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Detection of bio-signature by microscopy and mass spectrometry

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Abstract

We demonstrate detection of micro-sized fossilized bacteria by means of microscopy and mass spectrometry. The characteristic structures of lifelike forms are visualized with a micrometre spatial resolution and mass spectrometric analyses deliver elemental and isotope composition of host and fossilized materials. Our studies show that high selectivity in isolation of fossilized material from host phase can be achieved while applying a microscope visualization (location), a laser ablation ion source with sufficiently small laser spot size and applying depth profiling method. Our investigations shows that fossilized features can be well isolated from host phase. The mass spectrometric measurements can be conducted with sufficiently high accuracy and precision yielding quantitative elemental and isotope composition of micro-sized objects. The current performance of the instrument allows the measurement of the isotope fractionation in per mill level and yield exclusively definition of the origin of the investigated species by combining optical visualization of investigated samples (morphology and texture), chemical characterization of host and embedded in the host micro-sized structure. Our isotope analyses involved bio-relevant B, C, S, and Ni isotopes which could be measured with sufficiently accuracy to conclude about the nature of the micro-sized objects.

1. Introduction

Searching for the instrumentation and method capable of the detection of life and bio-relevant material on the other planets is important task of current planetology and space research. This involves usually preparation of the instruments capable of analyses with high spatial resolution. Planetary materials are typically highly heterogeneous on the micrometre-level and both material visualisation and possibility to interrogate the small surface area for the chemical analysis are necessary. Chemical information on the surface composition typically can be delivered by optical and mass spectrometric analyses. In both cases optical microscopy is necessary to visualise the surface details. Typically after this inspection the chemical analyses can follow up. We demonstrate that by combining a miniature microscope-camera and a miniature mass spectrometer is possible to deliver multiple information on the origin of the investigated material. The isolation of the material, accuracy and precision of the laser mass spectrometer is sufficiently high to deliver conclusive information on the surrounding host and entrapped inclusion including its possible bio-origin. Our 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 the 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].

2. Experimental

For chemical analysis of heterogeneous solid surfaces we have combined a miniature laser ablation mass spectrometer (LMS) and microscope-camera system. The microscope (spatial resolution ~2um, depth 30 um) yields the optical characterisation of the surface material including morphology and sample texture providing also some insights into mineralogical sample context. It helps to find the micrometre-sized objects such as fossilised structure or mineral grains across the rock surface. Using microscope-camera system one can define accurately the location of the objects of interest for the direct mass spectrometric analysis by the LMS instrument. The LMS instrument combines an fs-laser ablation ion source (775 nm, 180 fs, 1 kHz; the spot size of ~20 um) [4], [5], [6] and a miniature reflectron-type time-of-flight mass spectrometer (mass resolution (m/Δm) 400-600; dynamic range 10^7-10^8).

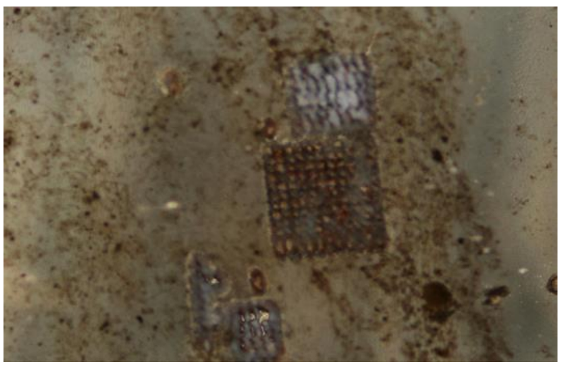

Figure 1: Photograph of a Gunflint sample with microbials phase (small spheres, rods and filaments) embedded in the silica. The microbials structure sizes are less than 10 micrometres in size and their age is determined to be close to 2 billions. The spot-like matrix are laser ablation craters.

Both stepwise surface analysis (chemical mapping of the surface) and depth profiling (layer-by-layer) can provide deep insights into the surface and subsurface mineralogy (as derived from the element correlation analysis).

3. Results and discussion

A number of heterogenous rock samples containing micrometre-sized fossils and mineralogical grains were investigated together with appropriate Standard Research Materials (SRM) for controlling the quantitative performance of the instrument.

Both elemental and isotope analysis of fossilised microbial structures (spheres, rods, filaments) of age from hundred thousand to billions of years embedded in aragonite or silica phases and hosted in rock materials were investigated. Large fraction of the measurements could be conducted with sufficiently high accuracy and precision allowing the analysis of isotope fractionation effects. With combined optical mineralogical, elemental and isotope analysis the assignment of analysed features to fossilised microbials or mineralogical grains could be made conclusively.

The analysis of the micro-sized objects can be conducted with high selectivity; the host composition was typically readily different 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], [7], [8]. 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.

4. Summary and Conclusions

Laser mass spectrometer (LMS) combined with a microscope-camera system can be to be important instrumentation for the investigation of micro-sized microbials. Current studies show that by combining optical visualization, mineralogical, elemental and isotope composition one can conclusively derive nature of the putative fossilized materials.

Acknowledgements

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