EFFECT OF THERMAL MATURITY ON NANOMECHANICAL PROPERTIES AND POROSITY IN ORGANIC RICH SHALES
(A BAKKEN SHALE CASE STUDY)

by

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ABSTRACT

Unconventional resources (Shale Plays) have been the game changer of energy supply worldwide. The ever improving technologies and expanding of knowledge related to unconventional hydrocarbon accumulations has generated an enormous opportunity for countries with these resources towards energy self-sufficiency.

For successful development of these resources, we need remote techniques that allow for spatially extensive in-situ reservoir characterization and sweet spots detection. In self-sourcing mudrocks, maturity (extent of oil generation), porosity and abundance of natural fractures are the main parameters to make them economical. Understanding the elastic properties of self-sourcing formations and their correlation with maturity can provide crucial information about amount of generated hydrocarbon, petrophysical properties and geomechanical characteristics from well logs and seismic surveys.

As kerogen matures and decomposes to lighter hydrocarbons, its physical and chemical properties change. Kerogen decomposition and consequent shrinkage also change the load bearing state of the minerals and organic matter and affect pore system since early stages of maturation.

Generating representative rock models to describe the behavior of organic-rich rocks is challenging due to complex textural properties of these rocks and the uncertainties in pore morphology and mechanical properties of some of the major components. Despite previous studies on the texture of organic-rich rocks in relation to their elastic properties, anisotropy and mechanical characteristics of the grains there is limited available data on the characteristics of some essential components such as clays and organic matter. Moreover, changes in properties of kerogen and clay minerals
during the course of thermal maturation are poorly understood. Consequently, any rock models must rely on anecdotal or extrapolated data about various types of kerogen.

The focus of this thesis was to determine underlying nano-scale changes in textural characteristics, mechanical properties and porosity evolution in organic-rich shales as these are main controlling factors of bulk properties.

Textural and nano-mechanical properties of Bakken Shae samples from a wide range of thermal maturity were studied at natural state and after hydrous pyrolysis using FESEM imaging, nanoindentation and nano-DMA techniques. Laminated texture of shales at low maturity levels (caused by abundance of organo-clay mixtures) changed to increased stiff grains contact and isolated kerogen particles. We found lowering of Young’s modulus of kerogen particles and organo-clay components with natural and synthetic maturation.

Significant amount of bitumen is generated and retained in the source rocks due to thermal maturation or synthetic hydrous pyrolysis which fills the kerogen and clay porosity. Lack or presence of bitumen in the pore system may introduce significant discrepancy in our evaluation of porosity and pore characteristics. In this research, successive solvent extraction was performed to determine what portion of the pore space is excluded from quantification due to oil trapped in pores and to understand the storage and flow capacity of source rocks in the oil window. The PSD and SSA measured after each extraction shows revival of the pore system with successive cleaning. Most significant was the recovery of kerogen-hosted pores with removal of soluble, oil-like organic material. Using successive extractions we were able to determine the evolution of organic matter porosity through maturation which was
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CHAPTER 1
INTRODUCTION

“We do not grow absolutely, chronologically. We grow sometimes in one dimension, and not in another; unevenly. We grow partially. We are relative. We are mature in one realm, childish in another. The past, present, and future mingle and pull us backward, forward, or fix us in the present. We are made up of layers, cells, constellations.”

— Anaïs Nin

Energy is the driving force of modern civilization. Oil and gas has been, and will remain for more decades to come, one of the most important sources of the world’s energy. There is a firm agreement that unconventional resources (Shale Plays) are the game changer of energy supply worldwide. Developments of these resources worldwide not only positively affect world’s economy and political stability; it brings peace and comfort to mankind. The ever improving technologies and expanding of knowledge related to unconventional hydrocarbon accumulations has generated an enormous opportunity for countries with these resources towards energy self-sufficiency. While North America is aiming for decreasing its foreign oil dependency, unconventional resources have gained tremendous attention.
The term “Shale”, as is used nowadays, encompasses a wide range of lithology. The inconsistency arises mostly due to the lack of a more general term when referring to ultra-tight, fine grained rocks. Shales are laminated and fissile fine-grained (<32μm) rocks which often have high clay content and may be organic rich. Mudrock is a more inclusive classification for describing sedimentary rocks with clay size grains (siltstone, claystone, mudstone, slate, and shale). Hydrocarbon accumulations in mudrocks are often referred to as unconventional accumulations. Unconventional reservoirs are different from conventional reservoirs in the governing trapping and migration mechanisms. In unconventional accumulations, due to very high capillary pressure caused by small pore and pore-throat sizes, buoyancy forces no longer control the hydrocarbon segregation or migration; thermal maturity of the charging source rock defines the fluid phase. As a result, lighter products are expected at deeper and more mature parts of the basin (unlike conventional accumulations). These petroleum accumulations are also called “reverse systems” or “deep basin accumulations”.

Many unconventional plays are the source rocks for conventional accumulations. These tight rocks store considerable volume of non-expelled hydrocarbon. The migration mechanism in the unconventional part of the petroleum systems is primary migration (hydrocarbon expulsion) within the tight body of the reservoir. Based on this characteristic, other terminologies like “Self-sourcing Mudrocks” are also used when referring to hydrocarbon charged tight rocks. Target zones in self-sourcing petroleum systems differ depending on the level of organic maturity, type of organic matter and kerogen content.
The complexity of production in ultra-low permeability mudrocks and associated challenging economics increases the risk of investment. Although advances in drilling and completion technologies have increased profitability of production from these accumulations, the profit margins remain fairly low for many of these plays when oil prices are low.

For successful development of these resources, we need remote techniques that allow for spatially extensive in-situ reservoir characterization and sweet spot detection. In self-sourcing mudrocks, maturity (extent of oil generation), porosity and abundance of natural fractures are the main parameters to make them economical. Understanding the elastic properties of self-sourcing formations and their correlation with maturity can provide crucial information about amount of generated hydrocarbon, petrophysical properties and geomechanical characteristics from well logs and seismic surveys.

This dissertation is focused on petrophysical and mechanical characterization of self-sourcing mudrocks for hydraulic fracturing design, well log analysis and seismic interpretation applications.

Nanoindentation, nano-dynamic modulus mapping, SEM imaging, nitrogen adsorption pore characterization, and geochemical analysis techniques are utilized to study mechanical properties, textural characteristics, and pore morphology of mudrocks as they evolve through thermal maturation.

Evolution of porosity in the source rocks with maturity, interaction of byproducts of hydrocarbon generation with other minerals, and their effect on conventional log responses and pore morphology are studied. These studies help us to understand how the log responses must be interpreted at the presence of organic matter and clay.
minerals. We have further developed practical workflows for integrating geochemical data with well logs for petrophysical characterization of mudrocks (presented in Appendix A).

1.1 Organization of the thesis

This thesis consists of six chapters. Chapters 2 through 5 are four articles that are already published in or submitted to peer reviewed journals. The core results of my research are presented in these four chapters and Chapters 1 and 6 provide an introduction and a wrap up conclusion to these chapters. In the following, I will explain the main contents of each chapter and explain my contribution to published articles.

Chapter 1 provides the problem statement and introduces the main focus of this thesis as it follows in the next chapters.

Chapter 2 presents the results of studying textural and mechanical changes of organic rich rocks through natural and synthetic thermal maturation. These findings set the stage for the next steps of my PhD research. We observed bitumen generation and occupancy of pore space by bitumen as well as softening of the organo-clay portion of the matrix during maturation which could not be explained without further analysis as is presented in the later chapters. This chapter is published in Geophysics journal with the same title. My contribution to this article was as the principle researcher and first author.

Chapter 3 presents the results of analyzing pore structure throughout the thermal maturation from immature state to gas window. The findings not only shed light on our understanding of porosity development in the kerogen but also explain mechanical properties of the kerogen as presented in chapters 2 and 5. This chapter is submitted to
Fuel journal with the same title. My contribution to this article was as the principle researcher and first author.

Chapter 4 introduces nanoDMA technique and describes advantages and limitations of the application of this technique to shales through varying sample preparation and scanning procedures. This chapter is published in the Journal of Material Science with the same title. My contribution to this article was in designing the experiments, sample selection and characterization, sample preparation, performing the nano-DMA experiments, and co-author. This chapter was solely added with permission from co-authors to provide an introduction to NanoDMA technique, sample preparation and the filtering scheme that is utilized in chapter 5.

Chapter 5 demonstrates the results of mechanical characterization of organic rich shales using nanoDMA technique and the main factors that control the kerogen moduli. This chapter is submitted to Geophysics journal with the same title. My contribution to this article was as the principle researcher and first author.

Chapter 6 summarizes the main conclusions of this dissertation and provides recommendations for future work to expand this research.

1.2 List of publications

Published in Peer Reviewed Journals


  
  Submitted to Peer Reviewed Journals

• Effect of Thermal Maturity on Elastic Properties of the Kerogen. (submitted to Geophysics)

Conference Proceedings and Abstracts


CHAPTER 2
ORGANIC MATURITY, ELASTIC PROPERTIES AND TEXTURAL CHARACTERISTICS OF SELF RESOURCING RESERVOIRS

A paper published in the journal of Geophysics
Saeed Zargari, Kenechukwu C. Mba, and Earl D. Mattson, Manika Prasad

“Maturity is when your world opens up and you realize that you are not the center of it.”
— M.J. Croan

2.1 Abstract

Organic-rich rocks have long been recognized as source rocks for clastic reservoirs, but more recently they have gained importance as reservoirs. However, the processes of kerogen maturation and hydrocarbon transport and storage are still poorly understood. Some empirical relations have been developed to relate the increase in elastic modulus with increasing maturity. A systematic study of the cause for this increase in elastic modulus is still lacking, and information about seismic and mechanical properties of kerogen and its alteration products is scarce. Consequently, any rock models must rely on anecdotal or extrapolated data about various types of kerogen.
Our experiments address this paucity of data by grain-scale modulus measurements coupled with careful FESEM microstructural assessments on organic rich Bakken formation shale samples with a range of maturities. Carefully acquired and detailed FESEM images help to understand the microstructural controls on the reduced (nanoindentation) Young’s modulus of minerals, clay particles, and kerogen matter with maturity in naturally matured shales. Using hydrous pyrolysis, we further investigate the cause for change in modulus with maturity and the mobility of the pyrolized organic matter.

In naturally matured shale samples, we find a direct relationship between the reduced Young’s modulus and the Total Organic Content or Hydrogen Index. Significant lowering of Young’s modulus is observed after hydrous pyrolysis due to bitumen generation. We measured modulus of the extruded bitumen to be less than 2 GPa. The presence of bitumen comingled with the organic matter also reduces its modulus, in excess of 30%. These results are critical to help understand how organic rich sediments evolve with burial and maturation. The modulus measurements can be used for modeling modulus variations during maturation.

2.2 Introduction

Kerogen is expected to undergo significant changes during maturation. As kerogen in the shale matures and expels hydrocarbon, its physical properties change. The amount of organic material in the shale decreases and shale matrix becomes stiffer (Mba et al., 2010; Prasad et al., 2011); sonic velocities increase and geomechanical properties of the rock improve. Despite general understanding of the bulk properties in kerogen-rich shales, inverting bulk measurements for kerogen properties remains
problematic. Isolating kerogen as another alternative also only results in concentrated kerogen. Moreover, complete removal of inorganic components requires treatments with different acids and solvents which have the potential of altering kerogen properties.

The organic content and maturity of organic rich shales is traditionally determined by pyrolyzing core samples and drill cuttings. In this context, pyrolysis is the process through which organic rich sediments are subjected to higher temperatures in the presence or absence of water to synthetically convert kerogen to hydrocarbons. Some indirect techniques have also been documented in which maturity is related to different characteristics of shales such as mechanical properties, sonic velocities, bulk density, resistivity and porosity (Schmoker and Hester, 1983; Passey et al., 1990; 2010; Vernik and Liu, 1997; Prasad, 2001, Prasad et al., 2011).

Understanding the elastic behavior of self-resourcing formations and its interrelation with maturity can provide crucial information about amount of generated hydrocarbon and geomechanical characteristics of the formation from sonic logs and seismic measurements. Stimulation programs with hydraulic fracturing require knowledge about rock fracture properties, such as brittleness. If fracture gradient is relatively constant over the vertical interval, more brittle rocks are easier to fracture and tend to sustain open fractures. For successful development of these resources, we need remote techniques that allow for spatially extensive in-situ detection of maturity which indicates oil generation and existence of extensive natural fractures. Generating representative rock models to describe behavior of these organic rich rocks is challenging due to limited knowledge about mechanical properties of kerogen and clay minerals which compose a significant portion of these rocks. Achieving this goal
requires a better understanding of the maturation process in which kerogen undergoes significant chemical and mechanical modification. Studying shales at sub-micrometer scale provides insight in developing appropriate rock modeling and petrophysical characterization techniques. Therefore we suggest application of in-situ techniques in sub-micron scale to extract the properties of different components of shales.

In the most recent studies on application of different rock models for predicting seismic response of shales, Carcione et al. (2011) found a significant dependence of velocity on TOC when modeling oil saturated rock using Backus and Krief/Gassman models. Vernik and Milovac (2011) found that TOC content tends to decrease Vp/Vs, whereas Lucier et al. (2011) showed that in shale gas reservoirs, the effect of gas saturation on Vp-Vs relationship is considerably higher than the effect of TOC. This implies that TOC predictions from sonic response are feasible in general, but can be more complicated due to variable pore fluid compressibility.

Building rock models requires knowledge of mechanical properties of individual grains and the texture of the rock. The mechanical properties of different clastic minerals are widely studied and are available in the literature, whereas properties of kerogen and clays are poorly studied. Studying texture of the rock provides information about interaction between the grains in the matrix. Despite previous studies on the texture of organic rich rocks in relation to their elastic properties and anisotropy (Vernik and Nur, 1992) and mechanical characteristics of the grains (Prasad, 2001; Zeszotarski, 2004; Ahmadov, 2009; Mba et al., 2010) there is little firm knowledge about the characteristics of some essential components such as clays and organic matter.
Moreover, changes in their properties during the course of maturation are poorly understood.

Investigations and direct measurements of naturally mature samples are confounded by changing mineralogy along with maturity. Kerogen is expected to undergo significant changes during maturation. As kerogen in the shale matures and expels hydrocarbon, its physical properties change. The amount of organic material in the shale decreases and shale matrix becomes stiffer (Mba et al., 2010; Prasad et al., 2011); sonic velocities increase and geomechanic properties of the rock improve. Despite general understanding of the bulk properties in kerogen-rich shales, inverting bulk measurements for kerogen properties remains problematic. Isolating kerogen as another alternative also only results in concentrated kerogen. Moreover, complete removal of inorganic components requires treatments with different acids and solvents which have the potential of altering kerogen properties.

We used Bakken Shale samples from various depths to evaluate changes in mechanical properties of source rocks with increasing maturation. Five samples were analyzed before and after hydrous pyrolysis to determine effect of maturation on the mechanical properties. By using pyrolysis to change maturity, we were able to eliminate mineralogy effects. Pyrolysis affects mostly organic matter and clay minerals. Thus, a comparison of elastic properties in native state and in post-pyrolysis samples allowed us to specifically evaluate changes in these two constituents. Nanoindentation and nano-DMA® techniques were utilized for studying microscale elastic behavior of the samples. FESEM images were taken to better describe the modifications in texture and distribution of organic matter. Our study helps understand changes in various
constituents of organic rich shales with maturity and can be used as building blocks for rock models.

2.3 Materials and Methods

2.3.1 Samples

The samples used in this study varied in depth and in maturity. The samples belong to Upper and Lower shale members of the Bakken system. These shales form the source of hydrocarbon for the Middle Bakken member and for adjacent formations. The samples vary from immature (HI~600 mg HC/g TOC) to fairly mature (HI~100 mg HC/g TOC) states. A previous study has reported natural state properties such as acoustic wave velocities, well log derived properties, geochemical, mineralogical and elastic properties (Mba et al., 2010, see Table 2.1).

Table 2.1- Geochemical characteristics and mineralogy of Bakken Shale samples used in this study (sample depths were used as identifiers in the study) (Mba et al., 2010)

<table>
<thead>
<tr>
<th>Sample #/Depth</th>
<th>10792</th>
<th>10479</th>
<th>10368</th>
<th>7221</th>
<th>7216</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (wt%)</td>
<td>7.9</td>
<td>10.3</td>
<td>12.8</td>
<td>16</td>
<td>17.7</td>
</tr>
<tr>
<td>HI (mg HC/ g TOC)</td>
<td>126</td>
<td>234</td>
<td>371</td>
<td>636</td>
<td>633</td>
</tr>
<tr>
<td>S1 (mg/g)</td>
<td>1.5</td>
<td>1.6</td>
<td>2.3</td>
<td>3.8</td>
<td>4.2</td>
</tr>
<tr>
<td>S2 (mg/g)</td>
<td>9.7</td>
<td>21.2</td>
<td>47.7</td>
<td>101.8</td>
<td>112.3</td>
</tr>
<tr>
<td>S3 (mg/g)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Quartz (vol%)</td>
<td>42.2</td>
<td>20.4</td>
<td>51.1</td>
<td>47.9</td>
<td>23.6</td>
</tr>
<tr>
<td>Clays (vol%)</td>
<td>33.5</td>
<td>60.2</td>
<td>26.3</td>
<td>42</td>
<td>60.6</td>
</tr>
<tr>
<td>Pyrite (vol%)</td>
<td>3.8</td>
<td>2.9</td>
<td>3.2</td>
<td>1.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Calcite (vol%)</td>
<td>3.2</td>
<td>0.6</td>
<td>1.6</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Dolomite (vol%)</td>
<td>12.4</td>
<td>6.3</td>
<td>12.4</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Other Minerals (vol%)</td>
<td>4.7</td>
<td>9.4</td>
<td>5.2</td>
<td>7</td>
<td>11.6</td>
</tr>
</tbody>
</table>
In this study, the same samples were re-measured and retorted through hydrous pyrolysis. Geochemical properties were obtained by RockEval analysis, microscale elastic properties were measured by nanoindentation, and texture and distribution of organic matter were visualized by FESEM. We present here comparisons of measurements on naturally mature and pyrolyzed cores (Table 2.2).

2.3.2 Pyrolysis

Several studies (for example, Lewan et al., 1979; Lewan, 1985 and 1987) have shown that pyrolysis in the presence of water (hydrous pyrolysis) results in the production of oil-like hydrocarbons, which better mimics the natural generation of oil. Thus, our samples were exposed to high temperature hydrous retort conditions to change their maturity by further converting the organic matter and possibly expelling hydrocarbons. The thermal treatment was conducted at the Idaho National Laboratory using Parr high pressure / temperature retorting vessels. The Bakken samples were sealed in the 1 liter high pressure vessels with 450 ml of deionized water. The head space was evacuated and purged with argon several times to create an inert environment. The vessel was then heated to 350°C and maintained at this temperature for 72 hours (Figure 2.1 and Figure 2.2).

After treatment, the samples were allowed to cool down to room temperature. Samples were weighed to detect any material loss or gain. During this heating period, physical and chemical reactions are expected. Although laboratory pyrolysis duplicates the hydrocarbon generation to a reasonable extent, the lack of confining stresses and high rate of kerogen conversion fails to precisely simulate textural changes. Lack of confining stresses also causes less effective expulsion. Depending on the extent of
kerogen conversion, the amount of trapped bitumen in the pyrolized samples might be higher than in naturally mature samples.

Figure 2.1- Bakken shale preparation steps for retort testing. A) Raw Bakken shale sample glued on to rigid backing plate, B) Shale sample after cutting with rock core device, C) Shale sample contained in porous stainless steel cylinder, D) Sample in stainless steel cylinder with porous stainless steel cover disk.

Figure 2.2- Axial stress loading device for the INL shale retorter. A) Picture of the spring stress stainless steel in the hydrous retorting position, B) Schematic of the stress loading device in a 1 liter pressure vessel.
Our experiments on hydrous pyrolysis show the variations in textures inside as well as on the surface of the samples. Since our main goal was to measure changes in physical properties and in interactions between grains and matrix, large scale textural artifacts due to inadequate simulation of subsurface could be ignored.

### 2.3.3 Geochemistry and Mineralogy

Total Organic Content (TOC) was determined by oxidizing the organic matter in separate samples using the LECO TOC method. Geochemical properties of the samples were determined before and after hydrous pyrolysis using RockEval analysis. During this analysis, samples are gradually heated and the released hydrocarbons are measured continuously. Volatile free hydrocarbons are released at the first stage of heating which reaches a maximum rate known as S1 (mg HC/g TOC) peak. On further heating, hydrocarbons are generated due to thermal cracking of kerogen reaching maximum expulsion at the temperature of Tmax. The relative amount of generated hydrocarbons at this stage, S2 (in mg HC/g TOC) is called the generative hydrocarbon potential of the source rock. At the final stage, CO2 generation is an indication of oxygen content of the kerogen [S3 (mg HC/g TOC)].

The mineral composition of samples was measured by QEMSCAN automated mineralogy analysis (Table 2.1). The analyses were made at 2μm pixel size for highest resolution in differentiating fine grains in these rocks.
Table 2.2- Geochemical data from source rock analysis. Samples were analyzed before and after hydrous pyrolysis in order to determine initial properties at natural state and extent of change due to pyrolysis. Weight loss occurred due to chemical decomposition of kerogen to lighter molecules as well as clay dehydration. The weight loss is found to be a function of HI and clay content.

<table>
<thead>
<tr>
<th>Sample# /Depth</th>
<th>TOC (wt%)</th>
<th>S1 (mg/g)</th>
<th>S2 (mg/g)</th>
<th>S3 (mg/g)</th>
<th>Tmax (°C)</th>
<th>HI (mg HC/ g TOC)</th>
<th>Wt Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7216</td>
<td>17.74</td>
<td>4.2</td>
<td>112.2</td>
<td>0.85</td>
<td>428.6</td>
<td>633</td>
<td></td>
</tr>
<tr>
<td>7221</td>
<td>16.01</td>
<td>3.8</td>
<td>101.8</td>
<td>0.69</td>
<td>431.2</td>
<td>636</td>
<td></td>
</tr>
<tr>
<td>10368</td>
<td>12.87</td>
<td>2.3</td>
<td>47.7</td>
<td>0.3</td>
<td>448.9</td>
<td>371</td>
<td></td>
</tr>
<tr>
<td>10479</td>
<td>10.3</td>
<td>1.66</td>
<td>21.2</td>
<td>0.26</td>
<td>450.8</td>
<td>234</td>
<td></td>
</tr>
<tr>
<td>10792</td>
<td>7.9</td>
<td>1.54</td>
<td>9.7</td>
<td>0.23</td>
<td>457.1</td>
<td>126</td>
<td></td>
</tr>
</tbody>
</table>

2.3.4 Nanoindentation

We used the automated nanoindentation method to evaluate modulus and hardness of constituent minerals in our samples. Automated indentation method is a controlled cyclic penetration of an indenter into the sample while recording the loading and unloading force-displacement behavior. This method was initially used for measuring elastic moduli and hardness of small size grains and thin layers (Fischer-Cripps, 2006). Nanoindentation technique enables us to measure mechanical properties of material on the micrometer scale (see critical review of the technique in Fischer-Cripps (2006)). With application of a load, the indenter penetrates into the sample. By recording loads and corresponding displacements, Young’s modulus (E) is calculated from (Fischer-Cripps, 2006):

\[
E_r = \frac{\sqrt{\pi}}{2\gamma C \sqrt{A_p(h_c)}} \tag{2.1}
\]

where \(E_r\) is called the reduced modulus, \(\gamma\) is a geometric correction factor, \(C\) is the compliance of contact derived from the slope of unloading curve, \(A_p\) is the projection of
contact area between sample surface and tip at depth of $h_c$. In order to calculate the Young’s modulus $E$, knowledge about the Poisson’s ratio and properties of the indenter are needed.

$$E = \frac{1-v_s^2}{\frac{1}{E_s} - (1-v_i^2)/E_i}$$  \hspace{1cm} (2.2)

where $v_s$ is Poisson’s ratio of the substrate, $v_i$ and $E_i$ are Poisson’s ratio and Young’s modulus of the indenter respectively. Poisson’s ratio of the substrate is an unknown in calculating $E$. Calculations of $E$ by varying Poisson’s ratio from 0.1 to 0.4 resulted in 6% variations of $E$. A similar observation was made by Prasad et al. (2001) for clay moduli. To avoid uncertainties due to unknown Poisson’s ratio, we report here only the nanoindentation modulus also known as reduced modulus $E_r$ (Fischer-Cripps, 2006).

Hardness can be calculated from

$$H = \frac{F_{\text{max}}}{A_c}$$  \hspace{1cm} (2.3)

where $F_{\text{max}}$ is the maximum force applied by the indenter and $A_c$ is the residual deformation after unloading. In ideally plastic solids, hardness relates directly to the yield strength (Lawn and Marshall, 1979). However, brittle materials are known to yield by fracturing processes. Thus, Lawn and Marshall (1979) define fracture properties by Toughness ($T_c$), with

$$T_c = F_{\text{max}}c$$  \hspace{1cm} (2.4)

where $c$ is the crack length. The ratio of Hardness ($H$) to Toughness ($T_c$) has been called Index of Brittleness (Lawn and Marshall, 1979).

In our measurements of shales, we find that the heterogeneous and nano-granular nature of shales make the likelihood of probing single components far less than that of probing aggregates of various components. Thus, while we do occasionally indent
single components, nanoindentation in shales will mostly measure composite values depending on the ratio of each component under the probe. This is mainly due to the sharpness of the tip (typically 100 nm radius) being similar to or larger than the finest constituents in shales. Distinguishing between separate phases in composite materials depends on a difference between the size of the components and the indentation scale (Durst et al., 2004; Constantinides et al., 2006). Although in our study the indentation size did not probe individual constituents, it allowed us to detect changes in properties of the aggregate components. Thus, instead of showing distinct values of the components as shown in Figure 2.3-a, typical histograms of measured properties showed behavior of a mixture of particles as shown in Figure 2.3-b (after Constantinides et al., 2006).

![Figure 2.3](image)

**Figure 2.3**- Schematic distribution of indentation points in ideal case (left graph) and for small grain sizes (right graph). In the ideal case, where indentation size is smaller than grain size (as a rule of thumb at least one order of magnitude), mechanical properties of individual components will be measured along with the frequency of its occurrence. In this study, since the particles are smaller than the precision of the tip, we are not able to select the indentation depth small enough to extract the mechanical properties of individual grains. Therefore, in this case we will get few broad peaks instead of sharper individual peaks for each component (right graph) (after Constantinides et al., 2006).
Organic rich shales mostly comprise carbonates, quartz, pyrites, clays, and organic matter. All these inorganic minerals except clays have Young’s moduli above 40 GPa. The Young’s moduli of clay and kerogen lie below 15 GPa (Prasad, 2001; Zeszotarski et al., 2004; Pal Bathija et al., 2009). Mba et al. (2010) have assessed kerogen modulus changes with maturity by using a threshold of 25 GPa. In the current study, we present histograms of all data to show modulus changes with maturity.

2.3.5 Results

Table 2.1 presents geochemical and mineralogical description of the samples. The main mineralogy of the samples is quartz and clay; clay content varies between 20-60%, quartz volume ranges between 20-50%, and carbonate minerals are present in smaller proportions (2-15.5%). The organic content and maturity correlated closely with depth; deeper samples had lower TOC and lower HI indicating higher maturity.

2.3.6 Naturally Mature Samples

Our previous studies dealt with statistical analysis of kerogen maturity effects on well log-derived properties such as resistivity, density, sonic and neutron porosity (Prasad et al., 2011). Since organic rich rocks are composite materials comprised of kerogen, inorganic minerals, and hydrocarbons, evaluating changes in each component is not possible by macro scale measurements. Such measurements yield an average value for the composite material. Nanoindentation allows us to measure the components on smaller scale and for smaller aggregates of particles. Our new measurements of reduced Young’s modulus (E) confirm the findings by Vernik and Liu
(1997), Mba et al (2010), and Prasad et al. (2011): Elastic moduli decrease with increasing content of clay and organic matter in naturally mature samples (Figure 2.4).

Figure 2.4- An average reduced Young’s modulus Er of naturally mature samples is computed by averaging sixty-four E measurements from loading-unloading nanoindentation curves. Clays and kerogen are denoted as soft materials. 2×TOC (wt%) + Clay Content was used as a volumetric measure of these soft materials.

The histogram of indentation values (Figure 2.5) shows the distribution of sixty-four measured modulus values along with reported values for main rock-forming minerals. Comparing histograms of samples with varying maturities show a systematic change in mechanical properties with clay content, TOC, and level of maturity (Figure 2.5). The histograms of immature samples (Samples #7221 and #7216 have HI~630 mg HC/ g TOC) show distinct peaks around 20 GPa. These two samples have the highest TOC (about 16%) and clay content (40-60%) of all samples used in this study. Another sample with proximate amount of soft material is #10479 which has a different behavior. This sample also has high clay content (60%) but lower TOC (10.3%) and is at higher maturity level (HI=234 mg HC/ g TOC). The modulus histogram of sample #10479 (Figure 2.5) shows two distinct peaks around 15 GPa and 25 GPa. Considering that this sample has comparable mineralogy to samples #7221 and #7216, the effect of maturity
can be explained as splitting in the histogram and causing a modulus reduction in the softer fraction of the components. Samples #10368 and #10792 have higher quartz and lower clay contents, lower TOC, and higher levels of maturity. The modulus histograms from these samples show a broad distribution between 20 GPa to 40 GPa, peaking around 30 GPa. The stiffening effect of more abundant clastic minerals and lower TOC in these two samples causes this difference in their modulus histograms.

Figure 2.5- Histograms of Young’s modulus values measured from nanoindentation show systematic changes with mineralogy and maturity. Higher clay content and TOC (softer fraction of the rock) lowers modulus values.

Quite possibly minor variations in Young’s modulus of the soft components with increasing maturity can be explained by competing effects of changing kerogen properties with maturity and retention of bitumen and dissolved volatile hydrocarbons in
the kerogen. We investigated this hypothesis further in the following section by analyzing artificially pyrolyzed shales.

### 2.3.7 Pyrolyzed Samples

The pyrolyzed samples showed significant deformation, bulging, and color change (Figure 2.6). Results of source rock analysis on the pyrolyzed samples (Table 2.2) show significant reduction in HI after pyrolysis. Hydrocarbons stored in the pore space during the course of natural maturation are expelled at an accelerated pace in the pyrolysis experiments. Heat exposure also causes transition of the kerogen texture from “glassy” to “rubbery” that also causes deformation and releases hydrocarbon (Larsen and Kidena, 2002). However, since we are making nano-scale measurements of grains, the measured values will not be affected by the large-scale textural variations caused by the laboratory heating process.

RockEval analyses show significant increase in maturity level after pyrolysis. In samples with initially higher TOC, the drop in S1 and HI was significantly higher (Table 2.2).

We observe bulging and deformation as consequences of these processes. FESEM images also reveal generation of micro fractures in the shale that act as conduits for bitumen and hydrocarbon expulsion (Figure 2.7-a and Figure 2.7-b). Flow of bitumen toward the surface of the cores at relatively higher rate of expulsion also leads to extensive fines migration (Figure 2.7-e). In the following images, we present typical textures and modulus values observed on the surface of the samples as well as inside them.
2.3.7.1 Surface observations

Figure 2.7-a and Figure 2.7-b show FESEM images of the surfaces with extensive flow channels and viscous fingering of bitumen. There is extensive formation of bitumen globules on the surface (Figure 2.7-c and Figure 2.7-d). These globules appear to be formed by feeder channels of bitumen. Figure 2.7-a shows the microtexture and long cracks that form on the sample surface due to bitumen and gas generation. Details of the cracks with flow textures and viscous films are shown in Figure 2.7-b. To determine how much of this texture was due to the free interface at the sample surface, we cut the
Figure 2.7 - Micro-fractures are formed as a result of hydrocarbon generation in sample #7221 as are shown in these FESEM images (a and b). The fractures are filled with bitumen (a and b) and act as conduits for transporting bitumen to the surface of the cores (c and d). Flow of bitumen inside the cores mobilizes the finer grains and clay particles and carries them along the expulsion path (e).
samples length-wise and investigated textural changes; these results are presented in the next segment on Section Observations.

The surface FESEM images of some of the cooked samples show formation of a thick layer of bitumen (Figure 2.8). Nanoindentation studies confirmed that the surface is covered by a very compliant material. This layer of bitumen is formed due to expulsion of pyrolized organic material from the inside of the plug to the surface. Color change was found to be due to calcite formation on the surface of some samples during pyrolysis (Figure 2.9). Since extruded bitumen covered surfaces of most samples, all subsequent modulus measurements were made on sectioned samples.

![Image](image_url)  
**Figure 2.8**- These FESEM images show outer surface of sample #7221 after pyrolysis. This sample has initial TOC of 16% and HI of 636. The sample was greatly deformed and bulged after pyrolysis. Several FESEM images confirm generation of hydrocarbon in the sample due to pyrolysis that changed the distribution of grains and kerogen. Bubbles and a thick layer of bitumen are found at the outer surface of the sample.
Figure 2.9- Sample #10368 showed discoloration on the surface. FESEM images show that the outer surface of the sample is covered with calcite as confirmed by EDAX on the calcite pellets. This sample has initial TOC of 12.8% and HI of 371. The dissolution of calcite and re-precipitation in a botryoidal fashion is a possible sign of diagenesis in the dolomitic particles of the shale due to hydrous pyrolysis.

2.3.7.2 Section observations

Comparing SEM images from cross section of natural and cooked samples show that more textural changes have occurred in samples of less maturity with higher TOC (Figure 2.10 and Figure 2.11). In more mature shales with lower level of organic matter, textural changes are minor (Figure 2.12). The extent of physical changes during pyrolysis depends on susceptibility of the grains to applied thermal stress. Shale samples at lower level of maturity have higher organic matter content and higher hydrocarbon generative potential. Therefore, when subjected to higher temperatures, low maturity samples experience extensive textural modification.
Figure 2.10- Comparing immature sample #7221 before pyrolysis (left FESEM image) and after pyrolysis (right FESEM image) shows dramatic change in distribution of organic matter. The images show that the generated hydrocarbon/bitumen imaged inside a section of the cooked sample (right image) covers most grains; whereas in the natural state sample (left image), darker colored kerogen can be distinguished from lighter colored grains.

Figure 2.11- FESEM images of mature sample #10479 with 9% TOC and HI of 234 show bubbles of hydrocarbon produced after pyrolysis (* in right image from a section cut in the pyrolyzed sample). The proportion of kerogen to mineral grains decreases with decreasing TOC. In the natural state (left image), kerogen particles are smaller as compared with the organic-rich sample (Figure 2.10).
Figure 2.12- FESEM images from section of sample #10792 show minor textural changes after pyrolysis (right image) as compared with the natural state sample (left image). The sample has the lowest organic content and higher maturity level (TOC = 7.7% and HI = 126) in comparison with other studied samples.

2.3.8 Young's modulus measurements

Nanoindentation measurements were performed on surface of the pyrolyzed samples. Histograms of measured indentation modulus on natural and pyrolyzed samples are compared in Figure 2.13. Comparison of the histograms of modulus shows change in distribution of measured values due to pyrolysis. The frequency of lower modulus values increases after pyrolysis and the peak of frequency shifts to lower values.

Nanoindentation measurements were performed on cross sections of pyrolyzed samples. Frequency of measured indentation modulus on natural and pyrolyzed samples were compared (Figure 2.14). Comparison of the histograms of modulus shows change in distribution of measured values due to pyrolysis. The frequency of
lower modulus values increases after pyrolysis and the peak of frequency shifts to lower values.

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Figure 2.13- Histograms show the distribution the 64 indents on the sample before pyrolysis (upper graph) and the 96 indents after pyrolysis (lower graph). The very low modulus values measured on the outer surface of the pyrolyzed sample (lower graph) is due to formation of a thick layer of bitumen which was also observed in FESEM images.
Figure 2.14- Histograms show the distribution of the 64 indents on each sample before and after pyrolysis. Comparing the histograms of natural samples (before pyrolysis) show the frequency of higher elastic properties increase as the sample depth increases. (TOC decreases consequently due to maturation). Comparing the natural and pyrolized samples shows an increase in frequency of the lower bound of elastic properties (i.e. below 20 GPa) especially in high TOC samples (#7221 and #7216).
2.4 Discussion

Nanoindentation tests on natural cores show that more mature cores have higher Young’s moduli (Figure 2.4). This is largely because more mature samples have lower organic material content and consequently higher moduli. Furthermore, although clay content might not be related to maturity, it affects elastic properties (Han et al., 1986).

The high fraction of clay and kerogen in all samples suggests that stiffer mineral grains might be suspended in a matrix of compliant grains. Comparing texture of the organic matter in the mature and immature natural samples shows laminates of kerogen in immature samples that appear to surround inorganic mineral grains (Figure 2.15). The kerogen is a prominent part of the framework and might well be load-bearing. Therefore, any stiffening effect due to these minerals will be eliminated by the soft frame in which they are placed. This is the main reason for relatively low modulus values in these measurements. In order to compare mechanical properties measured from nanoindentation, mineralogical effects must be considered. Only samples that have similar mineralogy can be compared at different maturity levels to analyze maturity related changes. In more mature samples, the kerogen appears isolated between grains with a few exceptions of kerogen grains with a unique feature (Figure 2.16). Nonetheless, these kerogen particles are considerably larger than the average kerogen particles and appear to have a semblance of flow texture. Such features imply that these larger kerogen particles have experienced larger stresses that led them to flow between larger mineral grains. These textures are also seen in other mature samples (Figure 2.17).
Figure 2.15- FESEM images show laminated texture of kerogen in a section of low maturity natural sample (sample #7216; TOC=17.7% and HI= 633).

Figure 2.16- Different features of kerogen in a section of a low maturity natural sample (#10368: TOC = 12.8% and HI= 371).
During hydrous pyrolysis, two processes take place simultaneously: Hydrocarbons are generated due to the high retort temperatures, and volatile hydrocarbons evaporate. These changes control the changes in elastic properties. TOC reduces due to pyrolysis which causes a decrease in softer material content of the rock, but more bitumen and hydrocarbon is produced part of which is retained. In particular, immature samples generate more bitumen and hydrocarbon in excess of the evaporative loss of the volatile amounts. This bitumen is retained and is mixed with the other softer components (Figure 2.18).

Figure 2.17- Left image: a bulky kerogen particle in a section of naturally mature sample #10479 (TOC = 9% and HI = 234); Right image: section of pyrolyzed sample #10792 (TOC = 7.7% and HI =126). Note that the kerogen particle in sample#10792 which is the leanest sample appears to become porous after pyrolysis.

On the surface of the pyrolyzed samples, the bitumen can flow unrestricted, and so modulus measurements at the surface probed almost entirely this low modulus material. On the inner sections of the sample, the modulus values are still indicative of the presence of bitumen although other materials are probed as well. Despite the large changes in volatile hydrocarbons potentially generated during pyrolysis, FESEM images
show that considerable amounts of organic matter still remain. TOC measurements before and after pyrolysis confirm changes in organic content (Table 2.2).

Figure 2.18- FESEM image from section of pyrolyzed sample #7221 shows dramatic change in texture and distribution of organic matter in comparison with natural state (figure 2.10, left image). The texture of organic matter is very similar to more mature samples (i.e. Figure 2.12).

There are similarities between the texture of more mature rocks and the pyrolyzed immature rocks. Immature rocks usually have laminated kerogen layers with elongated kerogen particles whereas naturally mature rocks usually have smaller and more isolated kerogen particles. The kerogen is load-bearing at lower maturity states where there is an abundance of organic matter. As the rocks get more mature, kerogen undergoes volume reduction and the particles become more isolated (both in natural and synthetic mature states).

At higher maturity, organic matter becomes more pore-filling and the matrix more grain-supported and lenticular, consistent with observations by Vernik and Nur (1992).
These observations must be taken into account when selecting appropriate rock models.

Table 2.3- Comparison between statistical data from Young’s modulus measurements reveals the overall reduction in Young’s modulus due to pyrolysis. Note that samples 7216 and 10479 have 60% clay content that also lowers the Young's modulus. The differences between immature samples, 7216 and 7221 after pyrolysis is currently under investigations.

| Sample #/ | Before Pyrolysis | | | | After Pyrolysis | | | |
| -------- | -----------------| | | | Sample #/ | Depth | TOC (wt%) | HI (mg HC/g TOC) | Median E (GPa) | Mean E (GPa) | TOC (wt%) | HI (mg HC/g TOC) | Median E (GPa) | Mean E (GPa) |
| 7216    | 17.74            | 633 | 20.4 | 22.5 | 11.1 | 79.0 | 14.5 | 14.4 |
| 7221    | 16.01            | 636 | 20.0 | 21.0 | 9.53 | 53.8 | 8.0 | 8.5 |
| 10368   | 12.87            | 371 | 30.8 | 32.1 | 8.45 | 45.0 | 20.3 | 23.5 |
| 10479   | 9.07             | 234 | 21.6 | 27.7 | 11.6 | 35.6 | 14.7 | 16.8 |
| 10792   | 7.9              | 126 | 33.1 | 34.9 | 7.84 | 42.7 | 21.2 | 22.3 |

The decrease in Young’s modulus of the softer components can be explained by replacement of parts of kerogen with bitumen. We postulate that the decrease in kerogen volume with pyrolysis (Okiongbo, 2011) is compensated by the expelled bitumen within the kerogen. Our measurements of lower Young's modulus (below 2 GPa) in bitumen would explain the overall reduction of elastic modulus in the kerogen.

2.5 Summary

We have related changes in reduced Young’s modulus (Er) to organic maturity and bitumen generation. Our nanoindentation measurements were explained by detailed textural analysis using FESEM images. Furthermore, by comparing measurements on the outer surface with section measurements, we could extract bitumen modulus, flow textures and bitumen conduits. We find:
1- There is an increase in Young’s modulus with maturity in naturally mature shales related to the corresponding reduction in TOC content. This observation is consistent with earlier results on Bakken shales.

2- Films of bitumen, bitumen globules, and bitumen flow channels are observed on the surface of pyrolyzed samples that have low (below 2 GPa) values of Young's modulus.

3- At higher maturities, part of the produced bitumen is trapped within the kerogen. This is observed in SEM images and inferred from reductions in Young's modulus of the "softer" components of shales. This corresponds to observations of a direct correlation between velocity and maturity. Young's modulus of bitumen (below 2 GPa) is lower than that of the other soft components, kerogen and clays, that lie between 7 and 15 GPa.

4- A reduction in Young's modulus after pyrolysis implies that the volumetric reduction of kerogen with pyrolysis is compensated by the pockets of bitumen.
CHAPTER 3  
POROSITY EVOLUTION IN OIL-PRONE SOURCE ROCKS

A paper published in the journal of Fuel  
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“The highest possible stage in moral culture is when we recognize that we ought to control our thoughts.”

— Charles Darwin

3.1 Abstract

The origin of porosity and mechanisms of fluid flow in the presence of organic matter and clay minerals in source rocks are poorly understood. Burial and maturation of the source rock modify or create the pore systems in these rocks. Kerogen decomposition and consequent shrinkage may change the load bearing state of the minerals and organic matter and affect pore system since early stages of maturation. Geochemical evidence confirms that the hydrocarbon expulsion process (i.e. primary migration) is not 100% efficient. Expulsion of hydrocarbon is mainly driven by 1) pressure increase in the source rock due to solid kerogen conversion and volume increase and 2) continued compaction of the sediment. Converted organic matter is partly retained in the source rock diverse framework constituents. Quantitative measurement of and determining producibility of the retained hydrocarbon in the source
rock is to date highly debated. The source rock hydrocarbon storage capacity is controlled by pore-hosting particles, pore system topology and rock-fluid interactions.

The presence of organic matter and clay minerals affect log responses by generally overestimating porosity, because the low density kerogen is not accounted for, and together with low resistivity caused by presence of clay minerals can result in erroneous saturation calculations; thus, accurate reserve estimation often is challenged if the impact of low organic matter density is not explicitly addressed.

In order to understand porosity evolution and the interaction of organic byproducts (i.e. bitumen and pyrobitumen) with rock minerals during thermal maturation, one must study source rock samples with different maturities. For this reason, ten Bakken Shale samples with varying maturity and mineralogy were selected in this study. Pore size distributions (PSD), specific surface areas (SSA) and geochemical characteristics of the samples were measured in native state and after successive solvent extraction.

The PSD and SSA measured after each extraction shows recovery of the pore system with successive cleaning. Most significant was the recovery of kerogen-hosted pores with removal of soluble, oil-like organic material. Using successive extractions we are able to determine the evolution of organic matter porosity through maturation which is otherwise not feasible using visual techniques or other conventional laboratory procedures.

3.2 Introduction

Pore size distribution (PSD), tortuosity, pore aspect ratio, and surface properties are the main pore characteristics which are defined by rock composition, fabric and its
burial and diagenetic history. These aspects influence the petrophysical characteristics of the rock as well as our measurement of these properties. Accessibility of the pore system by the displacement fluid, wettability and surface properties of the grains are the main controls on acquiring reliable and consistent laboratory measurements.

In low porosity rocks with permeability in the nanoDarcy range, porosity measurement comes with unique challenges, e.g., due to, but not limited to, nanometer-sized pores and reactive clay minerals. Conventional methods to measuring porosity and PSD in fine grained, ultra-tight rocks usually yield inconsistent values (Katsube and Scromeda, 1991; Howard, 1991; Dorsch and Katsube, 1996). Defining effective porosity in ultra-tight self-sourcing reservoirs with clay minerals and/or organic matter presents yet another challenge. Clay porosity in conventional reservoirs is considered as an ineffective pore system in storage and flow. Recent studies have questioned this assumption and shown that at certain circumstances, the clay minerals could improve storage and/or flow of hydrocarbons in ultra-tight rocks (Kurtoglu, 2013).

Log-derived porosity is calculated from density, neutron and/or sonic logs. These calculations require knowledge of density, hydrogen index and mechanical properties of rock fragments. Kerogen has lower density, lower elastic modulus, higher Poisson's ratio and higher hydrogen content than inorganic minerals (Okiongbo et al., 2005; Prasad et al., 2011; Zargari et al., 2013; Wilkinson et al., 2014). Scarcity of accurate measurements of kerogen properties and high contrast between physical properties of kerogen and inorganic minerals makes conventional log interpretation techniques difficult to apply to organic rich rocks.
Pore systems in organic rich rocks matrix can be divided into three pore types as defined by Loucks et al. (2012). Two types of pores are associated with the inorganic minerals (as interparticle and intraparticle mineral porosity) and the third type is associated with the organic matter (intraparticle organic porosity). All types of pores evolve since the time of deposition due to burial, diagenesis and maturation. Clay minerals also undergo significant porosity reduction due to compaction (Kuila and Prasad, 2013).

Porosity in kerogen may exist in the original particle at the time of deposition (e.g., original cellular microstructure in plant material or recycled thermally mature vitrinite), but more commonly, in Type II organic matter it is generated during burial, with early stages of porosity development due to decomposition and catagenesis. Kerogen porosity (if preserved) is often filled with bitumen at early stages of maturation (Larsen and Kidena, 2002; Zargari et al., 2013). Confirming existence of intraparticle kerogen porosity using SEM image analysis techniques, based on material density contrast, is very challenging since the density of kerogen and bitumen are close. Kuila et al. (2014) studied nano-scale pore structure of source rocks by comparing the PSD before and after removal of organic matter by NaOCl treatment. They found significant reduction in abundance of nanometer-size pores after removal of organic matter in mature source rocks indicating storage space within the kerogen. Prasad et al. (2011) have shown that with increasing maturity, kerogen particles are sheltered in a supporting frame of stiffer minerals. It is speculated that intraparticle organic porosity in kerogen is well preserved if the kerogen particles are sheltered in a supporting frame of load bearing stiff minerals.
(Bohacs et al., 2013). Determining the fraction of organic matter that is sheltered by load-bearing framework of stiff detrital or diagenetic minerals is therefore essential.

The interaction between organic matter maturity and minerals changes effective porosity and other geophysical properties of the mudrocks (Lewan and Birdwell, 2013). Sorption and absorption of hydrocarbon in the organic matter and on the surface of clay minerals also affect the hydrocarbon storage capacity and fluid flow (Javadpour et al., 2007; Javadpour, 2009; Ross and Bustin, 2009; Zhang et al., 2012). Bitumen and other byproducts of kerogen maturation occupy clay and kerogen porosity in the early stages of oil generation (Zargari et al, 2013; Kuila et al, 2014). Different mechanisms through which clay minerals and organic matter may interact are widely studied (Lagaly, 1984; Kowalska et al, 1994; Theng, 1970, 1974; Warren et al., 1986). The interaction of clay minerals and organic compounds is mainly governed by the electrically charged surface of the clay minerals and the polar nature of some functional groups present in the bitumen (Kowalska et al, 1994). Based on tendency of some organic functional groups to be adsorbed at clay exchange sites (Lagaly, 1984; Kowalska et al., 1994; Theng, 1970, 1974), it is possible that some organic compounds form stronger bonds with external clay surfaces, replacing clay bound water and consequently dehydrating the source rock. This phenomenon may cause a dramatic increase in resistivity by eliminating the water from interparticle clay porosity and occupying cation exchange cites of the clays.

Previous studies on characteristics of the pore system in source rocks provide limited information about how their pore systems evolve. These studies are mostly focused on investigating the pore system in samples as received with limited pre-
treatments or with limited discussion on how pretreatments affect measurements of porosity and PSD (Bernard et al, 2012; Curtis et al, 2012; Loucks et al, 2012; Modica and Lapierre, 2012; Bohacs et al, 2013; Kuila et al, 2014). We previously observed that considerable amount of bitumen is generated and stored in the source rocks in the oil window (Zargari et al., 2013).

Lack or presence of bitumen in the pore system may introduce significant discrepancy in our evaluation of porosity and pore characteristics (Lordello et al., 2014; Wei et al., 2014 a and b; Saidian et al, 2015). However, there are no sharp boundaries between bitumen and hydrocarbons; converted kerogen (hydrocarbons or bitumen) are by definition soluble in organic solvents. If anything, it is the converted organic matter that can contribute to production from source rocks. Therefore, determining the amount of storage specified to the soluble hydrocarbons provides an estimate of effective porosity in organic rich shales. In this study, solvent extraction was performed to determine what portion of the total pore space is excluded from quantification due to oil trapped in pores and to understand the storage and flow capacity of source rocks in the oil window.

3.3 Material and Methods

3.3.1 Visual Techniques

One of the most debated topics related to pore systems in organic rich shales at the oil window is the contribution of each pore hosting grain in total voidage and accessibility and contribution of different pore types in hydrocarbon storage and ultimately, production. Mineralogy, organic richness and thermal maturity determine the
types of pores, interaction between generated hydrocarbons and minerals, and control changes in pore-hosting particles.

Visualization techniques have been widely used for petrographical analysis. SEM imaging ad thin section analyses are used to understand pore structure, pore morphology and effect of compaction and diagenesis on pore systems. Due to fine-grained nature of mudrocks and complex sub-micron sized pores, 2-D and 3-D SEM imaging techniques have received broad attention for studying porosity and pore structure of mudrocks (Loucks et al., 2009, 2010, 2012; Curtis et al., 2010; Diaz et al., 2010; Slatt and O'Brien, 2011). High resolution imaging and image processing techniques have led to development of a new branch of rock physics, the so-called “Digital Rock Physics”. However, since digital rock physics is dependent on high resolution images, it is biased towards visible porosity. A considerable portion of the pore system may remain saturated with bitumen and will be counted as a part of solid organic matter due to low optical and density contrast with the kerogen.

This study is focused on quantifying porosity in organic rich rocks at different maturities with emphasis on bitumen-filled porosity in the oil window. This porosity quantification can help understand evolution of porosity and porosity topology in organic rich shales as well as improve digital rock models.

In the following section, we discuss petrographic results of three Bakken Shale samples at immature, mature (oil window) and over-mature (gas window) states to visually and quantitatively examine porosity evolution with increasing thermal maturity.
3.3.2 Porosimetry

Conventional direct porosity measurement techniques often result in inconsistent and inaccurate results when performed on very tight mudrocks (Saidian et al., 2014b). These methods include helium porosimetry, mercury injection porosimetry (MICP) and immersion techniques. Low permeability, small grain and pore sizes, and complex surface properties limit accessibility to mudrock pore system. Luffel and Guidry (1989) suggested using crushed tight rock samples for porosimetry purposes to increase material surface area. This technique was later adopted by Gas Research Institute (GRI). The GRI technique includes measuring bulk volume using immersion technique, then crushing and cleaning the sample using Dean Stark solvent extraction. Ultimately the sample is dried and the pore volume is measured with helium pycnometry.

Kuila (2013) proposed water immersion porosity (WIP) technique for total porosity measurement in mudrocks. This technique, tested on several nano-Darcy permeability samples, produced more repeatable and reliable results than other methods. Since WIP technique only heats the samples to 200ºC to remove the formation fluid, there is a possibility that some heavy hydrocarbons are not completely removed and therefore introduce an error in the analysis. Another limitation of this technique is its application in mixed wettability rocks. Deionized water saturates most of the hydrophilic pores but high capillary pressure prevents water intrusion into extremely hydrophobic pores (unless through a forced imbibition process). The deionized water may also cause swelling of some clay minerals which results in overestimation of porosity using this technique (Kuila et al., 2014; Saidian et al., 2014a).
While total porosity represents total voidage in the rock, it doesn’t provide information about fluid flow and hydrocarbon storage in the pore system. Quantifying pore structure and mineral surface properties (i.e. pore size distribution, specific surface area, surface charges and cation exchange capacity) helps us in characterizing petrophysical properties of the rock. Different techniques are available for quantifying pore size distribution and specific surface area, for example, mercury intrusion porosimetry (MIP) (Ross & Bustin, 2009), NMR analysis (Latour et al., 1993), NMR cryoporometry (Strange and Rahman, 1993), thermoporometry (Ishikiriyama et al., 1996; Burn et al., 1997) and gas adsorption (Adesida, 2011; Chalmers et al., 2012; Clarkson et al., 2012 a,b; 2013; Kuila and Prasad, 2013).

Despite wide usage of MIP in conventional reservoir rocks and its ability in capturing a wide range of pores, it is limited to measuring pores with pore throat sizes larger than 3.6 nm. Gas adsorption technique on the other hand, is capable of characterizing pore size distribution in the pores 2-200 nm in diameter. MIP and sub critical gas adsorption techniques have been used as complimentary methods for characterizing a broader range of pore sizes in mudrocks (Ross & Bustin, 2009; Saidian et al., 2014b). Except when GRI technique is used, all these studies have assumed that pores are accessible to the measuring fluid. However, if some pores are occupied by hydrocarbons, porosity and PSD will be dependent on their pretreatment for hydrocarbon removals.
3.3.3 **Samples and Solvent Extraction**

We studied pore size distribution, specific surface area and geochemical properties of ten Bakken Shale samples after successive solvent extraction. The selection was made from a range of mineralogy and thermal maturity. Table 3.1 summarizes the physical properties of solvents used. Utilizing a range of solvents with varying polarity and chemical structure enabled us to target a wider range of organic compounds in a successive process, determining the effect of each solvent and to ultimately access larger portions of the pore system.

Aliquots were crushed and sieved with 100 meshes (149 μm). All aliquots were extracted with toluene and then with chloroform in a soxhlet extraction unit for 48 hours each. Five samples were further extracted using two solvents with higher polarities. First with a mixture of Methanol, Acetone and Chloroform (MAC) and then with N-Methyl-2-pyrrolidone (NMP). Geochemical analysis was performed before extraction on all aliquots and after each extraction on the samples that were only extracted with toluene and chloroform. 2-3 grams of aliquots were separated for PSD, SSA and geochemical analysis after each extraction step. LECO TOC method was used for determining organic content and RockEval II for geochemical characterization of the organic matter. It is worthwhile mentioning that there are errors associated with using HI from RockEval as a measure of maturity since these shale samples may not have had the same initial HI. Table 3.2 summarizes the properties of the samples before and after solvent extraction with toluene and chloroform. Since mostly micropores were expected to be recovered after extraction, subcritical nitrogen adsorption technique was used for PSD and SSA determination as suggested by Kuila et al. (2014). The aliquots were
degassed at 120°C under vacuum (10 μmHg) prior to performing nitrogen adsorption tests.

Table 3.1- Physical properties of organic solvents used for solvent extraction.

<table>
<thead>
<tr>
<th>Solvent Properties</th>
<th>Toluene</th>
<th>Chloroform</th>
<th>MAC</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point (°C)</td>
<td>110.6</td>
<td>61</td>
<td>57.5</td>
<td>202</td>
</tr>
<tr>
<td>Solubility in water (25°C %w/w)</td>
<td>0.052</td>
<td>0.82</td>
<td>--</td>
<td>total</td>
</tr>
<tr>
<td>Polarity (Water 100)</td>
<td>9.9</td>
<td>25.9</td>
<td>36.1</td>
<td>36</td>
</tr>
</tbody>
</table>

Three Bakken Shale samples were used for petrographical analysis. Samples were selected from eastern part of the Williston basin at immature state, central part of the basin at peak oil generation and western part of the basin at over-mature state (gas window) where the interval is above a laccolith.

3.4 Results

3.4.1 Image Analysis

Petrographical analysis of Bakken Shale shows a dramatic alteration in the nature of pores and pore-hosting particles with maturity. At immature state (Figure 3.1-a), two dominant types of pore systems were identified: intraparticle kerogen porosity and interparticle clay porosity. At mature state (Figure 3.1-b), interparticle porosity is rare; the majority of clay porosity is filled with organic matter while organic matter shows no visible intraparticle porosity. At gas window (Figure 3.1-c), the predominant pore type is intraparticle organic porosity.

1 MAC: 23 wt% Methanol, 30 wt% Acetone, 47 wt% Chloroform
Our observation confirms previous studies that had shown none to very low measurable or visible porosity in the Bakken Shale at oil window (Vernik and Liu, 1997). It is of great interest to understand the extent and controlling factors of storage in the source rocks in the oil window. Despite high resolution of available SEM imaging techniques (4-7 nm), a considerable part of the pore space may remain unresolved and it is impossible to distinguish between converted organic matter (bitumen) and kerogen. Therefore, it is not feasible to quantify the pore space that is preserved in the oil window but saturated with the bitumen using SEM imaging. However, presence of intraparticle porosity in the kerogen and interparticle porosity in clay minerals at immature state and in the gas window questions vanishing of porosity in the oil window. To quantify this amount, we utilized solvent extraction to remove the bitumen from the pore space and sub-critical Nitrogen adsorption for pore characterization.
3.4.2 Pore Characterization

Solvent extraction using toluene and chloroform resulted in significant recovery of the pore space in mature Bakken Shales samples (HI<300). Both the specific surface area (SSA) and porosity increased after solvent extraction. In some cases Specific Surface Area (SSA) increased from 3 to upwards of 53 m²/g and porosity increased from 5.1 to 15% (Table 2).

Table 3.2- Mineralogy, geochemical and pore characteristics of investigated samples before and after successive solvent extraction are shown in the order of decreasing maturity. Silicates= quartz+feldspars, Carbs= calcite+dolimte.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral Composition</th>
<th>TOC (wt%)</th>
<th>HI</th>
<th>Before Extraction</th>
<th>After Toluene Extraction</th>
<th>After Chloroform Extraction</th>
<th>After MAC Extraction</th>
<th>After NMP Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPU 119</td>
<td></td>
<td>25</td>
<td>62</td>
<td>10</td>
<td>3</td>
<td>12.5</td>
<td>6</td>
<td>28.8</td>
</tr>
<tr>
<td>10694</td>
<td></td>
<td>37</td>
<td>55</td>
<td>6</td>
<td>2</td>
<td>15.5</td>
<td>102</td>
<td>16.2</td>
</tr>
<tr>
<td>10792</td>
<td></td>
<td>28</td>
<td>50</td>
<td>17</td>
<td>5</td>
<td>7.9</td>
<td>126</td>
<td>3.8</td>
</tr>
<tr>
<td>11005</td>
<td></td>
<td>31</td>
<td>57</td>
<td>9</td>
<td>3</td>
<td>12.4</td>
<td>131</td>
<td>17.3</td>
</tr>
<tr>
<td>10479</td>
<td></td>
<td>37</td>
<td>48</td>
<td>10</td>
<td>5</td>
<td>10.3</td>
<td>234</td>
<td>0.8</td>
</tr>
<tr>
<td>9157</td>
<td></td>
<td>34</td>
<td>59</td>
<td>3</td>
<td>4</td>
<td>21.7</td>
<td>257</td>
<td>3</td>
</tr>
<tr>
<td>10368</td>
<td></td>
<td>28</td>
<td>51</td>
<td>16</td>
<td>5</td>
<td>12.8</td>
<td>371</td>
<td>1</td>
</tr>
<tr>
<td>7219</td>
<td></td>
<td>30</td>
<td>65</td>
<td>2</td>
<td>3</td>
<td>16.1</td>
<td>556</td>
<td>1.3</td>
</tr>
<tr>
<td>7216</td>
<td></td>
<td>43</td>
<td>46</td>
<td>5</td>
<td>6</td>
<td>17.7</td>
<td>633</td>
<td>2.6</td>
</tr>
<tr>
<td>7221</td>
<td></td>
<td>37</td>
<td>55</td>
<td>4</td>
<td>4</td>
<td>16</td>
<td>636</td>
<td>1.9</td>
</tr>
</tbody>
</table>

SSA after solvent extraction with toluene and chloroform are compared with native state in Figure 3.2. The green bars in this figure represents the SSA of each sample before extraction, blue bars show SSA after toluene extraction and orange bars show SSA after chloroform extraction. Higher initial and recovered surface areas are generally observed in the samples with HI of lower than 300 (mg HC/g TOC) except the sample 10479 (HI=234 in Figure 3.2). As mentioned before the current HI of the
samples is not only a function of maximum temperature they have experienced during the geological time, but also a function of initial kerogen types and their fractions. Therefore, current HI might not be a perfect indicator to compare the maturity levels for example between sample 10479 and other samples in the same range of maturity.

The maximum recovered SSA and porosity, after solvent extraction for the samples from oil window and without extraction for the sample from gas window, are plotted versus TOC respectively in Figures 3 and 4. Mature samples show higher SSA and porosity. The highest maturity sample did not show noticeable change in solvent color and so the PSD and SSA were assumed to not have changed. Porosity and SSA are correlated with TOC.

Figure 3.2- Specific surface area of the investigated samples before and after solvent extraction. The samples are identified by their maturity index (HI). Lower HI indicates higher maturity.
Figure 3.3- Maximum measured specific surface areas of the aliquots are plotted versus TOC. The color code indicates thermal maturity index (HI).

Figure 3.4- Maximum measured porosity are plotted versus TOC. The color code indicates thermal maturity index (HI). The porosity increases with TOC and more mature samples have relatively higher porosity.
Comparing pore size distribution (PSD) curves (Figure 3.5), shows that in less mature samples the pore size distribution does not change after toluene extraction whereas in more mature samples most of the change occurred after toluene extraction, subsequent chloroform extraction recovered very little additional pore space.

Pore size distribution curves for different maturity rocks also vary in shape. The dominant pores in higher maturity samples are mainly smaller than 10 nm (Figures 3.5 and 3.6), whereas in less mature samples larger pores are often dominant.

Figure 3.5- Example pore size distribution curves of three samples before and after solvent extraction.

The question that remains unresolved is why the SSA is so low at the early stages of oil generation despite abundance of intraparticle kerogen and interparticle mineral porosity at immature state. This phenomenon might be due to limited solubility of the heavy bitumen in the solvents used here. In order to further investigate existence of micro pores in less mature states, the successive extraction was continued with MAC and NMP on five samples. SSA and PSD were measured consequently after each extraction (Figure 3.6).
Additional recovery of pore space was observed in immature samples after MAC extraction while more mature samples show minimum change in PSD curve after MAC extraction. Effect of NMP on PSD was rather destructive except on larger pores of one of the immature samples (#7216, HI= 633 in Figure 3.6).

3.4.3 Geochemical Analysis

RockEval analysis was conducted on five samples after solvent extraction. Total organic content (measured using LECO TOC) and maturity index (Hydrogen Index) are compared with natural state (Table 3). In general, the results show no evident trend relatable to initial values of TOC, HI or mineralogy (Figure 7). The changes in the TOC and HI are, for the most part, within expected errors of these measurements.
Figure 3.7- Change of measured TOC and HI after solvent extraction as a function of clay content, initial TOC and initial HI. There is no significant trend in changes of measured geochemical parameters due to solvent extraction.
3.5 Discussion

Successive solvent extraction of source rocks revealed abundance of otherwise undetected porosity at the oil window. Mature samples showed higher SSA and porosity which increases with TOC. This is an indication of dominance of kerogen hosted porosity in mature samples consistent with findings of Kuila et al. (2014). At early stages of maturation, chemical decomposition of kerogen is found to produce insoluble organic compound and become rubber-like (Johnson et al., 1975; Schnackenberg and Prien, 1953). Both mechanisms may cause collapsing or filling of the kerogen hosted pores at the oil window (Kuila et al., 2014).

At higher maturity levels, most of the soluble pore-filling hydrocarbon can be extracted using toluene. However, at lower maturity the bitumen can be more efficiently dissolved using more polar solvents. This phenomenon suggests a possible difference in composition of the bitumen and/or its interaction with the pore-hosting grains.

While Chloroform and MAC improved the extraction of bitumen, NMP resulted in porosity reduction. Similar effect was observed when different clay minerals (i.e. Illite,
Smectite and Kaolinite) were exposed to NMP (Erico, 2014). This behavior is due to swelling of kerogen (and maybe clays) as found by Hruljova et al. (2013). It could also be partly due to mobilizing and transporting the bitumen by NMP from larger pores to smaller (potentially more oil wet) pores.

An increase in TOC or HI after solvent extraction was unexpected since some fraction of organic matter was removed from the source rock. This can only be explained by absorbing of utilized solvent in organic matter and/or adsorbing on the clay surfaces.

Presence of kerogen-hosted porosity affects petrophysical, mechanical and flow properties of the source rocks. Porous kerogen has lower stiffness modulus (Zargari et al., 2013) which causes softening the rock matrix frame especially if kerogen is load bearing. Kerogen porosity contributes in hydrocarbon storage in the source rocks however its significance in contributing to flow will depend on the overall pore system’s morphology.

### 3.6 Summary

Source rocks contain considerable porosity in the oil window which is often entirely or partially filled with bitumen. Porosity and pore morphology measurements using available techniques can be affected by occupancy of the pores by the bitumen. Solvent extraction enables us to access the pore space in order to produce a more complete image of the pore system in the mudrocks. Utilizing organic solvents increases accessibility to the pore system in organic rich rocks at the oil window, however very high polarity solvents (i.e. NMP) showed a destructive effect on pore morphology.
Based on the results with various solvents on the Bakken Shale, NMP is not recommended as a routine cleaning solvent for pore characterization purposes because of the potential swelling effect on kerogen.

Our SSA and PSD data confirms that there is an overwhelming population of kerogen hosted porosity in the nanometer-scale range (<10nm) at the oil window. We found that the kerogen porosity generation peaks at higher maturity samples with HI of less than 300 (mg HC/g TOC). The total porosity and surface area was also found to be directly related to TOC in the higher maturity samples.

We found no particular effect of rock mineralogy, especially clay content, on the porosity development in organic rich shales.
4.1 Abstract

An elastic modulus mapping technique based on spatially continuous dynamic nanoindentation is applied to map microscale variations in a fine-grained, kerogen-rich shale consisting of inorganic minerals with an interpenetrating network of microscale pores filled with organic matter. Advantages and limitations of the application of this technique to shales are explored through varying sample preparation and scanning procedures. Filtering techniques are developed to remove data that are negatively impacted by topography and other issues inherent to the mapping technique. As a result, spatial variations of elastic modulus in kerogen-rich regions are seen at substantially higher resolution than has previously been reported. Spatial resolution and continuous mapping across high stiffness-contrast material boundaries are further improved with stringent sample preparation and the use of a sharp tip. Typical modulus values measured by this technique include approximately 10 GPa for kerogen, 15-45 GPa for clay depending on the morphology and orientation, and 50-70 GPa for quartz.
4.2 Introduction

Organic-rich shales are heterogeneous composite sedimentary rocks that form in sedimentary basins where abundant masses of living organisms are deposited along with silicic and carbonate minerals. The organic material, kerogen, intertwines throughout the matrix of the shale (Ahmadov et al., 2009; Bobko and Ulm, 2008; Zeszotarski et al., 2004). As the shales are buried and exposed to high temperature and pressure, the kerogen matures to produce hydrocarbons that are stored in the mature organic rich shales as well as in adjacent formations. Economic hydrocarbon production is only feasible through high conductivity conduits generated by the process of hydraulic fracturing.

The mechanical properties of kerogen and the physical arrangement of the material within shale reservoirs are of interest for building upscaled rock models to predict fracture propagation for hydraulic fracturing design and to interpret exploration seismic data. Mechanical properties of shales have conventionally been assessed at the cm-scale and above, using uniaxial and triaxial compression tests (Vernik and Nur, 1992), but a growing interest in determining the properties on the microscale has emerged. Serial sectioning techniques, acoustic wave technology, and computed tomography have been used to understand the arrangement of kerogen and its properties at mm- to μm-scales (Prasad et al., 2011; Vega and Kovscek, 2014). Elastic modulus variation in clay minerals, shales and natural cements has been mapped using nanoindentation, in which a diamond probe of known geometry is pressed 10s to 100s of nanometers into a material while simultaneously measuring force to extract local mechanical properties (Ahmadov et al., 2009; Kopycinska-Müller et al., 2007; Prasad et
Arrays of quasistatic nanoindentations have revealed spatial variations in properties over areas of $\sim 150 \mu m \times 150 \mu m$ (Ahmadov et al., 2009; Zhu et al., 2007). When these pointwise modulus maps are compared to scanning electron or optical micrographs of the same area, good correspondence is generally seen in locations of stiff mineral components such as calcite and pyrite and softer intergranular regions; however, spatial variations below the scale of the array spacing of $\sim 10 \mu m$ have not been resolved with this technique. Relatively large elastic and plastic zone sizes are required to reliably extract properties using the Oliver and Pharr method from these materials, thus large spacing is required between test locations to avoid overlap (Constantinides et al., 2006). Nanoindentation is capable of giving distinct mineral moduli; however, the technique often gives average or aggregate modulus values due to large indentation volumes compared to material grain size. This limitation restricts the utility of array-based nanoindentation to scales far larger than the grain sizes of most constituent particles in organic-rich shales.

Modulus mapping with finer spatial granularity is available through scanning probe methods. In this technique, a probe tip is oscillated at low displacements, typically on the order of 1 nm, while in contact with the sample surface and is simultaneously rastered across the surface to collect data. Correspondence between the drive signal and material response are analyzed to produce a mechanical property measurement for each pixel of the scan, thus providing a spatial map of the mechanical property variation (Balooch et al., 2004). This technique has been applied to create modulus maps of biological materials and some manufactured composites (Balooch et al., 2004; Gaboriaud and Dufrêne, 2007; Ryou et al., 2013; Sahin and Erina, 2008),
demonstrating the ability to resolve microscale mechanical property variations. From these studies, it has been seen that the use of scanning probe methods for nano-dynamic mechanical analysis (nano-DMA) enables the acquisition of modulus maps with higher spatial resolution than has previously been possible with point-based methods such as quasistatic nanoindentation.

The work presented here extends the use of scanning probe modulus mapping to Bakken shale samples collected from the Williston Basin. Modulus maps are produced over areas 5 \( \mu \text{m} \times 5 \mu \text{m} \) in size and are compared to scanning electron micrographs of the same areas. Given the increasing use and necessity of nano-dynamic mechanical property measurements, we discuss the effects of sample preparation, and scanning procedures are presented; both effects can negatively impact data extraction if not properly completed. While this technique allows for the collection of data at higher spatial granularity, some issues associated with the interpretation of the data become particularly pertinent when dealing with a material with high stiffness contrast, such as organic-rich shales. Both topographic variations and low signal-to-noise ratios are seen to negatively influence the ability to accurately characterize local properties within the shale. Another drawback with this technique, as well as with quasistatic indentation, is sensitivity to the material that is below the surface of the tip and may not be visible in an image or surface scan. Modulus mapping using nanoDMA reduces the impact of subsurface interactions by reducing penetration distance to approximately 1 nanometer compared to quasistatic nanoindentation, which typically probes 10s to 100s of nanometers into the material. As will be discussed in this paper, these issues are addressed through optimization of scanning procedures, data filtering techniques, and
analysis to understand the spatial resolution of modulus maps measured on an organic-rich shale, demonstrating that this scanning probe technique can reveal property variations at significantly higher resolution than has previously been reported.

4.3 Materials and Methods

The materials used in this study consist of two samples of Bakken shale recovered from the Williston Basin in North Dakota. One came from a depth of approximately 7200 ft (hereafter referred to as Shale 1). The total organic content in the core from which Shale 1 was recovered was 16 wt%. Shale 1 was sectioned, and then polished with a focused gallium ion beam (FIB) using an acceleration voltage of 30 kV and beam current beginning with 30 nA and ending with 2.5 nA. The surface roughness was found to be approximately 10 nm across a 25 μm² area. Figure 4.1-a shows an example SEM image taken of Shale 1 after FIB polishing. The layered texture corresponds to clay minerals, quartz and calcite are larger polygonal crystals, pyrite is white and kerogen is black. For the most part, clays and kerogen are interspersed. A region of interest, shown in Figure 4.1-b, was selected for mechanical property mapping; it consisted of large regions of kerogen with small amounts of interspersed clay, a quartz grain, and several calcite grains.

The second shale came from a depth of approximately 7000 ft (Shale 2), with a total organic content of 14 wt%. Shale 2 was sectioned and then prepared using the same FIB parameters as those employed for Shale 1. However, for Shale 2 a large area was quickly and roughly polished at high beam currents to remove a substantial amount of material at once. After, Shale 2 underwent extensive milling using lower beam
currents in order to decrease the surface roughness to below 2 nm across a $25 \mu m^2$ area. Figure 4.2-a shows a representative SEM image taken of Shale 2. The region of interest used for mechanical property mapping is shown in Figure 4.2-b, consisting of kerogen regions, clays mixed with kerogen, and quartz grains.

Figure 4.1- (a,b) SEM micrograph (and corresponding enlarged region of the area of interest) of Shale 1 showing pyrite as white, calcite as light gray, and kerogen-rich regions as black. Data from the highlighted area are shown in Fig. 3
Figure 4.2- (a,b) SEM micrograph (and corresponding enlarged region of the area of interest) of Shale 2 showing quartz as light gray and kerogen-rich regions as black. Data from the highlighted area are shown in Figure 4.4
Topography and property mapping were conducted using a Hysitron TI 950 nanoindenter (Hysitron, Inc., Minneapolis, MN) equipped with nanoDMA III, a commercial nano-dynamic mechanical analysis package. Two nanoindenter tips were calibrated against a fused quartz sample using a quasistatic force setpoint of 2 μN to maintain contact between the tip and the sample surface while a dynamic force of 1 μN was superimposed on the quasistatic signal at a frequency of 200 Hz. Based on a calibration reduced modulus value of 69.6 GPa for the fused quartz, the best-fit spherical radius approximation for one tip was found to be 590 nm, while the other tip was found to be significantly sharper, at 85 nm, for the selected nanoDMA scanning parameters.

Modulus mapping was conducted using the larger radius tip on Shale 1 using a quasistatic force setpoint of 2 μN and a dynamic force of 1 μN applied at 200 Hz. Mapping of Shale 2 employed the smaller radius tip and was conducted with a quasistatic force setpoint of 2 μN and a dynamic force of 0.5 μN applied at 200 Hz. Differences in the dynamic force required to achieve similar displacement amplitudes for both samples were a consequence of tip radius. Data from regions approximately 5 μm × 5 μm in size were collected on both shales using a scanning frequency of 0.1 Hz. Each scan resulted in a 256 × 256 pixel data array. Elastic modulus values were calculated based on the measured stiffness at each pixel. The storage stiffness of the material, $K'$, which represents the in-phase mechanical response was calculated from the measured displacement amplitude, $X$, and phase shift, $\varphi$, according to

$$K' = \frac{F_0}{X} \cos(\varphi) + m\omega^2 - K_i$$  \hspace{1cm} (4.1)
where $F_o$ was the applied force, $\omega$ was the oscillation frequency, $m$ was the mass of the transducer, and $K_i$ was the machine stiffness (Syed et al., 2001). Assuming spherical contact of the indenter tip on the sample surface, the contact area over which this stiffness was distributed was calculated as a circular area with radius equal to the contact radius, $a$, given as

$$a = \left( \frac{3F_o R}{2K'} \right)^{\frac{1}{2}} \quad (4.2)$$

where $R$ was the tip radius. The reduced storage modulus was then calculated as

$$E' = \frac{K'\sqrt{\pi}}{2\sqrt{A}} \quad (4.3)$$

where $A$ was the projected contact area with contact radius, $a$ (Syed et al., 2001). This value should not be confused with Young’s modulus, though the two are related. Young’s modulus represents the tensile elastic modulus measured in a linear elastic material. Under the dynamic tests, the resulting modulus is a complex modulus, which can be decomposed into storage (elastic) and loss (damping) modulus components. Furthermore, moduli acquired through indentation or dynamic modulus mapping inherently include the elastic properties of both the test material and the indenter material, and are reported as ‘reduced’ moduli. The reduced storage modulus is equivalent to the reduced elastic modulus for materials that do not exhibit damping (Syed et al., 2001), where the reduced elastic modulus, $E_r$, is defined as

$$\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i} \quad (4.4)$$

In Eqn. (4.4), the subscripts of $s$ and $i$ correspond to the sample and indenter tip material, respectively, for the Young’s modulus, $E$, and Poisson’s ratio, $\nu$. Reduced
storage modulus is reported throughout the paper to avoid assumptions regarding the Poisson’s ratios of materials encountered in the scans.

### 4.3.1 Results and Analysis

Imaging samples and collecting modulus data is a straightforward process; however, it is necessary to ensure that the data are free from sample preparation and scanning procedure artifacts in order to extract reliable elastic modulus data for interpretation. In the section that follows, we present scanning results from both shale samples. The discussion begins with analysis of Shale 1, illustrating the data extraction and analysis techniques developed to remove artifacts. The results of Shale 2 are then discussed in a comparative fashion in order to show the impact of sample preparation and scanning procedure optimization on data quality and spatial resolution.

Figure 4.3-a, which represents storage modulus data for Shale 1, shows minerals and some clay regions exhibiting moduli from 60 to 160 GPa and kerogen-rich areas taking on lower values. Figure 4.3-b, shows that Shale 1 has stiff calcite and quartz grains, which appear higher, in red, on the topography map with surrounding kerogen in green, approximately 7 nm lower. In Figure 4.3, topography changes and variations in modulus are discriminated across sub-micron distances within the scans. Compared to prior studies that have utilized grids of quasi-static indentations spaced 10 to 14 μm apart to map similar materials (Ahmadov et al., 2009; Zhu et al., 2007), the application of modulus mapping to this shale shows the potential of this technique to reveal property variations with substantially higher spatial resolution. However, this technique has several fundamental issues regarding the interpretation of the data that have not
been addressed by previous studies, namely, (1) the influence of local surface roughness, (2) displacement amplitude variations associated with scanning a high-modulus contrast surface at fixed dynamic force, and (3) the effective spatial resolution with a scan.

The negative impact of local surface roughness on property extraction is readily observed in Figure 4.3-b where horizontal streaks from FIB track marks are seen. Their impact is translated into the corresponding modulus map (Figure 4.3-a) where ion tracks show up as property variations within relatively homogeneous materials and even across boundaries between materials in the scan. Additionally, large changes in surface height occur where softer materials have been preferentially polished away compared to harder minerals (c.f. the smearing on the right side of the trapezoidal calcite grain in the bottom of Figure 4.3-b). These local changes in topography can lead to an over- or underestimation of contact area between the tip and the sample surface, and thus introduce errors into the property extraction when converting stiffness to modulus. For example, Figure 4.3-b shows that the edges of the square grain of calcite are sharp and distinct from the kerogen-rich region. The property map in Figure 4.3-a shows a smearing of the calcite grain properties into the kerogen regions; therefore, areas of kerogen are sometimes negatively influenced by neighboring materials.

To reduce the impact of topographic variations on the interpretation of modulus maps, a filtering scheme is implemented. First, we consider the contact radius of the 590 nm tip with the sample under a quasistatic setpoint load of 2 μN to understand the extent of the area probed by the tip. In this calculation, the sample is assumed to have a completely flat surface so that there is a uniform contact area for the tip to probe the surface of the material. Based on reported values of elastic moduli of the materials identified within
Figure 4.3: (a) Modulus map collected for Shale 1 from the region highlighted in Figure 4.1. (b,c) Raw topographic scan and corresponding filtered (0.3 nm) topography scan. (d,e) Raw displacement amplitude scan and corresponding filtered (0.3 nm) displacement amplitude scan. (f) A filtered modulus map of Shale 1 based on topographic and displacement amplitude filters.
the sample, ranging from 10 GPa for kerogen to 306 GPa for pyrite (Ahmadov et al., 2009; Zeszotarski et al., 2004; Mavko et al., 2009), the contact radius varies from 11 nm to 35 nm for the stiffest and most compliant materials, respectively. Comparison of these bounding contact radii to the map pixel size of 19.5 nm x 19.5 nm for a 5 μm by 5 μm scan illustrates that material from nearest neighbor pixels within a scan influence the data gathered at each location for the compliant materials; therefore, a filter is implemented that evaluates the surface height difference between nearest neighbor pixels throughout the Shale 1 topography scan and masks data from pixels that exhibit a height difference of greater than 0.3 nm. This cut-off is empirically acquired and results in removal of most areas affected by ion track marks and other sharp topographic variations for the region studied here, making up approximately 20% of the scan. A filtered topographic scan can be viewed in Figure 4.3-c, where data is removed around the square calcite piece in the lower left hand corner of the image due to the large height difference that was created between the stiff calcite and the compliant kerogen during sample preparation. The ion track marks seen horizontally across Figure 4.3-b, in yellow, have also been removed. Regions where data has been removed would result in erroneous local contact area estimations and bias the storage modulus values reported in Figure 4.3-a.

A second issue apparent in Figure 4.3-a is questionable modulus values on several of the mineral components. Note, in Figure 4.3-a), the circular piece of pyrite in the upper left hand corner of the image shows modulus values of approximately 80 GPa; however, the reported values for pyrite are upwards of 300 GPa (Mavko et al., 2009). Closer examination of the raw data used to produce the modulus map reveals
that displacement amplitude in the stiff mineral regions overwhelmingly falls below 0.3 nm (see Figure 4.3-d). Displacement amplitudes below 0.3 nm are not sufficiently above the noise floor of the instrument (Hysitron Inc., 2012); thus it is unsurprising that quantitative values for modulus in the affected regions are erroneous. In regions where displacement amplitude is below 0.3 nm, error is magnified due to insufficient material strain in high modulus materials for the given test force. Displacement amplitudes in the kerogen-rich regions of the scan are 1 - 1.7 nm for the same scanning parameters. These higher displacement amplitude values are sufficiently above the noise floor and simultaneously low enough that plastic deformation is avoided, so property extraction from more compliant regions is less likely to be negatively impacted at low dynamic forces. Increasing the dynamic load can result in higher displacement amplitude to make property measurements on mineral phases; however, this approach would risk the fidelity of the measurements conducted in low modulus regions by causing plastic deformation or non-linear elastic deformation. Filtering is performed on the scan to mask any pixels with inadequate displacement amplitude to ensure that only data with sufficiently high signal-to-noise ratio is examined. Figure 4.3-e shows that the large calcite grain (lower left hand corner) and the piece of pyrite (upper right hand corner) have been removed due to low displacement amplitudes. Kerogen-rich regions remain intact throughout the image of Figure 4.3-e; however, final analysis shows approximately 30% of the scan was removed during filtering.

Once each filtering technique was completed, scans from Figure 4.3-c and 4.3-e were used to filter affected data from the modulus map in Figure 4.3-a. If a pixel was filtered due to either too much neighboring surface height variation or an insufficient
displacement amplitude, the data from that pixel location was removed from Figure 4.3-a and replaced with a white pixel. The resulting filtered modulus map is located in Figure 4.3-f, where the effects of filtering can be seen in comparison to Figure 4.3-a with ion track marks and several of the stiff minerals are masked while parts of two calcite grains and large, kerogen-rich areas are left behind. Shale 1 has intermixed clay and exhibits lower moduli values in the range of 20 - 50 GPa through the scan in Figure 4.3-f.

Though modulus mapping provides data at extremely high granularity, especially compared to quasi-static indentation arrays, it is relevant to consider the effective spatial resolution of the scans to identify the extent to which the properties indicated in a pixel are influenced by the surrounding volume of material. The modulus mapping technique used in this study uses fixed set-point and dynamic loads through an entire scan; however, the contact radius varies at each point based on the stiffness of the specific location under test within the inhomogeneous sample. Assuming Hertzian contact and isotropic elasticity under the contact, one can estimate the volume that is probed at each pixel location as a roughly hemispherical volume of radius equal to three times the contact radius. Areas located at distances greater than 3a (where a is the contact radius defined in Equation 4.1) from the center of contact contribute little as the stresses drop to less than 10% of their maximum values (Fischer-Cripps, 2007). This information is used to estimate the effective lateral spatial resolution in the scan as between 66-210 nm, where the lower bound corresponds to stiff mineral areas with a modulus of 306 GPa and the upper bound corresponds to compliant, organic-rich areas with a modulus of 10 GPa. Given the scan size examined here, this spatial resolution
corresponds to 3 - 10 pixels. Though the tip displaces into the surface by only ~ 1 nm, material within a zone extending 33 - 105 nm below the surface impacts local property measurements. This sub-micrometer resolution in determining elastic properties in an organic-rich shale, though not as fine as the granularity of data collected in the scans, represents significantly finer scale resolution than is acquired by point-wise quasistatic nanoindentation, which probes volumes with radii of hundreds to thousands of nanometers for indentation depths typically used for property measurement.

While Shale 1, and its subsequent analysis, has given insight into the nanoscale interactions of these stiff and compliant materials, a large amount of the data, almost 40% in total, was lost due to filtering. These filtering techniques removed data due to large surface height variations as well as low displacement amplitudes. Both issues would result in an inaccurate calculation of properties. In an attempt to improve data retention, changes were made to the sample preparation and scanning procedures for imaging Shale 2. An analysis of the data collected for Shale 2 is presented below.

Figure 4.4-a and b show a modulus map and corresponding topographic scan, respectively, of the region of interest for Shale 2. When Figure 4.4-a is used in conjunction with Figure 4.4-b, the storage modulus values for the given areas in the SEM show that quartz regions (yellow/orange/red regions) range from 50 to 80 GPa, while the kerogen-rich regions are located in blue and exhibit moduli between 10 to 20 GPa. The green regions seen throughout the scan are the mixed clay and kerogen regions, which correspond to moduli values between 30 to 45 GPa. These more uniform property values partially result from the improved surface condition, as seen in the topography map in Figure 4.4-b. While topography varied approximately 10 nm over a
25 \( \mu \text{m}^2 \) area for Shale 1 (Figure 4.3-b), this was reduced greatly to approximately 2 nm over an equivalent 25 \( \mu \text{m}^2 \) area for Shale 2 (Figure 4.4-b). This reduction in surface topography is a result of more stringent sample preparation as presented in the methods section. The stiffer minerals in Shale 2, such as quartz, can be seen in Figure 4.4-b as dark orange, and they are located throughout the scan, surrounded by a mixture of kerogen-rich regions (yellow regions in Figure 4.4-b) as well as areas of clays mixed with kerogen (light orange regions in Figure 4.4-b). Unlike Shale 1, the topography was much more uniform for Shale 2. It is also important to note that the improved ion milling removed the majority of the issues of track marks seen in Shale 1.

The same topography filtering technique used for Shale 1 was used to analyze Shale 2 to determine whether or not improved surface preparation could reduce the amount of filtered data, resulting in a more complete modulus map. Figure 4.4-c shows the corresponding filtered topographic image for Shale 2. A surface height variation of 0.3 nm was used again to analyze the scan. Previously, the filtering technique removed close to 20\% of the scan of Shale 1. Figure 4.4-c shows less than 5\% of the entire scan is removed due to surface height variations. When the calculations for the amount of material probed were conducted, it was found that the contact radius varied from 5 to 15 nm. For a 5 \( \mu \text{m} \times 5 \mu \text{m} \) scan, these numbers correspond to less than 1 pixel for both compliant and stiff areas of the scan. Thus, it is still sufficient to consider topographic variations only between nearest neighbor pixels. In fact, the use of the topography filter for Shale 2 may be overly conservative; even with drastic filtering, Figure 4.3-c remains largely intact. This is due to the dramatically sharper tip as well as the lower dynamic load being used. Reducing the dynamic load using the larger radius tip used for Shale 1
would not yield similar results, but instead would result in the majority of the scan falling below the noise floor of the machine due to insufficient strain.

Once topography filtering was completed, the displacement amplitude scan for Shale 2 was analyzed. Similarly to Shale 1, displacement amplitude data that fell below 0.3 nm in Shale 2 was masked and removed from the final analysis of the shale. Previously, approximately 30% of the scan of Shale 1 (Figure 4.3-e) was removed due to the displacement amplitude being below the noise floor of the machine. Figure 4.4-e has less than 5% of the scan removed due to displacement amplitude values below 0.3 nm. Again, the regions where data was removed fell within the stiffer mineral components. This can be seen in the upper left hand corner of Figure 4.4-e where data was removed from the quartz grain. Shale 2 scanning parameters were optimized for kerogen-rich regions, just as was done for Shale 1; however, with better sample preparation and a sharper tip, more data remained after filtering techniques were implemented.

These filtering techniques combined resulted in the filtered storage modulus map in Figure 4.4-f. Less than 5% of the collected data was removed from the scan due to topographic variations or inadequate displacement amplitude values. Figure 4.4-f is a drastic improvement over the 40% of data that was removed during the analysis of Shale 1 (Figure 4.3-f). Note that the areas of transition from compliant to stiff material are sharp, denoting a change in properties. For example, in the lower left hand corner of the image, the circular mineral piece is surrounded by pore filling mineral deposits (in green corresponding to ~40 GPa) and finally by softer mineral regions (in blue corresponding to ~15 GPa).
Figure 4.4- (a) Modulus map collected for Shale 2 for the region highlighted in Figure 4.2-(b,c) Raw topographic scan and corresponding filtered (0.3 nm) topography scan. (d,e) Raw displacement amplitude scan and corresponding filtered (0.3 nm) displacement amplitude scan. (f) A filtered modulus map of Shale 2 based on topographic and displacement amplitude filters.
The effective spatial resolution for Shale 2 varied between 30 – 90 nm, which corresponded to a spatial resolution of 2 to 5 pixels. This is another improvement over the resolution seen for Shale 1, which varied from 3 to 10 pixels. The analysis of Shale 2 found that a sharper tip and more stringent surface preparation resulted in the ability to collect data with a consistent uniform contact area as well as data above the noise floor of the machine. This ultimately led to a more intact final scan once the analysis and filtering techniques had been applied to the highly heterogeneous shale.

While Shale 1 offers some useful insight, a large portion of the scan is removed due to large topography variations and a lack of displacement amplitude; Shale 2 provides a largely intact scan, which allows for simultaneous analysis of both compliant and stiff regions. In both scans, the data shows sub-micron spatial variations in reduced storage modulus, however, with adequate sample preparation and a sharp tip, the amount of data that can be maintained for analysis of local modulus variations after filtering is greatly increased.

4.4 Summary

Two Bakken shale samples were characterized using a nanoindentation-based dynamic modulus mapping technique. The shales exhibited large stiffness contrasts that can jeopardize accurate data collection if proper preparation of a smooth surface is not ensured. We find here that a surface roughness of 2 nm is adequate for obtaining high resolution scans, but that roughness of 10 nm or larger results in an unacceptable amount of negatively impacted data. Implementing a filter that removes data where neighboring pixels differ by a height of more than 0.3 nm avoids locally inaccurate
contact radius assumptions due to topographic variation and resulting inaccurate elastic modulus values. The large stiffness contrasts of shale constituent materials also make it difficult to achieve reasonable displacement amplitude values that are both above the noise floor of the machine and do not result in plastic deformation of the sample, unless a sufficiently sharp tip and optimized dynamic force are utilized. Elastic modulus values acquired from regions where displacement amplitude falls below 0.3 nm reflect inaccurate data as a result of insufficient strain in the locally probed area. Filtering techniques were applied to mask areas negatively impacted by high roughness or low displacement amplitude, resulting in property maps that are more quantitatively accurate in interpreting local property variation. While this approach provides sub-micrometer spatial resolution in mapping modulus variations within microscale kerogen-rich regions, which are too small to be accurately probed by quasi-static nanoindentation, nano-dynamic modulus mapping techniques can be optimized by ensuring the highest quality FIB preparation and employing a sufficiently sharp tip to maintain more of the collected data. It was found that Shale 1 lost approximately 40% of its data due to filtering while Shale 2 lost less than 5%. Typical modulus values measured by this technique include approximately 10 GPa for kerogen, 15-45 GPa for clay depending on the morphology and orientation, and 50-70 GPa for quartz. This improvement in data extraction provides a better understanding of intergranular properties in shales and is applicable to other natural and manufactured composites containing stiff and compliant materials. The data presented here for organic-rich shales are the first of their kind and have the potential to inform procedures for upscaling to
representative volume elements and developing physics-based models for assessing deformation and fracture potential.
CHAPTER 5
EFFECT OF THERMAL MATURITY ON ELASTIC PROPERTIES OF KEROGEN

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5.1 Abstract

Spatially continuous nano-dynamic mechanical analysis (nano-DMA) was performed on four organic-rich shale samples with different thermal maturities in order to extract the elastic modulus of kerogen particles. Aliquots were rigorously prepared and three scans were acquired from each aliquot. Sub-critical Nitrogen adsorption pore characterization was performed to determine abundance of kerogen-hosted porosity. The samples from oil window also underwent pore characterization after solvent extraction with toluene and then with chloroform.

The statistical distribution of measured modulus values was analyzed to extract properties of shale particles.

In mature samples from peak of oil generation or gas window, kerogen porosity is the dominant pore morphology. We find significant lowering of kerogen particle modulus resulted from intraparticle kerogen porosity. The kerogen particle modulus in mature samples was measured lower (7-12 GPa) than the immature sample (15-20 GPa) due to gas- or bitumen-filled pores.
5.2 Introduction

In self-sourcing reservoirs (SSR), maturity (extent of oil generation), porosity and abundance of natural fractures are the main parameters that make these tight plays economical. Determining sweet spots using spatially extensive detecting techniques is essential for successful development of these resources. Understanding the elastic behavior of source rocks and its interrelation with organic content and maturity can provide crucial information about the amount of generated hydrocarbon, petrophysical properties and geomechanical characteristics from well logs and seismic surveys.

Generating representative rock models to describe the behavior of organic-rich rocks is challenging due to complex textural properties of these rocks and the uncertainties in mechanical properties of some of the major components. Despite previous studies on the texture of organic-rich rocks in relation to their elastic properties, anisotropy (Vernik and Nur, 1992) and mechanical characteristics of the grains (Prasad, 2001; Zeszotarski, 2004; Ahmadov, 2009; Mba and Prasad, 2010; Prasad et al., 2011; Wilkinson et al., 2014; Eliyahu et al., 2015) there is limited available data on the characteristics of some essential components such as clays and organic matter. Moreover, changes in properties of kerogen and clay minerals during the course of thermal maturation are poorly understood.

Nanoindentation has been widely used for measuring mechanical properties of thin films, fine-grained composites, and polycrystalline materials. The technique uses a diamond indenter to apply small scale forces to a material while measuring the resulting displacement. Recently, this technique gained tremendous attraction for the
characterization of geo-materials, especially fine-grained mudrocks (Prasad et al., 2001; Zeszotarski et al., 2004; Ulm and Abousleiman, 2006; Bobko and Ulm, 2008; Ahmadov et al., 2009; Kumar et al., 2012; Shukla, 2013; Zargari et al., 2013). The accuracy of measurements using this technique is limited by the sharpness of the tip, size of the grains (in granular materials) or the thickness of the films (in thin films) in the substrate.

Effects of underlying and surrounding grains on nanoindentation measurements in very fine grain materials like mudrocks can be significant. If the generated stress field exceeds the grain boundaries, measurements are affected by comingled properties of loaded grain(s) and the substrate and surrounding material (Constantinides et al., 2006; Ulm et al., 2010). This effect is shown in Figure 5.1. An organic-rich shale sample was polished and a geometric grid of nanoindentation (with 8000 μN force) was conducted. The indented area was investigated using Field Emission Scanning Electron Microscopy (FESEM). Co-located FESEM backscattered and topography images on the area of an indentation array highlight the imprint of indentations. As is evident in topographic images (on the left) and backscattered images (on the right), the majority of the grains in this shale sample are smaller than the indented area under the tip in this test of specific settings; implying that the results of nanoindentation in this test are potentially controlled by mechanical properties of the comingled particles sensed underneath and adjacent to the tip.

Visual inspection of indentation points is a useful approach to screen the data points for extracting the mechanical properties of the individual grains. Another concern that remains unresolved is the effect of surrounding and underlying material (if different
Figure 5.1- SEM images of the indented surface reveal the probed locations. By locating the indented area the mineral groups that were measured under the probe can be identified. It is evident that in this setting, the size of indentation is greater than shale grain sizes in some of the points; causing comingled property measurements from target material). This effect may be reflected as a change in the slope of the loading curve (Figure 5.2).

In another case, if the grain sizes are significantly finer than the indentation size, the loading curve might not reflect a slope change, behaving similar to a homogeneous material (Constantinides et al., 2006; Ulm et al., 2010). In this scenario, the measured values are close to the bulk properties of the composite material. Therefore, measuring mechanical properties of individual grains in fine-grained material using nanoindentation has limited applicability.
Figure 5.2: Stiffer underlying material causes a deflection in the indentation loading curve (left image around 2000 μN) in comparison with a typical loading curve extracted from indentation on a single component (right image).

In order to avoid potential errors associated with the indentation size and depth of investigation, high-resolution, spatially continuous, dynamic mechanical probing techniques have been used (Prasad, et al., 2002; Wilkinson et al., 2014; Eliyahu et al., 2015). Utilizing these techniques requires comprehensive sample preparation [Wilkinson et al., 2014].

In this study, we implemented the nano-DMA technique. This technique provides high resolution two dimensional continuous measure of mechanical properties. For a complete description of the technique and the sample preparation requirements in organic-rich shales, we refer the readers to Wilkinson et al. (2014). Since presence of kerogen-hosted porosity affects the modulus of kerogen particles, separate aliquots underwent solvent extraction followed by nitrogen adsorption pore characterization to determine the abundance of intraparticle kerogen porosity. Pore morphology characteristics were further integrated with nano-DMA results in order to explain mechanical behavior of kerogen particles.
5.3 Materials and Methods

Four Bakken Shale samples with varying thermal maturities were selected for analysis. One immature sample was selected from onset of oil generation, namely BK001, two mature samples from the peak of oil generation, namely samples BK002 and BK003, and one over-mature sample from the gas window, namely BK004. Hydrogen indexes (a measure of maturity) of these samples range from >600 to 6 (mg HC/g TOC). Total organic contents (TOCs) range from 21.7 to 7.9 wt%.

Cubical aliquots of approximately 1 cm³ were collected from each sample and an 80μm wide area was polished at the edge of each aliquot using a focused ion beam (FIB). The mechanical mapping was conducted using a Hysitron TI950 nanoindenter (Hysitron, Inc., Minneapolis, MN) equipped with nanoDMA III.

In composite materials with components of high mechanical contrast, the displacement response varies depending on stiffness of the probed grains. The quasi-static and dynamic load amplitudes are selected such that the displacement amplitude remains reasonably above the noise floor (0.3 nm for this machine) throughout probing of the surface. A quasi-static load of 2μN and dynamic load of 1μN at a frequency of 200 Hz was maintained on a diamond tip with 80 nm tip radius while scanning. Based on expected range of elastic modulus of probed grains, from 10 GPa for kerogen as the most compliant grains to 306 GPa for pyrite as the stiffest grains, the contact radius of used tip may vary between 5.8 to 18.2 nm respectively (Wilkinson et al.; 2014).

The nano-DMA analysis was performed on three 5×5 μm areas from the polished edge of each aliquot. The modulus maps were analyzed and filtered to remove
measurements that were affected by polishing artifacts using the algorithms suggested by Wilkinson et al. (2014). The filtered areas are excluded from analysis and appear white in the subsequent figures.

Since kerogen-hosted pores have been reported (Slatt and O'Brien, 2011; Loucks et al., 2012; Modica and Lapierre, 2012; Milliken et al., 2012), the samples were investigated for the presence of kerogen-hosted porosity by removing soluble hydrocarbons using solvent extraction followed by sub-critical Nitrogen adsorption pore size distribution (PSD) and specific surface area (SSA) determination. Solvent extraction was performed on the samples from the oil window to remove the bitumen and liquid hydrocarbon from the pore space. Porosity measured with nitrogen adsorption was found to increase after solvent extraction compared to before extraction.

The measured SSA and PSD curves from sub-critical Nitrogen adsorption tests are used to characterize the pore system and to determine abundance of kerogen-hosted porosity in each sample.

The screened measured values (pixels values that passed the filtering criteria) from all three scans of each sample were analyzed collectively to extract the elastic modulus of the kerogen particle and inorganic minerals. The PSD and SSA were integrated with elastic modulus maps to explain the effect of kerogen-hosted porosity on mechanical modification of the kerogen particles.

5.4 Results and Discussion

The results of modulus mapping, FESEM images of corresponding mapped areas, geochemical characteristics of the specimen and pore size distribution curves before
and after solvent extraction are shown in the following figures. The histograms show frequency of collected elastic modulus values in all three scans from each sample (after filtering). In addition to mechanical contrast between the grains, the high resolution of modulus maps reflect as much textural details as are observed in SEM images.

Sample BK001 is the most immature sample in our selection with HI of 633 (mg HC/g TOC). Total organic content (TOC) in this sample is 17.7 wt%.

The histogram of elastic modulus exhibits a bimodal distribution in the low range with peaks i) between 15-20 GPa and ii) around 23 GPa. We interpret the lowest values (15-20 GPa) as reflecting the elastic modulus of larger kerogen particles and the second peak (around 23 GPa) to correspond to thin layers of kerogen where the measurements could be affected by the surrounding grains. Moreover, multiple overlapping peaks exist between 40-80 GPa which correspond to clay minerals and quartz particles.

From Nitrogen adsorption analysis, this sample shows very low specific surface area (maximum of 7.29 m²/g) and porosity (maximum of 3.7%) before and after solvent extraction. The PSD curve shows a broad distribution of pore sizes throughout the measured interval.

Samples BK002 and BK003 are selected from higher maturity levels at the peak of oil generation with HI of 257 (mg HC/g TOC), TOC of 17.7 wt% and HI of 126 (mg HC/g TOC), TOC of 7.9 wt% respectively. The elastic modulus histogram of the sample BK002 shows a sharp peak between 7-10 GPa (interpreted as kerogen particle modulus) and overlapping peaks in the range of 15-70 GPa (Figure 5.4). The modulus histogram of the sample BK003 also show a copious population of low modulus values between 7-10 GPa (kerogen particles). BK003 has a more distinct bimodal distribution
Figure 5.3- (a) Geochemical properties and pore characteristics. (b) Nanomechanical maps from surface of the immature sample BK001 and the corresponding FESEM images. (c) The histogram of overall measured elastic modulus values at three areas. (d) Pore size distribution before and after solvent extraction using toluene and then with chloroform. The lowest measured values correspond to kerogen particle modulus, ranging between 15-20 GPa. It is worthwhile mentioning that the desication cracks observed in FESEM images have occurred after nano-DMA tests were performed and have not affected the modulus measurements.
between 15-70 GPa with peaks around 20 and 60 GPa followed by a very low amplitude broad peak between 100 and 150 GPa representing the modulus of the pyrite grain present in the second scan (Figure 5.5).

Solvent extraction of these samples resulted in significant increase in SSA (53 and 30 m$^2$/g respectively), the PSD curves also exhibited a dramatic change in shape, showing substantial increase in population of nano-pores (2-20 nm in diameter) which are indicators of an abundant presence of kerogen-hosted porosity in both samples (Kuila et al., 2014).

The two samples show different textural characteristics owing to high contrast in TOC (21.7 vs 7.9 wt%). SEM images of sample BK002 show laminated features associated with organo-clay mixtures. These thinly interstratified laminates are also reflected in corresponding modulus maps. However, the fine nature of these features cause interference of measured values, resulting in comingled property measurement in thinly interstratified particles. This effect might compromise a major portion of measured values in the sample BK002, as well as causing appearance of the broad peak in the range of 15-70 GPa.

**Sample BK004** is the most mature sample in our inventory with HI of 6 (mg HC/g TOC) belonging to the over mature gas window. TOC is 12.5 wt%. The nitrogen adsorption PSD shows an abundant presence of nanopores, indicating porosity in the kerogen. The kerogen particle modulus ranges between 7-12 GPa. We also observe a second peak between 15-30 GPa which corresponds to thin layers and small pockets of kerogen. The larger kerogen values (second peak) are affected by the underlying and
surrounding minerals. The clay minerals and the silicates range in modulus between 45-70 GPa represented by the third peak in the histogram.

<table>
<thead>
<tr>
<th>TOC = 21.7 (wt%)</th>
<th>Max Measured Porosity = 6.9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI = 257 (mg HC/g TOC)</td>
<td>Max BET SSA = 53 (m²/g)</td>
</tr>
</tbody>
</table>

Figure 5.4- (a) Geochemical properties and pore characteristics (b). Nanomechanical modulus maps and the corresponding FESEM images. (c) Histogram of measured modulus values for sample BK002 and (d) PSD before and after solvent extraction. Kerogen particles in this sample have elastic modulus between 7-10 GPa.
Figure 5.5- (a) Geochemical properties and pore characteristics. (b) Nanomechanical modulus maps, corresponding FESEM images. (c) Histogram of measured modulus values for sample BK003 and (d) PSD before and after solvent extraction. Kerogen particles in this sample have elastic modulus between 7-10 GPa.
Here we find a considerable presence of kerogen-hosted porosity at high maturities. The intraparticle porosity in the kerogen causes a reduction of the elastic modulus of kerogen particles, regardless of whether they are fluid or gas-filled. These measurements provide us with a good approximation of kerogen particle modulus which is applicable for rock modeling purposes. These modulus values correspond to the kerogen grains that also contain porosity (Table 5.1). The kerogen porosity may be filled with water, bitumen, oil or gas depending on the level of maturity.

These findings are consistent with our previous results where we studied samples of different maturity at natural and synthetically matured states (Zargari et al., 2013). We observed that the softer portion of the rock which is comprised of kerogen, clays and bitumen is undergoing modulus reduction with natural and synthetic maturity. We previously speculated that the porosity is increasing in the kerogen, causing this modulus reduction, but we were not able to visualize this phenomenon since most of the porosity was filled by the produced hydrocarbons and bitumen.

Differentiating between the nanometer/sub-nanometer pores and the solid kerogen to investigate the solid kerogen moduli requires higher resolution measurements or use of deconvolution techniques. In order to determine the solid kerogen moduli using the results of current study, we need knowledge of the fraction of porosity in the kerogen, the properties of pore-filling fluid and an appropriate model to perform reverse fluid substitution. Further analyses are required to determine these properties.
Figure 5.6- (a) Geochemical properties and pore characteristics. (b) Nanomechanical modulus maps, corresponding FESEM images. (c) Histogram of measured modulus values for sample BK004 and (d) PSD before and after solvent extraction. Kerogen particles in this sample have elastic modulus between 7-12 GPa.
Table 5.1- Variations of kerogen particle elastic modulus with maturity as measured using nano-DMA technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Level of Thermal Maturity</th>
<th>Kerogen Particle Modulus (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK001</td>
<td>Onset of oil generation (immature)</td>
<td>15-20</td>
</tr>
<tr>
<td>BK002</td>
<td>Peak of oil generation (mature)</td>
<td>7-10</td>
</tr>
<tr>
<td>BK003</td>
<td>Peak of oil generation (mature)</td>
<td>7-10</td>
</tr>
<tr>
<td>BK004</td>
<td>Gas window (over-mature)</td>
<td>7-12</td>
</tr>
</tbody>
</table>

5.5 Summary

The dynamic mechanical analysis was performed on four organic-rich shales with thermal maturities ranging from immature to gas window. Nitrogen adsorption pore characterization technique was performed on the samples in their original states and after solvent extraction with toluene and then chloroform to examine the state of kerogen-hosted porosity.

The immature sample contained minimum kerogen-hosted porosity as indicated by sub-critical nitrogen adsorption and exhibited maximum kerogen particle modulus (15-20 GPa).

At higher maturity levels (peak of oil generation and gas window) kerogen particle are more porous, exhibiting extractable hydrocarbons, high SSA and abundant nano-porosity that lead to lower kerogen particle moduli (7-12 GPa).
By integrating nano-scale pore characterization and dynamic mechanical analysis we showed the significant influence of intraparticle kerogen porosity on the modulus of kerogen particles.

Determining solid kerogen modulus, using the results of this study, requires further analysis to collect the information essential for deconvolving effect of intraparticle kerogen porosity from the kerogen particle properties.
CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

The main objective of this thesis was to understand and quantify the underlying changes in mechanical properties and porosity of organic-rich shales (ORS) throughout thermal maturation.

The fine nature of pores and grains in organic-rich rocks necessitated employing nano-scale pore and matrix characterization techniques. Nanoindentation, nano-dynamic mechanical analysis and sub-critical nitrogen adsorption techniques were utilized. The results of these analyses were integrated with geochemical and mineralogical characteristics. RockEval and LECO TOC methods were used for geochemical characterization. Mineralogy was determined by QEMSCAN and XRD analysis.

Sample preparation and pretreatment were also essential parts of this study. Hydrous pyrolysis was conducted to replicate thermal maturation and consequent textural and mechanical changes that it imposes on organic rich shales. Solvent extraction was performed to remove hydrocarbons from the pore space before pore characterization. Rigorous surface polishing using focused ion beam (Fib) was conducted to prepare samples for nano-dynamic mechanical analysis.

In the following sections, a detailed summary on effect of thermal maturation on textural and mechanical properties (6.1.1) and porosity (6.1.2) in organic-rich shales are presented. In section 6.2, recommendations for future studies are provided.
6.1 Conclusions

Throughout this study we were able to quantify some of fundamental changes in properties of organic rich shales which significantly affect mechanical and petrophysical properties of these rocks.

6.1.1 Textural and mechanical modifications of ORS

There are similarities between the texture of more mature rocks and the pyrolized immature rocks. Immature rocks usually have laminated kerogen layers with elongated kerogen particles whereas naturally mature rocks often have smaller and more isolated kerogen particles. The kerogen is load-bearing at lower maturity states where there is an abundance of organic matter. As the rocks get more mature, kerogen undergoes volume reduction and the particles become more isolated (both in natural and synthetic mature states).

Natural thermal maturation causes an overall increase in bulk elastic modulus of organic rich shales due to conversion of kerogen to hydrocarbons and consequent TOC reduction. However, nanoindentation results revealed that at smaller scale, the softer portion of the shales (mixture of clay minerals and kerogen) undergoes modulus reduction. The decrease in Young’s modulus of the softer components can be explained by developing intraparticle kerogen porosity and replacement of parts of kerogen with bitumen. This hypothesis was proved after performing nano-dynamic mechanical analysis and investigating abundance of kerogen-hosted porosity in shales of different maturity.
By integrating nano-scale pore characterization and dynamic mechanical analysis we showed the significant influence of intraparticle kerogen porosity on the modulus of kerogen particles.

The immature sample contained minimum kerogen-hosted porosity as indicated by sub-critical nitrogen adsorption and exhibited maximum kerogen particle modulus (15-20 GPa). At higher maturity levels (peak of oil generation and gas window) kerogen particles are more porous, exhibiting extractable hydrocarbons, high SSA and abundant nanometer-sized pores that lead to lower kerogen particle moduli (7-12 GPa).

### 6.1.2 Porosity evolution in ORS

We studied pore size distribution, specific surface area and geochemical properties of ten Bakken Shale samples after successive solvent extraction. The selection was made from a range of mineralogy and thermal maturity.

Solvent extraction was performed to determine what portion of the pore space is excluded from quantification due to presence of trapped oil in the pores and to understand the storage and flow capacity of source rocks in the oil window.

Our SSA and PSD data confirms that there is an overwhelming population of kerogen hosted porosity in the nanometer-scale range (<10nm) at the oil window. We found that the kerogen porosity generation peaks at higher maturity samples with HI of less than about 300 (mg HC/g TOC). The total porosity and surface area was also found to be directly related to TOC in the higher maturity samples. We found no particular effect of rock mineralogy, especially clay content, on the porosity development in organic rich shales.
The small size of the recovered pores after solvent extraction brings up doubts about how these pores may contribute in the flow of larger hydrocarbon molecules through the source rocks. These results must be cautiously interpreted for flow modeling purposes.

These measurements were conducted on crushed samples which provided increased surface area for the flow of hydrocarbons with possibility of changing the pore structure during mechanical crushing. Moreover the driving force in extraction experiments is the chemical potential which is different than the driving force in fluid flow in primary recovery in the reservoir which is pressure difference. The pressure drawdown in the reservoir might not be sufficient within the time frame of oil production to result in significant displacement of oil/bitumen through these rocks.

6.2 Recommendations for Future Studies

The findings of this thesis helps us better understand some of the most fundamental characteristics of organic rich shales while it opens up new questions regarding their properties. In this section, I would like to introduce some of these questions whose investigation was beyond the scope and time limit of this PhD thesis.

- We measured kerogen particle modulus using nano-DMA techniques and found reduction of elastic modulus of kerogen particles with increasing maturity. However, we were not able to quantify solid kerogen modulus. We speculate that the solid kerogen modulus may increase with maturity. Thermal maturation and release of hydrocarbons results in reduction in hydrogen and carbon atoms while increasing relative abundance of nitrogen, oxygen, sulfur and fluorine atoms in kerogen molecules. This chemical
change may in turn increase the polarity of atomic bonds in the molecular structure of kerogen. Further analysis is recommended for determining solid kerogen modulus using the results of this study. Therefore collecting information regarding amount of kerogen-hosted porosity and physical properties of filling hydrocarbon are essential for deconvolving the effect of intraparticle kerogen porosity from the kerogen particle properties.

- This study was also focused on quantifying porosity in organic rich rocks at different maturities with emphasis on bitumen-filled porosity in the oil window. The interaction between organic matter maturity and minerals changes effective porosity as well as other petrophysical properties of the shales such as resistivity. We showed how bitumen and other byproducts of kerogen maturation occupy clay and kerogen porosity in the early stages of oil generation. Based on tendency of some organic functional groups to be adsorbed at clay exchange sites, it is possible that some organic compounds form stronger bonds with clay surfaces, replacing clay bond water and consequently dehydrating the source rock. This phenomenon may cause a dramatic increase in resistivity by eliminating the water from interparticle clay porosity and occupying cation exchange sites of the clays.

- Studying changes in chemical and physical properties of the entrapped bitumen throughout the maturation process would be very insightful in predicting producibility of the bitumen and its interaction with minerals.


APPENDIX A
POROSITY CALCULATION FROM DENSITY LOG

The observations of porosity changes in self-sourcing mudrocks, call for improvements in total porosity and saturation estimation from conventional well logs. Here we suggest a similar approach to Sondergeld et al. (2010) to integrate geochemical data with well logs and mineralogy for more accurate porosity calculations in source rocks. We present calculations of matrix density to be used in porosity evaluation from density logs using material balance calculations.

We differentiate between the inorganic and the organic components of shales. Together, they constitute the shale matrix. Mineralogy can be estimated using ECS logs, XRD analysis or QEMSCAN that in turn is used to calculate density of inorganic mineral mixture (Eq. A-4). The organic content is derived from independent measurements, for example from cores or cuttings. We calculate matrix density by adding the organic matter and inorganic minerals (Eq. A-5). Porosity can then be calculated using this matrix density and the bulk density from well logs (Eq. A-7).

Kerogen density is one of the required parameters for the porosity calculations. Kerogen becomes denser as it matures (Patience et al., 1992; Okiongbo et al., 2005). In this study we use the data set from Okiongbo et al. (2005) to estimate density of type II kerogen (Figure A.1). Weight fraction of organic matter is usually measured using LECO TOC method, in which crushed core samples are cleaned using organic solvents, and then the powder is oxidized to determine the organic content. This technique provides an estimate of insoluble organic content of the source rock since some portion
of the hydrocarbon residing in the clays and kerogen porosity is dissolved out (depending on the solvent). The efficiency of the cleaning process will affect the geochemical data and TOC measurements.

Figure 8.1 - Type II Kerogen density as a function of HI presented by Okiongbo et al. (2005). The experimental data shows how kerogen density increases with maturity. Complete removal of soluble organic matter (bitumen) is a major challenge in extracting kerogen. This issue also exists in TOC measurements. These are the main concern in using such data set for petrophysical analysis.

Kerogen volume fraction can be calculated knowing matrix density, TOC and density of kerogen as followed:

\[
f_k = \frac{R_{HOM} \times TOC}{\rho_k}
\]  \hspace{1cm} (A - 1)

we calculated density of kerogen using Okiongbo et al. (2005) data set.

in the matrix:

\[
f_k + f_{min} = 1
\]  \hspace{1cm} (A - 2)
matrix density can be calculated from material balance as:

\[ RHOM = f_k \times \rho_k + f_{min} \times \rho_{min} = f_k \times \rho_k + (1 - f_k)\rho_{min} \quad (A-3) \]

Using ECS logs we get weight fraction of inorganic minerals and we calculate mineral density

\[ \rho_{min} = \frac{1}{\sum \frac{f_{ECS_i}}{\rho_i}} \quad (A-4) \]

where \( f_{ECS_i} \) is the mass fraction of different inorganic minerals.

Combining Equations A-1 and A-3:

\[ RHOM = \frac{\rho_{min}}{\left(1 - \frac{TOC}{\rho_k}\right)(\rho_k - \rho_{min})} \quad (A-5) \]

material balance for the bulk of rock is in the form of:

\[ RHOB = (1 - \emptyset)RHOM + \emptyset(S_w\rho_w + S_o\rho_o) \quad (A-6) \]

rearranging this equation for porosity gives:

\[ \emptyset = \frac{RHOB - RHOM}{(S_w\rho_w + S_o\rho_o) - RHOM} \quad (A-7) \]

Calculating saturations using resistivity log is not possible without knowing the porosity and effect of clay surface charges, therefore we may assume a range of values for the terms \( (S_w\rho_w + S_o\rho_o) \).

This method is based on several assumptions on the quality and availability of the data. The well log measurements are usually reported every half a foot; however their
actual resolution is two to three feet. On the other hand, the geochemical data can be acquired with higher frequency.

Calculated porosity using this approach is affected by the efficiency of extracting hydrocarbons before performing LECO TOC method. The extracted hydrocarbons are excluded from TOC measurements and therefore are accounted for in porosity calculations.
The following procedure was conducted for crushing, solvent extraction and pore characterization of the Bakken Shale samples:

1- 40 grams of chipped core sample was crushed and sieved using 100 mesh

2- Approximately 2 grams of crushed aliquots was collected for subcritical nitrogen adsorption porosimetry and Rock Eval analysis

3- The rest of the aliquot was placed in cotton thimble and first extracted with toluene in a soxhlet extractor for 48 hours

4- The thimble was removed and was placed under the hood until the powder is completely dry

5- The solvent was recycled using distillation apparatus while the concentrated extract was collected for future chemical analysis

6- 2 grams of solvent extracted powder aliquot was collected for subcritical nitrogen adsorption porosimetry and RockEval analysis

7- The thimble with remaining aliquots was returned to the soxhlet extractor and the steps 3 to 6 were repeated with chloroform, MAC and NMP