

## Influence of Winemaking Practices on the Concentration of Rare Earth Elements in White Wines Studied by Inductively Coupled Plasma Mass Spectrometry

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Influence of clarification, filtration, and storage on the concentration of rare earth elements (REEs) was studied in white wines by inductively coupled plasma mass spectrometry (ICP-MS). Smooth and parallel chondrite-normalized (CN) plots were obtained for wines which have never been in contact with fining agents. Clarification and filtration generally used in white wine production were simulated in the laboratory using nontreated reference wines, and CN plots were compared before and after treatments. Clarification by bentonites yields an overall increase in REE concentrations resulting in substantially parallel CN curves well above the plots of the corresponding nontreated wines. Filtration using silicate (SiO<sub>2</sub>), on the other hand, changes the CN profile in a nonparallel manner due to a higher release of La, Ce, Pr, Nd, and Gd, more than other elements studied. Filtration with cellulose powder causes a small increase in the concentration of light REEs, while the concentrations of other elements remain basically unchanged. Storage conditions could also affect the REE pattern of wine. We found that the influence of glass is greater than that of stainless steel and wood. In addition, we report that commercially available finished white wines from the same region show highly different REE patterns depending on the winemaking practices employed.

**KEYWORDS:** Wine; winemaking process; rare earth elements; ICP-MS; chondrite-normalized plots

### INTRODUCTION

The ability to trace and authenticate a food product is a growing concern for food industries and food authorities. Today, quality wines in many countries have labels stating where their grapes come from. Authentication of geographical provenance of wines with analytical methods is a highly discussed and debated topic, and one which has concerned the research community for the past 10 years. Finding parameters which can link a wine to the soil of its vineyard and/or to the specific region (geographical origin) could serve as a guideline for guaranteeing the authenticity of products. This could especially be used to certify brands already claiming authenticity, and to consequently protect consumers from false claims. Today, traditional and innovative analytical methods are being tested to monitor both organic and inorganic wine components in order to find a reliable approach and a suitable set of markers for wine authentication (1–5). Inorganic markers, either a large, nonselected or a selected group of elements, are often monitored in wine by means of inductively coupled plasma mass spec-

trometry (ICP-MS) using semiquantitative or quantitative methods (3, 4, 6–8). Correlation between the element composition of wine and that of soil, however, is often affected by several factors such as environmental pollution, use of fertilizers and pesticides, the winemaking process itself, and the different solubility and migration properties of inorganic compounds in the soil (9, 10). Statistical treatment of data derived from the analysis of large sets of elements has been performed by a number of authors (11–14) in order to define a set of elements not affected by the above-mentioned factors which can act as drawbacks for discrimination. For example, by analyzing a large set of elements with different physicochemical properties in 112 wines, Baxter et al. discriminated wines of three different geographical regions of Spain (15). More recently, Coetzee et al. and Taylor et al. have used a similar methodology to distinguish South African (16) and Canadian wines (17), respectively. With a different approach, a set of elements having similar physicochemical properties is chosen because of their even uptake from soil to plant. REEs are thought to form a good set due to their strong chemical similarities. The bioaccumulation of REEs in roots and leaves increases with increasing REE concentration in the soil (18). Many authors show that REE distribution patterns in different parts of the plant are very similar and reflect the characteristic of the host soil (19). REE

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**Table 1.** White Wine Samples (1–13) and Their Origin, Clearing, and Filtration Materials Used during Winemaking and Storage Conditions

no.	wine sample name	origin	fining treatment	container
1	Fiano "Bechar" Caggiano 2001	Irpinia (It)	membrane filtration	glass bottle
2	Fiano "Bechar" Caggiano 2002	Irpinia (It)	membrane filtration	stainless steel
3	Fiano "Bechar" Caggiano 2002	Irpinia (It)	membrane filtration	wooden barrel
4	Fiano Antica Hirpinia 2001	Irpinia (It)	Unknown	glass bottle
5	Fiano Casa dell'Orco 2001	Irpinia (It)	bentonite/silicate/cellulose	glass bottle
6	Fiano Casa dell'Orco 2001	Irpinia (It)	bentonite/silicate/cellulose	stainless steel
7	Fiagre Caggiano 2001	Irpinia (It)	membrane filtration	glass bottle
8	Greco di Tufo Caggiano 2002	Irpinia (It)	bentonite/membrane filtration	stainless steel
9	Greco di Tufo Casa dell'Orco 2002	Irpinia (It)	bentonite/silicate/cellulose	glass bottle
10	Greco di Tufo Casa dell'Orco 2002	Irpinia (It)	bentonite/silicate/cellulose	stainless steel
11	Greco di Tufo Mastro 2002	Irpinia (It)	bentonite/silicate/cellulose	glass bottle
12	Leányka (experimental) 2002	Eger (Hu)	non-treated	glass bottle
13	Leányka (experimental) 2002	Eger (Hu)	bentonite/cellulose sheet	glass bottle

distribution in the soil is found unmodified in the roots and the leaves and in the grape juices as well (20). Augagneur et al. reported that concentrations of rare earth elements can be used to discriminate wines on the basis of their geographical provenances (21). The value of data obtained by ICP-MS analyses of finished products in wine authentication, however, was questioned by Jakubowski et al. In this work, the striking differences of REE concentrations between nontreated young and finished wines were shown (20). The authors reported that REE concentrations in young wines left untreated after grape-pressing were more than 1 order of magnitude lower than those in finished wines due to contamination from bentonites used for removing haze forming components. More recently, Castiñeira et al. have also confirmed that REE concentrations were altered in white wines from Germany during clarification by bentonite at different steps of the winemaking process (22).

The general aim of the present work was to measure and compare REE concentrations of white wines at different stages of production and storage. First, we studied the effects of clearing and filtration using nontreated reference wines in order to determine how these winemaking steps contribute to the final concentration of REEs. Second, we compared finished wines from the same regional origin which underwent different winemaking processes. Finally, we studied the influence of storage containers on REE concentrations in white wines stored in three different containers: stainless steel tanks, wooden barrels, and glass bottles. It has been observed that different storage conditions (barrel types, storage times) considerably influence the volatile composition of a wine by modifying concentrations of several organic compounds, like amines, saccharides, and others (23–26). Storage conditions can also influence concentrations of elements such as Fe, Al, and Cr (9). For this reason, in some countries, these and other potentially toxic elements (As, Cd, and Pb) are routinely analyzed in finished wines. To our knowledge, however, there are no data regarding the influence of storage on the REE concentrations in wine.

## EXPERIMENTAL PROCEDURES

**Reagents and Solutions.** Water MilliQ (Millipore, Bedford) filtered with 0.22  $\mu\text{m}$  Millipack 4.0 molecular filter and 60% ultrapure  $\text{HNO}_3$  (Merck, Darmstadt, Germany) were used to prepare all sample, blank, and standard solutions. A mixture containing 16 rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y) purchased from Ultra Scientific (North Kingstown) was used as external calibrant. Blank and standard solutions were prepared in 6% ethanol, RPE purity (Carlo Erba, Rodano, Italy) to match the content of ethanol

in samples. Rh or In (as it is stated throughout the text), ultrapure (Merck, Darmstadt, Germany), was used as internal standard (IS) at concentration of 100 ng/L. Tuning and instrument calibration were performed daily using a multielement standard solution (Merck, Darmstadt, Germany). High purity argon (99.995%) purchased from Sol Group (Monza, Italy) was used as plasmogen.

Bentonites, silicate, and cellulose used to mimic the industrial processes of clarification and filtration are commercially available products commonly used in Italy and Hungary. Bentogran bentonite (AEB spa, Brescia, Italy), silicate, and cellulose powders were supplied by Azienda Agricola La Casa dell'Orco, San Michele di Pratola, Avellino, Italy. "Mádi" bentonite is commercially available and commonly used in Hungary.

**Wine Samples.** White wines from Italy (with Italian certified brand of origin D.O.C., Denominazione di Origine Controllata) and Hungary were collected and analyzed by ICP-MS. The finished wines were collected from the glass bottles by cautiously removing the corks, conditioning the necks by 5%  $\text{HNO}_3$ , and then aspirating the liquid with noncontaminating PPE pipettes. Nonmetallic devices were always used to collect and transport the samples from the wooden or stainless steel containers of the producers to our laboratory. Wine samples were diluted 1:1 with 5%  $\text{HNO}_3$ , filtered using 0.22  $\mu\text{m}$  Millex GV molecular filters (Millipore, Bedford), and spiked with IS. Samples were freshly prepared on the day of analysis unless otherwise stated. No sample pretreatment other than acidification and dilution was carried out. Though aspiration of ethanol-containing solutions into the ICP may cause significant matrix effects, accurate results were obtained by using matrix-matched blanks and standards.

Three different sets of samples were analyzed: (1) Two untreated white wines from the province of Avellino (Irpinia, Italy), Fiano di Avellino "Bechar" Caggiano 2001 (Table 1, sample 1) and Fiano di Avellino "Bechar" Caggiano 2002 (Table 1, sample 2), were analyzed before and after the following laboratory treatments. (a) Clarifications of sample 2 by different bentonites were performed according to the bentonite producer's instructions; 7.5 mg of AEB Bentogran, swelled for 15 min at room temperature by 125  $\mu\text{L}$  of  $\text{H}_2\text{O}$  (MilliQ), was added to 25.0 mL of wine in a Falcon PPE tube. After 10 days, the liquid phase was collected by decantation. In a parallel experiment, 7.5 mg of Mádi bentonite, previously swelled by 125  $\mu\text{L}$  of  $\text{H}_2\text{O}$  for 4 min at 100  $^\circ\text{C}$ , was added to 25.0 mL of sample 2 in a Falcon PPE tube. After 10 days the clarified wine was collected by decantation. (b) Clarification of sample 1 was performed according to the wine producer's instructions; 15.0 mg of Bentogran was suspended in 50.0 mL of wine in a noncontaminating PPE bottle. After 10 days the liquid phase was collected by decantation. (c) Filtration of sample 1 through silicate or cellulose powder was performed mimicking the solid/liquid ratio used by the producer; 20.0 mL of sample 1 was passed through 1.5 g of powder packed in a PPE 10 mL syringe by applying a gentle pressure on the syringe piston. Flowthrough was collected. (2) A second set of nine ready white wines known to be subdued to different winemaking processes (Table 1) were grouped according to their geographical origins in the following two subsets. (a) There were three wines made of "Fiano di Avellino" grapes (certified brand of origin

**Table 2.** ICP–MS Operating Conditions Used in This Study for the Analysis of Wine Samples

instrument parameter	condition		
cooling gas flow rate	15.00 L/min		
auxiliary gas flow rate	0.790 L/min		
sample gas flow rate	0.819 L/min		
RF forward power	1200 W		
sample uptake	0.3 mL/min		
extraction lens voltage	−2000.0 V		
focus lens voltage	−866.4 V		
X-deflection	4.44 V		
Y-deflection	4.44 V		

acquisition parameter	LR	MR	HR
scan mode	E-scan	E-scan	E-scan
mass window	20	125	100
integration window	20	20	80
samples per peak	50	20	15
sample time (s)	0.02	0.02	0.02

isotopes measured	
low resolution	$^{89}\text{Y}$ , $^{139}\text{La}$ , $^{140}\text{Ce}$ , $^{141}\text{Pr}$ , $^{142}\text{Nd}$ , $^{147}\text{Sm}$ , $^{149}\text{Sm}$ , $^{151}\text{Eu}$ , $^{158}\text{Gd}$ , $^{159}\text{Tb}$ , $^{164}\text{Dy}$ , $^{165}\text{Ho}$ , $^{166}\text{Er}$ , $^{169}\text{Tm}$ , $^{174}\text{Yb}$ , $^{175}\text{Lu}$
medium resolution	$^{45}\text{Sc}$
high resolution	$^{136}\text{BaO}$ , $^{152}\text{Sm}$ , $^{113}\text{In}^{40}\text{Ar}$ , $^{115}\text{In}^{38}\text{Ar}$ , and $^{153}\text{Eu}$
oxide formation	$^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce} = 0.01$
doubly charged ion formation	$^{136}\text{Ba}^{++}/^{136}\text{Ba}^{+} = 0.02$
shape	120.0 V
sensitivity for $^{103}\text{Rh}(\text{cps}/1\text{ng}/\text{L})$	200

D.O.C.) by different producers from the province of Avellino (Irpina), Italy (samples **1**, **4**, and **5**), three wines made of “Greco di Tufo” grapes (certified brand of origin D.O.C.) by different producers from the province of Avellino, Italy (samples **8**, **9**, and **11**), and one wine (“Fiagre”, sample **7**) made by a mixture 1:1 of “Fiano di Avellino” and “Greco di Tufo”. (b) There were two wines made of “Leányka” grapes from Eger, Hungary (samples **12** and **13**), by the same producer before and after fining. (3) A third set of six wines stored in different containers was used, divided in two subsets, according to their geographical origins and their producers. (a) There were two “Fiano di Avellino” wines stored in stainless steel containers (samples **2** and **6**), a “Fiano di Avellino” wine stored in a wooden barrel (sample **3**), and a ready “Fiano di Avellino” wine stored in glass bottle (sample **5**). (b) There were two “Greco di Tufo” wines (samples **9** and **10**) from the same producer but differently stored (glass bottle, stainless steel tank).

**ICP–MS Measurement and Data Processing.** A double-focusing high-resolution sector field (Nier–Johnson reverse geometry) ICP–MS (Element2, Thermo, Bremen, Germany) instrument equipped with concentric nebulizer, double wall Scott–Meinhard spray chamber, and peristaltic pump was used. Standard operating conditions and measurement parameters are given in **Table 2**. Quantitative analyses were carried out by using external calibration curves constructed by a minimum of six standard solutions in different ranges, where the inferior limit was commonly 1 ng/L, while the superior limit could assume values from 50 to 1000 ng/L depending on the experiment. The most abundant isotopes of the major part of the REEs ( $^{89}\text{Y}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{142}\text{Nd}$ ,  $^{158}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{164}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{166}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{174}\text{Yb}$ , and  $^{175}\text{Lu}$ ) are almost free of any isobaric interference; therefore, low mass resolution (LR) was used to measure them. The mass resolution used here is defined as  $m/\Delta m$  measured at 10% peak valley. On our instrument, the mass resolution equals 400 for low (LR), 4000 for medium (MR), and 10000 for high mass resolution (HR), respectively. For medium and high resolution the instrument was fine-tuned.  $^{40}\text{Ar}^{40}$ . Ar was used as lock mass for HR analysis.  $^{45}\text{Sc}$  was measured in medium resolution (MR) to avoid interference with  $^{14}\text{N}_2\text{OH}$ ,  $^{12}\text{CO}_2\text{H}$ ,  $^{29}\text{SiO}$ , and  $^{28}\text{SiOH}$ . Concentration values were normalized, and chondrite-normalized (CN) plots were calculated using the values of Anders

and Grevesse multiplied by the factor 1.36 (27). This factor gives  $\text{Sm} = 0.2000 \mu\text{g}/\text{g}$  and results in values for all REE in the vicinity of those for the early ordinary chondrite composites (28). In the CN plots of nontreated reference wines, unusually high values were observed for  $^{152}\text{Sm}$  and  $^{153}\text{Eu}$  isotopes, reasonably not related to the samples. Interferences of  $^{113}\text{In}^{40}\text{Ar}$  and  $^{115}\text{In}^{38}\text{Ar}$  from the internal standard In were confirmed to be the cause of the high  $^{153}\text{Eu}$  value, and therefore, Rh was used instead of In. HR measurements of barium oxide ( $^{136}\text{BaO}$ ) and  $^{152}\text{Sm}$  revealed that high Ba concentration caused the interference on  $^{152}\text{Sm}$  in LR. To correct this, measurements of  $^{152}\text{Sm}$  were performed by HR analyses, or alternatively,  $^{147}\text{Sm}$  and  $^{149}\text{Sm}$  isotopes were measured in LR. Three spectra were measured and averaged in one cycle, and three cycles (i.e., nine scans) were performed for all isotopes. Concentrations were evaluated as the average of the three cycles. Each sample was analyzed in triplicate.

## RESULTS AND DISCUSSION

**Influence of Clarification by Bentonites.** Almost all white wines require specific clarification processes. Excess protein responsible for haze formation, causing an unattractive cloudy appearance, is normally removed by fining (29). Several fining materials are used for clarifying white wines, bentonite being the most widely used in the industrial enological field. The original REE pattern of the wine after bentonite extraction may increase by REE originated from desorption process and dissolution of bentonite. The kinetics of these processes is controlled by the physicochemical properties of the extraction solution and the bentonite itself (ionic strength, pH, etc.) and the experimental conditions (winemaking practice) as well. Release of REEs from bentonite to different media has already been studied at various solid/liquid ratios (30). Fractionation of REEs during desorption was observed by different authors finding different trends. Mihaljevic et al., for example, observed that high mass REEs (HREE) are preferentially extracted into wine solution, while the fractionation of REEs is not apparent during dissolution of bentonite. On the basis of this, suffice it to say that fining with bentonite can lead to an increase in REE concentrations and/or alteration of REE profiles of wine, hence causing a loss of information about geographical provenance (20).

Two white wines from the province of Avellino (**Table 1**, samples **1** and **2**) which had not undergone clarification and filtration were chosen as references to study the influence of clarification by bentonite. Before treatment, REE concentrations in these reference wines were very low, falling in the range 1–170 ng/L depending on the elements (**Table 3**). An overall increase of 1 order of magnitude in the concentrations of REEs was observed when reference wine **2** was treated with two bentonites (sample **2** AEB and sample **2** Mádi, **Table 3**) yielding substantially parallel CN plots (**Figure 1**). A difference was observed between the effects of the two bentonites: “Mádi” contaminated significantly more than AEB. It may have been caused by the difference in the clarification conditions (i.e., temperature and time used for swelling), or by the difference in quality of the two products. A similar effect was observed when sample **1** was clarified with “AEB Bentogran” (sample **1** AEB, **Table 3**). Our results are in good agreement with previously reported work (20): the clarification process changes the REE concentrations to a high extent. The increase in REEs observed after fining is due to the sum of REE desorption and dissolution. In contrast with previous work (30), we have not observed significant fractionation of REEs which can be explained by the different bentonites and experimental conditions applied in the two studies. In fact, various types of bentonite coming from different geographical locations and



Table 3. Average Concentrations<sup>a</sup> of Rare Earth Elements in Wine Samples and Corresponding Relative Standard Deviations<sup>b</sup>

sample	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																		
1	48.6	5.7	104	2.3	149	1.3	172	1.3	41.6	1.3	86.5	0.3	15.9	1.8	34.4	2.4	29.5	5.6	14.7	2.1	21.9	3.7	18.0	5.1	20.9	2.7	17.1	1.6	22.7	4.5	14.0	1.2		
1 AEB	221	6.7	1662	0.8	729	0.5	1769	0.5	172	0.7	962	2.4	82.3	4.0	58.2	3.2	286	1.3	42.4	0.6	228	0.6	228	0.6	52.8	1.3	184	0.6	29.4	0.5	229	1.1	43.9	0.4
1 silicate	216	8.7	1776	1.5	1599	1.4	3448	2.4	343	1.6	1751	2.4	101	1.7	53.1	1.3	412	0.9	44.0	0.5	233	0.5	233	0.5	46.8	1.9	164	1.6	19.4	2.3	151	0.9	25.5	3.1
1 cellulose	31.8	8.0	320	1.3	320	0.8	528	1.9	58.5	1.5	282	1.0	129	3.1	75.6	2.6	68.7	1.5	3.3	3.7	36.2	0.8	4.5	1.2	25.3	3.7	0.9	40.7	2.4	2.3	3.8	7.0	3.7	
2	58.6	3.1	133	2.4	29.3	2.8	5.8	3.0	15.3	7.5	21.4	3.7	30.6	5.4	26.9	4.0	15.4	4.7	4.6	10.2	17.7	6.9	7.9	7.5	15.0	8.6	6.8	10.5	15.5	1.6	8.9	3.7		
2 AEB	94.2	8.5	548	1.9	167	2.0	333	3.1	48.9	2.4	218	0.3	44.3	2.6	56.4	4.9	81.9	5.6	15.0	2.2	76.9	1.6	21.6	3.8	61.4	2.1	12.9	5.2	66.7	3.7	18.2	2.4		
2 Mádi	763	12.6	2530	1.2	416	0.6	1037	1.0	128	2.3	693	0.5	153	0.9	73.2	3.3	329	1.1	58.7	2.3	336	1.7	81.2	1.0	241	1.8	37.0	1.4	214	0.8	41.4	1.4		
3	46.7	3.6	87.5	6.2	22.3	8.4	18.7	2.5	10.9	6.8	17.9	3.0	19.6	3.4	23.9	3.7	5.8	3.8	1.1	3.5	3.8	5.7	2.1	3.9	2.6	1.7	0.9	8.8	3.5	3.2	1.7	4.9		
4	68.4	4.5	939	0.9	249	1.1	523	0.4	61.8	0.6	358	0.8	161	1.9	82.6	1.9	94.3	1.2	7.2	4.6	102	1.6	20.3	1.2	102	3.2	10.9	4.1	157	0.4	23.2	0.9		
5	52.0	7.3	814	0.3	436	1.1	909	1.2	114	0.7	526	0.5	132	1.9	80.8	0.9	134	1.9	32.3	0.9	111	0.4	39.3	1.1	98.4	1.3	29.4	2.1	125	0.5	33.5	0.4		
6	50.1	9.3	376	0.5	157	0.7	306	1.3	51.1	4.3	202	1.8	112	4.1	75.4	2.7	62.0	2.5	20.6	2.9	55.6	4.6	24.4	2.1	53.2	4.0	21.0	6.7	71.4	2.3	22.6	2.0		
7	45.3	16.4	95.5	3.1	22.6	5.6	35.8	0.4	7.3	7.1	24.8	2.2	7.8	7.5	8.4	7.2	7.7	6.6	1.2	13.6	6.0	2.2	1.9	9.8	4.8	9.3	1.6	11.4	5.8	3.9	8.1	1.3		
8	142	8.3	337	0.9	61.5	2.0	75.8	3.1	20.2	6.8	71.2	4.8	84.3	4.3	55.5	4.7	32.9	6.6	0.8	4.7	26.4	2.6	3.7	5.9	19.5	5.4	1.4	3.5	22.2	2.4	4.0	2.3		
9	74.8	10.0	559	3.2	413	2.4	688	2.6	105	2.7	434	1.5	147	2.2	99.2	3.1	114	1.0	27.9	1.1	81.5	3.3	34.4	1.0	77.3	1.8	27.2	4.2	114	1.1	33.1	1.0		
10	114	7.7	390	0.4	211	4.0	373	1.0	69.5	2.2	250	1.6	147	4.6	90.2	1.3	69.4	3.4	23.1	2.3	58.0	3.7	28.5	2.0	64.4	1.6	25.4	3.1	102	2.6	31.6	1.9		
11	142	3.8	1486	0.2	440	0.6	1138	0.5	113	0.5	683	0.2	181	0.4	71.2	2.4	167	0.7	20.6	0.7	180	0.2	37.6	0.5	151	1.6	15.5	2.4	183	0.3	25.2	0.8		
12	83.2	7.4	216	2.1	93.3	0.9	130	0.8	34.5	5.1	116	2.7	46.1	0.8	38.8	3.5	36.0	7.6	8.6	4.1	30.7	1.3	12.8	8.5	33.9	4.9	11.9	1.9	49.9	1.8	17.9	2.3		
13	88.2	9.2	1347	1.2	228	1.0	526	1.3	111	1.3	521	2.1	111	0.7	74.8	4.4	197	3.8	33.7	0.4	187	0.7	54.5	1.9	195	1.1	41.3	1.7	294	0.2	65.1	1.1		

<sup>a</sup>Concentration values are expressed in ng/L and refer to REEs in wine without dilution. <sup>b</sup>Standard deviations are given in percentage (%) and refer to the wine samples analyzed.

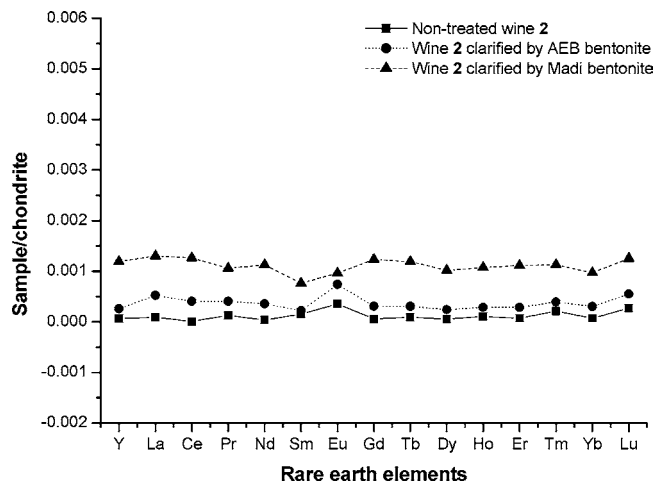
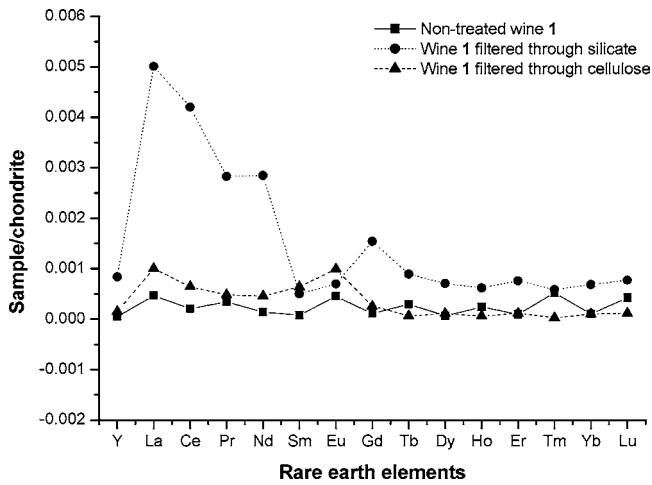


Figure 1. Chondrite-normalized plots of wine sample 2 (a nontreated wine) before and after clearing using two different bentonites (Mádi and AEB).

having different particle size, adsorption capacity, levels of purity, and swelling ability exist. The type and source of the bentonite used in fining can affect the protein removal efficiency due to the variations in the swelling and cation exchange capacity of the bentonite. Considering the experimental conditions we used here for fining (long time contact with bentonite: 10 days), we suppose that dissolution in our case has a significant contribution to REE release, which may attenuate the REE fractionation that originated from the desorption process.

**Influence of Filtration Using Silicate and Cellulose Powders.** Previous work has mainly been focused on the influence of the clearing agents (bentonites) on the REEs in wine, but most white and blush wines are not completely clear after fining, and some kind of filtration is often needed to ensure the required stability. Different studies have been reported on the influence of the filtration on the organic composition of wine (31), but there is a lack of information about the release of REEs from filtration materials to wine. Several types of membrane or molecular filters made of various materials (ceramic membranes, PTFE, PVPP, PES, and others) are currently used in enology to improve the process in terms of time and efficiency (microbiological safety and commercial appeal), and to avoid or limit the release of toxic metals. On the other hand, materials of natural origin, as silica from spent diatomaceous earth, or cellulose, are also commonly used and even recommended by authorities for the control of wine quality. Here we compare the different filtration methods in terms of the quantity of REEs released, regardless of the methods' effectiveness.

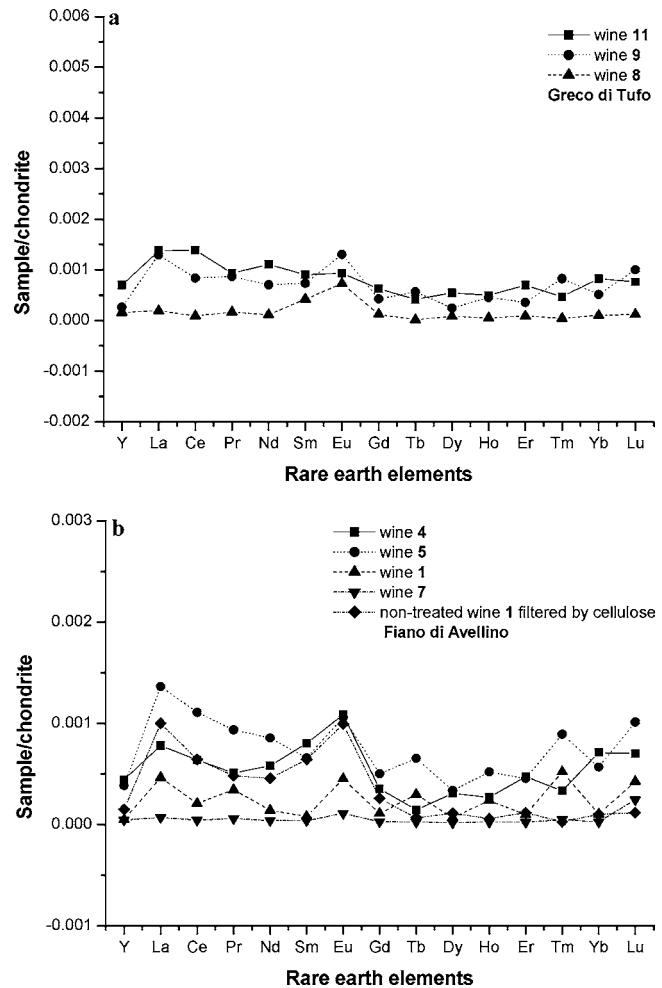
Reference wine 1 (Table 1) known to be filtered only through molecular filters during winemaking was filtered through silicate in the laboratory according to the producer's operating solid/liquid ratio. After filtration, REE concentrations increased by at least 1 order of magnitude for almost all the elements, but showed an even higher increase for La, Ce, Pr, and Nd (sample 1 silicate, Table 3). The same reference wine after filtration through cellulose powder showed an increase only in the concentrations of light REEs, from Y to Eu (sample 1 cellulose, Table 3). Comparing the CN plots of these samples (Figure 2), we made the following observations: (i) filtration through silicate powder causes a high increase in REE concentrations, (ii) the profile of the CN plot changes considerably after filtration through silicate compared to the original one causing



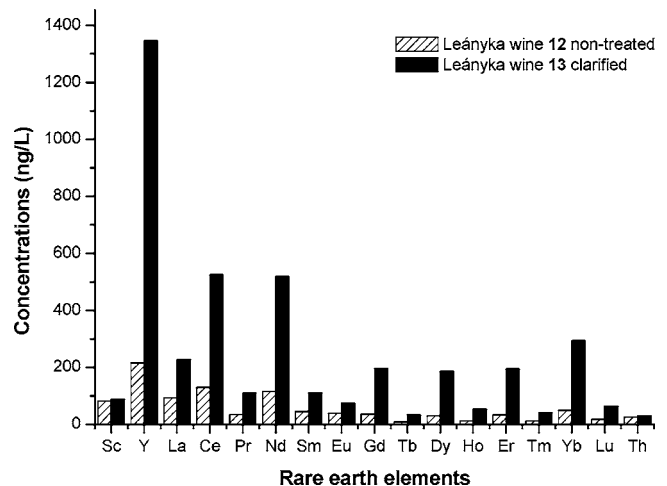
**Figure 2.** Effects of filtration through silicate and cellulose powders on the chondrite-normalized plot of sample 1.

the loss of the parallel shape, (iii) cellulose releases fewer REEs into wine than silicate powder does.

**Influence of Winemaking in Finished White Wines.** In our work, we aimed to compare the REE patterns of wines of the same origin in order to determine whether such patterns can represent a suitable fingerprint for authentication. Quality wines with the same certified origin but made by different producers who employ different winemaking processes were analyzed and compared. Comparing the CN plots of three “Greco di Tufo” D.O.C. wines from the province of Avellino (Irpinia, Italy), we found that two wines (Table 1, samples 9 and 11) which had been subjected to equal winemaking processes (clarification by bentonite followed by filtration with silicate and cellulose powders) have overlapping CN plots. In contrast, sample 8, filtered through membrane filters after clearing by bentonite, gave a different CN profile, which is under that of samples 9 and 11 (Figure 3a). A similar result was obtained for “Fiano di Avellino” D.O.C. wines (Table 1, samples 1, 4, 5, and 7), which were treated differently by the winemakers. Depending on the fining processes, the following general trends could be observed: REE concentrations of nontreated white wines were found to be very low, having values in the low nanogram per liter level, and their chondrite-normalized plots are smooth and parallel. Winemaking processes can influence both the absolute REE concentration values and the shape of the CN plots. In particular, filtration using silicate (Figure 3) and fining by bentonite can increase the REE levels to a great extent, while filtration using cellulose has less effect. REE concentrations are considerably higher (at least 1 order of magnitude) in wines known to be filtered through silicate (Table 3) than in nontreated, bentonite-clarified, or cellulose-filtered wines. Also, the CN plots are very characteristic of these wines due to a higher increase in the low mass REEs. It is worthwhile to note that wine 4 which underwent an unknown fining process showed a CN profile very similar to that of reference wine 1 after filtration through cellulose (Figure 3b). Analysis of the Hungarian wines (Table 1, samples 12 and 13) made from the same grape (Leányka) grown in the same vineyard, and supplied to us at different stages of winemaking, confirmed that the REE pattern is more linked to the enological fining practices than to the soil from which the grapes derive. In comparison to wine 12, which has never been in contact with bentonite or other fining agents, wine 13, clarified by bentonite and filtered through cellulose membrane, showed an overall increase in the concentrations for the various REEs (Figure 4). In conclusion, REE



**Figure 3.** Chondrite-normalized plots of Italian finished white wines made with the same grapes from the province of Avellino (Irpinia) (a) “Greco di Tufo”, and (b) “Fiano di Avellino” but produced using different winemaking practices (Table 1).



**Figure 4.** Rare earth elements pattern of two Hungarian white wines (“Leányka” varietal) from the same vineyard at different stages of winemaking (before and after fining).

concentrations and CN plots of finished white wines subjected to clarification and filtration processes are considerably higher than those of nontreated wines, suggesting that the pattern of REEs reflects the winemaking process itself more than the geographical origin of the grapes.

**Influence of Storage Conditions.** Different containers are used for storing wine, and it is stored at variable lengths of time depending on the enologist's decision for wine-aging. White wines are usually fermented and preserved in stainless steel tanks; however, they often stay in oak barrels for a few months as well. The use of different kinds of containers may result in completely different wine styles: stainless steel helps to preserve the freshness of wines, while oak releases extractable components, and more importantly, owing to its permeable properties, permits micro-oxidation. We compared wines derived from the same geographical origin (Irpinia, province of Avellino, Italy) but stored in different containers: some in green glass wine bottles, some in stainless steel tanks, and one in a wooden barrel. REE concentrations of wine preserved in a glass bottle for a year ("Fiano di Avellino", sample 5 in Table 1) are considerably higher than those for the same wine (sample 6) kept in a stainless steel tank for the same time (Table 3). Sample 9 ("Greco di Tufo Casa dell'Orco") kept in a glass bottle for only a month also showed an increased REE content with respect to the same wine (sample 10) conserved for the same time in stainless steel (Table 3). The concentrations of REEs in a wine conserved in *barrique* (sample 3) were slightly lower than those of the same wine (sample 2) kept in a stainless steel container, suggesting that wood releases fewer REEs into wine (Table 3).

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