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Grapevine rootstocks in K- and Ca-rich volcanic soils: the effect of mineral assemblage on nutrient uptake efficiency

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ABSTRACT

This study examines element mobility in volcanic soils to evaluate the relationships between mineral assemblage and the uptake capacity of rootstocks. The Gravesac rootstock, which appears to have a low capacity to selectively absorb K, Ca, Mg, and Na relative to one another, was used for this study. We analysed the chemical composition of rootstocks and the adhering soils. These soils were also mineralogically characterised and subjected to leaching using water over variable time periods and ammonium acetate. Chemical weathering of minerals significantly controls the mobility of base cations in vineyard soils and this should strongly impact root absorption and plant nutrient content. In the scarcely evolved volcanic soils (hereafter pozzolanic soils), where clinopyroxene is not significantly weathered, Ca has low availability in soil solution compared to evolved volcanic soils (hereafter clay-bearing volcanic (CBV) soils), despite higher Ca content in pozzolanic soils. This indicates that in pozzolanic soils, Ca and Mg are less mobile due to the minimal weathering of clinopyroxene. Rootstock absorption of Ca and Mg mirrors these findings, with lower uptake in pozzolanic soils despite higher total element content. Leaching experiments show that the bioavailability of Ca and Mg obtained in H_2O and ammonium acetate is inversely correlated with the uptake efficiency of rootstocks, which is instead positively correlated with the removal of Ca and Mg from the soils. In CBV soils, the intense chemical weathering of clinopyroxene increases the mobility and subsequent uptake of Ca and Mg by roots. On the contrary, leaching tests show that K bioavailability in pozzolanic soils, derived from leucite weathering, is higher than in CBV soils, which is consistent with their higher K content. The rapid dissolution of K in pozzolanic soils contrasts with its slower and more sustained release in CBV soils, linked to the weathering of phlogopite. This leads to higher K uptake in CBV soils despite their lower K content. The mineral assemblage in CBV soils, particularly the extent of phlogopite alteration, maintains high K activity in the soil solution, enhancing K bioavailability. The effect of mineral speciation (*i.e.*, the solid solution range and weathered form of a particular mineral) on the uptake efficiency of rootstocks is confirmed by the distinct chemical compositions of musts from Merlot grapes grown in the two soils. Our results highlight the pivotal role of mineral assemblage in shaping nutrient availability and rootstock uptake dynamics in viticultural systems.

KEYWORDS: rootstock, volcanic soils, Colli Albani, leucite, clinopyroxene, Gravesac, Merlot

INTRODUCTION

Relationships between textural soil characteristics, berry ripening traits, and volatile and phenolic compounds are known (De Santis *et al.,* 2017). However, finding a correlation between wine quality and nutrient content in soils appears a challenging goal (Seguin, 1986). On one hand, this correlation is hidden by the model's complexity of soil processes such as precipitation/dissolution, sorption/desorption, buffering, diffusion, and mass flow (influenced by water flow). On the other hand, the correlation between the wine composition to soil or parent rock composition is strongly demonstrated by the $^{87}Sr/^{86}Sr$ isotope ratio (Di Paola-Naranjo *et al.,* 2011; Marchionni *et al.,* 2013; Mercurio *et al.,* 2014; Tescione *et al.,* 2020). In any case, the selectivity for individual elements imposed at the absorbing root surface, as well as the mutual effect of chemical elements in inhibiting the uptake capacity of rootstocks, remains controversial (White, 2020). A commonly encountered issue in vineyards is high Na stress, which disrupts potassium-related physiological activities. In fact, a negative correlation between Na and K concentration in grape roots has been observed (Mohammadkhani *et al.,* 2015). However, certain rootstocks can withstand Na stress by restricting the uptake of Na from the soil (Chen *et al.,* 2024). Potassium deficiency can also be attributed to impaired K absorption caused by high Ca and Mg concentrations. On one hand, Ca enrichment could also inhibit Mg absorption by plants. On the other hand, excess Ca and Mg are consequences of high levels of total carbonates, active lime with high pH, and low organic matter in the soil (Yunta *et al.,* 2017). Different rootstock genotypes can have variable effects on the absorption and translocation of base cations to grapevines. Petiolar concentrations of macronutrients and micronutrients are notably influenced by the genotype of the rootstock. Comparative analyses have revealed that petiolar Na concentration remains unaffected by the rootstock genotype, whereas K, Mg, and Ca exhibit significant variations, with concentrations differing by more than two to threefold between the highest and lowest levels. Models based on the large-scale field experiments on root length distribution, measurements of exchangeable K and water balance at a given location (Gäth *et al.,* 1989), fail to adequately account for K mobilisation in the rhizosphere (*e.g.*, of sugar beet) (El Dessougi *et al.,* 2002) because of inadequate knowledge of the transfer mechanisms (Rengel *et al.,* 2008). One of the aspects that is rarely taken into account in these models is the mineral speciation. Potassium can derive from at least five mineral phases: feldspars, feldspathoids, micas, zeolites, and clay minerals (Sparks, 1987). Excluding the latter, the role of formers in the mobility of K in the soils is largely underestimated. These minerals are solid solution and their resistance to chemical weathering depends on their composition [*e.g.*, Fe/(Mg+Fe) of mica] or crystalline structure. The latter, for example, is the cause of the fast rate solubility of feldspathoids and zeolites at which should be added glasses, in the volcanic soils. This study focuses on element mobility in vineyard soils and aims to assess the relationships between mineral speciation and the uptake capacity of rootstocks. The vineyard soils are located in the Colli Albani volcanic district (Latium, central Italy) and originate from the Tufo di Villa Senni (TVS), a pyroclastic flow deposit dated to 365 ± 4 ka (Gaeta *et al.,* 2016). This deposit, with a volume exceeding 10 km³ (Freda *et al.,* 1997), consists of black to purple scoria clasts ranging in size from submillimeter to decimeter. These scoria clasts are enriched in clinopyroxene, leucite, and phlogopite and are associated with lithic clasts, within a consolidated, crystal-rich matrix. Among the lithic clasts, leucite-bearing granular rocks (*i.e.*, Italites; Gaeta *et al.,* 2000; Gaeta *et al.,* 2006; Fabbrizio *et al.,* 2018) are especially abundant. The bulk composition of the TVS ranges from phonotephritic to shoshonitic, while the rapidly cooled vitrophiric scoria clasts exhibit a K-foiditic composition (Gaeta, 1998; Gaeta *et al.,* 2021). The unique mineralogical and chemical composition of the TVS bedrock gives rise to soils containing minerals with varying resistance to chemical weathering and high concentrations of K, Ca, Mg, and Na (Gaeta *et al.,* 2022a). The uptake capacity of rootstocks in these soils is investigated using the Gravesac rootstock, a genotype that exhibits a low capacity for the fractionation of K, Ca, Mg, and Na (Gautier *et al.,* 2021). Emphasising the mineral speciation controlling the uptake capacity of rootstocks, our modelling supports the correlation between wine quality and mineral chemistry of soils or, more in general, between wine quality and geology.

MATERIALS AND METHODS

Soil and rootstock samples were collected in July 2022 at the Omina Romana farm (La Parata locality, Figure 1) on the southern slope of the Colli Albani volcano. This area is characterised by annual average temperatures ranging from 10.5 °C (minimum) to 21.9 °C (maximum), with an average yearly rainfall of approximately 1171 mm (minimum in July: 31 mm; maximum in November: 223 mm). These climate data were obtained from the RM10SPE meteorological station, located about 8 km from the study site, and are based on records from the past ten years. Soils occurring in the study site are classified as Luvic Phaeozems, according to the 1:250,000-scale soil map of Lazio (Napoli *et al.,* 2019). These soils are at an elevation between 90 and 110 m above sea level and are characterised by density values spanning from 1.01 to 1.35 g/cm³, neutral pH (6.9 ± 0.8), from low to moderate organic matter (0.70–2.55 wt%) and are rich in euhedral to subeuhedral crystals of clinopyroxene and phlogopite. In the lower topographic zones or directly above the bedrock, the soils at the study site exhibit a grey colour (Figure 1) and a high content of primary minerals—including those less resistant to chemical weathering (*e.g.,* leucite, analcime, and other zeolites)—a coarse texture, and an absence of vertical variations. These features indicate that these are scarcely evolved volcanic soils or leucite-bearing soils, as described by Gaeta *et al*. (2022b). In contrast, in the highest and flat topographic zones of the study site, brown soils are found (Figure 1). These soils are characterised by a higher amount of fine fractions, no evidence of an eluviation horizon,

low organic matter content, absence of carbonate, and the presence of primary clinopyroxene and phlogopite. These features identify them as moderately evolved volcanic soils or quartz-bearing soils, according to Gaeta *et al*. (2022b).

Ten root samples, including the adhering soil; were taken from the two previously described soils at a depth of 40 cm. The four plants sampled for this work are Merlot scions grafted onto Gravesac rootstock. The roots were taken at a similar diameter (2–4 mm) and collected from the lateral zone of the rootstocks and divided into two subsamples: one was immersed in a 50 mL Falcon tube containing 70 % alcohol for immediate cell fixation, while the other was placed on paper sheets to dry and subsequently frozen at –80 **°C.** The fixed roots were used for histological analysis to highlight any cyto-histological differences in the organ's tissues due to the different soil conditions. The frozen samples were used for chemical analysis to identify the elements present in the root cells and compare them with the chemical composition of the soil. To obtain the mineral and chemical compositions of the soils in contact with the analysed roots, the soil adhering to the roots was collected and quartered.



FIGURE 1. a) Location of vineyards within the landscape of the Colli Albani Volcanic District; b) macroscopic appearance of pozzolanic soils; c) macroscopic appearance of clay-bearing volcanic soils.

The mineral and chemical analyses were performed in the laboratories of the Earth Sciences Department and the Chemistry Department of the Sapienza University of Rome. X-ray diffraction analysis of bedrock and soils was conducted using a Bruker D8 Advance X-ray system equipped with Lynxeye XE-T silicon-strip detector. The instrument was operated at 40 kV and 30 mA using CuKα radiation (λ = 1.5406 Å). Samples were run between 2 and 70◦ 2θ with step sizes of 0.02◦ 2θ while spinning the sample. Data were collected with variable slit mode to keep the irradiated area on the sample surface constant and converted to fixed slit mode to identify whole-powder composition. The relative abundance of minerals was estimated by calculating peak areas and using mineral intensity factors as calibration constants (Moore & Reynolds, 1997). The sample treatment and elemental analysis of rocks, soils, and roots were carried out by previously published methods (Astolfi *et al.,* 2017; Conti *et al.,* 2023; Gaeta *et al.,* 2022a; Gaeta *et al.,* 2022b). Briefly, total acid digestion of rock, soil, and root samples was performed by microwave-assisted acid digestion using the Ethos1 Touch Control system (Milestone, Sorisole, Bergamo, Italy). About 0.1 g of rock or soil or 0.2 g of root was mixed with 3 mL HNO_3 (superpure; Carlo Erba Reagents, Milan, Italy), 1 mL HF (suprapure; Merck, Darmstadt, Germany), and 1 mL HCl (superpure; Carlo Erba Reagents, Milan, Italy), or 4 mL HNO_3 and 2 mL H_2O_2 (suprapure; Merck, Darmstadt, Germany), respectively, in a 100 mL polytetrafluoroethylene (PTFE) vessel, and then heated to 180 °C with microwave energy (at a power of 1000 W) for 40 min (Conti *et al.,* 2023; Gaeta *et al.,* 2022a; Gaeta *et al.,* 2022b). At the end, cooled samples were diluted to 10 mL of deionised H_2O (resistivity, ≤18.3 MΩ cm) and filtered (GVS Filter Technology, Indianapolis, USA; pore size, 0.45 mm). For the soil leaching tests, ~0.5 g of the samples were mixed with 10 mL deionised H_2O or 1.0 M CH_3COONH_4 (Merck, Darmstadt, Germany) (Gaeta *et al.,* 2022a; Gaeta *et al.,* 2022b). The samples were left under mechanical stirring for 1 and 16 h (water leaching) and 24 h (total soils, roots, and ammonium acetate leaching) by a rotary shaker (SB2, Cheimika, SA, Italy) at room temperature (21 °C). The extracted solutions were filtered and mixed with 1 % HNO_3. All the obtained solutions were analysed for 11 elements (Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti) by inductively coupled plasma emission spectrometry with optical detection (ICP-OES; Vista-MPX CCD Simultaneous, Varian, Victoria, Mulgrave, Australia). The ICP-OES operating parameters were reported elsewhere (Astolfi *et al.,* 2017). Calibration standards of all elements were prepared daily by diluting a single standard solution at 1000 mg/L (Merck, Darmstadt, Germany). Yttrium at 0.5 mg/L (from 1000 ± 2 mg/L; Panreac Química, Barcelona, Spain) was used as an internal standard for all measurements. The following wavelengths (nm) were used: Al 396.152, Ba 233.527, Ca 315.887, Fe 238.204, K 766.491, Mg 279.800,

Mn 257.610, Na 588.995, P 185.878, Si 251.611 and Ti 334.941. The analysed soil and root samples are relatively few (ten soil samples adhering to the roots and ten root samples), which does not allow for a detailed statistical analysis beyond the standard deviation. Nevertheless, the maximum and minimum values relative to the average indicate that the analytical differences are significant (Figure S1 and S2).

Chemical analyses of petioles and blades were not conducted in this study. However, the uptake capacity of the studied rootstocks was compared using the K and Ca contents of musts obtained from Merlot grapes (harvest 2022) grafted onto the sampled rootstocks. The must was obtained by combining the grape clusters from all the analysed plants and was analysed in the OMINA laboratory using the Hyperlab Smart multiparametric analyzer. The Merlot musts consist of only two samples (one for each soil type), which makes it impossible to perform statistical tests (*e.g.,* standard deviation). Nevertheless, the musts obtained from the studied vines were compared with those from control vines grown in the two different soil types.

The procedure described by Bozzano *et al*. (2006) was used to calculate the mass of 'immobile' and 'mobile' elements. Using Al as the immobile element, the mobility coefficient ($^{M}C_{m}$) values for the other elements were determined, along with the variation in total percentage mass ($\sum M\%$) at constant volume and the contribution of individual elements to the mass variation (ΔM_m). The following equations were applied:

$$^{M}C_m = (E_i^B \cdot E_m^S / E_m^B \cdot E_i^S);\ \sum M=(E_i^S/E_i^B-1);\ \Delta M_m = E_m^B \cdot((E_i^B \cdot E_m^S / E_m^B \cdot E_i^S)-1)$$

where E = element; m = mobile element; i= immobile element; B = bedrock; S = pozzolanic or CBV soils.

RESULTS

1. Mineral and chemical composition of soils

The root-adhering soils analysed in this study exhibit mineralogical characteristics (Table 1) identical to those described by Gaeta *et al*. (2022a) and Gaeta *et al*. (2022b) for samples collected in the La Parata locality (Figure 1). These volcanic soils from the Colli Albani are composed of both primary minerals (*e.g*., those inherited from the bedrock) and secondary minerals (e.g., those formed through alteration and not present in the bedrock). Among the primary minerals, leucite, analcime, chabazite, and phillipsite are particularly prominent in pozzolanic soils—an informal term used in the *terroir*, corresponding to the leucite-bearing soils described by Gaeta *et al*. (2022a) and Gaeta *et al*. (2022b). These soils differ from the bedrock due to their higher abundance of analcime (Table 1). Pozzolanic soils also contain minor amounts of secondary minerals, such as halloysite. The CBV soils—another informal term used in the *terroir*, corresponding to the quartz-bearing soils described by Gaeta *et al*. (2022a) and Gaeta *et al*. (2022b) are predominantly characterised by secondary minerals, including quartz, alkali feldspar (K-feldspar and albite), halloysite, smectite, and hematite, which collectively make up more than 70 wt% of the total composition (Table 1). These soils also contain weathered primary minerals, such as phlogopite and clinopyroxene, whose abundances are lower compared to those in Pozzolanic soils. Notably, the differences in the average abundances of phlogopite and clinopyroxene, as reported in Table 1, are statistically significant (P-value < 0.05, calculated using the Student's t-test). Prismatic crystals of clinopyroxene without weathering features are common in pozzolanic soils. On the other hand, weathered clinopyroxenes, characterised by a "gothic" texture (Gaeta *et al.,* 2022b), are common in CVB soils. The intense weathering of clinopyroxene, as well as those of phlogopite in the CBV soils is proved by X-ray diffraction analysis that indicates the decrease of these two minerals in the CBV soils respect their abundance in the bedrock (Table 1). Moreover, the position of the peak corresponding to (001) basal planes indicates that the weathering of phlogopite in the CBV soils causes structural changes in the mica. Actually, the weathered phlogopite in the CBV soils shows a shorter distance between the (001) crystallographic planes than the phlogopite from the pozzolanic soils with the migration of the first-order basal peak toward higher 2 Θ values (Gaeta *et al.,* 2022a). The weathered phlogopite is also characterised by a negative correlation between K and H_2O (Figure 2), as well as, between Fe and H_2O, whereas Ca is positively correlated with H_2O (Table 2). Both soil groups exhibit different chemical compositions, with lower Si, Ca, Na, K, and higher Al, Fe, and total water contents than the bedrock (Table 3). These differences are minor between the bedrock and the pozzolanic soils but are significant both between the CVB soils and the bedrock and between the two soil types (Table 3 and Figure S1). In fact, the CVB soils are characterised by a significant decrease in Mg, Ca, Na, K, and P, along with a strong Al enrichment compared to the bedrock (Table 3 and Figure S1). The chemical changes induced by the chemical weathering of bedrock and its conversion to pozzolanic and CBV soils can be quantified by mass balancing of

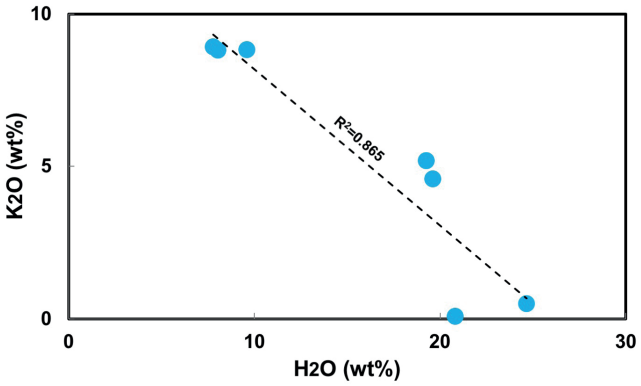


FIGURE 2. K and H_2O contents in weathered phlogopite of clay-bearing volcanic (CBV) soils of Colli Albani; linear equation: y = –0.513x+13.31.

TABLE 1. Mineralogical composition (wt%) of vineyard bedrock, soils, and soils adhering to roots.

RT/ST	Primary minerals								Secondary minerals					
	Anl	Lct	Cpx	Phl	San	Php	Ap	Cbz	Qz	Kfs	Ab	Hal-7	Sm	Hem
TVS bedrock	15	14	27	18	2	18	tr	6						
Pozzolanic soils	[a]38	4	13	25	2	10		5				3		
	(10)	(2)	(6)	(11)	(1)	(5)		(3)				(1)		
	[b]33	7	15	19	2	15	1	3				4		
CBV soils			[c]11	13					38	13	4	18	2	
			(8)	(7)					(16)	(4)	(2)	(7)	(2)	
			[d]3	6					66	10	4	9	1	1

[a]Average composition of 5 soil samples adhering to the roots; [b]representative analysis of pozzolanic soils (sample PA11 after Gaeta *et al* 2022a); [c]average composition of 5 soil samples adhering to the roots; [d]representative analysis of clay-bearing volcanic (CBV) soils (sample PA12 after Gaeta *et al.*, 2022a); ( ) standard deviation; RT/ST: rock type/soil type; Anl: analcime; Lct: leucite; Cpx: clinopyroxene; Phl: phlogopite; San: sanidine Php: phillipsite; Ap: apatite; Cbz: chabazite; Qz: quartz; Kfs: K-feldspar; Ab: albite; Hal-7: halloysite-7Å; Sm: Sm/mixed layers; Hem: hematite.

TABLE 2. Chemical analyses (wt%) of weathered phlogopite in the CBV soils (each column refers to different phlogopite crystals).

	CVB1			CVB2			
SiO_2	34.94	34.97	34.46	35.52	34.54	34.89	34.65
TiO_2	2.44	2.29	2.62	3.04	2.33	2.46	2.44
Al_2O_3	16.23	16.27	15.22	16.14	16.31	14.54	14.76
FeO	12.17	9.35	9.50	10.55	9.80	7.03	6.91
MnO	0.23	0.08	0.13	0.10	0.14	0.06	0.05
MgO	16.35	18.09	12.31	17.15	11.57	19.01	14.43
CaO	0.04	0.04	0.72	0.02	0.58	0.71	1.04
Na_2O	0.19	0.14	0.17	0.22	0.15	0.03	0.07
K_2O	8.93	8.84	5.19	8.81	4.60	0.07	0.48
F	0.68	0.33	0.40	0.42	0.39	0.41	0.50
Total	92.22	90.41	80.75	91.97	80.40	79.20	75.35
H_2O*	7.78	9.59	19.25	8.03	19.60	20.80	24.65

Analyses were obtained with an electron probe microanalyzer following the analytical procedure of Palummo *et al.* (2024). *Calculated with the difference method: H_2O = 100-Total.

"immobile" and "mobile" elements (Bozzano *et al.,* 2006). In our mass-balance computation, the "immobile" element is an element whose concentration passively changes as a result of weathering, depending on whether other elements, *i.e.*, the "mobile" elements, migrate into or away from the soil mass. Element mobility was inferred by graphic/analytical methods by comparing the concentrations of the analysed elements in x–y diagrams. Al, Fe, and Ti are the least mobile elements, as demonstrated by the high value of the regression coefficient ($r^2 = 0.93$) of the related regression lines passing through axes origin. Magnesium, Ca, K, P, and Mn are mobile elements as indicated by the absence of correlation with the origin of the axes in the covariation diagrams. However, pozzolanic and CBV soils show different element mobility as indicated by the comparison of K vs Al and Mg vs Al diagrams where K appears mobile in both types of soils, whereas Mg is mobile just in CBV soils. After taking Al as a reference for the immobile element, the mass balance of the "immobile" and "mobile" elements indicates that Si, Mn, Mg, Ca, Na, K, and P are mobile. The average negative balance for all these components in the analysed soils is indicated by $^{M}C < 1$ (Table 4); the average degree of mobility, which increases as $^{M}C_m$ decreases, following this trend K > Na = Ca > Mg > Mn > P > Si. Specifically, the transition from bedrock to pozzolanic soils is marked by significant mobility of K and Si, as illustrated in Figure 3 and Table 4. The depletion of these elements (±Ca, ±Na) leads to a mass reduction of 4–6 %, calculated using the compositions of average root-

TABLE 3. Bulk compositions (g/kg) of bedrock, soils, and soils adhering to roots.

	Bedrock		Pozzolanic soils				CBV soils		
	A1	σ	B1	A2	B2	σ	A3	B3	σ
	(8)				(5)			(5)	
Si	227	2.6	217	209	208	3.1	203	193	5.8
Al	97	3.3	88	94	92	2.1	129	127	3.7
Fe	54	4.2	53	59	56	7.6	73	74	6.2
Mn	1	0.1	1	1	1	0.2	1	1	0.2
Mg	19	1.8	18	20	19	2.0	4	6	1.2
Ca	57	3.5	58	58	56	3.3	4	9	2.9
Na	21	5.0	18	14	19	2.9	2	2	0.3
K	37	8.3	35	23	20	1.7	9	9	1.5
Ti	5	0.3	5	5	5	0.6	6	7	1.1
P	2	0.1	2	2	2	0.2	1	1	0.2
LOI	44	5.8	90	103	115	7.6	176	187	0.6

A1: average of 8 analysis of TVS (outside of studied vineyard); A2: representative analysis of pozzolanic soils (sample PA11 after Gaeta *et al.* 2022a); A3: representative analysis of clay-bearing volcanic (CBV) soils (sample PA12 after Gaeta *et al.* 2022a); B1: analysis of the TVS bedrock, in the studied vineyard; B2 and B3: analyses of 5 soils in contact with the analysed rootstocks. LOI: loss of ignition. σ: standard deviation. () number of analyses.

TABLE 4. Mobility coefficients ($^{M}C_{m}$) of chemical elements in soils and contribution of individual elements to mass variation ΔM_{m} in g/kg), calculated assuming Al as an immobile element.

	Pozzolanic soils				CVB soils			
	$^{M}C_{m}$		ΔM_{m}		$^{M}C_{m}$		ΔM_{m}	
Si	0.91	0.92	–19.0	–17.5	0.64	0.62	–77.3	–82.2
Al	1.00	1.00	0.0	0.0	1.00	1.00	0.0	0.0
Fe	1.04	1.00	2.1	–0.1	0.94	0.97	–3.3	–1.6
Mn	0.98	0.90	0.0	–0.1	0.47	0.60	–0.6	–0.4
Mg	1.07	1.02	1.2	0.3	0.17	0.22	–14.5	–13.6
Ca	0.94	0.93	–3.7	–4.2	0.05	0.11	–55.6	–51.8
Na	0.76	1.02	–4.2	0.4	0.07	0.08	–16.5	–16.5
K	0.61	0.55	–13.9	–15.8	0.17	0.18	–29.4	–28.9
Ti	1.06	0.99	0.3	–0.1	0.93	0.98	–0.3	–0.1
P	1.03	0.98	0.1	0.0	0.22	0.40	–1.5	–1.2

The mobility coefficients ($^{M}C_{m}$) and element depletion (ΔM_{m}) in the vineyard soils relative to the vineyard bedrock (B1 in Table 3) are calculated following the method of Bozzano *et al.* (2006), using Al as the immobile element and the average compositions of the pozzolanic (B2 in Table 3) and CBV soils (B3 in Table 3).

adhering soils (B2 in Table 3) and representative pozzolanic soil (A2 in Table 3). The $^{M}C_{Mg,P}$~ 1 (Table 4) indicates that clinopyroxene, phlogopite, and apatite are scarcely weathered in the pozzolanic soils. Potassium is highly mobile ($^{M}C_{K}$ = 0.6; Table 4), with a large depletion (42 %) with respect to the original content in the bedrock, caused by the weathering of leucite that is largely turned in analcime (Table 1). According to the buffer effect of analcime crystallisation, Na exhibits a relatively low mobility ($^{M}C_{K}$ = 0.9; Table 4) in pozzolanic soils with its content that remains constant or slightly decreases with respect to the bedrock. Consequently, the reaction of leucite-dissolution and analcime-crystallisation leads to an increase in the activity of both K and Si in the circulating soil fluids, resulting in an excess of silica moles. In CBV soils, in addition to K and Si, Mg ($^{M}C_{Mg}$ = 0.1), Ca ($^{M}C_{Ca}$ = 0.1), Na ($^{M}C_{Na}$ = 0.2), and P ($^{M}C_{P}$ = 0.3) become highly mobile (Table 4) due to the chemical weathering of primary minerals with a large depletion from the CBV soils (Figure 3).

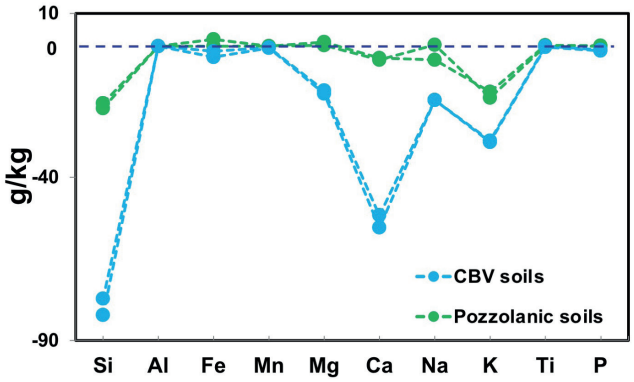


FIGURE 3. Element depletion in the vineyard soils relative to the parent composition of the vineyard bedrock (represented by the black dashed line) calculated following the method of Bozzano et al. (2006), using Al as the immobile element (see the text for details). Transitioning from bedrock to pozzolanic soils, K and Si are the main elements removed. In CBV soils, Mg, Ca, Na, and P are also depleted. The green and blue lines represent the element depletion calculated using the average values of the five soils in contact with the roots (B2 and B3 in the Table 3) and the representative soil sample (A2 and A3 in the Table 3), respectively.

Leaching experiments indicate that equilibrium conditions between water and soil are rapidly achieved (< 12 h) and confirm that element mobility is not dependent on the absolute concentration of elements in the soil (Figure 3). Indeed, in accordance with the high mobility in the CBV soils (Table 4 and Figure 3), Mg and Ca are released in greater quantities in leaching experiments conducted on CVB soils, despite the latter presenting significantly lower abundances of Mg and Ca with respect of pozzolanic soils (Table 3).

2. Root analyses and must compositions

Histological analyses display a few differences between the Gravesac rootstock growth in the two soil types. In particular, the rootstocks grown in CBV soils (R1 hereafter) show more evident raphides, druses, and prisms of Ca oxalate with respect to the rootstocks grown in pozzolanic soils (R2 hereafter). Additionally, the rootstock chemical analyses (Table 5) indicate that R1 and R2 are different in composition. On the one hand, the relatively low number of analyses does not allow for a deep statistical approach. On the other hand, the maximum and minimum values relative to the average values reported in Table 5 indicate significant differences between R1 and R2 (Figure S2). In R1, we observe Ca > K > Al > Mg > Fe > Na > Mn, whereas in R2, we have Ca > K > Al > Mg > Si > Fe = Na > Mn. In both cases, Al is relatively abundant, with concentrations lower than those of Ca and K, but always higher than those of Si, that in R1 is lower than the instrumental error. The distribution of elements between root (r) and soil (s), calculated by dividing the average element content in the roots (Table 5) by the average element content in the soils adhering to the roots (Table 3), indicated below as $^{i}D_{r/s}$ (i = element of interest), changes in the two soil types. Rootstocks R1 in CBV soils show higher $^{i}D_{r/s}$ ratios of base cations than those calculated for the rootstocks R2 grown in pozzolanic soils (Figure 5). In particular, the $^{Ca}D_{r/s}$ of R1 in CBV soils has the highest absolute value (0.74) and is approximately 5 times higher than the $^{Ca}D_{r/s}$ = 0.16 of R2 in pozzolanic soils. Similar differences are observed for $^{Na}D_{r/s}$ and $^{Mg}D_{r/s}$, respectively, 5 and 3 times higher in R1 grown in CBV soils. The $^{K}D_{r/s}$ are relatively similar. Silicon, Al, Fe, and Mn exhibit an opposite behaviour, being more effectively partitioned (*i.e.*, higher $^{i}D_{r/s}$ values) in R2 grown in pozzolanic soils. Ammonium acetate extraction of base cations (Table 5) provides similar indications to the distribution of elements between root and soil, except K. The ratio between elements extracted with ammonium acetate and those contained in the soil ($^{i}D_{am/s}$) indicates a greater ease

TABLE 5. Average compositions (mg/kg) of the rootstock roots and base cations extracted with ammonium acetate from the vineyard soils.

	Rootstocks				Ammonium acetate leaching			
	R1: roots in the CVB soils		R2: roots in the pozzolanic soils		CBV soils		Pozzolanic soils	
		σ		σ		σ	σ	σ
Si	-	-	1580	(273)				
Al	1673	(110)	3258	(108)				
Fe	990	(62)	1190	(37)				
Mn	13	(1)	27	(1)				
Mg	1454	(38)	1665	(7)	834	(5)	331	(18)
Ca	6879	(340)	9248	(460)	2735	(34)	5150	(257)
Na	530	(13)	1114	(32)	303	(101)	803	(69)
K	2428	(25)	3926	(461)	156	(13)	2237	(265)
Ba	645	(36)	43	(1)				

*σ: standard deviation calculated on five analyses.

TABLE 6. Composition of musts obtained from Merlot grapes (harvest 2022) grafted onto the Gravesac rootstocks.

Soil type		Sugar (g/l)	TA (g/l)	pH	MA (g/l)	YAN (mg/l)	FAN (mg/l)	AN (mg/l)	Ca (mg/l	K (g/l)
CBV	A	246	2.6	4.17	1.01	59	46	13	66	1.66
	B	231	2.8	3.97	0.75	67	52	15	55	1.60
Pozzolanic	A	258	4.1	3.59	0.31	67	41	26	57	1.51
	B	240	4.0	3.54	0.28	79	46	33	52	1.48

A: Merlot grapes grafted onto the analysed rootstocks; B: comparative Merlot musts; TA: tartaric acid; MA: malic acid; YAN: yeast assimilable nitrogen; FAN: free amino nitrogen; AN: ammoniacal nitrogen.

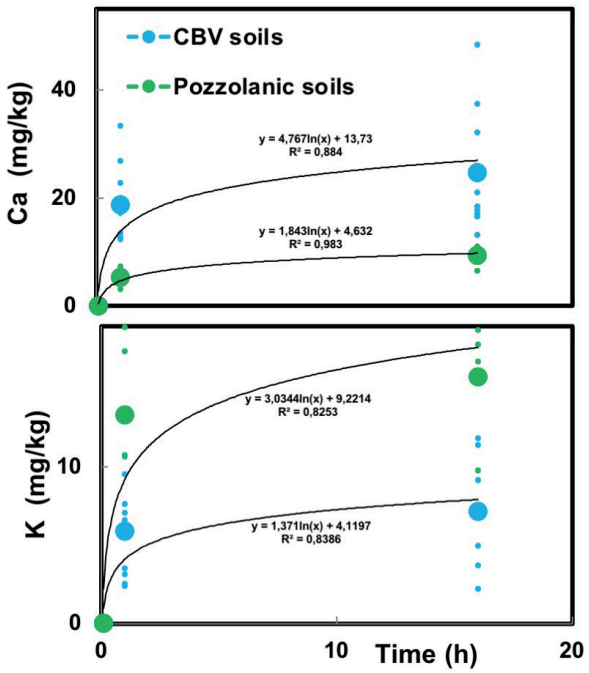


FIGURE 4. 1-h and 16-h-long leaching experiments in deionised water performed on the pozzolanic and clay-bearing volcanic (CBV) soils.

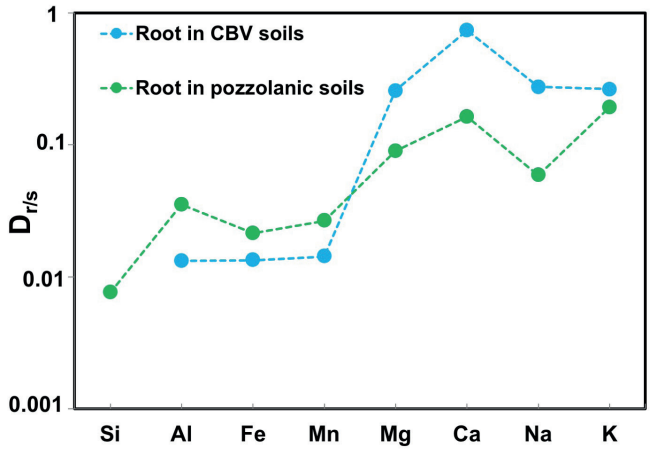


FIGURE 5. Distribution of elements Dr/s between root (r) and soil (s), for rootstocks grown in clay-bearing volcanic (CBV) and pozzolanic soils, respectively. The Dr/s ratios are calculated by dividing the average element content in the roots (Table 5) by the average element content in the soils adhering to the roots (Table 3).

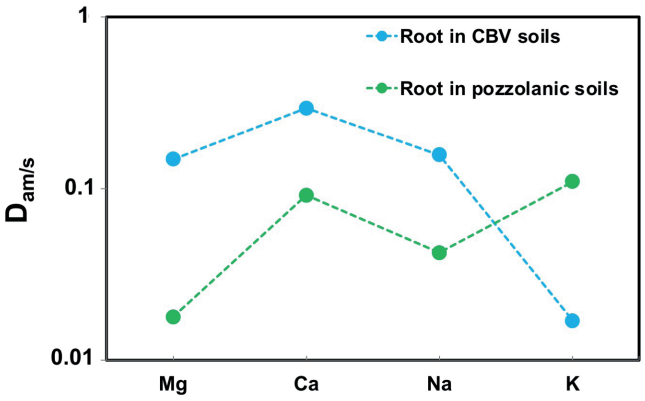


FIGURE 6. Distribution of elements Dam/s between those extracted with ammonium acetate (am) and those contained in clay-bearing volcanic (CBV) and pozzolanic soils, (s). The Dam/s ratios are calculated by dividing the average data of the ammonium acetate extraction (Table 5) by the average element content in the soils adhering to the roots reported in Table 3.

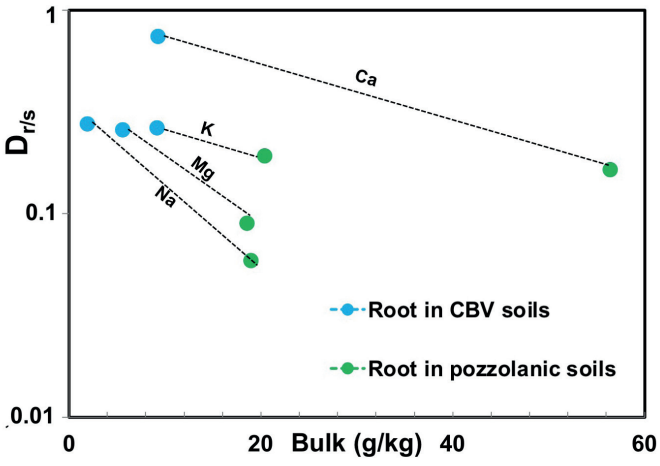


FIGURE 7. Covariation diagram showing the rootstock's capacity to extract base cation, expressed through Dr/s, vs the Ca, Mg, K and Na contents in the clay-bearing volcanic (CBV) and pozzolanic soils (B3 and B2 in Table 3, respectively).

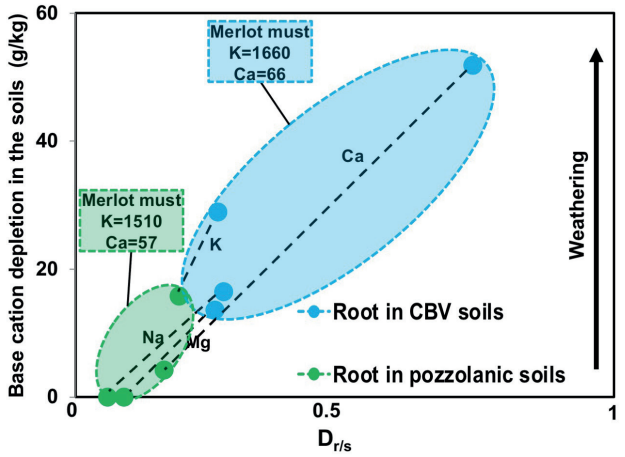


FIGURE 8. Covariation diagram showing the relationship between base cation removal from soils due to weathering (ΔMm in Table 5) and the rootstock's capacity to extract K, Ca, Mg, and Na expressed as Dr/s. The K and Ca contents (mg/L) measured in the musts from Merlot grapes grown on the studied rootstocks (Table 6) are also indicated in the coloured rectangles.

of Mg, Ca, and Na extraction from CBV soils. Conversely, the $^{K}D_{am/s}$ values are inverted, with pozzolanic soils exhibiting higher K release capacity than CBV soils (Figure 6). The must obtained directly from Merlot vines grafted onto Gravesac rootstock showed slight compositional differences (Table 6) that are peculiarly correlated with soil composition. Specifically, the Ca and K content in the musts from vines on pozzolanic soils is lower compared to the musts from vines on CBV soils, even though pozzolanic soils are richer in Ca and K.

DISCUSSION

In the soils of the Colli Albani, which derive from volcanic substrates with low glass content and low to moderate organic matter content and halloysite, the cation exchange capacity is not controlled by organo-clay mineral colloids but in large part by the primary mineralogical speciation (Gaeta *et al.,* 2022a). Leaching experiments (Figure 4) confirm that element mobility is not dependent on the absolute concentration of elements in the soil but on the chemical weathering of mineral species. In pozzolanic soil where clinopyroxene is unaltered, Ca is experimentally leached in lower amounts compared to CBV soils, despite pozzolanic soils having higher Ca content. In fact, Ca is scarcely mobile in pozzolanic soils (Table 4) because the clinopyroxene, the source of this element, is minimally weathered or unaltered. The absorption of Ca, as well as Mg, by Gravesac rootstocks, is consistent with leaching experiments in H_2O: roots in pozzolanic soils take up Ca and Mg with minor efficiency (Figure 5) even though the absolute quantity of these elements in the soil is higher (Table 3). Similar evidence is from leaching tests with ammonium acetate, showing lower Ca and Mg bioavailability in pozzolanic soils (Figure 6). However, Ca and Mg absolute content in the soil, as well as Ca and Mg amounts extracted with ammonium acetate, are inversely correlated with the rootstock's capacity to extract the elements, expressed through $^{Ca}D_{r/s}$ and $^{Mg}D_{r/s}$ (Figure 6). Conversely, $^{Ca}D_{r/s}$ and $^{Mg}D_{r/s}$ are directly correlated with Ca and Mg amounts removed from the soils as mobile elements (Figure 8). Specifically, in CBV soils, the weathering extent of clinopyroxene makes Ca and Mg extremely mobile, leading to their significant removal from the soil. Rootstock absorption of Ca and Mg appears to be controlled by the mobility of these elements, which in turn depends on the chemical weathering of the soil matrix. Rootstocks in CBV soils, which have lower Ca and Mg contents than those observed in pozzolanic soils, show higher $^{Ca}D_{r/s}$ and $^{Mg}D_{r/s}$ due to an advanced stage of clinopyroxene weathering. Noteworthy, the rootstocks grown in CBV soils are characterised by more abundant raphides, druses, and prisms of Ca oxalate. When looking at K, leaching tests in ammonium acetate and water provide different indications than those observed for Ca and Mg. Based on ammonium acetate leaching, the weathering reaction of leucite leads to a greater amount of bioavailable K in pozzolanic soils than in CBV soils (Figure 6), thus reflecting the absolute quantities of K in the two soils. Similar results are obtained in the time-dependent H_2O leaching experiments, from which K mobility is directly correlated with the abundance of the element in the soil (Figure 4). Furthermore, in the 1-hour-long experiments, the amount of K leached from the pozzolanic soil was almost double that leached from the CBV soil (Figure 4). Potassium removal is therefore a very fast process and should be considered independent of soil grain size, as the tests were carried out with grains of similar diameter (< 20 mm). The high rate of K dissolution in the pozzolanic soils is due to the mineral assemblage of the matrix because any analysis of element mobility in the soils must take into account the rates of formation of secondary minerals as well as the dissolution of primary phases (Lasaga *et al.,* 1994). The pozzolanic soils are characterised by not-weathered phlogopite (*i.e.*, with stoichiometric composition and abundance similar to those in the bedrock; Table 1) and analcime that originates from the reaction Lct + Na + H_2O = analcime. This reaction represents the main alteration mechanism, which begins in the syn-depositional eruptive phase (*i.e.*, at relatively high T) (Gaeta *et al.,* 2022a), continues at ambient temperature, and leads to the formation of the pozzolanic soils of Colli Albani. The leucite to analcime conversion is a reaction with low activation energy (65 ± 5 kJ/mol) and is fast even at low temperatures (~40 °C, Putnis *et al.,* 2007). However, despite the high rate of K dissolution, the $^{K}D_{r/s}$ of roots in the pozzolanic soil is lower than that of the roots in CBV soils (Figure 5). The lower $^{K}D_{r/s}$ of roots in the pozzolanic soils is due, on one hand, to the rapid reaction of analcime formation, which quickly removes leucite from the soil (Gupta *et al.,* 1975). On the other hand, it is due to the absence of mineralogical phases i) metastable minerals resulting from the alteration reaction of leucite and/or ii) newly formed K phases. The overall effect of the absence of these mineralogical phases is to increase the rate of K removal from aqueous solutions in pozzolanic soils. This effect, in turn, leads to $^{K}D_{r/s}$, decrease,

i.e., the root's capacity to extract K. The effect of mineral assemblage on the K uptake of the Gravesac rootstock is very evident even in CBV soils. In these soils, the rootstock has a higher Ba content than that in pozzolanic soils (Table 5). Barium, which is strongly partitioned in the phlogopite of the bedrock (Gaeta *et al.,* 2000), indirectly indicates that phlogopite is the main source of K for the roots in CBV soils. In fact, in CBV soils, there is a decrease in phlogopite content, whose abundance becomes less than half when compared to volcanic soil. Moreover, leucite and K-bearing zeolites are absent, and the alkali feldspar appears stable, as indicated by the increase of its abundance moving from pozzolanic to CBV soils (Table 1). Despite the absence of easily soluble K minerals, such as leucite and K-bearing zeolites, K bioavailability in aqueous solutions present within CBV soils seems higher compared to that in the aqueous solutions in pozzolanic soils. Actually, the $^{K}D_{r/s}$ of the Gravesac rootstock grown in CBV soils is higher (Figure 5) despite these soils containing less than half the K compared to pozzolanic soils (Table 3). In this case, mineral assemblage, and particularly the alteration extent of phlogopite, appears to be the factor that most controls K bioavailability in the soil. The negative correlation between K and H_2O contents in phlogopite (Figure 2 and Table 2) indicates that the weathering of this mineral in CBV soils occurs through reactions that lead to gradual K removal by forming micas with decreasing potassium content. Actually, prior to the full completion of phlogopite hydration (*i.e.*, the formation of vermiculite), a series of transitional species at various stages of evolution may emerge (Suvorov & Skurikhin, 2003). The formation of these minerals maintains a high K activity in the aqueous solutions within the solid matrix of CBV soils. The high K activity in the aqueous solutions in CBV soils is also indicated by K-feldspar, a phase virtually absent in both the bedrock and pozzolanic soils, but abundant in CBV soils. Therefore, unlike in pozzolanic soils, where K is quickly removed from the soil due to the lack of stable/metastable K minerals, in CBV soils, K is removed more slowly (Figure 4), and this is reflected by higher $^{K}D_{r/s}$ (Figure 5). High $^{K}D_{r/s}$ indicates greater K bioavailability in CBV soils than in pozzolanic soils, contrasting with results from leaching using ammonium acetate (Figure 6). The direct correlation between $^{K}D_{r/s}$ and K removal from soils, along with those observed for Ca, Mg, and Na (Figure 8), confirms that rootstock uptake capacity is strongly influenced by the mineral assemblage, as the latter is the main factor controlling element mobility caused by weathering. On the other hand, K levels measured in the musts obtained from Merlot grapes grown on the sampled rootstocks (Table 6) demonstrate higher K uptake by Gravesac rootstocks grown in CBV soils (Figure 8). A comparable trend is also observed for Ca contents, with similar results replicated in musts obtained from control grapevines grown in the two soil types.

CONCLUSIONS

The study highlights the implications of soil mineral assemblage on nutrient cycling and soil fertility management. Our results highlight the pivotal role of mineral assemblage in shaping nutrient availability and rootstock uptake dynamics in viticultural systems. Gravesac rootstocks demonstrate an adaptive response to the mineral diversity of soils. Their ability to extract Ca, Mg, and K appears finely tuned to the weathering dynamics of specific minerals present in the soils. Strategies aimed at enhancing nutrient bioavailability while minimising environmental impact could benefit from a nuanced understanding of mineral chemical weathering. Exploring the long-term effects of mineralogical changes on vine growth, fruit development, and wine quality would provide valuable insights into sustainable viticulture practices. Future studies could delve deeper into the biochemical mechanisms underlying rootstock adaptation to mineralogical variations. Meanwhile, any analysis of element availability in the vineyard should consider the rates of secondary mineral formation and primary mineral dissolution. Emphasising the mineral assemblage controlling the uptake capacity of rootstocks, our findings support the correlation between wine quality and the mineral chemistry of soils or, more generally, between wine quality and geology.

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