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Investigation of micrometre-sized fossils by a laser ablation mass spectrometer designed for in situ space research

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Abstract

Detection of extraterrestrial life is an ongoing goal in space exploration. The detection of signatures of life by means of chemical composition, elemental and isotopic, is one of the most important approaches. There is a need for advanced instruments and methods that can accomplish this task. We present the first investigations of chemical composition measurements of putative microfossils in natural samples using a miniature laser ablation/ionisation time-of-flight mass spectrometer (LMS). The primary aim of the study was investigation of the instrument's capabilities for element composition and isotopic abundance analysis of micro-sized samples.

1. Introduction

Fossilised microorganisms contain morphological, molecular and geochemical signatures concentrated in a defined micrometre-sized structure. Due to the small size of these features, the relevant information are not easy to obtain and to establish biogenicity is not an easy task, not even in terrestrial samples. Therefore, there is an urgent need for the development of new and more sensitive instrumentation capable of *in-situ* detection of molecular and elemental bio-signatures on other planetary bodies.

Endoliths fossils (microorganisms lived in the past in the rock interior) are interesting samples, because they are easily preserved over geological time due to fossilisation in the interior of rocks being embedded in vein- and vesicle filling mineral phases such as quartz or carbonates and naturally protected against destructive surficial processes such as chemical and physical weathering or radiation. In the present study we investigate micrometre-sized filamentous structures embedded in carbonate veins by microscopic imaging and laser ablation mass spectrometry. The chemical analysis of the micro-structures could be determined with high spatial (lateral and vertical) resolution. We discuss the implications of the *in situ* chemical analysis of microbials on planetary surfaces and its importance in the search of past life.

2. Experimental

The sample (1271B 4R1 23-26 cm) used in the current study is delivered from the slow-spreading Mid-Atlantic Ridge (MAR) during ODP Leg 209 and was collected from a depth of 26.9 m below seafloor (mbsf) (Bach et al. 2011). The sample contains aragonite veins hosted in serpentinised harzburgite. The age of the aragonite is > 54,900 years since it is radiocarbon-dead but not more than 1 Ma since that is the approximate time when the basement exhumed.

The mass spectrometric investigation was conducted by a miniature laser ablation/ionisation mass spectrometer (LMS) designed for *in situ* space research [2]. The instrument combines laser ablation/ionisation ion source with a reflectron time-of-flight mass analyser. The details of the technical realisation and principles of operation of LMS are described in previous publications [3], [4], [5]. The mass spectrometric analyses were conducted stepwise every 20 μm covering a surface area of 200 x 200 μm^2 (see Figure 1b, right panel). These studies yield chemical surface mapping. The instrument allows also high resolution chemical depth profiling [6]. In the latter studies the sample can be analysed layer by layer with a depth resolution down to sub-nanometre per laser shot. .

3. Results and Discussion

The measurements were conducted on dark filamentous micrometre-structures at the interface between the aragonite and the harzburgite host rock. The filaments have a uniform diameter of about 2 to 5 µm and range in length from about 20 µm to more than 100 µm (Figure 1). The filaments are anchored to the aragonite vein of size 5–10 mm at the walls of the host rock or occur closely associated with the vein walls embedded in the aragonite.

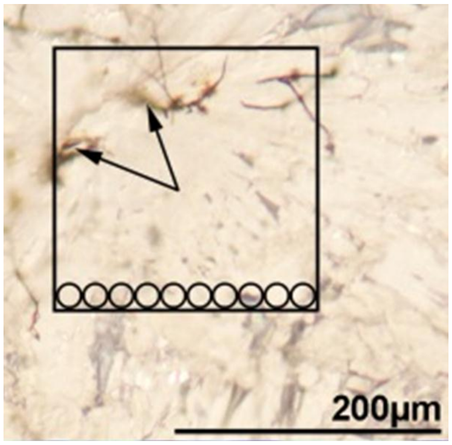

Figure 1: Detail of the sample surface used for systematic high resolution chemical mapping by mass spectrometry. The studies are conducted within a rectangular area containing filamentous micro-structures. The circles inserted in the picture are scaled to the laser spot size applied to ablate surface material.

The mass spectrometric measurements of carbonate host deliver composition of major elements: H, K, Na, Ca, C, O and Mg and confirm that the host is nearly pure calcium carbonate ($CaCO_3$). A typical mass spectrum of the investigated filaments is shown in Figure 2. In addition to major elements (O, Na, Mg, K, Ca, Mn, Fe, and Co) several minor elements (C, Si, S, Cl) and a few trace elements (B, N, F, Al, P, Ti, Cr and Ni) were measured.

4. Summary and Conclusions

The studies yield the element composition of the host material and filaments. The investigated filaments contain distinct atomic fractions of non-metallic (B, N, F, P, and S) and metallic (Li, Mn, Fe, Co, Ni, Se) elements in addition to the elements detected also in the aragonite matrix. Substantial differences between

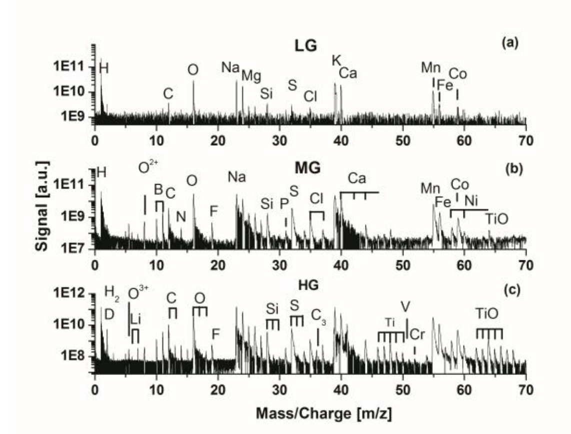

Figure 2: Typical mass spectrum measured at a filament location. In the LG spectrum the major and minor elements contained in the filament are identified .The Medium Gain (MG) (middle panel) and HG (bottom panel) spectra yield the detection of minor and trace elements as well as clusters and molecules.

the abundances of these elements in filaments and aragonite matrix were observed. The detection of high atomic fractions of bio-relevant elements including B, S, Mn, Co, Fe and Se is considered to be in favor of a bio-origin of the investigated filaments. Enrichment of the light isotope of S was measured for all investigated filaments but the accuracy of the measurement for isotopic investigations is presently too low. A few other abundant elements including B, F and Cl are observed in filaments. These can be important in metabolic processes but also be remnants of the ocean where the aragonite mineral was formed. The current studies form the basis for further investigations of these putative fossils by other analytical instrumentation.

Acknowledgements

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