Geographic determination of coffee beans using multi-element analysis and isotope ratios of boron and strontium

Hou-Chun Liu [a], Chen-Feng You [a,b,*], Chiou-Yun Chen [a], Yu-Ching Liu [b], Ming-Tsung Chung [c]

[a] Department of Earth Sciences, National Cheng Kung University, Tainan 70101, Taiwan
[b] Earth Dynamic System Research Center, National Cheng Kung University, Tainan 70101, Taiwan
[c] Ocean and Earth Science, National Oceanography Centre Southampton, University of Southampton Waterfront Campus, European Way, Southampton SO14 3ZH, UK

ARTICLE INFO

ABSTRACT

This study aims to evaluate the feasibility of using chemical and isotopic compositions of coffee beans to identify their geographic origins. Twenty-one *Coffea arabica* beans collected from 14 countries in 3 major coffee-producing regions, Africa, America and Asia, were analysed for multi-element of B, Rb, Sr, Ba, Fe, Mn and Zn, as well as isotopic compositions of B and Sr. Our results demonstrate that the geographic origin of coffee beans could be classified based on concentrations of Rb, Sr and Ba. However, the isotope ratios of B and Sr provide more sensitive information for the growth localities. Combined with literature data, this study indicates that B and Sr isotopes are excellent indicators of the origin of coffee beans.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Coffee is an important commodity and a popular beverage. Over a billion cups of coffee are consumed around the world every single day. The known amount of world coffee trade started with about 10,000 t per year, in 1700. By 2008, that number had grown considerably to 8,000,000 t per year (Oestreich-Janzen, 2010). Unfortunately, cheap counterfeit products of poorer quality have begun to enter the market, affecting the taste of coffee but also potentially posing a threat to human health if contaminated. Therefore, coffee authenticity and traceability have become key issues.

Many natural phenomena, known as physico-chemical effects, can lead to fractionation of isotopes in exogenic processes. This variability in abundance isotope ratios allows for wide applications in determination of food provenance (Kelly, Heaton, & Hoogewerff, 2005). Over the last two decades, several studies have applied isotopic methodologies to differentiate the geographic origin of coffee, including $^{11}B/^{10}B$, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{34}S/^{32}S$, and $^{87}Sr/^{86}Sr$ (Rodrigues, Máguas, & Prohaska, 2011; Rodrigues et al., 2009; Rodrigues et al., 2011; Serra et al., 2005; Wieser, Iyer, Krouse, & Cantagallo, 2001). Serra et al. (2005) proposed that a combined stable isotope of C, N and B was a good geographic indicator for coffee origins in different producing continents. However, overlapping isotopic variability for some provenances resulted in

lack of a complete discrimination. Rodrigues, Máguas, et al. (2011) suggested that a combination of O and Sr isotopes was a more robust approach to identify the geographical origin of coffee in small competitive regions. Such analysis does not allow a total discrimination amongst samples from different countries around the world. Application of an isotopic strategy on coffee origin, therefore, requires further systematic evaluation.

Boron has two naturally occurring stable isotopes, ^{10}B and ^{11}B. As a key component in many vital processes in the coffee plant (Leite, Brown, & Rosolem, 2007) and its large natural isotopic variation (up to 90‰, Hoefs, 2009), the B isotopic composition of coffee may provide novel insights into their physiology and provenance (Wieser et al., 2001). Similarly, the Sr isotope ratio has been successfully applied for food geographic discrimination on basis of varying $^{87}Sr/^{86}Sr$ ratios through their lithological differences (Hölzl, Horn, Rossmann, & Rummel, 2004; ODA, 2001). In the present study, the binary system of B and Sr isotopes were therefore chosen for provenance determination of coffee in continental or even smaller level.

Multi-element analyses have been applied to a wide range of food species to determine geographic origin (Kelly et al., 2005). Chemical analyses combined with methods of statistical pattern recognition have specifically been used to differentiate the geographic origin of coffee (Anderson & Smith, 2002). Previous studies suggested that the elements with significantly varying concentration, especially various chemicals in ppm to sub-ppm levels of Rb, Sr, Ba, Sc, Co, Cu, and Sc, may provide the information about coffee planting locations (Krivan, Barth, & Morales, 1993). For this reason, the current study evaluated the chemical concentrations of

---

* Corresponding author at: Department of Earth Sciences, National Cheng Kung University, Tainan 70101, Taiwan. Tel.: +886 6 2757575x65438; fax: +886 6 2740285.

E-mail address: cfy20@mail.ncku.edu.tw (C.-F. You).

the listed elements in coffee for potential application in geographic classification.

The main objectives were (1) to examine the geographic features of multi-elements and isotope ratios of B and Sr in worldwide collected *Coffea arabica* beans, and (2) to re-evaluate the potential isotopic methods of B, C, N, O and Sr isotopes for coffee origin discrimination based on the present study coupled with accumulated literature data. This information is critical for delineating beans growth under different geographic features.

2. Materials and methods

2.1. Sample origins

Twenty-one samples of *C. arabica* beans were collected from 14 countries in Asia, Africa and America (Fig. 1). The beans sampled in south-western and eastern Taiwan (Asia) were collected in August 2010. Oversea samples were obtained from coffee dealers able to supply samples with the assurance of the origin in late 2010.

For green coffee beans included in the analysis, the lithological settings and planting environments were quite different. As such, green coffee bean samples were simply divided into two groups: sedimentary or igneous weathering soils. For samples from Taiwan, sedimentary soils are common (i.e. alluvial soils) in south-western Taiwan (i.e. sample TWN-YL and TWN-PT), while metamorphic rock with volcanic or ophiolitic materials weathered soil in eastern Taiwan (TWN-TT). Other Asian samples from Papua New Guinea (PNG) and Sumatra in Indonesia (IDN-S) were generally collected in a volcanic zone, containing mainly ash and igneous weathered soils. Samples collected from middle- and south-America, El Salvador (SLV), Guatemala (GTM), Puerto Rico (PRI), Jamaica (JMB), Colombia (COL) and Brazil (BRA), were typically grown in igneous weathered soils. The geological settings for African samples were more complex. The surface lithology was generally an older continental crust in eastern Africa plateau. Inside the area, there are numerous peaks of active volcanoes developed along the rift zone of East African Rift. Thus, planation soils in Ethiopia (ETH), Tanzania (TZA), Malawi (MWI), Rwanda (RWA) and Uganda (UGA) greatly varied by location.

2.2. Sample pretreatment and digestion

Parchment and silver skin removed green coffee beans were first treated by a freeze-drying process for roughly 24 h. To confirm sample homogeneity, at least 5 g of each coffee bean specimen was pulverized. Approximately 50 mg of powdered sample was digested in a 2:1 solution of HNO_3 and H_2O_2 at 120 °C in a PFA vial for at least 2 h. The solution was then diluted to a final volume of 10 ml using Milli-Q water and stored for further chemical and isotopic analysis.

2.3. Analysis of chemical composition

For multi-element analysis, another 10-fold dilution of the final solution was prepared using 5% HNO_3. All chemical determinations were carried out using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Element II, Thermo Scientific, Germany). As recommended by the manufacturer, daily optimisation of the instrument was performed after a mass calibration check using 1 ng g^{-1} multi-elements standard solution. Matrix fitted standards (High-Purity Standards, USA) were prepared for concentration calibration. An international certified reference material (iCRM), NIST SRM 1515 (NIST, USA), was used to validate the standard operating procedure in the current study. The average analytical precision on metal concentration was approximately ±5% (2RSD).

2.4. Chemical separation and isotopic determination

To avoid potential matrix elements and isobaric interferences during isotopic analysis, chemical purification of B and Sr was conducted inside class-10 working benches. The procedure for boron matrix separation was modified from Rosner, Pritzkow, Vogl, and Voerkelius (2011). Approximately 60 ng B from the final sample solution was mixed with 180 μl of a 2% mannitol solution, then dried at 65 °C and converted in 0.5 ml of 0.02 N HCl. For B separation, 2 ml Bio-Rad AG50W-X8 resin (200–400 mesh) was packed in an acid-cleaned polypropylene column (5–5.5 mm in diameter). Before sample loading, the resin was washed using 5 ml 6 N HCl and pre-conditioned with 2.5 ml of 0.02 N HCl. The sample solution (0.5 ml) was carefully loaded into the column and eluted with 2.5 ml 0.02 N HCl. The B fraction was eluted by 3 ml of 0.02 N HCl, and collected for B isotopic determination. The elution curve was evaluated using NIST SRM 1515, and recovery was 102%. Excess B was potentially introduced by a minor chemical blank from resin and reagents. The introduced B blank through the chemical preparation may change the B isotope ratio of a processed sample,
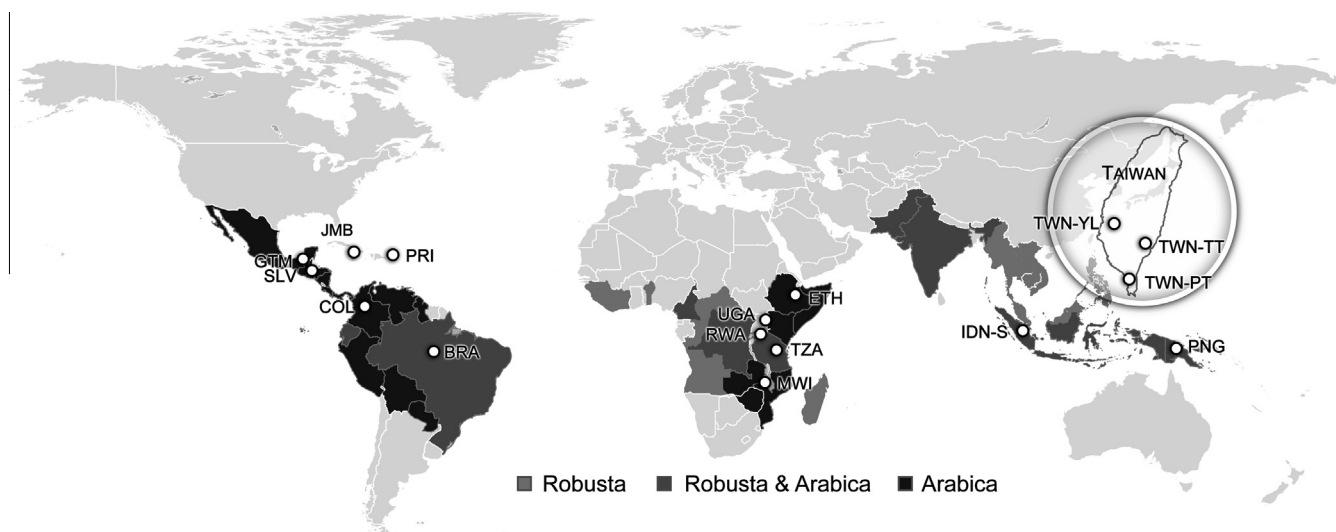

Fig. 1. Sampling locations among the major coffee-producing countries around the world (modified from Oestreich-Janzen (2010)).