A Method to Discriminate between Abiotic and Biotic Processes on Cryovolcanically Active Ocean Worlds

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A Method to Discriminate between Abiotic and Biotic Processes on Cryovolcanically Active Ocean Worlds – What to expect?

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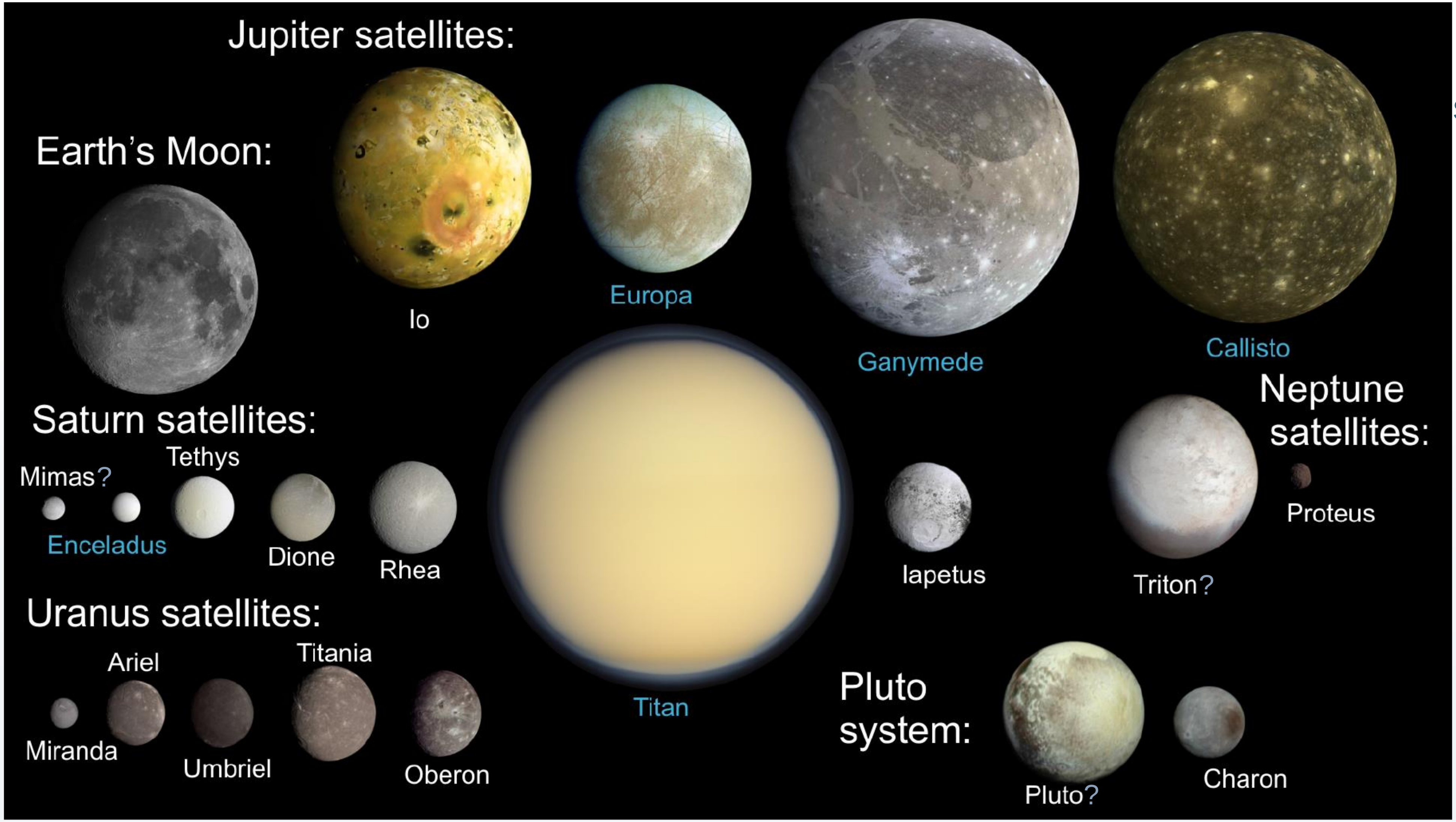
- Identifying and distinguishing between abiotic and biotic signatures of organic molecules is key to the search for life on extraterrestrial ocean worlds
- Impact ionization mass spectrometers can potentially achieve this by sampling ice grains formed from ocean water and ejected by moons (e.g., Enceladus)
- Here, we extend previous high-sensitivity laser based analogue experiments on biomolecules (Klenner et al. 2020a) to investigate the mass spectra of amino acids and fatty acids at simulated abiotic and biotic relative abundances
- Other organic and inorganic compounds are added to the biosignature mixtures to account for the complex background matrix expected to emerge from a salty Enceladean ocean that has been in chemical exchange with a carbonaceous rocky core
- Unfragmented molecular spectral signatures of amino acids and fatty acids reflect the original relative abundances of the parent molecules → Characteristic abiotic and biotic relative abundance patterns can be identified
- We also determine the detection limits of the biosignatures under Enceladus-like conditions

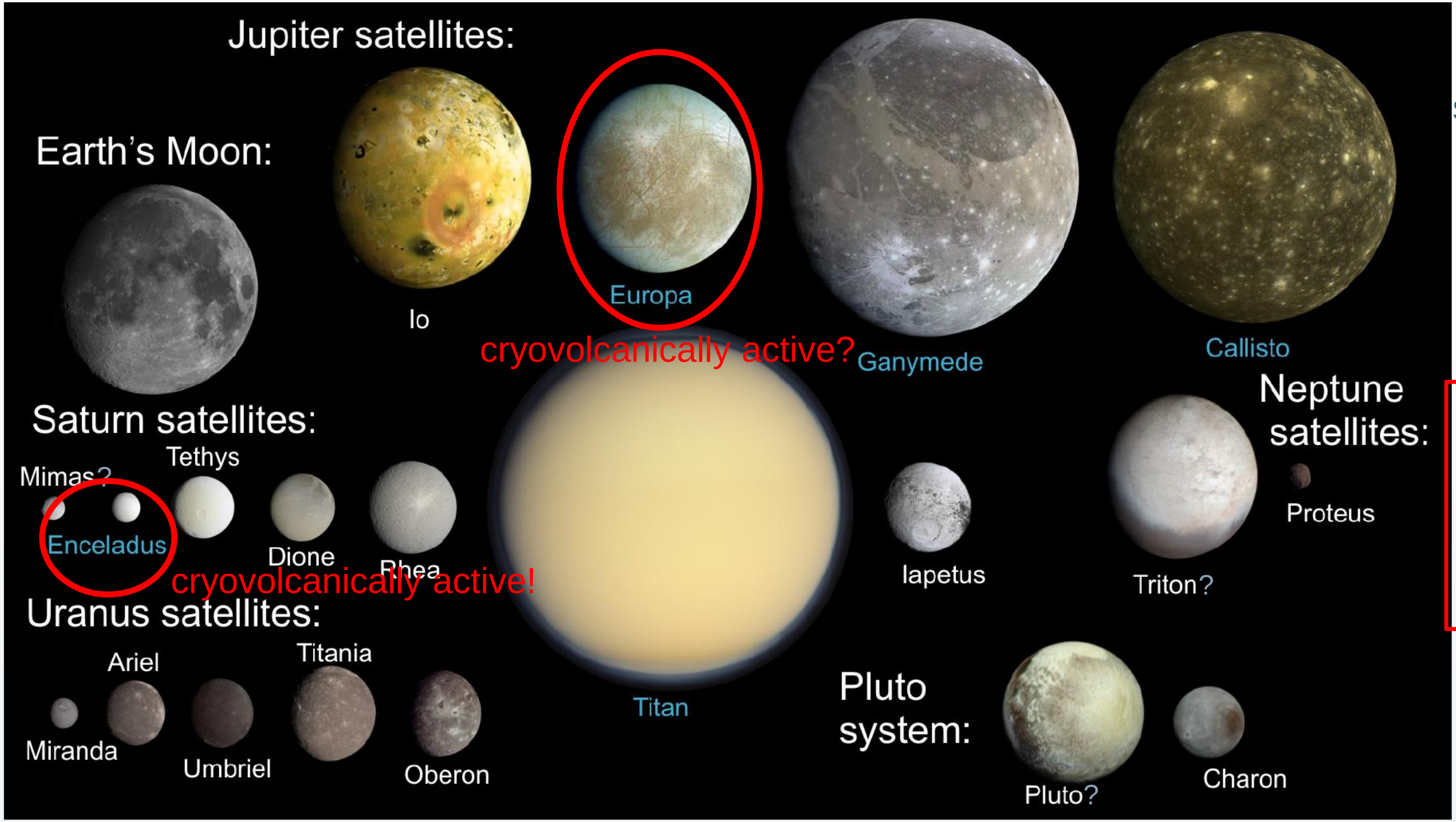
Ocean worlds in the Solar System



subsurface ocean confirmed

Nimmo & Pappalardo 2016

Ocean worlds in the Solar System



subsurface ocean confirmed

Enceladus and Europa's rocky cores are in contact with the subsurface ocean → Potential source of heat and biologically important elements

Nimmo & Pappalardo 2016

Enceladus feeds Saturn‘s E ring with ejected ice grains

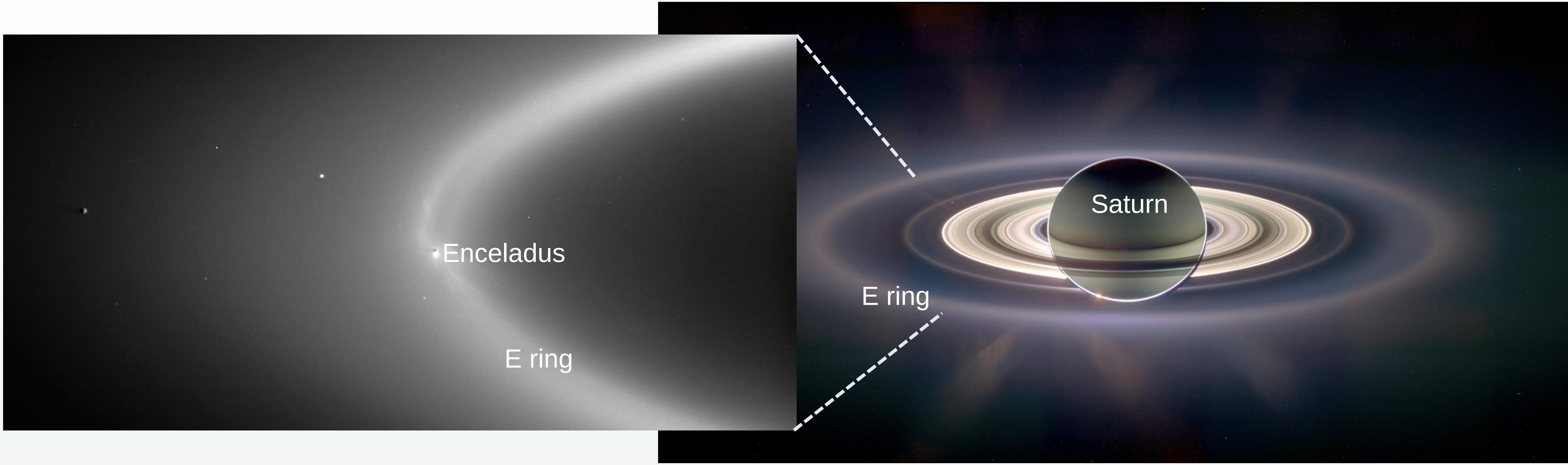


Image credit: NASA/JPL

Ice grain sampling by Cassini

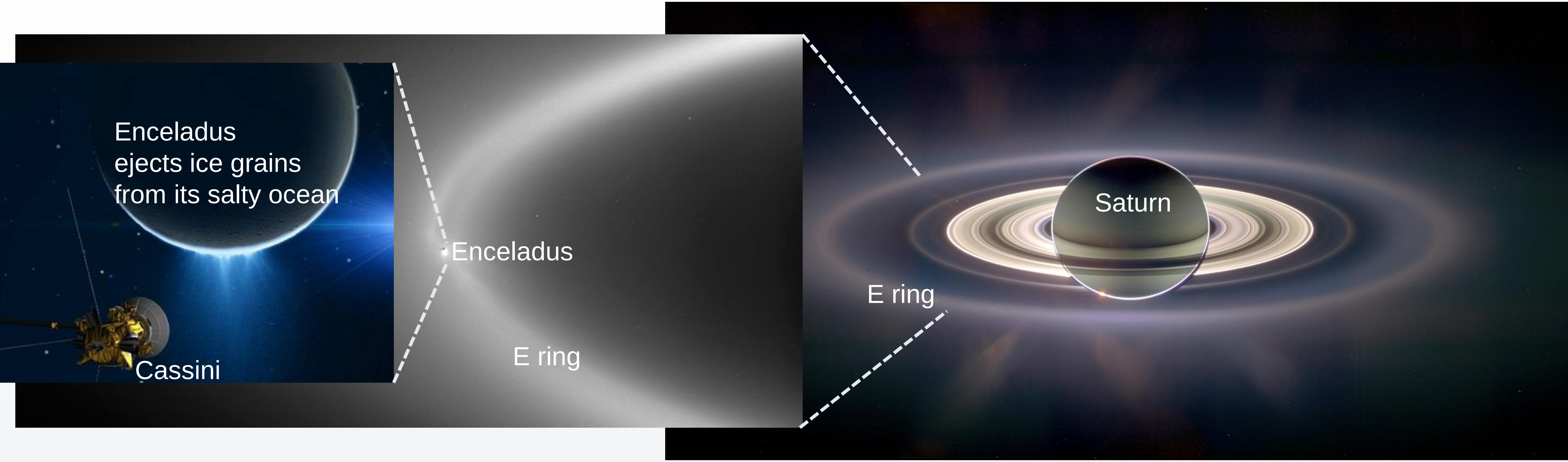
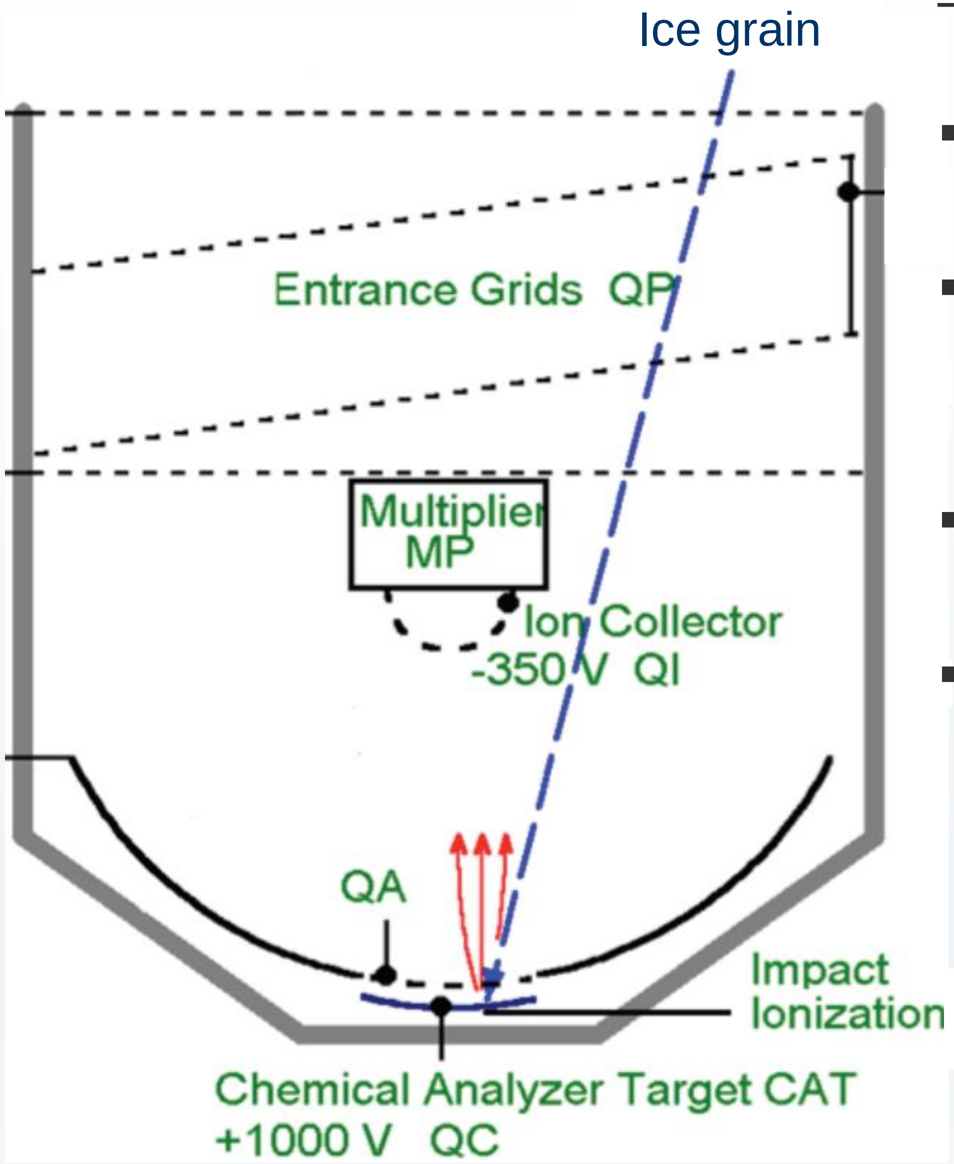


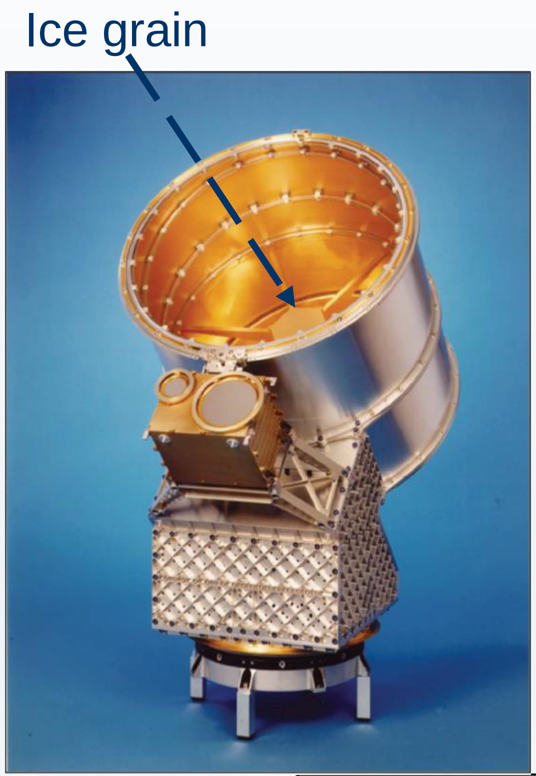
Image credit: NASA/JPL

The Cosmic Dust Analyzer (CDA) – The ice grain sampling instrument on-board Cassini



CDA generates impact ionization mass spectra of the ice grains!

- Sensitive to cations
- Determines impact rates, mass, speed, electric charge, and composition of the detected ice grain
- Mass resolution: 20 – 50 m/Δm
- Maximum recorded mass: ~ 200 u



Srama et al. 2004

CDA already sampled organics ejected by Enceladus

- Complex organic macromolecules (Postberg et al. 2018)

- Nitrogen- and oxygen-bearing organics that could act as amino acid precursors (Khawaja et al. 2019)

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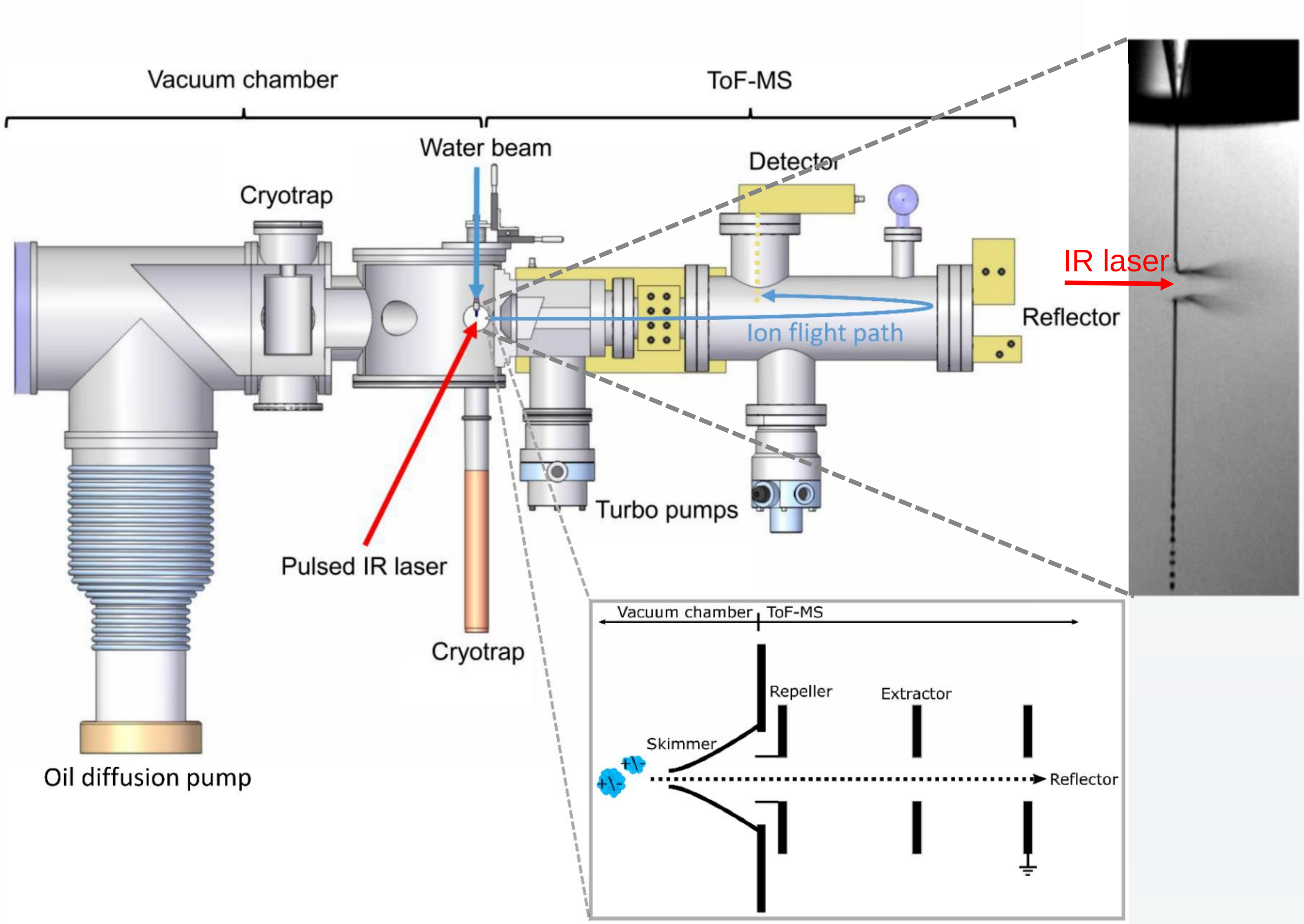
Could future impact ionization instruments also detect potential biosignatures (amino acids, fatty acids, peptides)?
→ YES: Klenner et al. 2020a

AND

Could future impact ionization instruments even discriminate between abiotic and biotic signatures in ice grains?
→ This work (Klenner et al. 2020b)!

Analogue experiment to reproduce impact ionization mass spectra: LILBID-ToF-MS (Laser Induced Liquid Beam Ion Desorption Time of Flight Mass Spectrometry)

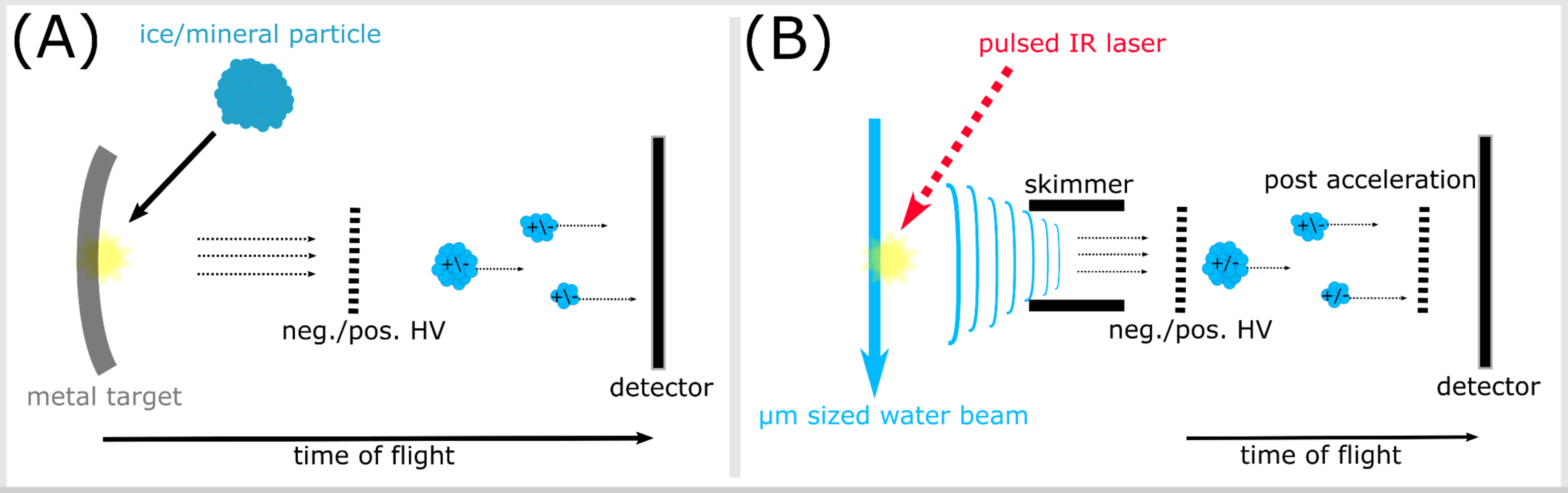


Klenner et al. 2019

- Liquid beam: r = 7 – 10 µm
- Vacuum chamber: P ≈ 5 x 10^{-5} mbar
- Laser: λ ≈ 2850 nm

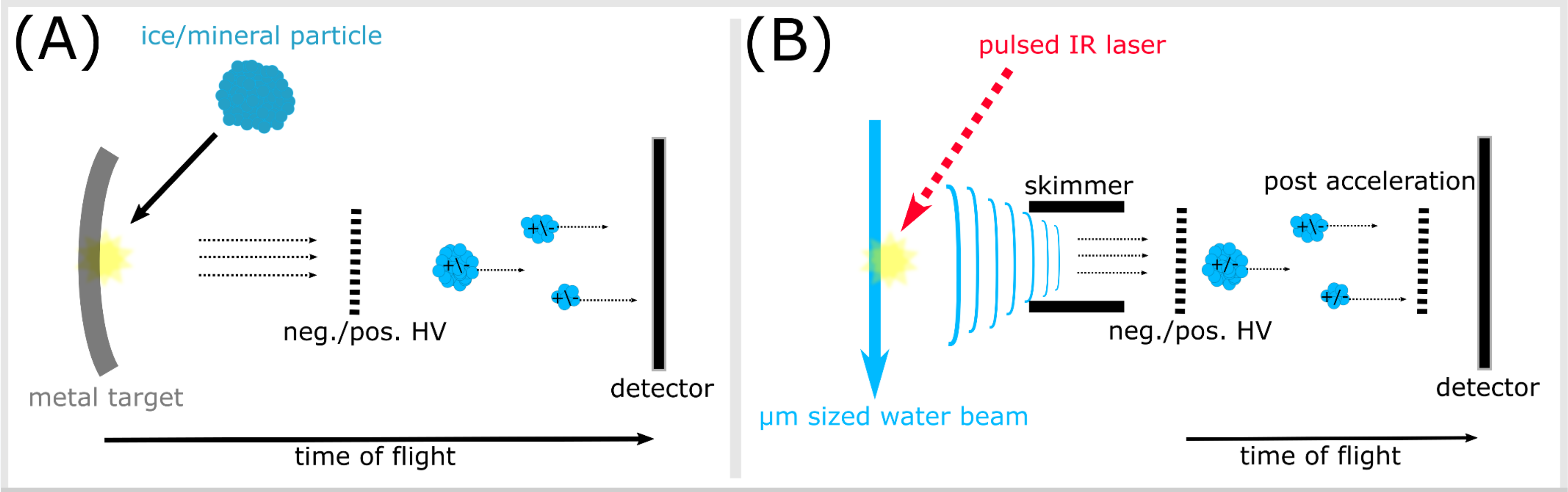
  I_{max} ≈ 1200 MW/cm^2
- ToF-MS: 600 – 800 m/Δm

(A) impact ionization in space and (B) laser desorption in the laboratory

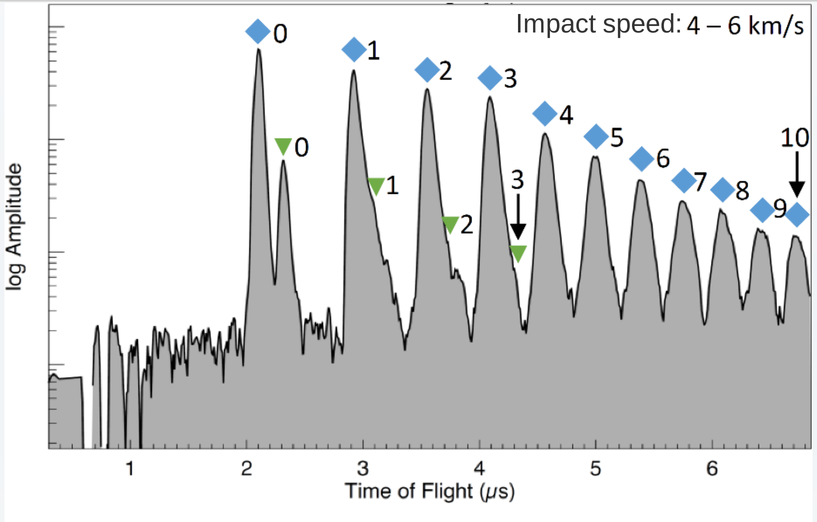


Klenner et al. 2019

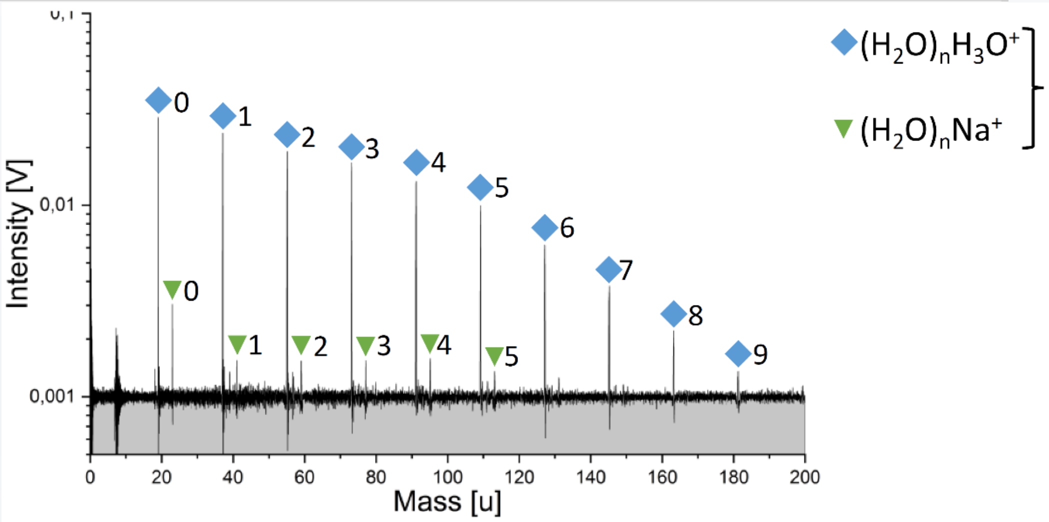
(A) impact ionization in space and (B) laser desorption in the laboratory



Klenner et al. 2019



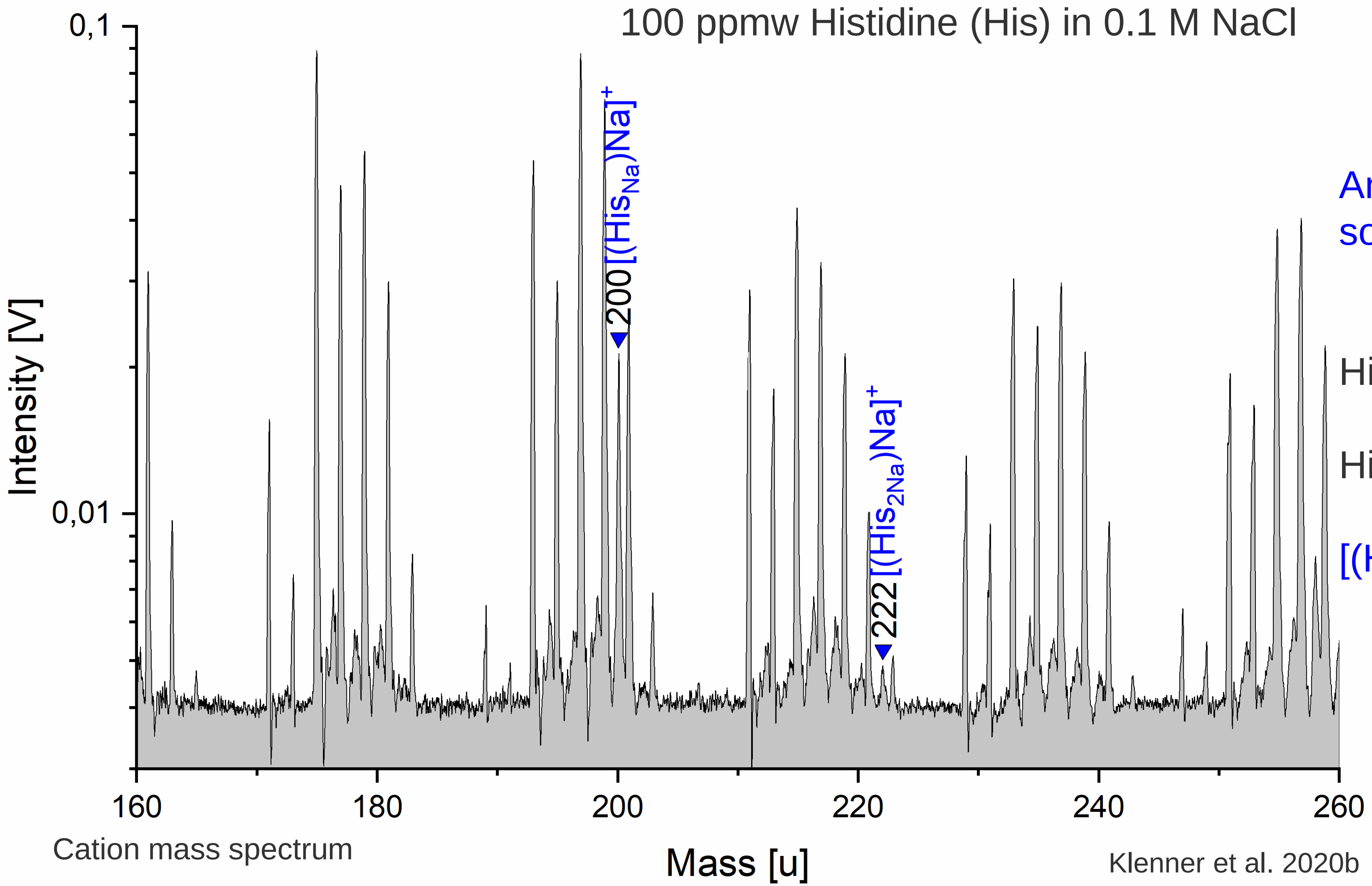
CDA spectrum of a nearly pure water ice grain



n is labeled besides the respective symbol.

Laboratory spectrum of a 10^{-7} M NaCl solution

Amino acids: spectral appearance in salty solutions



Cation mass spectrum

Klenner et al. 2020b

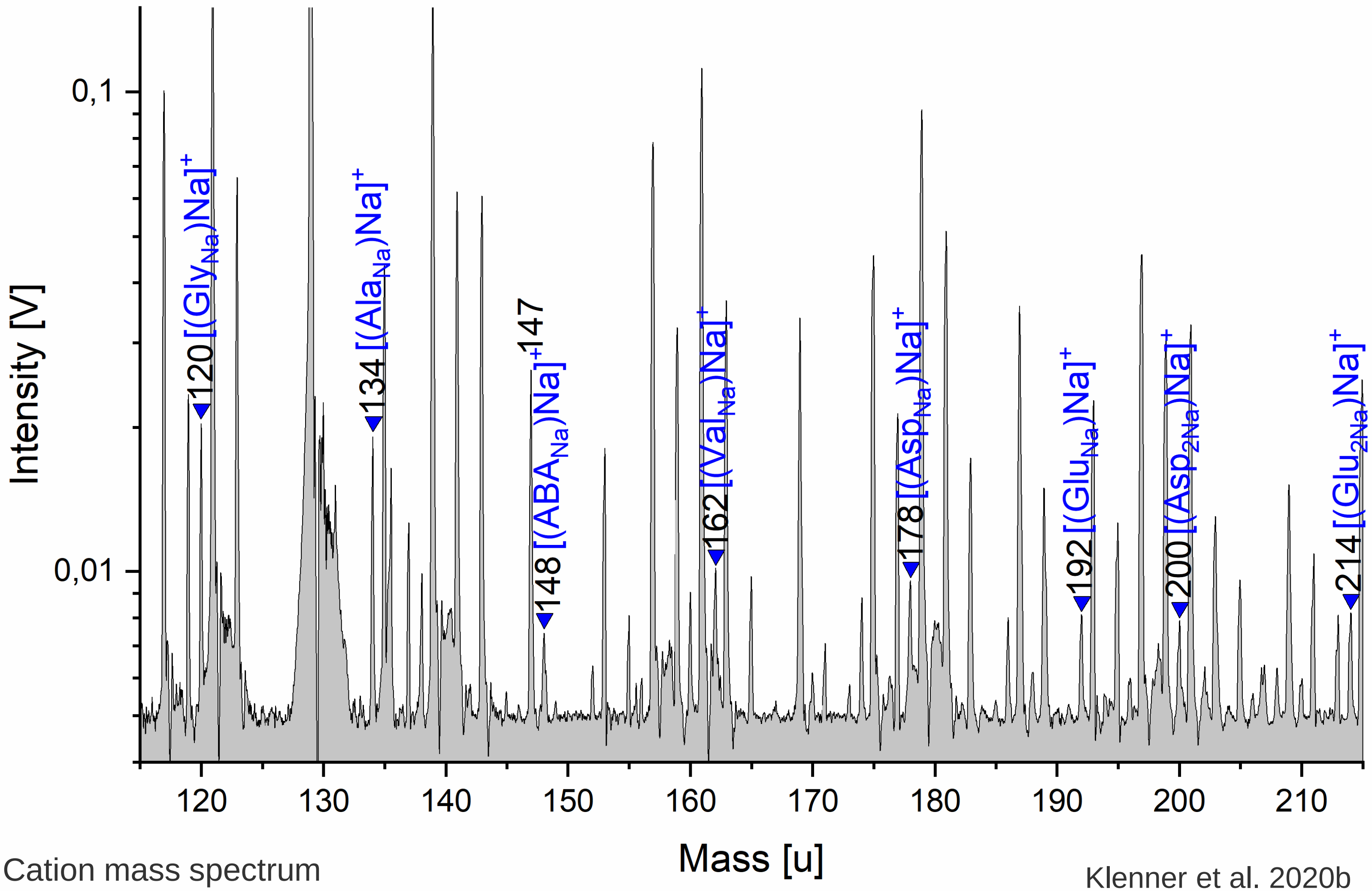
Amino acids are detectable as sodiated amino acid molecules

$His - [H]^+ + [Na]^+ \rightarrow His_{Na}$

$His_{Na} + [Na]^+ \rightarrow [(His_{Na})Na]^+$

$[(His_{Na})Na]^+ - [H]^+ + [Na]^+ \rightarrow [(His_{2Na})Na]^+$

Amino acids in abiotic abundance ratios in a salty Enceladus-like solution containing carboxylic acids



Cation mass spectrum

Klenner et al. 2020b

Sodiated peaks of Gly and Ala dominate the other sodiated amino acid peaks

Gly: Glycine
Ala: Alanine
ABA: Aminobutyric acid
Val: Valine
Asp: Aspartic acid
Glu: Glutamic acid

Detection limits of amino acids in a salty Enceladus-like solution

Amino acid	Molecular weight [u]	Detected ion		Detection limit [µmol/L]
		$[(AA_{Na})Na]^+$	$[(AA_{2Na})Na]^+$	
Glycine (Gly)	75			270
Serine (Ser)	105			19
Ornithine (Orn)	132			78
Histidine (His)	155			13
				161
Citrulline (Cit)	175			117
				286
Tyrosine (Tyr)	181			55
				11
Threonine (Thr)	119			83
Arginine (Arg)	174			56
				5740
Aspartic acid (Asp)	133			15
				4
Glutamic acid (Glu)	147			34
				3

AA: Amino acid

Klenner et al. 2020b

Fatty acids in abiotic and biotic abundance ratios

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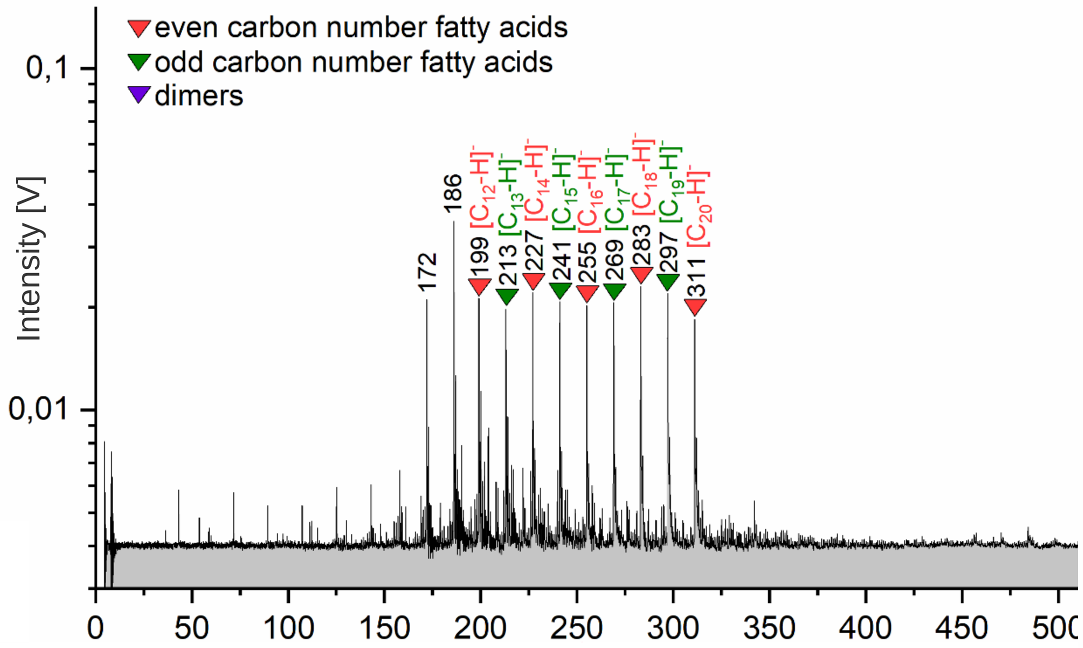
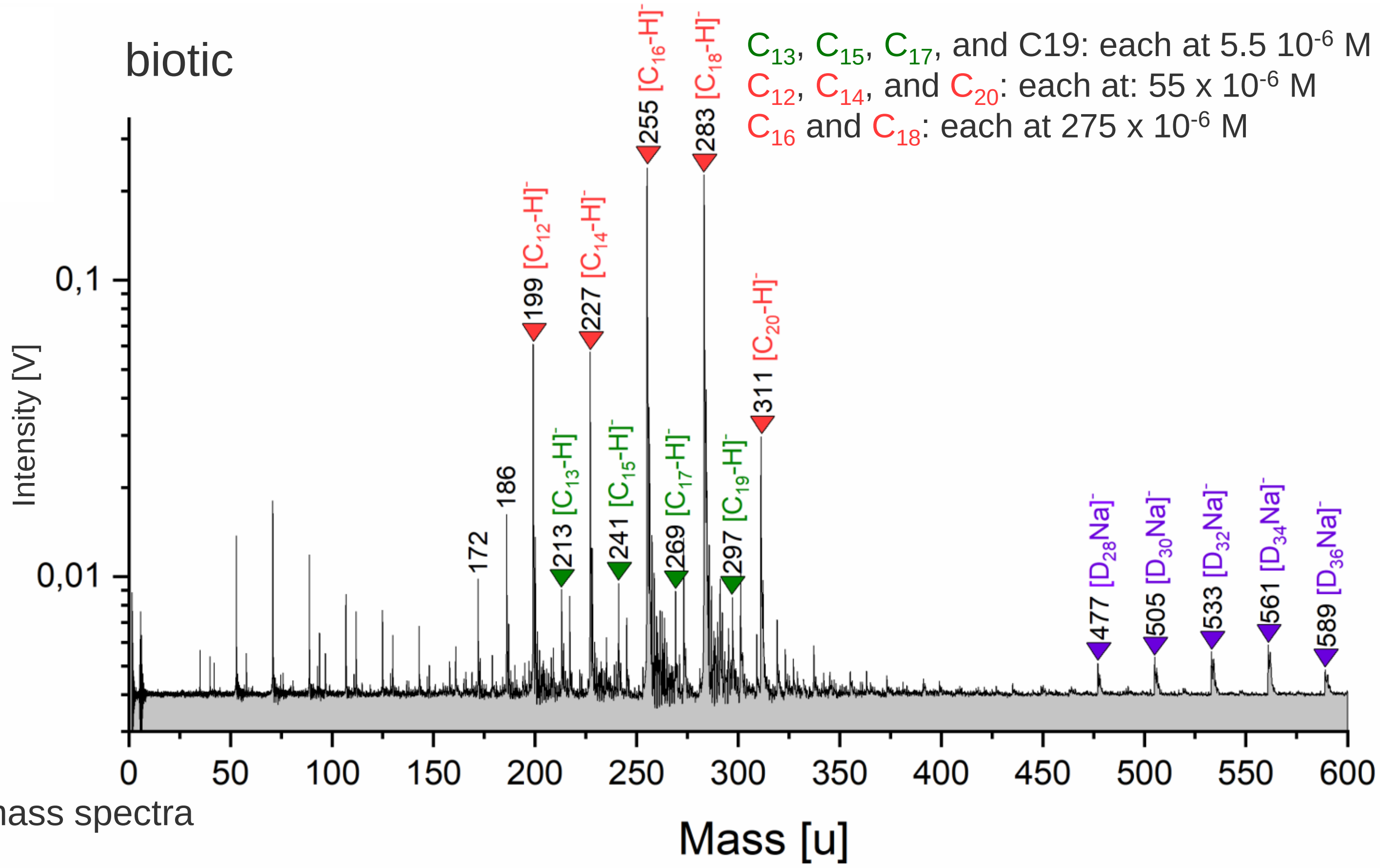
abiotic

each fatty acid at a concentration of 5.5 x 10^{-6} M



biotic

C_{13}, C_{15}, C_{17}, and C19: each at 5.5 10^{-6} M
C_{12}, C_{14}, and C_{20}: each at: 55 x 10^{-6} M
C_{16} and C_{18}: each at 275 x 10^{-6} M



Anion mass spectra

Klenner et al. 2020b

Approximately equally high peak amplitudes
(consistent with the equal fatty acid concentrations)

Peak amplitudes reflect the concentration differences!

Amino acids and fatty acids in biotic abundance ratios together in one solution with background compounds

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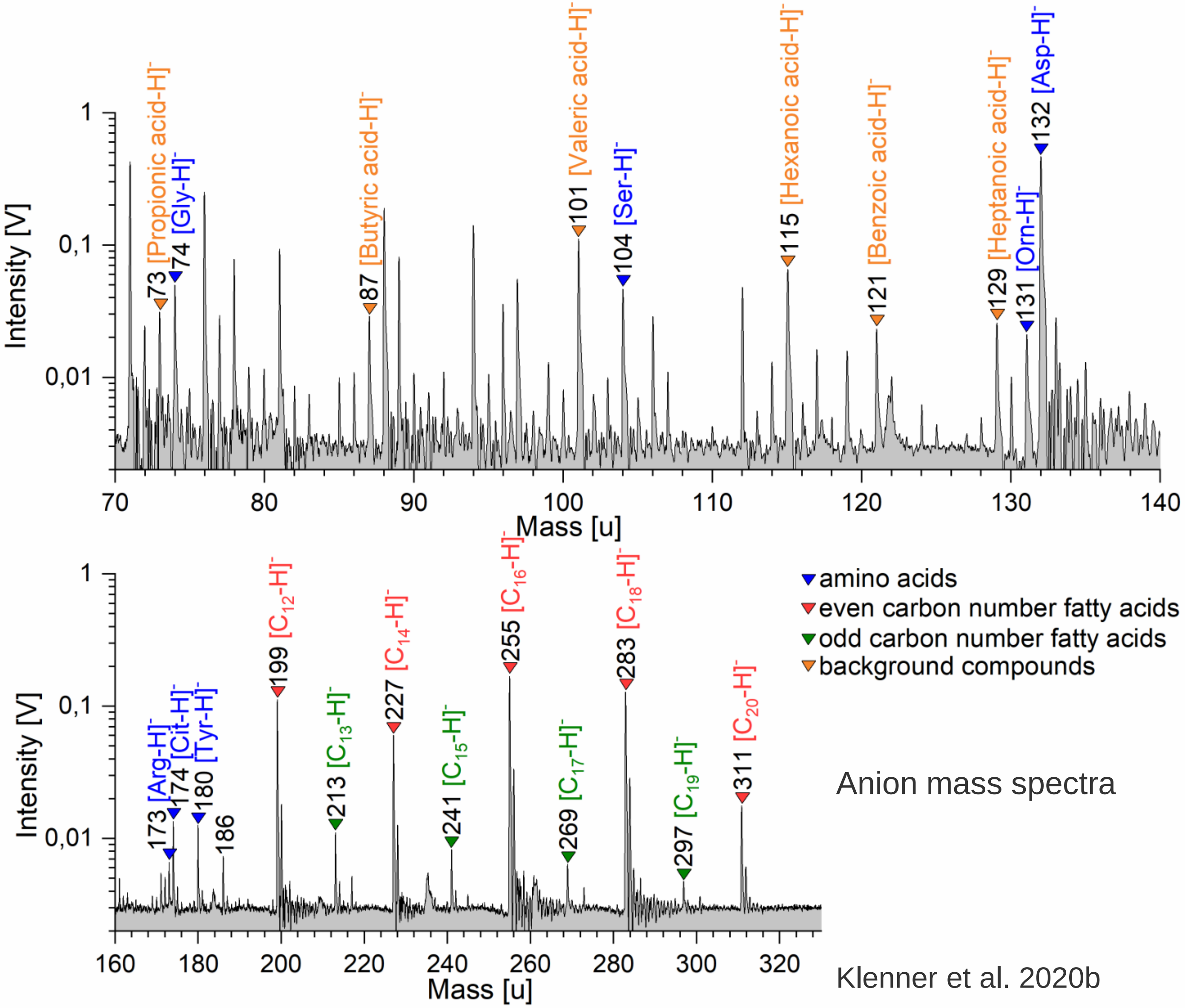


Anion mass spectra

Klenner et al. 2020b

- Amino acids and fatty acids clearly identifiable
- Amino acids other than Gly dominate
- Biotic abundance pattern of fatty acids observable
- Most background compounds detectable

Conclusions and outlook

- Laboratory laser desorption mass spectra are highly comparable to impact ionization mass spectra recorded in space
- Amino acids form characteristic sodiated molecular peaks in salty solutions
- Amino acids favor forming cations whereas fatty acids favor forming anions → Future flight instrument should be capable of detecting both cations and anions
- Detection limits of amino acids and fatty acids are, salinity dependent, at the µM or nM level → expected to be even lower for space instruments
- Abundances of the organics at given concentrations are reflected in the peak amplitudes of their characteristic molecular peaks
- The potential biosignatures can be recognized on icy moons with a subsurface ocean and characteristic abiotic and biotic signatures can be identified → Europa Clipper mission + other upcoming missions
- Laboratory detection thresholds transformed into recommended spacecraft-ice grain encounter velocities (Klenner et al. 2019) aids mission planning for future space missions → impact speeds of 4 – 6 km/s are found to be optimal to investigate potential biosignatures
- The survivability of organics appears to be significantly improved when the molecules are protected by a liquid or frozen water matrix
- Future work will be to investigate a wide range of organic compounds (e.g., E.coli DNA and cellular material) in matrices designed to mimic ice grains derived from a range of realistic oceanic compositions for Enceladus and Europa
- We are currently developing a comprehensive spectrum reference library for in situ space detectors from a wide variety of analogue materials in icy grains

Full citations of the used literature

- Khawaja, N., Postberg, F., Hillier, J., Klenner, F., Kempf, S., Nölle, L., Reviol, R., Zou, Z., and Srama, R. (2019) Low mass nitrogen-, oxygen-bearing and aromatic compounds in Enceladean ice grains. *Mon Not R Astron Soc* **489**:5231–5243.

- Klenner, F., Postberg, F., Hillier, J., Khawaja, N., Reviol, R., Srama, R., Abel, B., Stolz, F., and Kempf, S. (2019) Analogue spectra for impact ionization mass spectra of water ice grains obtained at different impact speeds in space. *Rapid Commun Mass Spectrom* **33**:1751–1760.

- Klenner, F., Postberg, F., Hillier, J., Khawaja, N., Reviol, R., Stolz, F., Cable, M.L., Abel, B., and Nölle, L. (2020a) Analog Experiments for the Identification of Trace Biosignatures in Ice Grains from Extraterrestrial Ocean Worlds. *Astrobiology* **20**:179–189.

- Klenner, F., Postberg, F., Hillier, J., Khawaja, N., Cable, M.L., Abel, B., Kempf, S., Glein, C.R., Lunine, J.I., Hodyss, R., Reviol, R., and Stolz, F. (2020b) Discriminating Abiotic and Biotic Fingerprints of Amino Acids and Fatty Acids in Ice Grains Relevant to Ocean Worlds. *Astrobiology* **20**:in press.

- Nimmo, F., and Pappalardo, R.T. (2016) Ocean worlds in the outer solar system. *J Geophys Res Planets* **121**:1378–1399.

- Postberg, F., Khawaja, N., Abel, B., Choblet, G., Glein, C.R., Gudipati, M.S.,Henderson, B.L.,Hsu, H.-W.,Kempf, S., Klenner, F., Moragas-Klostermeyer, G., Magee, B., Nölle, L., Perry, M., Reviol, R., Schmidt, J., Srama, R., Stolz, F., Tobie, G., Trieloff, M., and Waite, J.H. (2018) Macromolecular organic compounds from the depths of Enceladus. *Nature* **558**:564–568.

- Srama, R., Ahrens, T.J., Altobelli, N., Auer, S., Bradley, J.G., Burton, M., Dikarev, V.V., Economou, T., Fechtig, H., Görlich, M., Grande,M., Graps, A.,Grün,E., Havnes,O., Helfert, S.,Horanyi, M., Igenbergs, E., Jessberger, E.K., Johnson, T.V., Kempf, S., Krivov, A.V., Krüger, H., Mocker-Ahlreep, A., Moragas-Klostermeyer, G., Lamy, P., Landgraf, M., Linkert, D., Linkert, G., Lura, F., McDonnell, J.A.M., Möhlmann, D., Morfill, G.E., Müller, M., Roy, M., Schäfer, G., Schlotzhauer, G., Schwehm, G.H., Spahn, F., Stübig, M., Svestka, J., Tschernjawski, V., Tuzzolino, A.J., Wäsch, R., and Zook, H.A. (2004) The Cassini Cosmic Dust Analyzer. *Space Sci Rev* **114**:465–518.

Backup

Hypervelocity impact signals onto CDA

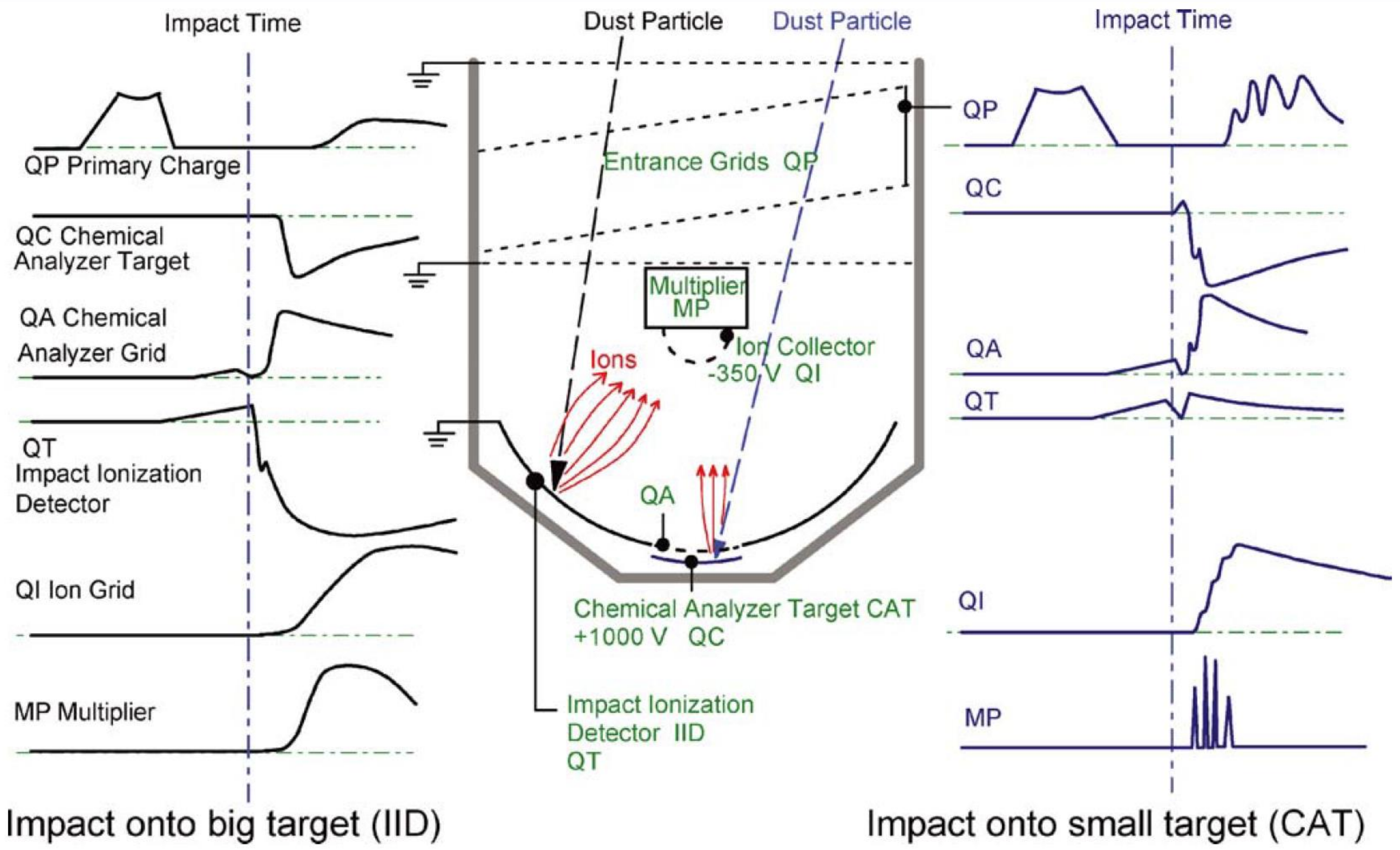
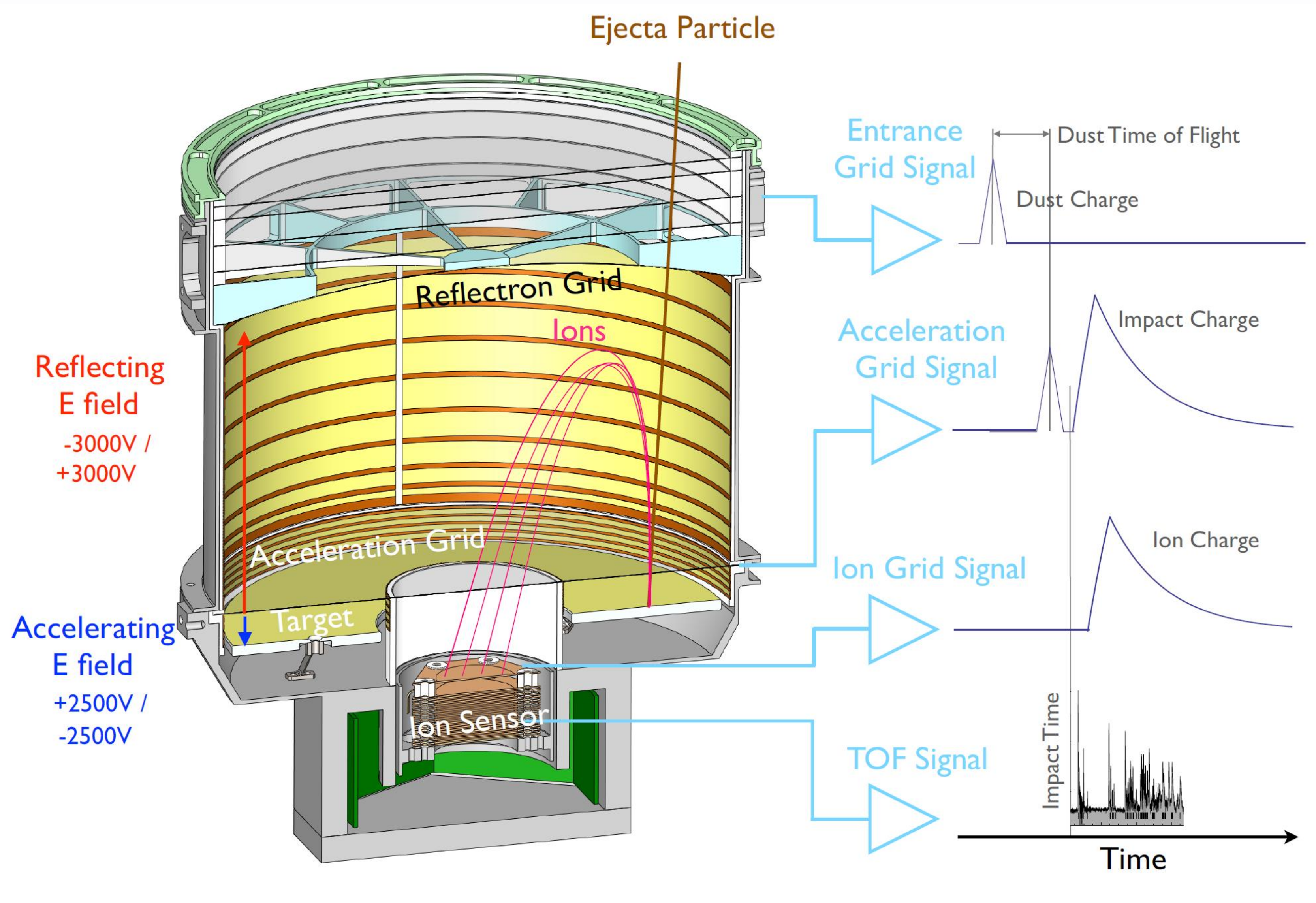


Figure 6. Hypervelocity impact signals of dust grains onto the big Impact Ionization Target (left) and onto the Chemical Analyzer Target (right). The chemical analyzer is a time-of-flight mass spectrometer and provides the elemental composition of the impacting dust grain.

Srama et al. 2004

SUrface Dust Analyzer (SUDA) on-board the Europa Clipper mission

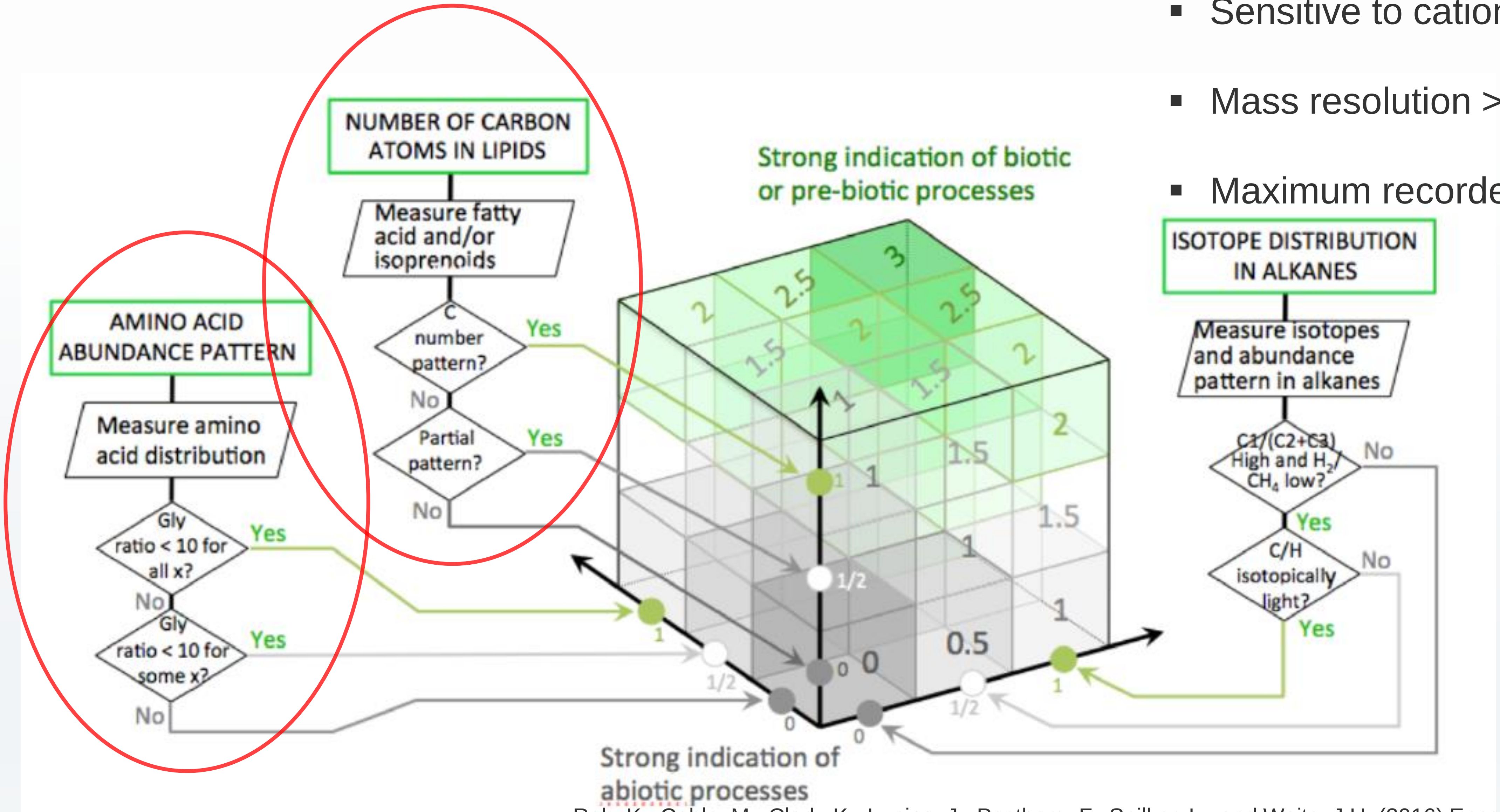


- Sensitive to cations and anions
- Mass resolution: 150 – 200 m/Δm
- Maximum recorded mass: 500 u

Kempf, S., Altobelli, N., Briois, C., Grün, E., Horanyi, M., Postberg, F., Schmidt, J., Srama, R., Sternovsky, Z., Tobie, G., and Zolotov, M. (2014) SUDA: a dust mass spectrometer for compositional surface mapping for a mission to Europa. *Eur Planet Sci Congr* **9**:EPSC2014-229.

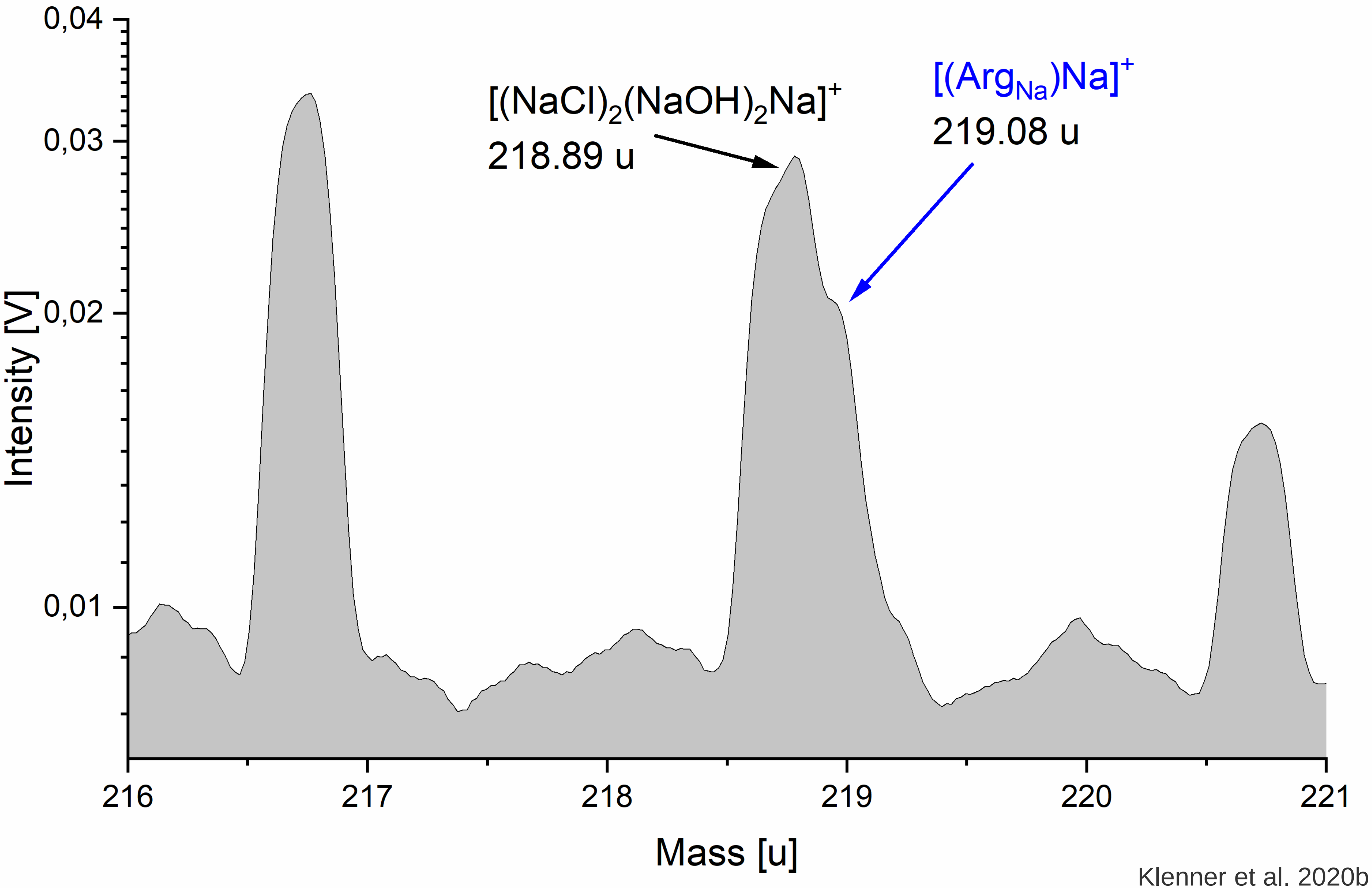
Proposed future impact ionization instrument: Enceladus Ice Analyzer (ENIA) to detect (a-)biotic chemistry

- Sensitive to cations and anions
- Mass resolution > 2000 m/Δm
- Maximum recorded mass: 2000 u



Reh, K., Cable, M., Clark, K., Lunine, J., Postberg, F., Spilker, L., and Waite, J.H. (2016) Enceladus life finder: the search for life in a habitable moon. *IEEE Aerosp Conf*, doi: 10.1109/AERO.2016.7500813.

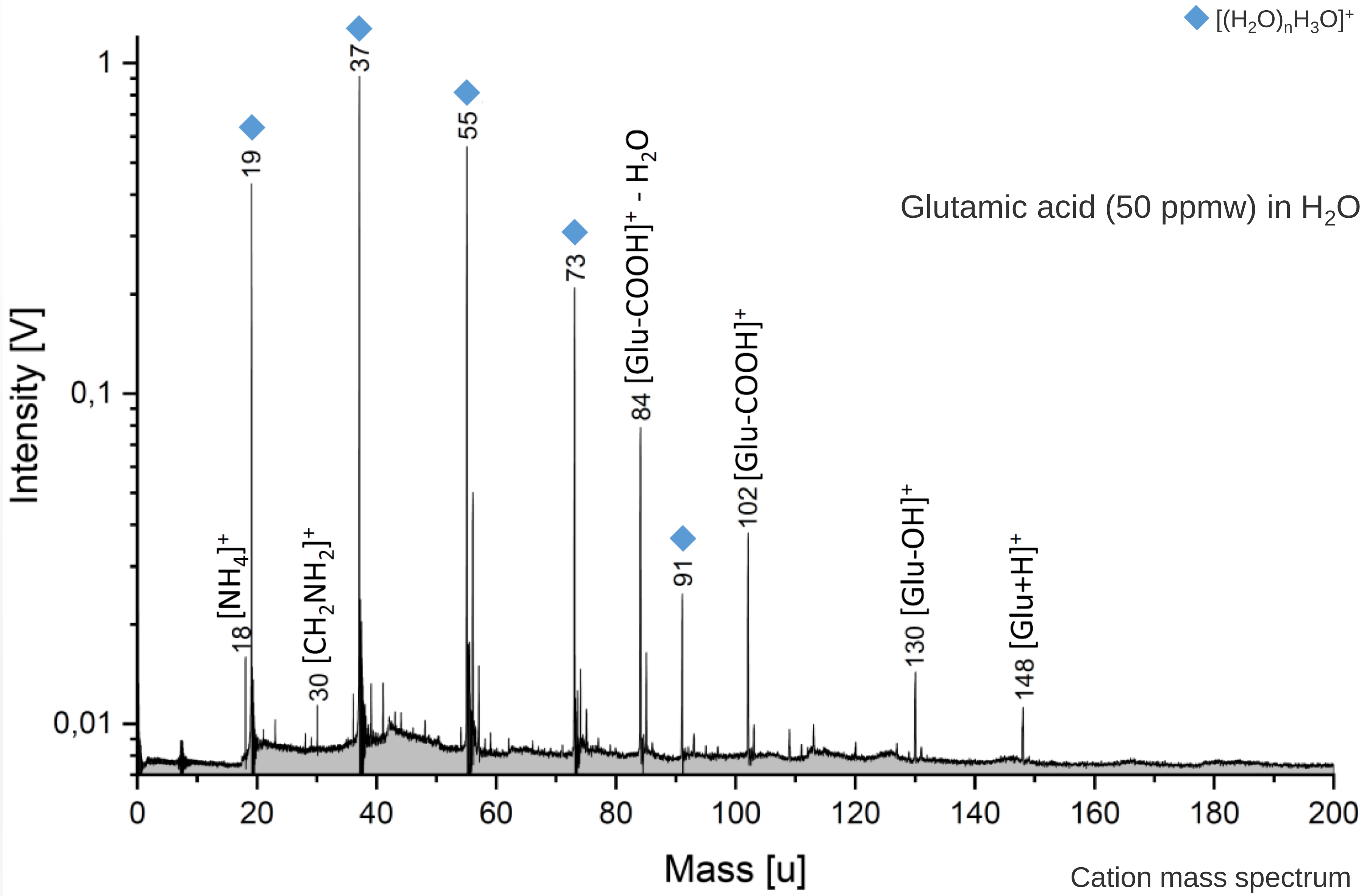
Interferences of ≈ 0.2 u can be resolved with the available mass resolution of 600 – 800 m/Δm



Arg: Arginine

Klenner et al. 2020b

Amino acids: spectral appearance in pure water



Klenner et al. 2020a

Amino acids: detection limits in pure water

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Amino acid	Molecular weight [u]	Detected ion		Detection limit [µmol/L]
		$[M+H]^+$	$[M-H]^-$	
Glycine (Gly)	75			7
				1
Serine (Ser)	105			10
				19
Ornithine (Orn)	132			0.02
				15
Histidine (His)	155			0.01
				13
Citrulline (Cit)	175			1
				6
Tyrosine (Tyr)	181			11
				11
Alanine (Ala)	89			2
Lysine (Lys)	146			0.001
Arginine (Arg)	174			0.001
Aspartic acid (Asp)	133			0.1
Glutamic acid (Glu)	147			0.1

M: Molecule

Klenner et al. 2020a

Peptides in pure water: spectral appearance in cation mass spectra

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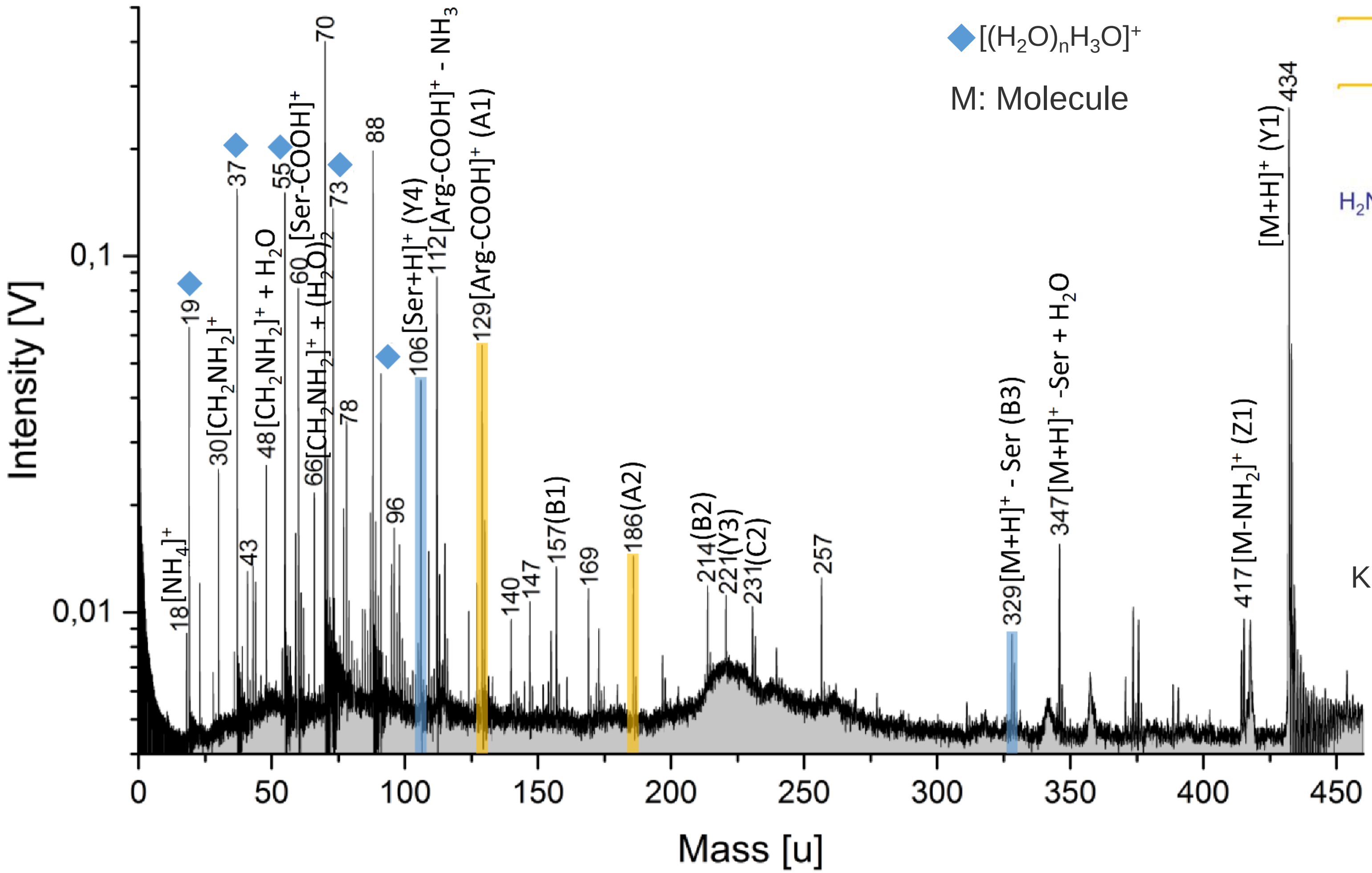
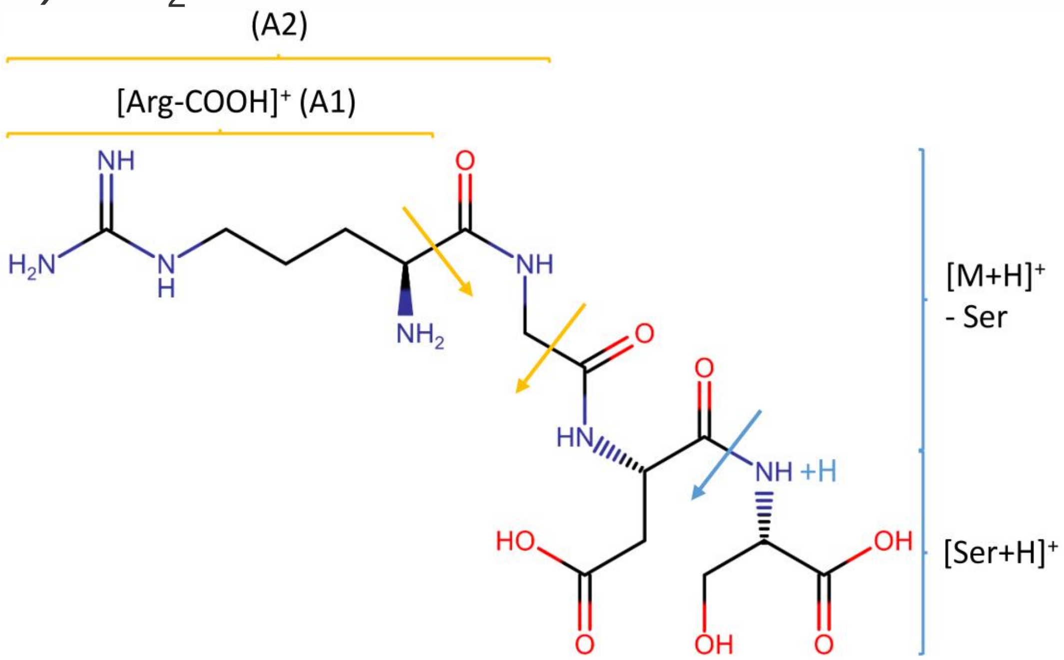
Arg-Gly-Asp-Ser (1000 ppmw) in H_2O





Klenner et al. 2020a

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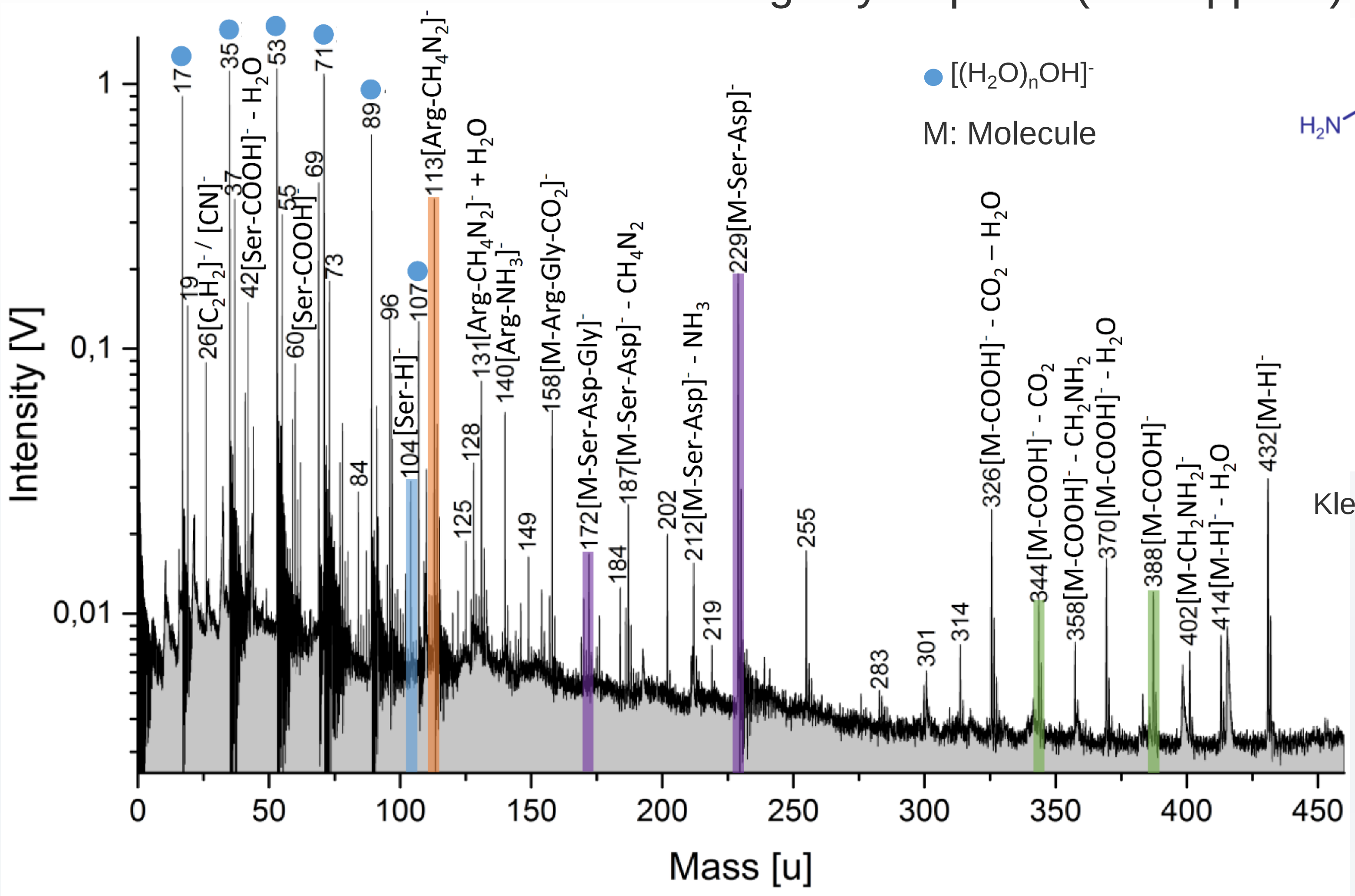

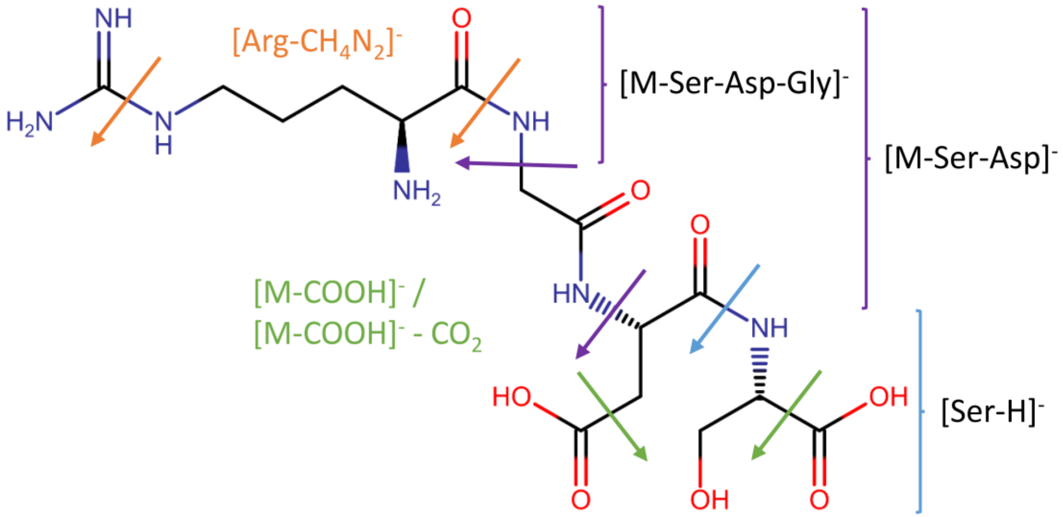

Klenner et al. 2020a