

PETROLOGICAL AND MINERALOGICAL APPLICATIONS TO WINES

MARIANO MERCURIO

Dipartimento di Studi Geologici ed Ambientali, Università del Sannio, Via dei Mulini 59/A, 82100 Benevento

SUMMARY

In order to investigate and emphasize the link between geology and food, a research on the uses of Campanian georesources, namely natural zeolites, in the process of the stabilization of white wines from Campania region (southern Italy) was carried out. The goals, set and achieved, were:

1. to identify a possible alternative to the established inorganic bentonite as a stabilizer in the production of white wines;
2. to get simultaneous protein and tartaric stability;
3. to lower the concentration of undesired cations (*i.e.* potassium) in wine, rather than getting a complete decationised product.

At the same time, a geotracerability study of the wine for a single cultivar (Piedirosso), produced on different volcanic areas of the Campania region, was also carried out. In particular, the main purpose of this research was to figure out the most suitable analytical methods to correctly define the geotracerability parameters, taking into account the relationship between the characteristics of the grape and the geological setting on which it developed. The goals, set and achieved, were:

1. enhancement of the historical indigenous grape variety of the volcanic areas of the Campania region;
2. identification of the relationship between the wine composition and the geology of the vineyard substrate on which it developed;
3. definition of a protocol for the formulation of the 'geofingerprint' based on trace elements and/or isotope ratios.

FIRST APPLICATION

Natural zeolites and white wines from Campania region (southern Italy): a new contribution for solving some oenological problems

The purpose of this first application is to provide a new mixture of the Campanian zeolitized tuffs for solving two specific problems in the production of white wines: the protein and tartaric stability. Actually, a frequent reason of turbidity and deposit formation for these wines is due to the spontaneous denaturation and flocculation of thermosensitive proteins occurring as colloidal suspensions (Boulton *et al.*, 1996; Høj *et al.*, 2000; Tattersall *et al.*, 2001; Ferreira *et al.*, 2002; Batista *et al.*, 2009), especially in summertime and during transportation. Their precipitation is known as protein Casse (break) mainly linked to inappropriate storage temperature and pH changes (Mesquita *et al.*, 2001); recently, the role of wine sulfate content has also been considered (Pocock *et al.*, 2007). Proteins bound to the Casse derive essentially from the grapes and are produced by the plant to shelter from pathogens (Waters *et al.*, 1996; Hayasaka *et al.*, 2001). Haze responsible proteins (Pathogenesis- Related (PR) proteins) are thaumatin-like (TL) proteins and chitinases, both deriving from grape berry (Waters *et al.*, 1996, 1998). In any kind of wine, proteins responsible of its instability show quite low molecular masses, ranging between 10-30 kDa, low isoelectric points, between 4.1 and 5.8 (Waters *et al.*, 1991; Ferreira *et al.*, 2000), and a variable glycolysis state (Moine-Ledoux & Parodi, 2007). Normally, to mitigate this risk, the wine producers use organic and inorganic stabilizers and clarifiers. The best known treatment, recognized also by the International Organisation of Vine and Wine (OIV), foresees the use of bentonite with a montmorillonite content not lower than 80%. The present study aims at evaluating the use of two high zeolite grade Italian volcanoclastites, such as the Neapolitan Yellow Tuff (NYT) and the Yellow Facies

of the Campanian Ignimbrite (YFCI), in the treatment of three peculiar white wines of the Campanian region: Falanghina, Fiano di Avellino and Greco di Tufo. As previously stated, another decay phenomenon worrying the wine producers is the tartaric instability due to the crystallization of potassium tartrate salts occurring in supersaturation states. The most used techniques to mitigate this risk are i) a chemical-physical method consisting in the addition of a metatartaric acid and, ii) a physical method involving prolonged cold stabulation. So far, both procedures showed objective limits due to the high exercise costs (physical method) and to the short durability starting from the bottling (chemical-physical method). These restrictions justify further researches aimed at improving the economic and qualitative aspects of the oenological production. On the other hand, the consolidated use of bentonite in the modern oenology did not motivate collateral studies concerning the use of other natural materials showing similar physico-chemical features.

In this frame, granulates were produced starting from tuff blocks as provided by quarries. Some grain size fractions have been prepared to investigate the zeolite content (phillipsite + chabazite + analcime) by X-ray diffraction (XRD). The 2-5 mm grain size fraction was chosen for NYT and the 5-10 mm for YFCI. Three Campanian monocultivar white wines were used for the test: the Falanghina 2006 grape harvest, the Fiano di Avellino DOCG 2007 grape harvest, and the Greco di Tufo DOCG 2008 grape harvest.

Forty-eight samples with mixture of the zeolitized tuffs, one sample with mixture of a synthetic zeolite A and one sample with mixture of a commercial sodium activated bentonite were prepared. Moreover the following tests and analyses were also carried out: i) ICP-OES analyses for the determination of the External Cation Exchange Capacity (ECEC); ii) ion chromatography analyses for the determination of some major cations; iii) turbidimetric tests for the definition of the protein stabilization process before and after treatments.

The present preliminary *in vitro* tests, mainly aimed at verifying the potential application of high zeolite

grade Campanian volcanoclastites in the resolution of some oenological problems, allowed to further confirm the high technological properties of this natural resource that is so widespread on the Campania region (Fig. 1).

The first approach to this research involved the use of untreated zeolitized tuffs, characterized by their natural cation composition. Benefits of their use in the treatment of white wines mainly consist in a significant decrease of potassium in solution, as a consequence of the high selectivity of phillipsite and, subordinately, of chabazite towards this cation. Actually, a correlation between phillipsite content and potassium exchange was clearly evidenced, which sometimes defines a decrease of this ion up to 25%. This aspect represents an undeniable advantage if compared to the use of other exchangers, such as polymeric resins, which show, as drawback, the almost

WHITE WINE MAKING STEPS

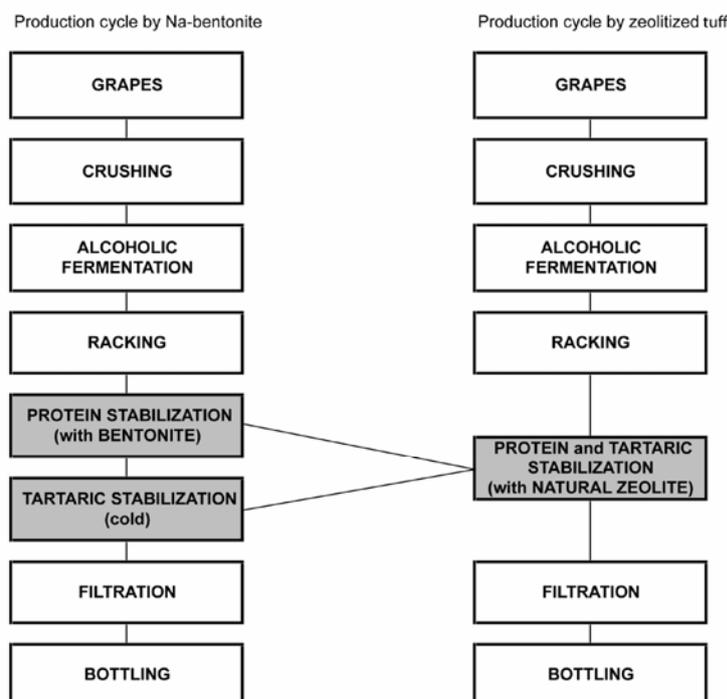


Fig. 1 - Comparison between the traditional production cycle (simplified) by using Na-bentonite (left) and the proposed one using zeolitized tuff (right) (from Mercurio *et al.*, 2010).

total decationization of the wine, as described by Wyss & Cuénat (2005). The same authors support the hypothesis that tartaric stability, in terms of potassium content, can be achieved by decreasing, from 10 to 30%, the starting amount of this ion.

It was demonstrated that the use of zeolitized tuff ensures protein stability conditions, measured in terms of turbidimetric units (NTU), as $\Delta \text{NTU} < 2$. On this account, one of the most striking effects induced by these experiments is that the total concentration of the alkali and alkali-earth cations increases after the interaction between zeolite and wines. These results may be due to the uptake of the positive charged proteins, on the surface of NYT and YFCI, since these long chain organic macromolecules should not have access to the zeolite cavities. The analysis of cations concentration in solution allowed to evaluate the ECEC for NYT and YFCI, which turned out to be 0.134 meq/g and 0.157 meq/g, respectively. This slight difference in terms of ECEC cannot be attributed to a different total zeolite content, inasmuch YFCI is characterized by an even lower total zeolite content (56 wt.% vs. 64 wt.%). By contrast, the different content of the two zeolites in NYT and YFCI could be responsible of this particular behaviour. A higher attitude of chabazite to external cation exchange should be hypothesized (Majdan *et al.*, 2006). In any case, the increase of the total cation concentration after the interaction still cannot be entirely attributed to the ECEC evaluated for the two samples.

In conclusion, phillipsite and chabazite of the Campanian volcanoclastites, at least from an experimental standpoint, resulted to be non noxious from the alimentary point of view, do not jeopardize the wine taste and showed marked potentials in the resolution of some problems linked to the biochemical processes occurring in three studied Campanian white wines (Mercurio *et al.*, 2010). These issues represent the basis of new scenarios in technological fields of oenological matter, for a georesource that, due to its abundance in Campania region, does not define high exploitation and commercialization costs, and can profitably replace bentonites, which are generally imported by quite far exploitation district. It was evidenced that high zeolitized tuff/wine ratios enable the protein stabilization whereas a significant decrease of potassium ion after the treatment with a zeolite-rich powder improves the tartaric stability, a serious problem in all the wine productions. The results of these tests refer to a laboratory scale research. A transfer of the experiment to a pilot plant scale is in progress.

SECOND APPLICATION

A 'geofingerprint' of the parent material-soil-wine chain in a high quality terroir. A first approach on Piediroso vineyards, Campania region, southern Italy

This second application encompasses the results of an interdisciplinary research involving geologists, chemists and pedologists, aiming at identifying a 'geofingerprint' univocally linking the wine to its origin, namely, the Piediroso vineyards growing on the campanian volcanic area. Since ancient times, vineyards were cultivated in this volcanic area due to its favorable climatic conditions and soil suitability, both contributing to the generation of a high quality wine terroir. The potassic alkaline volcanism of Campania region was characterized by the emplacement of a large amount of pyroclastic deposits and lava flows. The focal point of this research was the identification of the soil-vineyard-must chain by correlating the elements distribution and the isotopic ratios from the geological parent material to the ending wine must. In fact, during last years, several authors demonstrated that it is possible to recognize a wine fingerprint which guarantees the identification of the geological and geographical origin (Baxter *et al.*, 1997; Jakubowski *et al.*, 1999; Almeida & Vasconcelos, 1999, 2001, 2003a, 2003b, 2004; Coetzee & Vanhaecke, 2005; Boari *et al.*, 2008; González *et al.*, 2009 and references therein). All these authors assume that trace elements and/or isotope ratios possibly transfer from the geological substrate to the must, through a careful selection occurring during the biogeochemical processes that characterize the growth and productivity of the plant, namely vineyards. To this aim, a representative volcanic-soil from Piediroso vineyard system was identified and characterized, including the soil profile horizons. Four sites were selected: Pozzuoli (within Phlegraean Fields; "Cantine Babbo" Farm), Lettere (Somma-Vesuvius volcanic complex; "Casal di Lettere" Farm), Carano di Sessa Aurunca (Roccamonfina volcanic complex; "Masseria Felicia" Farm), and Orcoli-Dugenta (Benevento area, Phlegraean products, "Mustilli" Farm). The

samples from each soil horizon, as well as from vine branches, leaves, grapes, and must were collected and analyzed. All the samples were analyzed by MC-ICP-MS to determine their $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition, by ICP-QMS to measure Li, Be, B, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Ba, Tl, Pb, Bi, U and REE, and by XRD for the qualitative evaluation of the mineral phases occurring in the soil samples.

For example, the samples from the Phlegraean Fields (Pozzuoli, “Cantine Babbo” Farm) exhibit a soil profile with an Ap-Bw-BC-CB-C horization. The colour varies from dark brown in Ap to very dusky-red in C. Rock fragments ($\text{Ø} > 2\text{mm}$) represent 10-15% of the total volume. The soil texture is generally sandy loam. Water pH value ranges from weakly acid (5.2-5.8) in surface horizons to neutral (7.2) in depth along soil profile. For all horizons, the phosphate retention, the Cation Exchange Capacity, and the content of allophanic materials are very low, whereas the bulk density is high. The profile is classified as Vitrandic Haploxerepts (USDA-NRCS, 2010). Considering the Land Suitability analysis, soil belongs to S1 class, highly suitable for vineyards.

This study clearly shows that any interpretation of the elements distribution from both geological and pedological standpoints was not possible so far, whereas the use of a petrogenetic tracer such as $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition provided encouraging responses. In fact, the values of such ratio, within the entire chain studied, vary from 0.7076 to 0.7084, thus falling in the typical range for volcanites of Phlegraean Fields (0.7065-0.7086; Peccerillo, 2005).

Finally, the results of this study currently represent the unique study focusing on a geotracer, such as the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio, useful to identify the Campanian wine-producing chains from soil to end product.

REFERENCES

- Almeida, C.M. & Vasconcelos, M.T. (1999): Determination of lead isotope ratios in port wine by inductively coupled plasma mass spectrometry after pre-treatment by UV-irradiation. *Anal. Chim. Acta*, **396**, 45-53.
- Almeida, C.M. & Vasconcelos, M.T. (2001): ICP-MS determination of strontium isotope ratio in wine in order to be used as a fingerprint of its regional origin. *J. Anal. At. Spectrom.*, **16**, 607-611.
- Almeida, C.M. & Vasconcelos, M.T. (2003a): Lead contamination in Portuguese red wines from the Douro Region: from the vineyard to the final product. *J. Agric. Food Chem.*, **51**, 3012-3023.
- Almeida, C.M. & Vasconcelos, M.T. (2003b): Multielement composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin. *J. Agric. Food Chem.*, **51**, 4788-4798.
- Almeida, C.M. & Vasconcelos, M.T. (2004) Does the winemaking process influence the wine $^{87}\text{Sr}/^{86}\text{Sr}$? A case study. *Food Chem.*, **85**, 7-12.
- Batista, L., Monteiro, S., Loureiro, V.B., Teixeira, A.R., Ferreira, R.B. (2009): The complexity of protein haze formation in wines. *Food Chem.*, **112**, 169-177.
- Baxter, M.J., Crews, H.M., Dennis, J.M., Goodall, I., Anderson, D. (1997): The determination of the authenticity of wine from its trace element composition. *Food Chem.*, **60**, 443-450.
- Boari, E., Tommasini, S., Mercurio, M., Morra, V., Mattei, M., Mulinacci, N., Conticelli, S. (2008): $^{87}\text{Sr}/^{86}\text{Sr}$ of some Central and Southern Italian wines and its use as fingerprints for Geographic Provenance. Proc. O.I.V. 2008, 31st World Congress of Vine and Wine, Verona, Italy, CD-ROM, 6 p.
- Boulton, R., Singleton, V.L., Bisson, L., Kunkee, R.E. (1996): Principle and practices of winemaking. Chapman & Hall, New York, 150-166.
- Coetzee, P.P. & Vanhaecke, F. (2005): Classifying wine according to geographical origin via quadrupole-based ICP-mass spectrometry measurements of boron isotope ratios. *Anal. Bioanal. Chem.*, **383**, 977-984.
- Ferreira, R.B., Monteiro, S., Piçarra-Pereira, M.A., Tanganho, M.C., Loureiro, V.B., Teixeira, A.R. (2000): Characterisation of the proteins from grapes and wines by immunological methods. *Am. J. Enol. Vitic.*, **51**, 22-28.
- Ferreira, R.B., Piçarra-Pereira, M.A., Monteiro, S., Loureiro, V.B., Teixeira, A.R. (2002): The wine proteins. *Trends Food Sci. Technol.*, **12**, 230-239.
- González, A., Llorens, A., Cervera, M.L., Armenta, S., de la Guardia, M. (2009): Elemental fingerprint of wines from the protected designation of origin Valencia. *Food Chem.*, **112**, 26-34.
- Hayasaka, Y., Adams, K.S., Popock, K.F., Baldock, G.A., Waters, E.J., Høj, P.B. (2001): Use of electrospray mass spectrometry for mass determination of grape (*Vitis vinifera*) juice pathogenesis-related proteins: A potential tool for varietal differentiation. *J. Agric. Food Chem.*, **49** (4), 1830-1839.
- Høj, P.B., Tattersall, D.B., Adams, K., Pocock, K.F., Hayasaka, Y., van Heeswijck, R., Waters, E.J. (2000): The ‘haze protein’ of wine - a summary of properties, factors affecting their accumulation in grapes, and the amount of

- bentonite required for their removal from wine. Proc. ASEV 50th Anniversary Annual Meeting, June 19-23, 2000, Seattle, Washington, 149-154.
- Jakubowski, N., Brandt, R., Stuewer, D., Eschnauer, H.R., Gortges, S. (1999): Analysis of wines by ICP-MS: Is the pattern of the rare earth elements a reliable fingerprint of provenance? *Fresen. J. Anal. Chem.*, **364**, 424-428.
- Majdan, M., Pikus, S., Rzaczyńska, Z., Iwan, M., Maryuk, O., Kwiatkowski, R., Skrzypek, H. (2006): Characteristics of chabazite modified by hexadecyltrimethylammonium bromide and of its affinity toward chromates. *J. Mol. Struct.*, **791**, 53-60.
- Mercurio, M., Mercurio, V., de' Gennaro, B., de' Gennaro, M., Grifa, C., Langella, A., Morra, V. (2010): Natural zeolites and white wines from Campania region (Southern Italy): a new contribution for solving some oenological problems. *Per. Mineral.*, **79**, (1), 95-112.
- Mesquita, P.R., Piçarra-Pereira, M.A., Monteiro, S., Loureiro, V., Teixeira, A.R., Ferreira, R.B. (2001): Effect of wine composition on protein stability. *Am. J. Enol. Vitic.*, **52**, 324-330.
- Moine-Ledoux, V. & Parodi, G. (2007): Bentoniti: istruzioni per l'uso. *VQ*, **9**, 74-82.
- Peccerillo, A. (2005): Plio-quaternary volcanism in Italy. Petrology, Geochemistry and Geodynamics. Springer, Berlin, 365 p.
- Pocock, K.F., Alexander, G.M., Hayasaka, Y., Jones, P.R., Waters, E.J. (2007): Sulfate-a candidate for the missing essential factor that is required for the formation of protein haze in white wine. *J. Agric. Food Chem.*, **55**, 1799-1807.
- Tattersall, D.B., Pocock, K.F., Hayasaka, Y., Adams, K., van Heeswijck, R., Waters, E.J., Høj, P.B. (2001): Pathogenesis related proteins - their accumulation in grapes during berry growth and their involvement in white wine heat instability. Current knowledge and future perspective in relation to winemaking practices. In: "Molecular biology and biotechnology of the grapevine", K.A. Roubelakis-Angelakis, ed. Kluwer Academic Publishers, Dordrecht, Netherlands, 183-201.
- USDA-NRCS (2010): Keys to Soil Taxonomy, 10th edition. Agriculture Dept (U.S.), ed. Government Printing Office, Washington, DC.
- Waters, E.J., Wallace, W., Williams, P.J. (1991): Heat haze characteristics of fractionated wine proteins. *Am. J. Enol. Vitic.*, **42**, 123-127.
- Waters, E.J., Shirley, N.J., Williams, P.J. (1996): Nuisance proteins of wine are grape pathogenesis-related proteins. *J. Agric. Food Chem.*, **44**, 3-5.
- Waters, E.J., Hayasaka, Y., Tattersall, D.B., Adams, K.S., Williams, P.J. (1998): Sequence analysis of grape (*Vitis vinifera*) berry chitinases that cause haze formation in wines. *J. Agric. Food Chem.*, **46**, 4950-4957.
- Wyss, C. & Cuénat, P. (2005): Stabilisation tartrique des vins par traitement aux zéolithes. *Rev. Suisse Vitic. Arboric. Hortic.*, **37**, 341-347.