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Application of Kaolin and Italian Natural Chabasite-Rich Zeolitite to Mitigate the Effect of Global Warming in *Vitis vinifera* L. cv. Sangiovese

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Abstract: High temperatures and the anomalous distribution of rainfall during the growing season may have a negative impact on grapevine yield and berry composition. In recent years, many studies have focused on the application of agronomical techniques to reduce the negative impact of heat waves on secondary metabolites such as phenols. In particular, treatments with kaolin have shown positive effects on reducing canopy temperatures, enhancing the accumulation of anthocyanins. In regard to the above, three treatments were evaluated: untreated control (C), kaolin (CAO), and chabasite-rich zeolitites (ZEO) applications on cv. Sangiovese in order to verify the cooling effects on leaves and bunches, and the impact on gas exchange, yield parameters, berry composition, and on both chemical and sensory notes of wine. Minerals were sprayed twice around the veraison on the entire canopy at a 3% concentration. The results showed that the application of the minerals was able to reduce the berry temperatures in both years of the trial as compared to the untreated control (C), without affecting vine gas exchange, yield, and soluble solid accumulation. Furthermore, the cooling effect determined an increase in anthocyanin on both the grapes and the wine. At testing, CAO and ZEO wines stood out regarding greater color intensity and were preferred by the judges.

Keywords: climate change; particle film; temperature; organic acids; anthocyanins; wine

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1. Introduction

According to the latest OIV (International Organization of Vine and Wine) report [1], Italy was rated as the major world wine producer with 58.5 million hectoliters, and Sangiovese represented Italy's top variety, the only one whose cultivation exceeded 50,000 hectares [2]. Sangiovese (*Vitis vinifera* L.) participates in many of the Italian protected appellations, such as Chianti, Nobile di Montepulciano, and Brunello di Montalcino, appreciated all over the world.

Although Orlandini et al. [3] found a positive relationship between the recent thermo-pluviometric regime and the quality of Brunello di Montalcino wine, it is known that global warming could have a negative impact on the vine cultivation, yield, and composition of both grapes and wine [4].

It is well-known that Sangiovese berries have a low concentration of anthocyanins in their skin and have a composition mainly characterized by glycosylated anthocyanins [5]. In addition, Mattivi et al. (2006) showed that, on average, the values of anthocyanins for the Sangiovese grape (about 700 mg kg^{-1} of grape) were reduced by two-thirds in concentration as compared to the more widespread Cabernet Sauvignon cultivar.

There is evidence that elevated temperatures have negative impacts on the color of red berry grapevine varieties [6,7] and many studies have been aimed at increasing the anthocyanin content in the berry skins [8–11] and in the resulting wine [12,13]. The challenge of grape color which growers face in warm regions has become very complex in a perspective of climate change characterized by an ever-higher frequency of summer days surpassing the critical temperature of 35 °C [6,7]. Furthermore, Movahed et al. (2016) have reported that, around this temperature threshold, the biosynthesis of anthocyanins was suppressed at both the transcriptional and enzymatic levels, probably due to higher peroxidase activity [14]. Therefore, the role of peroxidases in the anthocyanin catabolism appears to be crucial in a global warming scenario.

However, in the Mediterranean basin, we are witnessing not only a radical increase in air temperature but also a change in the distribution of precipitation during the season [15,16]. Therefore, the vines are affected by a combination of several abiotic stresses which lead to physiological and biochemical changes in plant growth and fruit composition [17,18]. In particular, Dinis et al. (2020) have expressed concern regarding the combination of environmental stresses in some harsh regions where the water scarcity and elevated temperatures could damage leaf photosynthetic activity and berry metabolism [19]. Under similar stress conditions, it is common to have chlorosis and necrosis in the leaves, and a significant reduction in both growth and yield [20]. Heat waves may also induce an acceleration during ripening of soluble solid accumulation coupled with a faster depletion of organic acid, high pH, and atypical aroma compounds. Therefore, the resulting wines are less susceptible to aging, have poor color, and altered aromatic profiles [21].

In order to mitigate these adverse climate effects, new short-term agronomic techniques are now available, such as post-veraison shoot trimming or apical leaf removal [22–24], smart irrigation [25,26] and foliar application of particle materials, such as kaolin and zeolite.

Kaolin, $Al_2Si_2O_5(OH)_4$, is an aluminosilicate clay having the capability of reflecting a more elevated amount of potentially damaging radiation [27], resulting in a decrease in the temperature of spray organs, such as leaves and berries [28,29]. The effects of kaolin on plants has not yet been fully understood. However, recent literature has highlighted a different attitude of the mineral which exerts a positive action on gas exchanges under water shortage while mild or no effects on assimilation and transpiration have been recorded under non-limiting conditions [30,31]. In a one-year trial conducted on cv. Sangiovese, Frioni et al. (2019) showed that the effects of kaolin on vine gas-exchange drastically change according to the water status. This study demonstrated that kaolin, in absence of water stress, was able to improve the leaf cooling while slightly reducing photosynthetic and water loss rates. Furthermore, vines treated with kaolin showed better performances under severe water deficit, in terms of both carbon assimilation rate and water use efficiency (WUE) [32]. Although the author suggested the use of kaolin as an anti-transpirant under optimal water conditions, this does not happen under conditions of severe water stress. In the latter case, the mineral coating is able to preserve leaf function and viability, assuring a faster recovery once adequate water supply is replenished [32,33].

Likewise, Garrido et al. (2019) observed that kaolin applied to canopies increased the photosynthetic performance of berries growing under different light microclimates. In particular, kaolin improved the assimilation rate of both exocarps and seed teguments of berries growing under low light conditions due to the higher photosynthetically active radiation (PAR) reflections within the canopy [29]. At the same time, the maximum quantum efficiency of green berries grown under a high light ambience suggested that the mineral could protect the skin from light stress. Due to the ability of changing the reflective properties of the sprayed organs and the consequent cooling effects, kaolin is considered to be an important tool in reducing sunburn damage [34–36], having a positive effect on phenolic concentrations, such as those of anthocyanins present in the grapevine resulting in an average increase of 20% [30,31,35,37].

It is well-known that mineral particle application causes a modification in leaf and fruit texture, and a consequent variation in the reflected spectral signature of the plant which makes them less attractive to insects [38,39]. In recent years, the sustainable approach to pest and disease control has favored the use of innovative products, such as zeolites [40].

Zeolite-group minerals are aluminum silicates of the alkali and alkaline earth elements with open framework structures of linked (Si,Al)O_4 tetraedra [41]. In addition to the effect of zeolites against pests and diseases [42], they may also have beneficial effects on the treated plant itself. Due to the crystalline structure, the high cation exchange capacity, and the ability to retain water, zeolites are increasingly used in agriculture [43]. In a recent trial regarding cuttings of apple trees, zeolites were able to improve photosynthesis by increasing the absorption of carbon dioxide (CO_2) molecules [44]. In grapevines, zeolite-rich rocks—*zeolitites*—sprayed on the leaves has increased the concentration of anthocyanins in the berries and in the resulting wine except for those vines treated close to harvest [42].

It is from this assumption that, in recent years, not only kaolin but also zeolite has aroused interest in the sustainable fight against heat waves and multiple summer stress in vineyards. In this study, for the first time, the foliar application of kaolin and zeolite has been compared aiming to evaluate their possible effect on fruit cooling, gas exchange, and the grape and wine composition of cv. Sangiovese.

2. Materials and Methods

2.1. Plant Material and Treatments

The trial was carried out in the 2019 and 2020 seasons in Bologna (44°32′ N–11°22′ E) on a seven-year experimental vineyard, cv. Sangiovese (*Vitis vinifera* L.), clone 12T grafted on SO4. The vineyard was located on a flat land having clay loam and deep soil typical of the Po valley (Northern Italy). Three north-south oriented vine rows were trained to vertical shoot positioned (VSP) spur pruned cordons and were left with six two-bud spurs per vine. Vine spacing was 1 m × 2.8 m and, at flowering, each vine was uniformed for both number of shoots and bunches. During the growing season, the shoots were positioned by hand vertically, and slight shoot trimming was performed during the last days of June, leaving a canopy height of approximately 1.3 m. The vineyard was non-irrigated, and a standard disease control program was applied to control downy mildew, powdery mildew, and *Botrytis* sour rot.

The experimental design included 135 vines distributed in three randomized blocks along the rows. Each block consisted of 45 vines distributed in three treatments: (a) C, untreated control vines sprayed with water; (b) CAO, kaolin sprayed treatment; (c) ZEO, natural Italian chabasite-rich zeolitites sprayed treatment.

A formulation of 100% aluminum silicate (Bal.Co S.p.a., Modena, Italy) was mixed with water (3 kg hL^{-1}) and was sprayed on the entire canopy twice each year on the CAO vines. The first application was carried out on July 30 (day of year [DOY] 211) and July 27 (DOY 209) for the years 2019 and 2020, respectively. The second application was carried out on August 7 (DOY 219) and August 5 (DOY 218) for the two years of the trial, respectively. On the same days of the year, the treatments with Italian chabasite-rich zeolitite (ZEOVER, Verdi, Reggio Emilia, Italy) were carried out on the ZEO vines using an amount of 3 kg hL^{-1}. The two applications were carried out at the beginning and at the end of veraison—stages 34 and 35 according to Eichorn and Lorenz [45]. The suspensions were carefully sprayed on both canopy sides using a knapsack sprayer (Model M3, Cifarelli, Pavia, Italy).

2.2. Water Status and Leaf Gas Exchange Measurements

Midday stem water potential (Ψ_{stem}) was measured on fifteen vines per treatment using a Scholander-type pressure chamber (Model 3005, Soil Moisture Equipment Corp., Santa Barbara, CA, USA), at 1 pm on a mature leaf per vine on DOY 213, 221, 225 in 2019 and on DOY 213, 220, 232 in 2020. Each leaf was covered with a plastic bag and aluminum foil for 2 h before the measurements [46]. Leaf net assimilation (A_n) and stomatal conductance (g_s) rates were measured using a portable gas exchange Li-Cor 6400 system (Li-Cor Inc., Lincoln Nebraska, USA) on two well-exposed mature main leaves and on a lateral leaf inserted between nodes 8 and 12. Single leaf gas exchange measurements were taken in the morning (9:30–10:30) on the same day and on the same vines monitored for the Ψ_{stem} using a broad leaf chamber under a saturated light (1500 µmol $m^{-2}s^{-1}$) using an external lamp.

2.3. Microclimate Monitoring

The weather conditions were recorded by a meteorological station annexed to the experimental vineyard equipped with a rain gauge, thermocouples and relative humidity sensors (iFarming srl, Ravenna, RA, IT). Eight thermo probes (Spectrum technologies Inc., Aurora, IL, USA) per treatment were positioned in the sub-cuticular tissues of the berry skin. Four sensors were positioned on two different bunches, two located on the east side and two on the west side of the cordon. For each side, one thermo probe was inserted into a berry located in the external part of the bunch and one in the internal part. Each probe was then connected to a Watchdog 1000 Micro Station datalogger (Spectrum technologies inc., Aurora, IL, USA) which registered temperature data every 30 min during the seasons. These readings were averaged per cluster and plot. The berry temperatures were used to calculate the stress degree days (SDDs) accumulated over the August 2019 and 2020 seasons where SDD is defined as the difference between maximum berry temperature (T_{max}) and the threshold of 35 °C. The temperature of 35 °C or above are associated with anthocyanin degradation and consequent inhibition of anthocyanin accumulation [47].

On clear sky days, the mean leaf temperature was measured using an infrared thermometer (mod. Raynger ST, Raytek, Santa Cruz, CA, USA), measuring the same leaves analyzed for gas exchanges on DOY (day of the year) 213, 221, 225 in 2019 and on DOY 213, 220, 232 in 2020.

2.4. Vine Growth, Yield Components, and Berry Composition

The vines were individually harvested on 26 September 2019 (DOY 269) and 22 September 2020 (DOY 266), and crop weight, bunch number, and bunch weight were recorded. Pruning weight per vine was measured in both years during the winter.

At harvest, 50 berries per vine were collected and crushed. The must obtained was sieved and used for soluble solid analysis using a temperature-compensating CR50 refractometer (Maselli Misure Spa, Parma, Italy). A sample of 5 mL of the same must was then diluted seven times with bi-distilled water for titration using a Crison Compact Titrator (Crison, Barcelona, Spain) with 0.25 N NaOH (Sigma-Aldrich, St. Louis, MO, USA) to obtain pH and titratable acidity data (expressed as g L^{-1} of tartaric acid equivalents).

Total anthocyanins were analyzed by collecting 20 berries per vine and soaking the peeled skins in 100 mL methanol for 24 h [4]. High-performance liquid chromatography (HPLC) separation and quantification of anthocyanins [4] were performed on a Waters 1525 HPLC (Waters, Milford, MA, USA) equipped with a diode array detector (DAD) and a Phenomenex (Castel Maggiore, Bologna, Italy) reversed-phase column (RP18, 250 mm × 4 mm, 5 µM). The anthocyanins were quantified at 520 nm using an external calibration curve with malvidin-3-glucoside chloride as the standard (Sigma-Aldrich, St Louis, MO, USA), following the procedure reported by Mattivi et al. (2006).

2.5. Winemaking and Chemical Analysis

Soluble solid content and accumulation in the grape was used to determine the harvest date. In 2020, grapes from all the vines in each treatment group were harvested manually and kept separated for micro-scale vinification (three replications each for C, CAO, and ZEO). For each replication, 100 kg of grapes were destemmed, crushed, and transferred to fermentation tanks. Total of 8 g hL^{-1} of potassium metabisulfite was added to the musts and they were inoculated with 20 g hL^{-1} of *Saccharomyces cerevisiae*. About 20 g hL^{-1} of fermentation activators (diammonium phosphate + thiamine hydrochloride) were added at two different times during the process, at the beginning and before the end of fermentation. During the alcoholic fermentation, the mass temperature was maintained at 28 °C and the skins were punched down twice a day to keep the cap wet. After 5 days of skins maceration, the solid part was separated from the liquid, and the marc was pressed at maximum 1 bar. After ten days, at the end of the fermentation process, the wines were cold stabilized, sulphated with 6 g hL^{-1} of potassium metabisulfite, and stored at room temperature in 750 mL bottles closed with cork stoppers.

After 3 months, the wines were analyzed for alcohol concentration, total acidity, malic acid, and pH [48]. Wine color intensity (IC, Abs_{420} + Abs_{520} + Abs_{620}), color hue (HUE, Abs_{420}/Abs_{520}), and total phenols (Folin-Ciocalteau) were determined using spectrophotometry in accordance with the methods outlined in the official Journal of the European Community Regulations [49]. Total phenols were quantified at 725 nm using a calibration curve with gallic acid (Sigma Aldrich, St Louis, MO, USA). Determination of the anthocyanins in the red wine samples, filtered through 0.45 µm nylon filters, was carried out according to the OIV-MA-AS 315-11 method [50]. Thirty microliters of each sample were analyzed using HPLC, and total anthocyanin was quantified at 520 nm with malvidin-3-glucoside chloride (Sigma Aldrich, St Louis, MO, USA) using a calibration curve.

2.6. Wine Tasting

The wines underwent sensory analysis 3 months after bottling by a group of seven panelists (four males and three females between the ages of 22 and 60 years) with experience in wine scoring and trained to express their judgement per sample and per attribute based on an appropriate list of descriptors. The list of key attributes for the wine ratings was developed during three training sessions in which judges were instructed to recognize and rate the perceived intensity of the parameters which characterized the 'Sangiovese' profile: color intensity, red fruity aroma, finesse, spicy and vegetal aromas, wine body, acidity, astringency, bitterness, and an additional global assessment. Each attribute was rated on a 9 cm unstructured linear scale starting from the extreme left corresponding to imperceptible intensity to the right corresponding to high-intensity notes.

The wine tasting was carried out in one session conducted in separate booths at room temperature (20 °C). The wines were served at 18 °C, in standard coded ISO 3591 wine tasting glasses. Random codes identified each sample, and the tasting order varied across judges.

2.7. Statistical Analysis

Statistical analysis was carried out using SAS statistical package V9.0 (SAS Institute, Cary, NC, USA). The data underwent a mixed procedure, and the treatment comparisons were analyzed using the Tukey test. Stepwise forward canonical discriminant analysis (CDA) of the sensory determinations was carried out using R project V4.0.2 (R Foundation for Statistical Computing, Vienna, Austria) with a candisc function inside a candisc library regarding ten parameters—color intensity, red fruity intensity, finesse, spicy aroma, vegetal aroma, body, acidity, astringency, bitterness, global assessment—according to treatments and judges [51]. Significance testing was carried out on the CDA data using multivariate analysis of variance (MANOVA).

3. Results

3.1. Environmental Conditions, Leaf and Berry Temperatures

A careful analysis of the most important weather parameters during the two years of the trial showed that 2019 was a warmer and less rainy year than 2020 (Table 1). In particular, there was a difference of 1 °C in the average air temperature and a variance of approximately 94 mm of cumulative rainfall between the two growing seasons (April–October). Details of both precipitation and air temperature values at the time of veraison—when the treatments were applied—showed that 2020 was wetter (with 106.4 mm of rain in August) and slightly cooler than the previous year with a reduction of 1.3 °C in July and 0.4° C in August (Table 1).

Table 1. Monthly average temperature and rainfall recorded for the growth period (April–October) in 2019 and 2020 at a weather station close to the vineyard.

	2019		2020	
	T (°C)	Rainfall (mm)	T (°C)	Rainfall (mm)
April	14	57.2	14	31.5
May	15.4	136.6	18.7	29
June	25.7	26.4	22.2	106
July	26.3	36.2	25	34.3
August	26.2	19.8	25.8	106.4
September	20.9	41.2	20.9	86.9
October	17	38.2	13.8	55.6

Thermal readings taken on the leaves showed that the CAO and ZEO treatments had discordant effects on the canopy cooling, depending of the growing season (Table 2). In 2019, the mineral distributed on the foliage caused a significant drop in the leaf temperatures which lasted over time. This did not occur in 2020 when the application of both kaolin and zeolitite produced inconsistent thermal effects.

Table 2. Single leaf temperatures measured using an infrared thermometer in the 2019 and 2020 seasons. Readings were taken on three well-exposed leaves per vine. Different letters within a column indicate significant differences as calculated using the Tukey statistical analysis test ($p \leq 0.05$).

	2019			2020		
	DOY 213	DOY 221	DOY 225	DOY 213	DOY 220	DOY 232
C	33.2 [a]	33 [a]	31 [a]	35.3	32.4	33.3
CAO	32.6 [b]	31 [b]	30 [b]	36.0	32.4	32.9
ZEO	32.2 [b]	31 [b]	30 [b]	35.7	33.0	33.5

However, thermal cooling of the berries was recorded in both seasons for both the CAO and ZEO treatments as compared to the control vines (Figures 1 and 2). In particular, the maximum berry temperature was significantly reduced by CAO applications compared to the C berries.

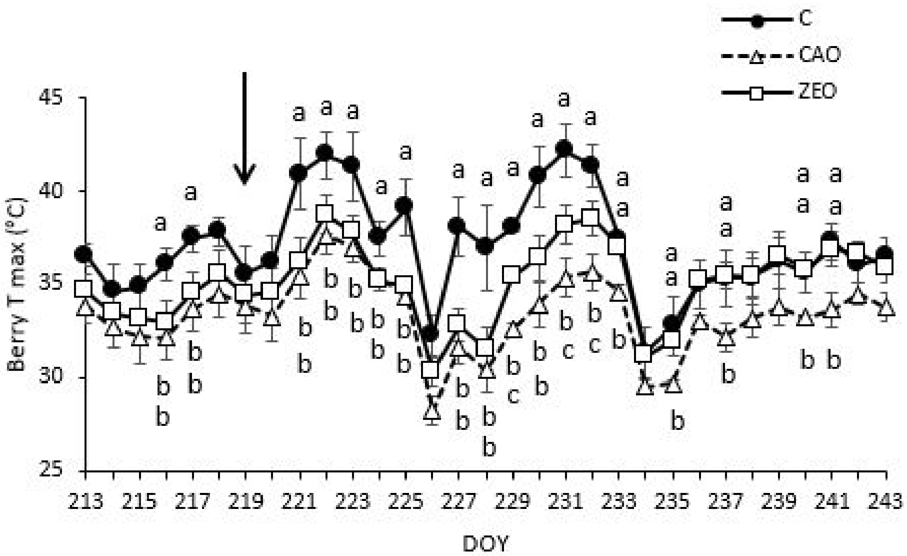

Figure 1. Trend of berry temperature (berry Tmax°C) measured using thermo probes in August 2019. The values are presented as mean ± standard error (SE) (n = 8 per treatment). Different letters indicate significant differences between treatments according to the Tukey test ($p \leq 0.05$). The arrow indicates the date of the second treatment with the mineral particles.

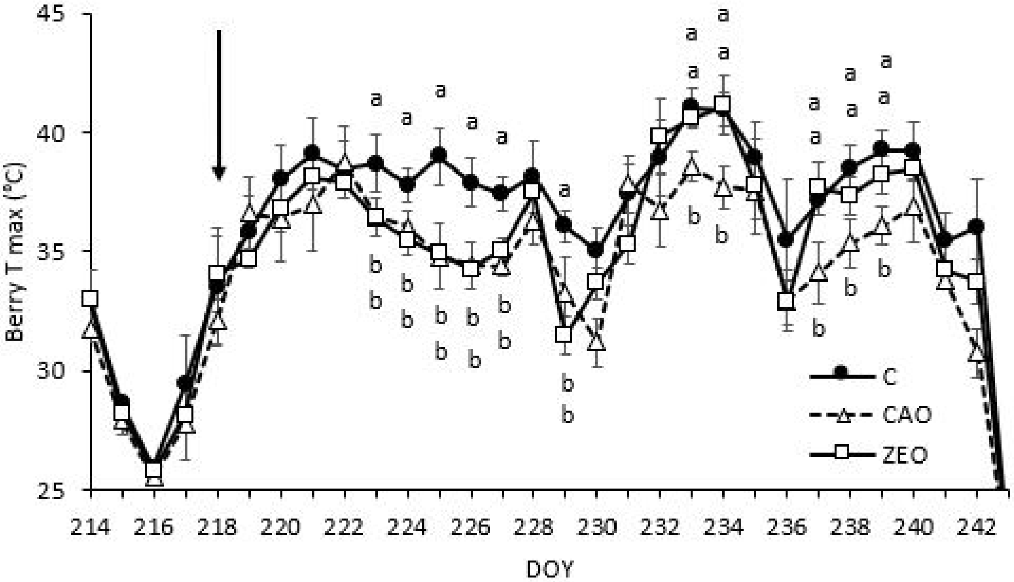

Figure 2. Trend of berry temperature (berry Tmax °C) measured using thermo probes in August 2020. The values are presented as mean ± SE (n = 8 per treatment). Different letters indicate significant differences between treatments according to the Tukey test ($p \leq 0.05$). The arrow indicates the date of the second treatment with mineral particles.

This thermal difference between the two treatments persisted in 2019 starting from the first treatment carried out on 30 July (DOY 211) throughout the entire month of August and corresponds to approximately 4 °C (Figure 1). In 2020, a significant difference between the maximum C and CAO temperatures characterized the entire month of August (Figure 2), starting from the second application on 5 August (DOY 218).

The same thermal drop was recorded on the grapes treated with ZEO with a substantial difference as regards the persistence of the mineral coating on the berries. While, in 2019, the maximum berry temperature was affected by ZEO for 18 continuous days, in 2020, the cooling effect was reduced to one week. Overall, the maximum temperatures were always higher in the C group while ripening during several heatwaves when values of approximately 40 °C were reached in both years. In particular, the maximum temperatures of the berries recorded for CAO and ZEO were consistently below the thermal limit of 35 °C in 2019 and only for eight days in 2020.

The calculation of stress degree days (SDDs) accumulated over August 2019 and 2020 was a strategic tool for analytically identifying the incidence of high temperatures on berry ripening. The SDDs showed a significant heat build-up for the control vines as compared to the treated vines. In particular, the SDDs reached 73 °C for C, 7 °C for CAO and 27 °C for ZEO in 2019. In 2020, the accumulation of the SDDs reached 75 °C, 34 °C, and 49 °C for C, CAO, and ZEO, respectively.

3.2. Vine Water Status and Leaf Gas Exchange

The different meteorological conditions of the 2019 and 2020 seasons as well as the treatments did not affect the stem water potential (Table 3). In fact, the experimental vineyard was located in fertile and deep soil with good water-holding capacity which helped keep the vines well hydrated.

Table 3. Midday stem water potential (Ψstem, bar) during the 2019 and 2020 seasons. Measurements were taken on one mature basal leaf per vine. Different letters within a column indicate significant differences as calculated by the Tukey statistical analysis test ($p \leq 0.05$).

	2019			2020		
	DOY 213	**DOY 221**	**DOY 225**	**DOY 213**	**DOY 220**	**DOY 232**
C	−4.3 [a]	−4.1 [a]	−4.1 [a]	−5.3 [a]	−6.0 [a]	−5.6 [a]
CAO	−5.6 [a]	−3.9 [a]	−3.9 [a]	−5.6 [a]	−5.8 [a]	−4.6 [a]
ZEO	−5.4 [a]	−3.8 [a]	−3.8 [a]	−5.2 [a]	−5.6 [a]	−5.8 [a]

From Table 4, it also appears evident that the use of both kaolin and chabasite rich-zeolitites did not limit stomatal conductance. Only in the warmest year did the kaolin significantly reduce gas exchange (g_s) two days after the second foliar application (DOY 219).

Table 4. Leaf stomatal conductance (g_s, mol $m^{-2}s^{-1}$) during the 2019 and 2020 seasons. Measurements were taken on three well-exposed leaves per vine. Different letters within a column indicate significant differences as calculated by the Tukey statistical analysis test ($p \leq 0.05$).

	2019			2020		
	DOY 213	**DOY 221**	**DOY 225**	**DOY 213**	**DOY 220**	**DOY 232**
C	0.17 [a]	0.23 [a]	0.21 [a]	0.18 [a]	0.14 [a]	0.21 [a]
CAO	0.17 [a]	0.19 [b]	0.22 [a]	0.19 [a]	0.20 [a]	0.21 [a]
ZEO	0.18 [a]	0.28 [a]	0.26 [a]	0.17 [a]	0.20 [a]	0.22 [a]

The leaf assimilation rate (A_n) was affected by the CAO treatment on DOY 213 two days after the first application, and DOY 232 two weeks after the second application, for 2019 and 2020, respectively (Table 5).

Table 5. The leaf assimilation rate (A_n, μmol $m^{-2}s^{-1}$) during the 2019 and 2020 seasons. Measurements were taken on three well-exposed leaves per vine. Different letters within a column indicate significant differences as calculated by the Tukey statistical analysis test ($p \leq 0.05$).

	2019			2020		
	DOY 213	**DOY 221**	**DOY 225**	**DOY 213**	**DOY 220**	**DOY 232**
C	23.4 [a]	17.5 [a]	17.1 [a]	14.0 [a]	10.5 [a]	16.8 [a]
CAO	15.3 [b]	15.3 [a]	16.4 [a]	14.8 [a]	10.9 [a]	14.2 [b]
ZEO	21.6 [a]	19.4 [a]	15.0 [a]	14.0 [a]	10.5 [a]	17.3 [a]

3.3. Vine Growth, Yield Components and Fruit Composition at Harvest

Starting from a normalized bunch number per vine (17 and 14 for the 2019 and 2020 vintages, respectively), no differences were reported among treatments in terms of yield components (yield per vine, weight of the bunch, or berry mass), soluble solids, and pH. Nonetheless, CAO showed a higher total acidity as compared to C and ZEO (Table 6) according to the statistical analysis. The anthocyanin concentration, expressed as mg per kg of grape, showed a significantly higher count in the CAO and ZEO vines than in the C vines in both years (Table 6) but no difference was recorded in terms of percentage of each anthocyanin (data not shown). Pruning weight reported no differences among treatments in either season; in 2019, it was 0.65 kg, 0.64 kg, and 0.60 kg for C, CAO, and ZEO, respectively while, in 2020, it reached the value of 1.0 kg per vine in all treatments.

Table 6. Yield parameter and fruit components recorded in Sangiovese vines undergoing Kaolin (CAO) and Chabasite-rich zeolitite (ZEO) treatments and the control (C) vines in 2019 and 2020. Different letters in a column for a given year indicate significant differences after the Tukey statistical analysis test ($p \leq 0.05$).

Vintage	Treatment	Yield per Vine (kg) [1]	Bunch Weight (g)	Berry Mass (g)	Soluble Solids (°Brix)	pH	Total Acidity (g/L)	Total Anthocyanins (mg/kg)
2019	C	5.82 ^{a}	338 ^{a}	2.54 ^{a}	20.0 ^{a}	3.5 ^{a}	6.84 ^{b}	509 ^{b}
	CAO	5.36 ^{a}	317 ^{a}	2.54 ^{a}	20.6 ^{a}	3.4 ^{a}	7.22 ^{a}	603 ^{a}
	ZEO	5.46 ^{a}	327 ^{a}	2.42 ^{a}	20.7 ^{a}	3.4 ^{a}	6.65 ^{b}	618 ^{a}
2020	C	4.57 ^{a}	326 ^{a}	2.79 ^{a}	21.9 ^{a}	3.5 ^{a}	6.79 ^{b}	613 ^{b}
	CAO	4.21 ^{a}	292 ^{a}	2.77 ^{a}	21.8 ^{a}	3.4 ^{a}	7.17 ^{a}	710 ^{a}
	ZEO	4.59 ^{a}	332 ^{a}	2.71 ^{a}	21.9 ^{a}	3.4 ^{a}	6.76 ^{b}	692 ^{a}

[1] The bunch number was standardized at 17 and 14 for the 2019 and 2020 vintages, respectively.

3.4. Wine Chemical and Sensory Analyses

The chemical results of the 2020 wines (Table 7) reflected berry composition (Table 6) with the exception of the acidity parameter. In detail, the higher titratable acidity levels which were found in the musts of CAO compared to the untreated control and the ZEO vines, flattened out in the resulting wines (Table 7). No differences were recorded in alcohol concentration, pH, and malic acid. Coherently with the berry composition, CAO and ZEO treatments significantly increased wine anthocyanin content and total phenols. Kaolin and chabasite-rich zeolitites contributed to the superior color intensity of the wine (IC) but had no effect on color hue (HUE) as reported in Table 7.

Table 7. Chemical analysis on wines obtained from kaolin (CAO) and chabazite rich-zeolitite (ZEO) treatments or the control (C) grapes in 2020. The wines were analyzed three months after harvest. Different letters in a column for a given year indicate significant differences after the Tukey statistical analysis test ($p \leq 0.05$).

	Alcohol (%vol)	pH	Total Acidity (g/L)	Malic Acid (g/L)	Total Phenols (mg/L)	Anthocyanins (mg/L)	IC	HUE
C	11.7 ^{a}	3.2 ^{a}	6.9 ^{a}	1.6 ^{a}	985.1 ^{b}	78 ^{b}	1.4 ^{b}	0.61 ^{a}
CAO	12.3 ^{a}	3.2 ^{a}	7.0 ^{a}	1.4 ^{a}	1164.8 ^{a}	97 ^{a}	2.2 ^{a}	0.61 ^{a}
ZEO	12.2 ^{a}	3.1 ^{a}	7.0 ^{a}	1.3 ^{a}	1159.1 ^{a}	98 ^{a}	2.1 ^{a}	0.58 ^{a}

Canonical discriminant analisys (CDA) was performed in order to examine the differences between treatments (C, CAO, and ZEO) according to the sensory analysis of wines.

CDA represents a transformation of the original parameters—colour intensity, red fruity intensity, finesse, spicy aroma, vegetal aroma, body, acidity, astringency, bitterness, global assessment—into a canonical space to obtain a new variables called canonical discriminant functions (Can1 and Can2). It is in fact very useful to reorganize the observations in a space with a reduced number of dimensions to improve the interpretation of the results.

CDA on the sensory traits of Sangiovese wines obtained from each treatments showed that canonical function 1 (Can 1, on x axe) represents the 66.2% of the variability while the canonical function 2 (Can 2, on y axe) represents only 33.8% (Figure 3). As reported in Figure 3, the centroid for C was located positively along Can 1 and negatively along Can 2. The centroid for CAO was located negatively along both Can 1 and Can 2. In contrast, the centroid of ZEO was located negatively along Can 1 and positively along Can 2.

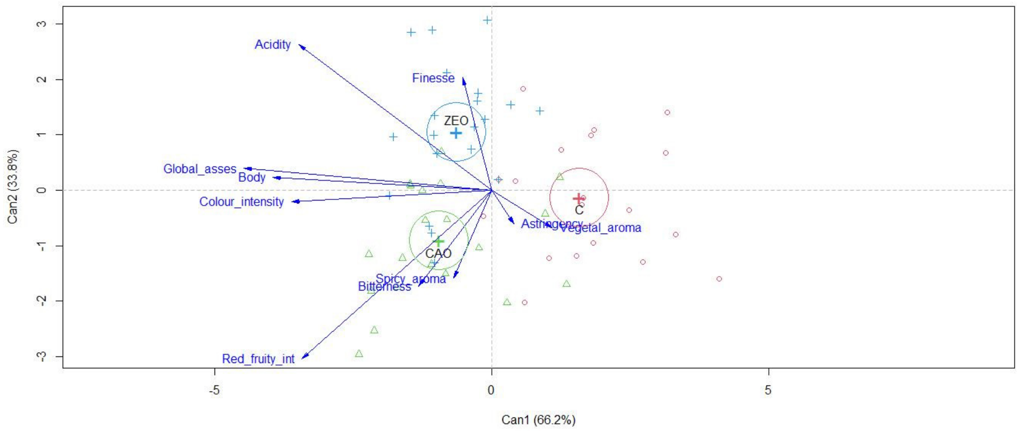

Figure 3. Canonical discriminant analysis (CDA) of the sensory traits for the Sangiovese wines obtained from kaolin (CAO, ∆) and chabasite-rich zeolitite (ZEO,+) treatments or the control (C, ○) vines in 2020. Treatment separation along the canonical discriminant function I (Can 1) and II (Can 2) with class centroids identified by the cross symbol (+).

Further elaboration according to Can 1, is reported in Figure 4 where the boxplot and the vector diagram showed that the segregation of the three groups of wines was attributable to the following variables: color and red fruit intensity, body, acidity, and global assessment. This approach highlights how the canonical variable relates to the original parameters for the interpretation of the results and for this reason, the canonical structure or canonical coefficients are taken into account.

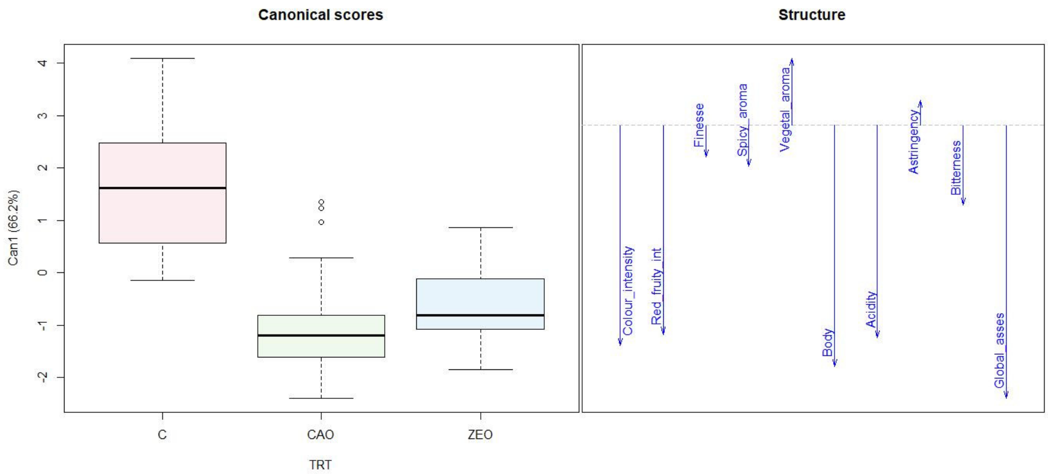

Figure 4. Boxplot of canonical scores (Can 1) and a vector diagram showing the magnitude of structure coefficients related to the sensory traits of Sangiovese wines obtained from kaolin (CAO) and chabasite-rich zeolitite (ZEO) treatments or the control (C) vines in 2020.

4. Discussion

Over the past few decades, a significant intensification of extreme weather events, i.e., heat waves, droughts, or increases in both the frequency and intensity of rainfall has been noted [52]. To address this scenario, the Paris Agreement has set the goal of limiting global warming in this century to below 2 °C above pre-industrial levels [53,54]. For this reason, it is important to act quickly in all sectors such as agriculture.

The impact of high temperatures on viticulture will be negative for areas which already falter from being too warm to produce quality grapes. In particular, several scientific reports have shown that high temperatures above 35 °C resulted in a lower anthocyanin concentration in berry skins [12,13,55]. Sangiovese is considered a medium-colored grape when compared to the average of anthocyanin concentration observed in the phenotyping screening carried out on various European grapevine cultivars [56]. It is therefore necessary to implement some strategies to ensure satisfactory productions avoiding the harmful effect of global warming on both the color of the grapes and the wine.

Based on the evidence that the spraying of mineral particles, such as kaolin, reflects solar radiation by reducing the surface temperature of vine organs, the aim of the two-year trial was to verify the effects of kaolin and chabasite-rich zeolitite on *Vitis vinifera* L. cv. Sangiovese in terms of temperature of the berries and leaves, gas exchanges, and yield and composition of both the grapes and the wine.

Over two years, the application of both kaolin and chabasite-rich zeolitite at veraison increased the quantity of phenolic compounds in the berries and in the resulting wines. As previously reported by some authors, kaolin was confirmed to improve the phenolic content in grape berries, as did anthocyanins [31,35,37,57], without affecting the yield and soluble solid concentration. It is well-known that the accumulation of anthocyanin in berries is impaired by high temperatures [12,55]; this suggests that the foliar application of minerals, leading to lowering the canopy temperature, promotes the biosynthesis of phenolic compounds [58] and decreases their enzymatic degradation [14,59].

Therefore, although several studies have reported a strong relationship between temperature and anthocyanin count in kaolin treated vines, the literature regarding the effect of zeolitites on canopy temperature, gas exchanges and berry composition at harvest is not yet available.

The present study showed that the application of chabasite rich-zeolitite as well as kaolin, led to a decreased berry temperature in both the 2019 and the 2020 seasons (Figures 1 and 2) while a reduction in leaf temperature was registered only for the warmer 2019 (Tables 1 and 2). The present results support the hypothesis of Brillante et al. (2016) who reported a significant decrease in leaf temperature only in stressed vintages [31]. However, since the vineyard was not affected by limiting conditions of water supply, no effects of each treatment emerged on gas exchange and photosynthetic response, except for CAO, in accordance with other findings reported by several authors. It is well-known that, under optimal water conditions, kaolin usually decreases the assimilation rate [60,61], unlike zeolite which maintains a high photosynthetic performance throughout the season [44]. Interestingly, the reduction in net assimilation for CAO occurred differently in the two-year trial. In particular, a decrease in photosynthesis was recorded immediately after the treatment in the driest year (2019), while in the wetter one (2020) the same decrease occurred only after the second treatment. This was probably due to the abundant rains recorded during the first week of August which affected the persistence of the clay on the leaves. Although CAO showed differences in gas exchanges, no variation was recorded between treatments, considering both yield and soluble solids concentration.

As has been reported by several authors, the reduction in kaolin sprayed organ temperature is a general event which is based on high reflection of ultraviolet (UV), PAR, and infrared (IR) radiation [29,31,62]. Furthermore, some authors have pointed out how the amount of temperature reduction was proportional to the amount of particle residue on the fruit surface [62]. This strong adhesion of clay on plant organs is not always considered to be positive, especially for fruit eaten fresh. For example, some authors have pointed out that treatment with kaolin on orchards has produced a residue on fruit which is difficult to wash off from the stem and calyx end [27,62]. Conversely, Huwei and others (2021) have recommended a pre-harvest treatment with natural zeolite (6%) to improve the shelf life of table grapes by acting on firmness and cuticle mechanical structure. In addition, the study reported that natural zeolite, as a nonchemical elicitor, showed good potential in enhancing the biochemical defense systems of table grapes which rely on a different secondary metabolite [63,64].

The present results revealed that kaolin and zeolitite, distributed twice at a 3% concentration around veraison, differ as regards the persistence of mineral coating on the berries. Compared to zeolitite, kaolin showed a longer cooling effect on the berries which lasted throughout the month of August. However, it should be noted that although kaolin was more persistent than zeolite, it appears that in rainy years—such as 2020—the effect on maximum temperatures was less evident as indicated by the accumulation of stress degree days. This data confirmed what has already been reported by Frioni et al. (2019) on potted Sangiovese vines [32]. Nevertheless, the effects of the two treatments on berry composition were similar. In detail, at harvest, grapes treated with CAO showed a higher amount of total acidity than C and ZEO in both years, and it was hypothesized that this positive effect could have been due to its longer-lasting sunscreen action [19,65]. It is known that heat waves from veraison through the ripening stages may reduce malic acid content due to the activity of the malate enzymes which increase with increasing temperatures up to 46 °C [66,67]. Although kaolin has better preserved berry acidity (Table 6), this has not been confirmed for the resulting wines in 2020 (Table 7). It has been proved that in humid seasons the absorption of potassium is favored and, consequently, it could be transported from the leaves to the berries after veraison [68]. Therefore, the authors hypothesized that the abundant summer rains increased the accumulation of cations in the vacuoles and the consequent precipitation of organic acids, such as potassium tartrate, during the winemaking process [69].

Although the wines from all treatments did not show any differences in terms of ethanol, pH, and organic acids, CAO and ZEO had a higher concentration of polyphenols and anthocyanins. The latter, extracted during the fermentation process, contributed to the greater color intensity of the wines obtained from the treated berries (Table 7). The present findings agreed with the results of other authors who imputed the increase in anthocyanin content to temperature regulation as a result of mineral coating [42,57].

It is interesting to note how both the CAO and ZEO treatments have determined an increase in the color intensity without affecting the hue of the resulting wines (Table 7). This result is probably related to the significant increase in absorption at 520 nm band which leads to a greater impact on IC and less on HUE values. However, it cannot be excluded that the two minerals act differently on grapevines and that zeolitite is able to enhance the production of different phytochemicals with powerful antioxidant activities as reported in Thompson Seedless grapes [63]. Furthermore, Calzarano et al. stated that zeolitite could negatively affect the extractability of anthocyanins during fermentation when applied close to the harvest date [42]. The present study highlighted how the positioning of just two treatments close to veraison, the crucial stage in anthocyanin synthesis [70], could improve the color of grapes and wines without altering their composition. Moreover, in a sensory analysis, wine from CAO and ZEO tasted by the judges reached the highest score. In particular, they were considered more attractive in terms of color intensity and red fruity aroma, and for having a better structure than the C-treated grapes. In the authors' experience, only a few studies regarding clay particles have reported effects on the sensory attributes of wines [19,31,71] and, surprisingly, this study is the first involving the natural zeolitite.

5. Conclusions

The use of both kaolin and chabasite-rich zeolitite appeared to be a promising strategy in abiotic stress alleviation for implementation in grapevines with moderate berry anthocyanin concentrations, such as Sangiovese cv.

In particular, the present findings revealed that the mineral particles applied twice at the beginning of veraison were able to both cool the grape clusters and improve the anthocyanin accumulation in comparison with the control vines (C) treated only with water. Kaolin and zeolitite differ in the persistence of the mineral coating on the berries. Although CAO produced a longer-lasting cooling of the berries than ZEO, the effects of the treatments on anthocyanin concentration were similar. On this basis, we may hypothesize a different mode of action of the two minerals on the biosynthesis and accumulation of anthocyanin. Nevertheless, further investigations are necessary to establish whether these treatments are linked to the temperature cooling effect and whether they might involve a nonchemical elicitor response affecting the secondary metabolism.

Sensory tests and chemical analyses of the wines produced in 2020 showed the positive characteristics of CAO and ZEO wines, associated mainly with a high intensity of color, body, and red fruity aroma.

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