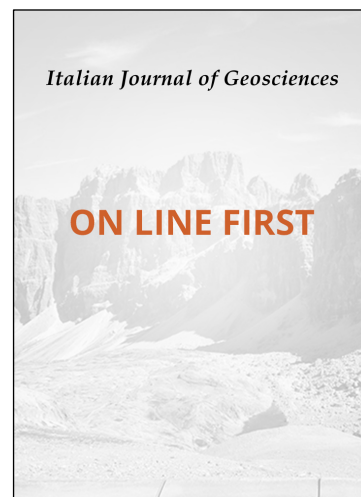


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Elemental and Sr-isotope characterization of the high-altitude Bosa vineyard in the Apuan Alps UNESCO Global Geopark (Italy)

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ABSTRACT

The Sr-isotope systematics and trace element analysis were applied to vine and wine collected during the 2015 harvest from the Bosa vineyard, a high-altitude farm in the Apuan Alps UNESCO Global Geopark in Italy, in order to investigate the links with geology in vineyards facing with a hostile environment. The results indicate a correspondence between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in wine and must [$^{87}\text{Sr}/^{86}\text{Sr} = 0.70843(1)$ and $0.70846(1)$, respectively] and the NH_4OAc extractable Sr from soil [$^{87}\text{Sr}/^{86}\text{Sr} = 0.70847(1)$]. However, detailed investigations reveal that Sr-isotope data on grape juice collected in different vines vary in the range between $0.70833(1)$ and $0.70844(1)$, reflecting a small-scale vineyard variability and indicating that the root system explores heterogeneous soil resources for nutrient uptake. Grape seeds and stems from one single vine both show identical $^{87}\text{Sr}/^{86}\text{Sr}$ of $0.70820(1)$, significantly lower with respect to corresponding juice [$^{87}\text{Sr}/^{86}\text{Sr} = 0.70844(1)$]: this finding is unexpected and reflects the uptake from isotopically different reservoir during the evolved dynamic of vine and fruit development. In particular, the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is attributed to the minor contribution of an unradiogenic carbonate component. These effects, however, do not mask the existing isotopic relationship between soil and wine at the vineyard scale. Trace elements in wine show a characteristic pattern that roughly mimics bedrock, suggesting a minor role of bedrock chemical weathering in developing the soil profile. Relatively high Fe and Mn contents are measured in wine, inherited from bedrocks, and high Zn, possibly applied to grapevines. Elements that are considered potentially toxic (As, Cd, Cu, Pb, Zn) are below the maximum acceptable limits established by OIV.

Despite preliminary, these data represent the first characterization for traceability of the high-altitude Bosa vineyard, giving some track of weathering and elemental availability in a particular microclimate setting and underlying the link between bedrock geology and element uptake in vines at high elevations with respect to valley grown grapes.

KEYWORDS: *trace element; Sr-isotopes; high-altitude vineyard; Apuan Alps UNESCO Global Geopark*

INTRODUCTION

The ability to trace the area of production for a wine is a priority for both consumers and producers (e.g. CIMINO & MARCELLONI, 2012), since the wine quality and characteristics are essentially due to the geographical and geo-pedological environment where vines grow. Indeed, the

geology of the vineyard substrate has an influence on the wine character (WHITE, 2003), providing inorganic nutrients for their growth (e.g. MORLAT & JACQUET, 1993; SMART *et alii*, 2006) and determining the content of naturally occurring metals in wine (POHL, 2007). The geochemical nature of the bedrocks, the degree of weathering (MORLAT & BODIN, 2006) and geomorphology of places where vineyards grow (e.g. ROBINSON, 2006) interacts with climatic factors. In this sense mountain and hillside vineyards distinguish from their flatland counterparts for the exposure to climate contrasts, temperature shifts, exceeding winds, snow cover, higher solar radiation and light intensity: these factors affect photosynthetic activity and the development of grape berries (FALCETTI & IACONO, 1996; MATEUS *et alii*, 2002; Oliveira *et alii*, 2004; VAN LEEUWEN & SEGUIN, 2007; Freeman & Kliewer, 1983; SPAYD *et alii*, 2002; ROBINSON, 2006). How the different elevation of production directly contributes to the distinct aromas and flavors in wine, for example by developing a more favorable phenolic profile, remains a debated topic (MALTMAN, 2008; CAPECE *et alii*, 2012). In Europe an altitude of about 500 m (a.s.l.) is generally thought to be the upper limit for reliable grapevine fruit ripening. However, higher-altitude areas for wine production in Italy and Europe occur, such as vineyards in the Lombardia, Valle D'Aosta, Alto Adige and Sicily Regions (Italy); in the Valais (Switzerland) and Pyrenees mountain range (France).

The multielement chemical composition of wine has been applied to differentiate production areas by statistical multivariate analysis (e.g. KMENT *et alii*, 2005; LARA *et alii*, 2005; MORET *et alii*, 1994; THIEL *et alii*, 2004); however, the selective uptake of elements from soils by plants, pollution and wine manufacturing practices may obscure the link between wine chemistry and vineyard soil. The Sr isotopic systematics has been demonstrated that is more likely to reflect the wine terroir, since any fractionation is in-run corrected (PETRINI *et alii*, 2015; VINCIGUERRA *et alii*, 2016; GHEZZI *et alii*, 2017; DURANTE *et alii*, 2018; TESCIONE *et alii*, 2018).

The Bosa Geopark Farm vineyard is located in the Apuan Alps UNESCO Global Geopark (www.apuanegeopark.it), at an altitude of 850 m (a.s.l.) representing the highest vineyard in the Tuscany Region and one of the highest of Italy. The idea of a micro-vinification experiment at Bosa starts from the awareness that modifications of landscapes and crops due to the climate change are underway and unavoidable, especially in the Mediterranean area (HANNAH *et alii*, 2013). The ongoing global warming process, moving plantations further North in latitude and higher in altitude,

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is revealing able to convert a land without winemaking tradition, such as the Apuan Alps area, into a potential area for high-altitude wine production. By considering its good capacities of adaptability in many climatic conditions, the Merlot grape variety was chosen and planted at Bosa, and vineyard is maintained under the same cultural practices (i.e. fertilizer, training system, irrigation and vigor control practices).

The project for the geo-pedological characterization of the area where grow the mountain vine, promoted by the Apuan Alps Geopark, started at the beginning of 2014 with the aim to define a new “terroir” (HUGGETT, 2006) in the inland side of the Apuan Alps. This study presents the results obtained from the first step in traceability and geochemical characterization of the Bosa wine.

AREA OF STUDY AND GEOLOGICAL OUTLINES

In the eastern sector of its territory, the Apuan Alps Geopark established the Bosa Geopark Farm (Fig. 1). Bosa is located in the inner slope of the Apuan Alps, near the village of Careggine, lying on a natural terrace facing west and overlooking the Vagli lake. It has an amazing panoramic position (Fig. 2), embracing the northern part of the Apuan Alps mountain range, from Mt. Sumbra to Mt. Pisanino.

The Bosa Geopark Farm is a rural district site used for the conservation of the wild and cultivated biodiversity and for agronomic experimentation. Here it is possible to maintain and look after old and local cultivars and breeds, promote typical agricultural and food products and introduce new agronomic techniques and plant and animal varieties suitable for the specific environmental and climatic conditions. This mission is being carried out in an ethical context of organic farming, good practice and the sustainable use of natural resources. Within this cultural framework, the Bosa vineyard has been planted on the terraces historically created to increase the crop acreage and prevent erosion by surface water and subsequent sliding. The terraced slope includes the bedrock as well as the Quaternary unconsolidated deposits derived from landslides and eluvial/colluvial processes.

The Bosa area is characterized by a perhumid climate with a mean annual temperature between 9 and 11 °C and 4/5 cold months (RAPETTI & VITTORINI, 2012). The precipitation data recorded by the nearby station at the Careggine village (Fig. 1) during the last 20 years (1999-2018) indicate a mean annual rainfall exceeding 1500 mm, ranging from the highest value of 2506 mm in 2014 to the lowest value of 1147 mm in 2015, with no months of complete dryness (Tuscan Regional Hydrological Service; www.sir.toscana.it).

From a geological point of view, the Apuan Alps correspond to the main tectonic window of the Northern Apennines (Fig. 1). Here the complete nappe stack of the Northern Apennine, resulted from the collision between the European plate and the African plate, is exposed. The resulting nappe stack is a complex fold and thrust belt with NE-directed tectonic transport including the highest ophiolite-bearing oceanic-derived Ligurian Units onto the units derived from the Adria continental margin, i.e. the Tuscan domain. In particular, the Apuan tectonic window allows the observation of the crustal

duplication of the continental Tuscan units. The lower tectonic units (Tuscan Metamorphic Units) underwent green-schist metamorphism during the Cenozoic time and constitute the deepest structural levels; the upper units are the corresponding unmetamorphosed sedimentary formations forming the Tuscan Nappe. The latter consists of a Mesozoic-Cenozoic succession evolving from shallow water to pelagic deposits, ending with siliciclastic foredeep turbidites of upper Oligocene-lower Miocene age (Macigno Formation). Inside the Tuscan Metamorphic Units, the Apuan Alps are a mountain range with steep slopes and high relief energy characterized by rugged profiles, jagged ridges and Dolomite-like peaks. On the contrary, the Tuscan Nappe rocks form more gentle and low-lying mountain areas.

The area of the Bosa Geopark Farm is located inside the outcrop area of the Tuscan Nappe. In particular, the bedrock is formed by the Scaglia Toscana Formation, belonging to the upper part of the Tuscan Nappe, and representing the transition between the underlying Lower Cretaceous pelagic carbonates (Maiolica Formation) and the overlying Macigno Formation. The Scaglia Toscana Formation has been subdivided into several members or lithofacies (PANDELI *et alii*, 2018 and references therein). The soil parental material (bedrock) in the studied vineyard shares common lithological and mineralogical features, being represented by varicoloured shales and siliceous marls with intercalations of grey to greenish siliceous

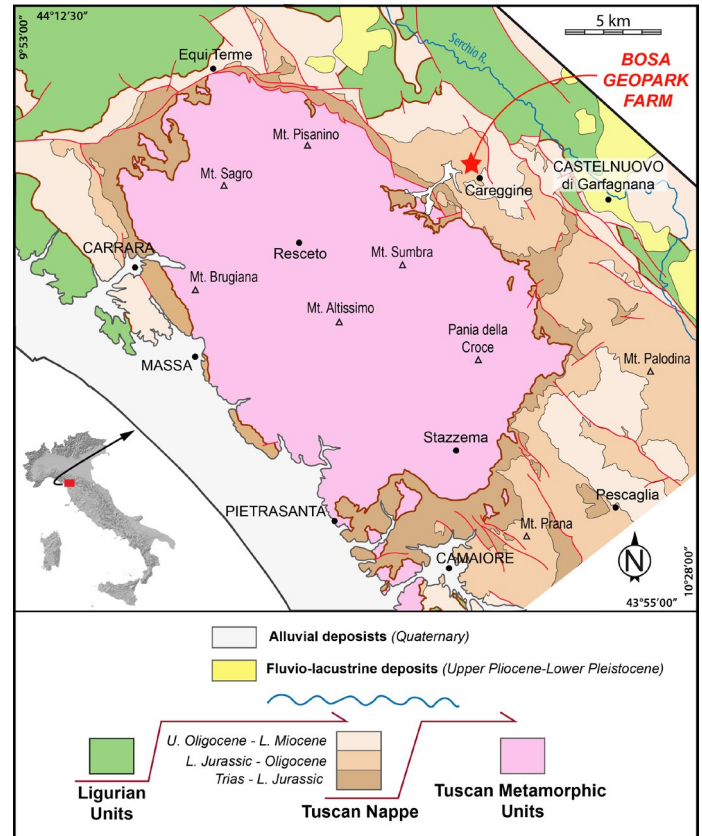


Fig. 1 - Geological sketch of the Apuan Alps (modified after CARMIGNANI *et alii*, 2000) with location of the Bosa Geopark Farm. The relationships among the main tectonic units and the unconformable continental deposits are shown.



Fig. 2 - The Bosa Geopark vineyard picture showing Merlot vines and pruning in the natural landscape of Apuan Alps.

calclutites and up to 25 cm thick beds of calcarenites. Based on lithostratigraphic correlations with better known successions of the Scaglia Toscana Formation, the lithofacies of the Bosa vineyard bedrock can be assigned to the “Argilliti e Calcareniti di Dudda Member” which is generally referred to the middle-late Eocene (48 – 34 Ma; PANDELI *et alii*, 2018).

THE SOILS OF THE BOSA VINEYARD

The vineyard is located on terraces that were renovated by the Bosa staff before the planting of vines. The terrace's slope gradient is between 2-8%, whereas the general slope is 25-30%.

Soil was characterized at the vineyard scale with the aim to identify the physical and chemical features of the Bosa vineyard terroir. The soil observations were carried out following the “Guidelines of the methods of soil survey and data informatization” (COSTANTINI, 2007).

The soil is closely related to the geological substratum of the Scaglia Toscana Formation, developing directly from the parental material through beginning processes of pedogenesis such as alteration. The distinguished soil sequence is given in Table 1 and consists of Ap, Bw, BC, Cr horizons. The Ap horizon is the plowed layer; Bw is the expression of the first signs of pedogenesis, it is rarely present inside the vineyard also because it has been affected by agricultural plowing during the terraces restructuring; BC represents the bedrock with light alteration, while Cr is the bedrock layer characterized by the varicoloured shales and siliceous calclutites of the Scaglia Toscana Formation. The soil is classified as loamy, mixed (nonacid), mesic, Typic Udorthents, following the Soil Taxonomy by the United States Department of Agriculture (USDA, 2010), or as Colluvic Regosols according to the Word Reference Base for Soil Resources (IUSS Working Group WRB, 2014). Soil horizons were sampled after the profile face was cleaned. Approximately from 1 to 1.5 kg of soil were collected from each layer. Soil test results are reported in Table 1. The soil is non-calcareous, well drained, from neutral to alkaline. It has a good content of organic matter (SOM; 45.3 g/kg in the Ap horizon, progressively lowering downward), which

is likely preserved by the climatic conditions typical of the mountain environment (cold winters and snow cover) that reduce reaction kinetics lowering the degradation rates. The organic matter affects the productivity and the physical properties of the soil and consequently its water retention and oxygenation. The cation exchange capacity (CEC) is moderately high [between 14.9 meq/100 g (Cr) and 25.5 meq/100g (Ap)], also reflecting the role of organic matter. It has to be noted that exchange sites are mostly for Ca, while a very low amount of exchangeable K and Na and low exchangeable Mg were measured, suggesting that these elements are mostly fixed within mineral phases. The supply of nitrogen is high, while the content of phosphorus, magnesium and potassium is low. Although the soil is suitable for grapevine grown and symptoms of nutrient deficiency are not observed, it might be planned to provide these elements through suitable fertilizers.

MATERIALS AND METHODS

A soil sample for Sr isotopic composition analysis (expressed by the measure of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) was collected at a depth of 60 cm, the depth of maximum root development, using a single-gauge auger set. The exchangeable fraction of soil for Sr isotopic analysis was extracted by using 1M ammonium acetate solution (NH_4OAc) buffered at pH 7 (FILGUEIRAS *et alii*, 2002; PETRINI *et alii*, 2015). The NH_4OAc -solution buffered at pH 7 extracts the labile component from soil without dissolving the carbonate fraction (e.g. Gompy *et alii*, 1998). The residual amount was extracted by conventional aqua regia (3:1 mixture of HCl and HNO_3) digestion on hot plate (URE, 1990). Elements that are not released by aqua regia are mostly bound to silicate minerals and are generally considered unimportant for estimating elemental mobility (NISKAVAARA *et alii*, 1997; CHEN & MA, 2001).

The wine from the 2015 harvest was analyzed for trace element and Sr isotopic composition. Must and grape juices obtained by gently squeezing with gloved hands grapefruits were also analysed for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, in order to evaluate the possible effects of vinification processes on isotope ratio and the isotopic heterogeneity in vines from different portions of the vineyard.

Stems and grape seeds from a single vine were also analysed for Sr isotopes. For isotopic analysis about 20 ml of unfiltered wine, must and juice and about 0.5 g of homogenized grape seeds and stems were digested by dry-ashing method (CAMPBELL & PLANK, 1998) using nickel crucibles and following the procedures reported by PETRINI *et alii* (2015). Analytical dry-ash represents a reliable method for decomposing plant tissue that does not introduce errors due to volatilization for strontium. Samples were removed from oven after internal temperature reached 30 °C, at this point ashes show a pale-grey color. 2 ml of ultrapure 2.5N HCl were then added to each digestion crucible and the solution centrifuged. The Sr isotopic composition in wine and soil extracts was determined by thermal ionization mass spectrometry (TIMS) using a Finnigan MAT 262-RPQ mass spectrometer, after separation of the ^{87}Rb isobar by conventional ion-exchange techniques. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was fractionation-corrected using the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. Repeated analysis of the NBS 987 isotopic standard gave an average value of $^{86}\text{Sr}/^{88}\text{Sr}=0.71025(2)$

TABLE 1.

Results of pedological analysis on soils from Bosa vineyard.

Soil horizon	Depth (cm)	Silt (g/kg)	Clay (g/kg)	Sand (g/kg)	N total (g/kg)	CaCO ₃ total (g/kg)	C/N	SOM (g/kg)
1Ap	0-60	412	283	305	3.14	5.3	8.5	45.3
2Bw	60-110	369	242	389	1.96	3.8	7.7	26.5
3BC	110-140	351	206	443	1.65	3.5	6.6	19.5
4Cr	140-180	146	153	701	0.51	3.1	5.6	4.8

	EC _{1:5} (dS/m)	pH	CEC (meq/100 g)	Assimilable P (mg/kg)	Exchangeable-Na (meq/100 g)	Exchangeable-K (meq/100 g)	Exchangeable-Ca (meq/100 g)	Exchangeable-Mg (meq/100 g)
1Ap	0.22	7.2	25.5	7	0.11	0.31	20.26	0.81
2Bw	0.07	7.6	23.6	3	0.12	0.21	19.25	0.45
3BC	0.05	7.8	23.3	2	0.11	0.20	21.27	0.45
4Cr	0.05	8.0	14.9	3	0.10	0.16	12.39	0.26

(n=28); no correction was applied to the measured ratios for instrumental bias. The reported uncertainties represent in-run statistics at 2s confidence level.

Trace element analyses on wine were performed using a PerkinElmer NexION 300X ICP-MS operating both in standard and in KED mode, using the procedures reported in GHEZZI *et alii* (2018). For wine digestion, 2 mL of sample were placed in 15 mL virgin polypropylene tubes and allowed to dry slowly at 70 °C. Ultrapure-grade concentrated HNO₃ was then added to the residue and digestion occurred until a clear solution was obtained (about two hours). The resulting solution was diluted with 13 mL of high-purity Milli-Q water providing a 6.6-fold final dilution of the wine with ~1.5% (v/v) HNO₃ matrix. The treated sample was analyzed within two hours. The relative standard deviation (RDS) was less than 10 % for Li, Be, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Mo, Cs, Ba, Ce and Tl and between 10 and 20 % for Sc, Ti, V, Fe, Cd, Sn, Sb and Pb. Recovery tests were carried out to evaluate the method accuracy. The recovery percentages in the wine sample were between 90 and 110% for Be, Sc, Cr, Mn, Zn, Ga, Rb, Sr, Mo, Sn, Sb, Ba and Pb and between 80 and 120% for Li, Ti, V, Fe, Co, Ni, Cu, As, Y, Zr, Cd, Cs, Ce and Tl.

RESULTS

The Sr isotopic data on wine, juices collected from grapes in different portions of the vineyard, grape seeds and stems and soil extracts are reported in Table 2. It is observed that the isotopic value in wine, must and in the NH₄OAc extractable fraction of soil closely approach [⁸⁷Sr/⁸⁶Sr = 0.70843(1), 0.70846(1) and 0.70847(1), respectively], even if deviation exceeds the error obtained by in-run statistics. These data indicate that the Sr-isotope ratio of wine and must is related to the local geology through the extraction by the 1 M NH₄OAc-solution of the Sr component which is mainly bound to the soil by low strength electrostatic forces. Indeed, this fraction best represents the readily soluble and plant-accessible strontium in the vineyard

(COMERFORD, 2005; GRYSCHKO *et alii*, 2005). It has also to be noted that the aqua regia extract from soil has a significantly more radiogenic signature with respect to wine [⁸⁷Sr/⁸⁶Sr = 0.70871(1)], indicating that this procedure is not able to recover the soil bio-available fraction and cannot be applied to represent biological processes. The correspondence observed between the ⁸⁷Sr/⁸⁶Sr ratio in wine and must indicates that the vinification process does not significantly alter the Sr budget (e.g. VINCIGUERRA *et alii*, 2015; MARCHIONNI *et alii*, 2016). It has to be noted that the ⁸⁷Sr/⁸⁶Sr ratio in berry juice from vines closely spaced in the vineyard range between 0.70833(1) and 0.70844(1) (Table 1). This reflects isotopic heterogeneities in the

TABLE 2

⁸⁷Sr/⁸⁶Sr ratio for the studied samples (soil extracts, wine, must, grape juice, grape seeds and stem)

Sample	⁸⁷ Sr/ ⁸⁶ Sr	abs. error*
acqua regia extract	0.708706	0.000005
ammonium acetate extract	0.708471	0.000006
wine	0.708428	0.000006
must	0.708464	0.000010
^a juice ₁	0.708440	0.000020
juice ₂	0.708337	0.000019
juice ₃	0.708436	0.000014
juice ₄	0.708327	0.000015
juice ₅	0.708389	0.000025
^b seeds	0.708202	0.000015
^b stem	0.708199	0.000012

* in-run statistics at 2s confidence level.

^a juices were obtained by grapefruits collected in different portions of the vineyard.

^b collected from a single vine corresponding to juice₁

extractable fraction of Sr from soil by vine roots; however, the observed soil-must-wine correspondence for the whole vineyard is not significantly affected by the within-area variability. Grape seeds and stems collected from a single vine both have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70820(1), showing a significantly less radiogenic signature compared with the corresponding juice [$^{87}\text{Sr}/^{86}\text{Sr} = 0.70844(1)$] (Table 1). This result is somewhat unexpected since Sr isotopic equilibrium has been previously reported among the different parts of a grape vine, despite the different Sr content (PETRINI *et alii*, 2015; DURANTE *et alii*, 2018).

The trace element analysis of the 2015 Bosa wine is reported in Table 3. Trace element contents are below the maximum contaminant limits specified by national and international regulations for consumption or export. In particular, the concentration of potentially toxic heavy metals As, Cd and Pb (1.8, 0.32 and 61 $\mu\text{g}/\text{L}$ respectively) are much lower compared with the concentration limits imposed by EU Regulation 1881/2006, OIV, WHO, Codex-San 193/1995, but also single Country regulations such as Deutsche Weinverordnung. Cr, Ni, Cu concentrations (respectively 17.9, 118 and 76 $\mu\text{g}/\text{L}$) are in the common range for trace metals in wine. A relatively high Zn content of 3596 $\mu\text{g}/\text{L}$ is measured; even if below the 5000 $\mu\text{g}/\text{L}$ threshold imposed by OIV and Italian Regulations (Italian Republic, DM 29, 1986), this may have detrimental effects on wine stability. Zn might derive from the agricultural practice, in particular fertilizers or specific dithiocarbamate-based fungicides, or be originated from the winemaking equipment. The wine is characterized by relatively high Mn content (1.4 mg/L), however below the 2 mg/L limit imposed by Chinese Authorities for the manganese content of wines imported into China, and very high Fe content (103 mg/L). The Fe content has an influence on the wine evolution during fermentation and affects its organoleptic properties. In addition, redox reactions (Pohl, 2007), may result in undesirable haze after aeration (iron casse, Jackson, 2008), and wines with high concentration of Fe may become unstable in the long term storage after bottling (Galani-Nikolakaki *et alii*, 2002). Even if at present there is not a threshold level for iron in wine, its amount should remain confined within reasonable levels so that the daily intake of iron for humans doesn't exceed 14 mg (EU Regulation No 1169/2011).

DISCUSSION

Although most of the vegetative matter in a vine is derived through pruning techniques and irrigation regimes (PELLEGRINO *et alii*, 2014), the primary minerals decomposing in vineyard substrate provide the inorganic nutrients that are essential for vine-root growth. Indeed, the nature of the bedrock and its degree of weathering influences the physical properties of the soil and the fate and cycling of nutrients (e.g. MORLAT & JACQUET 1993; COMERFORD, 2005; SMART *et alii*, 2006). In particular, clay minerals, carrying a net negative surface charge when in contact with soil water which derives from substitutions of cations in their structure, allow desorption and ion exchanges with soil water through protons liberated by roots, thus determining the bioavailability of nutrient and micronutrient (e.g. MARSCHNER, 1995; HOPKINS & HÜNER, 2004). Indeed, the trace element uptake by plants is

TABLE 3

Trace elements concentration in wine from the Bosa vineyard in the Apuan Alps UNESCO Global Geopark (Tuscany, Italy) together with bulk chemical composition of the bedrock.

Element	LOQ ^a ($\mu\text{g}/\text{L}$)	wine ^b ($\mu\text{g}/\text{L}$)	bedrock ^c (mg/Kg)
Li	1.67	<LOQ	84
Be	0.06	<LOQ	3.32
Sc	0.06	0.43	17.3
Ti	2.81	58	5520
V	0.80	0.95	146
Cr	2.51	17.9	109
Mn	3.49	1406	310
Fe	107	102985	54930
Co	0.20	8.8	23.9
Ni	7.0	118	67
Cu	39	76	
Zn	160	3596	
Ga	0.06	2.17	25
As	0.83	1.86	
Rb	5.1	1052	183
Sr	10.7	224	237
Y	0.01	0.04	28.4
Zr	0.26	2.67	155
Mo	1.60	5.9	
Cd	0.24	0.32	
Sn	0.70	1.66	
Sb	0.76	<LOQ	
Cs	0.01	11.7	13.1
Ba	10.6	38	240
Ce	0.05	<LOQ	87
Tl	1.31	<LOQ	1.51
Pb	3.70	61	25.1

^a LOQ values were calculated as the mean value of the blank solution concentration (ten replicates) plus ten times the standard deviation.

^b Wine collected during the 2015 harvest.

^c BRACCIALI, 2015.

controlled by the kinetics of release into soil solution by organic acid in the rhizosphere and by the rate at which elements are solubilized. Furthermore, the increasing of clay content increases soil water retention. The cation exchange capacity of clay minerals ranges from very high in montmorillonitic soils, such as those that form from sandstones or volcanic deposits, to relatively low values for kaolinitic soils, typically formed by granite weathering. The lithology and degree of weathering of the parent rock hence influences the amount and nature of clay materials and soil fertility, with effects on both vine behavior and wine character (MORLAT & BODIN, 2006).

High seasonal temperature gradients that characterize the highlands increase physical erosion and rock disaggregation, exposing bedrocks to meteoric waters and enhancing the water-rock contact time. However, even if active physical erosion and chemical weathering are strongly associated, field observations indicate that for the same lithology the physical erosion generally becomes the dominant process with respect to chemical weathering as increasing altitude (RIEBE *et alii*, 2004). In fact, even if eroded bedrocks at higher elevations are more exposed to infiltrating meteoric waters, and erosion may supply alterable rock fragments and minerals to soil, at high altitude the mineral dissolution rates are generally lowered by the decreasing average temperature, by the occurrence of thinner soils containing weatherable minerals, by the decline in vegetation and by the occurrence of snow cover in some season. Hence, in high-altitude sites weathering is more selective and solely the exchangeable cations and the most reactive minerals (such as calcite) produce ions that contribute to the solute load of soil solutions (DREVER & ZOBRI, 1992) and to the total plant available pool. The soil tests at Bosa highlight that the chemical decomposition of minerals of the bedrock is not promoted, limiting the occurrence of diagenetic clay minerals and hence reducing exchanges and availability for plant nutrients. Indeed, the trace element content measured in Bosa wine mimics the bulk chemical composition of the unaltered Scaglia Toscana Formation (BRACCIALI, 2015) (Fig. 3), suggesting that wine mostly reflects elements directly mobilized from the parental material. This confirms the pedological observations of limited Cambic horizons in soils, indicating that remobilization related to diagenetic minerals has limited effects on trace element partitioning during plant uptake. In particular, the trace element patterns highlight the relationship between the high iron content in wine and bedrock. It is known that iron represents an essential micronutrient for plant metabolism; however, Fe in soil is generally characterized by a low bioavailability since it readily forms ferric oxides and hydroxides precipitates under aerobic conditions with a very low solubility product (K_{sp}) when it is released from primary minerals by weathering. K_{sp} significantly increases by decreasing crystal size (SCHWERTMANN, 1991), and the Fe-oxyhydroxides dissolution rate pathways through which plants take up soluble iron from soil depends mostly on reduction and by

the occurrence of metastable Fe-oxydes (e.g. ferrihydrite). These processes, accounting for the high iron content measured in the Bosa wine, deserve further investigations.

The pattern of Fig. 3 shows the relative enrichment of Rb in wine with respect to Sr compared to the bedrock that might reflect the preferential Rb flux into the root from exchangeable sites and/or soil solutions. Further studies are necessary to determine the Zn concentration on bedrock, at present lacking, in order to investigate the lithogenic sources for this element in Bosa wine where Zn resulted to be 3.6 ppm (Table 3).

As already stated, grape juices from some vine deviate toward a less radiogenic signature compared with wine, must and the NH_4OAc -extracts from soil (Table 1). A shift from the $^{87}\text{Sr}/^{86}\text{Sr}$ measured in the labile fraction of soil and wine has been reported by BRASCHI *et alii* (2018) for single vine plants, despite the close correspondence between the Sr isotopic composition of wine and the labile fraction of soil when a statistical regression is applied to the whole samples. The Authors (BRASCHI *et alii*, 2018) interpreted this discrepancy as reflecting the different contribution of a carbonate and clay component characterized by isotopic heterogeneities to the Sr taken up by vine, not totally represented by the volume of soil collected. The role of leachable mineral phases with different $^{87}\text{Sr}/^{86}\text{Sr}$ during the uptake by vine roots has been also stressed by MARCHIONNI *et alii* (2013) in a traceability study of wines from different geographical localities in Italy. MERCURIO *et alii* (2014), addressing the application of the Sr-isotope systematics and trace elements for a “geo-pedo-fingerprint” of wines in the Phlegraean Field in Italy, also highlighted the variable partition of the weathering labile components extracted by NH_4OAc -solution in the different soil horizons, indicating that the labile fraction might not totally match the bioavailable nutrient pool.

The observed variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for grape juices collected in different vines (Table 1) are hence interpreted as due to the role of an additional unradiogenic source for Sr in soils that is not leached by the NH_4OAc solution at pH 7. On the basis of Sr-isotope stratigraphy, a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the range 0.7077-0.7078 is expected for middle-late Eocene (48 – 34 Ma) old marine carbonate rocks (McARTHUR *et alii*, 2001) as those characterizing the Bosa vineyard bedrock. The observed isotopic shift likely represents the contribution of a carbonate source

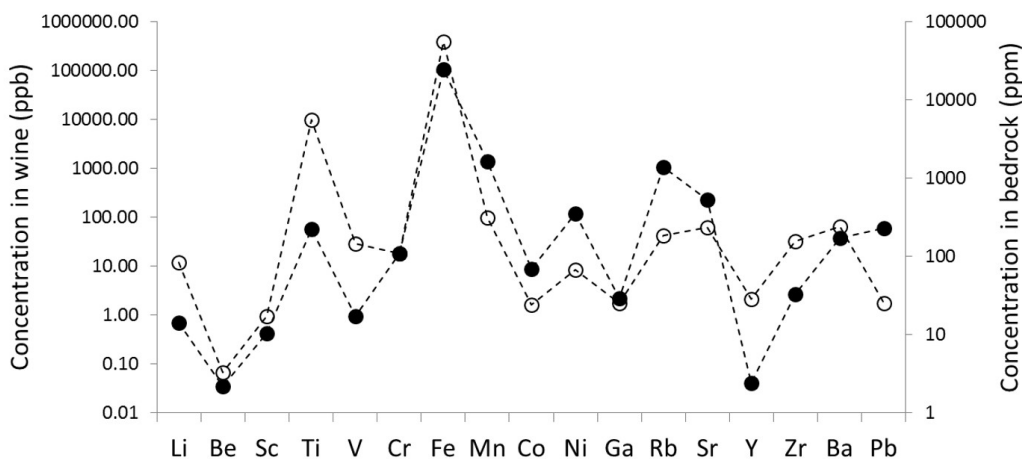


Fig.3 - Comparison of trace element concentrations in Bosa wine (filled circles) and in average bedrock (Scaglia Toscana Formation, BRACCIALI (2015)) (empty circles)

dissolved by root exudates. However, the strict relationship between the isotopic composition of wine/must and the soil sample suggests that wines smooth the occurrence of a local isotopic variability in the vineyard, also indicating that the soil sample and extraction procedure delineate the plant available Sr pool.

The lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured in seeds and stems with respect to juice from the same berry is somewhat unexpected since, despite a different Sr content, previous studies, in particular in the Lambrusco production district of Modena (Italy), indicate that the Sr-isotope ratio in vine branches matched the bio-available Sr fraction of soil (DURANTE *et alii* 2013, 2016, 2018). In addition, the lack of a significant Sr isotopic fractionation within the vine plant was observed in a study concerning the Prosecco wine traceability in the Veneto Region (Italy) (PETRINI *et alii*, 2015). It is noteworthy that seasonal patterns for the uptake and translocation of nutrients from roots to leaves to fruit occur in grape-vines (e.g. CONRADIE, 1981); a possible explanation for the observed isotopic heterogeneities might involve the rate at which trace elements are mobilized and the kinetics of released into solution by organic acid in the rhizosphere in the case of high-altitude soil. In particular, the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in grape seeds and stems may be related to the contribution of the low $^{87}\text{Sr}/^{86}\text{Sr}$ carbonate component more prone to be mobilized during a stage of growth, followed by the increasing contribution of Sr from more radiogenic sources (silicates) during the fruit maturity. However, this interpretation deserves additional investigations. The combined pedological, geochemical and isotopic approach offers the potential to better understand vine nutrition in particular in high-altitude settings.

CONCLUSIONS

The climate warming is impacting viticulture, in particular in the Mediterranean regions, shifting the establishment of vineyards at higher elevations and projecting mountain areas to become suitable for wine production in the future. Pedological and geochemical data reveal that at the high-altitude Bosa vineyard the bedrock chemical weathering has a minor role in developing the soil profile. Indeed, the trace element pattern in Merlot wine from the 2015 harvest mimic unaltered bedrocks, due to the lack of a well developed weathering complex. In the Bosa wine the heavy metals mostly derive from natural sources and are below the legal limits for wine consumption, when applicable. However, the wine is characterized by a very high Fe content that may affect the wine's quality on various accounts.

Sr-isotope data in must and wine closely resemble the isotopic composition of the labile fraction of Sr from soil; however, some isotopic heterogeneities on grape juice from single vines were observed, revealing a within-area variability that not significantly affects the soil-must-wine correspondence at the whole vineyard scale. Stems and grape seeds are isotopically distinct from juices, suggesting the uptake of Sr from a relatively unradiogenic reservoir during the different grapevine growth stages. This latter component is attributable to the carbonate fraction.

Despite additional investigations are needed, the obtained results highlight some of the processes determining the release of trace elements (micronutrients)

from the solid phase to wine, a requisite for the management of high-altitude vineyard in the Apuan Alps and wine authentication of provenance.

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