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Microscale molecular characterization of ancient microbial mats

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The biogenicity and/or the biological precursors of organic matter (OM) in Precambian rocks are difficult to constrain due to alteration, migration, and contamination processes. The composition of kerogen (insoluble macromolecular organic matter, assumed to be syngenetic with the host rock) is generally analyzed in bulk rocks [1], which cannot elucidate the composition of texturally, structurally and isotopically heterogenous organic microstructures [2]. Here, we present mass spectra and molecular imaging of semi-thin sections of sedimentary rocks using Time of Flight Secondary Ion Mass Spectroscopy with a Bi_3^+ probe a few µm in diameter. Soluble molecules were extracted from superficial OM with organic solvents. Airborne nano-deposits were removed with ion sputtering. Two samples were analyzed. First, thermally immature-OM-rich laminae of Kimmeridgian stromatolites (French Jura Mountains, Orbagnoux village [3]) show a dominance of aliphatic hydrocarbons over aromatic hydrocarbons at low mass, consistent with high bulk-rock H/C of the kerogen [3]. We imaged the distribution of C-S bonds (e.g., C_2S^-) and thiophene ($C_4H_4S^-$) formed during diagenetic OM sulfurization. Second, laminated OM-rich grains in a quartzite from the 3.4 Ga Strelley Pool Fm (Western Australia) show higher contents of aromatic compounds compared to Orbagnoux carbonaceous material, which is consistent with higher maturity. Moreover, aromatic isomers of relatively high mass (up to m/z=252) that were detected and imaged in some organic laminae of the Strelley Pool Fm are consistent with bulk kerogen compositions [2]. Overall, these results unveil great potential for microscale characterization of kerogen composition, and for distinguishing pristine, indigenous, organic compounds from contaminants.

[1] Marshall et al. (2007) *Precambrian Res.* **155** 1–2. [2] Lepot et al. (2013) *Geochim. Cosmochim. Acta* **112** 66–86. [3] Sarret et al. (2002) *Org. Geochem.* **33** 877-895.