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Stable isotope and multielement composition of coffee beans from different geographic origin

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Summary: This work combines the mineral and stable isotope profile to determine the geographic origin of 62 green coffee beans collected in 4 coffee growing region. The Canonical Discriminant analysis permits to achieve a good separation between samples of South and Central America, Africa and Asia with a 100% correct reclassification.

Keywords: coffee, IRMS, ICP-MS.

1 Introduction

Coffee is one of the world's most popular beverage and its market is one of the biggest worldwide. Depending on quality, taste and geographical origin the price of coffee beans, can range from 2 up to 77 $/kilogramme [1]. Fraud, where cheap coffee is sold as the more expensive one, is an important issue that concerns the coffee industry. In this framework, it is important to define an analytical/chemometric methods in order to decipher the geographical origin of coffee beans. Several authors have been trying to establish the provenance of coffee, either using their elemental concentration [1, 2] or using their isotope ratios [3, 4].

In this work we aim to couple the mineral profile (ICP-MS analysis) and the stable isotope ratios (IRMS analysis) of 62 green coffee beans endeavouring to find a tool for the determination of their geographical origin.

2 Experimental

Sixty-two samples of green coffee of known origin coming from the principal worldwide coffee-growing areas were collected. In detail, 17 samples were from Central America (Mexico, 5; Guatemala, 4; Honduras, 2; El Salvador, 2; Costa Rica, 2; Dominican Republic, 2); 14 from South America (Colombia, 4; Brazil, 7; Uruguay, 3); 14 from Africa (Côte d'Ivoire, 2; Cameroon, 2; Congo, 2; Central African Republic, 3; Ethiopia, 5) and 17 from Asia (India, 9; Indonesia, 8). The major part of the coffee bean were of the more valuable and appreciate *arabica* variety whereas 2 Central American, 1 South American, 7 African and 10 Asian samples were from the *robusta* variety.

The ratios $^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{34}S/^{32}S$ were directly measured on grinded coffee beans using an IRMS (DELTA V, Thermo Scientific, Germany) following total combustion in an elemental analyser (EA Flash 1112, Thermo Scientific or Vario EL III, Elementar Analysensysteme GmbH). The ratios $^{2}H/^{1}H$ and $^{18}O/^{16}O$ were measured using an IRMS (Finnigan DELTA XP, Thermo Scientific) coupled with a Pyrolyser (Finnigan TC/EA, Thermo Scientific).

The isotope values were expressed in δ‰ against international standards: Vienna-Pee Dee Belemnite (V-PDB) for $\delta^{13}C$, Air for $\delta^{15}N$, Vienna–Standard Mean Ocean Water (V-SMOW) for $\delta^{2}H$ and $\delta^{18}O$, Vienna-Canyon Diablo Triolite (V-CDT) for $\delta^{34}S$.

The coffee seeds were grinded and mineralized with HNO_3 in closed vessels using a microwave digester (MarsXpress, CEM, USA; max temperature 200°C). Analysis of Li, Be, B, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Tm, Yb, Ir, Pt, Au, Hg, Re, Tl, Pb, Bi and U was carried out using an ICP-MS (Agilent 7500ce Agilent Technologies, Tokyo, Japan) equipped with an Octopole Reaction System for the removal of principal polyatomic interferences.

Data analysis (Canonical Discriminant analysis) was performed with Statistica 8.0 (StatSoft Inc., USA) on standardized data.

3 Results

The $\delta^{13}C$ values ranged form -29.4‰ to -25.3‰; $\delta^{15}N$ values from 0.6‰ to 7.1‰, $\delta^{18}O$ values from 21.1‰ to 37.2‰, $\delta^{2}H$ from -83‰ to -20‰ and $\delta^{34}S$ from 2.6‰ to 12.8‰. As, Ge, Tm, Au, Tl and U were quantifiable in less than 50% of the samples whereas Pd and Sn in less than 10% of the samples. Te (<0.135 µg/kg dry weight), Ir (<0.622 µg/kg dw), Re (<0.055 µg/kg dw), Bi (<2.43 µg/kg dw) and Hg (<19.0 µg/kg dw) were always below the method's detection limit. Regarding the element present in at least an half of the samples: P, K, Mg and Ca median concentration was > 1 g/kg dw; Rb, Fe, Mn, Cu, B, Al, Na, Sr, Ba and Zn ranged between 1000 and 1 mg/kg dw; Ti, Ni, Mo, Co, Cr, Cs, Se, Pb, Ce, Li, la, Cd, Nd, V, Y, Ag and Ga ranged between 1000 and 1 µg/kg dw whereas Pr, Gd, Sm, Dy, Sb, Eu, Er, Yb, Be, and Pt were below 1 µg/kg dw. These orders of magnitude were generally in agreement with the literature [3, 5, 6].

The coffee beans of Central America were characterized by low values of $\delta^{15}N$, $\delta^{18}O$ and $\delta^{2}H$, high content of Sr and Ba and low level of Co, Mo and rare earth elements. The South American samples showed high values of $\delta^{13}C$, Mn and Co and low content of Mo. Coffee beans growth in Africa presented high values of $\delta^{15}N$, $\delta^{2}H$ and K and low level of Co and Mn. Finally, the Asian samples had high content of Co, K, Li and Na and low level of $d^{15}N$, $d^{18}O$, Mg and Mn. Manganese in particular, but also Al, Co, Cs, Na and Rb were considered suited as origin indicators by different authors [1, 5].

To assess the discrimination efficiency for coffee beans origin, a Canonical Discriminant analysis was performed using $d^{13}C$, $d^{15}N$, $d^{18}O$, $d^{2}H$, Li, B, Na, Mg, P, K, Mn, Co, Ga, Se, Sr, Mo, Cd, Sb, Cs, Ba, La, Ce and U data (Fig. 1). The combination of the first 2 canonical variables accounted for 88% of variability assuring a good discrimination of the samples of the 4 growth regions with a correct re-classification of 100% of the samples.

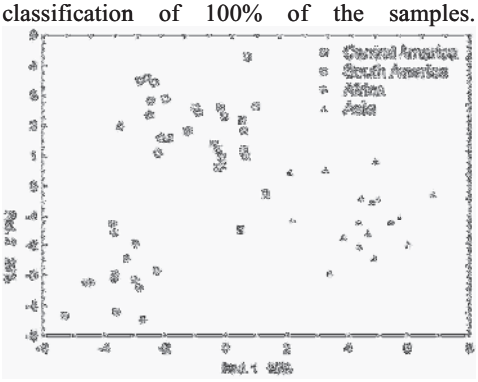

Fig. 1. Canonical Discriminant analysis of the isotopic and elemental composition of coffee beans from the 4 growing regions: scatterplot of the first two canonical variables.

4 Conclusions

This research shows that isotope and mineral composition can specifically characterize green coffee beans from the world's largest producing areas, proving that a combined use of this parameters can effectively trace their geographic origin, at least at continental level. The limited availability of genuine samples *per* each country did not permit the use of statistical analysis to further differentiate coffees at a more subtle level.

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