



Geographic origin of varietal apple and pear cake fillings differentiation based on fruit mineral content

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Abstract

Origin determination is crucial for foods under Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI), where risks of fraud are high. Authentication of fruit origin in cake fillings is particularly challenging, as pulps lose distinctive morphological traits during transformation, new ingredients are added, and for the same fruit variety the genetic information is independent of the geographic origin. Minerals, intrinsically linked to soil and environmental conditions, represent promising tracers of geographical origin. This may be disguised by the minerals present in the different technological ingredients added in manufacture of the cake fillings. This study hypothesized that even in these conditions, elemental profiles can serve as markers of fruit origin. For this, industrial apple (*Malus domestica* L. var. ‘Golden Delicious’) and pear (*Pyrus communis* L. var. ‘Rocha’) cake fillings from different orchards origin and the correspondent fresh fruit were analyzed by inductively coupled plasma–mass spectrometry. For apple samples, the geographic origin can be distinguished by the content of nine elements: B, La, Cs, Ce, Cr, Rb, Cu, Tl, and Mn, after the removal of Fe, Sr, Ba, Al, Pb and Zn, associated to the processing of the cake fillings ingredients. For pear samples, the geographic origin can be distinguished by the content of eleven elements: Zn, Cu, Ni, La, Pb, Rb, Mn, Co, B, Ba, and Cs, after removal of Fe, Cd, Ce, Al, Sr, Cr, and Tl. These elements, characteristic of soil, environment, and depth of tree roots, can be used as markers of authenticity of the fruit cake fillings.

Keywords *Malus domestica* · *Pyrus communis* · Element analysis · Fruit cake fillings · Geographic origin · Inductively coupled plasma mass spectrometry

Introduction

Apple and pear are usually the raw ingredients to prepare pastry fruit cake fillings by grinding the fruit and add sugar, water, and adjuvant ingredients to obtain jams traditionally used in various bakery and confectionery products [1]. The disruption of fruit tissues for cake filling preparation prevents the easy identification of the origin of the pulps. The differences between fruits from distinct geographical regions become less perceivable in the final product due to the reactions promoted by heating [1, 2]. This aspect is important when cake fillings use fruit from a Protected Designation of Origin (PDO) or Protected Geographical Indication (PGI) due to fraud issues. Fruits from other regions, usually of low value and quality, can fraudulently replace those with PDO or PGI label, and there are no available tools to detect the authenticity of the fruit [3–6]. While genetic markers can be useful to identify species, cultivars are not able to be distinguished, as demonstrated for apple

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cultivars from different geographical origins [7]. A strategy based on volatile organic compounds of PDO “Pera Rocha do Oeste” pear showed that it is possible to develop volatile signature for fruit from this origin, different from pear of the same variety but cultivated in other regions. Although this is valid for intact fruit, the strategy was not applied to processed fruit [8]. Inductively coupled plasma mass spectrometry (ICP–MS) and inductively coupled plasma optical emission spectrometry (ICP–OES) are tools to discriminate the geographical origin of lemon juices [4]. However, this is valid for whole juices, as the strategy was not applied to juices containing added ingredients.

Elements exist in soil as ions in pore waters or adhered to soil particles and, through the roots, plants absorb directly these ions or use an ion-exchange mechanism when elements are present in solid particles [9]. This means that soils with different compositions provide different mineral content to the plant that allowed to discriminate factors associated to their origin. Generally, soils from vineyards located on granite formations exhibit higher concentrations of Li, Be, Al, Fe, Ga, Ge, As, Rb, Sn, Cs, and rare earth elements compared to those from sedimentary geological formations and sandy soils [10]. In wines, constituted by blends of grapes, although Ba, Mg, and Mn content are important to distinguish the soil origin and, in this way, be authenticity markers, their B, K, and P content, associated with fertilizers and winemaking practices, Zn and As content, associated with phytosanitary products [11]. It is also already known that the distribution of elements in soils is usually stratified, as the potential toxic elements tend to be less superficial than the light element [9, 12].

As plants reflect the bioavailable elemental composition of their soils [6, 13], this study hypothesizes that the elemental profiles of fruit-derived products can serve as reliable markers of geographical origin, even after processing and despite the presence of additional ingredients. The primary criterion for success is the ability to discriminate between geographical regions, regardless of different orchards or harvest years. As pear tree has deeper roots than apple tree [14–16], it is hypothesized that the uptake of elements could be different from these trees on similar soils, allowed to trace fruit origin when processed as cake fillings.

Materials and methods

Sample collection and preparation

Fresh fruit

The apple samples (*M. domestica*, var. ‘Golden Delicious’) were all commercial, provided by the retailer SONAE MC

through the group of producers that supply the retail market associated under the brand “Clube de Produtores”. Apple samples were harvested in 2018 from 1 orchard ($n=5$) and from 2 orchards ($n=10$) in 2019, included in the delimited Alcobaça region, Portugal. All these apple samples were commercialized under a certified PGI “Maçã de Alcobaça” label by CODIMACO, Certificação e Qualidade, Lda. Also, for apples, 15 samples were obtained from 1 orchard in Carrazeda de Ansiães in 2018 harvest ($n=5$), 1 orchard in Armamar ($n=5$) and 1 orchard from Cova da Beira ($n=5$) both from 2019 harvest.

Pear samples (*P. communis* L. cv. ‘Rocha’) were also provided by the retailer SONAE MC through the group of producers. These Pear commercial samples were harvested in 2018 and 2019 from 9 different orchards in five localities, Caldas da Rainha ($n=25$), Lourinhã ($n=15$), Rio Maior ($n=25$), Cadaval ($n=20$), and Bombarral ($n=5$), all included in the delimited West region of Portugal. All these pear samples were commercialized under a certified PDO “Pera Rocha do Oeste” label by CODIMACO, Certificação e Qualidade, Lda. Also, non-PDO pear samples ($n=5$) from Alandroal in Alentejo, South of Portugal, were collected from the 2019 harvest, provided by SONAE MC. Since the non-PDO Rocha pear samples were exclusively from one region, to increase the quantity of non-PDO pear samples from different regions, samples were also obtained by direct contact with 3 local farmers. A total of 15 pear samples, harvested in 2019 in 3 different regions, Aveiro, North of Portugal ($n=5$), Leiria, West of Portugal ($n=5$), and Fundão, East of Portugal ($n=5$) were analyzed.

At the time of distribution of the fruit samples provided by the retailer, one box containing 40 fruit was received from each orchard for each harvest year, with no specification of the tree. From each box, 5 fruit were selected for elemental analysis by ICP. These commercial samples, obtained from cultivated orchards in different years, include the intrinsic variability related to soil fertilization and type, allowing a data set with a large dimension to select the elements with robustness to be used as geographical markers.

Fruit cake fillings

A total of 24 batches cake fillings were produced and supplied by Decorgel Produtos Alimentares S.A. The formulation of the cake fillings, performed industrially for commercial purposes, manufactured with the same formulation and production line of the commercial products, was constituted of 40% of fruit, water, glucose–fructose syrup, sugar, modified corn starch, lemon (from concentrate), gelling agent (pectin), antioxidant (ascorbic acid), preservative (potassium sorbate), and colorant (β -carotene). The fresh fruit samples from different regions and harvest years, used

in this work, gave origin to three batches of fruit cake fillings. In the case of PGI apple cake fillings from Alcobaça, 3 batches were processed with PGI apple samples of 2018 harvest, and 3 with PGI apple samples of 2019 harvest. Also, 3 batches apple cake fillings were processed with apple samples from Carrazeda de Ansiães and 3 batches apple cake fillings with apple samples from Armamar. Regarding PDO pear cake fillings, 6 batches were produced with PDO pear samples from the 2018 harvest and 3 batches with PDO pear samples from the 2019 harvest. Also, 3 batches pear cake fillings were produced with pear samples from Alandroal region.

The cake filling used include all the variability related to the ingredients used for their preparation, including the water and equipment, allowing to select only those elements that have robustness to be used as geographical markers.

Samples preparation

Upon arriving at the laboratory, each fruit sample was washed with deionized water, peeled, and cut into 1 cm × 1 cm × 1 cm cube. Afterwards pooled samples were frozen below −80 °C before being lyophilized (LaboGene Scanvac Coolsafe). Considering the fruit cake fillings, samples were freeze-dried. Moisture content of all samples was determined by measuring the mass before and after lyophilization. Freeze-dried samples were then homogenized into a fine powder using glass pestle. Samples were sealed in polyethylene flasks and kept until analysis in a desiccator containing phosphate pentoxide.

Elemental analysis

All reagents were of high analytical grades. Ultrapure 18.2 MΩ water was obtained from Milli-Q water system connected to an Elix one and was used in the preparation of all solutions. Concentrated nitric acid (65%; CAS number: 7697-37-2; VWR) and hydrogen peroxide (30%; CAS number: 7722-84-1; VWR) were used to digest samples. The apple leaves Standard Reference Material (SRM), SRM 1515, was used to evaluate the accuracy of the method. Percent recovery (%) of the certified reference material and limit of quantification (LOQ) (μg/g) were shown in Table S1.

Sample digestion

The digestion method was performed, adapted from the methodology described by Rodrigues et al. [11] and Bressy et al. [17], in closed microwave vessels (XP-1500 Plus Standard Vessel Assembly, CEM) and pressure/temperature control vessels (XP-1500 Plus Control Vessel Assembly,

CEM). A mass of around 200 mg of lyophilized sample were weighed and followed by the addition of 1 mL of concentrated nitric acid, 2 mL of hydrogen peroxide and 1 mL of ultrapure water. The microwave (Mars, Cem) used the following program: step (1) 4 min up to 130 °C, step (2) 4 min up to 160 °C, step (3) 3 min at 175 °C, step (4) 4 min at 195 °C and step (5) cooling down. After cooling to room temperature, the volume was made up to 25 mL with ultrapure water. All samples were analyzed in duplicate. Digested samples were kept at room temperature until further analysis.

Minerals quantifications

The element analysis was carried out in an ICP–MS (Thermo X series) with a Burgener MiraMist nebulizer. The spray chamber was cyclonic equipped with a Peltier device. Argon flow was 13 L/min and sample flow was ~1 mL/7min. The power used was 1400 W. Calibration curves were made with standard reference solutions (ICPMS 71 A and ICPMS 71B, Inorganic ventures, USA). For the analysis of Ca, Mg, K, and Na, the concentration range was 0–10,000 μg/L. For Fe, the range is 0 to 250 μg/L. For the remaining elements, the concentration ranged from 0 to 100 μg/L. For very concentrated samples, dilutions were performed to the standard concentration range.

To evaluate the concentration of elements in apple, pear, and their derived cake fillings, the set of 30 apple fruit, 110 pear fruit, 12 apple cake fillings, 12 pear cake fillings from different locations and harvested in two consecutive years were analyzed by inductively coupled plasma–mass spectrometry (ICP–MS). The concentration of all the elements was expressed in μg/g dry weight (d.w.).

Data processing

The web interface, MetaboAnalyst 5.0 software (McGill University, Montreal, QC, Canada), was used to autoscaling normalization of the data obtained from the concentrations expressed in μg/g of quantified element. A principal component analysis (PCA) was performed, to examine the differences in mineral content for all samples, for only apple and only pear samples and derived cake fillings. A partial least squares–discriminant analysis (PLS-DA) was used for geographical separation and discrimination. CV=5 as the default was considered to perform cross-validation using the k-fold method. The values of Q², which measures the model predictive capacity, and R², which indicates the data variability explain by the model were calculated from the prediction residuals of the validation folds. The optimal number of latent variables was selected based on the maximum Q² value, rather than the highest R², in order to

minimize overfitting. To assess the robustness of the model and the risk of overfitting, permutation tests (1000 permutations) were performed using the prediction accuracy and separation distance (B/W). For multiple comparisons, Tukey's post-hoc test was used. $P < 0.05$ was considered statistically significant for a 95% confidence interval. One-way analysis of variance (ANOVA) was applied using GraphPad Prism version 6.0 (GraphPad Software, San Diego, California, USA). The elements presenting values under LOQ were treated as zero when used for statistical analyses. This decision was supported by a sensitivity analysis where it was possible to demonstrate that the identified markers remained stable under alternative imputations such as 1/5 of the minimum positive value of each variable (used by software MetaboAnalyst) (Tables S3 and S7 and Figures S1 and S3).

Results and discussion

Minerals in fresh and processed apples and pears

A total of 46 elements of apple and pear fruit and derived cake fillings were analyzed by ICP-MS. Of these, 20 elements were quantified in samples (B, Al, Cr, Mn, Fe, Cu, Zn, Rb, Cs, Ba, La, Sr, Tl, Pb, Ni, Co, Cd, Ce, P, and Mg). A total of 26 elements (Be, V, As, Se, Mo, Ru, Rh, Pd, Sb, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Os, Ir, Pt, U, and Li) were below the limit of detection and were not considered.

For apple samples (Table 1), Co, Cd, and Ni were all below the limit of quantification (LOQ; Co and Cd $< 0.012 \mu\text{g/g}$ d.w. and Ni $< 0.13 \mu\text{g/g}$ d.w.) in both fruit samples and cake fillings. These elements are usually reported to be under the detection limit [18–21]. The major elements in fruit samples were P and Mg, on average 604 and 329 $\mu\text{g/g}$, respectively. These values agreed with literature, with ranges from 475 to 4190 $\mu\text{g/g}$ for P and from 140 to 750 $\mu\text{g/g}$ for Mg [18–24]. These two elements were also the highest in the respective cake fillings, 389 $\mu\text{g/g}$ for P and 86 $\mu\text{g/g}$ for Mg. The value of P in apple cake fillings was one half of the content found in fresh fruit while the Mg content was one-third. These results showed that the ingredients added to prepare the apple cake filling recipe changed the elemental composition of the major elements. For the cake fillings, the ingredients added decreased the macro-elements total content on a mass weight basis and on a different extent. The major elements composition of the cake fillings depends on the elemental composition and amount of the fruit and other ingredients used. Concerning the micro-elements, boron had the highest content, on average 24 $\mu\text{g/g}$ in raw apples fruit, approaching literature data (26–40 $\mu\text{g/g}$) [21, 24, 25], following by Rb, Fe, Al, Cu, Mn, and Zn (9, 7, 4.4, 2.7, 2.5, and 2.2 $\mu\text{g/g}$,

respectively). These data are within the range of the ones reported for apple fruit [18–23, 25], except for Rb that was reported with an amount ten times lower, ranging from 0.72 to 1.0 $\mu\text{g/g}$ [21]. For the apple cake fillings, Rb (2.3 $\mu\text{g/g}$) and Cu (0.73 $\mu\text{g/g}$) accounted for a quarter of the concentration found in fresh apple fruit, B (7.3 $\mu\text{g/g}$) and Mn (0.83 $\mu\text{g/g}$) content was one-third and Fe (3.7 $\mu\text{g/g}$) was half of the value found for the fresh fruit. These results demonstrate the dilution effect of these elements of the fruit promoted by the ingredients added for the preparation of the cake fillings, as observed for the macro-elements. The extent of their decrease allowed to infer a negligible contribution of Rb and Cu in cake-fillings, contrarily to Fe and Al. In fact, Al concentration was 4.0 $\mu\text{g/g}$ in apple cake fillings, almost the same as in apple fruit, possibly resultant from the water used in the process [26, 27]. The same origin can be attributed to Fe [28]. Although trace elements Ba (0.82 $\mu\text{g/g}$), Sr (0.68 $\mu\text{g/g}$), Cr (0.36 $\mu\text{g/g}$), and Tl (0.005 $\mu\text{g/g}$) were present in fresh apples fruit concentration in accordance with literature [18, 19, 24, 29]. Cs content (0.38 $\mu\text{g/g}$) was more than 100-fold higher (0.0025 $\mu\text{g/g}$) [21]. This high amount could be related to granite soil origin of apple samples [5, 30–33], contrarily to the sandy loam soil origin of the apples studied by Zhang et al. [21]. For Ce (0.041 $\mu\text{g/g}$) and for La (0.019 $\mu\text{g/g}$) no data was found in the literature for apple fruit. In apple cake fillings, the concentration of Cs (0.026 $\mu\text{g/g}$) was 15-fold lower than in apple fruit whereas the concentration of Tl (0.0013 $\mu\text{g/g}$) was 2.5-fold lower, close to the limit of quantification (LOQ; Tl $< 0.0011 \mu\text{g/g}$). In fact, this element was only quantified in cake fillings from Alcobaça region and not in those from other regions. The concentration of all the other trace elements, except Sr (0.58 $\mu\text{g/g}$) and Ba (0.53 $\mu\text{g/g}$), were 1.5-fold lower than that observed for apple fruit. For Sr and Ba in the cake fillings, the concentration was similar to the one found in fresh apple fruit, allowing to infer that the ingredients or the water [34, 35] may also contribute to increase Sr and Ba concentration in these apple cake fillings.

For pear fruit samples (Table 2), as observed for apple fruit, the major elements were P and Mg, on average 686 and 537 $\mu\text{g/g}$, respectively, comparable with the values reported in the literature (700–4700 $\mu\text{g/g}$ for P and 283–1890 $\mu\text{g/g}$ for Mg) [13, 19, 22, 36, 37]. The concentration of these two elements was also high in the respective cake fillings, 97 $\mu\text{g/g}$ for P and 89 $\mu\text{g/g}$ for Mg, 7- and 6-fold lower than the concentration found in pear fruit, respectively. Regarding the microelements, their concentration ranged from 14 $\mu\text{g/g}$ for Rb to 1.1 $\mu\text{g/g}$ for Sr, and the trace elements ranged from 0.49 $\mu\text{g/g}$ for Ni to 0.022 $\mu\text{g/g}$ for Cd, and their concentration, when available, was within the range found in literature [13, 19, 37–39]. For Ce (0.025 $\mu\text{g/g}$), Cs (0.023 $\mu\text{g/g}$), Tl (0.015 $\mu\text{g/g}$), and La (0.013 $\mu\text{g/g}$) in pear fruit samples,

Table 1 Mineral composition ($\mu\text{g/g}$, average $\pm$ standard deviation) of apple (fruit and cake fillings) by orchard origin, expressed by dry weight

Origin	Type	B	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Rb	Cd	Cs	Ba	La	Sr	Tl	Pb	Ce	P	Mg
PG1 Alcobaça	Fresh fruit	27.9	4.7	0.34	2.8	6.5	*	*	2.8	2.2	6.23	*	0.029	0.75	0.011	0.5	0.0032	0.036	0.031	490.01	410.8
		± 8.0	± 1.6	± 0.26	± 1.0	± 1.1	*	*	± 0.7	± 0.8	± 1.20	*	± 0.010	± 0.40	± 0.006	± 0.2	± 0.0005	± 0.024	± 0.17	± 260.91	± 39.5
	Cake fillings	7.5	4.2	0.16	0.9	3.4	*	*	0.6	2.0	1.79	*	0.013	0.40	0.008	0.4	0.0113	0.053	0.009	199.78	80.4
Carrazeda de Ansiães	Fresh fruit	± 0.9	± 0.8	± 0.08	± 0.1	± 0.9	*	*	± 0.1	± 0.6	± 0.13	*	± 0.003	± 0.07	± 0.001	± 0.1	± 0.0002	± 0.012	± 0.004	± 8.27	± 4.6
		26.7	4.2	0.52	3.1	7.4	*	*	3.4	2.2	10.96	*	1.097	0.87	0.026	1.0	0.0048	0.055	0.020	206.39	454.2
	Cake fillings	± 1.2	± 1.1	± 0.25	± 0.7	± 1.5	*	*	± 0.6	± 0.4	± 2.97	*	± 0.039	± 0.05	± 0.002	± 0.4	± 0.0018	± 0.010	± 0.001	± 61.39	± 184.3
Armamar/Douro	Fresh fruit	6.3	4.9	0.19	0.7	3.5	*	*	0.9	3.0	2.80	*	0.030	0.88	0.017	0.9	*	0.081	0.009	n.a.	88.7
		± 0.1	± 0.1	± 0.02	± 0.1	± 0.1	*	*	± 0.1	± 0.3	± 0.05	*	± 0.002	± 0.08	± 0.001	± 0.1	*	± 0.008	± 0.001	n.a.	± 0.7
	Cake fillings	15.5	4.7	0.31	1.5	7.3	*	*	2.3	1.5	11.16	*	0.967	0.96	0.052	1.2	0.0016	0.032	0.123	916.06	189.2
Cova da Beira	Fresh fruit	± 2.6	± 1.0	± 0.01	± 0.4	± 0.5	*	*	± 0.4	± 0.5	± 3.13	*	± 0.052	± 0.27	± 0.031	± 0.7	± 0.0001	± 0.005	± 0.051	± 25.69	± 20.8
		7.2	2.8	0.34	0.7	4.6	*	*	0.8	0.7	2.61	*	0.047	0.43	0.030	0.5	*	0.016	0.081	578.79	94.9
	Cake fillings	± 0.2	± 1.2	± 0.04	± 0.1	± 0.6	*	*	± 0.1	± 0.3	± 0.03	*	± 0.001	± 0.02	± 0.006	± 0.1	*	*	± 0.010	± 9.64	± 1.1
Total of apple fruit	Fresh fruit	20.1	3.2	0.30	2.1	7.4	*	*	2.1	2.9	14.70	*	0.129	0.80	0.003	0.6	0.0142	0.026	0.005	1033.51	260.6
		± 2.0	± 1.0	± 0.01	± 0.3	± 1.3	*	*	± 0.7	± 0.7	± 4.72	*	± 0.033	± 0.10	± 0.001	± 0.1	± 0.0009	± 0.009	± 0.004	± 88.51	± 30.3
	Cake fillings	24.3	4.4	0.36	2.5	7.0	*	*	2.7	2.2	99.25	*	0.380	0.81	0.019	0.7	0.0051	0.037	0.041	604.33	328.7
Total of apple cake fillings	Fresh fruit	± 7.5	± 1	± 0.21	± 0.9	± 1.2	*	*	± 0.8	± 0.8	± 4.16	*	± 0.473	± 0.31	± 0.021	± 0.4	± 0.0044	± 0.020	± 0.046	± 342.24	± 141.5
		7.2	4.0	0.22	0.8	3.7	*	*	0.7	1.9	2.25	*	0.026	0.53	0.016	0.6	0.0013	0.058	0.027	389.28	86.1
	Cake fillings	± 0.8	± 1	± 0.10	± 0.1	± 0.8	*	*	± 0.1	± 0.9	± 0.49	*	± 0.015	± 0.22	± 0.010	± 0.2	± 0.0001	± 0.022	± 0.033	± 207.75	± 7.1
* < LOQ (limit of quantification)	Fresh fruit	0.3	1.0	0.02	0.1	1.0	0.012	0.13	0.3	0.4	0.02	0.012	0.002	0.05	0.002	0.2	0.0011	0.012	0.004	0.02	7.0
		± 0.3	± 1.0	± 0.02	± 0.1	± 1.0	± 0.012	± 0.13	± 0.3	± 0.4	± 0.02	± 0.012	± 0.002	± 0.05	± 0.002	± 0.2	± 0.0011	± 0.012	± 0.004	± 0.02	± 7.0
	Cake fillings	0.3	1.0	0.02	0.1	1.0	0.012	0.13	0.3	0.4	0.02	0.012	0.002	0.05	0.002	0.2	0.0011	0.012	0.004	0.02	7.0

The concentration values are reported as mean $\pm$ standard deviation (SD)

n.a. not analyzed

no data were found in the literature. For the pear cake fillings, B (2.1 µg/g), Rb (1.6 µg/g), Zn (1.2 µg/g), Cu (0.67 µg/g), Sr (0.54 µg/g), Mn (0.41 µg/g), Ba (0.24 µg/g), and Cs (0.005 µg/g) presented concentrations lower than those found in the fruit samples. The Pb and La, although present in pear fruit, were below the quantification of pear cake fillings (LOQ; Pb < 0.012 µg/g; La < 0.002 µg/g). These results show that the processing had a negligible contribution to the concentration of these elements in the pear cake fillings. However, Fe (3.9 µg/g), Al (3.1 µg/g), Ni (0.15 µg/g), Cr (0.14 µg/g), Co (0.015 µg/g), Cd (0.014 µg/g), Tl (0.014 µg/g) and Ce (0.011 µg/g) showed values similar to those of pears fruit. As seen for apples fruit, the presence of Al was probably due to the water used in the process, similarly for the Cr [40, 41]. Tl could arise from different sources, natural or anthropogenic, including the acid treatments to obtain the pectin used as ingredient [42–44].

Comparing the concentration of elements in apple and pear fruit (Table S2), it can be stated that apples had significantly higher ($p < 0.05$) content of Cs (17-fold higher) and La (1.5-fold higher) than pears, and B and Cr were 2-fold higher than pears. On the other hand, the elements Fe, Cu, Zn, Rb, Ba, Sr, Tl, and Mg presented significantly lower values ($p < 0.05$) in apple samples, on average ranging from 1.5 to 4-fold than pears and Co, Ni, and Cd were below the limit of quantification in apple samples. Relatively to the cake fillings (Table S2), the content of B, Mn, and Cs, with high ($p < 0.05$) concentration in apple samples, and Tl, with high concentration ($p < 0.05$) in pears samples, in accordance with the respective fruit samples, can be indicators of fruit composition. The lower number of elements that are able to discriminate the pear cake fillings when compared with the fruit can be due to the raw materials of apple origin that are used for the preparation of this commodity. In fact, the negative charges of carboxyl groups in pectin, which are not fully methylesterified, are able to complex with positively charged ions, preferentially the divalent cations [45, 46].

To correlate the concentration of the elements with the two fruit species, including the derived cake fillings, a principal component analysis (PCA) was carried out with the 18 micro and trace elements (Fig. 1). The PCA scores plot (Fig. 1a) showed that samples were discriminated mainly by species independently of the product. PC1, representing 25.1% of total variance, placed samples containing apples in PC1 negative and those containing pears in PC1 positive. Nevertheless, PC2, representing 17.8% of total variance, also separated the cake fillings. The scores plot formed four clusters, one in each quadrant, showing that 42.9% of variance was enough to separate them. The samples containing apples were distinguished by seven elements (B, La, Cs, Pb, Ce, Cr, and Al) (Fig. 1b). The samples containing pears were discriminated by 11 elements (Rb, Mn, Ba, Cu,

Zn, Ni, Co, Tl, Cd, Sr, and Fe). Genetic factors shape tree's nutrient efficiency and their soil adaptability [47, 48]. Apple trees typically have fibrous root systems, while pear trees have deeper taproot-oriented systems, leading the roots to different soil zones for nutrient access. Elements like Al, Fe, Mg, and P are the most abundant in the earth crust [49, 50], whereas P, Mg, B, and Rb are the most abundant in both fruit (Tables 1, 2). These results are in accordance with the accumulation of P, Mg, and B, elements essential for the development of plants, contrary to Al, not a constituent, and Fe, a constituent but in lower levels than those present in earth crust. The accumulation of Rb seems to be related to the soil composition at a local level. The uptake of elements may also be distinguished from apple and pear fruit by their root length and surface density. The root length density reported for apple tree is 0.01–0.20 cm root/cm³ soil, with a surface density of 0.8–23.8 cm root/cm², lower than the root length density (0.12–0.56 cm root/cm³) and root surface density (7–69 cm root/cm²) reported for pear trees (Jackson, 2003). These differences also extend to their transporter proteins and ion channels specificity, enabling apple trees to have higher affinity for boron [51, 52]. Also, variations in rhizosphere interactions are described as apple trees releasing more organic acids to mobilize minerals than pear trees [51, 53, 54].

Although the mineral content is driven by species independently of their geographic origin, it is hypothesized that fruit elements concentration can be diagnostic of geographic origin, independently of their presentation form as raw or processed as cake fillings.

Identification of geographic origin of apple samples based on minerals contents

The multielement analysis by ICP–MS of apple fruit samples and derived cake fillings allowed to quantify 17 elements. The elements Co, Ni, and Cd were below the LOQ in all apple samples (fruit and cake fillings) and not considered for statistical analyses. Since P and Mg are the major elements and considered as macro elements, these were removed from the dataset and not considered for statistical analyses. The 15 elements used for statistical analyses were B, Al, Cr Mn, Fe, Cu, Zn, Rb, Cs, Ba, La, Sr, Tl, Pb, and Ce.

To identify the marker elements related to the geographical origin of apple samples, a PCA was carried out with the 15 micro and trace elements. A total of 25 apple fruit samples and respective apple cake fillings ($n=12$) from 3 regions were used (Fig. 2). The PCA scores plot (Fig. 2a) showed that apple samples were separated mainly by processing. PC1, representing 33.4% of total variance, placed mostly apple fruit in PC1 positive and their respective apple cake fillings in PC1 negative. The loadings plot shows that

Table 2 Mineral composition ($\mu\text{g/g}$, average $\pm$ standard deviation) of pear (fruit and cake fillings) by orchard origin, expressed by dry weight The concentration values are reported as mean $\pm$ standard deviation (SD)

Origin	Type	B	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Rb	Cd	Cs	Ba	La	Sr	Tl	Pb	Ce	P	Mg
PDO Oeste	Fresh fruit	12.5 $\pm$ 4.9	3.9 $\pm$ 1.6	0.17 $\pm$ 0.06	3.1 $\pm$ 1.3	9.8 $\pm$ 3.1	0.049 $\pm$ 0.030	0.51 $\pm$ 0.21	5.9 $\pm$ 2.1	8.8 $\pm$ 2.5	14.01 $\pm$ 7.06	0.023 $\pm$ 0.015	0.020 $\pm$ 0.016	1.32 $\pm$ 0.71	0.012 $\pm$ 0.011	1.0 $\pm$ 0.4	0.0146 $\pm$ 0.0107	0.025 $\pm$ 0.016	0.021 $\pm$ 0.014	649.44 $\pm$ 330.27	591.8 $\pm$ 154.1
	Cake fillings	1.8 $\pm$ 0.1	2.5 $\pm$ 0.4	0.13 $\pm$ 0.03	0.4 $\pm$ 0.1	3.7 $\pm$ 1.2	0.016 $\pm$ 0.003	0.15 $\pm$ 0.03	0.7 $\pm$ 0.1	1.2 $\pm$ 0.2	1.83 $\pm$ 0.23	0.014 $\pm$ 0.001	0.005 $\pm$ 0.001	0.24 $\pm$ 0.04	*	0.5 $\pm$ 0.1	0.0136 $\pm$ 0.0002	*	0.008 $\pm$ 0.003	95.64 $\pm$ 5.85	83.2 $\pm$ 9.6
Alandroal	Fresh fruit	19.0 $\pm$ 1.8	3.4 $\pm$ 0.9	0.14 $\pm$ 0.02	1.8 $\pm$ 0.2	9.8 $\pm$ 2.0	0.066 $\pm$ 0.012	0.40 $\pm$ 0.05	3.9 $\pm$ 0.7	6.2 $\pm$ 0.4	7.89 $\pm$ 0.59	0.017 $\pm$ 0.003	0.016 $\pm$ 0.003	1.49 $\pm$ 0.23	0.005 $\pm$ 0.002	2.2 $\pm$ 0.7	0.0162 $\pm$ 0.0008	0.018 $\pm$ 0.002	0.014 $\pm$ 0.003	971.14 $\pm$ 300.07	621.5 $\pm$ 139.1
	Cake fillings	2.8 $\pm$ 0.8	4.7 $\pm$ 3.1	0.17 $\pm$ 0.04	0.4 $\pm$ 0.2	4.3 $\pm$ 0.6	0.015 $\pm$ 0.001	*	0.7 $\pm$ 0.1	1.2 $\pm$ 0.1	1.03 $\pm$ 0.04	0.014 $\pm$ 0.001	0.004 $\pm$ 0.001	0.26 $\pm$ 0.03	*	0.6 $\pm$ 0.1	0.0139 $\pm$ 0.0001	*	0.020 $\pm$ 0.002	101.83 $\pm$ 3.11	105.6 $\pm$ 5.9
Aveiro	Fresh fruit	13.0 $\pm$ 1.2	3.2 $\pm$ 0.3	0.09 $\pm$ 0.01	1.3 $\pm$ 0.3	7.0 $\pm$ 1.5	0.015 $\pm$ 0.001	0.32 $\pm$ 0.15	4.1 $\pm$ 1.7	5.1 $\pm$ 1.2	38.07 $\pm$ 6.39	0.014 $\pm$ 0.001	0.080 $\pm$ 0.009	0.65 $\pm$ 0.24	0.018 $\pm$ 0.017	1.1 $\pm$ 0.2	0.0140 $\pm$ 0.0007	0.034 $\pm$ 0.007	0.045 $\pm$ 0.048	988.12 $\pm$ 173.97	275.4 $\pm$ 51.2
	Fresh fruit	9.3 $\pm$ 2.3	3.0 $\pm$ 1.0	0.08 $\pm$ 0.02	0.9 $\pm$ 0.2	5.3 $\pm$ 0.6	0.027 $\pm$ 0.006	0.52 $\pm$ 0.19	5.0 $\pm$ 0.9	8.4 $\pm$ 1.9	10.26 $\pm$ 3.19	0.014 $\pm$ 0.001	0.028 $\pm$ 0.010	1.29 $\pm$ 0.78	0.017 $\pm$ 0.017	0.6 $\pm$ 0.3	0.0138 $\pm$ 0.0008	0.112 $\pm$ 0.055	0.032 $\pm$ 0.031	712.29 $\pm$ 98.90	278.5 $\pm$ 44.4
Fundão	Fresh fruit	9.9 $\pm$ 0.7	5.5 $\pm$ 2.7	0.07 $\pm$ 0.01	1.8 $\pm$ 0.7	14.2 $\pm$ 4.2	0.036 $\pm$ 0.009	0.23 $\pm$ 0.05	3.9 $\pm$ 0.5	8.1 $\pm$ 5.9	9.53 $\pm$ 1.89	0.020 $\pm$ 0.004	0.017 $\pm$ 0.003	2.14 $\pm$ 0.69	0.029 $\pm$ 0.006	3.4 $\pm$ 1.2	0.0144 $\pm$ 0.0005	0.032 $\pm$ 0.00	0.074 $\pm$ 0.024	761.82 $\pm$ 78.12	421.6 $\pm$ 53.9
	Total of pear fruit	12.6 $\pm$ 4.7	3.9 $\pm$ 1.6	0.16 $\pm$ 0.07	2.8 $\pm$ 1.3	9.6 $\pm$ 3.3	0.047 $\pm$ 0.029	0.49 $\pm$ 0.21	5.6 $\pm$ 2.1	8.4 $\pm$ 2.7	14.45 $\pm$ 8.51	0.022 $\pm$ 0.014	0.023 $\pm$ 0.020	1.34 $\pm$ 0.72	0.013 $\pm$ 0.012	1.1 $\pm$ 0.7	0.0146 $\pm$ 0.0096	0.029 $\pm$ 0.026	0.025 $\pm$ 0.021	687.43 $\pm$ 321.52	536.8 $\pm$ 178.5
Total of pear cake fillings		2.1 $\pm$ 0.5	3.1 $\pm$ 1.8	0.14 $\pm$ 0.04	0.4 $\pm$ 0.1	3.9 $\pm$ 1.1	0.016 $\pm$ 0.002	0.15 $\pm$ 0.03	0.7 $\pm$ 0.1	1.2 $\pm$ 0.2	1.63 $\pm$ 0.41	0.014 $\pm$ 0.001	0.005 $\pm$ 0.001	0.24 $\pm$ 0.04	*	0.5 $\pm$ 0.1	0.0137 $\pm$ 0.0002	*	0.011 $\pm$ 0.006	97.19 $\pm$ 5.88	88.8 $\pm$ 13.2
	* < LOQ (limit of quantification)	0.3	1.0	0.02	0.1	1.0	0.012	0.13	0.3	0.4	0.02	0.012	0.002	0.05	0.002	0.2	0.0011	0.012	0.004	0.02	7.0

The concentration values are reported as mean $\pm$ standard deviation (SD)

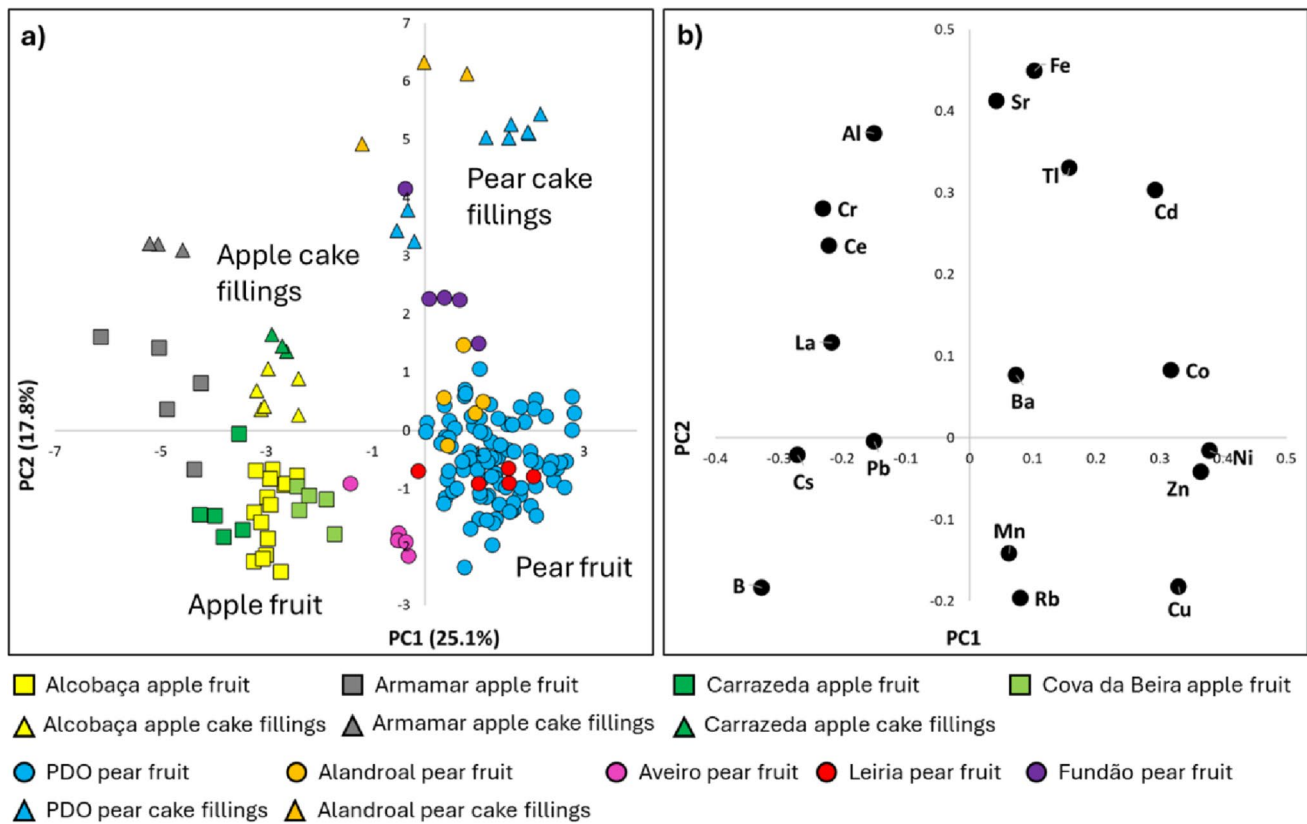


Fig. 1 Principal component analysis (PCA) using the data of the 18 elements analysed from 30 apple fruit samples, 12 apple cake fillings, 110 pear fruit samples, and 12 pear cake fillings. **a** Scores plot of PCA

(PC1 vs. PC2); **b** loadings plot of PCA (PC1 vs. PC2) of the 18 elements described in Tables S4, 5, 8 and 9

apple cake fillings samples were positively separated from apple fruit samples by 6 elements: Fe, Sr, Ba, Al, Pb, and Zn (Fig. 2b), showing that these elements can be influenced by processing. An internal cross-validation was performed by a PLS-DA (Fig. 2c and d, and Table S3), strengthening the separation of samples, confirming that these 6 elements are discriminated by the processing, now in Component 2 (28.3% of covariance). Q^2 increased up to 3 components ($Q^2 = 0.889$) and decreased thereafter. Although R^2 continued to increase with additional components (up to 0.956), Q^2 declined, indicating that additional components did not improve predictive ability and would likely introduce overfitting. Therefore, the 3-component model was considered optimal (Table S3). Aiming to find geographical origin markers independently of processing, a new matrix was built without these 6 elements.

A new PCA was carried out with 9 elements (Ti, Cr, Ce, La, Rb, Cs, Cu, Mn, and B) (Fig. 3). PC1, representing 38.7%, and PC2, representing 21.2% of total variance, separated the PGI apple samples (fruit and cake fillings) from Alcobaça area in PC1 positive, from the apple samples in PC1 negative from Armamar and Carrazeda de Ansiães (Fig. 3a). The loadings plot showed that PGI apple samples (Alcobaça) were mainly distinguished by Ti, Mn, and B,

the samples from Armamar by Rb, Cs, Ce, and La and the samples from Carrazeda de Ansiães by Cu and Cr (Fig. 3b). The PLS-DA plots (Fig. 3c, d) and the internal cross-validation parameters (Table S3) showed the same separation, reinforcing the hypothesis that the 9 elements (Ti, Cr, Ce, La, Rb, Cs, Cu, Mn, and B) can discriminate the different regions. For the model including 9 elements, Q^2 reached its maximum at 3 components ($Q^2 = 0.901$), remained stable, and then slightly decreased. This pattern indicates improved model stability and predictive performance compared with the full model. The fact that Q^2 does not increase monotonically with R^2 , but instead shows a clear maximum followed by a decline, suggests that the model complexity was appropriately controlled and that overfitting was avoided (Table S3).

To further assess robustness of the 9-variable model, it was compared with the full 15-variable one. It showed better predictive performance, with a maximum Q^2 of 0.901 (3 components), compared with 0.889 for the full model. Although the 15-variable model presented slightly higher R^2 values, reflecting a better model fit, the Q^2 of the 9-variable model showed higher predictive ability under cross-validation. Therefore, Q^2 instead of R^2 , was used as the main criterion for model selection. In addition, the 9-variable model

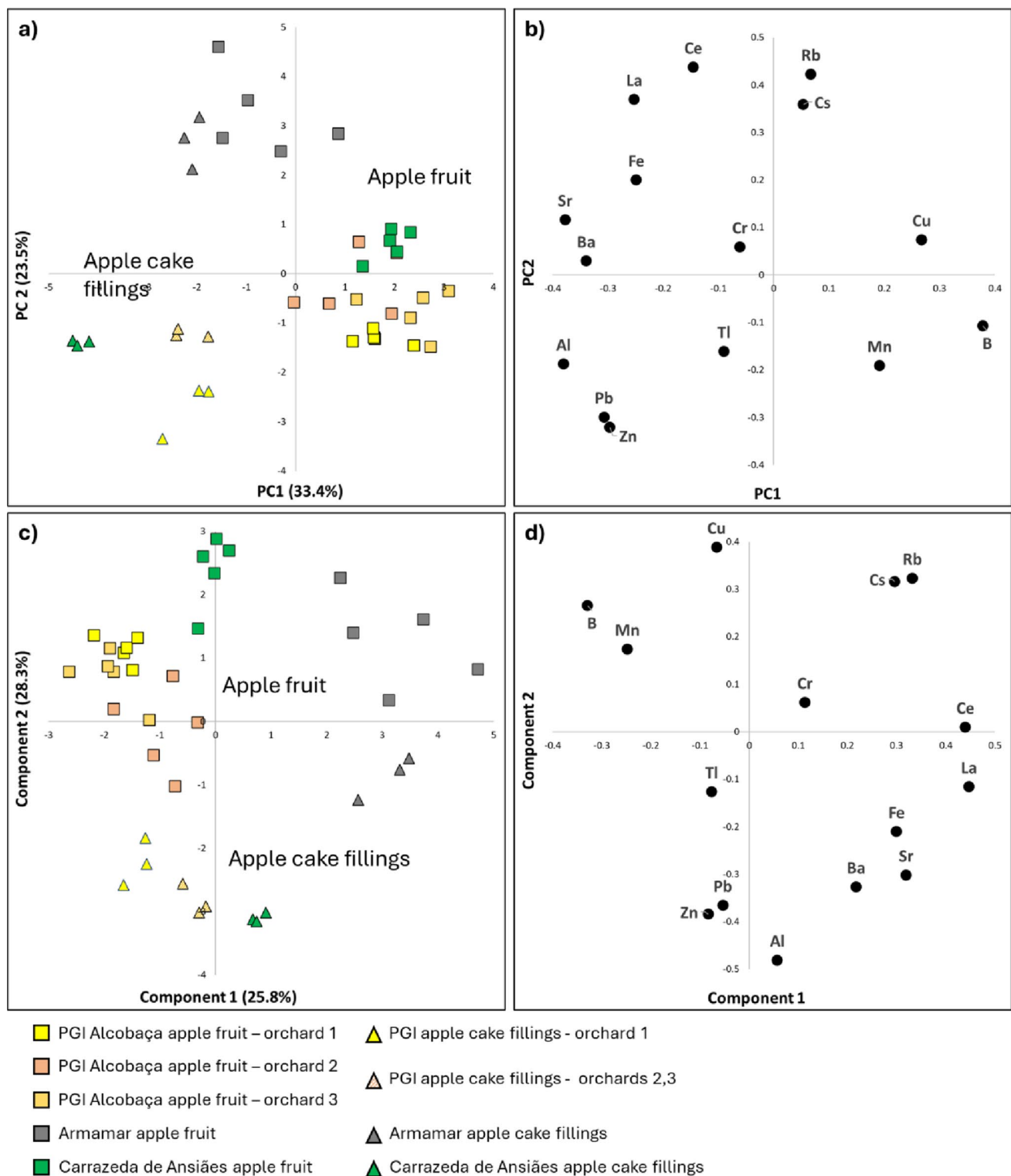


Fig. 2 Principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA) using the data of the 15 elements analyzed from 25 apple fruit samples and 12 apple cake fillings. **a** Scores plot of PCA (PC1 vs. PC2); **b** loadings plot of PCA (PC1 vs. PC2);

c scores plot of PLS-DA (Component 1 vs. Component 2); **d** loadings plot of PLS-DA (Component 1 vs. Component 2) of the elements described in Tables S4 and S5

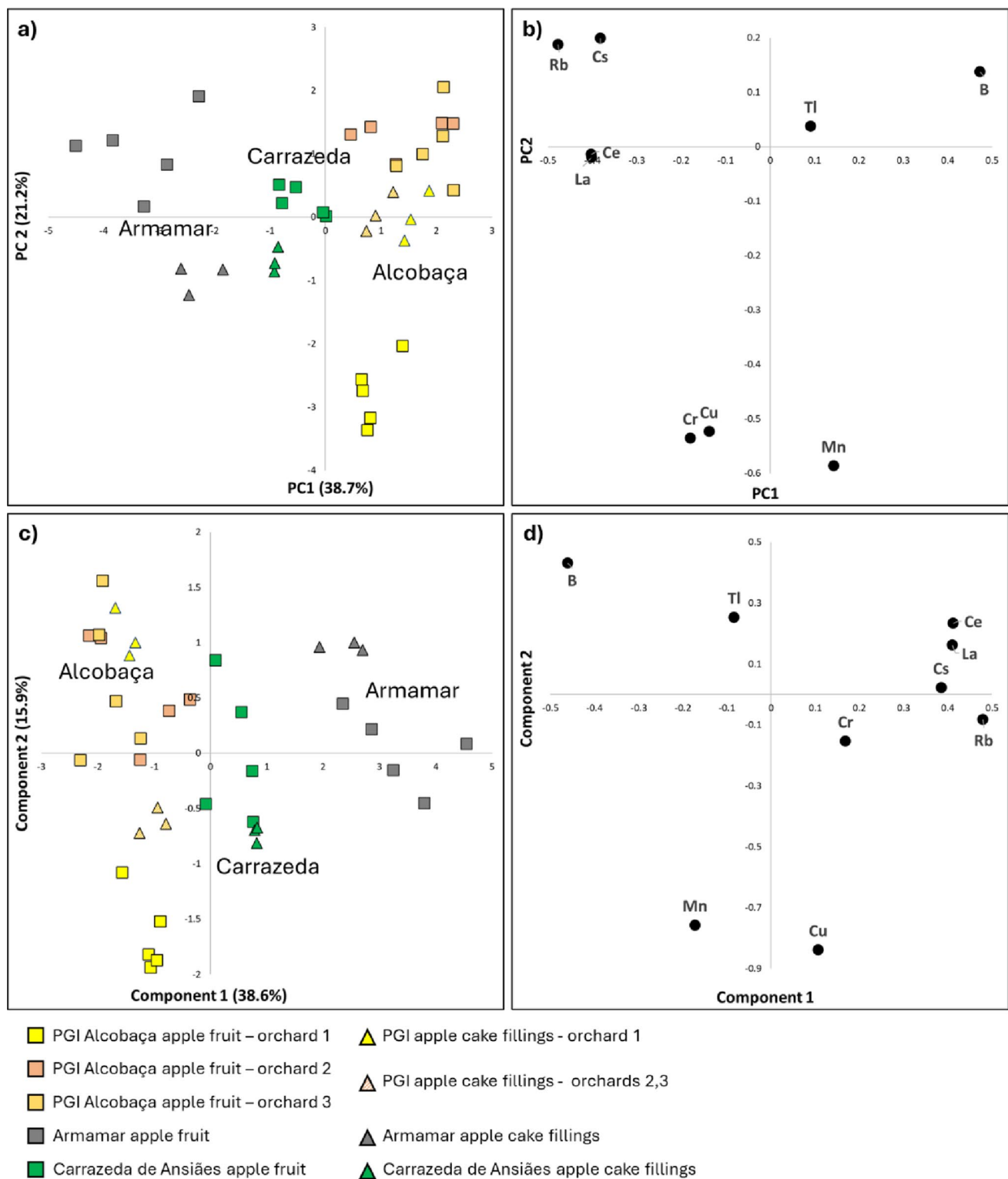


Fig. 3 Principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA) using the data of the 9 elements analyzed from 25 apple samples and 12 apple cake fillings. **a** Scores plot of PCA (PC1 vs. PC2); **b** loadings plot of PCA (PC1 vs. PC2); **c** scores

plot of PLS-DA (Component 1 vs. Component 2); **d** loadings plot of PLS-DA (Component 1 vs. Component 2) of the elements described in Tables S4 and S5

provides a more favorable samples-to-variables ratio (37/9 vs. 37/15), minimizing the risk of overfitting and improving model generalizability.

To further assess the risk of overfitting, permutation tests were performed with 1000 permutations. Using prediction accuracy as the test statistic, the empirical p -value was < 0.001 (0/1000 permutations), indicating the suitability of the 9-variable model. Consistent results were obtained when using between/within (B/W) separation distance ($p = 0.001$), separating the classes from the null distribution, demonstrating that the discrimination was not due to random chance (Figure S1). This result, together with the cross-validated Q^2 optimization and the improved samples-to-variables ratio in the 9-variable model, provides statistical evidence of model robustness and low overfitting risk. Alcobaca area is described by its calcareous soils with high clay content and moderate to high mineral availability [5, 31, 55]. These soils often contain high levels of boron and manganese due to the geological composition modulated by its coastal influence. It is possible that these elements have an uptake by the tree, accumulating in the fruit. Boron is essential for plant cell wall development and growth [56], complexing type II rhamnogalacturonan in middle lamella to form dimeric structures [51, 57]. Manganese is a cofactor involved in photosynthesis, where a multinuclear center with several Mn ions split the water in photosystem II complex, providing electrons to the electron transport chain in the chloroplasts, with the consequent release of molecular oxygen from water [58]. Manganese also involved enzymes such superoxide dismutase, and oxalate oxidase [59]. Thallium, on the other hand, is naturally present or even slightly enriched due to industrial activity, agricultural practices, or environmental deposition, especially in areas with mixed geological materials [60, 61].

The Armamar area is characterized by the predominance of slightly crystalline schists, corresponding to impermeable terrains which are, in part, highly metamorphosed (gneisses, mica, schists), and zones of granitic soils [62]. Schist-rich soils, along with Armamar's specific microclimate, seems to promote the uptake of alkali metals like rubidium and cesium, similarly to potassium [30–33]. La and Ce are two of the most abundant rare earth elements and are primarily found in soils derived from sedimentary and magmatic rocks such as granitic soils. In the environment, La and Ce has been reported to accumulate in soils through natural geological processes and anthropogenic activities such as mining, characteristic of Armamar region due to the former extraction of wolfram. La and Ce are rare earth elements that have been found to influence plant growth and development. Their impact on fruits seems to be particularly linked to their involvement in nutrient absorption, stress resistance,

and metabolic regulation. Further studies are needed to optimize their application in agriculture [63, 64].

Carrazeda de Ansiães soils are rich in metamorphic rocks and mineralized areas, where elements like chromium and copper are often more concentrated. These soils are typically well-drained, with abundant organic matter, and may contain trace amounts of metals like Cr and Cu due to the region's mineral-rich geology [31, 65–68]. Copper is commonly used in agriculture, especially in orchards, as a fungicide [61]. This region contains mines that also extracted chromium. The natural mineral content in these soils can make Cr more available for uptake by plants. Though not required by plants, trace amounts of Cr can still be absorbed and incorporated into fruit tissues, possibly marking it as a characteristic of apples from this region [30, 32, 33, 65].

To reinforce the assessment of the 9 elements (Tl, Cr, Ce, La, Rb, Cs, Cu, Mn, and B) selected as geographical markers, a new PLS-DA was carried out including in the data set apple fruit samples from another non-PGI region (Cova da Beira). The PLS-DA, constructed with 30 apple fruit and 12 apple cake fillings, showed a scores plot formed by four clusters when the first two components explained 48% of the variance, allowing to discriminate the samples from these 4 different regions. Q^2 increased up to 3 components ($Q^2 = 0.752$) and decreased thereafter and accuracy of 86%. Although R^2 continued to increase with additional components (up to 0.834), Q^2 declined, indicating that additional components did not improve predictive ability and would likely introduce overfitting. The 3-component model was considered optimal. This result showed that model was robust and had low overfitting risk (Figures S2 and S3, and Table S6).

Identification of geographic origin of pear samples based on minerals contents

To verify if the multielement analysis is also able to identify the origin of pear, fruit and derived cake fillings from distinct origins were analyzed. Pear fruit from five localities within a PDO region (Caldas da Rainha, Lourinhã, Cadaval, Rio Maior, and Bombarral) and pears out of the PDO (Alandroal), and their respective cake fillings, were used to identify the geographic origin of pear-derived products based on their component elements. The PCA carried out with the 18 micro and trace elements (B, Al, Cr Mn, Fe, Cu, Zn, Rb, Cs, Ba, La, Sr, Tl, Pb, Co, Ni, Cd, and Ce). The PCA separated in PC1 (28.7% of variability) the pear fruit samples (PC1 negative) from the pear cake filling samples, placed in PC1 positive (Fig. 4a). The loadings plot showed that the pear cake filling samples were positively distinguished from the unprocessed fruit by Fe, Cd, Ce, Al, Sr, Cr, and Tl (Fig. 4b). Due to the class imbalance in the dataset, both in fruit (95

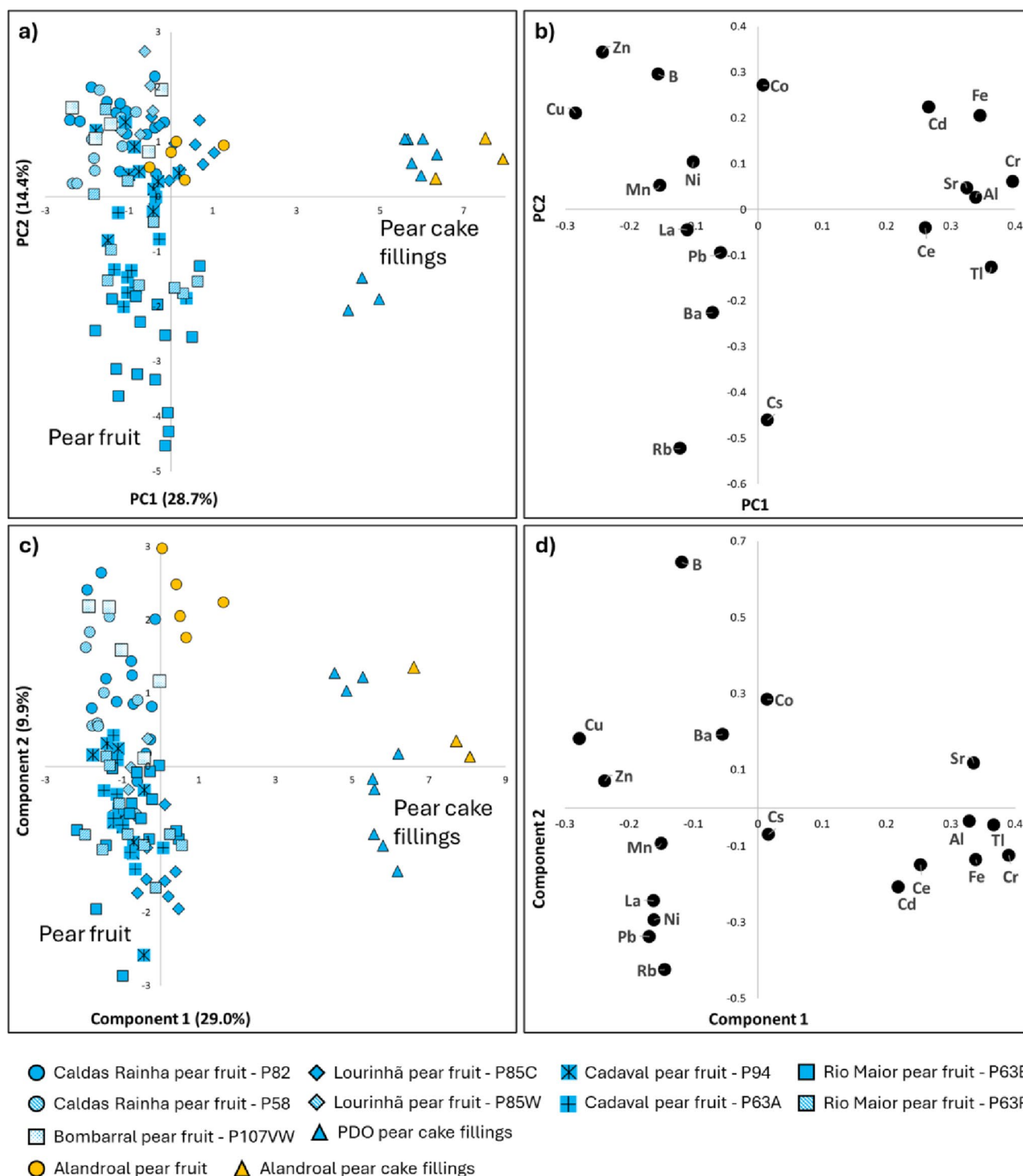


Fig. 4 Principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA) using the data of the 18 elements analyzed from 95 pear fruit samples and 12 pear cake fillings. **a** Scores plot of PCA (PC1 vs. PC2); **b** loadings plot of PCA (PC1 vs. PC2);

c scores plot of PLS-DA (Component 1 vs. Component 2); **d** loadings plot of PLS-DA (Component 1 vs. Component 2) of the elements described in Tables S8 and S9

pear samples) versus cake-fillings (12 cake-filling samples) and origin (99 PDO samples and 8 non-PDO samples), cross-validation and permutation testing were used to evaluate the existence of potential bias and robustness of the classification model. The internal cross-validation performed by a PLS-DA (Fig. 4c and d, and Table S7) showed that these 7 elements are discriminated by the processing. Q^2 increased up to 2 components ($Q^2 = 0.901$) and decreased thereafter, although R^2 continued to increase with additional components (up to 0.936). Therefore, the 2-component model was considered optimal (Table S7). The permutation tests ($n=1000$) showed empirical p -values <0.001 for prediction accuracy, indicating that the observed classification performance is significantly better than that expected by chance (Figure S3). Considering the separation distance test (B/W), the $p=0.837$ showed that the distance between the classes is only slightly higher than the distance within each class. This may be explained by the high number of PDO pear samples used in the dataset, resulting in a high spatial dispersion of samples when compared with the spatially concentrated non-PDO samples. This may be consequence of the unbalanced number of pear samples used in the dataset, not observed in the apple samples.

Elements such as Fe, Al, and Sr were in common with apple cake fillings process, showing that the processing apple and pear result in accumulation of different elements due to the use of different raw materials. As the processing seems to increase the concentration of all these seven elements, to find fruit geographical origin markers independently of processing, a new matrix was built without them.

The score plots of the PCA carried out with 11 elements (Zn, B, La, Ba, Cu, Co, Pb, Cs, Mn, Ni, and Rb) formed two distinct clusters, with 42.7% of variance. The pear samples (fruit and cake fillings) from PDO area were placed mainly in PC2 positive (17.7%) whereas those of Alandroal were placed in PC1 and PC2 negative (Fig. 5a). The loadings plot showed that the pear samples from Alandroal were mainly distinguished by Co, Ba, and B, and the PDO pear samples by Zn, La, Cu, Pb, Cs, Mn, Ni, and Rb (Fig. 5b). The PLS-DA plots (Fig. 5c, d) and the internal cross-validation parameters (Table S7) showed the same separation, reinforcing the hypothesis that the 11 elements (Zn, La, Cu, Pb, Cs, Mn, Ni, Rb, Co, Ba, and B) can discriminate these different regions. In this case, the model with 11 elements produced a prediction accuracy of 94%, suggesting that the classification result is not driven by a single variable configuration and that the selected elemental markers are stable. To further evaluate the robustness of the models and the potential risk of overfitting, permutation tests ($n=1000$) were performed by randomly shuffling class labels and recalculating model performance. The empirical p -values obtained for prediction accuracy were <0.001 , indicating that the observed

classification performance is better than that expected by chance (Figure S3). The separation distance test (B/W) with $p=0.987$ showed the same that the model training with 18 elements.

Both PDO region and Alandroal have predominantly alkaline and calcareous soils with high mineral content. However, Alandroal is closed to abandoned mines containing Co, which can be uptaken by plants [31, 56, 69, 70]. In addition, alkaline and calcareous soils can also be relatively rich in boron. Boron levels are often more stable in soils with lower organic matter and adequate drainage [60, 71], which is reported to be common in the Alandroal. The PDO region possesses diverse soil types, including clay-loam and sedimentary soils, which are typically high in trace metals such as Zn, Cu, and Mn. These soils have been reported to derive from both marine sedimentary rock and volcanic deposits, which may introduce trace elements like La and Ni into the soil [31, 56, 66, 67]. Trace elements such as Pb can occasionally result from industrial activities or pollution, which may influence areas with high agricultural activity in urbanized and industrial zones [67, 68, 72]. As these soils seem to be rich in potassium, the uptake of Rb and Cs, which are of the same group of the periodic table of elements, may justify their increased presence in pears from this region [66]. Ba and La are trace elements that can naturally occur in soils with marine and volcanic sedimentary deposits [60] as seem to be those of PDO region.

To reinforce the assessment of the robustness of the 11 elements (Zn, B, La, Ba, Cu, Co, Pb, Cs, Mn, Ni, and Rb) selected as geographical, a new PLS-DA was carried out including in the data set pear fruit samples from other 3 non-PDO regions (Aveiro, Leiria, and Fundão). The PLS-DA, constructed with 110 pear fruit samples and 12 apple cake fillings, showed a score plots formed by three clusters when the first two components explained 39% of the variance, allowing to discriminate the pear samples (fruit and cake filling) from PDO region from all non PDO pear samples. Q^2 increased up to 4 components ($Q^2 = 0.370$) and accuracy of 85%. Although R^2 continued to increase with additional components (up to 0.472), Q^2 declined, indicating that additional components did not improve predictive ability. The 4-component model was considered optimal. For prediction accuracy, the empirical p -value obtained was <0.001 , indicating that the observed classification performance is significantly better than that expected by chance (Figures S4 and S5, and Table S10). The separation distance test (B/W) with $p=0.809$ showed the same result as the model training with 18 elements.

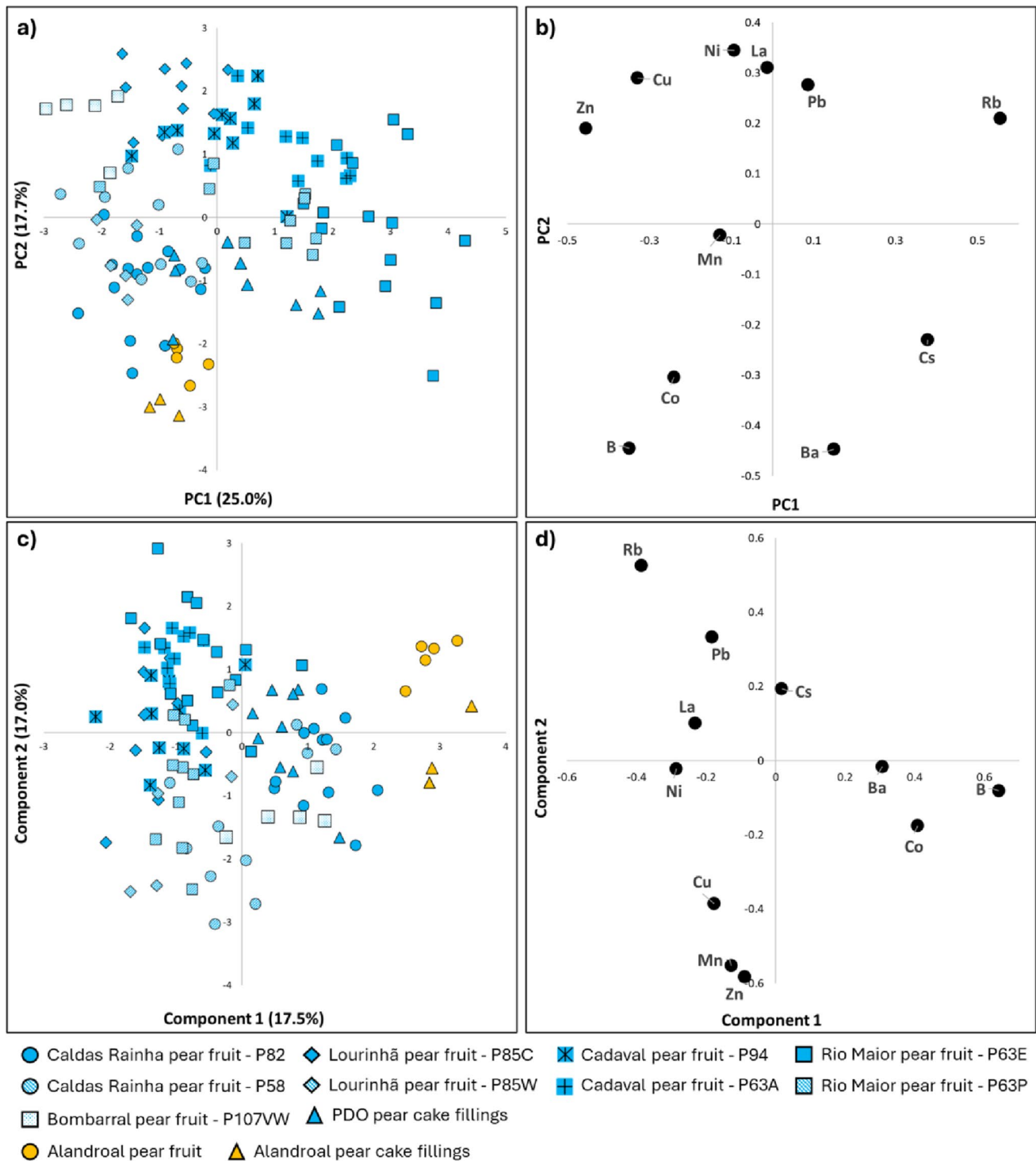


Fig. 5 Principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA) using the data of the 11 elements analyzed from 95 pear samples and 12 pear cake fillings. **a** Scores plot of PCA (PC1 vs. PC2); **b** loadings plot of PCA (PC1 vs. PC2); **c** scores

plot of PLS-DA (Component 1 vs. Component 2); **d** loadings plot of PLS-DA (Component 1 vs. Component 2) of the elements described in Tables S8 and S9.

Conclusion

This study demonstrated that the elements B, Tl, Mn, Rb, Cs, La, Ce, Cu, and Cr can be able to differentiate the different geographical origin of apple cake fillings, as their profile was not influenced by the production of the derived apple cake fillings. Similarly, for pear cake fillings, Zn, B, La, Ba, Cu, Co, Pb, Cs, Mn, Ni, and Rb, which were not affected by fruit processing, seem to be able to differentiate the geographical origin during pear cake fillings production. As these mineral markers remain detectable after processing, they can have potential for authenticity purposes and are a tool to contribute to the identification of the geographic provenance of fruit-derived products like cake fillings.

With this study, it was also possible to identify the distinctive elemental composition of apple and pear products that is independent of the geographical origins studied. In these regions, apple products were distinguished by the higher concentration of B, La, Cs, Pb, Ce, Cr, and Al, whereas pear products were distinguished by the higher concentration of Fe, Sr, Tl, Ba, Cu, Zn, Ni, Co, Cd, Mn, and Rb.

This research reinforces the usefulness of elemental analysis in food authenticity, particularly for processed fruit products labeled with Protected Geographical Indication (PGI) and Protected Designation of Origin (PDO) certifications.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00217-026-05142-4>.

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Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Ana M.S. Costa, Elisabete Coelho, Eugénio Soares, Eduarda Pereira, and Manuel A. Coimbra. The first draft of the manuscript was written by Ana M.S. Costa and all authors commented on previous versions of the manuscript. All authors discussed the results and commented on the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data availability The datasets generated and analysed during the current study are available on the manuscript and supplementary material.

Declarations

Conflict of interest All authors declare that they have no conflict of interest.

Consent to participate Not applicable. The manuscript does not report on or involve any animals, humans, human data, human tissue or plants.

Compliance with ethics requirements Not applicable. The study did not involve human participants or animal objects.

Human ethics declaration Not applicable.

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