ORIGIN: Towards *in situ* Laser Desorption Mass Spectrometry of Amino Acids, PAHs and Lipids on Ocean Worlds N.J. Boeren^{1,2}, K. Kipfer¹, N.F.W. Ligterink¹, C.P. de Koning¹, P. Keresztes Schmidt¹, V. Grimaudo¹, M. Tulej¹, R. Lindner³, P. Ehrenfreund^{4,5}, P. Wurz¹ and A. Riedo¹

¹Space Research and Planetary Sciences, Physics Institute, University of Bern, Bern, Switzerland (nikita.boeren@unibe.ch), ²NCCR PlanetS, University of Bern, Bern, Switzerland, ³Life Support and Physical Sciences Instrumentation Section, European Space Agency, ESTEC, The Netherlands, ⁴Laboratory for Astrophysics, Leiden Observatory, Leiden University, Leiden, The Netherlands, ⁵Space Policy Institute, George Washington University, 20052, Washington, DC, USA

Introduction: The detection of life, past or present, on Solar System bodies other than earth is a high priority topic in current space science. Reliable in situ detection of signatures of life poses several major challenges. Firstly, detection instrumentation should be suitable for flight, meaning robust and simple, which poses restrictions to, e.g., mass, volume, and power usage. In addition, low measurement sensitivity is required, while ideally a high dynamic range is simultaneously covered, as to not exclude highly abundant compounds. Whereas lab-based (earth-based) instrumentation can be very sensitive and cover a large dynamic range, such instruments are rarely suitable for use in space missions due to not meeting the physical and mechanical requirements. Lastly, the capability to detect compounds that are not expected to be of importance (unknowns) prior to the mission is a huge benefit to any instrument considered for use in space.

Signatures of life: Currently, the presence of life (extinct or extant) on several Solar System bodies is being investigated. The Galileo and Cassini-Huygens missions have recently uncovered information leading to two new astrobiological targets, namely Enceladus and Europa [1]. The probable presence of oceans under the ice shells of these moons are of high interest for the detection of signatures of life. These so-called 'Ocean Worlds' could harbor all ingredients necessary for life (as we know it), e.g., an energy source, liquid water, and a nutrient source.

Biosignatures could be present in the oceans themselves or preserved within (near) surface ice, where they are protected from harsh radiation environment. NASA Europa Lander Report [2] lists several groups of biomolecules of interest, which show high molecular stability, potentially retaining their molecular structure for several billion years. Among these molecules of interest are amino acids, lipids, and polycyclic aromatic hydrocarbons (PAHs). Therefore, detection and identification of these biomolecules is of high interest for the search for signs of life of future space exploration missions (on Ocean Worlds).

In our contribution, we will present the current measurement capabilities of our novel prototype Laser Desorption Mass Spectrometric (LDMS) system targeting various groups of biomolecules relevant to astrobiology.

Laser Desorption Mass Spectrometry: A novel prototype laser desorption mass spectrometer (LDMS), called ORIGIN (ORganics Information Gathering INstrument), was designed for *in situ* space exploration missions and constructed at the University of Bern, Switzerland [3]. The design of the instrument complies with all mechanical and physical requirements with respect to space instrumentation, meaning it is lightweight, compact and simple, and has low energy consumption. The fully-operational prototype allows for detection and identification of biomolecules of varying mass.

ORIGIN setup: The current setup consists of a miniature reflectron-type time-of-flight mass analyzer (160 mm x Ø 60 mm) and a nanosecond pulsed laser system (wavelength $\lambda = 266$ nm, pulse repetition rate of 20 Hz, pulse width of $\tau \sim 3$ ns) for the gentle desorption of analytes [4].

The laser system is installed outside the vacuum chamber with a beam guiding system that directs the pulsed laser beam towards the sample, which is located inside a vacuum chamber. The laser beam is focused through the mass analyzer onto the sample, which is placed in close vicinity to the entrance of the mass analyzer.

Every pulse reaching the sample surface causes desorption/ionization of the sample material. Positively charged ions are guided towards the field-free drift path of the time-of-flight mass analyzer. The ions are reflected at the ion mirror (reflectron), causing them to pass the drift tube a second time. Finally, ions hit the multi-channel detection plates at the bottom of the drift tube.

Generated, positively charged ions are separated in the TOF mass analyzer based on their mass-to-charge ratio (TOF principle). The detection of these ions over time result in a single mass spectrum for each laser shot.

Results: LDMS measurements of various sample solutions of amino acids standards, polycyclic aromatic hydrocarbons, and lipids standards were performed. Standardized measurement protocols, concerning, i.e., optimal laser desorption conditions, were established for biomolecule identification and limit of detection

studies. Three different groups of biomolecules were investigated thus far, namely amino acids, PAHs, and lipids.

For amino acids, detection sensitivity down to femtomol mm $^{-2}$ levels were shown. These results have recently been published [3]. PAHs and lipids were additionally investigated. Four different PAHs (coronene, perylene, pyrene, anthracene) were measured, all of which were detected with high sensitivity [5]. Measurements of six different lipids, all members of the prenol or sterol lipids, were performed [6]. Figure 1 shows the acquired mass spectra for vitamin K_1 and α -tocopherol, two of the investigated lipid molecules.

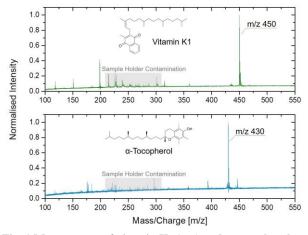


Fig. 1 Mass spectra of vitamin K_1 (top) and α -tocopherol (bottom). Intensities were normalized to the most intense peak.

Conclusions: ORIGIN is a powerful alternative to techniques more traditionally applied in space exploration missions, such as pyr-GC-MS. The implications of our results, specifically those pertaining to the suitability of the presented technique for future space missions to explore these Ocean Worlds in the search for signatures of life, will be discussed.

Acknowledgments: This work was supported by the Swiss National Science Foundation. NJB acknowledges support from NCCR PlanetS grant 200020_184657. NFWL is supported by the Swiss National Science Foundation Ambizione grant 193453.

References: [1] Lunine J.I. (2017) Acta Astronaut., 131, 123-130. [2] Hand K.P. et al. (2017) Report of the Europa Lander Science Definition Team. [3] Ligterink N.F.W. et al. (2020) Sci. Rep., 10, 9641. [4] Riedo A. et al. (2013) J. Mass Spectrom., 48, 1-15. [5] Kipfer K. et al. (2021) submitted to AAS. [6] Boeren N.J. et al. (2022) to be submitted.