

High-Precision $^{87}\text{Sr}/^{86}\text{Sr}$ Analyses in Wines and Their Use as a Geological Fingerprint for Tracing Geographic Provenance

Sara Marchionni,[†] Eleonora Braschi,[‡] Simone Tommasini,[†] Andrea Bollati,[§] Francesca Cifelli,[§] Nadia Mulinacci,[#] Massimo Mattei,^{*,§} and Sandro Conticelli^{*,†,⊥}

[†]Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy

[‡]U.O.S. Firenze, Istituto di Geoscienze e Georisorse, CNR, Via G. La Pira 4, I-50121 Firenze, Italy

[§]Dipartimento di Scienze, Università degli Studi di Roma TRE, Largo G. Murialdo 1, I-00146 Roma, Italy

[#]CeRA – Centro interdipartimentale di Ricerca per la valorizzazione degli Alimenti and Dipartimento di Scienze Farmaceutiche, Università degli Studi di Firenze, Via Ugo Schiff 6, I-50019 Sesto Fiorentino, Italy

[⊥]CISM – Mass Spectrometry Center, Università degli Studi di Firenze, I-50019 Sesto Fiorentino, Italy

Supporting Information

ABSTRACT: The radiogenic isotopic compositions of inorganic heavy elements such as Sr, Nd, and Pb of the food chain may constitute a reliable geographic fingerprint, their isotopic ratios being inherited by the geological substratum of the territory of production. The Sr isotope composition of geomaterials (i.e., rocks and soils) is largely variable, and it depends upon the age of the rocks and their nature (e.g., genesis, composition). In this study we developed a high-precision analytical procedure for determining Sr isotopes in wines at comparable uncertainty levels of geological data. With the aim of verifying the possibility of using Sr isotope in wine as a reliable tracer for geographic provenance, we performed Sr isotope analyses of 45 bottled wines from four different geographical localities of the Italian peninsula. Their Sr isotope composition has been compared with that of rocks from the substrata (i.e., rocks) of their vineyards. In addition wines from the same winemaker but different vintage years have been analyzed to verify the constancy with time of the $^{87}\text{Sr}/^{86}\text{Sr}$. Sr isotope compositions have been determined by solid source thermal ionization mass spectrometry following purification of Sr in a clean laboratory. $^{87}\text{Sr}/^{86}\text{Sr}$ of the analyzed wines is correlated with the isotopic values of the geological substratum of the vineyards, showing little or no variation within the same vineyard and among different vintages. Large $^{87}\text{Sr}/^{86}\text{Sr}$ variation is observed among wines from the different geographical areas, reinforcing the link with the geological substratum of the production territory. This makes Sr isotopes a robust geochemical tool for tracing the geographic authenticity and provenance of wine.

KEYWORDS: high-precision Sr isotopes, wine, geology and wine, geographic traceability

INTRODUCTION

The certification of authenticity and origin of food products is increasingly gaining importance within modern society. Health and safety of merchandise along with dictates on their quality standards have great consideration in present-day government legislation. Wines are no exception, and the laws affecting naming by geographic origin are the most well-known (i.e., *appellation contrôlée*). Geographic limits of designated wine production areas often correspond to the boundaries of specific geologic and geomorphologic features. Indeed, besides cultivar variety and enological practice, the soil type, geomorphology, and climate are thought to give wines distinctive attributes.

Major wine-producing countries have developed severe Appellation Control laws that regulate the use of regional names for wines. In Italy, Appellation Control laws have three levels of dictates that define (i) only the geographic origin for IGT (Typical Geographic Indication) wines and (ii) also the grape varietal use and production practices and limits, in the case of DOC (Denomination of Origin Verified) wines, along with (iii) the addition of yearly sensory evaluation for DOCG (Denomination of Origin Verified and Guaranteed) wines. In all cases the Appellation Control laws provide the reference for delimiting the geographical origin of the wines, which is

considered a fundamental indication of quality for consumers. To guarantee the geographic provenance several scientific methods have been established for wines and, in general, for foods to provide a further quality warranty for the consumer.^{1–10}

The challenge that scientists are called to face is to establish unambiguous parameters to identify the *terroir* in which the wines are produced. Chemical analysis is routinely performed in testing procedures to identify wine adulteration. Especially stable isotopes of light elements (e.g., $\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$) are widely used for this purpose. These stable isotope values can also be used for provenance determinations of wines, although a conclusive differentiation has not always been straightforward due to several factors controlled by yearly climatic variations.^{7,11,12}

A slightly simpler approach might be to measure the isotopic composition of inorganic trace elements, such as Sr, occurring in wines as inherited from the rock/soil on which the vine is

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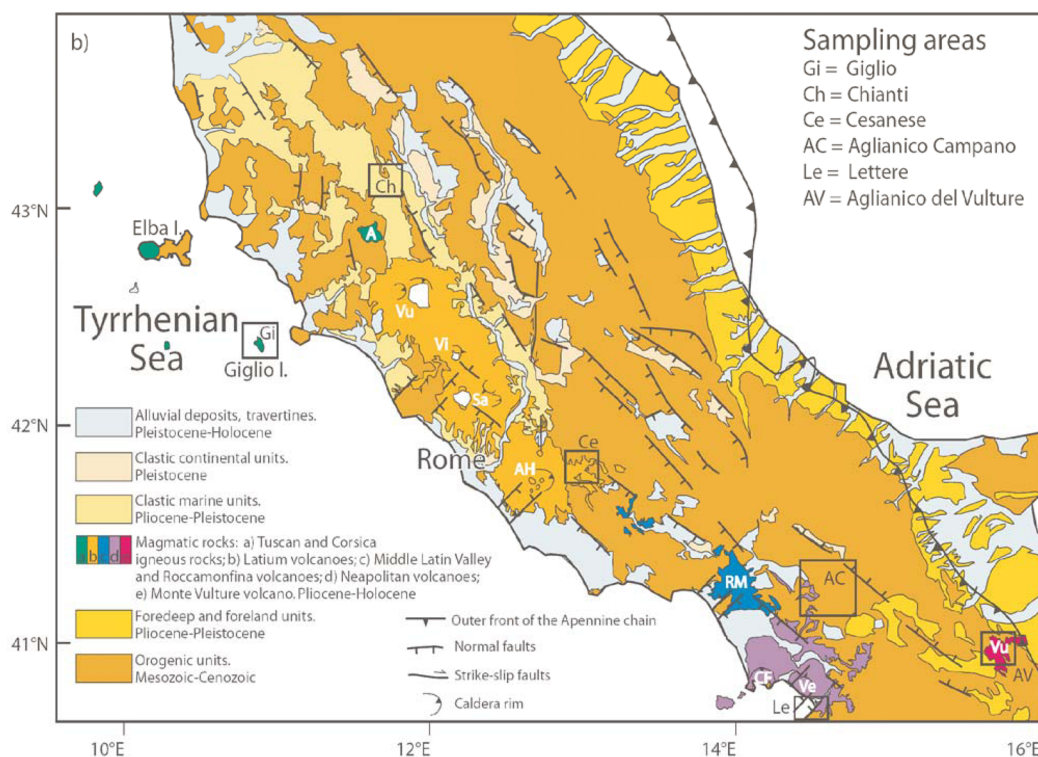


Figure 1. Geological sketch map of the central Italian peninsula. The six boxes indicate the wine areas under study in this paper.

grown.^{1,2,5–7,18,19} Sr is captured by the vine roots together with nutrients, among those leachable and hence available to biovegetative processes. The use of isotope ratios of certain key heavy trace elements (e.g., Sr, Nd, Pb) is a well-established tool in geology, geochemistry, and cosmochemistry for dating and tracing the origin of rocks and minerals.¹³ The well-established knowledge of Sr, Nd, and Pb isotopic ratios in rocks, in the past decades, and an increasing number of applications of isotope geology to environmental, archeological, forensic, medical, and food science have been successfully deployed.^{14–16}

The success of this geologic method of regional tracing resides in the fact that no Earth or extraterrestrial rocks have the same isotopic composition unless they were generated in the same environment and at the same time (i.e., they are the same rock).^{13,17} Indeed, the present day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of geological materials (i.e., rocks) is the result of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the time of the rock's formation and the ^{87}Sr added owing to the time-dependent radioactive decay of ^{87}Rb . Indeed, rock-forming geological processes are capable of significantly fractionating Rb from Sr up to 6 orders of magnitude ($0.001 > \text{Rb}/\text{Sr} > 1000$), making the Rb–Sr isotopic system an efficient method for dating rocks or, alternatively, if the age of rock formation is known, it may be used to derive the origin of the rock and to track geodynamic processes within the Earth's interior.²¹ Then old crystalline rocks have distinct $^{87}\text{Sr}/^{86}\text{Sr}$ values for each mineral species, as the result of different Rb/Sr of minerals and consequently different ^{87}Sr ingrowth due to ^{87}Rb decay.¹³ Young (<1 Ma) glassy volcanic rocks, due to their recent formation age and low crystalline contents, have bulk $^{87}\text{Sr}/^{86}\text{Sr}$ close to the initial value recorded at the time of their crystallization, with a highly homogeneous internal distribution. Then young volcanic rocks represent the ideal geological substratum for investigating in some detail Sr uptake from

plants and the use of $^{87}\text{Sr}/^{86}\text{Sr}$ as a possible geochemical tracer of foods provenance.

Grapes from different microregions within the same climate zone have similar $\delta^2\text{H}$ and $\delta^{18}\text{O}$, but in theory they can have different Sr isotope compositions.^{18–20} Then $^{87}\text{Sr}/^{86}\text{Sr}$ has the potential to supply an additional level of geographic resolution to high-quality wine provenance issues. Indeed, different lithologies can occur within the same wine district, implying that different Sr isotope compositions are liable to be measured in wines from a given vineyard and to differ from other adjoining vineyards.

Preliminary studies have shown the existence of some degree of $^{87}\text{Sr}/^{86}\text{Sr}$ variation in wines from different production areas.^{1,2,5–7,18–20} Despite these published data, however, the use of radiogenic isotopes of geological interest for tracing wine provenance is far from being a well-established method yet. The few published $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of wines show a large analytical uncertainty, ranging from 50 to 366 ppm and from 140 to 2770 ppm for TIMS and ICP-MS analyses, respectively.^{1,5–7,18–20} These values are far from the analytical quality expected for geochemical data.²⁰ Indeed, the error levels of the published $^{87}\text{Sr}/^{86}\text{Sr}$ data on wine cover the range of a large portion of terrestrial rocks and soil, including, for example, all limestones and most of the young volcanic rocks (<1 Ma) worldwide, hence preventing any possible real correlation with them.^{13,21} The published papers, however, demonstrated that the winemaking process does not affect the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio but neglected to study the possible variations in wines from different vintage years and the relationships with the geological substratum of the vineyards.^{1,2,18–20,23–25} In summary, the published studies have very limited application because they were performed on a very small set of samples and have very large error levels, which in some cases are not comparable to radiogenic Sr isotope variation in terrestrial soils and rocks.

In this study we present a new analytical procedure for the determination of $^{87}\text{Sr}/^{86}\text{Sr}$ in wines with reproducibility consistent with that generally reported for geological materials (~ 20 ppm).^{13,17} In addition, we accurately analyzed $^{87}\text{Sr}/^{86}\text{Sr}$ in wines produced with different grape vintage years from the same vineyard. Eventually, we applied the method to a large set of Italian commercial bottled certified wines (e.g., IGT, DOC, and DOCG) from four different wine regions of the Italian peninsula characterized by clear lithologic, and hence Sr isotope, differences to allow the evaluation of the presented analytical method as a possible tool for tracing wine provenance using combined wine and geochemical isotopic data.

ANALYTICAL PROCEDURE

Sampling Strategy. The wine regions selected for this study are distributed along the Italian peninsula, from Tuscany to Basilicata (Figure 1). The selected wines are Chianti Classico from Tuscany, Cesanese from Latium, Piediroso and Aglianico Campano from Campania, and Aglianico del Vulture from Basilicata. The Giglio Island wine from small vineyards on Giglio Island, Tuscany, has also been analyzed to have a first assessment of the behavior of Sr isotopes measured on white wines from vines on granitic soils. The wine Sr isotope compositions are then cross-checked with geological and isotopic data of the rocks of the production areas to verify the relationship, if any, between wines and their geological isotopic characteristics.

Only high-quality red wines have been selected, except the Ansonico white wine and Giglio Rosso from Giglio Island, to avoid potential isotopic contamination during the winemaking process. Indeed, bentonite (clay mineral) and limestone (calcium carbonate) powders are usually added during the production of white wines to help both complexation and precipitations of organic additive¹⁰ used to stabilize the winemaking process and to eventually clarify the final product.

The Cesanese, Piediroso, and Aglianico del Vulture wines have been selected because they are (i) from vineyards mainly planted on soils over young volcanic rocks (Figure 1) and (ii) from geologic substrata with distinct Sr isotope signature following the general northwest–southeast decreasing trend observed along the Italian peninsula.^{26–28} It should be considered, however, that Cesanese is divided in three consortia, namely, Cesanese d’Affile, Cesanese del Piglio, and Cesanese d’Olevano.

Wines from the Chianti Classico, Tuscany, and the Aglianico Campano, Campania, have been selected and analyzed because the geology of the substrata of their vineyards is made up by quartz-feldspatic and carbonate sedimentary rocks, respectively, rather than volcanic rocks. The Ansonico white wine from Giglio Island, Tuscany, has also been selected and analyzed to have a first assessment on wines from a substratum made up by young quartz-feldspatic igneous rocks (i.e., granite), albeit its Sr isotope composition may suffer from geological additives in the winemaking procedure.¹⁰

In a number of cases, wines of different vintage years but from the same vineyard have been collected to assess the constancy of $^{87}\text{Sr}/^{86}\text{Sr}$ with time.

Sr Isotope Analyses. The determination of any isotopic ratio of multielemental material has its critical point in the chemical treatment, measurement technique, and correction for isotope fractionation and isobaric interference. Cation exchange chromatographic methods performed in a clean laboratory are of the foremost importance in obtaining highly precise $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of wine by TIMS due to the comparable contents of Sr and Rb in wines, with the latter interfering on the measure of mass 87 in Sr (e.g., $\text{Sr} = 480\text{--}1600\ \mu\text{g L}^{-1}$ and $\text{Rb} = 370\text{--}1000\ \mu\text{g L}^{-1}$).⁵

Sample Preparation and Sr Purification. All samples have been prepared and measured at the Dipartimento di Scienze della Terra of the University of Florence, Italy. Sample preparation and purification prior to isotopic measurement have been performed in a clean laboratory (class 1000 environment). Sample digestion has been

performed within a horizontal HEPA-filtered laminar flow hood sited inside a fume cupboard, which ensures a low-blank working area. Subsequent purification has been performed using cation exchange chromatography within a vertical HEPA-filtered laminar flow hood (class 100 environment). High-purity chemical reagents and Milli-Q water ($18.2\ \text{M}\Omega\ \text{cm}^{-1}$) have been used throughout the entire chemical procedure.

Some 5 mL of wine sample was evaporated to dryness at $90\ ^\circ\text{C}$ in cleaned PFA beakers. The residue was dissolved twice in 3 mL of ultrapure quality H_2O_2 (30 wt %) at $40\ ^\circ\text{C}$ for 1 day and subsequently evaporated to dryness at $90\ ^\circ\text{C}$. The sample was then dissolved twice in 2 mL of suprapure quality HNO_3 (67 wt %) at $150\ ^\circ\text{C}$ for 1 day, evaporated to dryness, and dissolved again in 1 mL of 3 N HNO_3 for Sr chromatography. This procedure has been set up to oxidize organic matter to CO_2 .

Sr was finally purified by extraction chromatography using precleaned disposable Sr-Spec resins ($100\text{--}150\ \mu\text{m}$, Eichrom) placed in $140\ \mu\text{L}$ pure quartz microcolumns. After sample loading onto the column, some 14 column volumes (CV) of 3 N HNO_3 was added in three steps (including rinsing two times with 2 CV) to elute all major and trace element except Sr, which is retained in the resin bed. Sr was eventually collected in clean PFA beakers (Figure 2) using some 13

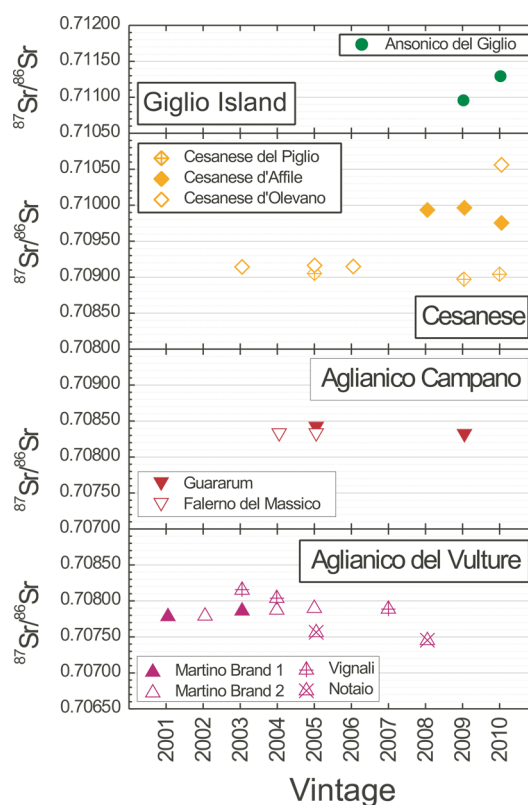


Figure 2. Bottled wine samples from the same winery but different vintage years to check the constancy of the Sr isotope geological signature through time. Note that the analytical error (2 SE) is smaller than the symbol size when error bars are not shown.

CV of Milli-Q water in three steps. The procedure was designed to collect >500 ng of Sr given a concentration range between 0.1 and 0.5 ppm determined by atomic absorption spectrometry in representative wine samples for each wine production area. Total procedural Sr blank was tested using an ^{84}Sr -enriched ($>80\%$) spike at a concentration of 0.92 ppb, yielding values between 100 and 300 pg, which are negligible with respect to the sample size.

Sr Isotope Measurements. Sr isotope compositions were measured using the last-generation Thermo Fisher (Bremen, Germany) Triton-Ti magnetic sector field thermal ionization mass spectrometer (TIMS)

designed to separate charged atoms or molecules on the basis of their momentum along their way through the magnetic sector field. The magnet has an effective dispersion of 810 mm and provides up to 16% mass dispersion. The laminated magnet allows fast peak jumping, and the magnetic field can be adjusted in such a way to give a mass range from 1 to 280 amu at 10 kV. Dynamic Zoom Optics enables slight change in the dispersion of the mass analyzer, ensuring maximum peak overlap and enhancing the precision attainable with multidynamic measurements. The multicollector system hosts 9 Faraday cups, of which 8 can be freely positioned with high precision. The Faraday cups have a dynamic range of 50 V (with a $10^{11} \Omega$ resistor).

Following cation exchange chromatography, 100–200 ng of Sr for each sample was dissolved in 1 μ L of 2 N HNO₃ and loaded on single Re filaments along with 1 μ L of TaCl₅ (activator) and 1 μ L of H₃PO₅ (fractionation suppressor). Each isotopic analysis is the result of 120 sets of measurements cycles, taken in 6 blocks of 20 cycles with 8 s integration time.

Multidynamic mass collection procedure (i.e., peak jumping) has been used to avoid further uncertainties due to bias among different signal collecting channels. In addition, the multidynamic mass collection procedure gives the possibility to obtain two simultaneous but independent measurements of the $^{87}\text{Sr}/^{86}\text{Sr}_{\text{double}}$ ratio during the run. The two $^{87}\text{Sr}/^{86}\text{Sr}_{\text{double}}$ exponential law corrected ratios are geometrically averaged to obtain a single $^{87}\text{Sr}/^{86}\text{Sr}_{\text{triple}}$ ratio, which is then a more accurate and precise value.²⁹ Indeed static measurement results are worse than dynamic ones in terms of internal ($2\sigma_m$, the standard error of the mean at 95% confidence level) and external precisions (2σ , the standard deviation of replicate analyses at 95% confidence level).²⁹ 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.²¹

The instrumental mass bias has been corrected offline with the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio measured on the main configuration (jump 2; Table 1)

Table 1. Statistics for 31 Replicate $^{87}\text{Sr}/^{86}\text{Sr}$ Analyses of the Same Wine Sample^a

		statistics	
wine consortium:	Aglianico Beneventano	mean	0.708439
type:	DOC	median	0.708439
cultivar:	Aglianico	mode	0.708439
winery:	La Guardiense	2 standard deviations (2σ)	0.000017
locality:	Guardia Sanframondi, Benevento, Campania	Kurtosis	−0.027
latitude:	41° 15′ 06″ N	skewness	0.243
longitude:	14° 34′ 32″ E	minimum	0.708423
wine:	Guardiolo	maximum	0.708455
year:	2008	count	31

^aStatistics about 31 Sr isotope replicate analyses of the same wine. Each analysis was performed with a new sampling from the bottle, through sample digestion and Sr purification. After Sr purification, the samples were measured by TIMS, and each $^{87}\text{Sr}/^{86}\text{Sr}$ value was the mean of 150 measurements (see text for further explanation) and has its own 2σ . The complete set of analyses is available as Supporting Information.

using the natural value ($^{88}\text{Sr}/^{86}\text{Sr}_N = 8.375209$)²² and an exponential fractionation law.²¹ ^{85}Rb has been monitored on the L2 collector to correct for residual contribution (i.e., isobaric interference), if any, of ^{87}Rb to ^{87}Sr , using the natural $^{87}\text{Rb}/^{85}\text{Rb}$ (i.e., 0.386). The analysis time, including lens focusing, peak centering, and baseline measurement (32 s) before and after each block, was ~ 75 min; the warm-up procedure was ~ 35 min.

The accuracy and precision of the procedure were tested through replicate analyses of the NIST SRM987 reference standard, yielding a long-term mean value $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248 \pm 16$ (2σ , $n = 173$, equivalent to an error of 23 ppm), identical to the widely accepted

recommended value of Thirlwall²² $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248 \pm 11$. The within-run precision (i.e., $2\sigma_m$, internal precision) of $^{87}\text{Sr}/^{86}\text{Sr}$ measurements has been typically ≤ 10 ppm.

RESULTS AND DISCUSSION

Reproducibility of Sr Isotopes in Wines. The excellent external reproducibility shown by the NIST SRM987 reference standard during the measuring period might be considered not representative of that of the wine samples due to the different matrix between the wine samples and the reference standard. To tackle this issue we have processed and measured the $^{87}\text{Sr}/^{86}\text{Sr}$ values of 31 different aliquots of wine from a single bottle of the Guardiolo wine (Table 1 and Supporting Information). The internal precision (either $2\sigma_m$ or 2 SE, i.e., 2 standard errors of the mean at 95% confidence level) of the replicate measurements has been < 10 ppm, and the statistics performed on all of the 31 replicates provide a log-normal distribution (see kurtosis and skewness, Table 1) with excellent parameters: the average, median, and mode values are identical; the external precision at 95% confidence level (2σ) is ± 0.000017 (i.e., ± 23 ppm) (Table 1). This gives us confidence in the reliability of the Sr isotope compositions measured in wine samples and permits us (i) to propose to the scientific community our analytical procedure and (ii) to properly investigate the relationship between wine and geology for obtaining reliable information about wine traceability.

Sr Isotopes in Wines through Different Vintage Years.

Once $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of wines at the same uncertainty level of geological samples^{13,21,22} have been determined, they might be directly compared with the $^{87}\text{Sr}/^{86}\text{Sr}$ of the rocks/soil of the substrata to verify its provenance and lack of adulteration with foreign grapes. This might be possible only if the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the wine from a single winery remains constant through the production years. Then bottled wine samples from the same winery but different vintage years have been also analyzed to check the constancy of the Sr isotope signature through time.

In Figure 2, each wine brand from commercial stores displays a constant and reproducible Sr isotope composition independent of the wine vintage year. In detail, the wines from the different wineries of the Aglianico del Vulture area have different Sr isotope signatures showing an excellent reproducibility (150 ppm) throughout the different vintage years and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio appears to be a tracing characterizing the winery itself. The same holds true for the Aglianico Campano and Cesanese wines (Figure 2).

The only wines that apparently do not show a constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio through the vintage years are the Cesanese di Olevano and Giglio Island (e.g., Ansonico wine) wines (Figure 2). The Cesanese di Olevano wine is one of the few wine bottles not collected in commercial stores, but directly supplied by the winemaker, as the other Cesanese wines, so it was possible to check the reason for this extreme increase of the Sr isotopic value in 2010. The winemaker, starting from the 2010 vintage year, has grapes from a new vineyard, but it kept separated the wines produced from the two vineyards. The new vineyard has a substratum made up by sedimentary rocks, whereas the original vineyard of grapes of the 2003, 2005, and 2006 vintages has a substratum made up by pyroclastic rocks of the Colli Albani volcano. Then, sedimentary sandstones have a higher radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than the Colli Albani volcanic rocks (Table 3).^{13,25–27} Coherently, the Sr isotope composition of the Cesanese di Olevano wine ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710586 \pm 8$) from the 2010 harvest has a distinct and more radiogenic Sr

Table 2. Bottled Wines Analyzed^a

production area	cultivar	winery	locality	latitude	longitude	wine	AOC	year	⁸⁷ Sr/ ⁸⁶ Sr	2 SE
Aglianico del Vulture	Aglianico	Martino	Rionero in Vulture	40° 55' 40" N	15° 40' 31" E	Bel Poggio	DOC	2001	0.707812	±0.000006
Aglianico del Vulture	Aglianico	Martino	Rionero in Vulture	40° 55' 40" N	15° 40' 31" E	Bel Poggio	DOC	2003	0.707896	±0.000005
Aglianico del Vulture	Aglianico	Martino	Rionero in Vulture	40° 55' 40" N	15° 40' 31" E	Martino	DOC	2002	0.707824	±0.000006
Aglianico del Vulture	Aglianico	Martino	Rionero in Vulture	40° 55' 40" N	15° 40' 31" E	Martino	DOC	2004	0.707880	±0.000005
Aglianico del Vulture	Aglianico	Martino	Rionero in Vulture	40° 55' 40" N	15° 40' 31" E	Martino	DOC	2005	0.707897	±0.000006
Aglianico del Vulture	Aglianico	Venosa	Venosa	40° 57' 32" N	15° 48' 00" E	Vignali	DOC	2003	0.708175	±0.000005
Aglianico del Vulture	Aglianico	Venosa	Venosa	40° 57' 32" N	15° 48' 00" E	Vignali	DOC	2004	0.708036	±0.000006
Aglianico del Vulture	Aglianico	Venosa	Venosa	40° 57' 32" N	15° 48' 00" E	Vignali	DOC	2007	0.707896	±0.000006
Aglianico del Vulture	Aglianico	Notaio	Rionero in Vulture	40° 55' 32" N	15° 40' 39" E	L'Atto	IGT	2005	0.707589	±0.000006
Aglianico del Vulture	Aglianico	Notaio	Rionero in Vulture	40° 55' 32" N	15° 40' 39" E	L'Atto	IGT	2008	0.707479	±0.000006
Aglianico del Vulture	Aglianico	Clemente	Barile	40° 56' 47" N	15° 40' 24" E	Cantine Clemente	DOC	2005	0.706793	±0.000005
Aglianico del Vulture	Aglianico	Eleano	Pian dell'Altare	40° 55' 28" N	15° 42' 09" E	Dioniso	DOC	2002	0.707124	±0.000006
Aglianico del Vulture	Aglianico	Eubea	Rionero in Vulture	40° 55' 32" N	15° 40' 39" E	Eubea	DOC	2002	0.707850	±0.000006
Aglianico Campano	Aglianico	I Favati	Cesinali	40° 53' 58" N	14° 49' 30" E	Taurasi	DOCG	2004	0.708439	±0.000006
Aglianico Campano	Aglianico	La Vinicola di Titerno	Massa di Faicchio	41° 15' 41" N	14° 30' 45" E	Aglianico Benevento	IGT	2009	0.708427	±0.000006
Aglianico Campano	Aglianico	Di Marzo	Santa Lucia	41° 00' 37" N	14° 49' 13" E	Irpinia Aglianico	DOC	2009	0.708277	±0.000006
Aglianico Campano	Aglianico	Cantine Astroni	Napoli	40° 50' 52" N	14° 09' 35" E	Guararum	DOC	2005	0.708445	±0.000006
Aglianico Campano	Aglianico	Cantine Astroni	Napoli	40° 50' 52" N	14° 09' 35" E	Gaurarum	DOC	2009	0.708342	±0.000005
Aglianico Campano	Aglianico	Rapuanò	Paupisi	41° 11' 43" N	14° 40' 02" E	Torre Pagus Taburno	DOC	2006	0.708432	±0.000006
Aglianico Campano	Aglianico	Sepe	Nola	40° 52' 41" N	14° 30' 33" E	Aglianico Benevento	IGP	2009	0.708646	±0.000005
Aglianico Campano	Aglianico	La Guardiense	Guardia Sanframondi	41° 15' 06" N	14° 34' 32" E	Janaré	DOC	2008	0.708614	±0.000007
Aglianico Campano	Aglianico	La Guardiense	Guardia Sanframondi	41° 15' 06" N	14° 34' 32" E	Guardiolo	DOC	2008	0.708442	±0.000006
Aglianico Campano	Aglianico	Mastroberardino	Atripalda	40° 55' 23" N	14° 49' 54" E	Aglianico	IGT	2004	0.708222	±0.000006
Aglianico Campano	Aglianico	Mustilli	Sant'Agata dei Goti	41° 05' 12" N	14° 30' 10" E	Cesco di Nece	DOC	2004	0.708219	±0.000006
Aglianico Campano	Piedirosso +Aglianico	Masseria Felicia	San Terzano	41° 13' 02" N	13° 54' 49" E	Falerno del Massico	DOC	2005	0.708349	±0.000005
Aglianico Campano	Piedirosso +Aglianico	Masseria Felicia	San Terzano	41° 13' 02" N	13° 54' 49" E	Falerno del Massico	DOC	2004	0.708351	±0.000006
Piedirosso	Piedirosso +Aglianico	no name	Lettere	40° 42' 17" N	14° 33' 05" E	Lettere	DOC	2002	0.707723	±0.000006
Piedirosso	Piedirosso	Cantine Astroni	Napoli	40° 50' 52" N	14° 09' 35" E	Piedirosso Astroni	DOC	2009	0.707991	±0.000006
Piedirosso	Piedirosso	Mustilli	Sant'Agata dei Goti	41° 05' 12" N	14° 30' 10" E	Piedirosso Mustilli	IGT	2009	0.707958	±0.000006
Cesane di Affile	Cesane	Colline di Affile	Colle Faggiano	41° 52' 48" N	13° 06' 27" E	Cesane di Affile	DOC	2005	0.709046	±0.000006
Cesane di Affile	Cesane	Colline di Affile	Colle Faggiano	41° 52' 48" N	13° 06' 27" E	Cesane di Affile	DOC	2009	0.708978	±0.000006
Cesane di Affile	Cesane	Colline di Affile	Colle Faggiano	41° 52' 48" N	13° 06' 27" E	Cesane di Affile	DOC	2010	0.709025	±0.000006
Cesane del Piglio	Cesane	Coletti Conti	Colle Cotoverio	41° 43' 13" N	13° 06' 11" E	Romanico	DOCG	2008	0.709965	±0.000006
Cesane del Piglio	Cesane	Coletti Conti	Colle Cotoverio	41° 43' 13" N	13° 06' 11" E	Romanico	DOCG	2009	0.709989	±0.000005
Cesane del Piglio	Cesane	Coletti Conti	Colle Cotoverio	41° 43' 13" N	13° 06' 11" E	Romanico	DOCG	2010	0.710010	±0.000009

Table 2. continued

production area	cultivar	winery	locality	latitude	longitude	wine	AOC	year	$^{87}\text{Sr}/^{86}\text{Sr}$	2 SE
Cesanese di Olevano Romano	Cesanese	Damiano Ciolli	San Giovenale	41° 50' 53" N	13° 02' 24" E	Silene	DOC	2003	0.709168	±0.000005
Cesanese di Olevano Romano	Cesanese	Damiano Ciolli	San Giovenale	41° 50' 53" N	13° 02' 24" E	Silene	DOC	2005	0.709177	±0.000005
Cesanese di Olevano Romano	Cesanese	Damiano Ciolli	San Giovenale	41° 50' 53" N	13° 02' 24" E	Silene	DOC	2006	0.709174	±0.000007
Cesanese di Olevano Romano	Cesanese	Damiano Ciolli	Cerreto	41° 50' 53" N	13° 02' 24" E	Silene	DOC	2010	0.710586	±0.000008
Giglio Island	Sangiovese	no name	Isola del Giglio	42° 22' 31" N	10° 52' 31" E	Giglio Rosso	IGT	2008	0.709371	±0.000006
Giglio Island	Ansonico	Greppe del Giglio	Isola del Giglio	42° 21' 37" N	10° 54' 56" E	L'Ansonaco	IGT	2009	0.710969	±0.000005
Giglio Island	Ansonico	Greppe del Giglio	Isola del Giglio	42° 21' 37" N	10° 54' 56" E	L'Ansonaco	IGT	2010	0.711305	±0.000007
Chianti Classico	Sangiovese + Merlot	La Spinosa	Barberino Val D'Elsa	43° 32' 24" N	11° 09' 54" E	Gorgottesco	DOC	2006	0.709000	±0.000006
Chianti Classico	no name	no name	Figline Valdarno	43° 38' 23" N	11° 25' 19" E	Chianti	DOCG	2006	0.710689	±0.000006
Chianti Classico	Sangiovese + Canaiolo	Poggerina	Figline Valdarno	43° 36' 38" N	11° 26' 22" E	Chianti - La Poggerina	DOCG	2006	0.709849	±0.000006

$^{87}\text{Sr}/^{86}\text{Sr}$ in wines from six different areas of the Italian peninsula. Each value is the mean of 150 measurements on the same sample (see text for further explanation). 2σ reports the internal reproducibility of the method.

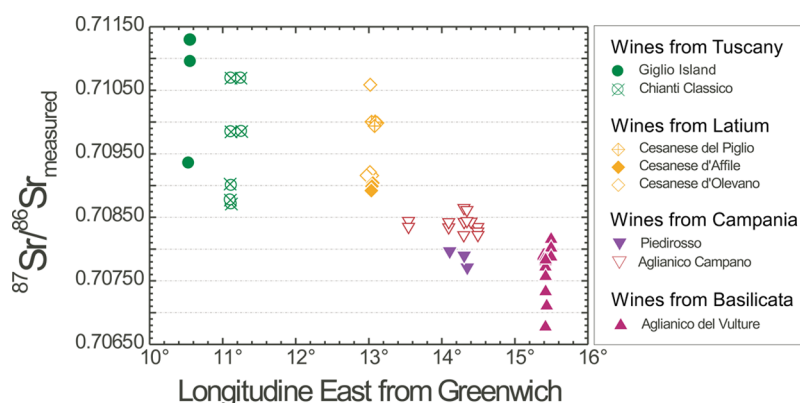


Figure 3. $^{87}\text{Sr}/^{86}\text{Sr}$ versus longitude east from Greenwich for bottled Italian wines from central Italy. Note that analytical error (2 SE) is smaller than the symbol size when error bars are not shown.

isotope signature than the other Cesanese di Olevano wines made with grapes from the original vineyard cultivated over the Colli Albani volcanic rocks, which have an identical Sr isotope signature within analytical error independent of the vintage year (i.e., $^{87}\text{Sr}/^{86}\text{Sr}_{2003} = 0.709168 \pm 5$; $^{87}\text{Sr}/^{86}\text{Sr}_{2005} = 0.709177 \pm 5$; $^{87}\text{Sr}/^{86}\text{Sr}_{2006} = 0.709174 \pm 7$; Table 2). These results show the great potential of Sr isotopes in tracing changes in the vineyard substratum even within the same wine brand.

On the other hand, the Ansonico wine is a white wine, and this implies, as stated above, that either bentonite or limestone silt was added during the winemaking process. Despite these additives being completely filtered and then removed, the data suggest that they have likely modified the Sr isotope composition of the wine with respect to that directly inherited from the geologic substratum of the vineyard (Table 2). Although further data are necessary to demonstrate this issue, we can tentatively propose that Sr isotope geology for wine provenance tracing should perhaps be limited to red wines.

In summary, replicate high-precision $^{87}\text{Sr}/^{86}\text{Sr}$ data on wines of the same vineyard but different vintage years remain

unchanged unless either the vineyard has been enlarged and then geology of the substratum has changed or geological material was added during winemaking of white wines. Then this represents a further argument to reinforce the hypothesis that $^{87}\text{Sr}/^{86}\text{Sr}$ data of red wines may represent a robust tool to verify the geographic provenance of wines and to check possible wine adulteration at the scale of a single vineyard.

Sr Isotope Compositions of Wines along the Italian Peninsula. The analyzed wines from the six different Italian wine areas selected for this study are reported in Table 2. They show $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.70762 to 0.71069, with a regular decrease of radiogenic isotope composition from Tuscany (Chianti Classico and Giglio Island wine areas) to Latium (Cesanese wine area), Campania (Aglianico and Piediroso wine areas) and Basilicata (Aglianico del Vulture wine area). In Figure 3, $^{87}\text{Sr}/^{86}\text{Sr}$ values of wines are plotted versus longitude east from Greenwich, showing a regular decrease of the radiogenic signature possibly dependent upon the nature and “petrographic” characteristics of the rocks of the different vineyard substrata rather than climatic variation as

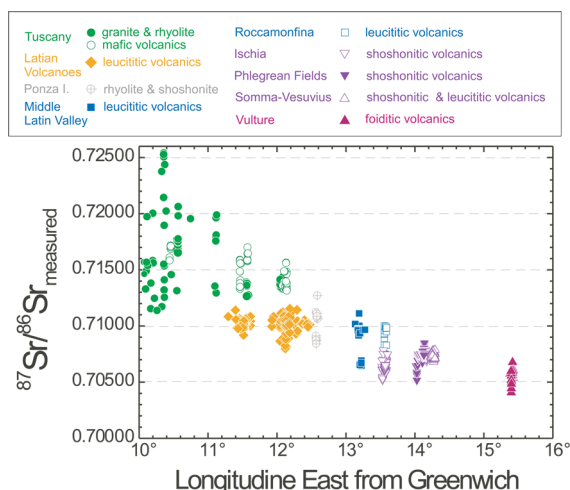


Figure 4. $^{87}\text{Sr}/^{86}\text{Sr}$ versus longitude east from Greenwich for volcanic terrains in central Italy. Note that analytical error (2 SE) is smaller than symbol size when error bars are not shown. Data are from refs 25–37 and references cited therein.

shown by stable isotopes in wines.^{5,8,9} The regular variation observed proceeding from northwest to southeast (Figure 3) should be in some way related to geology (Figure 1), the wine areas of the present study being selected in a way to have clearly different rocks in their substrata.

Sr Isotope Compositions of Rocks of the Areas of Grape Provenance. Four of the six wine areas under consideration in this study are characterized by vineyards cultivated mainly or partially on volcanic terrains. They namely are Aglianico del Vulture, from Monte Vulture volcanic area; Piedirosso from Neapolitan volcanic district, Aglianico Campano, from areas of the Campania plain and Taburno Mounts where pyroclastic rocks from Roccamonfina and Phlegrean Field volcanoes occur; Cesanese from Colli Albani volcanic district (Figure 1). One of the six, the Giglio Island wine area, is characterized by vineyards cultivated on granitic terrains, whereas the last one, the Chianti Classico wine area, is characterized by vineyard cultivated on sedimentary terrains (Figure 1).

One of the most peculiar characteristics of the Italian volcanic rocks is the high and variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which decreases regularly from northwest to southeast (Figure 4).^{27–30} Sedimentary rocks in southern Italy (including the Benevento and Irpinia areas) are mainly carbonate with narrow $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition;^{26,31–33} the highest and largest $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values are shown by the Giglio granite and by the siliciclastic rocks of Tuscany. Among sedimentary rocks from Tuscany, limestones show the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ measured values (0.70755–0.70767)²⁷ with clays, siltstones, and sandstones showing among the highest $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.72156–0.73823),³⁵ along with metasedimentary rocks.³⁵ Marlstones, which are a mixture of two components, limestone and clay to siltstone, have intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70879–0.71123)^{27,31–35} on the basis of the variable amount of each sedimentary component present in the rock (i.e., siliciclastic vs carbonate).

In Latium, the Cesanese wine area (Figure 1) is dominated by a substratum made up by volcanic rocks from the Colli Albani volcano with $^{87}\text{Sr}/^{86}\text{Sr}$ values within the range of 0.71006–0.71068²⁷ (Figure 4).

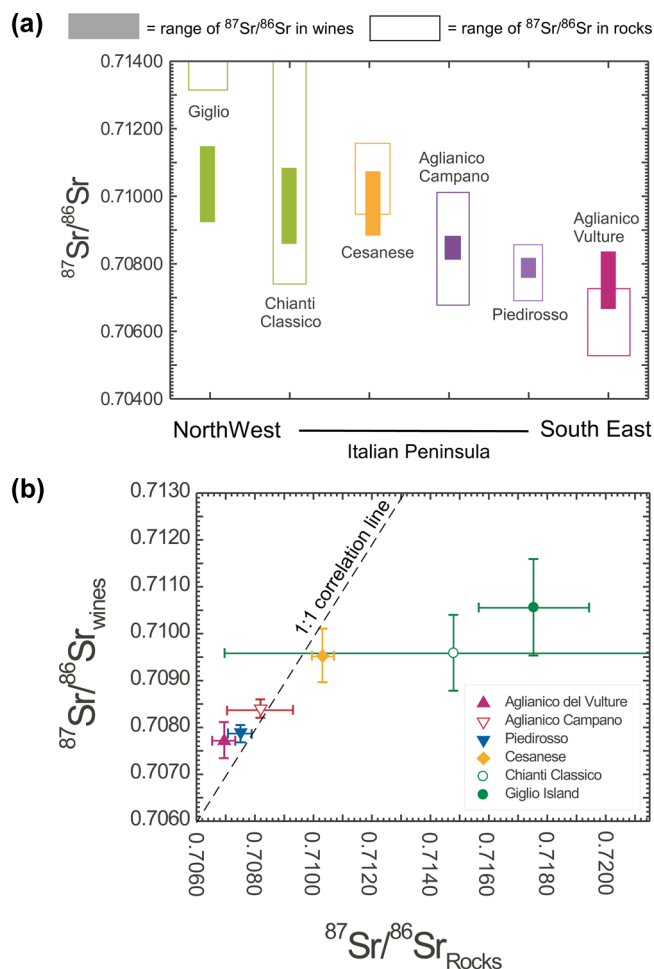


Figure 5. Diagram showing possible overlapping between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of wines (solid bars) and those of rocks from the wine area in which vines are cultivated (open boxes). $^{87}\text{Sr}/^{86}\text{Sr}$ values reported are maximum and minimum values of the rocks from the substrata of each wine area deriving from Table 3 where descriptive statistics of $^{87}\text{Sr}/^{86}\text{Sr}$ for rocks and wines are reported. (b) Diagram correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of wines and rocks of each wine area selected for this study with 2 standard deviation reported in the error bars. Data are from Table 3 where descriptive statistics are reported.

In Campania the wines are from two distinct areas, both characterized by pyroclastic volcanic rocks deposited over older sedimentary limestones. In the Piedirosso wine area Somma–Vesuvius volcanic rocks dominated, whereas the Aglianico Campano wine area is dominated by indifferetiated volcanic rocks from Phlegrean Fields and Roccamonfina rocks are present. There the limestone has the highest value ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.70884),^{31–33} whereas volcanic rocks have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70678–0.70797)^{28,30} (Figure 4).

The Aglianico del Vulture wine area is the southeasternmost one among the selected wine areas (Figure 1) with vineyards cultivated mainly on volcanic rocks,³⁰ although a few peripheral vineyards have a sedimentary substratum. Volcanic rocks from the Monte Vulture volcano have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values among the Italian rocks investigated in this study (e.g., 0.70522–0.70694; Figure 4).³⁰

Correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ Ratio in Wines and Rocks. At first glimpse, the observed variation of $^{87}\text{Sr}/^{86}\text{Sr}$ in wines (Figure 3) and rocks (Figure 4) with geographical parameter is strongly suggestive of strict relationships between

Table 3. Statistics of the $^{87}\text{Sr}/^{86}\text{Sr}$ Values of the Wines from the Same Production Area and Those of the Volcanic and Plutonic Rocks of the Substratum^a

	mean	median	standard deviation	min	max	no. of samples
rocks of substrata						
Vulture volcanic rocks	0.70695	0.70696	0.00040	0.70522	0.70705	54
Neapolitan volcanic rocks	0.70746	0.70746	0.00027	0.70678	0.70860	214
Roccamonfina volcanic rocks	0.70820	0.70831	0.00123	0.70656	0.71003	44
central Latium volcanic rocks	0.71038	0.71036	0.00038	0.70944	0.71134	52
southern Tuscany sedimentary rocks	0.71472	0.71123	0.00842	0.70746	0.72947	9
Giglio Island granite	0.71755	0.71760	0.00189	0.71322	0.72071	11
wines						
Aglianico del Vulture	0.70771	0.70785	0.00038	0.70679	0.70818	13
Piedirosso	0.70789	0.70796	0.00015	0.70772	0.70799	3
Aglianico Campano	0.70840	0.70843	0.00013	0.70822	0.70865	13
Cesanese	0.70951	0.70918	0.00057	0.70898	0.71059	10
Chianti Classico	0.70958	0.70942	0.00081	0.70877	0.71069	8
Giglio Island	0.71055	0.71097	0.00103	0.70937	0.71131	3

^aStatistics reported in the table refer to regional variability of the rocks and wines of an area. Source of data for rocks are from several papers^{25–37} and references cited therein, whereas for wines the data are from Table 2 from Boari et al.²

wines and geology. In several cases, the $^{87}\text{Sr}/^{86}\text{Sr}$ value of wines overlaps the values of the rock of the substratum of the vineyards from which the wines are produced. This is the case for the wines Cesanese, Aglianico Campano, and Piedirosso (Figure 5a). In other cases, Chianti Classico and Giglio Island wine areas, a large discrepancy is observed (Figure 5a). The Aglianico del Vulture wines display a slightly higher value than those of the dominant rock of their geological substrata (Figure 5a).

To better define the correlation between wine and geological data $^{87}\text{Sr}/^{86}\text{Sr}$ average, median, and standard deviation for the rocks of the wine areas selected and the wines analyzed are reported in Table 3, and then average values with their standard deviations are plotted (Figure 5b). In Figure 5b the deviatoric behavior of wine–rock pairs for Chianti Classico and Giglio Island is more clear. On the other hand, wine–rock pairs for Aglianico del Vulture, Aglianico Campano, Piedirosso, and Cesanese wine areas plot, within the standard deviation, on the 1:1 correlation line, suggesting a strict relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ value of wine and that of the rocks of the substrata (Figure 5b).

It is worth noting that the wines showing $^{87}\text{Sr}/^{86}\text{Sr}$ matching those of the substrata are mostly from vineyards grown on volcanic rocks, covering limestones. On the other hand, those deviating from the correlation are either from vineyards on sedimentary substrata, the Chianti Classico wine–rock pairs, or from granitic rocks, for the Giglio Island ones.³⁶

The high internal lithological variability of the rocks of the Chianti Classico vineyard substrata might be responsible for the preferential uptake by vine roots of leachable mineral phases with different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from their bulk rocks (e.g., feldspar, clay, calcite, etc.), due to differences in Rb/Sr developing time-integrated differences in $^{87}\text{Sr}/^{86}\text{Sr}$.

For the Giglio Island wines, in which the deviatoric behavior is extreme (Figure 5b; Table 3), the reason is still related to the addition of geologic additives during winemaking of white wines, a characteristic already observed in the metal distribution of German white wines.³⁷

In summary, we can observe a clear correlation between the Sr isotope composition of wines and the geological substratum of the corresponding vineyards (Figure 5b). Deviation from this

rule is observed when (i) the geological substratum is made up by old lithology characterized by textural and mineralogical heterogeneities (i.e., different components or rock-forming minerals with variable Rb/Sr ratios and hence different time-integrated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios); (ii) the grapes are from vineyards grown over different lithological substrata with different isotopic signature, then the resultant Sr isotope composition of wine depends upon the relative amount of grapes from the different vineyards used during the winemaking process; (iii) white wines with geological additives, such as bentonites and limestone powders, are used. To clarify the mechanisms related to these weak correlations between the Sr isotope composition of wines and old heterogeneous geological substrata, more detailed studies are needed.

The benchmark of this reasoning is that all grapes growing in the same geological substratum (i.e., rocks/soil) have the same Sr isotope composition, and because $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary widely among rocks and soils, and therefore grapes, around the world, the isotopic composition of Sr can be used to validate the geographic provenance of wines. If the correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of wines and highly heterogeneous and old rocks is confirmed, the determination of Sr isotopes in wines might become a fingerprint for the regional provenance. Then there would be no need for the use of combined $^{87}\text{Sr}/^{86}\text{Sr}$ with multielement analyses. Indeed, the isotopic procedure is very precise and does not require additional and sometimes operator-dependent statistical procedures to validate the geographic provenance of a given wine. The rationale of this method relies on the fact that neither biological processes nor Sr uptake from soil by vineyard nor wine fermentation and aging fractionate strontium isotopes in grapes and wine.^{38,39}

■ ASSOCIATED CONTENT

§ Supporting Information

Additional table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Both senior authors endorse the scientific responsibility and are available for correspondence and scientific feedback: sandro.coticelli@unifi.it, massimo.mattei@uniroma3.it.

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