Petrophysics, Geochemistry, Mineralogy, and Storage Capacity of the Niobrara Formation in the Aristocrat PC H11-07 Core, Wattenberg Field, Denver Basin, Colorado.

by

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ABSTRACT

The Niobrara Formation in the Denver Basin is an unconventional oil and gas play composed of highly cyclic, alternating chalk and marl intervals. These intervals act as the source, seal and trap for hydrocarbons generated in the organic-rich marl beds of the Niobrara Formation. The organic-rich marls act as source rocks and represent periods of varying anoxia and organic preservation. The calcareous, carbonate-rich chalks act as reservoirs and represent periods of carbonate production under varying oxygen paleo water conditions. Understanding the reservoir quality and the petrophysical, mineralogical, geological, and geochemical characteristic of the different members of the Niobrara Formation is key for future exploration and development. XRD, ICP-MS, XRF, TOC, nitrogen adsorption, WIP porosity, and well log data on the Aristocrat PC H11-07 core was used in this study.

Petrophysical evaluation of the well logs shows that the chalks possess higher porosity values that average between 11-13% than the marls that have average porosities less than 11%. The density porosity method provided the best estimate of log derived porosity as opposed to the commonly used neutron-density porosity method. Water saturation is highest in the marls and was best estimated using the dual water saturation petrophysical model. A petrophysical workflow was developed that allowed generating rock types from physical core data and predicting the same rock types from petrophysical logs. This facilitates the integration of core-scale geologic elements to petrophysical analysis.

The hydrocarbon potential of the Niobrara Formation is highly dependent on its organic content and maturity. Passey Delta Log R, Schmoker, and the Uranium method are widely used empirical relationships from logs for quantitative TOC estimation. The Schmoker and Passey Delta Log R methods present inconsistent results in Niobrara Formation. The Schmoker method over estimates TOC in the Niobrara Formation, while the Delta log R method underestimates TOC. The GR log and the uranium spectral log are the best proxies of organic richness in the Niobrara Formation. The uranium method provides the best estimate of log derived TOC. XRF, XRD and ICP-MS data was utilized to model the mineralogy in the Niobrara Formation using the concept of linear programming/optimization. The developed Matlab computer code “El Com” was successful at calculating mineralogy from available ICP-MS data. To study the storage capacity of the Niobrara Formation, WIP, nitrogen adsorption
and FESEM work was performed on selected chalk samples. Results show that WIP method for porosity measurement is repeatable, yet not suitable for the Niobrara Formation due to the presence of swelling clays such as smectite. This method overpredicts porosity in clay-rich samples and underestimates porosity in tight samples with small pores. Nitrogen adsorption and FESEM analysis revealed a significant portion of both meso and macropores in the Niobrara Formation. Nitrogen adsorption data shows a consistent trimodal micro and meso pore size distribution with distinct peaks between 50-100nm (e.g. intraparticle pores between clay aggregates), at 3nm (e.g. intraparticle pores within clay platelets), and between 1.7-2nm (e.g. organic matter associated pores). Organic matter and clays contribute to the microporosity of the Niobrara Formation and provide the highest specific surface area for gas adsorption. FESEM analysis confirmed the presence of organic pores, interparticle and intraparticle pores that vary in morphology. Analysis suggests interparticle and intraparticle macro sized pores that range in size from 3 microns to less than a micron. The Niobrara Formation exhibits a mixed pore system with the pores being mainly interparticle confined between crushed coccolith grains and micrites. This is followed by intraparticle pores between clay aggregates and organic pores. Fracture porosity was not documented in the core and is not a main contributor to porosity in the Niobrara Formation.
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Al Hamdullelah
CHAPTER 1
INTRODUCTION

The Niobrara Formation in the Denver Basin is an unconventional, self-sourced oil and gas play composed of alternating chalk and marl units. New technologies involving horizontal drilling and multi-stage hydraulic-fracture stimulation are unlocking reserves that previously were not obtainable. This chapter provides an overview of the study area, motivation and purpose of the study, and the dataset and methodology adopted in this research.

1.1 Motivation

With a long history of development, beginning in 1970, the Wattenberg field has entered a new phase of development since 2009 with the exploitation of the Niobrara Formation. Due to its low porosity and permeability, this “tight” formation is considered unconventional and requires detailed characterization from a macro-field scale to a nano-pore scale. Key characterization parameters that provide an understanding of the distribution of source potential within the Niobrara Formation include: total organic carbon (TOC), maturity level, storage capacity, mineralogy, thickness and organic matter type. This thesis aims to address the qualities of the Niobrara that make it a successful play from a well to a core and pore scale. Petrophysical, geochemical, and mineralogical properties of the Niobrara Formation will be analyzed and modelled. It also looks into the reservoir quality and storage capacity of the Niobrara Formation which remains not fully understood. The work of this thesis aims to address this gap in knowledge by answering questions related to organic richness, petrophysical properties, storage capacity and mineralogy of the Niobrara Formation in the Wattenberg Field.

1.2 Objectives and Purpose

The purpose of this study is to examine and model the mineralogy, organic richness, petrophysics and storage capacity of the Niobrara Formation in Wattenberg Field in the Denver Basin. The organic-rich marls within the Niobrara Formation act as source rocks while the chalks act as reservoirs. The hydrocarbon potential of a source rock is highly dependent on its organic content and maturity. Different empirical relationships were
developed to estimate TOC from logs. This study will look into and compare the different methods of quantifying TOC from logs and how they apply to the Niobrara formation. Most of these methods were initially developed for siliceous Devonian Shales (Passey et al., 1990; Schmoker 1980). With the Niobrara being a calcareous Cretaceous Shale, there is a need to test and analyze those methods and their applicability within the Niobrara Formation.

The mineralogy of the Niobrara has direct control on its reservoir quality. Mineralogy of the Niobrara will be studied and modelled and a method of quantifying mineralogy from elemental data in the Niobrara will be introduced. The commercial success of the Niobrara has also sparked interest in understanding pore structure and storage capacity. This study will also look into the storage capacity of the Niobrara chalks, porosity distribution and variability in pore structure with mineralogy, organic richness, and maturity. This study will incorporate field emissions scanning electron microscopy (FESEM), x-ray diffraction (XRD), total organic carbon (TOC), inductively coupled plasma mass spectrometry (ICP-MS), x-ray fluorescence (XRF), water immersion porosimetry and nitrogen adsorption analyses to characterize the mineralogy, organic richness and storage capacity of mature Niobrara samples.

1.3 Study Area

The location of this study is limited to the Wattenberg field which is located in the center of the Denver Basin in northeastern Colorado and is one of the largest oil and gas fields in the United States. The studied well, the Aristocrat PC H11-07, is located in section 11, 3N 65W, SWNE of the Wattenberg Field close to the highly mature, gas producing central part of the field (Figure 1-1).

1.4 Dataset and Methodology

The Aristocrat PC H11-07 core donated by Noble Energy was used in this study. The core was carefully described on a half foot interval. The lithologies, facies, and sedimentary structures were documented. The core was then sampled for FESEM, XRD, ICP-MS and Rock-Eval TOC analysis. XRF data was collected on the Aristocrat PC H11-07 core by Nakamura (2015) on an every foot interval. A few core analysis data was donated by Noble Energy and included: saturation data, porosity, permeability, grain density, bulk density, and
fluid density. The chalk members of the Niobrara Formation were sampled for water immersion porosimetry testing for total porosity. In addition, nitrogen adsorption test was performed on the same samples to analyze the pore size distribution within the chalks in the Aristocrat PC H11-07 core. Digital open hole logs on the Aristocrat PC H11-07 core were donated to the Colorado School of Mines Niobrara Consortium by Noble Energy.

The software, Techlog, was used to analyze log data and perform petrophysical calculations. Within Techlog, the logs were normalized and corrected. Core to log depth shifts were performed to compare core data to log data. The open hole logs were used to calculate water saturation, porosity, build a petrophysical mineral model, and perform rock typing in the studied interval. Well logs and core TOC data were used to test the different methods of calculating TOC from logs. A Quanti-Elan mineralogy model was generated using the Quanti-Elan module on Techlog. This model predicts mineral composition based on well log responses and was validated by core XRD data. In order to analyze storage capacity in the Niobrara Formation, samples from the chalks were collected, ion milled, and analyzed using the FESEM. Pore sizes, shapes and morphologies were studied and characterized on a microscopic level. Nitrogen adsorption and water immersion data was used to characterize porosity and pore size distribution. It was also used to validate observations made by FESEM analysis. XRD, XRF and ICP-MS data was used to build a mineral model that predicts mineralogy from elemental data using Matlab. The mineral model was validated to core XRD data. The detailed methods used in this study will be addressed and discussed in each chapter separately.
Figure 1-1: Left: structure map of the Denver Basin, Wattenberg field is highlighted in red. Right: vitrinite reflectance (Ro) contour map across the studied area. The Aristocrat PC H11-07 well lies within the 1.2 Ro contour indicating that it’s a mature, gas producing well.
CHAPTER 2
GEOLOGIC OVERVIEW

This chapter provides an overview of the Denver Basin and its regional and structural setting. In addition, the Niobrara Formation stratigraphy, depositional setting, and reservoir characteristics are introduced and discussed.

2.1 Denver Basin

The Denver Basin is one of the largest basins in the Rocky Mountain region. It extends more than 70,000 square miles across eastern Colorado, southeastern Wyoming, and southwestern Nebraska (Figure 1-1; Higley et al., 2007). It is an asymmetric Laramide-age (65-30 Ma) foreland basin with a gentle east flank with 0.5° west dip and a folded and faulted west flank with steep dips (Figure 2-1). Its axis is parallel with and close to the mountain front. The deepest part of the basin lies near Denver, where there are more than 13,000 feet of sediments (Higley et al., 2007). Bounding the basin on the west are the Front and Laramie Ranges of Colorado and Wyoming. Other tectonic features surrounding the basin include the Hartville uplift on the northwest, the Black Hills on the north, the Chadron-Cambridge Arch on the northeast, the Las Animas arch on the southeast, and on the south and southwest, the Sierra Grande and Apishipa uplifts. The Wattenberg field is located within the Denver Basin and is a large gas producing field. The field covers more than 2,000 square miles between the cities of Denver and Greeley, and includes more than 20,000 wells producing from a number of Cretaceous formations including the Niobrara Formation (Weimer et al., 1986).

2.2 Regional Structural Setting and Stratigraphy

Prior to the Late Cretaceous, the Denver Basin and adjacent Rocky Mountains and Great Plains consisted of a flat, stable platform underlying the shallow Cretaceous Western Interior Sea. Subsidence of this platform during Early and Late Cretaceous is marked by deposition of the Dakota and Benton Groups, Niobrara Formation, Pierre Shale, Fox Hills and Laramie Formations. The spatial distribution and thickness of these formations has been attributed to flexure of the North American craton by loading by the Sevier thrust belt about 700 km further West (Longman et al., 1998). The Sevier thrust belt has been attributed to the subduction of the Farallon Plate (Figure 2-2a; Longman et al., 1998). After the Sevier orogeny, the Laramide orogeny occurred between approximately 67.5 and 50 million years
ago, as a result of the shift to shallow low angle subduction of the Farallon Plate (Figure 2-2b; Longman et al., 1998). This major tectonic event folded originally flat-lying rocks, forming the Denver Basin, and uplifting the Rocky Mountains to the west. Within the basin, a complex tectonic history resulted in NE trending wrench faults and extensive normal faulting across the basin. This has also resulted in folding and displacing some of the stratigraphic units within the Denver Basin.

Figure 2-1: West-East cross section across the Denver Basin showing the distribution of the Niobrara Formation (modified from Sonnenberg, 2012).

Figure 2-2: Shallow angle subduction of the Farallon Plate (Longman et al., 1998).
2.3 Niobrara Depositional Setting

The Upper Cretaceous Niobrara was deposited in a foreland basin setting in the Cretaceous Western Interior Seaway (CWIS) of North America during a time of a major marine transgression (Figure 2-4; Longman et al., 1998; Kauffman, 1997). This transgression represents a near maximum sea-level highstand during the Cretaceous. The Cretaceous Western Interior Basin was an asymmetric foreland basin with the thickest strata deposited along its western margin (Kauffman, 1997). The basin was bordered by mountainous areas to the west including zones of plutonism, volcanism, and thrust-faulting that formed the Cordilleran thrust belt, and a broad stable craton to the east (Longman et al., 1998; Kauffman, 1997). The foreland basin subsided in response to thrusting and synorogenic sediment loading, allowing for further depositional accommodation space (Longman et al., 1998; Kauffman, 1997).

The Niobrara Formation was deposited in the Western Interior Basin during the Coniacian, Santonian, and lower Campanian (Figure 2-3) (Weimer, 1984). It consists of intervals of calcareous chalk and organic-rich shale units. Within the Niobrara, four chalk intervals, limestone interval and three marl intervals are defined, both in outcrop and on petrophysical logs, including in ascending order the Fort Hays Limestone, D chalk-marl, C marl, C chalk, B marl, B chalk, A marl and A chalk (Figure 2-3). Niobrara deposition in the Western Interior Basin was strongly influenced by the interplay of warm north-flowing currents from the paleo-Gulf of Mexico and cooler southward-flowing currents from the Arctic region, along with sea level fluctuations (Figure 2-4; Kauffman, 1997). Warm waters from the Gulf brought in rich carbonate flora of coccoliths and promoted carbonate production and deposition. Siliciclastic input from the west and cooler Arctic currents inhibited and diluted carbonate production and deposition to the north and west. The interbedded marls are caused by an increase in fresh-water runoff caused by increased rainfall, perhaps related to climatic warming in combination with slightly lower sea level that allowed more detrital clays to be carried across the seaway from the east and west.

Four transgressive cycles occurred during the Niobrara cyclotherm, resulting in the deposition of the Fort Hays Limestone, C chalk, B chalk, and A chalk intervals. During the transgressive cycles, higher relative sea level allowed for carbonate-rich waters from the south to invade the area of the CWIS which is now Colorado. Three regressive cycles took
place during the Niobrara cyclotherm, resulting in the deposition of the D chalk-marl, C marl, B marl, and A marl intervals (Longman et al., 1998; Kauffman, 1997). During the regressive cycles, the currents from the south were reduced, and the southward flowing Arctic currents inhibited carbonate production and deposition (Longman et al., 1998; Kauffman, 1997). Figure 2-3 shows a schematic of these transgressive-regressive cycles of the Niobrara cyclotherm. In addition to the fluctuating currents, a gradual deepening of the CWIS resulted in time periods when bottom waters throughout parts of the Western Interior Seaway were suboxic to anoxic, favoring the preservation of organic matter.

Figure 2-3: Schematic of the transgressive-regressive cycles of the Niobrara Cyclotherm and the stratigraphy (modified from Kauffman, 1977).
Figure 2-4: The Western Interior Cretaceous Basin during Niobrara time. Source area for clastics is dominantly to the West, total organic carbon content in the Niobrara increases to the East, carbonate content generally increases on the eastern side of the Western Interior Cretaceous seaway and to the southeast (modified from Longman et al., 1998).

2.4 Niobrara Stratigraphy

The Niobrara Formation is divided into two members: The Fort Hays Limestone and the Smoky Hill member (Figure 2-3). The Fort Hays Limestone member is a relatively pure limestone that thickens to the southeast (Weimer et al., 1986). The Smoky Hill member is divided into six intervals; three carbonate rich chalk intervals and three mud and carbonate mixed marls. Conformably overlying the Fort Hays Limestone is the lower D chalk-marl. The D chalk-marl is a heavily bioturbated interval that represents a transition from the Fort Hays limestone into the C marl. The C marl is the most organic rich interval in the Denver Basin with total organic carbon (TOC) up to 7.0 % by weight. The lithology is thinly laminated with 35-65% flattened chalk pellets in a silty matrix (Longman et al., 1998). Gradational with the C marl is the overlying C chalk. This facies is composed of 65-85%
chalk pellets, and is slightly burrowed. Above the C chalk bench is the middle shale or B marl. The B marl is dark olive gray in color with wispy to parallel laminations, an abundance of shell fragments, and TOC of 2.7 wt. % (Longman et al., 1998). Above the B marl lies the middle chalk, also titled the B chalk bench. The B chalk bench is also 65-85% chalk pellets. The remainder is composed of *Inoceramus*, foraminifera and micrite, with traces of burrowing and parallel laminations (Longman et al., 1998). Above the B chalk bench is the upper shale or A marl. The A marl is massively bedded with bentonite lamina, up to 25% silt, common pyrite, and 6 wt. % TOC (Longman et al., 1998). The A chalk bench is the uppermost member of the Niobrara and is chalk pellet rich with foraminifera, *Inoceramus*, oysters, and micrite.

### 2.5 Niobrara Reservoir and Source Rock Characteristics

In the Wattenberg field, the chalk benches have a slightly lower TOC (1-3%) than the marls (2-6%), and kerogen is dominantly Type II (oil-prone) (Weimer, 1996; Sonnenberg and Weimer, 1993; Jarvie, 2012; Sonnenberg, 2012). An unusually high temperature gradient is present within the Wattenberg area. This “hot spot” is associated with high heat flow caused by intrusives at depths, allowing kerogen maturation and subsequent hydrocarbon generation.

While the marls are better source rocks, the chalks are better reservoirs. However, the porosity and permeability are low enough to be classified as tight and unconventional and this has been widely discussed by many authors in literature. Most agree that the single most important factor affecting porosity within the Niobrara Formation is burial depth. Burial related diagenesis within the Niobrara has resulted in low matrix porosities and permeabilities in the Niobrara (Figure 2-5). Porosity loss within the Niobrara can be attributed to mechanical and chemical compaction. Mechanical compaction is an early burial processes resulting in dewatering and grain reorientation and breakage. This can be seen in flattened pellets and collapsed foraminifera tests found. Chemical compaction is a processes characterized by calcite dissolution, formation of stylolites, pressure solution at grain to grain contacts, and the precipitation of calcite as overgrowths resulting in a welded fabric (Pollastro and Scholle, 1986). Matrix porosities within the Smoky Hill member of the Niobrara Formation in the Denver Basin range between 8 - 16% and permeability is generally
< .01 millidarcy. Average porosities in the Wattenberg field range from 4-12%. With rocks this tight, fractures (both natural and induced) are critical to production. The Niobrara Formation has relatively low clay content in the chalk intervals, resulting in relatively brittle rocks, an essential index for production. Production in the Niobrara Formation corresponds with high micro and meso-porosity in both the chucks and marls enhanced by natural fractures.

Figure 2-5: Niobrara porosity and permeability with burial (modified from Pollastro and Scholle, 1986).
CHAPTER 3
CORE STUDY

This chapter discusses the different facies and lithologies identified in the studied Aristocrat PC H11-07 core and how they were defined. It provides an overview of the mineralogy and elemental characteristics associated to the different facies in the Niobrara Formation and how they relate to the depositional setting.

3.1 Lithofacies

In the Aristocrat PC H11-07 core, five different lithologies were identified based on the ratio of carbonate to clay content (Figures 3-1, 3-2). Figure 3-1 shows the core photos of the studied interval.

Figure 3-1: Core photos of the Niobrara study interval from Sharon Springs to the Fort Hays member (top left is the top of the core). The white sections represent core that is missing or is preserved.

The core shows high cyclicity and frequent changes from chalks to marls over small intervals. Within the chalk members there are marly (i.e. more clay rich) intervals and within the marl
members there are chalky (i.e. more carbonate rich) intervals. Cyclicity within the Niobrara Formation has been explained by Milankovich related cycles (Locklair and Sageman, 2008). The lithologies identified are:

1. **Chalk**: Composed of mainly carbonates and less than 5 wt. % clays. It is generally light grey in color and has a speckled appearance due to the abundance of Foraminifera, pellets and shell fragments. It has less organic content than other facies.

2. **Marly chalk**: This lithology is also carbonate rich but contains more clays with up to 15 wt. % clay content. They are generally planar laminated or bioturbated.

3. **Chalky marl**: Clay content is high can be up to 20% with carbonate content less than 60 wt. %. Chalky marls within the Niobrara core can also be planar laminated or bioturbated. Chalky marl and marly chalk lithologies are difficult to discern without a grey scale chart and XRD data.

4. **Marl**: Highly rich in clays with clay content reaching up to 30 wt. %. It has a black appearance and is the most organic rich.

5. **Bentonite**: Ash beds that are generally pyritized and their color ranges from white to greenish white. Their thickness is generally less than a few inches.

![Lithologies present within the studied Niobrara Interval. (A) Chalk (B) Marly chalk (C) Chalky marl (D) Marl (E) Bentonite.](image)

These lithologies were recognized based on a grey color scale of the rock paired with available XRD and TOC data. Generally the lighter colored intervals are more chalky and the
darker colored intervals are more marly. The lithologies have been further categorized into different facies based on the speckled nature of the rock, bioturbation, and presence of planar laminations. Every lithology exhibited bioturbated and laminated facies that were influenced by changes in anoxic and suboxic marine environments. Scattered thin bentonite layers are also found within the studied interval and seem to be less frequent within the C interval of the Niobrara Formation as opposed to the A and B intervals. Bentonite layers range in thickness from less than an inch to a couple of inches in thickness.

Another noticeable feature in the studied core is the speckled nature of the rock that frequently changes from one interval to the other. The abundance of speckles (e.g. foraminifera or pellets) was qualitatively assessed on a pellet index that ranges from 0 to 3 (Figure 3-3 3-3). The A chalk, B marl and C chalk intervals are highly rich in pellets with the B marl interval being rich in broken shell fragments (e.g. icneceramid and oyster shells). The C marl and the middle marly section for the C chalk, also known as the “K” zone (Smagala, 1984), are the most organic-rich intervals within the core. In terms of bioturbation, the most bioturbated facies are found within the D chalk-marl and Fort Hays Limestone of the Niobrara Formation reflecting oxic to suboxic marine conditions. The D chalk-marl may be considered as the transition zone from the Fort Hays Limestone into the Smoky Hill member. Changes in the level of bioturbation otherwise known as bioturbation index was tracked and described in the core according to the bioturbation index defined in Aplin and Macquaker (2011) (Figure 3-4). The bioturbated facies tend to have less organic matter preservation than planar laminated non-bioturbated facies. Bioturbation is not only prevalent in the D chalk-marl and Fort Hays Limestone but also throughout the Smoky Hill member at lower bioturbation indices. The A chalk and marl intervals of the Smoky Hill member are mainly planar laminated and with little to no bioturbation throughout possibly indicating more anoxic marine settings and suboxic to oxic settings in the lower Smokey Hill member into the Fort Hays Limestone. The A chalk, A marl, B chalk, B marl, C chalk, C marl, D chalk-marl, Fort Hays Limestone members are general classifications used to describe the different mappable units within the Niobrara Formation observed on logs. It must be noted, however, that as the core description shows that within the marl members there are chalk facies and vice versa.
Figure 3-3: Core description of the Aristocrat PC H11-07 core showing the different lithologies and facies identified within the Niobrara Formation combined with XRD total carbonates, total clays, and TOC data.

Figure 3-4: Naturally occurring examples of a mudstone unit with an equivalent Bioturbation Index (BI) shown next to the modeled fabric A&B = BI1; C&D = BI2; E&F = BI3; G&H = BI4; and K& J = BI5).
3.2 Mineralogy

Mineralogical data is obtained using x-ray diffraction analysis (XRD) analysis, a semi-quantitative process of determining the percentage by weight of minerals present within the rock. This technique allows for mineral identification based on unique inter-lattice spacing of individual minerals. Figure 3-5 shows the XRD mineral abundances and distribution within the different chalk and marl members of the Niobrara Formation. The Niobrara Formation is composed of calcite, illite/smectite clays, quartz, dolomite, albite and pyrite. This data shows that the Niobrara Formation is dominantly composed of carbonates and clays.

Mineral results are grouped into three groups with the carbonate group comprising calcite and dolomite; the clastic group comprising quartz and albite; and the clay group comprising illite, smectite, and chlorite. Chlorite is not a dominant clay within the Niobrara Formation and was found in minimal amounts in a few analyzed samples. Based on the XRD mineralogy of the Niobrara Formation, the dominant lithofacies type is clay-rich to mixed carbonate mudstones. The Fort Hays Limestone, A chalk, B chalk and C chalk show carbonate dominated lithofacies (Figure 3-6).

Figure 3-5: Niobrara XRD bulk mineralogy with depth.
Elemental Characterization

Elemental geochemistry is very useful in characterizing various mudrock facies and obtaining various information on organic richness, paleo-productivity, and provenance of detrital sediments. Elemental data may be obtained using a handheld XRF analyzer that emits high energy x-rays that excite individual atoms to emit X-ray photons of a characteristic energy or wavelength. By counting the number of photons of each energy emitted from a sample, the elements and associated concentrations may be semi-quantitatively determined. When elemental data is plotted as a function of sampling depth of the core, variability in elemental concentrations may be analyzed and compared with core facies.

All geochemical data was provided by Nakamura (2015). A detailed account on geochemical data collection procedure and interpretations can be found in Nakamura (2015). Relationships between major and trace elements measured by the XRF analyzer must be recognized and analyzed. Principle component analysis (PCA) is a statistical tool that has been widely applied on XRF data to find relationships between elements and classify them.
into groups based on calculated correlation coefficients (Cliff, 2014; Al Ibrahim, 2014). PCA allows for pattern identification in data and expresses the data in such a way to highlight their similarities and differences. PCA analysis performed on the studied interval suggest that elements fall into five categories (Figure 3-7).

- **Group 1**: Al, Si, Ti, Rb, Zr, K and Th. These elements are associated to terrigenous minerals including clay minerals, feldspars, and quartz.
- **Group 2**: Cu, V and Cr. This group is associated with organic matter, redox conditions and is indicative of suboxic environments.
- **Group 3**: S, Mo, Ni, Fe, U and Zn. These elements are associated to anoxic conditions.
- **Group 4**: Ca and Sr. These elements are associated with carbonate. This is consistent with other studies that relate these elements to diagenesis and aragonite to calcite alterations (Al Ibrahim, 2014; Pingitore Jr., 1978).
- **Group 5**: Consists of Mn element that is associated to oxic to suboxic conditions.

![Figure 3-7: Results of PCA applied to XRF data of the studied Interval. Results show the data falling into 5 different groups. Group 1 is associated to clays and terrigenous minerals. Group 2 is associated to suboxic conditions. Group 3 is associated to anoxic conditions. Group 4 is associated to carbonates while Group 5 is associated to oxic to suboxic conditions.](image)
Groups 2 and 3 plot on the same side of the grid because they are related to redox conditions but are different. Group 2 is related to suboxic conditions while group 3 is related to anoxic conditions. Piper et al. (2009) provides a detailed account of the conditions under which elements begin to precipitate. MnO$_2$ is reduced to a soluble valence state (Mn$^{2+}$) under anoxic conditions, but is stable within the oxic realm. Chromium (Cr) precipitates as a hydroxide or is adsorbed onto settling particles under mildly suboxic (denitrifying) to anoxic conditions (Piper et al., 2009). Under oxic conditions, Cr is in the oxidized and more soluble CrO$_4^{2-}$ valence state (Piper et al., 2009; Murray et al., 2007). Under suboxic to anoxic conditions, the limiting nutrient NO$_3^-$ is consumed and remaining oxygen acts as an electron acceptor. In addition, dissolved Cr, U, and V act as trace subordinate electron acceptors and are reduced to less soluble ionic states and eventually precipitate (Piper, 2009). Anoxic conditions prevail when oxygen accumulations have been essentially exhausted. In the transition between suboxic to anoxic environment, Cu$^{2+}$ is first reduced and precipitated. Under complete anoxic conditions, FeS, CdS, ZnS, MoS$_2$ and NiS are precipitated from redox reactions (Figure 3-8) (Piper et al., 2009).

![Figure 3-8: Schematic representation of bacterial respiration versus water-column depth in marine basins experiencing O2 depletion in the bottom water. The different colors are intended to identify the oxic photic (light blue) and aphotic zones (dark blue), suboxic zone (orange), and anoxic zone (green) (Piper et al., 2009).](image-url)
After the elemental groups were identified, they were then related to the different facies recognized in the Aristocrat PC H11-07 core. Group 1 elements are associated with terrigenous minerals and clays and show an increase in the marly, clay-rich facies within the Niobrara Formation (Figure 3-9). Cross-plots of some of Group 1 elements (Ti, Al, Rb, Si) with total clay content show a positive trend with good correlation coefficients ($R^2 > 0.7$) (Figure 3-10). This indicates that these elements are more associated to changes in lithology and clay content as opposed to variations in bioturbation and in paleo-oceanic oxygen water conditions.

Figure 3-9: Group 1 elemental data (Al, Ti, Si, Zr, K and Rb respectively) plotted as a function of core sampling depth, along with the core description.
Figure 3-10: Cross-plots of Group 1 elements against XRD total clay showing a positive trend.

XRF analysis qualitatively shows the abundance of Si in clay rich intervals but it is difficult to differentiate whether it is biogenic or detrital. Si, as a proxy for quartz can be cross-plotted with elements such as Zr to differentiate biogenic from detrital Si in the system. Presence of detrital Si will show a positive trend with Zr while biogenic Si will show a negative trend. Samples from the Niobrara Formation show a positive, terrestrial trend with Zr indicating that the Si in the system is detrital (Figure 3-11).

Figure 3-11: Cross-plot of XRF Si and Zr showing a positive trend indicating a detrital source for silica.
Group 4 elements include Ca and Sr and are associated to carbonate content in the analyzed interval. Chalk lithologies show the highest Ca and Sr readings that decrease in marly intervals (Figure 3-12). Similar to Group 1, Group 4 elements are more linked to changes in carbonate sediment supply as opposed to paleo-oceanic oxygen water conditions. Cross-plots of Group 4 elements with total carbonate content of the studied interval show a positive correlation with good correlation coefficients showing that these two elements are good proxies for carbonate content in the Niobrara Formation (Figure 3-13).

Figure 3-12: Group 4 elemental data (Ca and Sr respectively) plotted as a function of core sampling depth, along with the core description.
Organic matter is best preserved in source rocks under anoxic, reducing marine conditions. Group 2 and 3 elements are redox sensitive elements that precipitate under varying levels of anoxia. Group 2 elements precipitate in suboxic conditions while Group 3 elements precipitate in anoxic, highly reducing conditions (Figure 3-8). Group 2 and Group 3 elements show a positive trend with measured core total organic carbon (TOC) (Figure 3-14). Both elemental groups are highest in the marly, organic rich, planar laminated facies suggesting that these facies are deposited under reducing, dysoxic to anoxic water conditions (Figures 3-15, 3-16).

The D chalk-marl represents the transition from the Fort Hays Limestone into the Smoky Hill member. The D chalk-marl and Fort Hays Limestone both are heavily bioturbated. Oxygenated marine conditions were prevalent during the deposition of both intervals that allowed for burrowing organisms to thrive. Group 5 element Mn is stable and precipitates
under oxic conditions. With less oxygenated marine conditions Mn becomes more soluble and dissolves into the seawater. Manganese elemental data shows a gradual decrease from the Fort Hays Limestone up into the D chalk-marl and stabilizes at a minimum in the Smoky Hill member (Figure 3-18). This suggests that during the Fort Hays Limestone member deposition, marine water conditions were oxic and began to switch to suboxic conditions during the D chalk-marl deposition. Marine conditions within the Smoky Hill member alternated from suboxic to dysoxic conditions evident in the alternation from planar laminated organic-rich facies to bioturbated organic-lean facies. A cross-plot of Mn and core TOC shows a negative relationship (Figure 3-17).

Figure 3-15: Group 2 elemental data (Cr, V and Cu respectively) plotted as a function of core sampling depth, along with the core description.
Figure 3-16: Group 3 elemental data (S, U, Zn, Mo, Fe and Ni respectively) plotted as a function of core sampling depth, along with the core description.

Figure 3-17: Cross-plots of Group 5 element (Mn) against XRD total carbonates showing a weak negative trend.
Figure 3-18: Group 5 elemental data (Mn) plotted as a function of core sampling depth, along with the core description.
CHAPTER 4
PETROPHYSICS

This chapter provides an overview of the petrophysical properties and characteristics of the Niobrara Formation in the Aristocrat PC H11-07 core. It also provides an analysis of the different petrophysical models for calculating water saturation and porosity in the Niobrara formation. Results from the petrophysical models were compared to core data to identify the model that provides results consistent to core data. Calculated water saturation values were used to assess the hydrocarbon potential of the different intervals of the Niobrara Formation in the Aristocrat PC H11-07 core.

4.1 Introduction

A type log of the Niobrara Formation in the Wattenberg field (Figure 4-1) shows typical log responses for the various chalks and marls in the high maturity parts of the basin. Compared to the marls, the chalks generally have a lower gamma ray, a higher resistivity, and neutron-density porosity crossover.

![Figure 4-1: Niobrara type well log (after Matthies, 2014).](image)
Very little work has been published on the petrophysics and petrophysical properties of the Niobrara. Schlumberger (2011) has published some results on a study of the Niobrara Formation within the Denver Basin. The Niobrara Formation shows elevated resistivity at the chalk intervals. The bulk density and neutron porosity curves crossover due to lithology effects and the presence of hydrocarbons. Within the marls, an increase in clay and quartz content with a decrease in carbonate content can be illustrated by ECS log data (Figure 4-2). The presence of elevated clay content within the marls results in an increase in clay bound water. The presence of clay bound water suppresses resistivity resulting in even lower resistivity readings within the marls. Analysis of a spectral gamma ray log shows elevated thorium readings within the C and B marl intervals. Thorium is generally associated to the presence of heavy minerals and volcanic ash. Uranium log signatures within the marls increase due to an increase in organic matter content. Within mudrock systems, spectral gamma ray logs are essential. The gamma ray log is a summation of uranium, potassium and thorium spectral logs. Spectral gamma ray measurements offer several advantages. They can help with clay typing, because variations in the relative amounts of potassium, thorium, and uranium are associated with specific shale minerals. Cross-plots are useful to highlight fundamental differences. Different clay minerals may sometimes array themselves in different locations within the thorium-potassium cross-plot. The increase in organic matter may increase the gamma ray log signature, inaccurately suggesting increased clay content. The same is true for the reverse, increased clay content suggesting increase in organic content. Therefore, spectral gamma ray logs and producing a gamma ray log with thorium-potassium count rates is critical for better clay analysis.

4.2 Petrophysical Characterization

Open hole logs available for the studied core are gamma ray (GR), spectral uranium log (URAN), spectral thorium log (THOR), spectral potassium log (POTA), formation deep resistivity (Rt), photoelectric factor (PEF), bulk density (RHOB), neutron porosity (NPHI) and compressional slowness (DTC). The logs were analyzed using Techlog software for petrophysical characterization of the different lithologies and facies present within the
Niobrara Formation. Figure 4-3 shows the open hole log signatures associated to the Niobrara Formation members in the Aristocrat PC H11-07 well.

The RHOB log measures the bulk density of the formation and is a function of matrix density, porosity, and density of fluids in the pores. It has a relatively shallow depth of investigation and can be used to detect gas bearing zones. The DRHO curve indicates how much correction has been added to the bulk density curve during processing due to borehole effects. Whenever the DRHO curve exceeds 0.2 g/cm³ the value of the bulk density obtained from RHOB should be considered suspect and possibly invalid (Asquith et al., 2004). In the Aristocrat PC H11-07 well the DRHO curve does not exceed 0.2 g/cm³ and so the RHOB log data is considered valid.

Figure 4-2: Petrophysical evaluation of the Niobrara Formation, Watternbern field (Luneau et al., 2011).
Figure 4-3: log view of open hole logs of the Aristocrat PC H11-07 showing GR log and caliper (track1), URAN spectral log (track2), THOR spectral log (track3), POTA spectral log (track4), Rt log (track5), PEF log(track 6), NPHI and RHOB logs showing the gas effect.

The A, B and C chalks show lower RHOB readings (~2.4 g/cm³) influenced by the presence of gas in these reservoir intervals. Calcite has lower RHOB (~2.71 g/cm³) than illite-smectite clays (~2.78 g/cm³). Since RHOB log also responds to changes in matrix density, RHOB is lower in the chalks (A, B, C chalks) that are high in calcite content and are gas saturated while the illite-smectite clay rich marls and D chalk-marl have higher RHOB (Figure 4-3). In addition, the presence of pyrite (~5.1 g/cm³) results in increased RHOB signatures. Pyrite is associated to anoxic, organic-rich facies that form the marl intervals. The presence of organic matter can also have an effect on RHOB. Because solid organic matter in source rocks is less dense than the surrounding rock matrix, the presence of organic matter results in a reduction in RHOB log response (Schmoker, 1979; Schmoker, 1980; Passey et al., 1990). Chapter 5 discusses in depth the effect of organic matter on RHOB log response in the Niobrara Formation.
Neutron logs are porosity logs that measure the hydrogen concentration in a formation. Whenever pores are filled with gas rather than oil or water, the reported NPHI is less than the actual formation porosity. This occurs because there is a lower concentration of hydrogen in gas than in oil or water. When plotted on the same track with reversed scales, both logs will crossover due to gas effect. The magnitude of crossover is related to gas saturation; yet, it is also strongly influenced by formation pressure. Moreover, the presence of clays results in higher clay bound water and the hydrogen associated to the clay bound water is sensed by the neutron tool. This extra hydrogen in the clay-bound water is interpreted as being part of the porosity and results in increased NPHI readings. This phenomena is referred to as the shale effect. In gas bearing mudrock systems, the NPHI readings become complicated by both the shale and gas effect. RHOB and NPHI logs for the studied interval show a typical log crossover in the A, B, and C chalk members and the Fort Hays member. This crossover is caused by gas and lithology effect in the gas bearing A, B and C chalk reservoir intervals and the carbonate rich Fort Hays Limestone member. The marl intervals and D chalk show little to no crossover.

The DTC log is a sonic tool that measures interval transit time of a compressional sound wave traveling through the formation along the axis of the borehole. The interval transit time measured is dependent upon lithology, porosity and organic matter content. Presence of organic matter results in higher DTC log response (Passey et al., 1990). DTC is highest in the marl intervals that are organic rich and clay rich. Cross-plots of DTC log data against XRD total carbonate and clay content show a negative trend with total carbonates and a positive trend with total clays (Figure 4-4). In the studied well, the DTC log is mainly responsive to changes in lithology and organic content. Higher TOC is accompanied by higher DTC log readings (Figure 4-4).

The Rt log is used to determine hydrocarbon bearing versus water bearing zones. It can also be used to calculate porosity and water saturation using Archie’s equation. Archies equation, however, was developed for conventional clean sandstone cases. In mudrock systems such as the Niobrara Formation, Archie’s equation inaccurately overestimates water saturation. Overestimation has been attributed to suppressed resistivity from clay-bound water in clay-rich mudrocks (Boyce, 2010). Rt in the studied interval shows lower resistivity in
clay-rich, marly intervals due to clay-bound water. The clean chalk lithologies show elevated Rt compared to the other intervals due to the presence of hydrocarbons and less clay and therefore, less clay bound water.

Figure 4-4: Cross-plots of DTC against XRD total carbonate, total clay content, and core TOC respectively. DTC shows a negative trend with total carbonate content, a positive trend with total clay content and a positive trend with TOC.

The GR log measures the natural radioactivity in formations and is used for identifying lithologies, source rocks and correlating zones. The response of a normal GR log is made of the combined radiation from uranium, thorium, potassium and a number of associated daughter products of radioactive decay. Because these different radioactive elements emit gamma rays at different energy levels, the radiation contributed by each element can be analyzed separately. Total GR response can be separated into the gamma rays related to each of these elements. The spectral GR log processes the total measured GR into separate representative curves of thorium (THOR) uranium (URAN) and potassium (POTA) present in the formation. Spectral GR logs are particularly useful in source rock evaluation and clay typing. THOR and POTA logs are generally used as clay indicators in mudrock systems while URAN log is used as a proxy for organic richness. The use of URAN log as a proxy for organic richness is discussed in details in chapter 5. In mudrock systems, anomalous GR values are attributed to organic matter content, therefore, analysis of GR minus URAN (i.e. GRKT) allows for better clay analysis. Cross-plots of GRKT with XRD total clays shows a positive trend (Figure 4-5). Figure 4-6 shows that intervals with very high GR could be mistaken to be clay-rich intervals while in fact they are organic-rich intervals. Analysis of the GRKT removes the influence of organic matter on the GR log and becomes representative solely of clay content. THOR and POTA cross-plots are useful in identifying the different
types of clays present within the studied interval. Figure 4-7 shows that the Aristocrat PC H11-07 contains mixed layer clays of illite and smectite which has also been confirmed by XRD analysis.

![Graph of GRKT against XRD total clay content.](image)

**Figure 4-5**: Cross-plots of GRKT against XRD total clay content. GRKT shows a positive trend with XRD total clay content.

![Log view of GR (track1), GRKT (track2), URAN (track3), THOR (track4), POTA (track5).](image)

**Figure 4-6**: Log view of GR (track1), GRKT (track2), URAN (track3), THOR (track4), POTA (track5) for the studied well. GR log is influenced by URAN measurements. GRKT is the GR log minus URAN and is representative of the THOR and POTA portions of the GR log.
To get a better understanding of the relationships between the different logs and what they measure, PCA analysis was performed on the available log suite. Similar to the elemental application, PCA analysis will identify any patterns, similarities and differences between the logs. Variable that are closely related plot close to each while variables that are unrelated plot far away from each other. Results show the open hole logs grouped into five different groups:

- **Group 1**: RHOB sensitive to changes in mineralogy and gas effect.
- **Group 2**: POTA and THOR spectral GR logs that are indicators of the amount of clay present.
- **Group 3**: DTC and NPHI both responsive to changes in lithology, organic content and gas saturation.
- **Group 4**: GR and URAN both mainly responsive to organic matter. An increase in organic matter is reflected in an increase in both GR and URAN spectral log.
- **Group 5**: PEF and Rt affected mainly by changes in lithology coupled with clay bound water effects.
Porosity

The porosity of the Niobrara was evaluated in order to determine the reservoir potential and hydrocarbon storage of each interval. Density and neutron-density porosity was calculated and compared to core porosity data to assess the best petrophysical technique for porosity calculation in the Niobrara. Most petrophysical porosity calculation methods have been developed and effective in conventional sandstone reservoirs. In unconventional mudrock systems, the presence of organic matter and microporosity can affect the density or neutron porosity log readings and lead to incorrect porosity determinations.

Figure 4-9 shows a comparison of the log derived neutron-density (PHIT\_ND) and density porosity (PHIT\_D) and how it compares to core porosity data. The calculated PHIT\_D provided the best estimate of porosity compared to core porosity. When calculating PHIT\_D, fluid density was assigned to be 0.7 g/cm³ for gas and the matrix RHOB was assigned to be 2.68 g/cm³. RHOB matrix value was based on available core analysis data.

Porosity may also be calculated from sonic logs. This method requires knowledge of the sonic velocity of the rock matrix and fluids present. In addition, in gas bearing formations, the sonic log must be corrected for gas before calculating porosity. Core calibrated PHIT\_D porosity log shows higher porosity in the Smoky Hill members of the Niobrara Formation as opposed to the Fort Hays Limestone. Within the Smoky Hill member the chalk intervals and
the C marl show the highest porosity compared to other marl intervals and the D chalk-marl. Table A-1 summarizes the average porosity calculated for each member of the Niobrara Formation.

![Log view of RHOB and NPHI crossing over (track1), neutron-density total porosity and core total porosity (track2), density total porosity and core total porosity (track3).](image)

**Figure 4-9:** Log view of RHOB and NPHI crossing over (track1), neutron-density total porosity and core total porosity (track2), density total porosity and core total porosity (track3).

### 4.4 Water saturation

Different water saturation models such as Archie’s, modified Archie’s, dual water and Waxman Smith were compared and analyzed. Water saturation logs were constructed for the Aristocrat PC H11-07 well using Archie’s equation, modified Archie’s equation, and dual water saturation model. The constructed water saturation logs were compared to core analysis $S_w$ values to evaluate the best method of calculating water saturation in the studied well. Archie’s equation (Eqn. (4.1)) is a popular saturation model that has been used to calculate water saturation in conventional sandstone reservoirs.

$$S_w_{AR} = \left(\frac{R_w \ast a}{(\phi_l^m \ast R_i)}\right)^{\frac{1}{n}}$$  \hspace{1cm} \text{Eqn. (4.1)}
Where, $a$ is tortuosity factor, $R_w$ is formation water resistivity, $R_t$ is formation resistivity, $\phi_t$ is the fractional total porosity, $m$ is cementation exponent, $n$ is saturation exponent. For this study, $a = 1$ and $m = n = 2$. The calculated PHIT_D log was used for porosity and the resistivity log for $R_t$. A value of 0.03 was used for $R_w$. The calculated $S_w$ log using Archie’s equation (i.e. $S_w_{-AR}$) is shown in Figure 4-10. Compared to core $S_w$ values, Archie’s equation overestimates water saturation due to the presence of clays and clay-bound water. Developed by Boyce (2010), a modified Archie formula (Eqn. (4.2)) incorporates components of the spectral gamma-ray log such as thorium and uranium to account for clay-bound water.

$$S_w_{-AR\_mod} = \left( \frac{R_w \cdot a \cdot THOR}{\phi_t^m \cdot URAN \cdot R_t} \right)^{1/n}$$

Eqn. (4.2)

Where, $R_w$ is resistivity of interstitial water; $R_t$ is formation resistivity; $a$ is tortuosity; THOR is the concentration of thorium in ppm from the spectral gamma-ray log; $\phi_t$ is fractional total porosity; $m$ is the cementation exponent; URAN is concentration of uranium in ppm from the spectral gamma-ray log; and $n$ is the saturation exponent. The calculated PHIT_D log was used for porosity, resistivity log for $R_t$, thorium spectral GR log was used for THOR, and uranium spectral GR log was used for URAN. A value of 0.03 was used for $R_w$; $a = 1$ and $m = n = 2$. The calculated $S_w$ log using the modified Archie equation (i.e. $S_w_{-AR\_mod}$) is shown in Figure 4-10. The modified Archie model provides a better estimate of water saturation compared to the Archie’s model; yet, the modified Archie model also over predicts water saturation.

The dual water saturation model and Waxman Smith models seek to use the electrical properties of the clays in formations to predict a more accurate water saturation that accounts for clay bound water. The dual water model postulates two different types of water in a clay rich formation, an immovable water layer next to the clay surfaces (i.e. clay bound water) and movable water that can be displaced by hydrocarbons (i.e. free water). The Waxman smith model requires the clay cation exchange capacity (CEC) to calculate water saturation. CEC is the quantity of positively charged ions (cations) that a clay mineral or similar material can accommodate on its negatively charged surface. The dual water saturation model faces the reality that there is no way to measure CEC directly from logs and that CEC measurements on cores are rare. Instead it uses the volume of shale ($V_{shale}$) to calculate bound water saturation. Due to lack of CEC data, the dual water saturation model was used to calculate $S_w$. 

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in the studied interval (Figure 4-10). $V_{\text{shale}}$ was calculated from the GRKT log (i.e. GR minus uranium) and was validated by comparison to core XRD total clay data.

$$\frac{a}{(R_t \times \varphi_t^m)} = (1/R_w) * S_w^n + ((\varphi_{sh} \times V_{sh})/\varphi_t) \times ((1/\varphi_{sh}^2 \times R_{sh}) - (1/R_w)) \times S_w^{(n-1)} \quad \text{Eqn. (4.3)}$$

Where, $R_w$ is resistivity of interstitial water; $R_t$ is formation resistivity; $a$ is tortuosity; $V_{\text{shale}}$ is the volume of shale; $\varphi_t$ is fractional total porosity; $\varphi_{sh}$ is the porosity reading in 100% shale; $R_{sh}$ is the resistivity value in 100% shale; $m$ is the cementation exponent; and $n$ is the saturation exponent. A constant 0.03 was used for $R_w$; $m$ and $n$ both used the constant 2; $\varphi_{sh}$ was assumed a constant of 0.05; and $R_{sh}$ was assumed a constant 5ohm.m. Asquith et al. (2004) recommend the use of 0.35 for the tortuosity factor ‘a’ for petrophysical analysis in the Rocky Mountain region.

Figure 4-10: Log view of calculated water saturation $S_w$ using three different saturation models: Archie’s model water saturation $S_{w_{\text{AR}}}$ and core $S_w$ (track1), Archies model water saturation using $a=0.35$ and core $S_w$ (track2), modified Archie’s model $S_{w_{\text{AR}_{\text{mod}}}}$ and core $S_w$ (track4).
The calculated $S_w$ log using the dual water saturation model (i.e. $S_{w\_DUAL}$) is shown in Table A-1. Results show that the dual water saturation model provided the best estimate of water saturation compared to the other saturation models. In addition, the use of the tortuosity factor $a = 0.35$ is a valid assumption. Recalculating water saturation using the Archie model and $a=0.35$ as opposed to $a=1$ provides a comparably good estimation of water saturation to that of the dual saturation model. Recalculated Archie $S_w$ using $a=0.35$ (Sw_AR_035a) is shown in Figure 4-10. Calculated water saturation values in the studied well are highest in the marls and the D chalk-marl due to the presence of clay bound water. Total hydrocarbon saturation is the quantity of interest and is usually determined by the difference between unity and $S_w$. Figure 4-11 shows that, based on the calculated $S_{w\_DUAL}$, the hydrocarbon saturation is highest and averages around 80% in the Smoky Hill member of the Niobrara Formation. Table A-1 summarizes the average petrophysical properties of the different members of the Niobrara Formation in the Aristocrat PC H11-07 well.

![Figure 4-11: Log view of GR log (track 1), density porosity log (track 2), calculated hydrocarbon saturation (HCC) against calculated water saturation (SW_DUAL) (track 3) and petrophysical mineral model (track 4). Total hydrocarbon saturation is highest in the Smoky Hill member of the Niobrara Formation and is a function of the calculated Sw values.](image)
4.5 Petrophysical Rock Typing

Log data has historically been used to deduce information on the organic content of source rocks, mechanical properties, and reservoir quality of formations of interest. Core data is commonly expensive and limited across the prospect and vertical interval of the formation. Open hole logs, however, are continuous and are widely available in most drilled wells. This chapter introduces an integrated petrophysical workflow of generating rock types from physical core data and predicting the same rock types from petrophysical logs. The ultimate objective of this workflow is to provide a consistent methodology to systematically integrate both core-scale geologic elements with petrophysical logs.

4.5.1 Generating Rock Types

The proposed method of generating rock types from core data is derived from the theory behind the Stratigraphic Modified Lorenz Plot (SMLP) graphical tool used by reservoir engineers to identify flow units, baffles, and barriers within a geologic framework. When high-resolution core porosity or permeability data is plotted against depth, the different flow units may be recognized by analyzing slope breaks in the data. Intervals showing high change in porosity or permeability with depth (i.e. with gentle slopes) represent flow units. While intervals that show little to no change in porosity or permeability (i.e. steep slopes) represent baffles or barriers to flow. In addition, points that lie along the same slope represent similar flow units and different slopes represent different rock behaviors.

Due to a lack of high resolution continuous core porosity and permeability data, the SMLP tool was tested on high resolution (1 ft. interval) core TOC data. Normalized core TOC data from the Aristocrat PC H11-07 well were plotted against normalized depth values and the resultant slopes were analyzed. An available python script assigned points that lie along the same slope a color and each color was assigned a number. The results show five different distinct slopes differentiated by five different colors: blue, red, green, yellow, and black. These colors and their associated numbers were then translated into a log format and compared to core TOC data (Figure 4-11). The different colors corresponded to a different range of core TOC values. The dark blue group corresponds to the highest core TOC values followed by the light blue, green, orange, and red respectively. The red group corresponds to the lowest TOC values found in the D chalk-marl and Fort Hays Limestone. The
comparability of the generated groups (i.e. rock types) with the core TOC suggests that each color corresponds to a different rock type based on organic content (Figure 4-11). The dark blue group represents the most organic-rich source rock intervals while the red group represents the most organic-lean rocks. The dark blue group also corresponds with the C marl, the most organic-rich interval in the Niobrara Formation. Results suggest that by analyzing changes in slopes in a plot of any normalized core property against normalized depth one can distinguish different rock types based on the property being studied (e.g. TOC in this case).

4.5.2 Predicting Rock Types

After the rock types have been defined and geologically validated with core data, the next step is to predict the same rock types from well log data. To do this decision tree, a statistical tool, was used to classify the variable values (well logs) into a qualitative curve through pre-existing qualitative data (core based rock types). The decision tree analysis tool allows the user to relate a set of variables (well logs) to predefined geologic classifications (i.e. rock types) by learning the log signatures associated to every classification. In wells with no core data, a decision tree looks for the same log signatures and deduces a classification based on what it had previously learned.

PCA analysis on the Aristocrat PC H11-07 well logs shows that the GR and spectral uranium logs are closely related and are the best proxies of organic richness. These two logs are the best log combinations that can be most predictive of organic facies. Figure 4-12 shows the petrophysical workflow adopted to predict rock types. The decision tree incorporates these two logs with the pre-defined classification groups or rock types generated. The Aristocrat PC H11-07 well was both used as a learning and a blind application well. This process makes it possible to compare the actual classification groups with the predicted ones and evaluate the rock predicting efficiency using the used log combinations. Results show that the predicted and actual rock types match 72 % of the time (Figure 4-12).

This workflow is particularly useful with multiple wells that lack core data. If one well has both core data and well log data, it may be used to generate the geologic rock types using the slope based technique. The log signatures associated to the defined rock types can be determined using a decision tree. Other wells with well logs and lacking core data can then be analyzed using the decision tree to deduce specific rock types from available well logs.
Figure 4-12: Plot of normalized wt. % TOC against normalized depth on left with five distinct slopes. Points that lie along the same slope are represented by the same color and belong to the same rock type. The different slopes represented by different colors represent different organic rock types. Right: log view of GR log (track1), core TOC log and the slope based rock types translated with depth (track2). The different rock types correspond to different core TOC ranges. The most organic-rich rock type is the dark blue and consistently corresponds to the highest core TOC values. The most organic-lean rock type is the red which consistently corresponds to the lowest core TOC.
Figure 4-13: Petrophysical Workflow of predicting rock types from open hole logs using decision tree analysis. Rock types are generated based on available core data using the slope theory.
CHAPTER 5
TOC MODELLING

The hydrocarbon potential of a source rock like the Niobrara Formation is highly dependent on its organic content and maturity. This chapter discusses the organic richness of the Niobrara Formation in the Aristocrat PC H11-07 core. It also looks into the different methods of estimating TOC from open hole logs.

5.1 Introduction

Conventional approaches for TOC estimation either use log data as qualitative TOC indicators or employ empirical relationships from logs for quantitative estimation. Numerous papers have documented the use of well logs to identify and quantify source rocks (e.g. Schmoker, 1980; Schmoker, 1979; Passey et al., 1990). Qualitative log indicators of elevated TOC include elevated neutron porosity, low bulk density, high sonic transit time, and high gamma ray or uranium. However, these measurements respond to more than just organic matter; therefore, interpretation of these logs in terms of organic matter requires accounting for the effect of mineralogy and fluids. Different empirical relationships were developed to estimate TOC from logs. Two widely used empirical approaches developed to quantitatively estimate TOC from log data are the Schmoker density log technique and the combination sonic or density and resistivity log technique known as Δ log R (Passey et al., 1990; Schmoker, 1979). Other common methods for TOC estimation include using uranium or gamma ray logs as indicators of organic matter, although they often require a local calibration. This chapter will compare the different methods of quantifying TOC from logs and how they apply to the Niobrara formation. Most of these methods were initially developed for siliceous Devonian Shales (Passey et al., 1990; Schmoker 1980). For the Cretaceous calcareous Niobrara Formation, there is a need to test and analyze these methods and their applicability.

5.2 Background Information

Organic matter accumulation and formation of source rocks is a result of the interaction of three complex environmental processes. Bohacs et al. (2005) provided a detailed account of the processes that result in organic matter accumulation. Organic matter accumulation in depositional environments is controlled by complex interactions between rates of organic
matter production, destruction and dilution (Figure 5-1). Therefore, organic-rich intervals may show high vertical variability in TOC due to stratigraphic and biotic controls.

![Diagram of organic richness controls](image)

Figure 5-1: Controls on organic richness showing the interconnected influence of organic production, destruction and dilution on organic rich rocks accumulation (Passey et al., 2010).

The core based analytical methods most frequently used for source rock organic richness evaluation is Rock-Eval Pyrolysis and vitrinite reflectance analysis. Whether a rock is a source interval or a reservoir interval, its maturity, and its potential to generate oil/gas is evaluated by Rock-Eval data. The data derived from Rock-Eval analysis includes TOC, S1, S2, S3, S4 and Tmax. From this data various ratios can be calculated to aid in interpreting the rock characteristics such as Hydrogen Index (HI), Oxygen Index (OI), S2/S3, Production Index (PI) and normalized oil content (NOC). TOC is expressed as a weight percent and indicates the total amount of organic carbon present in the sediment (Ronov, 1958; Espitalie et al., 1985). S1, expressed in milligrams of hydrocarbon per gram of rock, represents the free, thermally extractable hydrocarbons present in the whole rock sample. Based on thermal extract chromatograph analysis, this includes hydrocarbons up to C75+ (Jarvie et al., 2000). Heavier, hydrocarbons will vaporize only at higher temperatures and will be included in the S2 Peak (Clementz, 1979). S2, also expressed as milligrams of
hydrocarbons per gram of rock, represents higher molecular weight hydrocarbons that did not vaporize in the S1 peak. It also represents the present-day source potential of the sample; thus, it is considered an important parameter in source rock evaluation. The temperature at which S2 hydrocarbons are evolved is referred to as Tmax. S3 is the third peak recorded by a Rock-Eval pyrolysis pyrogram and it represents organic carbon dioxide evolved during low temperature pyrolysis, yet it is not generally considered in source rock evaluation. S4 represents the amount of carbon dioxide (CO2) and carbon monoxide (CO) released during combustion of the organic matter remaining after pyrolysis. A typical pyrogram of the S1, S2, S3, S4 peaks and Tmax of a mature Niobrara sample is shown in Figure 5-2.

Figure 5-2: Rock-Eval pyrogram of one of the analyzed Aristocrat PC H11-07 Niobrara samples.

Rock Eval analysis directly determines S1, S2, S3, S4 and Tmax which may be used to calculate TOC and ratios such as HI, OI and PI. HI is an indicator for the amount of hydrogen present in organic matter and can be measured directly with elemental analysis (Durand and Monin, 1980) or can be estimated indirectly from measured S2 values by Rock-Eval Pyrolysis (Espitalie et al., 1977). Measuring HI from S2 values is a relatively fast and inexpensive procedure and is commonly used. OI represents the normalized oxygen content of the rock sample and helps in identifying the type of kerogen present. Finally, PI is the
transformation ratio and is indicative of the conversion of kerogen into free hydrocarbons. These ratios are calculated from Rock-Eval data as follows:

$$\text{TOC} = \frac{S_4 + (0.83(S_1 + S_2))}{10}, \text{HI} = S_2 \times \frac{100}{\text{TOC}}, \text{OI} = S_3 \times \frac{100}{\text{TOC}}, \text{PI} = \frac{S_1}{(S_1 + S_2)} \quad \text{Eqn. (5.1)}$$

NOC is another ratio that can be calculated from Rock-Eval data, showing the ratio of free hydrocarbons to total organic carbon. It may be used to identify reservoir rocks or the thermal maturity of tight source rocks. Mature source rocks have higher NOC ratio than immature source rocks (Jarvie and Baker, 1984).

$$\text{NOC} = S_1 \times \frac{100}{\text{TOC}} \quad \text{Eqn. (5.2)}$$

Dembicki (2009) provided a detailed account on how to understand and interpret TOC Rock-Eval data. Although a good source rock should have a high TOC, some organic matter will generate oil, some will generate gas, and some will generate nothing (Dembicki, 2009; Tissot et al., 1974). Hence, TOC generative potential becomes closely associated with the type of kerogen present. Moreover, TOC by itself is not necessarily a good indicator of how much hydrocarbon a sediment can generate. For organic matter to generate hydrocarbons, the carbon has to be associated with hydrogen (Dembicki, 2009). The more hydrogen associated with carbon the more the hydrocarbons it can generate; thus, the maturity and hydrogen index become important variables to consider. By combining TOC and S2, it is possible to understand how much organic matter is present and how much hydrogen is associated with it (Dembicki, 2009).

Care must be taken when evaluating mature source rocks because as the rock matures and expels hydrocarbons, the amount of TOC, S2 and HI values will decrease due to the consumption of kerogen. It must always be noted that as a source rock matures, it will gradually appear less like a source rock. Because, there is more to source rock than organic richness, knowing about the maturity of the source rock for proper interpretation is crucial.

The four basic kerogens recognized are Type I, Type II, Type III, and Type IV. HI (hydrogen to carbon atomic ratio) and OI (oxygen to carbon atomic ratio) are parameters that are generally used to classify the organic matter type. Type I kerogen has high initial
hydrogen to carbon atomic ratio (H/C) and low initial oxygen to carbon (O/C) atomic ratios. It is derived primarily from algal amorphous material deposited mainly in lacustrine environments. Type II has moderately high H/C and moderate O/C atomic ratios derived from autochthonous or herbaceous algal organic matter deposited under reducing conditions in marine environments that produce mainly oil during thermal maturation. Type III has low initial H/C and high initial O/C atomic ratios derived from terrestrial woody material such as plant debris deposited in an oxidizing environment that produces mainly gas upon maturation. Type IV has very low initial H/C and a variable initial O/C atomic ratio and is inert organic matter with no hydrocarbon generating potential. The HI and OI data are commonly plotted on a pseudo-Van Krevelen diagram to determine the type of kerogen present as shown in Figure 5-3. The pseudo-Van Krevelen diagram shows H/C (Hydrogen Index) and O/C (Oxygen Index) trends of different kerogen types that diverge between immature kerogen types and converge between over-mature kerogen types towards the origin (Passey et al., 2010).

Figure 5-3: Types of Kerogen shown on a Van Krevelen diagram (Passey et al., 2010).

Another important maturation parameter to be considered is vitrinite reflectance (Ro). Vitrinite is a type of kerogen particle formed from humic gels thought to be derived from the lignin cellulose cell walls of higher plants and is a common component of coals (Dembicki, 2009). With an increase in time and temperature, Ro also increases accordingly; therefore, it
relates to the hydrocarbon generation history of sediments (Dembicki, 2009). Ro can indicate if hydrocarbon generation is possible and what type(s) of hydrocarbon could be formed. However, Ro cannot directly indicate when hydrocarbon generation might have started or tell how much hydrocarbon has been generated and this is where burial history modeling and Rock-Eval become important.

5.3 Organic richness of the Niobrara

In this study Rock Eval Pyrolysis was performed to acquire TOC data to evaluate the Niobrara Formation source rock organic richness in the Aristocrat PC H11-07 core within the study area. Ro data was based on available literature. Smagala et al. (2011) studied Ro variations in the Niobrara Formation within Weld County in the Denver Basin. In his study he used 23 control wells with Ro data and generated Ro contour maps across the basin. Ro contour maps show that the study area within the Wattenberg field lies within the gas window vitrinite reflectance contour (Ro >1) (Smagala et al., 2011). The Aristocrat PC H11-07 well has high thermal maturity and lies within a 1.2 Ro contour and is therefore a mature gas well (Figure 5-4).

![Figure 5-4: Left: Wattenberg Field in the Denver Basin, Right: Vitrinite reflectance contour map showing the Aristocrat PC H11-07 well (black star) within the 1.2 Ro contour.](image)

The Aristocrat PC H11-07 core shows TOC values that range from 2.0 to 6.0 wt. % in both chalks and marls (Figure 5-5). The C marl interval is the most organic-rich interval.
with the highest TOC values. Original TOC within the Niobrara must have been higher but has been reduced due to maturity and hydrocarbon generation. Left over S2 values range from 1.0 to 4.0 mg HC/g rock (Figure 5-5). This being after the rock has matured indicates that the source rocks in the Niobrara have very good source rock potential (Table A-2). However, HI values have been greatly reduced due to thermal maturity to values less than 100. If the rock’s maturity level is not taken into consideration, the Niobrara source rocks may be mistakenly interpreted as an immature, Type IV, poor source rock system (Table A-7). Based on maturity knowledge and interpretation of data, one can conclude that it is in fact a mature, Type II generative system. S2/S3 is a ratio that was utilized by Clementz et al. (1979) as an indication of kerogen type in the absence of TOC data. This ratio reflects the ratio of hydrogen to oxygen, which is similar to the ratio of HI and OI. Calculated S2/S3 values are greater than 5.0 confirming that the organic matter in the studied core is Type II kerogen (Table A-4). NOC values range between 50 and 100 mg HC/g rock indicating that the Niobrara Formation is a stained, tight source rock (Table A-3). In addition to Ro data, calculated PI ratios are greater than 0.5 demonstrating that the studied core is in the gas window (Table A-6).

The Van krevelen diagram shows the data confined around the Type III and Type IV kerogen. Considering the maturity of the well, original HI values must have been much higher indicating a Type II kerogen instead (Figure 5-6A). Tmax values in this core are very high and range between 450°C and 475°C. HI against Tmax plots confirm that the source intervals in the studied core are mature and within the gas window (Figure 5-7B; Table A-5). A few data points that belong to the D chalk and the Fort Hays Limestone show very low Tmax and HI values (<420°C) (Table A-5). This is because these intervals are organic lean (i.e. low TOC) and do not act as source rocks in the Niobrara Formation.

Physical core TOC data is obtained using Rock-Eval analysis if a core is available or may be derived from well logs if a core is not available. Various petrophysical methods have been developed to estimate physical core TOC data from well logs. Such methods include the Schmoker, Passey Delta Log R and Uranium methods. These methods will be discussed in detail in the subsequent sections.
Figure 5-5: Geochemical Logs for the Aristocrat PC H11-07 core.
Figure 5-6: (A) Van krevelen diagram of the analyzed samples (B) Kerogen type and maturity plot of the analyzed samples.

Figure 5-7: Kerogen quality plot of the Aristocrat PC H11-07 analyzed Niobrara samples.
One of the empirical methods developed to calculate TOC from logs is the Schmoker density-log technique. The Schmoker technique uses the bulk density log and assumes that the change in density of the formation is due to the presence or absence of low-density organic matter (1.0 g/cm³) versus normal minerals’ density of 2.6-2.8 g/cm³. The Schmoker method was developed in Devonian shales in the Appalachian Basin using bulk density logs (Schmoker, 1979; Schmoker, 1980) and was later refined in the Bakken shale of the Williston Basin (Schmoker, 1983). Based on the response of the bulk density measurement to low-density organic matter (1.0 g/cm³), the Schmoker method, as it is commonly called, computes TOC using the following empirical correlation:

$$\text{TOC} = \frac{154.497}{\rho_b} - 57.261 \quad \text{Eqn. (5.3)}$$

Where, $\rho_b$ is the bulk density in g/cm³ and TOC is reported in wt. %. This equation assumes a constant mineral composition and porosity throughout the formation. Although the method was developed and refined for one specific environment, it is frequently used for TOC estimation in a wide variety of shale formations.
The original Schmoker equation proposes that with other rock properties remaining constant, bulk density can be directly used to quantify the total organic carbon content in the formation. However, a change in mineralogy will affect the grain density and in turn the measured bulk density. As shales are typically heterogeneous, this change in grain density needs to be taken into account so that any mineralogy influences on the bulk density are removed.

5.4.1 Schmoker Method in the Niobrara

Schmoker began deriving his equation by accounting for the presence of pyrite in the Bakken shale and the effect it has on bulk density readings. Pyrite has a density of 5 g/cm³ and its presence could increase bulk density readings. Studies performed on the relationship between pyrite and TOC in Devonian shales of the western Appalachian Basin suggested a linear positive relationship between both (Eqn. (5.4)).

$$\emptyset_p = 0.135 \emptyset_o + 0.0078$$  \hspace{1cm} \text{Eqn. (5.4)}

Where, $\emptyset_p$ and $\emptyset_o$ are fractional volumes of pyrite and organic matter, respectively. The relationship between pyrite and organic matter used for Appalachian Devonian shales (Eqn. 5.4) is assumed to be applicable to the shale members of the Bakken Formation and was used in deriving the Schmoker TOC equation. Analysis of pyrite and TOC data in the studied interval show a nonlinear relationship between TOC and pyrite (Figure 5-9). Moreover, pyrite is known to be disseminated within the Niobrara formation and a regional analysis of pyrite and TOC data in the Wattenberg field is required to account for the effect of pyrite in the Schmoker equation. Even though there is no linear trend between TOC and pyrite, the density effect of pyrite on bulk density readings must be accounted for.

![Figure 5-9: TOC and Pyrite cross-plot in the studied interval. There is no direct linear relationship between pyrite and TOC in the Aristocrat PC H11-07 well.](image-url)
By representing the Bakken Formation as a four component system consisting of rock matrix, pores, pyrite, and organic matter (represented by the sub-scripts m, i, p, and o, respectively), Schmoker defined bulk density as follows:

$$\rho = \phi_o \rho_o + \phi_p \rho_p + \phi_i \rho_i + (1 - \phi_o - \phi_p - \phi_i) \rho_m$$  \hspace{1cm} \text{Eqn. (5.5)}

To reduce unknowns in the equation, Schmoker assumed that porosity does not vary enough in the Bakken formation to alter formation density significantly and removed it from the equation.

$$\rho = \phi_o \rho_o + \phi_p \rho_p + (1 - \phi_o - \phi_p) \rho_m$$  \hspace{1cm} \text{Eqn. (5.6)}

In the Niobrara Formation, however, such an assumption is not valid. Available porosity data on the studied interval show that porosity varies significantly from 1% to 16% in both chalks and marls. Moreover, the variation in porosity has an effect on the recorded bulk density readings as shown in Figure 5-10. As porosity increases, recorded bulk density readings decrease accordingly. As a result, bulk density must remain a function of porosity when analyzing the Niobrara Formation.

![Figure 5-10: RHOB and porosity cross-plot in the studied interval showing a negative linear relationship between both.](image)
By substituting various defined pyrite and TOC relationships into Eqn. (5.6), the resulting equation becomes:

\[
\text{TOC} = \frac{(100 \rho_o) (\rho - 0.9922 \rho_{mi} - 0.039)}{[(R\rho) (\rho_o - 1.135 \rho_{mi} + 0.675)]} \quad \text{Eqn. (5.7)}
\]

Where, \( \text{TOC} \) is the total organic carbon of the rock, \( R \) is the ratio of weight percent organic matter to weight percent organic carbon, \( \rho_o \) is the density of kerogen, \( \rho_{mi} \) is the rock matrix density, and \( \rho \) is the bulk density of the rock.

By estimating \( \rho_o \), \( \rho_{mi} \) and \( R \) from available Bakken data, Schmoker was able to simplify his equation into its currently widely used form (Eqn. (5.8)).

\[
\text{TOC} = \frac{A}{\rho_{HOB}} - B \quad \text{Eqn. (5.8)}
\]

Where, \( A = 154.497 \) and \( B = 57.261 \).

It must be noted that the \( A \) and \( B \) parameters defined in the Schmoker TOC equation were specifically calculated for the Bakken shales based on an organic-matter density (\( \rho_o \)) of 1.01 g/cm\(^3\), a matrix density (\( \rho_{mi} \)) of 2.68 g/cm, and a ratio between weight percent of organic matter and organic carbon (\( R \)) of 1.3. The parameters \( A \) and \( B \) must be recalculated and refined for the particular formation, member, or area it will be used for. Okiongbo et al. (2005) showed that kerogen density changes with maturity and HI values (Figure 48). As HI of the rock decreases, the kerogen density increases and could vary in density from 0.9 to 1.4 g/cm\(^3\). According to the results presented by Okiongbo et al. (2005), \( \rho_o \) in the studied well should be higher than 1 g/cm\(^3\); averaging around 1.2 g/cm\(^3\).

Based on core analysis data, the \( A \), \( B \) and \( C \) chalk members in the studied interval show average matrix densities (\( \rho_{mi} \)) of 2.67 g/cm\(^3\). As for the marls, matrix densities average to 2.7 g/cm\(^3\). By taking the ratio of TOC and \( S_2 \), the ratio \( R \) was recalculated for the Niobrara Formation to be 1.5.

As previously discussed, the Schmoker equation relies on the effect TOC has on reducing bulk density log response. Such relationships were analyzed in the studied interval to see if TOC and the bulk density log show a relationship. Chalks and marls were separated and cross-plots of TOC against bulk density log for each were analyzed. Within the chalks
there are organic rich intervals with TOC values as high as that found in the marls. As a result, the chalks and marls are expected to exhibit similar behavior in reduction of bulk density with TOC if such a relationship does exist.

![Figure 5-11](image1.png)

**Figure 5-11**: Type II Kerogen density as a function of HI (Okiongbo et al., 2005).

![Figure 5-12](image2.png)

**Figure 5-12**: (A) RHOB and TOC data cross-plot for the A, B and C chalk members. (B) RHOB and TOC data cross-plot for the A, B and C marl members.

The chalks have shown no correlation or relationship between TOC and bulk density log indicating that the bulk density log response is not as sensitive to changes in TOC as Schmoker’s equation predicts and is in fact responding to changes in porosity and mineralogy. Factor analysis of available triple combo logs (discussed in section 4.2) shows that the bulk density log is unrelated to TOC sensitive logs such as the GR and spectral uranium logs (Figure 4-8). On the other hand, the marls display a slightly higher correlation ($R^2=0.118$)
between TOC and bulk density where bulk density decreases with TOC. This indicates that the bulk density log within the marly intervals seems to be also sensitive to changes in TOC in addition to porosity and mineralogy.

The Schmoker equation was used to calculate TOC from the bulk density log of the studied interval and the results were compared to core TOC data. Results show that the Schmoker equation works better in the marls than it does in the chalks. It still overestimates TOC but gives the correct TOC trends. In the chalks, however, the Schmoker equation fails and highly over predicts TOC and gives the wrong the trends. Core TOC data shows that the chalk intervals may be as TOC-rich as the marls and so a method is required capable of calculating TOC in both the chalks and marls taking into consideration lithology changes.

Figure 5-13: Petrophysical logs showing GR (track 1), GRKT (i.e. GR minus uranium, track 2), RHOB (track 3), calculated Schmoker TOC and core TOC (track 4), XRD mineralogical data (track 5) and petrophysical mineral model (track 6).
5.5 Passey Delta Log R

The second approach to calculating TOC from logs, known as the Δ log R technique, relies on separation of the sonic (or density) and resistivity curves to identify areas containing organic matter. Derivation of TOC may be calculated from the separation of the two curves based on the level of organic maturity (Passey et al., 1990). A sonic log is typically used for the porosity curve. However, if one is not available, a bulk density log may be used. The method relies on the porosity and resistivity curves overlaying each other in organic-lean rocks, whereas in organic-rich rocks, the two curves separate. The separation between the two curves, Δ log R, gives the method its name and is calculated as follows:

\[
\Delta \text{log} R = \log_{10} \left( \frac{R}{R_{\text{baseline}}} \right) - \text{Scaling Factor} \left( \frac{\rho_b - \rho_{\text{baseline}}}{\rho_b} \right)
\]

Eqn. (5.9)

Where \( R \) is the resistivity in ohm/m, \( R_{\text{baseline}} \) is the resistivity in the baseline organic-lean zone in ohm/m, \( \rho_b \) is the bulk density in g/cm³, and \( \rho_{\text{baseline}} \) is the bulk density in the baseline organic-lean zone in g/cm³. The scaling factor is calculated after baselining the two curves in the organic-lean zone and its calculation is further discussed in the methodology section. The Δ log R separation of the two curves is then related to the maturity of the formation to determine the TOC in wt. % in the organic-rich zones:

\[
\text{TOC} = (\Delta \text{log} R) \times 10^{(2.297 - 0.1688 \text{LOM})}
\]

Eqn. (5.10)

Where LOM is the level of organic maturity (Hood et al., 1975). The LOM can be determined from a variety of measurements including vitrinite reflectance, Tmax, or Rock-Eval if the type of organic matter is known. Therefore, if two formations have the same Δ log R values but different LOM values, estimated TOC will be different. However, in over-mature shale reservoirs with LOM values greater than 10.5; the limit of calibration of maturity to TOC is reached. In these formations, a LOM value of 10.5 should be used (Passey et al., 2010).

The application of the Δ log R method to log data is more complex. First, bulk density and resistivity curves are plotted on the same track using the default limits for each curve. Next, the two curves must be baselined in an organic-lean zone, which can be identified by finding where the two curves parallel each other. A gamma ray curve or knowledge of the local geology can help to identify these zones. Once the organic-lean interval has been identified, the curves are baselined by adjusting the limits of each curve so they end up
overlying each other in the selected interval. One or both of the limits can be adjusted, as long as the limits are within the range of the actual values. The scaling factor shown in the equation below is now calculated from the adjusted limits of the bulk density and resistivity curves:

$$\text{Scaling Factor} = \frac{\text{#Resistivity divisions}}{(\rho_{b-upper} - \rho_{b-lower})} \quad \text{Eqn. (5.11)}$$

Where the number of resistivity divisions is an integer and is counted from the track divisions on the log plot, $\rho_{b-upper}$ is the value of the upper adjusted bulk density limit, and $\rho_{b-lower}$ is the value of the lower adjusted bulk density limit. The scaling factor is then entered into Eqn. (5.9) along with the baseline bulk density ($\rho_{baseline}$) and resistivity ($R_{baseline}$) values to calculate the $\Delta \log R$ separation. Because the baseline is usually set over an interval and not at an exact depth, the $R_{baseline}$ and $\rho_{baseline}$ values chosen are the approximate average values for that interval. Finally, the calculated $\Delta \log R$ separation is used as an input to Eqn. (5.10) along with an LOM value for the formation.

5.5.1 Passey Delta Log R in the Niobrara

The Passey Delta Log R method was applied on the studied interval. Setting the baseline in the Niobrara formation is troublesome. Three baseline cases were considered: 1. setting the baseline at the most organic lean marl interval (case 1), 2. Setting the baseline at the cleanest, non-source and organic lean interval in the chalk (case 2), 3. Setting the baseline at the D chalk-marl interval as a non-source organic lean interval (case 3) (Figure 5-15). Moreover, since the studied well has an Ro of 1.4 and is highly mature, an LOM of 10.5 was used as suggested by Passey in his study. In addition, the sonic log was used as a porosity log along with the resistivity log. Results show that the Delta Log R method fails to predict TOC in the Niobrara Formation at different baseline settings (Figure 5-14). It also generally under predicts TOC and provides a wrong TOC trend when compared to core TOC. This is mainly due to the resistivity log behavior in the Niobrara. The resistivity log in the Niobrara shows very high resistivity values at the chalk intervals and this seems to be more associated to their higher porosity, less clay bound water, and presence of hydrocarbons. Passey’s method is based on resistivity log and porosity log deviations caused by a reduction in DTC and RHOB with organic matter and increase in resistivity in highly mature source rocks. As illustrated in Section 5.4.1 the RHOB log in the Niobrara Formation does not show a
consistent reduction in RHOB with TOC. Moreover it responds to many other mineralogical factors in addition to TOC.

Many factors can compromise the Delta Log R model in the Niobrara Formation. The chalks within the Niobrara Formation show very high resistivity values that are associated to the carbonate content and hydrocarbon content of the chalks as carbonate rich reservoirs. Moreover, the known presence of smectite and illite clays in the studied interval has a direct impact on the bound water and hence on the resistivity of the rock. Presence of clay bound water generally decreases resistivity. Another concern is the LOM factor being frequently used to tune the TOC model without a real understanding of the parameters involved. Partial conversion of TOC into bitumen could greatly affect the resistivity log response and possibly pyrite where it forms conductive circuits. In addition, the sonic (DTC) log is heavily impacted by compaction/decompaction caused by burial and uplift, subsequently affecting Delta Log R. Furthermore, neither DTC nor the resistivity curve are directly related to TOC alone. DTC can be directly impacted by the pore pressure increase commonly associated with mature source rocks with tight permeability matrix, where the converted fluids are retained in the pore space in the near vicinity of the source rock. By modifying the LOM and showing a saturation limit, Passey (2010) has indirectly concluded that at a certain point in the maturity cycle, resistivity will not increase proportionately to maturity because all the conductive fluids in the matrix would have been substituted with hydrocarbon. But he fails to account for continuing changes in DTC because of buildup of pore pressure as further maturity is achieved. In addition, Passey (2010) has not provided an LOM solution for wells with Ro values greater than 1. It is incorrect to treat wells at different Ro values greater than one to have the same LOM. Moreover, there is no clear definition as to where the baseline should be set.

The Niobrara Formation studied in the Aristocrat PC H11-07 core is has Ro values that are greater than 1. Therefore, estimating an LOM value will present error to the measurements. Moreover, The Niobrara chalk intervals exhibit a distinctively high resistivity signature that is not associated to maturity levels but instead is associated to lithology effects. Picking a baseline for Delta Log R calculations in the Niobrara Formation is difficult due to
its heterogeneity and cyclicity. Moreover, PCA analysis has shown that none of the logs is directly related to TOC alone.

Figure 5-14: log view of total GR (track 1), GR minus uranium (track 2), Resistivity (track 3), Sonic log (track 4), Delta Log R TOC and core TOC with case 1 baseline (track 5), Delta Log R TOC and core TOC with case 2 baseline (track 6), Delta Log R TOC and core TOC.
Figure 5-15: Log view of GR log (track1), sonic log and resistivity log (track2) and core TOC (track3) showing three different baseline cases for the Delta Log R method in the Niobrara Formation.
5.6 Uranium Method

Meyer and Nederlof (1984) reported that organic content can be estimated by developing a correlation with uranium content. They postulated that organic rich intervals are uranium enriched because planktons absorb uranium ions that are present in seawater.

Organic shales are generally associated with elevated Gamma Ray (GR) activity due to the concentration of uranium in these sediments. Schmoker (1981) proposes main controls on shale radioactivity such as uranium content of water at time of deposition, type of organic matter deposited, water chemistry near the water-sediment interface and finally the rate of sediment deposition. It must be noted that the GR activity recorded is a response to the presence of uranium as opposed to kerogen and the quantity of uranium measured is dependent upon differences in kerogen types, water chemistry and sedimentation rate (Gonzalez et al., 2013). Since kerogen is generally associated to elevated uranium measurements, one can assume that the zones with higher GR readings or uranium readings are more TOC rich. This relationship, however, is not always linear and can vary from one organic shale to the other as it is a function of many other controls in addition to TOC. Moreover, differences in clay types (i.e. smectites) and quantity can have a radioactive effect on potassium and thorium content which in turn can elevate the GR reading. Therefore, GR spectral logs become important in evaluating shale systems. When analyzing GR logs, it is generally best to separate the GR log into a GR minus uranium log from spectral uranium logs. GR minus uranium logs can be used as clay indicators because they will be recording clay associated radioactivity while the uranium log will be recording TOC related radioactivity. Empirical relationships can be derived between uranium content and TOC; however, some errors may arise due to the presence of other uraniferous minerals like phosphates that could be misidentified as TOC and sedimentation rate effects (Jacobi et al., 2008). The Niobrara Formation contains trace amounts of phosphatic apatite.

5.6.1 Uranium Method in the Niobrara

Analysis of how the Niobrara total GR log and spectral uranium log compare to core TOC, shows that the total GR and spectral uranium logs mimic the core TOC log (Figure 5-16). GR and spectral uranium logs are high where core TOC is high and low where core TOC is low. This shows that these logs are most sensitive to the presence of TOC than any of the other open hole logs previously discussed.
A linear relationship exists between the spectral uranium log and TOC. Despite the presence of a linear relationship, low correlation coefficients could be attributed to data scatter caused by TOC sampling error (Figure 5-17A). Cross-plots between total GR and core TOC also show a similar linear trend with a better correlation coefficient ($R^2=0.32$) (Figure 5-17B). The better correlation of the GR log compared to the uranium log may be because it includes radioactivity from clays that are also associated to the TOC-rich, marly intervals.

The linear relationships defined between core TOC, spectral uranium log and GR were used to calculate TOC across the Niobrara Formation. The results for both GR and spectral uranium log methods correlate well with core TOC (Figure 5-18). Both the GR and spectral uranium logs present the best proxies for TOC in the Niobrara Formation as opposed to the other open hole logs. Calculating TOC using these two logs may be the optimal method of
obtaining TOC data in the Niobrara Formation. It must be noted that not a single set of
coefficients in the linear relationships defined between TOC, GR and spectral uranium logs
in one well will work for the other. These methods require a local calibration to core data
and the use of normalized logs.

Figure 5-17: (A) cross-plot between core TOC and spectral uranium showing a linear
relationship. (B) Cross-plot between core TOC and GR log showing a linear relationship.
Figure 5-18: log view of total GR (track1), GR minus uranium (track 2), spectral uranium log (track3), uranium spectral log TOC and core TOC (track 4), GR TOC and core TOC (track 5), XRD mineralogical data (track6), petrophysical mineral model (track 7).
CHAPTER 6
MINERAL MODELLING

Quantification of minerals and their compositions can help determine geochemical and geological processes in all types of rocks. This chapter discusses how mineralogy can be predicted or calculated from elemental data. A *Matlab* computer code, hereafter named “El Com”, will be introduced for normative analysis of mineralogy using linear programming and optimization in the Niobrara formation.

6.1 Introduction

Determining the mineralogy of rocks from their bulk composition is referred to as normative analysis. Normative analysis was initially applied to study igneous rock mineralogy by distributing elements present in igneous rocks into a series of hypothetical minerals that would be present in the rock. Available methods of quantifying mineralogy include point counting, image analysis and XRD analysis. These methods work adequately in estimating the mineralogy of the rock but may present limitations in terms of efficiency, accuracy, time, and cost effectiveness in fine grained mudrocks. These analyses tend to be semi-quantitative and do not produce quantitative mineralogical analyses for most rocks. Clay minerals are especially difficult to quantify because they commonly have various compositions. Moreover, individual members of clay mineral groups, like smectite, are generally difficult to differentiate using XRD analysis methods if present all together in rocks. These semi-quantitative methods when combined with chemical analyses may provide more valuable information. Cross et al. (1902) were the first to quantify mineral amounts from chemical analyses and introduced the concept of normative mineral calculations for igneous rocks. Other work that combines XRD and chemical analysis to determine mineralogy in clay bearing rocks was later performed (Imbrie and Poldervaart, 1959; Miesch, 1962; Pearson, 1978).

6.2 Linear Programming and Optimization

Linear programming can be defined as “mathematical method to allocate scarce resources to competing activities in an optimal manner when the problem can be expressed using a linear objective function and linear inequality constraints” (Ferguson, 1958). Linear programming in mineralogical analyses allows the distribution of the analyzed oxides or
elements into minerals according to a set of linear equations or functions which are solved simultaneously using mathematical algorithms that allow optimization. A linear function has the following form:

\[ a_0x_0 + a_1x_1 + a_2x_2 + a_3x_3 + \ldots + a_nx_n = 0 \quad \text{Eqn. (6.1)} \]

In general, ‘\( a_i \)’ represents the coefficients of the equation and are generally constant while ‘\( x_i \)’ are the variables of the equation that are allowed to take on a range of values within the limits defined by the constraints. The variables in a linear program are a set of quantities that need to be determined in order to solve the problem. The problem is solved when the best or optimum values of the variables have been identified and this is referred to as linear optimization.

To further illustrate the concept of linear optimization, consider the following hypothetical example of optimizing the amount of water ‘\( P \)’ that must be allocated to two different plants ‘\( x \)’ and ‘\( y \)’. Such a problem may be represented mathematically as a linear equation defined by the following function:

\[ P(x, y) = 60x + 80y \quad \text{Eqn. (6.2)} \]

To maximize this equation most of the water will be allocated to plant ‘\( y \)’. However, there exists some constraints where the volume of water allocated to plant ‘\( y \)’ can’t be more than twice that allocated for plant ‘\( x \)’ and less than 50 liters expressed by: \( y \leq 2x \), \( y \leq 50 \), other constraints may include \( x + y \leq 70 \). The constraints are graphically represented in Figure 6-1. The shaded area enclosed by the constraints is called the feasible region, which is the set of points satisfying all the constraints.

Consequently, when working with minerals and oxides, linear optimization seeks the best numerical solution to a set of linear equations that govern the distribution of oxides into minerals. Any linear programming problem requires an objective function that is to be maximized and is subject to constraints. A linear program consists of a set of variables, a linear objective function indicating the contribution of each variable to the desired outcome, and a set of linear constraints describing the limits on the values of the variables. A linear programming problem may be defined as the problem of maximizing or minimizing a linear
objective function ‘Z’ subject to a set of ‘n’ linear constraints. The constraints may be equalities or inequalities.

\[ Z = \sum_{j=1}^{m} (X_i) \quad \text{Eqn. (6.3)} \]

\[ b_i \geq \sum_{j=1}^{m} (a_{i,j}X_i), \quad (i = 1, n) \text{ and } X_j \geq 0, \quad (j = 1, m) \quad \text{Eqn. (6.4)} \]

Where \( X_j \) is the abundance in wt. % of mineral ‘j’ in the rock, \( b_i \) is the proportion in weight % of oxide of ‘i’ in the rock measured by chemical analysis, and \( a_{i,j} \) is the weight ratio of oxide of ‘i’ in mineral ‘j’ and is calculated using Eqn. 6.5.

\[ a_{i,j} = \frac{MW_i}{MW_j} \times \frac{S_{[i],j}}{S_{[j],i}} \quad \text{Eqn. (6.5)} \]

Where, \( MW_i \) and \( MW_j \) are the molecular weights of oxide of i and of mineral ‘j’, respectively, and \( S_{[i],j} \) and \( S_{[j],i} \) are the stoichiometric coefficients of element ‘i’ in mineral ‘j’ and of element ‘i’ in oxide of ‘i’, respectively. Eqn. 6.3 dictates that the total mineral abundances be maximized. Ideally, if all the elements were analyzed with absolute accuracy and the composition of all phases in the rock were known, ‘z’ should equal 100 wt. %. In practice, however, ‘z’ is generally less than 100 wt. %. Moreover, Eqn. 6.4 represents a greater than or equal relationship accounting for the fact that a proportion of the analyzed oxides may potentially be tied up in minerals that have not been considered. Therefore, in order to avoid ‘\( \geq \)’ relationships, or mixtures of inequalities and equalities, all oxide distribution equations (Eqn. 6.4) are transformed into equalities by introducing slack variables on the right-hand sides. The objective function also is altered to take these slack variables into account (Eqn. 6.6). Thus, the linear optimization problem becomes:

Maximize the objective function z:

\[ Z = \sum_{j=1}^{m} (X_i) - \sum_{i=1}^{n} (\lambda_i) \quad \text{Eqn. (6.6)} \]

Subject to a set of ‘n’ constraints and a set of ‘m + n’ basic constraints of the general form:

\[ b_i \geq \sum_{j=1}^{m} (a_{i,j}X_i) + \lambda_i, \quad (i = 1, n) \quad \text{Eqn. (6.7)} \]
\[ X_j \geq 0, \ (j = 1, m) \ \text{and} \ \lambda_i \geq 0, \ (i = 1, n) \quad \text{Eqn. (6.8)} \]

Where, \( \lambda_i \) is the slack variable for oxide of \( i \), and all other symbols are defined previously. The slack variable represents the amount of any oxide that can’t be accounted for, given the bulk rock geochemistry and mineral compositions provided. Therefore, the sum of the slack variables is an indication of how well the mineral compositions fit the rock's composition.

Figure 6-1: Graphical representation of a linear optimization problem subject to constraints.

Linear programming problems may be solved using various mathematical optimization algorithms such as simplex, dual simplex, interior point, and active-set algorithms. The active-set algorithm, however, reaches an optimal solution by minimizing the objective function at each iteration over a subset of constraints until it reaches a solution. Simplex algorithm method may be used to find the optimal solution to multivariable problems by examining corner points in a methodical fashion until it arrives at the best solution. All forms of the simplex method reach the optimum by traversing a series of basic solutions. Since each basic solution represents an extreme point of the feasible region, the track followed by the algorithm moves around the boundary of the feasible region. A new technique to solve linear programs was proposed by Karmarkar (1984) whose goal was to approach the optimal solution from the strict interior of the feasible region. This led to a series of interior point
methods that combined the advantages of the simplex algorithm and other algorithms. In this study, the interior point algorithm is used by “El Com”.

6.3 Niobrara Mineral Model

Using ICP-MS, XRF and XRD data a mineral model was constructed for the Aristocrat PC H11-07 well. This model calculates mineralogy in the Niobrara Formation from elemental ICP-MS or calibrated XRF data. This is performed using the constructed “El Com” Matlab code. This section will discuss the analytical tools used, the data inputs, methodology, and the results of the constructed mineral model.

6.3.1 Analytical Tools

Elemental and mineralogical data and their associated relationships must be understood in order to build a comprehensive mineral model. Elemental and mineralogical data can be extracted from rocks using various analytical methods including: XRF, XRD, and inductively coupled plasma mass spectrometry (ICP-MS) analyses. Each method has different advantages and disadvantages related to efficiency and accuracy. The Niton handheld XRF analyzer is a convenient, simple, and efficient tool for elemental analysis. XRF is a nondestructive technique that does not require lengthy sample preparation (Beckhoff et al., 2006). ICP-MS is also an analytical technique used to determine elements but in a more quantitative manner than the handheld XRF analyzer. Nelms (2005) provided a detailed account of the technique. Although considered very accurate compared to other methods such as XRF, sample preparation and measurement time is considerably longer. Despite relatively small sample size, this method is destructive. In ICP-MS, samples are introduced to the plasma as an aerosol using an analytical nebulizer, laser ablation, electrothermal vaporization, or torch vaporization. Plasma, commonly generated from argon gas, ionizes the sample. The ions are passed into the mass spectrometer and are separated based on mass-to-charge ratio. The detector measures the intensity of each element and reports it back to the user. ICP-MS analysis is very powerful tool for detecting and analyzing trace elements. Over the past years, ICP-MS has become the technique of choice in many analytical laboratories for providing the accurate and precise measurements needed for today’s demanding applications and for providing required lower limits of detection. Using ICP-MS data and a calibration table, semi-quantitative XRF data may be converted into
quantitative data (Row et al., 2012). Elemental data obtained using ICP-MS and XRF analysis can also be used to define various proxies of organic richness, paleo-productivity, and provenance of the rock.

6.3.2 Data

For this study, the Aristocrat PC H11-07 core was sampled and a representative sample of each facies present within the chalk and marl members of the Niobrara was collected. The samples were pulverized and homogenized in the lab and were sent to an outside vendor for XRD and ICP-MS analysis. Moreover, XRF analysis was performed using a Niton handheld XRF analyzer on the flat bedding surface of the rock samples collected. The XRD, ICP-MS, and XRF data collected on the samples is shown in Table A-8, A-9, and A-10, respectively in Appendix A. This data was used to understand the mineralogy of the Niobrara Formation and build a mineral model that predicts XRD mineralogy from elemental XRF or ICP-MS data.

6.3.3 Data Validation

The main objective of a mineral model is to predict mineralogy from elemental XRF or ICP-MS data. XRD analysis as described earlier is a semi-quantitative analysis and may report error in the calculated mineralogy. In order to validate the model’s mineralogical predictions, XRD mineralogical data must be used for comparison. Therefore, it becomes important for the reported XRD data to be valid and accurate and consistent with the ICP-MS data. For example, the amount of iron (Fe) measured in a sample using ICP-MS analysis must be equivalent to the total amount of Fe calculated in XRD reported Fe bearing minerals such as pyrite and illite. XRD data collected (Table A-8) were validated against ICP-MS data (Table A-9).

The total amount of each element in wt. % present in XRD reported mineral data was calculated and compared to the amount of that element in wt. % measured by ICP-MS analysis (Table A-11). It is difficult to know the exact mineral phases of the minerals and clays reported by XRD and so the basic, general mineral phase chemical formulas were considered in the calculations. The presence of clays such as illite or smectite can be problematic since they can have many different mineral phases or compositions compared to other minerals such as pyrite, quartz, and albite which have consistent mineral phases and
compositions. Calcite can also be problematic since there can be several phases of calcite that can vary from pure calcite to low-Mg to high-Mg calcite to dolomite. Figure 6-2 shows the difference between the calculated wt. % element from XRD data and that reported by ICP-MS for all the analyzed Niobrara samples. The maximum calculated deviation between both ICP-MS and XRD wt. % of element is 3.0 wt. % for calcium. Highest deviations were found in calculated Al, Fe and Ca from XRD in relation to that reported by ICP-MS. Such deviation could be attributed to the semi-quantitative nature of XRD analysis, difficulty in quantifying clays with XRD analysis, or could be due to the presence of different clay and calcite mineral phase compositions that have not been taken into consideration in the calculation.

![Figure 6-2: Difference between calculated wt. % element from XRD and that reported by ICP-MS for all the analyzed Niobrara samples.](image)

6.3.4 Data Analysis

The general mineralogy of the Niobrara Formation is consistent in terms of the types of minerals present. Their abundances, however, vary from one facies to the other and from one member of the Niobrara Formation to the other. The chalk members have generally higher carbonate content and less clay content than the marly members of the Niobrara Formation. The marls, however, are richer in clays and quartz. The main types of clays present within the Niobrara Formation are discrete illite clays and mixed layer illite–smectite
(Figure 6-3). This has been confirmed by XRD data, SEM analysis, and energy dispersive analysis (EDS) performed on the samples.

![Figure 6-3: FESEM X1500 SEI image of mixed layer illite-smectite layers surrounding a Foram and authigenic illite filling the Foram’s interior in the C chalk.](image)

Figure 6-3: FESEM X1500 SEI image of mixed layer illite-smectite layers surrounding a Foram and authigenic illite filling the Foram’s interior in the C chalk.

The main minerals present in the Niobrara and are to be solved for using the mineral model are calcite, illite, smectite, quartz, albite, dolomite, and pyrite. Chlorite and gypsum were only reported in one sample in the C chalk and another in the A chalk, respectively, and will not be considered as main mineral constituents of the Niobrara Formation.

Close relationships exist between major elements measured by XRF and ICP-MS analysis and common rock forming minerals identified using XRD analysis. This is expected since the primary control on whole rock inorganic geochemical data is the component of mineralogy. Relationships between XRF and ICP-MS elemental data and XRD mineralogical data must be understood to allow for a better understanding of which elements are contributing to which mineral phases within the mineral model (Figure 6-4).
Silica (SiO$_2$) measured by ICP-MS data should go into minerals that contain Si that are known to be present in the Niobrara including quartz, illite, and albite, a type of plagioclase feldspar. Cross-plots between ICP-MS SiO$_2$ and Si containing minerals show good correlation coefficients with illite and quartz that are greater than 0.7 (Figure 6-5). Albite, however, did not show a good correlation with the recorded SiO$_2$ by ICP-MS. This indicates that most of the SiO$_2$ measured by ICP-MS or XRF analysis is associated to illite and quartz present within the Niobrara Formation.

Calcium oxide (CaO) measured by ICP-MS analysis must contribute to the carbonate forming minerals identified within the Niobrara such as dolomite and calcite. Cross-plots between ICP-MS measured wt. % CaO and XRD wt. % dolomite and calcite show very high correlation coefficient ($R^2$) values greater than 0.9 with calcite as opposed to dolomite (Figure 6-6). This indicates that most of the CaO contributes to the formation of calcite in the Niobrara system. In addition, a negative trend is seen between ICP-MS wt. % CaO and wt. % dolomite. This trend could be associated to the replacement of Ca with Mg.

Alumina (Al$_2$O$_3$), as measured by ICP-MS, is generally associated with clay minerals (e.g. illite and smectite) and feldspars (e.g. albite). Al$_2$O$_3$ shows very good correlation coefficients, with illite showing an almost one to one relationship (Figure 6 7). This means that most of the Al$_2$O$_3$ or Al measured by ICP-MS or XRF is going into forming the illite clays as opposed to albite which shows a much lower correlation coefficient.
Figure 6-5: Cross-plots of wt. % ICP-MS SiO2 and the wt. % of silicon containing minerals within the Niobrara Formation: quartz, illite and albite respectively.

Figure 6-6: Cross-plots of wt. % ICP-MS CaO and the wt. % of Calcium containing minerals within the Niobrara Formation: Calcite and Dolomite respectively.

Figure 6-7: Cross-plots of wt. % ICP-MS Al2O3 and the wt. % of Al containing minerals within the Niobrara Formation: Albite and Illite respectively.
Iron oxide (Fe$_2$O$_3$) or iron (Fe) is also generally associated to clays, but also to the common sulfide pyrite. Fe$_2$O$_3$ measured by ICP-MS data shows good relationship with pyrite with an $R^2$ of 0.7 as opposed to illite that shows a lower $R^2$ value of 0.46 (Figure 6-8). Hence, the Fe$_2$O$_3$ being measured is mainly going into forming pyrite in the system and the remaining is going into the clays such as illite or smectite. Solving for pyrite first in the mineral model will allow the redistribution of the remaining iron into the clays. Moreover, since pyrite has a single known mineral phase FeS$_2$ as opposed to the clays which could have several different mineral phases, it is best to solve for the pyrite first.

Sodium oxide (Na$_2$O) measured by ICP-MS data is associated to minerals that contain sodium (Na) within the Niobrara such as albite and illite. A closer relationship is found between the Na$_2$O measured by ICP-MS and the amount of illite measured by XRD as opposed to albite (Figure 6-9). Most of the Na$_2$O is going into forming the illite in the system as opposed to the albite. Albite with a chemical formula of NaAlSi$_3$O$_8$ shows low correlation coefficients with Al, Na, and Si. XRD data shows that the concentration of albite is low (<5.0 wt. %) and the abundant presence of other aluminum silicates (e.g. illite) results in a low correlation coefficient for albite.

Potassium oxide (K$_2$O) and sulphur (S) are the limiting elements as to how much pyrite and discrete illite there is in the system. The only mineral that contains K in the system is illite and so all the K$_2$O measured by ICP-MS data must go into forming the illite clays as there are no other minerals in the system that require K in their mineral composition. Hence, there can only be as much illite in the system as there is K. In addition, there can only be as much pyrite as there is S in the system. This applies as pyrite is the only mineral present that requires S in its mineral composition. Hence, S and K$_2$O will act as constraints on illite and pyrite in the mineral model. Both K$_2$O and S show almost a one to one relationship with illite and pyrite respectively (Figure 6-11).

By evaluating correlations between ICP-MS or XRF data and XRD data, relationships may be defined and one can be used to predict the other in situations where mineralogy is not expected to vary much across the basin. Where $R^2$ values between a mineral and an element exceeds 0.8, the linear regression between the two can be used to model mineral abundances within that well (Ratcliffe et al., 2010).
Figure 6-8: Cross-plots of wt. % ICP-MS Fe2O3 and the wt. % of Fe containing minerals within the Niobrara Formation: pyrite and illite respectively.

Figure 6-9: Cross-plots of wt. % ICP-MS Na2O and the wt. % of Na containing minerals within the Niobrara Formation: Illite and albite respectively.

Figure 6-10: Cross-plots of wt. % ICP-MS MgO and the wt. % of Mg containing minerals within the Niobrara Formation: Illite and dolomite respectively.
6.3.5 XRF Data Calibration

As previously mentioned, XRF data is a semi-quantitative indicator of elements present within a rock. ICP-MS data, however, quantifies elements in a more robust, quantitative and accurate manner. Cross-plots of ICP-MS against XRF measured elements can be used to identify relationships between the two measurements that can be used to convert one into the other. Where, $R^2$ values between elements measured by both analyses exceeds 0.8, ICP-MS data can be used to calibrate XRF semi-quantitative measurements into a more quantitative measurement (Nakamura pers. comm., 2015). Figure 6-12 shows the $R^2$ values between the major elements measured by ICP-MS and XRF analysis in this study. All major elements S, Ti, Mn, Fe, K, Si, Ca, and Al show correlation coefficients greater than or equal to 0.8 indicating an almost one to one relationship between XRF and ICP-MS measured elemental data (Figure 6-12). Mg, however, shows a lower $R^2$ value of 0.5 indicating that the Mg readings are less reliable than the other elements. Na is not included in the list as it is one of the elements that the Niton handheld XRF analyzer does not measure. XRF data was recalibrated to ICP-MS data before using it in the mineral model using the relationships shown in (Figure 6-12).
6.3.6 Methodology

As described in Section 6.1, linear programming is a method that seeks the best numerical solution to a set of linear equations that govern the distribution of oxides into minerals. These set of linear equations may be expressed as a function of the element oxide measured by ICP-MS analysis and the minerals being solved. Several normative analysis programs had been developed in the past for normative analysis of sedimentary rocks (Caritat
et al, 1994; Cohen et al., 1991; Merodio et al. 1992). Caritat et al. (1994) developed a normative analysis FORTRAN program called LPNORM and applied it to the Bersham mudstone and provided a detailed account of the program, how it works and the linear optimization/programming theory behind it and its applicability. This section applies similar concepts as proposed by Caritat et al. (1994) in a Matlab code “El Com” that performs a similar task in predict mineralogy in the Niobrara Formation.

In order to illustrate the concept of how the proposed mineral model “El Com” works, let us first consider a fictional rock that has reported ICPMS calculated composition of 40 wt. % SiO$_2$, 30 wt. % CaO, 25 wt. % Al$_2$O$_3$ and 5 wt. % K$_2$O and XRD identified mineral compositions of muscovite of known composition (KAl$_3$Si$_3$O$_10$(OH)$_2$), kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) quartz (SiO$_2$), and calcite (CaCO$_3$). This linear programming problem at hand, based on the equations introduced in section 6.1, can be stated as thus:

Maximize the objective function:

Eqn. (6.9)

$$ z = \text{quartz} + \text{calcite} + \text{muscovite} + \text{kaolinite} - \lambda_{\text{SiO}_2} - \lambda_{\text{Al}_2\text{O}_3} - \lambda_{\text{CaO}} - \lambda_{\text{K}_2\text{O}} $$

Where, $\lambda_{\text{SiO}_2}, \lambda_{\text{Al}_2\text{O}_3}, \lambda_{\text{CaO}}, \lambda_{\text{K}_2\text{O}}$ represent slack variables introduced to the objective function to represent the amount of any oxide that cannot be accounted for, given the bulk rock geochemistry and mineral compositions provided. Quartz, calcite, muscovite, and kaolinite represent the mineral abundances (in wt. %) of those minerals in the rock, subject to the following constraints:

Eqn. (6.10)

$$ 40 = (a_{\text{SiO}_2, \text{quartz}} \times \text{quartz}) + (a_{\text{SiO}_2, \text{muscovite}} \times \text{muscovite}) + (a_{\text{SiO}_2, \text{kaolinite}} \times \text{kaolinite}) + \lambda_{\text{SiO}_2} \quad (1) $$

$$ 30 = (a_{\text{CaO, calcite}} \times \text{calcite}) + \lambda_{\text{CaO}} \quad (2) $$

$$ 25 = (a_{\text{Al}_2\text{O}_3, \text{muscovite}} \times \text{muscovite}) + (a_{\text{Al}_2\text{O}_3, \text{kaolinite}} \times \text{kaolinite}) + \lambda_{\text{Al}_2\text{O}_3} \quad (3) $$

$$ 5 = (a_{\text{K}_2\text{O, muscovite}} \times \text{muscovite}) + \lambda_{\text{K}_2\text{O}} \quad (4) $$
In other words, the proposed problem in the previous example may be re-written in a matrix form \( A \times X = B \). Where, ‘A’ represents a matrix of the \( a_{i,j} \) coefficients, ‘X’ represents a matrix of minerals to be solved for (calcite, quartz, kaolinite, and muscovite in Wt. %) and ‘B’ represents a matrix of ICP-MS or XRF measured elements or element oxides (SiO\(_2\), CaO, Al\(_2\)O\(_3\), K\(_2\)O in wt. %) that are to be allocated to the different mineral phases present as shown in Eqn. (6.11). The set of linear equations (Eqn. (6.10)) may also be expressed in a matrix form as follows:

Eqn. (6.11)

\[
\begin{bmatrix}
    a_{SiO2,quartz} & a_{SiO2,muscovite} & a_{SiO2,kaolinite} & 0 & 0 \\
    0 & 0 & 0 & a_{CaO,calcite} & 0 \\
    0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\begin{bmatrix}
    \text{quartz} \\
    \text{muscovite} \\
    \text{kaolinite} \\
    \text{calcite} \\
\end{bmatrix}
= \begin{bmatrix}
    SiO2 - \lambda_{SiO2} \\
    CaO - \lambda_{CaO} \\
    Al2O3 - \lambda_{Al2O3} \\
    K2O - \lambda_{K2O} \\
\end{bmatrix}
\]

The \( a_{i,j} \) coefficients represent the weight ratio of oxide of ‘i’ in mineral ‘j’, \( MW_i \) and \( MW_j \) are the molecular weights of oxide of ‘i’ and of mineral ‘j’, respectively, and \( S_i \) and \( S_j \) are the stoichiometric coefficients of element ‘i’ in mineral ‘j’ and of element ‘i’ in oxide of ‘i’, respectively. \( a_{i,j} \) coefficients defined in Eqn. (6.10) are calculated as follows:

\[
a_{SiO2,quartz} = \frac{MW_{SiO2}}{MW_{Quartz}} \times \frac{S_{SiO2,Quartz}}{S_{Si,SiO2}} = \frac{60.8}{60.8} \times \frac{1}{1} = 1.0000
\]

\[
a_{SiO2,muscovite} = \frac{MW_{SiO2}}{MW_{muscovite}} \times \frac{S_{SiO2,muscovite}}{S_{Si,SiO2}} = \frac{60.8}{398.315} \times \frac{3}{1} = 0.4579
\]

\[
a_{SiO2,kaolinite} = \frac{MW_{SiO2}}{MW_{kaolinite}} \times \frac{S_{SiO2,kaolinite}}{S_{Si,SiO2}} = \frac{60.8}{258.16} \times \frac{2}{1} = 0.4655
\]

And also subject to the following basic constraints:

\[
\text{quartz} \geq 0, \quad \text{muscovite} \geq 0, \quad \text{kaolinite} \geq 0, \quad \text{calcite} \geq 0,
\]

\[
\lambda_{SiO2} \geq 0, \quad \lambda_{CaO} \geq 0, \quad \lambda_{Al2O3} \geq 0, \quad \lambda_{K2O} \geq 0
\]

Using the specified constraints, a linear program in this example would solve the linear equations (Eqn. (6.10)) simultaneously using an optimization algorithm to calculate the amount of quartz, kaolinite, muscovite, and calcite that provide an optimal solution to the
linear problem. This is done by maximizing the predicted wt. % of minerals close to a 100% while minimizing the slack variables (i.e. error) as close to zero as possible in the objective function (Eqn. (6.9)).

For mineral modelling of the Niobrara a similar approach was applied. A Matlab code “El Com” was written to allow the user to specify the ICP-MS or XRF inputs and perform similar calculations as demonstrated by the example to predict mineralogy in the Niobrara Formation. ICP-MS data collected from the Niobrara Formation was used and input into the model. ICP-MS measures the major element oxides that are known to contribute to the mineral composition of minerals identified by XRD analysis. Such element oxides include: MnO, MgO, CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, Na$_2$O, and K$_2$O. P$_2$O$_5$ and TiO are also measured by ICP-MS analysis but may be ignored as they don’t directly contribute to the chemical composition of minerals identified by XRD analysis. Level of ignition (LOI) is another measurement made by ICP-MS analysis that is ignored. It represents the wt. % of gases and fluids (ex. CO$_2$ and H$_2$O) that have been removed from the rock during analysis. With P$_2$O$_5$, TiO and LOI data removed from the ICP-MS inputs to the model, the remaining oxides must be re-normalized to sum to 100 wt. %. “El Com” takes the ICP-MS or calibrated XRF data specified by the user and renormalizes them to a 100 wt. %. XRD data collected on the Niobrara samples show that the minerals expected to be present within the Niobrara formation that the model needs to predict are calcite, quartz, dolomite, albite, illite-smectite clays, and pyrite. Those minerals are specified in the model to govern the code’s distribution of element oxides or elements into minerals. With eight input elements to be distributed over 7 minerals, the problem may be expressed as an A* X = B matrix problem with ‘A’ representing a 7×8 matrix as shown in Eqn. (6.12). It must be noted that if the user, for example, specifies 8 oxide inputs represented by 8 linear equations, he may only solve for 8 or less unknowns or minerals.

Eqn. (6.12):

$$ A \times X = B $$
To solve this matrix problem and optimize it an objective function ‘z’ must be defined.

Eqn. (6.13)

\[ z = \text{Quartz} + \text{Calcite} + \text{Dolomite} + \text{Illite} + \text{Pyrite} + \text{Ankerite} + \text{Albite} \]

\[ -\lambda_{\text{SiO}_2} - \lambda_{\text{Al}_2\text{O}_3} - \lambda_{\text{Fe}_2\text{O}_3} - \lambda_{\text{MgO}} - \lambda_{\text{Na}_2\text{O}} - \lambda_{\text{CaO}} - \lambda_{\text{K}_2\text{O}} - \lambda_{\text{MnO}} \]

The constraints to this optimization problem will be the set of linear equations defined by the matrix \( A^*X = B \) in addition to the following basic constraints:

\[ \text{Quartz} \geq 0, \quad \text{muscovite} \geq 0, \quad \text{kaolinite} \geq 0, \quad \text{calcite} \geq 0, \]

\[ \lambda_{\text{SiO}_2} \geq 0, \quad \lambda_{\text{CaO}} \geq 0, \quad \lambda_{\text{Al}_2\text{O}_3} \geq 0, \quad \lambda_{\text{K}_2\text{O}} \geq 0 \]

“El Com” computer code was first validated by running it on previously published datasets of the Bursham mudrock from the Caritat et al. (1994) LPNORM study. The results were compared to the LPNORM generated results published in Caritat et al. (1994). The same results were obtained which suggests that the algorithm and the optimization method used in “El Com” is working reliably. The LPNORM code uses dual simplex algorithm for its optimization method. In this study, however, the interior point algorithm will be used instead as it is more sophisticated in reaching optimal solutions.
Next it becomes a matter of understanding the minerals and mineral compositions that are present in the Niobrara and must be solved for by “El Com”. Minerals with varying mineral compositions and phases such as clays were further studied and characterized using a JEOL JSM-7000F FESEM and an EDAX Genesis Energy Dispersive Spectroscopy (EDS) to get a better understanding of their mineral phases. Minerals to be solved for, their mineral phases and ICP-MS data were input into “El Com”. Through linear programming and optimization, mineralogy was calculated and validated against available core XRD data. Since clays have varying mineral compositions, trial and error sensitivity analysis was performed until the calculated total clays by the model matched the XRD total clays. After the model was constructed using ICP-MS data it was then applied to calibrated XRF data.

6.4 Results and Discussion

Calcite and quartz having constant mineral compositions are less problematic to calculate than illite and smectite. The intrinsic chemical variability of minerals like clays adds a measure of uncertainty to the results. Moreover, XRD chemical analysis of clays represents a source of error as they are difficult to evaluate. Analysis of clay minerals using XRD analysis is considered excellent if the results are accurate to about 10% of the amount present (Reynolds, 1989). A detailed XRD analysis of clays would be required for accurate clay modelling.

Based on XRD analysis, the minerals that were solved for by “El Com” are calcite, quartz, dolomite, pyrite and illite-smectite clays. Albite has been removed from the model because it did not correlate well with any of the elemental data and its presence will add to the complexity of the model. Moreover, it will impact the distribution of Al and Na in the illite and smectite clays. Illite and smectite were added to the model as separate minerals as FESEM and XRD analysis confirmed the presence of a mixed layer illite smectite. Detailed clay XRD analysis dataset was not available on the studied samples. Only bulk XRD analysis data was available for comparison with “El Com” calculated mineralogy.

“El Com” mineralogical results were grouped into total carbonates, total clays, quartz and pyrite and were compared to available XRD data. Lack of detailed clay XRD data makes it difficult to accurately quantify the different types of clays present using “El Com”. Since illite and smectite clays have varying mineral phases and compositions, EDS work was
performed to confirm their types and estimate their mineral phases. EDS results confirmed the presence of discrete illite platelets and mixed layer illite-smectite clays. High Si, Al and K peaks coupled with smaller peaks of Mg and Fe suggests the presence of discrete illite. Discrete illite has the general chemical formula of \((K, H_3O) (Al, Mg, Fe)_2(Si, Al)_4O_{10}[OH]_2(H_2O)\). Some matrix illite spectrums were also coupled with small Ti and Mo peaks indicating their detrital origin. Authigenic illite forming on foraminifera surfaces did not show the Ti and Mo peaks (Figure 6-3). Lack of any K-spars suggests that the potassium in the system is going into forming the illite. And so it was used to limit the amount of discrete illite solved for by the model. In addition to discrete illite, mixed illite and smectite layers were identified. High Si, Al peaks coupled with smaller K, Fe, Mg and Na peaks suggesting the presence of mixed illite-smectite layers.

To get a better estimate of the clays, discrete illite and smectite were solved for separately and the resultant summation of both was compared to available XRD total clays data. Sulphur was also used as a constraint on the amount of pyrite present in the system. The minerals that can be constrained such as discrete illite and pyrite were solved for first so that any remaining elements are redistributed into other minerals solved for by the model. The calculated pyrite by “El Com” was refined by redistributing the Fe into the clays until an acceptable match was achieved between XRD pyrite and “El Com” calculate pyrite. A sensitivity analysis was performed on the clays and different chemical formulas were used in the model until the results were somewhat satisfactory.

The mineralogy calculated by “El Com” was comparable to available XRD data for calculated total carbonates, pyrite and quartz. Figure 6-13 shows the calculated mineralogy by “El Com” compared to the reported XRD mineralogy. Cross-plots of total carbonates, pyrite and quartz correlate well with XRD data. The calculated total clays were less than that reported by XRD analysis. This is also coupled with pyrite being over predicted by “El Com” in a few samples. The trends obtained for pyrite and total clays can be explained by more Fe being assigned into forming the pyrite than the clays. Hence, knowledge of clay composition and mineral phases could help eliminate this problem.
Results suggest that linear optimization is a viable, efficient and a quick method for calculating mineralogy from elemental data. “El Com” can be further refined or constrained for better clay results by incorporating surface area data. This will help in constraining the clays and improve their quantification. Clay minerals, particularly swelling clays (e.g. smectite), generally have greater surface areas than non-clay minerals (Table 6.1).

Table 6.1: Surface area of common clay minerals and fine grained sand (Passey et al., 2010).

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>Internal Surface Area (m²/g)</th>
<th>External Surface Area (m²/g)</th>
<th>Total Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectite</td>
<td>750</td>
<td>50</td>
<td>800</td>
</tr>
<tr>
<td>Illite</td>
<td>0</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Fine Quartz Sand</td>
<td>0</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>
CHAPTER 7

STORAGE CAPACITY

This chapter studies the porosity of representative Niobrara Formation chalk samples using a standardized Water Immersion Porosimetry (WIP) technique by Kuila (2013). In addition, pore-size distribution will be studied using nitrogen adsorption tests in order to understand the pore network within the chalks in the Niobrara Formation. Field Emission Scanning Electron Microscope (FESEM) work performed on the same samples will characterize the texture of the pore spaces present.

7.1 Introduction

Porosity is defined as the “fraction of the bulk volume of the porous sample that is occupied by pore or void space” (Dullien, 1991). This definition, however, becomes more complex when dealing with unconventional mudrock systems.

In order to characterize and understand pore structure, two measurements are required. These include porosity and pore size distribution. Porosity represents a “single–value quantification” that describes the general volume of pore spaces present (Nimmo, 2004; Kuila, 2013). It does not account for heterogeneities in pore sizes and structure. Pore size distribution gives a representation of the pore network and pore sizes present.

Permeability is generally expressed as a function of porosity. A linear relationship is assumed between both variables with an increase in porosity leading to an increase in permeability. In mudrocks and carbonate systems such as the Niobrara Formation, such models tend to show nonlinear variability caused by diagenesis, micro-fractures, high clay content and very low permeability. Pore size distribution, however, does account for all these factors and is, therefore, an important property to understand in carbonate mudrock systems. In general, there is no relationship between porosity and permeability in carbonate mudrocks unless pore-size distribution is included and understood.

7.2 Porosity Quantification

The term ‘total porosity’ is defined as total water–accessible porosity. ‘Effective porosity’ is defined as total porosity minus the clay-bound water. Despite the commercial
importance of mudrock formations, measuring total porosity in core samples remains challenging. The lack of an accurate measurement technique can lead to significant uncertainties in assessing these plays. Direct porosity measurements in mudrocks is complicated by the fine grained texture, the presence of extremely small pore sizes (often <10 nm), nanodarcy range permeability, and the strong interaction of water molecules with the clay mineral surfaces and associated exchangeable cations. Nanodarcy permeabilities make traditional core measurement techniques extremely difficult. To overcome these problems, Luffel & Guidry (1989) suggested a crushed rock methodology to obtain total porosity in such tight rocks. This technique has been adopted by the industry for routine shale core analysis and is referred as the GRI (Gas Research Institute) technique.

In the GRI method, bulk density is measured by mercury immersion using Archimedes’ Principle on a large (~300 g) block of intact untreated core material. The sample is then crushed in order to accelerate the extraction and pretreatment stages and also to facilitate complete invasion of helium in the pore space during the subsequent grain volume measurement. The crushed sample is solvent extracted with hot toluene using the Dean Stark method, and then dried in an oven at 200°C. Grain volume of the crushed material is measured by helium pycnometry using Boyle’s law. Difference between bulk volume and grain volume represents pore volume or total porosity.

The aggressive sample treatment in the GRI technique and the lack of a standardized protocol can reduce the accuracy of GRI results (Karastathis, 2007; Passey et al., 2010; Sondergeld et al., 2010, Spears et al., 2011). Significant discrepancies exist in porosity and grain density values of comparable samples measured by different commercial laboratories using the GRI method. These discrepancies are attributed to different and often undisclosed experimental procedures. The reported deviation in GRI porosity measurements between different laboratories range from 0.5 porosity unit (p.u.) (Karastathnis, 2007; Passey et al., 2010) to 1.5 p.u. (Sondergeld et al., 2010; Spears et al., 2011).

Inconsistent crushing, sample handling procedures, and measurement techniques can introduce such discrepancies. Moreover, these clay bearing rocks have high hydration potentials and abundant microporosity making them sensitive to changes in the relative humidity of the environment. An unknown quantity of water molecules may be adsorbed or
desorbed during an uncontrolled experiment due to the hydration capacity of clays and the condensation potential of micropore systems in moderate relative humidity (Kuila, 2013). This can significantly affect the measured grain density (Figure 7-1) and produce even greater uncertainties in porosity calculations. Figure 7-1 shows the discrepancy between whole rock grain density measured by helium pycnometry of the samples, preheated at 200°C, when kept dry under a controlled vacuum chamber compared to when equilibrated to room conditions.

![Figure 7-1: Effect of humidity on grain density measurements (Kuila, 2013).](image)

Another disadvantage of most GRI protocols is that they require crushing a large mass of valuable core material (~300 g) which results in small mass loss during the crushing procedure (Kuila, 2013). Moreover, fluid extraction using Dean Stark procedures can result in dissolved solid bitumen which could result in artificial porosity that results in higher grain density measurements (Kuila, 2013).

### 7.2.1 Water Immersion Porosimetry (WIP)

An alternative, immersion based porosity measurement technique was standardized by Kuila (2013) to measure porosity in mudrocks. The saturation and immersion technique determines porosity by saturating a sample with a liquid with known density, and calculating the pore volume from the weight difference between the fully saturated and dehydrated states. The total volume of the sample is determined using Archimedes’ principle. Bulk density, grain density, and porosity are determined from the same experimental sample. The choice of
saturating fluid in such immersion techniques becomes important as the accuracy of porosity measurements would depend on the saturating fluid that will efficiently saturate the entire pore network and be stable in laboratory conditions (Melnyk & Skeet, 1986; Kuila, 2013). Saturating fluids require low surface tension and low viscosity to allow as much saturation as possible (Kuila, 2013). Moreover, they require to be stable with low reactivity with the porous material they saturate and have known densities. The WIP technique employs the use of de-ionized water as it has distinct advantages in saturating mudrocks that would have significant clay mineral content and cation exchange capacity (Kuila, 2013). The polar nature of water molecules has a strong affinity for exchange cations and the high specific surface area of clay minerals. Thus, saturating the pore system with water molecules is ideal because water will penetrate small pores and capillaries associated with clay mineral aggregates. The simplicity of WIP methodology makes it especially attractive for routine mudrock core total porosity measurements.

7.3 Pore Size Distribution (PSD) Quantification

The pore-structure of a porous media influences properties such as elastic and mechanical behavior and fluid flow through that porous media. Pore structure and pore size distribution must be well understood for appropriate modeling of porous media behavior. Total porosity, as described earlier, is a ‘single-value quantification’ (Nimmo, 2004; Kuila, 2013) and does not provide insight into textural and morphological aspects of the pore-structure. Pore–size distribution (PSD) of a rock is a quantitative indicator of the relative volume associated to a specific pore size. The recommended classification of pore sizes by the International Union of Pure and Applied Chemistry [IUPAC] as proposed by Sing et al. (1985) and Rouquerol et al. (1998) is as follows:
1. Micropores: pores with pore-size below 2 nm (0.02 um)
2. Mesopores: Pores with pore-size between 2 nm (0.02um) to 50 nm (0.5 um)
3. Macropores: Pores with pore-size greater than 50 nm (0.5um)
Loucks et al. (2012) provided a modified classification of pore-size for mudrock pores. He introduced new pore classes such as a picopore defined as being less than 1 nm (0.01um) and a nanopore defined as being equal to or greater than 1 nm (0.01um) and less than 1 um (Figure 7-2).
Mudrocks exhibit multiple, complex pore–structures compared to conventional reservoir rocks. Advanced imaging techniques on mudrocks show the presence of nanometer scale pore structures within clays and organic matter (Loucks et al., 2009; Passey et al., 2010; Curtis et al., 2011; Curtis et al., 2012; Milliken et al., 2013). In addition to PSD, another important pore-structure parameter to describe porous media is specific surface area expressed as surface area per unit mass of sample. Smaller pores have higher specific surface areas. Therefore, nanoporous materials such as mudrocks typically possess large specific surface areas.

Characterization of pore space has been generally based on imaging techniques such as FESEM. FESEM provides a qualitative visual description of pore space but cannot resolve pores smaller than 5 nm and thus cannot image a significant portion of the pore structure (Chalmers et al., 2012). Most mudrocks including the Niobrara Formation contain pore spaces that are less than 5 nm. Such pore size distributions and specific surface areas of mudrocks may be quantified using several methods. The two most popular and widely used methods are mercury intrusion porosimetry (MIP) and N$_2$ gas adsorption. Historically, MIP has been the preferred technique for pore-size analysis of macroporous conventional reservoirs. However, in tight, microporous, unconventional mudrock systems MIP deforms the rock matrix and reports error in readings. Gas adsorption techniques are widely used in
the soil, chemical, and ceramic industries to characterize the pore structures and surface areas of powders and fine particles. Subcritical N\(_2\) gas adsorption techniques can be used to investigate fine pores in the range of 1.7–200 nm that are prevalent in mudrocks (Kuila, 2013). N\(_2\) gas adsorption cannot, however, resolve macropores greater than 200nm in size.

### 7.3.1 Nitrogen Adsorption Theory

Adsorption may be defined as the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. Adsorption experiments can be done with different gases and at different pressure-temperature conditions (Kuila, 2013). Lower temperatures and higher pressures make the adsorption process more prominent and easier. Adsorption studies conducted at higher pressures, where the gas is in supercritical phase, give information about the nature of surface and its adsorption potential of gases. It does not, however, give information about pore-sizes since the gas does not reach the condensation phase at such supercritical, high pressure conditions (Kuila, 2013). In low pressure adsorption experiments the temperature-pressure regime is kept below the critical fluid phase. These experiments yield valuable information about the textural properties of porous material, such as surface area and pore structure. Since the gas is below its critical point, capillary condensation becomes important in these experiments which give us the information of pore–sizes. Nitrogen gas (at 77K) is the most commonly used gas for surface area and mesopore characterization, however, alternative gases can also be used, such as krypton (at 77K), argon (at 87K), carbon dioxide (at 273 K). For this study subcritical N\(_2\) gas adsorption at liquid nitrogen temperature and sub-atmospheric pressure is used for characterizing surface area and pore-structure of the Niobrara Formation.

### 7.3.2 Interpretation of N\(_2\) Isotherms

Kuila (2013) provided a detailed account of the different shapes of isotherms and hysteresis patterns associated to different pore types. The shape of the isotherm and its hysteresis pattern collected during N\(_2\) adsorption experiments can provide useful information on the adsorption process and the pore size distribution within the rock. A detailed account of adsorption isotherms and hysteresis patterns was provided in Sing et al. (1985) and Rouquerol et al. (1998). They described six types of adsorption isotherms (Type I to VI), along with four hysteresis pattern types (H1 to H4). The different hysteresis patterns H1 to
H4 are characteristic of different mesopore shapes according to the Rouquerol et al. (1998) pore size classification. A detailed description of the IUPAC isotherm classification is presented in Sing et al. (1985) and Rouquerol et al. (1998). Three isotherm patterns described by Rouquerol et al. (1998) are relevant to mudrock pore systems and are described in Figure 7-3. For isotherm interpretations in this study, Rouquerol et al. (1998) pore size classifications will be used.

Sing et al. (1985) and Rouquerol et al. (1998) describe a type I isotherm which shows that a purely microporous adsorbent will exhibit a concave-shaped isotherm with very high adsorption at low relative pressure (P/P₀<0.01) before it reaches a plateau (Figure 7-3a). This isotherm behavior is due to micropore filling and the limiting uptake (plateau) depends on the cumulative accessible micropore volume present in the sample. Type II isotherm shows that a non-porous or a macroporous material will exhibit a completely reversible isotherm (Figure 7-3b) where the adsorption and desorption process follow exactly the same path. These isotherms initially have a concave shape at lower relative pressures (P/P₀<0.2), followed by a linear region and finally a convex shape at higher relative pressure (P/P₀>0.4). This isotherm profile represents a monolayer-multilayer adsorption mechanism of the gas on the open and stable solid surface (Kuila, 2013; Rouquerol et al., 1998). The concave part at low relative pressure indicates a relatively high heat of adsorption resulting in molecules adsorbed into a layer one molecule thick. The sharp inflection point at the transition between the concave and the linear part of the isotherm is considered to represent the completion of monolayer coverage and beginning of multilayer coverage. The amount adsorbed at this point is directly related to the surface area of the solid. The third important isotherm is the Type IV isotherm which shows that a dominantly mesoporous material will have a characteristic hysteresis loop (Figure 7-3c) which is associated with capillary condensation and evaporation taking place in mesopores. At lower relative pressure (P/P₀<0.4) the isotherm profile is similar to the Type II isotherms indicating a monolayer to multilayer adsorption mechanism on the walls of meso and macropores. At higher relative pressures, the gas condenses in the mesopores to bulk liquid at pressures below the saturation vapor pressure with the formation of a gas–liquid meniscus due to capillary condensation. The isotherms profile exhibit a plateau with reduced adsorption at high P/P₀. The limiting
adsorption plateau at high P/P₀ indicates complete filling of mesopores and subsequent adsorption on the external surfaces.

Figure 7-3: Typical isotherm shape exhibited by (a) purely microporous material; Type I isotherm profile (b) non-porous and macroporous material; Type II isotherm profile and (c) purely mesoporous materials; Type IV isotherm profile (Kuila, 2013, Modified from Sing et al., 1985).

The characteristic H₁ to H₄ hysteresis patterns (Figure 7-4) as described by Sing et al., 1985 result from different mesopore shapes. The H₁ hysteresis loop (Figure 7-4 a) types are mainly seen in materials with a narrow distribution of cylindrical or tubular pores. The H₂ hysteresis (Figure 7-4 b) types indicate a complex, interconnected pore structure with narrow pore openings. The H₃ hysteresis loop (Figure 7-4 c) types are mostly found in materials with platy particles having slit-shaped pores. The H₄ hysteresis loop (Figure 7-4 d) types also result from slit-shaped pores, but are associated with micropores in general.

Figure 7-4: The four characteristic hysteresis shapes of adsorption isotherm usually found by subcritical N₂ adsorption (Kuila, 2013, Modified from Sing et al., 1985).
Isotherms with characteristics of more than one Type such as the mixed Type I/IV and mixed Type II/IV do not fit into any of the above classifications and exhibit a distinctive isotherm shape classified as Type IIB (Rouquerol et al., 1998), which is characteristic of mudrocks such as the Niobrara Formation (Figure 7-5). Another important feature observed in many hysteresis patterns is the forced closure of the desorption branch where the isotherm ‘closes’ at P/P₀ relative pressures around 0.41–0.48 for N₂ isotherms (Figure 7-5). The presence of ‘forced closure’ in the isotherm shape may indicate a significant volume of pores with diameters smaller than 4 nm (Kuila, 2013).

Figure 7-5: Type IIB, N₂ adsorption isotherm of a representative mudrock sample from the Haynesville Formation (Kuila, 2013).

7.4 Textural Characterization of Pore Spaces

Mudrocks remain poorly understood compared to conventional reservoirs due to their complex pore systems that vary between mudrock systems within the same play. Mudrocks were known to contain organic matter but it was not until the discovery of pores in the organic matter using ion milling and FESEM that the organic matter was considered a contributor to the porosity network (Loucks et al., 2009). As previously discussed, the pore type, size, connectivity, structure and surface area are important parameters that affect a mudrock’s ability to generate, store, and produce hydrocarbons. Electron microscopy techniques are widely used to examine rocks and their associated pore networks on a nano-scale because of their high resolution. In this study, scanning electron microscopy (SEM) techniques were also used for visual understanding and characterization of pore systems within the Niobrara.
Loucks (2012) pore size classification is used to describe pores in this section (Figure 7-2). Loucks et al. (2012) provided a review of the spectrum of pore types and networks that are present in mudrock systems. He grouped pores into matrix related pores (interparticle and intraparticle pores), organic pores and fracture pores. Organic matter pores are pores that are present within organic matter. Such pores have been reported in various mudrock systems (Curtis, 2012; Loucks, 2012) and have been described to be effective due to their oil wettability (Passey, 2010). Matrix related pores, however, can be of two types: Interparticle or intraparticle. Interparticle pores are pores present between grain particles or crystals, while intraparticle pores are present within the minerals or crystals themselves. Mudrocks may contain one dominant pore type or a combination of pore types. Understanding the types, abundances, distribution, and spatial interrelationships of each pore is important as each type may contribute to permeability differently.

### 7.5 Experimental Procedures

This section summarizes the experimental procedures and methods used in acquiring total porosity measurements using the WIP experiment, pore size distribution using nitrogen adsorption tests and finally evaluating pore texture using FESEM analysis.

#### 7.5.1 WIP Experimental Procedure

Kuila (2013) provided a good, detailed review of the WIP technique and its experimental procedure. He proposed a standardized procedure that was followed in this study. Figure 7-6 summarizes the experimental procedure followed in the WIP experiment.

Four to six grams of rock chips were used per sample and were degassed in vacuum at 200°C for two days to expel any adsorbed gases or water. The dry weight of the samples (DryWt.Air) was measured in a moisture analyzer Mettler Toledo HB43™ with 0.1 mg readability. Samples were heated at 200°C for 15 minutes and dry weight recorded at the end of heating cycle. Use of a moisture analyzer and measuring the dry weight at the 200°C condition prevents readsorption of moisture from the air during the dry weight measurement after drying in the oven. After the samples we dehumidified and weighed, they were taken into a Vinci Manual pressure saturator™ connected to an ultra-high vacuum pump to evacuate the air in the sample prior to the introduction of water to ensure maximum possible
saturation. A vacuum was pumped and de-ionized water was allowed to flow in overnight under a pressure difference of 2000psi to saturate the samples. The samples were then immersed in de-ionized water for 24 hours. Using a high-precision jolly balance, with an accuracy of up to 0.01mg, weights of samples in air and submerged in water were measured for bulk density calculations. The saturated samples were weighed three times while submerged in a beaker of de-ionized water (Sat.Wt.Sub) and in air (Sat.Wt.Air) and water temperature was recorded.

The total porosity of any sample measured by WIP (φWIP) is determined by the relationship:

\[ \phi_{WIP} = \frac{\rho_{B} - \rho_{G}}{\rho_{H2O} - \rho_{B}} \times 100 \quad \text{Eqn. (7.1)} \]

Where, \( \rho_{G} \) is the grain density, \( \rho_{B} \) is the bulk density of the water-saturated sample, and \( \rho_{H2O} \) is the density of water at the measurement temperature \( T \) °C calculated using Eqn. (7.2). This equation is obtained by fitting a second order polynomial to published water density data where \( T \) is temperature of the water during measurement (Haynes et al., 2012; Kuila, 2013).

\[ \rho_{H2O} = -0.0000053 T^2 + 0.0000081 T + 1.0001627 \quad \text{Eqn. (7.2)} \]

The bulk density (\( \rho_{B} \)) is determined by Archimedes’ Principle. Thus, by weighing a fully saturated sample in air and submerged in de-ionized water, bulk density (\( \rho_{B} \)) can be calculated using Eqn. (7.3).

\[ \rho_{B} = \left[ \frac{\text{Sat.Wt.Air}}{\text{Sat.Wt.Air} - \text{Sat.Wt.Sub}} \times (\rho_{H2O} \ - \rho_{air}) \right] + \rho_{air} \quad \text{Eqn. (7.3)} \]

Where, Sat.Wt.Air is the weight of the saturated sample in air and Sat.Wt.Sub is the weight of the saturated sample submerged in de-ionized water and \( \rho_{air} \) is the air density (0.0012 g/cm³) (Kuila, 2013). The dry grain density (\( \rho_{G} \)) is determined by weighing the completely dehydrated sample weight in air and the completely saturated sample submerged in water as shown in the equation below where, DryWt.Air is the weight of completely dehydrated sample (Kuila, 2013).

\[ \rho_{G} = \left[ \frac{\text{DryWt.Air}}{\text{DryWt.Air} - \text{Sat.Wt.Sub}} \times (\rho_{H2O} \ - \rho_{air}) \right] + \rho_{air} \quad \text{Eqn. (7.4)} \]
7.5.2 Nitrogen Adsorption Experimental Procedure

For this study, the N\textsubscript{2} gas adsorption experiments were conducted on a Micromeritics ASAP 2020\textsuperscript{TM} instrument according to the experimental procedure described in (Kuila, 2013; Webb & Orr, 1997). One to three grams of pulverized, homogenous sample was degassed at 200°C for 24 hours under vacuum prior to analysis. This ensures removal of any adsorbed clay–bound or capillary water. After the degassing procedure, the tube and sample are weighed to determine the analysis weight of the sample. The sample tube is then placed on the analysis port of the instrument and the adsorption/desorption isotherms are collected. In this experiment, the degassed sample is exposed to nitrogen gas at constant cryogenic liquid nitrogen (LN2) temperature (~197.3°C) at a series of precisely controlled pressures. The volume of adsorbed gas on the solid surface is measured at discrete pressures over the relative equilibrium adsorption pressure (P/P\textsubscript{o}) range of 0.075–1.0 at a constant temperature, where P is the absolute equilibrium pressure and P\textsubscript{o} is the condensation pressure of nitrogen at laboratory conditions. The experiment is carried out by systematically increasing the pressure up to the condensation pressure at the adsorption branch followed by reduction of pressure.
from $P_0$ at the desorption branch. The gas-adsorption isotherm is reported as the volume of gas adsorbed as a function of $P/P_0$. The shape of the isotherm and the hysteresis pattern provide useful information regarding the mechanism of the physisorption process. Those hysteresis patterns can then be used to qualitatively predict the types of pores present in the adsorbent.

### 7.5.3 FESEM Analysis Procedure

Representative Niobrara samples were prepared for ion milling and imaging from the core being studied. The larger samples were mechanically ground and polished using grinding/polishing wheels to smaller 1mm by 5 mm sizes. The surfaces perpendicular to bedding that are of interest were ion milled using an Argon Bal-Tec RES100 ion mill. The polished and ion milled samples were mounted to SEM stubs using a conductive carbon paste and tape and coated with an alloy of gold. A JEOL JSM-7000F FESEM and an EDAX Genesis EDS, was used for sample imaging.

### 7.6 Results and Discussion

This section summarizes the results of the WIP, nitrogen adsorption and FESEM analysis performed on the analyzed chalk samples of the Aristocrat PC H11-07 core. The results provide a better understanding of the storage capacity and pore size distribution of the analyzed mature Niobrara samples.

#### 7.6.1 WIP Results

WIP analysis was performed on 17 representatives Niobrara chalk samples from the Aristocrat PC H11-07 core. Bulk density values range from 2.4 to 2.6 g/cm$^3$, with a mean value of 2.5 g/cm$^3$. WIP experimental results are shown in Table A-12 in Appendix A. It must be noted that the bulk density reading obtained with WIP analysis is bulk density with full de-ionized water and does not represent the in-situ bulk density as measured by bulk density logs. Grain density values range from 2.46 to 2.75 g/cm$^3$, with a mean value of 2.6 g/cm$^3$. Calculated WIP total porosity ranged from 3.0 to 13%. Results show that the WIP experiment is repeatable. Calculated dry bulk and grain density readings were similar in all three experiments. The maximum absolute difference calculated between the three different experimental results was 0.03 g/cm$^3$ for bulk density, 0.02 g/cm$^3$ for grain density and 2%
for WIP porosity (Figure 7-7). The WIP porosity results have shown the highest uncertainty. Calculated WIP porosity was highest in the A chalk, B chalk, C chalk, and D chalk. The D chalk-marl having high porosity values is questionable as it is known to have the lowest porosity in the Smoky Hill Member. The D chalk-marl is rich in illite and smectite clays and as the samples are submerged in water and saturated some of the smectite clays begin to swell and break off the sample. This results in a reduction in sample weight measured and an increase in the calculated WIP porosity. This was reflected in the WIP results of the D chalk-marl samples. Additional limitations in the WIP porosity measurement techniques include possible incomplete saturation and water soluble mineral dissolution. WIP porosity calculated for Niobrara chalk samples with low clay content are reliable and are comparable to nitrogen adsorption calculated porosity (Figure 7-12). The WIP technique will overestimate porosity in the presence of swelling clays but works well in low clay samples. Changing the saturating fluid into kerosen may yield better results for WIP porosity calculation in the Niobrara Formation.

![Figure 7-7: WIP experimental results of dry bulk density (g/cm³), dry grain density (g/cm³) and WIP porosity (%) per sample in increasing depth. Plots show the results of the three repeated experiments and the average calculated value.](image-url)
7.6.2 Nitrogen Adsorption Results

The mesopore and micropore size distributions (1.7-200 nm) within 8 Niobrara chalk samples were measured by subcritical nitrogen adsorption analysis at 77.3 K. The analyzed chalk samples show a typical Type IIB isotherm with forced closure implying an abundance of mesopores (Figure 7-11). Figure 7-8 shows the pore size distribution obtained from adsorption branch of the N2 isotherm of all analyzed chalk samples. The parameter dV/d(logD) is used to represent pore-size distribution. The area under the curve between any two pore diameters is proportional to the partial pore volume for that pore diameter range (Kuila, 2013). Mesopores are abundant in all 8 studied chalk samples and range in width from 50 nm to 100 nm. A trimodal pore size distribution is present within the Niobrara with a major peak between 50-100 nm, a small peak at 3nm and a big peak between 1.7-2 nm (Figure 7-8). Samples with the highest TOC content show higher peaks between 1.7-2 nm than samples with low TOC (Figure 7-9). In addition, samples with high clay content show higher peaks at 3 nm than samples with low clay content (Figure 7-10). Both organic matter and clay content have a direct effect on pore size distribution. The pore sizes between 1.7-2nm are interpreted to be mainly associated to organic matter, while the 3 nm and pore sizes are mainly associated to intraparticle pores within clay platelets. The 50-100 nm pore sizes are interpreted to be mainly associated to intraparticle pores between clay aggregates.

Figure 7-8: Pore size distribution of all analyzed chalk samples.
Figure 7-9: (A) Pore size distribution of low TOC chalk samples. Samples show lower < 2nm micropore size distribution highlighted with the red circle. (B) Pore size distribution of high TOC chalk samples. These samples show higher micropore < 2nm pore size distribution highlighted with the red circle.

Figure 7-10: (A) Pore size distribution of high clay chalk samples. (B) Pore size distribution of low clay chalk samples.
Figure 7-11: Nitrogen adsorption and desorption isotherm plots for all the analyzed Niobrara chalk samples.
The nitrogen adsorption pore volume results were used to calculate nitrogen porosity and were compared to WIP porosity values. Samples with high clay content show higher WIP porosity than nitrogen porosity due to swelling clay effect (Figure 7-12). Nitrogen porosity only includes pore sizes between 1.7-200 nm and does not represent total porosity. WIP porosity accounts for larger pores and accounts for macropores present. A few low clay samples have shown lower WIP porosity than nitrogen porosity. This can be explained by the samples being too tight for full water saturation during the WIP experiment or could be due to experimental measurement errors that caused this. In order to fully understand porosity and pores size distribution in the Niobrara Formation, multiple porosity measuring methods must be incorporated and compared.

![Figure 7-12: Calculated nitrogen and WIP porosity for the analyzed Niobrara chalk samples.](image)

Specific surface area (SSA) results for the studied Niobrara samples are summarized in Table 7.1. Figure 7-13 shows the measured surface area at different pore sizes. The smallest pore sizes < 2 nm show the highest pore surface area. Figure 7-14 shows that the D chalk samples and the B chalk samples have high SSA (~8.3-8.5 m2/g) and (~8.8 m2/g), respectively. These samples show much higher SSA than the remaining samples. The D chalk samples are clay rich and the increase in surface area is attributed to the micropores...
associated to clays. The B Chalk sample, however, has high TOC and the high surface area measured could be interpreted to be associated to organic and clay associated micropores. Both clays and organic matter host micro-sized pores that are less than 3 nm in size and are the main contributors to the surface area measured in the samples. Figure 7-15 shows that samples with high TOC or high clay content have the highest specific surface area. High calculated surface area suggests high surface area for gas adsorption.

Table 7.1: Nitrogen adsorption specific surface area results for the analyzed Niobrara chalk samples.

<table>
<thead>
<tr>
<th>Core Depth</th>
<th>Sample #</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6822.85</td>
<td>J-A Chalk</td>
<td>4.6791</td>
</tr>
<tr>
<td>6857.3</td>
<td>Q-B Chalk</td>
<td>8.7988</td>
</tr>
<tr>
<td>6869.9</td>
<td>K-B Chalk</td>
<td>7.2936</td>
</tr>
<tr>
<td>6875.6</td>
<td>H-B Chalk</td>
<td>6.2928</td>
</tr>
<tr>
<td>6947.3</td>
<td>D-C Chalk</td>
<td>6.3194</td>
</tr>
<tr>
<td>6975.3</td>
<td>G-C Chalk</td>
<td>5.9975</td>
</tr>
<tr>
<td>7032.4</td>
<td>M-D Chalk</td>
<td>8.5096</td>
</tr>
<tr>
<td>7055.7</td>
<td>O-D Chalk</td>
<td>8.2783</td>
</tr>
</tbody>
</table>

Figure 7-13: Pore surface area at different pore size distributions for all the analyzed Niobrara chalk samples.
Figure 7-14: Bar graph showing the variation in specific surface area measured in the different chalk members of the Niobrara Formation.

Figure 7-15: A. Cross-plot of Total Clays against SSA for the studied Niobrara chalk samples. B. Cross-plot of TOC against SSA for the studied Niobrara chalk samples. Samples with high clay, low TOC samples and low clay, high TOC samples show the highest surface areas. Both TOC and Clay content contribute to the total specific surface area.
7.6.3 FESEM Results

The rock texture, pore morphology and pore sizes were qualitatively assessed using an FESEM. The FESEM results complement the nitrogen adsorption pore size results and confirm the presence of pores that range in size from 3 microns to less than 5nm. The maximum pores size that can be resolved by nitrogen adsorption analysis is 200 nm which is equivalent to 0.2 microns. Pores with sizes greater than 1.0 microns, unresolvable by nitrogen adsorption tests, were identified in the Niobrara Formation. By combining FESEM, WIP and nitrogen adsorption results, the Niobrara Formation contains macropores, mesopores and micropores. These pore sizes vary in size based on mineralogy and organic content. In the marls micropores and mesopores are more abundant than macropores. While in chalks, macropores and mesopores are more abundant than micropores.

These pores are also classified in type, based on Louck’s (2012) classification, to be interparticle, intraparticle and organic matter pores. The presence of micro-fractures, however, was rare in all the analyzed FESEM samples making fracture porosity in this core minimal. Interparticle pores were mainly present between recrystallized calcite crystals (i.e. micrites) and clay platelets (i.e. illite-smectite layers). However, primary interparticle porosity has been greatly reduced due to compaction. Secondary interparticle porosity may be found between grain boundaries due to the effect of compaction on rigid non ductile grains (Figure 7-16). Moreover, intraparticle pores were found within a few partially intact coccoliths, their tubular tests and within illite-smectite clay aggregates (Figure 7-16).

Different pore shapes were found to be associated to different pore types (Figure 7-17). Pores present within clay particles are elongate and slot-like in shape whereas the organic pores and intraparticle pores within coccolith fragments are more circular in shape. According to Curtis et al. (2010) slot like pore geometry may be prone to collapse due to increased effective pressure as gas is drawn out of the pores and the closure of these pores would drastically reduce permeability. Irregularly shaped pores are generally intercrystalline interparticle pores found between calcite crystals (i.e. micrite) and coccolith fragments.
Figure 7-16: FESEM- SEI images showing organic pores, interparticle and intraparticle pores identified in the analyzed Niobrara chalk samples.
Variations in mineralogy and diagenesis profoundly affect porosity within the analyzed chalk samples. Different minerals exhibit different elastic behavior and respond differently to diagenesis and compaction. Clays, organic matter and fecal pellets are considered ductile components of the rock that distort due to compaction and close interparticle pore spaces and plug pore throats (Loucks, 2012). Rigid grains include quartz, feldspars, dolomite, coccoliths, calcite grains, and foraminifera. These grains exhibit higher resistance to compaction, and when/if they do break, create new pore spaces around them. Some, however, such as dolomite, feldspars, coccoliths and calcite grains can be chemically unstable and undergo dissolution forming secondary intraparticle dissolution porosity. Such dissolution porosity is found in the analyzed Niobrara chalk samples and is less than a 100 nm in size (i.e nanopores). Figure 7-19 shows an example of dissolution of calcite and coccolith fragments and its recrystallization in the C chalk. The process of calcite dissolution and recrystallization into smaller calcite crystals (i.e. micrites) is also referred to as micritization. Micrites can vary in morphology and can be either porous or tight and non-
porous (Figure 7-18). Deville de Periere et al. (2011) provided a detailed account on the relationship between micrite morphology and porosity (Figure 7-18). Micrite morphology and texture within the Niobrara varies from subhedral to euhedral, rhombic shaped micrites to anhydral, tight and compact micrites (Figure 7-20). In addition to dissolution and micritization, compaction within the Niobrara has resulted in the crushing of coccoliths grains and the coalescence of some of the micrite grains into a more compact, tight form thus, reducing porosity (Figures 7-20, 7-22).

Figure 7-18: Micrite textures found in Cretaceous limestones in the Middle East. Note that micrite texture can determine porosity potential (Al-Ibrahim, 2014, modified from Deville de Periere et. al., 2011).

Figure 7-19: FESEM-SEI X20,000 image showing dissolution of calcite and coccolith fragments and its recrystallization into micrite crystals, C chalk.
Figure 7-20: FESEM SEI images showing crushed coccolith fragments and broken coccolith tests due to compaction. Different micrite morphology is present. There is fused non porous micrite and porous euhedral and subhedral micrite that have recrystallized due to the dissolution of broken coccolith fragments.
Petrographic analysis of the Niobrara Formation shows the abundance of calcite rich and clay rich fecal pellets within the different Niobrara facies (Figure 7-21). The calcite rich fecal pellets within the Niobrara play an effective role in terms of storage capacity. Calcite rich fecal pellets within the chalk facies generally consist of recrystallized euhedral and subhedral micrites and broken coccolith fragments. As the Niobrara undergoes compaction, the material present within the fecal pellet experience less compaction than the surrounding matrix. Therefore, the fecal pellets maintain some of their porosity as opposed to the external matrix (Figure 7-22).

FESEM images of the Niobrara Formation show nano-sized pores (<100 nm) within the thermally mature organic matter (Ro>1.4). This suggests that there is development of secondary nanoporosity with an increase in thermal maturity from oil to gas window (Bernard et al., 2012; Curtis et al., 2011a; Heath et al., 2011; Schieber, 2010). There were, however, a few reported exceptions found with organic matter exhibiting nanoporosity in the oil window. Reed et al. (2012) reported pore development in organic matter at around 0.8% Ro maturity. Within the Niobrara both porous organic matter and non-porous organic matter can be found (Figure 7-23). The probable explanation for this is that multiple organic matter types are present. The non-porous organic matter is woody terrestrial organic matter (Type III) that was brought into the system along with detrital material (e.g. Curtis et al., 2012). Another possibility for the difference in structure is that the non-porous region of organic matter is kerogen and the porous region is pyrobitumen (Bernard et al., 2012, Curtis et al. 2012). The presence of non-porous kerogen in the system may hinder pore connectivity and prevent access to other mesopores present within clay aggregates and coccolith fragments. Analysis of the texture of the organic matter shows it encapsulated within fossil fragments, clay platelets and micrite suggesting that it might have been mobile at some point and could be a bitumen network that has formed post hydrocarbon maturation and migration. The size of those organic pores is considerably small and is generally found to be a few nanometers in diameter (<100 nm) (Figure 7-24). Such small pores can be effective and allow for greater pore surface area and increased surface area for hydrocarbon adsorption. Moreover, it has been argued that those organic pores can contribute to effective porosity due to their wettability to oil. Work by Passey et al (2012) and Sondergeld et al. (2012) suggests that the
wettability of an inorganic-associated pore system should be different than that of a pore system that is mainly within the organics and should be more oil wet.

Figure 7-21: (A) 10 X PL thin section micrograph of a B Chalk sample. (B) 10X XPL thin section micrograph of the same sample. A and B show the abundance of calcite rich and clay rich fecal pellets.

Figure 7-21: (A) 10 X PL thin section micrograph of a B Chalk sample. (B) 10X XPL thin section micrograph of the same sample. A and B show the abundance of calcite rich and clay rich fecal pellets.
Figure 7-22: (A) FESEM-SEI image at X1500 magnification of a fecal pellet that is rich in micrite and broken coccolith fragments, B chalk. (B) X5000 close-up image of the inside of the fecal pellet. Fecal pellet is surrounded by mixed layer illite-smectite clays and contains euhedral and subhedral micrite and crushed coccolith fragments.
Figure 7-23: (A) FESEM X3000 SEI image showing identified woody non-porous organic matter, C chalk (B) FESEM X10,000 SEI image showing organic pores within organic matter, C chalk.
Figure 7-24: (A) FESEM X15000 BSE image showing intercrystalline pores within micrites, itraparticle pores within coccolith fragments, and porous organic matter. (B) FESEM X40,000 BSE close up image of the area highlighted with a red box in figure A. Image B clearly shows nano-sized organic pores that are <100 nm in size that were not visible under lower magnifications of X15000.
To get a better understanding of pore type’s distribution in the Niobrara Formation, the different pores within a C chalk ion milled sample were point counted under the FESEM. Only pores that were visible at the working magnification were considered in addition to those with clearly distinguished pore types. Organic pores were difficult to quantify and count at high magnifications such as X2000 due to their very small size (<100 nm). Hence, point counts of organic pores at low magnifications report lower number of organic pores than those at higher magnification. To be able to capture the number of organic pores, a high magnification is needed and thus, the area of investigation becomes smaller and may not be entirely representative of the entire sample. Point counts performed in this study were more qualitative and based on eye observations and the abundance of one pore type over the other. At higher magnification the number of organic pores counted was much higher than interparticle and intraparticle pores (Table 7.2). Based on observations made, the Niobrara pore system may be classified as a mixed pore system type with approximately 20% organic pores, 30 % intraparticle (i.e. mainly pores within coccoliths and clay aggregates), and 50% interparticle pores (i.e. intercrystalline) (Figure 7-25). Depending on the organic matter content of the studied samples, these percentages may change with organic pores being most abundant.

Table 7.2: Point count of the different type of pores present in an analyzed ion milled C chalk sample at different magnifications.

<table>
<thead>
<tr>
<th>Magnification</th>
<th>Number of organic pores</th>
<th>Number of Interparticle pores</th>
<th>Number of Intraparticle pores</th>
<th>Total Number of pores</th>
<th>Area (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X10,000</td>
<td>153</td>
<td>34</td>
<td>25</td>
<td>212</td>
<td>49.21</td>
</tr>
<tr>
<td>X9500</td>
<td>160</td>
<td>46</td>
<td>20</td>
<td>226</td>
<td>98.42</td>
</tr>
<tr>
<td>X8000</td>
<td>172</td>
<td>30</td>
<td>21</td>
<td>223</td>
<td>103.89</td>
</tr>
<tr>
<td>X2000</td>
<td>68</td>
<td>105</td>
<td>51</td>
<td>224</td>
<td>492.11</td>
</tr>
</tbody>
</table>
Figure 7-25: Spectrum of pore types and networks in mudrocks (modified from Loucks, 2012). The Niobrara samples show a mixed pore system.
CHAPTER 8
CONCLUSIONS

1. The Niobrara Formation is highly cyclic with both the chalk and marl members as source rocks and reservoirs.
2. The density porosity method provided the best estimate of porosity that is comparable to core porosity.
3. Water saturation using Archie’s equation and the dual water saturation model is best calculated using $a=0.35$.
4. The dual water saturation method accounts for clay bound water and provides the best estimate of water saturation in the Niobrara Formation.
5. The Passey Delta Log R method and the Schmoker density log method do not work in the Niobrara Formation. The Schmoker method overestimates TOC in the Niobrara Formation, while the Delta log R method underestimates TOC.
6. The GR log and the uranium spectral log are the best proxies of organic richness in the Niobrara Formation. The uranium method provides the best estimate of log derived TOC.
7. Complete smectite to illite conversion does not occur at high temperatures. There remains smectite in super mature samples of the Niobrara Formation which must be accounted for in any mineralogical modeling.
8. “El Com” is an effective linear programming code for predicting mineralogy from XRF or ICP-MS data.
9. The WIP method for porosity measurement is repeatable, yet not suitable for the Niobrara Formation due to the presence of swelling clays such as smectite.
10. WIP method overpredicts porosity in clay-rich samples and underestimates porosity in tight samples with small pores.
11. The Niobrara Formation contains a significant portion of both meso and macropores.
12. N2 adsorption data shows a trimodal pore size distribution with distinct peaks between 50-100nm, at 3nm, and between 1.7-2nm.
13. Organic matter and clays contribute to the microporosity of the Niobrara Formation.
14. Organic pores and clay associated pores contribute the highest specific surface area for gas adsorption.
15. Organic pores, interparticle and intraparticle pores were identified using FESEM analysis. Fracture porosity was not documented in the core and is not a main contributor to porosity in the Niobrara Formation.

16. The Niobrara Formation exhibits a mixed pore system. Pores are mainly interparticle pores confined between crushed coccolith grains and micrites. This is followed by intraparticle pores between clay aggregates and organic pores.

17. The Niobrara Formation contains both calcite and clay rich fecal pellets. The calcite rich fecal pellets in the Niobrara Formation are the main preservatives of porosity in the Niobrara Formation.
CHAPTER 9
FUTURE WORK

1. Perform basin wide analysis of the relationship between TOC and different petrophysical log responses in the Niobrara Formation. This will help in deriving basin wide empirical relationships that can be used to derive TOC from logs.

2. Perform a detailed mineralogical study on clays and identify their mineral phases and chemical compositions in the Niobrara for more accurate clay modeling. Detailed clay XRD analysis will help in understanding the mineral abundances of clays and their mineral phases.

3. Analyze the smectite and illite clays within the Niobrara and potential inhibitors to complete illitization.

4. Obtain surface area data that can be used as to constraint the clays in the “El Com” model. The more mineral associated data incorporated into “El Com” the more constrained the model will be and the more accurate the results will be.

5. Additional WIP work should be carried out with other wetting liquids such as kerosene to eliminate the effect of swelling clays on the calculate density and porosity values. Comparing the results from kerosene immersion to water immersion will provide further insight on the immersion technique procedure, accuracy, and its applicability in studying the Niobrara Formation.

6. Perform a detailed FESEM study on all the Niobrara Formation members and compare porosity in the marls to that in the chalks. This will provide further insight on the contribution of organic pores to the pore system in the Niobrara Formation.

7. Perform a detailed point count analysis on pores identified using an FESEM to quantify the abundances of the different pore types present more accurately.
REFERENCES CITED


APPENDIX A

Table A-1: Calculated average petrophysical properties of the Smokey Hill and Fort Hays member of the Niobrara Formation in the Aristocrat PC H11-07 core.

<table>
<thead>
<tr>
<th>Variable</th>
<th>A chalk</th>
<th>A marl</th>
<th>B chalk</th>
<th>B marl</th>
<th>C chalk</th>
<th>C marl</th>
<th>D chalk</th>
<th>Fort Hays</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sw (v/v)</td>
<td>0.16</td>
<td>0.24</td>
<td>0.18</td>
<td>0.36</td>
<td>0.15</td>
<td>0.22</td>
<td>0.74</td>
<td>0.23</td>
</tr>
<tr>
<td>RHOB (g/cc)</td>
<td>2.43</td>
<td>2.49</td>
<td>2.44</td>
<td>2.50</td>
<td>2.45</td>
<td>2.46</td>
<td>2.60</td>
<td>2.57</td>
</tr>
<tr>
<td>DTC (µspf)</td>
<td>71.04</td>
<td>74.32</td>
<td>70.11</td>
<td>76.86</td>
<td>70.19</td>
<td>78.99</td>
<td>71.71</td>
<td>58.19</td>
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<tr>
<td>RT(ohm.m)</td>
<td>27.41</td>
<td>15.12</td>
<td>36.37</td>
<td>11.37</td>
<td>33.72</td>
<td>20.65</td>
<td>9.25</td>
<td>52.13</td>
</tr>
<tr>
<td>GR (api)</td>
<td>160.91</td>
<td>193.62</td>
<td>139.18</td>
<td>133.70</td>
<td>108.32</td>
<td>135.79</td>
<td>76.36</td>
<td>26.02</td>
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<td>PE (b/e)</td>
<td>4.90</td>
<td>4.91</td>
<td>4.57</td>
<td>4.29</td>
<td>4.64</td>
<td>4.32</td>
<td>4.28</td>
<td>4.83</td>
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<td>POTA(wt.%)</td>
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<td>0.98</td>
<td>0.81</td>
<td>1.29</td>
<td>0.79</td>
<td>1.27</td>
<td>1.51</td>
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<td>THOR(ppm)</td>
<td>3.02</td>
<td>3.88</td>
<td>3.42</td>
<td>5.29</td>
<td>3.13</td>
<td>5.34</td>
<td>6.13</td>
<td>1.79</td>
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<tr>
<td>URAN (ppm)</td>
<td>14.84</td>
<td>17.63</td>
<td>12.30</td>
<td>10.28</td>
<td>9.14</td>
<td>10.59</td>
<td>3.54</td>
<td>1.56</td>
</tr>
<tr>
<td>PHIT_D (v/v)</td>
<td>0.13</td>
<td>0.11</td>
<td>0.12</td>
<td>0.08</td>
<td>0.12</td>
<td>0.11</td>
<td>0.05</td>
<td>0.06</td>
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Table A-2: S2 (mg HC/g rock) and source potential (from Espitallie, 1982)

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<tr>
<th>S2 (mg HC/g rock) (from Espitallie, 1982)</th>
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<tr>
<td>0 - 2</td>
</tr>
<tr>
<td>2 - 5</td>
</tr>
<tr>
<td>&gt; 5</td>
</tr>
</tbody>
</table>

Table A-3: S1*100/TOC (mg HC/g rock) and source rock potential (Jarvie and Baker, 1984)

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<th>S1 *100/TOC (mg HC/g rock) (Jarvie and Baker, 1984)</th>
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<td>0 – 50</td>
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<td>50 – 100</td>
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<td>&gt; 100</td>
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Table A-4: S2/S3 and kerogen type (from Clementz et al., 1979)

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<th>S2/S3 (from Clementz et al., 1979)</th>
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<tr>
<td>2.5 - 5</td>
</tr>
<tr>
<td>&gt; 5</td>
</tr>
</tbody>
</table>
Table A-5: Tmax variation with kerogen type and maturity (from Espitallie, 1985)

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<th>Maturity</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
</tr>
</thead>
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<tr>
<td>Immature</td>
<td>440-448</td>
<td>&lt;425</td>
<td>&lt;435</td>
</tr>
<tr>
<td>Oil Window</td>
<td>425-450</td>
<td>435-465</td>
<td></td>
</tr>
<tr>
<td>Gas Window</td>
<td>&gt;450</td>
<td>&gt;465</td>
<td></td>
</tr>
</tbody>
</table>

Table A-6: PI variation with maturation window (from Espitallie, 1982)

<table>
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<th>PI (from Espitallie, 1982)</th>
<th>Immature</th>
<th>Oil Window</th>
<th>Gas Window</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 0.08</td>
<td>Immature</td>
<td>Oil Window</td>
<td>Gas Window</td>
</tr>
<tr>
<td>0.08 – 0.5</td>
<td>Oil Window</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt; 0.5</td>
<td>Gas Window</td>
<td></td>
<td></td>
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Table A-7: relationship between HI and kerogen type (from Espitallie, 1982)

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<th>HI (from Espitallie, 1982)</th>
<th>Type</th>
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<tr>
<td>&lt; 50</td>
<td>Type IV gas prone</td>
</tr>
<tr>
<td>50 - 200</td>
<td>Type III (gas/oil prone, usually terrestrial)</td>
</tr>
<tr>
<td>200 - 350</td>
<td>Mixed Type II/III (mixed oil/gas prone)</td>
</tr>
<tr>
<td>350 – 700</td>
<td>Type II (oil prone, usually marine)</td>
</tr>
<tr>
<td>&gt; 700</td>
<td>Type I (oil prone, often lacustrine)</td>
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Table A-8: XRD analysis results for Niobrara chalk and marl samples.

<table>
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<tr>
<th>Sample #</th>
<th>Member</th>
<th>Quartz</th>
<th>Albite</th>
<th>Muscovite/Illite</th>
<th>Chlorite</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Pyrite</th>
<th>Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A Chalk</td>
<td>5.3</td>
<td>4.6</td>
<td>1.6</td>
<td>0</td>
<td>78.7</td>
<td>5.8</td>
<td>2.8</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>A Marl</td>
<td>9.3</td>
<td>3.1</td>
<td>9.2</td>
<td>0</td>
<td>69.5</td>
<td>7</td>
<td>1.9</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>B Chalk</td>
<td>3</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>89.9</td>
<td>0.7</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>B Marl</td>
<td>17.2</td>
<td>1.4</td>
<td>17.6</td>
<td>0</td>
<td>55.7</td>
<td>5.8</td>
<td>2.3</td>
<td>0</td>
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<tr>
<td>5</td>
<td>C Chalk</td>
<td>5.2</td>
<td>1.3</td>
<td>2.8</td>
<td>0</td>
<td>89.7</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>C Chalk</td>
<td>5.3</td>
<td>0.4</td>
<td>24.4</td>
<td>4.1</td>
<td>63.8</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>C Marl</td>
<td>14</td>
<td>1.6</td>
<td>14</td>
<td>0</td>
<td>67.2</td>
<td>0.4</td>
<td>2.8</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>C Marl</td>
<td>22.2</td>
<td>2.8</td>
<td>21</td>
<td>0</td>
<td>49.7</td>
<td>3.3</td>
<td>1</td>
<td>0</td>
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<tr>
<td>9</td>
<td>D Chalk</td>
<td>30</td>
<td>3</td>
<td>23.3</td>
<td>0</td>
<td>34.5</td>
<td>4</td>
<td>5.2</td>
<td>0</td>
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<tr>
<td>10</td>
<td>D Chalk</td>
<td>12.4</td>
<td>1.9</td>
<td>8.5</td>
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<td>76.9</td>
<td>4</td>
<td>0.3</td>
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<tr>
<td>11</td>
<td>Fort Hays</td>
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<td>1.2</td>
<td>0</td>
<td>0</td>
<td>93.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0</td>
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<tr>
<td>12</td>
<td>Fort Hays</td>
<td>9.2</td>
<td>1.7</td>
<td>34.3</td>
<td>0</td>
<td>50.6</td>
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<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>Fort Hays</td>
<td>2.3</td>
<td>1.9</td>
<td>1</td>
<td>0</td>
<td>94.8</td>
<td>2</td>
<td>0</td>
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</tr>
</tbody>
</table>

Table A-9: ICP-MS analysis results for Niobrara chalk and marl samples.

| Sample # | Member    | SiO2   | Al2O3  | Fe2O3  | MnO   | MgO   | CaO   | Na2O  | K2O   | TiO2  | P2O5  | LOI   |
|----------|-----------|--------|--------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1        | A Chalk   | 8.63   | 2.13   | 2.34   | 0.015 | 0.79  | 44.18 | 0.14  | 0.18  | 0.069 | 0.07  | 35.67 |
| 2        | A Marl    | 16.32  | 4.32   | 1.69   | 0.012 | 1.1   | 39.68 | 0.4   | 0.84  | 0.163 | 0.11  | 33.42 |
| 3        | B Chalk   | 7.31   | 2.63   | 0.5    | 0.008 | 0.51  | 47.9  | 0.34  | 0.33  | 0.038 | 0.04  | 38.82 |
| 4        | B Marl    | 29.09  | 8.25   | 2.13   | 0.013 | 1.2   | 28.22 | 0.43  | 1.64  | 0.322 | 0.14  | 27.09 |
| 5        | C Chalk   | 8.93   | 2.48   | 0.85   | 0.008 | 0.34  | 46.25 | 0.2   | 0.44  | 0.092 | 0.09  | 38.24 |
| 6        | C Chalk   | 20.87  | 11.63  | 1.81   | 0.011 | 1.27  | 31.12 | 0.36  | 1.24  | 0.246 | 0.15  | 29.68 |
| 7        | C Marl    | 23.56  | 5.92   | 2.53   | 0.01  | 0.69  | 33.92 | 0.36  | 1.21  | 0.25  | 0.13  | 29.62 |
| 8        | C Marl    | 35.91  | 8.68   | 1.38   | 0.03  | 1.01  | 27.08 | 0.53  | 1.77  | 0.35  | 0.19  | 23.51 |
| 9        | D Chalk   | 41.95  | 9.81   | 4.07   | 0.017 | 1.06  | 17.56 | 0.61  | 1.99  | 0.405 | 0.16  | 22.03 |
| 10       | D Chalk   | 19.05  | 4.19   | 0.98   | 0.061 | 0.94  | 39.8  | 0.25  | 0.87  | 0.168 | 0.09  | 32.23 |
| 11       | Fort Hays | 6.56   | 0.9    | 1.04   | 0.168 | 0.44  | 50.31 | 0.11  | 0.12  | 0.032 | 0.05  | 39.04 |
| 12       | Fort Hays | 29.37  | 12.5   | 3.05   | 0.062 | 2.7   | 23.38 | 0.56  | 2.57  | 0.45  | 0.16  | 24.76 |
| 13       | Fort Hays | 5.54   | 1.96   | 0.85   | 0.1   | 0.53  | 49.58 | 0.19  | 0.32  | 0.052 | 0.14  | 39.21 |
Table A-10: XRF analysis results for Niobrara chalk and marl samples.

**XRF Analysis (wt. %)**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Member</th>
<th>Al %</th>
<th>Ca %</th>
<th>Fe %</th>
<th>K %</th>
<th>Mg %</th>
<th>Mn %</th>
<th>P %</th>
<th>S %</th>
<th>Si %</th>
<th>Ti %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A Chalk</td>
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<td>43.74</td>
<td>1.53</td>
<td>0.49</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
<td>2.75</td>
<td>3.93</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>A Marl</td>
<td>2.31</td>
<td>37.15</td>
<td>0.83</td>
<td>1.13</td>
<td>0.33</td>
<td>0.02</td>
<td>0.00</td>
<td>1.34</td>
<td>8.70</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>B Chalk</td>
<td>2.01</td>
<td>43.00</td>
<td>0.22</td>
<td>0.70</td>
<td>0.59</td>
<td>0.03</td>
<td>0.00</td>
<td>0.52</td>
<td>4.96</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>B Marl</td>
<td>4.49</td>
<td>26.01</td>
<td>1.31</td>
<td>1.28</td>
<td>1.30</td>
<td>0.03</td>
<td>0.00</td>
<td>1.51</td>
<td>16.35</td>
<td>0.18</td>
</tr>
<tr>
<td>5</td>
<td>C Chalk</td>
<td>1.55</td>
<td>42.10</td>
<td>0.40</td>
<td>0.89</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
<td>0.81</td>
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<td>C Chalk</td>
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<td>11.53</td>
<td>0.18</td>
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<tr>
<td>7</td>
<td>C Marl</td>
<td>3.84</td>
<td>28.30</td>
<td>1.77</td>
<td>1.10</td>
<td>0.92</td>
<td>0.02</td>
<td>0.00</td>
<td>2.19</td>
<td>15.20</td>
<td>0.21</td>
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<tr>
<td>8</td>
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<td>4.76</td>
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<td>0.54</td>
<td>1.42</td>
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<td>21.25</td>
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<td>0.02</td>
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Table A-11: XRD data validation with ICP-MS data.

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<th>6</th>
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<th>13</th>
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<td>8.72</td>
<td>10.25</td>
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<td>0.18</td>
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<td>0.92</td>
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<td>1.54</td>
<td>0.56</td>
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</tr>
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<td>0.71</td>
<td>0.28</td>
<td>1.38</td>
<td>0.37</td>
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<td>1.46</td>
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<td>0.73</td>
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<td>0.15</td>
<td>0.19</td>
<td>0.60</td>
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</table>
Table A-12: Bulk density, grain density and WIP porosity obtained using water immersion porosimetry for the analyzed Niobrara chalk samples.

<table>
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<tr>
<th>Member</th>
<th>Sample #</th>
<th>( \rho_B \text{ Av.} )</th>
<th>( \rho_G \text{ Av.} )</th>
<th>WIP Porosity Av.</th>
</tr>
</thead>
<tbody>
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<td>2.40</td>
<td>2.61</td>
<td>12.82</td>
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<td>A marl</td>
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<td>2.49</td>
<td>4.76</td>
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<tr>
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<td>2.48</td>
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<tr>
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</table>
APPENDIX B

1. “EL Com” Matlab code used for calculating mineralogy from ICP-MS or calibrated XRF data:

    %clc, clear all, close all

    % User-Defined Variables

    ICPfileName = 'Data.xlsx';
    ElComFineName = 'ElComConstants.xlsx';

    mineralToUse = {'Calcite', 'Quartz', 'Dolomite', 'Illite', 'Pyrite'};

    oxidesToUse = {'SiO2', 'Al2O3', 'Fe2O3', 'MgO', 'Na2O', 'CaO', 'K2O', 'MnO', 'S'};

    % minerals to use allows the user to specify minerals to be solved for. If a mineral is not specified it will not be read from the mineralToUse.xlsx sheet.
    mineralToUse = {'Calcite', 'Quartz', 'Dolomite', 'Illite', 'Pyrite'};

    oxidesToUse = {'SiO2', 'Al2O3', 'Fe2O3', 'MgO', 'Na2O', 'CaO', 'K2O', 'MnO', 'S'};

    % Read Data
    [ICPMSData, header] = readICPData(ICPfileName);
    [mineralMWs, OxideInfo, elementMineralRatios] = readElComConstants(ElComFineName);

    % Prepare Variables
    nMinerals = numel(mineralToUse);
    nOxides = numel(oxidesToUse);
    nSamples = size(ICPMSData,1);

    % Filter ICPMSData
    isIncluded = ismember(header, oxidesToUse);
    ICPMSDataFiltered = ICPMSData(:,isincluded);
    ICPMSDataFilteredNormalized = ICPMSDataFiltered ./ repmat(sum(ICPMSDataFiltered, 2), 1, size(ICPMSDataFiltered,2));

    Aprime = [];

    % Built A in Ax = b
    for oxideIndex=1:nOxides
        oxide = oxidesToUse(oxideIndex);
        oxideMembers = ismember(OxideInfo(:,1), oxide);
        oxideMW = cell2mat(OxideInfo(oxideMembers,2));
    end
oxideElementRatio = OxideInfo{oxideMembers,3};

for mineralIndex = 1:nMinerals

    mineral = mineralToUse(mineralIndex);
    mineralMembers = ismember(mineralMWs(:,1), mineral);
    mineralMW = mineralMWs{mineralMembers,2};

    mineralMembers = ismember(elementMineralRatios(:,3), mineral);
    oxideMembers = ismember(elementMineralRatios(:,2), oxide);
    ratioIndex = mineralMembers & oxideMembers;
    eleMinRatio = elementMineralRatios{ratioIndex, 4};

    Aprime(oxideIndex, mineralIndex) = (oxideMW/mineralMW) * eleMinRatio/oxideElementRatio

end

end

clear AprimeCell
AprimeCell = cell(nOxides+1, nMinerals+1)
AprimeCell(1,2:end) = mineralToUse;
AprimeCell(2:end,1) = oxidesToUse;
AprimeCell(2:end,2:end) = num2cell(Aprime)

% Define the objective function
f = [0*ones(1,nMinerals) +1*ones(1, nMinerals)']
%f = [ones(1,numel(mineralToUse)) -1*zeros(1, numel(mineralToUse))]

% Insert slack variables into Aprime
A = [Aprime eye(size(Aprime))];

% Boundary Conditions for each variable
lb = zeros(1,2*nMinerals);
ub = ones(1,2*nMinerals);

% Sum Condition
Aeq = [ones(1,nMinerals) zeros(1, nMinerals)];
beq = 1;

resultsCell = cell(nSamples, nMinerals);
resultsCell(1,:) = mineralToUse;

for sampleNumber = 1:nSamples

    % Define b
    bprime = ICPMSDataFilteredNormalized(sampleNumber,:);
    b = bprime';
    %xInitial = mldivide(Aprime,b);

end

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% Run the Optimization
opts = optimoptions('linprog','Algorithm','interior-point');
opts.TolFun = 10^-10;
[x,fval,exitflag,output,lambda] = linprog(f,A,b,Aeq,beq,lb,ub,[],opts);

% Put the results
if isempty(x) == false
resultsCell(sampleNumber+1,:) = num2cell(100*x(1:end/2)');
end

end

resultsCell

2. Mineral and oxide inputs:

2.1. Data.xlsx file:

This is an excel file that allows the user to specify the ICP-MS or calibrated XRF data available to be used in modelling mineralogy. Data must be specified in fractional values not as wt. %.

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</thead>
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2.2. El Com Constants.xlsx file:
This is an excel file composed of several sheets that allow the user to specify the minerals to be solved for, their MW and element to mineral molar ratios.

a) **MW_Mineral sheet:**

This sheet allows the user to input the minerals that are to be solved for by “El Com” and their molecular weights.

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<th>Mineral</th>
<th>Molecular Weight (g/mol)</th>
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b) **Elemnet_Mineral sheet:**

This sheet allows the user to specify the element/element oxide to mineral ratios that will be used to calculate the $a_{ij}$ coefficients in the matrix $A_{prime}$. This sheet gives the user the freedom to change the chemical composition of the mineral to be solved. This is particularly useful for clays with varying chemical compositions.

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### Oxide_Info sheet:

This sheet allows the user to specify the MW of oxides or elements that are input into the model from ICP-MS or calibrated XRF data. If an oxide is used as input, the user must specify the ratio of the element into the oxide. If the user inputs calibrated XRF data the ratios may be kept as 1.

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