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Multiscale analysis of Jurassic rocks with sulfur-rich organic matter using laser desorption/ionization mass spectrometry

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The Mars organic molecular analyzer (MOMA) of the Rosalind Franklin rover (ExoMars project) will combine laser desorption-ionization mass spectrometry (LDI-MS) and gas-chromatography mass spectrometry (GC-MS) to assess the origin of organic matter on planet Mars. In order to further assess the type of molecular information that can be retrieved with the former technique, we applied high-resolution laser two-step mass spectrometry (L2MS) to fossil organic matter of sedimentary rock from the Jurassic deposit of Orbagnoux, France. Abundant sulfur-rich microbial organic matter has been thoroughly documented in this deposit [1]. This sample has been chosen following the detection of thiophenes at Gale Crater on Mars by the Sample analysis at Mars (SAM) instrument [2]. In our L2MS instrument [3], the samples are irradiated with a pulsed desorption laser (532 or 266 nm), which generates a plume of chemical species that can be further ionized with a second orthogonal laser beam (266 nm). A radiofrequency ion guide is used to carry the ions to an orthogonal time-of-flight mass spectrometer (oToF-MS system by Fasmatech), yielding high-resolution mass spectra (m/Δm ~10000 at 128 m/z). Focusing of the desorption laser using a reflective objective and automated micro-positioning of the sample were used to generate hyperspectral raster mappings. Subsamples included solvent-extracted molecules (bitumen and maltene fractions), insoluble macromolecular organic matter (kerogen), rock powder and a polished slice. Our analyses showed that we can extract chemical information with LDI-MS from both soluble and insoluble organic fractions of the Orbagnoux samples and that various chemical families can be distinguished even in mineralized samples. Carbon clusters, including sulfurated and hydrogenated species could be detected in all subsamples. With the exception of the rock slice, polyaromatic hydrocarbons could be detected in all samples. Oxygenated molecules and alkylbenzenes could only be detected in extracts, which generated rich and intense mass spectra. Various inorganic ions were also generated in all sample fractions. Using focused desorption beams, carbon clusters (including sulfurated clusters) and inorganic species could be detected and mapped in the polished slice with <50 µm lateral resolution. L2MS thus shows great promise for fast screening of organic/inorganic species on Mars, and for microanalyses applied to paleontological questions.

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