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Mass spectrometry

Tracing the origin of food using MC-ICP-MS

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Goal

To show how non-traditional isotopes can be used for tracing the origin of food.

Introduction

Tracing the origin of food is important for both producers and consumers. For producers, there are various schemes of origin designation that exist (e.g. Regiokorn® - Südtiroler Bauernbund) that pay producers from specific regions significantly above the global market price for that commodity. European legislation on regional food protection considers authenticity as a quality criteria for the food. Food labels (e.g. Protected Denomination of Origin [PDO] and Protected Geographical Indication [PGI]) provide a means to preserve and protect regionally produced foods from generic versions, ensuring quality for the consumer and protection for the regional producers from cheaper imitations.

However, food labeling can be manipulated and used fraudulently. Objective analytical methods are important for reliable food tracing, protecting the authenticity and reputation of high-quality horticultural products labeled with geographical indications.

Traditionally, stable isotopes (e.g. oxygen, hydrogen, carbon) have been used to separate out products of different geographical origin. This has proved to be a powerful technique to identify coffee or beef produced in different parts of the globe (**AN 30418**, **AN 30572**) with distinct climatic regimes. However, for finer differentiation between specific regions or even neighboring valleys, other approaches are required.

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Strontium isotope analysis is an established tool for determining the geographic origin of a wide variety of agricultural products.[1–3] Strontium is usually easily absorbed from soil by plants, even though there is no clear evidence of any metabolic function of the element in plants. Hence, the strontium isotopic signature ($^{87}Sr/^{86}Sr$ ratio) is a fingerprint representative of the soil on which plants were cultivated. Once absorbed, strontium is distributed to other parts of the plant such as leaves or fruits, turning it into a constituent of foodstuffs and thus entering the food web. Subsequently, strontium isotopes can be used to pinpoint the geographical origin of a wide variety of foodstuffs. By combining strontium isotope ratios with the stable isotope ratios of light elements (e.g. H and O) and multi-element analysis, it is possible to gain a complete picture of the environment in which that crop was grown and therefore accurately determine the geographical origin of that foodstuff.

Here we summarize a number of recent publications using the Thermo Scientific™ Neptune™ MC-ICP-MS for strontium isotope analysis in combination with H and O stable isotope analysis and multi-element analysis to determine food provenance.[2–5]

Method
Sampling
Apples (cv. Golden Delicious®, rootstock M9) were collected from orchards within the protected areas for the cultivation of 'Val di Non apples PDO', 'South Tyrolean apples PGI' (from three main cultivation districts, namely Bressanone, Val d'Adige, Val Venosta), 'Valtellina apples PGI', in addition to other cultivation areas located in northern Italy where apples with no geographical indication (GI) are produced (non GI apples) (Fig. 1A). Cereals (rye and spelt) where collected from orchards located in South Tyrol, Trentino and Tyrol (Fig. 1B). From selected orchards, soil samples at the root depth for apple tree and cereals were collected. From two experimental orchards, it was possible to collect samples from different apple tree varieties (Fuji, Golden Delicious, Granny Smith, Royal Gala) and cereal species (barley, oat, rye, spelt) grown in close proximity within the same plot. At each sampling site, the number of biological replicates varied from 5–10 in the apple orchards and 3-5 in the cereal fields, for a total of 610 and 660 samples, respectively.
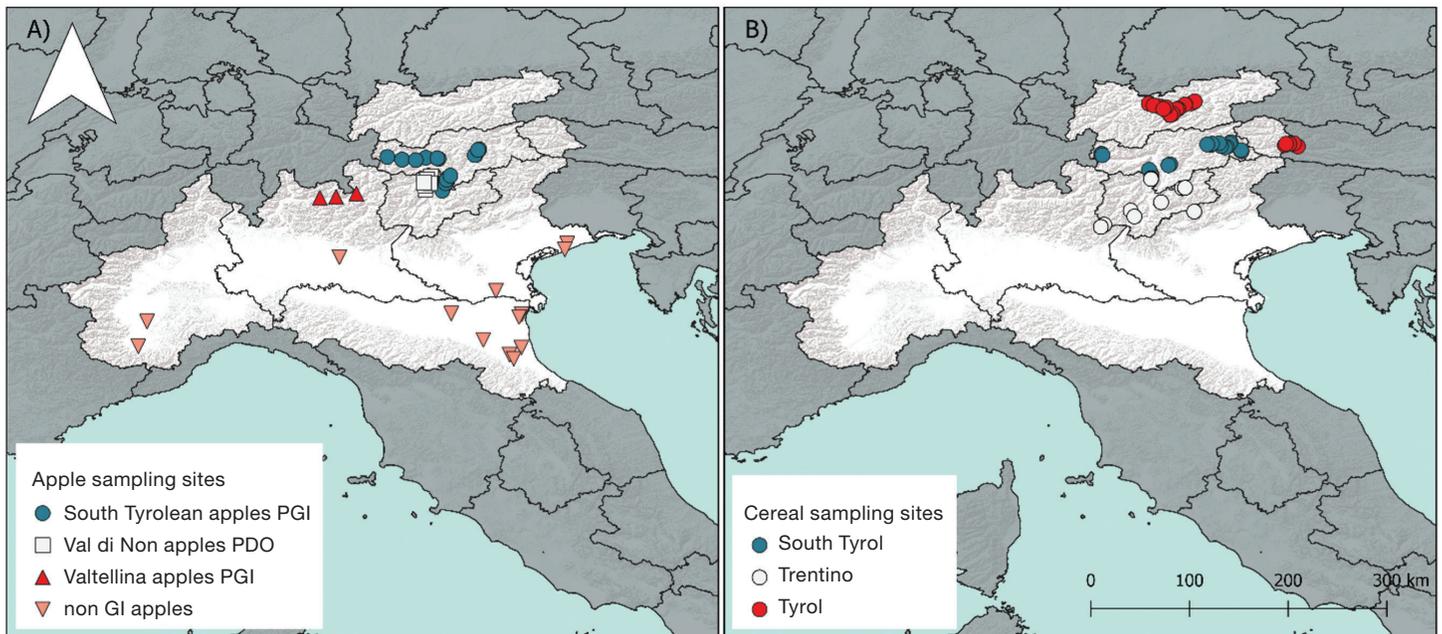

Figure 1. Map showing the location of the sampling sites for A) apples and B) cereals, grouped according to the cultivation area

Multi-element analysis

Apple and cereal samples were acid digested with nitric acid in a microwave digestion system.[3,4] The bioavailable mineral fraction from soil samples was obtained via extraction using a buffer solution according to DIN ISO 19730. After filtration, an aliquot of each sample was diluted for multi-element analysis. Quantitative analysis of the multi-element composition was performed using the Thermo Scientific™ iCAP™ Q ICP-MS. The following elements were quantified: beryllium (Be), sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), rubidium (Rb), strontium (Sr), molybdenum (Mo), silver (Ag), cadmium (Cd), antimony (Sb), barium (Ba), thallium (Tl), lead (Pb), and uranium (U). Elements for which the concentration was below the quantification limits were excluded from data analysis.

Strontium isotope analysis

Strontium was separated from the matrix using a Sr-specific resin following the manual procedure described by Durante *et al*.[1] Typical throughput of samples is 60/24 h, limited by the number of available positions into the vacuum manifold.

The $^{87}Sr/^{86}Sr$ ratio was measured after Sr/matrix separation using a Neptune Plus MC-ICP-MS. Measurements were performed as standard-sample bracketing using NIST® SRM 987 as the reference standard. Raw data correction included blank subtraction, mass bias correction after normalizing the $^{88}Sr/^{86}Sr$ value to the IUPAC value of 8.3752,[6] and interference correction of ^{86}Kr and ^{87}Rb. Finally, the values obtained for the NIST SRM 987 in each sequence were averaged and used for the correction factor calculation to correct for the possible instrumental drift. External reproducibility was $2\sigma < 0.00002$ (n = 134).[2,3]

Hydrogen and oxygen isotope analysis

For apples only, powdered samples were preventively oven-dried at 65 °C for 48 h to remove water traces. Samples were weighted into silver cups for hydrogen and oxygen isotope analysis using a Thermo Scientific™ TC/EA High Temperature Conversion Elemental Analyzer coupled to a Thermo Scientific™ DELTA™ V Advantage Isotope Ratio Mass Spectrometer (IRMS).[4]

Results & Interpretation

Strontium isotope analysis

Strontium isotopes are a useful tracer of food origin as the isotopic composition of the food stuff mirrors that of the soil from which it is grown. This was verified both for fruit trees and cereal crops, for which a clear 1:1 relationship between soil and produce $^{87}Sr/^{86}Sr$ ratio can be observed (Figure 2).
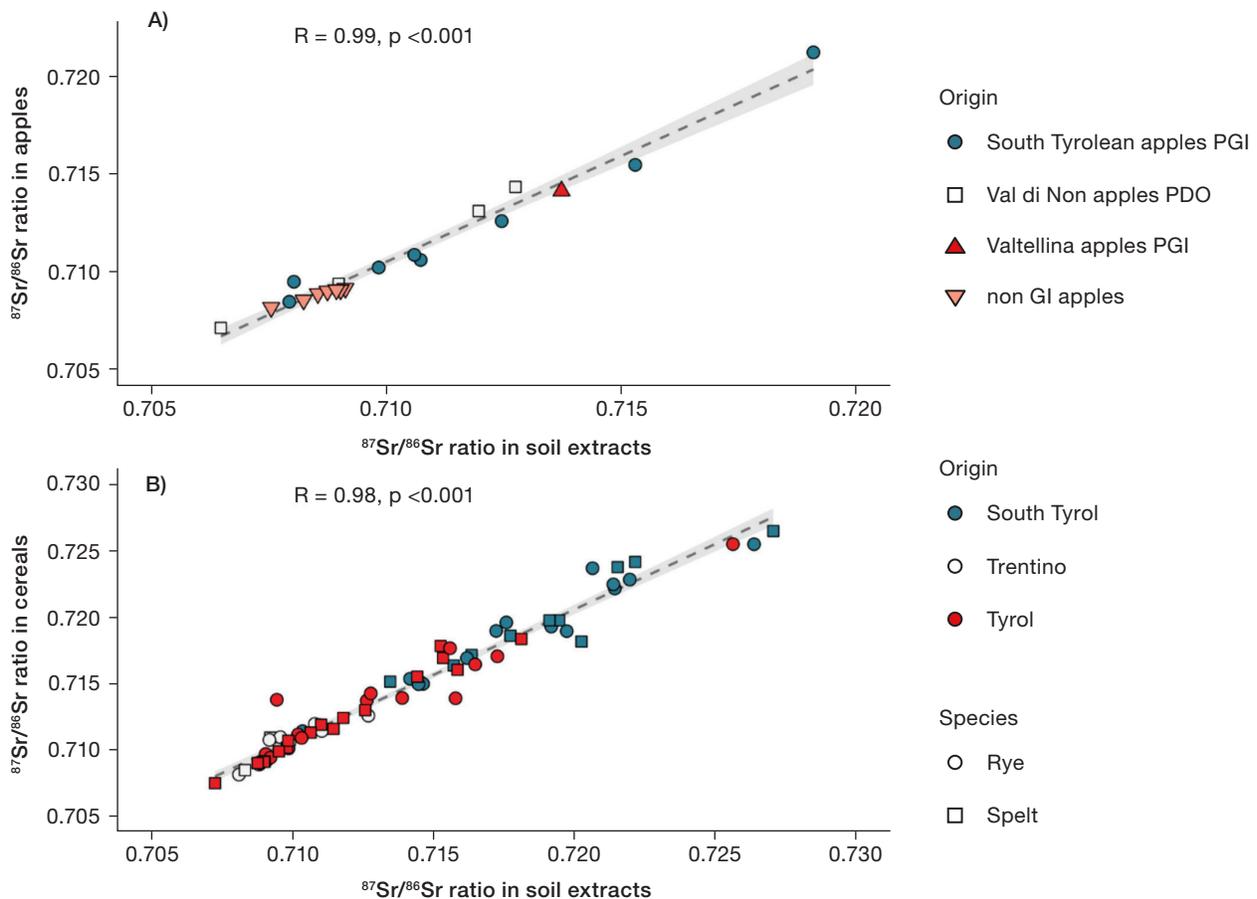

Figure 2. Correlation between the soil $^{87}Sr/^{86}Sr$ and produce $^{87}Sr/^{86}Sr$ for A) apples and B) cereals from Northern Italy

Furthermore, results obtained for different apple varieties and cereal grain species grown on small parcels of land in close proximity within the same experimental field fell in a narrow range of isotope values (Figure 3). Differences among groups were not significant (Kruskal-Wallis, p >0.05) and the data variability is likely to be attributed to the soil characteristics and the spatial distribution of the samples rather than isotope fractionation among different varieties or species. This allows the creation of regional databases for the strontium isotope ratio that can be used as reference regardless of the analyzed products.[5]

Grouping the produce based on cultivation areas, it is possible to identify different regions by the strontium isotope composition (Figure 4). In the case of cereals, regions can be statistically separated (Kruskal-Wallis, p <0.01) based on the sample Sr isotope ratios. However, substantial variability can be found from site to site within each cultivation area, with many regions having similar and overlapping $^{87}Sr/^{86}Sr$ values, due to similar geolithological features, which cannot be statistically separated, as in the case of the apple study (Figure 4A).
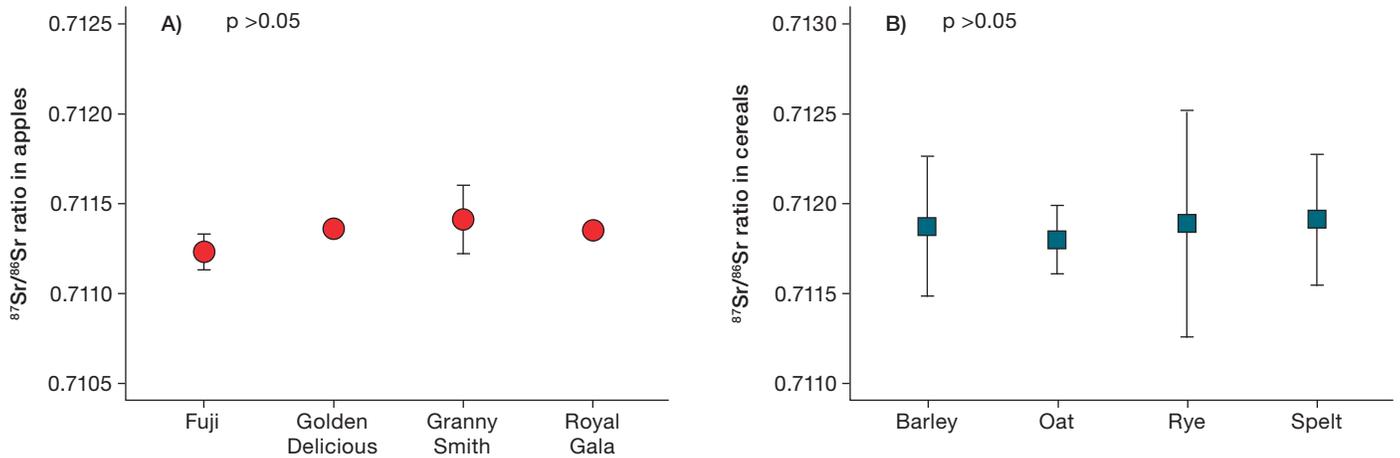

Figure 3. Comparison of the $^{87}Sr/^{86}Sr$ ratio of different A) apple varieties and B) cereal species grown in close proximity
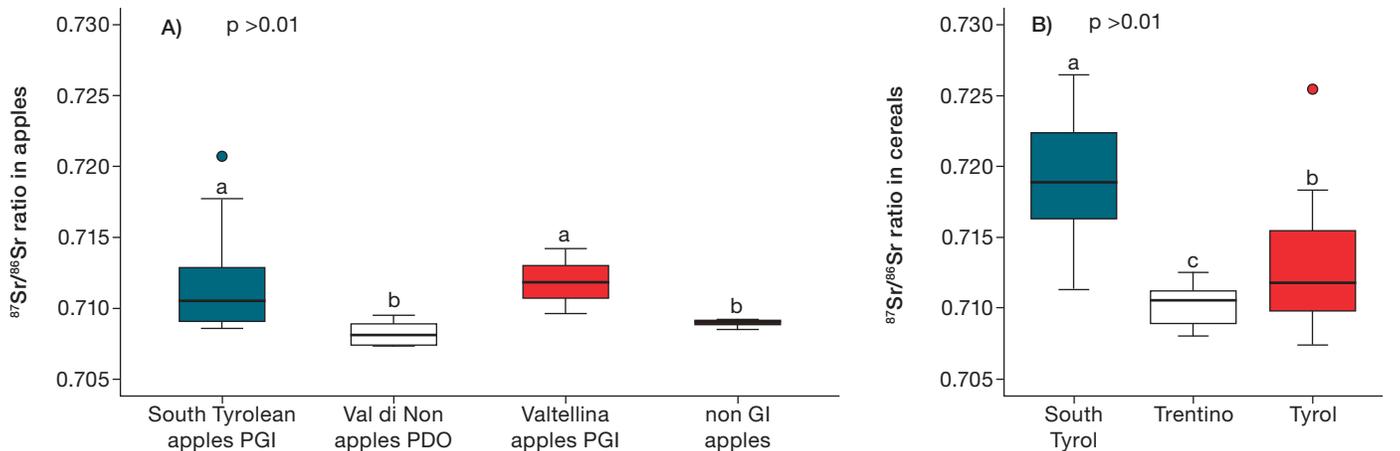

Figure 4. Comparison of regional $^{87}Sr/^{86}Sr$ ratios for A) apples and B) cereals

A multivariate approach

In order to better differentiate regions, it can be helpful to combine strontium isotope data with other isotopic and elemental data. Supervised multivariate data analysis, such as linear discriminant analysis (LDA), can be applied for the development of classification methods to obtain a comprehensive evaluation of the multi-element and multi-isotope composition of apples and cereals cultivated in different regions, respectively.

For the apple study, LDA was applied to develop an origin classification model for apple samples based on their multi-isotope and multi-element composition. The model balanced accuracy was higher than 95%, with a false discovery rate as low as 7%. The first three linear discriminant (LD) functions explained respectively 54%, 31% and 15% of the total variance. LD1 clearly discriminates Val di Non apples PDO from other apples (Figure 5A). The separation of the samples from the three other cultivation areas can be clearly appreciated plotting the second and third discriminant function (Figure 5B). The variables with the highest contribution to classification in LD1, identified by means of their discriminant coefficients, were given by three concentration ratios: Ca/Ba, Sr/Ba, and Ca/Sr. The concentration

of Ca, Mn, and Ba contributed mostly to LD2. The three main contributors to LD3 were Sr and Ca concentrations and the Sr/Ba concentration ratio.

A second model was developed with a specific focus on South Tyrolean apples PGI. Results of the LDA showed that the three apple districts of South Tyrol, namely Bressanone, Val d'Adige, and Val Venosta, can be perfectly distinguished, with a 100% model accuracy (Figure 5C). The variance explained by the two discriminant functions was 63% and 37%, respectively, with the $^{87}Sr/^{86}Sr$ ratio, Rb concentration, and Fe concentration contributing mostly to LD1 and the Ca/Sr concentration ratio, Sr concentration, and Cu concentration to LD2.

For the cereal study, the best LDA model to classify samples based on their origin was obtained including a restricted number of variables, namely the Sr isotope ratio and the K, Mo, and Sr concentrations. Independently from the sample species, this combination of variables led to a satisfactory sample separation (Figure 6), with good accuracy at discriminating all cereal samples based on origin (90% balanced accuracy, 14% false discovery rate).
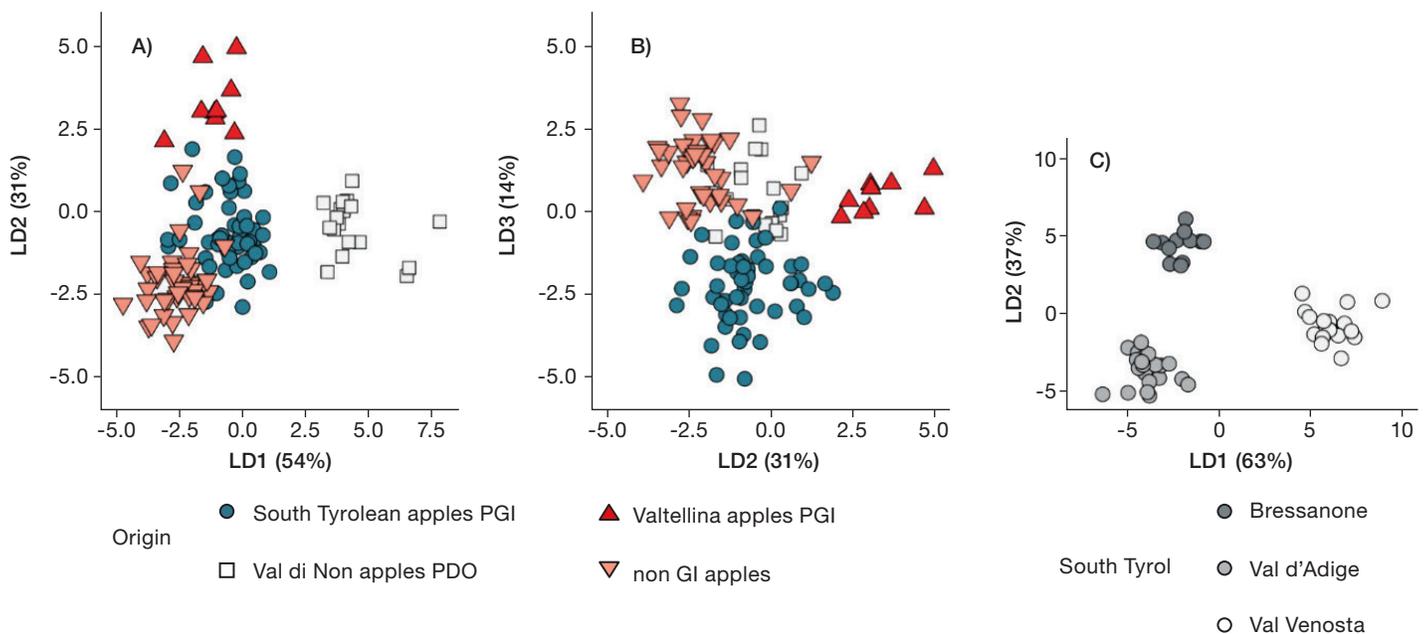

Figure 5. Two-dimensional-score plots of the LDA for apple samples cultivated in A) and B) Northern Italy, C) South Tyrol
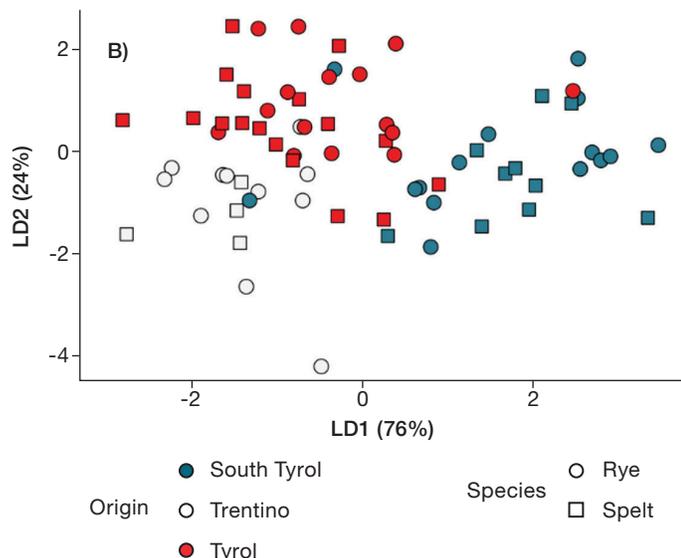
Figure 6. Two-dimensional-score plot of the LDA for cereal samples using the sample origin as grouping factor.

The future of MC-ICP-MS in food provenance

MC-ICP-MS is a powerful tool for food provenance analysis. In addition to strontium, there are a number of other non-traditional isotope systems that have been used for determining the origin of food, such as lead and boron. Lead is continually emitted from natural and anthropogenic sources into the atmosphere and deposited on the terrestrial surface with dust and rainfall.[7] During circulation in the atmosphere and the lithosphere, some lead is absorbed by plants in the form available for bioaccumulation. The lead isotopic signature in plants is caused both by mixing of anthropogenic and natural lead emissions with different contributions. Boron uptake by plants is controlled by soil properties, such as clay composition and pH. Natural variations of boron isotope ratio of the soil are therefore reflected in the plants. By combining lead, boron and strontium isotopes, it is possible to gain insights into the atmosphere, soil and geology from which the food was grown. The use of lead and boron isotopes as a tool in provenance and authentication studies has been successfully demonstrated on wine.[8–10]

The latest MC-ICP-MS from Thermo Fisher Scientific, the Thermo Scientific™ Neoma™ MC-ICP-MS, makes food origin studies even easier. Neoma MC-ICP-MS is controlled by the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) platform software, a workflow-driven software that can be operated in compliance with 21 CFR part 11. Furthermore, Qtegra ISDS Software controls a number of other Thermo Scientific instruments, such as the Thermo Scientific™ DELTA™ Q IRMS and the 253 Plus™ 10kV IRMS for Gas IRMS, and the iCAP™ TQ ICP-MS and iCAP™ PRO ICP-OES for trace elemental analysis. This common workflow across multiple instruments means that cross-device training and adoption of new instrumentation is faster and easier than ever before, dramatically improving laboratory productivity.

Neoma MC-ICP-MS potentially offers further improvements in productivity with the MS/MS option. This option contains patented pre-cell mass filter technology, which allows matrix elements to be removed without the need for column chemistry. For some food stuffs, such as wine, the MS/MS option potentially allows users to measure a dilute sample directly without any pre-treatment.

Conclusions

Strontium isotope analysis techniques are a powerful tool for determining the provenance of food. We have demonstrated the principle on apples and cereal grains using the Neptune Plus MC-ICP-MS. The $^{87}Sr/^{86}Sr$ of crops directly correlates to the $^{87}Sr/^{86}Sr$ of the soil and rock that the crops were grown in. There appears to be no inter-species fractionation in apples and cereals. By combining Sr isotope ratios with H and O isotope ratios and multielement profile, it is possible to create models to accurately allocate crops to particular regions. This is a valuable tool for authenticating food origin claims, protecting regional agricultural practices and ensuring quality for consumers. The development of new analytical solutions that ease sample preparation and analysis could further improve the research and applications in this field.

Acknowledgments

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