



Chemical analyses of micrometre-sized solids by a miniature laser ablation/ionisation mass spectrometer (LMS)

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Investigation of elemental and isotope compositions of planetary solids with high spatial resolution are of considerable interest to current space research. Planetary materials are typically highly heterogeneous and such studies can deliver detailed chemical information of individual sample components with the sizes down to a few micrometres. The results of such investigations can yield mineralogical surface context including mineralogy of individual grains or the elemental composition of other objects embedded in the sample surface such as micro-sized fossils. The identification of bio-relevant material can follow by the detection of bio-relevant elements and their isotope fractionation effects [1, 2].

For chemical analysis of heterogeneous solid surfaces we have combined a miniature laser ablation mass spectrometer (LMS) (mass resolution (m/Dm) 400-600; dynamic range 10^5 - 10^8) with in situ microscope-camera system (spatial resolution $\sim 2\mu\text{m}$, depth 10 μm). The microscope helps to find the micrometre-sized solids across the surface sample for the direct mass spectrometric analysis by the LMS instrument. The LMS instrument combines an fs-laser ion source and a miniature reflectron-type time-of-flight mass spectrometer. The mass spectrometric analysis of the selected on the sample surface objects followed after ablation, atomisation and ionisation of the sample by a focussed laser radiation (775 nm, 180 fs, 1 kHz; the spot size of $\sim 20\mu\text{m}$) [4, 5, 6]. Mass spectra of almost all elements (isotopes) present in the investigated location are measured instantaneously.

A number of heterogeneous rock samples containing micrometre-sized fossils and mineralogical grains were investigated with high selectivity and sensitivity. Chemical analyses of filamentous structures observed in carbonate veins (in harzburgite) and amygdales in pillow basalt lava can be well characterised chemically yielding elemental and isotope composition of these objects [7, 8]. The investigation can be prepared with high selectivity since the host composition is typically readily different comparing to that of the analysed objects. In depth chemical analysis (chemical profiling) is found in particularly helpful allowing relatively easy isolation of the chemical composition of the host from the investigated objects [6]. Hence, both the chemical analysis of the environment and microstructures can be derived. Analysis of the isotope compositions can be measured with high level of confidence, nevertheless, presence of cluster of similar masses can make sometimes this analysis difficult. Based on this work, we are confident that similar studies can be conducted in situ planetary surfaces delivering important chemical context and evidences on bio-relevant processes.

[1] Summons et al., *Astrobiology*, 11, 157, 2011. [2] Wurz et al., *Sol. Sys. Res.* 46, 408, 2012. [3] Riedo et al., *J. Anal. Atom. Spectrom.* 28, 1256, 2013. [4] Riedo et al., *J. Mass Spectrom.* 48, 1, 2013. [5] Tulej et al., *Geostand. Geoanal. Res.*, 38, 423, 2014. [6] Grimaudo et al., *Anal. Chem.* 87, 2041, 2015 [7] Tulej et al., *Astrobiology*, 15, 1, 2015. [8] Neubeck et al., *Int. J. Astrobiology*, 15, 133, 2016.