Orbitrap-HRMS for calibration of hypervelocity ice grain space detectors: OLYMPIA

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MOTIVATION

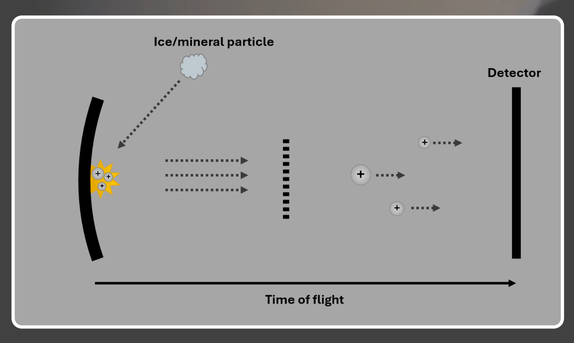
Laser-Induced Liquid Beam Ion Desorption (LILBID) coupled with a time-of-flight (ToF) has been the primary laboratory tool to replicate space hypervelocity impacts of water **ice grains from icy moons**, playing an essential role in interpreting Cassini-CDA (Cosmic Dust Analyser) data from Enceladus[1,2].

Born from an international collaboration, **OLYMPIA (Orbitrap anaLYser MultiPle IonisAtion)** is capable of reproducing high-velocity impact analogues of icy grains (20 km/s)[3]. Recent modifications have further enhanced this powerful instrument, providing even better analytical capabilities such as high mass resolution, high mass accuracy, broad mass range and high sensitivity, which are crucial to support NASA's Europa Clipper (SUDA) and ESA's L4 mission to Enceladus.

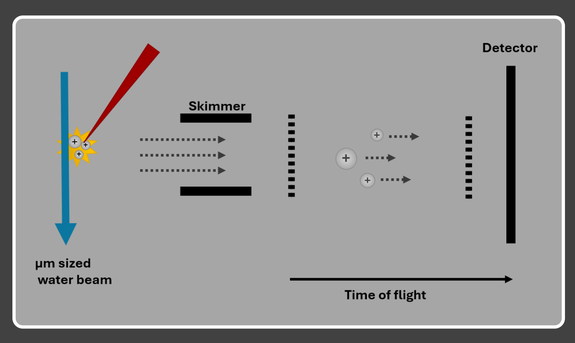
These exceptional analytical characteristics, together with its small size, highlight the strong potential that **Orbitrap-based** mass spectrometers offer for **future planetary missions**, as an alternative to broadly used time-of-flight (ToF) mass spectrometers.

METHODS

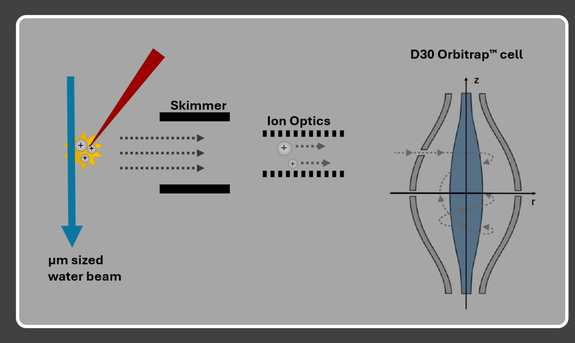
Impact Ionisation



LILBID - ToF



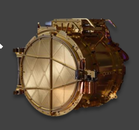
LILBID - OLYMPIA



LOW RESOLUTION — HIGH RESOLUTION

CDA
R(m/Δm) ~ 20-50

Direct in-situ sampling of Saturn's E-ring and Enceladus' plume. Discovered salty ice grains, silica nanoparticles, and organic precursors [4,5]

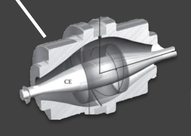


SUDA
R(m/Δm) ~ 250

Onboard Europa Clipper. Positive and negative mode. Capable of identifying amino acids, fatty acids, and DNA nucleobases

LILBID-ToF
Laboratory analogue experiments
R(m/Δm) ~ 800

Simulates ice grain impacts across a wide range of impact speeds in the lab; limited by peak overlaps in complex organic mixtures



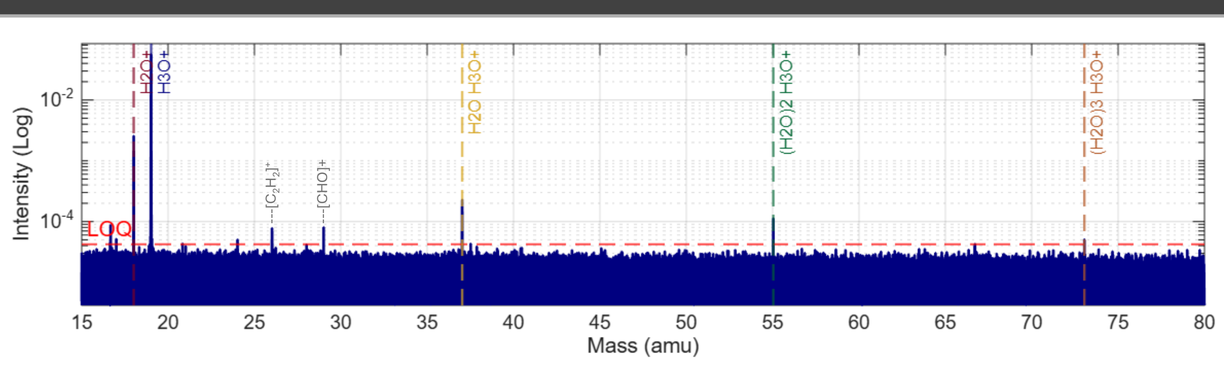
OLYMPIA
R(m/Δm) ↑100000

LILBID coupled with an Orbitrap mass analyzer
Simulates ice grain impacts and enables precise isotopic analysis and unambiguous separation of isobaric peak overlaps

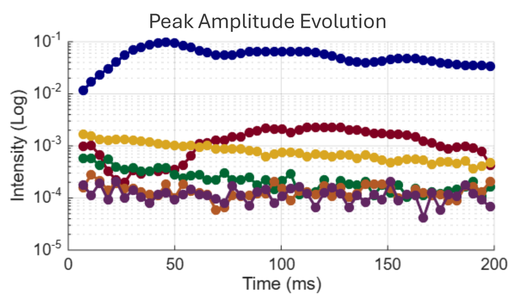
RESULTS

IR Laser / LILBID Coupling

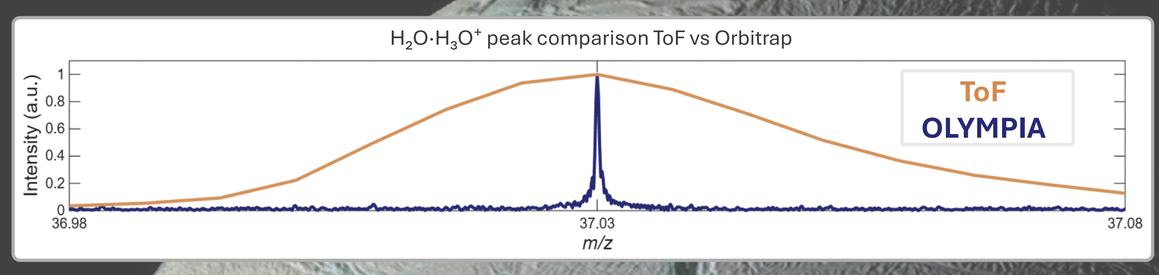
- Successful coupling of LILBID to the Orbitrap enabled the **capture of water ions and water clusters**, which is of vital importance for analogue velocity matching[2]



- Water clusters are not only present but also exhibit **stability over time**, which is a key parameter, as longer transient times lead to higher mass resolution
- Performance comparisons demonstrate superior analytical capabilities over previous instrument generations

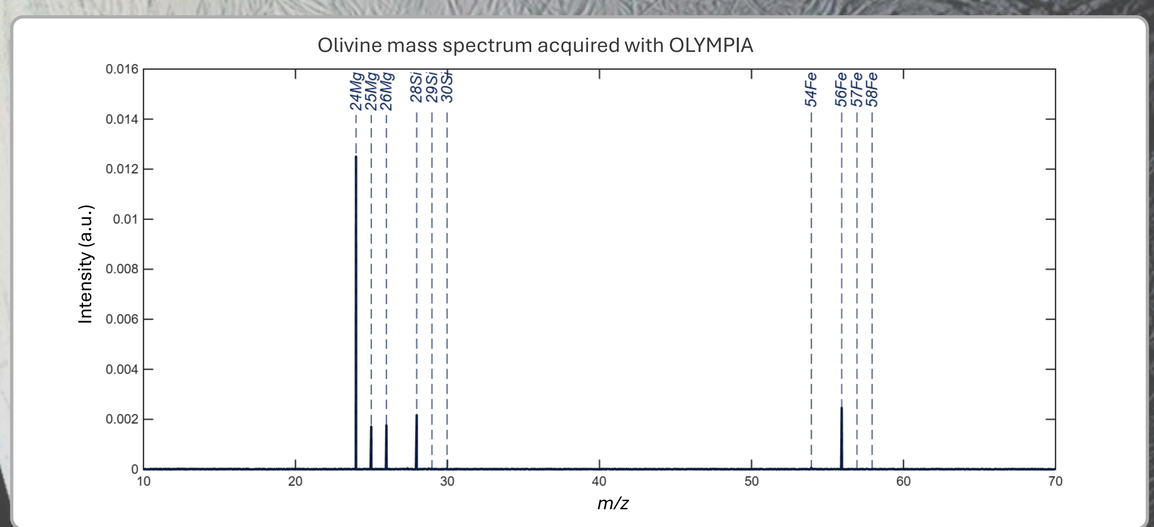


Ion	Exp Mass	R(m/Δm)	SNR	Acc(ppm)
H2O+	18.0099	82250.7	604.0	-4.0
H3O+	19.0178	114443.2	13341.6	+0.0
H2O H3O+	37.0278	91399.8	53.8	-0.3
(H2O)2 H3O+	55.0378	48551.6	26.6	-0.8
(H2O)3 H3O+	73.0478	61138.4	12.0	-1.1



UV Laser Ablation

- **UV ionization was evaluated and reference mineral spectra was obtained. The data collected exhibit expected values of resolution and sensitivity, therefore making the combination valuable for laser ablation/desorption purposes.**



CONCLUSSIONS

- We have **successfully captured water ions** in the orbitrap and more importantly, **water clusters** at an unprecedented resolution. This opens viability to use the orbitrap in the study of analogue hypervelocity ice grain impacts.

- Compatibility of OLYMPIA with UV Lasers and IR Lasers showcase the versatility of the instrument, supporting the use of Orbitrap for planetary exploration.

Check out our lab!

EUROPA CLIPPER

WHAT'S NEXT?

- In the near future, optimization efforts will focus on accurately replicating analogue spectra taken at slower velocities (~5 km/s)[2]. This can be achieved by working at lower laser energy density (< 15,000 MW/cm²) and controlling the delay time of ion extraction.

- Additionally, testing planetary/astrobiology-relevant compounds will build reference databases for the Europa Clipper mission, while demonstrating OLYMPIA's versatile coupling establishing Orbitrap technology for future space exploration

References:

[1] Srama, R., Ahrens, T. J., Altobelli, N., Auer, S., Bradley, J. G., Burton, M., ... & Zook, H. A. (2004). The Cassini Cosmic Dust Analyzer. *Space Science Reviews*, *114*(1–4), 465–518. [2] Klenner F, Postberg F, Hillier J, et al. Analogue spectra for impact ionization mass spectra of water ice grains obtained at different impact speeds in space. Rapid Commun Mass Spectrom. 2019;33:1751–1760. [3] Sanderink, A., Klenner, F., Zymak, I., Žabka, J., Postberg, F., Lebreton, J. P., ... & Briois, C. (2023). OLYMPIA-LILBID: A new laboratory setup to calibrate spaceborne hypervelocity ice grain detectors using high-resolution mass spectrometry. *Analytical Chemistry*, *95*(7), 3621–3628. [4] Postberg, F., Khawaja, N., Abel, B., Choblet, G., Glein, C. R., Gudipati, M. S., ... & Perry, M. E. (2018). Macromolecular organic compounds from the depths of Enceladus. Nature, 558(7711), 564–568. [5] Hsu, H.-W.; Postberg, F.; Sekine, Y.; Shibuya, T.; Kempf, S.; Horanyi, M.; Juhasz, A.; Altobelli, N.; Suzuki, K.; Masaki, Y.;Kuwatani, T.; Tachibana, S.; Sirono, S.; Moragas-Klostermeyer, G.; Srama, R. Ongoing Hydrothermal Activities within Enceladus. Nature2015, 519, 207–210.

Let's connect!
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