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1 **Laser Desorption Mass Spectrometry with an Orbitrap Analyzer for *in situ* Astrobiology**

2

3 **Ricardo Arevalo Jr.^{1,2}, Lori Willhite², Anais Bardyn², Ziqin Ni², Soumya Ray², Adrian Southard³,**
4 **Ryan Danell⁴, Andrej Grubisic⁵, Cynthia Gundersen⁶, Niko Minasola⁶, Anthony Yu⁵, Molly Fahey⁵,**
5 **Emanuel Hernandez⁵, Christelle Briois⁷, Laurent Thirkell⁷, Fabrice Colin⁷, and Alexander**
6 **Makarov⁸**

7

8 **¹Corresponding Author: rarevalo@umd.edu**

9 **²University of Maryland, College Park, MD USA**

10 **³CRESST II, College Park, MD USA**

11 **⁴Danell Consulting, Winterville, NC USA**

12 **⁵NASA Goddard Space Flight Center, Greenbelt, MD USA**

13 **⁶AMU Engineering, Miami, FL USA**

14 **⁷Laboratoire de Physique et Chimie de l'Environnement et de l'Espace, Orléans, FR**

15 **⁸Thermo Fisher Scientific, Bremen, DE**

16

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23 **Keywords: astrobiology; biomarker; life detection; mass spectrometry; Enceladus; Europa; ocean**
24 **worlds**

25 **Abstract (limit 150 words unreferenced; currently 150 words)**

26 **Laser desorption mass spectrometry (LDMS) enables *in situ* characterization of the organic content**
27 **and chemical composition of planetary materials without requiring extensive sample processing.**
28 **Coupled with an OrbitrapTM analyzer capable of ultrahigh mass resolving powers and accuracies,**
29 **LDMS techniques facilitate the orthogonal detection of a wide range of prospective biomarkers and**
30 **classification of host mineralogy. Here, an Orbitrap LDMS instrument that has been miniaturized**
31 **for planetary exploration is shown to meet the performance standards of commercial systems and**
32 **exceed key figures of merit of heritage spaceflight technologies, including those baselined for near-**
33 **term mission opportunities. Biogenic compounds at area densities relevant to prospective missions**
34 **to ocean worlds are identified unambiguously by redundant measurements of molecular ions (with**
35 **and without salt adducts) and diagnostic fragments. The derivation of collision cross-sections serves**
36 **to corroborate assignments and inform on molecular structure. Access to trace elements down to**
37 **ppmw levels provide insights into geological context.**

38 **Main text (upper limit 3500 words, excl. abstract, methods, references and legends)**

39 Future astrobiology missions to Europa, Enceladus, and other potentially viable ocean worlds will be
40 challenged to distinguish biological signatures without bias towards features associated with terrestrial
41 life [1]. Payload instruments need to support agnostic and discovery-based approaches to distinguish
42 relics of biological processes from the limited complexity and apparent randomness of abiotic sources [2].
43 A critical capability of next-generation technologies will be the orthogonal (or independent) detection of a
44 variety of biomarkers, including (but not limited to): organic abundance patterns; stable isotope ratios;
45 biogenic minerals; and, morphologies indicative of microbial activity [3]. Multiple distinct proxies
46 observed across a range of spatial scales provide a framework to gauge the probability of biogenicity [4].

47 Laser desorption mass spectrometry (LDMS) enables investigations into the organic inventory and the
48 elemental/isotopic composition of planetary materials *in situ*, providing: i) access to multiple classes of
49 biomarkers, most notably refractory organic matter; and, ii) identification of host mineralogy, ergo
50 geological context for detected organic compounds. Unsupervised data-driven approaches can increase
51 operational autonomy and enhance the confidence in organic/inorganic assignments (e.g., [5]). Laser
52 microprocessing is well suited for life detection objectives as such methods require minimal sample
53 processing and support 2D chemical imaging without requiring physical contact with the sample; standoff
54 instruments reduce the risk of cross-contamination and planetary protection violations. The spatial
55 resolution of an LDMS experiment is controlled by the profile of the beam focused onto the sample
56 surface, allowing for targeted analyses of micron-scale mineral phases, individual dust particles,
57 microfossils, finely laminated biofabrics, and discrete strata captured in sample cores. Each laser shot
58 only ablates the uppermost <100 nm of the sample even at elevated fluences (e.g., [6]), resulting in an
59 effective sample mass on the order of ng; thus, LDMS is ideal for surface analysis and/or depth profiling.
60 However, this can be a limiting capability if bulk measurements are required to meet specific planetary
61 science objectives.

62 Due to these analytical advantages, a standoff LDMS instrument called LIMA-D was launched onboard
63 Phobos 2 in 1988; however, communication with the spacecraft was lost during the approach towards
64 Phobos, compromising the mission [7]. A derivative of LIMA-D, named LAZMA [8], was later launched
65 in 2011 onboard the Phobos-Grunt mission, but a propulsion failure left the spacecraft stranded in low
66 Earth orbit. Thus, LDMS techniques have yet to be applied in an extraterrestrial planetary environment.
67 However, LDMS instruments have been developed for the ExoMars rover [9], Dragonfly rotorcraft [10],
68 and Luna-Glob (Luna-25) and Luna-Resurs-1 (Luna-27) missions [11], illustrating the impetus to exploit
69 such *in situ* techniques to address high-priority science questions in the planetary community.

70 Here, we describe an LDMS instrument that combines an OrbitrapTM mass analyzer, solid-state UV (266
71 nm) laser system derived from heritage designs, and custom series of ion optics that accelerate and focus
72 ions generated at the sample surface into the analyzer. A prototype of the LDMS instrument (**Fig. 1**) has
73 been highly miniaturized relative to the proof-of-concept breadboard reported previously [12] but without
74 a compromise in analytical performance (as discussed further below), representing an engineering model
75 of a spaceflight design that fits within the limited resources expected for a mission to the outer Solar
76 System (e.g., the Europa Lander [13]; see Supplement).

77 The Orbitrap analyzer, originally developed for commercial laboratories [14] but recently adapted for
78 planetary applications [12], delivers 100× higher mass resolution and mass accuracy compared to the
79 legacy quadrupole sensors that have explored the inner and outer reaches of the Solar System [15]. Such
80 analytical capabilities are essential to separate isobaric interferences (defined by the same nominal mass-
81 to-charge ratio, or integer m/z) and unambiguously identify molecular stoichiometry without additional

82 subsystems (e.g., resonance lasers and gas chromatographs). Because the Orbitrap analyzer uses
83 electrostatic fields to trap ions [16], the sensor does not require magnets, RF electronics, or consumable
84 detectors, limiting failure modes and minimizing resource requirements. The basic operation of the
85 Orbitrap analyzer involves injection and trapping of analyte ions, which then exhibit harmonic axial
86 oscillations at frequencies proportional to $(m/z)^{-1/2}$. Ion motion recorded as image current in the time
87 domain transient can be converted into frequency space via fast Fourier transform (FFT).

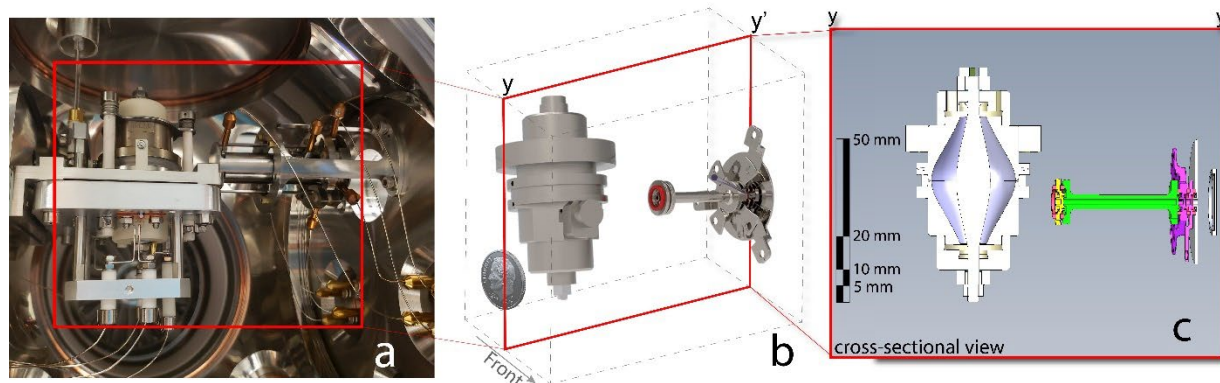
88 The effective mass range in a given experiment is influenced by the distance the ions travel from the
89 source to the trap, and the timing and slew rate of the voltages applied to the center and deflector
90 electrodes, which together enable electrodynamic squeezing of the incoming ions [14]. During an LDMS
91 analysis, the primary limit to the upper end of the mass range is the capacity of the laser source to ionize
92 macromolecular organic material without incurring excessive fragmentation of the parent molecule. The
93 mass resolving power is controlled principally by the observation time (i.e., transient length) and temporal
94 spread within a single m/z ion packet. Given these timing requirements and sensitivity to temporal
95 smearing, a pulsed laser system is a natural choice to serve as an ion source.

96 Previously, an Orbitrap analyzer extracted from its commercial packaging and interfaced directly to an
97 industrial laser was shown to characterize the mineralogy of a variety of planetary analog samples and
98 detect amino acids down to < 100 fmol/mm² concentrations (based on signal-to-noise ratios) with only a
99 single laser shot and no spectral stacking [17]. However, this breadboard was not designed to minimize
100 mass, volume, and power requirements, but rather to validate experimentally the scientific reach of
101 LDMS techniques that leverage an ultrahigh resolution mass analyzer.

102 In comparison, the footprint of the LDMS instrument described here has been miniaturized for mission
103 science by interfacing an Orbitrap analyzer with a laser system that leverages the side-pumped
104 Cr:Nd:YAG oscillator design flown on the Lunar Orbiter Laser Altimeter (LOLA) [18], with a
105 fundamental wavelength of 1064 nm and nominal pulse width of 5 ns. A fourth harmonic generator
106 produces an output wavelength of 266 nm (4.7 eV/photon), enhancing photon-substrate coupling with
107 aromatic organics [19] and many geological phases [20]. The laser generates >450 μ J/pulse at 266 nm
108 [21], more than three times the maximum energy of the laser for the state-of-the-art Mars Organic
109 Molecule Analyzer (MOMA) instrument onboard the ExoMars rover [9]. Fine attenuation control down
110 to 1% of the maximum output energy is achieved by controlling the polarization of incident 532 nm light
111 prior to conversion to 266 nm in the fourth harmonic; for comparison, the MOMA laser output energy can
112 only be reduced to 10% of the maximum value by thermal detuning of the fourth harmonic crystal [22].

113

114



115
 116 **Fig. 1. A prototype of the highly miniaturized Orbitrap LDMS instrument described here, which**
 117 **has been designed to minimize mass, volume, and power requirements without compromising the**
 118 **capabilities of the proof-of-concept breadboard reported previously [12], exceeds key performance**
 119 **metrics of the MOMA flight instrument [9], including: mass resolution and accuracy; laser output**
 120 **energy; and dual polarity ion detection. (a) Photograph of the Orbitrap analyzer and ion optical**
 121 **lenses mounted within a planetary simulation chamber. (b) Solid model and (c) cross-sectional view**
 122 **showing the orientation and compact geometry of the analyzer, lens stack, and sample plate.**

123
 124 A longstanding issue for LDMS techniques has been the deduction of quantitative information,
 125 particularly relative and absolute abundances of elemental and molecular species. The reproducibility of
 126 LDMS peak intensities is limited by: i) the heterogeneity of the sample; ii) shot-to-shot variability of the
 127 laser output energy; and, iii) dynamic changes in sample morphology induced by extended laser
 128 irradiation, which affect photon-substrate coupling. However, the empirical determination of *relative*
 129 *sensitivity factors* of elements with distinct electronic configurations, which have been shown to control
 130 laser induced fractionation [23], can enable the quantification of concentration ratios (*e.g.*, [24]) in solid
 131 samples. Absolute abundances can be further derived if an internal standard is known (*e.g.*, [25]). Such
 132 approaches, which are commonplace for laser ablation inductively coupled plasma mass spectrometry
 133 (LA-ICPMS), offer promise for the quantitation of spectral signals derived from LDMS analysis.
 134 However, significant work remains to validate these models.

135 Measuring the relative abundances of organic molecules is even more challenging as observed signal
 136 intensities are sensitive to the absorption characteristics, bond strengths, and ionization energy of the
 137 compound, as well as the physicochemical properties of the sample matrix and dynamics of the plasma
 138 plume. In spite of these challenges, linear responses between analyte concentrations and peak intensities
 139 normalized to an internal standard have enabled the quantitative analysis of amino acids [26],
 140 oligonucleotides [27], and a range of other organics (*e.g.*, [28]) via LDMS techniques.

141 Due to their identical electronic configurations and comparable physicochemical properties, isotopes of
 142 the same element (and isotopologues of the same molecule, to a lesser extent) are more easily preserved
 143 during an LDMS experiment. Isotopic precision is controlled largely by signal-to-noise ratios, and thus
 144 the dynamic range of the sensor. The Orbitrap analyzer, which can accommodate up to 10^6 elementary
 145 charges during a single analysis [29], has been shown to support a linear intrascan dynamic range up to
 146 10^4 [30], providing access to low abundance isotopes down to 0.1 mol%. Although space charge effects
 147 can incur isotope fractionation during transient acquisition (*e.g.*, [31]), precise and accurate $^{13}\text{C}/^{12}\text{C}$ ratios
 148 measured for single species (*e.g.*, $^{13}\text{C}^{12}\text{C}_2\text{H}_8\text{O}_2\text{N}^+ / ^{12}\text{C}_3\text{H}_8\text{O}_2\text{N}^+$ in nominally pure alanine) within

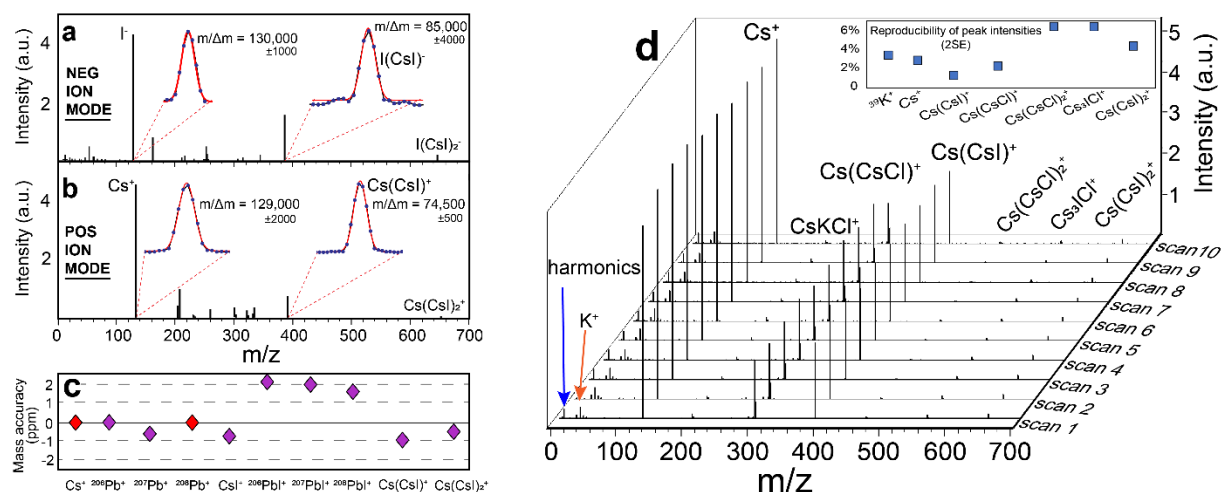
149 multicomponent sample mixtures have been recorded following careful calibration efforts, such as mass
150 pre-filtering, transient length shortening, and/or external standardization with a matrix-matched reference
151 material [32].

152

153 **Results**

154 A typical LDMS experiment comprises: i) desorption/ionization of the sample via pulsed laser light; ii)
155 acceleration, focusing, and adjustment of the reference potential of analyte ions through the ion optics
156 lens stack; iii) ion injection and electrodynamic squeezing in the trap; and, iv) detection of ion packets
157 according to their respective axial frequencies, and hence m/z . Tunable laser energy (and by extension
158 fluence, J/cm^2 , and irradiance, W/cm^2) promotes the ionization of refractory organics and mineral phases
159 via multiphoton absorption, supporting controlled fragmentation and disproportionation reactions to
160 derive molecular structure by in-source decay (e.g., [33]). The beam radius at the sample surface (r) is a
161 customizable parameter within the limits of diffraction; with an effective focal length of 140 mm, nominal
162 UV beam diameter of 3.0 mm, and beam quality factor $M^2 < 1.5$, the 266 nm laser system leveraged in
163 this study could approach a diffraction limited radius of $r < 12 \mu m$. Such fine spatial resolution comes at
164 the expense of total analyte throughput, which tracks with r^2 at a given fluence/irradiance. A MEMS
165 steering mirror inside the laser head, coupled with a set of deflector electrodes within the ion optics,
166 allows the construction of 2D chemical images with a nominal 500 μm diameter field of view (see
167 Supplement) without requiring translation/rotation of the sample, facilitating the identification of
168 biofabrics *in situ*.

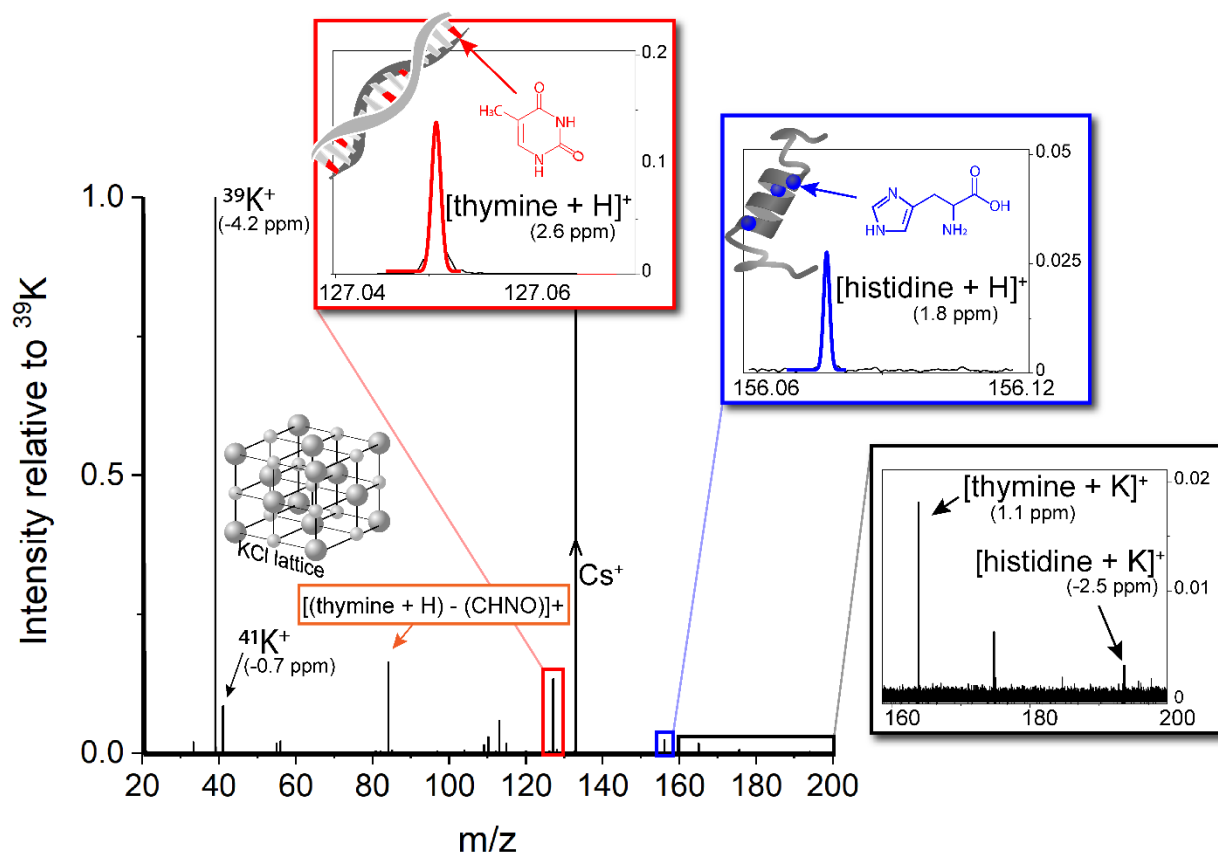
169 The measurement of both positively and negatively charged particles provides complementary
170 perspectives of complex chemical mixtures, empowering the detection of organic molecules with acidic
171 and basic side chains, as well as mineralogical indicators with high and low electronegativities. For
172 example, positive and negative mass spectra of a finely ground CsI disc (**Fig. 2**), a common laboratory
173 standard with identical composition to the calibrant for the MOMA flight instrument, provide multiple
174 molecular fingerprints diagnostic of the substrate. In positive mode, CsI is exemplified by a high intensity
175 Cs^+ peak (m/z 132.9054), but also $Cs(CsI)^+$ (m/z 392.7153) and $Cs(CsI)^{2+}$ (m/z 652.5253) clusters at lower
176 signal intensities. In negative mode, the spectrum is dominated by I^- (m/z 126.9045) followed by $I(CsI)^-$
177 (m/z 386.7144) and $I(CsI)^{2-}$ (m/z 646.5243). The mass resolution (e.g., $m/\Delta m > 100,000$, FWHM at Cs^+)
178 and ppm-level mass accuracy of these spectra, collected on the miniaturized prototype shown in **Fig. 1**,
179 meet the performance specifications of commercial instruments; for example, the Thermo Q ExactiveTM
180 offers mass resolution up to $m/\Delta m = 140,000$ (FWHM) at m/z 200 with < 3 ppm mass accuracy (RMS
181 with external calibration). Such analytical capabilities support the unambiguous identification of
182 elemental and molecular signatures for both commercial and spaceflight applications.



183
 184 **Fig. 2. In both negative and positive mode, the miniaturized Orbitrap LDMS instrument achieves**
 185 **mass resolving powers ($m/\Delta m > 10^5$, FWHM at m/z 100) comparable to commercial standards. (a, b)**
 186 **Spectra represent averages of 10 scans in the time domain, each acquired with an 800 ms transient**
 187 **(high-resolution) and sampling rate of 5 MHz (see Methods). Reported uncertainties of the mass**
 188 **resolving powers of individual peaks are determined by the fit of a Gaussian curve to the raw data.**
 189 **(c) Using $^{133}\text{Cs}^+$ as a single point internal standard, and subsequently $^{133}\text{Cs}^+$ and $^{208}\text{Pb}^+$ to apply a**
 190 **secondary linear calibration, peaks fall within ppm of exact monoisotopic masses. (d) Ten single**
 191 **scans collected in positive mode, acquired sequentially with 200 ms transients (medium-resolution)**
 192 **and 5 MHz sampling rate, illustrate the reproducibility of the experiments (see Supplement). As**
 193 **shown in the inset, the peak intensities of $^{39}\text{K}^+$, Cs^+ , and $\text{Cs}(\text{CsI})^+$ all vary by less than 5% (2SE)**
 194 **across all scans. Irradiance $0.1 \text{ GW}/\text{cm}^2$.**

195
 196 Chloride salts, such as NaCl and KCl, are important planetary materials because they can depress the
 197 freezing point of liquid water in cryogenic environments and concentrate dilute monomers of more
 198 complex biomolecules (*e.g.*, RNA) via enhanced adsorption onto mineral surfaces [34]. Such salts have
 199 been observed on the surface of Europa [35], within the Enceladus plume [36], and inside Occator crater
 200 on the dwarf planet Ceres [37]. Consequently, to address high-priority astrobiology mission objectives
 201 [38, 39], future payload investigations need to characterize salt-rich sample matrices to gain insights into
 202 the provenance of detected organics.

203 Assuming the composition of Enceladus approximates that of a comet, as suggested by comparable
 204 volatile abundances and D/H ratios recorded in the plume [40] and those observed in cometary comae
 205 [41], measurements provided by the Cassini payload implicate up to ppmw concentrations of individual
 206 amino acids in the subsurface ocean [42]. Area densities exceeding $200 \text{ pmol}/\text{mm}^2$ are projected if 1 mL
 207 of water ice, the sample volume baselined for each instrument onboard the Europa Lander [38], was
 208 sublimated onto a cm^2 sample plate. The analysis of a salt-rich planetary analog sample containing similar
 209 levels of a proteinogenic amino acid (*i.e.*, histidine) and nucleobase (*i.e.*, thymine) demonstrates the
 210 capacity of the Orbitrap LDMS instrument to simultaneously access both organic and inorganic fractions
 211 of multicomponent sample mixtures representative of those that may be collected by future missions to
 212 ocean worlds (**Fig. 3**).



214

215 **Fig. 3.** Analysis of a residue of a salt-rich (0.32 wt.% KCl) solution doped with trace levels of
 216 thymine and histidine, both prospective biomarkers containing aromatic groups that effectively
 217 absorb UV radiation (see Supplement), without desalination of the sample. The area densities of
 218 thymine (180 pmol/mm²) and histidine (210 pmol/mm²) approximate those expected if 1 mL of ice
 219 derived from Enceladus' subsurface ocean was sublimated onto a cm² sample plate (see main text).
 220 Detection of protonated molecular ions ([M+H]⁺ shown with Gaussian fits), diagnostic fragments
 221 ([M+H-CHNO]⁺), and potassiated peaks (e.g., [M+K]⁺) provide corroborative identification of the
 222 analytes. The isotopic composition of K derived from the salt matrix falls within natural values.
 223 This spectrum represents a single scan acquired with an 800 ms transient and sampling rate of 5
 224 MHz. ¹³³Cs⁺, sourced from the collocated CsI target, was used as an internal standard; ³⁹K⁺, ¹³³Cs⁺,
 225 and ²⁰⁸Pb⁺ were used to apply a linear calibration. Irradiance 0.3 GW/cm².

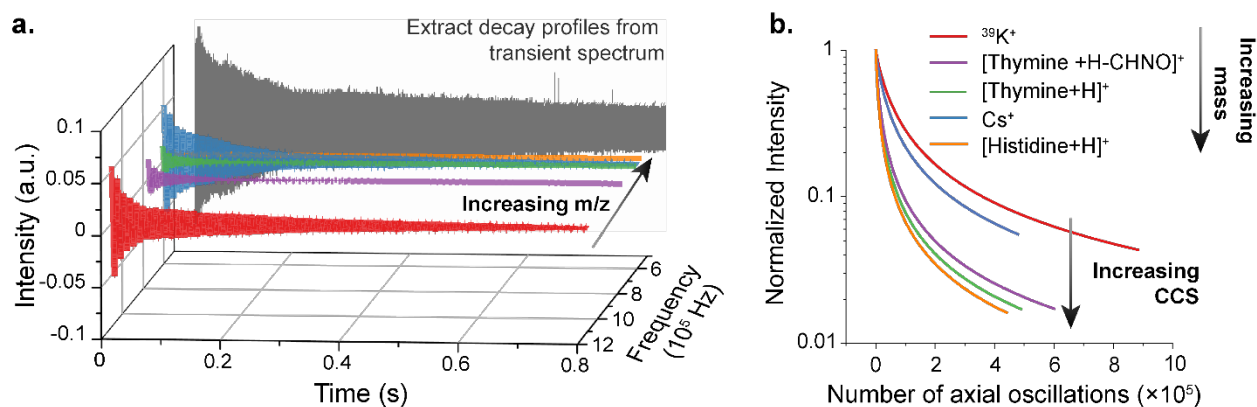
226

227 The elucidation of molecular structure, including the differentiation of structural isomers, represents an
 228 orthogonal means to establish the identity of prospective biomarkers and inform on the probability of
 229 biogenicity based on molecular complexity [2]. The finely controlled output of the laser source pioneered
 230 here enables in-source decay, a technique that has been shown to induce molecular fragmentation and
 231 facilitate the identification of peptides based on diagnostic amine-bond cleavages [43], and sequencing of
 232 proteins from the determination of N-terminal fragments [44] via matrix-assisted LDMS techniques.
 233 Another emerging capability specific to the Orbitrap analyzer involves determining the distinct decay rate
 234 of each compound during time-resolved transient signal acquisition in order to calculate of collision cross

235 section (CCS), a measure of ion size and conformation unique to each chemical species [45]. As a packet
236 of ions of a specific m/z oscillates around the center electrode, individual ions de-phase due primarily to
237 elastic collisions with background gas, ion-ion interactions, and other factors (*e.g.*, high-voltage ripple
238 and field perturbations derived from mechanical imperfections) [46]. The additive effect of these
239 processes results in degradative signal loss of ion packets as a function of time within the analyzer.

240 As shown in **Fig. 4**, the decay profiles of select chemical species identified in **Fig. 3** can be extracted from
241 a single transient spectrum via FFT, followed by inverse FFT. The observed signal losses reflect the
242 specific experimental conditions (*e.g.*, pressure, temperature, and voltages) in addition to the additive
243 decay factors described above. Chemical species that exhibit faster decay rates represent compounds with
244 larger cross-sections, which reflect both m/z and molecular structure. Previous work has shown that the
245 cross-sections of biogenic amino acids directly correlate with molecular weight, but aliphatic and
246 aromatic compounds tend to be larger than the average trend due to inefficient folding [47]. Thus, CCS
247 determinations provide a complementary means to identify organic compounds and differentiate
248 molecular structures, supporting agnostic detection techniques for the characterization of putative
249 biomarkers.

250



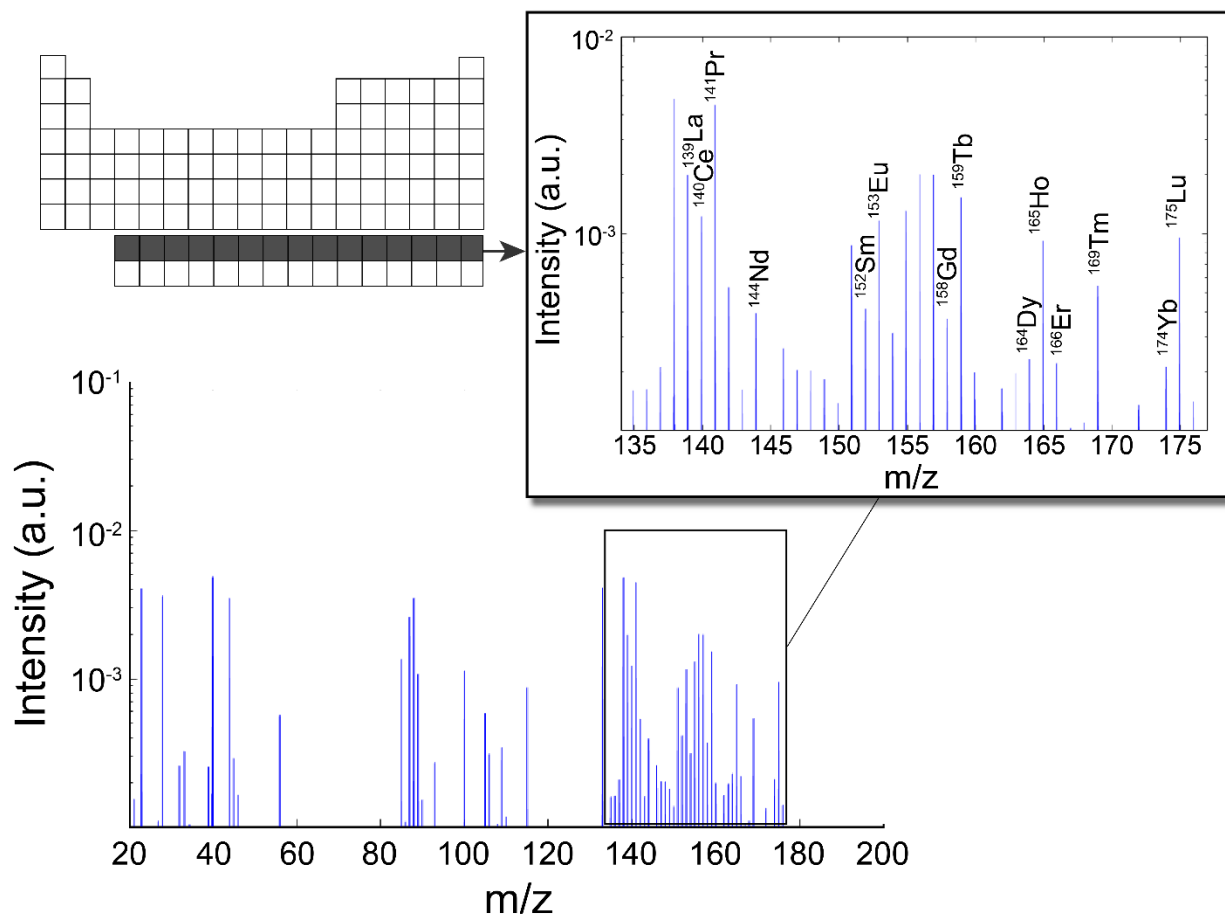
251 **Fig. 4 (a)** The total transient signal (grey) may be decomposed into decay profiles of individual
252 chemical species based on their distinctive frequencies (or m/z) via FFT and subsequent inverse
253 FFT. The signal intensities of select peaks identified in Fig. 3 correlate with ion abundances (and to
254 a lesser extent radial distribution about the center electrode). (b) The decay rates of signal
255 intensities reflect ion losses as a function of time, informing on molecular weight and structure.

257

258 The detection of organic compounds alone is insufficient to characterize the habitability potential of a
259 cryogenic environment and/or assign prospects for extant or extinct life with high confidence. Exogenous
260 infall can deliver significant quantities of organic material to the surface of any planetary body; for
261 reference, more than 10^7 kg of exogenous material is delivered to the Earth every year [48]. Although
262 infall rates scale with planet mass and interplanetary dust fluxes vary as a function of heliocentric distance
263 [49], significant quantities of organic materials are continually being accumulated on Europa, Enceladus,
264 and other ocean worlds. Associations between detected organic compounds and host mineralogy,
265 informed by major, minor and trace element abundances, are powerful tools for establishing the
266 provenance of organic matter. Rare earth elements (REE; *i.e.*, La through Lu) are particularly valuable
267 proxies for geological sources as this suite of trace elements shares a common valence state (X^{3+}) and
268 systematic contraction in ionic radii, resulting in predictable partitioning behaviors. Consequently, REE

269 are routinely used to understand the chemistry, formation, and evolution of major terrestrial reservoirs
270 [50]. The miniaturized LDMS described here can measure REE down to ppmw levels in solid samples
271 (Fig. 5), enabling insights into the sourcing of detected organic molecules, including prospective
272 biomarkers. However, a systematic evaluation is needed to constrain the accuracy of quantified elemental
273 concentrations and the reproducibility of observed abundance patterns of organic molecules.

274



275

276 **Fig. 5. The Orbitrap LDMS instrument can detect trace elements down to ppmw concentrations, as**
277 **illustrated by the measurement of REE in NIST SRM610. Observed signal intensities reflect the**
278 **distinct isotopic compositions and first ionization energies of each element. The detection limit for**
279 **Pr, which is monoisotopic and has the lowest first ionization energy of the REE, is 1.8 ppmw based**
280 **on the observed signal-to-noise ratio in this single spectrum. Summing multiple scans can reduce**
281 **the noise floor and improve detection limits when time and energy resources are available.**
282 **Irradiance 0.6 GW/cm².**

283 **Methods**

284 **Sample preparation.** A 2.2 mm thick CsI finely ground disc (7.49 mm diameter) produced by
285 Almaz Optics, Inc. was secured via interference fit inside a counter bore machined into the
286 stainless sample plate and analyzed daily to tune the voltages applied to the ion optical lenses
287 (see Supplement), verify ion transmission and baseline performance, and monitor for
288 instrumental drift. In order to simulate a salt-rich ice sample from a potentially viable ocean
289 world, a volume of deionized water (Milli-Q, 18.2 M Ω ·cm resistivity at room temperature) was
290 physically admixed with 0.32 wt.% KCl (Sigma-Aldrich P9541; purity \geq 99.0%), approaching
291 the observed alkali salt content of Type III Enceladus plume ice particles collected by the Cassini
292 CDA [36] and modeled salinity levels in Europa's ocean based on brine mobility in the ice crust
293 [51]. The salt solution was doped with 190 ppmw thymine (Alfa Aesar A15879; 97%) and 280
294 ppmw L-histidine (Sigma Aldrich P500108; 99.9%), both prospective biomarkers (see
295 Supplement). The organic-bearing sample was then agitated with a vortex mixer (2800 rpm) to
296 promote dissolution and homogenization. Prior to drop-casting, the sample plate was cleaned
297 with isopropyl alcohol and acetone in sequence. 40 μ L of the analog solution were deposited
298 onto the surface of the stainless steel sample plate over an area of 350 mm² and allowed to
299 evaporate on a hot plate (115 °C) in a chemical fume hood; this desiccation step produced a
300 heterogenous residue in line with what might be expected if an aliquot of ice was sublimated on
301 a warm sample plate on a landed mission to Europa or Enceladus. The resultant sample residuum
302 had an average area density of 180 pmol/mm² thymine and 210 pmol/mm² histidine.

303
304 **Measurement protocol.** The Orbitrap analyzer was located inside a Kimball Physics spherical
305 cube vacuum chamber at pressure conditions found on the surface of Europa (*i.e.*, $\leq 10^{-6}$ Pa). A
306 load lock chamber equipped with a dedicated pumping system and manual gate valve enabled
307 isolation of the stainless steel plate during sample exchange, minimizing communication
308 between the simulation chamber and laboratory atmosphere. After the sample was loaded onto
309 the target plate, it was introduced to the Orbitrap chamber through the load lock via a linear-
310 rotary actuator. The pressures in both chambers were monitored via hot-cathode ionization
311 vacuum gauges; all analyses were conducted at pressures $\leq 4 \times 10^{-6}$ Pa. Light emitted from the
312 laser source (266 nm) passed through a fused silica viewport window ($>90\%$ transmission at 266
313 nm) installed on the main vacuum chamber and irradiated the sample at an incident angle of 45°.
314 The laser beam profile at the sample surface was measured at 80 \times 120 μ m, enabling fluences
315 between 0.06 J/cm² (at 1% max energy output) and 6 J/cm² (at 100% max energy output), and
316 irradiances between 0.01 GW/cm² and 1 GW/cm². An external photodiode served to both detect
317 each laser pulse and trigger subsequent operations (*e.g.*, voltage slewing) via a precise timing
318 engine implemented in an FPGA. Different sampling locations on the target plate were accessed
319 by rotating the actuator.

320
321 **Data processing.** Each spectrum was collected at a sampling rate of 5 MHz for either 200 ms
322 (medium-resolution) or 800 ms (high-resolution) transients. A custom LabVIEW based software
323 package [52] was used to regulate experimental sequences, including timing operations, voltage
324 settings and ramp rates, data acquisition, and data processing. Standard data processing
325 techniques included applying Hanning apodization and zero filling raw transient spectra prior to
326 converting the signals to the frequency domain signal via FFT (see Supplement). Each frequency
327 spectrum was calibrated and translated into a conventional mass spectrum using a single peak

328 (*e.g.*, $^{133}\text{Cs}^+$) as an internal standard, and two or more well-characterized peaks (*e.g.*, $^{133}\text{Cs}^+$ and
 329 $^{208}\text{Pb}^+$) to apply an additional linear term to the calibration. Mass accuracy was calculated as the
 330 deviation of the determined mass from the exact mass in parts per million. Mass resolving
 331 powers, calculated at Full Width at Half Maximum (FWHM) peak intensities, were determined
 332 using Gaussian peak fitting functions. To determine CCS, a peak of interest was isolated in the
 333 frequency domain and moved artificially to a lower frequency (reducing computing
 334 requirements); an inverse FFT enabled reconstruction of the decay profile of the selected ion
 335 packet. Chemical species with low signal to noise ratios (*e.g.*, $S/N < 10$) were excluded from this
 336 practice because the high noise floor distorted peak shapes, resulting in inaccurate inversions of
 337 the decay profiles.

338
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342
 343 **Author contributions are as follows:**

NAME	WRITING	EDITING	DATA COLLECTION	DATA ANALYSIS	INSTRUMENT DESIGN	CONCEPT OF OPERATIONS
Ricardo Arevalo Jr.	X		X	X	X	X
Lori Willhite	X	X	X	X		
Anais Bardyn	X	X	X	X		
Ziqin Ni	X	X		X		
Soumya Ray		X	X	X		
Adrian Southard		X	X		X	X
Ryan Danell		X			X	X
Andrej Grubisic		X			X	X
Cynthia Gundersen		X			X	
Niko Minasola		X			X	
Anthony Yu		X			X	
Molly Fahey		X			X	
Emanuel Hernandez		X			X	
Christelle Briois		X			X	
Laurent Thirkell					X	
Fabrice Colin					X	
Alexander Makarov					X	

345 **References**

- 346 1. Johnson, S.S., et al., *Fingerprinting Non-Terran Biosignatures*. *Astrobiology*, 2018. **18**(7): p. 915-
347 922.
- 348 2. Marshall, S.M., A.R.G. Murray, and L. Cronin, *A probabilistic framework for identifying*
349 *biosignatures using Pathway Complexity*. *Philosophical Transactions of the Royal Society A:*
350 *Mathematical, Physical and Engineering Sciences*, 2017. **375**(2109): p. 20160342.
- 351 3. Chan, M.A., et al., *Deciphering Biosignatures in Planetary Contexts*. *Astrobiology*, 2019. **19**(9): p.
352 1075-1102.
- 353 4. Neveu, M., et al., *The Ladder of Life Detection*. *Astrobiology*, 2018. **18**(11): p. 1375-1402.
- 354 5. Lukmanov, R.A., et al., *On Topological Analysis of fs-LIMS Data. Implications for in Situ Planetary*
355 *Mass Spectrometry*. *Frontiers in Artificial Intelligence*, 2021. **4**.
- 356 6. Johnston, S., et al., *Small-volume U–Pb zircon geochronology by laser ablation-multicollector-*
357 *ICP-MS*. *Chemical Geology*, 2009. **259**(3): p. 218-229.
- 358 7. Sagdeev, R.Z. and A.V. Zakharov, *Brief history of the Phobos mission*. *Nature*, 1989. **341**(6243): p.
359 581-585.
- 360 8. Managadze, G.G., et al., *Study of the main geochemical characteristics of Phobos' regolith using*
361 *laser time-of-flight mass spectrometry*. *Solar System Research*, 2010. **44**(5): p. 376-384.
- 362 9. Goesmann, F., et al., *The Mars Organic Molecule Analyzer (MOMA) Instrument: Characterization*
363 *of Organic Material in Martian Sediments*. *Astrobiology*, 2017. **17**(6-7): p. 655-685.
- 364 10. Grubisic, A., et al., *Laser Desorption Mass Spectrometry at Saturn's moon Titan*. *International*
365 *Journal of Mass Spectrometry*, 2021. **470**: p. 116707.
- 366 11. Chumikov, A.E., et al., *LASMA-LR Laser-Ionization Mass Spectrometer Onboard Luna-25 and*
367 *Luna-27 Missions*. *Solar System Research*, 2021. **55**(6): p. 550-561.
- 368 12. Briois, C., et al., *Orbitrap mass analyser for in situ characterisation of planetary environments:*
369 *Performance evaluation of a laboratory prototype*. *Planetary and Space Science*, 2016. **131**: p.
370 33-45.
- 371 13. Willhite, L., et al., *CORALS: A Laser Desorption/Ablation Orbitrap Mass Spectrometer for In Situ*
372 *Exploration of Europa*. *IEEE Aerospace*, 2021.
- 373 14. Makarov, A.A., *Mass spectrometer (Patent 5,886,346)*. 1999, HD Technologies Limited,
374 Manchester, United Kingdom. p. 10.
- 375 15. Arevalo Jr, R., Z. Ni, and R.M. Danell, *Mass spectrometry and planetary exploration: A brief*
376 *review and future projection*. *Journal of Mass Spectrometry*, 2020. **55**(1): p. e4454.
- 377 16. Makarov, A., *Electrostatic Axially Harmonic Orbital Trapping: A High-Performance Technique of*
378 *Mass Analysis*. *Analytical Chemistry*, 2000. **72**(6): p. 1156-1162.
- 379 17. Arevalo Jr, R., et al., *An Orbitrap-based laser desorption/ablation mass spectrometer designed*
380 *for spaceflight*. *Rapid Communications in Mass Spectrometry*, 2018.
- 381 18. Yu, A.W., et al. *The Lunar Orbiter Laser Altimeter (LOLA) laser transmitter*. in *2011 IEEE*
382 *International Geoscience and Remote Sensing Symposium*. 2011.
- 383 19. Mallocci, G., G. Mulas, and C. Joblin, *Electronic absorption spectra of PAHs up to vacuum UV*.
384 *A&A*, 2004. **426**(1): p. 105-117.
- 385 20. Cloutis, E.A., et al., *Ultraviolet spectral reflectance properties of common planetary minerals*.
386 *Icarus*, 2008. **197**(1): p. 321-347.
- 387 21. Fahey, M., et al., *Ultraviolet Laser Development for Planetary Lander Missions*. *IEEE Aerospace*
388 (Big Sky, MT), 2020: p. 11 pp.
- 389 22. Büttner, A., et al. *Optical design and characterization of the MOMA laser head flight model for*
390 *the ExoMars 2020 mission*. in *Proc.SPIE*. 2019.

- 391 23. Jenner, F.E. and H.S.C. O'Neill, *Major and trace analysis of basaltic glasses by laser-ablation ICP-*
392 *MS*. *Geochemistry, Geophysics, Geosystems*, 2012. **13**(3).
- 393 24. Humayun, M., F.A. Davis, and M.M. Hirschmann, *Major element analysis of natural silicates by*
394 *laser ablation ICP-MS*. *Journal of Analytical Atomic Spectrometry*, 2010. **25**(7): p. 998-1005.
- 395 25. Longerich, H.P., D. Günther, and S.E. Jackson, *Elemental fractionation in laser ablation*
396 *inductively coupled plasma mass spectrometry*. *Fresenius' Journal of Analytical Chemistry*, 1996.
397 **355**(5): p. 538-542.
- 398 26. Alterman, M.A., N.V. Gogichayeva, and B.A. Kornilayev, *Matrix-assisted laser*
399 *desorption/ionization time-of-flight mass spectrometry-based amino acid analysis*. *Analytical*
400 *Biochemistry*, 2004. **335**(2): p. 184-191.
- 401 27. Sarracino, D. and C. Richert, *Quantitative MALDI-TOF MS of oligonucleotides and a nuclease*
402 *assay*. *Bioorganic & Medicinal Chemistry Letters*, 1996. **6**(21): p. 2543-2548.
- 403 28. Chumbley, C.W., et al., *Absolute Quantitative MALDI Imaging Mass Spectrometry: A Case of*
404 *Rifampicin in Liver Tissues*. *Analytical Chemistry*, 2016. **88**(4): p. 2392-2398.
- 405 29. Zubarev, R.A. and A. Makarov, *Orbitrap Mass Spectrometry*. *Analytical Chemistry*, 2013. **85**(11):
406 p. 5288-5296.
- 407 30. Makarov, A., et al., *Dynamic range of mass accuracy in LTQ orbitrap hybrid mass spectrometer*.
408 *Journal of the American Society for Mass Spectrometry*, 2006. **17**(7): p. 977-982.
- 409 31. Hoegg, E.D., et al., *Isotope ratio characteristics and sensitivity for uranium determinations using*
410 *a liquid sampling-atmospheric pressure glow discharge ion source coupled to an Orbitrap mass*
411 *analyzer*. *Journal of Analytical Atomic Spectrometry*, 2016. **31**(12): p. 2355-2362.
- 412 32. Hofmann, A.E., et al., *Using Orbitrap mass spectrometry to assess the isotopic compositions of*
413 *individual compounds in mixtures*. *International Journal of Mass Spectrometry*, 2020. **457**: p.
414 116410.
- 415 33. Hardouin, J., *Protein sequence information by matrix-assisted laser desorption/ionization in-*
416 *source decay mass spectrometry*. *Mass Spectrometry Reviews*, 2007. **26**(5): p. 672-682.
- 417 34. Franchi, M., J.P. Ferris, and E. Gallori, *Cations as Mediators of the Adsorption of Nucleic Acids on*
418 *Clay Surfaces in Prebiotic Environments*. *Origins of life and evolution of the biosphere*, 2003.
419 **33**(1): p. 1-16.
- 420 35. Trumbo, S.K., M.E. Brown, and K.P. Hand, *Sodium chloride on the surface of Europa*. *Science*
421 *Advances*, 2019. **5**(6): p. eaaw7123.
- 422 36. Postberg, F., et al., *A salt-water reservoir as the source of a compositionally stratified plume on*
423 *Enceladus*. *Nature*, 2011. **474**: p. 620.
- 424 37. De Sanctis, M.C., et al., *Fresh emplacement of hydrated sodium chloride on Ceres from ascending*
425 *salty fluids*. *Nature Astronomy*, 2020. **4**(8): p. 786-793.
- 426 38. Hand, K.P., et al., *Report of the Europa Lander Science Definition Team*. 2017, NASA HQ:
427 Washington, DC.
- 428 39. Hendrix, A.R., et al., *The NASA Roadmap to Ocean Worlds*. *Astrobiology*, 2018. **19**(1): p. 1-27.
- 429 40. Waite Jr, J.H., et al., *Liquid water on Enceladus from observations of ammonia and 40Ar in the*
430 *plume*. *Nature*, 2009. **460**(7254): p. 487-490.
- 431 41. Altwegg, K., H. Balsiger, and S.A. Fuselier, *Cometary Chemistry and the Origin of Icy Solar System*
432 *Bodies: The View After Rosetta*. *Annual Review of Astronomy and Astrophysics*, 2019. **57**(1): p.
433 113-155.
- 434 42. Guzman, M., et al., *Collecting amino acids in the Enceladus plume*. *International Journal of*
435 *Astrobiology*, 2018. **18**(1): p. 47-59.
- 436 43. Takayama, M., *In-source decay characteristics of peptides in matrix-assisted laser*
437 *desorption/ionization time-of-flight mass spectrometry*. *Journal of the American Society for*
438 *Mass Spectrometry*, 2001. **12**(4): p. 420-427.

- 439 44. Katta, V., D.T. Chow, and M.F. Rohde, *Applications of In-Source Fragmentation of Protein Ions for*
440 *Direct Sequence Analysis by Delayed Extraction MALDI-TOF Mass Spectrometry*. Analytical
441 Chemistry, 1998. **70**(20): p. 4410-4416.
- 442 45. Sanders, J.D., et al., *Determination of Collision Cross-Sections of Protein Ions in an Orbitrap Mass*
443 *Analyzer*. Analytical Chemistry, 2018. **90**(9): p. 5896-5902.
- 444 46. Makarov, A. and E. Denisov, *Dynamics of ions of intact proteins in the Orbitrap mass analyzer*.
445 *Journal of the American Society for Mass Spectrometry*, 2009. **20**(8): p. 1486-1495.
- 446 47. Anupriya, C.A. Jones, and D.V. Dearden, *Collision Cross Sections for 20 Protonated Amino Acids:*
447 *Fourier Transform Ion Cyclotron Resonance and Ion Mobility Results*. *Journal of the American*
448 *Society for Mass Spectrometry*, 2016. **27**(8): p. 1366-1375.
- 449 48. Chyba, C. and C. Sagan, *Endogenous production, exogenous delivery and impact-shock synthesis*
450 *of organic molecules: an inventory for the origins of life*. *Nature*, 1992. **355**(6356): p. 125-132.
- 451 49. Poppe, A.R., *An improved model for interplanetary dust fluxes in the outer Solar System*. *Icarus*,
452 2016. **264**: p. 369-386.
- 453 50. Taylor, S.R. and S.M. McLennan, *The significance of the rare earths in geochemistry and*
454 *cosmochemistry*, in *Handbook on the Physics and Chemistry of Rare Earths*. 1988, Elsevier. p.
455 485-578.
- 456 51. Steinbrügge, G., et al., *Brine Migration and Impact-Induced Cryovolcanism on Europa*.
457 *Geophysical Research Letters*, 2020. **47**(21): p. e2020GL090797.
- 458 52. Danell, R., et al., *A Full Featured, Flexible, and Inexpensive 2D and 3D Ion Trap Control*
459 *Architecture and Software Package*. *Proceedings of the 58th ASMS Conference on Mass*
460 *Spectrometry and Allied Topics (Salt Lake City, UT), 2010*.

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