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1       **Strontium elemental and isotopic signatures of Bordeaux wines for**  
2                   **authenticity and geographical origin assessment**

3

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25

26

27 **Abstract**

28

29 The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and Sr concentrations of 43 authentic Bordeaux wines from the world's most prestigious  
30 châteaux are presented in the context of their relation to the geographical origin of wine and authenticity.  
31 The results demonstrate relatively narrow spans of variabilities observed for  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and Sr  
32 concentrations in authentic Bordeaux wines, which can be used with reasonable certainty as specific  
33 parameters for identifying regional wineries. For comparison, a set of imitated Bordeaux wines was studied  
34 for Sr isotopic and elemental compositions. A significant excess of both parameters in suspicious wines  
35 were found in reference to authentic values. Such natural and anthropogenically induced variations offer  
36 an enhanced discriminating potential of Sr. The unique Sr binary signature may detect imitated wines and  
37 trace genuine products from different regional wineries. The obtained results shown a promising  
38 perspective for wine authenticity control by means of Sr isotopic and elemental composition.

39

40 **Key words:**

41

42 Wine authenticity; Geographical origin; Bordeaux wine;  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio; Sr concentrations; Terroir;  
43 Multi-collector ICP-MS.

44

## 45 Article

46

### 47 1. Introduction

48 Bordeaux, a territory in South West France, is one of the most famous and largest world viticultural regions  
49 and constitutes a conglomerate of vineyards extending over 112 000 ha. Its production represents almost  
50 half of French wines, far ahead of the rest of other world wine producing regions: a global bulk volume of  
51 about 6.5 million hectoliters and more than 850 million bottles of wine that are produced and delivered  
52 every year with wine qualities ranging from everyday table wines to some of the most expensive and  
53 prestigious wines in the world (Lecat, Brouard & Chapuis, 2016). To promote quality, the concept named  
54 “appellation” (French: “*Appellation d’Origine Contrôlée*”, AOC) has been developed, and takes into account  
55 the very careful selection of grape varieties and the approved winemaking practices for each of the  
56 Bordeaux's 57 appellations. The appellations are geographically localized and cover sub-regions, individual  
57 villages or even specific vineyards. Bordeaux wines are known by their “*terroir*” – the combination of  
58 various environmental factors that have an impact on the wine taste and link the style of the wines to the  
59 specific locations (Médoc, Graves, etc.) (Wilson, 1999; Bourrouilh, 2006). Individual wineries or “*châteaux*”  
60 – are most of the time a traditional term to name a winemaking estate.

61 Wine traceability and authenticity are extremely important issues for the wine production and distribution  
62 sectors due to enormous economic damage caused by forgeries. Despite of the fact that fake wines have  
63 always existed, today the damage from this when assessed only the French wine market is around 36  
64 million euros (Lecat et al., 2016). The traceability of prestigious Bordeaux wines is becoming crucial, since  
65 they are among the most copied. Anti-counterfeiting technologies such as serial and individual numbering,  
66 laser engraving of the glass of the bottle, using variety of stickers, etc., has been introduced in order to  
67 reduce the turnover of counterfeited wines. However, all these measures are only applied to wine bottle  
68 recognition, even though the wine itself can be falsified. Therefore, wine fraud is still a serious and  
69 increasing problem. This leads not only to commercial losses, but also results in important health risks in  
70 case the counterfeited wine contains dangerous compounds and contaminants.

71 The determination of the geographical provenance and definitive authentication of wine requires the use  
72 of highly sophisticated analytical techniques. The number of recognized analytical approaches based on  
73 determination of elemental composition, organic components, stable isotope ratios of light elements, and  
74 genetic specifications of vitis varieties have been successfully applied to provenance determinations of  
75 wines (Médina, Salagoity, Guyon, Gaye, Hubert & Guillaume, 2013; Cozzolino & Smyth, 2013). Among the  
76 different methods briefly mentioned above, the natural variation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is a relatively new  
77 approach addressing its geographical origin (Balcaen, Moens, & Vanhaecke, 2010). This method initially  
78 has been applied to provenance study in archeology, and later approved in the food sector. Indeed, its first  
79 attempt for food provenance assessment was performed on wine (Horn, Schaaf, Holbach, Hötl &  
80 Eschnauer, 1993). Since then, the Sr isotope ratio method has been successfully tested on various food  
81 matrices and now, its application in the field of geographical origin identification of food products is  
82 growing steadily (Baffi & Trincherini, 2016; Coelho, Castanheira, Bordado, Donard & Silva, 2017).

83 Strontium (Sr) is neither an essential nor a nutritional element for the vine, which is continuously supplied  
84 throughout the plant's growth by uptaking from the water-soluble fraction of soil (Horn et al., 1993; Green,  
85 Bestland & Walker, 2004). Then Sr is assimilated in all parts of the vine including grapes (Mercurio et al.,  
86 2014), and transferred into wine without being altered during the winemaking process (Almeida &  
87 Vasconcelos, 2004). Therefore, Sr contained in wine directly originates from soil in which the vine is grown  
88 and can be used to refer the plant's geographical origin. Following the first promising results, a series of  
89 studies have been performed aimed at the investigation of the correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the  
90 system soil-water-grapes-wine (Almeida & Vasconcelos, 2001; Barbaste, Robinson, Guilfoyle, Medina &  
91 Lobinski, 2002; Almeida & Vasconcelos, 2004; Vorster, Greeff & Coetzee, 2010; Di Paola-Naranjo et al.,  
92 2011, Vinciguerra, Stevenson, Pedneault, Poirier, Hélié & Widory, 2016). In the view of vineyards from  
93 around the world, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio has been applied for the geographical origin classification of wines  
94 from South-Africa (Vorster et al., 2010), Argentina (Di Paola-Naranjo et al., 2011), Canada (Vinciguerra et  
95 al., 2016), Portugal (Almeida & Vasconcelos, 2001) and Romania (Geană, Sandru, Stanciu & Ionete, 2017).  
96 Recently, some new information and interest has been raised on this topic following the publication of a  
97 series of studies performed on Italian wines. Using an extra-large sample selection of authentic samples it

98 was confirmed that: 1) Sr isotope composition of wine remained constant for different vintages (Mercurio  
99 et al., 2014; Durante et al., 2015; Petrini, Sansone, Slejko, Bucciati, Marcuzzo & Tomasi, 2015; Marchionni  
100 et al., 2013; Marchionni et al., 2016); 2) the ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  is not altered during the winemaking  
101 (Marchionni et al., 2016; Petrini et al., 2015; Tescione, Marchionni, Matte, Tassi, Romano & Conticelli,  
102 2015); and 3) the ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  in wine can be forecast on the basis of pedological settings (Durante et al.,  
103 2013; Mercurio et al., 2014; Durante et al., 2015, Marchionni et al., 2013; Petrini et al., 2015; Marchionni  
104 et al., 2016). The scientific and the practical importance of these studies is connected with the clear  
105 demonstration of the matching of Sr isotopic ratios in wine and those from the soil substratum of  
106 vineyards, obtained with precision and accuracy required for geological studies. Also they hold an  
107 extensive data base of Sr isotopic variations in Italian wines and are thus widely cited as main arguments of  
108 the Sr isotopes method applicable to wine geographical origin assessment. In 2014–2018, a comprehensive  
109 project aimed at establishing the  $^{87}\text{Sr}/^{86}\text{Sr}$  specification for Italian Lambrusco PDO wines was implemented  
110 (Durante et al., 2018).

111 Among the analytical methods traditionally used for the Sr isotopic analysis, the first reliable results were  
112 produced with thermal ionization mass spectrometry (TIMS). Recent instrumental developments made  
113 using multicollection inductively coupled plasma mass spectrometry (MC-ICP-MS) offer competitive  
114 information with data obtained by TIMS as the reference technique in the field of isotopic analysis  
115 (Walczyk, 2004). Since then considerable attention has been devoted to the development of  
116 methodologies and strategies with this new analytical detector, which finally made MC-ICP-MS the  
117 confirmed technique used to provide highly precise and accurate isotopic measurements (Irrgeher &  
118 Prohaska, 2016). In comparison to the previous generation ICP-MS instruments with quadrupole detection  
119 (Q-ICP-MS), whose analytical precision was tested and recognized to be insufficient for detection of the  
120 small variations of  $^{87}\text{Sr}/^{86}\text{Sr}$  in wines (Green et al., 2004), the introducing of MC-ICP-MS has resulted in  
121 significant improvements in the field of Sr isotopic analysis. The precision of detection with MC-ICP-MS  
122 yields variations between the interval of 0.002-0.005% (Mercurio et al., 2014; Durante et al., 2015) versus  
123 0.53% obtained on Q-ICP-MS instruments (Geană et al., 2017). The accuracy with MC-ICP-MS varies from  
124 0.004% to 0.016% (Horsky, Irrgeher & Prohaska, 2016) and it is far better than that obtained by Q-ICP-MS

125 under the best conditions - 0.16% (Geană et al., 2017). Currently, the Sr isotopic analysis of wine is  
126 successfully carried out using both methods, TIMS (Marchionni et al., 2013; Petrini et al., 2015; Tescione et  
127 al., 2015; Marchionni et al., 2016; Vinciguerra et al., 2016) and MC-ICP-MS (Mercurio et al., 2014; Durante  
128 et al., 2015) to identify the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio as a reliable guaranteed indicator of wine provenance.

129 In this study, an analytical approach for an accurate and precise determination of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in wine by  
130 ICP-MS has been developed for subsequent application for authenticity issues and geographical origin  
131 assessment. It has been tested on a wide selection of Bordeaux wines with the specific objective of  
132 identifying their Sr signatures with respect to individual wineries and detecting the imitated wine with a  
133 suspicious declaration of provenance.

134

## 135 **2. Materials and method**

### 136 **2.1. Sample origins**

137 ***Authentic Bordeaux wine.*** In this study, a series of 43 authentic wines from prestigious Bordeaux AOC,  
138 produced between 1969 and 2012 (most of them after 2000), some are classified as First Growth (*French -*  
139 *“Grand Cru”*), were provided by winemaking estates, territorially located on a restricted area of about 50  
140 km radius, encompassing the famous Bordeaux viticultural lands of Médoc, Graves and Libourne. These  
141 wineries belong to the following appellations: Pomerol (11 red wines, vintages 1969-2010), Saint-Émilion  
142 (4 red wines, vintage 2011), Pessac-Léognan (15 red wines and 9 white wines, vintages 2009-2012), and  
143 Pauillac (4 red wines, vintages 2004-2007). All wines conform to the applicable AOC regulations, are made  
144 entirely on the winery's property from grapes owned by the winery and do not ever leave the property  
145 during fermentation, ageing, or bottling.

146 The geographical location of vineyards under consideration can be seen in Fig. 1. Pomerol and Saint-  
147 Émilion represent the famous appellations of Bordeaux from the *Libournais* viticultural sub-region,  
148 situated on the right bank of the Dordogne River. The vineyards of Saint-Émilion are located on the slope  
149 of a large calcareous plateau where soils is rich in sands and clays. The vineyards of Pomerol are  
150 traditionally grown in soils containing some deep fine clays with a mixture of sand resting on calcareous  
151 molasse deposits. Geographically, these two winemaking estates are very close, with the distance not

152 exceeding 5 km, but have very distinctive soil compositions (Bourrouilh, 2006). Pessac-Léognan and  
153 Pauillac represent two viticultural sub-regions of the left bank of the Garonne River – *Graves* and *Médoc*,  
154 respectively. The vineyards of Pessac-Léognan are located within the Bordeaux urban activity zone, where  
155 the typical soil consists of gravel, pebbles and stone, overlaying a complex basis of sand and limestone. The  
156 vineyards of Pauillac are situated in the northern section of the viticultural strip of the Médoc peninsula.  
157 The soil on the low gravelly terrace mounds of Pauillac is derived from the ferruginous climatic residual  
158 crust, resting on a marly calcareous foundation with inclusions of varying proportions of sand, gravel and  
159 significant quantities of unique clay in layers of varying depth (Bourrouilh, 2006).

160 ***“Other wines” acquired from China.*** The discriminative capability of the Sr isotope marker was also tested  
161 on a set of 17 red wines, produced in 1998 – 2009 and purchased directly from China. This group included  
162 3 samples of wine of authentic Chinese production and 14 samples of wine labeled “Bordeaux”. For some  
163 bottles, the indicated “Bordeaux” origin caused an evident mistrust due to incorrect labels containing  
164 spelling mistakes in the names of the well-known wineries, or even not-existent names of wineries. The  
165 real geographical origins for these wines were unknown. Exact names of production regions of original  
166 Chinese wines were also not specified. The complete sample list of can be seen in the Supplementary  
167 material, Table S1.

168

## 169 **2.2. Instrumentation**

170 For the Sr elemental quantification analysis, a quadrupole Q-ICP-MS NexION 300X (PerkinElmer, USA) was  
171 used in a standard operation mode. For the precise Sr isotopic ratios determination, a high resolution MC-  
172 ICP-MS Nu Plasma-HR (Nu Instruments Ltd., UK) equipped with a cyclonic spray chamber, a micro-  
173 concentric nebulizer with flow rate of 200  $\mu\text{L min}^{-1}$ , and nickel plasma cones (Type A) were used. The  
174 operating conditions for both instruments and the list of elements/isotopes determined are given in Tables  
175 S2 and S3 in the Supplementary material. For sample digestion, a microwave Mars 5 (CEM Corporation,  
176 USA) was used. A laboratory heating block HotBlock (Environmental Express, USA) was used for sample  
177 evaporation.

178



### 179 **2.3. Reagents and materials**

180 All sample handling was performed in a cleanroom class ISO 7. All FEP and PTFE vessels, vials and tubes  
181 were pre-cleaned with HNO<sub>3</sub> (10% v/v, 69.0-70.0%, Instra Analysed Reagent, J.T.Baker®, Fisher Scientific,  
182 France) and rinsed with ultrapure water obtained from the Milli-Q system (resistivity of 18.2 MΩ cm,  
183 Millipore USA, Molsheim, France) prior to use. Sample pre-digestion was performed in 30 mL PFA Savillex  
184 vials (Savillex Corporation, USA) using hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (30%, ULTREX® II Ultrapure Reagent,  
185 J.T.Baker®, Fisher Scientific, France) and high purity subboiled HNO<sub>3</sub>, obtain by distillation of analytical  
186 reagent grade HNO<sub>3</sub> (69.0-70.0%, Instra Analysed Reagent, J.T.Baker®, Fisher Scientific, France) in an acid  
187 distillation system DST 1000 (Savillex, USA). All subsequent dilution steps involved in preparation of  
188 standards, samples and reagents for elemental and isotopic analysis were performed with HNO<sub>3</sub> solutions  
189 (2% v/v and 3 mol L<sup>-1</sup>), made of ultrapure water and HNO<sub>3</sub> (67-70%, ULTREX® II Ultrapure Reagent,  
190 J.T.Baker, Fisher Scientific, France).

191 For the elemental quantification analysis, a multielemental standard CCS-4 (Inorganic Ventures, USA) and  
192 the SLRS-5 certified reference material of river water for trace metals (NRC, Ottawa, Canada) were used for  
193 preparation and control of the calibration solutions.

194 The matrix purification was performed in ion-separation columns (2 mL, Triskem International, France)  
195 filled with 100 mg of Sr-selective resin Eichrom® (SR-B50-S, Triskem International, France) using 3 mol L<sup>-1</sup>  
196 HNO<sub>3</sub> Ultrex® and ultrapure water. The isotopic standard reference material SRM 987, (pure SrCO<sub>3</sub>, NIST,  
197 USA), previously dissolved in HNO<sub>3</sub> was used for the quality control and instrumental mass bias correction  
198 during isotopic analysis.

199 Each analytical procedure (including cleaning of all types of equipment, sample digestion, laboratory  
200 sample preparation, and instrumental analysis) incorporated blanks and controls to minimize  
201 contamination impact and ensure the quality of results.

202

### 203 **2.4. Elemental analysis Q-ICP-MS**

204 For the elemental quantification of Sr and Rb, 0.5 mL of wine was digested with 0.2 mL of HNO<sub>3</sub>. The  
205 obtained solution was then diluted with 10 mL of ultrapure water. A series of calibration solutions was

206 prepared in the range of 0.01-100  $\mu\text{g kg}^{-1}$ . During ICP-MS analysis a drift correction for ICP-MS data was  
207 controlled using normalization to  $^{103}\text{Rh}$ . Three blanks were subjected to a similar analytical procedure, the  
208 levels of Sr and Rb were below the method detection limits: 0.005  $\mu\text{g kg}^{-1}$  and 0.003  $\mu\text{g kg}^{-1}$ , respectively.

209

## 210 **2.5. Sample preparation for Sr isotopic analysis**

211 Sample preparation for Sr isotopic analysis consisted of steps of digestion followed by the Sr/matrix  
212 separation. In order to ensure quality control, several procedural blanks, counting one for every eleven  
213 wine samples mineralized and going through all steps of the procedure, were prepared.

214 Due to low Sr content in some samples, a pre-concentration was necessary. With that, a complete  
215 decomposition of organic matter during mineralization must be achieved, thus it was performed in three  
216 phases. Firstly, about of 10 mL of wine were evaporated in a Savillex vial until a volume of approximately  
217 1 mL was reached. A full evaporation of the sample was avoided, since it makes further manipulations  
218 more difficult. Secondly, 5 mL of  $\text{HNO}_3$  were gradually added to the wine concentrate and left to react at  
219 room temperature. Lastly, 1 mL of  $\text{H}_2\text{O}_2$  was added the next day, and then the resulting solution was  
220 microwaved to a temperature of 200°C and power of 1600W with the following timing: ramping - 20 min,  
221 heating - 20 min, and cooling - 20 min. After cooling, the solution was transferred into 50 mL  
222 polypropylene tubes and diluted with ultrapure water up to 30 mL.

223 The presented protocol is a modified version from the one proposed by Durante et al. (2015), where only  
224 5 mL of wine were combined with 5 mL of  $\text{HNO}_3$  and microwaved. In fact, some of Bordeaux wines had  
225 such low Sr concentrations that large volumes are required to be mineralized to ensure sufficient amounts  
226 of Sr for the isotopic analysis. Additionally, the maximum volume allowed for an effective digestion in the  
227 microwave system MARS 5 is limited to 10 mL. Thus, for safety and efficiency reasons, a soft pre-  
228 concentration combined with the addition of  $\text{H}_2\text{O}_2$  has been applied. The low temperature mineralization  
229 without heating (Durante et al., 2015) was deemed to be ineffective for studying red wines: after reacting  
230 for 12 hours, the solutions containing 5 mL of wine and 5 mL of  $\text{HNO}_3$ , were still colored typically for the  
231 presence of non-destroyed organic matter (pale yellow color). When these samples were subjected to the  
232 subsequent Sr/matrix separation using Eichrom® resin, the fractionation of the solution on the column was

233 observed due to the resin depletion by presented organic matter. Hence, recoveries obtained for Sr after  
234 the matrix separation were in the range not acceptable for the isotopic determination (30-50%). In  
235 contrast to this, all samples subjected to the presented microwave digestion protocol had a clear  
236 uncolored appearance and were carried out easily for the following matrix separation. Finally, this method  
237 was considered as the preferred and allowing to reach required efficiency in sample preparation for  
238 isotopic analysis.

239 A precise and accurate determination of Sr isotope ratios by MC-ICP-MS requires a separation of Sr from  
240 the sample matrix, specifically from Rb, which can produce an isobaric interference of  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$ . The  
241 following procedure was applied: the aliquots of a digested wine samples with an approximate content of  
242 2-2.5  $\mu\text{g}$  of Sr (necessary amount for a reliable isotopic ratio determination) were evaporated in 30 mL  
243 Savillex vials using a hot block at  $80^\circ\text{C}$  close to dryness and then re-dissolved in 4 mL of  $3\text{ mol L}^{-1}\text{ HNO}_3$ . An  
244 amount of 100 mg of the Eichrom<sup>®</sup> Sr-selective resin was put into a 2 mL column fitted with appropriate  
245 filters to fix the resin inside the column to ensure a slow constant flow rate of about  $0.5\text{ mL min}^{-1}$  required  
246 to obtain an acceptable recovery rate. At first, to avoid any contaminations, the packed resin was  
247 prewashed with 5 mL of  $3\text{ mol L}^{-1}\text{ HNO}_3$  and rinsed with 20 mL of ultrapure water. Then, the resin was  
248 conditioned with 2 mL of  $3\text{ mol L}^{-1}\text{ HNO}_3$  to ensure the sufficient activation of the binding groups. Next, the  
249 re-dissolved samples were loaded into the columns. The matrix removal was accomplished by flushing  
250 each column twice with 4 mL of  $3\text{ mol L}^{-1}\text{ HNO}_3$ . Finally, the Sr elution was obtained by rinsing the columns  
251 with 10 mL of ultrapure water. The resulting solutions contained Sr in the levels of about  $200\text{ }\mu\text{g L}^{-1}$ , and  
252 were ready to be analyzed by MC-ICP-MS without any supplementary dilution. The concentrations of Sr  
253 and Rb in wine samples and procedural blanks were controlled using a Q-ICP-MS before and after  
254 Sr/matrix separation, the obtained recoveries of Sr were in the range of 90-105% (only for samples  
255 containing Sr).

256

## 257 **2.6. Sr isotope ratio analysis**

258 The operating parameters of the MC-ICP-MS were daily optimized using the standard solution  
259 NIST SRM 987 with a concentration of  $200\text{ }\mu\text{g L}^{-1}$  to achieve the maximum sensitivity and stability for Sr

260 beam, the typical signal for the isotope  $^{88}\text{Sr}$  was about 7V. Measurements were performed using a  
261 conventional Sample-Standard-Bracketing calibration sequence with the NIST SRM 897 used as bracketing  
262 standard. After instrumental blank subtraction using the On Peak Zero approach (OPZ), the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  
263 was corrected for mass bias using the constant ratio  $^{86}\text{Sr}/^{88}\text{Sr}$  of 0.1194, and from the potential remaining  
264 interferences from traces of  $^{87}\text{Rb}$  using the ratio  $^{85}\text{Rb}/^{87}\text{Rb}$  of 2.5926. A second correction was then applied  
265 to the bracketing standard in agreement with the study of Albarède, Telouk, Blichert-Toft, Boyet, Agranier,  
266 & Nelson (2004). The value of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for NIST SRM 987 applied for data processing was 0.710255,  
267 according to Waight, Baker & Peate (2002).

268 Contamination from the presence of Sr in the samples was evaluated by preparing two procedural blanks:  
269 (1) - the procedural blank containing only reagents used in mineralisation, and (2) - the same procedural  
270 blank but spiked with an amount of SRM NIST 987 up to  $200\ \mu\text{g L}^{-1}$ . Both of them followed all the analytical  
271 stages, from mineralization to analysis, including matrix purification. The obtained average voltages on  $^{88}\text{Sr}$   
272 were 0.014 V and 7.4 V for the Sr-free procedural blank and for the spiked procedural blank, respectively.  
273 Comparison of  $^{87}\text{Sr}/^{86}\text{Sr}$  in spiked procedural blank ( $0.710271 \pm 0.000018$ ) with the reference value of NIST  
274 SRM 987 ( $0.710255 \pm 0.000026$ ) have shown that the influence of Sr contamination can be considered as  
275 negligible.

276 Concentrations of Rb in samples after matrix purification were first controlled using Q-ICP-MS and  
277 secondly by monitoring the  $m/z=85$  with MC-ICP-MS. Concentration of Rb in the two procedural blanks  
278 were below the limit of quantification of Q-ICP-MS ( $0.01\ \mu\text{g kg}^{-1}$ ). MC-ICP-MS showed low and relatively  
279 comparable voltages for  $^{85}\text{Rb}$  in procedural blanks (the average is less than 0.0001V) and instrumental  
280 blank (the average is less than 0.00002V), respectively. Some samples after matrix purification were still  
281 containing Rb in the level up to  $0.5\ \mu\text{g kg}^{-1}$  (the voltage on MC-ICP-MS reached 0.024 V for  $^{85}\text{Rb}$ ). However,  
282 a ratio Rb/Sr for these samples was  $\leq 0.006$ , which is lower than the maximal acceptable value of 0.015  
283 mentioned by Yang, Wu, Xie, Yang & Zhang (2011), and thus an exponential law using  $^{85}\text{Rb}$  correction can  
284 be reasonably applied.

285 The combination of the different methodological approaches mentioned above allowed to achieve an  
286 optimal measurement strategy for high-precision and accurate determination of  $^{87}\text{Sr}/^{86}\text{Sr}$  by MC-ICP-MS

287 with an external reproducibility for Sr isotope ratio measurement equivalent to 25 ppm calculated as  
288 standard deviation with 95% confidence interval of 75 individual measurements of NIST SRM 987 solution  
289 ( $200 \mu\text{g L}^{-1}$ ) under daily altered conditions. The average measured value of NIST SRM 987 was  
290  $0.710280 \pm 0.000013$  which is in good agreement with the reference value of  $0.710255 \pm 0.000023$  (Waight  
291 at al., 2002).

292 The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the wine samples were calculated as the mean from independently digested  
293 triplicates and measurement uncertainties were estimated as 2SD.

294

### 295 **3. Results and Discussion**

#### 296 **3.1. Strontium elemental concentrations**

297 The Sr elemental content in wine is an important criterion addressed to the geographical origin since its  
298 concentrations in grapes are strongly regulated by the vineyard's soil composition (Green et al., 2004). The  
299 box plots in Fig. 2 graphically display the mean values and variation intervals of Sr elemental content across  
300 the studied wine samples. In authentic Bordeaux wines, the Sr concentrations are quite homogenous with  
301 respect to individual wineries and not exceed the level of  $0.52 \text{ mg kg}^{-1}$ . A comparative analysis of variability  
302 shows a high degree of consistency of the results obtained for wines from Saint-Émilion, Pessac-Léognan  
303 (white, red wines), and Pauillac with the Sr concentrations ranging between  $0.16$  and  $0.19 \text{ mg kg}^{-1}$ .  
304 However, the wines from Pomerol are characterized by a slightly higher level of Sr concentrations detected  
305 in the interval of  $0.33 - 0.52 \text{ mg kg}^{-1}$ .

306 When comparing the average Sr concentrations in authentic Bordeaux and suspicious "Bordeaux" acquired  
307 from China, an obvious difference between those two groups can be seen immediately (Fig. 2).  
308 Furthermore, statistical distributions of the groups "suspicious Bordeaux" and "suspicious Pauillac" display  
309 a significantly higher degree of dispersion and an evident abnormal skewness. In terms of Sr  
310 concentrations, the levels vary in the suspicious samples from  $0.29$  to  $2.16 \text{ mg kg}^{-1}$  with the mean value  
311 significantly higher than that for authentic Bordeaux, but similar to wines from the group "China". As  
312 mentioned previously, Sr in wine mostly originates from the soil, hence, the large variability of Sr  
313 concentration in wine reflects the wide diversity of underlying geological bedrocks and soils formed on

314 them. Therefore, the widely scalable results of Sr concentrations in suspicious wines reflect the substantial  
315 heterogeneity of geological background of its origin, which is not consistent with the rather homogeneous  
316 sedimentary basin of Bordeaux (Wilson, 1999; Bourrouilh, 2006). And vice versa, a smaller dispersion of Sr  
317 concentration observed in authentic Bordeaux achieve full harmonization with the above noted. Thus,  
318 comparing only the Sr concentrations in authentic and dubious wines can reveal some significant  
319 divergence that can be regarded as a sign of falsely declared geographical origin.

320

### 321 **3.2. Strontium isotope ratios**

322 Following the Sr elemental analysis, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in studied wines were determined for further  
323 evaluation of their discriminating potential regarding the geographical origin. The ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  obtained  
324 for studied wines, authentic and suspicious, are listed in Table S1 (Supplementary material) and graphically  
325 presented in Fig. 3.

326 ***Authentic Bordeaux wine.*** The isotopic ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  in the authentic Bordeaux wines vary within a  
327 comparatively narrow range, between 0.70829 and 0.71022 (Fig. 3). When considering in detail the  
328 samples originating from individual wineries (in recognition of the analytical precision of measurements),  
329 the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured in wines from Pomerol lies in the range of 0.70968 – 0.71022, which is slightly  
330 higher than those observed in the wines from Saint-Émilion (0.70829 – 0.70895), and moderately  
331 overlapped with wines from Pauillac (0.70906 – 0.70953) and Pessac-Léognan (0.70900 – 0.70980). Indeed,  
332 the wine from Saint-Émilion demonstrates a lower  $^{87}\text{Sr}/^{86}\text{Sr}$  value due to relatively low content of the  
333 radiogenic isotope  $^{87}\text{Sr}$ . Wines of Grand Cru of Saint-Émilion are cultivated in soils developed on a large  
334 limestone plateau formed during the Lower Oligocene (about of 32 million years ago), and preserved the  
335  $^{87}\text{Sr}/^{86}\text{Sr}$  value of seawater during corresponding period. At that time, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio was in the range of  
336 0.7078-0.7080 (Jones, Jenkyns, Coe & Hesselbo, 1994), and it has been recorded in these limestones, and  
337 therefore it continues to be a major factor contributing for the low values of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in plants that  
338 grow on it, and ultimately becomes apparent in wine (Fig. 4). It is noticeably in wines from Pauillac and  
339 Pessac-Léognan, but even to a greater extent with respect to samples from Pomerol. In Pomerol, vines are  
340 cultivated on more recent alluvial terraces relating to the Pleistocene (< 2 million years ago) formed of

341 sands, pebbles and clays from the glacial erosion of the Central Massif and the Pyrenees. The slow and  
342 continuous dissolution of these siliceous elements of the Earth's crust (the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ranged from  
343 0.715 to 0.730) can only raise the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of seawater of the Pleistocene (about 0.7090-0.7092), that  
344 can be observed in Pomerol wine: 0.7098 - 0.7102.

345 Comparing early published results, the  $^{87}\text{Sr}/^{86}\text{Sr}$  data reported here for wine from Saint-Émilion is  
346 consistent with the only reliable study of Barbaste et al. (2002), where the Sr isotopic composition of four  
347 wines from the homonymous appellation (however, unknown vineyards) were recorded within the interval  
348 of 0.70943 – 0.71005. The limited sample size in both studies, and recent improvements of the signal  
349 treatment (Waight et al., 2002; Albarède et al., 2004; Horsky et al., 2016) can explain a slight discrepancy  
350 between them.

351 When examining the largest group of red and white wines originating from Pessac-Léognan, the obtained  
352 values of  $^{87}\text{Sr}/^{86}\text{Sr}$  do not vary significantly for red and white wines: 0.70910 – 0.70960 (mean of  
353  $0.70939 \pm 0.00031$ ,  $n=15$ ) and 0.70900 – 0.70980 (mean of  $0.70935 \pm 0.00058$ ,  $n=9$ ), respectively. This  
354 finding is consistent with the recent observations (Di Paola Naranjo, et al. 2011, Vinciguerra et al., 2016):  
355 different grape varieties equally accumulate Sr from the labile fraction of soil within the same geological  
356 substrata. With regards to Bordeaux wines, these facts are extremely important since the winemaking  
357 traditions in Bordeaux integrate the practice of wine varietal blending (*fr. "l'assemblage des cépages"*),  
358 when a final wine is produced by mixing of mono-varietal wines (i.e., Cabernet Sauvignon, Merlot,  
359 Cabernet Franc etc. - for red wines, and Sauvignon blanc, Semillon, Muscadelle, etc. – for white wines), and  
360 the assembled proportions may vary according to vintage. Further, as observed earlier (Durante et al.,  
361 2015; Petrini et al., 2015; Marchionni et al., 2013; Marchionni et al., 2016), the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in wine from  
362 a definite vineyard is generally stable from one vintage to another. Indeed, a certain variability observed in  
363 the samples of Pessac-Léognan (0.071% for red wines and 0.092% for white wines) represents a variability  
364 not depending on the year of production (Fig. C.3), and it is not likely due to the practice of vine varietal  
365 blending, because such differences have previously been observed for Italian Cesanese mono-varietal  
366 wine, produced during a period of 7 years by a particular winery (Marchionni et al., 2016). However,

367 additional contributions to the Sr isotopic compositions of wines from winemaking processes and  
368 agricultural practices are possible and will be further discussed.

369 The studied authentic wines characterized by a relatively narrow range of  $^{87}\text{Sr}/^{86}\text{Sr}$  variations mainly  
370 attributed to overall homogeneous geological settings of the Bordeaux region. Indeed, the local geology of  
371 the region is extensively described, with specific consideration given to the regional viticulture (Wilson,  
372 1999; Bourrouilh, 2006). This territory is a part of Gironde-Aquitaine sedimentary basin formed by erosion  
373 of the Pyrenees and the Massif Central between the end of the Tertiary and the beginning of the  
374 Quaternary periods. The soils are formed on a large limestone bedrock originated from expanses of alluvial  
375 sediments deposited by the Garonne and Dordogne rivers with gravel inclusions. According to Voerkelius  
376 et al. (2010), the typical values of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in geological samples from this region can be expected  
377 to range between 0.70701 and 0.71100. All ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  obtained in this study for authentic Bordeaux  
378 wines are within the predicted limits (Fig.3).

379 When comparing the average of Sr isotope ratios obtained for authentic Bordeaux wines and those from  
380 other wines worldwide (Fig. 3), it is notable that they have some important overlaps which certainly  
381 highlights the similarity of geological and pedological characteristics of provenancing territories. In order to  
382 achieve a reliable qualitative comparison, we used only results obtained by MC-ICP-MS and TIMS. Indeed,  
383 recent studies on Italian wines report the values of  $^{87}\text{Sr}/^{86}\text{Sr}$  that overlap Bordeaux signatures: Cesanese  
384 wines 0.70894 – 0.71062 (Marchionni et al., 2016), and Lambrusco 0.70840 – 0.70964 (Durante et al.,  
385 2015). The whole interval of the ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  which can be potentially found in Bordeaux wines has been  
386 recorded in Prosecco wines (Petrini et al., 2015), while a significant overlay with Aglianico wines is unlikely  
387 (Marchionni et al., 2013). When examining the Sr isotopic ratios in wine originated from other continents,  
388 the span of the  $^{87}\text{Sr}/^{86}\text{Sr}$  expressed in lower values has been recorded for wine from Argentina 0.7071 –  
389 0.7093 (Di-Paola Naranjo et al., 2011). On the contrary to studied Bordeaux samples,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in  
390 wines from Quebec vary with a wide range of values, from 0.70988 up to maximum 0.71546, indicating a  
391 relative enrichment by the radiogenic isotope  $^{87}\text{Sr}$  in Precambrian intrusive and metamorphic rocks  
392 composing the Canadian Shield. (Vinciguerra et al., 2016).



393 ***“Other wines” acquired from China.*** The wines from this group are characterized by large variations in  
394  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.70523 to 0.71266), significantly exceeding the upper and lower limits of the values  
395 observed in authentic Bordeaux. From 17 samples included in this set, only 12 wines (specifically: 9  
396 suspicious “Bordeaux” and 3 original from China) have the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio within the reference interval of  
397 typical Bordeaux  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Fig. 3). The  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the remaining 5 samples go beyond the  
398 lines defining the limits of typical Bordeaux geology and can be considered most likely as not originating  
399 from Bordeaux. According to spatial prediction maps (Voerkelius et al., 2010; Marchionni et al., 2013), a  
400 wine with  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.70523 could be produced from grapes planted in soils developed on volcanic,  
401 ophiolites or intrusive rocks. On the contrary, more radiogenic values of  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.711 – 0.713) can be  
402 caused by soils of vineyards developed on igneous or metamorphic, granitoidic rocks. These types of  
403 bedrock are very different from the typical geological structure of the Bordeaux region, which is a large  
404 sedimentary basin (Wilson, 1999; Bourrouilh, 2006). Such wide variability of  $^{87}\text{Sr}/^{86}\text{Sr}$  was observed also for  
405 Italian Prosecco wines 0.70706 – 0.71215 (Petrini et al., 2015) and wines from Quebec (Vinciguerra et al.,  
406 2016), in both cases studied vineyards were planted on territories of a wide geological diversity.  
407 These overall results are important since they demonstrate that different wines represent a certain  
408 specification of Sr isotopic composition depending on their geographical origin. However, its practical  
409 application is partly limited when considering it as the only independent discriminating criterion. In the  
410 present case, the declared Bordeaux origin could be contested on the basis of Sr isotopic signatures only  
411 for five suspicious wines with obvious outliers of  $^{87}\text{Sr}/^{86}\text{Sr}$  values. At the same time, the isotopic signatures  
412 of the remaining 9 wines labeled “Bordeaux” acquired from the China market do not detect  
413 nonconformities despite the other containing evidence of imitated wine. Moreover, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  
414 some Italian wines, such as previously mentioned Cesanese, Lambrusco, Prosecco and Chinese wines from  
415 this study have the ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  also disposed in the same range as Bordeaux. Thus, it is important to  
416 state that the Sr isotope ratio cannot be the distinctive criterion singularly applied for geographical origin  
417 assignment due to possible cases of similarity of regional lithology in different regions of the world.

418

419 **3.3. Combination of  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentrations**

420 In geosciences, an enhanced discriminating potential of Sr lies with the joint interpretation of its two  
421 characteristics - elemental concentration and isotopic composition (Green, et al. 2004). We attempted to  
422 find such interaction on example of authentic Bordeaux wines with consideration of relevant wineries, and  
423 then to use it for the differentiation of geographical origins of authentic and suspicious Bordeaux wines.

424

### 425 3.3.1. The case of Pomerol wine

426 At first, the correlation of these two parameters depending on vintages was appraised using an exceptional  
427 long-term series of wines produced in a winery in Pomerol in 1969 – 2010. This small winemaking estate  
428 has kept in-house developed wine production technology for many decades. In these wine samples, a  
429 significant mirroring dependency of Sr concentration versus the ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  from the years of wine  
430 production can be seen in Fig. 5. Indeed, despite rather narrow variations of both parameters, such a trend  
431 is clearly observed due to the high precision of isotopic measurements on MC-ICP-MS. For the studied  
432 wines, those produced during the first 20 years, from the late 1960s until around 1990, we can note a  
433 slight enrichment in the radiogenic isotope  $^{87}\text{Sr}$ , then followed by a moderate depletion in  $^{87}\text{Sr}$  for the  
434 wines of more recent production. Such variability would be expected to be seemingly dependent upon the  
435 quality of the vintage, since the excellence or poorness of a vintage is directly due to annual  
436 meteorological conditions. However, the wine produced in the poor 1969 year (*French -“Millésime*  
437 *mediocre”*) and in the best 2009 year (*French -“Millésime exeptionnel”*) have the same Sr concentrations:  
438  $0.429 \pm 0.011 \text{ mg kg}^{-1}$  and  $0.425 \pm 0.012 \text{ mg kg}^{-1}$ , while the values of  $^{87}\text{Sr}/^{86}\text{Sr}$  differ fairly:  
439  $0.71010 \pm 0.00002$  and  $0.70976 \pm 0.00005$ , both parameters are given respectively for 1969 and 2009.

440 Such interesting opposite relationship of elemental and isotopic signatures can be explained in particular  
441 by changing the source of available Sr either during vine growing or winemaking. Indeed, viticulture and  
442 winemaking involve various practices and operations (Pohl, 2007), that can potentially change the Sr  
443 elemental and isotopic content in grapes and later those in wine. Taking into consideration the lack of  
444 detailed information of vineyard- and winemaking management due to commercial confidentiality, only a  
445 hypothesis for explaining such a behavior can be made. For example, the use of substances containing Sr of  
446 marine origin for pH regulation purposes on vineyard soil in the 1990's could explain the simultaneous

447 increase in Sr concentrations with the shift of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio toward the  $^{87}\text{Sr}/^{86}\text{Sr}$  value of sea water -  
448 0.70918 (Allègre, Louvat, Gaillardet, Meynadier, Rad & Capmas, 2010). Other additives used during  
449 winemaking, such as bentonite, can also affect the Sr isotopic composition of wine. These observations  
450 clearly underline that even within a narrow range of the  $^{87}\text{Sr}/^{86}\text{Sr}$  variability, slight significant differences in  
451 the ratio may help to unravel the viticultural and winemaking features when considering a specific set of  
452 samples.

453

### 454 **3.3.2. Variability of Sr isotope and Sr elemental content and its application to discriminate between** 455 **Bordeaux's viticultural sub-regions**

456 To trace regional variabilities of Sr elemental and isotopic signatures in studied wines for further  
457 evaluation of their cumulative impact upon provenance discrimination, the ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  were plotted  
458 versus inverse Sr concentrations (Fig. 6). Such diagrams are primarily used to trace the geochemical  
459 development of soils horizons and estimate chronosequences of evaporation/sedimentation processes. In  
460 the case of wine samples this allows us to assess their potential origins: whether they are from the same or  
461 different geological regions. It can be clearly seen that this graph groups together most of the authentic  
462 Bordeaux wine samples with a slight distinction for Pomerol wines due to their higher Sr content. All  
463 authentic Bordeaux wines from this study form an elongated cloud of points bounded by limits of typical  
464 regional values  $^{87}\text{Sr}/^{86}\text{Sr}$  (Voerkelius et al., 2010), which is a true sign of the common geological  
465 provenance. (Fig. 6A). On the contrary, the suspicious "Bordeaux" wines are remarkable by the extreme  
466 diversity of Sr isotope ratio and Sr concentrations, which can be explained by their likely origins from  
467 certainly very distinctive geological areas. Moreover, three suspicious samples from this group are located  
468 in close proximity to the wine from Pomerol. From their disposition on the Sr elemental/isotopic scatter  
469 plot, the origin of these three dubious wines could be interpreted as from Bordeaux. Nevertheless, these  
470 wines have been identified as not veritable Bordeaux origin because they did not comply with the AOC  
471 regulations applicable to the labels (indications of production sites, winery's names, and grape varieties).  
472 From the closer examining of the series of Bordeaux wine (Fig. 6B), it can be observed that red wines from  
473 Pomerol, Saint-Émilion, and white wines from Pessac-Léognan are characterized by significant variabilities

474 of Sr elemental and isotopic composition, which exceed by several times the measurement uncertainties of  
475 analytical determinations. Furthermore, a typical trend applicable to most of the samples and expressed in  
476 an inverse relationship between total Sr concentrations and Sr isotopic compositions can be highlighted  
477 (Fig. 6B): lesser values of  $^{87}\text{Sr}/^{86}\text{Sr}$  correspond to higher Sr elemental levels without a direct correlation  
478 with years of wine production. Indeed, samples from Pomerol represent the period of 40 years, white wine  
479 from Pessac-Léognan – 4 years, and wine from Saint-Émilion were produced from the same vintage. This  
480 trend is most likely due to geochemical processes in soils, such behavior has been previously observed in  
481 soils from irrigated and non-irrigated vineyards (Green et al., 2004). Apart from the fact that soil profiles  
482 may be constituted by layers differing in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, we can hypothesise a difference in Sr isotopes  
483 mobility, because the radiogenic isotope  $^{87}\text{Sr}$  is being presented in a larger proportion under a lower Sr  
484 total concentrations. This was observed in wines, where Sr transferred through biotic and abiotic  
485 processes from soil to water and then to plants and grapes (Fig.5).

486 Such correlation between Sr elemental and its isotopic composition gives means to discriminate among  
487 Bordeaux's wine production sub-regions. For the studied Bordeaux wines, a certain distinction when  
488 plotting specifically the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios versus inverse Sr concentrations can be seen in Fig. 6B: the wines  
489 originating from Pomerol and Saint-Émilion plotted very differently with respect to other samples, mainly  
490 due to the difference in geological structures of these two sub-regions that referred in paragraph 3.2. On  
491 the contrary, there is a significant overlap for the samples originating from Pessac-Léognan (red wines),  
492 Pessac-Léognan (white wines) and Pauillac. Nevertheless, without a special consideration of four samples  
493 from Saint-Émilion, the most complete discrimination of a single winery by means of Sr isotopic- and  
494 elemental specifications was achieved for the wines from Pomerol.

495

### 496 **3.3.3. Testing of wine authenticity by means of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentrations**

497 Sr isotopic specification had already been tested for wine authenticity issues (Durante et al., 2015; Geană  
498 et al. 2017). The authenticity of doubtful "Bordeaux" was verified using Sr elemental- and isotopic  
499 approach. In the set of suspicious Bordeaux, four wines were labeled as a prestigious wine of high  
500 commercial value from a winery from the Pauillac appellation. By visual control, these bottles were

501 indistinguishable from the authentic ones. In order to evaluate their authenticity, we compared their Sr  
502 isotopic and elemental signatures with those of authentic samples from the same winery and the same  
503 years of production. Regarding the Sr concentrations in two comparative groups “suspicious Pauillac” and  
504 “authentic Pauillac”, a significant discrepancy can be observed immediately (Fig. 2): the suspicious samples  
505 contained 1.52, 0.74, 0.95, and 0.89 mg kg<sup>-1</sup>, while the concentrations for authentic wines were more  
506 homogeneous: 0.17, 0.17, 0.19, and 0.18 mg kg<sup>-1</sup>, for 2004, 2005, 2006, and 2007 respectively. Further, the  
507 <sup>87</sup>Sr/<sup>86</sup>Sr ratios in suspicious wines varied largely from 0.70523 to 0.71266 (Fig. 3, uncolored circles marked  
508 by letters A, B, C and D). The version about Bordeaux provenance of two wines with the maximal (0.71266)  
509 and the minimal (0.70523) values can be immediately rejected, because this value do not correspond to  
510 the Sr isotopic variation in geology of the region (Fig.3). Values of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio for two samples  
511 marked by uncolored circles B (0.71014 ± 0.00004) and C (0.70861 ± 0.00009) in Fig. 3, are within the  
512 typical range for Bordeaux region, but differ significantly from those of the authentic wine (green circles)  
513 ranging in the interval of 0.70906-0.70944. The combination of <sup>87</sup>Sr/<sup>86</sup>Sr and Sr concentration, presented in  
514 the insertion chart in Fig. 6B, immediately clearly indicates that 2 comparing groups do not belong to the  
515 same set of samples, and the actual geographical origin of suspicious wines does not correspond to the  
516 declared one. This example illustrates how the binary Sr signature, isotopic and elemental, can help to  
517 characterize wine for authentic purposes.

518

#### 519 **3.3.4. Factors of influence on variability of Sr isotopic and Sr elemental content**

520 As presented above, the use of the combined information of Sr elemental- and isotopic composition of  
521 wine can give evidence about its geographical origin. In this context it is important to estimate the  
522 allowable variation range of both parameters and factors affecting them. Apart from the crucial role of  
523 soil, there are several important factors that influence Sr elemental and isotopic variability in wine: climatic  
524 conditions, agricultural practices, management of wineries, winemaking techniques may be considered as  
525 the most significant.

526 **Climatic conditions.** The region of Bordeaux is influenced by atmospheric precipitations forming under the  
527 Atlantic Ocean, which can bring significant wet dissolved Sr elemental flux with a strong dependency on

528 seasonal to inter-annual scales (Maneux, Grousset, Buat-Ménard, Lavaux, Rimmelin & Lapaquellerie,  
529 1999). In the case of a high rainfall year, two effects are theoretically possible: 1) the flux of marine Sr with  
530 the isotopic signature of sea water - 0.70918 (Allègre et al., 2010) can result the slight shift of the  $^{87}\text{Sr}/^{86}\text{Sr}$   
531 ratio in wine to the value of sea water; 2) considerable precipitations can also change the hydrochemical  
532 dynamics in soil horizons resulting in the release of extra-amount of bioavailable Sr sourced from soil or  
533 sub-soil substrata (Nakano, Tanaka, Tsujimura & Matsutani, 1993). The climatic influence on the  $^{87}\text{Sr}/^{86}\text{Sr}$   
534 ratio in wine is a global factor and should be traced to a certain extent in all wines produced in the region.  
535 The global changing of environmental climatic conditions, such as an increasing of ambient air  
536 temperature and variation of water regime can potentially lead to changing of Sr elemental and isotopic  
537 composition in labile soil fraction and, consequently, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in wine.

538 **Managing of vineyards.** The root system of vines from non-irrigated Bordeaux's vineyards develops over  
539 the years and can reach 20 meters deep. In search of water, vine roots penetrate different layers of soil  
540 and sub-soil and uptake the bioavailable Sr. Therefore, wine produced from young vines with still evolving  
541 roots and wine from a mature vineyard can slightly differ in  $^{87}\text{Sr}/^{86}\text{Sr}$  due to geological heterogeneity of  
542 vineyard's soil profiles. Another factor affected directly Sr quantitative and qualitative content in wine is  
543 the application of fertilizers on vineyard soil. For example, lime and clay added for pH regulation purposes,  
544 contain some Sr with an individual value of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (Marchionni et al., 2016).

545 **Managing of wineries.** The increasing/decreasing of vineyards through the purchase/sale of neighboring  
546 sites differing by pedological settings, as well as wine-making estate mergers may lead to one-off changes  
547 of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the corresponding period. Modification and renovation of winemaking and storing  
548 facilities (tanks, reservoirs, etc.), composition of glass bottles and possible migration of Sr, should be also  
549 taken into account.

550 **Features of production process.** The particular features of winemaking within an individual winery, such as  
551 the longtime usage of special equipment, adding of yeasts and bentonite during vinification could cause  
552 the specification in both, Sr elemental and isotopic composition of wine, with a certain regularity. Bottling  
553 and storage the wine is also an important stage for Sr specification due to possible migration of Sr from the  
554 glass (Chesson, Tipple, Mackey, Hynek, Fernandez & Ehleringer, 2012). These factors are the most difficult

555 changes to correct, because of the commercial confidentiality of the process. However, in the context of  
556 food authenticity, these features can be used to specify the Sr elemental and/or isotopic signatures of final  
557 products (Epova et al., 2018).

558 Analyzing all of the above, the internal variability of  $^{87}\text{Sr}/^{86}\text{Sr}$  within the studied wines could have various  
559 sources. For the winery from Pomerol, a visible continuous influence from a new source of Sr starting  
560 around the late 1990's is apparent, that might be due to application of fertilizers or modification of the  
561 winemaking process. For other wineries, it is a difficult to single out a specific idea from the number of  
562 those available, thus, further studies are required.

563

#### 564 **4. Conclusion**

565 This is the first study that concerns the Sr isotopic and elemental compositions of a large selection of  
566 authentic Bordeaux wines. The results of 43 genuine wines from four regional wineries demonstrate a  
567 moderate variability of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and Sr concentrations with a strong possibility to assigned Sr  
568 specifications for individual winemaking estates. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio found to be relatively stable in varietal  
569 blended wine and wine from different vintages. However, applied solely, the Sr isotope ratio method is not  
570 intended to be relied upon to definitely identify the geographical origin due to world-wide geological  
571 diversity and numerous factors masking the geological signature of wine, as it has been demonstrated  
572 using the case of imitated Bordeaux wines.

573 A clearer discrimination of geographical origin can be obtained through a combination of Sr isotopic and  
574 elemental signatures of wines. Such an approach provides the specific terroir-inherent and winemaking-  
575 related tracer for authenticity and provenance assessment. With it, the studied wines produced by a  
576 winery from Pomerol AOC were successfully distinguished from the other authentic Bordeaux wines, and  
577 the wines of doubtful declared Bordeaux origin were denoted as imitated or mislabeled products, due to  
578 radically different elemental and isotopic compositions with respect to authentic samples.

579 To approve this method within the legal and scientific framework and corroborate the Sr isotopic- and  
580 elemental compositions as fingerprints for Bordeaux wines, isotopic analyses at TIMS and MC-ICP-MS

581 quality levels, with precision and accuracy comparable to those of geological studies should be performed  
582 and compared with isotopic data of control samples from the soil substratum of regional vineyards. With  
583 this study authors emphasize a serious potential in the expansion of work aimed to establish the individual  
584 Sr isotopic- and elemental signatures of Bordeaux wines which are able to objectively support the  
585 authenticity of Bordeaux wines.

586

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### 593 **Associated content**

594 Supplementary material: list of studied wines, Sr elemental concentrations and Sr isotope ratios are listed  
595 in the Table S1. The operating parameters of the Q-ICP-MS and MC-ICP-MS can be seen on Table S2 and  
596 S3, respectively.

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### 598 **Conflict of interest statement**

599 All the authors declare that there are no conflicts of interest.

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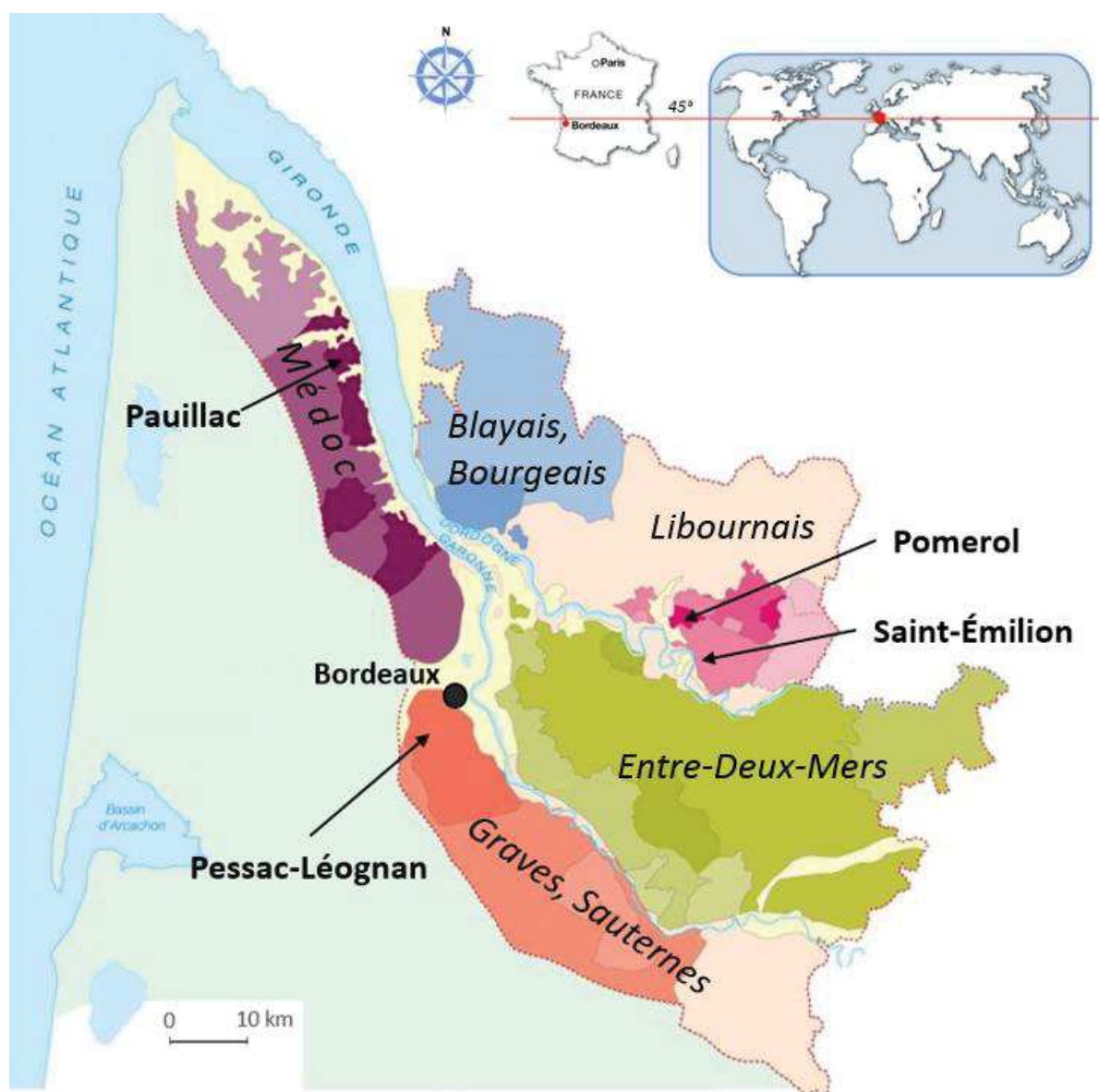


Fig. 1. Geographical origins of studied authentic Bordeaux wines, appellation of Pomerol, Saint-Émilion, Pauillac, Pessac-Léognan on a sketch map of Bordeaux region (France), modified from "The Bordeaux vineyard map", CIVB©. For the full list of appellations please check <https://www.vinexpo-newsroom.com>. Italics are used to refer to the main viticultural sub-regions.

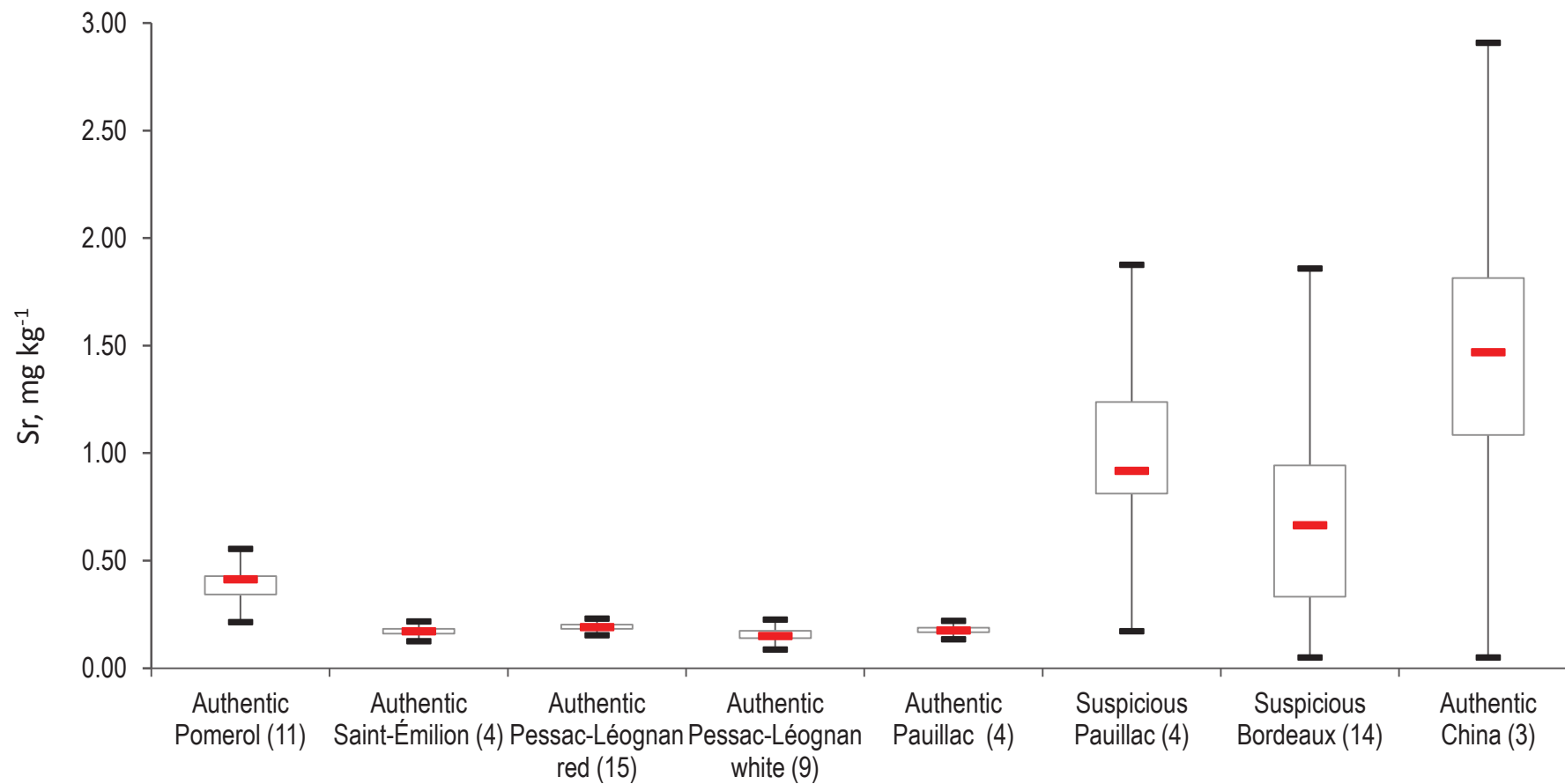
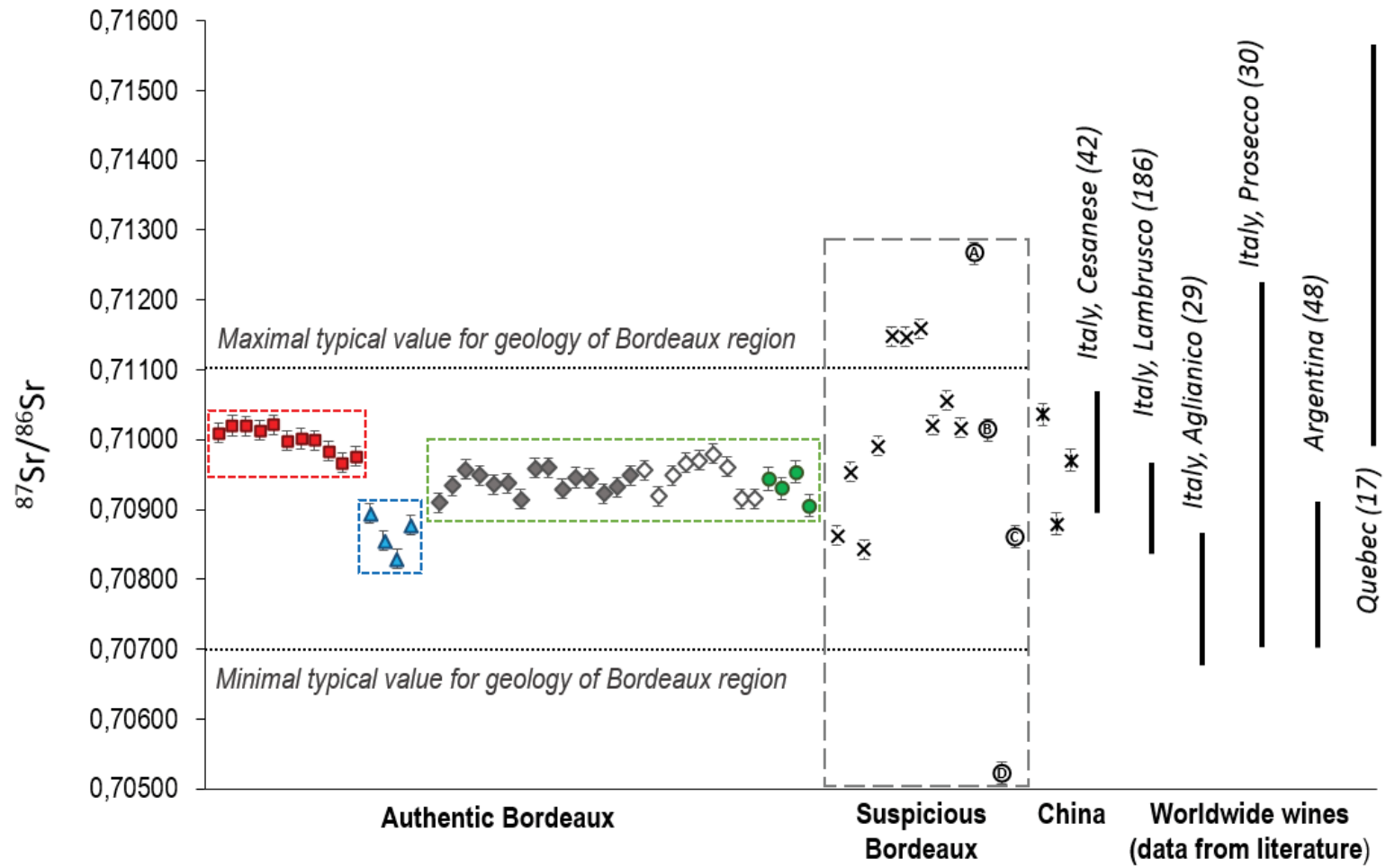


Fig. 2. The mean values and variation intervals of Sr elemental concentrations across the studied wine samples (number of samples is presented in the brackets).



■ Authentic Pomerol

▲ Authentic Saint-Emilion

● Authentic Pauillac

◆ Authentic Pessac-Léognan red

◇ Authentic Pessac-Léognan white

× Authentic China

× Suspicious Bordeaux

○ Suspicious Pauillac

Fig. 3.  $^{87}\text{Sr}/^{86}\text{Sr}$  in the studied wines and comparison with wines from different world origins, as reported in the literature. Legend: within individual groups, samples are sorted in ascending order of production year. Horizontal dotted lines defining the limits outside of which the values can be considered not belonging to the typical Bordeaux geology values, according Voerkelius et al., 2010. Wine samples of suspicious Pauillac are marked as A, B, C and D as described in the text. References used for wines worldwide: Argentina (Di Paola-Naranjo et al., 2011); Italy (Marchionni et al., 2013; Durante et al., 2015; Marchionni et al., 2016; Petrini et al., 2015); Quebec (Vinciguerra et al., 2016), number of samples is presented in the brackets.



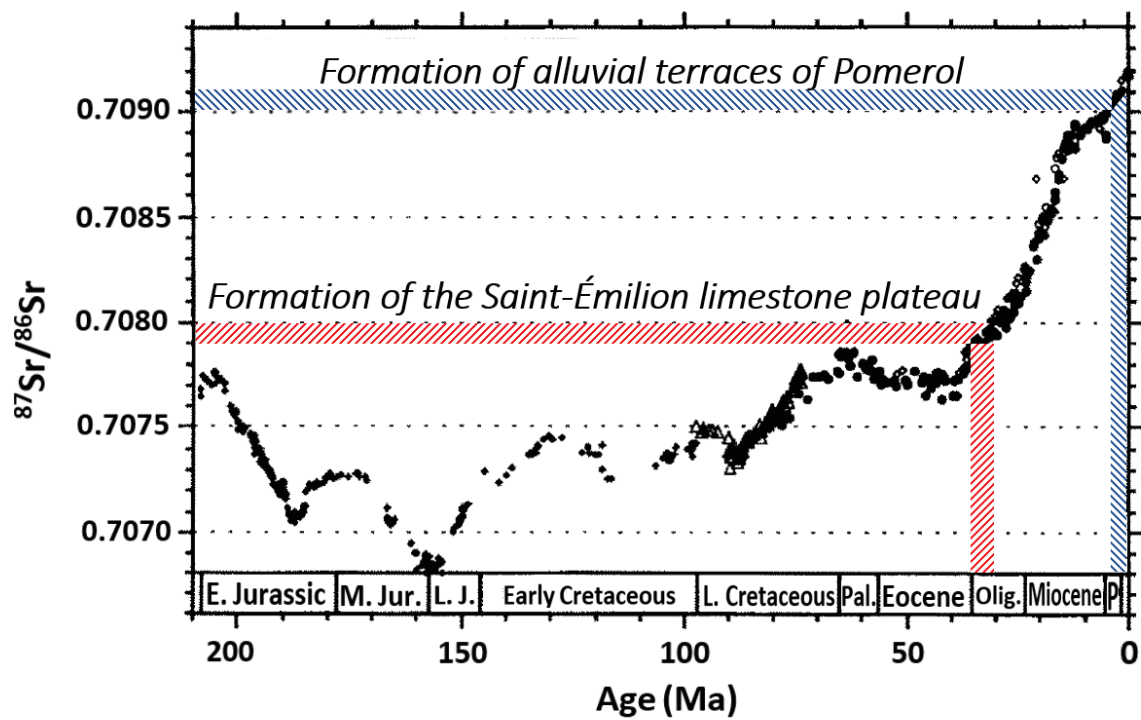


Fig. 4. Evolution of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in Jurassic and Cretaceous sea water with respect of periods of geological formation of the Saint-Émilion limestone plateau and alluvial terraces of Pomerol.

Modified after: Jones et al., 1994.

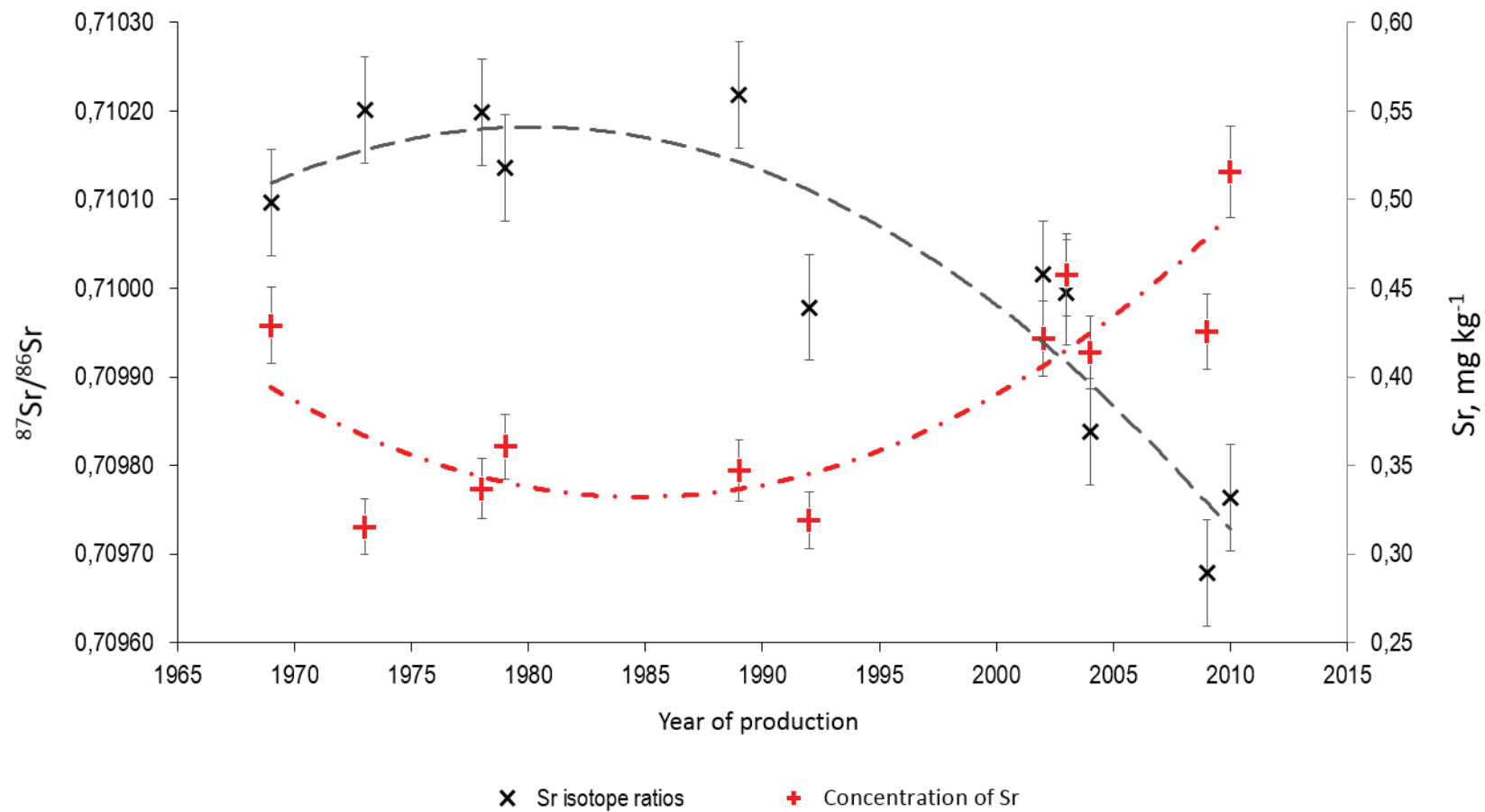


Fig. 5. Time dependent changes of Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios observed in wines from a winery of Pomerol AOC produced in the period 1965-2015.

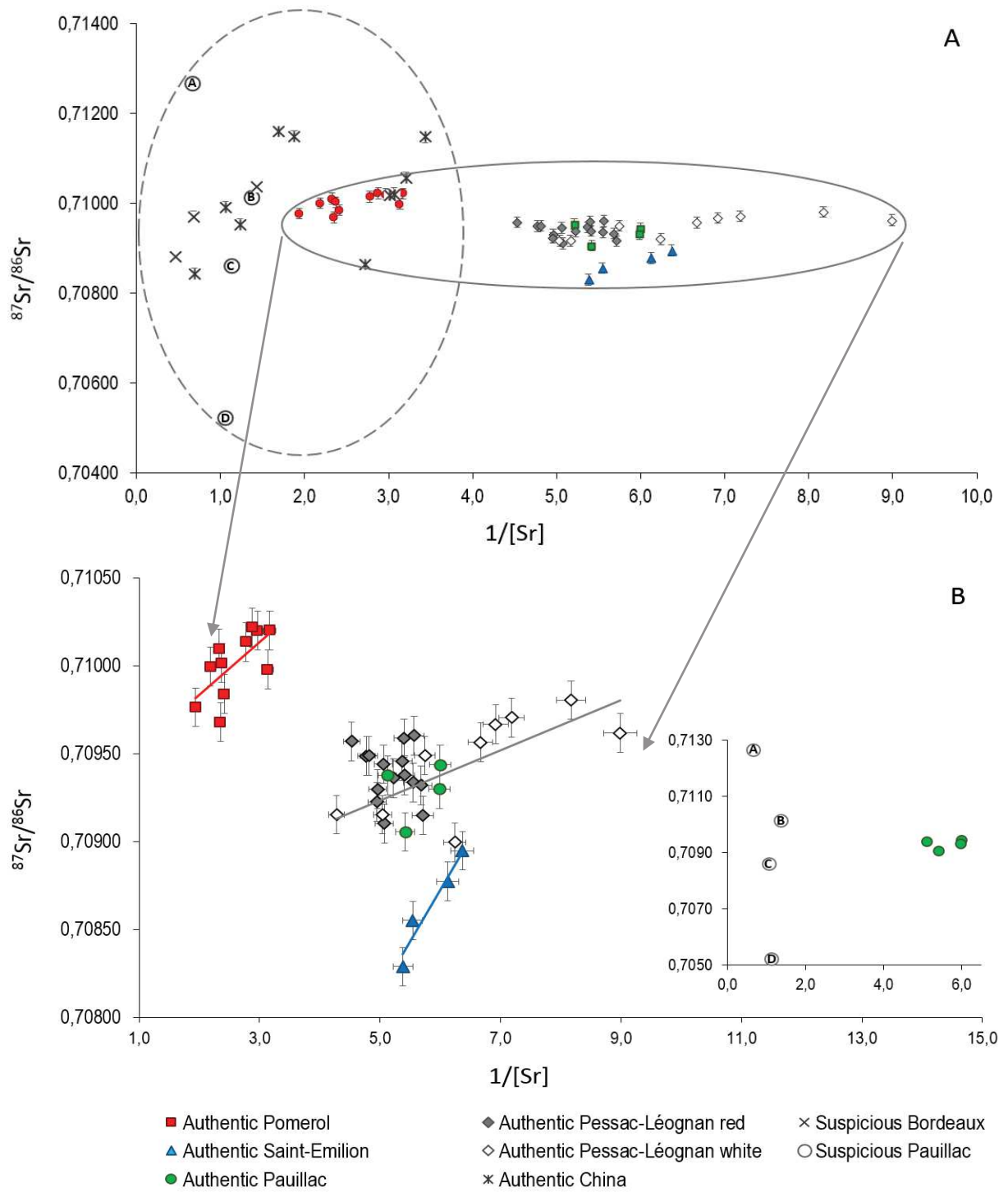


Fig. 6. Ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$  as a function of  $1/[\text{Sr}]$  concentrations in the wines studied: A – wines of authentic and suspicious Bordeaux origins; B – wines of Bordeaux origin. The error bars are smaller than the marks when not indicated. Samples of suspicious Pauillac are marked as A, B, C, and D, as described in the text of paragraph 3.3.3.

**Supplementary Material**

[Click here to download Supplementary Material: Supplementary materials Rev3.xlsx](#)

**Highlights:**

- Sr elemental and isotopic composition of 43 Bordeaux wines is determined
- Differentiation of authentic Bordeaux wines on the basis of their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio
- Relationship between Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  in wine
- Detection of wine counterfeits on the basis of  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentrations
- Sr isotope ratio is a promising parameter for wine authenticity control

**Conflict of interest statement**

All the authors declare that there are no conflicts of interest.