

MAPPING AND DEPTH PROFILING OF ORGANIC COMPOUNDS IN GEOLOGIC MATERIAL AT THE MICRON SCALE: FEMTOSECOND - LASER DESORPTION POSTIONIZATION - MASS SPECTROMETRY (fs-LDPI-MS) M. J. Pasterski¹, G. Barry², L. Hanley², F. Kenig¹. ¹University of Illinois at Chicago (Department of Earth and Environmental Sciences MC 186, 845 W Taylor Street, Chicago, Illinois, 60607-7059, email: Mpaste3@uic.edu), ²University of Illinois at Chicago (Department of Chemistry MC 111, 845 W Taylor Street, Chicago, Illinois, 60607-7059).

Introduction: One of the major challenges within the field of organic geochemistry is to determine whether an observed biomarker signature was emplaced during sedimentation (indigenous), after sedimentation via the post-depositional migration of fluids (non-indigenous), or during sampling, storage, or analysis (contaminant). Current geochemical techniques (e.g. gas chromatography-mass spectrometry, GC-MS and GCxGC-MS) can effectively determine the composition and structure of the organic constituents of a sample. However, because of the multiple preparatory steps necessary prior to GC-MS analysis (sample crushing, solvent extraction, organic fraction separation), it is impossible to determine the spatial distribution of organic molecules within rocks or sediments.

To determine the spatial distribution of organic compounds within rocks and sediments, we have used an MS imaging method, femtosecond-laser desorption post ionization-MS (fs-LDPI-MS), to map organic compounds in geologic material.

Background on fs-LDPI-MS: fs-LDPI-MS has the ability to map organic compounds across the surface of samples by desorbing the surface material using 75 fs, 800 nm laser pulses [1]. The ultra-short laser pulses leave the undesorbed material directly beneath the desorbed portion of the sample intact; therefore, it is possible to perform multiple analyses in the same location on a sample to create a micron-scale depth profile of organic compounds [2]. After desorption, the desorbed material is ionized using a 10.5 eV vacuum ultraviolet (VUV) laser; the low ionization energy imparted by the VUV laser causes minimal to no molecular fragmentation [1], [2]. After ionization, the ions are detected using a time-of-flight (TOF)-MS.

Samples: The target samples were collected from: (1) an Antarctic igneous dike which was baked at 500°C prior to analysis to be used as a sample blank; (2) a ~93 million year-old (Ma) burrowed carbonate collected near Pueblo, CO; (3) ~164 Ma organic rich (75 to 95% marine organic carbon) mudstone collected in Southwestern England; and (4) a 2.7 billion year-old (Ga) argillaceous metasediment crosscut by post depositional Archean and Paleoproterozoic hydrothermal veins collected near Timmins, ON, Canada.

Approach: Prior to this study, all geologic samples had been extracted and analyzed by GC-MS to deter-

mine the lipid biomarker composition of each sample. Corresponding thick and thin sections were prepared for each sample, and petrographic maps were drawn for each thick section. The petrographic maps display, among many other features, mineral species, organic carbon, hydrothermal veins including fluid inclusions, and trace fossils (burrows). The thick sections were prepared in house using clean cutting (all retrofitted baked parts and tested distilled water) and clean grinding techniques (*ibid.*). All possible sources of contamination were monitored throughout sample preparation.

Fs-LDPI-MS analysis was performed on the mapped thick sections. Immediately before fs-LDPI-MS analysis, the surface of each thick section was cleaned using a CO₂ snow-jet cleaner. Surface cleaning was performed to remove laboratory atmospheric contaminants which may have accumulated on the surface of the sample during petrographic study.

After fs-LDPI-MS analysis, MS-maps were created in the open source software BioMap. Overlays of the MS-maps and the petrographic maps were created to determine the location of targeted organic compounds relative to host rock features including minerals, burrows, or post-depositional hydrothermal features (veins, minerals, fluid inclusions).

Conclusions: Fs-LDPI-MS is an effective method to map organic carbon across the surface and with depth of geologic samples. Fs-LDPI-MS analysis of geologic samples will be a valuable tool to determine the spatial distribution of organic compounds within rocks and sediments. The distribution of the organic compounds within a rock can be used to unambiguously relate the organic compounds to minerals, periods of deposition, post-depositional migration of sub-surface fluids, or sample collection, preparation, and analysis. Fs-LDPI-MS analysis will be extremely useful to determine the origin of organic compounds (i.e. indigenous, non-indigenous, contaminant) observed in ancient sediments and upon Mars sample return.

References: [1] Milasinovic S., Liu Y., Bhardwaj C. T., M. T. M. B., Gordon R. J., and Hanley L. (2012) *Anal. Chem.*, 84, 3945-3951. [2] Cui Y., Bhardwaj C., Milasinovic S., Carlson R. P., Gordon R. J., and Hanley L. (2013) *ACS Applied Materials and Interfaces*, 5, 9269-9275.