Possible structural deformation effects on the pore size characteristics of shale reservoirs: An example from the Lower Cambrian shales of the Eastern Upper Yangtze Platform, South China


Abstract
The effect of thermal maturity, organic matter (OM) type, physical and diagenetic processes, such as compaction, mineral dissolution, replacement and cementation in major unconventional shale gas resources have been widely addressed, however, the effect of structural deformation on shale reservoir properties, is not well understood. To examine possible effect(s) of structural deformation on the pore structure of shale reservoirs petrographic, low-temperature N2 and CO2 adsorption and mercury injection capillary pressure (MICP) analyses were carried out on fourteen Lower Cambrian shale samples from the Dabashan arc-like fold-thrust belt in northeastern Chongqing (Deformed Zone) and a slightly folded area in southeastern Chong (Non-deformed Zone). The shales in Deformed Zone (DZ) have a wider range of total organic carbon (TOC) content (mean = 7.8 ± 8.6 wt. %) than the Non-deformed Zone (NDZ) samples (mean = 6.2 ± 3.5 wt. %). Pore-filling pyrobitumen is the dominant organic matter constituent of the studied samples in the studied areas. Micropores are the dominant pores in both areas, while the mesopore and macropore surface area and volume are significantly higher in NDZ in comparison to DZ samples. The mean MICP porosity of DZ samples (1.4 ± 0.9%) is slightly higher than samples from the NDZ (1.1 ± 0.1%) samples. Detailed SEM observations of both sample sets reveal OM-hosted pores are the dominant type of pore in the NDZ samples while micro-fractures within the OM and at the interface of OM and minerals are dominant in the DZ samples. Mineral-hosted pores in carbonate minerals resulted from dissolution by corrosive fluids are abundant in both areas, while dissolution rims around carbonate minerals are more abundant in NDZ samples. A significant correlation between TOC and MICP porosity (R² = 0.83) suggest OM-hosted micropores are the major contributor to total porosity. The dominance of micropores in DZ samples in comparison to the NDZ samples suggests OM-hosted meso- (2-50 nm) to macropores (>50nm) in DZ samples are likely collapsed by the structural deformation related to tectonic compression, while micropores which have less impacted and subsequently are preserved. The initial results of this study suggest structural deformation may potentially change the pore structure of shale reservoirs.

Statement of the background
The nanometer- to micrometer-size pores, along with natural fractures, form the major storage space and flow path network for gas flow in shale reservoirs. Determining pore type, size distribution, is thus of central importance to evaluate the storage and flow capacity of hydrocarbon in shale reservoirs (Ambrose et al., 2010; Loucks et al., 2012; Milliken et al., 2013). OM- and mineral-hosted pores generally are the major contributor to the shale pore network. Therefore, kerogen composition, thermal maturity, organic matter richness, and diagenetic processes are the major controlling factors on organic porosity development in organic-rich shales (Loucks et al., 2012; Löhr et al., 2015; Katz and Arango, 2018). The effect of thermal maturity, organic matter (OM) type, physical and diagenetic processes, such as compaction, mineral dissolution, replacement and cementation in major unconventional shale gas resources have been widely addressed, however, the effect of structural deformation on gas storage properties, is not well understood.

Aims and Objectives

Previous studies on shale reservoir characteristics were commonly focused on shales from the same formation or different depositional environments but usually in the same tectonic setting. In contrast to the majority of North American shale gas resources that generally formed in relatively stable tectonic settings, the marine organic-rich shales in south China have experienced several episodes of intensive tectonic movements after hydrocarbon generation, such as the Indosinian (257 - 205 Ma), Yanshanian (199.6 - 133.9 Ma), and Himalayan (70 - 3 Ma) orogenies (Ma et al., 2004; Hao et al., 2013). A comparative study of the tectonic influence on shale OM porosity is thus of great significance for the understanding of shale reservoir systems. The Lower Cambrian and Upper Ordovician-Lower Silurian organic-rich shales in the Upper Yangtze Platform of South China are major regional target units for shale gas resource exploration and development (Zou et al., 2015; Zhao et al., 2016). Although measured shale gas content of the Lower Cambrian shales in the southern and northeastern part of Sichuan Basin is significantly high (gas yields of around 4.5 billion m$^3$), however, shale gas production of the Lower Cambrian shales is not economic. Therefore, a better understanding of major controlling factor(s) on reservoir properties of Lower Cambrian shale gas reservoir and possible effect(s) of structural deformation is essential to understand the properties and thus shale gas production behavior and potential in this prolific region.

Materials and methods

In order to investigate potential effect of structural deformation on shale reservoir characteristics, two set of samples from same stratigraphic interval (Lower Cambrian) from the Dabashan arc-like fold-thrust belt in the northeastern Chongqing (DZ; seven samples) and a slightly folded area in southeastern Chong (NDZ; seven samples) to compare their reservoir characteristics. TOC content (wt. %) was measured with a Leco-CS230 carbon and sulfur analyzer after the samples were treated first, with 10% hydrochloric acid to remove carbonate. Organic petrography, low-temperature N$_2$ and CO$_2$ adsorption, and mercury injection capillary pressure (MICP) analyses were performed on fourteen shale samples to investigate the possible effect of structural deformation on pore size characteristics of shale reservoirs. Scanning electron microscopy (SEM), Helium ion microscopy (HIM) were used to characterize OM and mineral-hosted pores as well as micro-fractures in the studied samples in order to differentiate any physical deformation in shale matrix and pores between DZ and NDZ. X-ray diffraction (XRD) and Quantitative Evaluation of Minerals by Scanning electron microscopy (QEMSCAN) were carried out to determine the mineralogical composition of studied samples and mineralogical composition variations.

Results and discussion

TOC content of the DZ samples is highly variable and ranges from 1.3 to 24.1 wt. % with a mean value of 7.8 ± 8.6 wt. %. The mean TOC value for NDZ samples is equal to 6.2 ± 3.5 wt. %, slightly lower than that of DZ samples with a range of variation from 2.5 to 10.9 wt. %. The mean random bitumen reflectance (%BRo), for DZ and NDZ samples, are 2.7 ± 0.1% and 3.6 ± 0.3%, respectively that indicates an over-mature maturity level. The OM (mainly pyrobitumen), in the studied samples occurs in three forms: (1) fine laminations of pyrobitumen that resemble the structure of precursor lamellar algae or algal accumulations; (2) pore-filling pyrobitumen; and (3) big fragments (25 – 100 µm) of bitumen engulfed within fracture-filled calcite and quartz.
Quartz, carbonate (calcite and dolomite), and clay minerals are major mineral constituents of the studied samples. Plagioclase, K-feldspar, and pyrite are the other mineral components in the studied samples. Illite is the major component of total clay content while chlorite has minimal contribution to the total clay content. Smectite and kaolinite are other clay minerals that are detected only in the NDZ samples. The mean quartz, illite, plagioclase, pyrite, and total clay content in NDZ samples are higher than those in DZ samples. Dolomite content in DZ samples is significantly higher than the NDZ samples while calcite content is almost similar in two sample sets.

Based on SEM observations, four major pore types were identified in the studied samples, those are (1) OM-hosted pores, (2) mineral-hosted or intra-crystalline pores, (3) micro-fractures within OM and minerals, and (4) dissolution rims around minerals. The dominant pore types in the sample with the highest TOC (24.1 wt. %) from DZ are intra-crystalline and micro-fractures within OM and minerals with sporadic OM-hosted pores. OM-hosted pores distribution in the DZ sample is sporadic while shrunk micro-fractures (e.g., Koo et al., 2016) within OM and at the OM mineral interface are the abundant type of OM-hosted porosity. Micro-fractures are also abundant in minerals in this sample. The majority of carbonate minerals in the rock matrix contain secondary pores that are the likely result of dissolution from organic acids during oil migration or degradation. OM-hosted pores in the NDZ samples, with pore diameters ranging from 5 to 100 nm (pores smaller than 5 nm are invisible under SEM), are the dominant pore types. The mineral-hosted pores and micro-fractures are also abundant in the NDZ samples. Dissolution rims around diagenetic minerals (i.e., calcite, dolomite), or between them, is another major type of pore in the NDZ samples.

The MICP porosity of DZ samples shows a wide range of variation from 0.4 to 2.6% (mean = 1.4 ± 0.9%, n = 5), with slightly higher than mean porosity of the NDZ samples that offers a small range of values from 0.9 to 1.2% (mean = 1.1 ± 0.1%; n = 4). The total pore area of DZ and NDZ samples do have a good correlation with MICP porosity, with a better correlation for DZ samples. The TOC content shows a significant correlation (R² = 0.83) with MICP porosity for all studied samples, while the correlations for DZ samples (R² = 0.87) is more significant.

The combination of CO₂ and N₂ adsorption derived pore size distribution (PSD) curves reveals that the majority of pores in both areas are in the range of micropores (Fig. 1A-B). However, some NDZ samples show unimodal peaks at approximately 5 nm in diameter (Fig. 1A) within the low end of the mesopore range. The PSD of NDZ samples is multi-modal spreading from 0.3 to 1 nm. The outcrop sample has multimodal peaks in the micropore range with one order of magnitude higher differential volume than the rest of the samples in the NDZ area. The PSD results further confirm the dominance of micropores in this sample that is not SEM-visible but can be detected with helium ion microscopy (HIM).

The BET specific surface area and BJH pore volume are significantly lower for the DZ samples in comparison to the NDZ samples (Fig. 1C-D). The BET specific area from the DZ samples, ranges from 0.7 to 8.2 (m²/g) with a mean value of 3.3 ± 3.2 (m²/g), while it ranges from 0.35 to 27.9 (m²/g) and a mean value of 15.4 ± 8.6 (m²/g) for the NDZ samples. The BJH pore volume for the DZ samples ranges from 0.003 to 0.004 (cm³/g), with a mean value of 0.004 ± 0.0006 (cm³/g), while it is highly variable and ranges from 0.0003 to 0.022 (cm³/g), with mean values of 0.012 ± 0.007 (cm³/g) in the NDZ samples (Fig. 1C-D).

Although OM-hosted (SEM-visible) pore network is not developed in the DZ samples, the majority of pores within the OM in this sample are micro-fractures and sporadic pores. Micro-fractures within OM usually do not visibly extend into the mineral matrix. Those micro-fractures, if not formed during sample retrieval from the subsurface, likely usually form due to devolatilization and natural fracturing during petroleum hydrocarbon generation and expulsion that lead to OM shrinkage (Sondergeld et al., 2013; Katz and Arango, 2018). In contrast to the DZ samples, the dominant SEM-visible pore space in the NDZ samples is OM-hosted pores that formed within pore-filling pyrobitumen. Overall, significant correlation (R² = 0.83; n = 9) between TOC and MICP porosity for all samples indicates that OM-hosted pores are likely the major contributor to total porosity of the studied samples.

Mineral-hosted or intra-crystalline pores in carbonate minerals are the dominant pore space in the DZ samples, which have higher dolomite and total carbonate contents in comparison to the NDZ samples. Intra-crystalline pores in matrix carbonate minerals are usually the result of chemical diagenesis and dissolution and are often secondary (Yang et al., 2016). Several hypotheses have been proposed for the formation of such pores including dissolution resulting from organic acid formation (Schieber, 2010) during kerogen transformation (Barth et al., 1988), or oil degradation (Seewald, 2003), or corrosive fluids related to oil migration (Ehrenberg et al., 2012) and/or acidic hydrothermal fluids. In a thermally mature shale, several of these hypotheses are improbable and in deformed settings, corrosive fluids may be redistributed within the basin.
Similar to conventional reservoirs the major processes that control pore space and shape in unconventional shale and tight reservoirs through time are depth related physical and diagenetic processes, such as compaction, dissolution, replacement and cementation (Ardakani et al., 2018; Fishman et al., 2012; Milliken and Curtis, 2016; Milliken and Olson, 2017; Mondol et al., 2007; Ross and Bustin, 2009 among many others). Compaction represents the first order control on shale and mudstone porosity; however, the degree of compaction is a function of mineralogy, effective overburden stress, burial temperature, and chemical alteration (Aplin and Macquaker, 2011; Krushin, 2014) and original pore size (Milliken and Curtis, 2016). In addition to all those parameters, structural deformation also potentially can transform pore structure in shale reservoirs (Akker et al., 2018; Ma et al., 2015; Liang et al., 2017; Zhu et al., 2019), however it is challenging to differentiate the influences of structural deformation from other factors that may control pore structure. Large pores tend to collapse earlier in response to increasing effective stress, therefore, generally in mudstone sedimentary rocks, much of the overall porosity loss occurs at shallow depths, during the collapse of pores larger than 15 nm (Yang and Aplin, 1998), while smaller pores (< 10 nm) are generally resistant to mechanical compaction (Loucks et al., 2009; Milliken and Curtis, 2016; Katz and Arango, 2018). As such, mechanical stress due to structural deformation has little effect on micropores due to the nanometer-scale of OM-hosted pores and they are less likely to be affected by structural deformation (e.g., Liang et al., 2017; Zhu et al., 2019).

OM-hosted porosity heterogeneity, in terms of pore size and distribution, may result from a combination of OM chemo-physical properties and the structural fabric of the rock (Mathia, 2016; Katz and Arango, 2018). Therefore, less rigid rock fabrics may or may not protect the OM-hosted pores from structural deformation stress and result in the loss of the small organic pores (i.e., mesopores). It appears that this is the case for the DZ samples with lower quantities of OM-hosted pores than micro-fractures within the OM and mineral matrix. In addition, increased OM plasticity as a result of compaction and/or structural deformation, may result in the destruction of pores within OM during burial or deformation (e.g., Lühr et al., 2015; Katz and Arango, 2018). Therefore, structural deformation and OM plasticity may potentially be a controlling factor for the destruction of OM-hosted pores in the DZ samples and the destruction of mesopores that are more susceptible to collapse.

Conclusions

Pore-filling pyrobitumen is the dominant OM constituent observed in the Lower Cambrian shales of both studied areas. Quartz, carbonate (calcite and dolomite), and clay minerals are major mineral constituents of the samples. The mean quartz, illite, plagioclase, pyrite, and total clay contents in the NDZ samples are higher than that of the DZ samples. Dolomite contents in the DZ samples are significantly higher than those in the NDZ samples while calcite content is similar in the two sample sets. Pore size characteristics of the DZ and NDZ shale samples show noticeable differences, with a dominance of micropores in the DZ samples, while the NDZ samples show a wider range of pores from micropores, to pores at the lower end of the macropore range. Mineral-hosted sub-micron pores within carbonate minerals resulted from dissolution, and micro-fractures within minerals and OM, likely formed during deformation of the area, are dominant pore types in the DZ samples, while meso- to macropores within OM are sporadic. In contrast, OM-hosted micropores to macropores, and sub-micron to micrometer-sized mineral-hosted pores and micro-fractures are abundant in the NDZ samples. OM-hosted pores in the NDZ samples show strong heterogeneity, as some pore-filling OM is devoid of any SEM-visible internal pore, while in close proximity, or in same particle SEM-visible pores are present. The presence of HIM-visible nano-pores, combined with the good correlation between CO₂ micropore surface area and TOC content suggest that micropores within OM are abundant in both the DZ and NDZ sample sets. The OM-hosted micropores are the major contributors to total porosity for the DZ samples while OM-hosted meso- to macropores contribute to the total porosity for NDZ samples. The substantial difference in SEM- and HIM-visible pore types, meso- and micropore size distribution between the DZ and NDZ shale samples, suggests structural deformation may potentially have a significant effect on the pore size characteristics and gas content of the Lower Cambrian shales in the Upper Yangtze Platform. Structural deformations from tectonic stress may have destroyed the meso- to macropores within the OM in the DZ samples, while OM-hosted micropores are retained due to their greater mechanical resilience.
References


