Strontium isotopic signatures for authenticity and wine geographical assessment

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Abstract: The assessment of wine authenticity is of utmost importance in the current context of a growing market globalization. In the last years several studies were developed on the application of $^{87}Sr/^{86}Sr$ isotopic ratio for the evaluation of wine geographical origin, involving wine producing regions worldwide, evidencing its reliability as a provenance marker. Aspects such as $^{87}Sr/^{86}Sr$ relation with the vineyard substratum, analytical methodologies, and effect of technological processes have been addressed. Data has been obtained for different wine regions/PDO. Nevertheless, some important issues remain, such as the interpretation of the data from the soil (it is crucial to know the soil geochemistry), and the need for better understanding of the impacts of anthropogenic factors. Precise and accurate $^{87}Sr/^{86}Sr$ data is required for origin discrimination and analytical methods used should be officially recognized or validated in order to support comparison. Sr isotopic data can be used to build an authentic wine reference database (e.g. official or wine organization, PDO consortium), or to integrate a global database (e.g. EU wine databank). $^{87}Sr/^{86}Sr$ data combined with other discriminating parameters, namely elemental composition, can provide increasingly robust results for the identification of wine provenance. This work reviews the main aspects of the topic and includes recent research results obtained by the author's team.

Keywords: Wine, authenticity, geographic origin, $^{87}Sr/^{86}Sr$ isotopic ratio.

1. Introduction

Wine traceability and the assessment of its authenticity are of utmost importance in the current context of a growing market globalization (OIV, 2007). To boost wine quality, promote good practices and minimise fraud, wine authenticity is commonly addressed by a regulatory "wine of origin" system in many countries. In European Union (EU), traceability systems are applied to promote and protect certain denominations, such as Protected Geographical Indication (PGI) and Protected Designation of Origin (PDO). These designations of origin are awarded to high quality wines, strictly linked to their geographic provenance and specific viticulture and enological practices.

The main issues related to wine authenticity concern adulterations (e.g. sugaring, and watering, in EU), geographic origin, grape varieties, and vintage year. The high value of some specific PDO wines make economically interesting the use of not certified grapes

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and wines to mislead consumers, producing wines under counterfeit mentions. This type of fraudulent actions is not rare, being known several cases of relabelling of imported wines under a prestigious PDO. Moreover, fraudulent practices are not only on prestige wines but also on medium quality wines.
The place of origin of food products is regarded as value-added information and as a guarantee of quality and authenticity. For wine in particular, geographical origin has a direct effect on its quality and commercial value, being one of the most studied products in terms of food authentication. In fact, information of wine's origin on the labels provides dignity to the wine in the eyes of consumers.

The development of analytical methodologies which can positively identify the geographical origin of a given product is one of the most challenging issues for scientific community. Stable isotope analyses ($^{2}H/^{1}H$, also referred as D/H, $^{13}C/^{12}C$ and $^{18}O/^{16}O$) recognized by the International Organisation of Vine and Wine (OIV) for detecting adulterations, inclosed in the european Wine DataBank (since 1990, updated every year), are limited in terms of interpreting the data and relating them to the wines provenance. Regional differences in sensory characteristics of wines have commonly been attributed to, among other factors (e.g. grape variety, technological processes, and vintage), local variations in soil composition.

Soil-related fingerprints justify special attention, given that there is a relationship between the chemical composition of wine and the composition of the provenance soil. In fact, the most explored fingerprinting techniques combine chemical analysis, namely element and isotope ratio analysis, and multivariate statistical analysis of the chemical data to classify wines according to the geographical origin. However the successful application of the techniques based on multi-element composition of a wine strongly depends on the selection of suitable elements that would reflect the relationship with soil geochemistry and therefore have discriminating potential (Catarino *et al*., 2011; Catarino *et al*., 2018), requiring deep knowledge of chemistry and technology of wine. The data on mineral elements in wine as a probe for origin determination has to be carefully interpreted since there are many environmental, agricultural and oenological factors that can easily mask vital elemental information (Catarino *et al*., 2008a,b).

2. The isotopic ratio $^{87}Sr/^{86}Sr$

The strontium isotopic ratio $^{87}Sr/^{86}Sr$ is a well-established tool for dating and tracing the origin of rocks and minerals (Faure, 1986), with special interest for wine traceability. Strontium occurs in nature as four isotopes. Isotopes ^{84}Sr, ^{86}Sr and ^{88}Sr, non-radiogenic, occur in constant relative proportions, whereas ^{87}Sr, radiogenic, gradually increases in minerals due to the radioactive β-decay of the ^{87}Rb isotope (half-life: 48.8×10^{9} years). The $^{87}Sr/^{86}Sr$ isotope abundance variations given by IUPAC fall in a range of 82.29–82.75 % for ^{88}Sr, 6.94–7.14 % for ^{87}Sr, 9.75–9.99 % for ^{86}Sr and 0.55–0.58 % for ^{84}Sr, respectively (Berglund and Wieser, 2011). Observed range in the nature for ^{87}Sr is 0.0694–0.0714 mole fractions while ^{86}Sr is 0.0975–0.0999 which gives the ratio range from 0.695 to 0.732.

The strontium isotopic ratio $^{87}Sr/^{86}Sr$, depending on the initial $^{87}Sr/^{86}Sr$, initial Rb/Sr ratio, and age of the rock (time), gives particular data in different geological regions. Differences in the relative abundance of ^{87}Sr vary with geological age, and consequently with geographic locations, providing a fingerprint for different rock types (Capo *et al*., 1998). Horn *et al*. (1993) stated that soils of respective vineyard regions have different $^{87}Sr/^{86}Sr$ ratios.

Weathering of the underlying rock and/or sediments is a significant source of strontium for the soil. Pre-Cambrian granitic bedrock and alluvial sands derived from felsic rocks show high $^{87}Sr/^{86}Sr$ (0.710-0.716) reflecting the age of the continental crust and high Rb/Sr from which these materials originated. Limestones have intermediated $^{87}Sr/^{86}Sr$ ratio values (0.706-0.709) and young oceanic basalts and their sediments show the lowest values (0.702-0.705) (Faure, 1986; Capo *et al.,* 1998).

As a provenance tracer, a crucial feature of Sr is that this element is assimilated by the vine plant roots in the same isotopic proportions in which they occur, under available forms (labile Sr); biological processes involved in vine metabolism do not significantly fractionate Sr isotopes (Horn *et al*., 1993; Capo *et al*., 1998; Song *et al*., 2015). According to the literature, vine plants reflect the environment of growth: bedrock, soil and soil water (Horn *et al*., 1993; Capo *et al*., 1998). Nevertheless, studies on the hypothetical influence of rootstock and grapevine variety are limited.

3. Sr isotopic ratio analysis

The radioactive decay of ^{87}Rb induces extremely low differences in Sr isotopic composition. For samples with very close $^{87}Sr/^{86}Sr$ values, the possibility of discriminating often lies on the fourth or fifth decimal places of the isotopic ratio. Thus, precision of the measured $^{87}Sr/^{86}Sr$ values represents a quality parameter of utmost importance to ascertain the goodness of the experimental results (Sighinolfi *et al*., 2018). Thermal ionization mass spectrometry (TIMS), the reference technique in the field of isotopic analysis, and more recently multicollection inductively coupled plasma mass spectrometry (MC-ICP-MS) are capable to provide precise (0.002 %, RSD) and accurate isotopic measurements (Barbaste *et al*., 2002; Rosner, 2010; Durante *et al*., 2015). Several studies have been published with these techniques for assessing $^{87}Sr/^{86}Sr$ ratio in soils and wines (Barbaste *et al*., 2002; Marchionni *et al*., 2013; Durante *et al*., 2015; Petrini *et al*., 2015; Epova *et al*., 2019).

The lower precision of quadrupole ICP-MS (Q-ICP-MS), typically below 0.1 % (RSD), can be a limiting factor, especially in studies involving samples with very close $^{87}Sr/^{86}Sr$ values. On the other hand, Q-ICP-MS is robust and less time consuming, and its precision allowed distinguishing the Sr isotopic composition of wines in several studies (Vanhaecke *et al.,* 1999; Almeida and Vasconcelos, 2001; Vorster *et al*., 2010; Martins *et al*., 2014; Catarino *et al*., 2019). Due to the isobaric overlap of ^{87}Sr and ^{87}Rb, an effective Rb/Sr separation is a pre-requisite for the accurate determination of Sr isotope ratios by Q-ICP-MS.

A sample preparation procedure for $^{87}Sr/^{86}Sr$ determination by Q-ICP-MS was optimized by the author's team (Martins *et al*., 2014), comprising three main analytical steps in sequence: 1) sample digestion by high pressure microwave digestion (HPMW), 2) chromatographic separation of ^{87}Sr and ^{87}Rb, and 3) determination of Sr and Rb content by Q-ICP-MS. For elimination of organic substances in order to prevent any interference during chromatographic separation, soil and wine samples were digested by HPMW. Separation of Sr was performed by using Dowex 50W-X8/400 (Sigma-Aldrich) mesh resin and EDTA as eluent. Separation consists of four phases which are resin activation/pre-treatment; resin conditioning; sample preparation/dilution and elution. Sr and Rb total content and $^{87}Sr/^{86}Sr$ isotopic ratio were measured by a Q-ICP-MS equipment. Determination of Sr and Rb total contents in Sr-containing fractions previously to the isotopic measurement is important in order to keep Rb concentration less than 1% of the Sr content in Sr-fraction. The SRM 987 ($SrCO_3$) from National Institute of Standards and Technology (NIST) was used as an isotopic reference material for correction of mass bias phenomenon.

4. Application of $^{87}Sr/^{86}Sr$ isotopic ratio for wine geographical assessment

Literature on the progress made since the first application of $^{87}Sr/^{86}Sr$ isotopic ratio for wine traceability purposes in the 1990's is available, with a significant increase number of studies developed in the last decade, and involving wine producing regions worldwide (Horn *et al*., 1997; Almeida and Vasconcelos, 2001; Barbaste *et al*., 2002; Almeida and Vasconcelos, 2003; Vorster *et al*., 2010; Di Paola-Naranjo *et al*., 2011; Durante *et al*., 2013; Marchionni *et al*., 2013; Martins *et al*., 2014; Mercurio *et al*., 2014; Durante *et al*., 2015; Marchionni *et al*., 2016; Vinciguerra *et al*., 2016; Durante *et al*., 2016; Geanã *et al*., 2017; Durante *et al*., 2018; Epova *et al*., 2019; Catarino *et al*., 2019).

Pioneer studies by Horn *et al.* (1997) demonstrated that the $^{87}Sr/^{86}Sr$ values of several wines were within the respective ranges for rocks and soils. A few years later Almeida *et al.* (2003) investigated the potentialities of both multi-element composition and Sr isotopic ratio as tracers, by studying the influence of the provenance soil. Wine and soil samples from Douro wine region (Portugal) were analysed by Q-ICP-MS. This combined strategy showed to be suitable to act as fingerprint of the origin of a wine. The $^{87}Sr/^{86}Sr$ isotope ratios in soils and wines of four South African wine-producing regions were determined by Q-ICP-MS (Vorster *et al.*, 2010). Only one producing region could be distinguished from the rest.

In the last years a series of significant studies were developed on Italian wines and PDO, namely Lambrusco, evidencing the matching of $^{87}Sr/^{86}Sr$ ratios in wine and those from substratum of vineyards (Durante *et al.*, 2013; Marchionni *et al*., 2013; Mercurio *et al.*, 2014; Petrini *et al*., 2015; Durante *et al*., 2018). Based on a representative number of authentic samples and Sr isotopic measurements acquired with high precision and accuracy, additional information of interest was obtained: the bio-available (labile) fraction of soil is the one of interest for Sr isotopic analysis (Durante *et al*., 2013); vine-branches $^{87}Sr/^{86}Sr$ values show traceability power, overcoming the problems associated with soil sampling as well as those related to the evaluation of the element bioavailable fraction (Durante *et al*., 2016); $^{87}Sr/^{86}Sr$ isotopic ratio seems not to be affected by vintage year (Marchionni *et al*., 2013). Data on $^{87}Sr/^{86}Sr$ ratios of soils, vine branches and wines sampled in Modena, were used to build maps to objectively support the Lambrusco PDO wines (Durante *et al*., 2018).

Two studies from Vinciguerra *et al*. (2015) and Geanã *et al*. (2017) announced very promising results by attributing a strong relationship between $^{87}Sr/^{86}Sr$ on grape and wine and soils from different vineyards in Quebec and in Romania, respectively. Geanã *et al*. (2017) classified with a 100% success, the geographical origin of twenty one red wines with denomination PDO or PGI, by combining the Sr isotopic ratio together with Ca/Rb value and other elements concentration (Ga, Sr, Al).
One study in Australia also justifies the robustness of the strontium isotopic ratio method to differentiate between Australian and non-Australian wines (Wilkes *et al*., 2016). Nevertheless, overlap of the strontium isotopic ratio from different countries was observed, suggesting that the use of only one fingerprinting method may

not be sufficient.

Recently, a study concerned the Sr isotopic and elemental compositions of a large selection of genuine Bordeaux wines from four regional wineries (Epova *et al.*, 2019). Results demonstrated a moderate variability of $^{87}Sr/^{86}Sr$ ratio and Sr concentrations with a strong possibility to assigned Sr specifications for individual winemaking estates. Furthermore, the $^{87}Sr/^{86}Sr$ ratio found to be relatively stable in in wine from different vintages.

Within a research program on strategies for wine fingerprinting carried out by the author's team, the transference of $^{87}Sr/^{86}Sr$ signature through soil-wine system was examined (Martins *et al*., 2014). The $^{87}Sr/^{86}Sr$ ratios of soils from four vineyards located in three Portuguese PDO (Dão, Óbidos and Palmela), established on distinct soil types, were determined, by Q-ICP-MS. Significant differences were found between soils of different PDO. As expected, the soil developed on granites, showed a higher $^{87}Sr/^{86}Sr$ ratio than the other soils, which were developed on sedimentary formations. The results show clearly that $^{87}Sr/^{86}Sr$ may represent a suitable fingerprint for these Portuguese PDO (Martins *et al*., 2014).

More recently, the variation of $^{87}Sr/^{86}Sr$ in wines from Douro Valley, taking into account the effects of vineyard location and grape variety, was examined (Catarino *et al*., 2019). A total of twenty-two varietal wines, from relevant white and red grapevine varieties for the Portuguese Douro region, and respective soils from six vineyards were analysed. The range of $^{87}Sr/^{86}Sr$ observed in soils and wines was of 0.708-0.725 and 0.711-0.717. No significant difference was observed between vineyards soils and wines (Catarino *et al*., 2019). This study represents a development background for building an authentic wine reference database (e.g. official or wine organisation, PDO consortium) to evaluate the provenance of wine labelled as Douro, or to be integrated

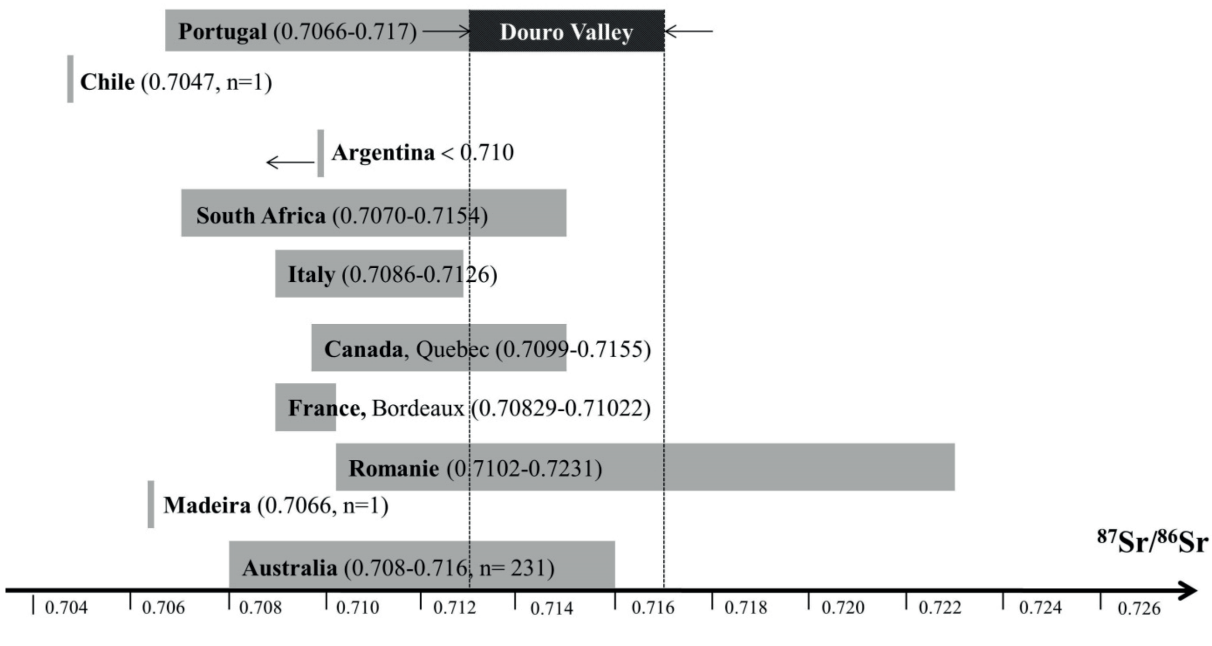

Figure 1. $^{87}Sr/^{86}Sr$ in wines on a global scale.

Data from Almeida and Vasconcelos, 2001; Barbaste *et al*., 2001; Vorster *et al*., 2010; Di Paola-Naranjo *et al*., 2011; Marchionni *et al*., 2013; Mercurio *et al*., 2014; Petrini *et al*., 2015; Durante *et al*., 2015; Durante *et al*., 2016; Marchionni *et al*., 2016; Vinciguerra *et al*., 2016; Wilkes *et al*., 2016; Geană *et al*., 2017; Moreira *et al*., 2017; Kaya *et al*., 2017; Catarino *et al*., 2019; Epova *et al*., 2019.

in a global wine database (e.g. EU wine databank) of great usefulness for industry. Nevertheless, despite the potential of $^{87}Sr/^{86}Sr$ for determining the provenance of wines, it seems it can be difficult to differentiate them both at the country and regional level only through $^{87}Sr/^{86}Sr$, as shown in Figure 1, suggesting that it should be used together with other discriminating parameters, e.g. elemental composition.

5. Influence of technological processes

The use of $^{87}Sr/^{86}Sr$ as a geographic origin marker is based on the assumption that there is a relationship between soil, plants and wine. Therefore, the $^{87}Sr/^{86}Sr$ ratio should not be modified significantly by agricultural and winemaking practices through the chain from vineyard to bottle. It is also important to take into consideration anthropogenic factors such as irrigation water, pollution and fertilizers that can contribute as mineral sources to the vine plants (Figure 2).
According to Horn *et al*. (1997), fining with bentonites, deacidification with carbonates and storage in glass showed little effects on wine $^{87}Sr/^{86}Sr$ ratio. Nevertheless, it is well known that the use of some technological aids, namely bentonite, can result in significantly concentrations of Sr (Catarino *et al*., 2008b). Almeida and Vasconcelos (2004) stated that although winemaking processes, and chemical applications in the vineyard change the element composition of must and wine, a strong correlation in terms of Sr isotopic ratio between wine and grape juice is still found. No influence of the production year or the winemaking process was observed in the $^{87}Sr/^{86}Sr$ ratio (Marchionni *et al*., 2013). Sr isotopic ratios of red and white wines were not affected by addition of fining agents during winemaking proving the close relation with the vineyard (Tescione *et al*., 2015). Durante *et al*. (2016) investigated the cellar practices that used different additives, such as clarification and deacidification agents as well concentrated musts. The hypothesis was that Sr concentration could be modified; hence the $^{87}Sr/^{86}Sr$ ratio of wine may be affected by these practices. Once again, the $^{87}Sr/^{86}Sr$ ratio was found to be a powerful tool discriminate the wines based on their

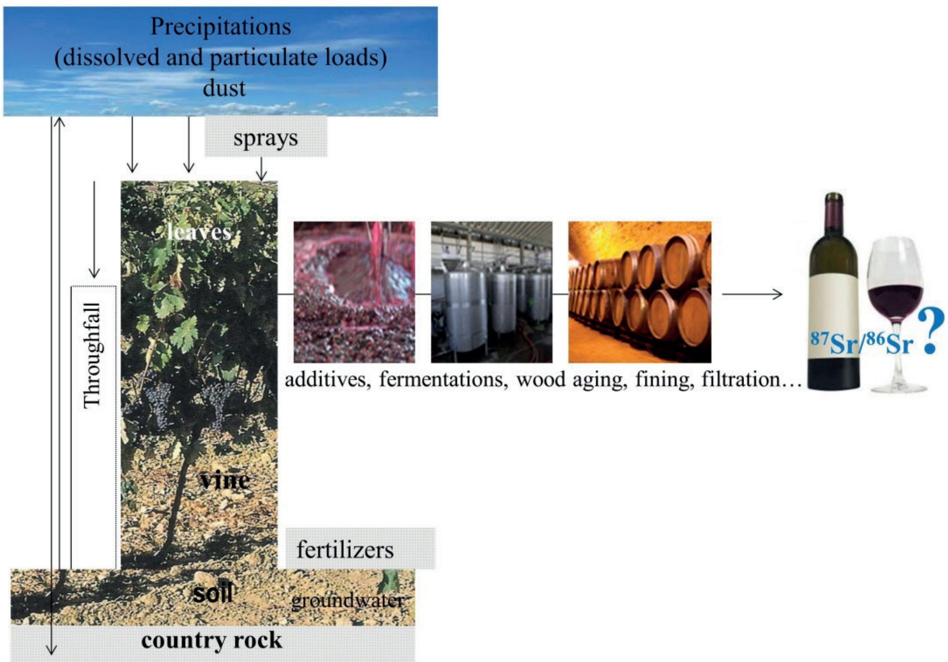

Figure 2. Reservoir scheme for Sr in wines, with possible transfer routes (adapted from Horn *et al.*, 1997).

region.
More recently the effect of two enological practices, namely nanofiltration for dehalcoholisation and wood aging, on the Sr isotopic ratio were investigated by the author's team. No significant differences in the $^{87}Sr/^{86}Sr$ of wines and corresponding permeate fractions were observed, suggesting that nanofiltration does not preclude the use of this isotopic ratio for wine traceability purposes (Moreira *et al.,* 2017). After three months of aging with oak staves in stainless steel vats, it was found that wood aging did not alter $^{87}Sr/^{86}Sr$ ratio of wine (Kaya *et al.*, 2017).

6. Principal current issues and future perspectives

The reliability of $^{87}Sr/^{86}Sr$ for wine fingerprinting is evidenced by the studies. Nevertheless, applied solely, this analytical approach shows some limitations to definitely identify the geographical origin. Soils from different wine regions and countries have been originated from similar geological formations, which can be a constraint in terms of interpreting the data and relating them to the wines provenance. Also, the heterogeneity of some wine regions and PDO in terms of soils and geological materials is well known, making it difficult to match wines with their substrata data. Further studies should be developed, on diverse lithological situations and other world regions, to confirm the feasibility of $^{87}Sr/^{86}Sr$ fingerprinting and enlarge data. A correct and representative soil sampling procedure is crucial in order to develop robust models.
Another issue concerns the interpretation of the data from the soil substratum. It is crucial to know the soil geochemistry background so a reliable wine origin relationship can be established. In particular, the discrepancy between the bioavailable fraction and the total amount of strontium in a soil may represent a limiting factor for the building of a reliable geographical traceability system.
The influence of the vintage year, in direct relationship especially with climate changes, requires further research. Also, a better understanding of the impacts of anthropogenic factors and technological processes on this marker is essential.
Analytical precision is a pivotal requirement for discriminating between samples with very close $^{87}Sr/^{86}Sr$ values. Furthermore, analytical methods should be officially recognized or validated (through interlaboratorial trials, proficiency tests) in order to support comparison.
For a statistical approach to the geographic origin of wine, a large database of precise and accurate values is needed in order to evaluate the indicator variability range of both the wine and the soils and to build robust classification models. Sr isotopic data can be used to build an authentic wine reference database (e.g. official or wine organization, PDO consortium), or to integrate a global database (e.g. EU wine databank).
At last, increasingly robust results for the identification of geographical origin can be achieved by combining Sr isotopic ratio and elemental signatures of wines. This approach supplies the distinguishing terroir-inherent and winemaking-related tracer for authenticity and provenance assignment.

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