



Stable isotope signatures of deuterium, oxygen 18, and carbon 13 ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$) in imported apples available in the markets of Vietnam

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ABSTRACT

This study examines whether fresh apples from the United States, New Zealand, and China sold in the markets of Vietnam can be distinguished based on the stable isotopic signatures of their water and carbon ($\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in apples from the United States were found to average -100.1‰ and -10.5‰ vs VSMOW, respectively, lighter than those from New Zealand and China. In apples from China, the $\delta^{13}\text{C}_{\text{VDBP}}$ averaged -25.8‰ , which is more enriched than apples from the United States and New Zealand. A clear distinction was shown in the $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ values in apple samples from the three regions based on the statistical treatment at a 95 % confidence level and $p < 0.05$. This method is reliable enough to control the import and export of agricultural products.

1. Introduction

Eating an apple a day really does keep the doctor away. This advice has been supported by ample scientific evidence over the years because apples not only provide essential nutrients and minerals but also contain a megadose of vitamins (Slavin & Lloyd, 2012). In particular, apples are one of the chief sources of dietary flavonoids, which show the strongest associations with decreased mortality. Apples have superlative antioxidant activity, inhibit cancer cell proliferation, decrease lipid oxidation, and lower cholesterol. Moreover, apples contain a variety of phytochemicals, including quercetin, catechin, phloridzin and chlorogenic acid—all of which are strong antioxidants. The phytochemical composition of apples varies greatly between different geographical sources of apples (Boyer & Liu, 2004).

Although apple trees cannot be grown in Vietnam due to the climate, apples have become one of the country's favourite fruits. Thus, Vietnam has become one of the five biggest importers of apples worldwide, having imported more than 280,000 tons in 2020. Apples are mainly imported into Vietnam from the United States, China and New Zealand (FAO, 2021). However, distinguishing imported goods by geographic origin is difficult for various reasons. One reason is the wide variety of prices of imported apples across Vietnam, which depend on their quality and geographical origin. It is possible to forge the apple origin label for profit.

Several techniques to verify the geographical origin of agricultural products have been established and successfully applied (Georgiou & Danezis, 2017). Among others, the stable isotope compositions of hydrogen ($\delta^2\text{H}$), oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) have been studied and applied to the problem of verifying the geographical origin of products (I. M. Chung et al., 2016; de Rijke et al., 2016; Franke et al., 2007; Liu et al., 2020; McComb, Sarker, Hoogewerff, Hayman, & Frew, 2019; Nietner, Haughey, Ogle, Fahl-Hassek, & Elliott, 2014; Portarena, Baldacchini, & Brugnoli, 2017; Yaeko Suzuki et al., 2012). Distinguishing the geographical origin of agricultural products is based on the relationship of the two isotopic components from the water extracted from the product, $\delta^2\text{H}$ and $\delta^{18}\text{O}$, with the global meteorological waterline. The composition of the isotopes $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ display regional characteristics because their values depend on the climatic, environmental and geographical characteristics of the regions where the agricultural products were grown (Chakraborty, Belekar, Datye, & Sinha, 2018; Chesson et al., 2014; Dawson, Mambelli, Plamboeck, Templer, & Tu, 2002; Fügél, Carle, & Schieber, 2004; Oerter et al., 2017; Portarena et al., 2017).

During growth, water or humidity is the only source of hydrogen for plants to photosynthesis, but plants can obtain oxygen from several sources, including the atmosphere and soil water. Therefore, the ^2H and ^{18}O composition of the water in the fruit must reflect the water from its place of origin. Plant physiology and transpiration during maturation

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play important roles in isotope fractionation processes. However, previous studies have shown that no isotope fractionation occurs during root uptake; that is, the isotopic composition of water does not change as it moves from the soil to the root (Barbour, 2007; Dawson et al., 2002; Dawson & Siegwolf, 2007; Kahmen, Schefuß, & Sachse, 2013). Therefore, the isotopic composition of water in the roots and stems reflects the isotopic composition of the water available to the plant. Several potential sources of water are available for plants: groundwater, rainwater, soil water and runoff. The isotope composition of groundwater, soil water and runoff represents the long-term average of the isotopic composition of precipitation in that area (Dawson, 1993). Based on this scientific foundation, the isotope ratios $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ are widely applied in authentication and geographical traceability research.

The geographical origin of agricultural products is essential because of the globalisation of the food market along with an increasing demand for food safety and high quality. Knowledge of the geographical origin of agricultural products not only protects consumers and producers from fraud but also helps to maintain economic profits (I.-M. Chung et al., 2016). Therefore, many scientists over the years have studied this topic.

To distinguish the geographical origin of fruit products, Rossmann et al. (2001) have applied the isotopic composition $\delta^{18}\text{O}$ to show regional differences in apple juice samples from several European countries, including Germany, Italy, Belgium, Finland, Hungary, Austria and the Czech Republic (Rossmann, 2001). Bat et al. (2012) have found that apple juice from various regions in Slovenia has different $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. The values of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$ have also been applied by Magdas et al. (2012) to confirm the geographical origin of apple juice in Transylvania. Yaeko Suzuki et al. (2012) have differentiated Japanese apples of the Aomori region from Chinese apples using stable isotopic signatures of carbon and oxygen. A new study by Strojnik et al. (2022) has applied stable isotopes, light elements and modelling methods to geographically distinguish and authenticate strawberries in Slovenia.

This study aims to determine the stable isotopic signatures of hydrogen and oxygen ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) in water extracted from fresh apples and the isotopic signature of carbon ($\delta^{13}\text{C}$) in apples imported from the United States, New Zealand and China. This study presents procedures for sample processing and analysis of the $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ in apple flesh legally imported from the countries mentioned above. The data derived from this study could serve as a database of the isotopic signatures of hydrogen, oxygen and carbon in imported apples, which market managers can use to authenticate imported products to protect consumers.

2. Materials and methods

2.1. Sampling and sample processing in the laboratory

In this study, 391 apple samples of different varieties imported from the United States (US, $n = 180$), New Zealand (NZ, $n = 124$) and China (CN, $n = 87$) were taken from the customs authority by the staff of the Institute for Nuclear Science and Technology (INST). The samples were processed and measured for $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the INST Isotope Hydrology laboratory. Water from the samples was extracted using cryogenic vacuum methods following the guidelines of the International Atomic Energy Agency's (IAEA) Tecdoc 1783 (IAEA-TECDOC-1783, 2016) to analyse $\delta^2\text{H}$ and $\delta^{18}\text{O}$. This extraction method has been proven acceptable for the stable isotope analysis of soil and plants (Chen et al., 2020; Millar, Pratt, Schneider, & McDonnell, 2018; Orłowski et al., 2018). After the extraction, the water sample was allowed to thaw at room temperature, and then it was transferred into 2-ml vials for isotopic composition analysis.

For the $\delta^{13}\text{C}$ analysis, apple samples were chopped into clean plastic bottles and placed in a freeze dryer (Thermo Savant, $T_{\min} = -55\text{ }^\circ\text{C}$, $P_{\min} = 100\text{ }\mu\text{bar}$). Freeze-drying is based on the principle of water sublimation in the solid state. The sample was rapidly cooled to $-55 \pm 5\text{ }^\circ\text{C}$ to freeze the water. Subsequently, the controlling program of the unit

Table 1
Reference materials information.

No.	Reference Name	Material	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	$\delta^2\text{H}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
1	IAEA-CH-7	Polyethylene	-32.15 ± 0.05		
2	IAEA-600	Caffeine	-27.77 ± 0.04		
3	IAEA-CH-3	Cellulose	-24.72 ± 0.04		
4	USGS62	Caffeine	-14.79 ± 0.04		
5	LGR 1C	Water		-154 ± 0.5	-19.49 ± 0.15
6	LGR 2C	Water		-123.3 ± 0.5	-16.24 ± 0.15
7	LGR 3C	Water		-97.3 ± 0.5	-13.39 ± 0.15
8	STD 4C	Water		-51.6 ± 0.5	-7.94 ± 0.15
9	VSMOW2	Water		0 ± 0.3	0 ± 0.02

initiated a suitable vacuum for the frozen water molecules to sublimate ($100\text{ }\mu\text{bar}$ – 50 mbar), and the material was dry after about 5 days. The dried samples were then homogenised by grounding them into a fine powder with a cold mill using liquid nitrogen. The dried samples amounted to 60 – $100\text{ }\mu\text{g}$ and were placed in tin capsules prior to $\delta^{13}\text{C}$ analysis.

2.2. Analytical method

The isotope compositions ($\delta^2\text{H}$, $\delta^{18}\text{O}$) in the apple water were measured using a laser spectrometer (LWIA-24D, Los Gatos Research). The ^{13}C composition was determined by continuous flow isotope-ratio mass spectrometry (CF IRMS) using an IsoPrime IRMS (Elementar, Cheadle, United Kingdom) equipped with an elemental analyser (EuroVector, Milan, Italy). The samples were measured in triplicate, and the standard deviations (SD) for $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ -values were $0.3\text{ }‰$, $0.1\text{ }‰$ and $0.3\text{ }‰$, respectively. The isotope compositions of the samples are expressed in delta notation (δ) per mill relative to the internationally accepted Vienna Standard Mean Ocean Water (VSMOW) for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}\text{C}$. The delta (δ) notation for deuterium, oxygen-18 and carbon-13 is expressed in per mill (‰) relative to the standards via the following equations:

$$\delta^2\text{H} = \left(\frac{{}^2R_{\text{sample}}}{{}^2R_{\text{Std}}} - 1 \right) \quad (1)$$

$$\delta^{18}\text{O} = \left(\frac{{}^{18}R_{\text{sample}}}{{}^{18}R_{\text{Std}}} - 1 \right) \quad (2)$$

$$\delta^{13}\text{C} = \left(\frac{{}^{13}R_{\text{sample}}}{{}^{13}R_{\text{Std}}} - 1 \right) \quad (3)$$

where ${}^2R_{\text{sample}}$, ${}^2R_{\text{Std}}$, ${}^{18}R_{\text{sample}}$, ${}^{18}R_{\text{Std}}$, ${}^{13}R_{\text{sample}}$, and ${}^{13}R_{\text{Std}}$ are the isotopic ratios of $[^2\text{H}]/[^1\text{H}]$, $[^{18}\text{O}]/[^{16}\text{O}]$ and $[^{13}\text{C}]/[^{12}\text{C}]$ in the samples to be analysed and the standards.

The standard used to determine the deuterium and oxygen-18 compositions in water was VSMOW2 (Vienna Standard of Mean Ocean Water, batch 2), supplied by the Isotope Hydrology Laboratory of IAEA based in Vienna, Austria. The reference materials used to calibrate $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were working standards LGR 1C, LGR 2C, LGR 3C and LGR 4C, supplied by the Los Gatos company. The standard for $\delta^{13}\text{C}$ determination was VPDB, which is a calcite mineral supplied by the IAEA. The working calibration standards used in the $\delta^{13}\text{C}$ determination were IAEA-CH3, IAEA-600 and IAEA-CO9. All information about the values of $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of the reference materials used in this study is detailed in Table 1.

Table 2

Statistical results for the $\delta^2\text{H}$ in water extracted from apple samples by country; n is the number of samples.

$\delta^2\text{H}_{\text{VSMOW}}$ (‰)	United States	New Zealand	China
Mean	-100.1	-45.0	-50.2
Min	-124.2	-65.1	-62.0
Max	-80.9	-29.4	-35.8
n	180	124	87

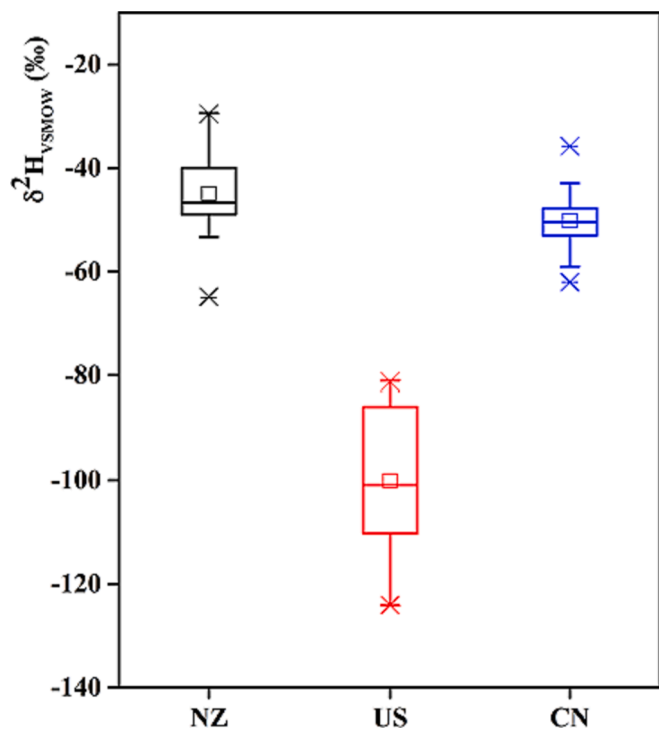


Fig. 1. Box plot of $\delta^2\text{H}$ values in apple water from New Zealand (NZ, n = 124), the United States (US, n = 180), and China (CN, n = 87).

2.3. Data processing

Excel and Origin Pro were used for data processing, drawing charts and creating tables. Data analysis included descriptive statistics for the mean, minimum, and maximum values and their SD. Statistical significance was calculated by the Kruskal–Wallis test to compare the stable isotope composition values of samples from the three countries. The Kruskal–Wallis test is a non-parametric test for multiple comparison samples among different groups that does not assume a normal distribution (Smalheiser, 2017).

For the control experiment and method comparison, apple samples were sent to the Isotope Laboratory of the Department of Chemistry at Otago University (OU), New Zealand, for comparative analysis using an elemental analyser isotope-ratio mass spectrometer (EA-IRMS). The results show the reliability of this experiment (Anh, Nhan, Frew, & Quynh, 2022).

3. Results and discussion

3.1. Evaluation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ results

A total of 391 values of $\delta^2\text{H}$ in water extracted from fresh apples were measured, of which data from 180 samples originated from the US (n = 180), 124 from NZ (n = 124), and 87 from CN (n = 87). Samples were tested using the Kruskal–Wallis method to assess whether there were significant differences between the three groups of $\delta^2\text{H}$ values. The

Table 3

Statistical results for the $\delta^{18}\text{O}$ in water extracted from apple samples by country; n is the number of samples.

$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	United States	New Zealand	China
Mean	-10.5	-8.8	-1.0
Min	-18.0	-14.0	-4.2
Max	-4.5	-5.7	-1.6
n	180	124	87

results are shown by country in Table 2 and Fig. 1. As seen in Table 2 and Fig. 1, the water in apples from the United States had the most depleted $\delta^2\text{H}$ among the three countries, while apples from NZ had the most enriched deuterium composition. The Kruskal–Wallis test showed significant differences in the $\delta^2\text{H}$ values of the apple water samples from the three countries. The Chi-square = 299.95, $p = 7.34\text{E} - 66$, and $df = 2$ were determined for the samples from the three countries at $\alpha = 0.05$.

With the same evaluation method, the results of $\delta^{18}\text{O}$ in 391 apple water samples are presented in Table 3 and Fig. 2. The Kruskal–Wallis test results confirm a clear difference in $\delta^{18}\text{O}$ values from water apple samples from US, NZ and CN (Chi-square = 212.44, $p = 7.40\text{E} - 47$, and $df = 2$, with $\alpha = 0.05$).

There were significant differences in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of apple samples from the US, NZ and CN. The differences in the isotopic composition in agricultural products due to their geographical location are known to be due to the isotopic fractionation effect during physical (e.g., phase transfer of water), chemical (e.g., isotopic exchange, equilibrium processes), biochemical reactions (e.g., photosynthesis), or diffusion processes (Dawson et al., 2002). Thus far, the results of most but not all studies of isotopic signatures in plants have shown no evidence for isotopic fractionation in the water uptake by the roots (Barbour, 2007; Dawson & Siegwolf, 2007; Flanagan, Bain, & Ehleringer, 1991). Thus, the isotopic compositions of the water in the roots and stems reflect the isotopic composition of water available to the plant. Two potential sources of water for plant roots are available: water can be obtained from deep groundwater or recent rainfall. However, the isotopic composition of groundwater represents a long-term average of the isotopic composition of precipitation occurring over an area (Loader, McCarroll, M.H, Robertson, & Jalkanen, 2007). Apples are perennial crops, so the isotopic composition of water from the tree reflects the long-term average isotopic composition of precipitation in that area.

Although no isotopic fractionation occurs during plant water uptake, cleavage occurs during transpiration (Majoube, 1971). The isotopic fractionation process is mainly due to the evaporation of water through the skin of the apple. The isotope fractionation coefficient for the liquid–vapour balance affecting the isotopic enrichment in the water of the apple depends on the geographical location and climate (Barbour, 2007; Dawson et al., 2002; Dunbar & Wilson, 1983). Hence, the stable isotope signatures of deuterium and oxygen-18 in apples from the US, NZ and CN can be discriminated against each other, as seen in Fig. 3.

As evaluated above, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the apple water are related to the local meteorological water. The value of the isotopic composition of local meteorological water is affected by longitude, latitude, the continental effect, and the distance of the locality from the sea (Craig, 1961). The impact of these factors explains why the isotopic compositions of the water from apple samples in different regions such as the US, NZ and CN are distinct.

3.2. Evaluation of $\delta^{13}\text{C}$ results

Carbon dioxide sources, water stress, nutrient stress, and light environment determine the variations in the carbon isotopic ratios of a single crop grown under different cultivation regimes due to chemical and biochemical processes (Ehleringer, 2017). Thus, the geographical origin of food could potentially also be identified based on their $\delta^{13}\text{C}$ values. The carbon stable isotopic compositions of 80 apple samples, of

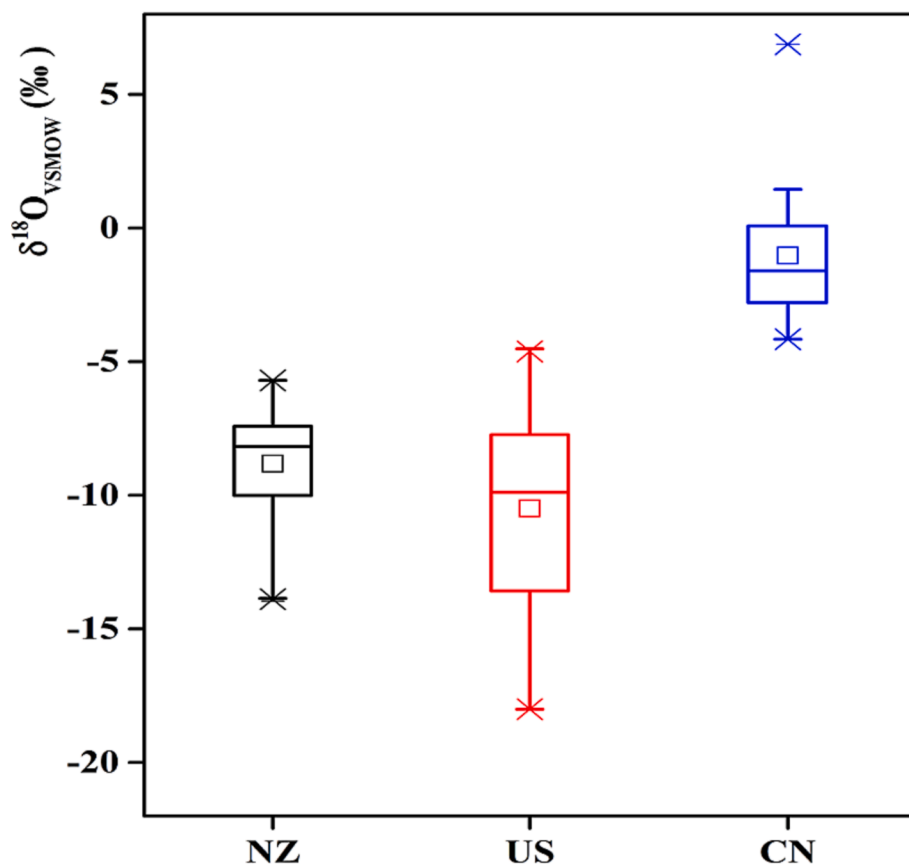


Fig. 2. Box plot of the $\delta^{18}\text{O}$ values of apple water from New Zealand (NZ, n = 124), the United States (US, n = 180), and China (CN, n = 87).

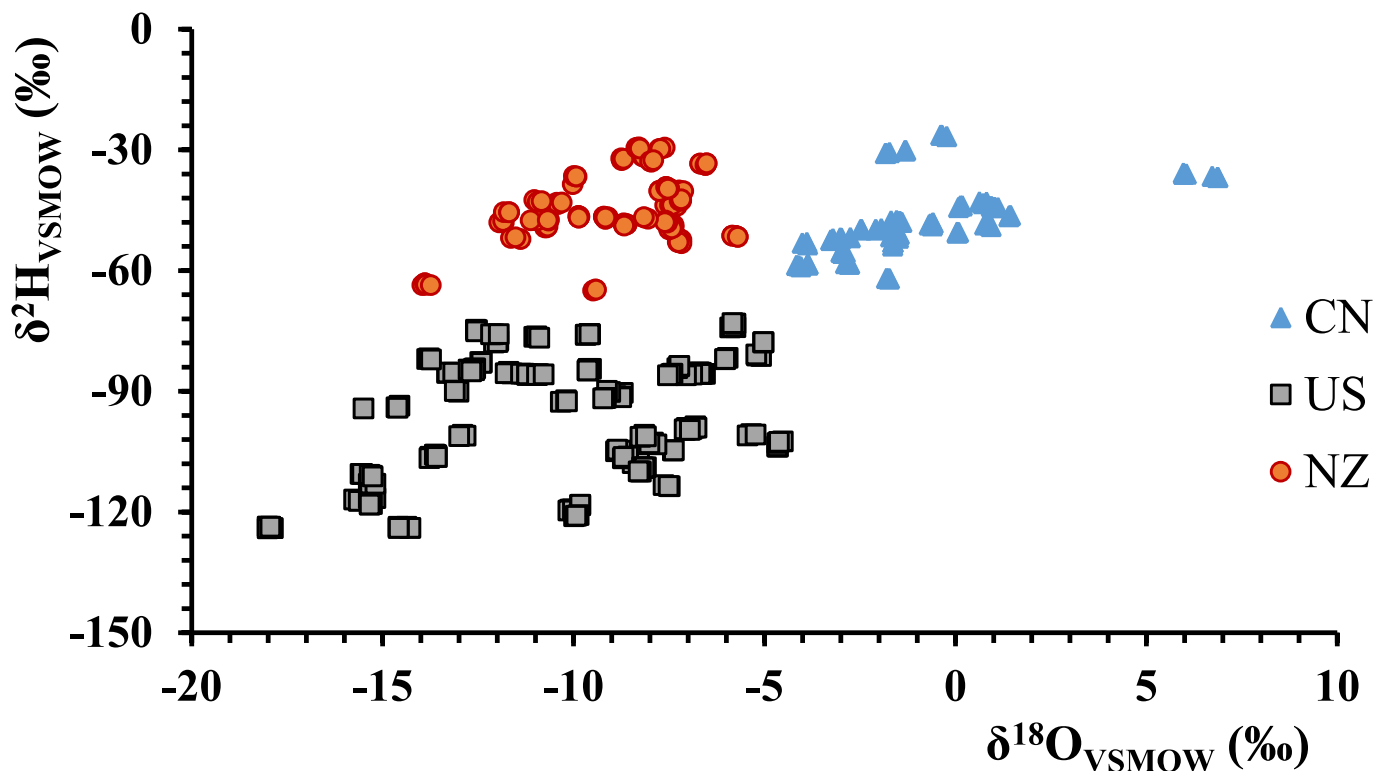


Fig. 3. Apple samples from different geographical origins (from the US, NZ and CN) were discriminated from each other based on the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in water extracted from the commodities.

Table 4
Results of statistical treatment of $\delta^{13}\text{C}$ values in apple flesh by country.

$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	United States	New Zealand	China
Mean	-26.2	-27.2	-25.8
Min	-28.1	-28.9	-26.8
Max	-23.8	-26.0	-24.1
n	39	32	9

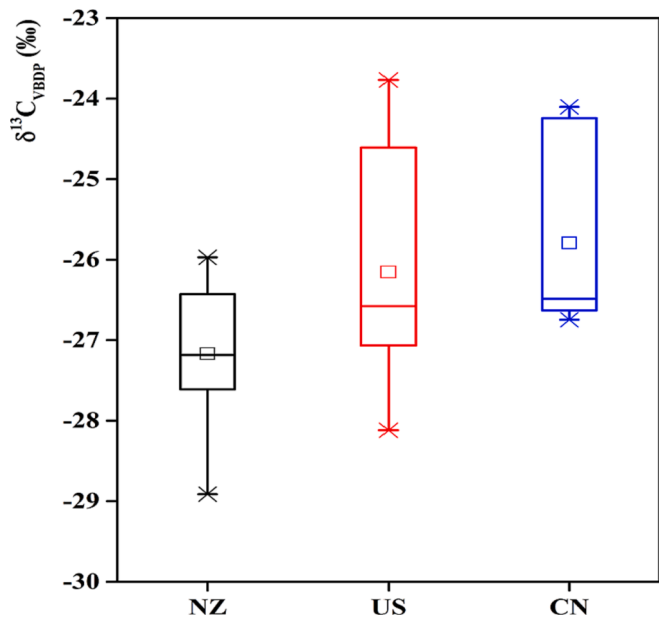


Fig. 4. Box plot of $\delta^{13}\text{C}$ values of apple flesh from New Zealand (NZ, n = 32), the United States (US, n = 39), and China (CN, n = 9).

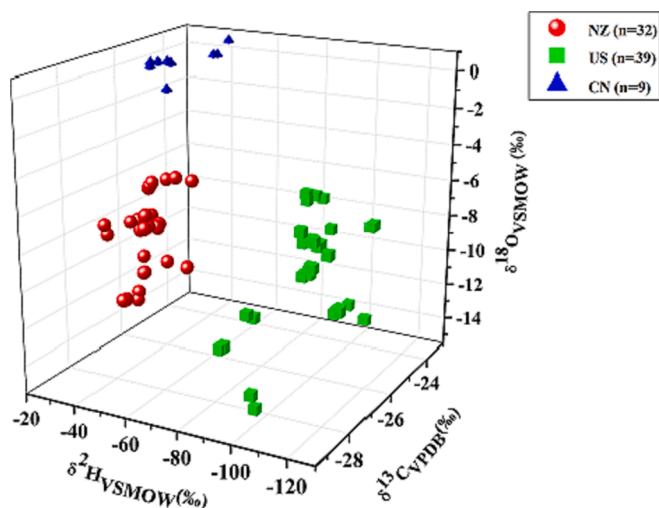


Fig. 5. Differentiation of 80 apple samples by their geographical origin based on $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ values in the products.

which 39 samples were from the US, 32 were from NZ, and nine were from CN, showed significant differences between the three sample groups (Table 4 and Fig. 4).

At a confidence level of $\alpha = 0.05$, the Kruskal–Wallis test showed significant differences in the $\delta^{13}\text{C}$ values of apple flesh originating from the US, NZ and CN: Chi-square = 11.49, $p = 0.003$, $df = 2$. The differences in the $\delta^{13}\text{C}$ in apple samples are explained by the factors affecting the isotopic fractionation of carbon isotopes during photosynthesis. In

addition, differences in the ratio of sugar to lignin to cellulose in apples from various geographic locations have been reported, which affects the resulting $\delta^{13}\text{C}$ value (Barbour, 2007; Loader et al., 2007). In addition, plants in humid environments consume more CO_2 . Thus, they develop a lower ratio of ^{13}C to ^{12}C than plants in drier environments (Anderson & Smith, 2006).

These distinctions form the scientific basis for using $\delta^{13}\text{C}$ to distinguish apples from various regions. Based on the $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, we can distinguish apples from different countries in the scatter plot (Fig. 5).

4. Conclusion

The isotopic compositions of deuterium, oxygen-18 and carbon-13 ($\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$) in imported fresh apples from the US, NZ and CN were analysed. The values of $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in apples from the three study regions differed significantly. This finding can authenticate the geographical origin of the imported apples, contributing to the protection of consumers' interests. Compared with other food traceability and authentication techniques, stable isotope ratios can be successfully used to characterise, classify and verify the labelling of the geographical origin of both local and imported fruit. This method also reduces fraud while improving consumer trust and confidence. Stable isotope analysis techniques also provide scientific support for stringent government regulatory policies. Thus, the technique is highly applicable and practical for consumers and is an effective tool for managers.

However, the stable isotopic compositions in the water and the organic matter of apples can be altered by climate and seasonal or annual fluctuations. Therefore, it will always be necessary to continuously analyse new authentic samples from specific locations. In this way, an isotope database could be set up to trace apples.

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.

Data availability

Data will be made available on request.

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