Sr ISOTOPES AND ROMAGNA WINES: AN OPPORTUNITY FOR BETTER TRADING?

LES ISOTOPES DU Sr ET LES VINS DE ROMAGNE: UNE OPPORTUNITE POUR UNE MEILLEURE COMMERCIALISATION?

GLI ISOTOPI DELLO Sr E I VINI DELLA ROMAGNA : UNA OPPORTUNITÀ PER UNA MIGLIORE COMMERCIALIZZAZIONE ?

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Summary

The Sr isotopic compositions of 11 wines from Romagna were determined with the aim of providing a new parameter to track the origin of these wines and serving for better trading. The ^{87}Sr values measured ranged narrowly from -0.07 to +0.33 permil, in agreement with the provenance of the parent grapes from an area characterized by substantial uniformity of soil composition. However, so far, it is possible to make a preliminary distinction of the *Sangiovese* wines from the other wines analyzed because the former contain slightly more radiogenic Sr. This may reflect the different soil geology of vineyards, as the *Sangiovese* wines are made from grapes mainly growing on flysch soils, while the other wines are from grapes growing on sedimentary and alluvial Pliocene-Quaternary soils.
The comparison of the data from Romagna wines with those of other Italian regions shows the potential of the ^{87}Sr to characterize most of these products. However, the data are ambiguous for distinguishing the wines from vinyards growing on similar lithologies, i.e. soils developed on Late Cenozoic sedimentary rocks. The application of Sr isotopes may be a promising tool for setting the fingerprints of wines when combined with other isotopic and chemical parameters.
Key words: *Sr isotopes, wines, origin, Romagna, Italy*

Résumé

La composition isotopique du Sr a été mesurée dans 11 vins de Romagne, parce que la détermination de ce paramètre peut être utile à tracer l'origine des produits pour une meilleure commercialisation.
Les ^{87}Sr mesurés se sont avérés homogènes au sein d'une faible amplitude de valeurs (-0.07 et +0.33 $^{o}/_{oo}$), en accord avec la provenance des raisins d'une zone caractérisée en grande partie par l'uniformité des sols. On peut distinguer de façon préliminaire, les vins *Sangiovese* des autres, parce que ces vins-ci contiennent plus de Sr radiogénique. Cela peut être expliqué par la différente composition

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géologique des sols, car les raisins de *Sangiovese* poussent surtout sur sols de flysch et, au contraire, les autres vins proviennent de terrains sédimentaires du Pliocène-Quaternaire.
En comparant les données isotopiques des vins de Romagne et d'autre régions italiennes, il semble possible que le ^{87}Sr soit un élément distinctif de la plus grande partie des vins, mais non de tous. Mais les données isotopiques sont ambiguës pour distinguer les vins de raisins développés sur sols issus de lithologies semblables, comme les roches sédimentaires du Cénozoïque supérieur. L'application des isotopes du Sr peut être un outil favorable pour définir les caractéristiques des vins, en conjonction avec d'autres paramètres isotopiques et chimiques.
Mots-clé: *Isotopes du Sr, vins, origine, Romagne, Italie*

Riassunto

È stata determinata la composizione isotopica dello Sr di 11 vini della Romagna, perché la determinazione di questo parametro può essere utile a tracciare l'origine del prodotto per una migliore commercializzazione. I $\delta^{87}Sr$ misurati sono risultati sostanzialmente omogenei, variabili tra -0,07 e +0.33 per mille, in accordo con la provenienza delle uve da un'area caratterizzata da sostanziale uniformità dei suoli. E' comunque possibile in via preliminare distinguere i vini *Sangiovese* dagli altri analizzati perché i primi contengono Sr leggermente più radiogenico. Ciò può riflettere la differente geologia dei suoli, perché le uve del *Sangiovese* crescono prevalentemente su terreni flisciodi, laddove le uve degli altri vini si sviluppano generalmente su suoli sedimentari e alluvionali di età pliocenica-quaternaria. Inoltre dal confronto dei dati isotopici dei vini della Romagna e di altre regioni italiane si evince la possibilità che il $\delta^{87}Sr$ sia un parametro distintivo, sebbene non in tutti i casi. Infatti i dati isotopici mostrano ambiguità per vini di uve che crescono su suoli sviluppatisi su simili litologie, cioè rocce sedimentarie tardo-cenozoiche. Tuttavia è possibile che l'applicazione degli isotopi dello Sr possa essere un promettente strumento di definizione della provenienza dei vini, in associazione con altri parametri isotopici e chimici.
Parole chiave: *Isotopi dello Sr, vini, origine, Romagna, Italia*

Introduction

Romagna is not a famed land of wines, at least as other Italian regions (e.g. Piedmont, Friuli-Venezia Giulia and Tuscany). Nevertheless, Romagna produces a number of wine brands, ranging from low-cost products such as *Tavernello* to higher-price products such as *Albana* and *Cagnina.* However, the typically common wines of the region are referred to as *Trebbiano* and *Sangiovese di Romagna.* The areas of wine production are mainly located in the foothill strip of the Apennines, stretching across the provinces of Forlì-Cesena, Ravenna, Rimini and Bologna (Fig. 1).
In this paper, we have applied the systematic of Sr isotopes to define the isotopic signature of several wines from Romagna. Sr is a quite mobile element in the soil

where it occurs mainly in minerals, generally to substitute for Ca. However, as the sources of Sr in the soil can also be anthropogenic (e.g. fertilizers, pH-amendments, etc.), the isotopes may help distinguish between natural and man-related sources (e.g. Lahd Geagea et al., 2008). As Sr isotopes do not fractionate when the element passes from the soil to the vine growing on, thus, the isotopic ratios are expected to be preserved in wines if no Sr-bearing substance is added during winemaking. In this context, Sr-isotope ratios can help trace the origin and, eventually, informing on winemaking treatment. Contributing to establish the fingerprints of a given wine, possibly along with other chemical and isotopic parameters, this may be useful in wine trade. As a whole, this research represents an attempt to set the traceability of Romagna's wines to serve for better trading.
The application of Sr isotopes to the study of wine origin dates back to the'90 (e.g. Horn et al., 1993; Horn et al., 1997; Wolff-Bönisch et al., 1998; Lancelot et al., 1999; Martin et al., 1999) and after 2000, has been used also associated with other techniques (e.g. Almeida and Vasconcelos, 2001, 2004a, b; Barbaste et al., 2002; Vorster et al., 2010). The first application of Sr isotopes to Italian wines has been carried out by Wolff-Börnisch et al. (1998) who studied the products from the Vesuvius and Etna volcanic areas. Recently, Mercurio et al. (2011) have presented a study of the *Piedirosso* vineyards in the Phlegrean Fields. On the basis of the number of wines so far analyzed throughout the world, it appears that Sr isotopes are not always fully successful to detect the provenance of wines because of possible overlapping of the isotopic signatures of the products from different districts (e.g. Vorster et al., 2010).

The studied wines and the geological setting of Romagna soils

11 wines have been analyzed for Sr isotopes in this study. They are: *Albana di Romagna, Cagnina di Romagna, Trebbiano di Romagna* (2 brands)*, Trebbiano di Ravenna, Trebbiano del Rubicone* (2 brands), *Sangiovese di Romagna* (2 brands), *Tavernello* and *Castellino*. In particular, the *Albana di Romagna* wine is labelled DOCG (Control of Authenticity of Origin Guaranteed), while the *Cagnina di Romagna, Sangiovese di Romagna* and *Trebbiano di Romagna* wines are labelled DOC and, lastly, the *Trebbiano del Rubicone* and *Trebbiano di Ravenna* wines are labelled IGT (Typical Geographic Indication).The area, where the related grapes grow on, generally covers the province of Forlì-Cesena, with minor extensions in the provinces of Bologna (Imola), Ravenna and Rimini (Fig.1). It extends mainly along the pedemountain strip of the Apennines. In contrast, the *Tavernello* wine, which is packaged in Forlì, is a blend of wines from different Italian areas; for instance, the studied wine specimen is a blend from Romagna, Emilia (Modena), Abruzzo (Chieti, Pescara, Teramo), Apulia (Brindisi) and Sicily (Trapani, Agrigento). For the *Castellino* wine, no information of grape provenance is available; only the site of packaging (Forlì) is known.

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The main lithologies outcropping in Romagna, which the wines are related to, are represented from downhill to uphill by Quaternary alluvial deposits of the Apenninian rivers, Pliocene sand and clay with associate Messinian gypsum and, lastly, Eocene-Miocene flysch, also known as Marnoso-Arenacea.

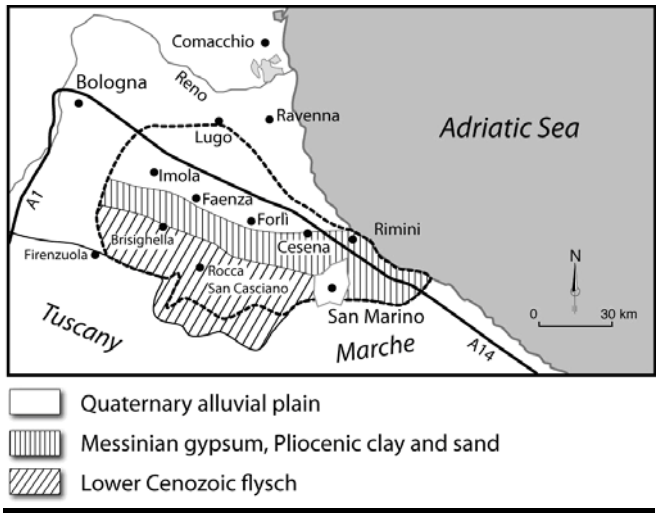

Figure 1

Sketchy geological map of Romagna; the area contoured by dash line represents the zone of the production of the studied wines

According to enological maps of Romagna released from www.vinostore.it, the areas where the grapes of the *Trebbiano-Cagnina-Albana and Sangiovese* wines grow on, overlap to large extent. However, in general, the *Sangiovese* vineyards extend almost exclusively uphill, whereas the *Trebbiano-Cagnina-Albana* vineyards stretch on foothill and the alluvial plain. Uphill lithologies are mainly represented by the Eocene-Miocene flysch, whereas downhill lithologies are composed of Pliocene clay and sand, as well as Quaternary alluvial deposits. Lastly, the Italian soils where *Tavernello* grapes grow on, are composed of sedimentary rocks of Tertiary age, with subordinate lithotypes of the Quaternary and Mesozoic. Fertilizers are generally used in the study area. However, the fertilizers commonly used in Romagna are represented by synthetic (K-N-P) products and subordinate organic matter. No Sr-bearing marine phosphorites are used because Romagna's soils are not P-deficient.

Analytical procedure

20 ml of wine sample were treated with 2 ml ultrapure HNO_3 and 4 ml H_2O_2 30% (v/v) under controlled temperature in order to avoid the decomposition of the organic matrix compounds. The digested samples were preconcentrated by heating at 80°C until the volume was reduced to approximately to 10 ml. Subsequently, 12 ml aqua regia (3:1, HCl/HNO_3) were added and the samples were heated on hot plate following the International Standard Procedure (ISO 11466). The digested samples were shaken at room temperature and, subsequently, filtered with

Whatman no. 42 paper, then evaporated and converted in chloride form with ultrapure 6N HCl.
Sr for isotopic analysis was separated in a 3 ml AG 50 W-X8 resin column. Isotopic analyses were carried out at IGAG-CNR c/o Dipartimento di Scienze della Terra, University of Rome "La Sapienza" using a FINNIGAN MAT 262RPQ multicollector mass spectrometer with Re double filaments in static mode. The internal precision (within-run precision) of a single analytical result is given as two standard error of the mean. Repeated analyses of standards gave averages and errors expressed as two standard deviation (2s) as follows: NBS 987 $^{87}Sr/^{86}Sr$ = 0.710241 ± 13 (n=20), $^{86}Sr/^{88}Sr$ normalized to 0.1194. Total procedural blanks were below 2 ng Sr and below 1 ng Nd for all samples. Sr-isotope ratios are expressed as δ values in permil relative to Sea Water standard (0.70917; Richter and De Paolo, 1987) according to the following formula :

$$\delta^{87}Sr = 10^3 [(^{87}Sr/^{86}Sr_{sample} / ^{87}Sr/^{86}Sr_{seawater}) -1] \quad [1]$$

Analytical results

The isotopic data are graphically shown in Figure 2.

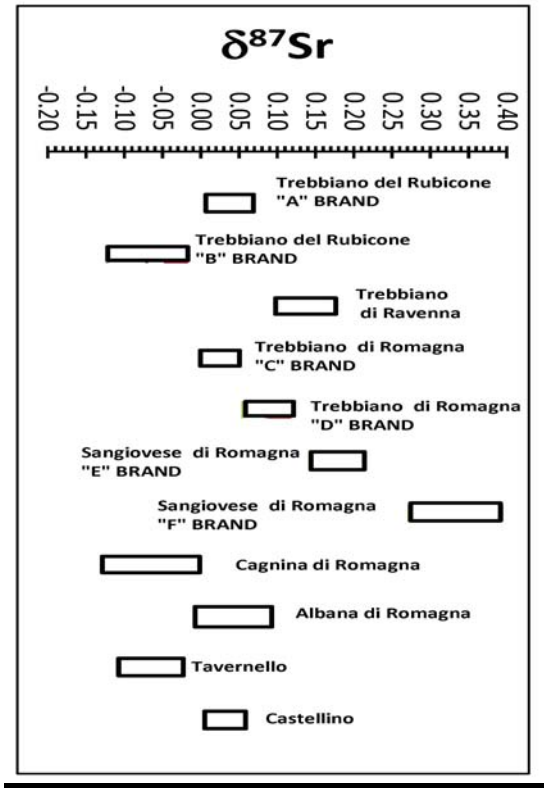

Figure 2

The variation of $\delta^{87}Sr$ of Romagna's wines studied in this paper; each box represents analytical value + error.

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The wine samples display a narrow isotopic range from -0.07 (*Trebbiano del Rubicone* "B" brand**,** *Cagnina di Romagna* and *Tavernello*) to +0.33 (*Sangiovese di Romagna* "F" brand). The two *Sangiovese* wines analyzed exhibit higher $\delta^{87}Sr$ than the other wines. The *Tavernello* and *Castellino* wines share similar $\delta^{87}Sr$ to the *Trebbiano del Rubicone* wines and, in general, the other white wines.

Discussion

The $\delta^{87}Sr$ of the *Cagnina di Romagna* and *Albana di Romagna* wines fall into the range of the five *Trebbiano* wines (-0.07 ÷ +0.15). This suggests origin of all these wines from grapes growing on soils developed on similar bedrocks. In particular, the $\delta^{87}Sr$ of these wines straddle the isotopic value of Quaternary seawater ($\delta^{87}Sr$ = 0, Richter and De Paolo, 1987), suggesting the Sr supplied from the soil to the vine is mainly derived from Pliocene-Quaternary marine carbonates.
Relative to the $\delta^{87}Sr$ of the *Sangiovese* wines, the lower values of the *Trebbiano* wines cannot reflect the distinction between white and red wines, although the two groups of wines can actually be distinguished according to the different color. In fact, Sr isotopic fractionation does no affect white or red grapes growing on the same soil. In contrast, the isotopic distinction between the *Sangiovese* and the other wines likely reflects the different lithologies of the two areas of grape production. In this context, the slightly higher $\delta^{87}Sr$ of the *Sangiovese* wines witnesses little contribution of radiogenic Sr beside that provided from the carbonate fraction of the flysch (Tab. 1).
Lastly, the similar $\delta^{87}Sr$ of the *Tavernello* and *Castellino* wines suggest a similar provenance of the related grapes. Moreover, as these wines display similar $\delta^{87}Sr$ to the *Trebbiano del Rubicone* wines, this may suggest that the bulk of the *Tavernello* and *Castellino* wines contain significant contributions from the grapes of the Rubicone river area.

Sample	Lithotype	□^{87}Sr
PV-4	Flysch Marnoso-arenacea (bulk sample)	+6.4
PV-3	Flysch Marnoso-arenacea (carbonate fraction)	-0.08
PV-8	Messinian gypsum	-0.37
PV-10	Pliocene clay and sand	-0.09
PV-11	Quaternary alluvium (bulk sample)	-0.03
Pa-4	Quaternary alluvium (carbonate fraction)	-0.62
Pa-5	Quaternary alluvium (carbonate fraction)	-0.65
Perd-2	Quaternary alluvium (carbonate fraction)	-0.61

Table 1

The isotopic composition of the main lithotypes outcropping in Romagna.

Comparison with other Italian wines

In Table 2 we report the $\delta^{87}Sr$ of wines from Abruzzo, Campania, Latium, Marche, Piedmont, Sardinia and Veneto. In particular, the W-31, W-32, W-35, W-36 and W-50 wines are produced from grapes growing on Tertiary-Quaternary sedimentary rocks, the W-4 wine is referred to vineyards from Quaternary volcanic

rocks of Latium and, lastly, the W-33 wine is produced in the Soave countryside between Verona and Vicenza, Veneto, where both basalts and limestones of the Tertiary crop out.

The comparison shows that Romagna's wines can be distinguished from the wines produced from grapes growing on volcanic areas, while they cannot be distinguished from wines related to sedimentary rocks and alluvial deposits of the Tertiary and Quaternary. In particular, the *Trebbiano* wines from *Romagna* and *Abruzzo* share very similar $\delta^{87}Sr$, reflecting similar lithologies of the two production areas. Therefore, as isotopic data may be ambiguous, this limits the potential use of Sr isotopes as an indicator of wine provenance. Probably, the application of Sr isotopes combined with the isotopes of other elements and/or element concentrations may solve data overlapping (Castorina and Masi, in preparation).

Table 2

The isotopic composition of wines from other Italian districts.

Sample	Brand name	$\delta^{87}Sr$
W-4	Frascati	+0.93
W-31	Vermentino Sardegna	-0.05
W-32	Falangina Benevento	+0.77
W-33	Soave Classico	-3.67
W-35	Verdicchio Jesi	-0.29
W-36	Cortese Monferrato	+0.85
W-50	Trebbiano d'Abruzzo	+0.03

Conclusions

The application of Sr isotopes to the study of several Romagna's wine specimens has yielded the first data that may help characterize the origin of these products. In fact, the $\delta^{87}Sr$ have unveiled the source of the Sr present in the wines, allowing for referring the parent grapes to soils of certain lithologies. In particular, it has been possible to distinguish between the soils which the *Sangiovese* grapes grow on, and the others, as the *Sangiovese* wines contain comparatively slightly more radiogenic Sr. No significant isotopic distinction has been found between DOC-DOCG and ITG wines, and between these wines except the *Sangiovese* ones, and the popular tetra-packaged *Tavernello* and *Castellino* wines.

The comparison between Romagna's wines and a selection of wines from other Italian regions, shows that Sr isotopes can be a suitable tool as indicator of provenance, but not in all cases. In fact, for wines derived from grapes grown on Cenozoic sedimentary rocks, it is not possible to provide a clear-cut distinction among the different areas. In contrast, Sr isotopes may allow for distinguishing Romagna's wines from those of Italian areas where volcanic, granitoid and metamorphic rocks crop out.

To improve the information provided by Sr isotopes in the case of overlap, it is advised to complement the data with those resulting from the application of other

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isotopes and/or trace-element analysis of wines, as suggested by Martin et al. (1999) and Almeida and Vasconcelos (2004a).

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