Solid Bitumen in Shales: Facies and Maturity Effects on Microstructures*

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Abstract

Solid bitumen is in the focus of recent research work on shale oil/gas plays as it might lower effective gas permeabilities due to the occlusion of pore throats, but also provide important hydrocarbon storage space and form migration pathways if a porous network of oil-wet pores is present. However, despite its significance for the quality of a shale reservoir, ambiguities about the various definitions of (solid) bitumen in organic geochemistry and petrography, as well as regarding the actual onset of compositional and microstructural transformations during thermal maturation and accompanying hydrocarbon generation, exist. In an attempt to visualize different solid bitumen types and transformation stages over a broad maturity range (0.5-2.7% Ro) in shales of varying primary kerogen composition, we reviewed optical and scanning electron microscopy data of shales with a Cambrian to Triassic age with emphasis on the petrographic characteristics of solid bitumen.

We were able to identify in-situ pre-oil solid bitumen as well as migrated post-oil solid bitumen at various maturity stages. We found solid bitumen to be surprisingly mobile already at marginal to early oil window maturity, arguing for significant influence of primary migration. Onset of porosity development in solid bitumen differs considerably between predominantly oil-prone (e.g. alginate) and gas-prone (vitrinite-rich) kerogen compositions; furthermore, solid bitumen (pyrobitumen at advanced maturity) in rocks with a terrestrially-dominated facies seems to be considerably less mobile compared to pre- and post-oil solid bitumen in oil-prone rocks. In most samples, several solid bitumen populations with varying reflectance were observed, complicating its use as a petrographic maturity indicator. Microstructural features such as irregularly distributed spongy porosity or detrital and authigenic mineral inclusions in the sub-micrometre scale were found to have a great influence on texture and reflectivity in lower-resolution optical microscopy. The formation of authigenic minerals (quartz, various carbonate phases, magnetite in Cambrian samples) was observed frequently in post-oil solid bitumen of oil-prone rocks; this points to a close genetic relationship between transformation products formed during hydrocarbon generation (e.g. acetate, carbon dioxide and methane) and the dissolution and precipitation of minerals during diagenesis.
Solid bitumen in shales: Facies and maturity effects on microstructures


AAPG ACE San Antonio - 2019/21/05
Outline

- **Cambrian**: Arthur Creek Fm., Australia
- **Ordovician/Silurian**: Graptolite Shale, Lithuania
- **Upper Visean**: Rudov Beds, Ukraine
- **Upper Jurassic**: Mandal Fm., Norway
- **Triassic**: Yanchang Fm., China
- **Miocene**: Vienna Basin, Austria

Data sources:
- Comparative optical and scanning electron microscopy
- Bulk geochemistry & source rock extracts
- Gas adsorption
- Mercury intrusion porosimetry

Image-based structure
Facies and maturity effects on SEM-visible *meso-* and *macropores*

Sorption-based structure
Facies and maturity effects on *micro-* and *mesopores*

Micromechanics
Facies and diagenetic effects on structural integrity
->fracture paths
→ **Solid bitumen** plays an integral role for:
- Maturity evaluation
- Mineral authigenesis
- Porosity evolution
- HC storage and expulsion

How to link both?
Visualize organic matter textures: BIB-SEM

- Spongy pores
- Pendular pores
- Complex mixture of pore types
- OM/CM interface pores

~1 mm

~5 µm
How to identify solid bitumen in the SEM?
Solid bitumen: remobilized vs. in-situ

In-situ: hardly distinguishable!

Remobilized:

- Flow textures
- Fossil impregnations
- Impregnations of authigenic minerals
- Impregnations of secondary dissolution pores
- Dissolved quartz cement
- Authigenic quartz
Fluorescence populations at early oil window:

- Wispy SB along alginites
- Network SB in microfractures
Mineral authigenesis

Two phase-fluid (oil/SB – water)
Solid bitumen porosity - organofacies

Oil-prone (Silurian – Triassic)

reactivity/mobility ↑

(~70 samples in total)
Solid bitumen porosity - organofacies

Gas-prone (Upper Visean)

reactivity/mobility ↑

reactivity/mobility ↓

(~70 samples in total)
Quantification: total vs. OM-hosted porosity

BIB-SEM: Segmentation of pores on representative areas

true porosity (total)
cracks (drying)
gypsum (core alteration)

Upper Visean (17 samples)

OM porosity (%OM) vs. total porosity (%)

- Correlation of $\phi_{total}$ vs. $\phi_{OM}$

- Weak correlation $\phi_{total}$ vs. wt% quartz
Influence of compaction on pores?

- Npog 74: < Qrz
- Ost 53: < Qrz
- Yan 198: > Qrz

Graphs showing correlation between pore orientation and quartz content.
Source rock extracts:
Composition suggests that solid bitumen pores are filled with a lighter HC phase

\[\text{↑ OM-pores} \rightarrow \text{↑ EOM & Sat/Aro}\]
Selective retention of NSOs by kaolinite (?)

Hydrocarbon retention/expulsion

* Yan 176, 65 % kaolinite

10 μm

solid bitumen / kaolinite

> 45 % Kaolinite
< OM pores

> OM pores

R² = 0.88

OM pores (%OM)
Hydrocarbon retention/expulsion

Upper Jurassic Mandal Fm. (Norway)

**Mixed type II/III kerogen**

- 30-60% of S2 peak extractable @ 430-450°C Tmax!

- Important information on hydrocarbon storage and expulsion efficiency

Petroleum Quality (PQ): \( S1/S1+S2_{\text{bitumen}} \)

Total Petroleum: \( S1+S2_{\text{bitumen}} \)

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No correlation!

Ziegs et al., 2017
Hydrocarbon retention/expulsion

Upper Jurassic Mandal Fm. (Norway)

Petroleum Quality (PQ): $\frac{S_1}{S_1+S_2}$

Nitrogen adsorption isotherms

- PQ 0.37, Tmax 431°C
- PQ 0.26, Tmax 431°C
- PQ 0.21, Tmax 431°C
- PQ 0.40, Tmax 449°C
- PQ 0.50, Tmax 447°C
- PQ 0.35, Tmax 447°C

![Graphs showing nitrogen adsorption isotherms and their correlation with petroleum quality and pore volume.](image)
Hydrocarbon retention/expulsion

<table>
<thead>
<tr>
<th>Heavy Fraction</th>
<th>Light Fraction</th>
<th>Sorption capacity</th>
<th>SEM-visible SB porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low PQ</td>
<td>Upper Jurassic</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>431°C; PQ 0.21</td>
<td>436°C; PQ 0.37</td>
<td>449°C; PQ 0.4</td>
<td></td>
</tr>
<tr>
<td>32 %S2_{bit}</td>
<td>49 %S2_{bit}</td>
<td>50 %S2_{bit}</td>
<td></td>
</tr>
<tr>
<td>total oil 6.03</td>
<td>total oil 17.50</td>
<td>total oil 9.51</td>
<td></td>
</tr>
</tbody>
</table>

| Low PQ         | Upper Visean  |                         |                         |
| 463°C; PQ 0.69 | 11 %S2_{bit} | total oil 1.9 mg/g    |                         |

- **High PQ**

- **Upper Jurassic**

- **Upper Visean**
Hydrocarbon retention/expulsion

**Microporosity** (< 2nm) dominated by $S_2\text{bitumen}$:

**Meso- & macroporosity** (2-200 nm) controlled by clay (mineralogy) & „SEM-porous“ solid bitumen:

**Organofacies & Maturity**
Cap rock integrity: BIB-SEM

Miocene cap rocks (Vienna Basin)

- Pore size distributions
- Geometry (Area, Perimeter, AR, Circ)

BIB-SEM study to investigate flow paths

\[
\text{Phicorr} = 1.98 \text{ vol}\% \\
\text{Phicorr} = 2.70 \text{ vol}\% \\
\text{Phicorr} = 9.56 \text{ vol}\%
\]
Cap rock integrity: MIP vs. BIB porosity

Miocene cap rocks (Vienna Basin)

-> Validation of petrophysical methods (e.g., Mercury Intrusion Porosity - MIP)

MIP porosity (vol%)

Corrected BIB porosity (vol%)

Mean \(\phi_{equ}(\text{nm})\)

Median \(\phi_{equ}(\text{nm})\)

Correlation coefficient: \(R^2 = 0.8873\)

Simplified pore model

Actual area

Simplified pore model

Mercury-filled drying cracks

Total clay minerals (wt%)

Correlation coefficients:

- Mean \(\phi_{equ}(\text{nm})\): \(R^2 = 0.5704\)
- Median \(\phi_{equ}(\text{nm})\): \(R^2 = 0.6296\)
Cap rock integrity: sorption

Miocene cap rocks (Vienna Basin)

Nitrogen adsorption isotherms

-> Trends are also observed in matrix mesopores (BET: 2-40 nm)

-> Influence on gas retention?
- Comprehensive understanding of depositional and diagenetic influences on storage/expulsion

- Input for **mechanical and transport modelling** of experimentally inaccessible material properties