

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

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ABSTRACT - The purpose of this research is to provide a new mixture of Campanian zeolitized tuffs for solving two specific problems in the production of white wines: the protein and tartaric stability. In fact, a very frequent cause of turbidity and formation of organic deposits in white wines is the occurrence of thermolabile and thermostable proteins colloidal suspensions which precipitate in time, especially in summertime and during the storage and transport. Normally, to mitigate this risk 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 paper 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 (Southern Italy): *Falanghina*, *Fiano di Avellino* and *Greco di Tufo*.

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). A 2-5 mm grain size fraction was chosen for NYT and a 5-10 mm for YFCI. Three Campanian monocultivar white wines were used for the test: the *Falanghina* 2006 vintage, the *Fiano di Avellino* DOCG 2007 vintage, and the *Greco di Tufo* DOCG 2008 vintage.

48 samples with mixture of the zeolitized tuffs, 1 sample with mixture of a synthetic zeolite A and 1 sample with mixture of a commercial sodium activated bentonite were prepared. ICP-OES analysis for the determination of ECEC, Ion Chromatography (IC) analyses for the determination of some major cations and Turbidimetric tests for the definition of the protein stabilization process before and after treatments were also carried out. 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

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transfer of the experiment to a pilot plant scale is in progress.

RIASSUNTO - In questo lavoro sono riportate le risultanze derivanti dall'applicazione di tufi campani come possibili stabilizzanti proteici e tartarici nella produzione dei vini bianchi. Difatti, una causa molto frequente della torbidità e della formazione di depositi organici nei vini bianchi è legata alla presenza, in sospensione colloidale, di proteine termolabili e termostabili che precipitano nel tempo, specialmente in estate, durante il trasporto e lo stoccaggio. Di norma, per mitigare tale rischio i produttori di vino utilizzano stabilizzanti e chiarificanti di origine organica ed inorganica. Il trattamento di gran lunga più utilizzato, riconosciuto anche dall'Organizzazione Internazionale della Vigna e del Vino (OIV) prevede l'impiego di bentonite con contenuto in montmorillonite superiore all'80%. A tal fine, in questa ricerca, sono state utilizzate vulcanoclastiti provenienti dalla regione Campania (Italia Meridionale) ad alto contenuto zeolitico quali il Tufo Giallo Napoletano (TGN) e l'Ignimbrite Campana in Facies Gialla (ICFG) per il trattamento di tre vini bianchi caratteristici della stessa regione: Falanghina, Fiano di Avellino e Greco di Tufo.

A partire dai blocchi di tufo, così come campionati dalle cave, sono stati prodotti alcuni granulati. Diverse frazioni granulometriche sono state preparate per determinare, mediante diffrattometria ai raggi X, il loro contenuto zeolitico in phillipsite, cabasite e analcime. I vini impiegati nel lavoro sono stati rispettivamente: Falanghina vendemmia 2006, Fiano di Avellino DOCG vendemmia 2007 e Greco di Tufo DOCG vendemmia 2008.

Nel complesso, sono stati preparati 48 campioni con miscele zeolitiche, 1 campione con zeolite sintetica 4A e 1 campione con bentonite sodica reperibile in commercio. Analisi in cromatografia ionica sono state impiegate per il dosaggio dei principali cationi, mentre analisi in ICP-OES sono state preferite per stimare la capacità di scambio cationico superficiale. Inoltre, le tecniche torbidimetriche sono state utilizzate per la definizione della stabilità proteica prima e dopo il trattamento con tufi a zeolite. I risultati hanno evidenziato che per alti rapporti zeoliti/vino la stabilità proteica è assicurata, mentre un significativo decremento dello ione potassio, dopo il trattamento con zeoliti, aumenta la probabilità che sia assicurata la stabilità tartarica che rappresenta parimenti un annoso problema

in tutte le produzioni vinicole.

Infine, occorre evidenziare che gli esiti di questa ricerca si riferiscono a prove *in vitro* e pertanto sperimentazioni a grande scala sono in fase di avanzamento.

KEY WORDS: *zeolitized tuffs, bentonite, white wines, protein stability, tartaric stability.*

INTRODUCTION

Wines are very complex matrixes characterized by different components which, due to their instability, may cause in time some modifications of the organoleptic features, that could be perceived by the consumer as a qualitative decay of the product (Bayly and Berg, 1967; Waters *et al.*, 1992).

The main oenological procedures aim at solving the problem of wine stability facing several aspects such as the protein and microbiological stability as well as the production of potassium and calcium bitartrate crystals. White wines are extremely sensible to these instability forms, being the protein and tartaric ones the most troublesome. 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), above all 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 (Hsu and Heatherbell, 1987a; Waters *et al.*, 1991; Ferreira *et al.*, 2000) and a variable glycolysis state (Moine-Ledoux and Parodi, 2007). Their low dimension as well as their high solubility make these components hard to be removed by a simple filtration (Eisenhour and Brown, 2009). This is the reason why wine producers, since quite long times, use organic or inorganic clarifiers and stabilizers to mitigate this risk (Ribéreau-Gayon *et al.*, 2004). Generally, the consolidated treatment, internationally acknowledged also by the International Organisation of Vine and Wine (OIV, 2003) accounts for the use of bentonite with a montmorillonite content not lower than 80%. The OIV disciplinary provides all the features that should be achieved to guarantee the quality and the functionality of the product. However, alternative methods have been studied: wine ultrafiltration, addition of oenological tannins, use of haze protective factors, protein adsorption on different matrix, polysaccharide finings and use of proteolytic enzymes (Peri *et al.*, 1988; Powers *et al.*, 1988; Flores *et al.*, 1990; Lagace and Bisson, 1990; Moine-Ledoux and Dubourdieu, 1999; Marchal *et al.*, 2002; Vincenzi *et al.*, 2005).

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 techniques most used to mitigate this risk are: i) a chemical-physical method by addition of a metatartaric acid and, ii) a physical one by prolonged cold stabulation (Laffort-Info, 2001). So far, both procedures show objective limits due to the high exercise costs (physical method) and short durability starting from the bottling (by addition). 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, the aim of the present research is the evaluation of the use of zeolitized Campanian volcanoclastites such as the Neapolitan Yellow Tuff (NYT) and the Yellow Facies of Campanian Ignimbrite (YFCI) with a high content of phillipsite and chabazite, as inorganic stabilizers of three important white wines produced in the Campania region: the *Falanghina*, the DOCG *Fiano di Avellino* and the DOCG *Greco di Tufo*. It was specifically verified the use of these natural materials both as protein stabilizers and cation exchangers.

It should be remarked however that the experimental conditions are somehow limited to the laboratory practice such as the high powder-to-wine ratio. Here follow the potential as well as the disadvantages of this new application.

PREVIOUS KNOWLEDGES

Bentonites and protein stabilization

Bentonites have been widely used to clarify and stabilize musts and wines since 30s' of the last century (Saywell, 1934; Ribéreau-Gayon *et al.*, 1980; Blade and Boulton, 1988; Achaerandio *et al.*, 2001). Europe produces about 3,500,000 tons/year of such geomaterials (Eisenhour and Brown, 2009) and only a small part (1%) is used in the oenological sector. Bentonite in wines has a deproteinizing effect even though some collateral effects such as the adsorption of flavorings and polyphenols which determine a qualitative sensorial loss cannot be disregarded (Celotti *et al.*, 2006). Bentonite is rarely used in oenological activities as raw material as it often undergoes some treatments such as activation with sulfuric acid or exchange processes with alkaline solutions so that acid, sodic or calcic

bentonites are obtained. Sodic bentonites are the most used in wine treatments inasmuch their higher swelling attitude in solution defines a higher capacity of protein trapping. As previously stated, the isoelectric point of proteins ranges between 4.1 and 5.8 so that they can assume a different electric charge as a function of the pH of the solution. Therefore, they are all positively charged if the pH of the solution is lower than 4; in these conditions proteins are adsorbed by bentonite. Since pH of white wines is almost always between 3.2 and 3.8 experimental results demonstrated that the more pH is close to 4 the more bentonite should be used to achieve a protein stabilization of the solution (Mercurio V., personal comm.). Thus, the optimal amount of bentonite necessary to ensure the protein stabilization, *e.g.* for a Sauvignon Blanc wine, ranges between 50 and 100 g/hL considering pH values of 3.4-4 (Hsu and Heatherbell, 1987b; Moine-Ledoux and Parodi, 2007; Laffort-Info, 2008). Finally, various methods have been proposed to determine the risk of wine protein instability (Dubourdiou *et al.*, 1988; Ribéreau-Gayon *et al.*, 2004).

Zeolites and wine

Due to their peculiar properties zeolites find wide uses in several industrial applications, including the feeding sector (Pond, 1995). Leaching tests demonstrated that this mineral group can be defined as a non-toxic product for human and animal health, as concentrations of residual elements are within the limits suggested by the specific sector rules (Lay and Meyer, 1989; Heili *et al.*, 1997; Mercurio *et al.*, 2009).

Unlike generally occurring for bentonites, few studies were finalized to the use of zeolites in the oenological sector. A possible explanation stands in the fact that during the 30s' of the last century that is, when the problem concerning the bottling of white wines and the consequent protein

stabilization arose, the technological properties of zeolites were not deeply known yet. As a result the scientific community promoted the use of other natural materials, namely bentonites.

Ciambelli *et al.* (1998) led laboratory tests aimed at evaluating the possible abatement of the volatile acidity in wines through a selective absorption of acetic acid with zeolite-based adsorbents. Results were quite encouraging as the total abatement was of about 60%. As far as the tartaric stabilization is concerned Wyss and Cuénat (2005) demonstrated that the selective reduction of the potassium ion in wines, namely 10-30% of the starting potassium amount, likely inhibits the precipitation of potassium bitartrate salts, but only if hydrogen ion concentration remains almost unchanged. The method used by these Authors accounts for the use of a synthetic zeolite column constituted by a mordenite Zeocat FM8/25 H⁺ having a 0.9 meq/g cation exchange capacity (CEC). It was also demonstrated that the concentrations of the most representative phenolic compounds do not vary after the zeolite treatment so that the taste and the aromatic quality of the treated wine is not significantly altered.

Surface properties of zeolites

One of the most interesting applications of zeolites, especially natural zeolites, are associated with their surface properties, making them able to interact with big organic molecules and cations, which are unable to enter their microporous structure. In fact, zeolites exhibit large external surfaces, negatively charged, balanced by hydrated inorganic cations, which results in possible interactions either with other cations or with polar molecules.

In order to evaluate the surface properties of zeolites, two important parameters have to be investigated: (1) the external surface area (ESA), usually evaluated through the BET adsorption nitrogen method (Brunauer *et al.*, 1938) and (2)

the external cation exchange capacity (ECEC) measured using Ming and Dixon method (Ming and Dixon, 1987) or a procedure suggested by Li and Bowman (1997). The first procedure is based on the zeolite surface cation exchange with TBA-Br (tetrabutylammonium bromide) whereas the second is based on the uptake of HDTMA-Br (esadecyltrimethylammonium bromide), since both the large organic cations are unable to enter the zeolite framework.

Two possible ways of using the surface properties of zeolites can be followed: directly, by exchanging the surface cations with large organic cations or indirectly, by forming surfactant micellae on the zeolite surface (surface modified zeolite, SMZ). In the first case the large organic cations, as proteins in some pH ranges, can be exchanged using the ECEC of the zeolitized material (Colella, 2007). In the latter case the ECEC is used to form a SMZ; the change of the surface zeolite charge from negative to positive, convert it in an anion surface exchanger. As a result of this modification, zeolites (a) retain the capability to exchange cations by using the inner extraframework cations, (b) attain a capability to exchange anions on the surface (Haggerty and Bowman, 1994), and (c) acquire a marked affinity for hydrophobic organic molecules, such as perchloroethylene (PCE) and benzene (Bowman et al., 1995).

Moreover, zeolites are able to form highly stable complexes with big organic molecules. In this case, bond formation has been credited to the hydrophilic environment created on the external surface of these minerals by hydrated cations. Cationic composition, and therefore the extent of surface hydration, was proved to be a relevant parameter in adsorption of polar organic molecules as micotoxins, pesticides, humic acids, etc. (Colella, 2007).

On this basis, natural zeolitized materials such as those used for the present research, could be used with a double advantage:

- 1) removal of some macromolecular proteins

occurring in wines which, being positively charged at wine pH and having sizes larger than zeolite channels, can only be exchanged on surface;

- 2) removal by cation exchange of some undesired cations occurring in wines such as potassium, towards which both phillipsite and chabazite show a good selectivity.

MATERIALS AND METHODS

According to de' Gennaro and Langella (1996) phillipsite and chabazite are natural zeolites widely occurring in the most widespread Quaternary volcanoclastic products of Campi Flegrei (Southern Italy): the Campanian Ignimbrite (CI) and the Neapolitan Yellow Tuff (NYT). CI represents the product of an eruption occurring about 39,000 ybp which covered an area > 30,000 km² (Cappelletti *et al.*, 2003; Deino *et al.*, 2004; Fedele *et al.*, 2008). From a petrographic point of view it is defined as a trachytic volcanoclastite made up of pumice and scoriae set in an ashy matrix. Two main different facies, both lithified, can be recognized: a grey one rich in epigenetic feldspar, and a yellow one characterized by phillipsite and chabazite. The NYT, linked to an eruption occurred about 15,000 ybp (De Vivo *et al.*, 2001), is a trachytic volcanoclastite constituted by pumices, lithics, obsidian fragments, and crystals set in an ashy matrix deeply altered to phillipsite, chabazite and smectite (de' Gennaro *et al.*, 2000).

Samples used for the present research come from a quarry (Liccar Block) of NYT located in Quarto (Naples) and of CI (Apostolico & Tanagro) in yellow facies (YFCI) located in Comiziano (Naples).

Starting from the dimension tuff blocks collected in the quarries different grain size fractions were obtained; quantitative XRD analyses using the RIR method (Bish and Chipera, 1988) allowed to select the zeolite richest fraction to be used for the experiments.

According to the method proposed by Cerri *et al.* (2002) the CEC was also evaluated. The external cation exchange capacity (ECEC) of the zeolite samples was determined by a method proposed by Li and Bowman (1997) and further modified (de' Gennaro *et al.*, 2008). Accordingly, 0.5 g of zeolite sample were shaken, in 50 mL sealed teflon bottles, with 20 mL of 20-mM solution of HDTMA-Br, under continuous stirring, at 25°C and for 24 h, time sufficient to attain equilibrium. After saturation with HDTMA, the samples were centrifuged and the supernatants analyzed in order to evaluate the released cations in solution by ICP atomic emission spectrophotometry (Perkin-Elmer Optima 2100 DV ICP-OES). All batch experiments were performed in duplicate.

As reference materials, other commercial products have been used such as a synthetic Zeolite A (Na-homocationic zeolite 4A, SASOL Italy SpA) and a Na-activated bentonite (bentgran-Na, AEB Group).

Three Campanian monocultivar wines have been tested: the DOCG *Fiano di Avellino* 2007 vintage, the DOCG *Greco di Tufo* 2008 vintage, both provided by the wine producer "I Favati" from Cesinali (Avellino), and the *Falanghina* 2006 vintage, provided by "Casal di Lettere" from Lettere (Naples). On the whole, 50 samples have been prepared in laboratory, 48 of which treated with natural zeolitized materials, 1 with the synthetic Zeolite A and 1 with the Na-activated bentonite. As far as zeolite A is concerned, its quite high pureness (80 wt.%) along with its Si/Al ratio equal to 1, accounted for a rather high CEC (4.54 meq/g), whereas Na-bentonite used as reference (blank) with a montmorillonite content higher than 80 wt.% showed a 0.9 meq/g CEC. The experiments lasted three years since the selected wines had the same affination period in cellar. Samples have been prepared with the following solid-to-liquid ratios: 1, 2, 3, 4, 5, 6, 7 and 8 g/L. The exchange reactions and the protein stability test were carried out using: a 1 L becker, a magnetic

stirrer, filtering systems and centrifuge. After shaking for one hour the wine/zeolitic material or wine/bentonite mixtures a centrifugation to 4000 rpm for 5 minutes of 200 mL was carried out. The solution was successively filtered on a 0.45 µm filter and turbidity, expressed in NTU (Nephelometric Turbidity Unit), evaluated with a HI 83749 turbidimeter (Hanna Instruments). One-hundred milliliter of the filtered solution was then hold in oven for 30' at 80° C. Once cooled for 45' at room temperature the turbidity was measured again. It should be reminded that were considered stable, that is sufficiently protected by protein precipitation, those wines which gave a $\Delta \text{NTU} < 2$ [$\Delta \text{NTU} = (\text{TURB2}) - (\text{TURB1})$] where TURB1 is the turbidity measured before the treatment and TURB2 the turbidity after the treatment and the heating stage (Laffort-Info, 2008). This test was carried out on the raw wines in order to verify if they were already stabilized prior to the treatments: values (TURB1) recorded for the three raw wines never exceeded 2 NTU whereas ΔNTU was always > 2 . Variation of cation content was measured on the filtered wines by ionic chromatography with a DIONEX - DX120 equipped with a CS12A cationic column and an isocratic elution system. Results are well comparable with those obtained with an Atomic Absorption Spectrophotometer (Da-ren *et al.*, 1985). The solution conductivity was measured with a Mod. 120 ANALYTICAL CONTROL conductimeter having a measuring field of 10-3000 µs/cm, whereas the pH was monitored with a mod.720A ORION pHmeter. Finally, the pleasantness index (PI) was calculated from the arithmetic average of the scores given by 10 expert tasters which expressed an opinion on the wines using a 1 to 10 scale and taking into consideration only the olfactory quality.

RESULTS

TABLE 1 reports the mineralogical

compositions, CEC, ECEC and exchangeable cations composition of the zeolitized tuffs used for the treatments. Bulk samples and grain size fractions evidenced a zeolite content ranging between 58 and 64 wt.% for NYT samples and between 54 and 56 wt.% for YFCI. As far as the kind of zeolite is concerned 2 mm < Ø < 5 mm grain size fraction of NYT showed 41 wt.% of phillipsite which never exceeded 30 wt.% in YFCI. By contrast, chabazite is in a larger amount in YFCI (24-26 wt.%) whereas ranges between 16 and 18 wt.% in NYT. Analcime only occurs in NYT (5-7 wt.%) and smectite content is higher in NYT (8-12 wt.%) than YFCI (5-6 wt.%).

(5 mm < Ø < 10 mm).

These results addressed the choice of the most favorable samples to be used for the following treatments to these grain size fractions. In order to improve the dispersion in solution during the treatment a further powdering of the sample (< 2 mm) was also carried out.

Figure 1a and figure 1b reports the concentrations (meq/L) of sodium, potassium, calcium and magnesium ions as a function of the tuff-to-wine ratios (0 ÷ 8) for the three investigated wines. Zero is the reference test without any addition. A solid vertical line defines a $\Delta NTU = 2$ referred to the results of the protein

TABLE 1
Representative mineralogical composition, CEC, ECEC, and exchangeable cations composition of zeolitic materials used for treatments.

Size Fraction	sme	bt	fd	phi	cha	ana	Total Zeolite	CEC	ECEC	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(meq/g)	(meq/g)	(meq/g)	(meq/g)	(meq/g)	(meq/g)
NYT (Bulk)	12	0.5	10	38	16	7	61	2.03	-	-	-	-	-
NYT 5 mm < Ø < 10 mm	8	0.1	12	35	17	6	58	2.00	-	-	-	-	-
NYT 2 mm < Ø < 5 mm	8	0.1	12	41	18	5	64	2.20	0.134	0.64	0.79	0.02	0.75
YFCI 5 mm < Ø < 10 mm	5	0.8	16	30	26	0	56	2.05	0.157	0.29	0.70	0.08	0.98
YFCI 2 mm < Ø < 5 mm	6	0.4	14	30	24	0	54	2.00	-	-	-	-	-
YFCI (Bulk)	5	1	16	30	26	0	56	2.08	-	-	-	-	-

NYT: Neapolitan Yellow Tuff; YFCI: Yellow Facies Campanian Ignimbrite; sme = smectite; bt = biotite; fd = feldspars; phi = phillipsite; cha = chabazite; ana = analcime.

A Cation Exchange Capacity of 2.08 meq/g and of 2.03 meq/g was measured for YFCI and NYT, respectively, in good agreement with the total zeolite amount. The highest CEC value (2.20 meq/g) was determined for the 2 mm < Ø < 5 mm grain size fraction of NYT as a consequence of its highest zeolite content (64 wt.%). As far as YFCI samples are considered, the best CEC performance (2.05 meq/g) was achieved by the other selected grain size fraction

stability test. This line identifies a stable field (right) and an unstable one (left). Encouraging results concern all those samples treated with a high zeolitized tuff-to-liquid ratio that is 7-8 g/L.

Generally, after the treatment and regardless the starting concentrations, the exchange reactions determined a substantial variation of the cations content. TABLES 2, 3 and 4 refer to samples with a solid-to-liquid ratio equal to 8, and report the concentrations of sodium, potassium, magnesium and calcium, the

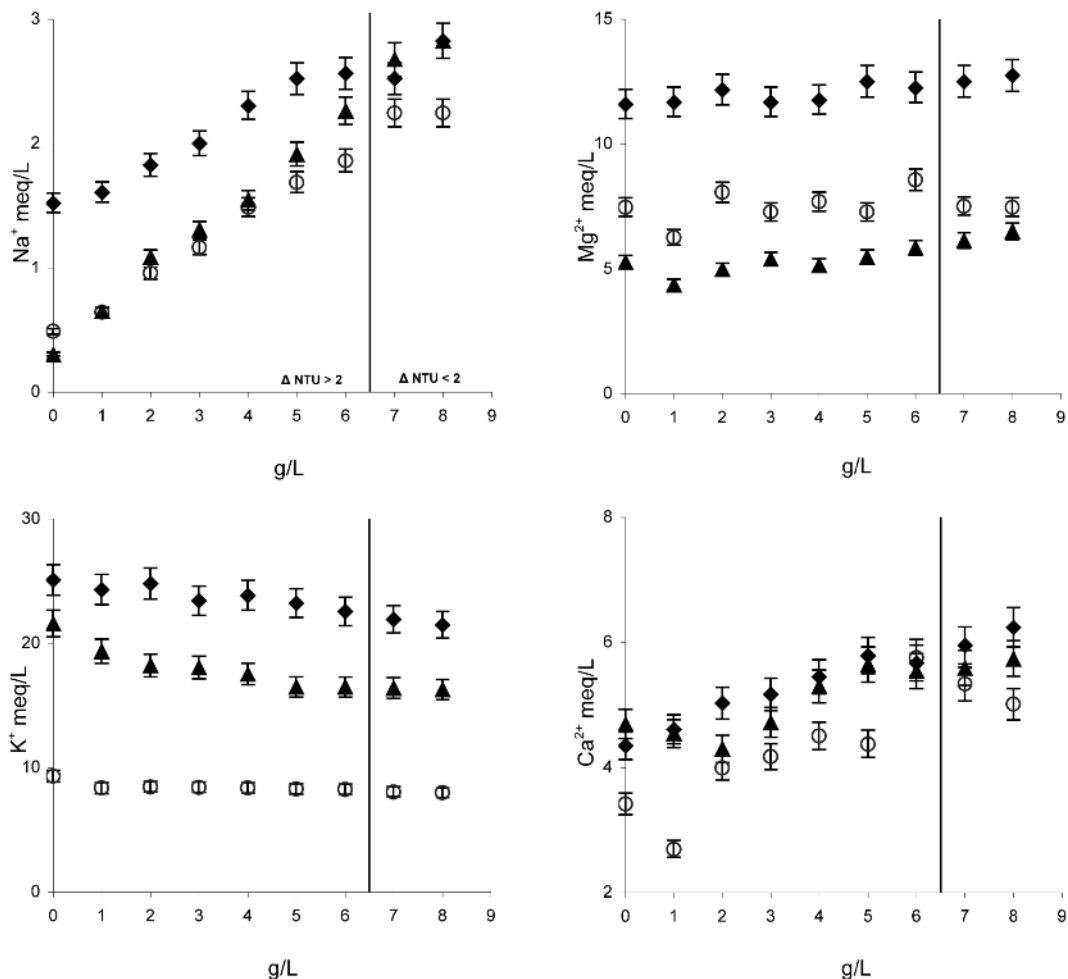


Fig. 1a - Cation concentrations (milliequivalent/Liter) released after the interaction between Neapolitan Yellow Tuff (2 mm <math>< \varnothing < 5 \text{ mm}</math>) and white wines as a function of the solid-to-liquid ratio. A solid vertical line defines the protein stability (right) and instability (left) fields. Diamonds: Greco di Tufo; triangles: Falanghina; circles: Fiano di Avellino. Error bar = $\pm 5\%$.

electrical conductivity of the solution, the hydrogen ion concentration and index parameters of protein (Δ NTU).

Data obtained after treatments with NYT and YFCI evidence for *Greco di Tufo* a potassium decrease associated with an enrichment of the other cations, with special reference to sodium (TABLE 2). The starting K⁺ amount in the untreated wine (25.070 meq/L) decreases to

21.463 meq/L in sample Z41 (NYT) and to 22.858 meq/L in sample Z49 (YFCI); by contrast, sodium of the starting solution (1.522 meq/L) increases to 2.827 meq/L in sample Z41 and to 3.262 in Z49. Mg content did not evidence substantial variations as well as for calcium with the exception of sample Z41 which recorded an increase from 4.342 up to 6.239 meq/L. The pH was always lower than 4 and slightly decreases

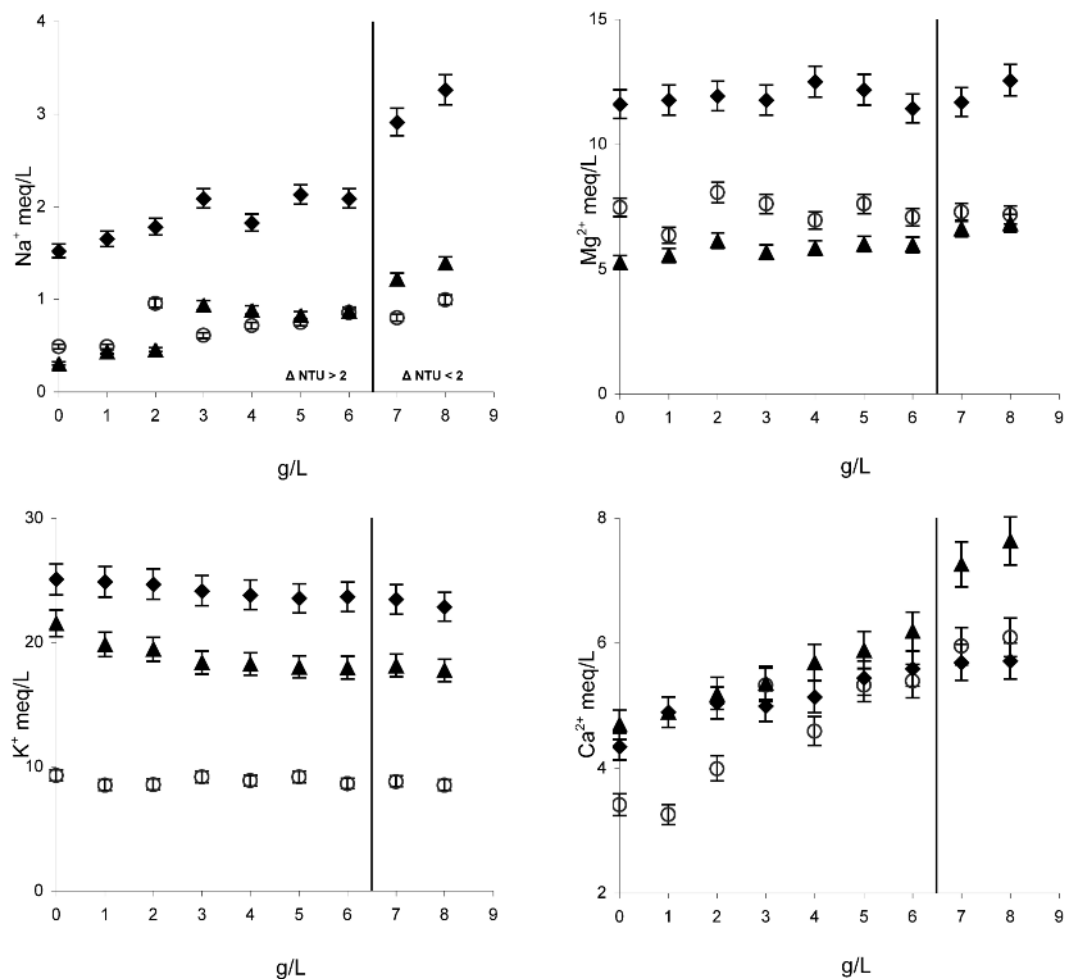


Fig. 1b - Cation concentrations (milliequivalent/Liter) released after the interaction between Yellow Facies Campanian Ignimbrite ($5 \text{ mm} < \varnothing < 10 \text{ mm}$) and white wines as a function of the solid-to-liquid ratio. A solid vertical line defines the protein stability (right) and instability (left) fields. Diamonds: Greco di Tufo; triangles: Falanghina; circles: Fiano di Avellino. Error bar = $\pm 5\%$.

if compared to the starting values (3.45) as well as the electrical conductivity.

Fiano di Avellino wine shows an overall similar behaviour (TABLE 3), with a remarkable decrease of potassium concentration in all the treatments carried out with the different Campanian volcanoclastites. It should be remarked however, that all the starting values are

definitely lower than those observed for the *Greco di Tufo* wine. In particular, K⁺ decreases from 9.291 meq/L to 7.971 meq/L in sample Z24 (NYT) and to 8.526 meq/L in sample Z32 (YFCI).

Falanghina wine (TABLE 4) records the most marked K⁺ decrease, from 21.540 meq/L to 16.245 and 17.754 meq/L for sample Z8 (NYT)

TABLE 2

Representative analyses of Greco di Tufo 2008 vintage after processing with NYT, YFCI. GT = untreated wine.

Sample ID	GT	Z41	Z49
Condition	bulk	8g NYT/L	8g YFCI/L
Na ⁺ (meq/L)	1.522	2.827	3.262
K ⁺ (meq/L)	25.070	21.463	22.858
Mg ²⁺ (meq/L)	11.605	12.757	12.560
Ca ²⁺ (meq/L)	4.342	6.239	5.715
Total Cations (meq/L)	42.539	43.286	44.395
pH	3.45	3.32	3.35
Conductivity at 20 °C (µs/cm)	2230	2180	2196
Δ (NTU)	> 2	< 2	< 2
Δ Na ⁺ (meq/L)		1.305	1.740
Δ K ⁺ (meq/L)		-3.607	-2.212
Δ Mg ²⁺ (meq/L)		1.152	0.955
Δ Ca ²⁺ (meq/L)		1.897	1.373
Balance		0.747	1.856
Δ Na ⁺ (meq/g)		0.163	0.217
Δ K ⁺ (meq/g)		-0.451	-0.277
Δ Mg ²⁺ (meq/g)		0.144	0.119
Δ Ca ²⁺ (meq/g)		0.237	0.172
Balance		0.093	0.232
ECEC NYT		0.134	-
ECEC YFCI		-	0.157
Δ ECEC		-0.041	0.075

TABLE 3

Representative analyses of Fiano di Avellino 2007 vintage after processing NYT, YFCI. FA = untreated wine.

Sample ID	FA	Z24	Z32
Condition	bulk	8g NYT/L	8g YFCI/L
Na ⁺ (meq/L)	0.487	2.244	0.992
K ⁺ (meq/L)	9.291	7.971	8.526
Mg ²⁺ (meq/L)	7.473	7.473	7.177
Ca ²⁺ (meq/L)	3.414	5.011	6.089
Total Cations (meq/L)	20.665	22.699	22.784
pH	3.36	3.29	3.31
Conductivity at 20°C (µs/cm)	1970	1958	1969
Δ (NTU)	> 2	< 2	< 2
Δ Na ⁺ (meq/L)		1.757	0.505
Δ K ⁺ (meq/L)		-1.320	-0.765
Δ Mg ²⁺ (meq/L)		0.000	-0.296
Δ Ca ²⁺ (meq/L)		1.597	2.675
Balance		2.034	2.119
Δ Na ⁺ (meq/g)		0.220	0.063
Δ K ⁺ (meq/g)		-0.165	-0.096
Δ Mg ²⁺ (meq/g)		0.000	-0.037
Δ Ca ²⁺ (meq/g)		0.200	0.334
Balance		0.254	0.265
ECEC NYT		0.134	-
ECEC YFCI		-	0.157
Δ ECEC		0.120	0.108

and Z16 (YFCI), respectively. A substantial stability of the electrical conductivity was also recorder, regardless the type of zeolitized tuff or wine used in the experiments.

Finally, table 5 reports the results obtained by only using reference materials. *Greco di Tufo*

wine treated with zeolite A recorded an even higher potassium decrease to 17.498 meq/L in sample Z50 with an increase of sodium to 14.137 meq/L of almost one order of magnitude; this is well consistent with the homocationic (Na) character of this synthetic zeolite. Sample Z50

TABLE 4

Representative analyses of Falanghina 2006 vintage after processing with NYT and YFCI. FL= untreated wine.

Sample ID	FL	Z8	Z16
Condition	bulk	8g NYT/l	8g YFCI/l
Na ⁺ (meq/L)	0.304	2.827	1.392
K ⁺ (meq/L)	21.540	16.245	17.754
Mg ²⁺ (meq/L)	5.267	6.502	6.831
Ca ²⁺ (meq/L)	4.692	5.740	7.637
Total Cations (meq/L)	31.803	31.314	33.614
pH	3.4	3.31	3.36
Conductivity at 20 °C (µs/cm)	2040	1980	2000
Δ (NTU)	> 2	< 2	< 2
Δ Na ⁺ (meq/L)		2.523	1.088
Δ K ⁺ (meq/L)		-5.295	-3.786
Δ Mg ²⁺ (meq/L)		1.235	1.564
Δ Ca ²⁺ (meq/L)		1.048	2.945
Balance		-0.489	1.811
Δ Na ⁺ (meq/g)		0.315	0.136
Δ K ⁺ (meq/g)		-0.662	-0.473
Δ Mg ²⁺ (meq/g)		0.154	0.196
Δ Ca ²⁺ (meq/g)		0.131	0.368
Balance		-0.061	0.226
ECEC NYT		0.134	-
ECEC YFCI		-	0.157
Δ ECEC		0.195	0.069

however, evidences a deep acidification as pH values decrease from 3.45 to 3.09. The reference sample Z33 of the *Fiano di Avellino* wine treated with bentonite generally does not evidence substantial variations of potassium concentration as well as for the other cations. It should be remarked however, that bentonite sample was prepared with a solid-to-liquid ratio one order of magnitude lower (0.6 g/L), as generally used in the oenological practice.

TABLE 5

Representative analyses of wines treated with reference materials: Zeo 4A (Na-homocationic zeolite 4A, SASOL Italy SpA) and Na-bent (Na-activated bentonite, bentogran-Na, AEB Group).

Sample ID	Z 50	Z 33
White wine	Greco di Tufo	Fiano di Avellino
Condition	8g Zeo 4A/L	0.6g Na-bent/L
Na ⁺ (meq/L)	14.137	0.609
K ⁺ (meq/L)	17.498	9.158
Mg ²⁺ (meq/L)	9.218	7.276
Ca ²⁺ (meq/L)	2.895	3.953
Total Cations (meq/L)	43.748	20.996
pH	3.09	3.31
Conductivity at 20 °C (µs/cm)	2116	1964
Δ (NTU)	< 2	< 2

DISCUSSION AND CONCLUSIONS

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 so widespread on the Campania region (Southern Italy). The first approach to the 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% (sample Z8). This aspect represents an undeniable advantage if compared to the use of other exchangers such as polymeric resins which show as drawback the almost total

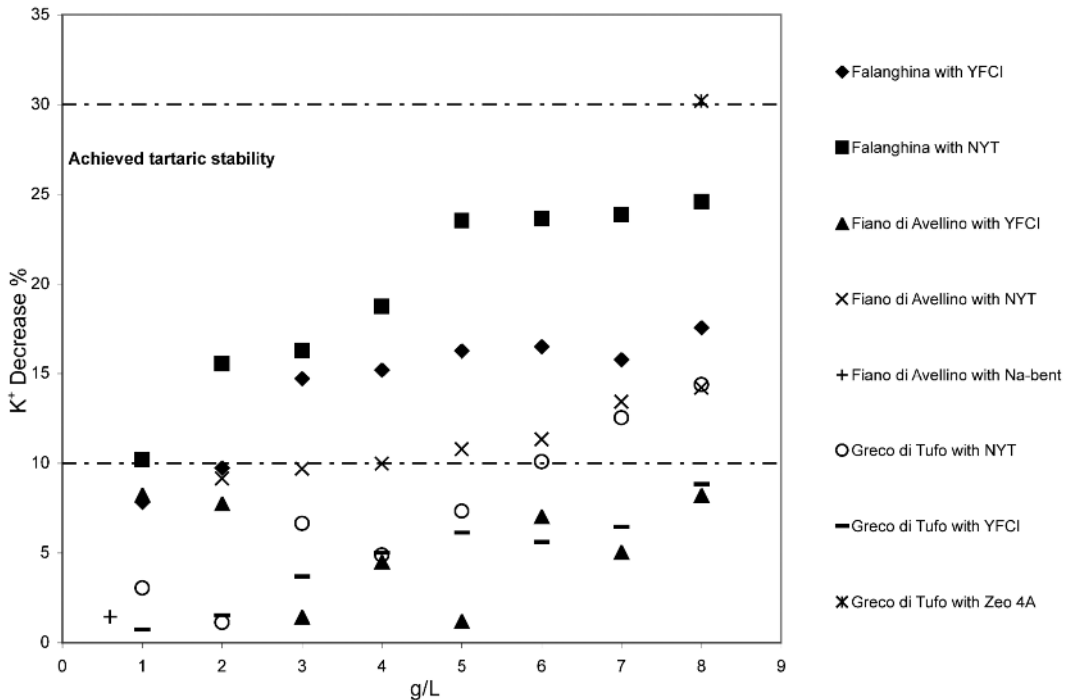


Fig. 2 - Potassium decrease (%) after interaction with different solid-to-liquid ratios. Horizontal dotted lines define a field of potassium decrease between 10 and 30% that, according to Wyss and Cuénat (2005), likely identify a tartaric stability achievement.

decaionization of the wine (Wyss and 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. Figure 2 reports the samples that achieved this requirement (achieved tartaric stability). The best results were recorded by the *Falanghina* wine + NYT or YFCI, with a potassium decrease up to 25% or ~ 15%, respectively. By contrast, *Fiano di Avellino* and *Greco di Tufo* treated with YFCI, even at the highest solid-to-liquid ratios, are always below 10%. The addition of bentonite (to *Fiano di Avellino*) does not allow the tartaric stability to be achieved.

It was demonstrated that the use of zeolitized tuff ensures protein stability conditions measured

in terms of turbidimetric units: Δ 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 (TABLES 2, 3 and 4). 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 external cation exchange capacity (ECEC) for NYT and YFCI which turned out to be 0.134 meq/g and 0.157 meq/g, respectively (TABLE 1). 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. It should be hypothesized a higher attitude of chabazite to external cation exchange (Majdan *et al.*, 2006).

In any case, the increase of the total cation concentration after the interaction still cannot be entirely attributed to the external cation exchange capacity evaluated for the two samples. TABLES 2, 3 and 4 report the balance expressed in meq/g between the increased amount of cations in solution and the experimental external cation exchange capacities. One of the possible explanations of these results is that some proteins may enter the zeolite framework thus determining the recorded extra cation exchange. On this account, some authors demonstrated that some long chain organic macromolecules, positively charged, could enter in the zeolites channel, especially chabazite (Majdan *et al.*, 2006). Also, an in-depth study of the chemical composition of the investigated wines, may provide further information on possible unconsidered cations concurring to the exchange process.

As far as the exchange process of *Greco di Tufo* with zeolite A (Na-form phase) is considered, the cation content difference is definitely lower than the experimental ECEC (about 0.5 meq/g; de' Gennaro *et al.*, 2009). In this case, the possibility that high dimension proteins may occlude some cation sites thus reducing the surface exchange should be invoked.

It is also relevant that significant pH variations did not occur after the treatment since a marked acidification could extensively alter the sensory features of the product; commonly, it is useful to optimize the exchange process trying to prevent a further contribution of H⁺ ions which could acidize the solution. This is the reason why zeolites highly selective towards monovalent

ions are more suitable for this treatment. These results were achieved by using 700-800 g/hL of zeolitized tuff that is, one order of magnitude higher than that used with bentonite (50 - 100 g/hL). By contrast, the use of these phyllosilicates implies some drawbacks: a 1:20 bentonite-water mixture added to the wine in many cases foresees a further addition of casein acting as filler of the voids still occurring within the T-O-T layers and thus promoting the coagulation. The addition of this second stabilizer is therefore necessary. The present research suggests a method that only requires the mixing of a powdered zeolitized tuff with the wine, for a time depending on the mass to be treated. After the contact time this powder is just left to settle. In figure 3 white wine production steps according to the usual procedure involving Na-bentonites are compared with those proposed in the present research. Definitely, this new approach is less complex, with an overall advantage in terms of energy involvement and, in the meanwhile, preserving the product quality. On this account, TABLE 6 reports the results of some olfactory wine tastings carried out by expert wine tasters. The sum of pleasantness indexes (PI) of each single panel test allowed to verify that, as far as *Fiano di Avellino* wine samples are concerned, no substantial variations of the olfactory profile was recorded, especially in wines treated with NYT compared to those treated with YFCI and bentonite. This condition should be further verified with sensorial analyses once the process will be reproduced at a pilot plant scale which foresees the use of wine masses close to those generally stocked in cellar wine tanks.

Treatments with zeolitized tuffs turned substantially positive even though two important remarks should be given. So far, it is not possible to estimate the consequences due to the slight increase of calcium recorded after the exchange process. It is well known in fact, that calcium amount of about 100 mg/L may define the

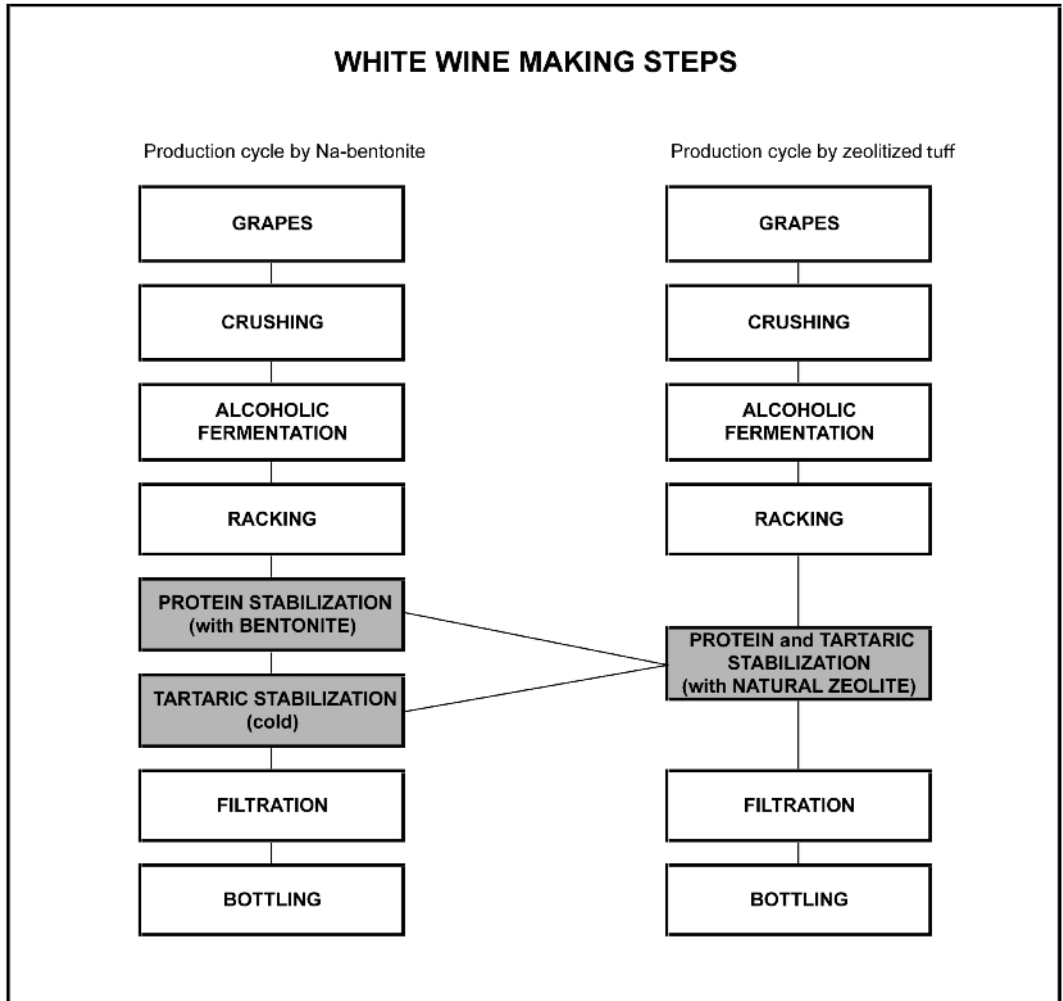


Fig. 3 - Comparison between the traditional production cycle by using Na-bentonite (left) and the proposed one using zeolitized tuff (right).

precipitation of Ca salts. This drawback could be avoided with a preventive Na-exchange of the zeolitized tuff even though this step of the process would increase the overall production costs. Another observation concerns the amount of zeolitized tuffs necessary to achieve the results so far described. This is definitely higher than bentonite thus determining the production of sediments in the wine tanks with consequent

disposal problems. A possible hypothesis of resolution should be the reuse of the powder for further treatments, or by regenerating it with appropriate treatments, or without any treatment if it is verified that a residual exchange capacity of the zeolitized tuff is still available.

All these aspects will be faced in detail in a more specific research that will take into consideration the set up of a pilot plant.

TABLE 6

Scores assigned to wine tastings performed on samples of Fiano di Avellino 2007 vintage processed with NYT, YFCI and Na-bent. PI = pleasantness index.

Sample ID	Powder/Wine (g/L)	PI
Z29	YFCI 5	78
Z30	YFCI 6	75
Z31	YFCI 7	84
Z32	YFCI 8	87
Z21	NYT 5	81
Z22	NYT 6	95
Z23	NYT 7	96
Z24	NYT 8	90
Z33	Na-bent 0.6	66
FA	untreated wine	98

In conclusion, phillipsite and chabazite of 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 Campanian white wines. 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 generally imported by quite far exploitation district.

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