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In-situ detection of biosignatures from 1.9 Ga Gunflint chert with LMS

Rustam Lukmanov (1), Marek Tulej (1), Reto Wiesendanger (1), Peter Wurz (1), and Andreas Riedo (2)
(1) Institute of Physics, University of Bern, Switzerland, (2) Sackler Laboratory for Astrophysics Leiden Observatory, University of Leiden, Leiden, Netherlands; (Rustam.lukmanov@space.unibe.ch)

Abstract

In this study, we show first data to demonstrate that miniaturized LA-TOF-MS (Laser Ablation – Time of Flight – Mass Spectrometer or LMS) combined with vacuum compatible microscopy system is a powerful tool in investigating the chemical composition of planetary bodies on the micrometer scale. Concerning questions related to the detectability of extinct or extant life, LMS is shown to be sensitive to highlight elemental abundances down to the ppb level and isotopic differences in the per-mil range of accuracy [2], [3]. These constitutes the primary challenge of planetary sciences and astrobiology, specifically, detectability of fossilized microbial colonies possibly preserved on planet Mars [1], [6]. We tested the instrument performance on a chert sample of 1.9 Ga age from the Gunflint Formation. Measurements are performed at infrared, infrared double pulse, visible, and ultraviolet wavelengths of laser irradiation in the fs time domain. We studied *in-situ* the chemical composition of a microfossils colony, different individual fossils, and host minerals. High spatial resolution of our microscope system with an updated procedure of the translation stage calibration allowed us to perform precise ablation of dense fossilized spots on the surface of stromatolite lamination and areas of surrounding Si-rich host.

Introduction

In-situ mass-spectrometry on the surfaces of planetary bodies is a promising technique which is of considerable interest for landed missions and also of particular interest in searches for extinct life on planet Mars. Regarding these question, single grain analysis coupled with sample probing on the macroscale and supported by satellite imaging on the regional level could help to investigate chemical composition of rock units, and gain insights into its formation and evolution [6],[7]. Sensitive elemental and isotopic studies with high lateral and depth resolution are considered to be the critical component for identification of single minerals, e.g. the host minerals of the fossils, and also for identification of putative microscopic fossils, which are usually preserved through permineralization [1], [4].

1. LMS Instrument

The LMS is small instrument suite which has low mass (1500 g), size (length – 120 mm; diameter – 60 mm), low power consumption, robustness in the harsh environments and ability to provide highly accurate measurements. Generally, all these aspects make the development of space instrumentation a challenging endeavour and frequently require lessening of precision of the instrument. In case of LMS, all necessary requirements have been fulfilled during continuous development over more than a decade. In the current state, the laboratory-based version of LMS is small-sized mass-spectrometer coupled with fs-laser ion source which can be switched from the fs-IR to the fs-UV range with an ability to provide two fixed harmonics at any given time (double-pulse). The suite is also coupled with the high vacuum compatible microscope with micrometer resolution. Detailed information about instrument could be found in our previous publications [2], [3], [5], [8].

2. IR and UV ablation studies of Gunflint chert as Martian analogue sample with LMS.

The 1.9 Ga Gunflint chert sample from Schreiber beach, Ontario, Canada, is considered in our study as Martian analogue sample. It was prepared in the form of the thin section and mounted on steel sample holder. Detailed mass-spectrometry studies on dense fossilized spots and clean host areas reveal differences in chemical composition. Main preservation type determined by results of our studies is pyritization of cell walls in mainly chalcedony host.

Fossilized colonies show high C, Mg, S, Fe content where at the same time measurements on pure host contain almost negligible or noticeably lower concentrations of these elements. The laser ablation rate for areas on the host mineral appears to be significantly lower in comparison to the fossils since pure chalcedony is nearly transparent at our IR wavelength. However, successful laser ablation in infrared was achieved by increased laser irradiation.

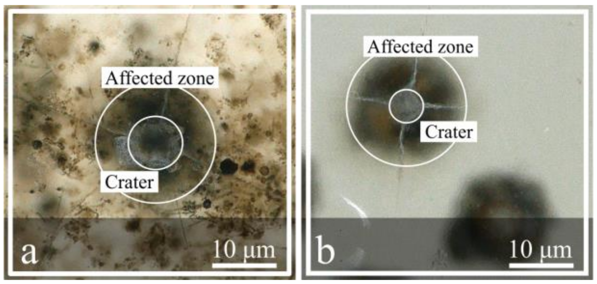

Figure 1: Laser ablation craters on the surface of the Gunflint chert sample obtained on two different areas with IR laser irradiation (equal amount of shots): a) Dense fossilized colony; b) relatively pure host

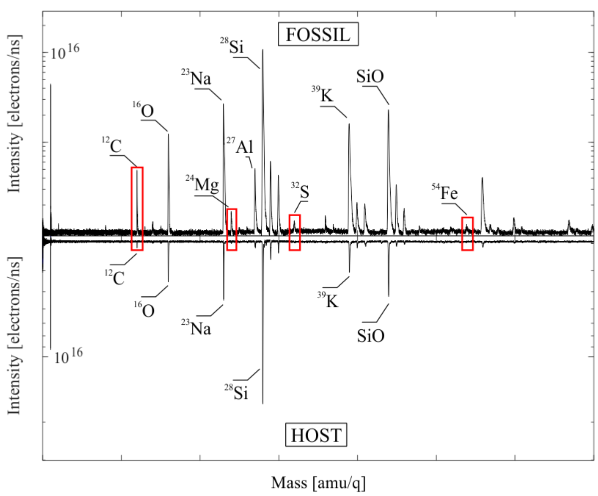

Figure 2: Comparison of two mass spectra from the Gunflint chert sample. The upper part of the plot corresponds to the crater shown in Figure 1a. The lower part of the plot corresponds to the crater shown in Figure 1b.

In comparison with the fs-IR-laser ablation ion source, measurements performed at UV range of laser irradiation offer better detection sensitivity and gentler ablation.

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