Investigation of aging processes in bitumen at the molecular level with high resolution Fourier transform ion cyclotron mass spectrometry and two-dimensional gas chromatography mass spectrometry

Supplemental material

Table S 1: Weighed portion of sample material for all measurements as well as the amount of non-evaporable residues weighed after the measurements. The red-marked sample "MP200 1D replicate 1" showed a negative value for the residue after the measurement and was considered as outlier.

Bitumen sample	crucible	sample	volatiles		residue	
	[mg]	[mg]	[mg]	[%]	[mg]	[%]
MP 200 original Replicate 1	22.44	1.00	0.84	84	0.16	16
MP 200 original Replicate 2	22.68	0.92	0.78	85	0.14	15
MP 200 original Replicate 3	22.31	1.05	0.91	87	0.14	13
MP 200 1D Replicate 1	21.92	0.98			-0.08	
MP 200 1D Replicate 2	22.30	1.09	0.89	82	0.20	18
MP 200 1D Replicate 3	22.20	0.96	0.82	85	0.14	15
MP 200 2D Replicate 1	22.39	1.09	0.89	82	0.20	18
MP 200 2D Replicate 2	22.40	1.02	0.82	80	0.20	20
MP 200 2D Replicate 3	22.56	1.14	0.94	82	0.20	18
MP 200 3D Replicate 1	22.56	1.04	0.91	87	0.13	13
MP 200 3D Replicate 2	22.37	1.00	0.86	86	0.14	14
MP 200 3D Replicate 3	22.48	1.14	0.88	77	0.26	23
MP 200 4D Replicate 1	22.54	1.04	0.91	87	0.13	13
MP 200 4D Replicate 2	22.35	1.10	0.91	83	0.19	17
MP 200 4D Replicate 3	22.46	1.10	0.93	85	0.17	15
MP 200 7D Replicate 1	22.24	1.06	0.85	80	0.21	20
MP 200 7D Replicate 2	22.28	1.12	0.86	77	0.26	23
MP 200 7D Replicate 3	22.35	0.98	0.71	72	0.27	28

Table S 2: GC×GC-HRTOF MS parameters.

Injection volume	1 µL (20 % wt solutions)
Injection temperature (PTV)	40°C – 2 °C/s – 400 °C (5 min hold)
Split flow	50 mL/min
Column flow	1.2 mL/min
Carrier gas	Helium (5.0)
1st Dimension Column	Phenomenex Zebron ZB-35HT Inferno (30 m × 0.25 mm; film: 0.1 µm)
2nd Dimension Column	SGE BPX1 (1.5 m × 0.1 mm; film: 0.1 µm)
Transferline	Agilent deactivated fused silica (0.8 m × 0.1 mm)
Modulation time	6 s (Hot pulses 2.5 s; Cold pulses: 0.5 s)
Primary oven temperature program	80 °C (5 min hold) – 2K/min – 400 °C (15 min hold)
Secondary oven temperature program	90 °C (5 min hold) – 1.95 K/min – 400 °C (15 min hold)
Modulator temperature program	105 °C (5 min hold) – 1.9 K/min – 400 °C (15 min hold)
Transferline Temperature	350 °C
MS acquisition delay	500 s
MS Acquisition rate	80 Hz
Mass range	40-800 m/z
Extraction frequency	1.5 kHz
Ion source temperature	300 °C
Ionization energy (EI)	70 eV
Mass calibration	PFTBA valve open during the whole run

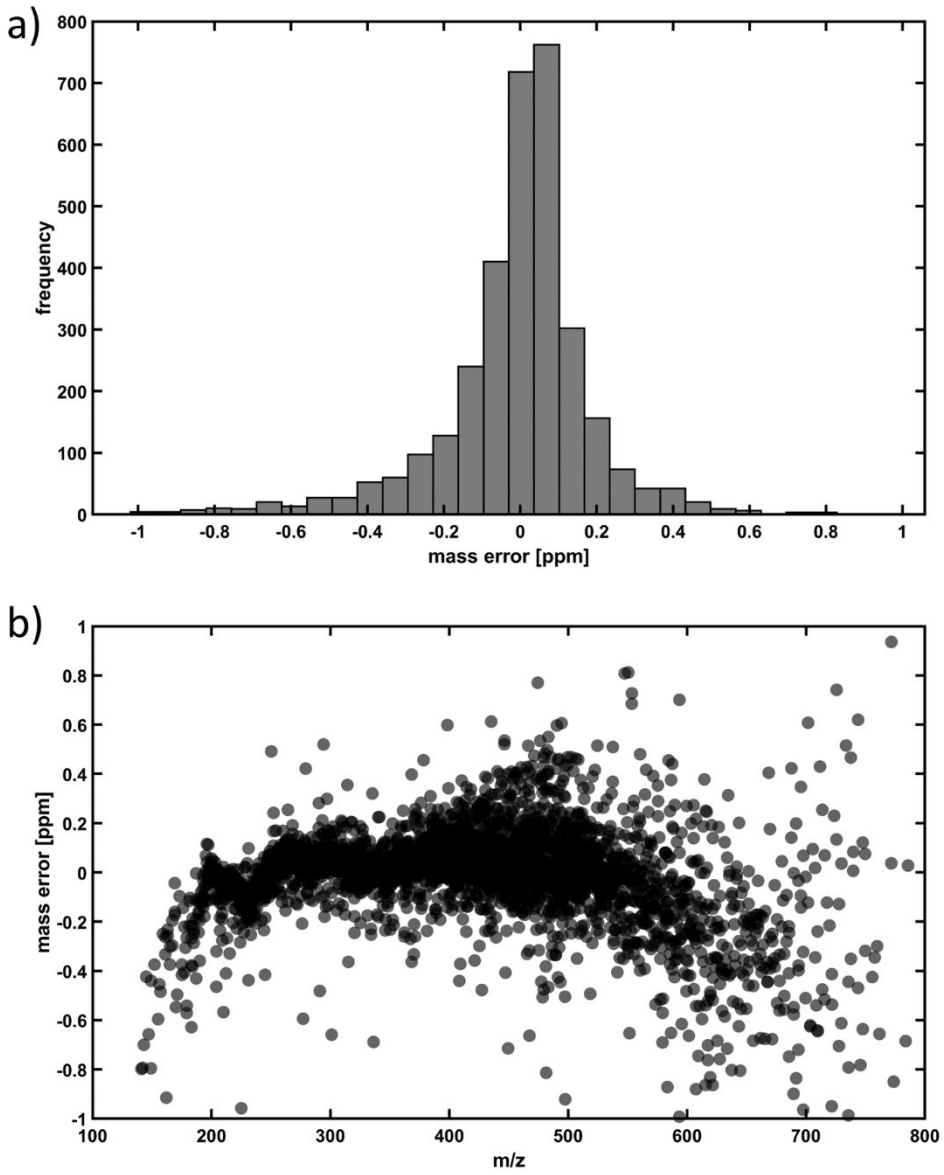

Figure S 1 Data quality of TG-FT-ICR MS data. a) Error histogram of the sum formula assignment exemplarily depicted for non-aged model bitumen. The error border for elemental composition calculation was set to 1 ppm. b) Mass error in ppm versus m/z. Generally, the root mean square error was below 0.28 ppm for MS-mode and below 0.31 ppm for MSMS-mode.

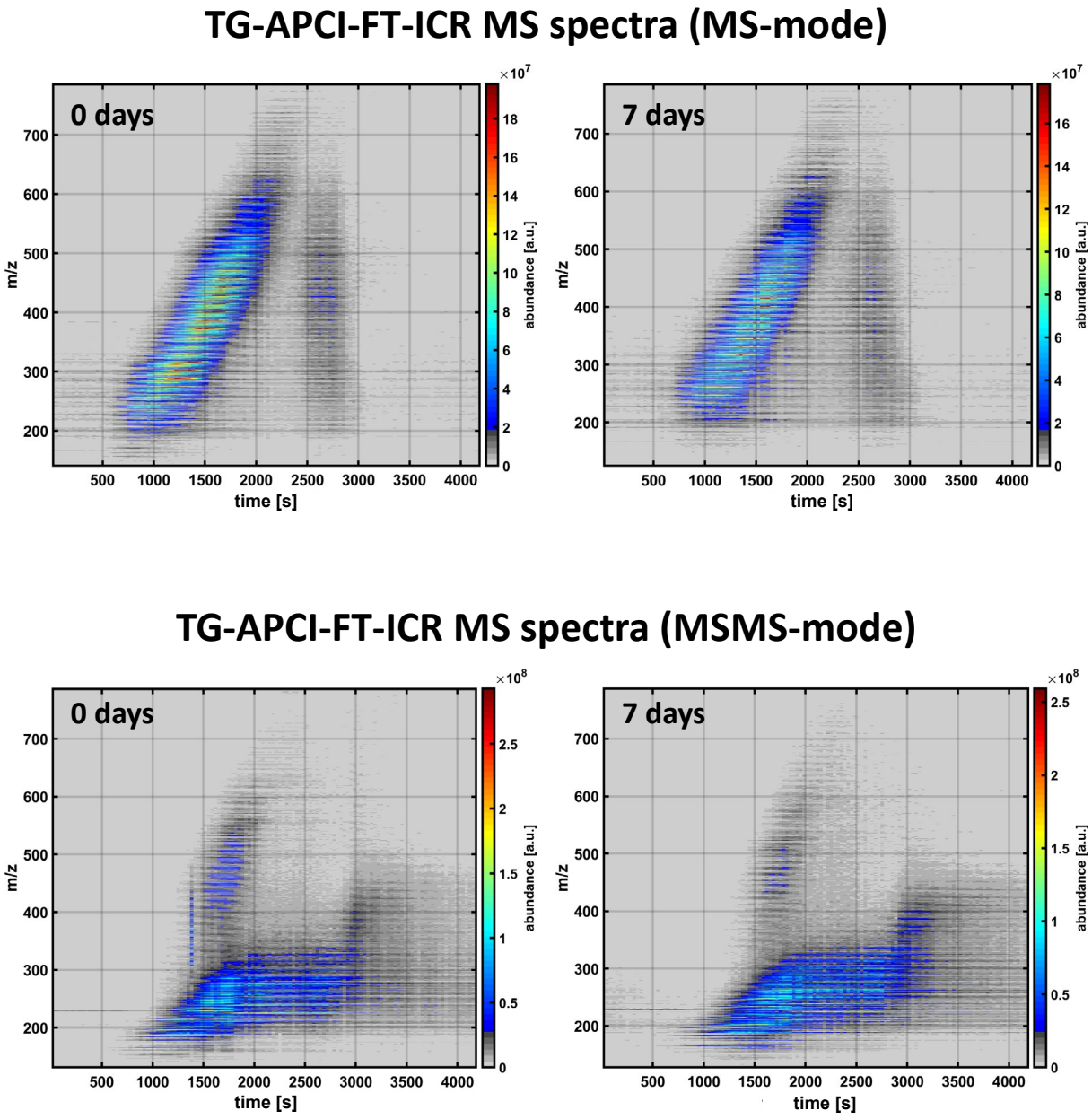

Figure S 2: Time resolved mass spectra of the TG-FT-ICR MS measurements for non-aged and 7 days-aged model bitumen. (top) Mass spectra obtained from intactly desorbed species and thermal fragments of pyrolyzed compounds. (bottom) CID-spectra of the alternating MSMS-mode.

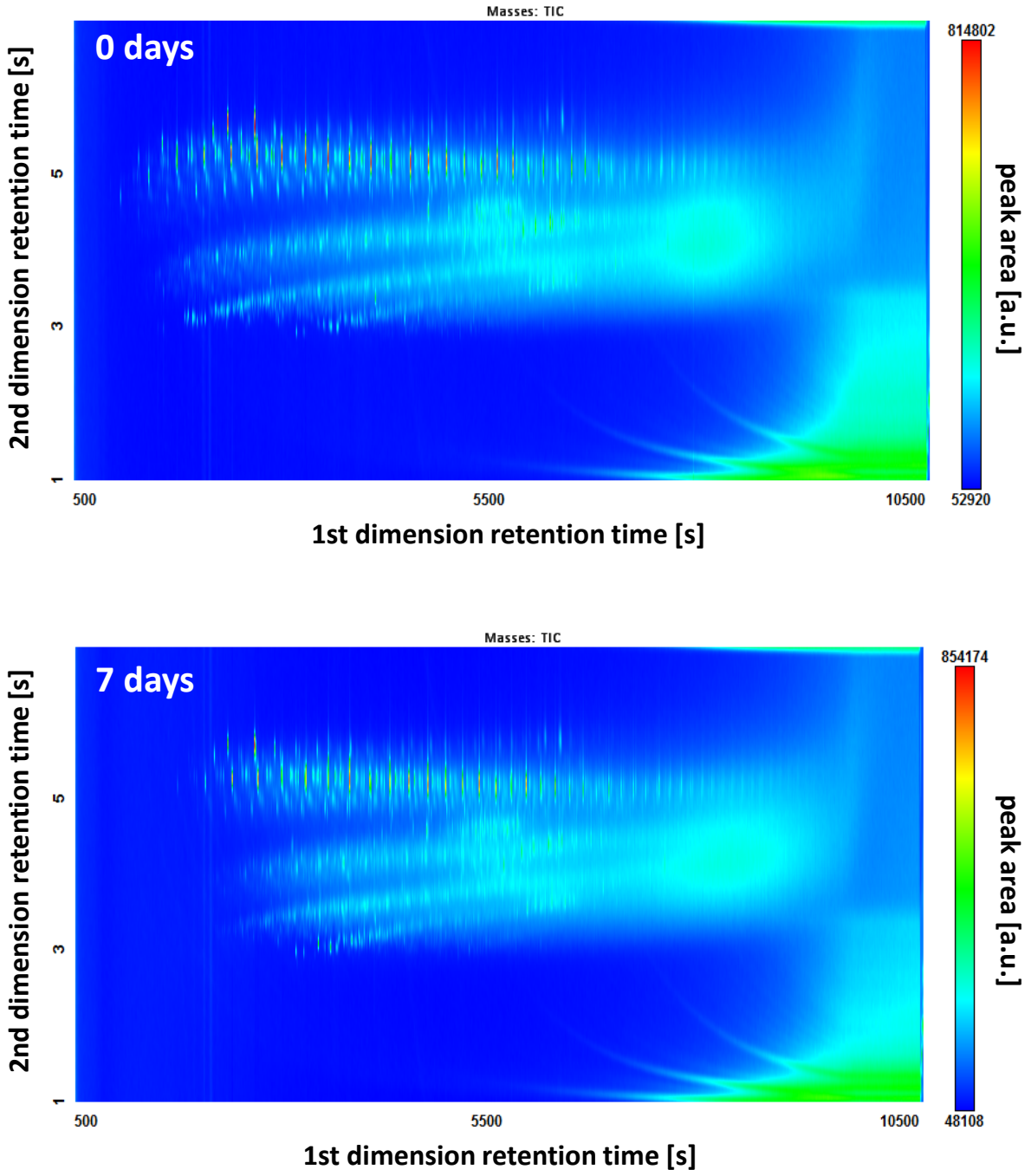

Figure S 3: Two-dimensional gas chromatograms obtained by GC×GC-HRTOF MS for non-aged and 7 days-aged model bitumen.

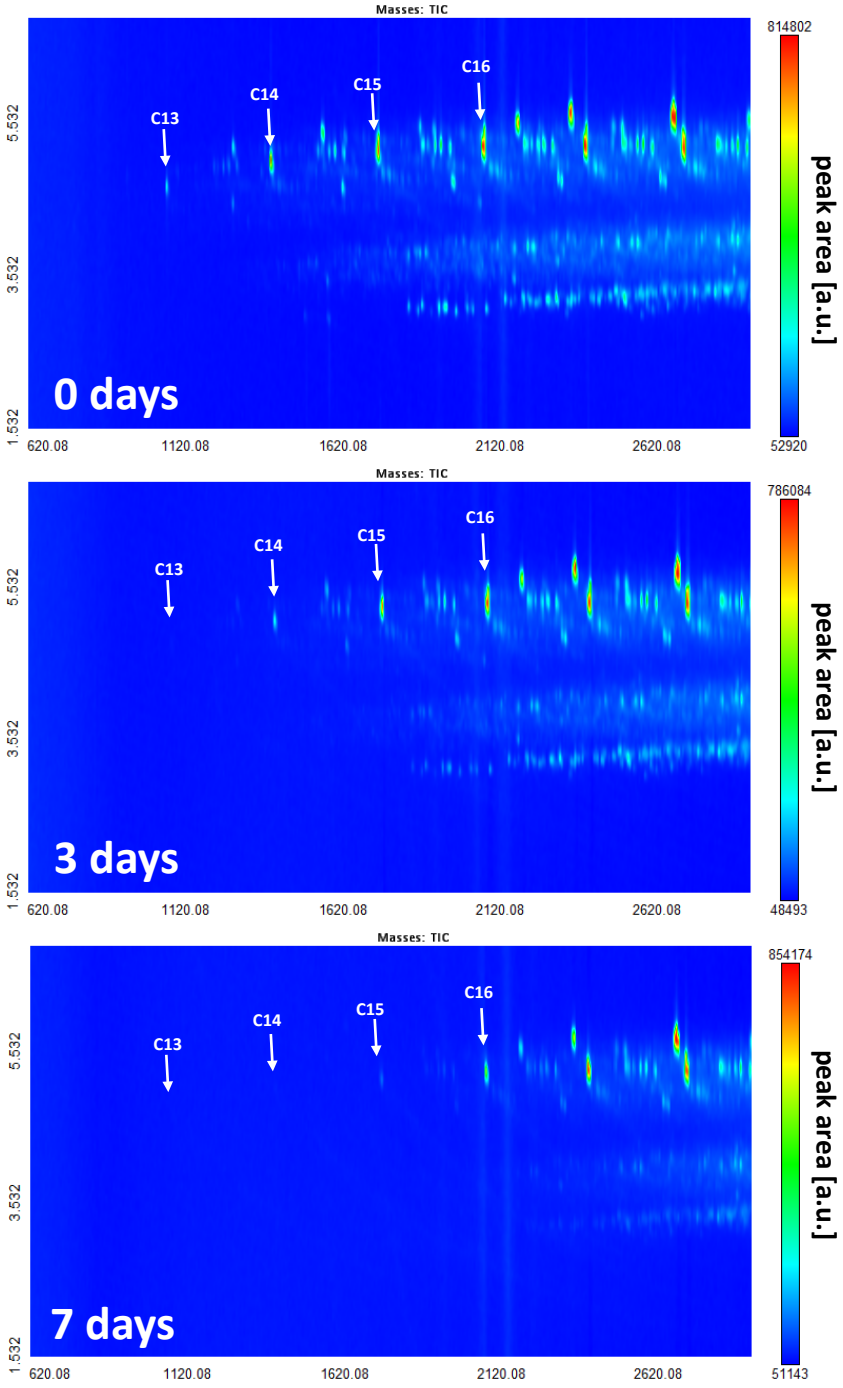

Figure S 4: Zoom in the region for low-boiling components of the GC×GC-HRTOF MS measurements. After severe aging, slight evaporation effects occur.

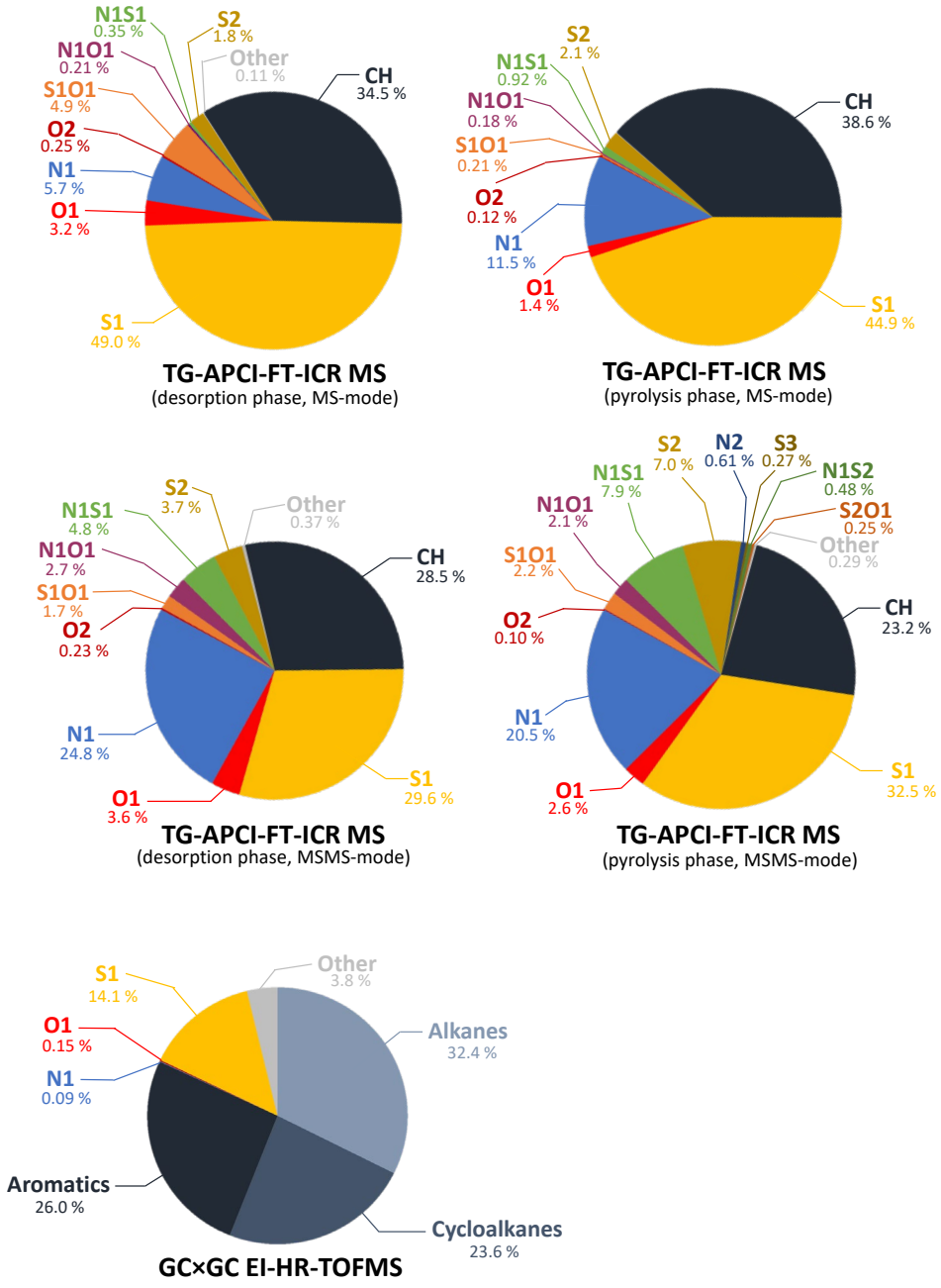

Figure S 5: Class distribution for non-aged model bitumen (average of three replicates) obtained by TG-APCI-FT-ICR MS and GC×GC-EI-HRTOF MS.

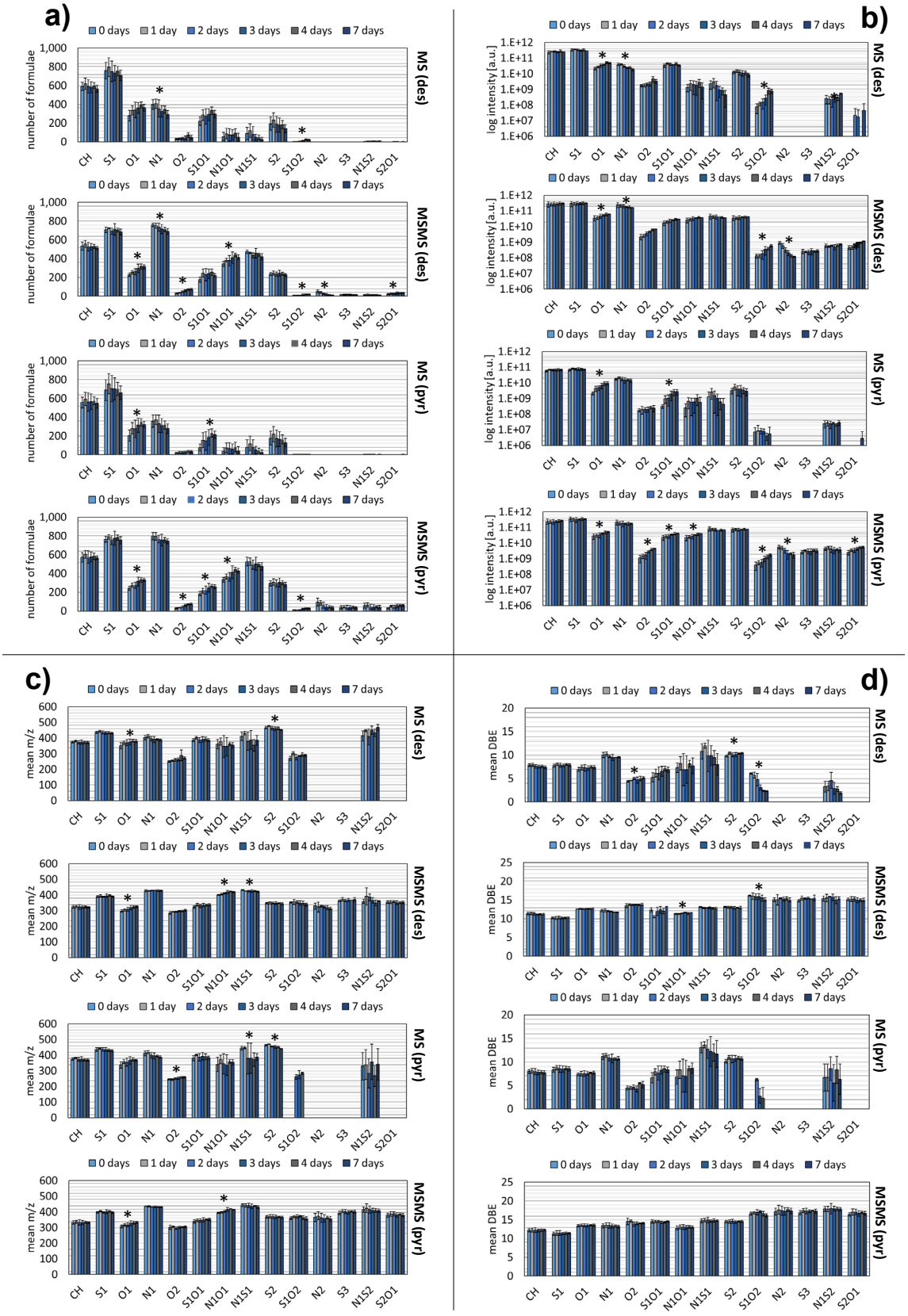

Figure S 6: Collection of average parameters for desorption and pyrolysis phase for MS and MSMS-mode. a) number of calculated sum formula, b) common logarithm for summed intensity, c) intensity-weighed mean m/z and d) intensity-weighed mean DBE.

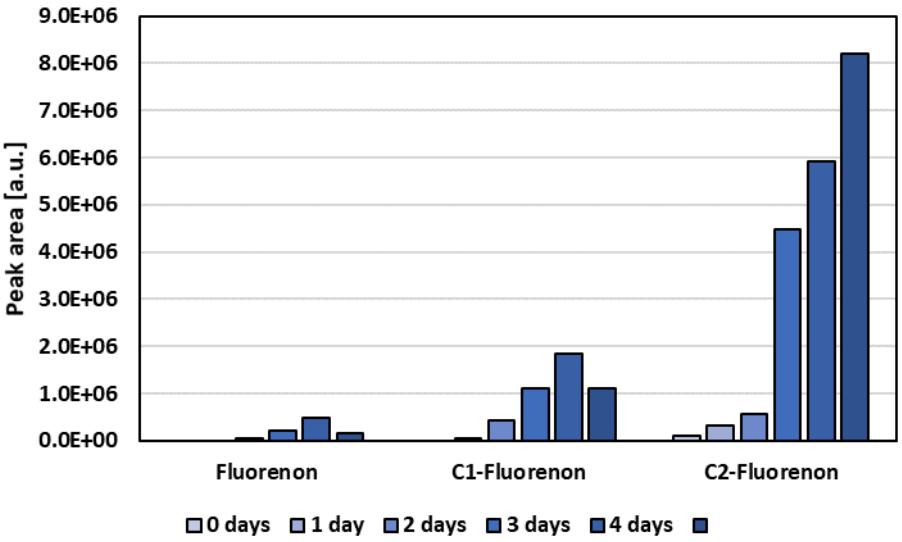

Figure S 7: Summed peak area of fluorenones with different alkylation degree revealed by GC×GC-HRTOF MS for all aging stages.

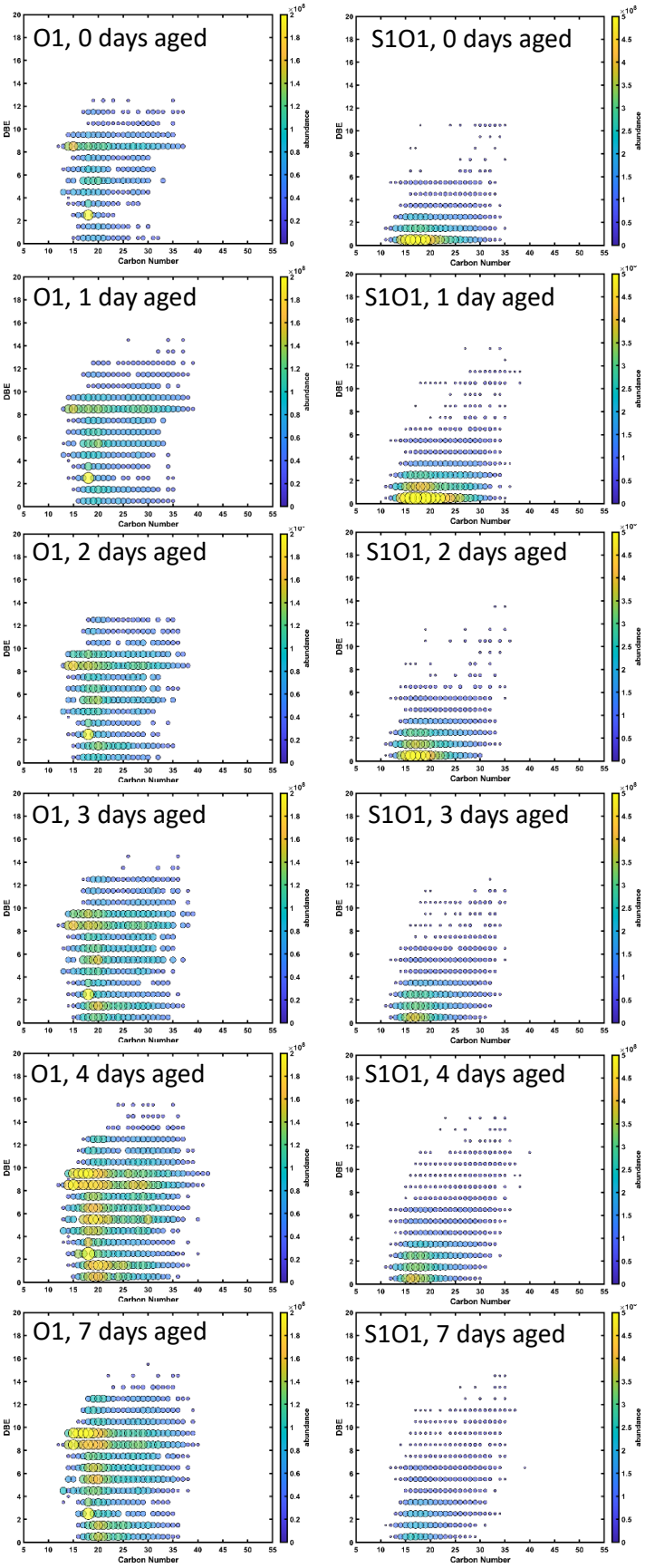

Figure S 8: Complete aging row for the O1- and S1O1-class of the desorption phase in MS-mode. While the O1-class shows a distinct increase for species with carbon numbers of 10 to 25 and a DBE of 1 to 10, the S1O1-class reveals a different behaviour. Species with DBE 1 to 2 in the S1O1-class show a slight increase after 1 day of aging and start to decrease after 2 days of aging. At the same time, species with higher DBEs are increasing.

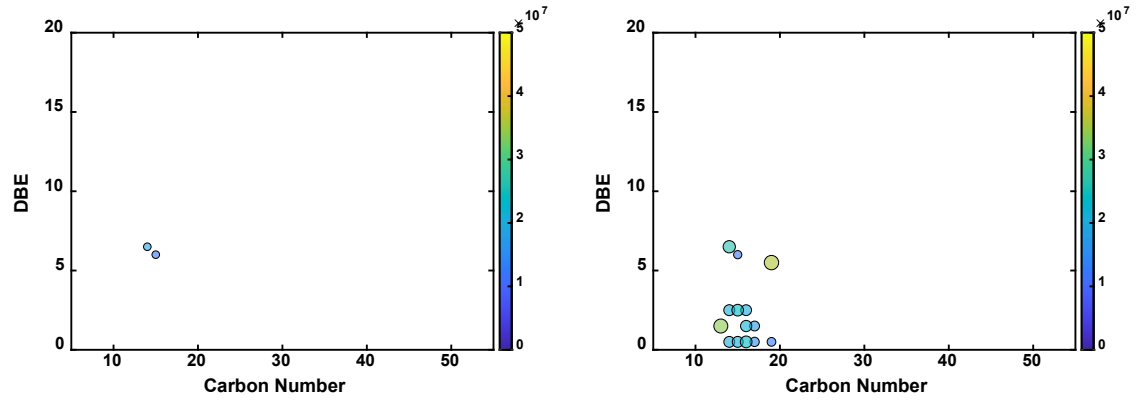

Figure S 9: Comparison of the S1O2-class for the desorption phase of the non-aged model bitumen (left) and 7 days-aged model bitumen (right). The increase in low DBE-species during aging may arise from the decrease of low DBE species observed in the S1O1-class due to further oxidation.

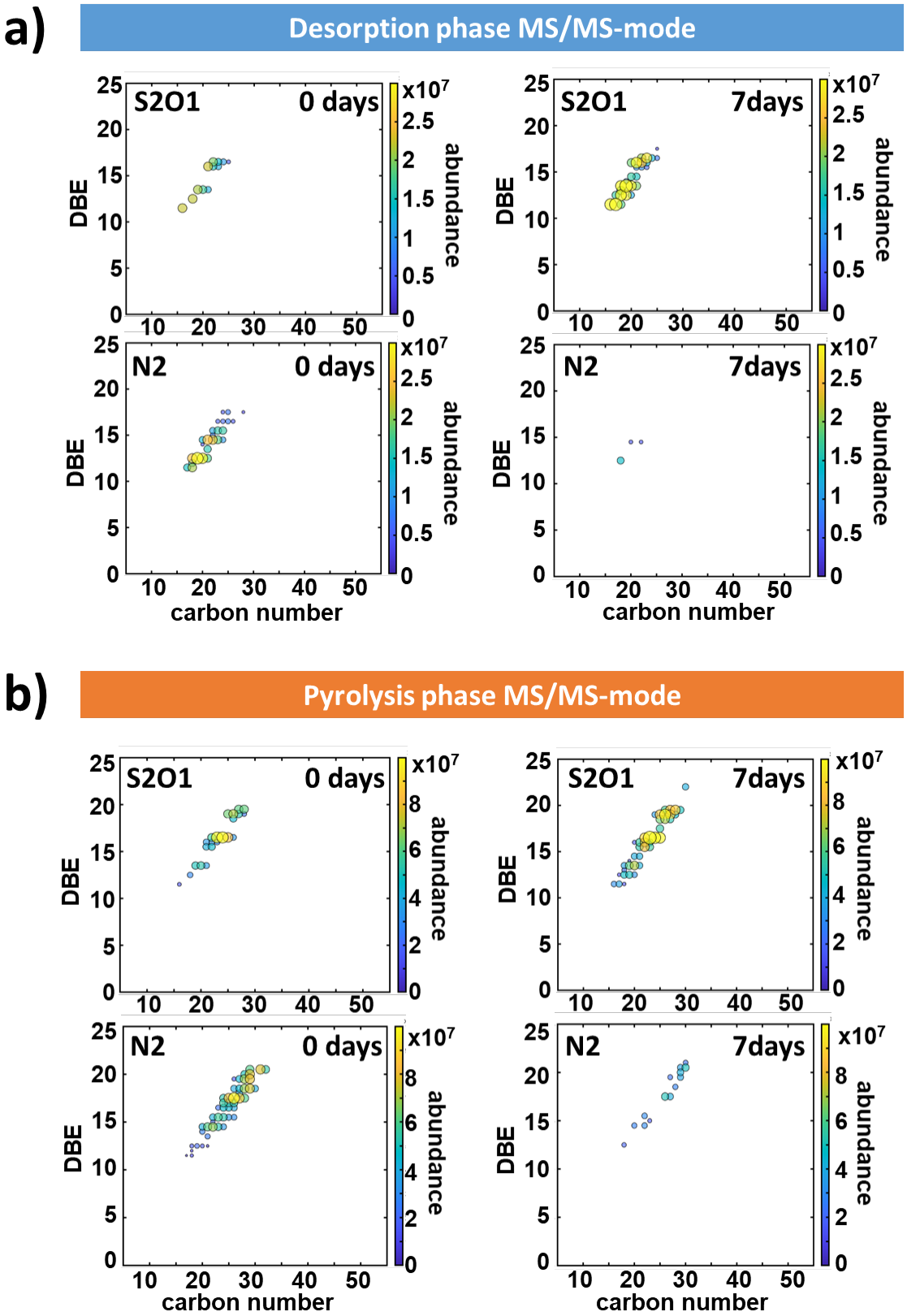

Figure S 10: DBE vs. #C diagrams of the S2O1- and N2-class for the desorption and pyrolysis phase. Due to very low intensity, both classes are only detected in MS/MS-mode.