



# Tracing geographical origin of Lambrusco PDO wines using isotope ratios of oxygen, boron, strontium, lead and their elemental concentration

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## ARTICLE INFO

### Keywords:

Isotopic ratios  
Lambrusco PDO wines  
Geographic traceability  
MC-ICP/MS

## ABSTRACT

Wine identification is one of the most important aspects in the classification of wines and consumer protection. In particular, assuring wine authenticity is a crucial issue on which researchers are focusing on. This study aims to evaluate the feasibility of using chemical (B, Pb and Sr concentration) and isotopic compositions ( $\delta^{11}\text{B}$ ,  $^{209}\text{Pb}/^{208}\text{Pb}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{18}\text{O}$ ) of wine samples to trace their geographic origins. Different PDO Lambrusco wines coming from a confined area of northern Italy were analyzed and all the isotopic systematics were monitored by using a multi collector inductively coupled plasma mass spectrometer (MC-ICP/MS).

The obtained results showed that boron isotope ratio measurements led to a satisfactory degree of accuracy and precision (measured value,  $n = 28$ ,  $^{11}\text{B}/^{10}\text{B}$  of NIST SRM 951a equal to  $4.04343 \pm 0.00178$ , ( $u = 2s$ ) with a certified value of  $4.04362 \pm 0.00136$  ( $u = 2s$ ). Furthermore, in the present study, it has been possible to highlight significant differences among samples by means of one-way analysis of variance (ANOVA) and post hoc Tukey-Kramer test. Finally, Principal Component Analysis (PCA) was also carried out in order to evaluate to which extent the different PDOs can be distinguished from each other, taking into account the whole set of geographical origin descriptors. Although  $\delta^{11}\text{B}$  provided more sensitive information, the obtained results highlighted the important to consider the synergistic combination of all the investigated parameters to trace the different samples and the need to combine the obtained values with the same parameters evaluated in the soil, water and fertilizer as well.

## 1. Introduction

Italian agriculture stands out for the great variety of traditional food, which represent regional excellences with unique characteristics. In a global market context, the consumer decision is increasingly influenced by quality, food safety and territoriality and, compliance with what is declared on the food label. Protecting and promoting these productions certainly leads to advantages from an economic point of view, and at the same time represents a political strategy that allows to highlight the national identity. In this context, a very important support is given by the European Union which introduced geographical indications, GI, (PDO protected designation of origin, PGI protected geographical indication and TGS traditional specialty guarantee) and issued many Regulations (Regulation (EU) No 1169/2011; Regulation (EU) No 1308/2013; Commission Delegated Regulation (EU) 2019/33) to

protect the several specific products and to promote their unique characteristics, linked to their geographical origin as well as to the traditional know-how.

The concept of 'origin' of a product is certainly linked to the wider concepts of food authenticity and geographical origin, in particular tracking and tracing processes (Regulation (EC) No 178/2002, GU n. 294/2005). Defining the origin of a food means reconstructing the food production chain, following the entire production process through a documentation which can be paper- or electronic-based. The weak point of this traceability system is that neither the paper nor the electronic procedures provide any guarantee that the information recorded is correct. As a result, the need for a 'scientific traceability' is gaining ground.

Among the different food, wine identification is one of the most important aspects in the classification of wines and consumer

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<https://doi.org/10.1016/j.crfs.2021.11.001>

Received 9 March 2021; Received in revised form 28 October 2021; Accepted 2 November 2021

Available online 8 November 2021

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protection, and both chemical and isotopic profiles have been widely applied in the literature to assure wine authenticity. In particular, the different analytical approaches are based on indicators, which can be divided in two categories: direct parameters, *i.e.* chemical characteristics of a food directly linked to the territory of origin (for instance, metal content or stable isotope ratios), and indirect parameters, *i.e.* chemical variables that relate the compositional characteristics of a product to its production process.

As far as the determination of direct indicators is concerned, one of the most promising approaches is based on the determination of the isotope ratios (IRs) of light and heavy stable elements (Wadood et al., 2020; Kamiloglu, 2019; Katerinopoulou et al., 2020). These analytical methodologies were successfully applied to a wide range of agricultural products, including wine (Camin et al., 2017; Braschi et al., 2018).

Furthermore, to verify the geographical origin of a wine, the measurement of stable isotopes of light elements by means of isotope ratio mass spectrometry (IRMS) is currently recognized as an official methodology. In particular, oxygen stable isotope ratio (IR) can be used to establish the authenticity of wines (Camin et al., 2017), since the non-homogeneous repartition of the oxygen-18 all over the globe, due to the hydrological cycle, provides useful information concerning plant growth localization and climate conditions (Dutra et al., 2011).

On the other side, among the IRs of medium-heavy elements, strontium surely represents one of the most studied geographical tracers. Reliability and validity of this indicator are widely consolidated and well documented (Horn et al., 1993; Almeida and Vasconcelos, 2001; Durante et al., 2013, 2016; Vinciguerra, 2016; Ghezzi et al., 2018; Braschi et al., 2018; Epova et al., 2019). Nevertheless, many studies recently reported the use of other potential geographical indicators, such as lead and boron, with encouraging results regarding the classification of wines with respect to their geographical origin (Epova et al., 2020; Mihaljevic et al., 2006; Almeida et al., 2016; Coetzee and Vanhaecke, 2005). However, a recent study demonstrated that it is not always possible to assess a direct link between the trend of Pb IRs in wine and the corresponding Pb IRs in soils (Lancellotti et al., 2020) since the presence of Pb in wine can be associated with both natural and anthropogenic sources.

Unlike lead, the essential role of boron in plant physiology is currently a matter of debate (Gonzales-Fontes, 2020). Coetzee and Vanhaecke (2005) reported a correlation between boron content in grapevine leaves and soil, highlighting that soil properties, such as clay composition and pH, play an important role in differentiating boron uptake by plants. Therefore, since the natural variation of boron isotope ratio of the soil is reflected in the vine and therefore in wine, the parameter  $\delta^{11}\text{B}$  may represent a valuable tool in provenance and authentication studies (Vorster, L. Greeff and P.P. Coetzee 2010; Almeida et al., 2017).

In the present work, the issue to trace the geographical origin of several PDO wines produced in three neighboring provinces in the north of Italy is tackled, considering the concentration of boron, lead and strontium together with the following isotopic signatures:  $\delta^{11}\text{B}$ ,  $^{206}\text{Pb}/^{208}\text{Pb}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{18}\text{O}$ .

Furthermore, isotope measurements in wine were carried out by using a multicollector ICP/MS spectrometer (MC-ICP/MS) and, to the best of our knowledge, this work represent the first approach aimed to test the potentiality of B isotope systematics together with all the others direct indicators in tracing geographic origin of different PDO wine samples coming from a small confined area.

In particular, in this study, the following PDO wines were analyzed: three PDOs from the province of Modena (Lambrusco Salamino di S. Croce, SAL; Lambrusco di Sorbara, SOR and Lambrusco Grasparossa di Castelvetro, GRA), one PDO from the province of Reggio Emilia (Lambrusco Reggiano, RE) and one PDO from Mantua (Lambrusco Mantovano, MN).

In order to highlight any statistically significant differences among the investigated PDOs, the obtained data were analyzed by means of

one-way analysis of variance (ANOVA) and post hoc Tukey-Kramer test. Furthermore, Principal Component Analysis (PCA) was carried out in order to evaluate to which extent the different PDOs can be distinguished from each other, taking into account the whole set of geographical origin descriptors.

## 2. Materials and methods

### 2.1. Reagents and standards

All the solutions required for the isotope ratio measurements were prepared by using high-purity de-ionized water TYPE1 (physical and chemical parameters for TYPE1 water comply with ASTM TYPE I and ISO3696 GRADE I purity specifications) obtained from a Milli-Q IQ 7000 system (Millipore, Bedford MD).

Ultrapure 65%  $\text{HNO}_3$ , obtained from analytical grade  $\text{HNO}_3$  (CarloErba, Milan, Italy) by means of a DST 1000 sub-boiling system (Savillex, Eden Prairie, MN, USA), was used throughout this work, while 37% HCl, 37%  $\text{H}_2\text{O}_2$  and 25%  $\text{NH}_4\text{OH}$ , of Suprapur® grade purity, were purchased from Merck (Darmstadt, Germany).

Standard reference materials, NIST SRM 951a ( $\text{H}_3\text{BO}_3$ ), NIST SRM 981 (Pb), NIST SRM 987 ( $\text{SrCO}_3$ ) and NIST SRM 997 (Ti), were purchased from the National Institute of Standards and Technology (NIST). The IR certified value of the boric acid standard, NIST SRM 951a,  $^{11}\text{B}/^{10}\text{B}$  is  $4.04362 \pm 0.000136$  (Catanzaro et al., 1970) (reported uncertainty,  $u$ , is expressed as twice the standard deviation,  $u = 2s$ ).

Isotopic certified values of the NIST SRM 981 and NIST SRM 987 standards, the resin used for solid phase extraction (SPE) of Sr and Pb and all the preparation procedure of the resin suspension were described in detail in previous works (Durante et al., 2013; Lancellotti et al., 2020).

Three natural water reference materials (IAEA-B1, IAEA-B2, IAEA-B3) from International Atomic Energy Agency (IAEA), with published B isotope compositions and B concentrations (Gonfiantini et al., 2003; Tonarini et al., 2003), were used to test the B-matrix separation and to check for possible isotopic fractionation introduced by the ion separation. In particular, the  $\delta^{11}\text{B}$  (‰) recommended values for IAEA-B1, IAEA-B2 and IAEA-B3 are  $37.67 \pm 2.09$ ,  $13.59 \pm 2.62$  and  $-21.33 \pm 0.90$  (mean  $\pm s$ ), respectively. As far as boron matrix separation is concerned, an Alltech Maxi-Clean™ IC-H cation exchange resin with 0.5 mL of sulfonic acid in the  $\text{H}^+$  form (Sepachrom, Milan, Italy), and an Amberlite IRA-743 anion exchange resin (Merck, Darmstadt, Germany) were used.

For  $^{18}\text{O}/^{16}\text{O}$  ratio analyses, three international reference materials were purchased from IAEA (VSMOW2, GRESP and IAEA-606). The  $\delta^{18}\text{O}$  (‰) certified values of VSMOW2, GRESP and IAEA-606 are  $0 \pm 0.02$ ,  $-33.39 \pm 0.04$  and  $2.43 \pm 0.04$  (mean  $\pm s$ ), respectively. Four working in-house standard water samples (STD1, STD2, STD3 and STD4), calibrated to the Vienna Standard Mean Ocean Water scale, were used to determine the isotope ratio of the samples. The  $\delta^{18}\text{O}$  (‰) values measured for these four internal laboratory water standards were  $10.04 \pm 0.04$ ,  $2.39 \pm 0.03$ ,  $-1.79 \pm 0.02$  and  $-8.73 \pm 0.04$  (mean  $\pm s$ ), respectively.

The IV-ICP-MS-71A standard solution (Inorganic Ventures, New Jersey, USA) was used for the determination of metals concentration in the samples.

### 2.2. Wine samples

For the present study, 40 PDO Lambrusco wines from the 2017 harvest coming from different producers were provided by the local Lambrusco Consortium of Modena. In particular, 11 Sorbara (SOR), 6 Grasparossa (GRA) and 7 Salamino (SAL) wine samples were from the province of Modena, 10 samples were from the province of Mantua (MN) and 6 samples were from the province of Reggio Emilia (RE). Furthermore, a Lambrusco wine sample from the province of Modena was

randomly selected as control sample and used to optimize the analytical procedure for boron IR determination, and to verify repeatability and reproducibility of the entire analytical procedure for the isotopic ratio determinations.

### 2.3. Sample pretreatment

Different sample pretreatments were used to determine the various isotopic ratios.

As for the determination of the  $^{11}\text{B}/^{10}\text{B}$  ratio, samples were acid-digested inside a 40 mL quartz tube, by means of a microwave autoclave system ultraWAVE (Milestone, Bergamo, Italy), equipped with a five-positions rack. In each quartz vessel, 2 g of sample were carefully weighed, then 1 mL 30%  $\text{H}_2\text{O}_2$  and 0.5 mL 65%  $\text{HNO}_3$  were added. The five-positions rack was always loaded as follows: three wine samples, one control sample and one method blank. The power of the instrument magnetron, 1500 W, is automatically managed by the ultraWAVE, to obtain a heating ramp in accordance with the parameters set (Table S1, reported as Supplementary material). At the end of the digestion process, the solution was brought to a final mass of 5 g with high purity water.

As regard the digestion of wine samples for lead and strontium isotopic ratios determination as well as the SPE separation, detailed information was reported in previous studies (Durante et al., 2013, 2015; Lancellotti et al., 2020). For  $\delta^{18}\text{O}$  determination no sample pretreatment was required.

### 2.4. Metals content measurement

Boron and lead content were determined using a quadrupole-based inductively coupled plasma mass spectrometer, ICP/qMS (XSeries II, Thermo Fisher Scientific, Bremen, Germany), while strontium concentration was measured by means of a PerkinElmer SIMAA6000 graphite furnace spectrometer (GFAAS), equipped with a Zeeman background correction system (PerkinElmer, Milan, Italy). Instrumental parameters are showed in Table S2 and Table S3 (reported as Supplementary Material).

### 2.5. Chemical separation by solid phase extraction

Strontium, lead and boron IR measurements require the isolation of the analyte from interfering matrix components that are still present after sample digestion pretreatment.

The analytical protocols for lead and for strontium separation were described in previous works (Durante et al., 2013; Sighinolfi et al., 2018; Lancellotti et al., 2020).

Boron separation was carried out through a two-step ion chromatography (Foster et al., 2013; Guerrot et al., 2011). Precisely, the Alltech Maxi-Clean™ IC-H cation exchange resin was used as first step to remove major cations. In particular, the resin was first activated and washed with 8 mL of  $\text{H}_2\text{O}$ , and then an aliquot of  $10 \div 12$  mL of sample solution, at about  $250 \mu\text{g kg}^{-1}$  of B, was loaded at a flow rate of  $1 \text{ mL min}^{-1}$ . The first 2 mL of eluate were discarded, while the following eluate was collected in polypropylene tubes for the subsequent phase.

The second chromatographic step was performed with an in-house made solid phase extraction column, using 10 mL capacity “Extract Clean™ Reservoir” (Sepachrom, Milan, Italy), loaded with 0.25 g of Amberlite IRA-743 anion exchange resin. Prior to separation, the pH of the sample solution was adjusted to 10 by adding 25%  $\text{NH}_4\text{OH}$ . Under these conditions, boron is present as borate anion and therefore is strongly absorbed by the Amberlite IRA-743 resin. The second chromatographic separation step scheme is reported in Table 1. The B amount in the sample loaded, 2 mL, was about 0.5  $\mu\text{g}$ , while the final boron concentration in the eluate was about  $50 \mu\text{g kg}^{-1}$ . Solution was collected in polypropylene tubes and subjected to instrumental analysis within few days.

**Table 1**

Second step sequence for SPE separation of boron.

| Step | Function           | Eluent                    | Volume (mL) |
|------|--------------------|---------------------------|-------------|
| 1    | Resin pre-washing  | 10% (v/v) $\text{HNO}_3$  | 12          |
|      |                    | $\text{H}_2\text{O}$      | 6           |
| 2    | Resin conditioning | 2M $\text{NH}_4\text{OH}$ | 6           |
| 3    | Sample loading     | Sample (pH>10)            | 2           |
| 4    | Resin rinsing      | 2M $\text{NH}_4\text{OH}$ | 6           |
|      |                    | $\text{H}_2\text{O}$      | 3           |
| 5    | B elution          | 4% (v/v) $\text{HNO}_3$   | 10          |

Both the boron reference solution (NIST SRM 951a) at  $250 \mu\text{g kg}^{-1}$  of B and an appropriate aliquot of the control wine sample were also systematically and periodically submitted to the analytical procedure for B separation, in order to check for possible chemical fractionation and to evaluate reproducibility and repeatability of the method.

### 2.6. Isotope ratios determination

IR measurements for boron, lead and strontium were accomplished with an MC-ICP/MS spectrometer (Neptune, Thermo Finnigan, Bremen, Germany). Data acquisition was performed in low resolution mode on a flat top peak signal for all the recorded ions and, regarding the Faraday cups, in static mode. The instrumental set up for boron, lead and strontium IRs determination is reported in Table S4 (reported as Supplementary Material).

Three different sample introduction systems were used. In particular, an APEX IR desolvating apparatus (Elemental Scientific Instruments, Huntingdon, UK) was used for Pb, since the concentration of this element in wine is lower than  $100 \mu\text{g kg}^{-1}$ . On the contrary, a quartz cyclonic-Scott dual spray chamber and a quartz cyclonic spray chamber were used for Sr and B IR measurements, respectively.

Samples were measured with the bracketing technique using NIST standards (Durante et al., 2013; Lancellotti et al., 2020) in order to check and to correct for any instrumental drift. The averaged intensities of the bracketing-blanks (4% v/v  $\text{HNO}_3$  for B and Sr analysis and  $3 \text{ mol L}^{-1}$  HCl for Pb determination) were subtracted from the measured intensities of the respective standards or samples. To check the instrumental precision, all the isotopic values of the NIST SRM 987 and 981 standard solutions, read during each measuring session, were used. In particular, the  $^{87}\text{Sr}/^{86}\text{Sr}$  mean value of NIST SRM 987 was  $0.71025 \pm 0.00002$  ( $u = 2s$ ,  $n = 50$ ) and the  $^{204}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  mean values of NIST SRM 981 ( $u = 2s$ ,  $n = 44$ ) were  $16.9310 \pm 0.0032$ ,  $15.4858 \pm 0.0030$ ,  $36.6834 \pm 0.0070$ ,  $2.16664 \pm 0.00021$  and  $0.914645 \pm 0.00021$ , respectively. Owing to the fact that samples were generally once measured, in this work, the uncertainties associated to the final IRs results were expressed as twice the standard deviations of the mean values of the control wine sample (interval with a level of confidence of 95%), which was always processed by applying the whole analytical procedure.

For  $^{11}\text{B}/^{10}\text{B}$  determination, all standards and samples were diluted to a final B content of about  $50 \mu\text{g kg}^{-1}$  before MC-ICP/MS measurement. To reduce the boron memory effect, before blank reading the washing time was set to 25 min, which yielded a  $^{11}\text{B}$  intensity of the blank lower than 3 mV. The measured  $^{11}\text{B}/^{10}\text{B}$  was corrected for the instrumental mass bias by applying an external correction method, using the fractionation factor ( $C_{\text{factor}}$ ), which was determined from the  $^{11}\text{B}/^{10}\text{B}$  measurements of the NIST 951a solution with isotopic ratio of  $4.04362 \pm 0.00136$ , ( $u = 2s$ ) (Catanzaro et al., 1970). In particular, the  $C_{\text{factor}}$  is calculated as the ratio between the certified value and the measured one. The mean of the  $C_{\text{factor}}$  values is used to correct the isotopic ratio of the unknown sample, in order to determine the correct  $^{11}\text{B}/^{10}\text{B}$  of the sample itself.

The boron isotope ratio results are commonly given as delta notation  $\delta^{11}\text{B}$  (‰) relative to the NIST 951a boric acid standard, and are calculated with a bracketing approach as follows:

$$\delta^{11}\text{B}(\text{‰}) = \left[ \left( \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}_1}}{((^{11}\text{B}/^{10}\text{B})_{\text{std}_1} + (^{11}\text{B}/^{10}\text{B})_{\text{std}_2})/2} \right) - 1 \right] \times 1000 \quad (1)$$

Determination of the  $^{18}\text{O}/^{16}\text{O}$  ratio of wine water was performed by using an Isotope Ratio Mass Spectrometer, IRMS Isoprime PrecisiON (Elementar, Langensfeld, Germany) connected to a water/ $\text{CO}_2$  equilibration system, Isoflow (Elementar, Langensfeld, Germany). The procedure is described in the OIV-MA-AS2-12 method (2009).  $\delta^{18}\text{O}$  values are reported in per mil unit (‰) on the relative  $\delta$ -scale, and refer to the international standard VSMOW (Vienna Standard Mean Ocean Water) scale. All standards and samples were processed in triplicate.

## 2.7. Statistical analysis

Univariate data analysis was performed using Student t-test, one-way ANOVA and post hoc Tukey-Kramer test. A 0.05 level of significance was considered for all statistical tests, that were performed using the “data analysis” macro of Microsoft Excel. A Principal Component Analysis (PCA) model was calculated on the whole set of variables to explore the correlations among all the considered geographical descriptors and their contribution in the characterization of the different PDOs. The PCA model was calculated using the PLS Toolbox (ver. 8.6, Eigenvector Research Inc., Wenatchee, WA, USA) running in the Matlab environment (ver. 9.3, The MathWorks Inc., Natick, MA, USA).

## 3. Result and discussion

### 3.1. Validation of the boron-matrix separation procedure

For the validation of boron-matrix separation procedure, a recovery test was carried out on the NIST SRM 951a standard solution and wine control sample as well. The recovery of the analytical procedure was calculated by measuring boron concentration in the standard solution and control sample analyzed with the same analytical procedure used for the investigated wines. In particular, Boron recovery was determined on 6 independent aliquots of wine control sample and 5 independent aliquots of NIST standard solution with a theoretical concentration of  $234 \pm 8 \mu\text{g kg}^{-1}$ , (mean  $\pm$  s,  $n = 5$ ). As regards the NIST standard, the B recoveries for the first and second ion chromatographic separation steps were  $(99 \pm 3) \%$  and  $(97 \pm 6) \%$  respectively, while the recovery for the

whole process was  $(96 \pm 8) \%$  (mean  $\pm$  s,  $n = 5$ ).

Concerning the wine control sample, the initial B concentration was  $6.93 \pm 0.36 \text{ mg kg}^{-1}$  (mean  $\pm$  s,  $n = 6$ ). The sample digestion and the first separation step showed a quantitative boron recovery, being 99 and 100%, respectively, while the second separation step led to a lower B recovery, equal to 92%. The overall sample preparation recovery was  $(92 \pm 4) \%$ , (mean  $\pm$  s,  $n = 5$ ).

Furthermore, in order to exclude any mass fractionation of the analyte during the SPE procedure, the  $^{11}\text{B}/^{10}\text{B}$  of the NIST SRM 951a was measured before and after the boron separation. Fig. 1 reports the trend of  $^{11}\text{B}/^{10}\text{B}$  data for the NIST 951a standard measured between September 2018 and February 2020 sessions, without matrix separation and after SPE separation. The mean values of boron IR values of the reference material measured before and after the matrix separation were equal to  $4.04350 \pm 0.00122$  ( $u = 2s$ ,  $n = 21$ ) and  $4.04326 \pm 0.00244$  ( $u = 2s$ ,  $n = 8$ ), respectively. Taking into account the uncertainty associated to the measurements and the results of the Student's t-test, the two sets of data are statistically equivalent ( $P = 0.48$ ). In addition, the overall experimental mean value of  $^{11}\text{B}/^{10}\text{B}$  of NIST 951a ( $4.04343 \pm 0.00178$  with  $n = 29$ ) resulted to be statistically equivalent to the certified one ( $P = 0.52$ ).

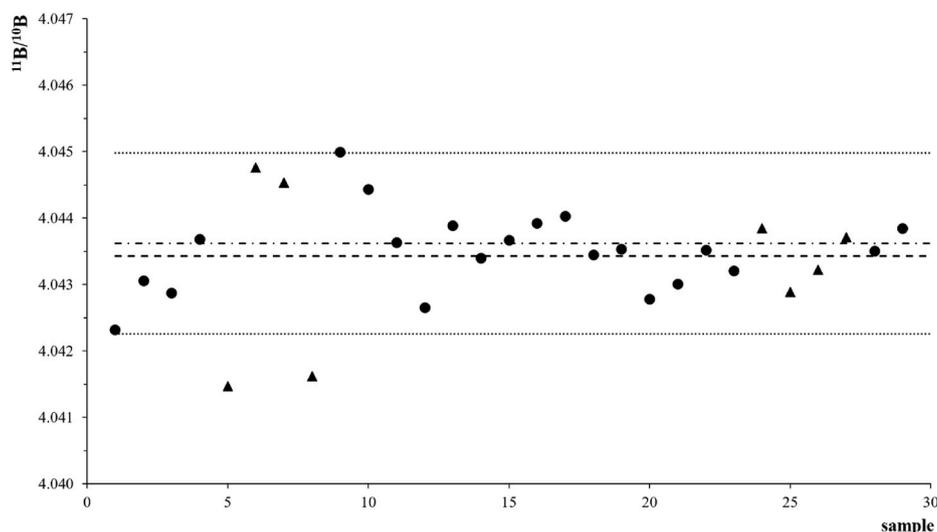
As far as the B isotopic values are concerned, the measured values of  $\delta^{11}\text{B}$  obtained for the certified water samples IAEA-B1, IAEA-B2 and IAEA-B3, after separation procedure are reported in Table 2. A Student's t-test made to compare the reference  $\delta^{11}\text{B}$  values (Gonfiantini et al., 2003) with the experimentally measured ones confirmed the absence of

**Table 2**

Reference and measured values (mean  $\pm$  s) of three certified IAEA water samples (IAEA-B1, IAEA-B2 and IAEA-B3), and results of Student's t-test comparison.

|   | IAEA-B1  | IAEA-B2  | IAEA-B3  |
|---|--|--|--|
|   | Mediterranean Sea  | Groundwater  | Groundwater  |
| $\delta^{11}\text{B}$ (‰) <sup>a</sup>    | $37.67 \pm 2.09$ ( $n = 11$ )  | $13.59 \pm 2.62$ ( $n = 9$ )   | $-21.33 \pm 0.90$ ( $n = 10$ )   |
| $\delta^{11}\text{B}$ (‰) <sup>meas</sup> | $37.00 \pm 1.35$ ( $n = 3$ )   | $14.23 \pm 0.41$ ( $n = 3$ )   | $-20.61 \pm 0.14$ ( $n = 3$ )  |
| <b>Student-test</b>                       | $t_{\text{cal}} = 0.52$<br>$t_{\text{tab}}(\text{df} = 12) = 2.18$<br>$P = 0.61$ | $t_{\text{cal}} = 0.41$<br>$t_{\text{tab}}(\text{df} = 10) = 2.23$<br>$P = 0.69$ | $t_{\text{cal}} = 1.34$<br>$t_{\text{tab}}(\text{df} = 11) = 2.20$<br>$P = 0.21$ |

<sup>a</sup> [Gonfiantini et al., 2003].



**Fig. 1.** Plot of  $^{11}\text{B}/^{10}\text{B}$  data for the NIST 951a standard, measured between September 2018 and February 2020 sessions. (●) standard solution without matrix separation, (▲) standard solution after SPE separation, (- -) mean value and (- - -) reference value. Dotted upper and bottom lines show the uncertainty value interval associated to the reference value:  $4.04362 \pm 0.00136$ .

statistically significant differences.

Based on these results, it is clear that the B-matrix separation does not influence the accuracy of boron IR values of the sample.

Finally, in order to acquire information in terms of reproducibility and repeatability of the whole analytical procedure, the wine control sample was analyzed several times, considering at least one sample for each IR measurement session. The  $\delta^{11}\text{B}$  mean value measured on the wine control sample was equal to  $16.17 \pm 0.61$  ( $u = 2s$ ,  $n = 11$ ); the variation along time of the measured values is reported in Fig. 2. The uncertainty estimated on the control sample measurements, expressed as twice the experimental standard deviation, was associated to the wine samples measurements.

### 3.2. Boron, lead and strontium contents in Lambrusco wines

All the experimental results are reported in Table S5 (reported as Supplementary Material). Table 3 reports the average values of the analytes concentration measured in the 40 samples of Lambrusco wine, along with the one-way ANOVA and the Tukey-Kramer multiple comparison test results.

Concerning the chemical composition of Lambrusco wines, in terms of B, Pb and Sr concentration values, some considerations can be drawn:

- Boron.** All the wine samples showed a boron concentration lower than  $14 \text{ mg kg}^{-1}$ , that represents the maximum allowed concentration proposed by the OIV (OIV, 2017). ANOVA highlighted significant differences among the different PDO Lambrusco wines, and a more in-depth analysis performed by means of Tukey-Kramer test revealed comparable boron concentration values for SAL-GRA, SAL-SOR and MN-RE. In particular, MN and RE showed a lower boron content with respect to the other PDO wines.
- Lead.** ANOVA test found no differences between the average Pb values of the considered Lambrusco wines. This may not surprise, considering that lead air pollution is widespread throughout the Po Valley (Canepari et al., 2014; Tositti et al., 2014), and that the vine plant slightly or probably does not absorb lead from soil (Lancellotti et al., 2020). Overall, Pb concentration varies between  $0.0025$  and  $0.0376 \text{ mg kg}^{-1}$ , that is significantly lower than the European limit, equal to  $0.15 \text{ mg L}^{-1}$ , established for products produced from the 2016 fruit harvest onwards (Stockley et al., 2020).
- Strontium.** Beyond the slight but statistically significant difference between the average Sr values of SOR and GRA samples, the difference between RE and all the other Lambrusco PDO wines was particularly notable. In fact, while for SOR, GRA, SAL and MN samples, the Sr content ranges from  $0.78$  to  $1.54 \text{ mg kg}^{-1}$ , with an average value of  $1.21 \text{ mg kg}^{-1}$ , the RE samples show a narrower range,  $0.73 \div 0.89 \text{ mg kg}^{-1}$ , with an average value of  $0.82 \text{ mg kg}^{-1}$ . In general, the measured Sr concentration values perfectly agree with

other published data concerning this element in the same matrix (Moreno et al., 2008; Diaz et al., 2003; Gonzalez et al., 2009; Angus et al., 2006).

### 3.3. Isotope signature of B, Sr, Pb and O in Lambrusco wines

All the experimental results are reported in Table S6 (reported as Supplementary Material). Table 3 reports the mean values of the measured isotopic ratios, along with the results of the one-way ANOVA and the Tukey-Kramer multiple comparison test.

- Boron.** Among the analyzed wines, RE samples show the lowest average value of  $\delta^{11}\text{B}$ , equal to  $11.6 \pm 3.4\%$  (mean  $\pm$  s). One-way ANOVA and Tukey-Kramer tests highlighted statistically significant differences between the Lambrusco PDO wines; in particular, this isotope ratio allows to differentiate RE wines from GRA, SOR, SAL and MN wines, for which  $\delta^{11}\text{B}$  values are in the range between  $15.5 \pm 3.9\%$  and  $16.7 \pm 4.1\%$  (mean  $\pm$  s).
- Oxygen.** In unadulterated wines  $\delta^{18}\text{O}$  is influenced by different variables, among which the climatic conditions of the vineyard location (Dutra et al., 2011; Santesteban et al., 2015). As regards the investigated wines, no particular behavior was highlighted even if a significant difference between the SAL and GRA samples was highlighted by applying ANOVA and Tukey-Kramer test.  $\delta^{18}\text{O}$  values range from  $0.06$  to  $2.10\%$ . Given the rather limited extension of the geographical area in which the considered Lambrusco PDO wines are produced, very similar climatic conditions are found, characterized by a humid temperate climate with very hot summers. Consequently, these results are not too surprising, although the observed difference between SAL and GRA will require further investigations in the future, planning a pilot study which might include the analysis of the isotopic pattern of local precipitation during the harvesting period.
- Lead.** Although the several isotopic values of Pb seem to overlap within experimental uncertainties, significant differences were found performing one-way ANOVA analysis. Lead has four isotopes, three of which ( $^{208}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$ ) are radiogenic, while  $^{204}\text{Pb}$  represents the only natural stable isotope and the least abundant one ( $1.4\%$ ). All the Pb – IRs seems to exhibit a similar trend; in particular, within each respective IR, differences between SOR samples with respect to all the other wines of the province of Modena were highlighted. Notwithstanding the presence of Pb in wine can be associated with both natural and anthropogenic sources of lead (Almeida et al., 2016), in this case the differences could be mainly attributed to anthropogenic sources since a recent study on similar samples demonstrated that it is not possible to assess a direct link between wine Pb IRs and the corresponding soil Pb IRs (Lancellotti et al., 2020). On the other side, it is worthwhile to notice that SOR production area is located in the most industrialized zone of the entire province with a high vehicular traffic. However, even if a correlation between vehicular/industrial sources and lead isotope pattern was shown in literature (Bollhofer and Rosman, 2001; Varrica et al., 2003), till now, no data concerning the province of Modena is available to support this hypothesis.
- Strontium.** Strontium uptake of vine plants strongly depends on the Sr bio-available fraction in the soil; nevertheless plants, and then wine, well reflect the Sr isotopic signature of the soil (Sighinolfi et al., 2018). As far as Modena Lambrusco wines are concerned, the obtained data are compared with those obtained within a previous long term study aimed to the development of Sr-isotopic map of Modena district (Durante et al., 2018). In all the three cases (SOR – SAL – GRA), the Lambrusco wines ratio fall into the Modena range obtained analyzing 198 soil samples which presented the following Sr-IR values: from  $0.70825$  to  $0.71230$ , from  $0.70847$  to  $0.70926$  and from  $0.70772$  to  $0.70955$  for GRA, SAL and SOR soils values, respectively. As regards the variability within the other Lambrusco varieties, the analysis with ANOVA and Tukey-Kramer test

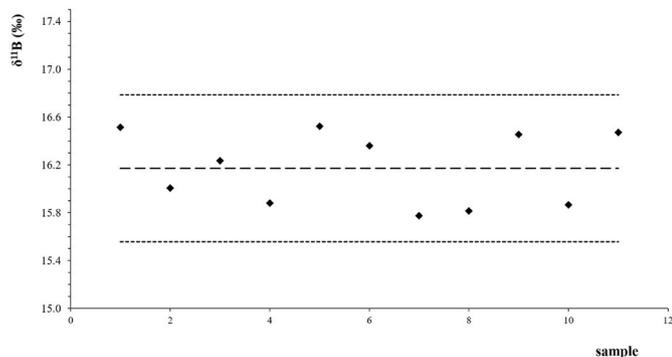


Fig. 2. Plot of  $\delta^{11}\text{B}$  (‰) isotopic ratio data for the separated control wine sample ( $n = 11$ ). Dotted upper and bottom lines show the uncertainty value interval associated to the mean value (---):  $16.17 \pm 0.61$ .

**Table 3**

Mean values and associated standard deviation data of the analytes concentration and IRs determined in Lambrusco wine samples, together with the one-way ANOVA results (df between = 5; df within = 35). Different superscript letters indicate statistical differences between different groups (Tukey-Kramer multiple comparison test, P = 95%).

|  | SAL                    |          | GRA                  |          | SOR                    |          | MN                    |          | RE                    |          | P-value*       |
|--|------------------------|----------|----------------------|----------|------------------------|----------|-----------------------|----------|-----------------------|----------|----------------|
| <b>B (mg kg<sup>-1</sup>)</b>            | 8.08 <sup>a,b</sup>    | ±0.48    | 7.85 <sup>a</sup>    | ±0.56    | 9.00 <sup>b</sup>      | ±0.67    | 6.22 <sup>c</sup>     | ±0.83    | 6.08 <sup>c</sup>     | ±1.27    | <b>3.0E-09</b> |
| <b>Pb (mg kg<sup>-1</sup>)</b>           | 0.0154                 | ±0.0114  | 0.0120               | ±0.0064  | 0.0172                 | ±0.0080  | 0.0135                | ±0.0070  | 0.0245                | ±0.0096  | 8.1E-02        |
| <b>Sr (mg kg<sup>-1</sup>)</b>           | 1.27 <sup>a</sup>      | ±0.11    | 1.06 <sup>a</sup>    | ±0.19    | 1.32 <sup>b</sup>      | ±0.12    | 1.17 <sup>a,b</sup>   | ±0.16    | 0.82 <sup>c</sup>     | ±0.07    | <b>4.1E-07</b> |
| <b>δ<sup>11</sup>B (‰)</b>               | 15.8 <sup>a</sup>      | ±4.0     | 16.7 <sup>a</sup>    | ±4.1     | 15.5 <sup>a</sup>      | ±3.9     | 16.6 <sup>a</sup>     | ±4.1     | 11.6 <sup>b</sup>     | ±3.4     | <b>3.8E-04</b> |
| <b><sup>208</sup>Pb/<sup>206</sup>Pb</b> | 2.0959 <sup>a</sup>    | ±0.0025  | 2.0962 <sup>a</sup>  | ±0.0016  | 2.0987 <sup>b</sup>    | ±0.0012  | 2.0972 <sup>a,b</sup> | ±0.0006  | 2.0970 <sup>a,b</sup> | ±0.0021  | <b>6.4E-03</b> |
| <b><sup>207</sup>Pb/<sup>206</sup>Pb</b> | 0.8569 <sup>a</sup>    | ±0.0020  | 0.8568 <sup>a</sup>  | ±0.0013  | 0.8595 <sup>b</sup>    | ±0.0014  | 0.8578 <sup>a,b</sup> | ±0.0004  | 0.8584 <sup>a,b</sup> | ±0.0015  | <b>7.2E-04</b> |
| <b><sup>206</sup>Pb/<sup>204</sup>Pb</b> | 18.213 <sup>a</sup>    | ±0.047   | 18.218 <sup>a</sup>  | ±0.030   | 18.148 <sup>b</sup>    | ±0.034   | 18.194 <sup>a</sup>   | ±0.014   | 18.184 <sup>a,b</sup> | ±0.037   | <b>4.1E-04</b> |
| <b><sup>207</sup>Pb/<sup>204</sup>Pb</b> | 15.605 <sup>a,b</sup>  | ±0.007   | 15.610 <sup>a</sup>  | ±0.005   | 15.598 <sup>b</sup>    | ±0.005   | 15.607 <sup>a,b</sup> | ±0.009   | 15.608 <sup>a,b</sup> | ±0.011   | <b>2.1E-02</b> |
| <b><sup>208</sup>Pb/<sup>204</sup>Pb</b> | 38.173 <sup>a</sup>    | ±0.055   | 38.188 <sup>a</sup>  | ±0.040   | 38.087 <sup>b</sup>    | ±0.052   | 38.157 <sup>a</sup>   | ±0.033   | 38.130 <sup>a,b</sup> | ±0.069   | <b>1.0E-03</b> |
| <b><sup>87</sup>Sr/<sup>86</sup>Sr</b>   | 0.70879 <sup>a,b</sup> | ±0.00005 | 0.70889 <sup>a</sup> | ±0.00016 | 0.70879 <sup>a,b</sup> | ±0.00011 | 0.70887 <sup>a</sup>  | ±0.00006 | 0.70872 <sup>b</sup>  | ±0.00004 | <b>1.4E-02</b> |
| <b>δ<sup>18</sup>O (‰)</b>               | 0.64 <sup>a</sup>      | ±0.35    | 1.38 <sup>b</sup>    | ±0.59    | 1.06 <sup>a,b</sup>    | ±0.49    | 0.88 <sup>a,b</sup>   | ±0.34    | 1.24 <sup>a,b</sup>   | ±0.32    | <b>3.4E-02</b> |

\*statistically significant differences (P-value < 0.05) are highlighted in bold.

highlighted a statistically significant difference between the average <sup>87</sup>Sr/<sup>86</sup>Sr value of RE samples and the average values of GRA and MN samples. This evidence was, more or less, already observed in a previous investigation although the <sup>87</sup>Sr/<sup>86</sup>Sr data range of the Modena Lambrusco wines holds the MN and RE values too (Durante et al., 2015). Experimental evidence confirms the difficulty in tracing Lambrusco varieties based only on their <sup>87</sup>Sr/<sup>86</sup>Sr ratio. This fact can be interpreted on the basis of a common origin of the Po valley whose geo-, litho-, and pedological characteristics are mainly influenced by the Po river basin. Therefore, more samples must be analyzed to build a robust data set for sample discrimination in terms of provenance.

3.4. Exploratory data analysis

In order to explore the overall contribution of the measured variables to the sample structure, PCA analysis was applied to the autoscaled data matrix composed by the 11 direct indicators (B, Sr and Pb content; δ<sup>11</sup>B, <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>208</sup>Pb/<sup>206</sup>Pb, <sup>207</sup>Pb/<sup>206</sup>Pb, <sup>208</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, <sup>206</sup>Pb/<sup>204</sup>Pb and δ<sup>18</sup>O) obtained for the 40 wine samples. Autoscaling was selected as the most appropriate data preprocessing, as the different indicators had different variances due to their different nature. In this first exploratory analysis, two-principal components seemed appropriate taking into account their explained variance (53.47%). In Fig. 3, the PC1 vs PC2 scores plot is reported, and the different wine samples are represented with different symbols and color according to their provenience.

From the PCA results some information could be obtained. In particular, Fig. 3 shows that significant separation could be observed among RE (negative PC2 score values) and SOR (almost all at positive

PC2 score values) wine samples. The main contribution to this separation seems to be given by higher concentrations of B and Sr and an higher δ<sup>11</sup>B values in RE samples and an higher concentration of Pb with higher δ<sup>18</sup>O in SOR ones, since they lie on the same side of the respective loadings plot (Fig. 4). This difference is in accordance with the results previously discussed in Sections 3.2 and 3.3.

The other different samples (MN, SAL and GRA) are rather overlapped and it is evident a ‘larger spread’ of GRA wines samples, that are uniformly distributed along the variability range of the higher PC1 and PC2 scores space. All of these samples seem to have similar isotopic systematics mainly as regard higher values of <sup>208</sup>Pb/<sup>204</sup>Pb, <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>87</sup>Sr/<sup>86</sup>Sr and δ<sup>11</sup>B (all at positive PC1 and PC2 loading values).

As regards δ<sup>11</sup>B values amongst various samples, they are likely to be due to difference in local growth conditions. Thus, the B supply from soils, water, and fertilizer may determine B isotopic composition in wines samples and this suggests considering the analysis of all these matrices in further studies.

Finally, it has to be remarked that PCA allows a straightforward interpretation of the whole data set. In particular, the obtained results show as it has been possible to use the synergistic information present in all monitored indicators in order to understand how all together were able to trace almost all the different monitored samples.

4. Conclusions

In the context of wine authentication, geographical traceability is

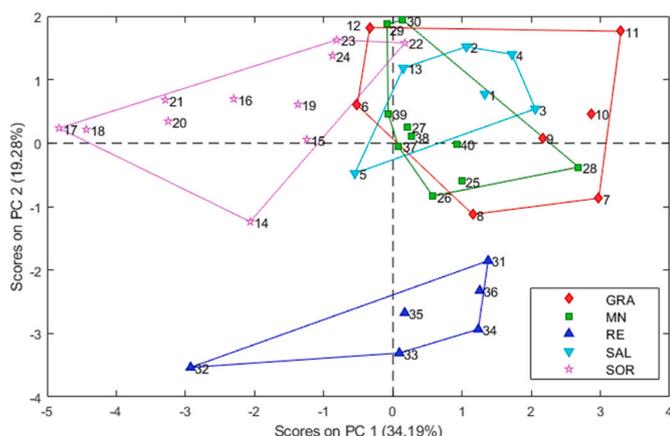


Fig. 3. PC1-PC2 score plot.

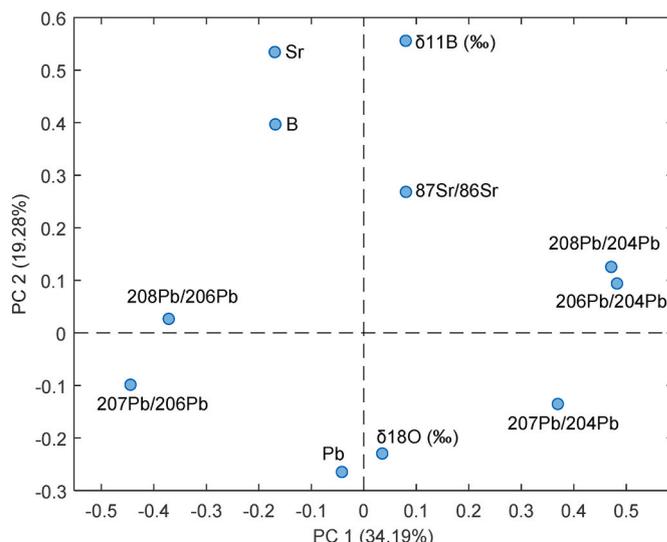


Fig. 4. PC1-PC2 loading plot.

certainly an important issue and for some time the scientific community has been focusing its efforts on the development of new technologies and analytical methodologies to improve knowledge and define new geographical traceability models. Moreover, there is a great interest by wine producers; in fact, the possibility of certifying the authenticity of the product through objective/scientific traceability indicators means attesting, through the label, that the wines are of high quality.

To fulfill these expectations, an elemental and isotopic methodology was tested on different PDO Lambrusco wines. The approach is based on the measurement of B, Pb and Sr concentration and their respective isotopic patterns, in addition to  $\delta^{18}\text{O}$ . Moreover, the  $^{11}\text{B}/^{10}\text{B}$  measurement procedure, carried out by means of a MC-ICP/MS, was optimized through the validation of the analytical method.

The results of the present study, that represents a preliminary exploratory data analysis of a set of PDO wines representative of Lambrusco production in northern Italy, highlighted that: a) boron isotope ratio measurements show a high degree of accuracy and precision (measured mean value  $^{11}\text{B}/^{10}\text{B}$  of NIST SRM 951a is  $4.04343 \pm 0.00178$ ,  $u = 2s$ ) when compared to the certified data ( $4.04362 \pm 0.00136$ ,  $u = 2s$ ); b) a separation was observed for Lambrusco wines from Sorbara (SOR) and for Lambrusco wines from Reggio Emilia (RE) with respect to the other PDOs; b) the differentiation observed for these PDOs is based mainly on boron and strontium, in terms of concentration and isotopic ratios, and on lead isotopic ratios.

In summary, the use of a multi-parametric approach, to ascertain the origin of wines proved to be promising, even if a limited number of samples were available and considering that the investigation was carried out on a very limited geographical scale. As a consequence, further studies are needed in order to increase the number of considered samples, which will also allow to develop robust classification models to improve the effectiveness of this methodology.

## Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## CRediT authorship contribution statement

**Lisa Lancellotti:** Investigation, Formal analysis, Writing – original draft. **Simona Sighinolfi:** Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Alessandro Ulrici:** Formal analysis, Methodology, Writing – original draft. **Laura Maletti:** Investigation. **Caterina Durante:** Methodology. **Andrea Marchetti:** Project administration. **Lorenzo Tassi:** Methodology.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.crfs.2021.11.001>.

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