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Brief Research Report

Sr isotope ratio in vegetable crops and apple trees depends on that of the soil environment while is unaffected by the genotype

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Abstract: The ^{87}Sr/^{86}Sr ratio is an effective geographical tracer for horticultural products. In plants this ratio reflects closely the characteristics of the growing area. However, information about the variability of this parameter when measured in different plant species or cultivars is still scarce. In this work, we have tested the hypothesis that, when plants are growing in the same environment, their ^{87}Sr/^{86}Sr ratio is independent from the plant species or cultivar. For this, four to six vegetable species were collected from two fields in different locations in South Tyrol (Italy), together with the corresponding soils. Additionally, within a single apple orchard located in the same area, apple leaves were collected from trees of five cultivars. The ^{87}Sr/^{86}Sr ratio was measured applying an established and validated method. In general, vegetable species growing in the same field had similar ^{87}Sr/^{86}Sr ratios and showed a lower variability compared to their corresponding soils, while a significant difference was found comparing the ^{87}Sr/^{86}Sr ratios of the two vegetable fields. Apple leaves sampled from different tree cultivars also did not show a significant difference in their ^{87}Sr/^{86}Sr ratio. We concluded that the ^{87}Sr/^{86}Sr ratio in vegetables and apple trees was affected by the soil, but not significantly by the type of species or cultivar. Therefore, within limited areas, the results of the ^{87}Sr/^{86}Sr ratio analysis based on samples of a certain species/cultivar can be extended to other similar plants growing in the same site.

Keywords: horticultural products; geographical tracer; ^{87}Sr/^{86}Sr; MC ICP-MS

1. Introduction

The geographical origin of food and agricultural products is becoming increasingly important for consumers. Recent studies reported that consumers generally prefer domestic over imported foods, and in emerging countries, people showed a preference for products derived from developed countries (Thøgersen et al., 2019). Hence, the origin of food is an important criterion for the consumers' purchase decisions. However, mislabeling (including all frauds related to misleading information on the label) was reported to be the most common type of food fraud in the EU in 2020, resulting in illegitimate economic competition (European Commission, 2020). To ensure food traceability and verify correct product labeling, innovative analytical methods are required to confirm the geographical origin of agricultural products. In the past years, various analytical techniques including NIR-Spectroscopy (e.g. Giraudo et al., 2019), multi-elemental and/or multi-isotope analysis (e.g. Liu et al., 2016; Richter et al., 2019) and many others (Danezis et al., 2016) have been tested for this purpose. Among the different types of origin tracers, the ^{87}Sr/^{86}Sr ratio is gaining increasing interest as it links the food to its production territory (Baffi and Trincherini, 2016; Marchetti et al., 2017).

The trace element Sr has four naturally occurring isotopes (^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr). Of these, ^{87}Sr is radiogenic and its amount increases over time due to the natural ß-decay of ^{87}Rb (half lifetime: 48.8 × 10^9 years). Hence, the amount of ^{87}Sr in a given rock or mineral depends on both its age and initial Rb/Sr ratio, which may cover a range of 2-3 order of magnitude, causing significant differences in the present ^{87}Sr/^{86}Sr ratios (Tommasini et al., 2018; Hoogewerff et al., 2019). Hence, older rocks (e.g., granitic rocks) may reach higher ^{87}Sr/^{86}Sr ratios compared to others (e.g., basaltic rocks) with the same initial Rb/Sr ratio (Capo et al., 1998). Mineral weathering, a series of complex processes that have a key role in soil formation, causes the release of Sr from the bedrock. As a result, the soil Sr isotope composition represents a weighted average of the Sr isotope composition of the underlying bedrock material (Drouet et al., 2007; Crowley et al., 2017). Additionally, wet and dry precipitations as well as the use of fertilizers and irrigation water may introduce external Sr sources in the soil, slightly modifying the original ^{87}Sr/^{86}Sr ratio. This is likely to have marginal repercussion on its use as geographical tracer (Rodrigues et al., 2011; Aoyama et al., 2017; Techer et al., 2017; Aguzzoni et al., 2018). In biological systems Sr does not play an essential role, however, due to its similarity with calcium (comparable ionic radius and valence), the two elements compete with each other for plant uptake and follow the same pathway (Capo et al., 1998). Knowing that the ^{87}Sr/^{86}Sr ratio tends to vary significantly depending on the local geo-lithological features and that the ^{87}Sr/^{86}Sr ratio of biological material closely reflects that of the growing area, this isotope ratio can be successfully applied as geographical tracer (Baffi and Trincherini, 2016; Gupta and Walther, 2017; Marchetti et al., 2017).

In the last decades, several studies have been published showing the capability of the ^{87}Sr/^{86}Sr ratio to distinguish several types of agricultural products based on their origin. They include north Italian apples (Aguzzoni et al., 2020), fresh and processed tomatoes from China and Italy (Trincherini et al., 2014), Japanese and Chinese vegetables (Aoyama et al., 2017) and Portuguese and French wines (Almeida and Vasconcelos, 2001). In preparation of a more extensive use of this parameter as a geographical tracer, it is interesting to verify whether, within small cultivation areas, the ^{87}Sr/^{86}Sr ratio varies depending on plant species or cultivar/variety. To the best of our knowledge, information about this aspect is still scarce and limited to a few case studies showing no effect of plant species (vegetables; Aoyama et al. 2017) or cultivar (grapevine; Tescione et al. 2015, 2018).

To advance research on this topic, we selected two vegetable fields and one apple orchard in South Tyrol (Italy) where different vegetable species and apple tree cultivars are present in proximity. Here, different vegetables (four to six species per field) with the corresponding soil and leaf samples from five apple tree cultivars were collected to determine their ^{87}Sr/^{86}Sr ratios and verify its variability among species/cultivars and between the two locations.

2. Materials and Methods

The applied analytical protocol was based on the previously developed and validated method reported by Aguzzoni et al. (2018).

2.1. Reagents

High purity deionized water (18.2 MΩ·cm, Merck-Millipore) and nitric acid 65% (v/v), sub-boiled through a duoPur microwave assisted distillation system (Milestone), were used for sample preparation and analysis. Cellulose acetate (CA) filters (0.45 µm) were purchased from GVS Filter Technology and polytetrafluoroethylene (PTFE) filters (0.45 µm) from Thermo Fisher Scientific. Ammonium nitrate (≥ 98%) was acquired from Honeywell. Mono-elemental standards of strontium (Sr) and rubidium (Rb) were purchased from ULTRA Scientific, calcium (Ca) from Agilent Technologies and yttrium (Y), scandium (Sc) and germanium (Ge) from Merck. A quality control sample for the ICP-MS instrument was obtained by diluting the TMDA-64.3 Lake Ontario water certified reference material (LabService Analytica Srl). For the MC ICP-MS, the SRM 987 (NIST) with a certified Sr isotope composition was used. Sr-selective resin (Sr-spec, SR-B100-S, particle size 50-100 µm) was acquired from TrisKem International. All chemicals were stored according to suppliers' instructions.

2.2. Sampling

For the present study, two representative fields were selected in the main vegetable growing areas in South Tyrol (Italy) and located in different valleys (Val Venosta, Val d'Adige). Both fields were used for commercial vegetable production under conventional farming. The first field was located in Oris (900 m a.s.l., 4.6 ha) and the second one in San Genesio (1100 m a.s.l., 3.4 ha). Soil type in Oris was silty clay and in San Genesio loamy sand. Soil type was determined according to the VDLUFA method D 2.1 (Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten, 2012). All samples were collected during the harvest period between September (Oris) and October (San Genesio) 2019. Four vegetable species were taken from both fields including: carrots (*Daucus carota*), potatoes (*Solanum tuberosum*), cauliflower (*Brassica oleracea var. botrytis* L.), and pumpkins (*Curcurbita pepo*). In Oris only, beetroot (*Beta vulgaris*) and radicchio (*Cichorium intybus*) samples were additionally taken. In proximity of the growing point of each vegetable sample, a soil portion was collected at 15-20 cm depth, as a representative soil sample layer with high root density. All samples were taken in biological triplicates (approximately 1 kg per vegetable sample, except for radicchio where approximately 300 g were taken), and from randomly distributed positions of each field. All vegetable samples were washed with distilled water, peeled (when needed), cut into cubes (3-4 cm diameter) and stored at -80 °C until further sample preparation steps.

Apple leaves were collected in an experimental apple orchard (243 m a.s.l., 0.4 ha) next to the Laimburg-Research Centre, located in Vadena (South Tyrol, Italy) in an important apple growing district (Bassa Atesina). In this orchard, guidelines for the integrated cultivation of pome fruits (AGRIOS, 2021) were applied. Within the same orchard and under identical soil conditions, five different apple cultivars (*Malus domestica,* 'Royal Gala', 'Granny Smith', 'Fuji', 'Golden Delicious' and 'Red Delicious'), alternated in rows with three to five trees for each cultivar, were present. Trees were older than 5 years and grafted on M9 rootstock. In April 2019, approximately 20-25 leaves per tree were randomly sampled from the central canopy (1.0-1.8 m above ground), washed with distilled water, and stored at room temperature till further sample preparation. Since a recent study demonstrated that the variability of the Sr isotope ratio among different tree parts (shoot axes, leaves, apple peels and pulps) is much lower (around 5 times lower) compared to the intra-orchard variability within the same area of this sampling (Aguzzoni et al., 2019), only leaves and no fruits or other parts were sampled for this experiment.

2.3. Sample preparation

Soil samples were oven-dried at 60 °C for two days and then sieved (2 mm diameter) to obtain homogeneous and representative samples. For the extraction of the Sr bioavailable fraction, a sample aliquot (10 g) was mixed with 25 mL of an aqueous NH_4NO_3 solution (1 M). Then, the samples were overhead shaken for two hours at room temperature, before being centrifuged at 2400 rpm for 5 min. The obtained supernatant was filtered with CA-filters (0.45 µm) and acidified with HNO_3 (65%, w/w) to obtain a final solution of 2% of HNO_3. Vegetable samples were freeze-dried (freeze drier from Labconco) for three days (0.045 mbar, -40 °C) and mechanically crushed. Leaf samples were oven dried for two days at 60 °C and ground with a swing mill (Retsch MM400) using zirconium jars and balls. Then, 0.5 g of the fine vegetable or leaf powder was weighted in a Teflon tube and mineralized using a microwave assisted UltraWAVE digestion system (Milestone) after adding 5 mL of HNO_3 (65%, w/w). Detailed instrument parameters were described by Aguzzoni et al. (2018). The digested material was filtered through PTFE filters (0.45 µm). Finally, water was added to reach a final volume of 10 mL.

2.4. Sr/matrix separation

Soil extracts and leaf and vegetable digested solutions were purified using a Sr-specific resin to remove interfering elements like Rb and Ca. The applied method followed the procedure described by Swoboda et al. (2008) and Durante et al. (2013; and following papers of the same authors) with some changes. The resin suspension was prepared mixing 10 g of powder in 50 mL of HNO_3 (1%, w/w), which was then overhead shaken overnight. The supernatant was removed and replaced with fresh HNO_3 (1%, w/w) to reach a final volume of 100 mL. Before use, the resin suspension was stirred for 30 min and then 2 mL were transferred into a SPE column and washed with 2 mL of distilled water. The resin was activated by the addition of 5.5 mL of 8 M HNO_3. Subsequently, the sample solution was loaded onto the column. After another washing step with 8 M HNO_3 (3.5 mL for the plant material, 4.5 mL for soil), the Sr-containing fraction was eluted with 8 mL of water (Sr recoveries > 85%, negligible Rb and Ca concentration). Finally, the eluate was acidified with HNO_3 (65%, w/w) to obtain a final solution of 2% HNO_3.

2.5. Element quantification by ICP-MS

Before and after the Sr/matrix separation, Sr, Ca, and Rb concentrations in the samples were determined by ICP-MS using an iCAP-Q instrument (Thermo Fisher Scientific). The prepared calibration curve ranged from 0.1-250 µg L^{-1} for Rb and Sr and 0.01-50 mg L^{-1} for Ca. A mixed solution of Sc, Ge, and Y was used as internal standard. The certified reference material TMDA-64.3 was analyzed to evaluate the instrumental accuracy, which ranged between 90 and 110%. Repeatability, within-lab reproducibility, and recoveries were measured as described by Aguzzoni et al. (2018) and results were comparable with those of the previous study.

2.6. Isotope ratio analysis by ICP-MS

The $^{87}Sr/^{86}Sr$ ratio was determined using a double focusing multicollector (MC) ICP-MS instrument (Neptune Plus, Thermo Fisher Scientific) with a forward Nier-Johnson geometry. The skimmer cone and sampler were made from nickel. Analysis was carried out in static mode and low resolution. The multicollector was equipped with nine Faraday cups, one fixed and eight movable (configuration: L4, ^{82}Kr; L3, ^{83}Kr; L2, ^{84}Sr, L1, ^{85}Rb; C, ^{86}Sr; H1, ^{87}Sr; and H2, ^{88}Sr) and 10^{11} Ω resistors as amplifiers. Soil and leaf samples were measured at 200 µg L^{-1} in wet plasma conditions, while vegetable samples, which had lower Sr levels, were measured at 20 µg L^{-1} in dry plasma conditions (CETAC Aridus apparatus as the aerosol drying unit and jet sample cone + H Ni skimmer cone).

Instrument tune was carried out daily and its accuracy was verified analyzing a NIST SRM 987 certified reference solution at the beginning, at the end and at each block of samples in the sequence (further information can be found in Aguzzoni et al., 2018). During the analytical period, the mean ratio of the replicated SRM 987 measurements was on average 0.71025 ± 0.00002 (2 sd), both in wet and dry plasma conditions (no significant difference in the SRM 987 ratios between the two settings). This is in agreement with the certified value (0.71034 ± 0.00026) and the "generally accepted" value (0.71026 ± 0.00002) with the uncertainty expressed as twice the standard deviation (Stein et al., 1997).

Raw data correction included blank subtraction, mass bias correction after normalizing the $^{88}Sr/^{86}Sr$ value to the IUPAC value of 8.3752 (Meija et al., 2016), and mathematical correction for the isobaric interference of ^{86}Kr and ^{87}Rb (Durante et al., 2013).

2.7. Statistical analysis

Results were tested for normal distribution using the Kolmogorov-Smirnov test ($p<0.05$). A student's t-test for unpaired samples ($p<0.05$) was used to assess the significance of the differences between vegetable and the corresponding soil samples. The non-parametric Kruskal-Wallis test ($p<0.05$)

with pairwise comparison was applied to assess the significance of the differences between groups of vegetable species and soils from the same location and among samples from the three locations. Data are reported as mean ± standard deviation (1 sd). All statistical analyses were carried out with MS Excel (Office 365) and SPSS (IBM).

3. Results

At Oris, the average $^{87}Sr/^{86}Sr$ ratio of vegetables crops was 0.7262 ± 0.0004 while that of soils was 0.7258 ± 0.0006. At San Genesio, the average $^{87}Sr/^{86}Sr$ ratio was 0.7099 ± 0.0010 for the vegetables and 0.7088 ± 0.0010 for the soils (Figure 1). At both locations, plant and soil samples had similar isotope ratios, even though at San Genesio, the $^{87}Sr/^{86}Sr$ ratio of soil samples were on average slightly lower than those of the corresponding plant species (Figure 1). Both plant and soil samples at Oris had higher $^{87}Sr/^{86}Sr$ ratios as compared to San Genesio ($p<0.001$). No significant differences among species were found in San Genesio, while at Oris the $^{87}Sr/^{86}Sr$ ratio was higher in cauliflower and potatoes samples than in those of pumpkin and in carrot. At San Genesio, plant and soil samples were not significantly different. At Oris the statistical analysis showed different results. While soil samples were statistically similar, we found a significant difference comparing the different vegetable species, with cauliflower and potato showing higher values than carrots and pumpkins (Figure 1).

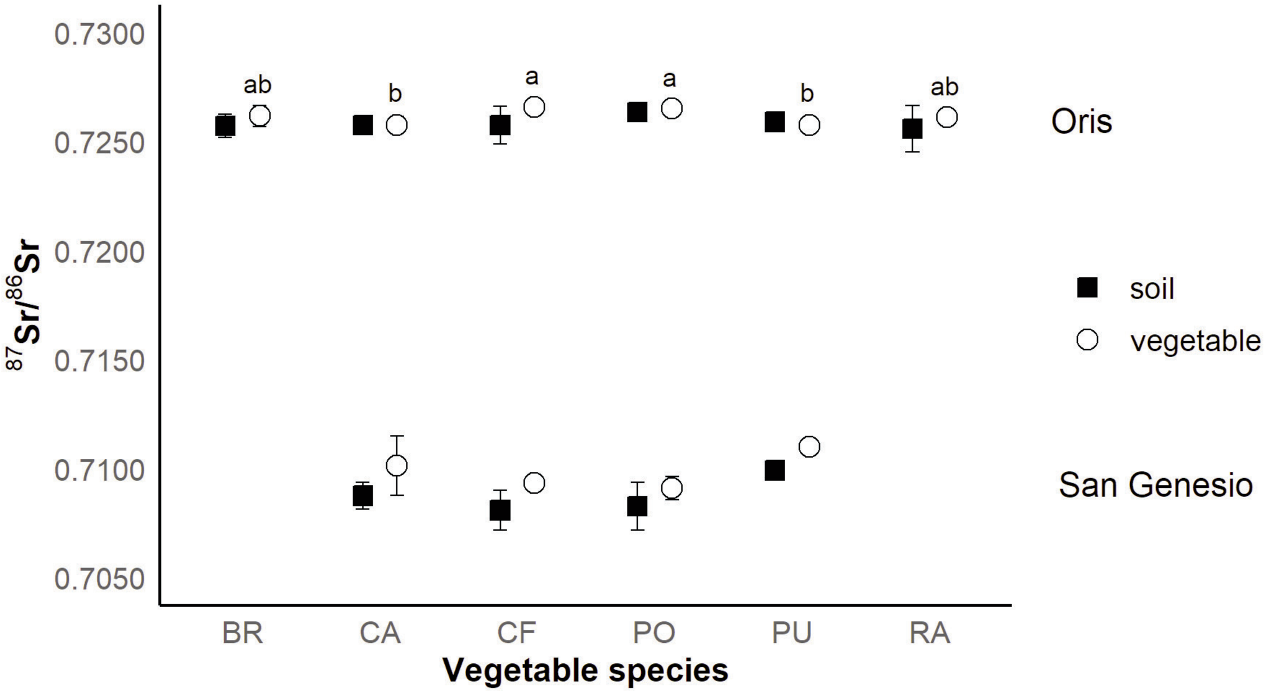

Figure 1. Average $^{87}Sr/^{86}Sr$ ratios for different vegetable species collected at Oris and San Genesio. Error bars indicates the standard deviation (n=3). Lowercase letters indicate significant differences ($p<0.05$) among vegetable crops. When no letters are shown, no significant differences could be found. BR = beetroot, CA = carrot, CF = cauliflower, PO = potato, PU = pumpkin, RA = radicchio.

The average $^{87}Sr/^{86}Sr$ ratio of apple leaves at Laimburg was 0.7114±0.0002 (Table 1). The isotope ratios of the different apple cultivars ranged from 0.7112 to 0.7117. No significant differences in leaf $^{87}Sr/^{86}Sr$ ratio were found among the different apple cultivars.

When we analyzed the plant samples from the three locations, highly significant differences ($p<0.0001$) in $^{87}Sr/^{86}Sr$ ratios were highlighted. Pairwise comparisons confirmed that all three locations differ from each other in their $^{87}Sr/^{86}Sr$ ratios (Figure 2).

Table 1. Average $^{87}Sr/^{86}Sr$ ratios for each apple tree cultivar (Royal Gala and Granny Smith n=5; Fuji, Golden Delicious, and Red Delicious n=3)

Cultivar	$^{87}Sr/^{86}Sr$, mean	$^{87}Sr/^{86}Sr$, sd
Royal Gala	0.7114	<0.0001
Granny Smith	0.7114	0.0002
Fuji	0.7112	<0.0001
Golden Delicious	0.7114	<0.0001
Red Delicious	0.7117	0.0002

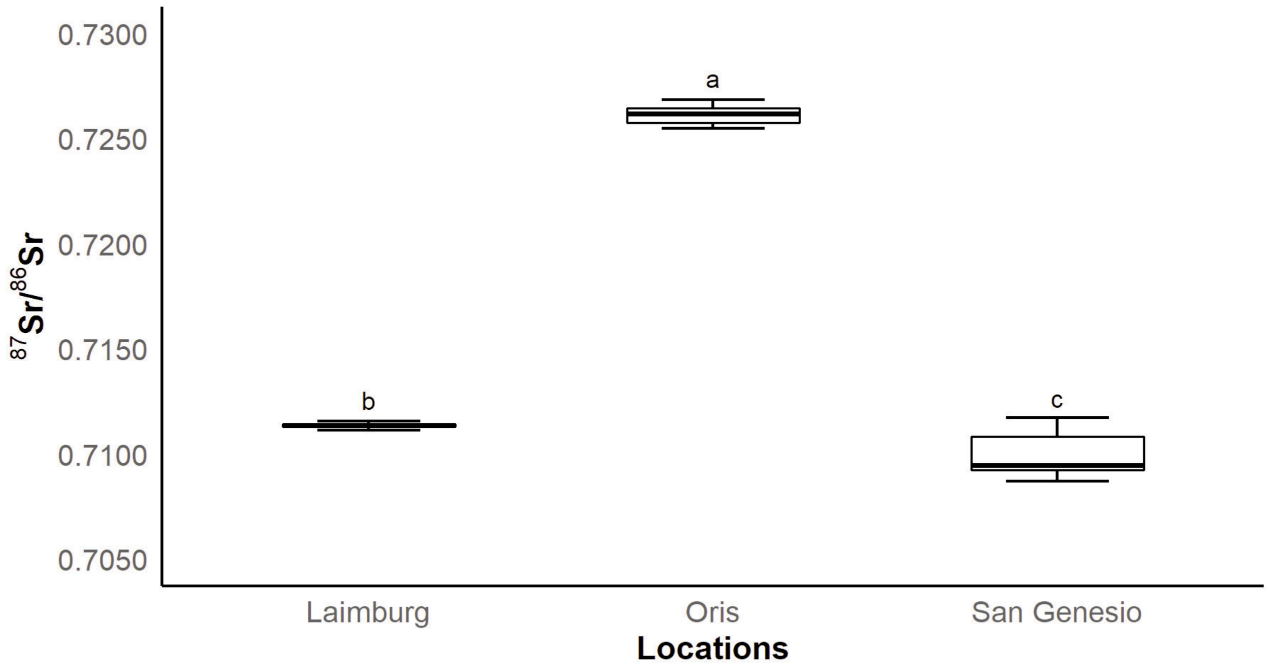

Figure 2. Boxplots showing the average distribution of the $^{87}Sr/^{86}Sr$ ratios measured in apple leaves in Laimburg (five cultivars, n=3-5 for each cultivar) and vegetables at Oris (six species, n=3 per species) and San Genesio (four species, n=3 per species). Lowercase letters indicate significant differences among groups ($p<0.05$).

4. Discussion

A first goal of our investigation was focused on the comparison of the $^{87}Sr/^{86}Sr$ ratio of vegetable crops from two locations of South Tyrol (Italy) with that of their corresponding soil. In both fields, the Sr isotope composition of plant organs matched that of the top soil, confirming that the $^{87}Sr/^{86}Sr$ ratio represents a chemical fingerprint of the growing area (Figure 1). In many cases, higher variability was found in $^{87}Sr/^{86}Sr$ ratios measured in the soil than in the vegetables. This might be due to the higher heterogeneity of the soil matrix and its complexity especially in slopes and in mountain areas (Prohaska et al., 2005; Crowley et al., 2017), such as those where the two fields, and particularly San Genesio, are located. Additionally, different authors reported that the correspondence between soil and vegetable samples could be affected also by the presence of external Sr inputs, such as those coming from the application of fertilizers, irrigation water, and other wet and dry precipitations (Rodrigues et al., 2011; Aoyama et al., 2017; Techer et al., 2017; Aguzzoni et al., 2018). As their penetration in the soil might be rather heterogeneous, it is likely that soil samplings at a single depth in proximity or under the plant, is not representative of the whole variability of the $^{87}Sr/^{86}Sr$ ratio, especially when no indication about the root distribution of the different sampled species is available. However, these aspects could explain in part the significant difference between the vegetables and their corresponding soils in the two fields and the higher standard deviations in soil and intra-field variability of the $^{87}Sr/^{86}Sr$ ratio measured particularly in the field of San Genesio. As suggested by Marchetti et al. (2017), given the occurrence of complex phenomena in the soil, it is more advisable to develop geographical traceability models based on plant instead of soil isotope data for in studies based on the $^{87}Sr/^{86}Sr$ ratio.

Our results suggest that different vegetable crop species at the same location do not significant differ in terms of $^{87}Sr/^{86}Sr$ ratios. The only differences among species were found at Oris and were of very low magnitude (Figure 1), which could be explained by some heterogeneity in the soil. Our results are in line with those of Aoyama et al. (2017), who found that the $^{87}Sr/^{86}Sr$ ratio of different vegetables in the main cultivation areas of Japan varied according to the local geological features, but was independent from the vegetable species. Despite local variability, combining the $^{87}Sr/^{86}Sr$ ratios with Sr concentrations they were able to reach a satisfactory discrimination between vegetables cultivated in Japan and in China. Similarly, apple tree samples from different cultivation areas can be discriminated according to their $^{87}Sr/^{86}Sr$ ratios (Aguzzoni et al., 2020).

A second aim of the study was to test the $^{87}Sr/^{86}Sr$ differences among apple tree cultivars. Our data indicate that when grafted on the same rootstock and grown in the same location, different apple cultivars do not differ as to their $^{87}Sr/^{86}Sr$ ratio. Sr isotope fractionation is supposed to be rather limited due to the small mass difference between the two Sr isotopes, although it has been reported during Sr root absorption and internal transport in the xylem system (Oeser and von Blanckenburg, 2020). However, for $^{87}Sr/^{86}Sr$ the effects of fractionation are mathematically corrected during data processing (Gupta and Walther, 2017; Marchetti et al., 2017). We cannot rule out the possibility that Sr root absorption could be affected by the rootstock or by the cultivars. However, all the trees used in our study were grown on the same M9 rootstock and this should eliminate the genomic influence of the roots. Moreover, since the $^{87}Sr/^{86}Sr$ ratios measured in different tree organs, including apple, grapevine and olive normally show homogeneous values (Aguzzoni et al., 2019; Durante et al., 2016; Guibourdenche et al., 2020, Marchetti et al., 2017; Petrini et al., 2015), the $^{87}Sr/^{86}Sr$ ratios obtained measuring one tree organ could be extrapolated to other tree organs, including the fruit.

Based on our results, we expect that different vegetable species and apple tree cultivars growing in the same area are characterized by the same $^{87}Sr/^{86}Sr$ ratio providing that their root apparatus is spread mainly in the same soil layers (hence plants absorb Sr from the same nutrient pool) or whenever the Sr-isotope ratio in the soil is very homogeneous along the soil profile (Aguzzoni et al., 2019).

This study also shows that different growing districts in South Tyrol are characterized by different $^{87}Sr/^{86}Sr$ ratios (Figure 2), in agreement with the results of previous publications (e.g. Aguzzoni et al., 2020). The highly significant differences between the three sampling sites were due to their respective geological features. Oris is located in the North-Western part of South Tyrol in a metamorphic basal complex with quaternary sediments. San Genesio is located in the south-alpine part of South Tyrol, an area with permic vulcanite bedrock. The same bedrock characterizes also the area of Laimburg (30 km south of San Genesio) and that lays on quaternary deposits (Autonomous Province of Bozen-Bolzano, 2021). These results confirm the use of the $^{87}Sr/^{86}Sr$ ratio as geographical tracer for food traceability and authenticity studies. However, when the complexity of the comparison increases (e.g. more sampling sites per studied area, comparison among several growing areas), it may be useful to combine the analysis of the $^{87}Sr/^{86}Sr$ ratio to other tracers of geographical origin, such as multi-element analysis, light element isotope ratios or other fingerprinting techniques to develop more accurate and precise estimation models (Luykx and van Ruth, 2008; Baffi and Trincherini, 2016).

5. Conclusions

The ^{87}Sr/^{86}Sr ratio in vegetable crops and apple trees is largely affected by the soil ^{87}Sr/^{86}Sr ratios, and is independent from the genotype. This aspect is relevant for traceability studies as databases or maps based on the ^{87}Sr/^{86}Sr ratio can be compiled for specific cultivation areas and used as a reference for unknown samples independently from their species/variety, with some limitations related to the heterogeneity of the ^{87}Sr/^{86}Sr ratio along the soil profile. By using the ^{87}Sr/^{86}Sr ratio analysis, we were able to distinguish the sample origins even in a small, but geologically complex area such as South Tyrol.

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Conflicts of Interest: The authors declare no conflict of interest.

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