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Wine Traceability with Rare Earth Elements

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Abstract: The traceability of foodstuffs is now a relevant aspect of the food market. Scientific research has been devoted to addressing this issue by developing analytical protocols in order to find the link between soil and food items. In this view, chemical parameters that can act as soil markers are being sought. In this work, the role of rare earth elements (REEs) as geochemical markers in the traceability of red wine is discussed. The REE distribution in samples from each step of the wine making process of *Primitivo* wine (produced in Southern Italy) was determined using the highly sensitive inductively coupled plasma-mass spectrometry (ICP-MS) technique. Samples analyzed include grapes, must, and wine samples after every step in the vinification process. The resulting data were compared to the REE distribution in the soil, revealing that the soil fingerprint is maintained in the intermediate products up to and including grape must. Fractionation occurs thereafter as a consequence of further external interventions, which tends to modify the REE profile.

Keywords: ICP-MS; rare earth elements; wine; traceability

1. Introduction

In the changing face of today's global wine industry, producers of traditional, quality wines are experiencing increased competition from low-quality, low-cost products. To combat potential frauds, the European Union has issued several regulations to ensure the authenticity of products labeled as coming from a specified geographic origin and produced according to a particular method. In addition, recently developed scientific techniques allow the origin of agricultural foodstuffs to be traced by using physical and chemical measurements of samples taken at different points throughout the entire production process, from the soil to the final edible product [1,2]. To be effective, these techniques need to take into account numerous factors that might influence the product, such as the climate and soil type, or the use of fertilizers and pesticides, not to mention the wine-making practices. As an example, techniques based on DNA analysis, which is independent from environmental influences, can be considered for traceability, especially for Protected Designation of Origin (PDO) products [3,4].

Inorganic parameters, especially isotopes of heavy elements such as lead and strontium, often turn out to be the most suitable for tracing a product's origin [5]. The isotope ratios of these elements have shown to be powerful tracers, allowing products to be linked to a particular soil. Isotopes of light elements—hydrogen, oxygen, nitrogen, and sulfur—are reliable indicators of food authentication, but their ratios are too variable to serve as tracers of the soil where a product originated [6].

Metals are another important group of chemical tracers. Of these, the rare earth elements (REEs) are the most reliable, and several studies have shown that trace metals, particularly REEs, can act as geochemical markers [7–9]. However, relatively little information is available on the use of REEs in

the traceability of foodstuffs. The high specificity of REEs derives from their compact grouping of 14 elements, from lanthanum to lutetium, with very similar chemical properties arising from their 4f electronic configuration. Another potential advantage of REEs is that they are much less heavily exploited in industry than other transition metals, and are thus not as ubiquitous in the natural environment. These characteristics make REEs useful as geochemical markers and attractive as agents for food traceability [10,11]. A further advantage of REEs is that they do not play a specific role in the metabolism of plants and are therefore taken up indiscriminately from the soil (although in diluted amounts) by the plant, with no fractionation of the original distribution. In fact, fractionation is an important consideration in the traceability study of a particular foodstuff: each passage in the production chain must be carefully inspected for whether or not it could induce fractionation in the original distribution of REEs.

Several studies have exploited the distribution of REEs and, more generally, of trace and ultra-trace elements to develop schemes of wines classification, as shown in recent reviews [12,13]. Most of these studies have been devoted to the *authentication* of wines, seeking to determine whether samples could be discriminated according to their geographical provenance [14], the variety of grape [15], or to oenological features such as ageing [16]. Very few studies have been devoted to the *traceability* of wine, in order to verify the link between a particular wine and the soil in which its grapes were grown. While authentication studies can be based on several types of chemical markers, e.g., trace elements, isotopic data [17,18], volatile compounds [19], and polyphenols [20], only the first two parameters have proven useful in traceability studies [21]. Hopfer et al. [22] in their study on Californian wines were able to classify the samples according to their vineyard origin and their processing winery, showing that the discrimination is possible according to both soil elemental content and viticultural practices. In one of the first studies on the traceability of wines, the soil–wine correlation in two wine-producing regions in Canada, Okanagan Valley, and the Niagara Peninsula was investigated [23]. They found that strontium was able to differentiate both soils and wines from the two regions. Another study analyzed four complete oenological production chains from Piedmont (Italy): *Gavi*, *Barbera*, *Brachetto d'Acqui*, and *Freisa* [24]. Samples of soil, grapes, must, and wine were analyzed with inductively coupled plasma-mass spectrometry (ICP-MS), giving particular care to REEs. The results showed that REE distribution was the same in the must as in the original soil, while fractionation occurred in the wine as a consequence of the winemaking process. Similar results were obtained on the production chain of a *Moscato d'Asti*: the distribution of REEs was the same in the soil, grapes, and must, but fractionation occurred in the wine after clarification with bentonites [25]. Significant correlation between soil and wine data sets were found in samples from three regions in Argentina, where both elemental composition and isotopic ratios ($^{87}Sr/^{86}Sr$) were used [26].

In this work, we further examined the role of REEs in the traceability of wine by analyzing the entire production chain of *Primitivo di Manduria* PDO wine (hereafter, *Primitivo*), a red wine produced in the area of Taranto and Brindisi, two main towns of the Apulia region, in Southern Italy. This wine has been awarded the Controlled Designation of Origin (CDO) mark according to an Italian Decree of 30 October 1974, and this mark was successively modified to a PDO. As a consequence, this wine is produced according to a stringent technical sheet, which specifies also the allowed production area. Samples, including soil, were taken at each step of production: grapes, must, and wine aliquots were taken following each step of vinification, including the process of fining in barriques (wooden barrels). Analysis of the grapes consisted in separate measurements taken on the pulp, skins, and seeds, so that the distribution of trace metals in different parts of the fruit could be compared.

Being REEs present at μg/L level or less in wine, a highly sensitive technique must be used in order to produce reliable data. We therefore employed inductively coupled plasma-mass spectrometry (ICP-MS), a multi-elemental technique with high sensitivity, accuracy, and precision.

2. Materials and Methods

2.1. Materials

High-purity water from a Milli-Q apparatus (Milford, MA, USA) was used in the study. 30% TraceSelect hydrogen peroxide, 69% nitric acid, 95% sulfuric acid, and 37% hydrochloric acid were purchased from Fluka (Milan, Italy). Polypropylene and polystyrene vials, used respectively for sample storage and analysis with an auto-sampler system, were kept in 1% nitric acid and then rinsed with high-purity water when needed. Porcelain capsules of a 30 mL volume were used for microwave dry ashing. Elements stock solutions (Inorganic Ventures, Lakewood, NJ, USA) were used for external calibration (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), stability testing (Li, Co., In, Ce, and U), and internal standardization (Rh, In, and Bi).

2.2. Sample Collection

A complete production chain was analyzed. Soil, grapes, musts, and wine samples were provided by a winery in Grottaglie (TA, Italy). At harvesting, 300 berries from a vineyard were picked from the upper, middle, and bottom parts of the bunches, from both shaded and exposed sides of the row, and then pooled. Sampling was carried out in August 2012. The collected berries were further divided into three groups of 100 berries, which were used as triplicates for the determinations. Grapes and must samples were kept frozen at −20 °C in order to stop all fermentation reactions; they were thawed for 4 h before sample treatment.

2.3. Sample Treatment

Being of different chemical nature, the various samples were treated with different procedures as follows:

1. Soil samples were treated according to a standardized procedure: soil was dried at 105 °C for 24 h, after which 1 g was sieved (ϕ 0.2 mm) and extracted with 20 mL of hydrogen peroxide for 20 min and then with 12 mL of aqua regia on a heating plate for 2 h under reflux. The resulting solution was diluted to volume in a 100 mL volumetric flask with high-purity water.
2. The grapes were processed as follows: skins were manually separated from the pulp and seeds and transferred to different Pyrex glass containers. All parts were separately subjected to dry ashing in porcelain crucibles in a Pyro 260 microwave ashing system (Milestone, Sorisole, Italy) with the following temperature cycle: 15 min to 150 °C, 60 min to 1000 °C, and 10 min at 1000 °C. The resulting ash was dissolved in 1 mL of concentrated nitric acid and brought to 50 mL to obtain a nitric acid concentration of approximately 1%. All solutions were prepared with high-purity water.
3. Musts (100 g) were dried overnight at 105 °C. The dried samples were transferred to porcelain crucibles and subjected to ashing with the following temperature cycle: 50 min to 750 °C, 10 min at 750 °C, 10 min to 900 °C, and 10 min at 900 °C. The resulting ash was dissolved in 1 mL of concentrated nitric acid and brought to 50 mL to obtain a nitric acid concentration of approximately 1%. All solutions were prepared with high-purity water.
4. Wine samples, obtained after every passage in the vinification, were treated with microwave ashing in the same condition used for must.

All samples (soil, grapes, must and wine) were analyzed in triplicate.

2.4. Vinification Processes

Once the grapes had been picked up and transported to the winery, they were treated with 20 mg/L of SO_2. The grapes were initially processed in a crusher-destemmer. The liquid formed after crushing and pressing is the must, which was transferred into "cold-soaked" tanks for two days, and the must was then inoculated with yeast, and fermentation began. It is noteworthy that the time

needed for fermentation varies according to the type of grapes and the method used by the winemaker. In the case of *Primitivo* wine, which typically has a high concentration of sugars, fermentation was carried out for a month. After fermentation, the juice (now wine) was pressed away from the skins into a holding tank, where it sat for a few days to allow sediment and dead yeast cells to settle out (P12SV). At this stage, P12SV wine was transferred into oak barrels for aging, and malolactic fermentation took place (with *Oenococcus oeni* bacteria inoculation). At the end of malolactic fermentation, monitored by HPLC, a sample was analyzed (P12FIN). This experimental wine created from *Primitivo* grapes was neither filtered nor stabilized.

Red wines may be aged from several months to several years, depending on the type and quality of the wine desired. For this study, we also analyzed wine samples coming from different vintages produced by the same winery (P08, P09, P10, and P11).

2.5. ICP-MS Analysis

Elemental analysis was performed with a Thermo Scientific (Waltham, MA, USA) X-Series II inductively coupled plasma mass spectrometer. The instrument is equipped with a quartz torch with a Plasma Screen device, a quadrupole mass analyzer, a lens ion optics based on a hexapole design with a chicane ion deflector and a simultaneous detector with real-time multichannel analyzer electronics, operating in either analogue signal mode or pulse counting mode. A high-efficiency ESI APEX-Q nebulizer (Epond SA, Vevey, Switzerland) was used as a nebulization system. The instrument and accessories were PC-controlled by PlasmaLab software. The instrument and measurement parameters were as follows: forward power: 1400 W; nebulizer gas flow: 0.92 L/min; auxiliary gas flow: 1.00 L/min; plasma gas flow: 13.1 L/min; dual mode detection with peak jumping; dwell time: 10 ms; 25 sweeps; 3 replicates for a total acquisition time of 180 s; the isotopes used were ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, and ^{175}Lu. Interferences were evaluated as follows: $CeO^+/Ce^+ < 1\%$ and $Ba^{2+}/Ba^+ < 1\%$. A stability test was performed before each analysis session by monitoring ^{7}Li, ^{59}Co, ^{115}In, ^{140}Ce, and ^{238}U masses and making sure precision was better than 2%: instrumental precision was better than 2% for the trace elements, while the overall uncertainty (involving both sample preparation and instrumental analysis), calculated on the basis of five genuine replicates, was better than 5%. Background signals were monitored at 5, 101, and 220 m/z to perform a sensitivity test on the above-reported analyte masses. External calibration was employed for quantification, using multi-elemental standards prepared at five concentration levels in the range of 10–10,000 ng/L, by diluting multi-elemental stock solutions (100 mg/L) in 1% nitric acid solution. Internal standardization was used to correct for instrumental drifts by monitoring signals from ^{103}Rh, ^{115}In, and ^{209}Bi isotopes, which were in-line added to all samples, standards, and blanks at a concentration level of 10 µg/L; responses from the three isotopes were interpolated to yield a better correction. Detection limits for the elements determined were in the range 1–10 ng/L, calculated as 3 times the background standard deviation.

2.6. Analysis of Certified Samples

To evaluate the performance and recovery of the proposed sample treatments, three certified standard materials were analyzed. BCR 668 (Mussel tissue) and BCR 670 (Duckweed) from IRMM were analyzed using the same ashing procedure used for the grapes and musts, while SRM 2586 (trace elements in soil containing lead from paint) from the National Institute of Standards and Technology (NIST) was analyzed according to the same treatment described for the soil samples. The results, detailed in Tables 1–3, showed good agreement between the certified and observed concentration values, as already reported in the literature [10].

Table 1. Analysis of BCR 668 certified biological material (mussel tissue).

Element	Certified Values (μg/Kg)	Uncertainty	Found (μg/Kg)	s.d. *
La	80	6	76.12	1.87
Ce	89	7	106.41	4.30
Pr	12.3	1.1	13.21	0.36
Nd	54	4	52.54	1.70
Sm	11.2	0.8	11.02	0.89
Eu	2.79	0.16	3.14	0.13
Gd	13	0.6	12.93	1.15
Tb	1.62	0.12	1.66	0.18
Dy	8.9	0.6	8.39	0.60
Ho	1.8 [1]	0.60 [1]	1.62	0.20
Er	4.5	0.5	4.27	0.31
Tm	0.48	0.08	0.60	0.02
Yb	2.8 [1]	0.5 [1]	3.05	0.47
Lu	0.389	0.024	0.59	0.04

[1] Indicative value. * s.d.: standard deviation

Table 2. Analysis of BCR 670 certified biological material (duckweed).

Element	Certified Values (μg/Kg)	Uncertainty	Found (μg/Kg)	s.d.
La	487	20	474.1	4.3
Ce	990	40	959	134
Pr	121	6	115.2	11.1
Nd	473	15	483.1	14.5
Sm	94	7	96.10	0.53
Eu	23.2	1.5	76.12	0.32
Gd	98	8	105.61	6.37
Tb	14	1.1	13.24	2.12
Dy	79	7	80.22	4.91
Ho	15.8	1.8	16.51	2.98
Er	44	2.8	46.11	1.62
Tm	5.7	0.7	5.23	1.13
Yb	40	4	43.32	6.14
Lu	6.3	0.5	7.11	0.93

Table 3. Analysis of SRM 2586 certified soil material (trace elements in soil containing lead from paint).

Element	Certified Values (mg/Kg)	Uncertainty	Found (mg/Kg)	s.d.
La	29.7	4.8	27.11	0.96
Ce	58	8	56.82	1.64
Pr	7.3 [1]		7.51	0.21
Nd	26.4	2.9	26.14	0.81
Sm	6.1 [1]		5.22	0.189
Eu	1.5 [1]		0.98	0.04
Gd	5.8 [1]		4.82	0.18
Tb	0.9 [1]		0.68	0.03
Dy	5.4 [1]		3.52	0.15
Ho	1.1 [1]		0.63	0.03
Er	3.30 [1]		1.86	0.03
Tm	0.5 [1]		0.23	0.02
Yb	2.64	0.51	1.31	0.04
Lu	[2]		0.15	0.02

[1] Indicative value; [2] Not determined.

2.7. Data Analysis

Multivariate data analysis was applied to compare the distribution of REEs in all samples, verifying the effect played by the oenological practices on the REE distribution. Data analysis and graphical representations were performed with XLSTAT v. 2012.2.02 (Addinsoft, Paris, France), a Microsoft Excel add-in software package.

3. Results and Discussion

As expected, the REE distributions in all samples followed the Oddo–Harkins rule, according to which even-numbered nuclides are more abundant than their odd-numbered counterparts; the distributions therefore show the typical saw tooth profile with decreasing abundances. The distribution shown in Figure 1a corresponds to the REEs detected in *Primitivo* vineyard soil. Promethium (Pm) has not been determined, given its extremely low concentration, but it is reported between neodymium and samarium in the graph, making it clear that the Oddo–Harkins rule is maintained.

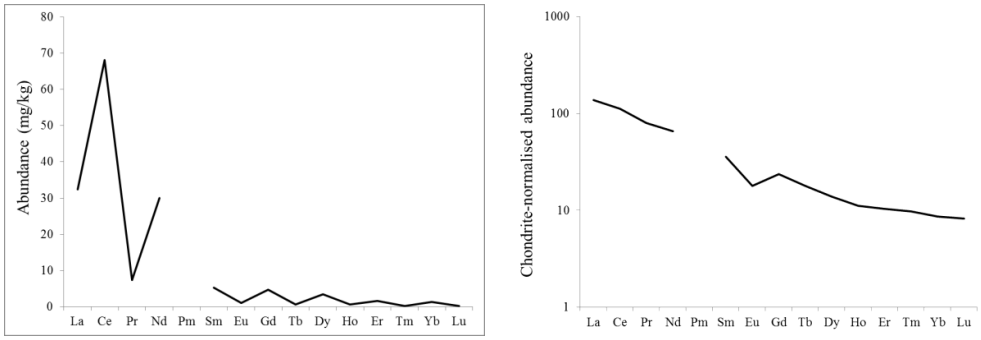


Figure 1. Distribution of rare earth elements (REEs) in *Primitivo* vineyard soil: (**a**) raw values; (**b**) chondrite-normalized values.

In geochemistry, it is common to compare data after normalization to typical patterns, such as those of *chondrite*, a meteoritic rock considered to be the best representative of the average concentrations of non-volatile elements in the solar system. Concentrations of single REEs in the samples are calculated according to Equation (1):

$$[\text{REE}]_{\text{chondrite-normalized}} = [\text{REE}]_{\text{sample}} / [\text{REE}]_{\text{chondrite}}. \quad (1)$$

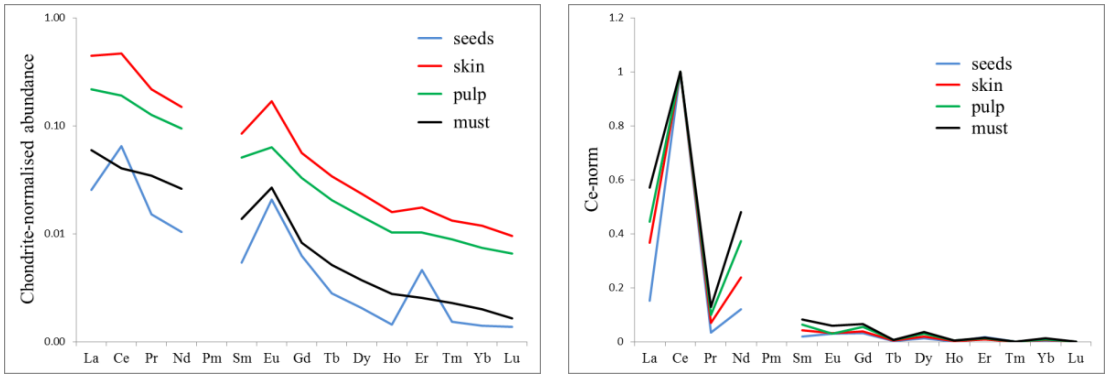
Normalized data are displayed in logarithmic scale (Figure 1b). In this study, we used the values of a CI chondrite [27]. In addition, we employed an alternative normalization method by dividing REE concentrations, for every sample of the production chain, by the corresponding concentration of cerium (Ce)—the most abundant REE—according to Equation (2):

$$[\text{REE}]_{\text{Ce-normalized}} = [\text{REE}]_{\text{sample}} / [\text{Ce}]_{\text{sample}}. \quad (2)$$

We believe that this internal normalization to Ce is more suitable for comparing samples whose concentrations are of different orders of magnitude. The REE concentration in soil, in fact, is approximately three orders of magnitude higher than in must and even higher than in wine.

3.1. Distribution of REEs in Different Parts of the Grapes

The concentrations of REEs were determined separately in the pulp, skin, and seeds of the grapes, to compare their distribution. REE concentrations increased in the order seeds/pulp/skin (Figure 2). As expected, the distribution of REEs in must is very similar to pulp.



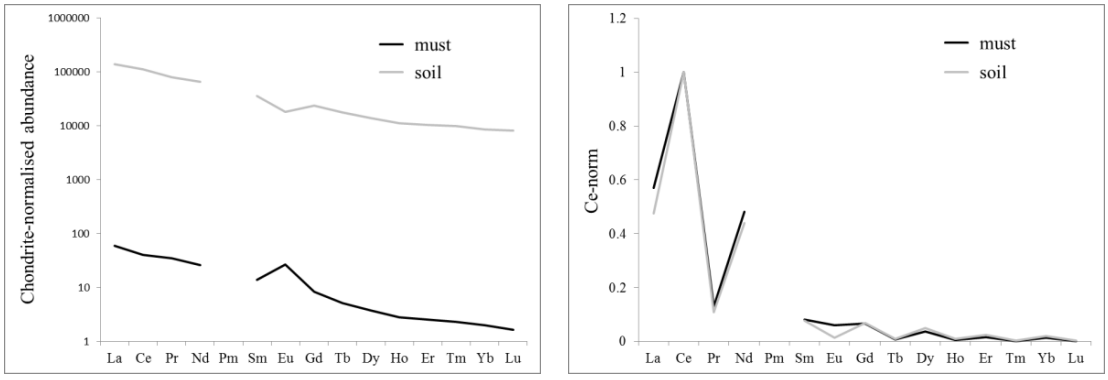
(**a**) (**b**)

Figure 2. Distribution of REEs in the different parts of *Primitivo* grapes and in must: (**a**) chondrite-normalized values; (**b**) Ce-normalized values.

Unlike the other REEs, Europium (Eu) concentrations seemed to vary in the samples at every production step. Rather than to the geochemical behaviour of this element, the anomaly can be explained in terms spectral interference in ICP-MS analysis. In fact, $^{135}Ba^{16}O^{+}$ and $^{137}Ba^{16}O^{+}$ polyatomic ions can cause positive interference on ^{151}Eu and ^{153}Eu isotopes, respectively [28]; this interference cannot be solved with the instrumental resolution obtainable by the quadrupole mass analyzer used in this study. Barium, as a natural substitute of calcium, can be actively absorbed by plants, resulting in unpredictable positive interference with Eu.

3.2. Comparison of Soil and Must

Previous works, based on the geochemical behaviour of REEs in the *Vitis vinifera*/soil system [29–31] indicated that there is no fractionation of REEs in the passage from soil to grapes and from grapes to must [24,25]. It was therefore interesting at this stage to check whether the distribution of REEs in soil forms a sort of fingerprint maintained in must. In the *Primitivo* chain taken into consideration in this study, it is apparent from Figure 3a that the original fingerprint of soil is well maintained in the must. The resemblance of the REE distributions in the soil and must is even more apparent when shown as a Ce-normalized concentration (Figure 3b). The anomalous behaviour of europium can be explained as before: Ba^{2+} is relatively more abundant in must than in soil due to the fact that it is actively absorbed by the vine as a substitute of Ca^{2+}; therefore, its positive interference on Eu isotopes is also higher in must than in soil.



(**a**) (**b**)

Figure 3. REE distributions in must and in soil: (**a**) chondrite-normalized values; (**b**) Ce-normalized values.

3.3. Effect of the Vinification Processes

The processes used for white winemaking cause fractionation of REE distribution, as obtained in the study on the traceability of a *Moscato* production chain [25]; this phenomenon is attributed to the release of REE ions from bentonites, which are clay materials widely used in oenology for wine clarification. Since bentonites are rarely used for red winemaking, the present study aims to determine whether REEs can act as suitable tracers all along the whole production chain of a red wine. In this case, two samples of wine were taken from the chain, one after alcoholic fermentation and another after malolactic fermentation. Both steps involve the addition of other substances: *Saccharomyces cerevisiae* yeasts were added to promote alcoholic fermentation, while *Oenococcus oeni* bacteria were added to promote malolactic fermentation. The possible contact of must/wine with surfaces, which can potentially release ions, should also be taken into consideration at this stage. The must was kept in stainless steel tanks until completion of alcoholic fermentation, and then the product was poured into barriques before malolactic fermentation. Figure 4 reports the REE distributions in the P12SV wine sample, withdrawn after alcoholic fermentation, and in the P12FIN sample, withdrawn after malolactic fermentation; the distributions in soil and must are included for comparison. Apart from the usual Eu anomaly explained by Ba interference, it seems evident that a certain degree of fractionation occurs after the alcoholic fermentation stage, making it hard to identify the original fingerprint given by the soil. The P12SV sample seems to be mainly depleted in Ce and Yb. Causes for this fractionation are attributable to the presence of inorganic additives in the biological products used for fermentation, including yeast nutrients, and in the release of metal ions from the surface of metallic tanks. The passage from P12SV to P12FIN seems less perceptible from a traceability point of view, possibly because storage in wooden barriques caused a negligible metal ions release.

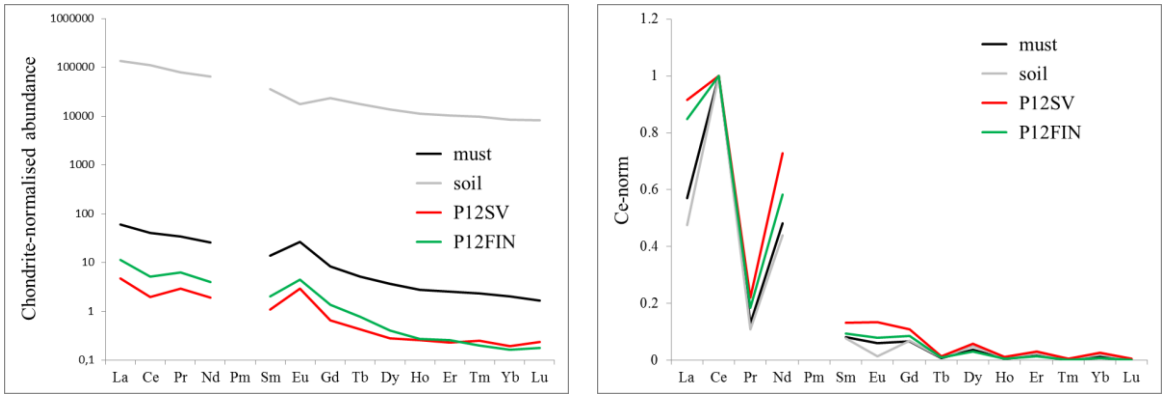


Figure 4. REE distributions in must, soil, and wines after fermentation processes: (**a**) chondrite-normalized values; (**b**) Ce-normalized values.

3.4. Effect of Vintage

In order to verify the effect of vintage, samples of *Primitivo* wines from different harvests were analyzed and compared. Samples labeled P08, P09, P10, and P11 come from the 2008, 2009, 2010, and 2011 harvests, respectively. Since *Primitivo* wine is aged one year in barriques before being bottled, it is obvious that Samples P08–P11 underwent a longer ageing process outside the cask than sample P12FIN, but we reputed that ageing in the bottle could at most cause only a phenomenon of precipitation of tartrates, which cannot induce fractionation in the distribution of REEs. When compared with each other and with the sample from the 2012 harvest (Figure 5), they show a high similarity. The P11 sample is rather anomalous, as far as La and Er concentrations are concerned.

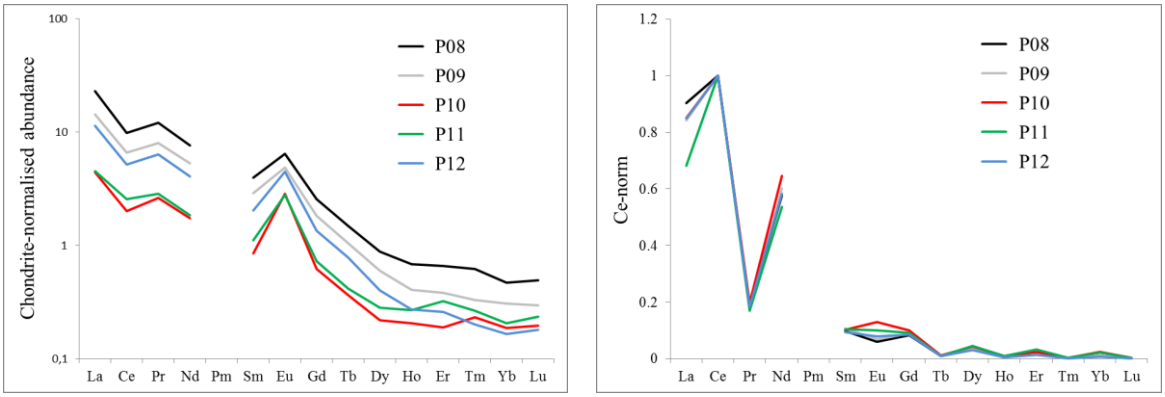


Figure 5. REE distributions in wines from different vintages: (**a**) chondrite-normalized values; (**b**) Ce-normalized values.

3.5. Multivariate Analysis

Multivariate chemometric analysis was performed on all data to verify the similarity between the various REE distributions. Agglomerative hierarchical clustering (AHC), using Euclidean distance as the similarity parameter and Ward's method as the agglomeration method, was selected for pattern recognition analysis. AHC was applied to Ce-normalized data after centering and scaling them; Ce and Eu were discarded as variables, the former being obviously equal to 1 in all samples and the latter being, in contrast, too variable due to barium interference. The result is displayed as a dendrogram in Figure 6: the similarity between *untreated* samples—the soil, must, and the various parts of grapes—is immediately apparent, while the *treated* samples, i.e., the wine samples, are grouped together in another cluster. The only exception is P11, which is grouped with the untreated samples; the reason for this behavior is due to its anomalous La and Er content, mentioned above.

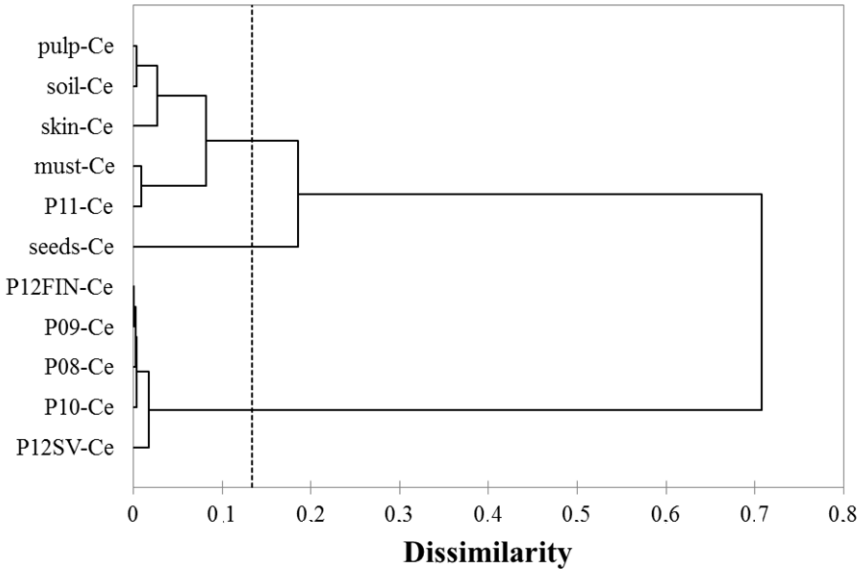


Figure 6. Dendrogram obtained with agglomerative hierarchical clustering (AHC) on Ce-normalized values.

4. Conclusions

REE distributions in samples taken at each step of a red wine making process showed that the original distribution in soil remains unaltered in every intermediate product up to and including the

grape must. Variation of REE composition occurs thereafter as a result of additives used to promote fermentation or because of the interaction with the surfaces of storage tanks.

In order to fully evaluate the validity of a link between the original REE fingerprint of soil and a finished wine, additional study on the variations induced by technical interventions in the winemaking process will be useful. Moreover, a further study comparing different production chains of wines obtained from grapes grown on the same territory will be advisable, and in particular further investigations would be required by carrying out a more extended sampling plan, representative of the whole production area of the *Primitivo di Manduria* PDO wine.

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Conflicts of Interest: The authors declare no conflict of interest.

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