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LIPID BIOMARKERS ARCHIVED IN GUANO ACCUMULATIONS FROM FRENCH CAVES

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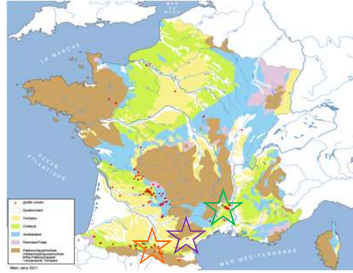
Introduction

Guano are accumulations over time of materials issued from bat excretions. Although they constitute potential archives of past environmental changes, they are yet unexplored, at least from an organic geochemistry point of view. Here we discuss biomarker imprints from 15 guano samples recovered from various French caves.

What?



Where?



| Sample | Site | Town | Age |
|----------|------------------|---------------------------|------------------|
| BROU-3 | Brouzet cave | Corconne | In progress ☆ |
| DEMOI-04 | Demosselles cave | Saint Bazuille de Puitis | In progress ☆ |
| ESCA-019 | Escalans cave | Saint Bazuille de Montmel | 4544 - 4368 BC ☆ |
| ESCA-020 | Escalans cave | Saint Bazuille de Montmel | 6067 - 5920 BC ☆ |
| FEES-001 | Fées cave | Tharoux | >45 000 BC ☆ |
| FEES-003 | Fées cave | Tharoux | ☆ |
| Lherm-4 | L'Herm cave | Lherm | In progress ☆ |
| Lherm-8 | L'Herm cave | Lherm | In progress ☆ |
| Lherm-11 | L'Herm cave | Lherm | In progress ☆ |
| MIG-013 | Miguro cave | Corconne | 5536 - 5373 BC ☆ |
| MIG-014 | Miguro cave | Corconne | In progress ☆ |
| ROQ-002 | La Roquette cave | Conqueyrac | 119 - 548 BC ☆ |
| TOUR-1 | Tourtoise cave | Tourtoise | Recent ☆ |
| TOUR-5 | Tourtoise cave | Tourtoise | Recent ☆ |
| TOUR-10 | Tourtoise cave | Tourtoise | Recent ☆ |

How?

Extraction: DCM:Isopropanol / ultrasonically

Separation: Aminopropyl-bonded silica

- Neutrals= DCM:isopropanol
- Acids= Formic acid-ether, ether
- Polars= MeOH

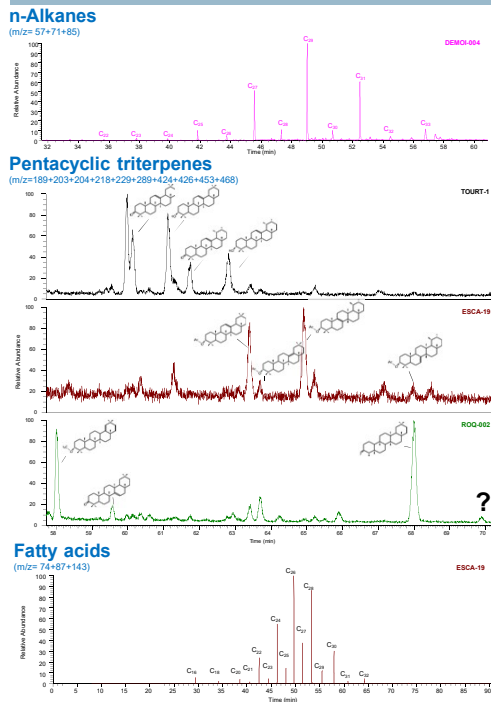


Identification/quantitation:

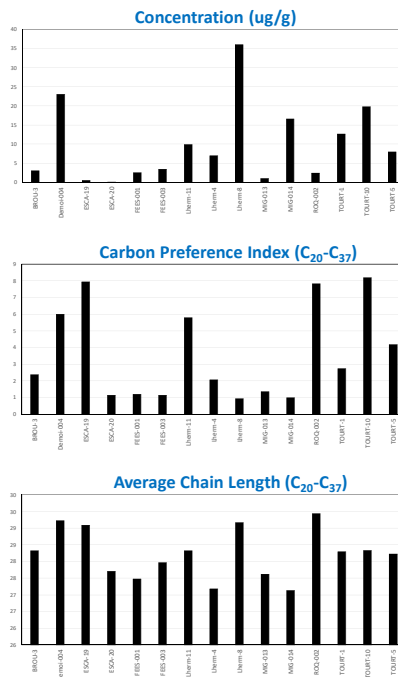
- GC: TRACE1300
 - BPX5 60 m, 0.32 mm id, 0.25 µm
- MS: Thermo Scientific ISQ QD



Biomarker distributions



Quantitations



Synthesis

Neutrals

| Samples | n-alkanes | | | MSEI | steroids | Pentacyclic triterpenes | | | | | | | Diols | Diols | Diols | Diols |
|----------|-----------|------------|-----|------|----------|-------------------------|-----------|-------|-----|-------|-----|-------|-------|-------|-------|-------|
| | Amount | Vol. ratio | CPI | | | Ok | Algae/bac | Algae | Bac | Algae | Bac | Algae | | | | |
| BROU-3 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| DEMOI-04 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| ESCA-19 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| ESCA-20 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| FEES-001 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| FEES-003 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Lherm-4 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Lherm-8 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Lherm-11 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| MIG-013 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| MIG-014 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| ROQ-002 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| TOUR-1 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| TOUR-5 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| TOUR-10 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |

Acids

| Samples | Amount | n-acids | | Diols | Hopanoic acid |
|----------|--------|------------|-----|-------|---------------|
| | | Vol. ratio | CPI | | |
| BROU-3 | + | + | + | + | + |
| DEMOI-04 | + | + | + | + | + |
| ESCA-19 | + | + | + | + | + |
| ESCA-20 | + | + | + | + | + |
| FEES-001 | + | + | + | + | + |
| FEES-003 | + | + | + | + | + |
| Lherm-4 | + | + | + | + | + |
| Lherm-8 | + | + | + | + | + |
| Lherm-11 | + | + | + | + | + |
| MIG-013 | + | + | + | + | + |
| MIG-014 | + | + | + | + | + |
| ROQ-002 | + | + | + | + | + |
| TOUR-1 | + | + | + | + | + |
| TOUR-5 | + | + | + | + | + |
| TOUR-10 | + | + | + | + | + |

Conclusions

- Alteration indices (CPI) and preservation of various oxygenated biomarkers indicate limited degradation, despite harsh acidic conditions, which is not related to the age.
- A strong contribution of biomarkers typical of vascular plants is evidenced by the distribution of n-alkanes.
- Its is confirmed by Angiosperms biomarkers such as oxygenated pentacyclic triterpenes, of which triterpenyl acetates (Asteraceae) and miliacin (Gramineae).
- Transfer from source to archive implies that insects that have been eaten by bats guano contributors have been in contact with (or even consumed) these plants.
- This plant->insect->bat->guano transfer does not appear to have significantly affected the properties of biomarkers.
- These first results are very promising for paleoenvironmental/paleoclimatic reconstructions.

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