NATIONAL HIGH MAGNETIC FIELD LABORATORY

FT-ICR MS as a Tool for Understanding Asphaltene Molecular Composition and Application for Production of Carbon Fibers

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NSF

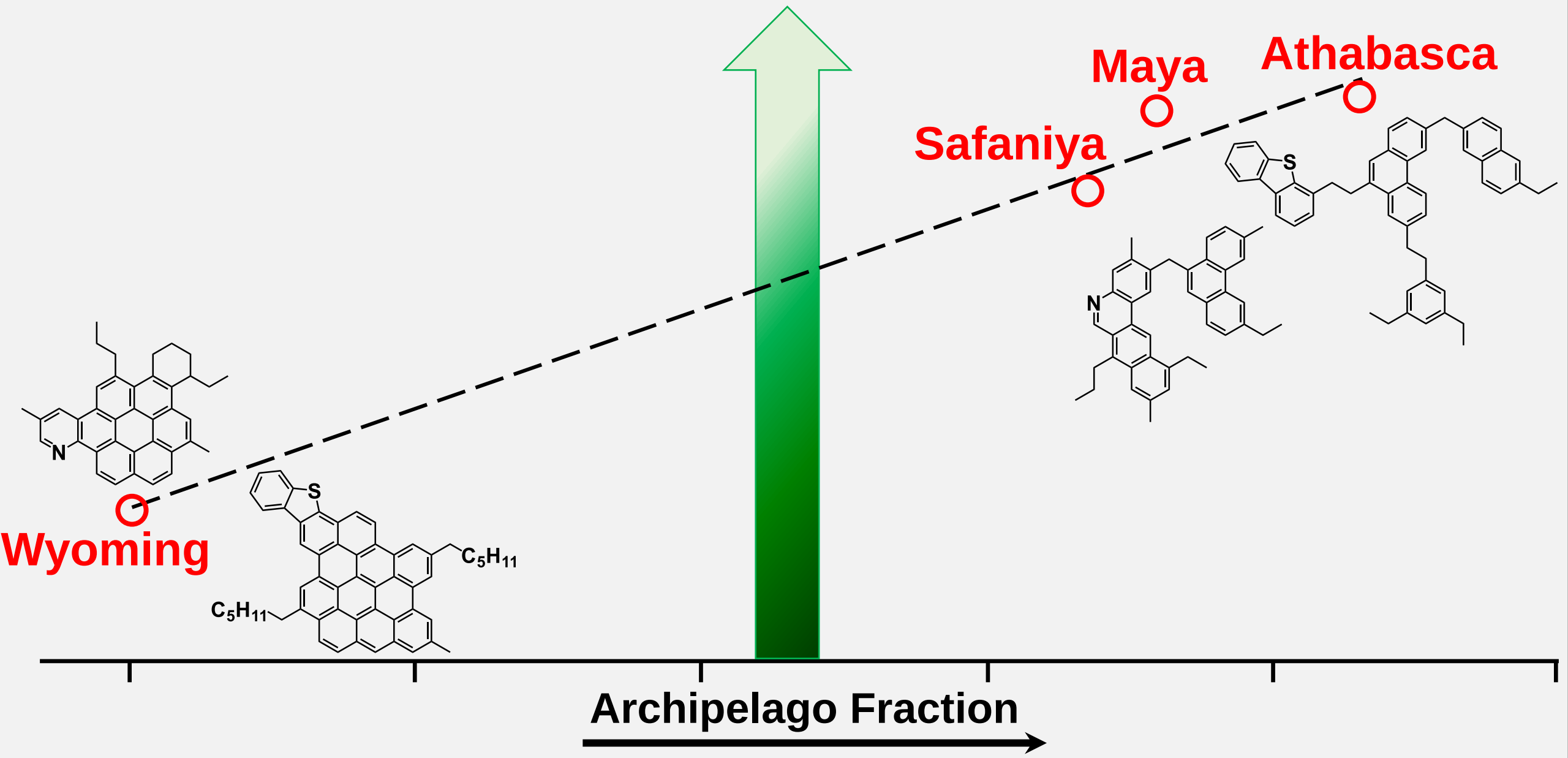
GULF OF MEXICO RESEARCH INITIATIVE

FLORIDA STATE UNIVERSITY 1851

UF UNIVERSITY of FLORIDA

Los Alamos NATIONAL LABORATORY

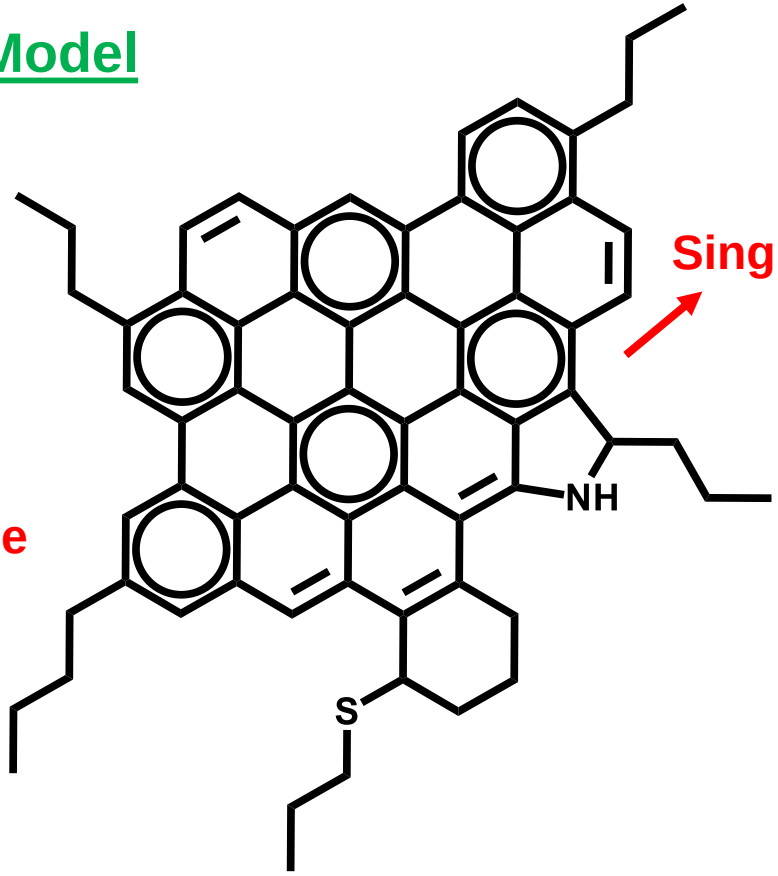
Amount of Distillable Products Upon Hydroconversion



Energy Fuels 2022, 36, 8, 4370−4380

Why the Controversy? Island *vs*. Archipelago Motifs

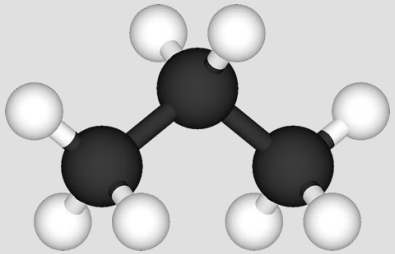
Island Model



Energy Fuels, 14 (1), 2000, 6-10

Pyrolysis / Thermal-Cracking Products

Coke



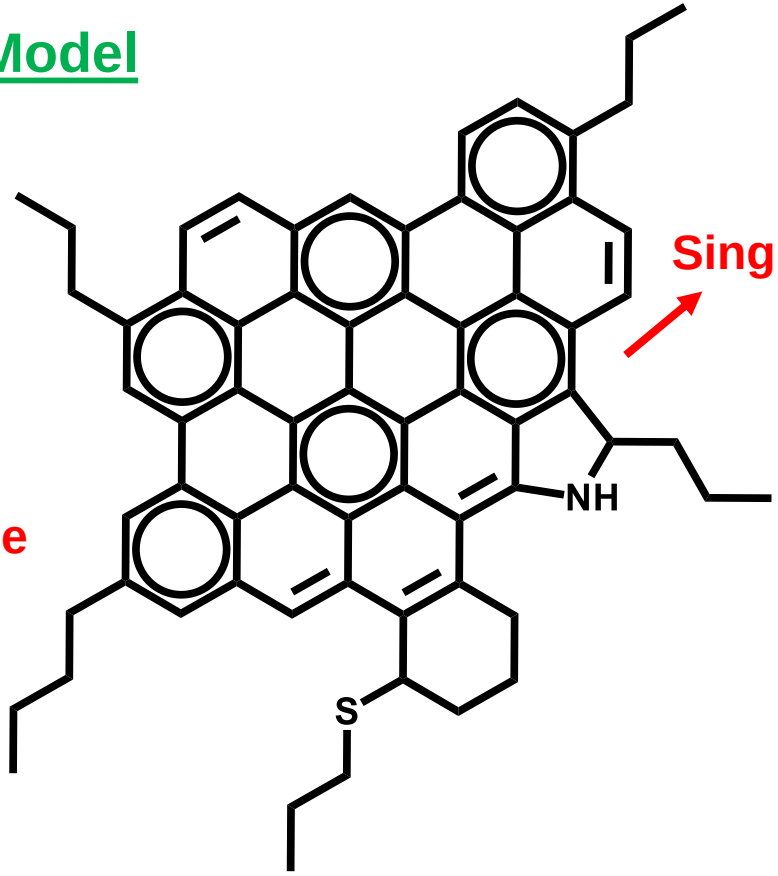
Gas

+

Naphtha
Alkanes

Why the Controversy? Island *vs*. Archipelago Motifs

Island Model



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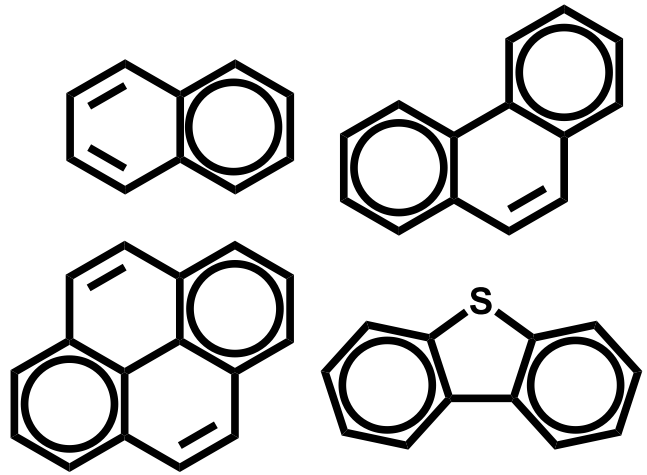

Pyrolysis / Thermal-Cracking Products

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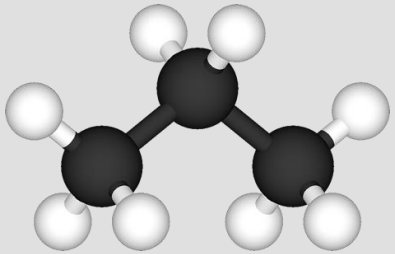


Gas

+

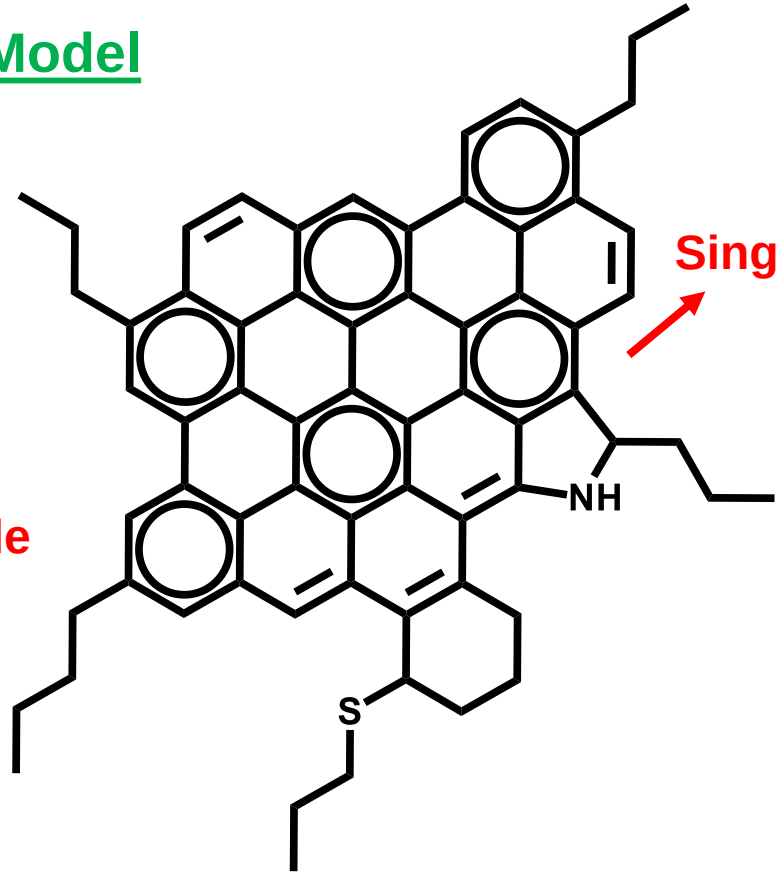
Naphtha
Alkanes

Distillable
1-5+ Ring aromatics

(Unique to Archipelago)

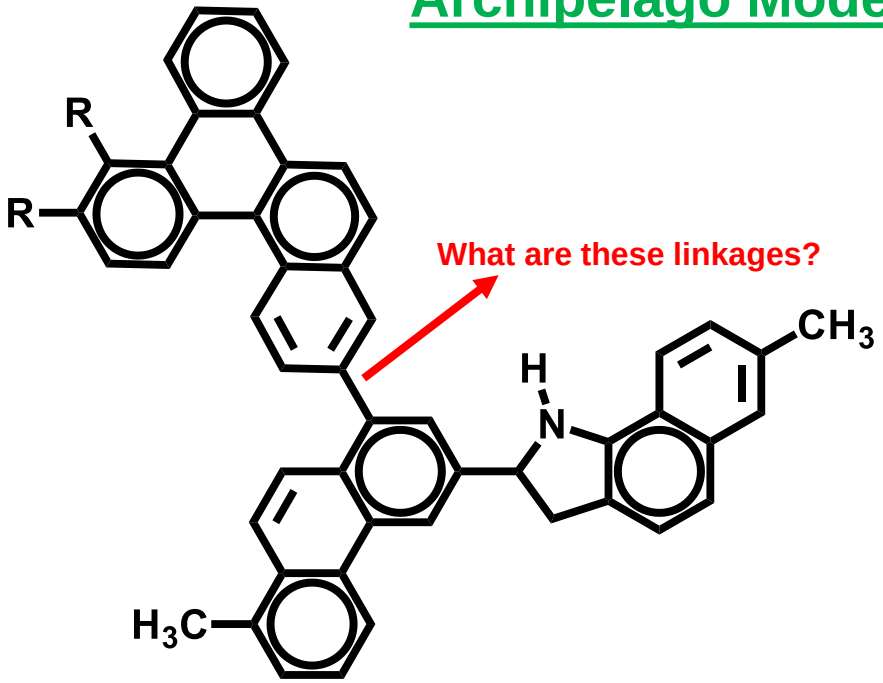
Why the Controversy? Island *vs*. Archipelago Motifs

Island Model



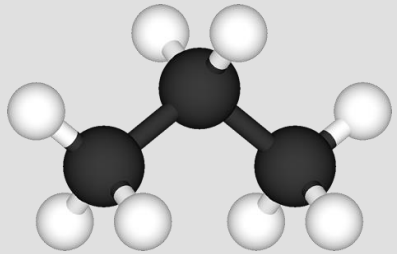
Energy Fuels, 14 (1), 2000, 6-10

Archipelago Model



Pyrolysis / Thermal-Cracking Products

Coke



Gas

\+

Naphtha
Alkanes

Distillable
1-5+ Ring aromatics

(Unique to Archipelago)

For ~20 years, Mass Spectrometry Supported the Dominance of Island Structures in Petroleum / Coal Asphaltenes

Why?

Asphaltene Petroleomics Requirements

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FT-ICR MS

Gas Phase Fragmentation

Sample Preparation

Sample complexity

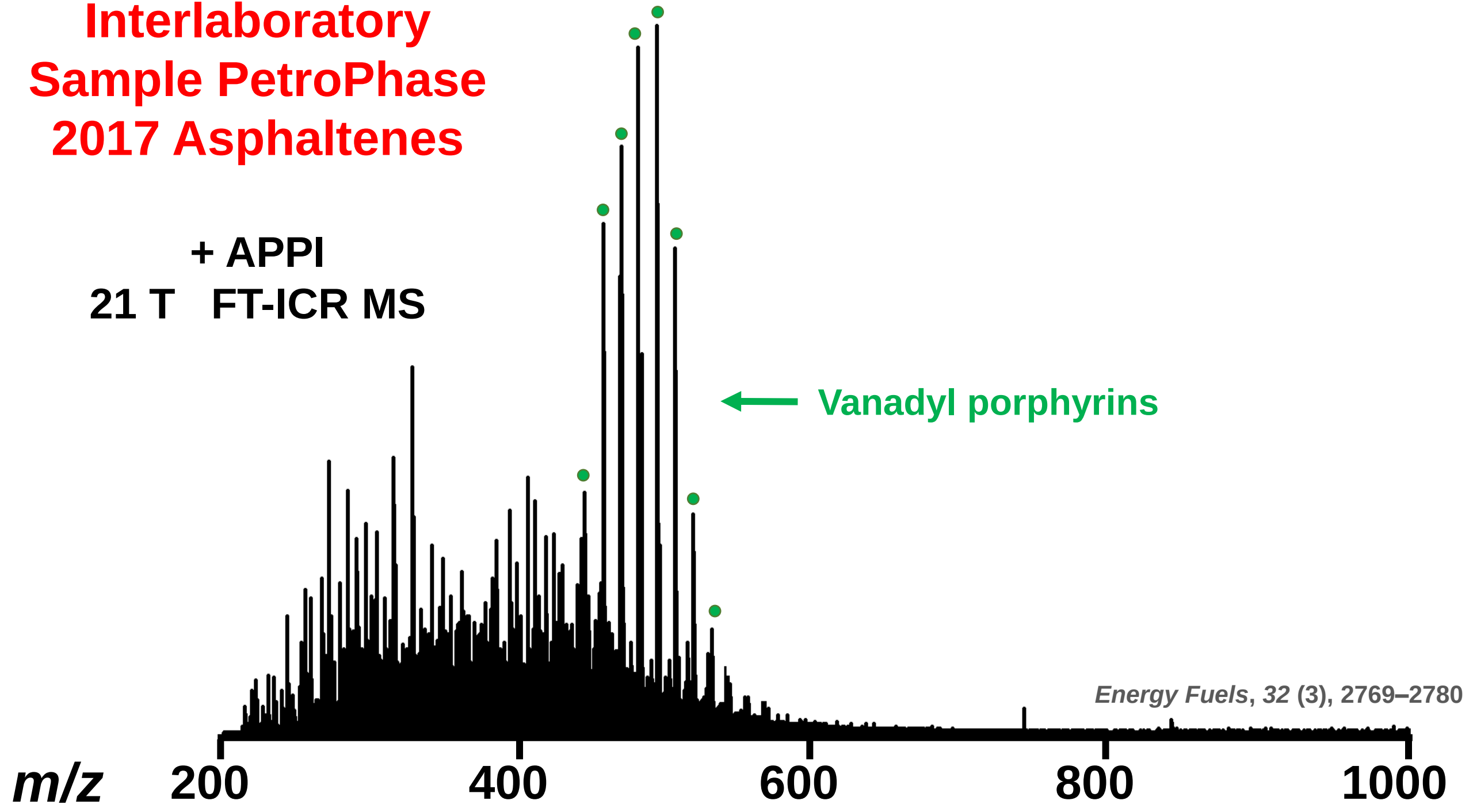
IRMPD / HE-CID

Selective Ionization

Interlaboratory Sample PetroPhase 2017 Asphaltenes

+ APPI

21 T FT-ICR MS



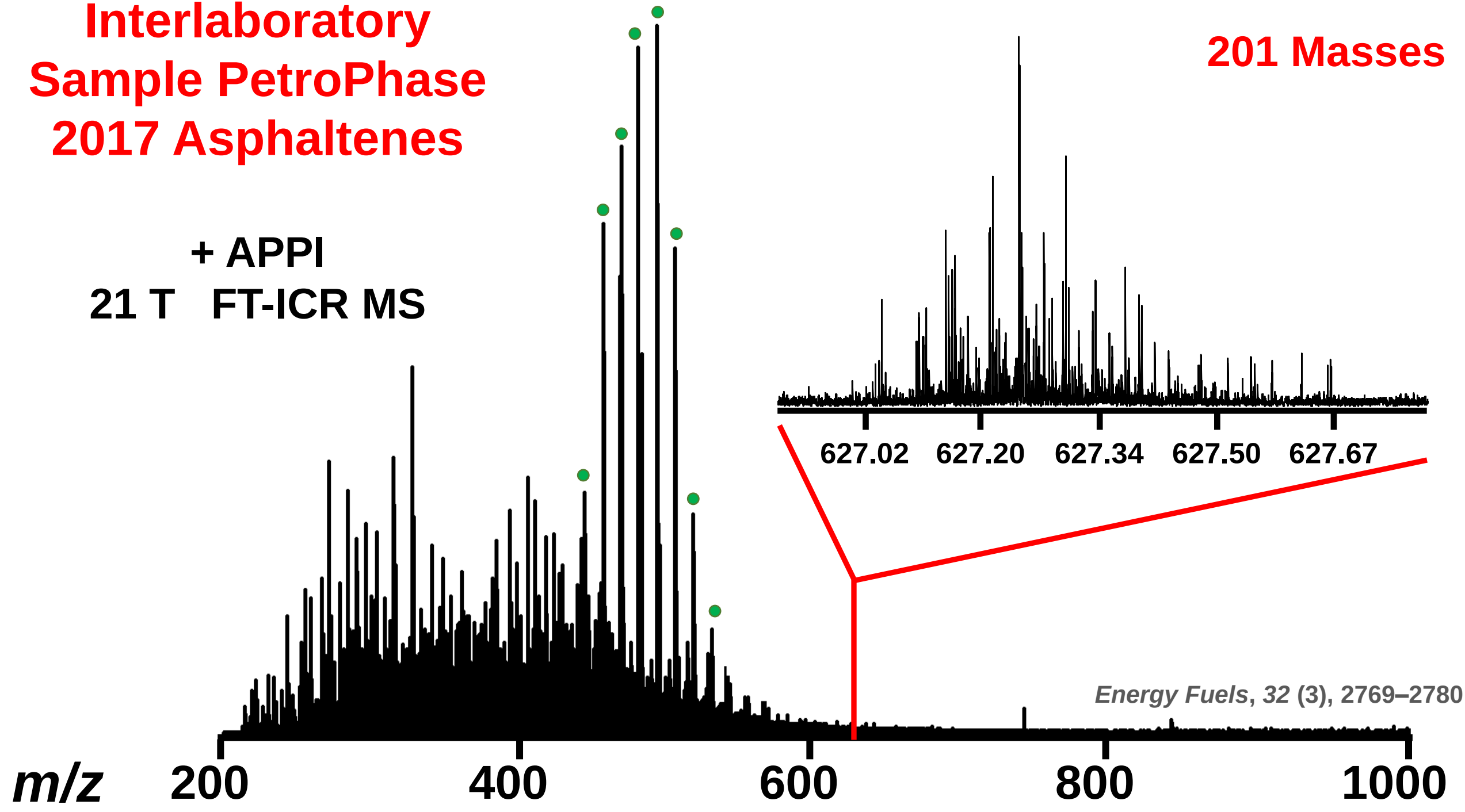
Energy Fuels, *32* (3), 2769–2780

Interlaboratory Sample PetroPhase 2017 Asphaltenes

+ APPI

21 T FT-ICR MS

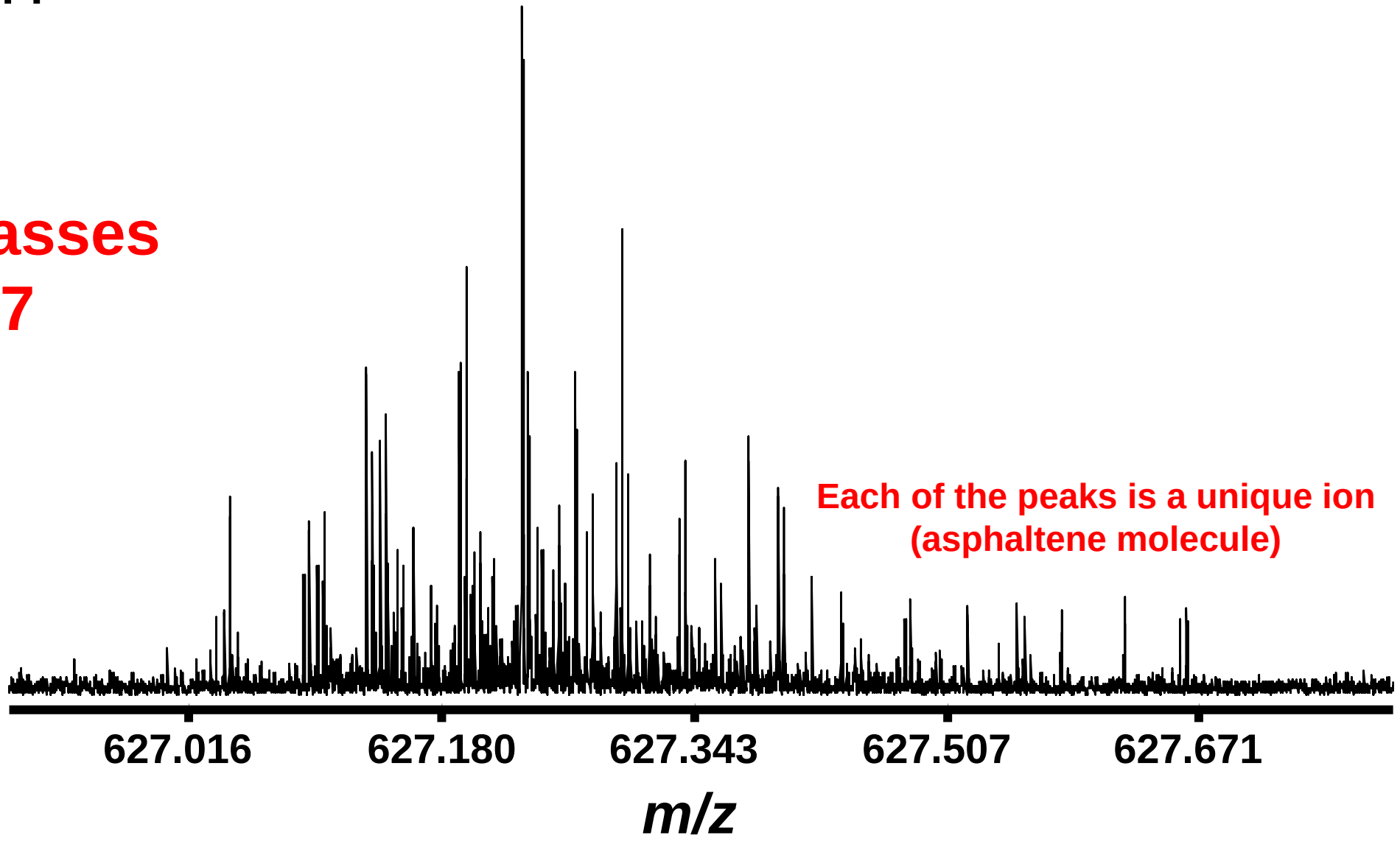
201 Masses

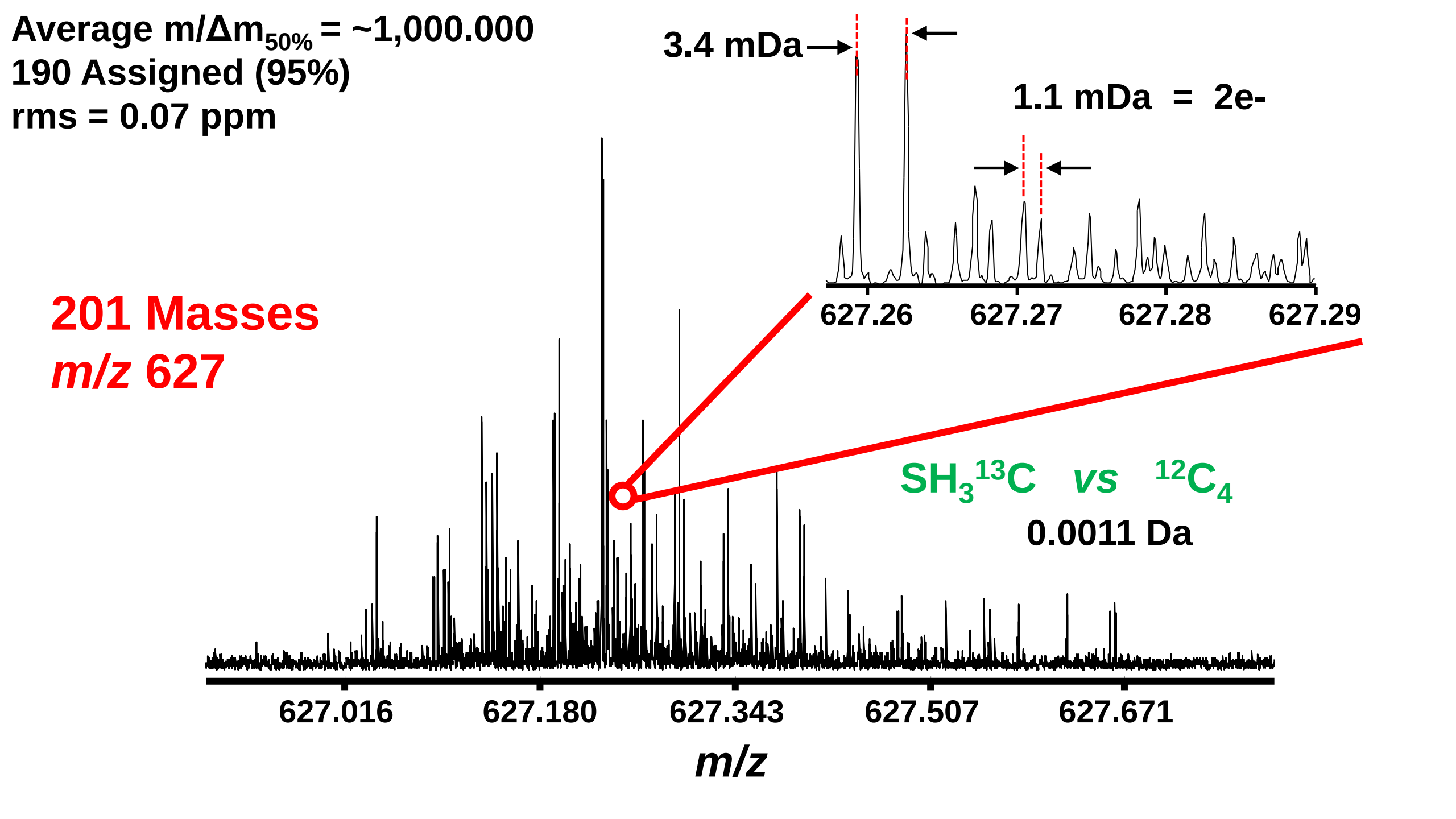


Energy Fuels, *32* (3), 2769–2780

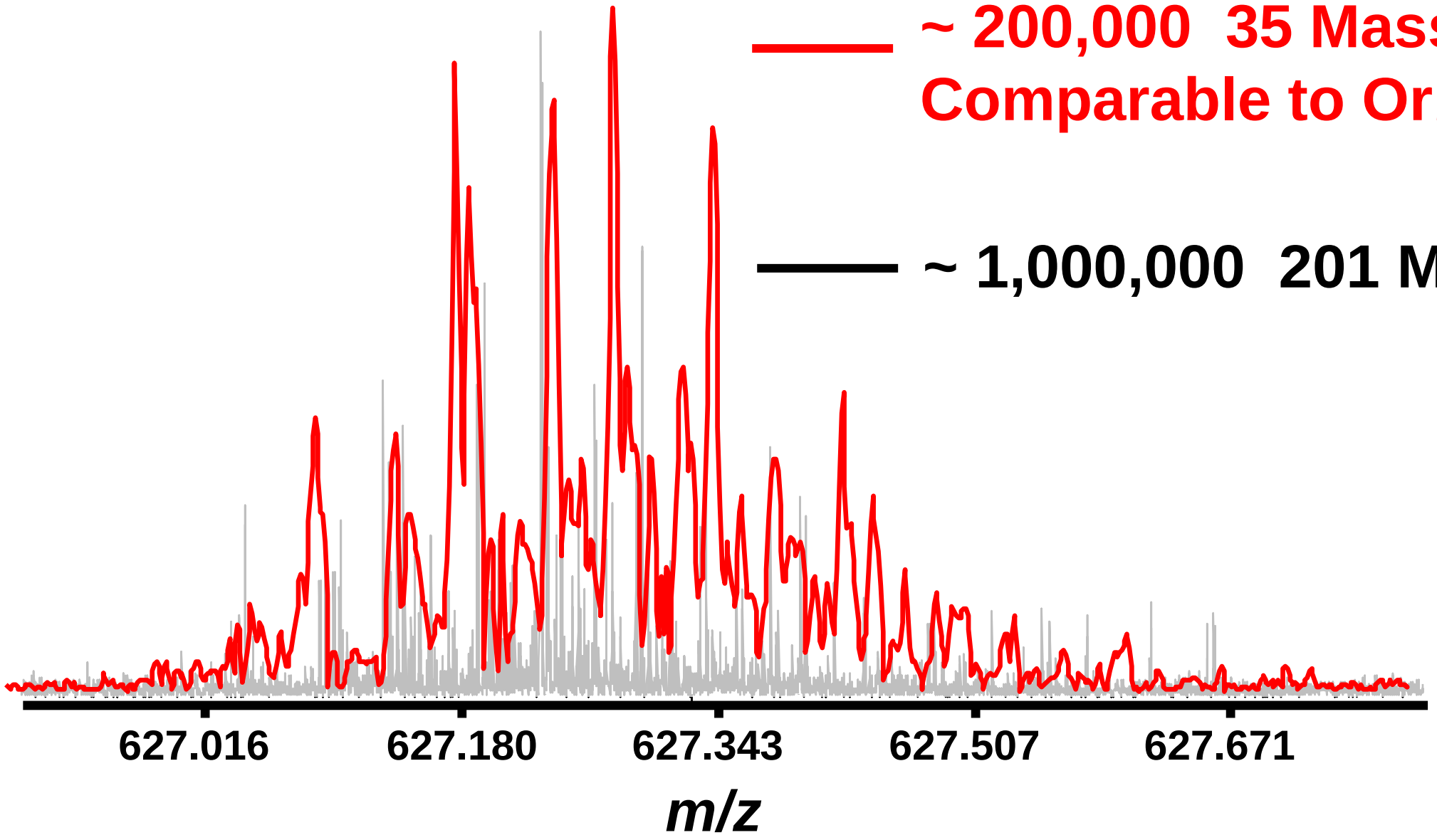
Average m/Δm$_{50\%}$ = 1,000.000
190 Assigned (95%)
rms = 0.07 ppm

201 masses
***m/z* 627**



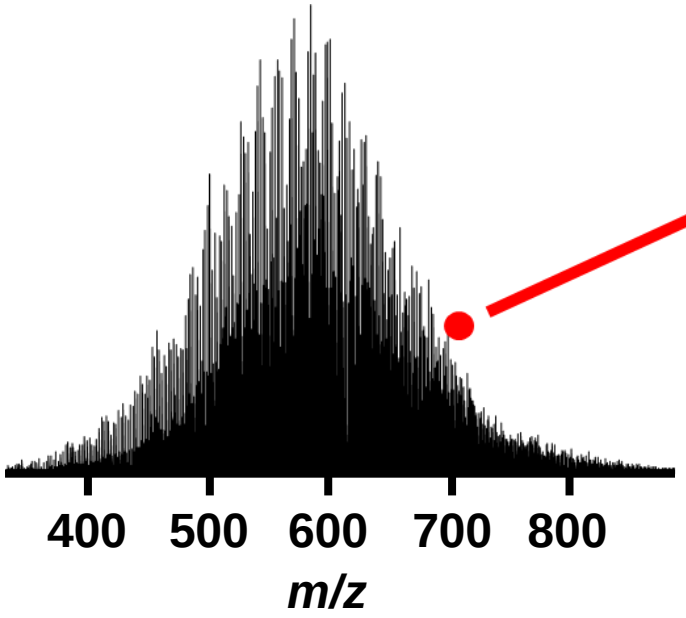

Average m/Δm50% = ~1,000.000
190 Assigned (95%)
rms = 0.07 ppm
3.4 mDa
1.1 mDa = 2e-
627.26
627.27
627.28
627.29
201 Masses
m/z 627
SH3 13C vs 12C4
0.0011 Da
627.016
627.180
627.343
627.507
627.671
m/z

Ultra-complexity within a Single Nominal Mass



How to Extract Molecular-level Information from Mass-Spec Data Useful for Understanding Challenges in the Petroleum Industry?

Data Processing and Visualization



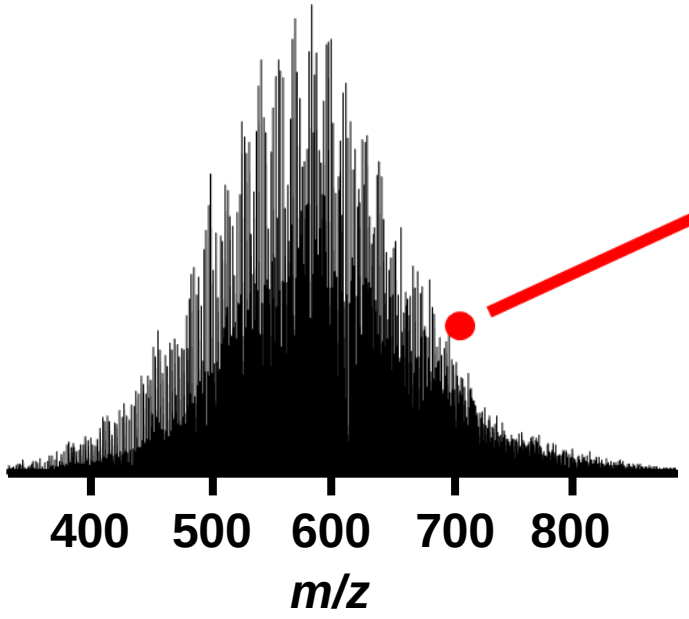
m/z **704.53510**

$[C_{50}H_{72}S_1 + H]^+$

50 - 200 ppb

FSU

Data Processing and Visualization



m/z 704.53510

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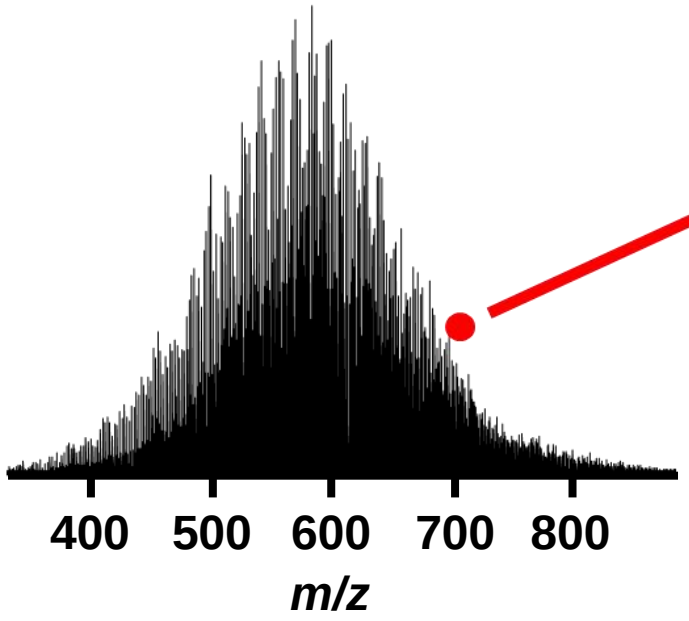
50 - 200 ppb

Data Processing and Visualization



m/z 704.53510

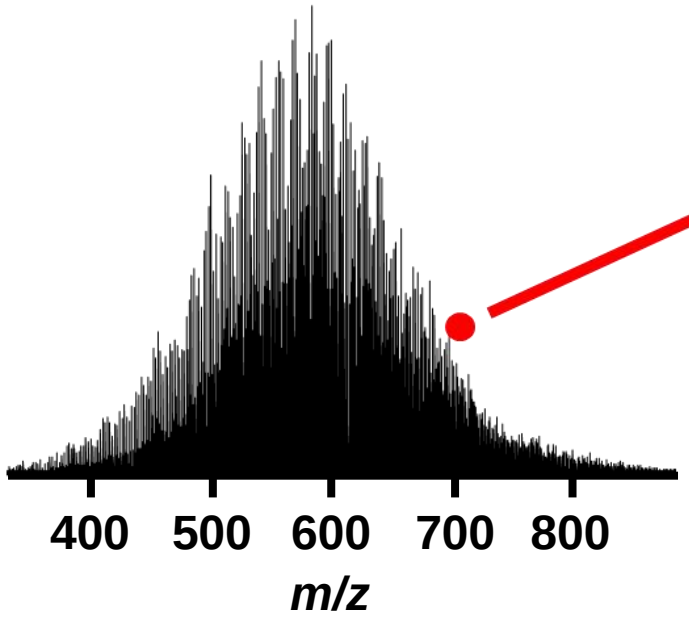
50 - 200 ppb

$[C_{50}H_{72}S_1 + H]^+$

1. Carbon number
2. Rings + Double Bonds

$$DBE = C - \frac{H}{2} + \frac{N}{2} + 1$$

Data Processing and Visualization



m/z 704.53510

50 - 200 ppb

$[C_{50}H_{72}S_1 + H]^+$

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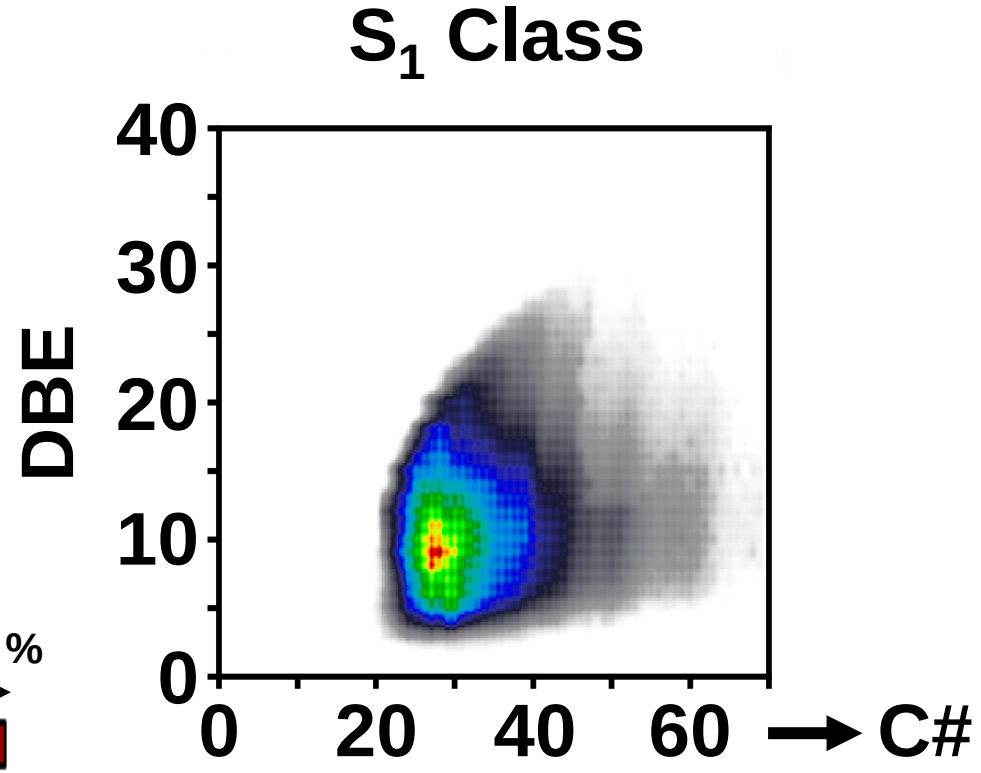
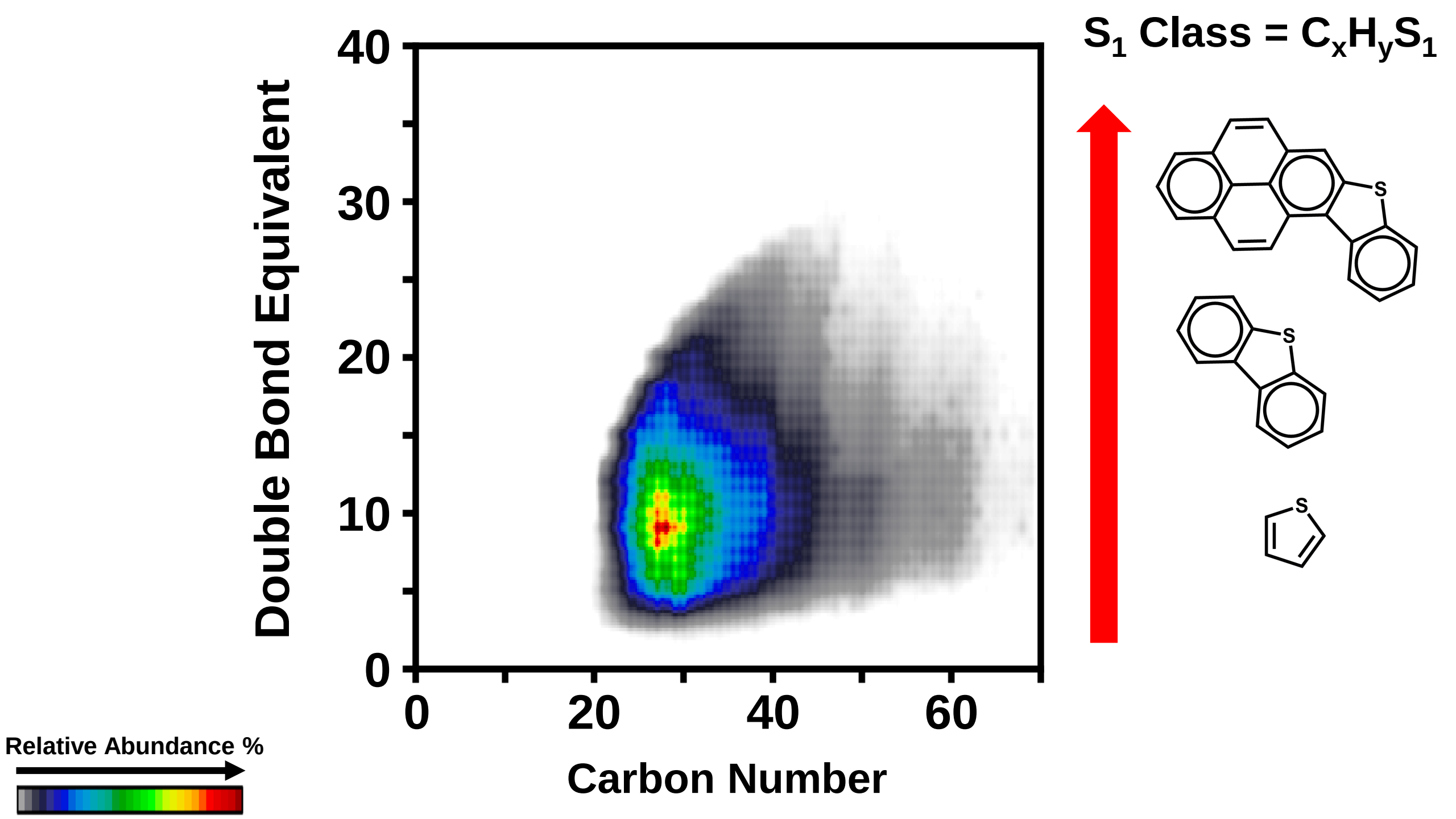
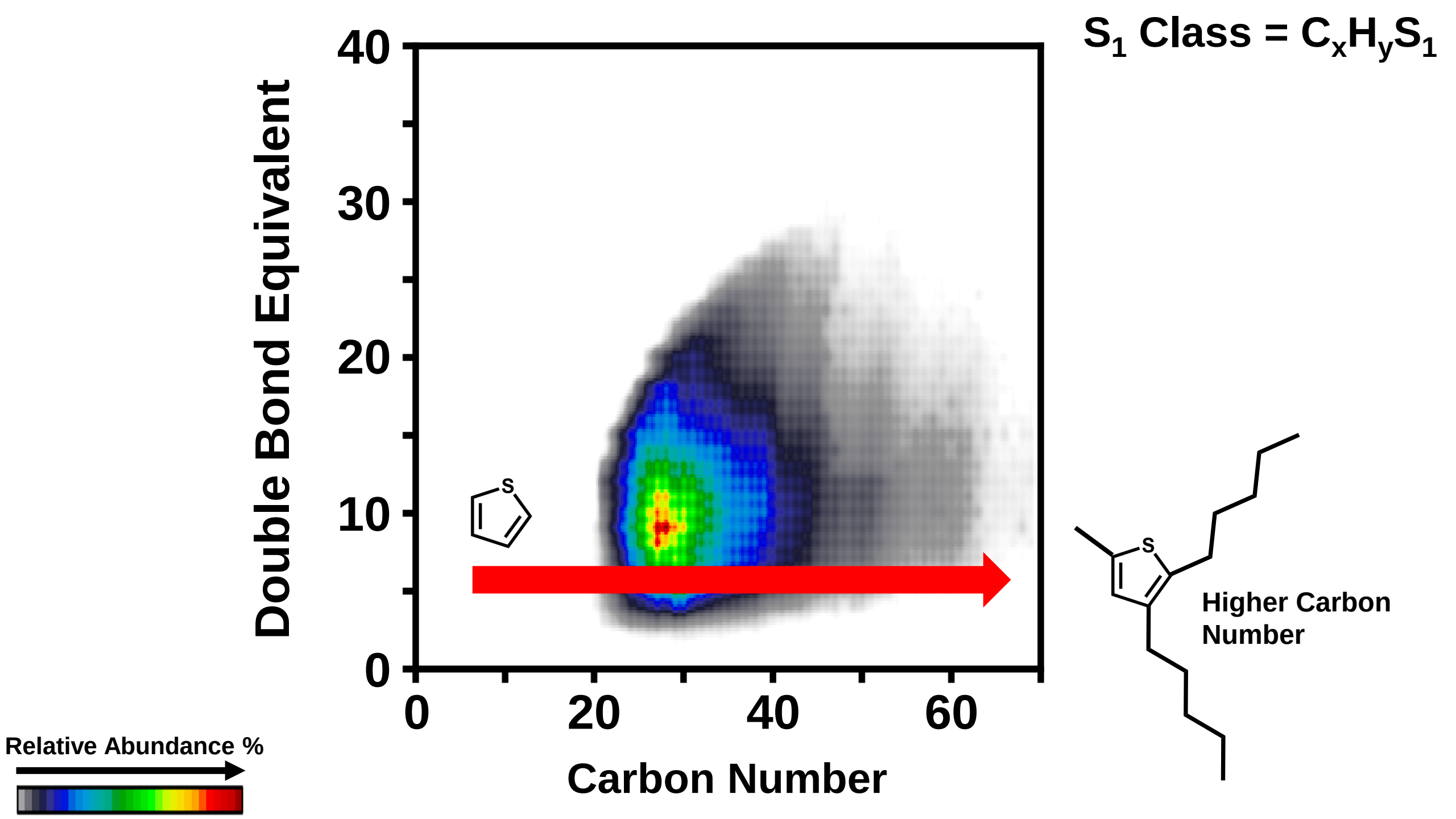
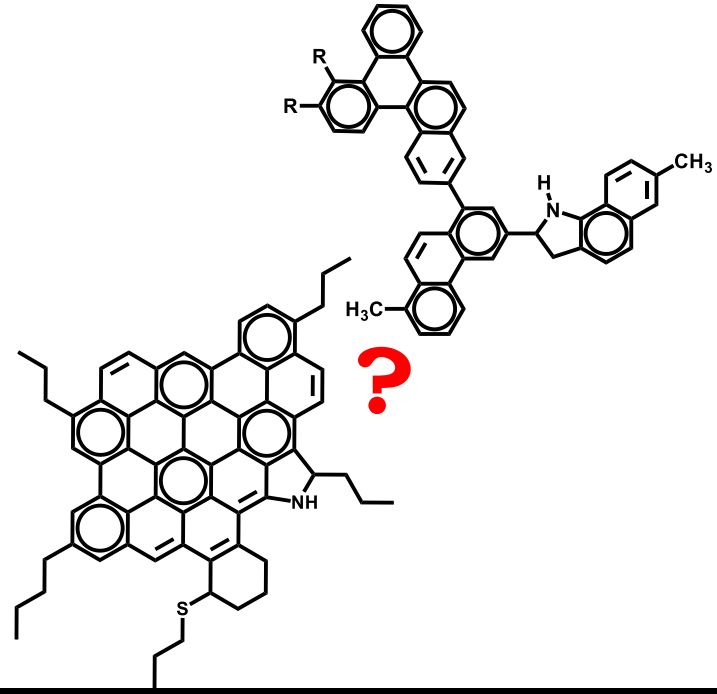



S_1 Class = $C_xH_yS_1$
Double Bond Equivalent
40
30
20
10
0
0
20
40
60
Carbon Number
S
S
S
Relative Abundance %


S_1 Class = $C_xH_yS_1$
Double Bond Equivalent
40
30
20
10
0
0
20
40
60
Carbon Number
S
Higher Carbon Number
Relative Abundance %

Asphaltene Petroleomics Requirements



FT-ICR MS

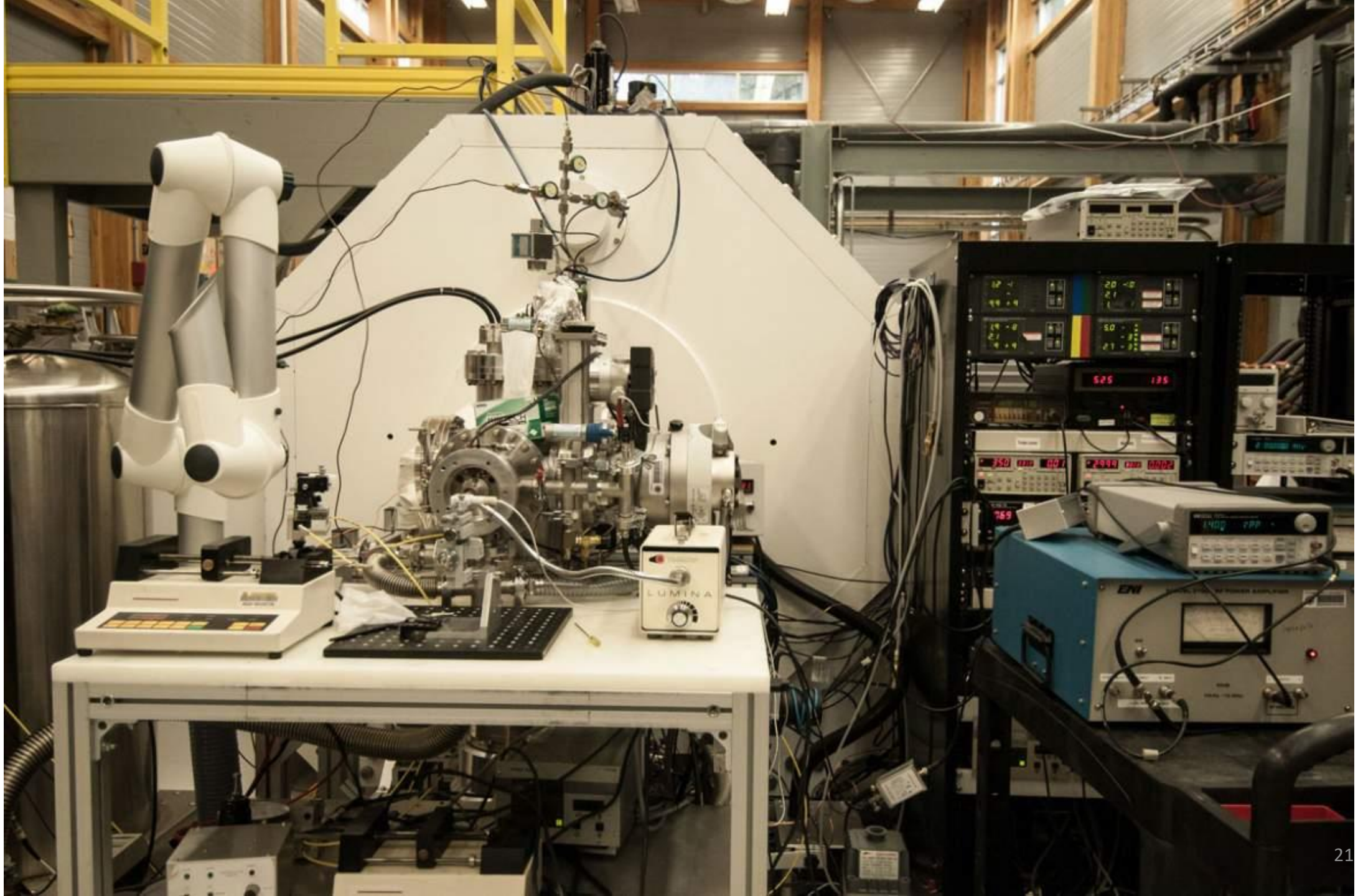
MS / MS Analysis

Sample Preparation

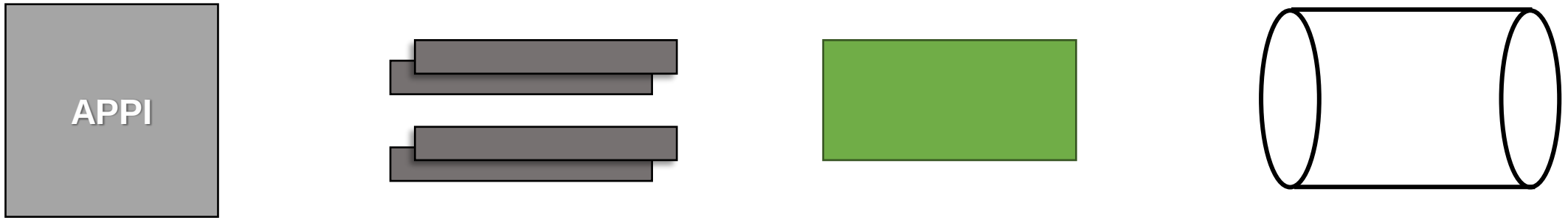
Sample complexity

IRMPD

Selective Ionization


LUMINA
ENI

General Configuration 9.4 T FT-ICR Mass Spectrometer

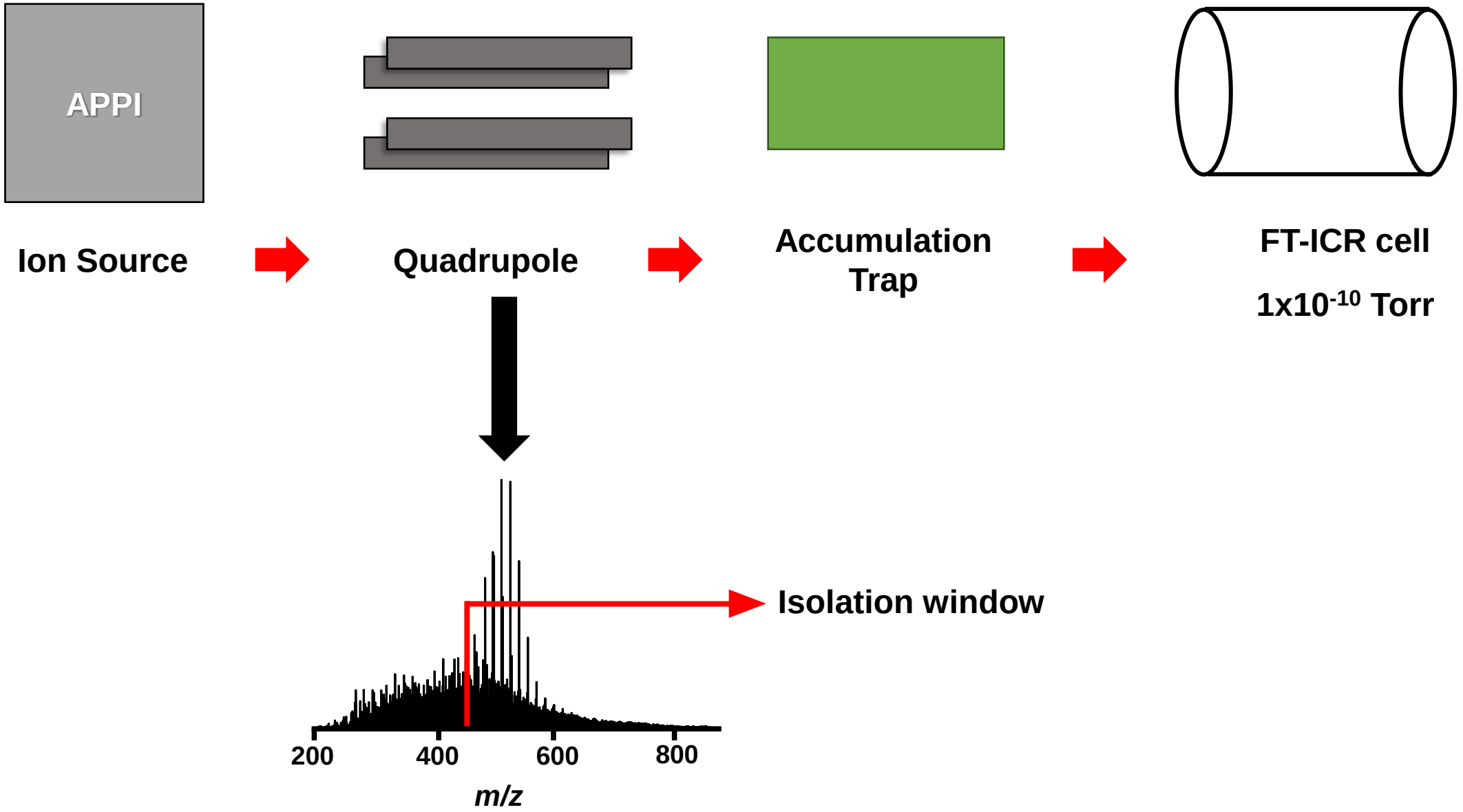


Ion Source → Quadrupole → Accumulation Trap →

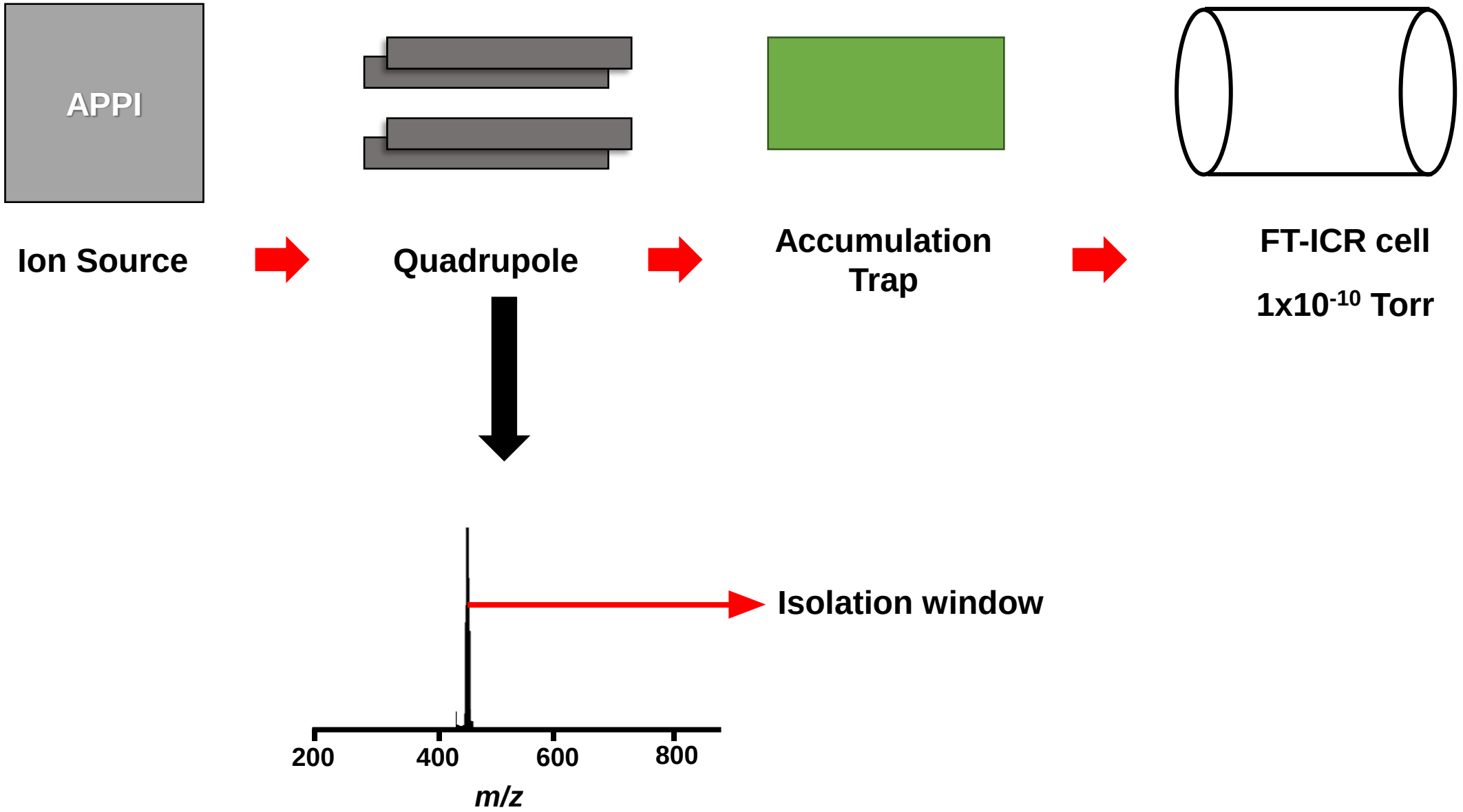
FT-ICR cell

$1x10^{-10}$ Torr

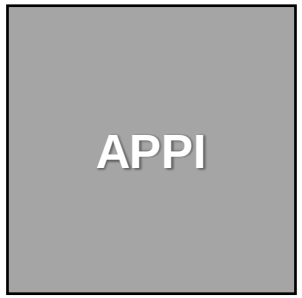
General Configuration 9.4 T FT-ICR Mass Spectrometer



General Configuration 9.4 T FT-ICR Mass Spectrometer



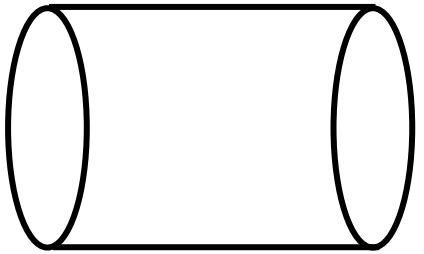
General Configuration 9.4 T FT-ICR Mass Spectrometer



Ion Source

Quadrupole

Accumulation Trap

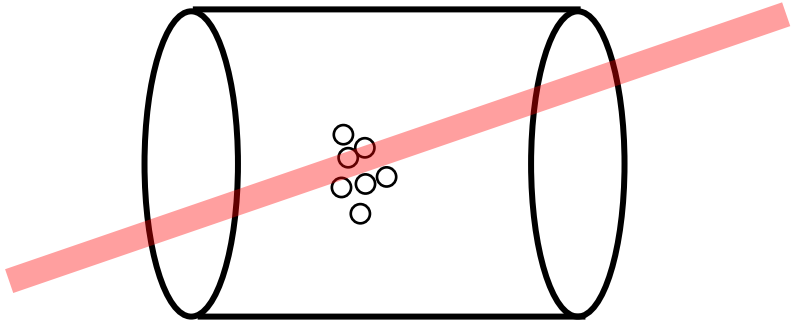


FT-ICR cell

$1x10^{-10}$ Torr

Infrared Multiphoton Dissociation

IRMPD

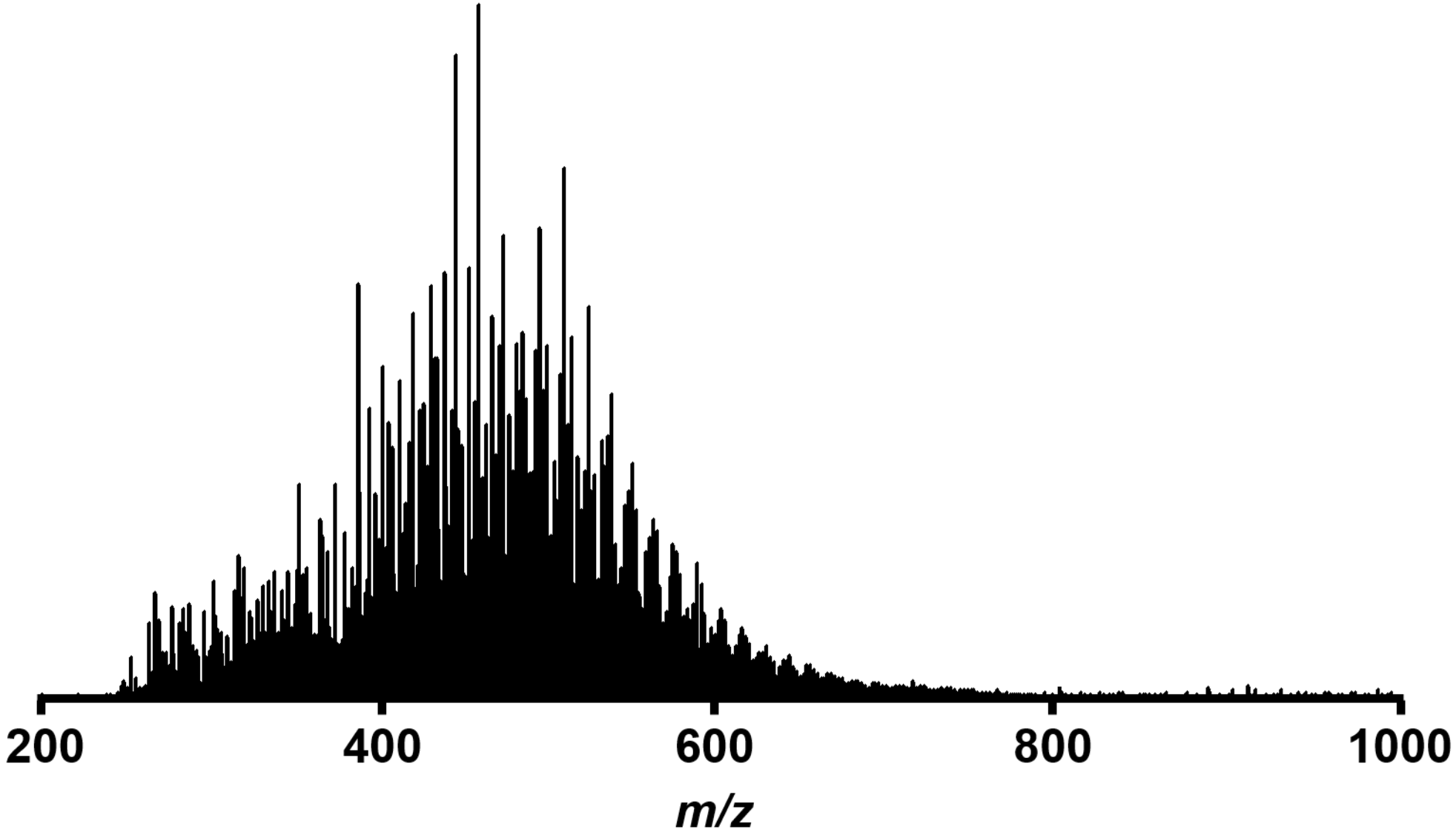


In ultra-high vacuum, secondary reactions (ion/ion reactions are unlikely)

Infrared Laser 10.6 μm
Irradiation time 500 ms
< 10^{-10} Torr

Mass Isolation Prior to IRMPD

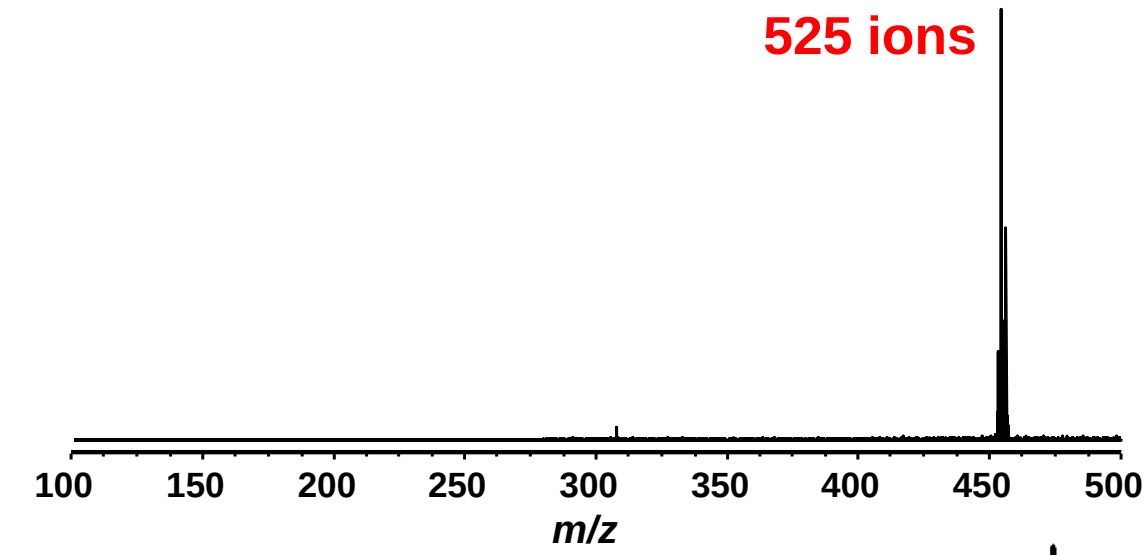
Wyoming Deposit C_7 Asphaltenes



Positive APPI @ 9.4 T

Mass Isolation Prior to IRMPD

Wyoming Deposit C_7 Asphaltenes

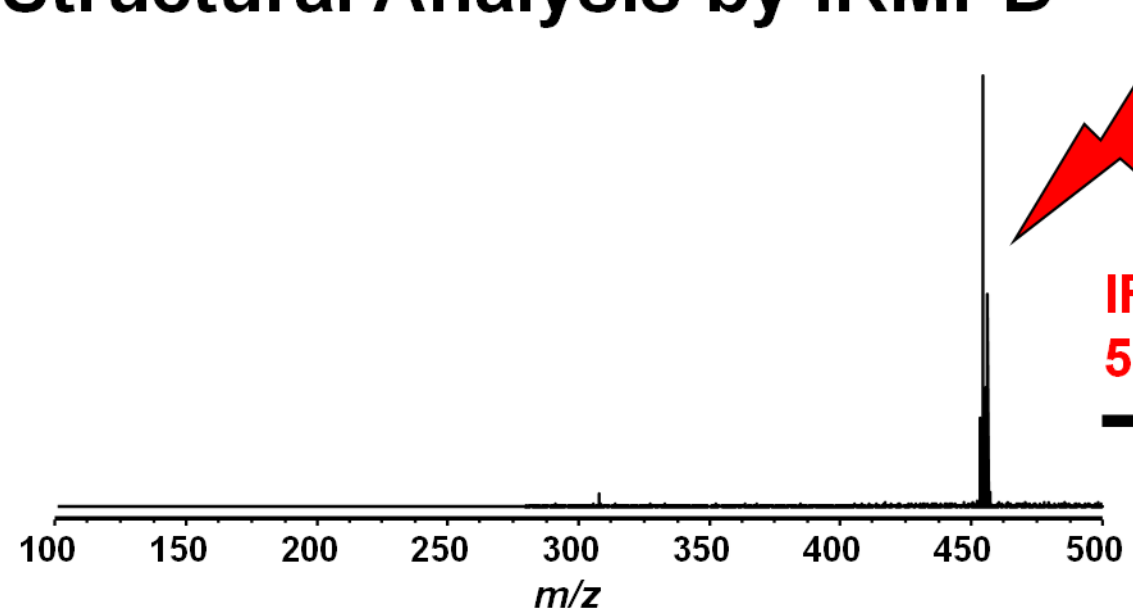


4 Da Quadrupole Isolation

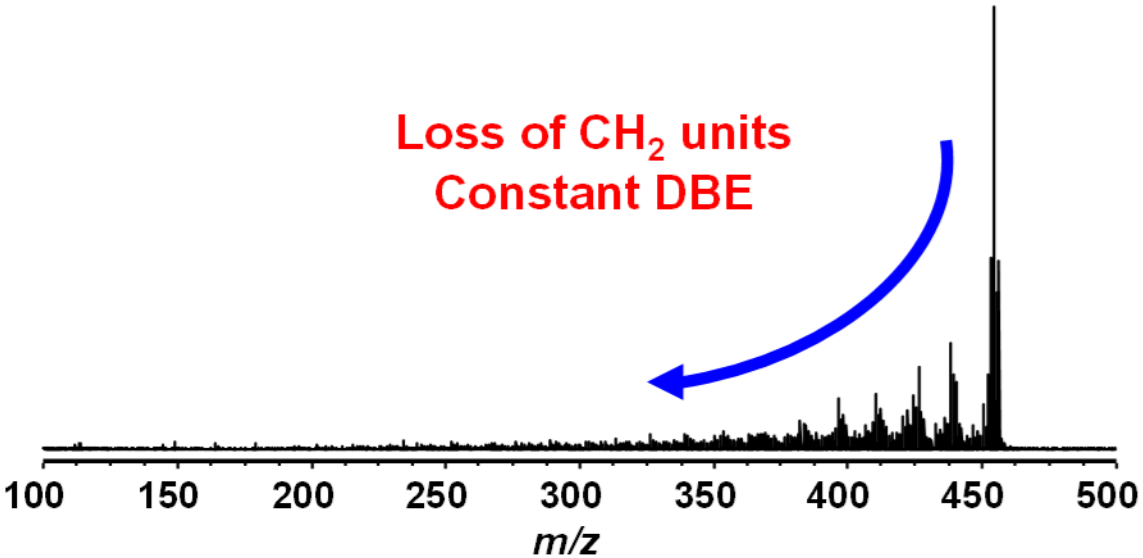
Positive APPI @ 9.4 T

Structural Analysis by IRMPD

Wyoming Deposit C_7 Asphaltenes



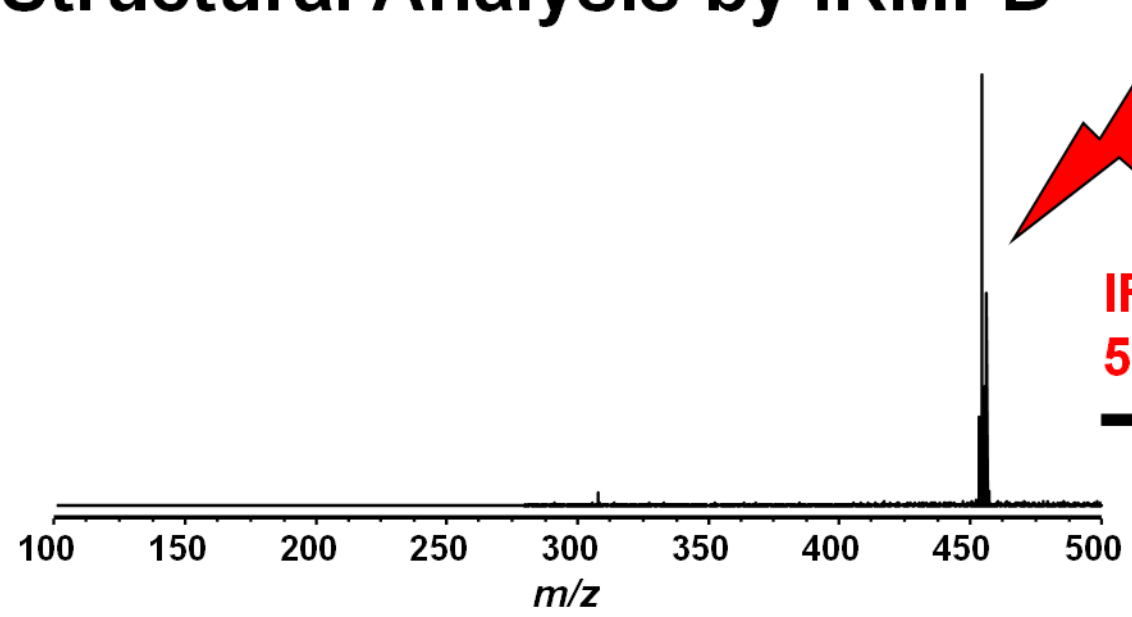
IR Photons
50-500 ms



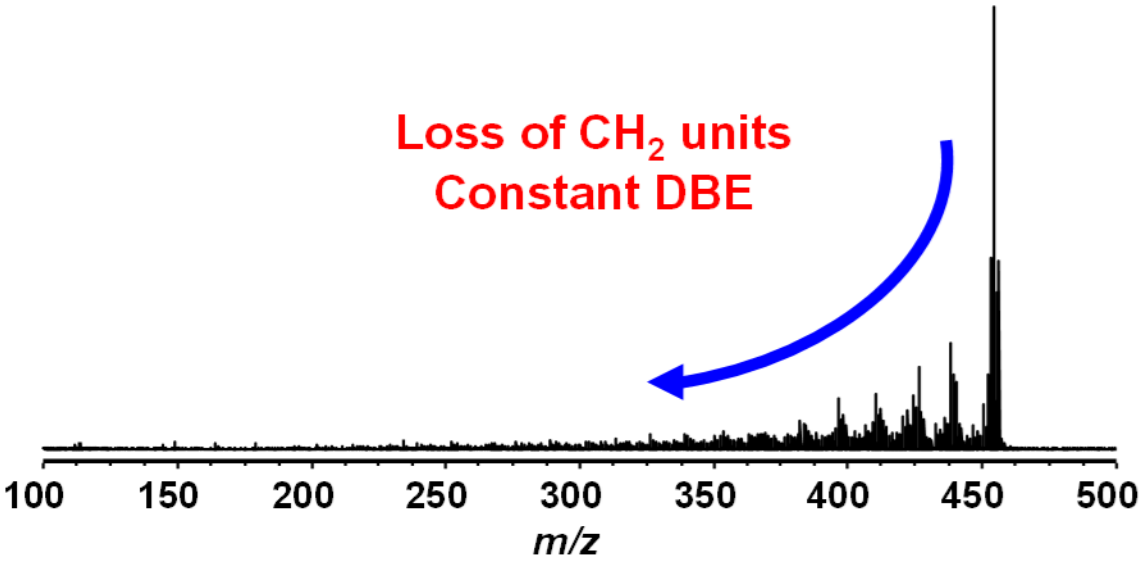
Energy Fuels 31, 12, 13509-13518

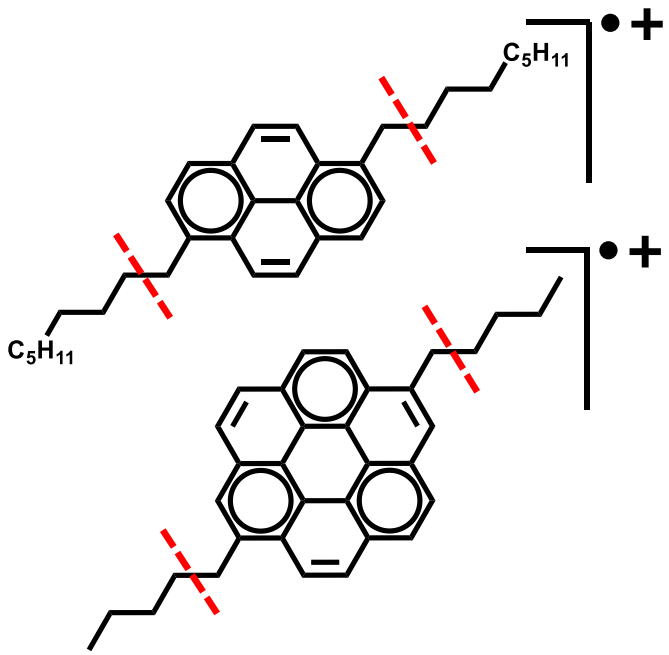
Structural Analysis by IRMPD

Wyoming Deposit C_7 Asphaltenes

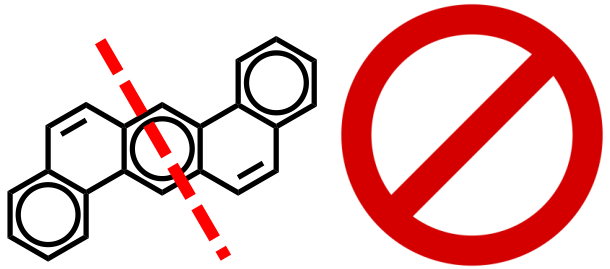


IR Photons
50-500 ms





Aromatic cores remain intact
Longer irradiation period (4000 ms)
→ Loss of H_2

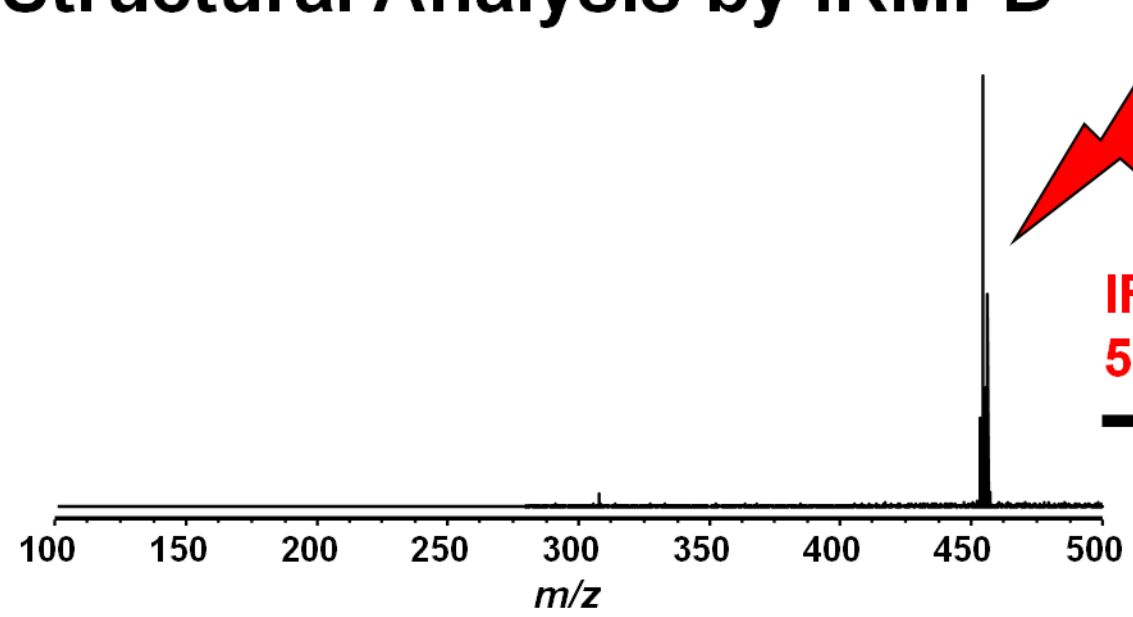


DBE constant

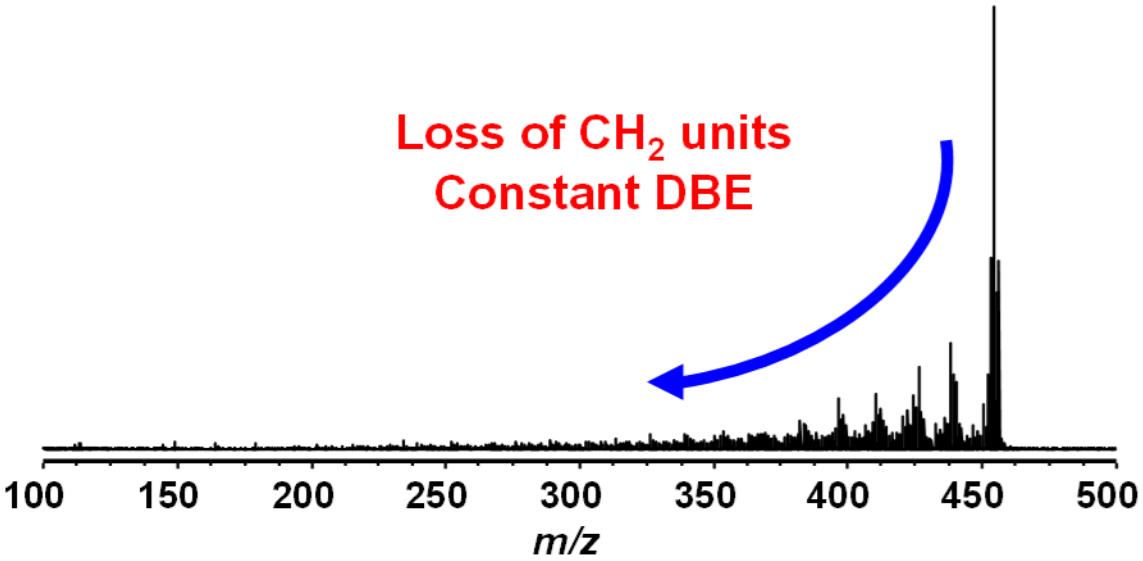
Energy Fuels 31, 12, 13509-13518

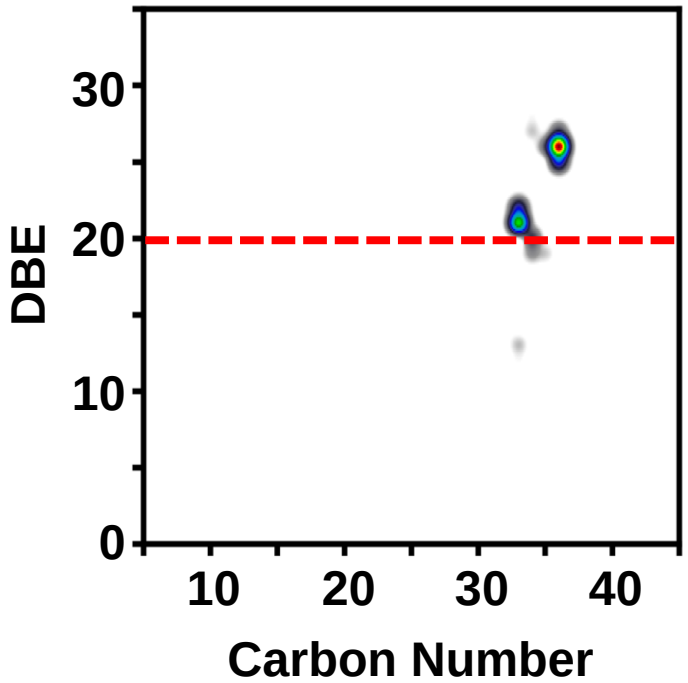
Structural Analysis by IRMPD

Wyoming Deposit C_7 Asphaltenes



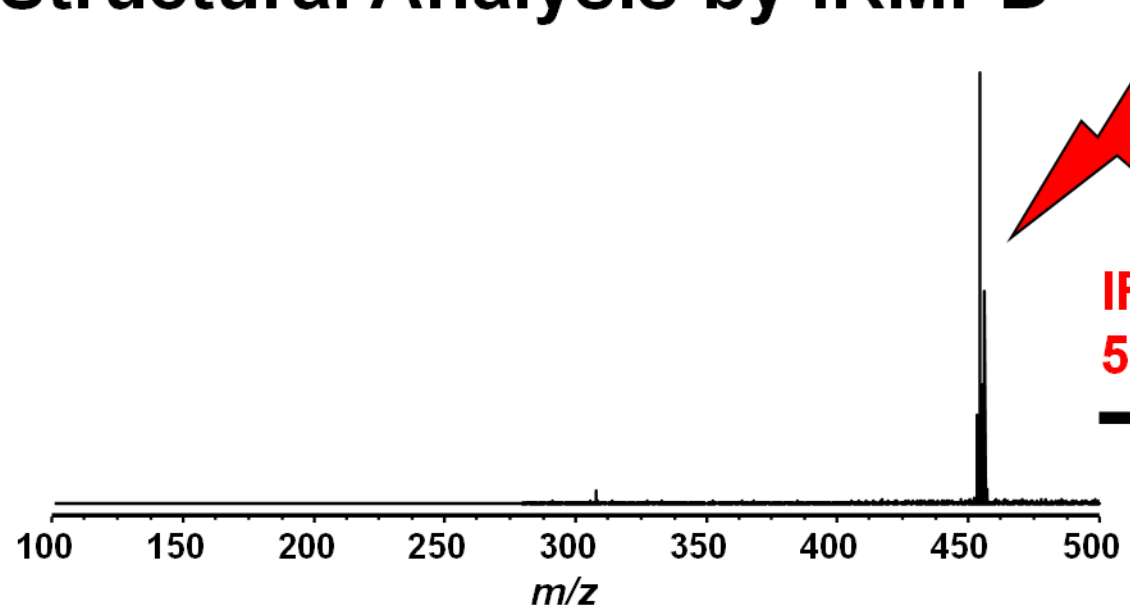
IR Photons
50-500 ms



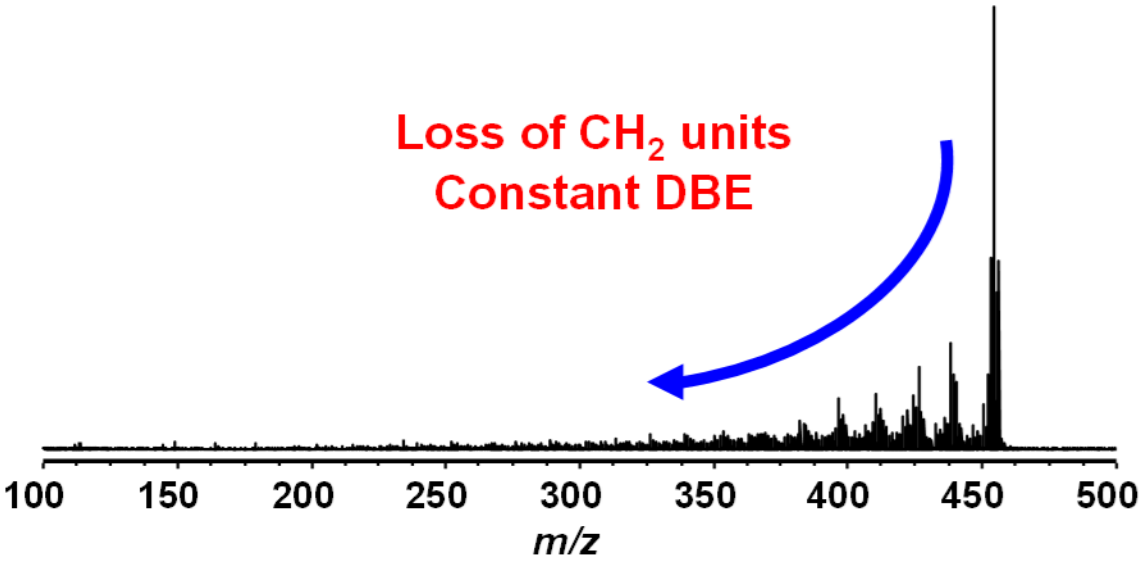


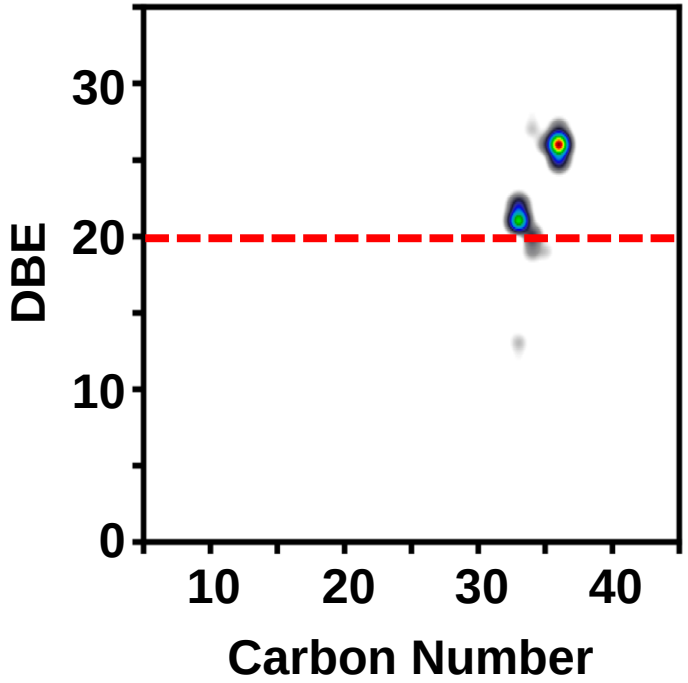
Structural Analysis by IRMPD

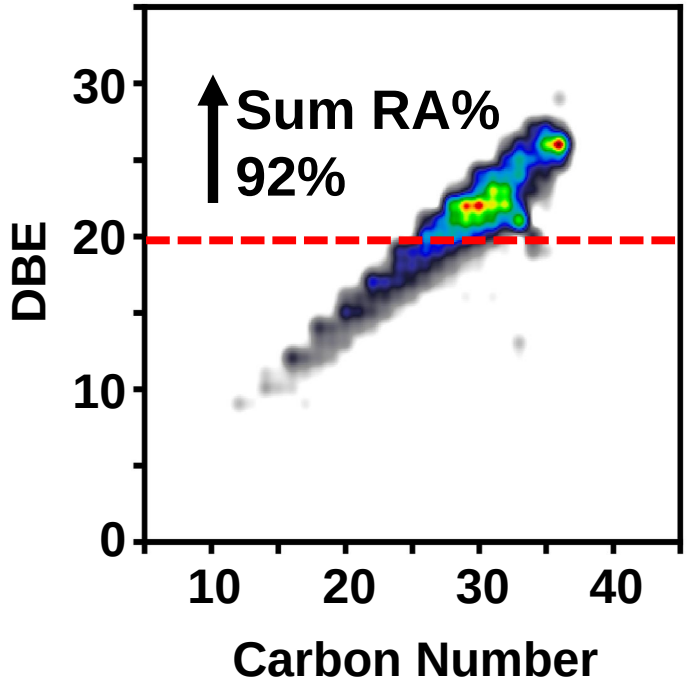
Wyoming Deposit C_7 Asphaltenes



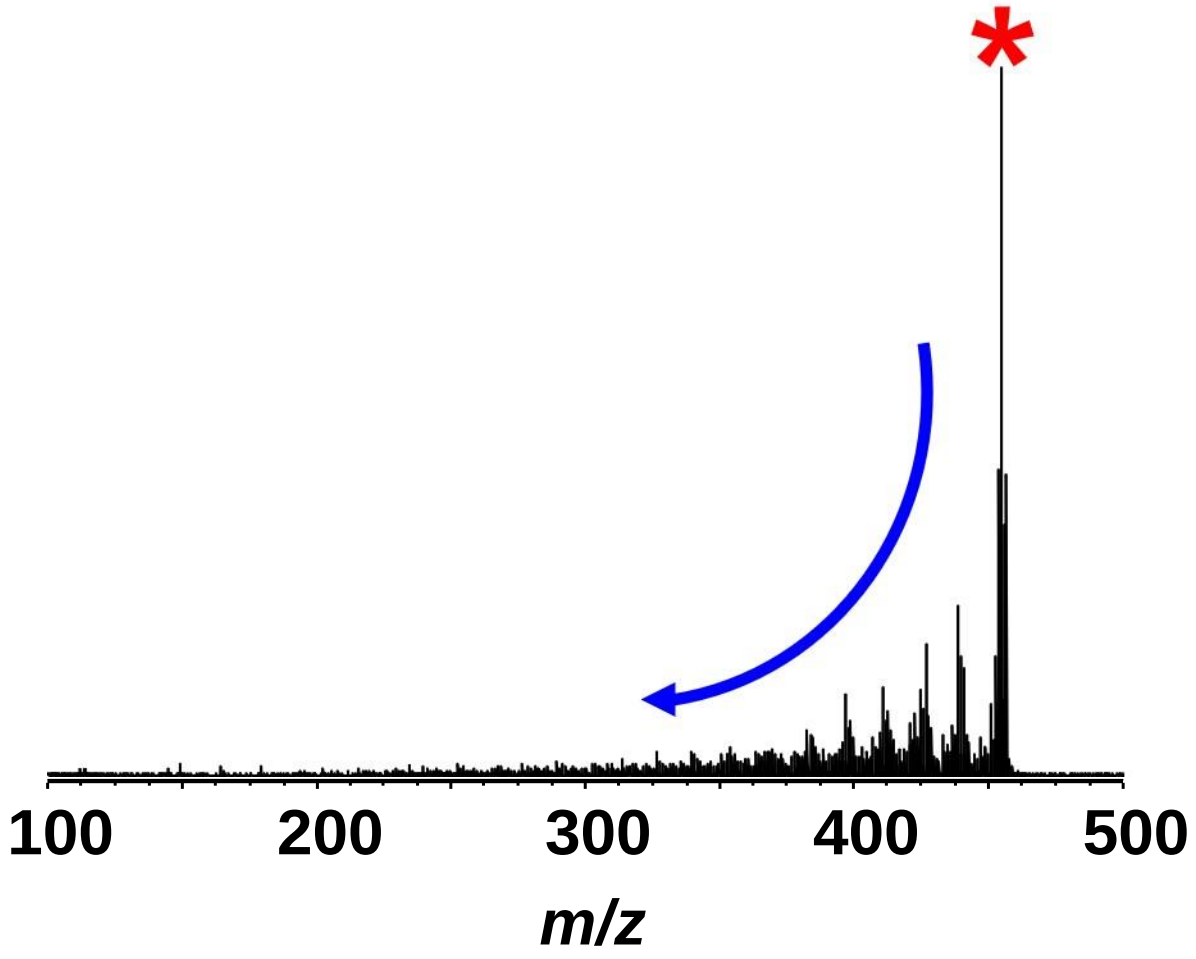
IR Photons
50-500 ms

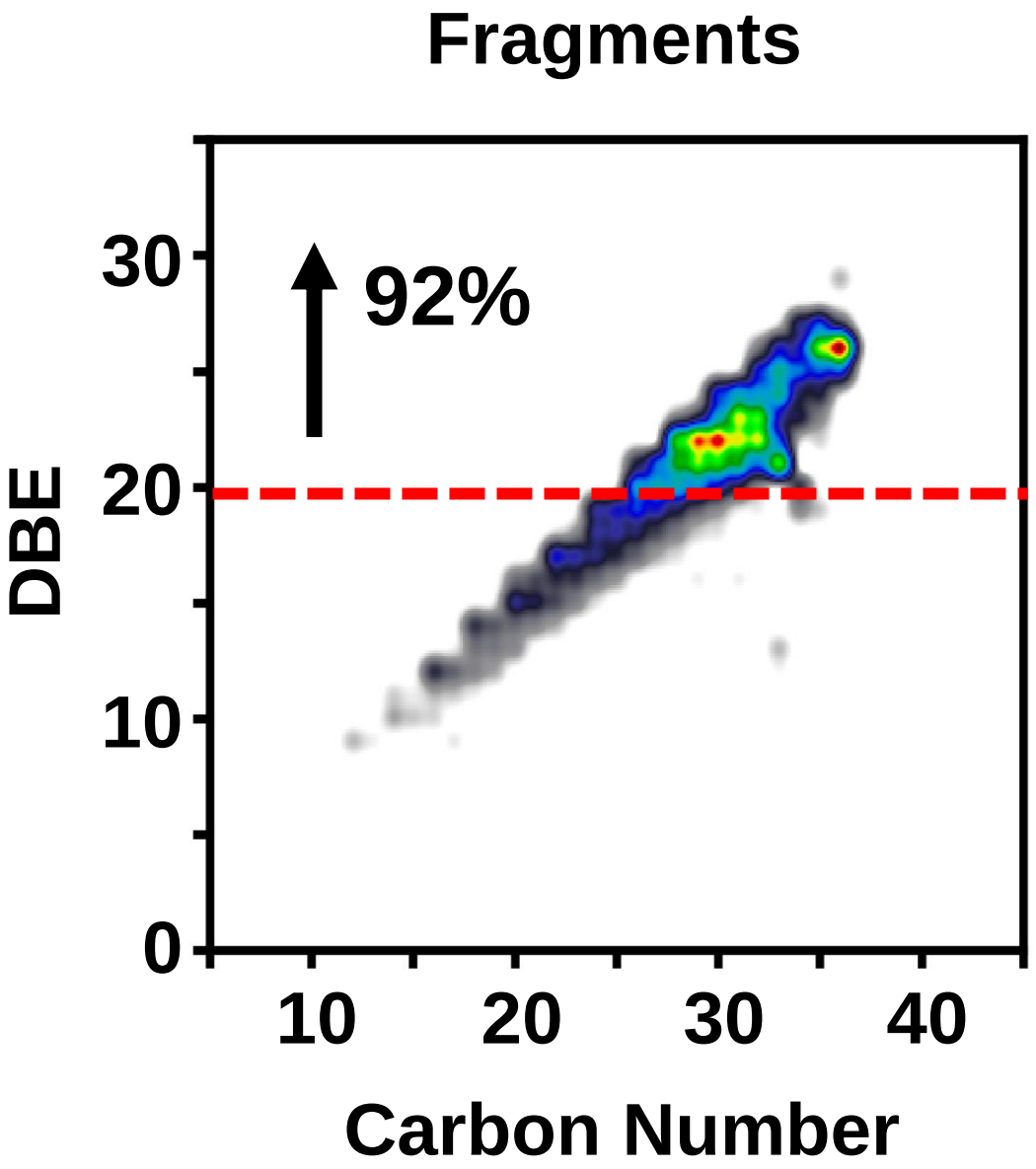






Wyoming Deposit – Island Dominant

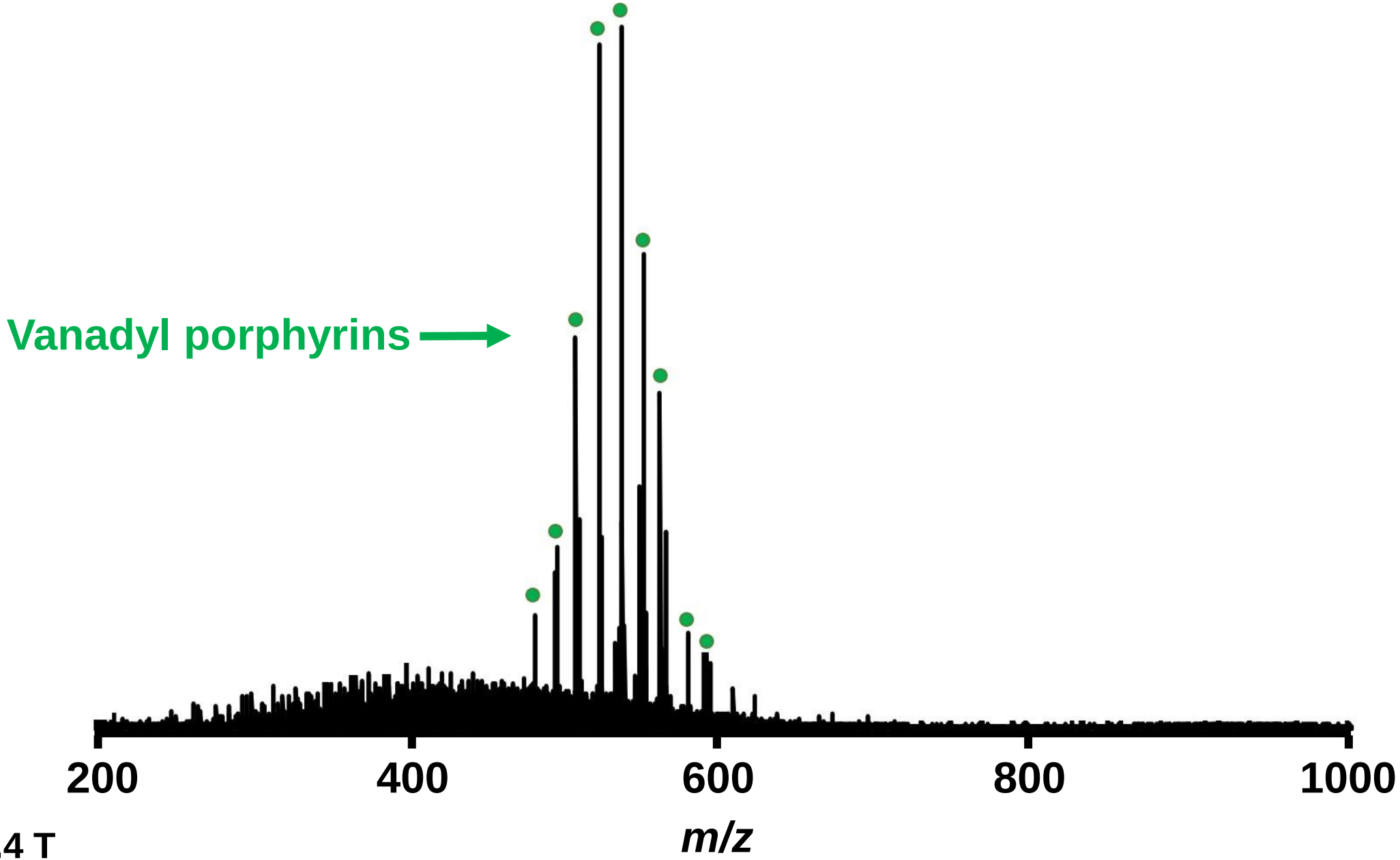




Relative Abundance %

Mass Isolation Prior to IRMPD

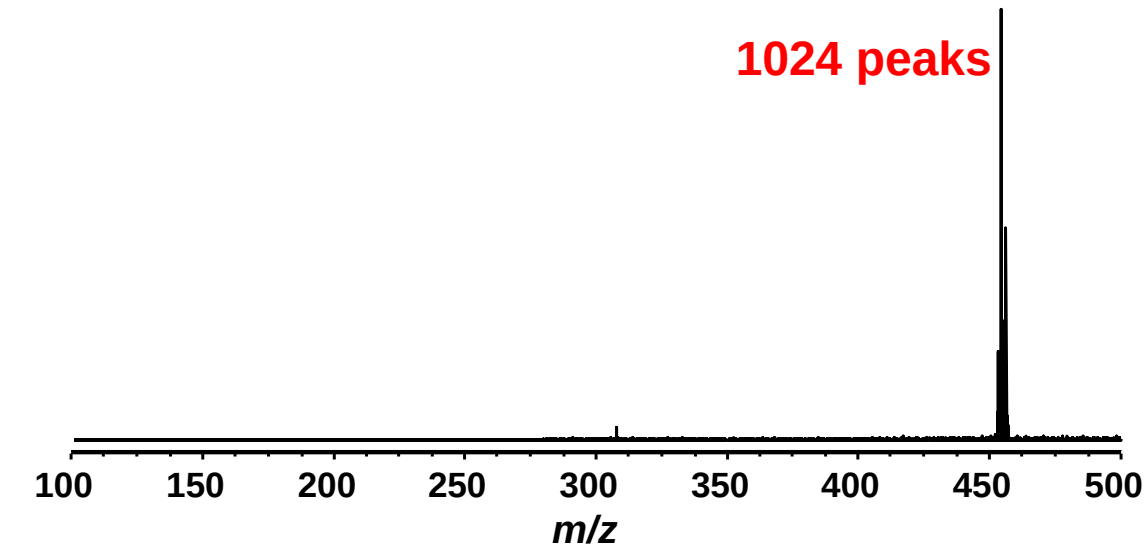
Athabasca Bitumen VR C_7 Asphaltenes



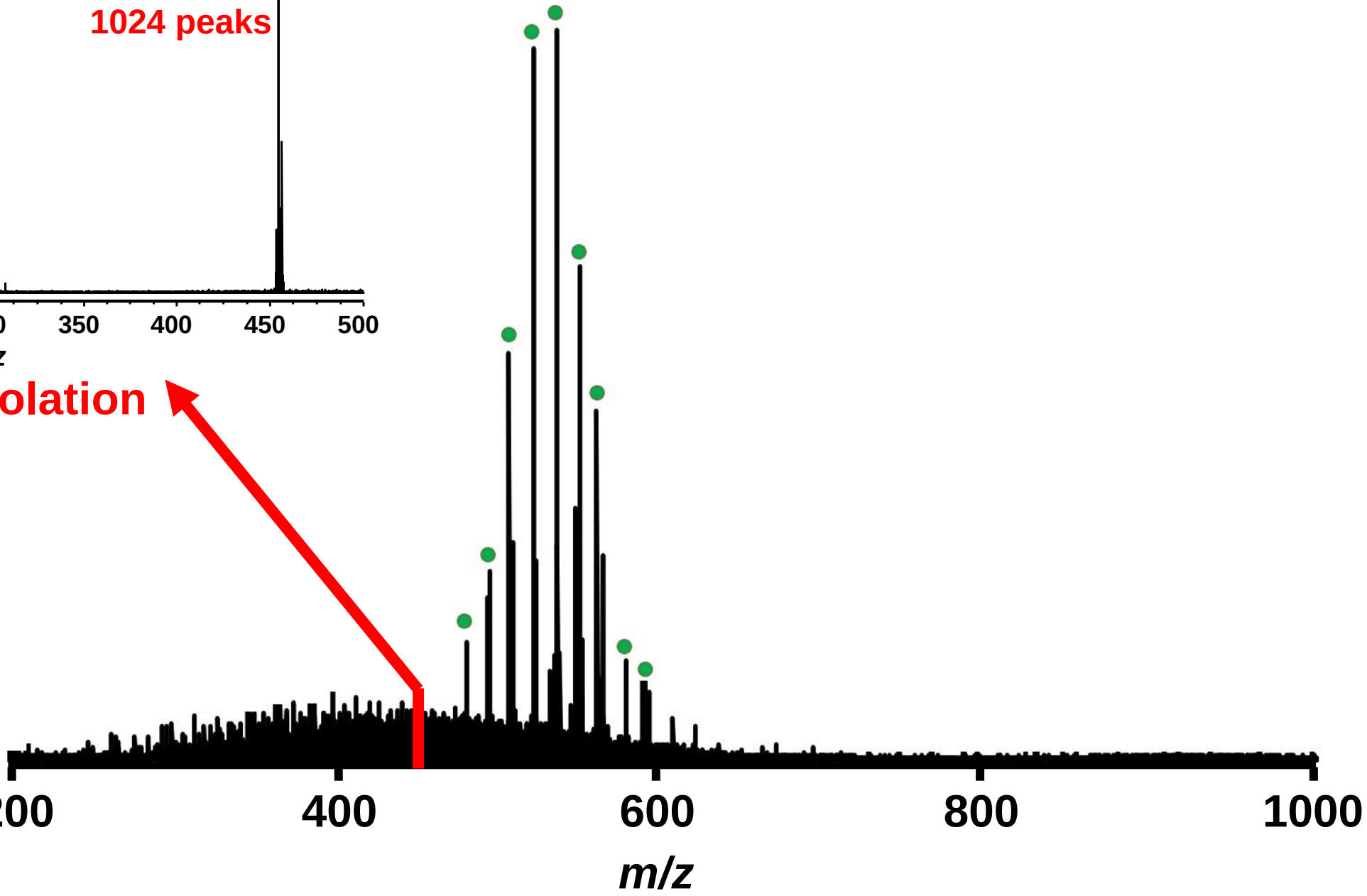
Positive APPI @ 9.4 T

Mass Isolation Prior to IRMPD

Athabasca Bitumen VR C_7 Asphaltenes



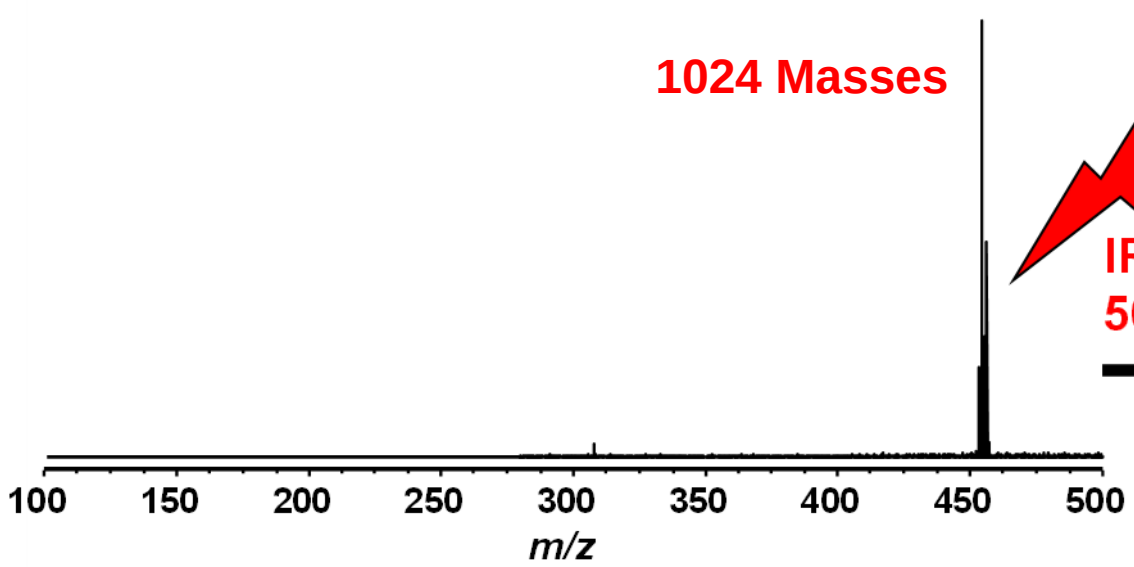
4 Da Quadrupole Isolation

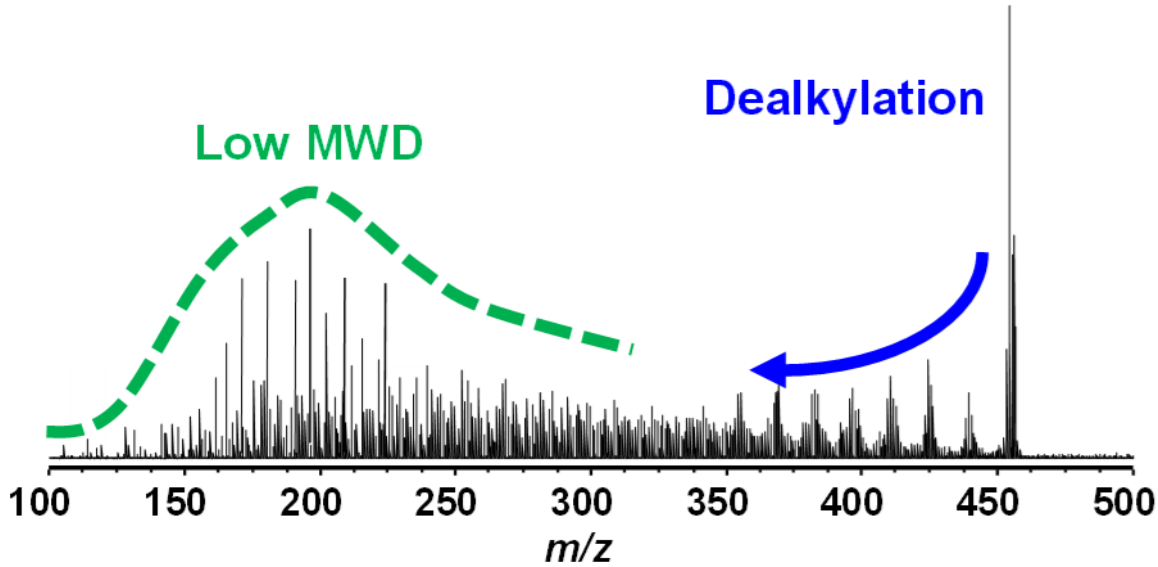


Positive APPI @ 9.4 T

Structural Analysis by IRMPD

Athabasca Bitumen VR C_7 Asphaltenes

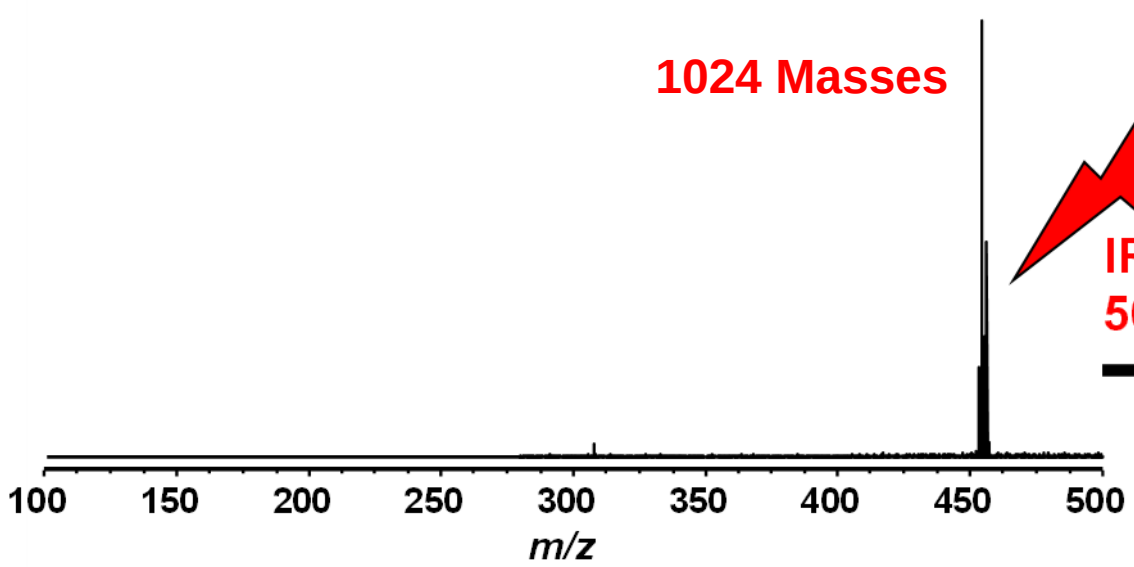


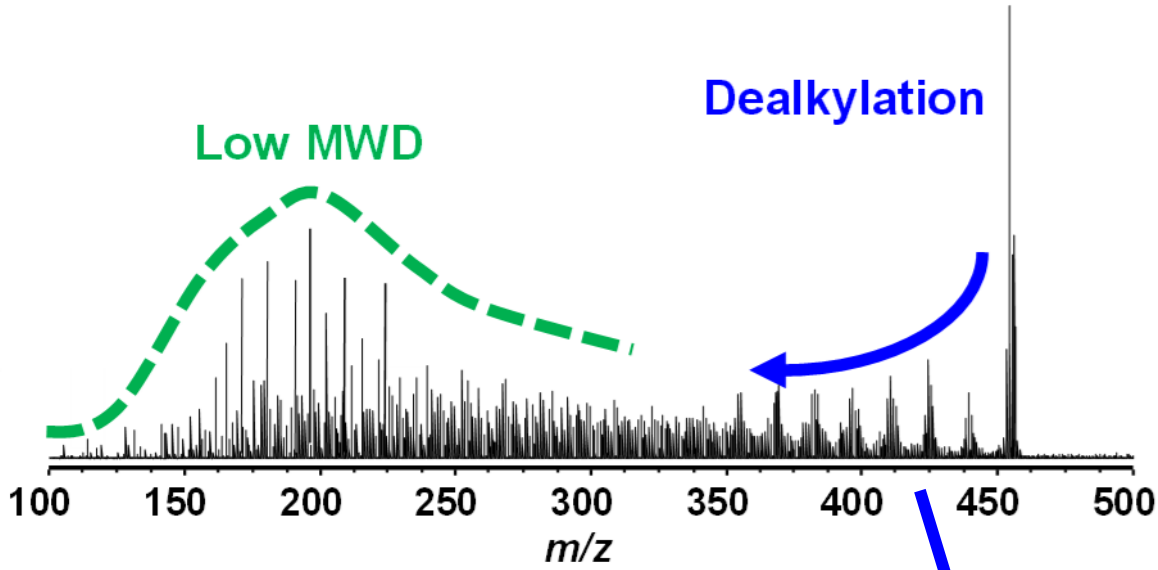


Energy Fuels 31, 12, 13509-13518

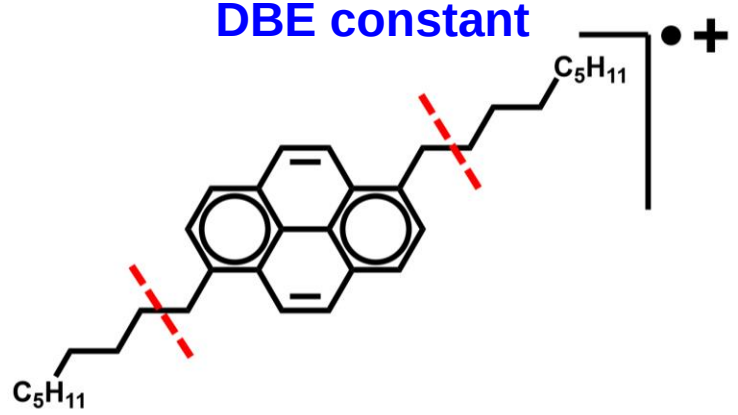
Structural Analysis by IRMPD

Athabasca Bitumen VR C_7 Asphaltenes





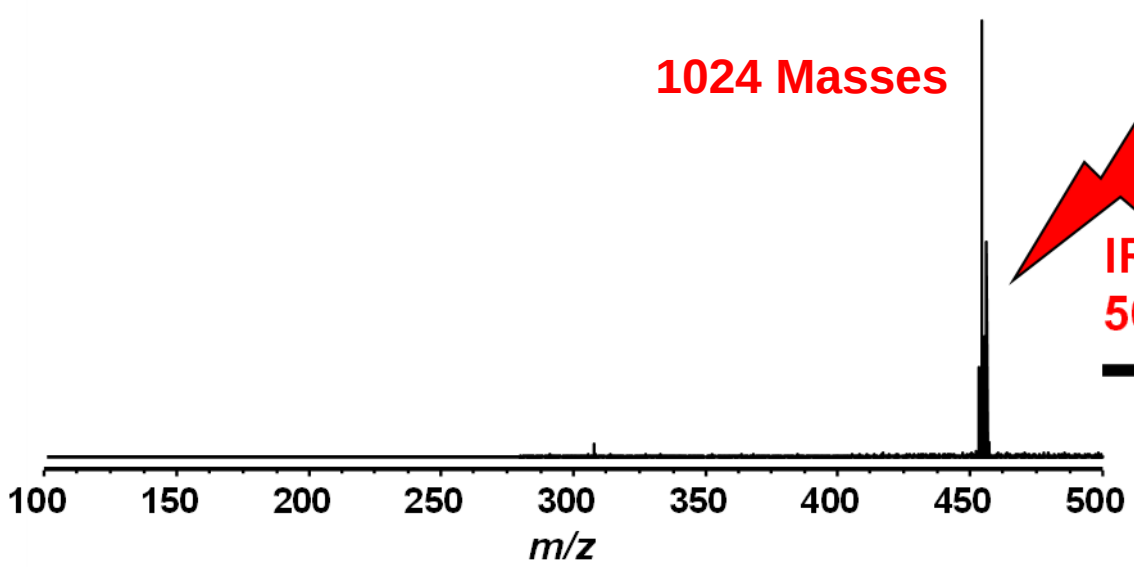
Loss of C#
DBE constant



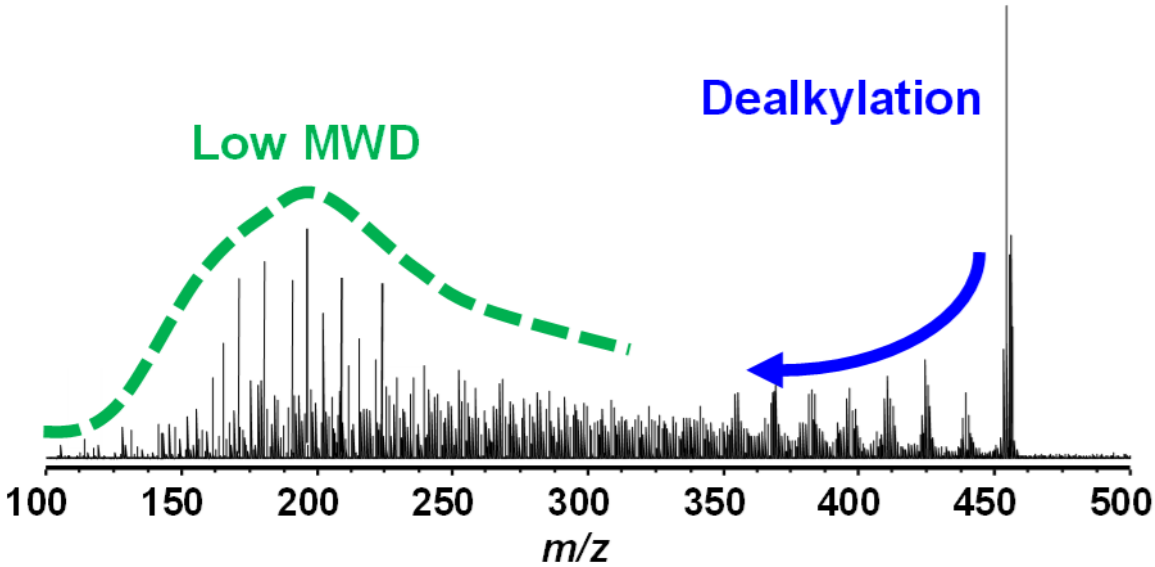
Energy Fuels 31, 12, 13509-13518

Structural Analysis by IRMPD

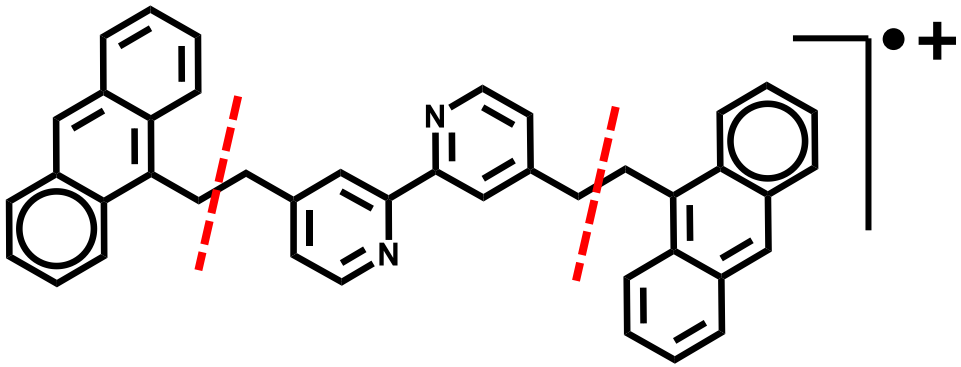
Athabasca Bitumen VR C_7 Asphaltenes

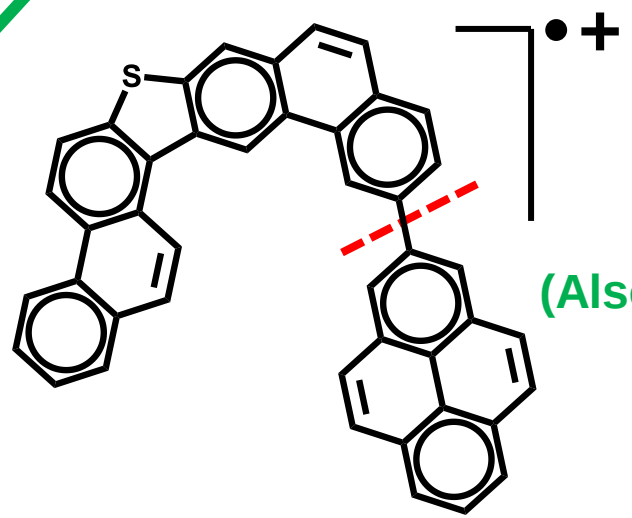


IR Photons
50-500 ms



Loss of Carbon Atoms
Loss of DBE



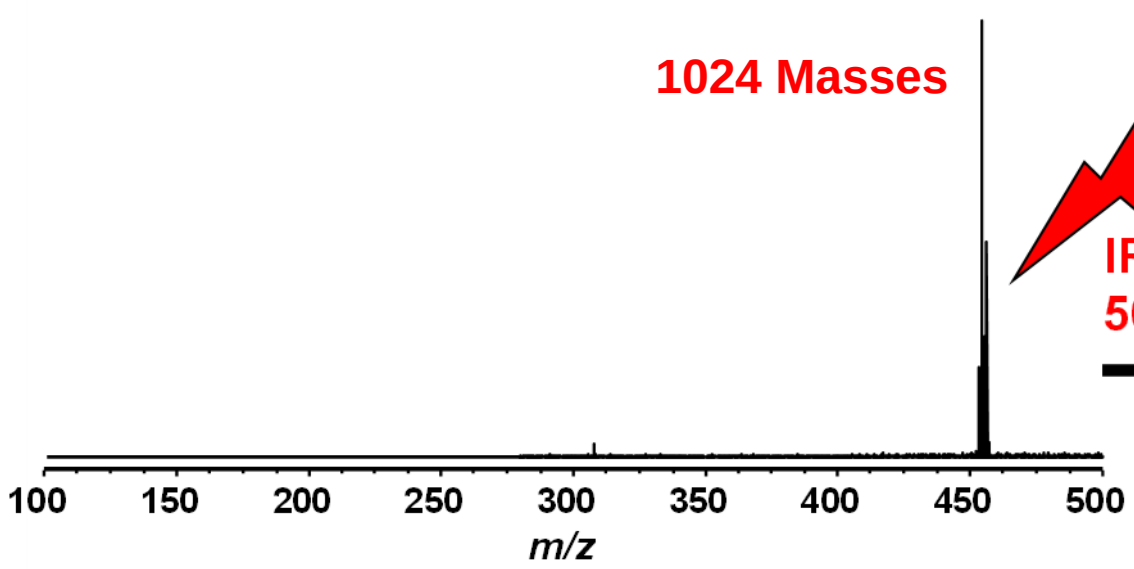


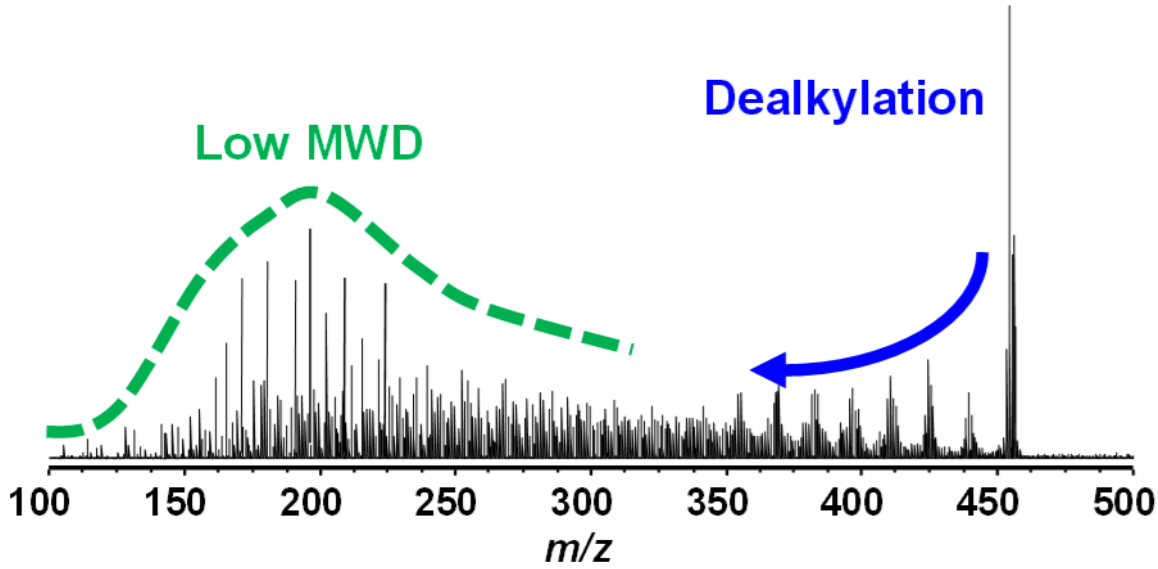
Archipelago
(Also known as multi-core structures)

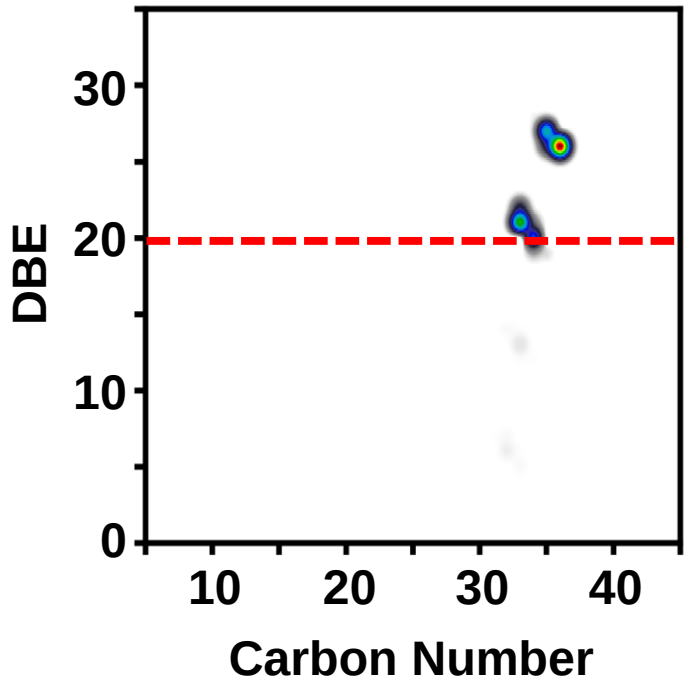
Energy Fuels 31, 12, 13509-13518

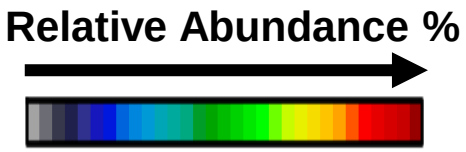
Structural Analysis by IRMPD

Athabasca Bitumen VR C_7 Asphaltenes



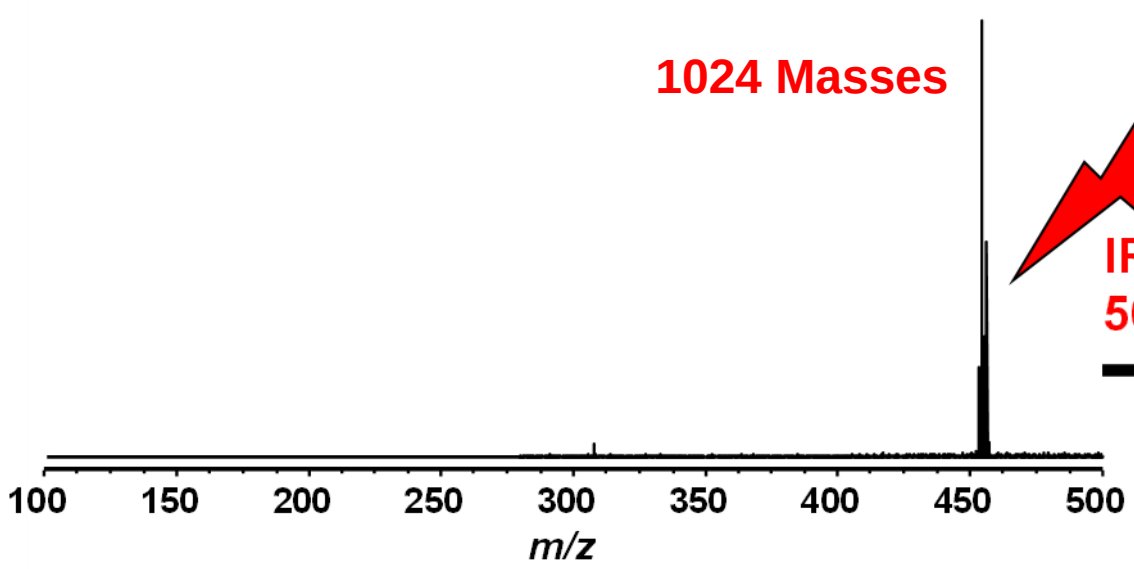


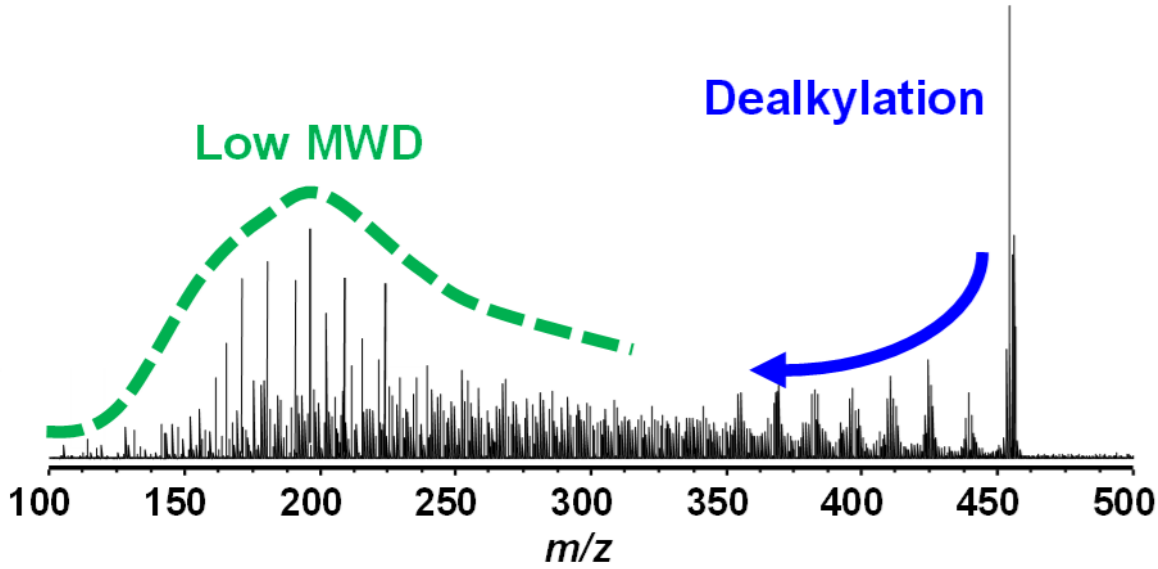


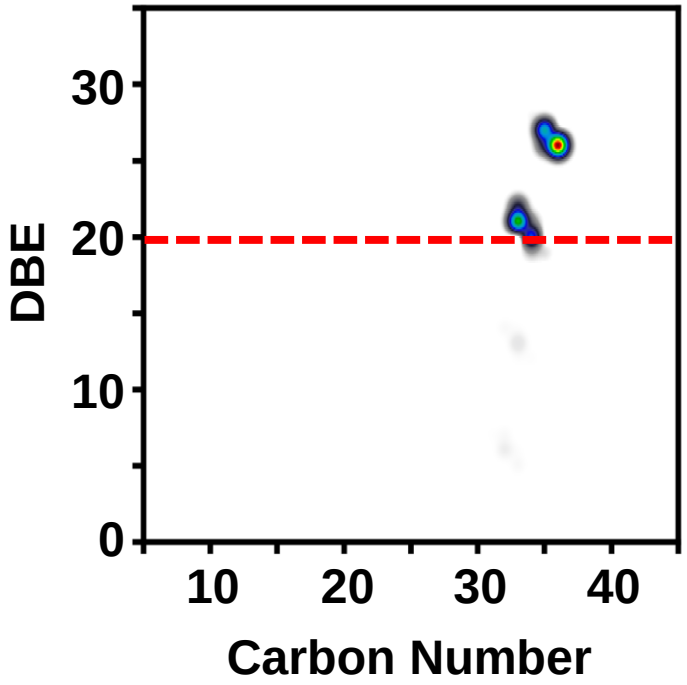


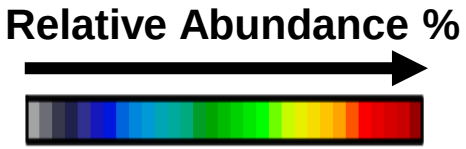
Structural Analysis by IRMPD

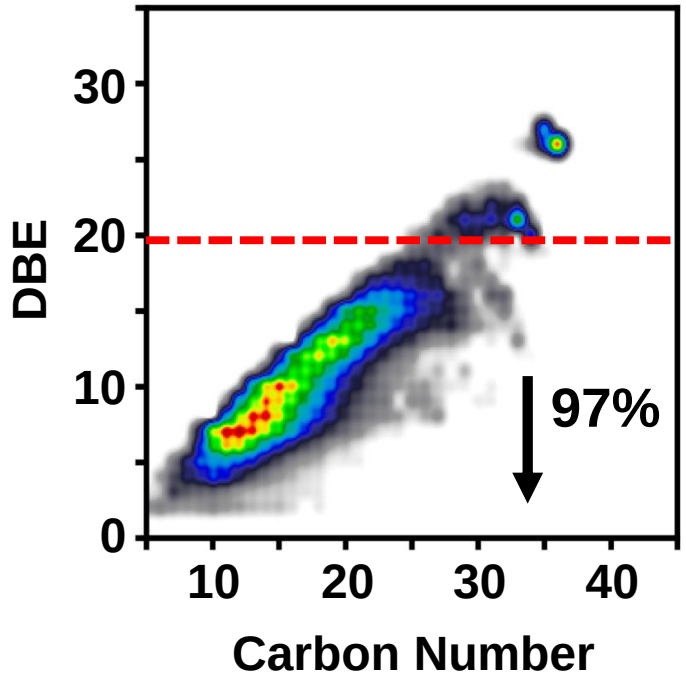
Athabasca Bitumen VR C_7 Asphaltenes



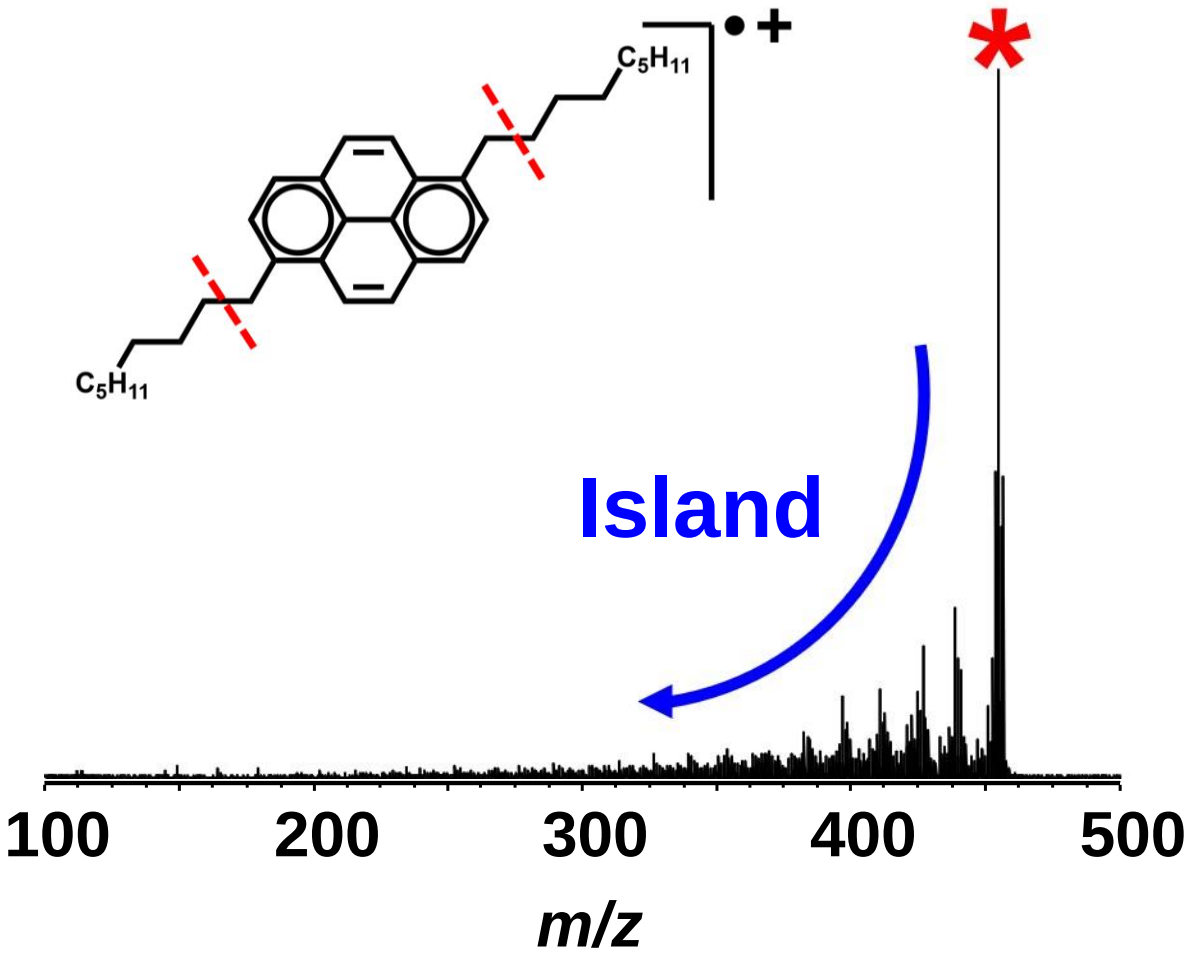




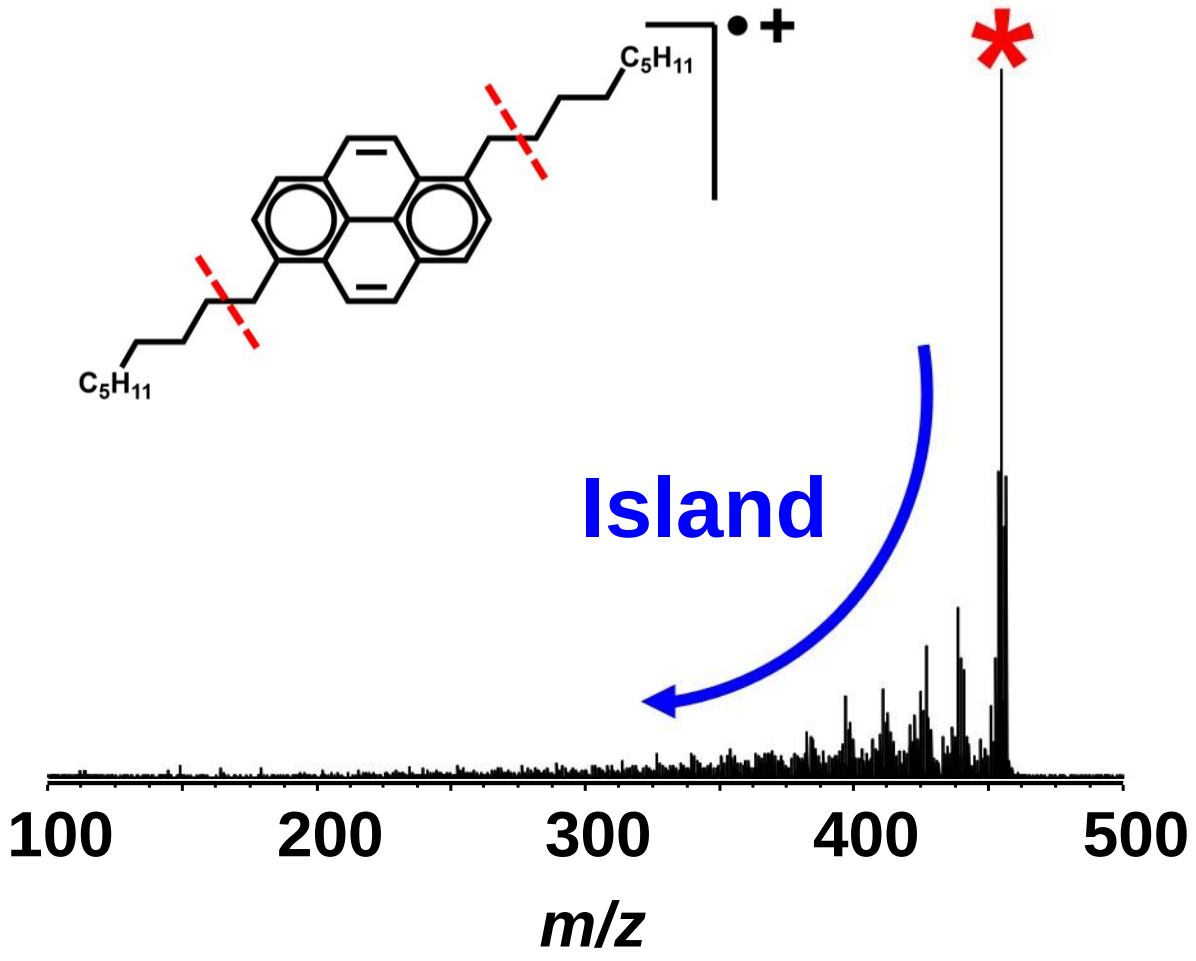


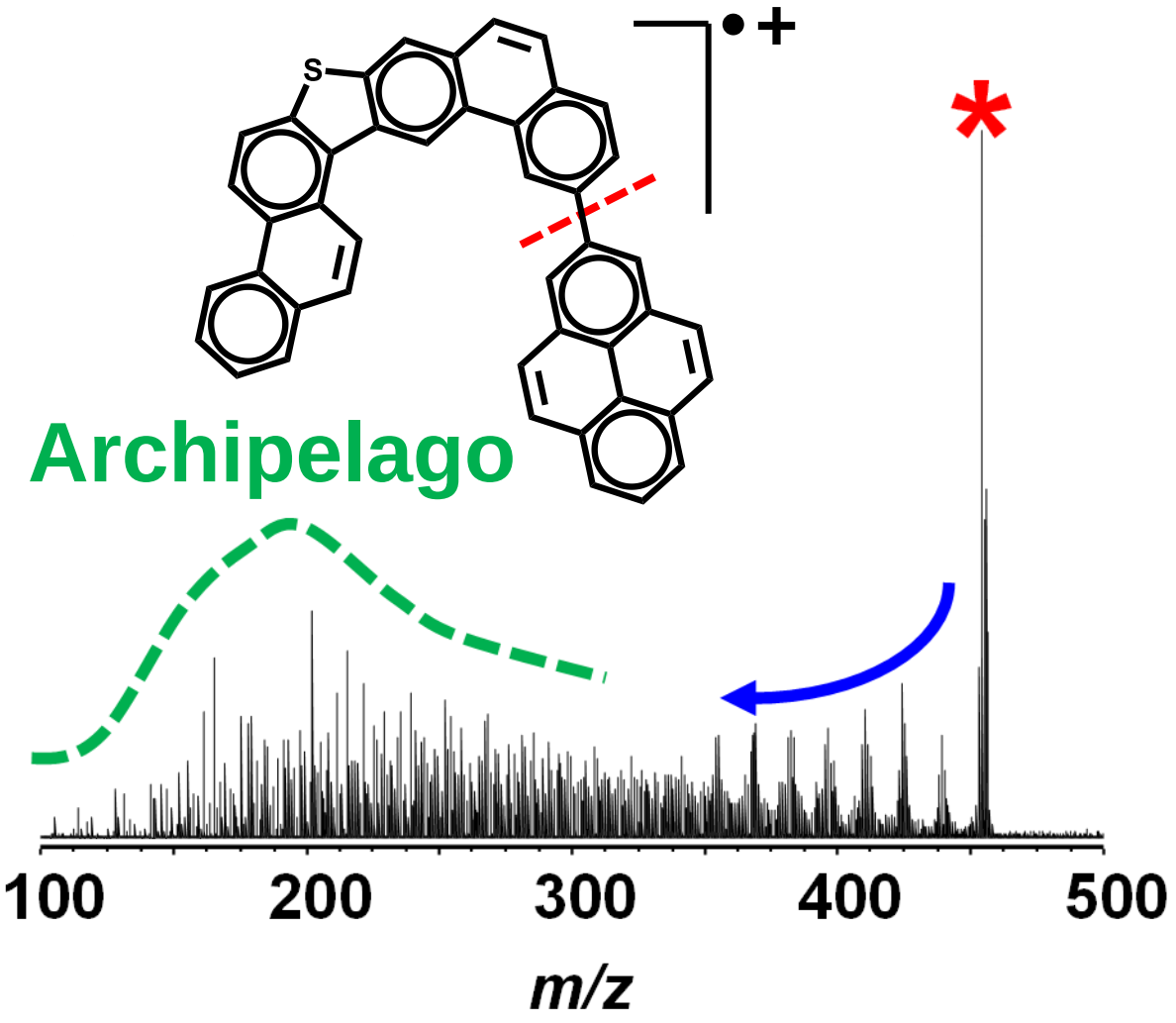


Island *vs.* Archipelago



Island *vs.* Archipelago





Asphaltene Petroleomics Requirements

FT-ICR MS

MS / MS Analysis

Sample Preparation

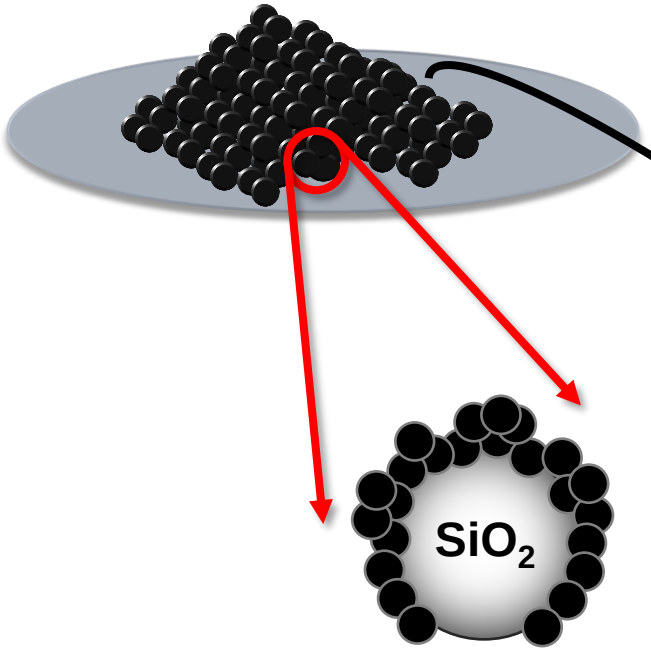
Sample complexity

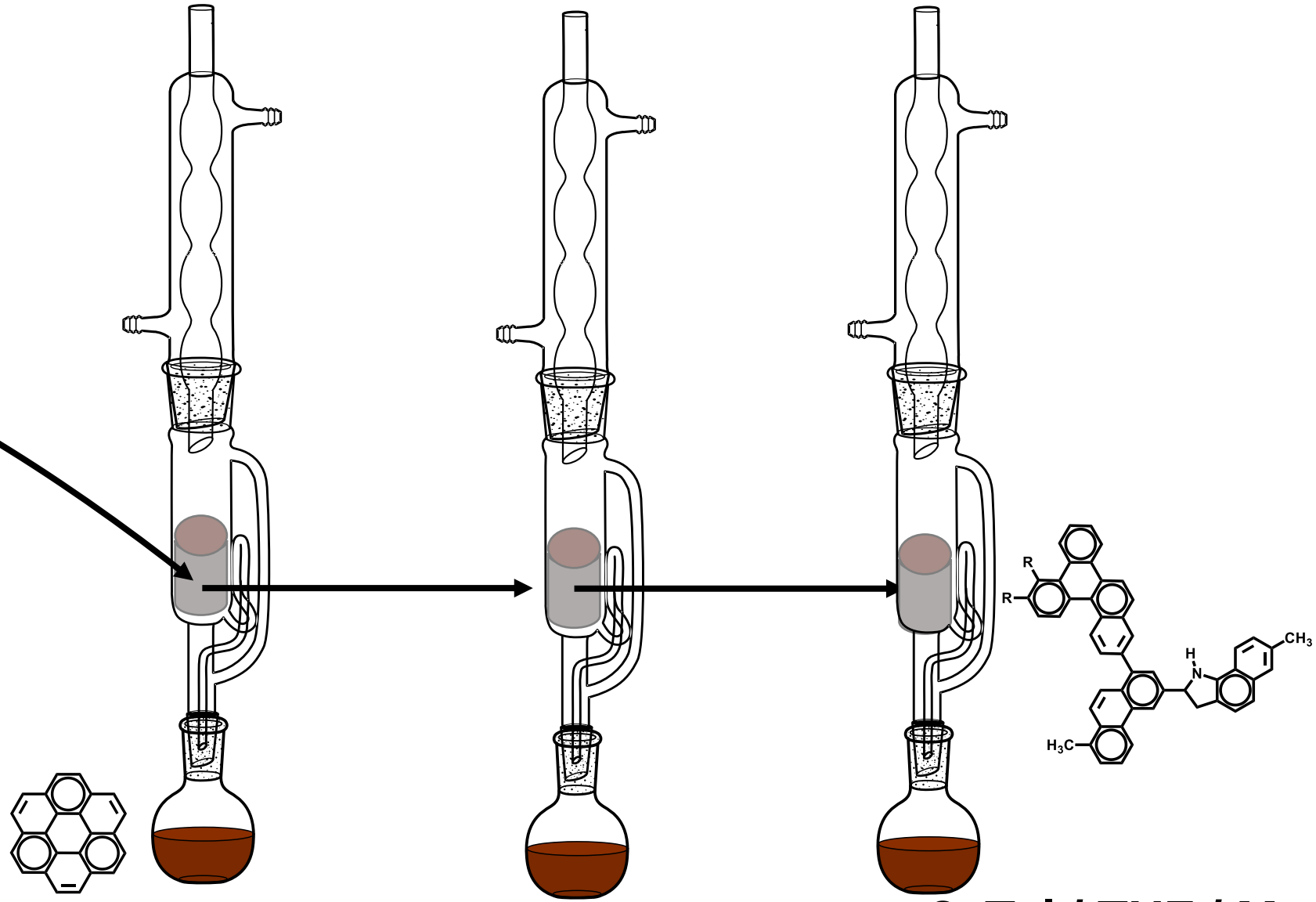
IRMPD

Selective Ionization

Extrography

Asphaltene Adsorption on Silica Gel





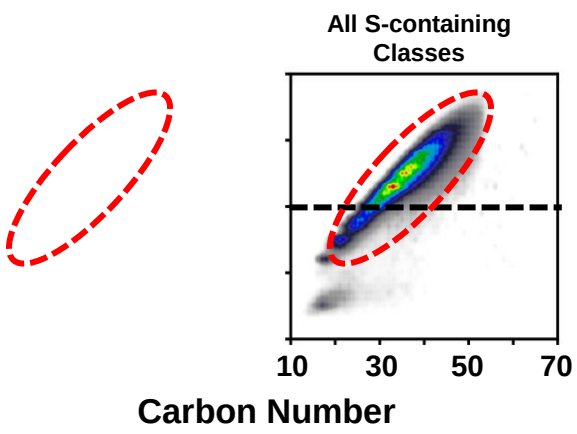
1. Acetone
***Dipolar* Interactions**

2. Hep / Tol
Alkyl-aromatics

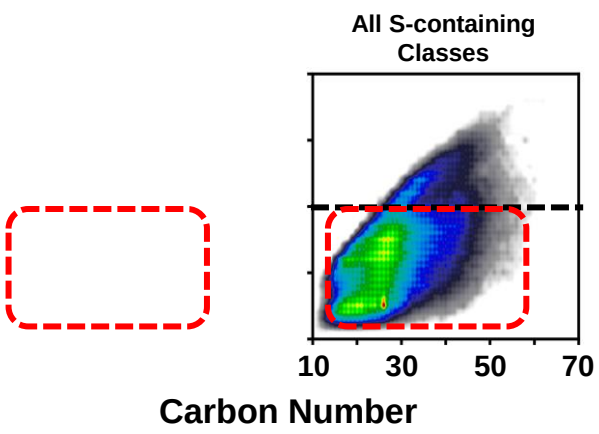
3. Tol / THF / MeOH
Hydrogen Bonding

Whole C_7 Asphaltenes

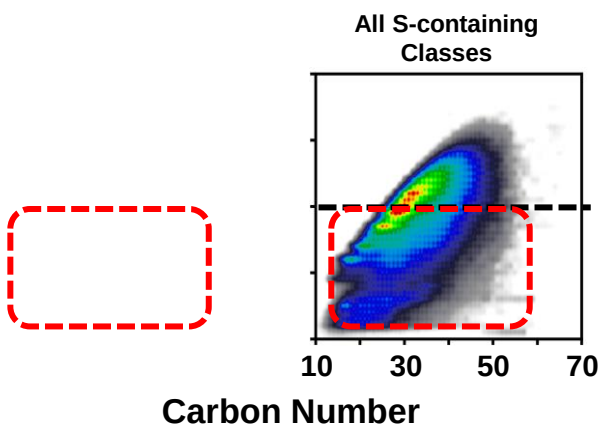
Wyoming Deposit

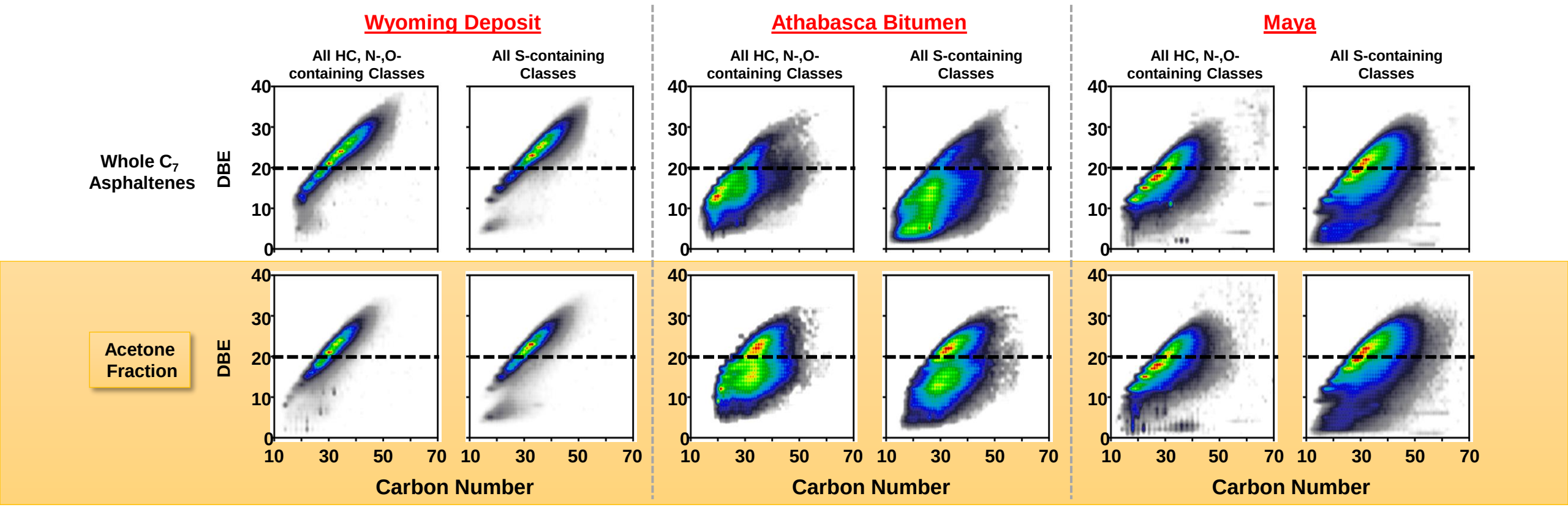


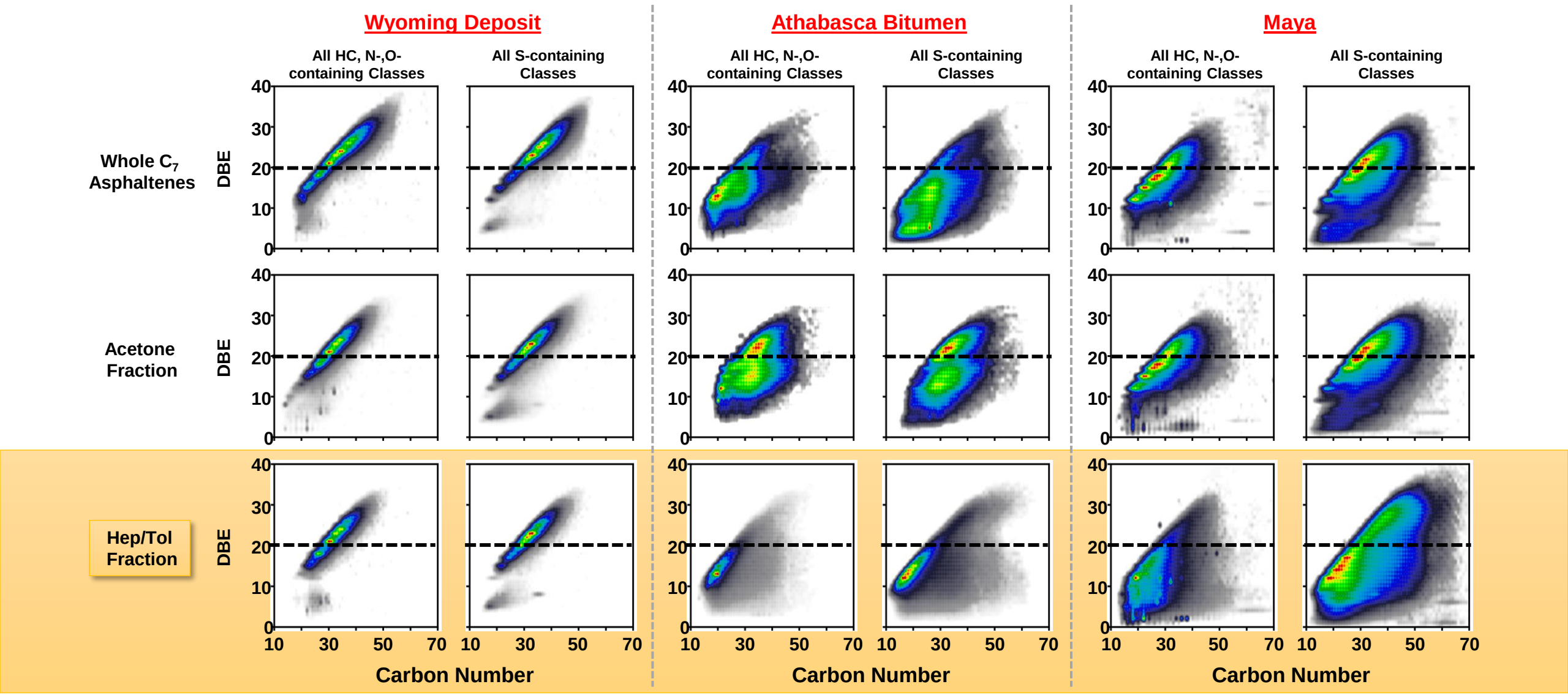
Athabasca Bitumen

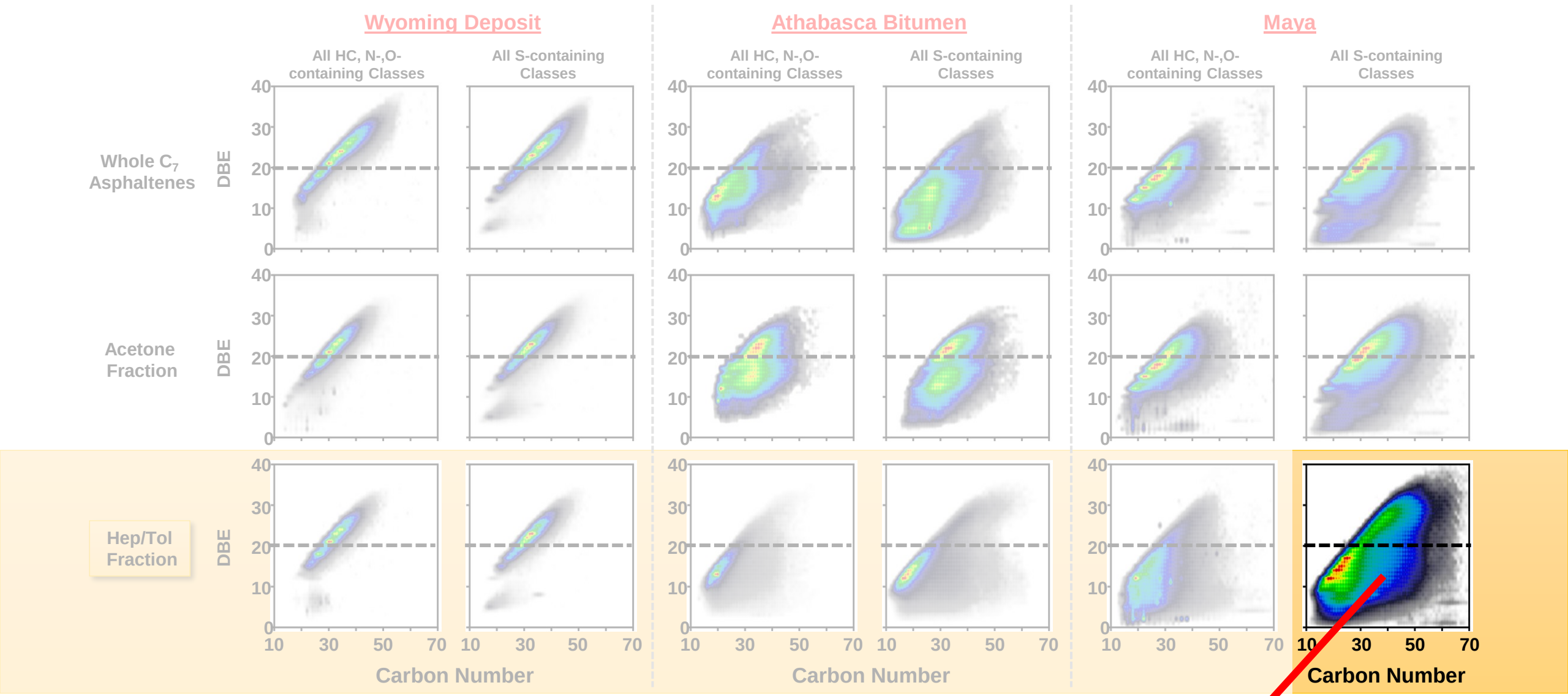


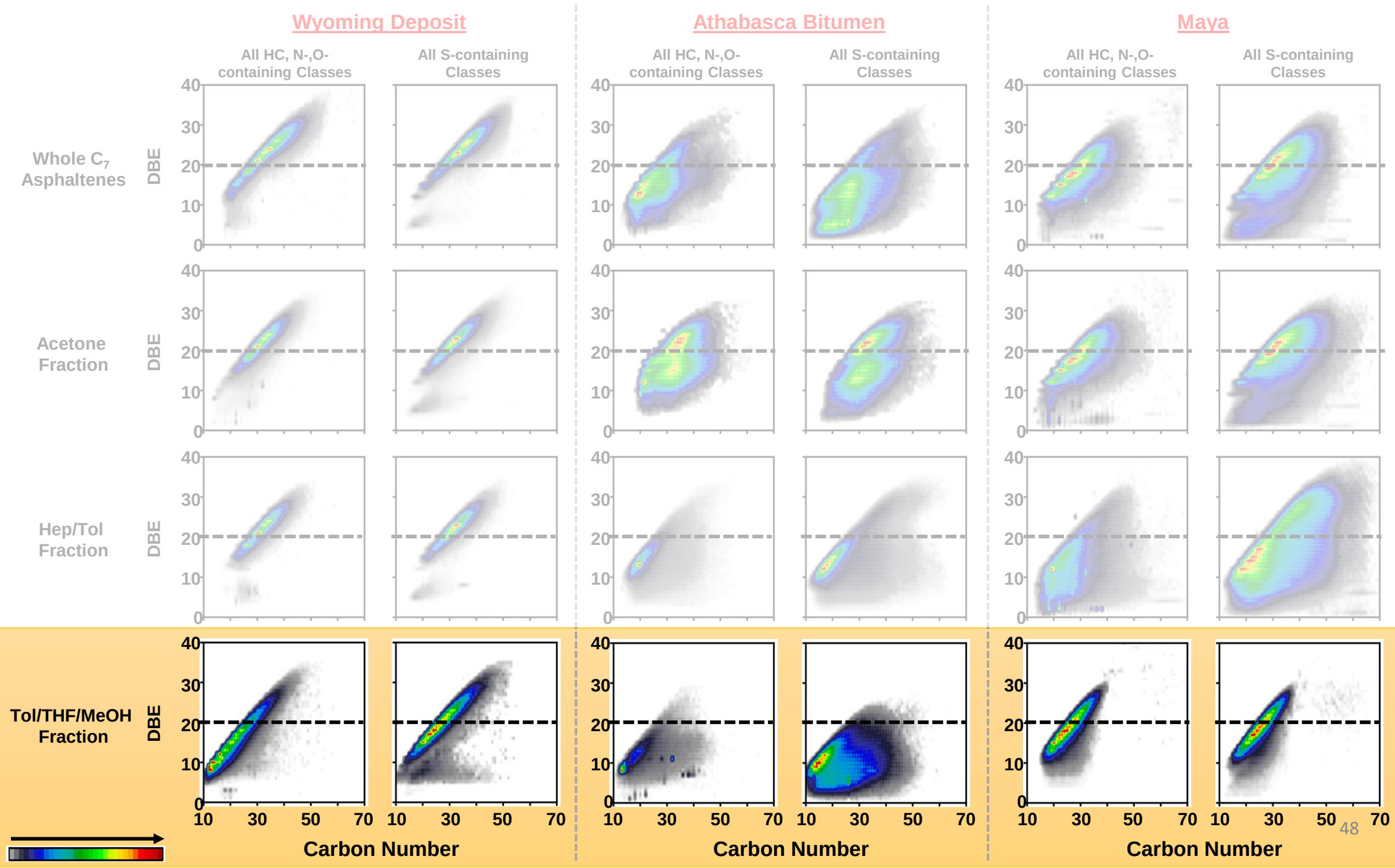
Maya

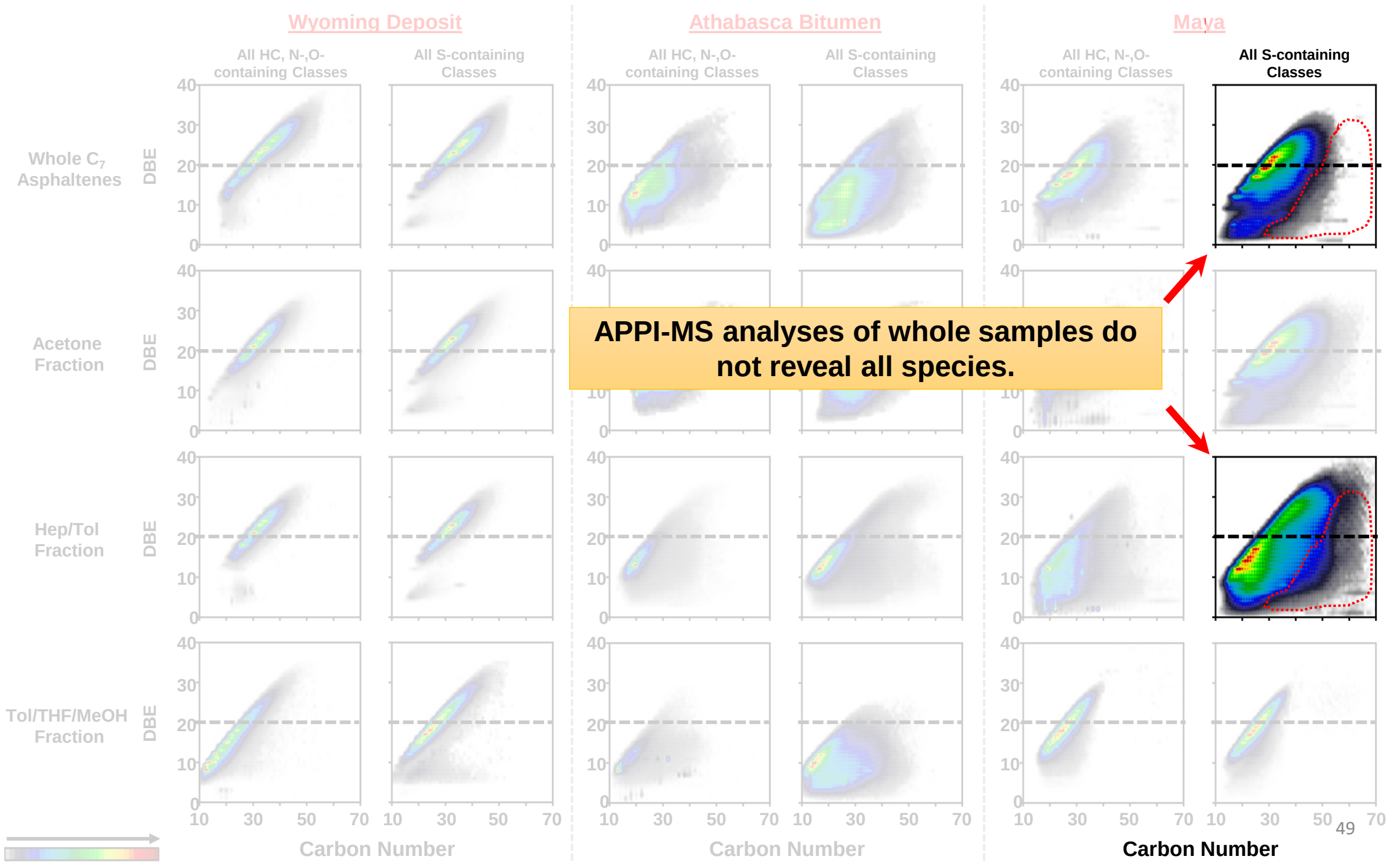


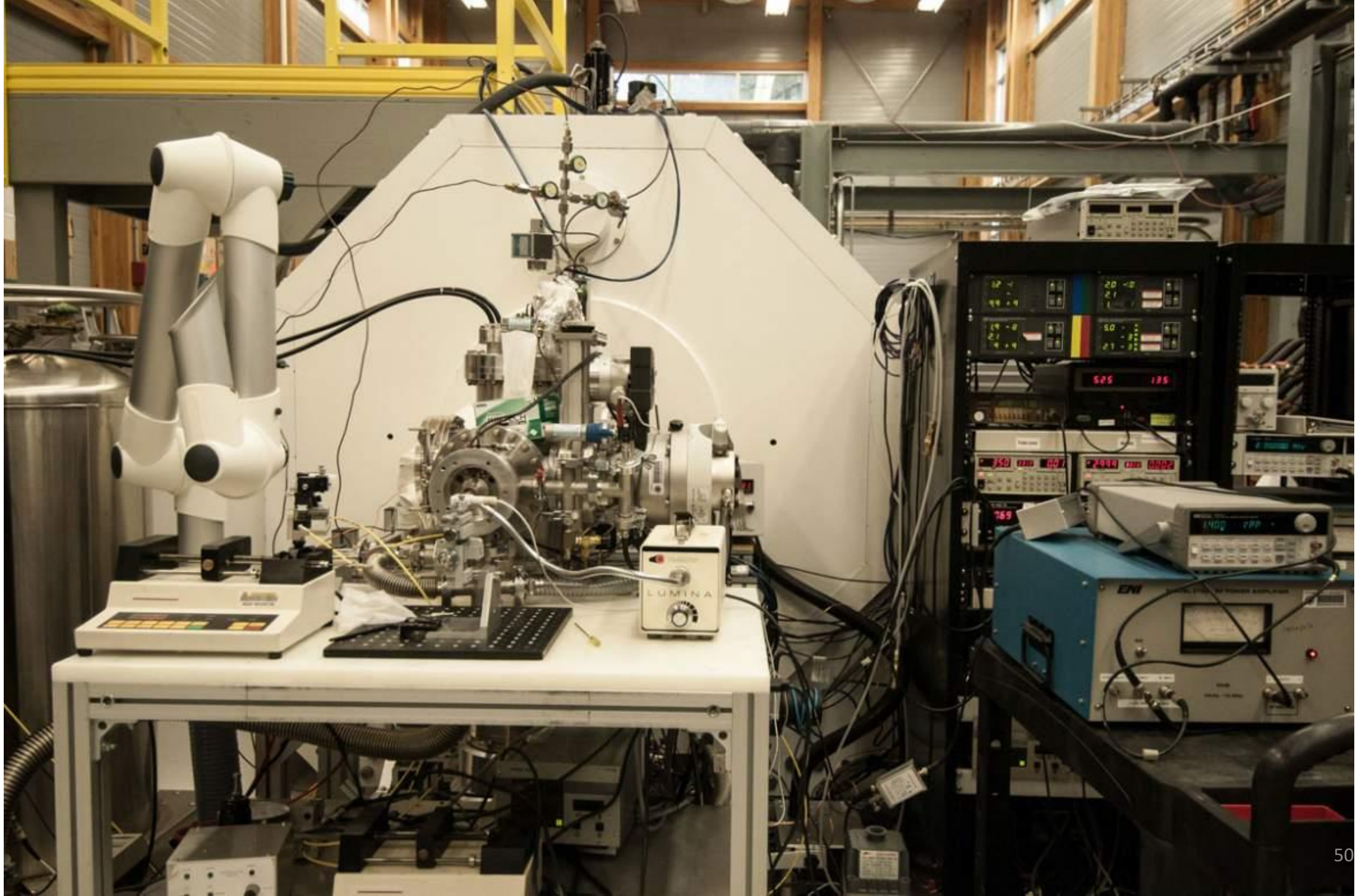

Wyoming Deposit
Athabasca Bitumen
Maya
All HC, N-,O-containing Classes
All S-containing Classes
Whole C7 Asphaltenes
Acetone Fraction
DBE
Carbon Number
0
10
20
30
40
10
30
50
70


Wyoming Deposit
Athabasca Bitumen
Maya
All HC, N-,O-containing Classes
All S-containing Classes
Whole C7 Asphaltenes
Acetone Fraction
Hep/Tol Fraction
DBE
Carbon Number

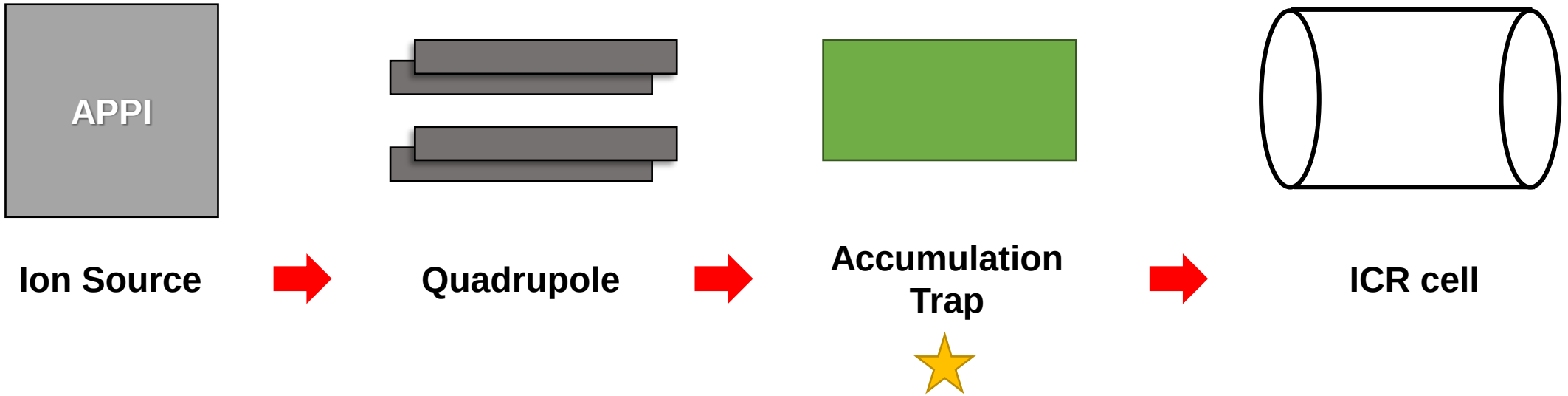

Wyoming Deposit
Athabasca Bitumen
Maya
All HC, N-,O-containing Classes
All S-containing Classes
Whole C7 Asphaltenes
Acetone Fraction
Hep/Tol Fraction
DBE
Carbon Number
Low DBE "atypical" asphaltenes


Wyoming Deposit
Athabasca Bitumen
Maya
All HC, N-,O-containing Classes
All S-containing Classes
Whole C7 Asphaltenes
Acetone Fraction
Hep/Tol Fraction
Tol/THF/MeOH Fraction
DBE
Carbon Number

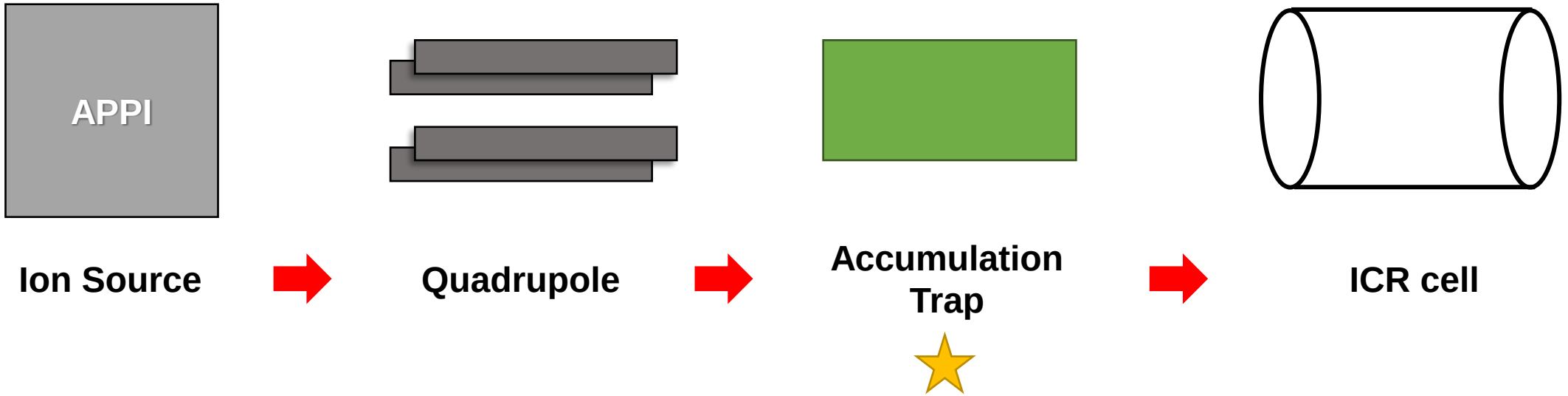

Wyoming Deposit
Athabasca Bitumen
Maya
All HC, N-,O-containing Classes
All S-containing Classes
Whole C7 Asphaltenes
Acetone Fraction
Hep/Tol Fraction
Tol/THF/MeOH Fraction
DBE
Carbon Number
APPI-MS analyses of whole samples do not reveal all species.

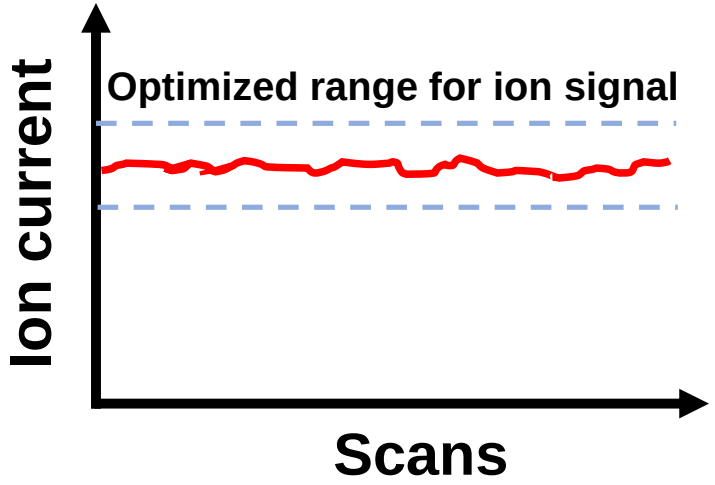

LUMINA
ENI

General Configuration 9.4 T FT-ICR Mass Spectrometer

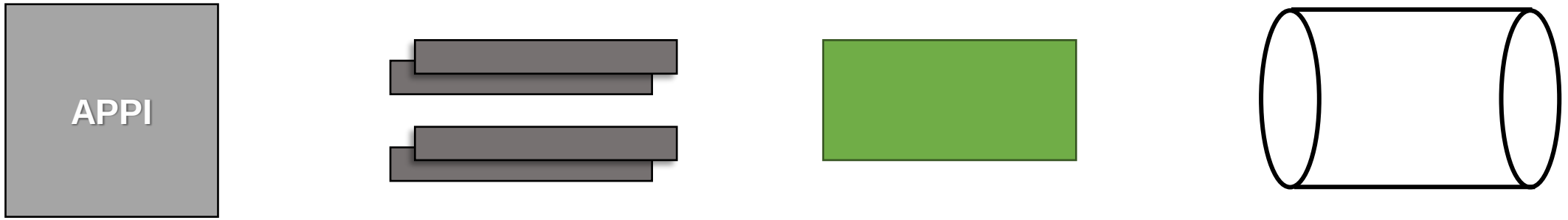


General Configuration 9.4 T FT-ICR Mass Spectrometer

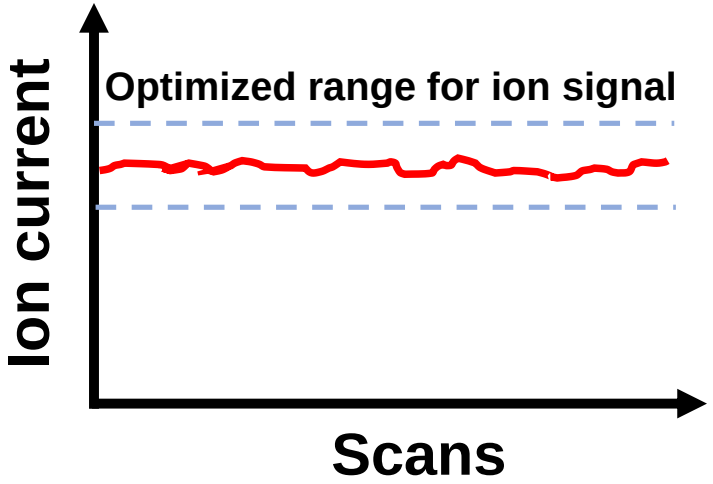




General Configuration 9.4 T FT-ICR Mass Spectrometer



Ion Source → Quadrupole → Accumulation Trap → ICR cell



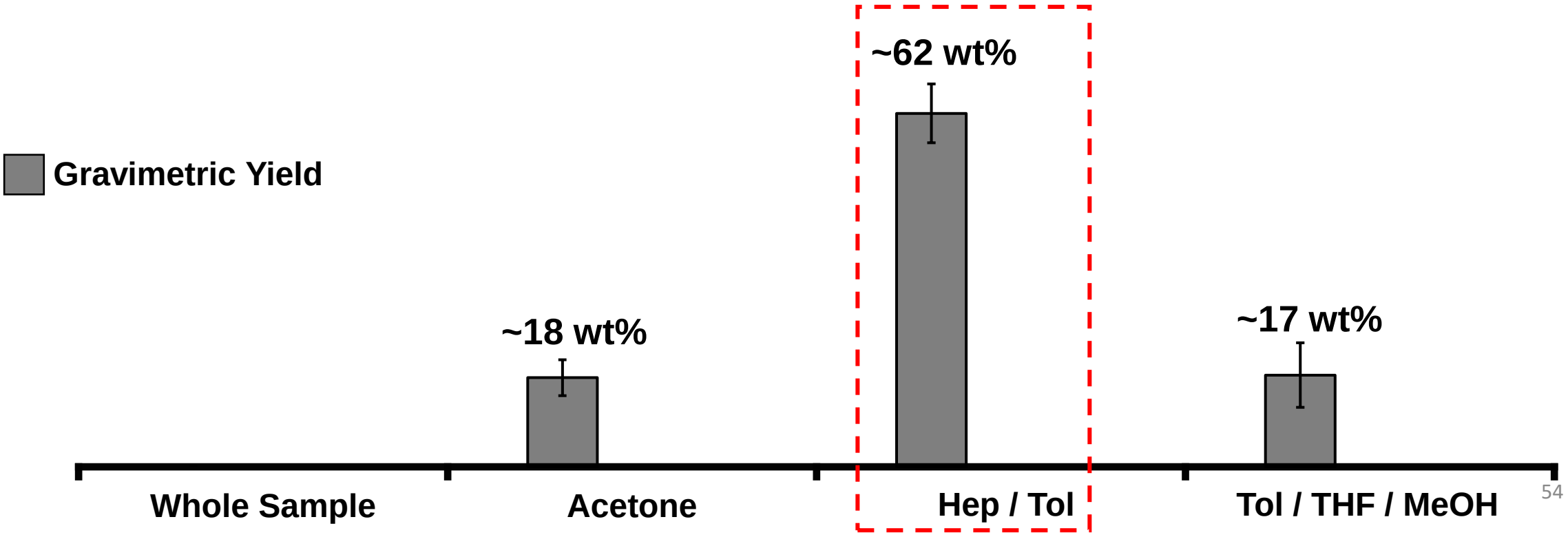
Short Accumulation — 5 – 20 ms

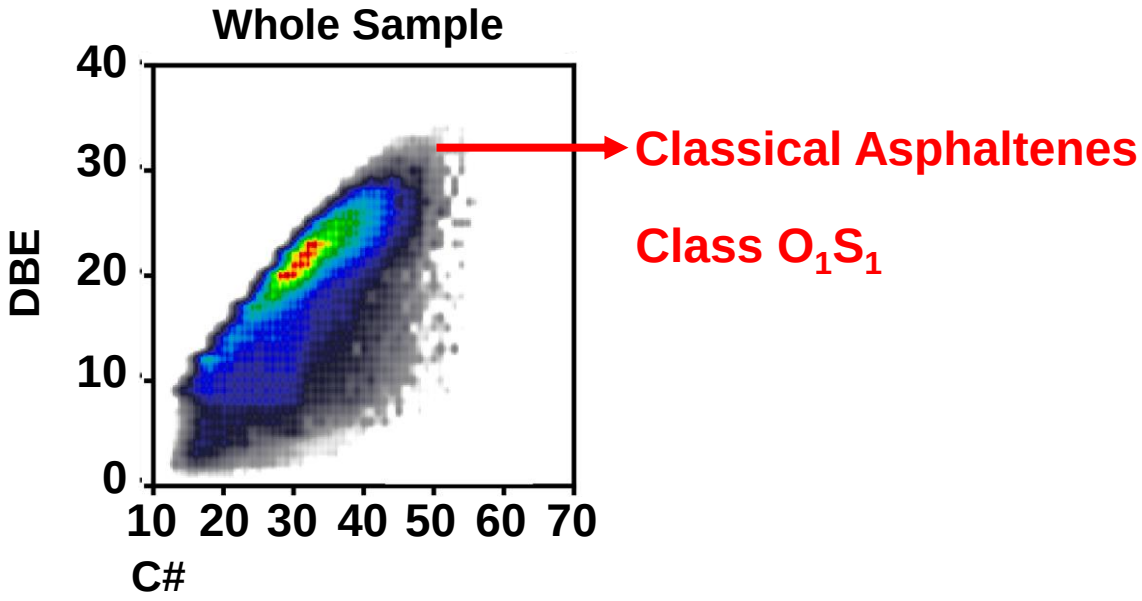
Aromatic fractions — PAHs

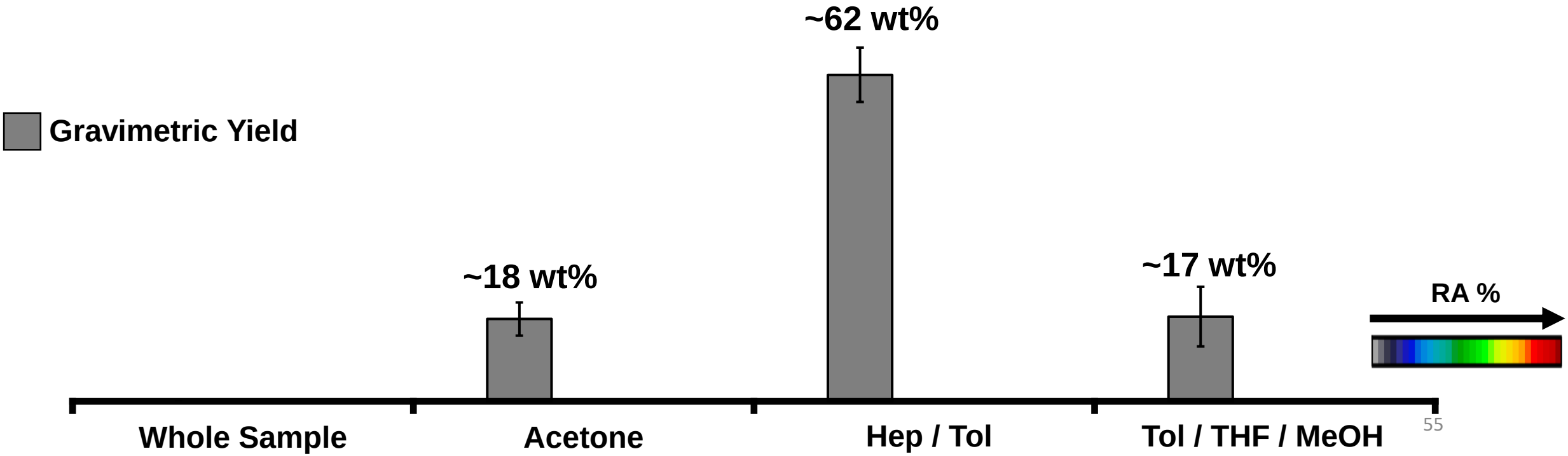
Asphaltenes → Longer Accumulation — 200 – 10000 ms

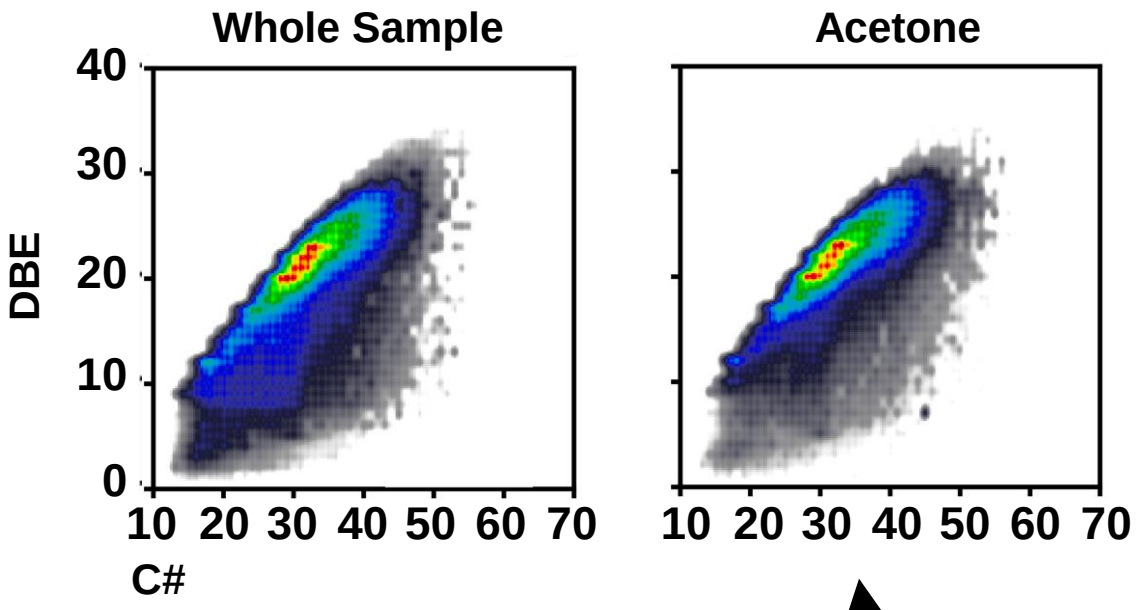
Ionization Efficiency ∝ 1 / ac. Time

Extrography Separation - Maya C_7 Asphaltenes Gulf of Mexico

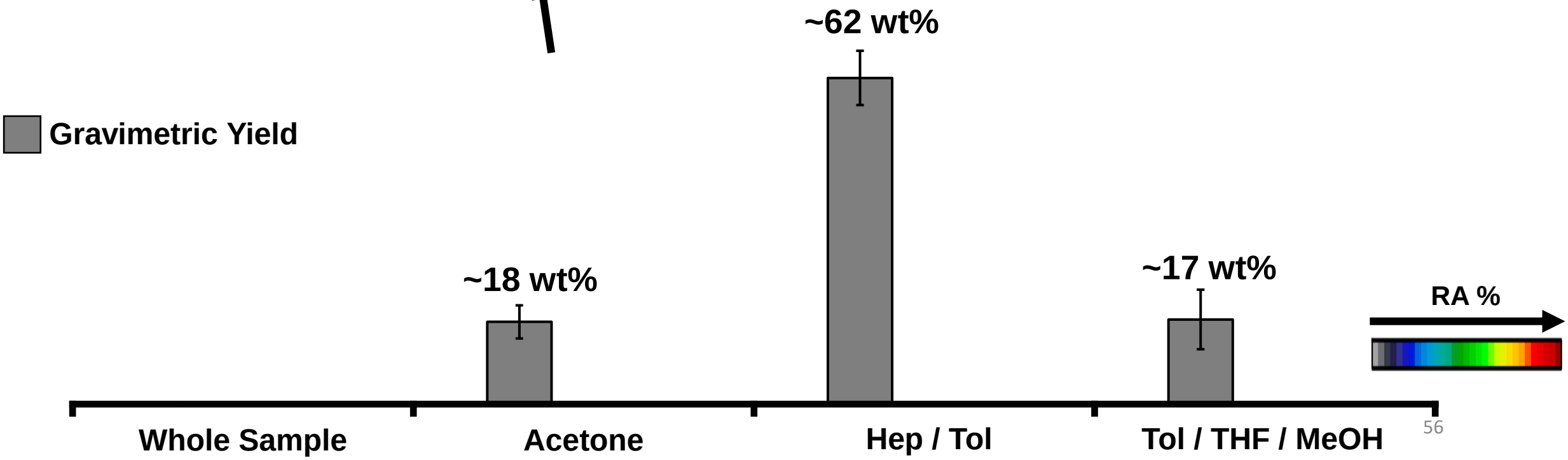


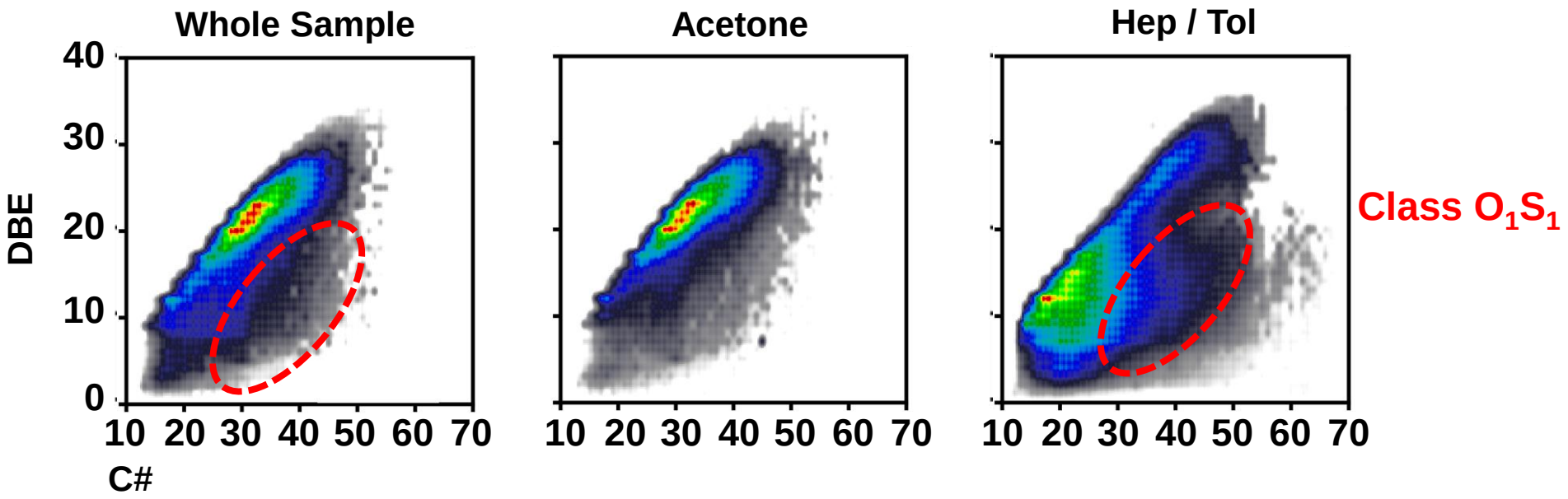

Whole Sample
40
30
20
10
0
DBE
10 20 30 40 50 60 70
C#
Classical Asphaltenes
Class O_1S_1

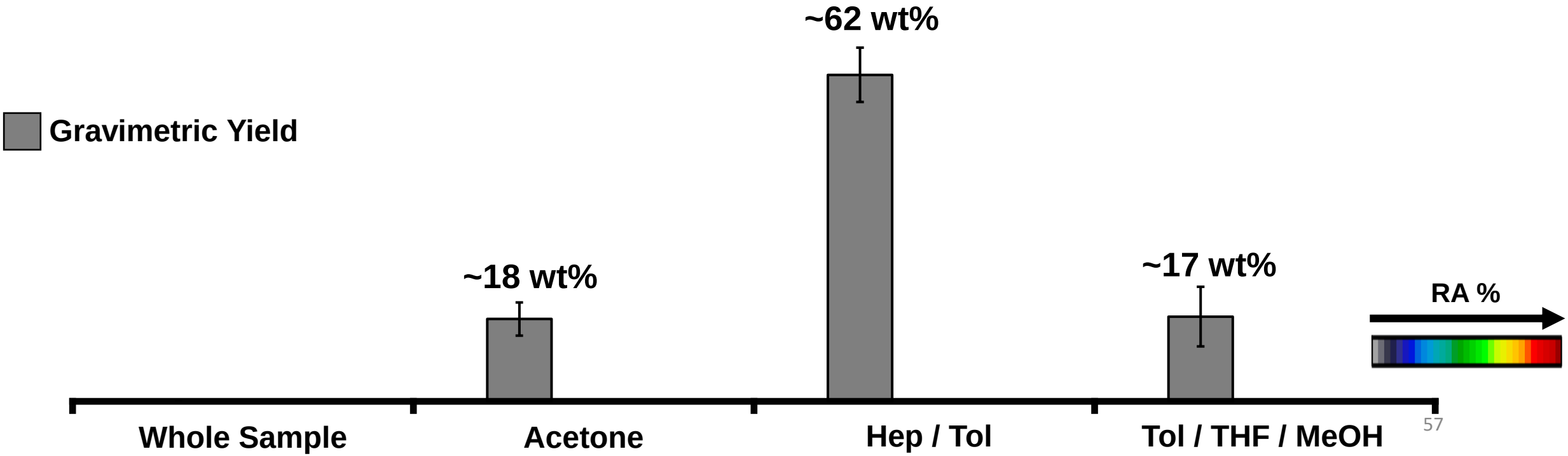

Gravimetric Yield
~62 wt%
~18 wt%
~17 wt%
RA %
Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH

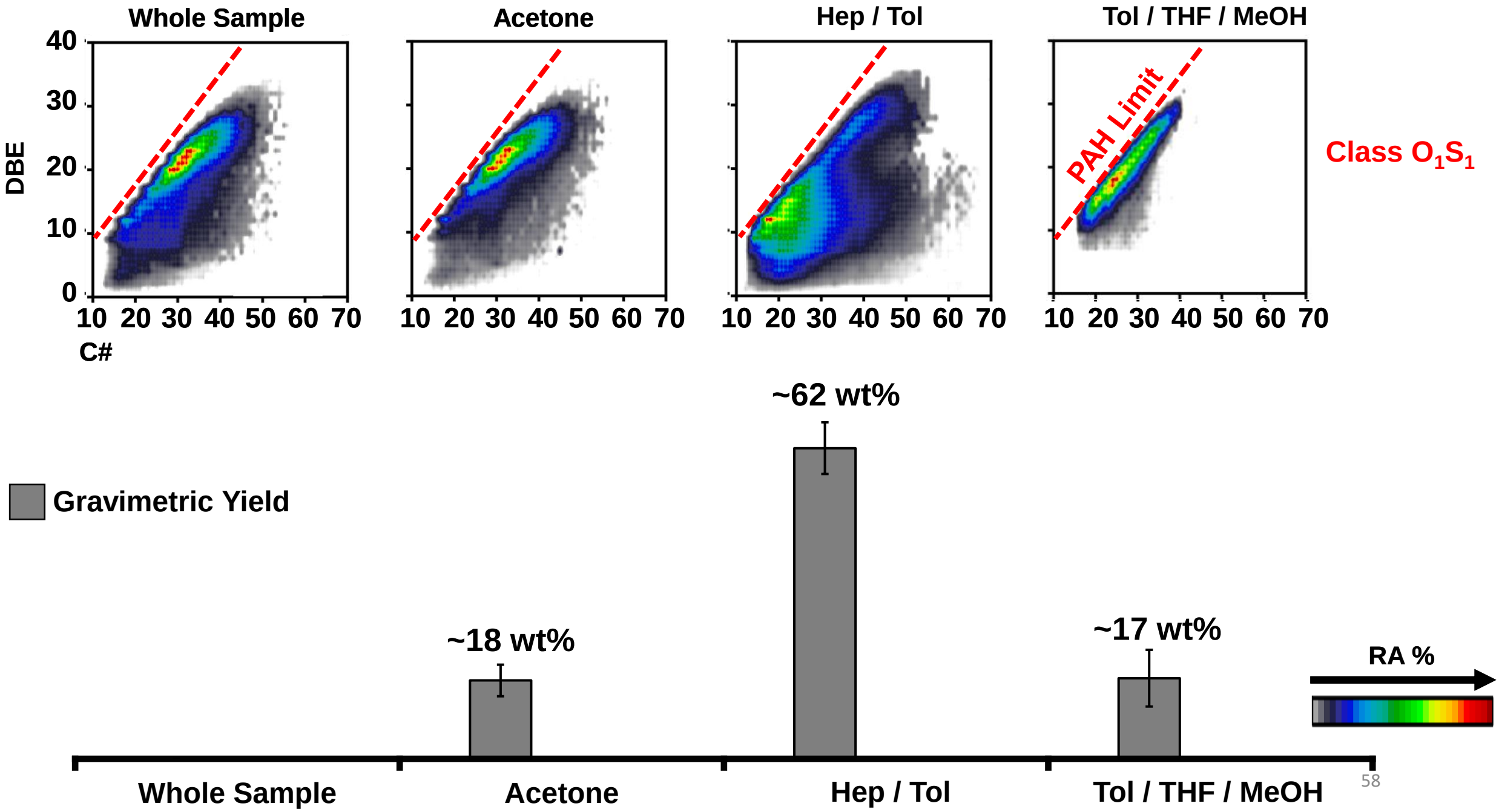

Whole Sample
Acetone
DBE
40
30
20
10
0
10 20 30 40 50 60 70
C#
10 20 30 40 50 60 70

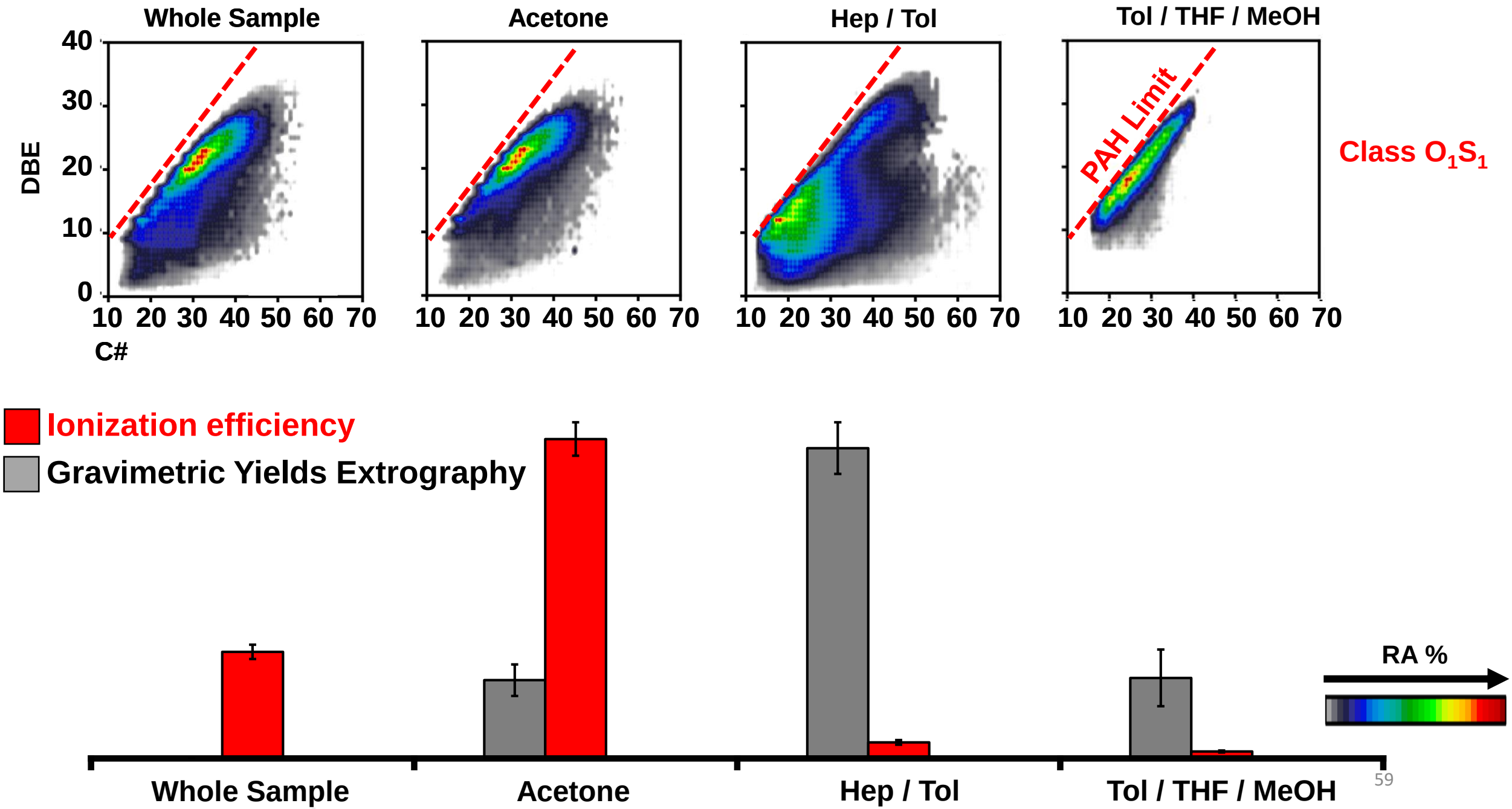
Class O_1S_1


Gravimetric Yield
~62 wt%
~18 wt%
~17 wt%
RA %
Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH


Whole Sample
Acetone
Hep / Tol
DBE
40
30
20
10
0
10 20 30 40 50 60 70
C#
Class O_1S_1

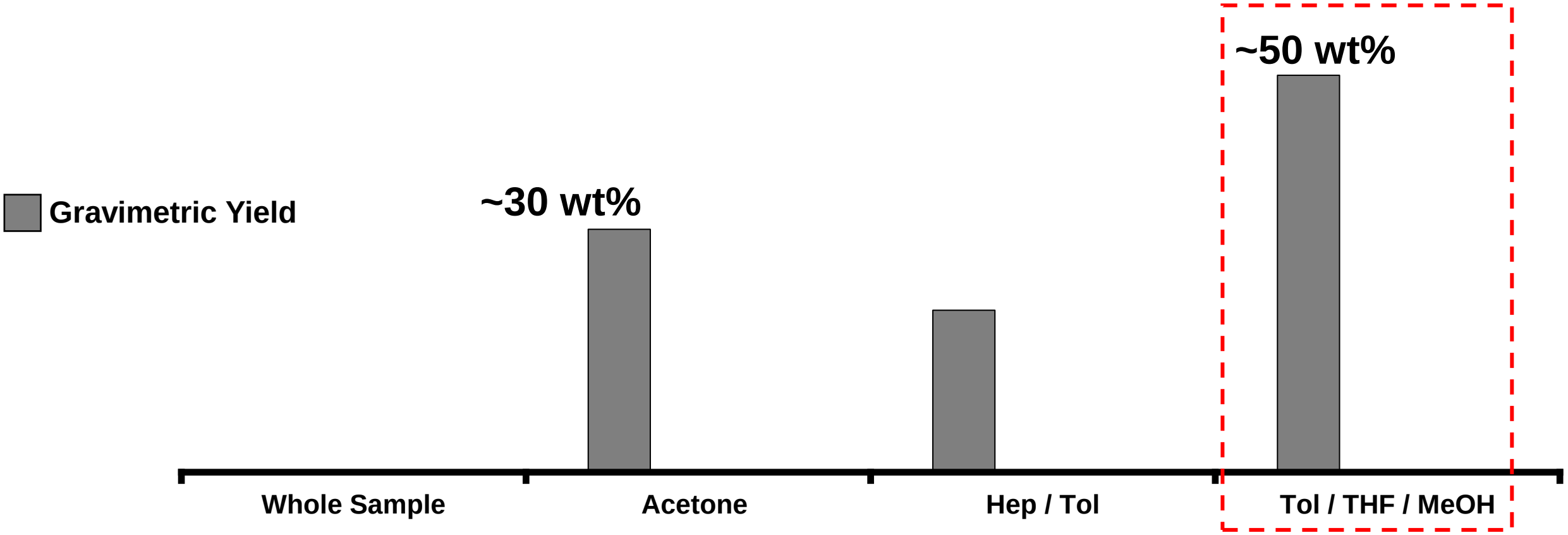

Gravimetric Yield
~62 wt%
~18 wt%
~17 wt%
RA %
Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH


Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH
PAH Limit
DBE
C#
Class O_1S_1
~62 wt%
~18 wt%
~17 wt%
Gravimetric Yield
RA %
Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH

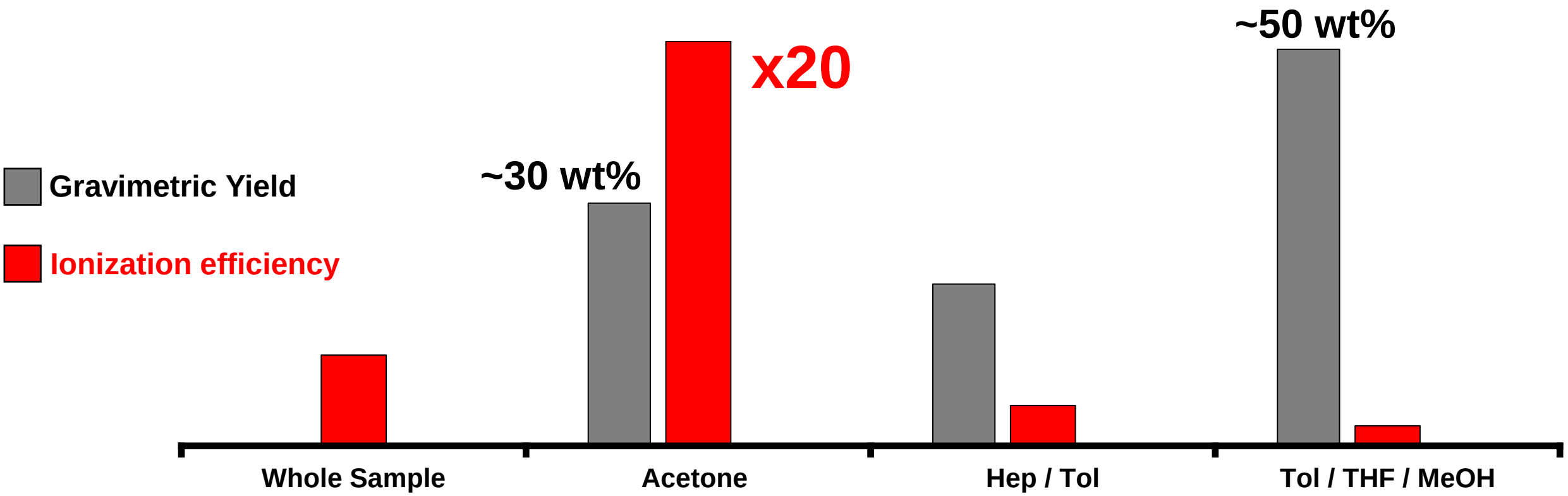

Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH
PAH Limit
DBE
C#
Class O_1S_1
Ionization efficiency
Gravimetric Yields Extrography
RA %
Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH

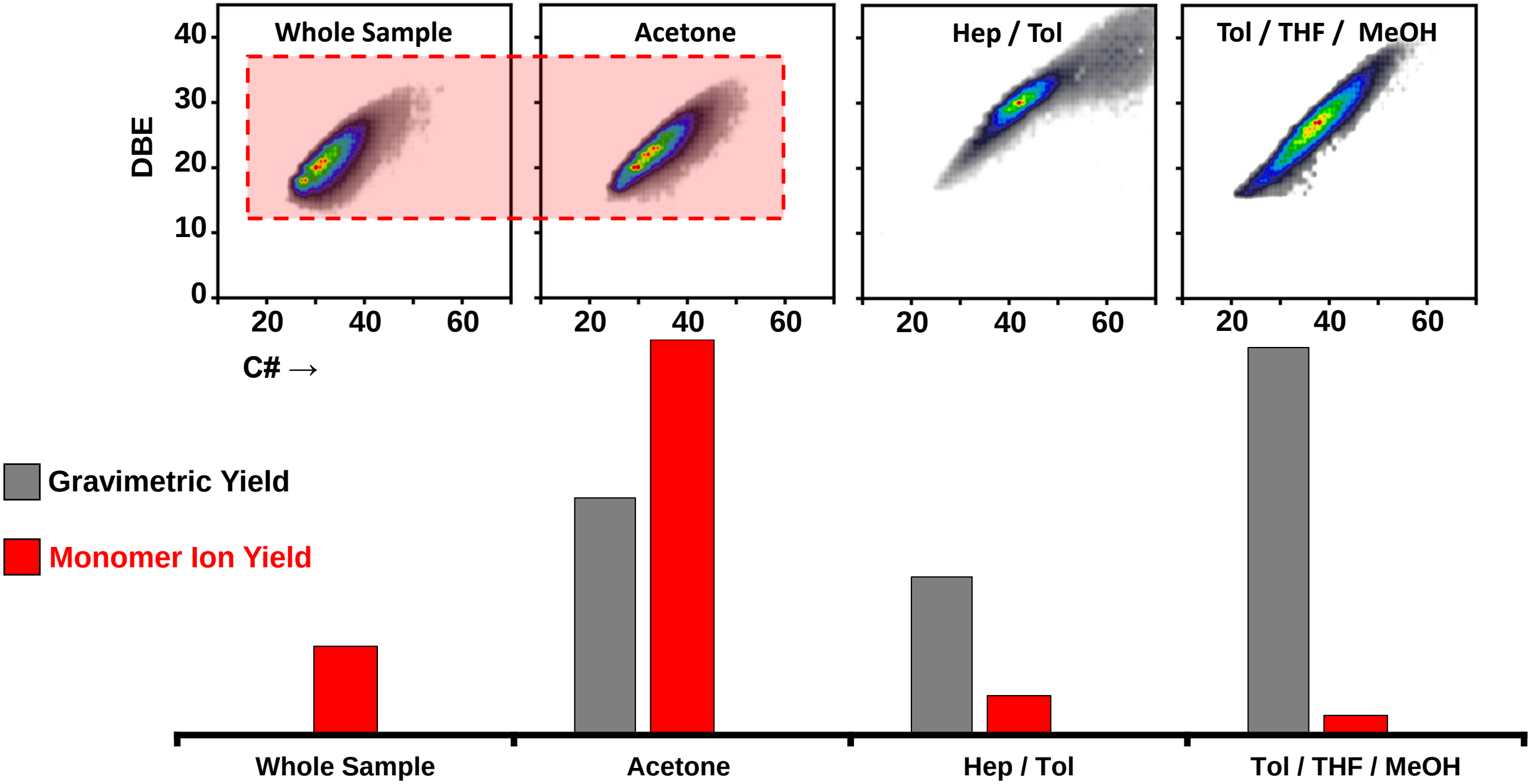
Selective Ionization has misled how we understand gas-phase fragmentation of asphaltenes.

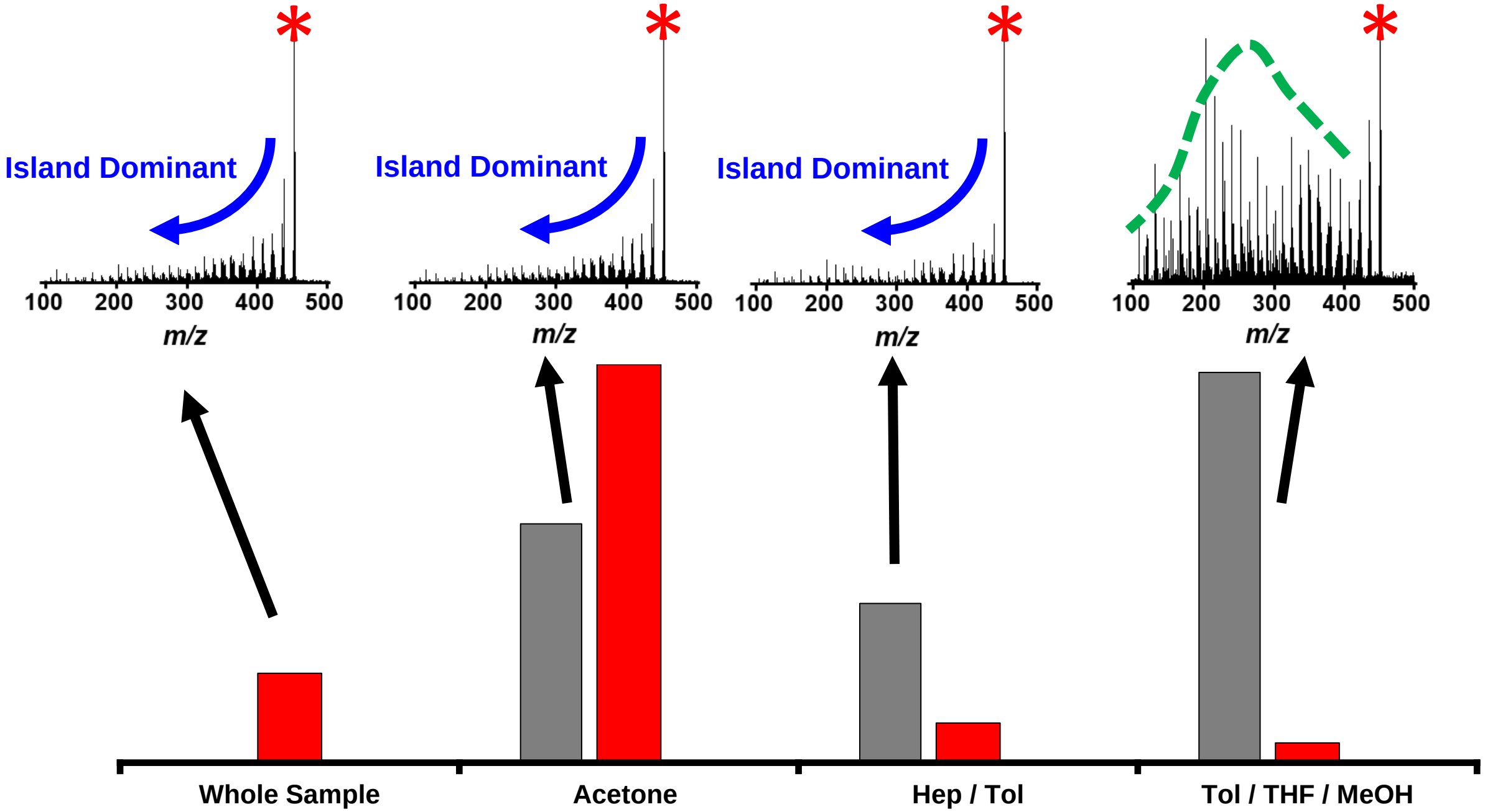
South American Medium Asphaltenes Archipelagos are only Accessed via Separations



South American Medium Asphaltenes

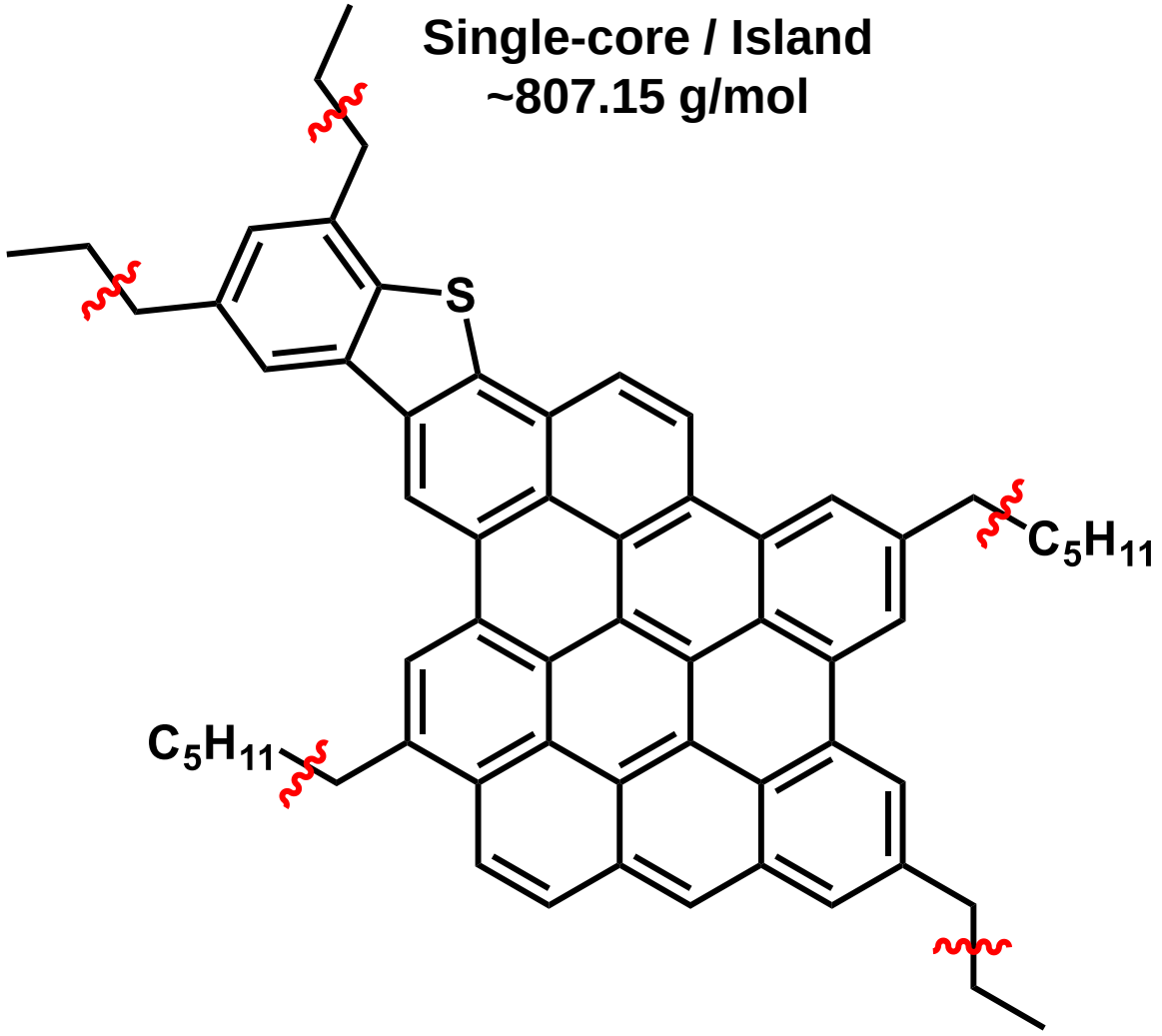



Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH
DBE
40
30
20
10
0
20
40
60
C# →
Gravimetric Yield
Monomer Ion Yield
Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH

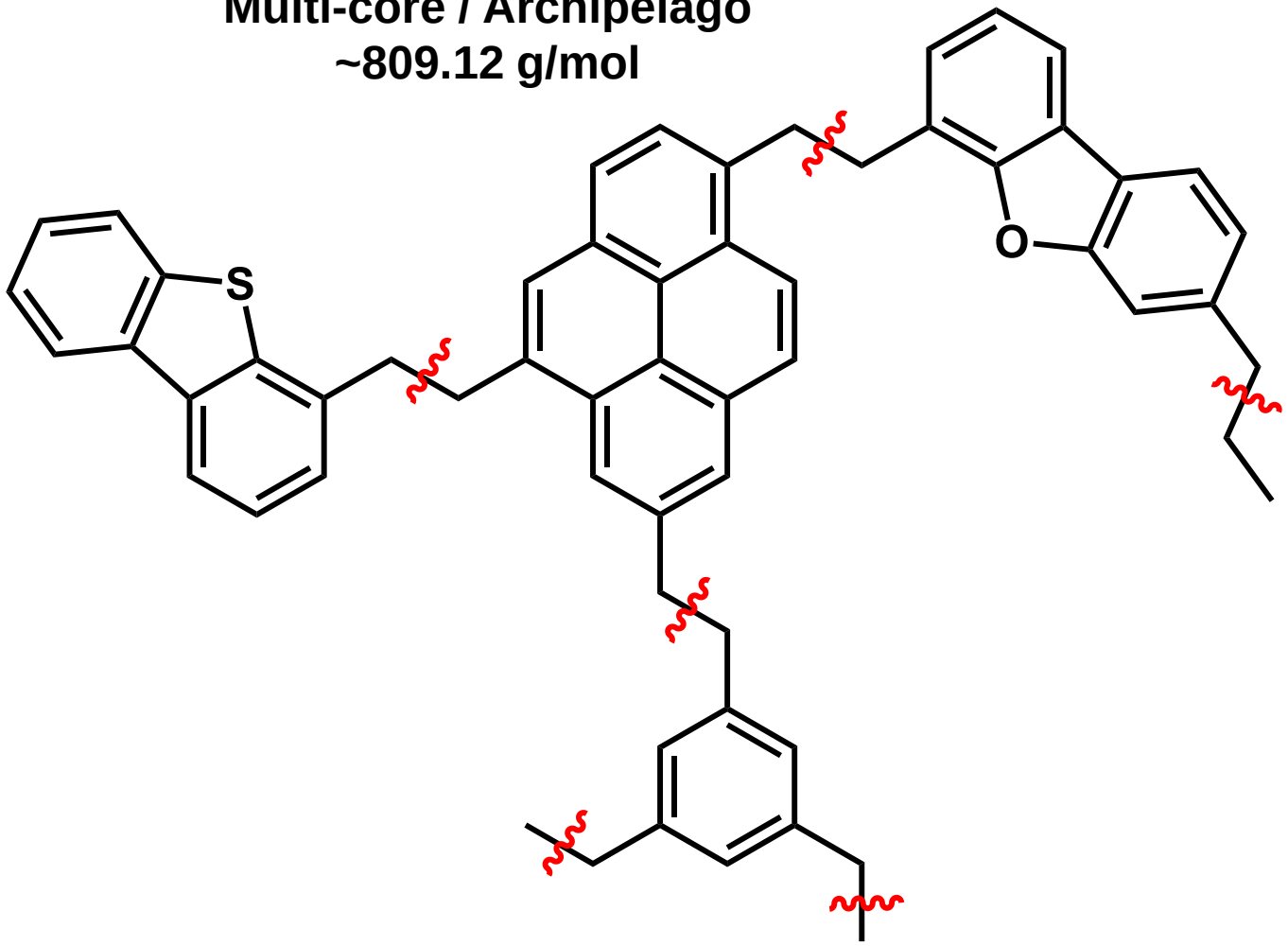

Island Dominant
Island Dominant
Island Dominant
100 200 300 400 500
m/z
Whole Sample
Acetone
Hep / Tol
Tol / THF / MeOH

Which one makes “good” carbon fibers?

Single-core / Island
~807.15 g/mol



Multi-core / Archipelago
~809.12 g/mol



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3-page research proposal

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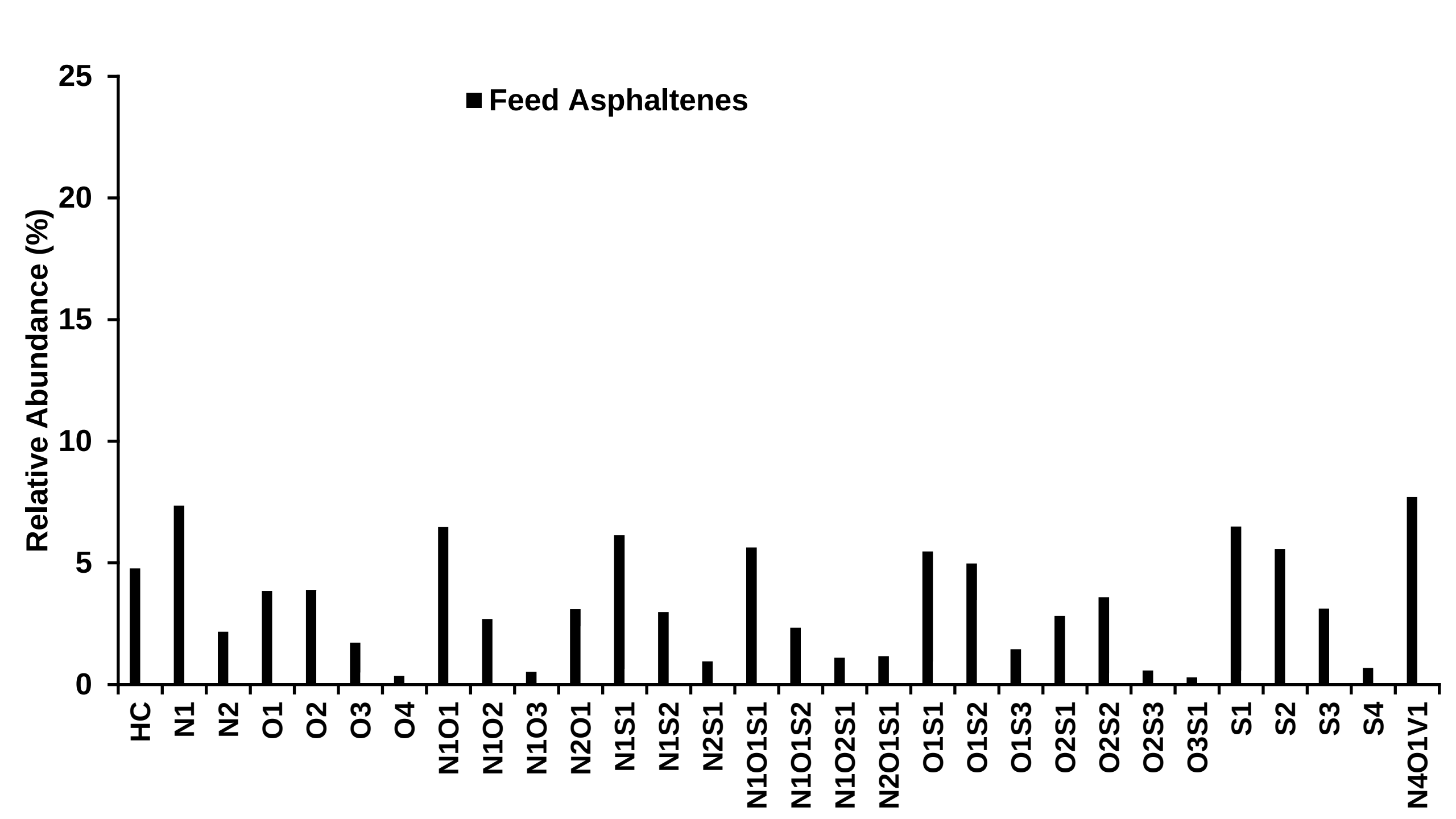
Feed Asphaltenes
Relative Abundance (%)
25
20
15
10
5
0
HC
N1
N2
O1
O2
O3
O4
N1O1
N1O2
N1O3
N2O1
N1S1
N1S2
N2S1
N1O1S1
N1O1S2
N1O2S1
N2O1S1
O1S1
O1S2
O1S3
O2S1
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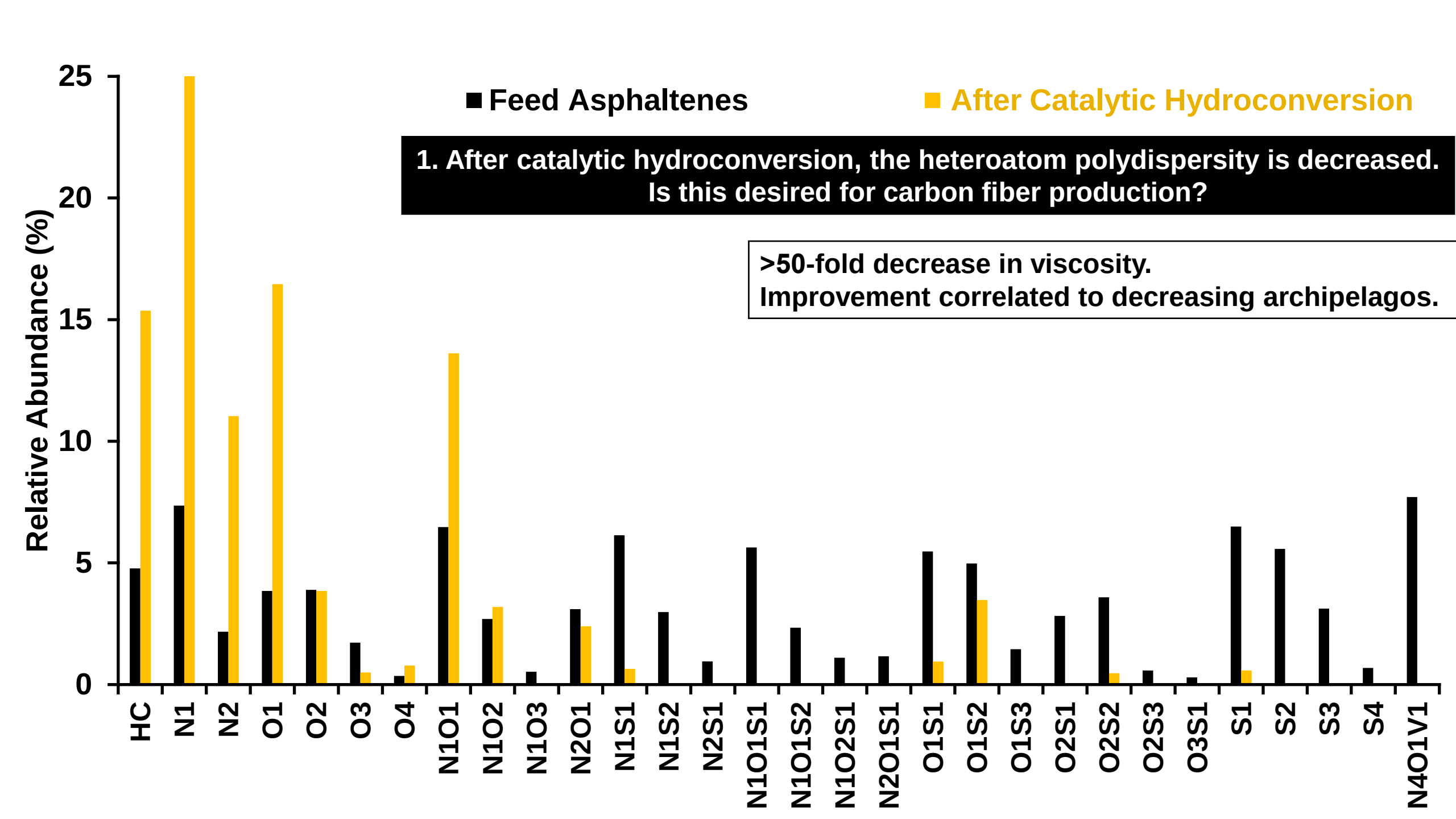
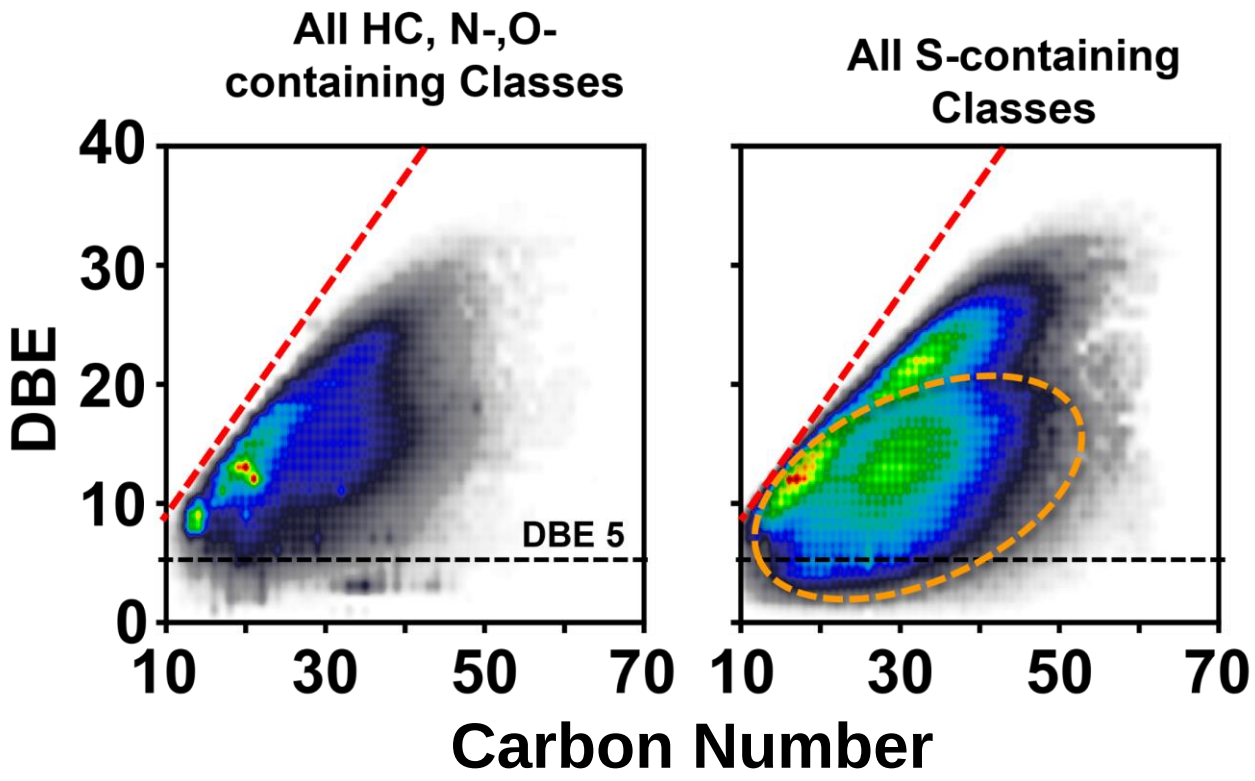
O3S1
S1
S2
S3
S4
N4O1V1


Feed Asphaltenes
After Catalytic Hydroconversion
1. After catalytic hydroconversion, the heteroatom polydispersity is decreased. Is this desired for carbon fiber production?
>50-fold decrease in viscosity.
Improvement correlated to decreasing archipelagos.
Relative Abundance (%)
25
20
15
10
5
0
HC
N1
N2
O1
O2
O3
O4
N1O1
N1O2
N1O3
N2O1
N1S1
N1S2
N2S1
N1O1S1
N1O1S2
N1O2S1
N2O1S1
O1S1
O1S2
O1S3
O2S1
O2S2
O2S3
O3S1
S1
S2
S3
S4
N4O1V1

2. Effect of Upgrading on the Molecular Composition: Cracking of CH_2 moieties

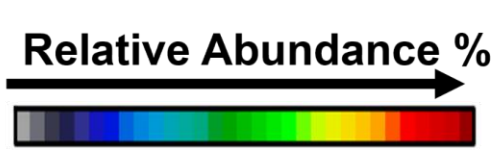
C_7 Asphaltenes
Athabasca Bitumen

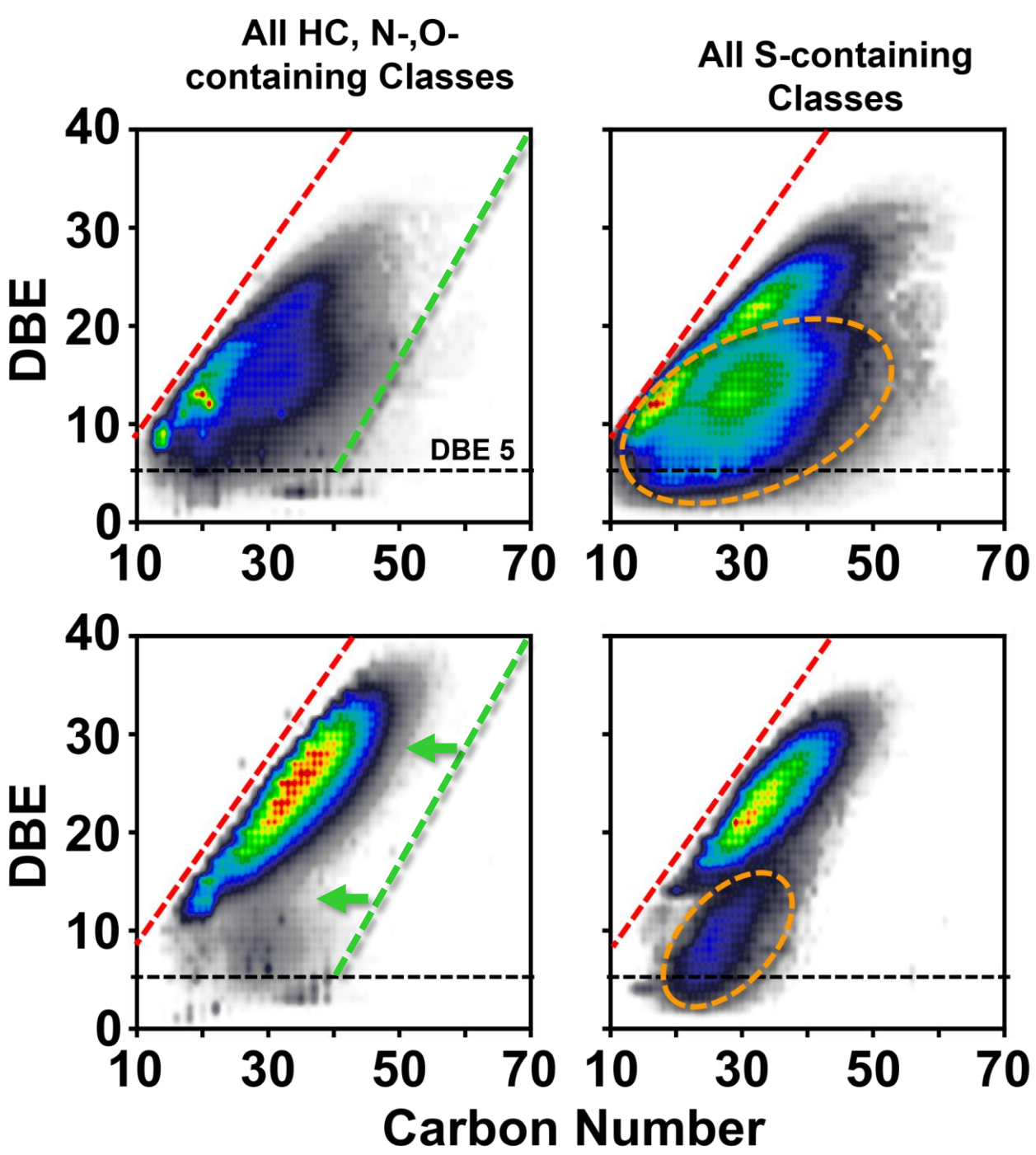


2. Effect of Upgrading on the Molecular Composition: Cracking of CH_2 moieties

C_7 Asphaltenes Athabasca Bitumen

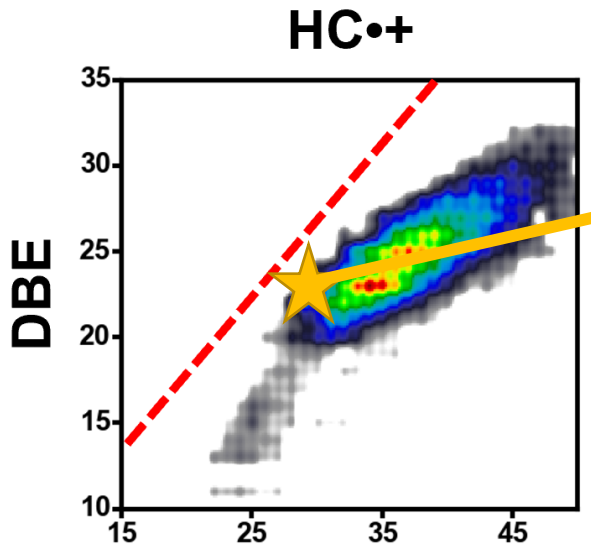
C_7 Asphaltenes Hydroconverted Athabasca Bitumen

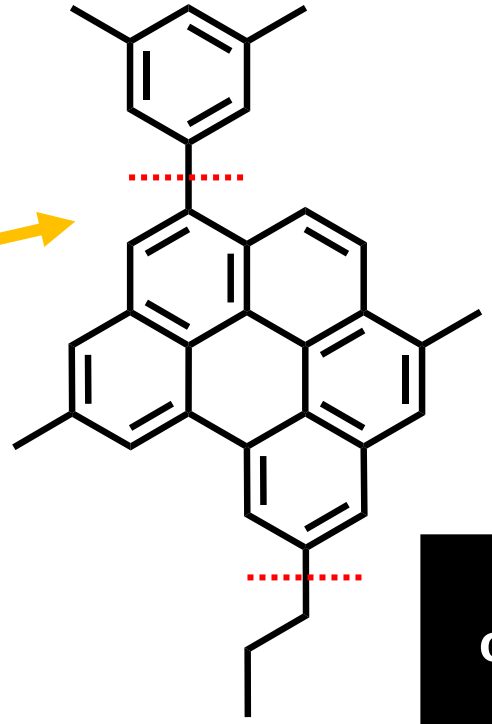




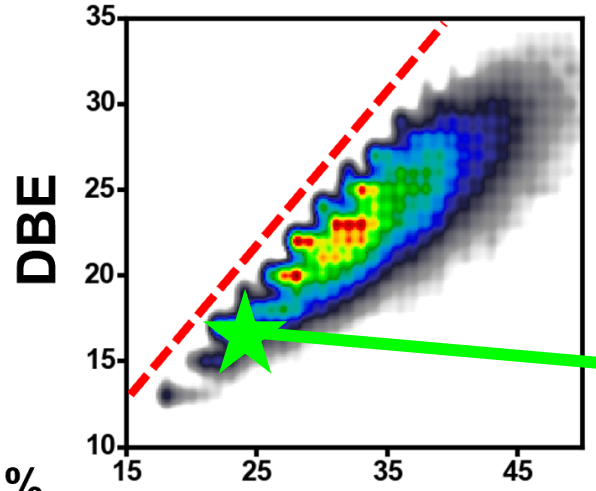
3. Effect of Upgrading on the Molecular Composition: Cracking of Archipelagos

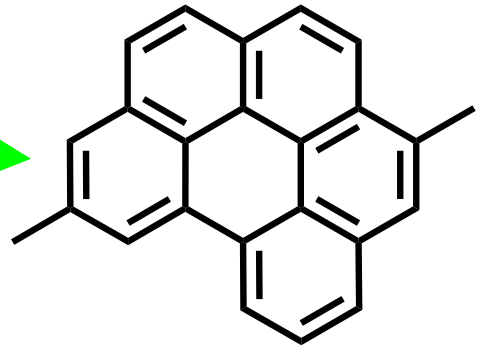
C_7 Asphaltenes Athabasca Bitumen





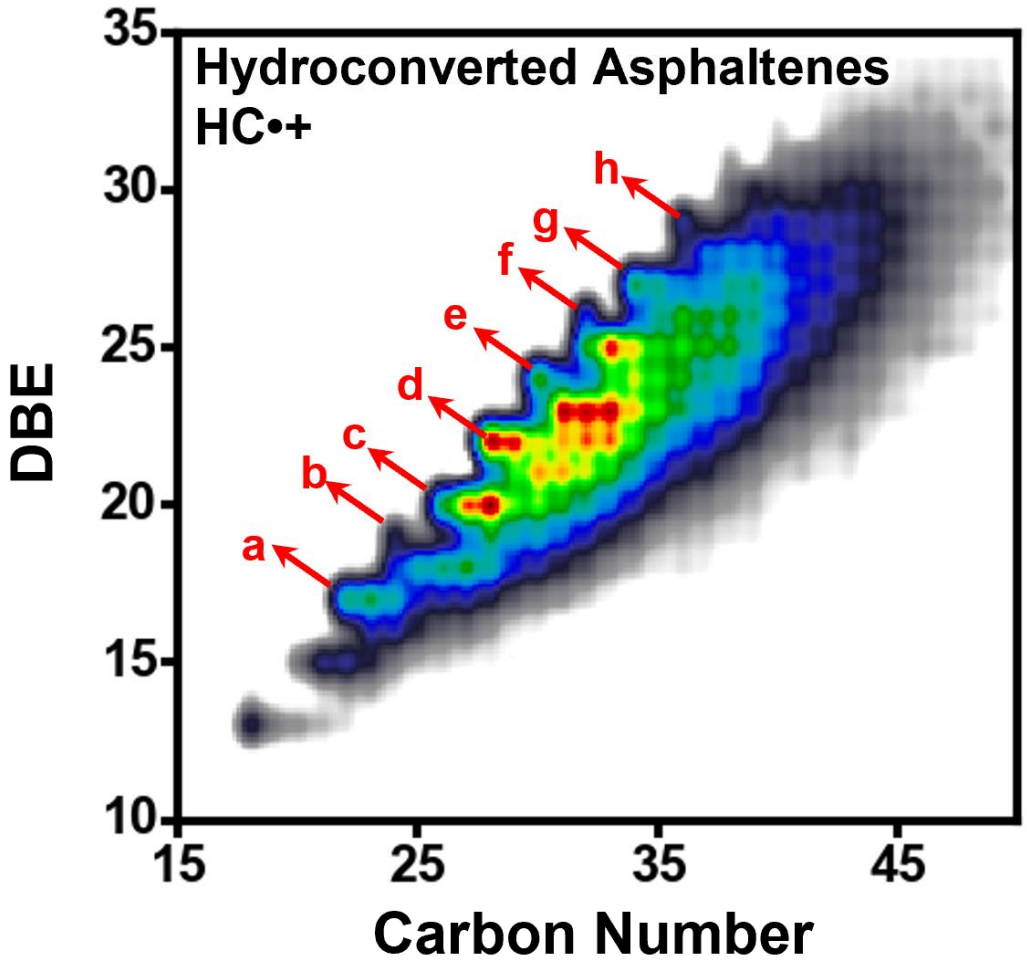
C_7 Asphaltenes Hydroconverted Athabasca Bitumen

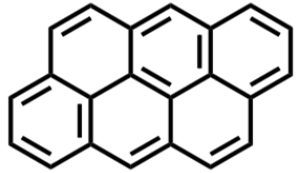




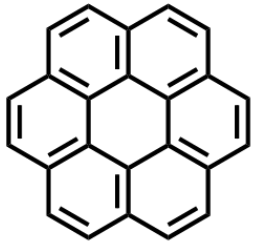
Relative Abundance %

4. Upgrading yields high-ring number bare PAHs

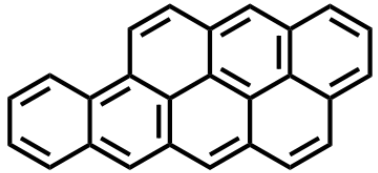




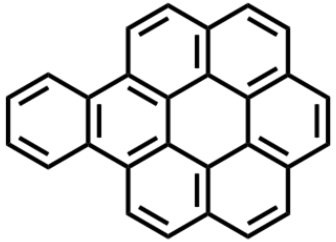
a) C# 22, DBE 17



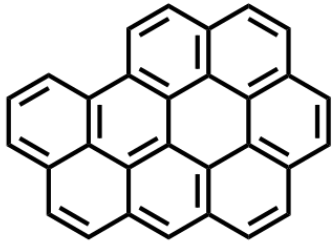
b) C# 24, DBE 19



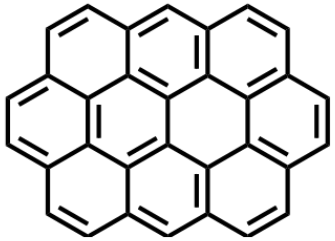
c) C# 26, DBE 20



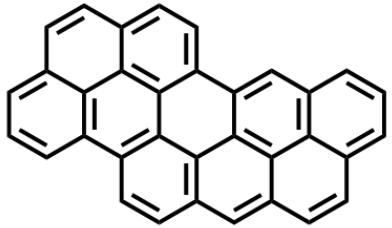
d) C# 28, DBE 22



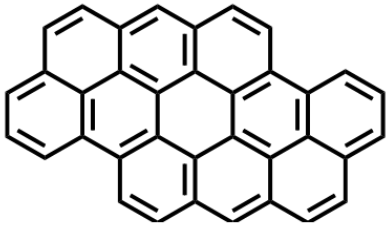
e) C# 30, DBE 24



f) C# 32, DBE 26

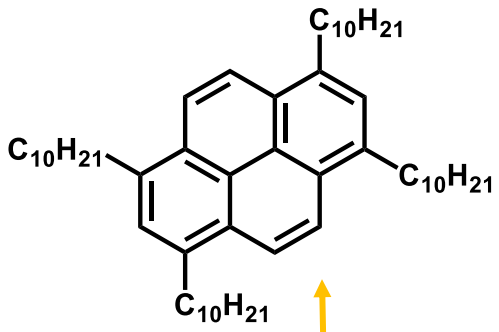


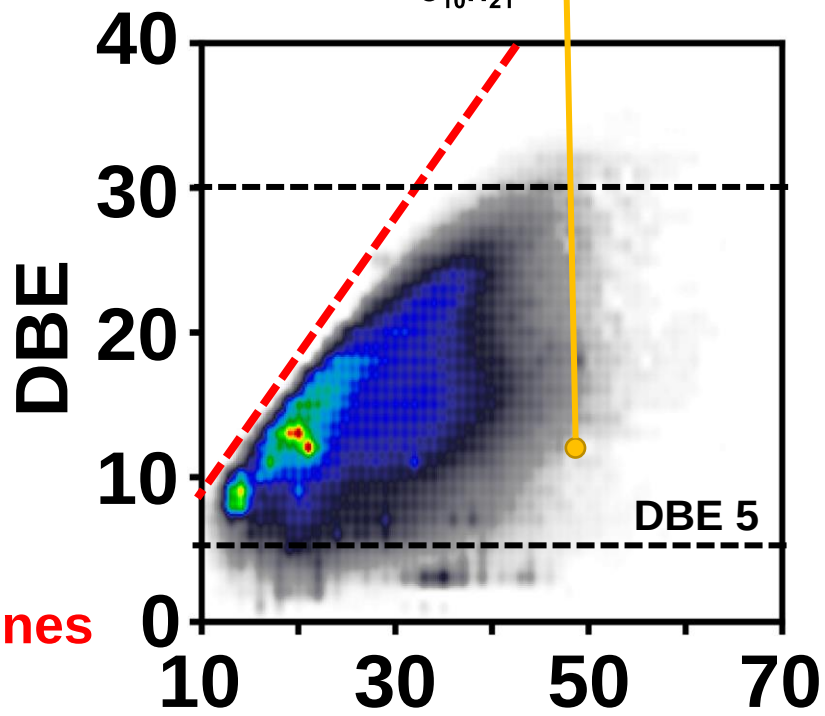
g) C# 34, DBE 27



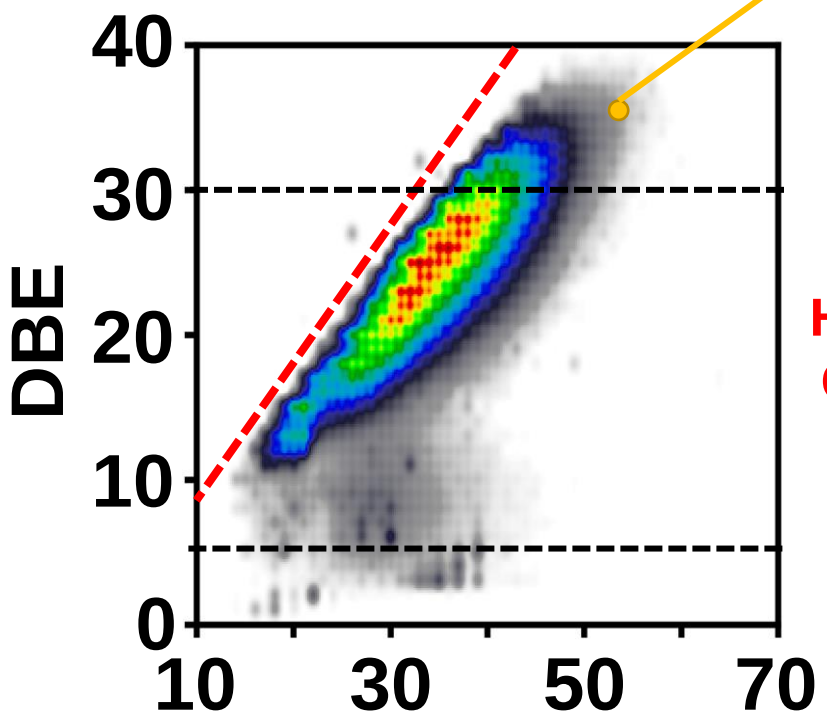
h) C# 36, DBE 29

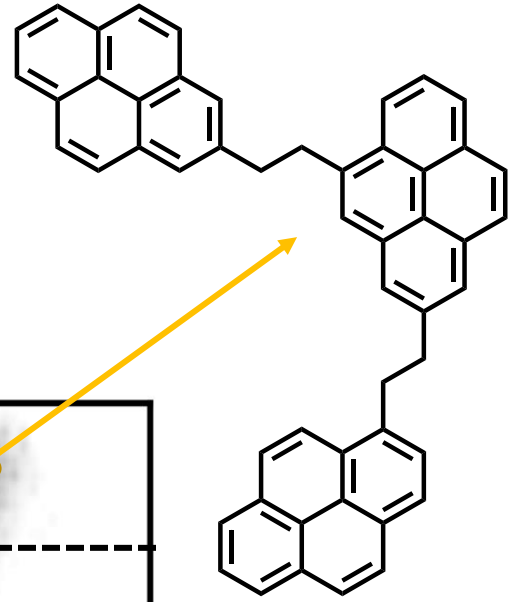
5. Upgrading <u>can</u> Produce Addition Reactions and produces archipelagos with a higher number of rings





C_7 Asphaltenes



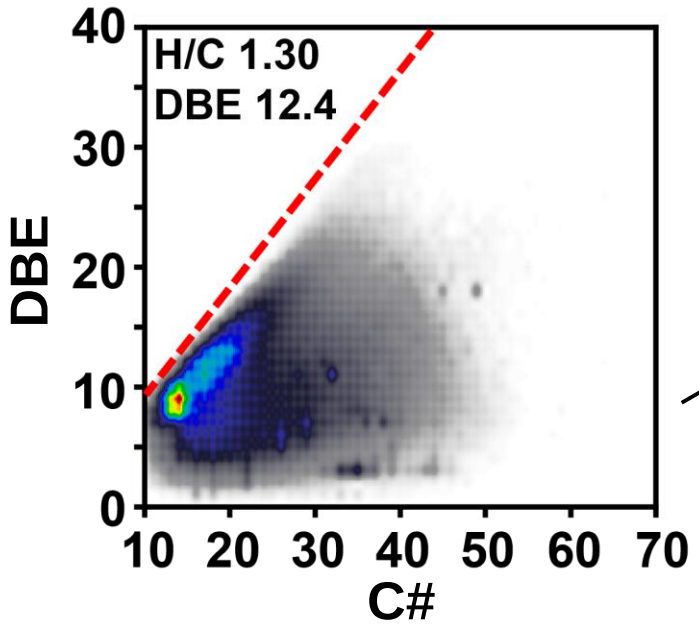


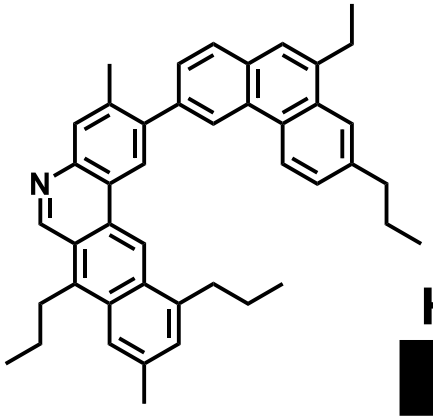
Hydroconverted C_7 Asphaltenes

Relative Abundance %

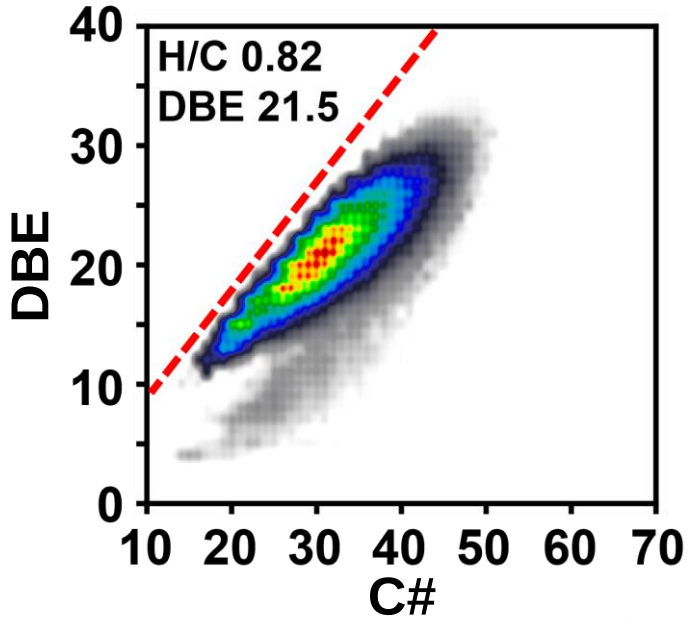
Carbon Number

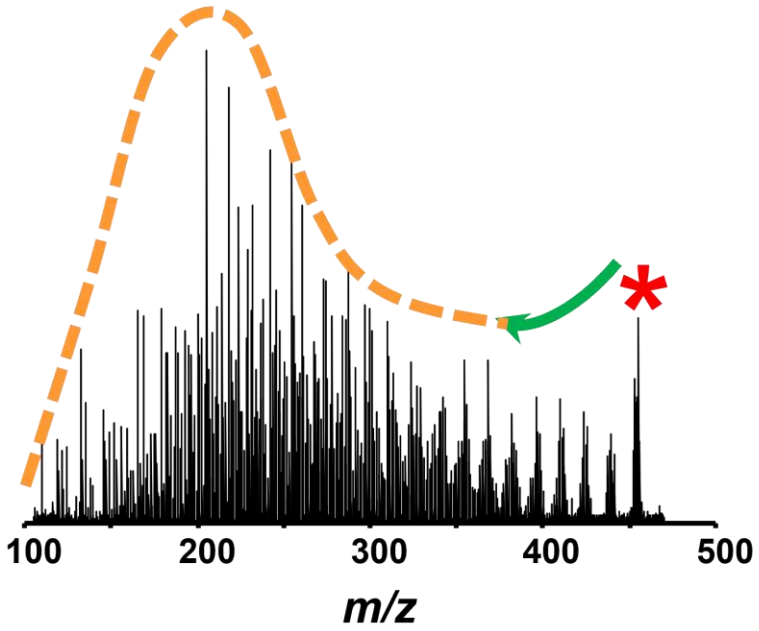
5. After hydroconversion, LMW species mostly reveal island structures

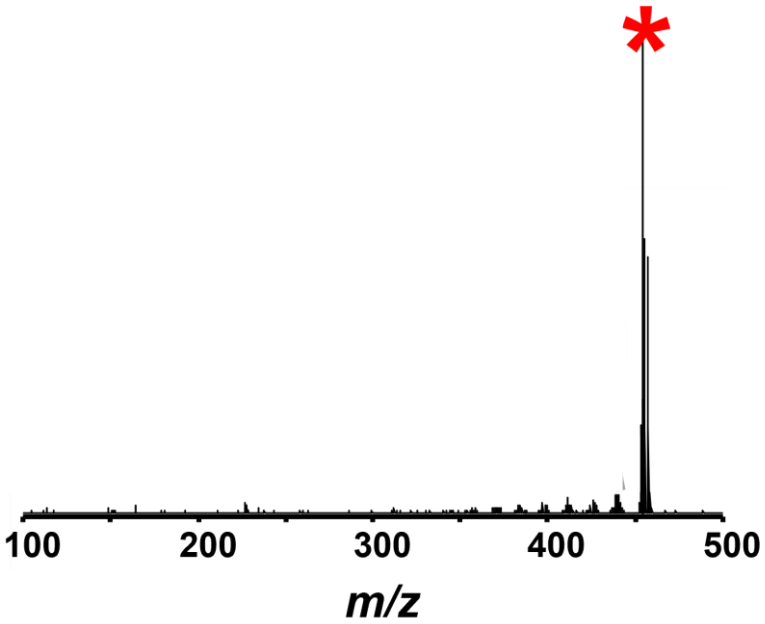




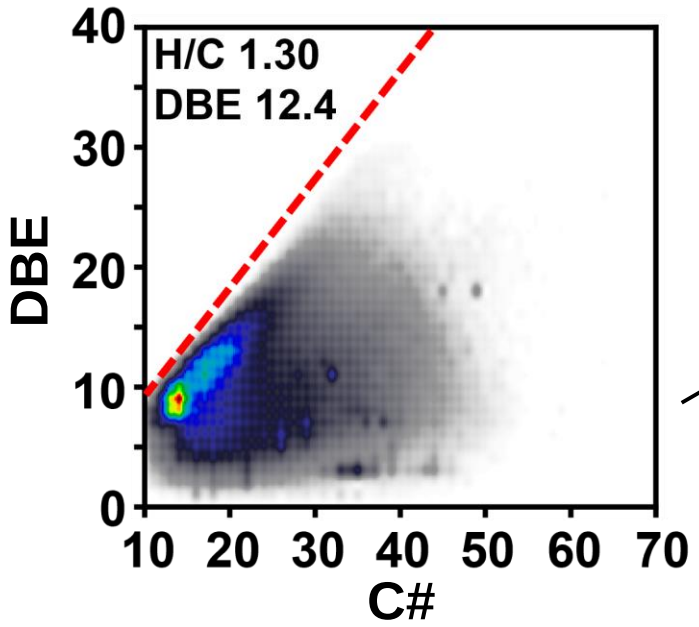
Hydroconversion

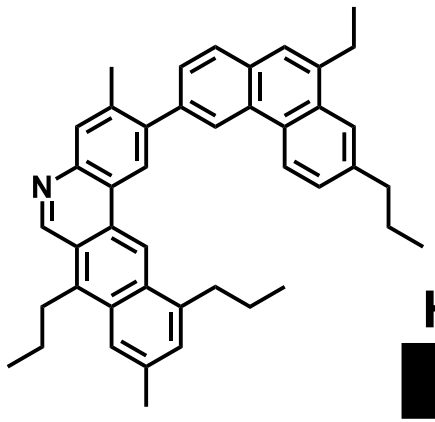




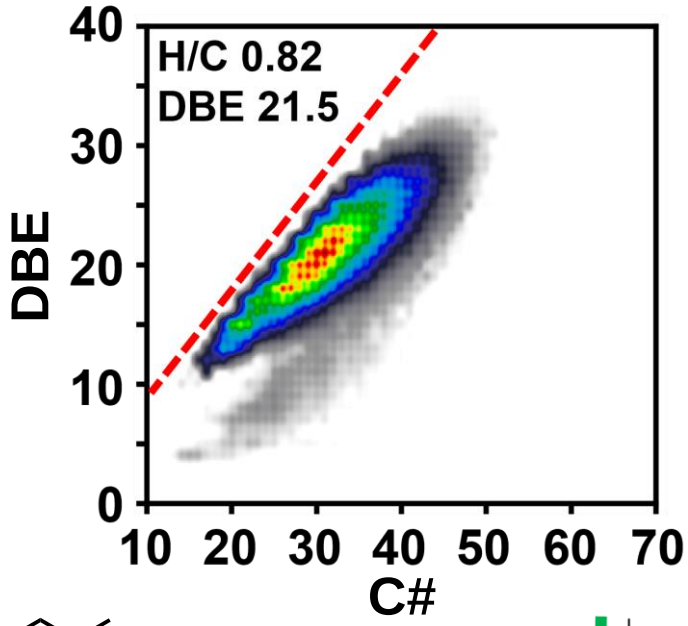


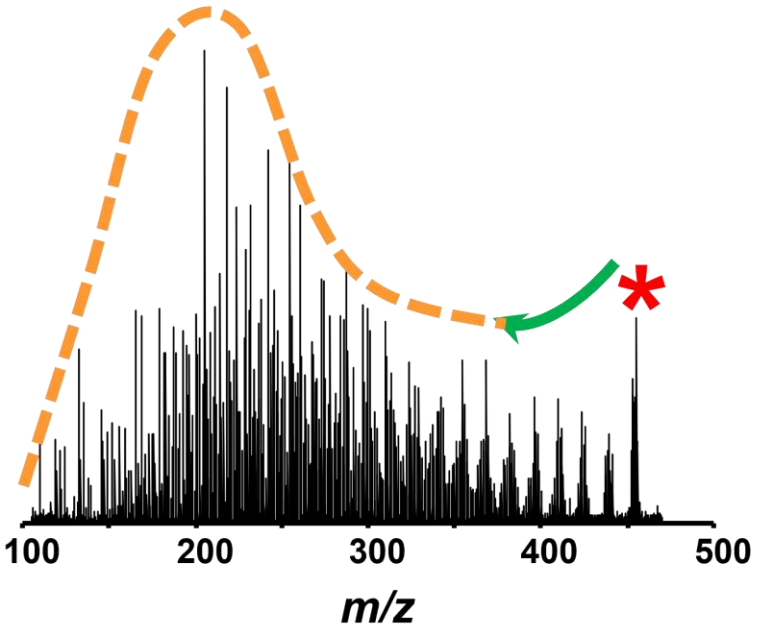
5. After hydroconversion, LMW species mostly reveal island structures

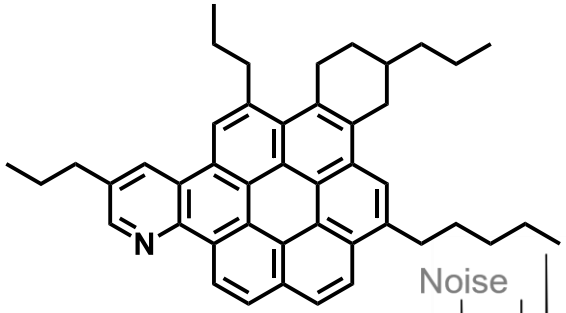


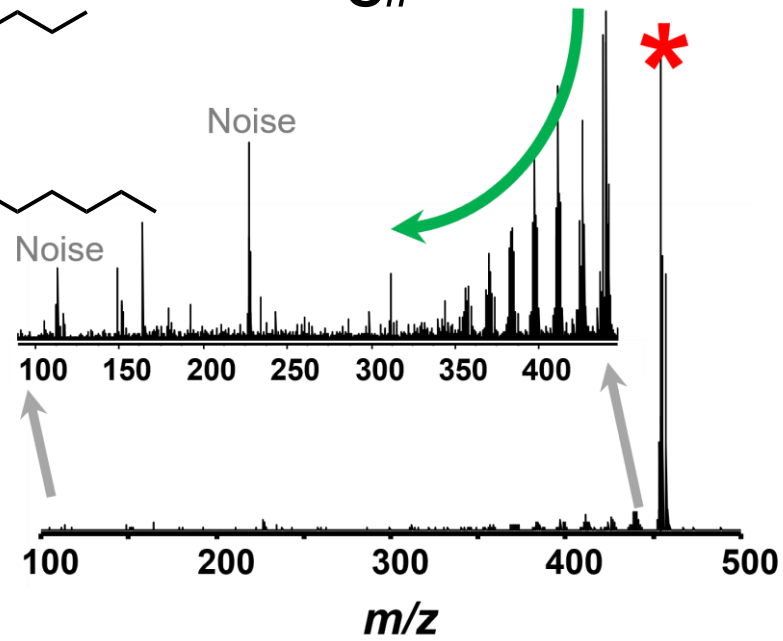


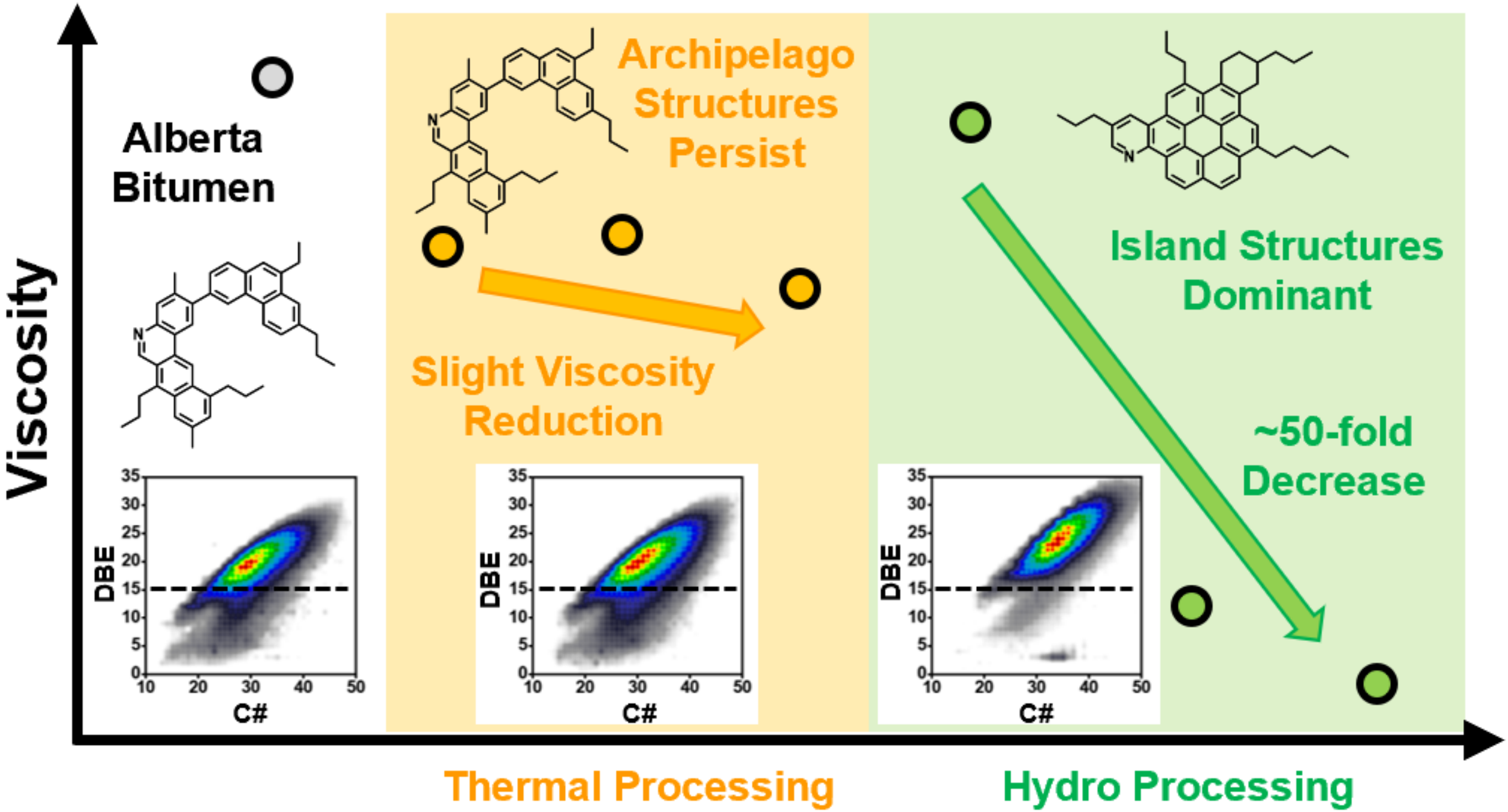
Hydroconversion











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