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Distribution of YLOID in soil-grapevine system (*Vitis vinifera* L.) as tool for geographical characterization of agro-food products. A two years case study on different grafting combinations

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ABSTRACT

The knowledge of a chemistry relationship between the soil and the agricultural products is an important tool for the quality assessment of food. We studied YLOID (Y, La and lanthanoids), recognized as very useful tracers due their coherent and predictable behavior, to trace and evaluate their distribution from soil to the grape in *Vitis vinifera* L. Because much of the world's viticulture is based on grafting, and rootstocks have proved affect vine growth, yield, fruit and wine quality, we carried out experimental trials to analyse the YLOID distribution of two different red cultivars, grafted onto six different rootstocks, on the same soil. The YLOID amounts, the relationship Heavy *vs* Light YLOID and the pattern of YLOID were calculated. The results showed that the different grafting combinations were not able to induce significant differences in YLOID uptake from the soil maintaining the same fingerprint (with the exception of Eu).

1. Introduction

The rising importance given from legislators and consumers to provenance of agrifood products purchased and/or eaten, in last years motivated several researches to identification of the geographical origin of agrifood products. In this context, the knowledge of one or more chemistry relationships between the soil and the agricultural products is an important tool for the quality assessment of food (Baroni et al., 2015; Drivelos & Georgiou, 2012; Durante et al., 2016; Gonzalvez, Armenta, & de la Guardia, 2009; Luykx & van Ruth, 2008; Marchionni et al., 2016; Reid, O'Donnell, & Downey, 2006; Zhao et al., 2013). Among the different techniques and compounds, or class of compounds, used to evidence these relationships, undoubtedly ICP-MS and trace elements have been exploited (Durante et al., 2015; Luykx & van Ruth, 2008; Reid et al., 2006). The significant role played by micro and trace elements in the growth and development of the plants is widely recognized from several studies (Kabata-Pendias, 2001, 2004). However, for any trace elements (i.e., YLOID) there is a lack of in-depth knowledge about their distribution and biological role in the natural system (Cao, Chen, Gu, & Wang, 2000; Tyler, 2004). On the Earth surface, YLOID are partitioned or separated, enriched or depleted, each other during geological processes because of differences in their chemical properties, and geochemists use the relative concentrations of YLOID to infer the chemical conditions under which a rock was formed. YLOID concentrations in soils vary according to parent material properties, history and weathering state of the soil itself and, for this reason, YLOID have recognized as very useful tracers (Laveuf & Cornu, 2009). Because of YLOID behavior, always occurring bunched together, their local differentiation, through mobilization and redistribution processes, could result in fractionation of any of these elements able to highlight and to trace the pedogenetic transformations, the latter being extremely long-term processes (Laveuf & Cornu, 2009). Often, relative enrichments of YLOID are difficult to appreciate at once as their abundance in soils is scattered. For this reason, in order to evaluate variation in YLOID abundance, they are normalized, i.e. the relative distribution of elements is compared to a geochemical or other type of reference, and then ratios are plotted on a logarithmic scale against the atomic number (Henderson, 1984; Laveuf & Cornu, 2009).

This plot, called "YLOID normalized pattern", evidences, promptly, enrichment or depletion of a group or of an individual YLOID relative to the others. These relative differences are called respectively fractionations or "anomalies", whose intensities are further expressed by ratios (Laveuf & Cornu, 2009).

Lu/La or Yb/La ratios, commonly, quantify the fractionation between HYLOID (Heavy YLOID from Tb to Lu plus Y) and LYLOID

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(Light YLOID from La to Gd). Because of the Yb and Lu contents, frequently too small to produce accurate measurements, the ∑HYLOID/∑LYLOID ratio is alternatively calculated. In all cases, the normalized concentrations are always used (Laveuf & Cornu, 2009). These tools, typical of geochemists, have been successfully applied to elucidate the mechanisms of YLOID intake by plants (Brioschi et al., 2013; Cao et al., 2000; Tyler, 2004).

Recent studies of YLOID in plant-soil systems, have often focused on several main aspect of metabolic mechanism (Johnson & Barton, 2007; Ouyang, Wang, Zhao, Yuan, & Wang, 2003), as well as of their distribution among plant organs of whole individual plant, and between an individual plant and the soil in which the plant grew (Bibak, Stürup, Knudsen, & Gundersen, 1999; Brioschi et al., 2013; Wahid et al., 2000; Xu, Zhu, Wang, & Witkamp, 2002).

According several authors, there is no fractionation of these elements during roots adsorption of soil solution, but they also reported a fractionation of YLOID during transfer from roots to leaves (Brioschi et al., 2013; FengFu, Tasuku, Sadayo, & Masaya, 2001; Li, Shan, Zhang, & Zhang, 1998; Liang et al., 2008; Wang & Sun, 1997). Therefore, the analysis of YLOID distributions among different media, from the inorganic soil interface to the coexisting fluid phase, and hence during their migration from soil to plant and its fruits, seem represent a promising tool to investigate processes in the plant-soil system. Only relatively few studies on the transport of YLOID from soil towards the aerial parts of *V. vinifera* were published (Aceto et al., 2013; Bertoldi, Larcher, Nicolini, Bertamini, & Concheri, 2009; Bertoldi et al., 2011; Ortiz-Villajos et al., 2012; Pepi, Sansone, Chicca, Marrocchino, & Vaccaro, 2016). Investigating lanthanoids and yttrium distributions in *V. vinifera*, most of data were treated according to a "classical" approach of a multivariate data analysis (Aceto et al., 2013; Bertoldi et al., 2011). In a relatively recent paper (Censi, Saiano, Pisciotta, & Tuzzolino, 2014), it has been demonstrated that YLOID patterns of aerial parts of three different rootstocks grown off-soil, were a suitable geochemical proxy, even if biological substrata (roots, vine shoots, leaves, etc.) are involved, of three soils of different nature. In order to evaluate the potential of this approach, highlighting the geochemical behavior of YLOID, this paper illustrates the distribution and relationships of YLOID, as geographical proxy, in soil-grapevine system. Furthermore, because most of the world's viticulture is based on grafting, we carried out the first, at our knowledge, systematic experimental trial on two years with two cultivars on six different rootstocks, to evidence if the different combinations (cultivar/rootstock) used, on the same soil, can influence the uptake and distribution of YLOID from soil to grape. To study the transfer of YLOID from soil to grape, and as a contribution toward deeper understanding the phenomena on which the geographical traceability of the soil-grapes line are based, we have chosen to determine the relative abundances of YLOID elements in soil both as bioavailable DPTA (diethylenetriaminopentaacetic acid) extract and as pseudo-total fraction.

2. Materials and methods

2.1. Chemicals

Concentrated nitric acid (65%) and hydrogen peroxide (30%) of ultrapure grade was purchased from Baker (Milano, Italy), DTPA (purity > 99%) was from Sigma-Aldrich (Milano, Italy). Ultrapure water 18.2 MΩ cm, produced with an EASYpureII (Thermo, Italy), was used for all standard solutions and sample preparations. Y, lanthanoids, Rh and Re standard solutions (1000 ± 5 μg mL^{-1}) were purchased from BDH, Merck and CPI International (Milan, Italy). Polypropylene and polystyrene vials, used respectively for sample storage and analysis, were kept in 1% nitric acid and then rinsed with ultrapure water upon request.

2.2. Plant material and sampling

The Piana Margio experimental vineyard, located at the "Regaleali" region (latitude 37°41′50.06″ N, longitude 13°50′51.05″ E and 428 m a.s.l., in Sicily, Italy), is constituted by a soil formed on a clayey sandy sediments. It is influenced by a Mediterranean climate, characterised by hot and dry summer and rainfall concentrated during the winter and spring period. Climatic data of the 2 years were collected from Informative Agrometeorological System of Sicily (www.sias.regione.sicilia.it) than only the usefully data were used and reported. The vines were spaced 2.4 m × 0.9 m on a clay soil (42% of clay and an amount of skeleton generally low) and trained onto 5-wires (cordon wire and two sets of movable wires) with vertical shoot positioned. Rows were E-W orientated and vines were pruned to two-buds spurs with a spur spacing of approximately 15–20 cm in a single cordon. Micro-irrigation system with low-volume were used to irrigate vines. Irrigation was applied from pea size to véraison with 500 m^3 ha^{-1}, according to deficit irrigation strategy (Di Lorenzo et al., 2005). The vineyard was managed following the local production integrated practices for commerce of wine. Two red cultivars, Nero d'Avola and Cabernet Sauvignon (ten years old) grafted onto six different rootstocks were sampled at technological ripeness. The six rootstocks were "SO 4", "420 A" (*V. berlandieri* × *V. riparia*), "1103 P.", "110 R", "140 Ru." (*V. berlandieri* × *V. rupestris*) and "41 B" (Chasselas × *V. berlandieri*). Each grafting combination was represented by six plots with five rows with a total of 150 vines per plot. One representative kilogram of grapes (three times replicated) was collected at technological ripeness: first sampling on September 2012, second one on September 2013. As well, soil samples (about 2 kg) in the vineyard plot corresponding to grape sampling were collected. To reduce the effect of any surface contamination (pollution and fertilizer) soil samples were from a depth of 10–40 cm at a distance of about 30 cm around each plant in the vineyard investigates.

2.3. Sample preparation

The grape samples were washed with ultrapure water and the berries separated from bunches. The whole samples were weighed, homogenized, dried in oven at 105 °C and newly homogenized. To berries aliquots of ~2.500 g (dried weight), in open vessels, in two steps, 2.5 ml of HNO_3 were added, to avoid the tumultuous formation of gas and leaks of sample. After about 1 h, the vessels were closed and digested (S.I. Table 1), adding 2.5 ml of H_2O_2, in a microwave system (Mars 5 Xpress, CEM, Milano, Italy). After digestion, the extracts, quantitatively transferred to a graduated polypropylene test tube, were diluted with ultrapure water to 15.0 mL. Each analytical sequence included a procedural blank (ultrapure water digested as the other samples).

The soil samples were dried in oven at 105 °C, gently crushed, sieved (∅ 0.5 mm) and homogenized. Aliquots of 0.500 g (DW) were digested using HNO_3 and H_2O_2 in a microwave system (pseudo-total fraction S.I. Table 1) as in the USEPA 200.7 method. After digestion, the extracts were quantitatively transferred to a graduated polypropylene test tube, and diluted with ultrapure water to 100 mL. Each analytical sequence included a procedural blank (ultrapure water digested as the other samples).

The determination of YLOID concentration in the bioavailable soil fraction was made by soil extraction with a DTPA solution (Rao, Sahuquillo, & Lopez-Sanchez, 2010).

Aliquots of 10.0 g for each soil samples were weighed into a 50.0 mL centrifuge tube and 20.0 mL of a DTPA 0.005 M (at pH 5.0 with NaOH) solution was added. The obtained mixtures were shaken in an end-over-end shaker at 300 rpm for 24 h at room temperature, successively centrifuged for 45 min at 5000 rpm and supernatant filtered through a Whatman N° 41 filter paper.

Each analytical sequence included a procedural blank (ultrapure water treated as the other samples). Prior to ICP-MS measurement, the solution was diluted 50 times with 1% (w/w) HNO_3 solution.

2.4. Certified reference material (CRM)

To evaluate the performance and recovery of the overall grapes samples treatments, the INCT-OBTL-5 Oriental Basma Tobacco Leaves certified standard material (tobacco leaves with certified and known YLOID composition) was analysed (Samczynski et al., 2012). The trueness of method was evaluated comparing obtained results by acid digestion, as above reported for the grape samples, with certified values. The recovery percent and its standard deviation were also estimated for the elements listed as information values in analysis certificate (data not shown). Recovery values of the certified elements (La, Ce, Nd, Sm, Eu, Tb, Er, Yb), ranged between 96% and 103%, while for the elements of the series listed as informative values, from 97 to 111%. Only Lu showed a low but still acceptable recovery of 85%.

The CRM 2711a Montana Soil II (NIST) was made up of moderately contaminated soil with certified and known chemical composition also for YLOID total content. To verify the quality of pseudo-total YLOID content of our samples, the CRM was exclusively subjected to oxidant mixture, HNO_3:H_2O_2 as in the USEPA 200.7 method. Five independent aliquots of CRM were carefully weighed (0.250 g), treated with 6 mL of the HNO_3:H_2O_2 (2:1 v/v) mixture and subjected to microwave digestion (S.I. Table 1). Because no YLOID value, though indicative, was reported as pseudo-total, we have considered our YLOID results acceptable, considering that the recovery results obtained for selected metals (Co, Cu, Mn. Zn, V, Cr), ranging from 89 to 98% of reported values and that the relative standard deviation of the five replicates for the YLOID amounts were lower than 10%.

2.5. Mineral element analysis

An ICP-MS instrument (Agilent Technologies 7500ce Series Spectrometer) was used and all instrumental parameters were optimized for the analyses of all the investigated trace elements. Each solution was measured three times and ICP-MS analyses were carried out with a classical external calibration approach, from 2.5 to 10,000 pg mL^{-1} for each investigated element, using ^{103}Rh and ^{187}Re (1000 pg mL^{-1}) as internal standard to compensate for any signal instability. The isotopes used to quantification were as follows: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{158}Gd, ^{159}Tb ^{163}Dy, ^{89}Y, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu. Instrument and measurement parameters were: forward power, 1550 W; nebulizer gas flow, 1.00 L min^{-1}; auxiliary gas flow, 0.80 L min^{-1}; plasma gas flow, 15 L min^{-1}; three replicates for a total acquisition time of 180 s. Interferences were evaluated as follows: CeO^+/Ce^+ and Ce^{2+}/Ce^+ ratios <1%. In particular, for a better determination of ^{151}Eu, we have carefully tuned the mass spectrometer with a solution containing 1.0 μg mL^{-1} of Ba in HNO_3 following and optimising both ratio $^{135}Ba^{16}O^+/^{135}Ba^+$ and $^{134}Ba^{17}O^+/^{134}Ba^+$ the higher amount of which was below 0.5%. Successively we have determined, in our real samples solutions for ICP-MS measurements, the amount of barium to a better control on $^{135}Ba^{16}O^+/^{135}Ba^+$ and a more accurate determination of Eu. A stability test was performed before each analysis session by monitoring ^7Li, ^{59}Co, ^{89}Y, ^{140}Ce and ^{205}Tl masses and verifying a precision better than 2%. The instrumental precision was better than 2% for YLOID elements, while the overall uncertainty (involving both sample preparation and instrumental analysis), which calculation based on three replicates, was better than 5%.

2.6. Data analysis

The software packages, Microsoft Office EXCEL 2007 (Copyright© Microsoft 2008) and SYSTAT® v.12, were used for statistical analyses and to produce figures. Cultivar, rootstock and year were considered as main factors, and a three-way analysis of variance (ANOVA) was performed ($\alpha = 0.1$, indicated the presence of a statistically significant difference, and $\alpha = 0.05$ was considered highly significant). Than a two-way analysis of variance (ANOVA) for each year was performed considering cultivar and rootstock as main factors. For significant main effect and their interactions, mean statistically differences were determined using the Tukey's HSD test ($\alpha = 0.05$). All the tables of statistical treatment were in Supplementary material (S.I. Tables 3–6).

The sequence of the distribution coefficient values (K_d), was calculated as $[YLOID]_1/[YLOID]_2$, between YLOID concentrations measured in two interfaced substances (for example, 1 = grape and 2 = P. Margio soil).

3. Results and discussions

3.1. Soil

The pedogenetic parameters and the mineralogy of the YLOID carrier phases in the soil and in the bedrock, essentially, determine the YLOID concentrations in soil. However, rather than the total YLOID amount of the bedrock, the soil mineral particles present in the rhizosphere area are the main source of YLOID for plants. Consequently, the origin of the YLOID taken up by plant itself, basically, derive from the soil water pool adsorbed on YLOID-bearing soil particles. Therefore, YLOID content of soil water is controlled mainly by solubility and stability of dissolved organic and inorganic YLOID complexes (Brioschi et al., 2013).

For these reasons, as reported in the introduction, to study the transfer of YLOID from soil to grape, we have chosen to determine the YLOID amounts as bioavailable and pseudo-total fractions and not their total content (S.I. Table 2). The first, to simulate as much as possible the capability of the vine roots to extract YLOID from the soil, the second to evaluate the highest YLOID contents in all phases released by soil avoiding the ones locked in silicates.

Moreover, it is important to remember and underline that the distributions of concentrations, rather than single absolute concentration values, must be taken into account (Henderson, 1984; Laveuf & Cornu, 2009). In geochemistry studies, YLOID concentrations are usually normalized with respect to different geochemical references. In our case we chose Upper Continental Crust (UCC) as reference, which being related with the most accessible part of our planet, has long been the standard of geochemical investigations (Wedepohl, 1995).

As reported in the introduction, to reduce any problems from the relatively low concentrations of Yb and Lu, we have considered the $(\sum HYLOID/\sum LYLOID)_{UCC}$ ratio and not the $(Yb/La)_{UCC}$ or $(Lu/La)_{UCC}$ ones. The Fig. 1 shows $\sum[HYLOID_{UCC}]$ *vs* $\sum[LYLOID_{UCC}]$ relation for all soil samples considering both methods. The linearity ($R^2 = 0.979$ and 0.996) enhance the homogeneity of YLOID distribution both in terms of pseudo-total and bioavailability content. The different amounts are obviously related to the different absolute values of YLOID determined with the two methods while the slopes are different because of the higher DTPA complexation constants of HYLOID than LYLOID ones (Byrne & Li, 1995). However, the hints obtained comparing the $\sum[HYLOID_{UCC}]$ *vs* $\sum[LYLOID_{UCC}]$ data, do not collect all the information available in the distributions and reciprocal ratios of all fifteen elements studied. The normalized patterns (Fig. 2) highlight these aspects and, as it is known, represent a soil sample fingerprint, able to estimate

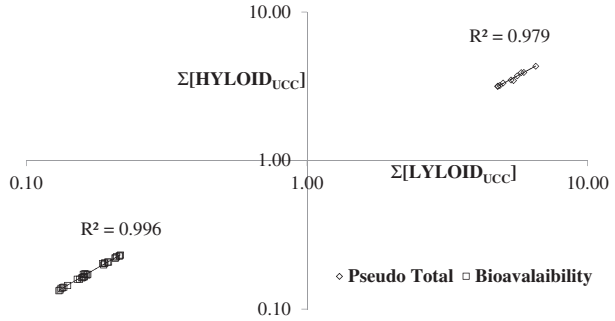

Fig. 1. $\sum$[HYLOID$_{UCC}$] *vs* $\sum$[LYLOID$_{UCC}$] relations for all Piana Margio soil samples considering both treatments (pseudo-total and bioavailability). The scales are logarithmic.

and evidence similarities or differences between different soils (as example, in S.I. are reported in Figs. 1–4, the relations $\sum$[HYLOID$_{UCC}$] *vs* $\sum$[LYLOID$_{UCC}$] and the patterns of Piana Margio soil in comparison to others Sicilian ones from literature Censi et al., 2014). The standard deviations values found among the soil samples reflect the good spatial homogeneity of the studied area, confirming the hypothesis of the "similar soil", in the YLOID distribution, experienced by the different roots of the different grapevines (grafting combination) in vineyard. The pseudo-total soil fractions show a flat YLOID distribution along the series with a progressive slight decrease from Gd until Lu, without any significant anomaly. Instead, YLOID pattern, in bioavailable soil fractions, is characterised by a slight increase from La to Gd with a small positive anomaly of Ce. From Gd to Lu the behavior is the same of pseudo-total fractions.

The differences between the two patterns are linked, for the total amounts, to the different oxidant and acid strength of the pseudo-total *vs* DTPA treatment while, for the different behavior of the LYLOID, and in particular to Ce anomaly, to the DTPA-YLOID complexation constant values.

3.2. Grape

The concentration of YLOID, from grape analysis for each grafting combinations (Table 1, reported as average values with standard deviations, in nmol kg^{-1} for the two years of sampling), were very low compared with soil data, but as expected and comparable to other published data, for what concerns all elements considered (Bertoldi et al., 2009, 2011). The behavior of YLOID in grape is consistent with the few data about trace element distributions in these materials, being YLOID less concentrated in grape compared to other aerial parts of grapevines (Bertoldi et al., 2009; Censi et al., 2014; Ortiz-Villajos et al., 2012). Considered that

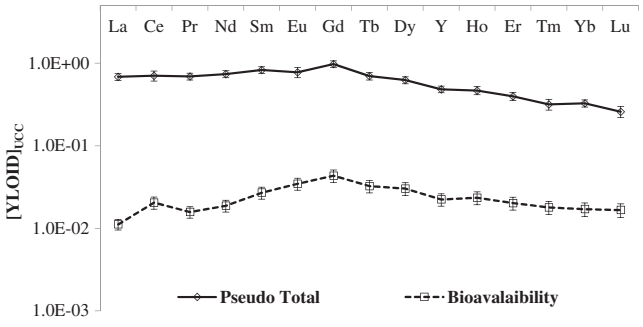

Fig. 2. UCC-normalised YLOID patterns of Piana Margio soils. Averaged values with standard deviation for both pseudo total and bioavailability treatments.

the "geochemical" treatment used with soil data is scarcely applied in agricultural or food fields, we initially have carried out a classic statistical approach. An ANOVA statistical analysis evidenced a significant effect of all main factors and their interactions on all the YLOID presence on the grapes but, according to the higher F-ratio, the principal influences was due to the year. Considering only the 2012 vintage, no significant differences (main factors scion, rootstock and their interaction) were recorded on grape YLOID content but, on 2013, ANOVA shows a significant effect of all factors. Reasonably, results are influenced, according to the season, by climatological conditions and different vine physiology (the different vigour expressions according to the grafting combinations) essentially due to the different rainfall of the two experimental periods. Total rainfall recorded in 2012 was 585 mm while 714 mm in 2013. Considering the two vegetative seasons (from March to September), the 2012 was characterised by 170 mm and the 2013 by 314 mm of rain, respectively. These differences of water supply, especially during summer, can explain the highest vine vigour in the 2013 (data not reported) and, finally, the differences in terms of YLOID content in the grapes between the two years. In fact, with a highest rainfall increase the amount of circulating water, allowing that a higher amount of YLOID dissolved could be available for the roots and for the grape.

Therefore, this approach is strongly influenced by absolute YLOID amount, and the information present in the distribution and ratios of all YLOID are evidently lost. For these reasons, we suggest a different approach, analogously to soil treatment a "geochemical" point of view, in the analysis of the YLOID data in which the potentialities of the ratio and the YLOID patterns can be exploited. However, as for soil samples, we have evaluated the $\sum$[HYLOID$_{UCC}$] *vs* $\sum$[LYLOID$_{UCC}$] and the UCC normalized pattern for the grape samples for each grafting combinations and for the two years of sampling.

The Fig. 3 shows $\sum$[HYLOID$_{UCC}$] *vs* $\sum$[LYLOID$_{UCC}$] relation for all grape samples. The result obtained is not so trivial: we found a high R^2 value, 0.934, independently by any grafting combination or year of sampling considered. Apart from any peculiar agronomic features, linked to the differences features of every rootstock (for example, vigour), all plant grafting showed the same correlation. More impressive appear the YLOID patterns: both every one of each grafting combination and those collected for cultivar (all patterns for each grafting combination are reported in S.I. Fig. 5–8) but, above all, the average concentration values of all grafting combinations, shown in Fig. 4. In fact, the average of all samples of the 2012 (separated for the two grafting combinations) are similar. Within the standard deviation, the differences between the data are negligible. For the analogous samples of the 2013, the patterns show differences, essentially, for the total concentration but not for the distribution. These strong similarities of all YLOID distributions without any significant fractionation with the exception, for all, of Eu, confirm the identical behavior of every grafting combinations in the uptake of YLOID. The strong Eu positive anomaly is enough common in plant YLOID uptake, suggesting that this element is preferentially mobilised from soil to grape, because of its great similarity with respect to Ca and relating to a possible involvement in biological processes (Brioschi et al., 2013; Liang et al., 2008; Yang & Sachs, 1989; Zeng et al., 2003). However, this result cannot give clear justifications whether the mechanism could be related to the Ca–Eu substitution during metabolic processes and its transportation, or if it could result from an enhanced Eu mobility induced by Eu^{3+} reduction to Eu^{2+}. In fact, under favourable Eu/Ca ratios in substrata (Zeng et al., 2003), it seem reasonable that a Eu–Ca substitution can be induced during physiological processes, as well as positive Eu anomalies also agree with the greater stability of organic-Eu complexes (e.g. proteins) with respect to Ca complexes (Kruk, Burda, Jemioła-Rzemińska, & Strzałka, 2003;

Table 1
Average amounts in nanomoles kg^{-1} and standard deviations of YLOID in Piana Margio grape samples (2012–2013).

	2012																							
	Cabernet Sauvignon												Nero D'Avola											
	110 R		1103 P		140 Ru		41 B		420 A		SO4		110 R		1103 P		140 Ru		41 B		420 A		SO4	
	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.
La	21.4	3.9	19.4	5.7	28.4	2.8	25.6	7.3	23.1	7.9	24.5	3.9	21.1	4.2	22.6	8.8	19.6	5.5	28.7	5.4	18.5	1.2	23.4	8.1
Ce	43.3	8.9	38.1	11.3	55.9	4.8	51.2	14.4	43.5	13.8	47.9	6.7	42.5	8.0	43.7	19.3	37.6	8.2	58.3	11.8	36.2	4.4	47.0	17.9
Pr	5.0	1.0	4.6	1.2	6.7	0.6	5.8	1.5	4.8	1.1	5.6	0.8	5.1	1.2	5.1	2.3	4.4	1.2	7.1	1.4	4.2	0.6	5.4	2.2
Nd	19.1	3.8	21.5	7.0	25.8	2.0	22.8	5.7	18.5	3.3	21.8	3.0	20.2	4.0	19.6	8.8	17.0	4.4	26.5	5.1	16.2	2.4	20.4	8.0
Sm	3.9	0.8	3.8	1.2	5.2	0.6	4.8	1.1	3.7	0.4	4.5	0.6	4.4	0.8	4.2	1.8	3.8	0.9	5.2	1.1	3.6	0.5	4.4	1.7
Eu	1.7	0.2	2.0	0.3	1.9	0.3	1.9	0.3	2.2	0.3	2.1	0.1	2.2	0.4	2.3	0.5	2.0	0.4	2.0	0.2	2.2	0.3	2.3	0.2
Gd	3.6	0.7	3.7	1.1	5.0	0.5	4.4	0.9	3.7	0.6	4.3	0.5	4.2	0.9	4.0	1.9	3.5	0.9	4.8	0.9	3.2	0.6	4.2	1.7
Tb	0.47	0.10	0.47	0.13	0.67	0.12	0.57	0.12	0.45	0.08	0.54	0.09	0.60	0.20	0.51	0.22	0.46	0.13	0.63	0.09	0.41	0.06	0.54	0.20
Dy	2.3	0.4	2.3	0.6	3.1	0.4	2.7	0.5	2.2	0.4	2.6	0.3	2.6	0.6	2.4	1.1	2.3	0.7	2.9	0.5	1.9	0.4	2.6	1.0
Y	21.0	3.9	20.8	5.5	28.9	4.0	24.2	3.9	20.4	3.8	25.1	3.6	26.3	6.9	23.0	10.5	21.8	7.3	26.3	5.0	18.8	3.7	25.9	10.2
Ho	0.39	0.08	0.39	0.12	0.57	0.12	0.47	0.07	0.37	0.07	0.46	0.06	0.50	0.18	0.41	0.18	0.40	0.13	0.50	0.11	0.34	0.07	0.45	0.17
Er	1.10	0.19	1.16	0.30	1.49	0.27	1.25	0.18	1.11	0.10	1.31	0.15	1.37	0.43	1.16	0.50	1.11	0.32	1.35	0.26	0.98	0.18	1.28	0.42
Tm	0.14	0.04	0.15	0.04	0.23	0.10	0.17	0.02	0.14	0.03	0.17	0.02	0.21	0.10	0.16	0.06	0.17	0.06	0.17	0.02	0.13	0.02	0.17	0.05
Yb	0.92	0.13	0.97	0.23	1.30	0.19	1.12	0.12	1.00	0.10	1.14	0.04	1.18	0.25	1.11	0.35	1.01	0.23	1.08	0.16	0.94	0.10	1.11	0.31
Lu	0.12	0.04	0.16	0.09	0.22	0.07	0.21	0.01	0.18	0.04	0.16	0.02	0.20	0.07	0.19	0.04	0.15	0.02	0.16	0.02	0.15	0.01	0.14	0.10
	2013																							
	Cabernet Sauvignon												Nero D'Avola											
	110 R		1103 P		140 Ru		41 B		420 A		SO4		110 R		1103 P		140 Ru		41 B		420 A		SO4	
	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.	avg	±s.d.
La	64.1	5.8	102.8	6.5	84.5	3.2	81.9	6.3	119.3	5.1	40.6	2.6	88.1	3.2	78.3	5.7	42.1	3.3	58.0	3.4	118.2	3.2	56.8	5.1
Ce	121.5	11.9	178.9	12.3	150.7	5.9	154.1	13.2	203.9	8.8	71.4	4.6	171.2	4.1	170.7	10.3	72.3	4.2	105.8	8.5	236.0	2.4	109.2	8.9
Pr	11.6	2.0	13.5	1.5	12.2	0.9	15.2	1.3	14.3	0.8	5.1	0.6	18.3	0.9	15.8	1.6	6.4	0.9	10.7	1.1	24.7	0.5	11.2	1.8
Nd	42.1	5.52	45.6	8.8	42.9	2.2	56.5	5.3	52.6	2.8	17.8	2.4	68.1	2.1	57.5	6.7	24.6	3.1	39.6	3.3	91.6	1.6	41.3	5.7
Sm	8.2	1.2	7.0	1.5	7.7	0.7	11.4	1.2	9.9	0.5	3.3	0.5	13.5	0.5	11.3	0.9	5.3	0.8	7.8	0.8	18. 2	0.3	8.2	1.2
Eu	2.8	0.3	2.4	0.4	2.3	0.3	3.0	0.2	2.9	0.3	1.33	0.05	4.0	0.3	3.3	0.4	2.3	0.3	2.5	0.2	4.6	0.2	2.6	0.1
Gd	9.0	1.1	8.4	1.4	8.3	0.7	11.8	0.7	10.7	0.6	3.6	0.4	14.3	0.5	11.8	1.5	5.4	0.8	8.3	0.7	18.4	0.4	8.7	1.1
Tb	1.06	0.15	0.96	0.15	0.95	0.13	1.49	0.10	1.30	0.08	0.46	0.08	1.74	0.18	1.44	0.18	0.65	0.13	1.02	0.08	2.4	0.1	1.04	0.13
Dy	4.9	0.6	4.4	0.7	4.0	0.4	7.1	0.5	6.1	0.4	1.9	0.3	7.8	0.4	6.7	1.0	3.3	0.6	4.9	0.4	11.4	0.3	5.0	0.6
Y	44.0	4.6	40.4	6.5	32.3	4.5	60.4	3.1	55.0	2.8	17.2	2.4	70.6	4.6	62.0	7.3	29.2	5.3	43.5	3.0	101.0	1.7	44.1	4.2
Ho	0.82	0.10	0.75	0.14	0.64	0.12	1.19	0.06	1.03	0.06	0.33	0.06	1.29	0.15	1.14	0.15	0.51	0.13	0.79	0.11	2.0	0.1	0.80	0.15
Er	2.3	0.2	2.2	0.4	1.8	0.3	3.2	0.2	2.9	0.1	0.92	0.11	3.5	0.3	3.3	0.3	1.58	0.28	2.3	0.2	5.3	0.2	2.3	0.3
Tm	0.27	0.05	0.30	0.04	0.22	0.10	0.40	0.02	0.35	0.03	0.13	0.02	0.45	0.10	0.41	0.06	0.17	0.06	0.26	0.02	0.73	0.02	0.27	0.05
Yb	1.65	0.18	1.68	0.30	1.40	0.22	2.4	0.2	2.1	0.1	0.76	0.05	2.6	0.2	2.5	0.3	1.17	0.20	1.70	0.15	4.0	0.2	1.66	0.21
Lu	0.19	0.04	0.21	0.09	0.17	0.07	0.31	0.01	0.27	0.04	0.09	0.02	0.33	0.07	0.33	0.04	0.12	0.02	0.20	0.02	0.58	0.01	0.20	0.10

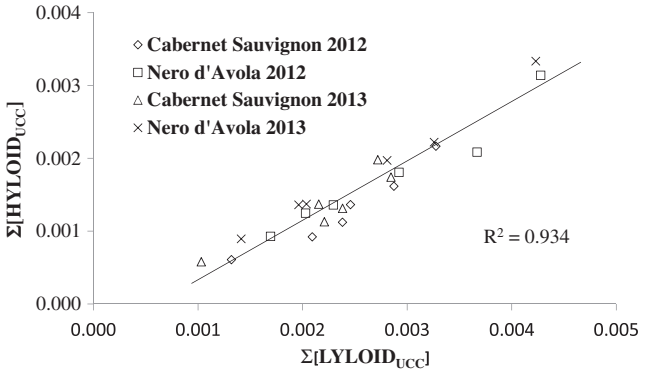

Fig. 3. $\sum$[HYLOID$_{UCC}$] *vs* $\sum$[LYLOID$_{UCC}$] relations for all Piana Margio grape samples separated for year and cultivar.

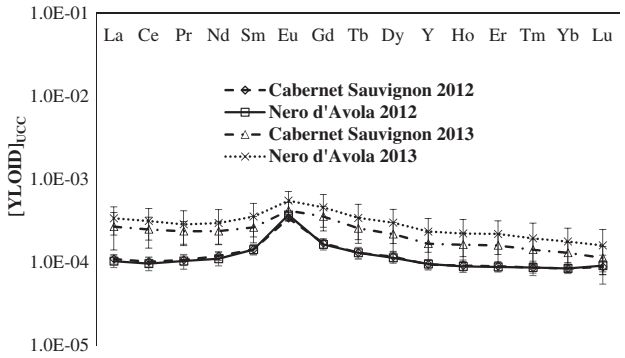

Fig. 4. UCC-normalised YLOID patterns of investigated grape samples separated for year and cultivar.

Sastri, Bünzli, Perumareddi, Rao, & Rayudu, 2003). Furthermore, positive Eu anomalies can result in enhanced Eu mobility and this process is related to the increasing nutrient transportation during metabolic processes in plants (Tian, Gao, Li, & Zeng, 2003), evidencing that, probably, a unique mechanism is responsible for transporting nutrients as well as trace elements and YLOID (Brioschi et al., 2013).

3.3. Plant/soil relationships

As above reported, the YLOID pattern, representing a sample fingerprint, can be used as a tool to compare similitude or differences of soil. The obtained results demonstrate that also the grapes of different grafting combinations, growth on the soil with similar YLOID pattern, have the similar YLOID one. Hence, the YLOID patterns could be a versatile tool to link soil and grape, for a geographical characterization. But, in order to recognise whether a relationship exists between YLOID contents in grape and amount determined on soil, it is useful to normalize the grape YLOID pattern in respect of the own soil. This normalization, a classic distribution coefficients succession $K_{d,}$ highlights the behavior of YLOID in the grapevine/soil system by features of the K_d values along the elements. The K_d coefficients were so calculated and graphically represented for both pseudo-total and labile fraction for the two samplings (Fig. 5). Unlike the absolute concentrations, the sequences of K_d values, as above the UCC normalized patterns, were always independent by sampling, cultivar and/or rootstock combination. These are all characterised by positive Eu anomaly. Flat features along the YLOID series, if calculated with respect both soil fractions, were present. Distribution coefficients pattern from

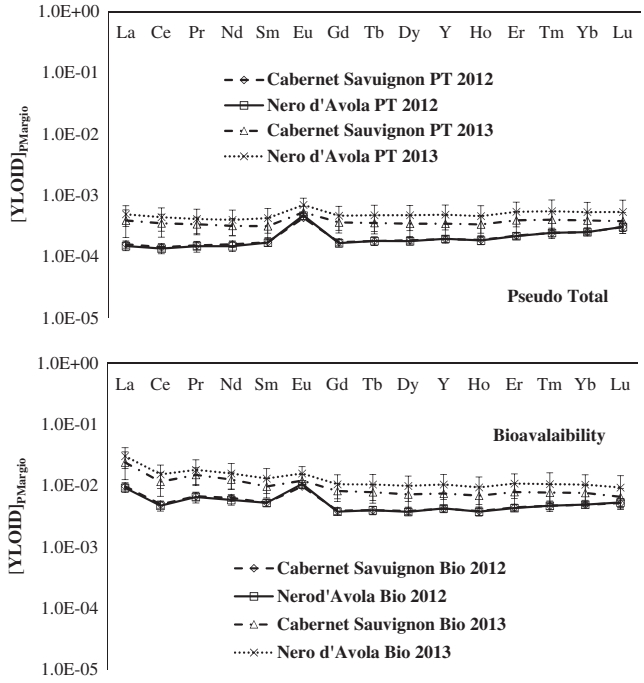

Fig. 5. Pseudo-total and Bioavailability Piana Margio-normalised YLOID patterns (Kd) of investigated grape samples separated for year and cultivar.

Gd to Lu were strongly similar while La, Pr, Nd and Sm are slightly lower than HYLOID in grape with respect to pseudo-total and slightly higher than HYLOYD with respect to bioavailable fraction. Considering the flat pattern UCC normalized of all grape samples, apart from the Eu, and the features of the two UCC normalized patterns of both pseudo-total and DTPA soil samples, we can derive easily all the characteristics above reported. In addition, the slight Ce-negative anomaly present in the grapevine with respect to DTPA soil fraction is in agreement with the distribution coefficient K_{Ce} where the denominator in the ratio is higher for the Ce-positive anomaly present in DTPA soil fraction with respect to other LYLOID. Similarly, for the Eu behavior.

All the results, in this case study, pointed out that in the YLOID uptake from the soil and in the transfer to the grapevine, the different rootstocks and the two cultivars were not able to selectively fractionate any YLOID (with exceptions of Ce and Eu), so maintaining the soil fingerprint. This last sentence motivate the geochemistry approach. In fact, Ce and Eu were the only elements that have shown different fractionation in soil and in grapevine, respectively, in relation to their specific chemical behavior (two possible oxidation state and, particularly for Eu, the similarity with Ca behavior). For this reason, in particular for the use of Ce as normalising factor for different approach (Aceto et al., 2013), in our opinion, delete, or at least hide, the ability of YLOID to strongly differentiate soil and/or grapevine of different provenance. The use of unique geochemistry normalising factors, as for example UCC, highlight the possible differences. This approach, and the K_d ratio, allow us to link more directly the system grape-soil pointing out, in particular, in terms of geographical traceability. Furthermore, these results suggest that grape sampling, in order to investigate the correspondence among grapes and soils in YLOID, could be done in any case even when the grafting combination is not known or doubt. The results obtained, at our knowledge, are the first reported data in which the role of the rootstock in the uptaking of YLOID was systematic studied and the scarce knowledge available on YLOID composition in Sicilian vineyard soils and grapes were update. Moreover, suggest the YLOID study as a

promising tool for the grape geographical origin characterization, both to grapevine and table grape products. These results open the way to further studies on the ability of $\sum[HYLOID_{UCC}]$ *vs* $\sum[LYLOID_{UCC}]$ relation, YLOID normalized patterns and K_d factors to trace and link the grape with geographical origin once the chemical signature of other regions will have been characterised.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2016.11.037.

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