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DIRECT SPECIFIC ISOTOPIC ANALYSIS OF COMPOUNDS RELEASED BY PYROLYSIS (Py-CSIA): NOVEL APPLICATIONS IN PALEOENVIRONMENTAL STUDIES

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Introduction

The combination of pyrolysis and compound specific isotopic analysis (Py-CSIA) and analytical pyrolysis (Py-GC/MS) opens new windows of information and is particularly useful to study solid materials that are not soluble and therefore not amenable by conventional GC/MS techniques. Py-CSIA is a rather novel hyphenated technique that combines the chromatographic separation of compounds released by pyrolysis (Py-GC) with an isotope ratio mass spectrometer (IRMS). The technique allows the measurement of stable isotope proportions i.e., $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$, $\delta^{18}O$ in specific compounds released by pyrolysis. The sample preparation is minimized and a molecular fingerprinting of the material is achieved.

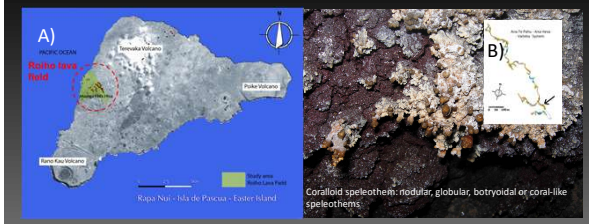
Experimental procedures

The analytical facilities used for conducting the direct pyrolysis compound specific isotopic analysis (Py-CSIA) consists of a micro-furnace double-shot pyrolyzer (Frontier Laboratories, model 3030D) attached to a Trace Ultra GC system. At the end of the chromatographic column the chromatographic flux is conducted to a GC-Isolink System equipped with micro-furnaces for combustion (C) and for pyrolysis (TC). The system is coupled to a Delta V Advantage IRMS via a ConFlo IV universal interface unit (Py-GC-C/TC-IRMS) (Fig. 1a). Specific peaks (structural information) are identified by comparing the mass spectra from a conventional Py-GC/MS system and Py-GC/IRMS chromatograms obtained using the same chromatographic conditions [1-2].

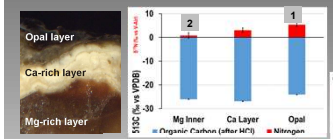
Case studies

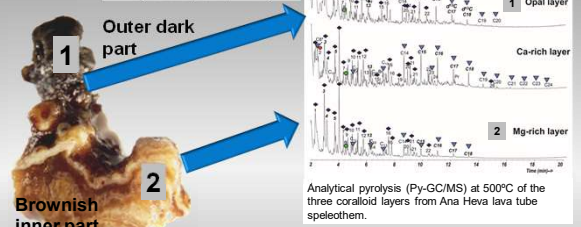
- **Coralloid speleothems from lava caves of Easter Island**
- **Remains of the fossil conifer *Frenelopsis oligoestomata* from central Spain**

Siliceous speleothems from Ana Heva lava tube – Easter Island



A) Geographical localization of Roiho lava field in Easter Island; B) sampling point in Ana Heva lava tube, and Coralloid-type speleothems collected.

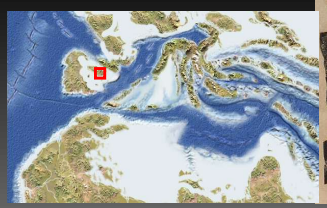


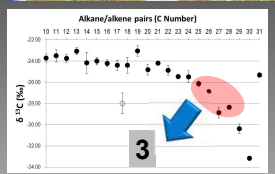


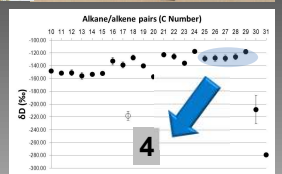
Analytical pyrolysis (Py-GC/MS) at 500ºC of the three coralloid layers from Ana Heva lava tube speleothem.

Frenelopsis oligostomata (coniferous fossil)

Age: 72 mya Senonian
Location: Central Spain

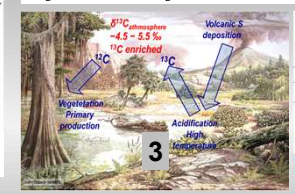


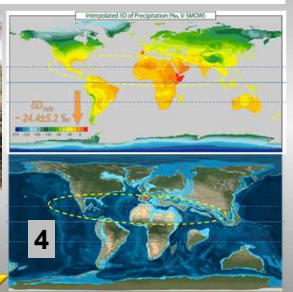




Due to the known source and stability of biopolymers, compound-specific analysis has been focused on lipids with various carbon chain lengths, such as C_{25}–C_{29} alkanes which are believed to derive exclusively from leaf waxes of higher plants.

From Py-CSIA [1] isotopic signatures of alkyl molecules we could estimate atmospheric CO_2 $\delta^{13}C$ and rainfall H_2O δD at the time the plant was alive.





Palaeo-environmental changes detected by Py-GC/MS, Py-CSIA & IRMS

Two stages of deposition during the last 12.000 years at Easter Island:

1. Subtropical climate
- Humid conditions
- Woody vegetation

2. Recent times
- Dry conditions
- Grass vegetation

Paleo-atmospheric CO_2 $\delta^{13}C$ and rainfall paleo-H_2O δD c.Iberian Peninsula 72 myr

3. $\delta^{13}C_{CO2}$ −5.0 ± 0.5 ‰
- Emissions of ^{13}C volcan
- Uptake of ^{12}C plants
- conditions

4. δD_{PW} −24.4 ± 5.2 ‰
- Warm environment
- Continental drift

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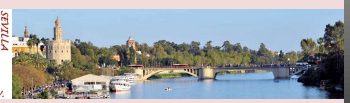
EA/IRMS

Py-GC/MS

Py-CSIA

Stable isotopes laboratory (MOSS group; IRNAS-CSIC)

REFERENCES:
[1] González-Pérez, J.A., et al. J. Chromatogr. A, 2015a, 1388, 236–243.
[2] González-Pérez, J.A., et al. J. Sci. Food Agr, 2015b, in press (DOI: 10.1002/jsfa.7169)
[3] De la Rosa J.M., et al. XVI-COLACRO, Lisbon (2016). Ed. J.M. Nogueira. Univ. of Lisbon (Portugal).



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