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## A comparative $^{87}\text{Sr}/^{86}\text{Sr}$ study in Red and White wines to validate its use as geochemical tracer for the geographical origin of wine

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### Abstract

Recently high precision  $^{87}\text{Sr}/^{86}\text{Sr}$  analyses have shown that Red wines keep the isotopic values of the vineyard substratum. Indeed, neither biological nor winemaking and aging processes are able to change the  $^{87}\text{Sr}/^{86}\text{Sr}$  values through the oenological food chain from grapes to Red wine. In addition,  $^{87}\text{Sr}/^{86}\text{Sr}$  of Red wines and those of rocks from the geological substratum of their vineyards correlate directly. The same holds not true for White wines, apparently. To investigate this discrepancy,  $^{87}\text{Sr}/^{86}\text{Sr}$  has been determined for the entire production chain, from terroir to final product, of Red and White wines from the same vineyard. Sr-isotope data have been also determined for the young pyroclastic rocks of the geological substratum, and the soil of the vineyard to disambiguate the original contribution to the  $^{87}\text{Sr}/^{86}\text{Sr}$  values of wines. Further Sr-isotope data have been determined on additives used for fining the White wine. The analytical results do not show significant differences between oenological food chains of Red and White wines. Preliminary data indicate that  $^{87}\text{Sr}/^{86}\text{Sr}$  does not change passing from grape juices to wine in all cases under consideration. As a corollary neither yeast nor bentonite added during vinification of both Red and White wines do affect their Sr-isotopic values. On the other hand,  $^{87}\text{Sr}/^{86}\text{Sr}$  of Red and White wines appears to be significantly lower than values observed in rocks of their substrata. Further experiments performed on this pilot winery would be useful to shed some lights on this issue.

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**Keywords:** Sr-isotope; Red and White wines; Terroir; Geologic traceability.

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## 1. Introduction

The increasing demand of high quality and safe food products in Europe promoted the development of rigid control laws to certificate their authenticity and geographical origin and to protect both producers and consumers from frauds. Among food products, wine is one of the most studied and protected with well-defined regulation for the certification of origin and provenance<sup>1</sup>. For this reason, the wine geographical traceability has gained importance in the modern society producing the need of valid scientific protocols able to trace geographic provenance of wines. These studies based on the fingerprint that the *terroir* leaves in the chemical composition of the final product, then allowing scientist to define a correlation between the food and its area of production. It is well known that a strict correlation does exist between the wine and its *terroir*, a precise area where climatic, physics, pedological, geological and viticultural factors interact and give the wine its typicalness<sup>2,3</sup>.

Stable isotopes of light elements are nowadays widely used to detect aroma and flavor sophistications in wines, notwithstanding they are not reliable for defining exactly geographic traceability of wines because their strong dependence upon local climatic and anthropic factors<sup>4</sup>.

In the last decades, isotopic ratios of heavy elements of geological interest, such as  $^{87}\text{Sr}/^{86}\text{Sr}$ , have gained interest in tracking regional provenance of foods and especially of wine<sup>6,7</sup>. It has been recently also shown that winemaking

process of Red wines does not affect the  $^{87}\text{Sr}/^{86}\text{Sr}$  of wine; this allows the direct link between the Sr-isotopes of wine and those of the vineyard substratum<sup>7-9</sup>. Recently, analytical protocols that provided Sr-isotope determinations in foods at the uncertainty levels of geological materials have been provided<sup>10-12</sup> allowing direct comparison between  $^{87}\text{Sr}/^{86}\text{Sr}$  of wine and of the substratum of the vineyard of production.

In figure 1 a detailed geochemical study, focusing on the relationship between the Sr-isotopes of high-quality Italian wines from five different regions along the Italian peninsula and the geology of their regions of production, is reported<sup>11</sup>. Red and some White wines have been studied in detail finding strict relationships between  $^{87}\text{Sr}/^{86}\text{Sr}$  of Red wines and of their *terroirs*<sup>11</sup>. On the other hand, White wines and some Red Wines from vineyards over sedimentary geological substrata in Tuscany have shown deviations from direct correlation with the geology of the region of production<sup>11</sup>. Discrepancies have also been found for White wines from other regions<sup>12</sup> confirming that possible cause might be found in the different winemaking procedure followed for vinification of Red and White wines.

To encompass the possible cause of the discrepancies between Red and White wines, an experimental study on the distribution of  $^{87}\text{Sr}/^{86}\text{Sr}$  in the oenological food chains of Red and White wines from the same winery has been undertaken.  $^{87}\text{Sr}/^{86}\text{Sr}$  on yeast and bentonites used for White wine vinification have been also determined. We report here the preliminary results of the first year of three for validating the experimental data.

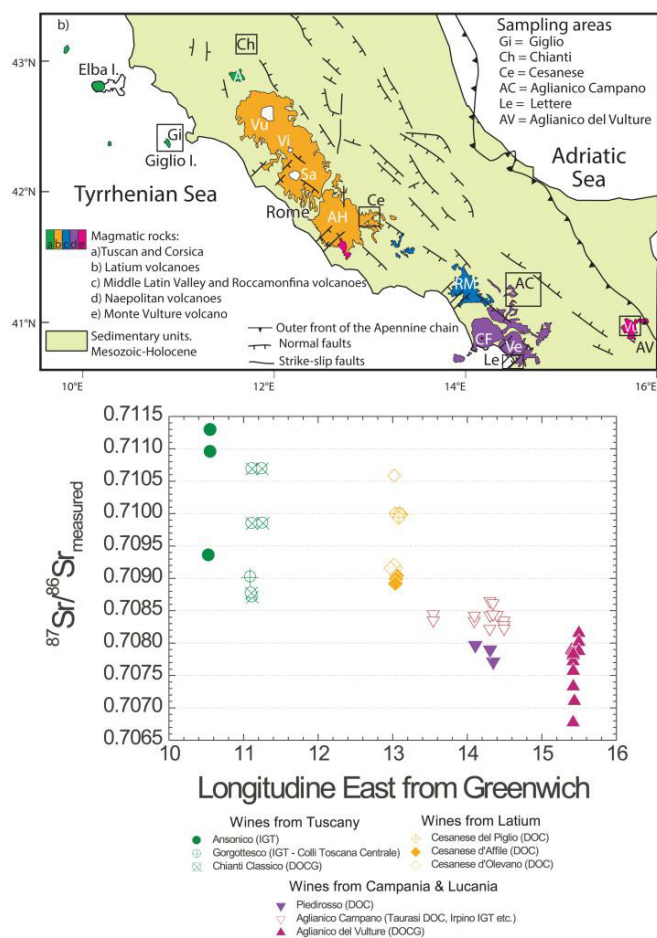


Fig. 1. The bottom diagram (a) shows variation of  $^{87}\text{Sr}/^{86}\text{Sr}$  of wines with respect of the geographic coordinates of their vineyards. The top geological map of Central Italy show the location of the five regions where the high quality wines are from Marchionni et al.<sup>11</sup>

## 2. Materials and Methods

A small winery producing high quality Red and White “Bio” wines has been selected for this study. A geological and pedological detailed study has been carried out separately to define the substratum nature of the two vineyards from which grapes are produced. Rocks and soils have been sampled and analyzed for trace elements and Sr-isotope. In addition, grapes of the different cultivars used for the vinification of the different wines, grape juices, and musts of different vintage years for oenological food-chains of both Red and White wines, as well as additives used for fining the latter, have been collected.

Rock and soil as well as grape, grape must, wine samples, yeast and bentonite have been treated and prepared for mass spectrometer analyses in a clean chemistry laboratory and underwent different digestion procedures according to methods previously described<sup>8,9,11,13</sup>. Bioavailable Sr was leached from soil using Unibest resin capsules (Unibest Inc., Bozeman MT) according to Marchionni et al.<sup>9</sup>. 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 3N HNO<sub>3</sub> as eluent and Milli-Q® water to collect Sr. Some 100-200 ng of purified Sr, accurately dissolved in 1 µl of 2N HNO<sub>3</sub>, were loaded onto single Re filaments using 1 µl of TaCl<sub>5</sub> (activator) and 1 µl of H<sub>3</sub>PO<sub>5</sub> (fractionation suppressor)<sup>9,11</sup>. Sr isotopes abundances have been measured in dynamic mode using a Thermo Finnigan™ Triton-Ti magnetic sector field thermal ionisation mass-spectrometer (TIMS) at the University of Firenze<sup>9,11,13</sup>. External precision of NIST SRM987 international reference sample for period of this study was <sup>87</sup>Sr/<sup>86</sup>Sr = 0.710251±10 (2σ, n=40), whilst the long-term mean value was 0.710248 ± 16 (2σ, n=213, equivalent to an error of 23 ppm).

## 3. Results and discussion

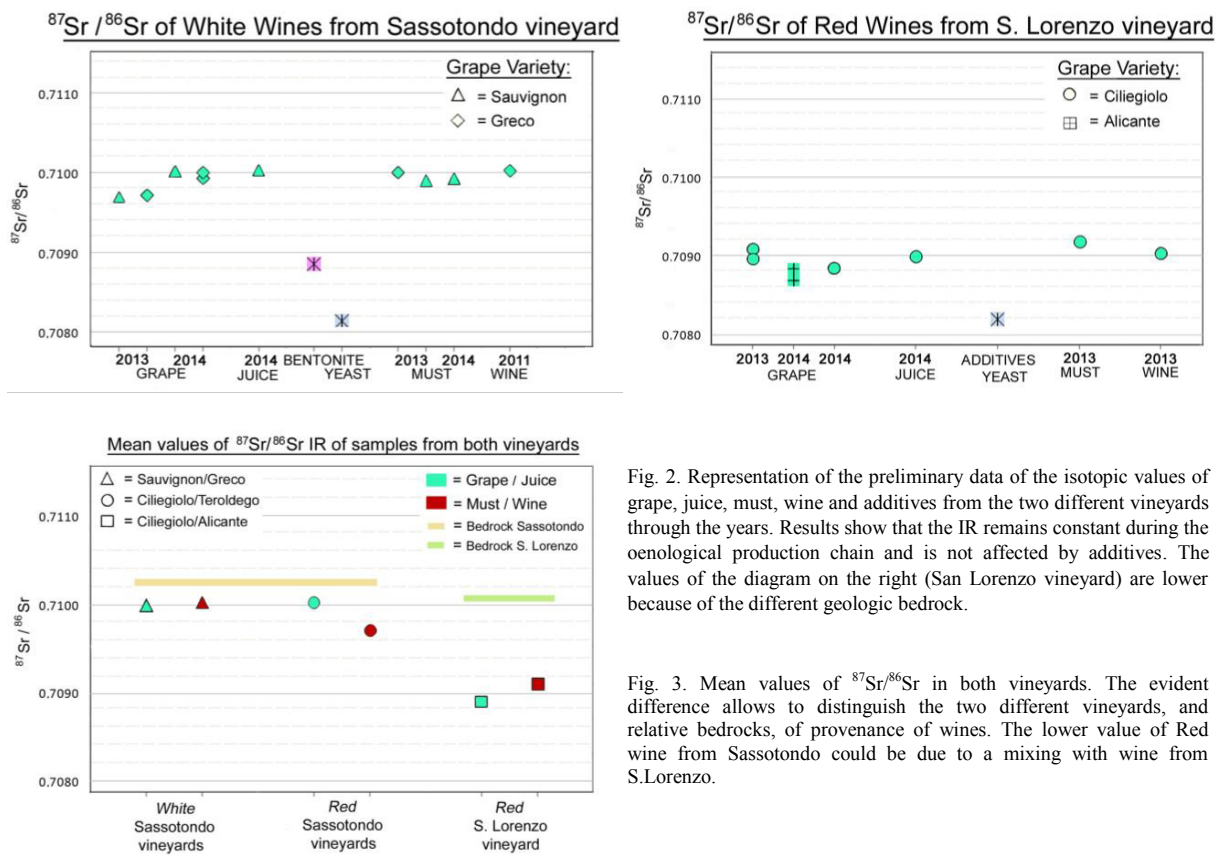


Fig. 2. Representation of the preliminary data of the isotopic values of grape, juice, must, wine and additives from the two different vineyards through the years. Results show that the IR remains constant during the oenological production chain and is not affected by additives. The values of the diagram on the right (San Lorenzo vineyard) are lower because of the different geologic bedrock.

Fig. 3. Mean values of <sup>87</sup>Sr/<sup>86</sup>Sr in both vineyards. The evident difference allows to distinguish the two different vineyards, and relative bedrocks, of provenance of wines. The lower value of Red wine from Sassotondo could be due to a mixing with wine from S.Lorenzo.

Preliminary results show two distinct groups of values relative to the “Sassotondo” and “San Lorenzo” vineyards lying on two different volcanic rock units. The isotopic values measured in grapes, grape juices, must and wines through the years are in a narrow interval at different levels depending upon the vineyard of provenance rather than to the addition of either yeast or bentonite. For example, the Greco cultivar for the vintage years 2013 and 2014 does not change significantly independently by the addition of yeast and bentonite.

The Sr-isotope data in grapes of different cultivars suggest that the isotopic ratio of the Sr absorbed by the roots does not depend upon the different type of vine cultivar, but the mechanism of elements absorption is the same for the different plants and it reflects the value of the respective geologic bedrock. The lower  $^{87}\text{Sr}/^{86}\text{Sr}$  observed in all products of the enological food chains with respect to the values of the bedrocks are not related to additives, but they possibly depend upon other geochemical factors. Further experiments on other vintage years are, however, needed to validate these preliminary findings and to better define the role of groundwater in controlling the final  $^{87}\text{Sr}/^{86}\text{Sr}$  of the wines.

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