

TOF-SIMS AND GC-MS ANALYSES OF MICROBIAL MATS FROM ASTROBIOLOGICALLY RELEVANT SETTINGS IN YELLOWSTONE NATIONAL PARK, USA. S. Siljeström¹, M. N. Parenteau², L. L. Jahnke² and S. L. Cady³, ¹Chemistry, Materials and Surface, SP Technical Research Institute, Drottning Kristinas väg 45, 114 28 Stockholm, Sweden (sandra.siljestrom@sp.se), ²Exobiology Branch, NASA Ames Research Center, Moffett Field, CA 94035, USA, ³Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99354, USA.

Introduction: One of that few techniques that is able to spatially resolve chemical data, including organic molecules, to morphological features in modern and ancient geological samples is time-of-flight secondary ion mass spectrometry (ToF-SIMS). This ability is key in interpreting the biogenicity of preserved remains in ancient samples. In particular, ToF-SIMS has been used in recent studies of both macro- and microfossils.

ToF-SIMS is surface sensitive mass spectrometric technique that analyses the top monolayers of a sample by bombarding the surface with energetic primary ions. The primary ions sputter positive and negative ions that are separated and analysed in a time-of-flight mass spectrometer. In addition to positive and negative mass spectra, ion images (chemical maps) of the sample surface are obtained as the ion beam is rastered over it.

However, due to the lack of reference data for geologically relevant samples and the ease with which samples can be contaminated, ToF-SIMS data may be difficult to interpret. In this project, we aim to build a ToF-SIMS spectral database for analysis of microbial communities from relevant astrobiological hydrothermal settings. This is done by performing parallel ToF-SIMS and gas chromatography-mass spectrometry (GC-MS) analyses of modern microbial mats that are actively being fossilized in different hot springs in Yellowstone National Park, USA. The microbial mats were collected in range of different hot spring settings including alkaline silica-depositing springs, acidic clays, and iron-depositing springs. We are building the library by analyzing samples of increasing complexity: pure lipid standards, solvent extracts of specific lipid fractions, total lipid extracts, pure cultures of dominant microbial members, and modern and increasing fossilized microbial mats.

Results: The results from the modern non-silified phototropic streamers from alkaline silica-depositing springs showed that important lipids and pigments originating from phototrophs found in the streamers could be detected by ToF-SIMS (e.g., wax esters, monogalactosyldiacylglycerol, digalactosyldiacylglycerol, sulfoquinovosyldiacylglycerol, chlorophyll *a*, bacteriochlorophyll *a* and *c*, alkanes, and β -carotene). Some of these lipids could also be spatially resolved to specific cell morphotypes within the streamer community

[1]. Similar results were seen for the modern microbial mat collected from the iron-depositing spring. This mat had a similar microbial community composition as the streamer the from silica-depositing spring.

Preliminary analyses of partly fossilized remains obtained from the three different hot spring settings indicated some organic signal remains and could be detected by ToF-SIMS.

Conclusion and outlook: The results show that ToF-SIMS is able to detect range of organic signals from microbial mats and their fossilized remains collected from hydrothermal settings.

The ability of ToF-SIMS to map organic signals to morphological structures, together with the developed spectral database, will be used to explore other microbial mats and their fossilized counterparts in ancient samples on Earth. This flight-relevant instrumentation is also relevant to characterizing organics on Mars *in situ* and on returned samples. ToF-SIMS offers significant advantages in determining the biogenicity of microbial samples over traditional extraction and analysis via GC-MS.

References: [1] Siljeström, S. et al. (2017), Organic Geochemistry, submitted.