Electron Microscopy Characterization of the Pore System in Gas Shale

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Philosophy by Yuxiang Lu

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Statement of Originality

I declare the work presented in this dissertation is original, except as acknowledged in the text. This work has not been submitted for a degree at any other university.

Yuxiang Lu
August 2016
Abstract

With the increasing demand of natural gas, unconventional natural gas reservoirs have drawn significant attentions. Many countries spend a large quantity of resources in studying unconventional natural gas. United States is the first country in the world to realize the commercial exploitation of shale gas. Though shale gas, one of unconventional natural gas, has been explored widely for commercial purpose in the past 10 years, the microstructure of most of these shale reservoirs are still lacking of research.

Unlike most conventional natural gas reservoirs, shale plays have extremely low permeability which make gases and fluids being stay within shale formations. Pores and natural fractures are the places where both compressed gas and sorbed gas are hided. In order to achieve better industrial production efficiency, it is essential to understand the microstructure of pores in shale reservoirs as pores are the places where natural gas trapped.

In this study, low pressure nitrogen adsorption, as a traditional core analysis technique, was used to determine the pore size distribution. It was found that mesopores with size of 20 - 40 nm were predominant in the shale. Investigation by scanning electron microscopy (SEM) on porosity of shale showed various morphologies of pores with complex structures. Energy dispersive spectroscopy (EDS) suggested the existence of quartz, pyrite framboids and organic matter. Transmission electron microscopy (TEM) explored the interconnectivity inside the shale volume, and TEM shows less frequency on the pore characterization of shales. In-situ dual beam system (FIB/SEM) was used on sequential milling and imaging and revealed much smaller pores (< 10 nm) in the shale. The datasets produced from FIB/SEM were failed to complete 3D reconstruction of the shale volume as a scientific threshold value could not be identified properly.
I would like to say thanks to my supervisor, A/Prof. Zongwen Liu for giving me the opportunity to conduct this study and I would not able to finish this project smoothly without his support, guidance and patience. Also, I would like to express my heartfelt gratitude to Dr. Cuifeng Zhou, for all the help from her on my SEM and TEM study. At the same time, I appreciate the kindness training and help for experimental instruments from Dr. Jeffrey. Without all these help and support from them, I cannot finish my project.

My family especially my parents has offered so many help and support on my study and life, it is them who encourage me and stand with me, I really appreciate the things they have done for me.

Meanwhile, my special thanks to the staffs at the School of Chemical and Biomolecular Engineering for their help all through my Masters.
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1. Introduction

1.1 Natural Gas Resources

Generally, natural gas is a fossil fuel which involves high percentages of methane and some of other hydrocarbons like ethane, propane, and butane (Table 1.1). Some gas reservoirs might contain rare gases like helium. Different gas reservoirs may have different gas compositions, even two wells in the same gas play could also yield products which are different in gas composition (Speight 2015).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Formula</th>
<th>Vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>&gt;85</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>3-8</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>1-5</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>1-2</td>
</tr>
<tr>
<td>Pentane⁺</td>
<td>C₅H₁₂</td>
<td>1-5</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>1-2</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
<td>1-2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>1-5</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

*Pentane⁺: Pentane and higher molecular weight hydrocarbons, including benzene and toluene.

Table 1.1 Constituents of Natural Gas (Speight 2013, Yuan, Luo et al. 2015).

There are two categories of natural gas resources that have been typically recognised so far: conventional and unconventional (Mokhatab and Poe 2012). Based on the different permeability of natural gas reservoirs, the gas plays with a permeability larger than 1 millidarcy (>1 mD) usually yield conventional gas which can be extracted by applying traditional techniques, and also up to present, conventional gas takes large proportion of global natural gas production. In the other hand, unconventional gas is typically explored in gas reservoirs with relatively low permeability (<1 mD), and therefore it cannot be acquired by conventional extraction applications and is relatively hard and expensive to yield commercially.
Figure 1.1 shows the geologic nature of the most major sources of the natural gas. Conventional plays have interconnected pore spaces that allow gas flow to the well, the gas producing in kerogen is more likely flowing to the more porous and permeable place such as sandstones and carbonates. Unlike conventional gas reservoirs, unconventional gas plays always trap natural gas with itself due to the low permeability, and because of it, particular technologies are needed to give additional permeability on these formations during the extraction.

1.2 Unconventional Natural Gas Reservoirs

People usually divide unconventional gas formations into four groups, they are very low permeability reservoirs, but the property and constituents may vary from each other. Because of rising demand of natural gas, unconventional gas reservoirs have been researched and developed in recent years. Rogner (1996) has estimated the worldwide unconventional gas resources, in terms of the amount of shale gas, tight gas and coalbed methane, which is shown in Table 1.2.

<table>
<thead>
<tr>
<th>Area</th>
<th>Shale Gas (Tcf)</th>
<th>Tight Gas (Tcf)</th>
<th>Coalbed Methane (Tcf)</th>
<th>Total volumes (Tcf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>3,842</td>
<td>1,371</td>
<td>3,017</td>
<td>8,228</td>
</tr>
<tr>
<td>Latin America</td>
<td>2,117</td>
<td>1,293</td>
<td>39</td>
<td>3,448</td>
</tr>
</tbody>
</table>
Western Europe & 510 & 253 & 157 & 1,019 \\
Central and Eastern Europe & 39 & 78 & 118 & 235 \\
Former Soviet Union & 627 & 901 & 3,957 & 5,485 \\
Middle East and North Africa & 2,548 & 823 & 0 & 3,370 \\
Sub-Saharan Africa & 274 & 784 & 39 & 1,091 \\
Centrally planned Asia and China & 3,528 & 353 & 1,215 & 5,094 \\
Pacific (Organization for Economic Co-operation and Development) & 2,313 & 705 & 470 & 3,484 \\
Other Asia Pacific & 314 & 549 & 0 & 862 \\
South Asia & 0 & 196 & 39 & 235 \\
World & 16,112 & 7,406 & 9,051 & 32,560 \\

<table>
<thead>
<tr>
<th>Western Europe</th>
<th>510</th>
<th>253</th>
<th>157</th>
<th>1,019</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central and Eastern Europe</td>
<td>39</td>
<td>78</td>
<td>118</td>
<td>235</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>627</td>
<td>901</td>
<td>3,957</td>
<td>5,485</td>
</tr>
<tr>
<td>Middle East and North Africa</td>
<td>2,548</td>
<td>823</td>
<td>0</td>
<td>3,370</td>
</tr>
<tr>
<td>Sub-Saharan Africa</td>
<td>274</td>
<td>784</td>
<td>39</td>
<td>1,091</td>
</tr>
<tr>
<td>Centrally planned Asia and China</td>
<td>3,528</td>
<td>353</td>
<td>1,215</td>
<td>5,094</td>
</tr>
<tr>
<td>Pacific (Organization for Economic Co-operation and Development)</td>
<td>2,313</td>
<td>705</td>
<td>470</td>
<td>3,484</td>
</tr>
<tr>
<td>Other Asia Pacific</td>
<td>314</td>
<td>549</td>
<td>0</td>
<td>862</td>
</tr>
<tr>
<td>South Asia</td>
<td>0</td>
<td>196</td>
<td>39</td>
<td>235</td>
</tr>
<tr>
<td>World</td>
<td>16,112</td>
<td>7,406</td>
<td>9,051</td>
<td>32,560</td>
</tr>
</tbody>
</table>

Table 1.2 Estimation of Worldwide Unconventional Gas Resources (Rogner 1997).

1.2.1 Tight Sand Gas Reservoirs

Tight gas formations are typical sandstone or carbonate reservoirs which have extremely low permeability (<0.1 mD). Some ultra-tight gas reservoirs can have in-situ permeability down to 0.001 mD. Naik (2003) injected blue epoxy into thin section of a conventional sandstone formation (Figure 1.2) and an unconventional sandstone reservoir (Figure 1.3), and the results show below.

Figure 1.2 Thin Section of Conventional Sandstone Reservoir (Naik 2003).
As shown in Figure 1.2 and Figure 1.3, the blue areas, which are pore space and may contain natural gas in a producing field, are the injected epoxy. In Figure 1.2, the spaces of each material remain larger than these in Figure 1.3. These spaces provide the paths for gas and oil to flow through. As demonstrated in Figure 1.3, the epoxy area, which is rock porosity, is much smaller compared with conventional sandstone formation in Figure 1.2. With such small pores and less appearance of potential pathway for gas and oil, permeability of tight gas formation stays much less than conventional sandstone reservoir.

![Figure 1.3 Thin Section of Tight Gas Formation (Naik 2003).](image)

1.2.2 Coalbed Methane

A variety of plant materials, mostly woody plant debris, have been buried under ground in high temperature and pressure environments for years (catagenesis). Those materials, with increasing burial period, are becoming a lithified organic sediment which is called coalbed (Law 1988).

The constituents of coalbed methane and conventional natural gas are almost same. Methane occupies nearly 100 percentages of coalbed methane while 90 percentages of conventional natural gas is methane and rest of 10 percentages is ethane, butane and other hydrocarbons. To get access to coalbed methane, the most common introduced way is vertical drilling combining with standard petroleum techniques and directional drilling. Sometimes in order to improve the
production efficiency, hydraulic fracturing is applied to help open fractures and pores where gas is stored.

1.2.3 Shale Gas Reservoirs

Shale is a geologically fine grained and organic rich sedimentary rock, which particles are mostly composed of silt and clay size materials (Blatt, Tracy et al. 2006). Clay minerals, such as illite, kaolinite and smectite, contributes 60 percentages of shale composition, while the rest 40% of shale is non-clay mineral particles such as quartz, chert and feldspar (Yaalon 1962). Due to the difference among environment conditions that shale formations are deposited, some materials such as organic matters, carbonate minerals, iron oxide minerals, sulfide minerals and heavy mineral grains could be found in shale rocks. Table 1.3 shows the work of Yaalon (1962) who summarised chemical composition of 10,000 shales.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay (mostly illite)</td>
<td>60</td>
</tr>
<tr>
<td>Quartz</td>
<td>20</td>
</tr>
<tr>
<td>Feldspar</td>
<td>10</td>
</tr>
<tr>
<td>Carbonates</td>
<td>6</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>3</td>
</tr>
<tr>
<td>Organic Matter</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1.3 Chemical Composition of Shales (Yaalon 1962).

Generally, shale formation, based on different organic contents, can be divided into two main varieties- dark shale formation and light shale rock (Yuan, Luo et al. 2015). The difference between them is that dark shale reservoirs contain more organic materials than light shale formation. The organic materials were prevented from decay because organic rich shale rocks usually were deposited in oxygen free places like water and marine, and because of it, it is more likely that organic matter is be able to transform into oil and gas, which give black colour to those black shale formations. Shales deposited in oxygen-rich environment usually gain light colour as the organic matters inside the rocks have reacted with oxygen, and it is easy to find tiny particles of iron oxide or iron hydroxide
minerals such as hematite, goethite and limonite in those shale formations. Particularly, it has been found that shale may have red colour as a consequent of the presence of hematite while the existence of limonite or goethite could result in yellow or brown shale formation (Tomlinson 1914).

1.3 The Natural Gas Resources Pyramid

The concept of the natural gas resources pyramid was first introduced in 1979, it stated that all natural resources were distributed log normally in natural (Masters 1979). Figure 1.4 shows reservoir rock endowment of conventional gas, tight gas, shale gas and coalbed methane combined with various parameters like delivery speed and production prices.

![Figure 1.4 World Gas Resources Pyramid (Adopted from (Aguilera, Harding et al. 2008))](image)

As it can be seen from Figure 1.4, the deeper into the resources pyramid, the lower permeability becomes, as well as decreasing delivery speed controlling the definitions of flow units and pore throat apertures. Normally, unconventional gas reservoirs have more endowment than conventional gas plays. However, more resources and time have to be put in further research in order to enhance the industrialization process.
1.4 Shale Gas Reservoirs History

United States of America is the first country that researched and developed shale gas resource. Up to present, US also has the largest shale gas reservoirs and yields the most shale gas products globally. As most of shale gas resources in other countries remain research and undeveloped, basically the history of world shale gas history is more likely to be the history of USA. In Europe, it has been reported that sizeable quantities of shale gas and other unconventional gas resources have been found in the United Kingdom, the Netherlands, Germany, France, Scandinavia and Norway (Nakićenović, Grübler et al. 1998). Those reservoirs have been in exploration, however, industry scale shale gas productions still remain doubtful as a result of economic, environment and governmental obstacles. Australia’s natural gas resources is enormous and fifty to sixty sedimentary basins have been investigated and verified (Mackie 1987, Roarty and Roarty 2008). However, in Australia, the current commercial production of shale gas stays unexploited, it is because that Australia’s domestic demand for natural gas is limited because of relatively small population. Besides, those shale gas formations are generally found in remote area, which makes it more difficult and more expensive to commercialise. The research and investigation of shale gas in Asia is not fully achieved, no large scale shale gas productions are existed. China began to explore shale gas in 2002, and first shale gas well was successfully drilled in 2009 (Fujie, Xiongqi et al. 2012). Table 1.4 summarizes historical background of shale gas industry in the world.

<table>
<thead>
<tr>
<th>Date</th>
<th>Events and Innovations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1821</td>
<td>USA first commercial shale gas well drilled in Devonian shales, Fredonia, New York.</td>
</tr>
<tr>
<td>1859</td>
<td>Commercial oil well drilled in USA.</td>
</tr>
<tr>
<td>1860’s –</td>
<td>Shale gas from the Appalachian and Illinois basins first appear in domestic markets.</td>
</tr>
<tr>
<td>1920’s</td>
<td></td>
</tr>
<tr>
<td>1930’s</td>
<td>Domestic transmission pipelines are built for gas transportation.</td>
</tr>
<tr>
<td>1940’s</td>
<td>Hydraulic fracturing first applies on a gas well Kelpper Well</td>
</tr>
</tbody>
</table>
NO.1 in Grant Country, Kansas.

1970’s  Directional drilling is introduced in industry.

1970’s – 1980’s  Department of Energy (USA) reports that America has great unconventional gas potential.

1980’s – 1990’s  To optimize large fracture designs, reservoir characterization and completion practices, Department of Energy (USA) and Gas Research Institute (USA) create multi-disciplinary projects, which make the Barnett Shale as a successful example using horizontal hydraulic multi-fracturing.


2005 - 2010  Other major shale basins start to develop.

2010  U.S. and Canada begin to discover shale gas overseas as shale in US becomes saturated.

Table 1.4 Shale Gas History Summary (Green 2012).

1.5 World Shale Gas Potential

In fact, the volume of world shale gas resources is great, estimated 16,000 to 25,000 Tcf excepting shales have not been found (Rogner 1997, Kawata and Fujita 2001). Table 1.5 illustrates the estimated shale gas volumes worldwide, similar to conventional natural gas resources, the evaluation of shale gas potential is somehow related to the research level on the regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>Estimated Shale Gas (TCM)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>108.79</td>
<td>23.8</td>
</tr>
<tr>
<td>Central Asia</td>
<td>99.90</td>
<td>21.9</td>
</tr>
<tr>
<td>Middle East</td>
<td>72.15</td>
<td>15.8</td>
</tr>
<tr>
<td>North Africa &amp; Oceania</td>
<td>65.50</td>
<td>14.4</td>
</tr>
<tr>
<td>Latin America</td>
<td>59.95</td>
<td>13.1</td>
</tr>
</tbody>
</table>
Table 1.5 Worldwide Shale Gas Potential (Kang and Yundong 2009).

As shale gas attracts increasing attentions of governments, scientists and companies, it is quite necessary to update the estimates of shale gas resources over the world, and because of this, Advanced Resources International, Inc. (ARI) and the U.S. DOE’s Energy Information Administration (EIA) evaluated the shale gas potential in 14 regions including 32 countries. Figure 1.5 demonstrates worldwide major shale gas resource in 32 countries.

![Figure 1.5 48 Major Shale Gas Resources Map (Adopted from (Administration and Kuuskraa 2011)).](image)

As shown in Figure 1.5, in North America, shale formations are mainly located in western Canada and southern USA, while these shale reservoirs can be found in centre and edge of Latin America. Eastern Europe has found significant shale gas resources in Ukraine, Romania and Bulgaria. Meanwhile, abundant shale gas
has been found in northern and central China, remote area of Australia and northern and southern Africa.

With the development of prospection techniques, the accuracy of shale gas evaluation has been significantly improved. To be more comparable, it has been summarised by using data from Rogner (1997) and Administration and Kuuskraa (2011). Table 1.5 shows the world estimates of shale gas resources at different times.

<table>
<thead>
<tr>
<th>Area</th>
<th>H.H. Rogner World Estimates (Tcf)</th>
<th>ARI/EIA World Estimates (Tcf)</th>
<th>ARI/EIA Risked Gas in Place (Tcf)</th>
<th>ARI/EIA Risked Technically Recoverable (Tcf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>3,842</td>
<td>7,140</td>
<td>3,856</td>
<td>1,069</td>
</tr>
<tr>
<td>South America</td>
<td>2,117</td>
<td>4,569</td>
<td>4,569</td>
<td>1,225</td>
</tr>
<tr>
<td>Europe</td>
<td>549</td>
<td>2,587</td>
<td>2,587</td>
<td>624</td>
</tr>
<tr>
<td>Africa</td>
<td>1,548</td>
<td>3,962</td>
<td>3,962</td>
<td>1,042</td>
</tr>
<tr>
<td>Asia</td>
<td>3,528</td>
<td>5,661</td>
<td>5,661</td>
<td>1,404</td>
</tr>
<tr>
<td>Oceania</td>
<td>2,313</td>
<td>1,381</td>
<td>1,381</td>
<td>396</td>
</tr>
<tr>
<td>Others</td>
<td>2,215</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Total</td>
<td>16,112</td>
<td>25,300</td>
<td>22,016</td>
<td>5,760</td>
</tr>
</tbody>
</table>

Table 1.6 World Estimates of Shale Gas at different times (Rogner 1997, Administration and Kuuskraa 2011).

As it can be seen from Table 1.5, the result of shale gas potential estimated by ARI/EIA is much larger than Rogner’s estimation, 25,300 and 16,112 respectively. Also there is a huge difference of shale gas estimates in Europe, Africa and North America.

1.6 World Shale Gas Production

The first commercial exploitation of shale gas was in 1621, starting at eastern America, moving into large scale production in early 20th. It has been found that the shale formations in eastern America are mostly organic rich and easily
applying fracturing techniques, these reservoirs become the main targets which may be high production plays. It has been recognised that the Barnett shale of central Texas, USA, is the first producing shale gas reservoir (WARWICK and HACKLEY 2014). From 1970, due to increasing demand of natural gas and improvement of gas exploration techniques, shale gas explorations have been extended to central and western America. At the same time, production from shale gas reservoir is greatly increasing, this makes US being able to export natural gas from a former natural gas importer (Arora and Cai 2014). Consequently, it has enabled the United States to stabilize the energy security and helped reduce carbon emissions successfully (Jacoby, O’Sullivan et al. 2011, Medlock, Jaffe et al. 2011). Canada is the second country who has achieved the industry scale exploitation of shale gas. These successful examples also stimulates China to develop shale gas industry, and it has attained commercial production of shale gas in 2012 (Yuan, Luo et al. 2015).

Figure 1.6 shows the increasing volume of shale gas production in US. Apart from this, it can also be seen that the percentage of shale gas in annual is increasing from 2007 to 2014. In 1998, shale gas only took 1.6% of natural gas production in US, then with the development of shale gas industry, it reached 3.0%
and 4.5% in 2003 and 2004, respectively (Kang and Yundong 2009). Up to 2014, shale gas took almost half percent of US natural gas production (40%), and due to crucial shale gas potential and certain technical breakthroughs, this number may increase (Jacoby, O'Sullivan et al. 2011, Yuan, Luo et al. 2015).

1.7 Research Scope

The storage of natural gas and its flow behaviour are largely influenced by the pore systems in the shale. this study combines both indirect and direct methods to characterize the shale sample, including conventional analysis like low pressure nitrogen adsorption and radiation probe techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The examined shale samples were provided by A/Prof. Zhiping Lai, King Abdullah University of Science and Technology. Originally, the samples were sent by a natural gas company in Norway, and due to commercial secrets, more details such as specific location, name of reservoir and company remain confidential in this study.

First, to prove the existence of pores with size around 100nm, low pressure nitrogen adsorption method will be applied to investigate the pore size distribution of the sample. The morphologies of shale will be observed with the help of scanning electron microscopy (SEM), while transmission electron microscopy (TEM) provides internal insights through sample, which indicates potential pores and throats that cannot be seen in SEM. Focused ion beam and SEM dual beam system will be applied to reveal ultra-small pores (around 10nm) and build up 3D reconstruction model of the sample, and with this, shale properties such as porosity, permeability and TOC could be calculated.
2. Literature Review

2.1 Standards for the Selection of Potential Shale Gas Reservoirs

To determinate whether a shale gas reservoir has the potentiality to explore commercially or not, its geochemical and petrophysical properties need to be known via using geological, geochemical, geomechanical and petrophysical analytical techniques. It is necessary that a shale must have a certain amount of mature organic matter, which is generally called as total organic carbon (TOC %wt.), to become a potential source rock or an unconventional shale gas formation (Speight 2013). Further investigation for shale gas in place assessment cannot be done unless certain amount of total organic content can be found in the shale. Mineralogical character of the shale is going to be researched when the organically rich and mature intervals of it have been investigated. The mineralogical character can be used to evaluate free porosity, adsorption and desorption characteristics and geomechanical character. These parameters provide essential information to apply hydraulic fracturing on the shale for generation of artificial permeability. The hydrocarbon storage mechanism varies significantly in a potential shale gas reservoir and its rock characters are extremely heterogeneous, this means a lot of techniques for its characterization are needed before commercial explorations start. It takes 17 years to finally achieve commercial natural gas production from the Barnett hale reservoir (Sondergeld, Newsham et al. 2010).

Usually, reservoir characterization of potential shales is divided into 3 phases. First phase is source rock identification which assesses the lateral extension and vertical thickness of the rock. Then it will identify the type of source rock and kerogen, total organic carbon and maturation level. Based on these information, hydrocarbon generation potential could be predicted. Next phase will mainly evaluate the petrophysical characters of the source rock. During this phase, further investigation will be done, in relation to type and amount of minerals, pores classification and gas flow mechanism. After the identification of shales, last phase focuses on the play development and production strategy, which includes well locating, horizontal drilling and hydraulic fracturing as shown in Table 1.6.
Table 2.1 Characterization phases for potential gas shale (Shaw, Reynolds et al. 2006, Deshpande 2008, Sondergeld, Newsham et al. 2010, Ahmad 2014).

A number of investigation techniques and research methods are included in 3 characterization phases of potential gas shales. For different petrophysical or petromechanical properties, evaluation methods could vary as given in Table 1.7.
<table>
<thead>
<tr>
<th>Evaluation technique</th>
<th>Techniques</th>
</tr>
</thead>
</table>
| Thickness and lateral extension           | 1. Self potential  
2. Gamma ray  
3. Correlation of logs data |
| Maturity                                  | 1. Core analysis                                                          |
| Mineralogy                                | 1. Scanning Electron Microscopy  
2. X-ray Diffraction  
3. Energy dispersive spectroscopy  
4. Fourier transform infrared spectroscopy |
| Total organic carbon                      | 1. Kerogen type  
2. Acidification  
3. Oxidation                                                              |
| Amount of free and adsorbed gas           | 1. Canister desorption and Langmuir isotherm                               |
| Porosity                                  | 1. Helium porosimetry  
2. Mercury injection capillary pressure  
3. Nuclear magnetic resonance  
4. Small angle neutron scattering and ultra-small angle neutron scattering |
| Water saturation                          | 1. Core analysis  
2. Self-potential  
3. Gamma ray                                                                |
| Pore size classification                  | 1. Mercury injection capillary pressure  
2. Scanning electron microscopy and focused ion beam milling               |
| 3D modelling                              | 1. Scanning electron microscopy and focused ion beam milling  
2. Computed tomography                                                           |

Table 2.2 Evaluation techniques for potential gas shale characterization (Shimadzu and Analyzer, Deshpande 2008, Elgmati 2011, Ahmad 2014).
2.2 Mineralogy

A number of minerals can be found in shales, due to different environment where shales are deposited, some shales could have minerals that others do not have, as well as minerals amount. So far, clay minerals like illite, kaolinite, smectite and chlorite are predominant while non-clay minerals (quartz, chert and feldspar) are mostly found in shales. Usually, construction of clay minerals is built up from two basic blocks, first is a tetrahedral silicate sheets with oxygen ions locating at the corners while the other one is an octahedral shape with hydroxyl ions or aluminium ions at the corners (Grim 1968), as showed in Figure 2.1.

![Figure 2.1](image)

The most abundant clay mineral in shale can be found is illite, which takes around 60% of shale (Yaalon 1962). It is non-expanding 2:1 type layer clay and the structure is built up with the repetition of tetrahedron-octahedron-tetrahedron (TOT) layers based on prototype minerals like muscovite and phlogopite (Murray 2006). Normally, tetrahedral sheets are the places that substitutions happen in illites, and potassium generally acts as the compensating cation who constitutes two structural types of illite – 1M and 2M, which gives chemical formula as (K,H$_3$O)Al$_2$Si$_3$AlO$_{10}$(OH)$_2$. Illite is usually found in deep-buried shales and it is more likely to be derived from pre-existing shales. Moreover, increasing temperature helps to form muscovite while slow sedimentation produces more glauconite which is an iron rich mineral.

The generation of kaolinite requires special environment such as abundant rainfall, well drainage and acid waters, which is common in tropical or subtropical areas. Geologists use kaolinite as an indicator to find ancient marine
basins as kaolinite is normally seen near shore. Kaolinite has been defined as a multi-layer silicate mineral on one tetrahedral sheet and its chemical formula is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Deer, Howie et al. 1992). Kaolinite is very friable and usually is white or grey colour unless iron oxide makes it become pink, red and orange colour.

Chlorite has been frequently found as a green colour mineral of which the surface coating with other minerals like quartz. Actually the term chlorite is the group name of around 10 related minerals, but it can be used to describe the group in general or any typical member of chlorite group. The three most common individual group members are cookeite, clinochlore and chamosite (Árkai and Ghabrial 1997). The structure of chlorite is a T-O-T layer with an interlayer brucite sheet or one with simple octahedrally coordinated cations (de Caritat, Hutcheon et al. 1993). Mostly $\text{Mg}^{2+}$, $\text{Fe}^{2+}$, $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ are the cation substitutions in chlorite.

### 2.3 Kerogen Type

As stated before, total organic carbon plays a key role in shale analysis because natural gas and oil are produced from organic materials, these organic materials deposited in shale are also call kerogen geochemically. This organic geochemistry term means that organic materials could be separated from sediments by using hydrochloric or hydrofluoric acid (Hunt 1979, Durand 1980, Hutton, Bharati et al. 1994). Kerogen has very complex formulas since it contains a range of organic matters with great molecular weight (insoluble in organic solvents) and bitumen (soluble in organic solvents), and it is basically a result of anaerobic decomposition of organic matters which are from dead plants and animals (Elgmati 2011, Ahmad 2014). The kerogen in shale can be transformed through liquid bitumen into liquid petroleum product with the effect of deeper burial, high temperature and high pressure, then if this liquid product is trapped in the shale rock, it is high possibility to have cracking of oil into gas as consequence of the overburden and the high temperature (Tiab and Donaldson 2015). It has been reported that weight and volume of kerogen could have impact on the petrophysical evaluation of the shale formation (Glorioso and Rattia 2012).
The classification of kerogen has been studied for many years and a special experimental technique has been developed and it is called Rock Evaluation Pyrolysis (Espitalie, Madec et al. 1977, Ahmad 2014). This technique provides information about amount and type of hydrocarbon (oil and gas), which has been generated transformation of organic matter into kerogen in shale rock. The basic procedure of this experiment follows 3 steps:

- Burn a known amount of crushed shale rock in oxygen free chamber, to generate hydrocarbon vapours for geochemical analysis.
- Vapours are split into 2 stream and are passed to flame ionization detector.
- Output is generated from flame ionization detector.

The grade of a source rock can be used TOC %wt. to classify – poor (0.50 – 1.00 wt.%), fair (1.00 – 2.00 wt.%), good (2.00 – 5.00 wt.%), excellent (>5.00 wt.%), it has also been reported that prediction of type of hydrocarbons generation potential can be made by using ratios between hydrogen and oxygen organic matter gained from Rock Evaluation Pyrolysis (van Krevelen 1961, Peters and Cassa 1994, McCarthy, Rojas et al. 2011). Table 2.3 shows 4 type of kerogen based on Rock Evaluation Pyrolysis techniques.

<table>
<thead>
<tr>
<th>Kerogen Type</th>
<th>Deposited Condition</th>
<th>Organic Matter Source</th>
<th>Hydrocarbons Generated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Oxygen deficient lacustrine or shallow marine lagoonal environment.</td>
<td>Chlorococcale algae, prasinophyte algae, cyanobacteria and thiobacteria.</td>
<td>Mainly oil.</td>
</tr>
<tr>
<td>Type IIa</td>
<td>Marine and lacustrine anoxic environments.</td>
<td>Marine plankton and fibrous algae.</td>
<td>Both oil and gas.</td>
</tr>
<tr>
<td>Type IIb</td>
<td>Plant spores and pollens.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type III</td>
<td>Marine or non-marine environments.</td>
<td>Woody matter.</td>
<td>Mostly gas.</td>
</tr>
</tbody>
</table>
Table 2.3 Type of kerogen (Hunt 1979, Tissot 1984, Tyson 1993, Passey, Bohacs et al. 2010, Glorioso and Rattia 2012, Killops and Killops 2013).

| Type IV | Oxygen sufficient swamp and marine environments. | Oxidized and carbonized phytoclasts. | Mostly coal. |

2.4 Thermal Maturation

Within kerogen analysis of source rock, the kerogen metamorphism/maturity level can also be identified, there are 3 maturity levels to be used: diagenesis (immature), metagenesis (mature) and catagenesis (postmature). When the kerogen is in immature level, this means most of kerogen remain stable instead of convertible, kerogen tends to generate oil and gas in mature level while oil cracking largely happens in overmature level (Peters and Cassa 1994). Generally, different degree of thermal maturation affects the colour changes in the exine of fossil palynomorphs, so this has been most often used to investigate the maturation of the source rock. Figure 2.2 illustrates the colour chart of spore/pollen.

The kerogen generates oil and gas slowly with the maturation of organic matters, most of generated hydrocarbons is oil in the beginning, but at overmature level, gas becomes the main product and most of oil cracking into gas (Oehler 1983). And as a result, shale gas formations, which have postmature organic matters, have trapped gas instead of oil.
2.5 **Total Organic Carbon (TOC)**

To measure the potential of the source rock, total organic carbon is an important character, except this, a range of other characters needs to be involved, such as total reservoir volume, depth, temperature, pressure, porosity and mineralogical composition (Passey, Bohacs et al. 2010). The hydrocarbon generation potential of the prospective shale gas reservoir is determined by the kerogen type, total organic carbon content, thermal maturity and reservoir volume (Ahmad 2014). Jarvie (1991) has defined TOC values as weight percentage of organic carbon, that is, 1 wt.% of TOC means 1 gram of organic carbon in 100 gram of sediment sample. A minimum limit 0.4 wt.% of TOC is used to distinguish whether a source rock has potential to produce a certain amount of natural gas.

In a source rock, total organic carbon has been divided into 3 basic parts:
1) Organic carbon in the retained hydrocarbons when undergone measurement (Jarvie, Hill et al. 2007);
2) Organic carbon which can generate hydrocarbons (Jarvie 1991) or alive/reactive carbon (Cooles, Mackenzie et al. 1986);

2.6 Micro/Nano-Scale Studies of Shale

Shales belong to unconventional reservoirs which have different pores networks, permeability and gas flow mechanism from conventional carbonated reservoirs. It is a sedimentary rock containing illite, kaolinite and quartz, those minerals have complicated structures and they distribute heterogeneously in shales. Their sizes can range from nanometre to micron. Heavy minerals like pyrite and calcite, found in shales, have their own morphology, size and shapes. A greatly complex compositional matrix of a shale has been made by the accumulation of the clays, the plant debris and animal bodies for a long time, and various physical and chemical changes happen and finally it becomes a multi-layer geological formation (Speight 2013). To better investigate the pores distribution, morphology, permeability and connectivity between pores, instruments with ultra-high magnification and resolution are introduced.

Bennett, O’Brien et al. (1991) suggested scanning electron microscopy (SEM) and transmission electron microscopy (TEM) could improve the understanding of organic and inorganic matrix in shale. However, it costed a long time and lots of money to complete, therefore this application did not achieve many breakthroughs in 20th century.

Scanning electron microscopy and focused ion beam (SEM/FIB) has been recognized as an important experimental tool for characterization of shale, and this application has been used and developed widely and intensively in recent years. There are two reasons that SEM/FIB is becoming progressively popular in the use of shale submicron investigation. First is that it can give a more accurate
insight into shales to research the flow properties with high magnification and resolution at submicron level, and secondly initial gas can be determined in-situ.

Tomutsa, Silin et al. (2007) firstly applied SEM/FIB technique on the 3D reconstruction study of rocks. They used FIB to mill the sample and took SEM images in each milling, then built up 3D pore structure by stacking these 2D images. The maximum-inscribed-spheres (MIS) image-processing method was introduced to compute the petrophysical properties. At the same time, Bustin, Bustin et al. (2008), Jacobi, Gladkikh et al. (2008) and (Rokosh, Pawlowicz et al. 2009) reported that they were facing significant challenges when applied conventional techniques on shale characterization and results remained doubtful. They highly recommended to implement the use of the radiation probe techniques like SEM, TEM, FIB.

Loucks, Reed et al. (2009) used in situ dual beam instrument (SEM/FIB) to evaluate the pore system in mudrocks from the Mississippian Barnett Shale of the Fort Worth Basin, Texas. They had successfully characterized pore structure at nano-scale (down to 5nm), and they reported 3 main modes of pores were found in the research, which are intraparticle pores, interparticle pores and pyrite frambooid intercrystalline pores (Figure 2.3). In the paper, they emphasized that the key to achieve the characterization of nanopores was to use Ar-ion-beam milling, it gave much flatter surface for high magnification imaging.
Rokosh, Pawlowicz et al. (2009) run a SEM experiment to investigate the shale fabric and mineralogy of the Upper Colorado Group, Banff and Exshaw shales sample from Western Canadian Sedimentary Basin. Semi-qualitative elemental analysis was applied by using PGT x-ray analysis system (Energy Dispersive X-ray, EDAX). They aimed to reveal the potential for enhanced vertical and lateral fluid flow in shale by studying effective porosity in the fabric or microfabric of potential gas shale reservoirs.

Wang and Reed (2009) studied potential effects of organic matter on petrophysical properties, pore networks and fluid flow in the Barnett Shale in the Fort Worth Basin, North Texas based on pore images and geochemical data. They found 4 types of porous media in shale: nonorganic matrix, organic matter, natural fractures and hydraulic fractures. The pores in organic matter were the most important pores as they were largely used to trap adsorb gas and free gas. They suggested when characterising shales, it is better to give more works on the investigation of organic matter matrix, pores distributions and morphology.

A review of pore-throat sizes in sandstone reservoirs was done by Nelson (2009). He combined previous research data from mercury injection capillary pressure (MICP), small angle neutron scattering (SANS) and scanning electron microscopy (SEM) to review pore distributions of gas reservoirs in U.S., Canada and other countries. In the paper, he mentioned that porosity varies in different shale reservoirs, as well as pore-throat size. For example, porosity ranges from 5.1% to 12.6% in Pliocene Shales of Beaufort-Mackenzie Basin, Canada while shale reservoirs in USA have porosity ranging from 4.3% to 12.7%.

Kale, Rai et al. (2010) did a further investigation on petrophysical characterization of Barnett Shale by applying LECO-pyrolysis techniques, MICP, helium porosimetry, fourier transform infrared spectrometry (FTIS). They mainly focused on hydrocarbon generation potential and core description as well as the impact of varying lithology/mineralogy on porosity.
Schieber (2010) examined 6 different shale successions (from Cambrian to Cretaceous), and he found that there were some common pore types even these samples had different compositions, deposition environments and compaction history. He classified these pore into 3 types: phyllosilicate framework pores (PF pores), carbonate dissolution pores (CD pores) and organic matter pores (OM pores). The PF pores found in phyllosilicates range in size from 5nm to more than 1000nm while the CD pores are 50nm to 1000nm in dolomite and calcite grains. The OM pores dominate within kerogen blebs and organic-clay aggregates range in size from 10nm to 100nm. SEM and TEM combined with ion milling equipment were used to investigate the location, morphology and distribution of these pores. Based on the results, he predicted pre and post-depositional changes in the sedimentary rocks.

Milner, McLin et al. (2010) used SEM/FIB to image shale samples from Haynesville, Horn River, Barnett and Marcellus Shale reservoir. They proved that the maximum size of pores in organic matter is determined by the size of the kerogen mass or the geometry of enclosing crystals. This 2D image analysis and 3D volumetric reconstruction study combined with thin section textural analysis and XRD also involved the consideration of rock microtexture and the various pore types.

Passey, Bohacs et al. (2010) examined the gas potential in the shale applying geologic and petrophysical characterization techniques such as XRD, vitrinite reflectance, TOC, adsorbed/canister gas, detailed core and thin-section descriptions, porosity and permeability. SEM/FIB has ability to reveal pore structure at micro/nano-scale and to build up 3D volumetric model. They also mentioned when estimating initial gas in place, the 3D model does not have representativeness of the whole shale gas reservoir.

Sondergeld, Ambrose et al. (2010) reported that porous matrix in a shale reservoir can control its porosity and permeability directly. They applied SEM/FIB device to characterize the shale sample and a 3D volumetric model to give better insight into shale to observe connectivity, then they compared this result with helium porosimetry and NMR outcomes from same samples. Nanopores contribute largely in the pore volume while some of them could be removed during milling, particularly while using SEM/FIB system to explore
porosity, pores whose thickness is less than 10 nm are more likely not to be included in the final total pore volume as the thickness of each slice is 10nm.

Ambrose, Hartman et al. (2010) found a new methodology to estimate shale gas in place, which combined the Langmuir equilibrium adsorption isotherm with the volumetrics for free gas and formulate a new gas in place equation accounting for the organic pore space taken up by the sorbed phase. They also mentioned in the paper that natural gas absorbing in clays and organic matter takes some space in various pores in the shale reservoirs, thus the total pore volume before desorption and after desorption is different.

Loucks, Reed et al. (2010) reviewed previous related paper and introduced an extensive pores classification. They described major pore types and showed example of these pores, meanwhile, a ternary diagram, which can be used as a classification of relative abundances of nanopore and micropore types in mudrock, is presented in the paper. Based on the morphology, pores, cracks and fractures are classified into 5 types: interparticle, intraparticle, intercrystalline, intracrystalline and microfracture.

Handwerger, Keller et al. (2011) run an investigation on fluids saturation estimation in shale gas reservoir. They developed an analytical technique for characterizing shale reservoirs on core with the use of crushed material to give better insight into pore space, also retort analysis is used to measure separately free, bound and structural water saturations as well as distinguish water from oil while the determination of permeability is made by pressure transient analysis.

Curtis, Sondergeld et al. (2012) applied SEM/FIB dual system to investigate 9 shale samples from Barnett, Eagle Ford, Fayetteville, Haynesville, Horn River, Kimmeridge, Marcellus and Woodford Shales. A complex microstructure with variations is shown by backscattered electron images (BSE) of FIB cross sectioned shale surfaces. Energy dispersive spectroscopy (EDS) demonstrate that clay, carbonate, quartz, pyrite and kerogen are commonly found in the shale cross sections. 3D reconstruction model shows that pore volume takes 0.2 to 2.3% of the reconstructed shale volumes while kerogen volume takes 0 to 90.0%. Nanopores with diameter around 5nm are predominated in the estimation of pore size distribution. Colours are used to identify pores (black), kerogen (grey black),
clays (light grey) and heavy minerals (white) in 3D reconstruction by setting up the grey scale intensity.

Glorioso and Rattia (2012) reviewed previous researches on shale reservoirs and discussed the cutting-edge technologies on characterization of shale gas plays. They introduced some ideas on the criteria and techniques for the evaluation of cores and logs combined with the recent and previous experiences of researchers. A large quantities of laboratory tests and results are presented in the paper, including log responses in the presence of kerogen, log interpretation techniques and estimation methods for different volumes of gas in situ. They highly suggested the application of SEM/FIB on shale characterization, pore size distribution and minerals identification when correlated with the outcomes from NMR, MICP and helium porosimetry.

Fishman, Hackley et al. (2012) analysed organic source richness, kerogen maturity and gas generation potential of the Upper Jurassic Kimmeridge Clay Formation, offshore United Kingdom. The Kimmeridge Formation has various levels of thermal maturity in shale system. They focused on the evaluation of porosity which has impact on organic macerals and thermal maturity. XRD has been used for rock and mineralogical qualitative and quantitative analysis and TOC identification is done by rock evaluation pyrolysis. However, pore size classification and total porosity evaluation are not included in the paper.

Wu and Aguilera (2012) used scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) to investigate shale structure at nanoscale. Shale samples from the Western Canada Sedimentary Basin are imaged with high magnification and resolution to be compared with images from other papers. They proposed a criterion on the determination of the porosity exponent and the evaluation of the water saturation in shales based on their observations of the nanopores structure.

Houben, Desbois et al. (2013) did an experiment to study the microstructure and porosity of Opalinus Clay Shale, Switzerland. They used broad ion beam (BIB) combined with SEM which provide much better insight into nanopores in shale. Pore size distribution from BIB/SEM is compared with one from MICP while they found that the pores and minerals are homogeneously distributed in 3D.
reconstruction model and there are non-porous regions with similar pore structures.

Most pores in the Marcellus Formation of Pennsylvania have been found in organic matter than in nonorganic matrix detected by field-emission scanning electron microscopy (FE-SEM), as Milliken, Rudnicki et al. (2013) stated. According to the studies of two wells, they found that thermal maturity has less impact on organic matter (OM)-hosted porosity than TOC. Positive correlation between TOC and porosity occurs only with TOC less than 5.5 wt.%, no increase in porosity with greater TOC (>5.5 wt.%). However, due to the varying TOC in the same formations and the 2D image-based observations at submicron scale, this methodology for total porosity determination remain doubtful when used as a criterion.

Pearce, Timms et al. (2013) investigated the mechanism of carbonated mineral replacement and its effect on porosity of samples from 1.95 Moz Junction gold deposit, Western Australia. A semi-qualitative elemental map is prepared by SEM/EDXS for identification of simultaneous magnesium in the rocks. They described the fluid-mediated carbonate reaction textures microchemically and microstructurally at hydrothermal conditions.
3. Shale Pore System Characterization

The pore system acts as a crucial role in shale, not only because it is the place trapping both compressed gas and adsorbed gas but also it has significant impact on the flow behaviour which somehow determines whether this shale reservoir is worth exploring or not. To better understand the pore system and the petrophysical characteristics of shale, we decide to use direct and indirect evaluation method in this project. Gas adsorption has been widely used as a conventional analysis on the characterization of pore size distribution and porosity, this technique provides indirect insight into pore system down to nanometre scale, whereas scanning electron microscopy directly demonstrates various pores in the shale by images.

3.1 Low-Pressure Nitrogen Adsorption (LPNA)

Low-pressure nitrogen adsorption has been widely applied on the characterization of porosity of porous materials. Shales, classified as porous material, have been investigated the porosity via using physisorption technique. Ross and Marc Bustin (2009) combined CO\textsubscript{2} and N\textsubscript{2} adsorption with mercury porosimetry on the studies of the porosity of the Western Canadian Sedimentary Basin. Previous comparative studies on porosity of shales by implementing a number of indirect and direct techniques have showed that the pore size distribution in shales may range from less than 2nm micropores to macropores exceeding 50nm (Chen, Zhu et al. 2011, Chalmers, Bustin et al. 2012, Mastalerz, He et al. 2012, Clarkson, Solano et al. 2013, Kuila and Prasad 2013, Mastalerz, Schimmelmann et al. 2013, Wang, Zhu et al. 2014). In the studies of physisorption, pores in the porous materials are generally classified into 3 categories (Clarkson and Bustin 1996):

- Macropores with widths exceeding 50nm;
- Mesopores with widths between 2nm and 50nm;
- Micropores with widths less than 2nm.
This classification first introduced by the International Union of Pure and Applied Chemistry and has been commonly used in shales studies. It has been reported that pore size distribution (between 1 and 20nm) in organic rich and microporous materials (shales) could be efficiently measured with the application of low-pressure N\textsubscript{2} adsorption (Gan, Nandi et al. 1972, Dubinin 1975, Dubinin 1989, Lamberson and Bustin 1993, Larsen, Hall et al. 1995, Wang, Zhu et al. 2014).

3.1.1 LPNA Methodology

1) Determination of Adsorption Isotherm

To determine an adsorption isotherm, a confined volume containing the adsorbent at constant temperature is required, which can let a known quantity of pure gas adsorb on the adsorbent under a wide range of relative pressures. An adsorption isotherm is then acquired by measuring the amount of adsorbed gas across the relative pressures while a converse desorption isotherm is obtained by measuring the desorbed gas when reducing the pressures.

Adsorption isotherms are typically presented in 6 types. Figure 3.1 demonstrates the types of physisorption isotherms.

![Figure 3.1 Types of Physisorption Isotherms (Brunauer, Deming et al. 1940).](image-url)
The Type I isotherms are obtained from microporous solids, whose pores are typically microporous with the exposed surface locating almost exclusively inside the microspores, which once filled with adsorbate, or no external surface for further adsorption.

The Type II isotherms are frequently found with the adsorption on macroporous materials. Point B in the middle of the isotherm indicates that the completion of first adsorbed monolayer.

The Type III isotherms are mainly characterised by heats of adsorption less than the adsorbate heat of liquification, adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface.

The Type IV isotherms occur on porous adsorbents with pores in the range of 1.5 – 100 nm. At higher pressures, the slope shows increased uptake of adsorbate as pores become filled, inflection point typically occurs near completion of the first monolayer.

The Type V isotherms are observed where there are small adsorbate-absorbent interaction potentials (similar to type III), and are also associated with pores in the 1.5 – 100 nm range.

The Type VI isotherms represent stepwise multilayer adsorption on a uniform non-porous surface. Ordinarily this isotherm is obtained with argon or krypton on graphitized carbon blacks under liquid nitrogen temperature.

Physisorption hysteresis generally occurs with capillary condensation in mesoporous materials which have multilayer adsorption. The shapes of hysteresis loop are supposed to have possibility to identify with some specific pore structures. Figure 3.2 spotlights 4 types of hysteresis loop.
The Type H1 hysteresis loop is generally obtained from some porous materials with narrow distribution of pore size as the materials have agglomerates in fairly regular array. The most common loops in physisorption is Type H2 with the association of many porous adsorbents like inorganic oxide gels and porous glasses, it is mainly recognised as an indicator which there is a difference in mechanism between evaporation and condensation processes occurring ink bottle pores (pores with narrow necks and wide bodies). The Type H3 loop and the Type H4 loop do not exhibit any limiting adsorption at high relative pressure, the difference between them is that the H3 loop is observed with aggregates of plate-like particle giving rise to slit-shaped pores while the H4 loop is often characterized from narrow slit-like pores.

Figure 3.2 Types of Hysteresis Loop
2) Determination of Surface Area

It is believed that the Brunauer-Emmett-Teller (BET) gas adsorption methodology is the most common applied standard procedure for the determination of the surface area of porous materials. The BET equation is normally described as below (Brunauer, Deming et al. 1940):

\[
\frac{1}{W \left( \frac{P}{P_0} - 1 \right)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \left( \frac{P}{P_0} \right)
\]

Where \( W \) is weight of gas adsorbed, \( \frac{P}{P_0} \) is relative pressure, \( W_m \) is weight of adsorbate as monolayer and \( C \) is BET constant.

The BET equation needs a linear plot of \( \frac{1}{W \left( \frac{P}{P_0} - 1 \right)} \) against \( \frac{P}{P_0} \), thus slope \( (s) \) and intercept \( (i) \) can be described as:

\[
s = \frac{C - 1}{W_m C} \quad i = \frac{1}{W_m C}
\]

Therefore, weight of monolayer can be expressed as:

\[
W_m = \frac{1}{s} = i
\]

And then total surface area \( (S_t) \) can be derived as:

\[
S_t = \frac{W_m N A_{cs}}{M}
\]

Where \( N \) is Avogadro’s number \( (6.023 \times 10^{23}) \), \( M \) is molecular weight of adsorbate and \( A_{cs} \) is adsorbate cross sectional area \( (16.2 \ \text{Å}^2 \text{ for nitrogen}) \).

Specific surface area \( (S) \) can be determined by total surface area by sample weight \( (w) \):

\[
S = \frac{S_t}{w}
\]

For microporous materials associated with the Type I isotherms, the Langmuir equation is introduced to describe this gas adsorption behaviour (Langmuir 1918). It is assumed that the adsorption only occurs to one monolayer and is expressed as below:
\[
\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m}
\]

Where P is adsorbate pressure, V is amount of adsorbed gas, \(V_m\) is volume of monolayer and b is constant.

A linear plot is made of \(P/V\) against P to calculate b and \(V_m\) based on slope and intercept. When using nitrogen as adsorbate, surface area (\(S_L\)) can be described as:

\[
S_L = 4.63 \times \frac{V_m}{W}
\]

Where W is sample weight.

3) Porosity

The total pore volume (\(V_p\)) is usually obtained by measuring the amount of vapour adsorbed at a relative pressure close to unity, it is assumed that the pores are filled with liquid adsorbate. So the total pore volume (\(V_p\)) may be described as below:

\[
V_p = \frac{P_a V_{ads} V_m}{RT}
\]

Where \(P_a\) is ambient pressure, \(V_{ads}\) is volume of adsorbed gas, \(V_m\) is molar vol. of liquid adsorbate, T is ambient temperature and R is constant.

The pore size distribution, which the distribution of pore volume with respect to pore size, is commonly derived from Kelvin equation (Lancaster 1966) which is shown below:

\[
\frac{2\gamma V_m}{rRT} = \ln \frac{P}{P_0}
\]

Where \(\gamma\) is surface tension, \(V_m\) is molar vol. of liquid adsorbate, r is Kelvin radius, R is constant, T is ambient temperature and \(P/P_0\) is relative pressure.
3.1.2 Experiment Procedure

1) **Sample preparation:** a small piece of shale sample with the weight of around 3g was cut from big rock sample by using diamond saw. Then a ball-milling machine was used to crush the small piece into powder. Due to the limitation of ball-milling machine, the particle size is around 200 mesh (74 micron). For gas adsorption experiment, samples need to be crushed to less than 250 microns to meet the vacuum threshold. Figure 3.3 shows the diamond saw machine and the prepared small piece specimen.

![Diamond Saw Machine and Prepared Sample](image)

**Figure 3.3** A. Diamond Saw Machine; B. Prepared Sample.

2) **Experiment Operation:** Nitrogen adsorption experiment was performed via using a autosorb iQ/ASiQwin gas adsorption system from Quantachrome Instruments Corporation. Around 0.2g of sample powder (as displayed in Figure 3.4) was first outgassed for 8 hours at 150°C in the instrument and then N$_2$ adsorption isotherms were collected at 77 K on the same apparatus. The data obtained from powder sample was then analysed by applying Brunauer-Emmett-Teller (BET) and Langmuir method for surface area and Barrett-Joyner-Halenda (BJH) equation for pore size distributions, Gregg, Sing et al. (1967) have introduced and interpreted comprehensively these methods in their studies.
3.1.3 Results Analysis and Discussion

Based on the studies of Gregg, Sing et al. (1967), the N₂ adsorption isotherms from this shale rock sample is the Type II, which represents unrestricted monolayer-multilayer adsorption so that Brunauer-Emmett-Teller (BET) equation can be applied on the analysis. Figure 3.6 exhibits the N₂ adsorption isotherm with red line A (adsorption) and blue line D (desorption).
This isotherm type has been discussed in the previous studies, however, it has been somehow recognised as the Type IV isotherm (Mastalerz, He et al. 2012). Also, Kuila and Prasad (2013) mentioned that the Type IV isotherm is common for shales as the presence of mesoporous pores and mainly the Type II isotherm is characterized from macroporous materials. With a closer inspection of our isotherm, it suggests that this isotherm should be classified into the Type II isotherm which is reported in the studies of Clarkson, Solano et al. (2013). It is also found that there is a forced closure of the desorption branch where the isotherm closes at relative pressure about 0.35-0.45. This phenomenon is called the “Tensile Strength Effect”, indicating that evaporation from pores is obviously different process from condensation within the pores, which suggests that capillary condensation occurs within the pores with diameter less than 4nm (Groen, Peffer et al. 2003). The hysteresis loop in the isotherm could be identified as the H3 type, which implies the presence of slit-shaped pores according to the classification of Gregg, Sing et al. (1967).

<table>
<thead>
<tr>
<th>BET Surface Area (m²/g)</th>
<th>N₂ Pore Volume (cm³/g)</th>
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<tbody>
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</tr>
</tbody>
</table>

Table 3.1 BET Surface Area and Total Pore Volume.
We compared BET surface area and pore volume (Table 3.1) gained from N$_2$ adsorption experiment with the comprehensive studies by Clarkson, Solano et al. (2013). They characterized pore structure of 10 shale gas reservoir samples from North American, those reservoirs are known as industry scale gas shales and have been explored for commercial purpose. By comparing with these organic rich and thermally mature shale formation, this sample exhibits a medium surface area and a high pore volume. The BET surface area from the N$_2$ physisorption is much larger than the surface area (2.05 m$^2$/g) of the tight gas reservoir characterized by Clarkson, Freeman et al. (2012). In some cases, Nitrogen BET surface area trends to increase with increasing micropore volumes.
(Ross and Marc Bustin 2009). In the research of Mastalerz, He et al. (2012), they investigated two Pennsylvanian coal samples and two Upper Devonian-Mississippian shale samples by using N$_2$ gas adsorption, the results showed that the samples with higher TOC content are more likely to have larger surface area and pore volume, this has also been reported in the study of Mastalerz, Schimmelmann et al. (2013).

![Figure 3.8 Pore Size Distribution Defined by Differential Pore Surface Area.](image)

With the respect of the pore size, the distribution of pore volume can be shown as cumulative, incremental and differential distribution curves (Wang, Zhu et al. 2014). A differential distribution plot of the derived pore volume with respect to pore diameter is shown in Figure 3.9, which exhibits unimodality with a peak around 40 nm, whereas the plot of the derived pore area with respect to pore diameter as demonstrated in Figure 3.8 suggesting two peaks (20 nm and 40 nm, respectively). This sample shows increasing pore volume and pore area with a decrease in pore diameter, particularly the greatest contribution to both pore volume and pore area is from pores within the mesopore range (2-50nm).
Figure 3.9 Pore Size Distribution Defined by Differential Pore Volume.

Chalmers, Bustin et al. (2012) used N₂ gas adsorption to explore pore system of shale sample from Barnett, Marcellus, Woodford and Haynesville, they reported that the most pores they found in those organic rich formation are micropores with size less than 2nm. Compared to other studies on shale gas reservoirs which have been explored commercially and researched comprehensively, especially in North American, we found that this sample has more pores with size of 10-50nm than micropores (less than 2nm). It may attribute to the limit of the gas adsorption apparatus, micropores are not explored properly, and besides, it is believed that the particle size of nitrogen is too large compared to other probe gas like CO₂ and Helium so it makes nitrogen hard to penetrate through the micropores (Groen, Peffer et al. 2003, Chalmers, Bustin et al. 2012, Clarkson, Freeman et al. 2012, Mastalerz, Schimmelmann et al. 2013, Wang, Zhu et al. 2014).

3.2 Scanning Electron Microscopy

It has been advised in 1990’s that direct techniques like scanning electron microscopy and computed tomography are able to provide better insight in pore system of shale (Ōya, Miyagawa et al. 1990, Bennett, Bryant et al. 1991, Bennett, O’Brien et al. 1991). From then on, SEM, known as a radiation probe technique,
has experienced a huge development on investigation and imagination of pore structure and morphology of shale reservoirs. Compared with light microscopy, SEM has much larger magnification and can reveal higher levels of detail and complexity with better resolution by using focused electron beam. Figure 3.10 represents the basic schematic diagram of SEM apparatus.

![Figure 3.10 SEM Schematic Diagram](image)

A two dimensional (2D) image is produced in SEM by detecting the interaction of the surface of a specimen and an electron beam, this interaction produces a range of signals which are detected by the detector and imaged a 2D image (Reimer 2000, Goldstein, Newbury et al. 2012). Electrons bounced back out of sample are recognised as backscattered electrons (BSE) while these knocking into sample with displacement of atoms are called as secondary electrons (SE). The interaction volume involved in the production of SE, BSE and X-rays can vary with change of the accelerating voltage, aperture and spot size of beam as well as the landing energy, the atomic number of the sample and the density of the sample and it generally forms as a tear drop to a semi-circle within the specimen. The amount of backscattered electrons is determined the atomic
number of specimen, and consequently, BSE images is mainly used to demonstrate compositional contrasts within a sample and also suggest the average atomic number of the sample. The difference of BSE and SE images is that SE images show texture and topography as more secondary electrons can be captured from the edges and sharps, which are looked brighter and showed more details than other area. Figure 3.11 demonstrates the interaction volume of specimen and electron beam in SEM imaging procedure.

Figure 3.11 Interaction Volume of sample surface and electron beam during SEM imaging with various signals produced (Adopted from (Salh 2011)).

3.2.1 Experiment Procedure

1) **Sample Preparation**: some shale rock samples were cut into pieces measuring around 5*5*2mm by using diamond saw (Figure 3.3 A), while some of them remained original size and shape. We took two samples from each group and mounted them into epoxy base by applying epoxy mounting apparatus (as shown in Figure 3.12), these sample were then processed to grinding and polishing stages with the use of two machines shown in below (Figure 3.13). These samples were attached on the SEM stub using carbon adhesive tabs and then coated with gold and covered with silver to give better conductivity (Figure 3.14). Also, several shale samples were polished with fine sand paper to reduce the roughness of sample surface and minimise the
curtaining effect (Desbois, Urai et al. 2010, Desbois, Urai et al. 2010), and then they were put on the stub and coated with gold. All samples were using their “fresh” side to run SEM experiment. Fresh surface refers to surfaces of the specimens have been polished or grinded to reduce the contamination during the shipment and transportation. Besides, sample power (Figure 3.4) prepared by ball milling was introduced in this study at the same time, the powder sample was attached on the SEM stub without coating.

Figure 3.12 Epoxy Mounting Machine.

Figure 3.13 A. Polishing Wheel B. Grinding Machine.
2) **Experiment Operation:** Investigation was performed by using Zeiss ULTRA Plus SEM system housed at Australia Centre for Microscopy and Microanalysis, the University of Sydney. In the experiments, we used low acceleration voltage of 2-5 kV, with working distance of 2-8 mm and magnification of 3000×-50,000×. Lower magnification always used to get a general information of overlook on sample surface whereas higher magnification gave more details of features found on the samples. Both secondary electron and backscattered electron detectors were applied in this study, and an energy dispersive spectroscope (EDS) system equipped within SEM was introduced to form element mapping. Figure 3.15 shows the SEM machine used in this study.
3.2.2 Results and Discussion

In SEM investigation, shale pores have usually been classified into 3 groups: interparticle pores (interP pores), intraparticle pore (intraP pores) and organic matter pores (OM pores). This classification has been recommended in many previous studies and been used widely (Loucks, Reed et al. 2009, Loucks, Reed et al. 2010, Schieber 2010, Fishman, Hackley et al. 2012, Milliken, Rudnicki et al. 2013). Interparticle pores can be found at the area with quartz, pyrite or other crystals. Intraparticle pores are usually found within pyrite framboids (between individual crystals) or fossils, for example, moldic pores after dissolution and along cleavage planes in micaceous grains. Organic matter pores are associated with grains of organic matter which is divided into solid (low thermal maturity), pendular (intermediate thermal maturity) and spongy (high thermal maturity). Examples of these pore groups are showed in Figure 3.17.

![Four SEM Images of Powder Sample Under InLens Model.](image-url)
Charging effect occurs frequently during the SEM imaging of shale powder samples, this phenomenon is a result of lack of conductivity on sample surface. A number of unexpected artefacts are produced such as abnormal contrast, image deformation and drift. As it shows in Figure 3.16, a range of unwanted bright flash occur on the images. Particularly, as the piece sample was crushed into powder, it may increase the surface roughness and destruct its original structures, which makes it harder to investigate the morphology and the porosity of the sample. However, from the images, it somehow tells us that the sample is heterogeneous and a lot of fractures can be observed. In general, the use of shale powder on the characterization of pore system still needs further consideration.

Figure 3.17 SEM Images of Shale Pore Types Under InLens Model. A: Intraparticle pores found within pyrite framboid, interparticle pores surrounded pyrite and organic matter pores along pyrite particles. B: Shale surface displays
number of cracks and pores. C: Intraparticle pores found within crystal grains. D: Intraparticle pores within quartz and interparticle pores around it.

Based on the SEM investigation of this sample, we find that it is better to recognize and group the pores into two general types according to their sizes: micropores (pores with the diameters >1µm) and nanopores (pores having the diameters <1µm). In this sample, nanopores are the most common pore type and usually associated with organic matter whereas micropores show more appearance around or in pyrite, quartz and clay grains. Natural fractures and cracks are also observed in this sample, and they are recognized as a storage and transport mechanism for hydrocarbons in shales (Dewhurst, Yang et al. 1999). Thermal maturity has some impacts on genesis and development of pores, and apart from it, other conditions like organic matter composition and deposit environment may also affect porosity (Jiao, Yao et al. 2014). It is believed that interparticle pores and intraparticle pores form in the stage of shallow- to intermediate-bury (low maturity), and organic matter pores are mostly developed in the deep-burial stage which hydrocarbons highly generate (Loucks, Reed et al. 2010, Loucks, Reed et al. 2012).

Most of micropores have been found within pyrite frambooids, microfossils or fragmentary fossil material (Figure 3.17 A, C, D). These fossil-related intraparticle pores are usually filled with pyrite cement, silica or carbonate. Compared with the study of Barnett shale reservoir by Loucks, Reed et al. (2009), the silica-related pores in our sample seems to be less present. The size of nano- to microintercrystalline pores associated with pyrite frambooids changes with the size of the frambooids. Pores with the size of around 200nm are usually found within small frambooids (300-500nm in size) while large frambooids show pores with the diameter over 1µm (Figure 3.17 A).

Interparticle pores are commonly observed at the margins of large grains (Figure 3.17 B) and they are dispersed over fine-grained clays. A group of “card house” like flocculated clay mineral aggregates is illustrated in the clay matrix, this structure is built by individual edge-face- or edge-edge-oriented flakes and/or domains of face-face-oriented flakes as showed in Figure 3.20 (O’Brien 1971, Wang, Zhu et al. 2014). The pores between the flocs are recognised as
intraparticle micropores with the sizes over 2µm. Intraparticle organic nanopores contribute largely in organic matters with the shapes varying from nearly spherical to irregularly polygonal (as showed in Figure 3.18 A, B). The distributions of the organic matter vary widely and greatly as well as the sizes and shapes, typically the size of organic matter grain in our sample is less than 100nm, however the grains over 1 micron are also observed. The shapes of organic matter remain irregularly angular with rounded or unrounded pores. Complex grains may imply that the formation is more related to early compaction and has been elongated parallel to bedding (Loucks, Reed et al. 2009). These organic matter are generally made from algal matter, transported terrestrial and other marine plants.

Figure 3.18 Three SEM Images of Organic Matter Pores Under InLens Model. A and B: Intraparticle organic nanopores; C: Organic pores observed on clay surface.
Nanopores within organic matter are usually present as irregularly ellipsoidal shapes, but some other morphologies are observed (Figure 3.18C). Some of them show increased rugosity with high magnification and resolution. It may suggest that the complexity of the pores is derived from coalescence of various ellipsoidal pores. In general, organic matter hosted pore system from this sample suggests irregularly rounded or ellipsoidal shapes. Large pores (over 1µm) seem to be more complex than small pores on cross-sections. Some nanopore (natural fracture) shows linear shapes along with grains, which may relate to underlying structure or heterogeneity. And mostly, organic matter hosted nanopores tend to be grouped together instead of appearing isolated. Nanopores in our sample seem to be smaller than the result of Barnett shale investigated by Loucks, Reed et al. (2009). Actually, morphology of pores can be changed by number of influence. For instance, the genesis of pores can be affected by anisotropic pressure, pore area extends with combining of pores during hydrocarbon generation and form the pores into more complex one like moniliform and irregular polyhedral (Jiao, Yao et al. 2014). The shapes of pores have been observed in our sample, which is similar to what have been presented in the studies for the Barnett Shale (Loucks, Reed et al. 2009, Passey, Bohacs et al. 2010, Slatt and O'Brien 2011, Bernard, Wirth et al. 2012, Curtis, Sondergeld et al. 2012); the Marcellus Shale (Curtis, Sondergeld et al. 2012); the Woodford Shale (Curtis, Ambrose et al. 2011); the Horn River Shale (Curtis, Sondergeld et al. 2012); the Eagle Ford Shale (Walls and Sinclair 2011, Curtis, Sondergeld et al. 2012); the Gothic Shale (Heath, Dewers et al. 2011); the Tuscaloosa Shale (Heath, Dewers et al. 2011); the Haynesville Shale (Elgmati, Zhang et al. 2011, Curtis, Sondergeld et al. 2012); the Utica Shale (Elgmati, Zhang et al. 2011); the Fayetteville Shale (Elgmati, Zhang et al. 2011, Bai, Elgmati et al. 2013); and the Toarcian Posidonia Shale (Bernard, Brown et al. 2013).
Permeability is a significant petrophysical characteristics on shale reservoir engineering, it controls behaviour and movement of fluids and gases through shale formations. From Figure 3.19 A, we can see some long and narrow throats connect to both micropores and nanopores, these throats with width less than 10nm and length around 50nm are too narrow to image properly. Just like other throats in conventional reservoirs, traces of the throats in sample are presented as

Figure 3.20 SEM Images of Flocculated Clay Mineral Aggregates. (A). Overview of Aggregates. (B). Close-Up of the Panel A.
smoothly curving. Pores found in fossil have been observed to be well connected to clay matrix and to each other (Figure 3.19 B). In pyrite framboids, the connectivity of pores is great and the pores are also connected with the clay matrix. Cracks (fractures) are commonly found in the clay matrix, they provide the way to let gases and fluids go through from mineral to clay matrix (Figure 3.17A). The intraparticle pores showed in Figure 3.20B may be interconnected to develop permeability pathways inside the flocculated clay mineral aggregates.

To better investigate the materials and identify the mineral composition, EDS system within SEM was introduced. Several certain areas were chosen for element mapping as showed in Figure 3.21 3.22 3.23.

Very large pore showed in Figure 3.21A may be considered as a big trap where a relative huge amount of gases and fluids hided inside. From the element mapping results, we find that the organic matters distribute along with carbonates. Carbonates have been reported to have 8% of total mineral composition of average shales (Gromet, Haskin et al. 1984). Calcite (CaCO$_3$) is predominant in this area as Ca takes 37.8% of element spectrum. The EDS results prove the existence of pyrite framboids (FeS$_2$) in Figure 3.22. Fe and S distribute centrally where pyrites framboids can be clearly seen and take percentage of 17.1 and 15.6 %, respectively. Last EDS (Figure 3.23) shows that the various chemical composition found on the surface of shale, clay minerals like illite, smectite and chlorite can be found more than non-clay minerals such as quartz and pyrite. Relative studies about chemical and mineral composition of shales were done by Wedepohl (1971), Vine and Tourtelot (1970), Gromet, Haskin et al. (1984) and Yaalon (1962).
Figure 3.21 A: Selected Area for Element Mapping. B: Close-Up of Selected Area. C: 3 Main Highlighted Element Mapping. D: Element Spectrum of Selected Area.
Figure 3.22 Element Mapping Results with 4 Main Elements Present.
Figure 3.23 Element Mapping of Selected Area with All Detected Elements.
3.3 Transmission Electron Microscopy

Similar to X-ray imaging technique, transmission electron microscopy (TEM) uses electron beams instead of X-rays. Even SEM and TEM are both introduced to help on the creation of image, the difference between SEM and TEM is that electrons pass through a sample and hit a detector on the other side during TEM imaging rather than interact with the surface of the sample like in SEM. Basically, a dark area in a TEM image means that electrons do not pass through the sample whereas brighter regions show that electrons are unscattered.

Figure 3.24 Left: Various Signal for TEM and SEM Imaging. Right: Basic TEM Schematic Diagram.

And because of the imaging process, TEM samples are always needed to be thin enough to let electrons pass through them. Actually, with the change of the electron energy or acceleration voltage and the average atomic number of the specimen, the electron transparency thickness can vary from nanometre to micron. However, it has been suggested by Williams and Carter (1996) that thinner samples with size less than 100nm are always preferable. Therefore, preparation for better quality TEM samples requires precisely mechanical
polishing facility like ion-beam thinner to gently thin specimens to electron transparency.

Just like SEM, an energy dispersive spectroscopy (EDS) system is usually equipped within TEM. By selecting a specific point, a certain area or drawing a line in a sample, EDS will calculate the chemical composition. What is more, electron diffraction is usually introduced to help on research of the crystal symmetries and identification of the crystal phases of different grains inside of shales. Therefore, TEM diffraction imaging and EDS are considered as a better way to analyse crystal phases and pores filled with organic matter or other minerals.

3.3.1 Experiment Procedure

1) **Powder Sample Preparation:** Powder sample from ball milling was used in TEM experiment (Figure 3.4). Powder was mixed up with ethanol (about 1:3) as ethanol does not have reaction with shales, then it was put in the ultrasonic wave oscillator for 10 minutes to make powders well-distributed in the ethanol. Next, a drop from the mixture was put on the copper grid by using a pipette. It has been suggested that one drop should be enough with this proportion (1:3) of the powder and the ethanol, but it still needs to be checked under TEM (Rao, Muraleedharan et al. 2010).

2) **Slice Sample Preparation:** Rock sample was cut into pieces measuring around 8×6×4mm by using diamond saw (Figure 3.3A), and then a grinding technique, which is called Tripods introduced by Adam Sikorski, Australian Centre for Microscopy & Microanalysis, The University of Sydney, was used for grinding manually to reach a relative thin section before going to last stage. After Tripods grinding, samples were put into precision ion-polishing system (PIPS) to finalise electron transparency for TEM observation (Figure 3.2). Every half an hour, these samples were taken out from PIPS and put under light microscopy to check progress (the sample is ready if the marginal starts disappearing observed under light microscopy). Each sample was taking around 2 hours for PIPS polishing.
3) **Experiment Operation:** Observation was performed by using JEOL 2200FS Transmission Electron Microscope housed at Australian Centre for Microscopy & Microanalysis, The University of Sydney. Imaging was conducted by Gatan Ultrascan 2k ×2k camera with an accelerating voltage of 200 kV, and element mapping was done by using EDS and scanning transmission electron microscopy (STEM) system. Figure 3.2 shows the TEM system used in this study.
3.3.2 Results and Discussion

The pores observed with TEM are still using the same classification designed by Loucks, Reed et al. (2009). As the large magnification we used in TEM, almost all the pores we have observed are nanopores (<1 µm). Shale powder samples are interpreted first, followed by shale piece samples. The advantage of TEM compared with SEM is that TEM could visualise the internal connectivity which is recognised as permeability pathway of gases and fluids. Previous research on the characterization of pore system of shales remains rare, few we can learn from. The interpretation of micropore structure, location and size could need further research.
Figure 3.27 Transmission Electron Microscopy (TEM) Images of Shale Powder Sample.
Large number of interparticle pores is observed under TEM, as illustrated in Figure 3.27A, C-E, however, TEM does not show the morphology of features we have found, so the interparticle pores we have identified could be intraparticle pores or organic matter pores. Most of interparticle pores are associated with clay sheets (Figure 3.27D) and found between quartz and clay grains. The intergranular porosity within pyrite framboids or other clay grains could be considered as potential permeability pathway for gases and fluids. It may be because the samples have been destructed structurally during the process of ball milling, which makes more difficult to locate the features we look for, and also, the powder sample has not been thinned so it gives challenges on the thin section finding. Besides, the samples distribute unorderly and unsystematically due to the method used to prepare samples.

Huge amount of small nanopores (<5 nm) are found in the shale slice samples (3.28A-C), we identify these nanopores as intraparticle pores because they seem to locate in the irregular wall surface which has been mentioned by Chalmers, Bustin et al. (2012) in their study on the Barnett, Woodford, Haynesville, Marcellus and Doig Shale. They suggested that this irregular wall surface could be built by a number of very small nanopores. These mineral grains in shale matrix are measured around 5 nm (Figure 3.28B). High magnification scanning transmission electron microscopy (STEM) images show the morphology of irregular wall surface (Figure 3.28D, E). They are more likely to be the organic matter intraparticle pores we found in SEM (Figure 3.18A & B, 3.21B), also the shapes of the fine nanopores trend to be irregular ellipsoidal or unrounded, clay particles have diameter of about 6 nm under STEM image (Figure 3.28E). Interparticle pores are observed associated with clay sheets (Figure 3.28 F). The change of sample thickness highly influences the electron density and the presence of fine nanopores, whereas sample composition is more likely not having impact on those.
Figure 3.28 A-C: TEM Images of Shale Slice Samples. D-F: STEM Images of Shale Slice Samples.
Figure 3.29 TEM Image of Shale Slice Sample with Numbered Areas Identified by EDS (see Table 3.2).

<table>
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<tr>
<th>Atomic (%)</th>
<th>C</th>
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</tbody>
</table>

Table 3.2 Elemental Composition (atomic percent) of Numbered Area in Figure 3.29, Measured by EDS.
Figure 3.30 TEM Image of Shale Slice Sample with Drawn Line Identified by EDS (see Figure 3.31).

Figure 3.31 Element Spectrum of Drawn Line in Figure 3.30, Identified by EDS.
Figure 3.32 TEM Image of Shale Slice Sample with Point Identified by EDS (see Table 3.3).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic (%)</td>
<td>95.48</td>
<td>3.32</td>
<td>0.10</td>
<td>0.16</td>
<td>0.66</td>
<td>0.18</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 3.3 Elemental Composition (atomic percent) of Point A in Figure 3.32, Measured by EDS.

EDS investigation on the irregular wall surface place suggests the essentially high content of carbon (Figure 3.31, Table 3.2 & 3.3) with some other elements such as Al, Si and Ca showing much less appearance varied from different morphologies. In Figure 3.29, the darker area with clay grains aggregating intensively, marked as Object 498, shows the highest atomic percent of carbon (78.7 %) compared to Object 499 which has less clay aggregates and Object 497
with almost no aggregates demonstrated visually. S and Fe found in Object 498 have a relative high content (8.10 and 6.06 %, respectively) which may be a consequence of pyrite (FeS2). Quartz and other non-clay minerals may be contained more in Object 497 and Object 499 as the Al and the Si have much higher atomic percent than in Object 498 (Table 3.2). A line EDS result is showed in Figure 3.31, different spectrums of 6 elements on the points of the line suggest the highest carbon content and few Si involved. Sulfur has higher occurrence rate along with the line than other elements like Al and Ca. Point check with EDS results presents in Figure 3.32 and Table 3.3. A point in the darker place within the irregular wall surface area exhibits carbon as a predominant element (95.48 %), the existence of other metallic elements like Al and Fe or mineral elements such as Si, S and Ca remains highly infrequent.

The darker areas containing clay aggregates found in the irregular wall surface may be believed as the organic matter associated with clays and non-clay minerals like quartz and pyrite. Comparison of 3 areas with different morphologies suggests that Object 498 could be sulfur-rich immature organic matter referring to the Lower Toarcian Posidonia Shale study done by Bernard, Brown et al. (2013), they found that in thermally mature and overmature shales, sulfur showed less content in organic and lack of Fe in clays, conversely, thermally immature shale demonstrated high content of sulfur and Fe in organic matter and clay respectively. EDS on point A (Figure 3.32) might reinforce the existence of organic matter.

3.4 Focused Ion Beam Milling and Scanning Electron Microscopy

The dual beam microscopy, which is called focused ion beam milling and scanning electron microscopy (FIB/SEM), has been believed to be a better technique used to characterize submicrometer grains and pores at high magnification and large resolution (Bernard, Brown et al. 2013). Previous studies highlight the significant effect on investigation of permeability pathways with ultra-high magnification (Desbois, Urai et al. 2009, Loucks, Reed et al. 2009, Desbois, Urai et al. 2010). Besides, as this system offers in-situ investigation with simultaneously sequential milling, it is more applying on the 3D rendering
of microstructure of shales (Carl Sisk, Elizabeth Diaz et al. 2010, Elgmati 2011, Curtis, Sondergeld et al. 2012, Bai, Elgmati et al. 2013). The FIB/SEM technique is also used in TEM sample preparation by extracting ultra-thin sections from interested area (Heaney, Vicenzi et al. 2001, Benzerara, Menguy et al. 2005, Wirth 2009). Figure 3.33 shows the basic schematic diagram of FIB/SEM system.

Figure 3.33 Schematic Diagram of FIB/SEM.

3.4.1 Experiment Procedure

1) **Sample Preparation:** shale sample was cut into small pieces by diamond saw (Figure 3.3A), then they were polished into smaller pieces measuring around 5×5×1.8mm with the use of fine emery paper. It has been suggested that smaller sample could have less charging effect during FIB/SEM process (Elgmati 2011). These specimens were attached on the SEM stub using conductive type and coated with gold to create more conductivity.
2) **Experiment Operation:** FIB/SEM system work was done by the help of Zeiss Auriga FIB/SEM instrument located in Australian Centre for Microscopy & Microanalysis, The University of Sydney.

![Platinum Strip](image)

Figure 3.34 A 20×10×2 µm Strip of Platinum Deposited on the Interested Area.

A relative flat area was selected for the FIB/SEM investigations, then the specimen stage was tilted 54° for the next process. The use of platinum (Figure 3.34) was to protect the targeted area or minimize curtaining artefacts during milling (Curtis, Sondergeld et al. 2012). The next stage was to remove bulk shale around platinum strip with 30 kV accelerating voltage and 21 nA ion current to dig a swimming pool liked hole (Figure 3.35). Swimming pool requires wider and deeper as it may avoid re-deposition of milled material and curtain effect (Elgmati 2011).
To increase conductivity and reduce charging during FIB/SEM imaging, one more platinum strip with size of around 20×5×1µm was put between the previous strip and shale surface as showed in Figure 3.36.

Figure 3.36 New Platinum Strip Added on.
Before the performance of sequential FIB milling and SEM imaging, the cross section was needed to gently mill to create a flatter surface with low current. We used a 30 kV accelerating voltage and a 50 pA current to clean the surface slowly and gently. Once cleaning phase was completed, a volume of shale with size of 5×2×10 µm was chosen to perform serial sectioning and imaging with the same current used for cleaning. The thickness of each slice was 8 nm, and each individual image took 5 minutes for milling and imaging with high resolution of 3072×2304 pixels. 250 images were resulted from this procedure and they were reconstructed into 3D model with the help of Avizo® Fire 9 imaging software. At the same time, some 2D images were used to investigate microstructure of nanopores found in FIB/SEM.

3.4.2 Results and Discussion

FIB/SEM has ability to expose the extremely small nanopores (<10 nm) which cannot be offered by only SEM. Due to the gold coating, the gold particles could block these very tiny pores resulting almost 0 observation on them. However, with focused ion beam milling system, it actually creates a new surface used in the characterization and remains conductivity on the samples at the same time.

This sample demonstrates 3 main features on the SEM images of cross section as showed in Figure 3.37. A number of nanopores ranging from few to hundreds nanometre can be found in clays and quartz grains. Intraparticle quartz pores usually have size of 40 – 100 nm as illustrated in Figure 3.37B-D. Very tiny nanopores are usually found in clays and predominant on number. These nanopores located in organic matter are more likely to have much smaller size (around 10 nm) than the isolated nanopores with size over 100 nm or even larger. This is matched with previous studies on investigation of nanopores by using FIB/SEM (Sondergeld, Ambrose et al. 2010, Elgmå 2011, Curtis, Sondergeld et al. 2012, Bernard, Brown et al. 2013, Jiao, Yao et al. 2014). Quartz and organic matter are the other two main features observed in FIB/SEM images (Figure 3.37B-D), both of them distribute unsystematically and unorderly with different size and shapes. The shapes of very tiny nanopores found in organic matter are mostly irregular elliptic, rounded or unrounded. Bigger nanopores associated
with quartz and clays stay relative complex shapes just like the pores showed in SEM investigation. Pore throats are not observed by our FIB/SEM investigation, the connectivity between these nanopores cannot be found, however, it does not mean that there is no permeability as the pore throats could be observed in other direction, and because of this, 3D characterization is needed on the characterization of pore system, especially at this magnification.

Figure 3.37 FIB/SEM Images of Shale Sample.
However, when we imported the images we took in FIB/SEM into Avizo® Fire 9 image processing software, we found that the images in FIB stacks do not identify a suitable threshold value because of charging issues. And what is more, image drifting was another important issue we have met during slicing and imaging process, the images kept drifting around all the time, which gave more challenges on 3D rendering work. The charging of the specimen could also cause the ion beam to miss during the slicing process resulting multiple image slices appearing identical to each other for periods during the stack. These issues happened in experimental stage make it harder in 3D reconstruction, which is the identification of features within the image. The datasets gained from FIB/SEM have a lot of charging effect showed in images and illustrate no clear boundary between the pores and the surrounding materials. To obtain information about pores or other materials, it is highly necessary to perform thresholding of the dataset to mark pixel/voxel of interest. As there is no ideal threshold value existed, any result could be produced by choosing any threshold value. Even the automatic threshold values provide widely varying masks, and the number of identified pores in 3D building changes significantly with the varied threshold values (Figure 3.39).

Figure 3.38 Left: Automatic Threshold Values Chosen for Different Methods. Right: Possibly Identified Pores (Black Spots) with a Threshold Value Ranging from 11-62.
### Raw Pore Data

<table>
<thead>
<tr>
<th>Threshold Value</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Volume (µm³)</td>
<td>4,968.23</td>
<td>4,968.23</td>
<td>4,968.23</td>
<td>4,968.23</td>
<td>4,968.23</td>
<td>4,968.23</td>
<td>4,968.23</td>
<td>4,968.23</td>
<td>4,968.23</td>
</tr>
<tr>
<td>Minimum Volume (µm³)</td>
<td>111.356</td>
<td>111.356</td>
<td>111.356</td>
<td>111.356</td>
<td>111.356</td>
<td>111.356</td>
<td>111.356</td>
<td>111.356</td>
<td>111.356</td>
</tr>
<tr>
<td>Maximum Volume (µm³)</td>
<td>362,686</td>
<td>643,190</td>
<td>95,1757</td>
<td>1.19E+06</td>
<td>1.39E+06</td>
<td>1.58E+06</td>
<td>1.74E+06</td>
<td>1.95E+06</td>
<td>2.50E+06</td>
</tr>
<tr>
<td>Median Volume (µm³)</td>
<td>113.045</td>
<td>112.891</td>
<td>126.612</td>
<td>111.782</td>
<td>114.103</td>
<td>113.194</td>
<td>111.359</td>
<td>111.359</td>
<td>111.359</td>
</tr>
<tr>
<td>Number of Pores</td>
<td>177</td>
<td>275</td>
<td>501</td>
<td>800</td>
<td>965</td>
<td>1,219</td>
<td>1,248</td>
<td>11,346</td>
<td>56,045</td>
</tr>
</tbody>
</table>

### Filtered Pore Data (Excluded Pores < 10 Voxels)

<table>
<thead>
<tr>
<th>Threshold Value</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Volume (µm³)</td>
<td>70,998.5</td>
<td>78,728.5</td>
<td>85,468.8</td>
<td>127,967</td>
<td>129,014</td>
<td>161,923</td>
<td>171,123</td>
<td>150,659</td>
<td>126,241</td>
</tr>
<tr>
<td>Minimum Volume (µm³)</td>
<td>1,781.69</td>
<td>1,224.91</td>
<td>1,336.27</td>
<td>1,447.62</td>
<td>1,224.91</td>
<td>1,336.27</td>
<td>1,224.91</td>
<td>1,224.91</td>
<td>111.356</td>
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<tr>
<td>Maximum Volume (µm³)</td>
<td>362,686</td>
<td>643,190</td>
<td>951,757</td>
<td>1.19E+06</td>
<td>1.39E+06</td>
<td>1.58E+06</td>
<td>1.74E+06</td>
<td>1.95E+06</td>
<td>2.50E+06</td>
</tr>
<tr>
<td>Median Volume (µm³)</td>
<td>22,633</td>
<td>14,245.9</td>
<td>14,867.9</td>
<td>29,918</td>
<td>58,386.4</td>
<td>15,892.2</td>
<td>26,935.6</td>
<td>10,753.3</td>
<td>7,272.12</td>
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<td>Number</td>
<td>12</td>
<td>23</td>
<td>34</td>
<td>34</td>
<td>49</td>
<td>55</td>
<td>70</td>
<td>104</td>
<td>162</td>
</tr>
</tbody>
</table>
Table 3.4 3D Reconstruction Volume and Number of Pores Based the Best-Guess Estimates with 9 Possible Threshold Values.

Based on the best-guess estimates, we assumed a voxel size of $3.337 \times 3.337 \times 10$ nm and 9 possible threshold values out of 255. Results are show in Table 3.4. Even the pores less than 10 voxels are excluded, the number of pores has been counted still changes significantly. Any one or none of the thresholds we have tested might be right and we cannot find a way to validate any of them, this means the results are entirely subjective depended on the threshold chosen in the analysis. The pore size distribution, porosity and permeability drawn from any of these are not scientific and defendable if we do so. Successful examples on 3D reconstruction of shale were done by Curtis, Sondergeld et al. (2012), Bai, Elgmati et al. (2013), Elgmati (2011), Groeber, Haley et al. (2006), Uchic, Groeber et al. (2006) and Carl Sisk, Elizabeth Diaz et al. (2010). However, Curtis, Sondergeld et al. (2012) have also pointed out that it is completely subjective to set thresholds on the grayscale of 3D reconstruction. Both overestimation and underestimation of small pores could happen as a consequence of high and low thresholding respectively. Due to heterogeneity of shales, a 3D rendering can only represent a very small volume within a greatly large formation. Further research on how to upscale this information for large shale volume will be needed.
4. Conclusions

1) Low pressure N\textsubscript{2} adsorption experiment exhibits the Type II adsorption isotherm which is not common for shales as shales normally contain more mesopores. The H3 type of hysteresis loop suggests the presence of silt-shaped pores in shale. Compared with other organic-rich and thermally mature gas shale reservoirs, this sample shows a medium BET surface area and a high pore volume.

2) Pore size distribution shows that mesopores with the size of 20 – 40 nm are predominant in this sample. Micropores (< 2 nm) do not show occurrence in N\textsubscript{2} physisorption, it could be a consequence of lack of penetration through micropores. Nitrogen have larger particle size than other probe gas like CO\textsubscript{2} and helium, which may influence on this.

3) Shale powder samples are not suitable for SEM investigation because of the destructive sample preparation and the unexpected artefacts showed in images. Rough and unsmooth surface makes it harder to find features. Serious charging effects happened during the experiment procedure, which brings more obstacles on identification of pores.

4) Relative satisfied images are obtained with the use of polished shale rock sample. A number of intraparticle pores and interparticle pores are found associated with quartz grains, pyrite framboiids and other minerals. Organic matter pores generally have smaller pore size than clay-hosted pores and intercrystalline pores.

5) Shape of the pores observed by SEM is mostly irregularly ellipsoidal, rounded or unrounded. Large pores show more complex morphologies which could be because of combination of pores. Pore throats showed in pyrite, clay and quartz grains suggest potential permeability pathways for gases and fluids.

6) EDS equipped in SEM shows the organic matters associated with carbonates and the existence of pyrite framboiids. Clays are the main minerals with less occurrence of other non-clay minerals like quartz and pyrite.

7) Lots of interparticle pores are showed in shale powder sample with the use of TEM. Challenges coming from the destructive sample preparation and
unpolished surface and unsystematically distribution result more difficult observations.

8) Clay particles are frequently illustrated in TEM images of shale piece samples. The particles are believed to have average size around 5 nm. Huge amount of nanopores are observed on the shale surface by using STEM.

9) Dark areas in TEM images are believed as organic matter associated with clay aggregates proved by the results of TEM/EDS. EDS Area identification shows high content of iron and sulfur in organic matter, which may be pyrite. Both line and point EDS identification suggest large percent of carbon.

10) FIB/SEM dual beam system reveals the tiny pores (< 10 nm). These nanopores are found as irregularly rounded, unrounded and ellipsoidal as observed in SEM images. Pores are found mostly isolated instead of connected under such magnification.

11) 3D reconstruction work fails as we could not find a scientific threshold value when stacking images gained from FIB/SEM. Any thresholding may produce various results, so the properties including permeability and porosity calculated from 3D model should not be accelerated and defendable.
5. Reference


Desbois, G., J. L. Urai and M. De Craen (2010). "In-situ and direct characterization of porosity in Boom Clay (Mol site, Belgium) by using novel combination of ion beam cross-sectioning, SEM and cryogenic methods."


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