

**LASER ABLATION IONIZATION MASS SPECTROMETRY FOR ACCURATE IN SITU MEASUREMENTS OF SULFUR ISOTOPE FRACTIONATION.** A. Riedo<sup>1</sup>, V. Grimaudo, J.W. Aerts<sup>2</sup>, M. Tulej<sup>1</sup>, R. Lindner<sup>3</sup>, P. Wurz<sup>1</sup> and P. Ehrenfreund<sup>4,5</sup>, <sup>1</sup>Space Research and Planetary Sciences, Physics Institute, University of Bern, Bern, Switzerland (andreas.riedo@space.unibe.ch), <sup>2</sup>Molecular Cell Physiology, Faculty of Earth and Life Sciences, VU University Amsterdam, Amsterdam, The Netherlands, <sup>3</sup>Life Support and Physical Sciences Instrumentation Section, European Space, <sup>4</sup>Laboratory for Astrophysics, Leiden Observatory, Leiden University, Leiden, The Netherlands, <sup>5</sup>Space Policy Institute, George Washington University, 20052 Washington DC, USA.

**Introduction:** Six groups of promising signatures of life were identified and discussed in detail by the Mars Science Definition 2020 team, ranging from prominent organic molecules (i.e., amino acids or lipids) to microscopic structures (i.e., microfossils), which are of high relevance for future space exploration missions devoted to the detection of life [1, 2]. Signatures of isotope fractionation belong to one of these six groups. Isotope abundances compared to molecular compounds, e.g., organic molecules, are more robust to changing physical conditions such as temperature, expose to radiation and ionization conditions. Sulfur isotopes are of particular interest. On Earth, several microorganisms that use sulfur for their metabolic process have been identified. Furthermore, it was shown that specifically the sulfur reducing bacteria have the capability to fractionate the sulfur isotopes to a level of about -70 ‰  $\delta^{34}\text{S}$ , whereas geochemical processes were observed to fractionate the sulfur isotopes only to a level of about -20 ‰  $\delta^{34}\text{S}$ . Hence, the identification of a fractionation beyond 20 ‰  $\delta^{34}\text{S}$  would be highly indicative of the presence of life, extinct or extant.

In this contribution, we present a novel measurement protocol using Laser Ablation Ionization Mass Spectrometry (LIMS) that allowed the analysis of sulfur fractionation with an accuracy at the level of ~ 2-3 ‰  $\delta^{34}\text{S}$  [3]. Measurements were conducted on five samples relevant to astrobiology, collected from three different extreme sites on Earth, including Río Tinto, Spain, and two caves in Romania. The accuracy is sufficiently high to differentiate between abiotic (geochemical) and biotic processes that might yield fractionation beyond the 20 ‰  $\delta^{34}\text{S}$  level.

**Laser Ablation Ionization Mass Spectrometry (LIMS):** The prototype space system used for these measurements comprises a miniature reflectron-type time-of-flight mass analyzer and a laser ablation ionization source. The principles of operation are discussed in detail in a previous scientific publication [3], hence only a brief description is provided in the following.

The mass analyzer (160 mm x Ø 60 mm) is located within a vacuum chamber and an optical system is

used to guide the laser pulses from the laser system (installed outside the vacuum chamber, wavelength  $\lambda = 775$  nm, operated in double pulse mode [4-5]) towards the mass analyzer. A lens system installed just above the mass analyzer focuses the laser pulses through the analyzer towards the sample surface to spot sizes of ~10 – 20  $\mu\text{m}$  in diameter. Each laser pulse removes a distinct layer of material and partially ionizes the just removed material. Only positively charged species can enter the ion optical system of the mass analyzer, by which they are accelerated, reflected at the ion mirror, and subsequently detected. The ions reach the detector system sequentially according to their mass-to-charge ratio (time-of-flight measurement principle). Sample material was placed into cavities on a steel sample holder and were positioned below the mass analyzer using an xyz-translation stage.

**Sample material:** For the elaboration of the measurement protocol, five samples were investigated. The samples differ in their sulfur abundance (ranging from abundances of 97.5 ‰ down to about 5.7 ‰, weight-%) and in their isotope fractionation signatures (from about -7.1 ‰  $\delta^{34}\text{S}$  to +8.6 ‰  $\delta^{34}\text{S}$ ). Three samples are from the well-known Río Tinto environment (sample names RT1, RT2 and RT6), Spain, one sample from the Movile Cave (sample name MC), Romania, and one sample from the Sulphur Cave (sample name SC), Romania. Two out of the five samples were used as internal standards. More details about the field sites can be found in the recent scientific publication [3].

**Measurement Results and Discussion:** On each sample, a laser irradiance campaign was conducted; laser pulses in the range of 0.3 – 1.7  $\mu\text{J}$  were applied. For each measurement a new sample location was investigated. Typically, each measurement consisted of 200 – 400 recorded mass spectrometric files, each representing a histogram of 50 single laser shot spectra. The analysis of the recorded mass spectra allowed the identification of a peak-like trend of  $^{34}\text{S}/^{32}\text{S}$  with applied pulse energy. Comparing the maxima of these peaks with the two internal standards (RT2 and SC) facilitated the analysis of  $\delta^{34}\text{S}$  with an accuracy of about 2-3 ‰  $\delta^{34}\text{S}$ . The measurement results are displayed in Fig. 1.

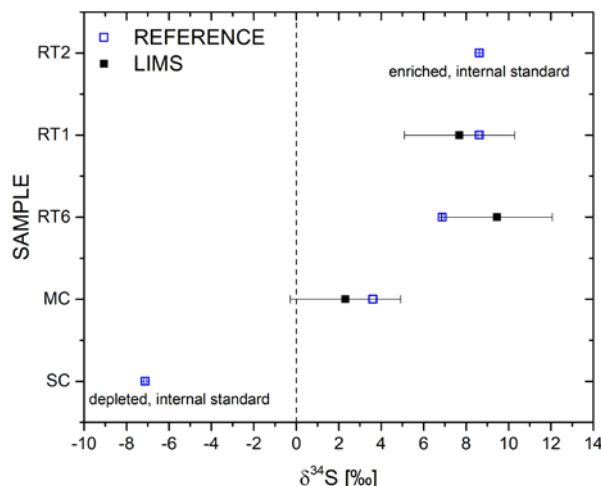


Fig. 1: Comparison between measured (black) and reference (blue) values for  $\delta^{34}\text{S}$ . The two samples RT2 and SC were used as internal standards for the LIMS measurements. Image taken from [3].

In addition to the analysis of the isotope fractionation signature, the recorded spectra allowed for element analysis of each sample. It was shown that the element composition matches the description of the sampling environment.

**Conclusions:** Isotope fractionation signatures belong to one of the six groups of promising signatures of life relevant to astrobiology. Sulfur isotopes are of particular interest because microbes have been identified on Earth that can fractionate sulfur isotopes beyond abiotic limits of about 20 ‰  $\delta^{34}\text{S}$ . In this study, LIMS measurements were conducted on five sulfur samples, differing in their sulfur abundance and fractionation signature. The measurements demonstrate that the analysis can be conducted with an accuracy of about 2-3 ‰  $\delta^{34}\text{S}$ . This accuracy is sufficient to, e.g., differentiate between abiotic (i.e., geochemical) and biotic process that might yield fractionation beyond 20 ‰  $\delta^{34}\text{S}$ . Application scenarios of this measurement protocol using the afore mentioned LIMS system might be Mars as well as the icy moon Europa (see e.g., [6]).

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