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Research paper

BIB-SEM characterization of pore space morphology and distribution in postmature to overmature samples from the Haynesville and Bossier Shales

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Four Haynesville Shale and four Bossier Shale samples were investigated using a combination of Scanning Electron Microscopy (SEM) and Broad Ion Beam (BIB) polishing. This approach enables the microstructure and porosity to be studied down to the mesopore size (<50 nm) in representative areas at the scale of the BIB cross-sections. The samples vary in mineralogy, grain size and TOC and the maturity ranges from 2.42 to 2.58 VR_r in the Haynesville Shale to 1.79–2.26 VR_r in the Bossier Shale. This variety within the samples enabled us to study controls on the porosity distribution in these shales. Visible pores exist as intraparticle pores mainly in carbonate grains and pyrite framboids and as interparticle pores, mainly in the clay-rich matrix. Pores in organic matter show a characteristic porosity with respect to the type of organic matter, which mainly consists of mixtures of amorphous organic matter and minerals, organic laminae and discrete macerals. A clear positive trend of organic-matter porosity with maturity was found. Pore sizes are power law distributed in the range of 4.4 μm to at least 36 nm in equivalent diameter. The differences in power law exponents suggest that a more grain supported, coarse-grained matrix may prevent pores from mechanical compaction. Porosities measured in the BIB cross-sections were significantly lower in comparison to porosities obtained by Mercury Intrusion Porosimetry (MIP). This difference is mainly attributed to the different resolution achieved with BIB-SEM and MIP and type of pore network. Extrapolation of pore size distributions (PSDs) enables the BIB-SEM porosity to be estimated down to the resolution of the MIP and thus to upscale microstructural observation at the confined space of the BIB-SEM method to bulk porosity measurement. These inferred porosities are in good agreement with the MIP determined porosities, which underpins the assumption that pores segmented in BIB-SEM mosaics are representative of the MIP methodology.

1. Introduction

Organic-rich shales are key petroleum source rocks and have become key gas and oil reservoirs. They are heterogeneous and the controls on the evolution of porosity, pore geometry and permeability are incompletely understood (Jarvie, 2012; Soeder, 1988). Also, analyses of conventional porosity measurements on these fine-grained rocks with low porosities and permeabilities can be difficult because, for example, of core damage. In addition, direct observation of pore space is still challenging because most of the pores are below micrometer in size. The link between bulk measurements and microstructures remains elusive but is essential for understanding of the pore properties at various scales.

Bulk measurements of porosity and permeability of such clay-rich and fine-grained rocks can be achieved by different methods. The most popular and quick technique is Mercury Intrusion Porosimetry (MIP). MIP provides a bulk porosity for the connected porosity with pore throat sizes down to 3 nm in diameter, at equivalent intrusion pressures according to the Washburn equation (Washburn, 1921). The intrusion volumes per pressure step are interpreted as a pore (throat) size distribution. Another widely used porosimetry technique is gas adsorption (N_2, CO_2, CH_4, Kr), which provides the surface area and the pore size distribution of pores

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from 300 nm down to the micropore (<2 nm) size range. The above mentioned techniques provide quantitative and reproducible porosity data, but they are not able to give direct information about real pore geometries and their connectivity. Moreover, pore size distributions (PSD) derived from such indirect methods are based on models of tube, slit or spherical-shaped pores, which are not observed in the actual samples (see e.g., Desbois et al., 2009; Loucks et al., 2009; Schieber, 2010). Furthermore, MIP does not account for side effects such as: deformation (Horseman et al., 1996), which may result in pore collapse; the ink-bottle effect (Münch and Holzer, 2008), which underestimates pore sizes; omnidirectional intrusion (Hildenbrand and Urai, 2003), which may lead to effective stresses and mask microstructural anisotropy (Esteban et al., 2006); and core damage. Imaging these fine-grained rocks at high magnification would provide insight in the actual pore sizes, their morphology and distribution, anisotropy of the microstructure and core damage like cracks because of drying, stress release and sample preparation.

A recent alternative to directly study the pore network in fine-grained rocks is based on the combination of Focused Ion Beam (FIB) with a gallium ion (Ga^+) source to prepare high quality cross-sections, and Scanning Electron Microscopy (SEM). This technique, known as FIB-SEM, allows the three dimensional pore network to be constructed down to the SEM resolution of various rocks (Ambrose et al., 2010; Curtis et al., 2010; Desbois et al., 2009; Holzer et al., 2004; Keller et al., 2011; Tomutsa et al., 2007). With FIB-SEM only a limited sample volume can be investigated (typically around $10 \times 10 \times 10\ \mu m^3$), which may not be representative, even in fine-grained materials (Houben et al., 2013; Klaver et al., 2012).

Broad-Ion-Beam (BIB) polishing in combination with SEM (Desbois et al., 2010, 2009, 2011b; Houben et al., 2013; Klaver et al., 2012) provides (a) an alternative to study larger areas, i.e., up to 2 mm^2, at the resolution of an SEM (<5 nm) and (b) the potential to do serial sectioning (Desbois et al., 2013). The use of Argon ion beam milling reveals new insights into the combination of pore and microstructures, which were previously poorly resolved, and opens a new field of up-scaling microstructural investigations. Desbois et al. (2009) first described different pore types in clay using this method. Loucks et al. (2009) presented an investigation using BIB-SEM on the pore morphology, genesis, and the pore size distribution of a prolific shale gas producer, the Barnett shale in Texas, USA. Other researchers described various pore types in fine-grained rocks using a similar approach (e.g., Curtis et al., 2010; Heath et al., 2011; Milner et al., 2010; Schieber, 2010). A comprehensive overview of pore classification in mudrocks is given in Loucks et al. (2010, 2012). The quantification of pore microstructures on representative areas of prominent cap rock, Opalinus Clay, and source rock, Posidonia Shale, was carried out by Houben et al. (2013) and Klaver et al. (2012) respectively. Both studies found that the pore sizes follow a power-law distribution. This enables the extrapolation of porosity, for comparison with MIP, to be undertaken with higher confidence. In these two studies, the authors found that each mineral phase have their own pore characteristics. This link suggests a novel porosity model based on "elementary building blocks" (Desbois et al., 2011a).

Previous studies dealing with microstructure imaging in the Haynesville Shale focused mainly on the qualitative description of porosity and fabrics (Chalmers et al., 2009, 2012; Curtis et al., 2010, 2012b, 2011b). Curtis et al. (2010, 2011b; 2012b) found that the Haynesville Shale is different from other US shales as it contains little kerogen and its porosity is mainly associated with phyllosilicates. Pores of 3 nm width in clay using STEM were imaged (Curtis et al., 2011b). According to Curtis et al. (2010; 2012b), the Haynesville Shale has a porosity of 2 % in a 3D FIB-SEM reconstruction, located mainly in triangular and linear pores associated with phyllosilicates, suggesting a sheet-like, connected pore network. Hammes et al. (2011) described lithofacies in the Haynesville shale with the help of BIB-SEM and reported organic and moldic pores. To our knowledge, there are no quantitative, published evaluations of pore systems on Haynesville and Bossier Shales using BIB-SEM.

Porosity associated with organic matter is an important part of the pore system of gas-mature source rocks and may be critical for both gas storage and production (Bernard et al., 2012; Chalmers et al., 2009; Curtis et al., 2012a; Fishman et al., 2012; Jarvie et al., 2007; Milliken et al., 2013).

This paper focuses on the qualitative and quantitative physical porosity (Pearson, 1999) of the Haynesville and Bossier Shales with a special focus on pore morphologies, pore size distributions, visible porosities and organic-matter porosity. The relative roles of TOC, thermal maturity, mineralogy and grain size on porosity are discussed. Pore characteristics for each mineral phase are described which enable up-scaling scenarios based on "elementary building blocks" (Desbois et al., 2011a) and are relevant for reservoir evaluation and flow modeling (Clarkson et al., 2011; Jiang and Spikes, 2013). Finally, the PSDs are compared with the MIP bulk porosities of these shales. These findings and their implications for storage and transport are addressed in the final part of the discussion.

2. Materials and methods

2.1. Samples

This contribution focuses on the detailed study of eight shale samples selected to cover a broad range in mineralogy, Total Organic Matter (TOC) and porosity. Four samples from both the Haynesville Shale formation and four samples from the Bossier Shale formation in Louisiana, provided by SHELL Global Solutions International B.V., were analyzed. The range of in TOC, maturity, mineralogy and grain size enabled us to study the controls of these parameters on the porosity distribution in the shales.

The mineral content of all samples was provided and determined using x-ray diffraction. The Haynesville Shale samples (SBI 9-4, SBI 8-2, SOM 4-4 and SOM 9-2, Table 1) consist of 40 wt. % quartz and feldspar. The carbonate and clay content range from 16–32 wt. % and 28–44 wt. % respectively (Table 1). The TOC varies from 2.8–5.6 wt. % with MIP connected porosities between 9.2 and 7.5 %. Lithology ranges thus from silty argillaceous shale to silty calcareous shale (Table 1).

The four Bossier Shale samples (SHSI 6-2, SHSI 1-6, SCN 3-6 and SMY 4-2) have a quartz and feldspar content between 11–32 wt. %, with large differences in carbonate and clay contents of 11–79 wt. % and 10–60 wt. % respectively. TOC was only given for two samples and values are lower compared to the Haynesville Shale: 0.5 % for SHSI 1-6 and 1.4 % for SCN 3-6. MIP connected porosities are also lower and range from 2.2 to 6.9 %. Lithologies differ even more than in the Haynesville Shale and vary from argillaceous mudstone/shale to marly (dolomitic or calcareous) mudstone (Table 1).

2.2. Organic petrography

Polished sections of whole rocks were prepared perpendicular to bedding planes in order to study the samples in incident white light to measure vitrinite reflectance. Solid bitumen reflectance was measured when vitrinites were scarce. The solid bitumen reflectance measurements were converted to vitrinite reflectance using the correlation of Schoenherr et al. (2007). The authors refer to Littke et al. (2012) for preparation procedures and microscopic methods. Vitrinite and solid bitumen reflectance was conducted in oil immersion at 500 times magnification according to standard