

DISENTANGLING THE EFFECTS OF SEDIMENTARY COMPONENTS ON LASER DESORPTION IONIZATION OF LIPID BIOMARKERS

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Mass spectrometry imaging, the spatially resolved detection of relevant analytes on undisturbed sample surfaces, has profoundly influenced several research fields, and, when applied to geological samples, has the potential to fundamentally advance our insights into (bio)geochemical and paleoceanographic processes. The initial application of Laser Desorption Ionization coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (LDI FTICR-MS) to geological samples investigated archaeal tetraether lipids in sediment cores at an ultrafine spatial resolution (Wörmer et al., 2014). In this study, the Crenarchaeol-Caldarchaeol tetraether index (CCaT), a sea surface temperature proxy based on a ratio of ubiquitously distributed archaeal membrane lipids, was proposed as an indicator to successfully reveal environmental variability at nearly annual resolution. In contrast to the conventional gas or liquid chromatography-based lipid analysis, the laser-based protocol enables detection of lipid biomarker directly on a flat surface of the sediment core, which means that ionization processes occur on a real sediment surface rather than in (vaporized) sediment extracts. However, our knowledge of potential impact of factors from laser-related parameters and sedimentary components on the measurement of lipid biomarkers is still at its infancy. Thus, this study aimed to constrain the influence of parameters such as interactions with various minerals with and without organic matter coating and salt content on the laser-based lipid detection and test its application for the determination of lipid-derived proxies in natural environments.

The evaluation of these parameters is achieved by a two-pronged approach that includes a series of laboratory-based experiments with pure compounds, and the evaluation of environmental samples. To better understand the impact of mineral matrices, a GDGT-rich total lipid extract with or without added NaCl was homogeneously sprayed onto the flat surfaces of ten different pure minerals and an aluminum plate as reference. Variation of laser power in the range of 10% - 100% was examined systematically to examine the responses of GDGTs and the derived CCaT values to different minerals. Additionally, in order to simulate minerals in their natural sedimentary context, we evaluated the impact of organic matter coatings on lipid ionization.

The results demonstrate the benefits of salt addition as ionization agent, as well as a selective response of different mineral surfaces to the laser power gradient (Figure 1), especially in the case of the Fe-bearing minerals goethite and pyrite. Interestingly, none of the minerals exhibit analyte ionization in the laser power range used for natural sediment samples, suggesting that the effects of mineral components may be masked by the predominant effect of the organic matrix naturally present in the system. This hypothesis is further validated by the addition of natural organic matter to the experimental setup and by the investigation of environmental samples, which reveal the importance of analyte concentration and total organic carbon content on the ionization of archaeal GDGTs. Ultimately, our results offer a case study in combining sedimentary component and laser-based ionization to improve our tools for the interpretation of the geological record.

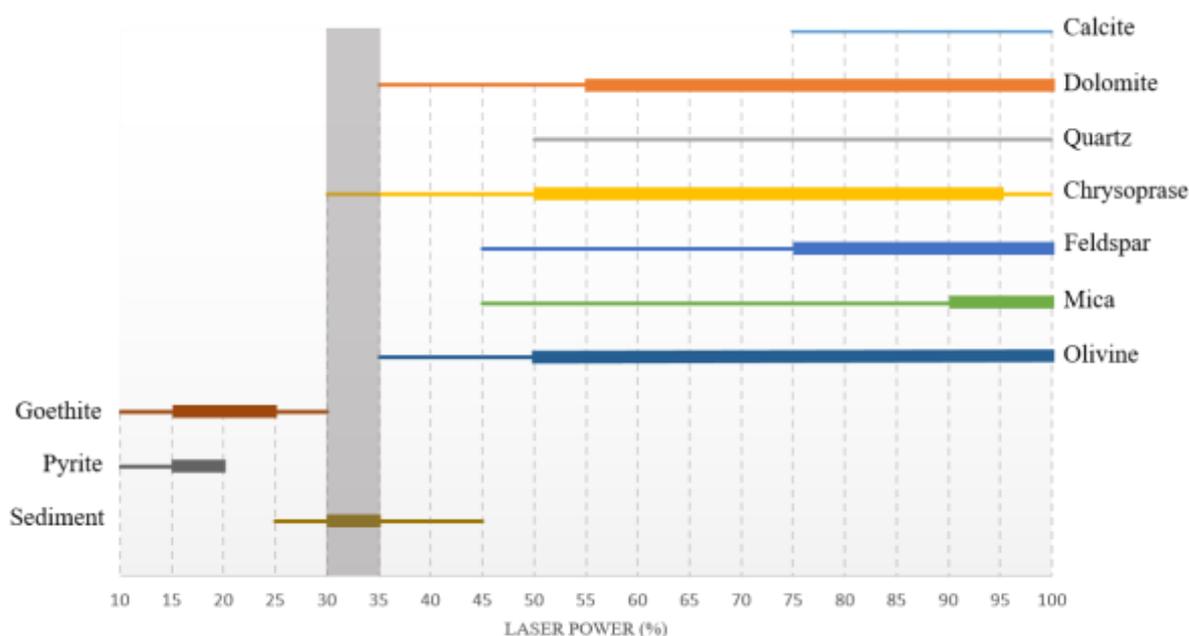


Figure 1 The laser power range of different minerals and typical sediment samples. The thicker line indicates the optimum range of laser energy, in which the valid scans can reach to more than 90%, and in the case of sediments, the best match is observed between LDI- and APCI-MS-based CCaT values. The darker grey bar with laser power ranging 30 – 35% indicates a typical laser power range for lipid ionization at sediment surface.

Reference

Wörmer, L., Elvert, M., Fuchser, J., Lipp, J.S., Buttigieg, P.L., Zabel, M., and 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 of the United States of America* 111, 15669–15674.