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# $^{87}$SR/$^{86}$SR ISOTOPIC CHARACTERIZATION AS A TOOL FOR THE DESIGNATION OF ORIGIN AND GEOGRAPHICAL INDICATION: APPLICATION TO VOLCANIC ROCKS, SOILS, LEAVES, GRAPES AND WINES FROM BRAZIL AND ITALY

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*"O pessimista reclama do vento, o otimista espera que ele mude, o realista ajusta as velas"*

Unknown author

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# ABSTRACT

Science advances, an increased interest by consumers in the origin of the products they are buying, as well as the multifunctionality of research groups have increased the recent number of publications focusing on the use of strontium isotope ratios ($^{87}Sr/^{86}Sr$) as a geographic tracer of agri-food products. Determining the geographical origin of wines using Sr isotope composition has been made within the last three decades in many countries, including Italy, South Africa, Romania, Canada, Portugal, Argentina, France, Chile, China, Kosovo, U.S.A., and Australia. The method is based on the principle that plants absorb bioavailable elements from the soils they are growing on, inherently carrying information related to their corresponding geology settings. Due to their similar valence and ion radius, Sr behaves similarly to calcium (Ca) in many geological and biological processes, and they can thus substitute one for the other. Strontium is first absorbed by the roots of the plants, then passes to the grapes and finally to the produced wine, without any isotope fractionation compared to the initial $^{87}Sr/^{86}Sr$ value in the soil and rocks. Thus, the analysis of the Sr isotope ratio in the final product (i.e., wine) directly correlates to its geological origin. The present work aims at using the $^{87}Sr/^{86}Sr$ systematics to authenticate wine origin in volcanic districts from Italy (Ponza Island, Ventotene Island, Somma-Vesuvio, Salina Island, Mount Etna, and Pantelleria Island) and Brazil (Vale dos Vinhedos). Nine soil samples, 9 grape samples, 9 leaf samples and 9 bottled wine samples from 6 different wine producers in Italy and 3 soil samples, 3 grape samples and 3 leaf samples from 3 different wine producers in Brazil have been sampled, during the 2018 harvest. Additionally, a study of a soil profile in the Somma-Vesuvio area was performed, including a detailed $^{87}Sr/^{86}Sr$ characterization of the various soil horizons as well as of parts of the grapevine (root, steam, grape, grape pulp, grape seed and grape skin). Soil characterization from Italian sites has also been used in order to better understand the complex equilibria in the soil-plant chain. The results indicate that the analyzed samples from different districts can be actually distinguished from each other based on $^{87}Sr/^{86}Sr$ values.

## OUTLINE OF THE THESIS

This thesis consists of five chapters: Introduction (Chapter 1); Characterizing wine *terroir* using strontium isotope ratios: a review (Chapter 2); $^{87}$Sr/$^{86}$Sr characterization as a tool for authenticating the geographical origin: application to bottled wine, microvinification, grape, leaf and soil samples in volcanic vineyards from Italy (Chapter 3); $^{87}$Sr/$^{86}$Sr characterization of cabernet sauvignon microvinification, leaf and soil samples in volcanic vineyards from Vale dos Vinhedos, south Brazil (Chapter 4); Conclusions (Chapter 5).

Chapter 1 provides the setup for the entire thesis and contains background information about food traceability and how $^{87}$Sr/$^{86}$Sr values can be applied to the characterization of wines.

Chapter 2 presents the main body of this thesis. During a first stage of this research project, a thorough bibliographic research was performed aimed at gathering all the available information about the published research papers presenting $^{87}$Sr/$^{86}$Sr data on wine samples, focusing on wines from 12 different countries, and totaling 695 $^{87}$Sr/$^{86}$Sr analyses. These data have been used to develop a georeferenced database which is currently being elaborated and critically revised in a review article that will be submitted for publication soon.

Chapters 3 and 4 contain the analytical results, respectively for wine samples from Italy and Brazil.

Chapter 3 presents $^{87}$Sr/$^{86}$Sr characterization for soil (labile fraction and bulk), bottled wine, microvinification, grape and leaf samples from vineyards grown in the volcanic districts of Ponza Island, Ventotene Island, Mount Somma-Vesuvio, Salina Island, Mount Etna and Pantelleria Island. Soil characterization was carried out through XRPD, HCl test, pH, organic matter, and CEC. In addition, a detailed study of a soil profile in the Mount Somma-Vesuvio area was carried out, including the Sr isotopic characterization of the different soil horizons and different parts of the grapevine (root, steam, grape, grape pulp, grape seed, and grape skin).

Chapter 4 contains the $^{87}$Sr/$^{86}$Sr characterization of cabernet sauvignon microvinification, leaf and labile fraction soil samples from 3 vineyards from Vale dos Vinhedos, south Brazil. This the first study carried out using the Sr isotopic technique applied to Brazilian wines.

Chapter 5 is a concluding section summarizing the general conclusions from this thesis.

# Chapter 1 – INTRODUCTION

## INTRODUCTION

Determining the geographical origin of a wine is of particular interest as it is one of the most important factors that contribute to its commercial value in the world market and to the recognition of a specific *terroir*. The term t*erroir* indicates the complex interplay of geology, soil, climate, and viticulture, all of which influence the character and quality of a wine from a given grape variety, rootstock and viticultural practice (Seguin, 1986; Meinert, 2018). The *terroir* impacts the taste of grapes wines, which elevates the reputation of the wine and even of a region. It is related to the French system of *Appellation d'Origine Contrôlée* (AOC, denomination of controlled origin), used as a model for wine designation and regulation worldwide, thus being considered as a fundamental indication of quality.

The authenticity of a *terroir* has been a major concern that has challenged researchers to develop reliable technologies for food traceability purposes, due to the increasing demand for quality and safety of food and beverages.

In 2002, the European General Food Law defined traceability as “The ability to trace and follow a food, feed, food-producing animal or substance intended to be, or expected to be incorporated into a food or feed, through all stages of production, processing and distribution” (EU, 2002). Olsen and Borit (2013) defined traceability as “The ability to access any or all information relating to that which is under consideration, throughout its entire life cycle, by means of recorded identifications”.

In the last few decades, the study of traceability has gained recognition with the increase in food frauds. Food fraud is a global problem that involves all steps in the food chain, including products and materials. Food fraud is described by Spink and Moyer (2011) as “A collective term used to encompass the deliberate and intentional substitution, addition, tampering, or misrepresentation of food, food ingredients, or food packaging; or false or misleading statements made about a product for economic gain”.

Fraudulence acts are not a novelty, and several records have been identified even in ancient times. Food adulterations were widespread since the antiquity, as evidence has been found about Roman merchants selling adulterated olive oil and wine. For the poor and middle class of Rome, local bar establishments seemed to have an unlimited supply of the prestigious Falernian wine for unusually low prices. In this context, Roman civil law included decrees against commercial fraud or contamination of food such as watering of wine or adding of sweeteners (Holmberg, 2010).

The problem of determining the geographical origin of beverages and foods has been widely discussed in the last three decades in many countries and several analytical techniques have been employed, including isotope analyses (e.g., Gremaud et al., 2004; Suhaj and Korenovska, 2005; Kelly et al., 2005; Rodrigues et al., 2011).

Among these latter, the application of strontium isotope systematics, expressed through variations of the $^{87}$Sr/$^{86}$Sr ratio, has proved to be a valuable tool for tracking the origin of different agricultural products (Stewart and Chadwick, 1998; Oda and Hirata, 2002; Kawasaki et. al., 2002; Franke et al., 2008; Ghidini et al., 2006; Berglund et. al., 2011), along with wine (Horn et al., 1993; Wolff-Boenisch, 1998; Barbaste et al., 2001, 2002; Almeida and Vasconcelos, 2001, 2004; Boari et al., 2008; Vorster et al., 2010; Di Paola-Naranjo et al., 2011; Marchionni et al., 2013, 2016; Mercurio et al., 2014; Martins et al., 2014; Durante et al., 2015, 2018; Petrini et al., 2015; Tedeschi et al., 2015; Vinciguerra et al., 2015, 2016; Geana et al., 2017; Bora et al., 2018; Braschi et al., 2018; Epova et al., 2019; Catarino et al., 2019; Guibourdenchen et al., 2020).

In wine traceability studies, strontium isotope ratios in soil-plant system are extremely important for geographic determination (Mercurio et al., 2014; Marchionni et al., 2013, 2016). The soil-wine connection seems to have some support in the fact that many wines possess some “chemical fingerprints” that can be used to trace their origin (Taylor et al. 2002; Greenough et al. 2005; Koundouras 2018; Meinert, 2018). Elements within the soil are absorbed by the roots of the plants, thus passing to the grapes and wines with the same isotopic ratio as they occur in the soil and rocks (Mercurio et al., 2014: Petrini et al., 2015; Vinciguerra et al., 2015, 2016; Bora et al., 2018; Braschi et al., 2018**)**. As a consequence, by analyzing the isotopic ratio of a final product (wine), it is possible to infer its geological origin. The soil provides water, minerals, and anchorage to the vine, as well as a specific temperature regime in the root zone (Leeuwen and Rességuier, 2018). The mineral portion of a soil is responsible for the supply of chemical nutrients (mainly N, P, K, Mg, Ca Fe, B, Mn and Zn; **Figure 1.1**) to the plants.

Strontium is a very reactive lithophile metal that quickly oxidizes (Nielsen, 2004). It naturally occurs as $Sr^{2+}$, which might substitute for $Ca^{2+}$ in a variety of rock-forming minerals such as feldspars, gypsum, apatite and, more importantly, calcite and dolomite (e.g., Waight, 2013).

Strontium has four naturally occurring stable isotopes whose abundances range from 0.55 to 0.58% for $^{84}$Sr, from 9.75 to 9.99% for $^{86}$Sr, from 6.94 to 7.14% for $^{87}$Sr, and from 82.3to 82.8% for $^{88}$Sr (Berglund and Wieser, 2011). $^{87}$Sr is the only stable isotope of strontium that is radiogenic. The radioactive decay of $^{87}$Rb (half-life 9.23 x $10^9$ years; Audi, 2012) to the radiogenic $^{87}$Sr leads to an increase in the natural relative abundance of the last, which is more significant for both higher concentrations of Rb and age of a system. Therefore, the quantity of $^{87}$Sr in nature has progressively increased, with the consequent increase of the $^{87}$Sr/$^{86}$Sr ratio. The $^{87}$Sr/$^{86}$Sr ratio of every geological formation is thus a function of the age of the rock and its initial Rb/Sr ratio. Consequently, $^{87}$Sr/$^{86}$Sr is considered a valuable tracer of strontium in rocks and minerals since it can be related to their Rb/Sr (De Souza et al., 2010), providing valuable information on both age and geochemical origin (Capo, 1998; Scher et al., 2014). The $^{87}Sr/^{86}Sr$ values of geochemical reservoirs and rocks are generally between 0.702, the typical value for the depleted, low Rb/Sr mantle, and might be as high as 0.943 for old continental crust (Rosner, 2010).

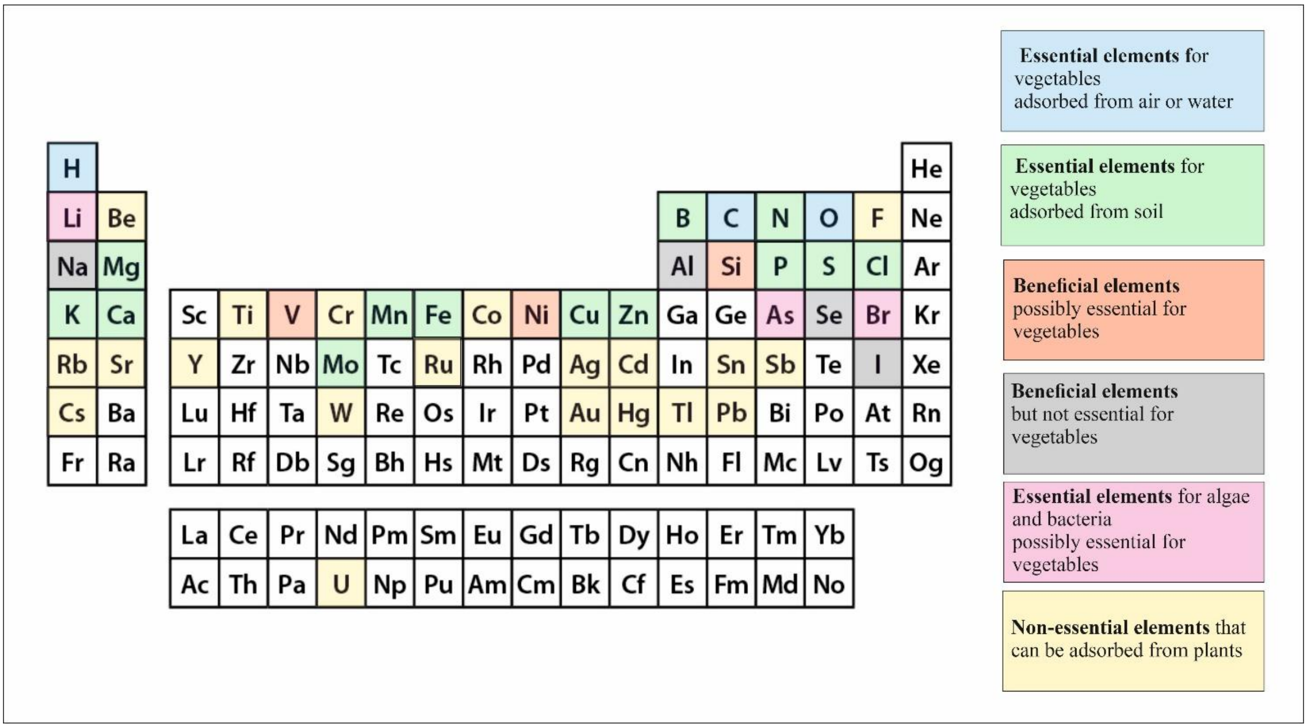

**Figure 1.1.** Periodic table of chemical elements adsorbed from plants (modified from https://www.unirc.it/documentazione/materiale_didattico/1462_2017_432_27687.pdf)

## OBJECTIVES

The present work aims to contribute to the characterization $^{87}Sr/^{86}Sr$ as a marker of wine origin in volcanic districts from Italy (Ponza Island, Ventotene Island, Somma-Vesuvio, Salina Island, Mount Etna and Pantelleria Island) and Brazil (Vale dos Vinhedos). This might provide new insights in the use of geological investigations for agri-food products traceability purposes. The study is based on the analysis of the soil, grape, leaf, and wine from 14 selected vineyards, belonging to nine different wineries (6 from Italy, 3 from Brazil).

Despite the large amount of $^{87}Sr/^{86}Sr$ data available for Italian wines, it is worth noting that studies carried out are concentrated in the northern and central regions, in vineyards on sedimentary terrains. Lesser data are available for Italian wines from the southern regions, where vineyards founded on volcanic terrains. In addition, it is known that Italian volcanic rocks display some sort of isotopic zoning for $^{87}Sr/^{86}Sr$, which decreases from northeast to southwest (e.g., Conticelli et al., 2002, 2009; Peccerillo, 2017). Therefore, an additional aim of this work might be also that of testing if this zoning can be observed also in the wines and in other geological/biological matrices (e.g., soils, leaves, grapes) which have been also sampled in the selected vineyards.

On the other hand, Brazilian samples of soil, wine and leaf were selected as a pioneering study applied to the characterization of wines from Vale dos Vinhedos, the most important wine region in the country, positioned a volcanic substratum.

The results of this research project will thus contribute to increasing the recognition of $^{87}Sr/^{86}Sr$ a marker for the geographical origin of wines and possibly in promoting similar research works in other important wine producing regions in both Italy and Brazil.

The project involves a scientific cooperation with the Geotop laboratory of the *Université du Quebéc à Montréal* (Montreal, Canada), the *Dipartimento Di Agraria* of the *Università degli Studi di Napoli Federico II* (Portici, Italy), the *Dipartimento Di Scienze e Tecnologie* of the *Università degli Studi del Sannio* (Benevento, Italy) and the Brazilian Agricultural Research Corporation (*EMBRAPA- Empresa Brasileira de Pesquisa em Agricultura*).

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## Chapter 2 – CHARACTERIZING WINE *TERROIR* USING STRONTIUM ISOTOPE RATIOS: A REVIEW

### INTRODUCTION

In the last 25-30 years, the augmented consumer interest in the origin of the products and the multifunctionality of the research groups have all contributed to increasing the number of agri-food traceability studies. The basic principle is that plants absorb bioavailable elements from the soil, therefore providing a medium for carrying information about the geological substratum on which they grew to the food and beverages that are produced from them.

Recently, the $^{87}$Sr/$^{86}$Sr systematics have turned out to be the most efficient method for traceability studies, mostly because i) Sr isotopes do not fractionate when Sr is assimilated by the plants and ii) $^{87}$Sr/$^{86}$Sr present rather large variations owing to the lithology and its age (Horn et al., 1993; Capo et al., 1998; Petrini et al., 2015; Braschi et al., 2018; Guibourdenchen et al., 2020).

The application of this technique, focused on the values of the$^{87}$Sr/$^{86}$Sr ratio, has proven to be a valuable tool for tracking the origin of different agricultural products, and especially for wines (Horn et al., 1993; Wolff-Boenisch, 1998; Barbaste et al., 2001, 2002; Almeida and Vasconcelos, 2001, 2004; Boari et al., 2008; Vorster et al., 2010; Di Paola-Naranjo et al., 2011; Marchionni et al., 2013, 2016; Mercurio et al., 2014; Martins et al., 2014; Durante et al., 2015, 2018; Petrini et al., 2015; Tedeschi et al., 2015; Vinciguerra et al., 2015, 2016; Geana et al., 2017; Bora et al., 2018; Braschi et al., 2018; Epova et al., 2019; Catarino et al., 2019; Guibourdenchen et al., 2020).

The study of $^{87}$Sr/$^{86}$Sr in the soil-wine system is important to understand whether the processes of winemaking, external addition of strontium concentrations, heterogeneities of geology and pedology or the instrumentation can influence the final product, and if it is effectively useful as a tool for geographical origin discrimination. The available $^{87}$Sr/$^{86}$Sr studies carried out on wines from all over the world focused on different topics, including the possible influence of winemaking procedures, different grape varieties, vintages, soils and geological substratum on Sr isotopes (Almeida and Vasconcelos, 2004; Boari et al., 2008; Mercurio et al., 2014; Marchionni et al., 2013, 2016).

This chapter attempts to present a review of the published literature on worldwide Sr isotope studies performed for the purpose of discriminating the geographical origin of wines. Particular emphasis will be devoted to the specific analytical procedures and techniques adopted by the authors, in an effort of comparing all the published results despite the undeniable overall heterogeneity of the investigated set of data.

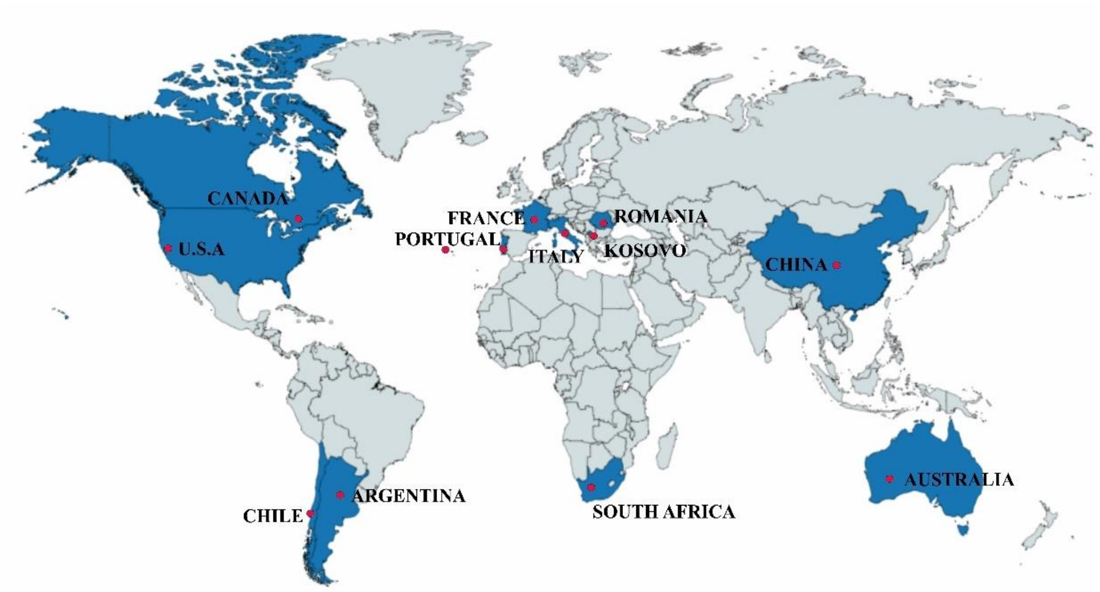


**Figure 2.1**. World map showing the distribution of available $^{87}Sr/^{86}Sr$ data on wine samples.

## MATERIALS AND METHODS

Twenty-five peer-reviewed studies were included in the present review, with the objective of discussing the potential for $^{87}Sr/^{86}Sr$ analyses of wines to be used as a provenance proxy. A special focus was made on the different procedures (sampling strategy, sample preparation and analytical instrumentation) adopted by the authors of these studies.

### *Sampling procedures employed by the authors*

In order to accurately identify the provenance of agri-food products, systematic sampling is an essential prerequisite. Among the available publications, Sr isotope analysis was carried out on three different matrices: bottled wine, wine made from controlled microvinification or must, and soils. Analyses on wines made from red grapes represented the largest part of the dataset, with 87% of total data against 13% for white grapes. Bottled wine samples make the 92% of the total data (either purchased by the authors or made available by wineries). As the vinification process may alter the original $^{87}Sr/^{86}Sr$ of the grape juice, mainly due to the addition of additives used to filter or attenuate the taste of wine (Tescioni et al., 2015; Marchioni et al., 2016;), a limited number of authors (8%) analysed microvinification (Mercurio et al., 2014; Vinciguerra et al., 2015, 2016; Guibourdenche et al., 2020) or must samples (Tescioni et al., 2015; Petrini et al., 2015; Braschi et al., 2018). Microvinification is a winemaking technique used for experimental wine studies where a limited amount of grape is pressed and fermented in small vats. Therefore, microvinification presents the advantage of preventing potential contamination resulting from the industrial winemaking procedure operated in a winery. It also limits the possible variations of the $^{87}Sr/^{86}Sr$

ratio related to the heterogeneities in the isotope ratios of the associated soils, due to the fact that the grapes used for the microvinification are sampled in one single vineyard. Moreover, large wineries often use grapes from different vineyards, potentially coming from areas with different geological substrata.

Over a total of 695 wine $^{87}Sr/^{86}Sr$ data, only 317 present corresponding data on soil samples (Vorster et al., 2010; Di Paola-Naranjo et al., 2011; Mercurio et al., 2014; Petrini et al., 2015; Vinciguerra et al., 2016; Marchionni, et al. 2016; Durante et al., 2018; Braschi et al. 2018; Guibourdenche et al., 2020). Among these, while most of the authors measured the $^{87}Sr/^{86}Sr$ values only for the labile fraction of the soil samples (n=277), Guibourdenche et al. (2020), Petrini et al. (2015), Vinciguerra et al. (2016), Braschi et al. (2018), Tescioni et al. (2015, 2016) and Marchionni et al. (2016) compared these with those for the corresponding bulk soil samples (n=40). The labile fraction of the soil refers to its compounds or substances that are easily transformed by biological activity. This fraction is generally considered representative of the solutions and nutrients that derive from the weathering and leaching of minerals in the soil, which are absorbed by the plant roots (Poszwa et al., 2004; Hajj et al., 2017; Guibourdenche et al., 2020). Consequently, the labile fraction represents the most likely reservoir in the soil that can provide Sr to the plant (Horn et al., 1993; Marchionni et al., 2016; Vinciguerra et al., 2016, Guibourdenche et al., 2020).

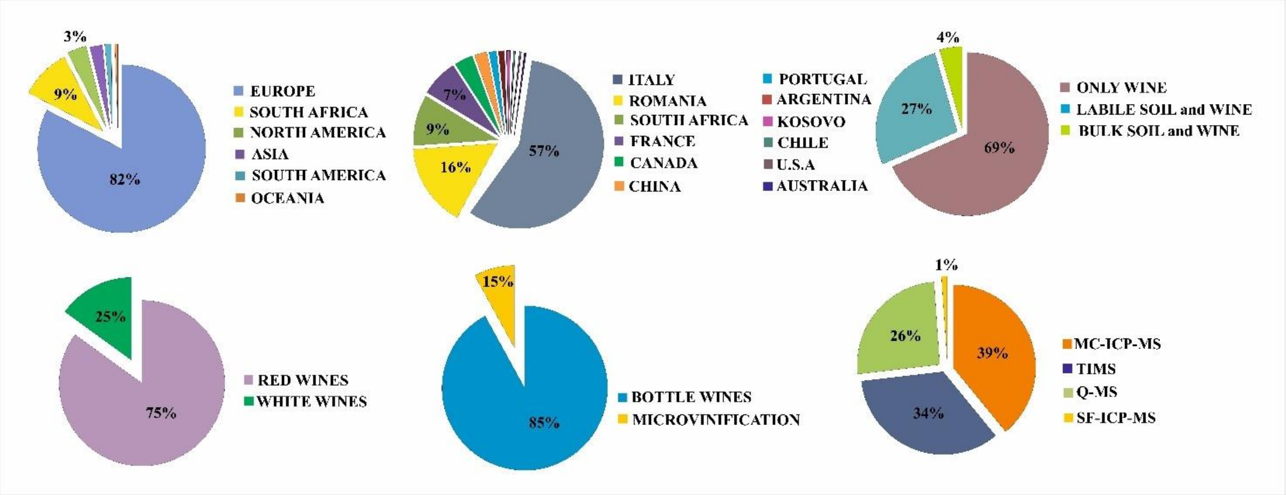


**Figure 2.2.** Pie charts for worldwide $^{87}Sr/^{86}Sr$ data on wine samples showing provenance, kind of data, type of wine (both whether red or white and whether commercial or microvinification) and analytical instrumentation employed. See text for further information. Data sources: Argentina (Di Paola-Naranjo et al., 2011); Australia (Barbaste et al., 2001); Canada (Guibourdenche et al., 2020; Vinciguerra et al., 2016); Chile (Barbaste et al., 2001); China (Epova et.al, 2019); France (Horn et al., 1993; Epova et.al, 2019); Italy (Horn et al., 1993; Barbaste et al., 2001; Marchionni et al., 2013, 2016; Mercurio et al., 2014;Teschini et al., 2015; Petrini et al., 2015; Durante et al., 2015,2018; Braschi et al., 2018); Kosovo (Horn et al., 1993); Portugal (Barbaste et al., 2001; Martins et al., 2014; Catarino et al., 2019); Romania (Geana et al., 2019; Bora et al., 2018); South Africa (Vorster et al., 2010); U.S.A. (Barbaste et al., 2001).

### *Sample preparation*

The different protocols used by authors for sample preparation (wines and soils) are summarized in **Figure 2.3** and **Table 2.1**. In brief, biological, and geological samples are first acid-digested, then Sr ions are separated and purified from other metal ions by chromatographic methods (i.e., through ion exchange resins) in a clean laboratory before their $^{87}Sr/^{86}Sr$ can be measured (Rossmann et al., 2000). To ensure an accurate $^{87}Sr/^{86}Sr$ measurement, in-run isotopic fractionation and isobaric interference must be accounted for and corrected.

### *Mass Spectrometry instrumentation*

Measuring the $^{87}Sr/^{86}Sr$ values for a geological or biological sample with a targeted precision of 0.01% (Horn et al., 1998) requires the use of a high-performance mass spectrometer. Reaching this precision depends on the ionization capacity of the instrument used, as well as on the mass-dependent isotope fractionation that occurs over the course of the analysis. The precision of the isotope measurements is usually evaluated by the repeated analysis of a certified international standard: NIST SRM 987 strontium carbonate ($SrCO_3$) with a certified $^{87}Sr/^{86}Sr$ value of 0.710245 ± 0.000011 (Thirlwall, 1991). Of the 1012 wine and soil samples that were analysed in the collected dataset, 401 samples were analysed using a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS), 342 a Thermal-Ionization Mass Spectrometer (TIMS), 258 a Triple Quadrupole Mass Spectrometer (TQ-MS) and 11 a Sector Field Multi-Collector Inductively Coupled Plasma Mass Spectrometer (SF-MC-ICP-MS). The main difference between these instruments relies on how the sample is introduced into the instrument and how the sample is ionized. Other differences are related to detection limits, resolution, mass interferences, data quality, associated costs, ease of use and the availability of a validated methodology. The type of instrument influences the accuracy of the data. **Figure 2.4A** shows a comparison among $^{87}Sr/^{86}Sr$ values reported by the different authors for the NIST SRM-987 standard. Results show that while the accuracy for TIMS, MC-ICP-MS and SF-MC-ICP-MS varies from to 0.00001% to 0.0001%, that of TQ-MS varies from 0.001 to 0.1% (**Figure 2.4A).**

The relations existing between the Sr isotope ratios measured in wines and soils were discussed on the basis of the difference between the two values for each sample. The objective was to eventually relate these differences to the influence of the pedology, wine processes and precision of the different instruments used by the authors.

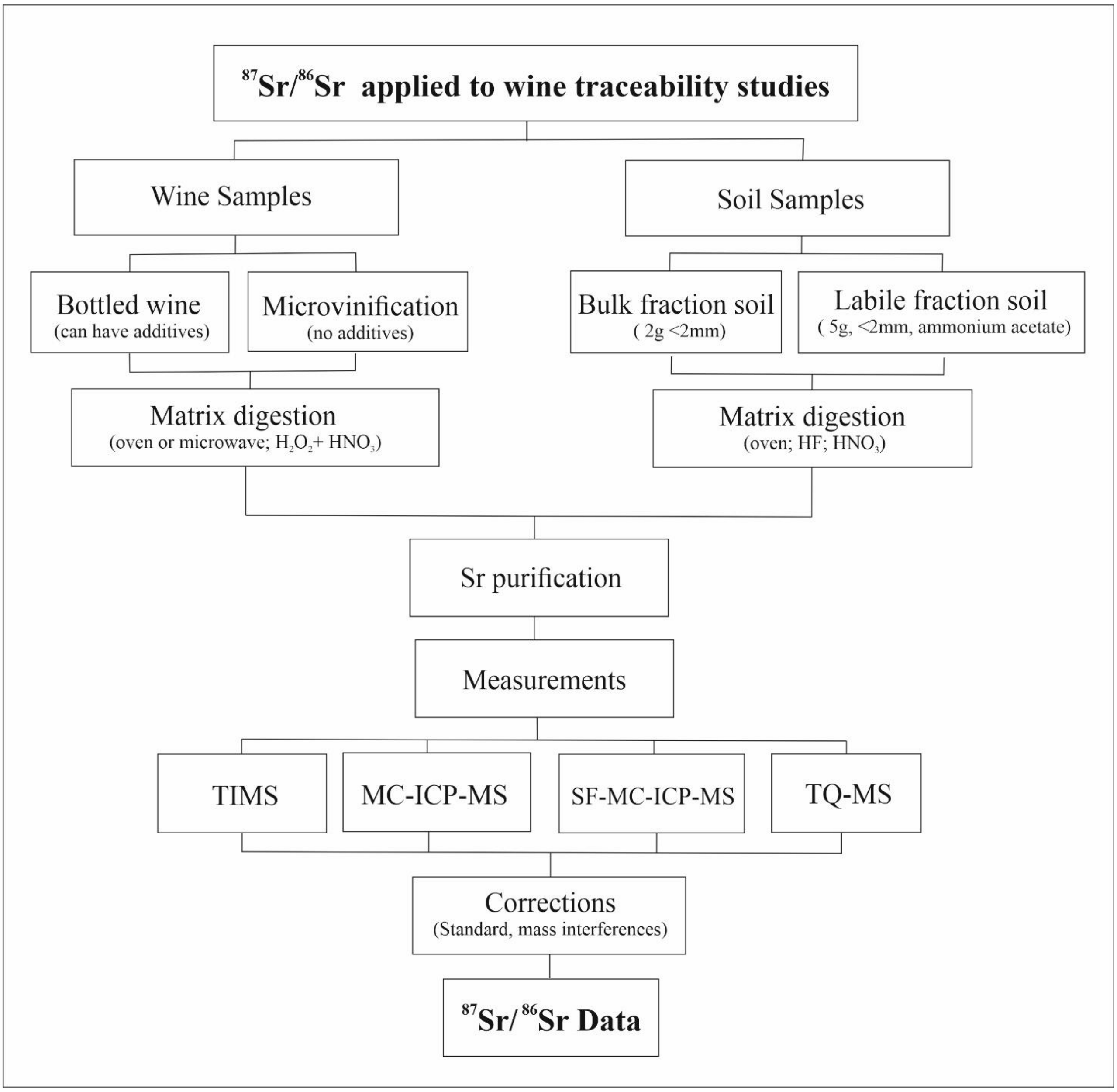


**Figure 2.3.** Flow chart summarising the procedures undertaken in the reviewed literature studies on Sr isotope analyses on wine samples. Additional details on the types of samples, employed instrumentation and precision of the measurements are reported in **Table 2.1**.

**Table 2.1**. Sample preparation procedure applied by consulted articles. n.a. = not analyzed.

| COUNTRY | REREFENCE | TYPE OF WINE SAMPLE | WINE SAMPLE PREPARATION | FRACTION OF SOIL | SOIL SAMPLE PREPARATION | INSTRUMENT USED | SRM- 987 STD | ERROR (%) |
|---|---|---|---|---|---|---|---|---|
| Argentina | Di Paola-Naranjo et al. (2011) | Bottled wine | 250 mL of sample were heated at low temperature for 24 h. Residues were digested in a muffle furnace at 550 °C for 20 h. Ashes were treated with concentrated nitric acid on a hot plate. | Labile | 20 g of sieved (2 mm) soil sample was dried at 40 °C and then 50 mL of $NH_4NO_3$ (1 M) were added. The solution was shaken for 2 h at room temperature. After 1 h samples were filtered using 0.45 µm filters and 0.5 mL of $HNO_3$ were added. | TIMS | 0.71008 | 0.00026 |
| Australia, Chile, USA, Italy, France, Portugal | Barbaste et al. (2001) | Bottled wine | 10 mL of sample was dissolved in 5 mL of concentrated $HNO_3$ followed by evaporation to dryness. The residue was dissolved in 5 mL of 6 M HCl and re-evaporated to dryness. The residue was dissolved in 2.5 M HCl and the solution was centrifuged for 20 min at 3500 rpm (revolutions per minute). | n.a. | n.a. | SF-MC-ICP-MS | 0.71020 | 0.00010 |
| Canada | Vinciguerra et al. (2015, 2016) | Microvinification | 4 mL of sample was mixed with 2 mL of 3:1 $HCl/HNO_3$ and 1 mL of $H_2O_2$ for 24 h. The process was followed by oven digestion at 600 °C for 1 h. | Labile and bulk | 0.4 g of bulk soil was heated for 6 h at 700 °C. 2-5g of labile soil was extracted using a $NH_4NO_3$ solution. Labile soil was filtered using 0.45 µm membrane. | TIMS | 0.71025 | 0.00003 |
| France and Chine | Epova et al., (2019) | Bottled wine | 10 mL of wine sample was evaporated and $H_2O_2$ was added. The residue (5 mL) was diluted with 5 mL of $HNO_3$ left to react at room temperature. Finally, 1 mL of $H_2O_2$ was added after 24h and then the solution was digested using a microwave at 200 °C) in different times: ramping – 20 min, heating – 20 min, and cooling – 20 min. The solution was then diluted with ultrapure water up to 30 mL. | n.a. | n.a. | MC-ICP-MS | 0.71028 | 0.00001 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Italy | Durante et al., (2016) | Bottled wine | 1mL of wine samples were microwaved adding 6 mL $HNO_3$, 1 mL $H_2O_2$ and 3 mL $H_2O$. | Labile | 100 g of each soil sample were dried and sieved within the 50–250 µm range size. Labile fraction was extracted using 1 mol L−1 $NH_4NO_3$ and then filtered with cellulose acetate membrane (pore size 0.20 µm) and then 10 mL of 65% sub boiled $HNO_3$ was added. | MC-ICP-MS | 0.71027 | 0.00100 |
| | Mercurio et al., (2015) | Microvinification | 5 mL was microwaved followed by addition of concentrated double-sub boiled $HNO_3$ (6 mL) and $H_2O_2$ (1 mL). | Labile | 20 g of sieved soil was used adding 50 mL of 1 mL of $NH_4NO_3$. Samples were shaken with an overhead shaker for 2 h at 20 rpm at room temperature and filtered with Whatman no. 42 filter paper into 50 mL vials, hen 0.5 mL of concentrated $HNO_3$ were added. | MC-ICP-MS | n.a. | n.a. |
| | Petrini et al., (2015) | Must | Wine samples were dried at 60 °C (using nickel crucible) and heated in an oven at 700 °C for 1 h. The residue has been dissolved with ultrapure 2.5 N HCl. Also, to test destruction of organic matter, 5 g of dried sample (60 °C for 12 h) was diluted, adding 5 mL of concentrated ultrapure $HNO_3$ and $H_2O_2$ and then heated at 120 °C for 2 h. The residue has been dried at 60 °C and then procedure was repeated until complete destruction of the organic matter. Finally, the residue was dissolved with ultrapure 2.5 N HCl. | Bulk, labile, carbonate | Bulk soil: first, samples have been digested using a mixture of ultrapure HF and $HNO_3$ at 100 °C followed by ultrapure HCl dissolution of the residue. Second, 10 g of the <2 mm soil fraction was mixed by adding 50 mL of 1 $NH_4O$. Acetate ultrapure grade buffered at circum-neutral pH.. Labile: samples were filtered through 0.45 ml nylon filters. Dissolution of carbonate: $NH_4OAc$ and 1 M HCl. | TIMS | 0.71025 | 0.00002 |
| | Marchioni et al., (2013, 2014, 2016) | Bottled wine | 5 mL of wine sample was evaporated at 90 °C, dissolved using 3 mL of $H_2O_2$ (30 %) at 40 °C for 24 h and then evaporated again to dryness at 90 °C. The residue was dissolved twice in 2 mL of supra pure quality $HNO_3$ (67 %) at 150 °C for 1 day, evaporated and dissolved again in 1 mL of 3 N $HNO_3$. | n.a. | n.a. | TIMS | 0.71025 | 0.00002 |
| Portugal | Almeida and vasconcelos, (2001) | Bottled wine | 5 mL of wine plus 5 mL of $H_2O_2$ (30%) and 15 mL of deionized water were added. The residue was microwaved for 1 h. | n.a. | n.a. | TQ-MS | 0.72100 | 0.41000 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Romania | Geana et al., 2017 | Bottled wine | Wine samples (5 mL) were mineralized using a microwave adding 6 mL of concentrated nitric acid. | n.a. | n.a. | TQ-MS | 0.70971 | 0.53000 |
| Romania | Bora et al., 2008 | Bottled wine | 0.5 mL of wine was set to react with 7 mL $HNO_3$ (65%) and 1 mL $H_2O_2$ as an initial procedure. After 15-30 min samples were microwaved in the following steps: step I, 10 min., at 200 °C, step II 15 min at 200 °C and step III 60 min. for ventilation at 35 °C. After that, samples were filtered using 0.45 mm filter and brought to a volume of 50 mL. | n.a. | n.a. | TQ-MS | 0.71117 | 0.49000 |
| South Africa | Voster et al., 2010 | Bottled wine | 1 mL of wine was evaporated in an oven at 70 °C. 4 mL 65 % $HNO_3$ and 2 mL 30 % $H_2O_2$ were added and then microwaved for 20 min at 180 °C. | Labile | First, 1 g of soil was dissolved using 4 mL 65 % $HNO_3$ and 2 mL 30 % $H_2O_2$. Second, soil has been heated using a microwave for 20 min at 180 °C and then filtered using 0.45 µm cellulose nitrate filters. | TQ-MS | n.a. | n.a. |

## RESULTS AND DISCUSSION

### *Influence of the mass spectrometry instrumentation on the determination of $^{87}$Sr/$^{86}$Sr of wine and soil samples*

**Figure 2.4A** shows results for the NIST SRM987 standard obtained in the collected literature studies as a function of the instrument used.

In general, TIMS is more precise and less sensitive to isotope fractionation than MC-ICP-MS (Heumann et al., 1998). Nevertheless, chemical separation of the element from the matrix makes measurements by MC-ICP-MS nearly as time consuming as by TIMS. MC-ICP-MS has a higher ionization efficiency (almost 100%), which makes it more sensitive as the instrument operates in a steady state mode, resulting in a mass fractionation that is constant over the course of the analysis. MC-ICP-MS were developed to improve the accuracy of ICP-MS in order to attain the high precision required for isotope-ratio measurements. SF-MC-ICP-MS yield similar performance compared to both TIMS and MC-ICP-MS (Barbaste et al., 2001). TQ-MS are robust, easy to use and cheaper than MC-ICP-MS, but they have a lower resolution and accuracy when measuring masses, which makes them not fully appropriate for certain precise isotope analyses. In summary, TIMS and MC-ICP-MS ensure the highest precision and an overall better data quality when studying $^{87}$Sr/$^{86}$Sr in wines and soils, followed by SF-MC-ICP-MS (**Figure 2.4A**). Finally, the large variability of TQ-MS data could represent a severe obstacle when trying to identify small regional Sr isotope variations, which may have some significant bearing in wine isotope studies. **Figure 2.4B** reports the values for the differences between $^{87}$Sr/$^{86}$Sr in wine and corresponding soil samples. Results suggest that the dispersion may be at least partly related with the accuracy of the employed analytical instrument. Other potential parameters influencing such differences are further discussed in the next section.

### *$^{87}$Sr/$^{86}$Sr of natural and anthropogenic additives*

A prerequisite before applying the $^{87}$Sr/$^{86}$Sr approach to authenticate agri-food products is to know which are the possible external additives that can affect strontium along the cycle from its original source (i.e., the bedrock on which vines are growing) to the final product (here, the wine). It is thus necessary to consider the possibility that Sr is added either by natural or/and by anthropogenic sources (Almeida and Vasconcelos, 2004; Petrini et al., 2015). In the case of wine studies, many of the additives that are commonly used contain calcium (Ca), so they may also add Sr, as Sr can substitute to Ca in minerals (Petrini et al., 2015). This will ultimately modify the original $^{87}$Sr/$^{86}$Sr of soils and plants, and thus of the wines. Identifying natural and external sources of Sr for soils and wines is difficult as they depend on the type of soil of each vineyard, their intrinsic heterogeneities as well as on the agricultural and winemaking practices of each winery. While natural sources of Sr are related to the weathering of the parent rock, anthropogenic sources are related to the use of organic and mineral fertilizers, of inorganic pesticides, and to environmental pollution (Şen and Tokatli, 2014).

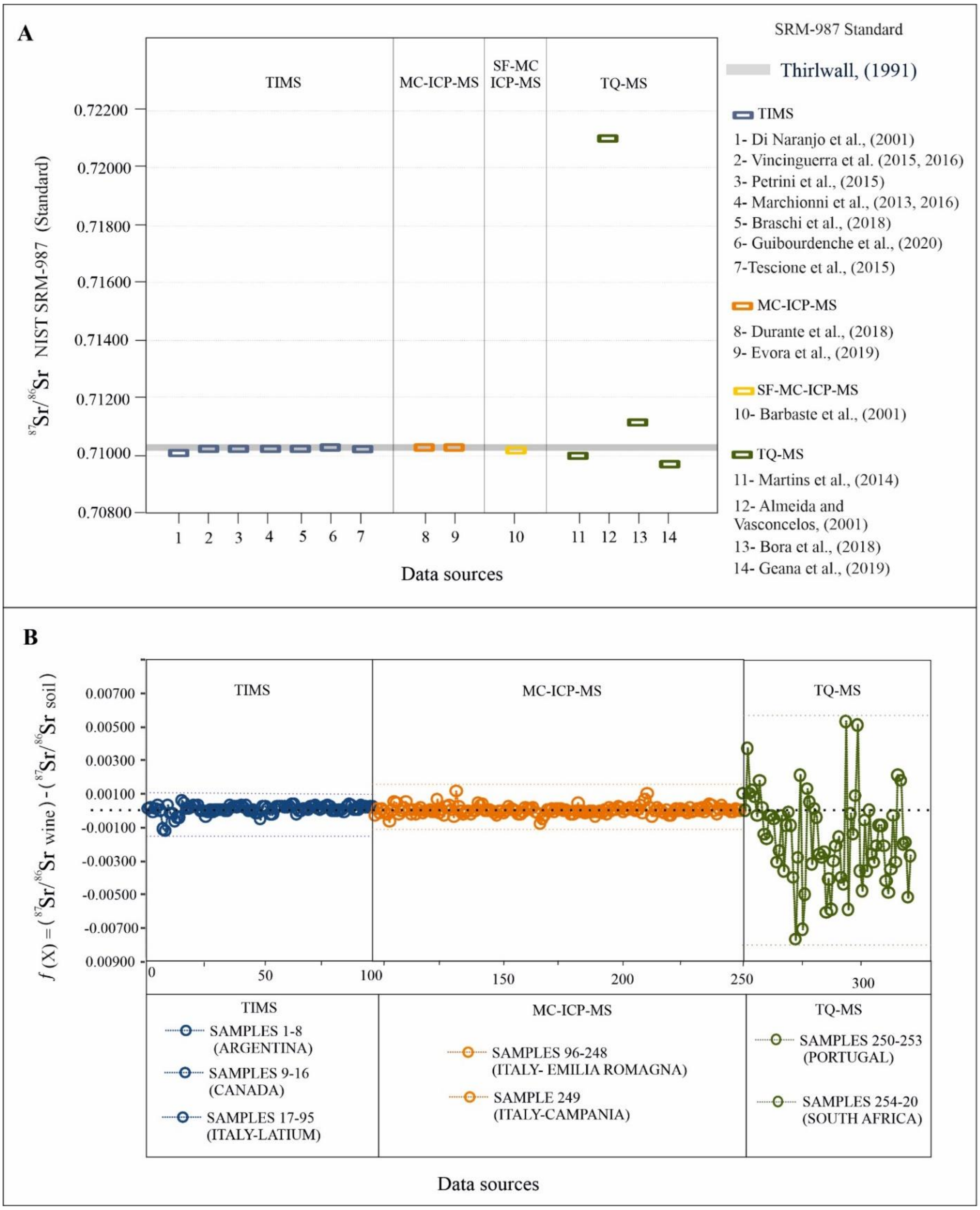


**Figure 2.4. A)** $^{87}$Sr/$^{86}$Sr values for the SRM-987 standard measured in the literature papers on wine samples compared with the certified values of Thirlwall, (1991) reported as a grey line (0.0.710245 ±0.000011). Results were separated based on the employed analytical instrument. **B)** difference between $^{87}$Sr/$^{86}$Sr values for wine and corresponding soil samples from the collected literature papers separated based on the employed analytical instrument.

In a study on four different grape varieties (two red and two white wines) from the Sassotondo and San Lorenzo vineyards (Tuscany region). Tescione et al. (2015) concluded that Sr and Ca absorption from the soils is homogeneous for the different grape varieties and is controlled by the geology and the soil geochemical heterogeneities. The $^{87}Sr/^{86}Sr$ values for wine samples resulted significantly lower than the values observed in the rocks of their volcanic substrata. However, the difference in values allows to discriminate the two areas, showing the efficiency of the method to differentiate the provenance of wines at a small scale with the application of the control of Sr external factors. Petrini et al. (2015) reported an $^{87}Sr/^{86}Sr$ value of 0.70769 ± 0.00002 for an organic fungicide. However, these kinds of additives, widely used to prevent or eradicate fungal infections from plants or seeds, have a very variable composition, depending on the country or region of manufacture, and thus can have a rather unpredictable effect on modifying$^{87}Sr/^{86}Sr$ values. The general winemaking procedure itself includes grapes collection, maceration, extraction, aging and a final refinement phase. During this latter, bentonite $[(Na, Ca)_{0,3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$; Montmorillonite] is widely used as a fining agent to clarify and stabilize insoluble matter suspended in the wine prior to bottling. The addition of bentonite during winemaking results in an increase of calcium and concomitantly of strontium, potentially altering the original $^{87}Sr/^{86}Sr$ of wines (Almeida and Vasconcelos, 2004). However, in the aforementioned work from Tescione et al. (2015), the authors concluded that $^{87}Sr/^{86}Sr$ values remain constant during the vinification process, even after the addition of yeast or bentonite.

### *Soil bulk and labile fractions and vintage control*

The chemistry of a soil is determined by rock weathering. During this process, Sr migrates from the hosting rocks to the soil as disaggregated primary minerals, secondary minerals, and dissolved in water and is then absorbed by vines' roots. The organic and inorganic compounds of a soil are not evenly distributed but are generally retained to be more concentrated in the so-called labile fraction (see previous section). Therefore, $^{87}Sr/^{86}Sr$ values for this fraction can be different from that for the bulk soil (Petrini et al., 2015; Marchionni et al., 2016; Vinciguerra et al., 2016; Guibourdenche et al., 2020).

Marchionni et al. (2016) studied the relationships existing between Sr isotope ratios in red wine samples and samples of soil form the corresponding vineyard in the Latium region of Italy. Soils were sampled at various depths and the bulk and labile fractions were separated to ultimately assess the $^{87}Sr/^{86}Sr$ variability. The presence of bioavailable Sr in the soil labile fraction can alter the expected $^{87}Sr/^{86}Sr$ correspondence between the soil and the wine. This was also observed by Vinciguerra et al. (2016) and Guibourdenche et al. (2020) in a study performed in vineyards from the Quebec province in Canada. The authors observed a good correspondence between $^{87}Sr/^{86}Sr$ of wine samples with those of the soil labile fraction. Petrini et al. (2015) in a study on different prosecco vintages in the Veneto region (Italy) reports a good correlation between the $^{87}Sr/^{86}Sr$ measured in samples of must and of the corresponding soil labile fraction. Studies that focused on the different soil fractions and wine samples showed that the soil labile fraction generally yields a lower $^{87}Sr/^{86}Sr$ value compared to the bulk one and are better correlated with the values for the corresponding wine samples, both for white and red varieties (Marchionni et al., 2016; Vinciguerra et al., 2016, Guibourdenche et al. 2020).

Additionally, they demonstrated that $^{87}Sr/^{86}Sr$ remains constant with time (years 2010, 2011 and 2012 were tested). Braschi et al. (2018) also monitored the $^{87}Sr/^{86}Sr$ of wine samples during a period of four consecutive vintage years (2010, 2011, 2012 and 2013) and compared them with their respective soil labile and bulk fractions, in order to identify the possible components that might alter the $^{87}Sr/^{86}Sr$ values during the grapevine bio-vegetative cycle. Results confirmed the constancy of the $^{87}Sr/^{86}Sr$ with time and the correspondence between wine and the soil labile fraction samples. Based on such results, it can be confidently assumed that $^{87}Sr/^{86}Sr$ in wine samples does not change during the vine cycle and thus may represent a reliable geochemical proxy to authenticate the geographical origin and *terroir* of any given wine.

### $^{87}Sr/^{86}Sr$ *from worldwide vineyards*

To date, there are 695 $^{87}Sr/^{86}Sr$ values reported for wine samples from 12 different countries, in 25 articles published between 1998 and 2020. Of this dataset, ~66% of data refer to wines from Italy (**Figure 2.2**), with the remaining being mainly represented by data from Romania (~16%), South Africa (~9%), France (~7%) and Canada (~3%). About half of them (317 data) coupled soil and wine Sr isotope characterization: Argentina (3), Canada (31), Italy (211), Portugal (4) and South Africa (68).

Below the results of such studies are briefly presented.

#### *South America*

Data from Argentina were obtained for red wines (Malbec, Cabernet Sauvignon and Syrah vines) from three different regions, and yielded $^{87}Sr/^{86}Sr$ ranges of 0.70710-0.70730 (Mendonza), 0.70810-0.70840 (San Juan) and 0.70920-0.70930 (Cordoba; Di Paola-Naranjo et al., 2011). These regions are underlain by different geological formations: Ternary conglomerates and sandstones (Mendonza); Ternary clastic, alluvial and eolian deposits (San Juan); Paleozoic magmatic rocks (Cordoba). $^{87}Sr/^{86}Sr$ of the associated soils mirror these lithologic variations, with corresponding ratios of 0.70720 (Mendonza), 0.70810 (San Juan) and 0.71040 (Cordoba). For Chile, a single red wine sample coming from a vineyard located on volcanic deposits/basaltic soil (no detailed information available) was analyzed, and gave a value of 0.70471 (Barbaste et al., 2001).

*North America*

Two detailed studies were carried out in the Quebec province (Canada) on microvinified red wines and soils samples (Vinciguerra et al., 2016; Guibourdenche et al., 2020), aiming at isotopically characterizing vineyards located in two different geologic areas: the St. Lawrence Platform and the Appalachian province. While wines from the St-Lawrence Platform vineyards cover an $^{87}$Sr/$^{86}$Sr range of 0.70988-0.71138, those from the Appalachian province range from 0.71108 to 0.71546. Both articles also included a systematic study of the soil-plant system. For the St. Lawrence Platform $^{87}$Sr/$^{86}$Sr values of 0.71211 and 0.70986 were obtained for soils developed on a substratum consisting of grey shale, sandstone, siltstone, and limestone deposits, 0.71203, 0.71538 and 0.71036 for those having a substratum of mudrock, slate, dolostone and sandstone deposits, and 0.71012 for soils from limestone, shale, dolostone and sandstone deposits. On the other hand, the Appalachian province yielded the following $^{87}$Sr/$^{86}$Sr values for soils: 0.71335 (mudrock, sandstone, conglomerate, and limestone deposits); 0.71174 and 0.71363 (phyllite, schist, slate, sandstone, quartzite, dolostone and conglomerate deposits); 0.71012 (limestone, shale, dolostone and sandstone deposits); 0.71546 (mudrock, conglomerate, sandstone, and limestone deposits). To our knowledge, only a single $^{87}$Sr/$^{86}$Sr datum is available for the United States, referring to a Californian vineyard (Barbaste et al., 2001). The authors report an $^{87}$Sr/$^{86}$Sr of 0.70688 for a vine growing on a basaltic soil.

*Asia and Oceania*

Epova et al. (2019) studied bottled wine samples purchased from Chinese wine stores. Among them, some red wine samples were identified as a certified Chinese production ($^{87}$Sr/$^{86}$Sr ranging from 0.70880 to 0.71036), while the others were labelled as ”Bordeaux“ (France) and had no information on the region of production. These samples had $^{87}$Sr/$^{86}$Sr varying from 0.70523 to 0.71266. The available $^{87}$Sr/$^{86}$Sr data for wines from Australia (no information available about the region of production) consist of a single analysis of a red wine sample that yielded an $^{87}$Sr/$^{86}$Sr value of 0.70963 (Barbaste et al., 2001).

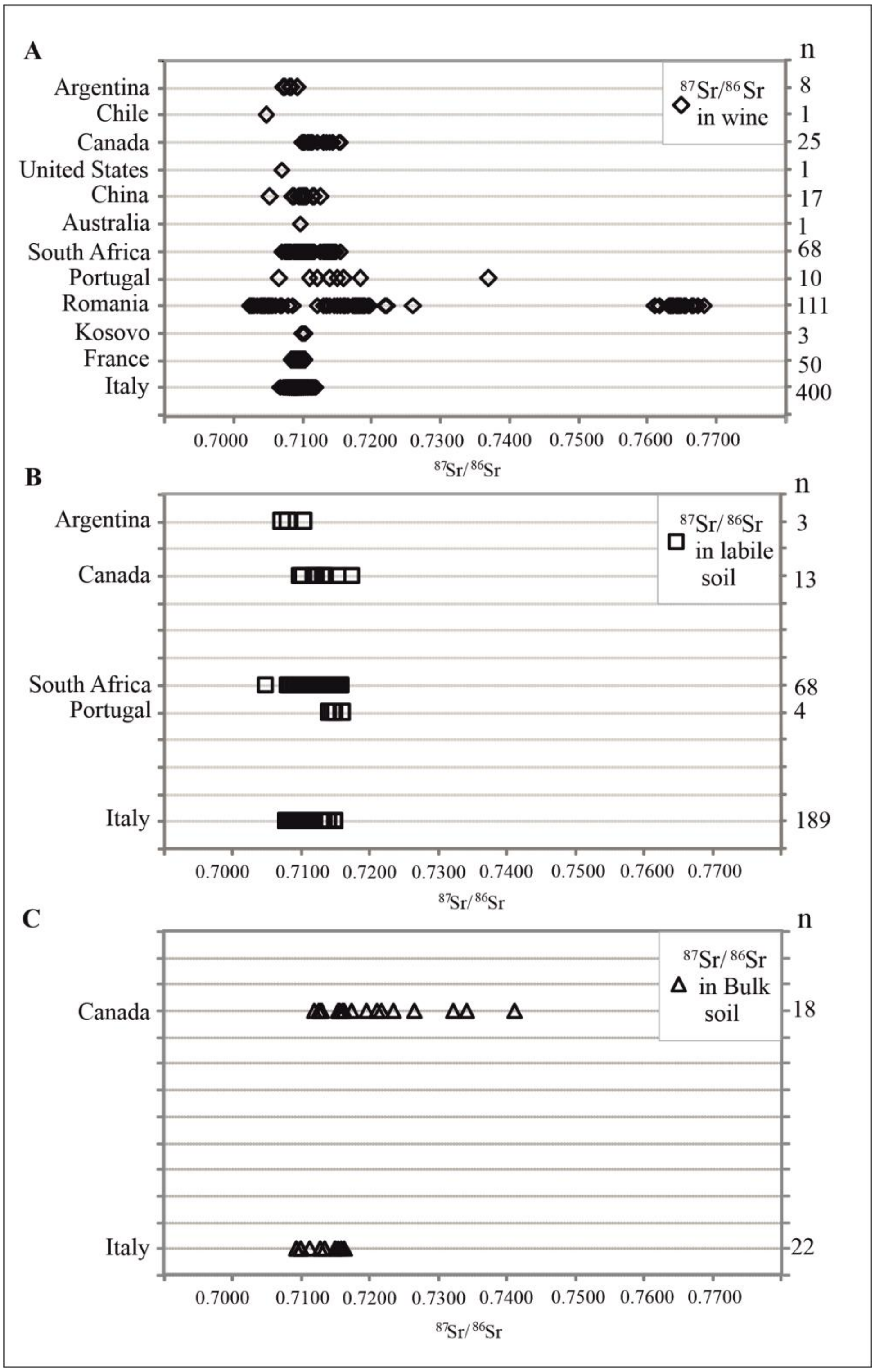


**Figure 2.5.** Ranges of worldwide $^{87}Sr/^{86}Sr$ values in a) wine, b) soil labile fraction and c) bulk soil samples displayed based on the provenance country, each showing the number of analysed samples (on the right). Data sources as in **Figure 2.2.**

*Africa*

Coupled wine-soil studies were carried out by Vorster et al. (2010) in four different South African vineyards (red and white varieties). $^{87}Sr/^{86}Sr$ measured in wines from the Robertson region rang from 0.711300 to 0.71540, slightly higher than those from the Stellenbosh region (0.70700-0.71100) and moderately overlapping with those from the Swartland (0.70750-0.71410) and Walker Bay (0.70780-0.71310) regions. However, the authors observed a poor correlation with the isotope values obtained on the corresponding labile soil samples: 0.71280-0.71550 (Robertson), 0.70820-0.71590 (Stellenbosh), 0.70480-0.71500 (Swartland) and 0.70920-0.71380 (Walker Bay).

*Europe*

A total of five Portuguese red wine regions have been characterized using Sr isotopes (Barbaste et al., 2001, Catarino et al., 2019; Martins et al., 2014; Almeida and Vasconcelos, 2001, 2004): Madeira (0.70660), Dao (0.73700), Obitos (0.71400), Douro Valley (0.71400-0.71600) and Palmela (0.71100). Vineyards located on Madeira Island have a substratum consisting of basaltic rocks that explains their lowest $^{87}Sr/^{86}Sr$ ratios (Barbaste et al., 2001), whereas the highest values were observed for wines from Dao, with a substratum consisting of granitic rocks (Martins et al., 2014). The Douro Valley vineyards grow on a metamorphic substratum (Catarino et al., 2019), while vineyards from Pamela and Obito areas have a sedimentary substratum (Almeida and Vasconcelos, 2001, 2004; Martins et al., 2014). Soils were also analysed in the Douro Valley, showing a range of 0.71600-0.71800 (Catarino et al., 2019). Horn et al. (1993) studied red wines from the Amselfelder region (Kosovo, southeastern Europe), yielding isotope ratios from 0.70981 to 0.71033. In Romania, Bora et al. (2018) measured an $^{87}Sr/^{86}Sr$ range between 0.70230 and 0.76810, the highest values referring to samples from the Ștefănești-Argeș (0.76810) and Dealu Bujorului (0.71700) regions, the lowest value for a sample from the Murfatlar area (0.70230).

The largest Sr isotope study for wines from France was conducted by Epova et al. (2019). The following red wine samples were analysed: Pomerol (0.70968-0.71022), Saint-Émilion (0.70829-0.70895), Pessac-Léognan (0.70900-0.70980) and Pauillac (0.70966-0.70953). Additional data for French wines include Muscadet white (0.70931-0.70996; Horn et al., 1993) as well as red wines from Saint-Emilion (0.70943-0.71005) and Chablis (0.70868) regions (Barbaste et al., 2001). The wine samples from Epova et al. (2019) come from vineyards with a sedimentary substratum represented by the Gironde-Aquitaine sedimentary basin (Tertiary to early Quaternary).

The majority of available $^{87}Sr/^{86}Sr$ for the European wines is represented by Italian wines that totalize 400 data from 6 different regions, reported in 12 articles published between 1998 and 2018. The data distribution between the Italian regions, listed here from North to South, is as follows: 31

for Veneto (7.8% of the total), 214 for Emilia Romagna (53.5%), 113 for Tuscany (28.3%), 12 for Latium (3%), 17 for Campania (4.2%) and 13 for Basilicata (3.2%). More than a half of these (234) are coupled with data for corresponding soils: 30 for Veneto, 154 for Emilia Romagna, 79 for Tuscany and 1 for Campania. In the following, data for each of the various regions of production is briefly summarised.

In the Veneto region, Petrini et al. (2015) investigated the applicability of the Sr isotopic approach to authenticate the geographic origin of Prosecco wine (white variety). The wine samples have an $^{87}$Sr/$^{86}$Sr range of 0.70921-0.71266. The corresponding soil samples, developed on a sedimentary substratum of Pleistocene-Holocene age, cover a more restricted range of $^{87}$Sr/$^{86}$Sr, from 0.70772 to 0.71097. Additionally, a single $^{87}$Sr/$^{86}$Sr value of 0.70872 is available for a Merlot di Piave (red variety) vineyard in this region (Horn et al., 1993).

The available $^{87}$Sr/$^{86}$Sr data for the Emilia Romagna region are mostly for wines from Lambrusco di Sobarba, Lambrusco di Gasparossa and Lambrusco di Salomino vineyards (red variety). Their $^{87}$Sr/$^{86}$Sr values range between 0.70823 and 0.71179 (Durante et al., 2015, 2018). Lambrusco vineyards are rooted on soils developed on Meso-Cenozoic terrigenous deposits whose $^{87}$Sr/$^{86}$Sr are in the range of 0.70773 and 0.71209 (Durante et al., 2015, 2018). Valpolicella red wine samples were also analysed in this region by Horn et al. (1998), yielding $^{87}$Sr/$^{86}$Sr values between 0.70889 and 0.70900.

The $^{87}$Sr/$^{86}$Sr data for red wines from the Tuscany region include Chianti, Sangiovese and Ansonaco vineyards (Marchionni et al., 2013; Braschi et al., 2018). Investigated samples were obtained by microvinification and were compared to soil samples in order to evaluate the potential Sr isotope impact of additives. Chianti wines range between 0.70813 and 0.71068 (Marchionni et al., 2013; Braschi et al., 2018), coming from grapes grown on soils that originate from limestone and marlstone deposits, mainly from the Ligurian oceanic domains. In the westernmost part of the Tuscany region soils are rooted on sedimentary rocks belonging to the Tuscan nappe, represented by feldspar sandstones to siltstones, shales, and marly schists (Costantini et al., 2012). The range of $^{87}$Sr/$^{86}$Sr in these soils is between 0.70804 and 0.70903 (labile fraction). Additional strontium isotope analyses are available for white and red wines from the Giglio Island (Arsonaco and Sangiovese wines), with $^{87}$Sr/$^{86}$Sr from 0.70909 to 0.71209. The Giglio Island is formed by young quartz-feldspathic igneous rocks (granite), showing an $^{87}$Sr/$^{86}$Sr range between 0.71322 to 0.72071 (Marchionni et al. 2013).

In the Latium region analysed wine samples correspond to the Frascati, Cesanese di Affile, Cesanese di Piglio and Cesanense di Olivano Romano vineyards, with an overall $^{87}$Sr/$^{86}$Sr range of 0.70897-0.71058 (Marchionni et al. 2013, 2016). The most important study in the Latium wine region was performed on Cesanese vineyards located on a volcanic substratum formed by pyroclastic rocks ($^{87}Sr/^{86}Sr$=0.71032-0.71148) of the Villa Senni, Pozzolane Rosse and Madonna degli Angeli formations from the Colli Albani volcanic field (Avanzinelli, et al., 2009; Boari et al., 2009; Conticelli et al., 2015). On the other hand, the vineyards labelled as "hill" (in flat areas) by the authors are characterized by a substratum consisting of Mesozoic to Tertiary sedimentary rocks such as limestone, marlstone, sandstone ($^{87}Sr/^{86}Sr$=0.70885-0.71785) from the Arenaceous-Pelitic and Madonna degli Angel formations (Critelli et al., 2007). Marchionni et al. (2013, 2016) showed a good correspondence between $^{87}Sr/^{86}Sr$ in wines and their geological substrata, especially for wines rooted on volcanic soils ($^{87}Sr/^{86}Sr$ from 0.70994 to 0.71138). Frascati white wine samples were studied by Horn et al. (1993) who reported $^{87}Sr/^{86}Sr$ values between 0.70835 and 0.70943.

As for the Campania region, the Aglianico Campano and Piedirosso vineyards are located on geological substrata represented by rocks from the Roccamonfina, Somma-Vesuvius and Campi Flegrei volcanic districts, as well as on the sedimentary rocks of the Campana plain (including the Benevento, Irpinia and Lettere areas). While Aglianico Campano wines display $^{87}Sr/^{86}Sr$ values between 0.70822 and 0.70865, Piedirosso ones range from 0.70772 to 0.70839 (Marchionni et al. 2013; Mercurio et al., 2015). Rocks from the Campania plain (represented by Tertiary terrigenous arenite, clay deposits with subordinate evaporite and limestone layers) show an $^{87}Sr/^{86}Sr$ value of 0.70884. Volcanic rocks from the afore mentioned districts display an $^{87}Sr/^{86}Sr$ interval between 0.70650 and 0.70860 (Conticelli et al., 2002; Peccerillo, 2017; Boari et al., 2009). Mercurio et al. (2014) conducted a detailed study coupling the analysis of Piedirosso wine samples, a soil profile, as well as samples from other matrices (grapes, leaves, branches) in the volcanic area of Campi Flegrei. The authors showed an overall agreement between the biological samples, including wines (0.70776-0.70844), and the soil samples from the different horizons (0.70788-0.70813).

Investigated vineyards in the Basilicata region are rooted on pyroclastic deposits from the Mount Vulture volcano Studies have also been conducted in the Aglianico vineyards (red variety), yielding $^{87}Sr/^{86}Sr$ values from 0.70679 to 0.70817 (Marchionni et al., 2013). The overall range of rock $^{87}Sr/^{86}Sr$ for Mount Vulture volcano is between 0.70522 and 0.70705 (Conticelli et al., 2002; Boari et al., 2009).

### *$^{87}Sr/^{86}Sr$ results and their overlap*

**Figure 2.5** reports the general distribution of $^{87}Sr/^{86}Sr$ in worldwide wines. The data highlight that there is a large overlap of $^{87}Sr/^{86}Sr$ for wine samples between countries, meaning that Sr isotope ratios are not efficient when trying to make a distinction between provenance areas at such a large scale of observation. For example, the $^{87}Sr/^{86}Sr$ range measured in Bordeaux wines (France) overlaps with that for wines from U.S.A., Italy, China and Argentina (**Figure 2.5).** Barbaste et al. (2001) compared $^{87}$Sr/$^{86}$Sr of wines from vineyards rooted on volcanic (Chile, Madeira-Portugal, California-U.S.A.), granitic (Douro-Portugal) and sedimentary bedrocks (St. Emillion-France). Wines from volcanic (basaltic) rocks show lower $^{87}$Sr/$^{86}$Sr values compared to wines from granite vineyards in Portugal. French wines, coming from sedimentary vineyards, showed intermediate $^{87}$Sr/$^{86}$Sr values. I attempted to discriminate $^{87}$Sr/$^{86}$Sr volcanic wines in the world (**Figure 2.6**). Results show that volcanic wines from California (U.S.A.) and the Madeira Island (Portugal) have low $^{87}$Sr/$^{86}$Sr and can be discriminated from Italian and Chileans wines. On the other hand, Chilean wines overlap Italian ones, showing that rocks can have similar isotope signature even if from different volcanic systems. It confirms that the $^{87}$Sr/$^{86}$Sr approach is inaccurate if attempting to distinguish wine-producing areas on a large scale.

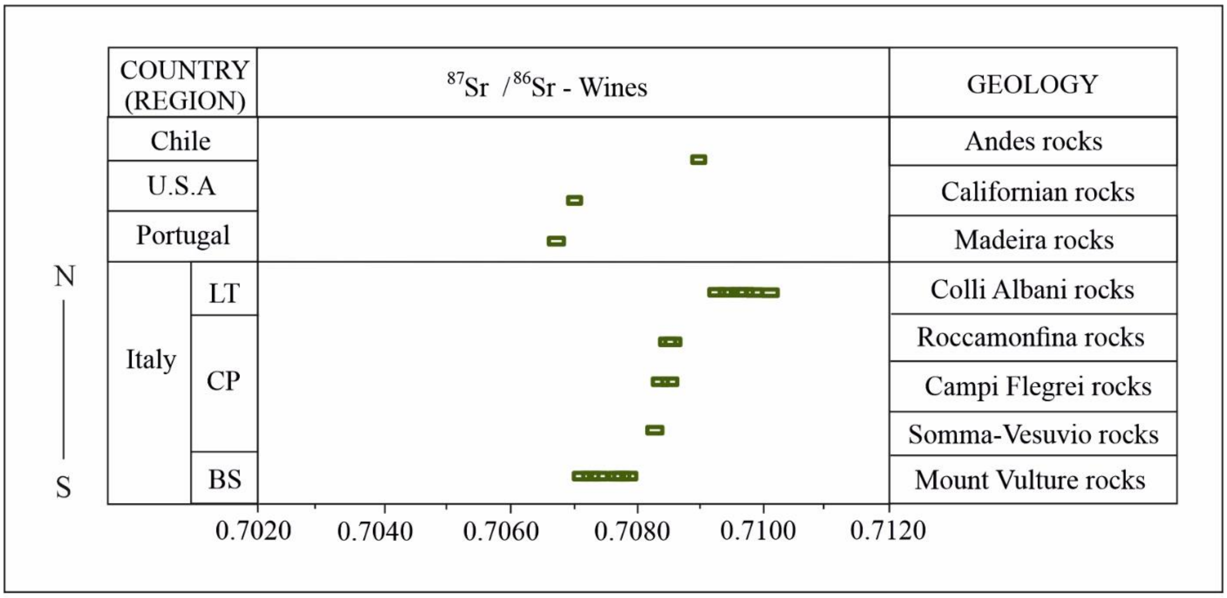


**Figure 2.6**. Distribution of $^{87}$Sr/$^{86}$Sr values in wine samples coming from areas with a volcanic substratum. Data sources as in Figure 2.2. Wines from Italy are listed from north to south, separated by the different regions (LT=Latium, CP=Campania, BS=Basilicata).

Italian wine samples, though making up the largest part of the existing dataset for wine Sr data, show a rather narrow range of $^{87}$Sr/$^{86}$Sr values, with vineries being founded on soils developed on a limited range of lithologies, from sedimentary to volcanic and granitic. $^{87}$Sr/$^{86}$Sr values for wines growing on volcanic lithologies show a clear isotope gradient, with a general decrease in values from North to South, being overall constant in the Latium, Campania, and Basilicata regions (Braschi et al., 2018; Mercurio et al., 2014; Marchionni et al., 2013, 2016). This zoning trend mimics the one observed in rocks (Conticielli et al., 2002, 2009), further supporting the conclusion that Sr isotope ratios in wine and substrate rocks are correlated. On such basis, it seems reasonable to conclude that wines from the Italian volcanic vineyards can be efficiently discriminated at a small to medium scale of investigation, thus possibly representing a useful tool for detecting frauds in wine appellation.

# Chapter 3 – $^{87}$Sr/$^{86}$Sr CHARACTERIZATION AS A TOOL FOR AUTHENTICATING THE GEOGRAPHICAL ORIGIN: APPLICATION TO BOTTLED WINE, MICROVINIFICATION, GRAPE, LEAF AND SOIL SAMPLES IN VOLCANIC VINEYARDS FROM ITALY

## INTRODUCTION

The assignment of geographical origin of beverage and food is of substantial importance within the European Union. The DOP (Protected Designation of Origin) and IGT (Typical Geographical Indication) products in Europe represent the excellence of European agri-food production and are both the result of unique combination of human and environmental factors characteristic of a specific territory (Barjolle and Chappuis, 2000; Raynaud et al., 2005; Sylvander and Martine, 2006; Belletti et al., 2007).

Italy is the European country with the largest number of agri-food products with designation of origin and geographical indication recognized by the European Union. Among these products, wine is the most protected, with clearly defined regulations for the certification of origin and provenance. The production of wine in Italy is characterized by a large diversification of types of wines, many of great prestige both nationally and internationally. For this reason, Italian institutions such as the *Ministero delle Politiche Agricole Aimentari e Forestali* (Ministry of Agricultural, Food and Forestal policies), *Camera di Commercio* (Chamber of Commerce) and the *Regioni* (Regions) have the aim of encouraging the consolidation of the success of quality productions, recognizable by the brands DOCG, DOC and IGT (https://www.politicheagricole.it/). These are defined as

- DOCG (*Denominazione di Origine Controllata e Garantita*, Controlled and Guaranteed Denomination of Origin): these are the finest wines, the brand guarantees the origin and the quality and allows the numbering of the bottles produced. The law requires that the following information must be found on the labels: name of the region from which wines come; name or company name of the bottler together with the mention of the Municipality and the Member State in which the bottler has its main office; nominal volume in liters, centiliters, or milliliters; actual alcoholic strength and production batch to identify the wine produced or packaged under identical conditions.
- DOC (*Denominazione di Origine Controllata*, Controlled Denomination of Origin): these are quality wines, originating in limited areas, whose production cycle must comply with the production regulations. Before being marketed, they are checked qualitatively by the tasting commissions, which submit them to chemical, physical and organoleptic analyses to check the correspondence to the legal requirements.

- IGT (*Indicazione Geografica Tipica*, Typical Geographical Indication): these products represent a recognition of quality attributed to table wines that do not have a particularly restrictive discipline and the production areas are quite large. IGT wines after five years they can aspire to become DOC.

Currently, wine production in Italy includes 74 DOCG, 334 DOC and 118 IGT, distributed in all the 20 Italian regions.

In the traceability system, it is important to distinguish the geographical source of food products to verify the origin often indicated on labels and to prevent adulterated products from reaching consumers. In this way, the traceability of wines is certainly a key topic.

The applicability of the Sr isotopic systematics has been evaluated in relation to qualification and to geographic traceability of wine products. Determining the geographical origin using wine $^{87}Sr/^{86}Sr$ has been widely discussed in the last three decades in many countries including Italy, South Africa, Romania, Canada, Portugal, Argentina, France, Chile, China, Australia, Kosovo and U.S.A. (Horn et al., 1993; Wolff-Boenisch, 1998; Barbaste et al., 2001, 2002; Almeida and Vasconcelos, 2001, 2004; Vorster et al., 2010; Di Paola-Naranjo et al., 2011; Marchionni et al., 2013, 2016; Martins et al., 2014; Mercurio et al., 2014; Durante et al., 2015, 2018; Petrini et al., 2015; Vinciguerra et al., 2015, 2016; Bora et al., 2018; Braschi et al., 2018; Guibourdenche et al., 2020). Italy represents the country with the largest number of available studies directed to the application of strontium isotopes in wines (Mercurio et al., 2014; Durante et al., 2015, 2018; Petrini et al., 2015; Marchionni, et al. 2013, 2016; Bora et al., 2018; Braschi et al., 2018). Among these, some are focused on vineyards grown on Cenozoic volcanic substrata (Mercurio et al., 2014; Marchionni et al., 2013: Braschi et al., 2018).

The $^{87}Sr/^{86}Sr$ methodology assumes that plants absorb labile elements in the same isotopic proportions that occur in the rocks and soils (Comerford, 2005). Cenozoic central-southern Italian volcanic rocks have a variable Sr isotopic composition, which decrease constantly from northwest to southeast (Conticelli et al., 2002, 2010; Avanzinelli et al, 2008, 2009). Thus, $^{87}Sr/^{86}Sr$ values of wines from volcanic vineyards in Italy were selected and compared with their respective bedrock values, aiming to investigate the relationships between wines and geology.

This chapter shows a new Sr isotope data for soil, grape, leaf, bottled wine and microvinification samples collected in nine vineyards from six different Italian volcanic districts: Ponza Island, Ventotene Island, Somma-Vesuvio, Salina Island, Mount Etna and Pantelleria Island (**Figure 3.1**).

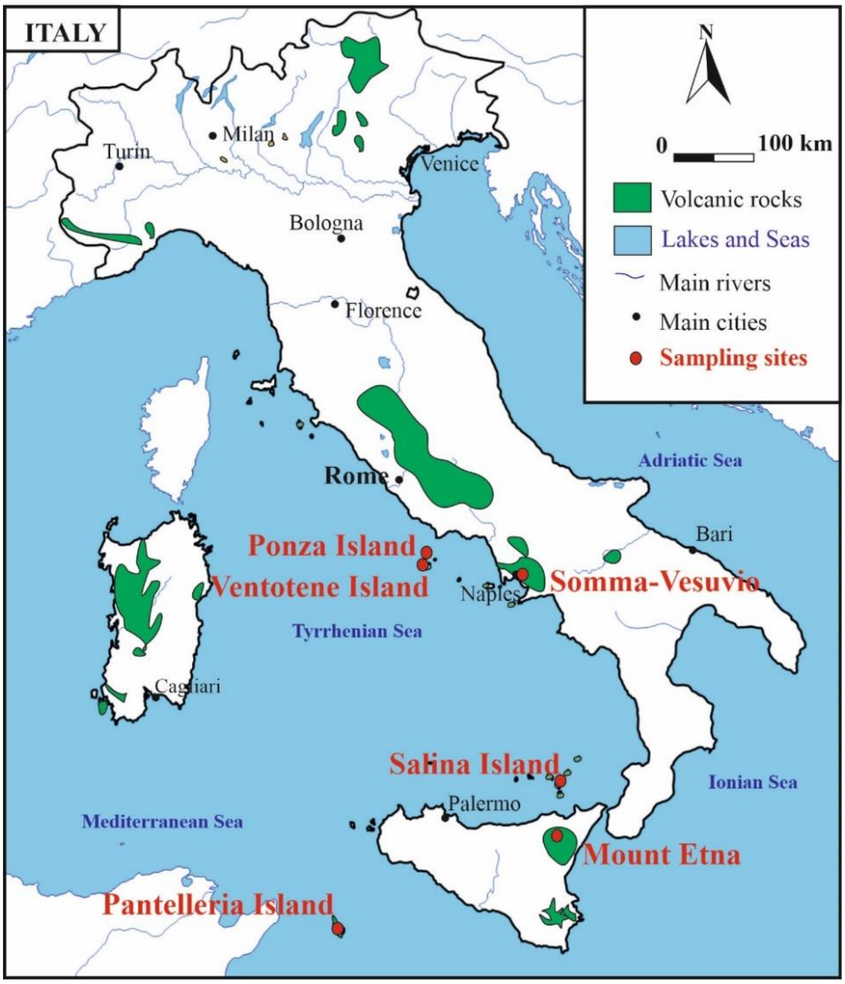


**Figure 3.1.** Distribution of volcanic rocks in Italy and location of vineyards selected for the present study (modified from Tacchia et al., 2004).

Studies of the labile fraction of soils reveal that this generally has a lower $^{87}Sr/^{86}Sr$ compared to its bulk soil, showing a better correlation to $^{87}Sr/^{86}Sr$ in wines (Almeida and Vasconcelos, 2001, 2004; Marchionni et al., 2016; Vinciguerra et al., 2016; Braschi et al., 2018; Guibourdenche et al. 2020). For this reason, both labile fraction and the bulk soil samples have been analyzed here. As a complement, a detailed characterization of the investigated soil samples was performed in order to assess whether the soil is able to provide chemical elements to the plant. Furthermore, to encompass the possible cause of the discrepancies between microvinification and bottled wine, samples from the same winery, grape variety and harvest has been undertaken.

In addition, a detailed $^{87}Sr/^{86}Sr$ characterization has been undertaken on a soil profile and on vine components from the Somma-Vesuvio district, to investigate possible variations of Sr isotopic composition from the soil to the plant, on a small and detailed scale.

## SAMPLE COLLECTION AND MICROVINIFICATION PROCESS

In 2018, soil (17 samples), root (1 sample), leaf (11 samples), grape (7 white, 3 red) and bottled wine (2 red, 9 white) samples have been collected for the present study (**Tables 3.1, 3.3, 3.4, 3.5, 3.6, 3.7 and 3.8**).

The selected sampling areas have been chosen considering the criteria of productivity (small wineries), grape variety (different grape varieties for all sampling sites) used and host rock/soil type (volcanic rocks of different composition and age) in the producing regions. Small wineries were selected on different volcanic rocks in Italy in 3 regions: (Latium, Campania, and Sicily) with the selected grape variety being different for each vineyard. The methodology applied follows that reported for a similar project carried out by Vinciguerra et al. (2016) and Guibourdenche et al. (2020).

Soil samples were collected from the corresponding vineyards (approximately weighing 2 kg each) at a depth of 0.30 m, close to the vine roots, using stainless steel collectors. All the sampling sites have been carefully geo-referenced. The color of the soil samples was described using the Munsell color chart (Miller, 1958). The Munsell Soil Color Charts is a quickly and easily tool to evaluate the type of soil and helps understand soil composition and classify. The soil is matched to the color and the color name and color code are registered. The presence of some elements in a soil can be detected established on its colors. For example, white color indicates the predominance of silica, or the presence of carbonate or salts, red is associated with iron oxide and brown and black indicate the level of organic matter. However, a higher precision is necessary using laboratory tests (i.e., HCl test for carbonate identification and organic matter quantification).

**Table 3.1**. Selected vineyards for the present study.

| Region | Vineyard district | Winery | Coordinates | Grape variety |
|---|---|---|---|---|
| Latium | Ponza Island | Antiche Cantine Migliaccio | 40°53'08"N; 12°57'06"E | Biancolella (white) |
| | | | 40°53'14"N; 12°57'04"E | Aglianico (red) |
| | Ventotene Island | Candida Terra | 40°47'33"N; 13°25'25"E | Fiano (white) |
| Campania | Somma-Vesuvio | Florami | 40°47'23"N; 14°26'21"E | Falanghina (white) |
| Sicily | Salina Island | Caravaglio | 38°33'35"N; 14°49'51"E | Malvasia (white) |
| | | | 38°33'34"N; 14°49'53"E | Corinto Nero (red) |
| | Mount Etna | Quantico | 37°50'16"N; 15°07'47"E | Carricante (white) |
| | | | 37°50'16"N; 15°07'44"E | Nerello Mascalese (red) |
| | Pantelleria Island | Federico Paulsen | 36°46'13"N; 12°01'55"E | Zibibbo (white) |

A soil profile (for a total thickness of 1.20 m) was described and sampled in the Florami winery (Somma-Vesuvio area) close to the sampled vine. Six soil samples were collected from different soil horizons (Ap=0-0.16 m, C=0.16-0.21 m, BC1=0.21-0.40 m, BC2=0.40-0.70 m, 2C=0.70-0.83 m and 3C=0.83-1.2 m), for which a detailed description is reported in the Results section.

Approximately 20 grape bunches (with an average weigh of 300 g each) have been collected in each vineyard from a single plant. The grape components (must, skin, seeds, and stem) used for the detailed characterization undertaken in the Somma-Vesuvio vineyard, have been separated with the use of gloves. A root sample was collected in the Somma-Vesuvius soil profile, found in horizons BC2 and 2C. Leaves from the sampled vine plants were also collected, for a total of 100 g. All the collected samples were stored in plastic bags and frozen at -10 °C.

Samples of bottled wine were provided by the wineries where the previously described samples have been collected. The wines (belonging to the same grape variety and harvest of the collected grapes) were made available by wineries after one year, going through the winemaking processes and regulations of each denomination of origin of each producer. Bottled wine samples from Mount Etna were the only ones which were not provided by the wineries. In addition, the Caravaglio winery of Salina provided a sample of *Passito* wine, produced from the same grape varieties and harvest with respect to the collected grape samples. Similarly, the Federico Paulsen winery supplied also a sample of wine made of a mixture of zibibbo grapes from different vineyards in Pantelleria Island (Barone winery).

The process of microvinification can help to define the characteristics of a wine obtained from a single vine plant, without the use of the chemical additives commonly used in commercial wines, which might change the original isotopic ratio of a wine (Almeida and Vasconcelos, 2004). The collected grapes samples were subjected to the microvinification procedure, entirely performed at the DiSTAR laboratories. In the first stage of microvinification procedure, grapes were thawed (24 h before the preparation), washed with distilled water, and then squeezed using a stainless-steel winepress. Each squeezed sample was collected in a stainless-steel bucket, transferred to a 2-liter glass bottle using a stainless-steel funnel, and then covered with cotton stopper. The samples were stirred once a day and kept below 30 °C (constantly checked through adhesive thermometers) until the end of the fermentation (for an estimated time of 32 days) in a chemical hood. The bottles were then closed with plastic stoppers and held horizontally at a temperature of 18 °C. A caustic soda solution of 0.5 mol/l was used to clean all materials before and after each microvinification, followed by washing with tap and distilled water. A blank was made before each microvinification, where distilled water was passed through winepress, bucket and funnel and then stored in a glass bottle.

## *TERROIR* CHARACTERIZATION

In order to fully define the sum of the factors that contributed to the peculiar features of the wines from the investigated districts, the geological, pedological, climatic, viticulture and winemaking characteristics of these are described below, in an attempt to define their specific *terroir*.

### *Ponza Island*

Ponza (Latium region) is the largest island of the Italian Pontine Islands Archipelago, located 33 km south of Cape Circeo in the Tyrrhenian Sea, between the 40°56′05.07″N, 13°00′03.75″E, and 40°52′39.75″N, 12°57′13.00″E coordinates. The island is approximately 8.9 km long and 2.4 km at its widest, with maximum altitude of about 270 m. Eutric leptosol, andic, eutric, thapto andic, and calcaric cambisol, haplic luvisol (vitric), vitric and mollic vitric andosol, thephric and eutric regosol are the main soil types at Ponza Island (Costantini et al., 2012). The vegetation is typically Mediterranean, with the prevalence of agaves, prickly pears, brooms, phillyrea and myrtle. The climate has subtropical Mediterranean characteristics with moderate thermal excursions, with average annual rainfall of 658 mm and temperatures ranging from 8 to 27 ºC (www.ilmeteo.it).

In 1734, Carlo di Borbone colonized the island, assigning various plots of land to Neapolitan settlers. He assigned to Pietro Migliaccio, coming from Ischia Island, the area of the Fieno, in the southern sector of Ponza Island. Pietro Migliaccio brought the typical vines from Ischia: Biancolella, Forastera, Guarnaccia, Aglianico and Piedirosso. (www. antichecantinemigliaccio.it). These, together with Chardonnay and Malvasia, are the typical grapes used by Ponza wine producers.

Wineries from Ponza Island obtained the IGT Latium appellation, established in 1995 in Latium region. Numerous are the production rules that must be followed in order to achieve the Latium IGT denomination, including that the zone of production must be within the Latium region. According to such regulations, the minimum alcohol level is of 9.0% for *Passito* (16.0% potential), 10.0% for *Spumante*, 10.5% for white, *Rosé*, and *Rosé* varietals, 11.0% for red varietals and Novello, 12.0% for *Vendemmia Tardiva* (15.0% potential; https://italianwinecentral.com/ denomination/igp-Latium/).

Ponza Island represents the product of the oldest felsic magmatic manifestation in the central Tyrrhenian area (Cadoux et al., 2005; **Figure 3.2**). Volcanic rocks are represented by Pliocene submarine rhyolites, Pleistocene subaerial trachyte and comendite lavas (Scutter et al., 1998; Conte and Dolfi, 2002). Rhyolites show poorly porphyritic textures with phenocrysts of plagioclase (about $An_{30-60}$), sanidine, biotite, orthopyroxene and salitic clinopyroxene, set in a glassy to microgranular groundmass. Trachytes are poorly porphyritic with phenocrysts of plagioclase (about $An_{30-65}$), alkali feldspar, salitic clinopyroxene and biotite, set within a microcrystalline groundmass made of alkali feldspar, fewer clinopyroxene and Fe-Ti oxides (Conte and Dolfi, 2002). K/Ar dating's on sanidine crystals indicate that rhyolitic volcanism at Ponza Island took place between 4.2 and 3.0 Ma. Trachytes were erupted at about 1.0 Ma (Cadoux et al., 2005). $^{87}Sr/^{86}Sr$ in Ponza Island rocks ranges from 0.70850 to 0.71387 (n=12; Conte and Dolfi, 2002).

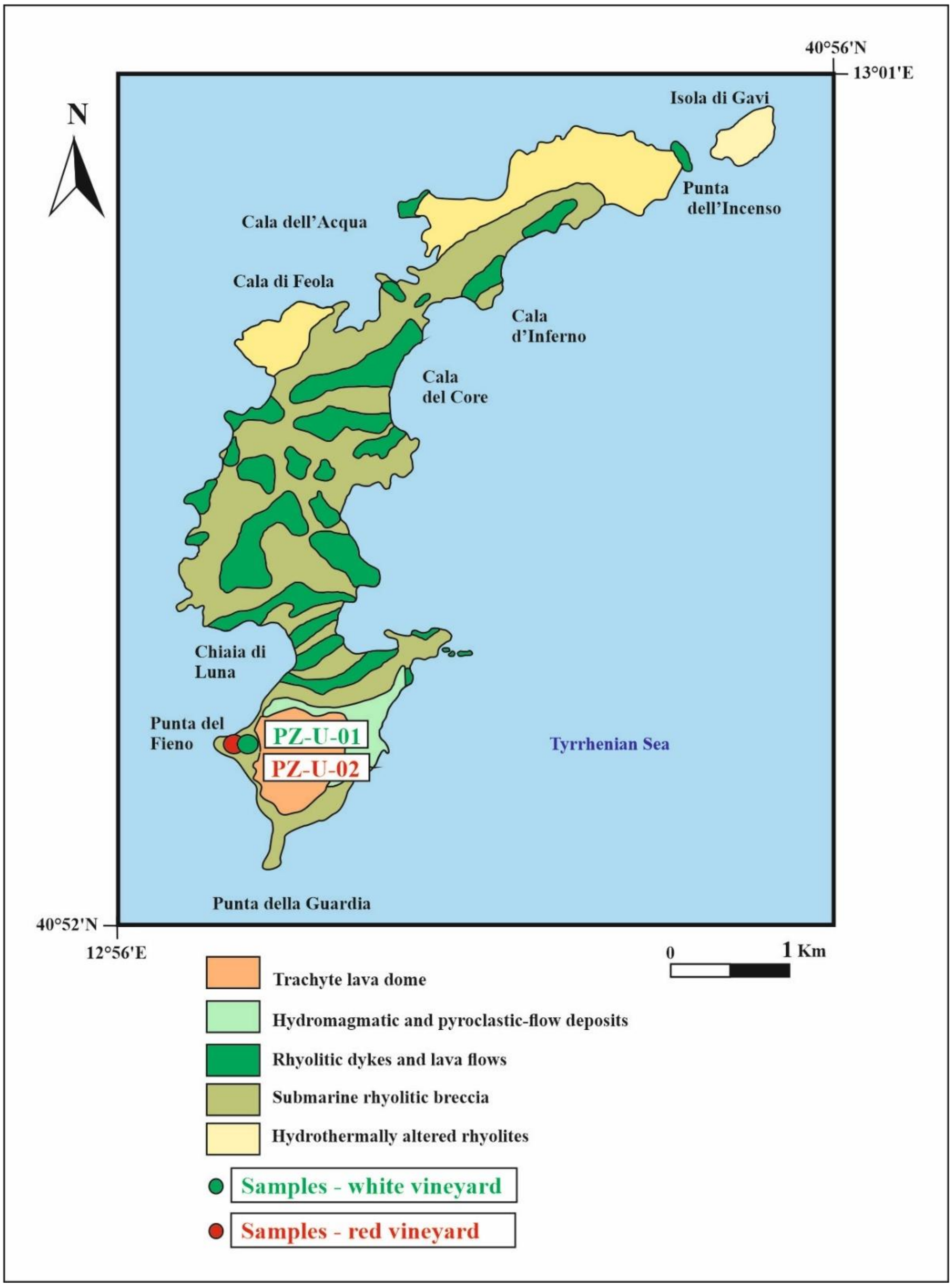


**Figure 3.2.** Geological map of the Ponza Island (modified after Cadoux et al., 2005) with sample locations.

**Table 3.2**. Sampling data sheet for the Ponza Island district.

| | |
|---|---|
| **Winery** | Antiche Cantine Migliacco (Punta Fieno) |
| **Sampling date** | 08/09/2018 |
| **Soil samples** | 2 samples (30 cm deep), 20 cm in front of the plants (PZ-S-01 and PZ-S-02) |
| **Amount of grapes** | Total 12kg: 6 kg (sample PZ-U-01) and 6 kg (sample PZ-U-02) |
| **Grape typology** | Biancolella (PZ-U-01, white grape) and Piedirosso (PZ-U-02, red grape) |
| **Leaf samples** | PZ-F-01 and PZ-F-02 |
| **Microvinification samples** | Biancolella (PZ-V-01) and Piedirosso (PZ-V-02) |
| **Bottle wine samples** | Biancolella (PZ-W-01) and Piedirosso (PZ-W-02) |
| **Wine classification** | IGT Latium |
| **Age of vine** | 220 years (Biancolella); 30 years (Piedirosso) |
| **Geology** | Submarine rhyolitic breccias (**Figure 3.2**) |
| **Coordinates** | 40°53'08"N, 12°57'06"E (Biancolella); 40°53'14"N, 12°57'04"E (Piedirosso) |
| **Altitude** | 60m |

### *Ventotene Island*

Ventotene (Latium region; **Figure 3.3**) is one of the Pontine Islands in the Tyrrhenian Sea, 46 kilometers off the coast of Gaeta right at the border between Latium and Campania, between the 40°48′12.38″N,13°25′50.24″E, and 40°47′07.98″N,13°24′31.94″E coordinates. The island shows a length of 3 km and a maximum width of about 800 m. The main soil types at Ventotene Island are represented by vitric, epileptic, mollic, eutric and melanic andosol (Costantini et al., 2012). The climate of the island is a very mild subtropical one, characterized by very mild and rainy winters with scarce daily thermal excursions, and by hot but breezy summers with an annual rainfall of 930 mm and temperatures ranging from 3 to 30 °C (www.ilmeteo.it).

In 2015, the winery Candidaterra was born, the name referring to Santa Candida, Patron Saint of the island. Pandataria is the name of its first white wine (a blend of Falanghina, Fiano and Greco grapes), the first wine of Ventotene Island. This wine obtained the IGT Latium appellation.

The Island of Ventotene consists of a basal series of thin mafic lava flows cut by a caldera rim and covered by intermediate to felsic pyroclastic products (Perrotta et al., 1996). Rock compositions range from basalt and trachybasalt to phonolite, with emplacement ages ranging from 0.8 Ma to < 130 ka (D'Antonio et al., 1999). Basalts and trachybasalts have a porphyritic texture with phenocrysts of olivine, diopsidic to salitic clinopyroxene and plagioclase, set into a holocrystalline groundmass formed by the same phases plus Fe-Ti oxides and alkali feldspars (D'Antonio et al., 1999).

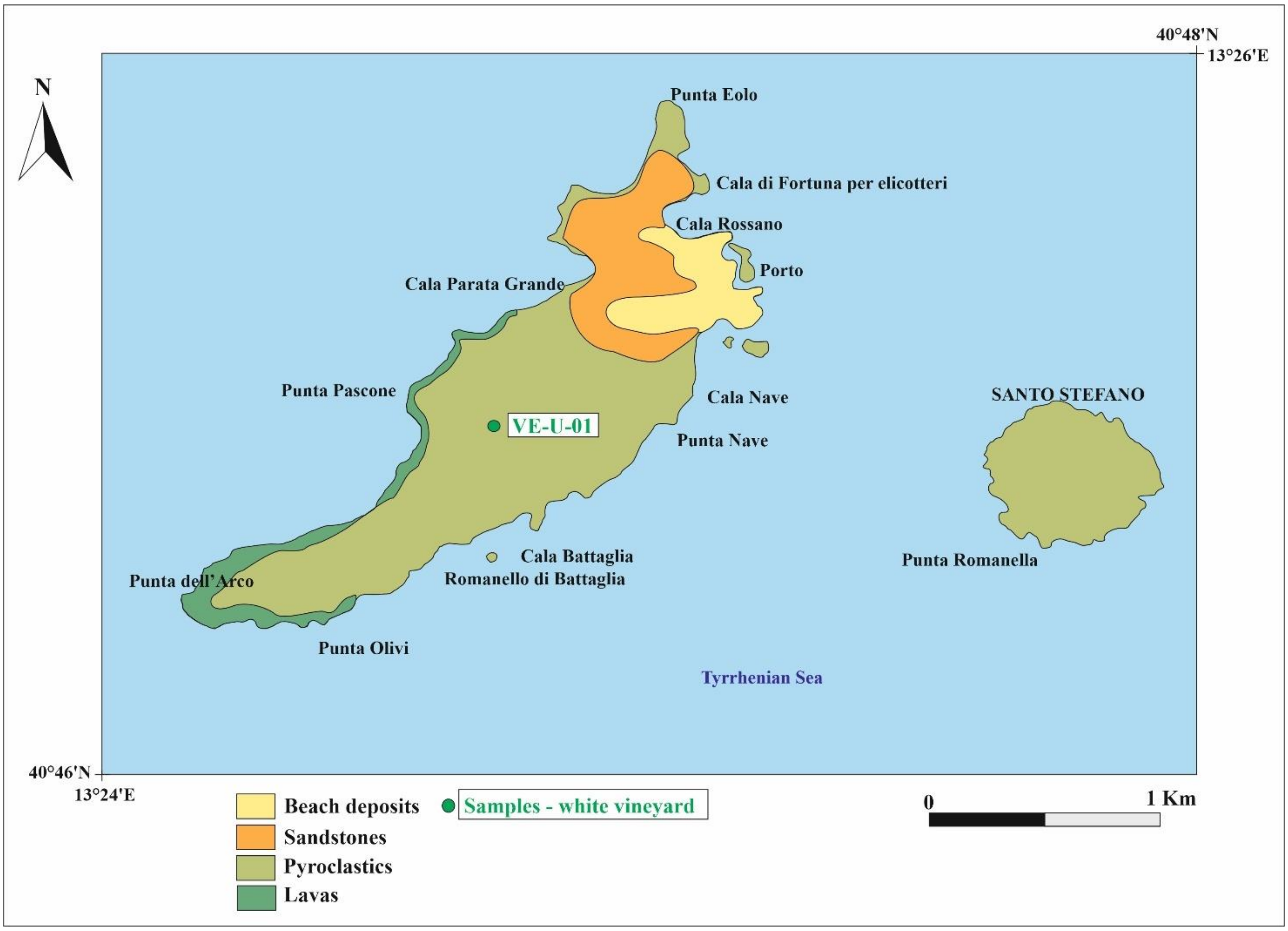


**Figure 3.3.** Geological map of the Ventotene Island (modified after Perrota et al., 1996) with sample locations.

**Table 3.3**. Sampling data sheet for the Ventotene Island district.

| | |
|---|---|
| **Winery** | Canditerra (via Calanave, 16) |
| **Sampling date** | 08/09/2018 |
| **Soil sample** | 1 sample (30 cm deep), 20 cm in front of the plants (VE-S-01) |
| **Amount of grapes** | Total 6 kg (sample VE-U-01) |
| **Grape typology** | Fiano (VE-U-01, white grape) |
| **Leaf sample** | VE-F-01 |
| **Microvinification sample** | Fiano (VE-V-01) |
| **Bottle wine sample** | Fiano (VE-W-01) |
| **Wine classification** | IGT Latium |
| **Age of vine** | 3 years |
| **Geology** | Pyroclastics (**Figure 3.3**) |
| **Coordinates** | 40°47'33"N, 13°25'25"E |
| **Altitude** | 40 m |

Latites have similar phenocryst assemblage as trachybasalts but contain biotite also and sometimes are characterized by the coexistence of two distinct types of clinopyroxene (D'Antonio et al., 1999). Phonolites have phenocrysts of sanidine, plagioclase, potassic ferropargasitic amphibole and Fe-Ti oxides. Haüyne and nepheline are found in some latites and trachytes (Metrich et al., 1988;

D'Antonio and Di Girolamo, 1994; D'Antonio et al., 1999). Isotope ratios for Ventotene Island whole rock samples range from 0.70709 to 0.71003 (n=22; D'Antonio and Di Girolamo, 1994; D'Antonio et al., 1996; 1999; Conticelli et al., 2002, 2010).

***Somma-Vesuvio***

The cone known as Vesuvio (elevation of 1,281 m), which grew within the caldera of the Mount Somma volcano, is located between 40°51′55.98″N, 14°26′21.54″E, and 40°46′49.24″N, 14°25′31.97″E coordinates (**Figure 3.4**). The climate of the district is a borderline Mediterranean and humid subtropical one, with annual rainfall of 1010 mm and temperatures ranging from 0 to 33 ºC (www.ilmeteo.it). Mount Somma-Vesuvio (Campania region) shows a typical Mediterranean vegetation, with artificially grown pinewoods and ilex trees. Vitric, epileptic, mollic, utric and melanic andosoil are the main soil types (Costantini et al., 2012).

Winemaking in the Somma-Vesuvio area dates back to centuries before Christ. Aristotle wrote that the ancient people of Thessaly in Magna Grecia planted the first vineyards on the volcano slopes in the 5th century b.C. After the rise of Christianity, monks who lived there continued producing this "Greek" wine, and in time the local peasants combined these two historic facts to form the name of the city of Torre del Greco, or "Greek Tower" (https://www.cantinadelvesuvio.it/). Lacryma Christi (literally "tears of Christ") is the name of wines (white and red) produced on the slopes of Mount Somma-Vesuvio. White wine is made mainly from Verdeca and Coda di Volpe grapes, with smaller proportions of Falanghina, Caprettone and Greco di Tufo. Red Lacryma Christi, made from Piedirosso and Sciascinoso grapes, is the nearest equivalent to wines drunk by the Ancient Romans, based on recent archaeological evidence represented by microscopic residues found on the taps of some casks (Robinson et al., 2012). The wine sample collected at Mount Somma-Vesuvio vineyards obtained the IGT Campania appellation, established in 2004. Principal white grape varieties are Asprinio, Bellone, Biancolella, Bombino Bianco, Chardonnay, Coda di Volpe, Falanghina, Fiano, Forastera, Gewürztraminer, Greco, Guarnaccia, Malvasia, Montonico Bianco, Moscato, Pinot Bianco, Pinot Grigio, Riesling, Sylvaner Verde, Trebbiano, Verdeca, Welschriesling (Riesling Italico). On the other hand, red grape varieties include Aglianico, Aleatico, Barbera, Cabernet Sauvignon, Casavecchia, Cesanese, Ciliegiolo, Greco Nero, Lambrusco, Malvasia Nera, Merlot, Montepulciano, Piedirosso, Pinot Nero, Primitivo, Sangiovese, Sciascinoso, Uva di Troia. A minimum alcohol level of 11.5% is required for both white and red wines (https://italianwinecentral.com/denomination/igp-campania/).

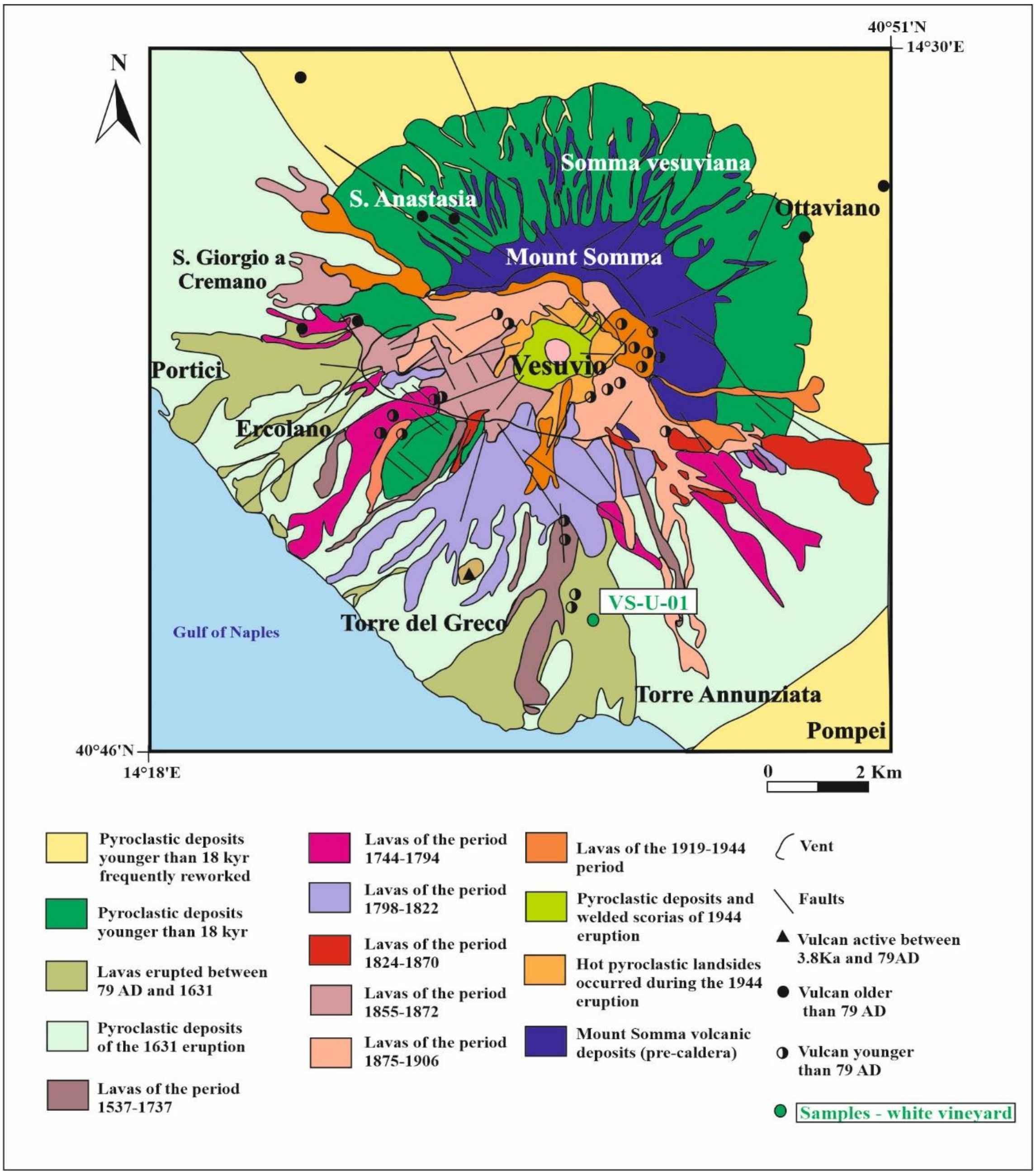


**Figure 3.4.** Geological map of Mount Somma-Vesuvius (modified after Orsi et al., 2003) with sample locations.

Mt. Somma-Vesuvio is a strato-volcano consisting of a recent cone, the Vesuvio, which evolved within the older Somma caldera (Santacroce, 1987; Rolandi et al., 2004). The oldest evidence for volcanic activity is represented by lavas and tephra deposits dated to >30 ka (Sparice et al., 2017a). The older period of activity (39-22 ka) built up the Mount Somma strato-volcano mainly by the emplacement of lava flows with rarer pyroclastic deposits from sporadic low-energy explosive events (Di Renzo et al., 2007; Santacroce et al., 2008; Sparice et al., 2017b). The collapse of Mount Somma and the development of the caldera started with the earliest major Plinian eruption (Pomici di Base) at 22 ka and was completed with the 79 AD Pompeii eruption (Santacroce et al., 2008).

The Vesuvio cone developed within this caldera after the 79 AD eruption, mostly by the emplacement of intermediate to mafic lava flows and leucite-rich tephra, with low-energy open-conduit activity (Piochi et al., 2006). Lava emissions were interrupted by only two sub-Plinian events in 472 and 1631 AD (Santacroce et al., 2008). Since its last eruption in March 1944, the Vesuvio has remained dormant without signs of unrest (Piochi et al., 2006). Mount Somma-Vesuvio rocks are mostly highly potassic, widely variable in terms of their degree of silica undersaturation (Di Renzo et al., 2007; Piochi et al., 2006). Whole rock Sr isotope ratio show a range from 0.70624 up to 0.70807 (n=215; Cortini and Hermes, 1981; Santacroce, 1987; Civetta and Santacroce, 1992; Caprarelli et al., 1993; Ayuso et al., 1998; Somma et al., 2001; De Vivo et al, 2003, Cortini et al., 2004; Civetta et al., 2004; Piochi et al., 2006; Di Renzo et al., 2007).

**Table 3.4**. Sampling data sheet for the Somma-Vesuvio district.

| | |
|---|---|
| **Winery** | Florami (Bascotrecase) |
| **Sampling date** | 13/09/2018 |
| **Soil sample** | 1 sample (30 cm deep), 20 cm in front of the plant (VS-S-01) |
| **Amount of grapes** | Total of 6 kg (sample VS-U-01) |
| **Grape typology** | Falanghina (VS-U-01, white grape) |
| **Leaf sample** | VS-F-01 |
| **Microvinification sample** | Falanghina (VS-V-01) |
| **Bottle wine sample** | Falanghina (VS-W-01) |
| **Wine classification** | IGT Campania |
| **Age of vine** | 3 years |
| **Geology** | Lavas erupted between 79AD and 1531 (**Figure 3.4**) |
| **Coordinates** | 40°47'23''N, 14°26'21''E |
| **Altitude** | 300m |

### *Salina Island*

The Salina Island (**Figure 3.5**), belonging to the Aeolian Islands Archipelago (Sicily region), has a total surface area of 27 km$^2$, located between 38°34′48.06″N, 14°50′26.23″E, and 38°32′04.86″N, 14°51′27.52″E coordinates. It is composed of six volcanoes, the oldest of which are preserved at the Pizzo di Corvo, Monte Rivi and close to Capo Faro, although these are only barely recognizable from a morphological point of view. On the other hand, the Monte Fossa delle Felci volcano (the highest peak in the entire archipelago, peaking at 968 m) and Monte dei Porri (886 m) are both almost perfectly preserved. Eutritic leptosol, andic, eutric, thapto andic, and calcaric cambisol, haplic luvisol (vitric), vitric and mollic andosol, tephric and eutric regosol are the main soil type of the island (Costantini et al., 2012). The climate of Salina Island is temperate, typical of the central-Mediterranean zones, with medium annual temperatures varying from 21 to 16 °C. The mountain sides of the island are covered with ferns, poplars, chestnut trees, and typical Mediterranean vegetation including with caper bushes, prickly pear cactus and a variety of orchards, olive groves and vineyards.

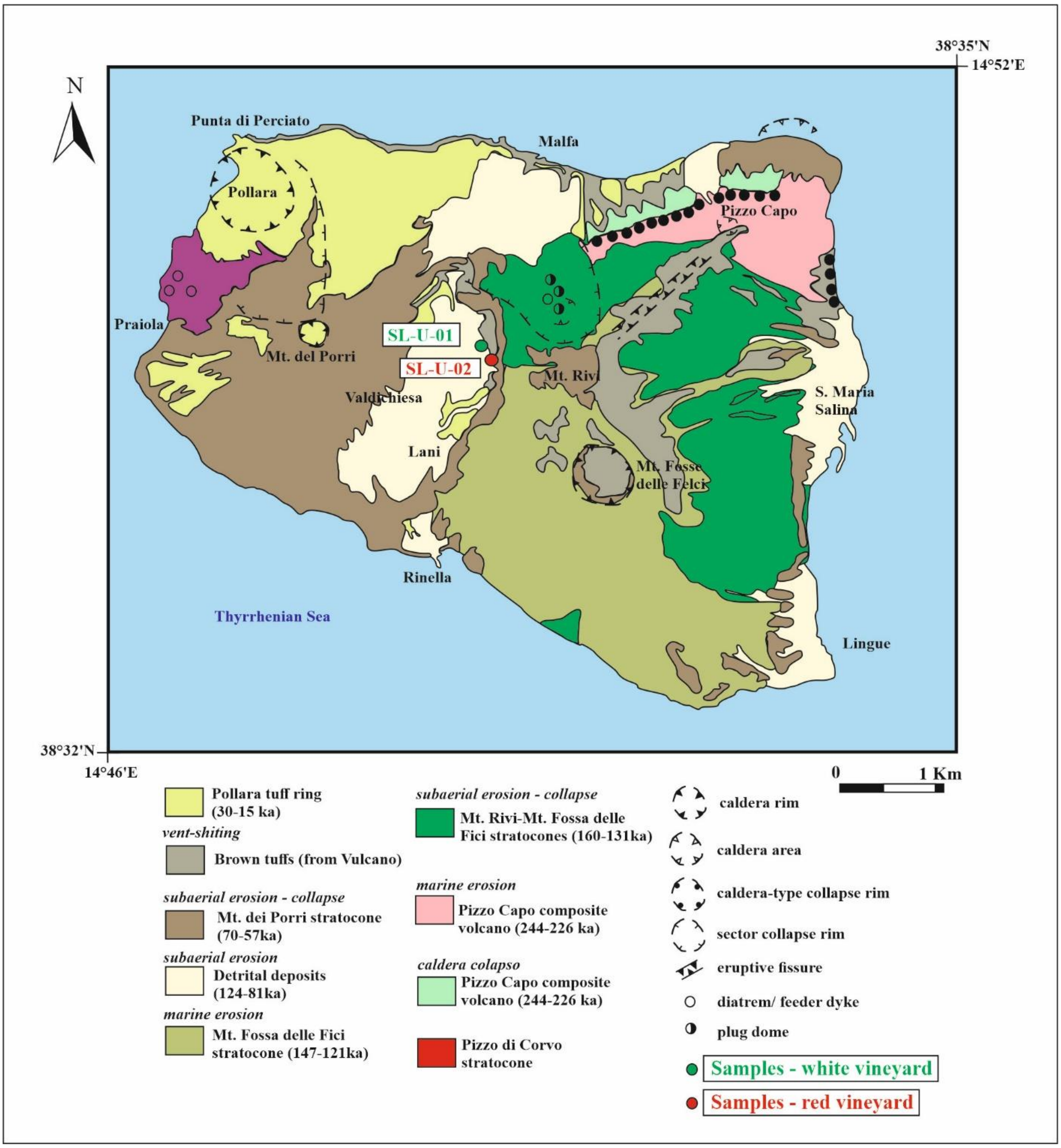


**Figure 3.5.** Geological map of Salina Island (modified after Lucchi et al., 2013) with sample locations.

Salina Island is renowned for Malvasia, a famous white wine that is only produced at Salina. Its name likely derives from Monemvasia, a Greek city of southern Peloponnesus. According to other sources, the term instead derives from Malta Island, where this wine was originally produced. Roman emperors were gluttonous for this wine, which they used to largely import to the capital using amphorae. In the middle ages, Malvasia gradually spread across England, and soon throughout Europe. The production of this wine had its peak during the 19th century thanks to the fleet of a hundred of sailing ships. At the beginning of the last century, the Phylloxera disease destroyed the greatest part of vine varieties, causing a collapse of local economy. After some decades of stasis, around the ‘50s, some of winemakers restarted its production.

In 1973, Salina wines obtained the DOC identification (Lipari DOC). The Lipari DOC rules include: a minimum alcohol level of 8.0% for white (11.5% potential), about 15% for *Passito* (18.0% potential) and 16.0% for *Liquoroso* (20.0% potential). Residual sugar has a minimum of 60 g/l (6.0%) for *Passito* and *Liquoroso.* The aging for *Passito* has a minimum of 4–6 months for *Liquoroso*, and minimum 6 months after fortification (https://italianwinecentral.com/denomination/malvasia-delle-lipari-doc/).

**Table 3.5**. Sampling data sheet for the Salina Island district.

| | |
|---|---|
| **Winery** | Caravaglio (Valdichiesa) |
| **Sampling date** | 10/09/2018 |
| **Soil samples** | 2 samples (30 cm deep), 20 cm in front of the plants (SL-S-01 and SL-S-02) |
| **Amount of grapes** | Total 12kg: 6 kg (sample SL-U-01) and 6 kg (sample SL-U-02) |
| **Grape typology** | Malvasia (SL-U-01, white grape) and Corinto Nero (SL-U-02, red grape) |
| **Leaf samples** | SL-F-01 and SL-F-02 |
| **Microvinification samples** | Malvasia (SL-V-01) and Corinto Nero (SL-V-02) |
| **Bottle wine samples** | Malvasia (SL-W-01), Corinto Nero (SL-W-02), *Passito*-Malvasia (SL-W-03) |
| **Wine classification** | DOC Lipari |
| **Age of vine** | 30 years (Malvasia); 30 years (Corinto Nero) |
| **Geology** | Brow tuff (**Figure 3.5**) |
| **Coordinates** | 38°33'35"N, 14°49'51"E (Biancolella); 38°33'34"N, 14°49'53"E (Biancolella) |
| **Altitude** | 60 m |

The Salina Island was built by subaerial volcanic activity of different stratovolcanoes between ~ 244 ka and 15.6 ka, interrupted by prolonged periods of dormancy and sudden volcano-tectonic collapses under the control of the main NE–SW and NNW–SSE structural trends (Lucchi et al., 2013; Romagnoli et al., 2013). The morphology of the island is dominated by two main volcanoes (Monte Fossa delle Felci and Monte Porri) and two major depressions (between the volcanoes and Pollara; Lucchi et al., 2013). The erupted products belong to a subduction-related calcalkaline magmatic series, with rock compositions ranging from basalts and basaltic andesites to rhyolites (Sulpizio et al., 2016). Whole rock $^{87}Sr/^{86}Sr$ values (n=15) range from 0.70400 to 0.70548 (Barberi et al., 1974; Keller, 1980; Ellam et al., 1989; Francalanci et al, 1993; Martelli et al., 2008).

### *Mount Etna*

Mount Etna (**Figure 3.6**) is a 3330 m high active volcano (the largest in Europe) that dominates the northeastern corner of the Sicily Island region, between 37°53′11.08″N, 15°00′19.86″E, and

37°35′44.70″N, 14°58′45.37″E coordinates, covering an area of 1200 km$^2$ (Romano, 1982; Tanguy and Condomines, 1997; Clocchiatti et al., 2004). The vineyards are located on the northern flank of the volcano, on a lava flow dating back to 1556 CE. Lepitic umbrisol, dystric leptic cambisol, eutritic regosol, mollic cleptosol (vitric), mollic vitric and silandic andosol represent the principal soils of region (Costantini et al., 2012).

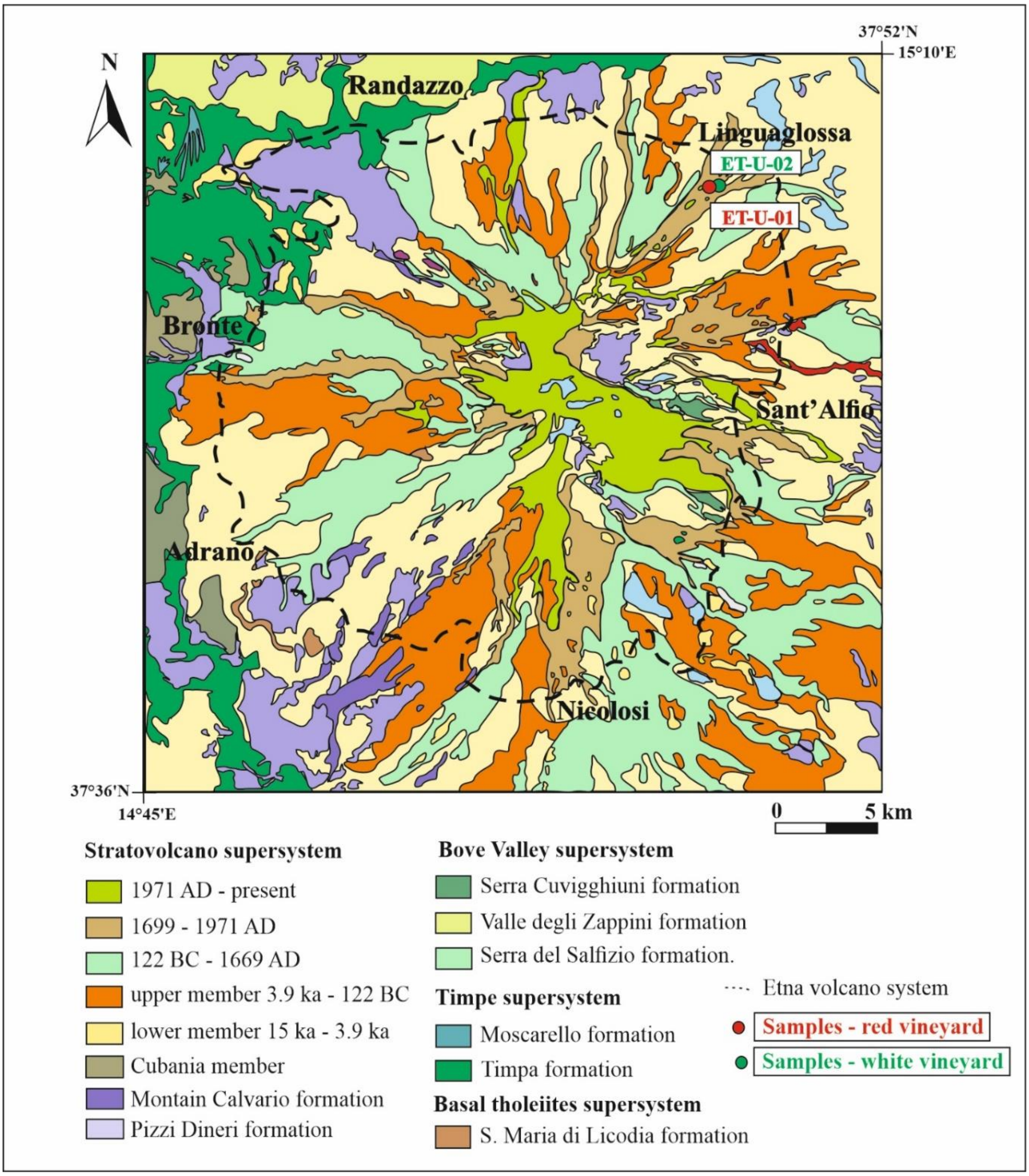


**Figure 3.6.** Geological map of Mount Etna (modified after Tanguy and Condomines, 1997) with sample locations.

The Etna wine brand was the first wine appellation in Sicily, created in August 1968. The Etna appellation was established as a DOC in 1968. Inzolia, Carricante, Grecanico, Nerello Cappuccio, Nerello Mascalese and Merlot represent the grapes most frequently used for Etna wine production. The Etna DOC regulations include a minimum alcohol level of 11.0% for *Spumante*, 11.5% for white, 12.0% for Superior, 12.5% for *Rosé* and Red, and 13.0% for Reserve. *Spumante* may be brut or Extra Dry. For vintage *Spumante*, minimum 18 months, whereas for Reserve minimum 4 years, including 12 months in barrel (https://italianwinecentral.com/denominations-region/).

Mount Etna represents a complex stratovolcano consisting of several overlapping volcanic centers (Romano, 1982; Branca et al., 2004, 2008). Volcanism began some 500,000 years ago with sparse effusions of subaphyric olivine tholeiites showing primary magma characteristics. At 300 ka, pigeonite tholeiites were emitted, soon followed by increasingly porphyritic transitional tholeiites, slightly evolved porphyritic alkali basalts and trachybasalts/hawaiites rich in calcic plagioclase phenocrysts Tanguy and Condomines, 1997). Since 200 ka, porphyritic trachybasalts represented the main products, accompanied by more differentiated products whose emplacement eventually culminated in a caldera collapse (Tanguy and Condomines, 1997). In the last 14 kyr, Mount Etna has continued to erupt porphyritic trachybasalts and rarely aphyric basalts (Tanguy and Condomines, 1997). $^{87}$Sr/$^{86}$Sr isotope ratio in Mount Etna rocks (n=213) cover a range from 0.70304 to 0.70400 (Armienti et al., 1989, 1994; Corsaro and Cristofolini, 1997; Tonarini et al., 1995; D'Orazio et al., 1997; Tanguy and Condomines, 1997; Viccaro and Cristofolini, 2008; Viccaro et al., 2011; Nicotra and Viccaro, 2012; Correale et al., 2014; Di Renzo et al., 2019**)**.

**Table 3.6**. Sampling data sheet for the Mount Etna district.

| | |
|---|---|
| **Winery** | Quantico (Linguaglossa) |
| **Sampling date** | 26/09/2018 |
| **Soil samples** | 2 samples (30 cm deep), 20 cm in front of the plants (ET-S-01 and ET-S-02) |
| **Amount of grapes** | Total 12kg: 6 kg (sample ET-U-01) and 6 kg (sample ET-U-02) |
| **Grape typology** | Carricante (ET-U-01, white grape) and Nerello Mascalese (ET-U-02, red grape) |
| **Leaf samples** | SL-F-01 and SL-F-02 |
| **Microvinification samples** | Carricante (ET-V-01) and Nerello Mascalese (ET-V-02) |
| **Bottle wine samples** | No available |
| **Wine classification** | DOC Etna |
| **Age of vine** | 11 years (Carricante); 78 years (Nerello Mascalese) |
| **Geology** | porphyritic trachybasalts, lavas erupted between 1669 and 1971(**Figure 3.6**) |
| **Coordinates** | 37°50'16''N, 15°07'47''E (Carricante); 37°50'16''N, 15°07'44''E (Nerello Mascalese) |
| **Altitude** | 60 m |

***Pantelleria Island***

The island of Pantelleria (**Figure 3.7**) covers an area of 83 km$^2$ and is located 100 km southwest of Sicily and 60 km east of the Tunisian coast, between 36°50′17.78″N, 11°57′01.58″E, and 36°44′07.93″N, 12°01′34.20″E coordinates. Leptic and luvic phaeozem, leptic and chromic luvisol, haplic calcisol, calcic chernozem, calcic regosol, calcaric cambisol, calcaric leptosol, calcaric arenosol are the main soil types of the island (Costantini et al., 2012). In Pantelleria the climate is Mediterranean, with average temperature of 12 °C in January and February, 25.5 °C in August. The lowest recorded temperature in the winter months is slightly above freezing, the highest in the summer months are up to 41-42 °C. Rainfall is not abundant, being around 500 millimeters per year.

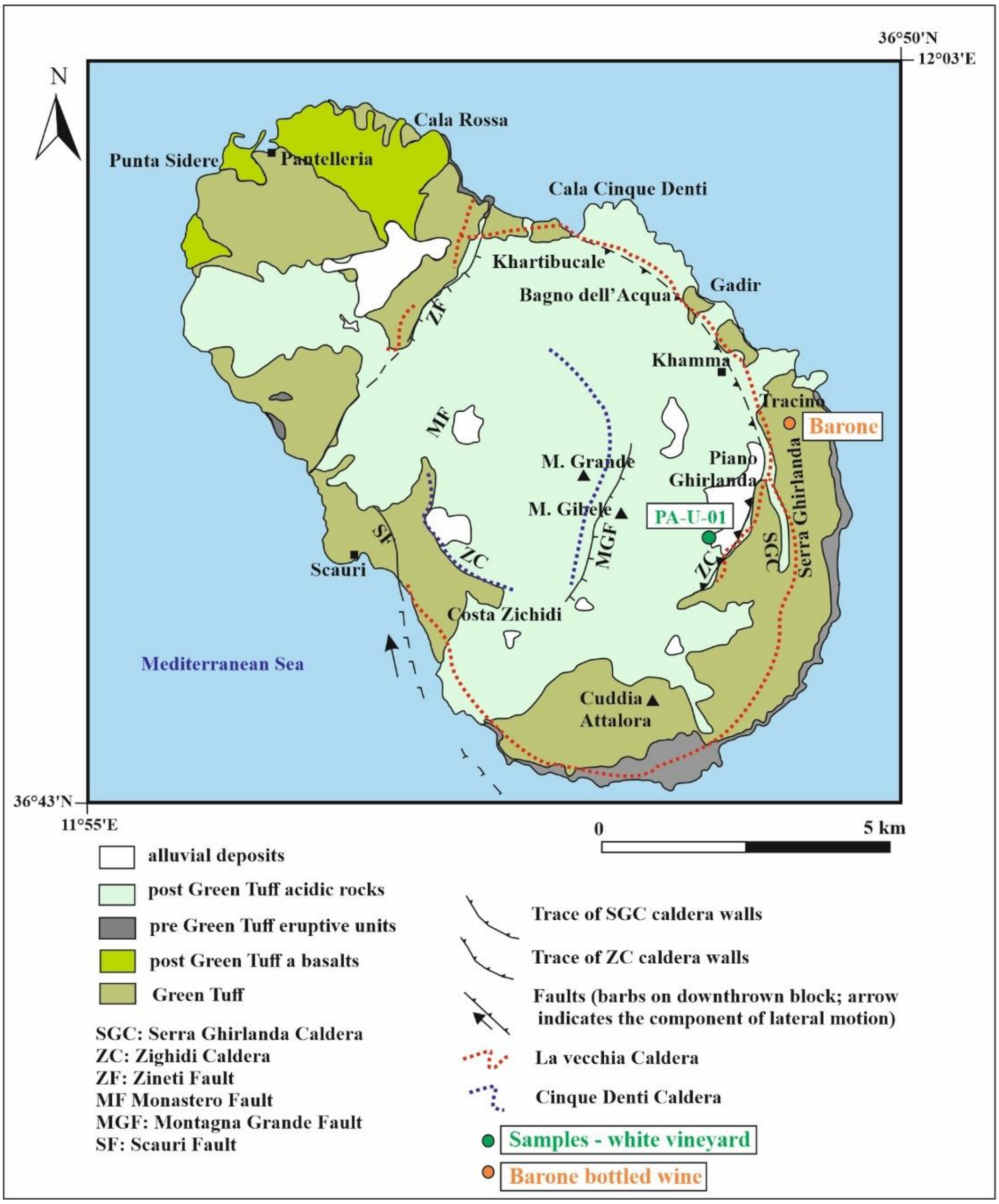


**Figure 3.7.** Geological map of Pantelleria Island (modified after Civetta et al., 1988) with sample location.

Pantelleria Island (Sicily region) is well-known for its sweet wines, Moscato di Pantelleria and Moscato *Passito* di Pantelleria, both made from the local Zibibbo grape. The appellation of Pantelleria wines was established as the Moscato di Pantelleria DOC in 1971. Grapes for Moscato *Dorado* must be dried on or off the vine to achieve a minimum sugar level of 250 g/l (25.0%). Zibibbo *Dolce* cannot exceed 1.7 atmospheres of pressure. The minimum alcohol level is of 6.0% for Zibibbo *Dolce* (10.0% potential), 6.0% for Moscato *Spumante* (12.0% potential), 11.0% for Moscato (15.0% potential), 11.5% for white, 14.0% for *Passito* (20.0% potential), 15.0% for Moscato *Liquoroso* (21.0% potential), 15.0% for *Passito Liquoroso* (22.0% potential) and 15.5% for Moscato *Dorado* (21.5% potential). Residual sugar has a minimum of 100 g/l (10.0%) for Moscato *Dorado*. The aging for *Passito Liquoroso* has a minimum of about 1–2 months, whereas that for the *Passito* is of about 6–8 months. (https://italianwinecentral.com/denominations-region/).

**Table 3.7**. Sampling data sheet for the Pantelleria Island district.

| | |
|---|---|
| **Winery** | Federico Paulsen (Contrada Dietro Isole, 22) |
| **Sampling date** | 26/08/2018 |
| **Soil samples** | 1 sample (30 cm deep), 20 cm in front of the plants (PA-S-01) |
| **Amount of grapes** | Total 6 kg (sample PA-U-01) |
| **Grape typology** | Zibibbo (PA-U-01, white grape) |
| **Leaf sample** | PA-F-01 |
| **Microvinification sample** | Zibibbo (PA-V-01) |
| **Bottle wine sample** | Zibibbo (PA-W-01); Zibibbo from Barone area (PA-W-02) |
| **Wine classification** | DOC di Pantelleria |
| **Age of vine** | 15 years |
| **Geology** | Alluvial deposits (**Figure 3.7**) |
| **Coordinates** | 36°46'13"N, 12°01'55"E |
| **Altitude** | 60 m |

The Pantelleria Island is made of volcanic products that vary in composition from pantellerite, pantelleritic trachyte and comenditic trachyte, to alkali basalt (McDonald, 1974; Mahood and Hildreth, 1986; Civetta et al., 1988; Di Genova et al., 2013). The oldest rocks have ages of 324.2 ± 10.5 ka (Mahood and Hildreth, 1986; Di Genova et al., 2013). The most recent activity occurred in the northern part of the island, represented by two submarine eruptions in 1831 and 1891 (Washington, 1913, 1914; Di Genova et al., 2013). The dominant volcano-tectonic features are represented by two calderas of different ages, located in the central part of the island: the 114 ka La Vecchia caldera and the 45 ka Cinque Denti caldera (Mahood and Hildreth, 1983; Di Genova et al., 2013). The latter followed the 50 ka eruption of the Green Tuff (Wright, 1980; Orsi and Sheridan, 1984; Di Genova et al., 2013). A resurgent block is situated inside the younger caldera (Orsi et al., 1991). Pantelleria Island rocks are characterized by $^{87}Sr/^{86}Sr$ value (n=47) ranging from 0.70280 to

0.70854 (Civetta et al.,1984; Esperança and Crisci, 1995; Civetta et al., 1998; Avanzinelli et al., 2004; Avanzinelli et al., 2014), with the highest value being interpreted as due to contamination with crustal material (Civetta et al.,1984).

## SOIL CHARACTERIZATION METHODS

Volcanic soils are developed across geological time through the weathering of volcanogenic products, including both mechanical and chemical processes. Biological activity is an accelerating factor and adds organic matter to the soil.

Soil is a complex mixture of several compounds and fractions of sand, silt, clay, organic matter and metal oxide contents. The determination of the various minerals, present in soil, and of its chemical properties are used to understand their connections to soil behavior.

Various types of analyses have been carried out in order to characterize the collected soil samples, including X-ray powder diffraction (XRPD), HCl test for determining the presence of carbonate minerals, determination of the soil pH, of the soil organic matter (SOM), and of the soil cation exchange capacity (CEC) and of exchangeable cations. Sample preparations and agronomical analyses were performed at the *Dipartimento Di Agraria* of the *Università degli Studi di Napoli Federico II (Portici)*, whereas XRPD analyses were performed at the DiSTAR laboratories.

Only the sample referring to the first horizon of the Mount Somma-Vesuvio soil profile (Ap) was determined through XRPD, prioritizing the mineralogical characterization of the most superficial soil horizon. The sample between 0.70-0.83 cm (2C horizon) was excluded from the soil characterization due to the low amount of the <2 mm soil fraction, which is essential for agronomical studies.

Soil samples have been dried at 40 °C, hammered to reduce agglomeration, disintegrated, and homogenized in a porcelain mortar and passed through a 2 mm sieve.

### *XRPD analysis*

The X-ray powder diffraction (XRPD) technique is one of the most regularly used methods to identify the minerals present in a soil. A total of 10 soil samples were analyzed in two different granulometric groups: <0.002 mm and 0.2 to 0.002 mm. For the first group, analyses were performed using three different methods, namely the normal clay method, the heating method at 550 °C and the glycolate method (<0.002 mm). The samples of the second granulometric group were analyzed using the normal sand and silt fraction analysis.

Since the organic matter possibly present in a soil sample might produce background interference and prevent parallel orientation of clays minerals during preparation (Douglas and Fiessinger, 1971), knowledge of the oxidation of soil organic matter is required for mineralogical studies of soils (Harada and Inoko, 1977). This was determined at the *Dipartimento Di Agraria*. Twenty grams of each soil sample (< 2 mm fraction) were transferred to a 500 mL beaker. Hydrogen peroxide (2.4%) was added (450 mL), then the solution was shaken with a glass rod and heated to 100 °C. After 90 days, when the effervescence ceased, samples were transferred to a glass beaker with distilled water (400 mL) and heated to 100 °C to remove $H_2O_2$.

After the oxidation of organic matter, the clay fraction of the soil samples was separated from the sand and silt fractions. Dried soil samples are transferred in centrifugation tubes of 100 mL with distilled water and weighed. The soil samples are homogenized by mixing with a spatula and immediately centrifuged using a Z366K Hermle Centrifuge at 1500 rpm (revolutions per minute) for 2 minutes and ten seconds. Larger particles have been isolated by gravity sedimentation. The suspended clay material is deposited in a 3l beaker and the process is repeated until no suspended material is present. An antiflocculant ($CaCl_2$ -50%) is added in each beaker and after 24 h samples are washed with distilled water. To remove the antiflocculant, samples are placed into 100 mL centrifugation tubes, cleaned with a solution of 80 mL of water and 80 mL of ethanol, and centrifuged at 3000 rpm for 5 minutes. The procedure is repeated 3 times, then the samples are washed with acetone and water (1:1) and centrifuged again. Finally, the samples are dried for 24 h at 60 °C (M).

Quantitative XRPD analysis of clay minerals require oriented clays in order to increase detection limits of the analyses (Cody and Thompson, 1976). Therefore, after clay separation by gravity and centrifugal sedimentation procedures, oriented mounts were prepared following Cavalcante and Belviso (2005).

A quantity of 0.188 g of dried clay samples was placed on 50 mL centrifugation tubes adding 10 ml of distilled water. Samples were suitably homogenized for 5 minutes in an ultrasonic bath. One ml of the clay suspension was smeared on a glass slide and then dried at room temperature for 24 h. The identification of the clays was made according to the position of basal reflection 001 in three XRPD patterns: 1) natural sample, 2) solvated sample and 3) heated sample.

The solvation procedure, usually employing ethylene glycol (Bradley, 1945) or with glycerol (MacEwan, 1944), consists in the introduction of these polar substances among the TOT packets of the smectites. This treatment modifies the dimensions of the basal distance ($d_{001}$) and is used to identify and characterize clay minerals such as smectites and the interstratified clays containing a smectitic component (Cavalcante and Belviso, 2005). Solvation with ethylene glycol was carried out by exposing the oriented samples to the reagent vapors for 8 hours at 60 °C in a thermostatically controlled oven.

The heating procedure allows distinguishing the different clay minerals based on their ability to lose water molecules and to modify their structure when subjected to different temperatures. Heating to 500-550 °C was used to distinguish kaolinite or halloysite from chlorite (Cavalcante and Belviso, 2005).

Sand and silt fractions (1.6 g of >0.002 mm fraction) were micronized in an XRPD-Mill McCrone (Retsch) using 10 mL of deionized water as grinding agent for 10 minutes. In addition, 0.2 g (10%) of alpha alumina ($\alpha$-$Al_2O_3$) was added as an internal standard for quantitative phase analysis. After drying (50 °C for 24 h), samples were ground in an agate mortar in order to prepare slides containing non-oriented powder samples.

Data were collected with a D2 Phaser XRPD diffraction system in the $2\theta$ range from 4° to 70° (>0.002 mm fraction) and 3° to 50° (>0.002 mm fraction - oriented aggregate) with CuKα radiation ($\lambda = 0.15045$ pm) at 30 kV and 10 mA. Measurements were carried out at room temperature. XRPD patterns were obtained using the software Panalytical X'Pert Highscore Plus 3.0.

### *Test for estimation of total carbonate presence*

The presence of carbonate minerals in a soil can affect soil productivity by influencing pH, structure, and water flow. Calcareous soils have a high buffer capacity, i.e., a high resistance to changes in pH. This is due to free carbonates being able to effectively neutralize acids in the soil. Various primary and secondary carbonates are found in soils (Doner and Lynn, 1989). Calcareous soils are defined as those that have free calcium carbonate ($CaCO_3$) and pH values in the range of 7.0 to 8.3 (Zhu et al., 2015).

Carbonate minerals are unstable in the presence of hydrochloric acid, following the reaction $CaCO_3 + 2HCl \rightarrow CO_2 + Ca^{2+} + 2Cl^-$, which produces carbon dioxide gas ($CO_2$), water ($H_2O$), dissolved calcium ($Ca^{2+}$), and dissolved chlorine ($Cl^-$; King, 2013). The carbon dioxide bubbles are evidence that the reaction is formed. When that occurs, calcite or another carbonate mineral is present (Zhu et al., 2015).

The HCl test is used to determine the presence of carbonate minerals as these might cause chemical exchanges between soil and plant. Two drops of HCl (30%) were added to 2 g of each soil sample (< 2 mm fraction) in a watch glass, and appropriate effervescence was assigned to the reaction after 2 minutes (**Table 3.8**).

**Table 3.8.** Effervescence classes used to describe the soil matrix through the HCl test (Soil survey Division Staff, 1993).

| Effervescence | Criteria | N° |
|---|---|---|
| Non effervescent | No bubbles detected | 0 |
| Very slightly effervescent | Few bubbles seen | 1 |
| Slightly effervescent | Bubbles readily seen | 2 |
| Strongly effervescent | Bubbles form low foam | 3 |
| Violently effervescent | Thick foam forms quickly | 4 |

### *pH determination*

The pH controls many of the properties of a soil, such as fertility (Sposito, 2008), and has an influence on biogeochemical processes in general (Bååth et al., 1995). Climate and content of inorganic carbon are the major factors that can modify soil pH (Hong et al., 2019). Plant roots can only absorb nutrients after these have been transformed into certain ionic forms. Only within certain pH ranges sufficient amounts of these nutrients can be transformed into such ionic forms. When the soil pH is outside the range of 6.2-6.8, the nutrients are not in a form useful to plants. A pH test is thus important in order to figure out whether the plant was able or not to receive the elements available in the soil, including strontium.

**Table 3.9.** Soil classification based on pH (Soil survey Division Staff, 1993).

| Classification | pH |
|---|---|
| Extremely acid | Below 4.5 |
| Very strong acid | 4.5 – 5.0 |
| Strongly acid | 5.1 – 5.5 |
| Mildly acid | 5.6 – 6.0 |
| Slightly acid | 6.1 – 6.5 |
| Neutral | 6.6 – 7.3 |
| Mildly alkaline | 7.4 – 7.8 |
| Moderately alkaline | 7.9 – 8.4 |
| Strongly alkaline | 8.5 – 9.0 |
| Very strongly alkaline | 9.1 and higher |

Ten milligrams of dried soil (< 2 mm fraction) were put in a 50 mL polypropylene centrifuge tube together with 25 mL of distilled water and stirred at 200 Hz for 2 h. The pH values were measured using a pH-meter (XS instrument, model number 8) previously calibrated with buffer solutions with pH values of 4.7 and 10. In order to minimize the influence of contact times between solution and soil on soil pH readings, all measurements were done after 30 minutes of agitation. The soils were classified based on the values of pH (**Table 3.9**).

### *Soil organic matter (SOM)*

Determining the soil organic matter (SOM) is essential parts of any soil characterization since these components can markedly influence how chemicals will react in the soil (Lehmann and Kleber, 2015).

Soil organic matter (SOM) is a general term for the fraction of the soil consisting of plant and animal residues in various stages of decomposition (Neumann, 2007).

The determination of SOM was performed through the Walkley and Black (1934) method. For each soil sample (< 2 mm fraction), 0.5 to 1.5 g were placed into 500 mL conical flasks. Ten milliliters of 0.167 potassium dichromate ($K_2Cr_2O_7$) were added, followed by addition of 20 mL of concentrated sulfuric acid ($H_2SO_4$), constantly stirred in order to ensure adequate interaction between the organic substance and the reagents. After 30 min, 200 mL of distilled water were added to interrupt the reaction. Ten drops of ferroin indicator solution [$Fe(C_{12}H_8N_2)_3SO_4$] were then added. The dichromate that was not reduced in the reaction has been determined by volumetric titration using ammonium ferrous sulfate [$Fe\ (NH_4)_2(SO_4)_2 6H_2O)$]. The calculation of total carbon was carried out with the introduction of an empirical factor (0.77), which considers the oxidized fraction in adopted conditions. Considering an average carbon content of organic matter equal to 580 g/kg, a second factor (1.724) has been introduced to transform organic carbon to organic matter (Walkely and Black, 1934).

### *Soil Cation Exchange Capacity (CEC) and determination of exchangeable cations*

The cation-exchange capacity (CEC) is a measure of how many cations can be retained on soil particle surfaces, i.e., it basically relates to the ability of a soil to hold and exchange cations (Saidi, 2012). It is defined as the total of the exchangeable cations that a soil can hold at a given pH (Aprile and Lorandi, 2002).

This parameter gives a measure of the availability of some elements present in the soil (including strontium) for plant absorption and is thus retained extremely relevant for the scopes of the present research project.

The cation exchange capacity has a significant influence on the physical and chemical behavior of a soil (Khaledian et al., 2017a,b). It depends on the physical (soil texture), chemical (pH, mineralogy), and biological (soil organic matter) characteristics of the soil (Mukherjee and Zimmerman, 2013), but is mostly related to the content of clay minerals and organic matter (Aprile and Lorandi, 2002).

The most important exchangeable cations in the soil are aluminum ($Al^{3+}$), ammonium ($NH_4^{2+}$), calcium ($Ca^{2+}$), hydrogen ($H^+$), magnesium ($Mg^{2+}$), potassium ($K^+$), and sodium ($Na^+$; Aprile and Lorandi, 2002).

Soil clay minerals and organic matter are likely to be negatively charged, and thus attract cations on their surfaces by electrostatic forces. Cations remain in the root zone of the soil and are not simply lost through leaching. The term "cation exchange" is related to the adsorbed cations that can easily exchange with other cations in the soil solution. Adsorbed cations replenish ions in soil solutions when concentrations decrease due to absorption by plant roots (Sonon et al., 2014).

Soil negative charges are a consequence of isomorphic substitutions in phyllosilicate structures. Electrostatically retained cations are easily exchangeable with other cations in soil solution and are readily available for plant absorption. Therefore, a high CEC is a key parameter for maintaining adequate amounts of $Ca^{2+}$, $Mg^{2+}$ and $K^+$ in the soil (Jaremko and Kalembas, 2014). The CEC of the soil can be defined as the total number of negative charges per unit weight of the soil.

The CEC of the investigated soil samples was determined by the Barium chloride and triethanolamine method (Mehlich, 1938). The following chemical solutions were prepared:

1. Barium chloride solution: 100 g of $BaCl_2.2H_2O$ was dissolved in 800 mL of distilled water with the addition of 22.5 mL of triethanolamine $N(CH_2OHCH_2)_3$. The pH of the solution was lowered to 8.1 with the addition of 83 mL of 37% HCl in 817 mL of distilled water.
2. Magnesium sulfate: $MgSO_4.7H_2O$, solution 0.05 mol/L (12.324 g of magnesium sulfate was dissolved in 1:l of distilled water).
3. Buffer solution at pH 10: 54 g of ammonium chloride $NH_4Cl$ was dissolved in 500 mL of water in a 1000 mL volumetric flask, 350 mL of ammonia was transferred to a 1000 mL volumetric flask and 650 mL of distilled water were added.
4. Indicator: in a porcelain mortar, 20 g of sodium chloride (NaCl) were homogenized with 0.2 of eriochrome R ($C_{23}H_{15}Na_3O_9S$).
5. EDTA: (Disodium salt of ethylene diaminotetra acetic acid): 0.025 mol/L solution (9.305 g of EDTA in 1000 mL of distilled water).

After solution preparation, 3.0 g of dried soil sample were weighed and transferred to a tightly stoppered polyethylene centrifuge tube. Twenty-five mL of Ba-chloride solution were added and mixed (3000 rpm) for 3 min. After 5 min, the clear liquid was transferred to a centrifuge tube. This operation was repeated twice, and then the samples were washed with distilled water and weighed again. Successively, 25 mL of the magnesium sulfate solution were added and mixed, then 10 mL of the clear liquid (without disturbing the sediment), 100 mL of distilled water, 10 mL of the buffer solution (pH = 10) and 1 g of indicator were added in a 250 mL conical flask. For blank determination, 10 mL of magnesium sulfate solution have been utilized. The samples were tritiated with the EDTA solution until the color changed from pink to blue. The amount added of EDTA (in mL) was used to calculate the CEC and amount of exchangeable cations, expressed in centimoles of positive charge per kilogram of soil (cmol$^{(+)}$ kg$^{-1}$).

The measurement of the amount of exchangeable cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$) was carried on diluted samples (1:20) by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) Thermo Scientific ICAP 4200.

## $^{87}$Sr/$^{86}$Sr ANALYSES OF BIOLOGICAL AND GEOLOGICAL SAMPLES

The $^{87}$Sr/$^{86}$Sr analyses of biological and geological samples have been carried out at the Geotop laboratories of the UQAM (Université du Québec à Montréal, Canada). Sample preparation procedure was performed in the Geotop laboratories in a clean room (ISO 5 standard, 100 particles/ft$^2$). Nitric (70%) and hydrochloric acids (35%) were produced by distillation (sub-boiling). Sample preparation is a significant factor that can affect the precision of TIMS analyses.

Samples were completely dissolved in order to separate the strontium from the matrix of the sample. The determination of Sr concentrations requires separation between the elements Rb and Sr due to the isobaric interference of the $^{87}$Rb and $^{87}$Sr during the spectrometric analysis. For high precision analyses, careful isolation of Sr from matrix elements present in geological and biological materials is necessary. Consequently, different procedures were employed for different types of samples, and different chromatography calibration procedures were adopted.

The preparations of the biological and geological samples were carried out following the method described by Vinciguerra et al. (2016) and Guibourdenche et al. (2020).

### *Soil*

The soil samples have been dried at 60 °C for 48 h, passed through a 2 mm sieve, hammered to reduce agglomeration, disintegrated, and homogenized in a porcelain mortar.

The labile and bulk soil fractions were prepared differently. The labile fraction of the soil was analyzed in order to identify the possible source of strontium for the biological samples, i.e., grapes, leaves and wines.

In order to extract the labile fraction from each of the soil samples, 2 g of soil sample (<2 mm) was set to react twice with 15 mL of super pure ammonium acetate ($NH_4CH_3CO_2$) for 8 h at room temperature. Supernatant portions were passed through 0.45 μm polypropylene syringe filters, dried at room temperature, and then dissolved in 3N $HNO_3$ at 85 °C. In addition, fractions up to 2 mm (*) from the C, 2C and 3C horizons were tested to identify variations in different soil granulometry.

Bulk soil fraction samples have been redried through a progressive four-step heating: 10 min at 200 °C, 10 min at 400 °C, 10 min at 600 °C and finally 7 h at 800 °C. Samples were weighed (0.7 g) and placed inside beakers adding 2 drops of 15N $HNO_3$ and 5 mL of HF 29N and reacted for 5 days at 85 °C. Samples were then dried and 30% $H_2O_2$ (1 drop) was added. The procedure was repeated until the organic matter was completely dissolved.

In order to extract the iron, present in large quantities, from the soil samples (both bulk and labile fractions) a chromatographic procedure was undertaken using AGI-X8 resin (2 mL) in a 10 mL Bio-RadTM column and 6N HCl (10 mL for rising washing) and 1N HCl (10 mL for rising and recovery sample) sub-boiling acids. At the end of the chromatography procedure, samples were dried at 80 °C, for 24 h, and 3 mL of 6N $HNO_3$ were added.

### *Grape, grape components, leaf, and roots*

For each of the investigated biological samples (grape and grape components, i.e., skin, seed, pulp and stem, leaf and roots) an amount of 2 g was set into a ceramic beaker and dried through a progressive four-step heating: 10 min at 200 °C,10 min at 400 °C, 10 min at 600 °C and finally 7 h at 800 °C. After cooling, samples were dissolved by adding 2 mL of nitric acid (6N $HNO_3$) and one drop of ultrapure hydrogen peroxide (30% $H_2O_2$) reacting for 72 h and then evaporated to dryness using a hot plate at 80 °C. This was repeated until complete oxidation of the organic matter (no bubbles).

### *Microvinification and bottled wine*

Microvinification and bottled wine samples were used in different amounts due to the different concentrations of organic matter present. This difference occurs because the microvinification process was carried without the must, differently from the regular oenological procedures, which thus implies that in the bottled wines the concentration of organic matter is higher.

Nine ml of microvinification sample was mixed with 1 mL of Mill-Q $H_2O$ in a 15 mL Teflon tube. On the other hand, 2 mL of bottled wine samples were diluted with 8 mL of Mill-Q $H_2O$. In both type of samples approximately 0.5 mL of $^{84}Sr$ spike was added for isotopic corrections.

For both types of samples, the organic matter was extracted using a AG50X-8 resin (2 mL). For both processes, 10 mL Bio-RadTM columns and 1N HCl (three times for rising) and 6N HCl (two times for sample recovery) sub-boiling acids were used. At the end of the process, the samples were dried at 80 °C for 24 h, and 3 mL of 6N $HNO_3$ was added.

### *Extraction of Sr*

As a last step, strontium was extracted from the investigated biological and geological samples by cation exchange chromatography using 0.25 mL of Eichrom Sr-spec resin in a 1 mL Bio-RadTM column. Three mL of 3 M $HNO_3$ has been added to dry samples, which were placed in an ultrasonic bath for 10 min and then centrifuged for 10 min before loading into the separation columns. Resin was washed using 2 mL of Mill-Q $H_2O$ (one time) and 2 mL of 3N $HNO_3$ (three times). Samples were loaded (0.25 mL of sample in four times), rinsed (using 0.5 mL of 3N $HNO_3$ for six times) and recovered (using 0.25 mL of 0.05N $HNO_3$ for five times). At the end of the procedure, samples were dried at 85 °C for 24 h.

## Sr ISOTOPE ANALYSES

The $^{87}Sr/^{86}Sr$ values of the investigated soil, grape, leaf, microvinification and bottled wine samples have been measured by Thermal Ionization Mass Spectrometry (TIMS) on a ThermoTriton PlusTM multi-collector instrument with Faraday cup type detectors ($10^{11}$ Ω resistance).

The Sr concentrations were determined following the procedures described by Guibourdenche et al. (2020) and Vinciguerra et al. (2016), using a TIMS Plus (Thermo Fisher Scientific®) mass spectrometer.

A Thermal Ionization Mass Spectrometer is a magnetic sector mass multi-collector spectrometer instrument, composed of three primary components: ion source, analyzer, and collector.

The sample is loaded on a filament, which is then mounted in the sample turret of the mass spectrometer (21 sample holders available,) and pumped down to high vacuum. The sample is atomized and ionized by heating the filament to the required temperature by passing an electric current through it. The ions generated on the filament are accelerated across an electrical potential gradient and focused into a beam via a series of slits and electrostatically charged plates, then separated into individual beams based on the mass/charge ratio of the ions by an electromagnet and then collected in faraday cups.

Rhenium filaments (non-reactive metal) were manually prepared and degassed in a filament bakeout device instrument (ThermoFisherScientific®) at a temperature of 1000 °C for 90 min. Samples are loaded on the filaments following this sequence: i) a physical barrier preventing the solution from spreading on the filament and to allow positioning the samples at the center of the filament is set up using a piece of parafilm (5x5 cm) heated by passing a 1.0 V current in the filament; ii) 0.5 µl of tantalum activator solution is loaded on filament and heated until it changes to black-red (at ~2V); iii) 1µl 16N $HNO_3$ sample solution is loaded and heated at 2V; iv) 0.3 µl tantalum oxide activator solution is loaded on the filament and heated at 2V.

### *Sr isotope measurements accuracy*

The external reproducibility of the performed measurements was evaluated and controlled through repeated analyses of the international standard SRM-NBS-987 certified by NIST (National Institute of Standards and Technology). The results obtained during a five-month period yielded an $^{87}Sr/^{86}Sr$ value of 0.710267 ± 0.00001 (**Figure 3.8)**, consistent with the certified values (0.710245 ± 0.000011; Thirlwall, 1991). The measured Sr isotope ratios were fractionation-corrected by normalizing to an $^{86}Sr/^{88}Sr$ ratio of 0.1194. The total procedure blank was less than 50 pg of Sr.

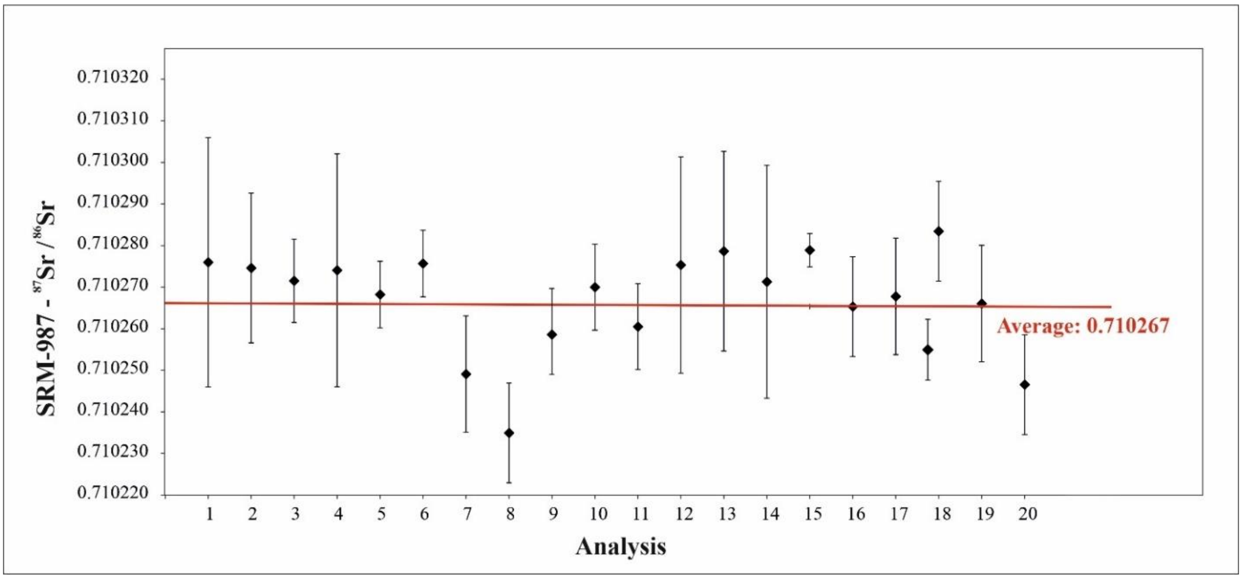


**Figure 3.8.** Results of the $^{87}Sr/^{86}Sr$ measurements for the NIST SRM-987 standard over a period of 5 months. The error bar represents the uncertainty, expressed as twice the standard deviation (2 SD).

## RESULTS AND DISCUSSION

### *Soil characterization*

In **Table 3.15** is reported a summary of color codes and mineralogical features of the investigated soil samples from Ponza Island, Ventotene Island, Somma-Vesuvio (including the Ap soil horizon from Somma-Vesuvio soil profile), Salina Island, Mount Etna, and Pantelleria Island. The XRPD patterns are presented in **Figures 3.9, 3.10, 3.11, 3.12, 3.13, 3.14, 3.15, 3.16, 3.17** and **3.18.** Somma-Vesuvio soil profile is described in **Figure 3.19**.

Soils from the Ponza Island (PZ-S-01 and PZ-S-02) are light yellowish brown and olive yellow in color (i.e., color codes 2.5Y 6/4 and 2.5Y 6/6, according to the Munsell chart), with sandy-silty texture, small sub-angular to rounded blocky structure. Feldspar (very present), quartz (frequent), kaolinite and illite (scarce) represent the minerals occurring in both samples PZ-S-01 and PZ-S-02, while amphibole (traces) is reported only for PZ-S-02.

Ventone Island soils (VE-S-01) show olive color (color code 2.5Y 6/4), silty texture and no blocky structure. XRPD patterns revealed the presence of feldspar, calcite, pyroxene (frequent), hematite, smectite and illite (scarce). Among the soils analyzed in the present study, Ventotene Island soil represents the most clayey and the only with carbonate minerals. High amount of carbonate in the soil was also observed in the field due to its light color.

The Somma-Vesuvio soil samples VS-S-01 are olive (color code 5Y 5/3), show sandy texture and angular block structure. XRPD patterns for both samples VS-S-01 and Ap horizon of the profile revealed the presence of feldspar, pyroxene, leucite (from scarce to frequent), and low amount of illite/mica (from scarce to frequent). In addition, Ap also features some kaolinite (traces).

Soil samples from Salina Island (SL-S-01 and SL-S-02) are light olive brown and olive yellow (color codes 2.5Y 5/4 and 5Y 6/6, respectively), showing sandy–silty texture, with small sub-angular blocky structure. Mineralogy is dominated by feldspar (frequent), pyroxene (scarce), hematite (traces), kaolinite/halloysite and illite-smectite (traces).

Mount Etna soil samples (ET-S-01 and ET-S-02) are olive brown to dark grayish brown (color codes 2.5Y 4/4 and 2.5Y 4/2, respectively), silty textured with small sub-angular to angular blocky structure. The dark color of these soil samples is a clue for the presence of large amounts of organic matter. Feldspar (frequent), pyroxene (scarce) and traces of kaolinite and illite were identified from XRPD patterns.

The soil samples from Pantelleria Island (PA-S-01) are light olive brown (color code 2.5Y 5/4), sandy textured with small sub-angular blocky structure. XRPD patterns revealed the presence (frequent) of feldspar, quartz, low amounts of amphibole (scarce) and traces of illite and kaolinite.

The results of the HCl test and of the chemical analyses (for the determination of CEC, exchangeable cations, BS, SOM and pH) are reported in **Table 3.16**.

The CEC values of the studied soils are as a whole low to moderate (2.3 to 28.1 cmol$^{(+)}$ kg$^{-1}$). From the comparison of the soil samples properties, it can be observed that the Somma-Vesuvio soil has the lowest CEC value (2.3 cmol$^{(+)}$ kg$^{-1}$) while Etna has the highest (28.1 cmol$^{(+)}$ kg$^{-1}$) value. Soil samples from the same district but of different grape varieties show similar CEC, as observed for Ponza Island (white: 9.8 cmol$^{+}$/kg; red: 9.3 cmol$^{(+)}$ kg$^{-1}$), Salina Island (white: 9.8 cmol$^{(+)}$ kg$^{-1}$; red: 11.4 cmol$^{(+)}$ kg$^{-1}$) and Mount Etna (white: 20.4 cmol$^{(+)}$ kg$^{-1}$; red: 28.1 cmol$^{(+)}$ kg$^{-1}$). The CEC values obtained for the various soil horizons of the investigated Somma-Vesuvio profile range from 6.0 to 12.7 cmol$^{(+)}$ kg$^{-1}$, linearly declining with soil depth (0.0-0.16 m: 12.6 cmol$^{(+)}$ kg$^{-1}$; 0.16-0.21 m: 9.2

cmol$^{(+)}$ kg$^{-1}$; 0.21-0.40 m: 6.8 cmol$^{(+)}$ kg$^{-1}$; 0.40-0.70 m: 6.7 cmol$^{(+)}$ kg$^{-1}$; 0.83-1.20 m: 6.0 cmol$^{(+)}$ kg$^{-1}$).

The highest values of exchangeable Ca$^{2+}$ were observed for the Etna soil (15.2 cmol$^{(+)}$ kg$^{-1}$, red grape vineyard) followed by Ventotene (14.8 cmol$^{(+)}$ kg$^{-1}$), whereas samples from Ponza Island (red: 1.9 cmol$^{(+)}$ kg$^{-1}$, white: 2.2 cmol$^{(+)}$ kg$^{-1}$) and Pantelleria Island (2.2 cmol$^{(+)}$ kg$^{-1}$) showed the lowest values, likely due to the presence of strongly evolved low-Ca basement rocks (rhyolites and pantellerites). The various horizons of the Somma-Vesuvio soil profile display variable values of exchangeable Ca$^{2+}$, ranging between 0.3 cmol$^{(+)}$ kg$^{-1}$ (3C horizon) and 7.8 cmol$^{(+)}$ kg$^{-1}$ (Ap horizon), and generally decreasing with depth.

The highest values for exchangeable K$^{+}$ were found for one Ponza Island soil sample (2.0 cmol$^{(+)}$ kg$^{-1}$, red vineyard), followed by Salina (white: 1.8 cmol$^{(+)}$ kg$^{-1}$1; red: 1.3 cmol$^{(+)}$ kg$^{-1}$), whereas the lowest values were found for the deepest horizon of the Somma-Vesuvio soil profile (3C: 0.1 cmol$^{(+)}$ kg$^{-1}$).

The highest values of exchangeable Na$^{2+}$ were found for Ponza and Ventotene Islands soil samples (both 0.6 cmol$^{(+)}$ kg$^{-1}$), with the remaining samples showing significantly lower values (in the range of 0.0-0.2 cmol$^{(+)}$ kg$^{-1}$).

The highest values of exchangeable Mg$^{2+}$ are observed for Ventotene Island sample (3.2 cmol$^{(+)}$ kg$^{-1}$) followed by Mount Etna and Salina Island soils (ET-S-01= 1.7 cmol$^{(+)}$ kg$^{-1}$; SL-S-01= 1.4 cmol$^{(+)}$ kg$^{-1}$). The lowest exchangeable Mg$^{2+}$ are found for the deepest horizons of the Somma-Vesuvio profile (3C: 0.0 cmol$^{(+)}$ kg$^{-1}$).

Base saturation varied between 34% and 100%. Ponza Island soil (PZ-S-01 and 02) represented the lowest values (34 and 59%%), indicating an undersaturated exchangeable complex confirmed by the low soil pH (3.9 and 4.4). Then, Mount Etna soil has a base saturation between 50 and 61%, while soil samples from Ventotene Island and Somma-Vesuvio soil showed 100% of the sum of exchangeable cations. Samples referring to the soil profile of Somma-Vesuvio reveled a constant percentage of 95%, regardless of depth.

The SOM in the studied soils ranges between 0.0% (in the 3C horizon of the Somma-Vesuvio soil profile) and 6.9% (Mount Etna red vineyard). In the Mount Etna soils, the presence of organic matter is also evidenced by olive brown to dark grayish brown color soil. In Somma-Vesuvio profile, as expected, SOM values show a clear linear decline with increasing depth, likely reflecting the effects of the presence of considerable amounts of deposited plant residues in the uppermost portions of the vineyard soil, as well as due to amendment practices.

The soil reaction of the investigated soil samples ranges from extremely acid (Ponza Island: pH = 3.9 and 4.4, respectively for white and red vineyard) to moderately alkaline (Ventotene Island pH=

8.3). There appears to be no significant difference between soil samples from the same district but different grape varieties (Ponza Island: pH = 3.9-4.4; Salina Island: pH = 5.0-5.3; Mount Etna: 6.2-6.4). Interestingly, the only soil samples with neutral pH were found in the Somma-Vesuvio districts, with no significant difference between the various soil horizons (pH = 7.3-7.5).

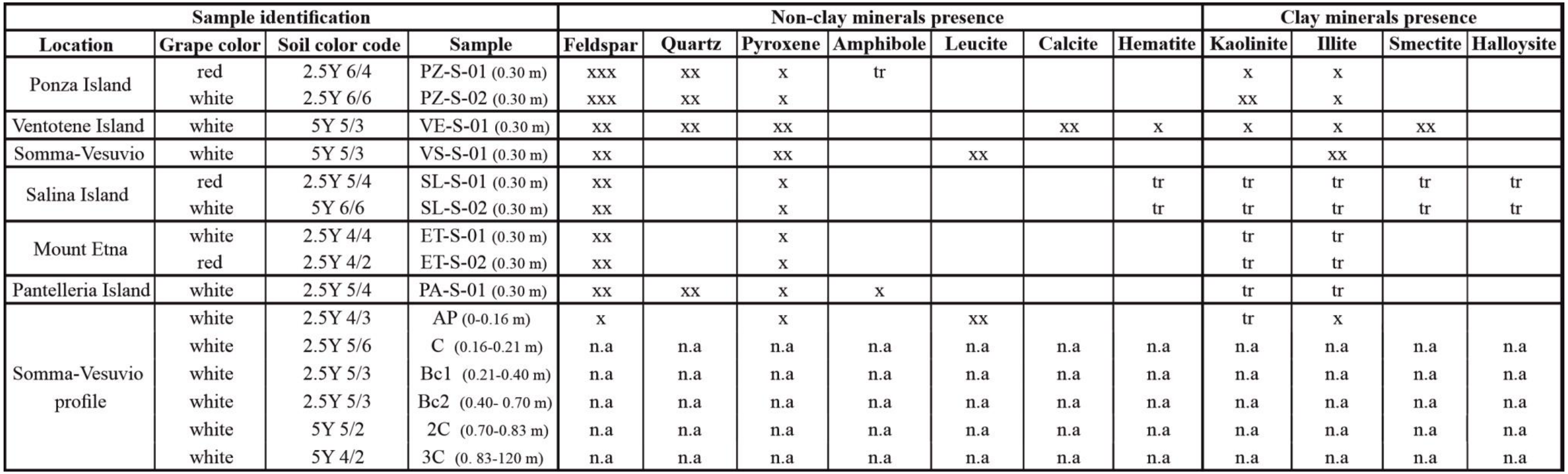
In general, the type of clay, presence of carbonate, CEC, SOM, and pH influence the availability of important soil micronutrients and other elements to the plant. A soil with higher CEC has a better capacity to preserve sufficient quantities of $Ca^{2+}$, $Mg^{2+}$ and $K^+$, but a soil with higher CEC is not necessarily more fertile than another because high CEC could also correspond to a high content of acid cations such as $H^+$ and $Al^{3+}$ (FAO, 2017).

Ventotene soils showed high CEC (19.2 cmol$^{(+)}$ kg$^{-1}$), high exchangeable $Ca^{2+}$ (14.8 cmol$^{(+)}$ kg$^{-1}$) and $Mg^{2+}$, (3.2 cmol$^{(+)}$ kg$^{-1}$), an optimal Mg/K ratio (4.8) assuring a balanced nutrition for plants. The presence of carbonates (XRPD and HCl test) and the moderately alkaline reaction (pH = 8.3) can generally predispose these soils to a reduced availability of nutrients, while the medium-low content of soil organic matter (1.9%) can have effects on soil chemical fertility. Among the samples analyzed, Mount Etna soils (ET-S-01 and ET-S 02) have the highest CEC values (28.1 and 20.1), which is consistent with the high content of organic matter (6.0 and 6.9%).

Indeed, the presence of organic material can increase the soil CEC over time. CEC is a good indicator of soil quality and productivity when combined with other measures of soil fertility (Ross and Katterings, 2011). The content of organic matter improves also many physical, chemical, and biological soil properties (i.e., water holding capacity, pH, micronutrients). The loss of organic matter can contribute to soil erosion, loss of fertility, compaction, and land degradation (FAO, 2017).

The base saturation indicates the sum of base ($Ca^{2+}$, $Mg^{2+}$, $K^+$, and $Na^+$) and acid ($H^+$ and $Al^{3+}$) cations adsorbed by the soil. The base saturation increases with increasing soil pH (Bache, 2006), as observed for Ventotene Island soil showing a 100% of base saturation and the highest pH values identified among the sampled sites (8.3), while soil samples from Ponza Island (PZ-S-01 and PZ-S-02) show the lowest base saturation (39 and 59%, respectively) and extremely acid pH values (3.9 and 4.4). The soil pH depends on many factors, among which the rock type from which the soil was formed and on the weathering processes, climate, vegetation, and topography, tending to increase in acidity over time due to agricultural activities (FAO, 2017).

**Table 3.15.** Soil color code (according to Munsell color chart) and semi-quantitative non-clay / clay mineralogy for the investigated soil samples from Ponza Island, Ventotene Island, Mount Somma-Vesuvio, Salina Island, Mount Etna and Pantelleria Island soils, including soil samples from the Somma-Vesuvio profile (*, with indication of their depth from the surface). Legend: xxx= abundant; xx= frequent; x= scarce; tr=traces; n.a. = not analyzed.



| Sample identification | | | | Non-clay minerals presence | | | | | | | Clay minerals presence | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Location** | **Grape color** | **Soil color code** | **Sample** | **Feldspar** | **Quartz** | **Pyroxene** | **Amphibole** | **Leucite** | **Calcite** | **Hematite** | **Kaolinite** | **Illite** | **Smectite** | **Halloysite** |
| Ponza Island | red | 2.5Y 6/4 | PZ-S-01 (0.30 m) | xxx | xx | x | tr | | | | x | x | | |
| | white | 2.5Y 6/6 | PZ-S-02 (0.30 m) | xxx | xx | x | | | | | xx | x | | |
| Ventotene Island | white | 5Y 5/3 | VE-S-01 (0.30 m) | xx | xx | xx | | | xx | x | x | x | xx | |
| Somma-Vesuvio | white | 5Y 5/3 | VS-S-01 (0.30 m) | xx | | xx | | xx | | | | xx | | |
| Salina Island | red | 2.5Y 5/4 | SL-S-01 (0.30 m) | xx | | x | | | | tr | tr | tr | tr | tr |
| | white | 5Y 6/6 | SL-S-02 (0.30 m) | xx | | x | | | | tr | tr | tr | tr | tr |
| Mount Etna | white | 2.5Y 4/4 | ET-S-01 (0.30 m) | xx | | x | | | | | tr | tr | | |
| | red | 2.5Y 4/2 | ET-S-02 (0.30 m) | xx | | x | | | | | tr | tr | | |
| Pantelleria Island | white | 2.5Y 5/4 | PA-S-01 (0.30 m) | xx | xx | x | x | | | | tr | tr | | |
| Somma-Vesuvio profile | white | 2.5Y 4/3 | AP (0-0.16 m) | x | | x | | xx | | | tr | x | | |
| | white | 2.5Y 5/6 | C (0.16-0.21 m) | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a |
| | white | 2.5Y 5/3 | Bc1 (0.21-0.40 m) | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a |
| | white | 2.5Y 5/3 | Bc2 (0.40- 0.70 m) | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a |
| | white | 5Y 5/2 | 2C (0.70-0.83 m) | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a |
| | white | 5Y 4/2 | 3C (0. 83-120 m) | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a |

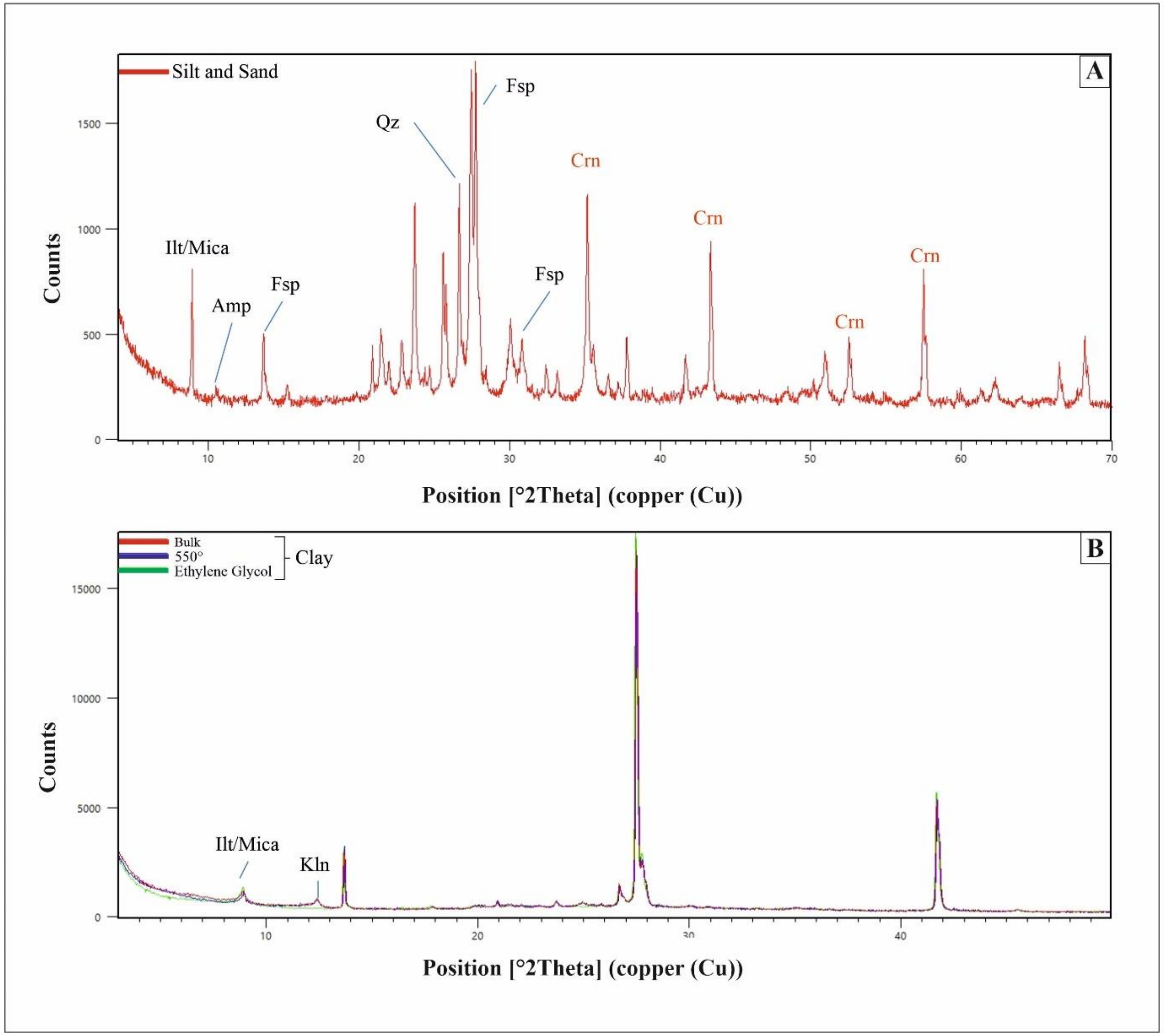


**Figure 3.9.** XRPD patterns for the soil sample from Ponza Island (PZ-S-01). A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Qz = quartz, Px = pyroxene, Amp = amphibole, Kln = kaolinite, Ilt = illite, Crn = corundum (internal standard, in red).

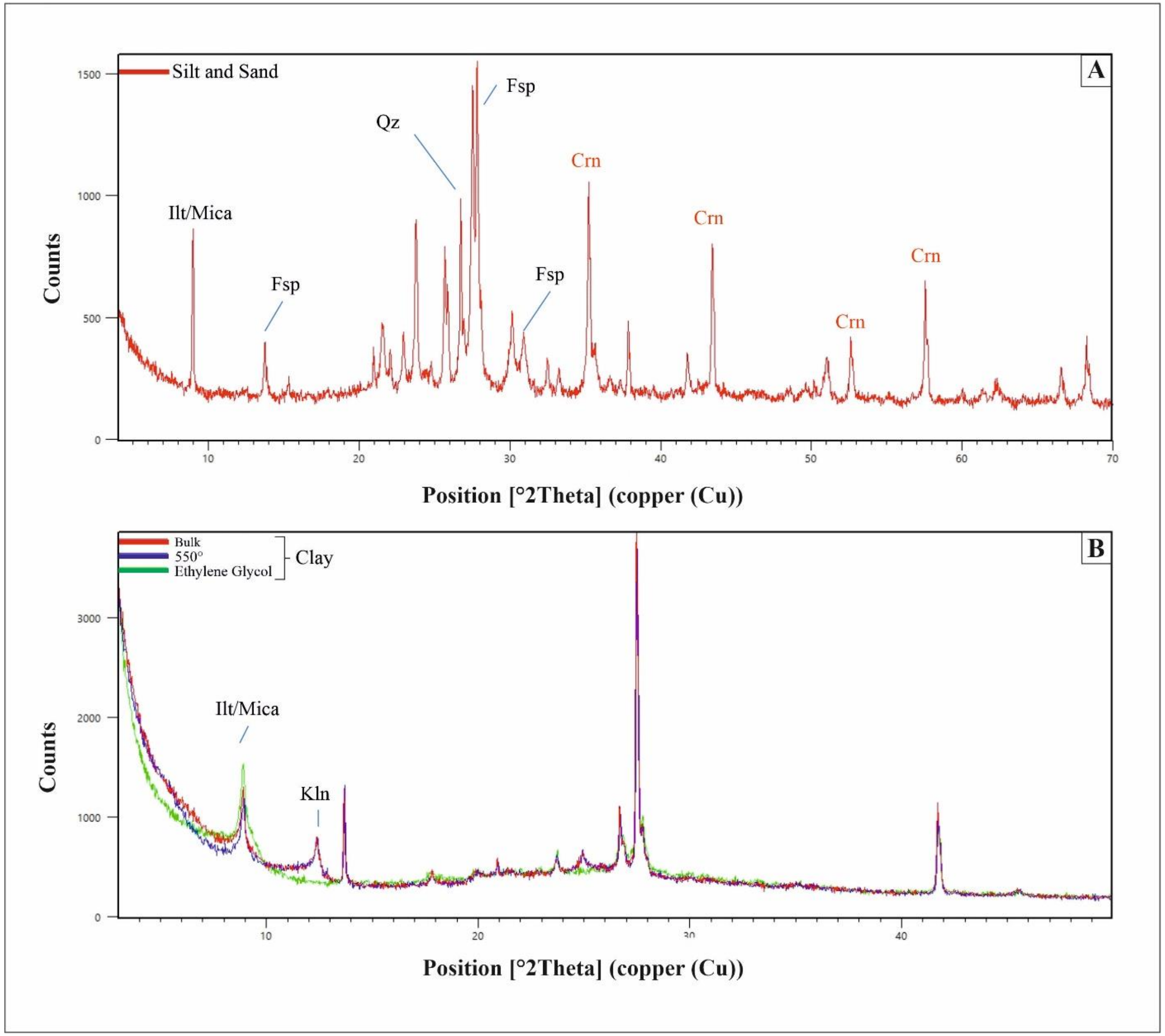


**Figure 3.10.** XRPD patterns of the soil sample from Ponza Island (PZ-S-02). A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Qz = quartz, Px = pyroxene, Kln = kaolinite, Ilt = illite, Crn = corundum (internal standard, in red).

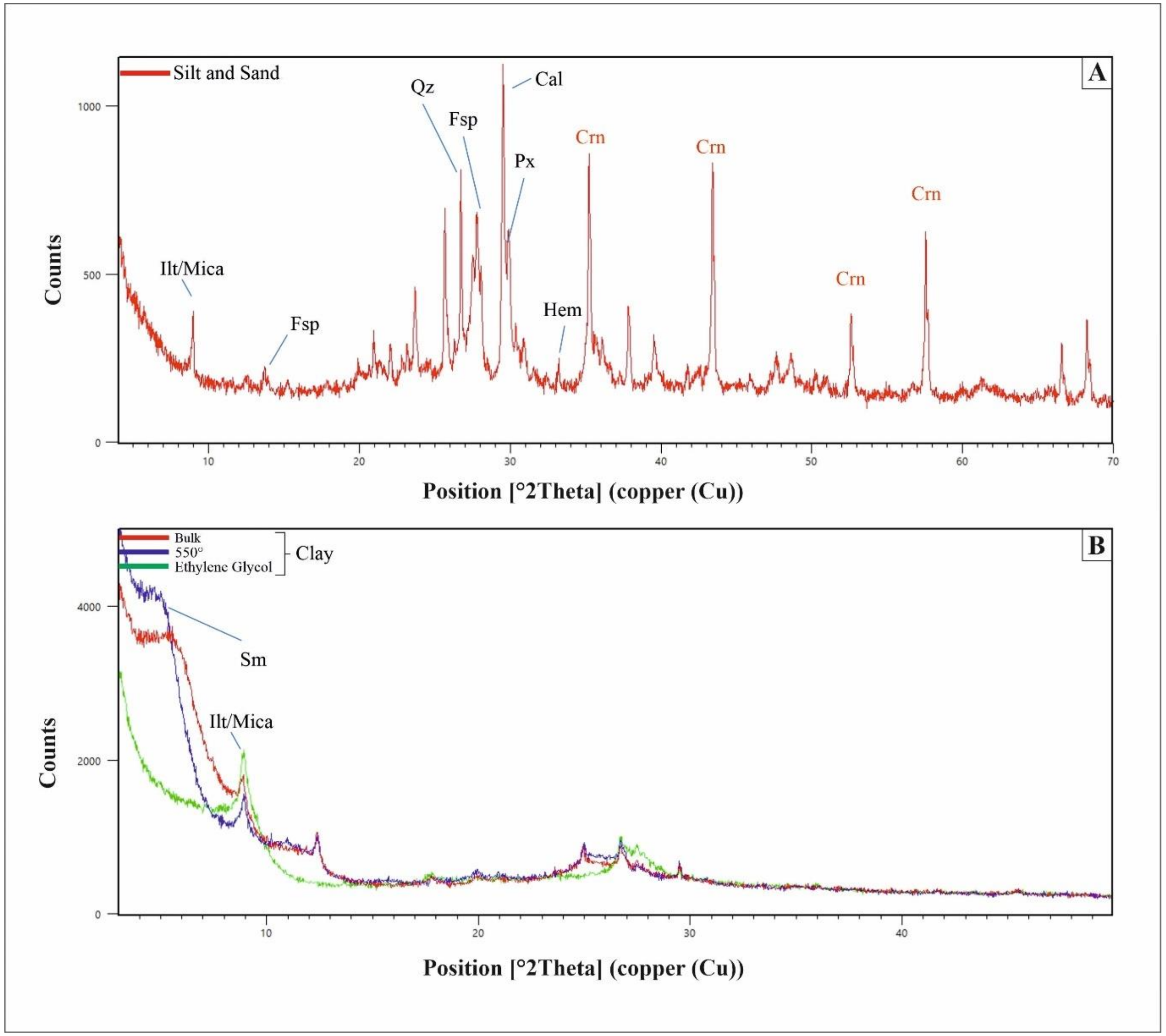


**Figure 3.11.** XRPD patterns of the soil sample from Ventotene Island (VE-S-01). A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Cal = calcite, Px = pyroxene, Hem = hematite, Kln = kaolinite, Ilt = illite, Sm = smectite, Crn = corundum (internal standard, in red).

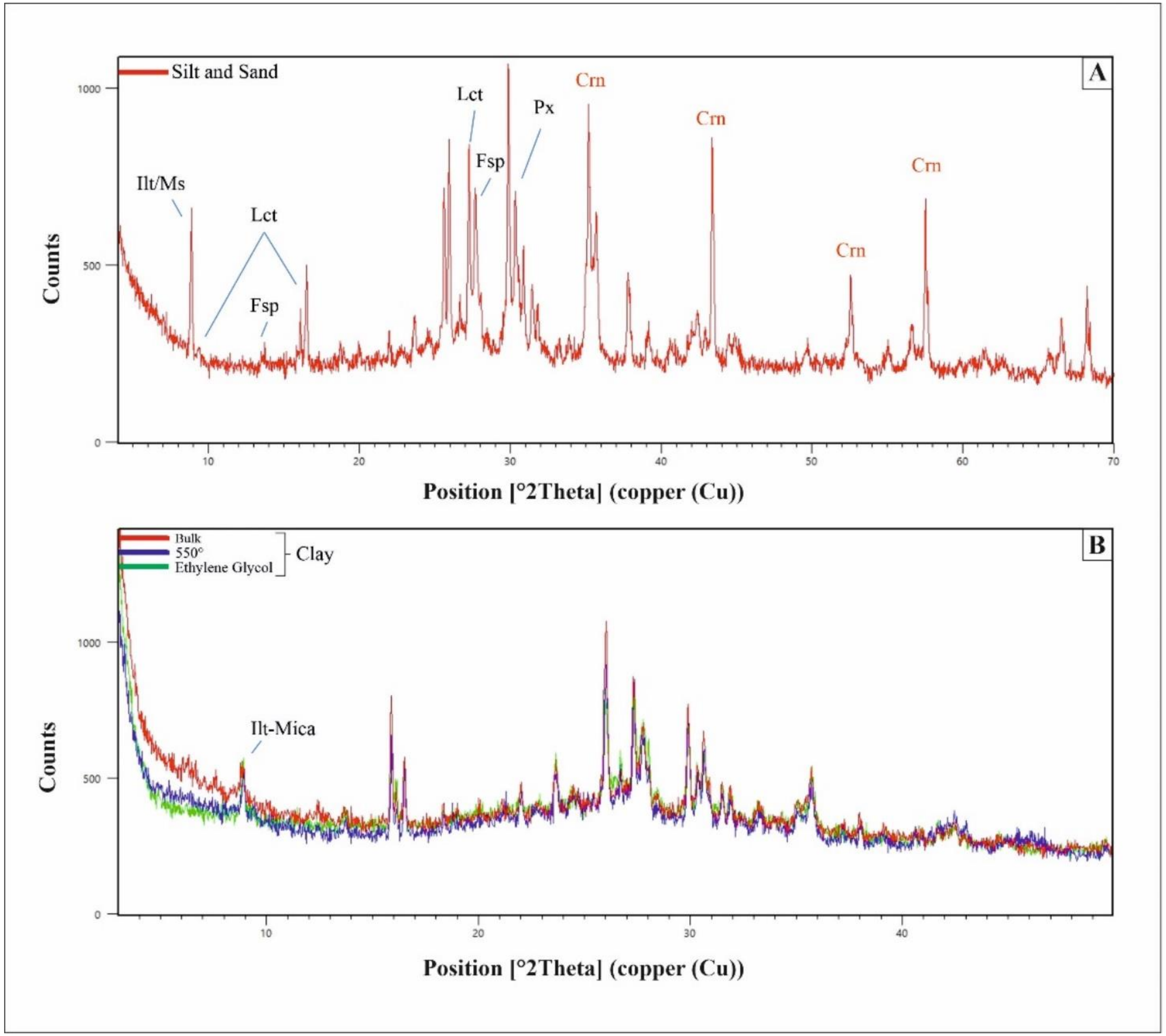


**Figure 3.12.** XRPD patterns of the soil sample from Somma-Vesuvio (VS-S-01). A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Px = pyroxene, Lct = leucite, Ilt = illite, Crn = corundum (internal standard, in red)

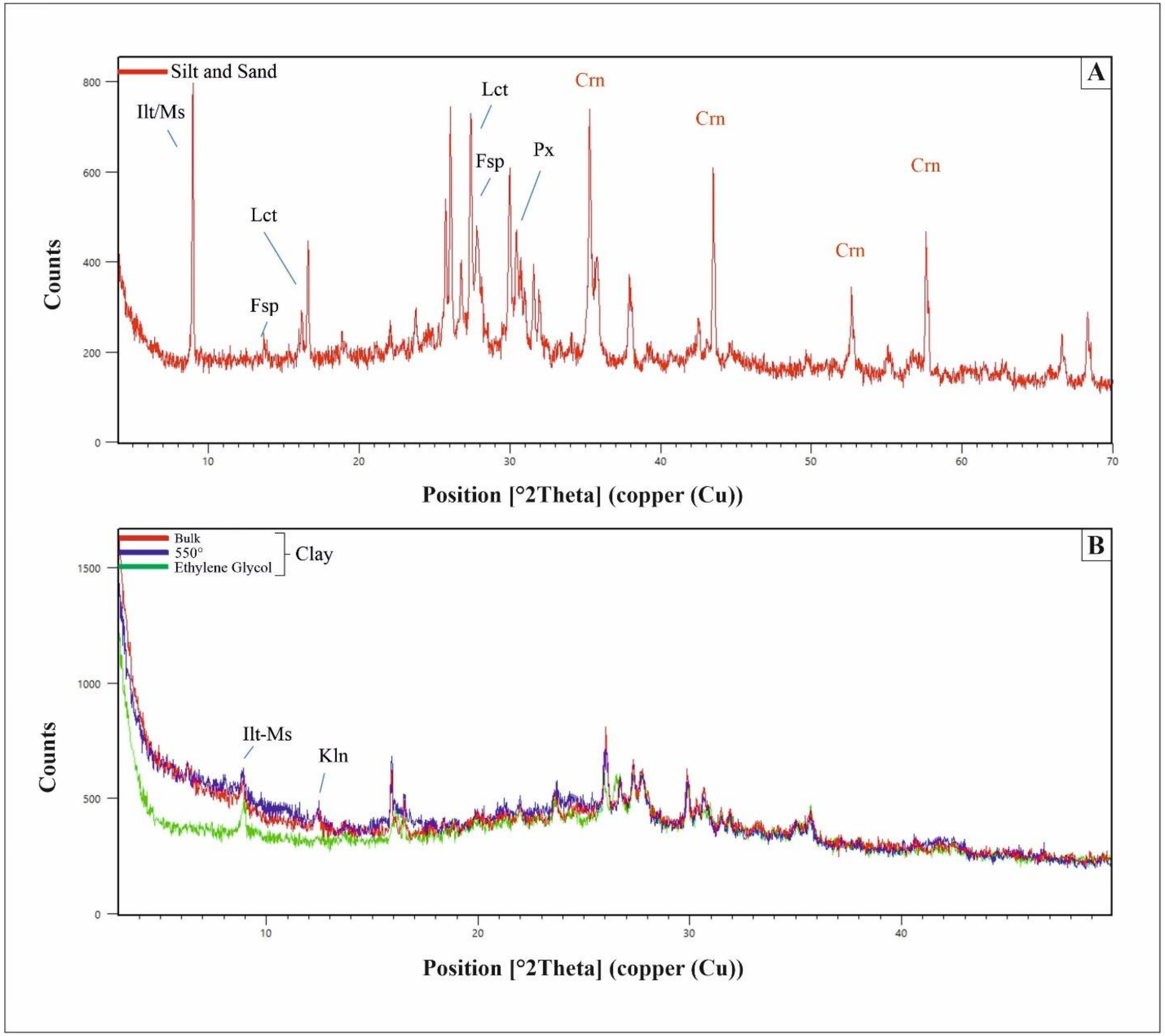


**Figure 3.13.** XRPD patterns of the soil sample from horizon Ap of the Somma-Vesuvio soil profile. A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Px = pyroxene, Lct = leucite, Ilt = illite, Kln = kaolinite, Crn = corundum (internal standard, in red).

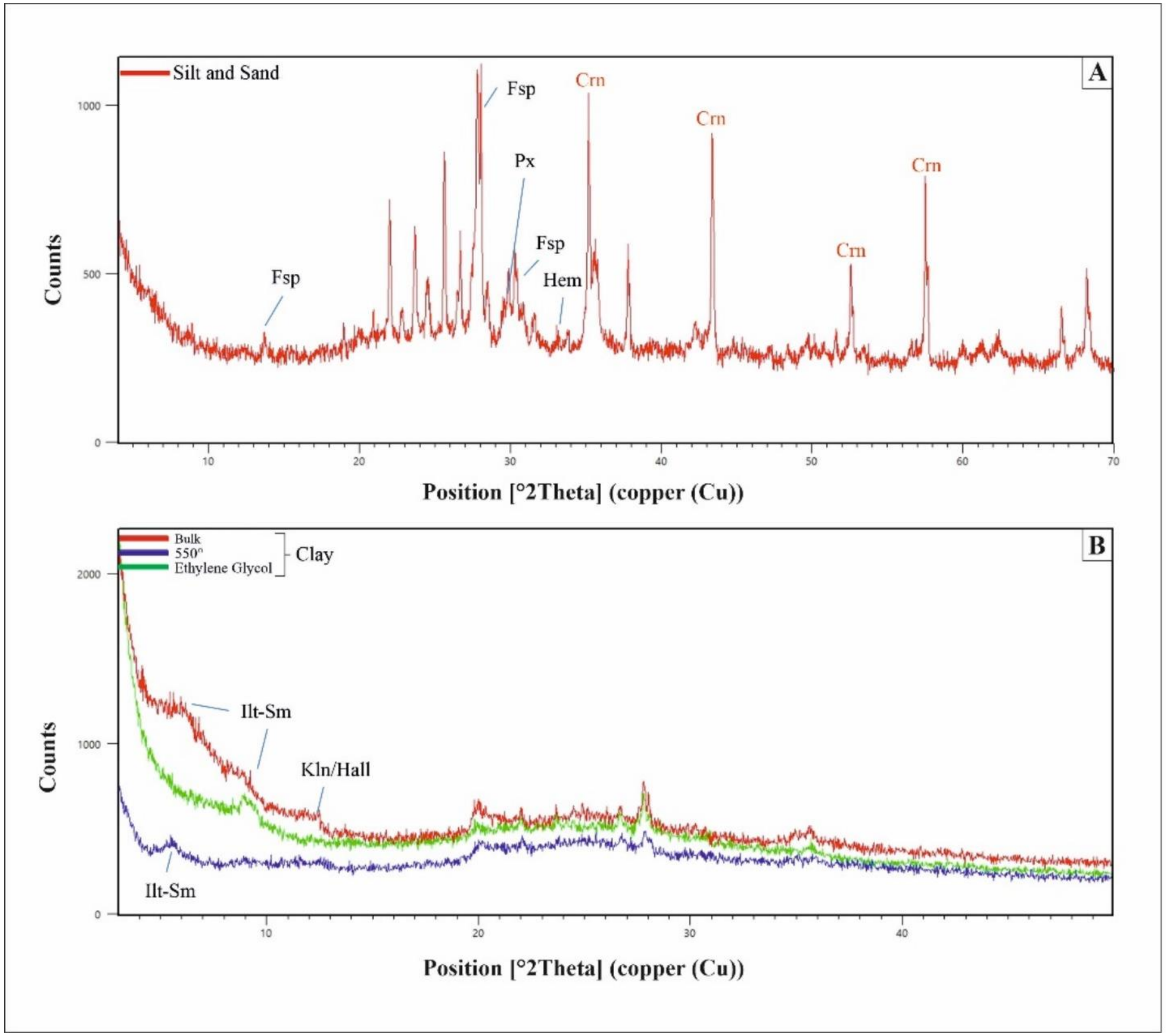


**Figure 3.14.** XRPD patterns of soil sample SL-S-01 from Salina Island. A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Px = pyroxene, Hem = hematite, Kln = kaolinite, Hall = halloysite, Ilt = illite, Sm = smectite, Crn = corundum (internal standard, in red).

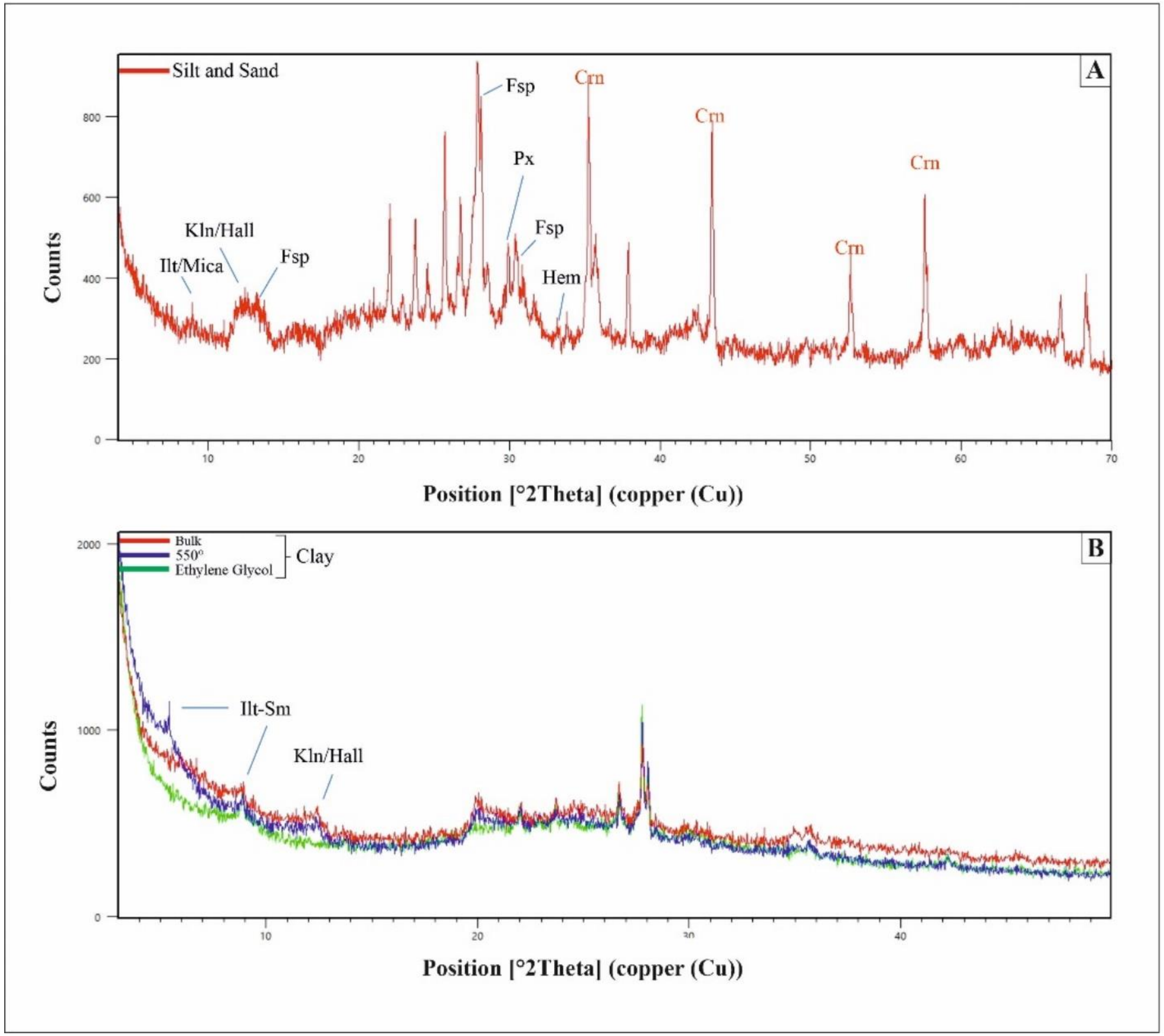


**Figure 3.15.** XRPD patterns of soil sample SL-S-02 from Salina Island. A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Px = pyroxene, Hem = hematite, Kln = kaolinite, Hall = halloysite, Ilt = illite, Sm = smectite, Crn = corundum (internal standard, in red).

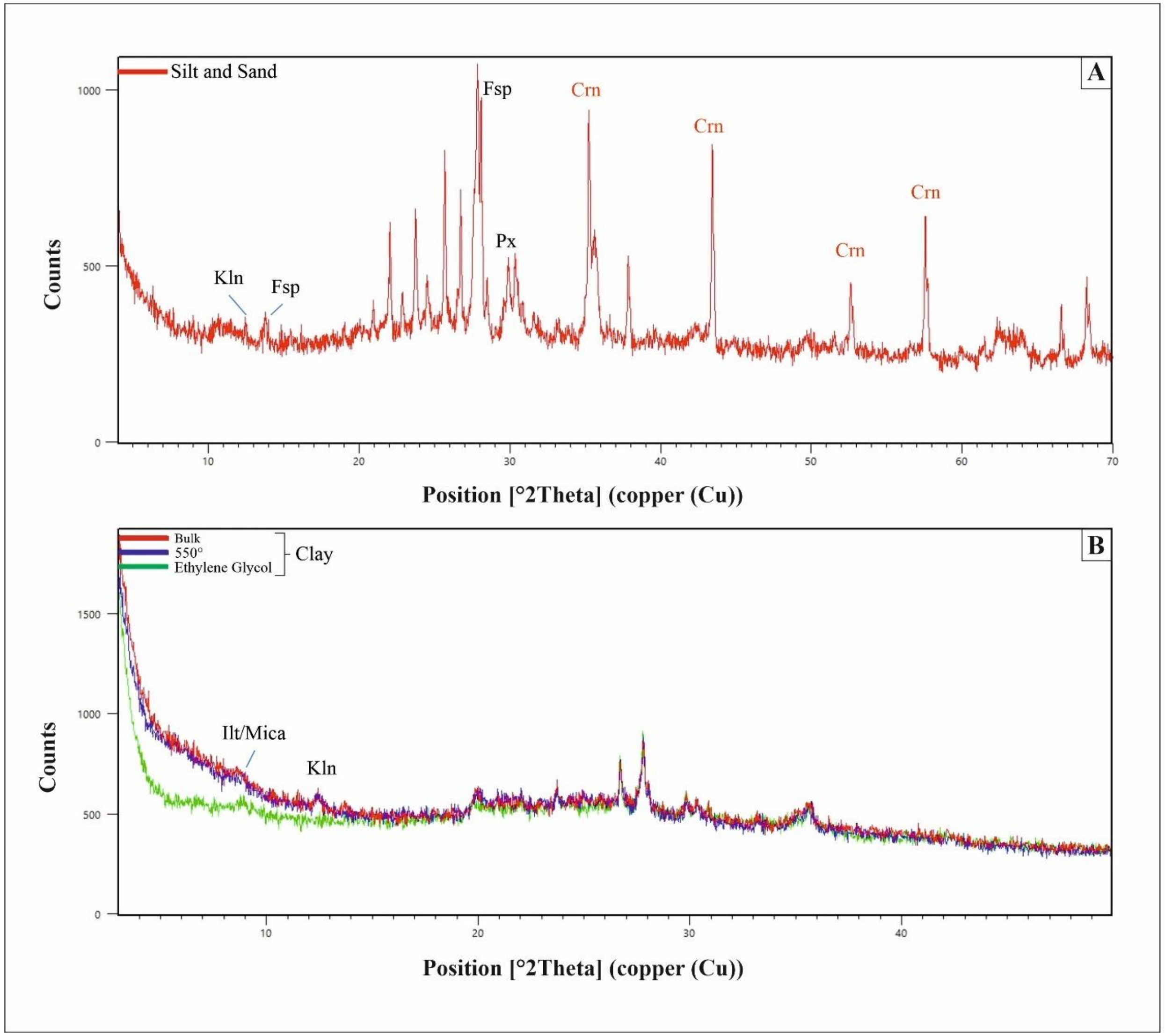


**Figure 3.16.** XRPD patterns of soil sample ET-S-01 from Mount Etna. A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Px = pyroxene, Kln = kaolinite, Ilt = illite, Crn = corundum (internal standard, in red).

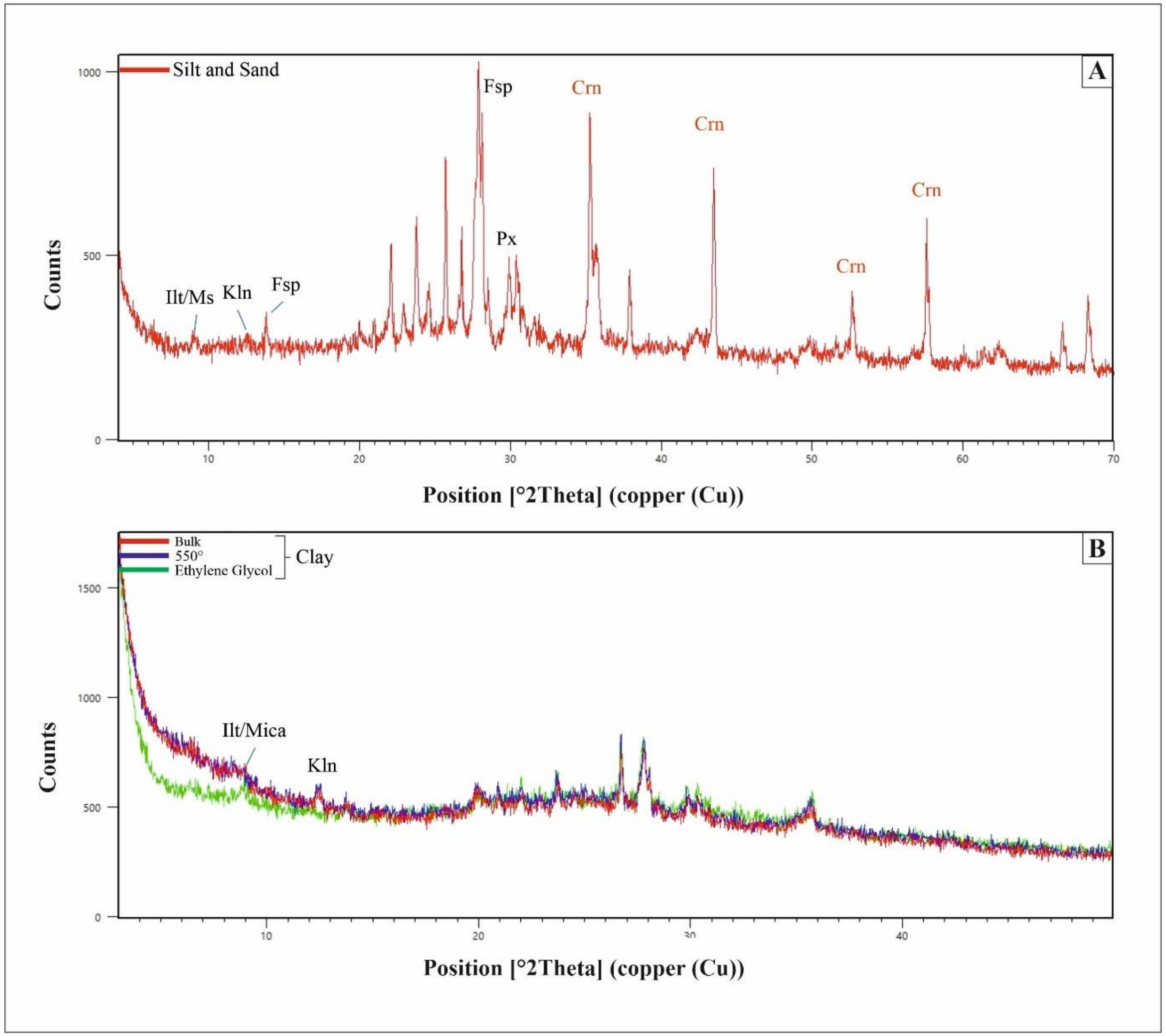


**Figure 3.17.** XRPD patterns of soil sample ET-S-02 from Mount Etna. A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Px = pyroxene, Kln = kaolinite, Ilt = illite, Crn = corundum (internal standard, in red).

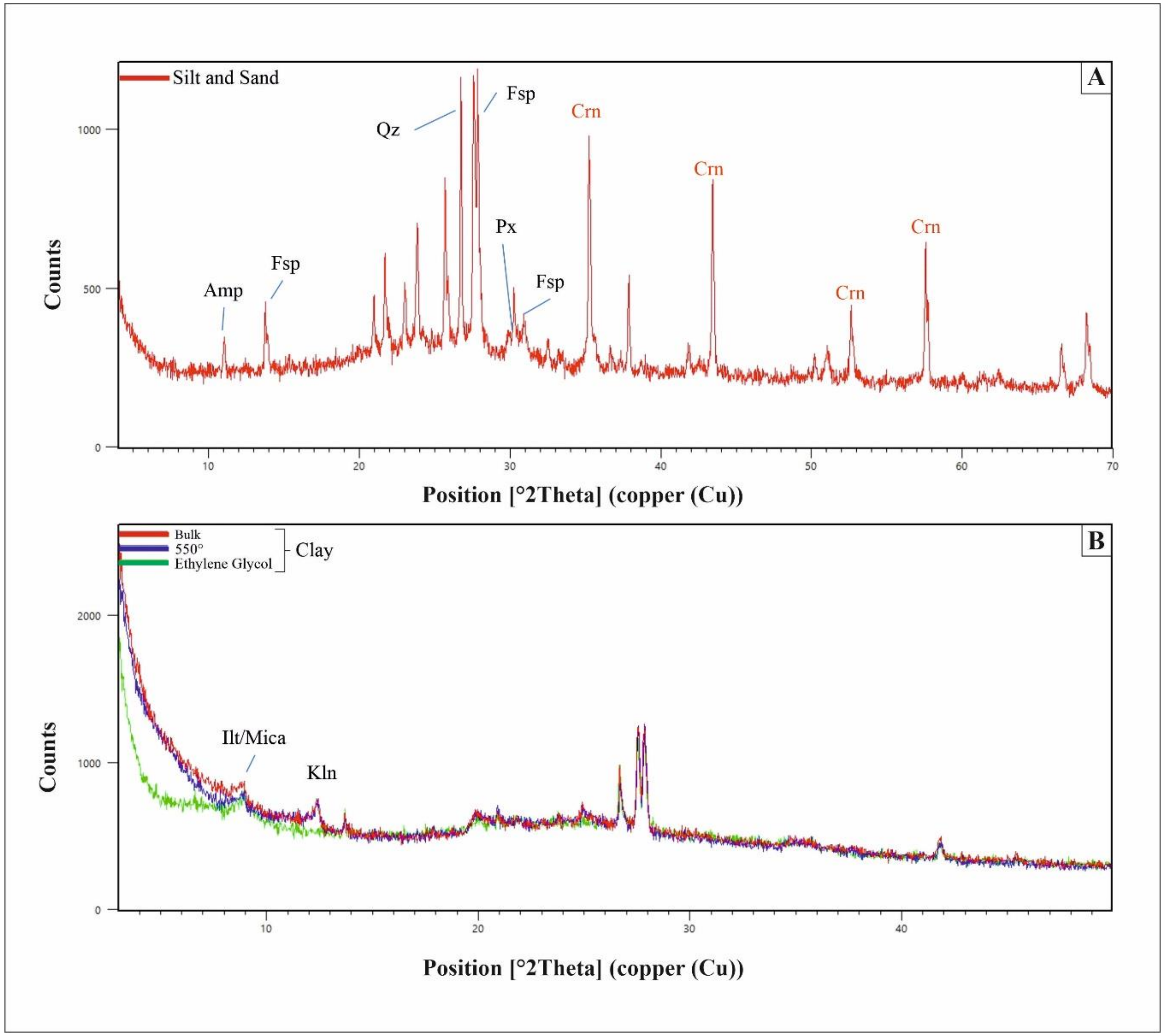
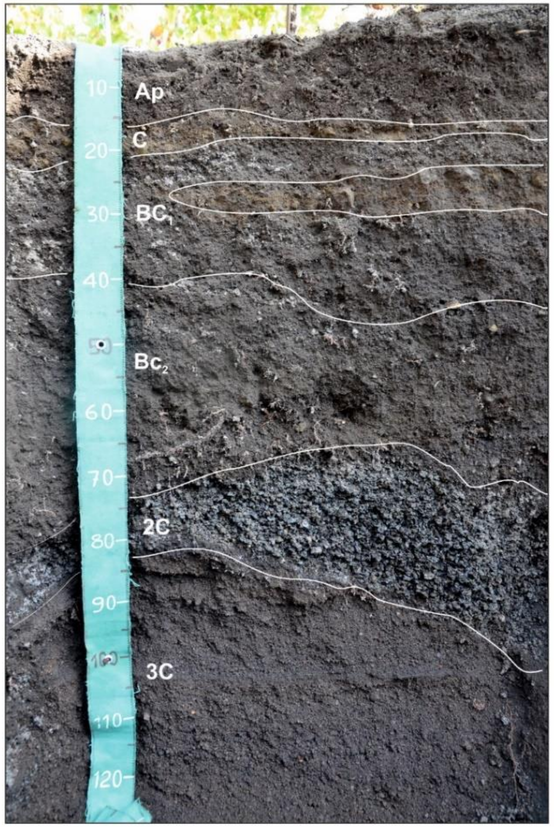


**Figure 3.18.** XRPD patterns of the soil sample from Pantelleria Island (PA-S-01). A) silt and sand fraction; B) clay fraction (red: normal; blue: heated at 550 °C; green: with the addition of ethylene glycol). Mineral abbreviations (Whitney and Evans, 2010): Fsp = feldspar, Qz = quartz, Px = pyroxene, Amp = amphibole, Kln = kaolinite, Ilt = illite, Crn = corundum (internal standard, in red).



**Ap**: 0- 0.16 m - Olive brown color (2.5Y 4/3), weakly developed subangular blocky structure of fine size, common (10-50%) very fine (<1mm) roots, the boundary is abrupt (<2.5cm) and discontinuous.

**C:** 0.16-0.21 m - Light olive brown color (2.5Y 5/6), weakly developed subangular blocky structure of fine size, common (10-50%) very fine (<1mm) roots, the boundary is abrupt (<2.5cm) and discontinuous.

**Bc1:** 0.21-0.40 m - Light olive brown color (2.5Y 5/3), weakly developed subangular blocky structure of fine size, common (10-50%) fine (1-2 mm) roots, the boundary is clear (2.5-6 cm) and linear.

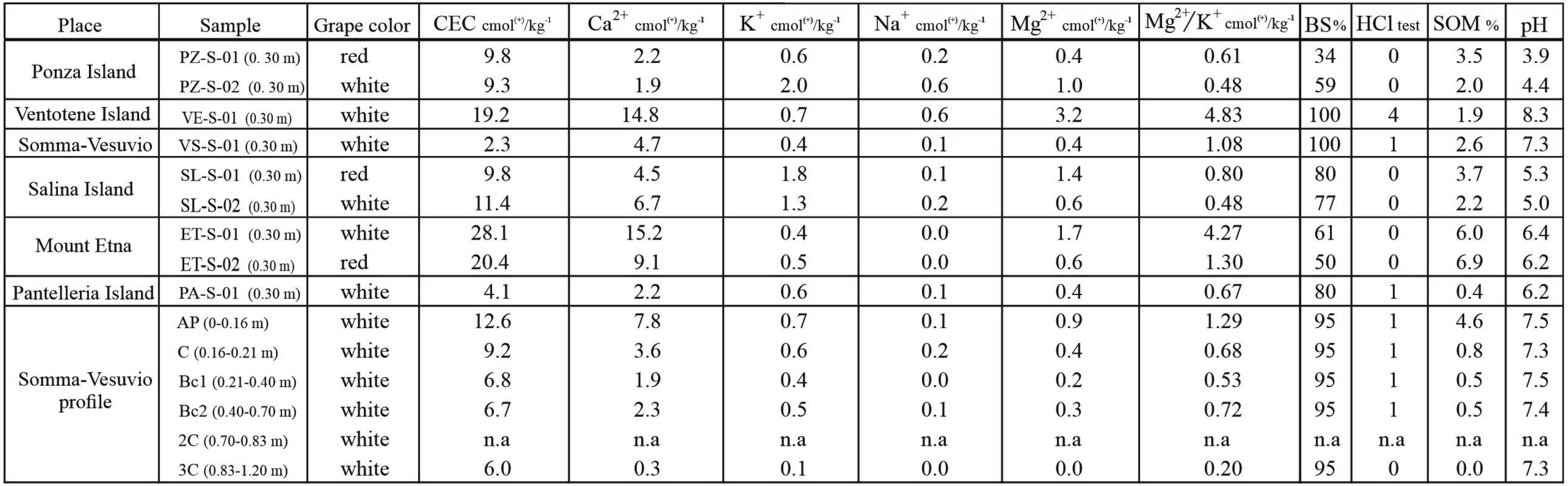
**Bc2:** 0.40-0.70 m - Light olive brown color (2.5Y 5/3), weakly developed subangular blocky structure of fine size, many (50-70%) large (> 5mm), medium (2-5mm) and fine (1-2mm) roots, the boundary is abrupt (<2.5cm) and wavy.

**2C:** 0.70-0.83 m - Olive gray color (5Y 5/2), weakly developed subangular blocky structure of fine size, few (<10%) large (> 5mm) roots, the boundary is abrupt (<2.5cm) and wavy.

**3C:** 0.83-1.20 (+) m - Olive gray color (5Y 4/2), weakly developed subangular blocky structure of fine size, few (<10%) fine (1-2 mm) roots, the boundary is unknown.

**Figure 3.19.** Somma-Vesuvio soil profile with description of soil horizons.

**Table 3.16.** Cation Exchange Capacity (CEC), exchangeable $Ca^{2+}$, $K^{+}$, $Na^{+}$ and $Mg^{2+}$, base saturation (BS%), results of HCl test, soil organic matter (SOM) and pH values for the investigated soil samples from Ponza Island, Ventotene Island, Mount Somma-Vesuvio, Salina Island, Mount Etna and Pantelleria Island soils, including soil samples from the Somma-Vesuvio profile (*, with indication of their depth from the surface). n.a. = not analyzed.



| Place | Sample | Grape color | CEC cmol$^{(+)}$/kg$^{-1}$ | $Ca^{2+}$ cmol$^{(+)}$/kg$^{-1}$ | $K^{+}$ cmol$^{(+)}$/kg$^{-1}$ | $Na^{+}$ cmol$^{(+)}$/kg$^{-1}$ | $Mg^{2+}$ cmol$^{(+)}$/kg$^{-1}$ | $Mg^{2+}/K^{+}$ cmol$^{(+)}$/kg$^{-1}$ | BS% | HCl test | SOM % | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ponza Island | PZ-S-01 (0. 30 m) | red | 9.8 | 2.2 | 0.6 | 0.2 | 0.4 | 0.61 | 34 | 0 | 3.5 | 3.9 |
| | PZ-S-02 (0. 30 m) | white | 9.3 | 1.9 | 2.0 | 0.6 | 1.0 | 0.48 | 59 | 0 | 2.0 | 4.4 |
| Ventotene Island | VE-S-01 (0.30 m) | white | 19.2 | 14.8 | 0.7 | 0.6 | 3.2 | 4.83 | 100 | 4 | 1.9 | 8.3 |
| Somma-Vesuvio | VS-S-01 (0.30 m) | white | 2.3 | 4.7 | 0.4 | 0.1 | 0.4 | 1.08 | 100 | 1 | 2.6 | 7.3 |
| Salina Island | SL-S-01 (0.30 m) | red | 9.8 | 4.5 | 1.8 | 0.1 | 1.4 | 0.80 | 80 | 0 | 3.7 | 5.3 |
| | SL-S-02 (0.30 m) | white | 11.4 | 6.7 | 1.3 | 0.2 | 0.6 | 0.48 | 77 | 0 | 2.2 | 5.0 |
| Mount Etna | ET-S-01 (0.30 m) | white | 28.1 | 15.2 | 0.4 | 0.0 | 1.7 | 4.27 | 61 | 0 | 6.0 | 6.4 |
| | ET-S-02 (0.30 m) | red | 20.4 | 9.1 | 0.5 | 0.0 | 0.6 | 1.30 | 50 | 0 | 6.9 | 6.2 |
| Pantelleria Island | PA-S-01 (0.30 m) | white | 4.1 | 2.2 | 0.6 | 0.1 | 0.4 | 0.67 | 80 | 1 | 0.4 | 6.2 |
| Somma-Vesuvio profile | AP (0-0.16 m) | white | 12.6 | 7.8 | 0.7 | 0.1 | 0.9 | 1.29 | 95 | 1 | 4.6 | 7.5 |
| | C (0.16-0.21 m) | white | 9.2 | 3.6 | 0.6 | 0.2 | 0.4 | 0.68 | 95 | 1 | 0.8 | 7.3 |
| | Bc1 (0.21-0.40 m) | white | 6.8 | 1.9 | 0.4 | 0.0 | 0.2 | 0.53 | 95 | 1 | 0.5 | 7.5 |
| | Bc2 (0.40-0.70 m) | white | 6.7 | 2.3 | 0.5 | 0.1 | 0.3 | 0.72 | 95 | 1 | 0.5 | 7.4 |
| | 2C (0.70-0.83 m) | white | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a | n.a |
| | 3C (0.83-1.20 m) | white | 6.0 | 0.3 | 0.1 | 0.0 | 0.0 | 0.20 | 95 | 0 | 0.0 | 7.3 |

***Sr isotope composition***

The Sr isotope compositions of soil (labile and bulk fractions), wine, microvinification, grape, grape-components and leaf samples from Ponza Island, Ventotene Island, Mount Somma-Vesuvio, Salina Island, Mount Etna and Pantelleria Island are reported in **Table 3.17.**

The $^{87}$Sr/$^{86}$Sr values of biological samples (grape, leaf, microvinification and bottled wine are homogeneous for a given vineyard (labile fraction and bulk soil). As a whole, regardless of the different type of samples analyzed, the measured $^{87}$Sr/$^{86}$Sr values show a large variability among the different districts, ranging between 0.70371 and 0.70919 with a systematic decrease from Ponza and Ventotene Islands to Somma-Vesuvio, Pantelleria Island, Salina Island and Mount Etna. Three different groups can be recognized: i) the Latium group: Ponza and Ventotene Islands (0.70865-0.70974); the Campania group: Somma-Vesuvio (0.70731-0.70786) and the Sicily group: Salina Island, Mount Etna and Pantelleria Island (0.70362-0.70673).

In Ponza Island the $^{87}$Sr/$^{86}$Sr for samples from the Biancolella (white) vineyards vary from 0.70883 to 0.70952, while the Aglianico (red) vineyard results display higher values, between 0.70905 and 0.70974, falling inside the range of the Ventotene Island Fiano (white) vineyard (0.70865-0.70910).

Samples from the Somma-Vesuvio Falanghina vineyard (white) showed quite homogeneous $^{87}$Sr/$^{86}$Sr values (0.70731 to 0.70786) including the analytical results of the different parts of the vineyards and soil horizons. These latter will be further discussed in the section ***Soil profile from the Somma-Vesuvio vineyard.***

The $^{87}$Sr/$^{86}$Sr measured for samples from Salina Island lie in the range of 0.70469 to 0.70655 for the Malvasia (white) vineyard and 0.70473 to 0.70591 for the Corinto Nero (red) vineyard.

The Etna samples from the Nerello mascalese (red) vineyard vary from 0.70362 to 0.70492, while the Carricante (white) vineyard samples display a somewhat larger range of values, between 0.70371 and 0.70548.

The $^{87}$Sr/$^{86}$Sr of Pantelleria Island samples (Zibibbo vineyard) range from 0.70578 to 0.70673, the lowest being for the bottled wine sample (PA-W-01).

**Figure 3.17** displays binary variation diagrams comparing $^{87}$Sr/$^{86}$Sr values for the labile and bulk fractions of the soil with those for grape, leaf, microvinification and bottled wine samples analyzed in the various investigated districts.

The $^{87}$Sr/$^{86}$Sr of bulk soil samples range from 0.70362 to 0.70919, whereas the labile soil fractions are limited between 0.70475 and 0.70905, the latter also being generally more radiogenic (with the only exception of Ponza Island samples). These results are in contrast with studies that demonstrated that the labile fraction of the soil is generally less radiogenic than the bulk soil (Petrini et al., 2015; Vinciguerra et al., 2016; Guibourdenche et al., 2020). However, the $^{87}$Sr/$^{86}$Sr values of the labile soil samples are more in line with those for the biological samples, showing that this is more suitable for traceability studies (**Figure 3.17**).

**Table 3.17.** Results (with standard deviation values, 2SD) of the $^{87}Sr/^{86}Sr$ analyses of the biological (leaf, grape, microvinification and bottled wine) and geological samples (soil, both bulk and labile fraction) from the investigated Italian volcanic districts. (*) Soil fractions up to 2 mm from the C, 2C and 3C horizons (Somma-Vesuvio soil profile).

| PLACE | GRAPE | VARIETY | TYPE | SAMPLE | $^{87}Sr/^{86}Sr$ | 2SD |
|---|---|---|---|---|---|---|
| PONZA ISLAND | WHITE | Biancolella | BULK SOIL | PZ-S-01 (0.30 m) | 0.70899 | 0.00001 |
| | | | LABILE SOIL | PZ-S-L-01 (0.30 m) | 0.70883 | 0.00002 |
| | | | MICROVINIFICATION | PZ-V-01 | 0.70896 | 0.00001 |
| | | | BOTTLED WINE | PZ-W-01 | 0.70905 | 0.00001 |
| | | | GRAPE | PZ-U-01 | 0.70896 | 0.00001 |
| | | | LEAF | PZ-F-01 | 0.70893 | 0.00002 |
| | RED | Aglianico | BULK SOIL | PZ-S-02 (0.30 m) | 0.70919 | 0.00001 |
| | | | LABILE SOIL | PZ-S-L-02 (0.30 m) | 0.70905 | 0.00002 |
| | | | MICROVINIFICATION | PZ-V-02 | 0.70906 | 0.00002 |
| | | | BOTTLED WINE | PZ-W-02 | 0.70906 | 0.00001 |
| | | | GRAPE | PZ-U-02 | 0.70905 | 0.00001 |
| | | | LEAF | PZ-F-02 | 0.70974 | 0.00041 |
| VENTOTENE ISLAND | WHITE | Fiano | BULK SOIL | VE-S-01 (0.30 m) | 0.70889 | 0.00001 |
| | | | LABILE SOIL | VE-S-L-01 (0.30 m) | 0.70900 | 0.00001 |
| | | | MICROVINIFICATION | VE-V-01 | 0.70865 | 0.00003 |
| | | | BOTTLED WINE | VE-W-01 | 0.70910 | 0.00002 |
| | | | GRAPE | VE-U-01 | 0.70899 | 0.00002 |
| | | | LEAF | VE-F-01 | 0.70897 | 0.00001 |
| SALINA ISLAND | WHITE | Malvasia | BULK SOIL | SL-S-01 (0.30 m) | 0.70469 | 0.00001 |
| | | | LABILE SOIL | SL-S-L-01 (0.30 m) | 0.70577 | 0.00001 |
| | | | MICROVINIFICATION | SL-V-01 | 0.70599 | 0.00003 |
| | | | BOTTLED WINE | SL-W-01 | 0.70522 | 0.00011 |
| | | | BOTTLED WINE | SL-W-03 | 0.70655 | 0.00002 |
| | | | GRAPE | SL-U-01 | 0.70597 | 0.00002 |
| | | | LEAF | SL-F-01 | 0.70589 | 0.00001 |
| | RED | Corinto Nero | BULK SOIL | SL-S-02 (0.30 m) | 0.70473 | 0.00001 |
| | | | LABILE SOIL | SL-S-L-02 (0.30 m) | 0.70591 | 0.00001 |
| | | | MICROVINIFICATION | SL-V-02 | 0.70583 | 0.00001 |
| | | | BOTTLED WINE | SL-W-02 | 0.70641 | 0.00003 |
| | | | GRAPE | SL-U-02 | 0.70596 | 0.00002 |
| | | | LEAF | SL-F-02 | 0.70589 | 0.00001 |
| MOUNT ETNA | RED | Nerello Mascalese | BULK SOIL | ET-S-02 (0.30 m) | 0.70362 | 0.00001 |
| | | | LABILE SOIL | ET-S-L-01 (0.30 m) | 0.70478 | 0.00001 |
| | | | MICROVINIFICATION | ET-V-02 | 0.70330 | 0.00004 |
| | | | GRAPE | ET-U-02 | 0.70473 | 0.00001 |
| | | | LEAF | ET-F-02 | 0.70492 | 0.00003 |
| | WHITE | Carricante | BULK SOIL | ET-S-01 (0.30 m) | 0.70371 | 0.00001 |
| | | | LABILE SOIL | ET-S-L-02 (0.30 m) | 0.70477 | 0.00001 |
| | | | MICROVINIFICATION | ET-V-01 | 0.70465 | 0.00002 |
| | | | GRAPE | ET-U-01 | 0.70458 | 0.00001 |
| | | | LEAF | ET-F-01 | 0.70548 | 0.00009 |
| PANTELLERIA ISLAND | WHITE | Zibibbo | BULK SOIL | PA-S-01 (0.30 m) | 0.70613 | 0.00001 |
| | | | LABILE SOIL | PA-S-L-01 (0.30 m) | 0.70673 | 0.00005 |
| | | | MICROVINIFICATION | PA-V-01 | 0.70623 | 0.00003 |
| | | | BOTTLED WINE | PA-W-01 | 0.70655 | 0.00002 |
| | | | BOTTLED WINE | PA-W-02 | 0.70578 | 0.00002 |
| | | | GRAPE | PA-U-01 | 0.70657 | 0.00002 |
| | | | LEAF | PA-F-01 | 0.70633 | 0.00001 |

| PLACE | GRAPE | VARIETY | TYPE | SAMPLE | $^{87}$Sr/$^{86}$Sr | 2SD |
|---|---|---|---|---|---|---|
| SOMMA-VESUVIO | WHITE | Falanghina | BULK SOIL | VS-S-01 (0.30 m) | 0.70748 | 0.00001 |
| | | | LABILE SOIL | VS-S-L-01 (0.30 m) | 0.70768 | 0.00001 |
| | | | SOIL PROFILE - LABILE | AP ( 0.0 to 0.16 m) | 0.70785 | 0.00002 |
| | | | SOIL PROFILE - LABILE | C (0.16 to 0.21 m) | 0.70786 | 0.00002 |
| | | | SOIL PROFILE - LABILE | C* ( 0.16 to 0.21 m) | 0.70786 | 0.00002 |
| | | | SOIL PROFILE - LABILE | BC1 (0.21 to 0.40 m) | 0.70786 | 0.00002 |
| | | | SOIL PROFILE - LABILE | BC2 (0.40 to 0.70 m) | 0.70784 | 0.00001 |
| | | | SOIL PROFILE - LABILE | 2C (0.70 to 0.83 m) | 0.70756 | 0.00001 |
| | | | SOIL PROFILE - LABILE | 2C* ( 0.70 to 0.83 m) | 0.70755 | 0.00001 |
| | | | SOIL PROFILE - LABILE | 3C (0.83 to 1.20 m) | 0.70773 | 0.00001 |
| | | | SOIL PROFILE - LABILE | 3C* (0.83 to 1.20 m) | 0.70776 | 0.00001 |
| | | | MICROVINIFICATION | VS-W-01 | 0.70748 | 0.00001 |
| | | | BOTTLED WINE | VS-V-01 | 0.70755 | 0.00002 |
| | | | GRAPE | VS-U-01 | 0.70733 | 0.00001 |
| | | | PULP | VS-PULP | 0.70731 | 0.00001 |
| | | | SKIN | VS-SK-01 | 0.70741 | 0.00001 |
| | | | SEED | VS-SE-01 | 0.70732 | 0.00001 |
| | | | LEAF | VS-F-01 | 0.70752 | 0.00001 |
| | | | STEM | VS-ST-01 | 0.70744 | 0.00002 |
| | | | ROOTS | VS-RA-01 | 0.70738 | 0.00002 |

Indeed, several $^{87}$Sr/$^{86}$Sr soil-plant studies revealed that Sr in plants mostly derives from the soil labile fraction and that the $^{87}$Sr/$^{86}$Sr of plants reflects that of the soil labile fraction (Goitom Asfaha et al., 2011; Song et al., 2014, 2015; Trincherini et al., 2014; Dotaniya and Meena, 2015; Aoyama et al., 2017; Coelho et al., 2017).

A comparison of $^{87}$Sr/$^{86}$Sr values for grape and respective microvinification samples shows a remarkably good correspondence for Ponza (white and red vineyards), Ventotene Island, Somma-Vesuvio, Salina Island (white) and Pantelleria Island (**Figure 3.18**). On the other hand, higher concentrations have been observed for grape samples from the Salina Island and Mount Etna red vineyards with respect to the corresponding microvinification samples.

Finally, in the case of the Mount Etna (white vineyard), grape samples have lower $^{87}$Sr/$^{86}$Sr with respect to microvinification ones. Further studies must be carried out on these samples to determine these variations, which may be related to isotopic variations in grapes or contamination of samples in the microvinication process.

As for leaf samples, $^{87}$Sr/$^{86}$Sr values are of the same order of magnitude as grape samples in the case of Ponza Island (white), Ventotene Island, Somma-Vesuvio, Salina Island (white) and Pantelleria Island vineyards. The $^{87}$Sr/$^{86}$Sr is higher in leaf samples from Etna (white and red) and lower in leaf samples from the red Salina Island vineyard. It could be speculated that the wide use of fungicides on grapes and leaves might modify their original isotopic composition.

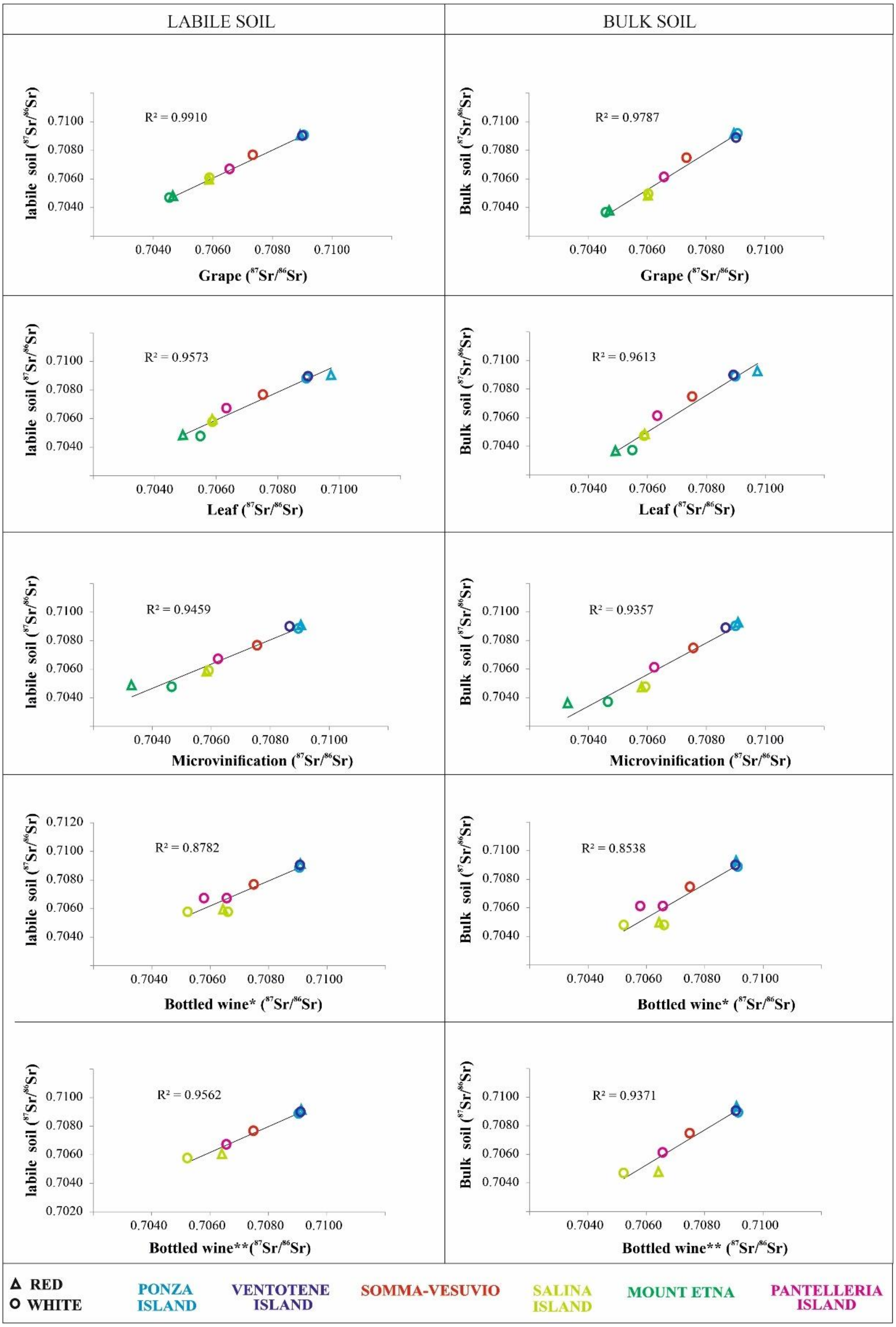


**Figure 3.17.** Binary diagrams comparing $^{87}$Sr/$^{86}$Sr in soil (labile and bulk fraction) and grape, leaf, microvinification and wine from sampled vineyards. In general, labile soils display a better correspondence with biological samples compared to bulk soil, except for leaf samples (see values for the correlation coefficient R$^2$). Sampled wine samples were separated into different graphs. (*) represents bottled wines of the same grape variety and vineyards sampled for microvinification; (**) represents bottled wines from different vineyards (for example, samples SL-W-03: *Passito* wine

from Salina and Lipari vineyards; PA-W-02: Zibibbo bottled wine from Barone area). The lowest $R^2$ values are observed for bottled wine** (from external vineyards), while values for bottled wine* (from same grape sample vineyards) display a better correlation, close to microvinification coefficient of determination.

The general effect of such additives is rather unpredictable, as their composition is highly variable, especially in terms of Ca (and consequentially of Sr). At the present, a single study has been made in order to try to assess how the use of pesticides can affect Sr isotope ratios in grape and must samples, showing that copper-based fungicides might have $^{87}Sr/^{86}Sr$ as low as 0.70769, while the values of must and grapevine samples varied between 0.70965 and 0.70978 (Petrini et al., 2015). The authors concluded that pesticides do not influence the isotopic ratio of the different parts of the vineyards. In this way, a detailed study of the specific product that is used in each investigated vineyard would be necessary to have a better understanding of the effects of the products on the vineyards and wines. In order to evaluate the possible effects of the winemaking processes, bottled wine samples have been compared to grape and microvinification ones.

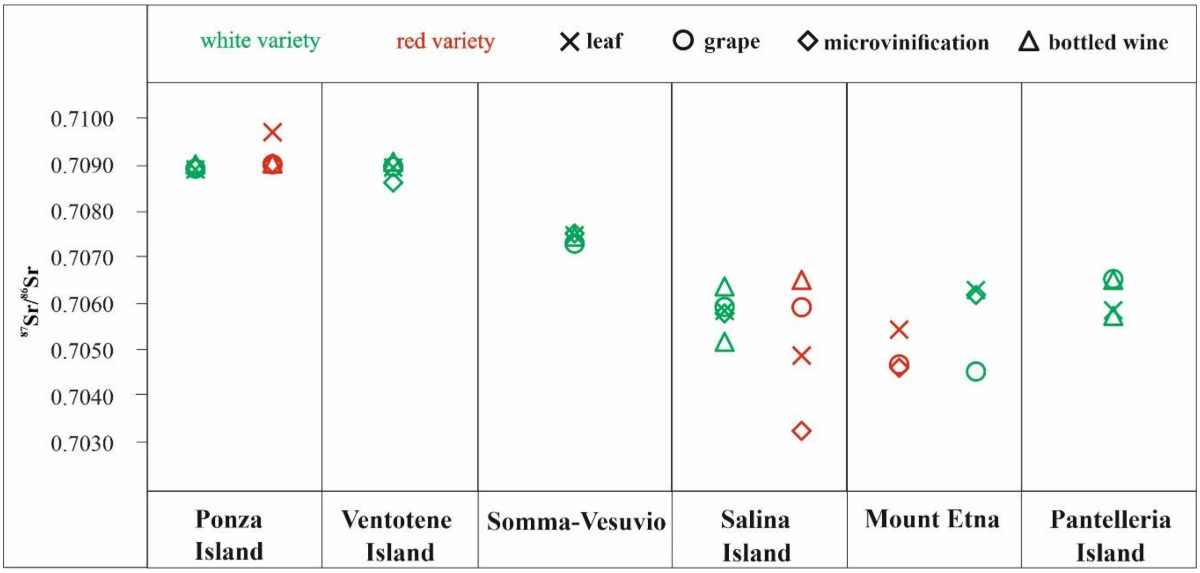


**Figure 3.18**. Distribution of $^{87}Sr/^{86}Sr$ for the biological samples from the studied districts.

A general good correspondence is observed between wine and microvinification samples from the same grape variety and vineyard, with samples from Ponza Island, Ventotene Island, Somma-Vesuvio and Pantelleria Island again showing a better match. As for Pantelleria Island samples, wine sample PA-W-02 yielded a slightly lower $^{87}Sr/^{86}Sr$ with respect to both wine sample PA-W-01 and microvification sample PA-V-01. The PA-W-02 sample is originally from the Barone winery is positioned 2 km away from the sampled vineyards, presenting a different geological substrate (green tuff), which may explain the lower values obtained (Figure 3.7). Meantime, the absence of soil, grape and microvinification samples corresponding to PA-W-02 bottled wine sample (provided by the winery) makes it difficult to understand the lower values in relation to the samples referring to Federico Paulsen winery.

In the Salina Island case, biological samples from the red vineyard generally display a larger dispersion of $^{87}Sr/^{86}Sr$ values with respect to those from the white vineyard, which also shows a better correspondence between wine and microvinification samples. Notably, the lowest value measured in white wine from Salina Island is for a sample of a *Passito* wine, which is made by a desiccation process (the so-called “appassimento”), whereby grapes are in part dried on pallets at the open air, in order to obtain a higher concentration of flavor and sweetness in the grapes prior to the vinification. However, it is not clear whether the “appassimento” process could modify a wine's isotopic signature of a wine.

One possible additional cause for some inconsistency between $^{87}Sr/^{86}Sr$ values measured for wine and microvinification samples might be due to the inclusion of additives, (e.g., to clarify, add flavors, or to filter) during the winemaking processes. As previously observed for the fungicides, also these additives might contain Ca, which consequently adds external Sr and modifies the original isotopic signature of a wine. On the other side, samples of bottled wines are made with a large quantity of grapes, collected from different vineyards, reflecting a greater soil heterogeneity and consequently could represent a more useful $^{87}Sr$ / $^{86}Sr$ value for traceability purposes of a region. This differs from microvinification samples, made by small amounts of grapes, representative of a single vineyard and their roots are limited by a particular type of soil and Sr composition.

### ***Relationships with substratum geology***

The $^{87}Sr/^{86}Sr$ of the various types of samples analyzed at the Ponza Island, Ventontene Island, Somma-Vesuvio and Pantelleria Island vineyards yield overall comparable values with respect to those for the rocks of the local substratum (**Figure 3.20**).

As previously remarked, a clear decrease in $^{87}Sr/^{86}Sr$ moving from northwest to southeast is known to characterize the Cenozoic volcanic rocks from central-southern Italy (Conticelli et al., 2002, 2009, 2010; Peccerillo, 2017). Except for Pantelleria Island, this zoning is clearly evident also from the investigated biological and geological samples. Rocks from Pantelleria Island show systematically lower $^{87}Sr/^{86}Sr$, ranging between 0.70280 and 0.70494, with the only exception of a single value of 0.70854 that was interpreted to reflect the effects of some crustal contamination (Civetta et al., 1984). However, it is to note that the investigated vineyards are located near an alluvial deposit (see **Figure 3.7**), therefore suggesting that the local basement might actually consist of a mixture of different types of rocks (ranging from basalt to strongly evolved rocks) coming from different source areas in Pantelleria Island. Another possible explanation is related to the influence of sea water on the soils of the Pantelleria Island (personal communication, by Massimo D'Antonio) which has an approximate value of 0.70919 (Arienzo et al., 2020).

The $^{87}Sr/^{86}Sr$ isotope ratios of Salina Island and Mount Etna vineyards are slightly different (more radiogenic) from the ratios of their rocks. Agricultural practices such as addition of fertilizers to the soil for agricultural use can also affect the $^{87}Sr/^{86}Sr$ ratios of the labile and bulk fractions of soil (Stewart et al., 1998; Bélanger et al., 2012; Techer et al., 2017). Alternatively, variations in the isotopic composition of Strontium in soils mainly due to climatic factors (different rainfalls) are common and easily observable in certain contexts (Stewart et al., 1998), and attributed to the double effect of the Strontium dissolved in the water and that deriving from the atmospheric dust. In both cases, the addition of secondary strontium may modify the original isotopic signature of the soil, and therefore, the plant and its products (Green at al. 2004).

### *Soil profile from the Somma-Vesuvio vineyard*

The $^{87}Sr/^{86}Sr$ values obtained for vine-grape components (root, stem, grape, skin, pulp, and seed) and soil horizons (Ap, C, BC1, BC2, 2C, 3C) sampled at the Somma-Vesuvio vineyard overlap with each other within analytical uncertainty, indicating that no detectable fractionation occurs for Sr isotopes amongst the different parts of the grapevine and soil horizons (**Figure 3.19**).

More in detail, the most radiogenic values are found for the shallowest Ap, C, BC1 and BC2 horizons (i.e., between 0.0 and 0.70 m of depth, $^{87}Sr/^{86}Sr$ = 0.70784 to 0.70786), whereas the deepest 2C and 3C horizons have slightly lower values faintly decreasing towards the deepest parts of the soil profile (from 0.70756 to 0.70776). Fractions up to 2 mm (*) from the C, 2C and 3C horizons were tested to identify variations in different soil granulometry, resulting in small differences within the analytical uncertainties (C= 0.70786, C*= 0.70786; 2C=0.70756, 2C*=0.70755; 3C= 0.70773, 3C*= 0.70776).

Soil physicochemical characteristics, impermeable layers, rootstock variety, and practices used in cultivation affect the development of grapevine-root systems (Rijal and Bergh, 2016). Most of the grapevine root system develops in the first 100 cm of soil, a small number of roots can be found at deeper depths, and rarely roots at depths more than 10 meters. Almost all fine roots are at depths of 10 to 60 cm, with the highest density in the upper 20 cm of soil. Indeed, the main roots are usually developed between 18 and 80 cm (Rijal and Bergh, 2016). The coarse soil regulates the size of the roots of the vine, presenting less dense roots than those in fine-textured soils. Soils with layered profile changes, for example layers containing large boulders or clay layers, have irregular root distribution. In the investigated Somma-Vesuvio soil profile, the highest density of roots was found at depths between 0.40 and 0.83 m (in BC2 and 2C horizons). The 2C soil horizon (0.70-0.83 m) shows a coarse texture, containing manly fragments of rocks of pyroclastic origin (mostly pumice and scoria clasts), with low or no presence of clay material. The $^{87}Sr/^{86}Sr$ of 0.70756 obtained for this soil horizon show a better correspondence with values obtained for both vegetative components (i.e., root=0.70738, stem=0.70744, grape=0.70733, skin=0.70741, pulp=0.70731 and seed=0.70732) and for microvinification (0.70748) and bottled wine (0.70755) samples.

The absorption of calcium (and consequently of strontium) in the grapevine begins after sprouting and continues until the fruit ripens. One second absorption period occurs in the weeks before the leaves fall. The skin, leaves, followed by the woody are the plant parts that retains more calcium (Conradie, 1981).

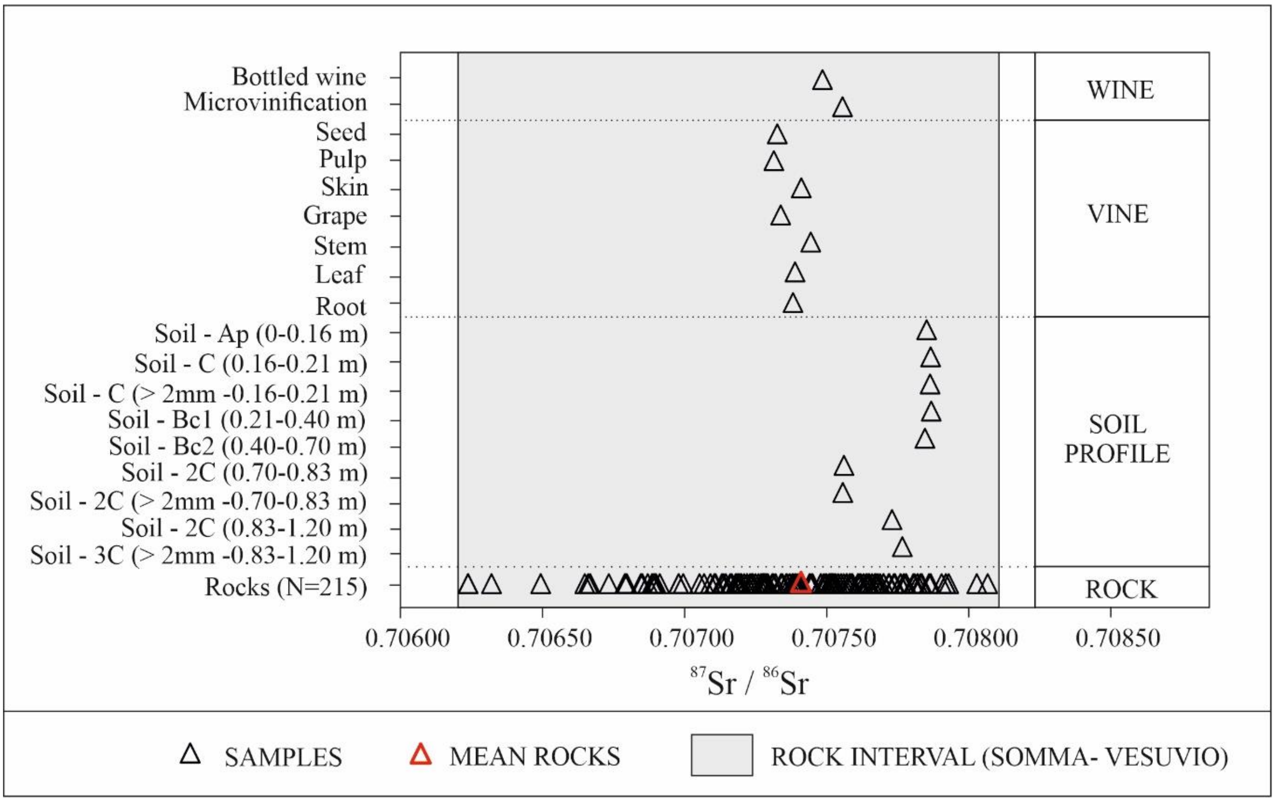


**Figure 3.19.** Comparison of $^{87}Sr/^{86}Sr$ values for the investigated samples from the detailed Somma-Vesuvio soil profile with those for the local volcanic rocks (data sources as *Terroir characterization* section).

The analyzed components of the grapevines sampled at the Somma-Vesuvio show overall similar $^{87}Sr/^{86}Sr$ values, with only a slight decrease moving from leaf to stem, skin, root, grape, seed, and finally pulp samples. Both microvinification and bottled wine samples (0.70748 and 0.70755) show slightly higher values compared to those for the correspondent grape (0.70733), and a better correlation with the $^{87}Sr/^{86}Sr$ of the 2C horizon (0.70756).

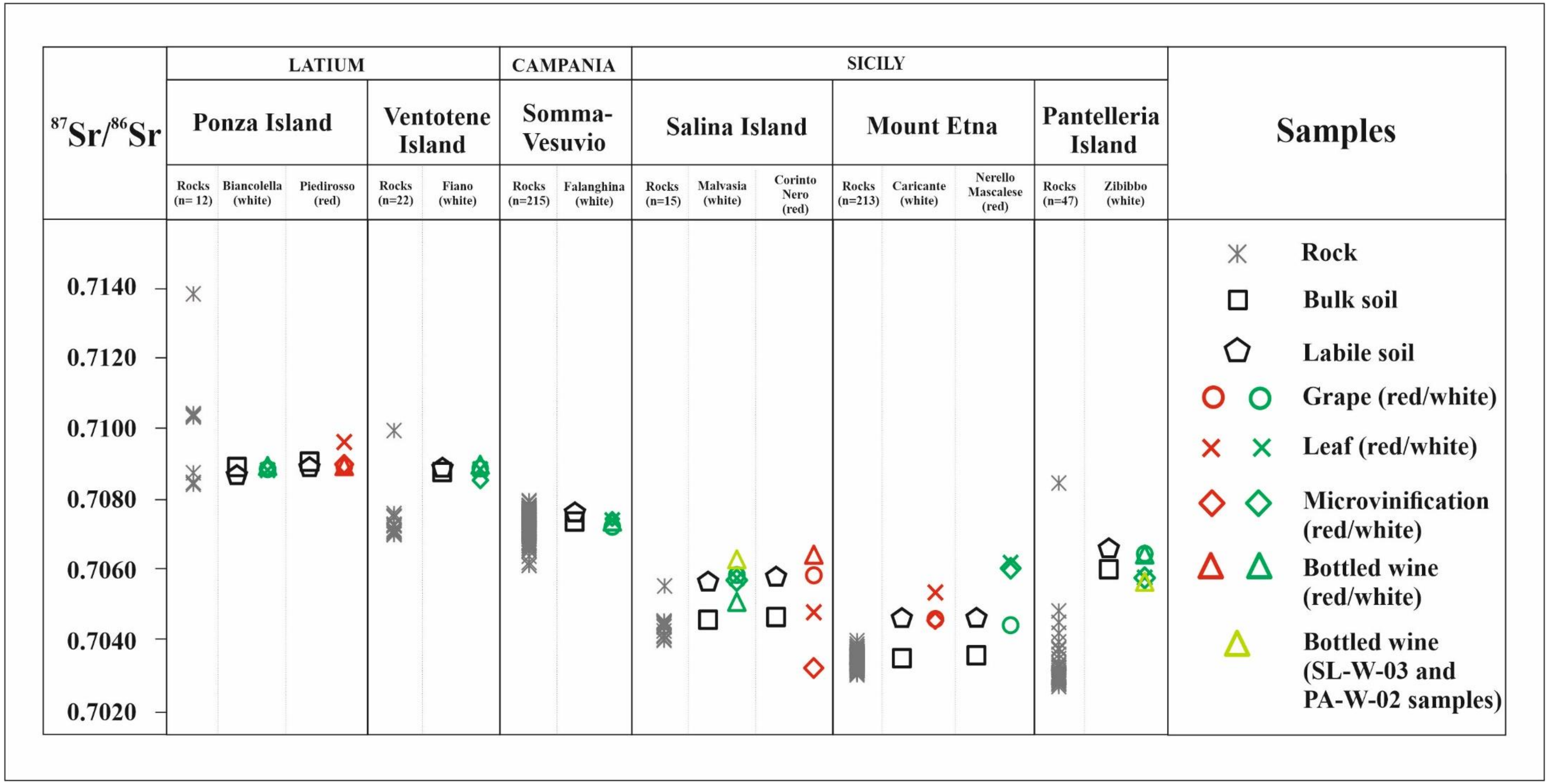


**Figure 3.20.** Comparison of $^{87}Sr/^{86}Sr$ for the different types of analyzed samples from Ponza Island, Ventotene Island, Somma-Vesuvio, Salina Island, Mount Etna and Pantelleria Island districts with those for rocks of their respective geological substratum (data sources as reported in the *Terroir characterization* section).

# Chapter 4 – $^{87}Sr/^{86}Sr$ ISOTOPE CHARACTERIZATION OF CABERNET SAUVIGNON MICROVINIFICATION, LEAF AND SOIL SAMPLES IN VOLCANIC VINEYARDS FROM VALE DOS VINHEDOS, SOUTH BRAZIL.

## INTRODUCTION

Brazil is the third largest wine producer in South America. According to Robinson et al. (2012), grapevines first arrived in Brazil in the mid-16th century, introduced by early Portuguese colonists. By the 20th century, Brazil had become home to more Italian descendants than Brazilians, and each of them had their own vineyard. In the 1970s and 1980s, Brazil began producing wines of true export quality. Small producers in Brazil imported new winemaking technologies, vineyard-management techniques, and the French grape varieties (i.e., Chardonnay, Semillon, Merlot and Cabernet Sauvignon) which were rapidly gaining popularity all over the world.

Despite 30 years of production, Brazil's wine industry has developed relatively slowly, particularly when compared to that of Chile or Argentina. Brazil does not have a Mediterranean climate, as Europe, or a dry climate such as Argentina and some areas of Chile. The humid and sub-humid climate of Brazil harms some grape varieties, causing a decline in concentration and alcohol content, but favors fresher, aromatic, and delicate wines.

The production of wines in Brazil totals 82,000 thousand hectares of Vitis vinifera grapes, divided into seven main regions with approximately 1200 wineries (usually of small production) with an annual production of around 3 million of liters (OIV, 2019).

In Brazil, the Law n° 9279/1996 (Brasil, 1996) defines two types of geographical indications (GI): the indication of origin and the denomination of origin. According to art. 177, “a geographical indication is considered the geographical name of a country, city, region or locality of its territory that has become known as a center for the extraction, production or manufacture of a particular product or the provision of a particular service”. Additionally, the art. 187 defines “a designation of origin (DO) as the geographical name of a country, region, city, or locality of its territory, designating a product or service whose qualities or characteristics are due exclusively or essentially to the geographical environment, including natural and human factors” (Valente et.al, 2012).

In 1995 Brazil became a member of the International Organization of Vine and Wine (OIV, *Organizzazione Internazionale della Vigna e del Vino*) and in 2002 the first Brazilian geographical indication (GI) recognized in the country was the Vale dos Vinhedos region that included also the first designation of origin (DO). Currently, there are seven Brazilian regions that received the GI brand in the country (**Figure 4.1**). In addition to the Vale dos Vinhedos wines, certified Brazilian wines include red, white, and sparkling wines from Pinto Bandeira, Monte Belo, Farropilha, Altos

Montes, Campanha Gaúcha (Rio Grande do Sul State), Vale da Uva Goeth (Santa Catarina State) and Vale do Sao Francisco (Bahia and Pernambuco State; Tonietto et al, 2013). Cabernet Sauvignon, Merlot, Chardonnay and Semillon are the most used grape varieties for wine production and are recognized as grape varieties authorized for designation of origin. The Cabernet Sauvignon grape variety (imported from Bourdeux, France) is considered one of the most important, especially in the Vale dos Vinhedos.

The Serra Gaúcha region, that includes the Vale dos Vinhedos, represents the most important wine producing region of Brazil, covering approximately 40,000 hectares, including five GI areas. The Vale dos Vinhedos, in the Rio Grande do Sul State (south Brazil) is responsible for 80% of Brazilian wine production and covers an area of approximately 73 km$^2$ (26% of the total area of the region) between the municipalities of Bento Gonçalves, Garibaldi and Monte Belo do Sul (EMBRAPA, 2015).

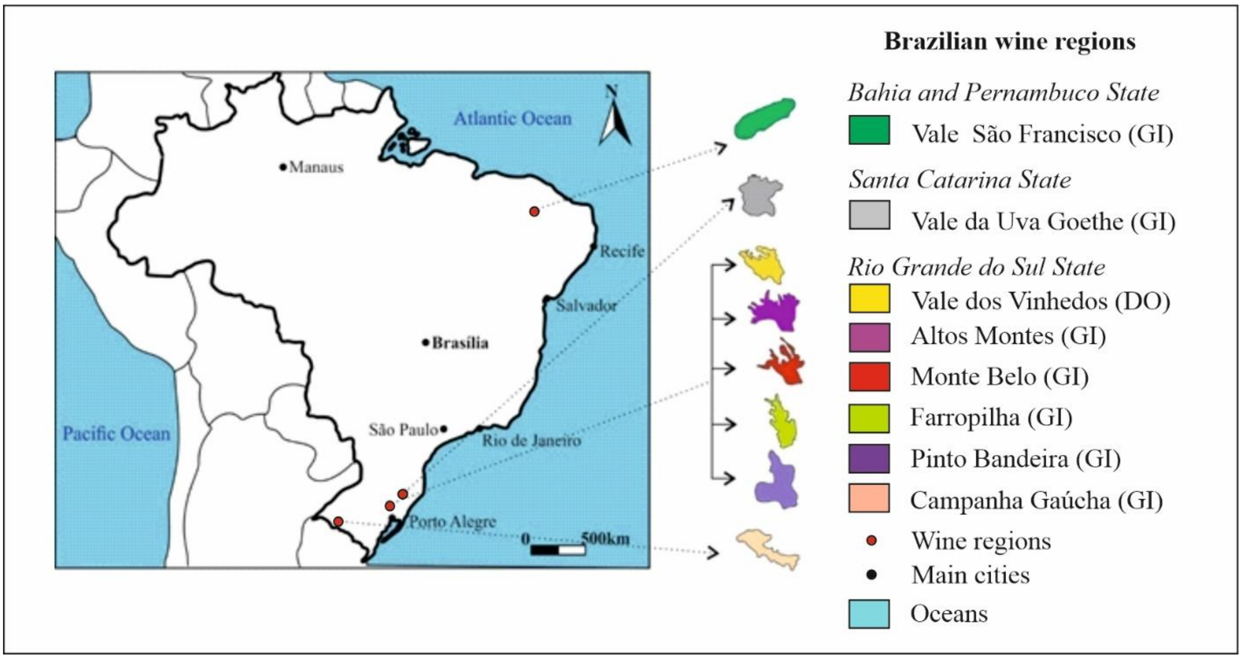


**Figure 4.1.** Map of Brazilian wine regions (modified from Tonietto et al, 2013**).**

The Vale dos Vinhedos region has a rugged topography (hilly to mountainous) and its vineyards are located at altitudes of 200 to 800 m. Soils are based on a substratum made of basaltic and rhyolitic rocks from the Paraná-Etendeka Province, a Large Igneous Province (LIP) covering an area of approximately 917,000 km$^2$ which developed from 134 to 119 Ma (Stewart et al., 1996). The range of $^{87}$Sr/$^{86}$Sr in the Paraná volcanic rocks ranges between 0.70600 and 0.72618 (Peate et al., 1992; Garland et al., 1995; Marques et al., 2006).

The aim of this study is to use the $^{87}Sr/^{86}Sr$ technique in order to perform the provenience study of Cabernet Sauvignon wine (2018 vintage) from Vale dos Vinhedos vineyards (Brazil). We compared the analytical results of soil, wine, and leaf samples to $^{87}Sr/^{86}Sr$ database from rocks that represent the substrate of its sampled vineyards.

## METHODOLOGY

The samples used for this study (i.e., grape, leaf, and labile soil) are from three different wine producers of the Vale dos Vinhedos (**Table 4.1**; **Figure 4.2**). Among the selected wineries, two are located on a rhyolitic substrate (Larentis and Don Laurindo) and one on a basaltic substrate (Barcarola).

Cabernet Sauvignon red grape samples were collected at the optimal maturity stage during the 2018 harvest. Approximately 150 grape bunches (with an average weigh of 300 g each) have been sampled per vine. All the collected grape samples were stored in plastic bags and immediately submitted to microvinification process.

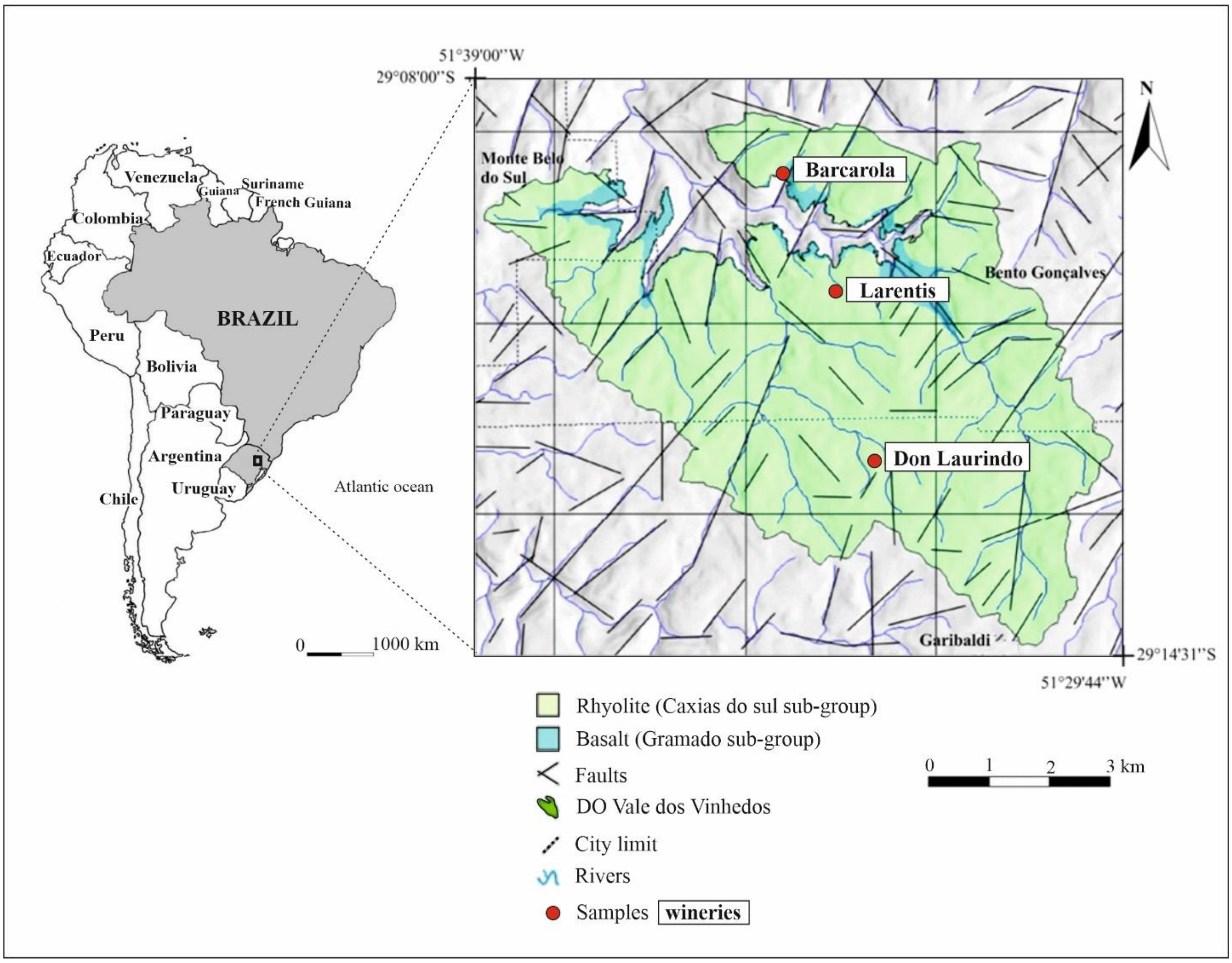


**Figure 4.2.** Geological sketch map of the Vale dos Vinhedos with sampling locations (modified from Tonietto et al, 2013).

The grapes were squeezed using a stainless-steel winepress then collected in a glass container with a capacity of 10 l and covered with a cotton stopper. After 30 days of fermentation, the microvinificated samples were covered with plastic stoppers and held at a temperature of 18 °C.

The organic matter fraction has been extracted from the soil samples by cation exchange chromatography using Ag50 X-8 resin in a 10 mL Bio-RadTM column. Detail procedure used to cation exchange chromatography is shown in ***$^{87}$Sr/$^{86}$Sr analyses of biological and geological samples section*** **(Chapter 3).**

A total of 100 g of leaves was collected from each of the investigated grapevines, then dried and frozen at -10 °C. Leaf samples were then thawed, placed in ceramic beakers, and dried in an oven through progressive heating at 200 °C (15 min), 400 °C (15 min), 600 °C (15 min), and 800 °C (8 h), followed by cooling (8 h). Once the drying procedure had been completed, $H_2O_2$ and 3N $HNO_3$ (at 85 °C) were added to each sample. Finally, samples have been dried again and dissolved in $H_2O_2$ and 3N $HNO_3$ (at 85 °C).

**Table 4.1.** Sampling data sheet for the investigated Brazilian vineyards.

| **Winery** | Barcarola | Larentis | Don Laurindo |
|---|---|---|---|
| **Coordinate** | 29°10'34"S; 51°34'08"E | 29°10'31"S; 51°33'54"E | 29°12'04"S; 51°33'16"E |
| **Altitude (m)** | 430 | 510 | 530 |
| **Date sampling** | 01/03/2018 | 01/03/2018 | 01/03/2018 |
| **Grape variety** | Cabernet Sauvignon | Cabernet Sauvignon | Cabernet Sauvignon |
| **Age of vine** | 1999 | 2000 | 2007 |
| **Wine-grape** | BA-U-01 | LA-U-01 | DL-U-01 |
| **Leave** | BA-F-01 | LA-F-01 | DL-F-01 |
| **Soil** | BA-S-01 | LA-S-01 | DL-S-01 |
| **Geology** | Basalt (Gramado sub-group) | Rhyolite (Caxias do Sul sub-group) | Rhyolite (Caxias do Sul sub-group) |

The soil samples were collected at sites close to the sampled vines (20 cm away from the root, approximately 2 kg each) using stainless steel collectors at a depth of 30 cm. All samples have been stocked in plastic bags and sampling positions have been carefully recorded by GPS coordinates.

First, soil samples have been dried at 60 °C (48 h) passed through a 2 mm sieve, hammered to reduce agglomeration, disintegrated, and homogenized in a porcelain mortar. Then, samples (2 g) were twice reacted with 15 ml of ammonium acetate ($NH_4CH_3CO_2$) for 6 hours at room temperature to extract labile soil fraction. Supernatants were passed through 0.45 µm polypropylene syringe filters, dried (at room temperature) and dissolved in 3N $HNO_3$ (at 85 °C).

The Sr fraction has been extracted, for all the different types of samples, by cation exchange chromatography using Eichrom Sr-spec resin (50-00 mesh) in a 1 mL Bio-RadTM column following the protocol described in ***$^{87}Sr/^{86}Sr$ analyses of biological and geological samples section* (Chapter 3).**

## GEOLOGICAL SETTING

Samples from Brazil have been collected in vines rooted on a substratum made of basaltic (Gramado sub-group) and rhyolitic rocks (Caxias do Sul sub-group) of the Paraná-Etendeka Igneous Province.

The Paraná-Etendeka is a Large Igneous Province (Coffin and Eldholm, 1992; Bryan and Ernst, 2008; Self et. al, 2008) covering 1,500,000 $km^2$, consisting of voluminous volcanic successions, 90% of which over the central-eastern sector of the South America continent (southern Brazil, eastern Paraguay, northwestern Uruguay, and northern Argentina; **Figure 4.3**), the remaining being found in Namibia, Africa (Cordani and Vandoros, 1967; Peate, 1997).

The Province is a succession of Cretacic volcanic tholeiitic basalts (90%), basaltic andesites (7%) and rhyolites and rhyodacites (3%; Bellieni et al, 1984; Piccirillo et al., 1988; Peate et al., 1992). Major intra-continental magmatism that occurred in the Paraná Basin (130-119 Ma) was developed from a fissural system related with the Tristan da Cunha Plume, emplacing lava flows, dikes and sills (Renner, 2010) over the Botucatú Formation (late Paleozoic to Jurassic continental aeolian red sandstones), then overlain by aeolian sandstones of the Bauru Group (Late Cretaceous).

The Paraná basaltic rocks have been grouped into six distinct magma types: Low-Ti (Gramado, Esmeralda, Ribeira sub-groups) and High-Ti (Urubicí, Pitanga, Paraná panema sub-groups; Peate et al., 2002). High-Ti rocks ($TiO_2$>2.75 wt.%) have low initial $^{87}Sr/^{86}Sr$ (0.70470 to 0.70650), whereas the low-Ti rocks ($TiO_2$<2.50 wt.%) have a wide range initial of $^{87}Sr/^{86}Sr$ (0.70470 to 0.71630) (Mantovani et al., 1985 a, b; Petrini et al., 1987; Piccirillo et al., 1987, 1989).

Rhyolitic magma types have been distinguished in various types based on incompatible trace element contents. The group with the lowest incompatible element contents is known as the Palmas-type, whereas the incompatible element richest group is called the Chapecó-type (Peate et al., 1992).

The Chapecó-type rhyolites have been further distinguished into three sub-groups, called Ourinhos ($^{87}Sr/^{86}Sr$= 0.70490-0.70764; northern Paraná state), Guarapuava ($^{87}Sr/^{86}Sr$= 0.70552-0.70604; central Paraná) and Sarusas (no $^{87}Sr/^{86}Sr$ information; northern Etendeka). Chapecó-type rhyolites from central Paraná have $^{87}Sr/^{86}Sr$ values similar to the high-Ti basaltic magma types ($^{87}Sr/^{86}Sr$ = 0.7056-0.7059). On the other hand, Palmas-type rhyolites show a wide compositional range, and were subdivided into three sub-groups named Santa Maria ($^{87}Sr/^{86}Sr$= 0.72166-0.72618), Anita Garibaldi ($^{87}Sr/^{86}Sr$= 0.71367-0.71465) and Caxias do Sul (0.71373-0.72049; Garland et al., 1995).

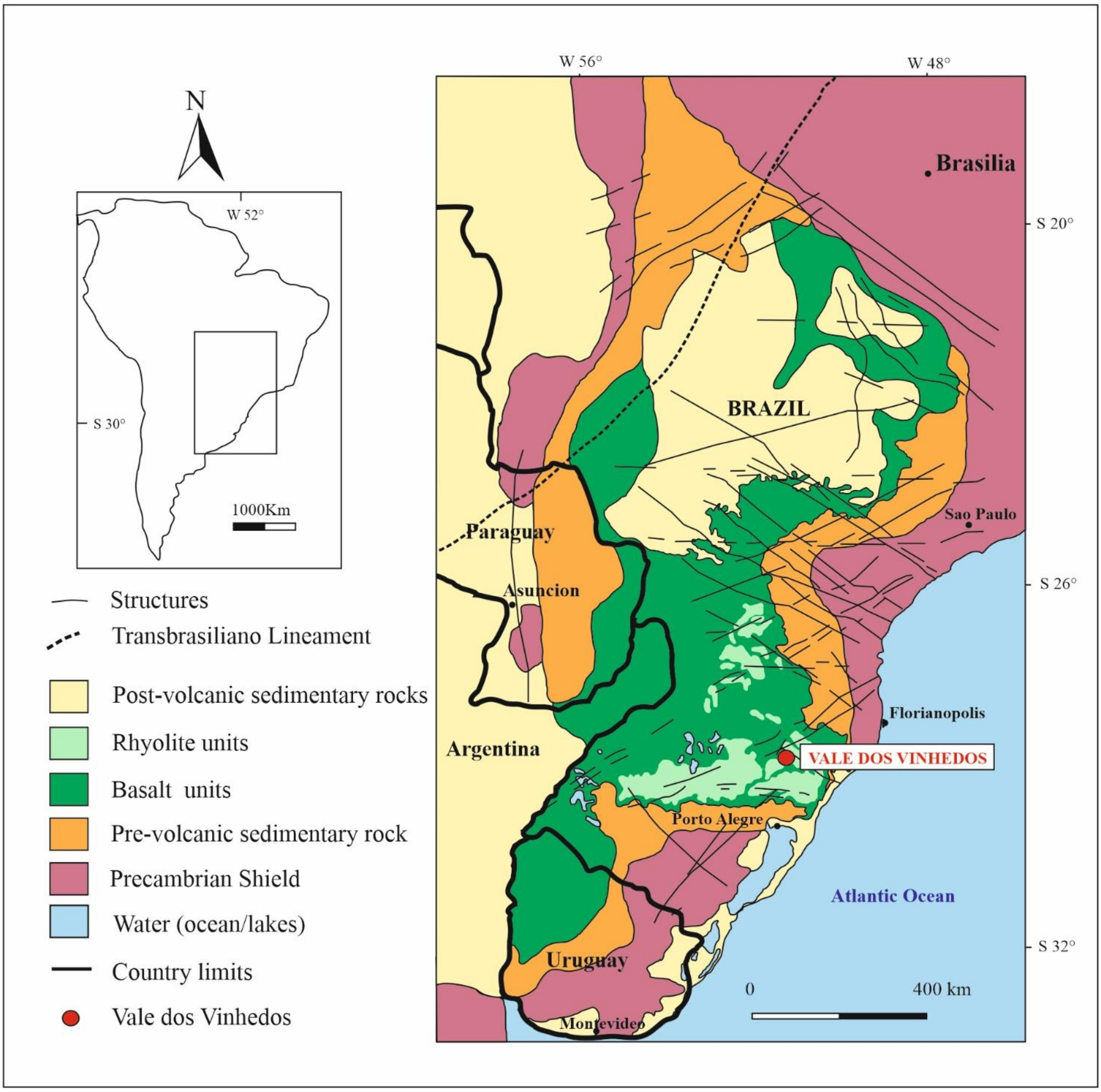


**Figure 4.3.** Geological map of the Paraná Igneous Province with location of the Vale dos Vinhedos area (modified after Renner, 2010).

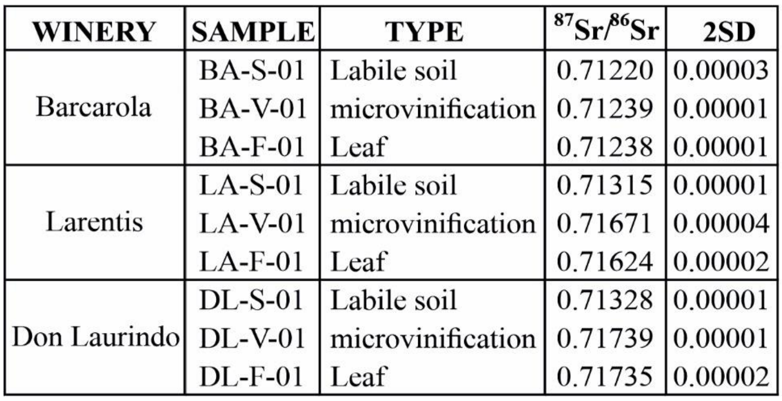
## RESULTS AND DISCUSSIONS

The results of $^{87}$Sr/$^{86}$Sr analyses for soil (labile fraction), microvinification and leaf samples from Brazil are reported in **Table 4.2**. The results revealed marked differences between the various types of samples (**Figure 4.4**).

The geomorphology of the Vale dos Vinhedos region consists of heavily dissected and fragmented levels with embedded valleys (Falcade and Mandelli, 1999). The soil samples are of volcanic origin (basaltic and rhyolite), with low pH and a sandy-clayey structure (Valduga, 2011).

In the study area, volcanic clasts are very abundant in the soils up to a depth of 100 cm, then they become much rarer in the deeper soil horizons (Flores et al., 2012). In the Barcarola vineyards soil have a reddish color, small and medium sub-angular blocks, sandy-clayey structure and are plastic and sticky. The soils of the Larentis and Don Laurindo vineyards have a brown color, small and medium subangular blocks, sandy-clayey structure, slightly hard, firm, plastic, and sticky.

**Table 4.2.** Results (with standard deviation values, 2SD) of the $^{87}Sr/^{86}Sr$ analyses of the soil (labile fraction), microvinification, and leaf samples from the investigated Brazilian vineyards.



| WINERY | SAMPLE | TYPE | $^{87}Sr/^{86}Sr$ | 2SD |
|---|---|---|---|---|
| Barcarola | BA-S-01 | Labile soil | 0.71220 | 0.00003 |
| | BA-V-01 | microvinification | 0.71239 | 0.00001 |
| | BA-F-01 | Leaf | 0.71238 | 0.00001 |
| Larentis | LA-S-01 | Labile soil | 0.71315 | 0.00001 |
| | LA-V-01 | microvinification | 0.71671 | 0.00004 |
| | LA-F-01 | Leaf | 0.71624 | 0.00002 |
| Don Laurindo | DL-S-01 | Labile soil | 0.71328 | 0.00001 |
| | DL-V-01 | microvinification | 0.71739 | 0.00001 |
| | DL-F-01 | Leaf | 0.71735 | 0.00002 |

The $^{87}Sr/^{86}Sr$ for labile soil samples from Larentis and Don Laurindo vineyards (both with a rhyolitic substratum) range between 0.71315 and 0.71328, being higher than the labile soil sample from the Barcarola vineyard, rooted on a basaltic substratum, with value of 0.71220.

The $^{87}Sr/^{86}Sr$ values for microvinification and leaf samples from the rhyolitic vineyards exhibit significantly higher values (0.71624 to 0.71739) when compared to their soils. On the other hand, no significant differences have been observed between $^{87}Sr/^{86}Sr$ values for microvinification, leaf and labile soil samples from the Barcarola basaltic vineyard (0.71239, 0.71238, 0.71220) and those for the substratum rocks (**Figure 4.5**).

A reasonable explanation for mismatches observed in the Larentis and Don Laurindo samples may be the external addition of strontium in the soil-plant chain.

As already observed in the case of the investigated Italian vineyards, among the factors that may cause a change in the Sr isotopic ration of grapes and leaves is the use of copper-based fungicides, widely applied for controlling vine diseases. Various types of fungicides are widely applied to grapes and leaves in the Vale dos Vinhedos vineyards, including sulfur powder, lime sulfur, copper sulfate, lime Bordeaux mixture, copper hydroxide, cuprous oxide, etc.

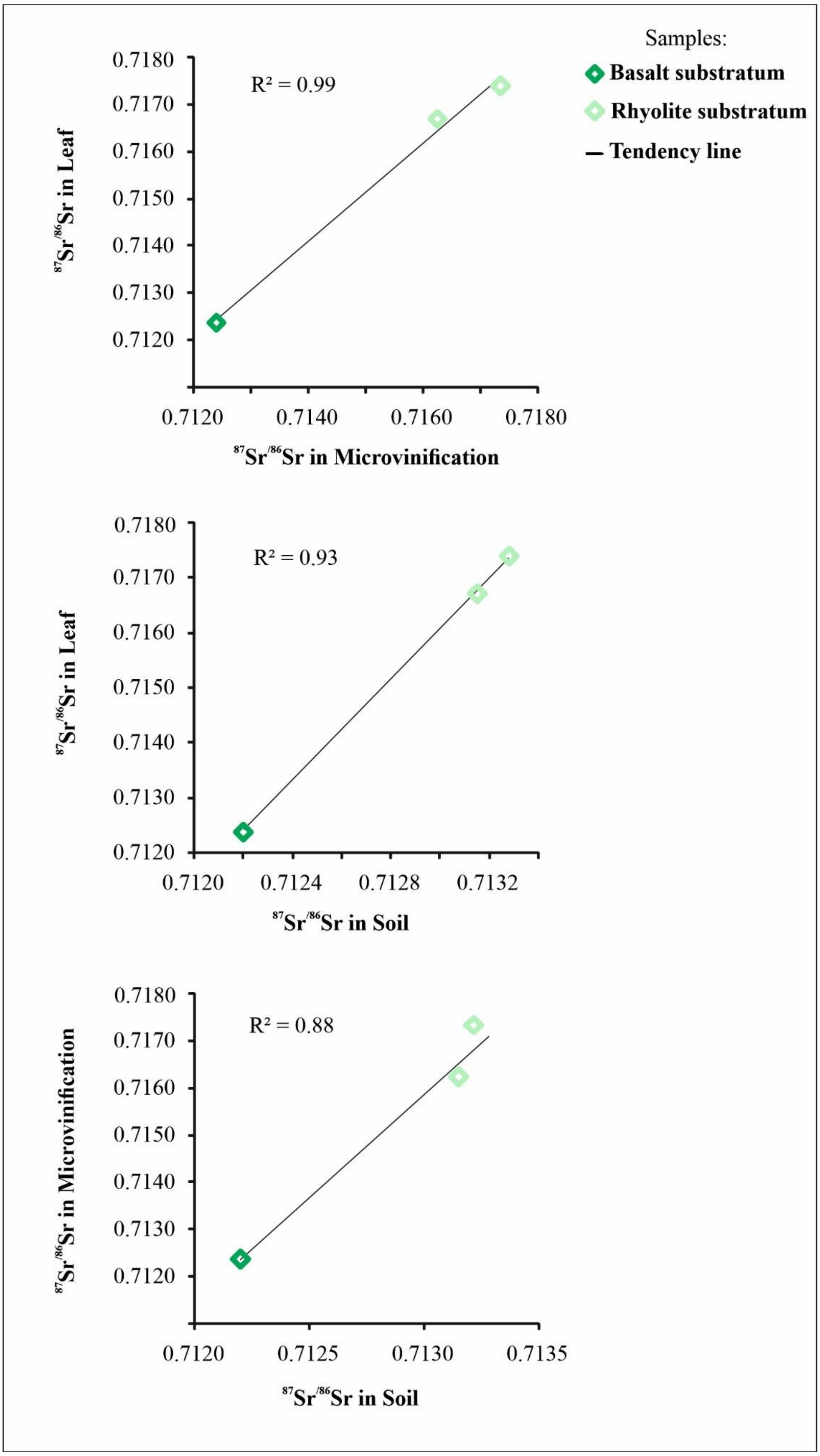


**Figure 4.4.** Binary diagrams comparing $^{87}Sr/^{86}Sr$ values in wine and leaf samples with respective soil samples (basalt and rhyolite substratum) from the Vale dos Vinhedos.

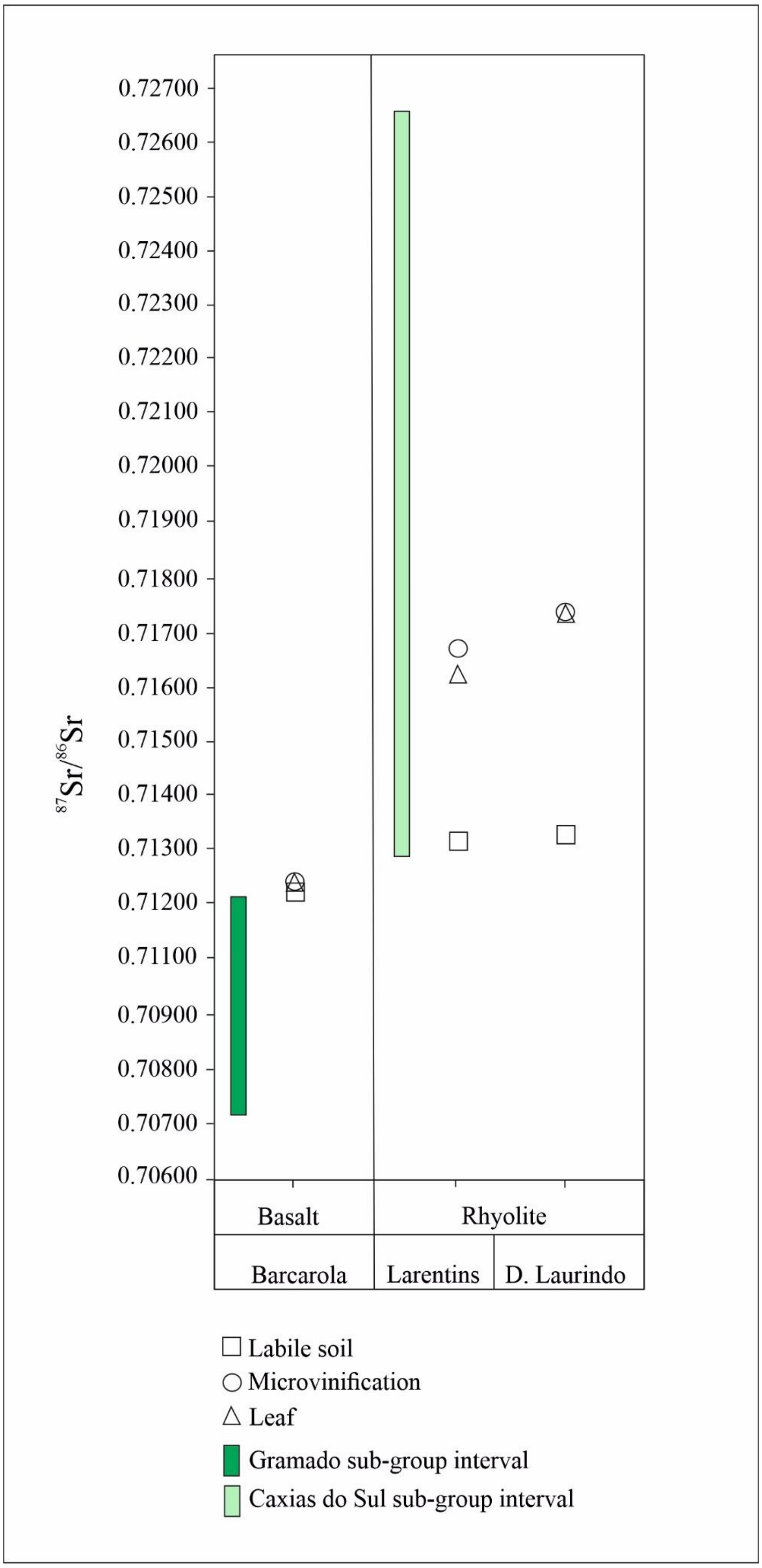


**Figure 4.5**. Distribution of $^{87}Sr/^{86}Sr$ values in microvinification, leaf and soil samples. Rock database is from Garland et al. (1995) and Marques et al. (2006).

A comparison between the values of $^{87}Sr/^{86}Sr$ of the rocks from the three vineyards in relation to the obtained results is shown in **Figure 4.5.** The isotopic composition of these rocks shows a wide variation between 0.71373 and 0.72643 (Caxias do sul sub-group; Garland et al., 1995) and 0.70780 to 0.71226 (Gramado sub-group; Marques et al., 2006) with a large overlap, showing that the technique is effective for the Sr isotope characterization in vineyards from the Vale dos Vinhedos.

In **Figure 4.6** the results for the Vale dos Vinhedos wine samples are compared with data for volcanic wines from Chile, Portugal, U.S.A., and Italy. The geological substratum from Vale dos Vinhedos vineyards is made up by old rocks (134 to 119 Ma; Bruckmann et al., 2014) with variable Rb/Sr, and hence different time-integrated $^{87}Sr/^{86}Sr$. The high values of $^{87}Sr/^{86}Sr$ in Brazilian wines can be explained by the fact that older rocks have higher Sr isotope ratio, consequently, wines from these old substrata may be distinguished from wines from younger volcanic terrains. The results of this study show that Brazilian wines have higher concentrations of $^{87}Sr/^{86}Sr$ showing an effective technique such as fingerprint of Brazilian wines compared to other wines from volcanic terrains in the world.

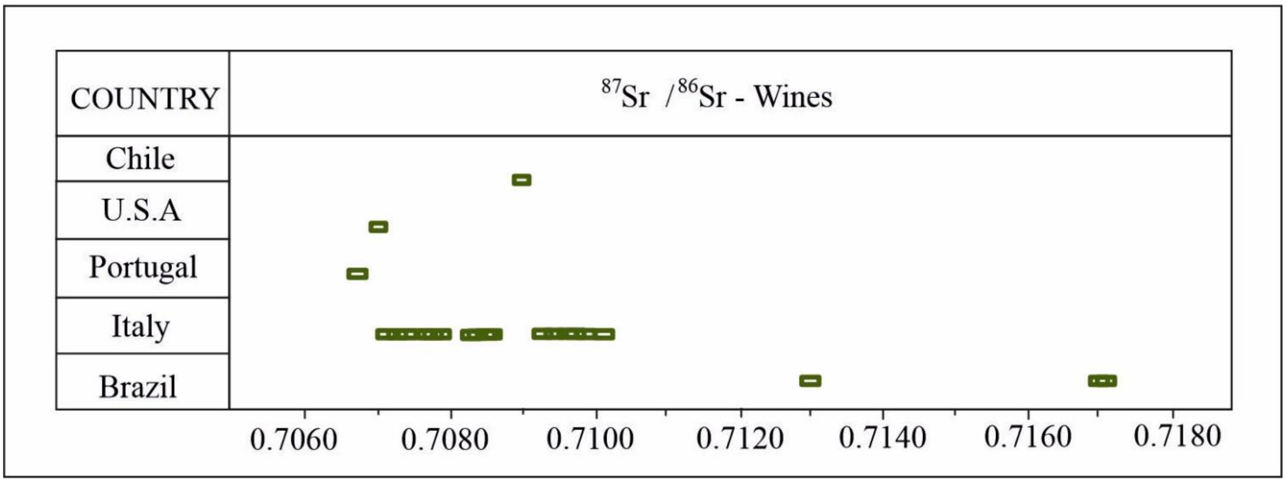


**Figure 4.6**. Distribution of $^{87}Sr/^{86}Sr$ for wines from worldwide volcanic vineyards (data sources: Chile, USA, Portugal: Barbaste et al. 2001; Italy: Marchionni et al. 2013; Mercurio et al., 2015; Braschi et al., 2018).

# Chapter 5 – CONCLUSIONS

In the present study, as a first step, the available $^{87}Sr/^{86}Sr$ dataset from published studies dedicated to implement this approach to wine authentication has been reviewed. Among the different parameters studied the ones that may control the wine $^{87}Sr/^{86}Sr$ signature were discussed, including geology, soil fraction, colour (i.e., white, and red), vintage, winemaking, and agriculture processes. All studies demonstrate that the $^{87}Sr/^{86}Sr$ of a wine derives from its vineyard pedogenetic substratum, incorporating its geological heterogeneities. Moreover, its Sr isotope signature is independent of the winemaking process (Marchionni et al., 2016; Petrini et al., 2015; Tescione et al., 2015), vintage (Durante et al., 2015; Marchionni et al., 2013, 2016; Mercurio et al., 2014; Petrini et al., 2015) and grape variety (Boari at al., 2008, Braschi et al., 2018). Results showed that the Sr isotope approach, as a single proxy, is a reliable tool to characterize the region of production at a rather local scale (i.e., regional, national) but appears more limited when trying to implement it at a larger scale. This approach must be carried out using a detailed protocol, precise instrumentation (TIMS, MC-ICP-MS or SF-MC-ICP-MS but not TQ-MS) and requires a good knowledge of the geological settings underlying the studied vineyards.

The presented new results allow to conclude that $^{87}Sr/^{86}Sr$ may be efficiently used for distinguishing volcanic wine-producing regions in South Italy, i.e., as a tracer for the geological origin of wines. A clearer discrimination of geographical origin was obtained in volcanic wines which makes it is possible to separate into 3 different groups according to Sr isotope ranges: Ponza and Ventotene island wines (group 1); Somma-Vesuvio wines (group 2) and Salina Island, Mount Etna and Pantelleria Island wines (group 3).

The $^{87}Sr/^{86}Sr$ values obtained for the investigated wine and soil samples from Brazil have a limited value as a provenance indicator since the analytical results of microvinification and leaves showed a significant difference in relation to the respective soils in rhyolitic terrain. On the other side, wines from basaltic substratum (Barcarola winery) show a good correspondence between geological and biological $^{87}Sr/^{86}Sr$ values. Therefore, more studies are necessary to test the reliability of this method in the Vale dos Vinhedos area.

However, the wines produced in South Brazil in comparison to the wines from volcanic terrains described by literature show that Brazilian wines can be differentiated from Chilean, American, Portuguese, and Italian wines due to the higher isotopic concentration of $^{87}Sr/^{86}Sr$ (**Figure 5.1**) coming from vineyards positioned in old rocks.

Partial overlaps can be observed with Chilean, American, Portuguese wine results when compared to Italian wines. The large amount of $^{87}Sr/^{86}Sr$ data available in Italian volcanic wines show a clear zonation, with a decrease in isotopic values of Sr, from north to south Italy (**Figure 5.1**), accompanying the isotopic zoning of the volcanic rocks described previously.

The new results obtained in this study referring to the vineyards of Brazil and Italy show that the technique is more efficient when the soil is studied in detail through a soil profile, using labile fraction, as was done at Somma-Vesuvio sampling site. This protocol allows a better understanding of the position of the grapevine root in relation to the sampled soil horizon, and consequently have a better correlation in the results.

Finally, considering its overall efficiency, the $^{87}Sr/^{86}Sr$ isotope ratio demonstrated its reliability as a tool for controlling wine authentication and thus it should be adopted by international wine regulatory organizations as a new application model for traceability.

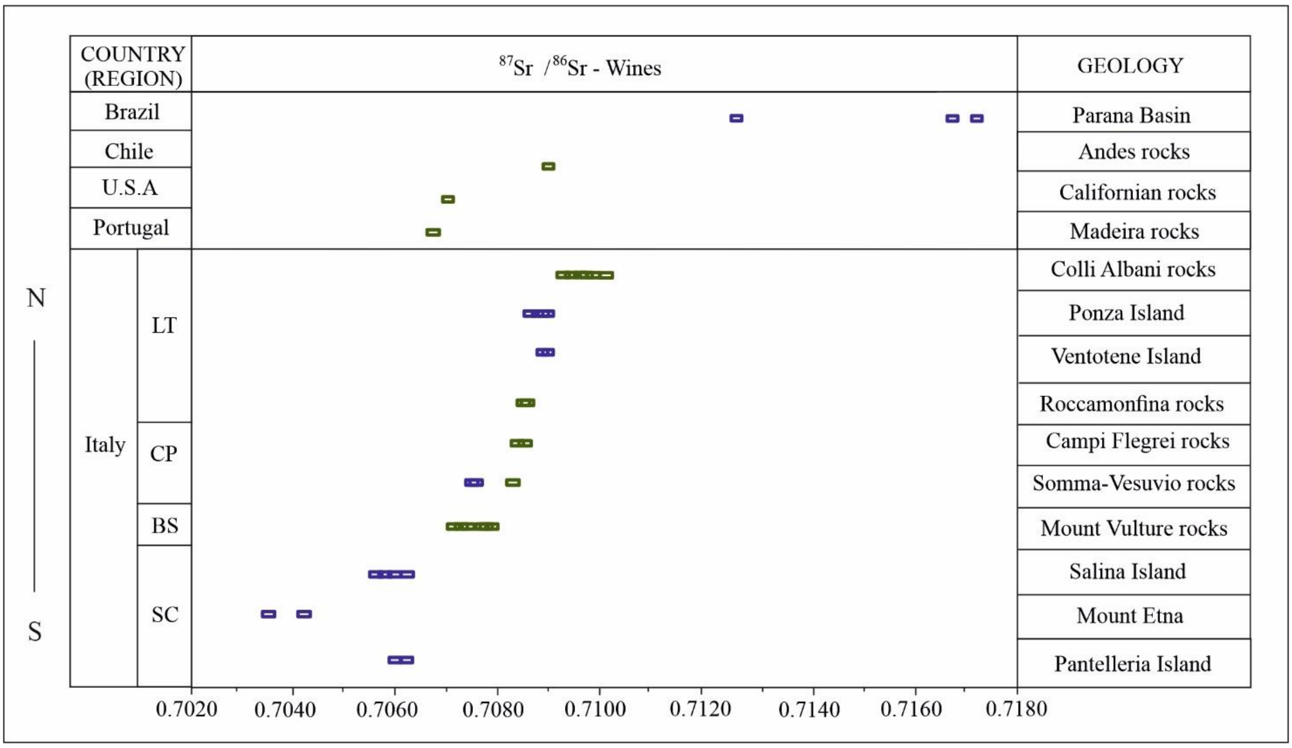


**Figure 5.1**. Distribution of $^{87}Sr\ /^{86}Sr$ from worldwide volcanic wines (data source in green: Chile, U.S.A., Portugal: Barbaste et al. 2001; Italy: Marchionni et al. 2013; Mercurio et al., 2015; Braschi et al., 2018; data source in blue: present work). Italian wines are separated by region: LT=Latium, CP=Campania, BS=Basilicata, SC= Sicily.

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