MASS SPECTROMETRY IMAGING OF SEDIMENTS – A SAMPLE PREPARATION PIPELINE FOR LASER-BASED ANALYSIS OF ARCHAEAL LIPID BIOMARKERS

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Introduction

In 2014 Wörmer and colleagues introduced a new, extraction-free, ultra-high-resolution method to detect archaeal biomarkers in marine sediments at an unprecedented spatial resolution. Laser Desorption Ionization was coupled to a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (LDI FTICR-MS) to create µm-scale images of lipid biomarker distributions on an intact sediment core section. This first laser-based detection of marine environmental biomarkers can be described as a bold beginning of mass spectrometry imaging (MSI) in geosciences. Sample preparation is crucial to the success of MSI (e.g. Goodwin, 2012), given the need to provide a smooth, even, non-disturbed and stable surface, without compromising biomarker distribution and sedimentary fine structure. It was our goal to implement a sample preparation pipeline for sediment samples that satisfies these criteria, and at the same time is compatible with MSI in terms of ion suppression and signal disturbance. This first protocol focuses on the optimized detection of thaumarchaeal glycerol dialkyl glycerol tetraethers (GDGTs), which are sensitive recorders of past sea surface temperatures and are used in the paleotemperature proxies TEX_{86} (Schouten et al., 2002) and the MSI-based CCaT (Wörmer et al., 2014). Besides the development of a scheme for the routine investigation of GDGTs with Matrix Assisted (MA)LDI FTICR-MS, this study also defines the ideal sample preparation protocol for the acquisition of congruent molecular and elemental maps. The prior analysis of the sample with non-destructive micro X-Ray Fluorescence Spectroscopy (µXRF) enables the investigation of biomarkers in the context of their sedimentary matrix.

Results

A mixture of eastern Mediterranean Sapropel layers (GeoB15103-2) served as a test sediment for the different steps of the sample preparation pipeline, which included drying, embedding, sectioning and matrix application.
Sample stability and handling strongly benefits from embedding the freeze-dried sediment in a gelatine-based mixture. This approach also enables sectioning of the sample into sub-mm slices. Slices of different thickness were analysed with µXRF and (MA)LDI FTICR-MS to evaluate the influence of this parameter on both methods. The MALDI-based proxy data (Crenarchaeol-Caldarchaeol Tetraether index; CCaT) showed very consistent results throughout the different section thicknesses (Fig. 1 C). Only in terms of signal intensity, thinner sections appear to be beneficial (Fig. 1B). As µXRF results are more reliable for thicker sections (Fig. 1A), 100 µm thick slices seem to be best for obtaining congruent elemental and biomarker imaging data of high quality. Moreover, we systematically examined the effect of different chemical matrices applied prior to MALDI analysis; these results will be presented as part of our recommendation for an optimal MALDI protocol for the analysis of sedimentary GDGTs.

Conclusions

This study provides an optimized sample preparation pipeline for combined elemental and archaeal biomarker imaging in marine sediments.

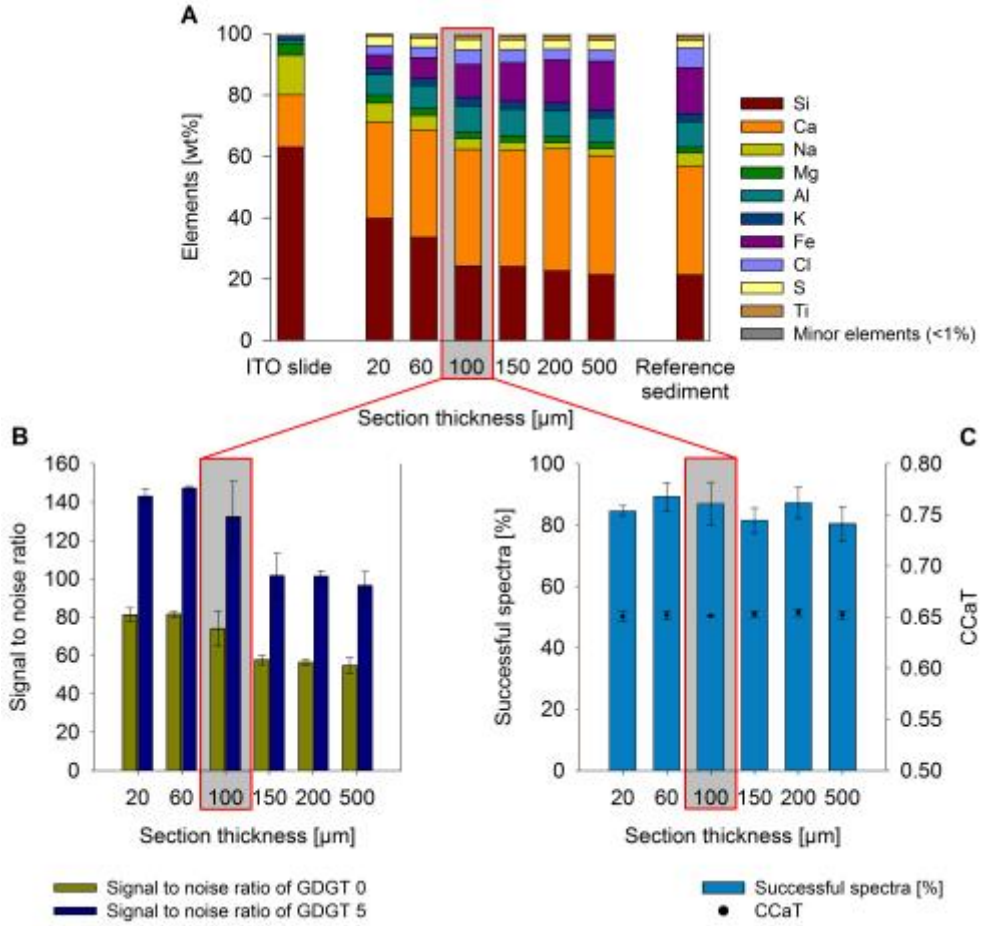

Figure 1*: Influence of section thickness on µXRF (A) and MALDI FTICR-MS (B, C). The grey boxes indicate the best section thickness for a combined molecular and elemental imaging analysis. The indium tin oxide (ITO) coated glass slide in A is the background signal of the sample holder. Successful spectra (C) are defined as spectra in which GDGT 0 and 5 are detected with a signal to noise ratio of ≥ 8. About 900 spectra per section were generated by (MA)LDI FTICR-MS. Samples were prepared and analysed in triplicate. The presented results are averaged values of triplicates with corresponding standard deviations.*

References

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