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Origin Authentication of European and American Ash (*Fraxinus* spp.) Based on Stable Isotope Ratio and Elemental Characteristics Combined with Chemometrics Methods

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Abstract: The research into and applications of wood origin traceability technology are of great significance for promoting the standardization and legality of the global timber trade. This paper focuses on analyzing the content of ten mineral elements and the ratios of stable isotopes $\delta^{13}C$ and $\delta^{15}N$ in ash samples. Furthermore, multivariate statistical analysis was conducted to assess the clusters and differences in mineral elements, as well as $\delta^{13}C$ and $\delta^{15}N$, among the samples, for identifying the different factors used to trace the origin of ash imported from different regions. Through unsupervised clustering and supervised discriminant modeling, a highly accurate method for discriminant analysis was developed. The results reveal significant differences ($p < 0.05$) in the contents of Mg, Cu, and Sr, as well as $\delta^{15}N$, between European and American samples. Additionally, the normalized results of mineral elements and isotope ratios were then subjected to partial least squares–discriminant analysis (PLS-DA), resulting in the highest level of separation. This analysis achieved an overall accuracy of 96.2% in discriminating between samples of European and American ash. The chemometrics analysis method integrating stable isotope analysis with elemental analysis exhibited potential for discriminating between samples from European and American ash.

Keywords: wood identification; origin traceability; mineral elements; isotope ratios; chemometrics; *Fraxinus* spp.; ash

1. Introduction

Ash (*Fraxinus* spp.) is a type of commercial timber that is particularly popular for furniture, floors, and upscale building supplies [1]. China, as a significant consumer of timber, relies substantially on timber imports. The majority of ash imports come from America and Europe. In China, imported ash is classified into two types, namely, *Fraxinus americana* and *Fraxinus excelsior* [2]. Timbers of different species within the same genus often exhibit similar characteristics when observed with the naked eye or under a microscope, and ash is no exception. The mainstay of conventional identification methods is physical recognition, which relies on a mix of macroscopic and microscopic characteristics. These methods, however, can only be used to determine the genus of timbers [3,4]. According to prior research, the micro-characteristics of European and American ash exhibit variations only in a few parts, such as leaves and pollen [5,6]. However, there is a lack of research regarding the identification of species and origins of traded ash that is made up solely of the trunk.

The advancement of modern measuring techniques has facilitated the application of various analysis methods to the identification and origin traceability of plant products. These methods include gas chromatography–mass spectrometry (GC-MS), infrared spectroscopy (IR spectroscopy), high-performance liquid chromatography–mass spectrometry

(HPLC-MS), direct analysis in real time–time of flight mass spectrometry (DART-TOFMS), multi-element analysis, and stable isotope analysis [7,8]. Although infrared spectroscopy technology has the specific advantages of non-destructive testing and simple operability, the spectral region of the infrared spectrum has the disadvantages of wide spectral band, serious band overlap and low absorption intensity, and the results are easily affected by the external environment and testing conditions [4]. Based on the different metabolomic fingerprints of wood from different regions, chromatography, chromatography–mass spectrometry, and DART-TOFMS can be applied to develop wood origin traceability. The main issues that need to be investigated in the development of those techniques are to understand the reasons for differences in metabolomic fingerprints in wood from different locations, and how much of that difference can be attributed to environmental or genetic effects. In the test process, there are still some shortcomings, such as difficulties in identifying characteristic chemicals, and interference caused by overlapping adjacent chromatographic peaks affecting the detection results [4,9].

Plants exhibit isotopic fractionation due to the influence of climate, environment, and biological metabolism, resulting in varying isotopic abundances at different origins. This characteristic can be utilized for origin identification and traceability [10,11]. Isotope ratio mass spectrometry (IRMS) has been widely used in tracing the origin of agricultural and forestry products, such as grains, fruits, coffee, plant oils, and wines [12–17]. Additionally, the application of origin traceability for timber has also been investigated, as mentioned in previous studies [18–20]. The elemental characteristics of plants can indicate differences in their growth conditions, and analyzing the mineral elements in plant products from different origins can provide reliable geographical and fingerprinting data. Previous studies on wood origin traceability often used only a single chemical method, and the discrimination effect was not ideal. To enhance the accuracy of identification, researchers have recently been integrating stable isotope analysis with elemental analysis in specific agricultural domains [21–23]. However, limited research has been conducted on the origin traceability of timber. At present, in the process of the timber trade, there is a lack of effective technology for identifying and tracing the origins of ash wood in Europe and America. This paper proposes a novel approach that combines stable isotope analysis and elemental analysis with chemometrics methods, thereby developing a more efficient method for discriminating between European and American ash. The creativity of this study combines stable isotope and characteristic element analysis traceability techniques for application in the field of wood traceability, uses data fusion for chemometric analysis, and establishes the best discrimination method through model comparisons.

The use of DNA technology has also been reported in the field of wood species identification, and its main problems and difficulties are that the extraction of DNA from wood tissue is difficult compared to extracting DNA from fresh tissue cells, due to DNA degradation; further, the accuracy of individual sequences or even combinatorial sequences is not high, making it difficult to identify species with complex genomic information [24,25]. Our research group has also carried out some research on the use of DNA for wood identification, mainly encountering the above problems. Moreover, the DNA sequence difference between closely related species is too little to make accurate wood identifications. Therefore, this paper uses elemental analysis and isotopic techniques with higher feasibility in the study of the origin traceability of ash in Europe and America, without using DNA technology.

In the global timber trade, there are variations in the quality, price, and trade measures of timber across different countries and regions. This, along with the challenge of legally identifying endangered wood species, has increased the urgency for research and the application of technologies to identify and trace timber origins. As such, the objectives of this study are to (1) evaluate the differences in stable isotopes and elemental characteristics of European and American ash; (2) employ statistical analyses to identify variables that exhibit significant differences, and utilize chemometric modeling to trace the origins of samples from different regions; and (3) enhance the stability and accuracy of the origin

traceability of European and American ash by collecting samples at various time intervals. This study represents an innovative mode of exploration that can provide technical support for standardizing timber trade and ensuring the legality of timber protection, particularly for countries that import timber.

2. Materials and Methods

2.1. Samples

From 2021 to 2022, different batches of ash wood samples were collected from Ningbo Port (China) and Shenzhen Port (China), including 16 samples imported from America, and 10 samples imported from Europe.

2.2. Apparatus

An Inductively Coupled Plasma Mass Spectrometer (NexION 350X, Perkinelmer, Shelton, CT, USA), an Elemental Analyzer (Vario Isotope cube, Elementar, Hanau, Germany), an Isotope Ratio Mass Spectrometer (BiovisION, Elementar, Germany), an ultra-centrifugal mill (ZM 200, Retsch, Haan, Germany), a microwave digestion system (CEM Mars 5, CEM Corporation, Matthews, NC, USA), and an ultra-pure water system (Milli-Q, Millipore, Billerica, MA, USA) were used.

2.3. Reagents

All standard solutions of mineral elements (1000 µg/mL) and internal standard solutions (Sc, Ge, Y, In, and Tb, 100 µg/mL) used in mineral elements tests were purchased from the National Analysis and Testing Center for Nonferrous Metals and Electronic Materials (Beijing, China). Nitric acid (electronic grade) was purchased from Jiangsu Jingrui Co., Ltd. (Suzhou, China). International isotope standards B2155 (δ^{13}C = −26.98‰, δ15N = 5.94‰), USGS40 (δ^{13}C = −26.39‰, δ^{15}N = −4.52‰), USGS64 (δ^{13}C = −40.81‰), IAEA-CH-6 (δ^{13}C = −10.45‰) and IAEA-N-2 (δ^{15}N = 20.30‰) were purchased from Elemental Microanalysis Ltd. (Okehampton, UK), United States Geological Survey (Reston, VA, USA), and International Atomic Energy Agency (Vienna, Austria). Tin capsules were purchased from Elementar Analysensysteme GMBH (Hanau, Germany).

2.4. Experimental Methods

2.4.1. Determination of Mineral Elements

The wood samples were cut into small pieces with a saw, then made into powder with the mill. A precise amount of 0.2 g powder was weighed and put in the digestion vessel. Then, 5 mL of concentrated nitric acid was added into the vessel, and the vessel was immediately sealed with a lid. The vessel then was put into the microwave digestion system under the temperature control mode was initiated. After the end of the cool-down, the solution was filtered through a membrane filter with a pore size of 0.45 µm and then diluted to 200 mL with ultra-pure water. Finally, the elemental analysis was carried out via ICP-MS, and the results have been quantified using the internal standard method.

2.4.2. Determination of Stable Isotope Ratios δ^{13}C and δ^{15}N

Here, 3~5 g ash wood samples were taken into the mill, and ground into powder. The powder was sieved through a 0.25 mm standard metal sieve. The sieved samples were accurately weighed to 20 mg, wrapped in tin capsules, and placed in the sample tray of the elemental analyzer. The sample injection program for the element analyzer was set up, and the samples were injected in sequence. The temperatures of the oxidation furnace and reduction furnace in the elemental analyzer were 1150 °C and 850 °C, respectively. The carbon and nitrogen elements in the samples were converted into CO_2 and N_2, and then introduced into the stable isotope ratio mass spectrometer (IRMS) for the determination of δ^{13}C and δ^{15}N.

The isotope compositions are denoted in delta values versus international standards (Vienna-Pee Dee Belemnite (VPDB) for carbon; air for nitrogen). The formula for calculating the ratios of stable isotopes $\delta^{13}C$ and $\delta^{15}N$ is:

$$\delta = [(R_{sample}/R_{standard}) - 1] \times 1000 \qquad (1)$$

where R_{sample} is the ratio of ^{13}C abundance to ^{12}C abundance or ^{15}N abundance to ^{14}N abundance in the measured sample, and $R_{standard}$ is the ratio of heavy isotope to light isotope abundance in the standard sample.

2.5. Data Processing

SPSS 26.0 statistical software (IBM) was used to conduct independent sample T-test statistical analyses on the sample data, and variables with $p < 0.05$ were regarded as having significant differences. The statistical software SIMCA 14.1 (Umetrics) was used for the clustering and discriminant analysis of ash sample data from different regions. OmicStudio tool (https://www.omicstudio.cn/tool (accessed on 13 June 2023)) was used for multivariate statistical data analysis.

3. Results

Ten mineral elements were tested, including Mg, Al, Cr, Mn, Fe, Ni, Cu, Rb, Sr, and Ba. The content results of elements in ash from America and Europe are shown in Table 1. The experimental results show that the content of Mg is significantly higher than the contents of other elements tested, which are 118~349 mg/kg. The contents of Fe, Ni, Mn and Cu are lower than Mg and between 2 and 50 mg/kg. The contents of Cr and Rb are below 3 mg/kg. The demand for different metal elements varies among trees. In wood composition, mineral elements can be classified into essential elements, rare earth elements and other elements. Among the 10 elements studied in this article, Mg, Fe, Ni, Mn and Cu belong to the essential elements, and the other 5 elements belong to other elements [26]. Fe, Ni, Mn and Cu are often found as microelements related to wood growth, and Mg is present as a medium element. The results of this experiment also show that the distribution of the content of elements in ash wood conforms to this pattern.

The intricate process of mineral element accumulation in trees is impacted by a number of variables, including time, space, and human activity. However, it is closely linked to growth conditions and climate factors. Therefore, the content of mineral elements in timber may differ significantly depending on the origin. In this study, ten mineral elements were subjected to Mann–Whitney tests using SPSS to explore if there were any significant differences in the experimental data between samples of European and American ash, as shown in Table 1. $p < 0.05$ indicates a statistically significant difference between groups. The results of the significance analysis reveal that the significance levels of Mg, Cu, and Sr in the samples were all less than 0.05—specifically, 0.003, 0.004, and 0.006, respectively. This suggests that there are significant differences in the contents of Mg, Cu, and Sr in ash samples from the two origins. This study also conducted subsequent studies on some rare earth elements such as La, Ce, Pr and Nd, and found that the contents of these elements were relatively low, and there was no significant difference between European and American white ash wood. In the chemometric analyses, the importance of these four elements to the discriminant analysis was determined to also be small, so they were not included in this article. This study did not analyze all the elements in wood, so further research may be needed to identify if there are any differences in those elements.

Table 1. The mean values, standard deviation (SD), variable importance in projection (VIP) and Mann–Whitney test results of mineral element content and stable isotope ratios of ash samples from the two regions.

Elements/Isotope	America Mean	America SD	Europe Mean	Europe SD	VIP	*p* Value
Mg (mg kg^{-1})	187.00	45.40	264.50	54.40	1.74	0.003
Al (mg kg^{-1})	12.10	3.93	14.8	4.59	0.84	0.220
Cr (mg kg^{-1})	0.73	0.53	0.63	0.26	0.33	0.938
Mn (mg kg^{-1})	3.07	0.51	4.39	2.96	0.63	0.036
Fe (mg kg^{-1})	48.70	21.70	48.1	7.75	0.41	0.310
Ni (mg kg^{-1})	16.90	13.10	12.2	6.60	0.53	0.517
Cu (mg kg^{-1})	15.50	11.00	6.68	1.60	1.04	0.004
Rb (mg kg^{-1})	1.18	1.30	2.55	2.10	1.23	0.023
Sr (mg kg^{-1})	4.97	1.97	6.78	1.74	1.07	0.006
Ba (μg kg^{-1})	7.85	4.35	8.32	5.79	0.60	0.979
δ^{13}C (‰)	−24.40	0.48	−24.8	0.57	1.04	0.068
δ^{15}N (‰)	3.78	0.80	2.35	1.17	1.44	0.002

Additionally, an analysis of δ^{13}C and δ^{15}N values was performed on samples from European and American ash. The results were subjected to Mann–Whitney testing using SPSS to determine their significance, as shown in Table 1. The analysis of δ^{13}C values between samples from the two origins showed a significance level of 0.068. The significance level of δ^{15}N between the two groups of samples was determined to be 0.002, indicating an even more significant difference. The calculation of standard deviation (SD) revealed that the SD values of δ^{13}C in the American and European samples were 0.602 and 0.495 times that of δ^{15}N, respectively. This suggests that δ^{13}C, by contrast, has a smaller degree of dispersion. Furthermore, the relative standard deviation (RSD) values of δ^{13}C in the American and European samples were 1.99% and 2.32%, respectively. These values are lower than the RSD of mineral elements, indicating that δ^{13}C is the variable factor with the smallest dispersion degree in this study.

The δ^{13}C value reflects the balance between the supply and demand of CO_2 during photosynthesis. It is affected by various factors, including the isotope effect in photosynthesis, respiratory metabolism, the activities of the enzymes related to carbon metabolism, environmental temperature, changes in precipitation, differences in tree species, and habitat conditions [27–29]. The δ^{15}N value, by contrast, is influenced by nitrogen deposition in the atmosphere, climate conditions during timber growth, and nitrogen content in the soil [28]. The differences between the SDs of δ^{13}C and δ^{15}N, as shown in Table 1, also indicate that the fractionation effect of δ^{15}N in timber is more significant and more influenced by the factors mentioned above.

4. Discussion

4.1. Cluster Analysis Conducted on Testing Results

The results for ten mineral elements, as well as δ^{13}C and δ^{15}N, were processed using log$_{10}$ and Z-score measures. The results were then subjected to hierarchical cluster analysis (HCA) performed with the hclust function and the complete linkage method. The resulting heatmap, displayed in Figure 1A,B, reveals their patterns. Based on the data presented in Figure 1A, it is evident that the European samples exhibit a higher content of Rb compared to the American samples. Additionally, the European samples display lower contents of Ni, whereas the American samples show higher contents of Cu. However, there are no significant differences in the contents of Fe and Ba between the two groups of samples. Based on the cluster analysis, the samples from ash of different origins can be divided into two clusters. The majority of European samples can be found in the right cluster. However, there is some overlap between the samples with different origins. This indicates that the unsupervised clustering analysis may have lower discrimination accuracy compared to the supervised discriminant analysis, resulting in less effective separation. In Figure 1B, the

American samples with higher ratios of stable isotopes $\delta^{13}C$ and $\delta^{15}N$ are predominantly situated in the left cluster. The European samples with lower ratios of stable isotopes, by contrast, are primarily found in the right cluster. Nevertheless, there are a few samples with overlapping $\delta^{13}C$ values between the two clusters. Additionally, the distribution of $\delta^{15}N$ shows a higher level of aggregation compared to $\delta^{13}C$.
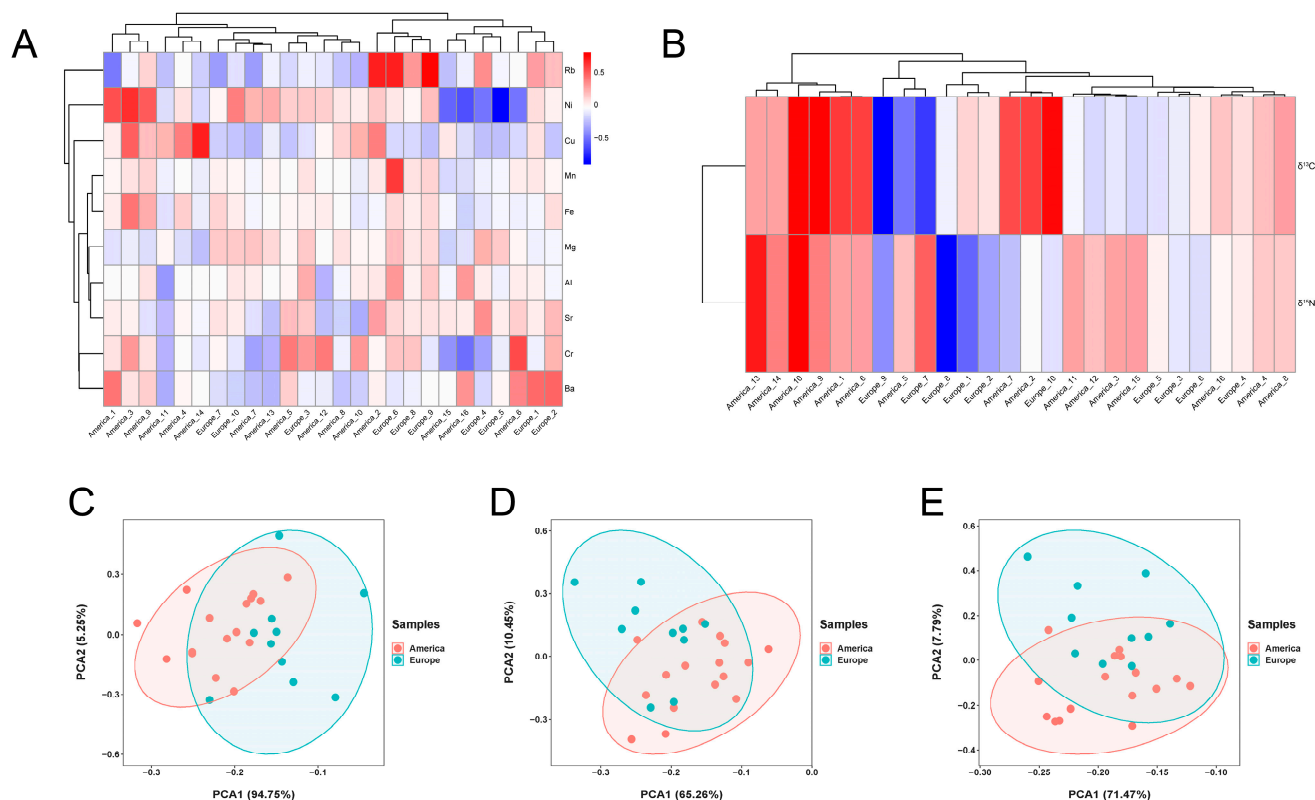

Figure 1. (**A**) Heatmap of elemental characteristics; (**B**) heatmap of isotope ratios; (**C**) PCA clustering plots based on isotope ratios; (**D**) PCA clustering plots based on elemental content; (**E**) PCA clustering plots based on data fusion.

Furthermore, principal component analysis (PCA) was performed on element content and isotope ratios after applying data normalization. The PCA results based on isotope ratios and element content are shown in Figure 1C,D, respectively. The PCA results using data fusion can be observed in Figure 1E. According to Figure 1C, PC1 and PC2 explain 100% of the total variance. However, the discriminative effect is not significant, possibly due to the limited inclusion of isotopes (carbon and nitrogen) in the data. Furthermore, subsequent PCA analyses using element content and data fusion did not yield satisfactory separation results. In PCA, Mn, Al, Rb, Sr and Mg mainly contributed to the isolation of European samples, while Ba, Fe, Cr, Ni, Cu, $\delta^{13}C$ and $\delta^{15}N$ are important variables for sample separation in the American samples. Partial least squares discrimination analysis (PLS-DA) is a supervised discriminant analysis method of multivariate statistical analysis. Discriminant analysis is a commonly used statistical analysis method for determining how a research subject is classified based on the values of a number of variables observed or measured. PLS-DA maximizes the differences between groups according to predefined classifications and obtains a better separation than PCA. As a result, PLS-DA was employed to discriminate between ash from Europe and America.

4.2. PLS-DA Model for Analyzing Element Content and Isotope Ratios

Wood has a unique characteristic—a longer growth cycle—that sets it apart from other agricultural products. Typically, it takes 40–50 years for an ash tree to reach maturity.

Throughout this lengthy growth cycle, various factors like climate and environment can influence the mineral elements and stable isotopes present in timber [20]. This poses challenges when it comes to identifying the species and origins of ash. To enhance the accuracy of discriminating between the two types of timber, this paper conducts a study integrating element content and isotope ratios. To ensure a more precise analysis, the contents of ten mineral elements and the values of δ^{13}C and δ^{15}N were normalized to dimensionless numbers ranging from 0 to 1 before conducting the PLS-DA analysis.

Figure 2 displays the PLS-DA score plots based on isotope ratios, element content, and data fusion, denoted as A, C, and E, respectively. B, D, and F represent the 200-displacement cross-validation results for each plot [30]. Upon observing the score plots, it is evident that the PLS-DA model utilizing data fusion achieves the highest level of separation, with a discrimination accuracy of 96.2%. This marks a 7.7% improvement compared to the discrimination accuracy (88.5%) of the PLS-DA model using isotope ratios (Table 2). The discrimination accuracy of the PLS-DA model using element content is 92.3%. In terms of sample discrimination, only 1 American sample out of the 16 was incorrectly classified as a European sample, indicating a significant discriminative effect. According to the cross-validation result plots (Figure 2), all Q^2 values were found to be below 0, signifying that the model does not over-fit, and has good stability [31]. In Figure 2, Cor represents the correlation coefficient indicating the degree of permutation, and value represents the Q^2 and R^2 scores. This suggests that the model is effective, and this method can be employed for the identification and origin-tracing of European and American ash.
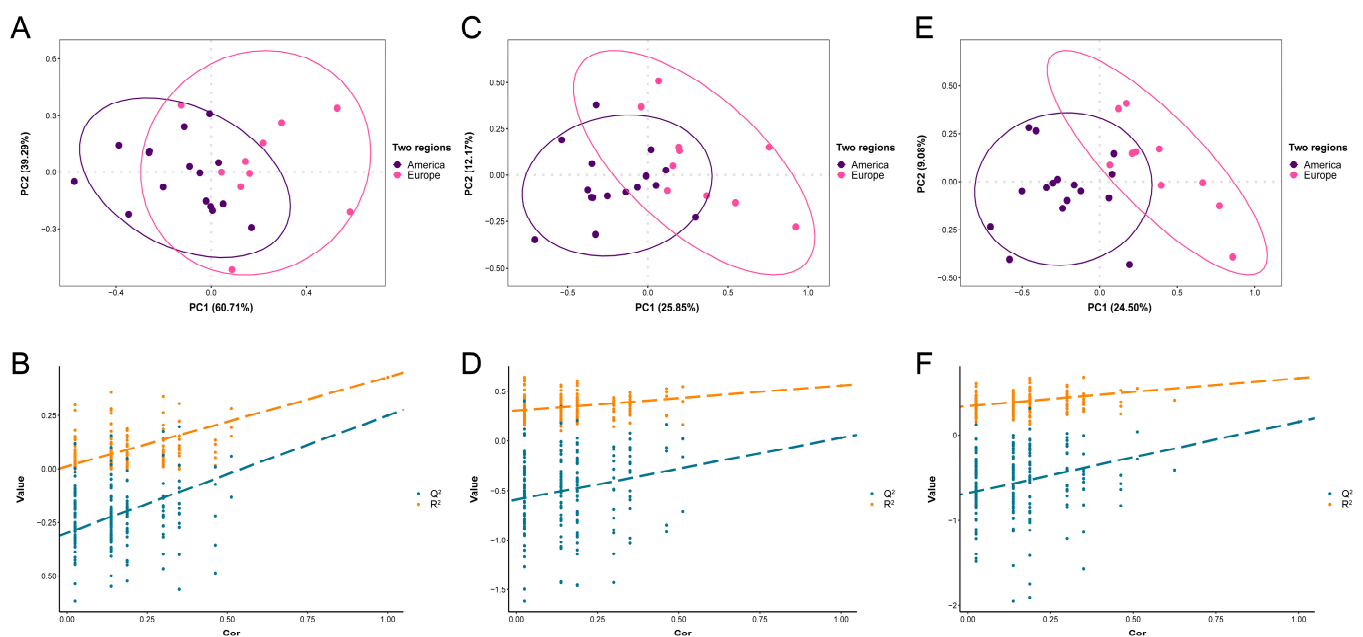

Figure 2. (**A**) PLS-DA score plots based on isotope ratios; (**C**) PLS-DA score plots based on element content; (**E**) PLS-DA score plots based on data fusion; (**B**) cross-validation result plot of PLS-DA model based on isotope ratios; (**D**) cross-validation result plot of PLS-DA model based on element content; (**F**) cross-validation result plot of PLS-DA model based on data fusion.

Table 2. Discriminant accuracies of ash wood samples from two origins determined using PLS-DA modeling based on stable isotope, mineral element and data fusion, respectively.

Modeling	Origins	Members	Accuracy	Total Accuracy
Stable isotope	America	16	100%	88.5%
	Europe	10	70%	
Mineral element	America	16	93.75%	92.3%
	Europe	10	90%	
Data fusion	America	16	93.75%	96.2%
	Europe	10	100%	

Based on the results from the PLS-DA model using data fusion, six components with variable importance in projection (VIP) scores greater than 1 were considered to be significant difference factors. The results of the VIP scores are shown in the Table 1. Subsequently, box plots, as shown in Figure 3, were generated to visually depict the significant differences in the distributions of six components between the two origins. Specifically, upon examining the box plots for Cu, Mg, Rb, and Sr, it is evident that Mg exhibits a significant discriminative effect, and the discrete degrees in the two types of timber are also comparable. Rb and Sr are both found at higher levels of abundance in European ash and exhibit better discrimination. The $\delta^{13}C$ values in both groups of samples show a relatively even distribution, although there is some overlap. However, the mean value and range of $\delta^{13}C$ in American ash are greater than those in European ash, suggesting a certain level of discrimination. Both groups of samples demonstrate significant discrimination based on the $\delta^{15}N$ values. Although one data point from American ash deviates slightly towards the third and fourth quartiles of European ash, there are clear differences between the two groups of samples. Among the top six most important components in the PLS-DA model, 5 of them were confirmed to be consistent with the significance analysis results of SPSS software. The significance *p*-value obtained by SPSS analysis has a strong correlation with the VIP score in the discriminant model analysis.
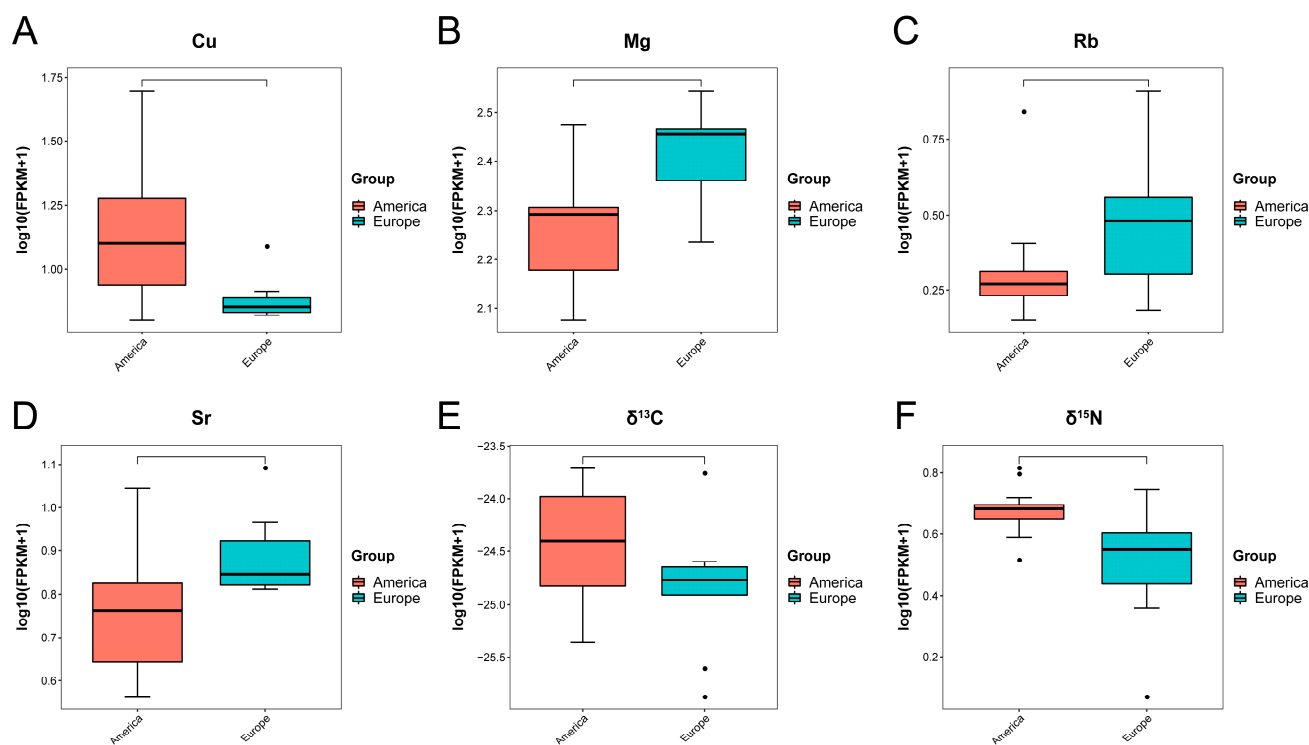
Figure 3. (**A**) Box plot of Cu content; (**B**) box plot of Mg content; (**C**) box plot of Rb content; (**D**) box plot of Sr content; (**E**) box plot of $\delta^{13}C$; (**F**) box plot of $\delta^{15}N$ of ash samples from America and Europe.

5. Conclusions

This paper focuses on analyzing the contents of ten mineral elements and the ratios of two stable isotopes in samples of European and American ash. The significant differences ($p < 0.05$) in Mg, Cu, Sr, and δ^{15}N between samples of European and American ash are also shown via a difference analysis using SPSS. The results indicate that δ^{13}C had the smallest dispersion degree, whereas δ^{15}N exhibited a more significant difference. When performing cluster analyses like HCA and PCA, it was demonstrated that the results of mineral elements and isotope ratios could be discriminated to some extent. The degree of separation attained, nonetheless, was deemed insufficient. To improve the separation effect, PLS-DA, a mode of supervised discriminant analysis, was utilized for modeling analysis. The normalized results of mineral elements and isotope ratios were subjected to PLS-DA analysis, resulting in the highest level of separation between samples of European and American ash. The analysis achieved an overall accuracy of 96.2% in discriminating between samples from European and American ash. Based on the analysis, six components were considered to be difference factors (VIP > 1), which closely aligns with the results from the analysis performed using SPSS. This paper provides property parameters for discriminating between European and American ash and offers an effective method for the origin traceability of ash from these two continents. It can be particularly useful for countries involved in the international trade of European and American ash, as it addresses technological challenges related to the identification and origin traceability of timber.

References

1. Pautasso, M.; Aas, G.; Queloz, V.; Holdenrieder, O. European ash (*Fraxinus excelsior*) dieback—A conservation biology challenge. *Biol. Conserv.* **2013**, *158*, 37–49. [CrossRef]
2. *GB/T 18513-2022*; Names of Main Woods Imported into China. Standards Press of China: Beijing, China, 2022.
3. Cheng, Y.; Zhong, L.; Sun, Y. Review of Wood Identification Technology. *Agric. Technol. Equip.* **2021**, *373*, 125–128. [CrossRef]
4. Zhang, J.; Yuan, P.; Li, J. Review of Wood Identification and Authentication Technology. *Hubei For. Sci. Technol.* **2015**, *44*, 30–35.
5. Kremer, D.; Stabentheiner, E.; Borzan, Ž.; Grubešić, R.J. Micromorphological differences between some European and American *Fraxinus* (Oleaceae) species. *Biologia* **2008**, *63*, 1111–1117. [CrossRef]
6. Aydoğan, B.; Cittan, M.; Çelik, A.; Kenan, D.O. A Comprehensive Analysis to Determine the Phytochemical Characteristics of *Fraxinus Americana* and *Fraxinus Excelsior* Leaves Extracts: Influence of the Extraction Method. *Celal Bayar Univ. J. Sci.* **2020**, *16*, 103–107.
7. Ma, Y.; Guo, B.; Wei, Y. An Overview of Analytical Approaches for Determining the Geographical Origin of Plant-derived Foods. *Food Sci.* **2014**, *35*, 246–250. [CrossRef]
8. Yan, T.; Chen, Y.; Shang, L.; Wang, Q.; Li, G. Discrimination of Volatile Components in Santalum album Heartwood from Different Habitats. *China Wood Ind.* **2019**, *33*, 18–21+26. [CrossRef]
9. Deklerck, V. Timber origin verification using mass spectrometry: Challenges, opportunities, and way forward. *Forensic Sci. Int. Anim. Environ.* **2022**, *3*, 100057. [CrossRef]
10. Wang, P.; Shen, J.; Tan, W. Progress in application of stable isotope in forest product traceability and adulteration detection. *J. Zhejiang A&F Univ.* **2018**, *35*, 968–974.

11. Hong, H.; Tian, X.; Wen, F.; Cui, Y.; Peng, K.; Cao, W.; Wang, M.; Liu, Y.; Xu, Y. Research progress in origin traceability and authenticity identification of agricultural products using stable isotope. *J. Food Saf. Qual.* **2022**, *13*, 6889–6897. [CrossRef]

12. Ma, M.; Feng, R.; Li, J.; Zhang, J.; Liu, Y.; Shi, T.; Cao, G.; Chen, X.; Yin, J. Origin traceability of imported barley based on ^{87}Sr/^{86}Sr and δ^{13}C. *J. Food Saf. Qual.* **2021**, *12*, 7857–7862.

13. Perini, M.; Giongo, L.; Grisenti, M.; Bontempo, L.; Camin, F. Stable isotope ratio analysis of different European raspberries, blackberries, blueberries, currants and strawberries. *Food Chem.* **2018**, *239*, 48–55. [CrossRef]

14. Feng, R.; Cheng, Y.; Qian, N.; Ma, M.; Yang, X.; Chen, X.; Cao, G.; Yin, J. Research on Traceablility of Geographic Origin for Myrica rubra from Zhejiang Province by ^{87}Sr/^{86}Sr Isotope Ratios Using Thermal-Ionization Mass Spectrometry. *J. Wuhan Univ. (Nat. Sci. Ed.)* **2022**, *68*, 687–692. [CrossRef]

15. Weckerle, B.; Richling, E.; Heinrich, S.; Schreier, P. Origin assessment of green coffee (*Coffea arabica*) by multi-element stable isotope analysis of caffeine. *Anal. Bioanal. Chem.* **2002**, *374*, 886–890. [CrossRef]

16. Taous, F.; Amenzou, N.; Marah, H.; Maia, R.; Maguas, C.; Bahmad, L.; Kelly, S. Stable isotope ratio analysis as a new tool to trace the geographical origin of Argan oils in Morocco. *Forensic Chem.* **2020**, *17*, 100198. [CrossRef]

17. Horacek, M.; Ogrinc, N.; Magdas, D.A.; Wunderlin, D.; Sucur, S.; Maras, V.; Misurovic, A.; Eder, R.; Čuš, F.; Wyhlidal, S.; et al. Isotope analysis (^{13}C, ^{18}O) of wine from central and eastern europe and argentina, 2008 and 2009 vintages: Differentiation of origin, environmental indications, and variations within countries. *Front. Sustain. Food Syst.* **2021**, *5*, 638941. [CrossRef]

18. Watkinson, C.J.; Rees, G.O.; Hofem, S.; Michely, L.; Gasson, P.; Boner, M. A case study to establish a basis for evaluating geographic origin claims of timber from the Solomon Islands using stable isotope ratio analysis. *Front. Forests Glob. Chang.* **2022**, *4*, 645222. [CrossRef]

19. Watkinson, C.J.; Gasson, P.; Rees, G.O.; Boner, M. The development and use of isoscapes to determine the geographical origin of Quercus spp. in the United States. *Forests* **2020**, *11*, 862. [CrossRef]

20. Correia, I.; Almeida, M.H.; Aguiar, A.; Alia, R.; David, T.S.; Pereira, J.S. Variations in growth, survival and carbon isotope composition (δ^{13}C) among Pinus pinaster populations of different geographic origins. *Tree Physiol.* **2008**, *28*, 1545. [CrossRef]

21. Griboff, J.; Horacek, M.; Wunderlin, D.A.; Monferrán, M.V. Differentiation Between Argentine and Austrian Red and White Wines Based on Isotopic and Multi-Elemental Composition. *Front. Sustain. Food Syst.* **2021**, *5*, 657412. [CrossRef]

22. Bin, L.; Wang, C.; Liu, Z.; He, W.; Zhao, D.; Fang, Y.-Y.; Li, Y.; Zhang, Z.; Chen, P.; Liu, W.; et al. Geographical origin traceability of muskmelon from Xinjiang province using stable isotopes and multi-elements with chemometrics. *J. Food Compos. Anal.* **2022**, *106*, 104320. [CrossRef]

23. Muñoz-Redondo, J.; Bertoldi, D.; Tonon, A.; Ziller, L.; Camin, F.; Moreno-Rojas, J. Multi-element and stable isotopes characterization of commercial avocado fruit (*Persea americana Mill*) with origin authentication purposes. *Food Control* **2022**, *137*, 108975. [CrossRef]

24. Jiao, L.; Lu, Y.; He, T.; Guo, J.; Yin, Y. DNA barcoding for wood identification: Global review of the last decade and future perspective. *IAWA J.* **2020**, *41*, 620–643. [CrossRef]

25. Zhang, R.; Yin, Y.; Xu, X.; Ye, K. Application of DNA Technology for Wood Origin Identification. *China Wood Ind.* **2015**, *29*, 31–34.

26. Boeschoten, L.E.; Sass-Klaassen, U.; Vlam, M.; Comans, R.N.; Koopmans, G.F.; Meyer-Sand, B.R.V.; Tassiamba, S.N.; Tchamba, M.T.; Zanguim, H.T.; Zemtsa, P.T.; et al. Clay and soil organic matter drive wood multi-elemental composition of a tropical tree species: Implications for timber tracing. *Sci. Total Environ.* **2022**, *849*, 157877. [CrossRef]

27. Han, X.; Yan, C.; Chen, L.; Mei, X. Stable carbon isotope characteristics of some woody plants in warm temperate zone. *Chin. J. Appl. Ecol.* **2000**, *11*, 497–500.

28. Liao, C.; Miao, S. Application of Stable Carbon and Nitrogen Isotopes in Tracing the Geographical Origin of Plants. *J. Anhui Agric. Sci.* **2022**, *50*, 19–21.

29. Chai, H.; Zhong, S.; Cui, H.; Li, J.; Sun, W. Variation in the carbon isotope composition of CO_2 derived from plant autotrophic respiration. *Acta Ecol. Sin.* **2018**, *38*, 2616–2624.

30. Zhao, J.; Liu, W.; Chen, Y.; Zhang, X.; Wang, X.; Wang, F.; Qian, Y.; Qiu, J. Identification of markers for tea authenticity assessment: Non-targeted metabolomics of highly similar oolong tea cultivars (*Camellia sinensis* var. sinensis). *Food Control* **2022**, *142*, 109223. [CrossRef]

31. Wang, H.; Cao, X.; Yuan, Z.; Guo, G. Untargeted metabolomics coupled with chemometrics approach for Xinyang Maojian green tea with cultivar, elevation and processing variations. *Food Chem.* **2021**, *352*, 129359. [CrossRef]