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1  **$^{87}\text{Sr}/^{86}\text{Sr}$  isotopes in grapes of different cultivars: a geochemical tool for geographic**  
2 **traceability of agriculture products**

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15 **Highlights**

- 16 –  $^{87}\text{Sr}/^{86}\text{Sr}$  in fresh grapes from different genotype vines (cultivar)  
17 –  $^{87}\text{Sr}/^{86}\text{Sr}$  differences between white and red grapes and among harvest years  
18 –  $^{87}\text{Sr}/^{86}\text{Sr}$  in bioavailable fraction of soils, soils, and rocks beneath vineyards of production  
19 – Geologic heritage in food stuff as a fingerprint for geographic traceability

20 **Abstract**

21  $^{87}\text{Sr}/^{86}\text{Sr}$  was determined on fresh red and white grapes, soils and rocks from three selected  
22 vineyards to verify the isotopic relationships between the fruit of the vine and geologic substrata  
23 of vineyards.  $^{87}\text{Sr}/^{86}\text{Sr}$  were determined on sampled grapes of four different harvest years and  
24 different grape varieties, on bioavailable fraction of soils, on whole soils, and on bedrocks from the  
25 geo-pedological substratum of the vineyards. The vineyards chosen for the experimental works  
26 belong to an organic farming winery and thus cultivation procedures were strictly controlled.

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

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

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

## 34 **1. Introduction**

35 The increasing demand of high quality food products promoted the development of rigid  
36 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  
37 request of suitable scientific protocols able to confirm the authenticity of food products by  
38 tracking their geographical origin. These studies aim to find scientific parameters inherited by the  
39 area of production of the agricultural products, which may be considered a fingerprint for  
40 geographic traceability of food (Kelly, Heaton & Hoogewerff, 2005).  
41

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

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

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

62 The experimental studies on the distribution of  $^{87}\text{Sr}/^{86}\text{Sr}$  in wines available in the scientific  
63 literature focused mainly on the evaluation of the consistency of the Sr-isotopic value through the  
64 winemaking process from the soil to the wine (e.g., Almeida & Vasconcelos, 2004; Durante et al.,  
65 2013, 2016; Marchionni et al. 2016). These papers, however, did not check in detail the Sr-isotopic  
66 traceability of grapes from different vines, in comparison with the Sr-isotopic variability of the  
67 substrata of the vineyards (e.g., soils and rocks). Indeed, grapes are not only important for the  
68 wine consumers, but also for the consumers of the fresh fruit itself. Presently, there are no  
69 detailed Sr-isotopic studies on grapes in general, notwithstanding grape production represents the  
70 world's most important fresh fruit crop with the highest total value of production (FAO-OIV Focus,  
71 2016), with half used for wine production, and the greatest quantity of the remaining part  
72 destined to the global market to be consumed as fresh fruit.

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

## 84 **2. Materials and Methods**

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

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

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

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

## 105 2.1 Sampling

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

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

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

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

## 124 2.2 Sample preparation and analysis

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

132 *Grape samples* were first washed and rinsed with Milli-Q<sup>®</sup> water for three times to be sure to  
133 have not any dust during further sample preparation. Then grapes were crushed with skin and  
134 seeds. A fraction of the collected juice was treated as follow: 5 ml were evaporated to dryness in a  
135 PFA beaker on a hot plate at 90°C, then 3 ml of H<sub>2</sub>O<sub>2</sub> 30 vol.% UpA were added to the dried sample  
136 and left overnight at room temperature and later evaporated to dryness at 80°C. This step of the  
137 digestion procedure was repeated twice. To assure a complete digestion of the organic matter 2  
138 ml of HNO<sub>3</sub> 65 vol.% were added, the beaker was covered and left overnight on the hot plate at  
139 170°C and evaporated to dryness. This step was repeated twice, too.

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

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

151 *Rock samples* were first mechanically crushed and then pulverised with an agate ball mill; an  
152 amount of 50 mg of homogenised sample were digested in a solution of 1:4 HNO<sub>3</sub> + HF at 140°C  
153 for 1-2 days, then they were brought to dryness. Two further additions of HNO<sub>3</sub> and dissolution in  
154 6 N HCl at 120°C and eventually evaporation to dryness followed.

155 All the digested samples underwent to Sr-purification by cation exchange chromatography  
156 using Sr-Spec<sup>®</sup> resins in 140 µl pure quartz micro-columns with 3N HNO<sub>3</sub> as eluent and Milli-Q<sup>®</sup>  
157 water to collect Sr. Sr purification was performed using a cation exchange chromatography in a  
158 “Class 100” vertical HEPA-filtered laminar flow hood and high-purity chemical reagents  
159 (Avanzinelli et al., 2005). The extracted Sr (about 100-200 ng) was dissolved in 2N HNO<sub>3</sub> and  
160 loaded on single Re filaments using 1 µl of TaCl<sub>5</sub> and 1 µl of H<sub>3</sub>PO<sub>5</sub> as activator and fractionation  
161 suppressor, respectively.

162 Sr-isotope abundance (<sup>88</sup>Sr, <sup>87</sup>Sr, <sup>86</sup>Sr, <sup>84</sup>Sr) was measured by thermal ionisation mass-  
163 spectrometer (TIMS), in dynamic mode, using a Thermo FinniganTM Triton-Ti<sup>®</sup> magnetic sector  
164 field equipped with nine moveable collectors (Avanzinelli et al., 2005). Each Sr-isotope ratio  
165 reported in Table 1a is the average of about 120 sets of cycles, with each cycle itself representing  
166 the average of three measurements performed during triple-jumping dynamic measurement. The  
167 120 sets of cycles were collected in 6 blocks, each consisting of 20 cycles with 8 seconds  
168 integration time. An idle time of 3 seconds was set before the start of the collection after each  
169 jump, to eliminate possible memory effect due to the decay of the signal in the faraday cups.

170 Procedural blank was <200 pg resulting in negligible sample correction. The external precision  
171 of NIST SRM987 international reference sample for the time of this study was <sup>87</sup>Sr/<sup>86</sup>Sr = 0.710251  
172 ±0.000010 (2σ, n = 20), while the long-term mean value was <sup>87</sup>Sr/<sup>86</sup>Sr = 0.710248 ±0.000016 (2σ, n  
173 = 173, equivalent to an error of 23 ppm). The within run precision (i.e., 2σ<sub>m</sub>: internal precision) of  
174 <sup>87</sup>Sr/<sup>86</sup>Sr measurements has been typically ≤10 ppm.

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

178 composition, yielding a  $2\sigma = \pm 0.000017$  (i.e., 23 ppm), which is consistent with that of the  
179 international reference standard.

### 180 **3. Results and Discussion**

181 The values of  $^{87}\text{Sr}/^{86}\text{Sr}$  in fresh grapes, soil bioavailable fractions, bulk soils, and whole rocks  
182 are reported in Tables 1a and 1b. The results for each cycle of measurement performed are  
183 reported as Electronic Supplementary Material (ESM-Tab. 2, Electronic Supplementary Materials  
184 2).

#### 185 *3.1 The $^{87}\text{Sr}/^{86}\text{Sr}$ does not vary with time*

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

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

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



207 (1 $\sigma$ )] than samples from *San Lorenzo* vineyard [average value  $0.708986 \pm 0.000121$  (1 $\sigma$ )]. This bias  
208 depends upon the different  $^{87}\text{Sr}/^{86}\text{Sr}$  shown by the substrata of the two vineyards (ESM-Fig. 2,  
209 Electronic Supplementary Materials 1) as discussed in the next paragraph.

210 In summary, excluding the *Greco* and *Sauvignon* grape samples harvested in the 2013, which  
211 display lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values than other grapes from the same vineyard, the grape samples  
212 collected for this study display no significant  $^{87}\text{Sr}/^{86}\text{Sr}$  variations through time (Fig. 2), as shown in  
213 previous experimental studies for musts and wines of different vintage years (Marchionni et al.,  
214 2013, 2016). On the other hand, systematic large  $^{87}\text{Sr}/^{86}\text{Sr}$  variations are observed among grapes  
215 from vineyards farmed on geological substrata with different chemical composition and  $^{87}\text{Sr}/^{86}\text{Sr}$   
216 signatures.

### 217 3.2 The $^{87}\text{Sr}/^{86}\text{Sr}$ of bioavailable soil fraction, soil, and bedrocks

218 Marchionni et al. (2013) have already shown the strong correlation existing between the  
219  $^{87}\text{Sr}/^{86}\text{Sr}$  of bottled red wines and the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the bedrocks of the area of production, although  
220 a discrepancy might be observed between the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the wine and that of the geological  
221 substratum of the area of production. This bias increases passing from wine production areas  
222 characterised by a substratum made of young volcanic rocks to wine production area  
223 characterised by older either sedimentary or granitic rocks (Marchionni et al., 2013). Other studies  
224 have also shown that the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the bioavailable fraction is a better proxy of the *terroir* of the  
225 area of provenance of the food product from agriculture (e.g., Tescione, Marchionni, Mattei, Tassi,  
226 Romano, Conticelli, 2015; Vinciguerra, Stevenson, Pedneault, Poirier, Hélie, Widory, 2015, 2016;  
227 Petrini et al., 2015; Durante et al., 2016; Marchionni et al., 2016).

228 These findings are confirmed by our data when the  $^{87}\text{Sr}/^{86}\text{Sr}$  of bedrocks are compared with  
229 whole soils and soil bioavailable fraction of the three vineyards taken under consideration in this  
230 study (Table 2 and ESM-Fig. 2; Electronic Supplementary Materials 1). Indeed, the *Pian de' Conati*  
231 vineyard shows slight differences among the mean values of  $^{87}\text{Sr}/^{86}\text{Sr}$  of the bedrock [*Grotte di*  
232 *Castro Formation* =  $0.710213 \pm 0.000037$  (1 $\sigma$ )], the total fraction of whole soil [ $0.710114 \pm$   
233  $0.000054$  (1 $\sigma$ )], and its bioavailable fraction [ $0.710077 \pm 0.000049$  (1 $\sigma$ )]. On the other hand, in the  
234 *Piana San Lorenzo* vineyard the  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the three components of the substratum are  
235 slightly to significantly lower than those observed for the *Pian de' Conati* vineyard. In particular  
236 large isotopic differences among geologic bedrock [*Pitigliano Formation* =  $0.710052 \pm 0.000032$

237 (1 $\sigma$ ), whole soil total fraction [0.709595  $\pm$  0.000225 (1 $\sigma$ )], and its bioavailable fraction [0.708948  $\pm$   
238 0.000091 (1 $\sigma$ )] are observed. Similarly, in the *Crucignano* vineyard the large difference between  
239 the whole soil [0.710265  $\pm$  0.000041 (1 $\sigma$ )] and its bioavailable fraction [0.709642  $\pm$  0.000117 (1 $\sigma$ )]  
240 does also occur (Table 2 and ESM-Fig. 2; Electronic Supplementary Materials 1).

241 The different amount of  $^{87}\text{Sr}/^{86}\text{Sr}$  depletion from bedrock to soil and to bioavailable fraction in  
242 the three different areas can be related to the different nature of soils outcropping in the area  
243 (Pedological Map of the Tuscany region: [http://www.lamma.rete.toscana.it/territorio/cartografia-](http://www.lamma.rete.toscana.it/territorio/cartografia-tematica/pedologia/carta-dei-suoli)  
244 [tematica/pedologia/carta-dei-suoli](http://www.lamma.rete.toscana.it/territorio/cartografia-tematica/pedologia/carta-dei-suoli)). Different soils may release the bioavailable fraction to the  
245 plants due to their different texture and inorganic composition, leading to different relationships  
246 among  $^{87}\text{Sr}/^{86}\text{Sr}$  values in bedrock, soil, vine, and wine (e.g., Marchionni et al., 2013; Petrini et al.,  
247 2015). Notwithstanding the significant difference observed between  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the  
248 *Ciliegiolo* grapes from *Pian de' Conati* and those from *San Lorenzo* vineyards depends clearly upon  
249 the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the bioavailable fraction rather than any other geological (i.e., bedrock, soil) and  
250 biological (e.g., vine, cultivar) component (Table 2), as previously found by other studies on  
251 isotopes of wines (e.g., Tescione et al., 2015; Vinciguerra et al., 2015, 2016; Petrini et al., 2015;  
252 Durante et al., 2016, Marchionni et al., 2016).

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

### 257 3.3 The $^{87}\text{Sr}/^{86}\text{Sr}$ does not vary among cultivars, but depend upon different vineyard substrata

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

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

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

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

276 Regarding the discrepancies observed in the box plot of *Sauvignon* these are caused by the  
277 lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the 2013 harvest year, shown in figure 2. The same was observed for the  
278  $^{87}\text{Sr}/^{86}\text{Sr}$  of *Greco* in the same harvest year but that did not affect greatly the box plot. Tentatively  
279 the sole explanation that we can find for these 2013 samples can be found in the low number of  
280 cycles during the experimental runs (i.e., 55-75; Table 1a).

### 281 3.4 $^{87}\text{Sr}/^{86}\text{Sr}$ as a tool for geographic traceability at different scales

282 The potential of  $^{87}\text{Sr}/^{86}\text{Sr}$  for food geographic origin applications has been abundantly  
283 investigated in many studies, at a wide scale, on different products: orange juice from 14  
284 producing countries in the world were analysed by Rummel et al. (2010), and García-Ruiz et al.  
285 (2007) attempted the geographical discrimination of ciders from 4 different European countries.

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

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

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

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

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

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

#### 309 **4. Summary and Conclusions**

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

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

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

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## 466 **Table headings**

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

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

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

## 470 **Table captions**

471 **Tab. 1** – Values here reported are the mean values of one single squeezed grape batch for the  
472 2013, harvest year, three squeezed grape batches for the 2014 harvest year, and two  
473 squeezed grape batches for the 2015 and 2016 harvest years.

## 474 **Figure Captions**



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

478 **Fig. 2** –  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of *Ciliegiolo*, *Greco*, *Sauvignon* and *Teroldego* cultivars collected in  
479 the *Pian de' Conati* (Vineyard a) and *Piana S. Lorenzo* (Vineyard b) areas through the  
480 2013 – 2016 harvest years interval. *Ciliegiolo* red grapes harvested in *San Lorenzo*  
481 vineyard are represented with empty squares and show lower mean values. The yellow  
482 triangles and circles are related to white grape cultivars (*Sauvignon* and *Greco*  
483 respectively), the red squares and diamonds represent the red grape cultivars (*Ciliegiolo*  
484 and *Teroldego*), all of them grown in *Pian de' Conati* area. The error bars represent the  
485 standard deviation ( $1\sigma$ ).

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

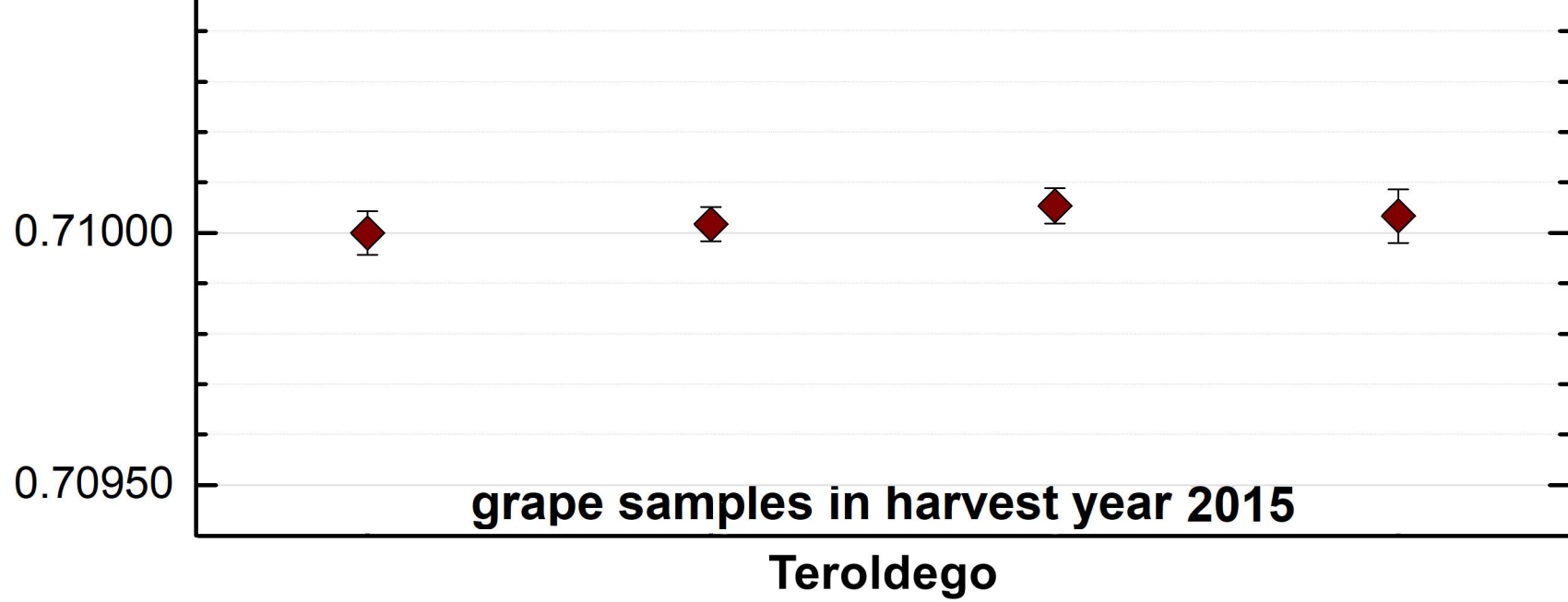
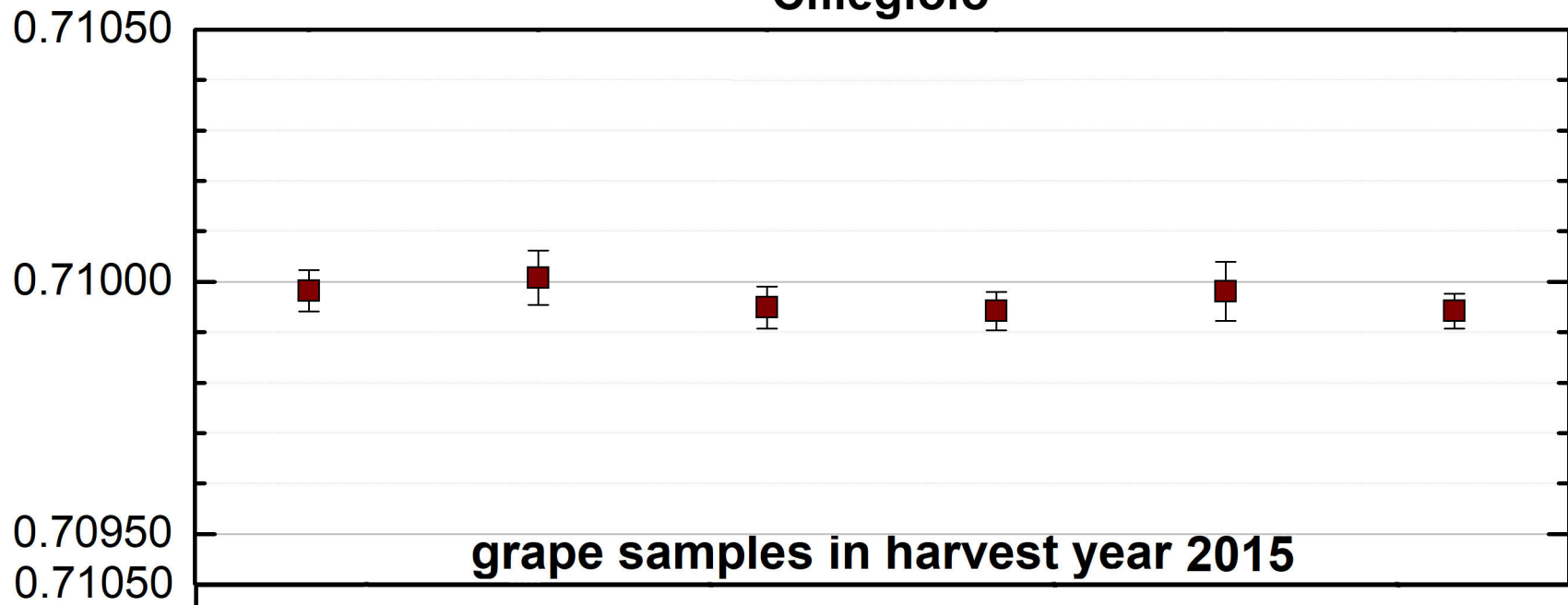
Table 1.a -  $^{87}\text{Sr}/^{86}\text{Sr}$  of analysed grapes from different harvest years

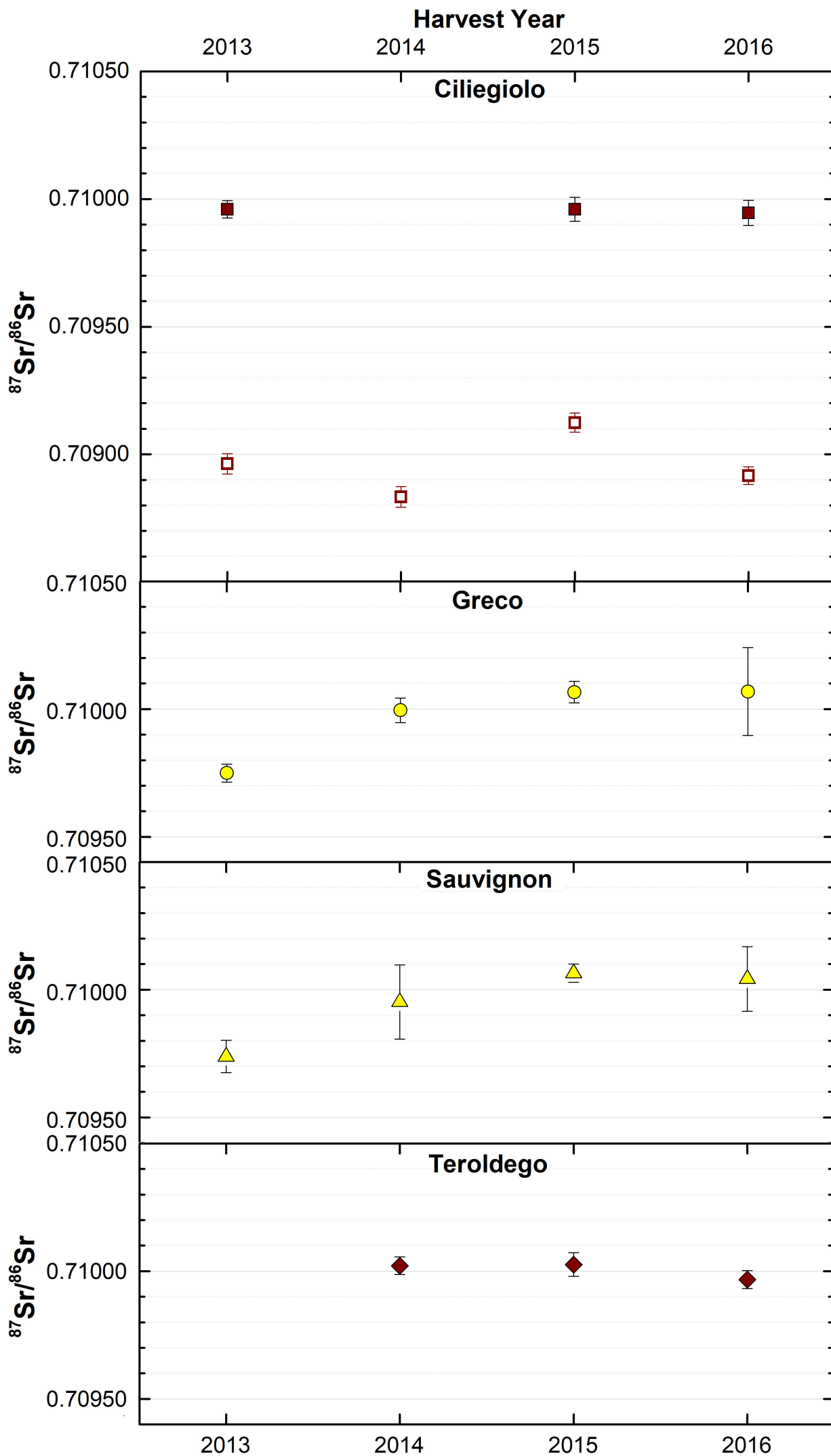
Grapes						
Sample Type	Harvest Year	Variety	$^{87}\text{Sr}/^{86}\text{Sr}$	$1\sigma$	n	
<b>Vineyard A - Pian de' Conati</b>						
W h i t e	2013	Greco	0.709749	$\pm 0.000036$	55	
		Sauvignon	0.709738	$\pm 0.000064$	75	
	2014	Sauvignon 1	0.709749	$\pm 0.000036$	55	
		Sauvignon 2	0.710048	$\pm 0.000039$	116	
		Greco 1	0.709960	$\pm 0.000031$	112	
		Greco 2	0.710029	$\pm 0.000036$	117	
	2015	Trebbiano 1	0.710069	$\pm 0.000045$	115	
		Trebbiano 2	0.710049	$\pm 0.000043$	114	
		Greco 1	0.710082	$\pm 0.000042$	116	
		Greco 2	0.710050	$\pm 0.000035$	115	
		Sauvignon 1	0.710065	$\pm 0.000036$	81	
		Sauvignon 2	n.d.	n.d.	n.d.	
	2016	Sauvignon 1	n.d.	n.d.	n.d.	
		Sauvignon 2	0.710042	$\pm 0.000126$	81	
		Greco 1	n.d.	n.d.	n.d.	
		Greco 2	0.710068	$\pm 0.000172$	65	
		Trebbiano 1	0.710081	$\pm 0.000042$	115	
		Trebbiano 2	0.710082	$\pm 0.000040$	91	
	R e d	2013	Ciliegiolo	0.709960	$\pm 0.000034$	113
		2014	Teroldego 1	0.710014	$\pm 0.000033$	113
Teroldego 2			0.710028	$\pm 0.000035$	113	
Sangiovese 1			0.710020	$\pm 0.000033$	116	
Sangiovese 2			0.710050	$\pm 0.000034$	115	
2015		Teroldego 1	0.710000	$\pm 0.000043$	117	
		Teroldego 2	0.710017	$\pm 0.000034$	113	
		Teroldego 3	0.710053	$\pm 0.000035$	117	
		Teroldego 4	0.710033	$\pm 0.000053$	111	
		Ciliegiolo 1	0.709982	$\pm 0.000041$	113	
		Ciliegiolo 2	0.710008	$\pm 0.000053$	23	
		Ciliegiolo 3	0.709949	$\pm 0.000042$	98	
		Ciliegiolo 4	0.709942	$\pm 0.000038$	115	
		Ciliegiolo 5	0.709981	$\pm 0.000058$	76	
		Ciliegiolo 6	0.709942	$\pm 0.000035$	116	
		Merlot 1	0.710044	$\pm 0.000041$	77	
		Merlot 2	0.710216	$\pm 0.000079$	115	
Sangiovese 1		0.710031	$\pm 0.000045$	102		
Sangiovese 2		0.710008	$\pm 0.000036$	114		
2016		Teroldego 1	0.709967	$\pm 0.000035$	113	
	Teroldego 2	n.d.	n.d.	n.d.		
	Ciliegiolo 1	0.709951	$\pm 0.000050$	96		
	Ciliegiolo 2	0.709940	$\pm 0.000048$	94		
	Merlot 1	0.710040	$\pm 0.000037$	66		
	Merlot 2	0.710035	$\pm 0.000036$	118		
<b>Vineyard B - Piana San Lorenzo</b>						
R e d	2013	Ciliegiolo	0.708963	$\pm 0.000040$	117	
	2014	Ciliegiolo	0.708834	$\pm 0.000040$	119	
	2015	Ciliegiolo 1	0.709119	$\pm 0.000041$	94	
		Ciliegiolo 2	0.709128	$\pm 0.000034$	114	
	2016	Ciliegiolo 1	n.d.	n.d.	n.d.	
		Ciliegiolo 2	0.708916	$\pm 0.000035$	116	
<b>Vineyard C - Crucignano</b>						
Red	2016	Trebbiano 1	0.709527	$\pm 0.000039$	115	
		Trebbiano 2	0.709525	$\pm 0.000038$	114	

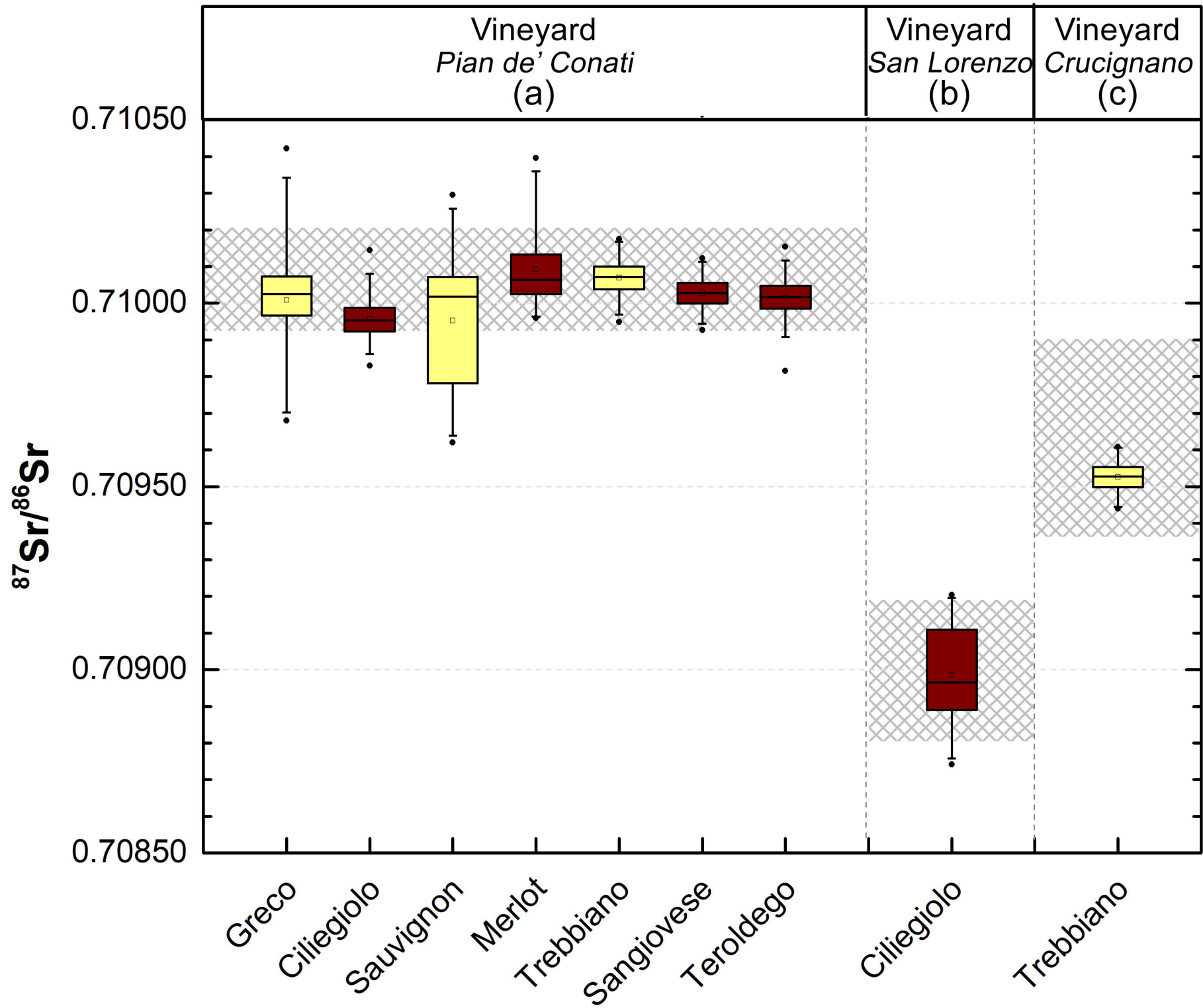
**Table 1.b -  $^{87}\text{Sr}/^{86}\text{Sr}$  of substrata of the vineyards**

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

# Ciliegiolo







## Electronic supplementary materials - 1

### <sup>87</sup>Sr/<sup>86</sup>Sr isotopes in grapes of different cultivars: a geochemical tool for geographic traceability of agriculture products

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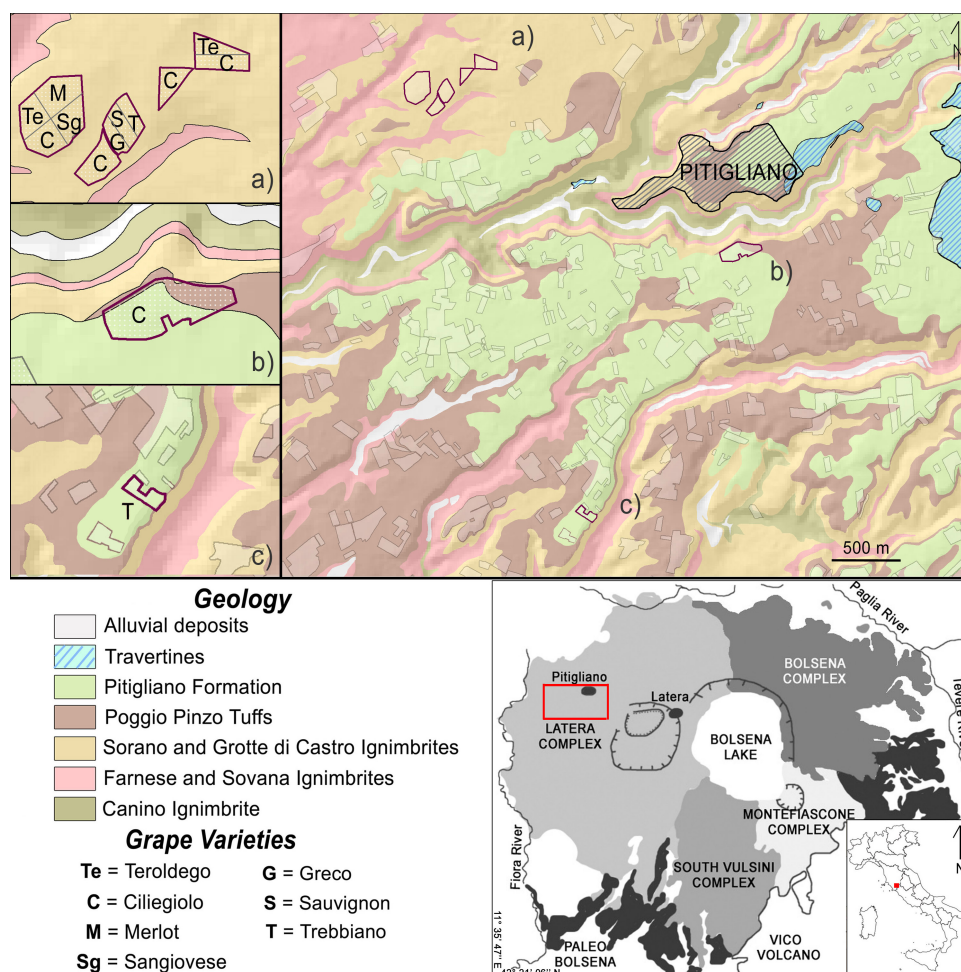
#### Focus on the geological setting of the Vulsini Volcanic District

The Vulsinian District is a 2,000 km<sup>2</sup> 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 apparatus 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.

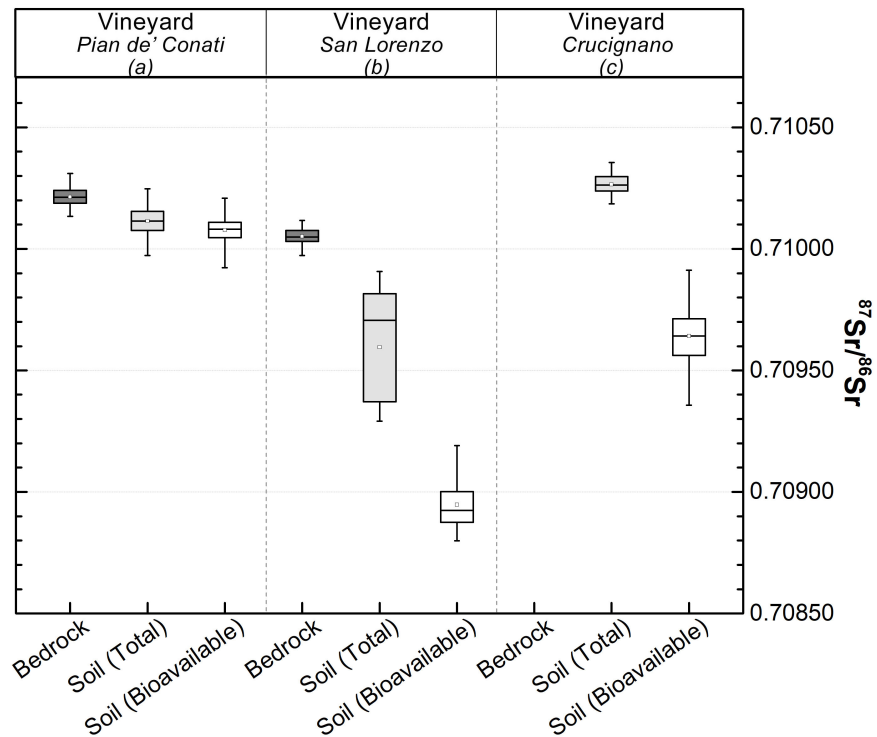
The *Sassotondo* farm, the winery used for the experimental work of this study, has vineyards lying on the volcanic succession of Latera volcano in the surroundings of the town of Pitigliano (Fig ESM-1). The vineyards develop in three different areas: a) *Pian de' Conati*, which has the soil

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’ Conati* Area, b = *Piana S. Lorenzo*, c = *Crucignano*, whereas the polygons represent the latera grape variety grown. In *Piana San Lorenzo* area only *Cilieggiolo* variety is grown, while in *Pian de’ Conati* area both red (*Cilieggiolo*, *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  $^{87}\text{Sr}/^{86}\text{Sr}$  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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