

Source rock evaluation and predicted petroleum compositions related to samples from the Adavale, Bowen, Cooper and Eromanga Basins, Queensland

Interim Report 6

GEOS4 Report 20161209

Nicolaj Mahlstedt, Brian Horsfield

Address:	GEOS4 GmbH Peter-Huchel-Chaussee 88 14552 Michendorf Germany
Telephone:	+49 3312881780
Telefax:	+49 3312881782
e-mail:	info@geos4.com
Report Title:	Source rock evaluation and predicted petroleum compositions related to samples from the Adavale, Bowen, Cooper and Eromanga Basins, Queensland Interim Report 6 GEOS4 Report 20161209
Authors:	N. Mahlstedt, B. Horsfield
Classification:	Confidential
Client:	
Client reference:	
Distribution:	Electronic files: Report (.pdf)



N. Mahlstedt



B. Horsfield

Contents

Introduction	4
Objectives	4
Aim of this part of the study	4
Samples and Methods	5
MSSV Pyrolysis – Late Gas Potential	5
Results	6
MSSV-Pyrolysis: Late Gas Potentials	6
References	9
Appendix A1 – MSSV Chromatograms	10
Appendix A2 – Tables.....	16

Introduction

The Department of Natural Resources and Mines (DNRM) of the Geological Survey of Queensland (GSQ) contracted GEOS4 to evaluate the petroleum geochemical characteristics of 48 samples from the Cooper, Eromanga, Bowen and Adavale basins of Queensland. GSQ provided the following background information:

Adavale Basin

The Adavale Basin is an under-explored basin in southern-central Queensland. Exploration in the 1960s resulted in the discovery of the Gilmore gas field, though no other discoveries have been made. The presence of the Gilmore gas field demonstrates a proven petroleum system.

Cooper Basin

The Cooper Basin forms part of one of Queensland's major petroleum provinces, and hosts several conventional oil and gas fields. There has also been recent exploration for unconventional gas resources in the deeper troughs of the basin. Knowledge of the generative capacity of the potential source rocks in this basin will give a better understanding of this unconventional gas potential.

Eromanga Basin

The Eromanga Basin overlies the Cooper Basin and is the other component of the Cooper-Eromanga petroleum province in south-west Queensland. Discoveries in the Eromanga Basin have been predominantly oil, and include the Jackson field, which is Australia's largest onshore oil field. The source for these fields is thought to be predominantly from source rocks in the Cooper Basin, though up to 25% may have been from source rocks within the Eromanga Basin itself.

Bowen Basin

The Bowen Basin forms part of the other major petroleum province in Queensland and is believed to host the principal source rocks for the Bowen and Surat basins conventional accumulations. Conventional reserves were first discovered in the basin in the 1960s, though recent development in the area has focussed on coal seam gas resources underpinning the world class CSG to LNG industry. Recent exploration has targetted deeper sections of the Taroom Trough for tight gas resources with a significant potential for additional unconventional resources such as deep shales and coals yet to be discovered.

Objectives

Our objective is to provide the GSQ and the petroleum industry with a better understanding of the petroleum systems and the petroleum resource potential within these basins through provision of pre-competitive data. There are two principal foci: compositional kinetics for potential sources in the Bowen and Eromanga Basins, and deep gas generation in the Cooper and Ardvale Basins.

Aim of this part of the study

To conduct closed-system MSSV-pyrolysis on selected samples from the study set in order to compositional information to evaluate the late gas potential of mature source rocks.

Samples and Methods

In accordance with the work plan laid out in GEOS4 Report 20161016 the following samples were selected for the Late Gas Potential determination:

Table 1: Sample overview.

GEOS4-ID	Basin	QLD i.d.	Rock Type	Rock Unit Name	Late Gas
COOPER BASIN	G016494	GSV01	Carb'ceous mst	Patchawarra Formation	1
COOPER BASIN	G016496	GSV03	Coal	Patchawarra Formation	1
COOPER BASIN	G016499	GSV06	Coal	Toolachee Formation	1
COOPER BASIN	G016500	GSV07	Coal	Toolachee Formation	1
COOPER BASIN	G016501	GSV08	Coal	Toolachee Formation	1
ADAVALE BASIN	G016508	GSV15	carbonate	Bury limestone	1
RUNNING TOTALS					6

MSSV Pyrolysis – Late Gas Potential

MSSV pyrolysis, or microscale sealed vessel pyrolysis (Horsfield et al., 1989), was performed using the Quantum MSSV-2 Thermal Analysis System®.

Milligram quantities of each sample were sealed in glass capillaries and artificially matured at 2.0K/min to two end temperatures, 560°C and 700°C, using a special MSSV prep-oven.

The tubes were then cracked open using a piston device coupled with the injector, and the released products were swept into the GC using a flow of helium. A HP5890 II instrument was used for GC analysis (column: BP-1, 50 m length, i.d. 0.32 mm, film thickness 0.52 µm) with flame ionisation detection.

Boiling ranges (C₁, C₂-C₅, C₆₊) were quantified for late gas potential evaluation. Quantification was performed by external standardisation using *n*-butane. Response factors for all compounds were assumed the same, except for methane whose response factor was 1.1.

Results

MSSV-Pyrolysis: Late Gas Potentials

Six mature samples from the Cooper and Adavale Basins, Queensland were subjected to closed-system high temperature pyrolysis to evaluate their late gas potential following the approach of Mahlstedt and Horsfield (2012b).

MSSV-pyrolysis gas chromatograms are shown in Figure A1 and individual compound and boiling range yields are listed in Table A1 and Table 2. Two MSSV pyrolysis experiments were performed for each sample using a heating rate of 2.0°C/min. One tube was heated from 200°C to 560°C and another one from 200°C to 700°C. The temperature range between 560°C and 700°C represents the main stage of late methane generation and occurs subsequently to primary C₁₊ generation as well as subsequently to secondary cracking of the major portion of C₆₊ compounds.

Total C₁₋₅ and C₆₊ product yields at MSSV temperatures 560°C and 700°C, calculated total late gas yields, late secondary gas (A) yields from oil cracking, and late secondary gas (B) yields from cracking of a refractory kerogen moiety, as well as late gas ratios LGP and LGT for all samples are given in Table 2.

Table 2: High temperature MSSV-Pyrolysis GC-FID

G-Number	Rr	C ₁₋₅	C ₁₋₅	C ₆₊	C ₆₊	Late Gas	sec. Gas (A)	sec. Gas (B)	LGP	LGT
		560°C	700°C	560°C	700°C					
	%	mg/g TOC							kg/kg	
G016494	1.25	108.1	147.4	22.4	17.5	39.2	1.5	37.8	0.58	1.34
G016496	0.96	101.7	147.8	22.6	4.3	46.1	5.5	40.6	0.59	1.38
G016499	0.95	75.9	120.4	18.3	2.9	44.5	4.6	39.9	0.61	1.50
G016500	0.78	97.9	141.2	29.3	5.4	43.3	7.2	36.1	0.59	1.34
G016501	1.44	64.8	113.0	11.2	3.0	48.2	2.5	45.8	0.64	1.68
G016508	1.20	41.4	58.0	16.0	4.9	16.6	3.3	13.2	0.58	1.30

Rr: assessed vitrinite reflectance taking into account T_{max} values as well as organic petrology
 Late Gas: Yield C₁₋₅(700°C) – Yield C₁₋₅(560°C)
 sec. Gas (A): Late Gas from late oil cracking: (Yield C₆₊(560°C) – Yield C₆₊(700°C))*0.3
 sec. Gas (B): Late Gas from refractory OM: Late Gas – sec. Gas (A)
 LGP: Late Gas Potential ratio: Yield C₁₋₅(700°C)/(YieldC₁₋₅(560°C) + Yield C₁₋₅(700°C))
 LGT: Late Gas Type ratio: Yield C₁₋₅(700°C)/(YieldC₁₋₅(560°C) + sec. Gas (A))

For all investigated samples gas yields at 700°C are higher than gas yields at 560°C. Those samples generate late gas and exhibit high late gas potentials (LGP >0.55). This means that generated late gas has to be largely explained by the cracking of a refractory kerogen moiety (formed during catagenesis) as input of secondary gas from oil cracking (sec. Gas (A)) is neglectable (LGT >>1). Late gas yields (sec. Gas (B)) range around 40 mg/g TOC for Cooper Basin samples and around 13 mg/g TOC Bury Limestone (G016508) from the Adavale Basin.

The two late gas potential ratios are shown in Figure 1 for investigated Queensland samples in comparison to earlier published results (Mahlstedt and Horsfield, 2012a) of Type II and Type III source rocks. All source rocks, despite of initial late gas potential develop high late gas potentials with increasing maturity, the ratios even exceeding borders previously defined by an immature sample set (Mahlstedt and Horsfield, 2012b). This maturity trend is systematic and can be described by a logarithmic function implying that late gas potentials increase up to infinity, which is of course only true for ratios but not for absolute yields, which will be shown in the following paragraphs. It should be stated here though that results for the samples from Queensland fit very well those of previously described coals and shales, as high late gas potentials are all associated with mature samples.

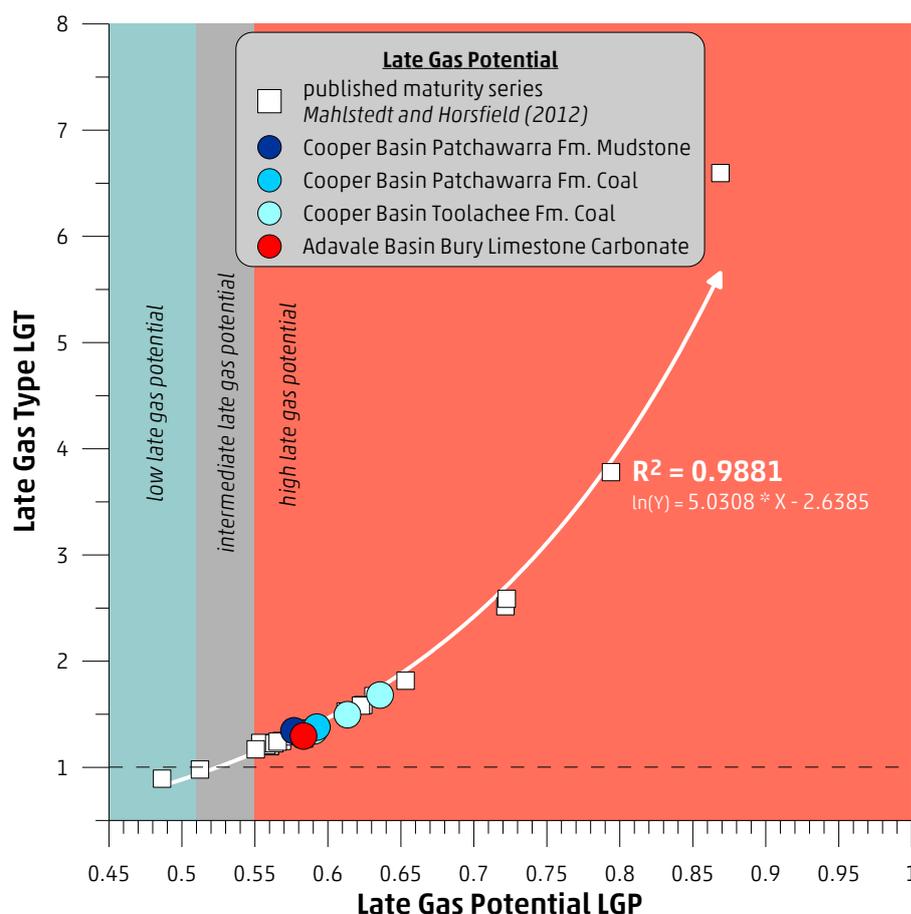


Figure 1: Late Gas Potential ratios evolution with maturity for Queensland samples (colored cricles) as well as for published (Mahlstedt and Horsfield, 2012a) maturity series samples (white squares). (Data in Table 2)

The evolution of late gas potentials as a function of maturity is shown in Figure 2 in comparison to earlier published results (Mahlstedt and Horsfield, 2012a) of Type II and Type III source rocks. For the latter it could be shown that late gas potentials are underestimates for immature samples and that late gas potentials increase during catagenesis up to values of ~40 mg/g TOC at 2.0% vitrinite reflectance for possibly any given kerogen type. Relevant late gas precursor structures, i.e. methyl-aromatics, are formed during catagenesis within the residual organic matter by chain shortening reactions via β -scission as well as by concentration of refractory kerogen. The late methane forming reaction itself can be described by a final demethylation of residual aromatic nuclei within spent organic matter via α -cleavage mechanisms involving condensation reactions of aromatic clusters.

Based on kinetic parameters published in Mahlstedt (2012) late gas generation takes place between 2.5 and 3.5% R_o for a simplified geological heating history ($3^{\circ}\text{C}/\text{ma}$ heating rate), a prediction directly confirmed by decreasing late gas potentials of naturally matured samples of Type II and Type III origin exhibiting vitrinite reflectance $>2.0\%$ R_o (Figure 2).

Late gas potentials of investigated samples from Queensland follow generally very well the previously described evolution trend for shales and coals with maturity, i.e. increasing late gas potentials going from low maturities ($<1\%$ R_r) to $R_r \sim 2.0\%$. The vitrinite-rich coals of the Toolachee and Patchawarra Fm. of the Cooper Basin exhibit high late gas potentials already at lower maturity stages than the Patchawarra Fm. mudstone sample. The late gas potential of $\sim 13 \text{ mg/g TOC}$ at $\sim 1.2\%$ VRcalc. for the Bury Limestone sample G016508 from the Adavale Basin fits very well to the trend of source rocks that have low LGP values at low maturity and only develop their late gas potential during catagenesis.

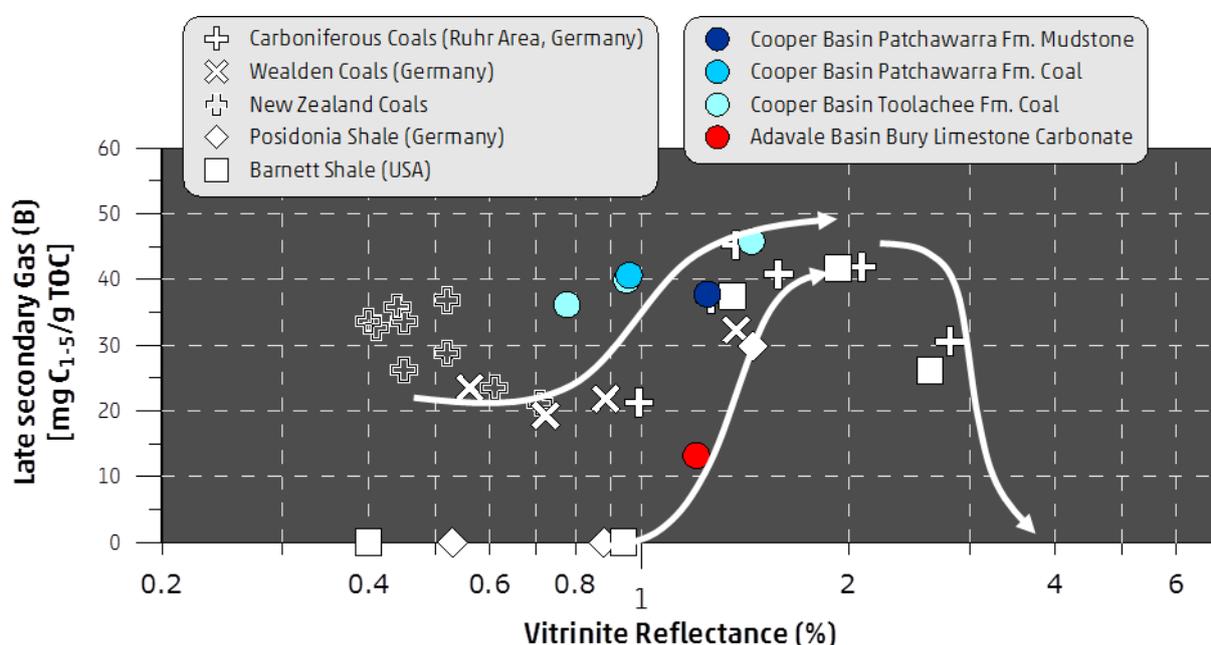


Figure 2: Late Gas potential evolution with maturity (vitrinite reflectance) for Queensland samples (colored circles) as well as for published (Mahlstedt and Horsfield, 2012a) maturity series samples (white symbols). White arrows indicate the evolution of late gas potentials with maturity. (Data in Table 2)

References

Horsfield, B., Disko, U., Leistner, F., 1989. The micro-scale simulation of maturation: outline of a new technique and its potential applications. *Geologische Rundschau* 78, 361-374.

Mahlstedt, N., 2012. Evaluating the late gas potential of source rocks stemming from different sedimentary environments. Dissertation. Technische Universität Berlin, Berlin, p. 342.

Mahlstedt, N., Horsfield, B., 2012a. Gas Generation at High Maturities (> Ro = 2.0%) in Gas Shales. *Search and Discovery Article #40873*.

Mahlstedt, N., Horsfield, B., 2012b. Metagenetic methane generation in gas shales I. Screening protocols using immature samples. *Marine and Petroleum Geology - Insights into Shale Gas Exploration and Exploitation* 31, 27-42.

Appendix A1 – MSSV Chromatograms

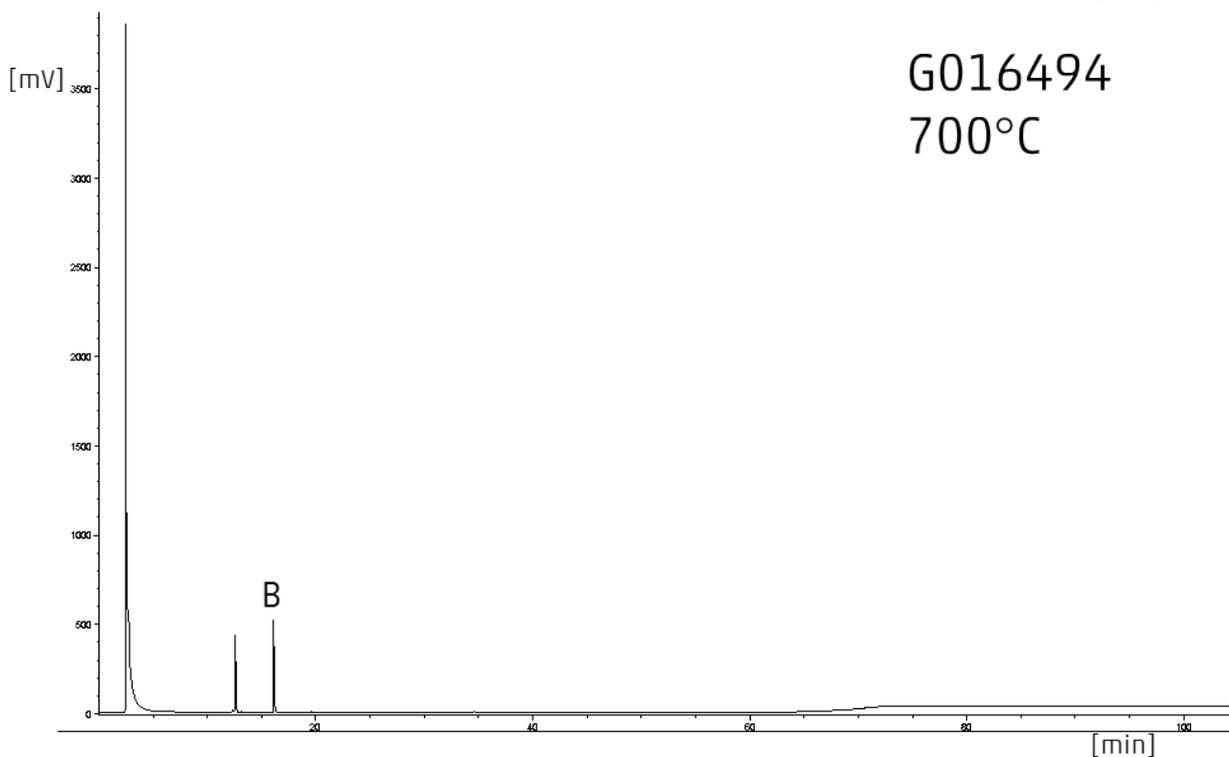
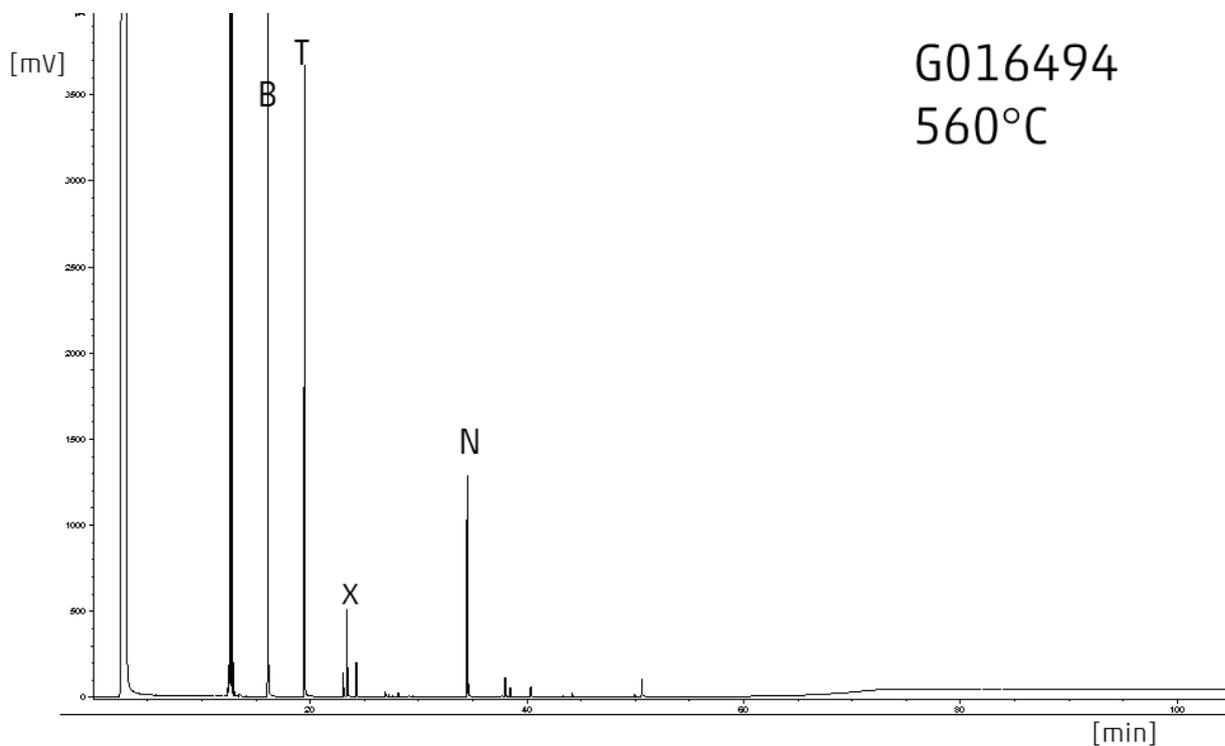


Table A1: MSSV-Pyrolysis GC-FID. Chromatograms Patchawarra Formation mudstone. For reference, selected peaks are marked: B= benzene; T= toluene; X= meta/para-xylene; N= naphthalene.

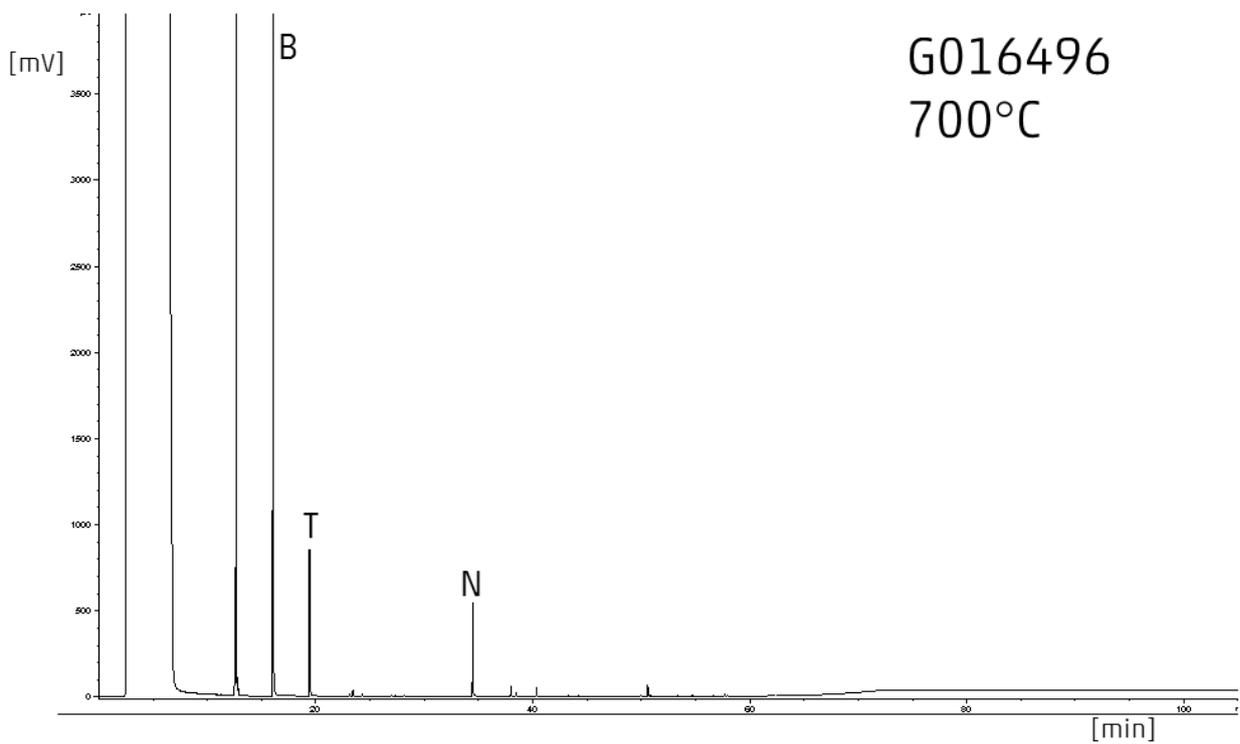
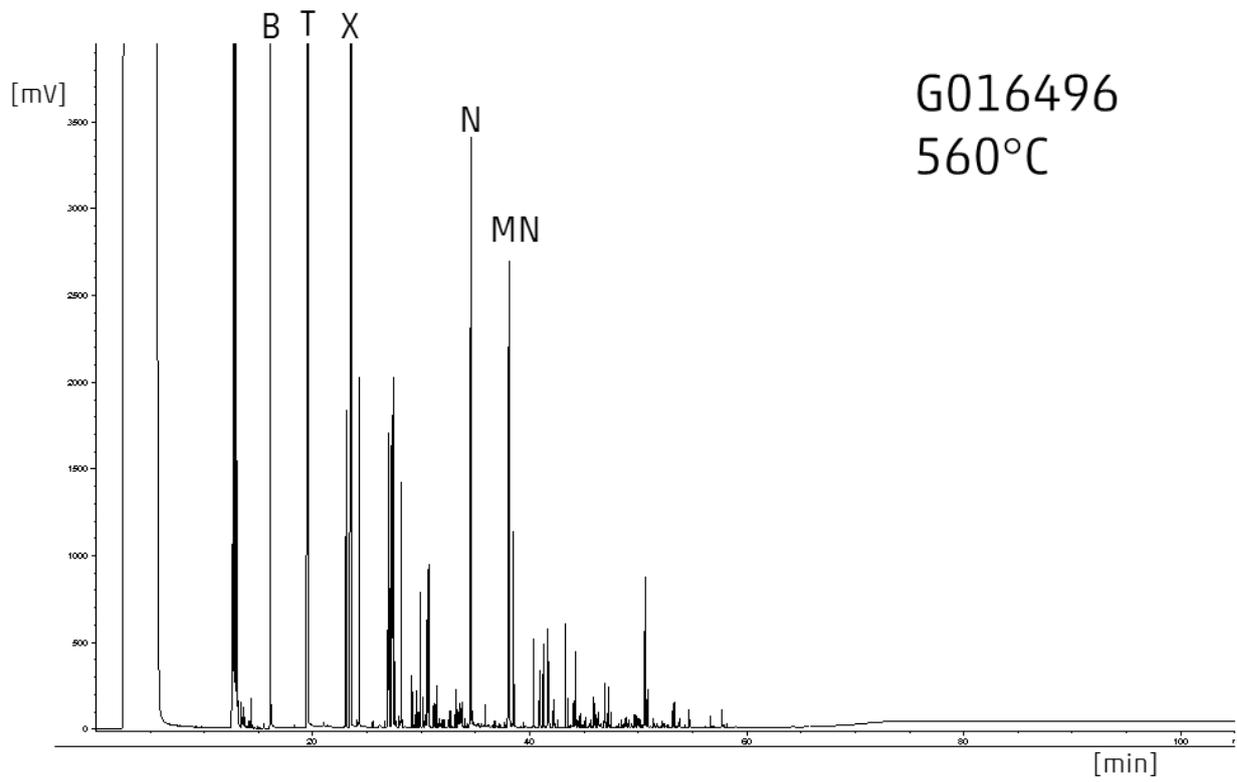


Table A1 (contd.): MSSV-Pyrolysis GC-FID. Chromatograms Patchawarra Formation coal. For reference, selected peaks are marked: B= benzene; T= toluene; X= meta/para-xylene; N= naphthalene; MN= methylnaphthalene.

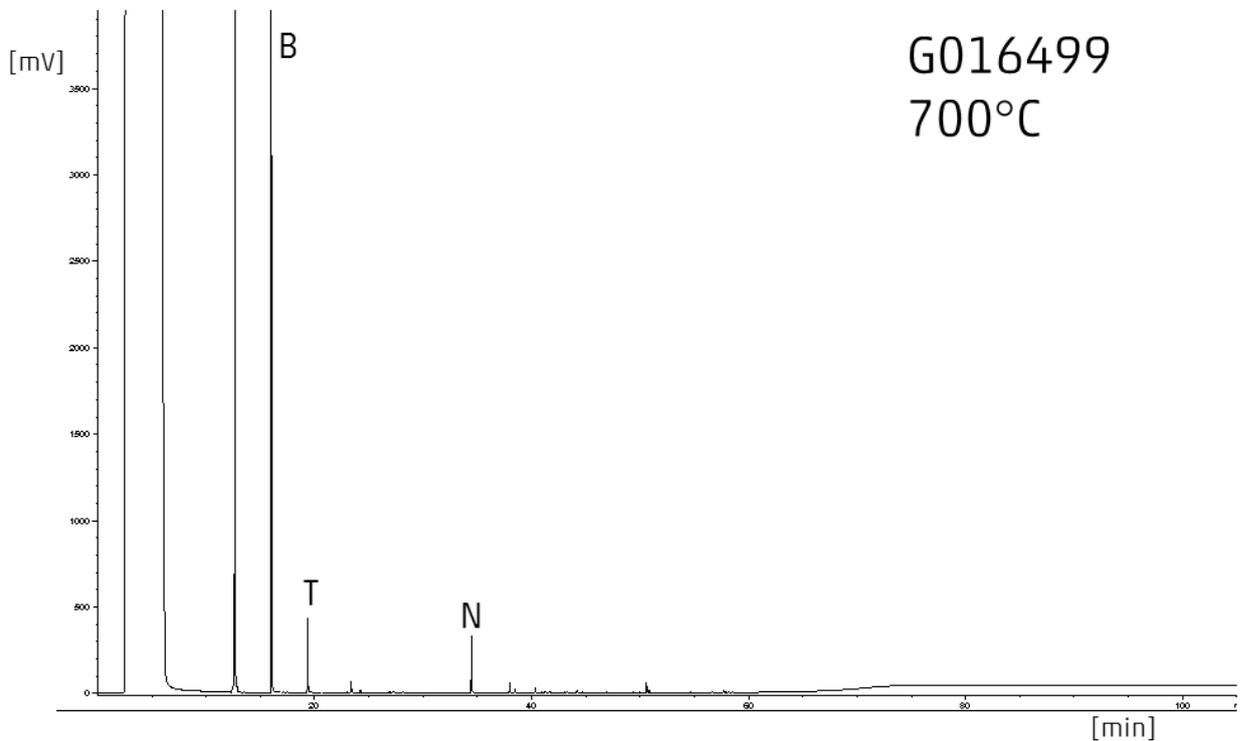
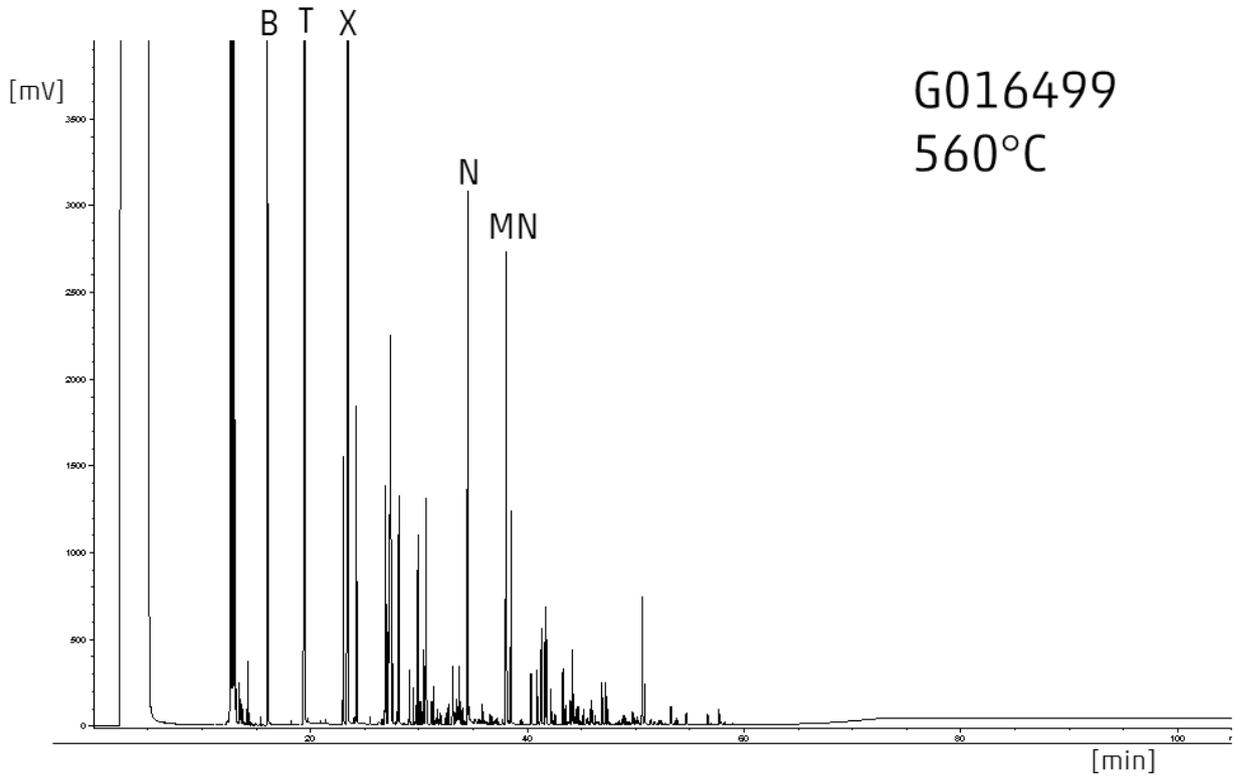


Table A1 (contd.): MSSV-Pyrolysis GC-FID. Chromatograms Toolachee Formation coal. For reference, selected peaks are marked: B= benzene; T= toluene; X= meta/para-xylene; N= naphthalene; MN= methylnaphthalene.

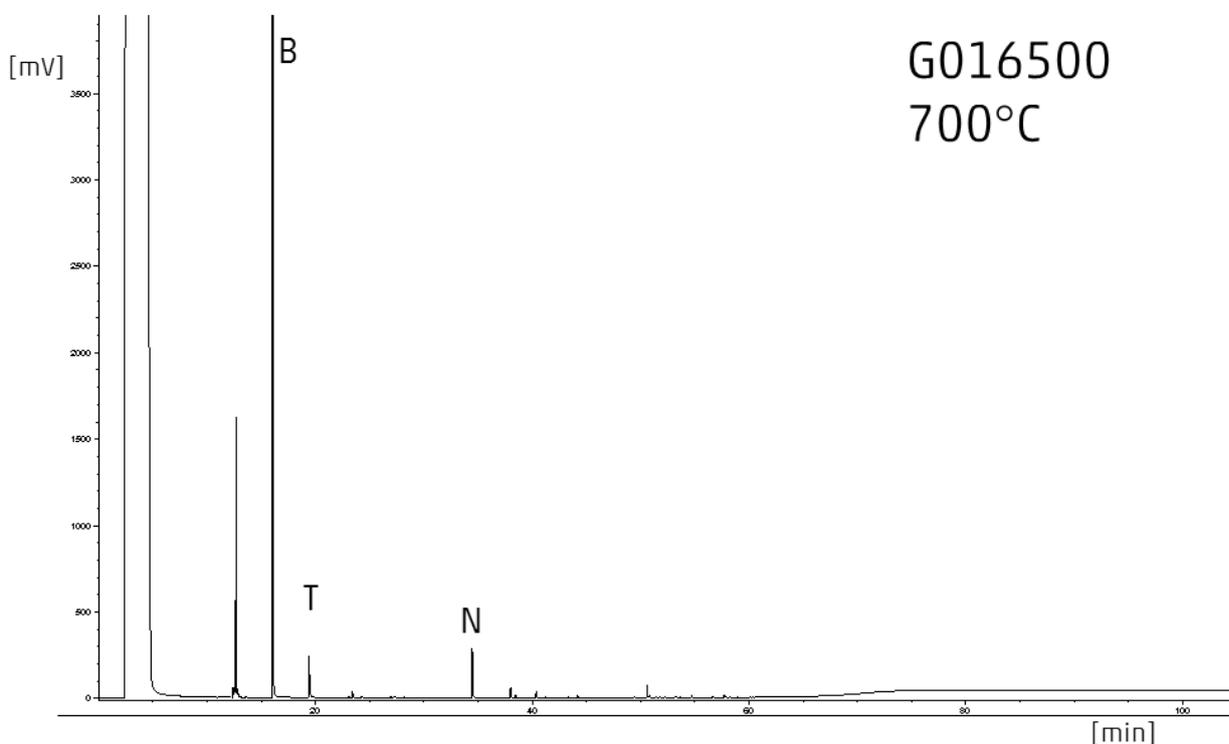
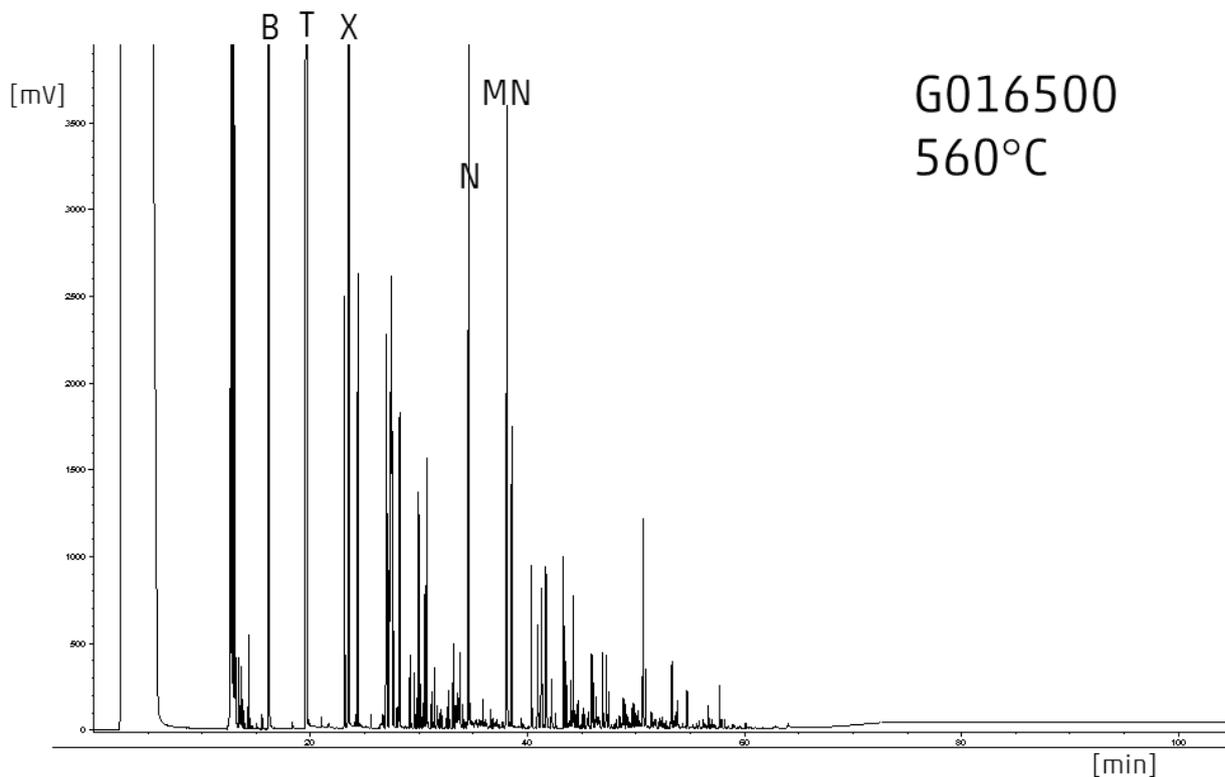


Table A1 (contd.): MSSV-Pyrolysis GC-FID. Chromatograms Toolachee Formation coal. For reference, selected peaks are marked: B= benzene; T= toluene; X= meta/para-xylene; N= naphthalene; MN= methylnaphthalene.

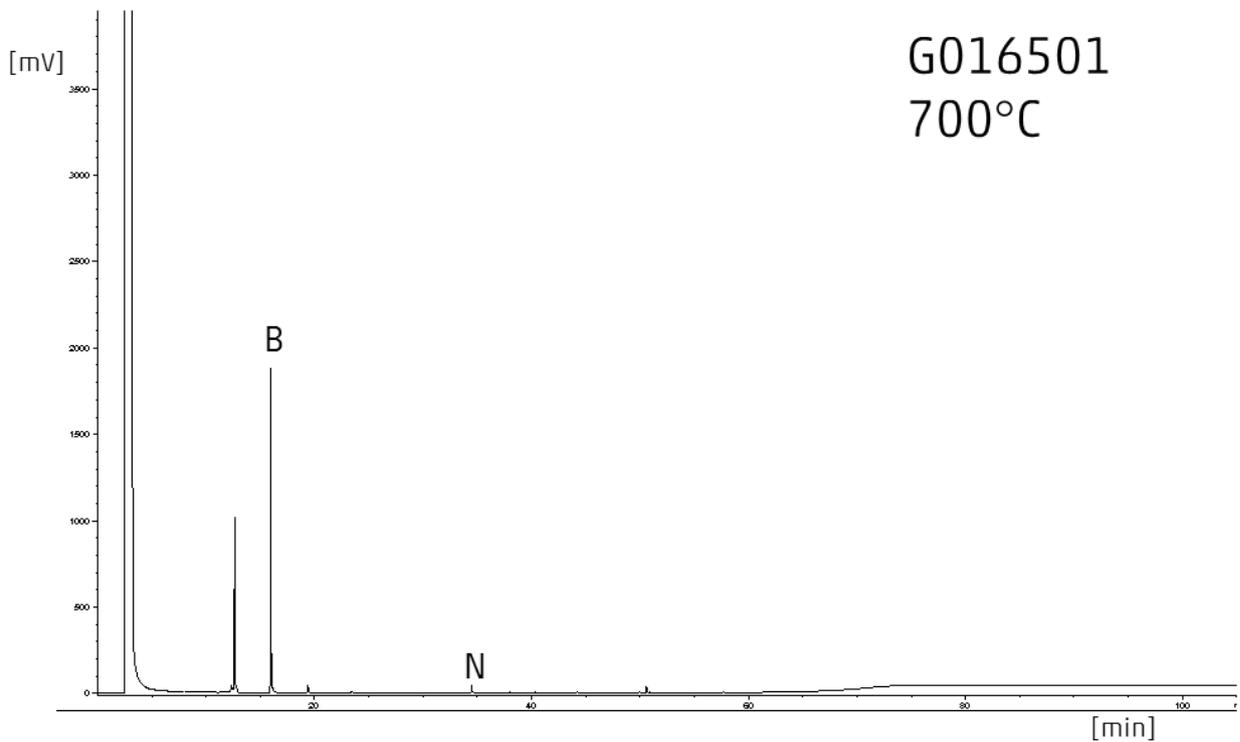
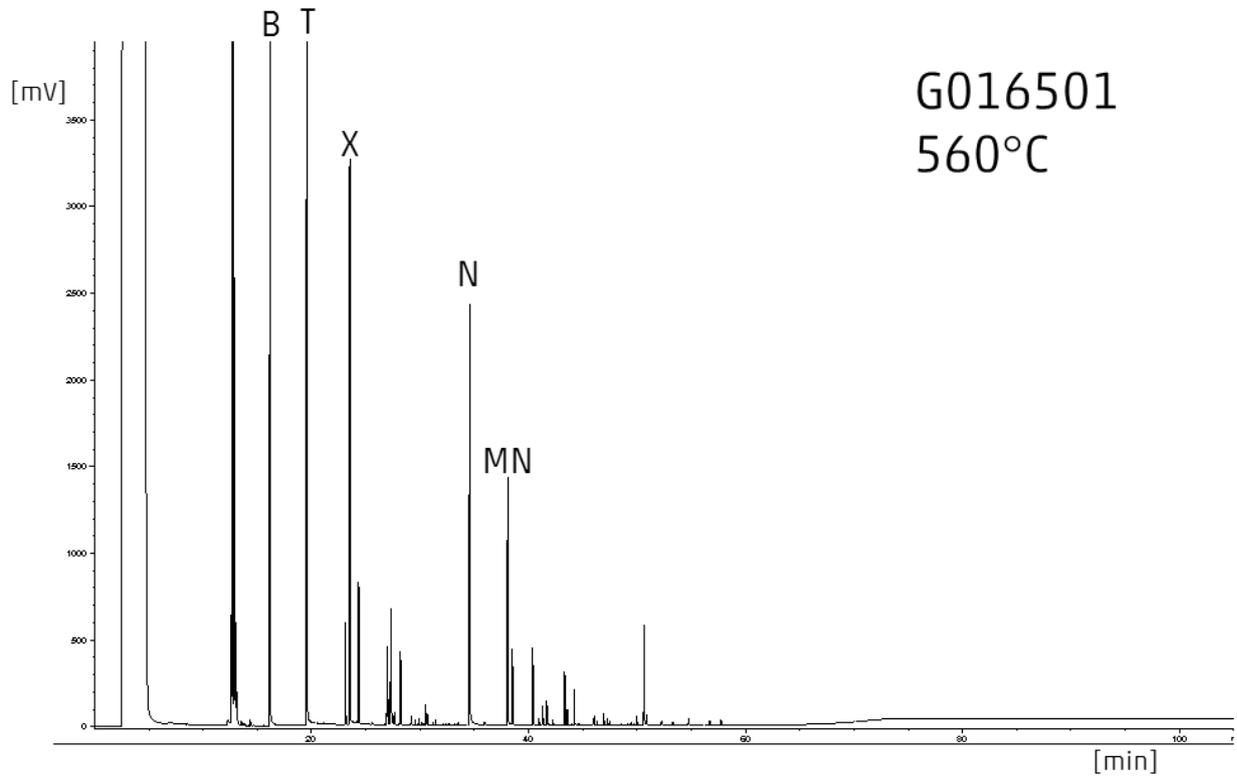


Table A1 (contd.): MSSV-Pyrolysis GC-FID. Chromatograms Toolachee Formation coaly shale. For reference, selected peaks are marked: B= benzene; T= toluene; X= meta/para-xylene; N= naphthalene; MN= methyl naphthalene.

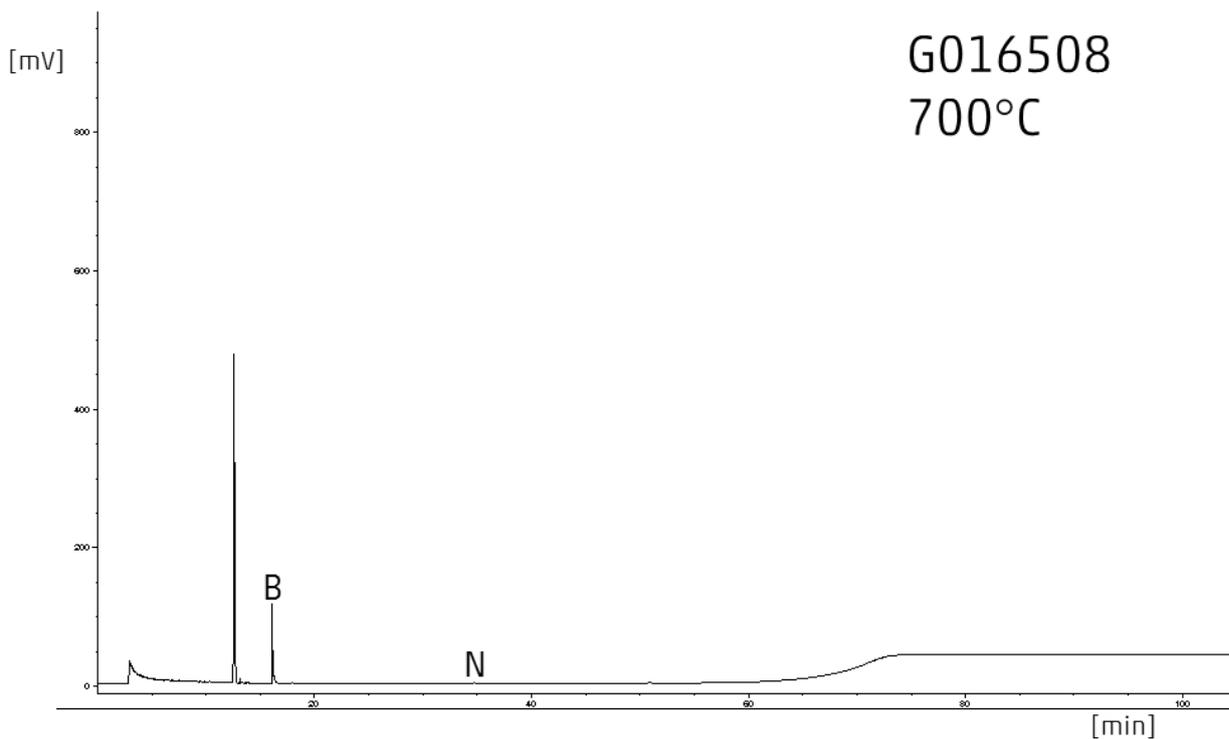
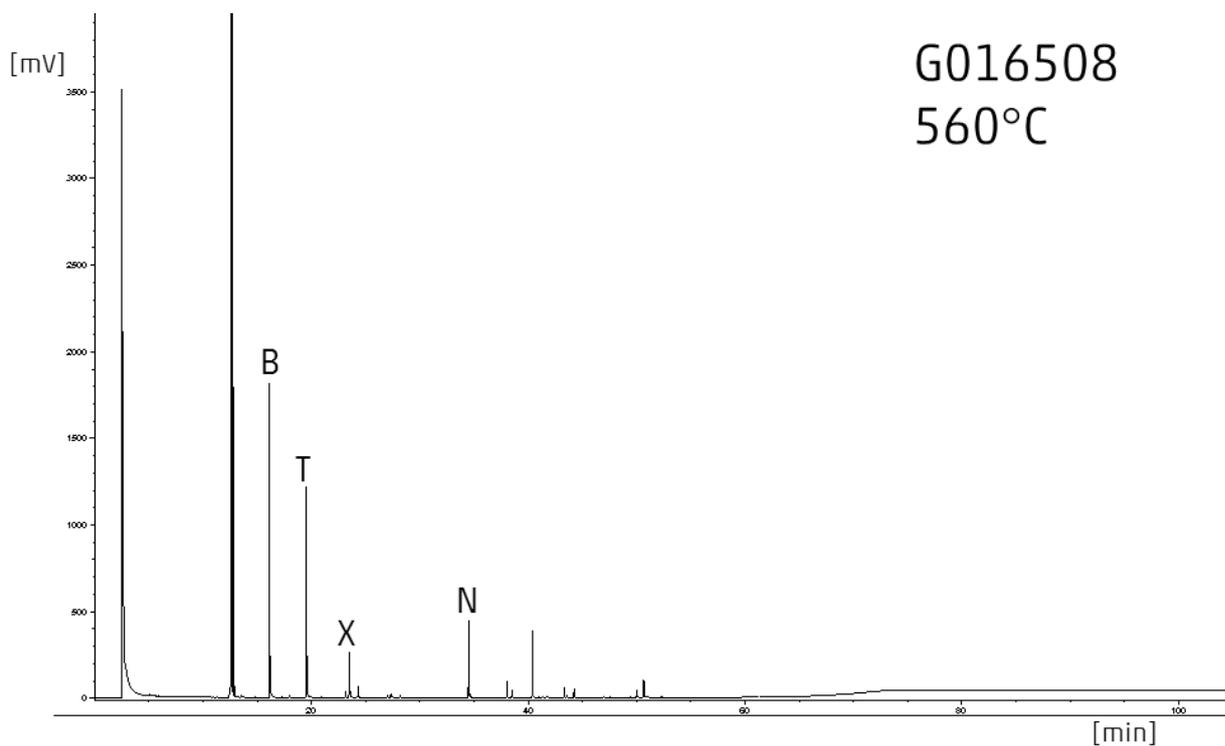


Table A1 (contd.): MSSV-Pyrolysis GC-FID. Chromatograms Bury limestone.
For reference, selected peaks are marked: B= benzene; T= toluene; X= meta/para-xylene; N= naphthalene.

Appendix A2 – Tables

Table A1: MSSV-Pyrolysis GC-FID. (Late Gas Potential)

Sample	G016494		G016496		G016499		G016500		G016501		G016508	
Heated to, °C	560	700	560	700	560	700	560	700	595	700	560	700
Weight, mg	38.90	6.18	6.18	4.10	6.48	4.11	6.60	2.20	17.84	3.10	36.04	3.93
	(µg/g sample)											
C1	1690	2979	58807	114725	44556	95732	52889	111687	13771	29073	355	550
C2-5	549	71	20889	1111	16288	794	25151	866	3195	533	117	111
C6+	463	362	17757	3387	14661	2347	23323	4290	2946	787	183	56