DOLOMITIZATION AND POROSITY EVOLUTION OF MIDDLE BAKKEN MEMBER, ELM COULEE FIELD AND FACIES CHARACTERIZATION, CHEMOSTRATIGRAPHY AND ORGANIC-RICHNESS OF UPPER BAKKEN SHALE, WILLISTON BASIN

by

Dipanwita Nandy
Copyright by Dipanwita Nandy 2017
All Rights Reserved
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Geology).

Golden, Colorado
Date: _________________

Signed: ___________________
Dipanwita Nandy

Signed: ___________________
Dr. Stephen A. Sonnenberg
Thesis Advisor

Golden, Colorado
Date: _________________

Signed: ___________________
M. Stephen Enders
Professor and Head
Department of Geology and Geological Engineering
ABSTRACT

This thesis is focused on improving the current geological understanding of the Bakken Shale Play, which currently produces with a rate of about 1 million BOPD and contributes about 12% of the total indigenous oil production of the US. In the first part of the thesis, I investigate the effect of dolomitization on the total porosity, pore architecture and pore-size of the Middle Bakken Member (MBM), which is one of the major producing intervals of the Bakken Shale Play. The second part of this research is focused on the organic-rich Upper Bakken Shale (UBS), which along with the Lower Bakken Shale, is the source rock interval for the Bakken Petroleum System. However, the potential of UBS as a future production interval is highlighted by the recent exploration successes and historical examples of production, which emphasizes the need for a comprehensive characterization of the UBS with respect to its facies and internal stratigraphic framework. I have investigated various aspects of the UBS, such as its facies types, their distribution in the basin and sedimentary processes. Moreover, chemostratigraphy was used to provide an internal stratigraphic framework for the UBS. The third part of this study is focused on understanding the role and interplay of the factors that controlled the organic-richness in UBS.

The first part of this research, which is focused on the MBM of the Elm Coulee Field, is based on the results of core description, thin section and scanning electron microscope (SEM) petrography, stable isotope of carbon and oxygen, routine core analysis (RCA), X-Ray Diffraction (XRD) and Mercury Intrusion Porosimetry (MIP). The relationships between dolomite content, total porosity, and pore size suggested that the porosity evolution in the MBM is closely linked with the dolomitization process. An increase in the dolomite content up to 60 wt.% results in an overall increase in the development of intercrystalline pores, total porosity, pore size, and dolomite crystal size. An increase in dolomite content above 60 wt.% marks overdolomitization of the MBM, which results in an increase in the size of dolomite crystals, and a decrease in both total porosity and pore size. My findings suggest that MBM of the Elm Coulee Field was dolomitized by seepage-reflux of the mesohaline brine. I propose that in the MBM, the dolomitization process involved an open-system volume-for-volume replacement of precursor calcite by dolomite, and the degree of dolomitization was dependent on the external supply of Mg\(^{2+}\) and (CO\(_3\))\(^{2-}\) ions. Dolomitization by volume-to-volume replacement results in an increase in the pore size, while the total porosity remains the same during the process. In MBM, an increase in porosity with an increase in dolomite content resulted from a relatively less compaction of dolomite-rich intervals, in comparison to the calcite-rich intervals, because the later is more susceptible to compaction. In the overdolomitization stage, dolomite crystals form interlocking fabrics, which in turn resulted in a decrease in the total porosity and pore size due to dolomite cement overgrowth.
I identify six lithofacies of the UBS from core description and thin-section petrographic study; however, 95% of the UBS consists of the three main facies: siliceous mudstone, massive to finely laminated silt-bearing mudstone, and macrofossil-bearing silt-rich mudstone. Three regionally correlatable chemostratigraphic packages (bottom to top): Sub-unit 1a, 1b, and Unit-2 were identified in the UBS. My study indicates that the maximum flooding surface is located in sub-unit 1b, near the contact of Unit-2 and sub-unit 1b. The results of this research show that during the deposition of the UBS, the basin was semi-restricted, had stratified water column, and the regeneration of the biolimiting nutrients such as P and N was one of the primary sources of nutrients. Moreover, the redox condition, paleoproductivity, and the influx of detrital and biogenic sediments varied during the deposition of the UBS, primarily due to a relative change in the sea level. This resulted in a temporal variation in TOC and the deposition of four distinct sub-units in the UBS (bottom to top): 1a, 1b, 2a, and 2b. Sub-units 1a and 1b were deposited in a strongly euxinic condition, which existed in the bottom water and extended to the photic zone intermittently. Whereas, during the deposition of sub-units 2a and 2b, the conditions were predominantly sub-oxic to anoxic along the sediment-water interface. Moreover, paleoproductivity was high during the deposition of sub-unit 1a and 1b, and paleoproductivity declined during the deposition of sub-units 2a and 2b.
# TABLE OF CONTENTS

**ABSTRACT** ........................................................................................................................................... iii  
**LIST OF FIGURES** ................................................................................................................................... viii  
**LIST OF TABLES** ..................................................................................................................................... xxi  
**ACKNOWLEDGEMENTS** ..................................................................................................................... xxiii  
**CHAPTER 1** **INTRODUCTION** .............................................................................................................. 1  
  1.1 Motivation .................................................................................................................................. 2  
  1.2 Research Objectives and Methods .......................................................................................... 3  
  1.3 Organization of the Thesis ........................................................................................................ 4  
  1.4 Conference Proceedings and Publication ............................................................................... 4  
  1.5 References .................................................................................................................................. 5  
**CHAPTER 2** **DOLOMITIZATION AND ITS EFFECT ON POROSITY EVOLUTION IN MIDDLE BAKKEN, ELM COULEE FIELD** ........................................................................................................... 7  
  2.1 Introduction ................................................................................................................................... 8  
  2.2 Literature review on origin of porosity in dolostones .............................................................. 8  
  2.3 Geological Setting .......................................................................................................................... 10  
  2.4 Methodology and Dataset ........................................................................................................... 11  
  2.5 Results and Interpretation ............................................................................................................ 14  
  2.5.1 Lithofacies Characterization ................................................................................................... 15  
  2.5.2 Diagenesis ............................................................................................................................... 16  
  2.5.3 Petrography and Stable Isotope of the Middle Bakken Dolomites ........................................ 25  
  2.5.4 Porosity Characterization ....................................................................................................... 26  
  2.5.5 Relationship between dolomite content and porosity .......................................................... 30  
  2.6 Discussion ...................................................................................................................................... 33  
  2.6.1 Dolomitization in Elm Coulee Field ....................................................................................... 33  
  2.6.2 Dolomitization process and porosity evolution ..................................................................... 37  
  2.6.3 Conceptual Model for Porosity Evolution ............................................................................. 39  
  2.7 Conclusions ..................................................................................................................................... 44  
  28 References ........................................................................................................................................ 44  
**CHAPTER 3** **FACIES CHARACTERIZATION AND CHEMOSTRATIGRAPHY OF ORGANIC-RICH UPPER BAKKEN SHALE, WILLISTON BASIN** ........................................................................................................... 50  
  3.1 Introduction ..................................................................................................................................... 50  
  3.2 Geological Setting ........................................................................................................................... 52  
  3.3 Methodology and Background ...................................................................................................... 55  
  3.3.1 Core and Dataset .................................................................................................................... 56
# Table of Contents

4.3.6 EF-Mo and EF-U relationship ................................................................. 140  
4.3.7 Mo-TOC Relationship and Basin Restriction ........................................ 141  
4.3.8 Redox-condition and OM preservation .................................................. 142  
4.3.9 Proxy for Paleoproductivity ................................................................. 143  
4.4 Discussion .............................................................................................. 145  
4.4.1 Depositional Setting ............................................................................. 145  
4.4.2 Model for Organic Richness in Chemostratigraphic Units of UBS ....... 148  
4.5 Conclusion ............................................................................................ 152  
4.6 References ............................................................................................ 153  

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK .... 159  
5.1 Conclusion ............................................................................................ 159  
5.2 Recommendations for Future Work ....................................................... 160  

APPENDIX A DIGITIZED CORE DESCRIPTION OF MIDDLE BAKKEN MEMBER, ELM COULEE FIELD ................................................................. 159  
APPENDIX B RAW DATA AND SOFT COPIES ............................................ 170  
APPENDIX C XRF MEASUREMENT QUALITY ASSURANCE AND QUALITY CHECK .... 170  
C.1 Sample Preparation ................................................................................ 172  
C.2 Optimal Detection Time ........................................................................ 173  
C.3 Reproducibility Test and XRF Measurement Validation ....................... 175  
C.4 Repeatability Test ................................................................................... 178  
APPENDIX D CHEMOSTRATIGRAPHIC PROFILES AND CORRELATIONS .......... 182
LIST OF FIGURES

Figure 1.1: (a) Chart showing the daily oil production rate of the US from 1920 to 2017 and the historical peak, which was attained in October 1970. The contribution of shale boom in the daily US oil production (purple color) post 2000 is also shown. (b) Chart showing a breakdown of the daily production of the different US shale plays and their relative contribution in the total US production. The chart shows, as of 2017, the Bakken contributes about 23% of the daily shale play production from the US. (Data Source for charts EIA, 2017) .......................................................... 2

Figure 2.1: Location map of the Williston Basin with subsea structure contour on the base of the Mississippian. Elm Coulee Field is located in northeast Montana, demarcated by the black ellipse. The limit of the Bakken Formation is shown by a dashed line. P=location of the Parshall field area; A=location of Antelope field. (modified from Sonnenberg and Pramudito, 2009). ............................................ 13

Figure 2.2: Late Devonian-Early Mississippian stratigraphic column of the Williston Basin showing the Bakken Formation and the underlying Three Forks Formation and overlying Lodgepole Formation. (modified from Webster (1984) and Sonnenberg and Pramudito (2009)). ................................................................................................ 13

Figure 2.3: Isopach map of the Middle Bakken Member with the location of the wells studied in this paper. The extent of the Elm Coulee Field is outlined by the green line. The red line is the boundary of the Richland County. Location of the wells which were studied for core description and routine core analysis (RCA) and X-ray diffraction (XRD) derived mineralogy were examined are shown by the yellow circles. Abbreviation of the well names shown in this map is given in Table 2.1. .... 15

Figure 2.4: The nine different lithofacies identified in the Middle Bakken Member (MBM) of the Bakken Formation in the Elm Coulee Field are shown in the core photographs. Detail description of each facies is listed in Table 2.2. .......................... 18

Figure 2.5: Core description of well Coyote Putnam showing lithofacies variation in the Middle Bakken along with the corresponding depth profiles of porosity and saturation obtained from routine core analysis and dolomite, calcite and clay content obtained from XRD analysis. MB-Middle Bakken, UBS-Upper Bakken Shale. Details about the degree of dolomitization is discussed later in Section 2.5.5. ............................................................................................................................. 19

Figure 2.6: The paragenetic chart is showing the different diagenetic events that the Middle Bakken Member (MBM) has undergone in the Elm Coulee Field. ......................... 21

Figure 2.7: (a) The core photograph is showing patchy calcite cementation (white dashed line) in the Middle Bakken facies B. CP, 10365.2ft. (b) The photomicrograph is showing the patchy calcite (red) cement in the Middle Bakken facies B. Plane light, BEL,10411.3ft. (c) The photomicrograph is showing micritization envelope which developed on bioclast while calcite cement precipitated within the bioclast in the Middle Bakken facies B. Plane light, BEL, 10411.3ft. ...................................................................................................... 22

Figure 2.8: (a) The photomicrograph is showing dolomitized matrix with unreplaced calcareous bioclasts. Plane light, BEL,10414.2ft. (b) The photomicrograph is showing zoned, planar euhedral dolomite rhomb in the matrix of the Middle Bakken facies B. Zoning in dolomite rhomb is shown by the pink arrows. Plane light, CP,10353.5ft. ......................................................................................................................... 22
Figure 2.9: The photomicrographs are showing different forms of pyrite in the Middle Bakken in Elm Coulee Field. (a) Pyrite within dolomite rhomb is indicated by the yellow arrow, whereas pyrite around the edge of the dolomite rhomb is shown by the white arrow. Pink haze in the matrix is due to impregnation of the thin section by red dye and indicates microporosity. Plane light, CP, 10353.41ft. (b) Pyrite is replacing calcareous fossil fragment. Plane light, BEL-10414.2ft. (c) and (d) Bioclast fragment is replaced by two generations of cement, microcrystalline silica (white arrow) and pyrite (yellow arrow). Plane light (c) and crossed polar (d). CP-10371.93ft.

Figure 2.10: Scanning Electron Microscope (SEM) image is showing: (a) authigenic quartz overgrowth (yellow arrow), and (b) authigenic pore bridging illite in intercrystalline pore between the dolomite rhombs. CP4, 10350.3ft.

Figure 2.11: Secondary anhydrite in different forms in the Middle Bakken in the Elm Coulee is shown in, (a) The core photograph is showing the anhydrite pseudomorphs burrows. CP, 10354.1ft (yellow arrow). (b) The core photograph is showing the anhydrite nodule (yellow arrow). LT, 10409.5ft. (c) and (d) The photomicrographs are showing poikilotopic anhydrite cement in plane light and crossed polars respectively (yellow arrow). (e) and (f) The photomicrographs are showing poikilotopic anhydrite cement in plane light and crossed polars respectively. Note the euhedral dolomite rhombs are floating in the anhydrite cement (yellow arrow).

Figure 2.12: δ¹⁸O versus δ¹³C crossplot comparing the completely dolomitized samples which were collected in this study from the Middle Bakken in Elm Coulee Field, with the reported values in the literature. Blue and green rectangles are stable isotope values of carbon and oxygen obtained from the Late Devonian and Early Mississippian unaltered brachiopods respectively from Mii et al. (1999) and Van Geldern et al. (2006). Gray shaded rectangle indicates expected stable isotope values in dolomite which is in equilibrium with the Late Devonian sea.

Figure 2.13: Box plot of routine core analysis (RCA) derived porosity of the Middle Bakken in the Elm Coulee Field, showing the porosity variation observed in the field. The median porosity of each of the facies is shown by a white line within the box plots. Data consists of samples from all the facies from eight cores whose locations are shown in Figure 2.3.

Figure 2.14: The photomicrographs are showing textural features corresponding to different dolomite content in the Middle Bakken facies B in the Elm Coulee Field. (a) Intercrystalline pores between dolomite rhombs which are sized between 10-15 µm are pointed by the yellow arrows. These pores are visible in petrographic thin section in completely dolomitized intervals. Plane light, SJ, 9731.35ft. This sample has RCA porosity of 7.07% and dolomite content of 50 wt.% obtained from XRD. (b) Intercrystalline pores between dolomite rhombs which are sized between 10-15 µm are shown by the yellow arrows. These pores are visible in petrographic thin section in completely dolomitized intervals. Plane light, CP, 10356.42ft. This sample has RCA porosity of 7.86% and dolomite content of 58 wt.% obtained from XRD. (c) Microporosity (sub-micron sized) between dolomite rhombs in the matrix is enhanced by the red dye in petrographic thin section. Micron sized pores are not present. Plane light, BY-10472.5ft. The sample has RCA derived porosity of 5.98% and dolomite content of 45 wt.% obtained from XRD. (d) Orange hue is showing the microporosity (sub-micron sized) between dolomite rhombs in the matrix. Epifluorescence, BY-10472.5ft.
This sample has RCA derived porosity of 5.98%, and XRD derived dolomite content of 45 wt.%. (e) Microporosity is not visible in thin section impregnated with red dye. Plane light, CP-10367.16 This sample has RCA porosity of 3.73% and dolomite content of 36 wt.% obtained from XRD. (f) No visible porosity in thin section impregnated with the red epifluorescence dye. Epifluorescence, CP-10367.16ft. Sample has RCA derived porosity of 3.73%, and XRD derived dolomite content of 36 wt.%.

Figure 2.15: The Scanning Electron Microscope (SEM) photomicrographs are showing pore architecture in the Middle Bakken facies B in the Elm Coulee Field. (a) Intercrystalline pores between dolomite rhombs are shown by yellow arrows. CP (2), 10356.42ft. This sample has RCA porosity of 7.86% and dolomite content of 58 wt.% obtained by XRD. (b) Yellow arrows show intercrystalline pores between the dolomite rhombs, which is filled by pore bridging authigenic illite. The presence of illite in between the dolomite rhombs results in a complex pore network and a decrease in the pore throat size. CP (6), 10359.29ft. This sample has RCA porosity of 8.85% and dolomite content of 50 wt.% obtained from XRD. (c) Intercrystalline pore between dolomite rhombs which is shown by the yellow line is filled by pore filling authigenic illite. CP4, 10350.3ft. The sample has RCA derived porosity of 5.93%, and XRD derived dolomite content of 51 wt.%. (d) Intercrystalline slot pores (yellow line) between dolomite rhombs which is filled by pore bridging authigenic illite. CP4, 10350.3ft. This sample has RCA derived porosity of 5% and dolomite content of 51 wt.% obtained from XRD.

Figure 2.16: Crossplot between X-ray diffraction (XRD) derived dolomite content, and routine core analysis (RCA) derived total porosity. Samples are color-coded by dolomite index (DI), which is a measure of the degree of dolomitization. Porosity increases as dolomite content increase up to 60 wt.%. Beyond that, porosity starts decreasing as dolomite content increases more than 60 wt.%.

Figure 2.17: Pore throat size distribution of the Middle Bakken samples from the Elm Coulee Field determined by Mercury Intrusion Porosimetry (MIP) is shown. Pore throat size distribution is color-coded by X-ray diffraction (XRD) dolomite content. Porosity and mineralogy details of the samples are given in Table 2.3.

Figure 2.18: (a) Subhedral, partially coalesced micritic particles of precursor limestone, corresponding to the Stage I of porosity evolution. Intercrystalline sub-micron sized pores between the micrite particles. BEL, 10402ft, Dol-13 wt.%, Calc-58 wt.%, porosity-3.64%. (b) Remnant microcrystalline calcite from the precursor micritic lime mud is present in between the euhedral dolomite rhombs in the partially dolomitized Middle Bakken facies B (stage II of porosity evolution). Dolomite rhombs are 15-20 µm in size. Note that micritic calcite is in direct contact with the dolomite rhombs. BY-13, 10457.6ft, Dol-36 wt.%, Calc-24 wt.%, porosity-2.39%. (c) Subhedral to anhedral fully coalescent remnant microcrystalline calcite from precursor lime mud is in direct contact with the 20 µm sized dolomite rhombs in the partially dolomitized Middle Bakken facies B (stage II of porosity evolution). (d) Intercrystalline pores between the euhedral dolomite rhombs, in the completely dolomitized interval of the Middle Bakken corresponding to the stage III of porosity evolution, is shown by yellow arrows. Dolomite rhombs are around 30-40 µm in size. CP (2), 10356.42ft. The sample has RCA derived porosity of 7.86%, and XRD derived dolomite content of 58 wt.%. (e) Euhedral dolomite rhombs from the overdolomitized interval (stage IV of porosity evolution) forming interlocking texture with compromised crystal
boundaries between dolomite rhombs is shown by the black arrow. Dolomite rhombs are more than 100 µm in size. BY-14, 10457.6ft, Dol-66 wt.%, porosity-4.25%. (f) Interlocking texture with compromised crystal boundaries (pink arrow) between euhedral dolomite rhombs in the overdolomitized interval (stage IV of porosity evolution) of the Middle Bakken is shown by black arrows. Dolomite rhombs are more than 100 µm in size. CP-3, 10353.25ft, Dol-63 wt.%, porosity-4.4%.

Figure 2.19: Schematic diagram illustrating an increase in the size of dolomite rhombs results in an increase in pore size.

Figure 2.20: Conceptual model illustrating porosity evolution both spatially and temporally due to seepage reflux dolomitization in a ramp setting. As seepage reflux continues from time T\textsubscript{1} through T\textsubscript{2} continues, limestones are progressively dolomitized, with the formation of dolomite cement near the source of the brine and anhydrite cement at the distal end, which in turn results in variation of porosity. (Jones and Xiao, 2005)

Figure 2.21: (a) At time T\textsubscript{1}, the precursor lime mud got deposited, and the entire sediment column has an overall high porosity. (b) At time T\textsubscript{2}, early patchy calcite cementation results in porosity loss at depths between d\textsubscript{0} to d\textsubscript{1}. (c) At time T\textsubscript{3}, seepage reflux of mesohaline brine has started. Sediment column from d\textsubscript{3} to d\textsubscript{2} is partially dolomitized, with the degree of dolomitization decreasing down the depth. No change in total porosity is observed between lime mud and partially dolomitized limestone due to dolomitization. However, pore space and pore size are modified as intercrystalline pores start to form between dolomite rhombs. Moreover, the formation of anhydrite cement may result in minor loss of porosity near depth d\textsubscript{1}. (d) At time T\textsubscript{4}, seepage reflux of mesohaline brine continues such that the partially dolomitized lime mud between d\textsubscript{3} to d\textsubscript{2} is completely dolomitized with no change in total porosity. While lime mud between d\textsubscript{2} to d\textsubscript{1} is partially dolomitized with the degree of dolomitization decreasing down the depth such that below depth d\textsubscript{0}, precursor lime mud remains unaltered. There is no change in total porosity due to dolomitization. However, pore space and pore size are modified as intercrystalline pores forms between dolomite rhombs. Moreover, the formation of anhydrite cement may result in minor loss of porosity between depth d\textsubscript{1} to d\textsubscript{0}. (e) At time T\textsubscript{5}, seepage reflux of mesohaline brine continues such that the completely dolomitized interval between d\textsubscript{3} to d\textsubscript{2} is overdolomitized with a loss in porosity due to the formation of dolomite cement. While partially dolomitized lime mud between d\textsubscript{2} to d\textsubscript{1} is completely dolomitized. Below depth d\textsubscript{1}, the precursor lime mud is partially dolomitized with the degree of dolomitization decreasing down the depth such that below depth d\textsubscript{0}, precursor lime mud remains unaltered. There is no change in total porosity due to dolomitization. However, pore space and pore size are modified as intercrystalline pores forms between dolomite rhombs. (f) At time T\textsubscript{5}, after cessation of the seepage reflux dolomitization, mechanical compaction of the sediment column occurs due to burial. This results in differential compaction of the sediment column such that the precursor lime mud is more compacted and therefore, loses more porosity in comparison to the dolostones.

Figure 3.1: (a) Map showing the distribution of the Bakken Formation in the Williston Basin and its equivalent Exshaw Formation and Lower Banff Formation in the Western Canada Sedimentary Basin (modified from Smith and Bustin, 2000). (b) Locations of the wells used in this study are shown in the isopach map of the
Upper Bakken Shale in the U.S. portion of the Williston Basin (source: Stephen Sonnenberg, personal communication). Abbreviations of the names of the wells used in this study are listed in Table 3.1.

Figure 3.2: Generalized stratigraphic column of the Williston Basin with an expanded section showing the stratigraphic details along with the conodont zones of the Late-Devonian-Early Mississippian age Bakken Formation (Sandberg et al., 1988; Karma, 1991; Hartel et al., 2012; Sonnenberg, 2015).

Figure 3.3: (a) Core photograph illustrating massive radiolarian-dominated siliceous mudstone (F1a). The characteristic ptygmatic pyrite-filled, sub-vertical fractures in facies F1a are shown by white arrows. Well: Rasmussen 1-21-6H, 10211ft. (b) Core photograph illustrating finely laminated radiolarian and silt-bearing mudstone (F1b). Well: Rasmussen 1-21-6H, 10214ft.

Figure 3.4: (a) Scanned petrographic thin section image showing ~14mm thick bed of massive radiolarian dominated mudstone (F1a). The sharp contact at the base and top of the facies F1a are indicated by the white arrow; Well: LTE, 10386 ft. (b) Optical photomicrograph of F1a showing the typical fabric of the massive radiolarian dominated siliceous mudstone (F1a). The high content of radiolarians, which are shown by the red arrow is evident from this photomicrograph. Wispy organic matter surrounding the radiolarians is shown by the yellow arrow. (c) Thin section photomicrograph of facies F1a showing radiolarian tests, which was replaced by chert (green arrow), sphalerite (yellow arrow) and pyrite (red arrow). Well: RT, 10663.60 ft. (d) Optical photomicrograph of facies F1a showing is radiolarians, which are replaced by calcite (green arrow) and pyrite (red arrow). As evident, it is difficult to distinguish the shape of the individual radiolarians as they are mostly dissolved out. Well: RT, 10661.9 ft.

Figure 3.5: (a) Optical photomicrograph showing a vertical ptygmatic fracture (red arrow) in massive radiolarian dominated mudstone (F1a). Well: RT, 10663.60ft. (b) Optical photomicrograph showing the vertical fracture (red arrow) in Figure 3.5a at higher magnification. Two generations of cement within the fracture, sphalerite (red arrow) followed by pyrite (yellow arrow) is observed. Well: RT, 10663.6ft..

Figure 3.6: (a) Scanned petrographic thin section image of laminated radiolarian and silt-bearing mudstone (F-1b). The double-headed yellow arrows show sub-mm scale laminae of F1b. Red arrows showing sphalerite-filled vertical fractures in the middle of the image Well: LT, 10390.1ft. (b) An optical photomicrograph of laminated radiolarian and silt-bearing mudstone (F-1b) showing discontinuous laminae of radiolarians (red arrows). Radiolarians (yellow arrows) along with silt grains are observed to be randomly distributed in an organic matter and clay-rich matrix in the lower part of the image. Well: LT, 10390.1ft.

Figure 3.7: (a) Core photograph showing the massive to finely laminated silt-bearing mudstone (F2). Discontinuous mm-size pyrite lenses (shown by the yellow arrow) is the most distinct macro-scale characteristics of F2. Well: R, 1265ft. (b) Optical photomicrograph of massive to finely laminated silt-bearing mudstone (F2) showing the presence and fecal pellets (p) and silt grains which are randomly dispersed in the matrix. Well LT, 10384.6ft, TOC: 14.3 wt.%. (c) Optical photomicrograph showing massive to finely laminated silt-bearing mudstone (F2a), which have characteristically high matrix content and proportionately less fecal pellets (<5%) compared to massive to finely laminated fecal pellet and silt-bearing mudstone (F2b). Well: BN, 10352.1ft. (d) Optical photomicrograph...
showing massive to finely laminated fecal pellet and silt-bearing mudstone (F2b), which have proportionately higher amounts of fecal pellets (p) (>5%) compared to massive to finely laminated silt-bearing mudstone (F2a). Well: 4-11-7-13W2, 1776.25 ft, TOC: 28.6 wt.% .......................................................... 66

Figure 3.8: (a) FE-SEM image of massive to finely laminated silt-bearing mudstone (F2) showing the presence of pyrite framboids (pyr fram), which are less than 10 µm in size and are randomly dispersed in clay and organic matter-rich matrix. Well: RT, 10668 ft, TOC: 14.7 wt.%. (b) Optical photomicrograph showing the occasional presence of radiolarians (rad) in massive to finely laminated silt-bearing mudstone (F2). Well: RT, 10665.5 ft, TOC: 12 wt.%.............................................. 67

Figure 3.9: (a) Optical photomicrograph from a parallel to bedding thin-section from massive to finely laminated silt-bearing mudstone (F2) showing the cross-section of type 1 fecal pellet, which is cylindrical in shape, clay-rich and organic poor. Well: LT, 10388.1 ft, TOC: 11.2 wt.%. (b) Optical photomicrograph from a parallel to bedding thin-section from massive to finely laminated silt-bearing mudstone (F2) showing the cross-section of type 2 fecal pellet, which is circular-shaped and silt-rich. Well: LT, 10388.1 ft, TOC: 11.2 wt.%. (c) FESEM image showing the shape of type 1 fecal pellet, which is cylindrical in shape and 200 µm in length. Well: RT, 10665.6 ft, TOC: 10.5 wt.%. (d) The SEM-EDAX image showing the near absence of organic matter (red) within the type 1 fecal pellet, while the matrix is rich in organic matter. Well: RT, 10665.6 ft, TOC: 10.5 wt.% .......................... 68

Figure 3.10: (a) Core photograph showing continuous and discontinuous lamination (yellow arrow) of sand and clay-bearing, silt-rich mudstone (F3). (b) Scanned image of a petrographic thin section showing planar silt laminations (yellow arrow) in the sand and clay-bearing, silt-rich mudstone (F3) well-LT, depth-10389 ft (c) Optical photomicrograph showing framework components of very-fine sand to coarse silt grains in a clay and organic-rich matrix in facies F3. (d) An optical micrograph showing massive to finely graded beds of facies F3. Presence of phosphatic fragments is indicated by the yellow arrows. Well: LT, 10387.1 ft. (e) The optical photomicrograph showing starved ripples and continuous planar silt lamina. Well: LT, 10389.8 ft.......................................................... 70

Figure 3.11: (a) Optical photomicrograph showing lenticular silt beds with a sharp base and overlain by a clay-rich lamina. The sample is from well LT, depth 10389 ft. (b) The optical photomicrograph is showing horizontal Planolites burrow indicated by yellow arrow in the clay-rich lamina overlying the silt lamina. Well: RT, 10670 ft.......................................................... 71

Figure 3.12: (a) Core photograph of macrofossil-bearing silt-rich mudstone (F4) showing horizontally aligned thin-shelled brachiopods (brac), which is a diagnostic characteristic of this facies. Well: RT, 10654 ft. (b) Core photograph of macrofossil-bearing silt-rich mudstone (F4) showing thin-shelled brachiopods in facies F4. Well: L, 10937.2 ft. (c) The optical photomicrograph showing articulated brachiopods (brac) in facies F4. Brachiopods are partial to completely pyritized. Well: RT, 10654.5 ft. (d) The optical photomicrograph showing articulated brachiopods (brac) in facies F4. Brachiopods are replaced by silica and pyrite. Well: RT, 10653.5 ft.......................................................... 72

Figure 3.13: (a) and (b) Optical photomicrograph in plane polars and crossed polars showing the presence of abundant silt content and homogeneous fabric in facies F4. Homogeneous fabric in facies F4 is probably a result of meiofaunal burrowing.
Abundant detrital dolomite (dd), authigenic dolomite and agglutinated benthic foraminifera (af) in this facies are observed at the lower right corner of the image. Well: RT, 10653.5ft TOC: 2.78 wt.%. (c) and (d) Optical photomicrograph in plane polar and crossed polars, showing agglutinated benthic foraminifera (af) in the facies F4 at a higher magnification. Presence of quartz silt in the wall of the benthic foraminifera can be seen in the wall of benthic foraminifera as pointed by the yellow arrow. Well-RT, 10650ft, TOC: 7.34 wt.%.................................................................73

Figure 3.14: (a) Optical photomicrograph is showing few silt grains thick discontinuous planar laminae with downlapping surface (shown by the yellow arrow) in macrofossil-bearing silt-rich mudstone (F4). Well: RT, 10354.5ft (b) Core photograph showing the presence of macroscale Planolites burrows (pl) in macrofossil-bearing silt-rich mudstone (F4). Well: L, 10934ft. ............................................................................74

Figure 3.15: (a) Core photograph showing macro-scale Planolites burrows (b) in burrow-mottled silt-bearing mudstone (F5) at the contact of UBS with the overlying Lodgepole Formation. Well: LT, 10383.2ft. (b) A core photograph is showing macro-scale Planolites burrows (b) in burrow-mottled silt-bearing mudstone (F5) at the contact of UBS with the overlying Lodgepole Formation. Well: RT, 10648ft. (c) Scanned image of petrographic thin section showing Planolites burrows (b) in facies F5. Well: LT, 10383.2ft. (d) Optical photomicrograph of facies F5 is showing that the burrow (b) filled by constituents, which are similar to the matrix, and is devoid of organic matter. Well: LT, 10383.2ft. ..........................75

Figure 3.16: (a) Core photograph showing mm-thick bed of phosphate clast and fossil-rich mudstone (F6). Well: R, 11026.6ft. (b) Core photograph showing cm-thick bed of phosphate clast and fossil-rich mudstone (F6). Well: BN, 10358.4ft. (c) Core photograph is showing cm-thick bed of phosphate clast and fossil-rich mudstone (F6) at the contact of UBS with the Middle Baken. Well: R, 11044.6ft. (d) Optical photomicrograph showing phosphate clasts, and sponge spicules (shown by red arrow) oriented randomly in phosphate clast and fossil-rich mudstone (F6). The base of this facies shows microscouring. Well: BN, 10352ft. ....................................................76

Figure 3.17: Four groups of element clusters shown on the crossplot between the two principal components determined from Principal Component Analysis (PCA) in XLSTAT™ of twenty elements. The PCA was performed on around 400 UBS sampled from sixteen cores.................................................................77

Figure 3.18: (a) Cross-plot of Al vs. Ti showing a strong positive covariance between the two elements, which indicates that Al has a detrital origin in UBS. (b) Crossplot of K vs. Ti showing strong positive covariance between the two elements indicating K has a detrital origin. Each crossplot includes all the samples from the sixteen wells for, which XRF data were collected in this study. All the data points are color-coded by the three different chemostratigraphic units of UBS which are described in Section 3.4.5. All the three crossplots form two clusters, which correspond to the two main chemostratigraphic units, namely Unit-1 and Unit-2. ............................79

Figure 3.19: (a) Cross-plot of Al vs. K showing a strong covariance between the two elements, which indicates that most of the Al and K are associated with clay minerals in UBS. (b) Crossplot between Ti vs. Si showing a negative correlation, which indicates that Si has both non-detrital origin biogenic/authigenic origin and detrital origin. All the data points are color-coded by the three different chemostratigraphic units of UBS which are described in Section 3.4.5. All the
three crossplots form two clusters, which correspond to the two main chemostratigraphic units, namely Unit-1 and Unit-2.

Figure 3.20: Box and whisker plot showing the variation in the absolute concentration for the three redox-sensitive trace elements: Mo, U, and V in UBS. Each plot comprises of all samples of UBS from all the sixteen wells for which XRF data was collected in this study.

Figure 3.21: (a) Crossplot of Mo vs. U showing a strong positive covariance between the two elements. (b) Cross-plot between Fe and S showing a positive covariance which indicates that most of the Fe and S are associated with pyrite. DOP_T (Degree of Pyritization) lines in the crossplot are based on Algeo and Maynard (2004). All the samples are color-coded by the three different chemostratigraphic units of UBS, which are described in Section 3.4.5.

Figure 3.22: (a) Cross-plot of Mo vs. V showing a weak covariance between the two elements. The data points from three different clusters which are indicated in by encirclements. (b) Cross-plot of U vs. V showing a weak correlation between the two elements. The data points from three different clusters are indicated by encirclements. All the samples are color-coded by the three different chemostratigraphic units of UBS, which are described in Section 3.4.5.

Figure 3.23: Depth profiles comparing the XRF data of major elements and XRD mineralogy of UBS in (a) Well LT, and (b) Well BF.

Figure 3.24: Core description and chemostratigraphic profile with elemental trends of biogenic, detrital, carbonate and redox-proxying elements from Rolf 1-20H core showing the chemostratigraphic sub-unit 1a, sub-unit 1b and Unit-2 of UBS. From left to right: Si-silicon; Al-aluminum; K-potassium; Ti-Titanium; Zr-zirconium; Ca-calcium; Mo-molybdenum; U-uranium; V-vanadium. MFS-Maximum Flooding Surface.

Figure 3.25: Core description and chemostratigraphic profile with elemental trends of biogenic, detrital, carbonate and redox-proxying elements from Roberts Trust 1-13H showing the chemostratigraphic sub-unit 1a, sub-unit 1b and Unit-2 of UBS. From left to right: Si-silicon; Al-aluminum; K-potassium; Ti-titanium; Zr-zirconium; Ca-calcium; Mo-molybdenum; U-uranium; V-vanadium; MFS-Maximum Flooding Surface.

Figure 3.26: Core description and chemostratigraphic profile with elemental trends of biogenic, detrital, carbonate and redox-proxying elements from core Graham USA 1-15 showing the showing the chemostratigraphic sub-unit 1a, sub-unit 1b and Unit-2 of UBS. From left to right: Si-silicon; Al-aluminum; K-potassium; Ti-titanium; Zr-zirconium; Ca-calcium; Mo-molybdenum; U-uranium; V-vanadium. MFS-Maximum Flooding Surface.

Figure 3.27: NE-SW chemostratigraphic correlation between wells RR Lonetree Edna, Round Prarie 1-17H, Rolf 1-20H, Sidonia 1-06H and Jorgensen 1-15H.

Figure 3.28: NW-SE chemostratigraphic correlation between wells Rasmussen 1-21-16H, Charlotte 1-22H, Roberts Trust 1-13H, and Miller 34X-9.

Figure 3.29: (a) Isochore map of the UBS showing north-northwest to south-southeast trend of maximum thickness in the basin depocenter. (b) Isochore map for sub-unit 1a showing a north-northwest to south-southeast trend of maximum thickness in the basin depocenter. Maximum thickness for sub-unit 1a is encountered in well C.
(6.5ft). (c) Isochore map of chemostratigraphic sub-unit 1b showing a north-northwest to south-southeast trend of maximum thickness in the basin depocenter. Maximum thickness for sub-unit 1b is encountered in well L (9ft). (d) Isochore map of chemostratigraphic Unit-2 showing the development of maximum thickness around wells L and RT in the southern part of the basin depocenter. Unit-2 loses its thickness drastically along the southern basin margin. Maximum thickness for Unit-2 is encountered in well RT (9.2ft). An inset map in each figure showing the isopach map of the entire UBS in US-portion of the Williston Basin and the shaded box in the inset map represents the study area. Locations of wells are shown by black dots. Abbreviations of well names used in the maps are listed in Table 3.1.

Figure 3.30: Correlation is showing the lateral and vertical facies distribution in the three different chemostratigraphic units. The boundaries of the three units marked in this correlation are picked from the chemostratigraphic profiles.

Figure 3.31: Correlation is showing the lateral and vertical facies distribution in the three different chemostratigraphic units. The boundaries of the three units marked in this correlation are picked from the chemostratigraphic profiles of the wells.

Figure 3.32: Vertical profile of gamma ray (GR) log and SRA derived total organic carbon (TOC) for UBS for wells: RT, BF, and S showing the presence of high GR peak near the base and top of UBS and an upward decreasing trend in the middle of UBS interval in all the three wells. In well RT, TOC profile mimics GR trend, whereas in the other two wells variation in TOC is insignificant and TOC profile does not follow GR.

Figure 3.33: Histograms showing the statistical distribution of Mo concentration in various chemostratigraphic units of UBS. a) For sub-unit 1a, more than 90% of the samples have Mo concentration more than 100ppm; b) For sub-unit 1b, more than 80% of the samples have Mo concentration more than 100ppm; b) For Unit-2, more than 60% of the samples have Mo concentration more than 100ppm.

Figure 3.34: Ternary plot representing $5\times Al_2O_3-SiO_2-2CaO$ relationship (after Brumsack, 1989) of the chemostratigraphic sub-unit 1a, 1b, and Unit-2 of UBS. The three axes of $(5\times Al_2O_3)$, SiO$_2$ and $(2\times CaO)$ represents clays, quartz and/or biogenic silica, and total carbonates respectively. The black data points represent XRD mineralogy from five wells, shape of the data points represents the three different chemostratigraphic units. The ternary plot includes all the samples from the sixteen wells for which XRF data has been collected in this study. All the data points are color-coded by the three different chemostratigraphic units of UBS. The data points form mainly two clusters, which correspond to the two main chemostratigraphic units: Unit-1 and Unit-2. Sub-unit 1b predominantly clusters below the 50% clay line, whereas Unit-2 plots above the 50% clay line.

Figure 4.1: Location of well Robert Trust 1-13H (RT) is shown by the red star in the isopach map of the Upper Bakken Shale (modified from Sonnenberg et al., 2017).

Figure 4.2: Schematic S-Fe-C ternary diagram showing the different degrees of pyritization (DOP) regions for suboxic, anoxic and euxinic conditions (modified from Rimmer et al., 2004).

Figure 4.3: Integrated profile of UBS in core Roberts Trust 1-13H (RT) showing different chemostratigraphic units of UBS, which were distinguished based on the vertical distribution of lithofacies, detrital and biogenic proxying elements of Si, Al, K,
Ti, Zr/Rb ratio, Ca and redox-proxying elements of Mo and U. Characteristics of each chemostratigraphic sub-unit are summarized in Table 4.1. The profile of TOC, stable isotope of $\delta^{15}$N$_{org}$, which is a proxy for the paleoproductivity, and stable isotope of $\delta^{13}$C$_{org}$, which acts as the proxy for the OM type, are also shown. TOCSRA represents TOC measured from source rock analysis (SRA) and TOCorg represents original TOC calculated from TOCSRA. The basis for identifying the Maximum flooding surface (MFS) was described in Section 3.5.5................................. 129

Figure 4.4: Samples from Well RT plotted on the modified Van Krevelen diagram showing sub-unit 1a, 1b and 2b predominantly consist of type II-III organic matter, while sub-unit 2a has a higher proportion of type III organic matter. ................................. 131

Figure 4.5: Box and whisker plot showing the stable isotope of carbon ($\delta^{13}$C$_{org}$) results for the different chemostratigraphic UBS units in Well RT. Mean values of $\delta^{13}$C$_{org}$ for each of the chemostratigraphic sub-units are labeled to the right of each of the boxes. Average values for $\delta^{13}$C$_{org}$ terrestrial-type III (-25‰ to -26 ‰) and marine-type II (-30 ‰) OM are also shown from Chen and Sharma (2016) by the green rectangle and brown line respectively............................................................ 132

Figure 4.6: Cross plot between Ti and Al show a positive linear covariance for Unit-1, which indicates that Al has a detrital origin. (b) Crossplot between Ti and K show a positive linear covariance for Unit-1, which indicates that K has a detrital origin, and for this unit, K can be used as a proxy for detrital illite clay. (c) Crossplot between Al and TOCorg show weak positive covarriance, which indicates that influx of clay did not result in dilution of organic matter as Al is a proxy for detrital clay minerals in UBS (Section 3.4.2, Chapter-3). (d) Crossplot between K and TOCorg show no covarricance, which confirms that influx of clay did not result in dilution of organic matter as K is a proxy for detrital clay minerals in UBS (Section 3.4.2, Chapter-3). (e) Crossplot between Ti and Al show a positive linear covariance for Unit-2, which indicates that Al has a detrital origin in this unit also. (f) Crossplot between Ti and K show a positive linear covariance for Unit-2, which indicates that K has a detrital origin, and for this unit, K can be used as a proxy for detrital illite clay. (g) Crossplot between Al and TOCorg for Unit-2 show a positive linear covariance, which indicates that influx of clay helped in organic matter preservation in Unit-2 as Al is used as proxies for detrital clay minerals (h) Crossplot between K and TOCorg for Unit-2 show a positive linear covariance, which confirms that influx of clay helped in organic matter preservation in Unit-2. ............................................................ 133

Figure 4.7: (a) Crossplot between Ca and TOCorg for Unit-1 show no correlation indicating influx of carbonates did not affect organic matter preservation. (b) Crossplot between Ca and TOCorg for Unit-2 showing a negative linear correlation, which indicates influx of carbonates especially detrital dolomites resulted in dilution of organic matter ............................................................ 134

Figure 4.8: For Unit-1, crossplots between (a) Si and Al, and (b) Si and Ti, showing no covariance, which indicates in Unit-1 has a considerable proportion of Si is associated with the radiolarians in siliceous mudstone (F1). It also indicates that biogenic silica had a dilution effect on the detrital clay. (c) Crossplot between Si and TOCorg for Unit-1 show a negative correlation indicating influx of biogenic Si had resulted in the dilution of organic matter. For Unit-2, crossplot between (d) Si and Al (e) Si and Ti show positive correlation indicating Si in Unit-2 has detrital origin. (f) Crossplot between Si and TOCorg for Unit-2 showing a
negative correlation, which indicates influx of detrital Si associated with silt-sized sediment had resulted in the dilution of organic matter. ......................................................... 135

Figure 4.9: (a) Crossplot between total iron (Fe$_T$) and total sulfur (S$_T$) for different chemostratigraphic sub-units of UBS is shown. S$_T$/Fe$_T$ stochiometric ratio of 1.15 represents pyrite shown by the black solid line in the plot, and the equivalent degree of pyritization (DOP) is equal to 1 for this line, which indicates the euxinic condition. The green broken line represents regression fit for Unit-1 and black broken line represents the regression fit for Unit-2. Unit-1 plots close to DOP=1 line indicating that most of the iron in Unit-1 is associated with pyrite and this unit was deposited in euxinic condition. Whereas Unit-2 plots below the DOP=1, which indicates that supply of iron was more compared to sulfur and pyrite formation was sulfur limited. This indicated Unit-2 was deposited at comparatively less reducing conditions than Unit-1. (b) Crossplot between $TOC_{org}$ and total sulfur (S$_T$) for the different chemostratigraphic units of UBS is shown. Solid line represents S and C trend for oxygenated normal marine conditions during organic matter deposited. Broken lines represent linear regression data for Unit-1 and Unit-2. The non-zero intercept of the linear regression lines for both Unit-1 and Unit-2 in the crossplot indicates that their deposition has taken place in reducing condition and not in oxygenated condition. ................................................................. 136

Figure 4.10: Fe-S-TOC$_{org}$ ternary diagram for UBS samples from well RT showing sub-unit 1a and 1b mostly plot along DOP=0.96, which indicates a strongly euxinic condition for these sub-units. Sub-unit 2a plots along DOP=0.56 suggesting suboxic condition for this sub-unit, while sub-unit 2b plots between DOP of 0.56-0.75, suggesting for 2b the paleoredox condition fluctuated from suboxic to anoxic with increasing intensity of anoxia compared to that in sub-unit 2a. ............. 137

Figure 4.11: Crossplot between (a) $TOC_{org}$ vs Mo; and (b) $TOC_{org}$ vs U showing three distinct covariation patterns. (c) Chart showing the expected pattern of relative enrichment of Mo and U at suboxic, anoxic and euxinic conditions (modified from Tribovillard et al., 2006), which suggest in suboxic condition, $TOC_{org} < 5$ wt.%; Mo has no enrichment while U shows limited enrichment. In anoxic condition, $5 < TOC_{org} < 12.5$ wt.%, both Mo and U shows moderate enrichment and has a good linear covariance pattern with $TOC_{org}$. In euxinic condition, $TOC_{org} > 12.5$ wt.%, concentration of Mo and U increases exponentially and shows poor correlation with $TOC_{org}$. ......................................................... 138

Figure 4.12: Crossplot between U Enrichment factors (U-EF) vs. Mo Enrichment factors (Mo-EF) showing three clusters of the UBS samples from core RT. The broken lines represent 0.3, 1 and 3 times of the average Mo/U of present-day seawater (SW). The general patterns of U-EF vs. Mo-EF variation in modern marine environments are represented by (i) gray field for unrestricted marine trend for eastern tropical Pacific Ocean, (ii) green field for semi-restricted Cariaco Basin, where particulate shuttle function for Mo enrichment within the water column and (iii) black solid line for strongly restricted Black Sea (adopted from Tribovillard et al., 2012). The yellow field represents areas, where the presence of sulfurized organic matter leads to very high enrichment of Mo in strongly euxinic conditions (Tribovillard et al., 2012). Sub-unit 1a and 1b plots in the zone of sulfurized organic matter (yellow field), whereas sub-unit 2b and part of sub-unit 2a and plots in the anoxic to the euxinic field (gray area). Finally, rest of the
samples from sub-unit 2a plot in the sub-oxic to the anoxic field in the gray area.

Figure 4.13: (a) Mo-TOC\textsubscript{org} crossplot for UBS in Well RT showing slope (m) for the regression line for chemostratigraphic sub-unit 1a, 1b and 2b are 21.1, 23.5 and 19.3 respectively. Value of m for these UBS sub-units is close to that of the semi-restricted Cariaco Basin, which m value close to 25. (b) m versus deepwater renewal times for modern anoxic silled basins showing an average m of 21 for UBS suggests the deepwater renewal in the Williston Basin during the deposition of UBS was around 25 years (modified from Algeo and Lyons, 2006).

Figure 4.14: (a) Box and whisker plot showing the results for the stable isotope of nitrogen (δ\textsuperscript{15}N\textsubscript{org}) for the chemostratigraphic units of UBS in well RT. The mean values of δ\textsuperscript{15}N\textsubscript{org} for each chemostratigraphic units are also labeled. (b) TOC\textsubscript{org} vs δ\textsuperscript{15}N\textsubscript{org} crossplot showing that sub-unit 1a and 1b have high TOC and lighter values of δ\textsuperscript{15}N\textsubscript{org}, whereas sub-units 2a has comparatively lower TOC and heavier values of δ\textsuperscript{15}N\textsubscript{org}. Sub-unit 2b has mixed values of δ\textsuperscript{15}N\textsubscript{org}. This crossplot indicates paleoproductivity during the deposition of Unit-1 was comparatively higher than that during the deposition of sub-unit 2a. The paleoproductivity increased marginally again during the deposition of sub-unit 2b.

Figure 4.15: Schematic diagram showing the prevailing depositional setting of the Williston Basin during the deposition of UBS. The basin was under the influence of the east-west trade wind as shown by the yellow arrow due to its location near the equator. The Williston Basin was semi-restricted in nature due to the presence of the Central Montana Uplift, which was situated at the south-west of the basin. Stratified water column developed due to the formation of a thermocline, which stabilized the chemocline, which in turn developed as a result of degradation of organic matter. The chemocline created a stagnant euxinic bottom water condition during the deposition of Unit-1 of UBS. However, when the depth of the thermocline is lowered due to fall in the sea level, the seasonal fluctuation of the thermocline disturbed the chemocline. This, in turn, decreased the reducing condition at the sediment-water interface during the deposition of Unit-2. The primary source of the nutrients was through regeneration of the biolimiting nutrients N and P in euxinic condition.

Figure 4.16: (i) Stratified water column shown developed during the deposition of sub-unit 1a due to the formation of a thermocline. Accumulation of OM continued incessantly, which exhausted the oxygen content in the bottom water and thereby resulted in the development of a stagnant euxinic condition below the chemocline. The biolimiting nutrients P and N were preferentially released in a euxinic condition, which resulted in high surface water productivity. Seasonal fluctuation of the depth of the thermocline also resulted in fluctuation of the chemocline which aided in releasing the nutrients back to the surface water. (ii) The relative rise in sea level during the deposition of sub-unit 1b increased the height of the oxygenated surface water column which decreased the export productivity since more OM were degraded while settling down through the water column. Primary productivity in the surface water was high. Bottom water conditions were still euxinic which extended to the photic zone intermittently. (iii) The sea level drop resulted in disappearance of radiolarians, and the depth of the thermocline dropped due to the fall in relative sea level during the deposition of sub-unit 2a. So, the thermocline became closer to the chemocline. Seasonal
fluctuation of the thermocline destabilized the chemocline due to the partial mixing of the water column. This resulted in the formation of sub-oxic to anoxic condition along the sediment-water interface. Paleoproductivity decreased as the biolimiting nutrients were less efficiently regenerated in sub-oxic condition. As more land area got exposed due to relative sea level fall, it was covered by vegetation which became the source of more terrestrial OM during the deposition of sub-unit 2a. (iv) During the deposition of sub-unit 2b, there was a minor increase in the depth of the thermocline due to a slight increase in relative sea level. As a result, the chemocline stabilized, and conditions were more reducing which enhanced the regeneration of the biolimiting nutrients (P and N). Therefore, the surface water productivity was higher compared to that of sub-unit 2b.

Figure C.1: Photograph showing two of the thirteen UBS-matrix specific sample standard cups, which were used in this study for XRF measurement QA-QC purpose.

Figure C.2: Optimal detection time for the Main, Low, High and Light filters for UBS is shown schematically. The effect of an increase in the detection duration on the measurement of absolute concentration and the error (2σ) also shown.

Figure C.3: The change in elemental concentration measurement and relative error for different excitation filters sequences (EFS) for Si, Al, K, Mo, U, and V is shown. Optimum time and EFS is characterized by stabilization of elemental concentration readings and relative error values. For light elements Si and Al, the optimum DT for the UBS samples with Niton handheld XRF were 180s and that for other elements was 120s.

Figure C.4: Niton-ICP/Element Analyzer cross plots for eighteen selected elements showing the relationships between Niton measured elemental concentrations and laboratory-grade measurements made by ICP-MS/ICP-OES and element analyzer. Best-fit linear regression lines are shown with associated R² values for each plot. For elements Al, Si, Ca, Fe, S, Mo, and U have a zero y-axis intercept.

Figure C.5: Profile of the representative suite of major and trace elements comparing Niton XRF and ICP-MS measurements. Visual identification of the elemental trend between the Niton XRF and ICP-MS measurement show consistency.

Figure C.6: Depth profiles of concentration show the repeatability test results for trace and major elements for eleven UBS samples (represented by sample depth) from well RT for each test runs. The error bars indicate the variability in elemental concentration measurement is for five test run for a sample of given depth. The red line connects the average of the five runs, whereas the blue line shows the spread of the measurement. Repeatability of the XRF measurement using Niton handheld XRF in TAG mode is confirmed by consistency in both major inflections and concentration changes for five test-run.

Figure C.7: Repeatability of the XRF element concentration measurements for the eleven UBS samples from core RT is shown in the heat-map, in which the numbers represent the variation σμ. The color-scale and the bar show the relative degree of repeatability for element concentration measurement by XRF. Cooler color (green) and lower percentages indicate better repeatability. Mg (Atomic No.-12), which was not used in this study, in general, shows poor repeatability because hand-held XRF and TAG mode used in this study is not suitable for detecting elements lighter than Al (Atomic No.-13).
LIST OF TABLES

Table 2.1: Name and location of the wells from the Elm Coulee Field from which cores, thin sections, routine core analysis (RCA) and X-ray diffraction (XRD) mineralogy are used in this study. ................................................................. 14

Table 2.2: Sedimentary and ichnologic characteristics of the sedimentary facies identified in the Middle Bakken in the Elm Coulee Field. ................................................................. 17

Table 2.3: Measured porosity from routine core analysis and dolomite, calcite, clay content derived from X-ray diffraction and dolomite index (DI) of the samples analyzed for mercury intrusion porosimetry (MIP) in Figure 2.16. ........................................ 32

Table 3.1: Names, abbreviations, APIs, and locations of the wells used in this study are listed. The available dataset used in this study are also listed. Description of abbreviations and symbol used in the table are as follows, Core Desc.: Core Description, Thin Sec.: Thin-section. ✓: Acquired in this study, ✗: not available, ✓#: Available from external sources.1-USGS, 2-Fishman et al. (2015), 3-(Jin, 2014), 4-(Kocman, 2014), and 5-NDGS. Sample for well 4-11-7-13W2 was available from Hui Jin (personal communication). ................................................................. 56

Table 3.2: Characteristic differences in terms of the biogenic, detrital, grain-size proxy, redox proxy and facies between Unit-1 and Unit-2 are listed. The signature of the boundary marker is also specified. ................................................................. 83

Table 3.3: The characteristic differences between sub-unit 1a and 1b in terms of the biogenic, detrital, grainsize proxy, redox proxy and facies are listed. The signature of the unit boundary marker is also specified. .................................................................... 83

Table 3.4: Thickness of different chemostratigraphic sub-units and units of UBS in all the eighteen wells used in this study. Well Abv- Abbreviation for well names. ................ 88

Table 4.1: The characteristic differences between sub-units 1a, 1b, 2a and 2b in terms of the biogenic, detrital, grainsize proxy, redox proxy and facies. .................................................. 128

Table 4.2: Organic geochemistry results for different chemostratigraphic units of Well RT as derived from the Source Rock Analysis (SRA). Legend: µ: mean; R: Range; σ: Standard deviation; HI: Hydrogen Index; OI: Oxygen Index; TOC SRA: SRA measured TOC; TOC Org: Original TOC calculated TOC SRA ........................................ 130

Table 4.3: Findings for the paleoredox conditions based on inorganic geochemical methods and petrographic observations. ................................................................. 144

Table B.1: Table listing the file description for data used in Chapter-2 of the thesis. .......... 170
Table B.2: Table listing the file description for the data used in Chapter-3 of the thesis. .... 170
Table B.3: Table listing the file description for the data used in Chapter-4 of the thesis. .... 171
Table B.4: Table listing the file description of additional data of the Upper and Lower Bakken Shale collected during the PhD curriculum. ........................................... 171
Table B.5: Table listing the file description for selected published papers and conference presentations during the PhD curriculum......................................................... 171
Table C.1: Table for coefficient of regression (R^2) and slope (m) for the best-fit linear regression lines for the Niton-ICP/Element Analyzer cross plots for eighteen selected elements showing the relationships between Niton measured elemental
concentrations and laboratory-grade measurements made by ICP-MS/ICP-OES and element analyzer. The XRF-measured concentration of elements which has been used quantitatively and semi-quantitatively in Chapter 3 are highlighted in red. ............................................................................................................................. 177

Table C.2: The results for element concentration measurements using Niton handheld XRF for the repeatability test is listed. The table lists the results for concentration of trace elements and major element, which were used in this study, for all five runs for each of the eleven samples (represented by their depth).................................. 178
ACKNOWLEDGEMENTS

This PhD would not have materialized without the sincere support, which I have received in these 5 years, from many individuals. I consider myself privileged to have such a prolific committee, and I take this opportunity to thank them for sharing their expertise and investing their time in my education.

- Steve Sonnenberg: I will be short of words in thanking you for all your support. Sincere thanks for entrusting me with all the freedom I enjoyed in driving this research at my own pace and way. Thanks for always believing in me and providing me with this opportunity. Your dedication and enthusiasm were a constant source of inspiration, and something, which will keep me motivated for my entire life.
- Mark Longman: You were always and will be a great source of knowledge and inspiration for me. Thanks for all your ‘thought-provoking’ questions and insights. Without them, my PhD research would never have taken this final shape.
- Piret Plink-Björklund: Your Applied Stratigraphy class made me more curious about the significance of sedimentary processes, which helped me immensely in my PhD research. Thanks for enriching me with all your inputs on mudrock depositional processes and for always provoking to think about an alternative interpretation.
- Manika Prasad: You were always inspirational in all our interactions, which were helpful in setting some of my research goals for this PhD. Thank you for supporting me on giving me direction for the research on the porosity characterization of the Middle Bakken Member. I would also like to thank you for giving me the opportunity to present my work at the OCLASSH consortium sponsors meetings.
- John Curtis: Thanks for agreeing to be on my committee at a very short notice. Thanks for all your kind suggestions and help, throughout this PhD curriculum.

I sincerely thank all the members and sponsors of the Bakken Consortium for funding this research and my PhD curriculum at CSM. I would also thank the Bakken Consortium for providing access to data and samples, which were used in this research. I would also like to extend my gratitude to North Dakota Geological Survey (NDGS) Grand Forks and US Geological Survey (USGS) core research center Denver for giving me access to their core libraries and allowing sample collection and data acquisition. I take the opportunity to remember Late Julie LeFever to express my sincere gratitude for sharing her immense knowledge about the Bakken Formation. I would like to thank Rocky Mountain Association of Geologists and Rocky Mountain-SEPM for the scholarships during my PhD. I would also like to thank John Humphrey for making me interested in carbonates specially in dolomites.
I thank Kathy Emme, Cheryl Medford, and Dorie Chen for providing all the administrative support during my tenure as a PhD student, including scheduling and planning to meet the thesis timeline. My colleagues in Bakken Consortium and Geology Department were a great support system with their cooperation and feedback, thanks to, especially Jingqi Xu, Cosima Theloy, Hui Jin, Mohammad Al Duhailan, Kazumi Nakamura, Claudia Gutierrez, Gary Listiono.

I also thank my alma-mater Presidency University Kolkata, and Indian Institute of Technology Roorkee for laying the foundation of my knowledge of Geology. My husband Sanyog Kumar has been more than just a constant support. Without his motivation and valuable inputs, this PhD would not have been materialized. I would also thank my father-, mother- and sister-in-law for their immense support. Finally, I thank my parents, without whom I would not have achieved anything. I would also thank my daughter Disha for her smiles, which kept me going while I was writing this thesis.
To Disha and Sanyog
CHAPTER 1

INTRODUCTION

Bakken Shale Play currently produces with an average rate of 1 million BOPD and contributes about 23% of the total production from U.S. shale plays. The production boom from Bakken and other American shale plays is one of the most dramatic growth stories the world of oil has ever seen. The 2017 edition of OPEC’s flagship publication *World Oil Outlook* (WOO) suggests that non-OPEC supply growth is dominated by the continuously increasing production from the U.S. shale plays. WOO (2017) further suggests that shale output is projected to rise from 5.1 million BOPD in 2017 to 7.5 million BOPD by 2021 and to 8.7 million BOPD by 2025. The growth is illustrated in Figure 1.1a, which shows historical U.S. daily oil production from 1920 to 2017 (data source: EIA); U.S. oil production peaked in October 1970 with an average daily rate of 10.1 MM BOPD, and then declined till 2007. After that year, it witnessed a steep rise, and daily production is currently near its historical peak in 1970. This remarkable rise is overwhelmingly driven by production from shale plays, as demonstrated by Figure 1.1b, which provides a breakdown of daily rate in terms of contribution from the major U.S. shale plays (EIA, 2017). In 2007 these so-called unconventional plays were contributing less than 10% of U.S. daily rate, whereas in 2017 their contribution was above 50%. However, despite the success story of U.S. shale play production, WOO (2017) also raised concerns regarding the possibility of a steep decline in their production after 2025. The report considered the excessively front-loaded nature of the shale projects, which are primarily driven by aggressive drilling programs, as the primary reason for this imminent decline. However, given the enormous in-place volume estimates for the shale resources, such premature decline would essentially leave a large volume of untapped reserves, which will be unrecoverable with current technology. Therefore, a holistic improvement in state-of-the-art technology for shale exploration and production is required to enhance hydrocarbon recovery efficiency. Bridging various knowledge gap in current geoscientific understanding can immensely improve the efficiency of exploration and production activities in shale plays. This thesis aims at developing a better understanding of the Bakken Shale Play, by contributing the following: 1) investigating the significance of the dolomitization process in porosity evolution of the Middle Bakken Member; 2) defining the lithofacies and chemostratigraphic sub-units of the Upper Bakken Shale; and 3) understanding the factors controlling the organic richness of the Upper Bakken Shale.
Motivation

The Bakken petroleum system consists of two major reservoir intervals: the Middle Bakken Member (MBM) of the Bakken Formation and the Three Forks Formation. The cumulative estimated ultimate recoverable (EUR) volume of these two intervals is 5 billion bbl (EIA U.S. Reserves Report, 2016). The history of oil production from the Bakken Formation dates back to 1953, which marked the discovery of the Antelope Field. However, the Bakken Formation came into the limelight in 2001, as the hydrocarbon production potential of the MBM was significantly improved by adopting a strategy of multi-stage hydraulic fracturing (HF) completion in horizontal wells. The first major success story of this development was the discovery of the Elm Coulee Field in Montana in 2001. Subsequently, in this field alone, more than 800 such horizontal wells were drilled and completed, the in-place volume is estimated to be 2 billion Bbl, and the EUR is around 300 MBbl (Theloy, 2014). The Elm Coulee Field has been extensively studied to understand facies characterization and diagenesis (Sonnenberg and Pramudito, 2009; Alexandre, 2011), structural interpretations from seismic data (Eidsnes, 2014; Rolfs, 2015), static and dynamic reservoir modelling (Almanza, 2011) and feasibility studies for Enhanced Oil Recovery (Todd and Evans, 2016). However, for the Elm Coulee Field, no detailed porosity characterization of the MBM has been performed. Therefore, for the MBM, there is a lack of understanding of the pore-types, pore-architecture, pore-size, the
effect of clay content, and the role of dolomitization, which was the most crucial diagenetic event in terms of the evolution porosity in MBM.

The naturally fractured Upper Bakken Shale (UBS) was a producing interval from 1976 to 2000 (Sonnenberg, 2014) in the Bakken Play. However, the scale of these production activities was not as enormous as that of dolomitic siltstone the MBM. This historical production and the recent success in exploration efforts in UBS in the southwest flank area of the Elm Coulee Field indicate the resource potential of the UBS (Sonnenberg, 2014). This emphasizes the necessity of developing a better understanding of the UBS for identification of target intervals and sweet-spots, which will aid in future exploration and production efforts. The UBS has been extensively studied to understand its depositional environment, source rock potential, and organic and inorganic geochemistry (e.g. Meissner, 1978; Price et al., 1984; Webster, 1984; Hayes, 1985; Smith and Bustin, 1996, 1998; Egenhoff and Fishman, 2013; Jin, 2014; Kocman, 2014; Longman et al., 2014). However, there still exist gaps in the understanding of the UBS with respect to its major lithofacies, and their lateral and vertical distribution, and basin-wide stratigraphic framework. The organic-rich UBS of the Bakken Formation is a world-class source rock with an average total organic content (TOC) of 11 wt.% (LeFever et al., 1991; Sonnenberg and Pramudito, 2009; Jin, 2014). However, there is limited understanding of the factors which have controlled this organic richness.

1.2 Research Objectives and Methods

The above-mentioned gaps in the understanding of the Bakken Formation have been the motivation for my research. The following have been my primary research objectives:

1) For the MBM in the Elm Coulee Field, to develop an understanding of the pore-types, pore-architecture, pore-size, the effect of clay content, and the role of dolomitization in porosity evolution. To fulfill these research objectives, firstly, the cores were described; this was followed by thin section petrographic studies, stable isotope analysis, scanning electron microscope (SEM) imagery, and mercury intrusion pore-size distribution study. The dataset from these analyses and experiments were integrated with routine core-analysis results and X-Ray diffraction (XRD) mineralogy data;

2) To identify the lithofacies of the UBS and their lateral and vertical distribution, and to define laterally correlatable chemostratigraphic units of the UBS, their depositional conditions, and their thickness variation in the basin. To fulfill these research objectives, firstly, lithofacies were identified by integrating core description results with thin-section petrographic observations. This was followed by XRF data acquisition on core slabs for chemostratigraphic analyses. The results of these two major analyses were integrated to understand the depositional conditions of the UBS;
3) To develop an understanding of the interplay of paleoproductivity, redox condition and dilution of Organic Matter in controlling the organic richness of the UBS and then to develop a conceptual model for its deposition. This research objective was fulfilled by integrating the findings of the ICPMS elemental concentration data, Source Rock Analysis (SRA)-derived Total Organic Content (TOC), and stable isotopes of carbon and nitrogen.

1.3 Organization of the Thesis

Chapters 2, 3 and 4 document my research as three journal-style papers, and each has an introduction, sections on geological settings, methodology, results and interpretation, discussion and conclusion. Chapter 5 summarizes the findings and applications of my research and lists recommendations for future work. Chapter-2 addresses my first research objective and the title of this paper is “Dolomitization and its effect on the porosity evolution in the Middle Bakken, Elm Coulee Field.” Chapter-3 focuses on my second research objective and the title of this paper is “Facies characterization and chemostratigraphy of Upper Bakken Shale, Williston Basin.” Chapter 4 addresses my third research objective, and the title of this paper is “Factors controlling organic richness of Upper Bakken Shale, Williston Basin.” General conclusions and recommendations for future work are provided in Chapter-5.

1.4 Conference Proceedings

I have presented my research findings at various conferences. In addition to the research findings, I present in this thesis, my presentations have included other contributions on the chemostratigraphy of the Lower Bakken Shale and the depositional model of the D-Facies of the MBM. Presentations given during various conference proceedings are as follows:


1.5 References


EIA, 2017, Crude Oil Production(Online), Available at: https://www.eia.gov/dnav/pet/pet_crd_crpdn_adc_mbbi_m.htm


CHAPTER 2

DOLOMITIZATION AND ITS EFFECT ON POROSITY EVOLUTION IN MIDDLE BAKKEN, ELM COULEE FIELD

The current state of the art on the characterization of sub-micron sized pores in tight carbonate rocks are mostly limited to limestones and chalks. But sub-micron sized pores are also common and are of significance in dolostones since they affect the hydrocarbon saturation and production performance. In this paper, I present a case study on the microporosity characterization of the Middle Bakken silty dolomites of the Elm Coulee field, Williston Basin. This paper also develops an understanding of the various dolomitization stages, which affects the evolution of porosity in the Middle Bakken silty dolostones. The shallow marine mixed-siliciclastic-carbonate deposits of the Middle Bakken Member (MBM) in Elm Coulee Field are dolomitized to varying degrees, and the dolomite content ranges from 5 to 65 wt.%. Dolomitization process in MBM of Elm Coulee Field was defined by a collective analysis of petrographic observation, X-Ray Diffraction (XRD) mineralogy, and stable isotope of C and O results of the core samples from eight wells of the field. Moreover, routine core analysis, Mercury Intrusion Porosimetry (MIP), and Field Emission Scanning Electron Microscope (FESEM) studies were performed on these core samples to determine the total porosity, pore-size distribution, and pore architecture.

Dolomite crystals with planar subhedral to euhedral fabric, stable isotope results, the presence of late anhydrite cement and overdolomitization indicate that the Middle Bakken dolostones in Elm Coulee Field are the product of seepage-reflux dolomitization in mesohaline conditions. Relationships between dolomite content, total porosity, and pore size suggest that the porosity evolution in the MBM is closely linked with the dolomitization process and is mainly dependent on the degree of dolomitization. A progressive increase in the dolomite content (up to 60 wt.%) results in an overall increase in the development of intercrystalline pores, total porosity, pore size and dolomite crystal size. However, with further increase in dolomite content beyond 60 wt.%, (overdolomitization), total porosity and pore size decrease as the size of the dolomite crystals increases. In the MBM, the dolomitization process involves volume-for-volume replacement of precursor calcite by dolomite in an open system. Moreover, the degree of dolomitization is dependent on the external supply of Mg and (CO$_3$)$_2^-$ ions. In this process, the total porosity remains same, while the pores size increases. However, as limestone is more susceptible to compaction than dolomite, so higher dolomite content in the MBM results in a comparatively lower porosity loss due to compaction. This explains the increase in porosity in the MBM with an increase in dolomite content. However, in the overdolomitization stage, dolomite crystals form interlocking fabrics, which in turn decreases the total porosity and pore size due to the formation of dolomite cement overgrowths.
2.1 Introduction

About a half of the world’s carbonate type petroleum reservoirs are dolostones (Al-Awadi et al., 2009); however, there are no modern-day analogs to the ancient massive dolostone systems. Therefore, the origin of dolostones and the process of dolomitization have been extensively studied in the past. Dolomitization commonly results in reservoirs with unique geometries and porosity distribution, which have a direct impact on exploration and production strategies. The role of dolomitization in porosity evolution was discussed by Powers (1962); Davies (1979); Allan and Wiggins (1993); Sun (1995); Warren (2000); Lucia (2004); Ehrenberg et al. (2006); Choquette and Hiatt (2008); Maliva et al. (2011); and Wang et al. (2015). After even five decades of research, the topic of the origin of porosity in dolostones is still controversial (Purser et al., 1994; Lucia, 2004; Ehrenberg et al., 2012). It has been observed that deeply buried, particularly Paleozoic dolostones, have better porosity than the associated limestone (Landes and Arbor, 1946; Murray, 1960; Longman et al., 1983; Schmoker et al., 1985; Purser et al., 1994; Sun, 1995; Saller and Henderson, 1998). However, because of this observation, it has been postulated that the dolomitization process results in an increase in porosity. This hypothesis gained further support in its favor due to the mole-for-mole replacement equation of dolomitization, which is $2\text{CaCO}_3 + \text{Mg}^{2+} = \text{CaMg(CO}_3\text{)}_2 + \text{Ca}^{2+}$. De Beaumont (1837) suggested that the mole-for-mole conversion of calcite to dolomite results in a 12.96% decrease in grain volume because the molar volume of dolomite is less than the molar volume of calcite. This contraction of grain volume is believed to cause a 12.96% increase in porosity of the dolomitized rock. Despite a multitude of case studies showing relatively higher porosity in dolostones, there are examples where a contrary relationship has been reported. For example, Lucia and Major (1994) observed that for the Plio-Pleistocene carbonates in Bonaire, Netherlands Antilles, the precursor limestones are more porous than the corresponding dolostones. Similarly, in their description of the upper Paleozoic buildup reservoir from the Horseshoe Atoll complex, Texas, Saller et al. (2004) noted that dolostones have lower porosity than the associated limestones. Furthermore, the Upper Jurassic Arab reservoirs of Saudi Arabia and Qatar show an overall decrease in porosity with dolomitization (Powers, 1962; Cantrell et al., 2004). Maliva et al., (2011) reported that the dolostones and associated limestones have nearly the same total porosity, thereby showing no change in porosity due to dolomitization. Therefore, the literature suggests that the porosity in dolostones can be enhanced or reduced, or it can remain same due to the process of replacement of calcite in limestones by dolomite. This ambiguity was explained by Morrow (1982) on the basis of the following volume-for-volume reaction: $(2-x)\text{CaCO}_3 + x(\text{CO}_3^{2-} + \text{Mg}^{2+} = \text{CaMg(CO}_3\text{)}_2 + \text{Ca}^{2+}$, where $x$=moles of external carbonate $(\text{CO}_3^{2-}$ ions added from the dolomitizing fluid. Therefore, depending on the amount of external $(\text{CO}_3^{2-}$ ions supplied to the system by the dolomitizing fluid, porosity of the resulting dolostone may increase, remain constant or decrease. Lucia (2004) suggested that
dolomitization does not create additional porosity; however, the external \((\text{CO}_3)^2-\) ions in the solution results in an occlusion of porosity.

This study focuses on the hydrocarbon bearing interval of the Middle Bakken Member (MBM) silty dolostones, in the Bakken Formation of the Elm Coulee Field, Montana. The porosity of the MBM ranges from 2% to 10% in the Elm Coulee Field, while the permeability varies from 0.02-0.04mD (Sonnenberg and Pramudito, 2009; O’Brien et al., 2012). Sonnenberg and Pramudito (2009) and Alexandre (2011) observed that the MBM in those sub-intervals and location, which are dolomite-rich, have better reservoir quality (porosity and permeability) and better hydrocarbon saturation. However, a detailed analysis of porosity, which is shown in this study, suggests that this may not always be true in all cases. Moreover, Alexandre (2011) has observed micropores in petrographic thin sections of the Middle Bakken from the Elm Coulee Field under an epifluorescence microscope. The term “micropores” from here onward refers to less than 1µm throat-size pores, according to the convention used by Pittman (1971) and Lucia (1995). However, by definition from Loucks et al., (2012), these sub-micron sized pores would be classified as nanopores, which is the convention of International Union of Pure and Applied Chemistry (IUPAC). However, recent studies focused on the evolution of sub-micron sized pores in carbonates are limited to limestones and chalks (Deville de Periere et al., 2011; Lucia and Loucks, 2013; Kaczmarek et al., 2015; Loucks and Ulrich, 2015). This study gives the opportunity to see the effect of dolomitization in the evolution of micropores in the Middle Bakken. Moreover, this study provides an explanation of these observations through the effect of dolomitization on different aspects of porosity evolution in the MBM.

Investigation of petrography and corresponding measured porosity and pore size distribution of carbonates, especially in the transition zone from limestone to dolostone in cores, could link the textural evolution to the porosity changes during the dolomitization process. In this chapter, I summarize previous studies on the formation mechanisms of porosity in dolostone and then investigate how the process of dolomitization affects porosity evolution in the MBM in the Elm Coulee Field by integrating core descriptions, petrography, core analysis and stable isotope data. The focus of this study is to understand the changes in texture, pore structure, porosity and pore size that occur through different stages of dolomitization.

The main objectives of this study with respect to the MBM in the Elm Coulee Field are:

1. Characterize the facies of the MBM from core description
2. Identify diagenetic stages based on petrographic studies
3. Identify dolomitization model based on petrographic and geochemical constraints
4. Characterize porosity both qualitatively and quantitatively
5. Investigate how the process of dolomitization affects porosity evolution in the MBM
2.2 Literature review on origin of porosity in dolostones

Dolostones are formed as a result of replacement of calcite in limestones by dolomite. Therefore, the origin of porosity in dolostones can be divided into three categories: pre-dolomitization, syndolomitization, and post-dolomitization, based on the relationship between the timing of porosity formation and the dolomitization process. When porosity in the dolostone is inherited from the precursor limestone and do not change due to dolomitization, it is termed as the pre-dolomitization origin of porosity. When porosity, pore space or pore size is altered during dolomitization, it is termed as the syndolomitization origin of porosity. When total porosity, pore types and pore size is altered after dolomitization and is controlled by fluids unrelated to the dolomitization process, it is termed as the post-dolomitization origin of porosity. The syndolomitization origin of porosity has been described in the literature either by the mole-for-mole replacement reaction or by the volume-for-volume replacement reaction. These two reactions are described in the section below.

Mole-for-mole replacement

When dolomite replaces calcite, Mg$^{2+}$ ions substitute half of the Ca$^{2+}$ ions from the crystal lattice. The reaction is expressed by the following equation (Tucker and Wright, 1990):

$$2\text{CaCO}_3 + \text{Mg}^{2+} = \text{CaMg(CO}_3\text{)}^2 + \text{Ca}^{2+}$$

(2.1)

De Beaumont (1837) proposed that the conversion of limestone to dolostone is based on this classic mole-for-mole replacement reaction, which causes an overall shrinkage in grain volume as the molar volume of Mg$^{2+}$ is less than that of Ca$^{2+}$. The decrease in grain volume, in turn, increases porosity in the dolostones. This theory has been extensively used to interpret the formation of porous dolostone, especially in deeply buried carbonate strata where dolostones are observed to be more porous than the surrounding limestones. However, the mole-for-mole replacement reaction is countered by many authors (Morrow, 1982; Land, 1983; Lucia, 2004) as it assumes that dolomitization takes place in a closed system, in which only Mg$^{2+}$ are added to the system from the dolomitizing fluid. Weyl (1960) countered this by demonstrating that (CO$_3$)$^{2-}$ ions are present in a minor fraction in the formation waters with respect to Mg$^{2+}$ and Murray (1960) suggested that (CO$_3$)$^{2-}$ ions involved in the dolomite precipitation are mainly derived from local carbonate sources. The mole-for-mole mechanism also fails to explain the occurrence of lower porosity in dolostones compared to the associated limestone. For example, in Plio-Pleistocene carbonates of Bonaire limestones and dolomitic limestones have similar ranges of 20–30% porosity, whereas the adjacent dolostones have the lower porosities of about 11% (Lucia and Major, 1994), which cannot be explained by the mole-for-mole replacement reaction. This also fails to account for the occurrence of dolomitic pore occluding cement. Such contrary observations suggest that external (CO$_3$)$^{2-}$ ions must be added to the replacement reaction during the dolomitization process to form the extra dolomite. Moreover,
most dolomitization processes are supposed to take place in open to semi-open systems (Land, 1983); the
dolomitizing fluid which brings Mg\(^{2+}\) ions can also bring in \((CO_3)^{2-}\) ions and remove the Ca\(^{2+}\) ions. 
Moreover, the Ca\(^{2+}\) ions released from the precursor calcite need to be taken out of the reaction site to
maintain the optimum Mg/Ca ratio required for precipitation of dolomite.

**Volume-for-Volume Reaction**

Many studies in the past have observed that the porosity remains unchanged as limestone is
dolomitized (Maliva et al., 2011). This was explained by Morrow (1982) based on the following volume-
for-volume replacement reaction:

\[
(2-x) \text{CaCO}_3 + x(\text{CO}_3)^{2-} + \text{Mg}^{2+} = \text{CaMg(\text{CO}_3)_2} + (1-x) \text{Ca}^{2+}
\]  
(2.2)

Where x is the number of moles of external \((\text{CO}_3)^{2-}\) ions added from the dolomitizing fluid. It is proposed
that the volume of \((\text{CO}_3)^{2-}\) ions required to replace the difference in molar volume is 0.1 for aragonite and
0.25 for calcite. Lucia (2004) suggests that in this condition of dolomitization, although the total porosity
in dolostones is inherited from the precursor limestone, dolomitization can modify the pore space and
thereby change the pore size. After all the precursor calcite has been replaced, but the dolomitizing fluid
have optimum Mg\(^{2+}\) and \((\text{CO}_3)^{2-}\)ions, then dolomite will continue to precipitate. This results in a decrease
in porosity and pore throat size and is termed as “overdolomitization” by Halley and Schmoker (1983).

Maliva et al., (2011) suggested that dolomitization affects porosity differentially on the scale of
individual crystals, beds, and formations. At the crystal scale, dolomitization occurs by volume-for-volume
replacement reaction in which the space occupied by the precursor calcite is replaced by a solid dolomite
rhomb with an associated reduction in porosity. However, as \((\text{CO}_3)^{2-}\) ions are passively scavenged from the
formation, so there is no change in porosity at formation scale. However, in bed scale, the creation of moldic
pores from allochems depends on the relative rate of calcite dissolution and the rate of dolomite
precipitation.

**2.3 Geological Setting**

The Elm Coulee Field is located along the southwestern margin of the Williston Basin within
Richland County in northeast Montana (Figure 2.1). Williston Basin is an elliptical intracratonic basin
located along the western edge of the Canadian Shield and covering an area of around 10,000 square miles
(Kent and Christopher, 1994). The basin is likely to have originated as a craton-margin basin and evolved
into an intracratonic basin during the Cordilleran orogen (Gerhard et al., 1990). The present-day basin
configuration is the result of the Laramide orogeny during Late Cretaceous and early Tertiary time (Kent
and Christopher, 1994). A continuous sediment column about 16,000ft thick accumulated in the Williston
Basin from the Cambrian to the Tertiary age (LeFever et al., 1991). Cyclical transgressions and regressions
characterize sedimentation in the basin with repeated deposition of carbonates and siliciclastics with many unconformities. Paleozoic strata consist mainly of cyclic carbonate deposits while Mesozoic and Cenozoic strata consist mainly of siliciclastics. Initial sedimentation during the Cambrian time started over an irregular Precambrian surface. The basin began to subside during the Ordovician Period and underwent episodic subsidence throughout the rest of the Phanerozoic period.

During the Late-Devonian-Early Mississippian age, the Bakken Formation was deposited in the Williston Basin. During its deposition, the basin was an area of active subsidence. The Three Forks Formation unconformably underlies the Bakken Formation and is overlain by the Lodgepole Formation (Figure 2.2). The Bakken Formation has been divided into three members, the organic-rich Upper and Lower Bakken Shale, which are the source rocks, and the silty carbonates of the MBM, which is the main reservoir interval. Previous studies suggest that the organic-rich Upper and Lower Bakken shale was deposited in an offshore marine anoxic environment during periods of sea level rise (Price et al., 1984; Webster, 1984; Smith and Bustin, 1998). The MBM shows a wide range of facies variability and is interpreted to have been deposited in a shallow marine environment in an epeiric platform setting following a rapid sea level drop, resulting in a regressive event (Webster, 1984; LeFever et al., 1991; Smith and Bustin, 1996; Angulo and Buatois, 2012). In the Elm Coulee Field, the MBM ranges in thickness from 10ft to 40ft and consists of silty lime wackestones to bioturbated siltstones, parts of which have been dolomitized to varying degrees. The lithology ranges from pure silty limestone to partially dolomitized silty limestones and pure silty dolostones (Sonnenberg and Pramudito, 2009). The Lower Bakken Shale approaches its erosional zero edge in the Elm Coulee Field (Sonnenberg and Pramudito, 2009; Alexandre, 2011; Rolfs, 2015).

2.4 Methodology and Dataset

Samples for this study were obtained from the cores of the MBM interval from the Elm Coulee Field wells as shown in Figure 2.3. Enerplus, which is the operator of the field, provided these cores along with petrographic thin sections, routine core analysis (RCA) data and X-ray diffraction (XRD) mineralogy from eight wells to the Bakken Consortium at Colorado School of Mines. Details of the wells, including well name, API, Township, Section and Range and available data including cores, thin sections, RCA and XRD used in this study is given in Table 2.1. Detailed core description was performed on all the eight cores for lithofacies identification. Sedimentary facies were described based on lithology, sedimentary structures, trace-fossil, and bioturbation index (BI). BI was estimated based on the scheme proposed by Taylor and Goldring (1993). Core plugs from the eight Enerplus cores, which were taken at a 1ft interval, were sent to Core Laboratories Inc. for RCA. The Core Measurement System-300 (CMS) was used to measure porosity and permeability. Mineralogy for these samples was obtained using XRD at Mineral Lab, Golden,
Colorado. The end trims of the core plugs were used for the preparation of the petrographic thin sections. Thin sections were impregnated with blue epoxy and stained with alizarin red and potassium ferrocyanide to distinguish calcite, dolomite, and ferroan-dolomite. Half of the thin sections were injected with a pink epifluorescent dye to highlight pore geometries when exposed to a fluorescent light under a microscope. A total of two hundred and twenty-four petrographic thin sections have been examined in this study.

Figure 2.1: Location map of the Williston Basin with subsea structure contour on the base of the Mississippian. Elm Coulee Field is located in northeast Montana, demarcated by the black ellipse. The limit of the Bakken Formation is shown by a dashed line. P=location of the Parshall field area; A=location of Antelope field. (modified from Sonnenberg and Pramudito, 2009).

Figure 2.2: Late Devonian-Early Mississippian stratigraphic column of the Williston Basin showing the Bakken Formation and the underlying Three Forks Formation and overlying Lodgepole Formation. (modified from Webster (1984) and Sonnenberg and Pramudito (2009)).
From the large inventory of core plug samples, twenty samples representing the range of porosity and dolomite content were selected for Field-Emission-Scanning Electron Microscopy (FE-SEM) in order to examine the pore architecture and identify the pore types. These twenty samples were examined under JEOL JSM-7000F FE-SEM at Colorado School of Mines. Pore throat-size distribution was obtained for seven representative samples using Mercury Intrusion Porosimetry (MIP). The opposite core plug end-trim was sent to Micromeretics Analytical Services for MIP analysis. Mercury intrusion and extrusion data were collected on the AutoPore IV 9500 V1.09 machines on sample masses ranging from 2-5 grams. Pore radius was calculated from the volume of mercury intrusion. Stable isotope of oxygen (O) and carbon (C) of twelve representative pure dolostone samples were analyzed from the powdered samples of whole rock, collected from the end trims of the core plugs by using a drill. It was ascertained through XRD mineralogy and thin section petrography that the samples selected for isotope analysis were pure dolostones and did not have calcite as a contaminant. Further details about sample selection for stable isotope analysis is discussed in Section 2.5.3. Stable isotope analysis was conducted on about 200 µg of powder were collected for each sample and were analyzed in Thermo Finnigan GasBench II coupled to a Thermo Delta Plus XL at the Stable Isotope Facility at University of Wyoming, Laramie. Oxygen and carbon isotope of carbonates are reported in per mil (‰) relative to the PDB (Pee Dee Belemnite) standard.

Table 2.1: Name and location of the wells from the Elm Coulee Field from which cores, thin sections, routine core analysis (RCA) and X-ray diffraction (XRD) mineralogy are used in this study.

<table>
<thead>
<tr>
<th>Well Name</th>
<th>API</th>
<th>T/S</th>
<th>Range</th>
<th>Sec.</th>
<th>Core</th>
<th>Thin Section</th>
<th>RCA</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR Lonetree Edna 1-13</td>
<td>LT</td>
<td>T23N</td>
<td>R56E</td>
<td>1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Coyote Putnam</td>
<td>CP</td>
<td>T23N</td>
<td>R57E</td>
<td>9</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Bullwinkle Yahoo 4-1-HSU</td>
<td>BY</td>
<td>T24N</td>
<td>R57E</td>
<td>4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Stockade Jayla 32-3-HID3</td>
<td>SJ</td>
<td>T25N</td>
<td>R51E</td>
<td>32</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Peanut Jimmy 22-3-HID3</td>
<td>PJ</td>
<td>T24N</td>
<td>R57E</td>
<td>22</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Jackson Rowdy 3-8</td>
<td>JR</td>
<td>T26N</td>
<td>R51E</td>
<td>3</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Brutus East Lewis 3-4-H</td>
<td>BEL</td>
<td>T24N</td>
<td>R57E</td>
<td>3</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Foghorn Ervin 22-3-H</td>
<td>FE</td>
<td>T23N</td>
<td>R58E</td>
<td>20</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

2.5 Results and Interpretation

This section, firstly, details the various lithofacies of MBM of Elm Coulee Field based on the core description. Thereafter, the major diagenetic events for the MBM is described. This section also provides the details of the mechanism of dolomitization in the MBM. Finally, the relationship between dolomite content and total porosity, pore size, and pore architecture is outlined.
Lithofacies Characterization

The Middle Bakken facies identified in this study in the Elm Coulee region, on the basis of lithology, sedimentary structures, trace fossils, and BI are similar to the facies described by previous authors (LeFever et al., 1991; Pramudito, 2008; Simenson, 2011; Gent, 2011; Angulo and Buatois, 2012). Nine sedimentary facies were identified from the cores of the MBM in the Elm Coulee Field. However, these nine sedimentary facies were grouped into five major facies, which from bottom to top are: A, B, D, E, and
F, in order to be consistent with the facies nomenclature scheme established by the Bakken Consortium at the Colorado School of Mines. Moreover, facies C of the MBM is not developed in the Elm Coulee Field region. Details of this classification scheme are referred from Gent (2011) and Simenson (2011). Table 2.2 lists a detailed description of the facies identified in the MBM of the Elm Coulee region. Representative core photographs of each of the nine facies are shown in Figure 2.4. Core description, along with the depth profile of the mineralogy obtained from XRD analysis and porosity and saturation data obtained from RCA of the Coyote Putnam well representing the MBM in the Elm Coulee Field, is shown in Figure 2.5. Core description panels of other seven wells are included in Appendix-A. Within an individual location in the field, such as the cored interval of the well Coyote Putnam (Figure 2.5), the dolomite content varies considerably along depth and between different facies of the MBM. There is an overall increase in the dolomite content and a decrease in calcite content from the bottom to the top of the Middle Bakken facies B. Moreover, there is a considerable variation in the abundance and distribution of dolomite and calcite content in the MBM, both spatially and temporally.

2.5.2 Diagenesis

A detailed petrographic examination was conducted to understand the diagenesis in Middle Bakken in the Elm Coulee Field. The diagenetic processes identified in the Middle Bakken in the Elm Coulee Field are mechanical and chemical compaction, early calcite cementation, early dolomitization, formation of pyrite, authigenic illite clay, quartz overgrowth and replacement, anhydrite cementation, minor ankerite (ferroan) dolomite overgrowth, fracturing and hydrocarbon production. Figure 2.6 shows the paragenetic sequence of the Middle Bakken in the Elm Coulee Field. Alexandre (2011) studied diagenesis and developed a paragenetic sequence for the MBM in the Elm Coulee Field. This study supports most of the diagenetic stages recognized by Alexandre (2011). However, this study contradicts the “dedolomitization” stage identified by Alexandre (2011). Alternatively, patchy calcite cementation is identified in the Middle Bakken in the Elm Coulee Field based on core description and petrographic analysis (Figure 2.7a & b). Prior to calcite cementation, bioclasts were subjected to micritization as evident from the presence of micritization envelope that developed on bioclasts (Figure 2.7c). Micritization indicates diagenesis in marine condition. Euhedral dolomite rhombs formed within calcite cement indicates that calcite cementation was followed by dolomitization. Similar early patchy calcite cementation that predates dolomitization has also been identified in the Middle Bakken in other parts of the Williston Basin (Brennan, 2016). Brennan (2016), based on stable isotope data from the Middle Bakken in North Dakota, demonstrated that the original source of calcium carbonate in these patchy calcite cement was most likely marine carbonate debris mixed internally throughout the member, which dissolved and reprecipitated as
calcite cement. The author also concluded that the dissolution of the internal carbonate has most likely taken place in the meteoric realm within the shallow subsurface.

Table 2.2: Sedimentary and ichnologic characteristics of the sedimentary facies identified in the Middle Bakken in the Elm Coulee Field.

<table>
<thead>
<tr>
<th>Facies</th>
<th>Lithology</th>
<th>Sedimentary structures</th>
<th>Bioturbation Index</th>
<th>Ichnofossils</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Light gray, whole fossils bearing brachiopod shells and crinoid dolomitic-to lime wackestone</td>
<td>Massive, burrow-mottled, storm beds present</td>
<td>0-1</td>
<td>burrow mottling</td>
</tr>
<tr>
<td>E2</td>
<td>Dark-gray, very thinly interlaminated, muddy siltstone, may be dolomitic or calcareous</td>
<td>Parallel lamination; locally current ripple and mudstone drapes</td>
<td>0-1</td>
<td>Planolites montanus</td>
</tr>
<tr>
<td>E1</td>
<td>Light-gray and buff colored, commonly pyritic in places, calcareous to dolomitic siltstone</td>
<td>Wavy lamination; mudstone drapes; microfaults and soft sediment deformation occur occasionally</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>Light gray, oolitic grainstone-sandstone</td>
<td>Massive to cross stratified, occasionally wavy lamination present</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>Light gray, fine-grained silty dolostone, mud drapes commonly present</td>
<td>Flaser-bedded with current ripples; climbing ripples and mudstone drapes are also common</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>Interbedded massive, light-gray to buff colored fine-grained silty dolostone with muddy partings</td>
<td>Massive with common intervals of wavy or parallel lamination, continuous shale laminae occur</td>
<td>3-4</td>
<td>Planolites montanus</td>
</tr>
<tr>
<td>B2</td>
<td>Interbedded light-gray to buff colored, massive, fine-grained silty dolostone, patchy calcite cementation present.</td>
<td>Bed boundaries are diffuse, locally continuous shale laminae occur</td>
<td>4</td>
<td>Nereites missouriensis and minor Phycosiphon incertum and Planolites montanus</td>
</tr>
<tr>
<td>B1</td>
<td>Light-gray or greenish-gray burrow-mottled calcareous to partially dolomitized siltstone, pyritic, brachiopod shell remains and discontinuous thin laminae of shale</td>
<td>Massive, Very rarely microhummocky and very thin parallel lamination occurs in the siltier intervals</td>
<td>5</td>
<td>Phycosiphon incertum and Nereites missouriensis</td>
</tr>
<tr>
<td>A</td>
<td>Greenish-gray burrow-mottled, very fine grained silty limestone, with fragments of brachiopod shells and crinoids may be dolomitic</td>
<td>Massive with burrow-mottled texture</td>
<td></td>
<td>Phycosiphon incertum</td>
</tr>
</tbody>
</table>

This was followed by dolomitization of the precursor micritic lime mud. The Middle Bakken dolostones predominantly consist of planar subhedral to euhedral dolomite rhombs with unreplaced (rarely partially) allochems (Figure 2.8a & b). Zonation within the dolomite rhombs (Figure 2.8b) is also observed, which indicates slight changes in the chemistry of the dolomitizing fluid. Alexandre (2011) mentioned the
presence of high-temperature saddle dolomite in minor quantities in the Middle Bakken in the Elm Coulee Field. However, saddle dolomite was not observed in any of the thin sections examined in this study. Late stage ankerite (ferroan dolomite) was observed only in very few samples, as thin rims of dolomite rhombs. Further details about dolomitization are discussed in the Sections 2.5.3 and 2.6.1. Pyrite occurs in many different forms throughout the diagenetic sequence. It is found both in the center and around the edges of the dolomite rhombs (Figure 2.9a). It replaces fossils (Figure 2.9b-d), occasionally fills burrows and fractures, and also forms small frambooids. Therefore, pyrite apparently began to form very early in the sequence and continued until the hydrocarbon generation process effectively stopped diagenesis.

Figure 2.4: The nine different lithofacies identified in the Middle Bakken Member (MBM) of the Bakken Formation in the Elm Coulee Field are shown in the core photographs. Detail description of each facies is listed in Table 2.2.
Figure 2.5: Core description of well Coyote Putnam showing lithofacies variation in the Middle Bakken along with the corresponding depth profiles of porosity and saturation obtained from routine core analysis and dolomite, calcite and clay content obtained from XRD analysis. MB-Middle Bakken, UBS-Upper Bakken Shale. Details about the degree of dolomitization is discussed later in Section 2.5.5.
After the dolomitization process ceased, authigenic quartz (Figure 2.10a), illite (Figure 2.10b) and secondary anhydrite (Figure 2.11 b-f) precipitated as cement and overgrowth. Silica and anhydrite replacement of burrows was also observed (Figure 2.11a). Formation of authigenic illite in the Middle Bakken was not recognized by Alexandre (2011). Pitman et al. (2001) suggested that the pore water became supersaturated with potassium due to the dissolution of K-feldspar framework grains, which precipitated as authigenic illite in the Middle Bakken. Finally, diagenesis in the Middle Bakken ended after hydrocarbon expulsion and formation of fractures. The continuation of hydrocarbon formation increased pressures within the shales, eventually causing them to fracture and expel hydrocarbons into the Middle Bakken reservoir (Pitman et al., 2001).

A detailed petrographic examination was conducted to understand the diagenesis in Middle Bakken in the Elm Coulee Field. The diagenetic processes identified in the Middle Bakken in the Elm Coulee Field are mechanical and chemical compaction, early calcite cementation, early dolomitization, formation of pyrite, authigenic illite clay, quartz overgrowth and replacement, anhydrite cementation, minor ankerite (ferroan) dolomite overgrowth, fracturing and hydrocarbon production. Figure 2.6 shows the paragenetic sequence of the Middle Bakken in the Elm Coulee Field. Alexandre (2011) studied diagenesis and developed a paragenetic sequence for the MBM in the Elm Coulee Field. This study supports most of the diagenetic stages recognized by Alexandre (2011). However, this study contradicts the "dedolomitization" stage identified by Alexandre (2011). Alternatively, patchy calcite cementation is identified in the Middle Bakken in the Elm Coulee Field based on core description and petrographic analysis (Figure 2.7a & b). Prior to calcite cementation, bioclasts were subjected to micritization as evident from the presence of micritization envelope that developed on bioclasts (Figure 2.7c). Micritization indicates diagenesis in marine condition. Euhedral dolomite rhombs formed within calcite cement indicates that calcite cementation was followed by dolomitization. Similar early patchy calcite cementation that predates dolomitization has also been identified in the Middle Bakken in other parts of the Williston Basin (Brennan, 2016). Brennan (2016), based on stable isotope data from the Middle Bakken in North Dakota, demonstrated that the original source of calcium carbonate in this patchy calcite cement was most likely marine carbonate debris mixed internally throughout the member, which dissolved and reprecipitated as calcite cement. The author also concluded that the dissolution of the internal carbonate has most likely taken place in the meteoric realm within the shallow subsurface.

This was followed by dolomitization of the precursor micritic lime mud. The Middle Bakken dolostones predominantly consist of planar subhedral to euhedral dolomite rhombs with unreplaced (rarely partially) allochems (Figure 2.8a & b). Zonation within the dolomite rhombs (Figure 2.8b) is also observed, which indicates slight changes in the chemistry of the dolomitizing fluid. Alexandre (2011) mentioned the
presence of high-temperature saddle dolomite in minor quantities in the Middle Bakken in the Elm Coulee Field. However, saddle dolomite was not observed in any of the thin sections examined in this study. Late stage ankerite (ferroan dolomite) was observed only in very few samples, as thin rims of dolomite rhombs. Further details about dolomitization are discussed in the Sections 2.5.3 and 2.6.1. Pyrite occurs in many different forms throughout the diagenetic sequence. It is found both in the center and around the edges of the dolomite rhombs (Figure 2.9a). It replaces fossils (Figure 2.9b-d), occasionally fills burrows and fractures, and also forms small framboids. Therefore, pyrite apparently began to form very early in the sequence and continued until the hydrocarbon generation process effectively stopped diagenesis.

After the dolomitization process ceased, authigenic quartz (Figure 2.10a), illite (Figure 2.10b) and secondary anhydrite (Figure 2.11 b-f) precipitated as cement and overgrowth. Silica and anhydrite replacement of burrows was also observed (Figure 2.11a). Formation of authigenic illite in the Middle Bakken was not recognized by Alexandre (2011). Pitman et al. (2001) suggested that the pore water became supersaturated with potassium due to the dissolution of K-feldspar framework grains, which precipitated as authigenic illite in the Middle Bakken. Finally, diagenesis in the Middle Bakken ended after hydrocarbon expulsion and formation of fractures. The continuation of hydrocarbon formation increased pressures within the shales, eventually causing them to fracture and expel hydrocarbons into the Middle Bakken reservoir (Pitman et al., 2001).

Figure 2.6: The paragenetic chart is showing the different diagenetic events that the Middle Bakken Member (MBM) has undergone in the Elm Coulee Field.
Figure 2.7: (a) The core photograph is showing patchy calcite cementation (white dashed line) in the Middle Bakken facies B. CP, 10365.2ft. (b) The photomicrograph is showing the patchy calcite (red) cement in the Middle Bakken facies B. Plane light, BEL, 10411.3ft. (c) The photomicrograph is showing micritization envelope which developed on bioclast while calcite cement precipitated within the bioclast in the Middle Bakken facies B. Plane light, BEL, 10411.3ft.

Figure 2.8: (a) The photomicrograph is showing dolomitized matrix with unreplaced calcareous bioclasts. Plane light, BEL, 10414.2ft. (b) The photomicrograph is showing zoned, planar euhedral dolomite rhomb in the matrix of the Middle Bakken facies B. Zoning in dolomite rhomb is shown by the pink arrows. Plane light, CP, 10353.5ft.
Figure 2.9: The photomicrographs are showing different forms of pyrite in the Middle Bakken in Elm Coulee Field. (a) Pyrite within dolomite rhomb is indicated by the yellow arrow, whereas pyrite around the edge of the dolomite rhomb is shown by the white arrow. Pink haze in the matrix is due to impregnation of the thin section by red dye and indicates microporosity. Plane light, CP.10353.41ft (b) Pyrite is replacing calcareous fossil fragment. Plane light, BEL-10414.2ft. (c) and (d) Bioclast fragment is replaced by two generations of cement, microcrystalline silica (white arrow) and pyrite (yellow arrow). Plane light (c) and crossed polar (d). CP-10371.93ft.

Figure 2.10: Scanning Electron Microscope (SEM) image is showing: (a) authigenic quartz overgrowth (yellow arrow), and (b) authigenic pore bridging illite in intercrystalline pore between the dolomite rhombs. CP4, 10350.3ft.
Figure 2.11: Secondary anhydrite in different forms in the Middle Bakken in the Elm Coulee is shown in, (a) The core photograph is showing the anhydrite pseudomorphs burrows. CP, 10354.1ft (yellow arrow). (b) The core photograph is showing the anhydrite nodule (yellow arrow). LT, 10409.5ft. (c) and (d) The photomicrographs are showing poikilotopic anhydrite cement in plane light and crossed polars respectively (yellow arrow). (e) and (f) The photomicrographs are showing poikilotopic anhydrite cement in plane light and crossed polars respectively. Note the euhedral dolomite rhombs are floating in the anhydrite cement (yellow arrow).
2.5.3 Petrography and Stable Isotope of the Middle Bakken Dolostones

The dolomitization process in the Middle Bakken has selectively replaced the matrix; however, the framework components (bioclasts) has remained unaffected as shown in Figure 2.8a. The matrix of the Middle Bakken dolostones predominantly consists of planar-subhedral to planar-euhedral dolomite rhombs, which vary from 10 to 150µm in size. The size of the dolomite rhombs increases with the dolomite content. Zoning is also observed in many dolomite rhombs as shown in Figure 2.8b. It was also observed that finely crystalline dolomite rhombs appear to be floating within a poikilotopic anhydrite cement (Figure 2.11 c-f).

![Figure 2.12: δ¹⁸O versus δ¹³C crossplot comparing the completely dolomitized samples which were collected in this study from the Middle Bakken in Elm Coulee Field, with the reported values in the literature. Blue and green rectangles are stable isotope values of carbon and oxygen obtained from the Late Devonian and Early Mississippian unaltered brachiopods respectively from Mii et al.(1999) and Van Geldern et al. (2006). Gray shaded rectangle indicates expected stable isotope values in dolomite which is in equilibrium with the Late Devonian sea.](image)

Stable isotope analysis of oxygen and carbon was performed to further understand the dolomitization model of the Middle Bakken in the Elm Coulee Field. This analysis was selectively performed only on those samples that consisted only of dolomite with no calcite impurity. XRD mineralogy data was considered to determine the dolomite and calcite content of these samples. Middle Bakken dolostones with more than 45 wt.% of dolomite content and dolomite index (DI) value of 1 (indicative of...
complete dolomitization) have a mean $\delta^{18}$O value of -2.40‰ and $\delta^{13}$C of 2.07‰. The $\delta^{18}$O values have a range of -2.03‰ to -2.39‰ and a standard deviation of 0.20‰. The $\delta^{13}$C values have a range of 1.01‰ to 2.98‰ and a standard deviation of 0.54‰. The oxygen isotope compositions of unaltered marine calcite from Late Devonian and Early Mississippian are well constrained to a range of about -4‰ to -5.5‰ relative to the PDB standard (Mii et al., 1999; van Geldern et al., 2006). Moreover, dolomite that originates from Late Devonian-Early Mississippian seawater is expected to have slightly heavier $\delta^{18}$O values ranging from -1.5‰ to -3‰ PDB because oxygen isotope fractionation between calcite and coevally precipitated dolomite is about 2.5 (Major et al., 1992; Rott and Qing, 2013). Therefore, the oxygen isotope data from Middle Bakken dolostones in the Elm Coulee Field matches with the expected oxygen isotope data in dolomites that originated from Late Devonian-Early Mississippian seawater as shown in Figure 2.12. Hence, the stable isotope data of oxygen indicate that the dolomitizing fluid of the Middle Bakken in the Elm Coulee Field was derived from the seawater which was probably slightly modified.

2.5.4 Porosity Characterization

The total porosity of the Middle Bakken in the Elm Coulee Field, which was measured by RCA, varies from approximately 2-10%. As shown in Figure 2.13, porosity varies considerably both within the facies and among the facies. Within an individual location in the field, such as the cored interval of the Coyote Putnam well (Figure 2.5), the porosity varies considerably along depth and between different facies of the Middle Bakken. Pore architecture in the samples was studied using thin section petrography through optical and epifluorescence microscopes and by observing whole rock samples under SEM. From thin section petrography, intercrystalline pores and intergranular pores were identified in few samples where the RCA derived porosity was between 7-10% and dolomite content was between 45-60 wt.%. As shown in Figure 2.14 a & b, these intercrystalline pores are 10-15 µm in size. These visible pores, which are large enough to be identified in thin sections through optical microscope, make up around 1% of the total porosity of the samples. However, for samples with RCA measured porosity between 4-6% and dolomite content less than 40 wt.%, thin sections study under an epifluorescence microscope indicated the presence of abundant sub-micron sized pores within the matrix as shown in Figure 2.14 c & d. Similar sub-micron sized pores were identified under epifluorescence microscope by Alexandre (2011). Furthermore, in samples with less than 4% porosity, microporosity was not observed under an epifluorescence microscope (Figure 2.14 e & f). However, it should be noted that the only indication of sub-micron sized pores under epifluorescence microscopes is a bright orange to yellow haze. Detailed pore geometry and architecture cannot be resolved at this magnification scale on an optical microscope. Therefore, SEM studies and MIP analysis were performed on samples of the Middle Bakken as they consisted of fine-grained dolostones with sub-micron sized pores as the dominant pore type.
Intercrystalline pores between dolomite rhombs were identified from SEM study as shown through the example of SEM photomicrograph in Figure 2.15a. However, most of the intercrystalline pores have pore bridging and pore filling authigenic illite, which results in the formation of a complex pore network (Figure 2.15b-f) and results in an overall decrease of the pore throat size. Patchy calcite cementation along with recrystallized remnant calcite and poikilotopic anhydrite cement in the Middle Bakken in the Elm Coulee Field also resulted in the occlusion of pore space and thereby a reduction in porosity (Figure 2.7a and b) and Figure 2.11c-f).

Figure 2.13: Box plot of routine core analysis (RCA) derived porosity of the Middle Bakken in the Elm Coulee Field, showing the porosity variation observed in the field. The median porosity of each of the facies is shown by a white line within the box plots. Data consists of samples from all the facies from eight cores whose locations are shown in Figure 2.3.
Figure 2.14: The photomicrographs are showing textural features corresponding to different dolomite content in the Middle Bakken facies B in the Elm Coulee Field. (a) Intercrystalline pores between dolomite rhombs which are sized between 10-15 µm are pointed by the yellow arrows. These pores are visible in petrographic thin section in completely dolomitized intervals. Plane light, SI, 9731.35ft. This sample has RCA porosity of 7.07% and dolomite content of 50 wt.% obtained from XRD. (b) Intercrystalline pores between dolomite rhombs which are sized between 10-15 µm are shown by the yellow arrows. These pores are visible in petrographic thin section in completely dolomitized intervals. Plane light, CP, 10356.42ft. This sample has RCA porosity of 7.86% and dolomite content of 58 wt.% obtained from XRD. (c) Microporosity (sub-micron sized) between dolomite rhombs in the matrix is enhanced by the red dye in petrographic thin section. Micron sized pores are not present. Plane light, BY-10472.5ft. The sample has RCA derived porosity of 5.98% and dolomite content of 45 wt.% obtained from XRD. (d) Orange hue is showing the microporosity (sub-micron sized) between dolomite rhombs in the matrix. Epifluorescence, BY-10472.5ft. This sample has RCA derived porosity of 5.98%, and XRD derived dolomite content of 45 wt.%. (e) Microporosity is not visible in thin section impregnated with red dye. Plane light, CP-10367.16ft. This sample has RCA porosity of 3.73% and dolomite content of 36 wt.% obtained from XRD. (f) No visible porosity in thin section impregnated with the red epifluorescence dye. Epifluorescence, CP-10367.16ft. Sample has RCA derived porosity of 3.73%, and XRD derived dolomite content of 36 wt.%.
Figure 2.15: The Scanning Electron Microscope (SEM) photomicrographs are showing pore architecture in the Middle Bakken facies B in the Elm Coulee Field. (a) Intercrystalline pores between dolomite rhombs are shown by yellow arrows. CP (2), 10356.42ft. This sample has RCA porosity of 7.86% and dolomite content of 58 wt.% obtained by XRD. (b) Yellow arrows show intercrystalline pores between the dolomite rhombs, which is filled by pore bridging authigenic illite. The presence of illite in between the dolomite rhomb results in a complex pore network and a decrease in the pore throat size. CP (6), 10359.29ft. This sample has RCA porosity of 8.85% and dolomite content of 50 wt.% obtained from XRD. (c) Intercrystalline pore between dolomite rhombs which is shown by the yellow line is filled by pore filling authigenic illite. CP4, 10350.3ft. The sample has RCA derived porosity of 5.93%, and XRD derived dolomite content of 51 wt.%. (d) Intercrystalline slot pores (yellow line) between dolomite rhombs which is filled by pore bridging authigenic illite. CP4, 10350.3ft. This sample has RCA derived porosity of 5% and dolomite content of 51 wt.% obtained from XRD.

2.5.5 Relationship between dolomite content and porosity

Figure 2.16 shows the cross plot between the XRD-derived dolomite content of the samples and the corresponding RCA derived total porosity of the eight well cores representing the Elm Coulee Field. The data points are color-coded by Dolomite Index (DI), which is defined as the ratio between total dolomite to total carbonate, and this indicates the degree of dolomitization the samples. The samples representing patchy calcite cement are not included in this plot because these samples do not represent the precursor
limestone. Following two trends were observed in Figure 2.16: 1) For dolomite content 0 to about 60 wt.%, porosity increases with an increase in the dolomite content, 2) For dolomite content more than about 60 wt.%, porosity decreases with an increase in the dolomite content. Figure 2.17 illustrates the effect of dolomite content on the average pore throat size through the MIP derived pore size distribution results for seven MBM samples, for which the mineralogical composition including the dolomite content is listed in Table 2.3. Figure 2.17 shows modal pore throat size increases with an increase in the dolomite content from 40 to 60 wt.%; however, with further increase in the dolomite content, the modal pore throat size decreases.

Figure 2.16: Crossplot between X-ray diffraction (XRD) derived dolomite content, and routine core analysis (RCA) derived total porosity. Samples are color-coded by dolomite index (DI), which is a measure of the degree of dolomitization. Porosity increases as dolomite content increase up to 60 wt.%. Beyond that, porosity starts decreasing as dolomite content increases more than 60 wt.%. 

Figure 2.17: Pore throat size distribution of the Middle Bakken samples from the Elm Coulee Field determined by Mercury Intrusion Porosimetry (MIP) is shown. Pore throat size distribution is color-coded by X-ray diffraction (XRD) dolomite content. Porosity and mineralogy details of the samples are given in Table 2.3.
Table 2.3: Measured porosity from routine core analysis and dolomite, calcite, clay content derived from X-ray diffraction and dolomite index (DI) of the samples analyzed for mercury intrusion porosimetry (MIP) in Figure 2.17.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP-1</th>
<th>BY-10</th>
<th>BY-9</th>
<th>CP-2</th>
<th>BY-8</th>
<th>FE-2</th>
<th>CP-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (ft)</td>
<td>10364.4</td>
<td>10472.3</td>
<td>10467.4</td>
<td>10356.2</td>
<td>10462.3</td>
<td>10508.7</td>
<td>10353.3</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>4</td>
<td>6</td>
<td>9</td>
<td>8</td>
<td>11</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Dolomite (wt.%)</td>
<td>39</td>
<td>45</td>
<td>47</td>
<td>58</td>
<td>59</td>
<td>61</td>
<td>63</td>
</tr>
<tr>
<td>Calcite (wt.%)</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dolomite Index</td>
<td>0.84</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Clay (wt.%)</td>
<td>13</td>
<td>8</td>
<td>8</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Based on the trend in the dolomite content vs. porosity cross plot, MIP results and SEM photomicrographs study, four stages of porosity evolution (Stage I to IV) were identified. Stage I is characterized by the lowest porosity (1-4%), less than 0.1 DI, and less than 15 wt.% dolomite contents. This is the onset phase of the dolomitization of the lime mud, and therefore, pore types are still dominated by intercrystalline pores between the partially coalesced subhedral micrite particles as shown in Figure 2.18a. Porosity increases in stage II to about 6% and dolomite content increases to about 45 wt.%, however, DI lies between 0.1 and 1. In this stage, subhedral to euhedral dolomite rhombs of 10-20 µm in size starts to form as shown in Figure 2.18b. Therefore, stage II is associated with partial dolomitization because the DI is still less than 1 and there is an occasional presence of dolomite rhombs. The dolomite rhombs at this stage are in direct contact with subhedral to anhedral fully coalescent microcrystalline calcite grains of the precursor limestone as shown in Figure 2.18c. Interstices between dolomite crystals are mostly filled by abundant residual microcrystalline calcites (Figure 2.16c). Intercrystalline micropores are fewer in number at this stage, and they selectively occur inside the clusters of dolomite crystals. Their selective occurrence is evident from the MIP results in Figure 2.17a, which indicate the lower frequency of the modal pore throat in the stage II samples. Moreover, the size range of the modal pore throat in these samples is between 0.015µm and 0.2µm, and they are associated with dolomite rhombs of size 10-20µm.

Stage III is marked by complete dolomitization of calcite in precursor lime mud. In this stage, porosity further increases to a maximum of about 10%, the dolomite content increases up to 60 wt.%, and DI attains a value of 1. The SEM photomicrograph for Stage III in Figure 2.18d shows that there is no remnant calcite micrite and intercrystalline pores between dolomite rhombs have increased to about 70µm in size. At this stage, these intercrystalline pores are abundantly present as evident from the MIP results in Figure 2.17a for the corresponding samples (CP-2 and BY-8), which suggest a higher frequency of the modal pore throat (0.3-0.4 µm). The increase in pore throat size from Stage II to Stage III is associated with an increase in dolomite rhomb size from 10-20µm to a maximum of 70µm. In Stage IV, overdolomitization takes place, resulting in an increase in dolomite content above 60 wt.% and a decrease in total porosity. In
this stage, the dolomite rhombs, which have compromised boundaries and interlocking texture, increase above 100µm in size (Figure 2.18 e-f). In this stage, intercrystalline pores are still present; however, their size and frequency of occurrence decreases. This is confirmed by the MIP results, which show that the pore throat size of samples from stage IV interval ranges between 0.05-0.2µm, which is lower in comparison to that in Stage III (Figure 2.17b).

As shown in Figure 2.5, all four stages of porosity evolution are observed in the cored interval of the Middle Bakken facies B of the Coyote Putnam well. The precursor lime wackestone of Stage I, with the lowest porosity (<2%), is identified in the lowermost interval of the Middle Bakken facies in this core (10371-10376ft). Stage II of the porosity evolution, which is associated with partial dolomitization, is observed in the interval between 10361-10371ft. In this interval, the dolomite content has an upward increasing trend reaching a maximum of about 40 wt.% (DI 0.1-1), while the average calcite content is around 20 wt.%. The porosity slightly increases in this interval and has a value in between 4-6%. This is followed by Stage III of porosity evolution, which is associated with complete dolomitization observed in the interval between 10354-10361ft. In this stage, the dolomite content varies between 45-55 wt.% and negligible calcite content according to the XRD measurements. The average porosity in this interval is 7.8 %, which is the highest among the entire Middle Bakken interval of this core. Stage IV of porosity evolution, which is associated with overdolomitization, is observed in this core between 10352.5-10354.5ft. In this interval, dolomite content increases more than 60 wt.%, while porosity decreases to about 5%.

2.6 Discussion

In this section, a plausible explanation for higher dolomite content in the Elm Coulee Field is discussed. A dolomitization model is also proposed for the Middle Bakken dolostone in the Elm Coulee Field based on the results of this study. Furthermore, the effect of dolomitization process in the evolution of porosity is discussed. And finally, a conceptual model of porosity evolution in the Middle Bakken of the Elm Coulee Field is proposed.

2.6.1 Dolomitization in Elm Coulee Field

More calcite-rich mud was deposited in the Elm Coulee Field and its surrounding area in comparison to other parts of the basin. During the Late Devonian-Early Mississippian time, the Williston Basin was located near the equator, so the climate was warm during the deposition of the Middle Bakken. This provided a favorable condition for the deposition of carbonates in the Middle Bakken. Moreover, the Middle Bakken is siltier on the eastern and northern side of the basin, so the Canadian Shield, which is located in the north-east of the basin, is often cited as the source of the siliciclastic sediments (Smith and Bustin, 1996). Therefore, the Elm Coulee Field, which is located along the south-western edge of the basin
parallel to the Late Devonian-Early Mississippian paleo-shoreline of the Williston Basin, lay at the farthest end of the siliciclastic sediment source during the deposition of the Middle Bakken (O’Brien et al., 2012). Hence, only a small portion of siliciclastic sediment could have been transported near the Elm Coulee Field (Alexandre, 2011; O’Brien et al., 2012). The clear, warm waters in the Elm Coulee region allowed more carbonates to form in this area than in other parts of the basin. Thus, the Elm Coulee Field and its surrounding area had more original lime mud, which was later dolomitized.

A collective analysis of stratigraphic and petrographic observations, along with stable isotope data, indicates that the seepage reflux dolomitization by slightly modified seawater resulted in the formation of the Middle Bakken dolostones in the Elm Coulee Field. The Middle Bakken dolostones consist of planar sub- to euhedral dolomite rhombs in the matrix with unreplaced calcareous bioclasts (Figure 2.8). Typically, planar -euhedral dolomite crystals form at lower temperature (<50° C) settings, while irregular, anhedral crystals and saddle dolomite form at higher temperatures (>50° C for anhedral crystals and 60°-150° C for saddle dolomite) (Radke and Mathis, 1980). Also, numerous examples of the pervasive replacement of the calcitic matrix by very finely crystalline, planar-subhedral type dolomite (4 to 20 mm) have been reported in the literature (Gregg and Sibley, 1984; Sibley and Gregg, 1987; Gregg and Shelton, 1990; Al-Aasm and Packard, 2000). The presence of these finely crystalline dolomite rhombs is often attributed to early dolomitization that takes place soon after deposition or during shallow burial. Therefore, these textural characteristics of the planar sub- to-euhedral dolomite rhombs indicate that most of the Middle Bakken dolomite was formed relatively early in the diagenetic history at lower temperature settings. Moreover, as discussed in Section 2.5.3 and shown in Figure 2.12, the δ18O values from the Middle Bakken dolostones in the Elm Coulee Field are also consistent with the typically expected δ18O values in dolomites that originated from Late Devonian-Early Mississippian seawater. This further supports the early origin of the Middle Bakken dolomites in the Elm Coulee Field and also supports the idea that the dolomitizing fluid was derived from the seawater, which was probably modified to some extent.

Generally, two models of dolomitization namely, the seepage reflux dolomitization (Adams and Rhodes, 1960) and the mixing-zone dolomitization (Humphrey and Quinn, 1989) are commonly accepted to explain the formation of dolomite at an early stage of diagenesis in low-temperature settings from seawater. Alexandre, (2011) and O’Brien et al., (2012) proposed a seepage reflux model of dolomitization for the Middle Bakken dolomites based on indirect evidence of arid paleoclimatic conditions. However, a seepage reflux model of dolomitization for the Middle Bakken dolomites is suggested in this study based on stratigraphic and petrographic evidence and also paleoclimatic conditions. Witzke and Heckel (1988) suggested that during the Late Devonian-Early Mississippian time, the Williston Basin and its surrounding area was located near the equator and was under the influence of arid climate conditions.
Figure 2.18: SEM images showing petrographic features representing various degrees of dolomitization and corresponding stages of porosity evolution in the Middle Bakken of the Elm Coulee Field. (a) Subhedral, partially coalesced micritic particles of precursor limestone, corresponding to the Stage I of porosity evolution. Intercrystalline sub-micron sized pores between the micrite particles. BEL, 10402ft, Dol-13 wt.%, Calc-58 wt.%, porosity-3.64%. (b) Remnant microcrystalline calcite from the precursor micritic lime mud is present in between the euhedral dolomite rhombs in the partially dolomitized Middle Bakken facies B (stage II of porosity evolution). Dolomite rhombs are 15-20 µm in size. Note that micritic calcite is in direct contact with the dolomite rhombs. BY-13, 10457.6ft, Dol-36 wt.%, Calc-24 wt.%, porosity-2.39%. (c) Subhedral to anhedral fully coalescent remnant microcrystalline calcite from precursor lime mud is in direct contact with the 20 µm sized dolomite rhombs in the partially dolomitized Middle Bakken facies B (stage II of porosity evolution). (d) Intercrystalline pores between the euhedral dolomite rhombs, in the completely dolomitized interval of the Middle Bakken corresponding to the stage III of porosity evolution, is shown by yellow arrows. Dolomite rhombs are around 30-40 µm in size. CP (2), 10356.42ft. The sample has RCA derived porosity of 7.86%, and XRD derived dolomite content of 58 wt.%. (e) Euhedral dolomite rhombs from the overdolomitized interval (stage IV of porosity evolution) forming interlocking texture with compromised crystal boundaries between dolomite rhombs is shown by the black arrow. Dolomite rhombs are more than 100 µm in size. BY-14, 10457.6ft, Dol-66 wt.%, porosity-4.25%. (f) Interlocking texture with compromised crystal boundaries (pink arrow) between euhedral dolomite rhombs in the overdolomitized interval (stage IV of porosity evolution) of the Middle Bakken is shown by black arrows. Dolomite rhombs are more than 100 µm in size. CP-3, 10353.25ft, Dol-63 wt.%, porosity-4.4%. 
Mixing-zone dolomitization usually takes place under humid conditions with a stable hydrologic setting, so it can be discarded as the likely dolomitization model for the Elm Coulee dolomites. Moreover, Alexandre (2011) suggested that since the Middle Bakken has limited fauna and ichnofacies, it was deposited in an arid and stressed environment which was not conducive for living organisms. And, in such arid and evaporitic condition, dolomitization of the precursor limestone commonly takes place by the seepage reflux process (Adams and Rhodes, 1960). Usually, such dolostones are closely associated with evaporite deposits; however, no bed-scale evaporite deposits have yet been discovered in the Bakken Formation. Secondary anhydrite as nodules, poikilotopic cement and pseudomorphs filling burrows are identified in both partially and completely dolomitized intervals of the Middle Bakken in the Elm Coulee Field as shown in Figure 2.11a-f. Adams and Rhodes (1960) suggested that the presence of secondary anhydrite in the dolomitized interval indicates that the seepage reflux is the likely process of dolomitization. Reactive transport models also suggest that in a seepage reflux model of dolomitization, anhydrite cement will result in porosity occlusion in the partially dolomitized interval (Jones and Xiao, 2005). Recent studies have shown that the absence of evaporites does not discard seepage reflux as a likely process of dolomitization. This is because mesohaline or penesaline brines, which are much below the saturation of gypsum or anhydrite, can be generated by very little evaporation and have the potential for dolomitizing limestone beds by penetrating downward under the influence of gravity (Simms, 1984; Whitaker and Smart, 1990; Melim and Scholle, 2002). There are also many reported examples in literature in which shallow water carbonates have been dolomitized extensively by the reflux of mesohaline to penesaline seawater driven by brine density and/or sea-level fluctuations without contemporaneous precipitation of evaporites (Sun, 1994; Qing et al., 2001; Vandeginste et al., 2006, 2009; Maliva et al., 2011; Rott and Qing, 2013). Therefore, the petrographic and geochemical evidence indicates that the Middle Bakken dolomites were formed at an early stage of diagenesis in the marine realm by a seepage reflux of slightly modified seawater, which formed the mesohaline to penesaline brine.

2.6.2 Dolomitization process and porosity evolution

This study suggests that the dolomitization process in the Elm Coulee Field has occurred by the volume-for-volume reaction. As discussed in Section 2.6, the Middle Bakken facies show an overall increase in total porosity, pore throat size and dolomite rhomb size as the dolomitization process proceeds from precursor lime mud to complete dolomitization. However, total porosity and pore throat size decreases and dolomite rhomb size increases as dolomitization proceeds further to the overdolomitization phase. The latter negative correlation between dolomite content and porosity in the Middle Bakken of the Elm Coulee Field suggests that dolomitization has resulted in an increase in the bulk volume. An increase in the bulk volume during dolomitization indicates the presence of an external source of \( \text{(CO}_3\text{)}^2^- \) ions during
dolomitization, which in turn suggests that dolomitization has taken place by the volume-for-volume reaction (Equation 2). Maliva et al., (2011) suggests that a direct contact between the precursor calcite and dolomite rhomb with no visible gap between the growing dolomite crystal and the precursor microcrystalline calcite indicates volume-for-volume replacement of calcite to dolomite. A direct contact between the dolomite rhomb with the precursor microcrystalline calcite is observed in the partially dolomitized Middle Bakken samples (Figure 2.18b-c). This further substantiates that dolomitization in the Middle Bakken primarily occurs by volume-for-volume replacement and the (CO$_3$)$^{2-}$ ions required in the process are primarily internally sourced, along with a minor external source. However, with continued dolomitization (stage III to stage IV), when all precursor calcite is exhausted, the externally sourced (CO$_3$)$^{2-}$ ions along with Mg$^{2+}$ and Ca$^{2+}$ are utilized for overdolomitization.

When bulk volume remains the same, an increase in grain or crystal size results in an increase in pore throat size as illustrated schematically in Figure 2.19. Therefore, from Stage I to Stage III, the dolomite rhomb size increases, which results in an increase in pore throat size. But in Stage IV, the addition of external (CO$_3$)$^{2-}$ ions results in the formation of additional dolomite, which causes an increase in the size of the dolomite rhombs and thereby an increase in bulk volume and a corresponding decrease in pore space. The pore space between the dolomite rhombs progressively decreases as the dolomite rhombs impinge upon each other and finally forms an interlocking texture (Figure 2.18e-f). This results in a decrease in both porosity and pore throat size as dolomitization proceeds from Stage III to Stage IV. Therefore, this study supports the thesis given by Lucia (2004) that the dolomitization process takes place by volume-for-volume replacement reaction and does not create porosity, rather it can create pore space and modify pore size.

However, in the Middle Bakken, there is an overall increase in porosity from Stage I to Stage III. The explanation for this observation is that limestones comparatively lose more porosity through burial compaction whereas dolostones resist compaction and retain much of their porosity (Schmoker and Halley, 1982; Lucia, 2004; Ehrenberg et al., 2006). Also, it has been observed in Cretaceous and Jurassic limestones that mud-dominated fabric becomes more compact and less porous compared to grain-dominated fabric (Cruz, 1997; Lucia et al., 2001; Lucia, 2004). Lucia (2004) predicted that this trend continued into the Paleozoic carbonates. This explains why an increase in porosity is observed in the Middle Bakken facies as precursor lime mud is progressively dolomitized.

Conceptual models also supported by reactive transport models predict that seepage reflux dolomitization results in the highest porosity in the distal path of dolomitizing fluid and the lowest porosity proximal to the brine source caused by the process of overdolomitization (Figure 2.20) (Jones and Xiao, 2005). In the Elm Coulee Field, all the four stages of dolomitization (stage IV to stage I) are present in the same section/location, from the top to bottom of the Middle Bakken facies B, such that porosity is low in
the topmost interval of the facies B, and the highest porosity is observed in the middle of the Middle Bakken facies B as shown in Figure 2.5. The bottom of the Middle Bakken facies B has the lowest porosity, as the precursor limestone is not dolomitized. This sequence of porosity evolution associated with the different stages of dolomitization indicates that the top of the Middle Bakken facies B was located proximal to the flow pathway of mesohaline brine. Also, locally in the Elm Coulee Field area, the brine mostly percolated downward into the precursor lime mud of the Middle Bakken and thereby progressively dolomitized the Middle Bakken.

2.6.3 Conceptual Model for Porosity Evolution

A conceptual model of porosity evolution in the Middle Bakken of the Elm Coulee Field is illustrated in Figure 2.21. As discussed in Section 2.5.5, in the Middle Bakken of the Elm Coulee Field, porosity is closely related to the dolomitization process, and it evolved in four different stages. This model is based on the theory of a volume-for-volume replacement reaction for the dolomitization process; therefore, the change in total porosity did not result from dolomitization, which only changes the pore space and pore size. However, the loss in the total porosity of the resultant dolostone was caused by the pre-dolomitization process of patchy calcite cementation, anhydrite cementation during dolomitization, overdolomitization, the post-dolomitization process of authigenic illite precipitation and mechanical compaction. However, at a given location, these processes take place in different proportions, which result in the observed variation in the porosity of the Middle Bakken in the Elm Coulee Field. As shown in Figure 2.21a, at time T₁, precursor calcareous sediment of the Middle Bakken consisting of silty lime mud was deposited in an epeiric platform in a shallow water setting.

![Porosity remains constant, Pore size increases](image1)

![Dolomite rhomb size increases](image2)

Figure 2.19: Schematic diagram illustrating an increase in the size of dolomite rhombs results in an increase in pore size.
At time $T_1$ the entire sediment column ($d_3$-$d_0$), which consisted of lime mud, was in Stage I of the porosity evolution. As shown in Figure 2.21b, at time $T_2$, the bioclasts present within the lime mud dissolved and got precipitated in the deeper sediment column ($d_1$-$d_0$) prior to any mechanical compaction, resulting in the formation of early patchy calcite cement (Section 2.5.2). This led to a slight reduction in the porosity of the sediment column $d_0$-$d_1$ prior to dolomitization; however, the entire sediment column was still in Stage I of the porosity evolution. This is followed by the seepage reflux of slightly modified seawater into the Middle Bakken sediment, almost contemporaneously with the deposition of the Middle Bakken at time $T_3$, as shown in Figure 2.21c. The arid climatic condition during deposition of the Middle Bakken resulted in an increased evaporation of seawater. This led to the formation of mesohaline brine, which percolated both downward and laterally in the precursor lime mud of the Middle Bakken facies. The mesohaline fluid preferentially flowed through the porous lime mud and avoided the impervious patchy calcite cement. As the reflux of mesohaline brine started, the shallow sediment column in interval $d_3$-$d_2$ was exposed to the
brine, which had the highest Mg\(^{2+}\)/Ca\(^{2+}\) ratio. As a result, dolomite rhombs of 10-20\(\mu\)m developed at the expense of calcite in the lime mud, and along with that, some intercrystalline pores also formed between the rhombs. Moreover, the modal pore throat size also increased at this stage as the overall grain size of the sediments in interval \(d_3-d_2\) increased due to the replacement of the smaller micritic calcite crystals (<1\(\mu\)m) by larger dolomite rhombs (10-20 \(\mu\)m). As shown in Figure 2.21c, as the mesohaline brine percolated in intervals deeper than \(d_2\), the Mg\(^{2+}\)/Ca\(^{2+}\) ratio progressively decreased. Therefore, the mesohaline brine fluid, which percolated below \(d_1\), or the deepest Middle Bakken sediments, had almost lost its dolomitizing potential. This, in turn, resulted in the precipitation of the secondary anhydrite cement in sediment interval \(d_2-d_1\) causing a minor loss in total porosity. So, at time \(T_3\), the interval between \(d_2-d_3\) was partially dolomitized with porosity evolution at Stage II, while interval below \(d_1\) was in Stage I, and the interval between \(d_2-d_1\) was in transition stage (Figure 2.21c).

The process of reflux of mesohaline brine and progressive decrease in the Mg\(^{2+}\)/Ca\(^{2+}\) ratio in deeper sections of Middle Bakken continued uninterruptedly. Therefore, the shallower interval between \(d_3-d_2\) was exposed to comparatively more pore volumes of mesohaline fluid with a higher Mg\(^{2+}\)/Ca\(^{2+}\) ratio in comparison to the deeper sections. Subsequently, at time \(T_4\), the remaining calcite in the partially dolomitized interval between \(d_3-d_2\) was completely replaced by larger dolomite rhombs of 20-50 \(\mu\)m, and along with that more intercrystalline pores were formed between the rhombs. The modal pore throat size in interval \(d_3-d_2\) also got enhanced in the process as the remaining micritic calcite was replaced by even larger dolomite rhombs. Therefore, as shown in Figure 2.21d at time \(T_4\), the interval \(d_3-d_2\) was completely dolomitized and was in Stage III of porosity evolution, and \(d_2-d_1\) was partially dolomitized or at Stage II, while the interval below \(d_1\) remained largely unaltered or in Stage I. As discussed previously, the total porosity of both completely dolomitized (\(d_2-d_3\)) and partially dolomitized (\(d_1-d_2\)) intervals remained same as the precursor lime mud, since dolomitization does not change the total porosity. However, porosity decreased in the partially dolomitized interval below \(d_1\) due to early patchy calcite cementation and secondary anhydrite cementation.

At time \(T_5\), additional dolomite was precipitated in completely dolomitized interval \(d_3-d_2\) as more mesohaline fluid percolated through it due to the continued availability of Ca\(^{2+}\), Mg\(^{2+}\) and (CO\(^3\))\(^{2-}\) ions. This resulted in the overdolomitization of interval \(d_3-d_2\) as shown in Figure 2.21e. As more dolomite was precipitated, the size of the dolomite rhombs continued to increase up to 150\(\mu\)m, thereby decreasing the porosity and the pore throat size. Even after overdolomitizing the \(d_3-d_2\) interval, the mesohaline fluid still had significant dolomitizing potential; however, the Mg\(^{2+}\)/Ca\(^{2+}\) ratio decreased.
Figure 2.21: Cartoon illustrating the progressive evolution of porosity in the Middle Bakken of the Elm Coulee Field from time T\textsubscript{1} through T\textsubscript{6}, due to seepage reflux dolomitization of precursor lime mud. Different depths in the sediment column are represented by d\textsubscript{0} to d\textsubscript{3}. (a) At time T\textsubscript{1}, the precursor lime mud got deposited, and the entire sediment column has an overall high porosity. (b) At time T\textsubscript{2}, early patchy calcite cementation results in porosity loss at depths between d\textsubscript{0} to d\textsubscript{1}. (c) At time T\textsubscript{3}, seepage reflux of mesohaline brine has started. Sediment column from d\textsubscript{3} to d\textsubscript{2} is partially dolomitized, with the degree of dolomitization decreasing down the depth. No change in total porosity is observed between lime mud and partially dolomitized limestone due to dolomitization. However, pore space and pore size are modified as intercrystalline pores start to form between dolomite rhombs. Moreover, the formation of anhydrite cement may result in minor loss of porosity near depth d\textsubscript{1}. (d) At time T\textsubscript{4}, seepage reflux of mesohaline brine continues such that the partially dolomitized lime mud between d\textsubscript{3} to d\textsubscript{2} is completely dolomitized with no change in total porosity. While lime mud between d\textsubscript{2} to d\textsubscript{1} is partially dolomitized with the degree of dolomitization decreasing down the depth such that below depth d\textsubscript{0}, precursor lime mud remains unaltered. There is no change in total porosity due to dolomitization. However, pore space and pore size are modified as intercrystalline pores form between dolomite rhombs. Moreover, the formation of anhydrite cement may result in minor loss of porosity between depth d\textsubscript{1} to d\textsubscript{0}. (e) At time T\textsubscript{5}, seepage reflux of mesohaline brine continues such that the completely dolomitized interval between d\textsubscript{3} to d\textsubscript{2} is overdolomitized with a loss in porosity due to the formation of dolomite cement. While partially dolomitized lime mud between d\textsubscript{2} to d\textsubscript{1} is completely dolomitized. Below depth d\textsubscript{1}, the precursor lime mud is partially dolomitized with the degree of dolomitization decreasing down the depth such that below depth d\textsubscript{0}, precursor lime mud remains unaltered. There is no change in total porosity due to dolomitization. However, pore space and pore size are modified as intercrystalline pores form between dolomite rhombs. (f) At time T\textsubscript{5}, after cessation of the seepage reflux dolomitization, mechanical compaction of the sediment column occurs due to burial. This results in differential compaction of the sediment column such that the precursor lime mud is more compacted and therefore, loses more porosity in comparison to the dolostones.
Continued downward percolation of this mesohaline fluid with reduced Mg\(^{2+}/\)Ca\(^{2+}\) ratio in the deeper section resulted in complete dolomitization of the previously partially dolomitized intervals d\(_2\)-d\(_1\). The precursor lime mud in interval d\(_1\)-d\(_0\) was partially dolomitized by this fluid, while the precursor lime mud below d\(_0\) remained unaltered. Therefore, as shown in Figure 2.21e at time T\(_5\), the interval d\(_3\)-d\(_2\) was overdolomitized and was in Stage IV of porosity evolution, and d\(_2\)-d\(_1\) was completely dolomitized and was in Stage III of porosity evolution. The interval d\(_1\)-d\(_0\) was partially dolomitized, while the interval below d\(_0\) remained largely unaltered or in Stage-I.

Finally, mechanical compaction due to burial started after the above-discussed dolomitization process was complete. As discussed in Section 2.2, dolostones can endure compaction more effectively than limestones. Therefore, porosity loss due to mechanical compaction in limestones is greater than the corresponding dolostones. Hence, as shown in Figure 2.21f., porosity loss due to compaction in the Middle Bakken in the Elm Coulee Field was in the following order: below d\(_0\)>d\(_0\)-d\(_1\)>d\(_1\)-d\(_2\)>d\(_2\)-d\(_3\). After dolomitization, authigenic illite clay was precipitated within the intercrystalline pore space, which further decreased both the total porosity and pore throat size. Thus, porosity evolution in the Middle Bakken of Elm Coulee Field was dependent on three diagenetic factors: the degree of dolomitization, burial compaction, and authigenic illite precipitation.

2.7 Conclusions

Based on this study, the following conclusions are drawn:

1. Integration of stratigraphic and petrographic observations along with the analysis of stable isotope data of oxygen and carbon indicates that precursor silty lime mud in the Middle Bakken in the Elm Coulee Field was dolomitized at varying degrees by seepage-reflux of mesohaline to penesaline brine. The seepage-reflux dolomitization of the Middle Bakken took place soon after the deposition of the lime mud.

2. The Middle Bakken consists of sub-micron sized intercrystalline pores between dolomite rhombs. The presence of pore bridging and pore lining authigenic illite clay within these intercrystalline pores results in a complex pore network thereby reducing the pore throat size.

3. Porosity evolution in the Middle Bakken silty dolostones of the Elm Coulee Field is closely associated with the degree of dolomitization. Four stages of porosity evolution (stage I to IV) were identified in the Middle Bakken based on the dolomite content, dolomite index (DI) and other textural features. Porosity evolution in Stage I is associated with the precursor lime mud (DI is less than 0.1, and the dolomite content is less than 15 wt.%). Porosity evolution in Stage II is associated with the partial dolomitization of the precursor lime mud (DI varies between 0.1 to 1 and dolomite content is less than 45 wt.%). Porosity evolution in Stage III is associated with the complete
dolomitization of the precursor lime mud such that DI=1 and the dolomite content is less than 60 wt.%. Porosity evolution in Stage IV is associated with overdolomitization of the precursor lime mud (DI=1 and dolomite content is more than 60 wt.%). Total porosity and pore throat size of the Middle Bakken increases from Stage I to III as the degree of dolomitization increases from the initial stages of dolomitization in the precursor lime mud to complete dolomitization. However, both total porosity and pore throat size start decreasing from Stage III to Stage IV as the degree of dolomitization increases further from complete dolomitization to overdolomitization.

4. Textural features of the Middle Bakken dolostones indicate that dolomitization has taken place by the volume-for-volume reaction such that the dolomitizing mesohaline fluid supplied (CO$_3^{2-}$ ions along with the Mg$^{2+}$ ions. So, dolomitization by replacement of calcite did not create porosity but modified the pore space and pore throat size in the Middle Bakken. However, overdolomitization resulted in a decrease in porosity due to an increase in the crystal size of the dolomite rhombs.

5. The total porosity of the completely dolomitized interval (Stage III) of the Middle Bakken is greater compared to the precursor lime mud (Stage I) because limestone loses more porosity due to burial compaction compared to dolostones.

6. Early patchy calcite cement, anhydrite cement, and authigenic illite clay are other diagenetic factors that reduce the porosity of the Middle Bakken.

7. A conceptual model of textual and porosity evolution in the Middle Bakken in the Elm Coulee Field is proposed. According to this model, the shallower intervals of the Middle Bakken were subjected to more pore volumes of the Mg-rich mesohaline brine fluid, and therefore have been overdolomitized. However, as the mesohaline fluid percolated downward into deeper intervals, the Mg/Ca ratio progressively decreased which resulted in gradually less dolomitized intervals.

2.8 References


Completions in the Bakken Formation, Elm Coulee Field, Montana: SPE Production & Operations, no. 1, p. 27–43.


CHAPTER 3

FACIES CHARACTERIZATION AND CHEMOSTRATIGRAPHY OF ORGANIC-RICH UPPER BAKKEN SHALE, WILLISTON BASIN

Recent exploration success and historical production from the Upper Bakken Shale (UBS) highlight its future resource potential. This emphasizes the need for comprehensive characterization of the UBS with respect to its facies and internal stratigraphic framework. This paper integrates results of thin-section petrography with the organic and inorganic geochemical analyses to characterize the facies, and to identify the laterally correlatable chemostratigraphic units of the UBS. Using these findings, this paper also addresses various gaps and inconsistencies in the current understanding of the prevailing sedimentary processes and depositional conditions for the organic-rich UBS.

In this study, handheld X-Ray Fluorescence (XRF) analyzer was used for elemental concentration data acquisition of sixteen well cores at 6-inch intervals. Thirteen well cores were described, and thin sections from five wells were examined. The cores used in this study were spread over both basin margin and basin depocenter areas. Six lithofacies, F1 through F6, were identified in the UBS from core descriptions and thin-section petrographic studies. 95% of the UBS consists of three main facies: siliceous mudstone (F1), massive to finely laminated silt-bearing mudstone (F2) and, macrofossil-bearing silt-rich mudstone (F4). Based on the trends of major and trace element concentrations obtained from the XRF data, three regionally correlatable chemostratigraphic packages (sub-units 1a, 1b, and Unit-2), were identified in the UBS. The elemental concentration data were also used as proxies to understand lateral and temporal variations in the detrital and biogenic sediment influx and to determine the paleoredox conditions of the basin during deposition of UBS.

Based on the results of this study it was proposed that influx of silt-size detrital sediments have multiple sources, especially during the deposition of Unit-2. Along with eolian silt from the northeast, some detrital silt was derived from the southern basin margin. Redox conditions varied both temporally and laterally during the deposition of the UBS. Sub-units 1a and 1b were deposited in a persistently euxinic condition in most locations across the basin. Unit-2 was deposited in a much less reducing condition, which varied from sub-oxic to intermittently euxinic. The maximum flooding surface was located in sub-unit 1b, below the Unit-2 and sub-unit 1b contact.

3.1 Introduction

The organic-rich Upper Bakken Shale (UBS) of the Bakken Formation is a world-class source rock with an average total organic content (TOC) of 11 wt.% (LeFever et al., 1991; Sonnenberg and Pramudito,
Although the dolomitic siltstone of the Middle Bakken reservoir is the primary target of current production activities in the prolific Bakken Play, the naturally fractured UBS was a resource play from 1976 to 2000 (Sonnenberg, 2014). The historical production and drilling activities in the UBS were primarily based in the Billings Nose structure, around the Bakken Fairway area (Sperr, 1990; Carlisle et al., 1992). Some recent exploration efforts in the UBS in the southwest flank area of the Elm Coulee Field, Montana, have yielded favorable results, which substantiates the resource potential of the UBS (Sonnenberg, 2014). This emphasizes the necessity of developing a basin-wide internal stratigraphic framework for the UBS for the identification of the target intervals and areas to aid future exploration and production efforts. The UBS, like other organic-rich shales and mudrocks, are particularly difficult to characterize, due to their macroscopic homogeneity and mineralogic complexity (Sano et al., 2013; Tinnin and Darmaoen, 2016). Complementing traditional analytical petrographic techniques with new methods, such as chemostratigraphic analysis, is expected to provide a better understanding of the UBS, with respect to identifying its regionally correlated sub-units and their depositional conditions.

Previous studies on the UBS describe it as a massively to finely laminated, fissile, siliceous, dark black, organic-rich shale with abundant pyrite content (Webster, 1984; Hayes, 1985; Smith and Bustin, 1996, 1998), but few studies in the past have focused on the possibility of lateral and temporal variations in the UBS with respect to its major lithofacies and their lateral and vertical distributions. For example, Egenhoff and Fishman (2013) identified three major facies in the UBS based on petrographic studies. The authors suggested that the UBS was deposited in a predominantly dysoxic setting based on the observation of extensive vertical microburrows and sedimentary structures indicating bedload transport processes observed in petrographic thin-sections. This interpretation, however, was later contradicted in a study by Schieber (2014), which suggested that the features in petrographic thin sections are essentially preparation artifacts. This highlights the need for integrating petrographic analysis with chemostratigraphic methods for characterizing organic-rich shales and their depositional conditions. Chemostratigraphic studies are based on inorganic geochemical results, such as elemental concentrations, which are more sensitive to the paleoenvironment and paleoredox conditions during their deposition (Sano et al., 2013; Nakamura, 2015; Nance and Rowe, 2015; Turner et al., 2016). Inorganic geochemical characterization helps define the chemostratigraphic packages in shales based on the abundancies of different elements, which in turn helps define a robust correlation framework in shales (Sano et al., 2013; Ramkumar, 2015). Moreover, the recent advancement in handheld energy dispersive X-ray fluorescence (ED-XRF) analysis provides a non-destructive method for the collection of high-resolution chemostratigraphic datasets directly from the cores (Mainali, 2011; Kocman, 2014; Nakamura, 2015). Kocman (2014) performed chemostratigraphic analysis of the UBS for seven cores along the eastern part of the Williston Basin, and thereby identified two laterally correlatable chemostratigraphic units of UBS; however, the significance of these chemostratigraphic units,
with respect to variations in lithofacies and depositional conditions for the UBS, was not discussed by the author.

In this study, I integrate core descriptions, thin-section petrography, chemostratigraphic analysis, and TOC results from multiple wells across the basin to accomplish the following objectives: i) identify lithofacies from core descriptions and thin-section petrography and interpret the sedimentary processes; ii) identify laterally correlatable chemostratigraphic units and integrate the lithofacies with inorganic geochemical data used as elemental proxies to understand the depositional condition of each unit; iii) determine the areal extent and distribution of these units in terms of their thickness; and iv) infer the stratigraphic position of the maximum flooding surface in the UBS.

3.2 Geological Setting

The Bakken Formation, which covers portions of western North Dakota and northeastern Montana in the U.S. and southern Saskatchewan and southwestern Manitoba in Canada, were deposited in the Williston Basin during the Late Devonian-Early Mississippian time, as seen in Figure 3.1 (LeFever et al., 1991; Smith and Bustin, 1996). The Williston Basin is an elliptical intracratonic basin located along the western edge of the Canadian Shield, and it extends over an area of around 100,000 square miles (Kent and Christopher, 1994). The basin is bordered on the east and north-east by the Sioux Arch and bounded on the north by the Punnichy Arch fronting the Saskatchewan Monocline. The exposed Precambrian Canadian Shield is commonly considered as the eastern and northern edge of the basin. The Sweetgrass Arch of northern Montana and southeastern Alberta limits the western extent of the basin, whereas the Black Hills Uplift and Miles City Arch mark the southern boundary of the basin (Gerhard et al., 1982; Kent and Christopher, 1994). In the Canadian region, the northeast trending Sweet Grass Arch separates the Williston Basin from the Alberta Basin, which is a northwest-trending trough in front of the Cordilleran Fold and Thrust Belt (Wright et al., 1994). As shown in Figure 3.2, a continuous sediment column of about 16,000 feet accumulated in the Williston Basin in between Cambrian and Tertiary ages (Gerhard et al., 1990; LeFever et al., 1991). Cyclical transgressions and regressions characterize the sedimentation in the basin, which has repeated deposition of carbonates and siliciclastics with several unconformities in between. Paleozoic strata are dominated by the cyclic carbonate deposits, while the Mesozoic and Cenozoic strata consist of siliciclastics. Initial sedimentation during the Cambrian time started over an irregular Precambrian surface (LeFever et al., 1991). The basin began to subside during the Ordovician Period and underwent episodic subsidence throughout the rest of the Phanerozoic Period. During the deposition of the Bakken Formation in the Late Devonian-Early Mississippian, the Williston Basin was an area of active subsidence (LeFever et al., 1991).
Figure 3.1: (a) Map showing the distribution of the Bakken Formation in the Williston Basin and its equivalent Exshaw Formation and Lower Banff Formation in the Western Canada Sedimentary Basin (modified from Smith and Bustin, 2000). (b) Locations of the wells used in this study are shown in the isopach map of the Upper Bakken Shale in the U.S. portion of the Williston Basin (source: Stephen Sonnenberg, personal communication). Abbreviations of the names of the wells used in this study are listed in Table 3.1.
Figure 3.2: Generalized stratigraphic column of the Williston Basin with an expanded section showing the stratigraphic details along with the conodont zones of the Late-Devonian-Early Mississippian age Bakken Formation (Sandberg et al., 1988; Karma, 1991; Hartel et al., 2012; Sonnenberg, 2015).

The paleogeographic reconstruction shows that the Williston Basin was located near the equator during the deposition of the Bakken Formation and the basin was inundated by a large shallow epicontinental sea, which had a very low gradient and extended over a large area (Parrish, 1982; Golonka et al., 1994; Smith and Bustin, 1998; Stasiuk and Fowler, 2004). As shown in Figure 3.2, the Bakken Formation lies unconformably over the Three Forks Formation and is underlain by the Lodgepole Formation (LeFever et al., 2011). Bakken Formation is subdivided into three members namely, the organic-rich Upper and Lower Bakken shales, and the mixed siliciclastic dolomitic siltstones of Middle Bakken (LeFever et al., 2011). However, recently the "Sanish" member has been included as a part of the Bakken Formation and has been renamed as the "Pronghorn" Member (LeFever et al., 2011; Johnson, 2013). The organic-rich Upper and Lower Bakken shales are believed to have been deposited in a moderately deep water setting (>200 m), while the siltstones and carbonates of the Middle Bakken were deposited in a shallow marginal-marine setting (LeFever et al., 1991; Smith and Bustin, 1996; Sonnenberg and...
Change in the relative sea level resulted in the shifting of the depositional environment from deep water to shallow water setting (Smith et al., 1995; Angulo and Buatois, 2012). During the deposition of the Bakken Formation, the Williston Basin consisted of two depocenters, one near the center of North Dakota and the other near Elbow sub-basin in Canada. These two depocenters were separated by the Regina-Melville and Swift Current Platform (Smith and Bustin, 1998). In Alberta, the Lower and Middle Bakken grades laterally into the Exshaw Formation, while the Upper Bakken Shale grades into the basal part of the Banff Formation (Richards, 1989; Smith and Bustin, 2000). Bakken Formation reaches the maximum thickness of about 150ft in North Dakota (LeFever et al., 1991).

UBS is a world-class source-rock with TOC averaging about 11.5 wt.% in the US portion (Webster, 1984;) and 17.6 wt.% in the Canadian portion (Chen et al., 2009) of the Williston Basin. UBS is the most geographically extensive member and represents the maximum depositional limit for the Bakken Formation (Cobb, 2013). The thickness of UBS ranges between 4-25ft reaching a maximum in North Dakota near the Nesson Anticline at basin center as shown in (Figure 3.1b) (Smith and Bustin, 1998). The deposition of UBS has continued through the Lower Siphonodella Crenulata conodont biozone (Karma, 1991) as shown in Figure 3.2. Different interpretations for the depositional setting of UBS ranges from the vast swamps to a deep offshore marine anaerobic environment (MacDonald, 1956; Kents, 1959; McCabe, 1959; Webster, 1984; LeFever et al., 1991; Smith and Bustin, 1996, 1998). Swamps are an unlikely possibility since the Bakken shales are dominated by sapropelic-amorphous type II kerogen with a minor presence of type III kerogen (land plants) localized at the basin margin (Webster, 1984; Jin and Sonnenberg, 2012). The widely accepted depositional model for UBS proposes that it was deposited by suspension sedimentation in a restricted basin with a depth of more than 200m, where a stratified water column resulted in an anoxic-euxinic bottom water condition (Smith and Bustin, 1998). However, Egenhoff and Fishman (2013) have reported the presence of vertical microburrows and sedimentary structures indicating bedload transport processes in the UBS. Based on these observations, Egenhoff and Fishman (2013) suggested that UBS was deposited in a dynamic environment with suboxic to dysoxic bottom water conditions.

### 3.3 Methodology and Background

This section, firstly, details the various UBS cores used in this study. Thereafter, the experimental methodology for the acquisition of various data is described. This section also provides the details of externally sourced data used in this study. Finally, the theoretical background for the analyses of this dataset is outlined.
3.3.1 Core and Dataset

Sub-surface cores of the UBS from a total of eighteen wells, located in North Dakota and Montana portion of the Williston basin, were used in this study. Table 3.1 lists these wells, including the abbreviated names used in this study, as well as the full name, API, and location. Well locations from which these cores were acquired are shown in Figure 3.1. The cores are available at the Wilson M. Laird Core Library of North Dakota Geological Survey (Grand Forks, ND), USGS Core Research Center (Denver, CO) and Triple O Slabbing core repository (Denver, CO). For each of these cores, Table 3.1 lists the acquired and external data, including their sources. XRF elemental data for the UBS section of cores from sixteen wells were acquired by a hand-held ED-XRF analyzer at 0.5ft intervals. The XRF data were used as proxies for detrital siliciclastic, carbonate and biogenic sediments, grain-size variations and redox-conditions for chemostratigraphic analysis. X-ray diffraction (XRD) data were acquired for well LT at Weatherford Laboratory, Golden, for qualitatively understanding the mineralogy-element association in the UBS. The externally sourced XRD data for the BF well was also used for this purpose. Thus, XRD data provided the reference for XRF-based analysis of the compositional differences between the UBS units.

Table 3.1: Names, abbreviations, APIs, and locations of the wells used in this study are listed. The available dataset used in this study are also listed. Description of abbreviations and symbol used in the table are as follows, Core Desc.: Core Description, Thin Sec.: Thin-section, ✓: Acquired in this study, X: not available, ✓*: Available from external sources.1-USGS, 2-Fishman et al. (2015), 3-(Jin, 2014), 4-(Kocman, 2014), and 5-NDGS. Sample for well 4-11-7-13W2 was available from Hui Jin (personal communication).

<table>
<thead>
<tr>
<th>Well</th>
<th>Well Full Name</th>
<th>API</th>
<th>State/ Country</th>
<th>Core Desc.</th>
<th>XRF</th>
<th>Thin Sec.</th>
<th>TOC</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT</td>
<td>RR Lonetree Edna</td>
<td>250832269500</td>
<td>MT</td>
<td>✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>Roberts Trust 1-13H</td>
<td>330250098200</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td>BN 1-23H</td>
<td>33007006600</td>
<td>ND</td>
<td>✓ X ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TT</td>
<td>5-1 Thompson Unit</td>
<td>330070118500</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF</td>
<td>Braaflat 11-11H</td>
<td>330610064100</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Sidonia 1-06H</td>
<td>330610088400</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RM</td>
<td>Rasmussen 1-21-16H</td>
<td>331050220400</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Rolf 1-20H</td>
<td>331050210000</td>
<td>ND</td>
<td>✓ ✓ ✓ X X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Charlotte 1-22H</td>
<td>33053035800</td>
<td>ND</td>
<td>✓ ✓ ✓ X X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>Linseth 13-12</td>
<td>330530369300</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Titan F-WP 32-14-H</td>
<td>330530271100</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP</td>
<td>Round Prairie 1-17H</td>
<td>330520714800</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Miller 34X-9</td>
<td>330570003500</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WT</td>
<td>Wayjetta 44-0311H</td>
<td>330610271700</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>Jorgensen 1-15H</td>
<td>330130149100</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST</td>
<td>Saratoga 12-1</td>
<td>330130166700</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Graham USA 1-15</td>
<td>330070069000</td>
<td>ND</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BY</td>
<td>Bullwinkle Yahoo</td>
<td>250832283700</td>
<td>MT</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Well 4-11-7-13W2</td>
<td>N/A</td>
<td>Canada</td>
<td>✓ ✓ ✓ ✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Core description was performed at a resolution of 0.5ft for thirteen of the total eighteen cores (Table 3.1). Among these thirteen cores, two wells RT and LT were considered as key wells for this study because of their strategic locations at the depocenter and basin margin, respectively (Figure 3.1). For the RT and LT cores, twenty-nine ultra-thin sections were prepared at Weatherford Laboratories, Golden for petrographic study. Twenty-one ultra-thin sections were perpendicular to bedding, whereas four were both perpendicular and parallel to bedding. Two additional thin sections were prepared for the immature UBS samples from the Canadian portion of the Williston Basin. All thin sections were impregnated with blue epoxy and stained with alizarin red and potassium ferrocyanide to distinguish calcite, dolomite, and ferroan-dolomite. An additional 23 thin sections from wells TT, BN, and BF were available from the USGS and Bakken Consortium, CSM. Source rock analysis (SRA) was also performed on the cores of RT and LT wells. High-frequency SRA for two wells were available from Jin (2014), and SRA for 2-3 samples for four other wells were available from NDGS.

3.3.2 ED-XRF Instrument Procedure and Interpretation Background

This study used ThermoScientific Niton XL3t GOLDD+ handheld energy dispersive x-ray fluorescence (ED-XRF) analyzer for acquiring elemental concentration data on the UBS cores. The analyzer was available at the Colorado School of Mines. The handheld ED-XRF instrument provided a nondestructive method for semi-quantitative elemental data acquisition. Niton ED-XRF includes three built-in spectral deconvolution algorithms, or modes: Mining, Soils, and TestAllGeo(TAG) (www.thermoscientific.com/niton). The Mining and Soils modes are suitable for the measurement of major and trace elements, whereas the TAG mode is a hybrid of the Mining and Soils modes and is designed for samples of the largely unknown composition. TAG mode gives the concentration of major, minor, and trace elements of a given sample in a single measurement. The study required concentrations of these three categories of elements; therefore, TAG mode was used for all the XRF data acquisition.

Procedures and results for optimum detection time, repeatability, and accuracy analysis for the XRF measurements are described in Appendix-C. These analyses used thirteen UBS matrix-specific standard cups, which were prepared following the methodology of Hall et al. (2011). The optimum detection time for samples used in this study was determined following procedures outlined by Kocman (2014), Lash and Blood (2014), and Nakamura (2015) and was 180 seconds in the TAG mode. Subsequently, the repeatability of the XRF measurements was analyzed by the procedure outlined by Fisher et al. (2014) and Nakamura (2015). The repeatability test indicated that variability in elemental concentration measurements using XRF was within 1-6%. XRF measurement accuracy for the twelve elements Si, Al, Ti, K, Ca, Fe, Rb, Sr, Mo, U, V, and Ni in UBS samples was confirmed by comparing the XRF results with the ICP-MS/ICP-OES and Costech ECS4010 elemental analyzer-derived measurements. For elements Mo, U, V, Ni, Ca, Fe, S, and
K, for which the regression coefficient ($R^2$) was more than 0.80, the XRF measurements were considered applicable for both quantitative and semi-quantitative analyses. Elements Al, Si, Ti and Rb, for which the regression coefficient ($R^2$) was 0.6-0.80, the XRF measurements were considered applicable for semi-quantitative analyses only. The log view of the elemental concentration shows similar stratigraphic trends between the ICP-MS and XRF measurements, which further validates the applicability of XRF measurements.

In this study, elemental concentrations were acquired on flat core surfaces at 0.5ft intervals for sixteen wells. The XRF data acquisition on the core samples was performed in the following steps: 1) a system precheck was run on the XRF analyzer to verify normal operation; 2) the previously described repeatability procedure (Appendix-C) was repeated after every 25 XRF measurements on the core samples to confirm whether the $R^2$ for ICP-MS and XRF measurements for the standards were consistent during the XRF acquisition of the samples, and 3) XRF measurements were taken on flat core surfaces.

### 3.3.3 Detrital, Biogenic, and Redox Proxies

XRF data were used in this study for chemostratigraphic analysis by utilizing elemental concentrations as proxies for detrital siliciclastic, carbonate and biogenic sediments, grain-size variations, and redox conditions. Ti always has a detrital origin, and is present in minerals such as ilmenite, rutile, and augite in the sand and silt-sized grains; Ti also exists in clays as cations (Calvert, 1976). Elements associated with siliciclastic sediments are considered to be of detrital origin if they plot with a positive correlation with Ti. Al is considered to be the principal conservative proxy for clay minerals in fine-grained clastic deposits (Arthur and Sageman, 1994; Calvert and Pedersen, 2007). K is usually associated with clay minerals, especially illite or with K-felspar; therefore, after ascertaining its detrital origin by correlating it with Ti, K was used along with Al as a proxy for siliciclastic detrital sediments. Moreover, a good covariation between Al, K, and Ti suggested that these elements are primarily associated with illite clay (Wedepohl, 1971).

Zr is preferentially enriched in coarser grain size fraction and is relatively immobile, such that its concentration does not change due to diagenesis or post-depositional weathering processes. Element Rb is commonly associated with clay minerals (Turner et al., 2015); therefore, in this study, Zr was used as a marker for chemostratigraphic correlation purposes, and the Zr/Rb ratio was used as a grain size proxy to determine variations in the proportion of silt-sized sediments. Si can have both detrital and biogenic and authigenic origins (Ross and Bustin, 2009). A negative correlation between Si and Ti implies the non-detrital origin of silica; if this is the case, Si can be used as a proxy for biogenic and/or authigenic sediment.

This study used the nomenclature proposed by Tyson and Pearson (1991) to describe the redox conditions. According to this nomenclature, oxic conditions refer to 8.0-2.0 ml/1 O$_2$ in water, dysoxic
conditions refer to 2.0-0.2 ml/l O₂ in water, suboxic conditions refer to 0.2-0.0 ml/l O₂ in water, and anoxic conditions refer to 0.0 ml/l O₂ and 0 ml/l H₂S in water. Many of the trace metals, such as Mo, U, and V, exhibit a variation in oxidation state, solubility, and/or change in host-phase as a function of redox condition of the depositional environment (Tribovillard et al., 2006). These redox-sensitive trace elements are more soluble and display a conservative behavior in oxic conditions, but are less soluble in reducing conditions, resulting in their authigenic enrichments in oxygen-depleted facies. This allows them to be used as proxies for evaluating redox conditions in paleomarine systems (Algeo and Maynard, 2004; Tribovillard et al., 2006). Euxinic or anoxic-sulfidic water lacks O₂ and contains free H₂S (Raiswell and Berner, 1985).

According to Tyson and Pearson (1991), the term “bottom water” refers to a water column less than one meter above the sediment-water interface. In oxic conditions, trace metal Mo in seawater is present in stable and unreactive molybdate ions (MoO₄²⁻). Marine sediments accumulating in oxic environments have limited authigenic enrichment of Mo, and they exhibit typical detrital background values of Mo concentration, ranging from 1-5 ppm (Zheng et al., 2000; McLennan, 2001; Morford et al., 2009). In a reducing environment and in the presence of very small amounts of dissolved HS⁻, MoO₄²⁻ ions become reactive and convert to a series of particle-reactive thiomolybdate ions (MoO₄Sₓ₋ₓ) (Helz et al., 1996; Zheng et al., 2000). Mo is rapidly sequestered by sulfurized organic matter, or becomes a solid-solution with Fe-S and precipitates as authigenic sulfide minerals (Helz et al., 1996; Tribovillard et al., 2004). At higher levels of dissolved hydrogen sulfide (H₂S)ₐq in an euxinic condition, authigenic uptake and burial rate of Mo increases by two to three times (Scott and Lyons, 2012); therefore, relative enrichment of Mo usually indicates the variation in the degree of reducing conditions in the bottom water.

Trace metal U is present mainly as soluble U(VI) in oxic-suboxic conditions, which reduces to less soluble U(IV) in an oxygen-depleted condition. U concentration in average shale is around 3.7 ppm (Wedepohl, 1991). Reduction of U commences at the Fe (II)-Fe(III) redox boundary and enrichment of U is controlled by microbially-mediated Fe redox reactions, rather than by the presence of HS⁻ (Zheng et al., 2002). The uptake of reduced Uₐᵤₙₖ by the sediment primarily occurs through the formation of organic metal ligands, or by precipitation of crystalline uraninite or a metastable precursor to uraninite (Klinkhammer and Palmer, 1991; Zheng et al., 2002). Concentration of trace metal V in average shale is 130 ppm (Wedepohl, 1971, 1991). In oxic waters, V is present as V(V) in the quasi-conservative form of vanadate oxyanions (HVO₅²⁻ and H₂VO₄⁻) (Tribovillard et al., 2006). Under mildly reducing conditions, V(V) is reduced to V(IV) and forms vanadyl ions (VO²⁻), hydroxyl species VO(OH)⁷⁻, and insoluble hydroxides VO(OH)₂. Under more strongly reducing or euxinic conditions, the presence of free (H₂S), released by bacterial sulfate reduction, causes V to be further reduced to V(III), which can be taken up by geoporphyrins or be precipitated as the solid oxide V₂O₃ or hydroxide V(OH)₃ phase. The two-step reduction process of V
may lead to the formation of separate V carrier phases of contrasting solubilities under non-sulfidic anoxic versus euxinic conditions (Algeo and Maynard, 2004; Tribovillard et al., 2006). This may result in relatively high enrichment of total V even when the conditions are non-sulfidic anoxic (Algeo and Maynard, 2004). High enrichment of V may also occur when anoxic conditions are present only within the pore water while the bottom water was not necessarily anoxic (Lewan and Maynard, 1982).

I have used variation trends of redox-sensitive trace elements Mo, U, and V, along with other proxies for identifying the chemostratigraphic packages in the UBS. Redox condition variations in the basin during the deposition of UBS were inferred from the absolute concentration of Mo. Along with the redox-sensitive trace elements, the degree of pyritization (DOP) was also used as a proxy to determine the redox condition of the basin during the deposition of the UBS. DOP is the ratio of pyritic iron (Fe) to reactive iron (pyritic iron plus HCl soluble iron) and is considered to be a reliable indicator of the depositional redox conditions in environments which are not limited by reactive Fe (Raiswell et al., 1988; Jones and Manning, 1994). DOP values less than 0.42 indicate normal marine oxygenated conditions, values ranging from 0.42 to 0.75 indicate dysoxic-anoxic conditions with a less strongly stratified water column, and values greater than 0.75 indicate anoxic conditions with a strongly stratified water column (Raiswell et al., 1988; Hatch and Leventhal, 1992; Algeo and Maynard, 2004). Uniformly high DOP values typically indicate deposition under euxinic conditions and suggest that nearly all of the available reactive Fe was utilized in the formation of pyrite (Raiswell et al., 1988; Lyons and Berner, 1992). Although the calculation of DOP values requires the determination of acid-soluble Fe and sulfide S concentrations via the chromium reduction method, Algeo and Maynard (2004) suggested that total concentration of Fe and S can be used to make an approximate assessment of total DOP or DOP\textsubscript{T} values from the crossplot of Fe (total) and S (total). Algeo and Maynard (2004) used DOP\textsubscript{T} to infer the redox condition of Pennsylvanian Kansas cyclothems. I have determined threshold DOP\textsubscript{T} values for dysoxic, anoxic, and euxinic conditions by following the technique of Algeo and Maynard (2004) through the crossplot between Fe (total) and S (total), and used them as redox proxies.

3.3.4 Core Description and Petrography

Core description and petrographic analysis were performed in the mudstone-dominated succession of the UBS to determine the lithofacies variability in both hand-specimen (mm-cm) scale and microscopic (sub-mm) scale. All thin sections used in this study were scanned in a flat-bed scanner (HP CLJ M477) at a resolution of 300 dpi to capture 1-10 mm-scale textures. Thereafter, the thin sections were studied using optical microscopy to obtain 0.1-1 mm-scale features. Micron-scale textural details were obtained for four of the thin sections by applying carbon coating and then examining them under a scanning electron microscope (SEM) using back-scattered electron (BSE) detector and energy dispersive spectroscopy.
SEM analysis was performed using the TESCAN MIRA3 LMH Schottky Field-Emission SEM at the Colorado School of Mines.

The lithofacies present in the UBS were described based on their compositional and textural features including grain size, grain origin (allochthonous, autochthonous, or diagenetic), sedimentary structure, and bedding geometries. I used the nomenclature scheme of Macquaker and Adams (2003) as follows: mudstones containing more than 90% of a particular component are termed as ‘dominated’ by that particular constituent; those containing 50-90% of a particular component are termed as ‘rich’ in that constituent; and those containing 10-50% of a constituent are termed as ‘bearing’ that constituent. The nomenclature of each facies of the UBS was finalized by combining the observations of core descriptions and microscopic petrography studies.

3.3.5 SRA and ICPMS Measurements

TOC was measured on all of the fifty core chips from both the RT and LT cores using the Weatherford Source Rock Analyzer (SRA) instrument at Colorado School of Mines, using the procedure described by Jin (2014). Prior to SRA, the samples were cleaned with deionized water and air-dried overnight to remove salt crust and drilling mud residues. Subsequently, the cleaned sample pieces were crushed by mortar and pestle to 200-mesh size powder. Aliquots of the powdered samples were then analyzed for TOC. Remaining aliquots of the powdered samples were used for determining the concentration of the minor and trace elements using inductively coupled plasma mass spectrometry (ICP-MS) at SGS Services, Canada. The ICP-MS results were used for making matrix-specific UBS standards for validation of ED-XRF-derived results. ICP-MS results will also be used in Chapter-4 for understanding the relationship of TOC to different geochemical proxies.

3.4 Results and Interpretation

In this section, I identify various lithofacies of the UBS and interpret their depositional processes. I then present the results of the chemostratigraphic analysis and describe the various chemostratigraphic units of the UBS and their regional correlations. Finally, I describe the distribution of various facies in the chemostratigraphic units.

3.4.1 Facies Description and Depositional Processes

Based on both compositional and textural features, six lithofacies of the UBS were identified. The UBS comprises of a variety of intergradational lithofacies, which are dominated by fine-grained (clay to silt-size) sediments, except for phosphatic skeletal lag beds. The six identified lithofacies of UBS are as follows: (i) siliceous mudstone (F1); (ii) massive to finely laminated silt-bearing mudstone (F2); (iii) sand
and clay-bearing silt-rich mudstone (F3); (iv) macrofossil-bearing silt-rich mudstone (F4); (v) burrow-mottled silt-bearing mudstone (F5); and (vi) phosphate and fossil-rich mudstone (F6). Out of these six facies, 95% of the UBS succession consisted of the three facies F1, F2, and F4. Facies F1 was the most dominant facies in the UBS, followed by facies F2. The presence of facies F4 in the UBS is localized. The remaining three facies make up less than 5% of the entire UBS. The next sub-sections describe characteristics of each of the facies.

**Facies F1- Siliceous mudstone**

Facies F1, which is characterized by the abundance of radiolarian tests, occurs as 1-40 mm thick mudstone beds intercalated within massive to finely-laminated silt-bearing mudstone (F2). This facies was further divided into two sub-facies: (i) Radiolarites, or massive radiolarian-dominated siliceous mudstone (F1a), as shown in Figure 3.3a, and (ii) Finely laminated radiolarian and silt-bearing mudstone (F1b) as shown in Figure 3.3b. Facies F1a are characterized by their massive fabric and are composed primarily (up to 90%) of radiolarian tests and spines (Figure 3.4a and b), which in turn are filled with microcrystalline silica, pyrite, sphalerite and/or calcite (Figure 3.4c and d). The matrix is composed of authigenic microcrystalline silica, pyrite cement, and organic matter, which gives the appearance of diffused wispy aggregates against the radiolarian tests. In some radiolarite beds, only a diffused outline of the radiolarian body exists, while the radiolarian tests appear to have dissolved out (Figure 3.4d).

Figure 3.3: (a) Core photograph illustrating massive radiolarian-dominated siliceous mudstone (F1a). The characteristic ptygmatite pyrite-filled, sub-vertical fractures in facies F1a are shown by white arrows. Well: Rasmussen 1-21-6H, 10211ft. (b) Core photograph illustrating finely laminated radiolarian and silt-bearing mudstone (F1b). Well: Rasmussen 1-21-6H, 10214ft.
Figure 3.4: (a) Scanned petrographic thin section image showing ~14mm thick bed of massive radiolarian dominated mudstone (F1a). The sharp contact at the base and top of the facies F1a are indicated by the white arrow; Well: LTE, 10386 ft. (b) Optical photomicrograph of F1a showing the typical fabric of the massive radiolarian dominated siliceous mudstone (F1a). The high content of radiolarians, which are shown by the red arrow is evident from this photomicrograph. Wispy organic matter surrounding the radiolarians is shown by the yellow arrow. (c) Thin section photomicrograph of facies F1a showing radiolarian tests, which was replaced by chert (green arrow), sphalerite (yellow arrow) and pyrite (red arrow). Well: RT, 10663.60 ft. (d) Optical photomicrograph of facies F1a showing is radiolarians, which are replaced by calcite (green arrow) and pyrite (red arrow). As evident, it is difficult to distinguish the shape of the individual radiolarians as they are mostly dissolved out. Well: RT, 10661.9 ft.

Facies F1a generally has a sharp basal and top contact. The thickness of facies F1a occasionally varies due to diagenetic overprint and is related to the silica dissolution and formation of early authigenic pyrite (Figure 3.3a) (Vecsei et al., 1989). The characteristic sub-vertical calcite, pyrite and/or sphalerite-filled ptygmatic fractures along with bitumen-filled horizontal fractures are frequently observed features in facies F1a and represent fluid-escape structures (Vecsei et al., 1989)(Figure 3.5a and b). Moreover, this facies was found to have the lowest TOC, ranging from 1-6 wt.%. Facies F1b is characterized by varying amounts (30-50%) of radiolarians, which are either dispersed randomly along with silt grains in an organic matter-bearing and clay-rich matrix or forms single test thick continuous to discontinuous laminae (Figure
Similar to F1a, the characteristic sub-vertical calcite, pyrite and/or sphalerite-filled ptygmic fractures are also present in F1b, but their occurrence is comparatively less frequent. The upper and lower contacts of facies F1b are commonly gradational. The TOC of facies F1b is more than those of facies F1a, F4, and F5, but comparatively lower than that of facies F2.

![Figure 3.5](image_url) (a) Optical photomicrograph showing a vertical ptygmic fracture (red arrow) in massive radiolarian dominated mudstone (F1a) Well: RT, 10663.60ft. (b) Optical photomicrograph showing the vertical fracture (red arrow) in Figure 3.5a at higher magnification. Two generations of cement within the fracture, sphalerite (red arrow) followed by pyrite (yellow arrow) is observed. Well: RT, 10663.6ft.

The presence of radiolarians indicates sediment accumulation in the outer shelf to deep basinal offshore settings at a water depth of more than 50m (Stasiuk and Fowler, 2004). Therefore, the occurrence of facies F1 indicates that the UBS was deposited in a setting, which had more than 50m of water depth. Facies F1a is interpreted to represent episodic radiolarian blooms related to eutrophication pulses, such that the radiolarians were rapidly deposited by suspension sedimentation (Garrison and Fischer, 1969; Jones and Murchey, 1986; De Wever and Baudin, 1996; De Wever et al., 2002). This interpretation is supported by the near absence of detrital sediments, massive structures, and the presence of sharp basal and top contact. The deposition of facies F1b represents the background sedimentation of organic matter, radiolarians, and fecal pellets along with detrital clay and silt which continued after episodes of radiolarian blooms. The single-test thick laminae of radiolarian tests in facies F1b is interpreted to represent shorter periods of radiolarian blooms during a constant rate of sedimentation of detrital sediments and organic matter (Jones and Murchey, 1986). Such radiolarian blooms may be quasiperiodic and related to seasonal fluctuations in nutrient supply.

Alternatively, if the single-test thick radiolarian laminae were deposited due to the hydrodynamic sorting of radiolarian tests by bottom water currents, it would have been a dynamic bottom water
environment (Vecsei et al., 1989). This would result in oxic to suboxic conditions at the sediment-water interface; however, lack of any bioturbation suggests that benthic conditions were not conducive for the survival of benthic organisms; therefore, it represents highly reducing conditions. This suggests that the benthic condition was stagnant, and bottom currents were sluggish and occasional (Smith and Bustin, 1996). The absence of any other bioclasts, coarse-grained sediments, or bedload transport sedimentary structures, such as ripples or grading, further indicates that the single-test thick radiolarian laminae were deposited by suspension sedimentation and were not produced by bottom current activities (Jones and Murchey, 1986; Vecsei et al., 1989). Therefore, deposition by predominantly suspension sedimentation of planktonic organisms, and lack of any major sedimentary structures indicating bedload transport processes and bioturbation suggest that benthic conditions were most-likely anoxic-euxinic during the deposition of facies F1.

Figure 3.6: (a) Scanned petrographic thin section image of laminated radiolarian and silt-bearing mudstone (F-1b). The double-headed yellow arrows show sub-mm scale laminae of F1b. Red arrows showing sphalerite-filled vertical fractures in the middle of the image. Well: LT, 10390.1ft. (b) An optical photomicrograph of laminated radiolarian and silt-bearing mudstone (F-1b) showing discontinuous laminae of radiolarians (red arrows). Radiolarians (yellow arrows) along with silt grains are observed to be randomly distributed in an organic matter and clay-rich matrix in the lower part of the image. Well: LT, 10390.1ft.

Facies F2- Massive to finely laminated silt-bearing mudstone

Facies F2 is massive to finely laminated in character, with gradational contacts, and is characterized macroscopically by the presence of mm-thick discontinuous pyrite lenses which occur abundantly along the fine laminations (Figure 3.7a). This facies is also characterized by the presence of detrital silt grains, fecal pellets, and organomineralic aggregates (a term defined by Macquaker et al., 2010; Ghadeer and Macquaker, 2012) as the major textural components (Figure 3.7b). Facies F2 was found to be the most
abundant facies type in the UBS and makes up about 75% of the entire UBS. The thickness of this facies can be up to 4ft.

Figure 3.7: (a) Core photograph showing the massive to finely laminated silt-bearing mudstone (F2). Discontinuous mm-size pyrite lenses (shown by the yellow arrow) is the most distinct macro-scale characteristics of F2. Well: R, 1265ft. (b) Optical photomicrograph of massive to finely laminated silt-bearing mudstone (F2) showing the presence and fecal pellets (p) and silt grains which are randomly dispersed in the matrix. Well LT, 10384.6ft, TOC: 14.3 wt.%. (c) Optical photomicrograph showing massive to finely laminated silt-bearing mudstone (F2a), which have characteristically high matrix content and proportionately less fecal pellets (<5%) compared to massive to finely laminated fecal pellet and silt-bearing mudstone (F2b). Well: BN, 10352.1ft. (d) Optical photomicrograph showing massive to finely laminated fecal pellet and silt-bearing mudstone (F2b), which have proportionately higher amounts of fecal pellets (p) (>5%) compared to massive to finely laminated silt-bearing mudstone (F2a). Well: 4-11-7-13W2, 1776.25ft, TOC: 28.6 wt.%. 

Based on the proportion of fecal pellets and the amount of matrix, I divided this facies further into two types: silt-bearing mudstone (F2a) (Figure 3.7c) and fecal-pellet and silt-bearing mudstone (F2b) (Figure 3.7d); however, facies F2a and F2b are distinguishable only under a microscope. Silt content in
both the sub-facies varies between 10-25%; however, in facies F2a, the matrix, which is composed of organic matter and clay minerals, varies between 65-85%, and fecal pellets are less than 2%. In facies F2b, the organic matter-bearing and clay-rich matrix may vary between 35-85%, and fecal pellets may vary from 5-45%. In both sub-facies F2a and F2b, silt is primarily composed of angular to sub-angular quartz, feldspar grains, and detrital and authigenic dolomite, along with pyrite framboïds (Figure 3.8a). Silt grains are randomly dispersed in the clay and organic matter-rich matrix. Occasionally, radiolarians, conodonts, and phosphatic bones are also present, making up less than 5% of all framework components (Figure 3.8b).

Facies F2 was interpreted to be deposited by suspension settling of organominerallic aggregates, fecal pellets, clay minerals, and silt grains on the basis of their fine planar laminations and the absence of sedimentary structures, which, in turn, indicates the absence of bedload transport processes. High TOC, along with the absence of bedload transport features and a lack of burrowing, indicated that the bottom-water conditions were predominantly anoxic to euxinic during the deposition of this facies. As shown in Figure 3.7b and d, the uniform size, appearance, and abundance of type 1 fecal pellets, which are OM-poor and clay-rich, suggested that they were most likely produced by a single type of organism (Macquaker et al., 2010; Lohr and Kennedy, 2015). Benthic macrofauna cannot thrive in anoxic conditions; therefore, the type 1 fecal pellets, which dominate this facies, were either produced by filter-feeding zooplanktons living in the oxic water column, or by deposit-feeding benthic meiofauna, which can survive in anoxic to euxinic conditions at the sediment-water interface (Cuomo and Bartholomew, 1991; Neira et al., 2001; Turner, 2002; Macquaker et al., 2010; Lohr and Kennedy, 2015).

Figure 3.8: (a) FE-SEM image of massive to finely laminated silt-bearing mudstone (F2) showing the presence of pyrite framboïds (pyr fram), which are less than 10µm in size and are randomly dispersed in clay and organic matter-rich matrix. Well: RT, 10668ft, TOC: 14.7 wt.%. (b) Optical photomicrograph showing the occasional presence of radiolarians (rad) in massive to finely laminated silt-bearing mudstone (F2). Well: RT, 10665.5ft, TOC: 12 wt.%.
As shown in Figure 3.9a and b, two types of fecal pellets were identified in facies F2. The dominant type 1 fecal pellets are poor in organic matter and rich in clay and have a distinct homogeneous texture compared to the matrix (Figure 3.9a, c, and d). They are cylindrical in shape with tapered ends and 100-500 µm in length. The rare type 2 fecal pellets are silt-rich, circular-shaped, and are generally up to 350 µm in length, as shown in Figure 3.7b. The TOC in the immature samples of this facies from the Canadian portion of the UBS was as high as 28.6 wt.% and was the highest TOC among all the facies studied.

Figure 3.9: (a) Optical photomicrograph from a parallel to bedding thin-section from massive to finely laminated silt-bearing mudstone (F2) showing the cross-section of type 1 fecal pellet, which is cylindrical in shape, clay-rich and organic poor. Well: LT, 10388.1ft, TOC: 11.2 wt.%.
(b) Optical photomicrograph from a parallel to bedding thin-section from massive to finely laminated silt-bearing mudstone (F2) showing the cross-section of type 2 fecal pellet, which is circular-shaped and silt-rich. Well: LT, 10388.1ft, TOC: 11.2 wt.%.
(c) FESEM image showing the shape of type 1 fecal pellet, which is cylindrical in shape and 200µm in length. Well: RT, 10665.6ft, TOC: 10.5 wt.%.
(d) The SEM-EDAX image showing the near absence of organic matter (red) within the type 1 fecal pellet, while the matrix is rich in organic matter. Well: RT, 10665.6ft, TOC: 10.5 wt.%.
The type 1 fecal pellets were identified as planktonic in origin based on the following observations — (i) cylindrical shape, and the tapered end of the type 1 pellets are characteristically produced by planktonic organisms (Cuomo and Bartholomew, 1991; Lohr and Kennedy, 2015), and (ii) continuous wispy organic matter and organominerallic aggregates along the fecal pellets indicate that the organic matter has not been disrupted by meiofaunal burrowing (Lohr and Kennedy, 2015). Therefore, the presence of planktonic fecal pellets indicates that the surface water was well oxygenated, but the bottom water condition was not conducive for living organisms. The presence of abundant pyrite frambooids further supports the hypothesis that the bottom water condition was anoxic to euxinic during the deposition of facies F2.

**Facies F3- Sand and clay-bearing, silt-rich mudstone**

Facies F3 is characterized by coarser framework components, consisting of very fine sand and silt-sized detrital grains of quartz, dolomite, and feldspar that are organized into sub-mm to 3 mm-thick laminae with a sharp base and a commonly gradational top, shown in Figure 3.10a, 10b, and 10c. The amount of detrital silt and sand varies from 30-60% in this facies. Phosphatic clasts are also present along with the detrital grains; however, their volume is less than 5% (Figure 3.10d) The volume of the matrix, which is composed of organic matter and clay minerals, varies considerably in the clay-rich laminae and in the silt-rich laminae. Facies F3 exhibits continuous planar laminations, starved ripples (Figure 3.10e), the lenticular fabric of coarse silt laminae (Figure 3.11a) and normal grading (Figure 3.10d). The normally graded beds with sharp bases are mostly overlain by silt-rich laminae, which grades upwards into more clay-rich laminae. Moreover, occasional horizontal burrows are also present in the clay-rich laminae. Facies F3 grades into massive to finely laminated silt-bearing mudstone (F2). As these mudstones are thin-bedded, accurate determination of TOC is difficult without contaminating the sample with facies F2.

Facies F3 is interpreted to be deposited by bedload transport processes. The lenticular nature of the coarse silt laminae and starved ripples indicate that these mudstones were likely deposited by storm-induced bottom water currents which carried silt grains and flocculated mud in bedload (Schieber et al., 2007; Schieber, 2011, 2016). Occasionally, phosphatic fragments accumulated along silty laminae, which indicates a weak or short duration of bottom current events (Li and Schieber, 2015). The presence of phosphatic clasts, along with the detrital silt and sand as normally graded beds with the micro-scoured base, suggest that some of these mudstone beds were probably deposited as distal tempestites by waning and storm-induced combined flows (Aigner and Reineck, 1982; Ghadeer and Macquaker, 2011; Schieber, 2016). The occurrence of rare horizontal burrows Planolites in the clay-rich laminae in Facies F3 indicates that after the deposition of these beds, the sediment-water interface was suboxic for a limited time. Because of this, the clay-rich tops of these units were colonized by diminutive organisms.
Figure 3.10: (a) Core photograph showing continuous and discontinuous lamination (yellow arrow) of sand and clay-bearing, silt-rich mudstone (F3). (b) Scanned image of a petrographic thin section showing planar silt laminations (yellow arrow) in the sand and clay-bearing, silt-rich mudstone (F3) well-LT, depth-10389ft. (c) Optical photomicrograph showing framework components of very-fine sand to coarse silt grains in a clay and organic-rich matrix in facies F3. (d) An optical micrograph showing massive to finely graded beds of facies F3. Presence of phosphatic fragments is indicated by the yellow arrows. Well: LT, 10387.1ft. (e) The optical photomicrograph showing starved ripples and continuous planar silt lamina. Well: LT, 10389.8ft.
Figure 3.11: (a) Optical photomicrograph showing lenticular silt beds with a sharp base and overlain by a clay-rich lamina. The sample is from well LT, depth 10389ft. (b) The optical photomicrograph is showing horizontal *Planolites* burrow indicated by yellow arrow in the clay-rich lamina overlying the silt lamina. Well: RT, 10670ft.

**Facies F4- Macrofossil bearing silt-rich mudstone**

Facies F4 is massive in character and is macroscopically distinguishable due to the presence of horizontally aligned, articulated and disarticulated brachiopod shells up to 10 mm in length, making up to 10% of the total volume of this facies, as shown in Figure 3.12a-d. Facies F4 has a mostly homogeneous texture and has the highest detrital silt content, varying from 20-60%, shown in Figure 3.13a and b. Detrital silt grains are primarily composed of quartz, dolomite, and felspar. Additionally, this facies is characterized by the presence of agglutinated benthic forams, demonstrated in Figure 3.13a and b. As indicated in the Figure 3.13c and d, the benthic forams observed in this study were either cherty or had silt-size quartz grains in their walls. Detrital silt grains, shell fragments, and benthic forams are randomly distributed in the F4 matrix, which is composed of clay minerals and organic matter. Figure 3.12c and d show that calcareous shells present in this facies were often replaced by pyrite and silica. Figure 3.14a shows that occasionally, a few silt grains-thick laminae exhibiting discontinuous planar or undulating geometries with downlapping surface were also observed in facies F4. Moreover, as shown in Figure 3.14b, macro-scale *Planolites* burrows, which are 2-5mm in size, were occasionally present in this facies. The maximum thickness of this facies is as high as 6ft. The average TOC of facies F4 varies from about 3-8 wt.%, which is comparatively lower than that in facies F2.
Figure 3.12: (a) Core photograph of macrofossil-bearing silt-rich mudstone (F4) showing horizontally aligned thin-shelled brachiopods (brac), which is a diagnostic characteristic of this facies. Well: RT, 10654ft. (b) Core photograph of macrofossil-bearing silt-rich mudstone (F4) showing thin-shelled brachiopods in facies F4. Well: L, 10937.2ft. (c) The optical photomicrograph showing articulated brachiopods (brac) in facies F4. Brachiopods are partial to completely pyritized. Well: RT, 10654.5ft. (d) The optical photomicrograph showing articulated brachiopods (brac) in facies F4. Brachiopods are replaced by silica and pyrite. Well: RT, 10653.5ft.

Loucks and Ruppel (2007) and Schieber (2009) reported the presence of agglutinated benthic forams from other Late Devonian - Early Mississippian black shales, such as the Mississippian Barnett Shale, and the Late Devonian Chattanooga Shale of Tennessee; however, for the UBS, which belongs to the same age, the presence of benthic forams have not been reported previously, and the likely reason for this is that facies F4 itself was not identified previously. This study found that benthic forams are abundantly present as this facies was closely examined through petrographic thin-section study. As the existence of
benthic forams requires at least some oxygen to persist at the seafloor (Schieber, 2009). Facies F4 was interpreted to be deposited in a suboxic condition, and the sediment-water interface was occasionally hospitable, which probably supported the survival of meiofaunal organisms. This is further supported by the presence of *Planolites* macroburrows; therefore, the bottom water conditions of facies F4 were probably suboxic and much less reducing compared to facies F1 and F2. As the benthic conditions were suboxic and macroburrows are occasionally present in this facies, the homogeneous texture is probably a result of meiofaunal burrowing (Lohr and Kennedy, 2015). Meiofaunal burrowing likely destroyed the primary laminations, and thus the depositional process could not be identified.

Figure 3.13: (a) and (b) Optical photomicrograph in plane polars and crossed polars showing the presence of abundant silt content and homogeneous fabric in facies F4. Homogeneous fabric in facies F4 is probably a result of meiofaunal burrowing. Abundant detrital dolomite (dd), authigenic dolomite and agglutinated benthic foram (af) in this facies are observed at the lower right corner of the image. Well: RT, 10653.5ft TOC: 2.78 wt.%.

(c) and (d) Optical photomicrograph in plane polar and crossed polars, showing agglutinated benthic forams (af) in the facies F4 at a higher magnification. Presence of quartz silt in the wall of the benthic foram can be seen in the wall of benthic foram as pointed by the yellow arrow. Well-RT, 10650ft, TOC: 7.34 wt.%.
The infrequent presence of undulating silt laminae with downlapping surface indicated occasional deposition by bedload transport processes under the influence of weak bottom water currents. Most articulate-disarticulated brachiopods present in this facies are assumed to have lived in well-oxygenated surface water conditions, which later settled down to the bottom sediment along with algae or other floating plant materials (personal communication with Mark Longman). Alternatively, as the benthic condition was suboxic, some of the shell fragments may belong to bivalve *Bositra*, which can also survive in soft muddy benthic condition (Leonowicz, 2016).

Figure 3.14: (a) Optical photomicrograph is showing few silt grains thick discontinuous planar laminae with downlapping surface (shown by the yellow arrow) in macrofossil-bearing silt-rich mudstone (F4). Well: RT, 10354.5ft (b) Core photograph showing the presence of macroscale *Planolites* burrows (pl) in macrofossil-bearing silt-rich mudstone (F4). Well: L, 10934ft.

**Facies F-5- Burrow-mottled silt-bearing mudstone**

Facies F5 is characterized by the presence of macro-sized horizontal burrows and is present primarily at the contact of the UBS with the overlying Lodgepole Formation, (Figure 3.15a and b). As shown in Figure 3.15, the elliptical-shaped horizontal burrows, which were identified as *Planolites*, are 2-10 mm in length and about 0.5-1mm in thickness. This facies consists of around 20-30% detrital silt grains of quartz, dolomite, and feldspar, dispersed randomly in an organic matter and clay-rich matrix. These burrows are distinguishable in the darker matrix because of their lighter color, as they are devoid of organic matter, shown in Figure 3.15d; however, the other constituents (non-organic) of the burrow-fill were similar to that of the surrounding matrix. TOC of this facies varies considerably from 2 wt.% in core RT to 11 wt.% in core LT and depends on the amount of bioturbation. Due to bioturbation, the depositional process of this facies cannot be identified; however, the presence of macro-scale burrows indicates that this facies was deposited in an oxic to suboxic condition.
Figure 3.15: (a) Core photograph showing macro-scale *Planolites* burrows (b) in burrow-mottled silt-bearing mudstone (F5) at the contact of UBS with the overlying Lodgepole Formation. Well: LT, 10383.2ft. (b) A core photograph is showing macro-scale *Planolites* burrows (b) in burrow-mottled silt-bearing mudstone (F5) at the contact of UBS with the overlying Lodgepole Formation. Well: RT, 10648ft. (c) Scanned image of petrographic thin section showing *Planolites* burrows (b) in facies F5. Well: LT, 10383.2ft. (d) Optical photomicrograph of facies F5 is showing that the burrow (b) filled by constituents, which are similar to the matrix, and is devoid of organic matter. Well: LT, 10383.2ft.

**F-6: Phosphate clast and fossil-rich mudstone**

Facies F6 is massive in character and is distinguished by an abundance of phosphatic fragments, conodonts, fish bones, and sponge spicules, which collectively form 20-70% of the total volume of this facies (Figure 3.16a-d). This facies occurs as 0.5-10 mm thick beds with mostly gradational bases. Basal microscouring is occasionally present in this facies, mostly at the contact of the UBS with the underlying Middle Bakken member (Figure 3.16b). The phosphatic fragments and fossils present in this facies are randomly oriented and do not show any grading. Detrital siliciclastic and dolomite silt grains form 10-20% of the volume of the framework of facies F6. The matrix content of this facies varies widely, as the framework components form a packstone-type texture with no matrix, or it may form a floating texture with
an abundant matrix composed of organic matter and clay minerals. This facies is interpreted to be deposited by the reworking of conodonts, fish bones, sponge spicules, and phosphate grains, which were concentrated by storm-induced bottom water currents and; therefore, represent lag deposits or distal tempestites (Aigner and Reineck, 1982; Ghadeer and Macquaker, 2011). The amount of matrix varies in this facies is probably dependent on the current intensity. Moreover, the absence of significant scouring surfaces suggests that the storm-induced currents were episodic and low in intensity. Smith and Bustin (1996) observed similar lag deposits in the Bakken Shale in the Canadian portion of the Williston Basin and concluded that they were produced by episodic bottom water circulation.

Figure 3.16: (a) Core photograph showing mm-thick bed of phosphate clast and fossil-rich mudstone (F6). Well: R, 11026.6ft. (b) Core photograph showing cm-thick bed of phosphate clast and fossil-rich mudstone (F6). Well: BN, 10358.4ft. (c) Core photograph is showing cm-thick bed of phosphate clast and fossil-rich mudstone (F6) at the contact of UBS with the Middle Baken. Well: R, 11044.6ft. (d) Optical photomicrograph showing phosphate clasts, and sponge spicules (shown by red arrow) oriented randomly in phosphate clast and fossil-rich mudstone (F6). The base of this facies shows microscouring. Well: BN, 10352ft.
3.4.2 Factor Analysis and Element Relationships using XRF data

Principal Component Analysis (PCA), which is a type of statistical factor analysis, was performed on the XRF elemental data of the sixteen wells (Table 3.1). XLSTAT, which is an add-in module of MS-Excel, was used to perform the PCA for twenty elements: silicon (Si), aluminum (Al), titanium (Ti), potassium (K), magnesium (Mg), zirconium (Zr), rubidium (Rb), niobium (Nb), iron (Fe), calcium (Ca), manganese (Mn), strontium (Sr), molybdenum (Mo), uranium (U), vanadium (V), nickel (Ni), zinc (Zn), copper (Cu), sulfur (S), and chromium (Cr). The crossplot between the two principal components, or the highest factors, shows a dominant relationship between the twenty elements. PCA results for XRF elemental data from all sixteen cores show four groups of elements, as shown in Figure 3.17. The four groups, or clusters, which were identified in the PCA, are as follows: 1) Al, K, Ti, Rb, and Nb; 2) Ca, Sr, Mn, and Mg; 3) Mo, U, Zn, Cu, Cr, Fe and S; and 4) Si.

![Figure 3.17: Four groups of element clusters shown on the crossplot between the two principal components determined from Principal Component Analysis (PCA) in XLSTAT™ of twenty elements. The PCA was performed on around 400 UBS sampled from sixteen cores.](image)

From the first group, it was inferred that elements Al, K, Rb, and Nb were detrital in origin since they cluster with element Ti, which is always associated with detrital minerals (Section 3.3.3). These detrital elements are commonly associated with detrital siliciclastic minerals such as clays, quartz, and feldspar. From the second group, it was inferred that elements Ca, Mg, Mn, and Sr are associated with carbonate minerals. Figure 3.17 shows that Zr plots near the carbonate group of elements. Zr is usually associated
with detrital silt or sand-sized sediments, suggesting that some of the carbonate silt may have a detrital origin in the UBS. From the third group, elements Mo, U, V, Ni, Zn, Cr, and Cu are assumed to be redox sensitive, and become enriched under reducing conditions (Tribovillard et al., 2006). Elements Fe and S plot in close proximity within the redox group because of their association with pyrite. V, Cr, and Cu cluster together and plot closer to the detrital group of elements in comparison to other redox-sensitive elements, such as U and Mo. Tribovillard et al. (2006) reported that Cr usually has a strong detrital influence; therefore, this suggests that along with Cr, V and Cu also have some detrital influence in the UBS. Finally, the fourth group consists of just Si, suggesting that a fraction of Si is of biogenic and/or authigenic origin as it plots opposite to the detrital group. This further substantiates the presence of the abundant radiolarians in facies F1 of the UBS as previously discussed in Section 3.4.1. Moreover, as the detrital group of elements in the UBS mostly reflects clay-sized sediments and Si has a biogenic origin, Zr does not plot with either of these two groups.

### 3.4.3 Crossplots between Elements Concentrations

In PCA, Al, K and Ti plot together and form the Group 1 cluster (Figure 3.17), which indicates that Al and K have a detrital origin. This is substantiated by the strong positive correlation observed between Ti vs. Al and Ti vs. K crossplots, as shown in Figure 3.18a, b. The Al vs. K crossplot also shows a strong positive correlation (Figure 3.19a); therefore, both Al and K were used as proxies for detrital clays since Al is mostly associated with clay minerals as described in Section 3.3.3. PCA suggested that Si in the UBS is of non-detrital origin, which is verified by a weak negative correlation between Si and Ti in Figure 3.19b. The scatter in the crossplot in Figure 3.19b is due to both the detrital and biogenic origins of Si in the UBS. This is consistent with the findings of the petrographic studies, which confirmed the presence of radiolarians in facies F1 (Figure 3.4a) and detrital quartz silt in facies other than F1 (Figure 3.7). Therefore, a combination of high Si and low Ti was used as indicators for radiolarian-rich intervals in the UBS.

The UBS was found to be enriched in the redox-sensitive trace elements of Mo, U, and V, as their values are higher than that in the average shale, as indicated by the box and whisker plot in Figure 3.20. This suggests UBS has a high enrichment of these redox sensitive trace elements; however, there are significant variations in the degrees of enrichment (Figure 3.20). Nonetheless, Mo and U show strong covariance (Figure 3.21a), which suggest that their enrichment occurs in similar proportions in the prevailing redox conditions. As shown in Figure 3.21b, the positive correlation between Fe and S indicates that these elements are mainly associated with pyrite. Moreover, the presence of abundant pyrite framboids was also observed in the petrographic thin sections (Figure 3.8) which further substantiates the association of these elements with pyrite. Also, both the elements plotted in the redox group 3 in the PCA plot (Figure 3.17), which further validates that Fe and S are associated with pyrite that formed under reducing conditions.
conditions. Therefore, DOP, determined from the Fe vs. S plot can be used a proxy to understand the redox condition of the basin during the deposition of UBS.

Figure 3.18: (a) Crossplot of Al vs. Ti showing a strong positive covariance between the two elements, which indicates that Al has a detrital origin in UBS. (b) Crossplot of K vs. Ti showing strong positive covariance between the two elements indicating K has a detrital origin. Each crossplot includes all the samples from the sixteen wells for which XRF data were collected in this study. All the data points are color-coded by the three different chemostratigraphic units of UBS which are described in Section 3.4.5. All the three crossplots form two clusters, which correspond to the two main chemostratigraphic units, namely Unit-1 and Unit-2.

Figure 3.19: (a) Cross-plot of Al vs. K showing a strong covariance between the two elements, which indicates that most of the Al and K are associated with clay minerals in UBS. (b) Crossplot between Ti vs. Si showing a negative correlation, which indicates that Si has both non-detrital origin biogenic/authigenic origin and detrital origin. All the data points are color-coded by the three different chemostratigraphic units of UBS which are described in Section 3.4.5. All the three crossplots form two clusters, which correspond to the two main chemostratigraphic units, namely Unit-1 and Unit-2.

The weak covariance between Mo or U with V (Figure 3.22a and b) suggests that enrichment of V during the deposition of the UBS was dependent on other factors or conditions. This is explained by the two-step reduction process of V, as previously described in Section 3.3.3. In the first step of V reduction,
which takes place in anoxic non-sulfidic conditions, the rate of V enrichment is rapid; however, the anoxic non-sulfidic conditions are not as conducive for the enrichment of Mo and U, which require sulfidic conditions for the high degree of enrichment similar to that observed in the UBS. Therefore, in anoxic non-sulfidic conditions, V will have relatively higher enrichment than Mo and U, whereas, in a sulfidic or euxinic condition, Mo and U will undergo higher enrichment than V. PCA suggested that the V enrichment is likely to have some detrital influence as well. Thus, relatively high enrichment of V compared to Mo and U does not always indicate a more reducing condition. Consequently, in this study, trends in variation in V concentration were used for chemostratigraphic correlation purposes, but absolute concentration was not used to infer the redox conditions of the different chemostratigraphic units. In contrast, Mo and U concentrations were used for both chemostratigraphic correlations and to infer the redox conditions in the UBS.

Figure 3.20: Box and whisker plot showing the variation in the absolute concentration for the three redox-sensitive trace elements: Mo, U, and V in UBS. Each plot comprises of all samples of UBS from all the sixteen wells for which XRF data was collected in this study.

Figure 3.21: (a) Crossplot of Mo vs. U showing a strong positive covariance between the two elements. (b) Cross-plot between Fe and S showing a positive covariance which indicates that most of the Fe and S are associated with pyrite. DOP (Degree of Pyritization) lines in the crossplot are based on Algeo and Maynard (2004). All the samples are color-coded by the three different chemostratigraphic units of UBS, which are described in Section 3.4.5.
Figure 3.22: (a) Cross-plot of Mo vs. V showing a weak covariance between the two elements. The data points from three different clusters which are indicated in by encirclements. (b) Cross-plot of U vs. V showing a weak correlation between the two elements. The data points from three different clusters are indicated by encirclements. All the samples are color-coded by the three different chemostratigraphic units of UBS, which are described in Section 3.4.5.

3.4.4 XRD-XRF comparison

This section illustrates the effectiveness of using major element (Si, Al, K, and Ca) concentrations obtained from ED-XRF measurements as a proxy for mineral content in the context of the UBS. For the Middle Bakken Member, Jin (2014) observed correspondence between Well B XRF data with the QEMSCAN derived mineralogy from Kowalski (2010). A side-by-side profile view of XRD mineralogy and elemental data from XRF in Figure 3.23 qualitatively compares the elements and the dominant minerals composed of these elements. The profile view of the XRD-derived mineralogy and ED-XRF elemental data for the UBS in wells LT and BF showed a definite correspondence between Si and quartz; Al and K with clay; and Ca with dolomite. For example, Figure 3.23a shows that for well LT at the 10389-10390ft interval, both Si and quartz content was high (35-53 wt.%); whereas in the 10383-10385ft interval, both Si and quartz content was low (14-24 wt.%). Similar trends for Si were observed in well BF and are shown in Figure 3.23b; Si was therefore assumed to be primarily associated with quartz in the UBS. In addition, the 10389-10390ft interval of well LT had low Al, K, and clay content (14-33 wt.%). This contrasts to the 10383-10385ft interval, which had higher Al and K content, and corresponded to a high clay content of 44-50 wt.%. As K-felspar remained constant over the entire section of the UBS in well LT, Al and K content variations can be attributed to the changes in the amount of clay. Moreover, at the 10386-10390ft interval in well LT, relatively less Ca content was observed as compared to that in the upper 10383-10386ft interval. Variation in Ca concentration correlates with the variation in carbonate content, especially dolomite. For example, the lower interval has dolomite content of 6 wt.%, while in the upper interval, dolomite content increased to 8-10 wt.%.
Figure 3.23: Depth profiles comparing the XRF data of major elements and XRD mineralogy of UBS in (a) well LT, and (b) well BF.
3.4.5 Elemental chemostratigraphic correlation

Based on the trends of the elemental proxies and lithofacies distribution, two chemostratigraphic units, Unit-1 and Unit-2, were identified in the UBS. Unit-1 is the stratigraphically lower interval of the UBS, while Unit-2 is located at its upper intervals. Unit-1 was further subdivided into the stratigraphically lower sub-unit 1a and the upper sub-unit 1b. Table 3.2 lists differences between Units 1 and 2, as well as the signature of the boundary marker.

Table 3.3 lists differences between sub-units 1a and 1b and their boundary marker signature. These differentiating signatures of the units and sub-units are further elaborated through examples of the chemostratigraphic profiles for wells R, RT, and G (Figure 3.24, Figure 3.25 and Figure 3.26). Profiles for the other wells are included in Appendix D.

Table 3.2: Characteristic differences in terms of the biogenic, detrital, grain-size proxy, redox proxy, and facies between Unit-1 and Unit-2 are listed. The signature of the boundary marker is also specified.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Biogenic, Detrital, Grainsize proxy</th>
<th>Redox proxy</th>
<th>Facies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High Si and low Al, K and Ti and Ca</td>
<td>High Mo and U content compared to Unit-2.</td>
<td>Dominated by massive to very finely laminated silt-bearing mudstone (F2) followed by siliceous mudstone (F1)</td>
</tr>
<tr>
<td>2</td>
<td>Low Si and high Al, K and Ti, and Ca and an upward increasing trend in Zr</td>
<td>V shows a characteristic blocky character, Mo and U less enriched than Unit-1</td>
<td>Dominated by massive to very finely laminated silt-bearing mudstone (F2) or Macrofossil-bearing silt-rich mudstone (F4)</td>
</tr>
</tbody>
</table>

Table 3.3: The characteristic differences between sub-unit 1a and 1b in terms of the biogenic, detrital, grain size proxy, redox proxy and facies are listed. The signature of the unit boundary marker is also specified.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Biogenic, Detrital, Grainsize proxy</th>
<th>Redox proxy</th>
<th>Facies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Al, K, and Ti in sub-unit 1a slightly lower compared to sub-unit 1a</td>
<td>Highest Mo and U content. Characteristic peak most prominently in V just below 1a and 1b contact.</td>
<td>Dominated by massive to very finely laminated silt-bearing mudstone (F2) followed by siliceous mudstone (F1)</td>
</tr>
<tr>
<td>1b</td>
<td>Al, K, and Ti in sub-unit 1b slightly high compared to sub-unit 1a</td>
<td>High Mo and U but comparatively less than that in 1a.</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.24: Core description and chemostratigraphic profile with elemental trends of biogenic, detrital, carbonate and redox-proxying elements from Rolf 1-20H core showing the chemostratigraphic sub-unit 1a, sub-unit 1b and Unit-2 of UBS. From left to right: Si-silicon; Al-aluminum; K-potassium; Ti-Titanium; Zr-zirconium; Ca-calcium; Mo-molybdenum; U-uranium; V-vanadium. MFS-Maximum Flooding Surface.
Figure 3.25: Core description and chemostratigraphic profile with elemental trends of biogenic, detrital, carbonate and redox-proxying elements from Roberts Trust 1-13H showing the chemostratigraphic sub-unit 1a, sub-unit 1b and Unit-2 of UBS. From left to right: Si-silicon; Al-aluminum; K-potassium; Ti-Titanium; Zr-zirconium; Ca-calcium; Mo-molybdenum; U-uranium; V-vanadium; MFS-Maximum Flooding Surface.
Figure 3.26: Core description and chemostratigraphic profile with elemental trends of biogenic, detrital, carbonate and redox-proxying elements from core Graham USA 1-15 showing the chemostratigraphic sub-unit 1a, sub-unit 1b and Unit-2 of UBS. From left to right: Si-silicon; Al-aluminum; K-potassium; Ti-Titanium; Zr-zirconium; Ca-calcium; Mo-molybdenum; U-uranium; V-vanadium. MFS-Maximum Flooding Surface.
The chemostratigraphic profile used in this study consists of the core description, GR log, and elemental concentration logs for Si, Al, K, Ti, Zr, Ca, Mo, U, and V. Figure 3.24 and Figure 3.25 show the chemostratigraphic profiles for wells R and RT. The profiles indicate that Unit-1 had comparatively higher Si, and lower Al, K, Ti, and Zr. Moreover, Unit-1 was characterized by an abundance of siliceous mudstone (F1), which is consistent with the high Si observed in the unit. This difference in chemostratigraphic characteristics between Units 1 and 2 manifests statistically through the clustering of data-points in two distinct groups in all crossplots of Figure 3.18. Sub-unit 1a had comparatively lower Al and K than sub-unit 1b, which is evident in the data-point clustering in the Al vs. K crossplot in Figure 3.18c. Furthermore, Unit-1 is enriched in the redox-sensitive trace elements Mo, U, and V, as their concentration was higher than average shale values (Section 3.3.3). This chemostratigraphic difference can be seen in the clustering of two distinct groups of data-points in Figure 3.21a to 3.20c crossplots.

Additionally, Mo vs. V and U vs. V crossplots in Figure 3.21b and c also suggest that Unit-1 had higher U and Mo and lower V compared to Unit-2, which had higher V and showed a characteristic blocky signature. For sub-unit 1b, Mo and U were less enriched, while V was slightly more enriched compared to sub-unit 1a. This is shown in the Mo vs. V and U vs. V crossplots in Figure 3.21b and c, in which they appear to form different clusters with some overlap. The unit and sub-unit boundaries are marked by peaks in the levels of redox-sensitive trace-elements. The V peak is the most predominant, appearing immediately below the 1a and 1b contacts and the Unit 1 and 2 contacts (Figure 3.24 and Figure 3.25).

### 3.4.6 Regional Distribution of Chemostratigraphic Units

All three chemostratigraphic units and sub-units within the UBS were developed in all cores used in this study. These units and sub-units of UBS are correlatable in wells across the study area from the northeast to southwest (Figure 3.27) and from the southeast to northwest (Figure 3.28); however, a considerable lateral variation in thickness was observed in the three different units. Table 3.4 lists the thickness of the UBS and its different chemostratigraphic units and sub-units. Isochore maps for UBS, its chemostratigraphic units and sub-units, which are shown in Figure 3.29, were prepared based on the thickness information of Table 3.4. The UBS attains its maximum thickness in the basin center following a north-northwest and south-southeast trend along the Nesson Anticline (Figure 3.29a). In this study, the thickest UBS interval was encountered in cores RT and L, which are 21.2 ft and 21.5ft thick.

The total thickness of Unit-1 ranged from 4ft in well BY, which is located along the southwestern margin of the basin at the Elm Coulee Field, to a maximum of 14 ft in well L, which is located at the center of the basin (Figure 3.29b). The maximum thickness trend of Unit-1 followed the similar north-northwest to south-southeast trend along the Nesson Anticline. Unit-1 loses its thickness along the southwestern
margin of the basin. The thickness of sub-unit 1a varied from 1.1ft in well BY, located at the southwestern basin margin, to a maximum of 6.5ft in well C, located at the basin depocenter (Figure 3.29c). The thickness of sub-unit 1a followed a north-northwest to south-southeast trend. Sub-unit 1b followed a similar north-northwest and south-southeast trend as that of sub-unit 1a and attained a maximum thickness of 9ft in well L, located in the southern part of the basin depocenter. The thickness of sub-unit 1b varied from 2ft in wells LT, T, and G, located at the southwestern basin margin, to a maximum of 9ft in well L, located at the southern end of the basin center (Figure 3.29d). Sub-unit 1b also loses its thickness along the southwestern basin margin.

Unlike sub-units 1a and 1b, the thickness variation of Unit-2 was uniform with localized maxima across the study area. Maximum thickness was developed along the southern end of the basin center in a localized area, where Unit-2 attains its maximum thickness of 9.2ft in well RT (Figure 3.29e). Unit-2 pinches out in the southwestern basin margin such that it has a mere 1.2ft thick interval of well BN. This indicates that Unit-2 was most likely not deposited further south towards the proximal end of the basin.

Table 3.4: Thickness of different chemostratigraphic sub-units and units of UBS in all the eighteen wells used in this study. Well Abv- Abbreviation for well names.

<table>
<thead>
<tr>
<th>Well</th>
<th>Well Abv</th>
<th>Sub-unit 1a (ft)</th>
<th>Sub-unit 1b (ft)</th>
<th>Unit 1 (ft)</th>
<th>Unit-2 (ft)</th>
<th>Total (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miller 34X-9</td>
<td>M</td>
<td>2.5</td>
<td>7</td>
<td>9.5</td>
<td>3.5</td>
<td>13</td>
</tr>
<tr>
<td>Jorgensen 1-15H</td>
<td>J</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>3.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Saratoga 12-1</td>
<td>S</td>
<td>1.5</td>
<td>5</td>
<td>6.5</td>
<td>5</td>
<td>11.5</td>
</tr>
<tr>
<td>Graham USA 1-15</td>
<td>G</td>
<td>2.9</td>
<td>2.3</td>
<td>5.2</td>
<td>1.7</td>
<td>6.9</td>
</tr>
<tr>
<td>Bullwinkle Yahoo</td>
<td>BY</td>
<td>1.1</td>
<td>3</td>
<td>4.1</td>
<td>1.7</td>
<td>5.8</td>
</tr>
<tr>
<td>Roberts Trust 1-13H</td>
<td>RT</td>
<td>4.5</td>
<td>7.5</td>
<td>12</td>
<td>9.2</td>
<td>21.2</td>
</tr>
<tr>
<td>BN 1-23H</td>
<td>BN</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>1.2</td>
<td>7.2</td>
</tr>
<tr>
<td>5-1 Thompson Unit</td>
<td>TT</td>
<td>3</td>
<td>4</td>
<td>7</td>
<td>1.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Braaflat 11-11H</td>
<td>BF</td>
<td>3</td>
<td>4</td>
<td>7</td>
<td>4.5</td>
<td>11.5</td>
</tr>
<tr>
<td>Sidonia 1-06H</td>
<td>S</td>
<td>4.8</td>
<td>5.9</td>
<td>10.7</td>
<td>5.3</td>
<td>16</td>
</tr>
<tr>
<td>Rasmussen 1-21-16H</td>
<td>RM</td>
<td>4.5</td>
<td>5</td>
<td>9.5</td>
<td>2.9</td>
<td>12.4</td>
</tr>
<tr>
<td>Rolf 1-20H</td>
<td>R</td>
<td>6</td>
<td>7</td>
<td>13</td>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td>Charlotte 1-22H</td>
<td>C</td>
<td>6.5</td>
<td>5.5</td>
<td>12</td>
<td>4.3</td>
<td>16.3</td>
</tr>
<tr>
<td>Linseth 13-12</td>
<td>L</td>
<td>5</td>
<td>9</td>
<td>14</td>
<td>7.5</td>
<td>21.5</td>
</tr>
<tr>
<td>Titan F-WP 32-14-H</td>
<td>T</td>
<td>3.5</td>
<td>2</td>
<td>5.5</td>
<td>1.75</td>
<td>7.25</td>
</tr>
<tr>
<td>Round Prairie 1-17H</td>
<td>RP</td>
<td>3.5</td>
<td>4</td>
<td>7.5</td>
<td>3</td>
<td>10.5</td>
</tr>
<tr>
<td>Wayjetta 44-0311H</td>
<td>W</td>
<td>4</td>
<td>5</td>
<td>9</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>RR Lonetree Edna</td>
<td>LT</td>
<td>2.5</td>
<td>2</td>
<td>4.5</td>
<td>2.5</td>
<td>7</td>
</tr>
</tbody>
</table>
Figure 3.27: NE-SW chemostratigraphic correlation between wells RR Lonetree Edna, Round Prairie 1-17H, Rolf 1-20H, Sidonia 1-06H and Jorgensen 1-15H.
Figure 3.28: NW-SE chemostratigraphic correlation between wells Rasmussen 1-21-16H, Charlotte 1-22H, Roberts Trust 1-13H, and Miller 34X-9.
Figure 3.29: (a) Isopach map of the UBS showing north-northwest to south-southeast trend of maximum thickness in the basin depocenter. (b) Map for sub-unit 1a showing a north-northwest to south-southeast trend of maximum thickness in the basin depocenter. Maximum thickness for sub-unit 1a is encountered in well C (6.5ft). (c) Map of chemostratigraphic sub-unit 1b showing a north-northwest to south-southeast trend of maximum thickness in the basin depocenter. Maximum thickness for sub-unit 1b is encountered in well L (9ft). (d) Map of chemostratigraphic Unit-2 showing the development of maximum thickness around wells L and RT in the southern part of the basin depocenter. Unit-2 loses its thickness drastically along the southern basin margin. Maximum thickness for Unit-2 is encountered in well RT (9.2ft). An inset map in each figure showing the isopach map of the entire UBS in US-portion of the Williston Basin and the shaded box in the inset map represents the study area. Locations of wells are shown by black dots. Abbreviations of well names used in the maps are listed in Table 3.1.
3.4.7 Distribution of Facies in Chemostratigraphic Units

The contact between the UBS and the Middle Bakken Member, which is essentially the base of sub-unit 1a, was found to be either gradational or sharp. Phosphate and fossil-bearing mudstone (F6) was commonly present in sub-unit 1a when the contact was sharp, indicating a transgressive lag deposit. These transgressive lag deposits at the basal contact of sub-unit 1a were usually 10-20 mm in thickness and were found in both the basin margin (e.g., Well BN, Figure 3.16b) and the depocenter (e.g., Well R, Figure 3.16c); therefore, the presence of transgressive lag deposits at the basal contact of sub-unit 1a reflects the local topography, rather than the proximity to the basin margin. The transgressive lag beds are usually thicker in the southern margin of the basin compared to other parts of the basin, which probably indicates that the area is located more proximal towards the basin margin.

This is followed by a 0.5-2ft interval in sub-unit 1a, which is dominated by massive to finely laminated silt-bearing mudstone (F2) with intercalations of sand and clay-bearing silt-rich mudstone (F3). Finer grain size in facies F3 was observed in the basin center compared to that in the basin margin, which implies that storm-induced bottom currents deposited coarser silt in proximal parts of the basin, while finer silt was deposited in the distal areas. Moving up in the section, sub-unit 1a was dominated by massive to finely laminated silt-bearing mudstone (F2) with intercalations of siliceous mudstone (F1). The frequency of siliceous mudstone (F1) beds varied laterally and was not laterally correlated, as shown in the correlation profiles in Figure 3.30 and Figure 3.31. There was no visual difference between sub-unit 1a and 1b with respect to the distribution of dominant facies type.

Sub-unit 1b was also dominated by finely laminated silt-bearing mudstone (F2) with intercalations of siliceous mudstone (F1); however, sand and clay-bearing silt-rich mudstone (F3) and phosphate clasts and fossil-bearing mudstone (F6) were only present within 2ft from the base of sub-unit 1a and were not present in sub-unit 1b. The presence of facies F3 along with facies F2 at the base of sub-unit 1a, which is followed by predominantly facies F2 and facies F1, indicates a change from a combination of bedload transport processes by storm-induced bottom currents and suspension sedimentation at the base of sub-unit 1a to dominantly suspension sedimentation in sub-unit 1b. This decrease in storm-induced current activity likely reflects a deepening of the basing due to relative sea level rise.

Unit-2 had an overall massive appearance and was distinguished by the absence of siliceous mudstone (F1). This absence of facies F1 is also reflected in the low Si content in the chemostratigraphic profiles (Figure 3.24). As shown in Figure 3.30 and Figure 3.31, Unit-2 is dominated by massive to faintly laminated silt-bearing mudstone (F2, such as in Well S), or by macrofossil-bearing silt-rich mudstone (F4, such as in well L), or it may have both facies present in variable proportions (such as in Well RM). Facies F4 was primarily developed in a small area along the southern portion of the basin depocenter. As shown
in Figure 3.25, for Well RT, if Unit-2 is dominated by facies F4, the chemostratigraphic profile shows high Ca, while Mo decreases to almost detrital background values (1-5 ppm; Zheng et al., 2000). On the western side of the basin depocenter in wells C and RM, Unit-2 had a greater proportion of massive to faintly laminated silt-bearing mudstone (F2) compared to macrofossil-bearing silt-rich mudstone (F4). Moreover, Mo enrichment was moderate in Unit-2 (Appendix D, wells RM and C). Along the eastern side of the basin depocenter, Unit-2 was mostly dominated by massive to faintly laminated silt-bearing mudstone (F2) and had very high Mo and U concentration (Appendix-D, e.g., Well S). As shown in Figure 3.30 and Figure 3.31, in the southern margin of the basin, Unit-2 thinned out and mainly consisted of massive to faintly laminated silt-bearing mudstone (F2) with intercalations of sand and clay-bearing silt-rich mudstone (F3), which indicated that storm-induced bottom current activity was more pronounced in the proximal part of the basin.

Phosphate and fossil-rich mudstone (F6) was present within the top 1-1.5ft of Unit-2 in many wells, such as wells S, R and LT (Figure 3.30), which probably indicates that the relative sea level has progressively descended, which increased the influence of storm-induced bottom water currents. The contact of the UBS with the Lodgepole Formation marked the upper limit of Unit-2 and was characterized by the presence of burrow-mottled silt-bearing mudstone (F5) (Figure 3.15). Occasionally, soft-sediment deformation was also present at the boundary.

3.4.8 Gamma Ray Log and TOC Trends

Figure 3.32 shows the GR log and TOC profile for wells RT, BF, and S. As shown in Figure 3.32, GR values are highest at the basal 2-4ft interval of the UBS; thereafter, it has a general decreasing upward trend for the next 2-8ft, which is followed by another subtle peak in the upper 2-4ft interval. GR typically attained the highest value in sub-unit 1a, which was around 400 units more than that of sub-unit 1b. The minimum value for GR was attained within the 2-5ft interval of the lower part of Unit-2. Temporal variation in TOC was insignificant in wells BF and S, which did not show any relation to GR log variations. In well R, TOC and GR values generally covary. For example, the TOC and GR logs showed an upward decreasing trend and two intermittent peaks in the middle and top of the UBS.
Figure 3.30: Correlation is showing the lateral and vertical facies distribution in the three different chemostratigraphic units. The boundaries of the three units marked in this correlation are picked from the chemostratigraphic profiles.
Figure 3.31: Correlation is showing the lateral and vertical facies distribution in the three different chemostratigraphic units. The boundaries of the three units marked in this correlation are picked from the chemostratigraphic profiles of the wells.
Figure 3.32: Vertical profile of gamma ray (GR) log and SRA derived total organic carbon (TOC) for UBS for wells: RT, BF, and S showing the presence of high GR peak near the base and top of UBS and an upward decreasing trend in the middle of UBS interval in all the three wells. In well RT, TOC profile mimics GR trend, whereas in the other two wells variation in TOC is insignificant and TOC profile does not follow GR.

3.5 Discussion

This section integrates the results and their interpretation of the previous section to develop an understanding of depositional conditions such as detrital sediment influx, sedimentation rate, depth of the basin, and the redox conditions which prevailed during the deposition of the UBS in Williston Basin. This section also discusses the likely position of the maximum flooding surface for the UBS and the associated sequence stratigraphic implications. Finally, the chemostratigraphic units of the UBS are ranked for their shale resource potential, primarily based on their mineralogical composition, natural fractures, and brittleness.
3.5.1 Detrital Sediment Influx

The Bakken Formation was deposited in the Late Devonian-Early Mississippian period when the Williston Basin was located near the equator. In this phase, the basin is believed to have been under the influence of the easterly trade wind system (Parrish, 1982; Golonka et al., 1994; Smith and Bustin, 1998). Smith and Bustin (1998) proposed that the detrital fine-grained sediments in the UBS were mostly eolian input from the surrounding Lauransian land mass to the east and north-east. The authors suggested that these sediments were transported offshore by the prevailing east-west trade winds and were deposited by suspension sedimentation. This interpretation of the sediment influx was probably based on two lines of evidence: (i) the absence of prograding clinoform along the margin of the Williston Basin, and (ii) present-day Saharan dust storms are reported to carry eolian material for 1000’s of miles offshore in the Atlantic ocean (Middleton and Goudie, 2001). This study agrees with the eolian influx for the UBS deposition; however, the findings of this study suggest that the sand and clay-bearing silt-rich mudstone (F3) was deposited by weak bottom water currents as distal tempestites. Facies F3 showed a decrease in grain size at the basin center (e.g., Well RT) compared to that in the southern basin margin (e.g., Well LT). This grain size decrease suggests that apart from the northern and northeastern sediment influx, some portion of the detrital silt and phosphatic clasts in facies F3 were probably derived from the southern basin margin. Nonetheless, facies F3 is mostly present within 2ft from the bottom of Unit-1 and the top of Unit-2 in proximal parts, and represents less than 5% of the entire UBS, suggesting that influx from the southern basin margin was minor. Unit-2 had a higher concentration of detrital proxying elements Al, K and Ti compared to those in Unit-1 in all wells, which indicates that Unit-2 has more detrital clay content. The higher clay content in massive to faintly laminated silt-bearing mudstone (F2) and macrofossil-bearing silt-rich mudstone (F4) in Unit-2 compared to Unit-1 is due to the dilution of detrital clay by biogenic silica in Unit-1, rather than by any actual increase in the influx of detrital clay during the deposition of Unit-2. This interpretation is based on the petrographic analysis which suggests the selective presence of radiolarians in facies F2 in Unit-1 and their complete absence in the massive to faintly laminated silt-bearing mudstone (F2) and macrofossil-bearing silt-rich mudstone (F4) facies in Unit-2.

Zr/Rb ratio is used in this study as a proxy for the variation of the silt-size grain content in the chemostratigraphic units (Section 3.3.2). Lateral variation in the Zr/Rb ratio in Unit-2 suggests that during the deposition of Unit-2, apart from eolian input from the northeast, at least a fraction of the detrital silt was locally supplied from the southern margin of the basin. High silt content in macrofossil-bearing silt-rich mudstone (F4) was predominantly present in Unit-2, especially in the southern part of the basin depocenter wells (e.g., well RT). Unit-1 was dominated by massive to finely laminated silt-bearing mudstone (F2) followed by siliceous mudstone (F1) in most locations. The contrast in silt content between Unit-1 and
Unit-2 in well RT is shown in Figure 3.25 by an increase in both Zr and the Zr/Rb ratio in Unit-2 in comparison to Unit-1. A similar trend of high Zr and Zr/Rb ratio in Unit-2 was also observed in well L; therefore, an increase in Zr/Rb ratio generally reflects the higher influx of detrital silt during deposition of Unit-2.

Where Unit-2 mainly consisted of dominantly massive to finely laminated silt-bearing mudstone (F2), the Zr/Rb ratio did not vary significantly between the Units. This indicated that influx of detrital silt remained same during the deposition of the Units in locations other than the southern part of the depocenter. These contradicting observations about detrital silt influx during the deposition of Unit-2 suggest that detrital silt was derived from multiple sources during the deposition of Unit-2, and result in lateral variation in facies. The increase in the Zr/Rb ratio and presence of facies F4 in Unit-2 which develops more towards the southern part of the depocenter in wells RT and L indicates that the additional detrital siliciclastic silt and detrital dolomite were sourced from the southern basin margin.

An increase in detrital silt content during the deposition of Unit-2 was localized and is associated with a facies change, which suggests that the influx of detrital sediment from the southern margin of the basin was likely carried to the basin interior by weak bottom water currents. A universally low Zr content in Unit-1 in comparison to that in Unit-2, however, has resulted from a dilution effect of biogenic silica associated with radiolarians in Unit-1. The increase in Zr content in Unit-2 was probably due to the absence of a dilution effect by biogenic silica in this unit. This should not be interpreted as an actual increase in the influx of detrital silt influx during the deposition of Unit-2. However, in wells G (Figure 3.26), T, LT, and BY (Appendix D), which are located along the southern basin margin, Zr content in Unit-1 was similar to that in Unit-2 and was comparatively higher than other parts of the basin. This probably indicates the presence of silt and sand-sized sediments associated with the facies F3, which is found more along the basin margin area.

### 3.5.2 Sedimentation Rate

Previous studies by Hayes (1985), Smith and Bustin (1996, 1998) and Longman et al., (2014) suggest that the UBS was deposited in an offshore environment by continuous suspension settling of fine-grained sediments and organic matter at a slow rate in stagnant and anoxic bottom water of the basin. Based on this model of deposition, the sedimentation rate of the UBS was proposed by Smith and Bustin (1998) as 2 mm/1000 years. Longman et al., (2014) proposed a sedimentation rate of 0.7mm/1000 years based on the total thickness of the UBS in well L adjusted to the geochronologic timescale given by Haq and Schutter (2008); however, there is controversy regarding the time span for the deposition of the UBS due to insufficient radiometric age control of the Bakken Formation, which would aid in the accurate
determination of the average sedimentation rate. Longman et al., (2014) suggested that the UBS was deposited over a period of 7MY, while Sonnenberg (2015) suggested that the UBS was deposited in a period of 1MY.

Petrographic characterization of the UBS in this study shows that sedimentary processes were not constant, and instead varied through time during the deposition of the UBS; therefore, sedimentation rate, which is dependent on the depositional processes, is also expected to vary for each facies type in the UBS. Massive radiolarian-dominated mudstone (F1a) was deposited as a result of episodic radiolarian blooms by suspension sedimentation. Sand and clay-bearing silt-rich mudstone (F3) and phosphatic clast and fossil-rich mudstone (F6), which represent distal tempestites, were deposited by bedload transport processes. Although these three facies (F1a, F3, and F6) were deposited by different physical processes, they all represent episodic sedimentation at a comparatively faster rate. In contrast, the massive to finely laminated silt-bearing mudstone (F2) was deposited predominantly by suspension sedimentation of organic matter, organominerallic aggregates, fecal pellets and detrital silt and clay. Macquaker et al., (2010) suggested that organic matter is generally deposited as organominerallic aggregates during episodic algal blooms as marine snow, and such organic-rich mudstones are stacked into mm-thin beds with sharp bases and are overlain by silt lags; however, organic-rich facies F2 in the UBS have gradational bed boundaries and laminasets, and silt lags were also not observed in this facies. This probably indicates that the organominerallic aggregates and fecal pellets were delivered to the basin continuously at a slow rate with occasional episodic algal blooms. Recent studies have shown that organominerallic aggregates or marine snow, phytoplankton, and fecal pellets of zooplanktons settle through the water column at a faster rate than individual grains (Shanks, 2002; Turner, 2002, 2015). Organominerallic aggregates and phytoplanktons have sinking rates in the range of 16-368 m/day and 100-150 m/day, respectively (Turner, 2002). This suggests that during the deposition of facies F2, the organic matter could have settled as marine snow at a comparatively faster rate.

3.5.3 Depth of Basin

Smith and Bustin (1998) proposed that the UBS was deposited below the storm wave base at a water depth of more than 200 m based on the laminated fabric of the organic-rich shales, the absence of storm deposits, and lack of bioturbation and body fossils. The suggested water depth by Smith and Bustin (1998) would demand repeated drastic changes in sea level over very short periods of time. Although the overall long-term, cumulative sea level rise could be as much as 250 m, individual third-order changes in sea level occurring over ~0.5 to 6 million years and rarely exceeded 150 m (Haq and Schutter, 2008). Another point of concern with such great water depths is the lack of clinoforms in the entire Bakken Formation, which should be expected on a slope of over 200m. Moreover, the depth of 200 m is a common
estimate for storm wavebase (Boggs, 1987). Recent studies by Peters and Loss (2012) have demonstrated that the wave base rarely exceeds 150 m in the Atlantic Ocean, and is even shallower, generally less than 100m, along with the Gulf Coast. Based on these observations, Scott et al., (2017) proposed a maximum water depth of 100-150 m during the deposition of the UBS.

Facies F3 and F6 of the UBS were interpreted to be deposited as distal tempestites by storm-induced bottom currents. This indicates that at least occasionally during the initial stages of transgression, the depth of the basin was near the storm wave base along the basin margin. In semi-enclosed epicontinental basins such as the Williston Basin, storm wave base is not deeper than a few tens of meters, down to a maximum of about 50 m (Shaw, 1964; Aigner and Reineck, 1982; Peters and Loss, 2012; Schieber, 2016). So, at least during the initial deposition of the UBS, the maximum water depth along the basin margin of the Williston Basin was probably about 50m. The presence of radiolarians, however, indicates accumulation of sediments in deep basinal offshore settings at a water depth of more than 50m (Stasiuk and Fowler, 2004). Therefore, the water depth was more than 50m during the deposition of sub-units 1a and 1b, which are characterized by an abundance of radiolarian beds associated with facies F1. The depth of the basin during the deposition of UBS was likely never higher than 200 m.

3.5.4 Redox conditions and bioturbation

There are two schools of thought regarding the paleo-redox conditions that prevailed during the UBS deposition. The first of these two interpretations is more widely accepted, and suggests that the UBS was deposited mainly by suspension sedimentation in a restricted basin in an anoxic-euxinic bottom water condition (Webster, 1984; Smith and Bustin, 1996, 1998; Sonnenberg and Pramudito, 2009; Longman et al., 2014). This interpretation is largely based on the following observations, 1) the presence of planar, thin laminations within the shales resulting in deposition below storm wave base in a tranquil condition; 2) the presence of planktonic algal spores (Tasmanites sp.), fish remains, cephalopods, ostracods, conodonts, and inarticulate brachiopods representing pelagic organisms or rafted skeletal debris derived from the oxygenated surface water; and 3) the rare presence of trace fossils or body fossils along with the presence of high amounts of organic and pyritic material, indicating benthic anoxia (Webster, 1984; Smith and Bustin, 1996; Longman et al., 2014). This interpretation was further supported by high enrichment of redox-sensitive trace elements like Mo, U, V, and Ni in the UBS, which in turn indicated that the UBS was deposited in anoxic to euxinic conditions (Kocman, 2014).

The second school of thought, proposed by Egenhoff and Fishman (2013), is based on petrographic study and proposes that the UBS was deposited in dysoxic conditions. Egenhoff and Fishman (2013) reported the presence of vertical microburrows and sedimentary structures, indicating bedload transport
processes in the UBS. Based on these observations, the authors interpreted that the UBS was predominantly deposited in a dynamic environment with suboxic to dysoxic bottom water conditions. Schieber (2014) argued that the features identified as vertical microburrows in the UBS by Egenhoff and Fishman (2013) were in fact artifacts in the petrographic thin sections.

My findings suggest that during the deposition of sub-units 1a and 1b, bottom water conditions were predominantly euxinic. This interpretation is based on the observation of the lack of bioturbation and body fossils, the presence of dominantly planktonic fecal pellets and abundance of pyrite frambooids in massive to finely laminated silt-bearing mudstone (F2), and the predominant suspension sedimentation of fine-grained sediments and radiolarians with only occasional weak bottom water current activity. Moreover, euxinic conditions in bottom water are supported by the high enrichment of Mo and U found in sub-units 1a and 1b. Scott and Lyons (2012) suggested that Mo concentration of more than 100 ppm in shales indicates that a persistent euxinia existed in the water column. More than 85% of all sub-unit 1a and 1b samples used in this study (from all wells) were found to have more than 100ppm Mo (Figure 3.33a and b). Moreover, 90% of the samples from sub-unit 1a and 70% of the samples from sub-unit 1b had DOP$_r$ values greater than 0.75. This further supports that sub-units 1a and 1b were deposited under euxinic benthic conditions, and represents deposition under strongly stratified water column based on the threshold values of DOP$_r > 0.75$ for euxinic conditions, as suggested by Raiswell et al. (1988), Hatch and Leventhal (1992), and Rimmer et al. (2004). Sedimentological features and inorganic geochemical results, therefore, indicate that sub-units 1a and 1b were deposited in predominantly euxinic bottom water conditions with occasional storm-induced bottom current activity.

Figure 3.33: Histograms showing the statistical distribution of Mo concentration in various chemostratigraphic units of UBS. a) For sub-unit 1a, more than 90% of the samples have Mo concentration more than 100ppm; b) For sub-unit 1b, more than 80% of the samples have Mo concentration more than 100ppm; b) For Unit-2, more than 60% of the samples have Mo concentration more than 100ppm.
Occasionally, smaller microscopic-scale Planolites burrows were observed in the clay-rich top laminae of facies F3 along the southern basin margin (Figure 3.11b). Discrete occurrences of these burrows indicate that after deposition of these beds by bedload transport processes, a slightly dysoxic bottom water condition developed for a limited time, which allowed the diminutive fauna to colonize the clay-rich tops of these mudstones. The high influx of organic matter, however, resulted in rapid exhaustion of the oxygen content in the bottom water and the sediment-water interface soon became anoxic to euxinic. In sub-unit 1a in well G, Mo concentrations were consistently between 25-100ppm along with low enrichment of U and V. Scott and Lyons (2012) suggested that a Mo concentration between 25-100ppm implies intermittent euxinic conditions. This indicates that in well G, which is located along the southern basin margin, benthic conditions were less reducing compared to other parts of the basin.

In most of the cores, Mo and U concentration in sub-unit 1a was the highest among all three chemostratigraphic units. Cores located in the central part of the basin, where the thickness of sub-unit 1b was at its maximum, both Mo and U concentration displayed an upward decreasing trend while progressing into sub-unit 1b. A decrease in the absolute concentration of Mo and U in sub-unit 1b suggests either a decrease in the availability of the dissolved Mo or U ions within the water column or a decrease in the supply of organic matter, which is the host-phase for these redox-sensitive trace elements. (Algeo and Lyons, 2006; Algeo et al., 2007). A decrease in the availability of Mo and U ions would suggest an increase in the degree of basin restriction due to a fall in relative sea level (Algeo and Lyons, 2006; Algeo et al., 2007), during the deposition of sub-unit 1b; however, as shown in Figure 3.26, in well G, which is situated close to the southern basin margin, sub-unit 1b had the highest Mo and U concentrations. A decrease in Mo and U concentration due to basin restriction would have affected the margin of the basin more strongly; therefore, Mo and U concentrations in sub-unit 1b in well G ideally would not have increased. This suggests that during the deposition of sub-unit 1b, the availability of Mo ions in the water column did not decrease due to increasing basin restriction, but rather the basin margin became more reducing probably due to a relative sea level rise. A decrease in Mo and U concentration in sub-unit 1b in wells located in the basin depocenter, therefore, suggests a decrease in the availability of the host-phase, i.e., organic matter.

Sub-unit 1a was characterized by strong enrichment in Mo concentration, and a DOP$_T$ > 0.75. This indicates that bottom water conditions were strongly reducing, which likely resulted in the higher preservation of organic matter. After the initial sea transgression, which brought nutrient-rich water, organic productivity increased, resulting in the high amount of deposition of organic matter that rapidly depleted the oxygen content at the bottom of the basin. This caused rapid development of euxinic conditions at the sediment-water interface, but the surface water remained well oxygenated and sustained high organic matter productivity, as evident from the presence of planktonic fecal pellets in massive to finely laminated
mudstone (F2) and the abundance of radiolarians in siliceous mudstone (F1). Egenhoff and Fishman (2013) suggested that the UBS is completely bioturbated by vertical micro-burrows identified as *Phycosiphon incertum*, but such burrows were not observed in any of the facies in sub-units 1a and 1b. Additionally, Schieber (2014) suggested that these shales undergo high compaction, and it is highly unlikely that any vertical burrow has remain uncompacted.

During the deposition of Unit-2, redox-conditions varied laterally across the basin from suboxic to euxinic. Variability in redox condition was also present in the lateral variability in a given facies. There was an overall decrease in Mo and U in all wells from both basin depocenter and basin margin (except wells S and ST, located in the north-eastern part of the basin). About 45% of all samples from Unit-2 from all wells had a Mo concentration of less than 100ppm, indicating an overall decrease in Mo concentration regionally (Figure 3.33c). Scott and Lyons (2012) suggested that Mo concentrations between 25-100 ppm indicate either or both of the following: i) intermittent euxinic conditions in the bottom water, ii) decrease in availability of dissolved Mo ions in the water column. In wells R (Figure 3.25) and L, which are located near the basin depocenter, Unit-2 was dominated by macrofossil-bearing silt-rich mudstone (F4). Mo and U concentrations were very low in most of the Unit-2 intervals, such that the Mo concentrations were as low as 2-3 ppm, equivalent to the average crustal values. Scott and Lyons (2012) suggested that a Mo concentration lower than 25 ppm indicates that euxinic conditions are restricted only within the pore space, while the sediment-water interface is in suboxic to anoxic conditions.

As discussed in Section 3.4.1, facies F4 was also characterized by the presence of agglutinated benthic forams and comparatively low TOC (3-8 wt.%); therefore, a limited enrichment of Mo and U, along with the presence of agglutinated benthic forams and low TOC, suggests that near the southern part of the basin depocenter, the sediment-water interface was suboxic to anoxic during the deposition of Unit-2. Development of suboxic conditions in basin depocenter suggests that the basin-wide lowering of Mo and U concentrations during the deposition of Unit-2 was probably the result of less reducing conditions across the basin. Because of this, in the northern and central parts of the basin where Unit-2 was dominated by F2 and Mo concentration was less than 100ppm, benthic conditions were only intermittently euxinic. Furthermore, the overall lowering of reducing conditions is supported by low DOP$_T$ values for Unit-2 samples.

As shown in Figure 3.21d, DOP$_T$ values from about 70% of the samples from Unit-2 varied from 0.75 to 0.5. Raiswell et al., 1988; Hatch and Leventhal, 1992; Rimmer et al., 2004 suggested that when the DOP$_T$ is less than 0.75 but greater than 0.42, it indicates the presence of anoxic to dysoxic conditions and a less strongly stratified water column. Results from the multiple redox-proxies of Mo, U, and DOP$_T$ suggest that during the deposition of Unit-2, the bottom water condition was less reducing compared to Unit-1 such
that in some areas it became suboxic. In wells S and ST (Appendix D), Mo concentration was persistently high (>100 ppm), along with a high enrichment of U in Unit-2, suggesting that persistent euxinic conditions were also present locally within the basin. The amounts of oxygen present within the water column along the sediment-water interface during the deposition of Unit-2, therefore, varied laterally within the basin.

Presence of macroscale *Planolites* burrows and the development of burrow-mottled silt-bearing mudstone (F5) at the contact of Unit-2 with the overlying Lodgepole Formation suggests that benthic conditions became progressively oxygenated with the onset of deposition of the Lodgepole Formation. This study demonstrates that redox conditions varied from strongly euxinic to suboxic both temporally and regionally during the deposition of the UBS. Moreover, the degree of bioturbation in the UBS was most likely overestimated by Egenhoff and Fishman (2013), and this has led to an incorrect interpretation that the Williston Basin was predominantly dysoxic during the deposition of the UBS.

### 3.5.5 Sequence Stratigraphic Interpretation

Most of the previous studies on the sequence stratigraphic interpretation of the Bakken Formation were focused on the Middle Bakken Member (Smith et al., 1995; Smith and Bustin, 2000; Kohlruss and Nickel, 2009; Angulo and Buatois, 2012). Theloy (2014) compiled the previously proposed sequence stratigraphic models for the Bakken Formation and concluded that in most models, the upper part of the Middle Bakken shows a fining upward lithology; therefore, it represents the beginning of a major transgression. Most previous studies included the upper part of the Middle Bakken and the entire UBS within the transgressive system tract (TST), while the overlying Lodgepole Formation was included within the highstand system tract (HST); however, one of the major issues with constructing the sequence stratigraphic framework in the organic-rich UBS is identifying the maximum flooding surface (MFS). This is because, unlike many other mudstones, MFS in the UBS is not marked by any distinct, recognizable condensed sections distinguished by the presence of phosphatic hardgrounds, regionally correlatable phosphatic granule layers, preferential cementation, sediment starvation, or unusual enrichment of organic content (Macquaker and Gawthorpe, 1993; Algeo et al., 2004; Macquaker et al., 2007).

Smith and Bustin (2000) suggested that the upper contact of the UBS should be considered as the MFS since sedimentation of fine-grained organic-rich sediment continued at a slow rate until sea level stopped rising and maximum water depth was reached. Deposition of the UBS ended with the establishment of a sea level highstand, and the associated changes in water circulation and sedimentation patterns resulted in the deposition of the overlying Lodgepole Formation. This interpretation, however, is inconsistent with the following three major findings of this study, i) basin-wide disappearance of radiolarians in Unit-2, ii)
overall lowering of the reducing condition during the deposition of Unit-2, and iii) deposition of macrofossil-bearing silt-rich mudstone (F4) in suboxic conditions at the basin depocenter.

As discussed in Section 3.4.1, radiolarians are deep-water planktonic organisms and are sensitive to changes in relative sea level that cause changes in surface-water temperature, salinity, and nutrient supply (De Wever and Baudin, 1996; Wang et al., 2006). The disappearance of radiolarians during the deposition of Unit-2, therefore, most likely indicates a relative sea level fall. The overall lowering of reducing conditions and the development of suboxic conditions at certain areas near the basin depocenter suggests that due to relative sea-level fall during the deposition of Unit-2, the stratified water column was disturbed, which led to the cessation of widespread euxinic condition across the basin. Moreover, a high Zr/Rb ratio in sub-unit 2 in areas where macrofossil-bearing silt-rich mudstone (F4) was deposited suggests that influx of detrital silt content increased during the deposition of Unit-2. This, in turn, suggests that more area along the basin margin became exposed due to falling sea levels, which resulted in more weathering of silt sediments. These evidence collectively suggest that relative sea level started falling with the deposition of Unit-2; thus, the contact between the UBS with the Lodgepole Formation is unlikely to be the MFS.

Jin (2014) suggested that the MFS corresponds to the most reducing conditions and can be identified in organic-rich shales from the maximum V and Ni enrichment near the upper contact of the UBS. Based on this theory, Jin (2014) identified a sharp peak in V concentration as the MFS value near the upper contact of the UBS in well BF (Appendix D). Although a sharp peak in V concentration was observed near the upper contact of the UBS in few wells such as BF and RT, in most wells used in this study, no such peak was observed. V showed a blocky character in Unit-2, and because of this observation, the sharp peak in V concentration observed by Jin (2014) cannot be regionally correlated. Moreover, as discussed in Section 3.3.3, V concentration in the UBS is not suitable to determine the maximum reducing condition because i) V has a detrital influence in the UBS, and ii) enrichment of V takes place by a two-step reduction process with separate carrier-phases, which may lead to the high enrichment of V at a relatively rapid rate even in less reducing conditions (Algeo and Maynard, 2004; Tribovillard et al., 2006; März et al., 2008). Lewan and Maynard (1982) also suggested that a high V enrichment can also suggest that anoxic or euxinic conditions existed only within the pore water, while the sediment-water interface and water column were less reducing. Since Unit-2 was deposited during a relative sea-level fall, this indicates that the MFS is probably located below Unit-2.

The contact between the Middle Bakken and Unit-1 of the UBS represents a transgressive surface and is marked by the presence of 10-20 mm thick phosphatic lag deposits (F6) in some places. Due to the lack of conodont data from the Middle Bakken, it is not clear whether the transgressive surface represents a significant hiatus in deposition (Figure 3.2). According to Wignall (1991), the basal part of transgressive
black shales is characterized by high GR and TOC values. Passey et al. (2010) suggested that in a platform/ramp setting like the Williston Basin, the maximum TOC value occurs in the basal TST and decreases stepwise to background values at the MFS. In almost all wells, the highest GR values were observed in sub-unit 1a of the UBS, which progressively decreases upward in sub-unit 1b and peaks again in Unit-2. In well R, TOC values mimic GR logs such that highest GR values are observed along with the highest TOC at sub-unit 1a; therefore, sub-unit 1a is part of TST, which is consistent with the proposition of Wignall (1991) and Passey et al. (2010).

The presence of sand and clay-bearing silt-rich mudstone (F3), along with massive and finely-laminated silt-bearing mudstone (F2), at the base of sub-unit 1a, which is followed by predominantly facies F2 and siliceous mudstone (F1), indicates a change from a combination of bedload transport processes and suspension sedimentation at the base of sub-unit 1a to dominantly suspension sedimentation with occasional weak bottom water current activity in sub-unit 1b. Moreover, in well G, located close to the south-western margin of the basin, the highest Mo and U concentration was observed in sub-unit 1b. This indicates that due to rising sea levels, maximum reducing conditions occurred during the deposition of sub-unit 1b, implying a gradual rise in the relative sea level during the deposition of sub-unit 1a to sub-unit 1b; and therefore, Unit-1 represents a transgressive cycle. The characteristic peaks in redox-sensitive trace elements represent a flooding surface, such as in Figure 3.25 and Figure 3.26, especially in V, which is present slightly below the contact boundary between sub-unit 1b and sub-unit 1a.

The basin-wide disappearance of radiolarians, an overall decrease in reducing conditions evident from low Mo and U concentrations and DOP$_T$ values less than 0.75, localized development of suboxic conditions, and an increase in the influx of detrital silt during the deposition of Unit-2 all suggest that Unit-2 was deposited during relative sea-level fall and represents a regressive cycle. The MFS for the UBS was thus most likely located near or below the contact between sub-unit 1b and Unit-2. A characteristic peak in redox-sensitive trace elements, especially in V, represents the MFS in the UBS. A carbonate concretion was also observed in well J (Figure 3.30) below the contact between Unit-1 and Unit-2. Concretionary carbonates generally precipitate in response to either complete breaks in sedimentation or to periods where sedimentation rates were very low (Macquaker and Gawthorpe, 1993); therefore, the presence of the carbonate concretion in well J probably indicates very low sedimentation rate, which in turn further supports that the MFS in the UBS is located just below the contact of Unit-1 and Unit-2. On the basis of the MFS identified in this study, Unit-1 is interpreted to be part of the TST, while Unit-2 and the overlying Lodgepole Formation is interpreted to be part of HST.
3.5.6 Mineralogy Based Resource Potential of UBS Chemostratigraphic Units

In this section, the chemostratigraphic units of the UBS are ranked for their shale resource potential based on their mineralogy, brittleness, and occurrence of natural fractures, which are among the key indicators for a successful liquid-rich shale play (e.g., Passey et al., 2010; Bohacs et al., 2013). Based on biogenic and detrital proxying elements, it was shown in Section 3.4.5 that the chemostratigraphic units of the UBS have different biogenic silica, clay, carbonate, and detrital silt contents. Silica associated with siliceous mudstone (facies F1) as radiolarians were attributed as the reason behind the high Si content in Unit-1 in comparison to that in Unit-2. Moreover, a fraction of silica in facies F2 is likely to be authigenic in nature (Schieber et al., 2000). Quartz associated with biogenic silica, which is present in Unit-1 only, is more brittle compared to detrital quartz because recrystallized biogenic and authigenic silica creates a rigid high modulus framework (Jarvie et al., 2007; Passey et al., 2010; Blood et al., 2013); therefore, Unit-1 should be more prone to natural fracturing, which is confirmed by the abundant presence of mineralized ptygmatic natural fractures in Unit-1, especially in facies F1. Unit-1 was additionally characterized by comparatively low detrital clay proxying elements Al, K, and Ti, which indicated lower clay content in Unit-1. Lower clay content in shales decreases the likeliness of the adverse effects of clays with respect to completion and production issues related to clay-swelling and fines migration (Passey et al., 2010; Blood et al., 2013). High silica content, low clay fraction, and presence of mineralized natural fractures (Figure 3.5a) collectively indicate that Unit-1 is comparatively more brittle than Unit-2.

Brumsack (1989) suggested that 5*Al₂O₃ is an indicator for clay, SiO₂ is an indicator for quartz, and 2*CaO is an indicator for carbonate minerals in rock samples. Thus, a ternary plot between 5*Al₂O₃-SiO₂-2*CaO can show the relative concentration of clay, quartz, and carbonate in given samples. According to Passey et al. (2010), in a quartz-clay-carbonate ternary diagram, currently producing shale plays generally lie below the 50% clay line since shale-plays that contain greater than 50 wt.% quartz or carbonate tend to be more brittle, and therefore are more fraccable.

In this study, the concentrations of Al₂O₃, SiO₂, and CaO were calculated stochastically from the absolute values of XRF data derived Al, Si, and Ca concentrations. Figure 3.34 shows a ternary diagram between 5*Al₂O₃-SiO₂-2*CaO for the different chemostratigraphic units of the UBS. The ternary diagram shows that samples from Unit-2 always plotted above the 50% clay line, suggesting that Unit-2 is less brittle and not a good target interval. Samples from sub-unit 1a and 1b, however, both plotted above and below the 50% clay line. This indicates that the silica-rich intervals below the 50% clay line would be relatively more brittle and therefore could be potential landing targets. This conclusion is further supported by the XRD data available from five wells. Based on the XRD mineralogy, all Unit-2 samples plotted above the 50% clay line in the ternary diagram in Figure 3.34, whereas all samples from sub-units 1a and 1b plotted
below the clay line. The ternary diagram shows that few samples from sub-unit 1a, which plots close to the quartz-rich corner, represent radiolarite or siliceous mudstone (F1). Based on the mineralogy and brittleness properties, Unit-1a and 1b are better target intervals than Unit-2.

![Figure 3.34: Ternary plot representing 5*Al₂O₃-SiO₂-2*CaO relationship (after Brumsack, 1989) of the chemostratigraphic sub-unit 1a, 1b, and Unit-2 of UBS. The three axes of (5*Al₂O₃), SiO₂ and (2*CaO) represents clays, quartz and/or biogenic silica, and total carbonates respectively. The black data points represent XRD mineralogy from five wells, shape of the data points represents the three different chemostratigraphic units. The ternary plot includes all the samples from the sixteen wells for which XRF data has been collected in this study. All the data points are color-coded by the three different chemostratigraphic units of UBS. The data points form mainly two clusters, which correspond to the two main chemostratigraphic units: Unit-1 and Unit-2. Sub-unit 1b predominantly clusters below the 50% clay line, whereas Unit-2 plots above the 50% clay line.]

3.6 Conclusions

The main conclusions from this study are as follows:

- The UBS consists of six different lithofacies identified from core descriptions and petrographic studies. These six lithofacies are: i) siliceous mudstone (F1); (ii) massive to finely laminated silt-bearing mudstone (F2), (iii) sand and clay-bearing silt-rich mudstone (F3), (iv) macrofossil-bearing silt-rich mudstone (F4), (v) burrow-mottled silt-bearing mudstone (F5), and (vi) phosphate and fossil-rich mudstone (F6). Out of these six lithofacies, 95% of the UBS is composed of Facies F2 and F1.
• Facies F1 and F2 were deposited by suspension sedimentation, whereas F3 and F6 were deposited by bedload transport processes; however, due to bioturbation, the depositional processes for F4, F6 were not identifiable.

• Internal stratigraphic framework for the UBS was provided by identifying two laterally correlatable chemostratigraphic units 1 and 2; Unit-1 was further subdivided into laterally correlated sub-unit 1b and sub-unit 1b. A total of three regionally correlatable chemostratigraphic packages were identified in the UBS.

• For both sub-unit 1a and 1b, the maximum thickness followed a northeast and southwest trend in the basin depocenter; for Unit-2, the thickness was localized and maximized near the southern part of the depocenter.

• Influx of silt-size detrital sediments had multiple sources, especially during the deposition of Unit-2. Along with eolian silt from the northeast, some detrital silt were also derived from the southern basin margin.

• Redox conditions varied both temporally and laterally during the deposition of the UBS. Sub-units 1a and 1b, in most locations across the basin, were deposited in a persistently euxinic condition. Unit-2 was deposited in a much less reducing condition, which varied from sub-oxic to intermittently euxinic.

• The maximum flooding surface is located in sub-unit 1b below the Unit-2 and sub-unit 1b contact; therefore, Unit-1 is part of the TST and Unit-2 is within the HST.

• Sub-units 1a and 1b have more biogenic and authigenic silica compared to Unit-2, which makes them comparatively more brittle than Unit-2. As such, sub-units 1a and 1b will be better reservoir targets compared to Unit-2.

3.7 Reference


Algeo, T. J., L. Schwark, and J. C. Hower, 2004, High-resolution geochemistry and sequence stratigraphy of the Hushpuckney Shale (Swope Formation, eastern Kansas): Implications for climato-
environmental dynamics of the Late Pennsylvanian Midcontinent Seaway: Chemical Geology, v. 206, no. 3–4, p. 259–288.


CHAPTER 4

FACTORS CONTROLLING ORGANIC RICHNESS OF UPPER BAKKEN SHALE, WILLISTON BASIN

Organic richness in shale is primarily controlled by the interplay of three factors: organic productivity, preservation, and dilution by sediments. This study is focused on understanding the impact of these factors on controlling the organic richness of Upper Bakken Shale (UBS), for which the Total Organic Carbon (TOC) varies between 3-20 wt.%. A conceptual model for the accumulation and preservation of organic matter (OM) in UBS is also proposed. The framework of this conceptual model includes the depositional setting of the basin, including basin morphology, paleogeography, paleoclimate, and probable nutrient sources.

This study is based on the results of the following three analyses: 1) source rock analysis (SRA) for TOC and OM characterization; 2) induced coupled plasma mass spectrometry (ICP-MS) for elemental concentration measurements; and 3) stable isotope measurements for carbon and nitrogen. These analyses were performed on 37 core chips of UBS from well Robert Trust 1-13H, which is located at the southern depocenter of the Williston Basin. Elemental concentration of Si, Al, K, Ti, and Ca were used for proxying the effect of dilution and preservation of OM by detrital and biogenic sediments. The concentration of the redox-sensitive trace elements (Mo, U) and degree of pyritization (DOP) were used as proxies for understanding the variation in redox condition during the deposition of the UBS. Stable isotopes of organic carbon and nitrogen were used to understand the OM type in the UBS and the paleoproductivity during its deposition.

The results of this study suggest that TOC and the factors which controlled the organic content varied in the southern depocenter of the basin during the deposition of the UBS. It is proposed that the basin was semi-restricted, with a stratified water column, and regeneration of the biolimiting nutrients such as P and N were the major source of nutrients. These conditions varied during the deposition of the UBS, primarily due to a relative change in sea level, which resulted in four distinct sub-units in the UBS: 1a, 1b, 2a, and 2b. Influx of clay helped in quick preservation of OM and thereby had a positive effect on organic-richness during the deposition of all four sub-units. Biogenic silica had a dilution effect during the deposition of organic matter in sub-units 1a and 1b. Detrital dolomite and siliciclastic silt also had a dilution effect during the deposition of sub-units 2a and 2b. Sub-units 1a and 1b were deposited in a strongly euxinic condition, which existed in the bottom water and extended to the photic zone intermittently. This prevented the degradation and resulted in better preservation of OM. During the deposition of sub-units 2a and 2b,
the conditions were predominantly sub-oxic to anoxic along the sediment-water interface, which resulted in more degradation of OM. Paleoproductivity was high during the deposition of sub-units 1a and 1b, and paleoproductivity declined during the deposition of sub-units 2a and 2b.

4.1 Introduction

Oil and gas production from shale plays has witnessed enormous growth over the last decade; however, there are challenges in terms of developing a better understanding of shale geology, which would assure the continuation of this growth. The organic richness and their controlling factors in both modern and ancient marine sediments is a fundamental but poorly understood area of shale geology. Currently, there are two very different schools of thought which seek to explain the higher organic matter (OM) accumulation in these organic-rich shales. The first theory emphasizes the role of increased primary productivity of OM (Demaison and Moore, 1980) to explain the organic richness of these shales. The second theory suggests that the primary reason for the organic richness in shales is the enhanced OM preservation due to a strongly reducing paleoredox condition (Calvert, 1987; Pedersen and Calvert, 1990; Tyson, 2005). However, recent studies have demonstrated that the total organic carbon (TOC) deposited in marine sediments is actually a function of three variables: OM production, OM preservation and OM dilution by detrital/biogenic sediments (Murphy et al., 2000; Werne et al., 2002; Sageman et al., 2003; Rimmer et al., 2004; Bohacs et al., 2005; Tyson, 2005). These three variables are in turn controlled by a complex interplay of multiple paleoceanographic and sedimentological factors, such as nutrient supply, sunlight, sedimentation rate, benthic-redox condition, size and depth of the basin, the degree of basin restriction, watermass mixing and changes in eustatic sea-level (Sageman et al., 2003; Bohacs et al., 2005). My study is focused on understanding the role of these factors in controlling the organic richness of the UBS by integrating the petrographic observations with the organic and inorganic geochemistry results.

The Early Mississippian UBS of the Williston Basin is a world-class source rock with an average TOC of 11.3 wt.% in the U.S. portion of the basin (Webster, 1984; Smith and Bustin, 2000). The UBS is an extensively studied shale system; the primary aims of these previous research efforts were to understand the source rock potential, organic and inorganic geochemistry, and depositional environment of the UBS (e.g. Meissner, 1978; Price et al., 1984; Webster, 1984; Hayes, 1985; Smith and Bustin, 1996, 1998; Egenhoff and Fishman, 2013; Jin, 2014; Kocman, 2014; Longman et al., 2014). Based on the geochemical analysis of the UBS, Smith, and Bustin (1998) concluded that enhanced organic productivity is the primary reason for the organic richness of the UBS. The authors also proposed that during UBS deposition, organic productivity varied, which in turn resulted in the observed temporal and spatial variation in OM richness of the UBS. Smith and Bustin (1998) also suggested that the UBS was deposited in an anoxic stagnant basin, which aided the preservation of OM. This interpretation was based on the presence of planar lamination,
abundant pyrite content and the lack of bioturbation and other body fossils. An anoxic stagnant condition in the basin during the UBS deposition was also suggested by Price et al. (1984), Webster (1984), Hayes (1985), Smith and Bustin (1996), Sonnenberg and Pramudito (2009), and Longman et al. (2014).

Smith and Bustin (1998) also used stable isotope of Nitrogen (N) as a proxy to determine paleoproductivity and suggested that OM productivity was higher at the onset of the UBS deposition compared to its levels in later stages. Moreover, based on the observation of spatial variation in TOC in the UBS (as high as 35 wt.% in the Regina-Melville Platform area), the authors also proposed that OM productivity varied regionally during the deposition. Smith (1996) used a quartz-to-illite and alkali feldspar-to-illite ratio as a proxy to understand the change in detrital sedimentation rate in the UBS. The author compared these ratios with TOC to understand the effect of siliciclastic sedimentation and dilution on OM preservation; they observed no correlation between TOC vs. change in either the quartz-to-illite ratios or TOC vs. alkali feldspar-to-illite ratios. Therefore, it was concluded that detrital sedimentation rate had almost remained constant over the period of UBS deposition, and it did not affect the preservation/dilution of TOC.

Scott et al. (2017), based on their inorganic geochemical analysis results, proposed that the deposition of the UBS resulted in a rapid development of a strongly euxinic condition with very high concentrations of dissolved \(\text{H}_2\text{S}\) (~10mM). They further suggested that this euxinic condition mostly remained close to the sediment-water interface and reached the photic zone episodically. These authors referred to UBS samples having Zn concentrations of more than 500 ppm and TOC >7 wt.%, as “hyper-enriched” with respect to Zn. It was proposed that hyper-enrichment of Zn reflects photic-zone euxinia and the presence of photoautotrophic sulfide-oxidizing bacteria (PSOB). Based on this hypothesis, Scott et al. (2017) concluded that UBS sections with hyper-enriched Zn concentration indicate the occasional development of photic zone euxinia during their deposition. They also proposed that neither high primary productivity nor a euxinic condition was the reason for the organic matter richness in the UBS. The authors also suggested that the shallow depth of the basin (100-150m) resulted in a short transit time of the OM through the water column, which after deposition degraded and resulted in the development of anoxic/euxinic conditions.

Previous studies have reported the presence of the biomarker isorenieratene in Bakken shales (Requeffo et al., 1991; Jiang et al., 2001). Isorenieratene is produced by PSOB Chlorobiaceae, which requires a water column with light and a sulfidic condition to survive. Based on the presence of the biomarker isorenieratene in Upper and Lower Bakken Shale, Requeffo et al., (1991) and Jiang et al., (2001) suggested that euxinic conditions were extending up into the photic zone during deposition. On the other hand, Egenhoff and Fishman (2013) proposed that the UBS was predominantly deposited in an overall
dysoxic condition (2.0-0.2ml O₂/ 1 H₂O according to Tyson and Pearson, 1991); their work was based on petrographic studies, which indicated the presence of burrows and sedimentary structures, indicating bedload transport processes. However, this study did not address the reservations regarding the reduced preservation potential of OM during UBS deposition in a dysoxic condition.

Jin (2014) calculated the original TOC of UBS from SRA data and prepared the original TOC map of the UBS. It was observed that along the eastern margin of the basin, the UBS is relatively lean in OM, with lower than 10 wt.% TOC, while in the central and intermediate parts of the basin in the North Dakota and eastern Montana areas, the UBS is generally organic-rich, with 17~20 wt.% original TOC. The author suggested that this spatial variation in TOC content is probably due to the low OM production, dilution of OM by terrigenous sediments, and poor preservation in a relatively dysoxic environment.

There is a clear disagreement over the interpretation of the redox conditions prevailing in the Williston Basin during the UBS deposition. In the current study, I have integrated the petrographic observations with organic and inorganic geochemistry results, which helped in providing a coherent understanding of the paleoredox condition of UBS. Moreover, my research findings are not different from the interpretation of Smith and Bustin (1998) which claimed constant anoxic conditions during the UBS deposition and suggests that the redox condition of the basin was not constant and has varied from euxinic to suboxic. The objectives of this study were as follows: 1) to develop an understanding of the interplay of paleoproductivity, redox condition and dilution of OM in controlling the organic richness of UBS; 2) based on this understanding, to provide a conceptual model for the UBS deposition. My results show that the redox condition, which controls the preservation potential of OM, should be considered along with paleoproductivity in order to understand the organic richness in the UBS. I also examined the effect on the organic richness of OM dilution by detrital and biogenic sediments.

4.2 Methodology: Sampling and analytical procedures

The study area and geological background are same as those used in Chapter 3 and were discussed in Section 3.2. The current study is based on the petrographic and geochemical analyses of the drill core of well Robert Trust 1-13H (RT), which is located near the southern part of the basin depocenter (Figure 4.1). In Well RT, the UBS thickness of 21.2ft is close to its maximum thickness in the basin; therefore, the core from Well RT is likely to have captured almost the full depositional history of UBS in the southern part of the basin depocenter. The core of well RT is curated at the North Dakota Geological Survey core repository center at Grand Forks (ND). About 40 core chips were collected at every 0.5 to a 1ft interval of the core for geochemical analysis, and thirteen paired thin-section billets were collected for petrographic thin section preparation. The methodology for thin section preparation was the same as that presented in Section 3.3.4.
The geochemical analyses I used were the following: 1) source rock analysis (SRA) for TOC measurements; 2) inductively coupled plasma mass spectrometry (ICP-MS) for identification of major and trace element concentrations; 3) Sulphur concentration measurements by an element analyzer; and 4) stable isotope measurements for organic Carbon and Nitrogen. Prior to the geochemical analysis, the core chip samples were cleaned with deionized water to remove salt crust and/or drilling mud residues, and subsequently, the samples were air dried for 24 hours. The cleaned samples were crushed by mortar and pestle to a 200-mesh size powder. Aliquots of thirty-seven samples were analyzed for TOC using the Weatherford Source Rock Analyzer (SRA) instrument at Colorado School of Mines using the procedure described by Jin (2014).

Figure 4.1: Location of well Robert Trust 1-13H (RT) is shown by the red star in the isopach map of the Upper Bakken Shale (modified from Sonnenberg et al., 2017).

Remaining aliquots of the powdered samples were used for determining major, minor and trace element concentrations by the SGS Mineral Services, Canada. This involved performing ICP-AES and ICP-MS analyses after sodium peroxide fusion of the powdered aliquots (SGS method GE ICM90A). ICP-AES and ICP-MS analyses were conducted on a total of thirty-six samples. Details about the protocol used in these analyses can be accessed at http://www.sgs.com/en/mining/analytical-services/geochemistry/digestion-and-fusion. Sulphur concentration measurements were performed using the Costech ECS4010
elemental analyzer Colorado Plateau Stable Isotope Lab at Northern Arizona University. Carbon and nitrogen isotope analyses were performed on the samples by the Stable Isotope Ratio Facility for Environmental Research at the University of Utah. For this analysis, the powdered samples were treated with 1mol/L hydrochloric acid (HCl) to remove the carbonate component. Thereafter, the samples were rinsed five times with distilled water followed by centrifugation, which was followed by drying the samples in an oven at a temperature of 50ºC. Finally, the dual C and N isotope (δ¹³Corg, δ¹⁵Norg) analyses were performed on these samples using the DELTA plus Advantage isotope ratio mass spectrometer configured through a CONFLO III interface for automated continuous-flow analysis. All values of δ¹³Corg and δ¹⁵Norg are reported in per mille (‰) relative to V-PDB and air, respectively. The measurement precision was assessed by a replicate of samples and internal lab standards and was determined to be ±0.15‰ for δ¹³C and ±0.2‰ for δ¹⁵N.

The role of detrital and biogenic sediments influx in the preservation of OM was analyzed using the geochemical proxies for detrital and biogenic sediments. The theoretical background for the geochemical proxying for detrital and biogenic sediments was discussed in Section 3.3.3. In this study, the stable isotope of Nitrogen (δ¹⁵Norg) was used as a proxy for paleoproductivity, whereas the stable isotope of Carbon (δ¹⁴Corg) was used as a proxy for the OM type (terrestrial vs. marine). The paleoredox condition was interpreted on the basis of different geochemical proxies, which are as follows: i) the absolute concentration of trace elements (TE) Mo; ii) the covariation pattern of TOC with Mo and U; iii) the slope of regression lines of TOC vs. the Mo crossplot; iv) the covariation pattern of the enrichment factor (EF) of U and the EF of Mo; and v) the degree of pyritization calculated from C-S-Fe (Carbon-Sulphur-Iron) systematics. These proxies have been used by various researchers for understanding the prevalent redox conditions in modern and ancient marine systems (Sageman et al., 2003; Algeo and Maynard, 2004; Rimmer et al., 2004; Tribovillard et al., 2006, 2012; Lash and Blood, 2014; Chen and Sharma, 2016). The EF of an element in each sample is calculated by comparing the Al-normalized trace element ratio to that of an average shale. In other words, the EF for element X (XEF) in a given sample is equivalent to the ratio (X/Al)sample/(X/Al)AS, where subscript AS refers to average shale (Wedepohl, 1971; Tribovillard et al., 2006). My study uses the nomenclature proposed by Tyson and Pearson (1991) to describe the redox conditions. According to this nomenclature, the oxic condition refers to 8.0-2.0 ml/l O₂ in water, the dysoxic condition refers to 2.0-0.2 ml/l O₂ in water, the suboxic condition refers to 0.2-0.0 ml/l O₂ in water, and the anoxic condition refers to 0.0 ml/l O₂ and 0 ml/l H₂S in water. Euxinic or anoxic-sulfidic water lacks O₂ and contains free H₂S (Raiswell and Berner, 1985). According to Tyson and Pearson (1991), the term “bottom water” refers to the water column, which is less than 1 meter above the sediment-water interface.
4.2.1 Proxies for paleoredox condition

Trace Element covariation

The theoretical background for the use of trace elements U and Mo for interpreting the paleoredox condition were discussed in Section 3.3.3. The trace metals Mo and U exhibit variability in an oxidation state, solubility, and/or change in host-phase as a function of the redox condition of the depositional environment. These redox-sensitive trace elements are more soluble and display a conservative behavior in oxic conditions but are less soluble in reducing conditions, which results in their authigenic enrichments in oxygen-depleted sedimentary facies. This makes these elements ideal proxies for evaluating redox conditions in paleomarine systems (Algeo and Maynard, 2004; Tribovillard et al., 2006). The concentration of these redox-proxying trace elements is very low in the continental crust, and they maintain a uniform concentration of seawater globally because of their long residence time. These trace elements are also present in low concentrations in plankton; therefore, their enrichment in marine sediments can be attributed to their authigenic uptake from seawater due to changes in paleoredox conditions. Furthermore, these elements are relatively immobile; therefore, their concentrations are generally not affected by diagenesis and thermal maturation (Algeo and Rowe, 2012).

In oxic conditions, the trace-metal Mo in seawater is present in the form of stable and unreactive molybdate ions (MoO$_4^{2-}$). Marine sediments accumulating in oxic environment have limited authigenic enrichment of Mo, and they exhibit typical detrital background values of Mo concentration, which range from 1-5 ppm (Zheng et al., 2000; McLennan, 2001; Morford et al., 2009). However, in reducing environments, in the presence of even very small amounts of dissolved HS$^-$, MoO$_4^{2-}$ ions become reactive and get transformed into a series of particle-reactive thiomolybdate ions (MoO$_4$S$_{4-x}$) (Helz et al., 1996; Zheng et al., 2000). Mo in this form is rapidly sequestered either by getting adsorbed in sulfurized organic matter or by forming a solid solution with Fe-S to get precipitated as authigenic sulfide minerals (Helz et al., 1996; Tribovillard et al., 2004). At higher levels of dissolved hydrogen sulfide in an euxinic condition, authigenic uptake and burial rate of Mo$_{auth}$ increases by two to three times (Scott and Lyons, 2012). Most of the Mo$_{auth}$ uptake occurs either along the sediment/water interface or within the pore water of the sediments (Zheng et al., 2000; Morford et al., 2009). Generally, low to moderate authigenic enrichment of Mo and its correlation with TOC indicates an anoxic environment of deposition, while very high enrichment of Mo indicates euxinic conditions with dissolved sulfide in water. However, along with the intensity of reducing conditions, authigenic Mo enrichment in sediment is also dependent on the aqueous concentration of Mo (source-ion availability) and the concentration of sedimentary organic matter (host-phase availability) (Algeo and Lyons, 2006; Algeo and Rowe, 2012). This relationship can be expressed as follows:
\[ [\text{Mo}]_{\text{sed}} \equiv [\text{TOC}]_{\text{sed}} \times [\text{Mo}]_{\text{aq}} \] (4.1)

\[ [\text{Mo}]_{\text{aq}} \equiv [\text{Mo}/\text{TOC}]_{\text{sed}}, \] (4.2)

where the subscripts \text{sed} and \text{aq} refer to the sediment and aqueous concentration of Mo, respectively. Based on this observation, Algeo and Lyons (2006) developed a method to understand the degree of basin restriction. Eq. (2) indicates that the ratio of Mo to TOC in the sediments is proportional to the concentration of aqueous Mo. Moreover, the concentration of aqueous Mo is dependent on the extent of deepwater renewal in the basin, which in turn is controlled by the degree of basin restriction and basin size. In restricted and silled basins with limited deepwater renewal, the uptake of Mo by sediment in a reducing environment decreases the aqueous concentration of Mo slowly. This condition results in a decrease in the rate of Mo enrichment in sediment over time, although the rate of OM accumulation may remain high due to the reducing condition, which thereby results in low \([\text{Mo}/\text{TOC}]_{\text{sed}}\]. However, in unrestricted open-marine basins, the aqueous concentration of Mo remains high due to strong deepwater renewal, and this results in high \([\text{Mo}/\text{TOC}]_{\text{sed}}\]. Thus, the positive covariation pattern between Mo and TOC concentration, specifically the slope \(m\) of the regression line in the Mo-TOC crossplot, exhibits a systematic relationship with the degree of basin restriction and deepwater renewal (Algeo and Lyons, 2006; Algeo and Rowe, 2012). Algeo and Lyons (2006) used this concept in studying modern silled basins at the Black Sea, Framvaren Fjord, Cariaco Basin and Saanich Inlet, and observed that an \(m\) value less than 10 is the characteristic of strong hydrographic restriction (Black Sea), whereas \(m\) between 10-25 represents moderate restriction (Framvaren Fjord and Cariaco Basin), and \(m\) greater than 25 represents weak restriction (Saanich Inlet). This concept was applied to various shale formations to study the ancient silled basins of the Devonian-Carboniferous time (Algeo et al., 2007). The degree of basin restriction affects the deepwater renewal time in the basin. Deepwater renewal time is dependent on \([\text{Mo}]_{\text{aq}}\), which in turn is dependent on the authigenic uptake of Mo by sediment. Algeo and Lyons (2006) used this background and estimated the deepwater renewal time from Mo flux for modern anoxic basins.

Trace-metal U is present mainly as a soluble U(VI) in oxic-suboxic conditions and is reduced to less soluble U(IV) in oxygen-depleted conditions. U concentration in average shale is around 3.7 ppm (Wedepohl, 1991). Reduction of U commences at the Fe (II)-Fe(III) redox boundary and the U enrichment is controlled by microbially-mediated Fe redox reactions rather than by the presence of HS\(^-\) (Zheng et al., 2002). The uptake of a reduced state of \(U_{\text{auth}}\) by the sediment primarily occurs through the formation of organic metal ligands, or precipitation of crystalline uraninite or a metastable precursor to uraninite (Klinkhammer and Palmer, 1991; Zheng et al., 2002). Thus, in comparison to \(M_{\text{auth}}\), \(U_{\text{auth}}\) enrichment in marine sediment starts at relatively less reducing conditions and at shallower depths within the sediment column (Morford et al., 2009).
These differences in geochemical behavior between Mo and U result in different relative enrichment of Mo and U for specific redox conditions. Algeo and Tribovillard (2009) applied this concept in modern marine settings and identified three unique covariation patterns of the EFs of U-Mo, which can be associated with different redox conditions and the processes specific to marine settings. The authors also observed that along with the EF covariation patterns of U and Mo, the ($\text{Mo}/\text{U}_{\text{auth}}$) ratio of the sediment, when compared to the ($\text{Mo}/\text{U}_{\text{aq}}$) molar ratio in seawater (SW) of $\sim$7.5-7.9, has the potential to provide new insights regarding the paleoceanography of organic-rich depositional systems. The first covariation pattern is characteristic of sediments from an unrestricted marine setting in the eastern tropical Pacific Ocean; it exhibits greater relative $\text{U}_{\text{auth}}$ enrichment but low or no $\text{Mo}_{\text{auth}}$ at low EFs ($\text{Mo}/\text{U}_{\text{auth}}$ $\sim$0.1-0.3×SW) and indicates a suboxic condition. However, for progressively greater relative $\text{Mo}_{\text{auth}}$ enrichment at high EFs ($\text{Mo}_{\text{auth}}$:$\text{U}_{\text{auth}}$ ratios >1×SW), the condition is increasingly more anoxic to euxinic in the water column. The second pattern is distinctive of sediments from the semi-restricted setting of the Cariaco Basin, which exhibits strong $\text{Mo}_{\text{auth}}$ relative to $\text{U}_{\text{auth}}$ enrichment at all EFs ($\text{Mo}_{\text{auth}}$:$\text{U}_{\text{auth}}$ ratios $>>$1 × SW, 3-10 × SW). This highlights the role of the Mn-oxyhydroxide particulate shuttle, which helps to transfer only the molybdate ions (not U ions) from the water column to the sediment-water interface and thereby enhances the relative enrichment of $\text{Mo}_{\text{auth}}$. The third covariation pattern is characteristic of sediments deposited below the pycnocline in the restricted and euxinic setting of the modern Black Sea. These sediments exhibit higher relative $\text{Mo}_{\text{auth}}$ enrichment than $\text{U}_{\text{auth}}$ for samples with lesser degrees of total enrichment ($\text{Mo}_{\text{auth}}$:$\text{U}_{\text{auth}}$ ratios $\sim$1 × SW) and progressively higher enrichment of $\text{U}_{\text{auth}}$ relative to $\text{Mo}_{\text{auth}}$ as total enrichment increases; this indicates the evolution of sub-pycnoclinal watermass chemistry due to sustained euxinia, which draws down the availability of aqueous Mo (source-ion) concentration with time (Algeo and Lyons, 2006; Algeo and Tribovillard, 2009). The validity of this U-Mo covariation pattern-based approach for analyzing the paleoredox conditions and processes during deposition of organic-rich shales were discussed by Algeo and Tribovillard (2009), Tribovillard et al. (2012), and Lash and Blood (2014).

4.2.2 C-S-Fe relationship

C-S-Fe systematics are used to differentiate between the varying redox conditions during the deposition of organic-rich shales. Dean and Arthur (1989), Arthur and Sageman (1994) and Rimmer et al. (2004) suggested that ternary Fe-S-C diagrams can be used to estimate Degree of Pyritization (DOP). A typical Fe-S-C ternary diagram used for this purpose is shown in Figure 4.2. Normal marine oxygenated samples are plotted along a line equivalent to a S/C ratio of 0.4 on this ternary diagram, whereas samples in which all iron is reactive and associated with pyritic sulfur (DOP=1), are plotted along the line having an S/Fe ratio of 1.15 (based on the stoichiometry of pyrite) that intercepts the Fe-S axis at 0.54. DOP lines and fields representing the dysoxic/suboxic and the anoxic conditions are also shown.
Carbon vs. Sulfur ($C_{org}$-$S_{pyr}$) crossplots are also used to distinguish normal marine and anoxic-euxinic environments (Rimmer et al., 2004). In $C_{org}$-$S_{pyr}$ crossplot, a strong positive correlation between these two variables is observed for normal marine sediments, which had accumulated below oxygenated water and the trend line has a zero intercept in the crossplot (Raiswell and Berner, 1985). This is because pyrite formation in normal marine sediments is controlled by the availability of OM. However, for euxinic sediments, pyrite formation is primarily controlled by the availability of reactive iron; therefore, the $C_{org}$-$S_{pyr}$ crossplot shows a non-zero sulfur intercept for the trend line, or it may show no correlation (Raiswell and Berner, 1985). Similarly, DOP, which is the ratio of pyritic iron to reactive iron (pyritic iron plus HCl soluble iron), is considered to be a reliable indicator for depositional redox conditions, especially in environments that are not limited by reactive Fe (Raiswell et al., 1988; Jones and Manning, 1994). DOP values less than 0.42 indicate normal marine oxygenated conditions; DOP values between 0.42 and 0.75 indicate dysoxic to anoxic conditions in a less stratified water column; and DOP values greater than 0.75 indicate anoxic conditions with strongly a stratified water column (Raiswell et al., 1988; Hatch and Leventhal, 1992; Algeo and Maynard, 2004; Rimmer et al., 2004). Uniformly high DOP values are typically interpreted to indicate deposition under euxinic conditions and suggest that nearly all of the available reactive Fe was utilized in the formation of pyrite (Raiswell et al., 1988; Lyons and Berner, 1992).

Figure 4.2: Schematic S-Fe-C ternary diagram showing the different degrees of pyritization (DOP) regions for suboxic, anoxic and euxinic conditions (modified from Rimmer et al., 2004).
4.2.3 Proxy for Paleoproductivity and Organic Matter type

In our current study, δ¹⁵N<sub>org</sub> was used as a proxy to assess the paleoproductivity in the UBS. Nitrogen (N) in the form of nitrate is an essential biolimiting nutrient for marine productivity. Phytoplanktons preferentially incorporate the lighter isotope of nitrogen (N<sup>14</sup>), which results in a relative enrichment of the heavier isotope of nitrogen (N<sup>15</sup>) in water (Marchitto, 2007). Therefore, in regions where the nitrate supply is heavily utilized, the surface ocean isotopic enrichment can be relatively large, which results in heavier δ¹⁵N<sub>org</sub> (Altabet and Francois, 1994). OM that has a light δ¹⁵N<sub>org</sub> value reflects conditions of high nutrient supply to the surface water relative to biological consumption, which indicates eutrophic conditions. Heavy δ¹⁵N values reflect a more limited supply of nitrate relative to consumption, which is indicative of oligotrophic conditions. Therefore, lighter δ¹⁵N values reflect an increase in the availability of nutrients, which indicates high primary productivity at the time of deposition. Heavier δ¹⁵N<sub>org</sub> values reflect a decrease in availability of nutrients and thus indicate reduced primary productivity at the time of deposition (Altabet and Francois, 1994; Altabet and Francois, 1994; Montoya, 1994). Caplan and Bustin (1998) and Smith and Bustin (1998) used δ¹⁵N<sub>org</sub> as a proxy to predict relative nutrient utilization and paleoproductivity of the organic-rich shales from the Bakken and Exshaw Formations. A stable isotope of organic carbon (δ¹³C<sub>org</sub>) was used in their study as a proxy to determine changes in organic matter sources. During the Devonian period, δ¹³C<sub>org</sub> was found to be about −30.5‰ for marine OM and −25‰ to −26‰ for the terrestrial organic matter, indicating marine organic matter is lighter in δ¹³C<sub>org</sub> (Maynard, 1981; Jaminski et al., 1998). My study also used a modified Van Krevelen diagram (hydrogen index(HI) vs. Tmax) to determine the OM type.

4.3 Results and Interpretation

This section presents the various experiments performed, their interpretation, and our results. I first present the chemostratigraphy, core description and petrographic results, and elaborate these based on the methods outlined in Section 3.3. I then discuss the results for TOC and OM types, obtained from SRA and oxygen stable isotope experiments. The effect of dilution on the organic richness of the UBS based elemental proxy is then described, and the results for various paleoredox proxying methods are interpreted. Finally, the paleoproductivity during the UBS deposition of is interpreted from the nitrogen stable isotope data.

4.3.1 Chemostratigraphy, Core description, and Petrography

Table 4.1 lists characteristic differences between the chemostratigraphic sub-units of the UBS in terms of vertical distribution of lithofacies, chemostratigraphic profiles of both detrital proxying elements (Si, Al, K, Ti, Ca, Zr/Rb) and redox-sensitive trace elements (Mo and U). Section 3.4.5 presented the
identification in well RT and 16 other wells of two chemostratigraphic UBS units: Unit-1 (lower) and Unit-2 (upper), and two sub-units of Unit-1 namely, 1a and 1b. In this chapter, I present a close examination of the trends in redox-sensitive trace elements for well RT, which helped me to further divide Unit-2 into sub-units 2a and 2b. In this study, it was observed that Mo and U had limited enrichment in sub-units 2a, whereas moderate to the high enrichment of these two redox-sensitive trace elements were observed in sub-unit 2b. The vertical distribution of the different lithofacies is shown in the core description of well RT presented in Figure 4.3. Here, the facies classification scheme and description methodology for the UBS is consistent with those of Section 3.3.4. As discussed in Chapter-3, the UBS consists of six different facies; however, in well RT, it primarily consists of only three facies: F1, F2, and F4. The characteristics and sedimentary processes of these facies were discussed in Section 3.4.1.

Table 4.1: The characteristic differences between sub-units 1a, 1b, 2a and 2b in terms of the biogenic, detrital, grain size proxy, redox proxy, and facies.

<table>
<thead>
<tr>
<th>Sub-units</th>
<th>Biogenic/Detrital/Grainsize proxy</th>
<th>Redox proxy</th>
<th>Facies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>High Si and low Al, K, and Ti, Ca and Zr/Rb ratios compared to those in Unit-2</td>
<td>Highest Mo and U content</td>
<td>Dominated by massive to very finely laminated silt-bearing mudstone (F2) followed by siliceous mudstone (F1)</td>
</tr>
<tr>
<td>1b</td>
<td>High Mo and U, comparatively less than that in 1a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>Low Si and high Al, K, and Ti Ca and Zr/Rb ratios compared to those in Unit-2</td>
<td>Limited enrichment of Mo and U</td>
<td>Macrofossil-bearing silt-rich mudstone (F4)</td>
</tr>
<tr>
<td>2b</td>
<td>Moderate enrichment of Mo and U</td>
<td></td>
<td>Macrofossil-bearing silt-rich mudstone (F4) and massive to very finely laminated silt-bearing mudstone (F2)</td>
</tr>
</tbody>
</table>

### 4.3.2 TOC, OM Characteristics, and Type

Table 4.2 lists the SRA-derived organic geochemistry results for four chemostratigraphic UBS sub-units of the UBS found in Well RT. These results and the TOC profile is shown in Figure 4.3, which indicate that TOC varies considerably among the different UBS sub-units in Well RT. For example, in sub-unit 1a, average TOC is about 12.9 wt.%, while in sub-unit 2a, average TOC is about 5.0 wt.%. The effect of thermal maturation of OM on measured TOC ($\text{TOC}_{\text{meas}}$) was corrected using the method described by Jarvie (2012), and thereby original TOC ($\text{TOC}_{\text{org}}$) was calculated. Most of our analyses which require TOC values were performed using $\text{TOC}_{\text{org}}$. Jin (2014) suggested that the onset of hydrocarbon generation in Bakken shales is marked by $T_{\text{max}}$ of 425°C, while $T_{\text{max}}$ of 435°C marks the peak of hydrocarbon generation, with $T_{\text{max}}$ of 445°C being the last stage of the oil window. Therefore, as the UBS $T_{\text{max}}$ in Well RT is between 440°C-448°C (average 445°C), the location of well RT is in the oil maturity window.
Figure 4.3: Integrated profile of UBS in core Roberts Trust 1-13H (RT) showing different chemostratigraphic units of UBS, which were distinguished based on the vertical distribution of lithofacies, detrital and biogenic proxying elements of Si, Al, K, Ti, Zr/Rb ratio, Ca and redox-proxying elements of Mo and U. Characteristics of each chemostratigraphic sub-unit are summarized in Table 4.1. The profile of TOC, stable isotope of $\delta^{15}N_{\text{org}}$, which is a proxy for the paleoproductivity, and stable isotope of $\delta^{13}C_{\text{org}}$, which acts as the proxy for the OM type, are also shown. $\text{TOC}_{\text{SRA}}$ represents TOC measured from source rock analysis (SRA) and $\text{TOC}_{\text{org}}$ represents original TOC calculated from $\text{TOC}_{\text{SRA}}$. The basis for identifying the Maximum flooding surface (MFS) was described in Section 3.5.5.
Table 4.2: Organic geochemistry results for different chemostratigraphic units of Well RT as derived from the Source Rock Analysis (SRA). Legend: μ: mean; R: Range; σ: Standard deviation; HI: Hydrogen Index; OI: Oxygen Index; TOC<sub>SRA</sub>: SRA measured TOC; TOC<sub>org</sub>: Original TOC calculated TOC<sub>SRA</sub>.

<table>
<thead>
<tr>
<th>Units</th>
<th>TOC&lt;sub&gt;SRA&lt;/sub&gt; (wt. %)</th>
<th>R</th>
<th>μ</th>
<th>σ</th>
<th>HI (mg HC/g OC)</th>
<th>R</th>
<th>μ</th>
<th>σ</th>
<th>OI (mg HC/g OC)</th>
<th>R</th>
<th>μ</th>
<th>σ</th>
<th>TOC&lt;sub&gt;org&lt;/sub&gt; (wt. %)</th>
<th>R</th>
<th>μ</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>10-17</td>
<td>12.9</td>
<td>1.9</td>
<td>248-350</td>
<td>312</td>
<td>26</td>
<td>1-3</td>
<td>2.0</td>
<td>0.6</td>
<td>13-20</td>
<td>16.2</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>9-14</td>
<td>10.8</td>
<td>1.7</td>
<td>249-326</td>
<td>273</td>
<td>26</td>
<td>1-4</td>
<td>2.2</td>
<td>0.7</td>
<td>13-17</td>
<td>14.2</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>3-9</td>
<td>5.0</td>
<td>2.1</td>
<td>129-249</td>
<td>184</td>
<td>41</td>
<td>5-10</td>
<td>7.6</td>
<td>2.5</td>
<td>3-11</td>
<td>5.5</td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>6-12</td>
<td>8.7</td>
<td>2.5</td>
<td>208-297</td>
<td>254</td>
<td>33</td>
<td>2-6</td>
<td>4.3</td>
<td>1.3</td>
<td>8-16</td>
<td>11.1</td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The TOC data for RT well were plotted on the modified Van Krevelen diagram shown in Figure 4.4. Both Table 4.2 and Figure 4.4 show that for sub-unit 2a, the average value of HI (184) is considerably lower than those in other sub-units (HI: 312-254). Such variation in HI can be explained either by variation in kerogen type (marine vs. terrestrial) or an alteration in thermal maturation (Tissot and Welte, 1984). However, in Well RT, T<sub>max</sub> varies in a narrow range (440ºC to 448ºC), which cannot justify the observed degree variation in HI. Therefore, the comparatively low average HI observed in sub-unit 2a suggests that this sub-unit consists of a different kerogen type. Figure 4.4 also shows that sub-units 1a, 1b, and 2b primarily consist of Type II-III OM; however, 2a has a greater amount of Type III (terrestrial) OM along with Type II OM. Jin (2014) suggested that the UBS primarily consisted of Type II and II-III kerogens near the basin depocenter, while inputs of type III OM are present exclusively along the eastern margins of the basin. However, type III (terrestrial) OM has not been reported for the UBS from the basin depocenter. For example, Stasiuk (1993), based on organic petrography, concluded that low maturity Bakken shales from Canada mainly consist of: i) bituminite, comprised of dark brown fluorescent to non-fluorescent amorphous granular groundmass, which forms micro-laminae, and ii) unicellular algae (alginites), which showed textures indicating partially degraded bituminite. Therefore, the author suggested that the Bakken shales primarily consisted of Type II kerogen. Hackley and Cardott (2016) studied matured UBS samples from the southern edge of the UBS in the Billings Nose area and observed that the UBS primarily consisted of non-fluorescent groundmass of solid bitumen with some fine-grained inertinite (wind-blown char).

Box and whisker plot in Figure 4.5 shows the result for the stable isotope analysis for δ<sup>13</sup>C<sub>org</sub> for the various chemostratigraphic sub-units of UBS in Well RT. Figure 4.3 shows the profile of δ<sup>13</sup>C<sub>org</sub> in the UBS interval, which demonstrates its variation among the different chemostratigraphic sub-units of the UBS in Well RT. The average δ<sup>13</sup>C<sub>org</sub> levels in sub-units 1a and 1b are -30.1‰ and -29.7‰; this is close to the average δ<sup>13</sup>C<sub>org</sub> of -30‰ observed in Type II OM (marine) in the Late Devonian and Early Mississippian. This suggests that the OM in sub-units 1a and 1b are of marine origin. The average δ<sup>13</sup>C<sub>org</sub> of sub-unit 2a is -25.4‰, which suggests sub-unit 2a is dominated by Type III OM (terrestrial), as the terrestrial OM have slightly heavier δ<sup>13</sup>C<sub>org</sub> (-25‰ to -26 ‰). The average δ<sup>13</sup>C<sub>org</sub> of sub-unit 2b is -28.1‰, which suggests that
sub-unit 2b has Type II-III OM. Therefore, the results of the stable isotope of C are consistent with the SRA data and further confirm that sub-unit 1a and 1b consist of marine (Type II) OM, while the OM in sub-unit 2a is mostly of terrestrial origin.

Figure 4.4: Samples from Well RT plotted on the modified Van Krevelen diagram showing sub-unit 1a, 1b and 2b predominantly consist of type II-III organic matter, while sub-unit 2a has a higher proportion of type III organic matter.

4.3.3 Effect of Detrital and Biogenic Sediment Influx on OM Richness

Principal component analysis (PCA) presented in Section 3.4.2 suggested that Al, K, and Ti in the UBS are of detrital origin; therefore, in our current study, the concentration of these elemental was used to study the effect of dilution by detrital influx on OM richness in the UBS. Figure 4.6 shows Al and K have strong positive covariance with Ti, which indicates that Al and K has a detrital origin in the UBS for both Unit-1 and Unit-2. Moreover, both Al and K can be used as proxies for detrital illite clay content in the
UBS, as described in Section 3.4.1. As was shown in Figure 4.3, Unit-2 has a higher concentration of the detrital proxying elements Al, K and Ti compared to those in Unit-1. However, the concentrations of Al, K and Ti in sub-units 1a and 1b do not vary considerably; therefore, these sub-units were considered as one single unit (Unit-1) for the purposes of analyzing the effect of detrital sediment influx on OM richness. Likewise, sub-units 2a and 2b were considered as one single unit (Unit-2) for this analysis.

As shown in crossplots between TOC with Al and K for Unit-1 in Figure 4.6 Al and K show no covariance with TOC, which indicates that the influx of clay did not affect OM richness in Unit-1. As Al and K do not have negative correlation in their respective crossplots with $TOC_{org}$, and according to Ibach (1982) and Werne et al. (2002), this suggests that the influx of clay did not dilute OM. However, as shown in Figure 4.6, $TOC_{org}$ correlates positively with both Al and K for Unit-2, which, according to Rimmer et al. (2004) and Passey et al. (2010), indicates that an influx of clay helped in preservation of organic matter as it was buried quickly. Alternatively, a clay surface area may also have played a role in OM preservation because this would provide a key site for OM adsorption and accumulation in organic-rich sediments (Kennedy et al., 2002).

Figure 4.3 shows that Unit-2 has a higher concentration of Ca than that in Unit-1, which is dominated by macrofossil-bearing silt-rich mudstone (F4). As discussed in Section 3.4.1, core description...
and the petrographic study confirmed the presence of articulate and disarticulated shells and detrital dolomites in facies F4. Therefore, Ca was used as a proxy to determine the effect of silt-sized detrital dolomite and bioclasts in the OM accumulation. As shown in Figure 4.7, the crossplot between TOC and Ca does not have any correlation for Unit-1, which suggests that the influx of carbonate sediments was minimum and had no influence in OM accumulation. However, TOC and Ca have a negative correlation for Unit-2, indicating an influx of silt-sized detrital dolomite and the presence of shell fragments, which has a detrimental effect on the preservation of OM.

Figure 4.6: Cross plot between Ti and Al show a positive linear covariance for Unit-1, which indicates that Al has a detrital origin. (b) Crossplot between Ti and K show a positive linear covariance for Unit-1, which indicates that K has a detrital origin, and for this unit, K can be used as a proxy for detrital illite clay. (c) Crossplot between Al and TOC_{org} show weak positive covariance, which indicates that influx of clay did not result in dilution of organic matter as Al is a proxy for detrital clay minerals in UBS (Section 3.4.2, Chapter-3). (d) Crossplot between K and TOC_{org} show no covariance, which confirms that influx of clay did not result in dilution of organic matter as K is a proxy for detrital clay minerals in UBS (Section 3.4.2, Chapter-3). (e) Crossplot between Ti and Al show a positive linear covariance for Unit-2, which indicates that Al has a detrital origin in this unit also. (f) Crossplot between Ti and K show a positive linear covariance for Unit-2, which indicates that K has a detrital origin, and for this unit, K can be used as a proxy for detrital illite clay. (g) Crossplot between Al and TOC_{org} for Unit-2 show a positive linear covariance, which indicates that influx of clay helped in organic matter preservation in Unit-2 as Al is used as proxies for detrital clay minerals (h) Crossplot between K and TOC_{org} for Unit-2 show a positive linear covariance, which confirms that influx of clay helped in organic matter preservation in Unit-2.
The principal component analysis (PCA) described in Section 3.4.2 suggested that a major fraction of Si in UBS is of biogenic or authigenic origin; therefore, I used Si concentration to study the effect of dilution by biogenic sediments on OM richness. As shown in Figure 4.3, Unit-1 has a higher concentration of Si in comparison to Unit-2. For Unit-1, Si shows no correlation with detrital proxying elements Al and Ti (Figure 4.8), which indicates that a major fraction of Si in Unit-1 is associated with biogenic and authigenic sources. Moreover, Figure 4.3 shows that Unit-1 consists of radiolarian-rich siliceous mudstone (F1), which confirms the presence of biogenic and authigenic Si in this unit. However, Si shows a negative correlation with $TOC_{org}$ for Unit-1 (Figure 4.8c), which indicates that the biogenic silica associated with radiolarians had a dilution effect in the accumulation of OM. The negative correlation between the detrital clay proxying elements of Al and Ti with biogenic Si for Unit-1 samples indicates that biogenic silica also had a dilution effect on the detrital clay influx. However, for Unit-2, Si correlates positively with Al and Ti, which indicates that the Si of Unit-2 has detrital origin. This is also supported by the absence of siliceous mudstone (F1) in Unit-2 (Figure 4.3). The Zr/Rb ratio, which is a proxy for the grain size of detrital sediment, increases in Unit-2, suggesting an increase in the coarser or silt-sized fraction of the detrital sediments in Unit-2. Therefore, for Unit 2, the absence of siliceous mudstone (F1) and an increase in the Zr/Rb ratio indicate that much of the Si in Unit-2 is associated with silt-sized quartz grains. This is further supported by the presence of silt content in macrofossil-bearing silt-rich mudstone (F4), which is predominantly present in Unit-2 (Figure 4.3). Therefore, Si was used as proxy a for silt-sized siliciclastic sediments for Unit-2. The crossplot of Si and $TOC_{org}$ for Unit-2 samples shows a negative correlation, which indicates that siliciclastic silt influx had a dilution effect during OM accumulation in Unit-2.
Figure 4.8: For Unit-1, crossplots between (a) Si and Al, and (b) Si and Ti, showing no covariance, which indicates in Unit-1 has a considerable proportion of Si is associated with the radiolarians in siliceous mudstone (F1). It also indicates that biogenic silica had a dilution effect on the detrital clay. (c) Crossplot between Si and $TOC_{org}$ for Unit-1 show a negative correlation indicating influx of biogenic Si had resulted in the dilution of organic matter. For Unit-2, crossplot between (d) Si and Al (e) Si and Ti show positive correlation indicating Si in Unit-2 has detrital origin. (f) Crossplot between Si and $TOC_{org}$ for Unit-2 showing a negative correlation, which indicates influx of detrital Si associated with silt-sized sediment had resulted in the dilution of organic matter.

4.3.4 Redox Proxy: C-S-Fe relationship

Figure 4.9a shows that the crossplot between total Fe ($Fe_T$) and total S ($S_T$) shows a strong positive correlation for all four UBS sub-units, indicating that Fe and S in the UBS are associated with pyrite. However, Unit-1 samples plot approximately on the DOP=1 or the stochiometric pyrite line, while Unit-2 Fe vs. S plots below the stochiometric pyrite line. This indicates pyrite formation in Unit-1 was not limited by the availability of Fe or S, while for Unit-2, pyrite formation was sulfur-limited. The $TOC_{org}$ vs. S plot in Figure 4.9b shows that all four sub-units have a positive covariance and the regression fit has a non-zero intercept, indicating that UBS deposition took place in reducing conditions and not in the normal oxygenated marine condition. However, the following trends are also visible from the plot in Figure 4.9b: 1) for Unit-1, $TOC_{org} > 12.5$ wt.% and total S varies between 2-4 wt.%; and 2) for Unit-2, $TOC_{org} < 12.5$ wt% and S vary between 0.5-2 wt.%. The trend-line for Unit-1 has a higher slope than that of Unit-2,
which indicates that sulphide formation increased substantially after a threshold TOC value of around 12.5%. Therefore, for Unit-1, sulfate reduction increased rapidly due to the higher availability of OM for degradation. This in turn increased the sulfide concentrations in the bottom waters, which resulted in a persistent euxinic condition in Unit-1. However, the trend-line for Unit-2 samples suggests less OM degradation has resulted in comparatively less sulfate reduction during the deposition of this unit, which gave rise to a less reducing condition for Unit-2.

Figure 4.9: (a) Crossplot between total iron (Fe<sub>T</sub>) and total sulfur (S<sub>T</sub>) for different chemostratigraphic sub-units of UBS is shown. S<sub>T</sub>/Fe<sub>T</sub> stoichiometric ratio of 1.15 represents pyrite shown by the black solid line in the plot, and the equivalent degree of pyritization (DOP) is equal to 1 for this line, which indicates the euxinic condition. The green broken line represents regression fit for Unit-1 and black broken line represents the regression fit for Unit-2. Unit-1 plots close to DOP=1 line indicating that most of the iron in Unit-1 is associated with pyrite and this unit was deposited in euxinic condition. Whereas Unit-2 plots below the DOP=1, which indicates that supply of iron was more compared to sulfur and pyrite formation was sulfur limited. This indicated Unit-2 was deposited at comparatively less reducing conditions than Unit-1. (b) Crossplot between TOC<sub>org</sub> and total sulfur (S<sub>T</sub>) for the different chemostratigraphic units of UBS is shown. Solid line represents S and C trend for oxygenated normal marine conditions during organic matter deposited. Broken lines represent linear regression data for Unit-1 and Unit-2. The non-zero intercept of the linear regression lines for both Unit-1 and Unit-2 in the crossplot indicates that their deposition has taken place in reducing condition and not in oxygenated condition.

Figure 4.10 shows the overlay of the UBS samples on a Fe-S-TOC<sub>org</sub> ternary diagram. This ternary diagram was used for DOP evaluation, which provides further clarity on the paleoredox condition of various sub-units of the UBS. Figure 4.10 shows that Unit-1 plots along a line that intersects the Fe-S axis at about 0.52, which is close to 0.54, where the DOP=1 line intersects the Fe-S axis. This suggests Unit-1 was deposited in an euxinic paleoredox condition in a strongly stratified water column, as described in Section 4.3.4. Moreover, an intersect of 0.52 at the Fe-S axis is equivalent to a DOP of 0.96, which suggests that
96% of the Fe in Unit-1 is associated with pyrite. Samples for sub-unit 2a plots along a line that intersects the Fe-S axis at approximately 0.30, which is equivalent to a DOP of 0.56; thus 56% of the iron in this sub-unit is associated with pyrite. However, sub-unit 2b plots between DOPs of 0.56 and 0.75, which indicates that the paleoredox condition fluctuated from suboxic to anoxic with an increasing intensity of anoxia compared to that observed for sub-unit 2a.

Figure 4.10: Fe-S-TOC$_{org}$ ternary diagram for UBS samples from well RT showing sub-unit 1a and 1b mostly plot along DOP≈0.96, which indicates a strongly euxinic condition for these sub-units. Sub-unit 2a plots along DOP≈0.56 suggesting suboxic condition for this sub-unit, while sub-unit 2b plots between DOP of 0.56-0.75, suggesting for 2b the paleoredox condition fluctuated from suboxic to anoxic with increasing intensity of anoxia compared to that in sub-unit 2a.

4.3.5 TOC-Trace Elements Relationship

Tribovillard et al. (2006) demonstrated that the covariance patterns between the concentration of redox-sensitive trace elements (TE) with TOC$_{org}$ can be used as a proxy to distinguish between various paleo-redox conditions. The redox-sensitive TE, Mo and U, used in this study show an overall positive correlation with TOC$_{org}$ in the scatterplots, as shown in Figure 4.11. However, this figure also shows the following three group of samples associated with the covariance pattern between TOC$_{org}$ and Mo, and TOC$_{org}$ and U: 1) Group 1 is characterized by TOC$_{org}$<5 wt.%, no enrichment of Mo and limited enrichment of U; 2) Group 2 has TOC$_{org}$ between 5-12.5 wt.%, and Mo and U are moderately enriched and show a good linear correlations with TOC$_{org}$; 3) Group 3 has TOC$_{org}$>12.5 wt.%, and shows highly
enriched Mo and U concentrations, which increase exponentially with increase in TOC$_{org}$. Figure 4.11c (modified from Tribovillard et al., 2006) shows the expected pattern of relative enrichment of Mo and U at suboxic, anoxic and euxinic conditions. Therefore, comparing Figure 4.11a, b with Figure 4.11c helped in distinguishing between the different redox conditions for UBS sub-units.

Figure 4.11: Crossplot between (a) TOC$_{org}$ vs Mo; and (b) TOC$_{org}$ vs U showing three distinct covariation patterns. (c) Chart showing the expected pattern of relative enrichment of Mo and U at suboxic, anoxic and euxinic conditions (modified from Tribovillard et al., 2006), which suggest in suboxic condition, TOC$_{org}$ < 5 wt.%; Mo has no enrichment while U shows limited enrichment. In anoxic condition, 5 < TOC$_{org}$ < 12.5 wt.%, both Mo and U shows moderate enrichment and has a good linear covariance pattern with TOC$_{org}$. In euxinic condition, TOC$_{org}$ > 12.5 wt.%, concentration of Mo and U increases exponentially and shows poor correlation with TOC$_{org}$.

As discussed in Section in 4.3.5, Mo enrichment starts only in the presence of dissolved HS$^-$ or a suboxic paleoredox condition. However, in the suboxic paleoredox condition, limited enrichment of U can take place as it does not require the dissolved of HS$^-$ to start the enrichment process. Therefore, during the
deposition of Group 1 samples, the paleoredox condition was suboxic, which explains no enrichment of Mo but the limited enrichment of U for these samples. Figure 4.11 shows that Group 1 consists of samples from the upper interval of sub-unit 2a, which suggests for 2a close to the 2b-2a boundary, the paleoredox condition was suboxic. For this interval of sub-unit 2a, Mo ranges from 2-6 ppm, which is close to the background levels of 1-5 ppm found in average shale (McLennan, 2001). These observations suggest that the upper sub-unit 2a was deposited in a suboxic benthic condition and dissolved sulfide was absent even in the pore water below the sediment-water interface.

For Group 2 samples, the moderate increase in Mo and U concentrations suggests that the paleoredox conditions were comparatively more reducing than those of Group 1 samples due to an increase in the dissolved HS\(^-\) concentration. Therefore, Group 2 samples were deposited in anoxic paleoredox conditions. Mo and U show good linear correlation with TOC\(_{org}\), as their uptake is dependent on the availability of suitable organic matter (Tribovillard et al., 2006). Based on this analysis, it was interpreted that the threshold 5 wt.% TOC\(_{org}\) is the boundary between the suboxic (Group 1) and anoxic (Group 2) conditions for deposition of the UBS. Figure 4.11 shows that Group 2 is dominated by samples from sub-unit 2b and the lower interval of sub-unit 2a, which suggests these two group of samples were also deposited in anoxic conditions. The bulk concentration of Mo for sub-unit 2b varies between 9-200 ppm, and according to Scott and Lyons (2012), this suggests predominantly anoxic conditions with either an intermittent euxinia or an increase in the degree of restriction in the basin. Lower sub-unit 2a samples (near the 1b-2a boundary) were also deposited in anoxic conditions; however, these sub-unit 2a samples have bulk Mo concentrations between 5-24 ppm, which are higher than the Mo concentration in average shale (~1.3 ppm). Scott and Lyons (2012) suggested that an Mo enrichment between the crustal average of 1-2 ppm (Wedepohl, 1991) and 25 ppm indicates the presence of dissolved HS\(^-\) that is restricted within the pore water; this suggests the euxinic conditions existed only below the sediment-water interface. This suggests that deposition of sub-unit 2a started in an environment where the benthic redox conditions along the sediment-water interface may have remained suboxic to anoxic, while euxinic conditions existed only within the pore water below the sediment-water interface.

For Group 3, both Mo and U show exponential increase in concentrations and their correlation with TOC\(_{org}\) disappears. Exponential enrichment of Mo is explained by the authigenic uptake and 2-3 times increased burial rate of Mo along with the sulfide minerals, which is associated with very high dissolved HS\(^-\) concentration (Scott and Lyons, 2012). High dissolved HS\(^-\) concentration indicates a euxinic paleoredox condition during the deposition for Group 3 samples. Mo resides primarily in pyrite, which results in a weak covariance of Mo with TOC\(_{org}\) (Tribovillard et al., 2004). This explains the poor covariance between Mo and TOC\(_{org}\) for the Group 3 samples in Figure 4.11. In euxinic conditions, U
resides in authigenic uptake consisting of metal sulfides and oxyhydroxides rather in the OM hosts, which explains the poor correlation between U with $TOC_{org}$. Therefore, the threshold $TOC_{org}$ of 12.5 wt.% marks the limit between anoxic and euxinic conditions for the deposition of UBS near Well RT in Williston Basin. Figure 4.11 shows that Group 3 is dominated by sub-units 1a and 1b, which indicates that these two sub-units were deposited in an euxinic condition. The bulk concentration of Mo for these sub-units varies between 100-400 ppm. Bulk concentration of Mo more than 100 ppm suggests the presence of dissolved hydrogen sulfide in the water column throughout the year (Scott and Lyons, 2012). This further substantiates the postulation of persistent euxinic conditions above the sediment-water interface for sub-units 1a and 1b.

4.3.6 EF-Mo vs. EF-U relationship

Enrichment factors (EF) of U and Mo for the chemostratigraphic sub-units of UBS exhibit three different clusters in the U-EF vs. Mo-EF plot for Well RT (Figure 4.12). For the first cluster, which is dominated by the samples from Sub-units 1a and 1b, Mo-EF is 350-900 and U-EF is 70-150 (Figure 4.12). Most Sub-unit 1a and 1b samples plot in the zone representing sulfurized OM, which is an extension of the euxinic field characterized by a Mo/U ratio that is 1-3 times of that in modern seawater. The second cluster, which is dominated by samples from both 2a and 2b, exhibit U-EFs of 20-30 and Mo-EFs of 20-100. As shown in Figure 4.12, this cluster of 2a and 2b samples plot in the zone between the anoxic and euxinic fields characterized by a Mo/U ratio that is 0.3-1 times of that of modern seawater. The third and last cluster, which consists of samples from 2a, exhibit U-EFs of 10-20 and Mo-EFs of 3-10. As shown in Figure 4.12, this cluster of 2a samples plot in the zone between suboxic and anoxic fields characterized by a Mo/U ratio that is 0.1-0.3 times of that of modern seawater. The crossplot between EF-U and EF-Mo (Figure 4.12) shows that organic matter in Sub-units 1a and 1b have been sulfurized. Similar, trend is shown by sulfurized Late Jurassic Kashpir oil shales of the Russian Platform (Tribovillard et al., 2012). Sulfurization of organic matter is described as the incorporation of reduced inorganic sulfur species or polysulfides into organic matter by reaction with functionalized organic molecules (Tribovillard et al., 2004). Sulfurization of organic matter takes place when hydrogen sulfide is formed in quantities exceeding the portion that can be scavenged rapidly by highly reactive iron to form pyrite. Tribovillard et al. (2004) have demonstrated that presence of sulfurized organic matter enhances Mo authigenic enrichment such that Mo is systematically more enriched relative to the other redox-sensitive/sulfide-forming elements studied (U, V, Ni and Zn). Thus, sulfurization indicates a strongly euxinic condition in the water column. In such euxinic conditions, Mo is rapidly sequestered by sulfurized organic matter and also goes into solid solution with sulfide minerals, so availability of both the host-phases in very high amount results in very high enrichment of Mo relative to U as observed in the unit 1a and 1b samples of UBS. Raven et al. (2016) demonstrated that
organic matter is rapidly sulfurized while sinking through the water column in the semi-restricted Cariaco Basin. They observed water column sulfurization is most extensive during periods of high primary productivity and appears to involve elemental S, possibly via polysulfides. They also suggested that the process has the potential to deliver substantial amounts of OM to the sediment by making it less available for remineralization in the water column; this, in turn, increases the preservation potential of organic matter.

![Figure 4.12: Crossplot between U Enrichment factors (U-EF) vs. Mo Enrichment factors (Mo-EF) showing three clusters of the UBS samples from core RT. The broken lines represent 0.3, 1 and 3 times of the average Mo/U of present-day seawater (SW). The general patterns of U-EF vs. Mo-EF variation in modern marine environments are represented by (i) gray field for unrestricted marine trend for eastern tropical Pacific Ocean, (ii) green field for semi-restricted Cariaco Basin, where particulate shuttle function for Mo enrichment within the water column and (iii) black solid line for strongly restricted Black Sea (adopted from Tribovillard et al., 2012). The yellow field represents areas, where the presence of sulfurized organic matter leads to very high enrichment of Mo in strongly euxinic conditions (Tribovillard et al., 2012). Sub-unit 1a and 1b plots in the zone of sulfurized organic matter (yellow field), whereas sub-unit 2b and part of sub-unit 2a and plots in the anoxic to the euxinic field (gray area). Finally, rest of the samples from sub-unit 2a plot in the sub-oxic to the anoxic field in the gray area.](image)

### 4.3.7 Mo-TOC Relationship and Basin Restriction

In anoxic to euxinic settings, the slope \( (m) \) of the regression line in Mo vs. TOC crossplot can be used as a proxy to determine the degree of restriction in the basin. As shown in Figure 4.13, the value of \( m \) for sub-units 1a, 1b and 2b are 21, 23.5 and 19.3, respectively. These \( m \) values are close to those of the modern day Cariaco Basin (Mo/TOC value ~25), which is a moderately restricted basin (Algeo and Lyons, 2006; Algeo et al., 2007; Algeo and Rowe, 2012). This suggests that sub-units 1a, 1b, and 2b were deposited in a semi-restricted basin, and, therefore, the water was subjected to intermittent deepwater renewal. However, since the value of \( m \) is higher in sub-unit 1a than in sub-unit 1b, the basin was progressively becoming less restricted due to sea level rise. The value of \( m \) decreases in Unit-2b, which indicates that the
basin became slightly more restricted during the deposition of sub-unit 1b. However, $m$ value cannot be used as a proxy for sediments deposited in oxic-suboxic conditions. Therefore, $m$ for sub-unit 2a, which was deposited in suboxic conditions, has no physical significance. Based on the procedure used by Algeo et al., (2007) for calculating the deepwater water renewal time in Devono-Carboniferous silled basins using $m$, the deepwater renewal time for the Williston Basin was estimated to be around 25 years (Figure 4.13b).

Figure 4.13: (a) Mo-TOC$_{org}$ crossplot for UBS in Well RT showing slope ($m$) for the regression line for chemostratigraphic sub-unit 1a, 1b and 2b are 21.1, 23.5 and 19.3 respectively. Value of $m$ for these UBS sub-units is close to that of the semi-restricted Cariaco Basin, which $m$ value close to 25. (b) $m$ versus deepwater renewal times for modern anoxic silled basins showing an average $m$ of 21 for UBS suggests the deepwater renewal in the Williston Basin during the deposition of UBS was around 25 years (modified from Algeo and Lyons, 2006).

### 4.3.8 Redox-condition and OM preservation

Different geochemical proxy based analyses show consistent results for the paleoredox condition of the chemostratigraphic units of the UBS. These paleoredox conditions identified from the inorganic geochemical analysis is consistent with the petrographic observations. Table 4.3 lists the findings for the paleoredox conditions based on inorganic geochemical methods and petrographic observations. These results indeed suggest that the redox-condition was changing during the deposition of the UBS. The bottom water conditions were strongly euxinic, which intermittently extended to the photic zone during the deposition of sub-unit 1a and 1b and this helped in the enhanced preservation of organic matter. However, during the deposition of sub-unit 2a, the benthic condition became less reducing and varied from suboxic to anoxic conditions. Suboxic conditions along the sediment-water interface resulted in more degradation of organic matter, which in turn decreased the total amount of preserved organic matter. This is one of the reasons for the low TOC in sub-unit 2a shown in Figure 4.3. However, as conditions became more anoxic
during the deposition of sub-unit 2b, the preservation potential of organic matter increased which resulted in the high TOC in Unit-2b. Therefore, the variation in TOC in the UBS is strongly dependent on bottom water redox-conditions.

4.3.9 Proxy for Paleoproductivity

As described in Section 4.3.9, I used the stable isotope nitrogen (δ\(^{15}\)N\(_{\text{org}}\)) as a proxy for the paleoproductivity in the UBS. Results of δ\(^{15}\)N\(_{\text{org}}\) for the different chemostratigraphic units of the UBS of Well RT are shown in Figure 4.14a. Figure 4.3 shows the δ\(^{15}\)N\(_{\text{org}}\) profile, which suggests that δ\(^{15}\)N\(_{\text{org}}\) has varied between Unit-1 and Unit-2 of the UBS in Well RT. The TOC\(_{\text{org}}\) vs. δ\(^{15}\)N\(_{\text{org}}\) crossplot in Figure 4.14b shows sub-units 1a and 1b have depleted average δ\(^{15}\)N\(_{\text{org}}\) of around 1.9; Sub-unit 2a has a much heavier δ\(^{15}\)N\(_{\text{org}}\) of 6.9. The depleted values of δ\(^{15}\)N\(_{\text{org}}\) in sub-units 1a and 1b suggest that the nutrient supply in the surface water was high; this suggests increased paleoproductivity in the surface water during the deposition of these sub-units. However, the relatively heavier values of δ\(^{15}\)N\(_{\text{org}}\) in sub-unit 2a suggests an increase in the utilization of the N\(^{15}\) isotope bearing nitrate, which was probably caused by a reduction in nutrient supply. This reduction in surface water nutrient supply resulted in a decrease in primary productivity during the deposition of sub-unit 2a. The δ\(^{15}\)N\(_{\text{org}}\) values in Sub-unit 2b are slightly depleted compared to those in sub-unit 2a, suggesting an increase in nutrient supply and thereby an increase in productivity during the deposition of sub-unit 2b.

Figure 4.14: (a) Box and whisker plot showing the results for the stable isotope of nitrogen (δ\(^{15}\)N\(_{\text{org}}\)) for the chemostratigraphic units of UBS in well RT. The mean values of δ\(^{15}\)N\(_{\text{org}}\) for each chemostratigraphic units are also labeled. (b) TOC\(_{\text{org}}\) vs δ\(^{15}\)N\(_{\text{org}}\) crossplot showing that sub-unit 1a and 1b have high TOC and lighter values of δ\(^{15}\)N\(_{\text{org}}\), whereas sub-units 2a has comparatively lower TOC and heavier values of δ\(^{15}\)N\(_{\text{org}}\). Sub-unit 2b has mixed values of δ\(^{15}\)N\(_{\text{org}}\). This crossplot indicates paleoproductivity during the deposition of Unit-1 was comparatively higher than that during the deposition of sub-unit 2a. The paleoproductivity increased marginally again during the deposition of sub-unit 2b.
Table 4.3: Findings for the paleoredox conditions based on inorganic geochemical methods and petrographic observations.

<table>
<thead>
<tr>
<th>Sub-units</th>
<th>C-S-Fe relationship</th>
<th>TOC-TE Relation</th>
<th>EF-Mo vs EF-U</th>
<th>Absolute Mo Concentration</th>
<th>Petrographic Evidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a, 1b</td>
<td>DOP$_T$ &gt;0.96</td>
<td>Exponential increase in Mo and U with TOC$<em>{org}$, weak covariance TOC$</em>{org}$ &gt;12.5wt.% Euxinic</td>
<td>Extreme enrichment of Mo relative to U Sulfurization of OM Strongly euxinic, photic zone euxinia</td>
<td>Mo &gt;100ppm Persistent euxinia in bottom water</td>
<td>Primarily suspension sedimentation Presence of planktonic fecal pellets (Section 3.4.1) Absence of bioturbation</td>
</tr>
<tr>
<td></td>
<td>Euxinic Strongly stratified Water Column</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>DOP$_T$ &lt;0.52</td>
<td>Lower: Moderate enrichment, Upper: No to limited enrichment Lower: good linear covariance; Upper: no covariance Lower 5.0&lt;TOC$_{org}$&lt;12.5wt.%; Upper&lt;5wt.%; Lower: Anoxic, Upper: suboxic</td>
<td>Lower: Moderate enrichment of both U and Mo Upper: More enrichment of U than Mo Lower: Anoxic to Euxinic, Upper: suboxic to anoxic</td>
<td>Lower: 5&lt;Mo&lt; 25ppm, Upper: Mo&lt; 5ppm Lower: Euxinic restricted to pore water, Upper: suboxic even in sediment column</td>
<td>Presence of agglutinated benthic forams (Section 3.4.1)</td>
</tr>
<tr>
<td></td>
<td>Suboxic Weakly stratified water column</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>0.75 &lt;DOP$_T$ &lt; 0.52</td>
<td>Moderate enrichment Good linear covariance 5.0&lt;TOC$_{org}$&lt;12.5wt.%; Anoxic</td>
<td>Moderate enrichment of both U and Mo Anoxic to Euxinic</td>
<td>Mo: 9-100ppm Anoxic to intermittent euxinia Basin getting restricted ($m$~19)</td>
<td>Occasional presence of agglutinated benthic forams (Section 3.4.1)</td>
</tr>
<tr>
<td></td>
<td>Suboxic to anoxic Weakly stratified water column</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.4 Discussion

In this section, a conceptual model for accumulation and preservation of OM in the UBS is proposed. This model provides the basis for the organic richness of four chemostratigraphic units of the UBS with respect to the interplay between OM production, preservation, and dilution. The framework of this conceptual model includes the effect of various depositional settings of the basin, such as basin morphology, paleogeography, paleoclimate, and probable nutrient sources. Therefore, to build a framework for the conceptual model, this section begins with selecting fit-for-purpose options for these depositional settings in the context of the UBS.

4.4.1 Depositional Setting

Basin Morphology

During the deposition of the UBS in Early Mississippian, Williston Basin was a very gently sloping epicontinental sea, which extended over hundreds of miles (Smith and Bustin, 1998). During the deposition of the UBS, the basin was located near the equator and had a maximum depth of around 150m (Section 3.5.3). As discussed in Section 4.3.7, average $m$ in $Mo$ vs. $TOC_{org}$ crossplot is 21, which indicates that the basin was semi-restricted during the deposition of the UBS. This finding is aligned with the physiographic presence of the Central Montana Uplift (Smith and Bustin, 1998), which formed a marginal sill to the west-southwest and limited frequent deepwater renewal (Figure 4.15). Moreover, as suggested by Smith and Bustin (1998), the Montana Trough along the south-western edge formed a connection between the Williston Basin with the open ocean conditions at the western margin of the North American Craton. It is proposed that this physiographic feature aided in the intermittent renewal of deep waters.

Paleoclimate

During the deposition of the UBS, the Williston Basin was characterized by a warm, tropical climate with seasonal precipitation (Ettensohn and Barron, 1981). In the Early Mississippian, Williston Basin was located within the tropics in the southern hemisphere and was under the influence of prevailing east-west trade winds, as shown in Figure 4.15 (Algeo et al., 2007; Blakey, 2005). However, due to the absence of any orographic barriers, the trade winds passed freely to the west and contributed very little towards precipitation (Smith and Bustin, 1998). As the Intertropical Convergence Zone (ITCZ) was also close to Williston Basin, the annual migration of the ITCZ probably caused seasonal rainfall, and a seasonal change in the direction and intensity of the trade wind (De Vleeschouwer et al., 2014).
Figure 4.15: Schematic diagram showing the prevailing depositional setting of the Williston Basin during the deposition of UBS. The basin was under the influence of the east-west trade wind as shown by the yellow arrow due to its location near the equator. The Williston Basin was semi-restricted in nature due to the presence of the Central Montana Uplift, which was situated at the south-west of the basin. Stratified water column developed due to the formation of a thermocline, which stabilized the chemocline, which in turn developed as a result of degradation of organic matter. The chemocline created a stagnant euxinic bottom water condition during the deposition of Unit-1 of UBS. However, when the depth of the thermocline is lowered due to fall in the sea level, the seasonal fluctuation of the thermocline disturbed the chemocline. This, in turn, decreased the reducing condition at the sediment-water interface during the deposition of Unit-2. The primary source of the nutrients was through regeneration of the biolimiting nutrients N and P in euxinic condition.

**Stratification of Water Column**

Ettensohn and Barron (1981), and Lineback and Davidson (1982) suggested that a stratified water column existed during the UBS deposition, which resulted in restricted circulation and mixing of surface water with the deeper bottom waters. I confirmed the presence of a stratified water column based on the DOP\_1 values for the UBS which are more than 0.75 (see Section 4.3.4). Stratification may form in a water column due to a difference in the density of surface and deeper water, which in turn may be caused by high fluvial discharge and surface run-off into the basin. Smith and Bustin (1998) suggested that fluvial run-off was minimum during the deposition of the UBS; therefore, the development of the stratified water column due to density differences is an unlikely scenario. Stratification in the water column may also be caused by temperature differences between the surface water layer with the deeper water. Tyson and Pearson (1991) suggested that a thermocline may develop in modern shelf seas and ancient epeiric seas in temperate climatic conditions due to seasonal variations in wind strength and temperature differences. However, the
Development of a thermocline stratifies the water column into three distinct layers: the surface mixed layer, the intermediate layers along the thermocline, and the deeper bottom water (Tyson and Pearson, 1991). These researchers suggested that in deep water areas in an epeiric sea, the water mass stratification can be so stable that it results in the formation of meromictic conditions. In such conditions, the deep bottom water resists seasonal overturn due to its higher volume and thus forms an isolated, deep, stagnant pool. In meromictic conditions, density differences in the stratified water column due to development of a thermocline eventually facilitate chemical differences between the surface water and the deep stagnant pool, which may result in the formation of a redox-boundary or chemocline in the deeper bottom water (Boehrer and Schultze, 2008). However, seasonal fluctuation of the thermocline and surface-water mixing results in fluctuation in the depth of the chemocline in the water column (Parkin and Brock, 1981). Therefore, it is proposed that the proximity of Williston Basin to the paleo-equator in a warm tropical climatic setting, and a seasonal variation in direction and intensity of the trade wind resulted in the development of a thermocline during the deposition of the UBS, which prevented vertical mixing of the surface water with the deep bottom water (Figure 4.15). Moreover, the physiographic sill of the Central Montana Uplift limited frequent deepwater exchange and thus did not disturb the deeper water. Therefore, for the UBS, the deposition of OM matter resulted in rapid depletion of oxygen content in the deep stagnant pool, which facilitated the development of a chemocline within the deeper water (Figure 4.15).

Paleoproductivity

Smith and Bustin (1998) suggested that during the deposition of the UBS, nutrients were supplied through upwelling and in-situ regeneration (of nutrients) by the process of remineralization of OM. Upwelling of nutrient-rich equatorial undercurrents was happening in the Central Montana Trough in an estuarine-like circulation pattern occurring above a stagnant anoxic pool. An estuarine-like circulation pattern generally takes place in environments with humid climatic conditions, which contribute to high river discharge and thus result in a stratified water column due to salinity differences (Algeo et al., 2008). However, during the deposition of the UBS, Williston Basin was characterized by a warm tropical climate with only seasonal precipitation and low fluvial discharge; therefore, an estuarine-like circulation pattern probably did not exist. Moreover, as the maximum depth of the basin was about 150 m, it is unlikely that the equatorial currents in the Pacific Ocean, which according to Jewell (1995) exist at depths of more than 100-200m, would have entered the shallow epicontinental sea of Williston Basin. Therefore, it is postulated that regeneration of biolimiting nutrients, such as P and N, was a major source of nutrients during the UBS deposition. In euxinic conditions, P and N are preferentially released from OM, which then diffuses upward from the sediment into a water column, and thus aids in the efficient recycling of nutrients (Ingall and Jahnke, 1994, 1997). Periodic mixing of the surface and mid-water along the thermocline may result in
fluctuation of the oxic-anoxic and anoxic-euxinic chemocline in the deeper stagnant water; this, in turn, probably aids in releasing the regenerated nutrients back to the surface water (März et al., 2008). In oxic-suboxic conditions, P is entrapped in sediment as a result of redox cycling of Fe with P (Tribovillard et al., 2006; März et al., 2008). This results in a decreased nutrient supply in the surface water, which in turn decreases surface water productivity. Therefore, based on the redox condition of the various chemostatigraphic sub-units of the UBS, P and N will either get preferentially released or will be entrapped within the sediments. As shown in Figure 4.15, for UBS chemostatigraphic sub-units, the preferential release will enhance the nutrient supply in the surface water during euxinic conditions, thereby increasing paleoproduction. Smith and Bustin (1998) suggested that most of the detrital sediment in the Bakken are windblown, supplied from the Canadian Shield by the east-west trade winds. Therefore, along with in situ regeneration of nutrients, it was hypothesized that during the deposition of UBS, the influx of clay into the Williston Basin from the Canadian Shield by the northeast trade winds brought Fe-rich nutrients, which augmented the OM productivity (Figure 4.15). This hypothesis is based on the positive covariance between TOC and detrital proxying elements (Al and K) and was discussed in Section 4.3.3. Filipsson et al. (2011) proposed a similar postulation for increased OM productivity on the northwest coast of Africa, due to the influx of Saharan eolian dust, which bring Fe-rich nutrients in the Atlantic Ocean.

4.4.2 Model for Organic Richness in Chemostatigraphic Units of UBS

Sub-unit 1a

Deposition of the UBS started with the onset of transgression/flooding of Williston Basin from the west (Section 4.4.1). This marks the beginning of the deposition of sub-unit 1a, which is the lower-most chemostatigraphic sub-unit of the UBS. Availability of more nutrients due to transgression enhanced the primary productivity, which in turn resulted in a higher flux of OM to the basin floor. This initiated the development of anoxic benthic conditions due to degradation of OM. Accumulation of OM at the basin floor continued incessantly, which exhausted the oxygen content in the bottom water and the reducing condition continued to get intense. Consequently, the concentration of dissolved HS within the bottom water increased due to sulfate reduction, and as a result, the paleoredox condition at the basin floor became euxinic. This resulted in the formation of a redox-boundary or chemocline in the bottom water, as shown in Figure 4.16a. For sub-unit 1a, persistently euxinic conditions in the bottom water with intermittent photic zone euxinia was confirmed by the geochemical redox-proxies and petrographic data (Table 4.3). Moreover, as previously described, thermal stratification in the water column prohibited the mixing of the sulfidic deep water with the oxygenated surface water, which helped in maintaining a stagnant euxinia at the bottom water. In such euxinic conditions, the biolimiting nutrients (P, N) were preferentially released from OM. As described in Section 4.4.1, a seasonal variation in the depth of the thermocline resulted in a
fluctuation in the depth of the chemocline, which aided in replenishing the surface water with the regenerated nutrients. Therefore, the surface water remained oxygenated and well-supplied with nutrients, which is evident from the depleted values of $\delta^{15}N_{\text{org}}$ in sub-unit 1a, resulting in its high organic productivity. This claim is further supported by the presence of planktonic fecal pellets in massive to finely laminated facies (F2) and the abundance of radiolarians in siliceous mudstone (F1) in sub-unit 1a. Therefore, high OM productivity along with high preservation potential due to bottom water euxinic conditions resulted in increased organic richness in this sub-unit. Sulfurization of OM during intermittent photic zone euxinia may have also helped in the enhanced preservation of OM during the deposition of sub-unit 1a. As discussed in Section 4.3.3, no covariance between detrital clay and carbonate proxying elements with TOC indicates that sedimentation of these elements was low, which did not aid in the dilution of OM. However, a negative correlation between Si and $TOC_{\text{org}}$ indicates that biogenic silica associated with radiolarians in siliceous mudstone resulted in the dilution of OM.

**Sub-unit 1b**

A flooding event marks the boundary between sub-units 1a and 1b as discussed in Section 3.5.5. Therefore, during the deposition of sub-unit 1b, there was a further rise in the sea level (Figure 4.16b). As a result, the basin became less restricted; this is also suggested by a higher value of slope ($m$) for sub-unit 1b in the TOC-Mo crossplot compared to that in 1a (Section 4.3.7). Due to rise in sea level, the height of the oxygenated surface water column increased, which in turn increased the travel time of OM through the oxygenated water (Figure 4.16b). Therefore, the export productivity was slightly lower during the deposition of sub-unit 1b because more OM was degrading before it was able to reach the euxinic bottom of the basin. This decrease in the export productivity of OM is confirmed by a slight decrease in the TOC of sub-unit 1b, in comparison to that of sub-unit 1a. However, during the deposition of sub-unit 1b, the primary productivity in the surface water remained the same, which is confirmed by the insignificant change in nitrogen isotope data (Section 4.3.9). All geochemical redox-proxies indicate that both sub-units 1a and 1b were also deposited in euxinic conditions (Table 4.3). However, as shown in Figure 4.3, for sub-unit 1b, Mo, U, and TOC show an increasing trend with depth. The decrease in Mo concentration either indicates low availability of host-phase (OM) or a decreased source-ion (aqueous Mo) availability (Section 4.2.1). However, a decrease in source ion-availability would be suggestive of a more restricted basin, which is not the case, as discussed earlier. Therefore, the decreasing trend in Mo is associated with a decrease in the availability of its host-phase or OM during the deposition of sub-unit 1b. The effect of the influx of detrital clay and dilution by biogenic silica in controlling OM richness in sub-unit 1b was the same as that for 1a (Section 4.3.3).
Figure 4.16: Schematic diagrams showing the depositional condition of the different chemostratigraphic sub-units of UBS at the location of well RT. (i) Stratified water column shown developed during the deposition of sub-unit 1a due to the formation of a thermocline. Accumulation of OM continued incessantly, which exhausted the oxygen content in the bottom water and thereby resulted in the development of a stagnant euxinic condition below the chemocline. The biolimiting nutrients P and N were preferentially released in a euxinic condition, which resulted in high surface water productivity. Seasonal fluctuation of the depth of the thermocline also resulted in fluctuation of the chemocline which aided in releasing the nutrients back to the surface water. (ii) The relative rise in sea level during the deposition of sub-unit 1b increased the height of the oxygenated surface water column which decreased the export productivity since more OM were degraded while settling down through the water column. Primary productivity in the surface water was high. Bottom water conditions were still euxinic which extended to the photic zone intermittently. (iii) The sea level drop resulted in disappearance of radiolarians, and the depth of the thermocline dropped due to the fall in relative sea level during the deposition of sub-unit 2a. So, the thermocline became closer to the chemocline. Seasonal fluctuation of the thermocline destabilized the chemocline due to the partial mixing of the water column. This resulted in the formation of sub-oxic to anoxic condition along the sediment-water interface. Paleoproductivity decreased as the biolimiting nutrients were less efficiently regenerated in sub-oxic condition. As more land area got exposed due to relative sea level fall, it was covered by vegetation which became the source of more terrestrial OM during the deposition of sub-unit 2a. (iv) During the deposition of sub-unit 2b, there was a minor increase in the depth of the thermocline due to a slight increase in relative sea level. As a result, the chemocline stabilized, and conditions were more reducing which enhanced the regeneration of the biolimiting nutrients (P and N). Therefore, the surface water productivity was higher compared to that of sub-unit 2b.
Sub-unit 2a

The absence of siliceous mudstone (F1) from sub-unit 2a is one of the major factors which makes it different from sub-units 1a and 1b. The absence of facies F1 in sub-unit 2a is associated with the disappearance of radiolarians, which thrive in a deeper water setting and are sensitive to falls in sea level (De Wever et al., 2002). Therefore, the absence of radiolarians from sub-unit 2a indicates that the deposition of this sub-unit is associated with a relative fall in sea level (Figure 4.16c). As discussed in Section 4.3.3, an increase in Zr/Rb ratio and Ca in sub-unit 2a supports the claim that the influx of detrital siliciclastic and dolomite silt sediment increased. The relative fall in sea level during the deposition of sub-unit 2a exposed more basin margin area, which resulted in an increased influx of silt-sized sediment due to weathering. This increase in the influx of the silt-sized sediments resulted in a dilution of OM, which was evident from the negative correlation in TOC-Si and TOC-Ca crossplots (Figure 4.6 and Figure 4.7). In contrast, the influx of detrital clay helped in the preservation of OM, as discussed in Section 4.3.3. Fe-rich clay also acted as a source of nutrients and thus enhanced the productivity, as discussed in Section 4.4.1. As more land area got exposed due to relative sea level fall, it was covered by vegetation, which became the source for the terrestrial Type III OM present in sub-unit 2a (Section 0).

As shown in Figure 4.16c, the depth of the thermocline dropped with the continued fall in sea level during the deposition of sub-unit 2a. As thermocline moved close to chemocline, the deeper bottom water below the chemocline, which was stagnant during the deposition of sub-units 1a and 1b, did not remain stagnant anymore due to the disturbance caused by the seasonal variation of the thermocline. This resulted in the partial mixing of the bottom water, which developed suboxic to anoxic conditions at the sediment-water interface. This was confirmed by the geochemical redox-proxy and petrographic evidence, which indicated that sub-unit 2a was deposited in predominantly suboxic to anoxic conditions (Table 4.3). An increase in oxygen content in bottom water resulted in a less effective regeneration of nutrients like P, which got retained within the sediment by getting co-precipitated with Fe-oxyhydroxides (März et al., 2008). This, in turn, decreased the nutrient supply and, as a result, the surface water productivity diminished, which was confirmed by the lower δ15Norg in sub-unit 2a in Figure 4.14. Suboxic conditions during the deposition of sub-unit 2b resulted in an increase in OM degradation and thus decreased the preservation potential at the bottom of the basin. Therefore, the decrease in TOC in sub-unit 2a is a combined effect of low preservation due to suboxic paleoredox conditions, low productivity, and more dilution by detrital silt-sized sediments and all three of these factors are related to a relative fall in sea level.

Sub-unit 2b

Geochemical redox proxies for sub-unit 2b indicate that benthic conditions were anoxic with intermittent euxinia (Table 4.3). Therefore, the paleoredox conditions during the deposition of sub-unit 2b
were more reducing compared to those of sub-unit 2a. It is proposed that during the deposition of sub-unit 2b, there was a minor rise in the sea level, which in turn raised the depth of the thermocline and surface water. As a result, the chemocline stabilized and thus increased the stagnation in the deeper bottom water below the chemocline, making the conditions more reducing than those of sub-unit 2a. Moreover, the intermittent euxinia resulted in a better regeneration of the biolimiting nutrients, thereby increasing the surface water productivity, which is evident from the higher $\delta^{15}N_{org}$ compared to that of sub-unit 2a (Figure 4.14). Dilution of OM by detrital silt-sized sediments was similar to that of sub-unit 2a, which is evident from the negative correlation in TOC- Si and TOC-Ca crossplots (Figure 4.6 and Figure 4.7). Therefore, organic richness in sub-unit 2b is a result of both enhanced paleoproductivity and better preservation potential due to development of intermittent euxinic conditions at the sediment-water interface.

4.5 Conclusion

- Two chemostratigraphic units, namely Unit-1 and Unit-2 were identified in Well RT. Unit-1 was further subdivided into two sub-units: 1a and 1b. Unit-2 was also subdivided into two sub-units: 2a and 2b. The subdivision of the UBS was primarily based on the trends of detrital and biogenic proxying elements and the variation in the response of the redox sensitive trace elements.

- The organic richness of the UBS at the location of Well RT or the southern part of the basin depocenter was controlled by paleoproductivity, bottom-water redox conditions, and dilution by detrital silt-size sediments and radiolarians. However, for the four sub-units of the UBS, these factors varied, primarily due to a relative change in sea level, which in turn affected the organic richness of these sub-units. Therefore, a variation in organic richness is observed in the four chemostratigraphic sub-units of the UBS.

- The slope ($m$) of the Mo-TOC crossplot indicated that the basin was semi-restricted in nature due to the presence of the Central Montana Uplift, which was located at the south-east of the basin. The higher value of $m$ in sub-unit 1b in comparison to that of 1a suggests that the basin was getting less restricted due to relative sea level rise. However, increase in the detrital sediment influx during the deposition of both sub-units 2a and 2b and the comparatively lower value of $m$ during the deposition of sub-unit 2b indicates that Unit-2 was deposited during a relative sea level fall.

- The degree of pyritization for Unit-1 indicated that a stratified water column existed in Williston Basin during the deposition of sub-units 1a and 1b. However, the stratification was disturbed during the deposition of Unit-2 due to fall in relative sea level and quasiperiodic fluctuation of the thermocline.
• Unit-1 was deposited in strongly euxinic conditions which existed in the bottom water and also extended to the photic zone intermittently. During the deposition of Unit-2, the conditions were predominantly sub-oxic to anoxic along the sediment-water interface.

• Paleoproductivity was high during the deposition of Unit-1 as more biolimiting nutrients (P, N) were getting preferentially regenerated due to the euxinic paleoredox conditions. However, as the paleoredox conditions became less reducing during the deposition of Unit-2, paleoproductivity declined due to the decreased regeneration of the nutrients.

4.6 References


CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The purpose of this thesis is to improve the current geological understanding of the Bakken Formation. The three primary objectives of this thesis were as follows: 1) to develop an understanding of the pore-types, pore-architecture, pore-size, and the role of dolomitization on porosity evolution in the Middle Bakken Member (MBM) of the Elm Coulee Field; 2) to identify the lithofacies of the Upper Bakken Shale (UBS) and their lateral and vertical distribution, define laterally correlatable chemostratigraphic units of UBS, their depositional conditions, and their thickness variation in the basin; and 3) to develop an understanding of the interplay of paleoproductivity, redox condition and dilution of OM in controlling the organic-richness of the UBS and develop a conceptual model for its deposition. These research objectives were attained by integrating multiple data-set and methods, which include core-description, thin-section, and SEM petrography, MIP, routine-core analysis data, XRF, XRD, ICP-MS, stable isotope of carbon, oxygen, and nitrogen, and TOC obtained from SRA. The conclusions of the thesis are summarized in Section 5; the recommendations for future work are listed in Section 5.2.

5.1 Conclusion

The general findings of this research are summarized in following five-points:

1) Dolomitization of the MBM in the Elm Coulee Field has taken place by the seepage-reflux of mesohaline to penesaline brine. As a major diagenetic event, the process of dolomitization has played a significant role in the porosity evolution of the MBM of the Elm Coulee Field. Early patchy calcite cement, anhydrite cement, and authigenic illite clay are the other diagenetic factors that reduce the porosity of the Middle Bakken.

2) The MBM in the Elm Coulee Field consists of sub-micron sized intercrystalline pores between the dolomite rhombs. Total porosity and pore throat size increases as dolomite content increases up to 60 wt.. When dolomite content increases more than 60 wt., total porosity and pore throat size start decreasing due to overdolomitization. Moreover, pore-bridging and pore-lining effect of the authigenic illite clay within the intercrystalline pores between the dolomite rhombs reduces the pore throat size and forms a complex pore network in the MBM.

3) Six different lithofacies (F-1 through F6) were identified in the UBS; however, 95% of the UBS primarily consists of facies F-1, F-2, and F-4. Basin-wide variation in the lateral and vertical distribution of these facies was observed.
4) Three laterally correlatable chemostratigraphic packages—sub-unit-1a, sub-unit 1b and Unit-2—were identified in UBS. Reducing conditions developed at the sediment-water interface and in the bottom waters due to degradation of organic matter (OM). Sub-unit 1a and 1b were deposited in a persistently euxinic condition, which existed in the bottom water and extended to the photic zone intermittently. However, Unit-2 was deposited in a less reducing condition, which varied from suboxic to intermittently euxinic. Unit-1 was deposited during an overall transgression and is a part of the transgressive systems tract (TST), while Unit-2 was deposited during a regression and represents the highstand systems tract (HST). Sub-units 1a and 1b have more biogenic and authigenic silica compared to Unit-2, which makes them comparatively more brittle than Unit-2.

5) The organic-richness of the UBS was controlled by paleoproductivity, bottom-water redox conditions, and dilution by detrital silt-sized sediments and radiolarians. For the different chemostratigraphic sub-units of the UBS, the effect of these factors varied, primarily due to a relative change in the sea level. This has resulted in a variation in the organic-richness and OM type of the chemostratigraphic sub-units of the UBS. Paleoproductivity was high during the deposition of Unit-1 as more biolimiting nutrients (P, N) were getting preferentially regenerated due to the euxinic paleoredox condition. This resulted in high TOC in the lower Unit-1 compared to that of the upper Unit-2 of the UBS in the southern part of the basin depocenter.

5.2 Recommendations for Future Work

1) The dolomitization model for the Elm Coulee Field proposed in this study should be compared with other parts of the basin. This will give an idea of the regional flow pattern of the dolomitizing fluid, which in turn will help to predict areas with better reservoir quality.

2) Stable isotope data for sulfur should be acquired from the MBM of the Elm Coulee Field samples, which consists of secondary anhydrite nodules and cement. This will give a better idea about the timing of the precipitation of anhydrite cement. Stable isotope of C and O from samples, which consists of patchy calcite cement, should be acquired to understand the genesis of calcite cement.

3) In this research, cathodoluminescence study was conducted on petrographic thin sections of the MBM; however, the petrographic thin sections were not optimally polished. Different dolomite zones indicating various stages of dolomitization can be further resolved by optimally polishing the thin section before studying them under a cathodoluminescence microscope.

4) In this study, the macrofossil-bearing silt-rich mudstone (F4) was found localized in the southern depocenter of the Williston Basin. Additional cores from the basin depocenter, north-western and eastern areas should be studied to verify the presence or absence of facies F4 in other parts of the
basin. This will help in developing a better regional understanding of the depositional setting of the UBS.

5) To further understand the relative hydrocarbon resource potential of the chemostratigraphic packages of the UBS, geomechanical and rock-physical properties of the different chemostratigraphic packages of the UBS should be studied. This will also help in predicting the extent of natural fracturing and the ease of performing hydraulic fracturing in these packages. Moreover, the porosity of these chemostratigraphic packages should also be characterized using SEM studies and nitrogen adsorption experiments to understand the pore architecture and pore connectivity.

6) In this study, the stable isotope data for organic carbon indicated the presence of type-III or terrestrial OM, in the upper sub-units (2a, 2b) of the UBS in the southern part of the basin depocenter. This new finding should be confirmed by a detailed organic petrographic study as this finding has implications on resource potential and regional hydrocarbon charging pattern in the producing intervals.

7) The methodology used in this thesis for understanding the stratigraphic framework, depositional conditions and organic-richness of UBS should be used to characterize the Lower Bakken Shale (LBS).
APPENDIX A: DIGITIZED CORE DESCRIPTION OF MIDDLE BAKKEN MEMBER, ELM COULEE FIELD

This appendix includes the core-description panel for all the well-cores used in the Chapter-1.

<table>
<thead>
<tr>
<th>Sedimentary structure</th>
<th>Lithology</th>
<th>Facies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Massive to finely laminated</td>
<td>Black Shale</td>
<td>UBS (Upper Bakken Shale)</td>
</tr>
<tr>
<td>Brachiopods and Crinoids</td>
<td>Sandy Dolostone</td>
<td>MB-F (Middle Bakken F)</td>
</tr>
<tr>
<td>Burrow NM</td>
<td>Silty Dolostone</td>
<td>MB-E (Middle Bakken E)</td>
</tr>
<tr>
<td>Burrow NM PI Minor</td>
<td>Calcareous Silty Dolostone</td>
<td>MB-B3 (Middle Bakken B3)</td>
</tr>
<tr>
<td>Burrow PI</td>
<td>Dolomitic Silty Limestone</td>
<td>MB-B2 (Middle Bakken B2)</td>
</tr>
<tr>
<td>Burrow PI NM minor</td>
<td></td>
<td>MB-B1 (Middle Bakken B1)</td>
</tr>
<tr>
<td>Burrow PM</td>
<td></td>
<td>MB-D (Middle Bakken D)</td>
</tr>
<tr>
<td>Ripple</td>
<td></td>
<td>MB-A (Middle Bakken A)</td>
</tr>
<tr>
<td>Planar lamination</td>
<td></td>
<td>LBS (Lower Bakken Shale)</td>
</tr>
<tr>
<td>Planar to Wavy Lamination</td>
<td></td>
<td>Pronghorn</td>
</tr>
<tr>
<td>Wavy-laminated</td>
<td></td>
<td>Three Forks</td>
</tr>
<tr>
<td>Cross Strata</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LBS Lag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Patey Calcite Cement</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Well name: Brutus East-Lewis 3-4-H

<table>
<thead>
<tr>
<th>Depth (ft)</th>
<th>Grainsize Sedimentary Structure</th>
<th>Lithology</th>
<th>Distribution Index</th>
<th>Facies</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>10385</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>UBS: Black colored, massive to finely laminated, siliceous, organic-rich mudstone</td>
</tr>
<tr>
<td>10390</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Massive: Massive, dark buff to gray colored, slightly burrowed at places, some continuous clay laminations</td>
</tr>
<tr>
<td>10395</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Planar to Wavy Lamination: Gray colored, planar to wavy-laminated, double mud drapes present, soft sediment deformation, microfaults</td>
</tr>
<tr>
<td>10400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Planar Lamination: Gray colored, massive to planar stratified, soft sediment deformation, slumping present at base</td>
</tr>
<tr>
<td>10405</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wavy-laminated: Light gray colored, wavy laminated, flaser ripples present</td>
</tr>
<tr>
<td>10410</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Burrow PM: Buff colored, massive, burrow mottled, wavy laminated present, Planolites montanus</td>
</tr>
<tr>
<td>10415</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Burrow NM: Buff colored, patchy calcite cementation, interbedded, massive burrow mottled, Nereites missouriensis</td>
</tr>
<tr>
<td>10420</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Burrow PI NM minor: Dark gray color, burrow mottled, patchy calcite cementation, brachiopods and crinoids present, Phycosiphon incertum dominated</td>
</tr>
<tr>
<td>10425</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Burrow PI: Greenish gray color, burrow mottled, brachiopods and some crinoids are present, patchy calcite cementation, Phycosiphon incertum</td>
</tr>
<tr>
<td>10430</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>LBS Lag: Phosphatic and pyritic lag deposit</td>
</tr>
<tr>
<td>10435</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Burrow PH: Pronghorn, burrow mottled</td>
</tr>
</tbody>
</table>

API# 250832250700
**Column Description**

<table>
<thead>
<tr>
<th>Depth (ft)</th>
<th>Lithology</th>
<th>Facies</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>10455</td>
<td>UBS</td>
<td>F</td>
<td>UBS: Black colored, massive to finely laminated, siliceous, organic-rich mudstone.</td>
</tr>
<tr>
<td>10460</td>
<td>Storm Bed</td>
<td>F</td>
<td>Storm Bed: Gray colored, massive to slightly burrowed, calcareous and fossiliferous, brachiopods present.</td>
</tr>
<tr>
<td></td>
<td>planar lamination</td>
<td>F</td>
<td>planar lamination: Gray colored, very thinly laminated, occasionally current ripples present.</td>
</tr>
<tr>
<td></td>
<td>Wavy laminated</td>
<td>F</td>
<td>Wavy laminated: Light gray colored, wavy-laminated, soft sediment deformation.</td>
</tr>
<tr>
<td></td>
<td>Burrow PM</td>
<td>F</td>
<td>Burrow PM: Buff colored, massive, burrow mottled, some planar lamination, Planolites montanus dominated.</td>
</tr>
<tr>
<td></td>
<td>Burrow NM</td>
<td>F</td>
<td>Burrow NM: Buff colored, interbedded, massive burrow mottled, Nerites missouriensis.</td>
</tr>
<tr>
<td></td>
<td>Burrow NM PI Minor</td>
<td>F</td>
<td>Burrow NM PI Minor: Gray color, patchy calcite cementation, massive burrow mottled, Nerites missouriensis dominated.</td>
</tr>
<tr>
<td></td>
<td>Burrow PI NM minor</td>
<td>F</td>
<td>Burrow PI NM minor: Dark gray color, burrow mottled, patchy calcite cementation, brachiopods and Crinoids present, Phycosiphon incertum dominated.</td>
</tr>
<tr>
<td></td>
<td>Burrow PI NM minor</td>
<td>F</td>
<td>Burrow PI NM minor: Greenish gray color, burrow mottled, brachiopods present, calcareous, Phycosiphon incertum dominated.</td>
</tr>
<tr>
<td></td>
<td>LBS Lag</td>
<td>F</td>
<td>LBS Lag: Phosphatic and pyritic lag deposit.</td>
</tr>
<tr>
<td></td>
<td>3 Forks</td>
<td>F</td>
<td>3 Forks: Planar laminated, silty-dolostone.</td>
</tr>
<tr>
<td>Depth (ft)</td>
<td>Lithology</td>
<td>Facies</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>7625</td>
<td></td>
<td>UBS</td>
<td>UBS: Black colored, massive to finely laminated, siliceous, organic-rich mudstone</td>
</tr>
<tr>
<td>7630</td>
<td></td>
<td>MB-F</td>
<td>Storm Bed: Gray colored, massive to slightly burrowed, brachiopods present</td>
</tr>
<tr>
<td>7635</td>
<td></td>
<td>MB-E</td>
<td>Planar to Wavy Lamination: Gray colored, planar to wavy laminated</td>
</tr>
<tr>
<td>7640</td>
<td></td>
<td>MB-D1</td>
<td>Wavy-laminated: Light gray colored, wavy laminated, quartz rich with dolomite cement</td>
</tr>
<tr>
<td>7645</td>
<td></td>
<td>MB-R3</td>
<td>Burrow PM: Buff colored, massive, burrow mottled, some planar to wavy laminations, Planolites montanus</td>
</tr>
<tr>
<td>7650</td>
<td></td>
<td>MB-B2</td>
<td>Burrow NM: Buff colored, interbedded, massive burrow mottled, patchy calcite cementation, Nerites missouriensis</td>
</tr>
<tr>
<td>7655</td>
<td></td>
<td>MB-B1</td>
<td>Burrow PI NM minor: Dark gray color, burrow mottled, patchy calcite cementation, brachiopods and crinoids present, Phycosiphon incertum dominated</td>
</tr>
<tr>
<td>7660</td>
<td></td>
<td>MB-A</td>
<td>Burrow PI: Greenish gray color, burrow mottled, brachiopods and crinoids present, patchy calcite cementation, Phycosiphon incertum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LBS</td>
<td>LBS: Black colored, siliceous organic-rich mudstone</td>
</tr>
<tr>
<td>Depth (ft)</td>
<td>Grainsize Sedimentary Structure</td>
<td>Lithology</td>
<td>Biota Index</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------</td>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td>10390</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10395</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10405</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10410</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10415</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Three forks</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX B: RAW DATA AND SOFT COPIES

In this appendix, the description of the files for XRF, XRD, MICP, TOC data, stable isotope, routine core analysis (RCA) data, chemostratigraphic profiles and correlations are arranged in a tabular format. These data for each chapter of this thesis are listed in the table, along with their directory location. Moreover, the file details of the published papers and conference presentation, and additional data collected during the PhD curriculum are also provided.

Table B.1: Table listing the file description for data used in Chapter-2 of the thesis.

<table>
<thead>
<tr>
<th>File name</th>
<th>Description</th>
<th>Directory location</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD_porosity.xlsx</td>
<td>XRD and porosity data for Middle Bakken interval in eight well of Elm Coulee Field</td>
<td>H:\Dipanwita Thesis\Chapter-2</td>
</tr>
<tr>
<td>Stable_isotope.xlsx</td>
<td>Stable isotope data for carbon and oxygen of Middle Bakken Interval from four wells of Elm Coulee Field</td>
<td>H:\Dipanwita Thesis\Chapter-2</td>
</tr>
<tr>
<td>Micromeretics_Elm Coulee_Drainage only MICP.xlsx</td>
<td>Mercury intrusion porosimetry data for pore-throat size distribution of four wells of Elm Coulee Field</td>
<td>H:\Dropbox\thesis\Chapter-2\MICP</td>
</tr>
</tbody>
</table>

Table B.2: Table listing the file description for the data used in Chapter-3 of the thesis.

<table>
<thead>
<tr>
<th>File name</th>
<th>Description</th>
<th>Directory location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compilation_XRF.xlsx</td>
<td>XRF data from UBS of nineteen wells collected by the author</td>
<td>H:\Dipanwita Thesis\Chapter-3</td>
</tr>
<tr>
<td>TOC.xlsx</td>
<td>TOC data from UBS of two wells collected by the author and available from external sources</td>
<td>H:\Dipanwita Thesis\Chapter-3</td>
</tr>
<tr>
<td>XRD_Chapter 3.xlsx</td>
<td>XRD data from UBS collected by the author and available from external sources</td>
<td>H:\ Dipanwita Thesis \Chapter-3</td>
</tr>
<tr>
<td>All chemostratigraphic profiles.pdf</td>
<td>Chemostratigraphic profiles for sixteen wells and correlation panels</td>
<td>H:\ Dipanwita Thesis \Chapter-3</td>
</tr>
<tr>
<td>Chemostratigraphic correlation I.jpeg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemostratigraphic correlation II.jpeg</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B.3: Table listing the file description for the data used in Chapter-4 of the thesis.

<table>
<thead>
<tr>
<th>File name</th>
<th>Description</th>
<th>Directory location</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-MS and Stable Isotope data.xlsx</td>
<td>ICP-MS elemental concentration data and SRA TOC for UBS in RT well</td>
<td>H:\ Dipanwita Thesis \Chapter 4</td>
</tr>
</tbody>
</table>

Table B.4: Table listing the file description of additional data of the Upper and Lower Bakken Shale collected during the PhD curriculum.

<table>
<thead>
<tr>
<th>File name</th>
<th>Description</th>
<th>Directory location</th>
</tr>
</thead>
<tbody>
<tr>
<td>C and N isotope Lonetree Edna.xlsx</td>
<td>Stable isotope of C and N of UBS for well LT</td>
<td>H:\ Dipanwita Thesis \Additional data</td>
</tr>
<tr>
<td>S isotope Lonetree Edna.xlsx</td>
<td>Stable isotope of S of UBS for well LT</td>
<td>H:\ Dipanwita Thesis \Additional data</td>
</tr>
<tr>
<td>ICP-MS Lonetree Edna.xlsx</td>
<td>ICP-MS of UBS for well LT</td>
<td>H:\ Dipanwita Thesis \Additional data</td>
</tr>
<tr>
<td>XRF_LBS</td>
<td>XRF data of Lower Bakken Shale and Pronghorn Member for eight wells</td>
<td>H:\ Dipanwita Thesis \Additional data</td>
</tr>
</tbody>
</table>

Table B.5: Table listing the file description for selected published papers and conference presentations during the PhD curriculum.

<table>
<thead>
<tr>
<th>File name</th>
<th>Description</th>
<th>Directory location</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB-D</td>
<td>Mixed Siliciclastic-Carbonate System of “D” Facies in the Bakken Formation, Williston Basin</td>
<td>H:\ Dipanwita Thesis \Additional data</td>
</tr>
</tbody>
</table>
APPENDIX C: XRF MEASUREMENT QUALITY ASSURANCE AND QUALITY CHECK

Chapter-3 of this thesis used elemental concentration data for chemostratigraphic analysis of the Upper Bakken Shale (UBS). XRF measurements were performed in this study using the Niton XL3t GOLDD+ handheld energy dispersive x-ray fluorescence (ED-XRF) analyzer in the TAG mode. In this appendix, procedures for the quality control and quality check (QA/QC) of these XRF measurements are described. Firstly, the samples used for QA/QC evaluation and their preparation steps are described. Thereafter, the evaluation steps and results for the optimum time required for achieving the maximum precision for XRF measurements are elaborated upon. Finally, the steps and results for XRF measurement reproducibility and repeatability are described.

8.1 Sample Preparation

Thirteen core-chips were collected from the core Roberts Trust 1-13H (RT) from the North Dakota Geological Survey (NDGS) Core Repository Center in Grand Forks, ND. The location, API, and other details of the core RT are given in Table 3.1. The core-chips were cleaned with deionized water to remove salt crust and/or drilling mud residues, and subsequently, the samples were air dried for 24 hours. The cleaned samples were crushed by mortar and pestle to 200-mesh size powder. About 5g aliquots of the powdered samples were used for determining major, minor and trace element concentrations by SGS Mineral Services, Canada. This involved performing ICP-AES and ICP-MS analyses after sodium peroxide fusion of the powdered aliquots (SGS method GE ICM90A). Around 15g aliquots of the powdered samples were used for making UBS matrix-specific standard cups, which is shown in Figure C.1, using the methodology described by Hall et al. (2011). The inventory description of the standard cups used in this study is as follows: ThermoPlastic® Seal Venting, External Overflow Reservoirs, Single Open End, 1.22" O.D. X 0.87" High. The standard cups were filled with powdered aliquots and covered with Mylar™ sheets, which allowed multiple uses by preventing spilling and contamination. The inventory details of the Mylar™ sheets used in this study are as follows: Mylar® 2.5μm 3.0" SpectroMembrane® Thin-Film Sample Supports, 0.1 mm thick, 76.2mm perforation.
Figure C.1: Photograph showing two of the thirteen UBS-matrix specific sample standard cups, which were used in this study for XRF measurement QA-QC purpose.

8.2 Optimal Detection Time

The precision of element concentration measurements using handheld XRF instruments depends on detection time. In general, longer detection times give more precise measurements. The handheld XRF instrument used in this study reports the measurement error as two standard deviations (2σ), which is equivalent to a 95% confidence interval. The optimum detection time for the sample-type (organic-rich shale samples in case of this study) is obtained by repeating measurements and gradually increasing the detection time. Both absolute measurements and error (2σ) show asymptotic trends with detection time, and at the optimum time, the absolute concentration values get stabilized, and error decreases to residual error or the instrument’s detection limit. Moreover, by appropriately changing the detection time (DT) for four different excitation filters (Main, Low, High, and Light), the detection precision for various elements can be optimized in the Niton XRF. Optimizing the Light filter DT increases the detection precision of Mg (atomic number 12) through Cl (17), whereas the measurement precision of K (19) up to Cr (24) is optimized by changing the Low filter DT. The Main filter DT is used to optimize the measurement precision of Mn (25) through Bi (83), whereas the changing the High filter DT optimizes the detection precision of Ag (47) through Ba (56) (Thermo Fisher Scientific, 2014). Kocman (2014) used the Niton ED-XRF, which was also used in this study, for XRF measurements of the samples from the Bakken Formation and suggested that correlative trends are achieved at both 75 seconds (Main-15s, Low-15s, High-15s, Light-30s) and 120s (Main-30s, Low-30s, High-30s, Light-30s). Nakamura (2015) used the same instrument to study the Niobrara Formation and suggested that the optimum detection time for the Niobrara samples is 180s (Main: 30s, Low: 30s; High: 30s and Light: 90s).

The optimal DT for four excitation filters for UBS samples was determined by performing multiple measurements on the UBS matrix-specific standard cup RT-UBS-20. As shown in Figure C.2, these measurements involved following four different excitation filters sequences (EFS): 1) Main-15s, Low-15s,
High-15s, Light-30sec (Total DT-75s); 2) Main-30s, Low-30s, High-30s, Light-30sec (Total DT-120s); 3) Main-30s, Low-30s, High-30s, Light-90sec (Total DT-180s); and 4) Main-60s, Low-60s, High-60s, Light-90s (Total DT-270s). Five measurements were taken for each of these four EFS; therefore, in total twenty measurements were taken on the RT-UBS-20 standard cup. In this study, the measurement precision for each element is represented by the relative standard deviation, ($\sigma/\mu$) or RSD, which allows the comparison of measurement precision for different elements used in this study. The results for the DT optimization analysis are shown in Figure C.3, which includes plots for absolute concentration and RSD for elements Si, Al, K, Mo, U, and V. Figure C.3 shows that for EFS-2 (total DT-120s), the absolute concentration is higher, and RSD is smaller for all elements except for light elements Al and Si, in comparison to that in EFS-1 (total DT-75s). However, for EFS-3 (total DT-180s), the absolute concentration is higher, and RSD is smaller for Al and Si, in comparison to that in EFS-2 (total DT-120s). Finally, for EFS-4 (total DT-270s), both absolute concentration and RSD show little change in comparison to that in EFS-3 (total DT-180s). The significance of these results is illustrated in Figure C.2, which suggests that the optimum DT for K, Mo, U and V is 120s and that for light elements Si and Al is 180s. Therefore, this analysis suggests that the optimum DT for UBS is 180s.

Figure C.2: Optimal detection time for the Main, Low, High and Light filters for UBS is shown schematically. The effect of an increase in the detection duration on the measurement of absolute concentration and the error (2$\sigma$) also shown.
Figure C.3: The change in elemental concentration measurement and relative error for different excitation filters sequences (EFS) for Si, Al, K, Mo, U, and V is shown. Optimum time and EFS is characterized by stabilization of elemental concentration readings and relative error values. For light elements Si and Al, the optimum DT for the UBS samples with Niton handheld XRF were 180s and that for other elements was 120s.

8.3 Reproducibility Test and XRF Measurement Validation

Niton measurements were validated by comparing XRF measurements with inductively coupled plasma mass spectrometry (ICP-MS) measurements. ICP-MS measurements were performed on all thirteen aliquots of powder, with which the thirteen UBS standard cups were made. XRF measurements were performed on all thirteen UBS standard cups at EFS-3 (Total DT 180s) in TAG mode. Theoretically, the concentration of elements measured by two methods are termed reproducible, if the straight line-fit in the crossplot between the measurements have the regression-fit coefficient ($R^2$) and slope ($m$) close to one, and the y-intercept close to zero. Therefore, in this study the elements for which, $R^2 > 0.9$, $0.9 < m < 1.1$ and $c=0$, XRF data were considered as suitable for both quantitative and qualitative analyses. Elements for which, $0.75 < R^2 < 0.9$, and $0.8 < m < 1.2$, XRF data were used for semi-quantitative and qualitative analyses. Finally, elements for which, $0.6 < R^2 < 0.75$, $0.5 < m < 2.0$, XRF data were used only for qualitative analyses. Figure C.4 shows the crossplot between these XRF and ICP-MS measurements on thirteen UBS standard cups for elemental concentrations of major and trace elements. Table C.1 summarizes the results of the straight-line regression fitting on the crossplots for elements and their analyses applications (quantitative, semi-quantitative, and qualitative) in this study. For qualitative analyses of the XRF data, the elements with a positive correlation and $R^2$ above 0.6 were observed to be suitable for trend reproducibility,
as it will be later shown. Moreover, as shown in Figure C.5, the log view shows similar stratigraphic trends between the ICP-MS and XRF measurements, which further validates the applicability of XRF measurements.

Figure C.4: Niton-ICP/Element Analyzer cross plots for eighteen selected elements showing the relationships between Niton measured elemental concentrations and laboratory-grade measurements made by ICP-MS/ICP-OES and element analyzer. Best-fit linear regression lines are shown with associated \( R^2 \) values for each plot. For elements Al, Si, Ca, Fe, S, Mo, and U have a zero y-axis intercept.
Table C.1: Table for the coefficient of regression ($R^2$) and slope ($m$) for the best-fit linear regression lines for the Niton-ICP/Element Analyzer cross plots for eighteen selected elements showing the relationships between Niton measured elemental concentrations and laboratory-grade measurements made by ICP-MS/ICP-OES and element analyzer. The XRF-measured concentration of elements which has been used quantitatively and semi-quantitatively in Chapter 3 are highlighted in red.

<table>
<thead>
<tr>
<th>Element</th>
<th>$R^2$</th>
<th>Slope/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.66</td>
<td>0.3</td>
</tr>
<tr>
<td>Al</td>
<td>0.67</td>
<td>0.65</td>
</tr>
<tr>
<td>Si</td>
<td>0.71</td>
<td>0.87</td>
</tr>
<tr>
<td>S</td>
<td>0.87</td>
<td>0.9</td>
</tr>
<tr>
<td>K</td>
<td>0.83</td>
<td>0.62</td>
</tr>
<tr>
<td>Ca</td>
<td>0.98</td>
<td>1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.6</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe</td>
<td>0.96</td>
<td>1.32</td>
</tr>
<tr>
<td>U</td>
<td>0.95</td>
<td>1.26</td>
</tr>
<tr>
<td>V</td>
<td>0.85</td>
<td>0.79</td>
</tr>
<tr>
<td>Mo</td>
<td>0.99</td>
<td>1.18</td>
</tr>
<tr>
<td>Ni</td>
<td>0.92</td>
<td>0.52</td>
</tr>
<tr>
<td>Cu</td>
<td>0.91</td>
<td>0.65</td>
</tr>
<tr>
<td>Zn</td>
<td>0.99</td>
<td>0.64</td>
</tr>
<tr>
<td>Sr</td>
<td>0.99</td>
<td>0.91</td>
</tr>
<tr>
<td>Mn</td>
<td>0.71</td>
<td>0.67</td>
</tr>
<tr>
<td>Rb</td>
<td>0.75</td>
<td>0.42</td>
</tr>
<tr>
<td>Th</td>
<td>0.57</td>
<td>1.21</td>
</tr>
</tbody>
</table>

Figure C.5: Profile of the representative suite of major and trace elements comparing Niton XRF and ICP-MS measurements. Visual identification of the elemental trend between the Niton XRF and ICP-MS measurement show consistency.
8.4 Repeatability Test

The repeatability of the XRF measurements was analyzed by following the procedure outlined by Fisher et al. (2014) and Nakamura (2015). A repeatability test was performed at eleven UBS core samples from well RT, and at each depth, measurements were repeated five times with the detection time of 180 seconds. The procedures for taking XRF measurement in TAG mode are described in Section 3.3.2. Five measurements at sample depth x were performed in different test-runs, such that each run includes measurements at all eleven depths before repeating measurements at sample depth x. Table C.2 lists the concentration of trace elements (Mo, U, Ni and V) and major elements (Si, Al, K, Ca, Fe, Ca, S, Ti), which were used in this study for all five runs on each of the eleven samples (represented by their depth). The result of the repeatability test is shown in Figure C.6, which plots depth profiles of concentration for trace and major elements for eleven UBS samples from well RT for each test runs. Repeatability of the XRF measurement using Niton handheld XRF in TAG mode is confirmed by Figure C.6, which shows consistency in both major inflections and concentration changes for five test-runs.

Table C.2: The results for element concentration measurements using Niton handheld XRF for the repeatability test is listed. The table lists the results for the concentration of trace elements and major element, which were used in this study, for all five runs for each of the eleven samples (represented by their depth).

<table>
<thead>
<tr>
<th>Depth</th>
<th>Test Run</th>
<th>Mo ppm</th>
<th>U ppm</th>
<th>Ni ppm</th>
<th>Fe %</th>
<th>V ppm</th>
<th>Ti %</th>
<th>Ca %</th>
<th>K %</th>
<th>S %</th>
<th>Al %</th>
<th>Si %</th>
<th>Mg %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10651</td>
<td>Run-1</td>
<td>8.34</td>
<td>17.5</td>
<td>127.3</td>
<td>2.00</td>
<td>634.35</td>
<td>0.29</td>
<td>7.11</td>
<td>2.48</td>
<td>0.72</td>
<td>3.71</td>
<td>20.91</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>7.27</td>
<td>14.9</td>
<td>142.1</td>
<td>2.02</td>
<td>626.92</td>
<td>0.29</td>
<td>7.08</td>
<td>2.48</td>
<td>0.73</td>
<td>3.80</td>
<td>20.97</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Run-3</td>
<td>8.62</td>
<td>16.6</td>
<td>147.8</td>
<td>2.02</td>
<td>673.24</td>
<td>0.29</td>
<td>7.14</td>
<td>2.48</td>
<td>0.72</td>
<td>3.80</td>
<td>21.06</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>Run-4</td>
<td>6.21</td>
<td>18.4</td>
<td>149.1</td>
<td>2.00</td>
<td>646.12</td>
<td>0.29</td>
<td>7.12</td>
<td>2.48</td>
<td>0.70</td>
<td>3.76</td>
<td>21.14</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Run-5</td>
<td>6.34</td>
<td>18.2</td>
<td>153.1</td>
<td>2.05</td>
<td>663.46</td>
<td>0.29</td>
<td>7.12</td>
<td>2.44</td>
<td>0.72</td>
<td>3.77</td>
<td>21.10</td>
<td>0.78</td>
</tr>
<tr>
<td>10651.5</td>
<td>Run-1</td>
<td>44.53</td>
<td>20.9</td>
<td>214.1</td>
<td>2.30</td>
<td>1209.59</td>
<td>0.32</td>
<td>5.40</td>
<td>2.71</td>
<td>1.02</td>
<td>4.62</td>
<td>22.21</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>45.66</td>
<td>22.1</td>
<td>222.5</td>
<td>2.35</td>
<td>1223.69</td>
<td>0.32</td>
<td>5.40</td>
<td>2.70</td>
<td>1.01</td>
<td>4.31</td>
<td>22.32</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Run-3</td>
<td>48.12</td>
<td>22.1</td>
<td>234.6</td>
<td>2.35</td>
<td>1187.89</td>
<td>0.32</td>
<td>5.39</td>
<td>2.69</td>
<td>1.02</td>
<td>4.24</td>
<td>22.25</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>Run-4</td>
<td>46.63</td>
<td>22.6</td>
<td>212.7</td>
<td>2.34</td>
<td>1221.04</td>
<td>0.32</td>
<td>5.37</td>
<td>2.69</td>
<td>1.01</td>
<td>4.34</td>
<td>22.23</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>Run-5</td>
<td>46.74</td>
<td>22.0</td>
<td>221.0</td>
<td>2.34</td>
<td>1227.70</td>
<td>0.32</td>
<td>5.38</td>
<td>2.74</td>
<td>1.01</td>
<td>4.32</td>
<td>22.43</td>
<td>0.78</td>
</tr>
<tr>
<td>10655.75</td>
<td>Run-1</td>
<td>20.11</td>
<td>18.2</td>
<td>208.7</td>
<td>1.91</td>
<td>877.79</td>
<td>0.32</td>
<td>7.15</td>
<td>2.48</td>
<td>0.67</td>
<td>4.45</td>
<td>23.36</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>19.88</td>
<td>16.8</td>
<td>200.6</td>
<td>1.88</td>
<td>896.09</td>
<td>0.32</td>
<td>7.12</td>
<td>2.50</td>
<td>0.68</td>
<td>4.42</td>
<td>23.41</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Run-3</td>
<td>19.04</td>
<td>18.6</td>
<td>230.3</td>
<td>1.89</td>
<td>930.41</td>
<td>0.33</td>
<td>7.13</td>
<td>2.48</td>
<td>0.68</td>
<td>4.42</td>
<td>23.43</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>Run-4</td>
<td>19.84</td>
<td>21.3</td>
<td>194.1</td>
<td>1.89</td>
<td>927.55</td>
<td>0.33</td>
<td>7.09</td>
<td>2.46</td>
<td>0.67</td>
<td>4.45</td>
<td>23.52</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Run-5</td>
<td>19.18</td>
<td>17.8</td>
<td>190.5</td>
<td>1.90</td>
<td>866.29</td>
<td>0.33</td>
<td>7.13</td>
<td>2.49</td>
<td>0.67</td>
<td>4.47</td>
<td>23.45</td>
<td>1.06</td>
</tr>
<tr>
<td>10658</td>
<td>Run-1</td>
<td>23.21</td>
<td>24.5</td>
<td>174.6</td>
<td>2.42</td>
<td>716.24</td>
<td>0.26</td>
<td>5.14</td>
<td>2.34</td>
<td>1.04</td>
<td>3.48</td>
<td>22.32</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>22.08</td>
<td>25.9</td>
<td>175.5</td>
<td>2.41</td>
<td>721.01</td>
<td>0.26</td>
<td>5.15</td>
<td>2.32</td>
<td>1.03</td>
<td>3.51</td>
<td>22.33</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Table C.2 continued

<table>
<thead>
<tr>
<th>Run</th>
<th>10661</th>
<th>10663</th>
<th>10664</th>
<th>10666.5</th>
<th>10667.5</th>
<th>10668.5</th>
<th>10669.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-1</td>
<td>55.2</td>
<td>323.05</td>
<td>238.65</td>
<td>412.73</td>
<td>415.42</td>
<td>331.93</td>
<td>369.28</td>
</tr>
<tr>
<td>Run-2</td>
<td>54.58</td>
<td>322.41</td>
<td>241.08</td>
<td>345.03</td>
<td>409.56</td>
<td>333.07</td>
<td>367.41</td>
</tr>
<tr>
<td>Run-3</td>
<td>53.38</td>
<td>318.94</td>
<td>239.86</td>
<td>350.07</td>
<td>405.61</td>
<td>343.56</td>
<td>378.59</td>
</tr>
<tr>
<td>Run-4</td>
<td>54.15</td>
<td>324.2</td>
<td>239.86</td>
<td>345.03</td>
<td>409.56</td>
<td>333.07</td>
<td>367.41</td>
</tr>
<tr>
<td>Run-5</td>
<td>54.16</td>
<td>323.05</td>
<td>243.88</td>
<td>324.2</td>
<td>239.86</td>
<td>240.98</td>
<td>348.19</td>
</tr>
<tr>
<td>Run-1</td>
<td>10661</td>
<td>10663</td>
<td>10664</td>
<td>10666.5</td>
<td>10667.5</td>
<td>10668.5</td>
<td>10669.5</td>
</tr>
</tbody>
</table>
Figure C.6: Depth profiles of concentration show the repeatability test results for trace and major elements for eleven UBS samples (represented by sample depth) from well RT for each test runs. The error bars indicate the variability in elemental concentration measurement is for five test run for a sample of given depth. The red line connects the average of the five runs, whereas the blue line shows the spread of the measurement. Repeatability of the XRF measurement using Niton handheld XRF in TAG mode is confirmed by consistency in both major inflections and concentration changes for five test-run.
The percentage variability ($\sigma/\mu$) in the measurement of concentration an element for a sample in five repeat-runs was determined by normalizing the standard deviation ($\sigma$) of the reading with average $\mu$. The variability results are shown in Figure C.7 in a heat-map format, in which the cooler color (green) and lower percentages indicates better repeatability. The last row in the heat-map in Figure C.7 shows the average of the variability for the eleven UBS samples from well RT, which shows that the measurement of trace element using Niton handheld XRF is repeatable within an average range of 2-5%, whereas for major elements, repeatability is within 0.2-2%.

<table>
<thead>
<tr>
<th>Depth (ft)</th>
<th>Mo</th>
<th>U</th>
<th>Ni</th>
<th>V</th>
<th>Fe</th>
<th>Ti</th>
<th>Ca</th>
<th>K</th>
<th>S</th>
<th>Al</th>
<th>Si</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>10651</td>
<td>13.2%</td>
<td>8.4%</td>
<td>7.0%</td>
<td>3.0%</td>
<td>1.0%</td>
<td>1.1%</td>
<td>0.3%</td>
<td>0.7%</td>
<td>0.6%</td>
<td>1.6%</td>
<td>0.5%</td>
<td>16.0%</td>
</tr>
<tr>
<td>10651.5</td>
<td>2.9%</td>
<td>2.8%</td>
<td>3.9%</td>
<td>1.3%</td>
<td>0.8%</td>
<td>0.9%</td>
<td>0.2%</td>
<td>0.7%</td>
<td>0.4%</td>
<td>1.0%</td>
<td>0.4%</td>
<td>9.3%</td>
</tr>
<tr>
<td>10655.75</td>
<td>2.4%</td>
<td>9.0%</td>
<td>7.7%</td>
<td>3.2%</td>
<td>0.6%</td>
<td>1.3%</td>
<td>0.3%</td>
<td>0.5%</td>
<td>0.6%</td>
<td>0.4%</td>
<td>0.3%</td>
<td>5.1%</td>
</tr>
<tr>
<td>10658</td>
<td>3.5%</td>
<td>3.9%</td>
<td>5.8%</td>
<td>1.9%</td>
<td>0.3%</td>
<td>1.1%</td>
<td>0.4%</td>
<td>0.5%</td>
<td>0.3%</td>
<td>0.6%</td>
<td>0.3%</td>
<td>14.6%</td>
</tr>
<tr>
<td>10661</td>
<td>1.2%</td>
<td>8.7%</td>
<td>5.4%</td>
<td>4.2%</td>
<td>0.7%</td>
<td>1.7%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>21.1%</td>
<td>2.0%</td>
<td>0.2%</td>
<td>27.0%</td>
</tr>
<tr>
<td>10663</td>
<td>0.6%</td>
<td>4.4%</td>
<td>2.7%</td>
<td>1.4%</td>
<td>0.2%</td>
<td>1.6%</td>
<td>1.3%</td>
<td>1.0%</td>
<td>0.3%</td>
<td>1.4%</td>
<td>0.2%</td>
<td>10.5%</td>
</tr>
<tr>
<td>10664</td>
<td>0.8%</td>
<td>5.0%</td>
<td>7.8%</td>
<td>2.3%</td>
<td>0.4%</td>
<td>2.0%</td>
<td>0.7%</td>
<td>0.3%</td>
<td>0.5%</td>
<td>2.3%</td>
<td>0.8%</td>
<td>19.7%</td>
</tr>
<tr>
<td>10666.5</td>
<td>1.0%</td>
<td>5.1%</td>
<td>2.1%</td>
<td>1.3%</td>
<td>0.7%</td>
<td>0.7%</td>
<td>0.6%</td>
<td>1.1%</td>
<td>0.6%</td>
<td>0.8%</td>
<td>0.5%</td>
<td>7.5%</td>
</tr>
<tr>
<td>10667.5</td>
<td>1.0%</td>
<td>4.0%</td>
<td>2.6%</td>
<td>1.0%</td>
<td>0.6%</td>
<td>2.1%</td>
<td>0.9%</td>
<td>0.3%</td>
<td>0.2%</td>
<td>0.6%</td>
<td>0.3%</td>
<td>10.4%</td>
</tr>
<tr>
<td>10668.5</td>
<td>1.3%</td>
<td>4.9%</td>
<td>2.4%</td>
<td>0.6%</td>
<td>0.3%</td>
<td>1.4%</td>
<td>0.6%</td>
<td>0.8%</td>
<td>0.8%</td>
<td>2.0%</td>
<td>0.5%</td>
<td>22.0%</td>
</tr>
<tr>
<td>10669.5</td>
<td>1.3%</td>
<td>3.0%</td>
<td>7.0%</td>
<td>1.5%</td>
<td>0.2%</td>
<td>1.1%</td>
<td>1.1%</td>
<td>1.1%</td>
<td>0.4%</td>
<td>1.1%</td>
<td>0.6%</td>
<td>13.0%</td>
</tr>
<tr>
<td>Average</td>
<td>2.7%</td>
<td>5.4%</td>
<td>5.0%</td>
<td>2.0%</td>
<td>0.5%</td>
<td>1.3%</td>
<td>0.6%</td>
<td>0.7%</td>
<td>2.3%</td>
<td>1.3%</td>
<td>0.4%</td>
<td>14.1%</td>
</tr>
</tbody>
</table>

Figure C.7: Repeatability of the XRF element concentration measurements for the eleven UBS samples from core RT is shown in the heat-map, in which the numbers represent the variation ($\sigma/\mu$). The color-scale and the bar show the relative degree of repeatability for element concentration measurement by XRF. Cooler color (green) and lower percentages indicate better repeatability. Mg (Atomic No.-12), which was not used in this study, in general, shows poor repeatability because hand-held XRF and TAG mode used in this study is not suitable for detecting elements lighter than Al (Atomic No.-13).
APPENDIX D: CHEMOSTRATIGRAPHIC PROFILES AND CORRELATIONS

Chemostatigraphic profiles for sixteen wells and chemosтратigraphic correlation for cross-sections I and cross-section II used in Chapter-3 are included in this appendix.
Well: Miller 34X-9

Well: Sidonia 1-06H

Well: Bullwinkle Yahoo

183