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A 'Geo-Pedo-Fingerprint' (GPF) as a tracer to detect univocal parent material-to-wine production chain in high quality vineyard districts, Campi Flegrei (Southern Italy)

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ABSTRACT

An interdisciplinary study, involving geologists, chemists and pedologists, started aiming at identifying a "Geo-Pedo-Fingerprint" (GPF) univocally linking the wine to its origin, namely, the *Piedirosso* vineyards growing in the Campi Flegrei volcanic area. The focal point of this research was the characterization of the whole parent material–soil–vineyard–wine system, achieved by correlating the elemental pattern – with special reference to micro-nutrients and Rare Earth Elements (REEs) – and Sr isotopic ratios, to identify a reliable and convenient 'GPF', as a guaranteed indicator of wine provenance. A representative soil/*Piedirosso* vineyard system was identified and characterized. Samples from each soil horizon as well as from vine branches, leaves, grapes and wine were collected and analyzed. All samples were analyzed by multi-collector inductively coupled mass spectrometry (MC-ICPMS) to determine their $^{87}Sr/^{86}Sr$ isotopic composition, by ICP-Quadrupole MS to measure multi-elemental composition including REE, and by X-Ray Powder Diffraction (XRPD) for the quantitative evaluation of the mineral phases occurring in soil samples.
Statistical analysis (Hierarchical Cluster Analysis, Factor Analysis) revealed the existence of separate correlations of element distribution between: i) soil, as nutrient pool source, and vegetative compartments, i.e. branches and leaves, as biochemical yards for nutrient elaboration and marshaling, ii) vegetative compartments and the productive compartment, i.e. grapes as the metabolic outcome of the vine, and, iii) the productive compartment and its artifact produced by man, i.e. wine. However, no sequential correlation of elements from soil to wine did appear, likely because clusters of elements were discriminated due to the varying takeup and fractionation processes in plants, as well as during vinification processes. Therefore, none of the investigated elements was a liable 'GPF' as a candidate tracer from soil to wine.
In contrast, the use of a petrogenetic tracer such as $^{87}Sr/^{86}Sr$ isotopic composition provided satisfactory responses. In fact, the values of such a ratio within the entire studied chain vary in a very small range from 0.7076 to 0.7084, thus falling within the typical range for volcanites of Campi Flegrei (0.7065–0.7086). These results currently represent the only study focusing on a geotracer, such as the $^{87}Sr/^{86}Sr$ isotopic ratio, linked with a pedological survey to identify the volcanic Campanian wine-producing chains from soil parent material-to-wine.

1. Introduction

The assorted combination of the different factors and processes active at the Earth's surface results in an impressive variety of unique pedological bodies with peculiar suitability to grow specific crops. On these bases, the concepts of 'unique farmlands', 'quality agro-food districts', and 'traditional–typical agro-food products' were developed and established over time, leading to the development of acceptability standards consistent with both the satisfaction of consumers' expectations and the competitiveness in domestic and global trade. This is mainly relevant for high-quality or high-value products, such as wine, the production of which crossed the traditional European boundaries and has spread to other countries, with special reference to Mediterranean-climate environments, including lands bordering the Mediterranean Sea as well as South-Western Africa, South-Western Australia, California, Chile, and several regions in China. As argued by Buondonno et al.

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(2008), in such a complex production/marketing system, vine-growers and wine-traders need to qualify their wine's production, enhancing and guaranteeing the unique 'typicalness' of grapevines and the quality of the whole wine production line. Concurrently, they also need to keep their quality wines safe from aggressive, low-cost marketing policies, especially from mass-product traders. To satisfy both of these demands, vineyards and wines have to be univocally linked to their 'homeland', where the peculiar interactions among the grapevines, soil, underlying geology and climate determine a unique, non-transferable set of environmental factors. These last, in turn, guarantee the origin and the quality of a given wine, provided that the other related factors, such as bio-genetic (species, cultivar) and anthropic (agrotechniques, vinification) ones, also perform optimally together.

Up to the present, the relationship among wine, vineyard and land has been inferred overwhelmingly by descriptive processes related to the concept of 'terroir' (Huggett, 2006; Van Leeuwen and Seguin, 2006; Van Leeuwen et al., 2004). Evocative and attractive as such a process is, it is almost empirical, as well as subject to individual interpretations and applications, and offers precise information neither on the nature and structure of the relationship, nor on the qualitative or quantitative measure of the relationship itself. Indeed, several models based on geological, pedological and landscape components have been proposed to characterize and survey viticultural lands (Bodin and Morlat, 2006; Deloire et al., 2005; Morlat and Bodin, 2006; Vaudour, 2002). Josling (2006) argued that the concept of 'terroir' has turned into a real 'war' in trade negotiations and disputes, as demonstrated by difficult controversies and quarrels about the correct protection of 'geographical indications'. As a matter of fact, beyond the academic and the trade terroir-linked cases, the true, pre-eminent concern is to fight label fraud and sellers who market shoddy wines. Such goals can be achieved by defining an objective, scientifically-based chain solely and clearly linking a given wine to its viticultural 'fatherland.'

New attractive and promising approaches do exist which seek to identify the possible 'tracers' able to be recognized along the soil-to-wine production chain, resulting in a wine fingerprint which guarantees the identification of the geological and geographic origin.

However, a number of methods and analytical techniques have been used which have provided contrasting results (Almeida and Vasconcelos, 1999, 2001, 2003a, 2003b, 2004; Augagneur et al., 1996; Barbaste et al., 2002; Baxter et al., 1997; Boari et al., 2008; Capron et al., 2007; Castineira-Gomez et al., 2004; Coetzee et al., 2005; Fortunato et al., 2004; Gonzálvez et al., 2009; Gremaud et al., 2004; Horn et al., 1993; Horn et al., 1998; Jakubowski et al., 1999; Kelly et al., 2005; Kment et al., 2005; Thiel et al., 2004; Vorster, 2008). These authors assume that trace elements and/or isotope ratios (e.g. $^{87}Sr/^{86}Sr$; $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) possibly transfer from the geological substrate to wine, through a specific selection occurring during the biogeochemical processes that characterize the growth and productivity of the plant, namely vineyards. As far as $^{87}Sr/^{86}Sr$ is concerned, it should be remarked that Capo et al. (1998) and Stewart et al. (1998) defined a wider concept, concluding that biological processes do not lead to a significant Sr isotope fractionation, thus enabling the use of this parameter as tracer of ecosystem courses.

Moreover, it is well known that the same isotope ratios have always been used in petrology as geochemical tracers to model the genesis of rocks and minerals (Faure and Mensing, 2004). Indeed, the $^{87}Sr/^{86}Sr$ isotope ratio represents a fundamental petrogenetic marker in the modelization of the magmatic processes, which allows us to link a narrow compositional variation of this parameter to a specific volcanic area. Most studies accomplished for provenance studies of wine have used only Sr isotope ratios of wines (Almeida and Vasconcelos, 2004; Barbaste et al., 2002; Boari et al., 2008; Horn et al., 1993; Vorster, 2008). Some studies have investigated soils along with the wine, but without paying particular attention to the associated pedogenetic development. Green et al. (2004) suggested that a comprehensive geological and pedological characterization of the site cannot be disregarded since the $^{87}Sr/^{86}Sr$ isotopic ratio of the wines is inherited from the substrate. In truth, without prejudices or quarrelsome intentions, we expect that such types of wine provenance studies must also embrace a thorough and congruent pedological characterization of the soil hosting the vineyard from which the wine of interest is produced. As a matter of fact, grapevines absorb elements, including Sr isotopes, from soil, nay from soil horizon in which they are rooted, irrespective of the features of the underlying geological substrate. Indeed, we must consider that the geological substrate is not always the genuine parent material from which the soil develops. Examples of allochthonous parent materials are volcanic ejecta, flood sediments, earthy materials from landslides or from aeolian depositions, and potting soils. In fact, if the soil parent material is different from the geological substrate, any genetic geo-pedological link does not exist, any isotopic measurement does not provide evidential data, and any wine provenance cannot be certified. On the other hand, it is well known that substrates belonging to different geological districts can be characterized by similar, overlapping $^{87}Sr/^{86}Sr$ ratios (e.g. Southern Italy; Peccerillo, 2005), as Italy and South Africa (e.g. Swartland area, Western South Africa, Jordaan et al., 1995): this paradoxically implies that a wine obtained by a given grape variety grown in Italy, e.g. Shiraz or Riesling, cannot be distinguished, using the $^{87}Sr/^{86}Sr$ ratio, from another wine obtained by the same grape variety grown in South Africa. All these circumstances inevitably entail that claiming the $^{87}Sr/^{86}Sr$ ratio – or a similar ratio – as a guaranteed indicator of wine provenance could be essentially worthless, unless this claim is supplemented by an exhaustive pedological survey including the isotopic characterization of horizons along the soil profile, thus proving that the soil is the liable link between the rock and the wine chain.

On these bases, the present interdisciplinary study – involving Geology, Chemistry and Pedology expertise – aims at identifying a 'Geo-Pedo-Fingerprint' (GPF) as a tracer univocally linking a wine to its own cropping 'homeland,' namely, the soil on which the vineyard is grown, and, inherently, the parent material from which the same soil has developed. The focal point of this research is the assessment and comparison of the transfer and the maintenance of elements, with special reference to micro-nutrients and Rare Earth Elements (REEs), and of the $^{87}Sr/^{86}Sr$ ratio throughout the whole parent material–soil–vineyard–wine system. Specifically, we plan to explore each system segment, from geological parent material to wine, through soil horizons, branches, leaves, and grapes. This is a preliminary approach aimed at evaluating whether such a complex "source-to-target" study is a reliable and convenient GPF as a provenance indicator for the valorization and the improvement of high-quality wine districts worldwide, able to solve the abovementioned concerns. As a paradigmatic case study, we focused on the celebrated wine district of 'Campi Flegrei' (Phlegraean Fields), a volcanic area in the Campania region of Southern Italy, investigating a representative vineyard/soil system called the *Piedirosso* which is cultivated on soil developed from recent pyroclastic phlegraean deposits.

2. Geological and pedological description of the site

The investigated site is located in the Campi Flegrei District (Fig. 1), a volcanic area situated in the *graben* of Campanian Plain, to the west of Naples. Campi Flegrei is a depression formed during the early Pleistocene as a consequence of calderic collapses subsequent to two high energy events: the Campanian Ignimbrite (CI) eruption (~39 ky b.p.; Fedele et al., 2008) and the Neapolitan Yellow Tuff (NYT) eruption (~15 ky b.p.; Deino et al., 2004). This volcanic field is permanently active, as testified by the 1538 eruption of Monte Nuovo (D'Oriano et al., 2005). However, the eruptive history of Campi Flegrei is quite debated; in recent years many studies have shed light on some questions concerning its genesis and evolution. More details can be found in Morra et al. (2010).