Gas Generation Reactions in Highly Mature Gas Shales

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Abstract

As a new and abundant energy resource, gas shales have already impacted worldwide energy supply. Currently, worldwide exploration activities are drastically increasing. This unconventional gas resource constitutes complex self-contained source-reservoir systems, in which three distinct processes together result in the formation of thermogenic gas: (1) the decomposition of kerogen to gas and bitumen; (2) the decomposition of bitumen to oil and gas; and (3) the secondary cracking of oil to gas and a carbon-rich coke or pyrobitumen residue. While the basic stoichiometries and source-sink relationships are understood, the chemical and structural variability of gas shales at the submicrometer scale is still poorly documented. Consequently, hydrocarbon generation and retention processes occurring within such unconventional systems are still poorly constrained.

As part of the European GASH project (GAs SHales) coordinated by the GFZ-Potsdam, organic-rich calcareous mudstone samples from Northern Germany at varying stages of thermal maturation have been characterized using an original combination of compositional organic geochemistry and spectromicroscopy techniques, including synchrotron-based STXM (scanning transmission X-ray microscopy) allowing in situ imaging of organic-rich samples with a chemical-based contrast at a 25-nm spatial resolution while providing spatially-resolved information of organic constituent speciation.

Within the selected gas shale samples, we document multi-scale chemical and mineralogical heterogeneities, from the bulk scale down to the nanometer scale. Different types of bitumen, very likely genetically derived from thermally degraded organic precursors, have been detected in close association with authigenic minerals. Macroscopic fracture-filling bitumen with the same organic chemical signatures as one family has been documented. Chemical rock-fluid interactions could be inferred in the case of another family. The porosity evolution with thermal maturation has also been documented using TEM at the nanometer scale. Our observations provide
key constraints on the thermal history of this gas shale formation and shed new light on the influence of the organic precursor chemistry on the thermal generation and retention of the various organic moieties which can be encountered in gas shales.

**Selected References**


Gas generation reactions in highly mature gas shales

Sylvain Bernard - Brian Horsfield
Hans-Martin Schulz - Richard Wirth - Anja Schreiber
Gas generation reactions in highly mature gas shales

Gas shales constitute self-contained source-reservoir systems of large and continuous gas accumulation.
Different processes may lead to thermogenic gas formation

Chemical heterogeneities of gas shales at the submicrometer scale?
Structural organic/inorganic relationships at the nanometer scale?
Identification of nanoscale pores within Barnett Shale samples

Origin of such nanoscale porosity: gaseous hydrocarbon generation?

→ Multiscale characterization of a maturation series using TEM + STXM

Loucks et al., 2009
**Posidonia Shales: Location and Maturity**

Lias ε level of the Lower Toarcian Posidonia Shales from the Hils syncline area

Maturity increases

Haddessen Well: 1.45 Ro
Harderode Well: 0.85 Ro
Wickensen Well: 0.55 Ro
Posidonia Shales: Rock-Eval Pyrolysis Data

Haddessen Well = Overmature gas shale

Bernard et al., Chemie der Erde, 2010
Bernard et al., Marine and Petroleum Geology, 2011
Soxhlet extraction of the soluble fraction

Solvent extraction and fractionation of the:
- Aliphatic fraction
- Aromatic fraction
- Polar NSO compounds
  - Asphaltenes
X-ray Absorption Near Edge Structure (XANES) Spectroscopy
or Near Edge X-Ray Absorption Fine Structure (NEXAFS)

Very high spectral resolution (0.1 eV) \rightarrow information on the bonding environment

XANES spectrum = information on speciation with a Beer’s Law response
Evolution of XANES signatures with increasing maturity: Aliphatic and Aromatic Fractions

Indexation
285.3 - Aromatic Groups (C=C) (1s → π*)
287.7 - Aliphatic Groups (CH1-3) (1s → 3p/σ*)
288 eV - Aliphatic Groups (CH1-3) (1s → 3p/σ*)
Evolution of XANES signatures with increasing maturity: Polar NSOs and Asphaltenes

Indexation
285.3 eV - Aromatic Groups (C=C) (1s→π*)
286.7 eV - Ketonic or Phenolic groups (1s→π*)
287.7 eV - Aliphatic Groups (CH1-3) (1s→3p/σ*)
288 eV - Aliphatic Groups (CH1-3) (1s→3p/σ*)
288.6 eV - Carboxylic Groups (COOH) (1s→π*)
Evolution of XANES signatures with increasing maturity: Insoluble Kerogen and Pyrobitumen

Indexation
- 285.3 eV - Aromatic Groups (C=C) (1s→π*)
- 286.3 eV - Unsaturated C-S bonds
- 286.7 eV - Ketonic or Phenolic groups (1s→π*)
- 287.7 eV - Aliphatic Groups (CH1-3) (1s→3p/σ*)
- 288 eV - Aliphatic Groups (CH1-3) (1s→3p/σ*)
- 288.6 eV - Carboxylic Groups (COOH) (1s→π*)
- 290.3 eV - Carbonate Groups (CO3) (1s→π*)
- 290.6 eV - Alkyl Carbon (1s→4p)
Deconvolution Procedure

- Collected C-XANES spectrum
- Arctangent function
- Gaussians functions
- Fit
- Difference

Haddessen Kerogen

X-ray Absorption

Energy (eV)
Posidonia shale kerogen: Chemical and structural evolution with increasing maturity

- With increasing maturity:
  1. The aromaticity of the kerogen increases
  2. The relative concentration of aliphatic carbon drastically decreases
  3. Sulfur and oxygen-containing functional groups are progressively lost

<table>
<thead>
<tr>
<th>Parameters extracted from XANES spectra</th>
<th>Kerogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wickenssen</td>
</tr>
<tr>
<td>Aromaticity - $S_A$</td>
<td>1.25</td>
</tr>
<tr>
<td>Ratio Alipatics/Aromatics - $R_{Aliph}$</td>
<td>0.96</td>
</tr>
<tr>
<td>Ratio (Phenols+Ketones)/Aromatics</td>
<td>0.62</td>
</tr>
<tr>
<td>Ratio Carboxylics/Aromatics</td>
<td>0.62</td>
</tr>
<tr>
<td>Ratio Oxygen/Aromatics - $R_{Oxygen}$</td>
<td>1.24</td>
</tr>
</tbody>
</table>
Microscope observations - Organic Petrography

Wickensen
- Inertodetrinite
- Semifusinite
- Faunal Relic
- Liptodetrinite
- Telalginite
- Lamalginite

Harderode
- Bituminite/Micrine
- Inertodetrinite
- Bitumen
- Pyrite
- Prasinophyte cysts

Haddessen
- 25 µm
- Inertinite
- Prasinophyte
- Liptinite

Maturity increases
Organic and inorganic heterogeneities at the micrometric scale.
Preparation of FIB sections for TEM and STXM characterization

In situ extraction of a ~10 µm x 5 µm x 100 nm slice of sample for TEM and STXM characterization

Heaney et al., 2001
STXM = Scanning Transmission X-ray Microscopy
Synchrotron radiation - Spatial Resolution: ~25 nm - Spectral Resolution: 0.1eV

Monochromatic X-ray at a single energy $E$

$I_0 \rightarrow I_1$

Absorption Measurement
$A = -\ln \left( \frac{I_1}{I_0} \right) = f(E)$

Spectromicroscopy = Both spectroscopy and microscopy at high spatial and spectral resolutions
**STXM = Scanning Transmission X-ray Microscopy**

*Synchroton radiation - Spatial Resolution: ~25 nm - Spectral Resolution: 0.1eV*

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**XANES spectrum : bonding environment of the compound**

@ 280 eV

@ 285.1 eV

**STXM image contrast = f (speciation)**

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**Spectromicroscopy = Both spectroscopy and microscopy at high spatial and spectral resolutions**

→ **Organic Geochemistry at the nanoscale**
XANES Spectroscopy: FIB sections - Wickensen Well - 0.5 Ro

285.1 eV & 285.3 - Aromatic Groups (C=C) (1s→π*)
286.3 eV - Unsaturated C-S bonds
288.6 eV - Carboxylic Groups (COOH) (1s→π*)
290.3 eV - Carbonate Groups (CO3) (1s→π*)

Bernard et al., Marine and Petroleum Geology, 2011
EDXS Mapping: FIB section - Wickensenn Well - 0.5 Ro

Nanoscale mineralogical heterogeneities - Complex organic/inorganic relationships

*Bernard et al., Marine and Petroleum Geology, 2011*
XANES Spectroscopy: FIB sections - Harderode Well - 0.85 Ro

285.3 - Aromatic Groups (C=C) (1s→π*)
287.7 - Aliphatic Groups (CH1-3) (1s→3p/σ*)
289 eV - Aldehyde Groups (C-OH) (1s→π*)
290.3 eV - Carbonate Groups (CO3) (1s→π*)

Bernard et al., Marine and Petroleum Geology, 2011
XANES Spectroscopy: FIB sections - Harderode Well - 0.85 Ro

285.3 - Aromatic Groups (C=C) (1s → π*)
287.7 - Aliphatic Groups (CH1-3) (1s → 3p/σ*)
289 eV - Aldehyde Groups (C-OH) (1s → π*)
290.3 eV - Carbonate Groups (CO3) (1s → π*)

Bernard et al., Marine and Petroleum Geology, 2011
285.3 - Aromatic Groups (C=C) (1s→π*)
286.7 - Ketonic or Phenolic groups (1s→π*)
287.7 - Aliphatic Groups (CH1-3) (1s→3p/σ*)
288.6 eV - Carboxylic Groups (COOH) (1s→π*)
289 eV - Aldehyde Groups (C-OH) (1s→π*)
290.3 eV - Carbonate Groups (CO3) (1s→π*)
XANES Spectroscopy: FIB sections - Harderode Well - 0.85 Ro

Bernard et al., Marine and Petroleum Geology, 2011
XANES Spectroscopy: FIB sections - Harderode Well - 0.85 Ro

Bernard et al., Marine and Petroleum Geology, 2011
EDXS Mapping: FIB section - Harderode Well - 0.85 Ro

Nanoscale mineralogical heterogeneities - Complex organic/inorganic relationships

Bernard et al., Marine and Petroleum Geology, 2011
Authigenic Albite containing nano-inclusions of NaCl crystals
EDXS Mapping: FIB section - Haddessen Well - 1.45 Ro

Intra-pyrobitumen nanoporosity: Evidence of gas formation
**Thermal maturation scenario of Posidonia Shale**

Authigenic Albite containing NaCl-inclusions = tracer of brine/carbonate interactions (*Spötl et al.*, 1999)

![Graph showing Raman Shift (cm⁻¹) for Albite, Quartz, Calcite, Pyrite, and Anatase](image)

Crystallisation of authigenic albite from evaporite-derived brines-carbonates interactions

Implications for the thermal maturation scenario of Posidonia Shales:

*Bernard et al., Marine and Petroleum Geology, 2011*
Identification of different generations of bitumen and pyrobitumen
(Mastalerz and Glikson, 2000; Hill et al., 2003)

→ New insights on gaseous hydrocarbon generation processes
Ongoing Research = to be continued...
Ongoing Research = to be continued...

Advanced Light Source synchrotron (Berkeley, CA) from outside

Future allotted STXM beamtime:
- June 2011: ALS, Berkeley, USA
- June 2011: CLS, Saskatoon, Canada
- July 2011: Bessy II, Berlin, Germany
Physical, chemical and biological processes contributing to shale gas formation are examined by experiments, monitoring, surveying and modelling.