POTENTIAL OF MULTI-ELEMENT ISOTOPIC APPROACH FOR GEOGRAPHICAL ORIGIN DISCRIMINATION OF TEA

*Ekaterina Epova[1], Sylvain Bérail[2], Bernard Médina[3], Julien Barre[1],
Julien Malherbe[1] and <u>Olivier F.X. Donard</u>[2]*

[1] UPPA, Pau, France ; [2] IPREM, Pau, France
[3] Société des Experts Chimistes de France, Paris, France

Abstract - The determination of strontium and lead isotope abundance ratios by MC-ICP-MS (multi-collection inductively coupled plasma mass spectrometry) has been applied to 28 authentic teas from various origin. A noticeably different value of $^{87}Sr/^{86}Sr$ has been obtained for Japanese tea. A distinctive trend of Pb-isotope ratios has been observed for the different geographic regions of sample origin. The combination of isotopic and elemental concentrations tremendously increases the discrimination possibilities compared to a single isotopic or elemental system.

Keywords: *geographic origin, food authenticity, strontium isotopes, lead isotopes, MC-ICP-MS*

1. INTRODUCTION

Traceability and authenticity are challenges in food production and distribution, and are of primary concern for customers, food producers and agriculture organizations. Elemental analysis, light stable isotopes (H, O, N) and selected non-traditional isotope approaches (Sr, Pb) have been already successfully used to distinguish among different origin of food products [1]. MC-ICP-MS is now recognized as a method of choice for the high precision measurement of non-traditional stable isotope ratios [2]. Isotopic fingerprinting is an individual characteristic which is based on the ratios of stable isotopes of a particular element present in samples. The use of multiple isotopic system allows exceptional new information to be obtained in terms of traceability [3, 4].

Strontium isotope ratios. Naturally occurring strontium is a mixture of four stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. Among them, only ^{87}Sr is radiogenic, i.e. produced by beta decay from the radioactive alkali metal ^{87}Rb with half-life of 4,88 x 10^{10} years. Over geological time scales, the abundances of isotopes ^{84}Sr, ^{86}Sr and ^{88}Sr are invariant, while the abundance of ^{87}Sr naturally increases with time, which results in distinctly different amounts of ^{87}Sr around the Earth over its 4,5 billion year history. Strontium released by weathering from parent rock to subsoil, groundwater, topsoil, and stream water ultimately becomes bioavailable for plants [5]. Therefore, the Sr isotopic signature of plant is strongly related to the exchangeable fraction of soil and groundwater [6], and has been found to be unaffected by the plant or animal metabolism [3]. It is a long-term stable parameter, which doesn't significantly depend on human activity, climate or season of production, but is regulated by local geological environment, particularly the age and the abundance of Rb in ambient rocks or soils [7]. Due to this features, the use of Sr isotope signatures becomes a promising tool to determine food authenticity and geographical provenance [1, 8].

Lead isotope ratios. Lead has four stable, naturally occurring isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, with the last three being end-members of the natural uranium–thorium decay series, so-called radiogenic Pb. The Pb isotopic composition of any natural material is the composite of three independent decay chains and different geochemical behavior of U, Th and Pb. It results in a greater variability of lead isotopic values in minerals compared to that for the Rb-Sr system. Lead stable isotopes are extensively used as an indicator for discrimination of anthropogenic contamination in environmental pollution research [9]. Due to features of industrial and urban activity lead in the atmosphere in each country has its own concentration and origin [10]. Tracing food origin using Pb isotope signatures consists in the determination of lead isotope ratios in food or raw

food material and their comparison with those in lead sources in the region considered. Most of the attention is paid to airborne lead because during their growth plants absorb lead mainly from the atmosphere through foliage [11, 12, 13]. The modern atmosphere is primarily affected by anthropogenic lead (e.g. vehicular exhaust, coal combustion, urban activity, etc.), and then by geogenic lead from natural emission (rock weathering, volcanic eruption, soil dust, etc.). As a consequence, lead isotope signature reflects the interaction of plant with its environment (and thus its origin) and the major sources of lead presented. The potential lead contamination during growth (e.g. fertilizers) and food processing must been considered during data interpretation.

The aim of this study was to determine the Sr and Pb isotope ratios in a variety of teas and then to assess the potential relationships between measured isotopic signatures of tea and its geographical origin.

2. MATERIALS AND METHOD

Samples, mineralization, matrix purification. Twenty eight tea samples were obtained from specialized tea stores with provenance information: China (n=13), Japan (n=11), South Korea (n=4). Samples were homogenized, mineralized using a microwave MARS 5 (CEM). The element concentrations were determined by a quadrupole ICP-MS NexION (PerkinElmer). Matrix purification for Sr and Pb isotopes determination has been done prior isotope ratio analysis.

MC-ICP-MS analysis. Isotopic analysis of the samples was performed using a MC-ICP-MS Nu Plasma II (Nu Instrument). For lead isotope ratios, the instrumental mass bias was corrected by spiking samples with a thallium solution (NIST SRM 997) and by following a standard/sample bracketing sequence against the NIST SRM 981. The solutions are introduced into the instrument via a desolvating nebulizer (DSN-100, Nu Instruments) with Pb concentration of 30 ng g^{-1}. The precision and accuracy of the Pb isotope determination were assessed through measuring a standard solution NIST SRM 981. The external reproducibility (2σ) was in average equal to ± 0,021% for $^{208}Pb/^{206}Pb$ and ± 0,008% for $^{207}Pb/^{206}Pb$.

For strontium isotope ratio measurement, general operating parameters were optimized to achieve the maximum ion intensity for ^{88}Sr using standard solution NIST SRM 987 with a concentration of 20 ng g^{-1}. The signal was corrected from mass bias using the constant ratio $^{88}Sr/^{86}Sr$ of 0,1194 and potential remaining interferences from ^{87}Rb. The precision and accuracy of the Sr measurement method were controlled using NIST SRM 987. The external reproducibility (2σ) was in average equal to ± 0,056 % for Sr isotope ratios.

3. RESULTS AND DISCUSSION

3.1. Strontium isotope ratios

The isotope ratio $^{87}Sr/^{86}Sr$ of tea leaves varied with the geographical origin to a large extent: China 0,7053-0,7454; Japan 0,7067-0,7107; and S. Korea 0,7115-0,7163.
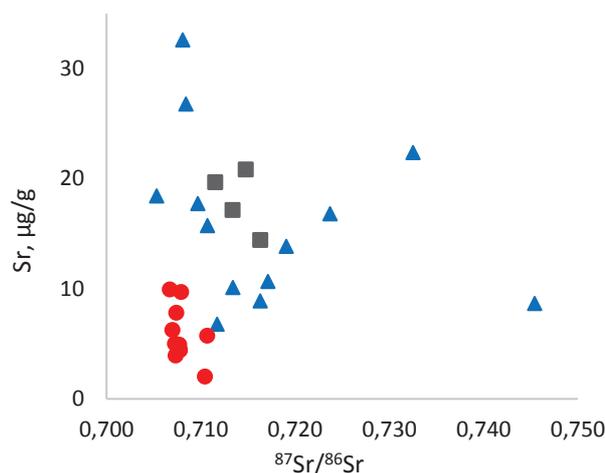

Fig. 1. Plot of $^{87}Sr/^{86}Sr$ *versus* Sr concentration for tea samples different origin: China - blue triangles, Japan – red circles, South Korea – gray squares.

It can be seen from the isotope-concentration plot (Fig. 1) that Japanese tea can be distinguished from South Korean tea by Sr isotope ratio and Sr concentrations, while Chinese teas is characterized by the large variability of these values. It is well known that $^{87}Sr/^{86}Sr$ is regulated by local geological environment, particularly the age and the abundance of Rb in ambient rocks or soils [7]. The geological structure of China is very variable and can be divided into several parts: the world's largest Quaternary loess deposit in Centre, the alluvial lands

at the East, high-altitude Tibetan plateau in the West, mountainous landscape on South dominated by sedimentary deposits. Obviously, the values of $^{87}Sr/^{86}Sr$ are more variable in China than those in Japan, which only consists in Mesozoic-Paleozoic sedimentary rock and Cenozoic intrusive rocks. Studied Korean tea samples origin from the south of Korean peninsula, where much older sedimentary and metamorphic Precambrian rocks are dominating the geological settings. This fact leads to the higher $^{87}Sr/^{86}Sr$ values observed for Korean tea in comparison with those in Japanese tea. Our data is in a great agreement with results of Song et al. [6], which measured an average $^{87}Sr/^{86}Sr$ of 0,71712 ± 0,00618 in Korean plants.

Fig. 2. Three-isotope plot for tea samples different origin: China - blue triangles, Japan – red circles, South Korea – gray squares.

3.2. Lead isotope ratios

Fig. 2 presents the variation of lead isotopic composition $^{208}Pb/^{206}Pb$ ($^{207}Pb/^{206}Pb$) according to tea samples origin: China 2,091-2,114 (0,845-0,859); Japan 2,100-2,117 (0,858-0,873); South Korea 2,104-2,129 (0,865-0,876). It can be seen from the three isotope plot that Japanese and Korean tea have a similar lead isotope composition. Also, tea from China has been more influenced by lead anthropogenic emissions than tea coming from Japan and South Korea.

Fig.2 illustrates the potential of the Pb system to discriminate tea origin. It has been shown that the atmosphere of continental China is characteristically different from that of Japanese islands and Korean peninsula in terms of lead isotope compositions [14]. The global character of lead atmospheric pollution and and the presence of few substantial pollutant sources prevent more detailed classification, as it can be seen for teas originating from South Korea and China (Fig.2). Pb isotope method has a great potential in distinguishing among products from geographical areas containing one specific anthropogenic lead pollutant source, such as local ores [11, 15].

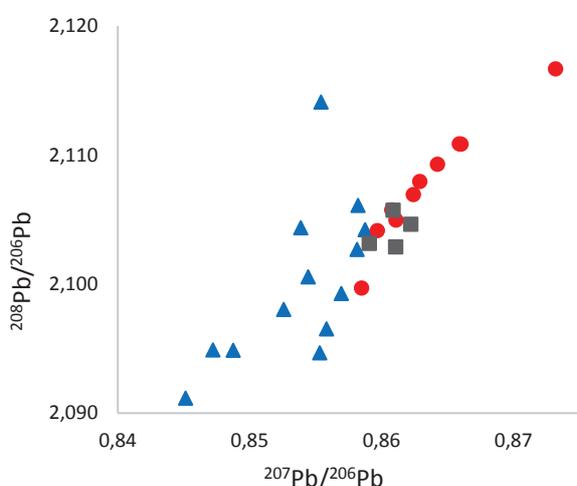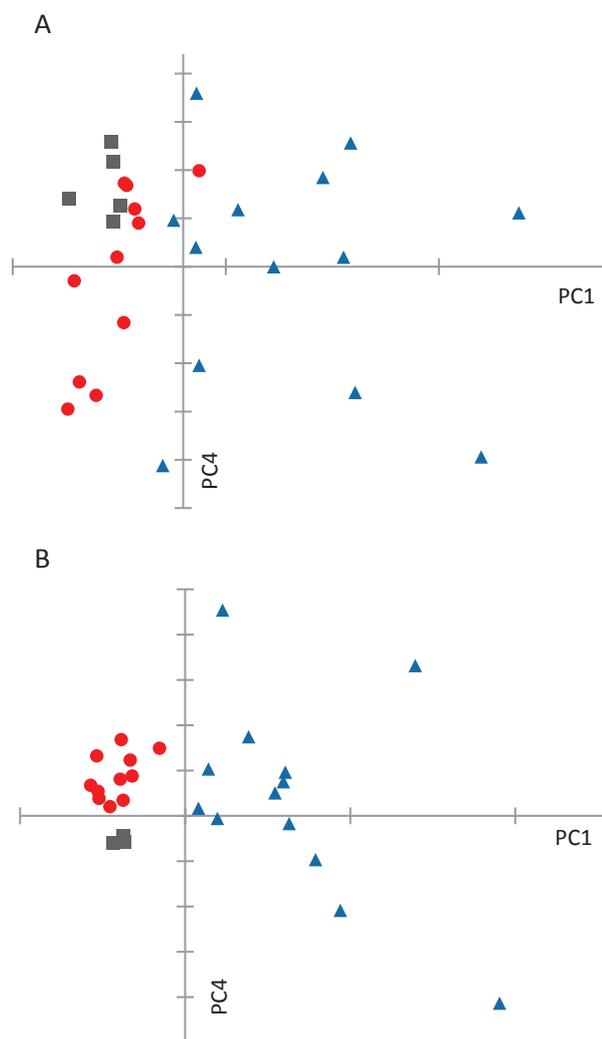## 4. MULTI-ELEMENT ISOTOPIC APPROACH

A

B

Fig. 3. Results of principal component analysis: (A) - with 16 elements; (B) - 16 elements with $^{208}Pb/^{206}Pb$ ($^{207}Pb/^{206}Pb$) and $^{87}Sr/^{86}Sr$; in tea leaves different origin: China - blue triangles, Japan – red circles, South Korea – gray squares.

In this work we would like to present the advantages of multi-elemental isotopic approach for geographical origin discrimination. Using only one isotopic system is not enough to discriminate clearly individual countries of origin. However, using a combination of two isotopic systems - one tracing the lithological settings, and the other tracing environmental ambient pollution, completed with elemental concentration gives maximal distinctiveness for origin discrimination. The importance of isotopes contribution to that might be illustrated by Fig. 3A and Fig. 3B: the best discrimination ability was obtain with use data from isotope analysis.

4. CONCLUSIONS

The presented study demonstrates the new potential of a model based on the combined high-precision determinations of non-traditional stable isotopes of Sr and Pb with MC-ICP-MS. This strategy can be used for determination of food origin, traceability and authenticity issues, detecting food frauds, including adulteration of high value products with cheaper substitutes, forgery and falsification.

AUTHOR INFORMATION

Corresponding author: E. Epova, e-mail: ekaterina.epova@univ-pau.fr

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