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Soil chemistry and meteorological conditions influence the elemental profiles of West European wines

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27 **Abstract**

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

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

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

41

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

44

45 **This manuscript was published under doi: 10.1016/j.foodchem.2019.125033 in Food Chemistry.**

46 **Highlights**

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

53

54

55 **1. Introduction**

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

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

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

77 Taylor et al. (2002, 2003) in North America, Fabani et al. (2010) in South America, and Angus et al.
78 (2006) or Martin et al. (2012) in Australia and New Zealand, but also studies such as those of Almeida
79 and Vasconcelos (2003), Baxter et al. (1997) or Jurado et al. (2012) in the European Old World. Only
80 one relatively old investigation (Kwan et al., 1979) compared elemental composition of wines from
81 different continents (Europe and North America). All studies covered a small number of wine-growing
82 regions, coupled with statistical methods and sometimes classical enological parameters, without
83 proposing biogeochemical mechanisms for the differences observed. To date, there is a lack of
84 elemental content studies on a global scale including a multitude of wine regions and an
85 unambiguous combination of elements allowing regional classification of wines. Still, some elements
86 are recurrent in the literature. Rubidium (Rb) was used in 15/22 studies, strontium (Sr) in 13/22
87 studies, manganese (Mn) in 13/22 studies and barium (Ba) in 12/22 studies, followed by magnesium
88 (Mg) used in 9/22 and cobalt (Co) 8/22. Subsequently, multiple elements start to be used equally.

89 In the previous cited literature, differences in wine composition were usually assigned to soil
90 or climatic influences, in a limited spatial area of investigation. Except for that of Greenough et al.
91 (2005), who studied wines from 6000 km across Canada, most of the studies investigated links
92 between soil and wine composition at the local scale and for a well-defined terroir, without covering
93 diverse biogeoclimatic conditions. Moreover, some of them link empirically the total or extracted
94 element contents of soil to wine composition. However, element mobility and plant uptake from soil
95 depend on physicochemical characteristics and bioavailability, rather than total content.

96 This study aims to contribute to the understanding of environmental factors (such as soil type
97 and properties, or climate factors) influencing the elemental composition of wines on an inter-
98 regional scale (Western Europe), with a rapid, easy-to-perform and inexpensive method using

99 inductively coupled plasma optical emission spectrometry (ICP-OES). By investigating 215 wines from
100 a spatially extended area with contrasting biogeoclimatic conditions (France and adjacent wine-
101 growing regions especially Spain, Italy and Germany), this study aims to identify global effects on the
102 elemental compositions of wine to elucidate which environmental factors control elemental
103 composition. Multivariate statistical methods were used to explore the contribution of various
104 parameters (wine color as a marker of wine-making process, “calcareous” or “non-calcareous” soil
105 conditions, and meteorological conditions) on the elemental compositions of wines. The novelty of
106 this work stems from the breadth of the dataset, making it different from previous studies that
107 analyzed a large number of wines from only a small number of regions.

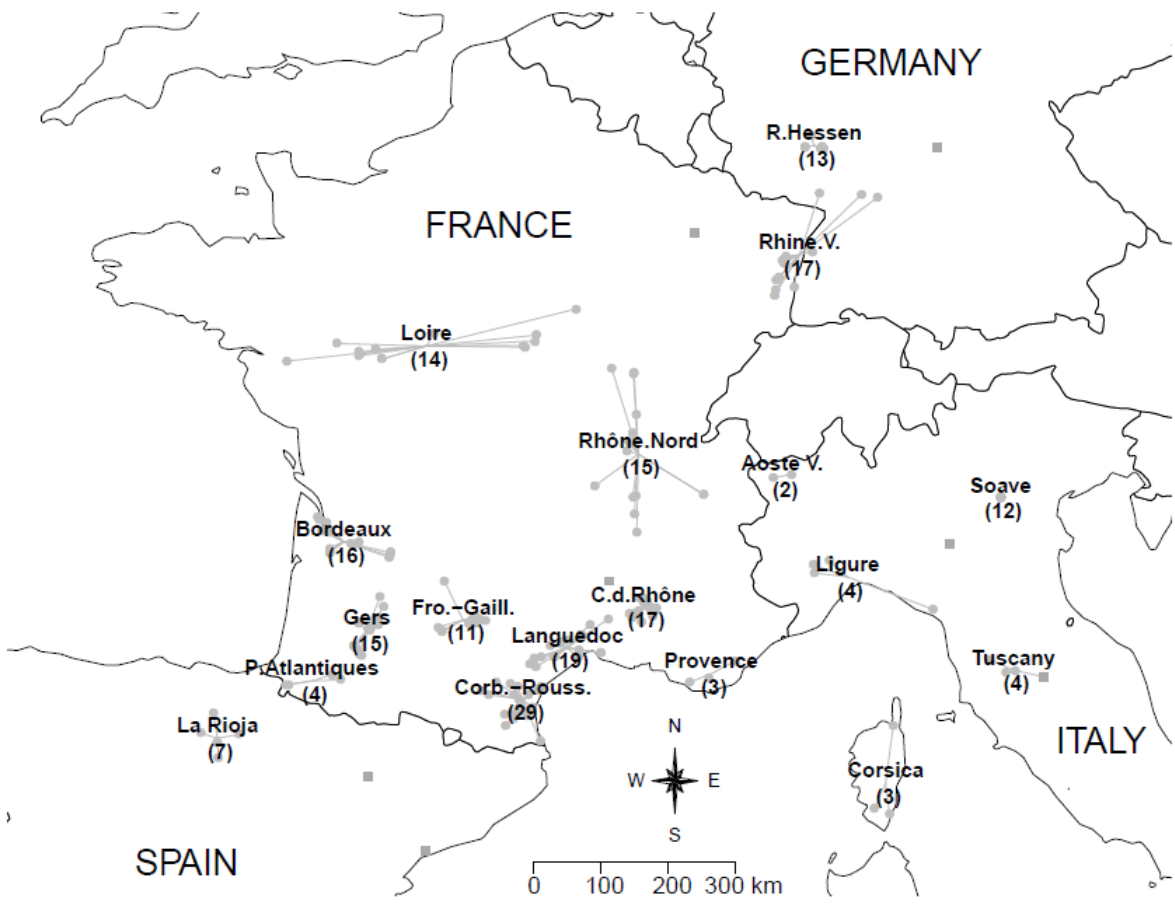
108

109 **2. Materials and methods**

110 ***2.1 Wine collection and storage***

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

120 alcohol oxidation and deposition) were checked using the same samples on several dates throughout
121 the 3 months of storage.



122
123 **Fig. 1.** Provenience of wines and their attribution to major wine-growing areas. Regions with only one
124 wine sample are marked by a square; otherwise, region names and number of wines are given. Gray
125 dots show provenience of wine samples. Aoste.V.: Aoste Valley; C.d.Rhône: Côtes du Rhône; Corb.-
126 Rouss.: Corbières et Roussillon; Fro.-Gaill.: Fronton and Gaillac; P.Atlantiques: Pyrénées Atlantiques;
127 R.Hessen: Rheinhessen; Rhine.V.: Rhine Valley.

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132 **2.2 Determination of soil type**

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

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

149

150 **2.3 Climatic conditions**

151 Coordinates of the actual grape-producing area was either known (n=33) or determined from
152 the address of the winery (n=53) or the village of provenience (n=46). Weather data for Germany
153 were taken from publicly available stations of the “Deutscher Wetterdienst” (DWD) and the weather

154 survey of Geisenheim University. French weather data came partly from data published by the NOAA
155 (National Oceanic and Atmospheric Administration, USA), but the majority was supplied by the
156 AgroClim Unit in Avignon, which manages the agroclimatic network of INRA. Spanish weather data
157 came from the AMET (Agencia Estatal de Meteorología, Spain). Data from NOAA, AMET and DWD are
158 publicly available online. The only Italian weather data used were measured by our working group in
159 the Soave region (Blotevogel et al., 2018, 2019). In each case, the closest available weather station
160 with data for the year of production was chosen. If the station was farther than 50 km, no weather
161 data were assigned. Monthly rainfall and average temperature were recorded from March to
162 September for the year of harvest for 132 wines.

163

164 **2.4 Chemical content analysis**

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

173 Ten wine samples (red and white) were mineralized in three steps for a calibration
174 experiment. HNO₃ and HCl used for this study were purified by double sub-boil distillation in our
175 laboratory. Suprapure H₂O₂ (30% v/v, 1 mL) was added to wine samples (10 mL) and left to react for 2

176 h to avoid explosion as a result of the reaction between ethanol and HNO_3 on addition of the HNO_3 .
177 Subsequently, 5 mL of HNO_3 was added slowly, and the mixture heated to 120°C in a closed Teflon
178 bomb digestion vessel (Savillex, Eden Prairie, MN, USA) for at least 4 h. Then, samples were
179 evaporated to dryness at 90°C . In the second digestion step, 4 mL of HCl (10 mol/L), 2 mL HNO_3 (14.5
180 mol/L) and 1 mL ultrapure HF (22.4 mol/L from Merck) were added to the digestion vessel, which was
181 heated to 120°C for at least 4 h. Then, samples were again evaporated to dryness, and a final
182 digestion step, using 5 mL of HNO_3 , was performed at 120°C for at least 4 h. After evaporation to
183 dryness, samples were dissolved in 20 mL HNO_3 20% (v/v), diluted 10 times and spiked with an in-
184 house In/Re standard. Measurements were performed on an Agilent 7500ce Q-ICP-MS (Santa Clara,
185 CA, USA). SLRS-5 certified reference materials (river water reference material for trace metals, from
186 the National Research Council of Canada NRC – CNRC) were also run to assure quality. Recoveries
187 were within a $\pm 10\%$ range of the certified values for the five elements considered.

188 Elemental contents of the wines were determined by ICP-OES, using ICP-MS to calibrate the
189 direct measurement method. 10 wines previously studied using ICP-MS were run as standards in the
190 ICP-OES batches to assure quality. Deviation of $\pm 10\%$ or less from ICP-MS measurements for each
191 element was accepted. For ICP-OES measurements, wines were diluted in ultrapure water (18.2 M Ω):
192 10 times for Ca, Mg, Mn and Sr measurements, and 3.5 times for Ba analysis.

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

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

199

200 **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
Stabilization time	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	

201

202

203 **2.5 Statistical treatments and data interpretation**

204 Data analysis was carried out using R software version 3.2.5. Elemental contents of the wines
 205 were log-transformed prior to statistical analysis. The script used to perform data analysis is provided
 206 as an R-file (Supplementary_Data_2_script.R). Linear discriminant analysis (LDA) was used to explore
 207 the relationship between elemental contents, color and soil type (calcareous/non-calcareous). Three
 208 LDAs were performed, the first using wine color only, the second using soil type only, and the third

209 using both factors. These LDAs were performed using data containing both soil type and
210 meteorological data (n=91), in preparation of the subsequent analyses (see below). The classification
211 ability of the three LDAs was evaluated by cross-validation using the remaining samples (n=124 for
212 the first LDA and n=61 for the second and third LDAs since 63 wines had no soil data).

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

223

224 **3. Results**

225 ***3.1 Effect of storage factors (aging, alcohol oxidation and deposition)***

226 We confirm that aging, alcohol oxidation, and precipitation did not influence element contents
227 more than the degree of analytical uncertainty by conducting repeated analyses over three months
228 storage. Average (\pm SD) concentrations, as a percentage of the initial measurement in the same wine

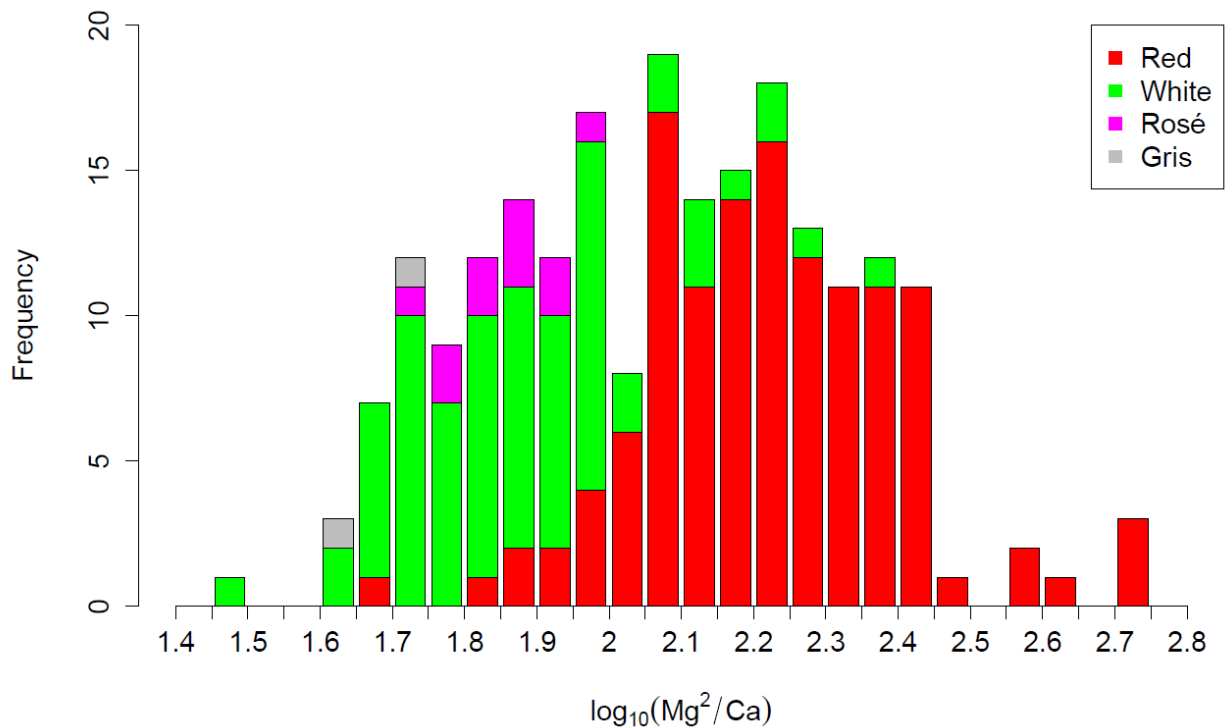
229 measured after 3 months of storage, were: Ba $94.5 \pm 5.5\%$, Ca $98.5 \pm 4.2\%$, Mg $95.6 \pm 4.0\%$, Mn
230 $102.9 \pm 5.7\%$ and Sr $103.2 \pm 9.6\%$.

231

232 **3.2 Effect of wine color on elemental composition**

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

248



249

250 **Fig. 2.** Mg and Ca composition of wines depends on wine color, more specifically differing between red
 251 wines and white/rosé/gris wines (red=red wine, green=white wine, violet=rosé wine and gray=*vin*
 252 *gris*). The ratio Mg²/Ca (x-axis; log₁₀-transformed) approximates the first axis of the LDA which
 253 connects wine color as a linear function of elemental composition (Mg, Ca, Mn, Sr, Ba). The y-axis
 254 counts wine samples; 89.8% of wines are correctly classified.

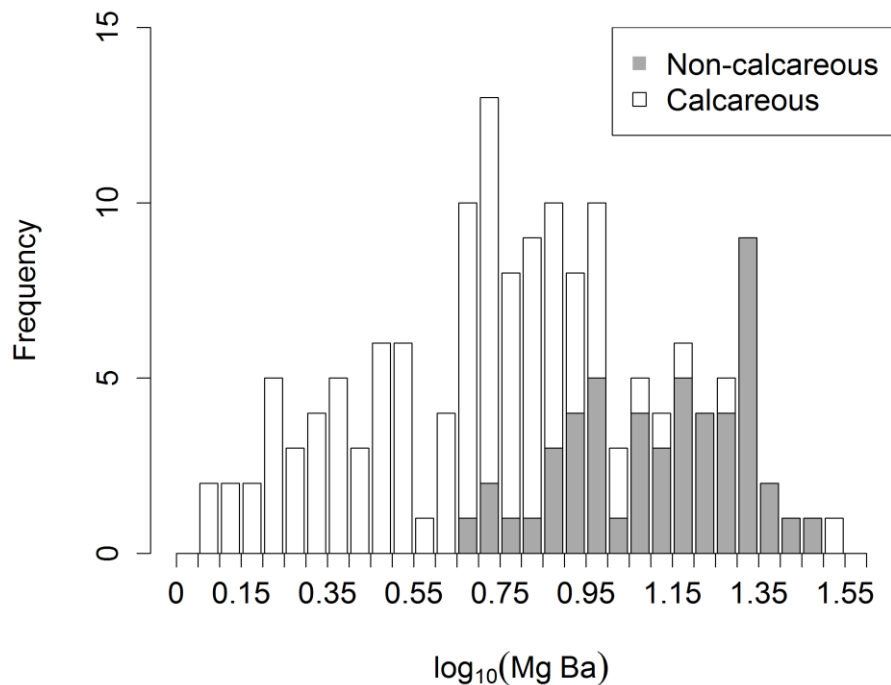
255

256 **3.3 Effect of soil geochemistry (calcareous vs non-calcareous) on elemental composition of wines**

257 The wine elemental contents also enabled identification of the soil type factor “calcareous”,
 258 containing the values “yes” and “no” (Fig. 3). Principal factors allowing separation were
 259 concentrations of Ba, Mg and Mn (Table SI-1, Supplementary_Data_3_Linear_Discriminants.xls). The
 260 influence of Ca concentration on the identification of soil properties was the lowest, about 20-fold
 261 less than that of Mg, the most influential element. Using all five elements, 89.0% of the wines with
 262 soil and meteorological data and 85.2% of the cross-validation dataset were classified correctly.
 263 Again, the criterion for classification could be reduced to two elements. The decision criterion
 264 ($\log_{10}([Mg] \cdot [Ba]) = 1.05$) was determined by an exhaustive search between 0 and 1.6 in 0.05 steps for

265 the 152 wines with soil data. Fig. 3 shows an LDA classifying correctly 84.9% of the 152 wines with soil
 266 data. If $[Mg]*[Ba] < 11.2$, then wines were assigned to the calcareous soil group. Otherwise, if
 267 $[Mg]*[Ba] \geq 11.2$, the wines were classified as coming from non-calcareous soil.

268



269

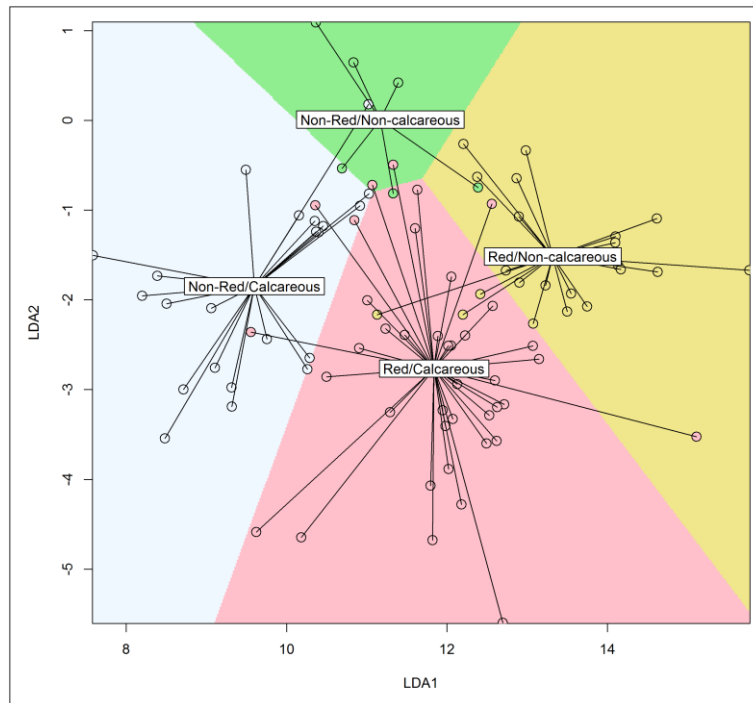
270 **Fig. 3.** Mg and Ba composition of wines depends on soil geochemistry, more specifically differing
 271 between wines grown in calcareous soils (white) and in non-calcareous soils (gray). The product Mg
 272 Ba (x-axis; \log_{10} -transformed) approximates the first axis of the LDA which connects soil geochemistry
 273 as a linear function of elemental composition (Mg, Ca, Mn, Sr, Ba). The y-axis counts wine samples;
 274 84.2% of wines are correctly classified.

275

276 3.4 Soil-color interaction

277 As the effects of wine color and soil type were determined on the same dataset, it is possible
 278 that some degree of interaction exists. Fig. 4 shows an LDA using four classes: “red+calcareous”,
 279 “red+non-calcareous”, “non-red+calcareous” and “non-red+non-calcareous”. Although the four

280 groups overlapped at the edges, and some clear outliers were visible, the centers of each group were
281 well separated. The influences of color and soil type were mostly orthogonal. RDA (Fig. SI-1,
282 Supplementary_Data_4_partial_RDA_calc_color.pdf) showed that the combined effects of soil type
283 and color accounted for 28.5% of the variance in the dataset.



284
285 **Fig. 4.** Elemental composition of wines can discriminate both soil geochemistry and color. Soil samples
286 (dots) are here projected onto the two first axes of the LDA analysis (first LDA axis on the x-axis;
287 second LDA axis on the y-axis) which connects soil geochemistry (as “calcareous” or “non-calcareous”
288 soil) and wine color (as red or white/rosé/gris) as a linear function of wine elemental composition
289 (from Mg, Ca, Mn, Sr and Ba content). Background color indicates the predicted assigned group
290 (groups are: red/calcareous, non-red/calcareous, non-red/non-calcareous and red/non-calcareous).
291 Point marker color highlights the observed group affiliation.

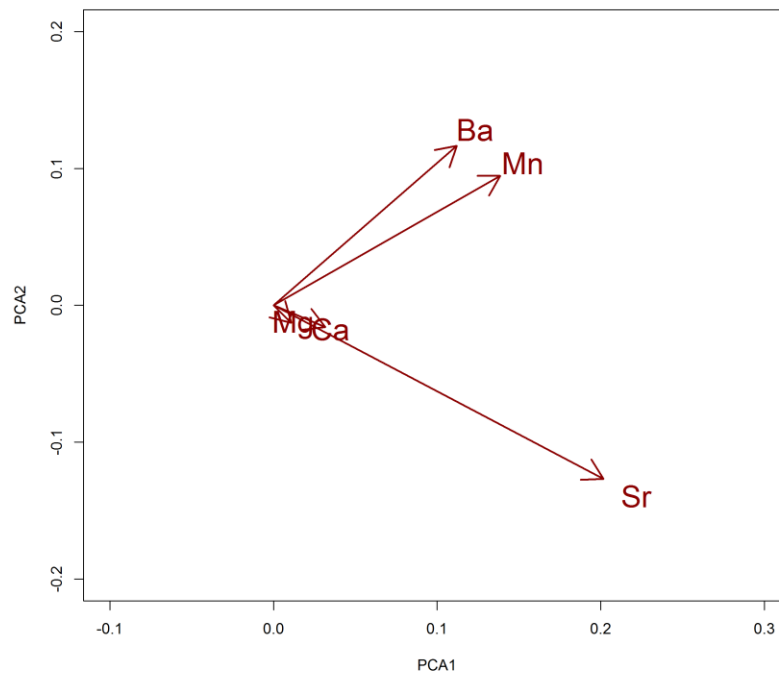
292
293 **3.5 Effect of climatic parameters on elemental composition of wines**

294 RDA was performed on the RDA residuals determining the effects of color and soil type on
295 elemental compositions (Fig. SI-2, Supplementary_Data_5_partial_RDA_meteo.pdf) and showed that
296 meteorological factors explained 23.4% of the remaining variance. The principal RDA axis can be

297 summarized as temperature minus rainfall in the summer months. Correlations of Ca and Mg
298 concentrations with this axis were weak, as their variance was largely exploited for color and soil type
299 classifications. The concentration of Sr correlated with higher temperatures, and Ba and Mn
300 concentrations with greater summer rainfall.

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

303



304

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

310

311 **3.6 Remaining variance**

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

317

318 **4. Discussion**

319 **4.1 Influence of wine color as an indicator of wine-making process on the elemental profiles of** 320 **wines**

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

333 4.2 Influence of environmental factors (soil and climate) on the elemental profile of wine

334 The presence of lime influences the major properties of soil chemistry. As highly soluble
335 mineral, dissolution of CaCO_3 controls soil pH by consuming protons to form HCO_3^- (George et al.,
336 2012; van Breemen et al., 1983). Thus, lime determines the solubility of mineral nutrients as well as
337 promoting competition between Ca ions and other bivalent nutrient ions during plant uptake (White,
338 2012). Furthermore, Ca is a powerful flocculating agent for clay minerals and organic matter and,
339 thus, also influences soil structure (Haynes & Naidu, 1998). Calcareous soils were historically thought
340 to produce “better wines” in terms of taste and flavor (Vermorel & Michaut, 1889; Viala & Ferrouillat,
341 1887). In contrast, the absence of lime usually translates to greater mobility of most metals, including
342 Al and Mn, which can have toxic effects on plants (George et al., 2012). For this reason, many non-
343 calcareous vineyard soils have a long history of liming and lime was part of the ‘Bordelaise mixture’
344 (Vermorel & Michaut, 1889; Viala & Ferrouillat, 1887). Today, however, Mn and Al toxicity are
345 prevented by rootstock choice and liming is rare. Nevertheless, this study allowed determination of
346 pedological proveniences of wines, based only on a combination of cations. The elements that were
347 measured (with exception of Mg) are not considered as mobile in the phloem and, as such, are
348 transported by the xylem fascicles (Marschner & Marschner, 2012). As they are transported via the
349 water supply system, environmental factors, such as transpiration rate or concentration in soil
350 solution, can be expected to have a greater influence.

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

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

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

374 Environmental factors also include the influence of climate on elemental compositions of the
375 wines. After subtracting the influences of maceration process and soil chemistry, weather conditions

376 explained 23.4% of the remaining variance in elemental composition. Higher concentrations of Ba and
377 Mn were associated with greater summer rainfall, but higher Sr contents were associated with higher
378 temperatures. Greenough et al. (2005) correlated high Sr contents in wines with arid conditions. The
379 main RDA axis opposed these factors and, thus, the main climatic effect could be interpreted as
380 drought stress, which decreased Ba and Mn concentrations and increased Sr concentrations, due to
381 evaporation processes and accumulation of carbonate salts in typical dry-climate soils. The correlation
382 of Mn and Ba concentrations with higher precipitation, especially in the summer months, could be
383 due either to greater mobility of these elements in wet soils with low redox potential or greater
384 acidification of soils receiving more rain.

385

386 ***4.3 Causes of leftover variance***

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

394 Sr content in limestone varied between 250 mg/kg in the Valanginian age and 1650 mg/kg in
395 the early Miocene, with important fluctuations over the past 140 million years (Renard, 1985). In
396 calcareous soils, the Sr:Ca variation should, thus, differentiate limestone formation of different ages
397 and geologic circumstances, and indicate the actual geological formation providing Ca nutrition. This

398 implies that the Sr:Ca ratio might be a good tool to discriminate vine-growing regions, where Sr:Ca
399 ratios differ locally. However, on a global scale, the same ratios are likely to be encountered in
400 different vineyard regions.

401 The unexplained variances of Ba and Mn might be due differences in soil pH, as a more
402 detailed measure of soil chemistry than the presence of carbonates alone. However, it could also be
403 influenced by redox potential and, thus, soil water status (Kabata-Pendias, 2004; Magalhães et al.,
404 2012).

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

412

413 **5. Conclusions**

414 In this analytical and statistical study, Mg, Ca, Mn, Sr and Ba contents in 215 wines from
415 different wine-growing regions in France, Germany, Italy and Spain were analyzed using an adapted
416 ICP-OES method. Chemical data were combined with meteorological data and information about soil
417 chemistry. Through multivariate statistical analysis, we provided evidence that elemental profiles of
418 the wines were controlled by soil chemistry (such as the calcareous profile of soils) and

419 meteorological conditions during the grapevine growth period. In particular, Mg and Ba contents
420 were higher in wines produced from non-calcareous soils. Sr contents were higher in wines from
421 regions with high summer temperatures, and Mn and Ba contents were higher in regions with high
422 summer rainfall. Furthermore, Mg:Ca ratios were linked to wine color and, thus, styles of wine-
423 making, likely due to Ca precipitation as tartrate during malolactic fermentation. Finally, systematic
424 differences in elemental profiles of the wines open up a potential route for investigating the
425 contribution of soil chemistry in the terroir effect.

426

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433 **References**Angus, N. S., O’Keeffe, T. J., Stuart, K. R., & Miskelly, G. M. (2006). Regional classification of New
434 Zealand red wines using inductively-coupled plasma-mass spectrometry (ICP-MS). *Australian Journal of*
435 *Grape and Wine Research*, 12(2), 170–176. <https://doi.org/10.1111/j.1755-0238.2006.tb00057.x>

436 Bates, T. R., Dunst, R. M., Taft, T., & Vercant, M. (2002). The Vegetative Response of “Concord” Grapevines to
437 Soil pH. *HortScience*, 37(6), 890–893.

438 Bavaresco, L., & Poni, S. (2003). Effect of Calcareous Soil on Photosynthesis Rate, Mineral Nutrition, and
439 Source-Sink Ratio of Table Grape. *Journal of Plant Nutrition*, 26(10–11), 2123–2135.
440 <https://doi.org/10.1081/PLN-120024269>

441 Benciolini, G., Tomasi, D., Pascarella, G., Lorenzoni, A., & Verze, G. (2006). Soave Viticultural zoning: the soil as
442 affecting wine quality. *BOLLETTINO DELLA SOCIETA GEOLOGICA ITALIANA*, 6, 135–146.

443 Blotevogel, S., Oliva, P., Sobanska, S., Viers, J., Vezin, H., Audry, S., Prunier, J., Darrozes, J., Orgogozo, L.,
444 Courjault-Radé, P., & Schreck, E. (2018). The fate of Cu pesticides in vineyard soils: A case study using δ
445 ^{65}Cu isotope ratios and EPR analysis. *Chemical Geology*, 477, 35–46.
446 <https://doi.org/10.1016/j.chemgeo.2017.11.032>

447 Blotevogel, S., Schreck, E., Audry, S., Saldi, G. D., Viers, J., Courjault-Radé, P., Darrozes, J., Orgogozo, L., & Oliva,
448 P. (2019). Contribution of soil elemental contents and Cu and Sr isotope ratios to the understanding of
449 pedogenetic processes and mechanisms involved in the soil-to-grape transfer (Soave vineyard, Italy).
450 *Geoderma*, 343, 72–85. <https://doi.org/10.1016/j.geoderma.2019.02.015>

451 Blum, J., Taliaferro, E., Weisse, M., & Holmes, R. (2000). Changes in Sr/Ca, Ba/Ca and Sr-87/Sr-86 ratios
452 between trophic levels in two forest ecosystems in the northeastern USA. *BIOGEOCHEMISTRY*, 49(1),
453 87–101. <https://doi.org/10.1023/A:1006390707989>

454 Bramley, R. G. V., Ouzman, J., & Boss, P. K. (2011). Variation in vine vigour, grape yield and vineyard soils and
455 topography as indicators of variation in the chemical composition of grapes, wine and wine sensory
456 attributes. *AUSTRALIAN JOURNAL OF GRAPE AND WINE RESEARCH*, 17(2), 217–229.
457 <https://doi.org/10.1111/j.1755-0238.2011.00136.x>

458 Coetzee, Paul P., Steffens, F. E., Eiselen, R. J., Augustyn, O. P., Balcaen, L., & Vanhaecke, F. (2005). Multi-
459 element Analysis of South African Wines by ICP–MS and Their Classification According to Geographical
460 Origin. *Journal of Agricultural and Food Chemistry*, 53(13), 5060–5066.
461 <https://doi.org/10.1021/jf048268n>

462 Coetzee, P.P., van Jaarsveld, F. P., & Vanhaecke, F. (2014). Intraregional classification of wine via ICP-MS
463 elemental fingerprinting. *Food Chemistry*, 164, 485–492.
464 <https://doi.org/10.1016/j.foodchem.2014.05.027>

465 Costantini, E. A. C., Bucelli, P., & Priori, S. (2012). Quaternary landscape history determines the soil functional
466 characters of terroir. *Quaternary International*, 265, 63–73.
467 <http://dx.doi.org/10.1016/j.quaint.2011.08.021>

468 Foroni, F., Vignando, M., Aiello, M., Parma, V., Paoletti, M. G., Squartini, A., & Rumiati, R. I. (2017). The smell of
469 terroir! Olfactory discrimination between wines of different grape variety and different terroir. *Food*
470 *Quality and Preference*, 58, 18–23. <https://doi.org/10.1016/j.foodqual.2016.12.012>

471 Frost, R., Quiñones, I., Veldhuizen, M., Alava, J.-I., Small, D., & Carreiras, M. (2015). What Can the Brain Teach
472 Us about Winemaking? An fMRI Study of Alcohol Level Preferences. *PLOS ONE*, 10(3), e0119220.
473 <https://doi.org/10.1371/journal.pone.0119220>

474 George, E., Horst, W. J., & Neumann, E. (2012). Adaptation of Plants to Adverse Chemical Soil Conditions. In
475 *Marschner's Mineral Nutrition of Higher Plants* (pp. 409–472). Elsevier. [https://doi.org/10.1016/B978-
476 0-12-384905-2.00017-0](https://doi.org/10.1016/B978-0-12-384905-2.00017-0)

477 Gonzalez-Barreiro, C., Rial-Otero, R., Cancho-Grande, B., & Simal-Gandara, J. (2015). Wine Aroma Compounds
478 in Grapes: A Critical Review. *CRITICAL REVIEWS IN FOOD SCIENCE AND NUTRITION*, 55(2), 202–218.
479 <https://doi.org/10.1080/10408398.2011.650336>

480 Greenough, J. D., Longerich, H. P., & Jackson, S. E. (1997). Element fingerprinting of Okanagan Valley wines
481 using ICP-MS: Relationships between wine composition, vineyard and wine colour. *Australian Journal*
482 *of Grape and Wine Research*, 3(2), 75–83. <https://doi.org/10.1111/j.1755-0238.1997.tb00118.x>

483 Haynes, R. J., & Naidu, R. (1998). Influence of lime, fertilizer and manure applications on soil organic matter
484 content and soil physical conditions: a review. *Nutrient Cycling in Agroecosystems*, 51(2), 123–137.
485 <https://doi.org/10.1023/A:1009738307837>

486 Hopfer, H., Nelson, J., Collins, T. S., Heymann, H., & Ebeler, S. E. (2015). The combined impact of vineyard origin
487 and processing winery on the elemental profile of red wines. *Food Chemistry*, 172, 486–496.
488 <https://doi.org/10.1016/j.foodchem.2014.09.113>

489 Imre, S. P., Kilmartin, P. A., Rutan, T., Mauk, J. L., & Nicolau, L. (2012). Influence of soil geochemistry on the
490 chemical and aroma profiles of Pinot noir wines. *JOURNAL OF FOOD AGRICULTURE & ENVIRONMENT*,
491 10(2, 1), 280–288.

492 Kabata-Pendias, A. (2004). Soil–plant transfer of trace elements—an environmental issue. *Geoderma*, 122(2–4),
493 143–149. <http://dx.doi.org/10.1016/j.geoderma.2004.01.004>

494 Kwan, W.-O., Kowalski, B. R., & Skogerboe, R. K. (1979). Pattern recognition analysis of elemental data. Wines
495 of *Vitis vinifera* cv Pinot Noir from France and the United States. *Journal of Agricultural and Food*
496 *Chemistry*, 27(6), 1321–1326. <https://doi.org/10.1021/jf60226a039>

497 Landesamt für Geologie und Bergbau Rheinland-Pfalz. (2017). *Großmaßstäbige Weinbergsbodenkarte von*
498 *Rheinland-Pfalz* [Map]. http://mapclient.lgb-rlp.de//?app=lgb&view_id=22

499 Magalhães, M. O. L., Sobrinho, N. M. B. do A., Zonta, E., Carvalho, M. M. de, & Tolón-Becerra, A. (2012). Effect
500 of variations in the redox potential of Gleysol on barium mobility and absorption in rice plants.
501 *Chemosphere*, 89(1), 121–127. <https://doi.org/10.1016/j.chemosphere.2012.04.060>

502 Maltman, A. (2013). Minerality in wine: a geological perspective. *Journal of Wine Research*, 24(3), 169–181.
503 <https://doi.org/10.1080/09571264.2013.793176>

504 Marschner, H., & Marschner, P. (Eds.). (2012). *Marschner's Mineral nutrition of higher plants* (3. ed). Elsevier,
505 Academic Press.

506 Martin, A. E., Watling, R. J., & Lee, G. S. (2012). The multi-element determination and regional discrimination of
507 Australian wines. *Food Chemistry*, 133(3), 1081–1089.
508 <https://doi.org/10.1016/j.foodchem.2012.02.013>

509 Mckinnon, A. J., Scollary, G. R., Solomon, D. H., & Williams, P. J. (1995). The Influence of Wine Components on
510 the Spontaneous Precipitation of Calcium L(+)-Tartrate in a Model Wine Solution. *American Journal of*
511 *Enology and Viticulture*, 46(4), 509.

512 Regierungspräsidium Freiburg, Landesamt für Geologie, Rohstoffe und Bergbau (Hrsg.). (2017). *Weinbauatlas*
513 *von Baden-Württemberg* [Map]. <http://maps.lgrb-bw.de>

514 Reynolds, A. C., Quade, J., & Betancourt, J. L. (2012). Strontium isotopes and nutrient sourcing in a semi-arid
515 woodland. *Geoderma*, 189(Supplement C), 574–584. <https://doi.org/10.1016/j.geoderma.2012.06.029>

516 Rodrigues, S. M., Otero, M., Alves, A. A., Coimbra, J., Coimbra, M. A., Pereira, E., & Duarte, A. C. (2011).
517 Elemental analysis for categorization of wines and authentication of their certified brand of origin.
518 *Journal of Food Composition and Analysis*, 24(4–5), 548–562.
519 <https://doi.org/10.1016/j.jfca.2010.12.003>

520 Rogers, S. Y., Greer, D. H., Hatfield, J. M., Orchard, B. A., & Keller, M. (2006). Mineral sinks within ripening grape
521 berries (*Vitis vinifera* L.). *Vitis*, 45(3), 115–123.

522 Styger, G., Prior, B., & Bauer, F. F. (2011). Wine flavor and aroma. *Journal of Industrial Microbiology &*
523 *Biotechnology*, 38(9), 1145–1159. <https://doi.org/10.1007/s10295-011-1018-4>

524 Tyler, G., & Olsson, T. (2001). Plant uptake of major and minor mineral elements as influenced by soil acidity
525 and liming. *PLANT AND SOIL*, 230(2), 307–321. <https://doi.org/10.1023/A:1010314400976>

526 van Breemen, N., Mulder, J., & Driscoll, C. T. (1983). Acidification and alkalization of soils. *Plant and Soil*,
527 75(3), 283–308. <https://doi.org/10.1007/BF02369968>

528 van der Linde, G., Fischer, J. L., & Coetzee, P. P. (2010). Multi-element Analysis of South African Wines and their
529 Provenance Soils by ICP-MS and their Classification according to Geographical Origin using Multivariate
530 Statistics. *SOUTH AFRICAN JOURNAL OF ENOLOGY AND VITICULTURE*, 31(2), 143–153.

531 van Leeuwen, C., TREGOAT, O., CHONÉ, X., BOIS, B., PERNET, D., & GAUDILLÈRE, J.-P. (2009). Vine water status
532 is a key factor in grape ripening and vintage quality for red Bordeaux wine. How can it be assessed for
533 vineyard management purposes? *J. Int. Sci. Vigne Vin*, 43(3), 121–134.

534 van Leeuwen, Cornelis, Friant, P., Choné, X., Tregoat, O., Koundouras, S., & Dubourdieu, D. (2004). Influence of
535 Climate, Soil, and Cultivar on Terroir. *American Journal of Enology and Viticulture*, 55(3), 207.

536 Vermorel, V., & Michaut, C. (1889). *Les engrais de la vigne*. Bibliothèque du Progrès agricole et viticole.

537 Viala, P., & Ferrouillat, P. (1887). *Les maladies de la vigne*. C. Coulet in Montpellier; A. Delahaye and E.
538 Lecrosnier in Paris.

539 White, P. J. (2012). Ion Uptake Mechanisms of Individual Cells and Roots. In *Marschner's Mineral Nutrition of*
540 *Higher Plants* (pp. 7–47). Elsevier. <https://doi.org/10.1016/B978-0-12-384905-2.00002-9>

541

543 **Supplementary Information**

544

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

549

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

554

555 **Table SI-1 (Supplementary_Data_3_Linear_Discriminants.xls).** Table showing the contribution of
556 each element to the first LDA axes. Three LDAs were conducted: wine color alone (two groups), soil
557 type alone (two groups), and both (four groups), all linear functions of elemental concentrations
558 (\log_{10} -transformed). The LDA axis of the two first LDAs were approximated into $\log_{10}(\text{Mg}^2/\text{Ca})$ and
559 $\log_{10}(\text{Mg Ba})$ and used to produce the plots of Figs. 2 and 3.

560

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

563

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