READING THE FINE PRINT: LASER-BASED DETECTION OF LIPID BIOMARKERS IN SEDIMENTS ON A MICROMETER SCALE

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In 2014 we demonstrated the feasibility of analyzing diagnostic lipid biomarkers in µm-scale sized spots directly on undisturbed sediments, without prior extraction (Wörmer et al., 2014). This study reconstructed high-frequency variations of sea surface temperature (SST) during Mediterranean sapropel formation using the CCaT ratio of the two major archaeal GDGTs, caldarchaeol and crenarchaeol. Analyte ionization and detection involves laser desorption ionization coupled to Fourier transform - ion cyclotron resonance - mass spectrometry (LDI FT-ICR-MS), with laser spot sizes being 200 µm in diameter or smaller, which in Late Quaternary sediments corresponds to temporal resolutions on the order of months to a few years, depending on the depositional setting. Stimulated by this initial finding and the prospects of advancing molecular stratigraphy to a new level, we have initiated a new project with a dedicated LDI FT-ICR-MS instrument. Our technical goal is to develop necessary protocols and expertise to fully establish LDI-based analysis as a powerful means to obtain precise and accurate measurements of a wide range of informative biomarker compounds. Scientifically, one of our major goals is to interrogate suitable archives, primarily laminated and dated sediment cores, to constrain the interrelationship between physical forcings such as SST and aquatic ecosystem properties with roughly annual resolution in settings sensitive to short-term climatic variations such as the El Niño Southern Oscillation.

On our way to advance this technology to the routine level, the following priorities govern our current efforts: (1) We developed suitable protocols for preparing intact sediment segments for analysis while maintaining the spatial integrity of the sample. This step involves embedding with stabilizing agents, cutting samples into thin slices and drying, and pretreatment with chemical additives to enable or maximize detection, with the latter step involving matrix assisted LDI (MALDI) (Alfken et al., this volume); (2) We conducted experiments to obtain a systematic understanding of how organic and inorganic sedimentary matrix components influence the analytical performance during instrumental analysis and to define the ideal instrumental settings that accounts for these factors (Wang et al., this volume); and (3) We have started to widen the analytical window of compounds accessible through MALDI analysis beyond GDGTs (Table 1). We aim primarily at ratios of chemically similar compounds rather than absolute abundances of individual compounds because the latter are prone to be influenced by changing sediment compositions.

Interestingly, we have been able to not only detect functionalized compounds. Using a silver-based matrix, we obtain good response of *n*-alkanes, providing access to meaningful proxy ratios such as average chain length distributions, which may inform us about short-term variations in continental vegetation. Similarly, polyaromatic hydrocarbons (PAHs) yield excellent signals using the 2,5-dihydroxybenzoic acid (DHB), α-cyano-4-hydroxycinnamic acid (HCCA) and graphite matrices and could be valuable tracers for studying records of natural and anthropogenic combustion at high temporal resolution. Long-chain alkenones, amenable with a graphite-based matrix, will be highly useful for SST reconstruction and complement information obtained by parallel analysis of GDGTs. While not necessarily

highly specific, sterol distributions are useful integrators of the bulk plankton community and changes in their relative distribution, which can be captured by appropriate molecular ratios, could inform us on ecosystem responses to environmental perturbations; the information encoded in sterols can be accessed through application of a graphite or silver-based matrix. Compounds such as bacteriohopanepolyols (BHP), carotenoids, phospholipids and specific pigments (e.g., the chlorophyll derivative pheophytin) will be highly useful for biogeochemical studies, e.g., of redox interfaces in sedimentary setting or in microbial mat systems, where we expect sharp successions of different functional microbial groups and using the appropriate matrix application, we can achieve excellent detection of these various compounds. This presentation will give an overview about the latest developments in this exciting initiative and showcase the first applications to sedimentary samples.

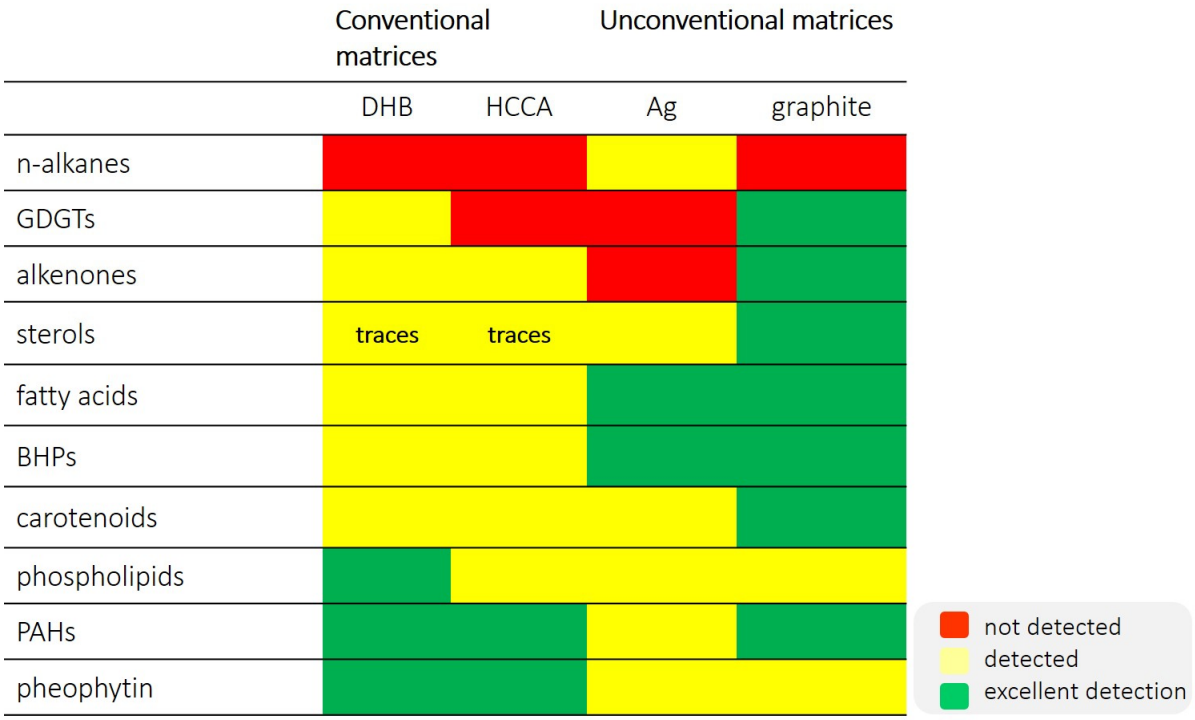

Table 1. *Overview of the detectability of various biomarker compound classes using different matrices for MALDI FT-ICR-MS detection; distinguished are three qualitative levels of detection, depending on the response signal per mass unit compound. Experiments have been performed on reusable MALDI ground steel targets.*

References

Alfken, S., Wörmer, L., Wendt, J., Lipp, J.S., Taubner, H., Wang, J.-X., Elvert, M., Heuer, V.B., Hinrichs, K.-U., 2017. Mass spectrometry imaging of sediments – a sample preparation pipeline for laser-based analysis of archaeal lipid biomarkers. International Meeting on Organic Geochemistry, Abstract Volume.

Wang, J.-X., Wörmer, L., Wu, T., Lipp, J.S., Alfken, S., Wendt, J., Taubner, H., Elvert, M., Heuer, V.B., Hinrichs, K.-U., 2017. Disentangling the effects of sedimentary components on laser desorption ionization of lipid biomarkers. International Meeting on Organic Geochemistry, Abstract Volume.

Wörmer, L., Elvert, M., Fuchser, J., Lipp, J.S., Buttigieg, P.L., Zabel, M., Hinrichs, K.-U., 2014. Ultra-high-resolution paleoenvironmental records via direct laser-based analysis of lipid biomarkers in sediment core samples. Proceedings of the National Academy of Sciences 111, 15669–15674.