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RESEARCH ARTICLE

Chemical elements as fingerprints of geographical origin in cultivars of *Vitis vinifera* L. raised on the same SO4 rootstock

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Abstract The uptake of major and trace elements in grapevine (*Vitis vinifera* L.) can be influenced by soil, climate, geographic origin, and rootstock type. Rootstocks were mainly selected to resist phylloxera and for specific tolerance to lime, mineral uptake, drought, and salinity. The relationship among concentrations of major, trace, and rare earth elements was studied in soil and leaves from two Italian grapevine cultivars, "Cabernet Sauvignon" and "Corvina," employed to produce renowned controlled designation of origin (DOC) wines. The cultivars were raised on the same rootstock SO4 in two different areas of the Veneto Region (Northern Italy). The elements were studied by X-ray fluorescence and inductively coupled plasma mass spectrometry, and data were elaborated by non-parametric tests and multivariate linear discrimination analysis. The related index of bioaccumulation was calculated to define the specific assimilation of the elements from soil to leaves. A statistically significant correspondence between soil and leaf samples was observed for Mg, Sm, V, and Zr. The results allowed to discriminate soil and leaf samples of the two cultivars according to geographical provenance, possibly providing geochemical markers (fingerprints) useful against fraudulent use of DOC wine labels.

Introduction

Rootstocks were developed before 1930 from American grape species to avoid damages caused by *Daktulosphaira* (syn. *Phylloxera*) *vitifoliae* F. on grapevine (*Vitis vinifera* L.) which in late nineteenth century destroyed European vineyards (Granett et al. 2001; Dry 2007; Serra et al. 2014). Besides the resistance to *D. vitifoliae*, rootstocks have valuable characteristics such as vigor in rooting and propagation, tolerance to salinity and lime, and selected uptake of major chemical elements (Granett et al. 2001; Keller et al. 2001; Fekete et al. 2012; Serra et al. 2014; Merli et al. 2016), depending on availability of water and nitrogen (Martínez de Toda 2002). The effects of rootstocks on grapevine growth, wine composition, and quality production have been widely studied (Paranychianakis et al. 2004; Boso et al. 2008; Ozden et al. 2010; Wooldridge et al. 2010; Serra et al. 2014) but it is still unclear whether these effects are directly exerted by rootstocks, or are due to locations where grapevines are raised, including microclimate (Boso et al. 2008; Ozden et al. 2010), or else to vineyard practices (Lee and Steenwerth 2011). Recently, rootstocks have been defined as reliable regulators of major element uptake and transport, especially for Mg, Fe and K in leaves and grapes (Keller et al. 2001; Ibacache and Sierra 2009; Lecourte et al. 2015; Zamboni et al. 2016).

The SO4 rootstock, an interspecific cross between *Vitis berlandieri* and *V. riparia* commonly used in Italian and

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European vineyards, has high resistance to *D. vitifoliae*, to wet soil and lime (Jackson 2008), is sensitive to lack of Mg, and induces early ripening (Fregoni 2013).

Recent studies maintain that SO4 rootstock favors the accumulation of K in grapes (Fregoni 2013). The correct amount of K is critical for wine stability and grape quality (Mpelasoka et al. 2003) and rootstock selectivity may alter the K/Mg ratio, inducing disorders such as berry shrivel and bunch stem necrosis with negative impact on fruit quality (Bavaresco et al., 2010).

Moreover, SO4, 110R, and 420A rootstocks may affect the content in anthocyanins, nitrogen distribution, and major and trace elements in grape (Hostetler et al. 2007; Lee and Steenwerth 2011; Merli et al. 2016). The amount of these compounds and of major and trace elements provide valuable information to evaluate the grape quality and the management practices (Lee and Steenwerth 2011; Pepi et al. 2016a). Several studies focused on the relationship between grapes and soil composition for tracing geographical origin (Oddone et al. 2009; Di Paola-Naranjo et al. 2011; Aceto et al. 2013; Cugnetto et al. 2014; Mercurio et al. 2014; Petrini et al. 2015), while others examined the translocation and bioaccumulation of chemical elements in the soil-plant system (Angelova et al. 1999; Amoros et al. 2011, 2013; Alagić et al. 2015; Vystavna et al. 2015; Pepi et al. 2016b). In detail, Cd, Cu, Pb, and Zn were shown to penetrate grapevines through the root system and to accumulate in aerials parts (Angelova et al. 1999), Pb and Ni were shown to preferentially accumulate in leaves and roots than in grape berries (Todic et al. 2006), and while Cr poorly translocated from roots to aerial plant parts (Ko et al. 2007). Other studies dealt with the possible toxicity by heavy metals and environmental conditions in grapes (Bertoldi et al. 2011; Fiket et al. 2011; Kabata-Pendias 2011; Alagić et al. 2015; Bravo et al. 2015). Several studies showed the connection among vineyards, soil, and geological origin based on geochemical composition (Cugnetto et al. 2014; Vystavna et al. 2015), also considering factors such as the grapevine element uptake, the bioavailability, and the human interference by soil management (Galgano et al. 2008; Di Paola-Naranjo et al. 2011; Kabata-Pendias 2011; Cugnetto et al. 2014; Wooldridge and Olivier 2014; Petrini et al. 2015).

Recent studies dealt with geochemical characterization of grape berries grown under different soil management (Pepi et al. 2016a). However, few studies concerned the relationship among rootstock, soil, and bedrock in grapevines. It is known that the uptake of major and trace elements could be affected by grape variety and rootstock: the accumulation may be different in grafts in comparison to rootstocks, and may also be different according to geographical characteristics (Fekete et al. 2012).

The major, trace, and rare earth elements (REE) were studied in soil and leaves of two renowned cultivars of *Vitis vinifera* L., "Cabernet Sauvignon" and "Corvina," from whose grapes many controlled designation of origin (DOC) wines of high quality are made. The two cultivars were raised on the SO4 rootstock in two vineyards from locations with DOC in the Veneto region (Northern Italy). The aim of the study was to identify possible geochemical markers as fingerprints of geographical provenance of Italian vineyards producing DOC wines, to expose falsification of the "Made in Italy" trademark according to the Italian and European laws.

Materials and methods

Geological setting and sampling areas

The samples analyzed belonged to two DOC vineyards respectively located in the area Mizzole (45° 28′ 22″ N, 11°3′ 8″ E) and Susegana (45°51′ 10″N, 12°15′29″E) in the Veneto Region, Northern Italy (Fig. 1). The pedological features within each catchment are quite homogeneous, with substrates characterized by alluvial and carbonate sediments. From a geological point of view, the substrate of Mizzole is characterized by colluvial deposits (Upper Pleistocene) and the substrate of Susegana by Montello conglomerate, mainly composed of carbonate and dolomite pebbles with clay and sand successions (Miocene) (Zampieri 2005).

The climate of the sampling area is characterized by low winds from East and North-East and average annual temperature 20 °C. The precipitations are more and less distributed along the year with averages about 800 and 1100 mm/year, respectively, in the low and high alluvial plain, and about 2000 mm/year on Prealps (Barbi et al. 2012).

Grapevines of *Vitis vinifera* L., cultivar "Cabernet Sauvignon" and "Corvina," were grafted on the rootstock SO4 (*V. berlandieri* and *V. riparia*) and trained with pruning method Guyot. The age of the vines were 12 years for Mizzole and 18 years for Susegana. Soil sampling was carried out in the two areas by an Edelman auger (Eijkelkamp Soil & Water, Giesbeek, The Netherlands). For each of the two areas, 10 soil samples were collected at regular intervals at the depth of 40 cm and at 50 cm of distance from the grapevine: each sample was collected in triplicate. At veraison time, that is at the phenological stage E-L 35 (Dry and Coombe 2005), 10 grapevine samples, each containing 15 leaves, were freshly picked from each sampling areas and put in polyethylene bags at 4 °C.

Sample treatments and analyses

X-ray fluorescence analysis

The soil samples were prepared as pressed powder pellets for X-ray fluorescence (XRF) analysis. The samples were dried at 105 °C for 24 h to eliminate the hygroscopic water,
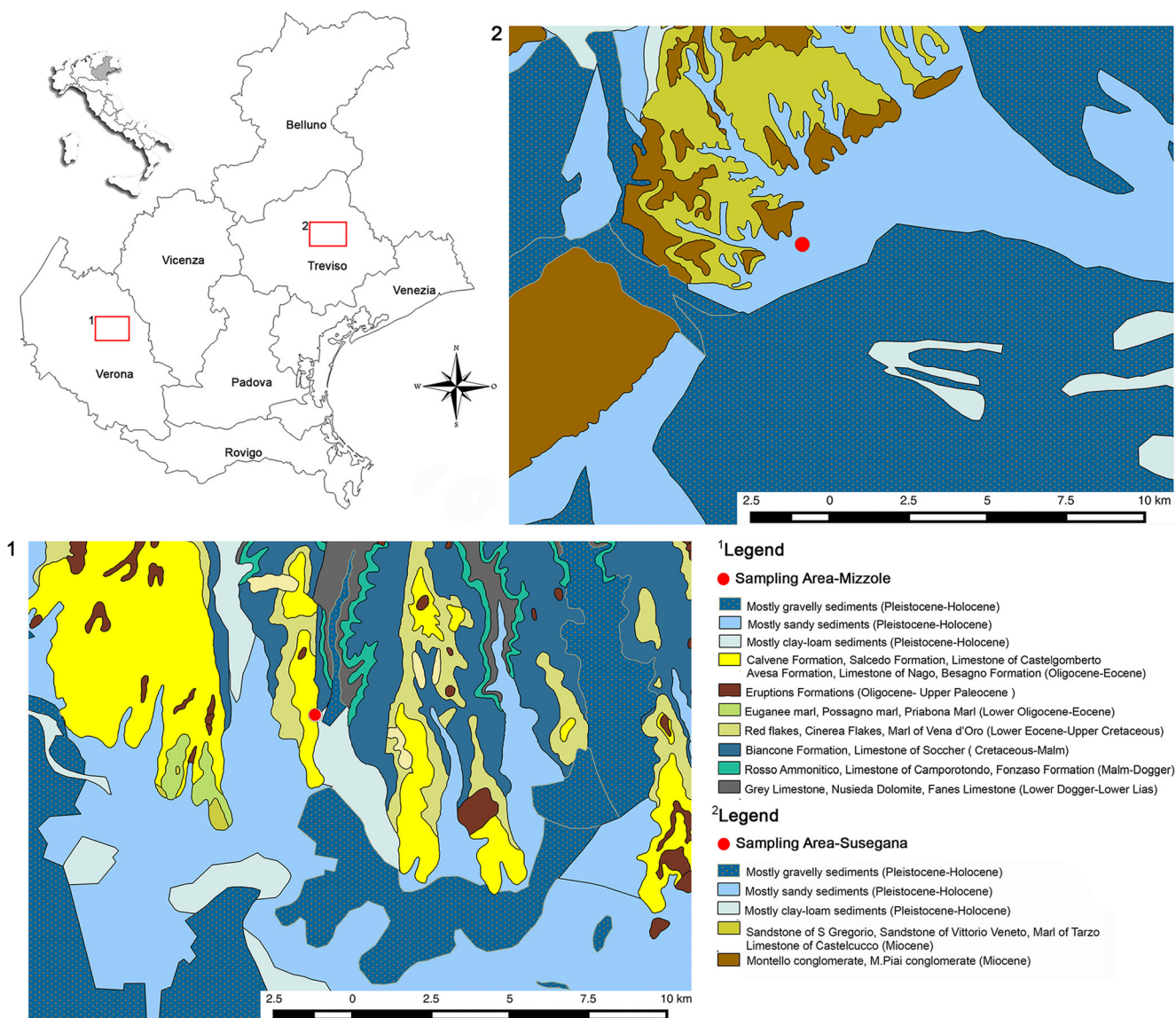
Fig. 1 Geological map of the Veneto Region (Italy) showing the location of the two wineries studied: Mizzole (1). Susegana (2)

and grounded in an agate mortar. About 3 g of powder was pressed over a base of boric acid in a hydraulic press to obtain pellets. The pellets were analyzed by a wavelength dispersive spectrometer ARL ADVANT'XP (Thermo Fisher Scientific, Waltham, Massachusetts). Simultaneously, 0.6 g of sample powder was heated for about 12 h in a muffle at 1000 °C for determining loss on ignition (LOI).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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). An amount of 0.20 g of powder was placed in a 50-mL Teflon digestion vessel, 43 × 60 mm (VWR International, Milan, Italy), adding 3 mL of HNO_3 (65% in distilled water, Suprapur®, Merck KGaA, Darmstadt, Germany) and 6 mL of HF (40% in distilled water, Suprapur®, Merck KGaA,

Darmstadt, Germany). The mixture was heated on a hotplate at 180–190 °C for 4–5 h until complete drying. Afterwards, 3 mL of NHO_3 and 3 mL of HF were added to the dried mixture, and heated on a hotplate for 3 h. The dry residue was resuspended in 4 mL of HNO_3 and heated until complete drying. Finally, the dry residue was resuspended in 2 mL of HNO_3.

Leaf samples were repeatedly washed with highly purified Milli-Q® water (resistivity 18.2 MΩ cm-1) and dried in an oven at 70 °C for 24 h. Once completely dried, the samples were ground in a spice grinder (MC3001-Moulinex, Italy). The ground leaf samples were prepared for ICP-MS as follows: (i) 0.4 g were placed in a 50-ml Teflon digestion vessel, adding 4 mL of HNO_3 (65% in distilled water, Suprapur®, Merck KGaA, Darmstadt, Germany) and 3 mL of H_2O_2 (37% in distilled water, Suprapur®, Merck); (ii) the mixture was

heated on a hotplate at 120–160 °C for 3 h until complete drying.; (iii) the dry residue was resuspended in 3 mL of HNO_3 and 2 mL of H_2O_2 and placed on hotplate until complete drying. The dry samples were finally resuspended in 2 mL of HNO_3. The final solutions of soil and leaf samples were transferred to plastic flasks and made up to 100 mL with highly purified Milli-Q® water. An internal element standard composed of Rh, Re, In, and Bi was added to each solution to a final concentration of 10 ppb. As standard reference materials, the SRM 1547 Peach Leaves and SRM 1567a Wheat Flour (National Institute of Standards and Technology, Gaithersburg, Maryland) and USGS GXR-2 (United States Geological Survey, Reston, Virginia) were employed.

The soil and leaf samples were analyzed by ICP-MS using a Thermo Electron Corporation X series spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts) for the reduction/exclusion of main polyatomic and isobaric interferences.

Statistical analyses

The Kruskal-Wallis non-parametric test (with post-hoc Dunn's test) was used to establish the differences among groups in all data from soil and leaf samples. The Pearson correlation test was used to evaluate the correlation in soil and leaf samples. Linear discriminant analysis (LDA) was chosen as multivariate analysis to ICP-MS data of soil and leaf samples. In LDA, the user must assign a classification group to all sample data: the differences among these predetermined groups describe combinations of variables (Rencher 2002). Stepwise LDA was applied to variables by a Wilks Lambda test (p value < 0.01) and an F-statistic factor (Rencher 2002). The variables were tested by cross validation (Rencher 2002), randomly choosing 10 samples out of 40 as outgroup and applying discriminant analysis. The results showed that all outgroup samples were included in the LDA model. The high percentage of cross validation in our samples supported a successful discrimination among groups. All data analyses were carried out by the software XLSTAT (Version 2015.5.02, Addinsoft, Paris, France).

Results and discussions

Soil characterization by XRF analyses

The data obtained by X-ray fluorescence (XRF) on geochemical composition of soil samples collected from the vineyards where the two cultivars were raised are reported in Table 1. Statistically significant differences ($p < 0.05$) were obtained for all major elements (expressed as oxides) and trace elements. The oxide with the highest concentration in both vineyards was SiO_2, followed by Al_2O_3, CaO, MgO, and Fe_2O_3. The oxides Al_2O_3, Fe_2O_3, and K_2O resulted significantly higher in Mizzole in comparison to Susegana. Concerning trace elements, the highest concentration was Ba in both vineyards, followed by Zr, Sr, and Cu. The concentration of the trace elements Ba, Zr, and Sr were higher in Mizzole in comparison to Susegana, whereas Cu was higher in Susegana.

Bivariate plots of abundances of oxides and trace elements versus SiO_2 and Al_2O_3 were used to identify the differences in soil composition, thus the minerals that could be present. The oxides Al_2O_3 and TiO_2 showed positive correlations with SiO_2 (Fig. 2a–c), suggesting the presence of quartz, feldspar, clay minerals, and/or hydroxides (Hossain et al. 2014). A high CaO/SiO_2 ratio (Fig. 2c) suggests the abundance of carbonate and dolomite minerals in according to geological features. The plots of oxides Fe_2O_3, K_2O, and MnO versus Al_2O_3 (Fig. 2d–f) showed a positive correlation suggesting a soil composition with abundant clay minerals and hydroxides (Schaetzl and Anderson 2005; Pepi et al. 2017). In detail, MnO/Al_2O_3 ratio showed a high value in soil samples from Mizzole suggesting the presence of Al/Mn hydroxides in alluvial deposits (Schaetzl and Anderson 2005; Pepi et al. 2017). Concerning trace elements, the higher values of V, Zn, and Ni versus Al_2O_3 (Fig. 2g–i) detected in soil vineyards are probably due to femic and clay minerals. In Mizzole vineyard, V, Zn, and Ni vs Al_2O_3 showed a well-defined regression line, suggestion a contribution of sediment from Lessini area (Siena and Coltorti 1989).

The data of Fig. 2 show a geochemical characterization by XRF analysis that could be useful to identify the geographical origin of the examined soils, since in almost all plots the data clearly grouped according to the location.

Distribution of elements in soil and leaf samples

Tables 2 and 3 report the concentrations expressed as ppm of major, trace, and rare earth elements in soil and leaf samples collected from the two vineyards and analyzed by ICP-MS. Statistically significant differences ($p < 0.05$ or lower) were obtained for all elements, except for Na and Lu in leaf samples (Table 3).

The data of concentrations of major (Ca, Mg, Mn, Na, and K) and trace elements (Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Nd, Ni, Ti, V, Y, and Zn) in soil samples detected by ICP-MS (Table 2) are in agreement with those obtained by XRF for the same samples. Concerning leaf samples examined by ICP-MS (Table 3), the highest concentrations of major elements in Mizzole vineyard were, respectively, Ca, K, P, and Mg, whereas in Susegana vineyard were Ca, K, Mg, and P. The highest values of trace elements in Mizzole were, respectively, B, Zn, Cu, and Sr, and in Susegana Cu, Zn, B, and Sr. The high values of Cu and Zn detected in Susegana for both cultivars, Cabernet Sauvignon and Corvina, are probably related

Table 1 Concentrations of major (%) and trace elements (ppm) in soil samples from Mizzole and Susegana vineyards, analyzed by X-ray fluorescence

	Mizzole						Susegana						
	Cabernet Sauvignon			Corvina			Cabernet Sauvignon			Corvina			
	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	p value
SiO$_2$	51.16	57.71	53.93	53.26	57.33	54.53	52.98	63.96	61.25	52.01	59.58	56.89	**
TiO$_2$	0.92	1.12	1.04	0.96	1.12	1.05	0.52	0.59	0.55	0.43	0.55	0.51	***
Al$_2$O$_3$	11.63	18.05	16.17	15.09	18.17	16.40	6.88	7.75	7.37	5.58	7.28	6.90	***
Fe$_2$O$_3$	4.93	8.92	7.38	6.71	8.63	7.30	2.86	3.27	3.11	2.45	3.30	3.04	***
MnO	0.19	0.26	0.23	0.21	0.26	0.22	0.09	0.10	0.09	0.09	0.10	0.10	***
MgO	1.50	1.99	1.63	1.59	2.19	1.72	8.34	12.05	9.45	10.31	13.20	11.53	***
CaO	9.58	26.43	17.58	9.99	19.08	16.41	15.32	23.16	17.47	16.80	24.93	19.61	*
Na$_2$O	0.05	0.07	0.06	0.02	0.06	0.05	0.09	0.14	0.12	0.10	0.14	0.11	***
K$_2$O	1.88	2.47	2.16	2.06	2.44	2.24	1.07	1.16	1.11	0.92	1.15	1.07	***
P$_2$O$_5$	0.19	0.30	0.21	0.19	0.23	0.21	0.07	0.12	0.09	0.09	0.12	0.10	***
Ba	204.20	451.90	342.55	313.00	399.30	351.10	106.50	134.50	125.75	87.80	141.10	111.30	***
Ce	44.50	99.90	81.05	65.20	89.40	81.00	25.00	29.90	29.35	19.90	29.90	26.60	***
Co	25.30	42.20	36.70	31.10	39.00	36.05	15.90	19.00	16.60	13.90	24.40	16.00	***
Cr	42.50	102.50	81.85	72.80	115.70	83.90	43.00	57.70	53.40	31.30	51.30	46.80	***
Cu	34.10	55.80	42.85	39.10	62.70	44.20	74.60	116.10	95.70	107.70	143.90	120.35	***
Ga	10.20	23.10	15.30	13.80	16.90	15.20	4.30	5.60	5.20	3.80	7.00	4.80	***
La	30.10	78.80	60.15	50.90	69.00	59.65	20.90	31.00	24.05	15.40	26.60	24.65	***
Nb	7.50	13.20	10.50	7.40	12.20	8.85	3.30	5.90	4.30	1.70	6.60	3.55	***
Nd	28.60	68.70	48.50	43.30	60.30	48.50	15.90	21.70	20.25	14.50	20.40	17.45	***
Ni	49.20	89.50	74.50	70.40	93.90	78.50	20.80	23.00	21.40	17.00	25.60	21.95	***
V	72.30	118.00	105.00	98.30	111.20	104.55	41.40	54.70	46.20	36.70	46.00	42.35	***
Y	17.90	40.60	32.60	25.00	38.60	28.95	6.90	9.80	7.85	4.30	9.20	7.20	***
Zn	6.60	62.00	41.50	32.40	53.10	41.55	16.30	36.00	20.85	21.40	44.00	23.95	**

A non-parametric multiple test (test di Kruskal-Wallis) was applied

p values; n.s. not significant;* < 0.05; ** < 0.01; *** < 0.001

to agronomic practices (Vitanović et al. 2008; Volpe et al. 2009; Fregoni 2013; Vystavna et al. 2014). In some vineyard soils in Italy and Slovenia, an accumulation of Cu was detected, due to the extensive use of copper-based fungicides, such as the Bordeaux mixture (Brun et al. 1998; Rusjan et al. 2007; Fregoni 2013).

The correlations among all elements in leaf samples from Mizzole and Susegana were also calculated (Supplementary Table). All elements in leaf samples showed significant positive correlations ($p < 0.05$), except U for Corvina and Cr, Ga, K, Tm, and V for Cabernet Sauvignon in Mizzole vineyard, and Cd and Pr for Corvina, and Cr and Ga for Cabernet Sauvignon in Susegana (Supplementary Table). Comparing these data, for Corvina, a significant positive correlation of K versus Mg was detected in Mizzole, but the same elements a significant negative correlation appeared in Susegana: these data suggest a different mobility of these elements according to the cultivars.

The concentration values of interchangeable elements in leaf samples of Table 3, such as Ca and Sr, Mg and Ni, P

and B, and Fe and Zn, were plotted in Fig. 3 together with the respective linear regression values. The elements Ca and Sr (Fig. 3a–b) showed a significant correlation for Cabernet Sauvignon in both vineyards. Previous studies supported the close relationship between Ca and Sr (Kabata-Pendias 2011; Fregoni 2013); Sr is also known to be interchangeable with Ca according to the plant metabolic requirements, since its uptake may be increased by Ca and probably by Mg, and decreased by K and Na (Kabata-Pendias 2004; Takeda et al. 2005).

The correlation values of Mg and Ni and of Fe and Zn are, respectively, shown in Fig. 3c, d and Fig. 3e, f and those of P and B in Fig. 3g, h. The elements Mg and Ni showed a significant positive correlation for Cabernet Sauvignon and Corvina in Mizzole vineyard and for Cabernet Sauvignon in Susegana. These data probably reflect the soil concentrations of these elements in the two vineyards, due to the different bedrocks. However, the ability of plants to absorb Ni may be affected by the displacement by Ni^{2+} of Mg^{2+} from the membrane (Kabata-Pendias 2011). Moreover, the metabolic control of Ni transport and mobility and its accumulation in leaves

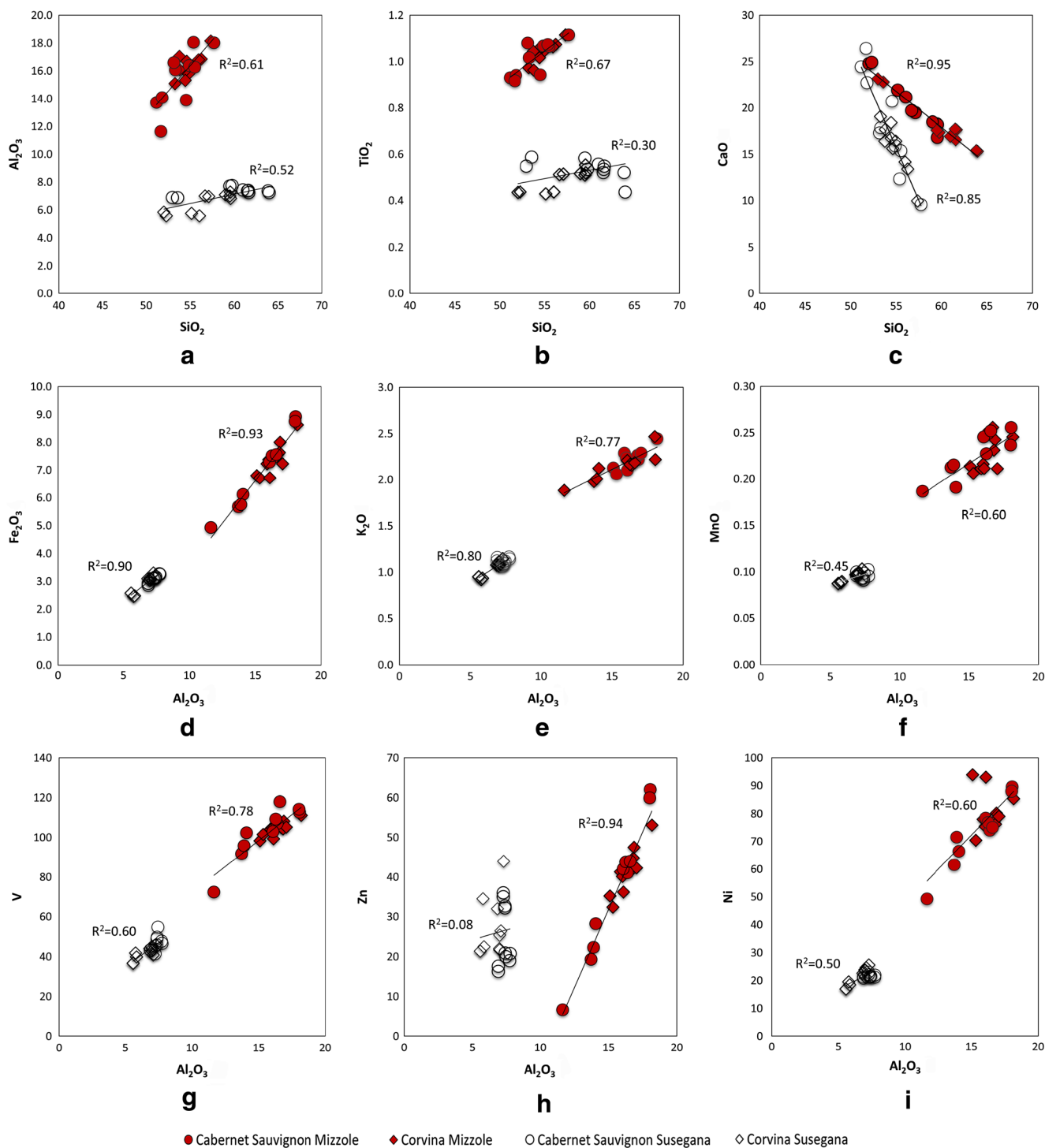**Fig. 2** Bivariate plots of abundances of SiO_2 vs Al_2O_3 (**a**), TiO_2 (**b**), and CaO (**c**), and of Al_2O_3 vs Fe_2O_3 (**d**), K_2O (**e**), MnO (**f**), V (**g**), Zn (**h**), and Ni (**i**), measured by X-ray fluorescence (XRF) in soil samples from the two vineyards Mizzole and Susegana on which the "Cabernet Sauvignon" and "Corvina" cultivars were raised. Values of trace elements are expressed in ppm and values of oxides in %

changes according to the plant species and the correlation of Ni with Mg support the absorption of plants by xylema (Kabata-Pendias 2011; Vázquez Vázquez et al. 2016).

The elements Fe and Zn (Fig. 3e–f) showed a significant correlation for Cabernet Sauvignon and Corvina in both

vineyards. The higher values of Zn in Susegana vineyard in comparison to those in soil suggest an accumulation due to fertilizers. Zn plays a relevant role as functional, structural, and regulatory cofactor of many enzymes (Fagaro 1994; Kabata-Pendias 2011; Fregoni 2013). The mobility of Fe

Table 2 Concentrations of elements in soil samples from Mizzole and Susegana vineyards, analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Values are expressed in ppm. All abbreviations as in Table 1

| | Mizzole | | | | | | Susegana | | | | | | p value |
| | Cabernet Sauvignon | | | Corvina | | | Cabernet Savignoun | | | Corvina | | | |
	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	
Li	28.92	50.45	40.93	30.97	48.74	39.39	14.30	22.82	17.34	14.35	20.13	17.77	***
B	15.28	39.51	31.15	12.88	30.48	22.34	5.46	22.49	10.92	7.33	28.41	12.80	***
Na	1060.67	3549.64	2608.64	2103.28	3862.00	2953.17	449.71	877.56	725.94	638.15	809.01	768.16	***
Mg	2075.34	3765.90	3055.55	1421.44	4578.74	2736.83	17,377.05	24,880.84	20,888.95	24,408.23	28,554.63	26,750.05	***
Al	26,032.29	59,632.60	49,877.57	32,721.46	54,400.00	39,979.47	13,471.55	21,882.93	17,615.92	15,762.16	19,744.35	18,282.15	***
P	653.55	883.14	725.65	608.91	896.50	723.13	278.78	435.63	342.30	336.04	431.75	411.81	***
K	4921.72	12,418.05	9226.17	7586.55	10,610.00	9217.56	3529.41	5482.93	5061.76	3453.38	4697.83	4333.99	***
Ca	40,741.09	124,285.02	93,096.57	55,300.00	92,470.47	74,944.91	7254.15	88,751.19	71,601.06	72,282.07	95,855.94	80,356.28	**
Ti	1069.96	1845.61	1530.71	1422.47	1986.00	1752.25	690.45	996.15	882.37	665.05	926.51	805.28	***
V	80.03	123.80	106.97	85.90	129.84	112.87	42.82	56.73	50.77	40.05	65.24	47.15	***
Cr	64.63	91.93	80.68	69.45	95.65	81.67	31.06	46.54	44.31	31.36	45.70	39.07	***
Mn	675.64	1515.95	1210.73	910.43	1289.35	1037.81	413.21	509.92	460.96	400.15	468.89	446.30	***
Fe	14,011.74	33,935.27	28,721.44	24,597.64	225,026.57	26,111.54	11,034.32	12,680.81	12,256.78	9649.73	12,678.15	11,224.29	***
Co	15.76	30.98	26.60	20.90	28.26	25.45	6.39	8.76	8.30	6.09	9.71	7.78	***
Ni	49.66	68.88	65.14	58.56	716.58	66.16	21.53	28.20	26.73	23.64	32.31	27.15	***
Cu	35.02	49.50	45.43	37.87	55.44	46.29	67.87	109.76	87.72	92.08	109.60	107.73	***
Zn	51.47	96.72	80.34	71.66	100.10	79.76	52.43	71.85	55.72	55.41	68.72	65.43	***
Ga	12.51	29.52	24.75	21.43	29.59	24.56	7.61	10.53	9.45	7.25	10.82	8.83	***
Rb	37.54	111.63	87.80	48.29	103.40	73.48	23.69	45.14	37.59	34.67	51.92	39.94	***
Sr	105.07	170.33	149.30	107.72	133.61	125.49	57.23	84.38	65.00	69.37	76.99	72.79	***
Mo	0.84	1.99	1.19	0.94	1.39	1.09	0.21	0.49	0.35	0.37	0.59	0.46	***
Cd	1.61	3.37	2.77	2.44	3.36	2.69	1.19	1.53	1.45	1.33	1.85	1.64	***
Sn	3.47	7.21	5.78	4.71	7.40	6.08	2.04	2.49	2.22	1.89	3.38	2.30	***
Sb	0.67	1.85	1.03	0.89	1.24	1.12	0.79	1.03	0.93	0.74	0.97	0.82	**
Te	0.58	0.87	0.77	0.66	0.90	0.75	0.28	0.48	0.42	0.28	3.97	0.78	**
Ba	171.58	350.40	322.77	257.43	323.50	278.29	102.17	151.56	134.76	98.27	130.31	117.12	***
Pb	15.83	36.88	29.14	22.56	32.94	26.34	16.33	19.63	18.22	17.04	22.08	18.58	***
U	1.65	3.00	2.37	2.11	2.77	2.41	1.80	2.02	1.94	1.88	2.74	2.14	***
Y	18.39	59.07	46.38	30.00	51.71	37.06	9.41	11.48	10.21	9.81	12.65	10.77	***
Zr	29.26	72.69	62.38	48.39	68.73	56.97	26.66	31.95	30.15	25.05	34.29	28.34	***
Nb	7.40	13.52	12.92	9.17	13.27	11.64	4.76	5.46	5.15	4.27	501.46	25.47	**
La	42.08	79.39	63.84	45.86	68.70	59.74	13.82	16.83	14.94	12.30	17.79	15.64	***
Ce	78.02	134.89	104.55	79.94	114.89	99.26	28.22	35.84	30.23	23.49	33.50	30.45	***

Table 2 (continued)

	Mizzole						Susegana						
Pr	8.68	14.44	11.70	9.15	13.43	11.59	3.16	3.82	3.35	2.83	3.67	3.60	***
Nd	32.60	57.46	47.14	36.05	53.48	46.33	12.38	14.95	13.40	11.05	14.95	13.88	***
Sm	6.56	10.70	8.82	6.64	9.95	8.56	2.35	2.84	2.55	2.14	2.82	2.66	***
Eu	1.41	2.18	1.84	1.38	2.06	1.77	0.48	0.58	0.51	0.45	0.57	0.52	***
Gd	6.33	10.57	8.59	6.61	9.74	8.27	2.21	2.65	2.40	2.04	2.88	2.44	***
Tb	0.96	1.56	1.29	0.96	1.44	1.23	0.32	0.39	0.35	0.30	0.40	0.35	***
Dy	4.84	7.70	6.39	4.63	7.16	6.02	1.60	1.89	1.69	1.52	1.76	1.62	***
Ho	1.01	1.58	1.31	0.94	1.46	1.19	0.33	0.39	0.35	0.31	0.37	0.35	***
Er	2.56	4.19	3.51	2.51	3.97	3.27	0.91	1.07	0.96	0.82	0.99	0.96	***
Tm	0.42	0.65	0.55	0.39	0.62	0.51	0.15	0.18	0.16	0.13	0.19	0.16	***
Yb	2.38	3.69	3.12	2.22	3.46	2.89	0.83	1.02	0.90	0.81	1.00	0.91	***
Lu	0.30	0.55	0.45	0.32	0.52	0.43	0.13	0.16	0.14	0.12	0.16	0.13	***

and Zn is very limited in plants and these elements need to be continuously absorbed during vegetative growth (Bergmann 1992). Plants absorb Zn mainly as Zn^{2+} ions and absorption and translocation of this element is influenced by age and vegetative state of the plant (Bergmann 1992; Farago 1994; Chopin et al. 2008; Fregoni 2013), as well as by interactions with Fe, in turn affected by soil and environmental factors (Alloway 1995; Fregoni 2013).

In Mizzole vineyard a significant correlation of P vs B was observed only for Corvina, while in Susegana vineyard, the same correlation was observed for both cultivars (Fig. 3g–h). The interactions between P and B are complex (Graham et al. 1987; Rogiers et al. 2006) and the interference of P ions with mobility of B may be related to similar reactions with OH groups (Kabata-Pendias 2011). Since the two elements are correlated in soils of both vineyards, probably the differences detected are due to different absorption by the cultivars.

To obtain more data about uptake of major and trace elements and REE in Cabernet Sauvignon and Corvina, the index of bioaccumulation (BA) was calculated as the ratio between the concentration of each element in leaves (Table 3) and the concentration of the same element in soil (Table 2) (Tyler 2004; Juang et al. 2012; Amorós et al. 2013; Alagić et al. 2015; Vystavna et al. 2015; Pepi et al. 2016a, 2016b). The BA provides information about the relative availability of elements in soil for uptake in plant tissues (Kabata-Pendias 2011). The BA values for major and trace elements and REE calculated in leaf samples for Mizzole and Susegana vineyard are, respectively, shown in Figs. 4 and 5.

The range of BA values in Mizzole vineyard are the following: 2–0.1 for K, Ca, Mn, Cu, and Zn in both cultivars; 0.1–0.01 for Rb, Sr, Ba, Ti, Cr, and Ni, in Cabernet Sauvignon and Rb, Sr, Ba, Mn, and Ni, in Corvina; 0.01–0.001 for Ba, V, Cr, Fe, Zr, and Co in Cabernet Sauvignon and Ti, Cr, V, Fe, Zr, Co, Ce, Eu, and Sm in Corvina; < 0.001 for all REE in Cabernet Sauvignon and for all REE except Eu and Sm in Corvina.

The range of BA values in Susegana vineyard are the following: > 2 for Cu and Zn in Cabernet Sauvignon and for Cu in Corvina; for both cultivars, 2–0.1 for K, Ca, Sr, Mn, Cu, and Zn; 0.1–0.01 for Rb, Ba, Co, and Ni; 0.01–0.001 for Ti, V, Cr, Fe, Zr, and REE.

Overall, the elements K, Rb, Ca, Sr, Ba, Mn, Co, Ni, Cu, and Zn elements had higher BA values in Mizzole than in Susegana vineyard, except for Ti, V, Cr, Fe, and Zr (Fig. 4). However, the BA values of K were higher in Susegana than in Mizzole for both cultivars (Fig. 4a–b). Moreover, the BA values of Cr and Fe (Fig. 4c–d) and those of Cu and Zn (Fig. 5e–f) were higher in Cabernet Sauvignon than Corvina in both vineyards. These data suggest a higher absorption of these elements in Cabernet Sauvignon in comparison to Corvina.

Table 3 Concentrations of elements in leaf samples of "Cabernet Sauvignon" and "Corvina" cultivars from Mizzole and Susegana vineyards, analyzed by ICP-MS. Values are expressed in ppm. All abbreviations as in Table 1

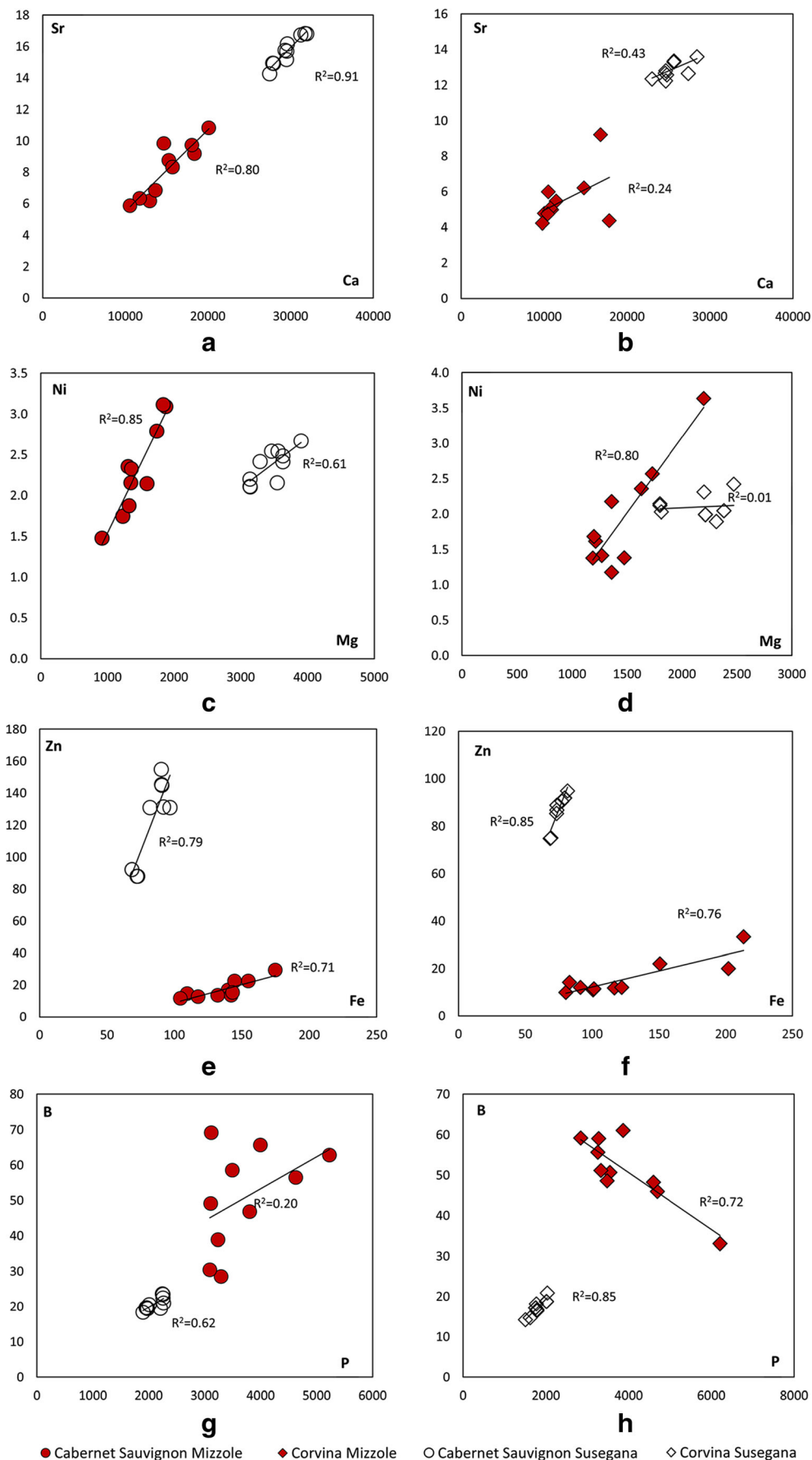|	Mizzole						Susegana						
	Cabernet Sauvignon			Corvina			Cabernet Savignoun			Corvina			
	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	p value
Li	0.01	0.06	< 0.01	0.01	0.04	0.01	0.12	0.29	0.18	0.11	0.16	0.15	***
B	28.50	69.11	52.78	33.09	61.09	50.91	18.38	23.59	20.08	14.24	20.85	17.18	***
Na	40.06	70.92	54.38	49.57	98.67	64.69	40.35	94.71	70.75	65.48	73.73	70.01	n.s.
Mg	917.23	1876.08	1355.86	1187.26	2200.00	1359.36	3138.16	3904.81	3502.68	1799.11	2472.56	2213.89	***
Al	12.87	32.87	20.43	10.26	55.46	19.59	64.00	80.69	71.82	52.99	80.86	65.69	***
P	3095.61	5231.56	3398.00	2838.93	6209.90	3511.96	1901.48	2265.95	2110.71	1504.40	2037.13	1777.56	***
K	6355.54	9392.08	7342.45	475.81	10,400.00	5175.95	5481.27	6835.97	6448.12	4619.91	7262.76	6405.49	*
Ca	10,592.65	20,135.16	14,987.81	9809.22	27,861.39	10,845.57	27,470.38	31,948.45	29,531.69	22,991.17	28,461.27	25,214.62	***
Ti	15.90	27.47	18.55	7.72	34.81	9.61	5.51	6.80	6.00	4.69	7.21	5.52	***
V	0.09	0.18	0.12	0.06	0.31	0.11	0.06	0.10	0.08	0.06	0.10	0.08	**
Cr	0.25	1.01	0.44	0.22	0.63	0.29	0.21	0.38	0.29	0.23	0.33	0.28	**
Mn	54.59	175.27	120.22	30.23	200.00	50.74	204.00	221.68	212.47	123.29	167.66	136.58	***
Fe	104.56	174.88	141.12	80.22	213.47	108.97	68.46	96.75	86.19	68.57	81.54	73.54	***
Co	0.02	0.14	0.09	0.05	0.17	0.06	0.22	0.30	0.25	0.18	0.30	0.21	***
Ni	1.48	3.12	2.24	1.18	3.64	1.65	2.10	2.67	2.41	1.89	2.42	2.04	*
Cu	9.37	19.51	12.41	6.84	16.92	8.10	119.45	199.72	190.45	159.95	220.75	168.05	***
Zn	11.55	29.34	14.90	9.97	33.39	12.05	87.90	154.86	130.97	74.85	94.79	88.74	***
Ga	0.13	0.23	0.18	0.13	0.38	0.17	0.31	0.41	0.37	0.32	0.45	0.39	***
Rb	2.41	5.75	3.20	1.84	5.78	3.10	1.35	1.83	1.66	1.10	1.95	1.39	***
Sr	5.85	10.84	8.52	4.22	9.22	5.02	14.26	16.83	15.74	12.24	13.59	12.73	***
Mo	0.23	0.58	0.43	0.12	1.05	0.34	0.02	0.07	0.03	0.07	0.10	0.08	***
Cd	0.01	0.02	0.02	0.01	0.03	0.02	0.05	0.07	0.06	0.04	0.05	0.05	***
Sn	0.05	0.12	0.10	0.04	0.18	0.06	0.11	0.22	0.18	0.12	0.22	0.15	***
Sb	< 0.01	0.02	0.01	< 0.01	0.02	0.01	0.01	0.04	0.03	0.02	0.04	0.02	***
Te	0.01	0.05	0.03	0.02	0.22	0.03	0.05	0.07	0.06	0.04	0.06	0.05	**
Ba	2.61	4.40	3.26	1.53	5.62	2.01	5.63	6.39	6.01	5.22	6.34	5.52	***
Pb	0.06	0.12	0.09	0.05	0.19	0.09	0.18	0.24	0.21	0.12	0.19	0.17	***
U	2.55	4.77	3.64	1.80	28.56	5.80	1.20	3.48	2.48	2.24	4.30	2.52	**
Y	10.85	24.90	17.99	16.50	60.18	23.32	25.62	39.83	32.05	30.94	39.57	33.67	***
Zr	42.35	94.94	65.65	71.22	153.23	94.15	134.33	187.20	150.64	154.26	188.23	167.56	***
Nb	10.76	31.82	16.00	7.67	897.73	89.04	6.40	72.02	44.37	6.40	78.63	18.84	*
La	13.93	40.41	26.58	20.11	76.79	26.60	43.37	72.78	50.86	50.73	64.06	52.96	**
Ce	24.27	66.06	37.76	30.73	177.70	63.23	42.22	76.16	56.79	51.29	64.90	60.20	**
Pr	2.98	5.98	3.95	4.05	26.63	5.75	7.31	10.72	8.71	7.92	10.00	8.53	**
Nd	11.83	24.29	17.45	15.70	76.93	24.38	27.37	41.44	36.67	35.81	37.91	36.54	***
Sm	2.28	5.22	3.34	3.25	34.87	5.02	5.41	8.26	7.02	6.46	7.22	6.97	***
Eu	1.04	2.38	1.52	1.58	2.95	1.99	2.76	4.11	3.41	3.31	4.26	3.79	***
Gd	2.45	4.91	3.30	3.33	21.17	4.72	4.72	7.34	6.24	6.03	7.17	6.29	***
Tb	0.36	0.64	0.53	0.43	2.82	0.74	0.71	1.20	1.03	0.86	1.09	1.01	***
Dy	1.71	3.32	2.57	2.34	6.77	3.54	3.50	5.00	4.26	4.13	4.97	4.46	**
Ho	0.36	0.70	0.48	0.40	0.77	0.63	0.71	1.04	0.80	0.81	1.08	0.91	***
Er	0.68	1.78	1.35	1.15	2.11	1.91	2.02	2.98	2.38	2.57	4.70	2.70	***
Tm	n.d.	0.24	0.21	0.17	0.28	0.23	0.26	0.51	0.40	0.39	0.50	0.46	***
Yb	0.71	1.48	1.11	1.00	1.51	1.34	1.45	2.65	1.85	1.91	2.78	2.20	***
Lu	< 0.01	0.27	0.21	0.17	0.28	0.23	0.19	0.49	0.23	0.19	0.43	0.24	n.s.

n.d. not detected, *n.s.* not significant

Concerning REE, the BA values were generally higher in Susegana than in Mizzole for both cultivars (Fig. 5), although the REE concentration in soil was about three times higher in Mizzole. Thus, the higher BA values in Susegana are apparently due to a higher accumulation of REE in leaves.

The concentration of REE has been shown to be related to P, Ca, Y, and Zr (Tyler 2004; Kabata-Pendias 2011; Censi et al. 2014): the soil of Mizzole vineyard contains a higher concentration of Ca and P, and this may explain the generally higher concentration of REE in soil in comparison to Susegana vineyard. In contrast, leaves of Susegana vineyard contain a higher concentration of Ca, Y, Zr, and REE. The Susegana vineyards is 6 years older than Mizzole: it is known that the concentrations of REEs increase significantly and linearly with plant age, because leaves are biological sinks of mineral nutrients and REEs which accumulate during growth

Fig. 3 Bivariate plots of major and trace elements of Ca vs Sr (**a**, **b**), Mg vs Ni (**c**, **d**), Fe vs Zn (**e**, **f**), and P vs B (**g**, **h**) determined by inductively coupled plasma mass spectrometry (ICP-MS) in leaf samples from the two cultivars raised in Mizzole and Susegana vineyards. Values of major and trace elements are expressed in ppm
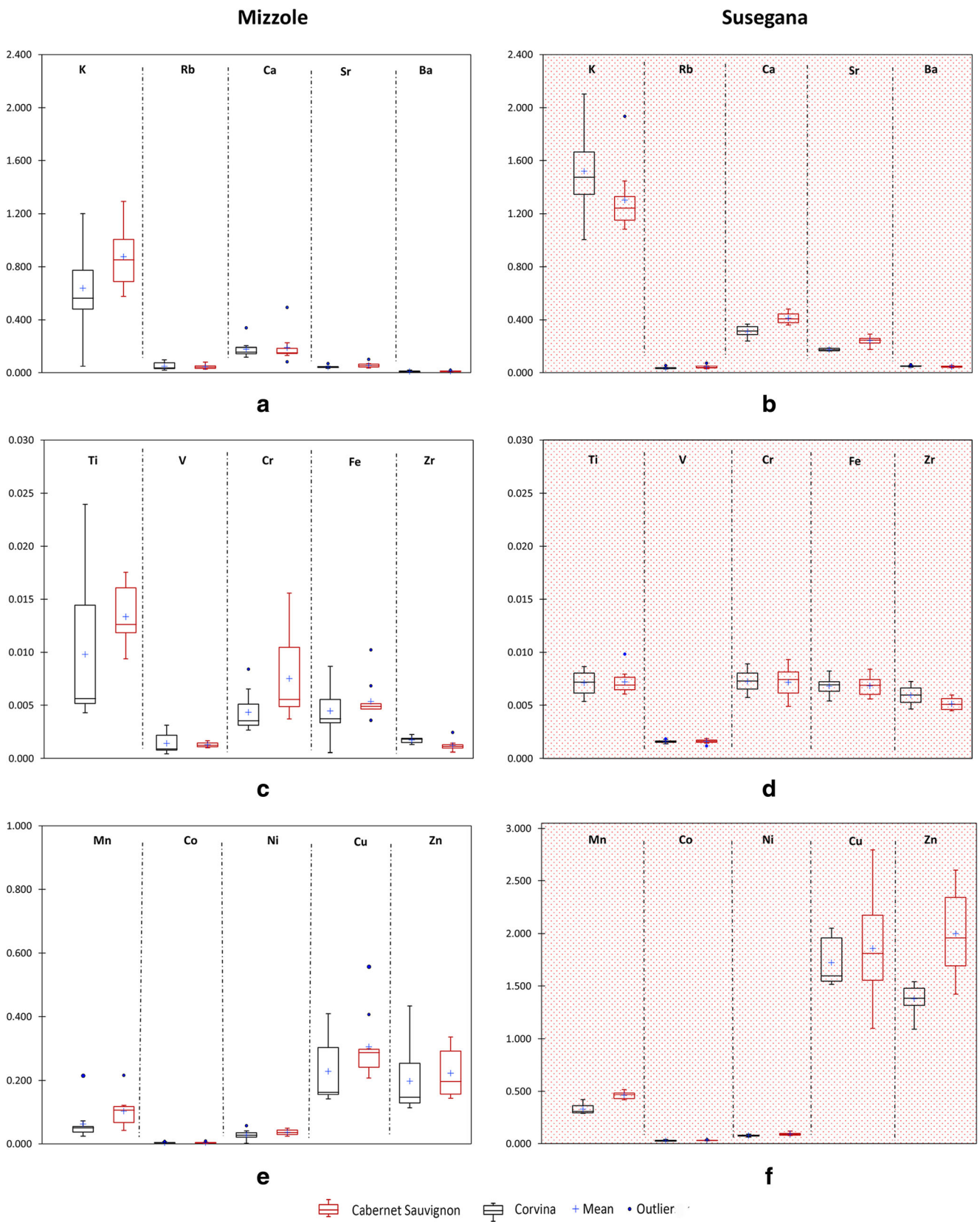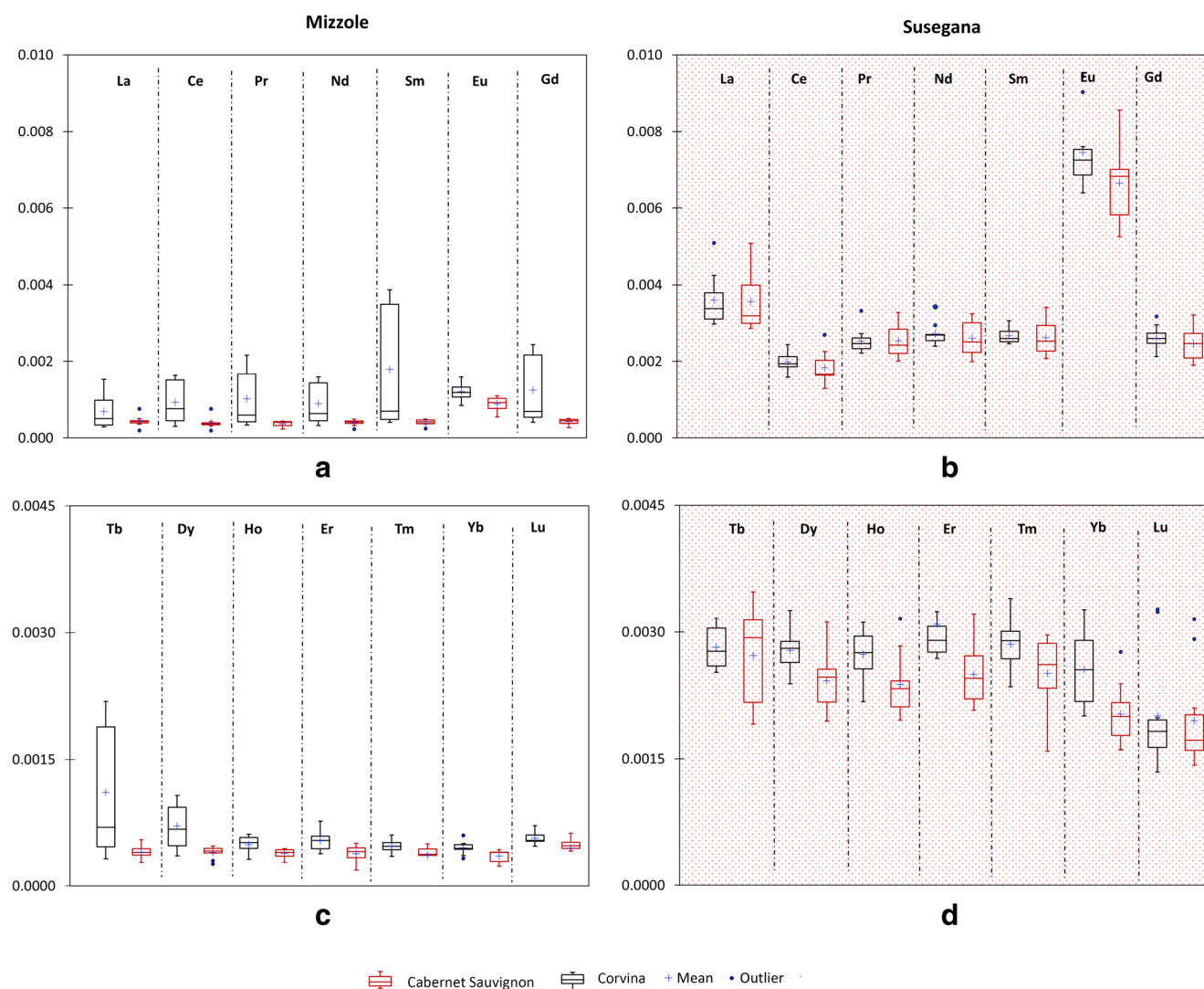
Fig. 4 Box plot of indices of bioaccumulation of the major and trace elements determined by ICP-MS in leaves of the two cultivars in Mizzole (**a**, **c**, **e**) and Susegana (**b**, **d**, **f**) vineyards. Values of major and trace elements are expressed in ppm

Fig. 5 Box plot of indices of bioaccumulation of light rare earth elements and heavy rare earth elements determined by ICP-MS in leaves of the two cultivars in Mizzole (**a**, **c**) and Susegana (**b**, **d**) vineyards. Values of rare earth elements are expressed in ppm

(Tyler 2004; Ding et al. 2005; Kabata-Pendias 2011; Brioschi et al. 2013; Censi et al. 2014). In plants, the trivalent charges and higher density of REE make them competitors of Ca^{2+} in several biological processes, interfering with the activity of calcium-dependent enzymes (Wei and Zhou 2000; Tyler 2004; Thomas et al. 2014). Among all REEs, Eu^{3+} has the highest similarity to Ca^{2+} and may easily substitute it, accumulating in aerial parts of plants (Zeng et al. 2003; Censi et al. 2014, 2017). The highest BA values of Eu^{3+} were detected in Susegana for both cultivars, in accordance to the higher Ca^{2+} concentration.

Among all REEs, the element with the highest concentration in soil and leaves was Ce, followed by La and Nd (Table 2). The concentrations of REEs were normalized according to upper crust continental (UCC) concentrations (Rudnick and Gao 2003) and the normalized distribution patterns in soil and leaves were reported in Fig. 6. In soil from each vineyard (Fig. 6a), the patterns of UCC-normalized

concentrations of REEs are characterized by a progressive decrease and by a slightly Gd-positive anomaly. In leaves (Fig. 6b), for Cabernet Sauvignon, the REE patterns of UCC-normalized concentrations are characterized in both vineyards by a progressive decrease along the light rare earth element (LREE) series and by Ce-negative and Eu-positive anomalies. However, in Corvina, the patterns of REEs in leaves are different according to the vineyard: those of Susegana follow the Cabernet Sauvignon ones, but in Mizzole, there is a progressive increase of concentrations along LREE and a decrease of high rare earth elements (HREE) concentrations, with Sm-positive and Eu-negative anomalies.

The Ce-negative anomaly in Cabernet Sauvignon (Fig. 6b) can be explained by the higher cationic charge (Ce^{4+}) of this element in comparison to all other REEs, which in soil-plant systems probably reduces the availability and uptake of Ce (Brookins 1989; Wyttenbach et al. 1998; Brown et al. 1990;
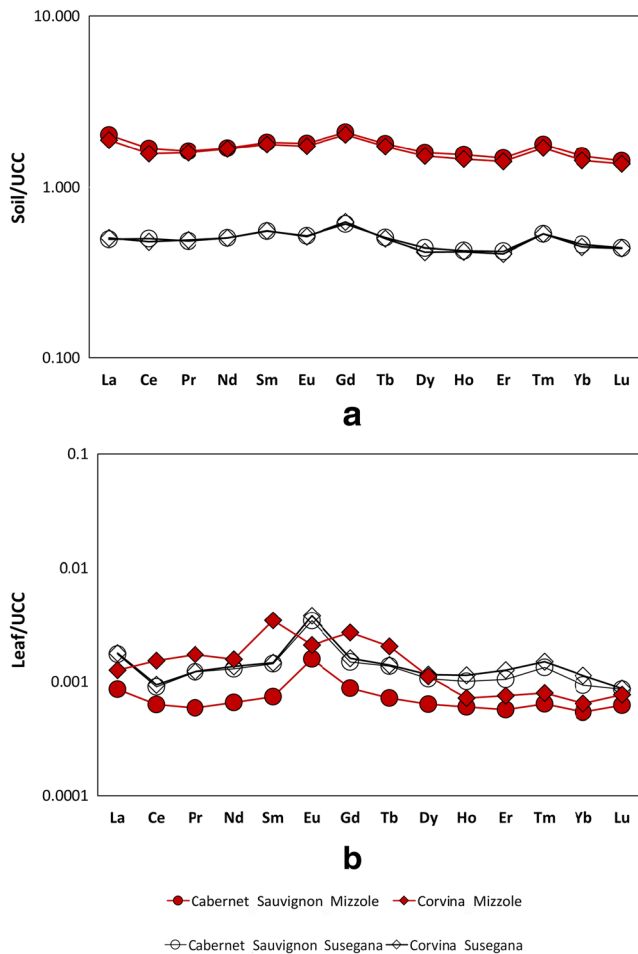
Fig. 6 Concentrations of rare earth elements determined by ICP-MS expressed in ppm and normalized by the upper continental crust values, in soil (**a**) and leaf (**b**) samples of the two cultivars from Mizzole and Susegana vineyards

REEs, but also to the fact that Eu^{3+}, the most reactive rare element, easily reduces to Eu^{2+}, increasing its ability to substitute Ca^{2+} in physiological processes (Kruk et al. 2003; Zeng et al. 2003; Censi et al. 2014, 2017). The Sm-positive anomaly suggests an environmental pollution due to an anthropogenic contamination of water used for irrigation (Brioschi et al. 2013; Kulaksiz and Bau 2013; Merschel et al. 2015).

Overall, the differences in BA profiles and distribution of REEs detected in the vineyards for Cabernet Sauvignon and Corvina, closely related to soil type and geographical origin (Tyler 2004; Kabata-Pendias 2011), suggest that they could be useful parameters to trace the geographical origin of grapes by analyses of leaves.

Correlations among elements in soil and leaf samples

The concentrations of chemical elements shown in Tables 2 and 3 were used to evaluate the correlations among all elements in soil and leaf samples for both cultivars. The concentrations in leaves were plotted against those in soil, calculating the linear regression values. Only four elements (Mg, Sm, V, and Zr) showed a significant correlation ($R^2 > 0.60$) with an internal and external 95% confidence interval (Figs. 7 and 8). In Mizzole, significant positive correlations were found for Sm in Cabernet Sauvignon and Zr in Corvina, whereas a significant negative correlation was found for V in Corvina (Fig. 7). In Susegana, a significant negative correlation was found for Mg in Cabernet Sauvignon and a significant positive one for V in Corvina (Fig. 8). The soil-leaf positive correlation for Sm could be related to the interchangeability of this element with macro and microelements, previously documented in plants (Tyler 2004; Kabata-Pendias 2011). The positive correlation of Zr could be related to the different solubility and bioavailability of Zr in soil and liquid media: in xylem,
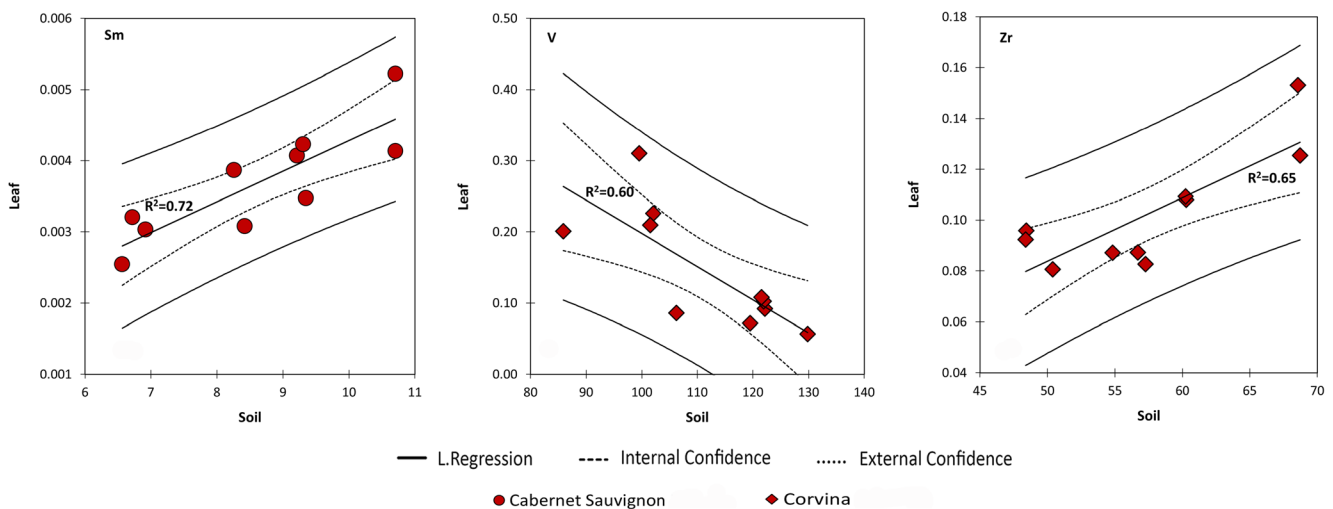
Censi et al. 2014). The Eu-positive anomaly (Fig. 3b) is related not only to the competition with Ca^{2+} similar to other

Fig. 7 Linear regression values of concentrations of Sm (**a**), V (**b**), and Zr (**c**) in soil vs leaf samples of the two cultivars from the Mizzole vineyard, showing a significant correlation ($R^2 > 0.60$) with an internal and external 95% confidence interval. Values of trace elements are expressed in ppm

Fig. 8 Linear regression values of concentrations of Mg (**a**), and V (**b**) in soil vs leaf samples of the two cultivars from the Susegana vineyard, showing a significant correlation ($R^2 > 0.60$) with an internal and external 95% confidence interval. Values of trace elements are expressed in ppm
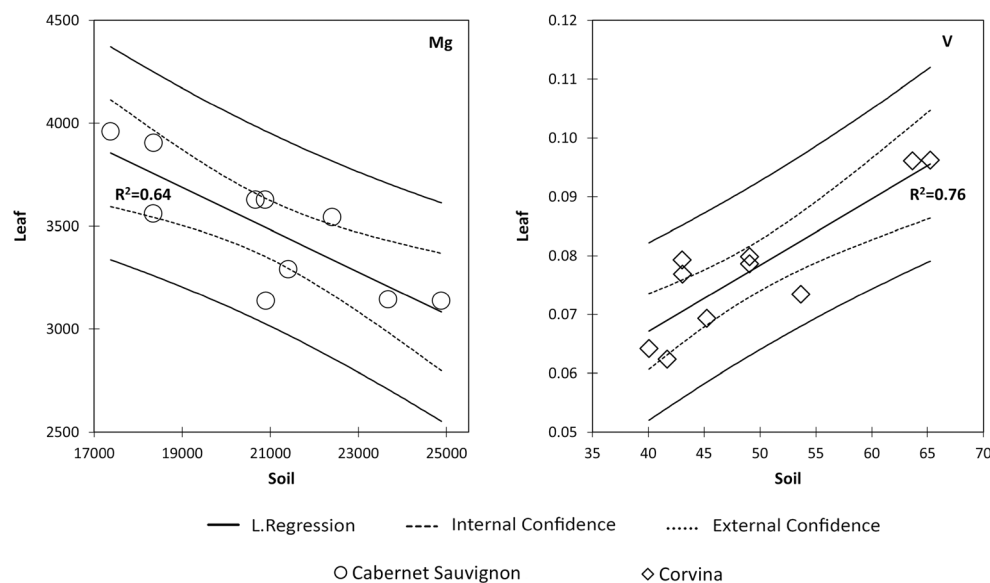
Zr may form complexes with amino acids or organic acids, or can be transferred in inorganic form (Ferrand et al. 2006; Kabata-Pendias 2011; Shahid et al. 2013). The BA values detected for Zr are in agreement with previously reported data (Shahid et al. 2013).

Concerning Mg, the negative correlation could be due to the high Ca^{2+} and K^+ in the Susegana soil, since it is known that these two elements may interfere with Mg absorption (Guo et al. 2016). The positive correlation for V in Susegana for Corvina could be explained by a soil richer in clay minerals, which may control its bioavailability (Kabata-Pendias 2011). In Mizzole, the negative correlation of V could be explained by the higher content of this soil in volcanic sediments rich in mica, pyroxene, and amphiboles with V impurities (Siena and Coltorti 1989; Hossain et al. 2014).

Overall, the significant correlation of Mg, Sm, V, and Zr between soil and leaf samples suggest the possibility to use these data to identify the geographical origin of the cultivars.

Multivariate analysis by LDA in soil and leaf samples

To establish the geochemical differences due to geographical origin and type of cultivar, the stepwise linear discriminant analysis (LDA) was applied to all data of major and trace elements in soils and leaves from the two vineyards (Tables 2 and 3) as described in the "Materials and methods" section. Among all functions calculated by the program, two were chosen as best discriminants among all data sets (Rencher 2002). Concerning the values of major and trace elements in soil shown in Table 2, the plot of the first discriminant function (F1) against that of the second one (F2) is shown in Fig. 9a. The LDA analysis is able to discriminate the soil samples according to their geographical origin, with a validation of 88.89%, confirming that it is possible to identify each winery in relation to cultivars (Fig. 9a). The highest

discrimination among soils is linked to F1, in which the elements selected (p value < 0.01) by the forward stepwise process for the discriminant plot are Mg, Mn, Co, Ti, V, Ga, Sr, Cd, Ba, Ce, and Sm.

For values of major and trace elements in leaf samples shown in Table 3, the LDA analysis in the same conditions. The elements selected by the forward stepwise process for the discriminant plot were Li, Mg, P, Ca, Ti, Mn, V, Ni, Cu, Cd, Sb, Pb, Zr, Eu, and Ho. The LDA model yielded 90.91% of sample validation for the leaf samples (Fig. 9b) and was able to discriminate all leaf groups for each winery according to their geographical origin and cultivar.

For both cultivars, Cabernet Sauvignon and Corvina, the results showed that plants accumulated elements in leaves depending on geochemical properties of the soils. The LDA multivariate analysis also enabled to discriminate the geochemical composition in relation to geographical origin of the two Mizzole and Susegana wineries. Based on LDA data, the elements useful as possible geochemical markers for Cabernet Sauvignon and Corvina are, in order of relevance are the following: Mg, Mn, Ti, V and Cd.

Conclusions

Major and trace elements in soil and leaves of *Vitis vinifera* cultivars Cabernet Sauvignon and Corvina, grafted to SO4 in the Mizzole and Susegana vineyards from the Veneto Region (Northern Italy), were evaluated as possible geographical markers. The results obtained by XRF showed that major and trace elements could be used to discriminate the two vineyards. The index of bioaccumulation based on ICP-MS analyses showed that major, trace, and rare elements were accumulated in a different way in leaves from Cabernet Sauvignon and Corvina in the two study areas.

Fig. 9 Linear discriminant analysis (LDA) plot of the concentrations of all elements in soil (**a**) and leaf samples (**b**) of the two cultivars from Mizzole and Susegana vineyards. Squares indicate the cross validation data
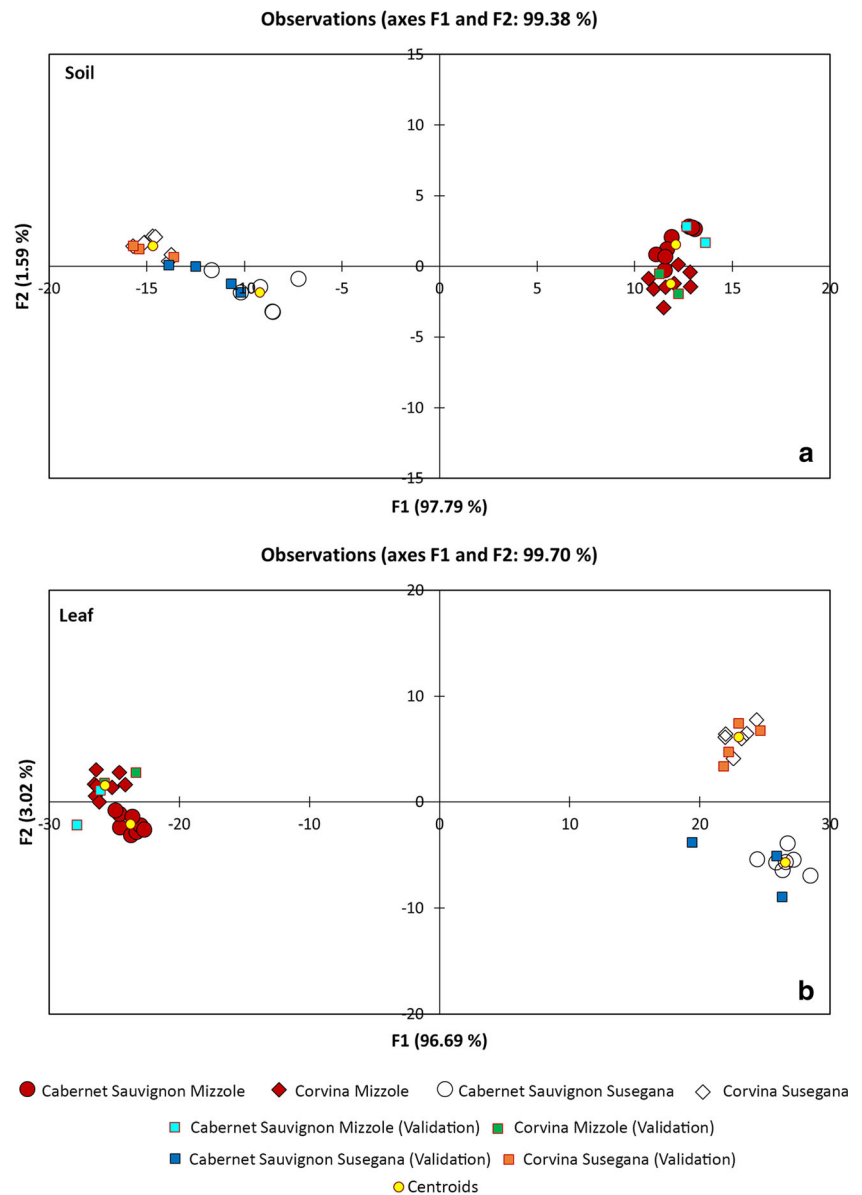
Comparing the results on soil and leaves, the elements that exhibited a high geochemical correlation were Sm in Cabernet Sauvignon and V and Zr in Corvina for Mizzole, and Mg in Cabernet Sauvignon and V in Corvina for Susegana. The LDA multivariate analysis allowed to detect geochemical correlations of other elements, Mg, Mn, Ti, V, and Cd. All the above elements, especially Mg and V, could establish a reliable correspondence between geolithological features of the vineyard soils and the chemical composition of grape leaves. Overall, these data support the use of major, trace, and rare elements as geochemical markers (geochemical fingerprints) to identify the geographical provenance of Cabernet Sauvignon and Corvina cultivars from Italian vineyards producing DOC wines, protecting the "Made in Italy" trademark according to the Italian and European laws.

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