



Conservation of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios during the winemaking processes of 'Red' wines to validate their use as geographic tracer



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ABSTRACT

$^{87}\text{Sr}/^{86}\text{Sr}$ has been determined in wines, musts grape juices, soils and rocks from six selected vineyards of 'Cesanese' wine area. Cesanese is a monocultivar wine from a small region characterised by different geologic substrata, a key locality to test the influence of both substratum and winemaking procedure on the $^{87}\text{Sr}/^{86}\text{Sr}$ of wines. Experimental work has been performed on wines from different vintage years to check possible seasonal variations. The data reveal that $^{87}\text{Sr}/^{86}\text{Sr}$ does not change through time, to validate the selection of wineries performed, and in addition no isotopic variations are observed during winemaking. Indeed, no significant isotopic variations have been observed in musts and wines. These findings reinforce the hypothesis that the isotopic signature of wines is strongly related to the bioavailable fraction of the soil rather than to its bulk. The data corroborate the possibility that Sr-isotopes of high-quality wines can be used as a reliable tool for fingerprinting wine geographic provenance.

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1. Introduction

Long lived isotope ratios of heavy elements of geological interest, such as $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, have in the last decades gained importance in tackling the issue of geographical food traceability, as well as in solving issues related with archaeological, environmental, medical and forensic sciences (Kelly, Heaton, & Hoogewerff, 2005; Podio et al., 2013; Voerkelius et al., 2010). This increasing consideration is mainly based on the fact that radiogenic isotopic ratios are extensively used either for tracking geological and environmental processes or in dating cosmological and Earth's materials (Capo, Stewart, & Chadwick, 1998; Horn, Schaaf, Holbach, Hölzl, & Eschnauer, 1993; Tommasini, Davies, & Elliott, 2000). In addition, radiogenic isotope ratios are fractionated neither by low-temperature nor by biogenic processes. Hence, their abundance in geological materials (i.e. minerals and rocks) depends upon: (i) the initial radiogenic isotopic abundance, (ii) on the age of the rock/mineral, and (iii) on their parent/daughter isotope ratio (Dickin, 2005; Stewart, Capo, & Chadwick, 1998; Stille et al., 2009).

Each geological substratum of vineyards is liable to have its own Sr isotope composition, which can potentially represent a *fingerprint* to trace the wine production provenance (Boari et al., 2008; Marchionni et al., 2013). The use of $^{87}\text{Sr}/^{86}\text{Sr}$ in tracking wine regional provenance was among the most pioneering applications of isotope geology to other sciences (Almeida & Vasconcelos, 2004; Barbaste, Robinson, Guilfoyle, Medina, & Lobinsky, 2002; Di Paola-Naranjo et al., 2011; Horn et al., 1993). In most of the cases, however, the analytical uncertainty observed in Sr isotopes analyses of wines from literature is larger than most of the rock/soil isotopic variability, creating major difficulties in matching data of wines with those from geological substrata of the vineyards. Recently, high-precision analytical methods for determining $^{87}\text{Sr}/^{86}\text{Sr}$ have been provided, enabling the direct comparison of data on wines with those of the geological and pedological substrata (Boari et al., 2008; Durante et al., 2015; Marchionni et al., 2013; Mercurio et al., 2014; Petrini et al., 2015).

Even with high-precision Sr isotopic measurement discrepancies have been observed between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in wine and those of geological material of the substrata of the vineyards (Boari et al., 2008; Marchionni et al., 2013). This might be due either to adulteration of the analysed wines or to contamination during vine life, with Sr uptake by its roots, and the winemaking

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processes. To encompass this issue a detailed study on the distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ in the complete chain of wine production of a 'DOC'-certified Italian 'Red' wine has been undertaken. This experimental study has the aim to verify the possible occurrence of $^{87}\text{Sr}/^{86}\text{Sr}$ decoupling between the wine and the geological substratum (i.e., rocks).

We determined $^{87}\text{Sr}/^{86}\text{Sr}$ in rocks, soil, grape, grape juice (must), and wine on six different farms from the 'Cesane' wine region in which we followed and verified the good winemaking practices during the years under consideration. The 'Cesane' cultivar is a red Italian grape variety that is grown primarily in the Latium district, Central Italy. The 'Cesane' Red wine is produced using 100% of the homonymous grape cultivar and its production is regulated and certified through three geographically distinct production areas protected by law regulation: the *Cesane di Affile* DOC (*Denomination of Origin Verified* according to the Italian appellation law for wines), *Cesane di Olevano Romano* DOC, and *Cesane del Piglio* DOCG (*Denomination of Origin Verified and Guaranteed*, where in addition to geographic provenance, sensory characteristics of wines are also guaranteed). The selected wineries cover the three distinct DOC areas and they are from a geologically well-defined region (Critelli et al., 2007; Giordano & the CARG team, 2010), from which a wide isotopic set of data for volcanic rocks is available (Boari, Avanzinelli, et al., 2009; Boari, Tommasini, Laurenzi, & Conticelli, 2009; Conticelli et al., 2010).

The final aim of this study is establish direct and unambiguous relationships between Sr-isotopes of wines and those of the substrata of their vineyards and to verify that neither the root nor the winemaking processes are able to change them through fractionation and contamination with additives, respectively.

2. Material and methods

The samples of the oenological chain used for this study (e.g., rocks, soil, grape, grape juice, must, and wine) are from six different wine producers of the three 'Cesane' wine areas. The selected wines are indeed from: (i) 'Cesane di Olevano Romano' consortium (i.e. *Silene*, *Colle Canino*, and *Attis* Red wines); (ii) 'Cesane di Affile' consortium (i.e., *Cesane di Affile* Red wine), and from the 'Cesane del Piglio' Consortium (i.e. *Romanico* Red wine).

The wines analysed in this experimental study are from small vineyards (some 1–4 ha), owned by high-quality farmers who ensured the grapes' provenance and the controlled winemaking procedure. According to the consortia regulation all wines analysed are made from the *Cesane* red grape variety (monocultivar); this ensure from possible differential elemental uptake from soil via the vine roots as seen to occur for Rare Earth Elements (Censi, Saiano, Pisciotto, & Tuzzolino, 2014).

Multiple wine and must samples have been collected directly from tanks before bottling. Previous studies have shown that $^{87}\text{Sr}/^{86}\text{Sr}$ in wines from different vintage years is preserved unless contamination occurs (Boari et al., 2008; Durante et al., 2015; Marchionni et al., 2013; Mercurio et al., 2014; Petrini et al., 2015). In this experimental work, however, we decided to use for each vintage 5–7 samples of wine and must from a number of vintage years population to check the conservation of the amount of radiogenic Sr for wines from the same vineyard through the years and to reinforce the significance of the data used for evaluating the winemaking process. Grape juices have been also sampled to check for the absence of external inputs during the winemaking processes and the oenological chain from raw agricultural fruit to bottled wine.

In addition to wine, must, and grape, volcanic and sedimentary bedrocks along with soils from the vineyards of grape production have been sampled to verify the $^{87}\text{Sr}/^{86}\text{Sr}$ of the geological substrata of the Cesane area in comparison with the available data

for similar rocks (Boari, Avanzinelli, et al., 2009; Boari, Tommasini, et al., 2009; Conticelli, Avanzinelli, Ammannati, & Casalini, 2015; Conticelli et al., 2010). In addition the $^{87}\text{Sr}/^{86}\text{Sr}$ from rocks and soil of the vineyards substrata are necessary to assess the existing relationships with the Sr isotope composition of wines.

In some cases soils were sampled at different depths to evaluate isotopic variability of the different levels. In addition whole soil and volcanic samples and extracted leached solutions from them have been analysed. This has been done to assess the different Sr isotope compositions between the soil and the soil solution that regulates bioavailability for bio-vegetative processes. Considering rock-forming minerals experiencing weathering processes, differential leaching is to be expected, and only by chance the soil solution will have the same inorganic trace element and isotopic content of the bulk source rock or soil.

2.1. Sample preparation, digestion and Sr-purification

Rock samples have been brought first to sand-size material (<2 mm) using a jaw crusher then mechanically split to obtain a representative sample and eventually pulverised to powder-size, grain-size smaller than 100 μm (<400 mesh), using a ball mill. An agate ball mill is used in place of any other pulverisation metal device, to avoid possible trace element contamination (Takamasa & Nakai, 2009). Soil samples before splitting and pulverisation have been dried at 60 °C. Grape samples have been washed several times with highly purified Milli-Q® water (18.2 M Ω cm $^{-1}$) before digestion. Grape musts and wines did not undergo any treatment before digestion.

Successively rock and soil as well as grape, grape must and wine samples have been treated and prepared for mass spectrometric analyses in a clean chemistry laboratory equipped with conditioned (ca. 20 °C) and overpressured air ('Class 1000' environment).

Rock, grape, grape must, and wine samples underwent different digestion procedures. Some 50 mg of bulk soil and rock samples were digested in cleaned PFA beakers using a 1:4 mixture of concentrated HNO $_3$ and HF. After 1–2 days at 140 °C, solutions were evaporated to dryness, nitrated twice, dissolved in 6 N HCl at 120 °C, and eventually evaporated to dryness and dissolved again in 1 mL 3 N HNO $_3$. Digestion was performed using clean PFA beakers within horizontal HEPA-filtered laminar flow work-stations sited inside a fume cupboard. This environment ensures a low-blank working area. High purity chemical reagents and water during sample treatment have been also used. Concentrated HNO $_3$ (65–69 wt%), and H $_2$ O $_2$ (30 wt%) were of ultra-pure quality; concentrated HF (40–49 wt%) was of supra-pure quality; concentrated HCl (37 wt%) of pro-analysis quality was distilled using a quartz sub-boiling distillation device. Water was treated with two steps of purification to obtain high resistivity Milli-Q® water (18.2 M Ω cm $^{-1}$). Sr-purification was performed using cation exchange chromatography within a vertical HEPA-filtered laminar flow hood ('Class 100' environment) and high-purity chemical reagents.

In order to emulate the composition of the bioavailable soil solution fraction we used *Unibest* resin capsules (Unibest Inc., Bozeman MT). *Unibest* capsules are filled with ion exchange resins able to mimic the action of plant roots during uptake of bioavailable substances from soil (Skogley & Dobermann, 1996). The use of *Unibest* capsules overcomes the problem of the purity level of reagents employed in the traditional soil sequential extraction procedure of the bioavailable component of the soil. It has been shown that *Unibest* resin capsules represent an efficient 'universal-bioavailability' system for measuring inorganics in soils of very different origin and composition (Johnson, Verburg, & Arnone, 2005; Jones, Webb, Cook, & von Jolley, 2012; Skogley & Dobermann, 1996).

The ion accumulation into the resin capsules is time-dependent (Dobermann et al., 1994). We performed preliminary experiments on the extraction time needed to obtain the correct amount of Sr for isotopic analyses. According to Skogley and Dobermann (1996) some 200 g of soil were mixed with Milli-Q water and the Unibest spherical capsule (2 cm diameter) was allowed to sink and stay within the obtained mud solution for some 10 days. Then the capsule was extracted from the mud solution and rinsed with Milli-Q® water to remove soil residue from the surface, and then put in a cleaned PFA beaker with 20 ml 2 N HCl, repeated three times, to extract the chemical elements absorbed from the soil solution. Each time the 20 mL 2 N HCl solution was evaporated to dryness and eventually was dissolved in 1 mL 3 N HNO₃ for Sr purification. Extracted and purified bioavailable Sr fraction was then loaded onto a filament for mass spectrometric measurement.

Some 5–10 mL of wine, grape must, and grape juice, the latter from the squeezing of grape samples were evaporated to dryness at 90 °C in cleaned PFA beakers. The residues were dissolved twice in 3 mL of H₂O₂ (30 wt%) at 40 °C for 1 day and subsequently evaporated to dryness at 90 °C. The samples were then dissolved twice in 2 mL HNO₃ (67 wt%) at 150 °C for 1 day, evaporated to dryness and dissolved again in 1 mL 3 N HNO₃ for Sr purification (see also Boari et al., 2008; Marchionni et al., 2013). Digested samples were subsequently treated for Sr fraction purification with conventional cation exchange chromatography using disposable Sr-Spec resins (100–150 µm, Eichrom®) in 140 µL pure quartz micro-columns with 3 N HNO₃ as eluent and Milli-Q® water to collect Sr. Care was taken in calibration of the Sr-Spec resins in order to avoid the presence of Rb and Ba in the eluted Sr-enriched fraction to be mounted on the filament, although possible presence of ⁸⁷Rb in ultratrace is efficiently burn out during step heating before mass spectrometry measurements.

2.2. Sample loading and mass spectrometry analyses

Following cation exchange chromatography, some 100–200 ng of Sr for each sample were dissolved in 1 µL of 2 N HNO₃ and loaded on single Re filaments along with 1 µL of TaCl₅ (activator) and 1 µL of H₃PO₅ (fractionation suppressor).

Sr isotopes abundance (⁸⁸Sr, ⁸⁷Sr, ⁸⁶Sr, ⁸⁴Sr) have been measured in dynamic mode using a Thermo Finnigan™ Triton-Ti magnetic sector field thermal ionisation mass-spectrometer (TIMS) equipped with nine moveable collectors at the Department of Earth Sciences, University of Firenze. Measurements have been carried out using *multi-dynamic* mass collection procedure (i.e., peak jumping) to avoid bias due to different Faraday cup efficiencies (Avanzinelli et al., 2005). An idle time of 3 s has been 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 (Thirlwall, 1991). *Multi-dynamic* mass collection procedure provides two simultaneous but independent measurements of the ⁸⁷Sr/⁸⁶Sr, which once exponential law corrected and geometrically averaged gives a more accurate and precise ⁸⁷Sr/⁸⁶Sr value (Avanzinelli et al., 2005). The instrumental mass bias has been corrected *off line* with the ⁸⁸Sr/⁸⁶Sr ratio measured on the *main* configuration using the natural value (⁸⁸Sr/⁸⁶Sr_N = 8.375209) and an *exponential fractionation law* (Thirlwall, 1991). ⁸⁵Rb has been also monitored during Sr measurements on the L2 collector to correct for residual contribution (i.e., isobaric interference), if any, of ⁸⁷Rb to ⁸⁷Sr, using the natural ⁸⁷Rb/⁸⁵Rb (i.e., 0.386). Each single isotope measurement, consisting of 120 cycles, was performed using a signal of ca. 4 V on mass 88. Procedural blank was <200 pg, resulting in negligible sample correction. The external precision of NIST SRM987 international reference sample for the period of this study was ⁸⁷Sr/⁸⁶Sr = 0.710251 ± 10 (2σ, n = 20), whilst the long-term mean value was ⁸⁷Sr/⁸⁶Sr = 0.710248 ± 16

(2σ, n = 173, equivalent to an error of 23 ppm), identical to the widely accepted recommended value of Thirlwall (1991), ⁸⁷Sr/⁸⁶Sr = 0.710248 ± 11. The within-run precision (i.e., 2σ_m: internal precision) of ⁸⁷Sr/⁸⁶Sr measurements has been typically ≤10 ppm.

2.3. Statistical analysis

Classical linear regression analysis was used to model the relationship of the ⁸⁷Sr/⁸⁶Sr isotopic value for musts (y) and wines (x) thus taking into account that only must (y) is the variable subjected to uncertainty. However in our case both values x and y are subject to errors and the linear Deming regression (Deming, 1943) was also applied for comparison. In this regression technique the errors on x and y are considered independent and the ratio of their variance known and equal to 1 when the measurement method is the same or, alternatively, different from 1 when the variance of the errors can be estimated.

One-way analysis of variance (ANOVA) was considered the appropriate tool (Scheffé, 1999) to simultaneously compare the behaviour of a variable (⁸⁷Sr/⁸⁶Sr isotopic value) measured on diverse data groups (rocks, musts and wines in our case). The requirements of the method are for independent observations, normally distributed data in each group and equal variances for all groups. Since these are rarely met when working with applied geochemical and environmental data, also the non-parametric version was used (Kruskal–Wallis one-way analysis of variance by ranks, Spurrier, 2003) to avoid mistakes in the interpretation.

3. Results and discussion

The Sr isotope compositions of wine, must, grape juice, and grape from the different vineyards are reported in Table 1a, whilst those of soil, soil leachate, and bedrock are reported in Table 1b. Descriptive statistics of the overall Sr isotopic measurements performed on the different sample populations are reported in Table 2, whilst results of the ANOVA test are reported in the [electronic supplementary material](#).

3.1. Evaluation of the samples populations

To ensure the possibility that Sr isotope composition of wine and must used for this experimental study are statistically representative for being considered as a geographic provenance tracer, no yearly variability should be observed. Marchionni et al. (2013) have shown that in bottled red wines from different vintage years of the same geological area the Sr-isotope composition is preserved unless there is possible contamination, although in some cases within-area variability has been observed, possibly due to mixing with products characterised by different isotopic signatures.

In Fig. 1 are shown the ⁸⁷Sr/⁸⁶Sr values in wines from five different vineyards of the ‘Cesane’ wine region through the vintage years. Each vineyard under consideration has its own geologic substratum, with vineyards of *Romanico*, *Attis* and *Silene I* wines rooted on volcanic rocks of the Colli Albani volcano (Boari, Avanzinelli, et al., 2009), and vineyards of *Silene II* and *Colline di Affile* wines rooted on sedimentary rocks. With the exception of *Silene* wines the *Romanico*, *Attis*, and *Colline di Affile* wines show constant and reproducible Sr-isotope compositions independently of the wine vintage year (Fig. 1; see 3.2 for the rationale to consider wine along with grape must and grape for statistical calculation). The *Romanico* wines from the 2008, 2009, 2010, and 2011 vintages have, indeed, an average ⁸⁷Sr/⁸⁶Sr = 0.709982 (RSD 0.043%). The *Attis* wine from the 2006, 2007, and 2010 vintages has an average ⁸⁷Sr/⁸⁶Sr = 0.709705 (RSD 0.164%). Incidentally, the wine from the

Table 1
 $^{87}\text{Sr}/^{86}\text{Sr}$ of (a) wine, must, grape from Cesanese wine region; (b) soils and rocks from the substrata of vineyards of the Cesanese wine region.

Wine production area	Cultivar	Winery	Vineyard	Wine	Sample	Vintage	$^{87}\text{Sr}/^{86}\text{Sr}_m$	2 s.e.
<i>(a)</i>								
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ia	Wine	2003	0.709168	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ia	Must	2005	0.709177	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2006	0.709673	±0.000007
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Wine	2008	0.709629	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2009	0.709590	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2009	0.709632	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Wine	2010	0.709670	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2010	0.709545	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	San Giovenale	Silene Ib	Must	2011	0.709595	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Wine	2010	0.710586	±0.000008
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Must	2010	0.710377	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Grape	2010	0.710622	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Damiano Ciolli	Cerreto	Silene II	Wine	2011	0.709774	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2006	0.709633	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2007	0.709548	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Must	2009	0.709512	±0.000007
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2009	0.709628	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2010	0.709923	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Must	2011	0.709684	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Ermes	La Selva	Attis	Wine	2011	0.709619	±0.000005
Cesanese di Olevano Romano-DOC	Cesanese	Colle Canino	Colle Canino	Colle Canino	Wine	2010	0.709674	±0.000006
Cesanese di Olevano Romano-DOC	Cesanese	Colle Canino	Colle Canino	Colle Canino	Wine	2010	0.709771	±0.000007
Cesanese di Olevano Romano-DOC	Cesanese	Colle Canino	Colle Canino	Colle Canino	Wine	2010	0.709873	±0.000008
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2005	0.709046	±0.000006
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2009	0.708978	±0.000006
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2009	0.709254	±0.000006
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2009	0.709145	±0.000006
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2010	0.709025	±0.000006
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2010	0.709042	±0.000006
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2010	0.709024	±0.000005
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Must	2010	0.708991	±0.000005
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Grape	2010	0.708938	±0.000007
Cesanese di Affile-DOC	Cesanese	Colline di Affile	Colle Faggiano	Cesanese d'Affile	Wine	2011	0.709007	±0.000006
Cesanese di Affile-DOC	Cesanese	Terre del Cesanese	Colle Passo	Terre del Cesanese	Wine	2010	0.709966	±0.000005
Cesanese di Affile-DOC	Cesanese	Terre del Cesanese	Colle Passo	Terre del Cesanese	Grape	2010	0.709627	±0.000007
Cesanese del Piglio-DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2008	0.709965	±0.000006
Cesanese del Piglio-DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2009	0.709989	±0.000005
Cesanese del Piglio-DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2010	0.710010	±0.000006
Cesanese del Piglio-DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Must	2010	0.709782	±0.000009
Cesanese del Piglio-DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Grape	2010	0.710189	±0.000024
Cesanese del Piglio-DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Wine	2011	0.709961	±0.000005
Cesanese del Piglio-DOCG	Cesanese	Coletti Conti	Colle Cotoverio	Romanico	Must	2011	0.710006	±0.000005
Wine production area	Rock type	Lithology	Sample description	Vineyard	Sample	Analysis	$^{87}\text{Sr}/^{86}\text{Sr}_m$	2 s.e.
<i>(b)</i>								
Cesanese di Olevano-DOC	Volcanic	Soil	Soil on Villa Senni Formation	San Giovenale	–25 cm	Whole	0.711386	±0.000006
Cesanese di Olevano-DOC	Volcanic	Soil	Soil on Villa Senni Formation	San Giovenale	–25 cm	Leached	0.709947	±0.000005
Cesanese di Olevano-DOC	Volcanic	Soil	Soil on Villa Senni Formation	San Giovenale	–60 cm	Whole	0.711421	±0.000007
Cesanese di Olevano-DOC	Volcanic	Soil	Soil on Villa Senni Formation	San Giovenale	–60 cm	Leached	0.710147	±0.000006
Cesanese di Olevano-DOC	Volcanic	Ignimbrite	Villa Senni Formation	San Giovenale	Rock	Whole	0.711238	±0.000006
Cesanese di Olevano-DOC	Volcanic	Ignimbrite	Villa Senni Formation	San Giovenale	Rock	Leached	0.710232	±0.000006
Cesanese di Olevano-DOC	Sedimentary	Sandstone	Arenaceous-Pelitic Formation	Cereto	Rock	Whole	0.717961	±0.000006
Cesanese di Olevano-DOC	Sedimentary	Sandstone	Arenaceous-Pelitic Formation	Cereto	Rock	Whole	0.715146	±0.000006
Cesanese d'Affile-DOC	Sedimentary	Marlstone	Orbulina Marl	Colle Faggiano	Rock	Whole	0.709136	±0.000006
Cesanese d'Affile-DOC	Sedimentary	Limestone	Briozoa Limestone	Colle Faggiano	Rock	Whole	0.708851	±0.000007
Cesanese del Piglio-DOCG	Volcanic	Soil	Soil on Pozzolane Rosse Formation	Colle Cotoverio	–10 cm	Whole	0.710562	±0.000006
Cesanese del Piglio-DOCG	Volcanic	Soil	Soil on Pozzolane Rosse Formation	Colle Cotoverio	–10 cm	Leached	0.710032	±0.000006
Cesanese del Piglio-DOCG	Volcanic	Ignimbrite	Pozzolane Rosse Formation	Colle Cotoverio	Rock	Whole	0.710560	±0.000006
Cesanese del Piglio-DOCG	Volcanic	Ashfall	Madonna degli Angeli Formation	Colle Cotoverio	Rock	Whole	0.711104	±0.000006
Cesanese del Piglio-DOCG	Volcanic	Surge	Madonna degli Angeli Formation	Colle Cotoverio	Rock	Whole	0.711489	±0.000006
Cesanese del Piglio-DOCG	Sedimentary	Ashfall	Madonna degli Angeli Formation	Colle Cotoverio	Rock	Whole	0.711049	±0.000006
Cesanese del Piglio-DOCG	Sedimentary	Ashfall	Madonna degli Angeli Formation	Colle Cotoverio	Rock	Leached	0.710302	±0.000006
Cesanese del Piglio-DOCG	Volcanic	Ignimbrite	Pozzolane Rosse Formation	Colle Cotoverio	Rock	Whole	0.710565	±0.000006

(a) $^{87}\text{Sr}/^{86}\text{Sr}$ values in wine, grape juice, must, and grape from the different vineyards and vintage years of the Cesanese Consortium wine area are reported. All analysed samples are from the Cesanese di Affile red grape variety. (b) $^{87}\text{Sr}/^{86}\text{Sr}$ values in soil, bedrock, and leachable soil solution fraction of the different vineyards of the Cesanese Consortium wine area are reported. Rock type and Lithology columns report the type of geological substratum of vineyards sampled and analysed, whilst the Sample description column reports the identification name of local geological formations (Giordano & the CARG team, 2010). 2 s.e. represent the within run two standard error of the mean referring to the last significant digits. The limestone sample (AF2) from the Colle Faggiano area does not correspond to the substratum of any vineyard; *: leached soil solution fraction using UNIBEST® resins; 2sm: within run two standard error of the mean referring to the last significant digits.

2010 vintage has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and different from the grape of the same vintage, which is similar to the other *Attis* samples (Table 1). This discrepancy is readily explained because the

producers during the 2010 winemaking processes added also grapes from another vineyard located to the south-east of Olevano Romano with geologic substratum consisting of Late

Table 2
Descriptive statistic of the samples from the oenological food chain and winery substrata.

Wineyard	Wine	Sample type	Mean	Standard error	Median	Standard deviation	Sample variance	Kurtosis	Sweekness	Range	Min	Max	Counts
San Giovenale		Rock	0.711235	0.000004	0.711235	0.000041	1.714E-09	0.304635	-0.370324	0.000212	0.711113	0.711325	120
San Giovenale		Rock leached	0.710231	0.000004	0.710231	0.000041	1.7183E-09	-0.485492	0.063509	0.000187	0.710145	0.710332	120
San Giovenale		Soil	0.711405	0.000003	0.711407	0.000048	2.2949E-09	-0.189918	0.228658	0.000231	0.711299	0.711530	240
San Giovenale		Soil leached	0.710049	0.000007	0.710047	0.000109	1.1809E-08	-1.538286	-0.027509	0.000413	0.709819	0.710233	240
San Giovenale	Silene Ib	Must	0.709608	0.000002	0.709608	0.000059	3.5309E-09	-0.234614	-0.031147	0.000329	0.709443	0.709772	600
San Giovenale	Silene Ib	Wine	0.709650	0.000003	0.709652	0.000044	1.9008E-09	0.009289	-0.020265	0.000247	0.709528	0.709775	240
San Giovenale	Silene Ia	Must	0.709182	0.000003	0.709183	0.000038	1.4414E-09	-0.074063	-0.141362	0.000195	0.709070	0.709266	120
San Giovenale	Silene Ia	Wine	0.709171	0.000004	0.709167	0.000040	1.6156E-09	0.224525	0.202043	0.000220	0.709062	0.709283	120
Cerreto		Rock	0.716557	0.000091	0.716544	0.001414	1.9985E-06	-2.013217	0.000335	0.003022	0.715045	0.718066	240
Cerreto	Silene II	Must	0.710379	0.000003	0.710378	0.000037	1.3924E-09	-0.162798	0.045294	0.000190	0.710287	0.710477	120
Cerreto	Silene II	Wine	0.710173	0.000026	0.709930	0.000409	1.6721E-07	-1.927388	0.076921	0.001152	0.709682	0.710834	240
La Selva	Attis	Must	0.709611	0.000003	0.709621	0.000074	5.4865E-09	-0.165869	-0.387209	0.000416	0.709391	0.709806	240
La Selva	Attis	Wine	0.709705	0.000009	0.709640	0.000164	2.6994E-08	-1.367571	0.502110	0.000555	0.709473	0.710029	600
Colle Canino	Colle Canino	Wine	0.709773	0.000014	0.709771	0.000272	7.3941E-08	78.563286	-5.525301	0.004537	0.706286	0.710823	355
Colle Faggiano		Rock	0.708995	0.000010	0.708997	0.000149	2.2164E-08	-1.645372	-0.010544	0.000531	0.708748	0.709279	240
Colle Faggiano	Cesanese di Affile	Grape	0.708950	0.000004	0.708949	0.000047	2.1631E-09	0.249664	0.327964	0.000242	0.708848	0.709090	120
Colle Faggiano	Cesanese di Affile	Must	0.709105	0.000005	0.709088	0.000112	1.2446E-08	-1.148793	0.286425	0.000459	0.708903	0.709362	480
Colle Faggiano	Cesanese di Affile	Wine	0.709020	0.000002	0.709020	0.000049	2.4082E-09	0.022683	-0.069918	0.000341	0.708847	0.709188	600
Colle Passo	Terre del Cesanese	Grape	0.709627	0.000005	0.709625	0.000053	2.778E-09	0.251209	-0.071310	0.000262	0.709493	0.709755	120
Colle Passo	Terre del Cesanese	Wine	0.709965	0.000003	0.709965	0.000036	1.3251E-09	0.040734	-0.049852	0.000199	0.709861	0.710061	120
Colle Cotoverio		Rock	0.710957	0.000015	0.711048	0.000365	1.3356E-07	-1.220042	0.144197	0.002033	0.709878	0.711911	600
Colle Cotoverio		Soil	0.710564	0.000004	0.710563	0.000043	1.8435E-09	0.052131	0.199281	0.000231	0.710453	0.710684	120
Colle Cotoverio		Soil leached	0.710030	0.000004	0.710025	0.000040	1.5955E-09	-0.572833	0.011641	0.000180	0.709934	0.710115	120
Colle Cotoverio	Romanico	Grape	0.710175	0.000103	0.710180	0.000959	9.1936E-07	53.137531	-5.238089	0.011807	0.702467	0.714274	87
Colle Cotoverio	Romanico	Must	0.709896	0.000008	0.709931	0.000126	1.595E-08	-0.494381	-0.464343	0.000638	0.709448	0.710086	240
Colle Cotoverio	Romanico	Wine	0.709982	0.000002	0.709981	0.000043	1.8248E-09	-0.325535	0.081127	0.000233	0.709875	0.710109	480

Dataset used for the statistics definition is made by the overall Sr-isotopes instrumental measurements.

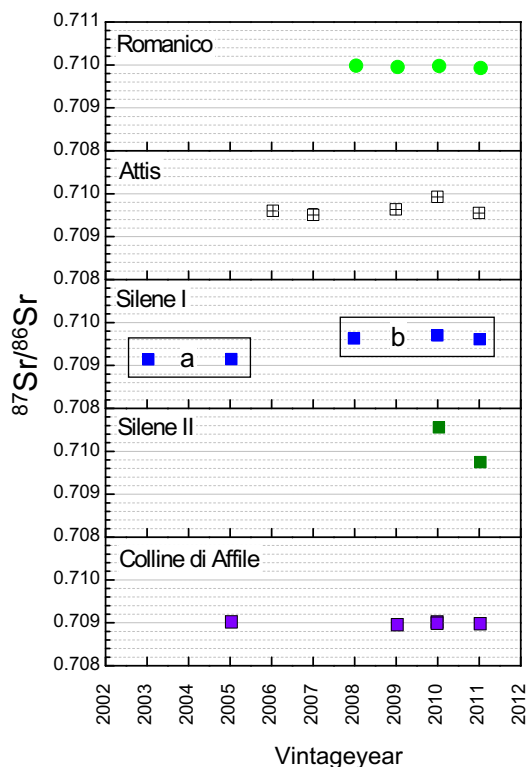


Fig. 1. $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of wines of the five sampled vineyards of the Cesanese consortia collected from the 2003 through 2011 vintage years.

Miocene sandstones with a highly radiogenic Sr isotope signature (Table 1b). Neglecting the 2010 wine sample, the *Attis* wines has an average $^{87}\text{Sr}/^{86}\text{Sr} = 0.709924$ (RSD 0.004%). The *Cesanese di Affile* wines from the 2005, 2009, 2010, and 2011 vintages have an average $^{87}\text{Sr}/^{86}\text{Sr} = 0.709020$ (RSD 0.049%). On the other hand, the *Silene* wines from the San Giovenale (I) and Cereto (II) vineyards (Table 1a) show large isotopic differences in the isotopic signature due to their different substrata (Table 1b). In addition, *Silene* wines from vineyard I (San Giovenale) show an abrupt jump of $^{87}\text{Sr}/^{86}\text{Sr}$ values from 0.709168 ± 5 (vintage 2003) and 0.709177 ± 5 (vintage 2005) to 0.709629 ± 5 (vintage 2008), 0.709670 ± 6 (vintage 2010), and 0.709595 ± 6 (vintage 2011). The farmer declared that during the 2003 grape growth season lime to the vineyard substratum of the vineyard I (San Giovenale) was added to correct the pH of the soil. The addition of lime, with a likely $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.709 (as the average value of seawater; Edmond, 1992; Palmer & Elderfield, 1985), is reflected in a lower Sr isotope composition of the 2003 vintage, with a protracted action thought the 2005 and 2006 vintages (Table 1a). The increase of the $^{87}\text{Sr}/^{86}\text{Sr}$, approaching the values of the volcanic substratum (Boari, Avanzinelli, et al., 2009), in the products since 2006 vintage year indicates that no further addition of lime was performed. The farmer also declared for the *Silene* wine of vineyard II (i.e., Cerreto) only the vintage 2010 was entirely made with grapes from the II vineyard whilst the 2011 was made with grapes from both vineyards, having different geological substrata, thus explaining the drop from 0.710586 ± 8 to 0.709774 ± 5 (Table 1).

In summary, replicate high precision $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of wines from the same vineyard and produced with harvests from different vintage years show the consistency of Sr-isotope values through time. As a confirmation the discrepancies observed are usually related either to mixing of grapes from different vineyards during the winemaking processes or to addition of lime to the soil of the

vineyard for agricultural purpose. Indeed, addition of lime to the vineyard substratum of *Silene* wine in the 2003 explains the lower $^{87}\text{Sr}/^{86}\text{Sr}$ values of 2003, 2005, and 2006 vintages with respect to values of the 2008, 2009, and 2010 vintages (Fig. 1). The Sr isotope composition of the 2010 vintage *Attis* wine is higher than other *Attis* wines and the 2010 grape (Fig. 1) because the producer added grapes from another vineyard located in a sandstone substratum. These preliminary checks helped to better refine the population used for the further steps of this study.

3.2. $^{87}\text{Sr}/^{86}\text{Sr}$ does not change during winemaking processes

To evaluate the effect of winemaking processes in the production of red wine, grape juice and must have been analysed and compared with the values of $^{87}\text{Sr}/^{86}\text{Sr}$ of wine samples (Table 1a). Grape juices, musts, and wines from the same vineyard and vintage years display similar $^{87}\text{Sr}/^{86}\text{Sr}$ values within the calculated standard deviation of each wine (Table 2). Indeed, considering that no variation has been observed in wines (Fig. 1), musts and grape juices (Table 1), the obtained data have been then used as a whole, calculating statistics for each type of product from the same vineyard. Then in Table 2 the statistics of the overall $^{87}\text{Sr}/^{86}\text{Sr}$ measurements obtained during the experimental work are reported.

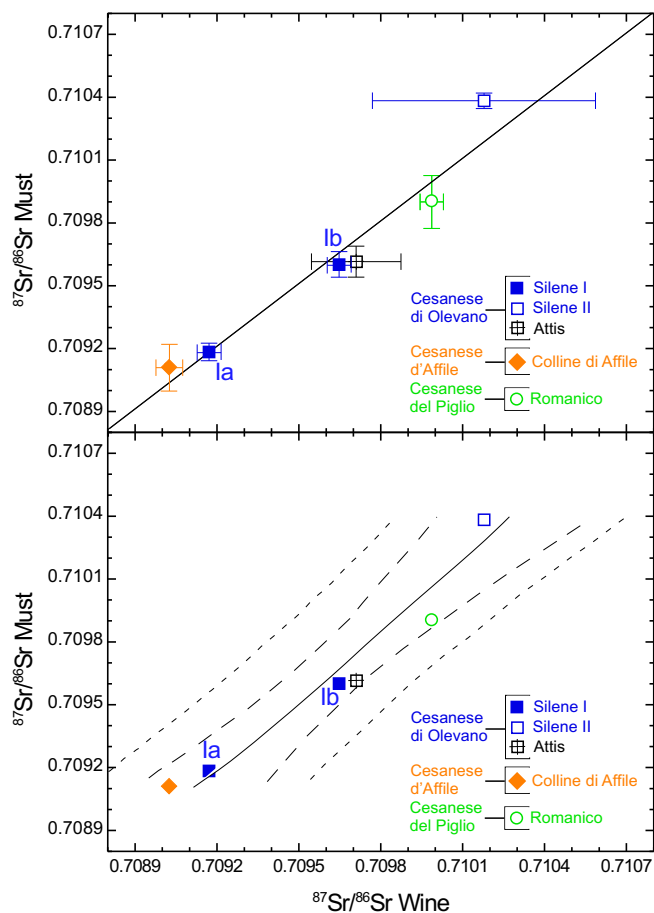


Fig. 2. (top) Relationships between $^{87}\text{Sr}/^{86}\text{Sr}$ in wines and in their original musts. Error bars represent the standard deviation of the mean values for the whole isotope analyses performed on the samples. (bottom) Linear regression model for $^{87}\text{Sr}/^{86}\text{Sr}$ in wines and musts. Internal dashed curves are the confidence bands defining the area that has a 95% chance of containing the true regression line. External dashed curves represent the prediction band, the area in which 95% of all data points are expected to fall.

Fig. 2a reports correlation between wines and musts from the same vineyard with values approaching the 1:1 correlation line, at least within the standard deviation brackets. The largest standard deviations, with mean values falling well outside of the 1:1 correlation line, are shown by the *Silene II* and the *Attis* wines (Tables 1a and 2). The two outliers observed correspond to the wines that were produced using mixing of grapes from vineyards with different geological substrata. Grape juice has been also analysed but not reported in Fig. 2 due to the few data available, but their $^{87}\text{Sr}/^{86}\text{Sr}$ plot well within the standard deviation of must and wines (Tables 1a and 2).

To obtain a model for the relationship between wines and musts a linear fitting was calculated and reported in Fig. 2b. Internal dashed curves are the confidence bands defining the area that has a 95% chance of containing the true regression line. External dashed curves represent the prediction band, which is the area in which 95% of all data points are expected to fall. The regression equation is given by $(^{87}\text{Sr}/^{86}\text{Sr} \text{ must}) = 0.01257 + 1.0177 (^{87}\text{Sr}/^{86}\text{Sr} \text{ wine})$ with r^2 equal to 0.94 and slope values statistically significant ($p < 0.01$). Deming regression (Deming, 1943), applied when both values x and y are subject to uncertainty as in our case, leads to the model $(^{87}\text{Sr}/^{86}\text{Sr} \text{ must}) = -0.04915 + 1.0693(^{87}\text{Sr}/^{86}\text{Sr} \text{ wine})$. If the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic value is considered a dependent variable measured on different groups of data as rock, must and wine, one-way analysis of variance (ANOVA) is appropriate to test for existing differences. Results are reported in the electronic supplementary material. These indicate that the data grouping is not statistically significant for the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic value; thus the correlations observed are statistically consistent. Similar results were obtained for the non-parametric version of ANOVA (Kruskal–Wallis one-way analysis of variance by ranks; Spurrier, 2003).

In summary, Sr isotopes are preserved during good winemaking practices for $^{87}\text{Sr}/^{86}\text{Sr}$ determination, performed at the precision levels of geological materials (Thirlwall, 1991), on high quality wines and related grape juices.

3.3. Matches between $^{87}\text{Sr}/^{86}\text{Sr}$ of oenological food chain and those of the substratum

The vineyards from flatlands of the Cesanese consortia are characterised by volcanic rocks in their geological substratum, dominated by pyroclastic rocks erupted by the Colli Albani volcano (e.g., Boari, Avanzinelli, et al., 2009; Giordano & the CARG team, 2010). On the other hands, vineyards from hills are characterised by substrata made up of Mesozoic to Tertiary sedimentary rocks (limestone, marlstone, sandstone; Critelli et al., 2007). $^{87}\text{Sr}/^{86}\text{Sr}$ determined on rocks and soils sampled from substrata of the vineyards used in the production of the wines considered in this study are well within the ranges of measured $^{87}\text{Sr}/^{86}\text{Sr}$ for volcanic and sedimentary rocks of the Cesanese area and of the Italian peninsula in general (Boari, Avanzinelli, et al., 2009; Boari, Tommasini, et al., 2009; Conticelli et al., 2015).

Marchionni et al. (2013) has shown that at a very large scale $^{87}\text{Sr}/^{86}\text{Sr}$ of wines matches the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values of the geological substrata of the areas of production, especially when the rocks of the substrata are of volcanic origin. This suggests that $^{87}\text{Sr}/^{86}\text{Sr}$ may represent a robust tool in tracing geographic provenance of wines. However, Marchionni et al. (2013) have also shown that in some cases $^{87}\text{Sr}/^{86}\text{Sr}$ variability in wines is larger than expected from the analyses of the geological substratum (i.e., rocks). In the present study to exploit the origin of radiogenic Sr, and to evaluate their influence we sampled in detail and analysed the rocks making the geological substratum of each vineyard (Table 1b). Fig. 3 reports the $^{87}\text{Sr}/^{86}\text{Sr}$ together with the 1:1 correlation line. If exception is made for the *Cesanese di Affile* wine from *Colle Faggiano* vineyard, which plots along the 1:1 line, the other

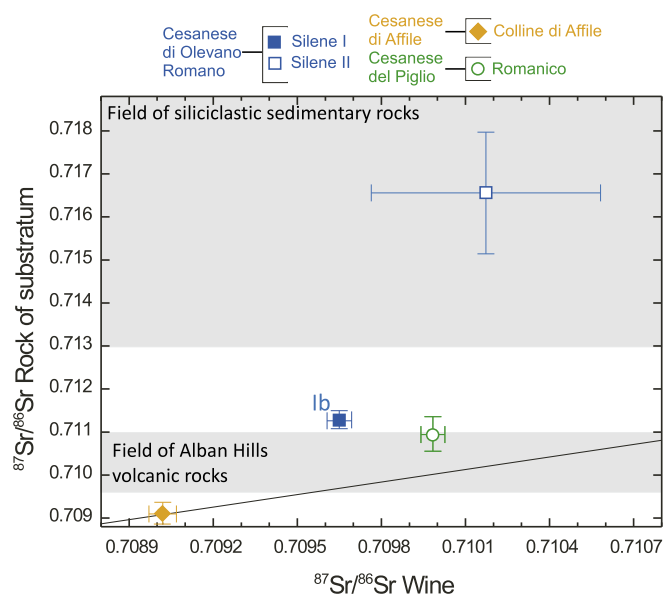


Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ of wines vs the Sr-isotope composition in the whole rocks of the substrata of their vineyards. Error bars represents the standard deviation of the mean values for the whole isotope analyses performed on the samples. Grey fields are drawn on the basis of data from the scientific literature (e.g., Conticelli et al., 2015; Melluso, Conticelli, D'Antonio, Mirco, & Saccani, 2003).

wine/rock pairs plot at higher $^{87}\text{Sr}/^{86}\text{Sr}$ with respect to 1:1 line, indicating that wines are less enriched in radiogenic Sr with respect to the rocks of the substrata of their vineyards (Fig. 3). This feature is mainly observed in wines from vineyards over sedimentary bedrocks rather than those on volcanic ones. Indeed, wines from vineyards on volcanic rocks plot not too far from the 1:1 line (Fig. 3) and well within the range of the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Alban Hills volcano (Boari, Avanzinelli, et al., 2009; Conticelli, D'Antonio, Pinarelli, & Civetta, 2002).

Halicz, Segal, Fruchter, Stein, and Lazar (2008) have shown that significant difference between the $^{88}\text{Sr}/^{86}\text{Sr}$ fractionation in soils could have an effect on the calculated fractionation factor and thus on the corrected value of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soils, but correction would only affect the values of high-precision measurements. In our cases the discrepancies observed are three orders of magnitude larger than those due to $\delta^{88}\text{Sr}/^{86}\text{Sr}$ fractionation in surficial environments (Halicz et al., 2008). Thus possible causes of the deviation of $^{87}\text{Sr}/^{86}\text{Sr}$ of wines from vineyards on sedimentary substrata from the expected geological $^{87}\text{Sr}/^{86}\text{Sr}$ values have been investigated in detail by Braschi (2015, Pers. Comm.). Here we investigated only the cases in which the deviation is observed in vineyards with geological substrata made of volcanic rocks.

For *Romanico* and *Silene Ib* vineyards we have measured $^{87}\text{Sr}/^{86}\text{Sr}$ in wines, musts, soils at different depths and underlying rocks (Tables 1 and 2). For soils we performed $^{87}\text{Sr}/^{86}\text{Sr}$ after leaching experiments, to assess the Sr isotope composition of the bioavailable fraction in soil solutions. The data on leached solutions reveal different Sr isotope compositions with respect to the corresponding soil and bedrock (Table 1). The Sr isotope composition of wines from vineyards located on volcanic substrata (*Romanico*, *Attis*, and the first *Silene* vineyard) are less radiogenic than the bulk soil/bedrock but similar to the leached soil solution. Indeed, all of the bioavailable fractions analysed have $^{87}\text{Sr}/^{86}\text{Sr}$ less radiogenic than the bulk material (Fig. 4), indicating the prevalent contribution to the Sr content of the soil solution of a 'relatively unradiogenic' phase (e.g. feldspar and glass rather than biotite). In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ values of leached solutions approach the values of final grape products (must/wine) with decreasing depth

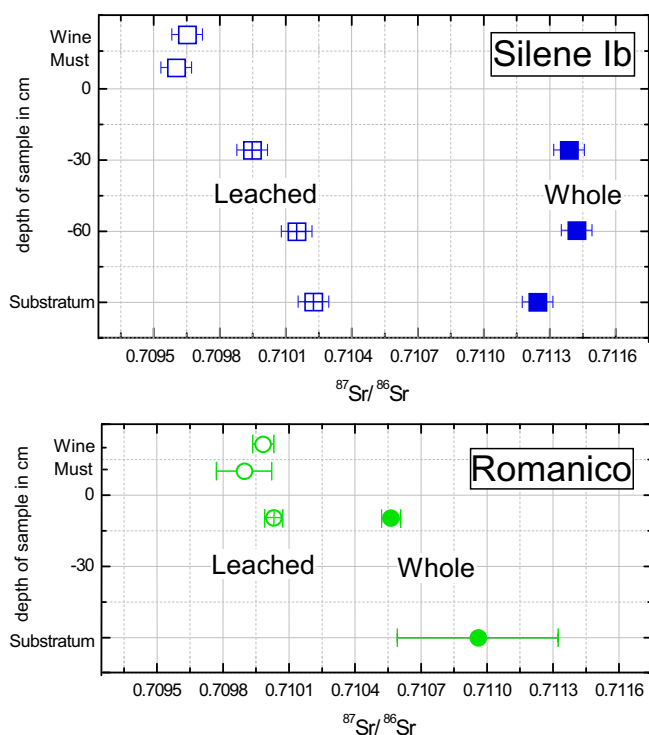


Fig. 4. Relationships among $^{87}\text{Sr}/^{86}\text{Sr}$ in wines and musts and the Sr-isotope values in the substratum (rock and soil). Note that samples are from different depths beneath the vineyards. In addition $^{87}\text{Sr}/^{86}\text{Sr}$ in soil horizons have been determined on both whole sample and extracted leached solutions, see text for further explanations.

finding the possible horizon of roots uptake between 20 and 30 cm depth (Fig. 4).

3.4. Summary and conclusions

In this study we have shown that, independently from wine-making procedure and vintage year, wine inherits its Sr isotope composition from the vineyard pedogenetic substratum, making $^{87}\text{Sr}/^{86}\text{Sr}$ a paramount candidate for being a robust and technologically advanced scientific tool for assessing of authenticity of the geographic provenance issues. As a corollary, the observed discrepancies in Attis wines reinforce the results of our study in that we could directly measure the Sr isotope variation in wine forced by external causes (i.e., lime addition and grape mixing).

The selective extraction of chemical elements by vine-roots, according to their bioavailability, limits the precise correspondence between $^{87}\text{Sr}/^{86}\text{Sr}$ in bulk soils and wines. Further detailed studies are needed to scientifically demonstrate the mechanism for Sr-isotope variability in wines from extremely complex sedimentary substrata. Indeed, the bioavailable organic and inorganic substances in soil solutions differ from the bulk soil composition and can be either extremely variable in clastic and polymineral weathered rocks (soils on sandstones, and granites), or negligible in more homogeneous weathered rocks (soils on marls, clays, limestones, glassy volcanic rocks) as shown in this study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2015.06.026>.

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