacer area of northern Germany to France, in southwestern Norway, and in the northern Sweden (Salpeteur, 2005).

There are also localities with Gadolinium anomalies located in eastern Greece associated with red earth soils and phosphorite mineralization.

The pattern of topsoil reflect those of the subsoil, with lower concentrations in Scandinavia and points of failure in the alkali basalt island of Gran Canaria in Spain. Gadolinium in the soil has strong correlations with other REEs. Its chemical behavior is very similar to the other HREEs.

Plant

Gadolinium is a highly toxic element for life forms. Few studies have been carried out and are usually not specific only on particular element but treat all the lanthanides, for this is usually difficult to understand the effects that the single element on the plant (Giussani, 1998) (Sun, 1997) (Yang, 1999). In the work of (Lidner, 2013) in particular, it was observed the absorption of gadolinium by L. Savitium plants, in controlled laboratory conditions. The study observed that the gadolinium placed on the solution into the ground, was quickly absorbed by the roots, and to accumulate in to a greater extent in the leaves than the roots or stem of the plant.

Terbium (Tb)

Terbium is a silver-gray metal, soft, malleable, ductile, and it is one of the rarest of REEs. It is reasonably stable in air, but it oxidizes and reacts slowly with cold water. It was never found in nature as a free element, but is found in many minerals including: xenotime YPO_4 and euxenite ((Y, Ca, Er, La, Ce, U, Th) (Nb, Ta, Ti)$_2$O$_6$) as well as in monazite containing up to 0.03% of terbium. Its average concentration in the Earth's crust is 1.2 milligrams per kilogram, while the oceanic average concentration amounts to 1.4×10^{-7}milligrams per liter.

The element was discovered in 1843 by a Swedish chemist Carl Gustaf Mosander. The scientist separated from gadolinite (Ce, La, Nd, Y)$_2$FeBe$_2$Si$_2$O$_{10,}$ three materials which called yttrium oxide, erbia and terbia. Because of the similarity of the names and properties of materials names were reversed by mistake since 1877. From these substances Mosander discovered two new elements terbium and erbium.

Now a day terbium is mainly obtained from monazite bearing sand, through a process of ionic exchange. But it may also derive from xenotime and euxenite.

terbium is used to dope some types of solid-state devices. Together with zirconium dioxide ZrO_2 it is used as a stabilizer in fuel cells that operate at high temperatures.

The terbium oxide, also called terbia, has the potential to be used as an activator for green phosphors in televisions. Finally another compound of erbium, the sodium terbium borate is used for the laser.

The main mining areas are located in China, US, India, Sri Lanka, Brazil and Australia. The reserves of terbium are estimated 300,000 tons; the world production is 10 tons per annum.

Soil

The average content in terbium in subsoil is in a range from 0.02 to 2.36 mg kg^{-1} with an average content of 0.64 mg kg^{-1}, into the topsoil by the compositional range is from 0.03 to 7.01 mg kg^{-1} and an average concentration of 0.60 mg kg^{-1}. The report topsoil / subsoil is equal to 0.910.

The European locations where the abundances of terbium are less than 0.45 mg kg^{-}1 are Northern Finland, the glacial drifts area from Netherlands to Poland, the Paris Basin in France, Hungary and Portugal, central, southern Spain and Eastern Europe. The European locations with high concentrations in excess of 0.90 mg kg^{-1}. The crystalline basement of the Iberian Massif between the north-western Spain and northern Portugal, the Massif Central in France, in alkaline igneous

provinces in Italy and central Macedonia in Greece (Plant, 2005), karst soils of Croatia and Slovenia, Austria and Hungary in the south, in the loess / palaeoplacer area of northern France to Germany, in southwestern Norway and lastly in northern Sweden (Salpeteur, 2005). There are also anomalies on time in Greece associated with red earth soils and phosphorite mineralization. The performance of topsoil perfectly mirrors that one of the subsoil, the lower concentrations in the topsoil of terbium are located in Scandinavia, and there is an anomaly on time in the Spanish island Gran Canaria due to the presence of alkali basalts.
Terbium in soil has very strong correlations with the other REEs, in particular the behavior is very similar to that one of the other HREEs.

Plant

The concentration of terbium in plants is generally very low. Out of 36 different species of plants analyzed in the city of Matsuyama (Japan) we have been found very low values, below the measurement limits of the instruments (Ichihashi, 1992).

Dysprosium (Dy)

Dysprosium looks silver, shiny and very soft. It is one of the most abundant REEs. It was never found as a free element, conversely it is found in many minerals, the most important being monazite and bastnasite. Its average concentration in the Earth's crust is 5.2 milligrams per kilogram, while the oceanic average concentration amounts to 9.1×10^{-7}milligrams per liter.

Dysprosium was discovered in 1886 by a French chemist Paul-Émile Lecoq De Boisbaudran, which I find as an impurity in the oxide of ernio, the erbia. In 1906, another French chemist, Georges Urbain succeeded in isolating the metal. While pure samples were obtained only from 1950 onwards.

Currently it is obtained through an ion exchange process from sand monazite (Ce, La, Th, Nd, Y) PO_4. World production is around 100 tons per year.

There are no commercial applications for dysprosium. Given its high ability to easily absorb neutrons and the high melting point, it may be bound with steel and be used in nuclear reactors. It is used as material for the construction of the laser when it is combined with the Vanadium and other elements of REEs. The dysprosia or oxide dysprosium Dy_2O_3, is combined with the Nickel and adds it to a particular type of cement that is used for the cooling of the rods of nuclear reactors.

Other compounds of dysprosium are: dysprosium fluoride (DyF_3), dysprosium iodide (DyI_3) and dysprosium sulfate ($DY_2 (SO_4)_3$).

Soil

The average content of dysprosium, in European subsoil is 3.66 mg kg^{-1} in a range from 0.1 to 12.7 mg kg^{-1} and for the topsoil is of 3.42 mg kg $^{-1}$ in a range ranging from 0.10 to 44.9 mg kg^{-1}, with an average ratio of topsoil and subsoil of 0.919.

In Europe dysprosium, is found in amounts less than 2.52 mg kg^{-1} in the central and northern Finland, in glacial drift extending from Poland to Netherlands, in the Paris Basin in France, Hungary and in central Portugal, in south and east of Spain and in the eastern sector of Greece.

Concentrations above 4.96 mg kg^{-1} are instead in the crystalline basement of the Iberian Massif located in northwestern Spain and Portugal, in the central and eastern Pyrenees, in the Italian alkaline magmatic provinces, in karst soils of Croatia and Slovenia, in the south of Hungary and Austria, in areas of Central Macedonia and Thrace in Greece, related to felsic rocks and mineralization, in the loess / palaeoplacer area of northern France to Germany, in southwestern Norway and in the northern part of Sweden (Salpeteur, 2005). Anomalies are also found in western Greece, associated with the soil of the Red Earth and phosphorite mineralization and Northern Ireland near the Mourne granite.

Also in this case the performance of the topsoil reflects that of the subsoil, with lower concentrations measured in Scandinavia and points of anomaly located in the island of Gran Canaria measured in alkali basalts. Dysprosium has strong and very strong correlation with the other REEs, especially its geochemical behavior is similar to that one of other HREEs.

Plant

The dysprosium, has a medium toxicity. Like most of the Rare Earths, has an established role in nature from the biological point of view, the lack of information is due to the fact that rare earths are almost always studied together, and studies related to a single item are extremely rare (Tyler, 2004).

Holmium (Ho)

Holmium is a ductile, malleable silver in color, it is one of the rarest REEs, it is obtained from monazite that contains up to 0.05% and bastnasite. Its average concentration in the Earth's crust is 1,3 milligrams per kilogram, while the oceanic average concentration amounts to 2.2×10^{-7} milligrams per liter.

The Swedish chemist Per Theodor Cleve, discovered holmium in 1879. The researcher found impurity oxides of other elements of REEs. Starting from erbia oxide, erbium Er_2O_3, removed all known contaminants, and after other treatments obtained two new materials, one brown and called holmia, and a green and called thulia. These two materials are the oxide holmium and thulium, respectively. The spectrum of holmium was observed at the beginning of the same year by two pharmacists, Swiss J.L. Soret and M. Delafontaine.

Now a days, holmium is obtained through an ion exchange process from monazite sand (Ce, La, Th, Nd, Y) PO_4. The main mining areas are in China, United States, Brazil, India, Sri Lanka and Australia. The world production is 10 tons for year, while the estimated reserves are 400,000 tons. There are no commercial applications regarding holmium. Even if its use in the future is not improbable because of its unusual magnetic properties. Nor are there any compounds of holmium important from the commercial point of view. Some of the holmium compounds: holmium oxide (Ho_2O_3), holmium fluoride (HoF_3) and holmium iodide (HoI_3).

Soil

We distinguish the average concentrations of holmium in European soils between subsoil and topsoil, subsoil is the average of 0.74 mg kg^{-1}, in a range from 0.02 to 2.58 mg kg^{-1}, the average concentration is slightly higher than that measured in the topsoil which is 0.68 mg kg^{-1} comprised in a range that goes from 0.03 to 9.16 mg kg^{-1}. The relationship between topsoil and subsoil is 0.923.

Lower concentrations of holmium, below 0.5 mg kg $^{-1}$, in the subsoil of Europe, are found in the northern part of Finland, in the glacial drift that extends from Poland to Netherlands, in France in the Paris Basin in the Western Alps and the Rhône valley, in the central parts of Portugal and Hungary, in the south and in the east of Spain, and in the eastern part of Greece (Salpeteur, 2005).

Holmium concentrations above 1 mg kg-1 are located in the crystalline basement of the Iberian Massif located between northern Portugal and north-western Spain, in alkaline magmatic provinces, which are in Italy and in northern Greece (Plant, 2005), in karst soils of Slovenia and Croatia, in the

southern part of Austria and Hungary, in Brittany, in the south west of Norway, in northern Sweden and finally in the loess / paleoplacer area of northern from France to Germany (Salpeteur, 2005).
Point holmium anomalies are found in the eastern part of Greece associated with "*Terra Rossa*" soils and phosphorite mineralization, other areas where there are point anomalies are in Northern Ireland, near the Mourne granite.
The trend of the subsoil is reflected in the topsoil where they also point to anomalies due to alkali basalts in the Spanish island of Gran Canaria.
Holmium in the soil has to be strong to very strong correlations with other REEs, its geochemical behavior is similar to that of other HREEs.

Plant

Studies, conducted primarily in China, have been performed on holmium (Qu, 2004), studies show positive effects on plant root elongation Vicia Faba, with small doses of holmium. There are not many studies that relate to the single element, the majority of studies usually regards all the REEs.

Erbium (Er)

Erbium is one of the most abundant REEs, it is a color silvery metal, bright, soft and pliable. It is very stable in air, reacts slowly with oxygen and water and dissolves in acids. The erbium is found in minerals xenotime YPO_4 and euxenite $(Y, Ca, Er, La, Ce, U, Th) (Nb, Ta, Ti)_2O_6$, but it is also found in monazite and bastnasite Its average concentration in the Earth's crust is 3,5 milligrams per kilogram, while the oceanic average concentration amounts to $8,7\times10^{-7}$milligrams per liter.
Erbium was discovered, along with terbium, by the Swedish chemist, Carl Gustaf Mosander in 1877, from the mineral gadolinite $(Ce, La, Nd, Y)_2FeBe_2Si_2O_{10}$ discovered in a quarry near the town of Ytterby, Sweden.
Today erbium can be obtained by a process of ion exchange from xenotime and euxenite. The main mining areas are in China and in the United States. The world production is around 500 tons per annum.
Erbium is associated with Vanadium, in order to make this last softer and easier to mold. Other uses of the element are in the fiber optic cable which is used as a doping agent to amplify the signal, and

in the field of nuclear energy. The erbium oxide Er_2O_3, erbia, pinkish in color, is used for coloring glass and enamels. Other compounds erbium are: erbium fluoride (ErF_3), erbium chloride ($ErCl_3$) and erbium iodide (ErI_3).

Soil

The average content of erbium is so divided: 2.18 mg kg^{-1} in subsoil and 1.98 mg kg^{-1} in the topsoil, the subsoil is comprised in a range from 0.1 to 7.42mg kg^{-1}, while the topsoil ranges from 0.12 to 26 mg kg^{-1}. The average ratio between topsoil and subsoil is 0.931.

Low concentrations of erbium, lower than 1.46 mg kg-1, found in the subsoil Europeans: in the northern and central Finland, in the glacial drift that covers a wide area from Netherlands to Poland, in the Paris Basin, located in France, the Western Alps and the Rhône valley, in the central parts of Hungary and Portugal, in the southern and eastern Spain, and in the east of Greece (Salpeteur, 2005). High concentrations, greater than 2.91 mg kg-1 are located mainly in the crystalline basement of the Iberian Massif, located between Portugal and northern Spain, in the provinces alkaline magmatic in Italy, in karst soils of Croatia and Slovenia, in Hungary, in Austria and southern in loess / paleoplacer area extending from northern Germany to France, in the south-west of Norway and northern Sweden (Salpeteur, 2005).

High values of erbium, which were found in Central Macedonia and Thrace, are associated with felsic rocks and mineralization. The points of anomaly of erbium that are located in Western Greece are associated with soils of Earth Red and mineralization of Phosphorite. The points anomaly, as well as in Greece were also found in the northern part of Ireland near the Mourne granite.

The pattern of topsoil and subsoil are very similar to each other. Note sign is the point anomaly in the topsoil, on the island of Gran Canaria in Spain, due to the alkali basalt. Erbium has a very strong correlation with the other REEs, especially his behavior is very similar to that of other HREEs.

Plant

The erbium has no known role from the biological point of view even if it has effects in the stimulation of metabolism. Studies carried out in this regard are still scarce, given the difficulty that you have in a study of individual REEs.

Thulium (Tm)

Thulium is the least abundant REE; it was never found in nature in pure form but it is found in small quantities in minerals with other REEs, it is extracted mainly from monazite, containing 0.007% of thulium and bastnasite containing 0.0008%. Its average concentration in the Earth's crust is 5.2×10^{-1} milligrams per kilogram, while the oceanic average concentration amounts to 1.7×10^{-7} milligrams per liter.

Thulium was discovered in 1879 by the Swedish chemist Per Theodor Cleve. While he is trying impurities in the oxide erbium Er_2O_3, coming to discover oxide holmium, holmia, and oxide thulium, thulia.

Thulium today is obtained through the ion exchange process from sand monazite (Ce, La, Th, Nd, Y) PO_4. The main mines where you can extract the thulium are located in China, US, Brazil, India, Sri Lanka and Australia. World production amounts to 50 tons per annum of oxide thulium, and world reserves are estimated at 100,000 tons.

The metal thulium is relatively expensive, for this reason it is not used for commercial purposes, although recently it has become more available. It is thought that one of its isotopes thulium^{169} can be used as the radiation source for X-ray machines portable. Currently it has important commercial values. Some of the compounds of thulium are: the thulium oxide (Tm_2O_3), thulium fluoride (TmF_3) and thulium iodide (TmI_3).

Soil

The average concentration of thulium in the subsoil of Europe is 0.31 mg kg^{-1} and for the topsoil is 0.30 mg kg^{-1}, the range in which is included the subsoil is between 0.02 to 1.08 mg kg^{-1}, while the topsoil is between 0.02 and 4.03 mg kg^{-1}. Their average ratio of 0.935.

In the European subsoil concentrations lower than 0.22 mg kg^{-1} are found in Finland, in northern Norway, in the glacial drift that goes from Poland to the Netherlands, in the Paris Basin in France, in the Western Alps and in the Rhône valley, in central Portugal and Hungary, in Spain and in southern part of Spain's north and east, and east and south of Greece (Salpeteur, 2005).

The greatest concentrations of 0.43 mg kg^{-1} are located in the crystalline basement of the Iberian Massif, located between Portugal and northern Spain, in the provinces of Italy alkaline magmatic, in residual soil on karst of Croatia and Slovenia, Hungary into Austria and southern, in the loess / palaeoplacer area of northern France to Germany, in southwestern Norway, and Sweden in the north

(Salpeteur, 2005). There are also point anomalies in western Greece, associated with soils of "*Terra Rossa*" and phosphorite mineralization, and in Northern Ireland near the Mourne granite. The Pattern of Topsoil and Subsoil are very similar to each other.

Thulium has strong and very strong correlations with other REEs, its geochemical behavior is very similar to that of other HREEs.

Plant

In large quantities the thulium has toxic effects, although usually the quantity of thulium which is located in the environment is very poor. It has no biological role, such as soluble salt stimulates the metabolism of living beings. Because of its low hazard for the biological sphere there are no studies about this single element, but only together with the other REEs.

Ytterbium (Yb)

Ytterbium is a silvery bright color element soft, malleable and rather ductile. It is found mainly with other REEs in several rare minerals as gadolinite, monazite and xenotime. Its average concentration in the Earth's crust is 3,2 milligrams per kilogram, while the oceanic average concentration amounts to $8{,}2\times10^{-7}$ milligrams per liter.

The history of ytterbium is complicated. In 1843 the Swedish chemist Carl Gustaf Mosander managed to separate from gadolinite yttrium oxide $(Ce, La, Nd, Y)_2FeBe_2Si_2O_{10}$ together with erbia and terbia, which are respectively erbium oxide and terbium oxide. In 1878 the Swiss chemist Jean Charles de Marignac Galissard discover that erbia consisted of two components, the ytterbia and erbia. He believed that the ytterbia was a compound of a new element, he called ytterbium.

But when other scientists studied it, trying to determine its properties, they got different results doing the same experiments. Initially such different results were due to faulty equipment or human error, but a French chemist Georges Urbain considered that ytterbium was a mixture of two elements. In 1907 he managed to separate the two elements which he called neoytterbium and lutetium.

Natural ytterbium is a mixture of seven stable isotopes. Usually it is recovered from monazite bearing sand, which contains about 0.03% of ytterbium. The main mining areas of ytterbium are in

China, US, Brazil, India, Sri Lanka and Australia. The world production of ytterbium amounts to about 50 tons per year, while world reserves are estimated at one million tons.

The uses of this element are not many. Ytterbium can be tied to stainless steel by improving its mechanical qualities, or is used as a doping agent in the fiber optic cables, where it is used as an amplifier. One of the isotopes of ytterbium is used as radiation source for portable machines X-ray.

Soil

In the European subsoil, the average concentration of ytterbium is 2.13 mg kg^{-1} including in a range from 0.05 to 7.37 mg kg^{-1}, the topsoil is the average concentration of 1.99 mg Kg^{-1} in a range from 0.09 to 25 mg Kg^{-1}, with an average ratio between topsoil and subsoil of 0.944.

The geochemical behavior of ytterbium is very similar to that of other HREEs.

In the subsoil of Europe, concentrations of ytterbium lower to 1.43 mg kg^{-1}: in central Finland, in the glacial drift that ranging from Netherlans to Poland, in the Paris Basin in France, in the western Alps and Rhône valley, in the central areas of Portugal and Hungary, and southern Spain. Concentrations above 2.83 mg kg^{-1} are located in the subsoil of the crystalline basement of the Iberian Massif, located between Portugal and northern Spain, in the provinces alkaline magmatic Italian, in the Massif Central, in France, in the residual soils on karst of Croatia and Slovenia, in southern Hungary and Austria, in southeastern Germany, in Brittany, in the loess / paleoplacer area located between the north of France and Germany, in the southwest of Norway and finally in northern Sweden (Salpeteur, 2005).

Point anomalies are present in the subsoil of Western Greece, associated with the Terra Rossa soils and mineralization of phosphorite, and in Northern Ireland near the Mourne granite. The pattern of distribution of topsoil subsoil reflects that of Europeans, the lowest concentrations are in ytterbium topsoil of Sweden and Norway.

Plant

Ytterbium is an element that has no role in the biological field, which is why the studies about it are very limited.

Lutetium (Lu)

Lutetium is a silvery white mineral relatively stable in air, it is also the hardest and densest of all REEs. It is one of the elements which are more difficult to prepare. It is produced by the reduction of anhydrous $LuCl_3$ LuF_3 or through an alkali or alkaline earth metal.

Lutetium is located in monazite (Ce, La, Th, Nd, Y) PO_4. Its average concentration in the Earth's crust is 8×10^{-1}milligrams per kilogram, while the oceanic average concentration amounts to 1.5×10^{-7}milligrams per liter.

Lutetium was discovered in 1907 by a French chemist Georges Urbain. Hovewer, the discovery actually consisted of a mixture of two elements ytterbium real and lutetium. Urbain realized that it was a mixture, because all the various experiments, which were conducted by other teams of scientists to evaluate the characteristics of ytterbium, gave different results. Urbain managed to separate the two elements that called lutetium neoytterbium. Meanwhile, another scientist Carl Auer von Welsbach, a German chemist, managed to separate the two elements. But the merit of the discovery was given to Urbain.

Today lutetium is extracted through an ion exchange process from bearing sand monazite. The main mining areas are in China, US, Brazil, India, Sri Lanka and Australia. Annually in the world about 10 tons of oxide lutetium, are extracted it is estimated that world reserves amount to 200,000 tons.

Lutetium as s metal has no practical uses because of its difficult extraction procedure. Some of its radioactive isotopes, however, can be used as catalyst in the cracking of petroleum products, and also as a catalyst in some polymerization processes and hydrogenation.

Soil

The average concentration in the subsoil Europeans is of 0.31 mg kg-1 in a range that goes from 0.02 to 1.06 mg kg-1, the topsoil has instead an average concentration of 0.30 mg kg-1, in a range between 0.02 and 3.21 mg kg -1, the average ratio between topsoil and subsoil is 0.947.

Lutetium concentrations are below 0.22 mg kg-1in northern and central Finland, in the glacial drift that extends from Poland to Netherland, in the Paris Basin in France, in the Western Alps and the Rhône River valley, in the areas central Hungary and Portugal and in Southern Spain (Salpeteur, 2005).

Concentrations above 0.42 mg kg-1 are instead: in the subsoil of the crystalline basement of the Iberian Massif that extends from northern Portugal to the north west of Spain, in the alkaline igneous provinces of Italy and of Central Macedonia in Greece (Plant, 2005), in soil on karst of

Croatia and Slovenia, in meridional Austria and Hungary, in the south-east Germany, in Brittany, in the loess / paleoplacer area stretching in a wide area stretching from northern France to the north of Germany, southwestern part of Norway and in the north of Sweden (Salpeteur, 2005).

There are also point anomalies of lutetium in western Greece that are associated with "*Terra Rossa*" soil and phosphorite mineralization, and other points are located in Northern Ireland near Mourne granite.

The pattern of lutetium topsoil are similar to those listed for the subsoil, the lower concentrations of lutetium in topsoil are found in Norway and Sweden.

The lutetium has strong to very strong correlations with the other REEs, in particular its geochemical behavior is very similar to that of the other HREEs.

Plant

The lutetium has no biological role. Midly toxic to the soluble state, whereas the insoluble state has low toxicity. Because of the difficulty and high cost of preparation it is usually not been studied as a single element in the biological sphere, but is included in the studies that include all REEs as (Tyler, 2004).

3.Sampling areas

The areas, which have been selected for the present thesis work, are located in eastern Sicily. The first area is located at the feet of Mt. Etna, the largest active volcano in Europe, the second area sits in the Hyblean Plateau, a carbonate platform located in the south-eastern Sicily.

In the first area, the choice fell on the vineyard of Don Saro, located in Linguaglossa paid east of Mt. Etna; in the of the Hyblean Plateau two vineyards were selected, a few kilometers distant from each other: the Avide wineries and the COS vineyard, both are located in the municipality of Comiso, in the administrative territory of the city of Ragusa.

Although both in eastern Sicily, the two areas have very different geological, morphological and climatic conditions.

Geology of the sampling area

Hyblean Plateau

The Hyblean Plateau is located in the south-eastern corner of Sicily. It is bordered to the north and to west by the Apennine-Maghrebian chain, and to the east by the Ionian basin through the Hybla – Malta Escarpment (Butler, 1992). The central portion is constituted by Hyblean Mountains; the overall extension is about 4500 km^2 with altitudes that reach up to 1000 m above sea level, surrounded by areas of low elevation and coastal areas. The Hyblean Plateau is characterized by steep gorges and small canyons, Mount Lauro is the highest point, with an elevation of 986 m above sea level. This is an geodinamically complex area, since it is the collision zone between the European and the African plate (Dewey, 1989).

The Hyblean Plateau is considered the northernmost portion of the non-deformed Pelagian Block, subducted beneath the European plate (Burollet, 1978); the emergence of the block is due to the clash between the African plate with the Peloritani-Calabrian Orogen that began in the Tertiary, with collisional events active until the Pliocene-Pleistocene (Catalano, 2000), (Lentini, 1996) (Scarascia, 2000). The Hyblean Plateau is sectioned by two major fault systems: the first, with a NE-SW trend it is extensional, and the second with trends NNW-SSE, is composed mostly of strike-slip faults (Catalano, 2011) (Grasso, 1988) (Torelli, 1998).

The Plateau consists of a thick carbonate succession mainly deposited as platform facies with age ranging between Mesozoic-Cenozoic and Quaternary. The exposed part of the sedimentary sequence consists of deep-water limestones of Upper Cretaceous to Cenozoic and Miocene and Pliocene-Quaternary open-shelf clastic, which are mostly located on the edge (Bianchi, 1987). The oldest rock outcrops date back to the Cretaceous, and are located in the portion of the Plateau overlooking the Ionian Sea (Lentini, 1984).

The sequence also shows interruptions, by various interbedded volcanic of different ages (Bianchi, 1987). The interbedded volcanic cropping out in the area have different mineralogical-geochemical characteristics. The first interbedded volcanic outcrops, date back to the Cretaceous period, the volcanic rocks of this period, both subaerial lava that those underwater, have a mainly basic composition (De Rosa, 1991) (Rocchi, 1998). The next volcanic phase, dates back to the Late Miocene and is located in the central part of the Plateau Hyblean. The diathermy pipes outcropping, suggest an explosive activity, it is found alkali basalts and basanites (Bianchini, 1998) (Bianchini, 1999). The last volcanic rocks date back to the Pliocene-Pleistocene and includes basalts, basanites and rare nephelinites (Beccaluva, 1998) (Trua, 1998). The oldest volcanics (not cropping out), found in drill hole are Triassic in age (Cristofolini, 1966).

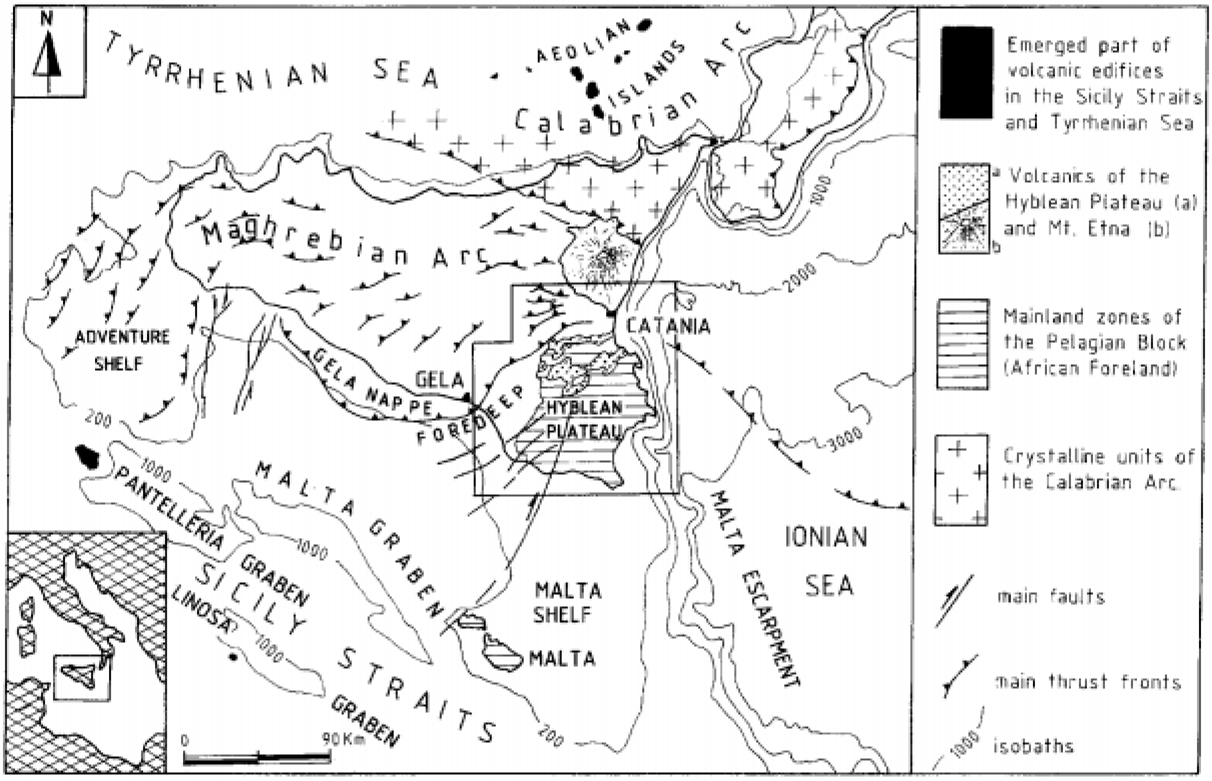
In various areas of the Hyblean Plateau many commercial wells are spread, reaching platform-type limestones dating back to the Triassic age at depths varying from 1 to 4.8 km. As for the nature of the pre Triassic bedrock , the only evidence is represented by xenoliths found in diatremes. The carbonate sediments, forming the Hyblean Plateau, in its central part reach thicknesses of 8-10 km according to the geophysical data (Bianchi, 1987) (Chironi, 2000), whereas the thickness of coeval sediments in northern and eastern Europe is around 5-6 km.

The Hyblean Plateau lower crust was considered, by many authors, be part of the African continental crust (Burollet, 1978) (Catalano, 2000) (Lentini, 1996). This hypothesis is primarily based on seismic data interpretation (Carrozzo, 1998) (Catalano, 2000).

Recently, a new hypothesis supposed to the Hyblean Plateau basement was formed in an oceanic or oceanic-continental transition environment. The hypothesis is based on the study of gabbro xenoliths found in diatreme pipes in Hyblean Plateau that seem derived from MORB liquid (Scribano, 2006).

In the Hyblean Plateau, the study area which is the subject of our study, sit on yellowish calcarenite. Age is between Middle Pleistocene, the formation consists of a yellowish calcarenite with stratification not very evident. The basis formation consist of several meters of sand, gravel and conglomerates with carbonate elements and reddish sandy matrix with thicknesses up to about ten meters, containing few remains of mollusks and calcareous algae.

In the area just to the north of the area studied, appears the Amerillo formation, which sit in the underlying position than the Ragusa formation. Age is between Upper Cretaceous and Lower Eocene; the formation consists of a sequence of layered limestone (calclutites) of whitish color, formed in a pelagic marine environment. Frequently there are layers, lists and nodules of flint. Are found also structures called "slumps" or "slumping" that testify to the geological instability of the environment of deposition (Bianchi, 1989) (Carbone, 1984) (Carbone, 1987).



Picture 2 Main Structural elements of Sicily areas. The boxed area includes the Hyblean Plateau (Yellin-Dror, 1997).

Mount Etna

The Mount Etna, located in eastern Sicily, north of the city of Catania, is the largest and most active volcano in Europe. It covers an area of 1200 km^2 and rises to an altitude of 3350m above sea level. Geographically it is bordered to the north by the Peloritani Mountains, east of the Ionian Sea, to the west by the Hyblean Plateau and by the Erei Mountains. Mt. Etna is a layer-alkaline volcano, which formed on a continental crust formed by clastic and carbonate deposits of Mesozoic age-Pleistocene (Lentini, 1982). The composition of its products ranges from alkali basalt to trachyte, although most of its lavas have hawaiitic composition (Tanguy, 1997).

Mt. Etna is at the margins between two great borders geodynamic, the Apennine Magrebide thrust system and Hyblean Foreland (Lo Giudice, 1982); the volcanic edifice is crossed by numerous faults which belong to the three main regional systems active: the escarpment Maltese, with trends NNW-SSE (Atzori, 1978) (Ghisetti, 1979); the faults of the system Giardini Messina with trends NE-SW (Ghisetti, 1980); and the fault system Mt. Kumeta-Alcantara, with WNW-ESE trend, located in the eastern flank of the volcano.

The volcanism of Mt. Etna is located near to the area of the collision between the African plate to the south and the Eurasian plate to the north; this area is located in a crustal weakness zone, that enables the surfacing of magma deep about 100 km. The area is between two important geodynamic domains: the Hyblean-Maltese escarpment to the south, consisting of African deformed crust, and the Apennine-Maghrebian chain to the North, this latter is constituted by a complex system of divergent flaps south that are part of the plate Eurasian (Bousquet, 2004).

The magmatism of Mt. Etna is determined by the greater curvature of the plan and the extension of the subduction fault system NW-SE to the north, this fault system is the continuation of the Hyblean-Maltese escarpment. Faults created deep extensional fractures that allow the rise in basic magmas typical of Etna activity (Branca, 2004).

The deep regional fracture systems, which are the cause of the formation of Mt. Etna, are active from Middle-Upper Pleistocene. The ascent of large volumes of magma from the mantle produces the formation of radial fractures that unfold from the center of effort. The magma coming into these fractures gives life to the activity side of the volcano resulting in the formation of numerous cones of which are concentrated mostly in the main directions of the faults (Branca, 2004).

The volcanic edifice has a grossly elliptical shape, in fact, the North-South axis is 47 km against 38 km east-west axis with a total perimeter of 150 mm, the asymmetric morphology reflects the history of the volcano, which is made by overlapping products issued by various apparatus eruptive, formed at different times, the centers of which have undergone a migration over time from east to west. Mount Etna is a very recent volcano, its first eruptions took place between 700,000 and 500,000 years ago (Romano, 1982). The history of the Mt. Etna can be divided into four main phases:

1) tholeiitic basalts;
2) alkaline ancient centers;
3) alkaline modern centers;
4) Mongibello (current phase).

The first phase includes submarine, activities located inside the pre Etnean gulf, the products of this phase are tholeiitic basalts with production of pillow lavas, ialoclastite and ialoclastic breccias (Corsaro, 2000) (Cristofolini, 1974) (Sturiale, 1968).

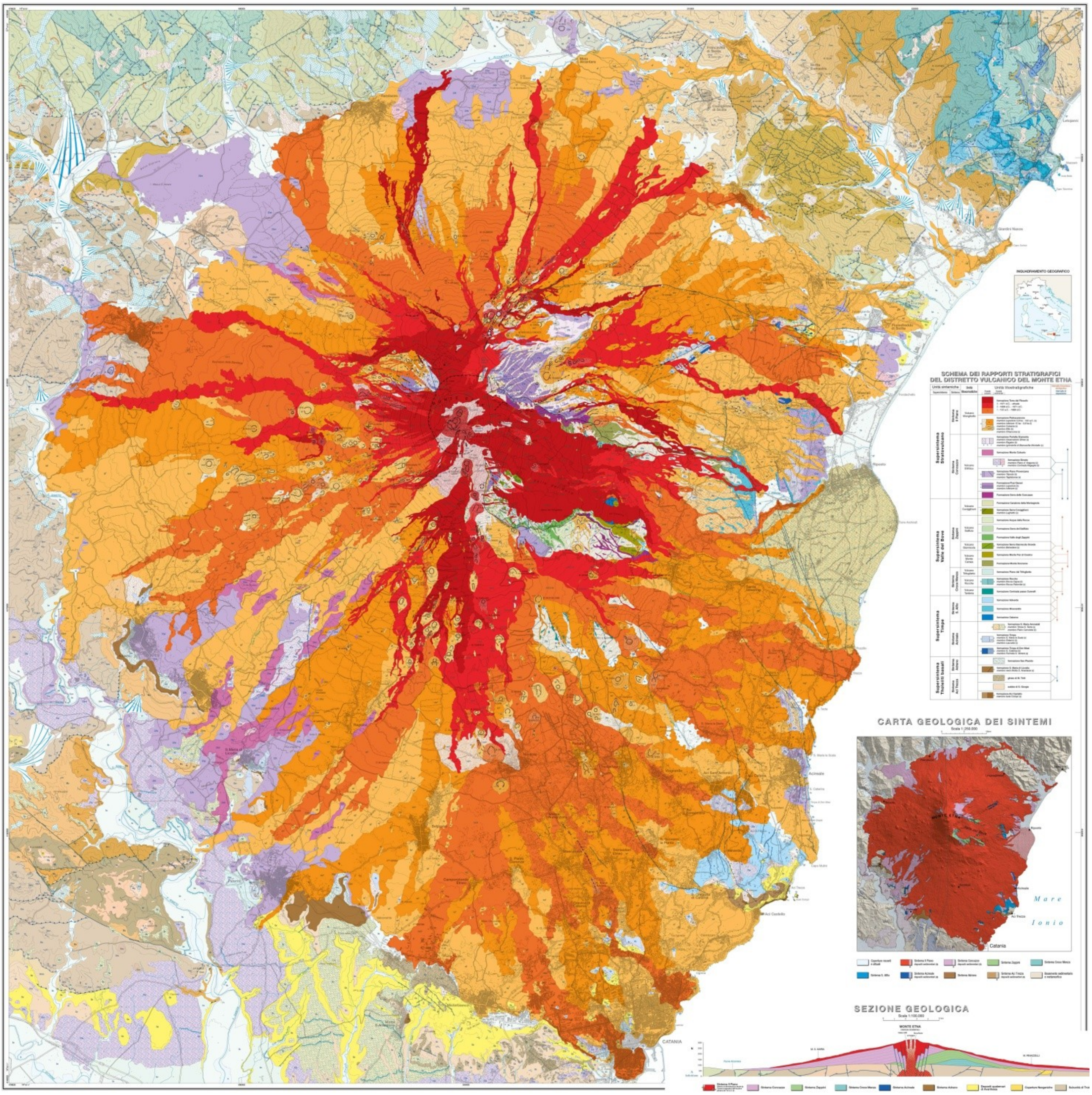
The second phase of the alkaline ancient centers began between about 200,000 and 100,000 years ago (Condomines, 1976); at this stage, there was a change in the chemical composition of the magma, from tholeiitic becomes alkaline and formed the first small eruptive centers. Two of these centers have been identified, and are the Calanna and Trifoglietto I (Romano, 1975).

The third stage begins 100.000 years ago with the formation of a complex layer volcano. In this phase change, the mechanism of rise of the magma, are formed small reserves of magma where this differentiates, towards more evolved terms. The major eruptive center of this phase is the Trifoglietto II, characterized by various eruptive centers, among which: Vavalaci, Belvedere and Serra Giannicola Piccola (Lo Giudice, 1970) (Lo Giudice, 1974).

At the end of activity in the Trifoglietto II, there is a shift in feeding towards the north-west, it forms a new eruptive center Mongibello, this is divided into old Mongibello and recent Mongibello, respectively. The ancient Mongibello is characterized by explosive activity, at the conclusion of which the phase of recent Mongibello began (which is the current phase). This phase begins approximately between 5000 and 3000 years ago, the products are poorly differentiated with effusive activity quite explosive, eruptive mechanism seems to again be powered by relatively deep fissures extensional (Romano, 1982).

The area where the vineyard is located sit in the municipality of Linguaglossa, oat the feet of Mount Etna on a lava flow dating back to the period between the 122 b. C. and 1669 a. C. (Branca et alii, 2011), the lava flow date should 1556 A.D. (Silvestri, 2015). The eruptive products issued, on these dates, belong to Mongibello which is the current phase of Mount Etna. Besides this casting another eruption came to lap the municipality of Linguaglossa in 2002, but the vineyards of the vineyard of

Don Saro interested in our study, were not involved.



Picture 3 Geological Map of Mount Etna (Branca et alii, 2011).

Soil

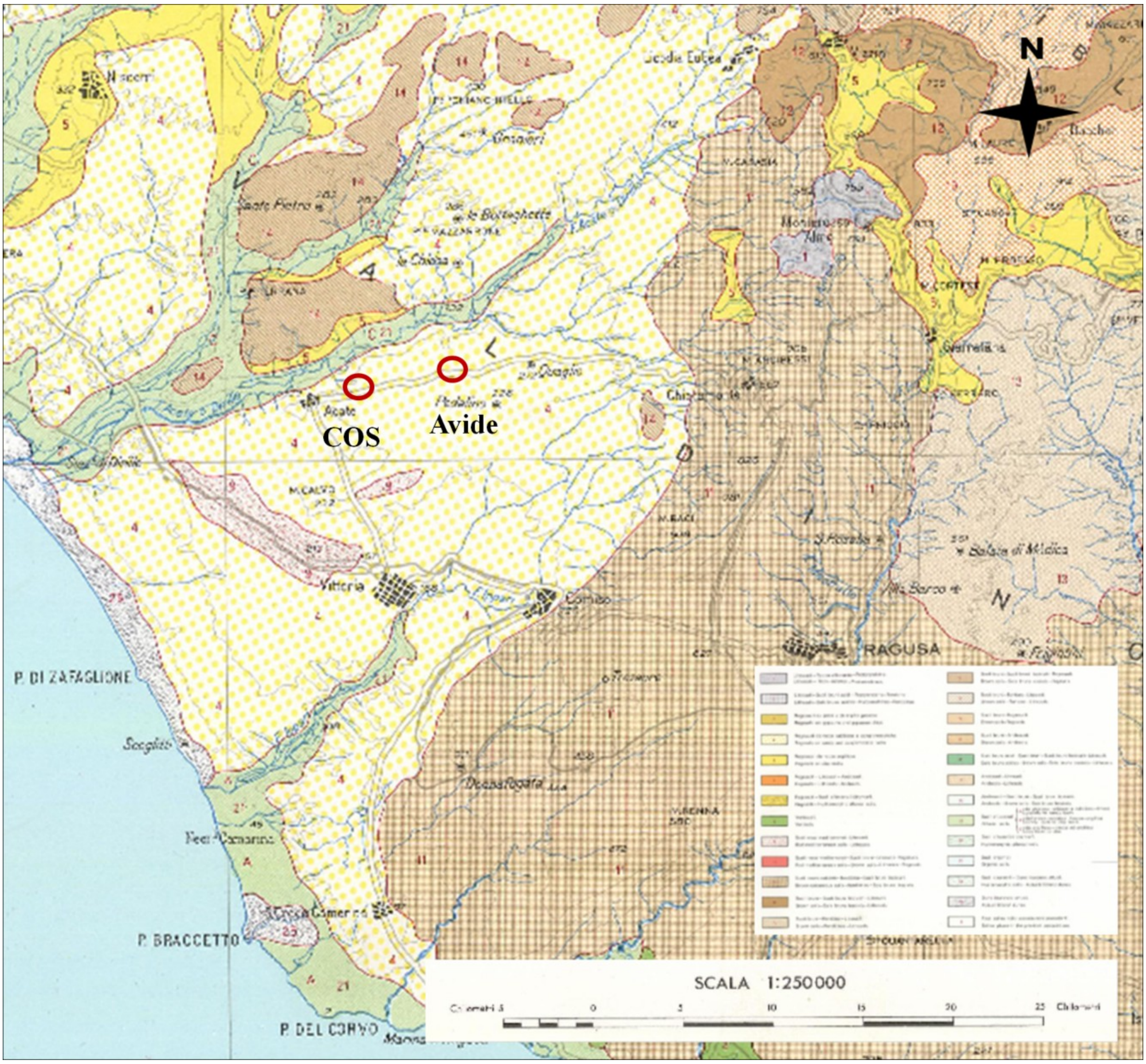
Soil is the primary factor of production for agriculture, without which it would impossible to plant cultivation. It plays a vital role in the ecosystem, so knowledge of the soil, and the elements of which it is composed is a key factor in the search. Plants take their nourishment from the soil, absorbing the fundamental elements for their growth, elements that therefore will enter in the food chain and reach humans.

It is essential to understand how sediments, geomorphology and hydrology interact to produce soil.

The sediment or materials from which soil develop determines the soil initial physical and chemical properties. Important features that affect the soil formation are: the depositional environment, intensity and duration of weathering processes, the age of the surface from which the material and the one where you go to deposit then this material and geomorphological history of area (Daniels, 1977).

The characteristics of the soils of the two areas are extremely different from each other. Sicily owns a great variety of geological features reflected on its soil. In addition to the lithological composition, there are many factors that can affect the characteristics of the soil. One of these factors is the composition of organic substance and how this is distributed across the profile. Other factors affecting the soil are the temperature, the amount and distribution of rainfall. The type of vegetation can affect the soil through root activity, the contribution of organic waste and the release of energy photosynthetically fixed, these are the mechanisms through which the vegetation influence the evolution of the physic - chemical characteristics of the soil (Benintende, 2002).

Soil of the Hyblean Plateau



Picture 4 Hyblean Plateau taken from Soil Map of Sicily (Ballatore, 1967). The red circles indicate the locations of COS and Avide vineyards.

Soils of the Hyblean Plateau are characterized by calcium-based soil, substrates formed by sands from the early Pleistocene. In areas covered by Mediterranean forests and hillsides less stable you notice a thickness of soil greater than the areas without vegetation. In areas covered by vegetation the soil composition is calcium and is rich in plant remains. The steeper slopes and the slopes of the valleys have a thickness of less land, because of greater exposure to erosion due to the lack of vegetation cover. The valleys are characterized by very deep, loamy soils with a rich component calcium. (Dazzi C., 2007) These types of soils on the valley floor are those that lend themselves to cultivation.

The calcareous rocks in the area of the Hyblean Plateau, undergo strongly weathering and they are subject to dissolution. The dissolution is a process that involves the formation of a solution, and then a liquid phase incorporating the ions of the minerals preexisting. Meteoric precipitations, passing through the lower atmosphere, are enriched in carbon dioxide, the water dissolves the calcium carbonate in solution bringing the calcite form of calcium bicarbonate:

$$\mathbf{CaCO_3+H_2O+CO_2 \Leftrightarrow Ca(HCO_3)_2}$$

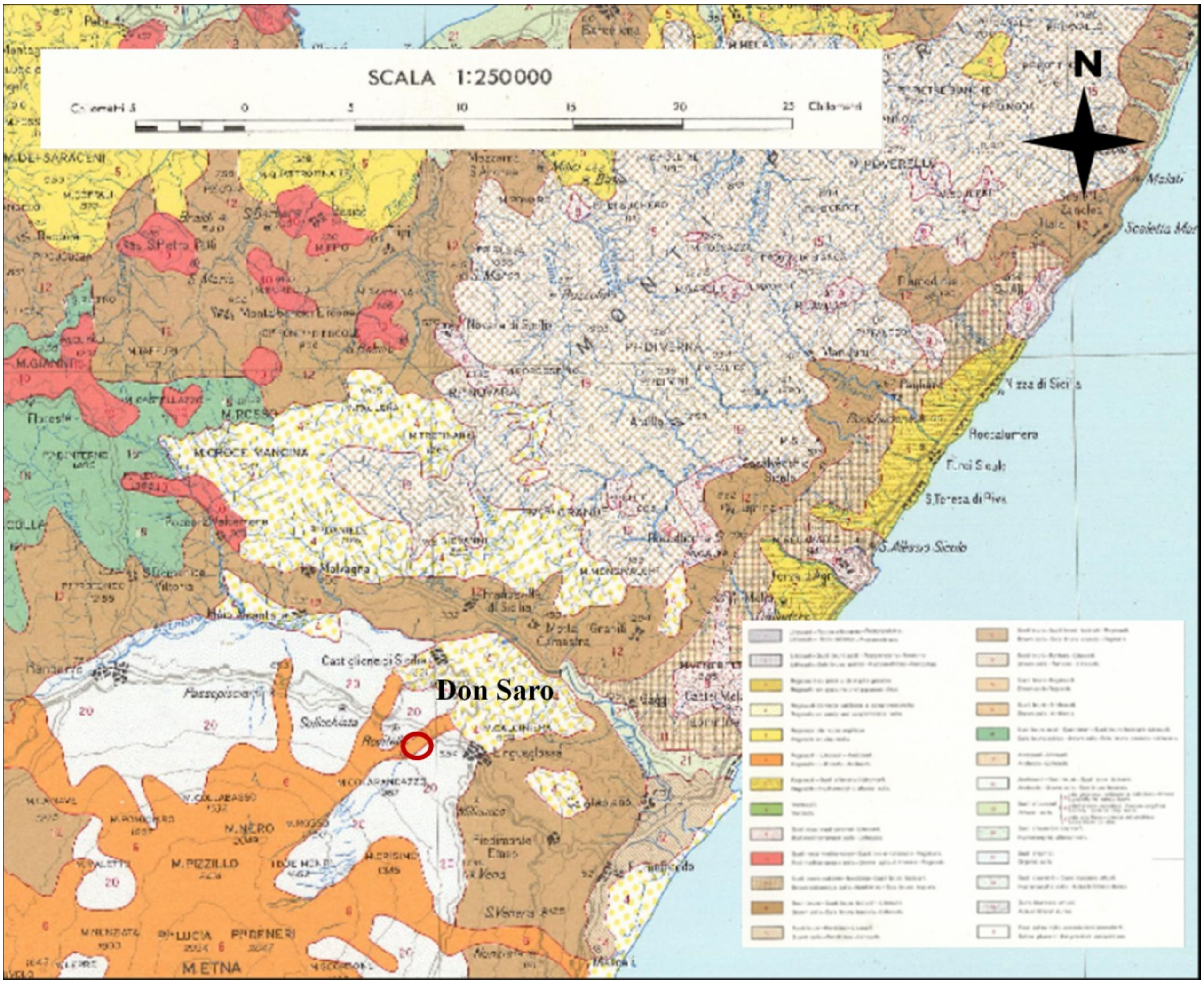
The dissolution of the carbonate persists until the CO_2 remains in solution; when environmental conditions (increase of T and / or decrease of P) do not guarantee the solubilization of CO_2, the bicarbonate is transformed into carbonate, and precipitates (Morbidelli, 2005).

What remains of the chemical dissolution of limestone; is a reddish soil called "Red Earth", almost always shallow deep, rich in iron and metal ores (Cita, 2003).

The limestone plateaus haven’t an ideal environment for the grape cultivation. To improve soil conditions, local farmers they used of the extra touches:

it was common practice to build low walls with limestone to protect plants and shatter limestone and mix with the "Red Earth" to make it less compact, these practices have followed for centuries in cultivated land of the Hyblean Plateau, obtaining land suitable for cultivation of the vine plant (Cita, 2003).

Soil of Mt. Etna



Picture 5 Linguaglossa taken from Soil Map of Sicily (Ballatore, 1967). The red circle indicate the location of Don Saro vineyard.

The soils of the area of Mt. Etna have been linked to volcanic matrix. The soil originates from the disintegration of volcanic rocks of basaltic and andesitic. The thickness is generally quite exiguous, rich of the component of skeleton, loose and very permeable, the color is more or less dark brown, often almost black. The soil of Mt. Etna 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 that following the various eruptions are deposited with thicknesses centimeter on the land of Mt. Etna (Giovannini, 1963) (Principi, 1961). As for the soil of Mt. Etna, these have a shape almost concentric circles from the center of the volcano, consisting exclusively of the rock outcropping with no soil, it evolves away to the suburbs in lithosols and regosols. At the foot of the mountain there is the presence of brown soils andic that pass near the sea association brown soils - alluvial soils (Sparacio, 2010).

The soils are mostly andosoils with brown soils leached, lithosoils and regosoils with profile very simple, usually from AC (Giovannini, 1963).

The andosols soils are very dark, even blacks, that develop from materials derived from volcanic eruptions (ash, lapilli, lava, pumice and powder). They have low apparent density and a high content of amorphous materials the primary (glazing) and secondary (allophane), with an abundance of iron and aluminum and a high reactivity FAO World Reference Base for Soil Resources.

The high temperatures and the high fluency of volcanic soils, especially as regards the summer months which are also characterized by an almost total absence of precipitation, determine the rapid destruction of the organic substance.

Viticulture insists for about 80% of brown soils andic and brown soils leached, and only the remaining 20% of alluvial soils and vertisols. The brown soils are those that host the terraced vineyards of Etna, (as vineyards of the vineyard of Don Saro), these have originated from the disintegration of one or more types of lava of different ages and from eruptive materials like ash and lapilli. The crumbling away from origin to typologies of soil composed of very fine particles, such as those of the town of Verzella and Caselle, or soils formed by abundant gravel and pumice of small dimensions, with high flow capacity, such as soils that are seen in the municipality of Monte Serra, Monte Gorna, this type of soil is called locally "ripiddu" (Sparacio, 2010). The thickness of these soils varies from area to area, the pH is typically sub-acid, soils are devoid of carbonates, rich in trace elements iron and copper in particular, and on average with potassium, phosphorus and magnesium, while they are poor in calcium and nitrogen.

Weather-climatic conditions

Sicily is located in the Mediterranean between the Sahara Desert and the mid-latitude storm rain band (Mariotti, 2002). The island has the typical characteristics of the Mediterranean climate with hot summers ranging from June to September and cold winters ranging from November to March. The model of Precipitation has a strong seasonal tendency with most rain falling in the winter and very little rain in the summer. Spring and autumn climatic conditions have intermediate between winter and summer (Pirrone, 2003).

The atmospheric circulation in the Mediterranean is very complicated due to the complex land-sea distribution, in fact are numerous, small basins, islands and peninsulas that affect the air flow within the Mediterranean basin. Another factor that complicates the study of atmospheric circulation of the Mediterranean is located in a transition zone climate, the air masses in the basin come from different areas depending on the season. The air movements cause fluctuations in the extension of the cells of high pressure, from October to March, the low pressure conditions are caused by cold fronts from the northern areas of the Atlantic Ocean, from Scandinavia and Siberia. In spring and summer, however, the atmospheric circulation is to the north-northeast with winds from North Africa to the shores of Europe.

Hyblean Plateau (Comiso area)

The Hyblean Plateau constitutes the most important aquifer of southeastern Sicily**,** because of its large size and high permeability of its carbonate rocks and volcanic deposits**.** The permeability is 10^{-5} m / s for volcanic aquifers and > 10^{-5} m / s for carbonate aquifers (Aureli, 1993).

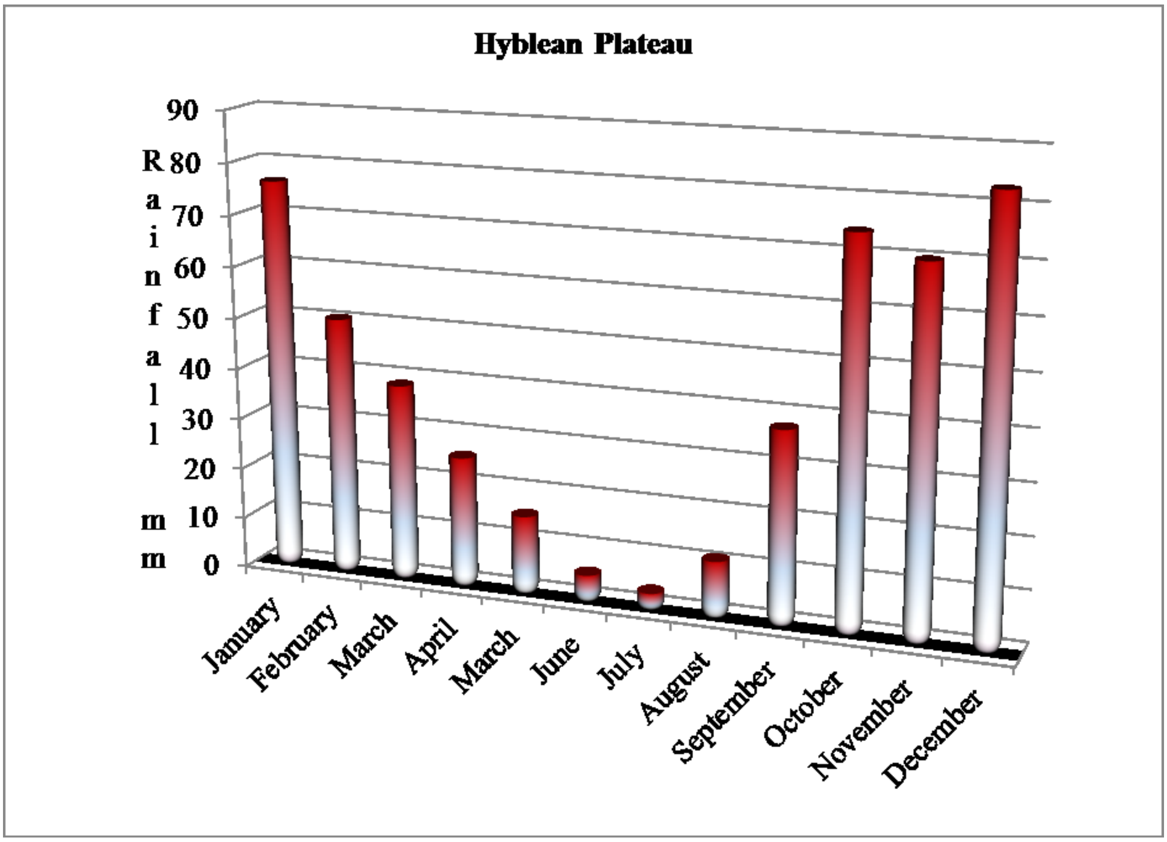
Observations of temperature and rainfall made by the Hydrographic Service of Civil Engineering for the period of time ranging from 1966 to 1990, recognized, within the Hyblean Plateau, two major sub-climatic areas. The first of them is the area of the morphological high, with a maximum altitude of 986 above sea level; the climate is temperate, with an average annual temperature between 13 and 15 ° C, rainfall is moderate with a range between 650 and 850 mm of annual rainfall and rare snowfalls in winter. The second area includes the inland and coastal areas with semi-arid climatic conditions, the temperature averages are higher included in a range of 16-19 ° C, the annual rainfall is less than the previous area, and range between 400-450 mm annual (Hydrographic Service of Civil Engineering from 1966 to 1990).

In both areas the rain falls from September to March with almost no rain during the summer.

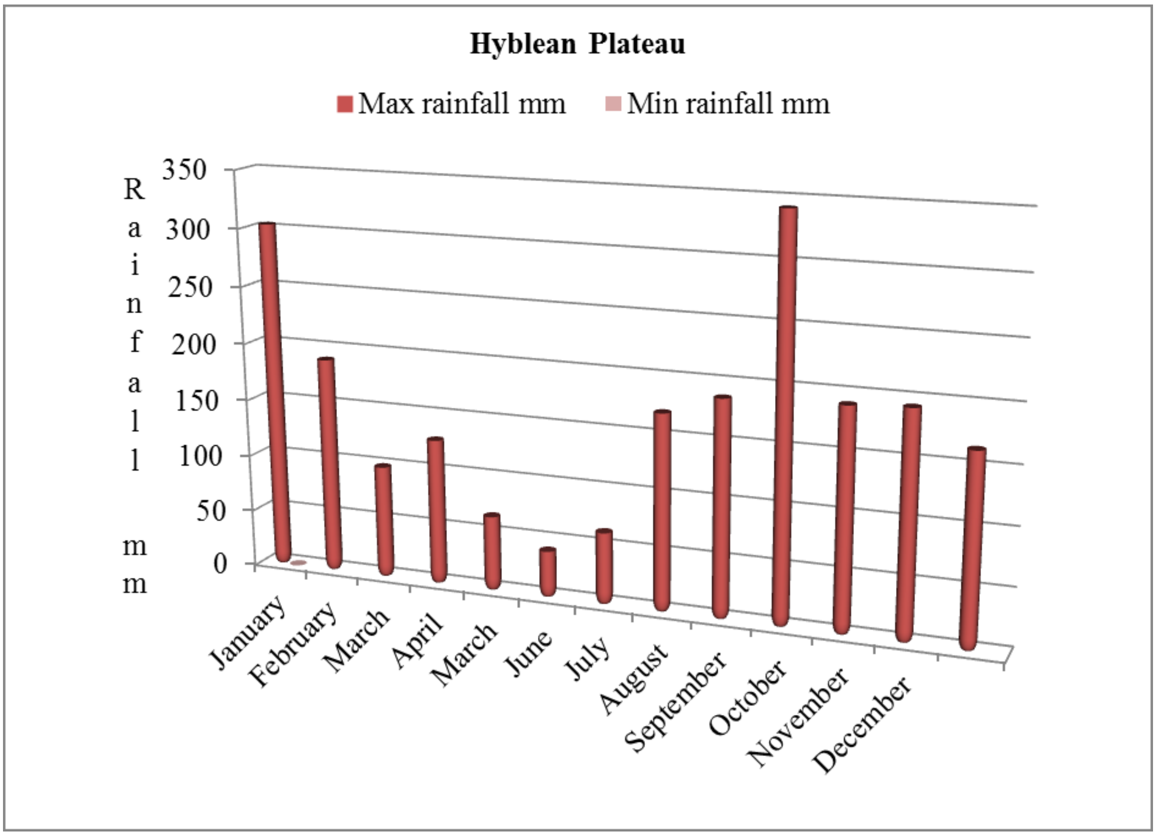
The average annual rainfall in the region of the Hyblean Plateau, is generally lower than the average values of 1/3 at the same elevation in northwestern Sicily. This is due to the loss of vapor caused by the partial condensation induced by orographic lift the clouds, in fact in the winter, when you experience the most rainfall, the Hyblean Plateau is downwind, the clouds coming from the north must pass through two large topographic barriers: the chain of the Peloritani Mountains and Mt. Etna, respectively.

Hyblean Plateau Month	Rainfall mm	Max rainfall mm	Min rainfall mm	Temperature °C
January	76,3	303,4	6	10,3
February	50,5	189,3	0,4	10,9
March	38,6	99	0	12,7
April	25,7	127,8	0	15
March	15,5	65,8	0	19,2
June	5,4	41	0	23,3
July	3,4	63,2	0	25,5
August	11,2	170,4	0	25,8
September	37,6	187,2	0	23
October	74,2	342	2,6	19,3
November	70	190,8	0,2	15
December	83,1	193,4	9	11,5
Average	40,96	164,44	1,52	17,63

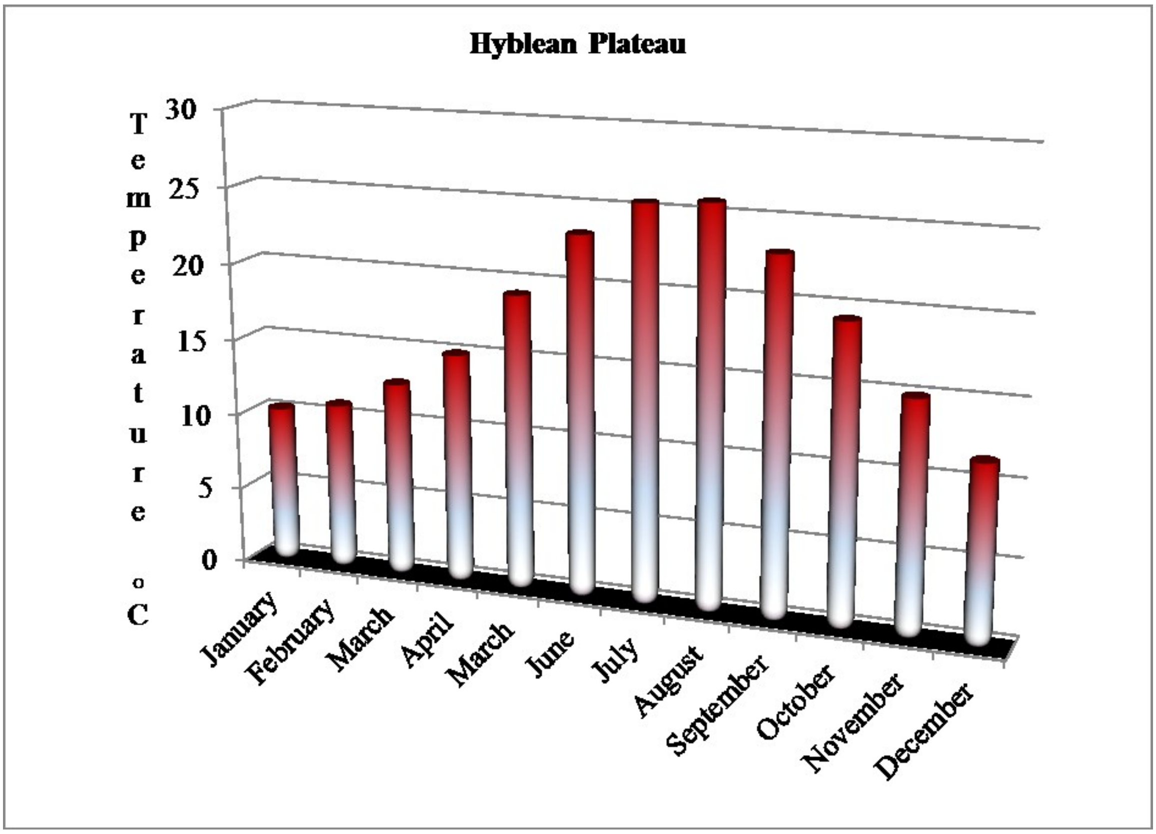
Table 3 Weather station Comiso (RG Hyblean Plateau), pluviometric data (for the period 1930-2010) and thermal (for the period 1951-2010)**.** Data source: (Onlusmeteonetwork).



Graph 1 Average monthly rainfall, Hyblean Plateau (referring to the period 1930-2010). Data source: (Onlusmeteonetwork).



Graph 2 Average monthly rainfall max and min, Hyblean Plateau (referring to the period 1930-2010). Data source: (Onlusmeteonetwork).



Graph 3 Average monthly temperature, Hyblean Plateau (referring to the period 1951-2010). Data source: (Onlusmeteonetwork).

Mt. Etna (Linguaglossa)

Mt. Etna, because of its size compared morphology nearby, exerts heavy control in the condensation of humid air masses, favoring a large meteoric recharge. The Etnean area, based on geophysical and geological studies it can be divided into three major hydrological basins:

- Tributaries of Alcantara north;
- Simeto south -west;
- Riverso s Sea Ionio east

The climatic conditions of the Mount Etna are different than the Mediterranean climate of the surrounding areas, because of its altitude and geographic position. At higher altitudes there is a change of regime thermometer that goes from subtropical to temperate until you get cold. The average annual temperature rose from 18 ° C at sea level until 1 ° C at an altitude of 2900m. Above 1000 meters the temperature gradient seems constant at 5.8 ° C / km for the entire volcanic edifice.
Factors influencing precipitation in Mt. Etna are two: the altitude and aspect. The more humid air masses come from the western sectors, in winter the incoming direction is north-west and in the summer from the southwest. Air masses after losing moisture through Europe and Africa buying vapor quickly when crossing the Mediterranean Sea (Gat, 2003). The moist air masses from the western sectors, drag moisture from the Atlantic Ocean. Finally, the ultimate source of humid air masses is the Ionian Sea, located in the eastern Mediterranean, which is the main source of moisture of Etna. The rainfall is concentrated mainly on the eastern slope of Mt. Etna due to the condensation induced by orographic lift of moist air.
The rainfall data collected from the region of Sicily for a time period of 30 years (from 1965-to 1994) made it possible to calculate the average annual millimeters of rain for the different sides. It calculated an average 800 mm of rain divided as follows: 400 to 700 mm of rain on the side of South-West, and from 1000 to 1200 mm on the East side, this measure was calculated for a share of 800 m (Regione Siciliana, 1998).
About 70-80% of the precipitation is concentrated between October and March. The highest peaks occur in the month of October, although several peaks of intensity is also in January. While for the summer months, there is very little rains, especially for the month of July, in which almost every year you have the total absence of precipitation.

At altitudes above 1500 m, most of the precipitation occurs in the form of snow, going high you have a gradual reduction of the amount of rain for snow (Ferrara, 1975).

There are climatic differences between different parts of the Mt. Etna, this is due to the fact that the volcano is spread over an area truncated - conical and the proximity to the sea affects the climate.

These factors mean that the climatic conditions are different for the different sides, so we distinguish three different areas:

- the first area is located on the eastern side, in the municipalities of Santa Venerina and Giarre, this is the area where the grapevine have matured earlier because of the exposure of the slope;
- the second area is located on the western side, in the municipalities of Biancavilla, Adrano and Bronte. The area is characterized by relative humidity lower than other areas with average annual rainfall of 500 mm;
- the third area is located on the northern side, in the municipalities of Randazzo, Castiglione and Linguaglossa, this area is characterized by lower temperatures, that will have a more late for the maturation of the grapes.

The thermal excursions, which have in the third area, are crucial to promote the synthesis and accumulation of the aromatic properties of the grapes (Sparacio, 2010).

Municipality of Linguaglossa sit on the north eastern Mt. Etna, in a position of windward of the currents northern and north-eastern. The location means that the area is subject to very heavy rains despite the altitude is not too high.

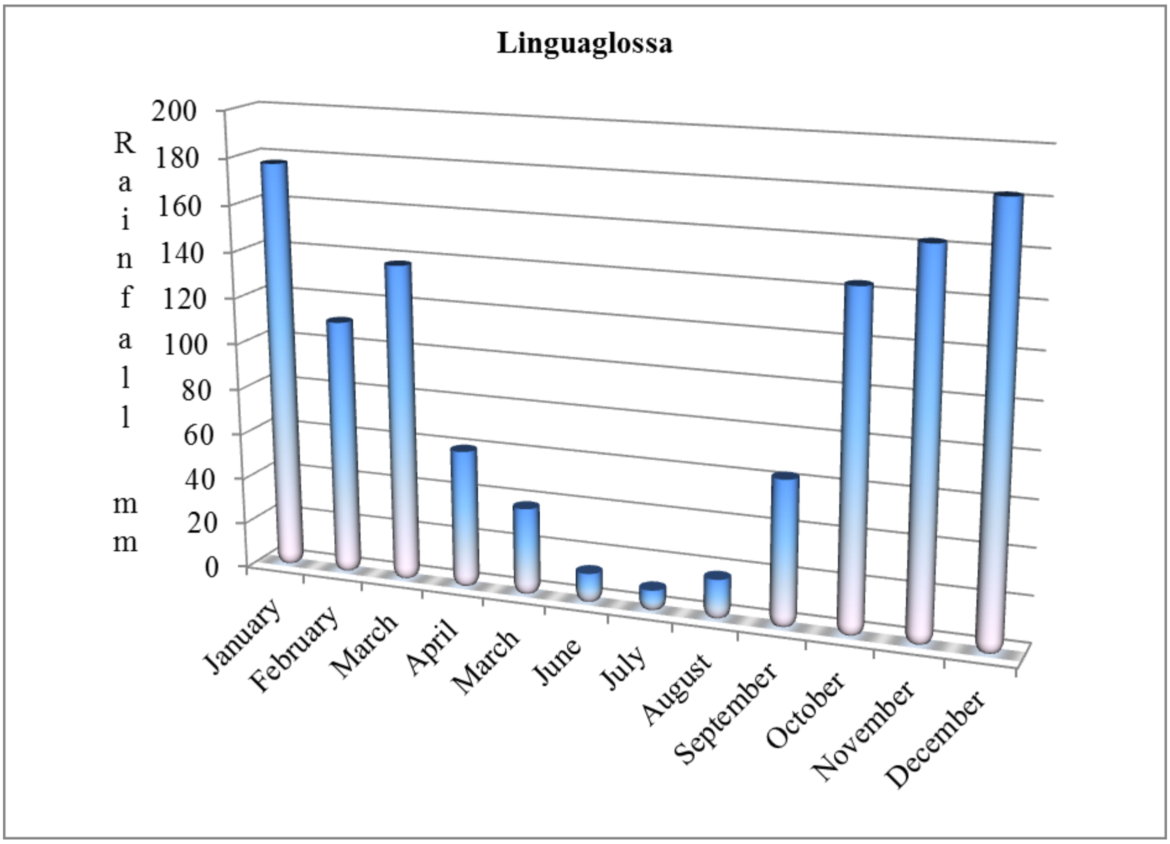
Linguaglossa

Month	Rainfall mm	Max rainfall mm	Min rainfall mm	Temperature °C
January	177,2	720,8	13,4	7,6
February	111,3	451,2	3,8	7,9
March	137,8	620,4	3	9,5
April	60,3	201,4	0	12
March	38,3	198,9	0	16,4
June	13,2	78,2	0	21,1
July	9,4	69,4	0	24,2
August	17,6	123,8	0	24,1
September	63,3	337	0	20,4
October	144,1	673,8	2	16,2
November	162,7	544,6	1,4	12,1
December	182,3	913,8	17	8,8
Average	93,13	411,11	3,38	15,03

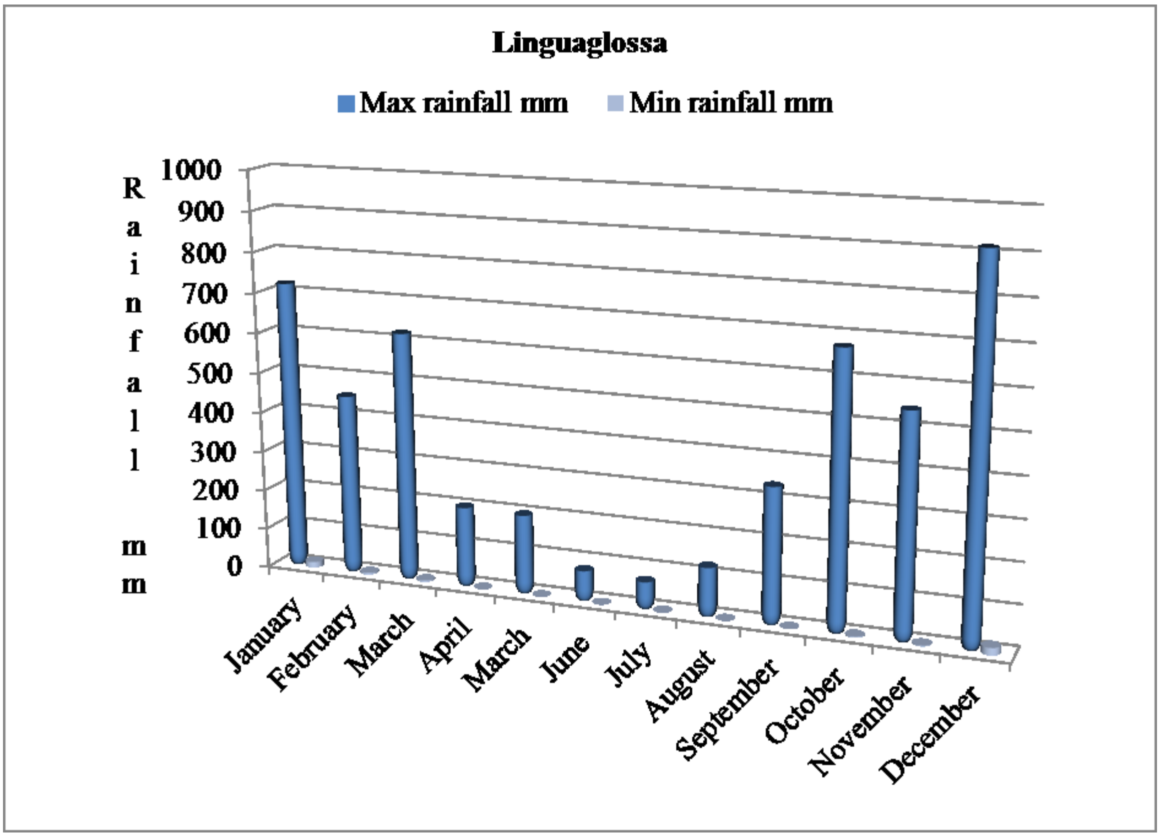
Table 4 Weather station Linguaglossa, pluviometric data (for the period 1930-2010) and thermal (for the period 1951-2010) Data source: (Onlusmeteonetwork).

From the data in the table and graphs obtained, it is found that the rainfall in the municipalities of Lingfield is significantly more abundant, with 1100 mm annual average than 650 mm in the region of Sicily. Precipitation is is concentrated from October to January and very low contributions occur from June to August, as in the rest of the region.

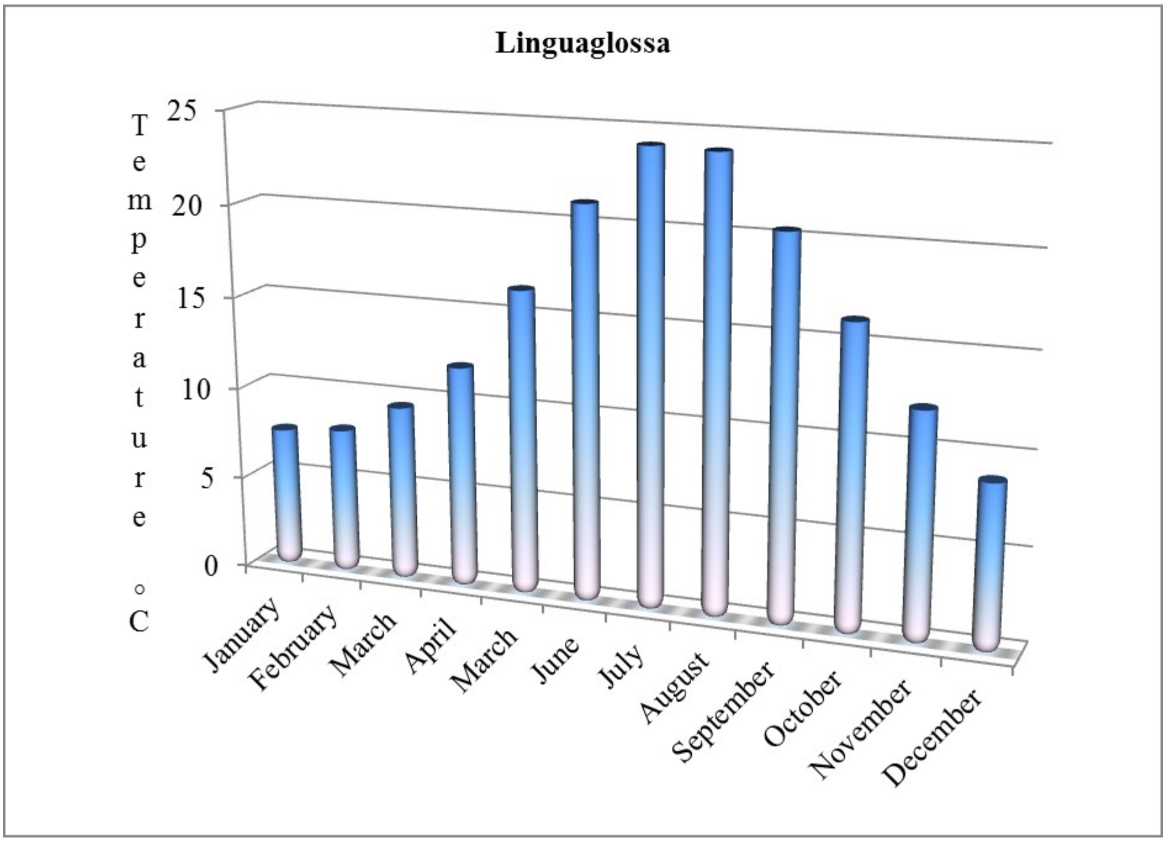
The abundance of rainfall in the winter stem mainly from the polar-continental from the northeast.



Graph 4 Average monthly rainfall, Linguaglossa (referring to the period 1930-2010). Data source: (Onlusmeteonetwork).



Graph 5 Average monthly rainfall max and min, Linguaglossa (referring to the period 1930-2010). Data source: (Onlusmeteonetwork).



Graph 6 Average monthly temperature, Linguaglossa (referring to the period 1951-2010). Data source: (Onlusmeteonetwork).

Type of grape

The vine plant needs special conditions for properly growing: a climate characterized by strong seasonal temperature, with cold winters and hot summers; a good exposure to the sun and ventilated; well-drained soil, preferably with slope (Cita, 2004).

Although Italian wines most sought abroad are: reds of Piedmont and Tuscany and the whites of the Veneto and Friuli, wines produced in southern Italy are very interesting, because of: the incredible variety; climate favorable for viticulture and the extreme versatility of the geological formation.

Worldwide, there are over 7,000 different cultivars of grapevine. The vine is one of the major crops in the Italian peninsula, with 800,000 ha cultivated, which are unequally distributed in all region.

According to the latest ISTAT figures (Istat, 2008), in Italy the area planted to wine grapes amounted to around 700 thousand hectares, of these 48% is located in southern Italy. Sicily owns 124,924 hectares found which are equal to 17.78% of the national total, the island is the Italian region with the most significant wine heritage. The Sicilian viticulture is mainly concentrated in the western part of the island, where Trapani, Agrigento and Palermo, holding 87% of the wine production of the island.

	2006	2007	2008	2009
Trapani	64,249	62,993	63,125	67,000
Palermo	16,430	15,880	15,973	13,888
Messina	1,629	1,628	1,639	1,870
Agrigento	20,661	20,517	20,685	23,306
Caltanissetta	5.930	5,914	5,910	7,100
Enna	505	504	501	900
Catania	4,156	4,221	4,209	5,000
Ragusa	1,261	1,313	1,405	1,400
Siracusa	1,776	1,852	1,875	2,460
Total surface	11’597	114,822	115,322	124,924

Table 5 Surface for the province, Sicily (ha) (ISTAT date**).**

It has prevalence of crops of white grapes, although in recent years there has been a reduction of the latter in favor of the red grapes, because of the growing demand from consumers for red wines.

	2004	2005	2006	2007	2008	2009
Total surface (ha)	130,018	125,393	117,569	118,926	119,893	118,580
White grape surface (%)	76,8	68,2	65,5	64,4	64,1	63,9
Red grape surface (%)	23,2	32,8	34,5	35,6	35,9	36,1

Table 6 distribution vineyard area Sicilian white grapes and red grape **(** IRVV processing of wine Registry 2000 / SRRFV and Ass. Reg. Agriculture and Forests).

The white grapes are mostly widespread in western Sicily (administrative territories of Trapani, Agrigento and Palermo), while the black grapes are widespread in eastern Sicily.

Sicily boasts a wide variety of cultivars, caused by: different environmental conditions, to the cultivation of various genotypes introduced by the multitude of human migrations that have followed in the island (Dangl, 2001) and the intersections, spontaneous or induced, between wildlife and domestic species (Arroyo-Garcìa, 2006) (Snoussi, 2004).

On agricultural holdings, various types of wines are produced, including both red berry and white grape. For this thesis, took into account both types for a total of 10 different cultivars. We have chosen 4 cultivars of white grapes: Carricante, Grecanico, Ansonica and Moscato; and 6 cultivars with red grapes: Cabernet Sauvignon, Frappato, Merlot, Nerello Cappuccio Nerello Mascalese and Nero d'Avola, sispectively.

Some of them are present in most vineyards, even in different areas, making it possible to compare the differences of the same cultivar grown on different soils.

Autocthones vine grapes

The Sicilian grapes have a high variability, due to the fact that they originated from a multitude of varieties, which have been subjected over the centuries to a selection by vine growers. This type of selection is still carried out by vine growers, who select multiple plants considered to be the best, using element to the home of the wild vine cuttings. Only recently, there was increasing awareness of the high potential of the wine grape varieties, which are the basic tools for the type verification and differentiation of wine production in the region (Bica, 2007).

In recent years, the Sicilian region, had aimed to recover and valuate some autochthones vine grapes of the wineries in the region.

White grape varieties

Ansonica (Inzolia)

Ansonica can also be called “*Inzolia*”, “*White Ansonica*”, “*Insolia*” and “*Nzolia*”. It is a white grape variety from which we get a sparkling white wine. This grape variety typically grows in Sicily and in Tuscany.

There were many different opinions on the origin of this grape variety, among which it is thought of to have originated in Greece because of the citation made by Pliny the Elder on a cultivar called Irzolia in his "Naturalis Historia" and because of the genetic profile similar to the Greek varieties Roditis and Sideritis (Labra, 1999).

The Sicilian origin of the grape variety is the most accepted (Giavedoni, 2006): as described in the "Guide to the vines of Italy", the grape variety (native of Sicily), first arrived to Sardinia and from here to the coastal area of Tuscany and to the islands of Elba and Giglio, where it is known as “Uva del Giglio” (Pastena, 1969).

Even (Dalmasso, 1938)and (Carimi, 2010) confirm its Sicilian origin. This latter highlighted a close genetic relationship of Ansonica with numerous Sicilian grape varieties: Frappato, Grillo, Moscato Yellow or Muscatedda and Nerello Mascalese.

The grape variety was already known in Italy in the XVI century, with the name of Ansolia, and already at that time it was widespread in Sicily, Calabria, Sardinia, in the coastal area of Tuscany, Elba and Giglio Island (Breviglieri, 1965). Anzonica was described in the past by many authors, it appears in the catalog of the “Hortus Catholicus” of (Cupani, 1696) which describes three varieties of Ansonica including two white grapes and red grapes, “*Ansonica White*” is also described by (Acerbi, 1825), (Mendola, 1868), (Nicolosi, 1869), (Paulsen, 1904).

The grape variety is located in Sicily, in particular in the areas of Palermo and Agrigento. Its grapes are used as a blending grape in many denominations DOC island.

In the recent years there has been a reduction in breeding of the grape variety, the surface of Sicily, cultivated Ansonica, has decreased from 11,670 ha in 2000 to 5500 in 2014 that amounted to 5.3% of the vineyard area of Sicily.

This cultivar is a white grape variety, it is characterized by an unusual level of tannin.

The wine produced from this grape variety contributes to the production of the following Sicilian DOC wines :Alcamo DOC, Contea di Sclafani DOC, Delia Nivonelli DOC, Erice Doc, Menfi DOC, Sambuca di Sicilia DOC, Santa Margherita di Belice DOC, Sciacca DOC, Sicilia DOC, and IGT: Salemi IGT.

The grape variety Ansonica has the following features:

- Leaf: medium, pentagonal;
- Grape: medium to large with a / two wings;
- Berry: medium-large, regular, Skin: yellow-amber;

(Bica, 2007), (Mendola, 1868), (Scalabrelli, 2013).

Picture 6 Ansonica grapevine and leaf respectively (Pecile, 2013).

Carricante

Carricante, also called "*Catanese*" or "*Catarratto Bianco*" o "*Nocera Bianca*" is an ancient white grape of eastern Sicily, it is bred for at least a thousand years on the slopes of Mount Etna. Its name is due to the high yields of the plant, the name Carricante means cargo.

The vine, is already described in 1774 by Sestini (Sestini, 1777). While testimonials on its territorial diffusion were described by (Geremia, 1835). In the nineteenth century he was attempted to introduce the vine also in other cities of Sicily, but weren't obtained good results, and is now grown almost exclusively in the area of Catanese. Its greater presence is found on the slopes of Etna oriental 950 meters above sea level and on the southern slope to 1050 m latitude. The cultivar has its best high-altitude soils derived from volcanic, where it is raised until to the altitude of 1200m above sea level. The grape has a late ripening and the harvest takes place between late September and mid-October (Bica, 2007). The cultivar is characterized by high acidity (Sestini, 1777).

Carricante is the most important grape of white DOC wines of Etna, is in fact required in all the white wines of the designation: Etna DOC, Sicilia DOC

The grape variety Carricante has the following features:

- Leaf: medium, sub-orbicular or pentagonal, three-lobed or five-lobed;
- Grape bunch medium, conical, simple or with wing, semi-sparse or sparse;
- Berry: medium, sub-ellipsoidal Skin: waxy and yellowish green;

(Bica, 2007)

Picture 7 Carricante grapevine and leaf respectively (Pecile, 2013).

Grecanico

Grecanico, also known as “*Golden Grecanico*” or “*White Grecanico*” is a white grape variety. Grecanico is part of the Sicilian grapes, whose origin, as for many other varieties of Southern Italy, can be traced back to Greece. Indeed, the variety, was introduced during the colonization time, which occurred from the seventh century BC. There is no written documentation on grape variety until the late Renaissance in 1696, when (Cupani, 1696) quoted it calling Grecani. The abbey Geremia describes it in his treatise "Stafulegrafia", indicating the location of the grape variety as the the municipality of Randazzo in the provinces of Catania and Trapani (Geremia, 1835), respectively. Since 1980 the hectares cultivated have been increasing, thanks to the establishment of the designation of origin. Currently 5,000 hectares of vineyards are dedicated to Grecanico, starting from only 500 hectares of the previous period.

Referred to 2010, the planted area has an extension of 4,083 hectares (ISTAT data).

The wine produced from this grape variety contributes to the production of DOC Sicilian wines: Alcamo DOC, Contea di Scaflani DOC, Delia Nivolelli DOC, Erice DOC,Menfi DOC, Sanbuca di Sicilia DOC, Santa Margherita di Belice DOC, Sciacca DOC, Sicilia DOC and IGT:SalemiIGT.

The maturation of this variety is late, usually it takes place in early October.

The grape variety Grecanico has the following features:

- Leaf: medium, pentagonal, five, more marked the upper lobes, uneven teeth very pronounced, flap a bit 'rough, dull green, almost hairless;
- Grape: bunch long, cylindrical, winged, with wings more or less pronounced, or semispargolo semicompact millerandage with more or less evident;

- Berry: is average, spheroid, of golden yellow, Skin: thick and consistent.

(Bica, 2007).

Picture 8 Grecanico grapevine and leaf respectively (Pecile, 2013).

Moscato Yellow

The yellow Moscato, also called "*Muscatedda*", is a white grape variety, whose cultivation is spread to almost all the Italian peninsula, since it is a cultivar with the largest vineyard area.

The grape variety belongs to the family of Moscati, aromatic grapes. The name comes from the Latin "*muscum*" which means moss, with a characteristic flavor of the grape. The cultivar was probably known both by the Greeks who called it "*Anathelicon Moschaton*" and Romans as "*grapes apiana*". The grape vine corresponds to the French "Muscat à petit grains".

It is thought that the grape variety has Greek origins; it is cultivated in all the countries bordering the Medditerranean Sea since many centuries. The vine was known after Catone, who named it "*Grapes apicia*", while Columella, Varro and Pliny mentioned it as "*Screw Apiana*" because of the predilection that bees have for this variety due to the sweet taste and sugary of the berries. (Mendola, 1868) evidenced by the presence of the grape in Sicily in the nineteenth century, witness also reported by Bulletins Ampelographic of those years that brought him back as in several provinces of Sicily.

The grape variety well tolerates summer drought and has a good and constant production.

The wine produced from this grape juice gives a pale yellow, intensely aromatic and musky fragrance, characteristics that make it to be used in withering, in sparkling wine and as a basis, in liqueur wines.

It is present in many of DOC Italian wines.
We recall here only those one in Sicily: Noto DOC, Sicilia DOC e Siracusa DOC. It also has a DOCG in Piedmont, Asti DOCG. Countless are the IGT of which none in Sicily.

The grape variety Moscato has the following features:

- Leaf: medium, pentagonal, three-lobed or five-lobed
- Grape: medium, cylindrical-pyramidal, from compact to semi-loose
- Berry: medium or medium-large, spherical or slightly flattened, Skin: thin, yellow-green, tending to gold if well exposed to the sun; slightly waxy; the pulp has the characteristic sweet and aromatic.

(Bica, 2007).

Picture 9 Moscato yellow grapevine and leaf respectively (Pecile, 2013).

Red grape varieties

Frappato

Frappato, also called "*Black Frappato*", "*Frappato of Victoria*", "*Black Captain*", "*Frappatu*" and "*Nerello*", is a red grape variety, widely grown on the southeast coast of Sicily and in particular in Syracuse and Ragusa territories (Bica, 2007).

The grape variety has ancient origins, there are written records of the existence of Frappato vineyards since the seventeenth century, in a letter sent by Comm. Rosario Cancellieri Baron Mendola (Ministero Agricoltura, 1879). It is not known if the cultivar was cultivated in that area before the foundation of the city of Victoria, around the seventeenth century, or the variety has been introduced at a later date, and that the name is derived later.

Frappato has a great historical importance. The vine contributes, along with the Nero d'Avola wine production Cerasuolo di Vittoria in 2005 became the first and only DOCG in Sicily. Frappato is also mixed with Nerello Mascalese, Nerello Cappuccio and Nocera. The wine produced from this cultivar has a low content of tannins and a light body.

The wine produced from this grape variety contributes to various Sicilian DOC: Alcamo DOC, Eloro DOC, Erice DOC, Sicilia DOC, Vittoria DOC and DOCG Cerasuolo di Vittoria DOCG.

The grape variety Frappato has the following features:

- Leaf: medium, pentagonal;
- Grape: medium to large, cylindrical or pyramidal, compact;
- Berry: medium, spheroidal or ellipsoidal, Skin: pruinose, thick and leathery, blue-violet color.

(Bica, 2007)

Picture 10 Frappato grapevine and leaf respectively (Pecile, 2013).

Nerello Cappuccio

Nerello Cappuccio, also known with the name of "*Nerello Mantellato*", is a red grape variety found in Sicily and in Calabria. The variety is mainly bred in the volcanic soils of Mount Etna, especially at higher elevations. It ripens earlier than the cousin Nerello Mascalese. The berries of this variety have a higher acidity of the grapes than average, combined abundance of tannin which is fitted to make it a good choice for making wine. Outside Sicily it is also raised within the DOC Calabria. Its origin is unknown, but is grown Sicily for hundreds of years. The first written records of this variety comes from the abbot Geremia (Geremia, 1839) which indicates crops in the area of Trecastagni and Viagrande (both located in the province of CT). Bulletins Ampereologic we speak of a "*Nerello Ammantellato*" that is grown in the Province of Catania in 1878 and a "*Nireddu Ammantiddatu*" in Palermo.

The wine produced from this grape is soft and richly colored, with a cherry flavor, often is used together with Nerello Mascalese to soften the taste. Only in the last two decades it has begun to take important as variety.

DOC has in Sicily and in Calabria, for Sicily: Faro DOC e Sicilia Doc, and for Calabria S. Anna Isola di Capo Rizzuto DOC e Savuto DOC.

While the IGT are only Calabresi: Arghillà IGT, Calabria IGT, Costa Viola IGT, Lipuda IGT, Locride IGT, Palizzi IGT, Pellaro IGT, Scilla IGT, Val di Neto IGT, Valdamato IGT.

The grape variety Nerello Cappuccio has the following features:

- Leaf: medium to large, wedge-shaped, whole or Triblade;
- Grape: medium, cylindrical or conical, compact;
- Berry: spheroidal , Skin: pruinose, consistent, blue-black color.

(Bica, 2007).

Picture 11 Nerello Cappuccio grapevine and leaf respectively (Foto Santa Maria La Nave).

Nerello Mascalese

Nerello Mascalese is a type of red grape of Sicily. The typical area of breeding are the volcanic slopes of Mt. Etna in Sicily, is raised up to share 1000 meters above sea level. There are also modest cultivations of Nerello Mascalese in the town of Faro, (in the province of Messina) even if

the cultivations do not reach the altitude typical of Mt. Etna.
This type of grape variety has a late ripening to mid-October, in most of the vineyards are grown with bush -vine method.

The cultivar is named the plain of Mascali, situated between Mount Etna and the coast of the Ionian Sea, where it is thought to have originated from a small portion of the ancient vines before the phylloxera of 1880. As the name refers to the Nerello very dark color of the grapes, this name is also shared by the Nerello Cappuccio, which is the most common partner melting Nerello Mascalese.

The grape variety is part, most likely, of the ancient group of varieties "Nigrelli" described by (Sestini, 1991), whereas the first mentions of the Nerello Mascalese are to be referred to the abbot Geremia speaking cultivation of the vine on the slopes of Mt. Etna (Geremia, 1839).

Recent DNA tests that have been carried out suggest that the grape variety comes from Sangiovese.

The variety is in the wine DOC of Mt. Etna. The wines produced from this cultivar are enjoying a increase in popularity in the last 10 years, thanks to their fresh fruity, herbaceous flavor, excellent minerality adding a trace of earth. The DOC Sicilian are: Alcamo DOC, Contea di Sclafani DOC, Etna DOC, Faro DOC, Marsala DOC, Riesi DOC, Sicilia DOC. Calabria has only one DOC**:** S. Anna isola di capo Rizzuto DOC. For IGT Sicily there is: Fontanatossa di cerda IGT, and for Calabria: Arghillà IGT, Calabria IGT, Costa Viola IGT, Lipuda IGT, Locride IGT, Palizzi IGT, Pellaro IGT, Scilla IGT, Val di Neto IGT, Valdamato IGT.

The grape variety Nerello Mascalese has the following features:

- Leaf: medium-large, three-lobed or entire, wedge-shaped or pentagonal;
- Grape: medium, often winged, more or less compact;
- Berry: medium-small, spherical or elliptical short, Skin: thick and consistent blue-violet color.

(Bica, 2007).

Picture 12 Nerello Mascalese grapevine and leaf respectively (Pecile, 2013).

Calabrese (Nero d'Avola)

Nero d'Avola, occurring in the register of Italian wines with the name "*Calabrese*", is the most important variety of red grapes and it has the largest area of cultivation of Sicily. It is also widely bred in Calabria. Nero d'Avola is the most important grape berry colored of Sicily. It nurtures it intensely in the provinces of Siracusa, Ragusa, Caltanissetta, Catania and Agrigento, but is also present in other provinces of Sicily (Bica, 2007).

The name comes from the town of Avola, located on the southeast coast of the island, which in the Middle Ages was a rich and prosperous commercial junction, and the wine produced from this grape until to then it was used to add body to the vines minor Italian. Its origins are still a source of debate.

There are various ongoing discussions on the origin of the grape, the name is thought that could have Calabrian origin but there is no evidence in support of this this hypothesis (Geremia, 1839).

An assumption shared by many, the name derives dialect "*Aulisi*" from "*Caia-Avola*" where V Avola has been converted into U, while "*Cala*" would be the dialect form of "*Calea*" or "*Caleu*" which Sicilians are synonyms of "*racina*" (grape) (AA.VV, 1996). It is certain that the area of Avola (located in the province of Syracuse), even if it was not the center of origin of cultivars, is certainly a center for the cultivation of the grape variety from ancient times. The oldest written records date back to Mendola reporting the presence of the vine in the provinces of Agrigento, Catania and Siracusa (Mendola, 1868).

For most of the 20th century, the grapes of this vine had been used as a blending grape, but in the

21st century it became a wine varietal type. Nero d'Avola is bred in the eastern part of Sicily, and you are looking to experience the breeding of the grape in Australia and in California.

The Nero d'Avola contributes to the production, together with Frappato, the Cerasuolo di Vittoria, who in 2005 became the first and only DOCG in Sicily. Sicily holds numerous DOC: Alcamo DOC, Contea di Sclafani DOC, Faro DOC, Mamertino di Milazzo or Mamertino DOC, Marsala DOC, Menfi DOC, Monreale DOC, Noto DOC, Riesi DOC, Salaparuta DOC, Sambuca di Sicilia DOC, Santa Margherita di Belice DOC, Sciacca DOC, Sicilia DOC, Siracusa DOC, Vittoria DOC.

La Calabria has two DOC Bivongi DOC and Terre di Cosenza DOC.

There are also several IGT, for Calabria: Arghillà IGT, Calabria IGT, Costa Viola IGT, Lipuda IGT, Locride IGT, Palizzi IGT, Pellaro IGT, Scilla IGT, Val di Neto IGT, Valdamato IGT; for Basilicata: Basilicata IGT, e for Siciliy : Fontanarossa di Cerda IGT.

The grape variety Nero d'Avola has the following features:

- Leaf: large, orbicular, whole;
- Grape: medium, conical, winged, moderately compact and often compound;
- Berry: medium, ellipsoidal or oval, Skin: waxy, medium thickness, very resistant, bluish.

(Bica, 2007).

Picture 13 Calabrese (Nero d'Avola) grapevine and leaf respectively (Pecile, 2013).

Autochthonous vines variety

In Sicily, since the 90's, production interest focused on the spread of grape varieties, especially black grapes such as Cabernet Sauvignon, Merlot and Syrah. The purpose of these introductions was to produce monovarietal wines or to be used in mixture with some autochthones vines variety

(Bica, 2007).

These varieties well adapted to climatic and weather conditions, and the types of Sicilian soil, so they are now bred in many vineyards in Sicily.

Cabernet Sauvignon

The Cabernet Sauvignon is the most popular red grape variety in the world.

The grape variety is a native of Bordeaux in France, and has been spreading successfully in almost all wine-growing regions of the world. Regardless of their origin wines produced from these grapes they have the common characteristic traits: deep color, good tannin structure, moderate acidity and aromas of black currants, tomato leaf, dark spice and cedar wood.

Cabernet Sauvignon is the grape variety originated from a spontaneous cross between "Cabernet Franc" and "Sauvignon Blanc, which occurred in the Gironde in France (Bowers, 1997) (Robinson, 2012).

Initially it appears, in the historical data, with the name of "*Petit Cabernet*" in 1763-1777, a few years later the name changes to "*Cavernet Sauvignon*", to get the current "*Cabernet Sauvignon*" in 1840 (Rézeau, 1997) (Robinson, 2012).

The ubiquity of the variety is due to two main factors. The first is that its strains are highly adaptable to different climates and soil types, a growth in the most diverse latitudes up to 50 ° North (Okanagan, Canada) at 20 ° South (northern Argentina) and in soils ranging from gravels Pessac-Leognan in France, to the red soil rich in iron in the area of Coonawarra (Australia). The second reason is that despite the diversity of the Terroir in which is bred grapes, the wines made from this grape retain an inimitable character called "Cab"

The grape variety has a high yield and a late maturing.

The Cabernet Sauvignon has numerous DOC in the various Italian regions. The DOC of Sicily are: Contea di Sclfani DOC, Contessa Entellina DOC, Erice DOC, Menfi DOC, Monreale DOC, Riesi DOC, Salaparuta DOC, Sambuca di Sicilia DOC, Santa Margherita di Belice DOC, Sciacca DOC and Sicilia DOC; and only one IGT: Fontanarossa di Cerdia IGT

The grape variety Cabernet Sauvignon has the following features:

- Leaf: medium size, pentagonal, five with breasts closed overlapping edges, almost hairless;
- Grape: medium-small, cylindrical, often with a wing evident, medium compact;
- Berry: medium, spheroidal, Skin:. blue-violet, consistent, some fleshy pulp and slightly grassy flavor.

(Scalabrelli, 2013)

Picture 14 Cabernet Sauvignon grapevine and leaf respectively (Pecile, 2013).

Merlot

Merlot is a red grape of French origin. It is the predominant variety in the areas of Saint-Emilion and Pomerol, where the grape originated. Genetic investigations indicate that the variety is closely related to the Cabernet Sauvignon and Cabernet Franc.

The first written reference, ascribable to grape variety there is in 1783 under the name "*Merleau*", in Gironde in France. The current name appears Merlot in 1824 on a wines treatise of the Medoc, which reveals that the name derives from Merlo, in fact these birds are fond of its grapes (Rézeau, 1997) (Robinson, 2012).

Molecular analysis, conducted to shed light on the origins of the grape variety, found that Merlot was originated from a spontaneous cross between "*Cabernet Franc*" and "*Magdeleine noire des Charentes*", which is a variety almost unknown, of which are found, to date, only a few specimens (Boursiquot, 2009) (Robinson, 2012).

This grape variety is widely grown in the wine regions around the world. In France it is the most bred variety of red wine. It is also widely distributed in northern Italy, in warmer areas of southern Switzerland, Chile and California. With volumes of wine produced comparable only to the Cabernet Sauvignon that is his partner for the production of Bordeaux. Although in recent years the popularity of the grape decreased.

The grape variety prefers hilly terrain, fresh and moist, but not against the drought climates.

The skins of the grapes, which is the area Where are tannins, are particularly thick, and the seeds are very large. The maturity of this type of cultivar is early, then mature even in cooler climates. The DOC that holds in the entire Italy, such as Cabernet Sauvignon, are numerous. The DOC of Sicily are: Alcamo DOC, Contea di Sclafani, Contessa Entellina DOC, Delia Nivonelli DOC, Erice DOC, Menfi DOC, Monreale DOC, Riesi DOC, Salaparuta DOC, Sambuca di Sicilia DOC and Sciacca DOC.

The grape variety Merlot has the following features:

- Leaf: medium, pentagonal, three-lobed and five lobes;
- Grape: medium, pyramidal more or less sparse, with one or two wings;
- Berry: medium, round, blue-black color, Skin: medium consistency, covered with itchy skin.

(Giavedoni, 2006) (Scalabrelli, 2013).

Picture 15 Merlot grapevine and leaf respectively (Pecile, 2013).

4.Methods of sampling and analysis

In the two sampling areas of Sicily, chosen for the doctoral thesis**,** samples of inorganic matter (soil and rock) and organic samples (juice, residue, skin, seed and leaf) were collected as set out on Table 7.

Summary sheet samples

Year 2013

SOILS

Vineyard	Soil type	Number of Samples
Don Saro	Volcanic	11
COS	Carbonate	11
Avide	Carbonate	9

JUICES

Vineyard	Soil type	Number of cultivars	Names of Cultivars	
			Red Berries	White Berries
Don Saro	Volcanic	5	Nerello Mascalese, Merlot, Nerello Cappuccio	Inzolia, Carricante
COS	Carbonate	7	Cabernet Sauvignon, Nero d'Avola, Frappato, Merlot	Moscato, Inzolia, Grecanico
Avide	Carbonate	3	Cabernet Sauvignon, Frappato, Nero d'Avola	--------

RESIDUES

Vineyard	Soil type	Number of cultivars	Names of Cultivars
Don Saro	Volcanic	5	Nerello Mascalese, Merlot, Nerello Cappuccio, Inzolia, Carricante
COS	Carbonate	7	Moscato, Inzolia, Grecanico, Cabernet Sauvignon, Nero d'Avola, Frappato, Merlot
Avide	Carbonate	3	Cabernet Sauvignon, Frappato, Nero d'Avola

Year 2014

ROCK

Area	Number of Samples
Linguaglossa(CT)	7
Comiso (RG)	10

JUICE

Vineyard	Soil type	Number cultivars	Names of Cultivars

Don Saro	Volcanic	5	Nerello Mascalese, Merlot, Nerello Cappuccio, Inzolia, Grecanico
COS	Carbonate	6	Grecanico, Frappato, Cabernet Sauvignon, Merlot, Inzolia, Nero D'Avola
Avide	Carbonate	3	Cabernet Sauvignon, Frappato, Nero d'Avola

SKINS

Vineyard	**Soil type**	**Number cultivars**	**Names of Cultivars**
Don Saro	Volcanic	5	Nerello Mascalese, Merlot, Nerello Cappuccio, Inzolia, Grecanico
COS	Carbonate	6	Grecanico, Frappato, Cabernet Sauvignon, Merlot, Inzolia, Nero D'Avola
Avide	Carbonate	3	Cabernet Sauvignon, Frappato, Nero d'Avola

SEED

Vineyard	**Soil type**	**Number cultivars**	**Names of Cultivars**
Don Saro	Volcanic	5	Nerello Mascalese, Merlot, Nerello Cappuccio, Inzolia, Grecanico
COS	Carbonate	6	Grecanico, Frappato, Cabernet Sauvignon, Merlot, Inzolia, Nero D'Avola
Avide	Carbonate	3	Cabernet Sauvignon, Frappato, Nero d'Avola

LEAVES

Vineyard	**Soil type**	**Number cultivars**	**Names of Cultivars**
Don Saro	Volcanic	5	Inzolia, Nerello Mascalese, Carricante, Merlot, Nerello Cappuccio
COS	Carbonate	6	Grecanico, Frappato, Cabernet Sauvignon, Merlot, Inzolia, Nero D'Avola
Avide	Carbonate	3	Cabernet Sauvignon, Frappato, Nero d'Avola

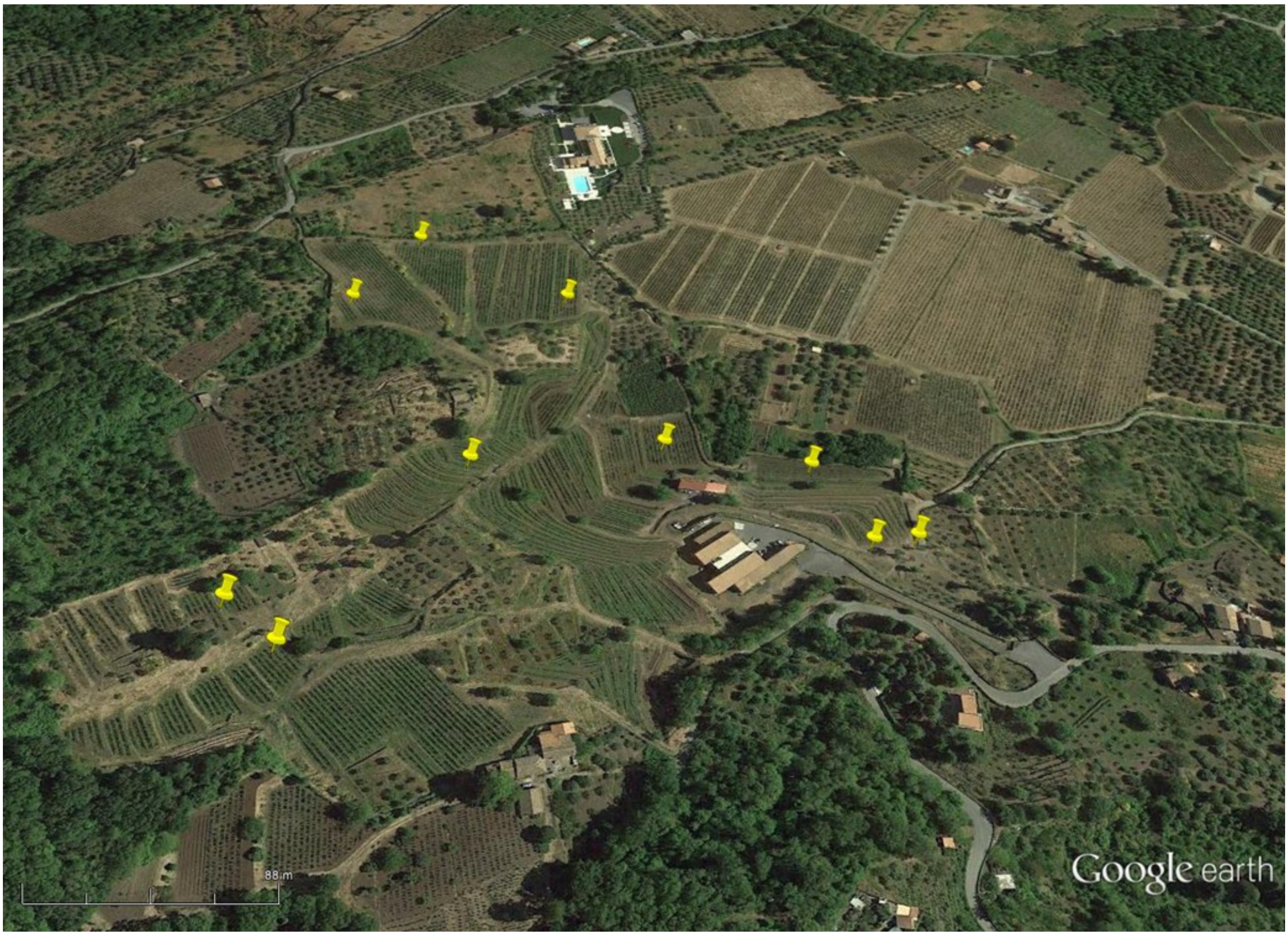
Table 7 sample list.

Sampling

Soil and Rock Sampling

In the selected areas**,** 31 soil samples were collected**,** on May 2013, their position being accurately mapped using a GPS device. Of these 11 were sampled in the vineyard of Don Saro in Linguaglossa town**,** 9 in the Avide vineyard and 11 in the COS vineyard, these two last are both located in Comiso. The first 10 cm of the soil surface were excised as any plants present in it, the sample was collected (about 500gr), through the use of a plant bulbs expansion, at a depth between 10 and 20 cm and placed in plastic bags and initialed sealed to prevent contamination. The samples were stored in the refrigerator to prevent contamination by bacteria and the proliferation of mold.

In addition to soil samples, rock samples were also collected in the selected areas for a total of 17 samples: 7 of them were collected in rocky outcrops in the winery of Don Saro (Mt. Etna), and 10 samples were collected in the rocky outcrops in one zone between Acate and Chiaramonte towns (Hyblean Plateau) where the Avide and COS wineries are located. Any residue of soil and plants was removed from before. The samples, collected through ice ax for geologist, were placed in sterile plastic bags for the sampling.



Picture 16 In the image are marked by Google Earth the soil sampling points measured using GPS the vineyard Don Saro, located in the municipality of Linguaglossa, Mount Etna.

Picture 17 In the image are marked by Google Earth the soil sampling points measured using GPS the vineyard COS, located in the municipality of Comiso, Hyblean Plateau.

Picture 18 In the image are marked by Google Earth the soil sampling points measured using GPS the vineyard Avide, located in the municipality of Comiso, Hyblean Plateau.

Plant Sampling

The plant samples were collected during the harvest period, by taking into account that for each areas this period is different; indeed, in the Etnean area the harvest occurs between late September and early October, whereas for the area of the Hyblean Plateau the harvest period runs from late August through the end of September. The different periods of time in which the harvest takes place depends on the different climatic conditions as well as on different geographical position of the two chosen areas. The sampling was carried out for the next two years 2013 and 2014. The samples of grapes were manually collected by clippers, then placed in bags of sterile sampling and frozen. The breakdown of samples in parties 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, to eliminate any possible residue present on it. The next step was the ungrapture manual of the berries from grape. After which, samples obtained foe each year were treated according two different methods, that were then compared.

For the harvest of 2013: the berries were centrifuged with a food centrifuge, in order to extract the juice and keep the residues. For each cultivar, two samples were collected of either juice and residue.

For the harvest of 2014: the grapes were peeled by hand, whereas the rest of the berry was centrifuged to split the seeds from the juice. Also in this case, samples were collected in duplicate of each cultivar, except for the seeds of which 4 samples for each cultivar were taken.

In 2014 sampling of grapevine leaves was also performed; leaves, these were harvested at the beginning of May, before the leaves were subjected to any type of treatment. The leaves were manually collected from the various cultivars, avoiding the leaves of the rootstock. At the laboratory of Chemistry Department of Biology and Earth Sciences of the University of Catania leaves were detached from the branches, weighed and subjected to washing with MilliQ water. The leaves were then placed on a special absorbent sterile paper not to suffer contamination and placed in a stove at 70 ° C for 48 hours according to the literature procedure (Zhang, 2001). The leaves, when dried, were again weighed to measure their weight loss, and milled by an agate mortar.

Samples treatment

Samples, before analyses, must undergo various treatments. Depending on the nature of the sample, treatments vary according to analytical technique. In this work it was decided to apply the X-ray fluorescence (XRF) for inorganic samples (i.e. soil and rocks), and the Mass-Inductively Coupled Plasma Spectrometry (ICP-MS) for both inorganic and for organic samples: juices, residues, peels, seeds and leaves. The analysis of the samples by XRF allows the determination of major, minor and trace elements, whereas the analysis by ICP-MS trace and ultra-trace elements. For XRF analysis samples were prepared into tablets of pressed powder, while in the case of the ICP-MS analysis, samples solutions were prepared.

Grain size analysis

The particle size analysis of samples was performed on 31 soil samples, by, weighing about 500 grams, collected on May 2013 as follows: 11 belonging to the area of Mt. Etna, and 20 belonging to the Hyblean Plateau (11 from COS and 9 from Avide the agricultural companies, respectively). The procedures for collecting the samples are those one previously described.

Each sample was placed on a tray and all of the evident pollution elements (e.g. plant remnants, residues of animals origin or paper, plastic fragments), if present, were removed. Once cleaned each sample was quartered, to make sure that the sample is as homogeneous and representative as possible.

In the next step, part of the quartered sample was put in a beaker where it was treated with hydrogen peroxide at 18 volumes, in order to remove the organic part that is not visible to the naked eye. Samples remained in immersion for a few days, after that they were rinsed with water and subjected to a coarse sieving to remove the largest stone fragments or other residues remained in the sample. A second fine mesh sieve will collect the sample while the water with the fine suspension is left to decant. Once extracted all the water this part will be analyzed by the silkscreen 500.

The sample collected from the second sieve was dried and sieved, it is passed through a column of progressively finer sized sieves. The withheld each sieve is weighed, obtaining the particle size analysis of the samples.

Sample preparation for XRF analysis

This technique has been applied to both soil (which had been previously removed organic matter) and rock samples. The method applied is the same for both types of sample, the only variation is that for the rock samples was carried out through the grinding crusher to reduce samples to a finer particle size.

The samples were subjected to drying, in a furnace, at a temperature of 105 ° C for 24h, these were weighed before and after to measure water loss.

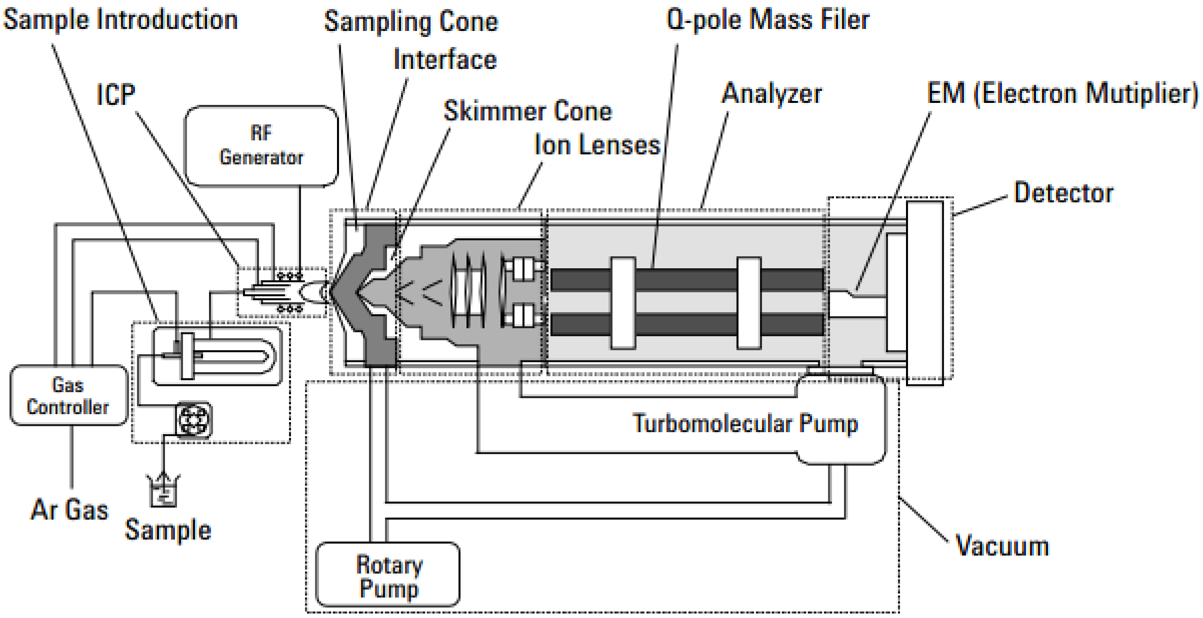
Subsequently, the particle size was reduces with both the hydraulic press that manually reducing the samples into a fine powder using a agate mortar. The samples were subsequently dried again in a muffle at a temperature of 500 °C, for 24h. They were weighed both before and after the treatment, the weight loss indicating the loss of the organic substance, still present in the sample, through the calcination.

The powders, so treated, were used to make the pellet. Approximately 0.2 grams of sample were mixed with a bonding agent and pressed on a support of boric acid through a hydraulic press. Pellets, thus obtained, were dried for 24 hours before being sealed in sterile polyethylene bags to avoid contamination of the tablets waiting to be analyzed. The "Loss on ignition" (LOI), fundamental for the analysis of dust samples by X-ray fluorescence, was calculated from the weight loss of 0,5g sample. The weight loss is obtained from the weight difference of the sample before and after being subjected to a temperature of 1000 °C for 24h in a muffle.

For XRF analysis it was used a spectrometer dispersion wavelength "ARL Advent-XP" at the department of Physics and Earth Sciences of the University of Ferrara. The tool has allowed the determination of major and minor elements: SiO2, TiO2, Al2O3, Fe2O3, MnO, MgO, CaO, Na2O, K2O, P2O5 (expressed as percentage by weight on the oxide) and minor elements: Ba, Ce, Co,Cr, La, Nb, Ni, Pb, Rb, Sr, Th, V,Y, Zn, Zr, Cu, Ga, Nd, S, Sc (in part per million ppm).

Inductively Coupled Plasma Mass Spectrometry (ICP- MS)

The Inductively Coupled Plasma Mass (ICP) techniques are based on the presence of an inductively coupled plasma source. The sample is atomized, by the source, to a temperature that can reach up to 10,000 K. The advantages of the use of a plasma source are: more complete atomization and less subject to chemical interferences, than that obtainable by the methods flame or oven, thanks to high temperatures that can be obtained with the plasma and at intervals of operating linearity of concentration by several orders of magnitude.



Piture 19 Inductively Coupled Plasma Mass Spectrometry scheme (Agilent, 2005).

The sample is aspirated by a system of peristaltic pumps and, at the level of the nebulizer, is rendered to the aerosols state. The nebulized sample is transported from the *carrier* (argon in Picture 17) and passes inside the torch, here is atomized and ionized, thanks to the presence of argon in the plasma state. The obtained ion beam, focused through a system of electrostatic lenses, is brought to the level of the quadrupole also called mass separator, where separation takes place on the basis of the mass / charge ratio (m / Z). The separator operates in conditions of vacuum (10-5 torr) to avoid that the path of the ions is altered by collisions with air molecules. Finally, the detector converts the stream of ions in an electric signal that can be processed (Agilent, 2005).

Preparation of the samples ICP-MS

ICP-MS investigation was carried out with a spectrometer X series, Thermo Electron Corporation, equipped with CCT® (Collisional Cell Tecnology) of the department of Physics and Earth Sciences of the University of Ferrara, which allows to reduce and control the spectral interferences, making the most precise measurements.

The samples were analyzed twice; in the first analysis the REEs are enclosed together with the other elements that are usually used for the petrological report: Rb, Sr, Y, Zr, Nb, La, Ce, Pr, Nd, Sm Eu, Gd, Tb, Dy, Ho Er, Tm, Yb, Lu, Hf, Ta, Th, U.

In the second analysis we determined Li, B, Na, Al, K, Rb, Ca, Sr, Ba, Mg, Mn, Fe, V, Cr, Co, Ni, Cu, Zn, Ga, As, Mo, Ag, Cd, Sn, Tl, Pb.

Samples, were prepared according to specific procedures. The material to be analyzed **(**both organic and inorganic) was dissolved with a mixture of strong acids and / or oxidants, the digestion system used for samples is the method "*Wet digestion*" also known as " Acid digestion". In this technique, the sample mixture of acids and / or oxidants**,** is placed into a sterile container (possibly Teflon**)** which will be heated**.** The reagents used vary based on the nature of the sample**,** but we usually use HNO_3, H_2SO_4 and H_2O_2.

Wet Digestion

The Wet digestion can be done according to two different procedures (Chao, 1992):

- Open / closed system;
- Dissolution by microwave.

In the **"open system"**, the sample, mixed acid, is heated on a plate. The heat of the plate and acids make that the dissolution of the sample occurs. Once the mixture reaches the incipient dryness, another known amount of acid will be added to sample, diluting the solution to the desired volume. Nevertheless, quite often one single heating cycle on the plate is not sufficient to dissolve the sample completely, so several cycles are needed to complete sample dissolution.

The cycles of dissolution and the choice of acid depends on multiple factors such as, the chemical-physical characteristics of the sample, the quantity of sample that is chosen to submit to dissolution, and the instrumentation which is then employed.

In **"dissolution by microwave**" technique, heating the mixture of the sample and acids takes place in sealed containers placed inside the microwave oven that may reach 300 ° C and pressures in the order of 800 psi. With this instrumentation, the digestion times are considerably reduced, as also the risk of contamination, and since the system is perfectly sealed, even the loss of volatile elements is drastically reduced. Moreover, the consumption of acid used is also reduced. The advantages of this system are due to the direct heating of the components and the use of high pressures is increased thanks to which the boiling point of the acids and by facilitating the dissolution of the samples (Chao, 1992) (De La Guardia, 2013).

In this work, the method of dissolution that has been used is the wet digestion on open systems in a hot plate. As already mentioned, there are many factors that affect the processes of dissolution and given the extreme variety of samples, it was necessary diversifying digestion techniques based on the characteristics of the sample. Five different digestion techniques were used, as described in detail in the following sections.

Soil and Rock digestion

A quantity of the sample between 0.1 and 0.2 g was placed in Teflon vessels of and covered with parafilm to prevent contamination by external agents. 6ml HF 40% Merck Suprapur and 3 ml of HNO_3 65% Merck Suprapur were added to sample, which was subjected to ultrasounds for 10 minutes and left to stand overnight. The next day, the samples were subjected to further 10 minutes ultrasound, after that they were left to dissolve at a temperature of 170 °C on a plate that distributes heat evenly on the various vessels in Teflon. Once dried, 3 ml HF 40% Merck Suprapur and 3 ml of HNO_3 65% Merck Suprapur were added, leaving to stand again overnight. The next day the samples were subjected to a further 10 minutes of ultrasound and dissolved at a temperature of 170 °C up to dryness, then further 4ml of HNO_3 65% Merck Suprapur and maintained on the plate up to that dissolve again. Once the mixture reaches the dryness**,** 2 ml of HNO_3 65% Merck Suprapur were added**,** and the mixture was poured into a volumetric flask. Multi-elemental internal standard with Re, Rh, In and Bi at a concentration of 10 ppb was also added. Last, the volumetric flask was filled up to the notch with 100 ml of MilliQ water**.**

Juice digestion

In this case the procedure is faster than the previous one describe for inorganic sample, since it requires only 1 step of dissolution. A sample quantity of 4 gr was placed in a Teflon vessel. 3 ml of HNO_3 65% Merck Suprapur and 3 ml H_2O_2 37% Merck Suprapur were added. The sample are left dissolve at a temperature of 150 °C on a plate that distributes heat evenly on the various vessels in Teflon. Once the mixture reaches the incipient dryness**,** 3 ml of HNO_3 65% Merck Suprapur were added**,** and the mixture was poured into a volumetric flask. Multi-elemental internal standard with Re, Rh, In and Bi at a concentration of 10 ppb was also added. Last, the volumetric flask was filled up to the notch with 100 ml of MilliQ water**.**

Residue and Skin digestion

The dissolution of these organic components requires a different procedure from the two previous ones; in this case we have two different steps of dissolution but the treatment, as in the case of juices, is all performed within a single day. A sample quantity of 2,5g was placed in Teflon vessel. 4 ml of HNO_3 65% Merck Suprapur and 3 ml H_2O_2 37% Merck Suprapur were added. The sample are leaves dissolve at a temperature of 150 °C on a plate that distributes heat evenly on the various vessels in Teflon. Once dried, add 2 ml HNO_3 65% Merck Suprapur and 2 ml of H_2O_2 37% Merck Suprapur, and dissolved at a temperature of 150 °C. Once the mixture reaches the dryness, 2 ml of HNO_3 65% Merck Suprapur were added, and the mixture was poured into a volumetric flask. Multi-elemental internal standard with Re, Rh, In and Bi at a concentration of 10 ppb was also added. Last, the volumetric flask was filled up to the notch with 100 ml of MilliQ water.

Seed digestion

The seeds digestion procedure, follows the same procedure and the same steps used in the case of residue and skins, which have been seen previously, the only difference lies in the amount of seeds. The weight of 0.5 grams is the same for each sample. This quantity corresponds to a number of seeds between 14 and 16 for the varieties with seeds smaller and 9-10 for seeds of larger dimensions. The different sizes of the seeds do not affect in any way the digestion procedure, and then was applied to the same procedure for all samples.

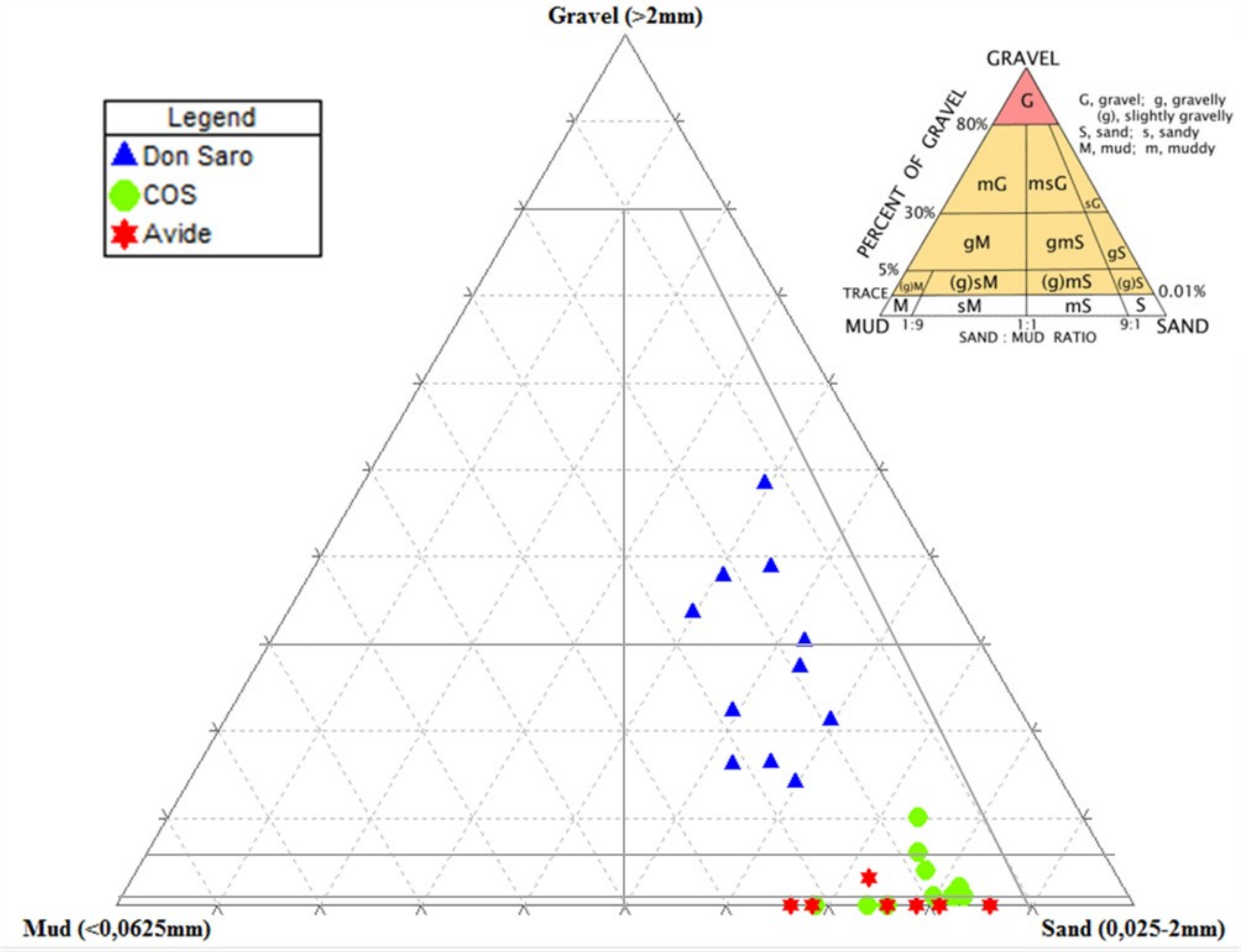
Leaf digestion

As in the case of residues and skins, including the leaves, two different steps of dissolution were performed within a single day. A sample quantity of 0,5 g was placed in vessel of Teflon and 4 ml of HNO_3 65% Merck Suprapur and 3 ml H_2O_2 37% Merck Suprapur were added. The sample are left to dissolve at a temperature of 150 °C on a plate that distributes heat evenly on the various vessels in Teflon. Once dried, in the second step add 3 ml HNO_3 65% Merck Suprapur and 2 ml of

H_2O_2 37% Merck Suprapur were adding, and dissolved at a temperature of 150 °C. Once the mixture reaches the dryness, 2 ml of HNO_3 65% Merck Suprapur were added, and the mixture was poured into a volumetric flask. Multi-elemental internal standard with Re, Rh, In and Bi at a concentration of 10 ppb was also added. Last, the volumetric flask was filled up to the notch with 100 ml of MilliQ water.

5.Results and Discussion

Grain size analysis



Graph 7 Folk ternary diagram of classification of mixtures of gravel, sand and mud of soil samples of three vineyards. Don Saro-member of the Etna, while COS and Avide belong to the Hyblean Plateau. Top right Folk ternary diagram of classification of mixtures of gravel, sand and mud (Folk, 1954) (Folk, 1974).

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The particle size and textural analysis, carried out on soil samples, highlighted the distinction between the two areas. The samples were compared with each other by the Folk chart (Folk, 1954) (Folk, 1974), which classifies soils according to the content of gravel, sand and mud. The diagram shows that samples the Hyblean Plateau plot into two categories "*muddy sand*" and "*gravel slightly muddy sand*"; samples of Mt. Etna show a range of distribution and mostly plot in "*muddy sandy gravel*" and "*gravelly muddy sand*".

As expected, the analysis reflects perfectly the division of investigated areas. Compared to samples from the Hyblean Plateau, the coarser particle size soil of the study area of Linguaglossa (Etna) is due to its relatively young age, since, it derives from the transformation of the lavas erupted in 1556. As regards the wide dispersion, it may be caused by the continuous paroxysmal explosive eruptions of the Mt. Etna. These eruptions disperse in the environment a huge amount of volcanic ash that, depending on the wind direction, deposited on the slopes of the volcano, and then also in soils. Despite the first 10 cm of soil have been removed, the ash deposited accumulated over the years as amalgamating with the pre-existing soil.

Samples collected in the Hyblean Plateau indicate a type of soil with a finer sandy-loam particle size distribution.

pH of the soil

The pH and conductivity of the ground are important characteristics of the soil. Being pH is the measure of the concentration of hydrogen ions (H +) in an aqueous solution, the pH of the soil is therefore the measurement of the concentration of hydrogen in the liquid phase which is located in the free spaces left by the solid parts (Giardon, 1990).

The pH of the soil affects the solubility of the various minerals, by determining elements accumulation in the soil and availability for plants or elements leaching to deeper layers.

Measurement of pH and conductivity in the soil of agricultural holdings was carried out. Three samples for each vineyard were collected at a depth of between 10 and 20 cm. The soil as it is, placed in bags of sampling, was immediately frozen at harvest time at the Department of Earth Sciences, University of Catania.

The evening prior to the measurements, the soil samples were placed in the laboratory at room temperature to thaw out slowly. The measurements were carried out in the next morning, after checking that the samples were completely thawed out;

5g of sample and 25 ml of MilliQ water in a ratio of 1: 5 were mixed in the plastic beaker at the temperature of 20 ° C.

The measurements were made on samples using the pH-meter and the conductimeter of the chemistry laboratory of the Department of Sciences Earth University of Ferrara. As seen from the results set out in table, the soils of vineyards show very different characteristics in the two areas of sampling. The average value of the pH value of the area of Mount Etna is 6.42 then are sub-acid soils. In contrast the average value of the pH of the soil for the area of the Hyblean Plateau is 8.33, the soils of this area are alkaline.

Very Acid	<5,4
Acid	5,4-5,9
Sub Acid	6,0-6,6
Neuter	6,7-7,2
Sub Alkaline	7,3-8,0
Alkaline	8,1-8,6
Very Alkaline	>8,6

Table 8 Classification of the soil according to the pH according to the scheme interpretative ARPAV.

Acid soils favor the solubilization of many nutritional elements, and often it can happen that they can be easily leached in deep horizons, or accumulate within soils at high concentrations that, if they are excessive, may be harmful to the health of plants. Apart the strong leaching, in acidic soils it is usually found an insufficient absorption of calcium, magnesium, potassium and phosphorus ions, and an increase in the availability of manganese, iron, aluminum, nickel and copper (Giardon, 1990).

The basic soils are characterized by the presence of some components, which affect the chemical-physical characteristics of the soils. The calcareous soils, typical of the Hyblean Plateau, unlikely exceed a pH value of 8 to 8.4; these soils are rich in calcium and magnesium carbonate. This type of soils have a lower availability in microelements, a retro-gradation of phosphorus with formation of insoluble phosphates and increase in the amount of calcium, which can also induce antagonism with magnesium and potassium and increase in the availability of molybdenum (Giardon, 1990).

Sample	Weight g	Vineyard	pH	Conductivity µs (ratio 1:5)	Real Conductivity
A1	5,0075	Avide	8,28	102,3	511,5
A2	5,0174	Avide	8,38	98,6	493
A3	5,0148	Avide	8,28	102,4	512
C1	5	COS	8,34	122,8	614
C2	5,0007	COS	8,34	120,3	601,5
C3	5,0049	COS	8,38	121,8	609
DS1	5,0046	Don Saro	6,44	54,8	274
DS2	5,0008	Don Saro	6,47	55,9	279,5
DS3	5,0001	Don Saro	6,35	52,6	263

Table 9 measuring pH and conductivity of the soil in agricultural holdings.

Soil conductivity

The electrical conductivity of the saturation extract of the soil or of suspensions Soil / water, is an excellent indicator for the diagnosis of salinity of soils. The soluble salts, present in the soil, are essential for the nutrition of the plants, provided that their concentrations do not exceed certain values. Besides the concentration, another important factor to consider is the water retention capacity of the soil.

The conductivity of the soil solution was performed by the use of a conductivity meter, of a soil suspension in water in the ratio (weight / weight) 1:5 ($EC_{1:5}$). The measurement was repeated for three samples of soil of each vineyard.

Conductivity of the soil of the two areas is significantly different with average concentration of 272.166 milliSeimens/centimeter (mS/cm) for the area of Mount Etna and 556.833 mS/cm for soils of agricultural holdings of the Hyblean Plateau.

The large difference in the conductivity of soils is due to different climatic conditions of the two zones. In fact, in the Hyblean Plateau, where the two vineyards (Avide and COS) are located, the temperature averages are included in a range between 16 and 19 ° C and the annual rainfall is in a range between 400-500 mm (Hydrographic Service of Civil Engineering from 1966 to 1990).

Conversely, on the side of Mount Etna, where the vineyard of Don Saro is located, the average annual rainfall is between 1000 and 1200 mm (Regione Siciliana, 1998).

The low rainfall the Hyblean Plateau is a major cause of the high conductivity.

Rainfall is concentrated between September and March in the Hyblean Plateau and between October and March on Mt. Etna. In summer time the rains are almost entirely absent, also the type of cultivation does not provide for almost any type of irrigation part cases of long drought.

The combination of these factors are the cause of the higher conductivity found in soils of the Hyblean Plateau than those ones of Mt. Etna.

XRF analysis

Soil

For the chemical and mineralogical characterization of soils, of the areas XRF analysis of major and minor elements have been carried out. Data were analyzed by binary diagrams of major, minor and trace elements, to go back to information on the mineralogical and textural nature of the soil.

The element analyzed are: major as weight and minor as ppm.

By taking into account the major elements, the soils of the two areas, are, as expected, very different. Soil from Linguaglossa (Mount Etna), where the vineyard of Don Saro is located,

Is characterized by low SiO_2 wt% content, compared to the area of the Hyblean Plateau. As regards TiO_2 wt%, Al_2O_3 wt%, Fe_2O_3 wt%, MnO wt%, MgO wt%, Na_2O wt% and P_2O_5wt% contents, soil of in the Etnean area have higher values than soils of the Hyblean Plateau. From the diagrams binary, it appears evident that the samples of the Etnean vineyard plot very gathered; on the contrary, results of the Hyblean soils present a greater dispersion, despite the samples of both vineyards plot close together.

The two vineyards of the Hyblean Plateau, have very similar soils; the most clear difference is the slightly higher concentration of Al_2O_3 wt% detected in Avide vineyard, compared to COS.

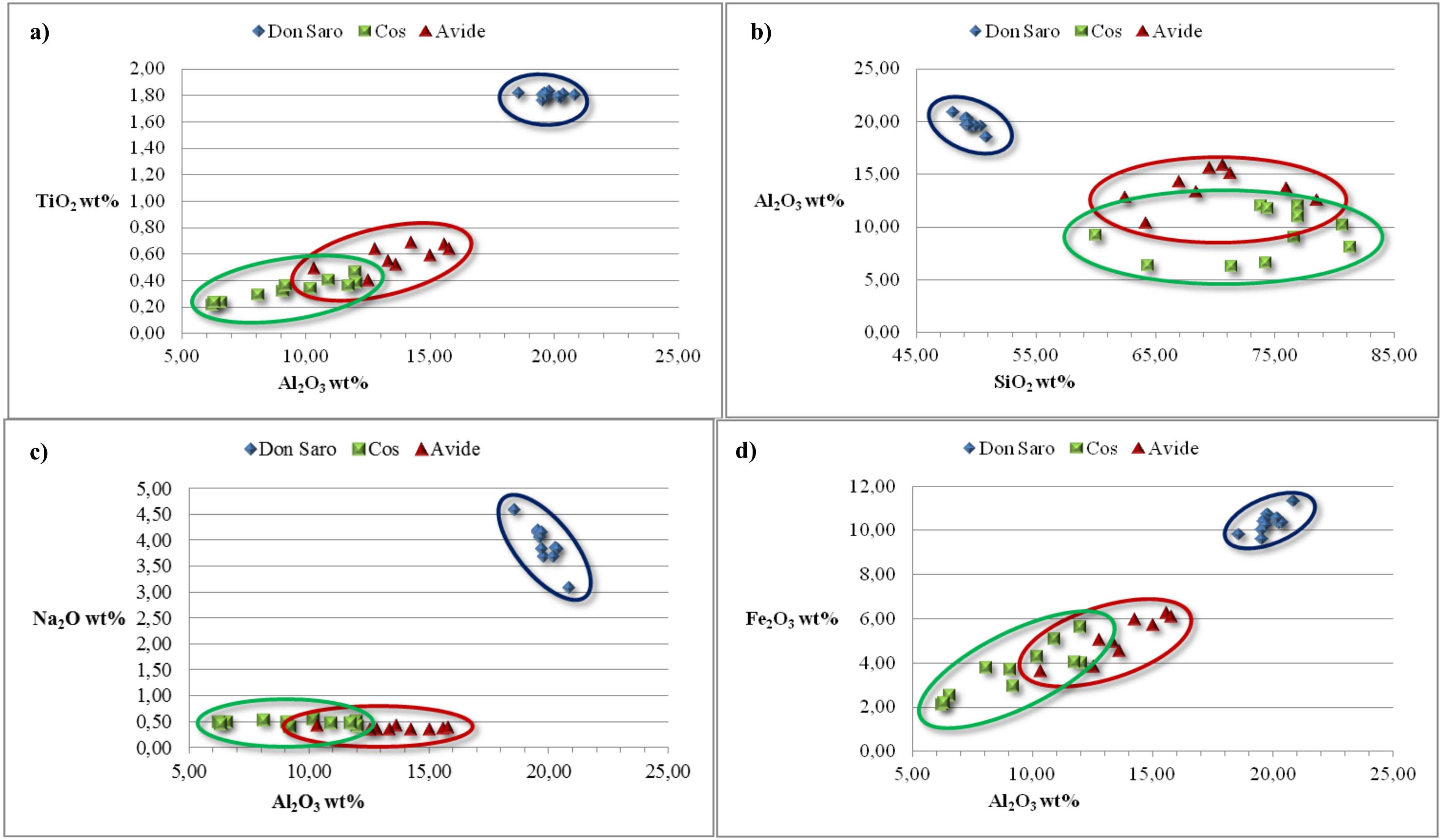
The soil of the Don Saro vineyard, comes from the 1556 year lava of Mount Etna, so it is very recent and not well developed, this is the reason because the samples are very uniform and do not show much dispersion.

On the contrary, the soil of the cellars of the Hyblean Plateau, has had more time to develop. The carbonate rocks, which entirely constitute of the surrounding mountains and hills, tend to be easily eroded, causing the accumulation CaO wt% in soils, which are also enriched in K_2O and SiO_2.

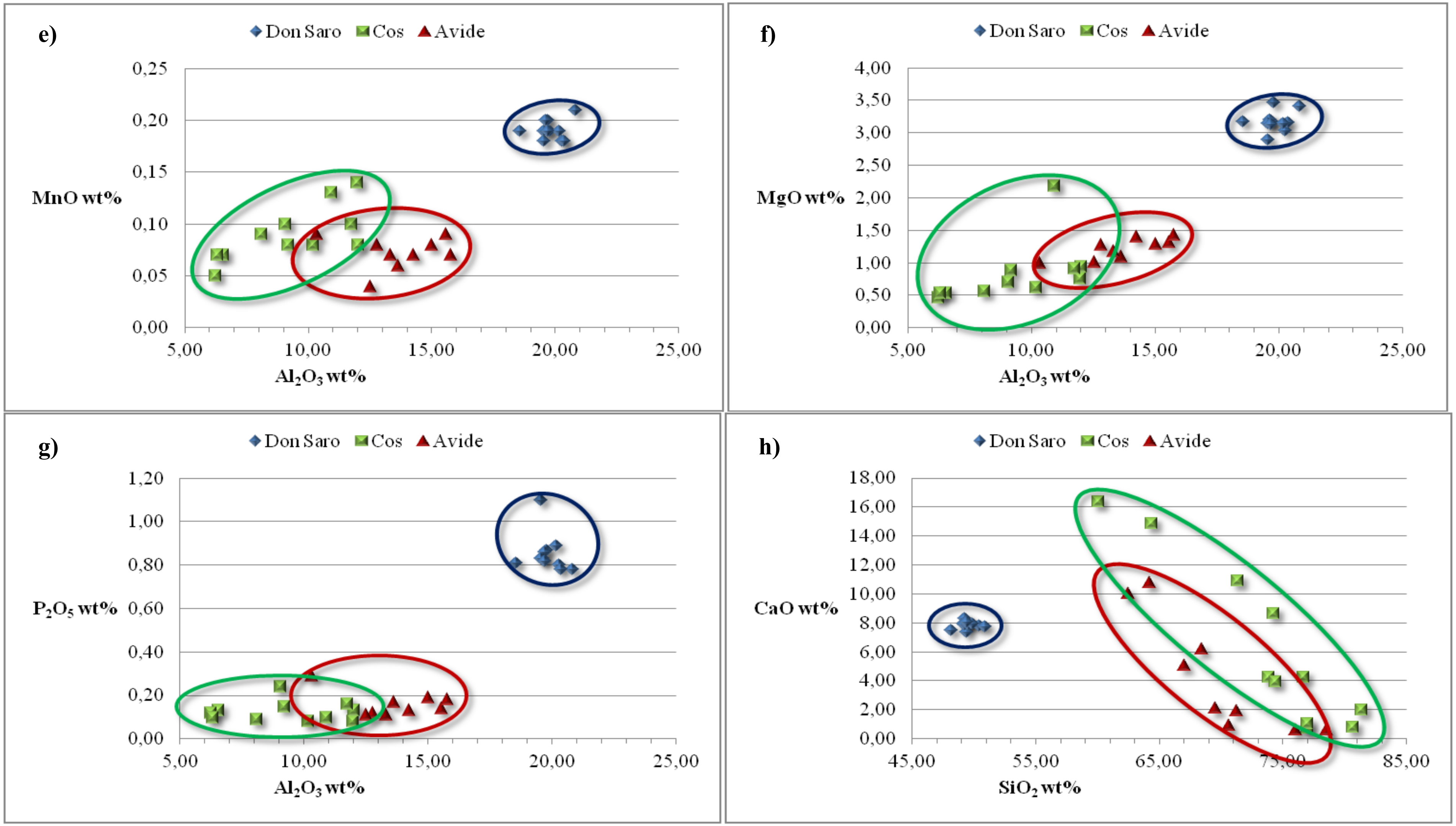
In the hills of the Hyblean Plateau, near to the area where the two studied vineyards of COS and Avide are located, lithotypes ascribed to the Ragusa Formation crop out, consisting of alternating calcareous whitish limestone and calcareous marl of Upper Oligocene. The total thickness of this alternance is about 100 meters.

The basal interval of the formation is characterized by massive and widespread phenomena of slumping, whose deposits are evident in the areas (Grasso, 2000).

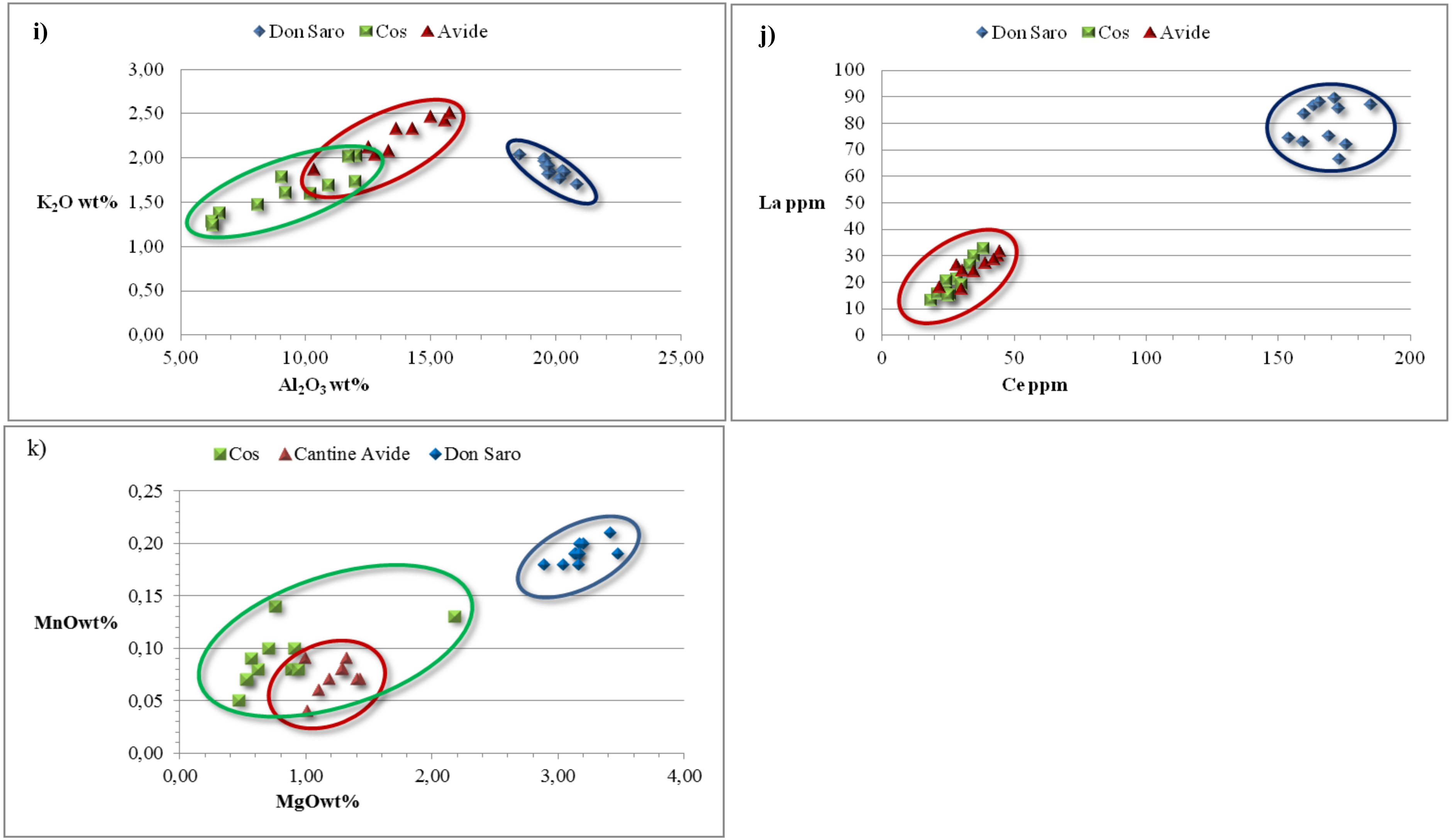
The material that deposits in the valley, mixes up with the underlying one that is constituted by weakly stratified yellowish calcarenites that at the base contain also several meters thick deposits of sand, gravel, conglomerate and carbonate elements with a reddish sandy matrix (Grasso, 2000). The mixture of these elements gave origin to soil of the valley on which the two vineyards are set.



Graph 8 (a), (b), (c), (d) Binary diagrams of selected major and minor elements of the soils of the three vineyards.



Graph 9(e), (f), (g), (h) Binary diagrams of selected major and minor elements of the soils of the three vineyards.



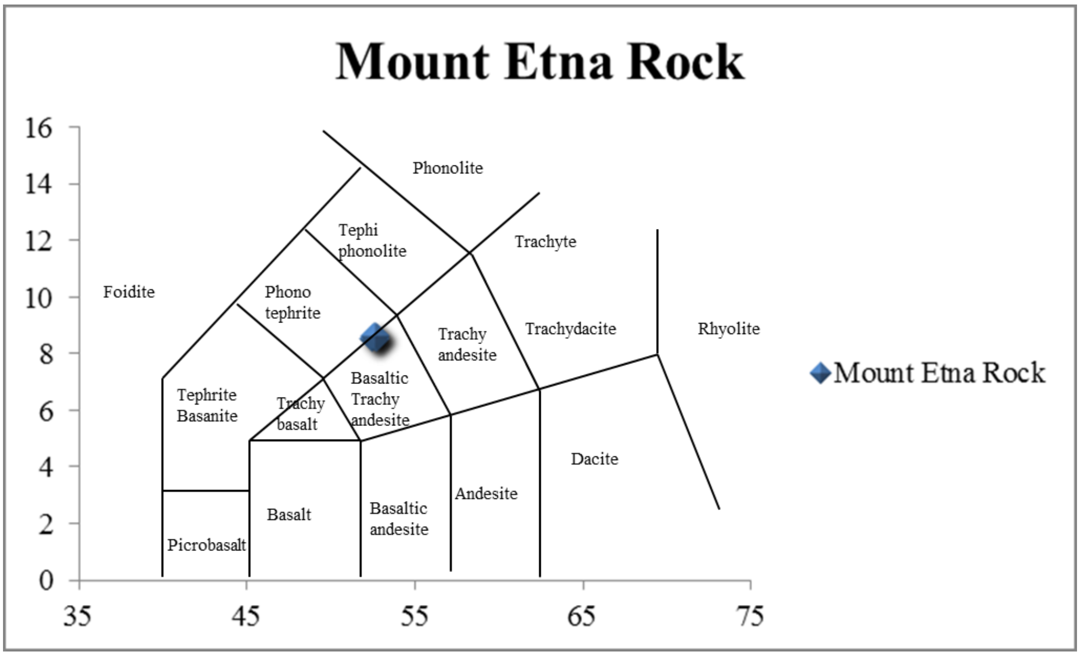
Graph 10 (i), (j), (k) Binary diagrams of selected major and minor elements of the soils of the three vineyards.

Rock

In order to better contextualize the data, 17 rock samples of the two areas were collected, of which 10 belong to the area of Linguaglossa (Mount Etna) and 7 to the Hyblean Plateau. The samples were collected in the formations that crop out in the vicinity of the vineyards, and were subjected to XRF and ICP-MS chemical investigation.

Rock samples collected at the outcrops in the area of Linguaglossa (Mount Etna), are volcanic rocks, which come from a flow that took place in 1556 (Silvestri, 2015). The samples were collected at the outcrops within the vineyard itself, which consists of a terraced amphitheater.

Etna samples have higher concentrations of most of the major elements than Hyblean Plateau rocks SiO_2, Al_2O_3, TiO_2, Na_2O_3, Fe_2O_3, MnO, K_2O and P_2O_5 and low content in MgO and CaO; according to the T.A.S. classification diagram they plot within the field of basaltic trachyandesite (graph 11).



Graph 11 TAS diagram of Mount Etna rock samples.

It is worth noting that soil samples from Don Saro vineyard reflect the composition of volcanites from which they derived.

Indeed, the concentrations of the major elements except for a few slight differences. Al_2O_3, TiO_2 and MnO have slightly lower values, MgO content is about half of the values found in soils, while Na_2O, K_2O and SiO_2 have higher values, as well as La and Ce.

Magnesium is leached from rocks and accumulates in the soil, for this reason its concentration in soil is higher compared to rock. The low concentrations of potassium in the soil compared to those ones of the rock can be explained by the plants, whose roots absorb much potassium (they use for growth) from the soil, about 5 times more than the magnesium absorbed, thus impoverishing the land in potassium (Manning, 2010) (Romheld, 2010).

The similarity between the values found in rock and soils is due to the fact that the soil of the vineyard of Don Saro is very young, rich in lithic portion which have not been affected for a long time by weathering. The soil also contain a fraction of volcanic ash brought by the wind.

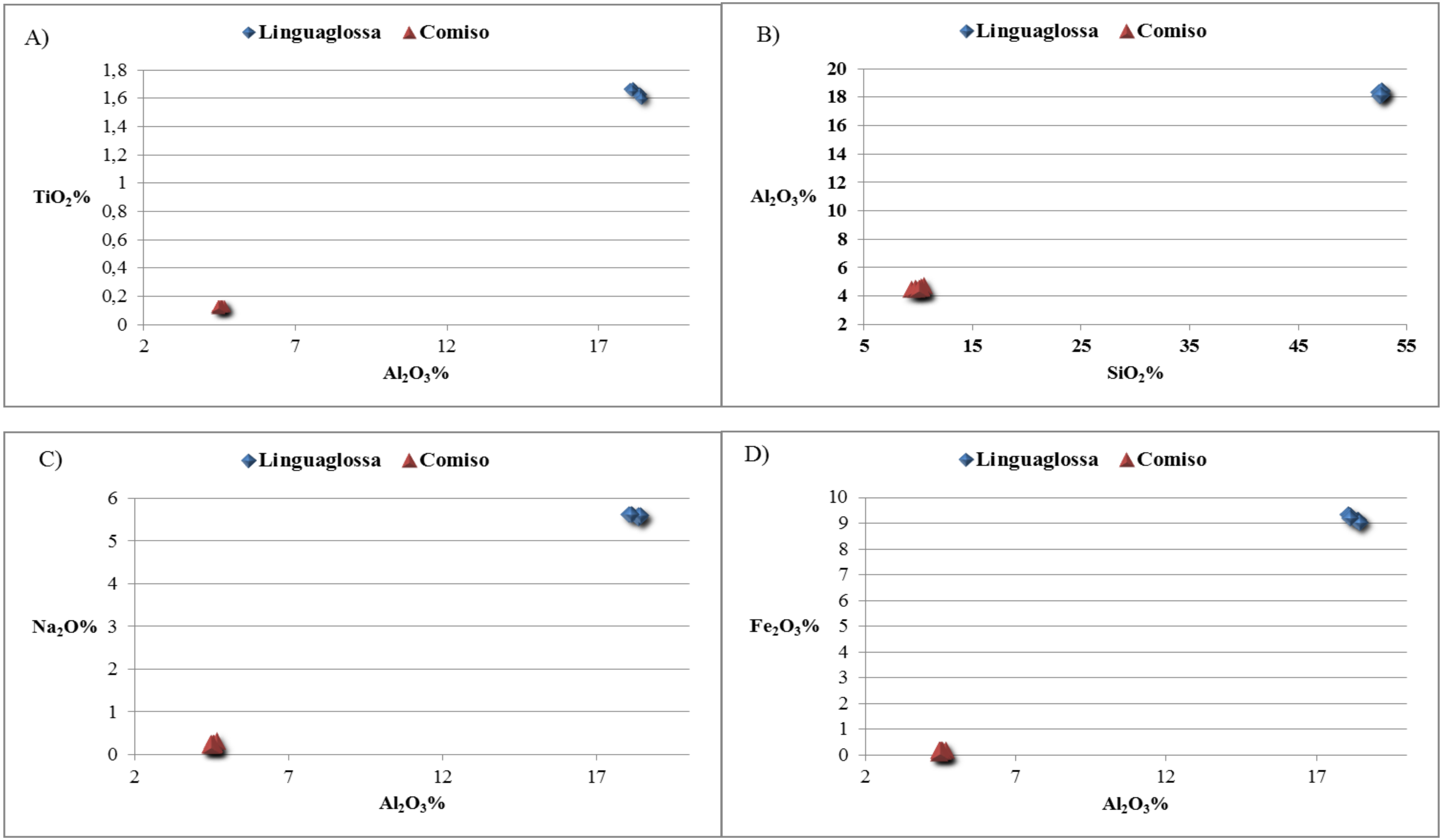
In fact, Mount Etna frequently meets at numerous events of paroxysmal eruptions, with large emission of volcanic ash that is deposited in the surroundings of the volcano, therefore the soil of the Don Saro vineyard is continuously enriched in these very fine powders.

The average content of La and Ce in the rock samples of Linguaglossa are 108 ppm and 218 ppm, respectively, much higher than values measured in the corresponding soils, whose the average values are 80 ppm for lanthanum and 180 ppm for cerium, respectively. The large difference in the concentrations of REEs between rock and soil is due to their low mobility, and to the young age of the soil, as well as the resistance to the effects of weathering and erosion by the rocks of Mount Etna.

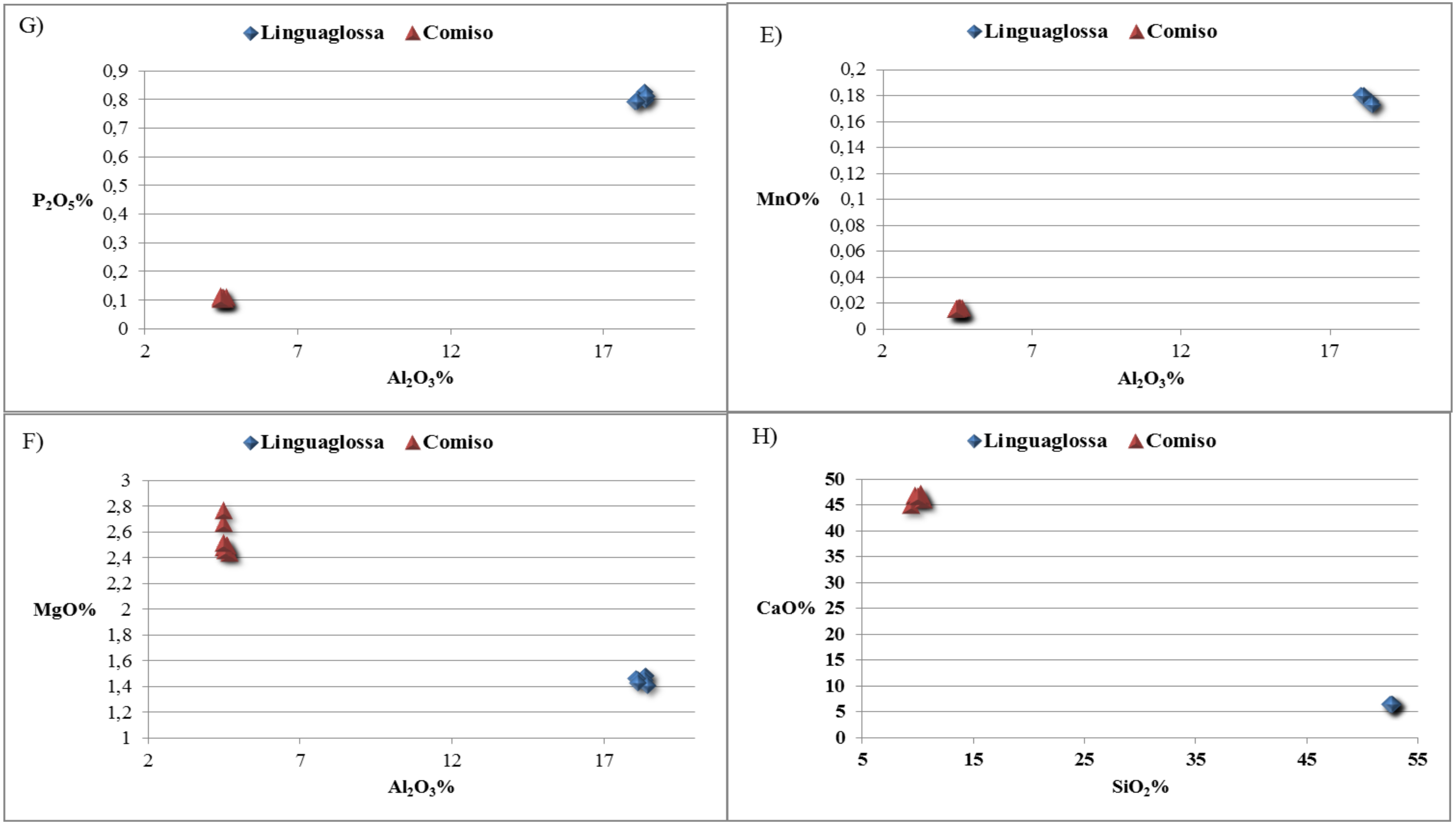
Samples of the Hyblean Plateau, have not been collected within the vineyards, because there were no rock outcrops. Samples were collected from outcrops in a hill located a few kilometers away from the two vineyards and belong to the Ragusa Formation, Leonardo member formed by alternating calcilutites and whitish marls with whitish marly limestones, this unit is also known as "Stone of Comiso", of Oligocene age (Grasso, 2000). The Formation consists of an alternance of calcilutites and marl with limestone marls of Upper Oligocene age (Grasso, 2000).

As a matter of fact the chemical compositions samples of the Hyblean Plateau samples is completely different from that one found in the samples collected at the Mount Etna. Hyblean carbonate rocks have a high content of CaO and MgO and low concentrations of the other major elements in particular for Al_2O_3, SiO_2, Na_2O, and Fe_2O_3.

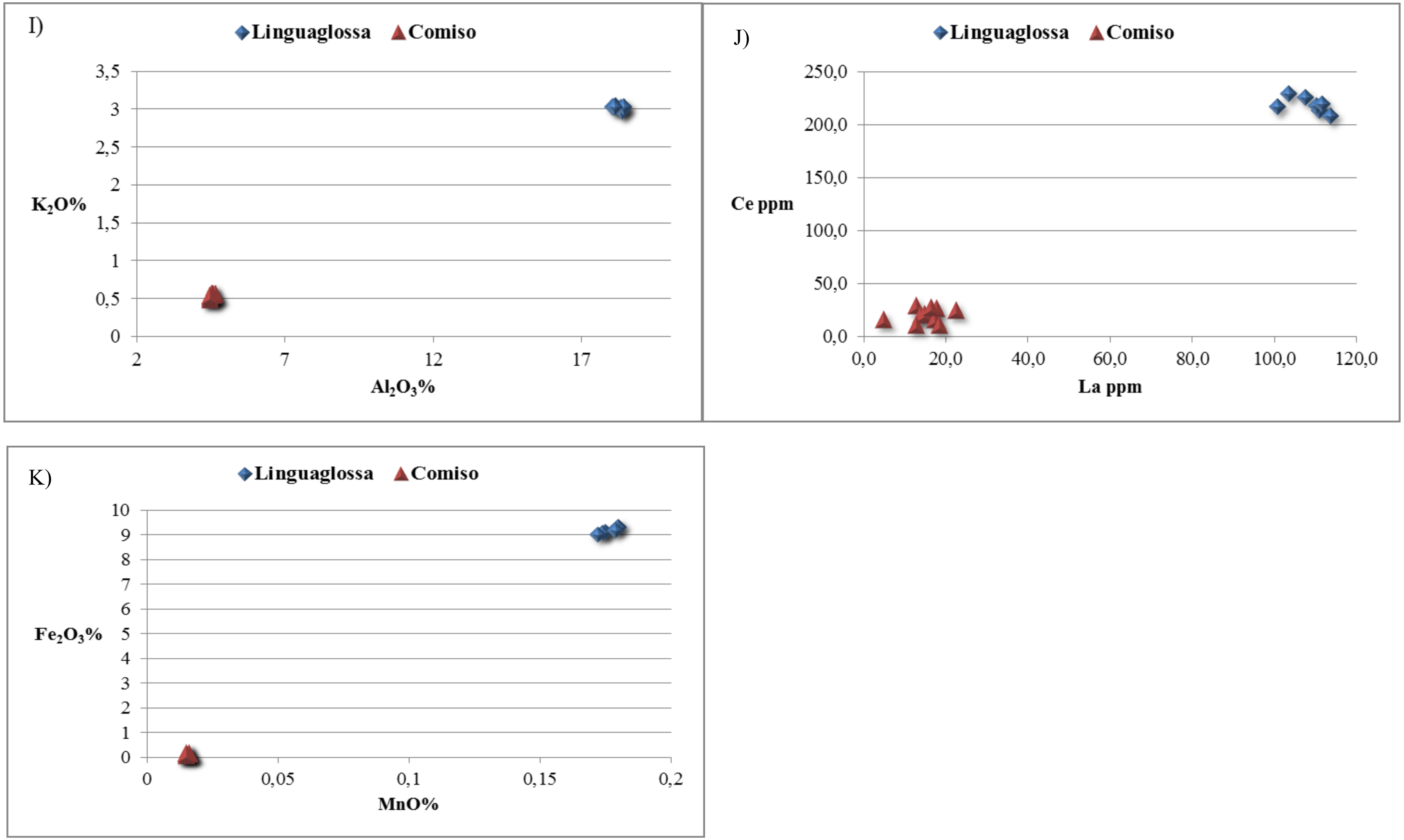
If we compare the results with those obtained from the rocks of the soils of the two vineyards, considerable differences are noticed. Indeed, soil samples do not reflect the composition of the rocks from which they derive. The soils have MgO and CaO values lower than the rocks, 1 wt% and 12 wt%, respectively against 2.5 wt% and 45 wt% of the rock. The differences are not confined here, TiO_2 is 0.1 wt% in rock to 0.40 in soil, Al_2O_3 wt% passes from 5 wt% in rocks to 10 wt% in soil, SiO_2 content, in particular, increases from 10 wt% in rocks to 74 wt% in soil. Compared to rock, Na_2O, Fe_2O_3, MnO and K_2O also increase in rock. The carbonate rocks are strongly subjected to the phenomenon of dissolution by the action of weathering, as well as the poor resistance of this lithotypes makes them easily prone to erosion. The dissolved material in the rocks and what is going to accumulate in “Terra Rossa” (i.e. “Red soil”) characteristic of these environments. The soils of the two vineyards sit on a wide plateau, surrounded by hills often subjected to slumping of overlying rock formations, which in this case are: Ragusa Formation, Member Irminio which consists of an alternance of grayish calcarenite with calcareous marl aged from Upper Burdigagliano Lower Langhian, and Tellaro Formation consisting of gray blue marl aged between Serravagliano to Tortoniano (Grasso, 2000). The content of lanthanum and cerium in the Hyblean rock samples are 15 ppm and 20 ppm, respectively, 25 to 35 ppm for lanthanum and cerium obtained in soil samples of vineyards. Compared to what found out at Mount Etna, this is a converse situation, since the soil of the Hyblean vineyards has a content in lanthanum and cerium higher than the rocks, despite the poor mobility of REEs, due to the dissolution of the rocks which enhance an accumulation of elements in the “*Terre Rosse*” of the Hyblean Plateau, where the vineyards are located. In the Plateau, soil is not subject to slumping and the action of weathering is limited.



Graph 12 (A), (B), (C), (D) Binary diagrams of rock samples of the three studied vineyards.



Graph 13 (E), (F), (G), (H) Binary diagrams of rock samples of the three studied vineyards



Graph 14 (I), (J) (K) Binary diagrams of rock samples of the three studied vineyards .

ICP-MS analysis

All of the samples, both inorganic (rock and soil) and organic (leaves, juice, residue, skins and seeds) were analyzed by Inductive Couple Plasma Mass Spectrometry, in order to detect the Rare Earth Elements (REEs) contents. Due to the large amount of samples used, in order to make the graphs clear to reader, we represented the average concentrations of the samples of the same type of each area.

In soil and rocks samples it was adopted Upper Crust normalization values by Rudnick and Gao (Rudnick R L & Gao S, 2003), because it has a close composition to that one of soils and rocks considered. The organic samples were hence normalized to the average concentrations of soil of corresponding vineyard.

Soil and Rock

A total of 31 soil samples (11 Don Saro, 11 COS e 9 Avide) and 17 rock samples (10 Linguaglossa, 7 Hyblean Plateau) were collected for Inductively Coupled Plasma Mass Spectrometry.

In graph 15 the average concentrations of REEs of the three vineyards were compared. The soils of the vineyard of Don Saro are extremely enriched in REEs, especially LREE, as you would expect from a andosoil derived from volcanic rocks. The concentrations of the two Hyblean vineyards are very similar, in particular La and Ce, while the other elements slightly deviate, results of COS vineyard shows values slightly higher than those ones of Avide vineyard. Soils also show positive anomaly of europium and thulium. The positive europium anomaly, found in the soil of Mount Etna, is of primary type inherited from the mother rock (i.e., plagioclase bearing), while the positive anomaly of thulium is probably caused by an systematic instrumental error. As for the anomalies of carbonate-type soil, the slight positive europium anomaly, found could be caused by the terrigenous portions occurring; in fact, as mentioned earlier, in the Hyblean Plateau, it was common practice for farmers to mix and shatter the rocks and go and mix with the red soil to improve soil quality (Cita, 2003).

Another aspect worth to be highlighted is the relatively high fractionation of LREEs in Don Saro, whereas the difference in fractionation between LREE, MREE and HREE is not so evident in the Hyblean Plateau vineyards.

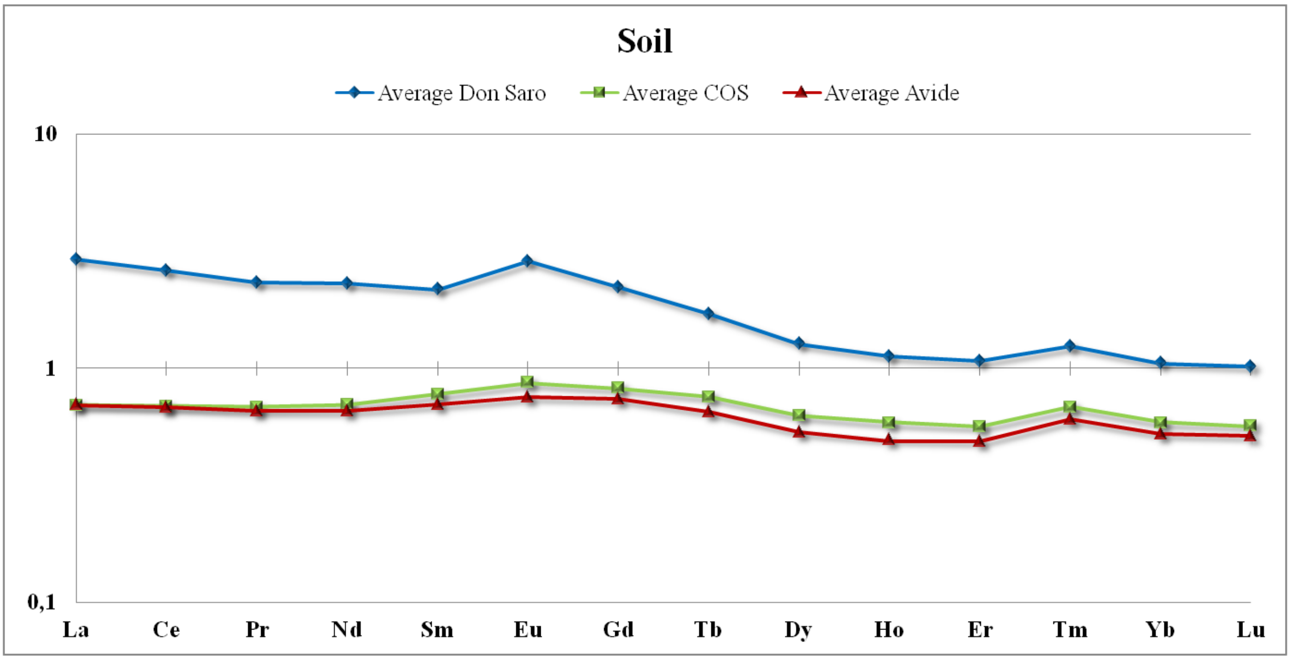
The average normalized pattern of rock samples are shown in the graph 16. The normalized values of the rocks of the two areas are very different from each other, with high values found in Mount Etna samples. From the graph the trend of normalized pattern is immediately evident, while Mount Etna samples show a normal pattern with LREEs and enrichment compared to MREEs and HREEs, Hyblean Plateau samples show an opposite situation with slight enrichment in MREEs and HREEs. This behavior observed for carbonate rock of the Hyblean Plateau was may be explained with the fact that, as previously mentioned, carbonate rocks of the Ragusa formation (Leonardo Member), easily undergo phenomena of dissolution and erosion. The REEs are usually motionless and relatively insoluble, but, in case of strong phenomena of dissolution and erosion, mobilize, and LREEs are the most movable, from the rock.

The negative cerium anomaly observed in Hyblean rocks, is typical of carbonate rocks ad attributed to calcium and magnesium occurrence (Elderfield, 1981) (Laveuf, 2009) (Masuda, 1975).

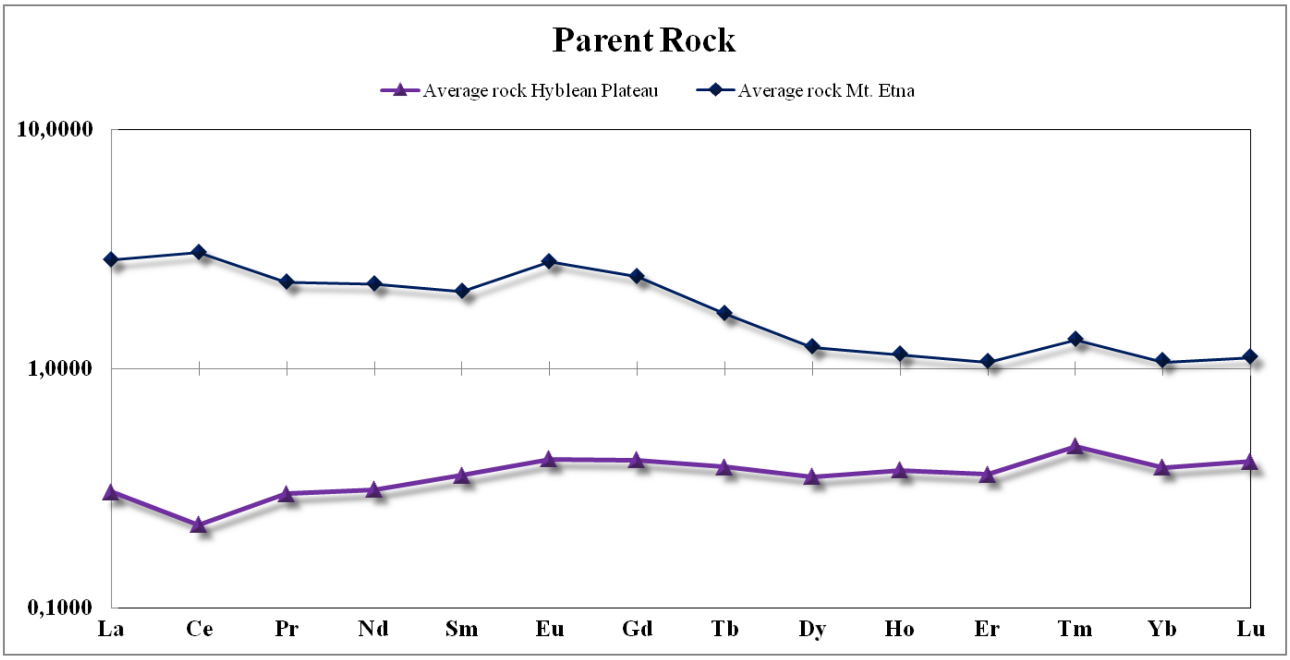
In the Etnean volcanic rocks, two positive anomalies are found: europium and thulium.

The positive europium anomaly is probably due to the presence of plagioclase in the rock, since this mineral phase commonly occurs, in the Etnean basalts (Forniciai, 2015) (Mongelli, 2013) (Landi, 2004).

The thulium anomaly which is also the average REEs patterns of Hyblean Plateau vineyards, has not been the subject of studies to date, and the fact that you find yourself in all samples is presumed to be due to a systematic error.



Graph 15 The graph compares the average normalized patterns of REEs in the soil of three vineyards, Cos and Avide in Hyblean Plateau, in Comiso and Don Saro in Mt. Etna, Linguaglossa. The values were normalized to the Upper Crust (Rudnick R L & Gao S, 2003).



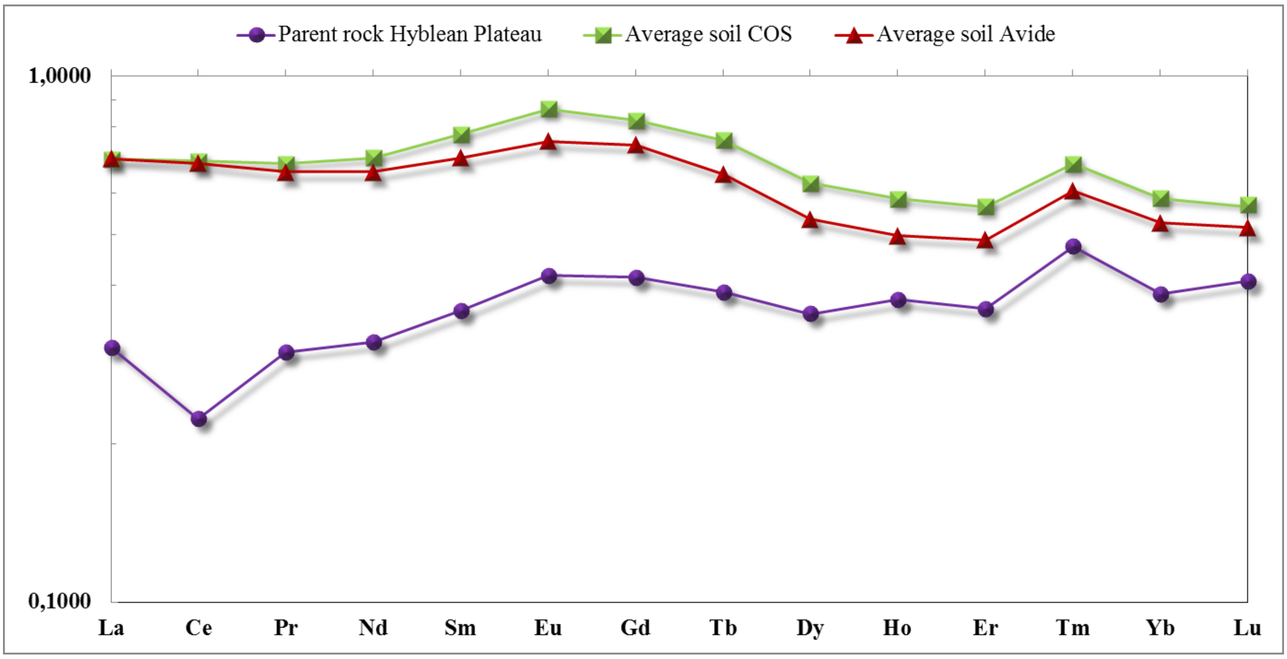
Graph 16 The graph compares the average normalized patterns of REEs in the rocky outcrops in the two areas under examination, Hyblean Plateau, in Comiso and Mount Etna, in Linguaglossa. The values were normalized to the Upper Crust (Rudnick R L & Gao S, 2003).

Comparison soil - parent rock

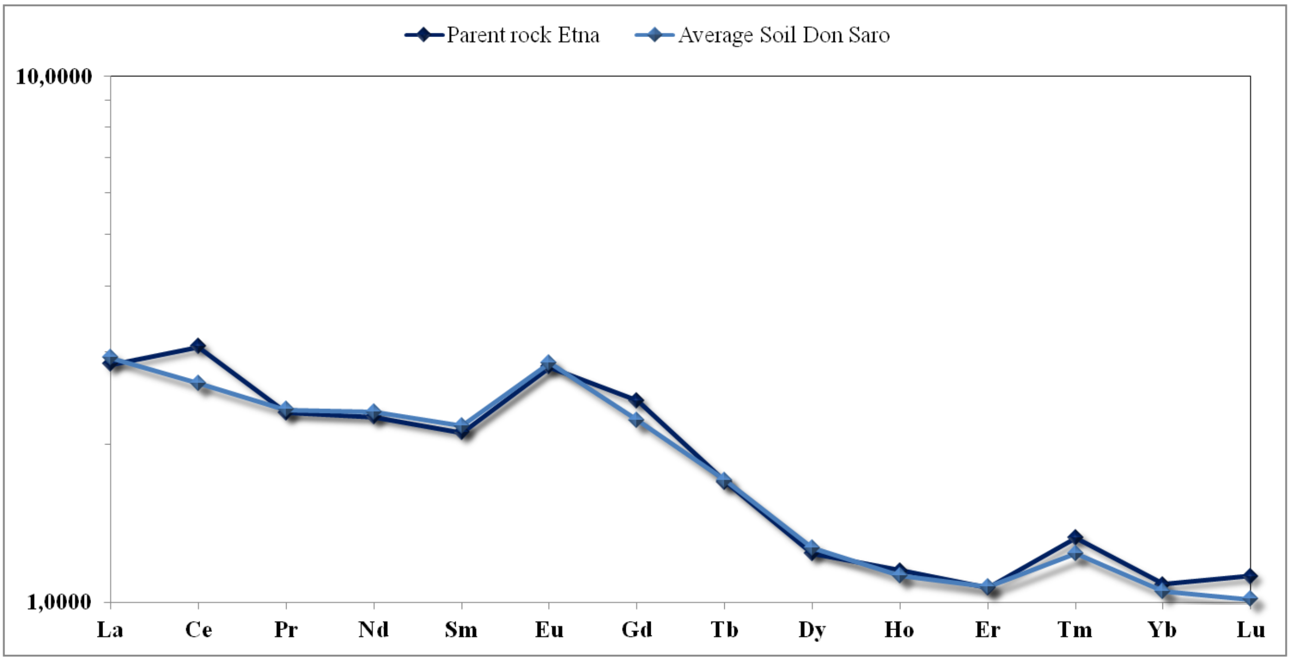
Samples of soil and rock were compared to obtain further information.

As far as the Hyblean Plateau, the comparison between the samples of rock and soil (graphic17) showed that. The REEs content in the soils of the two vineyards is higher than that one found in parent rock. In particular, the rocks are depleted in LREEs, such behavior was not found in soil samples. Cause of this behavior is the dissolution of carbonate rocks, and the subsequent accumulation of LREEs in soils. On the contrary MREEs and HREEs are relatively motionless and less soluble than LREEs.

In the graph 18 REEs patterns of soil on the vineyard of Don Saro and rocks in the area of Linguaglossa, Mount Etna were compared. The graph shows as the rock and soil samples have almost equal content of REEs, except for small differences. The pattern are almost identical, the only differences are some anomalies. Both soil and rock show europium positive anomaly. Cerium, gadolinium and lutetium positive anomaly have been observed in rock samples, but not in the soil. In Linguaglossa, the typical soil is the andosoil, this is very young, and perfectly reflects the characteristics of the rock from which it is derived, as was previously seen. Soil forms after the disintegration of rock and volcanic ash that are deposited on the slopes of Mount Etna as a result of frequent paroxysmal phenomena that occur on the volcano.



Graph 17 The graph compares the average normalized pattern of REEs of soil samples of agricultural holding COS and Avide, both vineyard in the Hyblean Plateau, area of Comiso, with mean values of the rock outcropping near the vineyard. The values were normalized to the Upper Crust (Rudnick R L & Gao S, 2003).



Graph 18 The graph compares the average normalized patterns of REEs of soil samples of agricultural holding Don Saro with rock samples of Mt. Etna, where the soil originated. The values were normalized to the Upper Crust (Rudnick R L & Gao S, 2003).

Plant sample2013 -2014

Samples were collected for two consecutive years (2013 and 2014), during the harvest. During the first year, we took into account only the division between residue and juice; the next year it was decided to undertake a further dismemberment of the samples by dividing the residue in the skins and seeds. It was decided to do this further separation aiming to see any preferred distribution of REEs in the residue.

However, the leaves were harvested at a different time to harvest, in early May, because in this period the vine leaves are already developed, and the usual treatment copper sulphate, whose values might alter the analysis, was not been done yet.

The concentrations of REEs in organic samples (leaves, juice, residue, skins and seeds), were normalized to the average concentration of the soil of the vineyard to which the samples belong. In the present PhD thesis, only the average concentrations of the sample are displayed in the graphs, and the same logarithmic scale was adopted to better display the comparison between samples of different type.

From the graphs we see that the various parts of the plant absorb the REEs in a different manner; samples of leaves (graph 19) have higher concentrations of REEs than the other organic components examined in this thesis work. In juices (graphs 20 and 21), in the residues (graph 22), in the skins (graph 23) and in the seeds (graph 24) the concentrations are gradually lower than the leaves. Seed show the lowest concentrations, in the majority of cases below the instrumental detention limits.

In particular, we noticed how the concentrations of COS and Avide vineyards, belonging to the Hyblean Plateau area, have higher values than those ones reported in the area of Mount Etna. Given the difference in REEs contents the two types of soil, one would expect the opposite, but studies in other plants (references) show that climatic conditions affect the plants. Plants grown in an arid environment with poor water supply, absorb a greater extent the elements contained in the soil. The rainfall area of Comiso (Hyblean Plateau) is 400-450 mm annual with 16:19 °C average temperature (Hydrograph Service of Civil Engineering from 1966 to 1990), while in the area of Linguaglossa (Mount Etna) there are 1200 mm of rain annual and an average temperature of 14 °C (Regione Siciliana, 1998) the more arid plateau lead the plants to absorb higher element contents, thus explaining what shown in graph 19.

A positive europium anomaly is also noted in the samples of both of Don Saro (Mount Etna) and Avide (Hyblean Plateau), whereas there is an evident negative anomaly cerium is only in the samples from Don Saro vineyard.

The REEs concentrations measured in the samples of juice (graphs 20 and 21) show lower values than those ones measured in the leaves. Also in this case concentrations of vineyards the Hyblean Plateau (COS and Avide) are higher than those ones of Mount Etna (Don Saro), with slightly higher concentrations in the samples of the COS. Although the two Hyblean vineyards are far each other only a few kilometers, they show some differences.

There are differences between the samples of juice collected during the two years, being the values of the concentrations higher in samples collected in 2013 than samples of 2014; this is more pronounced in Avide vineyards.

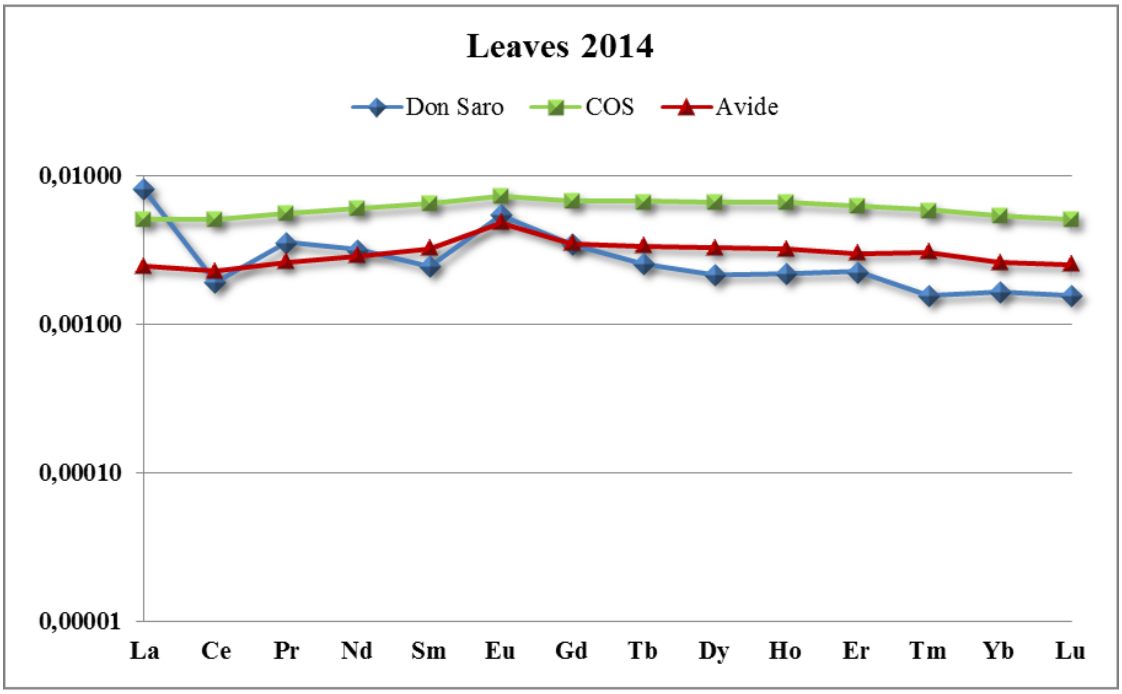
The differences could be explained by the water, contribution a water intake bottom found in the year 2013 with respect to 2014, as mentioned earlier in arid conditions the plant absorbs more, so that a smaller rainfall implies an increase in the absorption. The difference between Avide and COS in the year 2014 is not due to a changing climate conditions because the two vineyards are located too close; the difference may be due to a factor of irrigation. Usually in the vineyards, during summer time the vines are not irrigated, but the Avide vineyard is equipped with irrigation system to be used in case of prolonged drought, and this would explain the lower concentrations of REEs in juice samples collected in 2014.

In samples of juice of both years (graphs 20 and 21) a positive anomaly of samarium is visible, in the graphs is also known the negative anomaly of Thulium juices of 2013 than in the juice of 2014 becomes positive, it is considered that Thulium anomaly is due to an instrumentation lack, so it is discarded.

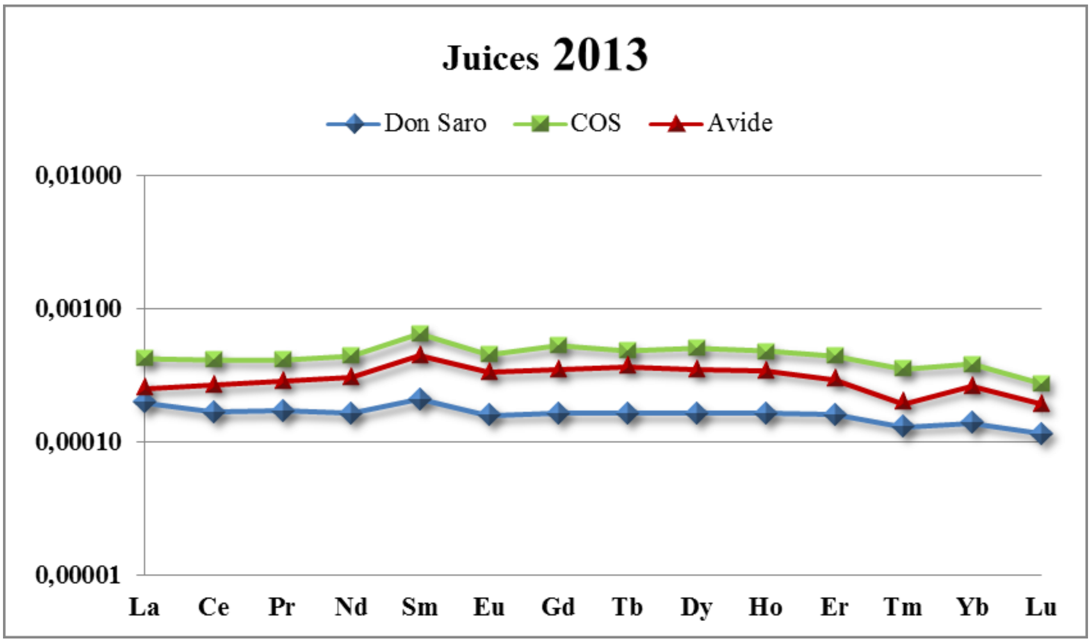
Samples of residual 2013 in graph 22 have REE concentrations higher than the samples of the skins and seeds of 2014 championships (graphs 23 e 24).

The sampling carried out in a different manner, allowed us to understand in which part of residues REEs are most concentrated: they result to be the skins, whereas seeds are found very low, often below the instrument detection limits. The positive anomaly of europium is observed either in the samples of residue and skins, then it would seem that is not due to a seasonal factor. It is noted that, in the samples of skins of 2014, there is a decreasing of REEs in samples of Avide than COS vineyard. It is thought to be due, as in the case of juices, to irrigation reinforcement, done in the dry season in Avide vineyards. The concentration difference between COS and Don Saro is rather due to, again to different climatic conditions of the two vineyards.

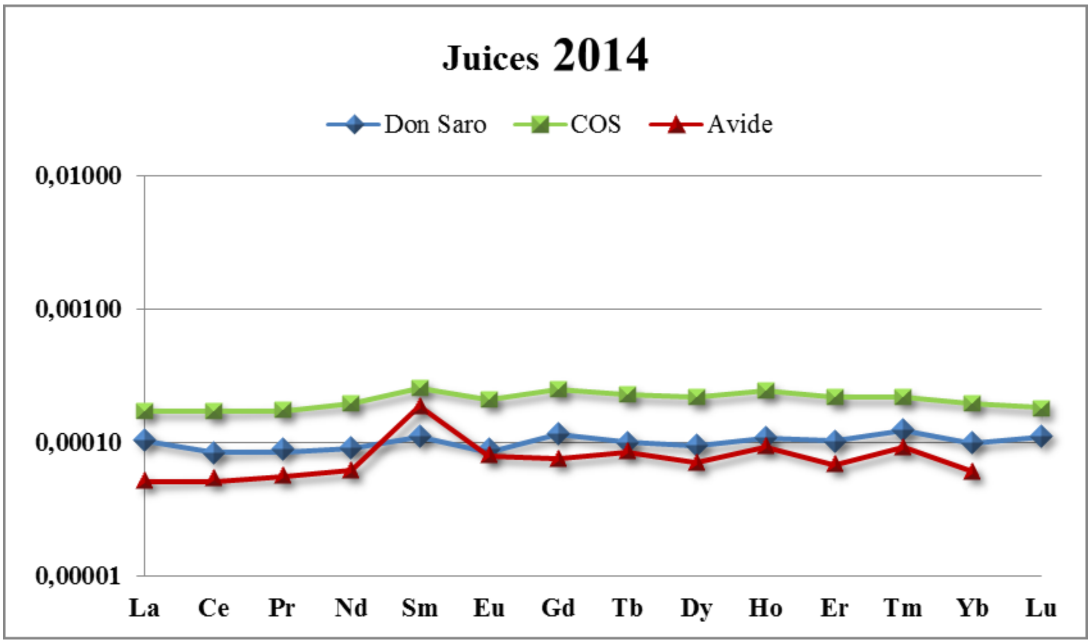
In seed samples the concentrations are too low to perform any kind of reasoning, as seen in the graph 24, there are missing values for many elements, and in the case of the Avide vineyard the concentrations are too low to be measured by the instrumentation.



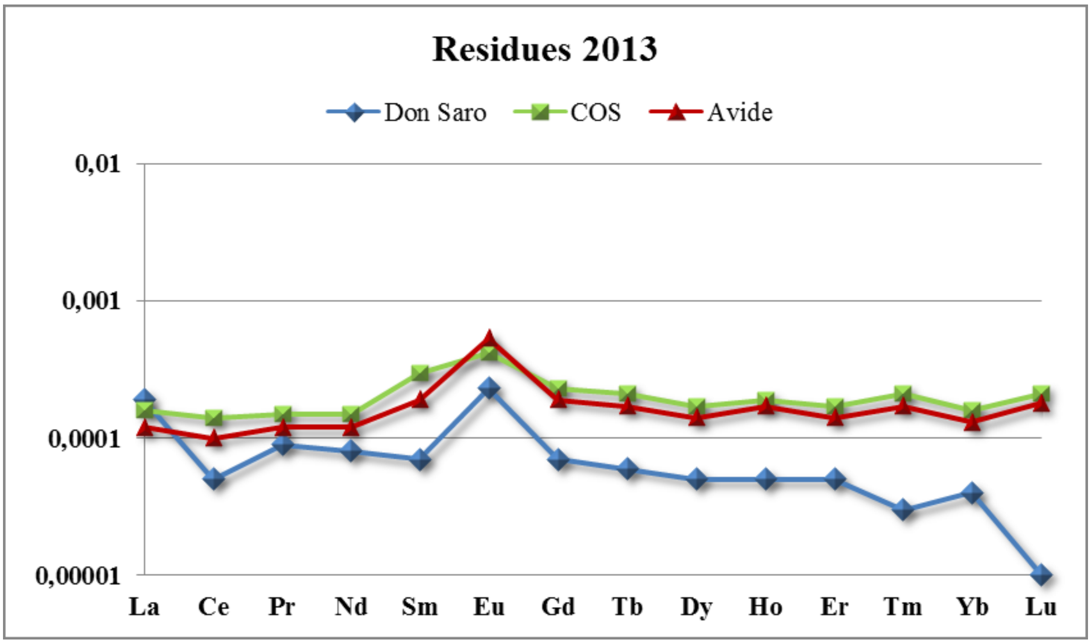
Graph 19 The graph compares the average normalized REEs patterns of leaves 2014 of grapes collected from three vineyards. The values are normalized to the average concentrations of the soils of the respective vineyard.



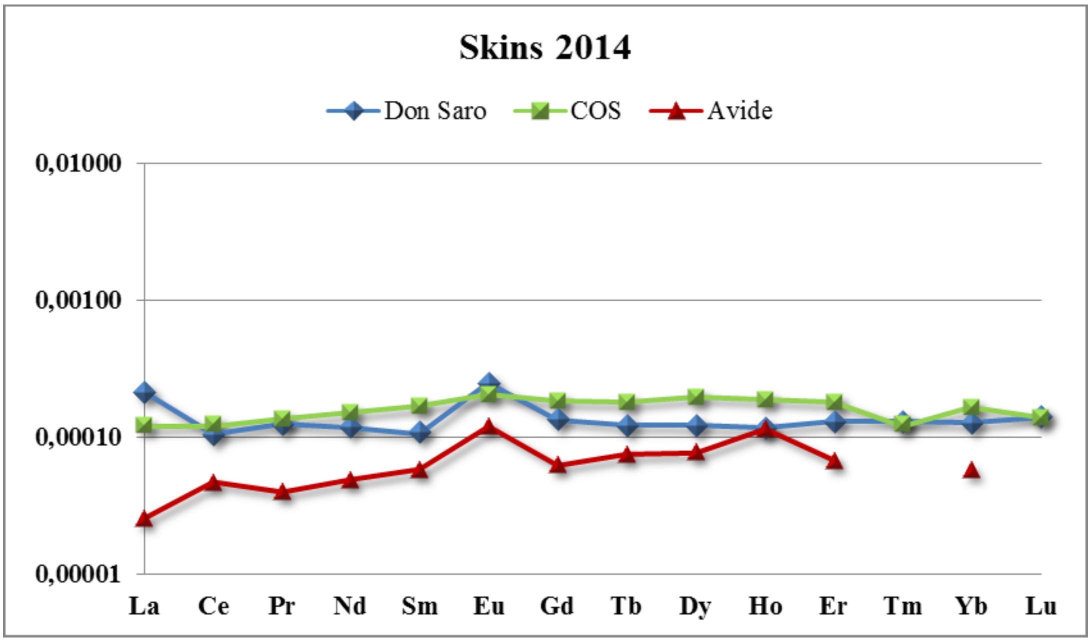
Graph 20 The graph compares the average normalized REEs patterns of juices 2013 of grapes collected from three vineyards. The values are normalized to the average concentrations of the soils of the respective vineyard.



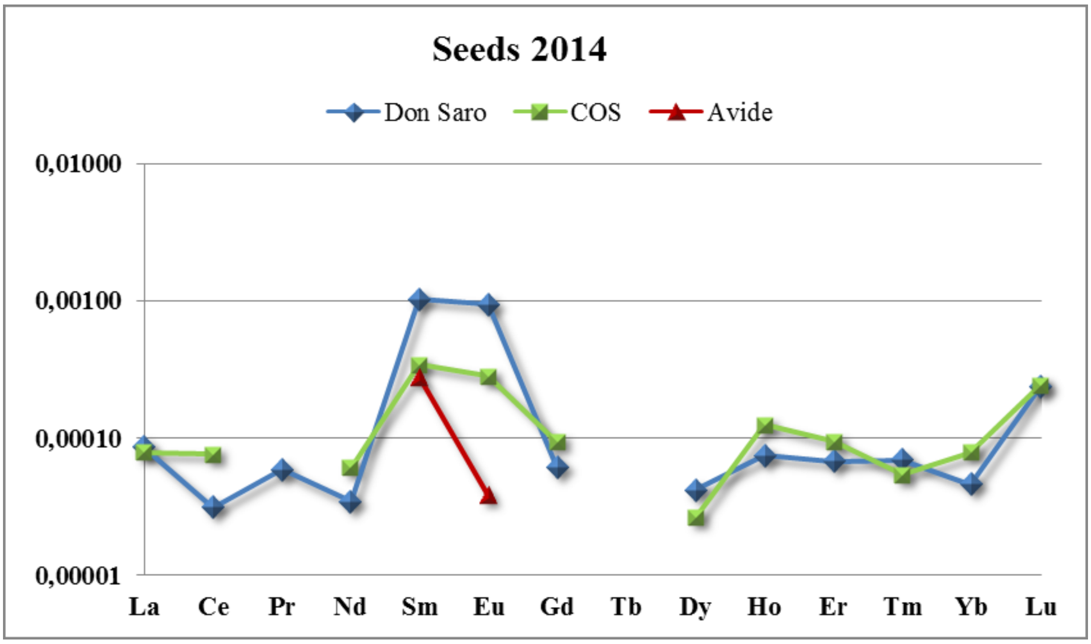
Graph 21 The graph compares the average normalized REEs patterns of juices 2014 of grapes collected from three vineyards. The values are normalized to the average concentrations of the soils of the respective vineyard.



Graph 22 The graph compares the average normalized REEs patterns of residues 2013 of grapes collected from three vineyards. The values are normalized to the average concentrations of the soils of the respective vineyard.



Graph 23 The graph compares the average normalized REEs patterns of skins 2014 of grapes collected from three vineyards. The values are normalized to the average concentrations of the soils of the respective vineyard.



Graph 24 The graph compares the average normalized REEs patterns of seed 2014 of grapes collected from three vineyards. The values are normalized to the average concentrations of the soils of the respective vineyard.

The next step was to compare the different cultivars within each vineyard, the comparison was carried out in all of the organic samples treated in this thesis work, and also in this case have been adopted the average values of each type of cultivar.
The types of cultivars analyzed are in table 10.

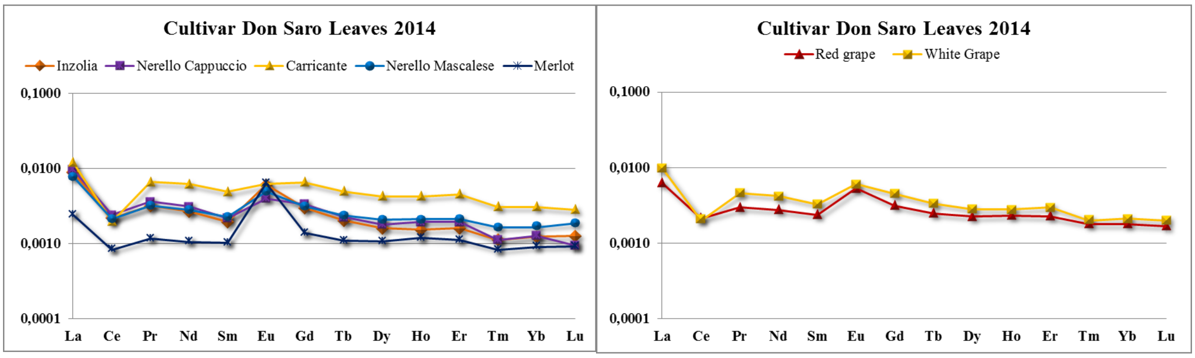
Vineyard	Red Grape	White Grape
Don Saro	Merlot Nerello Cappuccio Nerello Mascalese	Carricante Grecanico * Inzolia
COS	Cabernet Sauvignon Frappato Merlot Nero d’Avola	Grecanico Inzolia Moscato **
Avide	Cabernet Sauvignon Frappato Nero d’Avola	

Table 10 examined cultivar types. * Cultivar examined only for juice, seed and skin 2014,**Cultivars examined only for juice and residue 2013.

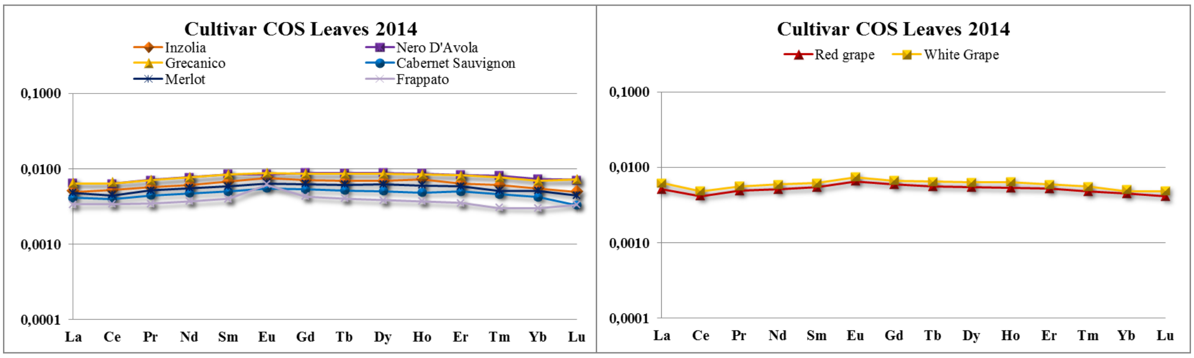
The best results were obtained in the samples of leaves (graphs 25-27) and of juices (graphs 28-33); unfortunately, in the samples of residues (graphs 34-36) and skins (graphs 37-39)it was not possible to obtain the concentrations of all REEs, because of the extremely low concentrations, while the samples of seeds (graphs 40-41) most showed extremely low REEs concentrations, below the detection limits.

From the graph 25 (A), it is evident that the leaves of most cultivars grown at Don Saro's have absorbed the REE in a slightly different way, although the plants are grown on the same soil type and under the same conditions weather and climate, indeed, from this graph we can see as the REEs pattern of Merlot and Carricante cultivar differ from the others. In the graph 25 (B) we compared the average pattern of REEs cultivars with white and red grapes of Don Saro vineyard, to see if there are differences, the white grapes have slightly higher values than red grapes.

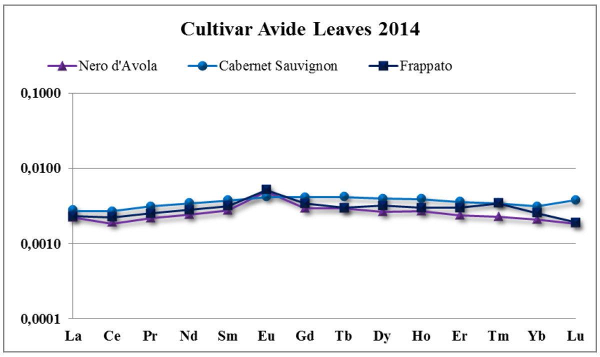
In Cos and Avide vineyards, the differences between the leaves average patterns REEs (graphs 26 and 27), are minor, the cultivars that differ more are Frappato and Grecanico for vineyard COS (graphs 26 A), while the differences between red and white they are almost nil in COS vineyard, The third vineyard, Avide, it was not possible to make this comparison because the types of cultivars considered are only red grapes cultivar.



Graph 25 Leaves sample 2014, vineyard Don Saro: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.



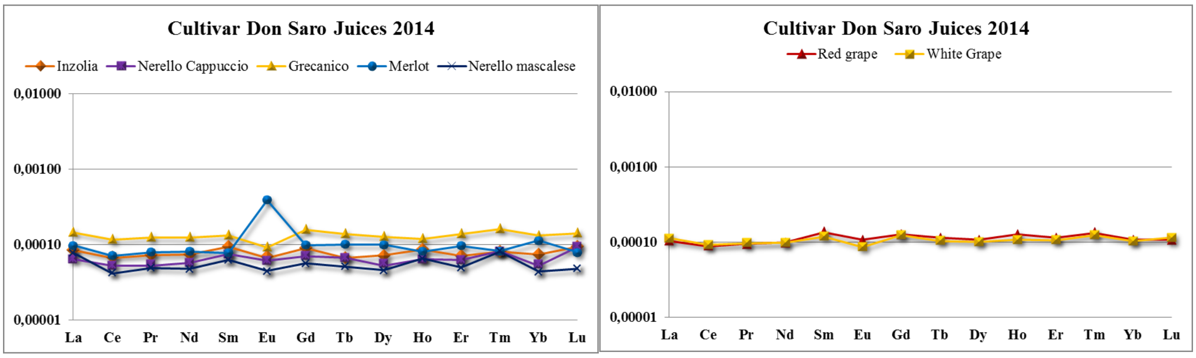
Graph 26 Leaves sample 2014, vineyard COS: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.



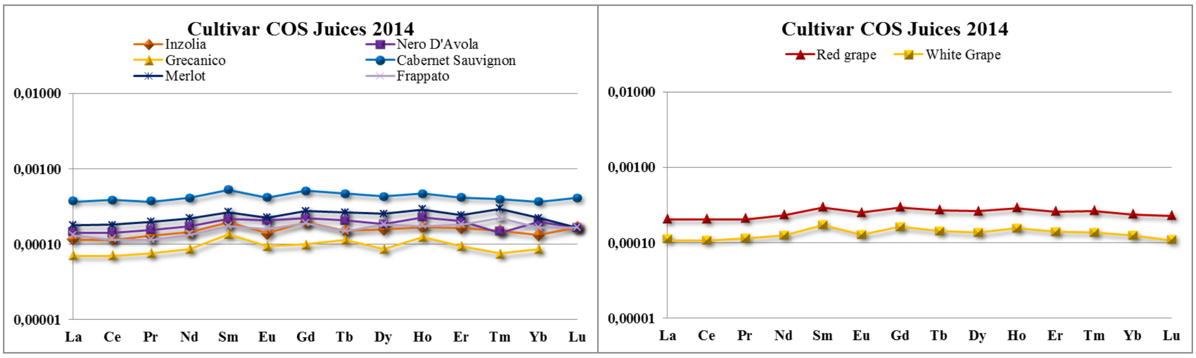
Graph 27 Leaves sample 2014, vineyard Avide: comparison average REEs pattern cultivar. The values are normalized to the average concentrations of the soils of the respective vineyard.

The different behavior of the cultivars can also be observed in the graphs 28 (A) showing juices of 2014, where Merlot has a different trend compared to other cultivars of the same vineyard (Don Saro), also Grecanico cultivars show differences in the average pattern REEs. Indeed, there are no differences in the average pattern of cultivar with different colored berries (graph 28 B).

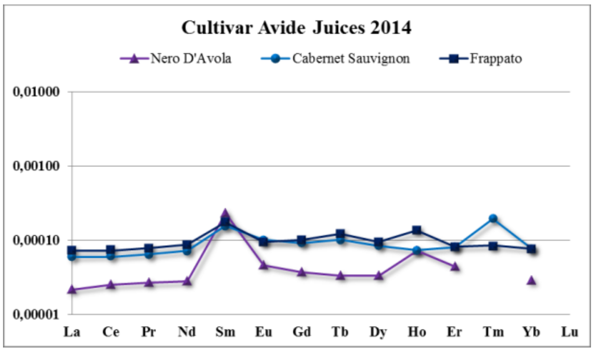
In 2014 juice samples of Hyblean Plateau vineyards, average pattern among cultivars are significantly different from each other (graph 29 and 30), in particular Cabernet Sauvignon vineyard of COS and Nero d'Avola Avide vineyard, they differ from other pattern. Another thing of note is that you also have a difference even in the average pattern of different colored cultivars, as you can see in the graph 29 B.



Graph 28 Juice sample 2014, vineyard Don Saro: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

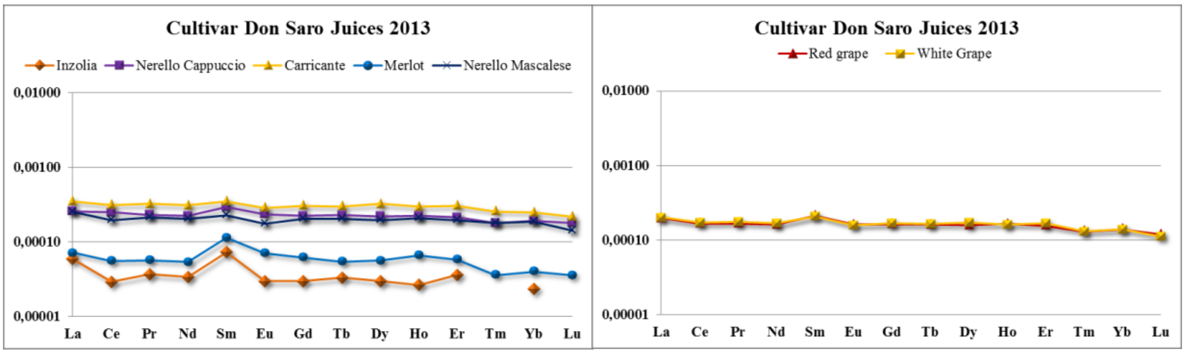


Graph 29 Juice sample 2014, vineyard COS: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

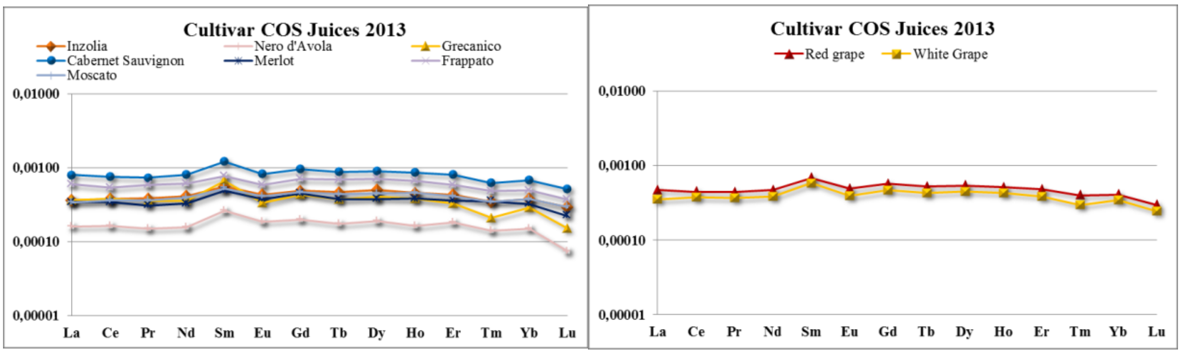


Graph 30 Juice sample 2014, vineyard Avide: comparison average REEs pattern cultivar. The values are normalized to the average concentrations of the soils of the respective vineyard.

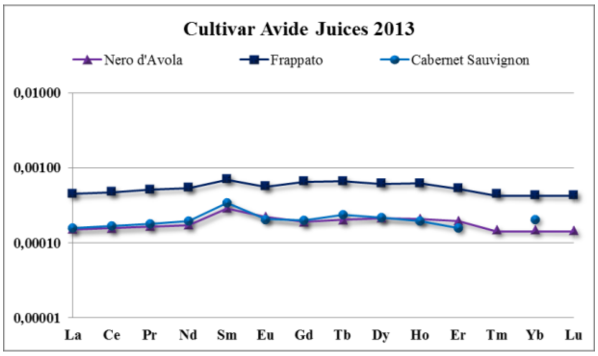
In graphs 31 A the juices of 2013 (Don Saro) Merlot and Inzolia have a low average pattern REEs than the pattern of other cultivars. Even in the graphs regarding vineyard Hyblean Plateau (graphs 32 A and 33 A), the average patterns show significant differences, such as Frappato and Grecanico of COS vineyard. The differences between cultivars of different colors, indeed, are null by Don Saro vineyard, and red grapes show a slightly higher pattern in COS vineyard (graphs 32 B and 33B).



Graph 31 Juice sample 2013, vineyard Don Saro: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.



Graph 32 Juice sample 2013, vineyard COS: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

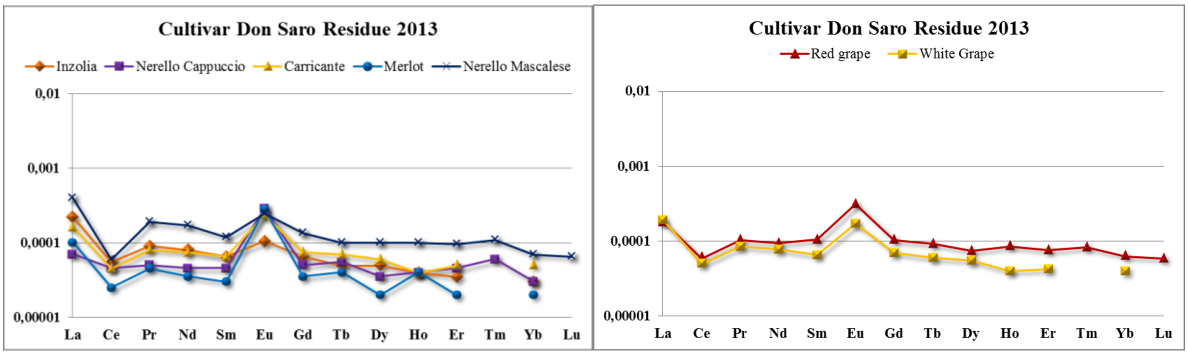


Graph 33 Juice sample 2013, vineyard Avide: comparison average REEs pattern cultivar. The values are normalized to the average concentrations of the soils of the respective vineyard.

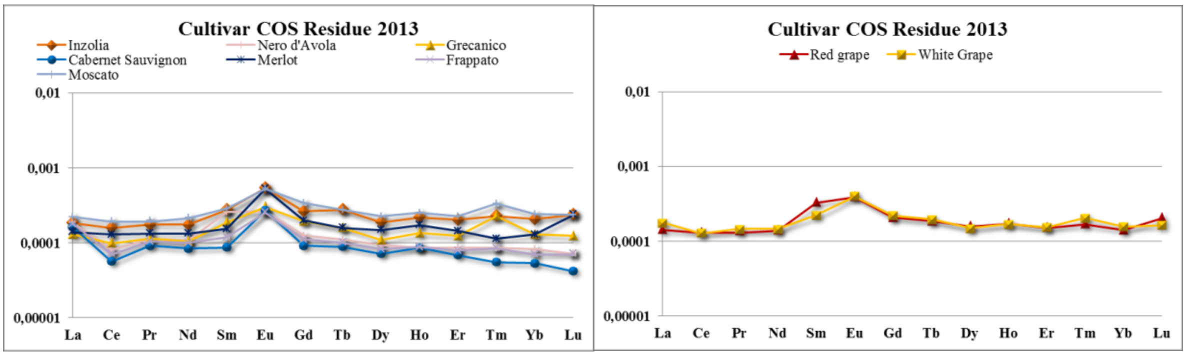
They were compared also cultivars of residual (graphs 34-36), skins (graphs 37-39), and seeds samples (graph 40-41), of the three vineyards (Don Saro, COS and Avide).

The differences among cultivars in samples of residue, are less clear than those found in the samples of leaves and juices, and the average pattern REEs are lower. In the graph 34 (A), Nerello Mascalese, Carricante and Inzolia have different patterns than other cultivars of Don Saro vineyard. The concentrations of HREEs of most cultivars are missing in the graph as below the instrumental detection limit. In graph 35 A the average pattern REEs of COS vineyard are with lower concentration than those ones analyzed in Don Saro vineyard, indeed, we see that Frappato and Cabernet Sauvignon show differences, presenting an evident negative anomaly cerium which is lacking in the other cultivars. The grape variety Cabernet Sauvignon shows lower pattern REEs than other cultivars, both in the graph on the vineyard and in the COS vineyard Avide, as seen from the graphs 35, A and 36, A.

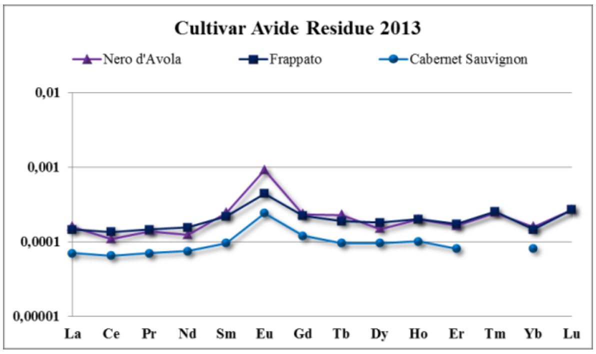
Comparing the two types of color berry cultivars, the vineyard of Don Saro (graph 34, B), the graph shows that the red grape cultivars have values slightly higher than the white grape cultivars, the difference between the two types is not present on the vineyard COS of Hyblean Plateau (graph 35, B).



Graph 34 Residue sample 2013, vineyard Don Saro: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.



Graph 35 Residue sample 2013, vineyard COS: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

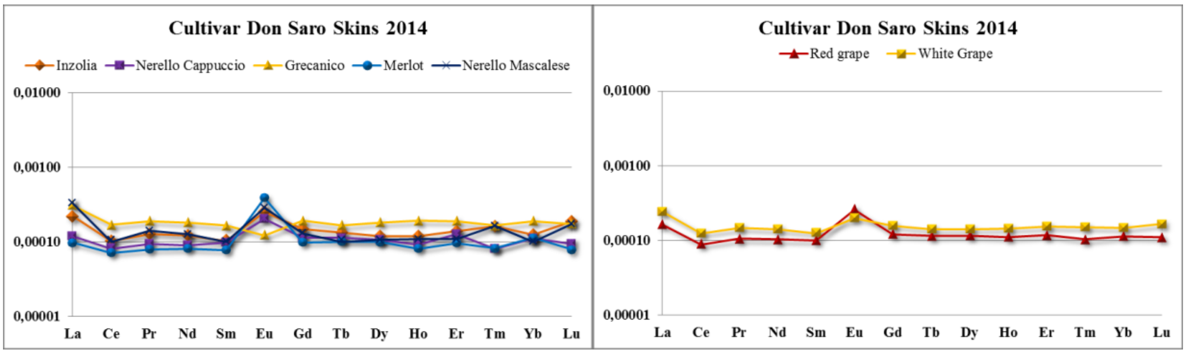


Graph 36 Residue sample 2013, vineyard Avide: comparison average REEs pattern cultivar. The values are normalized to the average concentrations of the soils of the respective vineyard.

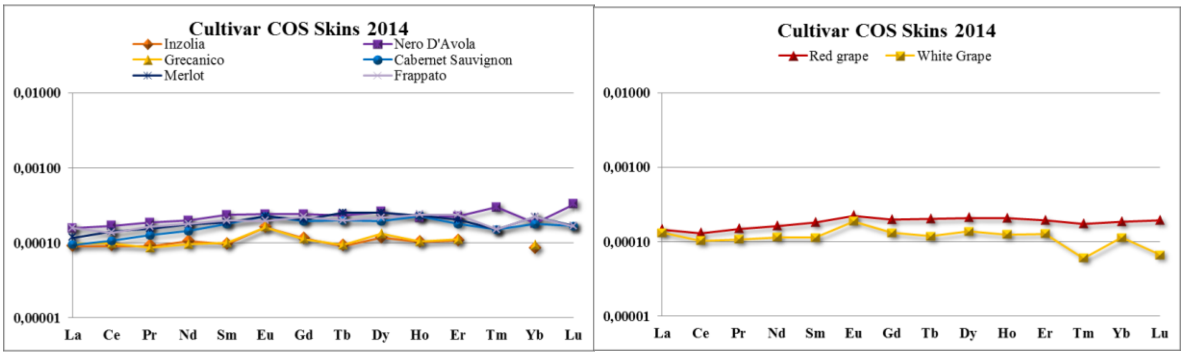
In the graphs of the skins (graphs 37-39), it is observed that the cultivar Inzolia of Don Saro vineyard (graph 37), behaves differently than other cultivars of the graph, showing negative anomalies of europium, when other cultivars show a positive anomaly of this element.

On vineyards in the Hyblean Plateau is a greater concentration of HREEs than the LREE. The Avide vineyard shows average pattern REEs (graph 39, A) extremely low.

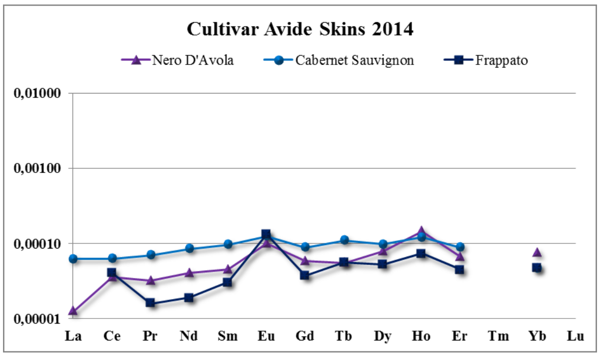
There are differences between average pattern red and white grape. In graph 37 B (Don Saro), white grape have highest value than red grape, except for positive europium anomaly in red grape pattern. In graph 38 B (COS vineyard), there is a reverse situation, with highest values for red grape.



Graph 37 Skins sample 2014, vineyard Don Saro: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

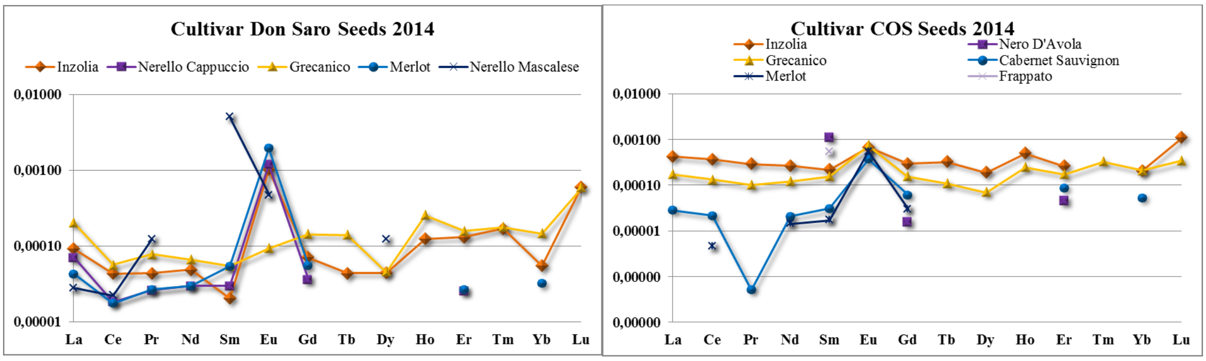


Graph 38 Skins sample 2014, vineyard COS: comparison average REEs pattern cultivar (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

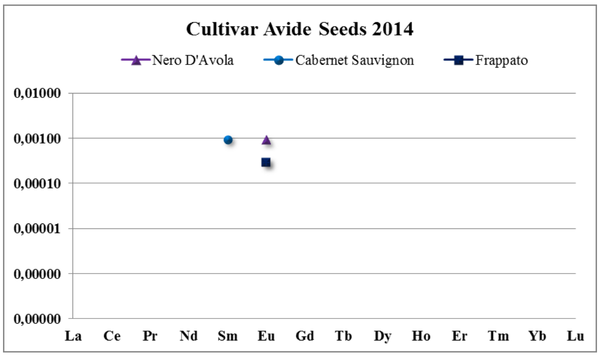


Graph 39 Skins sample 2014, vineyard Avide: comparison average REEs pattern cultivar. The values are normalized to the average concentrations of the soils of the respective vineyard.

In the seeds samples graphs 40-41, the value of REEs average pattern are too low to give valid results, especially in the vineyard Avide (graph 41), where most of the elements is below the instrumental detection limit of the equipment used, not allowing us to get any useful information.



Graph 40 Seeds sample 2014, comparison average REEs pattern cultivar Don Saro vineyard (A), comparison average REEs pattern of red and white grape (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

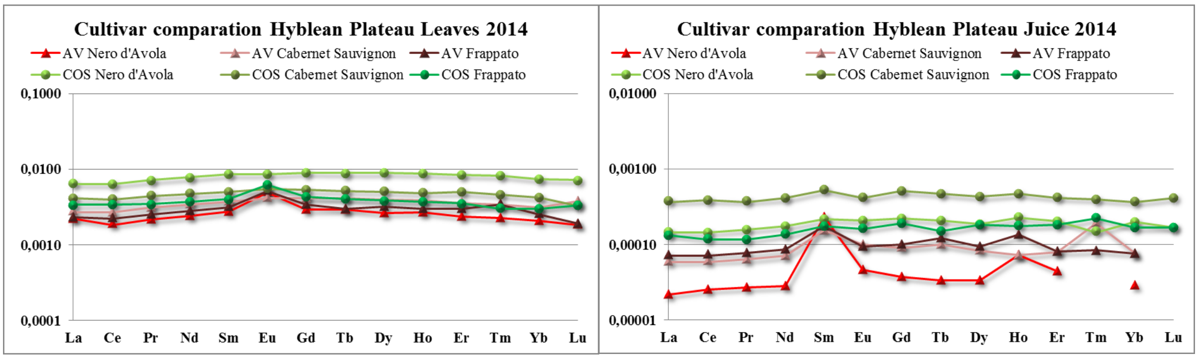


Graph 41 Seeds sample 2014, comparison average REEs pattern cultivar Avide. The values are normalized to the average concentrations of the soils of the respective vineyard.

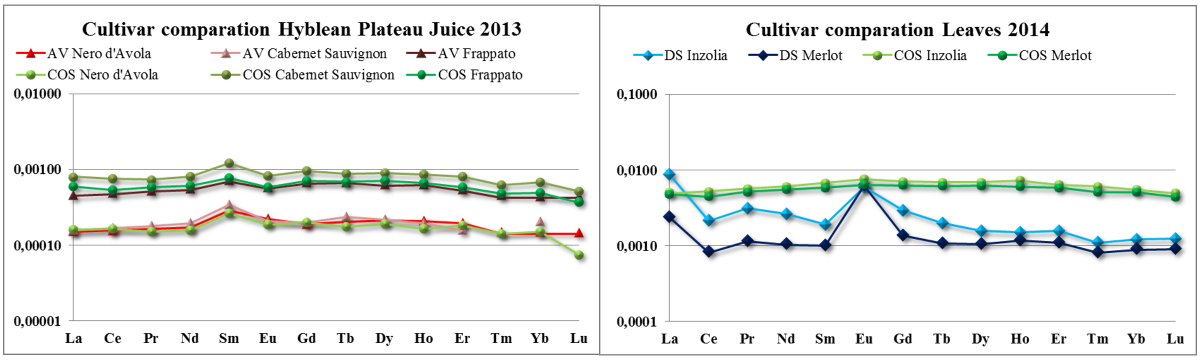
We eventually compared concentrations of REEs cultivars of the same type, grown in different vineyards. This comparison was carried out only on samples of leaves and juices, which have higher REEs content than residues, skins and seeds. The graphs 42 (A and B), 43 (A) show cultivars comparison in the two vineyards Hyblean Plateau: Nero d'Avola, Cabernet Sauvignon and Frappato. It notes that the three cultivars are grouped according to the vineyard to which they belong. In previous chapters, it has already been noted, as the soils of vineyards COS and Avide slightly differ in composition. This slight difference is also noticeable in the graphs, despite the climate and altitude are the same, slight differences in the composition of the soil are shown in the graphs, in particular, the average REE pattern of Nero d'Avola of the COS vineyard is located in opposite position with respect to that one of Avide vineyard (graph 42); the difference between the two vineyards, albeit at lesser extent, is also observed in samples of Cabernet Sauvignon and Frappato. So it would seem that some cultivars are variously affected by concentration of REEs in soil.

Such difference is not so clear in all samples; in juices of 2014 we saw the same differences in the samples of leaf, while in samples of juice of 2013, the difference can be seen only in samples of Cabernet Sauvignon, while the other two cultivars (Frappato and Nero d'Avola) do not show differences in concentration between the two vineyards, but if we look at the graph 42 (B) we see that the two varieties show different concentrations depending on the different cultivars.

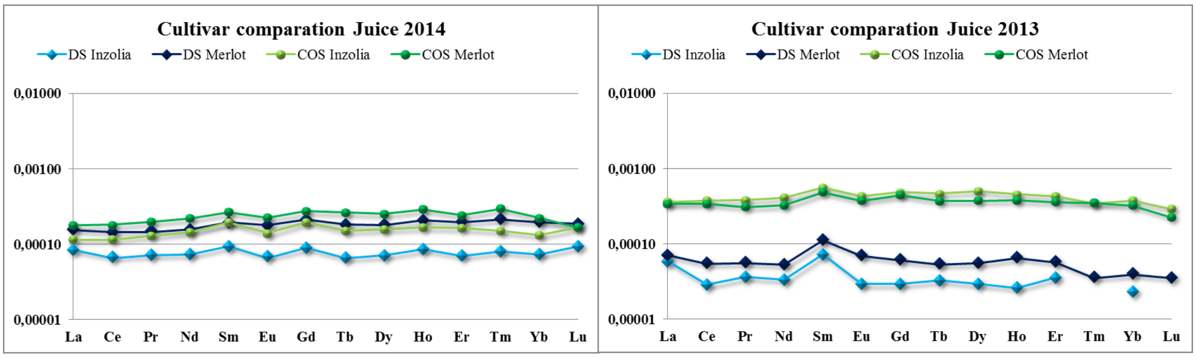
The better the results of comparisons between Inzolia and Merlot, grown on vineyards Don Saro and COS, in this case the soils are very different. Both in the samples of leaf (graph 43, B), than in those of juice of the two years (graphs 44 A and B), occur differences in concentration, in addition also the presence or absence of anomalies. This is a fact of considerable importance, in fact, the concentration and the patterns of REEs allowed us to discriminate the type of soil in which the plant is grown, allowing us to place it in a precise lithological context.



Graph 42 Cultivar comparison average REEs pattern Hyblean Plateau COS-Avide vineyard : Leaves sample 2014 (A); Juice 2014 (B). The values are normalized to the average concentrations of the soils of the respective vineyard.



Graph 43 Cultivar comparison average REEs pattern: Juice sample 2013 COS –Avide vineyard (A); Leaves 2014 Don Saro-COS vineyard (B). The values are normalized to the average concentrations of the soils of the respective vineyard.



Graph 44 Cultivar comparison average REEs pattern Don Saro-COS vineyard: Juice 2014(A); Juice 2013 (B). The values are normalized to the average concentrations of the soils of the respective vineyard.

6. Statistical approach

The data of the concentrations of Rare Earth Elements (REE) were also analyzed by the statistical point of view through the program "Statistica", version 8 is a suite of analytics software products and solutions originally developed by StatSoft (Weib, 2007), in order to obtain a model that allows a distinction among samples from different Sicilian vineyards. Indeed, data concerning various samples, belonging to three different vineyards: Don Saro, COS and Avide, respectively. The first vineyard (Don Saro) located at the Mount Etna, is characterized by a type of soil of volcanic origin; differently, the other two vineyards are located in carbonate derived soils, in Hyblean Plateau (SE Sicily). In the three vineyards various types of cultivars are cultivated: they include either white grapes (Inzolia, Carricante, Grecanico and Moscato) and red grapes (Nerello Mascalese, Nerello Cappuccio, Merlot, Frappato, Nero d'Avola and Cabernet Sauvignon).

The first step, with statistical computation, is to check any possible difference among the two main types of grapes that can can be influenced by the geographal differentiation.

To perform the statistical analysis, concentrations were analyzed without performing any normalization.

The increased technology of instrumental techniques, such as XRF, ICP-MS and many others not listed here, has greatly increased the number of components, both organic and inorganic, that can be identified and quantified, even for trace components. The advances in technology have increased the precision and quality of measurements, even though have dramatically increased the number of data to be analyzed.

The massive data sets are thus to be created, due to: the number of samples and related, number of constituents, that are very complex to analyze, especially for understanding the relationships between the samples and many important information that otherwise may be lost.

To deal with this problem multivariate analysis technique were done, for exploring the relationships between the obtained data.

Some recent papers indicate an increased attention to class modeling techniques and their use in food control problem (Esteban-Diez, 2007) (Marini, 2006) (Sanchez, 2005) (Sarabia, 2009).

The statistical approach covered in this chapter are:

- Box Plot; it is a graphical representation used to describe the distribution of a sample by means of simple measures of dispersion and location.;
- Principal Component Analysis (PCA); it is a technique for the simplification of the data used in the context of multivariate statistical. The main purpose of this technique is the reduction of a varying number of variables (representing as many features of the phenomenon) in some latent variables (feature reduction);
- Linear Discriminant Analysis (LDA) a method used in statistics to find a linear combination of features that characterizes or separates two or more classes of objects or events.

Box Plot

The Box Plot also called "*box and whiskers plot*", was proposed by Turkey in 1977; it is a graph quantitative analysis and describes the main features of a distribution. The graph allows us to have immediate information on the type of distribution, level of asymmetry, variability of the data and presence or not of abnormal values (Outliers). The box plot is useful for analyzing data sets which are few in number.

The more the lengths of the whiskers are similar to each other and the heights of the two sides of the box are between them similar, as far as distribution is symmetrical. The whiskers provide useful information on Outliers that are exceptional observations, highlighted by the whiskers themselves. It is obtained from 5 numbers that are: minimum, $1^{\circ st}$ quartile (Q1), median, 3^{ord} quartile (Q3) and maximum. The five numbers of synthesis are reported on one axis. The box of Box Plot has, as lower and upper bounds, Q1 and Q3, respectively, the median divides the box into two parts, whiskers are obtained joining Q1 and Q3 to the maximum to a minimum. The distance between the first and the third quartile, called " *interquartilic distance* ", is a measure of the dispersion of the distribution, 50% of the observations are located in between these values (Ciotoli, 2005).

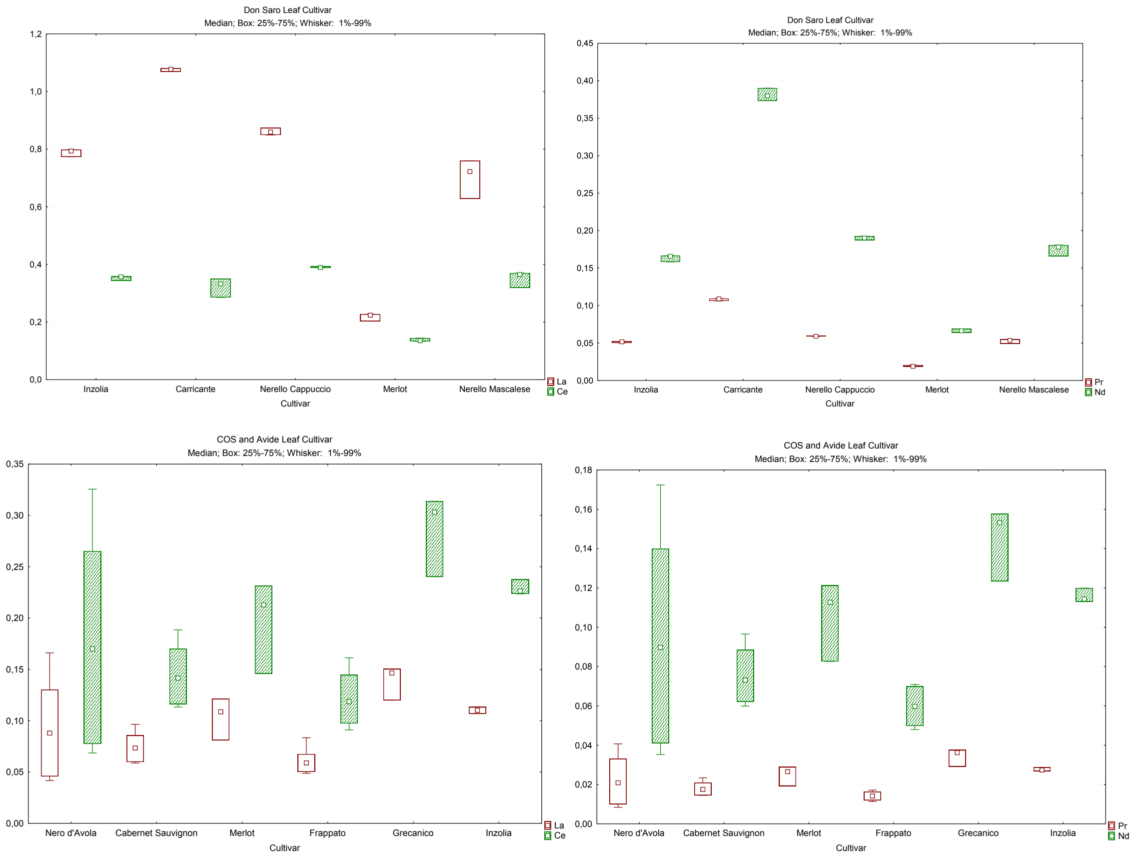
Through Box Plot it is possible to visualize the differences: as it is shown on graph 45 (A, B, C, D, E and F) the highest REE concentrations are in the samples of leaves and of the grape juices. The concentrations of REE decrease in samples of residue, of the skins and of the seeds.

Through the box plot we compared the main LREEs: La, Ce, Pr and Nd in relation to the different cultivars, in the vineyards of the two areas (Don Saro for the Etna area and COS and

Avide for the Hyblean Plateau), to see whether through these elements a distinction among the different grape varieties can be carried out. It is found that the concentrations of each element differ depending on the part of the plant taken into consideration, but do not allow to make a clear distinction among the grape varieties.

The data have not been normalized to facilitate the visualization of differences which could be concealed by normalization.

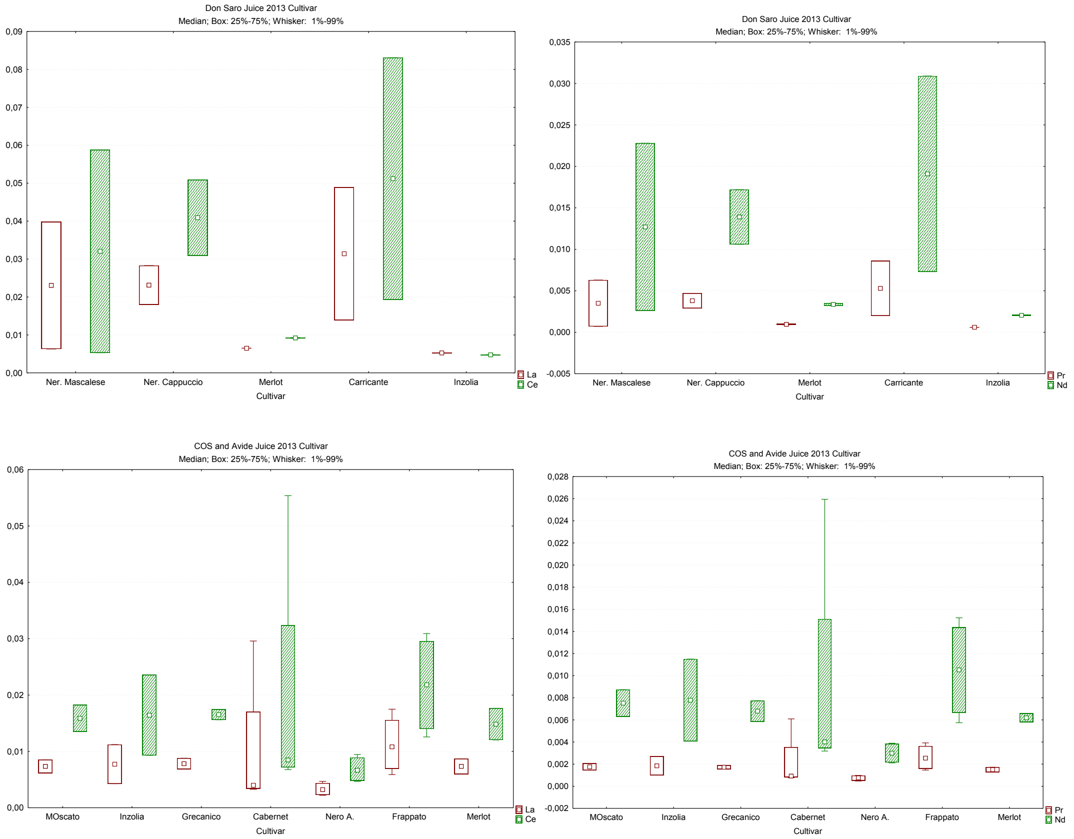
In graph 45 let us observe the concentration of leaves cultivar, as it is highlighted by graphs 45 (A, B, C and D), the different cultivars have differences in the concentration of the elements, in particular the differences are more readily apparent from the lanthanum and neodymium. In graph 45 it is evident that concentrations of REEs are greater than those measured in the Hyblean Plateau.



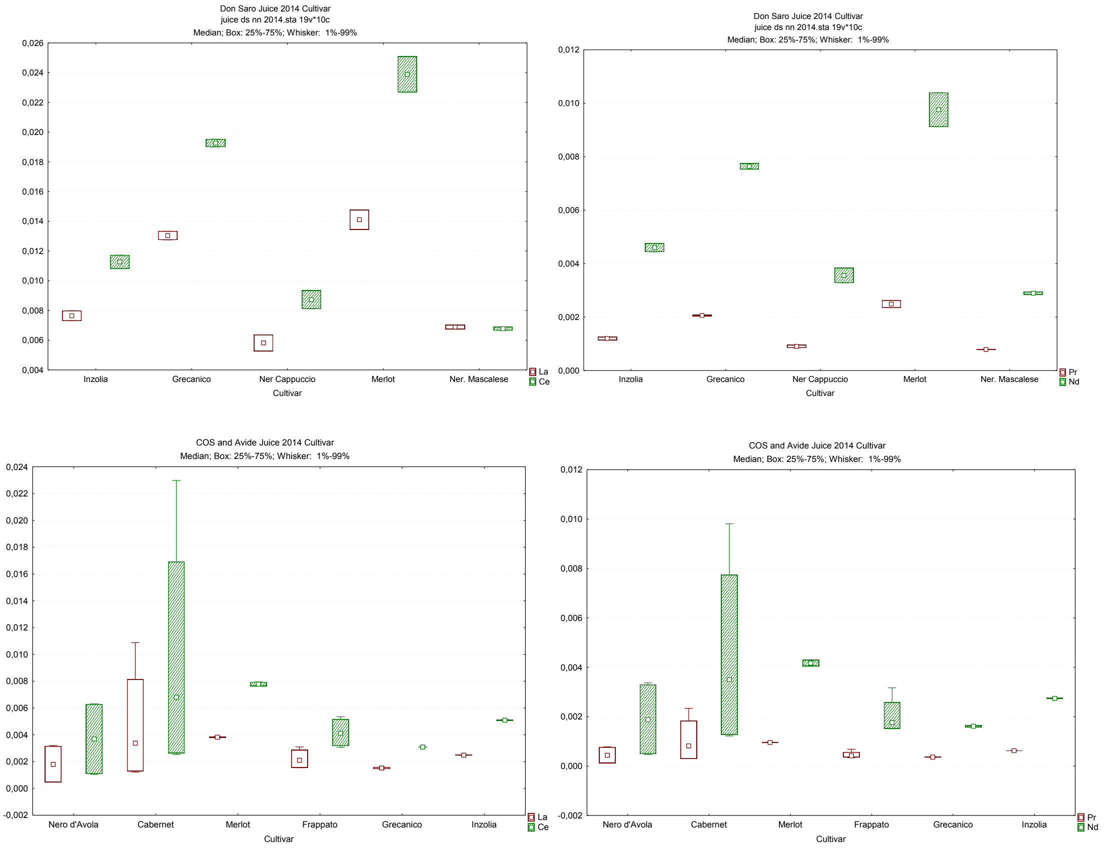
Graph 45 Box Plot cultivar leaf 2014, Don Saro(A and B) and COS and Avide (C and D).

Do not notice any obvious difference between the grapes and red grapes of Etna, while for leaves samples of Hyblean Plateau, concentrations of cerium and neodymium are slightly higher than those ones of the red grapes grown in the same area.

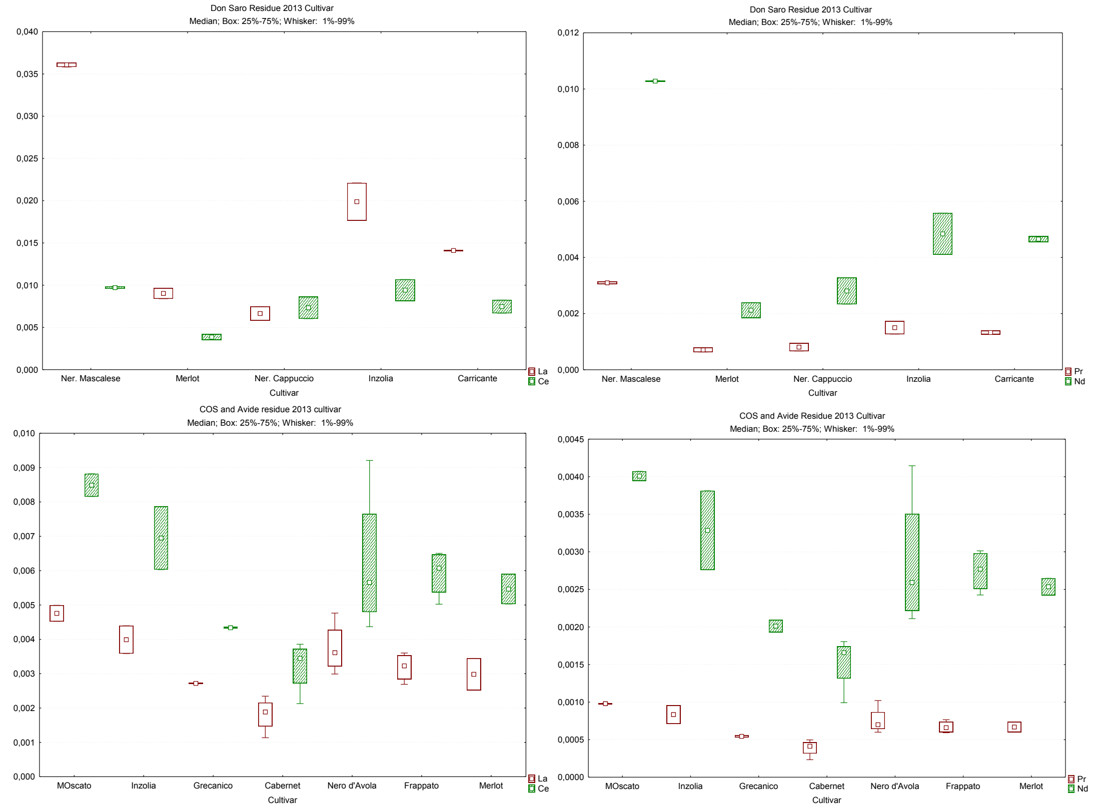
The concentration difference between cultivars of the same area is also evident in samples juices 2013 and 2014; respectively in graphs 46(A, B, C and D) and 47(A, B, C and D). The concentration differences between the two areas are more minor, and the elements that allow greater differentiation in these types of samples are cerium and neodymium.



Graph 46 Box Plot cultivar juice 2013, Don Saro(A and B) and COS and Avide (C and D).

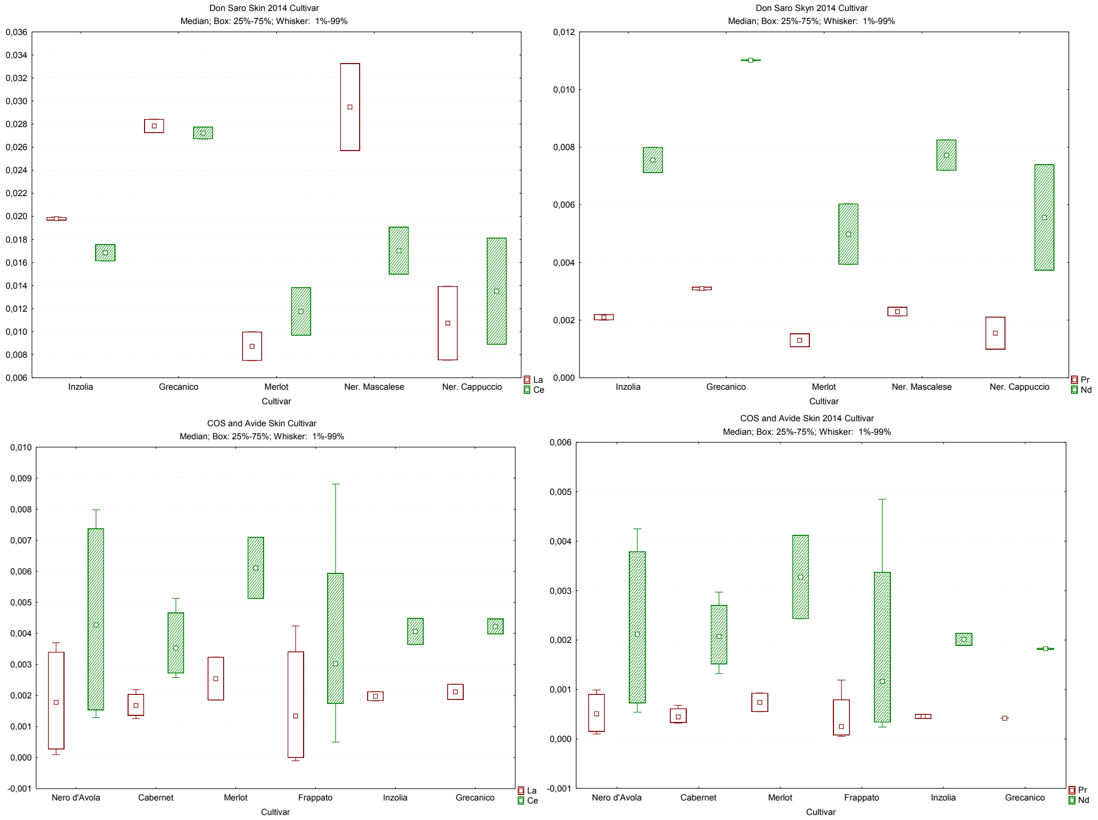


Graph 47 Box Plot cultivar juice 2014, Don Saro(A and B) and COS and Avide (C and D).

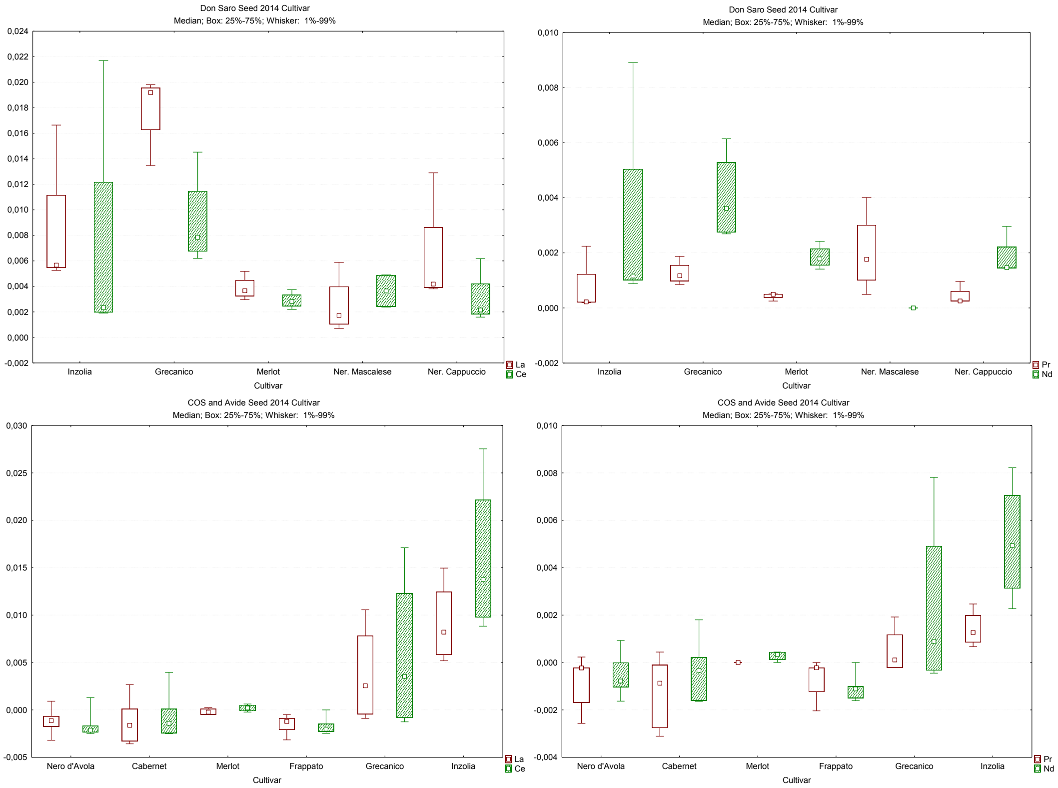


Graph 48 Box Plot cultivar residue 2013, Don Saro(A and B) and COS and Avide (C and D).

In sample of residue (graphs 48 A, B, C and D) and skins (graphs 49 A, B, C and D), lanthanum and neodymium are the elements that allow a greater degree of discerning cultivars, and in Hyblean Plateau the elements that favor the distinction are cerium and neodymium. In these graphs (48 and 49), there are obvious differences between the varieties of white grapes and the red grapes. This difference seems to be noted however in seeds graphs (graphs 50 A, B, C and D), the difference between cultivars with white grapes and the red grapes is especially noticeable among the varieties located in the Hyblean Plateau, while among the grapevines of Etna not have particular distinctions.



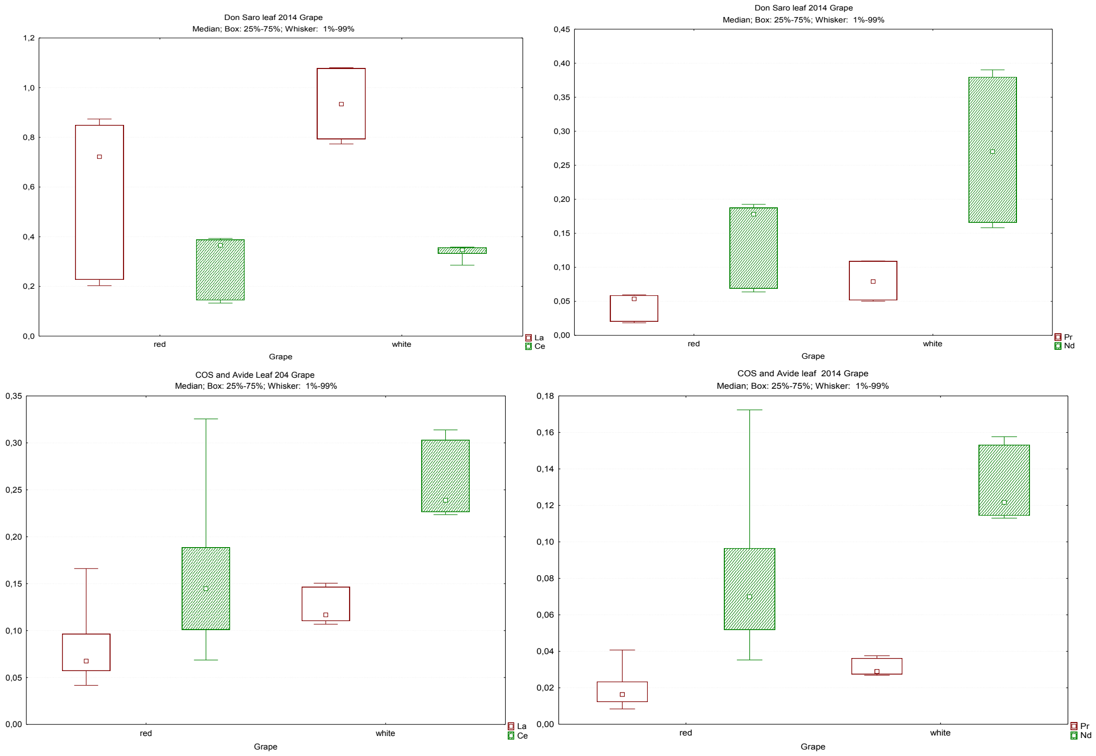
Graph 49 Box Plot cultivar skin 2014, Don Saro(A and B) and COS and Avide (C and D).



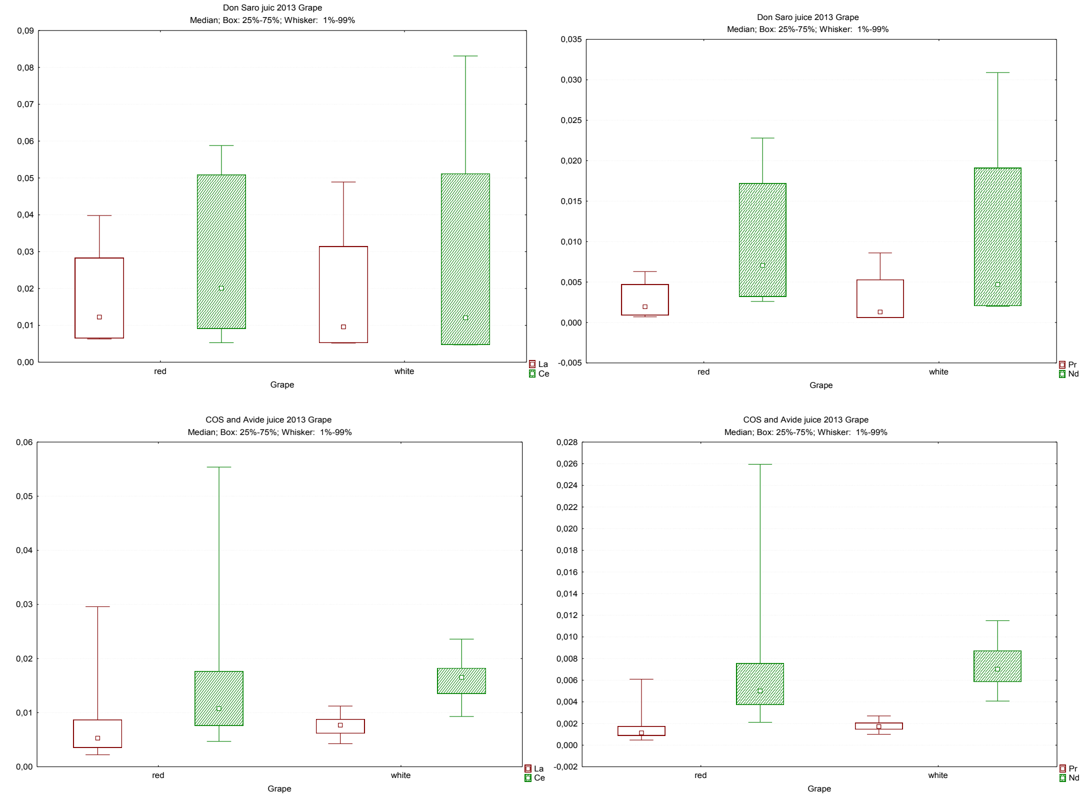
Graph 50 Box Plot cultivar seed 2014, Don Saro(A and B) and COS and Avide (C and D).

In the next step, we confronted white and red grape, based on LREEs distribution: La, Ce, Pr and Nd. As in the case of box plot seen above, were considered separately the two areas of interest, the winery of Don Saro is in the Etna area, and wineries COS and Avide represent the area Hyblean Plateau.

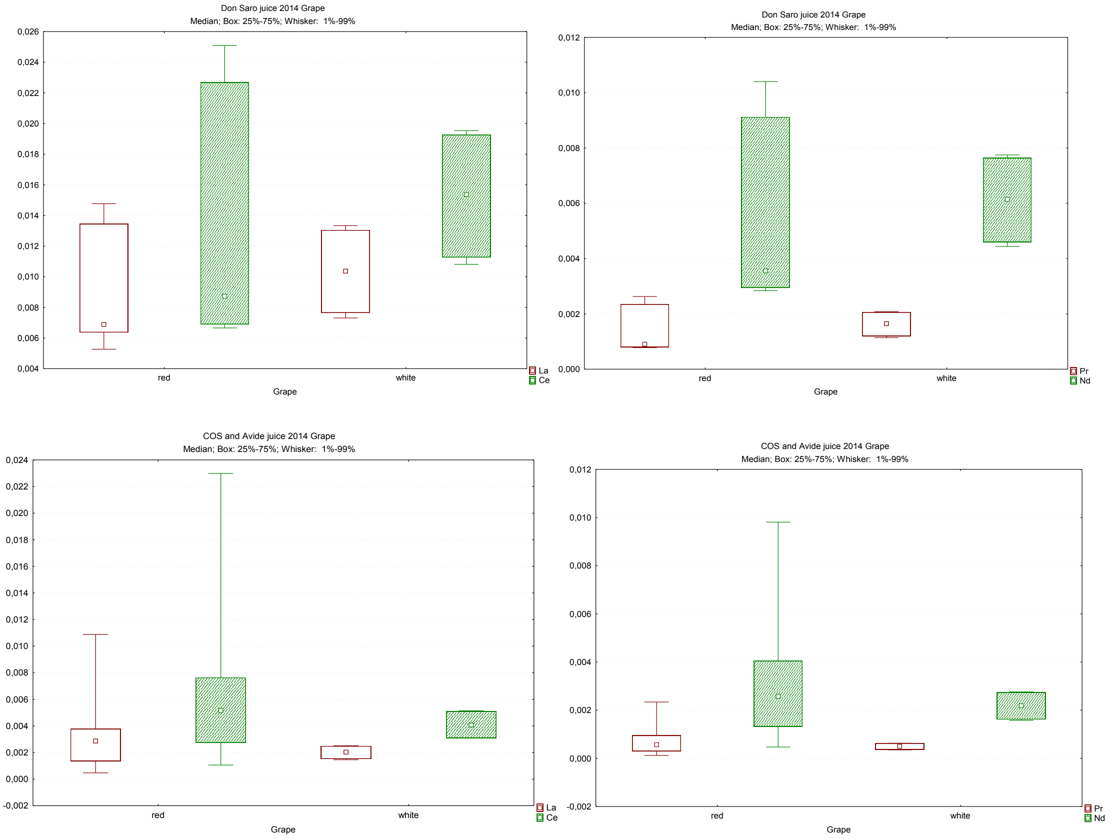
In both areas, the graphs appear to distinguish between the two types of grape varieties, thanks to the content of La and Nd in leaf samples (graphs 51 A,B,C and D). In samples of juice, we can see in the graphs 52 (A,B,C and D) and 53 (A,B,C and D), there are differences between the white and red grapes but you cannot discriminate as in the leaves graphs 50 (A,B,C and D), in view of the length of the measured values in the red, the white samples have concentrations with a narrower width values .



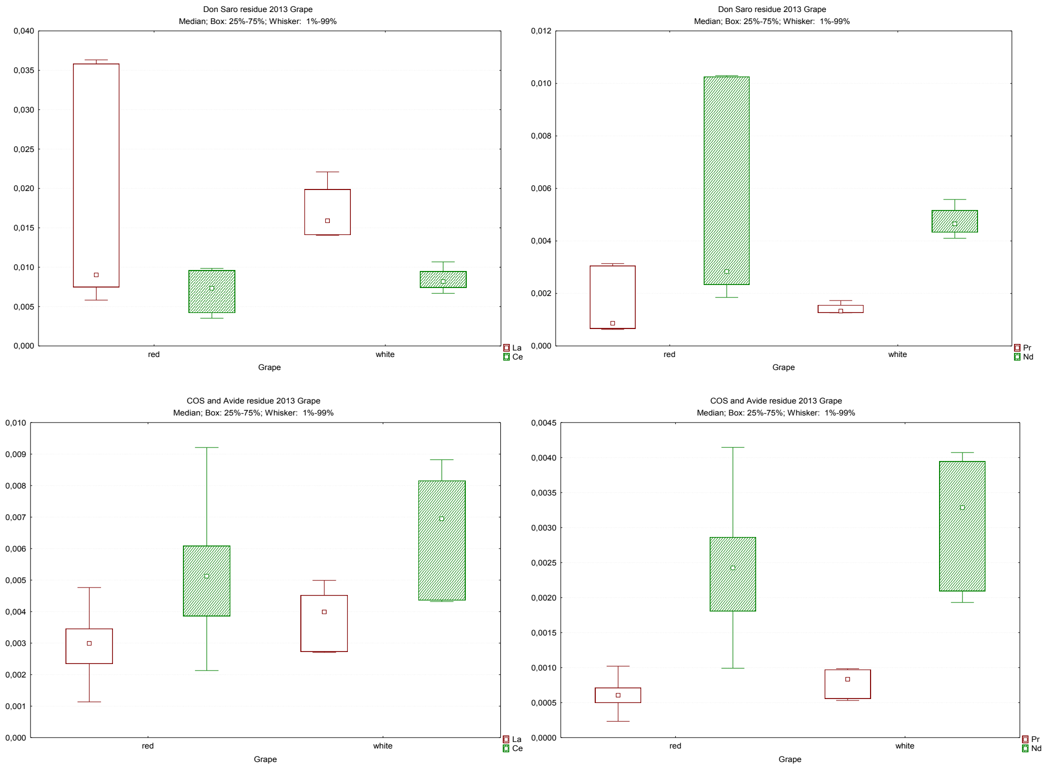
Graph 51 Box Plot leaf 2014 of grape variety of La, Ce, Pr, and Nd; Don Saro (A and B) and COS and Avide (C and D).



Graph 52 Box Plot juice 2013 of grape variety of La, Ce, Pr, and Nd; Don Saro (A and B) and COS and Avide (C and D).



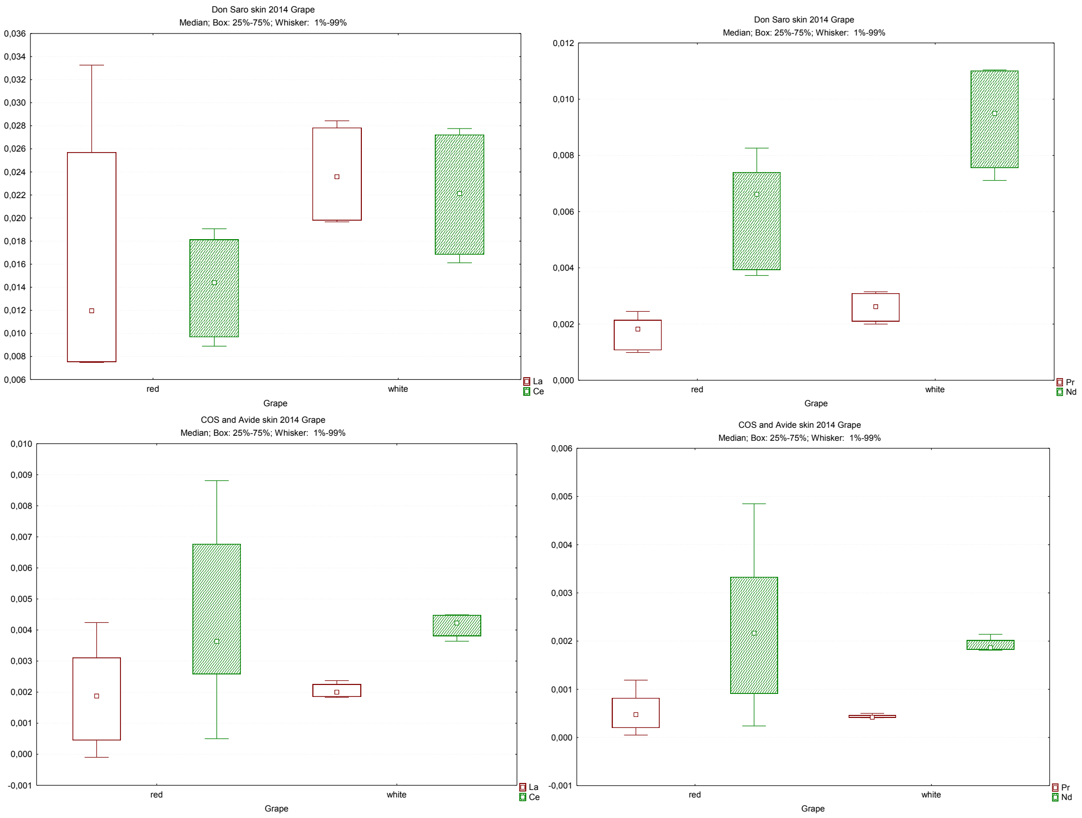
Graph 53 Box Plot juice 2014 of grape variety of La, Ce, Pr, and Nd; Don Saro (A and B) and COS and Avide (C and D).



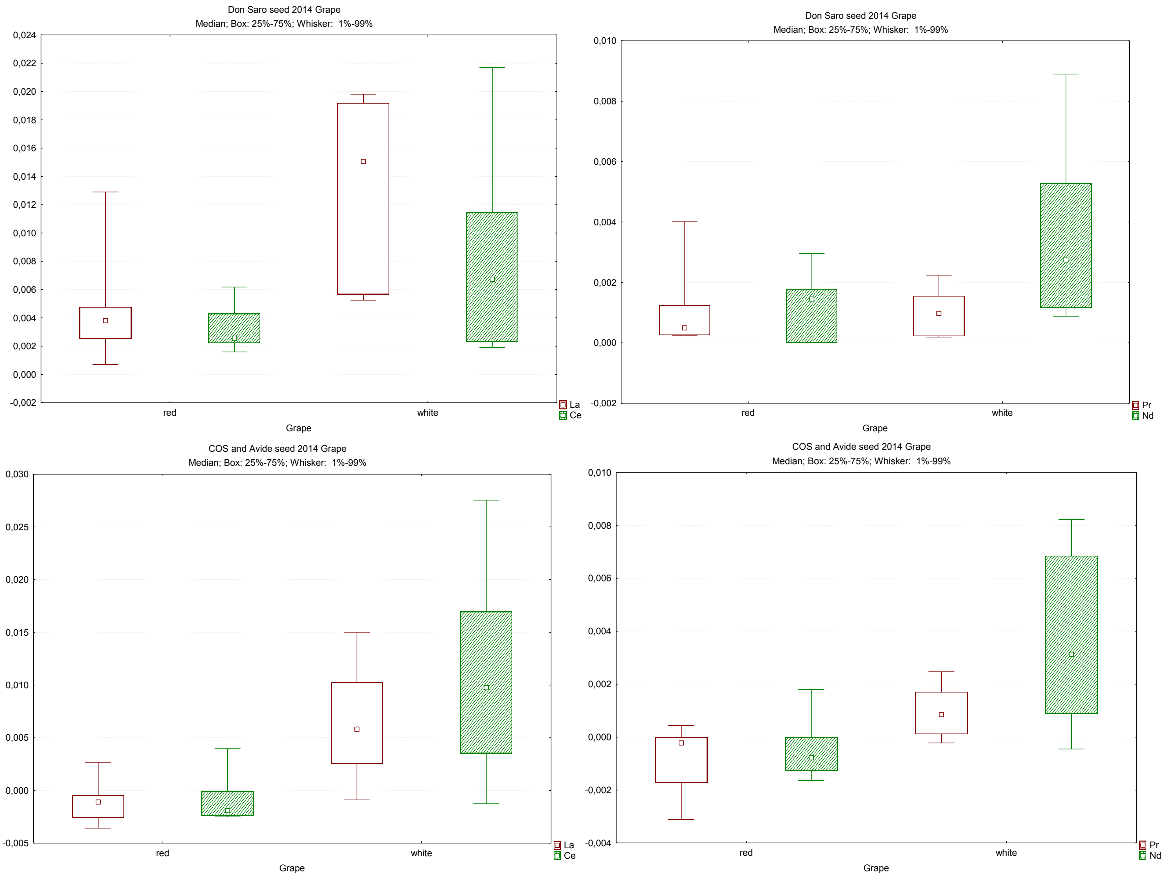
Graph 54 Box Plot residue 2013 of grape variety of La, Ce, Pr, and Nd; Don Saro (A and B) and COS and Avide (C and D).

In samples of residue (graph 54 A, B, C and D), you have the same situation already seen in the samples of juice, and you cannot make a clear distinction between the two types of grape variety. As regards the samples of the skins, shown in the graphs 55 (A, B, C and D) the white grapes have higher concentrations of neodymium than red berry cultivars of the Etna, but it does not happen the same with regard to the samples of the Hyblean Plateau.

Differences were most significant in the samples of seeds in the graphs 56 (A, B, C and D), where cerium, praseodymium and neodymium allow us to distinguish between the two types of grape varieties. Contrary to observations in other types of samples, the concentrations found in the samples of seeds of white grape varieties are superior to those found in red grapes varieties.

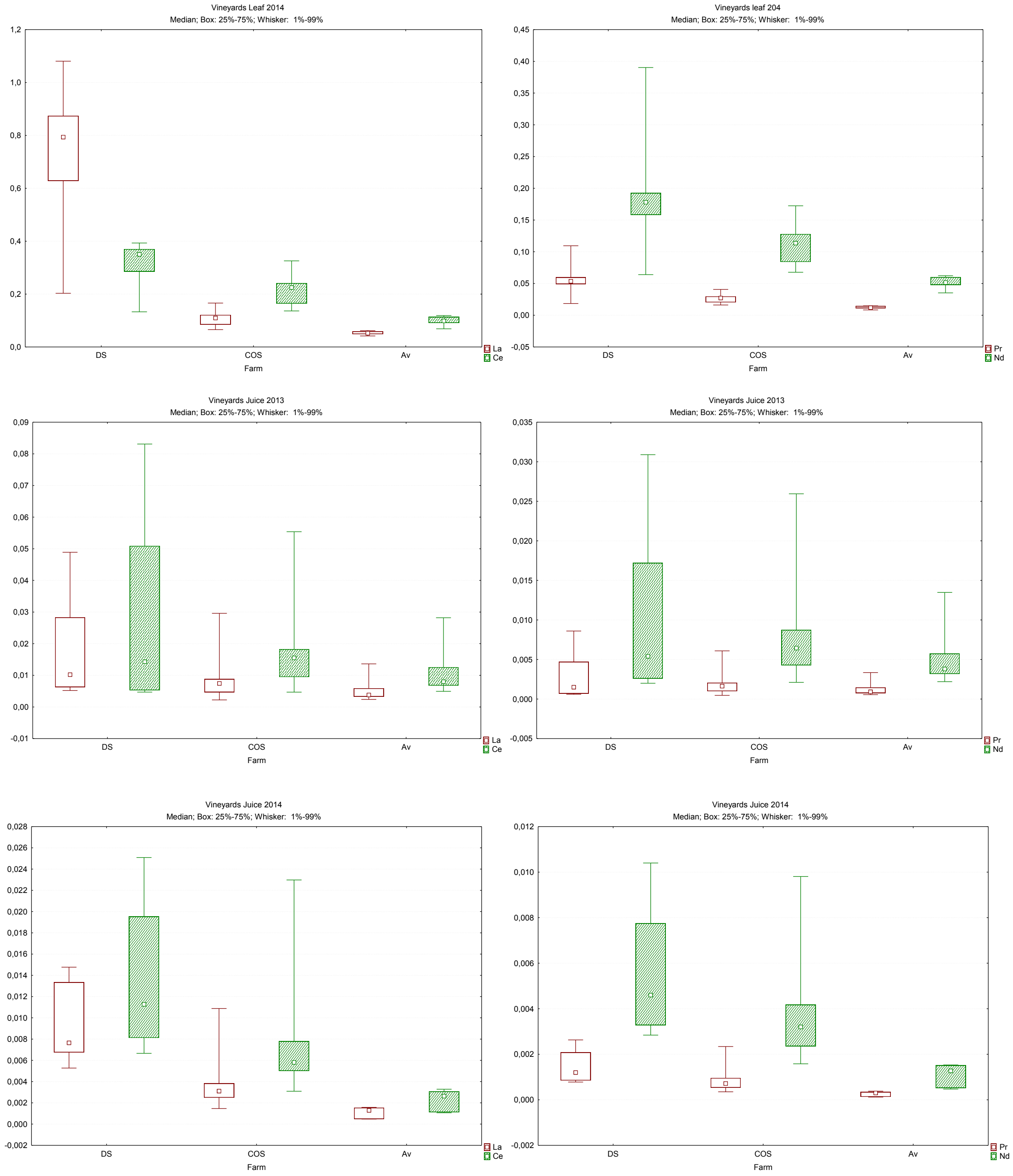


Graph 55 Box Plot skin 2014 of grape variety of La, Ce, Pr, and Nd; Don Saro (A and B) and COS and Avide (C and D).

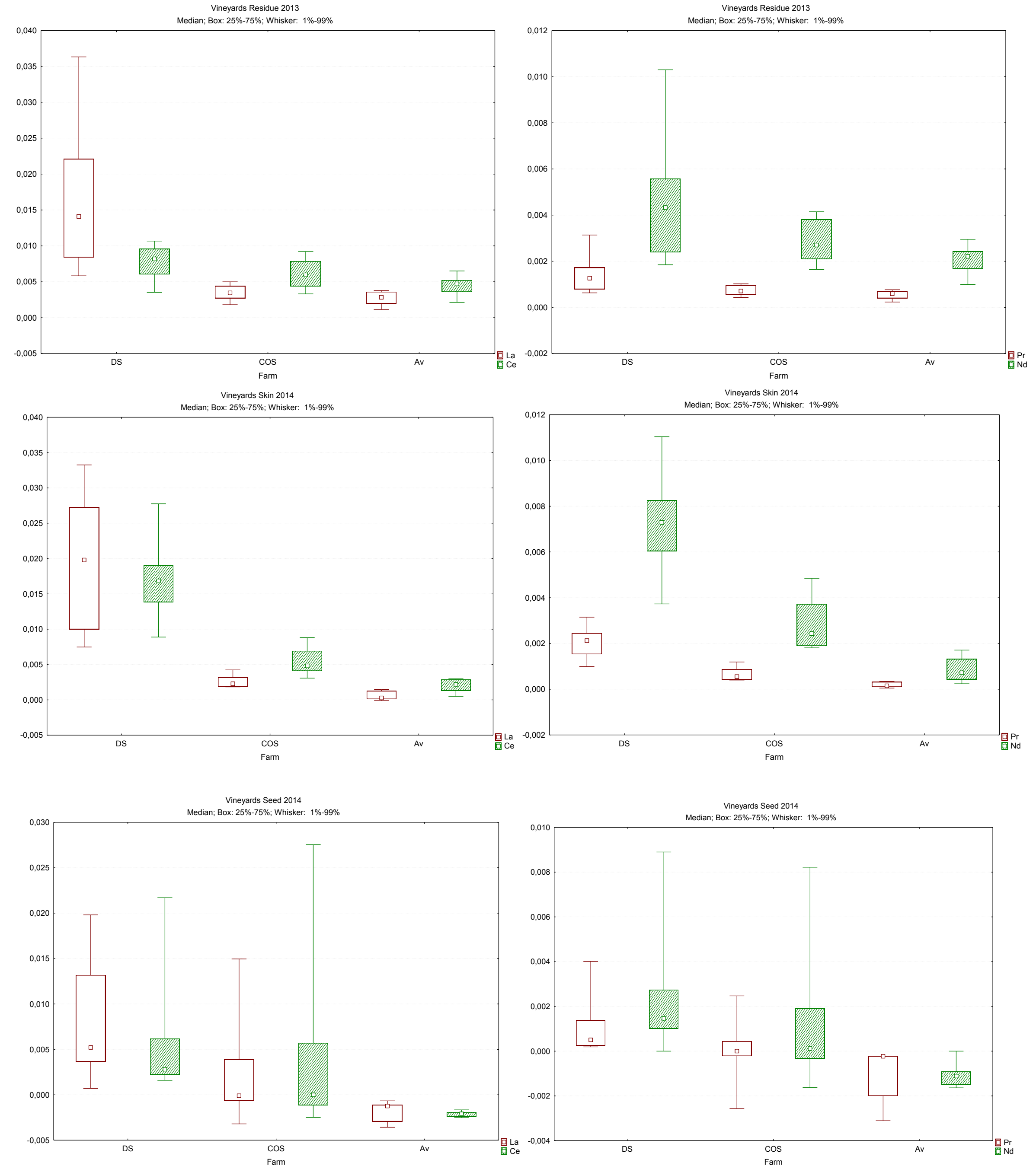


Graph 56 Box Plot seed 2014 of grape variety of La, Ce, Pr, and Nd; Don Saro (A and B) and COS and Avide (C and D).

Considering always the same LREEs, we did the comparison among the three vineyards respectively (Don Saro, COS and Avide). The distinction among Don Saro vineyard (Mount Etna) and COS and Avide vineyards (Hyblean Plateau) is evident (graphs 57 and 58). Samples of leaves collected at Don Saro vineyard, show the highest values, especially for lanthanum and neodymium (graph 57 A and B). There is also has a slight difference between the two vineyards of the Hyblean Plateau, although the values are similar, the samples of the COS vineyard having slightly larger distribution and a greater dispersion. Discrimination is also evident in the samples of juice in 2013 and 2014 (graph 57 C, D, E and F): samples of the COS have a greater scattering compared to Avide vineyard. The distinction between the Hyblean Plateau vineyards is less pronounced in the remaining 2013 samples and skins 2014, although samples of Don Saro have always concentrations and scattering higher than COS and Avide. The distinction is even difficult to detect in the samples of seeds (graph 58 E and F), because of their low concentrations of LREEs. However, Don Saro has always the highest values; a singular fact is the wide scattering presented by samples of vineyard COS, whilst those ones of Avide vineyard show extremely low concentrations and a minimum scattering.



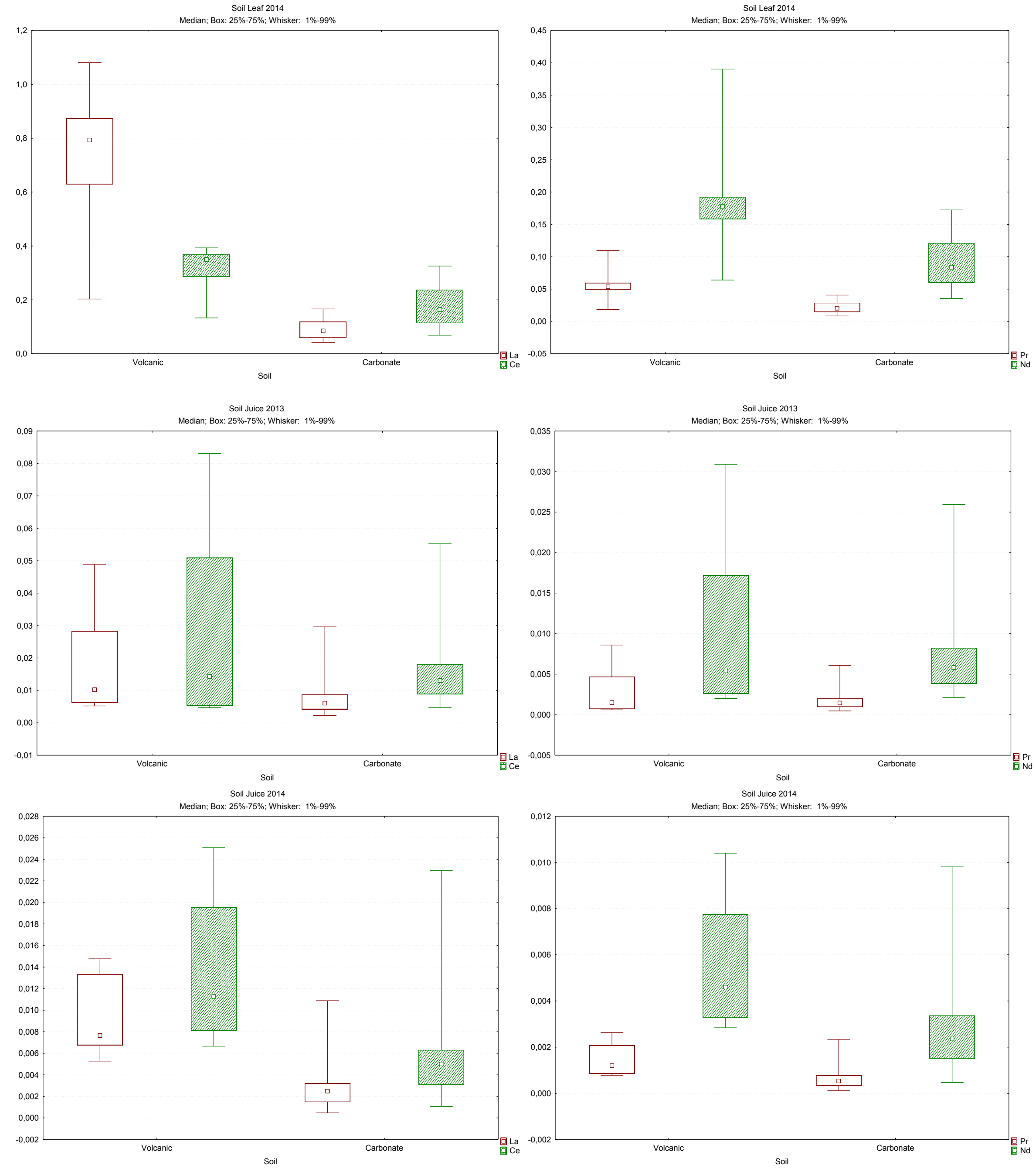
Graph 57 Box Plot leaf 2014 (A and B), juice 2013 (C and D), juice 2014 (E and F) of vineyard of La, Ce, Pr, and Nd.



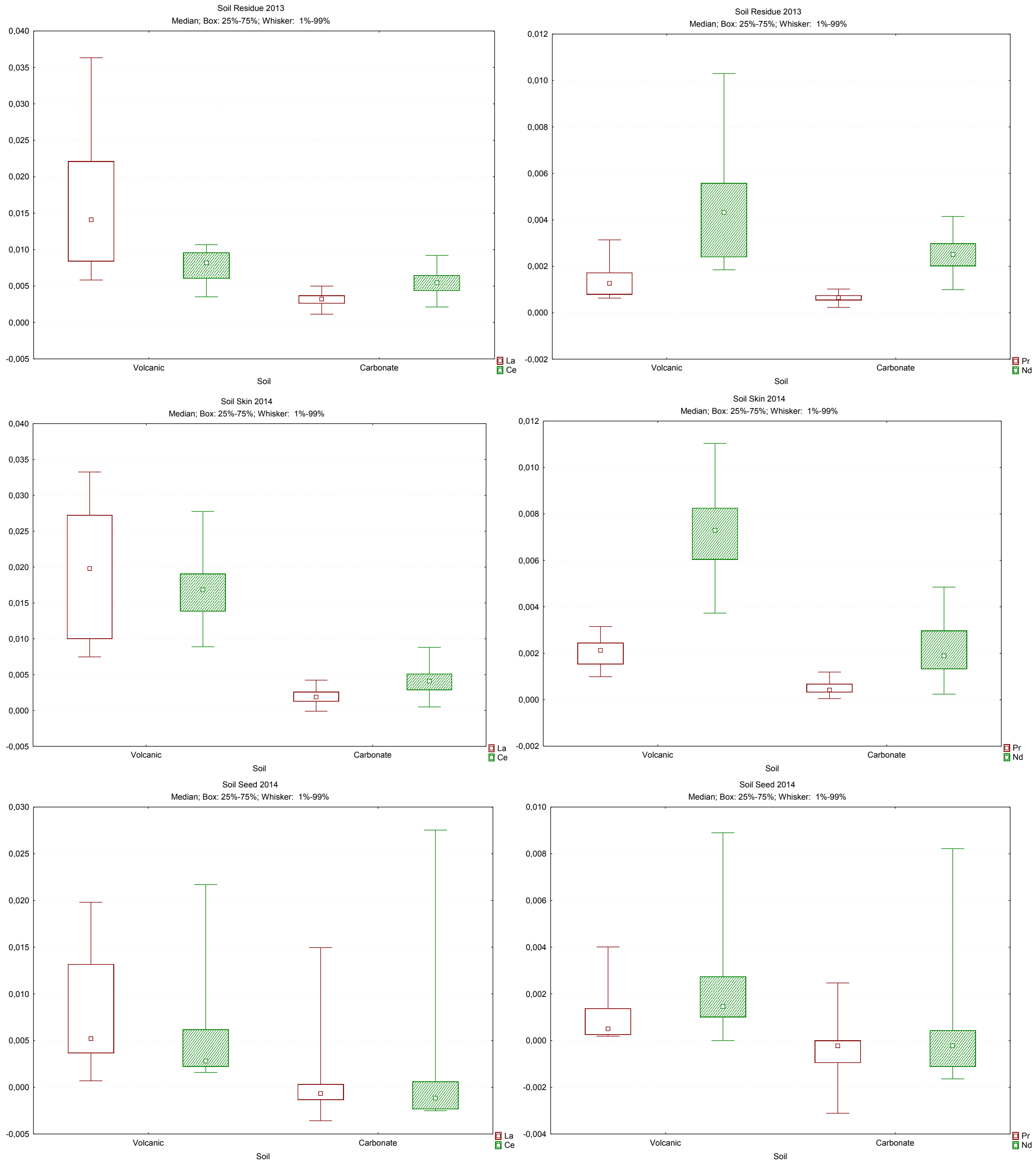
Graph 58 Box Plot residues 2013 (A and B), skins 2014 (C and D), seeds 2014 (E and F) of vineyard of La, Ce, Pr, and Nd.

In the last analysis we are going to compare whether La, Ce, Pr and Nd (i.e. LREEs) allow us to make a distinction between the plants grown in the two different types of soil: volcanic and carbonate, respectively, through the use of Box Plot.

In all of the Box Plots there is a clear distinction, on the basis of the soil in which the plant grew (graph 59 and 60). The volcanic soil has higher concentrations and less scattering in La, Ce, Nd and Pr. The difference is more evident in samples of leaves and juices (graph 59 A, B, C, D, E and F). In particular, (graph 59 and 60) the elements that better show the difference between the two types are La and Nd, while Ce and Pr show no as much difference as the first two LREEs. The "volcanic" samples, show a much wider scattering in concentrations than samples collected in the Hyblean Plateau. Also in this case, the seeds (graph 60 E and F), whose concentrations are very low, even below the detection limits for some elements, are the samples that show no difference between the two soils to which they belong, with a remarkable scattering of values in the graph for both types of soil taken into account.



Graph 59 Box Plot leaf 2014 (A and B), juice 2013 (C and D), juice 2014 (D and F) of soil of La, Ce, Pr, and Nd.



Graph 60 Box Plot residues 2013 (A and B), skins 2014 (C and D), seeds 2014 (E and F)of soil of La, Ce, Pr, and Nd.

Non parametric test

Non parametric tests, often referred to as “distribution-free statistics”, are tests that do not involve the estimation of statistical parameters such as mean, standard deviation, variance. They are easy to calculate and to interpret, effectiveness in highlight the differences is smaller than that one found in parametric type tests.
Advantage of non-parametric test are:

- The amplitude of the sample may also be very small;
- The tests are suitable to analyze data that are organized by ranks;
- There are types of nonparametric tests can analyze categorical or nominal data type;
- Some types of tests, analyze samples from different populations;
- immediate results (Ciotoli, 2005).

Because the test results give significant differences, require to be larger, it increases the risk of being able to accept a false null hypothesis (Tipe II error).
In this work we took into account two non-parametric tests: the first analyzes difference between two discrete levels of the independent variable Mann- Whitney U test; the second is the Kruskal Wallis test for comparing how paired groups of data relate to each other.

Mann-Whitney Test

The test was developed in 1945 by the Wilcoxon, for two samples of the same size; in 1947 was further developed by Mann and Whitney to cover different sample sizes of the test. The test is also called "Mann-Whitney-Wilcoxon (MWW)" or "testing two samples" (Ciotoli, 2005).
The Mann-Whitney U-test, is a statistical comparison of the mean. This non-parametric test is used to compare two population means that come from the same population, it is also used to test whether two population means are equal or not. It is used for equal sample sizes, and is used to test the median of two populations.
The method requires assumptions:

- The sample drawn from the population is random;

- Independence within the samples and mutual independence;
- Ordinal measurement scale.

Consider the case of having two samples of size n and m with m <n. We name x_i and y_i, respectively, sample observations less numerous and more numerous, the order of observation R (x_i) or R (y_i), if there are two observations with the same value to these will be assigned a value equal to the average of their orders. The sum of the orders for the two groups is:

$$Wx = \sum_{i=1}^{m} R(x_i)$$

$$Wy = \sum_{j=1}^{m} R(y_j)$$

The test is the sum of the orders of the observations of the sample less numerous (W_x in this case).

For samples with numerous observations W_x is distributed in a normal manner. The value of the mean and standard deviation is given by the formulas:

$$X = nm/2$$

$$s = \sqrt{\frac{nm(n+m+1)}{12}}$$

These are used to transform the value of the test Wx to a standardized form normal by the equation:

$$z = \frac{W_x - X}{s} = \frac{W_x - nm/2}{\sqrt{nm(n+m+1)/12}}$$

(Ciotoli, 2005).

In our case the test was performed to calculate the discrimination among the two types of soil and among white grapes and red grapes. The test was applied to all of the types of samples, the calculation was performed for each REEs.

The results show that lanthanum plays an important role in the distinction among the plants grown in the two types of soil, in particular in the case of juices; Ce, Pr, Nd and Eu are also able to make the distinction among the different soil. In the leaves, which are part of the plant with the highest concentration of REEs, the elements that allow the best discernment among the type of soils are; La, Eu, Pr and Nd followed by Gd, Tm, Lu, Yb and eventually Ce. If we consider the residual discrimination can be carried out by La, Lu, Yb, Tm, Ho and Pr especially, but Er, Eu, Nd, Dy and Ce have an important role in discerning the type of soil. From the samples of skins it is evident that almost all elements can permit a distinction among the two populations, especially the LREE. In seed samples, La, Pr, Eu, Ce, Nd, Gd and Dy must be taken into consideration for making a distinction.

The results so far confirm what was previously observed in the Box Plot calculation, indicating the elements which permit distinguish on the basis of the two types of soil on which the cultivar grew.

The method was also applied to make a distinction among the two populations of grape varieties (white and red grapes, respectively). The method does not show any evidence that could allow the distinction among the two populations, by considering juice and skins (in the residue of 2013 only the Nd allows for discrimination). Instead, the leaves and seeds allow to describe the two types. The elements that mainly allow the distinction, in the case of leaves, are: Sm, Tb, Pr, Gd, Nd, Eu, La and Ce, it is worth nothing that also the other REEs permit such a distinction, even though at the lesser extent. The seeds show very high values for the distinction, in particular, Ho, Er and Yb, and Lu which are all HREEs whose values, especially in the seeds are very low or below the detection limits in many cases, other REES, that allow the distinction are to follow La, ce, Tb, Nd, Gd, Pr and Dy. In this case it is reflected what was previously seen in the Box Plot approach, where the samples of leaves and seeds were the only ones that allowed a kind of distinction between the types of grapevine.

Kruskal-Wallis test

Kruskal-Wallis, named after its authors William Kruskal and W. Allen Wallis, is a nonparametric test to verify the equivalence between the average of several samples, it is the alternative non-parametric analysis of variance. The procedure used is very similar to the Mann-Whitney test. The observations of the K samples are joined together and arranged in ascending, for each sample the sum of ranks is given by:

$$Rk = \sum_{i=1}^{nk} R(x_{ik})$$

Where $R(x_{ik})$ represents the rank of the i-th observation of the k-th sample. The number of cases is: $N = \sum_{i=1}^{k} n_k$where n_k is the number of observations of the k-th sample.

Adding the number of the ranks to calculate the value of H Kruskal-Wallis:

$$H = \frac{12}{N(N-1)} \sum_{j=1}^{k} \frac{R_k^2}{n_k} - 3(N+1)$$

(Ciotoli, 2005) (Hollander, 1999). The test can be also applied to numerous samples.

The method was applied to samples of all parts of the plant; the discriminating elements allowed the distinction of the three vineyards.

In the case of leaf samples, Pr and Eu allow to discriminate the three vineyards, whereas other elements discriminate only in part: Dy, Ho, Er, Tm, Yb and Lu allow the distinction between Don Saro and COS and between COS and Avide, but not to distinguish among Don Saro and Avide vineyards.

Consider the samples of juices, which show different behavior among samples collected in 2013 and those ones collected in 2014; in the first group (i.e. 2013) only lanthanum allows to distinguish among Don Saro and Avide vineyards, whereas in the second sampling group (2014) all of the REEs, with the exception of the Thulium, can distinguish among Don Saro and Avide and, in case that we exclude Sm and La, among COS and Avide vineyards.

In the samples of seeds, La, Ce and Pr are useful in the distinction between the three vineyards (Don Saro, COS and Avide), while most of the other elements allows us to distinguish if the population of samples belongs to Don Saro or Avide.

In samples of skin, no elements allows the distinction between the three vineyards, whereas the distinction among Don Saro and Avide is evident from all of the REEs. The LREEs differentiate between Don Saro and COS and only Dy, Er and Yb distinguish among COS and Avide.

In residues samples, most REEs distinguishes among Don Saro and COS, whereas only La, Ce, Pr and Nd distinguish between Don Saro and Avide. However, there is no element that distinguishes the two Hyblean Plateau vineyards.

The method was also applied in the comparison of different cultivars. Samples of leaf allow you to make some distinctions between some of the cultivars, concerning LREE La, Ce, Pr and Nd.

In juice samples, there are elements that allow you to differentiate among the various cultivars as well as in samples of skins, whereas in the remaining sample the only significative difference, are limited in the distinction among Cabernet Sauvignon and Nerello Mascalese, carried out by La, Ce, Pr and Nd. Special mention is deserved to the seeds, from which it seems no possible to distinguish among the different cultivars, especially on the basis of La, Ce, Pr Nd, Sm, Eu, Gd and Dy. It must be pointed out that usually these distinctions are mostly evident for discriminating among white and red grapes cultivars, this particularly holds for Ansonica cultivar is distinguished, in the samples of seeds from other cultivars.

Principal Component Analysis (PCA)

Principal component Analysis (PCA), is the most used multivariate analysis technique, especially with regard to the scientific and engineering fields (Brown, 1995). With this method, the original measurement variables are transformed into new variables called "principal components". The main components are linear combinations of the original variables, enough so only a few major components to understand the information in the data, significantly reducing amount of variables to be analyzed. In fact, all of the original data are plotted into a coordinate system, which is defined by two or three principal components, in order to identify similarities and differences, if anything from the data constituting the key relationships to be extrapolated.

The method reduces the size of data sets while preserving the information contained in it, you can achieve this because the set of chemical data are redundant because of co-linearity among the measured variables. Co-linearity reduces in fact the information contained in the data (Lavine, 2015).

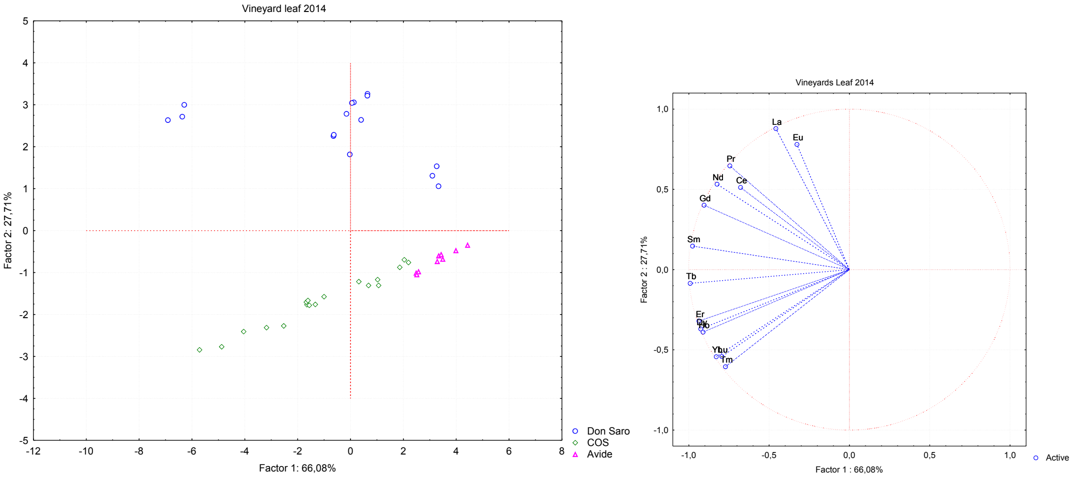
Collinear variables are those that have a great deal of redundancy or those highly correlated. In case of high linearity, you can create a new set of basis vector, this set will be connected with the changes in the data that will be used to create a new coordinate system. The principal components defines the variance based axes of the new coordinate system. The first principal component is formed by determining the direction of largest variation in the original measurement space. This can be represented as a line fitted by linear least square passing through the center of the data. The second largest main component, will pass through the center of the data and will be orthogonal to the first. The third in order of size, will also pass through the center of the data and will be orthogonal to the other two, and so on. Every major component describes different sources of information because it defines a different direction of the variance in the data.

The variance explained is a measure of the amount of information conveyed by each principal component and is called "eigenvalues". The main component are arranged in order of decreasing eingenvales. Each main component describes either an amount of signal and an amount of noise. The first principal component describes signal, whereas the last almost describes noise and very often this main component can be discarded (Lavine, 2015).

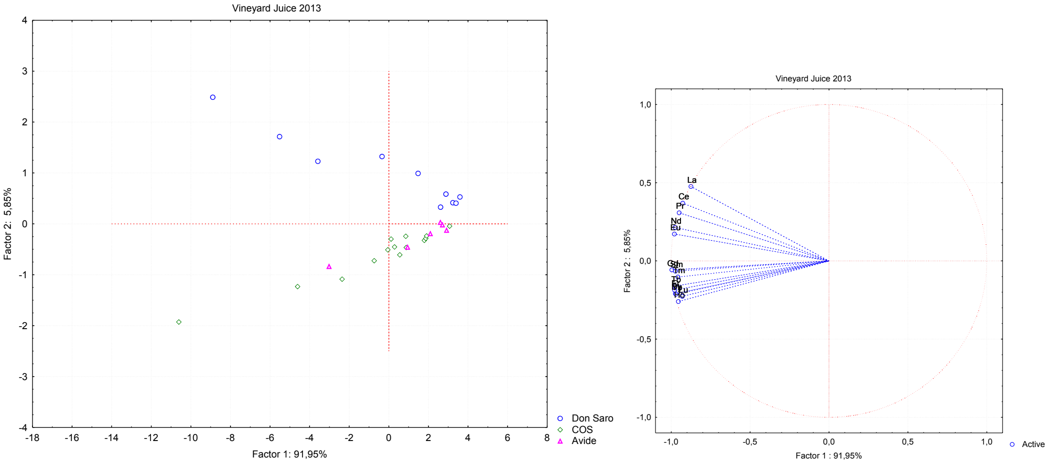
The PCA method is always performed prior to the application of discriminant methods, since it allows the simultaneous inclusion of information from all classes, allowing to easily subdivide them thanks to the discriminating methods (Brereton, 2011).

The PCA was performed on all of the collected organic samples. The comparison was even done for all of the covered categories: vineyards, soils, grape variety and cultivars.

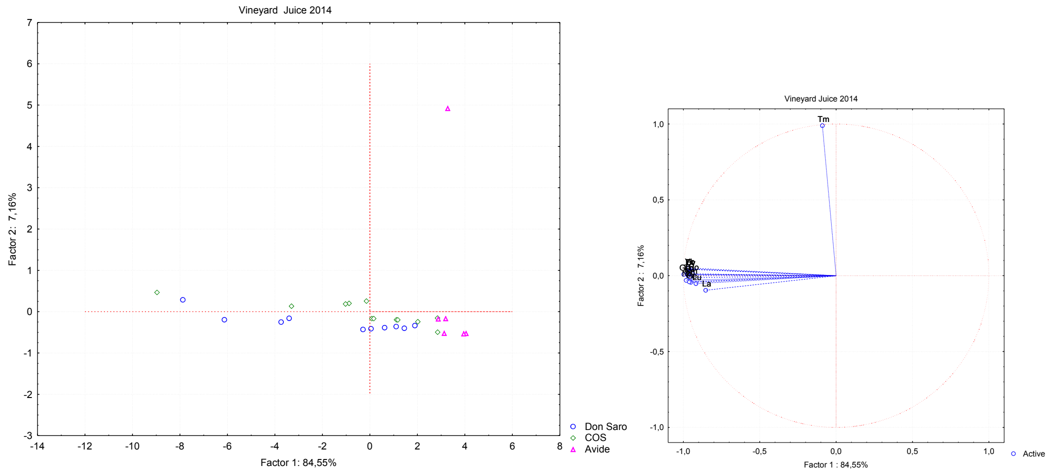
Consider first the comparison between the three vineyards:



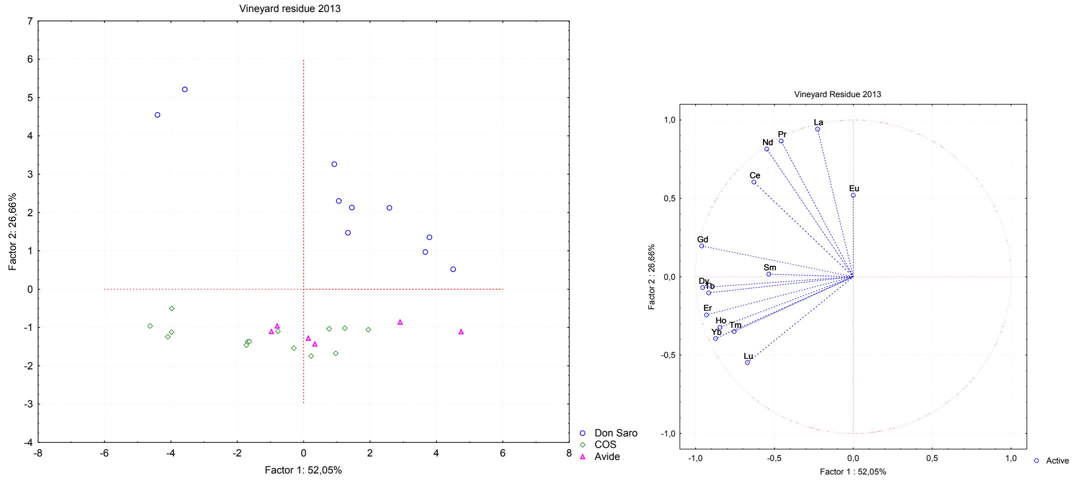
Graph 61 PCA vineyard Leaves 2014.



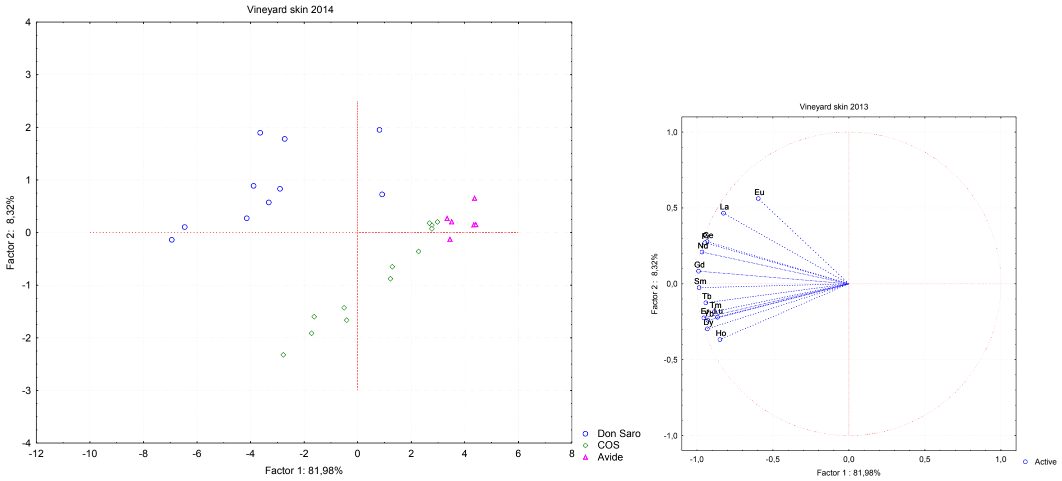
Graph 62 PCA Juice 2013 vs vineyard.



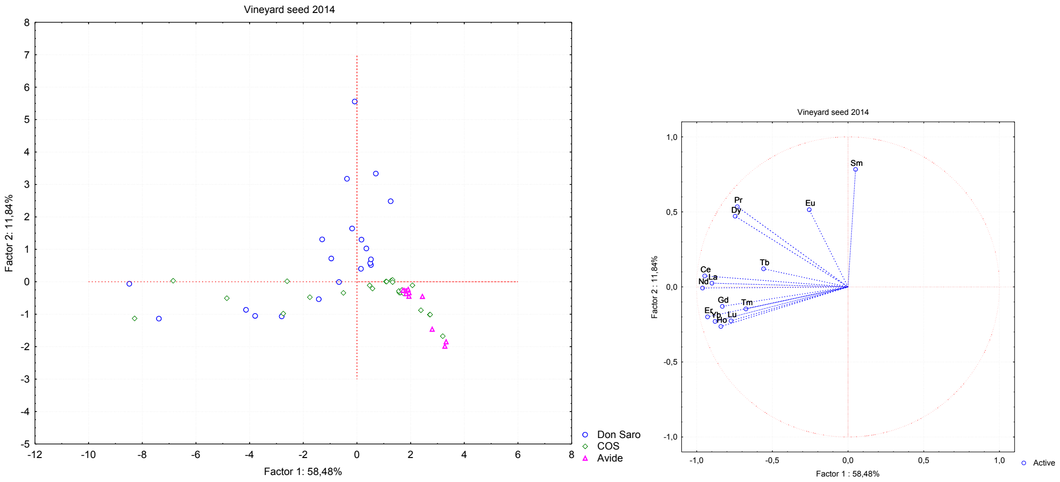
Graph 63 PCA Juice 2014 vs vineyard.



Graph 64 PCA Residue 2013 vs vineyard.



Graph 65 PCA Skin 2014 vs vineyard.



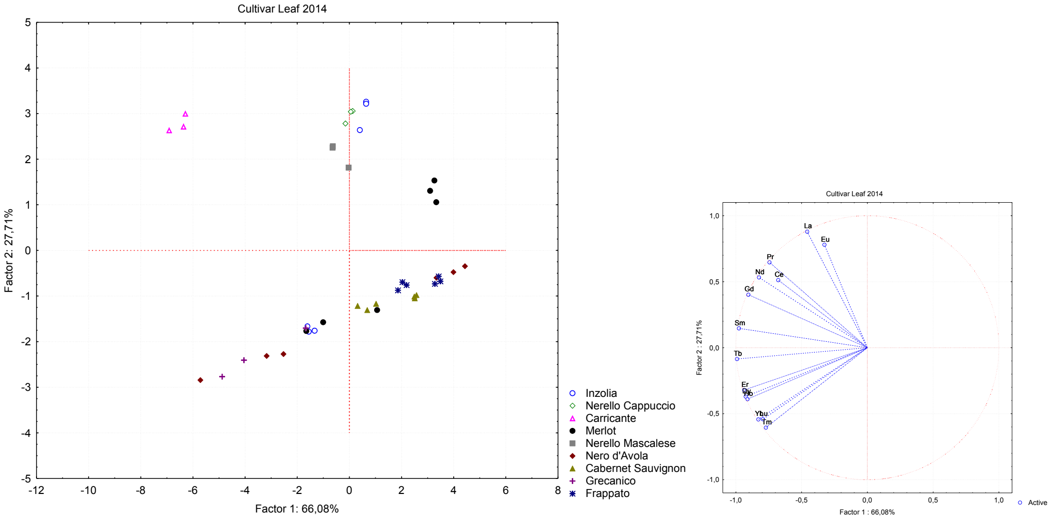
Graph 66 PCA Seeds 2014 vs vineyard.

As shown by the various graphs (graphs 61-65), the distinction among the two types of soil is perfectly respected, in fact the two cellars of the Hyblean Plateau (COS and Avide) completely differ from that one in the volcanic soil (Don Saro vineyard).

The best evidence of the distinction between the three vineyards is provided by samples of leaves and skins (graphs 61 and 65), from which the three vineyards are perfectly distinct. The samples of juice, 2013 and 2014 (graphs 62 and 73) and the remaining ones of 2013 (graph 64), always show the distinction between Don Saro and the other two vineyards, but the distinction between COS and Avid is not very clear, as can be seen from the graphs reported on graphs 62-64. In the samples of seeds (graph 66) the distinction among the vineyards is instead very confused, this is due to the fact that the seed samples have very low of REEs concentrations, and for some elements, such as the HREE concentrations are below the detection limits. PCA eliminate redundancy of data and the elements of which will be made this distinction are few, not allowing a clear discernment among the three vineyards on the basis of seeds sample.

The leaf samples were compared within the different types of cultivars, from the graph 67 it is seen that cultivars of the volcanic area are located at the top of the graph, while those of the Hyblean Plateau is located at the bottom of the axes. The samples of cultivars are gathered together in small groups, especially with regard to the samples volcanic. Is well known as the same cultivar grown in two different areas (Mount Etna and Hyblean Plateau) is placed in different parts of the graph 67. Take for example the Merlot, a black berry cultivar which is either cultivated in volcanic soils (Don Saro vineyard) and carbonate soil (COS vineyard): although the samples belong to the same cultivars, they plot in different parts of the graph 67.

The distinction of the cultivars is possible only if we take into account each individual vineyard, because provided that each cultivar absorbs the elements in a different way, the soil on which cultivars grow is crucial. Depending on the availability of the soil and on climate conditions, the same cultivars on different soils absorbs the elements in different way.

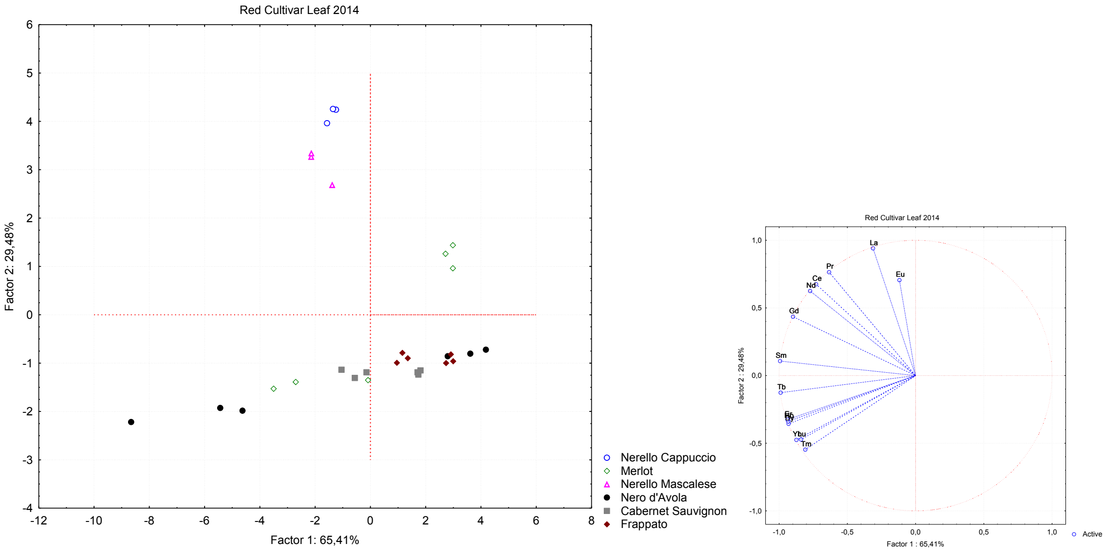


Graph 67 PCA Leaf 2014 vs cultivar.

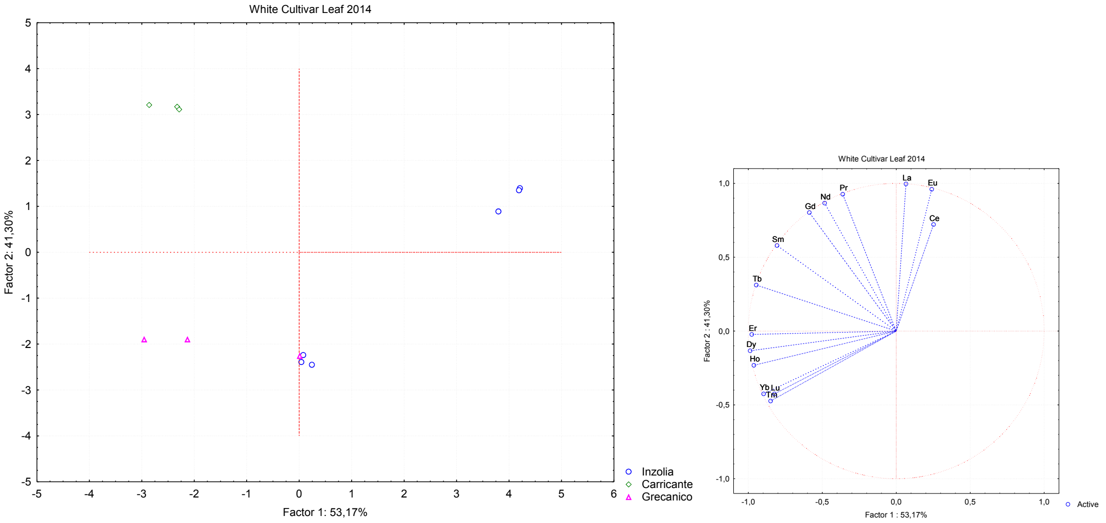
The following graph 68 pointed out a distinction among cultivars by taking into account only the red grapes. Frappato and Nero d'Avola are present in both vineyards of the Hyblean Plateau, then characterized by the same weather conditions and by the same type of land: after picture it is evident that the samples of the same cultivars plot close together. Nevertheless, the reasoning seems to not work for a cultivar, Nero d'Avola, which is grown in both vineyards of the Hyblean Plateau: as you can see in the graphs, sample plot far apart, probably there are some factors that affected this variety, which can be more sensitive than the other ones.

Cultivars Cabernet Sauvignon and Frappato (in the graph 68), belong to the same contest lithological (Hyblean Plateau), but the vineyards are different (COS and Avide vineyards), in this case the difference in plotting graphs is minimal, because the geological context it is the same, the two vineyards differ only a few kilometers.

In the case of white varieties, Inzolia (Ansonica) belongs to two different vineyards: Don Saro and COS, respectively and samples behave in the same way as those ones of Merlot as we can see in the graph 68. Despite the cultivar is the same, in the graph 68 is plotted in different parts of the graph because the geological context is different. The samples which are in the top of the graph 68, belong to the context of the volcanic basement of Don Saro, while those plotted in the lower part of that graph, belong to the lithological context of Hyblean Plateau (COS vineyard).



Graph 68 PCA Leaves 2014 vs red grape.



Graph 69 PCA Leaves 2014 vs white grape.

The same trend is also noticeable in the other samples (juices, skins, residues and seeds), whose samples reflect the same trend for the different organic samples taken into consideration.

However, no evident differentiation can be outlined between white and red grapes, since each type of cultivar behaves differently, no matter it is red or white.

Linear Discriminant Analysis (LDA)

Linear Discriminant Analysis (LDA), it is the first multivariate classification technique, developed by Fisher in 1936 (Fisher, 1936). This technique is based on the estimation of multivariate probability density functions, which are fully described by a minimum number of parameters, that is covariance and variances. It is based on the assumption that the probability density distributions are multivariate normal, with the same dispersion and correlation between variables with all categories in question.

The most famous formulation of LDA is that one given by the Fisher-Rao criterion, defining as:

$$J(V) = \frac{V^T A V}{V^T B V}$$

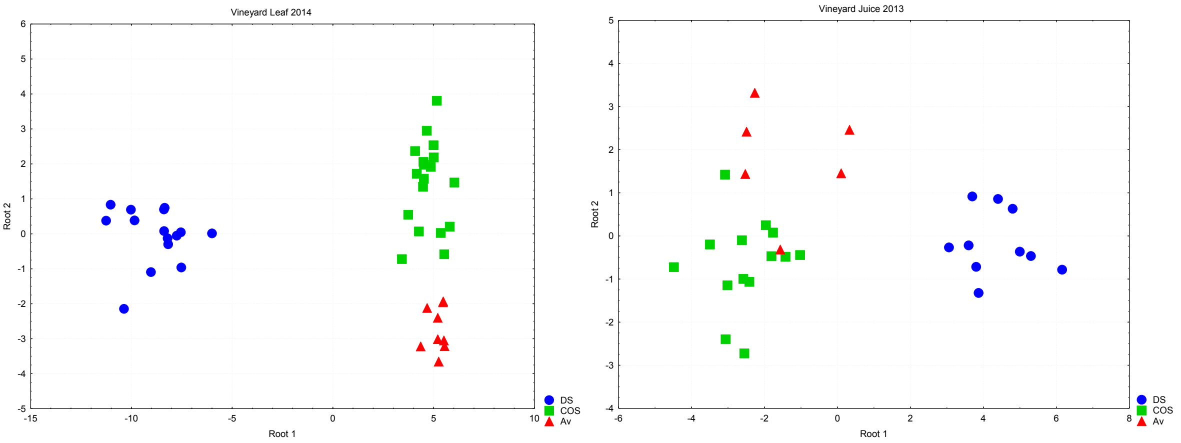
V are the discriminant feature vectors while A e B are two symmetric positive-definite matrices defining the metric to be maximized and minimized (Fisher, 1938) (Rao, 1948).

The main reason for the instability of JV) is due to the fact that some eigenvectors are associated to near-zero values. Some are due to their true underlying discriminant power, but other ones are caused by small noise in the observation. Ability to understand which are due to noise and what capabilities to discriminate is of utmost importance for the proper use of LDA. To work around this problem LDA was performed by following the PCA.

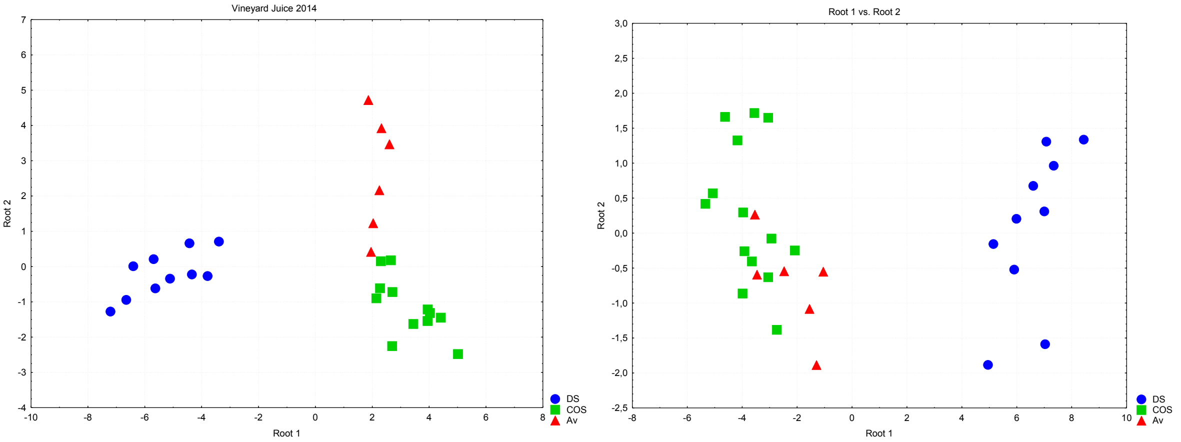
As it can be seen from the graphs set out in graphs 70-72 , plants belonging to the two types of soil (volcanic soil from the vineyard of Don Saro and carbonate soil of vineyards COS and Avide, respectively) are perfectly distinguishable.

Discrimination between the three vineyards is evident, as can be seen in the graph 70 (A), where they examined samples of leaves. The graph 70 (A) can also distinguish between the two types of soil, samples of Hyblean Plateau vineyards (COS and Avid), are plotted opposite to the samples of volcanic soil (vineyard Don Saro).

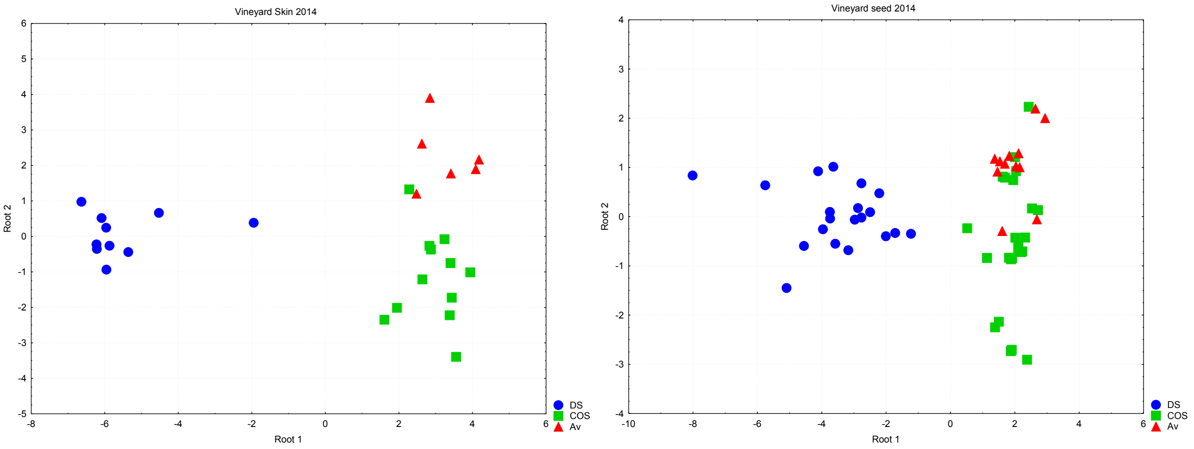
Similarly the samples of juice show (graphs 70 B and 71 A), they too, this net difference, as also the skims (graph 72 A), although to a lesser degree. From the graphs on the residue 2013 samples of seeds and 2014 (graphs 71 B and 72 B), the difference between the vineyards COS and Avide is not noticeable, whereas it remains clear the distinction between the two types of soil, carbonate and volcanic, respectively. The concentrations of the residues and of seeds do not allow us to make the distinction, despite the use of PCA and LDA approaches.



Graph 70 (A)LDA leaves 2014 vs vineyard, (B) LDA juice 2013 vs vineyard.



Graph 71 (A) LDA juice 2014 vs vineyard, (B) LDA residue 2013 vs vineyard.



Graph 72 (A) LDA skims 2014 vs vineyard, (B) LDA seeds 2014 vs vineyard.

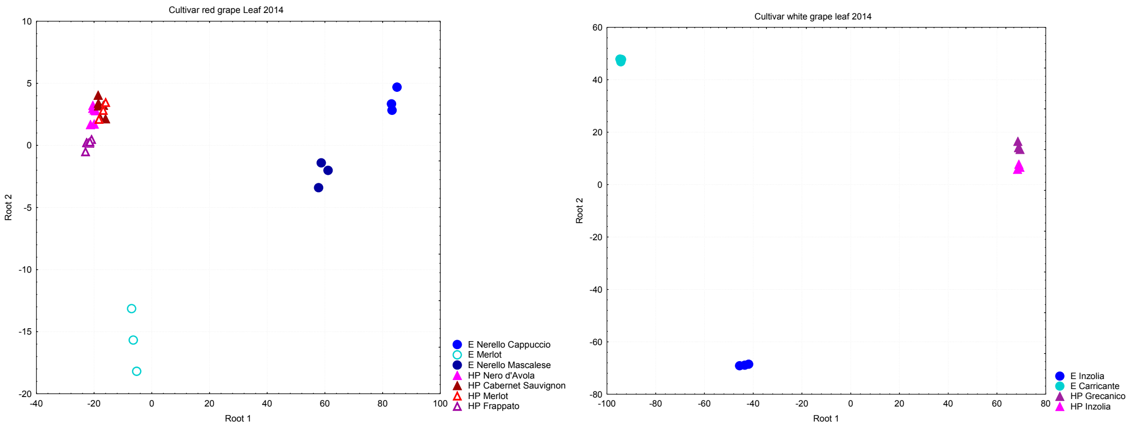
LDA approach was used to compare the cultivars with red berries and white. The results are different than those ones obtained with the PCA; indeed, in the graphs relating to the samples of leaves in graphs 73 A and B, there is marked distinction between the different cultivars, and also those ones belonging to the vineyard with a different type of soil appear closely grouped. This clear distinction was not so evident with PCA. The difference between the cultivars is most evident in the cultivars of vineyard Don Saro.

These satisfying results are maintained in the other parts of the plant; in the samples of juice of 2013 (graphs 74 A and B).

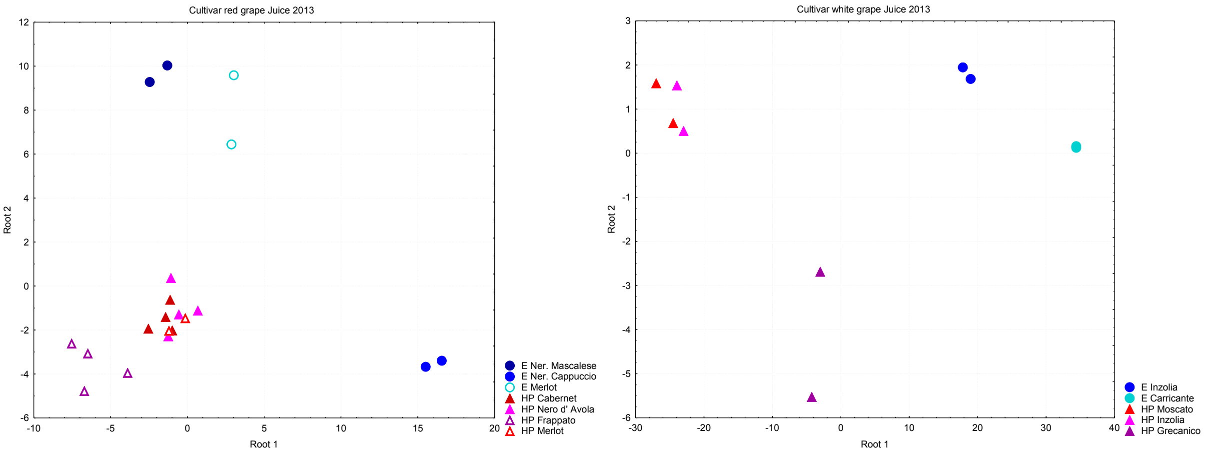
In juices of 2014, the variance between white grape is so small that it was not possible to obtain the LDA graph; while on the graph of red grapes notice the difference between the cultivars.

In particular, we can highlight the grape variety Merlot (graphs 73 A, 74 A and 75 A) that is grown in two different soil, the samples show significant differences in the absorption of REE allowing us to discriminate the area where the plants were grown.

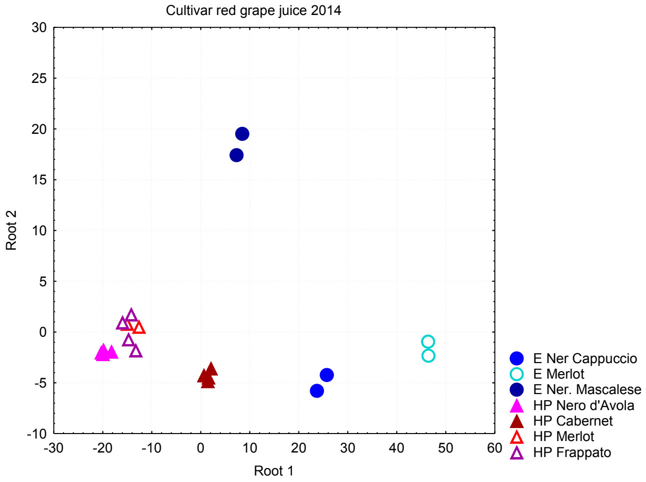
If we look at the graphs of the white grape cultivars, Inzolia, which is also present in the two different types of land, shows the same behavior shown by samples of Merlot as you can see in the graphs 73 B, 74 B and 75 B.



Graph 73 LDA leaves 2014 vs red grape (A), LDA leaves 2014 vs white grape (B).



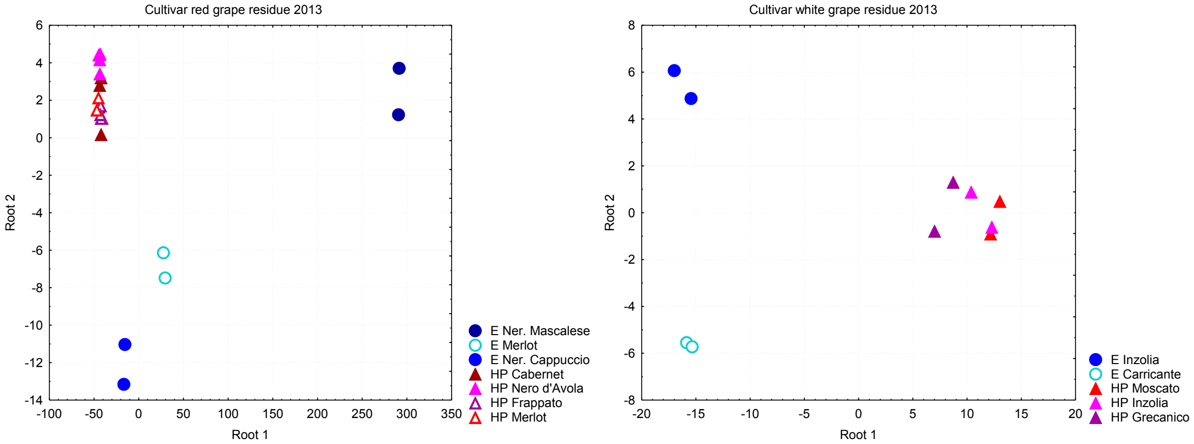
Graph 74 LDA juice 2013 vs red grape (A), LDA juice 2013 vs white grape (B).



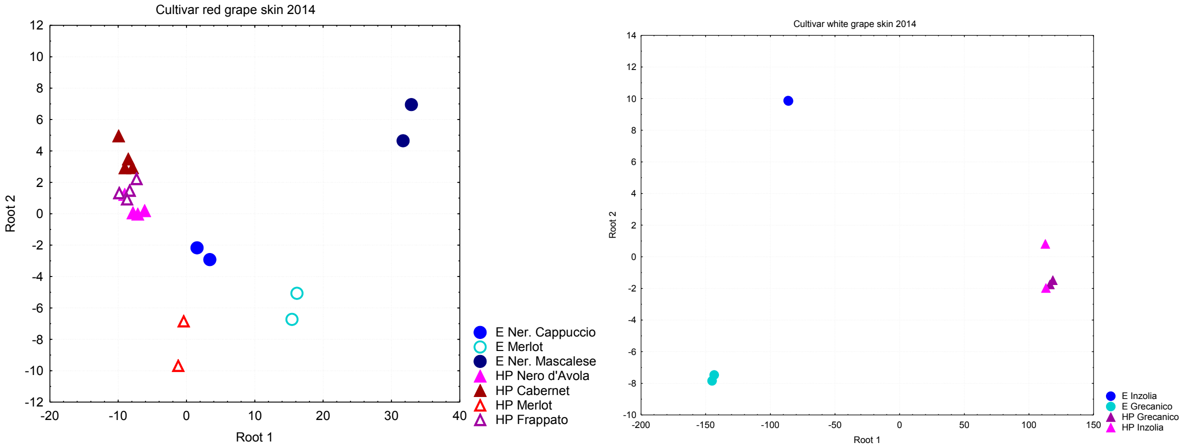
Graph 75 LDA juice 2014 vs red grape(A), it has not been possible to obtain the graph for the little variance for LDA juice 2014 vs white grape .

Samples of residual of 2013 (graphs 76 A and B) show good results where the different cultivars are located close to each other. It always notice the difference between Merlot and Inzolia belonging to the two areas, demonstrating how it is possible to identify the area where the plant is grown.

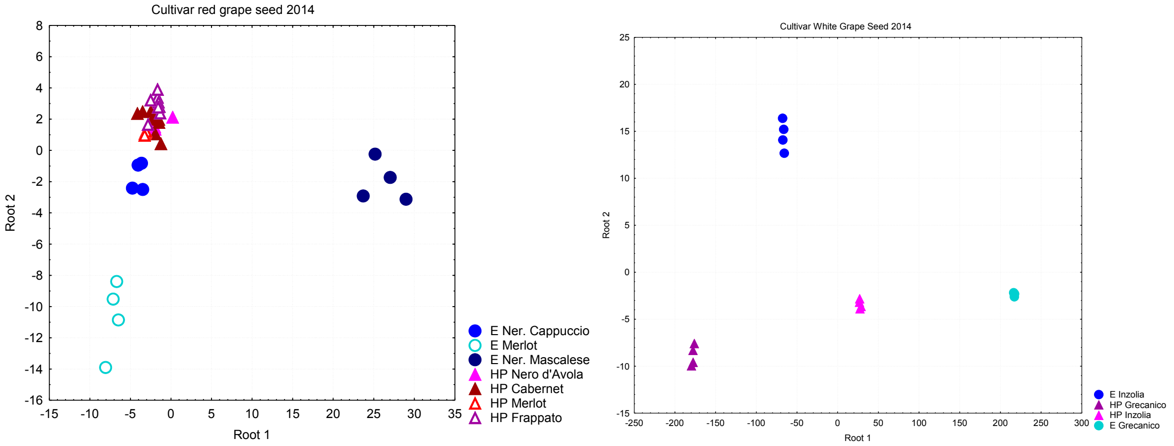
The skins again show a deterioration of the conditions as can be seen in the graphs of both the red and white variety, in the graphs 77 A and B, the difference between the same cultivars of two different areas is slightly lower than that found in graphs previously seen.



Graph 76 LDA residues 2013 vs red grape (A), LDA residues 2013 vs white grape (B).



Graph 77 LDA skins 2014 vs red grape (A), LDA skins 2014 vs white grape (B).



Graph 78 LDA seeds 2014 vs red grape (A), LDA seeds 2014 vs white grape (B).

The seed samples in the graphs 78 A and B, show the same differences between samples of cultivar Merlot, Inzolia and Grecanico that belong to different sampling areas, although in this case the variables that have allowed the differentiation between the cultivars to obtain the graph only include LREEs, since the values are too similar measure it regards the MREEs and HREEs.

To use the approach LDA, for the differentiation of cultivars, we have considered only some REEs, but the scarcity of elements considered due to the little difference in concentration between the REEs, makes these results not very reliable, especially with regard to samples with low concentrations of REEs as the seeds, skins and residues.

Instead the LDA approach is very useful for the discrimination of the three vineyards and the type of soil, view the graphs 70-72, in fact, these charts have been taken into consideration all the REEs.

7.Conclusions

In the present PhD thesis, the Rare Earth Elements functionality was investigated in order to assess whether they can be used as territorial markers on vine plants, so as to expand the methods used to prevent counterfeiting of the production areas of the wine, a product, whose ever-growing demand from developing countries, means that it is more and more subject to fraud and its territoriality must be preserved, as “made in Italy”.

The chemical composition of wine is influenced by many factors (i.e. grape variety, soil climate, agricultural practices, wine making practices, transport and storage), difficult to analyze all together, so we focused on the grapevine, looking for the criteria, if any, useful for grape varieties identification. By treating both authentication, namely, discriminated food of the same type, but different in their geographical origin, botany, variety, and is traceability, which connects to the food with the soil from which the raw material have been product.

Two areas of eastern Sicily were chosen, characterized by type of soil and content of REE extremely different from each other: A) the Comiso in Hyblean Plateau area; and B) the Linguaglossa area located at Mount Etna.

The soils of the Hyblean Plateau are sedimentary carbonate type whereas Etnean soils are of volcanic origin. The REEs content in the two areas is very different, being the volcanic soils rich in REEs, especially Light Rare Earth Elements (LREEs).

To evaluate the absorption of REEs in plants, a chemical analysis of the characteristics of the soil and also the parent rock was initially carried out, the Rare Earth Elements concentration in the soil, using grain size analysis, XRF and ICP-MS.

The Mount Etna soil is a andosoil, derived from volcanic rock, rich in REE, particularly Light Rare Earth Elements; normalized patterns of REEs pointed out a positive europium anomaly, which is of primary derivation due to plagioclase content in the parent rock. The Hyblean Plateau soil, is a carbonate soil with a terrigenous component; the content of REEs is lower than the values measured in the Etna soils, there is not a clear fractionation between LREE, HREE and MREE. The terrigenous component is the cause of the positive europium anomaly. The negative anomaly of cerium instead is typical of carbonate rocks, and due to the presence of calcium and magnesium.

Sampling was carried out into two years, 2013 and 2014, by following there criteria: in 2013 the organic samples were divided into juice and residue; the following year, 2014, it was decided to expand the organic samples, to observe more precisely the absorption of REEs, and the organic samples were divided into leaves, juice and the remaining was divided into the skins and seeds.

Each type of organic sample, due to differences in its nature (leaves, residue, seeds, juice and skin), was treated in a manner appropriate for ICP-MS investigation, as discussed in Chapter 4.

We selected both autochthonous (Frappato, Nerello Mascalese, Nerello Cappuccio, Nero d'Avola, Carricante, Grecanico, Inzolia, Moscato), and allochthonous (Cabernet Sauvignon and Merlot) cultivars, the choice was done to observe any possible difference in absorption of REEs, the selection includes both red grape and white grape cultivar, to observe whether the color of the grape variety has any influence on absorption.

Result showed that the measured concentrations of REEs in the organic component of vine plants (juice and remaining for harvest in 2013; juice, skins, seeds, and leaves for the harvest of 2014), considering plants grown on the same type of soil, differ depending on the part of the plant considered. The part of the plant which highest absorb REEs are the leaves, followed by juices, residues, skins, and finally seeds.

The differences between the two areas not only consist in the composition of the soil (i.e. carbonate and volcanic type), but also in climatic conditions, since the Hyblean Plateau area is characterized by an arid climate type, while the Etna area is characterized by a temperate climate.

The climatic conditions affect the absorption of REEs by plants, indeed, by relating the average REEs absorbed plant to average REEs concentration of soil, it is clear that the plants grown in arid climatic conditions of the Hyblean Plateau absorb the REEs from the soil to a greater extent compared to plants grown in a temperate climate, characterized by higher rainfall and lower temperature, as Mount Etna climate.

In fact, despite the measured concentrations of REEs in soil are greater Mount Etna, REEs plants absorb from the soil at a lesser extent than the grapevine plants of the Hyblean Plateau.

The characterization of the soil and of the organic samples, taken from different parts of the analyzed cultivars, allowed us to discriminate, through the concentrations of REEs analyzed, to which of the two soil types the plants belong.

Moreover, by comparing the average REEs patterns of organic samples, it was observed that the absorption of the plants depends not only by soil composition but even by climatic conditions.

Of the analyzed plant parts that show differences in the absorption of REEs, the leaves show the highest concentrations, even the juices have high values of REEs (although lower than those ones found in the leaves samples), the absorption is rather low in residue and skins samples, while in seeds samples concentrations are extremely low.

Comparing the same type of cultivars bred in different environments can be seen other differences, there are differences in the concentration of REEs between cultivars Frappato, Cabernet Sauvignon and Nero d'Avola bred on vineyards and COS Avide of the Hyblean Plateau.

The comparison was also done between cultivars belonging to different environments; Inzolia and Merlot are two cultivars bred both on the vineyard of Don Saro, with a component of the soil of volcanic origin, and in the vineyard of COS, whose soils are derived from carbonate. The comparison showed that depending on the content of REEs it is possible to distinguish the area where the plants were grown.

In order to get as much information as possible from the data obtained, a statistical approach was carried out for further discrimination. The approaches used are Box Plots, Principal Component Analysis (PCA), Linear Discriminant Analysis (LDA).

The statistical approaches confirm for the most part when stated before, and also add some new information. The Mann-Whitney Test says that the organic samples (i.e. leaves, juice, residues, skins and seeds) can be distinguished according to the the soils on which they grow based on the content of Light Rare Earth Elements (LREEs). The LREEs allow us to determine whether the soil, the vineyard of origin, thanks to Box Plot, elements that allow this distinction are lanthanum and neodymium.

The Principal Component Analysis, allows us to better distinguish between the two types of land, while the Linear Discriminant Analysis allows us to distinguish the vineyard of origin of the organic grapevine samples. The part which best allow you to make the distinction are the leaves and juices, which have higher REEs concentrations than other parts. The differences between the various cultivars are also highlighted, differentiating among cultivars grown in different environments.

Ultimately, it is thus possible to distinguish, based on the content of Rare Earth Elements, the area of origin where vine plants grew. The search should be extended to other types of terrain, and vineyards in another region to observe differences due to the climate as well as the type of soil, a database should be created and used to establish an unique geographical territoriality of food products.

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Appendix

Soil

	SiO_2%	TiO_2%	AL_2O_3%	Fe_2O_3%	MnO%	MgO%	CaO%	Na_2O%	K_2O%	P_2O_5%
Don Saro	49,49	1,8	19,83	10,35	0,19	3,17	7,86	3,92	1,87	0,85
COS	73,69	0,33	9,29	3,66	0,09	0,83	6,14	0,48	1,62	0,13
Avide	69,77	0,58	13,69	5,1	0,07	1,22	4,24	0,37	2,24	0,16

Table 11 Vineyards average soil major elements (wt%), the values are the average of 31 samples, 11 Don Saro, 11 COS and 9 Avide vineyard, respectively.

	Ba	Ce	Co	Cr	Cu	Ga	Hf	La	Nb	Nd	Ni	Pb	Rb	S	Sc	Sr	Th	V
Don Saro	947	168	30	56	136	27	9	80	60	76	14	18	34	3163	16	1022	12	221
COS	253	28	10	33	28	7	6	21	7	15	18	14	39	2330	11	92	4	37
Avide	250	35	10	42	30	9	9	25	11	20	18	15	45	1532	11	93	5	49

Table 12 Vineyards average soil minor elements (ppm), the values are the average of 31 samples, 11 Don Saro, 11 COS and 9 Avide vineyard, respectively.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Don Saro	2,918	2,608	2,326	2,302	2,167	2,857	2,221	1,707	1,269	1,125	1,071	1,237	1,049	1,016
COS	0,693	0,688	0,68	0,698	0,773	0,865	0,821	0,753	0,625	0,583	0,563	0,68	0,584	0,568
Avide	0,696	0,681	0,656	0,656	0,699	0,752	0,739	0,65	0,533	0,496	0,487	0,603	0,524	0,514

Table 13 Vineyards average REES the value are normalized to Upper Crust (Rudnick R L & Gao S, 2003), the values are the average of 31 samples, 11 Don Saro, 11 COS and 9 Avide vineyard, respectively.

Rock

	SiO_2%	TiO_2%	Al_2O_3%	Fe_2O_3%	MnO%	MgO%	CaO%	Na_2O%	K_2O%	P_2O_5%
Hyblean Plateau	10,06	0,12	4,54	0,14	0,01	2,52	46,46	0,24	0,54	0,11
Mount Etna	52,61	1,63	18,25	9,15	0,17	1,45	6,47	5,58	3,01	0,80

Table 14 Parent rock major elements average (wt%), the values are the average of 17 samples, 10 Hyblean Plateau and 7 Mount Etna, respectively.

	Sr	**V**	**Cr**	**Co**	**Ni**	**Zn**	**Rb**	**Y**	**Zr**	**Nb**	**Ba**	**La**	**Ce**	**Pb**	**Th**
Hyblean Plateau	1334	29	30	5	33,5	29,5	11,7	11,5	12,5	-	227,3	15	20	2,6	0,7
Mount Etna	1110	143	-	14	5	99,4	48	29	262	63,8	1219	108	218,0	3,6	14

Table 15 Parent rock minor elements average (ppm), the values are the average of 17 samples, 10 Hyblean Plateau and 7 Mount Etna, respectively.

	La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Hyblean Plateau	0,30	0,22	0,30	0,31	0,36	0,42	0,41	0,39	0,35	0,37	0,36	0,47	0,38	0,41
Mount Etna	2,84	3,07	2,29	2,25	2,10	2,80	2,42	1,69	1,24	1,15	1,07	1,33	1,08	1,12

Table 16 Parent rock average REES, the value are normalized to Upper Crust (Rudnick R L & Gao S, 2003), the values are the average of 17 samples, 10 Hyblean Plateau and 7 Mount Etna, respectively

Harvest 2013

Juice

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Don Saro	0,00021	0,00017	0,00017	0,00016	0,00021	0,00016	0,00016	0,00016	0,00016	0,00016	0,00016	0,00013	0,00014	0,00012
COS	0,00042	0,00042	0,00041	0,00044	0,00064	0,00045	0,00053	0,00048	0,0005	0,00048	0,00044	0,00036	0,00038	0,00028
Avide	0,00025	0,00027	0,00029	0,0003	0,00045	0,00033	0,00035	0,00037	0,00035	0,00034	0,0003	0,0002	0,00026	0,00019

Table 17 Juice average REEs, the values are normalized to the average concentration of the soil of the respective vineyard, the value are average of 30 samples, 10 Don Saro, 14 COS and 6 Avide, respectively, two for cultivar.

Residue

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Don Saro	0,00019	0,00005	0,00009	0,00008	0,00007	0,00023	0,00007	0,00006	0,00005	0,00005	0,00005	0,00003	0,00004	0,00001
COS	0,00016	0,00014	0,00015	0,00015	0,0003	0,00042	0,00023	0,00021	0,00017	0,00019	0,00017	0,00021	0,00016	0,00021
Avide	0,00012	0,0001	0,00012	0,00012	0,00019	0,00053	0,00019	0,00017	0,00014	0,00017	0,00014	0,00017	0,00013	0,00018

Table 18 Residues average REEs, the values are normalized to the average concentration of the soil of the respective vineyard, the value are average of 30 samples, 10 Don Saro, 14 COS and 6 Avide, respectively, two for cultivar.

Harvest 2014

Leaves

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Don Saro	0,0081	0,0019	0,0035	0,0031	0,0024	0,0055	0,0034	0,0025	0,0021	0,0022	0,0022	0,0015	0,0016	0,0016
COS	0,0051	0,0050	0,0055	0,0059	0,0064	0,0072	0,0068	0,0066	0,0066	0,0065	0,0062	0,0058	0,0054	0,0051
Avide	0,0025	0,0023	0,0026	0,0029	0,0032	0,0048	0,0035	0,0034	0,0033	0,0032	0,003	0,0031	0,0026	0,0025

Table 19 Leaves average REEs, the values are normalized to the average concentration of the soil of the respective vineyard, the value are average of 42 samples, 15 Don Saro, 18 COS and 9 Avide, respectively, three for cultivar.

Juice

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Don Saro	0,00011	0,00009	0,00009	0,00009	0,00011	0,00009	0,00012	0,0001	0,0001	0,00011	0,0001	0,00012	0,0001	0,00011
COS	0,00017	0,00017	0,00018	0,0002	0,00025	0,00021	0,00025	0,00023	0,00022	0,00024	0,00022	0,00022	0,0002	0,00018
Avide	0,00005	0,00005	0,00006	0,00006	0,00019	0,00008	0,00008	0,00009	0,00007	0,00009	0,00007	0,00009	0,00006	-

Table 20 Juice average REEs, the values are normalized to the average concentration of the soil of the respective vineyard, the value are average of 28 samples, 10 Don Saro, 12 COS and 6 Avide, respectively, two for cultivar.

Skin

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Don Saro	0,00021	0,00011	0,00013	0,00012	0,00011	0,00025	0,00013	0,00012	0,00012	0,00012	0,00013	0,00013	0,00013	0,00014
COS	0,00012	0,00012	0,00014	0,00015	0,00017	0,0002	0,00018	0,00018	0,0002	0,00019	0,00018	0,00013	0,00016	0,00014
Avide	0,00003	0,00005	0,00004	0,00005	0,00006	0,00012	0,00006	0,00007	0,00008	0,00011	0,00007	-	0,00006	-

Table 21 Skins average REEs, the values are normalized to the average concentration of the soil of the respective vineyard, the value are average of 28 samples, 10 Don Saro, 12 COS and 6 Avide, respectively, two for cultivar.

Seed

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Don Saro	0,00009	0,00003	0,00006	0,00003	0,00103	0,00094	0,00006	-	0,00004	0,00007	0,00007	0,00007	0,00005	0,00024
COS	0,00008	0,00008	-	0,00006	0,00034	0,00028	0,00009	-	0,00003	0,00012	0,00009	0,00005	0,00008	0,00024
Avide	-	-	-	-	0,00028	0,00004	-	-	-	-	-	-	-	-

Table 22 Seeds average REEs, the values are normalized to the average concentration of the soil of the respective vineyard, the value are average of 56 samples, 20 Don Saro, 24 COS and 12 Avide, respectively, four for cultivar.