Achieving Food Authenticity and Traceability Using an Analytical Method Focusing on Stable Isotope Analysis

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High-value agricultural products are characterized by the geographical conditions of the production areas such as climatic and soil conditions. These products are protected by the geographical indication (GI) protection system, which has been introduced in more than 100 countries. Because GI products are expensive in the market, products are often mislabeled as GI. Thus, there is an urgent need for the development of analytical methods that enable the tracing of geographical origins of food materials. Stable isotope analysis is used to trace the geographical origin of food materials. In this study, we review the applications for tracing the geographical origin of agricultural products (especially rice, beef, and honey) focusing on an analytical method for analyzing stable isotopes (δD, δ13C, δ15N, δ18O, and δ34S).

Keywords Stable isotope analysis, food authenticity, rice, beef, honey

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1 Introduction

There are many high value-labeled agricultural products that are obtained using traditional production processes and from a specific production area with unique geographical characteristics, such as climatic and soil conditions. Geographical indication (GI) is a system that protects the names of these products with intellectual property (IP) rights. Recently, because there is demand for exporting these GI products, the introduction of GI systems has received much attention worldwide. The GI system is positioned as an IP, and has been introduced in more than 100 countries. For example, the wines “champagne” and “chablis,” and the cheese “Parmigiano Reggiano” are well-known GI products.

In the European Union (EU), more than 3400 names of products are legally protected by GI systems. At the end of 2019, the new public database called eAmbrosia—the EU Geographical Indications registers—was launched. All GI products in the EU are now accessible on eAmbrosia. There are three schemes to protect and promote the GI products: protected designation of origin (PDO), protected geographical indication (PGI) and traditional specialties guaranteed (TSG). PDO products are required to have strong links to the production area. PDO products produced entirely from raw materials sourced from specific geographical areas. The reputation and characteristics of these products are closely related to the region of origin. For example, Kalamata PDO olive oil is produced entirely from olive varieties grown and harvested in the region of Kalamata, which is located in the south part of the Peloponnesse peninsula in Greece. PGI products are required to have factors of quality, reputation or other characteristics derived from geographical origin. PGI products are produced, processed or packaged in specific geographical areas, but the raw material is not necessarily sourced from that region. For example, Westfälischer Knochenschinken PGI ham is produced in the

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region of Westphalia in Germany,\textsuperscript{2} using the region’s traditional pig farming techniques. However, the meat does not originate exclusively from animals born and reared in that area. TSG designation requires the product to have certain traditional aspects, such as the way the product is made or its composition, but unlike PDO and PGI, there is no need for a relationship between the product and its geographical area. For example, Gueuze TSG beer is a type of lambic beer generally produced in and around Brussels, Belgium.\textsuperscript{2} Gueuze beer is produced from a centuries-old farmhouse brewing and blending recipe. This production method is protected but could be used to carry out production somewhere else.

In Japan, for GI designation, the quality, reputation and characteristics of the products must essentially be attributable to a specific geographical area. The names of the GI products are permitted for use only for products that meet the criteria for specific geographical origin and the production method specified by the groups of producers/processors. In 2015, the Geographical Indication Act was enforced to protect and promote Japanese GI products. Illicit use, including marketing of products similar to GI registered products, is monitored and regulated by the government. As of August 2020, 99 products have been registered,\textsuperscript{4} including KOBE BEEF and YUBARI MELOM. In addition, for these GI products to be protected overseas, GI protection is required in the export destination countries. The Japanese government has signed international agreements with foreign countries that employ the same GI protection system used in Japan. For example, 48 Japanese GI products and more than 200 EU GI products are mutually protected based on the Japan-EU Economic Partnership Agreement (EPA).\textsuperscript{5}

In order to protect product names from being copied and to promote and be able to easily identify GI products, symbols have been used on labels of these GI products.\textsuperscript{2,4} However, products are often mislabeled as GI in order to set higher retail price. Unfortunately, there are many cases in which the names and production areas of GI products have been used illegally. To protect the brands of high-value-labeled food products, such as GI products, there is a need for the development of analytical methods that enable the tracing of the geographical origin of food products.

There are two important types of methods for protecting these high-value products with food-traceable systems. First are electronic methods, such as barcodes, IC chips, tags, and QR codes. An electronic method system displays the number and the code attached to each product to access its history, such as the information on the producer, agricultural practices, and production area. This system provides consumer confidence because it can be easily accessed. However, these external codes may be inadvertently or deliberately modified on the labels, which results in incorrect or inappropriate information of the products. Another approach is to employ scientific methods, such as DNA analysis, trace element composition, and stable isotope ratios.\textsuperscript{5} These methods are used to analyze the food and agricultural products themselves. Stable isotope analysis is a useful method for food authentication.\textsuperscript{5-10} In this study, we review the applications of methods use to trace the geographical origin of the following food materials: rice, beef, and honey. It is performed using analytical methods that focus on analyzing the stable isotopes ($\delta$D, $\delta^{13}$C, $\delta^{15}$N, $\delta^{18}$O, and $\delta^{34}$S).

2 Experimental

2.1 Sample preparation

Food and agricultural products were dried using an oven or freeze-dryer and homogenized using mills, such as ball mill, stainless or ceramic blade mill, and/or an agate mortar and pestle.\textsuperscript{8,11} In the case of a sample with high lipid content, such as animal samples, the extraction of lipids is required because the lipids have relatively lower carbon isotope ratios.\textsuperscript{8,12} The homogenized samples were extracted with solvents such as chloroform/methanol and an iso-propanol/hexane mixture. The defatted samples were separated from the solvent by vacuum filtration, air-dried overnight in a fume hood, and rehomogenized. For the carbon, nitrogen, and sulfur isotope analysis, freeze-dried fine powdered samples were weighed into a tin capsule. Tin burns easily and initiates the combustion reaction. For the oxygen and hydrogen isotope analysis, freeze-dried fine powdered samples were weighed into a silver capsule. Silver capsules have a lower oxygen content, and they are more suitable for pyrolysis.

2.2 Elemental analyzer isotope ratio mass spectrometry (EA/IRMS)

Powdered samples were analyzed using an elemental analyzer/isotope ratio mass spectrometer (EA/IRMS) (Fig. 1). For carbon, nitrogen, and sulfur isotope ratios, carbon, nitrogen, and sulfur in each sample were converted into gases: carbon dioxide ($\text{CO}_2$), nitrogen ($\text{N}_2$), and sulfur dioxide ($\text{SO}_2$) at 1000°C using an elemental analyzer. For oxygen and hydrogen isotope ratios, the oxygen and hydrogen in each sample were converted into carbon monoxide ($\text{CO}$) and hydrogen ($\text{H}_2$) gases at 1450°C using a thermal conversion element analyzer (TCEA). The gases were separated using a column, and each separated gas was introduced into an IRMS. Generally, mass spectrometry (MS) continuously scans a large range of masses (e.g., 40–600 amu) to characterize the ion fragmentation of compounds. However, the IRMS continuously determines the isotope abundance of a couple of masses (the $m/z$ values of carbon are 44, 45, and 46, the $m/z$ values of N$_2$ gas are 28, 29, and 30, the $m/z$ values of sulfur are 64, 65, and 66, the $m/z$ values of hydrogen are 2 and 3, and the $m/z$ values of oxygen are 28, 29,
and calculates the isotope ratio. For example, the $^{13}C/^{12}C$ ratio was obtained by comparing the abundance of three major isotopes, $^{12}C^{16}O_2$ (m/z 44), $^{13}C^{16}O_2$ (m/z 45), and $^{12}C^{18}O^{16}O$ (m/z 46), to calculate $^{13}C/^{12}C$ ratios. The measured stable isotope values were normalized using isotope-known standards such as international standards. These standards were determined regularly (e.g., every 12 samples) to confirm the reproducibility of the measurements. The Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network was produced a guide on how to operate IRMS. This guide provides useful information about instrument set-up, calibration, taking measurements, data handling and uncertainty, quality assurance and troubleshooting.

The isotopic composition is reported, and it is denoted as $\delta$:

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where $R$ is the isotope ratio (i.e., $^{13}C/^{12}C$, $^{13}N/^{12}N$, D/H, $^{18}O/^{16}O$, and $^{34}S/^{32}S$) of the sample, and $R$ is the isotope ratio of the international standards: for carbon, Vienna PeeDee Belemnite (VPDB); for nitrogen, air; for oxygen and hydrogen, Vienna Standard Mean Ocean Water (VSMOW); and for sulfur, Vienna Canyon Diablo Troilite (VCDT). Isotope values were given per mil ($\%$). A positive $\delta$ value indicates enrichment in the heavy isotope relative to the standard, while a negative $\delta$ value indicates depletion in the heavy isotope.

3 Results and Discussion

Living organisms are composed mainly of light elements such as carbon, hydrogen, nitrogen, oxygen, and sulfur. These elements have different mass numbers, which are called isotopes. Isotopes have the same number of protons but different number of neutrons in the atoms. These isotopes include radioactive isotopes with radioactivity (e.g., $^{14}C$ for carbon) and stable isotopes (e.g., $^{12}C$ and $^{13}C$ in carbon). Stable isotopes are not radioactive, and they are naturally stable. The stable isotope ratio (e.g., $^{13}C/^{12}C$ in carbon) is influenced by chemical and biochemical reactions. For example, in the evaporation process of water, $^{18}O$ with lower mass generally tends to react more quickly than $^{16}O$ with high mass, so the water vapor tends to be slightly enriched. Therefore, the stable isotope ratio of organisms is actively used in fields such as geochemistry, ecology, environmental chemistry, and archeology, for applications involving the elucidation of material circulation, the structural analysis of food webs, and the food analysis of animals because they preserve information such as the origin of organisms, biosynthesis processes, and growth environments.

Plants are classified as $C_3$ plants, $C_4$ plants, and CAM plants based on the difference in the carbon fixed path during photosynthesis. Most plants belong to the $C_3$ plant category, but sugar cane and corn are classified as $C_4$ plants. The carbon isotope ratio of sugar produced from sugar cane and corn are significantly higher. Thus, the addition of these sugars to juices or honey can be detected by performing carbon isotope analysis. When comparing plants of the same type, there are differences in the carbon isotope ratios of plants that require moisture conditions for growth. The stomata not only facilitate carbon dioxide diffusion into the leaves but also controls water loss due to water vapor diffusion from the leaves (transpiration). The opening and closing of the stomata depend on the moisture available in the plants. Thus, carbon isotope ratios indicate climatic conditions during growth, such as the mean temperature, humidity, and mean precipitation amount. The nitrogen isotope ratios of the plants indicate those of nitrogen sources in the soil absorbed by the roots. The nitrogen isotope ratios of organic fertilizers, such as manure, are higher than those for chemical fertilizers. Some GI products are linked to the production method such as organic farming. For example, Edosaki Kabocha (pumpkin), which is a Japanese GI product, has rich and delicious taste compare with other pumpkin varieties because the production technique of growing to full ripeness. The production area for this area is suitable for squash production because of its high drainage capacity affected by volcanic ash soil and moderate rainfall throughout the year. In addition, because livestock farming has flourished in this area, the manure compost is used to cultivate Edosaki Kabocha. Thus, nitrogen isotope ratios could be indicators for tracing the geographic origin of food materials, focusing on this paper, we review the applications of the methods used to trace the geographical origin of food materials, mainly since 2000. In previous studies that traced the geographical origin of food materials using stable isotope analysis, mainly since 2000. In this paper, we review the applications of the methods used to trace of the geographical origin of food materials, focusing on rice, beef, and honey.

3-1 Tracing the geographical origin of rice

Rice is one of the most important crops in Asian food culture. According to the FAOSTAT (Food and Agriculture Organization Corporate Statistical Database), the contribution of Asian countries to rice production was about 90% of the world’s total production. Many countries actively export and import rice not just to and from Asia but also in other parts of the world. The rice cultivar and the cultivation area are important factors in determining the market value of rice. For example, Basmati rice, which is one of the most famous types of premium-quality rice, is cultivated in the Himalayan foothill regions of India and

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| Food group | Agricultural products | Country | Parameters | Reference |
|-----------|-----------------------|---------|------------|-----------|
| Cereals   | Rice                  | India, Pakistan, France, Italy, Spain, USA | $\delta^{18}O$, $\delta^{13}C$, and amino acids | Kelly et al. (2002) |
|           |                       | Australia, USA, and Japan | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Suzuki et al. (2008) |
|           |                       | Australia, USA, Thailand, China, Vietnam and Japan | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Korenaga et al. (2015) |
|           | Wheat                 | China | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Li et al. (2015) |
|           |                       | Thailand | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Chung et al. (2015) |
|           |                       | Australia, USA, Turkey, and Italy | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Chen et al. (2016) |
|           |                       | Canada, Australia, and China | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Kukusamude and Kongsri (2018) |
| Meats     | Beef                  | Australia, USA, and Japan | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Brescia et al. (2002) |
|           |                       | South Korea, Australia, New Zealand, and Mexico | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Luo et al. (2015) |
|           |                       | China | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Wadood et al. (2018) |
| Pork      |                       | South Korea, Denmark, Germany, France, Spain, Canada, and Mexico | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Heaton et al. (2008) |
| Poultry   |                       | China | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Nakashita et al. (2008) |
|           |                       | Brazil, France, Germany, Hungary, and Switzerland | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Nakashita et al. (2009) |
| Dairy     | Cheese                | Italy | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Horacek and Min (2010) |
|           | products              | Germany, Finland, Switzerland | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Orsio et al. (2011) |
|           |                       | France, Italy, Spain | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Aoyagi et al. (2013) |
|           |                       | Europe | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Zhao et al. (2013) |
|           |                       | Italy | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Zhou et al. (2015) |
|           |                       | China | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Zhao et al. (2020) |
|           |                       | Argentina | $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ | Shin et al. (2018) |
| Milk      |                       | USA | $\delta^{18}O$, and amino acids | Zhao et al. (2020) |
|           |                       | Europe | $\delta^{18}O$, and amino acids | Franke et al. (2008) |
| Olive oil |                       | Italy | $\delta^{18}O$, and amino acids | Rees et al. (2016) |
| Honey     |                       | Slovenia | $\delta^{18}O$, and amino acids | Manca et al. (2001) |
|           |                       | Europe | $\delta^{18}O$, and amino acids | Filonel et al. (2003) |
|           |                       | Italy | $\delta^{18}O$, and amino acids | Cimin et al. (2004) |
|           |                       | Italy | $\delta^{18}O$, and amino acids | Filonel et al. (2005) |
|           |                       | Italy | $\delta^{18}O$, and amino acids | Manca et al. (2006) |
|           |                       | 23 Countries | $\delta^{18}O$, and amino acids | Cimin et al. (2012) |
|           |                       | 11 Countries | $\delta^{18}O$, and amino acids | Pianezz et al. (2019) |
|           |                       | 15 Countries | $\delta^{18}O$, and amino acids | Chesson et al. (2010) |
|           |                       | 19 Countries | $\delta^{18}O$, and amino acids | Cimin et al. (2010) |
|           |                       | 21 Countries | $\delta^{18}O$, and amino acids | Chiocchini et al. (2016) |
|           |                       | 7 Countries | $\delta^{18}O$, and amino acids | Portaren et al. (2017) |
|           |                       | 16 Countries | $\delta^{18}O$, and amino acids | Krop et al. (2010) |
|           |                       | 19 Countries | $\delta^{18}O$, and amino acids | Schellonenberg et al. (2010) |
|           |                       | 20 Countries | $\delta^{18}O$, and amino acids | Dinca et al. (2015) |
|           |                       | 21 Countries | $\delta^{18}O$, and amino acids | Magdas et al. (2021) |
| Coffee    |                       | 16 Countries | $\delta^{18}O$, and amino acids | Rodrigues et al. (2009) |
| and tea   |                       | 19 Countries | $\delta^{18}O$, and amino acids | Rodrigues et al. (2011) |
| Tea       |                       | 7 Countries | $\delta^{18}O$, and amino acids | Santato et al. (2012) |
|           |                       | China | $\delta^{18}O$, and amino acids | Carter et al. (2015) |
|           |                       | 21 Countries | $\delta^{18}O$, and amino acids | Driscoll et al. (2019) |
|           |                       | 19 Countries | $\delta^{18}O$, and amino acids | Cengiz et al. (2017) |
|           |                       | 14 Countries | $\delta^{18}O$, and amino acids | Peng et al. (2019) |
|           |                       | 12 Countries | $\delta^{18}O$, and amino acids | Liu et al. (2019) |
|           |                       | 17 Countries | $\delta^{18}O$, and amino acids | Liu et al. (2020) |

Pakistan. It is sold at a price that is two to three times higher than that of other types of long-grain rice.\textsuperscript{77} Thai Hom Mali rice is internationally well-known as Thai jasmine rice. Thai Hom Mali rice is grown in the Thung Kula Rong Hai area, and it is the highest quality jasmine rice. It is recognized by the EU as a GI product.\textsuperscript{35} Koshihikari is a cultivar of Japanese rice, and it is the most famous premium-quality rice. Koshihikari is cultivated not only in Japan, but also in various countries such as Australia and the USA.\textsuperscript{78} Koshihikari is exported to foreign countries such as China. The Koshihikari rice that is produced in Japan was sold at a price that is approximately 50 times the price of ordinary Chinese rice in Chinese supermarkets in 2007.\textsuperscript{79} Thus, Koshihikari rice is often the subject of geographical origin mislabeling. A tracing system that identifies the origin based on
| Country of origin | Cultivation regions        | n  | δ¹³C, ‰   | δ¹⁵N, ‰ | δ¹⁸O, ‰ | δD, ‰ | δ³⁴S, ‰ | Reference          |
|------------------|---------------------------|----|-----------|---------|--------|-------|--------|-------------------|
| India            | Haryana                   | 4  | −27.7     | 20.4    |        |       |        | Kelly et al. (2002)²⁹ |
| India            | Punjab                    | 2  | −27.6     | 23.2    |        |       |        |                   |
| India            | Purchased in Madras       | 10 | −27.7     | 22.0    |        |       |        |                   |
| India            | Unknown                   | 7  | −27.7     | 23.0    |        |       |        |                   |
| India            | Unknown                   | 5  | −26.1     | 23.3    |        |       |        |                   |
| India            | Camargue                  | 3  | −24.1     | 25.1    |        |       |        |                   |
| Italy            | Bariago                   | 1  | −24.8     | 25.4    |        |       |        |                   |
| Italy            | Casalino                  | 2  | −25.8     | 23.7    |        |       |        |                   |
| Italy            | Ferrara                   | 1  | −25.5     | 25.2    |        |       |        |                   |
| Italy            | Santhia                   | 1  | −25.2     | 23.9    |        |       |        |                   |
| Italy            | Tricerro                  | 1  | −25.9     | 24.9    |        |       |        |                   |
| Italy            | Vercelli                  | 6  | −26.0     | 23.9    |        |       |        |                   |
| Italy            | Unknown                   | 6  | −25.7     | 25.0    |        |       |        |                   |
| Spain            | Seville                   | 4  | −25.6     | 28.2    |        |       |        |                   |
| Spain            | Unknown                   | 1  | −25.4     | 29.1    |        |       |        |                   |
| USA              | Arkansas                  | 6  | −26.1     | 27.0    |        |       |        |                   |
| USA              | Louisiana                 | 2  | −26.8     | 25.2    |        |       |        |                   |
| USA              | Mississippi               | 6  | −25.6     | 25.6    |        |       |        |                   |
| USA              | Texas                     | 6  | −26.8     | 26.6    |        |       |        |                   |
| Japan            | Hokkaido                  | 14 | 19.7      |        |        |       |        | Suzuki et al. (2009)³⁹ |
| Japan            | Nagano                    | 10 | 20.8      |        |        |       |        |                   |
| Japan            | Ibaragi                   | 5  | 22.5      |        |        |       |        |                   |
| Japan            | Okinawa                   | 11 | 25.1      |        |        |       |        |                   |
| Japan            | Fukushima                 | 4  | −27.8     | 21.6    |        |       |        | Korenaga et al. (2013)³¹ |
| Japan            | Nagano                    | 10 | −26.9     | 21.0    | −88    |       |        |                   |
| Japan            | Tochigi                   | 26 | −27.5     | 21.4    |        |       |        |                   |
| Japan            | Niigata                   | 44 | −27.4     | 21.2    | −92    |       |        |                   |
| Japan            | Chiba                     | 7  | −27.3     | 21.6    |        |       |        |                   |
| Japan            | Me                       | 3  | −27.4     | 22.7    |        |       |        |                   |
| Japan            | Ibaragi                   | 3  | −27.3     | 22.1    |        |       |        |                   |
| Japan            | Shimane                   | 4  | −27.3     | 1.7     | −94    |       |        |                   |
| USA              | California                | 50 | −26.4     | 25.8    | −85.7  |        |        |                   |
| Australia        | California                | 9  | −25.6     | 26.1    |        |       |        |                   |
| Thailand         | 21 −27.1 5.4             | 32.6 −72.6 |        |         |        |        | Li et al. (2015)³² |
| Vietnam          | 1 −26.6                  | 25  |        |       |        |        |                   |
| Vietnam          | 6 −26.3                  | 25.3 |        |       |        |        |                   |
| Australia        | 4 −26.87 5.61            | 26.70 −33.75 |        |         |        |        |                   |
| China            | 4 −26.92 5.98            | 17.36 −60.92 |        |         |        |        |                   |
| France           | 3 −26.86 4.18            | 19.84 −48.75 |        |         |        |        |                   |
| India            | 30 −27.49 3.23           | 21.72 −46.94 |        |         |        |        |                   |
| Italy            | 5 −26.78 4.90            | 20.86 −57.42 |        |         |        |        |                   |
| Japan            | 27 −26.98 3.25           | 19.58 −59.89 |        |         |        |        |                   |
| Japan            | 2 −25.92 4.14            | 21.27 −54.16 |        |         |        |        |                   |
| Malaysia         | 6 −28.42 1.29            | 19.89 −53.08 |        |         |        |        |                   |
| Myanmar          | 2 −27.26 1.84            | 19.07 −44.71 |        |         |        |        |                   |
| Pakistan         | 18 −27.37 2.83           | 22.32 −46.98 |        |         |        |        |                   |
| Spain            | 3 −26.14 8.76            | 21.90 −43.62 |        |         |        |        |                   |
| Taiwan           | 10 −27.26 3.56           | 20.66 −44.33 |        |         |        |        |                   |
| Thailand         | 64 −27.33 2.81           | 20.23 −52.25 |        |         |        |        |                   |
| USA              | 20 −26.62 2.61           | 21.90 −53.03 |        |         |        |        |                   |
| Vietnam          | 16 −27.69 1.80           | 19.35 −50.80 |        |         |        |        |                   |
| Korea            | Suwon                     | 9  | −27.54 6.3 | 23.3    | 2.10   | Chung et al. (2015)³³ |
| Korea            | Shanghai                  | 9  | −27.94 5.75 | 22.44   | 4.41   |                   |
| Philippines      | Los Banos                 | 9  | −28.88 3.58 | 20.77   | 9.02   |                   |
| China            | Fujin (superior spikelet) | 3  | −26.8 5.6 | 22.2 −81.4 | Chung et al. (2016)³⁴ |
| China            | Fujin (inferior spikelet) | 3  | −27.5 5.5 | 21.5 −82.8 |                   |
| China            | Wuchang (superior spikelet)| 3 | −26.3 5.7 | 20.9 −96.1 |                   |
| Thailand         | Sisaket province          | 7  | −27.09   | 24.53   |        |        |                   |
| Thailand         | Yasothon province         | 8  | −27.32   | 25.68   |        |        |                   |
| Thailand         | Roi Et province           | 13 | −27.28   | 25.54   |        |        | Kukusamude and Kongsri (2018)³⁵ |
| Thailand         | Surin province            | 4  | −26.79   | 24.07   |        |        |                   |
| Thailand         | Mahasaraksham province    | 5  | −27.41   | 25.54   |        |        |                   |
analytical methods is required to resolve these authenticity problems. Many studies have reported the use of stable isotope analysis to identify the cultivation area of rice samples. Kelly et al. (2002) reported the δ13C and δ18O values of rice samples from five countries (India, Pakistan, France, Italy, and Spain) (Table 2). The δ13C values of Indian and Pakistani rice (−27.4%) were relatively lower than those of European countries (−25.5%) and the USA (−26.2%). The δ18O values of Indian and Pakistani rice (+22.3%) were relatively lower than those of European countries (+25.3%) and USA (+26.3%). The Himalayan region is a high-altitude area, and precipitation in that region has lower δ18O values. These results indicate that the δ13C and δ18O values are significantly correlated with the geographical origin of rice samples. Suzuki et al. (2008) reported the δ13C and δ18O values of Koshihikari rice from Australia, the USA, and Japan (Table 2). In that study, 38 samples from Japan, 16 samples from Australia, and 9 samples from the USA were collected. Then, their carbon and oxygen isotope ratios were analyzed, and the possibility of determining the origin was verified. The δ13C values of Koshihikari from the USA (−25.6 ± 0.3%) were higher than those from Japan (−26.9 ± 0.4%) and Australia (−27.1 ± 0.3%). The δ18O values of Koshihikari were high in the samples from countries in the following order: Australia (35.2 ± 1.2%), USA (26.1 ± 1.8%), and Japan (22.6 ± 1.0%).

The δ13C and δ18O values of Chinese rice samples with unknown varieties were very close to those obtained for Japanese rice samples. Because geographical factors such as latitude and climate are similar in Japan and China, there are overlaps in the distribution of stable isotope ratios, and it is difficult to distinguish them using only stable isotope analysis. Suzuki et al. (2009) reported the δ13C, δ15N, and δ18O values of rice samples, soil, and water from the rice fields to verify the effect of growth conditions on rice samples. Comparisons between the δ13C values of rice grown in paddy fields and upland fields showed that the δ13C values of rice from the upland fields were about 1% higher than those from the paddy fields. Generally, there is a positive correlation between the water utilization efficiency (WUE) of plants and the carbon isotope ratio of plant tissues. This result indicates that the δ13C values of rice samples indicated the WUE in the rice field and could be an indicator for tracing the geographical origin of rice. A comparison of the δ15N values of rice and soil samples from rice fields showed positive correlations between the δ15N values of rice and soil. Moreover, organic rice samples showed higher δ15N values than conventional rice. Generally, organic fertilizers, such as cow, chicken, and pig manure, show higher δ15N values than chemical fertilizers. Thus, the δ15N values of rice samples would be an indicator for tracing the origin of organic rice. A comparison between the δ18O values of rice and water collected from rice fields showed positive correlations between the δ18O values of rice and water. The δ18O values of rice mainly indicate those of water supplied to the plants. The δ18O values of rainwater and groundwater depend on geographical factors, such as latitude, altitude, and inland effect. Thus, these results indicate that the δ13C and δ18O values of rice samples could be an indicator for tracing the geographical origin of rice.

Li et al. (2015) reported the δ13C, δ15N, and δ18O values of rice samples from 15 countries (Australia, China, France, India, Italy, Japan, Korea, Malaysia, Myanmar, Pakistan, Spain, Taiwan, Thailand, the USA, and Vietnam) (Table 2). The δ13C values of rice samples ranged from −28.85 to −25.52%. Malaysian rice samples showed the lowest δ13C values, ranging from −28.17 to −28.85%. The mean δ13C values of rice were compared with the mean annual temperature and mean water vapor pressure of the cultivation regions, which were obtained using an online climate estimator. Rice samples from countries with higher annual average temperatures tend to have lower δ13C values. The trend observed was that higher mean water vapor pressure decreases the δ13C values of rice samples. The δ15N values of rice samples ranged from 0.24 to 12.01%. Spanish rice samples showed the highest δ15N values, ranging from 6.55 to 12.01%. In this study, a comparison of the δ15N values of organic and conventional rice samples shows that a significant difference could not be observed, although the organic rice generally has a higher median δ15N value than the conventional rice. The δ18O and δD values of the rice samples ranged from 15.17 to 29.79% and from −70.95 to −26.81%, respectively. Australian rice samples showed significantly higher δ18O and δD values than those from other countries. A comparison of the δ18O and δD values of rice samples and precipitation for the rice cultivation regions showed a positive correlation. These results indicate that the use of the stable isotope analysis of rice samples can be used in various countries, and it could be a potential tool for tracing their geographical origin.

3-2 Tracing the geographical origin of beef
Meat is an important source of nutrition worldwide, and its global demand is increasing. Beef is one of the most commonly consumed meat forms globally, and its consumption is increasing with the increasing global population and consumer income. Beef has become a key source of protein, and this is a major factor driving the increase in demand for beef in the market. In 2019, global production of beef was 72.199 million tons. The major beef-producing countries are the USA (12.291 million tons), the EU (7.934 million tons), China (6.866 million tons), India (2.549 million tons), and Argentina (3.160 million tons). The USA is the largest consumer of beef, and the consumption in the EU, Argentina, and India is increasing with their production. The top three beef-exporting countries are Brazil (2.194 million tons), India (1.510 million tons), and Australia (1.541 million tons). Japanese beef “Wagyu” is one of the most well-known Japanese agricultural products. The high-grade “Wagyu” from Japan has been acknowledged for its rich marbling and taste. In recent years, Japan has exported beef to several foreign countries, such as the USA, Canada, Hong Kong, Macau, Mexico, New Zealand, Vietnam, Cambodia, Singapore, the Philippines, and since 2014, it has also exported to the EU. Moreover, Wagyu beef is also bred in Australia and the USA. The distribution and subsequent export of foreign-grown “Wagyu” has significantly expanded. Australia is now the largest Wagyu supplier in the global market. In Japan, much of the Wagyu is branded with the name of the production regions, which have established their own standards related to characteristics such as the growing methods and quality, and only the excellent meat that satisfies the standards is eligible for certification as branded beef. “Matusaka Beef” in Mie prefecture, “Kobe Beef” in Hyogo prefecture, “Omi Beef” in Shiga prefecture, and “Yonezawa Beef” in Yamagata prefecture are sold at high prices, and they are also well-known abroad. Each brand has its own appeal as a local specialty product.
Heaton et al. (2008) reported the δ¹³C, δ¹⁵N, δD, and δ¹⁸O values of beef samples from 17 countries (Table 3). The δ¹³C values of beef samples ranged from −26.32 to −11.05. Brazilian beef samples showed values above −13. Some samples from South America and England showed high δ¹⁵N values exceeding 9%. These high δ¹⁵N values may indicate the use of fishmeal or marine products such as seaweed in the cattle feed. These results indicate that the δ¹³C and δ¹⁵N values depend on the local feeding practice. The δ¹⁸O and δD values of lipids extracted from the beef samples ranged from 17.9 to 32.3 and from −220.1 to −140.5, respectively. Beef samples from higher latitudes, such as Scotland, New Zealand, Shetland, and England, showed lower δ¹⁸O and δD values. A comparison of the δ¹⁸O values of lipids and the distance of the production region from the equator showed a negative correlation. These results indicate that there are wide ranges of δ¹⁸O and δD values.

Table 3  Stable isotope ratios of beef samples obtained from previous studies

| Country of origin | Defatted beef | Lipid |
|-------------------|--------------|-------|
|                   | n     | δ¹³C | δ¹⁵N | δ¹⁸O | δD  | δ¹³C | δ¹⁵N | δ¹⁸O | δD  |
| England           | 78    | −24.34 | 6.7  | 17.9 | −196.9 |
| Scotland          | 19    | −25.75 | 7.1  | 18.2 | −208  |
| Ireland           | 26    | −24.52 | 6.6  | 18.3 | −189.8 |
| Denmark           | 4     | −22.56 | 6.6  | 17.7 | −211.3 |
| France            | 3     | −22.5  | 6.1  | 19.0 | −216.6 |
| Germany           | 28    | −22.53 | 6.2  |      |       |
| Austria           | 25    | −21.51 | 5.8  |      |       |
| Italy             | 26    | −21.24 | 4.7  | 18.3 | −220.1 |
| Spain             | 1     | −21.48 | 5.8  | 20.3 | −276.4 |
| Argentina         | 10    | −20.79 | 6.6  | 22.3 | −181.6 |
| Uruguay           | 3     | −20.28 | 6.8  | 22.8 | −180  |
| Brazil            | 22    | −11.36 | 6.7  | 21.4 | −183  |
| North America     | 2     | −11.05 | 6    | 17.9 | −214.2 |
| Australia         | 3     | −16.87 | 6.1  | 23.4 | −157.7 |
| New Zealand       | 6     | −26.32 | 5.8  | 19.4 | −214.6 |
| Namibia           | 1     | −12.46 | 7.3  | 32.3 | −151  |
| Swaziland         | 1     | −15.33 | 7.3  | 26.1 | −140.5 |
| Japan             | 20    | −19.3  | 7.9  | 10.4 |       |
| USA               | 17    | −12.6  | 6.0  | 10.8 |       |
| Australia         | 21    | −22.1  | 6.8  | 17.2 |       |
| USA               | 20    | −12.3  | 6.0  | 10.9 |       |
| Australia         | 53    | −22.5  | 6.6  | 16.0 |       |
| New Zealand       | 3     | −24.1  | 6.3  | 12.1 |       |
| Japan             | 66    | −18.5  | 7.5  | 10.9 |       |
| Japan (Tokachi, Hokkaido) | 20  | 9.1    | |
| Japan (Yamagata)  | 11    | 9.7    | |
| Japan (Matsuzaka, Mie) | 14  | 11.0   | |
| Japan (Ishigak, Okinawai) | 21  | 13.5   | |
| Austria           | 6     | −22.16 | 5.29 | −122.65 | 1.99 |
| Brazil            | 17    | −10.97 | 7.21 | −106.32 | 9.85 |
| France            | 4     | −19.62 | 7.21 | −108.73 | 2.68 |
| Germany           | 6     | −23.11 | 9.02 | −124.44 | 2.37 |
| Ireland, pasture  | 20    | −27.78 | 9.39 | −122.32 | 4.69 |
| Ireland, concentrate | 20   | −25.1  | 6.18 | −112.40 | 5.93 |
| Ireland, retail pasture | 18   | −27.02 | 4.99 | −113.99 | 10.49 |
| Ireland, retail unknown | 8    | −26.84 | 7.07 | −114.40 | 8.07 |
| Italy             | 18    | −20.25 | 4.97 | −105.88 | 1.50 |
| Spain             | 7     | −21.71 | 5.85 | −112.88 | 5.60 |
| United Kingdom    | 20    | −25.61 | 7.72 | −110.44 | 4.35 |
| U.S., retail pasture | 12   | −18.01 | 6.74 | −105.15 | 0.69 |
| U.S., retail unknown | 10   | −13.03 | 6.46 | −104.53 | −0.40 |
| Japan (Matsuzaka) | 6     | −21.4  | 6.6  | 12.3 |       |
| Japan (Hida)      | 4     | −17.1  | 6.3  | 11.6 |       |
| China (Jilin)     | 3     | −12.65 | 5.39 | −118.7 |     |
| China (Hebei)     | 3     | −16.92 | 4.78 | −122.6 |     |
| China (Ningxia)   | 3     | −19.62 | 5.58 | −113.6 |     |
| Canada            | 50    | −13.49 | 7.10 | 11.24 | −117.66 |
| Argentina         | 50    | −13.56 | 8.22 | 16.81 | −72.78 |
| Uruguay           | 50    | −16.38 | 8.30 | 16.98 | −103.82 |
| New Zealand       | 50    | −26.99 | 8.19 | 14.04 | −129.7 |
| Brazil            | 50    | −11.50 | 5.89 | 20.78 | −101.48 |
| China             | 42    | −15.52 | 4.52 | 8.78  | −119.03 |

Heaton et al. (2008) reported the δ¹³C, δ¹⁵N, δD, and δ¹⁸O values of beef samples from 17 countries (Table 3). The δ¹³C values of beef samples ranged from −26.32 to −11.05. Brazilian beef samples showed values above −13. The δ¹³C values of beef from England, Scotland, and Ireland were less than −20%. The δ¹³C values of beef were reflective of the proportion of C₃ and C₄ plant materials in the diets of the cattle. The δ¹⁵N values of beef samples ranged from 4.7 to 7.3%. Some samples from South America and England showed high δ¹⁵N values exceeding 9%. These high δ¹⁵N values may indicate the use of fishmeal or marine products such as seaweed in the cattle feed. These results indicate that the δ¹³C and δ¹⁵N values depend on the local feeding practice. The δ¹⁸O and δD values of lipids extracted from the beef samples ranged from 17.9 to 32.3% and from −220.1 to −140.5%, respectively. Beef samples from higher latitudes, such as Scotland, New Zealand, Shetland, and England, showed lower δ¹⁸O and δD values. A comparison of the δ¹⁸O values of lipids and the distance of the production region from the equator showed a negative correlation. These results indicate that there are wide ranges of δ¹⁸O and δD values.
of lipids in beef samples in various countries, and use of these values may be a potential tool for tracing their geographical origins.

Osorio et al. (2011) reported the δ13C, δ15N, δD, and δ34S values of beef samples from nine countries (Table 3).42 The δ13C values of beef samples ranged from −10.97 to −27.78‰. The beef samples from Brazil and the USA showed the highest 13C values. However, some pasture-fed beef samples from the USA showed similar δ13C values as those from other countries, such as Germany, Spain, and Austria. The δD values of the beef samples ranged from −130.7 to −94.4‰. The beef samples from higher latitudes and colder climate countries, such as Brazil and Italy. The highest mean δD values were found in the U.S. retail beef of unknown origin (−104.5‰) and Italian beef samples (−105.88‰). The δD values of animal tissues are indicative of feed and drinking water. The high δD values of U.S. beef samples may be explained by the effect of the warm and dry climate in the production regions as well as the high proportion of C₃ plants in the cattle diets. In the same region, the C₃ plants have higher δD values than C₄ plants. The δ34S values of the beef samples ranged from −4.3 to 12.5‰. The highest mean δ34S values were observed in the beef samples from Ireland (10.49‰) and Brazil (9.85‰). The beef samples from the USA showed the lowest δ34S values, ranging from −4.3 to 2.2‰. The δ34S values of animal tissues generally indicate the differences in the primary S source. The differences in the δ34S values of beef may indicate their diets, including the plants cultivated using marine sulfate as a fertilizer or by the deposition of sea-spray sulfate as an aerosol and crops close to the sea. The highest δ34S values were for Ireland beef grown in regions 30–40 km from the sea.

Nakashita et al. (2009) analyzed the stable isotope ratios of beef from Japan, Australia, the USA, and New Zealand, and examined the potential for determining their geographical origin (Table 3).43 The δ13C values of beef were higher in the following order: USA (mean ± standard deviation: −12.3 ± 1.1‰), Japan (−18.5 ± 1.0‰), Australia (−22.5 ± 1.5‰), and New Zealand (−24.1 ± 0.1‰). In general, the proportion of C₃ plants in the USA is extremely high in the diet of cattle. The difference in the proportion of C₃ plants in the cattle diets indicates the difference in carbon isotope ratios of beef in each country. The δ18O values of beef were significantly higher in Australia (16.0 ± 1.5‰) compared to those from Japan (10.9 ± 2.1‰) and USA (10.9 ± 1.1‰). Comparing the δ18O values of precipitation in production regions from the Global Network of Isotopes in Precipitation (GNIP) published by the International Atomic Energy Agency (IAEA), the value in New South Wales (−5 to −4‰) in Australia is higher than that in Japan (−10 to −6‰) and Central America (−10 to −6‰). Further, the δ18O values of Waygu beef produced in four regions within Japan showed different values. Ishigaki beef in Okinawa prefecture, which is the southernmost prefecture in Japan, shows the highest δ18O value (13.5 ± 0.9‰). The lowest δ18O value was obtained for Tokachi beef (9.1 ± 1.8‰) in Hokkaido Prefecture, which is the northernmost Prefecture. These results indicate that the use of stable isotope ratios would be a useful tool for determining the origin of beef.

3-3 Tracing the geographical origin of honey

Honey is a nutritious, healthy, and natural sweet liquid produced by honeybees that consume nectar from flowers. It contains several minerals, enzymes, vitamins, and proteins that possess nutritious and organoleptic properties. In 2018, world honey production totaled 1.851 million tons, including honey from all nectar sources (agricultural plants, wildflowers, and forest trees). The major honey-producing countries are China (447000 tons), the EU (259000 tons), and Turkey (114000 tons). World import and export quantities of honey currently averages 680000 and 64000 tons per year, respectively. Its exports have been increasing. Germany, Japan, the UK, and the USA are the major markets for honey. Manuka honey is one of the most well-known New Zealand honey varieties, and it is sold at a high price owing to its health-related benefits. Some of the premium honey products sold as Manuka honey are adulterated and mislabeled.

Schellenberg et al. (2010) reported the δD, δ13C, δ15N, and δ34S values of protein extracted from honey in 20 European countries.44 The δ13C values of honey protein ranged from −26.8 to −24.2‰. The δD values of honey protein from Iceland showed the lowest δ13C values. The δ13C values of honey protein from Sicily in Italy were the highest. The δ13C values of honey protein increased with an increase in the number of days of sunshine and higher mean temperature, and a decrease in mean humidity. The δ18O values were lower for honey from regions with lower mean temperatures or high humidity, such as Orkney in Scotland (−26.8‰), Mühlviertel in Austria (−26.7‰), Gäuboden in Germany (−26.3‰), or Jylland in Denmark (−26.3‰) than those of the Mediterranean honey, such as honey from Sicily in Italy (−24.2‰) and Carpentras in France (−24.6‰). The same floral from European countries showed relatively large variations depending on the climatic conditions of the area. For example, the acacia honey samples obtained from the moderate and Mediterranean regions were clearly distinguishable by δ13C values. The δ15N values of honey protein from Cornwall in the UK were the highest. The δ15N values of honey protein indicate the soil conditions of the areas where honeybees collected the honey. The high δ15N values of honey protein from Cornwall may reflect the fertilization of the grasslands with seaweed or other products from the marine ecosystem. The δD values of honey protein ranged from −149 to −32‰. The honey from Western Europe in regions close to the Atlantic Ocean showed the highest mean δD values. The lowest δD values were observed in honey from alpine regions or regions far away from the sea, such as Allgäu in Germany (−121‰) and Franconia in Germany (−118‰). The δD values of honey protein decreased with increasing distance from the sea, increasing altitude, and decreasing mean temperature. The δ34S values of honey protein ranged from −2.0 to 11.1‰. The European honey samples were divided into five groups. Group one consisted of samples from Sicily in Italy and Allgäu, which are areas that produce honey characterized by low δ34S values. The second group consisted of samples from approximately 60% of all sampling areas. The third group showed relatively high δ34S values, and included honey from Iceland (8.0‰). The other two groups were characterized by high δ34S values, and included honey from Iceland (9.3‰), Cornwall in the United Kingdom (9.5‰), Laconia in Greece (9.3‰), and the Orkneys in the United Kingdom (11.1‰). The δ34S values of honey protein indicate the soil geological composition of plants. The δ34S values of plants, including nectar and pollen grown in regions close to the sea, are influenced by the high δ34S values of sea-salt sulfate. In addition, there were very small variations in the δ34S values of honey protein in each region. Therefore, the δ34S values of honey protein would be a useful indicator to trace the
geographical origin of honey because these values are less likely to be affected by annual changes or the botanical origin of honey. The results show that the stable isotope ratios in honey protein can be applied to verify the origin of honey.

In Japan, the volume of honey consumed in 2018 was 47329 tons, but only 2826 tons were produced in Japan.64 Because domestic honey production cannot meet the domestic consumption requirement in Japan, 44421 tons were imported in 2018, mainly from China (70.8%).65 The price of Japanese honey is about five times higher than that of imported honey. The difference in price between Japanese and Chinese honey is about five times higher than that of imported honey.

The price of Japanese honey samples, a combination of other analytical methods, such as trace element analysis, is required.67

4 Conclusions

The stable isotope ratios of food and agricultural products indicate their growth conditions, such as geological factors and diets of the livestock, in the production regions. Therefore, the use of the multi-element stable isotope analysis may be a potential tool for tracing the geographical origin of various food materials. However, the creation of a database for the use in inspection of food and agricultural products requires the analysis of a large-volume of samples and verification of annual variation.68 Moreover, for some regions with similar climate conditions, such as Japan and China, it is very difficult to clearly differentiate products by stable isotope analysis. The combination of other analytical methods, such as trace element analysis6,7,10 and strontium (Sr) isotope ratios6,10,89–91 is required to distinguish products from such areas. Especially, the Sr isotope ratio has been used to distinguish between different source origins of agricultural products.6,48–50 For example, in 2002, Kawasaki et al. reported the Sr isotope ratio of Japanese brown rice samples (O. sativa L.) collected from Japan, Australia, California, China and Vietnam for tracing their geographical origin. The Sr isotope ratios of the Japanese rice samples (0.706 to 0.709) were lower than those of the Australian samples (0.715 and 0.717), as well as the Chinese and Vietnamese rice samples (0.710 to 0.711). The combination of Sr isotope and light element isotope ratios would improve the authenticity testing of rice samples.

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