Mass spectrometry imaging as a new tool for deep time ecological reconstruction

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Laser-based mass spectrometry imaging (MSI) enables mapping the µm-scale distribution of organic molecules. While firmly established in the life sciences, in recent years MSI has also proven itself as a powerful tool for paleoclimatic and ecological reconstructions. Previous applications comprise functionalized molecules recorded in unconsolidated sediments deposited within the most recent geological period, i.e., alkenone and tetraether based climate proxies [1,2], sterol based redox proxies [2] in Quaternary sediments, as well as intact polar lipids and pigments in a modern microbial mat [3]. Due to geological heating and transformation processes, organic molecules contained within sedimentary rocks that were deposited much earlier in Earth history have lost their functionalization and are mostly preserved as molecular fossils in form of saturated or aromatic hydrocarbons. Ionization of these compounds provides a new challenge for MSI analysis. Here, we present results of the first application of MSI to thermally mature Precambrian rocks, providing a pipeline for sample preparation and analysis for solid sedimentary samples. Using the exemplary 1640 million-year old Barney Creek Formation, which hosts some of the oldest molecular fossils preserved on Earth [4], we discuss the potential of MSI for deep time paleoecological reconstructions. MSI can be combined with complementary types of spatially congruent analyses such as µXRF, allowing for a direct comparison of organic molecules with their sedimentary matrix indicative of environmental and depositional conditions (Fig. 1).

A particular focus of this study will be on the potential of MSI for recognizing fossil microbial mat communities (Fig. 1). Even though microbial mats were widespread during the Precambrian and may have exerted a principal control on molecular fossil taphonomy [5], it is almost impossible to gauge the influence of microbial mat communities on proxy signatures in traditional extraction-based organic geochemical analysis [4]. Does MSI provide the long-sought tool for differentiating between pelagic and benthic molecular fossil signatures?

<u>References</u>

[1] Wörmer et al. (2014) PNAS 111, 15669-1567. [2] Alfken et

al. (2021) *Paleoceanogr. Paleoclimatology* 36. [3] Wörmer et al. (2020) *Geobiology*, doi:10.1111/gbi.12411 [4] Nettersheim (2017) PhD thesis, Australian National University, Canberra doi: 10.25911/5d5145163fd80. [5] Pawlowska, Butterfield and Brocks (2013) *Geology* 41(2): 103-106.



Figure 1. Microscale elemental and molecular fossil distributions in intact Paleoproterozoic rocks. A) Photograph overloid with MSI map (50 µm resolution) showing the distribution of molecules with the exact mass (±3 mDa) of aromatic derivatives of fossil triterpenoid lipids and B) µXRF elemental map (50 µm resolution) of Si, Ca, AI, Fe, S in the same partially silloffed putative microbial mat system.