

New objects of study for mass spectrometry by secondary-ion and laser desorption-ionization: Acritarchs, a pilot study of the species "*Gloeocapsomorpha prisca*"

ORAL PRESENTATION

Presented by Mathilde Bon

 Tuesday, 11 July 2023

 10:00 - 10:15

 [R13 \(Building B, Level 1, Lyon Congress Center\)](#)

Subsession: 6gO1 - Advances in molecular and light stable isotope techniques and their application to (bio)geochemical studies

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Theme: Theme 6: Novel methods: nanoscale techniques to big data

Abstract

Acritarchs are organic-walled microfossils of uncertain biological affinity. The species *G. prisca* (~10 μ m), a probable cyanobacterium, comprises the bulk of the insoluble organic matter (kerogen) from a rock type named "kukersite"¹⁻⁵. *G. prisca* has been studied by gas chromatography-mass spectrometry (GC-MS) using extraction, chemolysis, and pyrolysis¹⁻⁴.

Here we test the potential of laser-assisted mass spectrometry techniques to analyze the molecular composition of single microfossils. Bitumen and kerogen (dominated by the *G. prisca* microfossils) were analyzed after organic solvent extractions and demineralization of a sample from a 460 million year-old deposit of north-western Russia⁵. Using secondary ion time-of-flight mass spectrometry (ToF-SIMS), we carry out mass spectrometric imaging with ~1 μ m spatial resolution and high surface sensitivity. We perform high resolution two-step laser desorption-ionization mass spectrometry (HR- μ L2-MS) with a 140 μ m probe and laser desorption-ionization

Fourier transform ion cyclotron resonance mass spectrometry (LDI-FT-ICR-MS) with laser probes down to less than 20 μm .

The ToF-SIMS and HR- $\mu\text{L2-MS}$ analysis of microfossils are dominated by abundant (poly)aromatic hydrocarbons. Unique formula assignments were possible for the ions that dominate the signal between ca. 150-450 m/z in LDI-FT-ICR-MS. Thus, we identify a few thousands of molecular formulae and show aromatic hydrocarbons, oxygenated and nitrogenous compounds, with a major contribution of the O_{2-4} compounds. This predominance is consistent with the organic composition of the *G. prisca* wall deduced from pyrolysis- and chemolysis-assisted GC-MS analyses¹⁻⁴. Importantly, the bitumen and the microfossils showed distinct molecular signatures with all techniques.

The potential effects of desorption lasers in LDI-FT-ICR-MS, such as fragmentation and pyrolysis, were examined using principal component analysis. Our analytical method and data analysis workflow is expected to help future molecular discrimination of microfossils from heterogenous assemblages, and can help the search for molecular signatures for exobiology⁶.

¹ Blokker P *et al.* (2001) *Geochimica et Cosmochimica Acta* 65.

² da Silva TF *et al.* (2016) *International Journal of Coal Geology* 168.

³ Derenne S *et al.* (1990) *Organic Geochemistry* 16.

⁴ Derenne S *et al.* (1992) *Organic Geochemistry* 19.

⁵ Raevskaya E *et al.* (2004) *IGCP* 503.

⁶ Goesmann F *et al.* (2017) *Astrobiology* 17.

Presenting Author



Mathilde Bon

Univ. Lille, Univ. Lille,
CNRS, UMR CNRS, Univ.
8523 – Littoral Côte
PhLAM – d'Opale,
Physique des UMR 8187 –
Lasers LOG –
Atomes et Laboratoire
Molécules d'Océanologie
et de
Géosciences

Department
of Geology

(WE13),
Ghent
University

Authors



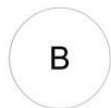
Kevin Lepot

Institut Universitaire de France (IUF)
Univ. Lille, CNRS, Univ. Littoral Côte d'Opale, UMR 8187 – LOG – Laboratoire d'Océanologie et de Géosciences



Yvain Carpentier

Univ. Lille, CNRS, UMR 8523 – PhLAM – Physique des Lasers Atomes et Molécules



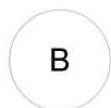
Fabrice Bray

Univ. Lille, CNRS, USR 3290 – MSAP – Miniaturisation pour la Synthèse, l'Analyse et la Protéomique



Armelle Riboulleau

Univ. Lille, CNRS, Univ. Littoral Côte d'Opale, UMR 8187 – LOG – Laboratoire d'Océanologie et de Géosciences



François Baudin

SU CNRS, ISTeP UMR 7193



Nicolas Nuns

Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide



Maxime Cyril Bridoux



Christian Rolando



CEA



R

Univ. Lille,
CNRS, USR
3290 – MSAP
–
Miniaturisation
pour la
Synthèse,
l'Analyse et la
Protéomique



S

[Philippe Steemans](#)
EDDy
Lab/Palaeobotany
and
Palaeopalynology,
Univ. Liège,
4000 Liège,
Belgium



V

[Thijs R. A. Vandenbroucke](#)
Department
of Geology
(WE13),
Ghent
University

