Using ToF-SIMS to study biomarkers

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Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a technique designed to analyze the composition and lateral distribution of molecules and chemical structures on surfaces. A beam of high-energy ions (primary ions) bombards the sample surface, resulting in the emission of secondary ions from the outermost molecular layers of the sample. Analysis of these ions with respect to mass yields a mass spectrum which contains chemical information about the sample surface. During the measurement, the primary ion beam is scanned over a selected analysis area and individual mass spectra are recorded from each raster point within this area. The acquired data can then be used to produce (i) ion images, which show the signal intensity of selected secondary ions across the analysis area, and (ii) mass spectra from selected regions of interest on the sample surface.

These capabilities have generated much interest in the use of ToF-SIMS for the characterization of lipids and other organic biomolecules at the microscopic (μm-) level (see [1] and [2] for reviews). Here we introduce static ToF-SIMS imaging mass spectrometry as a tool for organic geochemical analyses. After describing the ToF-SIMS analysis principles, experiments on selected sample types relevant in geobiology and organic geochemistry are reported, namely soft (microbial cell matter, sediments), hard (microbialites), and liquid (fluid inclusions) samples. This presentation aims to put the potential of ToF-SIMS for organic biomarker approaches up for discussion, considering not only the strengths, but also current drawbacks and limitations for which further development would be beneficial for the field.

[1] Winograd & Garrison (2010) *Annual Review of Physical Chemistry* **61**, 305–22. [2] Thiel & Sjövall (2011) *Annual Review of Earth & Planetary Sciences* **39**, 125–156.

Raison d’être of X-ray spectromicroscopy for geochemistry

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X-ray microscopy in the sub-keV X-ray energy range uncovers structures down to 10 nm size, at higher X-ray energies structure sizes down to 30 nm can be imaged. The technique is capable of imaging specimens directly in aqueous media. X-ray microscopy images can be used for tomographic reconstructions of thick samples. By choosing the used X-ray energy appropriately, it is possible to perform spectro-microscopy studies. X-ray fluorescence can be used as a highly sensitive method to identify trace elements. Comprising, the combination of microscopy and spectroscopy is a powerful tool for addressing key questions in many scientific areas, e.g. to study structures in the environment showing dimensions on the nanoscale. Applications to scientific issues in geochemistry, geomicrobiology, and in soil and environmental sciences will be used to show the significance of this tool for science. X-ray images show the appearance of structures on the nano- and microscale. X-ray tomography conveyed morphological changes of humic substances due to biologically induced redox changes. Using the spectromicroscopy potential, the distribution of organic and inorganic components in such samples has been studied. NEXAFS spectra have been analyzed for major chemical constituents. This reveals e.g. the influence of extraction methods on the properties of humic sub-stances. Spectromicroscopy allows the study of carbon nanotubes and their influence on the environment. X-ray fluorescence spectromicroscopy studies of the spatial distribution, the chemical state of sulfur and its co-localization with iron in soils were performed. X-ray spectroscopy and spectromicroscopy has been used to study the release of sulfur from war debris from World War II into urban soils, an issue of rising importance.