Gas Generation at High Maturities (> Ro = 2%) in Gas Shales*

Nicolaj Mahlstedt[1] and Brian Horsfield[1]

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[1]GFZ German Research Centre for Geosciences, Potsdam, Germany (nick@gfz-potsdam.de)

Abstract

Shale gas is most often of thermal origin. The secondary cracking of unexpelled oil at temperatures exceeding 150° C over geological time is usually viewed as the major pathway for generating the gas, corresponding to Ro = 1.5%, and kinetic models of secondary gas generation are used as part of GIP estimations to predict the extent of secondary cracking in time and space. Here we present new findings concerning a second later gas charge that is generated from some types of organic-rich shale at high maturity (Ro > 2.0%; T > 200°C). Using a large selection (~100 samples) of putative source rocks and gas shales, we have been able to demonstrate that high late gas potentials are associated with heterogeneous type III to type II/III organic matter that is aromatic/phenolic; low late gas potentials are associated with homogeneous Type I to Type II organic matter. This "High Temperature Methane" goes largely unnoticed when evaluation of immature source rocks is based on routinely used open-system pyrolysis screening-methods alone. Here we use a rapid closed-system pyrolysis method, which consists of heating crushed whole rock samples in MSSV-tubes from 200° C to two different end temperatures (560° C; 700° C) at 2° C/min, marking the main stage of late gas generation under laboratory conditions.

During natural maturation, chain shortening reactions via β-scission related to hydrocarbon generation might lead to a concomitant enrichment of methyl-aromatics and hence late gas precursor structures within the residual organic matter. Interestingly, late methane yields of various natural maturity series samples increase up to ~40 mg/g TOC by the end of the catagenesis stage, eg. Barnett Shale, indicating that predicted late gas amounts based on immature equivalents are underestimates. This interpretation is corroborated by increasing late gas potentials of pyrolysis residues prepared under both closed- and open-system conditions. Decreasing late gas potentials observed for highly mature source rocks (Ro > 2.0%) demonstrate that dry gas generation takes place under geologic conditions during metagenesis and indirectly confirm previous studies' and this studies' compositional MSSV-kinetic calculations.

Reference

Jarvie, D.M., R.J. Hill, T.E. Ruble, and R.M. Pollastro, 2007, Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment: AAPG Bulletin, v. 91/4, p. 475-499.

Gas generation at high maturities ($> R_0 = 2\%$) in gas shales

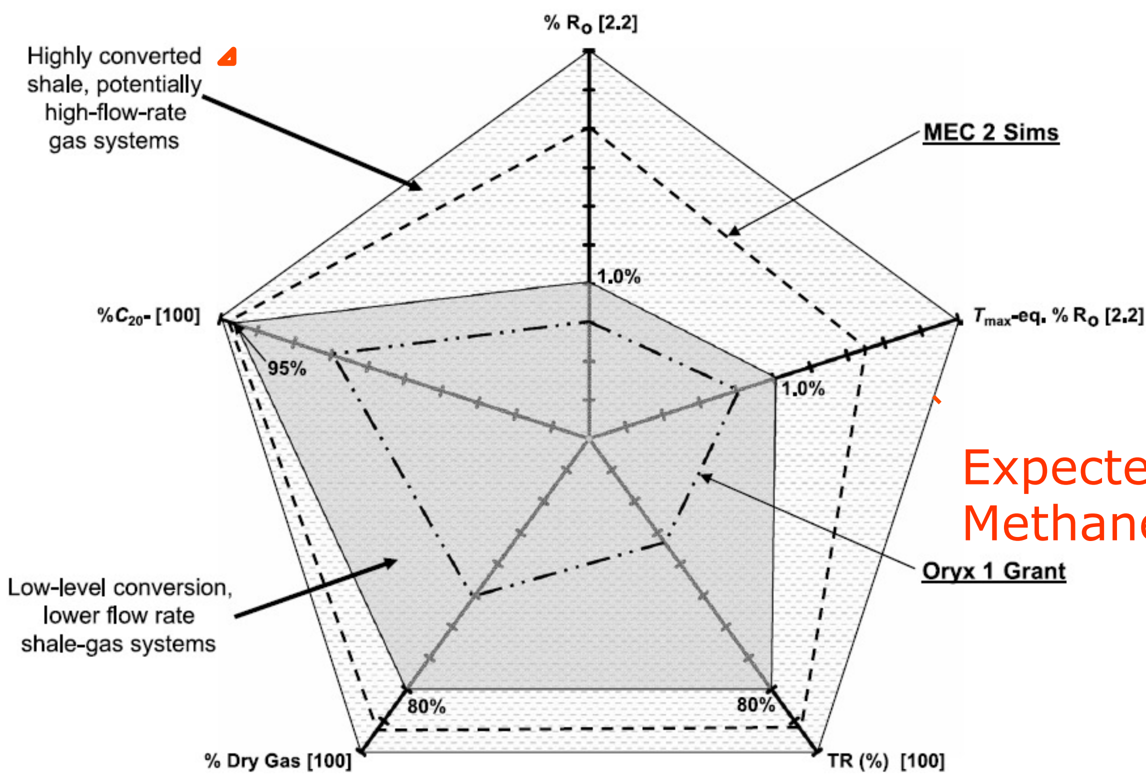
Nicolaj Mahlstedt and B. Horsfield

GFZ German Research Centre for Geosciences, D-14473 Potsdam, Germany

AAPG-ICE 2011, Milano

Unconventional Reservoirs

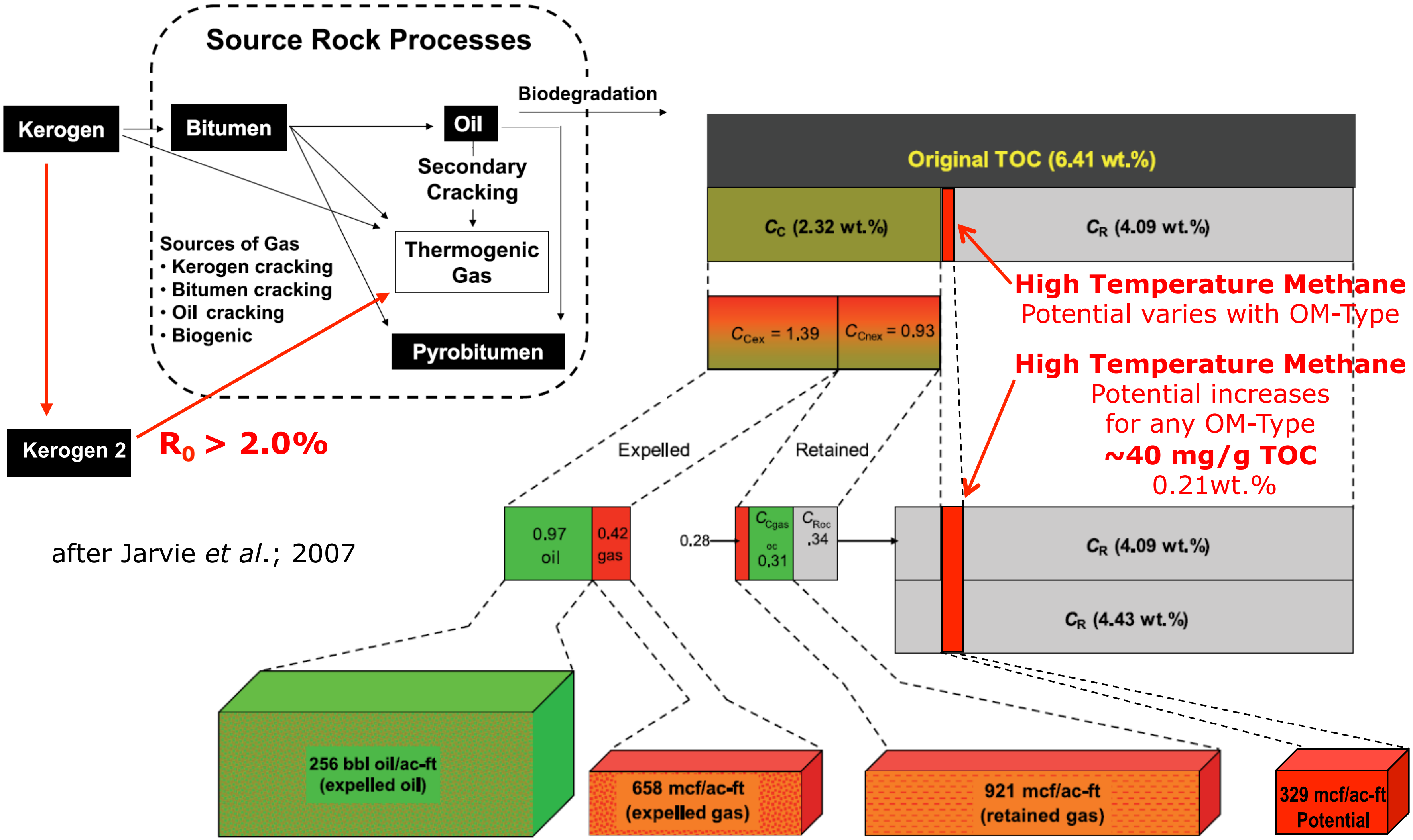
Shale Gas risk plot for low porosity – low permeability shales: High gas flow rates at high maturities with given fraccability



Expected High Temperature Methane Generation

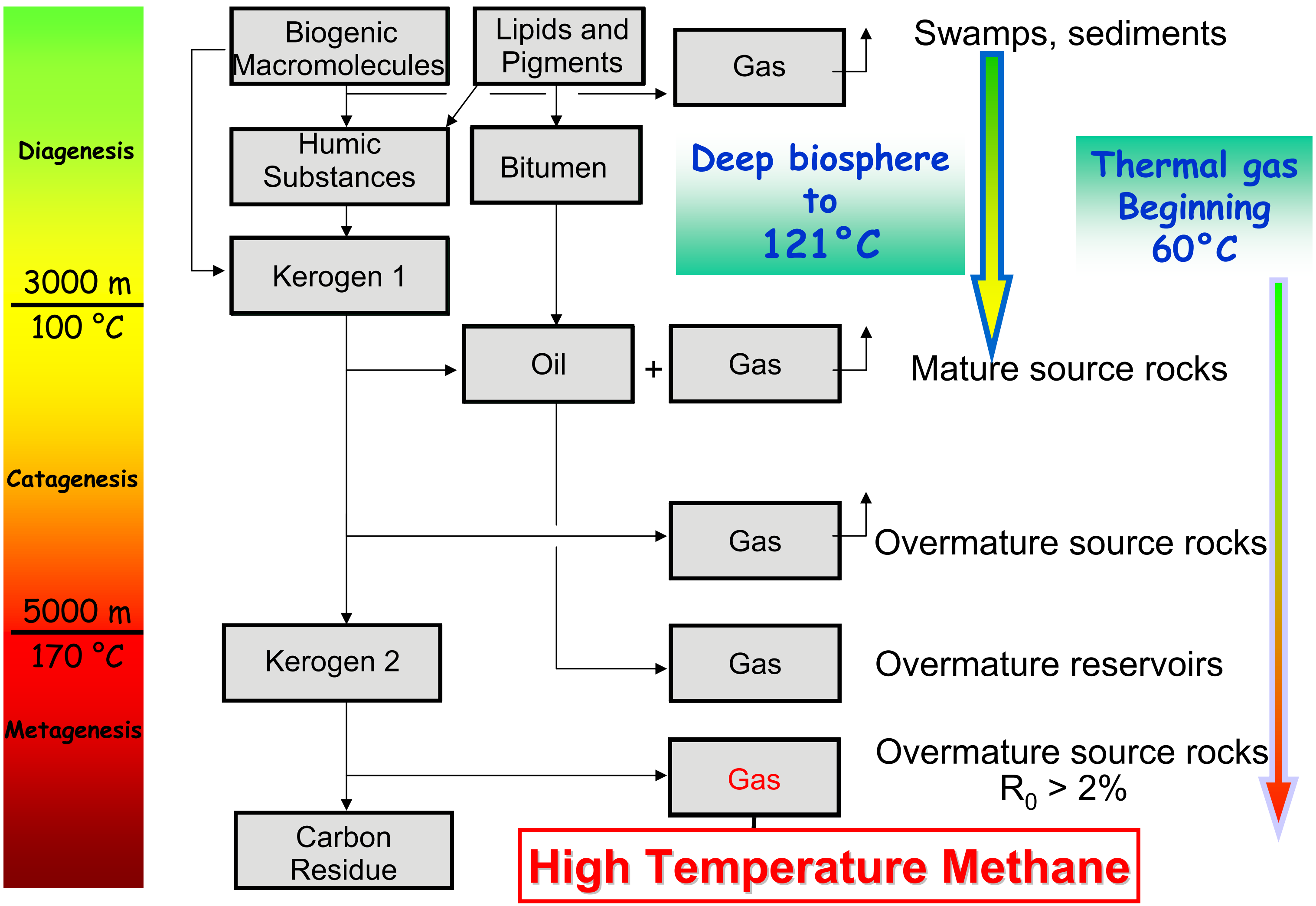
after Jarvie *et al*.; 2007

Take Home Message



after Jarvie *et al.*; 2007

Gas Generation Zonation



Late Gas Potential Evaluation

Sample Set		
~50 Immature Source Rocks	Natural Maturity Series 2 Type II; 2 Type III	Artificial Maturity Series (open/closed)

- high quality source rocks / wide range of geological ages
- All kerogen types / wide range of depositional settings

•**homogeneous alginitic/bacterial lacustrine** (Green River Shale, Wealden Shale) or **marine** (Alaskan Tasmanite) source rocks

•**more heterogeneous alginitic/bacterial marine source rocks**
→carbonates (Brown Limestone from Jordan – sulphur-rich)

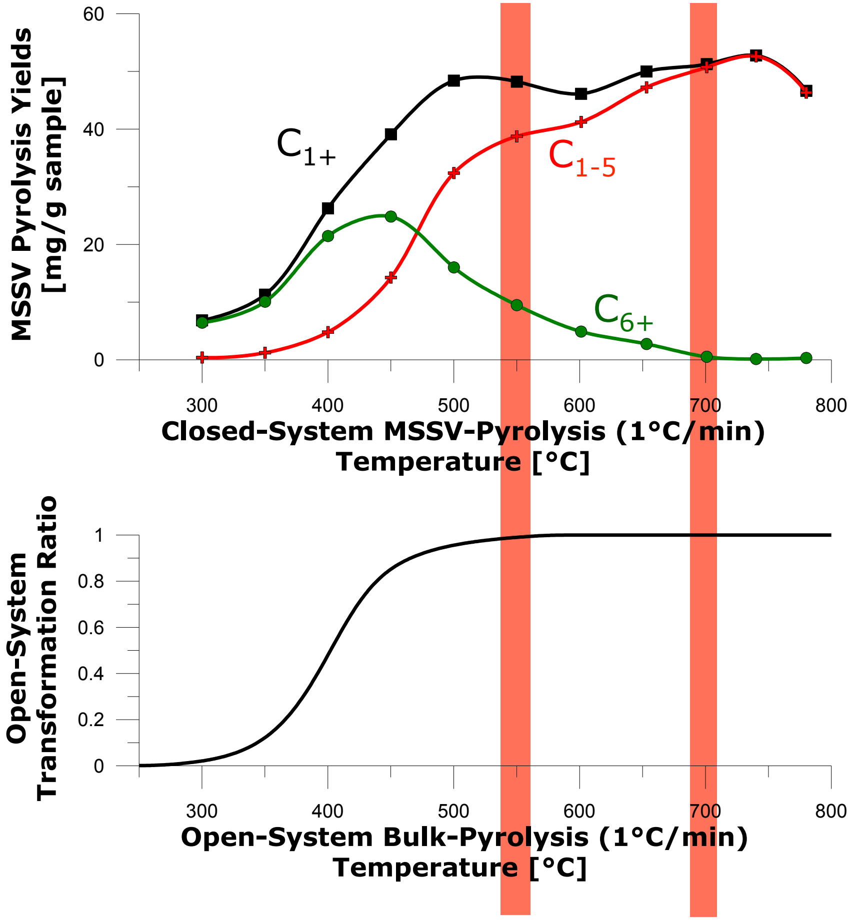
→black shales of Paleozoic age
(Cambrian Alum; Silurian Hot Shales from North Africa – Middle East - Russia; Devonian-Mississippian from North America e.g. Barnett, Bakken, Woodford)
→black shales of Mesozoic age (e.g. Posidonia; Norwegian Continental Shelf)

•**heterogeneous fluvio-deltaic – terrestrial or terrestrially influenced** coals and shales (Southeast Asia, New Zealand, German Wealden Coals or Carboniferous Ruhr Coals, Niger Delta)

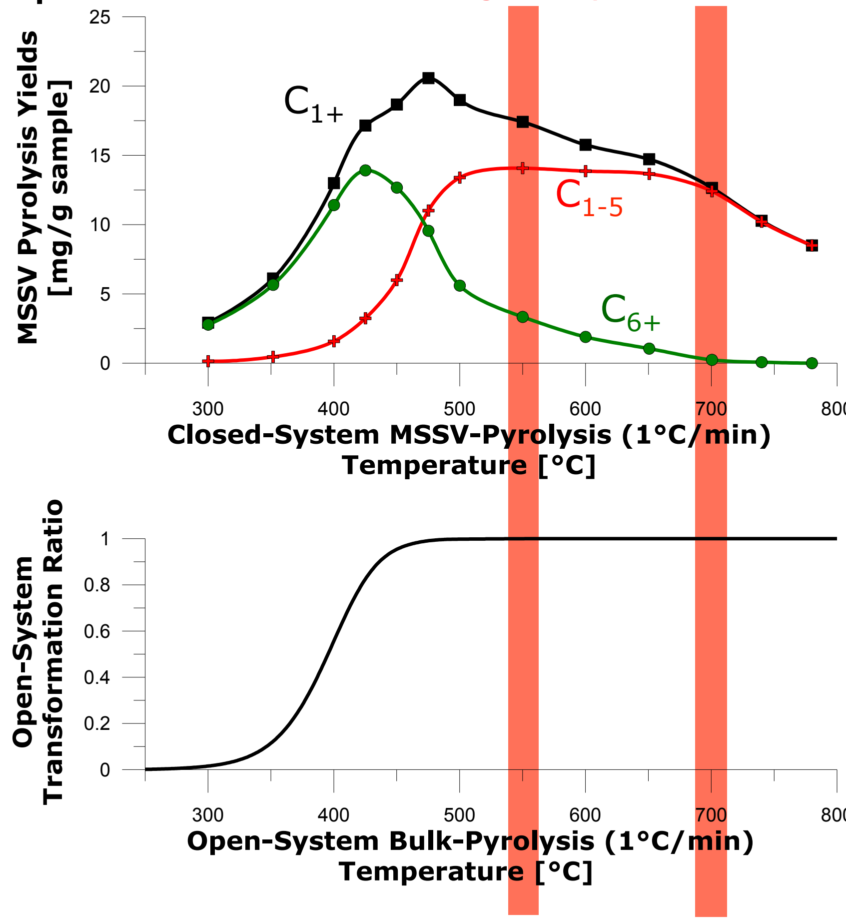
~50 Immature Source Rocks | Natural Maturity Series 2 Type II; 2 Type III | Artificial Maturity Series (open/closed)

Late Gas Potential Screening: **M**icro-**S**cale-**S**ealed-**V**essel Pyrolysis-GC-FID

Åre Fm. — Screening Temperatures



Spekk Fm. — Screening Temperatures

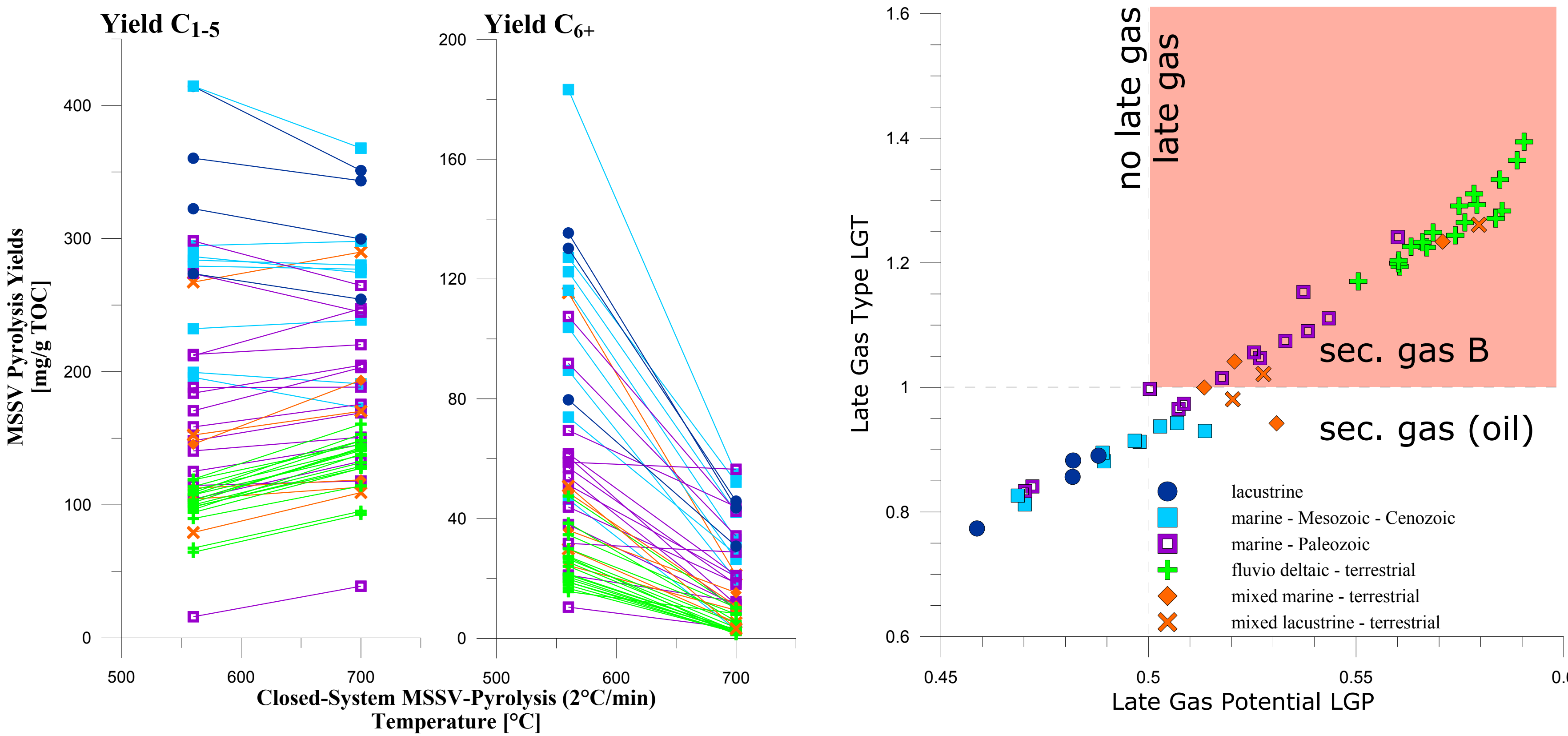


~50 Immature Source Rocks	Natural Maturity Series 2 Type II; 2 Type III	Artificial Maturity Series (open/closed)

Late Gas Potential Screening: (MSSV) Pyrolysis-GC-FID (2 temps.)

$$LGP = (C_{1-5}Yield700°C)/(C_{1-5}Yield560°C + C_{1-5}Yield700°C)$$

$$LGT = (C_{1-5}Yield700°C)/[C_{1-5}Yield560°C + sec.\ gas\ (oil)]$$



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High LGP´s:

terrestrial or terrestrially influenced coals and shales

intermediate

Silurian Hot Shales

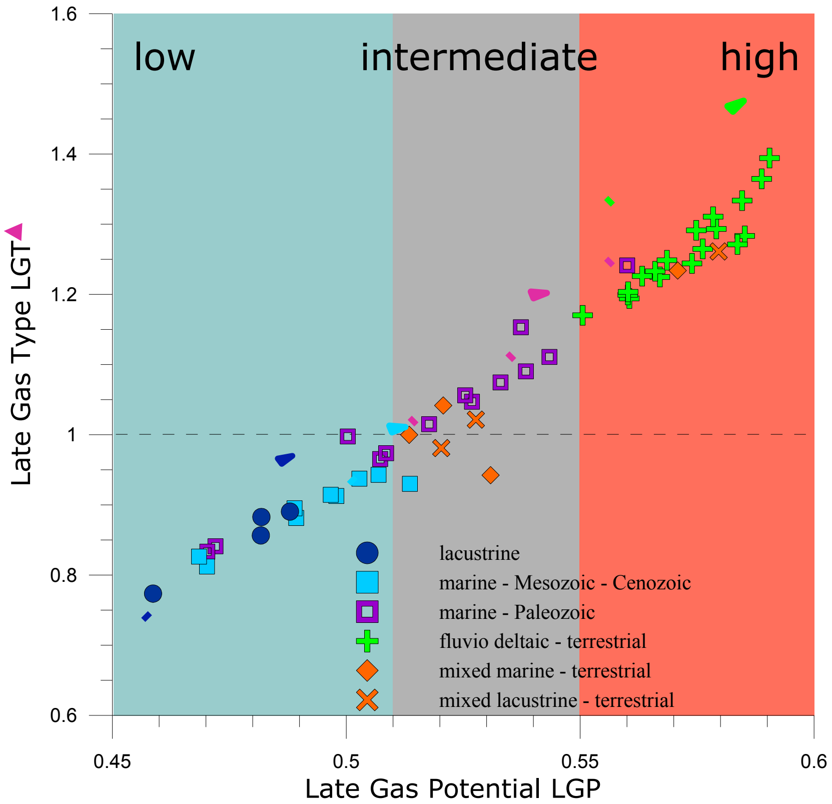
Cambrian Alum Shales

Barnett, Bakken, Woodford, New Albany, Caney Shales, etc.

Mesozoic shales – e.g. Posidonia Shale

Low LGP´s:

lacustrine and marine Alginites – Green River Shale; Wealden Shale



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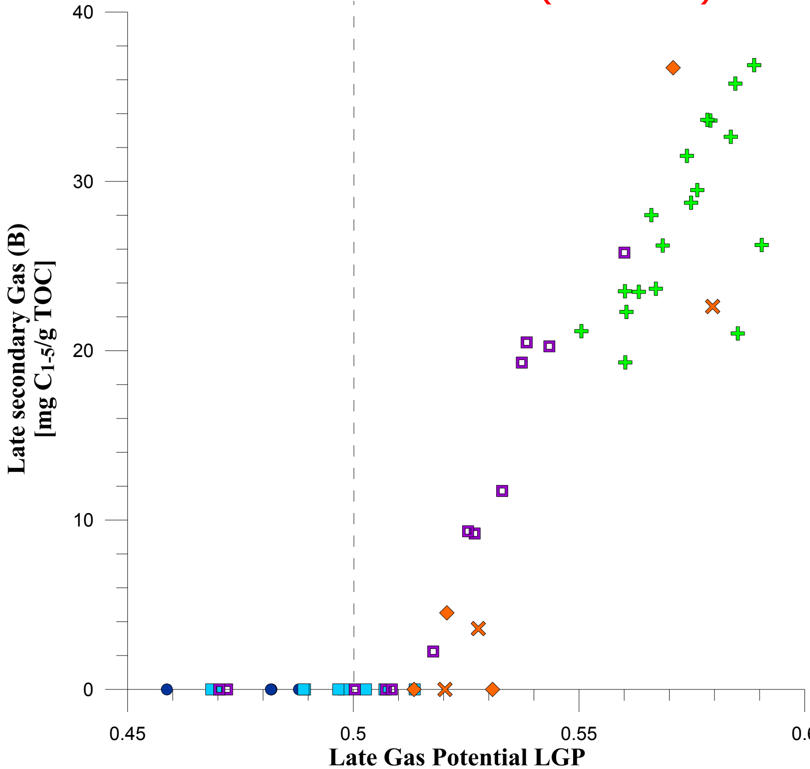
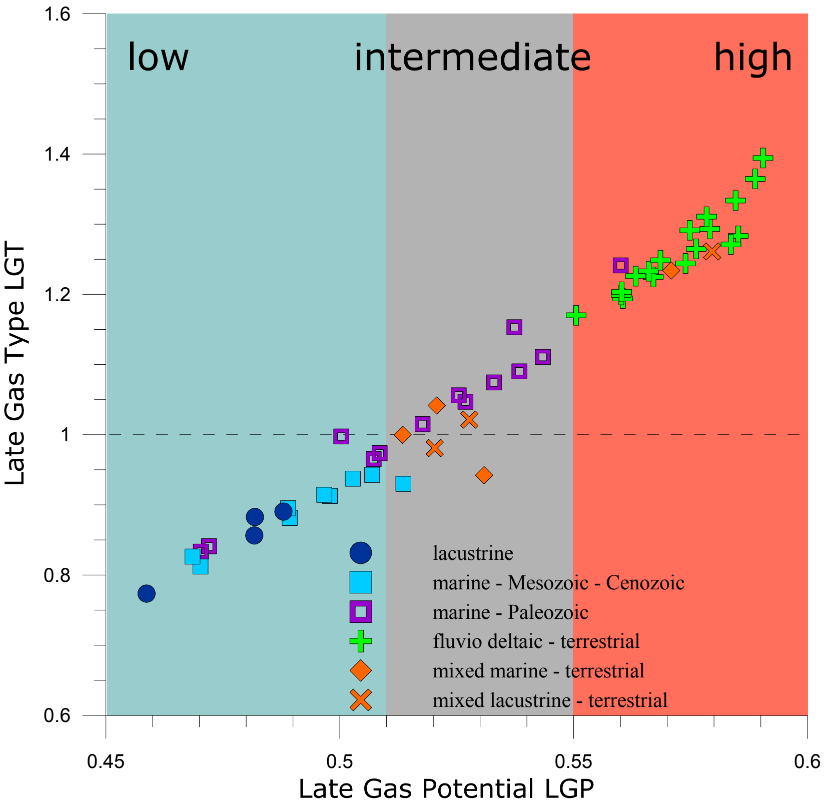
- Calculated Secondary Gas (B) Yield = Late Gas minus sec. Gas (from oil)





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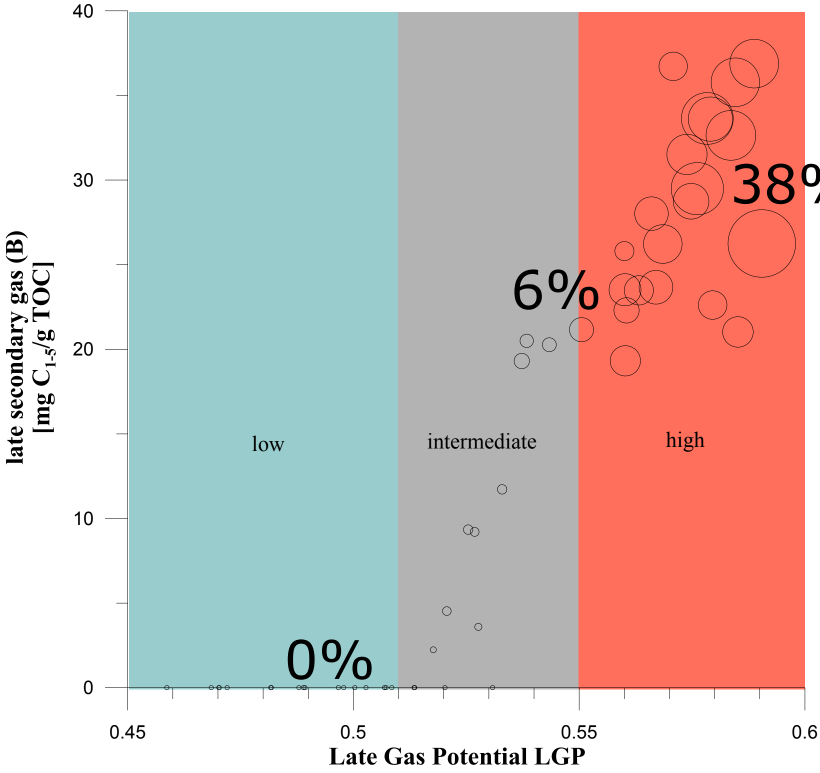
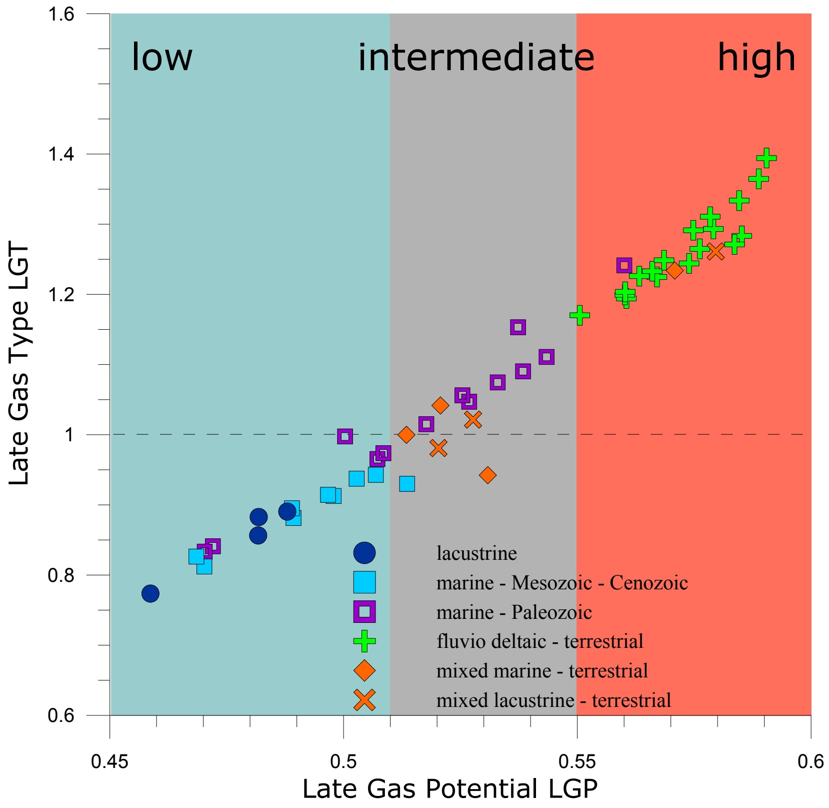
- Additional Sec. Gas (B) input as percent of primary petroleum potential (HI)





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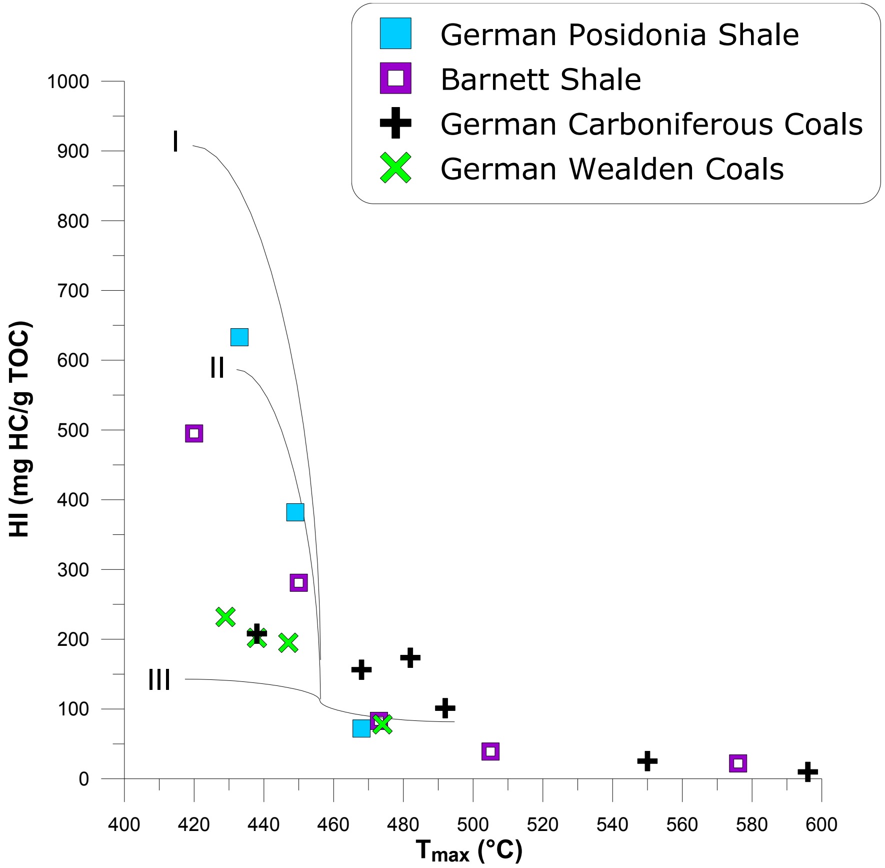
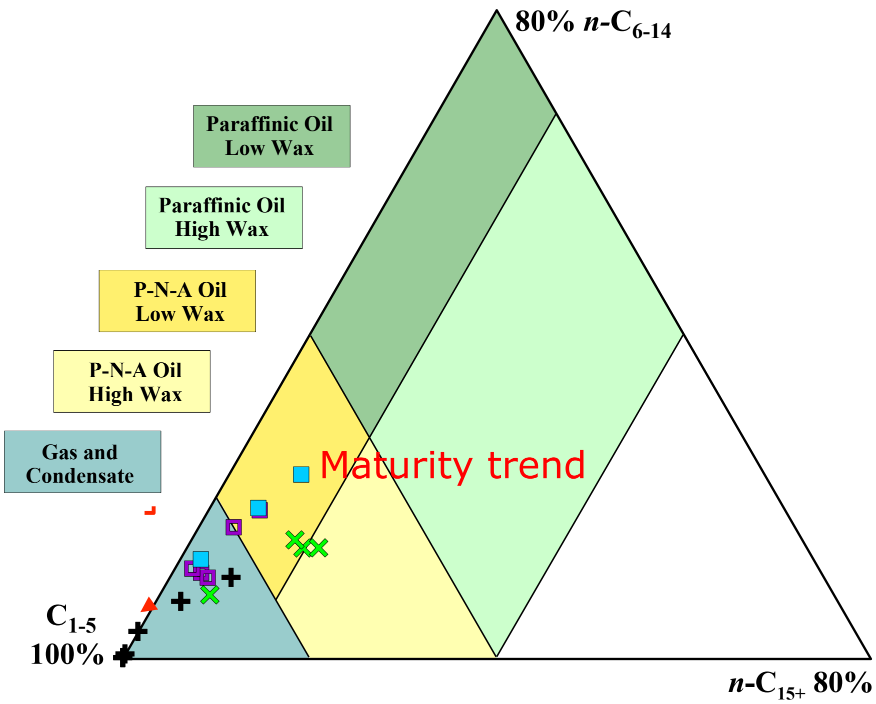
Geochemical Characterisation

TOC/Rock-Eval



Open Pyrolysis GC-FID



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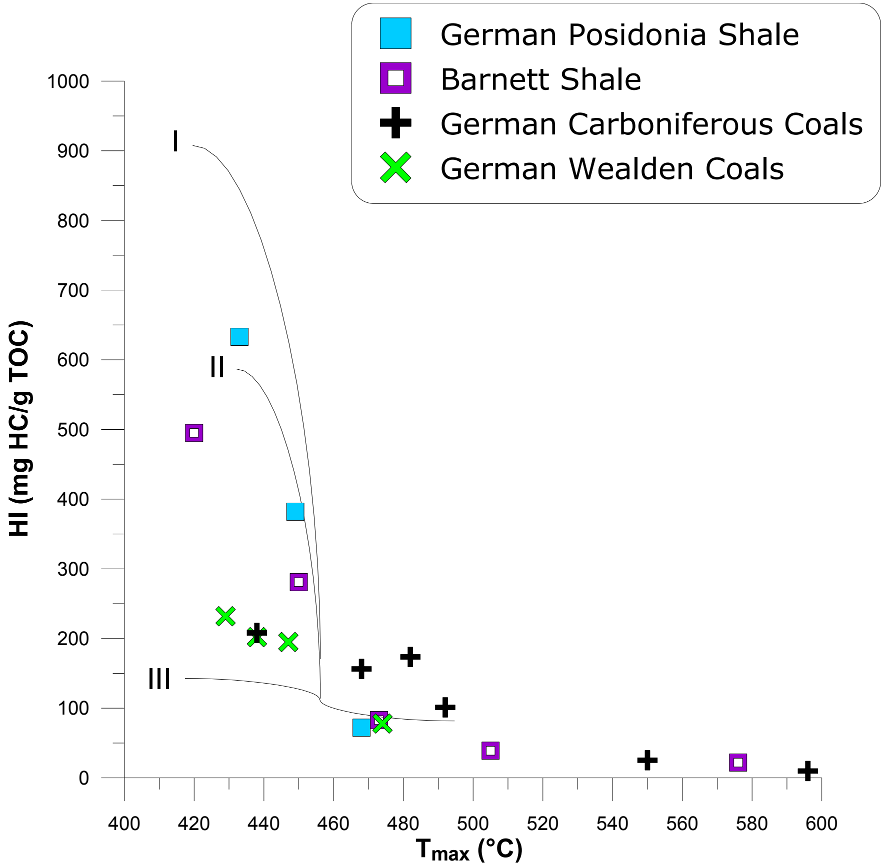
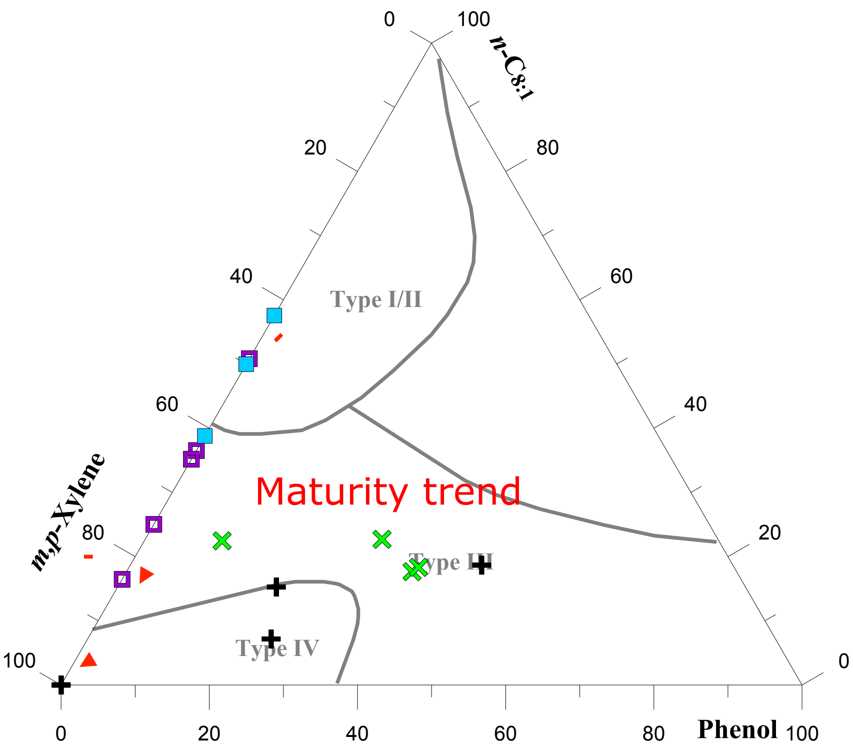
Geochemical Characterisation

TOC/Rock-Eval



Open Pyrolysis GC-FID

phenol content
-terrestrial input



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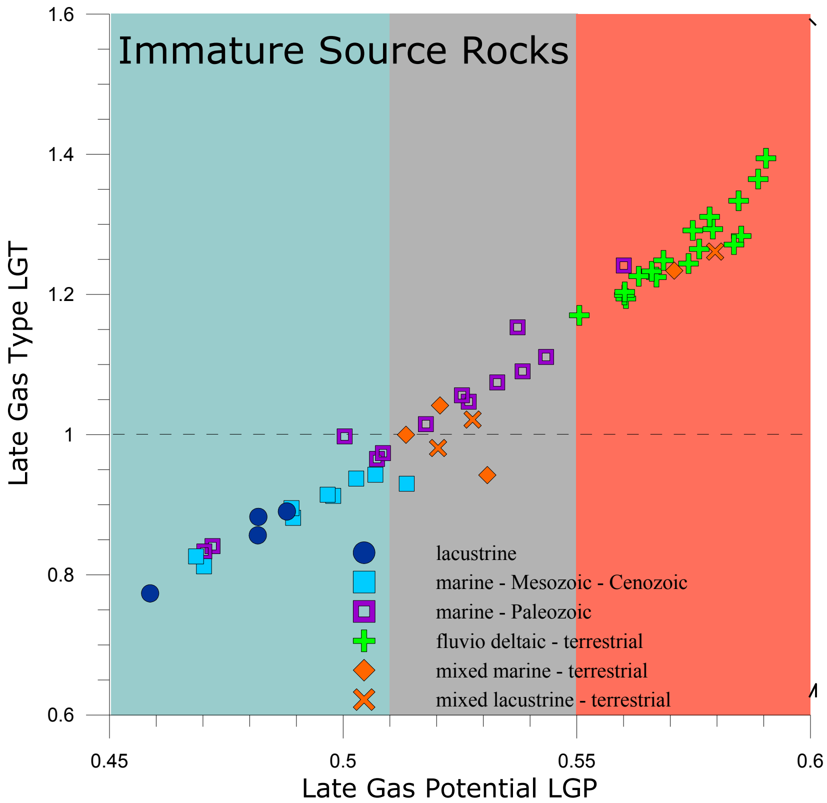

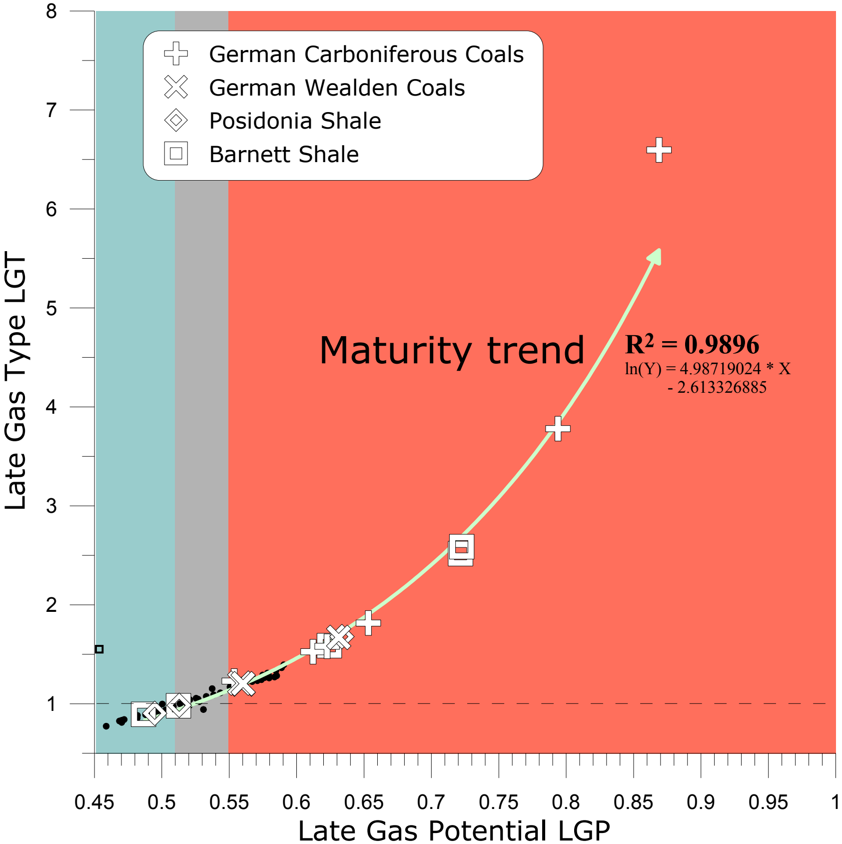

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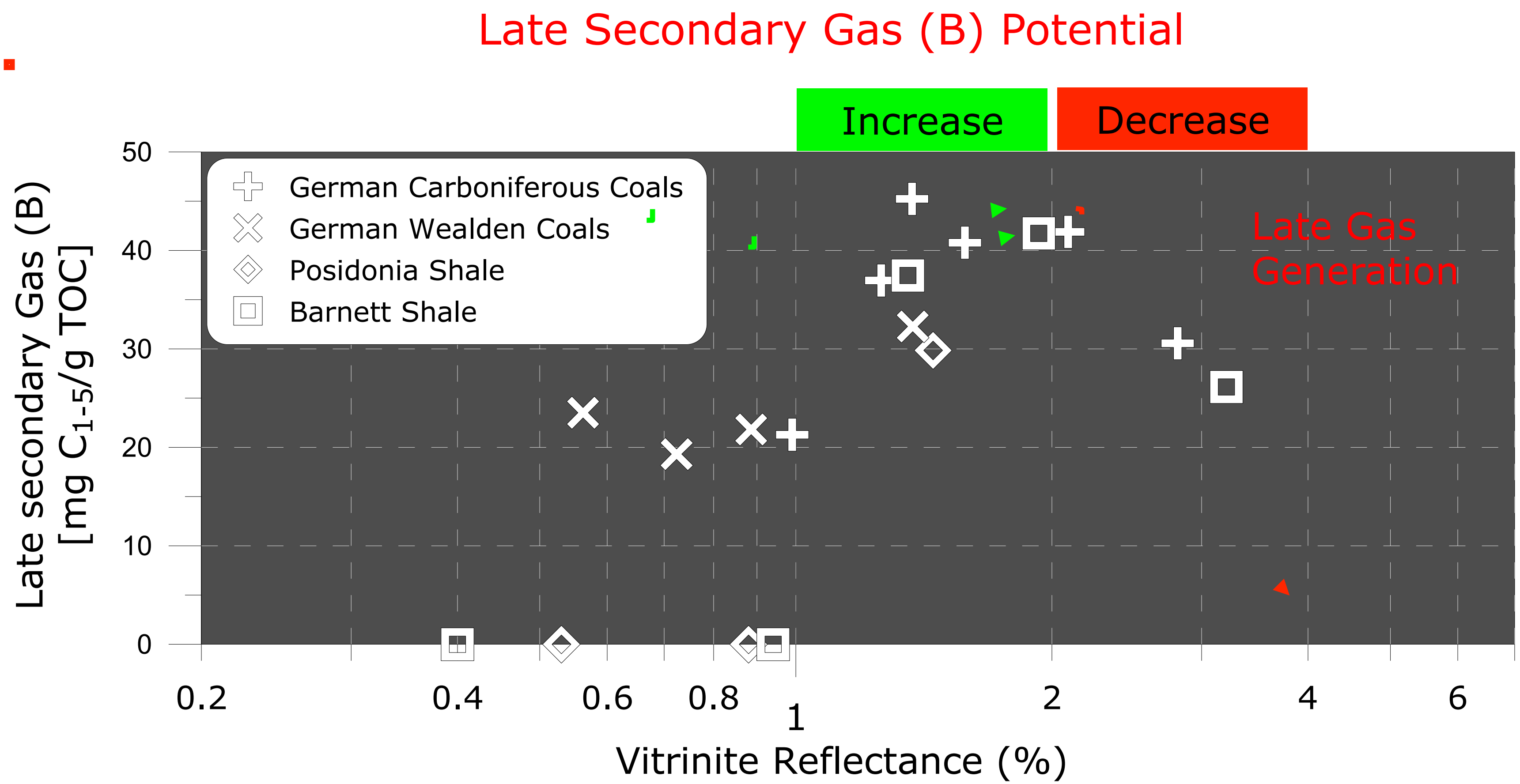
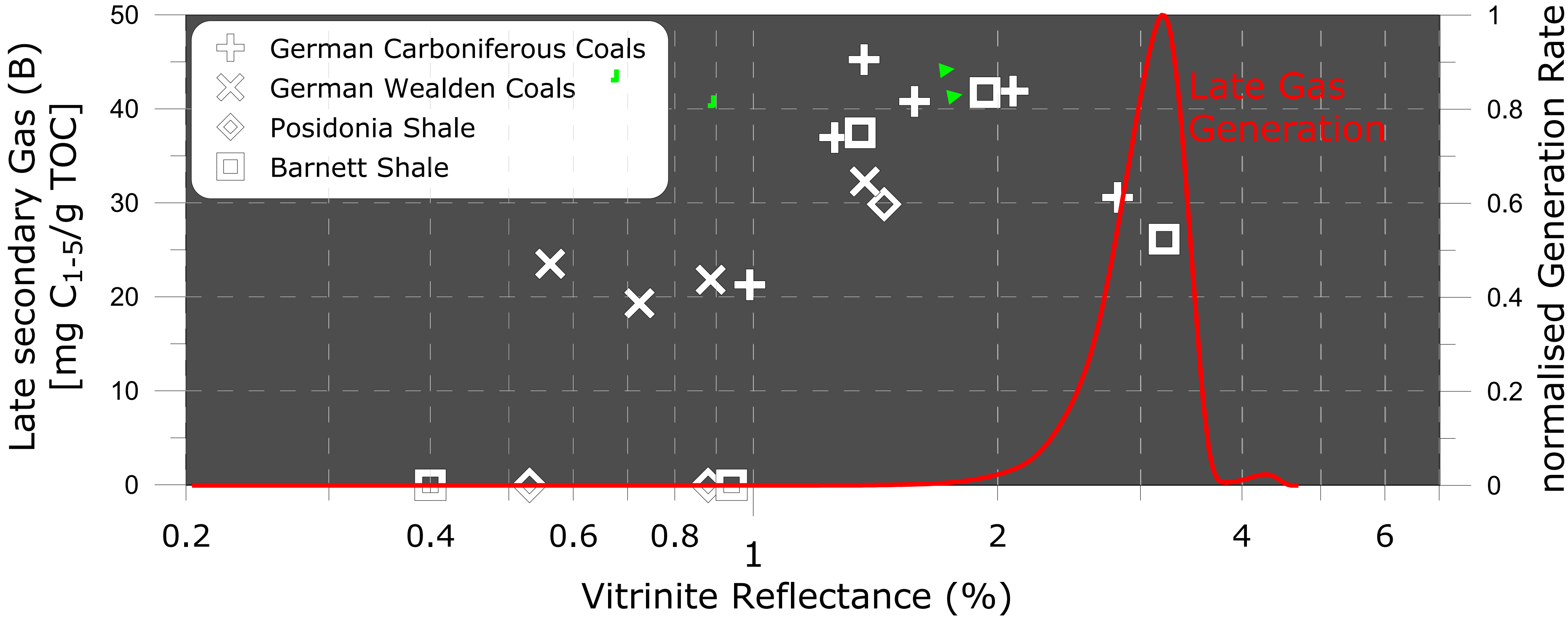


Kinetic Parameter of Late Gas Generation

stepwise (MSSV) Pyrolysis-GC-FID at 3 heating rates (0.1; 0.7; 1.0 °C/min)

- Sample: Immature Åre Fm Coal (~0.4% R_0)

→Prediction for a 3 °C/ma heating rate



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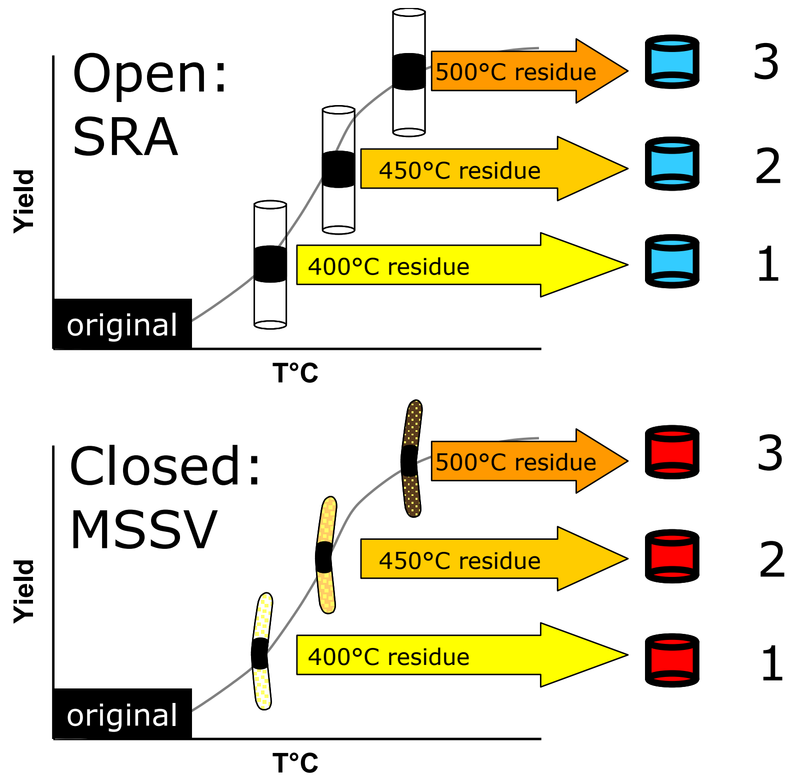
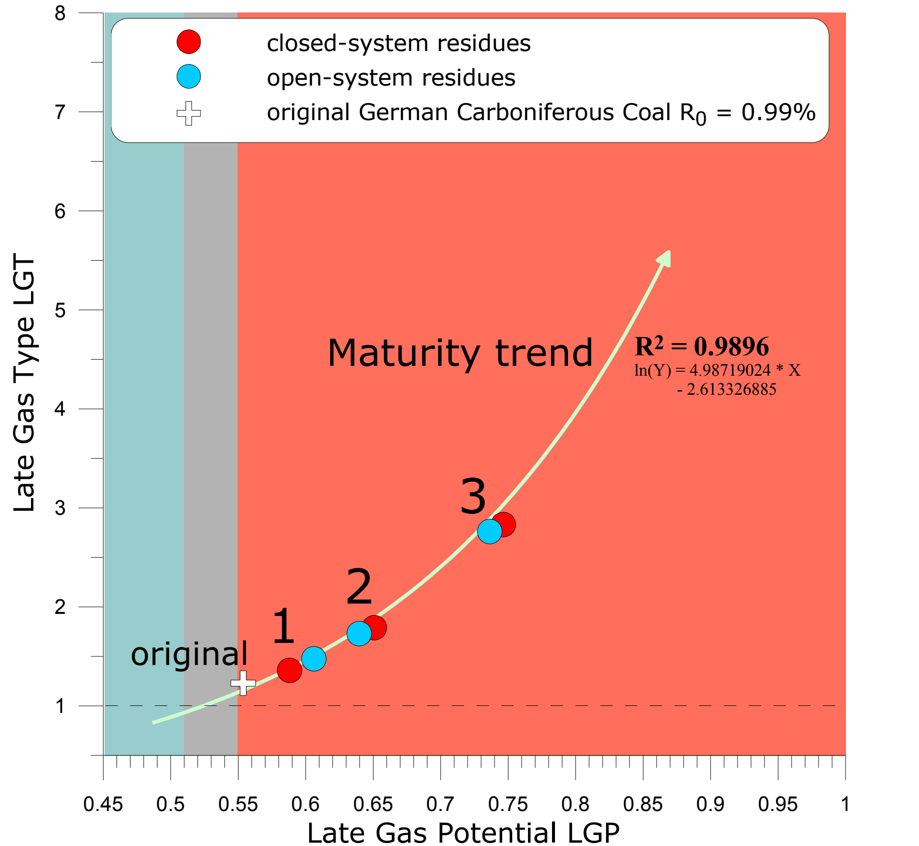
Residue Preparation

- 250°C to end temperature at 1°C/min



MSSV-Pyrolysis



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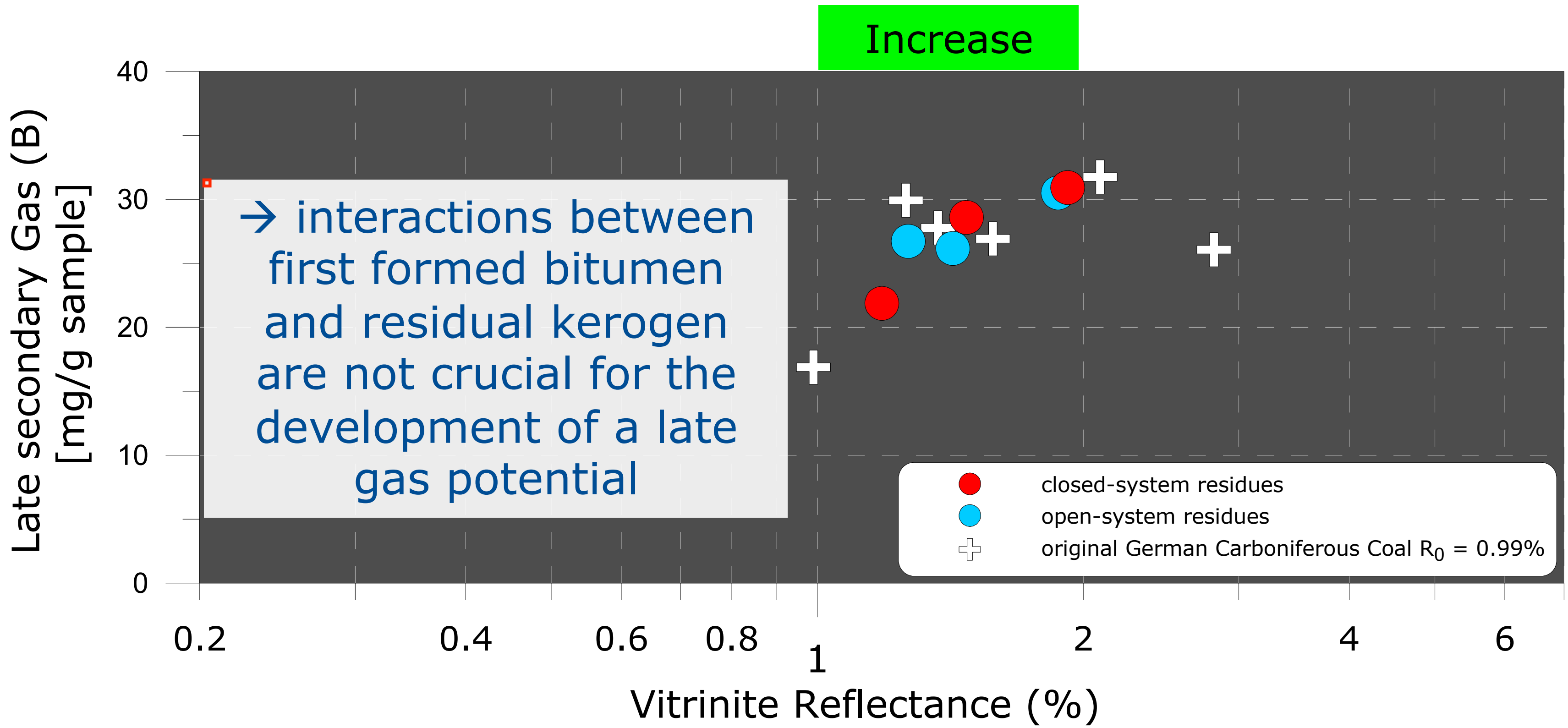
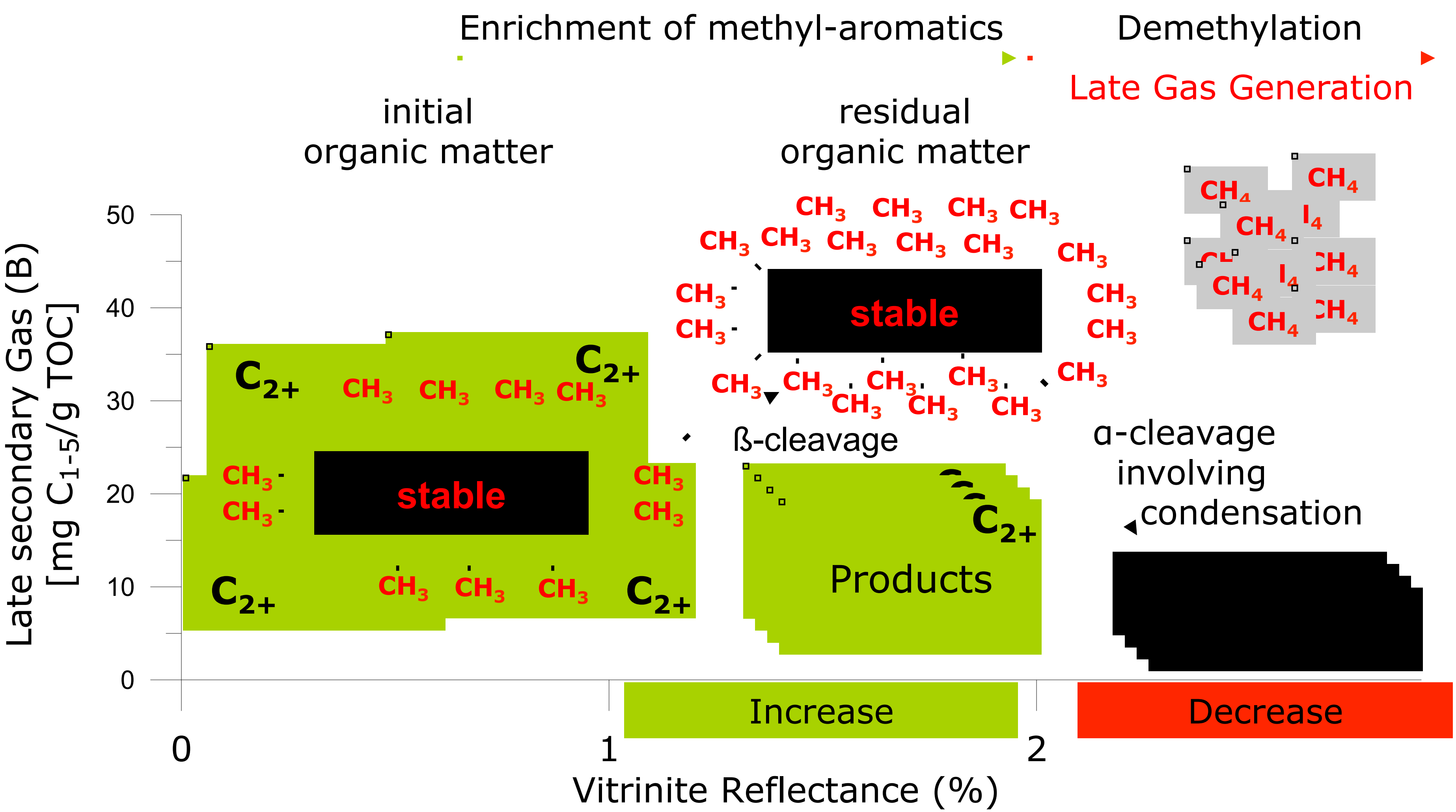
Late Secondary Gas (B) Potential



Hypothetical Mechanism



Major Conclusions

1. A method (tool) to evaluate the Late Gas Potential of immature as well as naturally and artificially matured source rocks was developed.

2. High Late Gas Potentials (LGP>0.55) are seen for immature source rocks of high initial aromaticity and for mature samples at the end of catagenesis **(40 mg/g TOC).**

   →Late Gas Potentials of immature samples are underestimates.

3. Decreasing Potentials at **R_0 >~2.0%** demonstrate that late dry gas is formed under natural conditions.

   →Kinetic Parameters correctly predict this late secondary gas (B) generation confirming previous results (Erdmann and Horsfield, 2006).
   →Calculated onset of high temperature methane generation is ~220°C or at a calculated R_0 of ~2.5% (geologic heating rate 3°C/ma)

4. The amount of late gas generated from a given mature source rock unit would be strongly coupled to initial TOC content and carbon loss during catagenesis.