

## Indigenous Organic Molecular Biosignatures are Detectable via ToF-SIMS of a Kerogen-rich Jurassic Clay

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**Introduction:** Organic molecular biosignatures (OMBs) detected within Mars Sample Return (MSR) samples could provide strong evidence for the existence of extraterrestrial life (Neveu et al., 2018). The utility of any OMB depends on its character, which can be: i) indigenous or syngenetic; ii) non-indigenous or incorporated during sub-surface fluid migration; or iii) contaminant. One way to determine the OMB character is to determine its spatial distribution within a host rock (Brock, 2011; Medina Ferrer et al., 2018). Traditional lipid analysis (sample crushing, solvent extraction) obscures the spatial relationship between OMBs and the host rock leading to potential ambiguities about the character of extracted lipids. Mass Spectrometry (MS) imaging used in conjunction with traditional organic geochemical analysis has been shown to be effective at determining the spatial distribution of OMBs (Thiel and Sjövall, 2011).

In natural samples, previous Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) MS imaging studies have detected indigenous OMBs in modern sediments (e.g., Thiel et al., 2007; Siljeström et al., 2017) as well as non-indigenous OMBs in ancient sediments (e.g., Sjövall et al., 2008; Siljeström et al., 2010). To date, the only detected ancient indigenous OMBs have been fatty acids within an ancient whale bone (Thiel et al., 2014). Here, ancient indigenous sterane molecular ions and fragments ions of isorenieratene derivatives (all excellent OMBs) were detected for the first time using ToF-SIMS within a kerogen-rich sample, the 164 million-year-old Oxford clay.

**Methods:** We collected data via gas chromatography – mass spectrometry (GC-MS), ToF-SIMS, secondary electron microscopy – energy dispersive X-ray spectroscopy (SEM – EDS), and traditional micrographic imaging. The data derived from these analyses were compared using statistical packages within the data analysis platforms R and Python.

**Results:** Steranes are detectable in ToF-SIMS spectra by the presence of their typical molecular ions. The sterane molecular ions reflect a subset of the complex sterane mixture that dominates the saturated/unsaturated hydrocarbons of the extractable

fraction observed via GC-MS. ToF-SIMS spectra and MS images indicate that steranes are heterogeneously distributed within the sample at the scale of 10's to 100's of  $\mu\text{m}$ . Additionally, typical fragment ions of isorenieratene derivatives including  $m/z$  133 and  $m/z$  237, were above noise level within ToF-SIMS spectra from the regions with observable sterane ions. Isorenieratene derivatives are the dominant constituents of the extracted aromatic fraction observed via GC-MS. SEM-EDS analysis indicates that the regions containing OMBs are high in organic carbon, likely reflecting the previously observed sulfur-rich kerogen (Kenig et al., 1994). The restricted spatial distribution of the OMBs to regions containing kerogen indicates that they are indigenous to the sample.

**Conclusions:** Indigenous OMBs are detectable via ToF-SIMS in ancient, kerogen-rich samples. The presence of an OMB molecular ion strengthens the interpretation of ToF-SIMS spectra of complex natural material. Finally, the spatial co-occurrence of kerogen and potential indigenous OMBs in ancient sediments is a valid test of their character. These conclusions are directly relevant to MSR sample selection as well as the analysis of MSR samples upon return.

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