

# CID fragmentation studies of asphaltenes at different precipitation times using Magnetic Resonance Mass Spectrometry (MRMS)



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## Introduction

The structures of asphaltenes are one of the hot topics in asphaltenes analysis because they might have an influence on aggregate formation. Since years ago, there has been a discussion about the existence of archipelago and/or island structures. Recently, studies have been performed by Podgorski et al. [1] using FT-ICR mass spectrometry combined with IRMPD to determine the ratio of archipelago and island structures.

In our study, two asphaltenes with a low heptane to crude oil ratio (HCOR) after short and long precipitation times have been studied by CID fragmentation using magnetic resonance mass spectrometry (MRMS). Asphaltenes were ionized by APPI and isolated with a quadrupole using a small mass window of 10 Da. The fragmentation of the asphaltenes were studied at different collision energies.

## Methods

### Data acquisition:

- solarIX 2xR MRMS with 7 T superconducting magnet and new dynamically harmonized analyzer cell and quadrupole detection
- mass range  $m/z$  151 – 3000
- ionization: APPI positive ion mode
- resolving power of 1300,000 at  $m/z$  400 using absorption mode processing
- 300 single scans were averaged for the final mass spectrum
- APPI: 100 ppm in 90% toluene, 10% MeOH

### Mass calibration:

- external calibration with NaTFA cluster
- internal recalibration with a known homologous HC and S1 series

### Molecular formula assignment:

- PetroOrg 10.0 (Florida State University)
- Max. molecular formula:  $C_{60}H_{10}N_3O_3S_3$
- H/C ratio:  $0.2 \leq H/C \leq 2.3$
- Electron configuration: odd and even
- Mass tolerance: 0.5 ppm

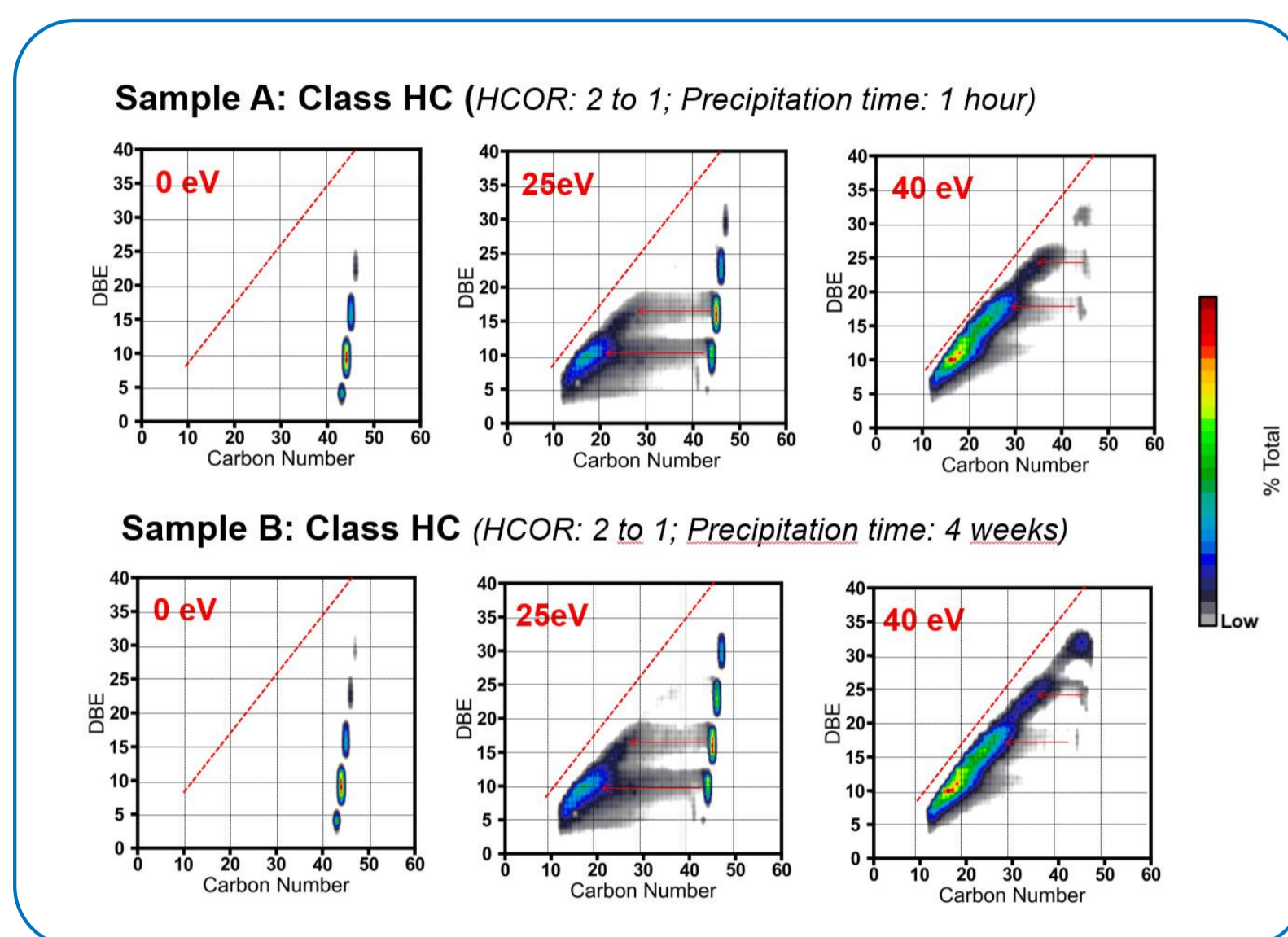


Fig. 1: DBE vs. C atom number plots of the HC class of sample A and B after Q-isolation ( $m/z$  595 – 605) and fragmentation at low and high collision energies.

## Results

Two asphaltenes with the same HCOR but with different precipitation times were analyzed concerning their structures using QCID fragmentation. Sample A with a short precipitation time (1 hour) has a much higher H/C ratio (1.54) than sample B (long precipitation time of 4 weeks) with a H/C ratio of only 1.38. Therefore, different structures might be expected (Table 1).

The DBE vs. C plots of the HC class after Q-isolation and at low and high collision energies of both samples are shown in Figure 1. No significant differences were found between both samples. At low collision energies (25 eV) only compounds with low aromaticity (low DBE) were fragmented. A shift close to the planar limit were observed only for structures with low DBE up to 18. Higher fragmentation energies resulted in fragmentation of high aromatic compounds with DBE up to 35. The fragmentation of the classes S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> of samples B are shown in Figure 2. All S<sub>x</sub> classes showed similar patterns in the DBE vs. C plots regarding fragmentation.

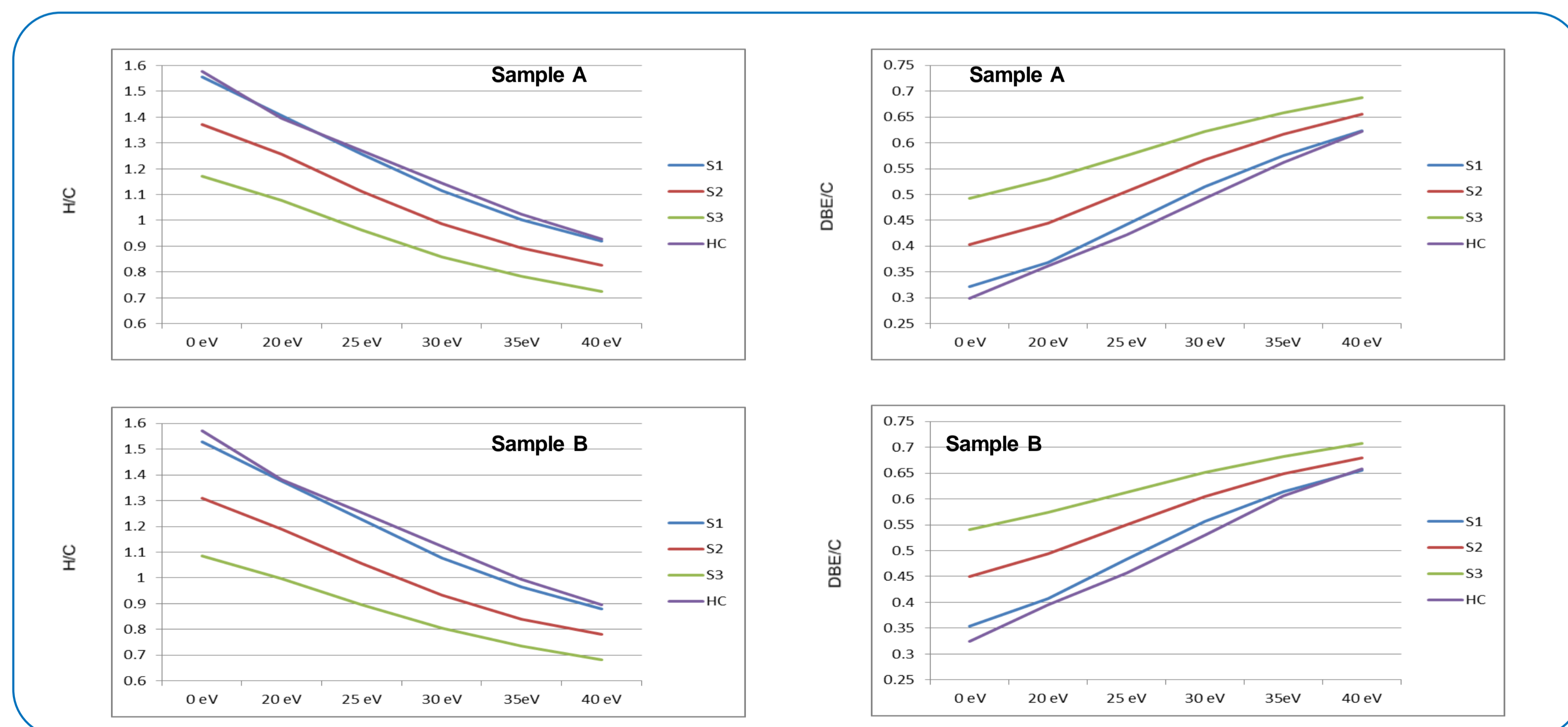


Fig. 3: Average H/C ratios of the S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> and HC classes before and after QCID fragmentation of a) sample A and b) sample B. Average DBE/C ratios of the S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> and HC classes before and after QCID fragmentation of c) sample A and d) sample B.

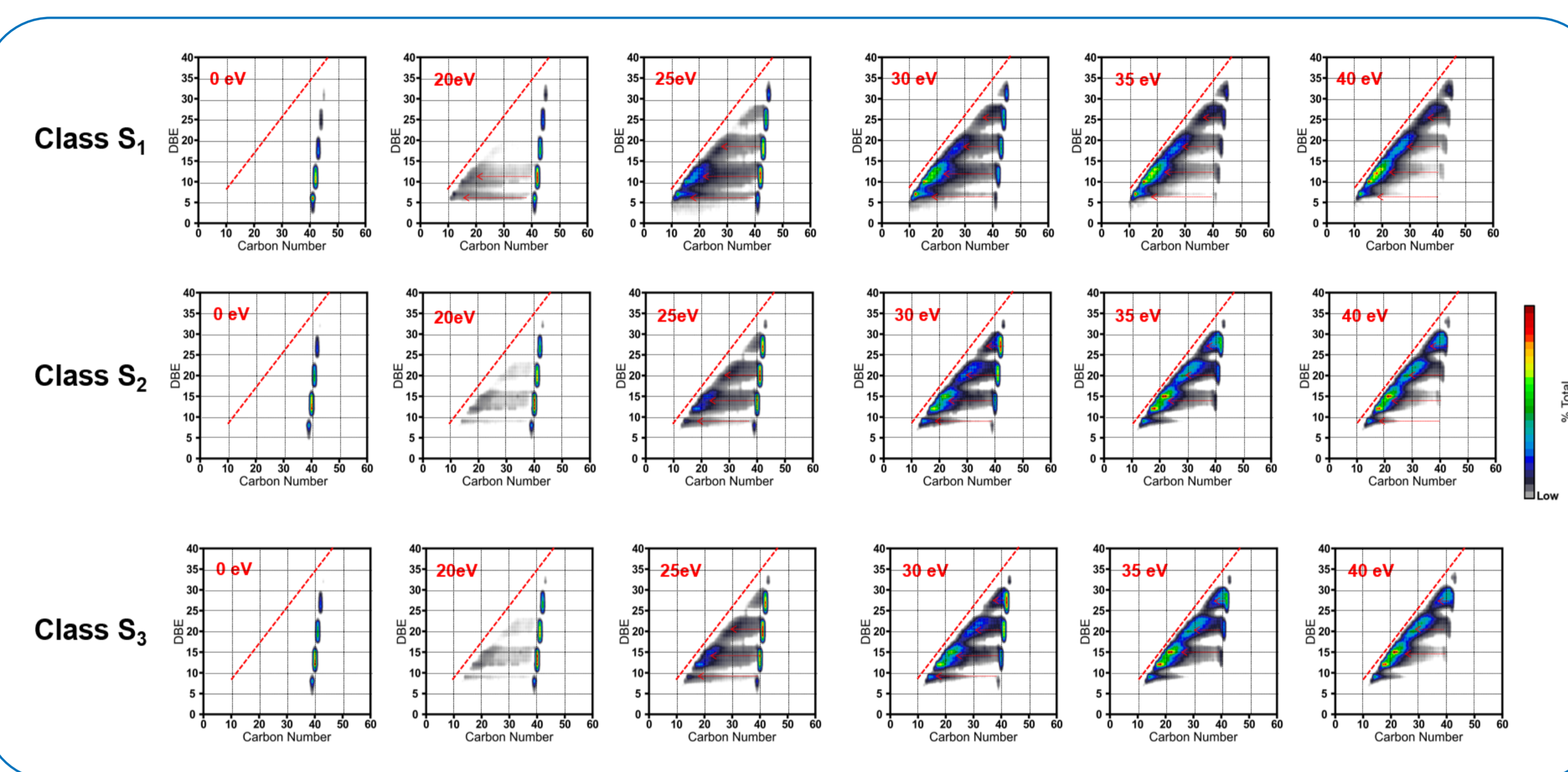


Fig. 2: DBE vs. C atom number plots of the S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> classes detected by APPI of sample B (HCOR: 2 to 1, precipitation time 4 weeks). Mass range  $m/z$  595 – 605 was selected by quadrupole and fragmented at different collision energies in the collision cell (Q-CID).

However, low DBE compounds (DBE  $\leq$  15) of class S<sub>1</sub> fragment already at low collision energies of 20 eV. At higher collision energies all S<sub>x</sub> classes show the same behavior generating fragments close to planar limit without changing the DBE. This was observed for structures up to DBE 35 indicating island structures. The average H/C ratios and the DBE/C ratios of the asphaltenes before and after QCID fragmentation are shown in Fig. 3. Both samples shows a similar trend with increasing collision energies. No significant differences between both samples were observed.

Table 1: Amount of carbon, hydrogen and H/C ratio of sample A and B

Asphaltenes	C	H	H/C
<b>Sample A:</b> HCOR 2 to 1, precipitation time 1 hour	84.62	10.87	1.54
<b>Sample B:</b> HCOR 2 to 1, precipitation time 4 weeks	83.11	9.53	1.38

[1] Podgorski et al. Energy Fuels 2013, 27, 1268-1276.

## Conclusions

- Low collision energies results in fragmentation of compounds with low aromaticity.
- High collision energies results in fragments close to planar limit for all compound classes.
- During fragmentation no reduction of DBE was observed. Fragmentation patterns of all observed classes correlate with island structures of the studied asphaltenes.

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