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

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ABSTRACT

This contribution reports on the study of the pore space morphology in two early mature ($VR_r = 0.59$ and 0.61) samples of Posidonia Shale from the Hils Syncline in Germany, using Broad Ion Beam (BIB) polishing and high resolution Scanning Electron Microscopy (SEM). This allows imaging pores with resolution down to 10 nm in equivalent diameter (d_{eq}), and quantitative estimation of porosity. Using a combination of BSE and SE detectors and semi-automatic segmentation of the gigapixel images, the representative elementary area of the samples, on the scale of a few mm, is inferred to be about $140 \times 140\ \mu m^2$. Pore morphologies and pore sizes are clearly related to the mineral fabric, with large differences: very large (typically several microns) pores with internal faceted crystal morphology in recrystallized calcite clasts, and smaller pores ($d_{eq} < 1024$ nm) in clay-rich matrix and in *cf. Schizosphaerella* nanofossils (typically 200 nm). Pores are less common in organic material and in pyrite aggregates. Pore characteristics are very similar for both samples, and porosity resolvable by BIB-SEM is 2.75 and 2.74%. Pore size distribution can be described by a power-law, with an exponent about 2.0 and 2.2, respectively, for the pore population excluding the fossils. Pores in the carbonate fossils show dual-power-law distribution with power-law exponents of about 1 and 3. By extrapolating the power-law distribution for each sample, total porosity is estimated to be 4.8% (−0.9, +1.7%), and 6.5% (−2.7, +7.2%), respectively. This estimate can be compared with 3.4–3.7 and 3.3–3.6% as measured by mercury injection porosimetry. We interpret this difference to reflect the unconnected (for mercury) part of the porosity. Comparison of imaged pores and mercury injection porosimetry suggest a very high pore body to pore throat ratio. This results in a pore model where large pores, represented mainly by pores in fossils and calcite grains, are connected via a low-porous (and low-permeable) clay-rich matrix with pore throats below 10 nm in both samples.

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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 wide-spread 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

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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 $10\times10\times10$ μm^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 mm^2) 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 claystones 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-derived 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_r 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 RWEP06 and RWEP08. 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 RWEP06 and RWEP08 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 RWEP06 and RWEP08 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 ($\sim0.5\times0.5\times0.5$ cm^3) 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 mm^2 (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

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