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Abstract

Elemental profiles of wines have been used successfully to distinguish their geographical provenience around the world; however, underlying mechanisms are poorly understood. In this study, Ba, Ca, Mg, Mn and Sr contents were determined in 215 wines from several West European wine-growing areas using an easy-to-perform analysis based on ICP-OES. Major environmental and wine-making parameters (soil type as "calcareous" or not, rainfall, temperature and wine color) were used to explain variations within the dataset.

The combined effects of wine-making processes (expressed by wine color) and soil type explained 28.5% of total variance. The effect of climatic conditions explained 24.1% of variance and could be interpreted as intensity of drought stress.

Finally, carbonate occurrence in soils and climatic conditions systematically influenced the elemental composition of the wines. These findings provide insights into the mechanisms underlying elemental fingerprinting and allow prediction of which wine-growing regions can easily be distinguished based on elemental profiles as a marker of the terroir in viticulture.

Keywords: Soil; Terroir; Wine composition; Elemental analysis; Origin tracing; Environmental parameters

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Highlights

- Lime content in soils partially determines the elemental composition of wines.
- Mg and Ca contents differ most between wine-color categories.
- Wine color and soil type explain jointly 28.5% of total variance in the dataset.
- Climatic conditions influence wine elemental composition slightly but significantly.
- Aging, alcohol oxidation and precipitation do not influence Ba, Ca, Mg, Mn and Sr contents after storage.

1. Introduction

The influence of soil chemistry on wine taste is controversial even in geologic literature (Maltman, 2013). The essence of these differences in opinion is the French notion of terroir, which can be described as an interactive ecosystem including topography, climate, soil, and vine characteristics such as rootstock and cultivar (Foroni et al., 2017) that affect characteristics of the wine. Human factors, such as viticulture techniques and landscape environment, can also be influential (Cornelis van Leeuwen et al., 2004), meaning each wine is a unique combination of these parameters (Frost et al., 2015). Even though the effects of climate, topography, biological material and production techniques have been studied thoroughly, the influence of soil chemistry remains unclear (van Leeuwen et al., 2004).

In 1997, a pioneering study (Greenough et al., 1997) investigated the relationships among composition, vineyard and color of wines from Okanagan Valley (Canada); they used element fingerprinting and multivariate exploratory and inferential statistics and were the first to highlight the influence of soil and climate. Later, Mackenzie and Christy (2005) reported a link between geological bedrock, soil chemistry and related wine products. Reports of soil properties influencing wine quality are more and more frequent in scientific literature (Cheng et al., 2014; Costantini et al., 2012; Foroni et al., 2017; Hopfer et al., 2015; Imre et al., 2012). The most likely way for soil chemistry to influence wine composition is via mineral nutrition of the grapevine plant (Maltman, 2013).

In efforts to demonstrate the authenticity of wines, an important body of scientific literature (about 22 studies, not all cited here) has been elaborated, showing that the elemental content of wines differs between wine-growing regions. Among this literature, we can highlight the studies of Coetzee et al. (2005) or van der Linde et al. (2010) in South Africa, Greenough et al. (1997; 2005) or

Taylor et al. (2002, 2003) in North America, Fabani et al. (2010) in South America, and Angus et al. (2006) or Martin et al. (2012) in Australia and New Zealand, but also studies such as those of Almeida and Vasconcelos (2003), Baxter et al. (1997) or Jurado et al. (2012) in the European Old World. Only one relatively old investigation (Kwan et al., 1979) compared elemental composition of wines from different continents (Europe and North America). All studies covered a small number of wine-growing regions, coupled with statistical methods and sometimes classical enological parameters, without proposing biogeochemical mechanisms for the differences observed. To date, there is a lack of elemental content studies on a global scale including a multitude of wine regions and an unambiguous combination of elements allowing regional classification of wines. Still, some elements are recurrent in the literature. Rubidium (Rb) was used in 15/22 studies, strontium (Sr) in 13/22 studies, manganese (Mn) in 13/22 studies and barium (Ba) in 12/22 studies, followed by magnesium (Mg) used in 9/22 and cobalt (Co) 8/22. Subsequently, multiple elements start to be used equally.

In the previous cited literature, differences in wine composition were usually assigned to soil or climatic influences, in a limited spatial area of investigation. Except for that of Greenough et al. (2005), who studied wines from 6000 km across Canada, most of the studies investigated links between soil and wine composition at the local scale and for a well-defined terroir, without covering diverse biogeoclimatic conditions. Moreover, some of them link empirically the total or extracted element contents of soil to wine composition. However, element mobility and plant uptake from soil depend on physicochemical characteristics and bioavailability, rather than total content.

This study aims to contribute to the understanding of environmental factors (such as soil type and properties, or climate factors) influencing the elemental composition of wines on an inter-regional scale (Western Europe), with a rapid, easy-to-perform and inexpensive method using inductively coupled plasma optical emission spectrometry (ICP-OES). By investigating 215 wines from a spatially extended area with contrasting biogeoclimatic conditions (France and adjacent wine-growing regions especially Spain, Italy and Germany), this study aims to identify global effects on the elemental compositions of wine to elucidate which environmental factors control elemental composition. Multivariate statistical methods were used to explore the contribution of various parameters (wine color as a marker of wine-making process, “calcareous” or “non-calcareous” soil conditions, and meteorological conditions) on the elemental compositions of wines. The novelty of this work stems from the breadth of the dataset, making it different from previous studies that analyzed a large number of wines from only a small number of regions.

2. Materials and methods

2.1 Wine collection and storage

We collected 215 wine samples through private consumption and research stocks at the GET (Geosciences Environment Toulouse) Laboratory and from the French Agronomic Institute INRA (Institut National de la Recherche Agronomique) in Gruissan and Bordeaux (France). Data collected for these wines including wine color, country of origin, appellation, greater wine region, soil type information and chemical and meteorological data are provided in the supplementary material (Supplementary_Data_1_wines.txt). The wines collected included 126 red wines, 76 white wines, 11 rosé wines and two *vins gris*. Wine provenience and the number of samples for each wine-growing area are reported in Fig. 1. Small samples were stored in 30-mL PP vials until ICP-OES analysis and for no longer than 3 months at ambient temperature and low light exposure. Effects of storage (aging, alcohol oxidation and deposition) were checked using the same samples on several dates throughout the 3 months of storage.

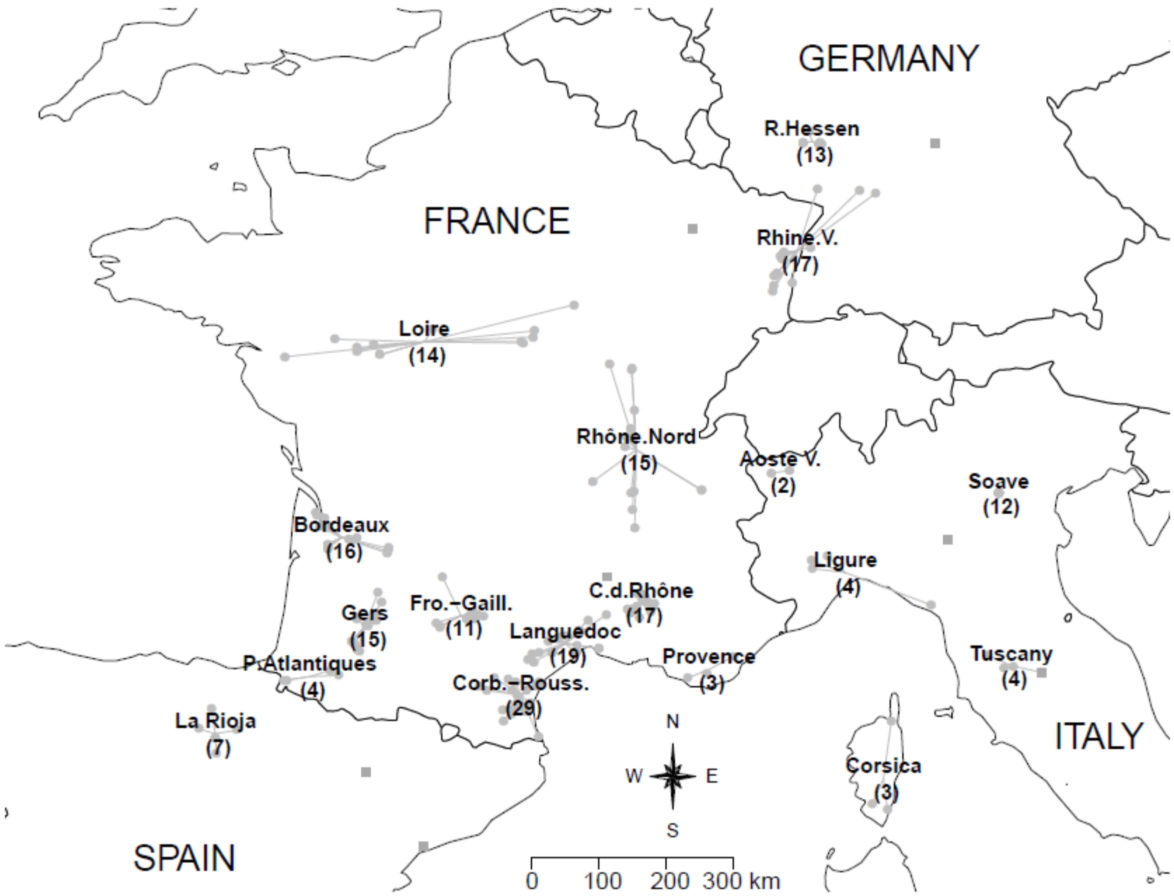

Fig. 1. Provenience of wines and their attribution to major wine-growing areas. Regions with only one wine sample are marked by a square; otherwise, region names and number of wines are given. Gray dots show provenience of wine samples. Aoste.V.: Aoste Valley; C.d.Rhône: Côtes du Rhône; Corb.-Rouss.: Corbières et Roussillon; Fro.-Gaill.: Fronton and Gaillac; P.Atlantiques: Pyrénées Atlantiques; R.Hessen: Rheinhessen; Rhine.V.: Rhine Valley.

2.2 Determination of soil type

Information on soil lime content was determined directly in the field for samples within the working group (n=23). For others, soil data were derived from pedologic maps of the wine region (n=33). Soil maps were obtained from the French INRA series and geological surveys of the German Länder. Based on these sources of soil information, wines were assigned to “calcareous” soil, when there was effervescence in the organomineral horizon, lime content given or when soil pH was higher than 7. If these conditions were not met, wines were assigned to the “non-calcareous” soil group. Otherwise, the product description from wine producers was used (n=96).

The presence of lime was accepted if indications were stated on the bottle, appellation description or promotion website, such as “chalky-clay soil”, “limestone” or similar. If soil or bedrock was described as “non-calcareous”, “gneissic”, “granitic”or “schistous”, wine samples were assigned to the “non-calcareous” group. One exception was the Maury area, where some wine growers explicitly stated carbonate-silicate schists as the bedrock and, thus, wines were assigned to the calcareous soil group. Soil data derived from vineyard descriptions (serving mainly for marketing purposes) were expected to be subjective and less quantitative than dedicated geochemistry analyses. The final dataset contained 51 wines grown on non-calcareous soils and 101 wines on calcareous soils; the remaining wines (n=63) had no soil information.

2.3 Climatic conditions

Coordinates of the actual grape-producing area was either known (n=33) or determined from the address of the winery (n=53) or the village of provenience (n=46). Weather data for Germany were taken from publicly available stations of the “Deutscher Wetterdienst” (DWD) and the weather survey of Geisenheim University. French weather data came partly from data published by the NOAA (National Oceanic and Atmospheric Administration, USA), but the majority was supplied by the AgroClim Unit in Avignon, which manages the agroclimatic network of INRA. Spanish weather data came from the AMET (Agencia Estatal de Meteorología, Spain). Data from NOAA, AMET and DWD are publicly available online. The only Italian weather data used were measured by our working group in the Soave region (Blotevogel et al., 2018, 2019). In each case, the closest available weather station with data for the year of production was chosen. If the station was farther than 50 km, no weather data were assigned. Monthly rainfall and average temperature were recorded from March to September for the year of harvest for 132 wines.

2.4 Chemical content analysis

Even though Greenough et al. (1997) proposed using a large number of elements with diverse geochemical characteristics, our study focused on five elements (Ba, Ca, Mg, Mn and Sr) that are frequently used as tracers in geographical origin to facilitate analysis of a larger number of wines. Our first objective was to develop a rapid, efficient and easy-to-perform method to determine the Ba, Ca, Mg, Mn and Sr contents in various wines, using ICP-OES (Ultima Expert by Horiba, Kyoto, Japan) without any pre-treatment (except dilution) or mineralization of samples. ICP-OES is used widely for determination of elemental content in foods and environmental matrices but, because of the age of the method for wine (Thiel and Danzer, 1997), new adjustments and calibration were needed.

Ten wine samples (red and white) were mineralized in three steps for a calibration experiment. HNO_3 and HCl used for this study were purified by double sub-boil distillation in our laboratory. Suprapure H_2O_2 (30% v/v, 1 mL) was added to wine samples (10 mL) and left to react for 2 h to avoid explosion as a result of the reaction between ethanol and HNO_3 on addition of the HNO_3. Subsequently, 5 mL of HNO_3 was added slowly, and the mixture heated to 120°C in a closed Teflon bomb digestion vessel (Savillex, Eden Prairie, MN, USA) for at least 4 h. Then, samples were evaporated to dryness at 90°C. In the second digestion step, 4 mL of HCl (10 mol/L), 2 mL HNO_3 (14.5 mol/L) and 1 mL ultrapure HF (22.4 mol/L from Merck) were added to the digestion vessel, which was heated to 120°C for at least 4 h. Then, samples were again evaporated to dryness, and a final digestion step, using 5 mL of HNO_3, was performed at 120°C for at least 4 h. After evaporation to dryness, samples were dissolved in 20 mL HNO_3 20% (v/v), diluted 10 times and spiked with an in-house In/Re standard. Measurements were performed on an Agilent 7500ce Q-ICP-MS (Santa Clara, CA, USA). SLRS-5 certified reference materials (river water reference material for trace metals, from the National Research Council of Canada NRC – CNRC) were also run to assure quality. Recoveries were within a ±10% range of the certified values for the five elements considered.

Elemental contents of the wines were determined by ICP-OES, using ICP-MS to calibrate the direct measurement method. 10 wines previously studied using ICP-MS were run as standards in the ICP-OES batches to assure quality. Deviation of ±10% or less from ICP-MS measurements for each element was accepted. For ICP-OES measurements, wines were diluted in ultrapure water (18.2 MΩ): 10 times for Ca, Mg, Mn and Sr measurements, and 3.5 times for Ba analysis.

Standards were prepared in ultrapure water containing 1.2% and 4% ethanol (Et-OH) by volume. One drop (about 30 mg) of double sub-boiled HNO_3 was added to 100 mL of Ba standards to assure solution stability. Machine settings are denoted in Table 1.

Different methods have been published for analyzing elemental contents of wine using ICP-OES but, there is no standardized method, and parameters need to be adapted to the material used, as red wines in particular have a strong impact on plasma stability.

Table 1. Analytical parameters and experimental set-up for wine elemental study by ICP-OES.

ICP-OES method	For Ca, Mg, Mn, Sr	For Ba
Dilution	×10	×3.5
Operating power	1200 W	1200 W
Nebulization pressure	1.98 bar	1.98 bar
Nebulizer flow	0.82 L/min	0.7 L/min
Nebulizer type	PEEK Mira Mist	PEEK Mira Mist
Rinsing time	60s	60s
Stabilizationtime	20s	20s
Integration time	4 s	4 s
Wavelength	Ba 455.403 nm, Ca 317.933 nm, Mg 279.079 nm, Mn 257.610 nm, Sr 407.771 nm	

2.5 Statistical treatments and data interpretation

Data analysis was carried out using R software version 3.2.5. Elemental contents of the wines were log-transformed prior to statistical analysis. The script used to perform data analysis is provided as an R-file (Supplementary_Data_2_script.R). Linear discriminant analysis (LDA) was used to explore the relationship between elemental contents, color and soil type (calcareous/non-calcareous). Three LDAs were performed, the first using wine color only, the second using soil type only, and the third using both factors. These LDAs were performed using data containing both soil type and meteorological data (n=91), in preparation of the subsequent analyses (see below). The classification ability of the three LDAs was evaluated by cross-validation using the remaining samples (n=124 for the first LDA and n=61 for the second and third LDAs since 63 wines had no soil data).

Finally, the relative contribution of the various predictors (wine color, soil type and meteorological variables) to the variability in elemental contents of the wines as well as the relationship between meteorological variables and elemental contents were computed using redundancy discriminant analysis (RDA). RDA is the extension of multiple linear regression to multiple explanatory variables. In our case, the elemental contents of wines (five variables) were expressed as a function of wine color (0 for red; 1 otherwise), soil type (0 for non-calcareous; 1 for calcareous) and meteorological variables (14 variables). A partial RDA was performed to measure the effect of meteorological variables, given that the effect of wine color and soil type were already accounted for. The remaining covariance structure of the elemental contents of wines was investigated by conducting principal component analysis (PCA) on RDA residuals.

3. Results

3.1 Effect of storage factors (aging, alcohol oxidation and deposition)

We confirm that aging, alcohol oxidation, and precipitation did not influence element contents more than the degree of analytical uncertainty by conducting repeated analyses over three months storage. Average (± SD) concentrations, as a percentage of the initial measurement in the same wine measured after 3 months of storage, were: Ba 94.5±5.5%, Ca 98.5±4.2%, Mg 95.6±4.0%, Mn 102.9±5.7% and Sr 103.2±9.6%.

3.2 Effect of wine color on elemental composition

Red wines contained higher Mg concentrations than white, rosé or *vin gris* wines. LDA using all five elements could not separate rosé and *vin gris* wines from white wines. However, when the LDA was performed using two groups (i.e. red *vs* white/rosé/*gris*), 92.3% of 91 wines with available soil and meteorological data were assigned correctly. Cross-validation using wines without soil and meteorological data classified correctly 84.7% of the wines. The relative contributions of the chemical elements to the LDA axis weights (Table SI-1, Supplementary_Data_3_Linear_Discriminants.xls) showed that Mg and Ca were the major contributors. These results also showed that the LDA axis can be approximated well with $[Mg]^2/[Ca]$ (Pearson correlation coefficient: $r= -0.98$). Fig. 2 shows the distribution of red, white, rosé and *vin gris* wines as a function of $[Mg]^2/[Ca]$ ($\log_{10}$-transformed). The cut-off value for $\log_{10}([Mg]^2/[Ca])$, which optimized classification of red wines *vs* white/rosé/*gris* wines, was 2 (using an exhaustive search of all wines between 1.4 and 2.8 every 0.01). The cut-off value of 2 led us to the following classification rule for red *vs* white/rosé/*gris* wines using Mg and Ca concentration: red wines > $[Mg]^2/[Ca]$ 100 < white/rosé/*gris* wines. This rule classified correctly 92.3% of the wines, using the learning dataset, and 87.7% of the wines using the cross-validation dataset. Applying this rule to the whole dataset classified correctly 89.8% of wines.

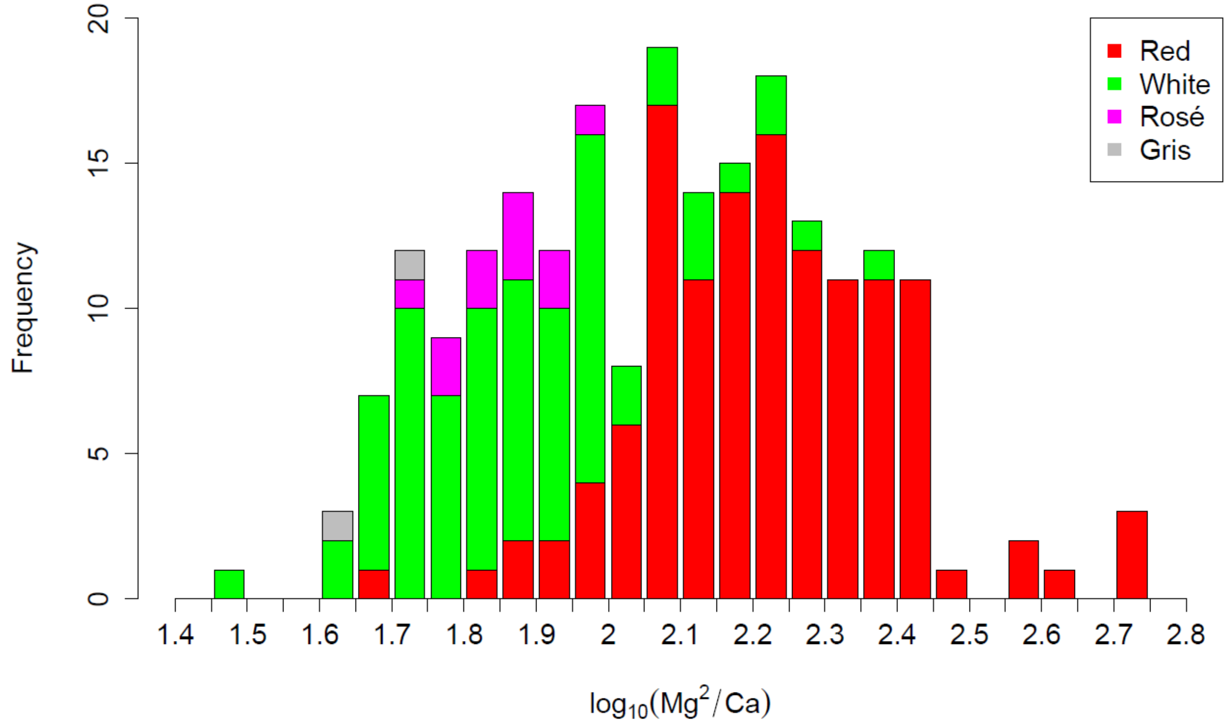

Fig. 2. Mg and Ca composition of wines depends on wine color, more specifically differing between red wines and white/rosé/*gris* wines (red=red wine, green=white wine, violet=rosé wine and gray=*vin gris*). The ratio Mg^2/Ca (x-axis; $\log_{10}$-transformed) approximates the first axis of the LDA which connects wine color as a linear function of elemental composition (Mg, Ca, Mn, Sr, Ba). The y-axis counts wine samples; 89.8% of wines are correctly classified.

3.3 Effect of soil geochemistry (calcareous vs non-calcareous) on elemental composition of wines

The wine elemental contents also enabled identification of the soil type factor "calcareous", containing the values "yes" and "no" (Fig. 3). Principal factors allowing separation were concentrations of Ba, Mg and Mn (Table SI-1, Supplementary_Data_3_Linear_Discriminants.xls). The influence of Ca concentration on the identification of soil properties was the lowest, about 20-fold less than that of Mg, the most influential element. Using all five elements, 89.0% of the wines with soil and meteorological data and 85.2% of the cross-validation dataset were classified correctly. Again, the criterion for classification could be reduced to two elements. The decision criterion ($\log_{10}([Mg]*[Ba]) = 1.05$) was determined by an exhaustive search between 0 and 1.6 in 0.05 steps for the 152 wines with soil data. Fig. 3 shows an LDA classifying correctly 84.9% of the 152 wines with soil data. If [Mg]*[Ba] < 11.2, then wines were assigned to the calcareous soil group. Otherwise, if [Mg]*[Ba] ≥ 11.2, the wines were classified as coming from non-calcareous soil.

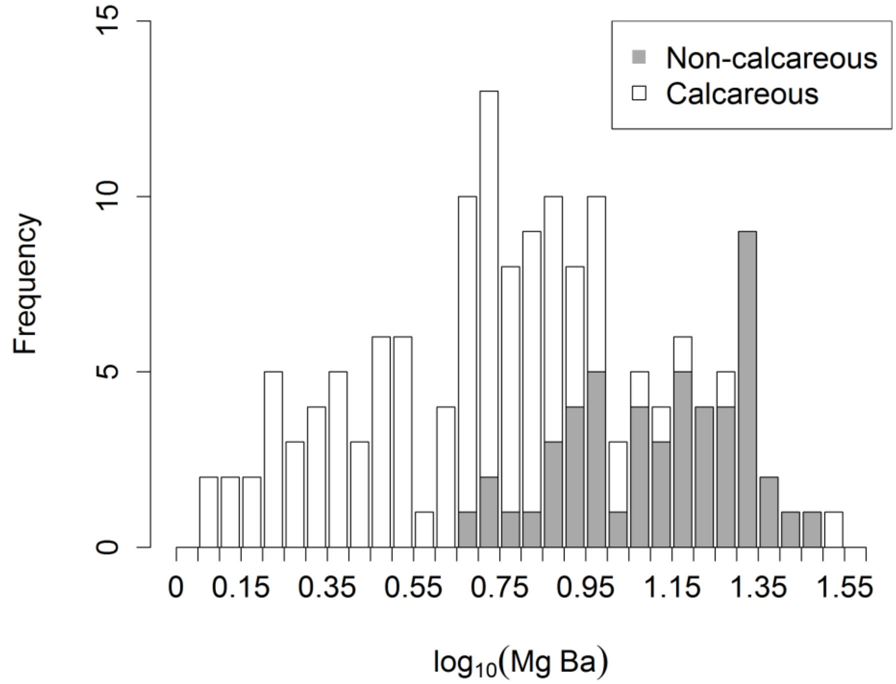

Fig. 3. Mg and Ba composition of wines depends on soil geochemistry, more specifically differing between wines grown in calcareous soils (white) and in non-calcareous soils (gray). The product Mg Ba (x-axis; $\log_{10}$-transformed) approximates the first axis of the LDA which connects soil geochemistry as a linear function of elemental composition (Mg, Ca, Mn, Sr, Ba). The y-axis counts wine samples; 84.2% of wines are correctly classified.

3.4 Soil–color interaction

As the effects of wine color and soil type were determined on the same dataset, it is possible that some degree of interaction exists. Fig. 4 shows an LDA using four classes: “red+calcareous”, “red+non-calcareous”, “non-red+calcareous” and “non-red+non-calcareous”. Although the four groups overlapped at the edges, and some clear outliers were visible, the centers of each group were well separated. The influences of color and soil type were mostly orthogonal. RDA (Fig. SI-1, Supplementary_Data_4_partial_RDA_calc_color.pdf) showed that the combined effects of soil type and color accounted for 28.5% of the variance in the dataset.

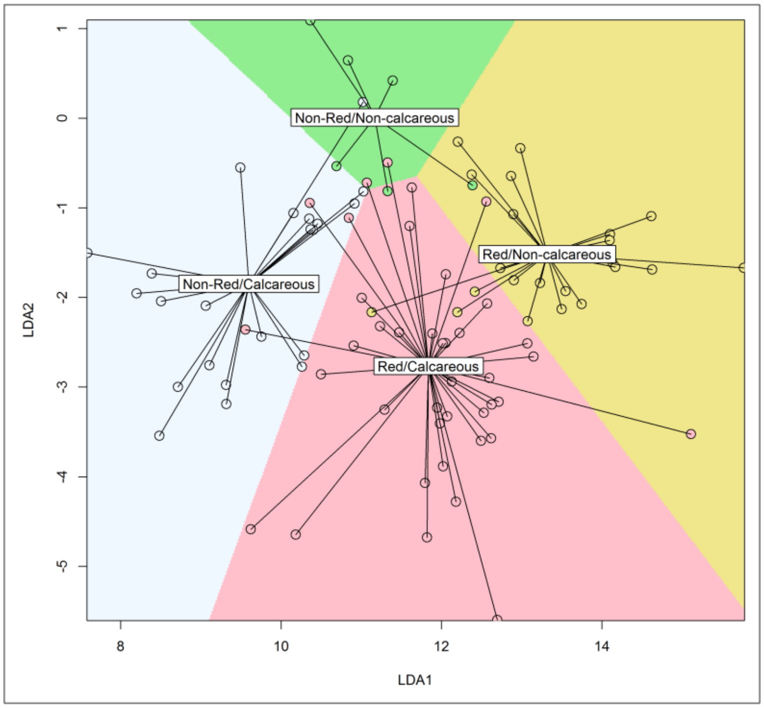

Fig. 4. Elemental composition of wines can discriminate both soil geochemistry and color. Soil samples (dots) are here projected onto the two first axes of the LDA analysis (first LDA axis on the x-axis; second LDA axis on the y-axis) which connects soil geochemistry (as “calcareous” or “non-calcareous” soil) and wine color (as red or white/rosé/*gris*) as a linear function of wine elemental composition (from Mg, Ca, Mn, Sr and Ba content). Background color indicates the predicted assigned group (groups are: red/calcareous, non-red/calcareous, non-red/non-calcareous and red/non-calcareous). Point markercolor highlights the observed group affiliation.

3.5 Effect of climatic parameters on elemental composition of wines

RDA was performed on the RDA residuals determining the effects of color and soil type on elemental compositions (Fig. SI-2, Supplementary_Data_5_partial_RDA_meteo.pdf) and showed that meteorological factors explained 23.4% of the remaining variance. The principal RDA axis can be summarized as temperature minus rainfall in the summer months. Correlations of Ca and Mg concentrations with this axis were weak, as their variance was largely exploited for color and soil type classifications. The concentration of Sr correlated with higher temperatures, and Ba and Mn concentrations with greater summer rainfall.

The same RDA performed on the dataset without subtracting the effect of color and soil type explained 24.1% of total variance.

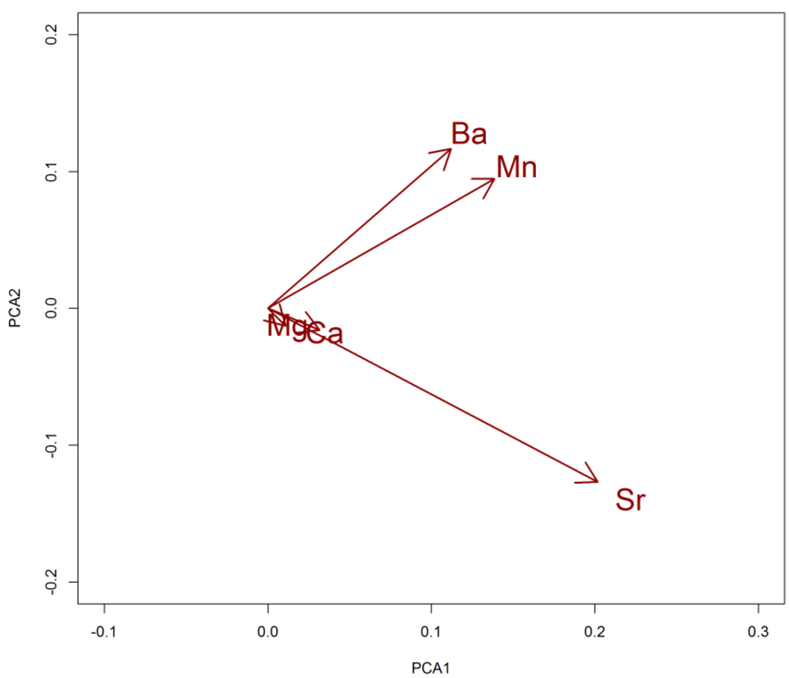

Fig. 5. Leftover variance of Ba and Mn is correlated whereas leftover variance of Sr is independent. Elemental composition variables (red arrows) are projected in reduced space (PCA first axis on the x-axis; PCA second axis on the y-axis). PCA was performed on the residuals of the RDA which connects elemental composition as a function of (1) wine color and soil and (2) meteorological variables, which conjointly explain 45.2% of the variance of elemental concentration data.

3.6 Remaining variance

After subtracting the effects of wine color, soil and meteorological factors, 54.8% of the total variance in the dataset remained unexplained. In a PCA performed on the RDA residuals described in Section 3.4, two nearly orthogonal contributions were visible (Fig. 5): Ba and Mn pointed in one direction whereas Sr pointed in another. The contributions of Mg and Ca were low, as their variance was largely exploited in color and soil type analysis.

4. Discussion

4.1 Influence of wine color as an indicator of wine-making process on the elemental profiles of wines

The comparison of Mg content in red wines with the content in white/rosé/*gris* wines suggested a slow extraction of Mg from the grape residues during maceration and fermentation. In the literature, Mg is reported to accumulate in grape seeds, which are present during red wine fermentation (Rogers et al., 2006). Mg has already been described as being part of the elements allowing separation of white from red wines (Greenough et al., 1997; Martin et al., 2012), even though it does not appear in other classifications of wine color. The Ca content of red wines tended to be lower than white/rosé and *gris* wines, especially when compared with Mg, as the separation axis can be summarized as $[Mg]^2/[Ca]$. This is probably due to malolactic fermentation of red wines, which is used less commonly in white wines. Malolactic fermentation consumes malic acid in the wine, a major inhibitor of Ca-tartrate precipitation (Mckinnon et al., 1995). Thus, this second fermentation facilitates removal of Ca from the wine.

4.2 Influence of environmental factors (soil and climate) on the elemental profile of wine

The presence of lime influences the major properties of soil chemistry. As highly soluble mineral, dissolution of $CaCO_3$ controls soil pH by consuming protons to form HCO_3 (George et al., 2012; van Breemen et al., 1983). Thus, lime determines the solubility of mineral nutrients as well as promoting competition between Ca ions and other bivalent nutrient ions during plant uptake (White, 2012). Furthermore, Ca is a powerful flocculating agent for clay minerals and organic matter and, thus, also influences soil structure (Haynes & Naidu, 1998). Calcareous soils were historically thought to produce "better wines" in terms of taste and flavor (Vermorel & Michaut, 1889; Viala & Ferrouillat, 1887). In contrast, the absence of lime usually translates to greater mobility of most metals, including Al and Mn, which can have toxic effects on plants (George et al., 2012). For this reason, many non-calcareous vineyard soils have a long history of liming and lime was part of the 'Bordelaise mixture' (Vermorel & Michaut, 1889; Viala & Ferrouillat, 1887). Today, however, Mn and Al toxicity are prevented by rootstock choice and liming is rare. Nevertheless, this study allowed determination of pedological proveniences of wines, based only on a combination of cations. The elements that were measured (with exception of Mg) are not considered as mobile in the phloem and, as such, are transported by the xylem fascicles (Marschner & Marschner, 2012). As they are transported via the water supply system, environmental factors, such as transpiration rate or concentration in soil solution, can be expected to have a greater influence.

In the LDA analyses, higher concentrations of Ba, Mg and Mn were associated with non-calcareous soils. Ba and Mn contents in plant tissues have been reported to be greatly decreased by the addition of lime (by a factor of 6 and 4, respectively) and, subsequently, pH rises from 5.2 to 7.8

(Tyler & Olsson, 2001). For Mn, this effect is due to increased solubility of Mn oxides at acid pHs, up to toxic levels inplants (George et al., 2012). The case for Ba is less clear: Carbonates are the primary source of Ca nutrition for plants, in contrast to silicate minerals in non-calcareous soils (Reynolds et al., 2012). But, Ba is virtually absent in most soil carbonates considered in this study (calcite, dolomite or aragonite), suggesting that Ba uptake might be influenced by its content in the Ca source and associated Ca:Ba ratios in soil (Blum et al., 2000), explaining the lower Ba contents in wines grown on calcareous soils. Higher Mg contents in wines from non-calcareous soils could be due to competitive absorption between Ca and Mg (White, 2012); Mg is also naturally more abundant in silicate rocks, with respect to Ca, than in carbonates. The influences of Ca and Sr were small but higher concentrations of Sr pointed to calcareous soils. Considering the greater mobility of Ca in calcareous soils, this pointed to active regulation of Ca content by the plant. In any case, soil pH and Ca-homeostasis mechanisms seem to condition differences in elemental compositions between wines grown on calcareous *vs* non-calcareous soils. The link between soil chemistry and wine elemental compositions shows, for the first time, the influence of macroscopic soil parameters on grape compositions. Furthermore, lime content controls soil pH, which is reported to influence grapevine quality (Bavaresco and Poni, 2003).

These clear effects of soil type on wine geochemistry are stated, even though separation performance would be expected to be higher, if the soil data were more comprehensive and quantitative. Finally, combining the effects of wine color and soil type showed that both factors were close to orthogonal, suggesting their influences are independent of one another.

Environmental factors also include the influence of climate on elemental compositions of the wines. After subtracting the influences of maceration process and soil chemistry, weather conditions explained 23.4% of the remaining variance in elemental composition. Higher concentrations of Ba and Mn were associated with greater summer rainfall, but higher Sr contents were associated with higher temperatures. Greenough et al. (2005) correlated high Sr contents in wines with arid conditions. The main RDA axis opposed these factors and, thus, the main climatic effect could be interpreted as drought stress, which decreased Ba and Mn concentrations and increased Sr concentrations, due to evaporation processes and accumulation of carbonate salts in typical dry-climate soils. The correlation of Mn and Ba concentrations with higher precipitation, especially in the summer months, could be due either to greater mobility of these elements in wet soils with low redox potential or greater acidification of soils receiving more rain.

4.3 Causes of leftover variance

Using the three factors examined (wine color, soil type and climate), 45.2% of the total variance in the dataset could be explained. PCA performed on the residuals (Fig. 5) showed an axis influenced by Sr concentration and another by Ba and Mn. Sr contents of the wines, as one of the parameters most used in fingerprinting schemes, as previously reported by Greenough et al. (2005), was not explained to any great extent by the environmental factors used in this study. As Sr chemistry is very similar to that of Ca, the ratio of these two elements should also depend on their signature in the substratum.

Sr content in limestone varied between 250 mg/kg in the Valanginian age and 1650 mg/kg in the early Miocene, with important fluctuations over the past 140 million years (Renard, 1985). In calcareous soils, the Sr:Ca variation should, thus, differentiate limestone formation of different ages and geologic circumstances, and indicate the actual geological formation providing Ca nutrition. This implies that the Sr:Ca ratio might be a good tool to discriminate vine-growing regions, where Sr:Ca ratios differ locally. However, on a global scale, the same ratios are likely to be encountered in different vineyard regions.

The unexplained variances of Ba and Mn might be due differences in soil pH, as a more detailed measure of soil chemistry than the presence of carbonates alone. However, it could also be influenced by redox potential and, thus, soil water status (Kabata-Pendias, 2004; Magalhães et al., 2012).

Some production procedures have also been shown to influence the elemental compositions of wines (Hopfer et al., 2015). As our dataset was composed of wines from 183 different wineries, no systematic effect was expected or observed. Influences due to root stock and cultivar species have been reported in the literature (Angus et al., 2006; Martin et al., 2012). However, as many wines in our dataset were blends, and we focused on wide geographical distributions, analysis of mono-cultivar was not significant. Moreover, data on rootstock were, unfortunately, not available in most cases.

5. Conclusions

In this analytical and statistical study, Mg, Ca, Mn, Sr and Ba contents in 215 wines from different wine-growing regions in France, Germany, Italy and Spain were analyzed using an adapted ICP-OES method. Chemical data were combined with meteorological data and information about soil chemistry. Through multivariate statistical analysis, we provided evidence that elemental profiles of the wines were controlled by soil chemistry (such as the calcareous profile of soils) and meteorological conditions during the grapevine growth period. In particular, Mg and Ba contents were higher in wines produced from non-calcareous soils. Sr contents were higher in wines from regions with high summer temperatures, and Mn and Ba contents were higher in regions with high summer rainfall. Furthermore, Mg:Ca ratios were linked to wine color and, thus, styles of wine-making, likely due to Ca precipitation as tartrate during malolactic fermentation. Finally, systematic differences in elemental profiles of the wines open up a potential route for investigating the contribution of soil chemistry in the terroir effect.

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Supplementary Information

Supplementary_Data_1_wines.txt. Dataset used for statistical analysis in the present article. The file contains (columns) data on geographical origin, appellation, wine color, vintage, soil type, chemical analysis and meteorological conditions for each wine (rows) of the 215 wine samples used in the article. The file is formatted in utf8, using ‘;’ as field delimiter and ‘.’ as decimal sign.

Supplementary_Data_2_script.R. Rscript used for the statistical analysis presented in the article. The script can be run using an R version newer than 3.2.5 using the packages specified in the script file in combination with the data from Supplementary_Data_1_wines.txt. Note that some packages are incompatible so that not all are called in the preamble but rather in the appropriate positions.

Table SI-1 (Supplementary_Data_3_Linear_Discriminants.xls). Table showing the contribution of each element to the first LDAaxes. Three LDAs were conducted: wine color alone (two groups), soil type alone (two groups), and both (four groups), all linear functions of elemental concentrations ($\log_{10}$-transformed). The LDA axis of the two first LDAs were approximated into $\log_{10}(Mg^2/Ca)$ and $\log_{10}(Mg\ Ba)$ and used to produce the plots of Figs. 2 and 3.

Fig. SI-1 (Supplementary_Data_4_RDA_calc_color.pdf). Triplot of the RDA using soil type and wine color as response variables, and elemental concentrations as explanatory variables.

Fig. SI-2 (Supplementary_Data_5_RDApartial_meteo.pdf). Triplotof the partial RDA using meteorological parameters as response variables, and elemental concentrations as explanatory variables, after subtracting the effect of soil and color.