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

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Acritarchs are organic-walled microfossils of uncertain biological affinity. The species *G. prisca* (~10µm), 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 pyrolysis[1–4].

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 Russia[5]. Using secondary ion time-of-flight mass spectrometry (ToF-SIMS), we carry out mass spectrometric imaging with ~1 µm spatial resolution and high surface sensitivity. We perform high resolution two-step laser desorption-ionization mass spectrometry (HR-µL2-MS) with a 140 µm 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-µL2-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 analyses[1–4]. 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 exobiology[6].

[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.