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Distribution of Rare Earth Elements in soil and grape berries of Vitis vinifera cv. "Glera"

--Manuscript Draft--

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Abstract:	The renowned Vitis vinifera L. cultivar "Glera" (Magnoliopsida Vitaceae) has been grown for hundreds of years in the Italian regions of Veneto and Friuli to produce the sparkling Prosecco wine, with Controlled Designation of Origin (DOC). We evaluated the relationship among the concentrations of rare earth elements (REE) in soil and in "Glera" grape berries in vineyards belonging to five different localities in the Veneto alluvial plain, all included in the DOC area of Prosecco. The concentration of REE in samples of soil and juice or solid residues of grape berries was determined by inductively coupled plasma mass spectrometry (ICP-MS) and the Index of Bioaccumulation was calculated to define the specific assimilation of these elements from soil to grape berries. The concentration of REE in soil samples allowed an identification of each locality examined and REE were mostly detected in solid grape berry residues in comparison to juice. These data may be useful to associate REE distribution in soil and grape berries to a specific geographical origin, in order to prevent fraudulent use of wine denomination labels.
Response to Reviewers:	Answer to the Reviewers Reviewer #1: General The manuscript is generally well written and provides useful descriptive data on rare earth elements in wine grape cultivation in Italy. Figures and tables are clear and the interpretation is logical. The authors could have explore more sophisticated multivariate statistics to determine chemical fingerprints, but the data were simple enough here that their graphical approach likely is sufficient. There was not mention in the figure legends what 'normalized' means and how it was calculated, which should be included. Answers to Reviewer #1

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Reviewer #2

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Answers to Reviewer #2

First of all we would like to thank Reviewer n.2 for his/her favourable judgement and interest in our work, and above all for his/her revision. Here are the detailed answer to his/her questions.

1. What specific insight or key discovery did you make that is applicable elsewhere, beyond the sites studied?

The aim of our study is to establish territorial fingerprintings of the V. vinifera cultivar “Glera”, employed in the production of the renowned Italian Controlled Designation of Origin (DOC) wine “Prosecco”. “Prosecco” is the sparkling wine most popular in the world (recently outscoring even Champagne) and its trade amounts to 3.5 billions Euro per year. The increasing international demand for sparkling wine had recently caused an increase of falsification and fraudulent use of denomination labels. The organoleptic characteristics of each wine reflect the soil geochemistry, the specific climate area and viticultural practices of each specific district (“terroir”). The precise identification of the

	“terroir” protects the wine producers from unfair competition and falsification, and the customers from any kind of commercial (or health) fraud. For these reasons, it is relevant to precisely identify the geographical area of production by REE and other geochemical fingerprintings. This method could be applied to many other products to precisely identify their area of production. 2. Please discuss in greater detail the mineralogy and texture of the soils -- and their affinity for sorbing each element studied (attaching to soil particles versus dissolving in soil water). For example, it would be very interesting to estimate Kd values through laboratory batch experiments. We thank the Reviewer for his/her valuable suggestion and added more sentences about the mineralogy and texture of the soils, in the Materials and Methods section (from line 101 onwards) and in the Results and Discussion section (from line 159 onwards). We also added another reference (Yanfei et al. 2016) to clarify the affinity of the studied elements for absorption on clay minerals. Concerning the Kd values, we are presently expanding our study through a new series of experiments. According to the Reviewer’s suggestion, we will include calculations of Kd values in a forthcoming paper.

Dear Dr Elvir,

the manuscript "Distribution of Rare Earth Elements in soil and grape berries of *Vitis vinifera* cv. Glera" by Pepi et al. (ref. EMAS-D-16-01575) has been extensively revised, following both Referees' suggestions. We highlighted in yellow the main corrections made to the manuscript and enclose with this letter the detailed answers to the Reviewers' comments.

We thank both Referees for the careful revision of the manuscript, and we hope that the revised manuscript is now suitable for publication on Environmental Monitoring and Assessment.

Thank you very much for your attention and best regards,

Salvatore Pepi

Salvatore Pepi, PhD

Department of Physics and Earth Sciences
University of Ferrara (Ferrara, Italy)

Answer to the Reviewers

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Distribution of Rare Earth Elements in soil and grape berries of Vitis vinifera cv. "Glera"

[1] Salvatore Pepi, [2]Luigi Sansone, [3]Milvia Chicca, [1]Elena Marrocchino, [1]Carmela Vaccaro

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Abstract

The renowned *Vitis vinifera* L. cultivar "Glera" (Magnoliopsida Vitaceae) has been grown for hundreds of years in the Italian regions of Veneto and Friuli to produce the sparkling Prosecco wine, with Controlled Designation of Origin (DOC). We evaluated the relationship among the concentrations of rare earth elements (REE) in soil and in "Glera" grape berries in vineyards belonging to five different localities in the Veneto alluvial plain, all included in the DOC area of Prosecco. The concentration of REE in samples of soil and juice or solid residues of grape berries was determined by inductively coupled plasma mass spectrometry (ICP-MS) and the Index of Bioaccumulation was calculated to define the specific assimilation of these elements from soil to grape berries. The concentration of REE in soil samples allowed an identification of each locality examined and REE were mostly detected in solid grape berry residues in comparison to juice. These data may be useful to associate REE distribution in soil and grape berries to a specific geographical origin, in order to prevent fraudulent use of wine denomination labels.

Keywords: *ICP-MS, Index of Bioaccumulation, grape berry, Veneto, Prosecco*

Introduction

The series of lanthanide elements of the Periodic Table, commonly called "Rare Earth Elements" (REE) includes 14 elements relatively abundant in rock and soil (Kabata-Pendias 2011; Aide and Aide 2012). The REE are divided in three groups: the first includes the light rare elements (LREE) from La to Gd, the second one the medium rare elements (MREE) from Sm to Ho, and the third one the heavy rare elements (HREE) from Tb to Lu. The REE typically exhibit trivalent oxidation states, except Europium and Cerium, which may also occur respectively as Eu^{2+} and Ce^{4+} (Kabata-Pendias 2011; Aide and Aide 2012; Atwood 2012; White 2013). Due to their large use in the electronics industry and agricultural practices, the REE concentration has greatly increased in the environment (Emsley 2001; Xu et al. 2002; Shtangeeva and Ayrault 2007; Gonzalez et al. 2014). In many agricultural practises the application of a controlled amount of fertilizer containing REE has been shown to increase yield and quality of crops (Diatloff et al. 1995; Liang et al. 2005). In recent years, there is increasing interest in direct application of REE to plants, but they can exert positive or negative physiological effects depending on the dosage and other conditions (Zhang et al. 2013). Controlled doses of REE have been shown to exert some effects on growth and germination in native Canadian herbs and other plant species (Thomas et al. 2014).

It is known that the REE distribution in rocks is maintained in soil and in plant tissues (Ichihashi et al. 1992; Wang et al. 1997; Zhang et al. 2002; Ding et al. 2006; Censi et al. 2014), and REE concentrations change according to species and soil type (Ichihashi et al. 1992; Wyttenbach et al. 1998; Oddone et al. 2009). The absorption rate of REE from the soil depends on the translocation rate towards the aerial plant organs: as expected, in *Triticum aestivum* (Liliopsida Poaceae) higher amounts of REE are observed in roots in comparison to shoots (Hu et al. 2002).

Concerning *Vitis vinifera* L. (Magnoliopsida Vitaceae), studies of REE concentrations in grape berry samples have been previously conducted by ICP-MS on cultivars Chardonnay (Bertoldi et al. 2009), Cabernet Sauvignon, Marselan and Italian Riesling (Yang et al. 2010). These results have encouraged the use of REE in studies of geographical origin of the cultivars Moscato d'Asti and Sauvignon Blanc (Aceto et al. 2013; Censi et al. 2014).
The capacity of plant to uptake the nutrients can be evaluated by the Bioaccumulation index (BA), that is the ratio between the concentration of a given element in plant and the concentration of the same element in soil (Kabata-Pendias and Mukherjee 2007; Kabata-Pendias 2011). BA can be measured in different parts of the plant (root, leaf or fruit) for a better evaluation of element behaviour in the soil-plant system and assess the influence of soil on the composition of plant products, often in relation to environmental contaminants (Chopin et al. 2008; Pessanha et al. 2010; Pèrez de los Reyes et al. 2013; Bravo et al.2015).
Recent studies (Amorós et al. 2013; Bravo et al. 2015; Pepi et al. 2016) dealt with uptake and bioaccumulation of major and trace elements in *V. vinifera*, but only one of them included two rare earth elements, La and Ce (Amorós et al. 2013).
The aim of this research was to investigate, by inductively coupled plasma mass spectrometry (ICP-MS), the concentrations of REE in soil and in "Glera" grape berries from vineyards of five different localities in the Region Veneto, all included in the Controlled Designation of Origin (DOC) area of the renowned Prosecco wine. The data on REE distribution in soil and grape berries may be useful to identify the specific geographical origin of the vineyards of the cultivar "Glera".

Materials and Methods

Study areas

The vineyards belonged to five wineries (Bottazzo, Gaiarine, Lonigo, Nardin and Pattarello), all located in the Region Veneto (Fig. 1). From a geological point of view, the substrate of all wineries is characterized by recent fine sediments aged from Pleistocene to Holocene, except in the Lonigo site, characterized by volcanoclastic deposits from the Holocene. The soils of the wineries were all classified as silt loam, according to the United States Department of Agriculture (Schoeneberger et al. 2002). They had a high content in clay and silicates related to the sediments from alluvial deposits: the clay minerals were montmorillonite, chlorite, illite, muscovite and kaolinite, and the silicates were quartz and K-feldspar (Petrini et al. 2015).

Vines of *Vitis vinifera* L., cultivar "Glera", grown for production of the renowned Controlled Designation of Origin (DOC) wine "Prosecco", were grafted on three rootstocks, 420A and Kober 5bb (*Vitis berlandieri* x *Vitis riparia*), and Richter 110 (*Vitis berlandieri* x *Vitis rupestris*). The vines were trained with vertically oriented canopies, according to "Sylvoz" and "Double Guyot" pruning methods. Rows were oriented N-S and vine spacing was 2.3 m x 1.1 m in each study site. Soil sampling was carried out by means of an Edelman auger (Eijkelkamp Soil & Water, Giesbeek, The Netherlands). For each of the five sampling areas, three vines were chosen at random and nine soil samples (about 2kg each) were collected at regular intervals at 50 cm of distance from each vine base, starting from the depth of 40 cm to the depth of 60 cm. At harvest time, for each of the five sampling areas 10 grape berry clusters were freshly picked at random and put in polyethylene bags at 4 °C. All clusters were completely destemmed in the laboratory and about 300 berries for each sampling area were immediately frozen at -20 °C for analysis.

Soil and grape berry treatment

Soil samples were dried at 105 °C for 24 h to eliminate the hygroscopic water and then grounded in a mortar grinder (Laarmann LMMG 100, Roermond, The Netherlands).

Afterwards, 0.20 g of soil powder were placed in a 50-ml Teflon digestion vessel, 43 x 60 mm (VWR International, Milan, Italy), adding 3 mL HNO_3 (65% in distilled water, Suprapur®, Merck KGaA, Darmstadt, Germany) and 6 mL HF (40 % in distilled water, Suprapur®, Merck KGaA). The mixture was heated on a hotplate at 180-190 °C for 4-5 hours until complete drying: 3 mL NHO_3 and 3 mL HF were then added and the mixture was heated on the same hotplate for 3 hours. The dry residue was resuspended in 4 mL HNO_3, completely dried on the hotplate and finally resuspended in 2 ml HNO_3.

Grape berry samples (about 300 berries each) were carefully washed with MilliQ® water (resistivity 18.2 MΩ cm^{-1}), taking care not to crush them to avoid juice loss. Each sample was centrifuged at 12600 rpm in a Centrika Metal centrifuge (Ariete, Florence, Italy) separating the juice residue (JR) from the solid residue (SR). A quantity of 4 g of JR and 2.5 g of SR were accurately weighed in a Teflon vessel, digested with HNO_3 and H_2O_2, heated and finally resuspended in 2 mL HNO_3, according to a previously established protocol (Pepi et al., 2016). All JR and SR samples were transferred to perfluoroalkoxy-copolymer flasks and made up to 100 mL with highly purified Milli-Q® water. All samples were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) in a Thermo Electron Corporation X series spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts) adding an internal Rh-Re standard to a final concentration of 10 ppb as a control. The accuracy of soil sample analyses was checked by NIST 2709 and USGS GXR-2 certified reference materials. The standard reference materials for ICP-MS were SRM 1547-Peach Leaves and SRM 1567a-Wheat Flour (National Institute of Standards and Technology, Gaithersburg, Maryland).

Statistical analysis

The data of soil, JR and SR samples from the five vineyards were statistically analysed by the non-parametric Kruskal-Wallis test, followed by Dunn's test to verify the significant values by a multiple comparison procedure (Rencher, 2002; Miller and Miller, 2010). All analyses were carried out by the software XLSTAT (Version 2015.5.02, Addinsoft, Paris, France).

Results and discussion

Soil. The chemical composition of soil samples collected from each vineyard is reported in Table 1. Statistically significant differences ($p<0.05$) among the five vineyards were obtained for La, Ce, Pr, Nd, Eu and Gd, using the non-parametric multiple test (Test di Kruskal-Wallis). In all vineyards, the highest REE concentration value was Ce, followed by La, Nd, Pr, Gd and Eu. Examining the concentration differences among vineyards, Ce, Eu and Gd were higher in Lonigo and Nardin vineyards in comparison to Bottazzo, Gaiarine and Pattarello. Among the REE whose p-value was non-significant, Sm resulted higher in Lonigo and Pattarello vineyards.

Generally, the REE concentrations apparently changed according to geographical origin of soils. The higher concentrations of REE in Lonigo and Nardin vineyards could be explained by the different soil origin: Lonigo originated from a substrate of volcanoclastic deposits, while Nardin originated from alluvional deposits rich in carbonates.

The concentration values of all REE in the five vineyards were divided by the Upper Continental Crust (UCC) values (Rudnick and Gao 2003) and plotted in Fig. 2. The REE distribution patterns indicate that all vineyard soils were enriched in light and medium REE, but showed a slight depletion in heavy REE.

A positive Eu anomaly was detected in Lonigo and Pattarello vineyards. The conditions causing Eu anomalies are complex and related to the redox potential environment for Ca mineralization the Ca minerals (Kabata-Pendias 2011; Aide and Aide 2012). In the case of Lonigo and Pattarello vineyards, the Eu anomaly is probably related to the content in feldspars (Petrini et al. 2015).

The mobility of REE in soil is linked to parameters such as pH, chemical availability, organic matter, fertilizers and conditioners, redox potential, clay content and soil texture (Kabata-Pendias 2011). The REE could be found in accessory minerals, such as hydrous oxides and oxides, formed during the weathering process (Tyler 2004), thus the adsorption of REE on clay minerals can be affected not only by leaching but also by weathering (Yanfei et al. 2016).

Juice and solid residue. The chemical composition of juice residue (JR) and solid residue (SR) of grape berries collected in the five vineyards are reported respectively in Tables 2 and 3. Overall, the REE concentration values are higher in SR than in JR, supporting previous data obtained with a slightly different protocol (Bertoldi et al. 2009). In JR, all concentration differences among vineyards were statistically significant ($p<0.05$), except for Dy and Yb (Tab. 2). In all vineyards, the highest REE concentrations in JR were respectively La, Ce, Nd and Pr. In SR, all concentration differences among vineyards were statistically significant ($p<0.05$) except Er, and the highest concentrations were respectively La, Ce, Nd, Sm and Gd (Tab. 3).

As for vineyard soils, also in JR and SR the REE concentrations showed differences related to the geographical origin. All JR and SR concentration values of REE were then normalized to UCC values, showing the results in Fig. 3. The REE showed a different distribution in each vineyard and REE concentration was always higher in SR than in JR. A higher amount of Eu was detected in both JR and SR in samples from Bottazzo, Pattarello, Lonigo and Nardin vineyards (Fig. 3). This positive anomaly could be due to the interchangeability of Eu^{3+} with Ca^{2+} during physiological processes of plant growth occurring in soil (Zeng et al. 2003) or to protein binding in photosystem II (Kruk et al. 2003). Higher concentrations of Eu in SR could also be related to accumulation of this REE in seeds in place of Ca (Ding et al. 2006; Rogiers et al. 2006; Bertoldi et al. 2009). The negative anomaly of Ce concentration in Lonigo samples suggests a depletion in absorption and translocation, probably due to the lower availability and mobility of Ce^{4+} (Wang et al. 1997; Wen et al. 2002).

Bioaccumulation of REE. In order to obtain more data about REE uptake in grape berries cv. Glera, the Index of Bioaccumulation (BA) was calculated as the ratio between the concentration of each element in JR or SR (Tab. 2-3) and the concentration of the same element in soil (Tab. 1) (Tyler 2004; Kabata-Pendias 2010; Amorós Ortiz-Villajos et al. 2013; Pepi et al. 2016). The BA provides information about the relative availability of REE in soil for uptake in plant tissues. The BA values for all REE examined in JR and SR for each vineyard are shown in Fig. 4. The range of BA values are the following: 1.00 - 0.1 for Eu in SR; 0.1 - 0.01 for La, Ce, Pr, Nd, Sm, Dy, Er in JR, and for La, Ce, Pr, Nd, Sm, Gd, Er in SR; 0.01 - 0.001 for Gd, Er, Yb, in JR, and for Dy, Yb in SR.

All SR ranges were higher than JR ones, thus REE accumulation was higher in SR in comparison to JR. Each vineyard showed a different BA for REE, therefore BA was related to soil type and geographical origin (Fig. 4) (Tyler 2004; Kabata-Pendias 2011). Concerning light rare elements (LREE) from La to Gd, the vineyard with the highest BA in JR was Bottazzo, followed by Gaiarine, Lonigo, Nardin and Pattarello. The highest BA of LREE in SR was Gaiarine, followed by Lonigo, Bottazzo, Nardin and Pattarello. The REE distribution in SR of grape berries of the cv. Glera from different vineyards confirms previous observations in grape berries of the cv. Chardonnay, in which skin and flesh resulted enriched in REE (Bertoldi et al. 2009). Moreover, LREE are known to be associated to chlorophyll (Hu et al. 2004) and could persist as a residue of the previous photosynthetic activity of the berry (Bertoldi et al. 2009).

Conclusions

The concentration of rare earth elements (REE) was evaluated by ICP-MS in soil and grape berries of *Vitis vinifera* L. cultivar "Glera" from vineyards of five different localities in Region Veneto (Italy) included in the DOC area of Prosecco. Each vineyard soil was geologically characterized and identified on the base of the different REE concentrations. The ICP-MS analyses of juice and solid residues of grape berries and the values of Index of Bioaccumulation supported the identification of each vineyard based on REE accumulation.

Overall, our data extend knowledge about uptake of REE in *V. vinifera* and about their behaviour in soil-plant relationships and could also be useful in characterization of geographical origin of vineyards based on REE concentration and distribution in soil and grape berries. The characterization based on geochemical markers is especially relevant to prevent frauds involving vineyards producing renowned Controlled Designation of Origin (DOC) wines.

Acknowledgments

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Figure Captions

Fig. 1. Geological map of the Veneto Region (Italy) showing the location of the wineries of *Vitis vinifera* cv. "Glera" studied: "Lonigo" (1), "Bottazzo" (2), "Pattarello" (3), "Gaiarine" (4), "Nardin" (5).

Fig. 2. Concentrations of Rare Earth Elements (REE) determined by inductively coupled plasma mass spectrometry (ICP-MS), expressed in µg/g and divided by the Upper Continental Crust (UCC) values, in soil from vineyards of the five wineries listed in Fig. 1.

Fig. 3. Concentrations of REE determined by ICP-MS, expressed in µg/g and divided by UCC values, in juice residues and solid residues from grape berries of the vineyards "Bottazzo" (a), "Gaiarine" (b), "Lonigo" (c), "Nardin" (d) and "Pattarello" (e). The concentrations of Tb, Ho, Tm, Yb and Lu were below the detection limit of ICP-MS.

Fig. 4. Index of Bioaccumulation of REE determined by ICP-MS in juice residues (top) and solid residues (bottom) from grape berries of the five vineyards of Fig. 3. The concentrations of Tb, Ho, Tm, Yb and Lu were below the detection limit of ICP-MS.

Table 1. Median concentrations, minimum (Min) and maximum (Max) values (μg/g) of REE in soil samples of the five vineyards of Fig. 1, analyzed by ICP-MS. A non-parametric multiple test (Kruskal-Wallis) was applied. P-values: ns= not significant; *< 0.05; ** < 0.01; *** < 0.001.

Table 2. Median concentrations, minimum (Min) and maximum (Max) values (μg/g) of REE in juice residues of grape berries of the five vineyards of Fig. 1, analyzed by ICP-MS. The non-parametric Kruskal-Wallis test was applied. P-values: ns= not significant; *< 0.05; ** < 0.01; *** < 0.001. The concentrations of Tb, Ho, Tm, Yb and Lu were below the detection limit of ICP-MS.

Table 3. Median concentrations, minimum (Min) and maximum (Max) values (μg/g) of REE in solid residues of grape berries of the five vineyards of Fig. 1, analyzed by ICP-MS. The non-parametric Kruskal-Wallis test was applied. P-values: ns= not significant; *< 0.05; ** < 0.01; *** < 0.001. The concentrations of Tb, Ho, Tm, Yb and Lu were below the detection limit of ICP-MS.

Figure

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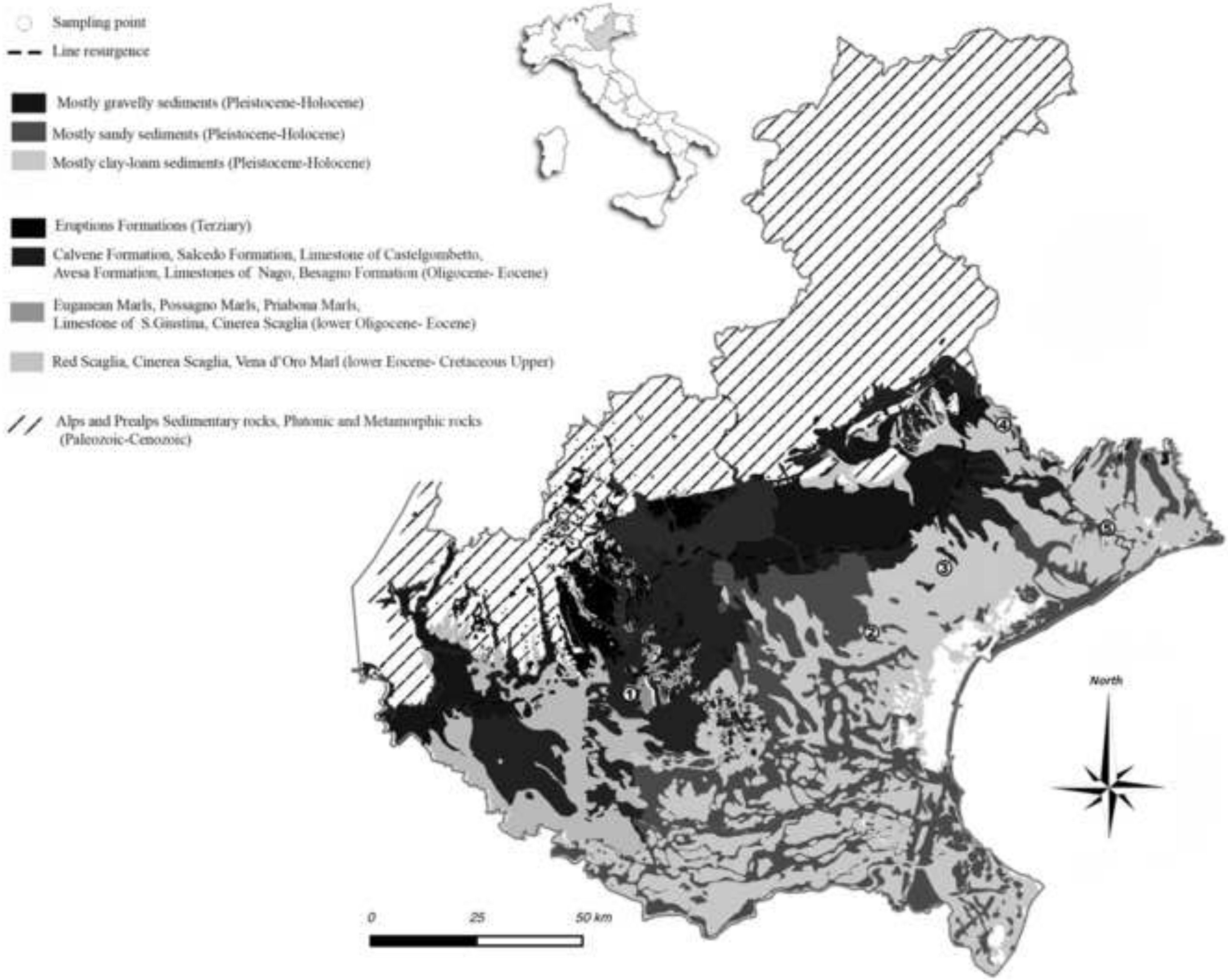

Figure2

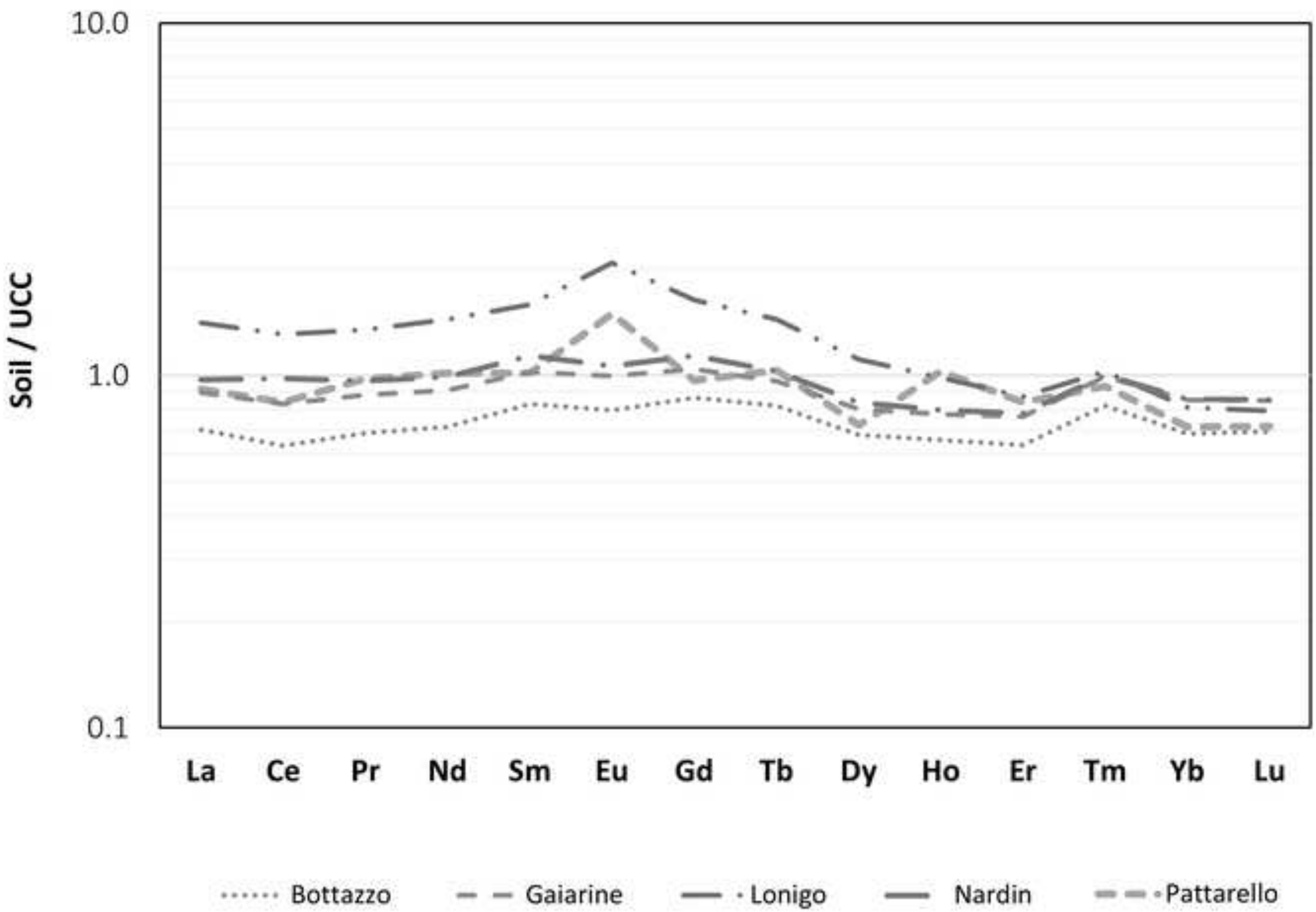

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Figure3

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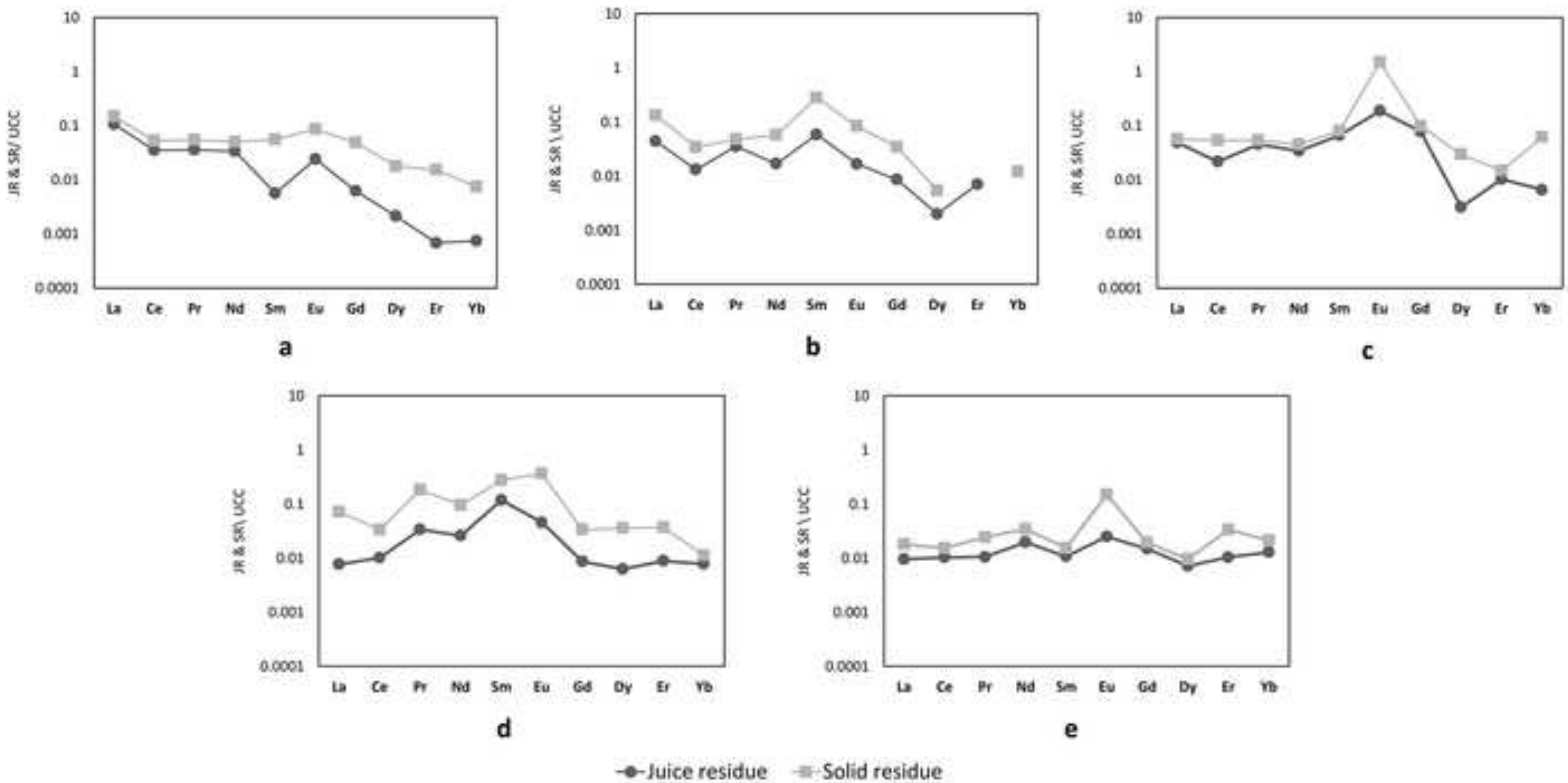

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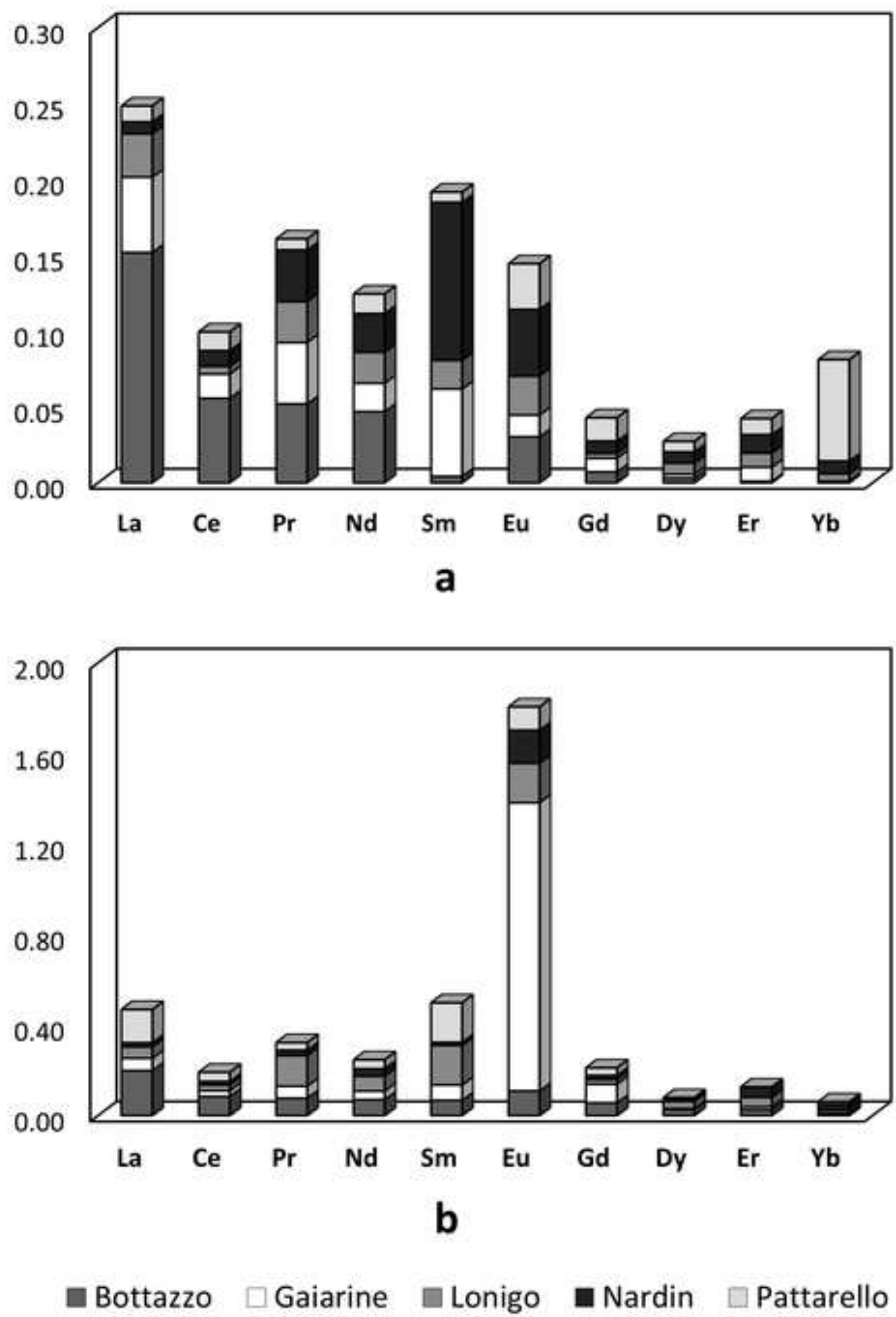

Table 1

	Bottazzo			Gaiarine			Lonigo			Nardin			Pattarello			p-value
	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	
La	18.993	24.161	22.167	18.850	34.636	29.555	39.670	47.250	44.409	28.501	31.853	30.106	25.964	32.862	26.225	*
Ce	36.772	41.890	40.735	39.000	67.376	50.268	72.074	88.729	87.000	56.751	67.282	60.912	43.959	67.343	47.326	**
Pr	4.375	5.323	4.936	4.646	7.652	6.487	9.052	9.967	9.676	6.657	7.063	6.815	5.704	17.383	7.760	*
Nd	17.341	21.151	19.366	18.625	29.707	25.250	37.743	40.370	38.814	26.262	27.173	26.961	21.700	70.086	30.589	*
Sm	3.489	4.280	3.936	3.696	5.777	4.925	7.255	7.729	7.392	5.286	5.406	5.330	4.154	13.274	5.901	ns
Eu	0.713	0.872	0.804	1.024	1.276	1.214	2.040	2.166	2.061	1.049	1.073	1.072	0.801	0.858	0.810	**
Gd	3.073	3.772	3.516	3.139	4.304	4.082	6.389	6.844	6.426	4.498	4.622	4.541	3.285	4.781	3.527	*
Tb	0.499	0.630	0.593	0.502	0.810	0.710	1.003	1.976	1.050	0.704	0.745	0.711	0.541	0.733	0.724	ns
Dy	2.352	2.873	2.701	2.379	3.800	3.226	4.227	4.498	4.273	3.233	3.303	3.274	2.303	7.415	3.219	ns
Ho	0.474	0.593	0.565	0.484	0.779	0.670	0.797	0.853	0.801	0.647	0.680	0.659	0.462	1.472	0.626	ns
Er	1.288	1.580	1.502	1.331	2.132	1.818	1.961	2.079	1.980	1.738	1.835	1.819	1.217	3.904	1.675	ns
Tm	0.206	0.273	0.259	0.218	0.358	0.316	0.287	0.329	0.308	0.286	0.321	0.294	0.209	0.671	0.264	ns
Yb	1.198	1.490	1.406	1.294	2.089	1.731	1.583	1.690	1.602	1.651	1.752	1.738	1.134	3.611	1.539	ns
Lu	0.180	0.237	0.227	0.194	0.314	0.280	0.230	0.261	0.246	0.251	0.284	0.259	0.182	0.578	0.227	ns

	Bottazzo			Gaiarine			Lonigo			Nardin			Pattarello			p-value
	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	
La	2.225	4.259	3.434	1.306	1.475	1.345	1.113	1.334	1.268	0.214	0.254	0.245	0.223	0.372	0.293	***
Ce	1.398	3.098	1.875	0.815	0.915	0.816	0.400	0.434	0.423	0.614	0.673	0.632	0.634	0.679	0.640	***
Pr	0.247	0.259	0.254	0.235	0.265	0.252	0.250	0.270	0.253	0.212	0.255	0.233	0.073	0.076	0.075	**
Nd	0.323	2.077	0.408	0.325	0.586	0.464	0.192	1.621	0.571	0.612	0.794	0.692	0.443	0.590	0.547	*
Sm	<0.001	0.025	0.025	0.243	0.425	0.247	0.125	0.149	0.147	0.500	0.599	0.549	0.049	0.063	0.049	***
Eu	0.022	0.025	0.024	<0.001	0.025	0.025	0.045	0.064	0.050	0.036	0.058	0.048	0.024	0.025	0.025	***
Gd	0.025	0.025	0.025	<0.001	0.082	0.022	0.020	0.022	0.022	0.022	0.041	0.040	0.049	0.065	0.065	**
Dy	<0.001	0.025	<0.001	<0.001	0.023	<0.001	0.023	0.049	0.023	<0.001	0.050	0.023	0.023	0.046	0.024	ns
Er	0.001	0.002	0.002	0.012	0.024	0.012	0.005	0.025	0.023	0.016	0.025	0.023	0.023	0.024	0.024	**
Yb	0.001	0.002	0.002	n.d	n.d	n.d	0.007	0.008	0.008	0.009	0.026	0.014	0.024	0.026	0.026	ns

Table 3 Click here to download Table Tab3.docx

	Bottazzo			Gaiarine			Lonigo			Nardin			Pattarello			p-value
	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	
La	4.018	4.818	4.162	4.020	4.198	4.186	1.385	1.620	1.531	2.116	2.329	2.202	0.534	0.577	0.555	***
Ce	3.127	3.500	3.339	2.061	2.274	2.125	1.227	1.383	1.358	2.030	2.178	2.080	0.920	0.981	0.979	***
Pr	0.344	0.435	0.365	0.327	0.363	0.333	0.240	0.364	0.355	1.256	1.377	1.256	0.121	0.173	0.172	***
Nd	1.336	1.392	1.366	1.457	1.690	1.629	0.875	0.945	0.945	2.404	2.721	2.524	0.842	0.995	0.885	***
Sm	0.223	0.343	0.223	1.283	1.383	1.383	0.234	0.356	0.347	1.227	1.368	1.311	0.063	0.079	0.075	***
Eu	0.084	0.089	0.087	0.081	0.091	0.083	0.346	3.552	0.575	0.240	0.444	0.368	0.137	0.183	0.153	***
Gd	0.189	0.196	0.196	0.101	0.154	0.128	0.308	0.322	0.315	0.108	0.212	0.122	0.062	0.097	0.088	***
Dy	0.034	0.088	0.088	0.013	0.038	0.013	0.011	0.014	0.012	0.128	0.183	0.128	0.035	0.039	0.037	**
Er	0.026	0.044	0.034	n.d	n.d	n.d	0.024	0.024	0.024	0.079	0.089	0.085	0.072	0.086	0.086	ns
Yb	0.012	0.016	0.016	0.023	0.025	0.025	0.001	0.001	0.001	0.021	0.023	0.023	0.038	0.049	0.039	**