

## ToF-SIMS imaging mass spectrometry of microbial systems

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Over the last years, imaging mass spectrometry has been emerging as a promising tool for the chemical analysis of biomaterials. Among a number of powerful spectral imaging methods, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is recently attracting the attention of the geobiological community, due to its potential to obtain elemental and molecular information at a sub- $\mu\text{m}$  lateral resolution, i.e. well within the range of microbial systems.

In ToF-SIMS, primary ions are applied to the sample surface in short pulses. The impact of these projectiles causes the emission of secondary ions characteristic for the composition of the surface analyzed. The secondary ions are accelerated into a time-of-flight mass spectrometer to give a high-resolution mass spectrum of the analysed spot. By scanning of the primary ion beam over the sample surface and recording the intensity of each detected secondary ion species, each rastered pixel can be displayed in an 'ion image', e.g. according to a colorscale. Thereby, information on the distribution of elemental as well as organic and inorganic chemical components can be obtained in a single measurement.

This talk gives an introduction into the principles, capabilities and limitations of ToF-SIMS imaging of biomaterials, with particular emphasis placed on the analysis of substances and samples of interest in biogeochemistry and geobiology. Examples introduced here encompass (i) imaging of complex lipid biomarkers in microscopic sections of microbial mats, (ii) organic and inorganic mapping of fossil biofilms along fracture fillings within deep granitic rocks, and (iii) detection of sterane and hopane hydrocarbon biomarkers in minute amounts of crude oils. Considering not only the strengths, but also current analytical drawbacks and limitations inherent to the method, an outlook is given on the potential of ToF-SIMS imaging mass spectrometry for interdisciplinary molecular approaches in the future.

## Mass independent isotopic fractionations: Discovery and recent applications in nature: Earth and the early Solar System

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A motivation for the experiments of Thiemens and Heidenreich [1, 2] was to test the basic assumption that the only mechanism by which meteoritic mass independent isotopic compositions could be produced was via a nuclear process. That work [1] has led to new theories and experiments in basic chemical physics and was the first to suggest that meteoritic oxygen and nitrogen isotopic compositions were the result of photochemical isotopic self shielding, now recently rediscovered. As in the case of the nuclear model, self shielding has several, crucial assumptions. 1) in the nebular dissociation process, the only fractionation derives from the optical filtration of photons by carbon monoxide. 2) Once the filtered light is absorbed, it leads to an immediate dissociation (quantum yield of one). These crucial assumptions have now experimentally been shown to be wrong [3]. The experimental test was formidable because: 1) the only short UV source of sufficient photon fluence is synchrotron radiation and 2) at relevant wavelengths all windows are opaque and experiments must be done in a window free mode. In [3], these obstacles were overcome and self shielding was probed directly. The crucial parameters; shielding depth, wavelength (specific quantum states), and temperature were tested. The beam profile of the radiation is also directly measured to quantify the states. It is directly shown that 1) the quantum yield is far different from unity, 2) there is a thousands of per mil fractionation associated with the process of dissociation itself, which has *nothing* to do with self shielding as it also occurs at wavelengths where shielding is not possible. Further, the fractionation pattern does not produce the equal  $^{17}\text{O}$ ,  $^{18}\text{O}$  composition required for shielding and therefore there is no experimental support for self shielding models.

The mass independent fractionation process has also been observed to occur in nature; in the Earth's atmosphere (pre Cambrian to present), Mars, and tests a multitude of geochemical processes [2] which will be discussed.

[1] Thiemens & Heidenreich III (1983) *Science* **219**, 1073-1075. [2] Thiemens (2006) *Ann. Rev. Earth Planet. Sci.* **34**, 217-262. [3] Chakraborty *et al.* (2008) *Science* **321**, 1328-1331.