Untargeted µm-scale imaging of sedimentary climate archives: A fresh look at existing data

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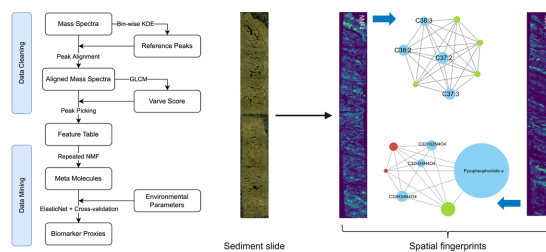
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Figure 1 left: the untargeted workflow for sedimentary MSI datasets; right: examples of spatially co-occurring molecular clusters with associated spatial fingerprints; GLCM=grey-level co-occurrence matrix; NMF=non-negative matrix factorization

Recently, we increased the resolution of molecular proxy records to the µm-scale by mass spectrometry imaging (MSI) of sedimentary archives. In annually varved sediment of the Santa Barbara Basin (SBB), such fine resolution allows deciphering sub-annual distributions of archaeal tetraether lipids, haptophyte-derived alkenones, and sterols, which are sensitive to changes in upwelling intensity, sea surface temperature, water column redox conditions [1,2]. Herein, we report a non-targeted data mining workflow (Figure 1, left) for dissecting the MSI datasets and extract information beyond conventional molecular proxies, enabling us to discover unique molecular fingerprints, which can be linked to environmental parameters.

We applied the proposed workflow to two datasets obtained by MSI of the upper ~10 cm of SBB box core SPR0901-05BC. The two datasets consist of 18625 and 18963 data points and cover a mass window of 520 – 580 Da and 375 – 525 Da, respectively. Using bin-wise kernel density estimation (KDE) and grey level co-occurrence matrix, a total of 1242 peaks were picked whose mass-to-charge ratios (m/z) were accurately assigned (<2 ppm for the theoretical m/z of some known compounds). Subsequent consensus clustering based on spatial co-occurrence revealed 23 molecular clusters with distinct spatial fingerprints (e.g., Figure 1, right), most of which likely belong to similar chemical taxonomies. With regularized linear regression and cross-validation, molecular clusters that spatially co-occur can be correlated to environmental data. We successfully validated the approach between the alkenone cluster and sea surface temperature data from the nearby hydrographic data station from the California Cooperative Oceanic Fisheries Investigations. Using the same approach, one molecular cluster with steroid-like chemical formulas is found to be closely related to bottom water redox conditions in the SBB between 1984 – 2008.

In conclusion, the untargeted workflow further expands our knowledge about the sedimentary MSI datasets, and it holds great potential for discovering novel, biogeochemically relevant biomarkers.

[1] Alfken et al. *Paleoceanogr. Paleoclimatol.* 2020, *35* (10), e2020PA004076.

[2] Alfken et al. *Paleoceanogr. Paleoclimatol.* 2021, *36* (12), e2021PA004354.