GEOW INSTITUT FÜR GEOWISSENSCHAFTEN

UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386

Mass Spectrometry of Astrobiologically Relevant Organic Material – Implications on Future Space Missions to Ocean Worlds in the Outer Solar System

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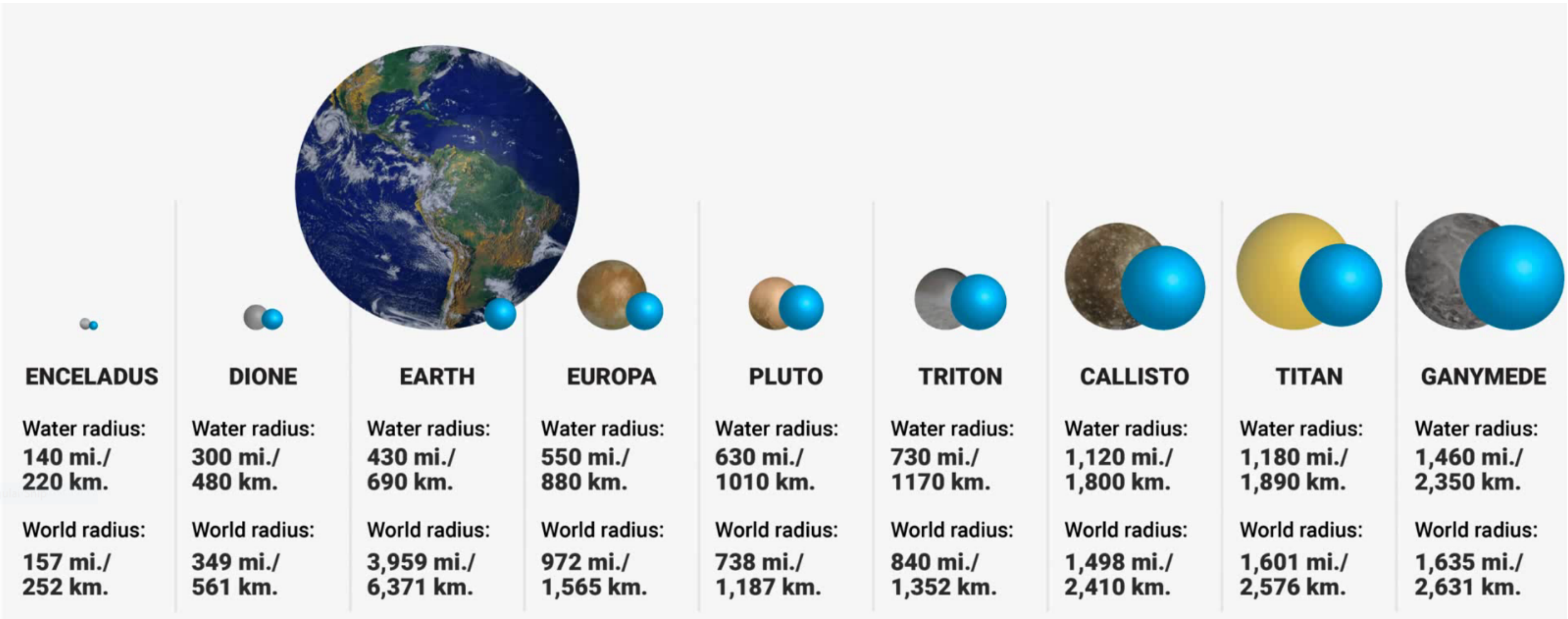
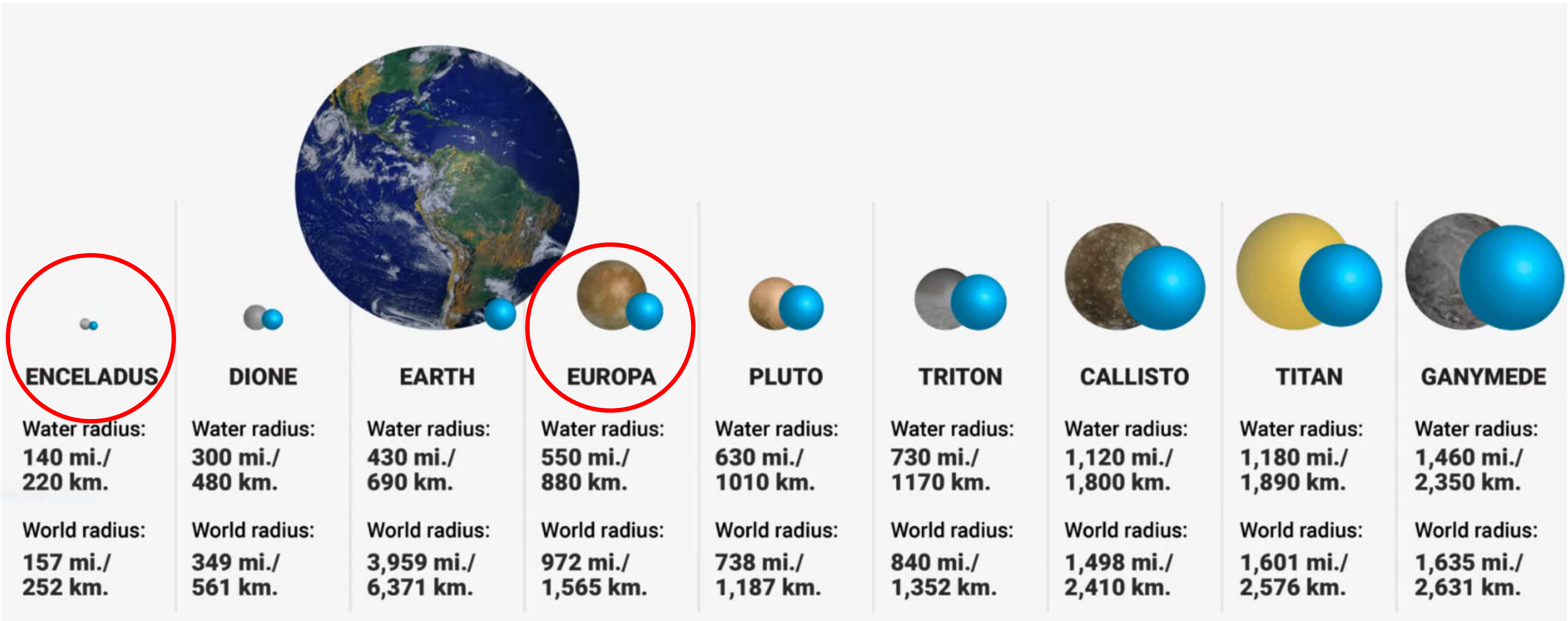
51st ESLAB Symposium - Extreme Habitable Worlds
ESA ESTEC, The Netherlands

The Solar System‘s ocean worlds



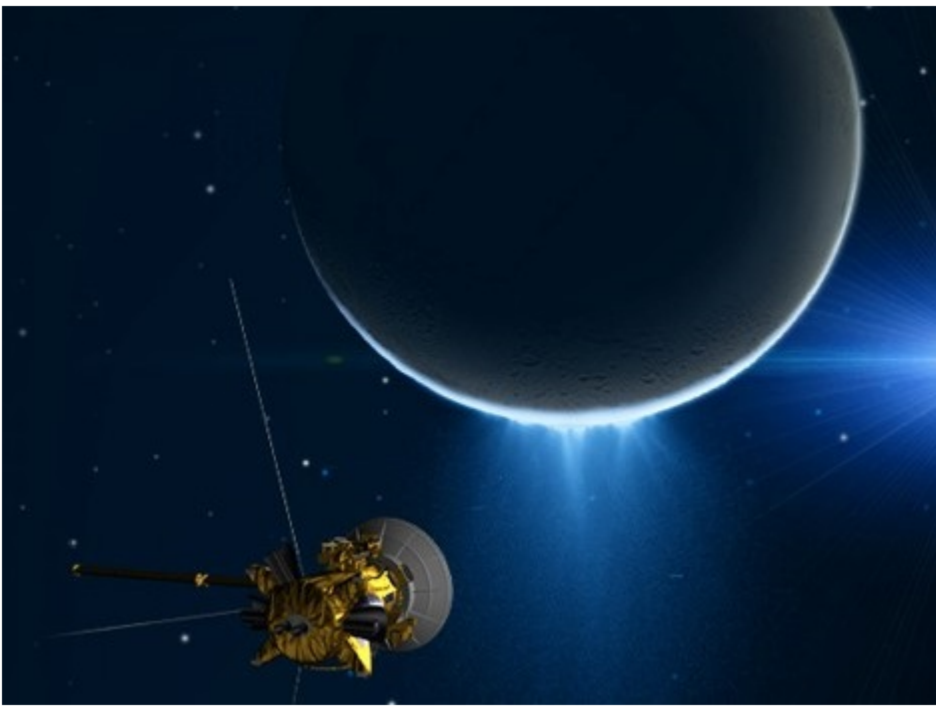
Steve Vance; NASA/JPL-Caltech

The Solar System's ocean worlds

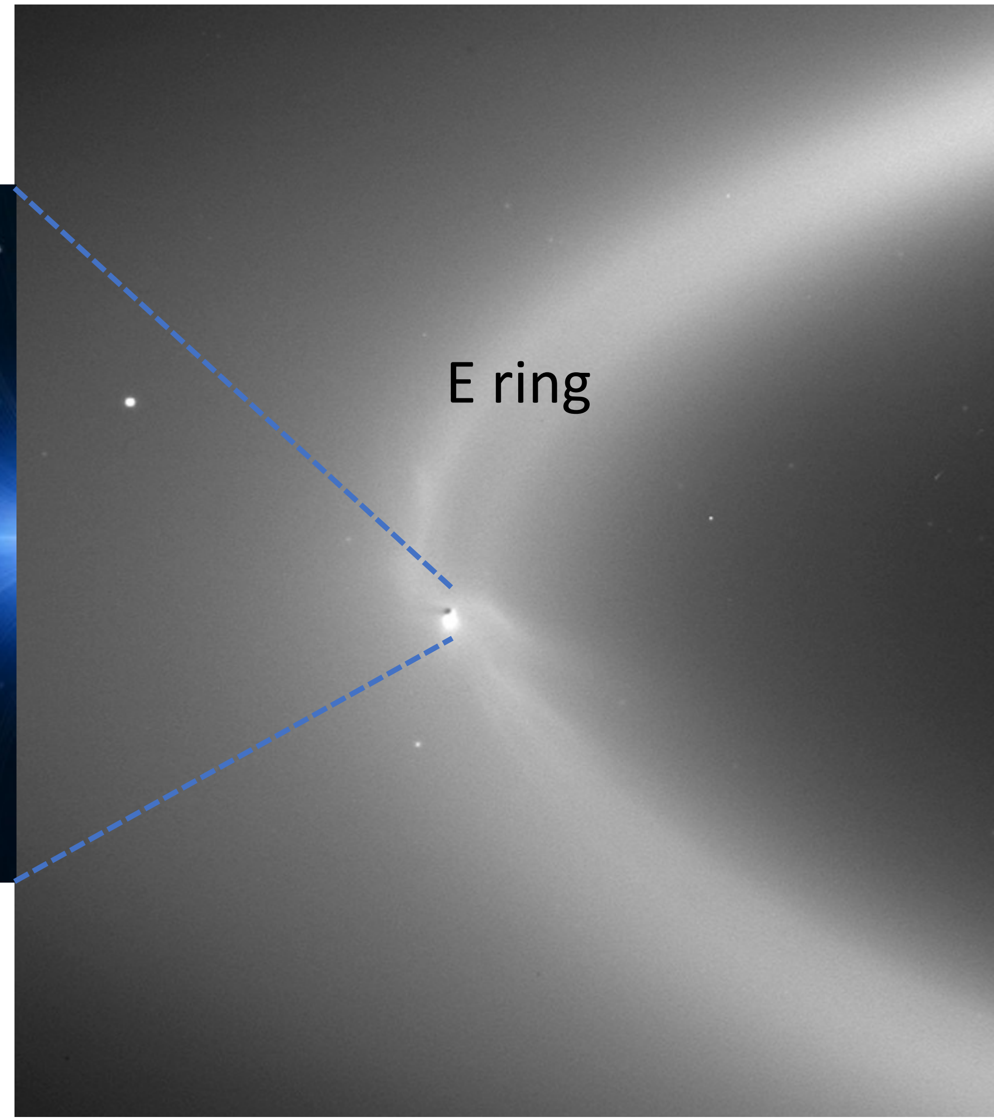


Steve Vance; NASA/JPL-Caltech

Sampling dust and ice particles in space

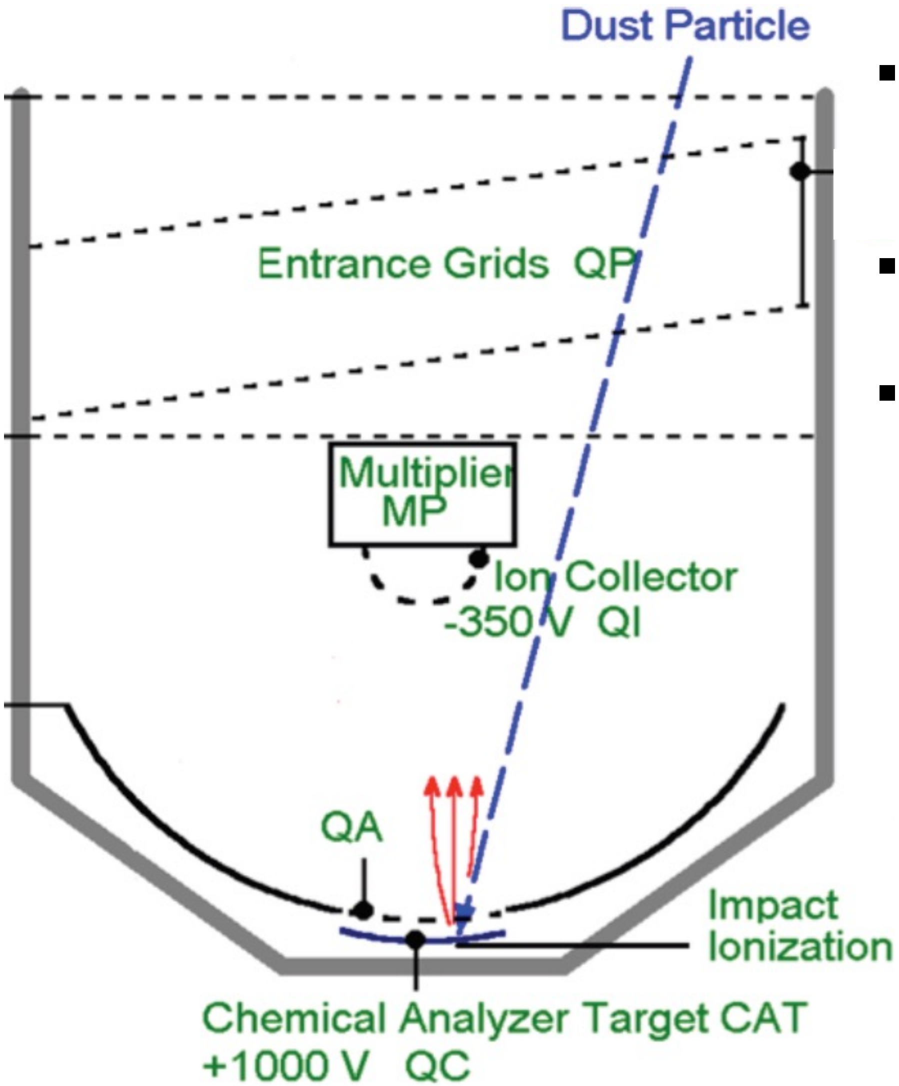


NASA/JPL

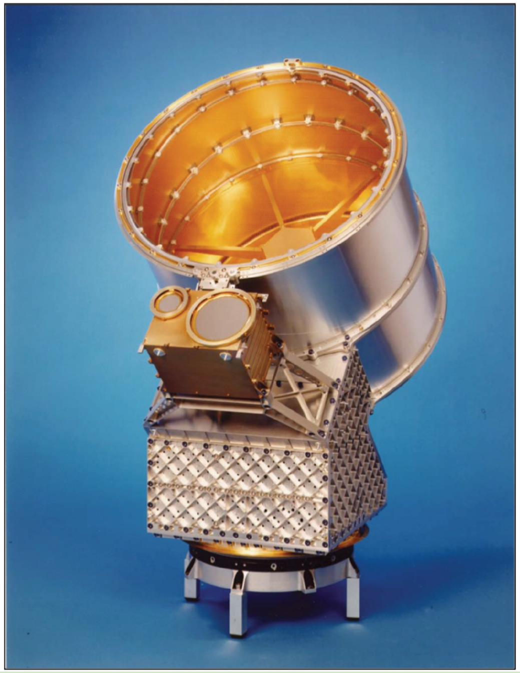


The Cosmic Dust Analyzer (CDA)

Chemical Analyzer subsystem (CA)

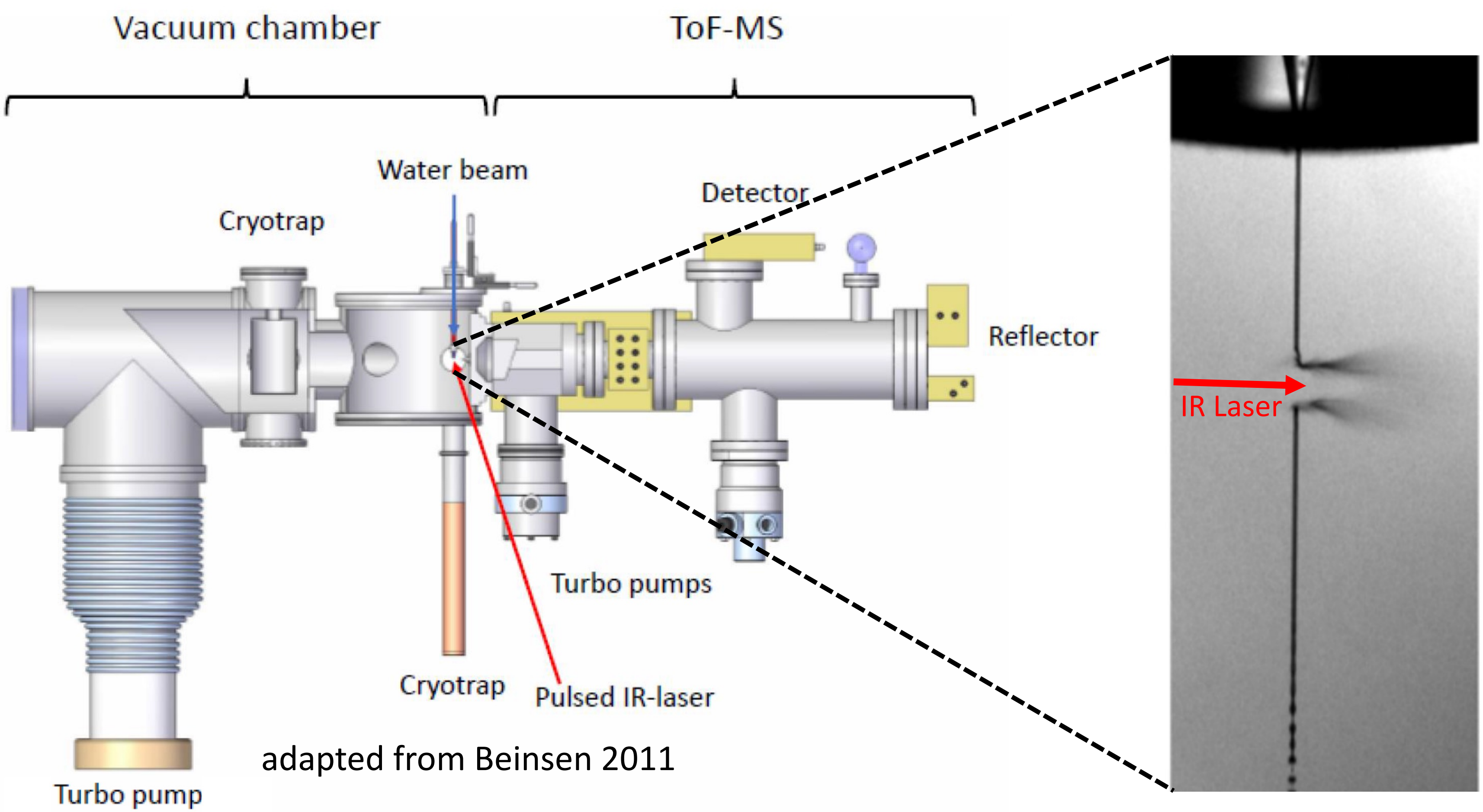


- Sensitive to cations
- Determines impact rates, mass, speed, electric charge, and composition
- Mass resolution: ≤ 50 $m/\Delta m$
- Maximum recorded mass: ca. 200 u



Srama et al. 2004

Analog experiment: IR-FL-MALDI-ToF-MS

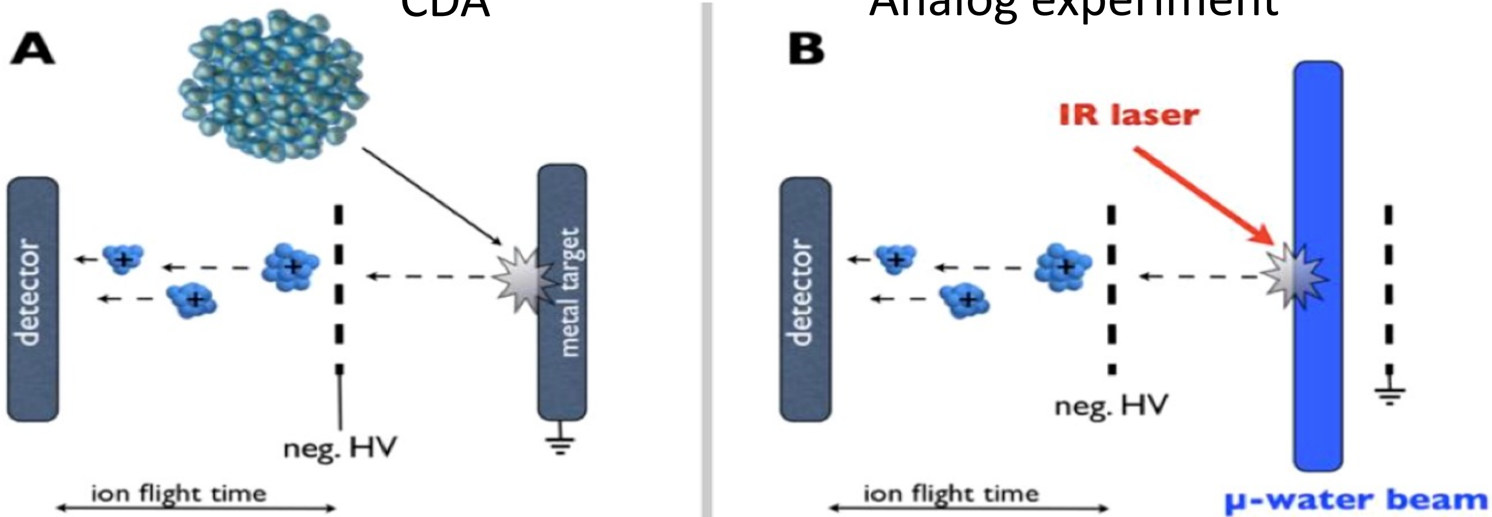


adapted from Beinsen 2011

- Liquid beam: r = 7.5 µm
- Vaccum chamber: P = 5 x 10^{-5} mbar
- Laser: λ = 2480 nm; I ≤ 1152 MW/cm^2
- ToF-MS: R = 700 – 800 m/Δm

Comparison of the impact mechanisms of CDA and the analog experiment

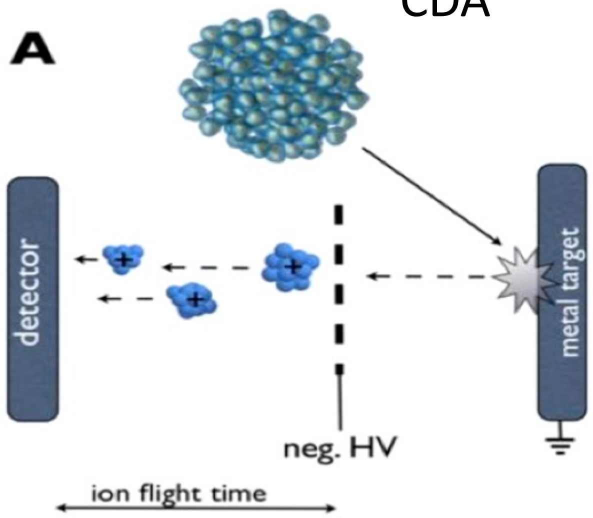
CDA | Analog experiment



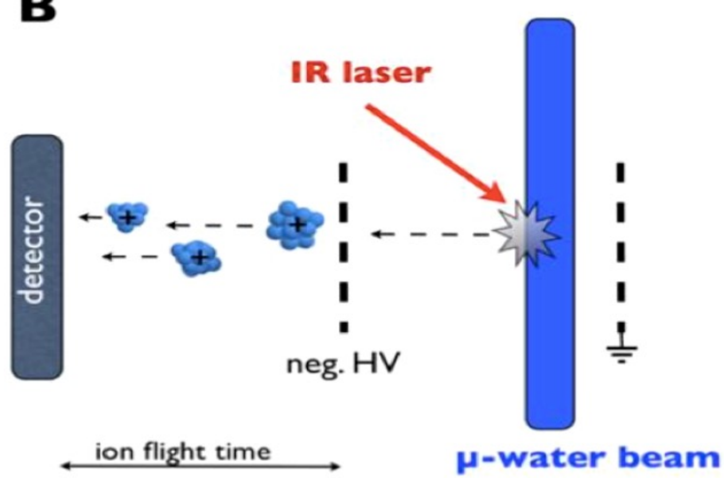
Postberg et al. 2009

Comparison of the impact mechanisms of CDA and the analog experiment

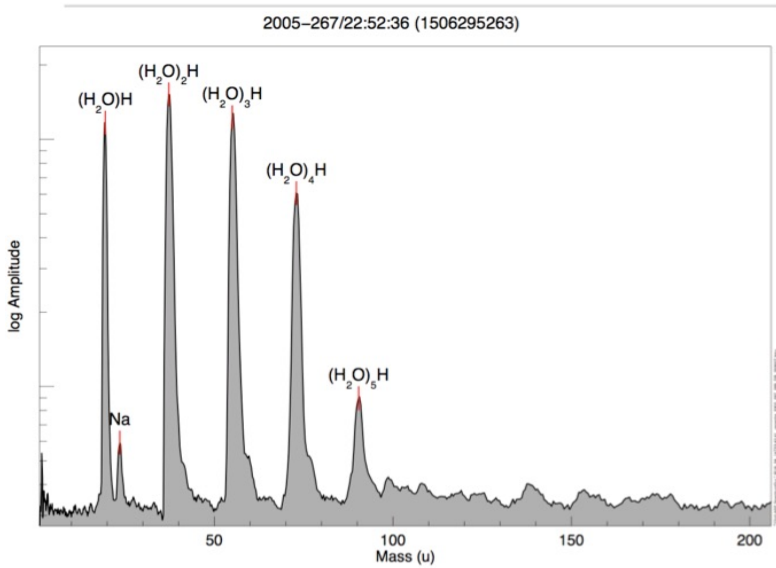
CDA

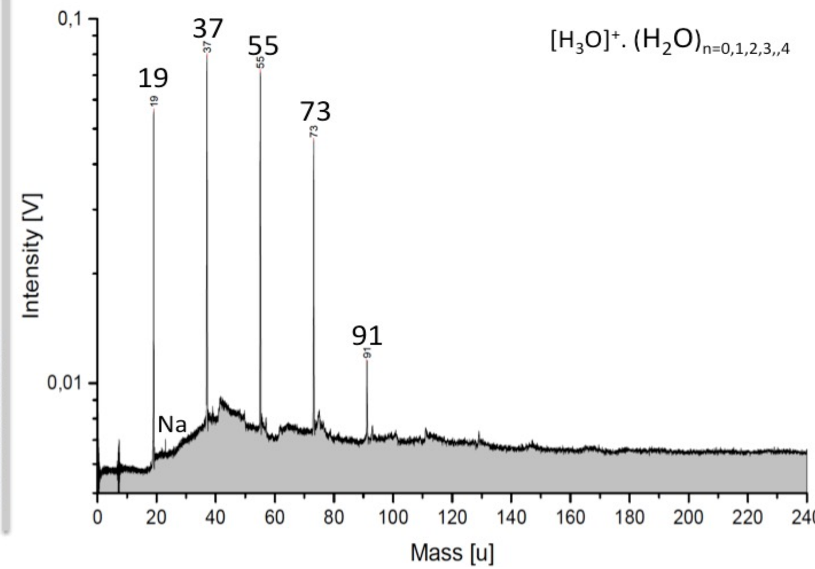


Analog experiment



Postberg et al. 2009

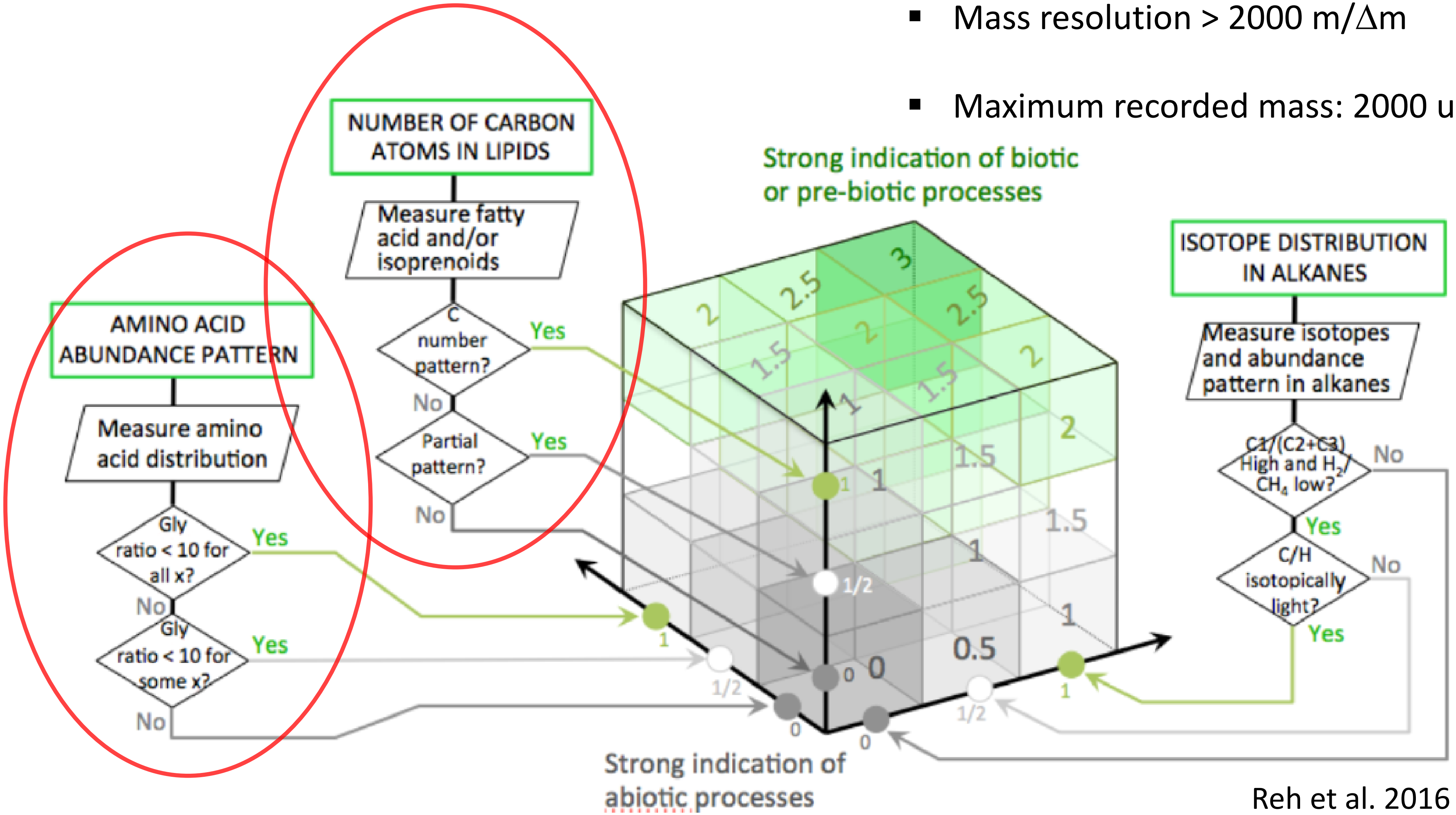




Khawaja 2016

Future missions and Enceladus Ice Analyzer (ENIA)

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



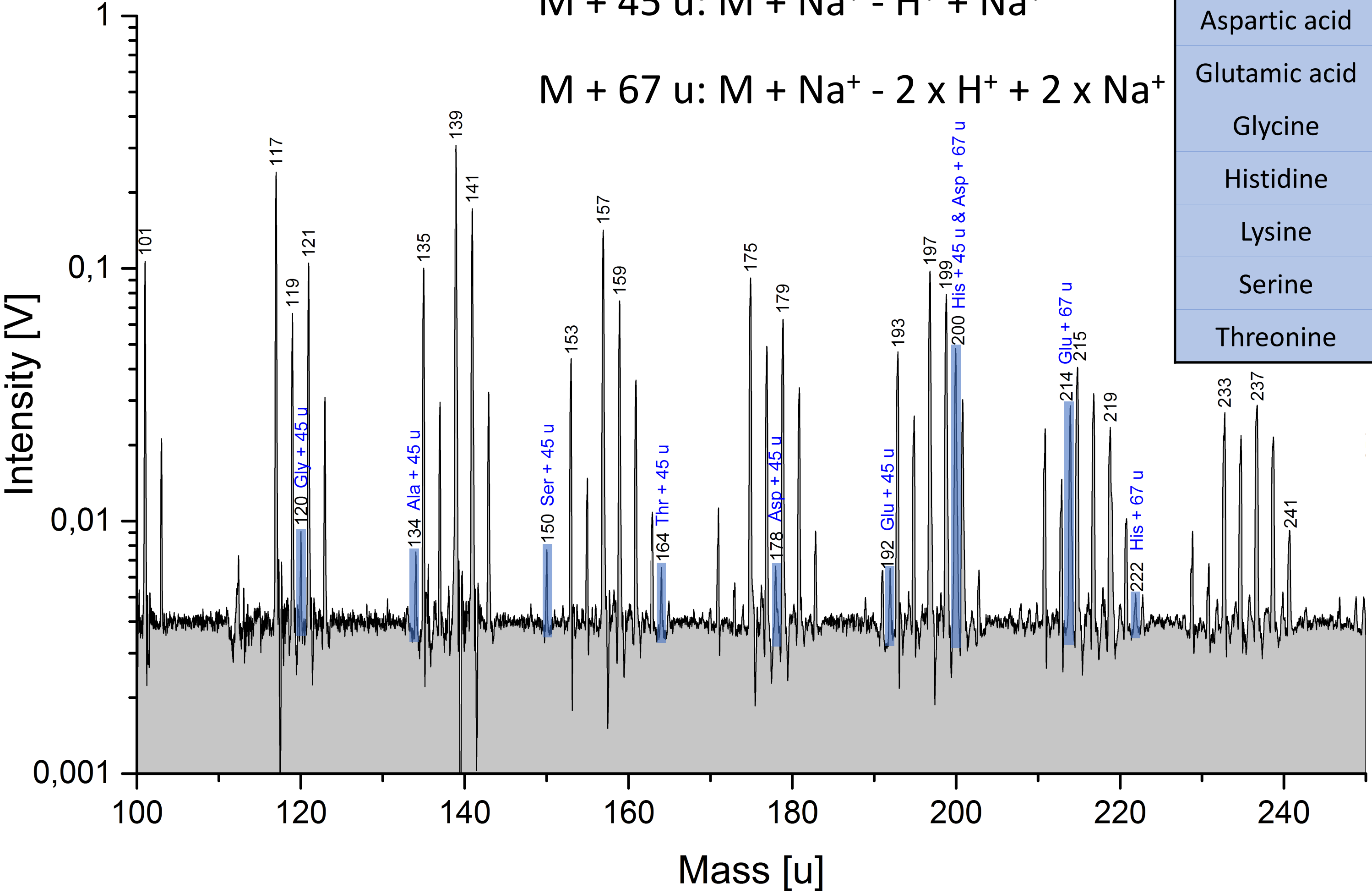
Reh et al. 2016

Sodium complexation of amino acids

9 Amino acids in 0.1 M NaCl

M + 45 u: M + Na^+ - H^+ + Na^+

M + 67 u: M + Na^+ - 2 x H^+ + 2 x Na^+



AMINO ACID	M* [u]	CONCENTRATION [PPM MOLAR]
Alanine	89	10
Arginine	174	5
Aspartic acid	133	7
Glutamic acid	147	6
Glycine	75	12
Histidine	155	6
Lysine	146	6
Serine	105	9
Threonine	119	8

*M: Molecular weight

Sodium complexation of amino acids

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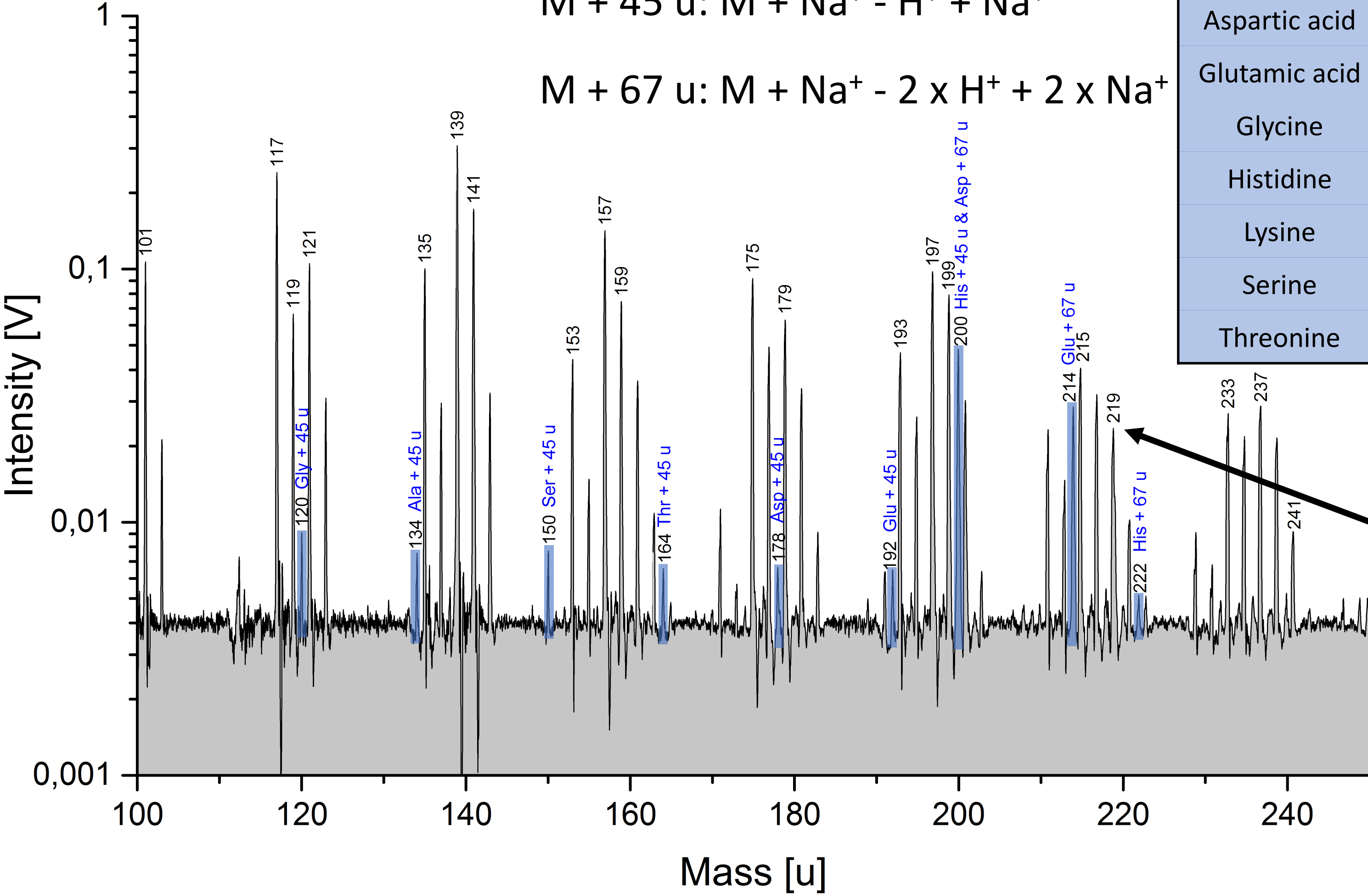
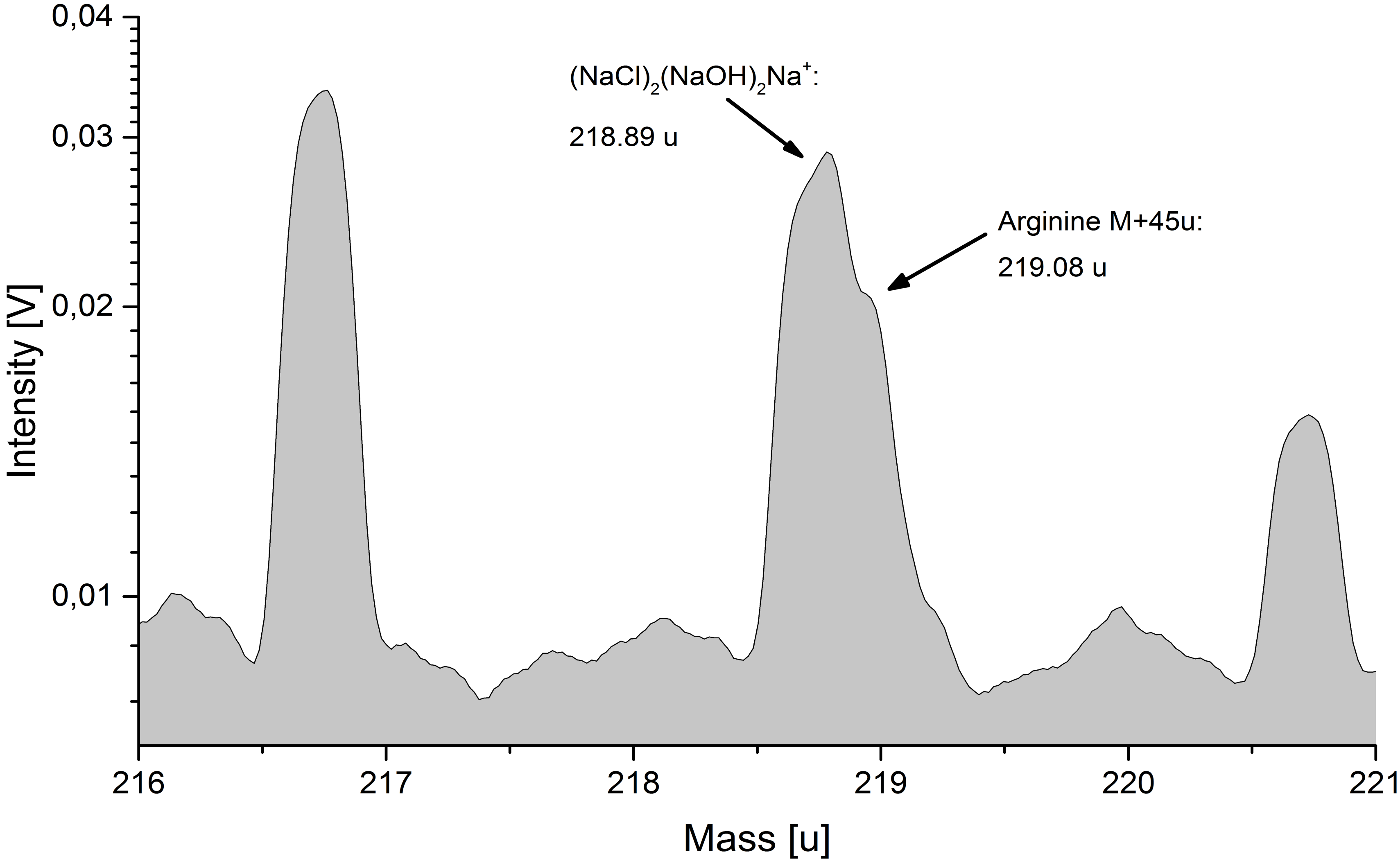


Interferences of salt peaks with amino acid peaks are possible, e.g. arginine + 45 u = 219 u

Detection of two species at the same integer mass



Detection limits of amino acids

Salt poor matrix: H_2O

AMINO ACID	MOLECULAR WEIGHT [u]	DETECTED PEAK	DETECTION LIMIT [PPB MOLAR]
Glycine	75	M* + 1 u	120
		M – 1 u	25
Serine	105	M + 1 u	170
		M – 1 u	340
Lysine	146	M + 1 u	0.02
Arginine	174	M + 1 u	0.02
Ornithine	132	M + 1 u	0.3
		M – 1 u	270
Histidine	155	M + 1 u	0.2
		M – 1 u	230
Citrulline	175	M + 1 u	20
		M – 1 u	100
Tyrosine	181	M + 1 u	200
		M – 1 u	200

Salt rich matrix: ≥ 0.1 M NaCl

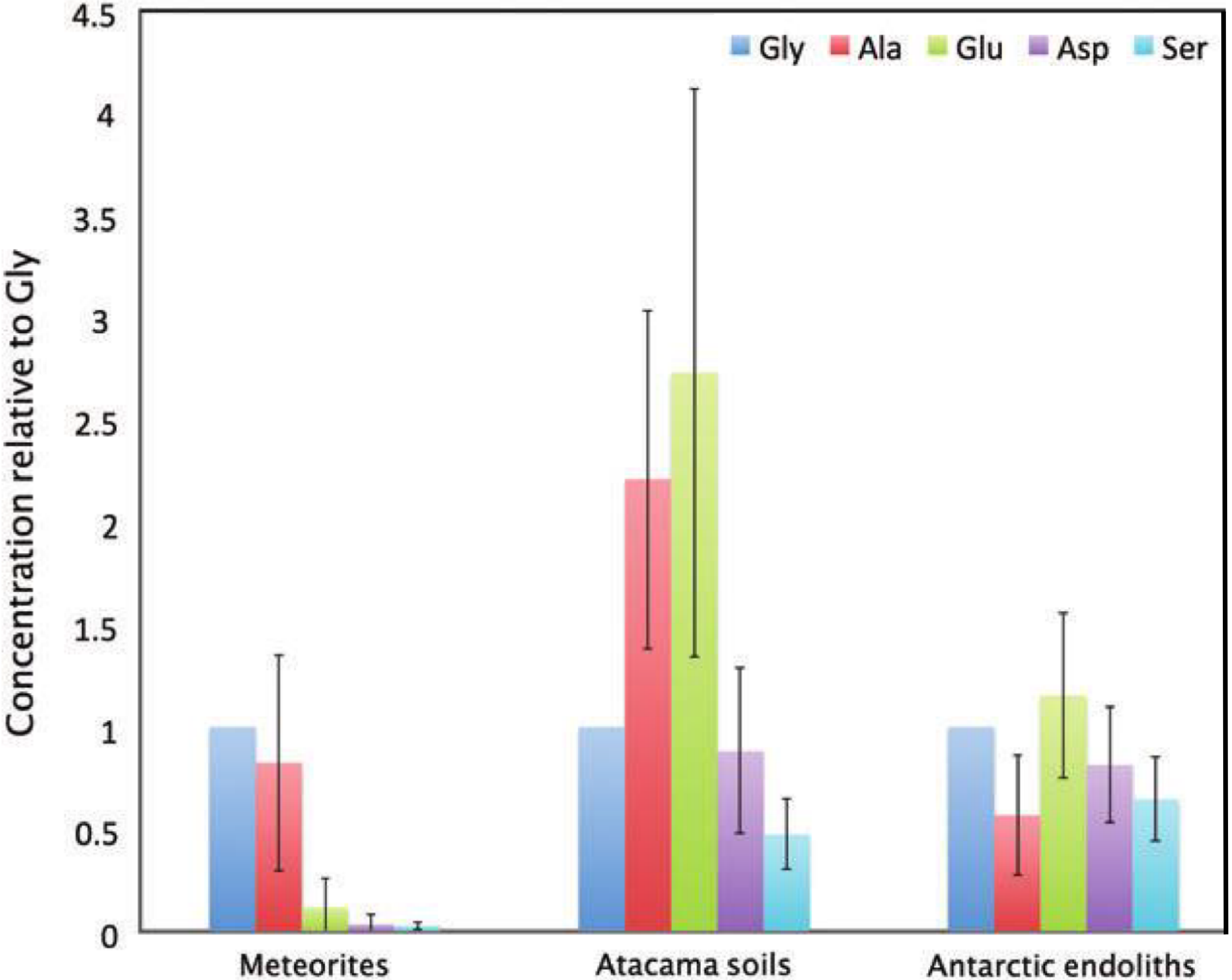
AMINO ACID	MOLECULAR WEIGHT [u]	DETECTED PEAK	DETECTION LIMIT [PPB MOLAR]
Glycine	75	M + 45 u	4800
Serine	105	M + 45 u	340
Threonine	119	M + 45 u	1500
Ornithine	132	M + 45 u	1400
Aspartic acid	133	M + 67 u	70
Glutamic acid	147	M + 67 u	60
Histidine	155	M + 45 u	230
Arginine	174	M + 45 u	1000
Citrulline	175	M + 45 u	2100
Tyrosine	181	M + 67 u	200

Amino acids detectable at 5000 x lower concentrations in a salt poor matrix than in a salt rich matrix

Cations detectable at 1000 x lower concentrations than anions

*M: Molecular weight

Amino acid abundances: abiotic/biotic



adapted from Davila & McKay 2014

Amino acids in the Enceladean ocean assuming a chondritic rocky core* and water-rock interaction

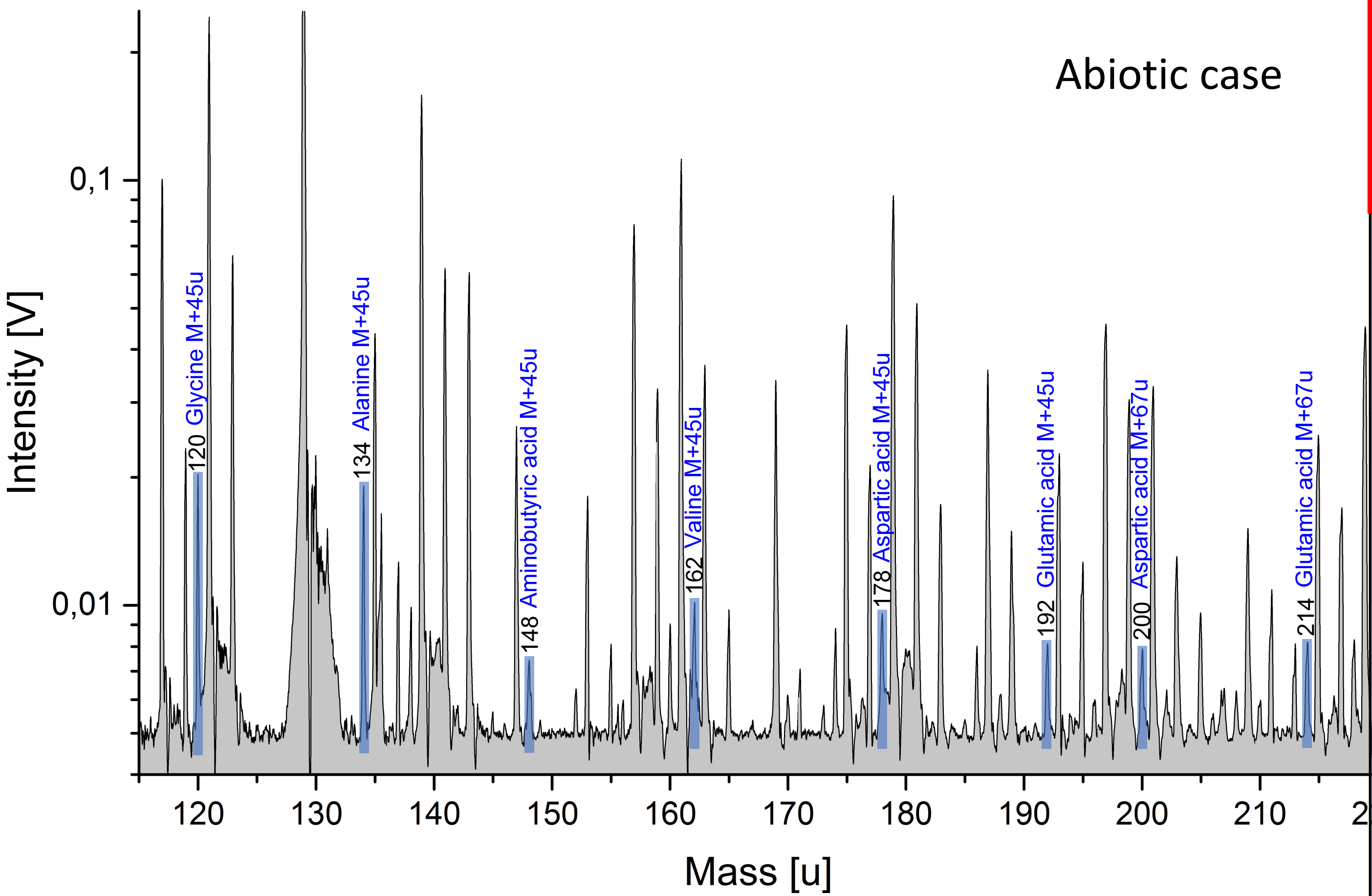
* Calculations based on Pizzarello et al. (2012) and Glavin et al. (2010)

Abiotic case

ACID	CONCENTRATION [PPM MOLAR]
Glycine	36.0
Alanine	30.3
Valine	11.5
Aminobutyric acid	7.0
Glutamic acid	0.6
Serine	0.5
Aspartic acid	0.3
Valeric acid	10.6
Methylbutyric acid	10.6
Hexanoic acid	4.6
Acetic acid	5.6
Butyric acid	4.1
Heptanoic acid	4.1
Octanoic acid	3.8
Nonanoic acid	3.4
Methylpentanoic acid	3.1
Ethylhexanoic acid	2.5
Benzoic acid	1.5
Formic acid	0.8
Ethylbutyric acid	0.8
Decanoic acid	0.5

Amino acids in the Enceladean ocean assuming a chondritic rocky core* and water-rock interaction

* Calculations based on Pizzarello et al. (2012) and Glavin et al. (2010)



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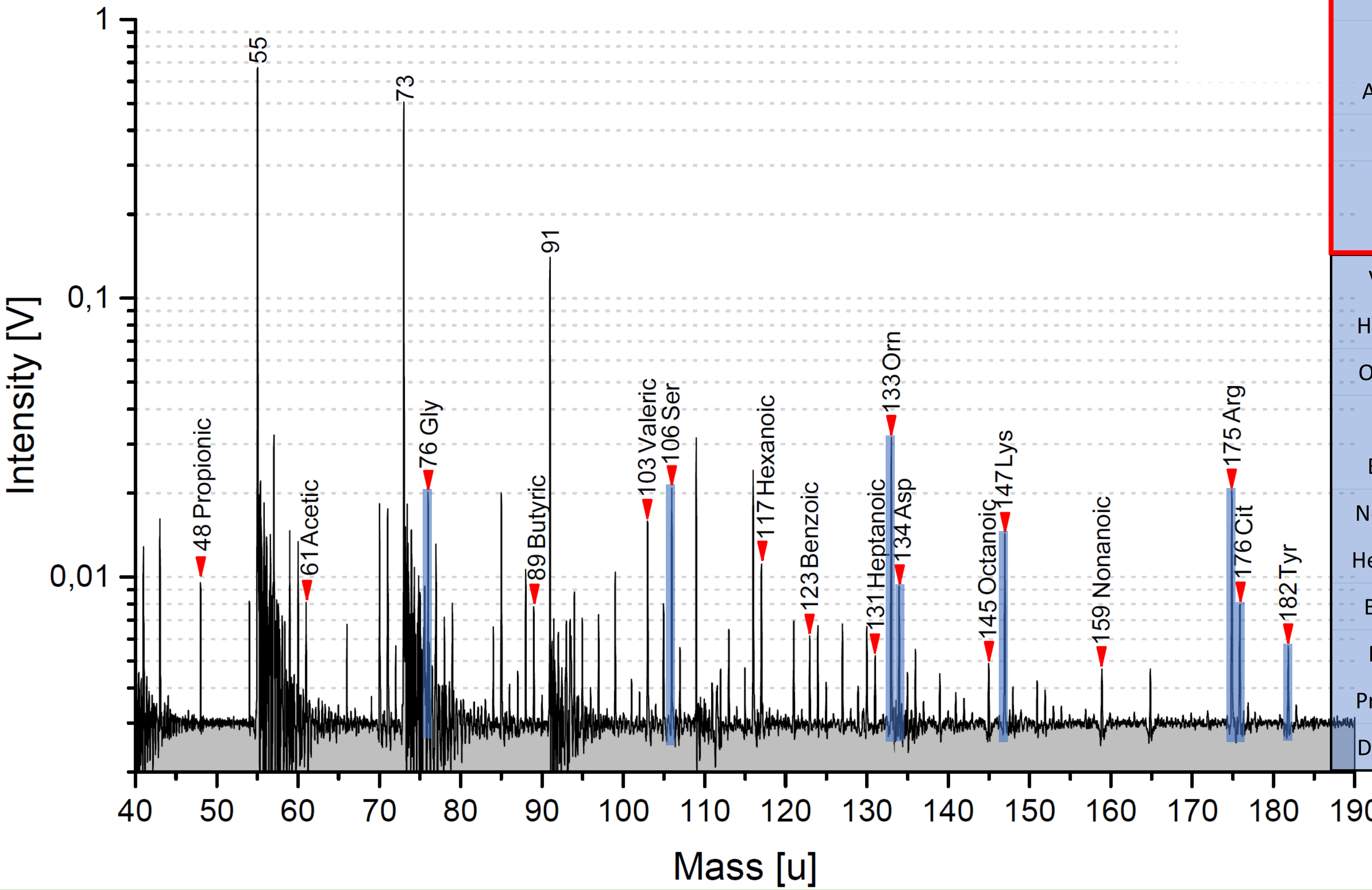
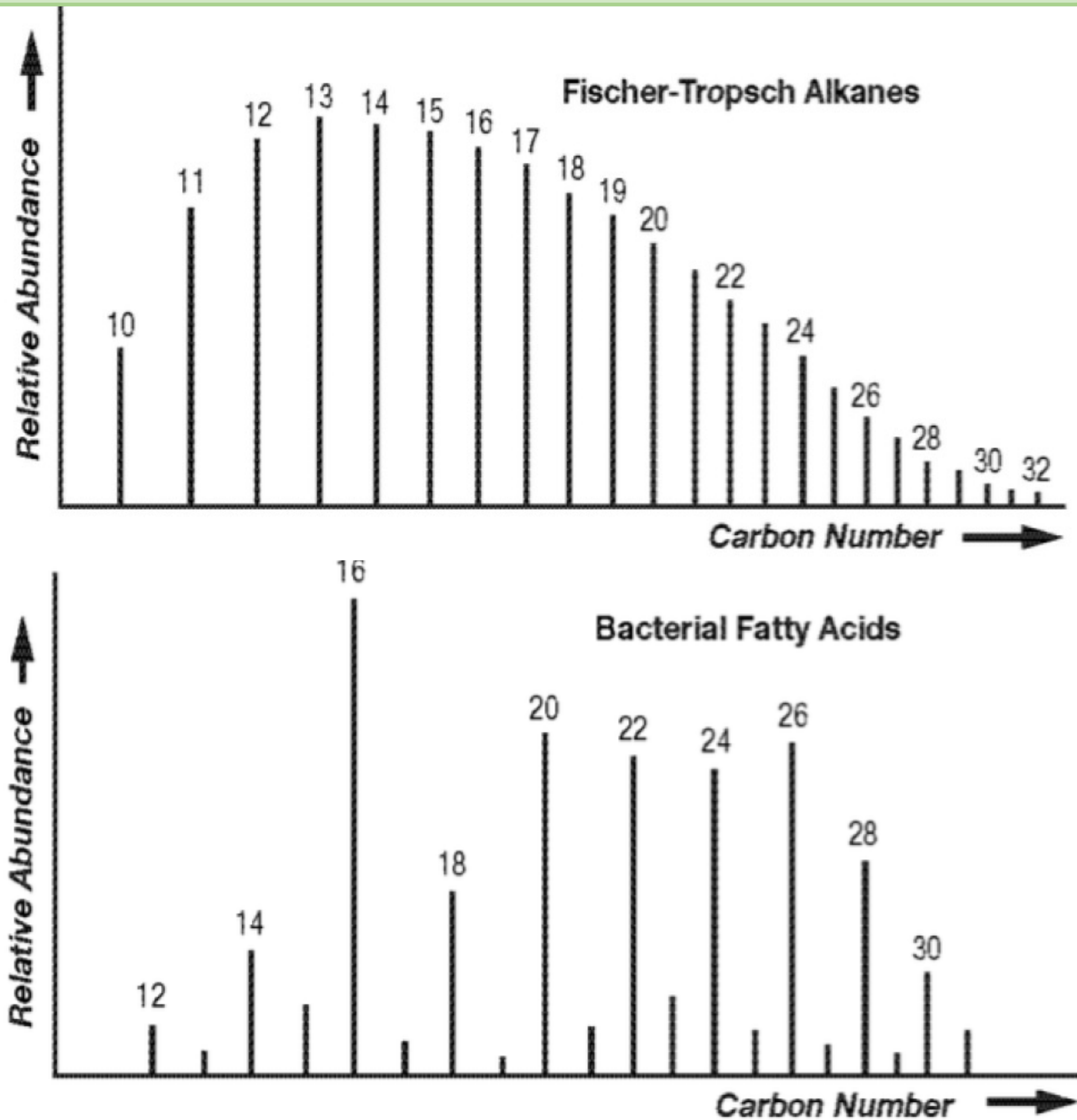
Methylbutyric acid	10.6
Hexanoic acid	4.6
Acetic acid	5.6
Butyric acid	4.1
Heptanoic acid	4.1
Octanoic acid	3.8
Nonanoic acid	3.4
Methylpentanoic acid	3.1
Ethylhexanoic acid	2.5
Benzoic acid	1.5
Formic acid	0.8
Ethylbutyric acid	0.8
Decanoic acid	0.5

Amino acids: Biotic case



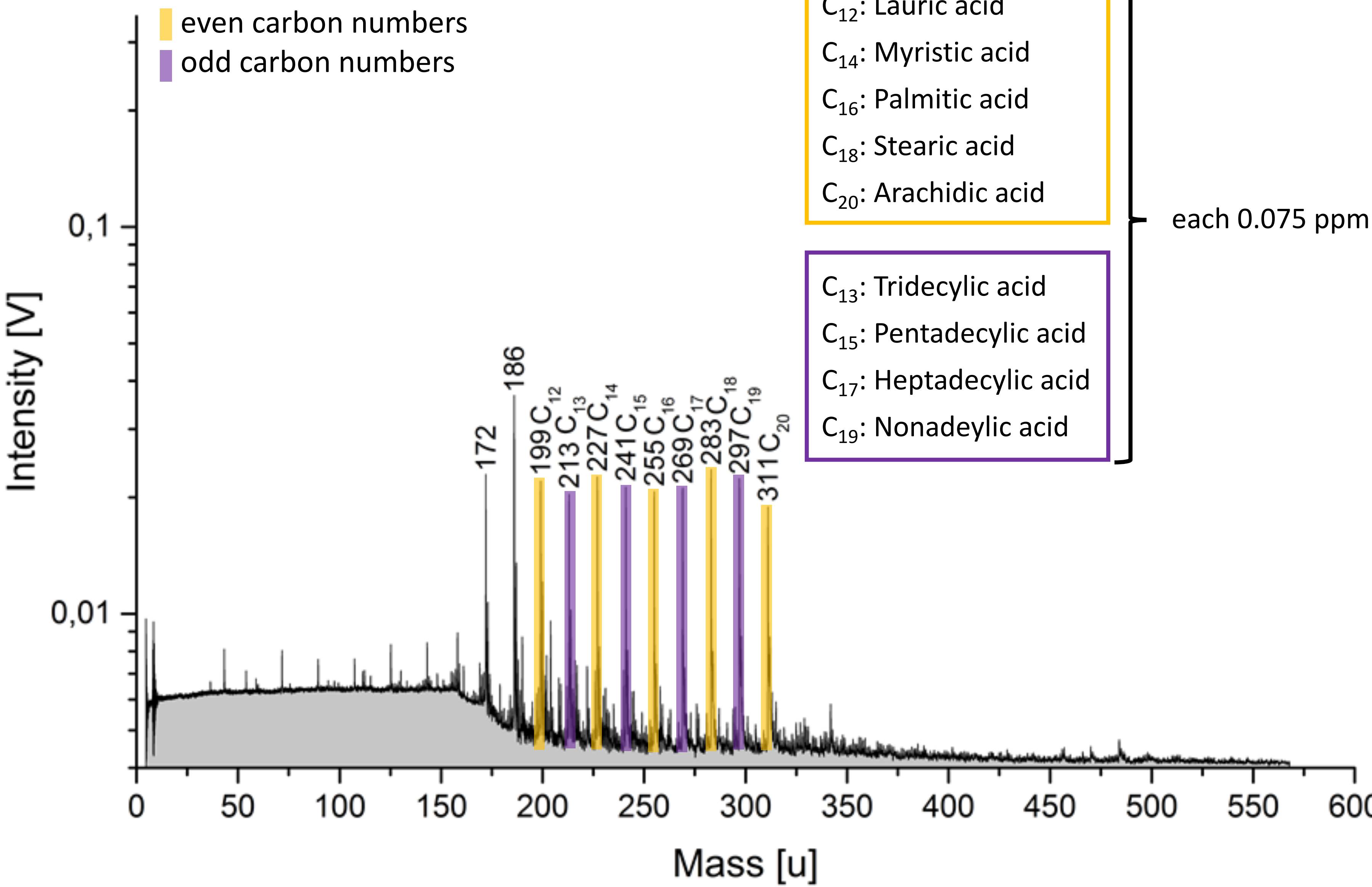
ACID	CONCENTRATION [PPM MOLAR * 10]
Serine	5.1
Glycine	4.8
Citrulline	2.1
Tyrosine	2.0
Aspartic acid	1.4
Ornithine	1.4
Lysine	0.6
Arginine	0.5
Valeric acid	167.6
Hexanoic acid	93.1
Octanoic acid	62.5
Acetic acid	45.0
Butyric acid	40.9
Nonanoic acid	28.5
Heptanoic acid	27.7
Benzoic acid	14.8
Formic acid	7.8
Propionic acid	7.7
Decanoic acid	5.2

Fatty acid abundances: abiotic/biotic



Lunine 2015

Fatty acids: abiotic case

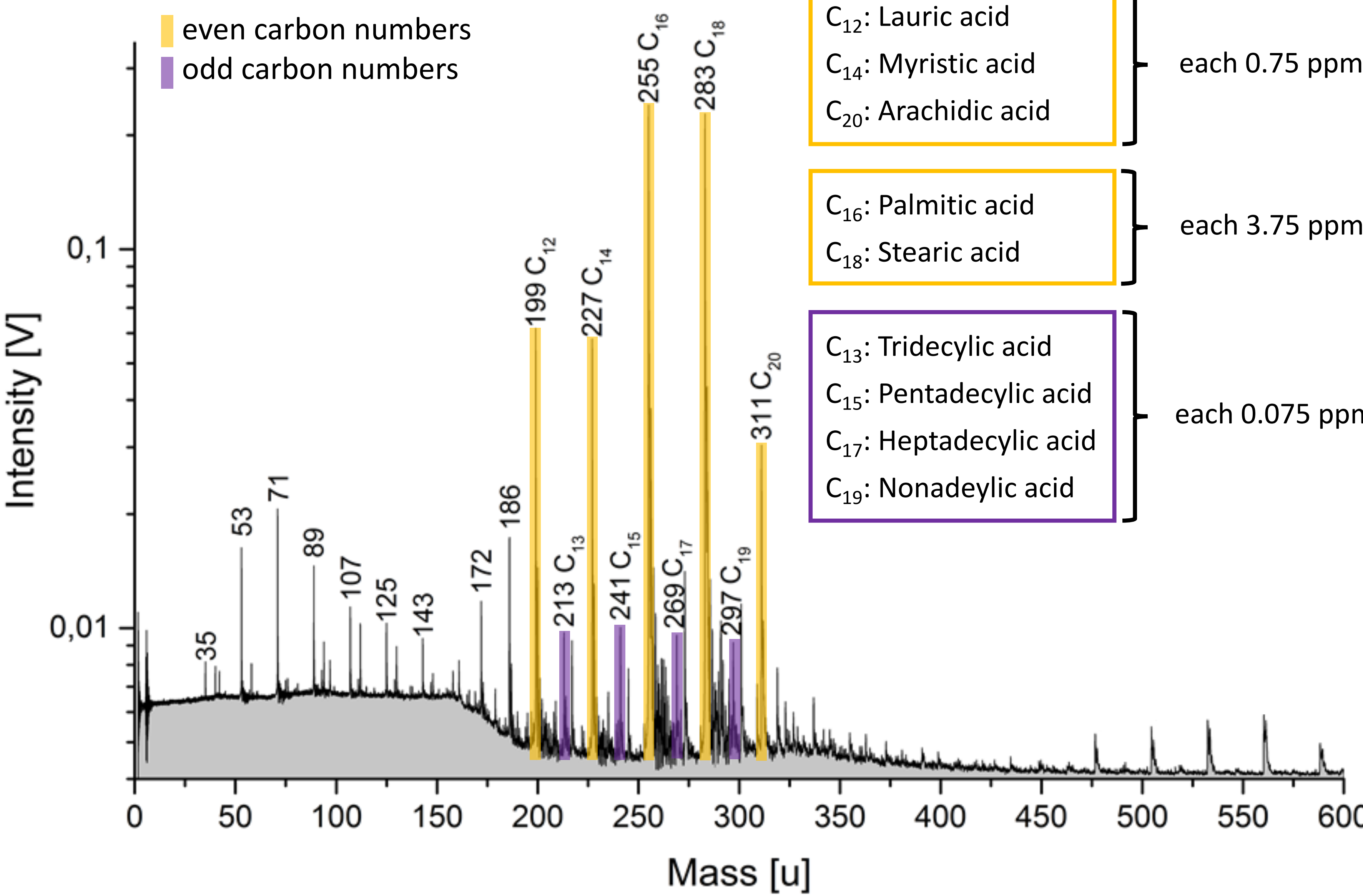


C_{12}: Lauric acid
C_{14}: Myristic acid
C_{16}: Palmitic acid
C_{18}: Stearic acid
C_{20}: Arachidic acid

C_{13}: Tridecylic acid
C_{15}: Pentadecylic acid
C_{17}: Heptadecylic acid
C_{19}: Nonadeylic acid

each 0.075 ppm molar

Fatty acids: biotic case



C_{12}: Lauric acid
C_{14}: Myristic acid
C_{20}: Arachidic acid

each 0.75 ppm molar

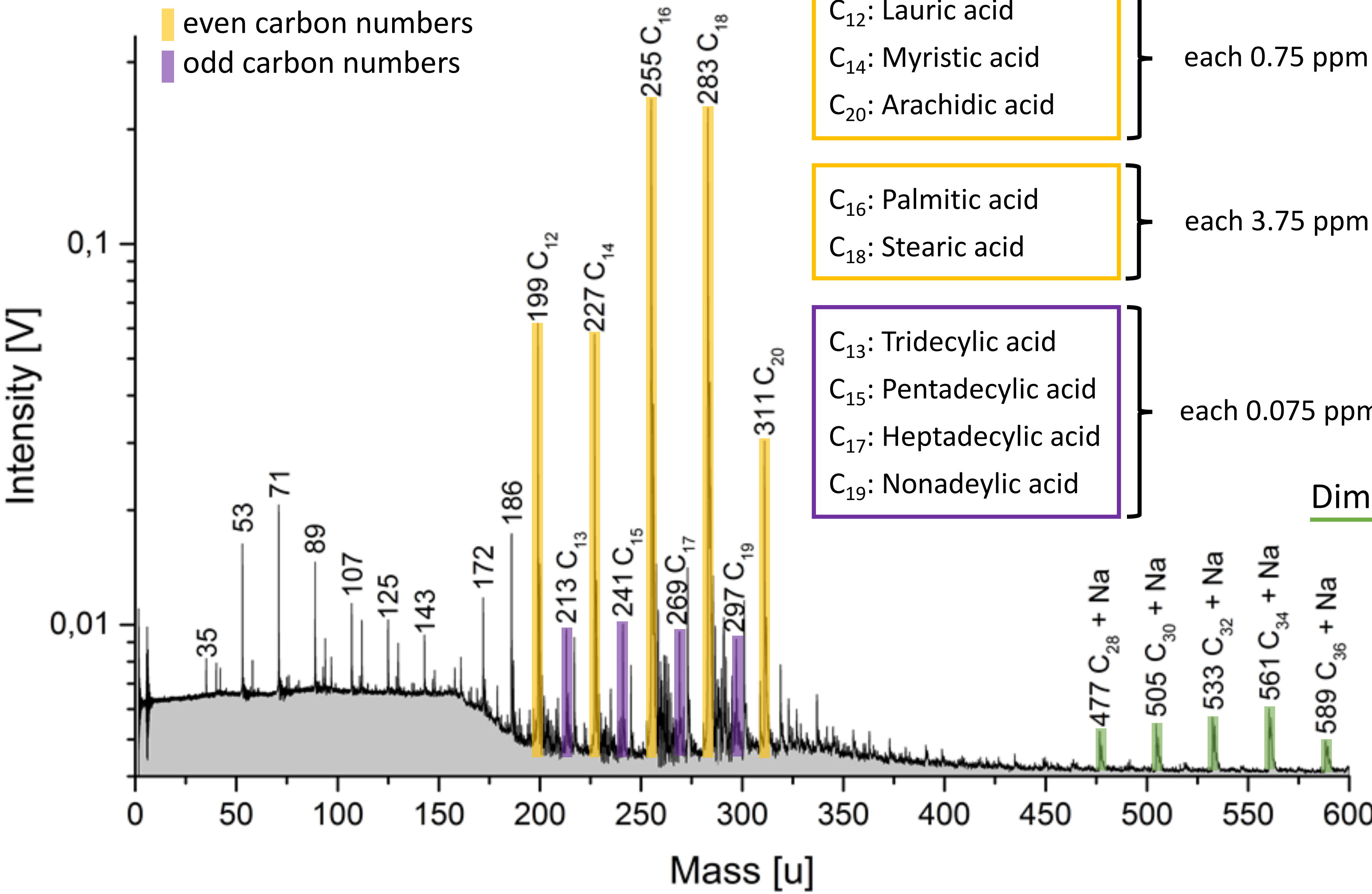
C_{16}: Palmitic acid
C_{18}: Stearic acid

each 3.75 ppm molar

C_{13}: Tridecylic acid
C_{15}: Pentadecylic acid
C_{17}: Heptadecylic acid
C_{19}: Nonadeylic acid

each 0.075 ppm molar

Fatty acids: biotic case



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each 3.75 ppm molar

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C_{17}: Heptadecylic acid
C_{19}: Nonadeylic acid

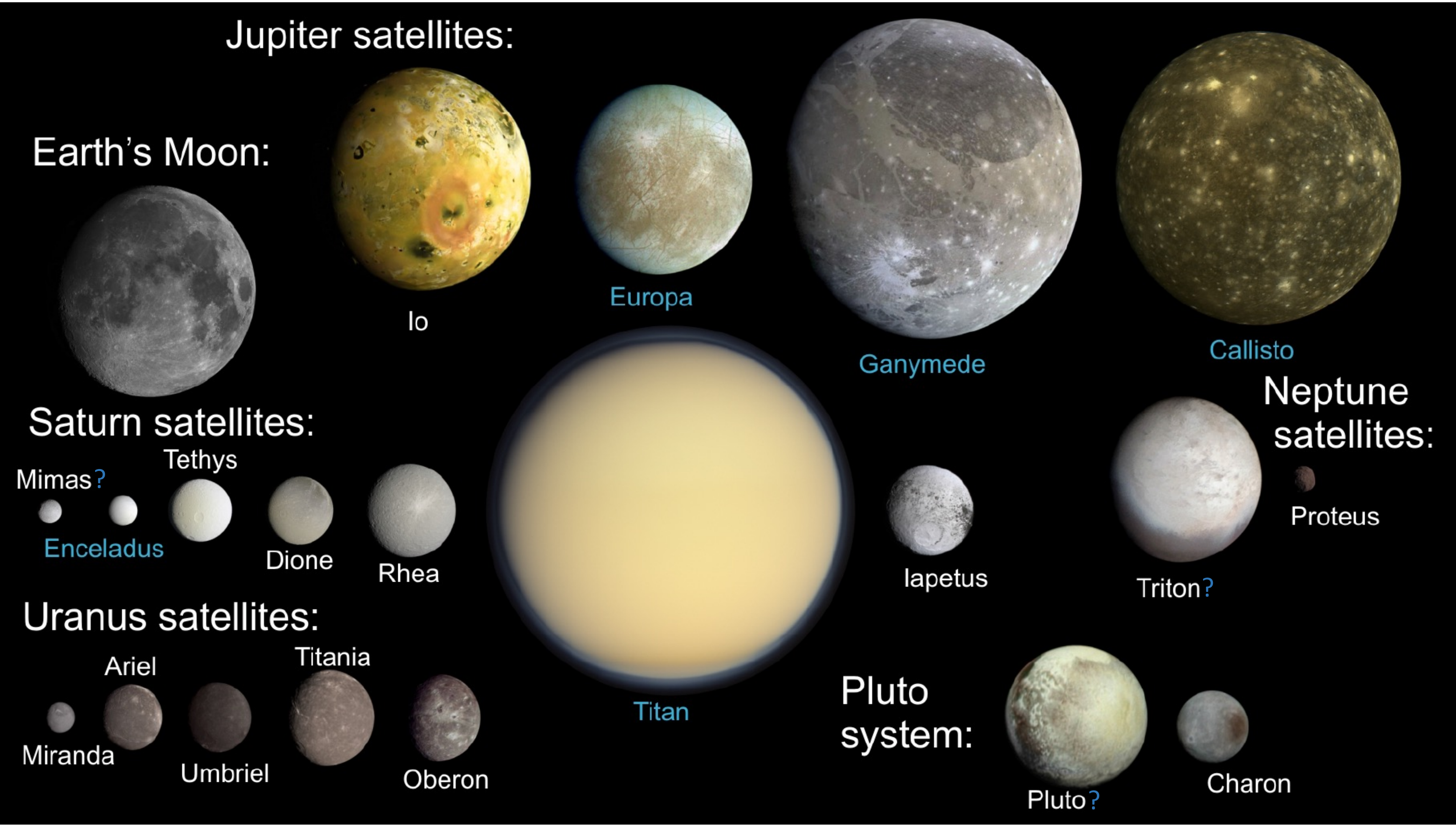
each 0.075 ppm molar

Summary and outlook

- Analog desorption mass spectra highly comparable to impact ionization mass spectra taken in space
- Most amino acids better detectable as cations, a few amino acids and fatty acids as anions
- Amino acids form sodium complexes M + 45 u and/or M + 67 u in a salt rich matrix (≥ 0.1 M); Fatty acids form complexed dimers
- Peptides have been investigated → Characteristic cleavages lead to characteristic fragmentation patterns diagnostic for its amino acid constituents
- Detection limits of amino acids and fatty acids depend on salt concentration but are in general below 1 ppm; Glu and Asp are the most sensitive amino acids in a salt rich matrix, Arg and Lys in a salt poor matrix
- Peak heights can be well ‘‘translated“ into concentrations of the organics → abiotic and biotic signatures can be easily distinguished
- By comparing the laboratory results with spacecraft data, we have the ability to recognize and distinguish such signatures on icy moons with a subsurface ocean → Europa Clipper mission + other upcoming missions
- We aim to create a comprehensive spectrum library for in situ space detectors from a wide variety of analog materials in icy grains

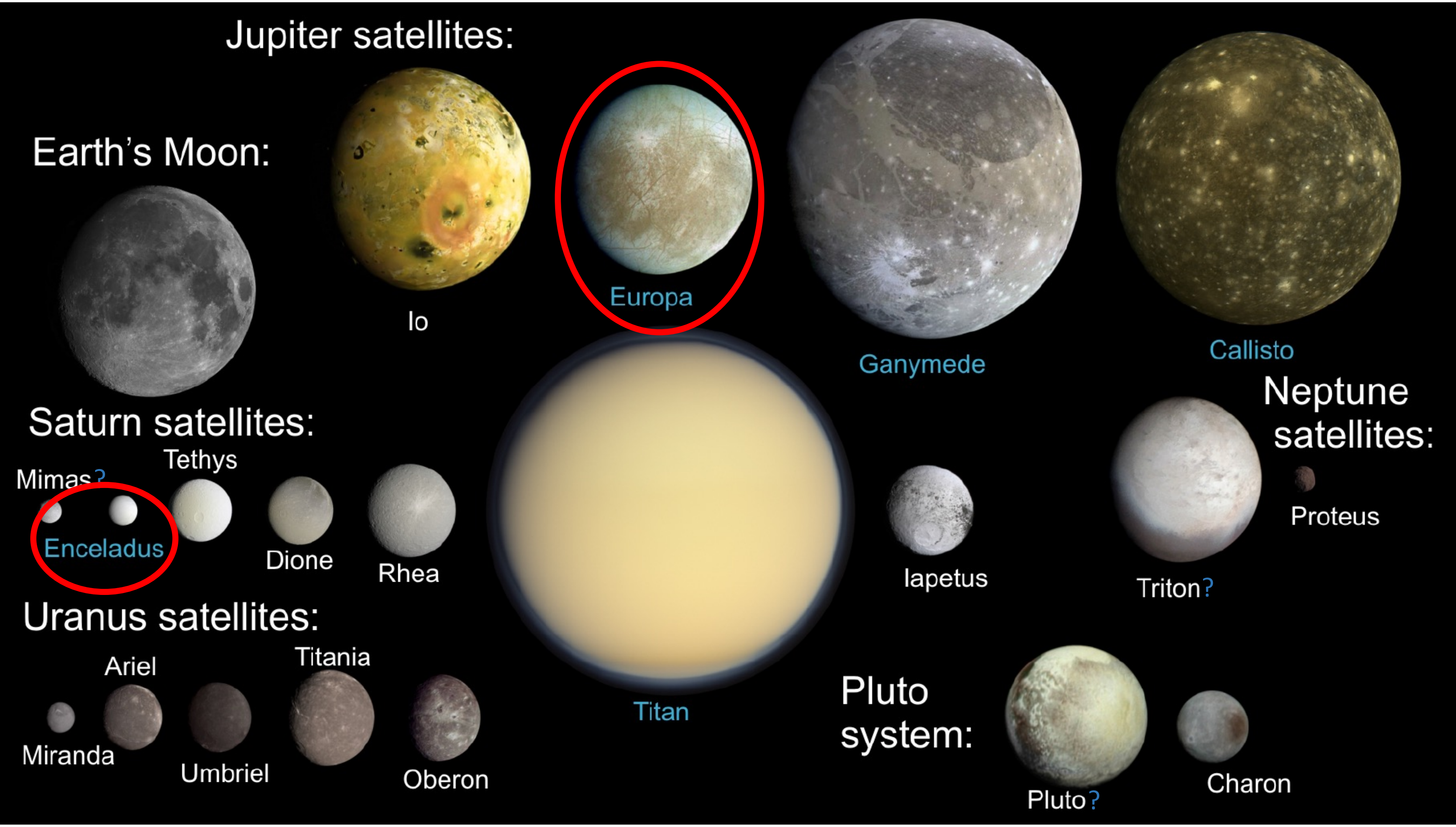
Backup

Backup: Which objects harbor liquid oceans?



Nimmo & Pappalardo 2016

Backup: Which objects harbor liquid oceans?



Nimmo & Pappalardo 2016

Backup: Hypervelocity impact signals (CA)

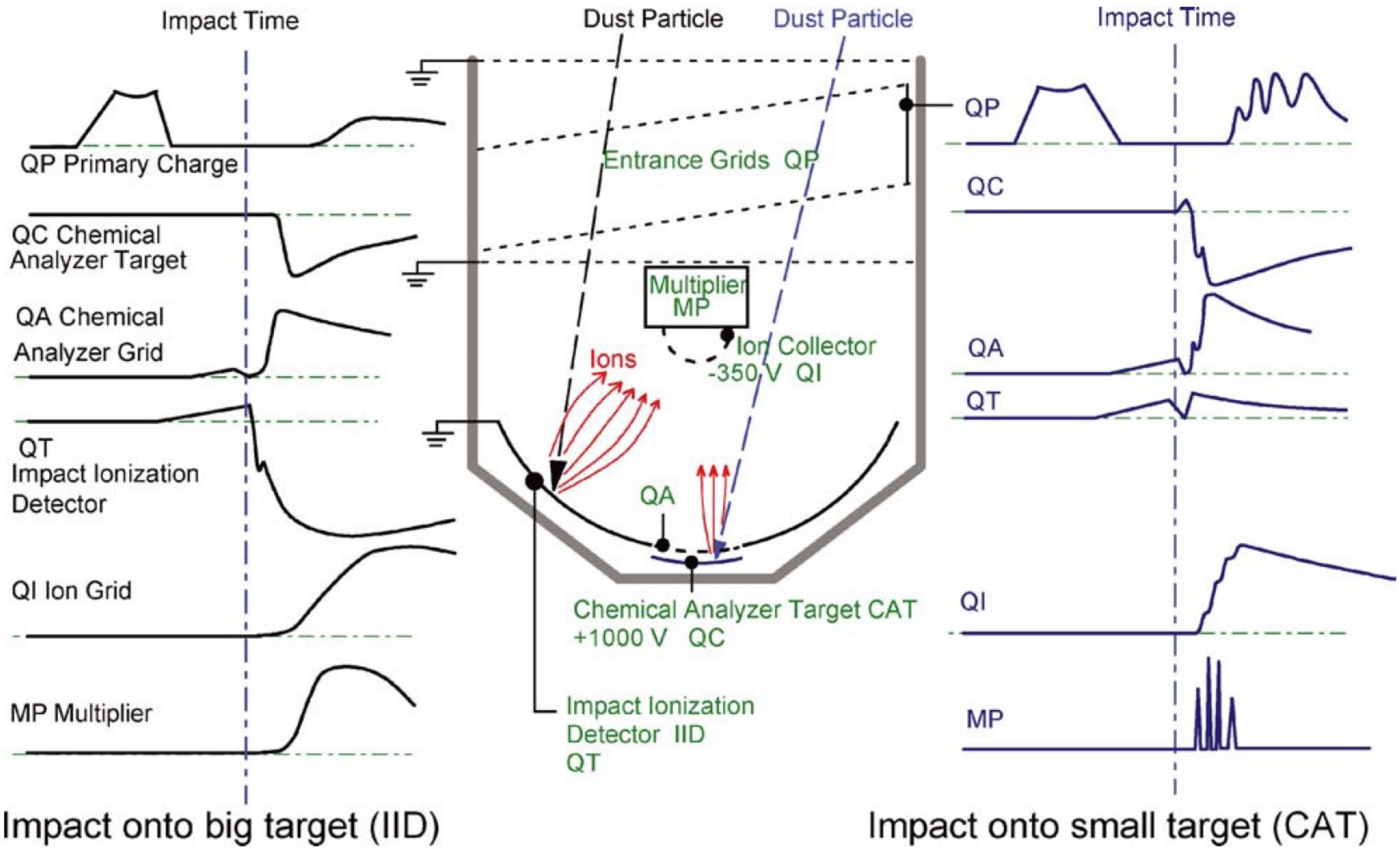
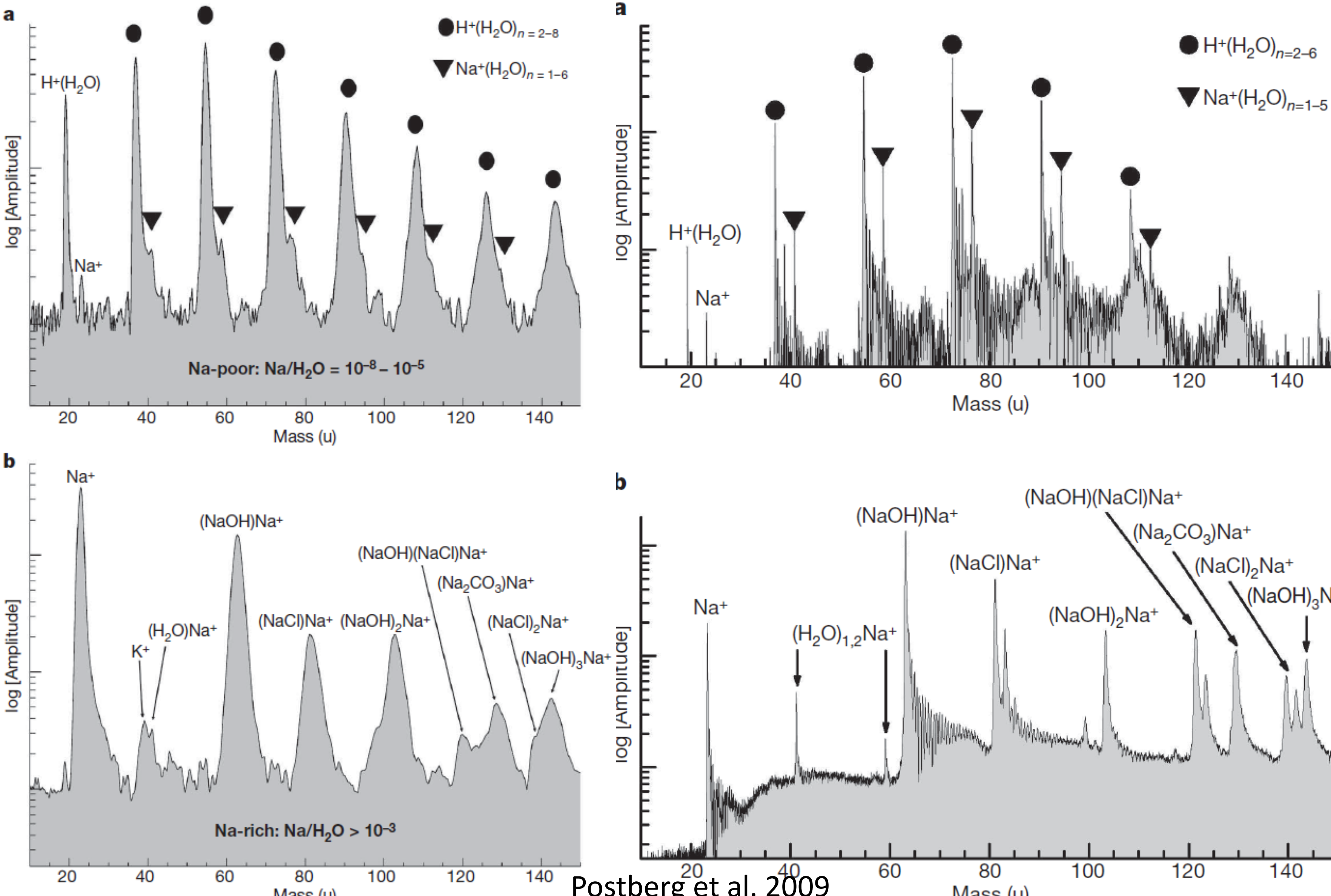


Figure 6. Hypervelocity impact signals of dust grains onto the big Impact Ionization Target (left) and onto the Chemical Analyzer Target (right). The chemical analyzer is a time-of-flight mass spectrometer and provides the elemental composition of the impacting dust grain.

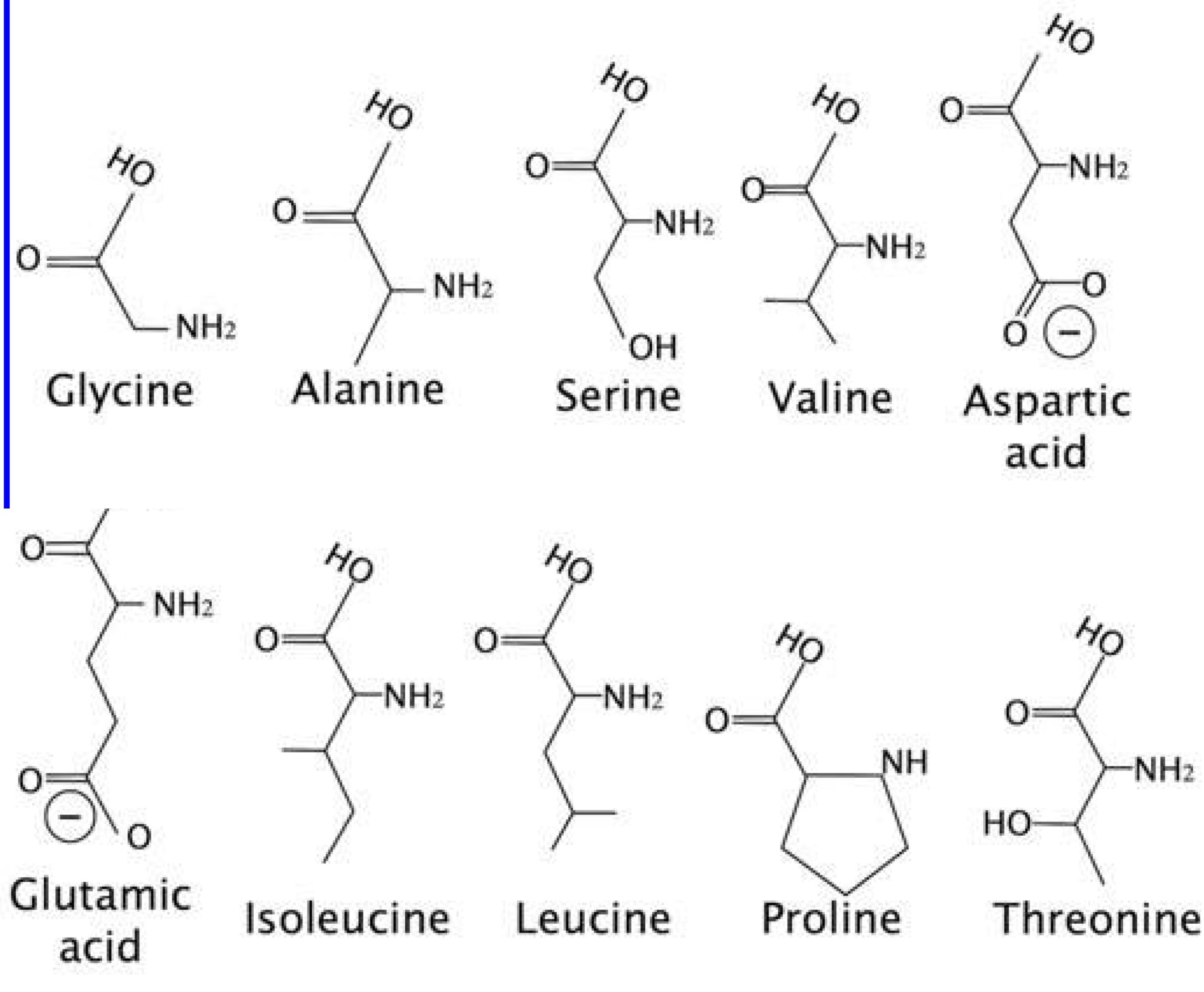
Srama et al. 2004

Backup: Mimicking Type-1 and Type-3 mass spectra



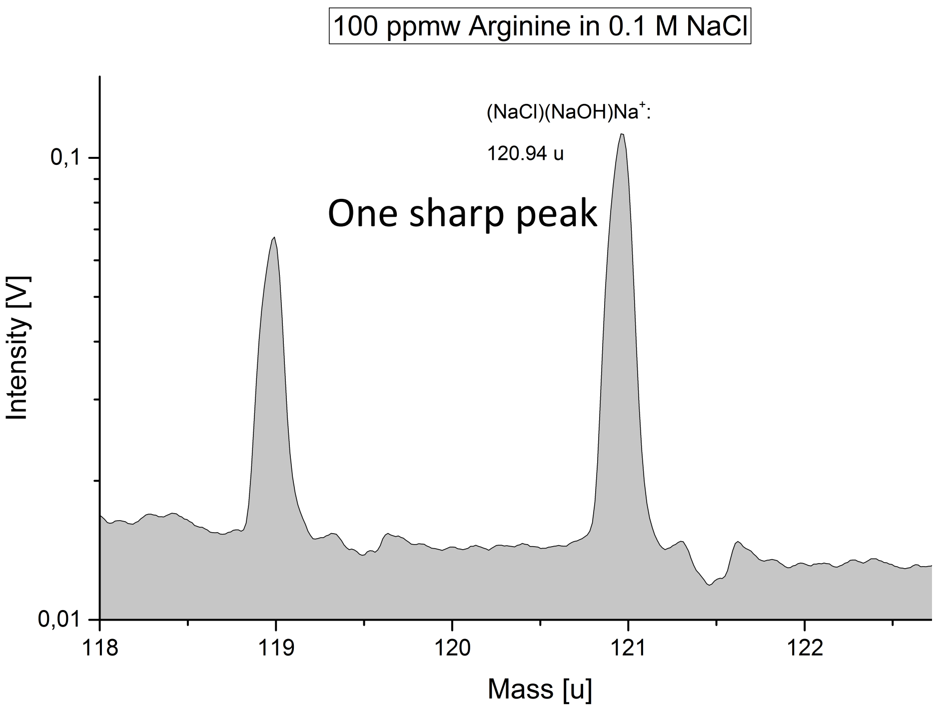
Postberg et al. 2009

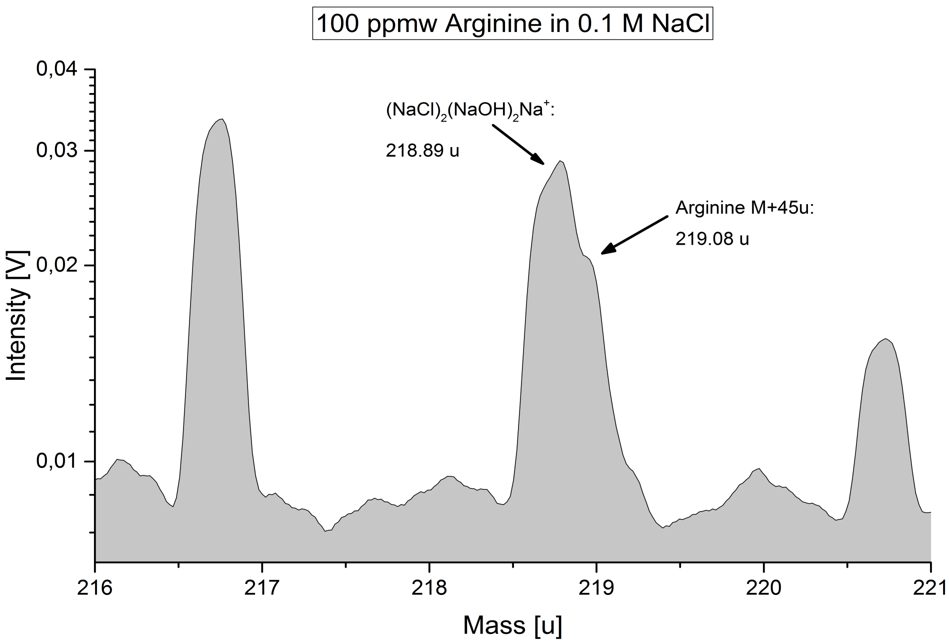
Backup: Some amino acid structures



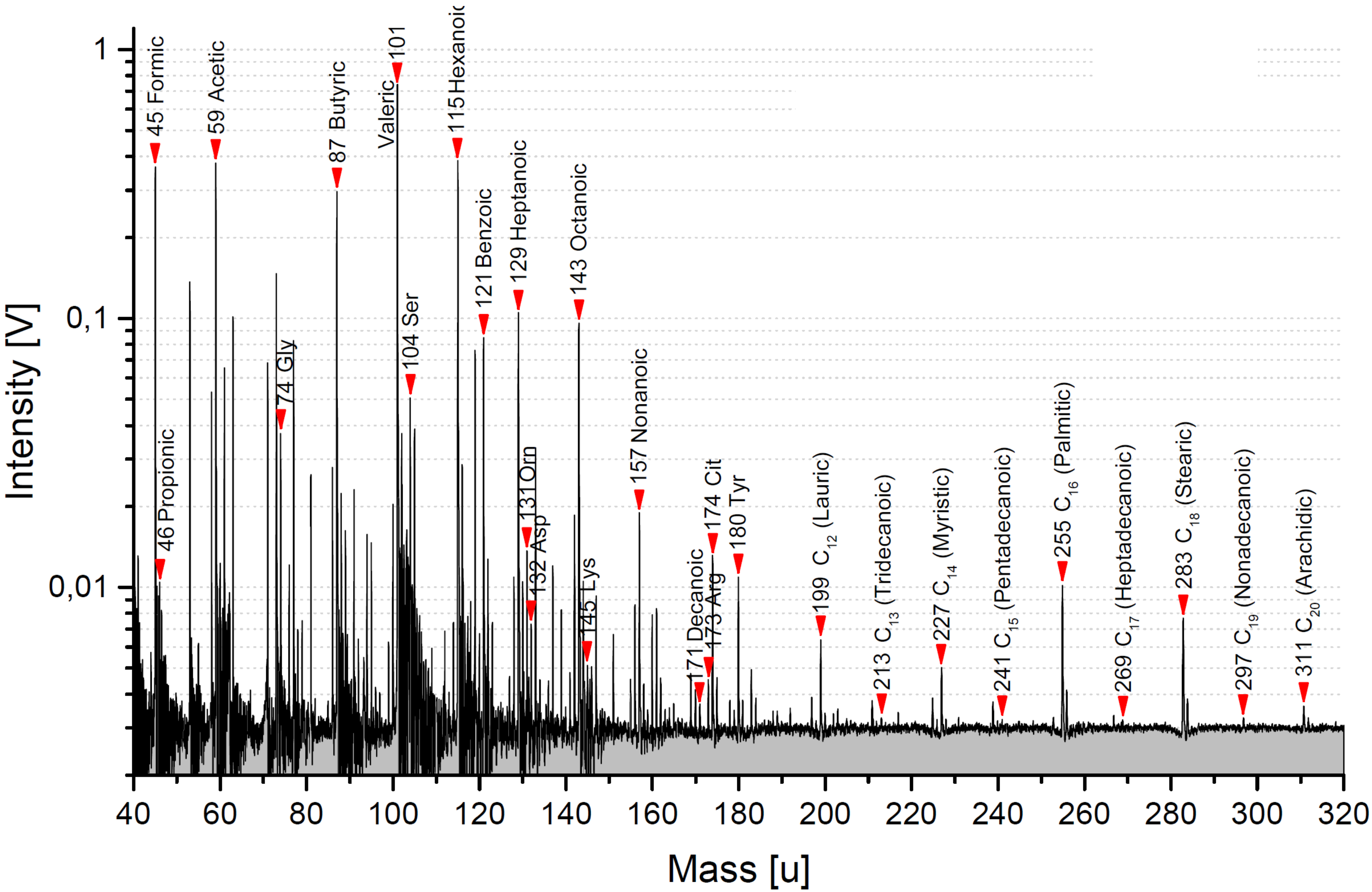
Davila & McKay, 2014

Backup: Confirmation of Arg Detection



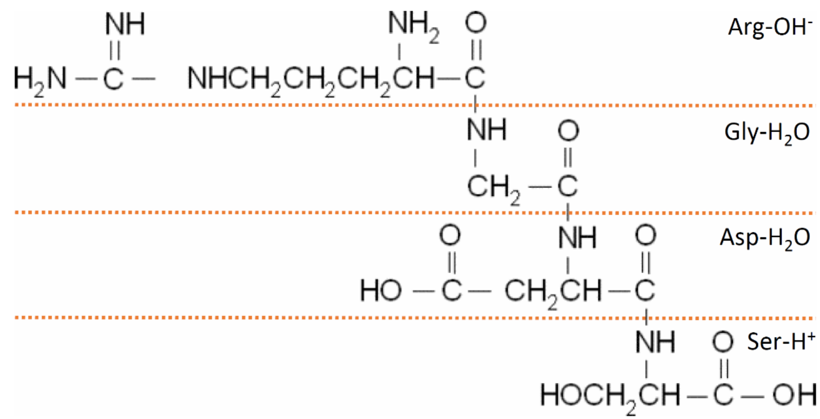


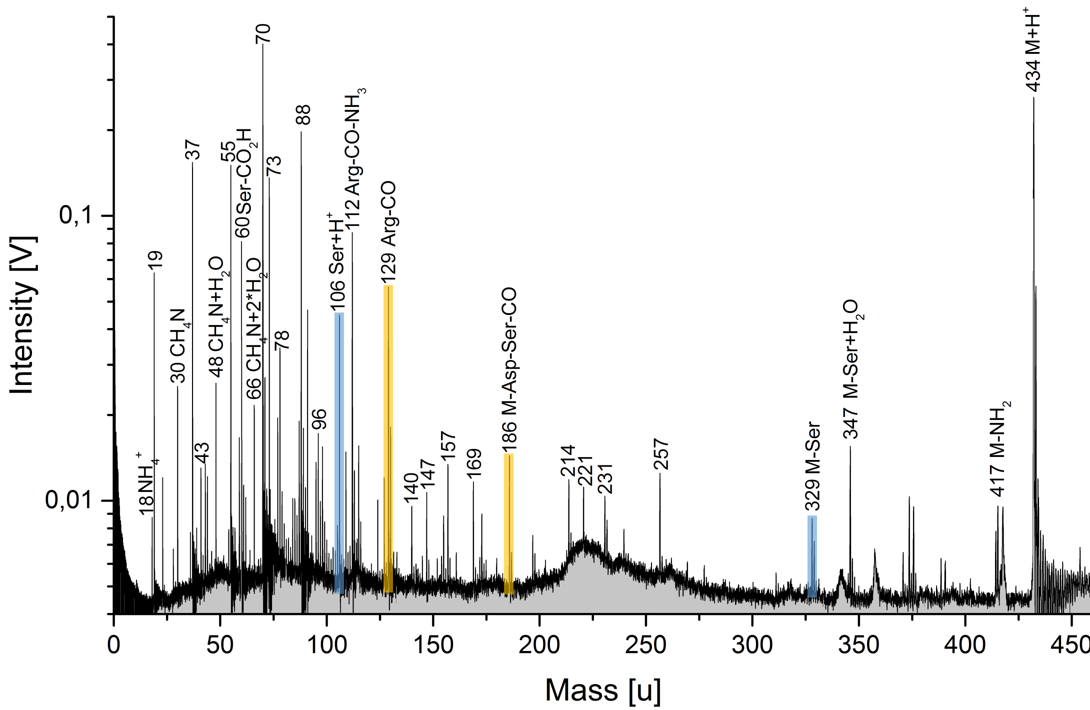
Backup: Amino acids & fatty acids: Biotic case

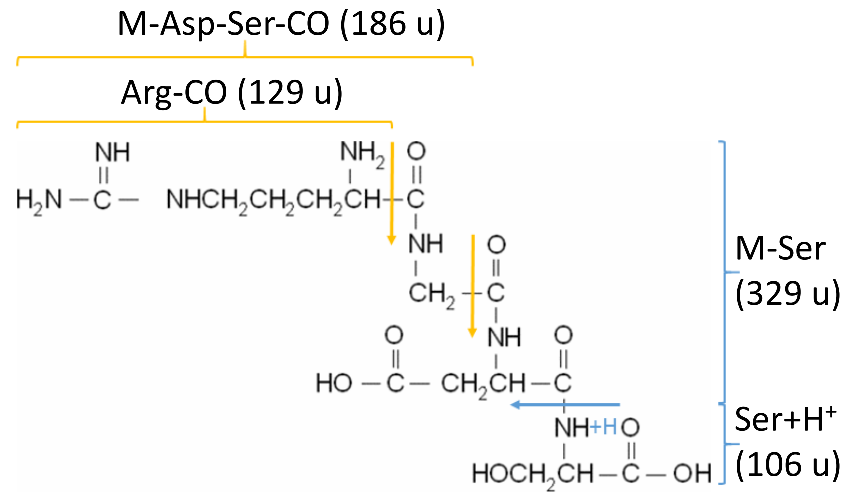


Backup: Peptides

42 ppm molar Arg-Gly-Asp-Ser in H_2O, positive ion mode

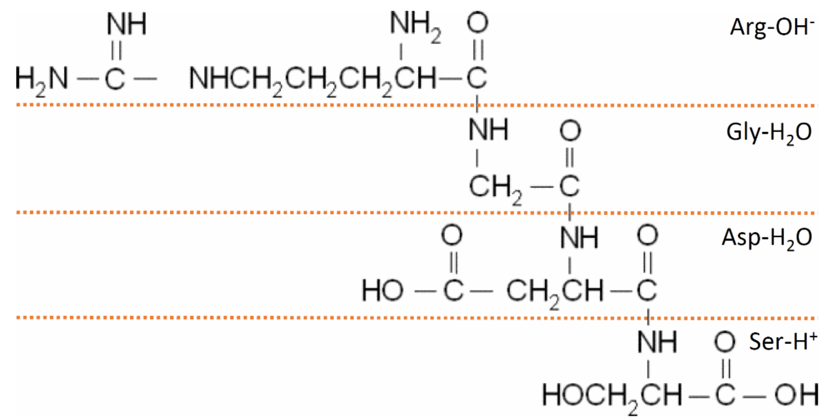


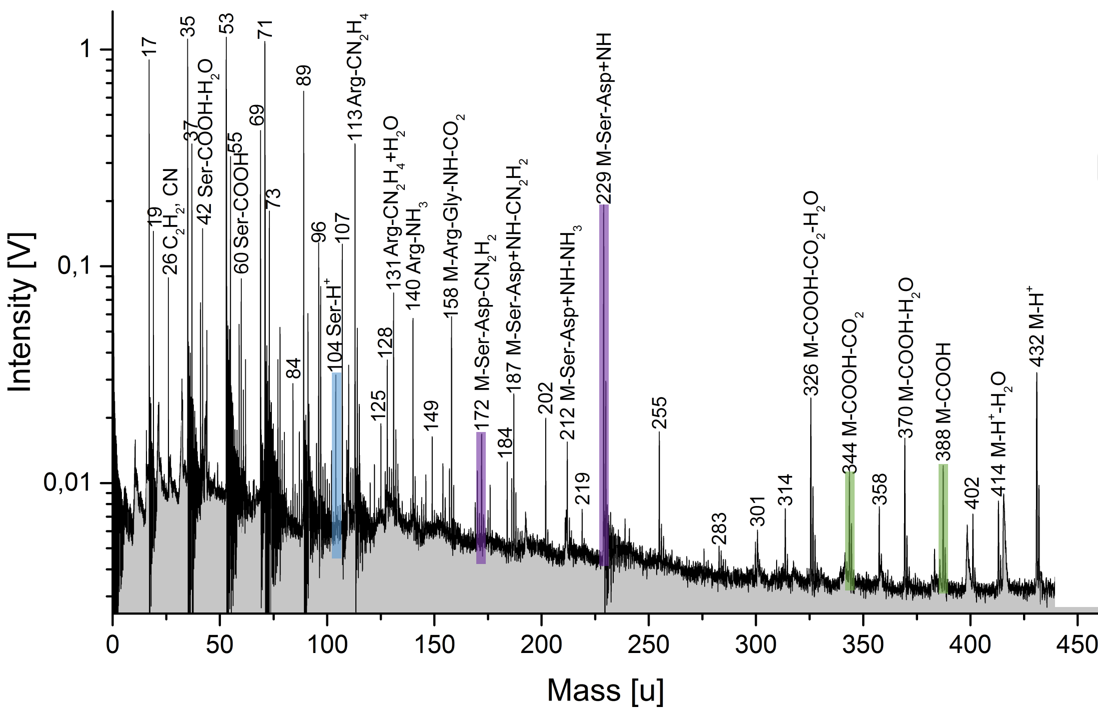


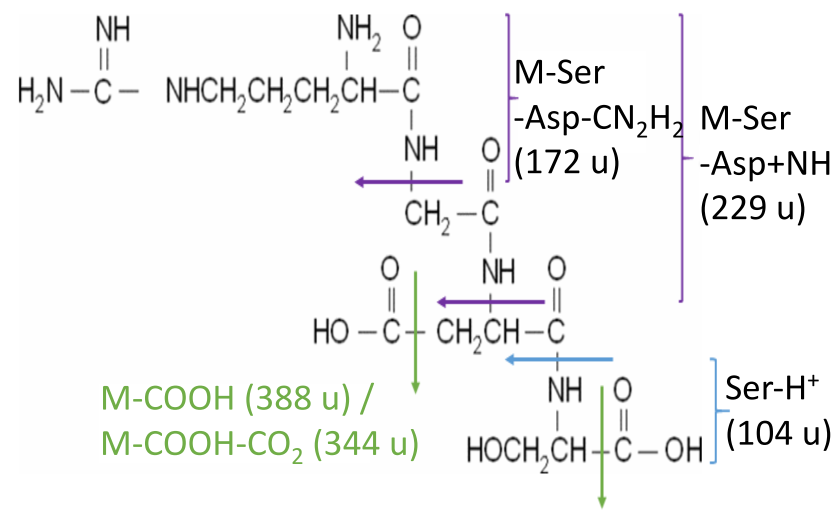


Backup: Peptides

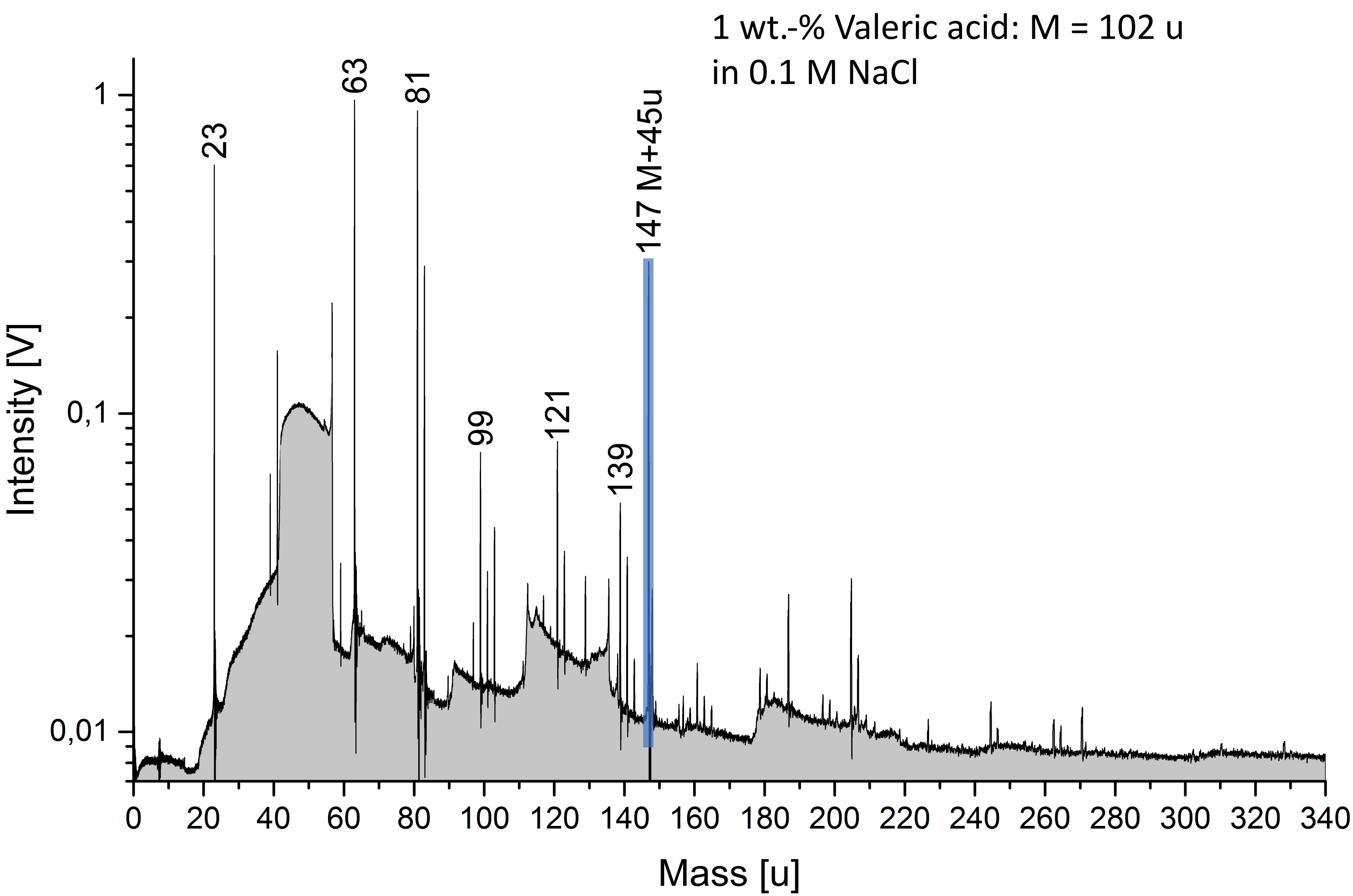
42 ppm molar Arg-Gly-Asp-Ser in H_2O, negative ion mode







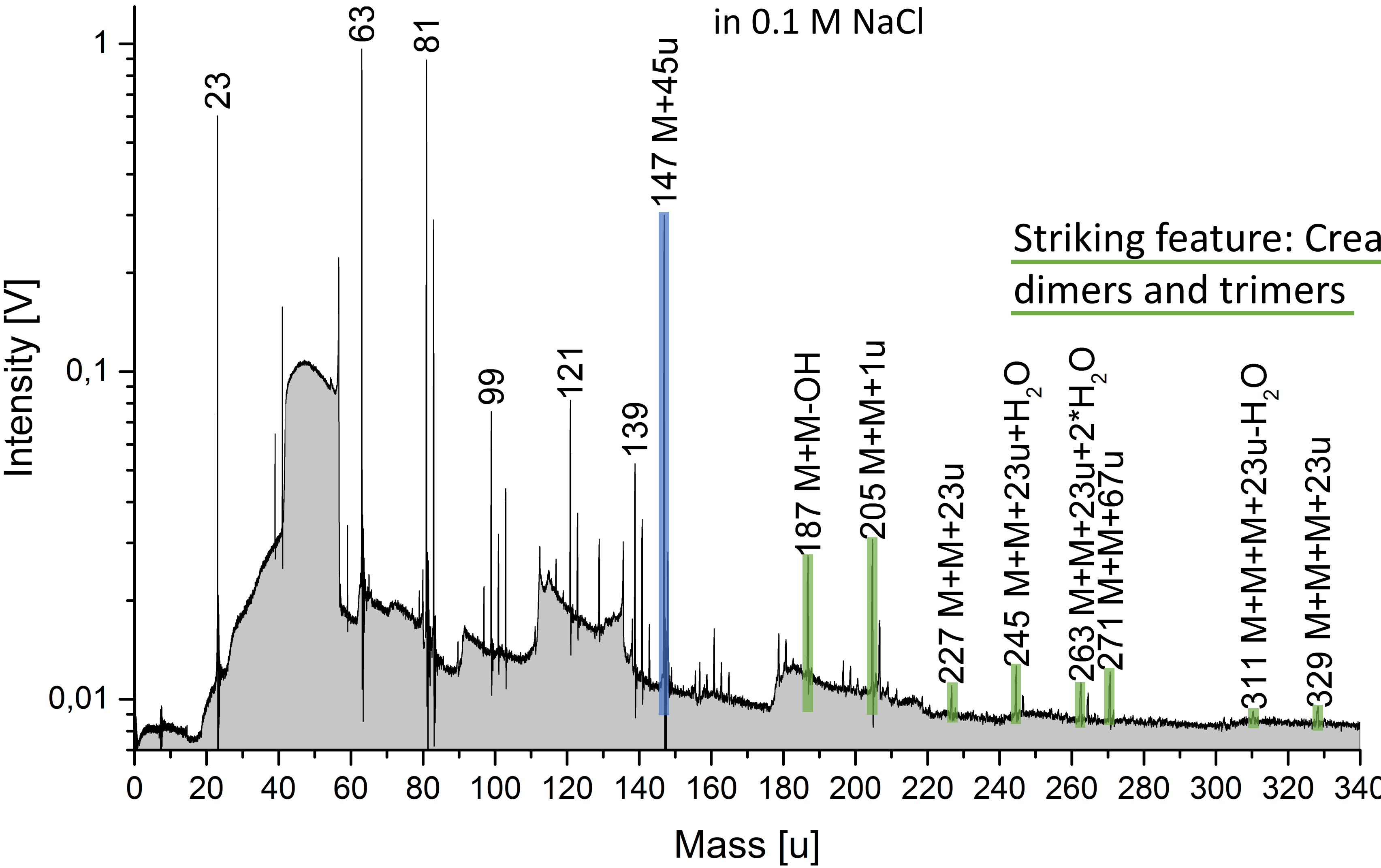
Backup: Sodium complexation of straight chained carboxylic acids



Backup: Sodium complexation of straight chained carboxylic acids

1 wt.-% Valeric acid: M = 102 u
in 0.1 M NaCl

Striking feature: Creation of dimers and trimers

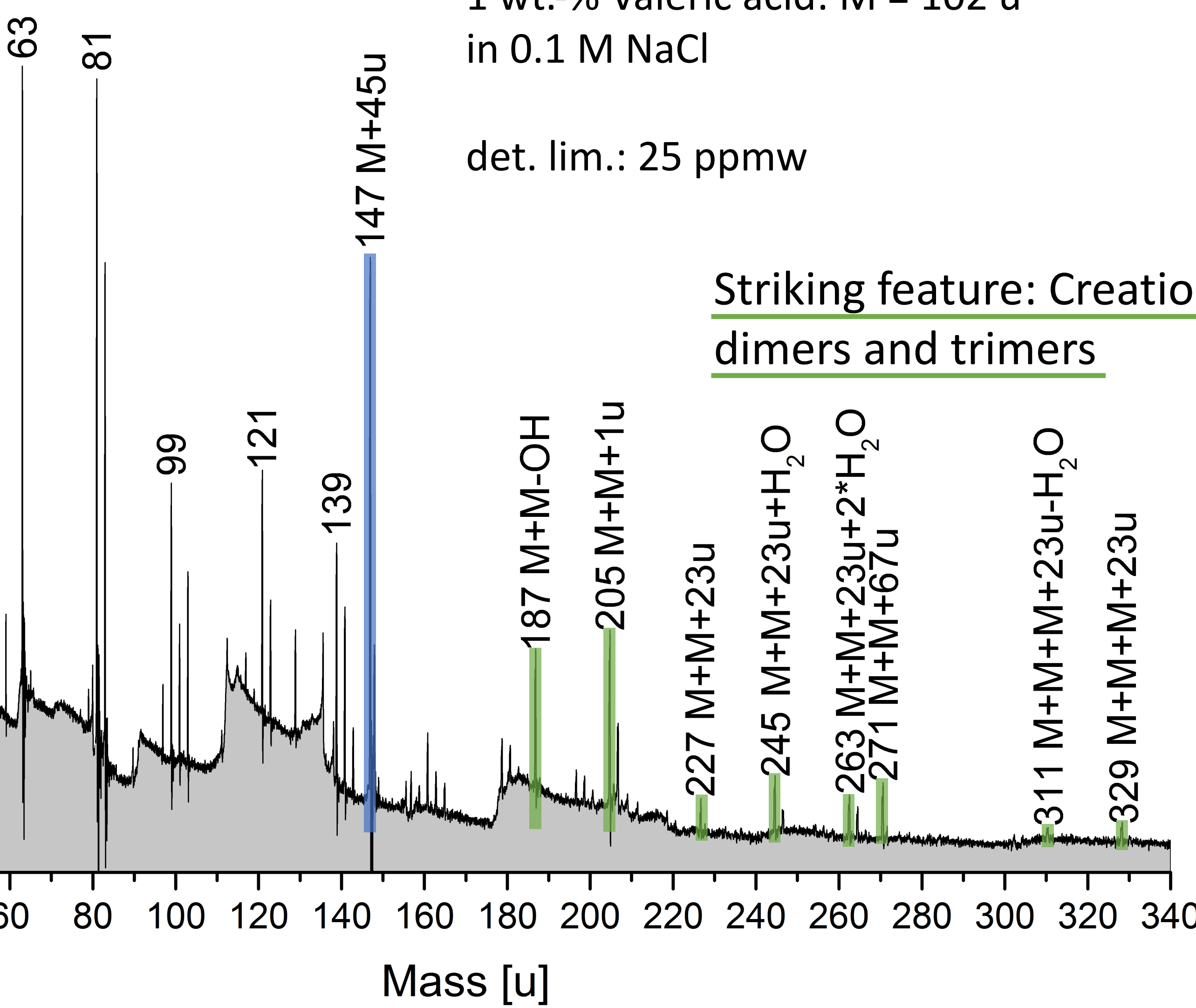


Backup: Sodium complexation of straight chained carboxylic acids and their detection limits

1 wt.-% Valeric acid: M = 102 u
in 0.1 M NaCl

det. lim.: 25 ppmw

Striking feature: Creation of dimers and trimers



Detection limits of fatty acids:

Lauric acid (C_{12}),
Tridecylic acid (C_{13}),
Myristic acid (C_{14}),
Pentadecylic acid (C_{15}):

each < 10 ppbw
(in H_2O, neg. spectra)