

# **Quantitative analysis of the pore structure of premature-to-postmature organic rich mudrocks using small angle neutron scattering**

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## **Summary**

The pore structure of organic rich mudrocks is associated with both inorganic and organic constituents. The contribution of organic matter to the pore structure has been investigated on Posidonia and Bossier Shale samples having different organic carbon content and thermal maturity. Development and distribution of organic matter pores were studied by using small angle neutron scattering technique at a broad pore scale size investigation, from 2 nm to 2  $\mu$ m. The pore structure of the mudrocks studied is highly complicated at which total pore volume and specific surface area are not significantly affected by thermal maturation, however, the maturity attribute contributes to different pore size distribution on meso- and macro-pores. Thermal maturation is likely to be the factor of amalgamating small organic matter pores into larger pores in overmature organic rich mudrocks, potentially causing an increase in pore volume at macroscale pores. Although not considerably, the increased macroporosity can enhance the permeability of pore network for viscous gas flow in organic rich mudrocks.

The pore structure of mudrocks is not only confined to the mineral-mineral interface (inter- and intra-particle pores), but it is also associated with organic matter (OM) (Javadpour, 2009). Inorganic- and organic-related pore network leads to the natural permeability pathways for fluid transport in mudrocks (Loucks *et al.*, 2009). OM pores appear to be intraparticle pores located within solid kerogen. These are likely to be part of an inter-connected pore network because of the interconnectivity of OM particles resolved in 3D Focused Ion Beam (FIB) SEM analysis (Loucks *et al.*, 2012). Varying from few micrometers to a few nanometers in size as well as interfacing large to small minerals (e.g. quartz/carbonates and clays, respectively), the contribution of OM to the pore structure of mudrocks is associated with all pore size scales from macro- to micropores (Kuila, 2013, Furmann *et al.*, 2016). Development and distribution of OM pores is controlled by thermal maturity, kerogen type, abundance of maceral groups, and organic richness, and all of these attributes contribute to both the total porosity, the pore size distribution (PSD) and proportions of micropore, mesopore, and macropore volumes (Curtis *et al.*, 2012, Mastalerz *et al.*, 2013). Image-based techniques are broadly used to semi-quantitatively characterise the pore structure of organic rich mudrocks, however pore morphologies can change at different scales because of depositional and burial diagenetic history (Chiou *et al.*, 1991), which remain challenging to resolve completely with such techniques. Neutron scattering provides a quantitative analysis of the inter- and intra-particle pore system at a broad pore scale range of ~1nm to ~20µm. In this study, small angle neutron scattering (SANS) combined with very small angle neutron scattering (VSANS) (Radlinski, 2006) have been conducted on Posidonia Shale and Bossier Shale samples of different maturity. The black shales are of interest in industry and academia due to the increasing demand to produce gas from shales around the world. The pore characteristics of these shales have been investigated to understand the fluid transport properties as well as the effect of thermal maturation on the pore structure. The results can provide influential information in order to adopt economically suitable scenarios to produce natural gas from these formations.

Two sample sets were studied from different locations, having different organic matter content, thermal maturity and burial depth. The differences in the nature of these samples allows investigating the thermal maturity controls on the pore structure. Mineralogical and petrophysical data are provided in Table 1.

- 1- Posidonia Shale: the Toarcian (Lias Epsilon) Posidonia Shale samples were obtained the Hills Syncline in northern Germany and are of Type II kerogen type. The shale intervals cored represent a large maturity range from very early mature to overmature gas window attributed to either Late Cretaceous magmatic heating or deep burial during the Late Jurassic and Early Cretaceous. Deposited in shallow marine environment with upper facies of calcareous shale and lower facies of marlstone, the samples have nearly similar mineralogy (Klaver, 2014, Klaver *et al.*, 2012).
- 2- Bossier Shale: these samples were obtained from the Bossier Shale formation in West Louisiana. They were deposited in a marine environment and lithologies vary from argillaceous to dolomitic or calcareous mudstone. The samples have different mineralogy and maturity, but limited TOC's over the ~100 m depth range (Klaver, 2014).

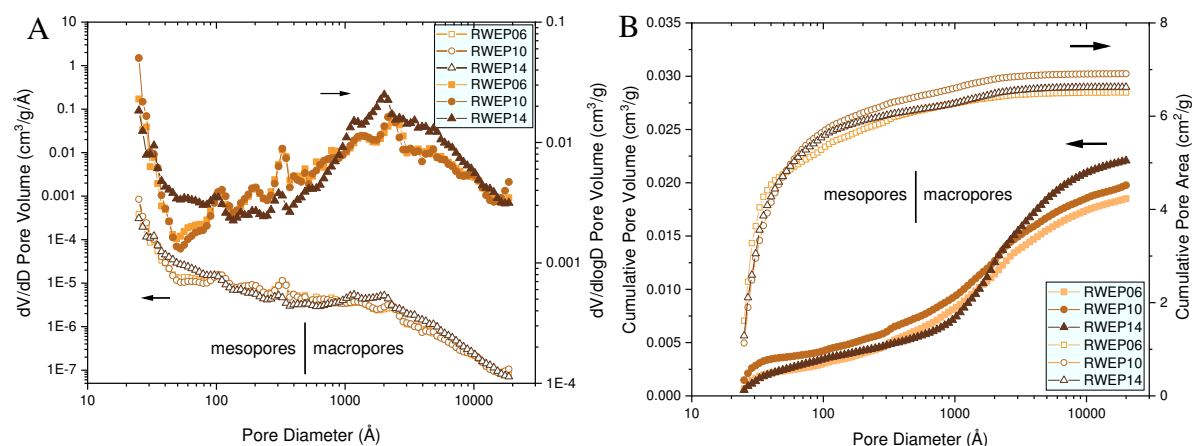
Sample	Quartz & K-feldspar	Carbonate Group	Clay Minerals	Burial Depth	TOC	Vitrinite Reflectance	Porosity	SSA
	%	%	%	ft	%	VRo, %	%	m <sup>2</sup> /g
<b>Posidonia Shale</b>								
<b>RWEP06</b>	17.3	42.6	23.4	NA	6.1	0.59	5.0	6.5
<b>RWEP10</b>	15.3	45.8	19.1	NA	4.4	0.91	5.5	6.9
<b>RWEP14</b>	14.0	45.8	18.4	NA	5.9	1.52	6.0	6.6
<b>Bossier Shale</b>								

<b>SHSI 1-6</b>	28.6	10.9	59.2	12012	1.3	1.81	2.6	6.4
<b>SHSI 6-2</b>	31.6	12.8	54.3	12050	1.3	1.79	3.2	6.9
<b>SMY 4-2</b>	10.9	78.1	9.9	12342	1.1	2.15	3.5	2.5

In order to characterise the pore structure of the mudrocks studied, SANS data was collected by two SANS instruments, each of which designed to scan a certain range of pore sizes. This was conducted at the Jülich Centre for Neutron Science (JCNS) outstation at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching, Germany. KWS-3 instrument is used to gain VSANS data at pore geometry between 5µm and 500nm (Pipich & Fu, 2015) and the KWS-1 instrument is utilised to deliver SANS data at pore size of 500nm to 1nm (Feoktystov *et al.*, 2015). Samples were cut parallel to bedding, fixed on quartz glass carriers, and polished to a thickness of about 200 µm. Samples were dried at room temperature, and measurements performed under ambient pressure and temperature conditions for standard measurements (Busch *et al.*, 2017). Specific surface area (SSA), porosity, pore size distribution (PSD) were calculated from scattering profile (I vs. Q data) by MATSAS for the entire sample set (Rezaeyan *et al.*, 2018).

## Results

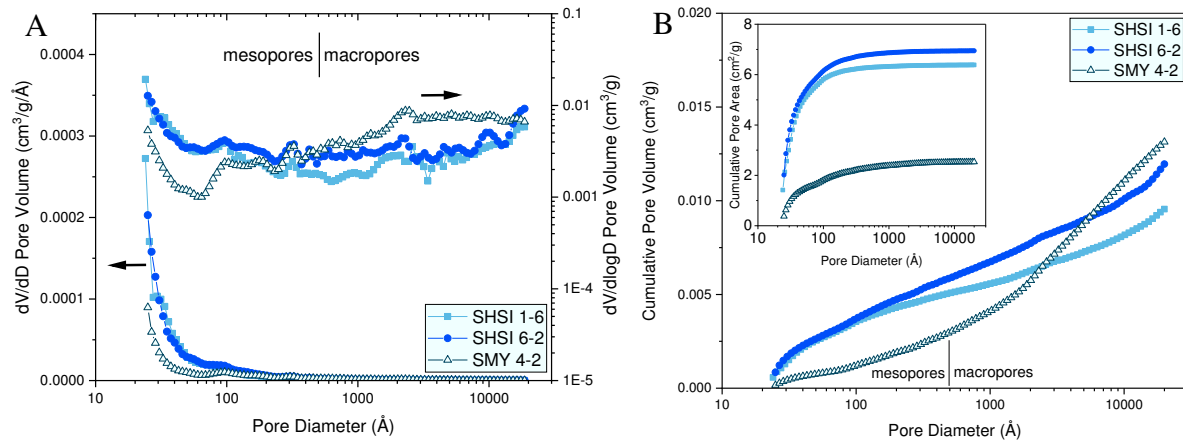
The three Posidonia Shale samples are mainly composed of carbonates (45 wt-%), followed by clay minerals (18-23 wt-%) and quartz and K-feldspar (14-17 wt-%, Table 1). As opposed to organic richness of the samples, ranging between 4 and 6 wt-%, vitrinite reflectance varies from 0.59 to 1.52 %. According to Table 1, the immature RWEP06 sample has a porosity of 5.0 % and SSA of 6.51 m<sup>2</sup>/g, the intermediate mature RWEP10 and overmature RWEP14 samples have similar porosities of 5.5 and 6.0 % and SSA of 6.91 and 6.62 m<sup>2</sup>/g, respectively. Thermal maturation has not appeared to notably change the total porosity and SSA of the mature and overmature samples, however, the effect of maturity is more apparent on the pore size distribution (Figure 1). The pore size distribution of immature and intermediate mature samples are similar on most of the pore scales as illustrated in Figure 1-A. Whereas, the pore structure of the overmature Posidonia Shale sample has obviously evolved at macropore sizes (Figure 1-B).



**Figure 1** Pore size distribution of Posidonia Shale with different maturity (A) and the cumulative pore volume and pore area (B).

The two argillaceous Bossier Shale samples, SHSI 1-6 and SHSI 6-2, have similar mineralogy and are dominated by clays (55-60 wt-%), quartz (~30 wt-%) and calcite (~12 wt-%). The two samples do not vary in TOC (1.3 wt-%) or maturity (VRo, ~1.8 %), and are recovered from almost the same depth. SMY 4 on the other hand is a calcareous mudstone mainly composed of calcite (~78 wt-%), followed by silicates (~10 wt-%) and clay minerals (~10 wt-%), and was buried 300 ft deeper than the other samples, therefore showing higher maturity (VRo, ~2.15 %). The porosity of Bossier Shale has not changed significantly (~3 %) with increasing burial depth, whereas in fact specific surface area has remarkably dropped by 2.5 times. Although similar in mineralogy and maturity, the argillaceous Bossier Shale samples feature slightly different pore size distribution at pore sizes >100 Å (Figure 2-A),

resulting in minor differences in pore volume and pore area (Figure 2-B). Compared to the argillaceous samples, the calcareous sample shows higher macroporosity and lower mesoporosity, leading to higher pore volume and lower SSA. Moreover, the pore structure of Calcareous Bossier Shale is highly complicated, and we expect that this is controlled by differences in compaction, mineralogy, and maturity attributes.



**Figure 2** Pore size distribution of Bossier Shale samples with different composition (A) and the cumulative pore volume and pore area (B).

## Discussion and Conclusion

Organic matter pores have appeared to be intraparticle porosity with different shape and size, which contribute to the effective pore network (Loucks et al., 2012). The size and number of OM pores control fluid conductivity in organic rich mudrocks in which kerogen type, organic richness, and thermal maturity can alter fluid flow properties. From previous studies on the same Posidonia Shale, the porosity and permeability of the overmature sample is higher than the mature one (Ghanizadeh *et al.*, 2014, Klaver et al., 2012), attributed to intraparticle micro- and mesopores within organic macromolecules. It was found that the slightly increased porosity of the overmature Posidonia Shale sample (RWEPI4), by one percent, is most likely associated with macropores. The same results were achieved for the Bossier Shale as well, where the amalgamation of small pores into larger pores during pore growth (Loucks et al., 2009) has led to a relative increase in macropore volume. The decline in SSA values as well as sharp increase in cumulative pore volume support the progressive amalgamation towards larger pores. This is attributed to the exsolution of gaseous hydrocarbons during the secondary thermal cracking of retained oil (Bernard *et al.*, 2012) and conversion of oil to solid bitumen followed by thermal cracking of bitumen to form porous pyrobitumen (Piane *et al.*, 2018), which generate additional smaller micropores to be amalgamated and preserved. Nonetheless, it should be noted that the development and distribution of pores in the organic matter of all organic-rich shales cannot be only controlled by thermal maturity (Curtis et al., 2012) since the transition of mineral-mineral interface, the development of organic-inorganic pores, and microfracture can alter the pore structure of Posidonia and Bossier Shales during thermal maturation.

However, small angle neutron scattering offer a full spectrum of pore size investigation (from ~2 nm to ~2  $\mu$ m) to quantify pores affected by thermal maturity. Although porosity has not increased significantly, it can be due to the rather closed nature of pore structure in such mudrocks as well as the low-to-intermediate maturity, the pore size distribution vary widely across the different pore sizes. The evolution of porosity in the overmature mudrock has led to a decrease in mesoporosity and increase in macroporosity where the fluid flow mechanism can be different. Regarding the increased permeability and porosity (yet, extremely low) as well as the preservation of abundant macropores in the overmature Posidonia and Bossier Shale intervals, and that the Darcy flow is the relevant dominant mechanism at macropores, the exploitation of the overmature intervals might economically be more favourable.

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