BIB-SEM study of the pore space morphology in early mature Posidonia Shale from the Hils area, Germany

Jop Klaver a,*, Guillaume Desbois a, Janos L. Urai a, Ralf Littke b

a Structural Geology, Tectonics and Geochemistry, Energy and Mineral Resources Group (EMR), RWTH Aachen University, Germany, Lochnerstrasse 4–20, 52056, Aachen, Germany
b Institute of Geology and Geochimistry of Petroleum and Coal, Energy and Mineral Resources Group (EMR), RWTH Aachen University, Lochnerstrasse 4–20, 52056 Aachen, Germany

1. Introduction

Petrophysical properties of organic-rich shales are of special interest due to the growth in exploration and production of gas shales. In central and western Europe, one of the potential gas shales is the Lower Jurassic (Toarcian) Posidonia Shale which is widespread and known as the principal source rock for petroleum in the North German Basin, the Upper Rhine Valley and the Paris Basin. A gas shale is both the source and the reservoir of the gas, and pores are the reservoirs of free gas (Bustin et al., 2008). Decrease of shale porosity with depth is well known (Aplin et al., 2006; Broichhausen et al., 2005) but the relative roles of mechanical compaction and diagenesis are still not well understood. Quantifying the pore structure is still challenging in low porous and low permeable rocks, due to a lack of an appropriate method to investigate directly sub-micrometer structures in representative area and volume. The most popular conventional bulk porosity measurements are performed by mercury injection porosimetry (MIP) and gas adsorption porosimetry. MIP measures pore size down to 3 nm in diameter but only from the connected part of porosity and interpretation of the measurements is based on a simplified model of cylindrical pore tubes (Washburn, 1921) which does not reflect the complexity of natural pore network. Therefore, pore sizes inferred from MIP are underestimated due to the ink-bottle effect (Münch and Holzer, 2008) and give only information about pore throat size. Moreover, during the omnidirectional injection at high pressure, pore collapse is possible when an effective stress is created by the capillary pressure and gradients in saturation in the sample (Hildenbrand and Urai, 2003; Hildenbrand et al., 2005). With gas adsorption BET, surface area can be measured (Brunauer et al., 1938), and pore size distribution can be calculated (Barrett et al., 1951; Schull, 1948) down to 0.3 nm in diameter. However, these data are still only related to the connected porosity and are based on a simplified model. Both methods lack direct information about pore morphologies and the relation of porosity to mineralogy and microstructures. In contrast, recent developments of ion beam milling allow study of porosity and microstructure on high
quality flat surfaces in SEM (Desbois et al., 2009). This research on nanopores in low porous rocks has grown rapidly in recent years (e.g., Bernard et al., 2012; Chalmers et al., 2009, 2012; Curtis et al., 2011a; Holzer and Cantoni, 2011; Milner et al., 2010; Passey et al., 2010; Schieber, 2010; Schneider et al., 2011; Slatt and O’Brien, 2011; Wang and Reed, 2009), see Loucks et al. (2012) for a thorough overview and pore classification. Serial cross-sectioning with focused ion beam (FIB) milling in combination with SEM is able to deliver a 3D model of pore space (Ambrose et al., 2010; Curtis et al., 2012; Desbois et al., 2009; Heath et al., 2011; Keller et al., 2011; Sisk et al., 2010; Sondergeld et al., 2010) but the studied volume is limited, typically $10 \times 10 \times 10 \mu m^3$ and usually not representative. Complementary to these methods, a combination of broad-ion-beam milling and scanning electron microscopy (BIB-SEM) allows imaging of large (greater than mm²) planar, undamaged surfaces. This technique is suitable for the qualitative and quantitative study of microstructures and porosity, in representative elementary areas. This combined BIB-SEM technique to quantify the pores was used on cleanstones from reference sites for waste disposal (Desbois et al., 2009; Hemes et al., 2011), salt (Desbois et al., 2012), tight gas sandstones (Desbois et al., 2011) and on other, organic-rich, shales (Loucks et al., 2009).

The major goal of this study is to obtain pore size distributions, quantify the porosity and to study the pore morphology in representative areas, on the scale of the BIB cross-section, of two early mature Posidonia Shale samples from the Hils Syncline, Germany, using BIB-SEM. In addition, the bulk porosity is estimated and compared to MIP. Here the physical porosity (Pearson, 1999) is studied in the meso- to macropores range (Nelson, 2009; Rouquerol et al., 1994). The BIB-SEM results are compared with MIP data to infer the properties of the pore network, and to formulate a conceptual pore model.

2. Samples and geological setting

Both samples are from a Toarcian shale interval known as the Posidonia Shale (or Lias Epsilon), from the Hils Syncline in northern Germany (Fig. 1). The Posidonia Shale in the Hils Syncline was drilled and completely cored in several shallow boreholes in the 80's and comprehensive studies were done by several authors (Bernard et al., 2012; Jochum et al., 1995; Littke et al., 1988, 1991a, 1991b; Mann, 1987; Mann and Müller, 1988; Rullkötter et al., 1988). The cored shale intervals represent a large maturity range from very early mature to overmature gas window. The reason for the partly high maturity in this area is discussed and attributed to either a Late Cretaceous magmatic heating or to deep burial during the Late Jurassic and Early Cretaceous (Bartenstein et al., 1971; Petmecky et al., 1999). The Posidonia Shale consists of two units: an upper calcareous shale, and a lower marlstone (Littke and Rullkötter, 1987). Mann (1987) found, based on XRD, that a typical calcareous shale consists of 43% clay minerals, 37% calcite, 15% quartz and feldspar and 5% pyrite; whereas a typical lower marlstone consists of 35% clay minerals, 50% calcite, 11% quartz and feldspar and 4% pyrite. The origin of the calcite are mainly coccoliths and other plankton-deposited microfossils (Littke et al., 1991a), of which a part is recrystallized depending on the thermal maturity (Rullkötter et al., 1988). Vitrinite reflectance varies from 0.48 in the southeast to 1.45 in the northwest (Rullkötter et al., 1988). MIP porosities have been measured and range between 2.4 and 22% (Mann, 1987) and a weak dependency of VR, is seen. One geochemical scanning transmission X-ray microscopy (STXM) and transmission electron microscopy (TEM) study has been done recently on the Posidonia Shale (Bernard et al., 2012) indicating intra-particle pores of 1–50 nm in the organic matter for the mature samples which is consistent with work done by others (Chalmers and Bustin, 2008; Chalmers et al., 2012; Curtis et al., 2011b; Loucks et al., 2009; Ross and Bustin, 2009; Sondergeld et al., 2010). This contribution is based on two samples, known as RWEPO6 and RWEPO8. Both samples are thought to be dry as they were stored under normal atmospheric conditions.

3. Methods and approaches

3.1. XRD analysis, incident light organic petrography and Rock Eval pyrolysis

X-ray powder diffraction (XRD) analysis was performed on both RWEPO6 and RWEPO8 using a Bruker D5000 at the Geological Institute Aachen (GIA) RWTH Aachen University. Quantification of the different minerals was done using the Rietveld Method (TOPAS), with special attention for clay (Kahle et al., 2002). In order to study the samples in incident white light and in an incident light fluorescence mode, polished sections of whole rocks were prepared in orientation perpendicular to bedding following the procedure described in Sachse et al. (2011). Vitrinite reflectance was measured in oil immersion with magnification of 50 times following standard procedures. An Yttrium-Alluminium-Garnet (R = 0.89%) was used for calibration. Reflectance measurements followed standard procedures as described in Taylor et al. (1998) and details of the microscopic equipment are described in Littke et al. (2012). Vitrinite reflectance was measured on 49–58 points of RWEPO6 and RWEPO8 respectively, and mean values were calculated. It should be noted that autochthonous vitrinite is rare in Posidonia Shale, whereas resedimented vitrinite and inertinite are much more common (Littke et al., 1988). However, the dominant macerals are liptinites (alginite). Rock-Eval pyrolysis was done according to Espitalié et al. (1977).

3.2. Sample preparation

Core fragments were stored at room temperature in a plastic air-tight container. Subsamples (~0.5 × 0.5 × 0.5 cm³) were cut with a saw blade and pre-polished using silicon carbide (SiC) sandpaper to reduce roughness from sawing down to 10 μm. Surface damage induced by SiC polishing was removed by argon BIB polishing which removed a 100 μm thick layer from the surface. The size of a typical BIB polished cross-section is 1–2 mm² (Fig. 2A). Samples were BIB argon polished in a JEOL SM-09010 cross-section polisher (8 h, 1 × 10⁻³–1 × 10⁻⁴ Pa, 6 kV, 150 μA) to produce a high quality, planar cross-section with topography less than ±5 nm as measured by AFM (Fig. 2B) and very sharp edges at pore boundaries. The BIB polished cross-sections were Au-coated and imaged in a Zeiss Supra 55 SEM with a back scatter detector (BSE) for phase contrast imaging and a secondary electron detector (SE2) for topography investigation up to a magnification of 30,000 corresponding to a pixel size of 10 nm. From BIB cross-sections, large areas were selected to be imaged (SE2) at magnifications of 10,000, 20,000 and 30,000 times using 10–20% of overlap to create a large representative mosaic made of hundreds of single images (Table 1) to study the pores down to the resolution of SEM. A minimum of 10 pixels was shown to be the practical pore resolution, i.e., all pores with a minimum size of 10 pixels are detected (Fig. 2C). Mosaics made with the BSE detector were imaged at a magnification of 1500, 2500, 5000 and 15,000 times to gain qualitative information about the mineralogy. An energy-dispersive X-ray spectroscopy (EDX) detector was used for semi-quantitative chemical composition analysis.

3.3. Image processing and pore segmentation

Single images were stitched together with a bicubic interpolation algorithm in Autopano 2 to build large mosaics preserving the pixel resolution. Pores were segmented semi-automatically in ArcGIS 10 from mosaics of SE2 images by using the contour tool in the 3D Analyst toolbar in ArcGIS 10 (Fig. 2C). With this tool the pore boundary of
each single pore is selected by the user and a contour at that specific gray value is drawn around the pore by ArcGIS. If the result is not satisfactory, the contour can be deleted or edited. Using this method, segmentation is faster than full manual interpretation. After segmentation pores were analyzed in MATLAB with PolyLX (Lexa, 2010). Cracks were interpreted as core damage due to stress relaxation after sample collection and were removed during analysis.

Segmentation of mineral phases was achieved by using gray value patterns from BSE images validated by a combination of EDX and XRD investigations. Because of low gray value contrast, quartz, mica and carbonate fossils were segmented manually (Fig. 3).

3.4. Representative elementary area

The representative elementary area (REA) was determined with the box counting method (Kameda et al., 2006) on the classified BSE mosaic of samples. Thus, (as shown in Fig. 4), gray values from BSE mosaics that were ranked in ArcGIS10 were first attributed to
the phases organic matter, clay matrix, calcite and pyrite. Then, a stepwise growing box was applied to the classified BSE image. At each increasing box size the amount of the different phases present in that box was calculated in the box. This process was repeated for several different starting points in the mosaic. At a given box size the individual contribution of each phase to the overall composition does not significantly change. This area is interpreted to be the REA on the scale of the BIB cross-section.

3.5. Pore size by mercury intrusion and extrusion

For comparison with the BIB-SEM-based pore data, MIP was performed on both samples at Micromeritics Analytical Services Europe, Aachen, Germany. Mercury intrusion and extrusion analysis was done in the 360–0.003 μm pore throat range. Samples to be analyzed were dried at room temperature in vacuum ($1 \times 10^{-4}$ Pa) for 30 h. No significant change in weight was measured, as expected. Pore throat radius distribution calculations are based on the Washburn equation (Washburn, 1921). Pressures used for intrusion were up to 414 MPa corresponding to a pore throat diameter of 3 nm (Hg surface tension $= 485$ dynes/cm, contact angle $= 130^\circ$). Extrusion of the mercury takes place at decreasing pressure steps. Difference in intrusion and extrusion mercury volumes give trapped mercury volumes due to the pore body to pore throat differences. Pore body to pore throat ratios can be calculated from MIP (Cerepi et al., 2002; Janssen et al., 2011; Webb, 2001). Measurements were corrected for blank errors and conformance errors (Sigal, 2009). After drainage, the samples were weighed to measure the amount of mercury remaining in the samples.

3.6. Power-law distribution and porosity nomenclature

For comparison of the pore size distributions in the different mosaics and samples, pore data are analyzed as normalized discrete frequency as a function of pore area:

$$\frac{N_i}{b_i S_{mosaic}} = C S^{-D}_{\text{pore}}$$

(1)

or alternatively:

$$\log \left( \frac{N_i}{b_i S_{mosaic}} \right) = -D \log (S_{\text{pore}}) + \log C$$

(2)

where $N_i$ is the number of pores with pore area $S_{\text{pore}}$ within bin $b_i$, where $b_i$ doubles each next bin, except for the first bin (1, 1, 2, 4, 8, etc., with corresponding boundaries at 1, 2, 4, 8, 16, etc.). $S_{mosaic}$ is the surface area of the current mosaic, $C$ is a constant and $D$ is the power-law exponent. When the pore size distributions follow a power-law we interpret this as self-similar. The pore size distributions are plotted and the best fit is calculated between the largest pore and the practical pore resolution (Fig. 3), which bounds the power-law distribution (Eq. (2)). This fit is later used for the extrapolation of the pore size distribution down to the pore sizes, which are not detectable at the resolution of the SEM. The 95% confidence levels and the outermost linear fits of the log–log data are plotted as a measure of uncertainty for the best fit.

We adopted the following nomenclature. The porosity of phase ($\theta$) in sample (N) inferred by the method (M) at the given resolution (X) is given by: $\phi_{M,N}^{X,\theta}$, if the porosity is extrapolated from data and not measured, the same porosity is then indicated by the symbol (*). Thus, in this case the symbol $\phi_{N}^{X,*}$. Therefore, for example, the total (T) porosity measured by BIB-SEM (BIB) method down to 36 nm in sample RWEP06 (06) made of organic matter (OM), clay matrix (CM), calcite (C), pyrite (P) and fossils (F) is written as follows:

$$\phi_{BIB,36,06}^{T} = \phi_{BIB,36,06,OM}^{T} + \phi_{BIB,36,06,CM}^{T} + \phi_{BIB,36,06,C}^{T} + \phi_{BIB,36,06,P}^{T} + \phi_{BIB,36,06,F}^{T}$$

(3)

where $\phi_{BIB,36,06,NF}$ represents the porosity associated with non-carbonate fossil phases. A list of symbols used to specify all possible M, X, N and $\theta$ terms used in this paper is given in Table 2.

---

**Table 1**

Mosaic properties for samples RWEP06 and RWEP08.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mosaic Magnification</th>
<th># Images</th>
<th>Pixel size [nm²]</th>
<th>Practical pore resolution [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RWEP06 I</td>
<td>30,000</td>
<td>120</td>
<td>$10 \times 10$</td>
<td>$= 36$</td>
</tr>
<tr>
<td>RWEP06 II</td>
<td>10,000</td>
<td>169</td>
<td>$29 \times 29$</td>
<td>$= 104$</td>
</tr>
<tr>
<td>RWEP08 I</td>
<td>20,000</td>
<td>144</td>
<td>$15 \times 15$</td>
<td>$= 54$</td>
</tr>
</tbody>
</table>

---

**Fig. 3.** Mineral fabric and classification of mineralogy in sample RWEP06. (A) BSE mosaic shows mineral phase contrast. (B) Identification of minerals by using the EDX detector which provides semi-quantitative chemical analysis of the BIB cross-section. Identified chemical elements are given in the legend. (C) Interpreted segmented mineralogy based on the BSE mosaic and EDX analysis, mineralogy is given in the legend.
4. Results

4.1. XRD analyses, organic petrography, organic carbon content and Rock-Eval pyrolysis

XRD analyses show that both samples RWEP06 and RWEP08 consist, respectively, mainly of calcite (44% and 57%), quartz (18% and 17%) and pyrite (4% and 4%), together with phyllosilicates of the muscovite/illite (14% and 8%) and kaolinite/clinochlore (9% and 6%). The other components consist of a mixture of albite, anhydrite, nacrite, chlorite, anorthite and siderite counting for about 10% of the total content (11% for RWEP06 and 8% for RWEP08). RWEP06 has a TOC of 6.05 with mean vitrinite reflectance (VRr) of 0.59% whereas RWEP08 has a TOC of 8.14 with average VRr of 0.61%. Rock-Eval S1 and S2 peaks indicate a type I-II kerogen (Fig. 6A). Table 3 summarizes all compositional data for the two samples. Moreover, both samples are rich in brightly fluorescing alginite, but only sample RWEP06 contains Tasmanales algae as a common constituent (Fig. 6B).

4.2. Representative elementary area

BSE gigapixel mosaic (Fig. 4A) combined with EDX chemical analyses allow identification of 5 different mineral phases: calcite, organic matter, clay rich matrix, pyrite and others (Fig. 4B). A first box counting analysis of the above 5 different mineral phases from a segmented BSE mosaic shows that the REA is between 100×100 and 200×200 μm² (Fig. 4C). Based on a more detailed approach, the minimum REA for both samples was interpreted to be 140×140 μm² (Fig. 4B–F). Below areas of 140×140 μm², the relative content of each mineral phase does change significantly for both samples (Fig. 4C–G). At the scale of the REA, the only feature that may not be representative is the organic matter, which shows some larger fluctuations (up to 5%) in some analysis (Fig. 4D, F) probably because the organic matter-rich regions are mostly distributed as rare large particles within the matrix (blue line in Fig. 4F, for example). Above the area of 140×140 μm² and at the scale of BIB-milled cross-section, the average mineral contents of sample RWEP08 are: pyrite = 2.3% ± 0.38%, organic

Fig. 4. Principle of representative elementary area calculation (REA). (A) BSE mosaic is segmented according to the different gray values and EDX analysis (B). A stepwise growing grid is placed on the segmented BSE mosaic in (B) to perform the box counting method. (C) Box counting analysis indicating REA is between 100×100 and 200×200 μm². (D–G) Evolution of mineralogy content with increasing box size and for different starting points for organic matter (D, F) and Pyrite (E, G) phases and both samples RWEP06 and RWEP08. Dashed line in (D–G) indicates the box size where the overall composition is stable, pointing to REA.

Please cite this article as: Klaver, J., et al., BIB-SEM study of the pore space morphology in early mature Posidonia Shale from the Hils area, Germany, Int. J. Coal Geol. (2012), doi:10.1016/j.coal.2012.06.012
matter = 9% ± 1.2%, calcite = 30% ± 2.1%, clay-rich matrix = 33% ± 0.9% and other = 26% ± 1.7. For sample RWEP06 the mineralogical composition is: pyrite = 1.6% ± 0.36%, organic matter = 14% ± 2.2%, calcite = 18% ± 3.6%, clay-rich matrix = 39% ± 3.4% and other = 28% ± 4.8. The differences are due to the intrinsic heterogeneity in the shale.

4.3. Description of mosaics

Two mosaics with different surface areas were imaged for sample RWEP06: mosaic-I covers 0.3 × REA (105 × 65 μm²), whereas the mosaic-II covers 1.1 × REA (231 × 94 μm²). In mosaic-I, close to 16,500 pores were detected at the magnification of 30,000 resulting in a visible porosity of 2.62% from SE image analysis (Fig. 7A). The BSE mosaic shows clearly the carbonate fossils, organic matter, quartz and calcite (Fig. 7B). The largest pores (>500 nm, up to a few μm) are seen in the carbonate fossils and calcite grains (Fig. 7C, D). In between carbonate fossils and calcite grains there appears to be a low-porous matrix showing typical pore sizes about a few 10 nm (Fig. 7C and D). In the mosaic-II, over 26,000 pores were segmented resulting in a visible porosity of 2.75% at a magnification of 10,000, with similar porosity fabric as seen for the mosaic-I: i.e. large pores in carbonate fossils and calcite grains surrounded by a low porous matrix.

One mosaic of 1.0 × REA area (163 × 119 μm²) was made of sample RWEP08, in which a total of about 55,000 pores were detected at the magnification of 20,000 times resulting in a visible porosity of 2.74% (Fig. 8A). Though in RWEP08, the BSE mosaic (Fig. 8C and B) shows a larger amount of calcite (Fig. 7B) and the carbonate fossils are more fragmented within the low porosity matrix (Fig. 8C, D), the overall porosity fabric has similar characteristics than those observed for RWEP06.

4.4. Pore morphologies

Pore morphologies are very similar in the two samples RWEP06 and RWEP08. Therefore, descriptions below are valid for both samples. Pores in the organic matter (Fig. 9A) are mainly at interfaces between organic matter and the low porous matrix. These elongated pores have high aspect ratios (3 ± 1.7). Straight and sharp edges matching both sides and lack of cementation suggest that they were formed by micro cracking after coring (Fig. 9A, B). Pores in and around organic matter are sub-parallel to bedding. The few mesopores detected were close to the pixel resolution (inset in Fig. 9A). It is well known that organic matter has pore sizes which are often below 3 nm (Chalmers and Bustin, 2008; Chalmers et al., 2012; Curtis et al., 2011a, 2012; Prinz and Littke, 2005; Ross and Bustin, 2009; Sondergeld et al., 2010) and thus below the resolution of the methods applied here.

Carbonate fossils can be porous (Fig. 9C–D) or non-porous (Fig. 9F). Porous fossils are usually U-shaped fragmented with sizes of up to 10–20 μm (Figs. 7 and 8). The non-porous carbonate fossils have shapes from round- to U-shaped and are generally smaller than porous carbonate fossils with sizes of up to 5 μm (Fig. 9F). Pores inside the carbonate fossils have sizes below 500 nm and are typically polygons with straight and sharp edges (Fig. 9D). Porous carbonate fossils in RWEP08 have some tendency to be more fragmented and may be more cemented with recrystallized calcite (Fig. 8D). The porous carbonate fossils are interpreted to be cf. Schizosphaerella (Bour et al., 2007; Veiga de Oliveira et al., 2007).

Pores related to calcite grains are relatively large (1–4 μm) with faceted calcite crystals growing towards the center of the open pore (Fig. 9G–J). These large pores have no preferred shape or orientation. They contribute 24 and 15% to the total visible porosity for RWEP06 and RWEP08, respectively. These large pores in calcite contribute significantly to the porosity (Table 4). However, most of the pores in calcite have sizes below 1 μm. Pores between two mica sheets are elongated

Table 2
Definitions of symbols and terms used to describe porosity.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>ϕ</td>
<td>Porosity</td>
<td>0–100%</td>
</tr>
<tr>
<td>N</td>
<td>Sample nr.</td>
<td>RWEP06–RWEP08</td>
</tr>
<tr>
<td>θ</td>
<td>Phase</td>
<td>T = Total, OM = organic matter, CM = clay-rich matrix, C = Calcite, F = Fossil, P = Pyrite, NF = Non-Fossil</td>
</tr>
<tr>
<td>M</td>
<td>Method</td>
<td>BIB = BIB SEM or MIP = MIP</td>
</tr>
<tr>
<td>x</td>
<td>Resolution</td>
<td>36, 104, 54 (for BIB-SEM), 3 (for MIP) nm</td>
</tr>
<tr>
<td>*</td>
<td>Extrapolated</td>
<td>-</td>
</tr>
</tbody>
</table>

Please cite this article as: Klaver, J., et al., BIB-SEM study of the pore space morphology in early mature Posidonia Shale from the Hils area, Germany, Int. J. Coal Geol. (2012), doi:10.1016/j.coal.2012.06.012
and parallel to the longest axis of the mica (Fig. 9I, J). These pores are rare and do not significantly contribute to the total visible porosity. Pyrite frambooids in RWEP06 have low porosities with equidimensional shapes controlled by the arrangement of single pyrite grain (Fig. 9F), whereas in RWEP08 the pyrite frambooids are non-porous and calcite-cemented (Fig. 9K, L).

Moreover, because of different magnifications used for SEM imaging, the practical pore resolution is different for each mosaic (Table 3) and this affects the pore statistics described below. The largest pores seen in a mosaic are between 500 and 4000 nm in diameter (Fig. 5).

### 4.5. Pore size distributions from BIB-SEM data

Because of the limited spatial resolution of the BSE and EDX detectors (about few μm) and the sub-micron grains in the clay matrix, pores in the clay matrix cannot be accurately classified by mineralogy like we did for pores in the carbonate fossils. Therefore, for the calculation of pore size distributions, the total porosity seen by BIB-SEM is written as the sum of the porosity associated with carbonate fossils and the porosity associated with non-fossil phases (see Eq. (3)).

Moreover, because of different magnifications used for SEM imaging, the practical pore resolution is different for each mosaic (Table 3) and this affects the pore statistics described below. The largest pores seen in a mosaic are between 500 and 4000 nm in diameter (Fig. 5).

#### 4.5.1. Pore size distributions of carbonate fossils

In both samples, regardless of the magnification and the mosaic area, pore areas in carbonate fossils follow a dual-power-law distribution (Fig. 10A-C). From bin center 1500, 12,300 or 3000 nm² to bin 24,600 nm², pore areas are power-law distributed with an exponent around 2 (D=3.02, 3.34 and 2.65 with Log C=−6.96, −6.39 and −6.87, for RWEP06_Mosaic-I, RWEP06_Mosaic-II and RWEP08, respectively). From bin 24,600 nm² to bin 196,600, 393,200 or 1,572,900 nm², the pores are also power-law distributed but with an exponent around 1 (D=3.02, 3.34 and 2.65 with Log C=−6.96, −6.39 and −6.87, respectively). Pores below bin 24,600 nm², contribute 32, 15 and 24% to the porosity associated with non-fossil phases (see Eq. (3)).

4.5.2. Pore size distributions of non-fossil pores

Size distributions were analyzed for the pore population excluding both the pores, which were interpreted as microcracks formed after coring and the pores in the carbonate fossils (Fig. 10). In both samples, regardless of the magnification and the mosaic area, pores in non-fossil phase follow a power-law distribution (Fig. 10D-F). From bin center 1500, 12,300 or 3000 nm² to bin center 6,291,500 or 12,582,900 nm², pore sizes are power-law distributed with an exponent around 2 (D=1.9±0.15, 2.02±0.07 and 2.2±0.12 with Log C=−3.3±0.76, −2.4±0.40 and −1.8±0.66, respectively).

### 4.6. Pore throat distributions inferred from MIP

Mercury porosimetry data indicate a 3D bulk connected porosity of 5.44% and 7.33% for RWEP06 and RWEP08, respectively (Fig. 11A, B). A significant amount of mercury is injected in the 60–240 μm (RWEP06) and 45–300 μm (RWEP08) pore throats range followed by a low intrusion curve (Fig. 11C, D) contributing to the total intruded porosity (Fig. 11A, B). However, these large pore sizes were never seen in the microstructural investigations on the BIB cross-sections. Injection volumes in these pore throat ranges are interpreted as cracks, filling of the container and surface roughness, also known as confinement errors (Sigal, 2009). MIP curves are thus corrected by subtracting the first part of the intrusion data from the total in order to provide realistic MIP porosity (Fig. 11A, B, C and D). The point from which the data should be subtracted is in the range between the largest pore imaged by the SEM and the start of the low intrusion seen in the MIP data (60 and 45 μm, respectively). The largest imaged equivalent pore diameters are deq =4.3 μm in RWEP06 and deq =4.5 μm in RWEP08. Thus, the MIP data are corrected by...
excluding data in the range from 60 to 4.5 μm and 45 to 4.5 μm for RWEP06 and RWEP08, respectively. Therefore, the porosity provided from corrected MIP data is in the range of 3.4–3.7% for RWEP06 and 3.3–3.6% for RWEP08. For sample RWEP06, the highest mercury porosity contribution (8%) is at a pore throat diameter of 6 nm and 67% of the mercury is injected in pore throats below 11 nm in diameter (Fig. 11C). Sample RWEP08 shows similar results with a highest mercury porosity contribution of 8.5% at a pore throat diameter of 7.2 nm and also 67% of the mercury is injected in pore throats below 11 nm in diameter (Fig. 11D). Comparison of intrusion and extrusion MIP curves (Fig. 11E, F) indicates that about half of the mercury remained in sample RWEP06 (Fig. 11E) and two third in sample RWEP08 (Fig. 11F). Probably the mercury remained in the pores due to the ink-bottle effect (Moro and Böhni, 2002). This is confirmed by the sample weight increase measured after the mercury intrusion-extrusion cycle, indicating a residual filled porosity of 1.13% (RWEP06) and 1.50% (RWEP08). Pore throat to pore body ratios are calculated (Fig. 11G, H) based on Janssen et al. (2011) and Webb (2001). Differences in mercury intrusion and extrusion curves point to pore body-pore throat diameters (Fig. 11I, J), we show that pore throat diameters are power-law distributed over the entire MIP pore size resolution (i.e., from 3 nm to 4622 nm pore throat diameter) with power-law exponents similar for both samples (D = 2.42 ± 0.07 for RWEP06 and D = 2.45 ± 0.08 for RWEP08).

5. Discussion

The combination of BIB milling for high quality surface preparation and SEM imaging gives access to much larger areas than FIB (Ambrose et al., 2010; Curtis et al., 2012; Desbois et al., 2009; Heath et al., 2011; Keller et al., 2011; Sisk et al., 2010; Sondergeld et al., 2010) so that representative areas in shales can be studied to quantify the microstructure and pore space. The comparison of BIB-SEM and MIP offers the possibility to link pore morphologies to bulk properties. Considering that the BIB-polished surfaces are flat, and that the edges of pores intersected by BIB are sharp with radii less than a nm, the BIB-polished surfaces can be considered as 2D sections through the material. Using the basic principles of stereology (Underwood, 1970), the 2D area fraction in a REA is a good estimate of the 3D bulk porosity. The differences between the BIB-SEM results and MIP will only be due to the unconnected porosity and differences in resolution of small pores.

5.1. Microstructural evaluation

Mineral content, vitrinite reflectance and TOC give results very similar to those of other studies of Posidonia Shale (Littke et al., 1988; Mann, 1987; Rullkötter et al., 1988). Our samples are typical of the upper calcareous shale unit at low maturity. An area of 140×140 μm² is interpreted to be representative (up to at least mm scale) based on the BIB cross-section in terms of mineralogy and porosity (Fig. 4), when large organic particles (about 15×100 μm² in Figs. 4, 6B) are not taken into account. Because of the low frequency and low porosity of such organic particles, this does not significantly affect the overall porosity in these samples. Pore morphologies and sizes are similar for both samples and are clearly related to the mineralogy (Fig. 9). At the scale of observations, the largest pore sizes (typically several microns) are found in large calcite grains (Figs. 7–9), and the smallest ones in the matrix. A significant part of the porosity visible in SEM images is associated with carbonate fossils (about 20% of porosity down to the practical BIB-pore resolution, Table 4), which are embedded in the matrix. Organic matter exhibits only few intra-particle
pores (<30 nm when visible) and most of the pores (with width around 200 nm and axial ratio about 3, Fig. 9A) related to organic matter are located at interfaces with matrix.

Pore areas detected by BIB-SEM, both in carbonate fossils and non-carbonate fossils, are interpreted to have power-law distributions (Fig. 10). This enables comparison of the pore size distributions. A power-law distribution of pore throats is also interpreted from the MIP data (Fig. 11I, J).

The dual-power-law distribution of pore areas in carbonate fossils (Fig. 10A-C) implies that pores smaller than bin 24,600 nm² contribute progressively less to the porosity of carbonate fossils. As the break in slope occurs both in the range where pores are fully resolved and at the same length scale in all three mosaics, the dual-power-law distribution of pore areas in carbonate fossils is interpreted to represent the porosity in the carbonate fossils. Because of the progressively lower contribution to porosity below bin 24,600 nm², we interpret that the total porosity associated with carbonate fossils is virtually resolved by BIB-SEM (Table 4). In Bour et al. (2007), rectangular-shaped, sub-micrometer-size pores have been observed corroborating our interpretations. Pore areas of the non-fossil phase follow a single power-law distribution with power-law exponents D of 2.02±0.07 and 2.2±0.12 for the representative mosaics of RWEP06 and RWEP08, respectively, which suggests that the small pores contribute significantly to the visible porosity in non-fossil phase.

Significant contribution of small pore throats to the overall connected porosity is also emphasized by the MIP data which show that pore throat diameters are power-law distributed with power-law exponents D of 2.42±0.07 and D=2.45±0.08 for RWEP06 and RWEP08, respectively (Fig. 11I, J). Because the carbonate fossils are fully embedded in matrix, we expected comparable power-law exponents from BIB-SEM measurements for non-fossil pores and MIP data. However, these are quite different; the contribution of small pores being significantly higher from results given by MIP data. This discrepancy suggests that a significant part of porosity in the matrix is not connected.

5.2. Estimation of bulk porosity from BIB-SEM microstructural data

The porosity resolvable with BIB-SEM is lower than porosities found in early mature Posidonia shale by Mann (1987) and measured with MIP. The reason for this is that MIP measures porosity connected by pore throats down to 3 nm in diameter compared to 36 nm corresponding to the minimum practical pore diameter imaged using BIB-SEM (Table 1). Resolvable porosities in BIB-SEM of a REA are comparable for both samples (2.75% and 2.74% for RWEP06 and RWEP08, respectively) and significantly higher than the porosity accessed by MIP at comparable pore throat diameter (Fig. 12A and B). In order to compare MIP porosity and BIB-SEM porosity at smaller pore sizes, the power-law distributions described above are used to extrapolate BIB-SEM pore data down to pore size of 3 nm in diameter. To do this, we assume that bulk porosity is given by

$$\phi_{\text{BIB}}^{\text{06}} = \phi_{\text{MIP}}^{\text{06};\text{NF}} + \phi_{\text{BIB}}^{\text{06};\text{F}}$$

and that pores un-resolved by the BIB-SEM approach follow the same power-law distributions defined in Section 4.5 and Fig. 10. This results in $$\phi_{\text{BIB}}^{\text{06};\text{NF}} = 4.34\%$$ (3.41–6.01%) and $$\phi_{\text{BIB}}^{\text{06};\text{F}} = 6.13\%$$ (3.47–13.36%). The extrapolated BIB-SEM porosities are thus higher than...
porosities measured by MIP (Fig. 12). These differences are discussed in the following section in order to link BIB-SEM microstructural observation with MIP data.

5.3. Linkage of BIB-SEM data with MIP data resulting in a pore model based on microstructures

In other studies good agreement has been found between pore data acquired by imaging and mercury intrusion in other comparable studies based on low permeable and low porous rocks (Curtis et al., 2010, 2011a; Heath et al., 2011; Loucks et al., 2009) but can also be problematic (Hildenbrand and Urai, 2003) if pore collapse occurs during mercury intrusion at high pressure. In the present contribution the intrusion of mercury into the pore space is demonstrated by the increase of sample weight after MIP experiment and hysteresis between intrusion and extrusion (see Section 4.6).

In Section 5.2, we noticed that $\phi_{\text{BIB}} - \phi_{\text{MIP}} > 0.06$ or $\phi_{\text{MIP}} > 0.06$ and $\phi_{\text{BIB}} - 0.104 > 0.06$ or $\phi_{\text{BIB}} > 0.06$ (Fig. 12). Because MIP measures only connected porosity, these discrepancies mean that a significant part of the pore space resolved in BIB mosaics is not connected at pressures corresponding

Please cite this article as: Klaver, J., et al., BIB-SEM study of the pore space morphology in early mature Posidonia Shale from the Hils area, Germany, Int. J. Coal Geol. (2012), doi:10.1016/j.coal.2012.06.012
to the practical pore resolution. This is also corroborated by MIP data that illustrates that most of the pore space (67%) is filled with mercury in pore throats smaller than 11 nm (Fig. 11A–D) for both samples, with maximum intrusion volumes measured for pore diameter of 6 and 7.2 nm (Fig. 11C, D; for RWEP06 and RWEP08, respectively). Therefore the pore space imaged in BIB mosaics is not representative of pore throats because they are not resolvable down to the practical pore resolution. In other words, this suggests that the pore space imaged in BIB-SEM mosaics is not representative of pore throats because they are not resolvable down to the practical pore resolution. In this case, the power-law exponent for pore throat distribution inferred from MIP data (D = 2.4–2.5, Fig. 11I, J) may be representative for the clay-rich matrix.

6. Conclusions

1. Porosity resolvable by BIB-SEM is 2.75 and 2.74% for the two samples RWEP 06 and RWEP08, respectively. This method can resolve pores of around 10 nm diameter, and allows qualitative and quantitative study of porosity.

2. Using a combination of BSE and SE detectors and semi-quantitative segmentation of the gigapixel images, we found that at the mm-scale the representative area of the samples is around 140×140 μm².

3. Different pore morphologies are found in fossils, calcite, organic matter and pyrite framboids.

4. Pore areas are power-law distributed with a power-law exponent of about 2 for the pore population that excludes the fossils. Pores in the fossils show dual-power-law distribution with power-law

Table 4

Porosity inferred from BIB-SEM analyses and MIP at the practical pore resolution in mosaics covering REA, for the carbonate fossils and in the large calcite pores (LCP).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BIB-SEM Mosaic</th>
<th>Fossil</th>
<th>LCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>RWEP06</td>
<td>1.99%</td>
<td>0.42%</td>
<td>0.66%</td>
</tr>
<tr>
<td>RWEP08</td>
<td>2.15%</td>
<td>0.41%</td>
<td>0.40%</td>
</tr>
</tbody>
</table>

In regards to these interpretations, porous carbonate fossils and large pores in calcite grains which contribute the most to the porosity in BIB-SEM data, (Table 4), are interpreted to be embedded in a low permeable and low porous matrix. We propose also that the pore connectivity of the matrix is controlled by the clay-rich matrix.

Fig. 10. Pore size distribution of pore area in the carbonate fossils and non-carbonate fossils phases inferred from BIB-SEM methods in mosaics I and II of sample RWEP06 and in sample RWEP08. Data are plotted as the logarithm of normalized frequency of pore as a function of the logarithm of binned pore area (Eq. (2), Fig. 5). As in Fig. 5, filled marks are pore area fully resolved whereas white-filled markers are pore area still detectable but not fully resolvable at BIB-SEM resolution. Vertical dashed lines bound the power-law distribution and middle vertical dashed lines indicate slope break observed for pore area distribution in carbonate fossil, equivalent pore diameter is given in the boxes below. Solid line through data is the best fit and surrounding dashed lines represent the error of the fits. Resulting power-law exponent (D) and Log [C] are given in each plot.

Please cite this article as: Klaver, J., et al., BIB-SEM study of the pore space morphology in early mature Posidonia Shale from the Hils area, Germany, Int. J. Coal Geol. (2012), doi:10.1016/j.coal.2012.06.012
Fig. 11. Results from MIP measurement performed in both samples RWEP06 (left) and RWEP08 (right). (A–B) Cumulative porosity as a function of pore throat diameter. Raw data are indicated by filled markers and corrected data by hollow markers. Indicated errors bars are based on cut-offs used to correct the data, see text for more details. (C–D) Contribution to the total porosity as a function of pore throat diameter. Raw data are indicated by filled markers and corrected data by hollow markers. The vertical dashed line indicate the pore throat which contributes the most to the total porosity. (E–F) Normalized cumulative filled pore space versus pore throat diameter for the corrected intrusion and extrusion measurements. (G–H) Pore body to pore throat ratio versus pore throat diameter. (I–J) Logarithm of the normalized frequency of pore throat diameter versus the logarithm of the pore throat diameter. The solid line represents the best fit of the data. Resulting power-law exponents (D) are given in each plot.
exponents of about 1 for pores smaller than bin middle 24,600 nm² ($d_{eq} = 177$ nm) and 3 for pore areas above this size. 5. Extrapolation of power-law for pore area unresolved by BIB-SEM to the pore resolved by MIP (hollow marker) as a function of equivalent pore (throat) diameters for the sample RWEP06 (A) and RWEP08 (B).

5. Extrapolation of power-law for pore area unresolved by BIB-SEM to the pore resolved by MIP (hollow marker) as a function of equivalent pore (throat) diameters for the sample RWEP06 (A) and RWEP08 (B).


Acknowledgments

We gratefully acknowledge an anonymous reviewer and Andrew Aplin for their constructive comments which much improved the manuscript. The authors would like to show their gratitude to U. Wollenberg for his help with the XRD analyses, BIB-milling and SEM imaging and to M. Houben and S. Hemes for the pleasant and fruitful discussions during the project. We would like to thank K.A. Wilkins for his help with the pore segmentation, and thank D.R. Aretz for the AFM analyses.

References


