



# The effect of roasting on boron isotope ratio in coffee beans: Implications for provenance studies of roasted coffee

D. Malinovsky<sup>a,\*</sup>, P.J.H. Dunn<sup>a</sup>, P. Rooke<sup>b</sup>, H. Goenaga-Infante<sup>a</sup>

<sup>a</sup> National Measurement Laboratory, LGC, Queens Road, Teddington TW11 0LY, UK

<sup>b</sup> British Coffee Association, Southill Barn, Southill Business Park, Charlbury, Oxon OX7 3EW, UK

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## ABSTRACT

We determined  $\delta^{11}\text{B}$  values of green and roasted coffee beans from 20 locations worldwide and conducted laboratory experiments with the aim to investigate boron isotope fractionation during roasting. Authentic single origin roasted coffees were found to be isotopically lighter than their green bean counterparts, with an average difference of 1.5‰. This isotope fractionation can be explained as arising from partial dissociation of boric acid in capillary water of green beans, where  $^{11}\text{B}$  isotopes are preferentially partitioned into molecules of undissociated boric acid and are then volatilised during roasting. However, boron isotope fractionation induced by roasting was significantly smaller than between-origin variations in  $\delta^{11}\text{B}$  values of green coffee beans that had the range of ~54‰. This implies that  $\delta^{11}\text{B}$  isotopic composition of roasted coffee retains the geographical origin information within  $\delta^{11}\text{B}$  values of green beans when regional differences in boron isotopic composition of coffee are considered.

## 1. Introduction

Coffee has long been one of the most commercialised and widely consumed beverages in the world (Farah, 2012). With global consumption of coffee steadily growing, a rise in adulteration and mislabelling of coffee products has also been observed (Burns et al., 2017; Sezer et al., 2018; Toci et al., 2016). High precision  $^{11}\text{B}/^{10}\text{B}$  isotope ratio measurements have shown potential as a useful tool for assuring authenticity of plant-based food and beverages (Coetzee & Vanhaecke, 2005; Drivelos & Georgiou, 2012; Laursen et al., 2016; Li et al., 2016; Zhao et al., 2014). The following properties of boron make it a particularly useful marker: (1) the element is essential for higher plants and present in them at concentrations sufficient for isotope analysis ( $\mu\text{g}/\text{g}$ ) (Chen et al., 2023; Xiao et al., 2022); (2) the range of natural variations in the isotopic composition of boron across all matrix types is wide, being ~100‰ (Marschall & Foster, 2018); (3) geochemical composition of soil is a major control of variations in the isotopic composition of boron in plants (Gaillardet & Lemarchard, 2018; Dembitsky et al., 2002).

Thus far, only the boron isotopic compositions of green coffee beans have been considered in provenance studies (Liu et al., 2014; Rodrigues et al., 2011; Serra et al., 2005; Wieser et al., 2001). However, the process

of bringing the harvested coffee fruits to consumers involves a series of bean processing steps, including roasting. It is roasted coffee that dominates the consumer market in developed countries. Ground, roasted coffee is also a highly complex matrix for investigating potential adulteration because mixing of different coffee products cannot be detected visually (Burns et al., 2017; Burns & Walker, 2020; Toci et al., 2016). Instrumental techniques are therefore of growing importance in analytical testing of roasted coffee.

Roasting results in mass loss of coffee beans and compound-specific volatilisation that leads to profound changes in the chemical composition of the roasted beans (Yeretizian et al., 2002). However, previous studies reported an agreement of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{18}\text{O}$  compositions between the same origin green and roasted coffee (Carter et al., 2015; Driscoll et al., 2020; Tian et al., 2022). It was only the isotopic composition of hydrogen in coffee beans that was affected by roasting (Tian et al., 2022). The potential for bias in oxygen isotope measurements of bulk roasted beans due to volatilisation of components was acknowledged in another study, and compound-specific isotope analysis of non-volatiles was suggested as a strategy to avoid it (Driscoll et al., 2020).

Boron and strontium hold promise in authentication of the provenance and have far fewer chemical species in coffee beans. Chemical

\* Corresponding author.

E-mail address: [dmitriy.malinovskiy@lgcgroup.com](mailto:dmitriy.malinovskiy@lgcgroup.com) (D. Malinovsky).

species of strontium in plants are considered non-volatile. However, volatility of boric acid, by far the predominant species of boron in plants (Dembitsky et al., 2002), is a well-known phenomenon and has been widely used for quantitative separation of the element from different sample matrices (Gaillardet et al., 2001; Liu et al., 2018; Wang et al., 2020).

When boron isotope fractionation associated with boron volatilisation is concerned, a review of the literature reveals controversial data. On one hand, the absence of boron isotope fractionation during boron volatilisation from acidic solution at moderate temperatures (60–65 °C) has been reported (Gaillardet et al., 2001). Some authors have also indicated that no boron isotope fractionation occurs during dry-ashing of plant material (Rosner et al., 2011; Xu et al. 2015, Xiao et al., 2019). On the other hand, moderate to strong boron isotope fractionation during boron volatilisation from an aqueous phase, with the isotope fractionation factor,  $(^{11}\text{B}/^{10}\text{B})_{\text{vapor}}/(^{11}\text{B}/^{10}\text{B})_{\text{solution}}$ , of up to 1.0064, has been observed numerous times (Kowalski & Wunder, 2018; Miyata et al., 2000; Rose-Koga et al., 2006; Van Hoecke et al., 2014; Wang et al., 2020; Xiao et al., 1997). Volatility of boron compounds has also been used as the physico-chemical basis for the separation of boron isotopes on industrial scale (Kiss et al., 1961). These findings suggest that occurrence and extent of boron isotope fractionation due to boron volatilisation can be controlled by ambient physico-chemical conditions and sample matrix.

In this work, we have studied the effect of roasting of green coffee beans on the isotopic composition of boron in the beans. The aim was three-fold: (1) to assess whether roasting of coffee beans results in change in the isotopic composition of boron, (2) to provide a plausible explanation of this fractionation, if it occurs, (3) to assess the suitability of boron isotope data of roasted coffee in authentication of geographical origin. The study involved boron isotope ratio measurements of single origin green and roasted coffee beans from different geographical locations and controlled experiments in the laboratory. Boron isotope ratios were determined by multicollector ICP-MS, the technique that allows resolution of small natural variations in the isotopic composition of boron. Experimental findings have been discussed in the context of significance and application of boron isotope ratio data as a tool to support provenance of coffee products.

## 2. Materials and methods

### 2.1. Samples and sample preparation

36 samples of air dried green and roasted Arabica and Robusta coffee beans from 20 single locations in 14 coffee-producing countries were provided by the British Coffee Association (Table S1). We use the terms “single origin coffee” and the “same origin coffee” to denote green and roasted coffee beans from a particular geographical location within a country where these beans were grown. Coffee beans were powdered using a commercial coffee grinder (Kenwood, BL430 series), with careful cleaning between samples. Approximately 0.3 g aliquots of powdered samples were transferred into Teflon microwave bombs and digested in 10 ml of 12 M HNO<sub>3</sub> (Romil, Cambridge, UK) in a microwave (Milestone, Sorisole, Italy) using an 1800 W power setting. Digested solutions were doped with *D*-mannitol (Sigma Aldrich, Gillingham, UK) to a concentration of ~ 10 µg/g, evaporated on a hot plate to near dryness, taken up in 4 ml of 0.08 M HNO<sub>3</sub>, and subjected to separation of boron by ion-exchange chromatography.

### 2.2. Laboratory experiments

To provide insight into mechanisms of boron isotope fractionation during roasting, the following sets of experiments were carried out. First, roasting of powdered green beans from different sample shipment was performed in laboratory oven at 200 °C for 60 min with the aim of determination of boron recovery in roasting. Second, to assess the effect

of different roasting temperature, aliquots of single origin green coffee were heated in the oven for 60 min at temperatures of 80 °C, 100 °C, 120 °C, 180 °C, 200 °C and 220 °C, respectively. <sup>11</sup>B/<sup>10</sup>B isotope ratios were determined in the above samples before and after thermal treatment. Third, changes in the isotopic composition of dissolved boric acid (NIST SRM 951a) were monitored in a water solution with pH of ~ 5.7, containing boric acid at concentration level of 10 mg L<sup>-1</sup>, placed on a hot plate at ~ 80 °C. The experiment was performed both without other substances added to the solution and with the addition of sucrose at concentration of ~ 800 mg L<sup>-1</sup>. Sucrose is the main form of sugar in coffee beans (Ky et al., 2001). Our aim in this experiment was to assess whether the presence of sucrose plays a role in suppressing volatilisation of boric acid from aqueous phase. It is worth noting that the pH value of ~ 5.7 was chosen because the median pH of 5.7 was reported for Robusta coffee beans roasted at different temperatures (Chindapan et al., 2019), with pH values of the xylem sap of plants shown as ranging from 4.5 to 7.4 (Teskey et al., 2008).

Lastly, possible isotope fractionation during sublimation of boron from solid B(OH)<sub>3</sub> was studied. It involved transferring 0.1 g aliquots of finely powdered boric acid (NIST SRM 951a) into nickel beakers and heating them in an oven at 200 °C for 72 h. The powder was then transferred into plastic 50 ml Falcon tubes, dissolved in 0.3 M HNO<sub>3</sub> and subjected to isotopic analysis. Further details of the laboratory experiments are given in [Supplementary Material](#).

### 2.3. Ion-exchange chromatography

Prior to isotope ratio measurement, ion-exchange separation of boron from concomitant elements of sample matrix was carried out to minimise spectral interferences and matrix effects. The procedure was modified after Liu et al. (2014) and Xiao et al. (2019) and made use of the fact that in acidic solution boron exists entirely in the form of neutral B(OH)<sub>3</sub> species, and therefore is not retained on a cation-exchange column. The columns were prepared from 5 ml disposable pipette tips, loaded with ~0.8 ml of strongly acidic cation exchange resin AG 50 W-X8 (Sigma Aldrich, Gillingham, UK) held in place with small plugs of cotton wool. They were cleaned by 10 ml 6 M HNO<sub>3</sub>, then by 5 ml deionised water and conditioned by 5 ml 0.08 M HNO<sub>3</sub>. Sample solutions were carefully loaded into the columns in 0.08 M HNO<sub>3</sub> and followed by a further wash with 1 ml of 0.08 M HNO<sub>3</sub>. Quantitative boron recovery was confirmed on aliquots taken before and after the separation. The absence of boron isotope fractionation in the procedure were also verified by measurements of <sup>11</sup>B/<sup>10</sup>B isotope ratios of boron isotope standard NIST SRM 951a run through the ion-exchange column.

### 2.4. Mass spectrometry and data presentation

A Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) was used in the measurements (Thermo Fisher Scientific, Bremen, Germany). Samples and standards were introduced into the plasma through a stable introduction system consisting of a peristaltic pump, a 50 µl microconcentric nebuliser, and a tandem quartz spray chamber arrangement (cyclone + Scott double pass). At the beginning of each measurement session, the instrument was tuned to maximise intensity of the signal by adjusting the torch position, gas flow rates, and lens voltages, with typical values of instrumental parameters reported elsewhere (Malinovsky et al., 2020). The analyses were conducted in low resolution mode. Signal intensities for <sup>11</sup>B<sup>+</sup> ions were ~ 10 V per mg L<sup>-1</sup>. The sample-standard bracketing technique was used to correct for instrumental mass bias. Concentrations of samples and bracketing NIST SRM 951a boron isotope standards were matched to within 20%. A 0.16 M HNO<sub>3</sub> solution containing 0.03% NaF was used to wash the sample introduction system between samples. It was also verified in the on-line scan window that signal from previous sample had dropped to the background level prior to starting the next measurement.

The on-line data processing included calculation of the ion beam

intensity ratios and removal of outliers using a  $2\sigma$ -test. Results of the measurements were expressed in the  $\delta$ -notation, as defined by the relationship

$$\delta^{11}\text{B}_{\text{SRM 951a}} = \frac{R(^{11}\text{B}/^{10}\text{B})}{R_{\text{SRM 951a}}(^{11}\text{B}/^{10}\text{B})} - 1 \quad (1)$$

These delta values were multiplied by a factor of 1000 and expressed in the per mil (‰) notation. Unless stated otherwise, measurement uncertainties reported are combined standard uncertainties obtained using the Kragten's approach (Kragten, 1994) and the ISO/IEC Guide 98-3:2008 (JCGM series, 2008).

### 3. Results

#### 3.1. $\delta^{11}\text{B}$ values of green and roasted coffee

The  $\delta^{11}\text{B}$  values of single origin green and roasted coffee beans from different coffee producing countries, analysed in this study, are shown in Fig. 1 and Supplementary Table 1. These data show that green and roasted coffee from the same location were characterised by similar  $\delta^{11}\text{B}$  values, whereas variations in  $\delta^{11}\text{B}$  values of coffee beans from different geographical regions were significantly larger. An interesting observation is that boron isotope composition of roasted coffee was consistently lighter than that of green coffee of the same origin, with the difference between them ranging from 0.1‰ to 3.3‰ and the mean value of 1.5‰ ( $n = 23$ ). Given that combined standard uncertainty of the measurements ranged from 0.2‰ to 0.7‰ and the median value of 0.4‰ (Tables S1 and S2), most of the above variations can be ascribed to boron isotope fractionation that occurs during roasting. Mass balance calculations using boron concentration data for homogenised green coffee powder before and after roasting in the laboratory indicate boron recovery of  $85 \pm 5\%$  ( $1 \sigma$ ;  $n = 6$ ). Fig. 2 and Supplementary Table 2 show  $\delta^{11}\text{B}$  values of the samples roasted in the laboratory.

#### 3.2. Experimental modelling of boron volatilisation

The  $\delta^{11}\text{B}$  values of green coffee exposed to high temperatures in the oven are shown in Fig. 3. They show that boron isotope fractionation already occurs at temperatures of 80 °C and 100 °C, with the magnitude of shift in  $\delta^{11}\text{B}$  values being similar to those observed at higher temperatures.

Results of the experiments on volatilisation of boric acid from solution at 80 °C are shown in Fig. 4 and Fig. 5. Experimentally determined  $\delta^{11}\text{B}$  composition of aqueous phase is shown in Fig. 4A. It can be seen that the isotopic composition of dissolved boron becomes progressively depleted in the  $^{11}\text{B}$  isotope with increasing fraction of boric acid lost from solution by volatilisation. Fig. 4B shows theoretically predicted  $\delta^{11}\text{B}$  values of volatilised boric acid which were calculated using mass balance approach and the Rayleigh distillation equation (Mariotti et al., 1981):

$$(\alpha - 1) \ln f = \ln \frac{\delta^{11}\text{B}_{\text{solution}} + 1}{\delta^{11}\text{B}_{\text{solution},0} + 1} \quad (2)$$

$$\alpha = \left( \frac{1 + \delta^{11}\text{B}_{\text{vapour}}}{1 + \delta^{11}\text{B}_{\text{solution}}} \right) \quad (3)$$

where  $\alpha$  is the  $^{11}\text{B}/^{10}\text{B}$  isotope fractionation factor between coexisting vapour and solution phases,  $\delta^{11}\text{B}_{\text{solution},0}$  and  $\delta^{11}\text{B}_{\text{solution}}$  are  $\delta^{11}\text{B}$  values of boron in solution at the beginning of the process and at time of sampling ( $\delta^{11}\text{B}$  values input into equations (2) and (3) were expressed in their native form rather than in per mil), and  $f$  is the fraction of boron remaining in solution. Details of the calculations are given in Fig. 4C and further explained in Supplementary material.

Fig. 5 shows the effect that the presence of sucrose in solution can have on boron isotope fractionation. The residues after evaporation of the sucrose-containing solutions were characterised by  $\delta^{11}\text{B}$  values of  $0.31 \pm 0.27\%$  ( $u_c$ ). Data obtained in this experiment show that sucrose

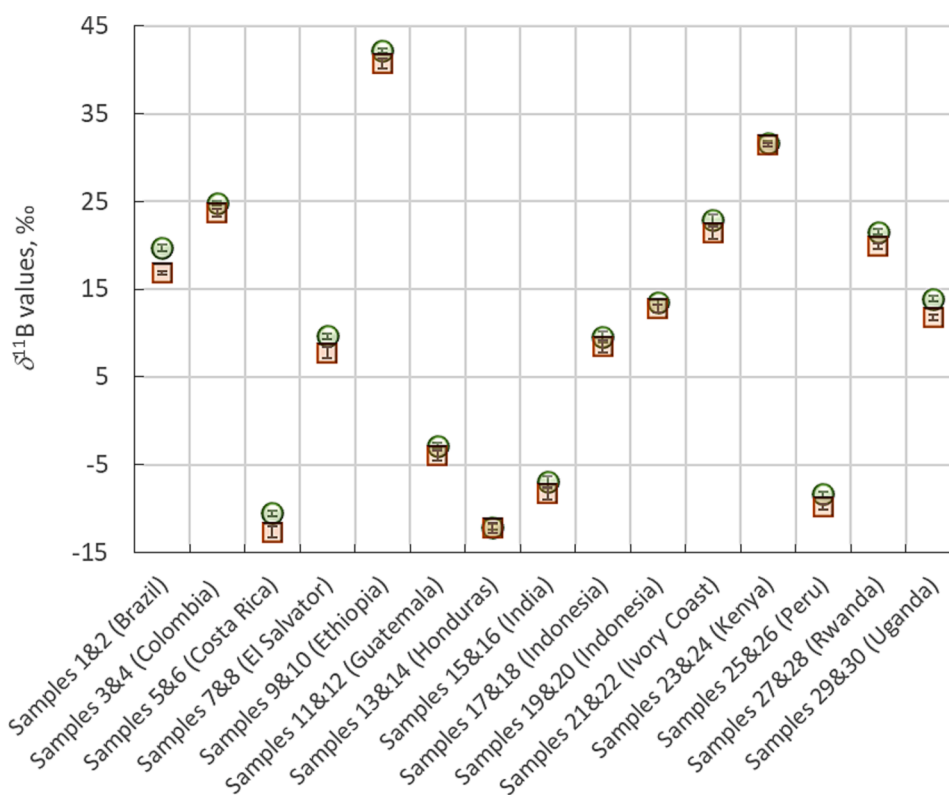
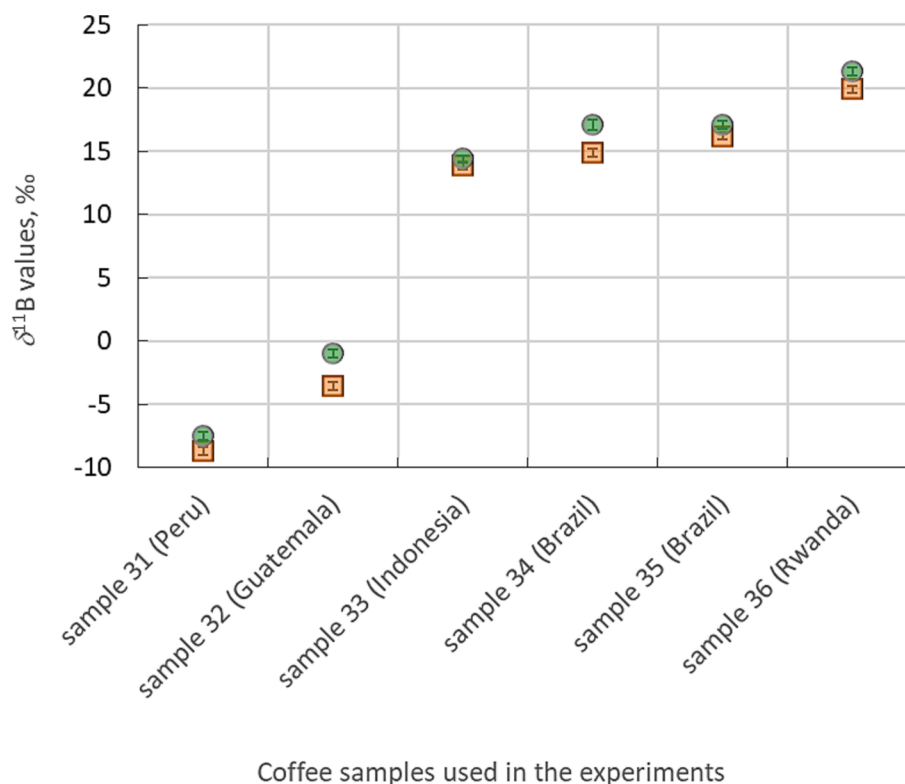
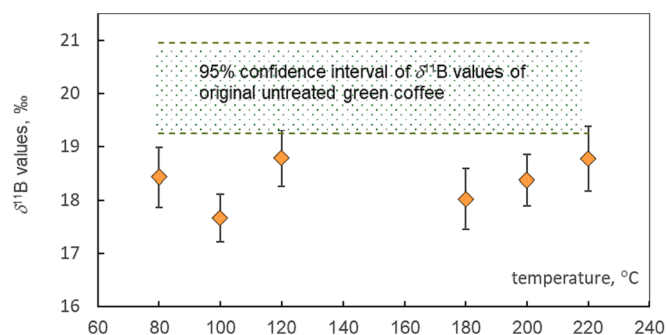


Fig. 1.  $\delta^{11}\text{B}$  values of green and roasted coffee beans from single location in different coffee producing countries. Circles represent green coffee samples; squares represent roasted coffee. Measurement uncertainties,  $u_c$ , are smaller than the data points. See section 3.1 and Supplementary Table 1 for details.



**Fig. 2.**  $\delta^{11}\text{B}$  values of green coffee beans of different geographical origin before and after roasting in the laboratory oven (see section 2.2 of Material & methods for details). Circles represent green coffee samples; squares represent roasted coffee. Measurement uncertainties ( $u_c$ ) are smaller than the data points. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.**  $\delta^{11}\text{B}$  values of independent aliquots of a single origin, powdered green coffee kept in the laboratory oven at the indicated temperatures for 60 min, relative to the original composition. Dashed lines denote the 95% confidence interval for the  $\delta^{11}\text{B}$  value of the original green coffee before heating ( $\delta^{11}\text{B} = 20.1 \pm 0.86$ ). Error bars are expanded uncertainties ( $U_c = 2 \times u_c$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can play a role in suppressing boron isotope fractionation during roasting.

Fig. 6 summarises the data obtained from the boron sublimation experiments. It can be seen from this figure that  $\delta^{11}\text{B}$  values of residual solid  $\text{B}(\text{OH})_3$  remain unchanged after heating to 200 °C for 72 h.

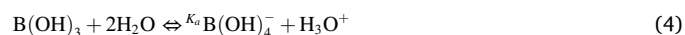
## 4. Discussion

### 4.1. Plausible mechanism of boron isotope fractionation

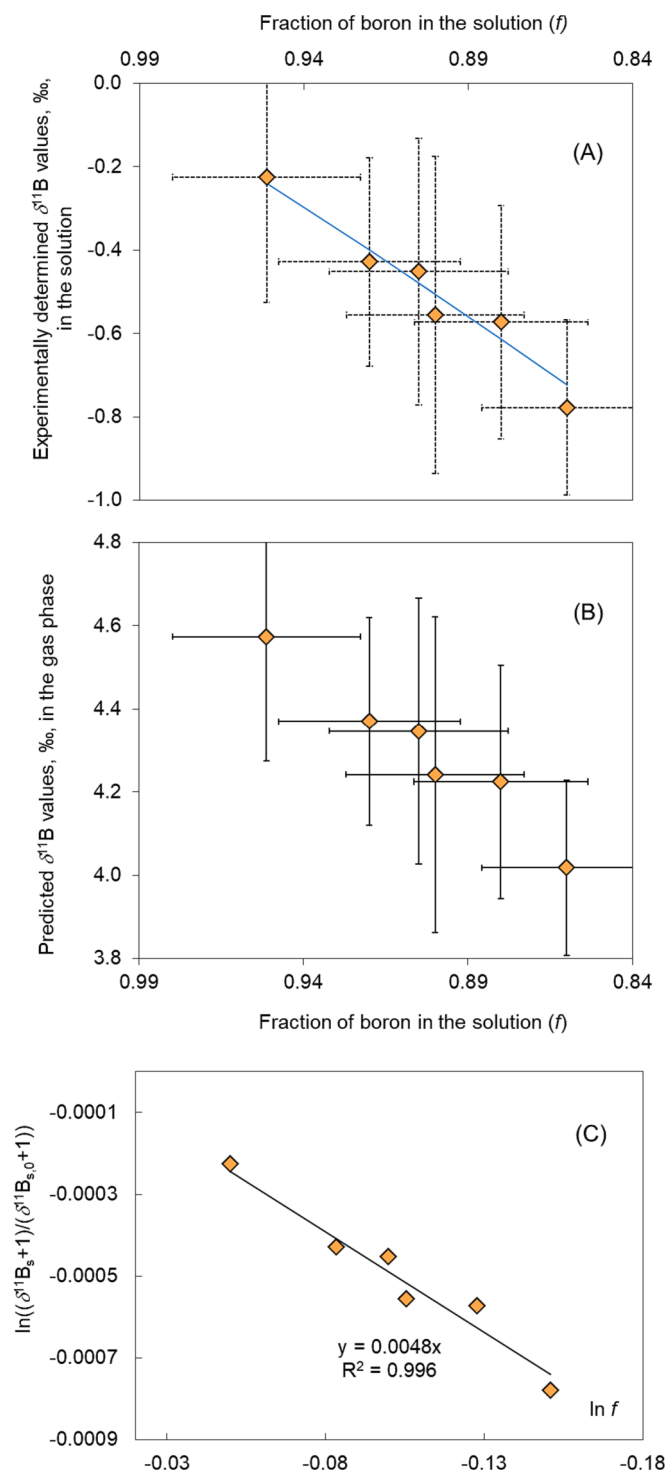
Due to their porous and hydroscopic nature, air dried green coffee beans have water content in the range of 8–13% (Franca and Oliveira,

2016). Three types of water environments are recognised in such plant materials, namely capillary (intercellular or free) water, intracellular water, and cell wall water (Khan et al., 2016). The latter two types are also commonly referred to as bound water and constitute a small fraction of total water in plants. During the initial phase of roasting, coffee beans gradually lose capillary water. As the temperature increases to above 130 °C, most of the bound water is also liberated and evaporated.

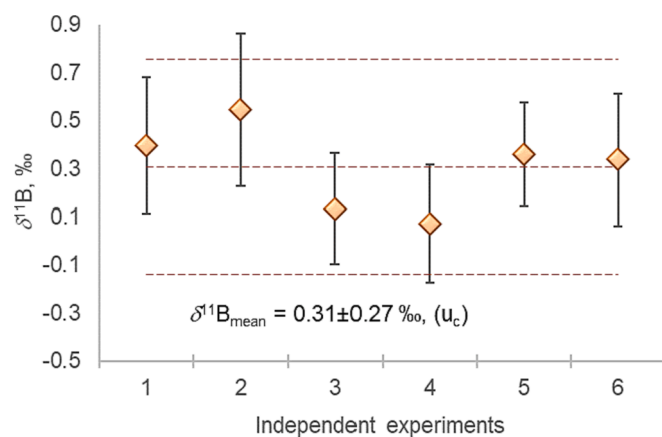
By analogy with other micronutrients, it is likely that speciation of boron in coffee beans exerts a major control on boron isotope fractionation. At physiological pH, boron exists mainly as undissociated boric acid (Hunt, 2003; Tanaka & Fujiwara, 2008), with passive transport of soluble boric acid being the most widely accepted mechanism of boron uptake and accumulation in plants (Dembitsky et al., 2002; Takano et al., 2002). At the same time, partial dissociation of boric acid can occur in any water solution through continuous boron-oxygen bond breaking and formation, stoichiometrically expressed as follows (Hunt, 2003)



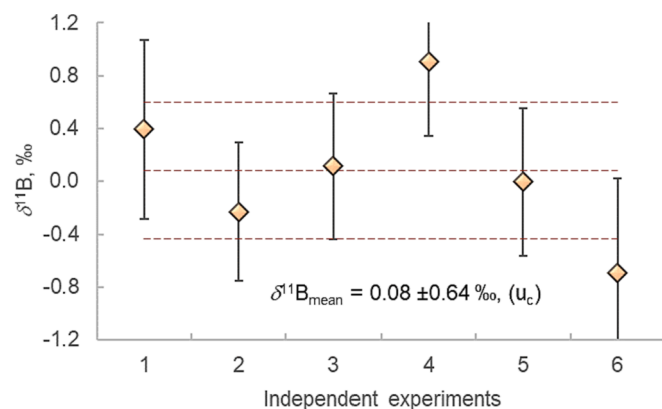
Boron distribution between  $\text{B}(\text{OH})_3$  and its conjugate base,  $\text{B}(\text{OH})_4^-$ , is controlled by pH, temperature and the chemical composition of the matrix, with fraction of  $\text{B}(\text{OH})_4^-$  increasing as temperature raises (Roy et al., 1993). It is also known that thermodynamically driven boron isotope fractionation occurs between undissociated boric acid and the borate ion,  $\text{B}(\text{OH})_4^-$ , resulting in preferential partitioning of  $^{11}\text{B}$  isotopes into the former (Kowalski & Wunder, 2018; Zeebe, 2005). First principle models have showed that the difference in  $\delta^{11}\text{B}$  values between  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  species at equilibrium at 25 °C is about 25‰ (Rustad et al., 2010; Zeebe, 2005). Selective enrichment of  $^{11}\text{B}$  isotopes in the vapour phase between coexisting vapor and liquid in natural systems have been documented by many studies previously in both natural settings and in laboratory experiments (Foster et al., 2010; Gaillardet et al., 2001; Gaillardet & Lemarchard, 2018; Leeman et al., 1992; Xiao et al., 1997, 2007).



**Fig. 4.** Summary of boron isotope fractionation associated with volatilisation of boric acid from water solution at temperature  $\sim 80$  °C. Panel (A) shows experimentally determined  $\delta^{11}\text{B}$  values of dissolved boron plotted versus the remaining fraction of boron in solution. The solid line through the data points was constructed using Eqn. (2) and the isotope fractionation factor,  $\alpha$ , equal to 1.0048 which was determined by regression from the data shown in the Panel (C). Panel (B) shows theoretically predicted  $\delta^{11}\text{B}$  values of volatilised boron plotted versus the remaining fraction of solution. Details of the calculations are given in Supplementary Material. Panel (C) shows a plot of experimentally determined  $\delta^{11}\text{B}$  values versus fraction of boron in solution in the ln-ln space which was used for the determination of the isotope fractionation factor in the experiment with volatilisation of boric acid from solution. Further details are given in Supplementary Material.



**Fig. 5.**  $\delta^{11}\text{B}$  values of the residues after evaporating the solution of boron NIST SRM 951a also containing sucrose. Dashed lines denote the mean value with 95% confidence interval.



**Fig. 6.**  $\delta^{11}\text{B}$  values of solid  $\text{H}_3\text{BO}_3$  after 72 h exposure at 200 °C, determined relative to the original composition. Dashed lines denote the mean value with 95% confidence interval. It can be seen that transition of boric acid directly from the solid to the gas state is not accompanied by boron isotope fractionation within the measurement uncertainty (see text in section 4.1).

The observed negative shift in  $\delta^{11}\text{B}$  values of roasted coffee is consistent with the hypothesis that boron isotope fractionation takes place at the early stage of roasting, concomitant with evaporation of capillary water from coffee beans. At the core of it lies the uneven partitioning of boron isotopes between undissociated  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  ions in aqueous solution. Volatilisation of  $\text{B}(\text{OH})_3$  molecules enriched in  $^{11}\text{B}$  isotopes from capillary water of coffee beans leads to the depletion of  $^{11}\text{B}$  isotopes in the isotopic composition of coffee beans after roasting.

Results of our experiments provide evidence for the crucial role of aqueous phase in the fractionation of boron isotopes during roasting. As can be seen from Fig. 3, nearly identical decreases in  $\delta^{11}\text{B}$  values of powdered green coffee beans relative to the original isotopic composition were observed after keeping the subsamples in the oven for 60 min at different temperatures, ranging from 80 °C to 220 °C. This indicates that the isotope fractionation was produced by a mechanism that could operate at the temperature below the boiling point of water.

Data obtained in the experiment on volatilisation of boric acid from the solution with the presence of sucrose indicate a crucial role of boron complexing substances in suppressing boron isotope fractionation (Fig. 5). It appears likely that sugars and other *cis*-hydroxyl group containing ligands in coffee beans can form strong association with boron and prevent volatilisation of the element. Sucrose is known to decompose at temperatures near to its melting point of  $\sim 186$  °C (Richards &



Shafizadeh, 1978). However, the thermal decomposition pathways are complex, with sucrose being not fully degraded at the temperatures of roasting (Richards & Shafizadeh, 1978).

It has also been shown previously that deposition of solid orthoboric acid occurs after complete evaporation of boron containing aqueous solution at acidic and near-neutral pH conditions (Kowalski & Wunder, 2018; Qi et al., 1991). Solid boric acid can therefore be formed in coffee beans if water is fully evaporated. At this stage, boron can escape into the gas phase by sublimation. However, our experiments show that sublimation of boric acid is not accompanied by boron isotope fractionation (Fig. 6).

#### 4.2. Implications for determination of coffee origin

Although boron isotope fractionation was detected during roasting green coffee beans, both during our laboratory experiments and from analysis of green and roasted coffees from the same origin, the extent of this fractionation is small and with predictable direction. Roasting degree does not seem to have an effect on the extent of this fractionation. Differences in  $\delta^{11}\text{B}$  values between green and roasted coffee of single origin were characterised by the mean value of  $1.5 \pm 0.75\%$  (1  $\sigma$ ,  $n = 23$ ). This value is much smaller than the observed range of variation in  $\delta^{11}\text{B}$  values of green coffee from different geographical locations, spanning the range of  $\sim 54\%$ . This implies that even though accuracy of  $\delta^{11}\text{B}$  values determination in roasted coffee can be biased towards lighter values relative to the starting green beans, the isotopic composition of boron in roasted coffee retains its potential to be a marker of coffee origin on a regional scale.

The observation of wide range of variations in  $\delta^{11}\text{B}$  values also underpins the potential of boron isotope data in provenance studies for coffee. However, limited data on chemical composition of the soils and the absence of other metadata do not allow us to make inferences on the factors that govern the observed isotopic differences between sampling locations.

## 5. Conclusion

Determination of  $\delta^{11}\text{B}$  values in single origin green and roasted coffee beans from different geographical locations together with experimental modelling allowed us to investigate in detail the influence of roasting on the isotopic composition of boron in coffee beans. Small differences in  $\delta^{11}\text{B}$  values between single origin green and roasted coffee was observed, with the mean value of  $1.5\% \pm 0.75\%$  (1  $\sigma$ ,  $n = 23$ ). However, this difference was larger than combined standard uncertainty of the measurements (typically at 0.4‰) and was attributed to boron isotope fractionation occurring during volatilisation of boron from coffee beans during roasting. The plausible mechanism accounting for this fractionation involves preferential partitioning of  $^{11}\text{B}$  isotopes into undissociated boric acid,  $\text{B}(\text{OH})_3$ , in capillary water of the beans and higher volatilisation rate of undissociated boric acid relative to  $^{11}\text{B}$  isotope depleted borate ions. The experimental modelling of boric acid volatilisation from solution showed that the presence of sucrose has a strong suppression effect on boron isotope fractionation. This effect, consistent with high affinity of boron-oxygen compounds for diol containing moieties in coffee beans, can be an important factor that prevents boron volatilisation losses during roasting and minimises associated boron isotope fractionation. In the light of applicability of boron isotope data in roasted coffee for provenance studies, the bias towards lighter  $\delta^{11}\text{B}$  values induced by roasting was found to be small relative to the wide,  $\sim 54\%$  range of  $\delta^{11}\text{B}$  values in coffee beans from different regions.  $\delta^{11}\text{B}$  isotopic composition of roasted coffee can therefore be used as a marker of regional differences in coffee origin.

#### CRedit authorship contribution statement

**D. Malinovsky:** Methodology, Formal analysis, Writing – original

draft, Writing – review & editing. **P.J.H. Dunn:** Methodology, Writing – review & editing. **P. Rooke:** Supervision. **H. Goenaga-Infante:** Supervision, Writing – review & editing.

#### 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.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2023.138128>.

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