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Chapter 22

C0110 # Coffee

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Chapter Outline

s0005 1 BRIEF DESCRIPTION OF COFFEE PLANT, FRUIT AND SEED

p0005 From its origins in Africa, coffee cultivation wandered east and west, eventually forming a belt roughly bounded by the Tropics of Cancer and Capricorn [1]. Nowadays, the top 10 coffee-producing countries are Brazil, Colombia, Indonesia, Vietnam, Mexico, Ethiopia, India, Guatemala, Peru and Honduras [2].

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p0010 According to the legend, coffee originated from Africa in A.D. 800. Kaldi, a legendary Ethiopian goatherd, noticed his herd dancing from one coffee shrub to another, grazing on the cherry-red berries containing the beans and picked some cherries to him and soon felt the effect of this plant. However, coffee, as we know it, originated in Arabia where the first roasted coffee beans were brewed around A.D. 1000. By the thirteenth century, Muslims drank coffee religiously and wherever the Islam went, coffee went too: North Africa, the eastern Mediterranean and India. In the eighteenth century, coffee blooms in Brazil and by 1800, Brazil's large harvests turned coffee from an elite indulgence to an everyday elixir, a drink for the people. Since then, coffee has become one of the most important merchandises commercialized in the world.

p0015 Coffee is the only food merchandise produced globally (except in Europe) associated with many sustainability, fair trading, health care and education projects implemented in the regions where it is cultivated. There is no doubt about the importance of the coffee market in the global economy. From the early 1970s onwards, public concerns over the social aspects of coffee production in producing countries rose first in the Netherlands, sometimes forcing retailers and roasting companies to stop selling coffee from countries with dictatorial regimes, such as Angola [3]. This is a political matter that, albeit very interesting for its complexity, is beyond the scope of this chapter. Nonetheless, to whom it may interest, the work of the sociologist Daniel Jaffee (*Brewing Justice*, *Fair Trade Coffee*, *Sustainability and Survival*) [4], and also the work of Goodman and co-authors (*Confronting the Coffee Crisis*, *Fair Trade*, *Sustainable Livelihoods and Ecosystems in Mexico and Central America*) [5], is recommended. At the same time, the international organic movement developed, which promoted agricultural practices in harmony with Nature. During the 1980s, the Max Havelaar and EKO standards[1] were introduced. As a result of the market trend for developing specialties, products with labels such as Fair Trade were able to penetrate the regular distribution channels. For producers, a major issue is to get access to the global market through channels that ensure a reasonable price. One way is to grow high-quality coffee, which is only possible if local ecosystems permit. An alternative is to grow organic coffee, but this involves a choice for one standard or another. Adopting a standard requires substantial additional fieldwork and administrative responsibilities, as well as up to 3 years of operating under more strict principles before a certificate can be obtained [3].

p0020 The issues of production methods, fair trade commerce or organically, along with consumers placing added value to products with label of origin made coffee authenticity confirmation through chemical/physical analysis important. In addition, coffee importing companies were interested in

np0005 1. Max Havelaar quality label for Fair Trade guarantees that products or raw materials were purchased on the basis of Fair Trade principles. EKO quality label represents the use of organic production methods in the country of origin.

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developing analytical tools that could be applied to demonstrate that the imported coffee had not been adulterated along the commercial chain. These different factors influencing coffee production and consumption had an impact on the coffee research field. Several studies have been developed in the past 10–15 years in order to achieve the geographical origin discrimination of coffees.

p0025 Recently, news concerning the effects of climate change on coffee cultivation became public (Reuters Agency). Rising temperatures and erratic weather patterns are changing historic trends in the coffee season [6,7]. Farmers also report that high altitude plants are maturing at times more typical of their lowland counterparts [6,8]. This is generating complete production disorder [6] and shifting the attention of coffee producer countries to the problems of climate change. Today, coffee-producing communities struggle to sustain their ecosystems, cultures and knowledge systems, and this will have a major impact on the future of coffee production and consumption, as well as scientific research. Coffee has been a case study in a large number of research fields, for example, biology, genetics, agronomy, ecology, plant physiology and analytical chemistry.

s0010 1.1 The Coffee Plant

p0030 The genus *Coffea* belongs to the family *Rubiaceae*. This family comprises many genera including *Gardenia*, *lxora*, *Cinchona* (quinine) and *Rubia*. The two main species of coffee tree cultivated on a worldwide scale are *Coffea arabica* and *C. canephora* var. *robusta*. Minor cultivated species include *C. liberica* and *C. excelsa*, which are mainly restricted to West Africa and Asia, and account for only 1–2% of global production [9]. The coffee plant takes approximately 3 years to develop from seed germination to first flowering and fruit production (Figure 1).

p0035 A well-managed coffee tree can be productive for up to 80 years or more; however, the economic lifespan of a coffee plantation is rarely more than 30 years [9]. The shrub is perennial evergreen dicotyledonous which can reach a height of 10 m in wild state. Plantation coffee is usually pruned to a maximum of about 3 m to facilitate harvesting and to maintain optimum tree shape. The primary branches are opposed, horizontally or drooping, and the leaves grow in pairs on short stalks. They are about 15 cm in length in *C. arabica* and longer in *C. canephora*, oval or lanceolate, and shiny dark green in appearance.

p0040 The first flowers are produced at an age of 3–4 years, creamy white and sweetly scented, appearing in clusters in the axis of the leaves. After flowers fade, the ovaries slowly develop into oval drupes up to 18 mm in length and 10–15 mm in diameter, at first green, ripening to a bright red or yellow (referred to as 'cherries'), at which stage they are ready for harvesting. It is common to find blossoms, green fruit and ripe cherries flourishing on the same branch, especially in regions where there is no annual rainfall cessation.

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f0005 **FIGURE 1** (A) coffee seedlings, (B) adult coffee plant, (C) ripe coffee cherries and (D) coffee bean samples for analysis: (1) green coffee beans, (2) ground green coffee beans, (3) green coffee beans with parchment, (4) dry coffee cherries with coffee bean still inside.

The coffee 'beans' are the seeds, of which two are normally found in each fruit [1,9]. Each bean is covered with a thin closely fitting tegument known as the silverskin, outside of which is a looser, slightly yellowish skin called the parchment, the whole being encased in a mucilaginous pulp which forms the flesh of the coffee 'cherry' (Figure 1) inside a tough skin. The beans, which develop inside the cherry, are used as the basic element for producing roasted and ground coffee, soluble coffee powders and coffee liquor.

p0045 Although it is possible to propagate coffee by grafting or by taking cuttings, the usual commercial practice is to raise the plants from seeds that have not been dried below 30%. On the plantation, the seeds are sown in carefully prepared seedbeds, sometimes covered by a layer of sand, with protection from strong sunlight. The seedlings may then be transplanted into nursery beds for final planting in the field when they are 20–30 cm high (Figure 1). A density of 2500–3000 plants per hectare is typical [1].

s0015 1.2 The Specificities of the Coffee Seed

p0050 The coffee bean consists of an endosperm containing an embryo, which is wrapped in two husks: the outer parchment and the silverskin (or integument) just underneath (Figure 2). The seed, called the green coffee bean, is hard and

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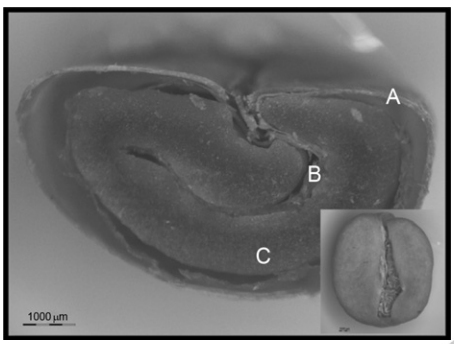

f0010 **FIGURE 2** Section of a green coffee bean. Legend: parchment (A), silverskin (B) and endosperm (C).

f0015 **FIGURE 3** Growth of the endosperm within the space formed by expansion of the integument.

bluish green in colour. The silverskin adheres tightly to the seed and above this follows the parchment and the mucilage. The parchment is rough and papery and, for that reason, is often called 'the pergamin' [10]. Before being shipped to a roaster, coffee is typically stored with the parchment attached since it serves as a protective barrier.

p0055 The coffee flower ovary, which contains the two fertilized ovules, starts to develop immediately following fertilization. During the first 2 months, however, the ovary grows very slowly but eventually becomes definitely visible in a dormant (if water stressed) pinhead stage. When adequate water breaks dormancy in the second to third month of development, the ovary increases in size more rapidly and the integument occupies almost the entire space in each ovule. The embryonic sac grows and fills with endosperm (Figure 3). From the third to the fifth month after fertilization, the fruit increases significantly in weight and volume. The endosperm slowly replaces the integument that is forced back to the periphery of the ovule. Between the sixth and the eighth month after fertilization, the fruit reaches maturity. The integument is now only represented by the silverskin (Figure 3).

p0060 In the endosperm that fills the whole grain, the zygotic embryo has evolved into the 'two-cotyledon' stage. During the last month of maturation, the fruit completes its growth and, depending on the variety, acquires a red or yellow colour. The time taken from flowering until the maturation of the coffee cherries varies according to the variety, climatic conditions and agricultural practices. As a general rule, *C. arabica* takes 6–9 months and

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f0020 **FIGURE 4** Air-drying of coffee beans. *(courtesy from Shawn Steiman).*

C. canephora takes 9–11 months to mature, although this period can increase at higher altitudes, where the air temperature drops by 1 °C per 180 m of elevation [9]. Once the cherries have been harvested, coffee processing begins. The cherries are pulped (the parchment covered seed is removed from the fruit), the mucilage is removed and the seeds are dried. There are two different methods of coffee processing: the 'wet method' and the 'dry method' [11].

p0065 The wet method is the most commonly used in the world. It begins with the removal of the pulp and the separation of the seed, after which the mucilage is disposed of by mechanical means or fermenting the coffee in water. Once free of the mucilage, the beans are rinsed and laid out on wood or concrete drying floors where they will air-dry (Figure 4). A variation on the wet method is to dry the pulped but not demucilaged seeds.

p0070 The objective of drying is to lower the moisture content of parchment or cherry coffee to between 8% and 12%, in order to preserve the beans safely in storage. This moisture level is set in industry as a global standard [12]. Coffee is dried by supplying energy to the bean to evaporate water and unsaturated air to carry away the water. This can be either by direct exposure to the sun, exposure to radiation from a heated surface (in the case of drying grounds), heated air or some combination of these. Convection (air movement) moves the saturated air away, thus effectively drying the coffee [13].

p0075 The dry method is an alternative process where the pulping and fermenting stages are skipped and the coffee cherries are dried with their seeds still inside (Figure 5). Even within the cherry, the seed moisture content will reach the appropriate level. The resulting coffee has fruitier flavour. It is a less commonly used method compared to the wet method. Recent market trends are more for dry processing.

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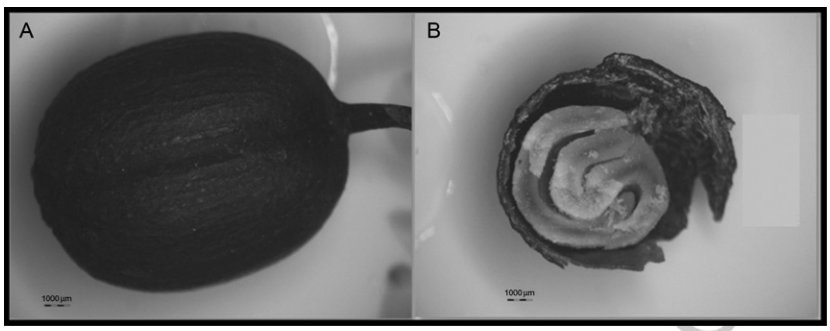

f0025 **FIGURE 5** Dried coffee cherry (A) and correspondent transversal section (B) showing a 'peaberry' (only one bean in the cherry; usually there are two coffee beans per cherry).

s0020 1.3 Coffee Distribution and Main Climate Characteristics Associated with Coffee Production

p0080 Coffee-growing areas extend from 25 °N to 25 °S of latitude [1]. The appropriateness of the climate for the cultivation of coffee depends on the latitude and the height above sea level. Every 100 m of altitude corresponds to a decrease in temperature of approximately 0.6 °C [14]. The positive effect of altitude on coffee quality is well known. Beans produced at higher altitude are harder and, therefore, more appreciated. Coffees cultivated at higher altitudes develop more acidity, aroma and flavour. Appropriate sites for coffee growing are selected based on six basic environmental factors, that is, temperature, water availability, sunshine intensity, wind, type of soil and topography of the land (all likely associated with altitude).

p0085 Temperature values and their fluctuations have a significant impact on the behaviour of coffee plants [15]. Sensitivity to cold, as well as to high temperatures, can vary between coffee species and varieties and even between individual plants. Both wind and air humidity can greatly influence the effect of air temperatures. The optimum mean annual temperature range for *Arabica* coffee is 18–21 °C [16]. Above 23 °C, development and ripening of fruits are accelerated, often leading to loss of quality [16]. It should be noted, however, that selected cultivars under intensive management conditions have allowed *Arabica* coffee plantations to be spread to marginal regions with average temperatures as high as 24–25 °C, with satisfactory yields, such as in the northeast of Brazil [17]. For *Robusta* coffee, the optimum annual mean temperature ranges from 22 to 26 °C [16]. *Robusta* is much less adaptable to lower temperatures than *Arabica* coffee. As temperature relates to altitude and latitude, *Robusta* coffee can be grown between sea level and 800 m, whereas *Arabica* coffee grows best at higher altitudes and is often grown in hilly areas. Coffee can also be grown at lower altitudes further away from the equator, unless limited by frost, as is the case of *Arabica* coffee in Brazil [16].

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p0090 Another crucial environmental factor is rainfall, which is the most important restrictive factor for coffee growing. Coffee requires sufficient and well-distributed rainfalls. Two inseparable elements must be taken into consideration: the total annual rainfall and its monthly or, better still, weekly distribution. A total annual rainfall between 1400 and 2000 mm is favourable for *Arabica* growing, whereas *Robusta* needs about 2000–2500 mm. Rates below 800–1000 mm for *Arabica* and 1200 mm for *Robusta*, even if they are well distributed, can be hazardous to the productivity of the coffee plantation, particularly if artificial irrigation is not possible [9]. The rainfall pattern should include a few months with little or no rain as this period is necessary to induce and concentrate flowering. However, water shortage during the critical period from weeks 6 to 16 after the fecundation may cause huge losses due to the development of empty beans, as the physiologic activity decreases during dry periods [14]. A dry season of 2–3 months, coincident with the harvest period, is ideal. Where there is no dry season (e.g. Colombia, Central America, Hawai'i), the production of beans is not concentrated, and selection during harvest or post-harvest is required for premium coffee.

p0095 The atmospheric humidity or relative humidity (RH) of the air also has a marked influence on the behaviour of the coffee plant, particularly in the case of *Robusta* [9,16]. Coffee species are evergreen, so transpiration is continuous [18]. A high level of RH will reduce water loss, whereas a low level will increase plant evapotranspiration.

p0100 Initially, coffee was farmed under natural or artificial shading conditions, in order to recreate the original forest environment, but nowadays coffee plantations are often established under direct sunlight. For best results, coffee requires an average of 2200–2400 h of sunlight per year [18]. However, shade still remains useful and even necessary in certain conditions, as it helps to attenuate the effects of extreme high and low temperatures. A further beneficial effect of shade has been revealed by recent studies indicating that it improves the quality of coffee. Shading also diminishes the risk of erosion, restricts weed growth and generates mulch which protects and enriches the soil with organic matter. In sun-exposed plantations, the temperatures of air, leaves and soil can be substantially higher than in shaded plantations, sometimes by more than 10 °C. High temperatures can reduce plant performance and coffee quality. In contrast, in almost environments, plants under at least 50% shade experience optimum air temperatures during the whole day, barely exceeding 25 °C at noon [14]. Also, the further the coffee fields are distant from the ideal altitude for coffee growing (either higher or lower), the more severely these microclimatic constraints will affect the coffee trees and, as a result, the need for shade will be greater. Although shade is often thought to be provided by companion trees, some places experience cloud cover that provides sufficient shade making other forms of shade detrimental to production.

p0105 The agronomy of the coffee plant is a complex matter and is related to many aspects, from disease control to the ecophysiology of the plant. This

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chapter does not intend to comprehensively cover all of these issues but, instead, aims at providing background information for the following sections on the analytics of coffee. However, to access a more detailed description of the coffee plant, its botany and genetics, as well as the breeding practices, the work of Sondahl and Baumann [19], Van der Vossen [20] and Wintgens [9] should be consulted.

2 GEOGRAPHICAL ORIGIN DIFFERENTIATION OF FOOD PRODUCTS: WHERE DO WE STAND WITH COFFEE?

p0110 A growing number of consumers demanding diversity and distinctiveness in food and an increasing public concern over issues such as health and ecology have changed public confidence in conventional food production. Thus, standards and certifications nowadays represent a means of demonstrating quality and gain confidence of consumers with whom the producer does not have a direct relationship. In other words, certification is a way of communicating with consumers living outside the region of production [21]. It is argued to have a number of benefits for consumers and producers and responds to the growing demand that exists in western nations for foods that are produced in ethical, environmentally sustainable and socially just ways [22]. This is also reflected in scientific research with attempts to respond to the increasing demand for developing analytical tools to prove food authenticity and/or quality.

p0115 In the case of coffee, several attempts have been made to determine the origin of green and roasted coffee beans. Analytical methods such as gas chromatography–mass spectrometry (GC–MS) [23] and near infrared spectroscopy (NIR spectroscopy) [24] were applied for the determination of organic compounds such as fatty acids profiles [25], tocopherols and triglycerides [26]. Stable isotope ratios of carbon, nitrogen and oxygen of specific compounds extracted from green coffee beans [27] were studied with promising results. Krivan and co-authors [28] demonstrated the potential of measuring elemental fingerprints in *C. arabica* coffee beans and quantified manganese (Mn) along with carbon (C), cobalt (Co), caesium (Cs), sodium (Na) and rubidium (Rb) in order to discriminate between green coffees from eight different origins. That study was complemented by Anderson and Smith [29] with the determination of the multi-element composition of roasted coffee beans from eight different origins of Central and South America, Indonesia and East Africa. Other authors studied variations in the boron (B) isotope composition of *C. arabica* beans, showing that the measured variation in B isotopic composition among different coffee beans is significant and can be related to differences between local growing conditions [30]. Based on previous studies, Serra and co-authors [31] determined the isotopic composition of C, N and B in green coffees from 19 different countries, showing that the isotopic composition of these three elements is a good indicator of geographical-dependent parameters, and therefore represents a useful tool to infer the region of production

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of green coffee. The authors suggested that the use of stable isotope ratios might be improved by the use of climatic data as an additional variable for the construction of a statistical model. These are important 'preliminary' studies although some of the authors acknowledge the relatively small number of authentic samples included in the studies. Recently, Techer and co-authors [32] have characterized the strontium (Sr) isotopic composition of all components of a cultivation system, that is, plants, rocks, soils and water in the frame of an intensive coffee-growing project on the Réunion Island, East of Madagascar. These studies indicate that measuring elemental concentrations and isotopic variation in regional coffees is arguably the best analytical strategy for accurately verifying coffee geographical origin. This approach results from global variations of isotopes abundance of 'light' bio-elements and 'heavy' geo-elements.

s0030 3 COFFEE GEOGRAPHICAL ORIGIN DIFFERENTIATION

s0035 3.1 *Arabica* Versus *Robusta* Coffee

p0120 *Arabica* coffees are considered to be of higher quality and of finer taste than *Robusta* coffees, which is reflected by distinctly higher prices by 20% on average and more than 200% when compared to the cheapest *Robusta* and most expensive *Arabica* coffees [33]. The price also depends on the geographic origin [33]. Many coffees from different geographical origins and of different types and grades are imported yearly by coffee roasting companies through a supply chain that usually involves several intermediates. To ensure that coffees had not been adulterated, analytical tools for coffee bean type and geographical origin discrimination are essential. For instance, visual inspection has been common practice to evaluate if a coffee is of *Arabica* or *Robusta* type, but it does not allow the safe detection of 'contaminations' of *Arabica* beans by small amounts of *Robusta* beans. Consequently, developments of more objective methods that can be certified are desirable. Analytical approaches which have been employed for green bean [24,34–39] as well as to roasted coffees [34–36,39–43] may be grouped into two classes depending on the processing of the coffee for testing. The first class, chemical methods, is based on traditional analytical methods in which coffee beans are mechanically and chemically processed for applying chromatographic techniques to distinguish between the two coffee species on the basis of different compositions of specific compounds, for example, hydroxycinnamic acids [44], sterols [45], chlorogenic acid, caffeine, trigonelline [46,47], amino acids [35,47], metals [48], fatty acids [25,40], polysaccharides [49], tocopherols [26,34] and diterpernoids [39,50,51]. The second class is based on spectroscopic techniques, mainly using mid-IR [52,53] and near-IR [41–43,52] spectroscopy which have been proven to be useful for discrimination between roasted *Arabica* and *Robusta* coffees. In addition, IR spectroscopy in combination with

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principal component analysis has been shown to distinguish between *Arabica* and *Robusta* instant coffees [54], and even 'Timor Hybrid' (Híbrido de Timor—HdT), which is a crossbreed of *Arabica* and *Robusta* coffees, was correctly identified by this method [24]. The two classes of analytical approaches are associated with specific advantages and disadvantages.

p0125 Chemical methods rely upon different chemical compositions in *Arabica* and *Robusta* coffees, but the quantitative analysis requires a time-consuming and costly sample processing in an adequately equipped chemical laboratory. On the other hand, the previously employed spectroscopic methods were applied to ground roasted or green beans without further chemical extraction procedures. However, the spectra analysis relies upon statistical calibration model procedures, which are sensitive to many factors such as year of harvest. Moreover, sample preparation has to follow a precise protocol since, for instance, water content and grain size may affect the spectra and thus the principal component analysis [55,56].

p0130 Other authors [57] have applied a Fourier-transform (FT) Raman spectroscopic approach capable of overcoming the drawbacks associated with the chemical and IR-spectroscopic techniques. High-quality Raman spectra were obtained which allowed identifying the characteristic vibrational bands of the specific compound kahweol. In a previous study, kahweol had already been detected in chemical extracts of processed green and roasted beans [39]. Due to the different content of this diterpenoid in *Arabica* and *Robusta* [50,51,54,58], these two coffee species could readily be distinguished on the basis of the kahweol Raman bands without sophisticated spectra analysis. Keidel and co-authors [57] used the FT Raman spectroscopy with 1064-nm excitation to monitor the characteristic Raman bands of kahweol in green coffee beans without chemical and physical processing of the coffee beans. The procedure was optimized on the basis of several measurements of whole and ground beans using coffee samples of different types (*Arabica*, *Robusta*) and different geographical origins. The relative contribution of the kahweol in individual beans could be determined quantitatively by means of a component analysis of the spectra, yielding a spectral kahweol index σ_{ka} that is proportional to the relative content of kahweol in the coffee bean (Figure 6). An unambiguous distinction between *Arabica* and *Robusta* samples was possible on the basis of single-bean measurements as the σ_{ka} values were larger and lower than 10 for *Arabica* and *Robusta*, respectively (Figure 6). In this study, measurements of whole and ground beans afforded very similar results, despite the heterogeneous distribution of kahweol within a coffee bean. Unlike conventional analytical techniques, the single-bean sensitivity of this approach may allow for a rapid detection of unwanted admixtures of low-value *Robusta* coffee to high-quality and more expensive *Arabica* coffee [57].

p0135 The spectral kahweol index introduced by these authors allowed us to characterize various coffees and to distinguish between *Arabica* and *Robusta*, with single-bean sensitivity. In contrast to the Raman spectroscopic approach,

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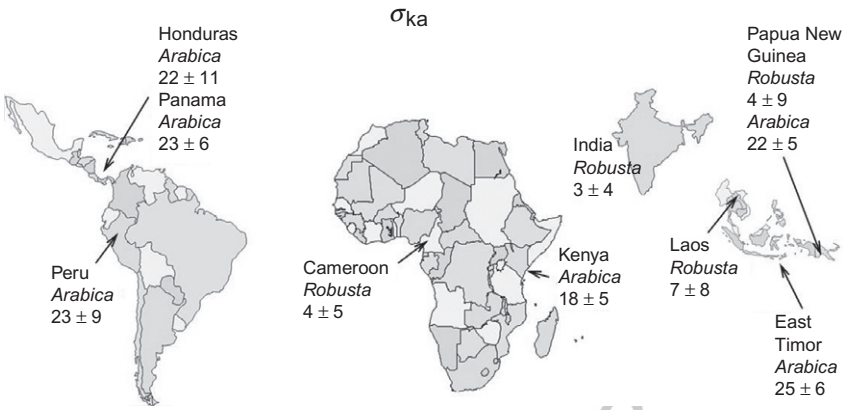

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f0030 **FIGURE 6** Spectral kahweol index (σ_{ka}) including standard deviation of *Arabica* and *Robusta* whole green coffee beans from different geographical origins (maps are not at scale). *Data source: [57].*

conventional analytical techniques, which lack this single-bean sensitivity and, instead, average over many beans, cannot distinguish between contaminations of coffee samples by Robusta beans and samples of pure Arabica coffee with somewhat lower kahweol content. However, it is still necessary to calibrate the spectral index on the basis of coffee samples of known kahweol content via chemical analyses. Such a calibration is a pre-requisite for further developing this Raman spectroscopic approach towards a highly accurate and rapid analytical tool for coffee quality control. However, already the spectral kahweol index that is readily derived from the Raman spectra represents a sound criterion to classify green coffee beans if the kahweol content is considered to be an adequate marker. The intriguing advantage of the present spectroscopic approach is that it can be performed without any time-consuming chemical processing of the coffee beans and even without mechanical pretreatment of the bean. Furthermore, this approach does not rely on pattern-matching spectral techniques which depend upon spectral differences regardless of the molecular origin or are sensitive to the sample (pre-) treatment (e.g. water content). Instead, it is based on the relative contribution of a specific chemical ingredient of the coffee beans (i.e. kahweol), and thus may be applied as an accurate tool in all cases where the kahweol content is a classification criterion, that is, distinction between *Arabica* and *Robusta*, detection of admixtures of *Robusta* to *Arabica* and possibly also the identification of different geographical origins [50].

s0040 3.2 Global Scale Coffee Geographical Origin Differentiation

p0140 Isotope analysis has been used as the most promising tool for coffee geographical origin differentiation. If necessary, it may also be combined with

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other analytical techniques for a higher degree of coffee differentiation. The isotopic fingerprint of the coffee bean should be a result of plant variety, cultivation practices, processing, and, most important, of the relation between plant and local environment. In this sense, variations in isotopic composition of coffee beans from different geographical origins, with their own climate and geology, should be expected. Several studies have shown that green coffee beans from different geographical origins have different elemental and isotopic compositions. Krivan and collaborators [28] demonstrated the potential of measuring elemental fingerprints of coffee beans to discriminate between different origins. This study was complemented by other authors as already shown in Section 2 of this chapter. However, the study of the relations between isotopes of the coffee bean and environmental factors is still recent [32,38,59,60]. The understanding of these relations allows interpreting isotopic composition differences observed among coffees from distinct geographical origins and provides an added ecological value to this merchandise. In a study developed at global scale, Rodrigues and co-authors [38,59,60] have measured isotope ratios of carbon, nitrogen, oxygen and strontium in green coffee beans and have searched for relationships between the isotope ratios and available information on environmental factors. Such studies are important in order to understand how the coffee seed (i.e. the coffee bean) integrates isotope fractionations occurring during its developmental period, which are associated to variations in local climate and geology. This may ultimately lead to the differentiation of the coffee-producing regions. The results of carbon, nitrogen and oxygen isotope analysis of green coffee beans as well as of carbon and nitrogen elemental analysis are shown in Table 1.

p0145 A global scale mean for coffee bean $\delta^{13}C$ of $-27.4‰ \pm 1.4‰$ was observed among 224 samples from different coffee-producing countries distributed throughout the African, Asian and American continents. This value is approximate to the 26‰ $\delta^{13}C$ value reported by Yakir and Sternberg [62] for plant tissues. The coffee bean $\delta^{13}C$ values ranged from $-31.4‰$ to $-22.1‰$ (Table 1), in accordance with previous results reported by Serra and co-authors [31] (with green coffee bean $\delta^{13}C$ values ranging from $-28.1‰$ to $-23.8‰$). As already mentioned in Chapter 4 of this volume, it is generally accepted that the $\delta^{13}C$ of plant organic matter will be a result of equilibrium and kinetic fractionations associated with the metabolic pathways involved in carbon fixation [63,64]. Factors changing stomatal conductance (g_s) and/or photosynthetic capacity (e.g. water deficit, light, vapour pressure deficit), thus changing the ratio of CO_2 partial pressure in the leaf interior sub-stomatal cavities and air surrounding the leaf, will change the values of $\delta^{13}C$ found for plant tissues. The variations observed among coffee beans' $\delta^{13}C$ values (Table 1) may be interpreted as reflecting differences in plant water availability, in local precipitation amount and temperature, and air RH. The observed 10‰ variation in the coffee bean $\delta^{13}C$ should be related to the occurrence of factors influencing stomatal conductance during its

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t0005 **TABLE 1** Mean, Standard Deviation and Range of Values of C and N% and of $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ of Green Coffee Beans from the United States ($n = 127$), Africa ($n = 63$) and Asia ($n = 34$) Continents (na, non available)

	C (%)			$\delta^{13}C$ (‰)		
Continent	*Mean*	*Std. Dev.*	*Range*	*Mean*	*Std. Dev.*	*Range*
The United States	45.9	1.5	41.5–52.5	−27.4	1.5	−22.1 to −31.4
Africa	46.4	1.8	42.7–51.9	−27.1	1.4	−24.5 to −29.9
Asia	44.7	1.7	39.5–49.3	−28	0.9	−25.4 to −29.5
Global scale	45.9	1.7	39.5–52.5	−27.4	1.4	−22.1 to −31.4

	N (%)			$\delta^{15}N$ (‰)		
Continent	*Mean*	*Std. Dev.*	*Range*	*Mean*	*Std. Dev.*	*Range*
The United States	2.2	0.3	1.2–2.8	2.7	1.3	0.2–5.8
Africa	2.2	0.3	1.2–3.3	3.5	1.5	−0.4 to 6.5
Asia	2.3	0.3	1.4–3	2.7	1.1	0.4 to 5.7
Global scale	2.2	0.3	1.2–3.3	2.9	1.4	−0.4 to 6.5

				$\delta^{18}O$ (‰)		
Continent				*Mean*	*Std. Dev.*	*Range*
The United States	na	na	na	27.2	2.9	18.7–33.2
Africa	na	na	na	30.4	3	23.9–39.8
Asia	na	na	na	24.3	2.5	18.3–29.4
Global scale	na	na	na	27.7	3.5	18.3–39.8

Source: [61].

developmental period [61]. However, the lack of knowledge on *how* these factors interact with the coffee plants at each location makes this interpretation difficult. Ecophysiology studies under field conditions are necessary to yield understanding on the processes that determine carbon fractionation not only at the coffee plant level but also at fruit and seed levels. In the case of N, the range of coffee bean $\delta^{15}N$ values observed varied from −0.4‰ to 6.5‰ (Table 1), with a global mean value of $+2.9‰ \pm 1.4‰$. These results suggest

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differences in coffee plants N metabolism that may eventually be associated with differences in local agricultural practices. A variation in the coffee beans $\delta^{18}O$ values was also observed, ranging from a minimum of +18.3‰ to a maximum of +39.8‰. The global mean of coffee bean $\delta^{18}O$ was +27.7‰ ± 3.5‰ (Table 1). This value is close to the 27‰ value reported for cellulose $\delta^{18}O$ in leafs [65]. Although oxygen fractionation events in plant seeds (e.g. the coffee bean) are not yet fully understood compared to other plant organs such as leafs and stems, it is expected that the green coffee bean $\delta^{18}O$ values reflect coffee plants source water oxygen isotopic composition. This is based on several authors works, showing that the oxygen isotope composition of plant organic material reflects that of source water and leaf evaporative conditions at the time the material was formed [63,66,67]. The oxygen stable isotope composition of organic molecules and of plant tissues is now providing one of the most useful archives of ecological change [68,69]. In what refers to water isotopes, there is no fractionation of water upon uptake into the plant, except perhaps under exceedingly unusual conditions [66]. Furthermore, there is no evaporation, and therefore no fractionation, of water until it reaches the leaves [70]. Therefore, the isotope ratio of xylem water can be used as a measure of the isotopic signature of the water being utilized by the plant. Differences in altitude, annual precipitation, water stress and processes such as evaporation and transpiration and also on the kinetics of the exchange of CO_2 with leaves will affect leaf water isotopic composition. Also, evaporative enrichment of water in the leaf is passed on to organic material due to exchange of carbonyl oxygen with water, resulting in a mean 27‰ enrichment of the organic oxygen compared to water at equilibrium [63]. Due to these relations between isotopes in plant organic matter and environmental factors, isotopes can often be used for fingerprinting food as they integrate the isotopic signature of its provenance. This supports the observed results obtained from oxygen isotope analysis of the coffee beans that seem to reflect local precipitation $\delta^{18}O$. Figure 7 shows that, in general, more depleted $\delta^{18}O$ values were observed in coffees from Asia in comparison to the American and African coffees. The results show that oxygen is an important element for coffee geographical origin differentiation.

p0150 Although the results allow an evaluation of the relationships between the coffee bean isotopic composition and several local environmental factors, they do not lead to global scale coffee geographical origin differentiation. In order to improve the degree of differentiation, it was necessary to proceed with the measurement of the isotopic composition of other element(s) besides the C, N and O. Previous food authenticity studies had already indicated that the analysis of strontium (Sr) isotope abundance ratios could improve the development of analytical tools towards food geographical origin discrimination, inclusively in the case of coffee. The advantage of using Sr isotopes is that soil $^{87}Sr/^{86}Sr$ remains a robust signature, even though concentrations in major elements released by weathering can be modified by the formation of

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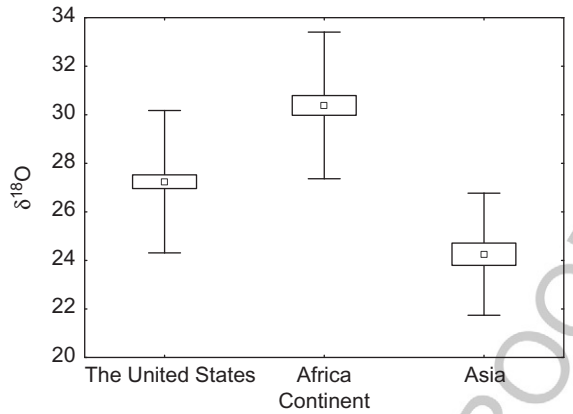

f0035 **FIGURE 7** Mean (small □), standard error (large □) and standard deviation (bar) of $\delta^{18}O$ (‰) values of green coffee beans from the United States ($n=127$), Africa ($n=63$) and Asia ($n=34$). *Source: [61].*

secondary minerals or exchange processes on the soil adsorbing complex [71]. By combining O and Sr isotope analysis, Rodrigues and collaborators [59] achieved a separation between coffee of selected origins and groups of provenances. According to these authors, coffees from East Timor differentiated from all other origins solely based on their $^{87}Sr/^{86}Sr$. In the region of South America, coffees from Brazil, Peru and Ecuador were discriminated based on their $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ values. Also, coffees originating from different islands (Papua New Guinea, Hawai'i, Indonesia, Jamaica and East Timor) differentiated on the basis of their $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ values (Figure 8).

p0155 Some of these coffees are considered *gourmet* as is the case of the Hawai'i and Jamaica. In spite of the combination of O and Sr isotope analysis of green coffee beans presenting a good approach to differentiate the geographical origin of coffee, the authors reported that the Sr isotopic signature of the atmospheric inputs and of the weathering endmember remains to be included in the study. Recently, Techer and collaborators [32] have characterized the Sr isotopic composition of all components of a cultivation system, that is, plants, rocks, soils and water in the frame of an intensive coffee-growing project on Réunion Island. The study revealed that Sr isotopic composition of coffee beans reflected the sources of strontium available during plant growth. Fertilizers may contribute to high Sr contents and high $^{87}Sr/^{86}Sr$ ratios that constitute the sources of the ^{87}Sr enrichment of the soil, eventually affecting $^{87}Sr/^{86}Sr$ values measured in the coffee beans. Thus, Sr ratios may also depend on local agricultural practices.

p0160 There was, however, evidence that most $^{87}Sr/^{86}Sr$ ratios of the green coffee beans were related to Sr isotope abundance ratio of the parent rock and/or soil. The isotopic composition of all sources of Sr such as soil, soil extracts, wet and dry precipitates, surface and groundwater, as well as water used for

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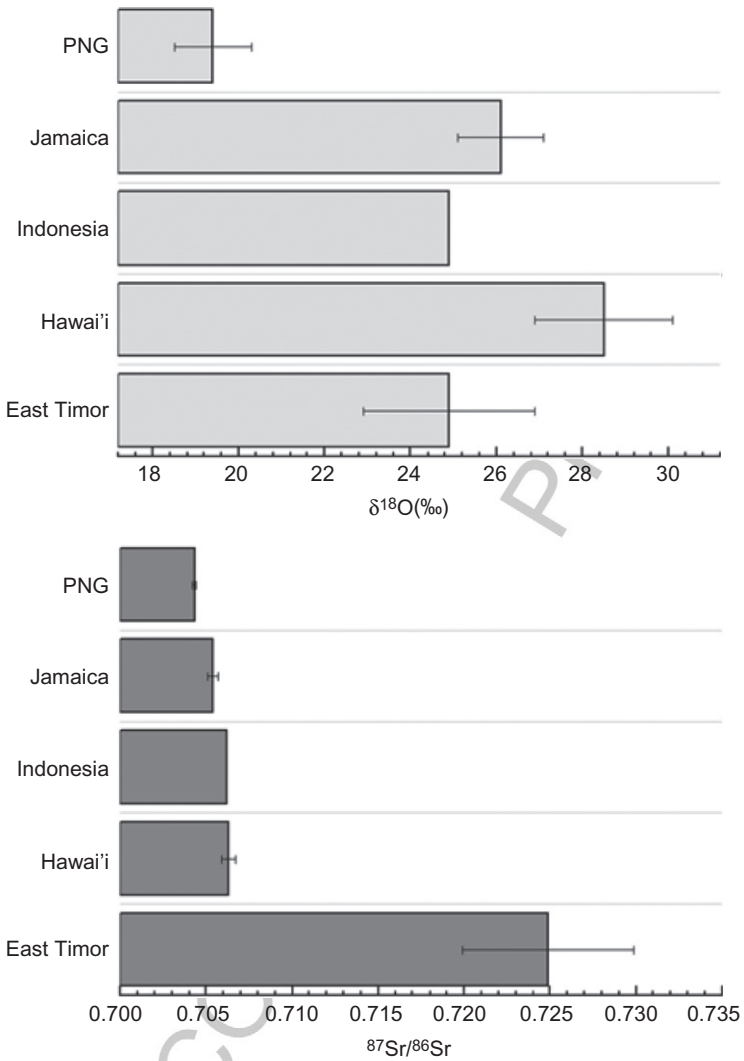

f0040 **FIGURE 8** $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ of green coffee beans from different islands. *Source: [59,60].*

watering, has to be subject to broader investigations for further interpretation of data obtained from the coffee bean isotope analysis. Also, a conclusive *Coffee Geographical Origin Discrimination Model* requires an increasing number of samples from consecutive harvest periods, as well as fundamental studies on influencing parameters and on how these evolve over time. In addition, the series of elements under analysis may be reinforced by the measurement of the isotopic composition of a wider range of chemical elements, depending on the coffee-producing region under study.

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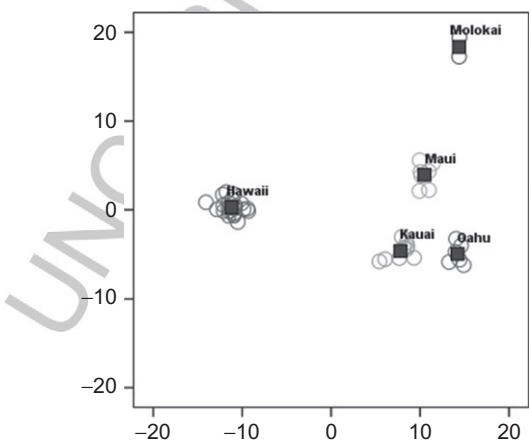
s0045 3.3 The Scale Down to the Hawai'i Coffee-Producing Regions

p0165 To assess the affect of climatic, geological and physiological processes, analytical approaches such as the 'bulk' coffee bean isotope method should be based on sufficiently small 'sampling entities'. For this reason, a scale down to smaller coffee-producing regions can improve the understanding of the processes leading to isotope fractionations at coffee plant and seed level. An interesting case study has been recently presented on the basis of the coffees from Hawai'i [59,60]. In this case, multi-element and sulphur isotope ratio analysis were applied in combination with C, N, O and Sr isotope analysis of the coffee beans, allowing discrimination of the Hawai'i coffee-producing regions (Figure 9).

p0170 The study demonstrates that combining isotope ratio and multi-element analysis is a promising tool for coffee authenticity studies. Instead of working on a 'global scale', the authors scale down to smaller coffee-producing regions allowed for a better characterization of the geographical area under study, which was advantageous when interpreting isotopic composition data from different coffee samples. When applying isotope analysis to food authenticity studies, a characterization of the region under study from climatic and geological point of view should be performed at the outset, if possible. Also, information on cultivation methods, species and varieties/cultivars, and processing should be important when building the most comprehensive database. Depending on this information, the series of chemical elements to be studied may have to be adjusted in order to achieve the highest degree of provenance discrimination. The fact that for the earlier mentioned study [38,59,60] information on exact geographical location and related environmental factors could be accessed allowed the correlation between



f0045 **FIGURE 9** Canonical analysis of isotopic and multi-element composition of 47 coffees from 5 different Hawai'i coffee-producing regions (squares indicate group centroids). *Source: [59,60].*

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experimental results and data available on, for example, altitude, latitude, $\delta^{18}O$ of precipitation and, in some cases, Sr amount and isotope composition of parent rock. This innovative approach in comparison to previous food authenticity studies contributes to a better knowledge on how and why isotope analysis can be useful for food products geographical origin discrimination. In the study conducted with the Hawai'i coffees, for each coffee sample known values of latitude and longitude, and altitude allowed calculating the correspondent values of $\delta^{18}O$ of local precipitation with the OIPC [72] (Bowen, 2010), obtaining a correlation between the $\delta^{18}O$ of coffee beans and of precipitation ($r = 0.56$; $p < 0.05$). The coffee bean $\delta^{18}O$ reflected the local precipitation oxygen isotopic signature which is in accordance with the view that O isotopes of plant water, organic molecules in plant tissues and the gases produced during plant metabolism all reflect important aspects of a plant's growth environment and physiological activity *at various spatial and temporal scales* [73]. In Figure 10, it is also possible to observe the variation of $\delta^{34}S$ values Hawaiian coffees in relation to altitude. The higher values were measured in coffees produced at altitudes under 200 m, closer to the ocean (at lower altitude values) [59,60].

p0175 Atmospheric deposition is an important sulphur source in the Hawaiian Islands, but its contribution decreases with increasing distance to the sea [74]. Monitoring atmospheric, volcanic ash, soil and precipitation, sulphate isotopes will be important in order to understand how sulphur isotopes of coffee beans reflect these important environmental impacts. In addition, further research on sulphur isotopes fractionation processes during coffee seed development is necessary to evaluate the differences in S-assimilation and isotope fractionation. In Hawai'i, the influence of volcanic activity, tropical storms, the distance to the coast and the altitude were inferred from the isotope ratios measured in the Hawai'i coffee beans (Figures 10 and 11) (Rodrigues [59,60]). These observations were supported by significant correlations between the green coffee bean isotopic composition and the various environmental factors. All this reflects the importance of the seed, the coffee bean, as a 'tool' to study climate and plant primary production spatial and temporal variations. The results of these studies may eventually support the development of a more robust analytical tool to obtain coffee geographical origin discrimination.

p0180 In reference to Sr, coffees from Ka'u district, in Hawai'i island, grown under a greater influence of the Kilauea volcano, showed lower mean values of $^{87}Sr/^{86}Sr$. These values were approximate to the reported values for Hawaiian lava (Figure 11). In the case of the coffees from Kualapu'u (Moloka'i), Waiahole and Waialua (O'ahu), the $^{87}Sr/^{86}S$ values were similar to the value reported for the Sr isotopic composition of sea salt aerosol (Figure 11). The Hawai'i islands are ideally suited for Sr isotopic studies because there are relatively few sources of Sr to the island ecosystems and these sources have distinct values that do not vary spatially or temporally [78] and are thus relatively well defined [79].

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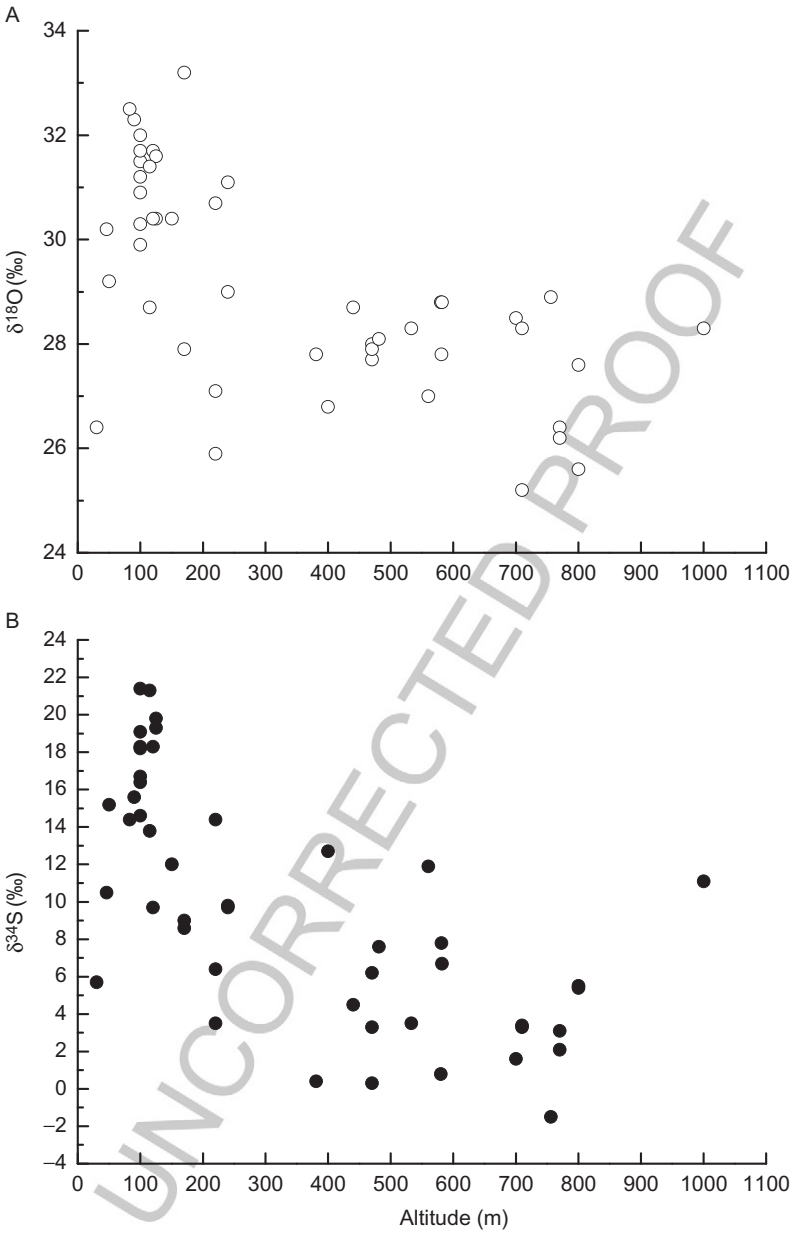

f0050 **FIGURE 10** $\delta^{18}O$ (A) and $\delta^{34}S$ (B) of the green coffee beans in relation to altitude. *Source: [59,60]*.

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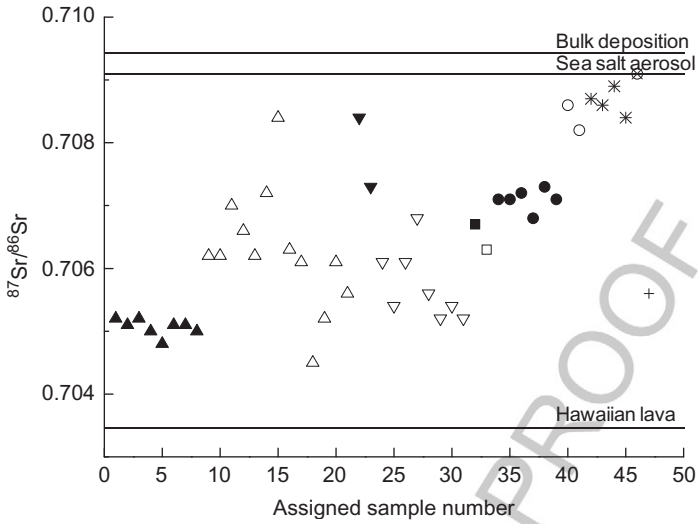

f0055 **FIGURE 11** Sr isotope ratio of green coffees from Hawai'i. Legend: (▲) Ka'u (Hawai'i), (Δ) Kona (Hawai'i), (▼) Puna (Hawai'i), (▽) Ele'ele (Kaua'i), (■) Kapahi (Kaua'i), (□) Kula (Maui), (●) Ka'anapali (Maui), (○) Kualapu'u (Moloka'i), (*) Waialua (O'ahu), (⊗) Waiahole (O'ahu), (+) Kunia (O'ahu). Bulk deposition: 0.7095 [75], sea salt aerosol: 0.70917 [76], Hawaiian lava: 0.7035 [77]. *Source: [59,60]*.

p0185 Atmospheric Sr is derived mainly from marine aerosol, and the atmospheric endmember can be considered equivalent to sea water with a minimal contribution of dust from Central Asia ($^{87}Sr/^{86}Sr = 0.7093$) [75,78]. The young basaltic substrate has accumulated minimal amounts of radiogenic ^{87}Sr since eruption, providing a weathering endmember of 0.7035 from all mineral phases [78]. The Hawaiian Islands are built of plume basalts with relatively minor compositional variation (compared to typical continental settings) [79], meaning that rock-derived Sr isotope ratios are relatively homogeneous within and among the islands. Sites corresponding to coffee beans with higher $^{87}Sr/^{86}Sr$ values (Kona, Puna, Kualapu'u, Waialua and O'ahu; Figure 11) have in common the proximity of the ocean (less than 3 km). In contrast, the coffees from Ka'u region, under a closer influence from Kilauea volcano, showed lower values of $^{87}Sr/^{86}Sr$ (Figure 11). Ka'u's coffees had $^{87}Sr/^{86}Sr$ values close to what is reported to Hawaiian lavas [77], whereas coffees from O'ahu show $^{87}Sr/^{86}Sr$ values approximate to what is referred for bulk deposition (dust) and sea salt aerosols [75–77] (Figure 11). However, in this work, Sr isotopic composition of local meteoric water has not been determined, in order to confirm if the Sr in the coffee plant derives from the atmosphere. Nonetheless, studies with other Hawaiian plant species indicate that Sr isotopic signature of plant leaves is a result of the contribution from the three main sources of Sr: Hawaiian lavas, mineral aerosol and sea salt aerosol [77,79]. In a study reported by Whipkey et al. [78], variations in annual precipitation, distance from the ocean and lava flow texture were the best

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predictors of foliar Sr isotopes. The same authors state that basalt weathering is still the dominant source of Sr in young ecosystems like in the southernmost part of Ka'u region. It was not possible to evaluate to what extension this was valid for coffee plants, specifically in the case of fruits and seeds, but the results of this work indicate that main sources of Sr in the coffee bean may be the Hawaiian lavas and the sea salt aerosols [59,60]. Fertilizers that provide high Sr contents and high $^{87}Sr/^{86}Sr$ ratios (0.7093–0.7135) could also constitute the source of the ^{87}Sr enrichment in soils [32]. But, in the case of the Hawaiian coffee beans, the Sr isotopic composition was lower than the range of values reported for fertilizers, suggesting that the latter were not the main source of Sr. This study suggested that the isotopic composition of coffees from different regions may to some degree be predictable. If so, this would support the use of stable isotopes as a tool for the verification of coffee origin. In addition, coffee plant seeds' isotopes may contribute to tracing environmental impacts occurring in Hawai'i in particular if related with volcanic activity, distance to the ocean, anthropogenic emissions and altitude.

p0190 The studies described in this chapter reflect the importance of coffee plant seed, for example, the coffee bean, as a 'tool' to study climate and the change in plant primary production over time and space. In order to apply isotope and/or multi-element analysis to coffee authenticity studies, it is important to know well the geographical area where coffee is grown. Moreover, isotope analysis allows approaching different ecosystem specificities, enclosing different spatial and temporal scales. Their study will allow for a better understanding on how environmental, biological and geological change occurs. When applied to a covering several different years, isotope delta values can give us a completely different perspective of nature cycles and plant physiological responses to the ever changing environment and reinforce food geographical origin discrimination models.

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Abstract

In this chapter, it is shown how spectroscopic techniques can be applied for the discrimination of different types of coffee and of their geographical origin. In a first approach, a study on the application of Raman spectroscopy to the differentiation of coffee type (*Arabica* vs. *Robusta*) is described, based on the determination of kahweol content, wherein the results obtained allowed coffee type discrimination. Then, isotope ratio mass spectrometry (IRMS) is addressed as a tool for the determination of the isotopic composition of carbon (C), nitrogen (N) and oxygen (O) of the green coffee bean, allowing coffee differentiation at continental level. Studies involving isotope analysis of the coffee bean have shown that oxygen is a fundamental element to achieve this differentiation, reflecting the hydrology of the coffee-producing regions. Subsequently, IRMS has been combined with inductively coupled plasma mass spectrometry, to determine the isotopic composition of strontium (Sr) in the coffee bean, in particular the ratio of the isotopes 87 and 86 ($^{87}Sr/^{86}Sr$). The study demonstrated that the isotope ratios of Sr and O can be promising for coffee authenticity, as these elements reflect the local geology and hydrology. However, in order to expand the understanding of how environmental factors determine the isotopic composition of the different elements in the green coffee bean, it may be necessary to study a model region of production, such as Hawai'i. A study performed at microscale, with coffees from different Hawai'i islands, allowed the detail analysis of how the various environmental factors prevailing in the location and time of coffee production were reflected in the elemental isotopic composition of the coffee beans. This approach allowed the discrimination of coffees from the different islands of Hawai'i. It has also revealed that the isotopic composition of O, Sr and S in the green coffee beans is related to known environmental factors, namely, the isotopic composition of the O of local precipitation ($\delta^{18}O_{prec}$), the distance to the coast and the volcanic activity characteristic of that region.

In short, this chapter describes the various tentative approaches to coffee geographical origin discrimination where isotope analysis may play an important role and also, how this tool can bring an additional value to each coffee (or provenance), an ecological value.

Keywords: Green coffee bean; Isotopes; Spectroscopy; Geographical provenance