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Pore Systems of the B Chalk and Lower A Marl Zones of the Niobrara Formation, Denver-Julesburg Basin, Colorado

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PORE SYSTEMS OF THE B CHALK AND LOWER A MARL ZONES OF THE NIOBRARA FORMATION, DENVER-JULESBURG BASIN, COLORADO

by

JULIAN MARTIN H. MICHAELS

B.A., Colgate University, 2011

A thesis submitted to the
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Denver-Julesburg Basin, Colorado
written by Julian Michaels
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Kevin H. Mahan

Date________________

The final copy of this thesis has been examined by the signatories, and we
find that both the content and the form meet acceptable presentation standards
of scholarly work in the above mentioned discipline.
Michaels, Julian Martin H. (M.S., Geological Sciences)

Pore Systems of the B Chalk and lower A Marl Zones of the Niobrara Formation,
Denver-Julesburg Basin, Colorado

Thesis directed by Dr. David A. Budd

ABSTRACT

This study identifies, characterizes, and analyzes the pore systems of the Niobrara Formation, and explores the linkage between measurable rock properties and the observed pore system. Pore system characterization was achieved using focused ion-beam scanning electron microscopy (FIB-SEM) and Avizo Fire™ image segmenting software. The study focuses on the B Chalk, the primary landing zone for horizontal wells, and overlying A Marl units.

Material was examined from four cores representing thermal maturities ranging from the oil window ($\text{Ro} \approx 0.7, \text{GOR} \approx 1,000$) to the dry-gas window ($\text{Ro} \approx 1.2, \text{GOR} > 20,000$). Electron microprobe elemental maps showed that detrital organic macerals are concentrated in the marl interlaminations, whereas finely disseminated organic matter occurs in the peloids. The maps also show peloids to be exclusively calcite whereas matrix varies from nearly pure calcite to dominantly alumino-silicates. Intercrystalline, mineral-associated micropores dominate all samples in both matrix and peloids. Total image porosity averages 4.3% with a range of 1.4% to 10%, with the highest porosity in peloids. Relationships between lithology, geochemistry, thermal maturity, and microfacies were tested for attributes such as shape, size, and abundance of mineral pores, residual hydrocarbon-filled pores, and pores within organic matter (OM pores). OM pores occur in residual hydrocarbon-filled pores in all wells, but not in all filled pores. These pores range in size from tens of nanometers to microns in diameter. Abundance of OM porosity
shows no increase with thermal maturity above ~0.7 R_0. OM pores are generally larger in the higher thermal maturity wells.

The abundance and size of mineral and organic pore systems does not vary significantly with respect to lithologies, microfacies and geochemical facies defined by redox and nutrient proxies. Predicting the nature of the pore systems is not possible from these larger scale rock attributes. Paucity of pores in the matrix of samples implies that matrix material may be a fluid flow barrier. Therefore, nearly all storage potential and flow capacity exists within peloid-rich laminae. Conversely, the amount of residual hydrocarbons within original mineral pores raises concerns about how much fluid may flow through the pore system.
ACKNOWLEDGMENTS

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I could not have gotten through graduate school without the unwavering support of my family and friends. For the couches, pep talks, adventures, distractions, and fun, I am forever grateful. Thank you to my mom, dad, sister, and extended family for supporting me through my longer-than-anticipated tenure as a student. Twenty years of formal education has been a long journey!

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Chapter 1- Introduction

The revolution in unconventional oil and natural gas exploration has completely changed the way the United States and the world views fossil fuel exploration and energy policy. By combining horizontal drilling and multi-stage hydraulic fracturing, reservoirs of fossil fuels in very low permeability (“tight”) rocks are now being exploited around the world (Curtis et al., 2010; Figure 1). Tight reservoirs have relatively low permeability due to small pore throat size (typically nanometers in scale), and in some cases, porosity less than 10% (Loucks et al., 2009; Zhang et al., 2012). The small pore throats are only large enough to pass a few molecules of hydrocarbon (Figure 2) and non-Darcian flow is potentially a significant component of production. Many tight reservoirs such as the Eagle Ford, Marcellus, Woodford, and Barnett shales that had previously been deemed uneconomic are now being drilled and completed with great success (Curtis et al., 2010). Before the technological advancements, these tight reservoirs were not targets for exploration. In some cases, these shale formations exist in areas where conventional oil and natural gas development has taken place in the past, and infrastructure costs are low due to previous exploration. This allows for experimentation with lessened midstream cost. In other cases, exploration is occurring in regions long ignored by most of the industry, such as the Appalachian Basin in New York and Pennsylvania. Across the U.S., oil and natural gas production from tight shale formations is bringing thousands of jobs and boosting many local economies. One independent study projects that more than 3.9 million jobs will be supported in the US by unconventional gas activity by the year 2025 (IHS, 2013, 7/16/2014). The Energy Information Agency estimated that the United States has increased its proved oil reserves to over 33 billion barrels and over 322 trillion cubic feet of proved wet natural gas (EIA, 2014,
Figure 2. Sizes of molecules and pore throats in silicilastic rocks on a logarithmic scale covering seven orders of magnitude. Measurement methods are shown at the top of the graph and scales used for solid particles are shown at the lower right. The symbols show pore-throat sizes for four sandstones, four tight sandstones, and five shales. Ranges of clay mineral spacings, diamondoids, and three oils, and molecular diameters of water mercury and three gases are also shown (Nelson, 2009).

Figure 1. Global distribution of unconventional hydrocarbon resources (http://pacwestcp.com/education/shaleunconventional-resources/)
The increases in reserves came from reevaluation of formations made possible by technological advances.

The Denver-Julesburg (DJ) Basin (Figure 3) is one area where increased unconventional exploration is occurring. Oil and natural gas have been produced from the DJ Basin since the early 20th century (USGS, 2007), beginning with exploration in the Pierre Shale at the McKenzie #1 well in Boulder, CO (historycolorado.org, 9/23/2013). Until the last decade, conventional (mostly vertical) drilling into porous and permeable sandstones was the primary method of extracting DJ Basin resources. With the development of directional drilling and hydraulic stimulation, the DJ Basin has been reassessed and different formations are now targeted for exploitation. These formations include the Cretaceous-age Niobrara Formation. The Niobrara Formation has been horizontally drilled and hydraulically stimulated for nearly a decade and is now the most prolific hydrocarbon producing intervals in the DJ Basin. This formation is an organic-rich and partially self-sourcing calcareous marine chalk. The underlying organic-rich Graneros Shale provides further hydrocarbon charging (Higley et al., 1995).

The Niobrara Formation in the DJ Basin consists of alternating chalk and marls (Figure 4). Chalks represent periods of decreased deposition of argillaceous material and/or higher rates of calcareous deposition associated with periods of maximum sea-level rise; in essence a condensed section (Locklair and Sageman, 2008). In contrast, marls typically contain calcitic material but also a large amount of argillaceous material, which dilutes the calcareous material (Figure 5). Locklair and Sageman (2008) suggest that the meter-scale cyclical alternations are due to the effects of climate change based on Milankovich orbital forcing mechanisms.

The Niobrara Formation is composed of mostly calcitic fecal material in the form of pellets, as well as dark, fine-grained mud particles or floccules (Hattin, 1981). Chalky material is
Figure 3. Inset map in upper left shows northern Colorado and extent of Denver-Julesburg Basin. Township and range map of northeastern Colorado (lower right) indicates location of wells used in this study (red dots). Greater Wattenberg Field shaded in pink. Gas-to-oil (GOR) ratios and Ro values reported for each well.
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iferai in a matrix that contains abundant calcite (brown coloring) but also some admixed clays as evidenced by the patchy and 
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abundant clays (Aristocrat 7127.9). Blue epoxy fills cracks in the 
fissile marl.
mostly derived from primary productivity of coccolithophores in the water column (Figure 6; Hattin, 1981). Pelagic foraminifera were also deposited, however, whole coccoliths, coccolith plates, and broken pieces of plates contribute the majority of the matrix in chalky and marly strata (Pollastro and Scholle, 1986). As the formation was deposited during the Cretaceous, most of the detrital material and argillaceous mud was likely derived from the distal Sevier Orogenic Belt (Figure 7; Hattin, 1981). Compaction, cementation, and recrystallization of the calcareous material (Figure 6A versus 6B) contributed to porosity loss with progressive burial (Hattin, 1981; Pollastro and Scholle, 1986). However, the high calcite content provides some of the desirable brittleness needed for artificial stimulation (Josh et al., 2012). The Niobrara Formation is considered to be tight shale and therefore requires stimulation to create an artificial permeability network more effective than that of the natural network.

The Cretaceous-aged Niobrara Formation is subdivided into two members, the Fort Hayes Limestone and the overlying Smoky Hill Member. The Smoky Hill Member is further divided into four informal chalk members, each separated from one another by an informal marl member (Longman et al., 1998). The chalks have been labeled alphabetically, with the stratigraphically highest chalk labeled "A" and the lowest labeled "D" (Figure 8). This largest scale of vertical heterogeneity occurs at the scale of decameters. Additional scales of vertical chalk-marl heterogeneity occur at the meter (core) scale and relate to parasequence cycles (Locklair and Sageman, 2008) and at the centimeter to millimeter (thin section) scale of individual laminations (Longman et al., 1998; Figure 9). These multiple scales of alternations between chalk and marl make it difficult to precisely define tops for the different members, and complicates definition of lithology (Sonnenberg, 2012).
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The most calcareous chalk, the B Chalk, has been the primary target of unconventional exploration in the DJ Basin, while the C Chalk is a secondary target (Stark and Coskey, 2011). The thickness, porosity, and permeability of both the B and C chalks make them favorable for landing horizontal wells. The brittle nature of the chalks also makes them better targets for hydraulic fracturing, as artificially induced fractures propagate best through brittle material such as calcareous chalk (Josh et al., 2012).

**Pore Systems in Unconventional Reservoirs**

FIB-SEM and other electron microscopy techniques have been used to identify and evaluate the nanometer- to micron-scale pores in many tight unconventional reservoirs. The small pore sizes, abundance of clays, and disseminated organic matter results in unique pore systems in many unconventional reservoirs. New types of pores have been documented in association with the organic material and they contribute to overall hydrocarbon storage and deliverability (Loucks et al., 2009; Milner, 2010; Heath et al., 2011; Curtis et al., 2011). Pore systems of the Barnett, Woodford, Horn River, Haynesville, Marcellus, Eagle Ford, and Fayetteville have been studied (Milner, 2010; Curtis et al., 2011; Heath et al., 2011; Zhang et al., 2012; Bai et al., 2013, Milliken et al., 2013), however the Niobrara Formation is still poorly understood and little work has been published.

A variety of pore types are documented in various unconventional reservoirs and Loucks et al. (2012) proposed a classification system for those pore types (Figure 10). The three main types of pores in these systems are 1) interparticle (between particles of the matrix), 2) intra-particle (within particles), and 3) organic (within bitumen or kerogen particles). Similarly, Schieber (2010) also suggested three types of pores: phyllosilicate framework (PF) pores,
Figure 10. Backscatter electron imagery of various types of shale porosity plotted on ternary diagram of pore types. A mixed pore network exists within most formations (from Loucks et al., 2010 and modified by Dahl et al., 2012).
carbonate dissolution (CD) pores, and organic matter (OM) pores (Figure 11). In most unconventional reservoirs, a mixture of these pore types occurs, however some units such as the Barnett and Pearsall are dominated by organic porosity and intraparticle porosity, respectively (Loucks et al., 2012). Other formations like the Haynesville, Eagle Ford, and Niobrara contain a mixture of just interparticle and organic porosity. Still others are dominated by just fracture porosity within organic matter (e.g. Dahl et al., 2012; Loucks et al., 2009). The dissolution pores emphasized by Schieber (2010) are not believed to play a major role in shale formations containing relatively low organic or carbonate content.

Interparticle pores identified by Loucks et al. (2012) include pores between detrital siliciclastics, microfossils, fossil fragments, recrystallized calcite, forams, and pyrite framboids. All of these pores and connecting pore throats contribute to total porosity and permeability. Curtis et al. (2010) defined three additional pore types that are sub-categories of interparticle pore types. These included crack-like, phyllosilicate, and organophyllic pores (Figure 12).

Intraparticle pores include pores associated with skeletal material and grains that have been recrystallized or undergone dissolution. Depending on the formation, they may be sparse and not connected with the overall porosity system. Loucks et al. (2012) found that intraparticle pores are the dominant pore type in the Bossier and Pearsall Shales, and that most intraparticle pores are primary with evidence of diagenetic origin. The age and burial history of a formation can impact the number of intraparticle pores, as compaction and cements tend to destroy this type of porosity.

Pores within organic matter are a relatively new pore type, only recently identified in unconventional systems (Loucks et al., 2009). Some correlation is noted between different types of organic material, total organic carbon, and pore types (Modica and Lapierre, 2012; Schieber,
Figure 11. Backscattered electron imagery of the three main pore types defined by Schieber (2010). A) Clay flakes at multiple orientations exhibiting phyllosilicate framework pores. B) Calcite grain exhibiting carbonate dissolution pores at the margins of a crystal. C) Organic material exhibiting organic matter pores in the thermally mature Geneseo Shale. All images from Schieber (2010).
Figure 12. Backscattered electron imagery from various shale formations that illustrate the clay-related interparticle pores defined by Curtis et al. (2010). A) Crack-like pores at top of image with porous organic material. All mineral-associated pores filled with migrated organic material which now exhibits various levels of organic matter porosity development. B) Phyllosilicate pores seen between clay platelets. These pores have been impacted heavily by compaction. C) Complex network of organophyllic pores throughout most organic material between mineral grains. Some pores are small, round pores while others are more elongate, complex shapes. Pyrite (white masses) is prevalent throughout the sample. All images from Curtis et al. (2010).
2010; Milliken et al., 2013). Organic porosity textures include bubbly, spongy, cracked and fractured, and sheet-like pores (Loucks et al., 2009; Curtis, et al., 2010; Schieber, 2010; Walls and Diaz, 2011; Heath et al., 2012; Figure 13). Pore types, their shape, and spacing yield different textures within the organic matter. The presence and abundance of these various pore types may depend on a number of variables explored throughout this study.

Thermal maturity has been found to impact the formation of organic matter porosity by multiple studies (Loucks et al., 2009; Curtis, et al., 2010; Modica and Lapierre, 2012; Bai et al., 2013; Milliken et al., 2013). Other studies, such as Dahl et al. (2012), have shown through experimental heating of organic shales that pores are created, as well as destroyed, due to thermal effects. It has been hypothesized that the various organic textures imaged may be directly related to thermal effects including cracking of oil (catagenesis) and pyrobitumen formation as a result of severe oil cracking (Bernard et al., 2012; Dahl et al., 2012; Modica and Lapierre, 2012). These studies also assert that some fractures associated with organic material, particularly along contacts of organic and matrix material, are likely due to expulsion of hydrocarbons with no available flow path. This creates overpressure leading to natural microfracturing. Finally, Ross and Bustin (2008) suggest that with increased thermal maturity, a greater amount of hydrocarbon, particularly gas molecules, may be sorbed to the surfaces of organic material, surfaces of clays, in the void space of the pores themselves, or as Curtis (2002) mentions, dissolved in kerogen and bitumen.

Research Objectives

This study involves three main research objectives, all intended to provide insight into the pore systems of the Niobrara Formation. First, what are the different pore types and porosity
Figure 13. Backscatter electron imagery of various types of organic porosity plotted on ternary diagram. Pore type end members include bubble, fracture, spongy, and solid. Most examples of organic pores fall within the diagram (Walls and Sinclair, 2011).
systems in the Niobrara Formation? It is hypothesized that different porosity systems exist within marl and chalk intervals and between different wells. As outlined above, pore systems in unconventional reservoirs like the Niobrara Formation can consist of varied components and the presence/absence of any pore type will depend on a multitude of variables. By utilizing ion milling and SEM imaging, pore types and porosity systems will be identified and categorized.

The second research question asks where and why different porosity systems might exist. Do pore systems vary as a function of microfacies, macrofacies, lithology, or stratigraphic interval? Do they vary laterally as a function of thermal history? This research question will be attacked by sampling a ~70 foot interval that spans from the base of the A marl to the base of the B Chalk in each of 4 wells distributed across a large geographic area. This strategy insures that pore systems will be analyzed in all microfacies, representative of chalk and marl intervals, and from settings with different thermal histories.

The third question involves predictive capability. Can pore systems be predicted from lithology, macro- or microfacies, geophysical logs, or geochemical profiles? Geophysical logs, geochemical profiles, and core facies are relatively high-resolution (foot scale) data that exploration geologists use to characterize and correlate the Niobrara Formation. If certain porosity systems can be linked to these attributes, specific target intervals with favorable pore types can be inferred.
Core Description and Sampling

Four cores totaling ~525 feet and positioned on a roughly SW-NE transect through the Denver-Julesburg (DJ) Basin were selected for the study (Figure 3; Table 1). The four were chosen based on the gas-to-oil ratios (GOR) for each well or for nearby wells. GOR values were calculated from the Colorado Oil and Gas Conservation Commission (COGCC) database. The highest GOR well (Aristocrat Angus 12-8) is in the southwest region of study area (center of the Wattenberg Field), and the lowest GOR value is from the Burbach 20-3H well in the northeast region of the study area.

Each of the four cores were described for various attributes at roughly the quarter-foot scale. Attributes from each core included lithology, gray scale, degree of bioturbation, sedimentary structure, grain size, grain richness, pellet roundness, and relative abundance of forams, innoceramid shell fragments, and pyrite. Most of the cores also contained ash beds, however many have been removed due to over-sampling and therefore were difficult or impossible to locate and identify. Reflective light microscopy was employed to judge grain size, grain richness, and pellet roundness. Grain richness and pellet roundness were subjective estimates of grain content and circularity of pellets within a footage. These estimates helped to inform sampling and allowed a cursory micro-resolution study of the cores.

Sampling of each core was not continuous, but material was collected to insure that each core was sampled in a similar pattern. Fifty-four samples across the four cores were selected from the lower A Marl through lower B Chalk. Most samples were taken from chalky footages.
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</table>

Table 1. List of wells used in this study with location, API numbers, general well information, U.S. Geological Survey core library numbers if appropriate.
Sampling generally involved two strategies. Representative samples of all apparent macrofacies where chosen. These macrofacies were identified visually, often using gray scale as a proxy for chalk or marl. Also, specific beds of interest and certain features were preferentially sampled.

X-ray fluorescence (XRF) data was collected using a Thermo Scientific Niton® XL3t 950 portable hand-held analyzer at the one foot scale for all four cores, half foot scale on the Aristocrat and Timbro and for individual samples cut from the Burbach and Gill cores. These measurements provided major, minor, and trace-elemental data for each sample. Before use each day, the instrument was auto-calibrated by measuring a standard sample supplied by the manufacturer to verify instrument accuracy. Each measurement took 115 seconds. From the raw data, enrichment factors of elements relative to the North American Shale Standard were calculated (Gromet et al, 1984). In the case of the Gill and Burbach cores, reported data are for collected samples from this study. Reported values for the Aristocrat and Timbro samples are from the closest half-foot analysis. Elemental data collected included Ca, Mo, Al, Zn, V, Cr, S, Ni, and Cu and are reported in Appendix 1.

Thin-Section Analysis

All 54 samples were trimmed, vacuum and pressure impregnated with blue dyed epoxy, and faced before being sent to Spectrum Petrographics, Inc. (http://www.petrography.com/) for thin section manufacturing. Each thin section was examined on the millimeter scale, described, and photomicrographed for textures, fabrics, grain types and sizes, and sedimentary structures. Each sample’s attributes were used to categorize the overall microfacies. These microfacies influenced high-grading samples for further study. Thin-section analysis was done using an
Olympus BH-2 polarizing microscope and photo documentation was done with a MagnaFire™ digital camera.

Eighteen thin sections were also analyzed for disseminated organic matter using a reflecting ultraviolet fluorescence microscope using long wavelength UV (365 nm) and blue light (~400-450 nm; Burress, 1991). This was done in an attempt to constrain areas of interest to later analyze using the FIB-SEM. The eighteen thin sections were chosen to be representative of most microfacies present in the full set of thin sections. Representative fluorescent images were acquired with a Zeiss Axiophot® reflected-light microscope. The microscope was fitted with 10x oculars and a 50x oil immersion lens, for a total of 500x magnification, and utilized incident light (100 W tungsten lamp) filtered to 546 nm (green). A 100-watt mercury lamp was used for illumination in the UV range.

Wavelength-dispersive spectroscopy (WDS) X-ray maps of carbon (C), calcium (Ca), silica (Si), and aluminum (Al) were acquired on a JEOL-8600 electron microprobe. Analytical conditions were 15 kV, 150 nA, and a focused electron beam of ca. 1 µm. Pixel size was set to 1.6 µm for each set of four elemental maps, with a dwell time of 28 microseconds per pixel. Detectors utilized were PET for Ca and Si, LDEC for C and TAP for Al. The Ca, Si and Al images were stacked using ImageJ (http://rsb.info.nih.gov/ij/) and the stacked composite converted to an RGB image. The result displays quartz in red, calcite in blue, and alumino-silicates (feldspars, clay minerals) in shades of reddish yellow to yellow to yellowish green depending on relative Al and Si abundance. The distribution of carbon was assessed by adjusting window and level settings, which effectively decreased intensity on the carbon map so that only finely disseminated carbon and organic macerals were evident (i.e., the carbon coating and carbon in carbonate minerals is suppressed).
Electron Microscopy

Electron microscopy was used to characterize the pore systems in nine high-graded Niobrara samples. All electron microscopy was conducted in the Nano-Characterization Facility, College of Engineering, University of Colorado, Boulder. Samples were chosen based on a combination of sedimentologic and geochemical attributes seen in the core analysis, thin section microscopy, and XRF readings. A sample from the A Marl and B Chalk (primary landing zone) from each of the four wells was analyzed, plus one sample from the Gill C Chalk that represented a black, organic-rich marl that had not been sampled in the selected eight samples. These samples represented the possible variations in macrofacies, microfacies, and geochemical facies across the thermal maturity gradient between the wells.

Focused ion beam scanning electron microscopy (FIB-SEM) was used to image pore systems. Samples chosen for FIB-SEM analysis were mechanically broken and cut using a table saw to a size no greater than 3 by 3 by 3 millimeters, then mechanically polished with quarter-micron grit to yield an optical polish. Samples were held under vacuum for over 6 hours each to remove gasses and any contaminants that could damage SEM equipment. All samples were then soaked in toluene for one week at ~30º C, methanol for 2 days, methanol (87%) and chloroform (13%) mixture for 3 days, and then tetrahydrofuran at ~30º C for 14 days in order to remove any soluble hydrocarbons. Samples were then mounted onto aluminum stubs using double sided carbon tape, and carbon paint was applied to the sides and small area on top of samples to enhance conductivity. After drying, samples were gold sputter-coated to further enhance surface conductivity though it does not do so completely.

The FIB-SEM used in this study was a dual-beam FEI Nova 600i. This instrument has a gallium (Ga⁺) ion source and is able to generate both secondary electron and backscatter electron
images. Backscatter electron (BSE) microscopy proved the most effective for recognizing pores, organic material, and different grain types.

In the FIB-SEM, fields of view for milling were chosen based on recognizable features and textural elements such as peloids or matrix material but in some cases was done randomly because textural components were impossible to distinguish on the mechanically polished, gold-coated surfaces. Once a feature was identified, the sample was tilted to 52 degrees so that the orientation of the ion column was perpendicular to the face of the sample and the SEM column was aimed perpendicular to the face to be milled. A platinum pad was then deposited on the sample surface atop the feature of interest to protect it from the Ga⁺ ion beam. Thick platinum was found to better protect the sample from milling artifacts. Typically, the pad was 30 µm by 20 µm by 2-4 µm thick. Milling was initiated by cutting a 40 µm long by 30 µm wide and 15 µm deep trench (ramp) using the standard cross section tool at the maximum milling amperage (21 nA). The resultant rock face was again milled using the cleaning cross section tool (rectangle) at 2.8 nA to clean it of redeposited debris and curtain artifacts (vertical lines due to uneven or rapid milling). Finally, another cleaning cross section was milled at .93 nA to give a final polish.

Once the rock face of interest was sufficiently flat and clean, it was initially imaged at 3500x to 6500x magnifications using BSE mode at 15 kV and .98 nA to give an overview of the entire face. One to four overview images were required depending on the size of the wall. Subsequently, individual pores, grains, and other features of interest were imaged using 8000x to 65,000x magnification. The features included pores of different types, organic material, peloid-matrix contacts, pyrite, carbonate grains, forams, skeletal debris, and clays. Many of these features were imaged at different magnification to give context and document each occurrence.
Pore analysis and quantification was done using the software program Avizo™ Fire. The program allows segmentation and quantification of pore, organic material, and matrix material (Figure 14). All images were processed using various combinations of smoothing filters including one or two Gaussian smoothing filters, as well as a Non-Local Means filter. Contrast and brightness were also adjusted to optimize image resolution. Using the threshold tool, as well as drawing tools, individual objects were identified. Avizo™ was also used to compute shape (elongation) and size (equivalent circular diameter) of all objects segmented in an image based on object parameters such as length, width, and area. This quantitative data allowed for size, shape, and area percent analysis of all objects. These could then be converted to image porosity and image total organic carbon (TOC). These measurements also allowed for analysis of pores and organic material between different lithologies, facies types, and thermal maturities.
Figure 14. A) Backscattered electron image of Burbach 7169.5 microfacies 3) that contains only mineral pores. B) Same image as in A, but segmented for mineral pores (blue). C) Backscattered electron image of Aristocrat 7140 (microfacies 2) that contains mineral pores, organic matter, and porosity in organic matter D) Same image as in C, but segmented for mineral pores (blue), organic material (green), and organic matter pores (yellow).
Chapter 3- Sample Characterization

Core Macrofacies

Sedimentary structures and color were the primary attributes used to define facies at the core scale. The core macrofacies included 1) laminated marl, 2) bioturbated marl, 3) laminated chalk, 4) bioturbated chalk, and 5) structureless chalk (Table 2). The core macrofacies occurred throughout all four cores and in no apparent pattern and at no regular spacing or thickness. Macrofacies designation of all samples is given in Appendix 1.

Thin-Section Microfacies

Thin-section microfacies were distinguished by four major features: 1) presence and abundance of peloids, 2) presence of marl laminations, 3) amount of calcareous or detrital matrix material between peloids, and 4) skeletal debris and foram content. Six distinct microfacies were identified (Table 3). They are 1) calcareous peloidal grainstone (Figure 5a), 2) calcareous peloidal packstone (Figure 15a), 3) marl-laminated calcareous peloidal packstone (Figure 15b), 4) marl-laminated skeletal-rich peloidal packstone (Figure 15c), 5) peloidal wackestone (Figure 5b), 6) marl-laminated peloidal wackestone (Figure 5c). The marl laminae in microfacies 3, 4, and 6 are discrete millimeter to centimeter thick marls that are composed at least 5% of the thin section. A few thin sections that contained multiple microfacies were categorized by the most dominant facies. Microfacies categorization for each sample can be found in Appendix 1.
Figure 15. Photomicrographs of Niobrara Formation samples illustrating progressively increasing amounts of clay between chalk and marl end-members. A) Calcareous peloidal packstone (microfacies 2, Aristocrat 7140) with abundant forams. Both large and small peloids exist in dark matrix material. B) Marl-laminated calcareous peloidal packstone (microfacies 3) containing both gra and black, compacted peloids with few foraminifera in a dark, laminated matrix (Gill 6752.1). Often contains dark, mari-rich crinkle laminae. C) Marl-laminated skeletal-rich peloidal packstone (microfacies 4) with abundant forams and skeletal debris. Often contains dark, mari-rich crinkle laminae (Gill 6784.5). Blue epoxy fills cracks in the fissile marl.
<table>
<thead>
<tr>
<th>Macrofacies</th>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Laminated Marl</td>
<td>Dark brown or black clay-rich marl with evident laminations, seen because of different colored laminae, shell or skeletal lags possible</td>
</tr>
<tr>
<td>2</td>
<td>Bioturbated Marl</td>
<td>Dark brown or black clay-rich marl with light-colored filled burrows, lamination often destroyed by bioturbation</td>
</tr>
<tr>
<td>3</td>
<td>Laminated Chalk</td>
<td>Light brown or gray calcareous chalk with evident lamination, shell and skeletal lags possible</td>
</tr>
<tr>
<td>4</td>
<td>Bioturbated Chalk</td>
<td>Light brown or gray calcareous chalk with evident burrows, lamination often not present or destroyed by bioturbation</td>
</tr>
<tr>
<td>5</td>
<td>Structureless Chalk</td>
<td>Calcareous chalk without evidence of bioturbation nor lamination, peloids and sedimentary structures not apparent</td>
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</tbody>
</table>

Table 2. Description of core-scale macrofacies.

<table>
<thead>
<tr>
<th>Microfacies</th>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Calcareous peloidal grainstone</td>
<td>Very chalk-rich, peloids so compacted individual peloids not visible. Bioturbation evident in some samples.</td>
</tr>
<tr>
<td>2</td>
<td>Calcareous peloidal packstone</td>
<td>Chalk-rich, large and small peloids with dark matrix material between peloids.</td>
</tr>
<tr>
<td>3</td>
<td>Marl-laminated calcareous peloidal packstone</td>
<td>Mostly chalk-dominated, all samples contain &gt;5% dark marl laminae, crinkles often present.</td>
</tr>
<tr>
<td>4</td>
<td>Marl-laminated skeletal-rich peloidal packstone</td>
<td>Abundant forams, laminations of shell lags present, black crinkles possible with &gt;5% dark laminae.</td>
</tr>
<tr>
<td>5</td>
<td>Peloidal Wackestone</td>
<td>Well-formed compacted peloids with light-colored matrix.</td>
</tr>
<tr>
<td>6</td>
<td>Marl-laminated peloidal wackestone</td>
<td>Well-formed compacted peloids with light-colored matrix, containing ~5% marl laminae.</td>
</tr>
</tbody>
</table>

Table 3. Description of thin-section scale microfacies.
**Geochemical Facies**

Calcium to aluminum ratio (Ca/Al) distinguishes lithology on a finer scale than visual core interpretation. Lithologies derived from Ca/Al ratios include chalk (~93-85% Ca), marly chalk (~85-60% Ca), marl (~60-30% Ca), and marly shale (<30% Ca) (after Longman et al., 1998). Geochemically defined lithologies for the 54 samples were chalk (n=15), marly chalk (n=24), marl (n=12), and marly shale (n=3; Figure 16). Neither end member, a pure chalk (100-95% Ca) nor a pure shale (5-0% Ca) were sampled in this study.

Samples were also examined using copper (Cu), zinc (Zn), vanadium (V), and molybdenum (Mo) (Figure 17). Cu and Zn are proxies for paleonutrient levels whereas V and Mo are proxies for benthic redox in bottom water and pore water at time of lithification (Piper, 1994; Ratcliffe et al., 2012; Sageman et al., 2003). Populations consisted of 1) a low range of values for Zn EF but a greater range of Mo EF values, and 2) a low range Mo EF values but a greater range of Zn EF values (Figure 17). These populations may represent two different redox conditions in Niobrara seas and pore waters when the unit was being deposited.

**Geophysical Log Attributes**

Samples were collected from a range of gamma-ray and density porosity values. The most chalk-rich core microfacies (microfacies 1) has a slightly lower gamma-ray signal and slightly higher porosity than the more marl-rich microfacies (microfacies 6; Figure 18). The intermediate microfacies do not reflect the same trends. The poor correlations between borehole log data and microfacies is interpreted to reflect differences in the scales of investigation. Borehole logs average rock properties over 6-12 inches, which means logs aggregate multiple microfacies. In contrast, thin section are of a smaller scale (1-2 inches) and average less rock
Figure 16. Percent Ca versus percent Al for all 54 core samples. Cut-offs for lithologies after Longman et al. (1998). Blue diamonds represent all data, red dots indicate group of samples for FIB/SEM analysis.
Figure 17. Cross plot of molybdenum and zinc enrichment factors as proxies for benthic redox (Mo EF) and paleonutrient levels (Zn EF) defines three populations: low, intermediate, and high Zn/Mo EF. Blue diamonds indicate all samples, red dots indicate samples for FIB/SEM analysis.
Figure 18. Cross-plot of geophysical properties, gamma-ray versus density porosity for all microfacies of the 54 samples analyzed. This shows little correlation between the microfacies, though the most chalk-rich (microfacies 1) has slightly higher porosity and lower gamma-ray values than the most marl-rich samples (microfacies 6). FIB-SEM samples are indicated in red.
heterogeneity. The highly intercalated chalk and marl creates variable log signatures that do not necessarily represent the sampled piece of rock. Thus, geophysical log properties were not considered in relation to the investigated pore networks.

**FIB-SEM Sample Characteristics**

High grading of samples for FIB-SEM analysis meant trying to simultaneously insure coverage of varied lithologies (Figure 16), macro- and microfacies (Tables 2, 3), varied nutrient and redox signals (Figure 17), and the range of thermal histories across the study area (Figure 3). A sub-set of nine samples were ultimately selected that captured most variability. Two samples from each well were selected, with one sample chosen from the primary landing zone (B Chalk) and the other from the overlying A Marl. This covered variability between lithofacies (chalk and marl), as well as between wells. The ninth sample was a very marl-rich sample chosen from the C Chalk (Gill 6819). These samples are indicated on Figures 16-18 by red symbols. Object attributes for each field of view from all samples are reported in Appendix 2.
Chapter 4- Results

**Organic Petrography**

Fluorescent microscopy reveal two types of organic matter (OM): 1) morphologically indistinct and finely disseminated OM throughout a thin section (Figure 19A), and 2) thick (0.25 to 0.75 µm), crinkled and discontinuous laminae of OM (Figure 19B). The latter is presumably organic macerals, with the thinnest examples probably being crushed algal cysts. Both types of OM were observed in most of the 18 thin sections examined by fluorescent microscopy, most often within the matrix of a sample (i.e., not in peloids). Black and thin (typically < 5 mm) crinkled marl laminae within chalky microfacies were observed to contain a disproportionally large amount of the OM laminae (Figure 20). Multiple colors of fluorescence were noted but no effort was made to relate color and intensity to OM type and thermal maturity (e.g., Suárez-Ruiz, 2012).

Elemental maps of carbon (C) proved more informative as to the distribution of OM. The most common occurrence of carbon is as finely disseminated organic matter within peloids (Figure 21). This type of carbon is found in all microfacies, however, not all peloids contain carbon. Both circular brown and elongate black peloids can contain carbon, yet when both are present the carbon seems to be preferentially concentrated in the blackish peloids more so than brown peloids (Figure 21). The carbon contained within peloids is thought to be migrated hydrocarbon, implying peloids contained an adequate pore network for hydrocarbon migration and storage.
Figure 19. UV fluorescence photomicrographs (left) and plane light photomicrographs (right) of the same field of view. A) Dispersed organic material (orange blebs) between peloids throughout matrix of sample (Gill 6860.5), B) Crinkled organic material, thought to be crushed algal cysts with some dispersed organic material (orange blebs) nearby in the
Figure 20. Paired UV Fluorescence and plane light photomicrograph of crinkled organic material (orange blebs, white arrows) within dark black laminae (outlined by thin white lines) within microfacies 3. These black, marly laminae contain a disproportionately large fraction of the organic material. Burbach 7169.5, B Chalk. Scale bar is 4 μm.
Figure 21. Paired elemental maps of carbon (left) and corresponding plane light photomicrographs (right). Both sets of images demonstrate the abundance of carbon (whiter material) within peloids and paucity of carbon in matrix between peloids. White arrows denote black peloids that have an abundance of carbon and yellow arrows indicate brown peloids that have a minimal amount, if any, carbon. A) Microfacies 5, A Marl), Aristocrat 7110.5. B) Microfacies 2, A Marl), Timbro 5675.6.
The carbon maps also show that lithology impacts the nature of organic carbon and its distribution in the Niobrara samples. Outside of the peloids, very little if any carbon was noted in the chalkiest microfacies and laminae (Figures 22, 23). In contrast, marl microfacies contain elongate carbon features (Figure 22C), which are interpreted to be compacted algal cysts and other types of original organic macerals. That is, this type of carbon is interpreted to be primary and emplaced during deposition of the laminae. This type of carbon almost exclusively occurs within siliciclastic-rich marl laminae.

**Millimeter-scale Lithologic Variability**

The elemental mapping of calcium (Ca), silica (Si), and aluminum (Al) revealed that all peloids are almost exclusively calcite, regardless of lithology and matrix mineralogy (Figures 22, 23). The mineralogical purity of peloids suggests they were not formed on the seafloor from mixed mineralogies in the sediments. Either peloids formed in the water column by organisms that exclusively fed on coccolithophores or the alumino-silicates were added to the sediment after formation of peloids by benthic organisms. Both scenarios imply episodic clastic influx and homogenization of the mixed sediments by bioturbation or bottom currents after peloid formation.

Mineralogy outside peloids is quite variable. Marl-rich microfacies (Figure 23A) contain a much larger quantity of quartz and alumino-silicates and much less calcite than chalky microfacies (Figure 23B). The chalkiest samples contain the highest amounts of Ca in their matrix, with alumino-silicates and quartz being minor components (Figure 23B). Alumino-silicates in all samples include rectangular-shaped feldspar crystals, authigenic clay in
Figure 22. Elemental map (A), thin section photomicrograph (B), and carbon map (C) of alternating chalk (blue in A, brown in B) and compacted marl laminae of a microfacies 3 sample (Burbach 7177.3, C Chalk). A) Elemental map shows that the marls’ matrix contains quartz (red), Al-silicates (orange, yellows, and greenish yellows), and minor calcite (blue). The chalk lamina are dominated by calcite (blue) with trace amounts of Al-silicates. Pyrite (black) is present throughout the sample. B) The marl laminae are black and crinkled. Foraminifera, with their interparticle pores filled with calcite, are the large white objects. C) Carbon (white) is primarily elongate crushed algal cysts within the crinkled marl laminae, however diffuse carbon also exists within the peloids in the chalk lamina. The organic material in the marls is interpreted to be detrital whereas the carbon in the peloids is interpreted to be residual migrated hydrocarbon. Scale bar in A is 300 μm.
Figure 23. Paired elemental maps (left) and thin section photomicrographs (right) illustrating the distribution and abundance of silica and Al-silicates in the matrix of A) a marly microfacies 5 sample (Aristocrat 7110.5, A Marl) and B) chalky microfacies 2 sample (Burbach 7183.5, B Chalk). Colors in the elemental maps indicate quartz (red), Al-silicates (orange, yellows, and greenish yellows), calcite (blue), and pyrite or epoxy-filled cracks (black). In all elemental maps, elongate peloids are almost 100% calcite (arrows). Only small amounts of Si are included within a few peloids. In the corresponding thin section photomicrographs, note that both blackish and brown peloids have the same calcite-dominated mineralogy. Scale bars are 400 µm.
interparticle voids within forams, and dispersed clays. The dispersed clays are the mineral phases that increase the most with increasing marl content, as witnessed by the increase in yellows and greens in Figures 24A and 24B.

**Observed Pore System**

Two general constituents were identified within all samples: 1) peloid, and 2) matrix material. Peloids often contain the majority of porosity within a given sample. Pores associated with peloids are dominated by intercrystalline mineral-associated pores. As discussed above, an argument could be made for intraparticle classification of these pores since they are within peloid grains, however on the scale of investigation in this study, classification as intercrystalline pores is more applicable because they occur between calcite crystals. These pores are often angular, sharp edged, and display calcite crystal terminations protruding into void space (Figure 24). This pore type is the most abundant throughout almost all of the samples, and especially within peloids.

Other, less abundant, pore types also occur. Porosity associated with clay particles was noted in many matrix samples. Clay-associated pores appeared to form between authigenic, void-filling clay minerals (Figure 25) that occur in the matrix of non-chalk microfacies. Minor amounts of small interparticle porosity was rarely observed between alumino-silicates and calcite in the marliest of matrices (Figure 25). Porosity was also noted between individual pyrite crystals of pyrite framboids (Figure 26). This type of porosity was never observed to be pervasive throughout all framboids within the same sample, and not all framboids exhibited porosity. Nonetheless, the fact that pyrite is common within the matrix of most samples means that trace
Figure 24. Backscattered electron images of intercrystalline mineral pores within peloids of A) Burbach 7169.5 (A Marl) and B) Aristocrat 7110.5 (A Marl). Nearly all pores occur between crystals of calcite with a very small amount being intraparticle pores within skeletal grains (black arrows), remnants of interparticle pores between detrital skeletal grains (yellow arrows), or an intracrystalline pore (red arrow). Pores are not uniform in color due to pore-backs or mineral grains protruding into void spaces (white arrows). Intercrystalline pores vary in size and are mostly angular. Growth of calcite cements evidenced by rhombic crystal terminations into pores, which occludes porosity.
Figure 25. Backscattered electron image showing an example of interparticle clay pores in the matrix of a microfacies 2 sample (Aristocrat 7140, B Chalk). Pores exist between individual clay mineral grains (black arrows). Pores are elongate and have some clay bridges within the void space (white arrows). The clay particles appear to grow authigenically within former interparticle pores, as the clays are not highly compacted. This pore type has been grouped with mineral pores. Other pore types are intercrystalline (e.g., lower right, yellow arrows) and remnants of other interparticle pores above the clay-related pores.
Figure 26. Backscattered electron image showing examples of intraparticle porosity associated with pyrite (bright white masses) in the matrix of a microfacies 2 sample (Aristocrat 7140, B Chalk). Pyrite occurs as framboids with large crystals (middle right), framboids with small crystals (top left), and as small and isolated individual pyrite crystals (cubic shapes) or framboids (circular shapes) throughout the image. Small pores exist within the large pyrite framboid between individual pyrite crystals (yellow arrows), however some of the void space between the pyrite crystals in that large framboid have filled with matrix material or organic material. Outside of the framboids, intercrystalline pores (angular black objects) between crystals of calcite dominate.
amounts of matrix porosity are associated with pyrite. Finally, intraparticle porosity within bioclasts was noted. This intraparticle porosity was found in association with the discs of coccolithophores, spicules (Figure 24, black arrows), and within foram tests. The latter were never observed to be completely open pores, rather tests were filled with authigenic calcite and less commonly clay (Figure 27). Minor, unconnected micro-porosity sometimes exists between crystal terminations within that cement infill. It was rarely noted and its paucity and isolation suggests it does not contribute greatly to the overall porosity system. Collectively, these mineral-associated pore types are hereafter termed mineral porosity. Overall, mineral pores were the most abundant pore type within all samples.

The Niobrara Formation has undergone significant amounts of diagenesis in the form of compaction, pressure-solution, and the subsequent reprecipitation of the pressure-solved calcite (Scholle, 1977; Pollastro and Martinez, 1985; Scholle and Pollastro, 1985). Reprecipitation of pressure-solved calcite formed cements and overgrowths on mineral grains and in pores, and overprinted original skeletal grains, including the individual crystals of coccoliths. The pressure-solution and reprecipitation occluded porosity and converted the original interparticle pores to the observed intercrystalline network. In the process, pore sizes were reduced. However, no evidence of complete porosity loss due to recrystallization was found, as all samples exhibited some amount of intercrystalline pores associated with the calcite in peloids.

A portion of open mineral pores are occluded or partially occluded by organic material (OM). The OM occurs most often within former mineral pores as evidenced by the organic matter’s angular, non-elongate nature, which appears very similar in size and shape to open mineral pores (Figure 28). The angularity arises from mineral crystals that terminate into the OM, a feature indicating the crystal was originally growing into an open pore prior to the OM
Figure 27. Backscattered electron image of a large foraminifer (outlined by white line) that is almost completely filled with calcite (Gill 6784.5, B Marl). Two intraparticle pore types exist within the foram: 1) large micrometer scale mineral pores (blue arrows), and 2) nanometer scale mineral pores (within yellow circles). These pores likely play very little role in the overall pore network because both pores types are isolated and unconnected to the overall pore network within the sample. Pores in that overall network are seen outside of the foraminifer are mineral pores, and include mineral pores filled with residual hydrocarbon (white arrows), elongate clay pores (black arrows), and pyrite-associated porosity (yellow arrows).
Figure 28. Backscattered electron images of mineral pores that are all filled with residual hydrocarbon (RHC). Both fields of view are of peloids. Filled pores clearly have the angularity and low elongations of mineral pores (compare to intercrystalline mineral pores show in Figures 29 and 31). The RHC is interpreted to have migrated into the intercrystalline pore network. OM pores are absent or very minor within the organic material. Image A is from Timbro 5742 (B Chalk), which is low thermal maturity, and image B is from Aristocrat 7140 (B Chalk), which is high thermal maturity (Figure 3). In spite of the thermal maturity differences, there is little visible difference in organic material morphology and OM porosity development.
invasion. The lack of elongation to this type of OM also argues against it being organic macerals deposited as sedimentary material. Gray-scale analysis in backscattered electron photomicrographs was the main criteria for distinguishing between open mineral pores and OM in former mineral pores. The OM is slightly lighter gray (less black) and more consistently one shade of gray than an open pore.

This pore-filling organic material is known to now be immobile because it remained after samples were subjected to Soxhelet-style hydrocarbon extraction. Since it currently fills mineral pores, it had to migrate into the intercrystalline pore system. Organic material that fills mineral pores is possibly pyrobitumen or some other type of now-immobile hydrocarbon, though no attempt was made to identify the exact type. This migrated, pore-filling OM is herein referred to as residual hydrocarbon (RHC).

Most RHC contains small- to medium-sized pores. They are generally round or subround bubble-shaped pores in the solid organic material (Figure 29). Pores occur as singular bubble pores, multiple unconnected bubble pores, and as a network of interconnected small bubble pores (Figure 30A, B). These pore types are herein referred to as OM porosity. In some cases, the OM pores within the RHC were crack-like, occurring between the organic material and mineral matrix (Figure 30C). Morphologically this is the same as the organic-mineral interface pore type of Loucks et al. (2010). Loucks et al. (2010) and Dahl et al. (2012) suggested that these crack-like pores may be due to desiccation, depressurization, or shrinkage causing delamination of the OM from the mineral host. All types of OM pores were noted throughout all wells and no one OM pore type was exclusive to one well. This indicates that the various OM pores are independent of thermal maturity.
Figure 29. Backscattered electron images of large OM pores within peloids. A) Field of view from Gill 6739.3 (A Marl) shows many relatively large (up to 1 micron in diameter) OM pores (white arrows). B) Field of view from Aristocrat 7140 (B Chalk) with only a few large OM pores (≤ 0.6 micron in diameter) with smaller OM pores throughout (black arrows).
Figure 30. Backscattered electron images of OM pores, all in residual hydrocarbons within peloids. A) Individual round to sub-rounded OM pores of large (black arrow) and small (white arrow) sizes (Gill 6754.7, B Chalk). B) Network of round pores (Timbro 5675.6, A Marl). C) Crack pores along organic-mineral contacts (white arrow; Timbro 5742, B Chalk). Note various scales of each image and heterogeneity of OM pore shapes and sizes.
Residual hydrocarbon in former mineral pores without any OM pores was noted within some samples and occasionally within samples that contained nearby RHC with OM pores (Figure 31). In particular, RHC within matrix were noted to be less likely to contain OM pores relative to RHC in peloids. Why a difference in OM pore development exists from one mass of RHC to another within the same sample is unknown. Curtis et al. (2012) suggested it could be due to differences in organic material or the impact of catagenesis. In the Niobrara, it is hard to imagine how different types of bitumen could have separately invaded pores just microns to millimeters apart. Catagenesis might be a more feasible explanation if one mass of OM is connected to open pore space that allows hydrocarbons to escape and yield OM pores, while another mass is isolated and hydrocarbons do not evolve as readily.

A second type of organic material exists outside the mineral pore system. This is the detrital organic matter (Figure 32) that has an elongate and sinuous morphology that is much different than the more equant and angular morphology of the residual migrated hydrocarbon that fills mineral pores (e.g., Figure 28). All examples of detrital OM were contained within matrix material. Both types of OM, those pores filled with RHC and detrital organics, were segmented as OM in this study. Attempts were made to divide detrital organics and RHC based on object size. Those objects identified as organics with an equivalent circular diameter of greater than 1500 nm were thought to be detrital, however since the two were not segmented separately, some OM may not have been correctly identified, particularly those detrital organics that are not large or were intersected at an oblique angle by the FIB. Detrital organic matter rarely contains OM pores, however it was interpreted to exist in a matrix field of view from Aristocrat 7110.5. The OM pores in detrital organics were similar to those noted in organic material interpreted as RHC. The OM pores were small, tens of nanometer-scale bubbles that
Figure 31. Backscattered electron image of various types of residual hydrocarbons within a peloid (Aristocrat 4140, B Chalk). Porous (white arrow) and non-porous (black arrow) organic material are present only a few microns from each other.
were not connected to each other. Only a few small OM pores were noted throughout the detrital organic material and none was well-connected with the mineral pores in 2D analysis (Figure 32).

The two large milled transects (~350 µm and ~200 µm in length) illustrate the differences in pore systems between matrix and peloids. These two fields of view indicate that the porosity of peloids and matrix are extremely different and heterogeneous (Figures 33, 34). Whereas peloids may have better than 8% porosity, the adjacent matrix can have less than 1% porosity. Pore morphology within matrix material is also much different than pores within peloids. Most matrix pores are more elongate and smaller than pores in peloids. Most of the pores in matrix material are associated with individual calcite crystals, clay minerals, or other detrital minerals. Large intercrystalline networks, like those found in the calcitic peloids are not common in matrix. Both long transects show that matrix contains clay porosity, where authigenic clay may have filled open pores but did not occlude all porosity (Figure 25).

Object Analyses

Abundance, shape, and size parameters were utilized to analyze mineral pores, OM pores, and organic material. Abundance is the relative proportion of a particular feature across an entire imaged field of view (FOV). Elongation is a shape attribute computed for each individual object and is the shortest distance across an object divided by the longest distance. Elongation is an expression of roundness or lack thereof, as an elongation value of 1 indicates a perfect sphere and a value approaching 0 indicates a very linear shape. Equivalent circular diameter (ECD) is the proxy for size. ECD is computed from:

\[ 2\sqrt{\frac{\text{AREA}}{\pi}} \]
Figure 32. Backscattered electron image of detrital organic material in the matrix of a microfacies 2 sample (Aristocrat 7140, B Chalk). The detrital OM are the dark objects. The piece of organic matter to the left is elongate and sinuous whereas the piece to the right is circular (center of image). The sinuous piece has no apparent internal OM pores, whereas the circular piece appears to be riddled with small circular OM pores.
Figure 33. Long wall (~350 µm) FIB-SEM photomosaic across multiple peloids (P) and intervening matrix (M) (Aristocrat 7140, B Chalk zone). Scale bar is applicable to all images. Images tie at B and C. Dashed white lines outline interpreted margins of peloids (P1, P2, P3, P4). Peloid 1 and 3 contain open mineral pores, residual hydrocarbon-filled pores (white arrows), some of which exhibit OM pores. Peloid 4 only contains open mineral pores. Detrital organic matter (black arrows) is mainly in the matrix. Overall, the large transect indicates extensive heterogeneity in pore abundance at the tens of micron scale and poor connectivity of pores through the matrix.
Figure 34. Long wall FIB-SEM photomosaic (Gill 6819) of ~200 um exposure. Scale is the same through all images. Yellow lines indicate where images fit together. Long wall exposes multiple constituents, including peloids and matrix material. A variety of porosity networks are present within this sample. White circles indicates peloids contain both open mineral pores and RHC-filled pores (white arrows), some of which exhibit OM pores. Yellow circles denote less-porous matrix material. Boundaries between peloid and matrix material is very difficult to identify in this sample. There are some indicators of matrix material, such as pyrite and clay porosity that does not appear within peloids in other samples. Skeletal debris is noted throughout the sample, not just within peloids. White dashed line indicates clear difference in gray scale (mineralogy?) and a likely boundary between peloid and matrix material. Due to the large number of mineral pores filled with RHC in this sample and the lack of connectivity, it could be hypothesized that this sample underwent greater diagenesis resulting in porosity reduction, as the filled mineral pores do not appear to be as well-connected as in Figure 33.
and corresponds to the diameter of a circle with the same area as the measured object. The larger the object, the larger the ECD. With these three parameters, objects of all different shapes and sizes could be compared by standardized metrics, regardless of their different morphologies. The varied size, shape and abundance attributes of mineral pores, OM pores, and organic material are first described below, then their parameters are compared and contrasted as a function of lithology, microfacies, geochemical proxies, and thermal maturity.

Abundance of mineral pores, OM pores, and organics varies among samples. Coarse-(magnification ≤ 6,500x) and fine-scale (magnification ≥ 10,000x) analyses yielded different results. Both scales captured larger objects, meaning nearly all mineral pores and all organic material. The fine-scale analysis simply captures fewer mineral pores and OM objects, but not appreciably smaller ones (Figure 35). Thus the coarse scale analysis is an accurate measure of the mineral pores and OM. However, OM pores occur across multiple scales and the coarse analysis only captured the larger OM pores. Coarse-scale analysis thus underestimates total OM porosity. In contrast, the small-scale analysis, which targeted OM, captured the true abundance of small and large OM pores within small masses of OM, but understates the abundance of mineral pores and overstates the abundance of organics. Figure 36 illustrates the differences between imaging at both scales for pores, which have been broken out for mineral pores and OM pores. Mineral porosity ranges from 2.5% to 5.2% in coarse analysis and 2.0% to 3.6% in fine analysis. OM porosity ranges from 0.1% to 0.2% in coarse analysis and 0.6% to 1.1% in fine analysis. A similar pattern occurs when comparing percentages of OM between coarse and fine analyses (Figure 37). OM content ranges from 0.5% to 4.3% in coarse analysis and 4.0% to 10.2% in fine analysis.
A

**ECD Mineral Pores, Coarse Scale**

<table>
<thead>
<tr>
<th>Material</th>
<th>Median Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aristocrat</td>
<td>268.7 nm</td>
</tr>
<tr>
<td>Gill</td>
<td>208.1 nm</td>
</tr>
<tr>
<td>Timbo</td>
<td>190.3 nm</td>
</tr>
<tr>
<td>Burbach</td>
<td>205.6 nm</td>
</tr>
</tbody>
</table>

B

**ECD Mineral Pores, Fine Scale**

<table>
<thead>
<tr>
<th>Material</th>
<th>Median Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aristocrat</td>
<td>102.3 nm</td>
</tr>
<tr>
<td>Gill</td>
<td>104.5 nm</td>
</tr>
<tr>
<td>Timbro</td>
<td>112.3 nm</td>
</tr>
<tr>
<td>Burbach</td>
<td>82.2 nm</td>
</tr>
</tbody>
</table>
Figure 35. Histograms of equivalent circular diameter (ECD) versus pore type and as a function of the scale of the imagery (e.g., coarse- vs fine-scales). All histograms are based on all fields of view collected in all samples in all wells. A, C) Histograms of mineral and OM pores in coarse-scale images, respectively. B and D) Histograms of mineral and OM pores based on fine-scale images, respectively. Fine-scale imagery targeted OM pores, thus large mineral pores are under-represented in the fine-scale data set, which explains the difference in median mineral pore ECD values (A vs. C). More importantly, the fine-scale analysis of mineral pores shows very few pores smaller than the resolution of the coarse-scale analysis (i.e., less than the 25-50 nm class), suggesting the coarse-scale analysis captures the vast majority of mineral pore sizes. In contrast, the coarse-scale images do not capture the small OM pores, which are very abundant (B vs. D). The coarse-scale images are thus biased to large OM pores, whereas the fine-scale images are not. The fine-scale images are thus the more accurate measure of ECD for OM pores. Median values are arranged in vertical sequence from the highest thermal maturity well to the lowest (Figure 3) and those values indicate a slight increase in ECD with higher thermal maturity for both mineral pores (A) and OM pores (D).
Figure 36. Bar graphs showing percentages of mineral pores (blue) and OM pores (orange) in the coarse- and fine-scale images. Average percentage of each pore type in each well is shown between the graphs. Coarse image analysis does not allow for accurate measurement of OM pores, while fine image analysis does not accurately capture mineral pores.
Figure 37. Bar graphs showing percentages of total organic matter (gray, detrital OM and residual hydrocarbons) and OM pores (orange) in the coarse- and fine-scale images. Average percentage of total organic matter and OM porosity in each well are shown between the two graphs.
Combining the two scales of analysis yields the most accurate estimates of the true abundance of OM porosity. The key is computing the percentage of the original amount of OM now represented by porosity at the fine scale, and then using that percentage and the total amount of original OM at the coarse scale to compute an estimate of total OM porosity (small and large pores) across coarse fields of view (Table 4). The results combine the two scales of imagery and indicate a wide range of average calculated OM porosity values, from 0.6% (Aristocrat 7140) to 7.0% (Gill 6739.3). In some cases, samples contained up to seven FOVs with OM porosity while others did not contain any OM pores.

ECD results are presented as a function of cumulative area percent for mineral pores at the coarse scale (Figure 38A), OM pores in the fine-scale analysis (Figure 38B), and for organic material in the coarse-scale analysis (Figure 38C). As argued above, the coarse scale adequately captures the mineral pores and OM as they both tend to be relatively large in all occurrences whereas the fine-scale best represents the OM pores as they have both large and small pore spaces. Matrix samples have mostly smaller mineral pores relative to peloids. ECD of mineral pores in matrix are typically under 600 nm while they range to 1,800 nm in peloids. Peloids also may have a few very large mineral pores that make up 10-20% of total mineral porosity (Figure 38A). In fact, all samples have at least one mineral pore that accounts for 8-11% of total porosity. Mineral pores tend to be larger than OM pores, with the largest mineral pores up to twice the ECD as the largest OM pores. High thermal maturity samples (Aristocrat and Gill) have generally larger OM pores than Timbro and Burbach samples (Figure 38B). Also, the largest organic material contributes a larger percent of cumulative area than the largest mineral pores. Lastly, mineral pores are slightly smaller and more similar in size to one another (Figure 38A) than organic material (Figure 38C).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Microfacies</th>
<th>Calculated Total OM Porosity (%) in Separate Field of Views</th>
<th>Average of Calculated OM Porosity (%) for the entire samples</th>
<th>Average TOC for all Fields of View</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aristocrat 7110.5, A Marl zone</td>
<td>5</td>
<td>4.1, 0.9, 0.5, 0.0</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Aristocrat 7140, B Chalk zone</td>
<td>2</td>
<td>0.0, 0.0, 0.9, 0.8, 0.9, 0.9</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Gill 6739.3, A Marl zone</td>
<td>5</td>
<td>6.8, 7.1, 7.2</td>
<td>7</td>
<td>7.1</td>
</tr>
<tr>
<td>Gill 6754.7, B Chalk zone</td>
<td>2</td>
<td>0.7, 0.9, 0.9</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Gill 6819, Crinkle</td>
<td>36</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Timbro 5675.6, A Marl zone</td>
<td>2</td>
<td>3.7, 3.8, 3.7, 2.4</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Timbro 5742, B Chalk zone</td>
<td>2</td>
<td>1.3, 9.6</td>
<td>5.5</td>
<td>5.3</td>
</tr>
<tr>
<td>Burbach 7169.5, A Marl zone</td>
<td>2</td>
<td>1.6, 1.8, 1.8, 0.0, 0.7</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Burbach 7183.5, B Chalk zone</td>
<td>2</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4. OM porosity utilizing both coarse and fine FOVs to calculate total OM porosity for each sample.
Figure 38. Cumulative area (percent) plots for equivalent circular diameter (ECD) classes. Each line represents one field of view. A) Mineral pores in coarse scale analysis, B) OM pores in fine scale analysis, and C) all organic material in coarse scale analysis. All FOVs were plotted for all four wells. In both A and B, the majority of mineral pores and OM pores in the FOV are small (< 500 nm), however a few very large mineral pores (> 10000 nm) and OM pores (>500 nm) exist. Mineral pore FOVs do not seem to differ due to thermal maturity. OM pores in the high thermal maturity wells are generally larger and more heterogeneous in size (Aristocrat and Gill), whereas all OM pores are small in the low thermal maturity wells.
Many FOVs contain large organic matter objects (ECD > 1500nm), whereas most mineral pores are smaller (ECD < 1500 nm).

In contrast to ECD, elongation does not vary between objects. Organic material (< 1500 nm ECD), mineral pores, and OM pores all have very similar distribution of elongation values (Figure 39). Median elongation values among all three types of features measured within each well range from 0.49 (Burbach OM) to 0.63 (Timbro OM pores). Generally, median values did not vary significantly, though the number of individual objects analyzed is very different between the four wells and among pores and organics, as mineral pores are the overwhelming majority of objects analyzed.

When size and shape are considered together there is little difference between the four wells. Mineral pores with large ECD (>1000 nm) tend to have 0.2-0.8 elongation values and in general, the larger the mineral pores, the closer the elongation value to 0.5 (Figure 40A). As noted previously, the more thermally mature wells (Aristocrat and Gill) exhibit slightly larger but not necessarily more elongate OM pores (Figure 40B).

Mineral pores and pores filled with RHC are quite different in their shapes (Figure 41). Objects identified as organic-filled pores have considerably larger median ECDs (300-700+ nm; Figure 41C) than mineral pores (150-375 nm; Figure 41A). Only a slight overlap exists between the two types of objects and their difference in size is statistically significant (Mann–Whitney $U = 15$, $n_1 = 21$, $n_2 = 27$, $z = 5.48$, $P < 0.0001$ two-tailed). This means that mineral pores filled with RHC are roughly double the size of open mineral pores. Elongations of the two
Figure 39. Histograms of elongation for all objects identified in all wells. Median elongation values posted next to well names in the legends (red= Aristocrat, orange= Gill, green= Timbro, blue= Burbach). A) Elongation of all mineral pores by well in coarse-scale analysis. B) Elongation of all organic material in coarse-scale analysis. C) Elongation of all OM pores in fine-scale analysis. Note different frequency scales due to large differences in number of observed objects.
Figure 40. Median field of view (FOV) elongation versus median FOV equivalent circular diameter (ECD) for mineral pores in coarse-scale analysis and OM pores in fine-scale analysis. A) Mineral pores from coarse-scale analysis. B) OM pores from fine-scale analysis. OM pores’ ECDs are generally smaller than mineral pores’ ECDs, indicating OM pores are smaller than mineral pores. Most OM pores occur within residual hydrocarbon that has migrated into former mineral pores. Median elongations of OM pores are slightly greater than mineral pores. Median values of all samples overlap.
Figure 41. Median elongation versus median equivalent circular diameter (ECD) for all objects in all fields of view (FOV). A) Mineral pores in coarse-scale analysis. Note the large range of ECD medians. B) Organic material in coarse-scale analysis. Note large range of median ECD values. C) OM pores in fine-scale analysis. Note the narrow range of ECD values and slightly larger range of elongation values. Median elongation and ERD values for each lithology are shown by diamonds and indicate slight differences in elongation and ECD. Organics (B) are roughly double the size of mineral pores (A), suggesting a major difference between organic-filled pores and open mineral pores.
types of features, however, are not different and range from ~0.5 to ~0.65 (two organic samples above 0.7; Mann–Whitney $U = 357, n_1 = 21, n_2 = 27, z = 1.527, P < 0.130$ two-tailed).

**Measured Rock Attributes Related to Pores and Organic Matter: Lithology, Geochemistry, Microfacies, and Thermal Maturity**

Abundance, shape, and size of pores and organic material has been compared for multiple measurable rock attributes. It does not seem that object abundance, shape, or size are dependent on lithology (Figure 41). A large range of mineral pore, OM pore, and organic material abundances and ECDs, and mineral pore and OM elongations are exhibited in each of the lithologic facies. There is a strong overlap in values for each metric and the Mann-Whitney test indicates that the lithologic population of median elongation values ($p < 0.048$) is marginally different while ECDs are not statistically different ($p < 0.810$). Median values of pore elongation for all lithologies ranged from 0.52-0.57 and ECD ranged from 182.9 nm (marl) to 259.6 nm (marly chalk). Slightly higher values were associated with chalk and marly chalk but the differences in median values do not seem to be well-supported by lithologic variability.

Mineral pores show no patterns in median elongation or median ECD as a function of geochemical facies (Figure 42). This is not surprising, as lithology and geochemistry are highly related in this study, as all chalks in this study are high Zn/Mo EF and all marls are low Zn/Mo EF (Figure 17). As object size and shape do not vary by lithology, nor should they vary by geochemical facies.

Only three microfacies are represented by the samples chosen for FIB-SEM analysis. The overlap between the three microfacies in both mineral pores and OM pores for median values of
Figure 42. Median FOV elongation and equivalent circular diameter plotted for high Zn/Mo EF and low Zn/Mo EF geochemical facies (Figure 17). A) All objects plotted for high and low Zn/Mo EF. Median values are plotted as circles. B) Same data as in A, but now distinguished by pore type.
elongation and ECD suggests little difference in these objects due to microfacies (Figure 43). Elongation does not seem to vary between the different microfacies with regards to mineral pores, organic material, or OM pores. A wide range of median ECDs exists between microfacies 2 and 5 with regards to organic material, though all microfacies 5 median values plot within the range of microfacies 5 values. A small number of laminated peloid packstone (microfacies 3) with >5% dark marl laminae were included, however the values are within the ranges of both microfacies 2 and 5 for all three features considered (Figure 43).

Thermal maturity may have an impact on certain rock attributes, however mineral pores are unaffected by differences in thermal maturity (Figure 40A). Histograms of mineral pore elongation (Figure 39) and ECDs (Figure 35) show no patterns as a function of thermal maturity, nor is there a thermal maturity trend in median mineral pore elongation and median mineral pore ECD (Figure 40A). Similarly, Figure 38C shows no trend in distribution of organic material ECD and there is no trend in OM elongation (Figure 39B).

Although OM pore abundance is not related to thermal maturity (Table 4), a number of lines of evidence suggest OM pore sizes are sensitive to thermal maturity. First, the fine-scale analysis does expose an increase in median ECD with increased thermal maturity (Figure-35). Median values for the Aristocrat (most mature) were nearly double (133.5 nm) that of less mature wells (Timbro= 61.0 nm, Burbach= 88.3 nm). Most convincingly, ECDs of OM pores as a function of cumulative area do indicate strong differences between highly thermally mature and less mature wells (Figure 38B). Low thermal maturity wells (Burbach and Timbro) are dominated by small OM pores under 400 nm ECD while high thermal maturity wells (Aristocrat and Gill) contain both small and large OM pores. The largest OM pores in high thermal maturity
Figure 43. Median equivalent circular diameter (ECD) versus median elongation as a function of microfacies for A) mineral pores (coarse-scale images), B) organic matter (coarse-scale images), and C) OM pores (fine-scale images). Data based on all fields of view from all samples analyzed. Data for mineral pores group very tightly suggesting little difference in mineral pores’ size and shape as a function of microfacies. Data for organic matter are limited to just two microfacies and show no difference in elongation as a function of microfacies. However, median ECD in microfacies 5 is much more variable than in microfacies 2. Data for OM pores shows a large amount of scatter but the scatter is independent of microfacies.
wells are 600-900 nm. Collectively, these data indicate that OM porosity enlargement is related to thermal maturity.
Chapter 5 - Discussion

Diagenetic Evolution of Mineral Pores

Many different pore types have been noted as contributors to overall porosity systems in unconventional reservoirs including intraparticle pores, clay pores, moldic pores, and fracture pores (Figures 10-13). Most of these pore types are present in the Niobrara Formation but are nowhere near as important as in other unconventional, and particularly shales. Instead, intercrystalline, mineral-associated interparticle pores dominate most samples due to the calcareous nature of the formation. This is particularly the case in peloid fields of view (FOV). The extensive diagenetic history of the Niobrara Formation has destroyed or modified many pores of various types due to compaction and dissolution/reprecipitation of calcite (Scholle, 1977; Pollastro and Martinez, 1985; Scholle and Pollastro, 1985). Crystal terminations protrude into voids creating angular pores, indicating that carbonate cements formed on the walls of former interparticle pores and partially occlude porosity. Cementation lead to overall reduction in pore size and impacted the shapes and abundance of mineral pores. In some FOVs, calcite crystals have grown together, partially destroying porosity and creating a solid, non-porous calcite mass in both matrix and peloids.

The Cretaceous Eagle Ford Formation, a highly productive unconventional reservoir along the Texas Gulf Coast, is the closest analog to the Niobrara, as both are chalks. Comparison of the pore systems in the two highlights the significance of diagenesis to the evolution of mineral pores in the Niobrara Formation. Pommer et al. (2013) documented the pore networks in the Eagle Ford and reported many of the same pore types and attributes documented herein for
the Niobrara. However, the Eagle Ford has substantial porosity between and within coccoliths and coccolithophore plates. Those detrital components are readily seen in imagery from Pommer et al. (2013), but were rarely imaged in the Niobrara. The Niobrara does not have the same diversity of pore types and overall has less porosity than the Eagle Ford. The average FOV porosity is ~4% (maximum 6%) in the Niobrara versus ~5% average (maximum 12.5%) in the Eagle Ford FIB-SEM imagery. These differences reflect the fact that the Niobrara has experienced more extensive compaction, pressure-solution and calcite recrystallization than is indicated by images of the Eagle Ford (Pommer et al., 2013). The interparticle mineral pores that prevail in the Eagle Ford, and other types of pores, have thus been reduced to the intercrystalline pores that dominate the Niobrara. The differential diagenesis between the two units highlights the importance of the calcite’s diagenetic history in the development of mineral pores in carbonate-dominated unconventional reservoirs.

**Organic Pores and Residual Hydrocarbon-filled Pores**

The presence of residual hydrocarbons (RHC) within pores, and the presence of OM pores within those RHC and detrital organic matter, are an important pore type in most North American and international unconventional reservoirs (Bai et al., 2013; Curtis et al., 2012; Loucks et al., 2012; Heath et al., 2011; Milliken and Reed, 2010; Curtis et al., 2010; Schieber, 2010; Milner et al., 2010). Three aspects of the RHC and their pores observed in the Niobrara Formation are worthy of discussion. (1) The size differences between the RHC-filled pores and open intercrystalline mineral pores. (2) Why some RHC have pores and others, often just
microns away, do not. (3) The variance in OM pore attributes as a function of thermal maturity. Each of these topics is considered in more detail below.

Size Differences in Mineral Pores versus Residual Hydrocarbon-filled Pores

Migrated RHC fills voids that are similar in shape to open mineral pores. Both exhibit connected angular morphologies between calcite crystals. The angularity defined by crystal terminations indicate growth of those crystals into open, or once open, pore space. This suggests that the RHC fills space that was once an open and well-connected portion of the mineral pore system. The filled and open pores, however, vary in size. Those pores filled with RHC tend to be substantially larger than the open mineral pores in the same samples and even FOVs (Figure 41). Multiple hypotheses may explain this occurrence. First, organic material-filled pores may have been enlarged by acid production associated with hydrocarbon generation. A pulse of acid immediately precedes hydrocarbon migration (Surdam et al., 1984). That could have enlarged pores just prior to hydrocarbon emplacement because of dissolution of carbonate material (Zuddas et al., 2003). Due to the size differences (Figure 41), the enlargement would have averaged many tens to even hundreds of nanometers, which means clearly corroded calcite crystal surfaces would have been seen in the FIB-SEM imagery. They were not, thus enlargement of the now hydrocarbon-filled pores by organic acid dissolution is rejected.

A second hypothesis is that an early phase of oil generation produced mobile hydrocarbons that filled void space between calcite crystals and skeletal grains before significant compaction could occur. The hydrocarbon would have acted to maintain pre-compaction pore size and shape. This hypothesis, however, can be rejected on two counts. First, mechanical
compaction in chalks is an early burial phenomena that is replaced at a few thousand feet of burial by pressure solution and concurrent calcite cementation (Scholle, 1977; Schmoker, 1984; Pollastro and Martinez, 1985; Scholle and Halley, 1985; Scholle and Pollastro, 1985). The cementation makes the rocks rigid, thus inhibiting further compaction. When mechanical compaction ceased in the Niobrara, the imagery of Scholle (1977), Pollastro and Martinez (1985), Scholle and Pollastro (1985) and the porosity with depth history of Schmoker (1984) suggest is was far more porous, and contained far larger pores than can be accounted for by the RHC-filled pores. Those residual hydrocarbons must have entered the rock long after mechanical compaction ceased.

Third, generation of gaseous hydrocarbon and OM pore development could have mechanically increased the size of pores filled with RHC (Dewhurst et al., 1999). Since there is no evidence of microfractures or deformation of the crystalline calcites around the pores, mechanical enlargement would have had to occur during a ductile phase of the formation’s diagenetic history. However, the abundance of calcite, and the presence of calcite cementation since early in the Niobrara’s burial history (Hattin, 1981; Pollastro and Scholle, 1986) argues against this hypothesis. That is, the calcite surrounding the now RHC was probably not particularly ductile when hydrocarbon migration occurred and therefore would not allow expansion of pores during further catagenesis.

Fourth, large residual hydrocarbon-filled pores could be larger than open mineral pores because the hydrocarbons coated pore surfaces and arrested the precipitation of calcite cements in the pores (Zuddas et al., 2003). Unfilled pores would have continued to grow smaller due to cementation and the differences in median sizes would have resulted. Due to the advanced nature of diagenesis and catagenesis in the Niobrara samples analyzed, there was no way to collect FIB-
SEM data to confirm this hypothesis. However, no observations were made that would negate the plausibility of this explanation.

A fifth and last explanation is that the RHC-filled pores represent the pores accessed by the largest pore throats, and thus they were filled with hydrocarbons when those hydrocarbons migrated. In contrast, the still open mineral pores were accessed by pore throats that were too small to allow hydrocarbon invasion at the time of migration. The size difference between the two sets of objects is thus the byproduct of capillary pressure effects at the time of hydrocarbon migration (Joe Beer, Encana Corp., personal communication, May 12, 2014). If this hypothesis is valid, it also means the still open mineral pores are connected by relatively small pore throats, which has implications to fluid migration during hydrocarbon production. As with hypothesis four, there is currently no data that allows the validity of this potential explanation to be evaluated.

**Micron-scale Heterogeneity in Presence of OM Pores**

Many FOVs of RHC from the four wells contain OM porosity; however, many FOVs also exhibit non-porous organic material. In some cases, porous and non-porous organic material can be found in the same FOV (Figure 31), indicating variability in OM pore generation. Fishman et al. (2012) suggested that this type of heterogeneity in OM porosity may be due to differences in organic material type, catagenetic impacts, and/or diagenetic effects. Applying their ideas to the heterogeneity in Niobrara OM porosity requires either different sources for the RHC that host the OM pores, or multiple influxes of hydrocarbons during catagenesis.
A variety of different sources are possible for the hydrocarbons within the Niobrara Formation. The RHC could be self-sourced from the Niobrara (Higley et al., 1995; Longman et al., 1995) or derived from the organic-bearing source rocks in the underlying Carlile, Greenhorn, Graneros, and Mowry sequence (Clayton and Swetland, 1980; Higley et al., 1995). Although self-sourcing is the generally accepted (Longman et al., 1995; Higley et al., 1995; Coskey, 2011), the variety of detrital organic matter found in the Niobrara (Clayton and Swetland, 1977; Kauffman, 1977; Hattin, 1981) could still mean different types of hydrocarbons evolved and migrated into different mineral pores. Whether externally or internally sourced, once the varied hydrocarbons migrated into the pores, subsequent catagenesis could yield varied OM pore generation due to chemical differences between the different hydrocarbons.

Alternately, OM pores in RHC may have been generated multiple times throughout the course of catagenesis (Jiang and Cheadle, 2012). If hydrocarbon migration is prolonged, then hydrocarbons could have migrated into pores, OM pores could form in those hydrocarbons, and then those OM pores could fill with new migrating hydrocarbons. Solid RHC would result where formerly porous RHC occurred. Multiple cycles of OM pore generation and fill would thus explain why some RHC does not contain OM porosity.

**Role of Thermal Maturity in OM Pore Generation**

All wells in this study exhibited some amount of OM porosity with only slight variation in OM pore morphology due to thermal maturity. Fishman et al. (2012), Curtis et al. (2012), and Jiang and Cheadle (2012) also reported no relationship between thermal maturity and the presence of OM pores in the Kimmeridge Clay Formation, Woodford Shale, and the Colorado
Group of the Western Canadian Sedimentary Basin, respectively. In those rocks, OM pores did not vary between immature (Ro<0.5%) to mature (Ro>1.3%) settings. These findings are consistent with the organically-lean Niobrara Formation, in that the Burbach well (oil generation; Ro=0.6%) contained similar abundances and types of OM pores to those in the Aristocrat well (dry gas generation; Ro=1.2%). Those prior works and this study thus suggest that thermal maturity is not the driver of OM pore development.

Yet thermal maturity must play a role as evidenced by the fact that OM pore size distributions in the Niobrara did vary with thermal maturity (Figures 35, 38). The Eagle Ford Formation is a good comparison to the Niobrara Formation, as carbonate and clay are the two major constituents in both formations. Total organic carbon is higher in the Eagle Ford, but both formations exhibit similar pore systems. Pommer et al. (2013) found that a greater amount of porosity can be attributed to OM pores in highly mature Eagle Ford wells (Ro=1.2-1.3%) relative to immature Eagle Ford wells (Ro=0.5%). Ozkan et al. (2013) corroborated that thermal maturity in the Eagle Ford has an impact on OM pore generation, as high thermal maturity samples have well-developed OM pores. The Niobrara Formation and the Eagle Ford Formation have different thermal histories, yet both are calcite-dominated, and differ from most other unconventional reservoirs in that regard. This suggests that their unique mineralogy, or the type of hydrocarbons generated in chalk systems (Type II-S) as opposed to shale systems (Type II), might be a key to the influence that thermal history has on OM pore generation. Such a hypothesis would require further testing.
Potential Impact of OM Pores on Hydrocarbon Migration and Storage

Residual hydrocarbon (RHC) are known to contain connected OM pores that range in scale from tens of nanometers to single microns in diameter, and likely contains single-digit nanometer- and picometer-scale pores below the resolution of this study (Curtis 2013; Loucks et al. 2012). Such a pore system could form a percolating network of nano-pores within a large portion of all organic material (Zhang et al., 2010). It can be hypothesized that a similar porosity network may exist within the RHC of the Niobrara Formation. If a picometer-scale OM porosity exists within the Niobrara organic material, the resulting porosity network could be quite extensive (Curtis et al., 2011), particularly within peloids where the majority of migrated RHC now exists. Combined with the documented OM pores, this nano-scale pore system could contribute to flow and storage of mobile hydrocarbons. This does seem plausible for the Niobrara Formation, as a large amount of mineral pores have been filled by RHC.

An alternative argument regarding pico- and nano-scale OM pores is that they will not be that significant to migration given that their associated pore throats are assumedly very small. Pore throats that would connect individual pico- and nano-scale OM pores would likely be so small that only a few molecules of oil, gas, or water might be able to pass, as a single methane molecule is roughly 0.38 nm and complex hydrocarbon chains are even larger (Figure 2, Loucks et al., 2012). Incredibly high capillary pressures for fluid migration would be required given such small pore throats. In addition, the micro- and nanometer-scale pore systems in most shale reservoirs means non-Darcy flow and diffusion would actually prevail (Heller et al., 2014; Ma et al., 2014). Given these complicating factors on flow within many unconventional reservoirs, the hypothesized nanometer and picometer-scale OM pore system would do little to facilitate hydrocarbon flow through the system (Cheng et al., 2013).
Nano-scale OM pore systems can be important to storage capacity. Assuming water does not consume the available adsorption sites (Ganor et al., 2009; Hao et al., 2013; Gasparik et al., 2014), the increased surface area of the organic material due to nano- and micro-scale OM pores allows for greater methane sorption capacity (Hui et al., 2013). Thus adsorption to organic material is likely an important type of hydrocarbon storage within organic shales since percentages of open porosity is mostly in the single digits. Indeed, Gasparik et al. (2014) and Hao et al. (2013) report that methane in the Barnett, Haynesville, and Eagle Ford Formations generally shows increased sorption potential with increasing TOC and thermal maturity, the latter presumably being taken as a proxy for increased OM porosity. In the Niobrara, adsorption of hydrocarbon molecules could occur in the migrated RHC that is in many peloids, as well as in the detrital organic material within the dark crinkled marly laminae. These adsorbed hydrocarbons could be an important part of the Niobrara resource.

**Connectivity**

Connectivity, or the lack thereof, between the two main constituents, peloid and matrix, was documented herein for two long milled transects (Figures 33, 34). These long exposures showed that porosity is many times greater within peloids than in matrix material, and also suggest that matrix pores are not well-connected, if at all. Matrix material may thus be a partial barrier to flow. This implies that connectivity will be best where matrix material is minimal, such as in very peloid-rich microfacies (e.g. microfacies 1-3; Table 3). Yet two fields of view, no matter how large, may also not be fully representative. Connection between porous peloid and less-porous matrix may vary extensively throughout the formation. There may be porous matrix
present in some microfacies or wells as matrix material does exhibit diverse pore types and some organic material that could produce porous and permeable connections. Clearly, more imaging of the peloid-matrix interface is needed, as fluid flow between peloid and matrix must occur for the Niobrara Formation to produce hydrocarbons.

While connectivity between micron-scale mineral pores in peloids is the dominant porosity network documented in this study, natural fracture networks in the formation play a role in porosity, permeability, and deliverability of hydrocarbons. Pollastro and Scholle (1986) noted that fractures in the Niobrara not only enhance hydrocarbon production, but also increase storage potential. Allen (2010) and Vincelette and Foster (2011) point to extensive fracture networks within the Niobrara Formation as a primary method for fluid migration at multiple periods throughout geologic history. The formation was severely impacted by the Laramide orogenic event (~70 Ma) and to a lesser extent the Sevier orogeny (through 50 Ma) during and after deposition (~85 Ma). These orogenic events, coupled with post-Laramide extension, created multiple fracture networks throughout the basin (Vincelette and Foster, 2011). Near-vertical fractures are often exploited during the horizontal drilling process, as intersection of many hydrocarbon-filled fractures is optimal for production (Zhao et al., 2014). The fracture networks within the Niobrara Formation could be an important part of the hydrocarbon deliverability system.
Uncertainty and Upscaling

As demonstrated herein, heterogeneity in the Niobrara Formation occurs at a variety of scales from the nano- to micro-scale of the pore systems, to peloid-matrix variability, to centimeter scale variability in lithology, microfacies and organic material distribution, to core scale variations in macrofacies, to stratigraphic variability in dominant lithologies, to regional variability in thermal maturity. Unconventional reservoirs like the Niobrara Formation are not a homogenous and continuous formation. Due to uncertainty associated with all the scales of heterogeneity, the author is unaware of any literature documenting the upscaling of pore network data from FIB-SEM scale to reservoir scales. The majority of past and current literature is focused on documentation, qualitative, and quantitative analysis of pore systems on a very fine scale (Loucks et al., 2009; Curtis et al., 2010; Milliken and Reed, 2010; Heath et al., 2011; Bai et al., 2013). The specific nature of the data collected with FIB-SEM analysis is applicable to individual lamina and grain types. Without data for every type of lamina, little can be said about the intervening material that was not sampled. The standard 6 inch sampling interval of geophysical log data proved to be too large for correlation to sample attributes (Figure 18), let alone FIB-SEM observations. Even XRF data with a spot size of about one inch can be biased due to incorporation of multiple laminae in each analysis. The variety of investigative scales complicates the ability to cross-correreate pore system attributes. An extremely rigorous and thorough analysis of pore systems that attacks the issue of the various scales of heterogeneity is necessary if an attempt to upscale to regional or reservoir scales is to be made. Until then, the results from this study and studies like it can be used to generally inform the oil and gas industry about the pore systems of certain unconventional formations but use of the data outside the individual types of lamina sampled may not be an accurate reflection of the overall formation.
Chapter 6- Conclusions

FIB-SEM technology has made pore imaging on the nano- and micron-scale possible and this study of the pore systems of the Niobrara Formation is one of the first of that unit in the public domain. Documentation, characterization, and quantification of the pore types answer three fundamental questions about the Niobrara pore system:

1) What are the different pore types and porosity systems in the Niobrara Formation?

- Porosity between mineral crystals is the dominant pore type in both peloid and matrix samples. These mineral-associated pores include pores between crystals of calcite and clay, pores within skeletal and pyrite grains, and minor amounts of pore between alumino-silicate framework grains and pyrite. Median equivalent circular diameters (ECD) of these mineral pores range from ~100 to 400 nm. Matrix material rich in alumino-silicates tends to have more clay, pyrite, and singular mineral pores with little connectivity. In contrast, calcite-dominated matrix and all peloids just contain intercrystalline pores between calcite crystals.

- Peloids are considerably more porous than matrix material because the dominant intercrystalline pores mainly occur within peloids. Thus, nearly all of the storage potential and flow capacity probably exists within peloid-rich laminae.

- Many mineral pores are now filled with residual hydrocarbon (RHC), particularly within peloids as evidenced by elemental maps of carbon. RHC-filled pores have a similar morphology and distribution as the open mineral pores, but larger median ECDs (300 to 900 nm). The RHC-filled pores were part of a well-connected porosity network prior to hydrocarbon migration. Their increased size relative to mineral pores may be due to the hydrocarbons having arrested diagenesis within their host pores.
Residual hydrocarbons host organic matter (OM) porosity with ECDs that range in size from ~10 nm to ~900 nm. The OM pores occur as single bubble pores, a few non-connected bubble pores, as well-connected complex networks, or along RHC-mineral contacts. OM porosity was the second-most abundant pore type and was present in most fields of view (FOVs) that contained RHC. In 2D imagery, OM pores did not seem to be well-connected with other OM pores, however 3D analysis would provide better data regarding connectivity.

Primary organic particles typically occur within matrix material and especially within millimeter-thick black and crinkled marl laminae. This organic material is sinuous and elongate as it is typically crushed and morphed around mineral or skeletal grains. This detrital organic matter can contain some OM porosity, though not all examples were porous. Individual OM pores within detrital organics were not as large and well-defined as those within RHC.

2) Do pore systems vary as a function of macrofacies, microfacies, lithology, or thermal maturity?

At the micron scale, pore types and the abundance of porosity vary between calcite-dominated (e.g., peloids) and alumino-silicate dominated (e.g., marl matrix) FOVs. However, core-scale macrofacies, thin section-scale microfacies, and XRF lithologies are all defined at much coarser scales. As such, the full range of peloid and matrix pore systems observed could occur within any microfacies, macrofacies, or lithology. It is thus not surprising that no correlation was noted between pore system attributes (e.g., elongation or ECD) and these coarser-scale analyses of Niobrara rocks.
Thermal maturity does not affect mineral pore abundance, elongation, or ECD. Samples from low maturity (0.6% Ro, oil window) to high maturity (1.2% Ro, dry gas window) all exhibit OM pores, indicating all wells had passed through the thermal threshold for OM pore formation. Abundance of OM porosity shows no increase with thermal maturity above ~0.7% Ro but the largest OM pores are in the higher thermal maturity wells. Comparison of the Niobrara OM pores to similar pores in the Eagle Ford Formation may prove appropriate in that their unique calcareous mineralogy, or type of hydrocarbons generated in chalk systems, might be a key to the influence that thermal history has on OM pore generation.

3) Can pore systems be predicted from the properties of geophysical logs or geochemical profiles?

- Correlation of geophysical data to pore-system data was deemed futile due to the large difference in spatial resolution of the two types of data. The decimeter scale at which geophysical logs are collected averages all the nanometer to decamicron differences observed in pore systems.
- Geochemical proxies for productivity (Zn EF) and redox (Mo EF) do not correlate to the elongation or ECD of mineral pores, organic material, or OM pores.
Recommendations for Further Work

1. Large milled trenches (> 200 microns long) should be used rather than small 20-30 \( \mu \)m pits. Trenches expose connections between peloids and matrix material, heterogeneity across a large area (100s of microns), and multiple examples of the various constituent particles within a sample.

2. Fine-scale (> 12,000x) imagery should be collected for all samples so as to capture single-nanometer OM pore system.

3. FIB-SEM analysis of the C Chalk, the intervening marl zones, and a greater diversity of B Chalk and A Marl samples will give a better understanding of the diversity of pore networks in the Niobrara Formation.

4. 3D cube analysis will help to resolve uncertainty in segmentation by providing a stack of images for object clarification. Long trenches and fine-scale image analysis should inform location of 3D cubes.

5. 3D cube analysis should also be used to clarify the true size, volume, and connectivity of the mineral and OM pores identified in this study.
Bibliography


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Zhang, S., Klimentidis, R. E., & Barthelemy, P., 2012. Micron to millimeter upscaling of shale rock properties Based on 3D imaging and modeling. Exxomobil Upstream Research Co., Houston, TX, USA. VSG-Visualisation Sciences Group, Burlington, MA, USA.

## Appendix 1- Attributes of FIB-SEM Samples

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1- See Table 3 for description of microfacies  
2- Lithology defined in Figure 16
### Appendix 2- Image Segmentation Results

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Appendix 3- Catalog of Pore Types in BSE Images

FIB-SEM imagery from all fields of view annotated for various features including mineral pores, organic material, and organic matter pores (see key below). In some cases, entire fields of view are dominated by one feature.

Key to Labeling

- **Mineral Pores**
- **Organic Material- Detrital**
- **Organic Material- Residual Hydrocarbon**
- **Mineral Pores- Skeletal Grains**
- **Organic Matter Pores**
Aristocrat 7110.5, A Marl, Peloid Pit
Aristocrat 7110.5, A Marl, Matrix Pit
Aristocrat 7140, B Chalk, Matrix Pit
Aristocrat 7140, B Chalk, Matrix Pit
Aristocrat 7140, B Chalk, Peloid Pit
Burbach 7169.5, A Marl, Fourth Matrix Pit
Burbach 7169.5, A Marl, First Peloid Pit
Burbach 7169.5, B Chalk, Left Matrix Pit
Burbach 7169.5, B Chalk, Right Peloid Pit
Timbro 5675.6, A Marl, Flat Peloid Pit
Timbro 5675.6, A Marl, Fourth Pit Matrix
Timbro 5675.6, A Marl, Middle Peloid Pit
Timbro 5675.6, A Marl, Third Pit Matrix
Timbro 5742, B Chalk, Pit 1 Peloid
Timbro 5742, B Chalk, Pit 2 Peloid