



Distinguishing the region-of-origin of roasted coffee beans with trace element ratios



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ABSTRACT

Determining coffee region-of-origin is most appropriately addressed through analyses of the product available to the consumer. We analyzed the concentrations of 44 trace elements in 53 samples of roasted Arabica coffee beans (*Coffea arabica*) from 21 different countries. Variations in absolute elemental concentrations of coffee beans arise through varying degrees of roasting (from green through dark roasts). Since trace elements are not volatilized at roasting temperatures, we conducted analyses of element ratios to evaluate concentration-related differences among beans of different origins. We used kernel density estimates to compare the distributions of 1892 element ratios for each of these countries with the combined distribution of coffee samples from the other countries. Using this quantitative approach, we demonstrated that many of the world's coffee-producing regions can be distinguished from other regions of the world on the basis of element ratios.

1. Introduction

Every day, over 1.5 billion cups of coffee are consumed worldwide, making coffee one of the most consumed beverages in the world (Luttinger & Dicum, 2012; Neves, Trombin, Lopes, Kalaki, & Milan, 2012). However, the taste, quality, and supply of coffee varies significantly by the region in which it is grown (International Coffee Organization, 2017a; Vasconcelos, Franca, Glória, & Mendonça, 2007). Many consumers have developed preferences for coffees that have unique flavor characteristics or are less abundant in the open market. As a result, coffee beans from the most coveted regions of the world can command prices many times higher than the average global price (International Coffee Organization, 2017b). Furthermore, it appears that cheaper coffees from less desirable regions may be fraudulently labeled in order to command higher prices (Southick, 2006). The ability to reliably identify the true region-of-origin of coffee beans sold to a consumer would be valuable for many stakeholders, including customers, regional farmers, traders, and distributors, and could protect brands and producers selling coffee from coveted regions.

There is an established literature showing that trace element measurements in coffee beans can be used to distinguish different coffee-producing regions (Akamine, Otaka, Nakai, Hokura, & Ito, 2010; Al-Jaf

& Saydam, 2019; Anderson & Smith, 2002; Habte et al., 2016; Haswell & Walmsley, 1998; Krivan, Barth, & Morales, 1993; Liu, You, Chen, Liu, & Chung, 2014; Muñoz-Valencia, Jurado, Ceballos-Magaña, Alcázar, & Hernández-Díaz, 2014; Oliveira, Ramos, Delerue-Matos, & Morais, 2015). The application of trace element concentrations offers an advantage over organic compound identification because organic matter can degrade during storage (Toci, Neto, Torres, & Farah, 2012). Additionally, the concentrations of trace elements in foods can be indicative of the soil type in which a crop has been grown (Gonzalez, Armenta, & de la Guardia, 2009).

Consumers in developed countries typically purchase roasted rather than green coffee beans. During roasting, a coffee bean loses 14–20% of its mass because of a reduction in moisture content and changes in carbohydrate, oil, and protein composition (Belitz, Grosch, & Schieberle, 2009). As a consequence, it is difficult to compare results of element analyses between green and roasted coffee beans. In fact, Farah (2012) summarized that the mineral concentration in Arabica coffee increased from 3.5 to 4.0% (w/w) to 4.5% during roasting. This effect was further demonstrated in Cuong et al. (2014) where all 9 different element concentrations measured in the study (K, Mg, Ca, Na, Fe, Cu, Mn, Zn, and Pb) were lowest in green beans and elevated in roasted beans, with some elements increasing proportionally to the duration of

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the roast. Consequently, variations in individual element concentrations in roasted coffee may obscure information about the region-of-origin. However, adopting a trace element ratio approach, in which the concentration of one element is divided by that of another element, is more robust. Since trace elements are not volatilized during the roasting process, trace element concentrations may increase, but the ratio of two trace element concentrations will stay relatively constant. While the concept of using element ratios to distinguish among differences in the regions-of-origin has not been previously applied to coffee beans, this approach has been effectively used in other biological studies such as honey (Czipa, Alexa, Phillips, & Kovács, 2018), sweeteners and oils (Banerjee, Kyser, Vuletich, & Leduc, 2015), onions (Ariyama, Horita, & Yasui, 2004), and wine (Bora et al., 2017; Di Paola-Naranjo et al., 2011). This element ratio approach is also commonly used in geosciences for identifying the composition or origin of geological features (Condie, 2005; Winchester & Floyd, 1977; Zhang, Zhao, Chen, Ji, & Liu, 2018).

Previous studies of element concentrations of coffee beans applied to forensic region-of-origin applications have some interpretation limitations. First, previous studies that involved roasted coffee beans (Anderson & Smith, 2002; Muñoz-Valencia et al., 2014; Oliveira et al., 2015) did not account for roasting-related changes in concentrations. Second, several previous studies have focused on green beans (Habte et al., 2016; Krivan et al., 1993; Liu et al., 2014) which may not be applicable for consumers. Third, previous studies have mostly focused on comparisons of fewer countries, constraining their applications with regard to wider global considerations in the coffee market. Lastly, for forensic applications, interpretations of most previous studies have relied on complex multivariate analyses that are often difficult to visually present to a non-scientific audience, such as a jury.

Here we used an alternative approach and analyzed only roasted coffee beans, since this is the product most widely available to consumers. First, we calculated kernel density estimates (KDEs) to represent the expected distribution of element ratios of coffee from each country. Then we identify which combinations of element abundance ratios have distinguishing capabilities. This is accomplished by calculating the percentage of the element ratio distribution of samples from a specific country that is shared with the distribution of that ratio in coffee samples from other countries. Second, we present biplots of two different element ratios to visualize those differences in coffee regions-of-origin. This approach is (a) more robust to roasting-related variations, (b) offers practical likelihood ratio determinations, and (c) allows for easier data interpretation via visualization for audiences without a statistical background. Here we distinguish coffee from 21 different coffee-producing countries, minimizing the differential effects of roast, and make the results visually presentable to audiences with various backgrounds.

2. Materials and methods

2.1. Sampling

Fifty-three roasted coffee bean samples were obtained from reliable sources from twenty-one different coffee-producing countries. Forty of our samples had more specific location information than just country of origin, and could be traced to a single sub-region within a country. The remaining samples were labeled with the country of production and may have consisted of blends from different farms within the country. This information is provided in [Supplementary Table 1](#).

2.2. Coffee sample preparation and measurement methods

Five grams of each roasted coffee bean sample was subsampled from the original package and ground with an agate mortar and pestle to eliminate potential contamination from metallic blades in electric grinders. A 0.5 g subsample of each grind was analyzed with

inductively coupled plasma mass spectrometry (ICPMS). Twelve subsamples of one coffee bean sample were analyzed a total of thirty-five times in several different analytical batches to measure within-sample and between-batch variability.

The determination of trace and ultratrace elements in ashed coffee bean samples was performed with a collision-cell quadrupole inductively coupled plasma mass spectrometer (ICPMS, Agilent 7500ce) at the ICPMS Lab in the Department of Geology and Geophysics at the University of Utah. About 0.5 g of coffee beans were weighed and ashed in a lidded porcelain 25 mL crucible in a muffle furnace (Yamato F0710CR) with the following temperature ramp: 1 hr at 120 °C, 2 hr at 350 °C and 8 hr at 550 °C. Two empty crucibles (chemical blanks) and one Standard Reference Material (SRM 1515 “Apple Leaves”, National Institute of Standards and Technology, USA) were included in each ashing batch of 17 coffee bean samples. Ashes were digested in ~4 mL of 5% HNO₃ (BDH ARISTAR Plus) added to the crucible and transferred into an acid leached 15 mL centrifuge tube. Aliquots of 2 mL 5% HNO₃ were subsequently used to rinse the crucible and added into the centrifuge tube, totaling about 10 mL of 5% HNO₃ (primary digest). A solution of indium (1 µg/mL) was added into the primary digest to a concentration of 10 ng/mL as internal standard. Tubes were mixed well and centrifuged at 3000 rpm for 5 min, and an aliquot of 0.5 mL of supernatant was transferred into a second tube and diluted to 10 mL, to which In was added to a concentration of 10 ng/mL (secondary digest). The secondary and primary digests were run in a quadrupole ICPMS using a double-pass quartz spray chamber; PTFE 50 µL/min nebulizer and syringe FAST introduction system (Elemental Scientific), platinum cones and sapphire injector in a quartz platinum-shielded torch. Elements determined in the secondary digest were Li, B, Na, Mg, Al, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Ba, Tl, and Th. For Na, K, Mn, Fe and Cu the collision cell was used with a flow of 5 mL He/min, and for As and Se a mixture of 1.5 mL H₂/min and 1.5 mL He/min was used. Elements determined in the primary digest were Be, V, Cr, Y, Mo, Cd, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Pb and U.

An external calibration curve with all the elements reported was prepared from 1000 mg/L single elemental standard solutions in HNO₃ (Inorganic Ventures). Samples, blanks and the calibration solutions were prepared in 5% HNO₃ (BDH Aristair Plus). Standard Reference Material (SRM) 1643e (“Trace Elements in Water”, National Institute of Standards and Technology, USA) was prepared at 1:20 dilution and run together with blanks, samples and calibration curve solutions. Indium at a concentration of 10 ng/mL was added to calibration curve, reference material, samples and blanks as internal standard. Twelve replicates were run for each element, with a total acquisition time of about 5 min for the secondary digest, and 3 min for the primary digest. Eighty-second rinses at 400 µL per minute were performed after samples, blanks, and SRM. Limit of determination (LoD) was calculated as three times the standard deviation of the blanks, multiplied by the dilution factor used for samples. The instrument is located in a filtered air positive pressure lab and sample handling and chemistry was performed in laminar flow benches. The measured values for Na in the SRM 1515 apple leaf standard was 4–5 times higher than the certified value, despite the chemical blank being below the threshold. This is likely due to leaching from the ceramic crucible glaze during ashing; it follows that the concentrations of Na in the samples are likely to be biased. For this reason, the Na values have been removed from the supplementary tables.

2.3. Statistical methods and data analysis

Trace element ratios with relative standard deviations greater than 30% in a repeatedly run sample were excluded from analysis. [Supplementary Table 2](#) contains a summary of all measurements made. Note that the standard deviations are for the entire dataset. [Supplementary Table 3](#) contains the average element concentrations for samples by country of origin. For measurements that were below the

LoD, the LoD was substituted as a proxy. All data were analyzed in R version 3.5.1 (R Core Team, 2018).

A KDE for each ratio for each country was calculated using the 'density' function in R, a Gaussian kernel type, and a lower limit at 0 (Scott, 1992). The default bandwidth was selected by utilizing the common Silverman's 'rule of thumb' technique (Silverman, 1986). If only one sample was analyzed, or the default bandwidth was lower than the standard deviation of the consistency sample (i.e., a single, repeatedly analyzed coffee bean samples), then the standard deviation of the consistency sample was used as a bandwidth. The KDE of each country for each elemental ratio is then compared to the KDE of all coffee samples from other countries. A percent overlap between the two density distributions is calculated by integrating the overlapping area between the two density estimates divided by the area under the KDE of the samples from other countries; this parameter identifies how much of one distribution of interest is shared with all of the other coffee-producing regions of the world. A visualization of a KDE with overlap is shown in Fig. 2. For each country, the element ratios that share less of their distribution with those of other countries' coffees are better able to distinguish that country. We used this method to identify the element abundance ratios that shared the lowest percentage of their distributions with other coffees.

We also present element ratios in the form of paired biplots, with one element ratio on each axis. Various methods exist for visually representing the confidence intervals of biplots, including drawing multiple density contours, using individual density contours (such as with the 'ks' package; Duong, 2019) or just plotting the points with transparency. Each of these visual aids has its own benefits and limitations but can effectively communicate element ratio data to audiences without scientific backgrounds.

3. Results and discussion

3.1. Distinguishing coffee origin on the basis of element abundance ratios

Fig. 1 shows the trace element abundance ratios with the greatest distinguishing capability for each coffee-producing country, and their corresponding percent distribution shared with coffee beans produced in other parts of the world. The lower the percent of distribution shared, the more effective the trace element ratio is at distinguishing the coffee region-of-origin. Certain coffee-producing regions are easier to distinguish than others. For example, coffee beans from Yemen were easily distinguished from all other regions with several trace element ratios involving either boron or cesium. Several of these element abundance ratios, such as B/Mg, shared less than 0.5% of their distributions with other coffee beans grown elsewhere in the world. Additionally, Hawaiian samples ($n = 6$) were easily distinguishable with Rb/Ni; these samples shared only 8% of their Rb/Ni distribution with other countries. This is in stark contrast to Guatemala ($n = 3$), where its most distinct ratio is Mn/Sr, which shared 26 percent of its distribution with samples from other countries. The origins of coffee beans from certain countries may have been more easily distinguishable than others due to a combination of within-country variation in soil characteristics, growing conditions, and farming practices, among others.

Often in distinguishing different countries on the basis of element ratios, a particular element stood out, indicating that this element contributed to a high discrimination capacity. Coffee beans from Yemen, for example, had very different B concentrations than other coffee samples around the world. When considering all regions, Mn, Fe, and Rb were the elements most frequently identified as having distinguishing capabilities (in the top 6 ratios from 15, 13, and 13 of 22 regions, respectively). The element ratios that contained these elements were not necessarily the best at distinguishing individual coffee-producing countries, but they were at least somewhat useful for distinguishing many countries when used in an element ratio approach. The strong distinguishing abilities of Mn is consistent with the findings of

Krivan et al. (1993) which considered green beans, and Oliveira et al. (2015), which analyzed espresso coffee samples.

Fig. 2 serves as an example to depict the kernel density estimates of the six ratios with the greatest distinguishing capabilities for Brazilian samples. Some ratios, including Ce/Dy and Ce/Nd, were effective at distinguishing Brazilian samples because their mean value is relatively far away from the mean value of other countries sampled. However, other element ratios, such as Sr/Ni for Brazil, were identified as useful by the KDE overlap method because they have a low range of measurements within the Brazilian samples relative to the range of values in other countries. As a result, it was still able to effectively distinguish that country from some, but not all, coffee-producing regions. In addition, certain element ratios may provide an indication about the region within a country, as Brazilian samples were analyzed from five farms in geographically distinct regions. La/Er and La/Ho, which have bimodal distributions, may illustrate regional differences within Brazil, whereas Ce/Dy and Ce/Nd cluster the Brazilian samples as a country.

The KDE approach has two interpretive advantages. First, it provides a foundation for likelihood ratio estimation. Likelihood ratios can help to communicate the odds that a sample is from a given location. This is useful because they are widely used in forensic applications and is easier for a non-scientific audience to understand. Second, it identifies elemental ratios useful for distinguishing one coffee-producing region from other regions of the world.

On the other hand, the limitations of the KDE approach are a requirement for large sample numbers and adequate bandwidth selection. While only one coffee bean sample from Vietnam was tested, it happened to be distinguishable from other coffee bean samples with a variety of different ratios. However, coffee beans from other regions may be more difficult to distinguish. In addition, over-smoothed bandwidths can ignore useful ratios that have distinguishing capabilities for a country, whereas under-smoothed bandwidths can potentially identify ratios that have too wide of a range in its distribution to be effective. We present multiple ratios to distinguish each coffee region because the exact percent shared between a given country's distribution and the distribution of other countries is likely to change with sample size, but the element ratios presented will likely still have strong distinguishing capabilities. Also, the method of cultivation was not considered for this analysis, but may alter the concentrations of certain elements (dos Santos, dos Santos, Conti, dos Santos, & de Oliveira, 2009; Singh, 1994).

3.2. Distinguishing coffee bean regions-of-origin with biplots

Some coffee beans, such as those from Yemen, were easily distinguished with a single trace element ratio. On the other hand, coffee beans from Peru, Colombia, Guatemala, and Brazil were more difficult to distinguish from other the regions. Using combinations of multiple element ratios proved more useful in distinguishing these countries from others. By combining pairs of element ratios having low overlap values into a biplot, coffee bean regions-of-origins could be further distinguished. Guatemalan coffee beans were effectively distinguished from other regions using a biplot of Mn/Sr and U/Yb (Fig. 3). While the scatter among the measurements is large, the values for Guatemalan samples in this plot are clearly distant from the majority of world measurements. A biplot of Ce/Yb and La/Er is able to very clearly distinguish four of the five Brazilian samples (Fig. 4). Furthermore, countries that were distinguishable with one element ratio were further distinguished with two element ratios. For example, coffee beans from Yemen were distinguished on the basis of a biplot of B/Mn and Ca/Cs, even though both B/Mn and Ca/Cs alone were able to distinguish Yemen coffee beans from samples in other parts of the world with ease (Fig. 5).

Usually, simply combining two element ratios that shared a low percentage of their distribution for country resulted in a useful biplot. Biplots may be easier for audiences without a statistical background to

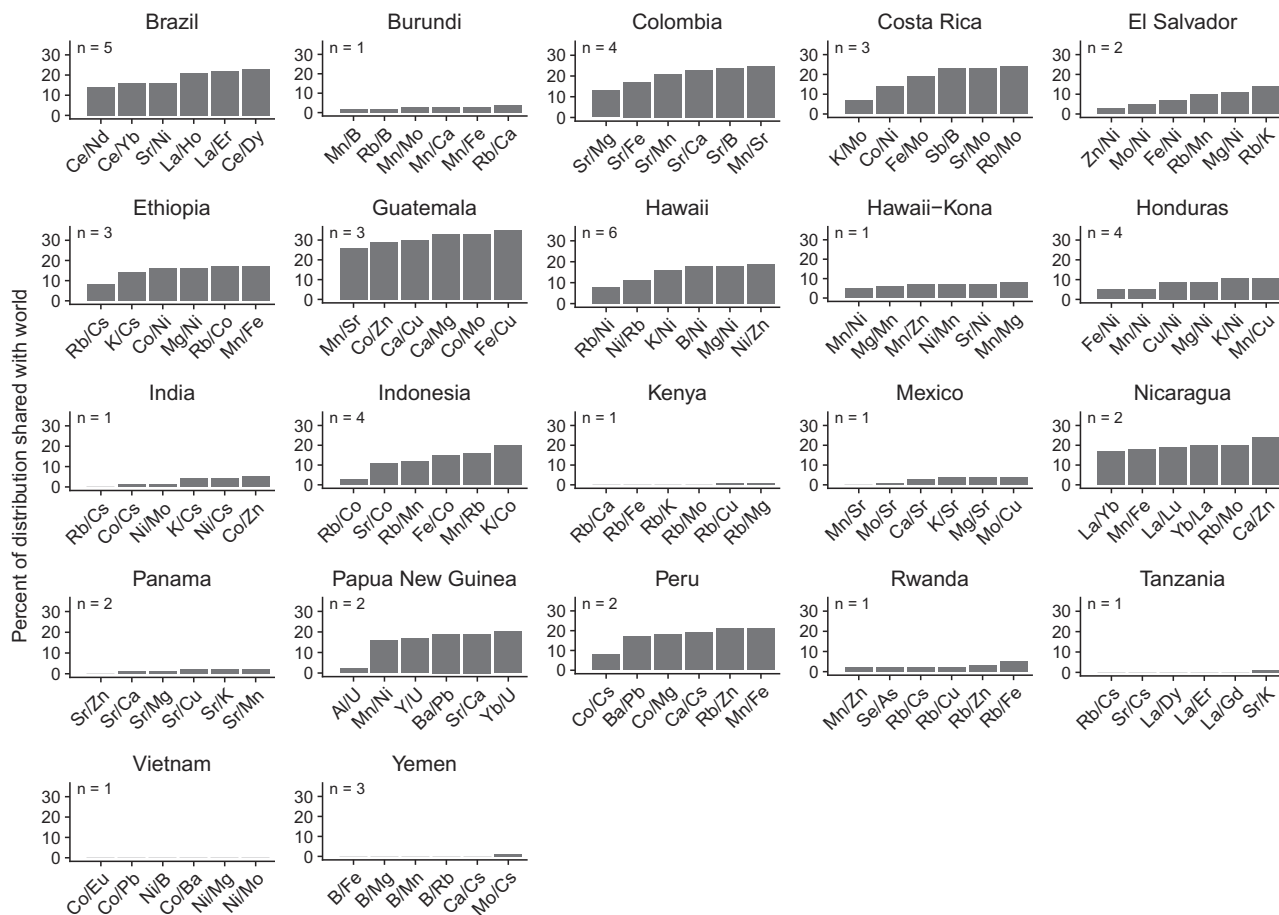


Fig. 1. Percent of the kernel density estimate of each ratio for samples from each country that overlaps with the kernel density estimate of coffees from other countries. For each country, the six element ratios with the lowest percent overlap are shown. Countries that have a lower percent of their distribution shared with other countries are more easily distinguishable than countries with a higher percent of their distribution shared with other countries. Ratios with no visible bar height have shared distribution of less than 0.5%.

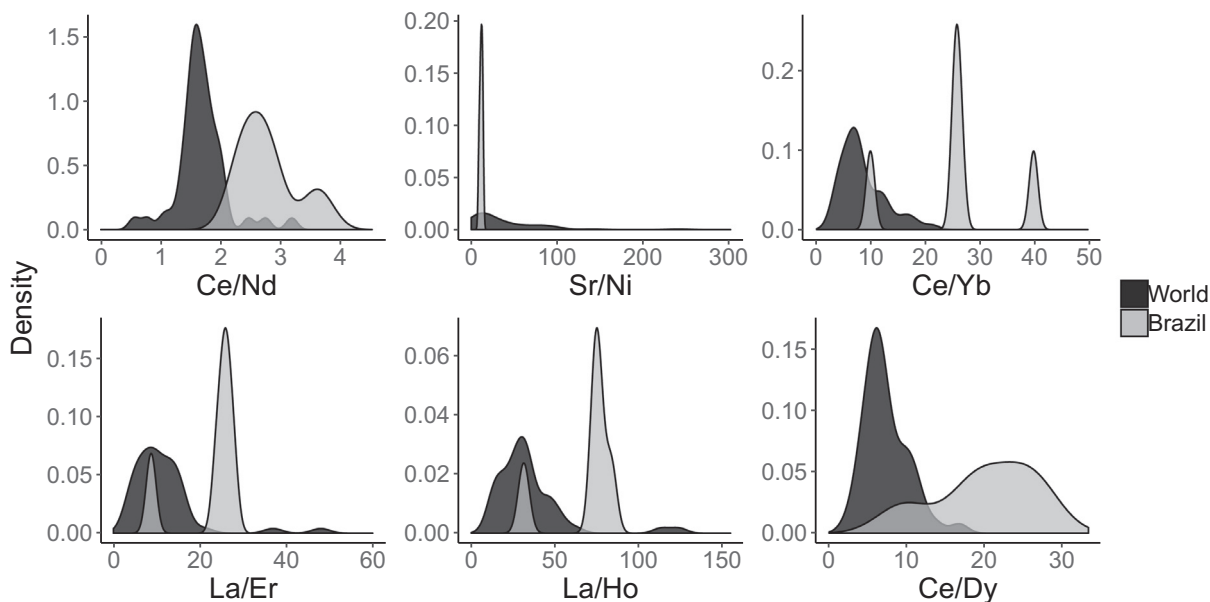


Fig. 2. Kernel density estimates for Brazilian samples (light grey) and samples from other sampled counties (dark grey) for the six ratios with lowest percent overlap between the Brazilian and global distributions. Percent overlaps were calculated by integrating the area under the overlapping curve and dividing by the area under the world distribution density. Ce/Nd or Ce/Dy may be the best choice for distinguishing Brazilian samples as a whole country.

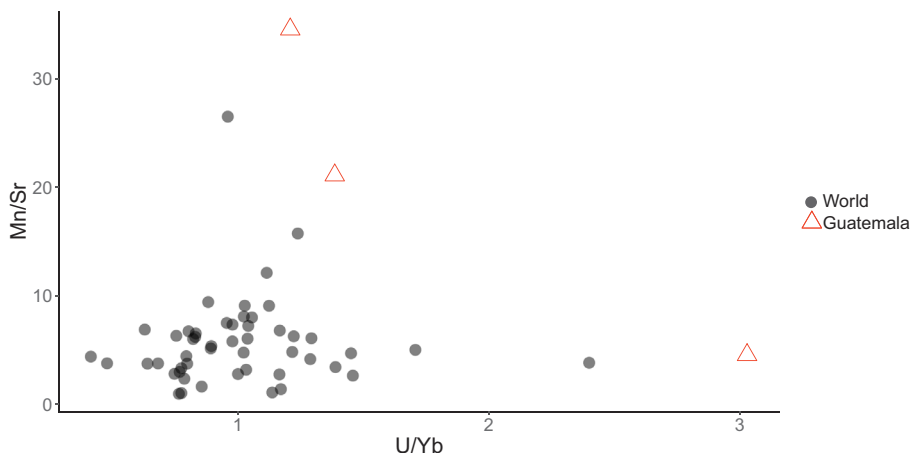


Fig. 3. Distinguishing Guatemalan samples with biplot approach. This biplot distinguishes Guatemala (red triangles) from other countries (grey circles) using the combination of U/Yb and Mn/Sr. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

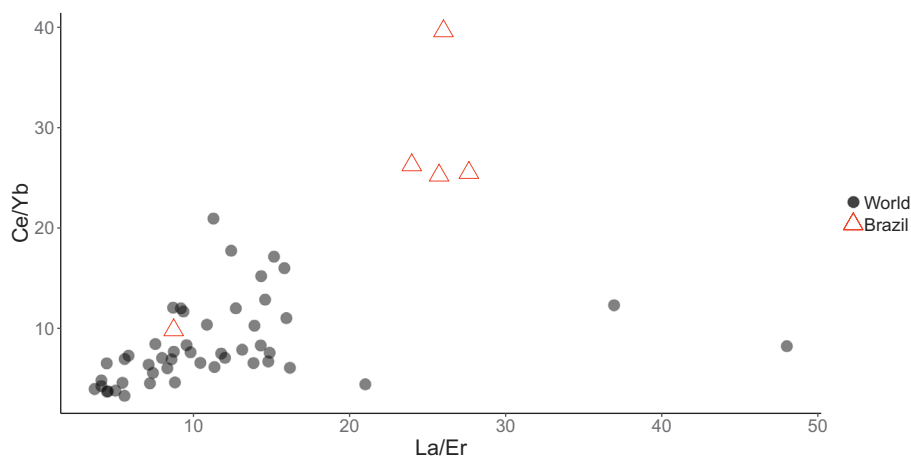


Fig. 4. Distinguishing Brazilian samples with biplot approach. Four of five Brazilian samples (red triangles) can be clearly distinguished from samples from other countries (grey circles) with a biplot of the element abundance ratios La/Er and Ce/Yb. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

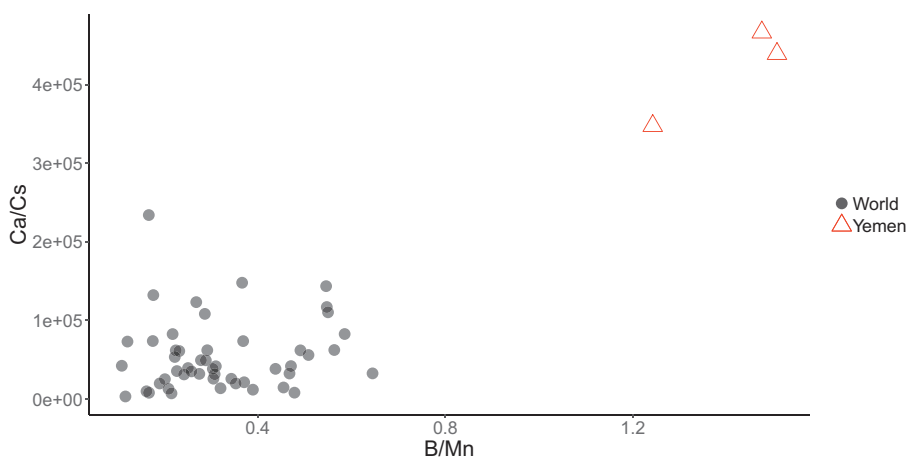


Fig. 5. Distinguishing Yemen samples with biplot approach. This plot distinguishes Yemen (red triangles) from other countries (grey circles) with a biplot of B/Mn and Ca/Cs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

interpret than other multivariate visualization methods because the axes contain measurements rather than statistical parameters. Biplots effectively convey that samples from a country of interest have measurements that are different than, or uncommon, among samples from the rest of the world.

4. Conclusions

The trace element concentrations of roasted coffee beans can be effectively used to distinguish coffees of different origins as they are linked to local soil composition. Because the concentrations of 44 trace elements were measured, the likelihood of finding distinguishable trace element ratios was quite high. Trace element ratios of roasted coffee are more robust to some of the complications encountered in previous

efforts to determine the region-of-origin of coffee, such as variations introduced by degradation during storage or chemical and/or mass balance changes during roasting.

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CRediT authorship contribution statement

Nicholas Q. Bitter: Writing - original draft, Software, Methodology, Formal analysis. **Diego P. Fernandez:** Resources, Investigation. **Avery W. Driscoll:** Writing - review & editing, Methodology. **John D. Howa:** Writing - review & editing, Methodology, Supervision. **James R. Ehleringer:** Writing - review & editing, Methodology, Supervision, Conceptualization, Project administration.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2020.126602>.

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