PYROLYSIS COMPOUND-SPECIFIC NITROGEN ISOTOPE ANALYSIS ($\delta^{15}N$ Py-CSIA): NOVEL ANALYTICAL APPROACH FOR ARCHAEOLOGICAL STUDIES

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BACKGROUND

The measurement of stable isotopes has become an important tool within the field of archaeology. The isotopic trace of human and animal tissues and components (bone, collagen, keratin, muscle, fat etc.) allowed insight into the diet of our ancestors in a specific period of time, as well as its relationship with various human pathologies. Furthermore, this technique informs about food origin and possibly also about their commercial routes, as well as population migrations.

Pyrolysis-compound specific isotope analysis (Py-CSIA) is a cutting-edge analytical approach able to provide, not only a precise identification of organic compounds in different complex matrices, but also valuable information on the nature and origin of the materials based on their isotope composition.

METHODOLOGY

Py-CSIA is based on the coupling of a micro-furnace pyrolysis unit to a gas chromatograph (GC) equipped with an isotope ratio mass spectrometer (IRMS) detector. The individual volatile pyrolysis products separated by GC are directed to a combustion or pyrolysis micro-reactor (GC-Isolink system). Subsequently, the isotope composition of the gases produced is measured in a continuous flow IRMS via an interface ConFlo IV unit (**Fig 1**). With this technique it is possible to make direct determinations of stable isotope ratios (i.e. $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$) of specific compounds separated by GC with minimum sample handling and pre-treatment, thus minimizing the chance of contamination and artefact production.

Fig. 1. Main Instruments at the MOSS group, stable isotopes laboratory

CASE STUDIES

Here, we introduce the Py-CSIA technique into the field of archaeology by determining the isotopic composition of human skeletons buried in medieval necropolises from the Center and South of Portugal (**Fig. 2**).

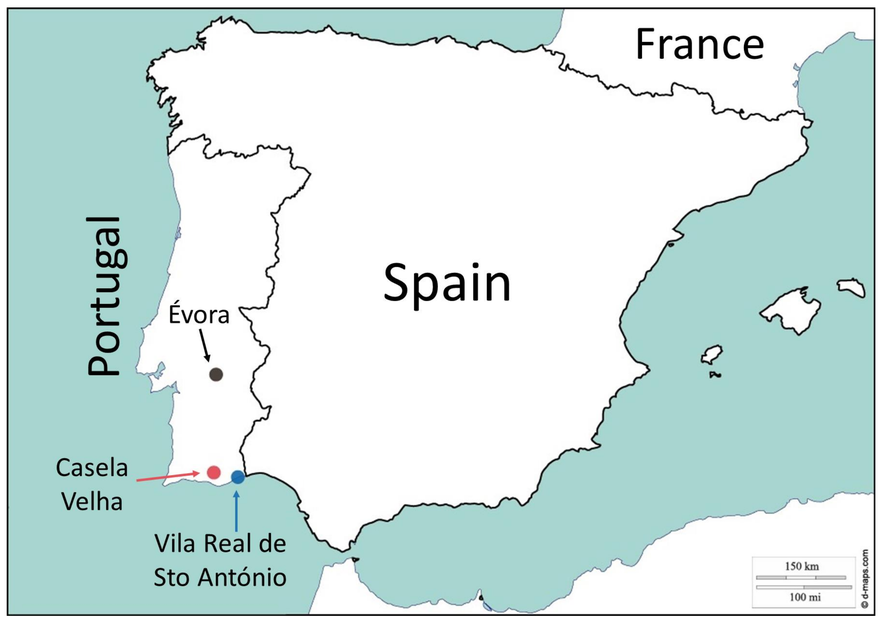

Fig. 2. Location of Portuguese medieval necropolises.

ADVANTAGES OF $\delta^{15}N$ Py-CSIA

- Small sample size: only a few milligrams of a single sample are required for measurement.
- Time saving: no pre-treatment nor extraction procedures are generally needed.
- Less handling: avoid artefact production.
- Robust technique.
- Complex materials or mixtures (including collagen), with varying structures and origins can be analyzed (**Fig 3 & 4**).
- Py-CSIA is an innovative approach in archaeological science, allowing us to assess trophic levels and paleodiets.

Py-GC/MS of Archaeological Collagen samples

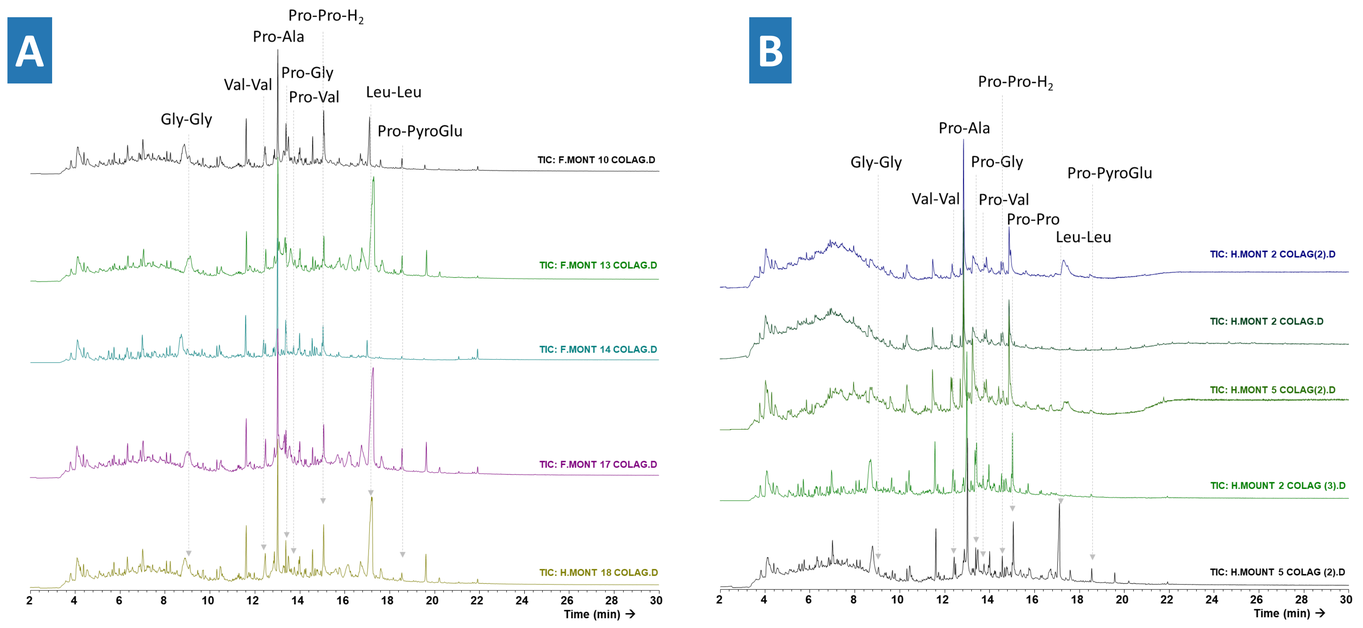

Fig. 3. Pyrograms of collagen extracted from bones found in Portuguese archaeological sites. A) Fauna, and B) Humans. The characteristic diketopiperazine (amino acid cyclations) compounds are detected in both set of samples. Pro = Proline, Gly = Glycine, Leu = Leucine, and Val = Valine

Py-CSIA of Collagen samples

Fig. 4. Example of compound specific isotope ($\delta^{13}C$ and $\delta^{15}N$) analysis (Py-CSIA) of a lizard scale. It was possible to detect the isotopic composition of various diketopiperazines (Pro-Pro and Pro-Leu), as well as other nitrogen compounds, such as indoles and alkylamines

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