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$^{87}Sr/^{86}Sr$ isotopes in grapes of different cultivars: a geochemical tool for geographic traceability of agriculture products

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Highlights

- $^{87}Sr/^{86}Sr$ in fresh grapes from different genotype vines (cultivar)
- $^{87}Sr/^{86}Sr$ differences between white and red grapes and among harvest years
- $^{87}Sr/^{86}Sr$ in bioavailable fraction of soils, soils, and rocks beneath vineyards of production
- Geologic heritage in food stuff as a fingerprint for geographic traceability

Abstract

$^{87}Sr/^{86}Sr$ was determined on fresh red and white grapes, soils and rocks from three selected vineyards to verify the isotopic relationships between the fruit of the vine and geologic substrata of vineyards. $^{87}Sr/^{86}Sr$ were determined on sampled grapes of four different harvest years and different grape varieties, on bioavailable fraction of soils, on whole soils, and on bedrocks from the geo-pedological substratum of the vineyards. The vineyards chosen for the experimental works belong to an organic farming winery and thus cultivation procedures were strictly controlled.

Grapes were sampled during the harvests of four different but consecutive years with $^{87}Sr/^{86}Sr$ that does not change reflecting the values of the soil bioavailable fraction. No variations among grapes from different vine cultivars were observed. A strict isotope relationship with soil bio-

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available fraction was observed. These findings demonstrate the reliability of $^{87}Sr/^{86}Sr$, even at a very small scale, for food products geographic origin assessment.

Key words: $^{87}Sr/^{86}Sr$ of fresh grapes, white and red grapes, geographic traceability, geologic and pedologic fingerprints, Pitigliano area, Vulsini Mountains, Central Italy.

1. Introduction

The increasing demand of high quality food products promoted the development of rigid regulations for certification of authenticity and protection from frauds (e.g., http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32002R0178). This is leading to an increasing request of suitable scientific protocols able to confirm the authenticity of food products by tracking their geographical origin. These studies aim to find scientific parameters inherited by the area of production of the agricultural products, which may be considered a fingerprint for geographic traceability of food (Kelly, Heaton & Hoogewerff, 2005).

In the last decades, geochemistry of light (H, C, O, N, B) and heavy (Sr, Pb) isotopes, sometimes combined with multi-elemental analysis and chemometrics, have been applied to the authentication and the tracking of geographic provenance of foods (e.g., Evans, Pashley, Richards, Brereton & Knowles, 2015; Medini, Janin, Verdoux & Techer, 2015; Techer, Lancelot, Descroix, Guyot, 2011) and processed beverages such as wine, one of the most investigated product derived from fermentation of fresh fruit (e.g., Di Paola-Naranjo et al., 2011; Durante et al., 2013, 2016; Petrini, Sansone, Slejko, Buccianti, Marcuzzo & Tomasi, 2015; Rummel, Hölzl, Horn, Roßmann & Schlicht, 2010; Vinciguerra, Stevenson, Pedneault, Poirier, Hélie & Widory, 2016).

A relevant aspect in isotope geochemistry studies is the variation of stable isotopic composition of light elements by climatic variation (e.g., Christoph, Roßmann, & Voerkelius, 2003; Christoph et al., 2004). On the other hand, isotopic composition of radiogenic heavy elements, such as Sr and Pb, show the advantage of correlating directly with the geological and pedological substrata with no effects related with climatic conditions, which allows to identify possible unambiguous association between the agricultural product and the geological setting of the production area (e.g., Horn, Schaaf, Holbach, Hölzl & Eschnauer, 1993; Marchionni et al., 2013; Tommasini et al., 2018, and references therein).

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Several authors, however, showed that Sr and Pb uptaken from soil with nutrients is differentially enriched in different parts of the vine (e.g., roots, branches, leaves, grapes; Amorós Ortiz-Villajos et al., 2017; Bravo et al., 2017; Censi, Saiano, Pisciotta & Tuzzolino, 2014; Tommasini, Davies & Elliott, 2000).

The experimental studies on the distribution of $^{87}Sr/^{86}Sr$ in wines available in the scientific literature focused mainly on the evaluation of the consistency of the Sr-isotopic value through the winemaking process from the soil to the wine (e.g., Almeida & Vasconcelos, 2004; Durante et al., 2013, 2016; Marchionni et al. 2016). These papers, however, did not check in detail the Sr-isotopic traceability of grapes from different vines, in comparison with the Sr-isotopic variability of the substrata of the vineyards (e.g., soils and rocks). Indeed, grapes are not only important for the wine consumers, but also for the consumers of the fresh fruit itself. Presently, there are no detailed Sr-isotopic studies on grapes in general, notwithstanding grape production represents the world's most important fresh fruit crop with the highest total value of production (FAO-OIV Focus, 2016), with half used for wine production, and the greatest quantity of the remaining part destined to the global market to be consumed as fresh fruit.

In this paper we report the first detailed research on the $^{87}Sr/^{86}Sr$ distribution in grapes from different cultivars from three different geologically well-constrained vineyards. This experiment is an extensive grape inter-varietal and site-specific study designed for evaluating the possible contribution to the $^{87}Sr/^{86}Sr$ of grapes of the cultivar versus the different geology/pedology of the vineyards substrata. Samples of grapes from different cultivars of four different harvest years and samples of soils and bedrocks were analysed for $^{87}Sr/^{86}Sr$ isotopic composition to shed some lights on the following issues: i) the consistency of $^{87}Sr/^{86}Sr$ isotopic ratio in different harvest years; ii) the influence of $^{87}Sr/^{86}Sr$ in grapes from vineyards with different geological substrata; iii) the possible influence of different cultivars on the $^{87}Sr/^{86}Sr$ composition of grapes. The findings of this study will bring further insights in the issue of food geographical traceability using radiogenic isotope of heavy elements of geological interest.

2. Materials and Methods

In the present pilot study a restricted area with vineyards characterised by young volcanic rocks with different $^{87}Sr/^{86}Sr$ was selected to minimise the effects of age variability among rocks of different ages and ^{87}Sr ingrowth due to time integration (Faure, 1986). In addition, because the

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pyroclastic volcanic rocks of the study area are rich in the glass fraction rather than in the crystalline one (Conticelli, Francalanci, Manetti, & Peccerillo, 1987) the possible $^{87}Sr/^{86}Sr$ bias between the geological substratum, the soil, and its bioavailable fraction is minimised.

The grape samples collected for this study are from a single winery in southern Tuscany, Central Italy. The *Sassotondo* farm, managed as a high quality organic farm, is located between the small towns of Pitigliano and Sorano on 72 hectares, 10 of which are destined to the vine (*Vitis vinifera* L.) cultivation (ESM-Fig. 1, Electronic Supplementary Materials 1). The vineyards produce both red grape (*Ciliegiolo*, *Sangiovese*, *Merlot*, and *Teroldego* cultivars) and white grape (*Trebbiano*, *Greco*, and *Sauvignon* cultivars). The trial was carried out in three different vineyards: *Pian de' Conati*, *Piana San Lorenzo*, *Crucignano*, which are located in the NW and in the S, and SE of Pitigliano, respectively (ESM-Fig. 1, Electronic Supplementary Materials 1). Each vineyard is characterised by different geological substratum.

The Pitigliano area is underlain by volcanic rocks belonging to the Latera volcano (Vulsinian volcanic district), which is made up by a succession of seven ignimbrites (e.g., Conticelli, Francalanci, Manetti, & Peccerillo, 1987; Conticelli, Francalanci, & Santo, 1991) each of them characterised by different Sr-isotopic compositions (e.g., Conticelli, Avanzinelli, Ammannati & Casalini, 2015).

2.1 Sampling

For this study, we collected 46 samples, 29 of red (14 *Ciliegiolo*, 4 *Sangiovese*, 4 *Merlot*, and 7 *Teroldego* cultivars) and 17 of white grapes (6 *Trebbiano*, 6 *Greco*, and 5 *Sauvignon* cultivars) varieties. They have been taken within four harvest years from 2013 to 2016, and collected in three different vineyards, each of them characterised by different bedrock and soil (a = *Pian de' Conati*, b = *Piana di San Lorenzo*, c = *Crucignano* vineyards; ESM-Fig. 1, Electronic Supplementary Materials 1). Each sample consists of a bunch of grapes picked from a single plant of the vineyard. Grape samples of the same cultivar and harvest year were collected from different plants of the same vineyard.

We collected whole soil samples from *Pian de' Conati* (4 samples), *Piana di San Lorenzo* (2 samples), and *Crucignano* (1 sample) at a mean depth of 20-30 cm (Marchionni et al., 2016) and of a unitary weight of about 500 g. Among bedrocks (Vezzoli et al., 1987), two samples are from *Pian de' Conati* (*Grotte di Castro Formation*), one sample is from *Piana di San Lorenzo* (*Pitigliano*

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formation), and one sample from *Crucignano* (*Pitigliano formation*) vineyards (ESM-Fig. 1, Electronic Supplementary Materials 1). In addition $^{87}Sr/^{86}Sr$ data from scientific literature and from an unpublished Sr-isotopic Authors' database are also used for investigating the relationships between grapes and vineyard of provenance (Conticelli et al., 2015).

A detailed scheme of the sample strategy adopted is reported in the Electronic Supplementary Material 1 (ESM-Tab. 1).

2.2 Sample preparation and analysis

All the collected samples have been prepared and measured in the Radiogenic Isotopes Lab of the Earth Science Department at the *Università degli Studi di Firenze*. The preparation protocols were different depending on the kind of material (grape, soil, rock, etc.); the treatment and preparation of the samples followed the procedure reported by Marchionni et al. (2016) and were performed in a clean chemistry laboratory "Class 1000" environment. High purity chemical reagents and Milli-Q® water were used during sample treatment to reduce the level of contamination.

Grape samples were first washed and rinsed with Milli-Q® water for three times to be sure to have not any dust during further sample preparation. Then grapes were crushed with skin and seeds. A fraction of the collected juice was treated as follow: 5 ml were evaporated to dryness in a PFA beaker on a hot plate at 90°C, then 3 ml of H_2O_2 30 vol.% UpA were added to the dried sample and left overnight at room temperature and later evaporated to dryness at 80°C. This step of the digestion procedure was repeated twice. To assure a complete digestion of the organic matter 2 ml of HNO_3 65 vol.% were added, the beaker was covered and left overnight on the hot plate at 170°C and evaporated to dryness. This step was repeated twice, too.

Soil samples underwent two different treatments: a first portion of the sample was prepared following the procedure for rocks described below to determine the isotopic composition of the bulk soil; the remaining part of the sample underwent to an extraction treatment using Milli-Q® water and Unibest® resin capsules (Dobermann et al., 1994) in order to determine the chemical composition of bioavailable fraction in soil solution. Unibest® resins are able to simulate the mechanism of nutrient uptake by the plant roots from soil (Skogley & Dobermann, 1996). The Unibest® resin capsule was immerged in a muddy mixture of 200 g of soil, without any pre-treatment, and Milli-Q® water for 10 days; subsequently the Unibest® resin capsules was

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extracted, rinsed, to remove any residues, treated three times with 20 ml of 2N HCl in a PFA beaker, dried to get the accumulated ions from the soil solution, and then dissolved in 0.3 ml 3N HNO_3 for Sr chromatography (Marchionni et al., 2016).

Rock samples were first mechanically crushed and then pulverised with an agate ball mill; an amount of 50 mg of homogenised sample were digested in a solution of 1:4 HNO_3 + HF at 140°C for 1-2 days, then they were brought to dryness. Two further additions of HNO_3 and dissolution in 6 N HCl at 120°C and eventually evaporation to dryness followed.

All the digested samples underwent to Sr-purification by cation exchange chromatography using Sr-Spec® resins in 140 µl pure quartz micro-columns with 3N HNO_3 as eluent and Milli-Q® water to collect Sr. Sr purification was performed using a cation exchange chromatography in a “Class 100” vertical HEPA-filtered laminar flow hood and high-purity chemical reagents (Avanzinelli et al., 2005). The extracted Sr (about 100-200 ng) was dissolved in 2N HNO_3 and loaded on single Re filaments using 1 µl of $TaCl_5$ and 1 µl of H_3PO_5 as activator and fractionation suppressor, respectively.

Sr-isotope abundance (^{88}Sr, ^{87}Sr, ^{86}Sr, ^{84}Sr) was measured by thermal ionisation mass-spectrometer (TIMS), in dynamic mode, using a Thermo FinniganTM Triton-Ti® magnetic sector field equipped with nine moveable collectors (Avanzinelli et al., 2005). Each Sr-isotope ratio reported in Table 1a is the average of about 120 sets of cycles, with each cycle itself representing the average of three measurements performed during triple-jumping dynamic measurement. The 120 sets of cycles were collected in 6 blocks, each consisting of 20 cycles with 8 seconds integration time. An idle time of 3 seconds was set before the start of the collection after each jump, to eliminate possible memory effect due to the decay of the signal in the faraday cups.

Procedural blank was <200 pg resulting in negligible sample correction. The external precision of NIST SRM987 international reference sample for the time of this study was ^{87}Sr/^{86}Sr = 0.710251 ±0.000010 (2σ, n = 20), while the long-term mean value was ^{87}Sr/^{86}Sr = 0.710248 ±0.000016 (2σ, n = 173, equivalent to an error of 23 ppm). The within run precision (i.e., $2\sigma_m$: internal precision) of ^{87}Sr/^{86}Sr measurements has been typically ≤10 ppm.

The reproducibility of the analytical method we used in this study is reported in Marchionni et al. (2013), where different aliquots (n = 31) of the same sample of wine (i.e., a similar organic matrix with respect to the samples of this study) were processed and measured for ^{87}Sr/^{86}Sr

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composition, yielding a 2σ = ± 0.000017 (i.e., 23 ppm), which is consistent with that of the international reference standard.

3. Results and Discussion

The values of $^{87}Sr/^{86}Sr$ in fresh grapes, soil bioavailable fractions, bulk soils, and whole rocks are reported in Tables 1a and 1b. The results for each cycle of measurement performed are reported as Electronic Supplementary Material (ESM-Tab. 2, Electronic Supplementary Materials 2).

3.1 The $^{87}Sr/^{86}Sr$ does not vary with time

In order to evaluate the consistency of the $^{87}Sr/^{86}Sr$ values over different years of harvest, first of all we tested the reproducibility of the isotopic measurements on multiple sampling of bunch grapes from the same cultivar (6 grapes of *Ciliegiolo* and 4 of *Teroldego*), of the same harvest year (i.e., 2015), from different sampling points of the same vineyard (i.e., *Pian de' Conati*). The results are reported in figure 1, showing a significant constancy of $^{87}Sr/^{86}Sr$ values in both cases under consideration. This is strongly suggestive that each bunch of grapes collected is representative of the whole vineyard and cultivar of provenance. Thus, in absence of any external cause (e.g., soil nourishment, additive addition to soil, use of chemical improver, etc.; Marchionni et al. 2016), the constancy and conservation of the isotopic composition over different harvest years is expected.

In figure 2 the $^{87}Sr/^{86}Sr$ of the grapes of the most representative cultivars sampled in the different years of harvesting and from the *Pian de' Conati* vineyard are reported. In these plots we observe for the majority of samples a fairly good conservation of the Sr-isotopic composition through the different harvest years, with values within the measurement uncertainty level (1σ). A first exception is shown by the *Greco* and *Sauvignon* grapes of the 2013 harvest year, which display $^{87}Sr/^{86}Sr$ values of 0.709749 ± 0.000036 (1σ) and 0.709738 ± 0.000064 (1σ), which are slightly off with respect to the Sr-isotopic composition of the 2014-2016 period. This discrepancy has no apparent explanations, neither analytical nor related to the farming practice. On the other hand, the *Teroldego* grapes display a perfect conservation of the $^{87}Sr/^{86}Sr$ values through the harvest period considered.

A further notable variation is observed for *Ciliegiolo* grapes (Fig. 2) with samples from *Pian de' Conati* vineyard showing consistent higher $^{87}Sr/^{86}Sr$ values [average value 0.709957 ± 0.000046

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(1σ)] than samples from *San Lorenzo* vineyard [average value 0.708986 ± 0.000121 (1σ)]. This bias depends upon the different $^{87}Sr/^{86}Sr$ shown by the substrata of the two vineyards (ESM-Fig. 2, Electronic Supplementary Materials 1) as discussed in the next paragraph.

In summary, excluding the *Greco* and *Sauvignon* grape samples harvested in the 2013, which display lower $^{87}Sr/^{86}Sr$ values than other grapes from the same vineyard, the grape samples collected for this study display no significant $^{87}Sr/^{86}Sr$ variations through time (Fig. 2), as shown in previous experimental studies for musts and wines of different vintage years (Marchionni et al., 2013, 2016). On the other hand, systematic large $^{87}Sr/^{86}Sr$ variations are observed among grapes from vineyards farmed on geological substrata with different chemical composition and $^{87}Sr/^{86}Sr$ signatures.

3.2 The $^{87}Sr/^{86}Sr$ of bioavailable soil fraction, soil, and bedrocks

Marchionni et al. (2013) have already shown the strong correlation existing between the $^{87}Sr/^{86}Sr$ of bottled red wines and the $^{87}Sr/^{86}Sr$ of the bedrocks of the area of production, although a discrepancy might be observed between the $^{87}Sr/^{86}Sr$ of the wine and that of the geological substratum of the area of production. This bias increases passing from wine production areas characterised by a substratum made of young volcanic rocks to wine production area characterised by older either sedimentary or granitic rocks (Marchionni et al., 2013). Other studies have also shown that the $^{87}Sr/^{86}Sr$ of the bioavailable fraction is a better proxy of the *terroir* of the area of provenance of the food product from agriculture (e.g., Tescione, Marchionni, Mattei, Tassi, Romano, Conticelli, 2015; Vinciguerra, Stevenson, Pedneault, Poirier, Hélie, Widory, 2015, 2016; Petrini et al., 2015; Durante et al., 2016; Marchionni et al., 2016).

These findings are confirmed by our data when the $^{87}Sr/^{86}Sr$ of bedrocks are compared with whole soils and soil bioavailable fraction of the three vineyards taken under consideration in this study (Table 2 and ESM-Fig. 2; Electronic Supplementary Materials 1). Indeed, the *Pian de' Conati* vineyard shows slight differences among the mean values of $^{87}Sr/^{86}Sr$ of the bedrock [*Grotte di Castro Formation* = 0.710213 ± 0.000037 (1σ)], the total fraction of whole soil [0.710114 ± 0.000054 (1σ)], and its bioavailable fraction [0.710077 ± 0.000049 (1σ)]. On the other hand, in the *Piana San Lorenzo* vineyard the $^{87}Sr/^{86}Sr$ values of the three components of the substratum are slightly to significantly lower than those observed for the *Pian de' Conati* vineyard. In particular large isotopic differences among geologic bedrock [*Pitigliano Formation* = 0.710052 ± 0.000032

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(1σ)], whole soil total fraction [0.709595 ± 0.000225 (1σ)], and its bioavailable fraction [0.708948 ± 0.000091 (1σ)] are observed. Similarly, in the *Crucignano* vineyard the large difference between the whole soil [0.710265 ± 0.000041 (1σ)] and its bioavailable fraction [0.709642 ± 0.000117 (1σ)] does also occur (Table 2 and ESM-Fig. 2; Electronic Supplementary Materials 1). .

The different amount of $^{87}Sr/^{86}Sr$ depletion from bedrock to soil and to bioavailable fraction in the three different areas can be related to the different nature of soils outcropping in the area (Pedological Map of the Tuscany region: http://www.lamma.rete.toscana.it/territorio/cartografia-tematica/pedologia/carta-dei-suoli). Different soils may release the bioavailable fraction to the plants due to their different texture and inorganic composition, leading to different relationships among $^{87}Sr/^{86}Sr$ values in bedrock, soil, vine, and wine (e.g., Marchionni et al., 2013; Petrini et al., 2015). Notwithstanding the significant difference observed between $^{87}Sr/^{86}Sr$ values of the *Ciliegiolo* grapes from *Pian de' Conati* and those from *San Lorenzo* vineyards depends clearly upon the $^{87}Sr/^{86}Sr$ of the bioavailable fraction rather than any other geological (i.e., bedrock, soil) and biological (e.g., vine, cultivar) component (Table 2), as previously found by other studies on isotopes of wines (e.g., Tescione et al., 2015; Vinciguerra et al., 2015, 2016; Petrini et al., 2015; Durante et al., 2016, Marchionni et al., 2016).

In the following paragraphs we only discuss the relationship among the $^{87}Sr/^{86}Sr$ of the bioavailable fraction of the soils and of cultivars in the three different vineyards selected, leaving the analysis of the processes, which are responsible of the different mean values of $^{87}Sr/^{86}Sr$ in bedrock, soil, and bioavailable fraction to future studies.

3.3 The $^{87}Sr/^{86}Sr$ does not vary among cultivars, but depend upon different vineyard substrata

In figure 3 the box plots for each grape variety under consideration in this study are reported. Each box plot was calculated using all $^{87}Sr/^{86}Sr$ values obtained from a single grape variety of different harvest years. In addition, in this figure the range of $^{87}Sr/^{86}Sr$ values of the soil bioavailable fraction is reported as hatched area in the background.

In this plot we observe, with the sole exception for the *Sauvignon* grape cultivar, that the box plot derived statistically by the $^{87}Sr/^{86}Sr$ of the different grape cultivars, indifferently by their variety (i.e., red or white), fall well within the range of the bioavailable fraction of the soil of their vineyards (Fig. 3). As a corollary, different $^{87}Sr/^{86}Sr$ values are observed for grapes from the same

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cultivar but harvested by vines grown in different vineyards (i.e., *Ciliegiolo* and *Trebbiano* cultivars; Fig. 3).

On the other hand the $^{87}Sr/^{86}Sr$ mean values of the whole set of grape samples fall, with no exceptions, well within the $^{87}Sr/^{86}Sr$ range of the bioavailable fractions. In addition the $^{87}Sr/^{86}Sr$ mean value of grapes from *Pian de' Conati* (vineyard a) is 0.710010 ± 0.000095 (1σ), which lies within the range of variation of the relative soil bioavailable fraction [0.710077 ± 0.000049 (1σ)], and it is discernible from grape collected in *San Lorenzo* (vineyard b) [0.708986 ± 0.000121 (1σ)] and *Crucignano* (vineyard c)[0.709526 ± 0.000038 (1σ)](Table 2). These findings consistently support the hypothesis that $^{87}Sr/^{86}Sr$ of grape depends on the $^{87}Sr/^{86}Sr$ of the-soil solution from which the vine roots absorb nutrients as bioavailable substances.

Regarding the discrepancies observed in the box plot of *Sauvignon* these are caused by the lower $^{87}Sr/^{86}Sr$ values of the 2013 harvest year, shown in figure 2. The same was observed for the $^{87}Sr/^{86}Sr$ of *Greco* in the same harvest year but that did not affect greatly the box plot. Tentatively the sole explanation that we can find for these 2013 samples can be found in the low number of cycles during the experimental runs (i.e., 55-75; Table 1a).

3.4 *$^{87}Sr/^{86}Sr$ as a tool for geographic traceability at different scales*

The potential of $^{87}Sr/^{86}Sr$ for food geographic origin applications has been abundantly investigated in many studies, at a wide scale, on different products: orange juice from 14 producing countries in the world were analysed by Rummel et al. (2010), and Garcìa-Ruiz et al. (2007) attempted the geographical discrimination of ciders from 4 different European countries.

One of the most tested products with Sr-isotopes, due also to its high economic relevance, is wine. In fact, several studies can be found in literature, aiming to discriminate wines from a global to a regional scale, according to the nations of production (Barbaste, Robinson, Guilfoyle, Medina, & Lobinski, 2001; Horn et al., 1993), to different regions in the same country (Boari et al., 2008; Marchionni et al., 2013; Vinciguerra et al., 2015, 2016), and to different wineries in the same producing region (Durante et al., 2013; Petrini et al., 2015; Marchionni et al., 2016).

In order to perform an inter-varietal investigation among various grapevine genotypes, the scale of the study area has been further reduced to a single producer.

The values of $^{87}Sr/^{86}Sr$ measured in the grapes of this study show that the relation with the geologic bedrock of the vineyard of provenance is not relevantly affected by the plant genotype

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(Fig. 3) and by the harvest year and, despite the reduced study area, the grape samples collected in the three different vineyards of production are isotopically well defined and differentiated by each other. This implies that the geographic provenance for grapes can be tracked at a very fine tuning, being possible to discriminate among single vineyards of the same geographic area. On the other hand, no direct information about the variety and the vine genotype can be obtained with Sr-isotopes.

The possibility of checking the origin of grapes at such high level of geographic detail has relevant implications in terms of geographic traceability control in agreement with the European regulation for Protected Denomination of Origins (PDO) and therefore the Sr-isotopic method represents a valid and robust support for the product authenticity assessment.

The robustness of this tool at the local scale of the vineyard has been verified and, as the geology of the bedrock is the only discriminant factor, its applicability at a regional scale to check the provenance of grape at the national or even global market is also encouraged.

4. Summary and Conclusions

In this study we have shown that grapes inherit their Sr isotope composition exclusively from the geologic substratum of the vineyard of production and that it does not depend on the variety of the cultivar. It is worth noting that the correspondence between $^{87}Sr/^{86}Sr$ in vine products and geologic bedrock can be limited due to the selective absorption of chemical elements by vine roots. This concern can be encompassed by correlating the $^{87}Sr/^{86}Sr$ of grapes with that of the bioavailable soil fraction. In addition, our data show that for harvest years 2013-2014-2015-2016 the Sr-isotope remains fairly constant, arguing for the lack of influence of the climatic variations on its value. Therefore, this study clearly shows that $^{87}Sr/^{86}Sr$ can be a useful analytical tool to check the geographical provenance of fresh grape fruits, using the $^{87}Sr/^{86}Sr$ of the bioavailable fractions, which is somehow related to the geological substratum of the vineyard.

The study was conducted at the small scale to demonstrate the reliability and reproducibility of data within a well-controlled operational farming practice and well constrained geological and pedological environments to prevent any kind of food fraud and to guarantee the final product origin. In addition the reduced scale of the study shows the potential application of this tool, on a wide regional scale, and on the vineyard scale, with the possibility of confirming the authenticity of food products grown by different producers in the same viticultural region.

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Our work demonstrates that Sr isotopes can be used to assess the geographical origin of grapes and may also be used to label wine production. Furthermore, they might be useful to guarantee the observance of the regulations and the control on the production chain of high quality wines.

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Table headings

Tab. 1.a – $^{87}Sr/^{86}Sr$ of analysed grapes from different harvest years

Tab. 1.b – $^{87}Sr/^{86}Sr$ of substrata of the vineyards

Tab. 2 – Descriptive statistics of the grape, bioavailable soil fraction, soil, and rock samples

Table captions

Tab. 1 – Values here reported are the mean values of one single squeezed grape batch for the 2013, harvest year, three squeezed grape batches for the 2014 harvest year, and two squeezed grape batches for the 2015 and 2016 harvest years.

Figure Captions

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Fig. 1 – $^{87}Sr/^{86}Sr$ values for the 2015 harvest year and *Pian de' Conati* vineyard (a) for different samples of *Ciliegiolo* and *Teroldego* cultivars. The error bars represent the standard deviation (1σ).

Fig. 2 – $^{87}Sr/^{86}Sr$ composition of *Ciliegiolo*, *Greco, Sauvignon and Teroldego* cultivars collected in the *Pian de' Conati* (Vineyard a) and *Piana S. Lorenzo* (Vineyard b) areas through the 2013 – 2016 harvest years interval. *Ciliegiolo* red grapes harvested in *San Lorenzo* vineyard are represented with empty squares and show lower mean values. The yellow triangles and circles are related to white grape cultivars (*Sauvignon* and *Greco* respectively), the red squares and diamonds represent the red grape cultivars (*Ciliegiolo* and *Teroldego*), all of them grown in *Pian de' Conati* area. The error bars represent the standard deviation (1σ).

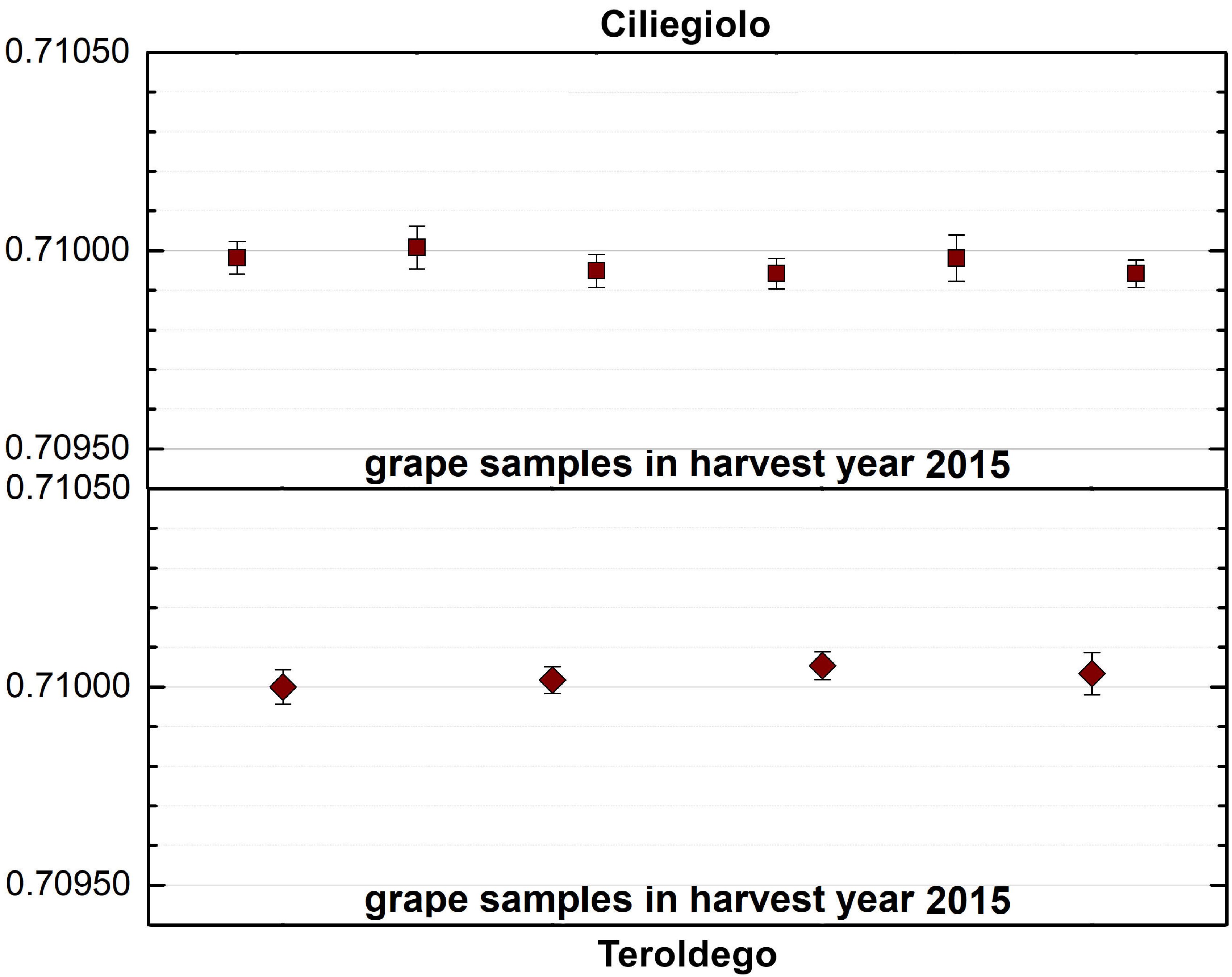
Fig. 3 - Box plot of the $^{87}Sr/^{86}Sr$ values distribution in different grape varieties from the three different areas compared to the soil bioavailable fraction. The hatched area represents the minimum and maximum values of the bioavailable fraction distribution. The yellow boxes are related to white grape cultivars (*Sauvignon*, *Greco*, and *Trebbiano*), the red boxes represent the red grape cultivars (*Ciliegiolo*, *Merlot*, *Sangiovese*, and *Teroldego*).

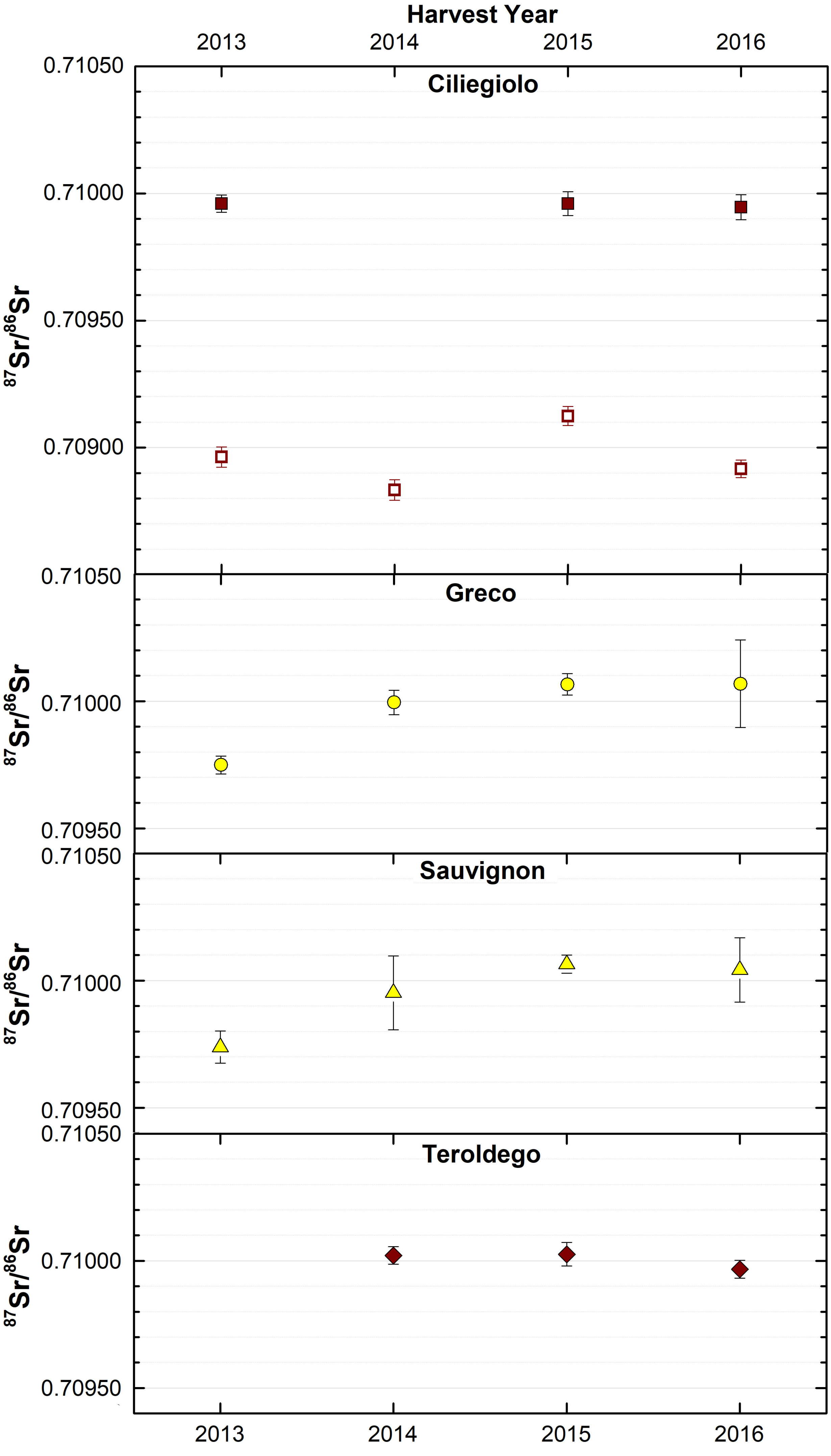
Table 1.a - $^{87}Sr/^{86}Sr$ of analysed grapes from different harvest years

Grapes					
Sample Type	Harvest Year	Variety	$^{87}Sr/^{86}Sr$	1σ	n
Vineyard A - Pian de' Conati					
White	2013	Greco	0.709749	± 0.000036	55
		Sauvingnon	0.709738	± 0.000064	75
	2014	Sauvignon 1	0.709749	± 0.000036	55
		Sauvignon 2	0.710048	± 0.000039	116
		Greco 1	0.709960	± 0.000031	112
		Greco 2	0.710029	± 0.000036	117
	2015	Trebbiano 1	0.710069	± 0.000045	115
		Trebbiano 2	0.710049	± 0.000043	114
		Greco 1	0.710082	± 0.000042	116
		Greco 2	0.710050	± 0.000035	115
		Sauvignon 1	0.710065	± 0.000036	81
		Sauvignon 2	n.d.	n.d.	n.d.
	2016	Sauvignon 1	n.d.	n.d.	n.d.
		Sauvignon 2	0.710042	± 0.000126	81
		Greco 1	n.d.	n.d.	n.d.
		Greco 2	0.710068	± 0.000172	65
		Trebbiano 1	0.710081	± 0.000042	115
		Trebbiano 2	0.710082	± 0.000040	91
Red	2013	Ciliegiolo	0.709960	± 0.000034	113
	2014	Teroldego 1	0.710014	± 0.000033	113
		Teroldego 2	0.710028	± 0.000035	113
		Sangiovese 1	0.710020	± 0.000033	116
		Sangiovese 2	0.710050	± 0.000034	115
	2015	Teroldego 1	0.710000	± 0.000043	117
		Teroldego 2	0.710017	± 0.000034	113
		Teroldego 3	0.710053	± 0.000035	117
		Teroldego 4	0.710033	± 0.000053	111
		Ciliegiolo 1	0.709982	± 0.000041	113
		Ciliegiolo 2	0.710008	± 0.000053	23
		Ciliegiolo 3	0.709949	± 0.000042	98
		Ciliegiolo 4	0.709942	± 0.000038	115
		Ciliegiolo 5	0.709981	± 0.000058	76
		Ciliegiolo 6	0.709942	± 0.000035	116
		Merlot 1	0.710044	± 0.000041	77
		Merlot 2	0.710216	± 0.000079	115
		Sangiovese 1	0.710031	± 0.000045	102
		Sangiovese 2	0.710008	± 0.000036	114
	2016	Teroldego 1	0.709967	± 0.000035	113
		Teroldego 2	n.d.	n.d.	n.d.
		Ciliegiolo 1	0.709951	± 0.000050	96
		Ciliegiolo 2	0.709940	± 0.000048	94
		Merlot 1	0.710040	± 0.000037	66
		Merlot 2	0.710035	± 0.000036	118
Vineyard B - Piana San Lorenzo					
Red	2013	Ciliegiolo	0.708963	± 0.000040	117
	2014	Ciliegiolo	0.708834	± 0.000040	119
	2015	Ciliegiolo 1	0.709119	± 0.000041	94
		Ciliegiolo 2	0.709128	± 0.000034	114
	2016	Ciliegiolo 1	n.d.	n.d.	n.d.
		Ciliegiolo 2	0.708916	± 0.000035	116
Vineyard C - Crucignano					
Red	2016	Trebbiano 1	0.709527	± 0.000039	115
		Trebbiano 2	0.709525	± 0.000038	114

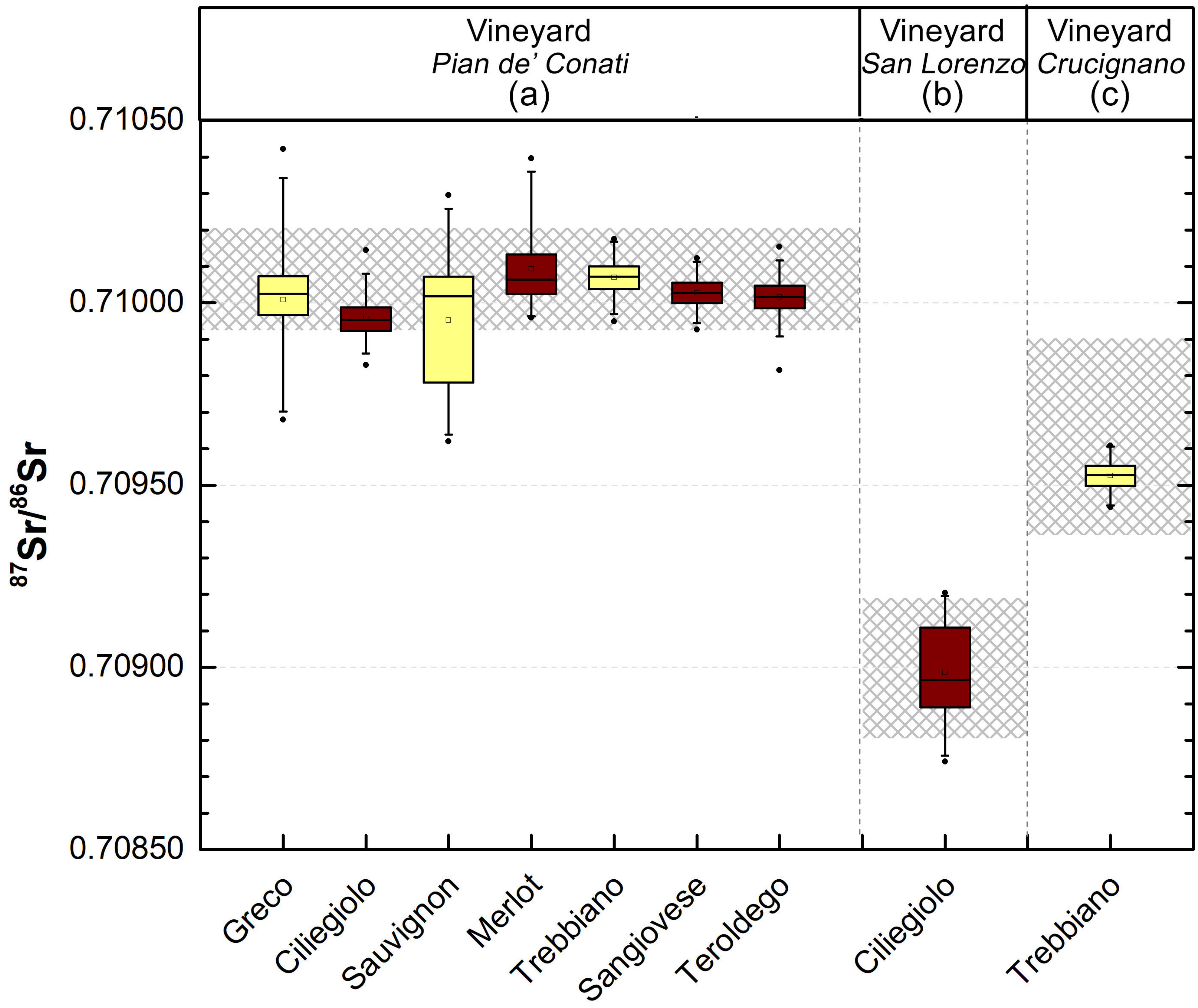
Table 1.b - $^{87}Sr/^{86}Sr$ of substrata of the vineyards

Bedrock and Soil					
Sample Type	**Formation**	**Fraction**	**Average $^{87}Sr/^{86}Sr$**	**1σ**	**n**
Vineyard A - Pian de' Conati					
Rock	Grotte di Castro Ignimbrite	whole	0.710204	± 0.000033	117
			0.710223	± 0.000039	114
Soil	Grotte di Castro Ignimbrite	whole	0.710145	± 0.000035	114
			0.710125	± 0.000037	114
			0.710133	± 0.000054	116
			0.710052	± 0.000032	112
	Grotte di Castro Ignimbrite	bioavailable	0.710095	± 0.000050	93
			0.710066	± 0.000039	115
			0.710096	± 0.000035	114
			0.710056	± 0.000056	117
Vineyard B - Piana San Lorenzo					
Rock	Pitigliano Formation	whole	0.710052	± 0.000032	112
Soil	Pitigliano Formation	whole	0.709371	± 0.000037	111
			0.709810	± 0.000055	116
	Pitigliano Formation	bioavailable	0.708884	± 0.000037	113
			0.709010	± 0.000084	114
Vineyard C - Crucignano					
Soil	Pitigliano Formation	whole	0.710265	± 0.000041	114
	Pitigliano Formation	bioavailable	0.709642	± 0.000117	114


Ciliegiolo
0.71050
0.71000
0.70950
grape samples in harvest year 2015
0.71050
0.71000
0.70950
grape samples in harvest year 2015
Teroldego



Harvest Year
2013
2014
2015
2016
Ciliegiolo
Greco
Sauvignon
Teroldego
$^{87}Sr/^{86}Sr$
0.71050
0.71000
0.70950
0.70900
0.71050
0.71000
0.70950
0.71050
0.71000
0.70950
0.71050
0.71000
0.70950
2013
2014
2015
2016



Vineyard
Pian de' Conati
(a)
Vineyard
San Lorenzo
(b)
Vineyard
Crucignano
(c)
$^{87}Sr/^{86}Sr$
0.71050
0.71000
0.70950
0.70900
0.70850
Greco
Ciliegiolo
Sauvignon
Merlot
Trebbiano
Sangiovese
Teroldego
Ciliegiolo
Trebbiano

Electronic supplementary materials - 1

$^{87}Sr/^{86}Sr$ isotopes in grapes of different cultivars: a geochemical tool for geographic traceability of agriculture products

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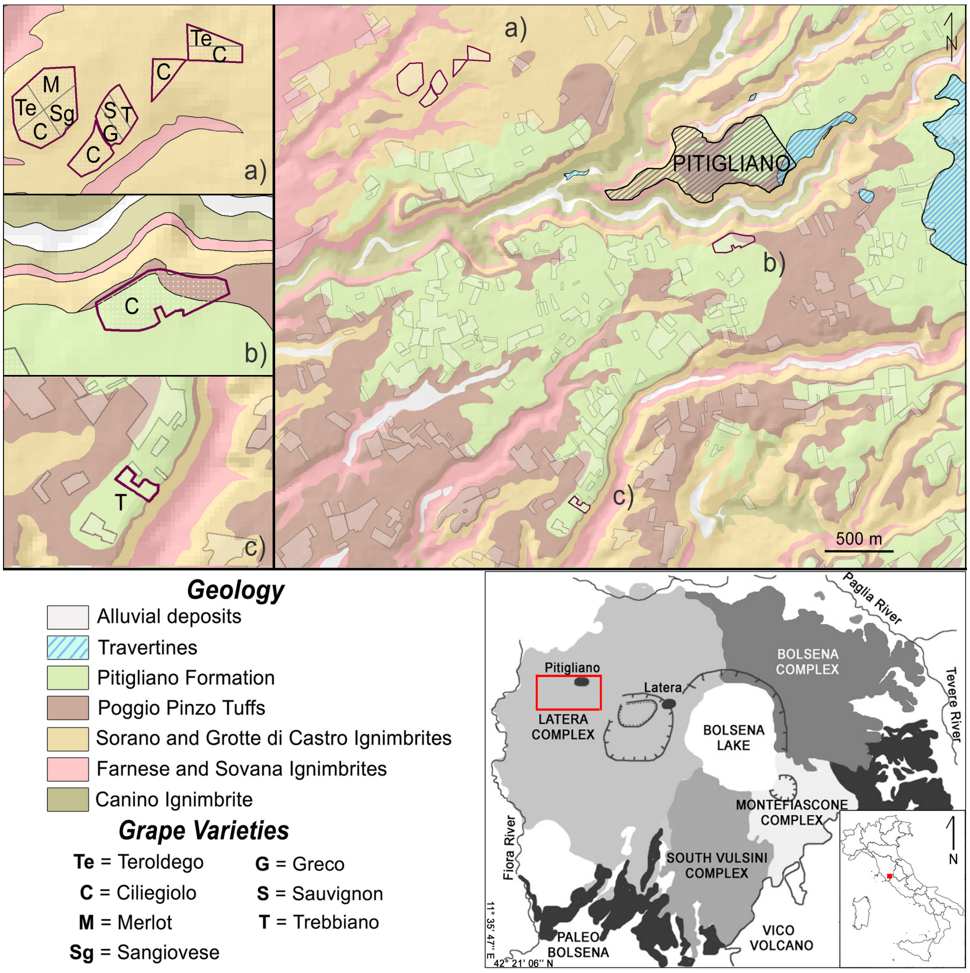
Focus on the geological setting of the Vulsini Volcanic District

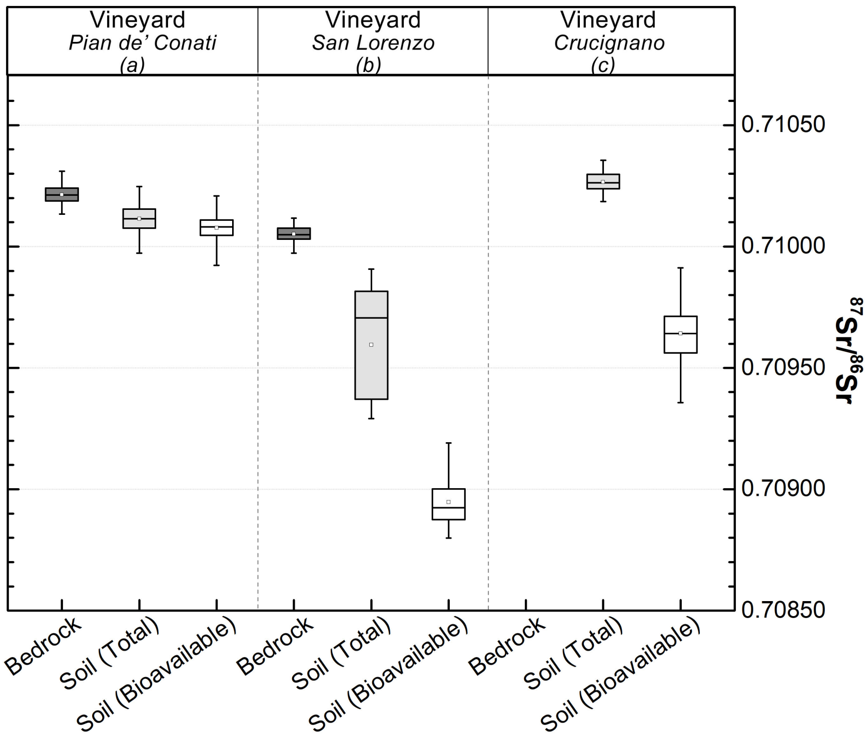
The Vulsinian District is a 2,000 km^2 widespread volcanic area formed about 600 – 100 kyr BP (Vezzoli et al., 1987; Conticelli et al., 2010). The volcanism produced a thick sequence of pyroclastic deposits and lava flows that formed the three main volcanic apparata of Bolsena, Latera and Montefiascone (ESM-FIG1). These coalescent volcanoes were characterized by similar eruptive styles with ignimbrite-forming eruptions preceded and followed by effusive and strombolian activities, usually taking place along peripheral circum-calderic fault system.

The volcanic activity in the Latera area developed from about 429 to 145 ka. Lavas were confined in the early and late stage of the volcano, whilst pyroclastic activity occurred between 278 and 166 ka, with the emplacement of six main ignimbrites inter-bedded to some events of pyroclastic fall and surges (Conticelli et al. 2010). A large polygenic caldera was formed.

The *Sassotondo* farm, the winery used for the experimental work of this study, has vineyards lying on the volcanic succession of Latera volcano in the surroundings of the town of Pitigliano (Fig ESM-1). The vineyards develop in three different areas: a) *Pian de' Conati*, which has the soil formed on the bedrock belonging to the Grotte di Castro formation; b) *Piana San Lorenzo*, which has the soil formed on both Poggio Pinzi Tuffs and Pitigliano Formation, but the grapes were from vines on the former bedrock; c) *Crucignano*, which has a soil formed directly on the Pitigliano Formation. The different soils are formed on the above mentioned pyroclastic bedrocks (i.e., ignimbrites and falls) and they range in terms of pedology, according to the Tuscany Pedological map - http://www.lamma.rete.toscana.it/territorio/cartografia-tematica/pedologia/carta-dei-suoli - from "*Molli Pachic Andosols*" (autoc. *Scopetone* soil) for *San Lorenzo* vineyard, to "*Epileptic Andosols*" (autoc. *Farmacista* soil) for *Crucignano* vineyard, and "*Eutric Epileptic Andosols*" (autoc. *Aia di Tufi* soil) for *Pian de' Conati* vineyard (IUSS WGW, 2006).



ESM-Fig. 1 – Geological map of the study area showing the three vineyards of the Sassotondo farm. On the left side insets a,b,c represent the three vineyards: a = *Pian de' Conat*i Area, b = *Piana S. Lorenzo*, c = *Crucignano*, whereas the polygons represent the grape variety grown. In *Piana San Lorenzo* area only *Ciliegiolo* variety is grown, while in *Pian de' Conati* area both red (*Ciliegiolo*, *Teroldego*, *Merlot*, and *Sangiovese* cultivars) and white (*Greco*, *Trebbiano*, and Sauvignon cultivars) grape varieties can be found. The inset below represents the distribution of the volcanic rocks of the Vulsinian District, Roman Magmatic province (Vezzoli et al., 1987).



ESM-Fig. 2 – Box plot of the $^{87}Sr/^{86}Sr$ value distribution of the different samples (i.e., bedrock, whole soil, and bioavailable fraction of soil) for the three vineyards analysed.

			2013	2014	2015	2016
Vineyard A - Pian de' Conati	White Grape	Greco	1	2	2	1
		Sauvignon	1	2	1	1
		Trebbiano			2	
	Red Grape	Teroldego		2	4	1
		Ciliegiolo	1		6	2
		Merlot			2	2
		Sangiovese		2	2	
		Trebbiano				2
Vineyard B - Piana San Lorenzo	Red Grape	Ciliegiolo	1	1	2	1
Vineyard C - Crucignano	Red Grape	Trebbiano				2

ESM-Tab. 1 – Schematic representation of the sampling strategy of the bunch grapes and of related materials to the vineyards (i.e., bedrocks, whole soil, bioavailable fraction of the soil).

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