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Marine Reyrolle[a], Gilles Bareille[a], Ekaterina N. Epova[b], Julien Barre[b], Sylvain Bérail[b], Thierry Pigot[a], Valerie Desauziers[a], Lydia Gautier[c] and Mickael Le Bechec[a*]

[a] Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IMT Mines Ales, IPREM, Pau, France, Institut des sciences analytiques et de Physicochimie pour l'environnement et les Matériaux, UMR5254, Hélioparc, 2 avenue du Président Angot, 64053, Pau cedex 9, France

[b] Advanced Isotopic Analysis (A.I.A.), Hélioparc, 2 avenue du Président Angot, 64000, Pau, France

[c] T Edition, 63 rue Vercingétorix , 75014 Paris, France

**Corresponding author at Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IMT Mines Ales, IPREM, Pau, France*

Email adress : mickael.lebechec@univ-pau.fr Phone: +335 59 40 75 84

Abstract

High value food products are subject to adulterations and frauds. This study aimed to combine, in our knowledge for the first time, inorganic chemical tracers (multi-elements and Sr isotopy) with volatile organic compound (VOCs) to discriminate the geographic origin, the varieties and transformation processes to authenticate 26 tea samples. By measuring Sr isotope ratio using the multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), 6 out of 11 regions were successfully discriminated. The combination with the ICP-MS inorganic pattern allowed to discriminate 4 more regions with a significance level of 0.05. VOCs fingerprints, obtained with selected ion flow tube mass spectrometer (SIFT-MS), were not correlated with origin but with the cultivar and transformation processes. Green, oolong, and dark teas were clearly differentiated, with hexanal and hexanol contributing to the discrimination of oxidation levels. With this multi-instrumental approach, it is possible to certify the geographical origin and the tea conformity.

Highlights

- VOCs profiles, $^{87}Sr/^{86}Sr$ ratio and multielement analysis were applied on tea
- $^{87}Sr/^{86}Sr$ ratio discriminated 6 of the 11 regions of the sample collection
- Inorganic pattern improved the discrimination of Sr isotope ratio up to 10
- Volatile fingerprints were mainly impacted by the type of Camelia cultivar
- Hexanal and hexanol were highlighted for the classification with oxidation rate

Keywords

Tea, traceability, authenticity of food products, inorganic pattern, volatile organic compounds profiling, Sr isotope ratio

1. Introduction

Food provenance assessment is a global concern for sanitary and quality control. Consumers expect more guarantees regarding food quality, i.e., information on composition, absence of health risks, product origin, quality, and transformation processes with reduced environmental impact. Thus, labels have been developed to meet these expectations providing information regarding the product origin (Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI)) along with environmental and social impact. These labels, provided by authorities, authenticate agri-food products regarding product origin and expected sensory quality. Unfortunately, certified products are *de facto* more expensive and profitable, which encourages the fraud development and fake products in the marketplace. This problem is particularly acute for old products consumed worldwide, such as tea.

For centuries, people have consumed tea and enjoyed its taste and aroma. Originally produced in China, tea is now mainly produced in Asia (India, China, Sri Lanka, Vietnam, and Japan), but also in Africa (Kenya) and in South America. Tea plants, *Camellia sinensis* (*C. sinensis*), are members of the family *Theaceae*. The first wild tea plants grew at the source of the Irrawaddy River in a triangle formed by Yunnan in China, Northeast India, Burma, and Tibet. Tea plants have spread naturally along rivers, giving rise to three main varieties: *sinensis*, *assamica*, and *cambodiensis*. Various national research institutes developed new varieties that were more adapted to local climatic conditions (e.g., resistant to certain pests, early or mature growth) and balanced productivity and quality. Thus, a large number of cultivars were created via cutting, grafting, layering, or suckering. The terroir, i.e., the composition of soil, climate, altitude, latitude, the plants grown alongside tea plants, picking methods and periods all play an essential role in developing the organoleptic qualities of tea.

Moreover, many changes in the transformation processes of *C. sinensis* leaves have led to the development of several types of tea (Feng et al., 2019). Therefore, based on the drying, fixation, fermentation, and enzymatic oxidation levels, teas can be classified into different colours: green, black, dark, red, white, oolong and yellow (Zhang et al., 2019). Nevertheless, only a few labels have been created, such as Darjeeling tea, a typical black tea from North India, which is one of the most famous teas. Currently, only 10,000 tons of Darjeeling tea is produced annually, while four times as much is sold worldwide. This information highlights the challenge of traceability of high-value food products. Beyond the product-origin information, consumers also want to be informed about typical product quality.

To protect producers, manufacturers, and consumers, labelled products must be cultivated and transformed in a defined geographic area. In order to obtain a label in addition to the declarative aspect, several fraud checks should be conducted by food industry sectors to assess product origin. The development of new analytical techniques for determining the geographical origin and authenticity of products has increased since the 1980s. Such techniques include stable isotopes, analysis of carbon, nitrogen, and oxygen, near-infrared spectroscopy, nuclear magnetic resonance spectroscopy, electronic nose sensing, multielement analysis, chromatographic techniques, evaluation

by mass spectrometry and sensory analysis (Luykx & van Ruth, 2008). Recent reviews gave a state of art of methods to trace the origin and quality of foods produced in China, including tea (Li et al., 2023; Shuai et al., 2022).

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used in multielement fingerprinting for the geographical assessment of various plant-based food products, such as olive oil (Nasr et al., 2021), coffee (Liu et al., 2014), wine (Epova et al., 2020), and tea (Liu et al., 2021). Plants grow in soil containing organic and mineral matter as well as water. Mineral elements are transferred to the plant tissues during cultivation and lead to different multielement signatures depending on product origin that reflect underlying geology and soil composition (Liu et al., 2021). Anthropogenic actions and environmental pollution may also contribute to elemental signatures (Zhao et al., 2017). Inorganic elements, such as Sr, Pb, B, Cd, Li, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, and Ba, may be good tea leaves markers before and after processing (Gomes et al., 2019). Moreover, post-processing (drying or roasting) and storage methods are more likely to affect the active organic compounds that may degrade or attenuate (Ni et al., 2018). Sr and especially the ratio of two of its four isotopes ($^{87}Sr/^{86}Sr$) has an advantage over element contents. Indeed, it has been shown that the $^{87}Sr/^{86}Sr$ isotope ratio does not change during biological processes (no biological fractionation) and, in plants, reflects the growth environment: mainly the bioavailable fraction of Sr derived from the mineral weathering processes of bedrock and soil (Bin et al., 2022), although atmospheric and anthropogenic sources, e.g., fertilisers, may sometimes play a role (Bataille et al., 2020).

In addition to geographic origin, consumers expect the taste and aroma of teas to match the label. This quality aspect of tea is closely related to agricultural practices, including growth and harvest conditions, as well as transformation processes and storage conditions. Tea experts can assess the expected quality of labelled samples, but this ability requires a long learning process. Analytical chemistry methods were thus developed to monitor the characteristic markers of types of tea (Lin et al., 2013; Zhang et al., 2013). Recently, a new global approach based on the identification of volatile compound fingerprints for product traceability has been developed using proton-transfer reaction–mass spectrometry (PTR-MS) (Yener et al., 2016). This method features the nontargeted measurement of volatile organic compounds (VOCs) emitted by a product using a rapid and non-destructive mass spectrometer with a soft chemical ionization source. Selected ion flow tube mass spectrometry (SIFT-MS) is also a direct-injection mass spectrometry (DIMS) technique that determine the volatile fingerprint of a product by monitoring the ions produced by volatile molecules and eight chemical precursors (Reyrolle et al., 2022).

Throughout this study, we performed and combined for the first time on a collection of tea samples, multielement signature measurements using -ICP-MS, Sr isotope ratio with multi collector ICP-MS and SIFT-MS volatile fingerprints to trace origin of production, cultivar type, transformation processes and therefore conformity. For this purpose, it was essential to work with tea samples with perfectly certified origins. To conduct this study, our collaborator, a tea expert collected 26 samples directly from the producers and factories in order to avoid blending along supply chain.

2. Material and methods

2.1. Samples

A tea expert collected 26 tea samples (Table 1) with certified origins directly from producers or factories, from 2011 to 2020. These tea samples were obtained from six countries: Nepal (n = 3), China (n = 11), Vietnam (n = 5), India (n = 3), Sri Lanka (n = 2), and Japan (n = 2), corresponding to 11 regions (Figure SI1). These tea samples displayed five colours: green (n = 6), black (n = 10), dark (n = 3), white (n = 4), and oolong (n = 3). Samples were stored in sealed aluminium bags (Jamo solution LTD, Orpington, Kent, United Kingdom) at 25°C ± 5 in the dark.

Sample	Country	Region	Colour	Cultivars
Tea-1	Nepal	Ilam Valley	White	Mix Clonal Cultivars
Tea-2	Nepal	Ilam Valley	White	Mix Clonal Cultivars
Tea-3	Nepal	Ilam Valley	White	Mix Clonal Cultivars
Tea-4	China	Zhejiang	Green	Jiu Hang
Tea-5	China	Zhejiang	Green	Jiu Hang
Tea-6	China	Zhejiang	Green	Jiu Hang
Tea-7	Japan	Kyushu	Green	Yabukita
Tea-8	Japan	Kyushu	Green	Yabukita
Tea-9	China	Jiangsu	Black	Xiao Ye
Tea-10	China	Jiangsu	Black	Xiao Ye
Tea-11	China	Jiangsu	Black	Xiao Ye
Tea-12	India	Darjeeling	Black	China Jat (Mix)
Tea-13	India	Darjeeling	Black	China Jat (Mix)
Tea-14	India	Darjeeling	Black	China Jat (Mix)
Tea-15	China	Taiwan Ali mountain	Black	Chin Shin
Tea-16	China	Taiwan Ali mountain	Oolong	Chin Shin
Tea-17	Vietnam	Lai Chau	Oolong	Jin Xuan
Tea-18	Vietnam	Lai Chau	Oolong	Jin Xuan
Tea-19	Vietnam	Lai Chau	White	Jin Xuan
Tea-20	Vietnam	Lai Chau	Black	Jin Xuan
Tea-21	Vietnam	Lao Cai	Green	Da Ye age
Tea-22	China	Yunnan	Dark	Da Ye
Tea-23	China	Yunnan	Dark	Da Ye
Tea-24	China	Yunnan	Dark	Da Ye
Tea-25	Sri Lanka	Ratnapura	Black	Assamica

Tea-26	Sri Lanka	Matara	Black	Assamica

Table 1: Tea samples description

2.2. Inorganic signature of tea

Three grams of tea were dry ground using a porcelain mortar. The obtained powder was transferred to a zipped polyethylene bag (Nalgene, Thermo Fisher Scientific, Illkirch-Graffenstaden, France) and stored in a dry, dark place until analysis. The tea powder (0.2–0.4 g) was combined with 7 mL of sub-boiled nitric acid (HNO_3; 69.0%–70.0%, Instra Analysed Reagent, J.T.Baker®, Fisher Scientific, France) and left to react overnight at room temperature. Then, 1 mL of hydrogen peroxide (H_2O_2; 30%, ULTREX® II Ultrapure Reagent, J.T.Baker®, Thermo Fisher Scientific, Illkirch-Graffenstaden, France) was added to the sample–acid solution. The final mixture was then digested in a microwave system (Ultrawave SRC technology, Milestones, Sorisole (BG), Italy) following an optimized gradual heating program up to 250° C, where the temperature was maintained for 20 min at P max = 110 bar. An aliquot of the resulting clear solutions was then used for multi-elemental analysis, and the rest of mineralized solution was transferred to clean PFA vials (Savillex Corporation, Eden Prairie, MN, USA).

2.2.1. Multielemental composition determination using quadrupole ICP-MS

Aliquots of diluted solutions were used for multielement analysis of tea samples using an ICP-MS Plasma Quant Elite spectrometer (Analytik Jena, Jena, Germany). All the samples were analysed to determine the total concentration levels of 21 elements: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Rb, Sr, Pb, V, and Zn. Instrument operating conditions and measured isotopes are presented in Table SI2. The analysis was performed using two operating modes: a standard "no gas" mode and an integrated collisional reaction cell (iCRC) mode. Helium (He) and hydrogen (H_2) (Air Liquide, Paris, France) were used as collision and reaction gases, respectively, to reduce spectral interference. For the external calibration, solutions were prepared at eight concentration levels, ranging from 0.01 to 500 µg L^{-1}, via an appropriate dilution of the multielement standard solutions, CCS-4 and CCS-6 (Inorganic ventures, Christiansburg, VA, USA). Yttrium, rhodium, and iridium at the concentrations of 2.5 µg L^{-1} were used as internal standards for the low, medium, and heavy masses, respectively, to correct instrumental drifts. Sample concentrations were calculated after applying the corrections for the analytical and procedural blanks as well as internal standards. Accuracy and precision of the measurements were controlled by analysing the following certified reference materials: NIST SRM 1643f (trace elements in water, The National Institute of Standards and Technology, Gaithersburg, MD, USA) and CRM NIES 23 (National Institute for Environmental Studies, Tsukuba-City, Ibaraki, Japan). Recoveries were within the acceptable limit of ±10%.

2.2.2. Sr Isotope analysis using the Multi-collector MC-ICP-MS

An appropriate volume of each digested solution sample was evaporated to dryness to obtain 4 µg of Sr. The residue was then dissolved in 3M HNO_3. Subsequently, Sr was separated from the matrix using columns containing Eichrom Sr-Spec resin (Eichrom Technologies Inc, Lisle, USA) via sequential elution with ultrapure water and 3M ultrapure HNO_3, as previously described by Martin *et a.*. Sr isotope analysis was performed using a Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham, UK) with wet plasma conditions and a self-aspirating micro concentric nebulizer (200 µL min^{-1}) combined with a glass cyclonic spray chamber. Measurements were performed using a conventional “Sample–Standard–Bracketing” calibration sequence with SRM 987 (Sr carbonate isotopic standard, NIST,

Gaithersburg, MD, United States) used as a bracketing standard after every two samples. After instrumental blank subtraction using the on-peak-zero approach, the $^{87}Sr/^{86}Sr$ ratios were corrected for instrument mass bias though an exponential law with a constant $^{86}Sr/^{88}Sr$ ratio of 0.1194 and for the potential remaining interferences from the traces of ^{87}Rb using the monitored ^{85}Rb and a $^{85}Rb/^{87}Rb$ ratio of 2.5926. The value of $^{87}Sr/^{86}Sr$ ratio was 0.710255 for SRM 987 applied for data processing, according to Waight *et al.*.

The $^{87}Sr/^{86}Sr$ ratio was normalized to the certified reference material NIST CRM 987 according to the following equation (Liu et al., 2014):

$$\delta^{87}Sr = \left[\frac{(^{87}Sr/^{86}Sr)_{sample}}{(^{87}Sr/^{86}Sr)_{NIST987}} - 1\right] \times 1000(‰).$$

Equation 1

2.3. Analysis of volatile components with SIFT-MS

SIFT-MS measurements were performed on headspace contents of tea samples. Ten grams of tea were introduced into a 1-L glass bottle (Schott, Colombes, France) fitted with a polypropylene screw cap with two tight connection ports fitted (Duran Wheaton Kimble, Holzminden, Germany) with 0.6-cm PFA tubes (Swagelock, Lyon, France). The first tube was connected directly to the SIFT-MS and the second to a 1-L Tedlar© bag (Supelco, Bellefonte, PA, USA), filled with zero dry air (ZeroAir Alliance ZA1500, F-DGSi, Evry, France). This bag compensated for analysed volume during SIFT-MS analyses. The closed bottle was incubated for 2 hours at 60°C to achieve equilibrium in the gas phase before performing the positive and negative SIFT-MS full scan analysis.

A SIFT-MS Voice 200 Ultra (SYFT Technologies, Christchurch, New Zealand) instrument equipped with a dual source producing positive and negative soft ionizing precursor ions (H_3O^+, $O_2^{\bullet+}$, NO^+, $O^{\bullet-}$, OH^-, $O_2^{\bullet-}$, NO_2^- and NO_3^-) was used in a single scan. This instrument used nitrogen (Air Liquide, Alphagaz 2, Paris, France) as the carrier gas; the sample was introduced through a heated (110°C) and flow-controlled (20 mL min^{-1}) sample line (High-Performance Inlet HPI®, SYFT Technology, Christchurch, New Zealand). The instrument was calibrated daily using a standard gas (ScottTM gas mixtures, Air Liquid, Breda, Nederlands), containing standards at 2.0 ppmV in nitrogen. A blank experiment was performed for each empty bottle before analysing all of them in triplicate. The full scan raw data files containing product ion intensities in the 15–250 m/z range were collected before compilation and pre-processing steps.

Compilation and pre-processing of the full scan raw data were performed as described in a previous study (Reyrolle et al., 2022) using Python language. Data was pre-processed by subtracting background noise (signal of bottles without samples) for each replicate. Triplicates of each sample were averaged to obtain a single value of signal intensity for each ion. This value was multiplied by the ICF factor corresponding to the instrument calibration correction. The dataset was cleaned by suppressing constant quantitative variables.

2.4. Statistical analysis

Statistical analysis, including non-supervised and supervised methods, was performed using the R language and MixOmics package (Rohart et al., 2017). Multielement analysis and Sr isotope data were evaluated via principal component and partial least-squares-discriminant analyses. For volatile fingerprint analysis, sparse principal component analyses (Sparse PCA) and sparse partial least-squares discriminant analyses (sPLS-DA) were used to show the dispersion or discrimination of the sample

based on many variables. Inorganic elemental contents and $^{87}Sr/^{86}Sr$ ratios were combined by normalizing the latter was normalized to the certified reference material NIST CRM 987 ($\delta^{87}Sr_{NIST987}$) using equation 1.

3. Results & Discussion

3.1. inorganic signatures

Studies on geographical origin of food products that use multiple markers (trace element fingerprints, stable isotope signatures) have been steadily increasing over recent years (Bandoniene et al., 2018). Trace element fingerprints can be used to determine origin of products, especially for plants in which the primary element composition is derived from the bioavailable fraction of elements in soil (Bataille et al., 2020). Sr isotopes, radiogenic ^{87}Sr vs. stable ^{86}Sr ($^{87}Sr/^{86}Sr$), were primarily used to infer geographical provenance and thus were often applied in fisheries or food sciences (Epova et al., 2019). The $^{87}Sr/^{86}Sr$ ratio has several advantages. First of all, Sr is absorbed into biological materials in a conservative manner, i.e., without biological fractionation across the food chain. Secondly, the Sr isotope ratio mainly depends on the bioavailable Sr in soil, a fraction largely controlled by differential weathering of minerals from parent bedrock and soil with varying Sr and Rb concentrations (Rb/Sr ratio). Ultimately, the combination of lithology, weathering, and additional Sr sources (atmospheric and anthropogenic) produces considerable variability in available $^{87}Sr/^{86}Sr$ ratios in the geosphere and thus the biosphere (Bataille et al., 2020).

The $^{87}Sr/^{86}Sr$ ratios in tea samples clearly discriminated six regions (China_Yunnan, India_Darjeeling, Nepal_Ilam Valley, Vietnam_Lao Cai, China_Taiwan Ali Mountain, and Japan_Kuyshu) from 11 collection sites (figure 1), confirming the success of this technique to determine geographical origin, as previously mentioned in the scientific literature. Globally, $^{87}Sr/^{86}Sr$ ratios found in our tea samples were consistent with those reported in recent provenance studies (Aoyama et al., 2017; X. Wang & Tang, 2020), strengthening the link between plants and bioavailable $^{87}Sr/^{86}Sr$ ratios (Bataille et al., 2020). Our high $^{87}Sr/^{86}Sr$ ratios for Darjeeling tea (average = 0.744 ± 0.004 and n = 3) correspond to those published for the same region (Lagad et al., 2013) (average = 0.745 ± 0.029, range = 0.726–0.829, and n = 9) but with a lower dispersion. The wide range of variation in $^{87}Sr/^{86}Sr$ ratios reported by Lagad et al is consistent with ratios in local water and soils developed from granitic to gneissic rocks (Galy et al., 1999). The narrow range in $^{87}Sr/^{86}Sr$ ratios we observed is due to the unique geographical origin of our three samples. Our analyses did not discriminate however the Darjeeling region from the Ilam Valley (Nepal = 0.736 ± 0.002 and n = 3) or Lao Cai (Vietnam = 0.7558 and n = 1). The combination of $^{87}Sr/^{86}Sr$ ratios and trace element concentrations of Ca, Sr, Ba, Cd, and K allowed such discriminations (figure 2). Moreover, Vietnam_Lao Cai teas were enriched in Rb and Fe compared to India_Darjeeling teas providing more reliability in the separation of these sources. A geographical association was assigned by the “Tea Board India” to protect Darjeeling tea and preserve iconic stature in India's cultural heritage. Thus, a combination of Sr isotope ratios and trace elements may demonstrate the authenticity of the product and highlight fake products labelled as “Darjeeling tea.” Finally, the volcanic substratum of the Kyushu province in Japan shows a characteristic $^{87}Sr/^{86}Sr$ ratio that set it apart from other sources worldwide (Aoyama et al., 2017). An additional factor in distinguishing these teas is the relatively large levels of Na that complete Sr isotope ratios.

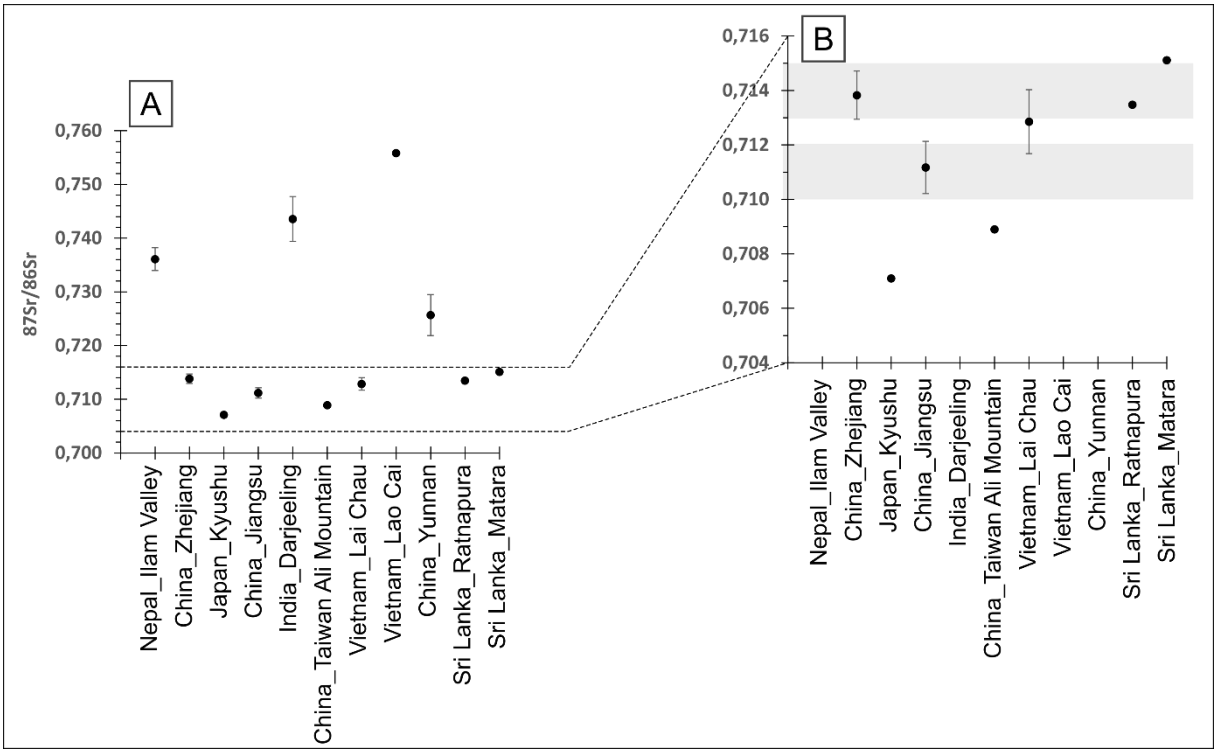

Figure 1: Sr isotope ratios ($^{87}Sr/^{86}Sr$) according to the regions. The mean values are represented with circles and the standard deviation with vertical lines. Figure 1B represents a zoom of figure 1A between 0.704 and 0.716 of $^{87}Sr/^{86}Sr$

$^{87}Sr/^{86}Sr$ ratios appeared to overlap between the following sites, Sri Lanka_Ratnapura and Sri_lanka_Matara, Vietnam_Lai Chau, and China_Zhejiang, on the one hand, and China_Jiangsu and Vietnam_Lai Chau, on the other. Nonetheless, we identified inorganic profiles among these sites that allowed differentiation. Similarities and differences in chemical fingerprints of teas were assessed across sites and countries of origin using a partial least square regression and a discriminant analysis to create a hierarchical clustering heatmap (Figure 2). Elemental concentrations and $\delta^{87}Sr$ are presented as variables (in columns), and regions and countries of origin are presented as observations (in rows). The two Sri Lankan sites were an exception. For instance, China_Jiangsu teas presented high levels of V, Co, Cr, Pb, and Cu compared to four other sites and those already discriminated using Sr isotope ratios. Higher concentrations are associated with surrounding mines and industrial activities. More specifically, elemental profiles in heavy metals were related to the presence of 12 mines, listed by the United States Geological Survey, that produce Fe, Cu, Zn, Pb, Cr, V, and Ag. Moreover, GEM, one of the largest battery recyclers in China that processes used battery and produces 10,000 tons of cobalt tetroxide in Jiangsu. These elements were, therefore, good markers of anthropogenic impact on multielement signatures and allow the identification of teas from this region. Furthermore, China_Zhejiang, Vietnam_Lai Chau, and Sri Lanka_Ratnapura/Matara teas differed in As concentrations and Ca/Mn and Na/Mg ratios, respectively. Our results confirmed that multielement signatures are useful indicators, especially for tea authentication, since they reflect climate, environment, and agricultural practices (Camin et al., 2017). Finally, combining Sr isotope ratios and elemental fingerprints enabled to distinguish 10 out of 11 tea samples with a significance level of 0.05. Nine origins displayed unique geochemical signatures, i.e., China_Jiangsu, Vietnam_Lao Cai, India_Darjeeling, Nepal_Ilam Valley, Japan_Kyushu, Vietnam_Lai Chau, China_Taiwan Ali Mountain, China_Zhejiang, and China_Yunnan, along with one group of two sites (two Sri Lanka provinces: Ratnapura and Matara districts). Four sites or groups of sites were primarily discriminated according

to their elemental content (China_Jiangsu, Sri Lanka_Ratnapura/Matara, Vietnam_Lai Chau, and China_Zhejiang), three sites mainly by their $^{87}Sr/^{86}Sr$ ratio (Nepal_Ilam Valley, China_Yunnan, and China_Taiwan Ali Mountain), and three sites according to the $^{87}Sr/^{86}Sr$ ratio ($\delta^{87}Sr$) as well as specific elemental concentrations (Vietnam_Lao Cai, India_Darjeeling, and Japan_Kyushu) (Figure 2 and Table SI2).

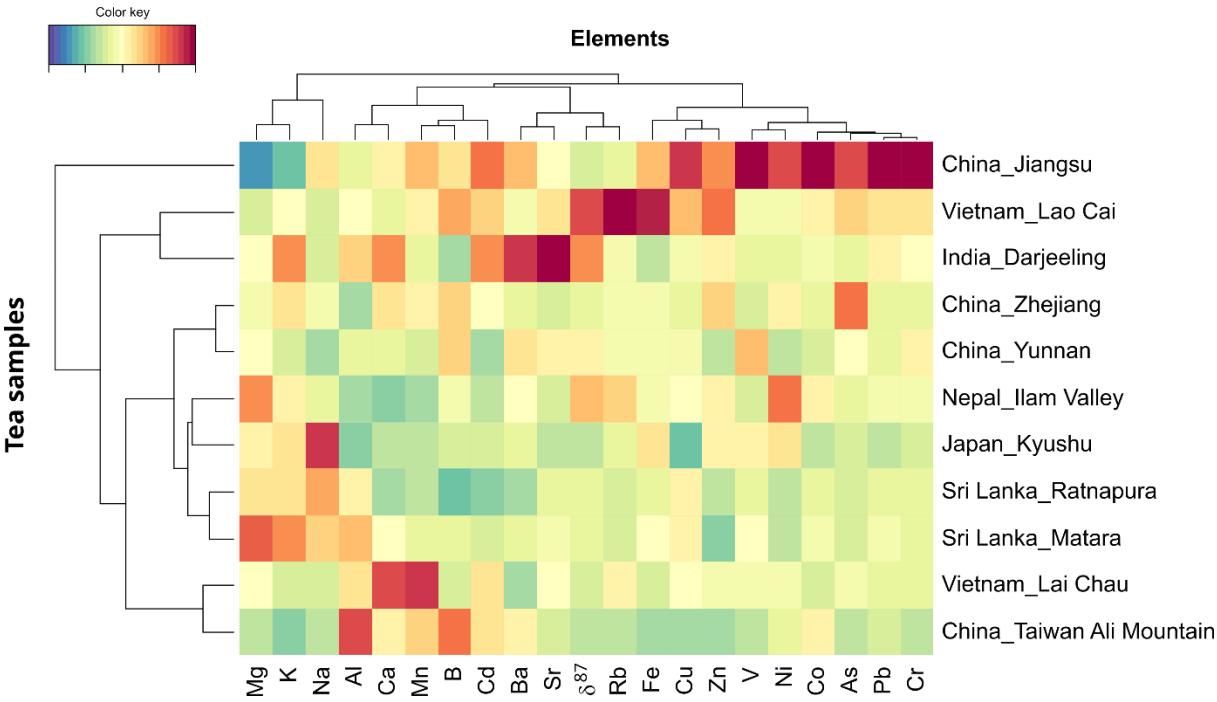

Figure 2: A clustered image map (CIM) based on PLS-DA and according to the "country_region of origin"parameter. The dendrograms represent hierarchical grouping for regions (horizontal) and for elements (vertical). The colour key indicates the under expression (in blue scale) or over expression (in red scale) of the element in each sample group in relation to the others.

3.2. Volatile fingerprints

VOCs released from food products have been studied for many years. VOCs are good markers of plant, animal, and microbial metabolisms involved in food production and transformation. Taste and aroma are generally sufficient to identify specific compounds because of the high complexity of human perception. New approaches, based on nonspecific analysis of food combined with statistical tools, allow use of correlations between qualitative attributes and chemical composition. Direct injection mass spectrometers, such as PTR-MS and SIFT-MS, are powerful instruments for investigating VOCs, thanks to their high chemical selectivity. Thus, specific biogenesis of volatile molecules in plants, such as olive oil (Ozcan-Sinir, 2020) or saffron (Nenadis et al., 2016), can be used to control processes, such as drying (Olivares et al., 2011), roasting (Dryahina et al., 2018), oxidation and fermentation (Van Kerrebroeck et al., 2015). Analyses can also be used to demonstrate typical profiles for dark chocolates and ewe cheeses (Deuscher et al., 2019; Reyrolle et al., 2022). Traceability of food products can be, in some cases, correlated with taste and flavour but it requires highly experienced experts. In this work, static headspaces of tea samples were analysed with SIFT-MS Voice 200-ultra creating volatile fingerprints with 1,880 variables by combining the raw signals in a full scan mode (15-250 m/z) obtained with the three positive precursor ions and the five negative precursor ions.

3.2.1. Unsupervised analysis of tea samples grouped by the region of origin

The power of the volatile fingerprint approach lies in the search for correlation of VOCs signals with descriptive values. An unsupervised sparse principal component analysis (sparse PCA) was performed on the volatile fingerprints obtained from 26 tea samples (mean of triplicates) by grouping them by region of origin and then representing them on the cluster image map (Figure 3).

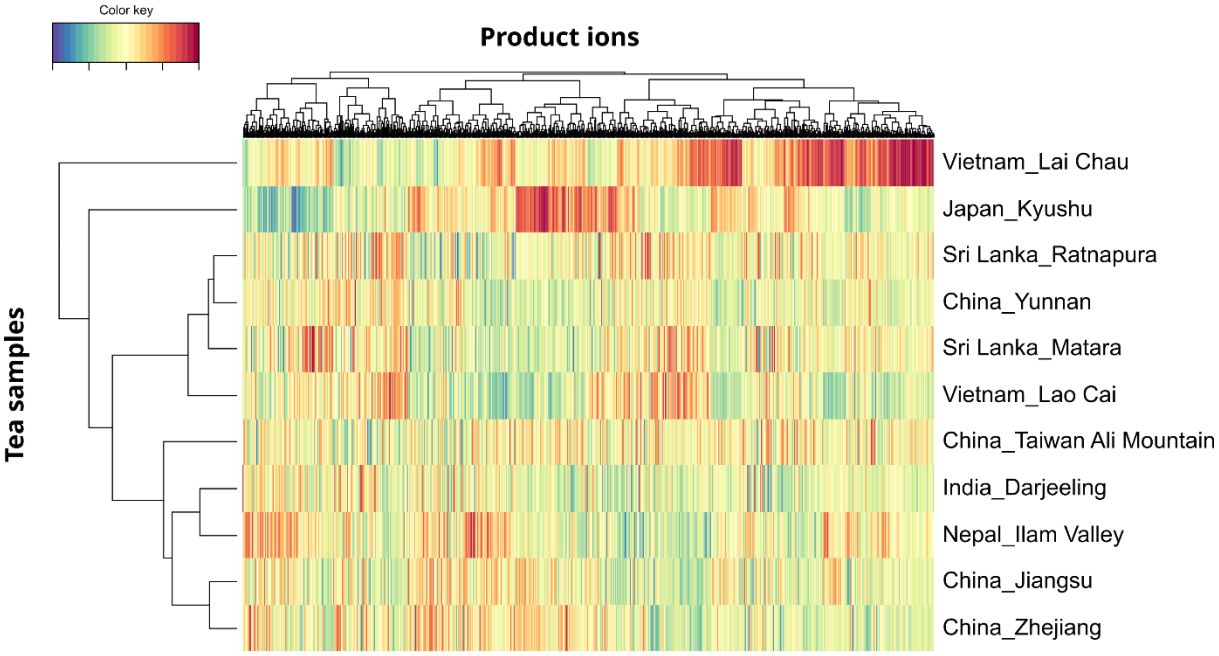

Figure 3: A clustered image map (CIM) based on Sparse PCA analysis of volatile compound fingerprints according to the parameter "country_region of origin". The horizontal dendrogram represents the hierarchical grouping per tea region and the vertical dendrogram for product ions. The colour key indicates the under expression (in blue scale) or overexpression (in red scale) of the product ion in each group sample in relation to the other samples.

No obvious classification of tea samples according to the country was observed (i.e., Chinese, Vietnamese, and Sri Lankan samples were not grouped). Vietnam_Lai Chau showed a completely different pattern to the rest of the dataset, with a large number of product ions overexpressed compared to the entire dataset. Surprisingly, this profile corresponds to the average of four different samples with different processes (oolong tea = 2, white tea = 1, and black tea = 1). Japan_Kyushu tea, presented another cluster of product ions that were overexpressed compared to the entire dataset and that separated these samples from the rest of the collection. Despite the lack of classification by country, the product knowledge allowed us to further interpret this cluster image.

Indeed, apart from these two origins with very different volatile profiles, the other samples seem to be classified in 2 clusters. A first cluster of region profiles included Sri Lanka_Ratnapura, Sri Lanka_Matara, China_Yunnan, and Vietnam_Lao Cai samples. The similarity of volatile fingerprints for these four regions cannot be explained by geographical proximity. However, this didn't come over surprised to our tea expert because the two cultivars grown in these four provinces are both large-leafed teas.

In the second cluster, the volatile fingerprints of tea samples from China_Zhejiang and China_Jiangsu were similar, which can be explained by the geographical proximity of the two production areas and the use of similar cultivars (Jiu Hang and Xiao Ye), small-leafed *C. sinensis var sinensis* tea bushes. Following the same trend, the volatile fingerprints of India_Darjeeling and Nepal_Ilam Valley teas were similar due to the geographical proximity of the two production areas and the use of a similar mix of

cultivars: a mixture of small-leaf teas from eastern China and *assamica* (large-leaf tea). The similarity of volatile fingerprints between the Darjeeling and Ilam Valley tea samples and those from Jiangsu and Zhejiang could be explain by the same cultivar base (small-leaf tea). The small-leaf tea plants in the mix of cultivars seem to contribute more to the typicality of the Darjeeling and Ilam Valley tea characteristics in a clone mix compared to the large-leaf tea plants.

The profiles of Japanese teas are consistent with a specific unique terroir, and also because Japanese research institutes have developed a new variety of *C. sinensis, Yabukita,* adapted to their climatic conditions. Teas from Vietnam_Lai Chau province are produced from a tea plant called *Jin Xuan* developed in Taiwan by the Tea Research and Extension Station and subsequently imported to this region. We were expecting similar volatile fingerprints between these two regions, Vietnam_Lai Chau and China_Taiwan Ali mountain however this was not the case. Therefore, this may suggest that growing areas also play a role in inducing differences between regions. The secret of the genetic selection of tea cultivars combined with the number of cultivars makes the understanding of phylogenetic relationships complex. The use of different cultivars in the two Vietnamese provinces notably affects volatile profiles (Figure 4).

3.2.2.Volatile fingerprints obtained from processing methods

Our partner collected samples directly from producers in different countries, thus recovering samples of various origins and colours, corresponding to the tea leaves transformation processes. Using colour labels of the tea principal component analysis does not enable to group tea together based on processing method, which therefore suggested that the process is not the predominant factor in the volatile footprint of tea. Then, a supervised analysis (sparse PLS-DA) was performed on the volatile fingerprints of the 26 tea samples to highlight the impact of transformation processes which can be seen on the cluster image map (Figure 4). This statistical tool allowed the identification of commonalities among volatile fingerprints and differences between classes. The dendrogram on the left of the map corresponds to the classification of tea based on volatile profiles, and the dendrogram at the top corresponds to the classification of product ions.

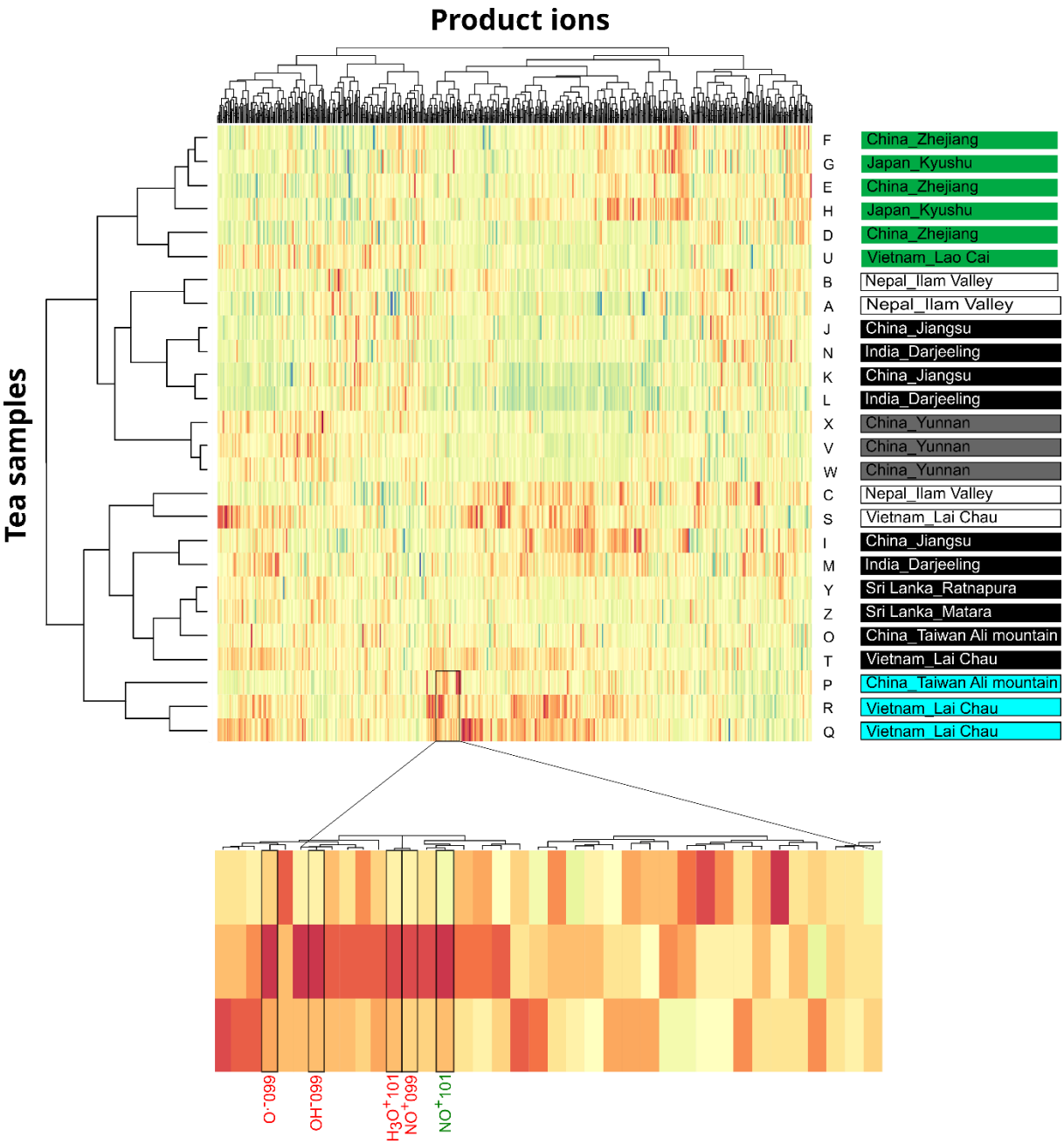

Figure 4: Clustered image maps (CIM) based on sparse PLS-DA analysis of volatile compound fingerprints based on colour/processing of tea. Green teas were highlighted with green, Oolong teas with blue, black teas highlighted with black, Dark teas highlighted with grey and white teas highlighted with white. The dendrograms represent hierarchical grouping for tea samples (horizontal) and for product ions (vertical). The colour key indicates the under expression (in blue scale) or overexpression (in red scale) of the product ion in each group sample compared to the other samples. A zoom was drawn to highlight the position of the different product ions coming from hexanal (red) and hexanol (green)

The supervised analysis of volatile fingerprints based on the dataset according to the colours of teas shows a good discrimination of green and oolong teas (Figure 4). The green teas were all grouped together and were furthest away from the oolong tea cluster. Green teas are not oxidised, whereas oolong teas are (Feng et al., 2019; Zhang et al., 2019). Recent studies observed that Oolong tea produced from several cultivars presented significantly different aroma profiles (Guo et al., 2022; Tan et al., 2022). We observed a quite high statistical distance between oolong teas with cultivar Chin Shin

from China_Taiwan Ali mountain and oolong teas with cultivar Jin Xuan from Vietnam_Lai Chau. But, in our sample set, these three Oolong teas were clearly grouped together and separated from the other colours.

A third cluster of dark teas from China_Yunnan province was observed at the center of the cluster image map, with short statistical distance, indicating a strong similarity in their volatile fingerprints. These teas are also called "Pu Erh," and correspond to post-fermented teas. (Zhang et al., 2013).

Black and white teas were mixed into two groups; some shared features with the oolong group and others with the dark group. In our dataset, volatile fingerprints did not clearly discriminate black and white teas into two separated clusters. Black tea is produced in large quantities with various process stages allowing different degrees of oxidation and roasting (Alasalvar et al., 2012). Finally, white tea is the least known, produced from buds or young leaves with a process of prolongated withering, allowing slight enzymatic oxidation and drying (Chen et al., 2019; Dai et al., 2017). Black and white teas were not discriminated using SIFT-MS. The worldwide diversity of cultivars, agricultural practices, and processing techniques produce several types of tea. Some of them were easy to identify (green, dark and oolong), whereas the other had too high level of similarity in term of VOCs to be grouped using this approach.

Volatile fingerprints allowed discrimination among dark (fermented), oolong (oxidized), and green (not oxidized) teas, which are very different. The plot Loadings figure (SI3) showed the 40 most discriminating product ions on the first component of the sPLS-DA. Unitary mass resolution of the instrument and possible ion conflicts affected the identification of molecules within the list. Nevertheless, five product ions corresponding to hexanal displayed positive discrimination for oolong teas (H_30^+ m/z 101, NO^+ m/z 99, $O^{\bullet-}$ m/z 99, $O_2^{\bullet-}$ m/z 99, and OH^- m/z 99). These particular teas are oxidised with higher levels of oxygenated molecules, such as aldehydes or alcohols among which hexanal and hexanol were previously identified (Zhou et al., 2020). The boxplot (Figure 5) shows the intensity of one ion produced by hexanal (NO^+ m/z 99) and by hexanol (NO^+ m/z 101) in different tea categories. Weaker signals were observed for green and dark teas that were consistent due to the lack of oxidation, and the strongest signals were observed for oolong teas. Black and white teas displayed intermediate levels for these product ions.

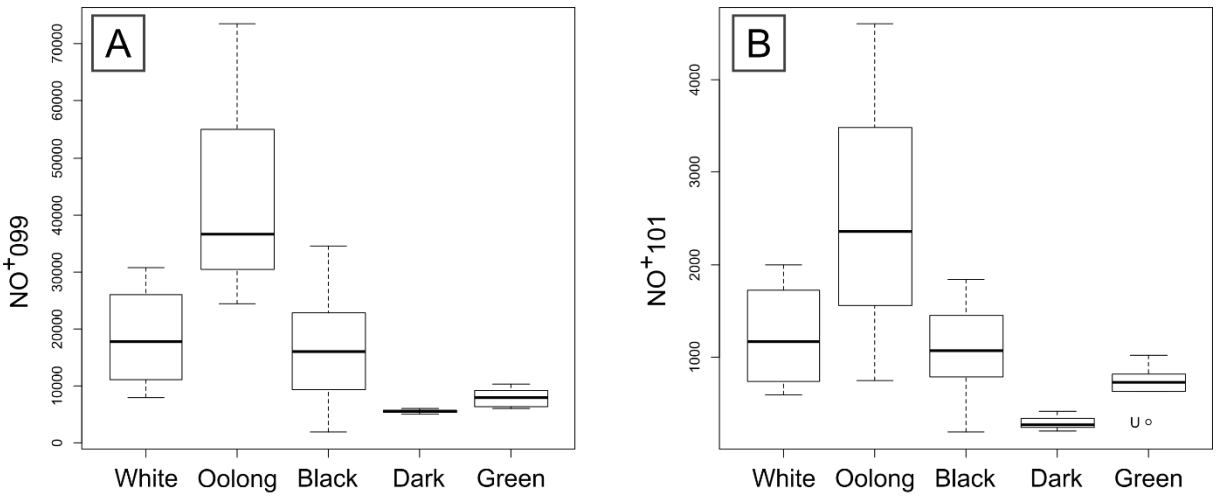

Figure 5: Boxplot of the intensity of product ions X3099 (NO^+ m/z 99) corresponding to hexanal (A) and X3101 (NO^+ m/z 101) corresponding to hexanol (B) for each colour of tea.

4. Conclusion

This work showed for the first time that the combination of volatile fingerprints with inorganic signatures can greatly improve the authentication of tea. $^{87}Sr/^{86}Sr$ ratio reflecting the bioavailable fraction of Sr derived from the mineral weathering processes of bedrock and soil was a well-known marker of geographical origin. It was demonstrated that completing this signature with elemental composition increased the ability to discriminate the 11 production regions of the studied tea samples (from 6 using only $^{87}Sr/^{86}Sr$ ratio to 10). Only the two locations in Sri Lanka seemed to share a common inorganic pattern. The origin of a food product is nevertheless not sufficient to ensure its conformity. For centuries, varietal selection of *Camelia sinensis* has led to a large number of cultivars that have developed their own aroma and cultivation properties. It is therefore very important for an authentic tea to be produced from the right cultivar that has undergone the appropriate processing steps. It was demonstrated that the main contributing factor of tea volatile fingerprints recorded with SIFT-MS was the type of cultivar. In a second approach, with a supervised statistical analysis, the different colours of tea reflecting different rates of oxidation were also separated. Oolong teas which are oxidized teas were clearly separated from the green ones, that are the least transformed teas and from dark / Pu Er samples which are fermented teas. We were not able to separate black and white teas because of the median level of oxidation of these types of tea and the variability of the different processes. Despite the technical limitations of the SIFT-MS instrument, i.e. its unit mass resolution and the presence of conflict ions, it was possible to show that the expression levels of the two molecules hexanal and hexanol were consistent with oxidation level. The statistical proximity of the ions corresponding to these two molecules in the vertical cluster means that these signals vary similarly in our dataset and may correspond to a metabolic pathway. The present study emphasizes the potential of combining instrumental and chemometric analyses to improve the traceability of teas and can also help to ensure product quality and safety throughout the food industry sectors. The application of the proposed analytical strategy on a collection of tea samples adapted in number and quality will enable the construction of a predictive model to answer questions related to product traceability and authenticity.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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