Chemostratigraphy and facies analysis of the Hare Indian Formation in the Mackenzie Mountains and Central Mackenzie Valley, Northwest Territories, Canada

by

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Abstract

The Hare Indian Formation, a Givetian aged organic rich mudstone, is the basal formation of the Horn River Group in the Northwest Territories, Canada. It is subdivided into two members: the basal Bluefish Member and the upper Bell Creek Member. Recent interest in unconventional resource plays sparked interest in the Hare Indian Formation and the overlying Canol Formation as targets for exploration. The Kee Scarp Reef near Norman Wells has produced oil sourced from the Canol Formation since the 1920s. There are aspects of the depositional model, paleoredox conditions and sequence stratigraphy of the Hare Indian Formation that are not well understood.

Here, a detailed examination of the sedimentology and sequence stratigraphy of the Hare Indian Formation is made. High-resolution portable X-ray fluorescence (pXRF) data is collected from four cores in the Central Mackenzie Valley and three outcrop locations in the Mackenzie Mountains. The pXRF data is used as geochemical proxies using elements like Al, Ti, K, Si, Ca, Mg, Mo and V to interpret terrigenous input and paleoredox conditions in order to construct a chemostratigraphic framework for the Hare Indian Formation. The results suggest a maximum flooding surface in the Bluefish Member and a maximum regressive surface at the top of the Bell Creek Member. Relative sea level transgression occurred during the onset of the deposition of the Bluefish Member, followed by relative sea level regression throughout the remaining deposition of the Hare Indian Formation. Redox sensitive trace metals support intermittent euxinia throughout deposition. The pXRF data is also used to interpret five

distinct chemofacies based on three cores using agglomerative hierarchical clustering (AHC) to compare to more traditional lithofacies and microfacies models using the same cores. Different facies types correspond locally, though different classification schemes have particular uses. Chemofacies are particularly useful in producing a high-resolution understanding of the geochemical ratios present in a succession, tracing the relative amounts of clay or silica. Microfacies show sedimentary processes and biogenic activity. The best use of facies models in fine-grained successions are often in conjunction with one another.

Preface

This thesis is original work by Brette Harris and has involved collaboration with other researchers. This work was completed in conjunction with Maya LaGrange's PhD thesis, which focuses on the geochemical properties and chemostratigraphy of the Canol Formation, and Sara Biddle's MSc thesis, which focuses on the microfacies and depositional models for the Hare Indian and Canol Formations.

Chapter 2 and Chapter 3 of this thesis will be submitted for publication.

“We'll be saying a big hello to all intelligent lifeforms everywhere and to everyone else out there, the secret is to bang the rocks together, guys.”

— Douglas Adams, The Hitchhiker's Guide to the Galaxy

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The past four years have been an incredible adventure, made possible only by all the people I have met along the way. I have spent many days in the basement of the South Academic Building with a pXRF analyser for company, but I have also been to the mudflats of Willapa Bay, the worm reef at the Baie Mont-St-Michel, and the Mackenzie Mountains. Plus, I experienced a hurricane in Moncton and giant Jenga at The Raven in Yellowknife. I am privileged enough to have had these experiences with everyone in the Ichnology Research Group: Carolyn, Aimee, Donald, Eric, Dave, Derek, Jared, Celine, Dan, Matt, Rob, Reed, Qi, Ryan, Chundi, Chenyang, Arzu, Scott and many others. Beyond the IRG, I am grateful to have met a great number of inspiring friends in the department, through ATLAS, GSA, and the AAPG student group.

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1 Introduction

1.1 Overview

The Hare Indian Formation is a Devonian aged, organic-rich mudstone located in the Northwest Territories. It is the oldest formation in the Horn River Group, a mixed clastic and carbonate succession spanning the Givetian to the Frasnian. The Horn River Group is of interest due to technological advances in the development of unconventional resource plays, as both the Hare Indian and Canol Formations have potential as oil producing shales. A sequence stratigraphic framework can be of use in predicting basin architecture and reservoir quality.

While some studies have applied the principles of sequence stratigraphy to the Horn River Group (e.g. Muir and Dixon, 1985) and others have begun to incorporate geochemistry in the form of chemofacies and paleoredox indicators (e.g. Kabanov, 2019; Pyle and Gal, 2016), no studies have integrated the two in an attempt to form a sequence stratigraphic framework. While sequence stratigraphy can be applied in fine-grained successions, the subtlety of sedimentological and lithological changes can make interpretations more difficult. The integration of geochemical data can aid or strengthen these interpretations.

1.2 Geological Background

The Horn River Group was deposited over the Middle Devonian, when the Northern Canadian Mainland Sedimentary Basin was a divergent passive margin setting (Morrell, 1995; Morrow, 2012; Pugh, 1983). The Horn River Group comprises mixed clastic-carbonate successions associated with environments ranging from basinal and basin margin, to platform and reef complexes (Muir and Dixon, 1984). It was deposited in a marine transgression that drowned the Eifelian shallow marine reef platforms: the Hume, Nahanni and Ogilvie Formations (Morrow, 2012). During the Givetian, carbonate production moved south, and the northern part of the basin was covered in fine siliciclastic material possibly derived from uplifts in the Selwyn Basin, coinciding with the Watt Mountain Regression (Morrow and Geldsetzer, 1988). Cretaceous and Paleocene uplift of the Mackenzie Arc during the Columbian and Laramide orogenies resulted in folding and thrusting of Paleozoic strata. This ended passive margin sedimentation, formed a foreland basin, and brought the Horn River Group to the surface in the modern-day Mackenzie Mountains (Law, 1971; Morrell, 1995; Morrow *et al.*, 2006).

The Horn River Group includes the Hare Indian Formation, The Ramparts Formation and the Canol Formation. The Hare Indian Formation is a Givetian-aged shale and limestone formation (Pyle and Gal, 2016; Uyeno, 1991). It overlies the Eifelian Hume Formation, a fossiliferous interbedded limestone. The Hare Indian Formation underlies the Givetian-Frasnian Ramparts and Canol Formations, except for the “dark facies” of the Bell Creek Member, which conodont dating suggests is age-equivalent to the Ramparts Formation (Gilbert, 1973; Pyle *et al.*, 2014; Pyle and Gal, 2016). The Canol Formation is an organic-rich, non-calcareous shale or mudstone unit (Norris, 1967). The Ramparts Formation is a carbonate succession split into three units: the ramp unit, the organic-rich Carcajou Member or marker, with as much as 7% total organic carbon (TOC), and the reef unit (Pyle and Gal, 2016).

The Hare Indian Formation is divided into two members: the Bluefish Member, an organic-rich, calcareous, fossiliferous shale unit and the Bell Creek Member, a variable grey, recessive, slightly calcareous shale unit interbedded with limestone, argillaceous limestone and siltstone (Pyle and Gal, 2016). The Bell Creek Member is often subdivided into either two or three facies or members (Kabanov and Gouwy, 2017; Pyle and Gal, 2016). In general, the Bell Creek is subdivided into a grey facies and a dark facies (Pyle and Gal, 2016). In terms of sedimentary structures, both the Bluefish and Bell Creek Members have massive appearing beds, planar and wavy laminae, both continuous and discontinuous, and pyrite nodules. There are fibrous calcite beds with cone-in-cone structures and calciturbidite beds observed in both core and outcrop in the Bluefish Member (Mackenzie, 1972). The Hare Indian Formation varies from less than 10 metres to more than 200 metres and is present as far north as the Anderson River, thinning eastward to at least the Snake River, northward towards Rumbly Creek, and as far south as the Ram River (Aitken, 1982; Basset, 1961; Tassonyi, 1969). The Bluefish Member has type II kerogen and TOC values ranging from 3% to 10%, while the Bell Creek Member has type II and type III kerogen and generally has TOC values of 3% or less, but occasionally up to 8% (Al-Aasm *et al.*, 1996; Haldari *et al.*, 2015; Pyle and Gal, 2016; Snowdon *et al.*, 1987).

The Hare Indian Formation has an impoverished, low-diversity fauna (Lenz, 1972). Fossils documented in the Hare Indian Formation include brachiopods (mainly *Atrypa* sp. and *Nudirostra* sp.), corals (*Favosites* sp.), *Tentaculites* sp., and *Styliolina* sp., acritarchs (*Leiosphaeridia* sp. and *Tasmanites* sp.) and ammonoids (Aitken *et al.*, 1982; Basset, 1961; Warren and Stelck, 1956; Tassonyi, 1969). Larger macrofauna are often concentrated near the base of the Bluefish Member.

The Hare Indian Formation is thought to have potential as an unconventional petroleum reservoir. The Horn River Group shales serve as a source rock for the Kee Scarp reefs at Norman Wells, which have produced over 274 million barrels of oil (NTGS and NEB, 2015). Reports link hydrocarbons produced at Norman Wells with the Canol Formation based on biological markers, though the Hare Indian Formation has the right conditions for hydrocarbon generation (Snowdon *et al.*, 1987). Vitrinite reflectance results have suggested that the entirety of the Horn River Group lies within the oil window and was buried during the Jurassic (Pyle *et al.*, 2014; Pyle and Gal, 2016). Markers suggest that bitumen recovered from the Hume Formation was generated in the Bluefish Member (Feinstein at al., 1988).

With the advent of unconventional resource plays, new interest has emerged regarding the reservoir potential of organic-rich shales in the Mackenzie region. The Horn River Group of the Northwest Territories is stratigraphically equivalent to the Evie Member of the Horn River Formation in northeast British Columbia, which is also considered a favourable prospect for oil and gas, and Facies F of the Pine Point Formation (Snowdon *et al.*, 1987). According to a NTGS and NEB report, the Bluefish Member has upwards of 8% porosity and greater than 6% organic carbon (2015). The Bluefish Member also has low clay and high silica content, making it ideal for hydraulic fracturing. The total estimated oil in place in the Bluefish Member is 7.366 billion m3 (46.346 billion barrels) (NTGS and NEB, 2015). Since 2011, seven wells have been drilled in the Central Mackenzie Valley targeting the Horn River Group (the E-76, O-06, P-20, N-20, N-09, H-64 and I-78).

In addition to potential as a petroleum resource, the Bluefish Member has been considered a possible source of minerals of economic value due to the presence of mineralization including fluorite, barite, calcite and quartz (Macqueen *et al.*, 1975).

1.3 Study Area

The study area for this project includes the Central Mackenzie Valley (also referred to as the Mackenzie Plain) and the Mackenzie Mountains (Figure 1.1). Four cores are analysed: the MGM Shell East Mackay I-78 core (64.795°N, 128.594°W), the Husky Little Bear N-09 core (64.981°N, 126.519°W), the ConocoPhillips Canada COP Loon Creek O-06 Core (65.097°N, 127.008°W), and the ConocoPhillips Canada COP Mirror Lake N-20 core (64.997°N, 126.800°W). Three outcrops are analysed: the Mountain River outcrop (65.23°N, 128.594°W), the West Powell Creek outcrop (65.277°N, 128.786°W), and the Dodo River outcrop (65.008°N, 127.344°W).

1.4 Previous Work

1.4.1 Nomenclature

The Hare Indian Formation was first described by Kindle and Bosworth as “the Hare Indian shale”, a calcareous shale unit with interbedded limestone and rare fossils (1921). The term “Horn River Group” originates from Whittaker’s report of a shale unit at Horn River (1921). In an attempt to simplify Devonian nomenclature, Hume and Link (1945) renamed the “Hare Indian shales” the “Middle Ramparts shale member”. Crickmay (1957) later suggested that the “Hare Indian shales” and the “Lower Fort Creek shales” (now the Canol Formation) were the same unit. During World War II, Canol project geologists frequently misidentified the Hare Indian Formation as the “Lower Fort Creek shale” (Canol Formation) (Tassonyi, 1969). As such, in literature predating the 1960s, the Hare Indian Formation is referred to as the “Hare Indian shale”, the “Middle Ramparts shale member”, and in some cases: the “Lower Fort Creek shale”. In 1961, Basset formally proposed the name Hare Indian Formation replace “Hare Indian shale” for the greenish-grey calcareous shale unit containing argillaceous limestone beds with a dark grey bituminous basal bed. Since Basset (1961), the name Hare Indian Formation has been widely accepted and the criteria for its definition has been further resolved (Caldwell, 1964; Tassonyi, 1969).

The name Bluefish Member was formalized by Pugh (1984) with the type section moving from Bluefish Creek to Powell Creek. The “upper grey shale member” was later formally named the Bell Creek Member and Mountain River was designated the type section for the entirety of the Horn River Group, due to improved exposure (Pyle and Gal, 2016). In addition, the authors suggested a supplementary reference section for the Bell Creek Member at Carcajou River due to the heterogenous nature of the unit. A different study attempts to separate the “upper grey shale member” of the south into two members rather than facies: The Francis Creek Member (grey shale) and the Prohibition Creek Member (dark shale), which together are laterally equivalent to the northern Bell Creek Member (Kabanov and Gouwy, 2017).

1.4.2 Sedimentology

The Hare Indian Formation has two members: The Bluefish member: the lower bituminous, calcareous, laminated black shale unit; and the Bell Creek Member: the upper grey-green calcareous shale with interbedded thin limestone beds (Tassonyi, 1969).

The Bluefish Member, the “spore-bearing” unit, was described as dark, “chocolate-black”, bituminous, variably calcareous and non-calcareous shales commonly containing well preserved trilete spore cases, *Tentaculites* sp. and *Styliolina* sp., brachiopod shell fragments and spines (sometimes pyritized), rare carbonate concretions and pyrite nodules (Muir and Dixon, 1984). Limestone beds in the Bluefish Member vary from lime mud beds to grainstone beds, often with abundant *Tentaculites* sp. and *Styliolina* sp. (Pyle and Gal, 2016). Towards the base of the Bluefish, there are beds containing thin, persistent fibrous calcite beds with cone-in-cone structures ranging from 2 to 7 centimetres thick that extend as far west as 132°W (Mackenzie, 1972). The origin of these beds is somewhat contested, although cone-in-cone structures are often associated with deep burial diagenesis. Muir (1988) suggested that the calcite beds are primary features because of shale inclusions within the beds. Mackenzie (1972) suggested that they formed in partly consolidated organic-rich mud, along a bedding plane close to the sediment-water interface because of physico-chemical environmental changes including temperature change, increased evaporation, change in sea level, or change in pH. Pyle and Gal (2016) reported these features as bed-oriented fibrous calcite veins. In addition, Gilman and Metzger (1967) suggested that cone-in-cone structures might form from syngenetic concretions of fibrous aragonite while surrounding clay is still soft. The aragonite later reverts to calcite. The trilete spore cases were later reidentified as *Leiosphaeridia* sp. and *Tasmanite* sp. acritarchs (Aitken *et al.*, 1982). The *Tentaculites* sp. and *Styliolina* sp. are often associated with thin, bituminous, crystalline limestone beds or sharp-based grainstone beds, more prevalent towards the base of the member (Tassonyi, 1969). In outcrop studies, these beds have been used to establish a westward paleocurrent based on cricoconarids at the base of these beds (Muir, 1988). Grainstone beds are thought to be due to pelagic mass kills caused by either short term water toxicity, variable productivity or low-density turbidity currents (Muir, 1988). Limestone beds decrease upwards through the Bluefish Member (Pyle and Gal, 2016). There are varying degrees of bioturbation reported throughout the Bluefish Member (Muir, 1988). The Bluefish Member ranges from less than 10 to 15 metres, with outliers as thick as 25 metres, however the Hare Indian Formation has been reported as thick as 400 m (Dixon, 1984; Morrow and Geldsetzer, 1988).

The upper member, the Bell Creek Member, was described as predominantly shale, with some interbeds of calcareous siltstone or argillaceous limestone (Tassonyi, 1969). The upper member is often greenish-grey or dark grey, and in some places bituminous, with very fine mica and calcareous grains (Pugh, 1983). There are also reports of variable bioturbation throughout the Bell Creek Member (Muir, 1988). There are fewer tentaculitids in the Bell Creek Member, and more ostracods up section (Braun, 1966). Tassonyi (1969) reported the upper member as being of variable thickness, averaging 200 metres. The Bell Creek member varies stratigraphically; where the Ramparts Formation overlies the Hare Indian, the unit is consistent with its typical definition (greenish-grey mudstone or shale) and often thicker (upwards of 100-150 metres), however where the Ramparts is absent, the unit is dark grey and more similar sedimentologically to the Canol Formation and Bluefish Member (Kabanov and Gouwy, 2017; Pyle and Gal, 2016). This change is suggested to occur at 65°20’N (Basset, 1961; Kabanov and Gouwy, 2017; Pugh, 1993). The Bell Creek Member is quite recessive and is often covered by scree in outcrop or eroded completely.

The grey facies of the Bell Creek Member is characterised by interbedded greenish grey to dark grey, calcareous and non-calcareous, micaceous shale, calcareous siltstone and argillaceous limestone (Pyle and Gal, 2016). There are ten-centimetre graded beds from tentaculitids to lime mud, fish scales are common. Kabanov and Gouwy (2017) distinguished the grey facies, or Francis Creek Member, from the typical Bell Creek Member as lacking calcareous material and benthic shelly fossils and having no significant bioturbation. The dark facies of the Bell Creek Member is characterised by dark grey, calcareous and non-calcareous shale with lime mudstone and grainstone beds, flaky or platy pyritic brown or dark grey shale interbedded with limestone in thin, fining-upward beds with erosive bases (Pyle and Gal, 2016). Kabanov and Gouwy (2017) described the dark facies, or Prohibition Creek Member as rich in pyritic calcareous nodules with calcareous beds, no fauna or trace fossils, but rare pyritized sponge spicules. This facies is typically 19-32 m thick.

Geochemically, the Bluefish Member is characterised by high gamma-ray counts, high TOC values, uranium enrichment, negative silica-zirconium ratios, higher calcium oxides, high redox-sensitive element enrichment and high amounts of terrigenous oxides (Pyle and Gal, 2016). The Bell Creek Member grey facies is characterised by low gamma-ray counts, low TOC values, lower uranium concentrations than the Bluefish Member, high amounts of terrigenous oxides, higher thorium-uranium ratios that the Bluefish Member (suggesting higher clay and terrigenous input relative to organic matter), more biogenic silica than the Bluefish Member but less than the Canol Formation, and elevated redox sensitive elements. The dark facies is characterised by high TOC values, elevated uranium concentration, more terrigenous oxides than the Bluefish Member or Canol Formation, and lower potassium and thorium concentration than the Canol Formation (Kabanov and Gouwy, 2017; Pyle and Gal, 2016). SiO2/Zr ratios suggest mainly terrigenous silica in the Hare Indian Formation and more biogenic silica in the Canol Formation, though there is more silica in parts of the Bluefish Member than would be expected from purely terrigenous input. The Hare Indian Formation is distinguished mineralogically from the Canol Formation by increased mixed-layer clays and chlorite, more abundant carbonate minerals and less abundant quartz (Pyle and Gal, 2016).

1.4.3 Contacts

The lower contact with the Hume Formation is sharp and conformable (Aitken *et al.*, 1982; Basset, 1961; Pyle and Gal, 2016; Tassonyi, 1969; Gilbert, 1973). This contact is interpreted as a rapid shift from normal, shallow marine conditions to a euxinic environment (Tassonyi, 1969). Some studies reported an erosional surface or hardground between the Hume Formation and the Bluefish Member however, conodont analysis suggests that there was no meaningful gap in time between the cessation of Hume Formation deposition and the beginning of Bluefish Member deposition (Kabanov and Gouwy, 2017).

The contact between the Bluefish Member and the Bell Creek Member can be difficult to recognise. In early research, the two are distinguished based mostly on colour change, from dark and bituminous to grey or green-grey and non-bituminous (Pugh, 1983). The contact is described as gradational from dark grey shale to silty shale and defined as the first appearance of argillaceous limestone interbedded with silty shale (Pyle and Gal, 2016). In the case of the dark facies, the Bluefish Member to Bell Creek Member contact is picked often based on changes in weathering: from dark grey and flaky Bluefish Member to dark grey, brownish grey and flaky or platy (Pyle and Gal, 2016). In addition, the nature of the limestone beds changes from nodular to lenticular in the Bluefish

Member to thin beds in the Bell Creek Member. These types of changes are not always present, especially in core, but the contact can also be picked at the top of a high gamma ray log trace.

The upper contact between the Bell Creek Member and the Ramparts Formation is usually sharp or gradational, and may be diachronous or conformable (Basset, 1961; Dixon, 1984; Gilbert, 1973; Pugh, 1983; Tassonyi, 1969). It has also been reported as interfingering with the lower Ramparts Formation (Pugh, 1983). Where the Canol Formation overlies the Hare Indian Formation, the contact is often gradational (Basset, 1961). It may be marked by a change in weathering from flaky weathering grey-black shale and limestone to siliceous dark grey-black shale (Pyle and Gal, 2016). The contact between these units is also determined based on changes in geochemistry. In western parts of the basin, the Canol Formation may overlie the Bluefish Member without any evidence of the Bell Creek Member (Pyle and Gal, 2016).

1.4.4 Depositional Environment and Sequence Stratigraphy

The Hare Indian Formation has been assigned several depositional settings over the years. Tassonyi (1969) suggested that the Hare Indian Formation was deposited as the result of a shallow marine clastic mud delta. Thinning of the Hare Indian Formation to the south and east is attributed to paleotopographic lows; in these areas, the darker, bituminous shales are associated with poorly oxygenated water at the flanks of a mud bank (Tassonyi, 1969). Snowdon *et al.* (1987) suggested slow sedimentation in anoxic or euxinic conditions in a deep (several 10s of metres), stratified water column. Morrow and Geldsetzer (1988) suggested that the Hare Indian Formation was deposited during a major transgression on the inner shelf and slope. Dixon (1984) suggested the Hare Indian Formation was deposited on a gradually shallowing slope environment. Muir *et al.* (1985) suggested shale clinoforms, with deposition from clay suspension and carbonate turbidite deposition.

The Bluefish Member is associated with anoxic or euxinic waters. This may be because of regional cut-off from open circulation due to north-eastern uplift or a stratified water column due to thermocline and salinity changes with depth resulting in reduced oxygen at greater depths (Muir, 1988). The Bluefish Member has been reported as a basinal facies, moving upwards into the basin margin facies in the Bell Creek Member (Muir and Dixon, 1984). The authors also addressed the calciturbidites, suggesting that they were deposited rapidly from an over-steepened slope, below the carbonate compensation depth, but quickly enough that they had little contact with undersaturated water. The Bell Creek Member may be a clinoform basin fill or deltaic shale lobes (Muir and Dixon, 1985).

Kabanov (2019) suggested an anoxic horizon based on molybdenum and uranium enrichment in the Bluefish Member that coincides with the Eifelian-Givetian boundary. This would be equivalent to the Kačák anoxic event in Europe and anoxic horizons of the Marcellus Formation in the Appalachian Basin, suggesting a global occurrence (Kabanov, 2019). It is proposed that greenhouse conditions expanded oxygen minimum zones on continental shelves worldwide, leading to coincident organic-rich mudrocks in different basins around the globe (Kabanov, 2019). This is hypothesised to be initiated by degassing from large igneous provinces (LIP).

Morrow and Geldsetzer found, in a regional study of the Canadian Cordillera, that there had been transgression during the deposition of the Hume Formation, regression during the Hare Indian Formation's deposition and further transgression during the deposition of the Ramparts and Canol Formations (1988). Williams (1987) found that the Horn River Group recorded a major transgression, a major regression and a subsequent major transgression controlled by cratonic subsidence rather than eustatic sea level changes. The Hume Nahanni and Lonely Bay carbonate platforms were drowned in the Keg River transgression and become sediment starved (Williams, 1987). The Watt Mountain regression occurred during the deposition of the Givetian strata, including the Hare Indian Formation and the Ramparts Formation. The Hare Indian Formation was the prodelta of a prograding westward delta at that time (Williams, 1987). The Swan Hills transgression resulted in conditions favourable for ensuing carbonate deposition.

Sequence stratigraphy has been applied to the Horn River Group by few studies. Muir (1988) identified shallowing-upwards cycles and correlated them across the basin. One "first order cycle" (cycles that are 100s of metres thick) is found in the Hare Indian Formation, several "second order cycles", (cycles that are 10-25 metres thick) indicating episodic relative sea level rise followed by periods of no change (Muir, 1988; Muir and Dixon, 1985). The mechanism behind this cyclicity is thought to be a combination of eustatic sea-level fluctuation and delta lobe switching resulting in progradation and regression (Muir, 1988).

1.4.5 Sediment Source

The sediment that formed the Hare Indian Formation is suggested to be sourced from Precambrian shield rocks to the East (Lenz, 1972). It is also noted that carbonate content increases upwards, eventually leading to reef build up (Lenz, 1972).

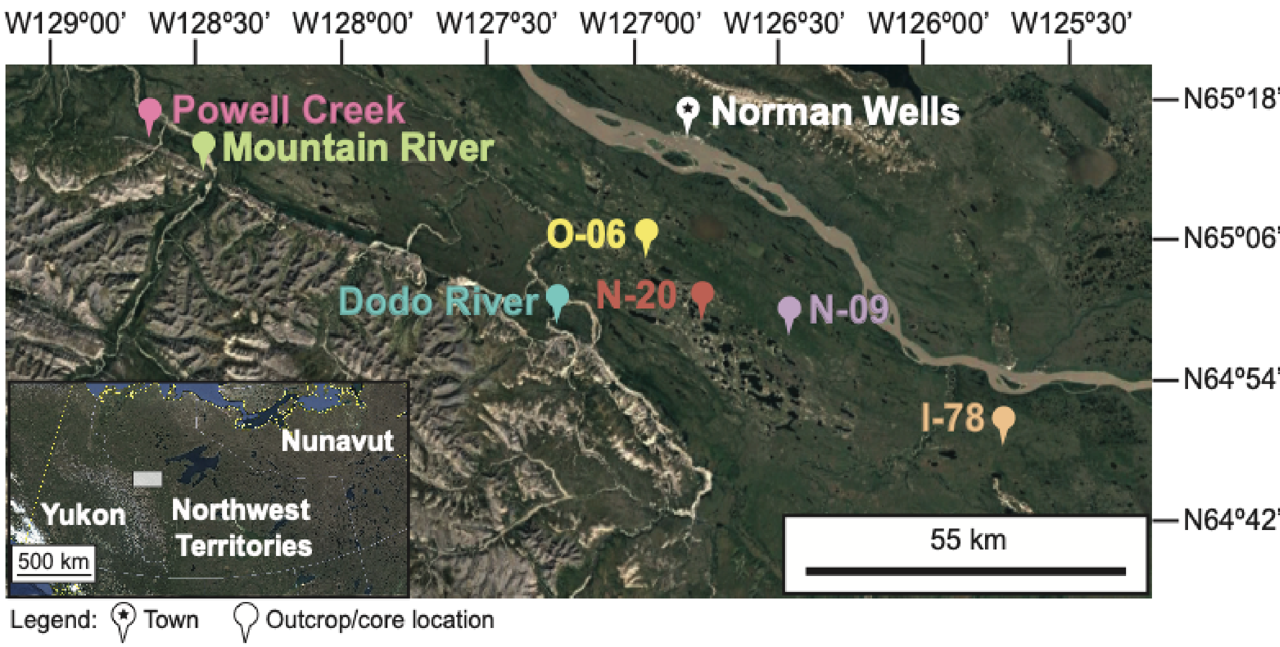

Figure 1.1 Map of the study area showing the location of the four cores and three outcrops considered in this study relative to Norman Wells, Northwest Territories, Canada. Images are modified from GoogleEarth.

2 Chemostratigraphy of the fine-grained Hare Indian Formation in the Mackenzie Mountains and Central Mackenzie Valley, Northwest Territories, Canada

2.1 Introduction

Unconventional reservoirs have become increasingly prevalent in the energy industry and, as such, organic-rich mudstones have become common targets of exploration and production in basins across North America. The Devonian Horn River Group is a potential unconventional reservoir located in the Northwest Territories, Canada. This group comprises three formations: The Hare Indian, the Ramparts, and the Canol Formations.

Conventional oil at Norman Wells is produced from the reefal part of the Ramparts Formation (Kee Scarp Reef) and sourced primarily from the Canol Formation (Snowdon *et al.,* 1987). The emergence of unconventional resource plays has renewed interest in the Horn River Group due to the unconventional potential in the Canol Formation and the Bluefish Member. The Bluefish Member has upwards of 8% porosity and often greater than 6% organic carbon while having low clay content, making it ideal for hydraulic fracturing (NTGS and NEB, 2015).

Recently, chemostratigraphy has emerged as a useful tool in order to better understand depositional environment and reservoir characteristics, particularly in organic-rich mudstone successions (*e.g.* Pearce *et al.,* 1999; Ratcliffe *et al.,* 2010, 2012; Sano *et al.*, 2013; Turner *et al.*, 2015, 2016; El Attar and Pranter 2016; Nyhuis *et al.*, 2016; Pyle and Gal, 2016; Playter *et al.*, 2018). Chemostratigraphy provides a means of correlation in successions where other datasets are of limited use (Pearce *et al.*, 2005; Ratcliffe *et al.*, 2012a). This method can be further used to correlate sequence stratigraphic surfaces and systems tracts from core and outcrop datasets using geochemical proxies such as terrigenous elements, redox-sensitive elements, and element ratios (Turner *et al.*, 2016; LaGrange *et al.,* 2020).

Using chemostratigraphic data collected from both core and outcrop locations, the purpose of this study is to investigate the sequence stratigraphy of the Hare Indian Formation. Additional objectives include interpretation of (1) the paleoredox conditions that prevailed in the basin at the time of deposition, (2) the relative proportions of different silica sources, and (3) variations in the relative abundance of terrigenous input, all of which give information about the nature of the depositional environment. This is achieved using data collected through high-resolution portable X-ray fluorescence (pXRF) and will broaden our understanding of environmental conditions in the present-day Central Mackenzie Valley and Mackenzie Mountains during the Givetian and shed further light on the reservoir potential of the Hare Indian Formation.

2.2 Geological Background

The Hare Indian Formation is a fine-grained, Givetian-aged mudstone unit located in western Northwest Territories, Canada (Pyle and Gal, 2016; Uyeno, 1991). First described by Kindle and Bosworth (1921), it was formalised by Basset (1961). It is part of the Horn River Group, a mixed clastic and carbonate succession deposited on a passive margin shelf and slope environment. Underlain by the Hume Formation, an Eifelian shallow marine reef platform, and overlain by the Imperial Formation, a Frasnian-Famennian silty shale and sandstone unit, the Horn River Group comprises the Hare Indian Formation, the Ramparts Formation and the Canol Formation (Figure 2.1) (Morrow, 2012). The Ramparts Formation includes three sub-units: the ramp unit, the organic-rich Carcajou Member, and the reef unit (Pyle and Gal, 2016) and the Canol Formation is an organic-rich, siliceous mudstone unit (Norris, 1967).

The Horn River Group was deposited during the Middle Devonian as part of the Northern Canadian Mainland Sedimentary Basin, located on the western passive margin of Laurussia, south of the equator (Morrell, 1995; Morrow, 2012; Pugh, 1983; Torsvik *et al.*, 2002). The cratonic shelf was stable from the Late Cambrian to the Middle Devonian (Pugh, 1983). During the Middle Devonian, clastic wedges began prograding westward over the Mackenzie Platform, forming the Horn River Group, starting with the Hare Indian Formation (Al-Aasm *et al.,* 1993). The succession was then deformed in the Late Cretaceous-Paleocene Laramide orogen (Norris and Yorath, 1981).

The Hare Indian Formation is divided into two members, the lower Bluefish Member and the upper Bell Creek Member (Pyle and Gal, 2016). Reported thicknesses of the Hare Indian Formation vary, ranging from 30 m to upwards of 125 m (Kabanov and Gouwy, 2017). In part owing to the changing definition of the Hare Indian Formation, some studies report the Hare Indian Formation as thick as 400 metres (Dixon, 1984; Morrow and Geldsetzer, 1988). In the study area, the Hare Indian ranged in thickness from 25 m to 45 m. The upper contact of the Hare Indian Formation with the Ramparts Formation is marked as a transition from recessive mudstone to resistant carbonate beds (Pyle and Gal, 2016). In this study, there are no occurrences of the Ramparts Formation, and the contact between the Bell Creek Member and the Canol Formation is more transitional. Here, the upper contact of the Hare Indian Formation with the Canol Formation is defined using geochemical trends. The contact is defined by decreased terrigenous inputs, increased silicon in relation to terrigenous inputs, and increased redox-sensitive trace metals.

The Bluefish Member is an organic-rich, commonly calcareous mudstone unit (Pugh, 1983). The interval is bituminous, with fibrous cone-in-cone calcite beds and basal graded limestone beds (Mackenzie, 1972; Pugh, 1993). Planar and wavy laminae, both continuous and discontinuous, and pyrite nodules are also present. The Bluefish Member fauna includes criconarids such as Tentaculitidae and Styliolinidae, acritarchs, ammonoids, rare brachiopods, rare coral, and plant material (Aitken *et al.,* 1982; Basset, 1961). Fossil distribution is concentrated towards the base of the unit. The thickness of the Bluefish Member varies from 10 to 25 metres and is controlled mainly by basin paleotopography as a result of bioherm development in the Hume Formation (Pugh, 1993).

The Bell Creek Member is a recessive mudstone unit interbedded with limestone and siltstone that varies significantly laterally and vertically (Pyle and Gal, 2016). The Bell Creek Member is informally subdivided into two units, a grey shale member and a black shale member (Pugh, 1993; Pyle and Gal, 2016). The grey shale member is present where it is overlain by the Ramparts Formation (Kabanov and Gouwy, 2017; Pyle and Gal, 2016). It is characterised by grey, micaceous shale interbedded with limestone and siltstone (Pugh, 1993; Pyle and Gal, 2016). The black shale member is present where the Ramparts Formation is not present, and it is overlain by the Canol Formation. It is characterised by black, bituminous shale that is variably micaceous and pyritic (Pugh, 1993; Pyle and Gal, 2016). Conodont age dating suggests that the black shale member is laterally equivalent to the Ramparts Formation and the grey shale member (Pyle *et al.,* 2014; Pyle and Gal, 2016).

Regional studies have suggested that the Hare Indian Formation is characterised by transgression, then regression, followed by renewed transgression culminating in the upper contact with the Ramparts Formation or Canol Formation (Morrow and Geldsetzer, 1988; Williams, 1987). It is generally associated with anoxic or euxinic depositional waters (Dixon, 1984; Snowden *et al*., 1987). It has been interpreted both as a mud delta deposited on the slope and shelf, and as a result of slower, basinal deposition characterized by clinoform development (Snowdon *et al.,* 1987; Tassonyi, 1969). Anoxic horizons in the Hare Indian Formation have been suggested to be equivalent to global anoxic events such as the Kačák event in Europe and the anoxic horizon of the Marcellus Formation in the Appalachian Basin (Kabanov, 2019).

Studies have interpreted one first order cycle (using an archaic sequence stratigraphic scheme meaning in this case, cycles on the order of hundreds of metres thick) and several second order cycles (*i.e.* cycles on the order of tens of metres thick) indicating episodic relative sea level rise as a result of eustatic sea level fluctuation or perhaps autocyclic stacking as a result delta lobe switching (Muir, 1988; Muir and Dixon, 1985), however authors speculated that tectonics likely played a role in shaping the Hare Indian Formation's stratigraphic expression as well. There are no recent studies that have applied sequence stratigraphy to the Hare Indian Formation. Accordingly, the objective of this study is to use high resolution portable energy-dispersive X-ray fluorescence (pXRF) data to produce a sequence stratigraphic framework for the Hare Indian Formation.

2.3 Methods

2.3.1 Portable energy-dispersive X-ray fluorescence

Geochemical data for this study is collected using an energy-dispersive portable X-ray fluorescence analyser, a non-destructive, cost and time efficient method for collecting elemental composition data at high resolutions. In this study, data is collected using a Thermo Scientific Niton XL3t portable XRF analyser. Helium purged analysis is used in order to decrease the limit of detection of lighter elements like Si and Al. The average error for Al is 797 ppm and the average error for Si is 1162 ppm.

Samples are obtained from three outcrops in the Mackenzie Mountains and four slabbed cores drilled in the Central Mackenzie Valley (Figure 2.2). Outcrop samples are collected along a measured section at varying intervals ranging from 10 to 50 centimetres, as well as features of interest (i.e. nodules, unique laminae, obvious mineralogical change). Outcrop samples are prepared by removing weathered sample by grinding and are homogenised by powdering using an automatic agate mortar and pestle. Powder is put in a plastic sample cup with a polypropylene film base. Slabbed core samples are cleaned and measured every 10 centimetres and at depths of interest.

Each sample is measured for 180 seconds and data is reported for 34 elements in parts per million. The analyser is calibrated by Thermo Scientific using a proprietary algorithm. A certified reference material, the Brush Creek Shale and a 99.995% silica blank were analysed every ten samples in order to oversee accuracy and precision of the instrument and data collected.

2.3.2 Principle Component Analyses (PCA)

Principal component analysis (PCA) is used in this study to show how elements associate or co-vary with each other within an interval (Pearce *et al.,* 2005; Pe-Piper *et al.,* 2008; Sano *et al.,* 2013; Svendson *et al.,* 2007). PCA is a type of multivariate statistical calculation that recalculates the position of axes that inform the variability of n-dimensional data. These axes, the principal components, explain the total variance observed in the dataset with fewest variables. Statistical calculations for this study were completed using XLSTAT (Addinsoft, 2019). In this study, pXRF elemental assessments are used for PCA.

2.3.3 Proxies Considered

We provide a sequence stratigraphic framework that is informed by geochemical data, which are used as proxies for the proportion of terrigenous sediment input, paleoredox conditions and proportion of biogenic sediment input (LaGrange *et al.,* 2020; Playter *et al.*, 2018; Sano *et al.,* 2013; Turner *et al.,* 2016). These proxies are used to assign stratigraphic surfaces and systems tracts and interpret paleodepositional environment.

Elements such as Al, K, Ti, Fe, and Zr have been used to assess siliciclastic input of fluvial or aeolian origin in marine settings (Chen *et al.,* 2013). Aluminum is derived mainly from aluminosilicates, and their weathering products, clay minerals. Additionally, Al and Ti have short residence times in seawater (<200 years), meaning they are derived mainly from continents (Murray and Leinen, 1996). The majority of K in marine sediments is derived from terrigenous sediment, despite K being a major cation in seawater (Wei *et al.,* 2003). Titanium and iron may be chemically weathered, but reprecipitate rapidly as oxides without significant transportation (Nesbitt and Markovics, 1997). Iron may be sourced from detrital material or authigenic precipitation (Chen *et al.,* 2013). Zirconium is primarily present in zircon, which is resistant to chemical weathering (Tole, 1985). In this study, these elements are collectively referred to as terrigenous input and based on associations identified using PCA, Al, K and Ti are used as proxy indicators of siliciclastic input into the basin (Figure 2.3). Because detrital input is related to the proximity of the coastline, these elements are in turn used as a proxy for relative sea level.

The origin of silica in the Hare Indian is also addressed in more detail. Silica is generally sourced from detrital input, biogenic activity or hydrothermal activity (Adachi *et al.*, 1986; Arsairai *et al.*, 2016). To distinguish hydrothermal silica from non-hydrothermal silica, an Al-Fe-Mn ternary diagram is used (Figure 2.4) (Adachi *et al.*, 1986; Arsairai *et al.*, 2016). Another proxy is used to distinguish the proportion of detrital silica from biogenic silica. This is measured by the ratio Si/Al (Turner *et al.,* 2016). Peaks in the Si/Al curve indicate increased biogenic silica, especially if the same trend is not present in Zr/Al or Ti/Al curves (Turner *et al.,* 2015; Gambacorta *et al.,* 2016). Crossplots of these elements (Si-Al, Si-Ti, Si-Zr, Si-K) are used to determine silica's origin, where a strong positive correlation indicates detrital silica (Figure 2.5) (Tribovillard *et al.,* 2006; Ratcliffe *et al.,* 2012b; El Attar and Pranter, 2016).

Certain elements are sensitive to redox conditions, becoming enriched under low oxygen, anoxic or euxinic conditions. Authors use various thresholds when defining paleoredox conditions (*e.g.* oxic, >4.5 uM; suboxic, 4.5 uM – 10 nM; anoxic, < 10 nM) (Morrison *et al.*, 1999; Tyson and Pearson, 1991; LaGrange *et al.*, 2020). Additionally, the term euxinia is also used here to describe anoxic conditions with hydrogen sulfide in the water column. Here, V and Mo are the redox-sensitive trace metals used as proxies.

Both elements are unreactive in modern oxygenated seawater, and are concentrated under oxygen-depleted conditions, and both are more often concentrated in organic-rich deposits (Emerson and Huested, 1991).

Of the V species, V(V) is present in oxygenated water, V(IV) is stable under low oxygen conditions, and V(III) is stable in anoxic environments (Algeo and Maynard, 2004; Sadiq, 1988; Tribovillard *et al.,* 2006). Vanadium (IV) and V(III) readily substitute into clay minerals, form insoluble hydroxides and complex or adsorb with particles (Francois, 1988; Szalay and Szilágyi, 1967; Huang *et al.,* 2015). Reduced V may also be complexed with organic matter, decreasing solubility (Ferrer and Baran, 2001). V can also be reduced by microorganisms, resulting in precipitates of V(IV) (Huang *et al.,* 2015).

Molybdenum is primarily present in seawater as molybdate (MoO_4^{2-}). Molybdate has low reactivity and a long residence time (~800,000 years) (Emerson and Huested, 1991). In oxygenated water, molybdate co-precipitates or adsorbs with Mn-oxyhydroxides as Mn nodules or ferromanganese crusts where sedimentation rates are low (Scott and Lyons, 2012). Studies have also shown that Mo can adsorb to Fe-oxides (Goldberg *et al.*, 1996). In anoxic environments, where hydrogen sulfide is present in the water column and/or sediment pore waters (euxinic environments), molybdate is converted to reactive thiomolybdate ($MoS_{4-x}O_x^{2-}$) and tetrathiomolybdate (MoS_4^{2-}) and precipitates as sulfide minerals or is incorporated into organics (Helz *et al.*, 1996; Scott and Lyons, 2012). Where sulfides are present only in pore waters, Mo concentrations do not exceed 20 ppm, whereas in euxinic environments with hydrogen sulfide in the water column continuously, and Mo is abundant due to unrestricted exchange with the open ocean, Mo may be enriched from 60 to 100 ppm (Scott and Lyons, 2012). Molybdenum enrichment does not happen when conditions are anoxic without sulfides as hydrogen sulfides are required for the reduction of molybdate to thiomolybdate (Helz *et al.*, 1996). In order to test the origin of Mo in the Hare Indian Formation, Mo is cross plotted with Mn, V and TOC (Figure 2.6).

Vanadium and molybdenum are expressed as enrichment factors relative to aluminum, which has low mobility during diagenesis (Tribovillard *et al.,* 2006). The enrichment factor is calculated by comparing the ratio of a certain element relative to Al in the sample to the ratio of the element relative to Al in the average shale. The element may be enriched or depleted relative to that of the average shale. The enrichment factor for element (X) is calculated as follows (Brumsack, 2006; Tribovillard *et al.,* 2006):

$$EF_X = (X/Al)_{sample} / (X/Al)_{average\ shale}$$

Molybdenum enrichment factors of 3 – 10 represent suboxic conditions and >10 suggest euxinic conditions (Tribovillard *et al.*, 2012). Vanadium enrichment factors greater than 1 are considered enriched (Tribovillard *et al.*, 2006). The values for average shale in this study are from the Post-Archean Average Shale (Taylor and McLennan, 1985). The disadvantage of using this method is that reference shales may not be representative of the shale in question and concentrations of these redox sensitive elements can vary greatly both globally and locally (Van der Weijden, 2002; Xu et al, 2013). Alternatively, total ppm concentrations of Mo can be directly compared. In this scheme, Mo concentrations <25 ppm suggest non-euxinic conditions where sulfides are restricted to pore waters, >100 ppm suggest persistent euxinic conditions and intermediate concentrations of 25-100 ppm suggest euxinia, but may be intermittent euxinia, dilution due to high sedimentation rates, depletion of Mo in the water column (in a restricted basin, for example) or pH variations (Scott and Lyons, 2012).

2.3.4 Sequence Stratigraphic Nomenclature

The nomenclature and criteria used in order to make sequence stratigraphic surfaces and systems tracts is provided in Table 2.1.

2.4 Results

Data is collected for 34 elements using a pXRF analyser including Ca, Sr, Mn, Sn, Mg, Ba, Cd, Zn, Ni, Mo, Cu, C, P, Si, As, S, Pb, Nb, Zr, Fe, Cr, Bi, Al, Ti, K, and Rb. PCA is used to identify co-variance among the measured elements.

In Figures 2.7-2.13, elemental data are presented for each location, as well as a gamma log and any data for total organic carbon (TOC). Trends are assessed for each location by combining proxies: terrigenous inputs (Al, K, and Ti), Si/Al, Ti/Al, Zr/Al, Mo enrichment factor, V enrichment factor, gamma, and TOC where possible (Figures 2.7-

2.13). Throughout the studied cores and sections, terrigenous inputs decrease stratigraphically upward, and typically there is a spike in Si/Al in the Bluefish Member, then terrigenous inputs typically increase approaching the top of the Bell Creek Member. These trends can be correlated across the study area (Figure 2.14).

2.4.1 PCA

PCA is conducted for the dataset of pXRF measurements (Figure 2.3). In this case, 50.64% of the total variation of the dataset of 34 elements is explained by two principal components. The first principal component (F1) accounts for 34% of the variance in the dataset. The second principal component (F2) explains 16% of the variance in the dataset. Elements associated with carbonate lithologies are covariant: these are Ca, Sr, Mn, Sn, and Mg. Elements associated with clay minerals are separately covariant, including Fe, Cr, Bi, Al, Ti, K and Rb. Elements similarly associated with heavy and detrital minerals are P, Sb, S, Si, As, Pb, Nb and Zr. Heavy and detrital mineral elements are more closely grouped with clay mineral elements as they are both associated with terrigenous input (Sano *et al.,* 2013). Some of these elements, specifically Al, Ti, and K, are used as terrigenous input proxies in this study. Elements that are redox-sensitive and associated with total organic carbon plot together as well and these comprise Ba, Cd, Zn, Ni, Mo, Cu, and V. In particular, Mo and V are used as proxies for redox conditions.

2.4.2 Silica Proxies

Silica is derived from three sources: detrital input, biogenic activity, and hydrothermal activity (Adachi *et al.*, 1986). In order to account for hydrothermal silica, data is plotted on an Al-Fe-Mn ternary diagram (Figure 2.4) (Adachi *et al.*, 1986; Arsairai *et al.*, 2016). The majority of the data plot in the non-hydrothermal area of the diagram. In order to further distinguish detrital and biogenic silica, Si is plotted against Zr, Al, K, and Ti, which are characteristically of detrital origin. A strong positive correlation suggests that silica is detrital, whereas a strong negative correlation is consistent with the predominance of biogenic silica (Ratcliffe *et al.,* 2012b). These data show a positive correlation (Figure 2.5). For Si-Zr in the Bluefish Member, r^2 is 0.86, in the Bell Creek Member r^2 is 0.88; for Si-Al in the Bluefish Member, r^2 is 0.88, in the Bell Creek Member r^2 is 0.95; for Si-K in the Bluefish Member, r^2 is 0.0.88, in the Bell Creek Member r^2 is 0.93; for Si-Ti in the Bluefish Member, r^2 is 0.86, in the Bell Creek Member r^2 is 0.95. For all of these corrections the p value is less than 0.0001. Visually, some data points in the Bluefish Member in particular appear to show a negative correlation, however the predominant positive correlation is strong.

2.4.3 Terrestrial Proxies

Aluminum, titanium and potassium are used as proxies for terrestrial input. The plots for the N-20 core (Figure 2.7) show a sharp increase at the base of the Bluefish Member, above the Hume Formation, coincident with the onset of clastic deposition. The terrestrial proxies decrease upwards with a minimum in the middle of the Bluefish Member. This depth coincides with increased Si/Al ratios. Terrestrial proxies then increase until the top of the Bell Creek Member. Similar trends are observed in the O-06 core (Figure 2.8), the I-78 core (Figure 2.9), the N-09 core (Figure 2.10), the Mountain River outcrop section (Figure 2.11), the West Powell Creek outcrop section (Figure 2.12), and the Dodo River outcrop section (Figure 2.13). These trends correlate across the study area (Figure 2.14).

2.4.4 Redox Proxies

Throughout the Hare Indian Formation, Mo and V are enriched. Vanadium enrichment factors are consistently above 2, and throughout the Bluefish Member they are consistently above 4. Molybdenum enrichment factors are consistently greater than 10 throughout the Hare Indian Formation. Molybdenum is consistently between 25 and 100 ppm throughout the Hare Indian Formation. The mean value for Mo in the Hare Indian is 53 ppm. Values are typically higher throughout the Bluefish Member (Figures 2.7-2.13), however Mo and V are enriched throughout the Hare Indian Formation compared to the average post-Archean Shale.

2.5 Interpretation and Discussion

The results described above are used to make several interpretations about the Hare Indian Formation. They are used to interpret the relative proportion of different sources of silica throughout the succession, paleoredox conditions during the Givetian in the Mackenzie Basin, and the sequence stratigraphy of the Hare Indian Formation.

2.5.1 Silica Source

A positive correlation of Si with detrital elements (*e.g.* Zr, Al, K, Ti) is interpreted as indicating a detrital source of silica. A negative correlation suggests that Si does not co-vary with detrital elements and is likely biogenic in origin (Piper and Calvert, 2009). The cross-plots of detrital elements and Si show a positive correlation (Figure 2.5) (Ratcliffe *et al.,* 2012b). However, Si values greater than 350,000 ppm are more negatively correlated with detrital elements indicating that silica in excess of 350,000 ppm may be biogenically sourced. Data points exceeding 350,000 ppm of Si occur more often in the Bluefish Member, suggesting that the proportion of biogenic silica in the Bluefish Member is higher than in the Bell Creek Member (Figure 2.5). This implies that the Bell Creek Member was deposited as pulses of detrital sediment, with a smaller proportion of silica sourced biogenically. In addition, there are spikes that occur in the Si/Al ratio, that do not correspond to spikes in the Ti/Al or Zr/Al ratios, supporting an interpretation of increased biogenic silica.

The presence of both detrital and biogenic silica indicates that it is unlikely that the Bluefish Member represents a deltaic depositional environment, as in that instance, the silica would be predominantly detrital in origin, rather than both detrital and biogenic. A distal shelf setting would be dominated by biogenic silica, rather than mixed with detrital silica. The increased proportion of biogenic silica to detrital silica may represent increased productivity or low clastic dilution. In the I-78 core, the N-20 core, and the O-06 core, TOC is high (6-8%) coinciding with the peak in silica, supporting low clastic dilution rates as a means of silica concentration.

2.5.2 Paleoredox Conditions

Paleoredox conditions are assessed by calculating the enrichment factor for Mo and V at each location. Molybdenum enrichment suggests the presence of H_2S in the water column or sediment, meaning conditions may be euxinic or intermittently euxinic (Scott and Lyons, 2012). When V is enriched, depositional conditions are interpreted as anoxic or euxinic at the sediment-water interface during deposition (Tribovillard *et al.*, 2006). Throughout the Hare Indian Formation, Mo and V are enriched. The enrichment factors for Mo and V are both higher in samples from the Bluefish Member (Figure 2.7-2.13). In addition, Mo is almost without exception present in amounts between 25 and 100 ppm. Based on Scott and Lyons (2012) scheme, this would indicate intermittent euxinia. Based on this interpretation, O_2 concentration levels in bottom waters would have been less than 0.2 ml O_2/l H_2O (anoxic), likely with free H_2S present in the water column (euxinic) intermittently throughout deposition (Tyson and Pearson, 1991; Tribovillard *et al.,* 2006). Paleoredox conditions have implications for the preservation of organic matter, as oxygen decreases preservation potential because of microbial degradation (Wignall, 1991). High productivity may also preserve organic matter (Pederson and Calvert, 1990). In this case, it is likely that oxygen was low or not present during the time of deposition and facilitated the preservation of organic matter, especially in the Bluefish Member.

Furthermore, Biddle *et al.*, (in review), found intervals in the Hare Indian Formation containing microbioturbation. Together, the ichnology and geochemical proxies would suggest that the sediment and/or water column was intermittently experiencing euxinia.

2.5.3 Sequence Stratigraphy

Using the geochemical proxies, a sequence stratigraphic framework comprising transgressive-regressive cycles can be established (LaGrange *et al.*, 2020). Trends were assessed in the proxies used for this study, the terrigenous elements (Al, K, and Ti), the Si/Al ratio, the Ti/Al ratio, the Zr/Al ratio, the Si/Zr ratio, the Mo enrichment factor, the V enrichment factor, gamma ray and TOC where possible. The outcrop sections make up the three locations in the northwest portion of the cross section. At West Powell Creek (WPC), a maximum flooding surface (MFS) is interpreted where the terrigenous elements are at a minimum, and the Si/Al ratio peaks, where the Ti/Al ratio and Zr/Al ratio decrease (Figure 2.12). This would indicate higher relative sea level, as less terrigenous material is being deposited, as well as either increased biogenic silica or decreased clastic dilution. Enrichment factors are both high throughout the samples below this level consistent with higher sea levels. Above the MFS, the terrigenous elements increase in abundance until the top of the section. At the Mountain River (MR) location, terrigenous elements decrease quickly above the Hume Formation contact, and then increase (Figure 2.11). Where terrigenous elements are at a minimum, there is a peak in the Si/Al ratio curve as well as high Mo and V enrichment factors both below and above the height of the minimum. The minimum is interpreted to be an MFS. Above this, enrichment factors decrease, but remain greater than 1 and the ratios follow similar profiles. Above the covered part of the section, the terrigenous elements are at a maximum, where a maximum regressive surface (MRS) is interpreted. The Dodo River (DD) section is the shortest section in the cross section. The trends are less apparent here due to coarser sampling rates, however the terrigenous element profile increases upwards in the section.

The four southeast locations comprise data measured from core. The ConocoPhillips Loon Creek O-06 core shows a decreasing trend in the terrigenous elements, followed by an increase (Figure 2.8). Mo and V enrichment factors are highest in the middle of the Bluefish Member but remain above 1 throughout the majority of the Hare Indian Formation, suggesting low oxygen levels throughout the deposition of the Hare Indian Formation. Here, an MFS is interpreted in the Bluefish Member, and an MRS is interpreted towards the top of the Bell Creek Member. In the ConocoPhillips Mirror Lake N-20 core, the terrigenous elements decrease in the Bluefish Member, then increase throughout the remaining Hare Indian Formation (Figure 2.7). At the minimum in the terrigenous elements, there is also a spike in the Si/Al ratio and the Si/Zr ratio that does not have a corresponding spike in the Ti/Al ratio of the Zr/Al ratio. Just below this depth, the Mo and V enrichment factors are high. This would suggest an MFS should be placed at this level. Above the MFS, the terrigenous elements steadily increase while enrichment factors decrease, then begin to increase again. At the terrigenous elements' maximum, and near the top of the Bell Creek Member, an MRS is interpreted. The Husky Little Bear N-09 shows very similar trends to the N-20 core (Figure 2.10). Terrigenous elements increase and are at a maximum where there is a spike in the Si/Al and Si/Zr ratios that does not correspond to a spike in the Ti/Al or Zr/Al ratios. At this depth, an MFS is interpreted. Similarly, the terrigenous elements increase upwards in the core. There is a spike in enrichment factors around 1815 m. There is an MRS interpreted at the top of the Bell Creek Member at 1806 m. The MGM Shell East Mackay I-78 core includes only the lower Bluefish Member (Figure 2.9). A similar decrease in terrigenous materials is present, though there are further smaller scale trends in the terrigenous element profile that are not present at other locations. At the minimum in the terrigenous elements, an MFS is interpreted. The V enrichment factor is high above this depth, but the Mo enrichment factor, while still greater than 1, does not appear to correspond as well with the V enrichment factor as at other locations.

The northwest to southeast cross section through the Mackenzie Mountains and the Central Mackenzie Valley encompasses the 3 outcrops and 4 cores discussed above (Figure 2.14). The trends and surfaces discussed above correlate readily across the locations. The result is that a TST is interpreted in the lower portion of the Bluefish Member, followed by an RST making up the uppermost part of the Bluefish Member and the entirety of the Bell Creek Member. These results also support an interpretation of an unrestricted setting because when detrital elements are at a maximum, suggesting maximum regression, redox sensitive elements are at their minimums, consistent with abundant dissolved oxygen levels at the sea floor during that time (LaGrange *et al.* 2020).

2.6 Conclusions

The Hare Indian Formation is an organic-rich mudstone with potential as an unconventional resource in the Northwest Territories, Canada. In this study, a sequence stratigraphic framework was produced using high-resolution pXRF data collected from outcrop and core materials. The applications of such a framework include more detailed regional mapping and core to outcrop correlation. The data was useful in correlating surfaces that are otherwise not apparent using traditional methods such as wireline tools or sedimentology and facilitated answering questions regarding the silica source and paleoredox conditions. There are two systems tracts present in the Hare Indian Formation, a TST in the lower Bluefish Member, and an RST making up the rest of the formation. Paired with the results of Biddle *et al.*, (in review) which showed microbioturbation present in horizons in the Hare Indian Formation, Mo and V enrichment support intermittent euxinia during deposition. There are often depths, particularly in the Bluefish Member with increased biogenic silica, increasing brittleness at these depths.

These findings provide a better framework through which to assess other aspects of the Hare Indian Formation, and Horn River Group. Future questions to be addressed include controls on the lithological variability within the Bell Creek Member, expanding the number of sections or cores studied in order to more broadly test these findings and this framework. Isotopic work (C and N) would shed further light on remaining questions of whether the biogenic silica is the result of productivity or clastic dilution. In addition, Mo isotope analysis may support the findings presented here regarding paleoredox conditions.

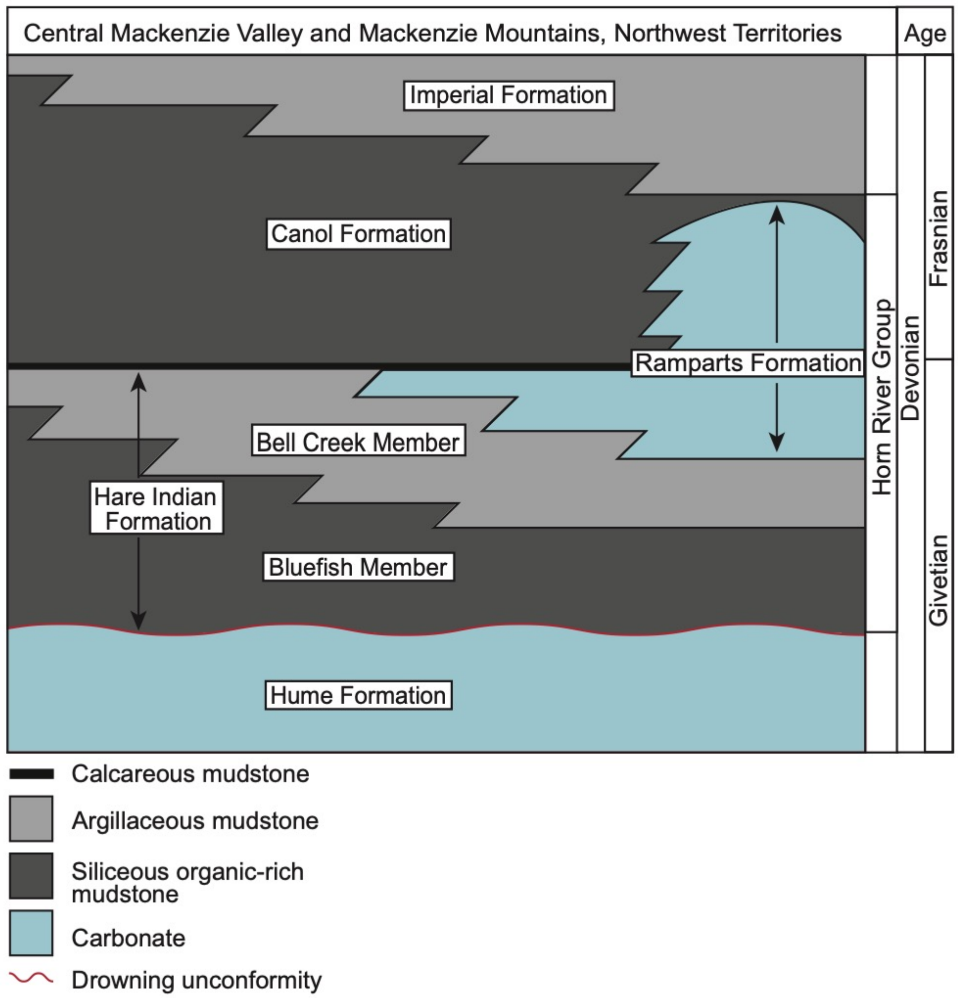

Figure 2.1 Schematic stratigraphic column of the Horn River Group and surrounding formations, spanning the Givetian and Frasnian of the Devonian in the study area of the Central Mackenzie Valley and the Mackenzie Mountains in Northwest Territories, Canada. Modified from Pyle and Gal (2016), Kabanov (2019) and LaGrange et al. *(2019).*

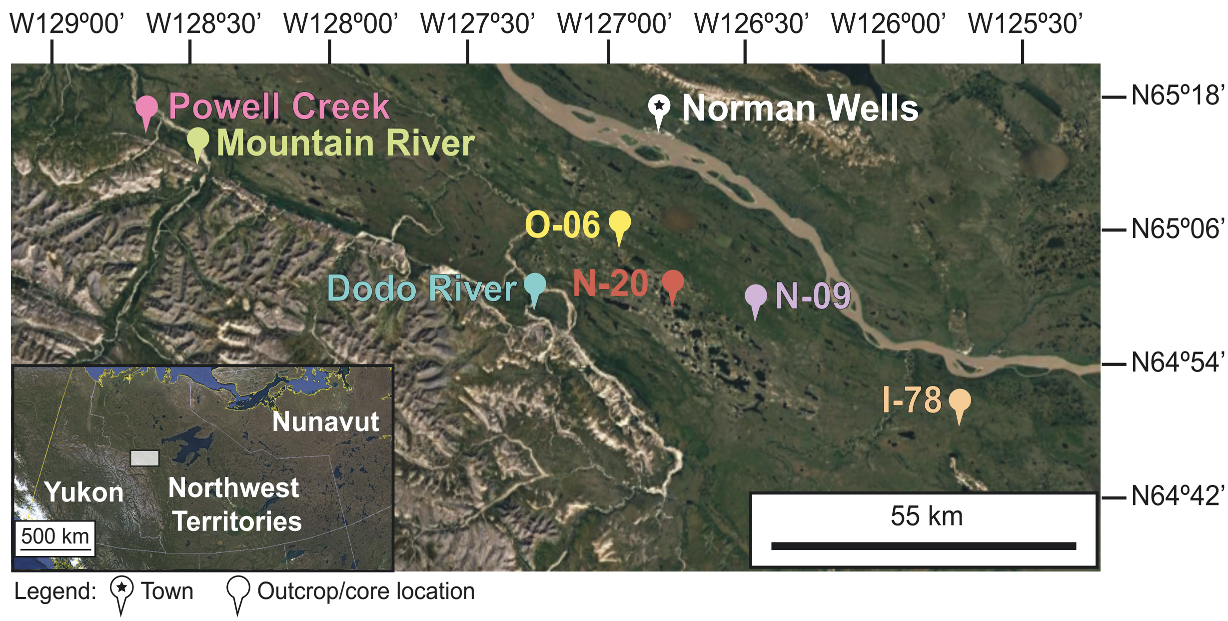

Figure 2.2 Map of the study area showing the location of the four cores and three outcrops considered in this study relative to Norman Wells, Northwest Territories, Canada. Images are modified from GoogleEarth.

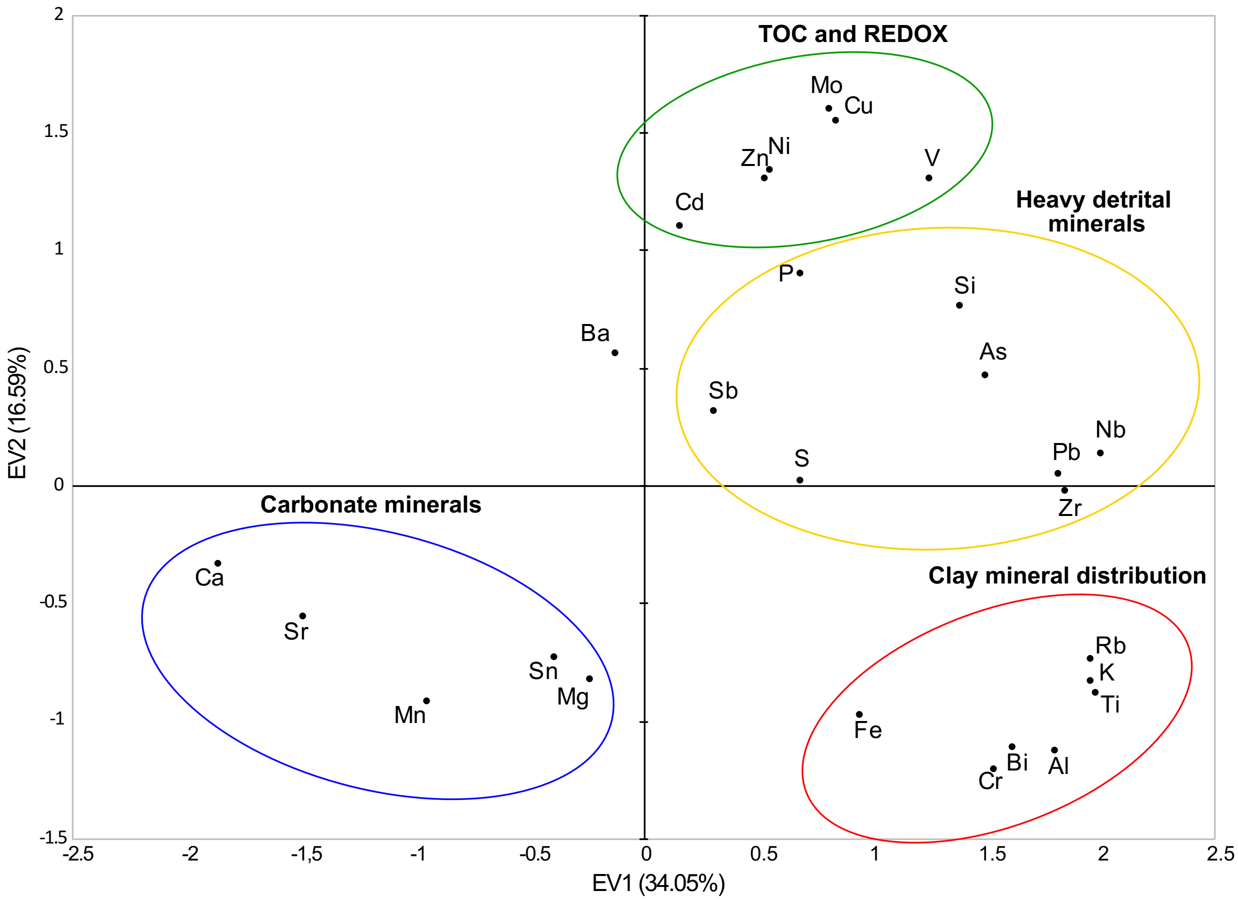

Figure 2.3 Biplot of eigenvectors derived by principal component analysis (PCA) of all pXRF data measured from the Hare Indian Formation. Elements cluster in four distinct groups interpreted as sharing depositional controls or sources. The first two eigenvectors account for 50.64% of the variation in this dataset. Generated using XLStat (Addinsoft, 2019).

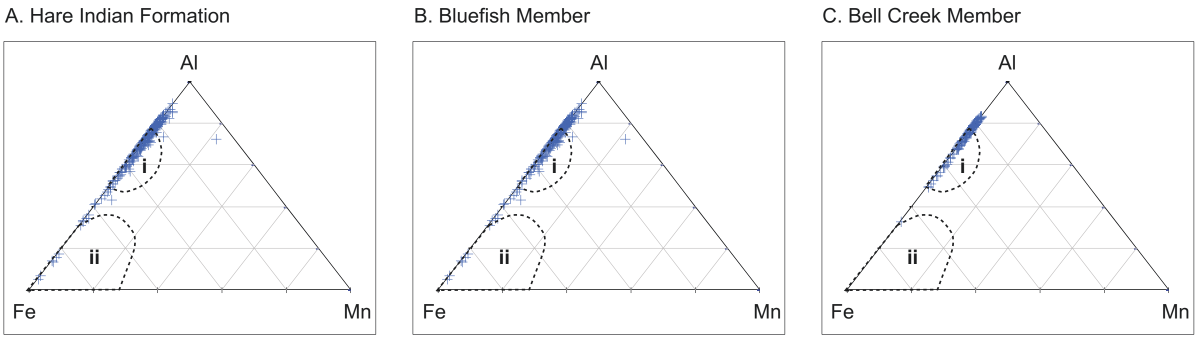

Figure 2.4 Al-Fe-Mn ternary diagrams of pXRF data collected from the Hare Indian Formation cores and outcrops included in this study where (i) represents the field where non-hydrothermal siliceous rocks plot and (ii) represents the field where hydrothermal siliceous rocks plot. Diagram (A) shows the data from the entirety of the Hare Indian Formation. Diagram (B) shows the data from the Bluefish Member. Diagram (C) shows the data from the Bell Creek Member. Modified from Adachi et al., (1986) and Arsairai et al., (2016).

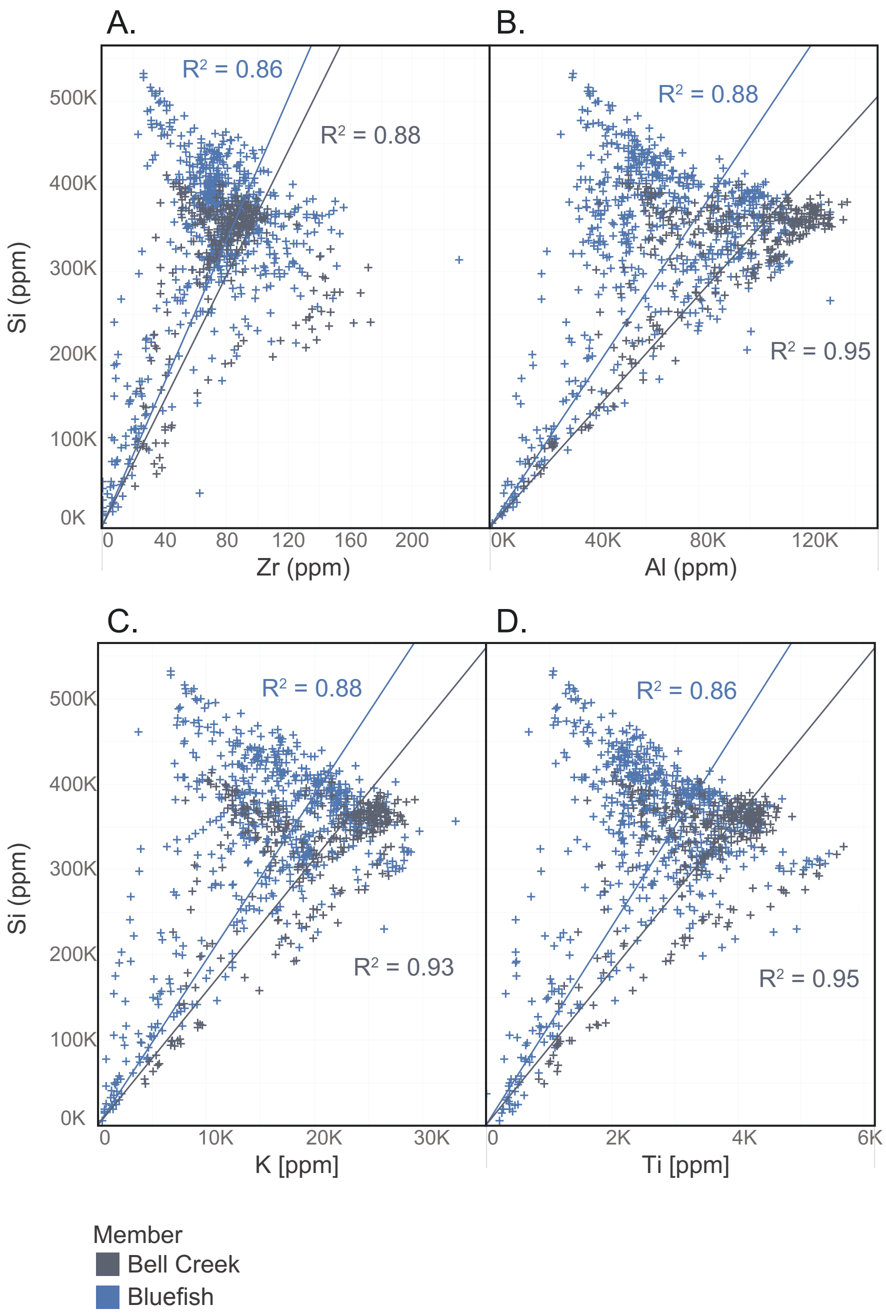

Figure 2.5 (A) Cross-plot of Si with Zr. The R^2 value in the Bluefish Member is 0.86. The R^2 value in the Bell Creek Member is 0.88. (B) Cross-plot of Si with Al. The R^2 value in the Bluefish Member is 0.88. The R^2 value in the Bell Creek Member is 0.95. (C) Cross-plot of Si with K. The R^2 value in the Bluefish Member 0.88. The R^2 value in the Bell Creek Member is 0.93. (D) Cross-plot of Si with Ti. The R^2 value in the Bluefish is 0.86. The R^2 value in the Bell Creek Member is 0.95.

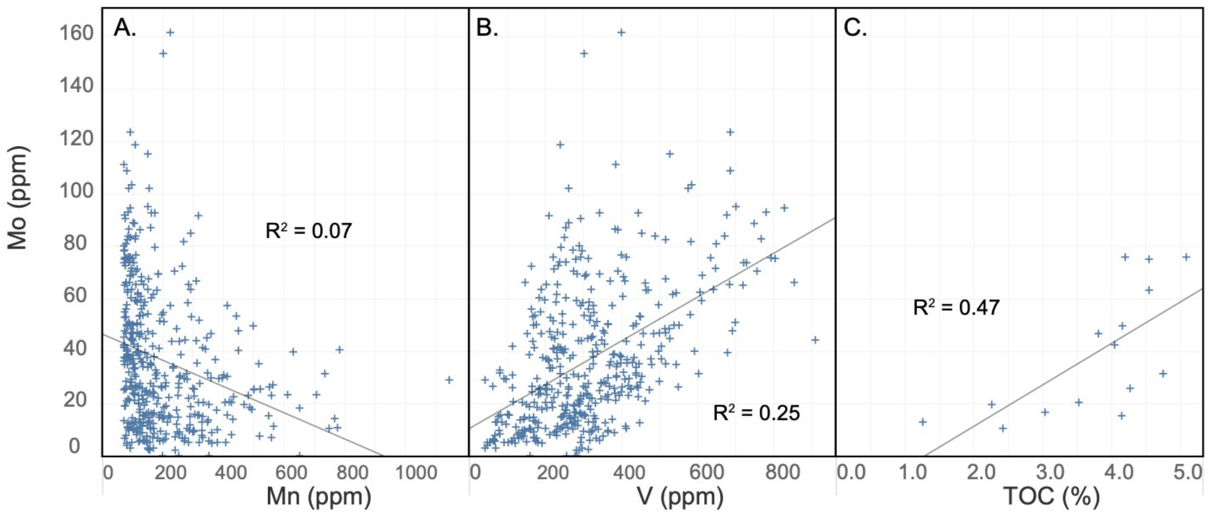

Figure 2.6 Cross-plots of pXRF data measured from the Hare Indian Formation cores and outcrop samples showing the relationship between Mo with Mn, V and total organic carbon (TOC). (A) Cross-plot of Mo and Mn. The R^2 value is 0.07. The p-value is less than 0.0001. (B) Cross-plot of Mo and V. The R^2 value 0.25. The p-value is less than 0.0001. (C) Cross-plot of Mo and TOC. The R^2 value 0.47. The p-value is 0.00266.

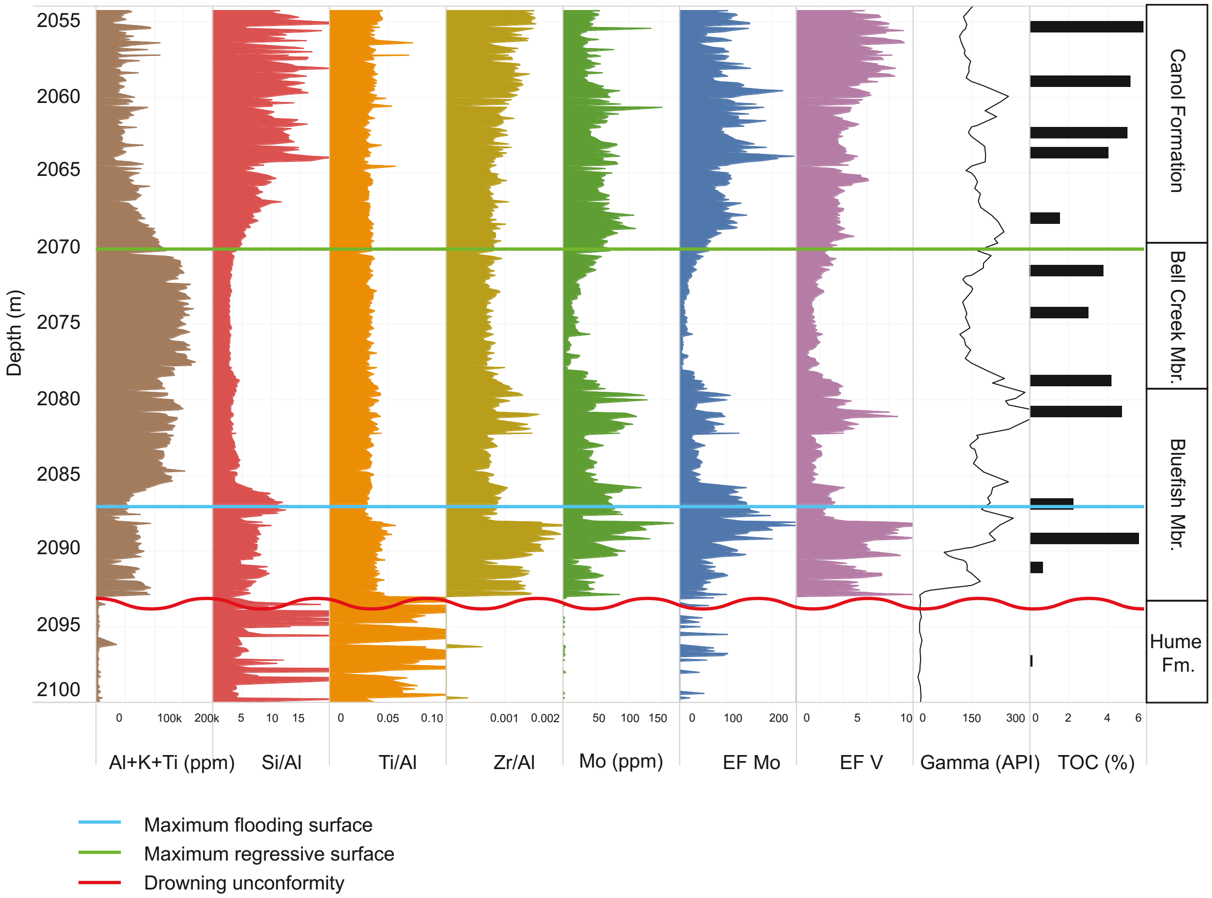

Figure 2.7 Plots of pXRF and well data from the ConocoPhillips Mirror Lake N-20 core. Plots from left to right are the concentration of detrital inputs (Al, K and Ti), the ratio of Si/Al, the ratio of Ti/Al, the ratio of Zr/Al, the concentration of Mo, the Mo enrichment factor, the V enrichment factor, a gamma ray plot, and total organic carbon (TOC). These geochemical proxies are used to interpret a drowning unconformity at 2094 m, a maximum flooding surface (MFS) at 2087 m, and a maximum regressive surface (MRS) at 2070 m.

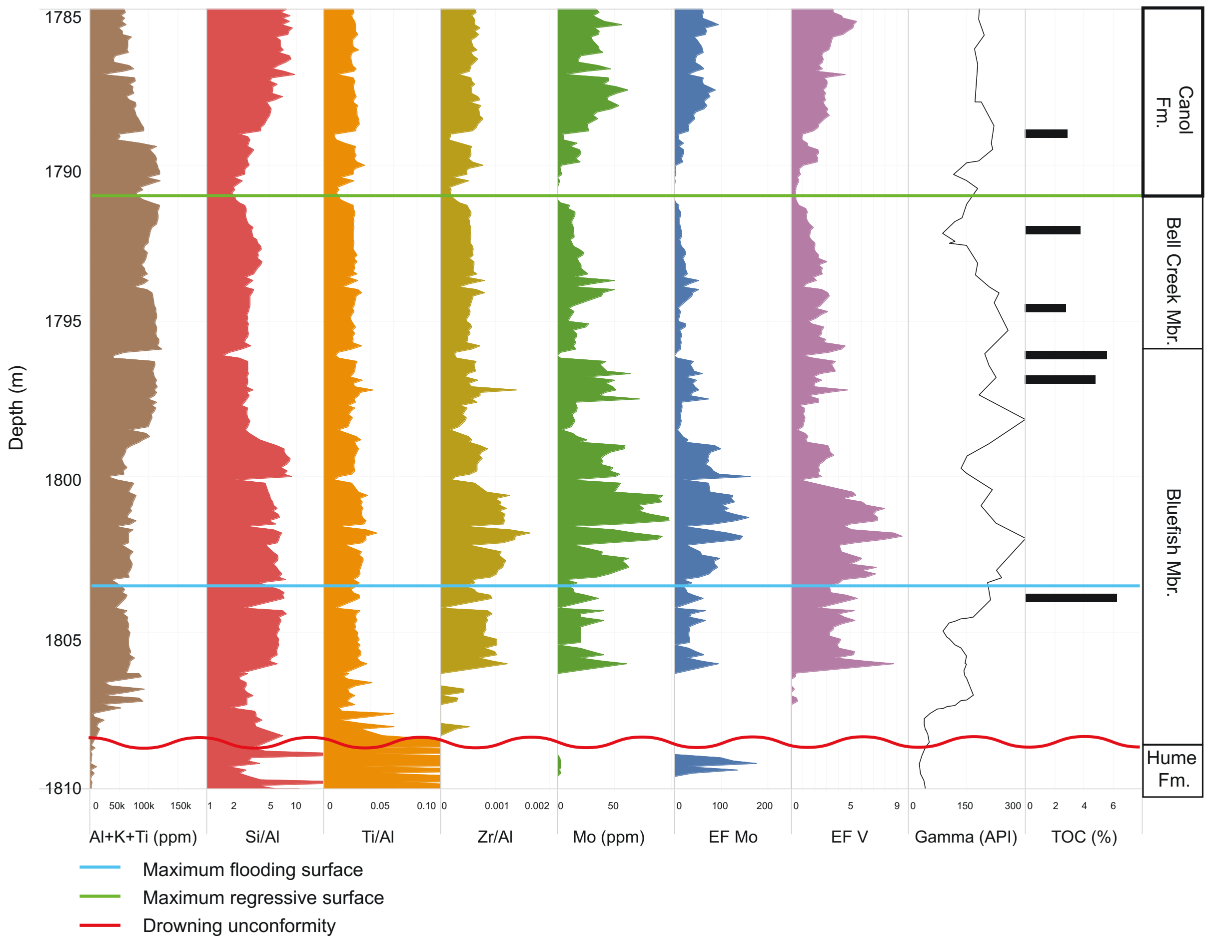

Figure 2.8 Plots of pXRF and well data from the ConocoPhillips Loon Creek O-06 core. Plots from left to right are the concentration of detrital inputs (Al, K and Ti), the ratio of Si/Al, the ratio of Ti/Al, the ratio of Zr/Al, the concentration of Mo, the Mo enrichment factor, the V enrichment factor, a gamma ray plot, and total organic carbon (TOC). These geochemical proxies are used to interpret a drowning unconformity at 1808 m, a maximum flooding surface (MFS) at 1804 m, and a maximum regressive surface (MRS) at 1791 m.

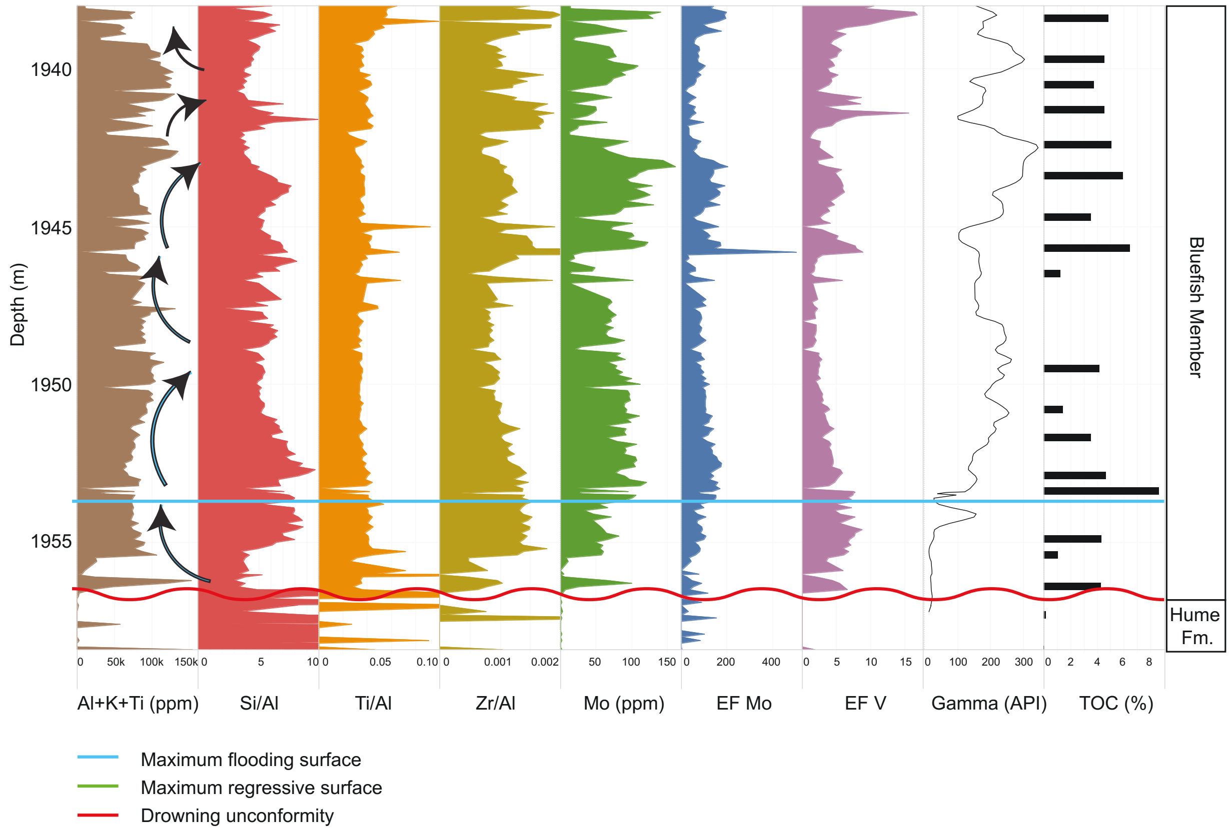

Figure 2.9 Plots of pXRF and well data from the MGM Shell East Mackay I-78 core. Plots from left to right are the concentration of detrital inputs (Al, K and Ti), the ratio of Si/Al, the ratio of Ti/Al, the ratio of Zr/Al, the concentration of Mo, the Mo enrichment factor, the V enrichment factor, a gamma ray plot, and total organic carbon (TOC). These geochemical proxies are used to interpret a drowning unconformity at 1957 m, a maximum flooding surface (MFS) at 1954 m.

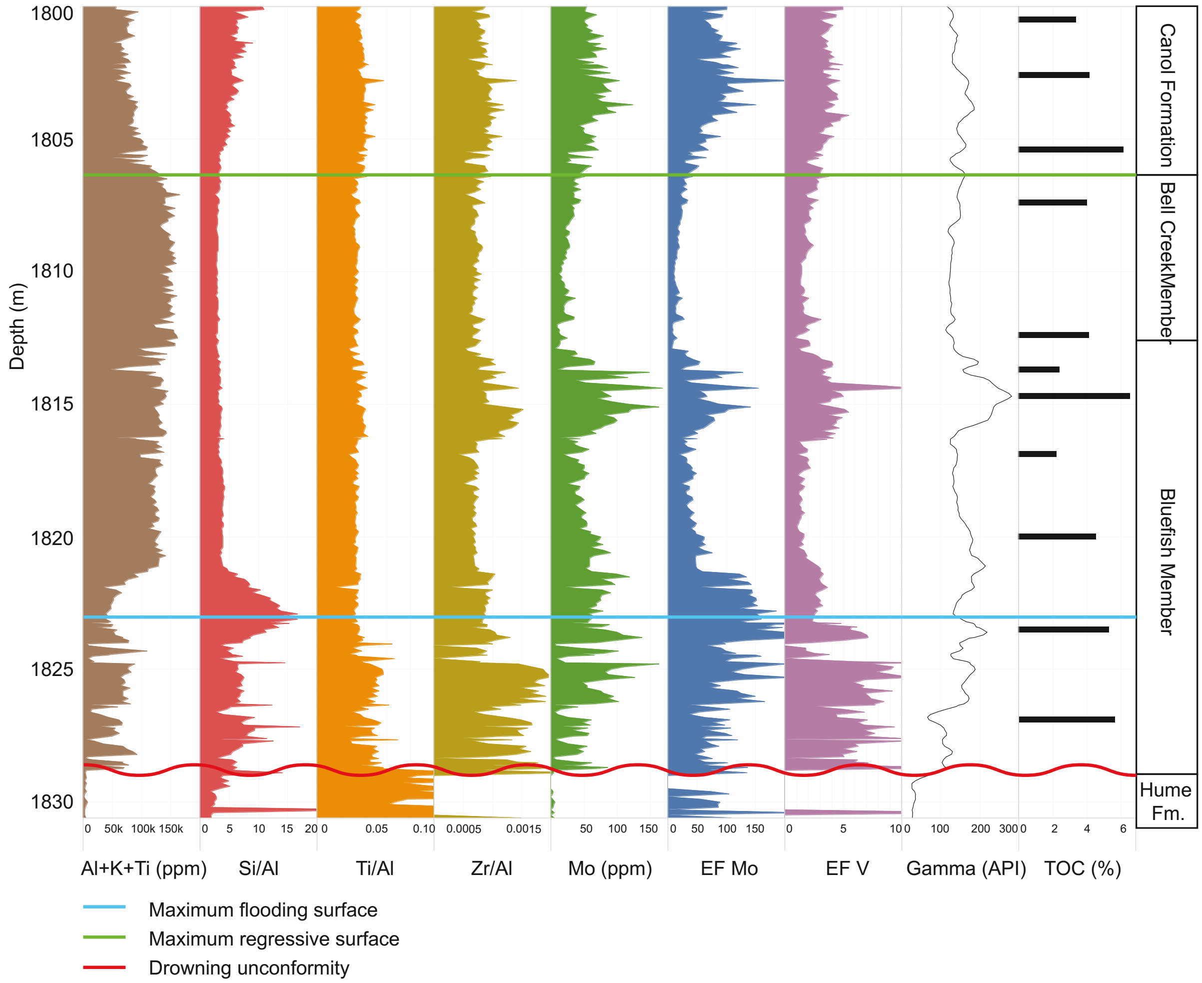

Figure 2.10 Plots of pXRF and well data from the Husky Little Bear N-09 core. Plots from left to right are the concentration of detrital inputs (Al, K and Ti), the ratio of Si/Al, the ratio of Ti/Al, the ratio of Zr/Al, the concentration of Mo, the Mo enrichment factor, the V enrichment factor, a gamma ray plot, and total organic carbon (TOC). These geochemical proxies are used to interpret a drowning unconformity at 1828 m, a maximum flooding surface (MFS) at 1823 m, and a maximum regressive surface (MRS) at 1806 m.

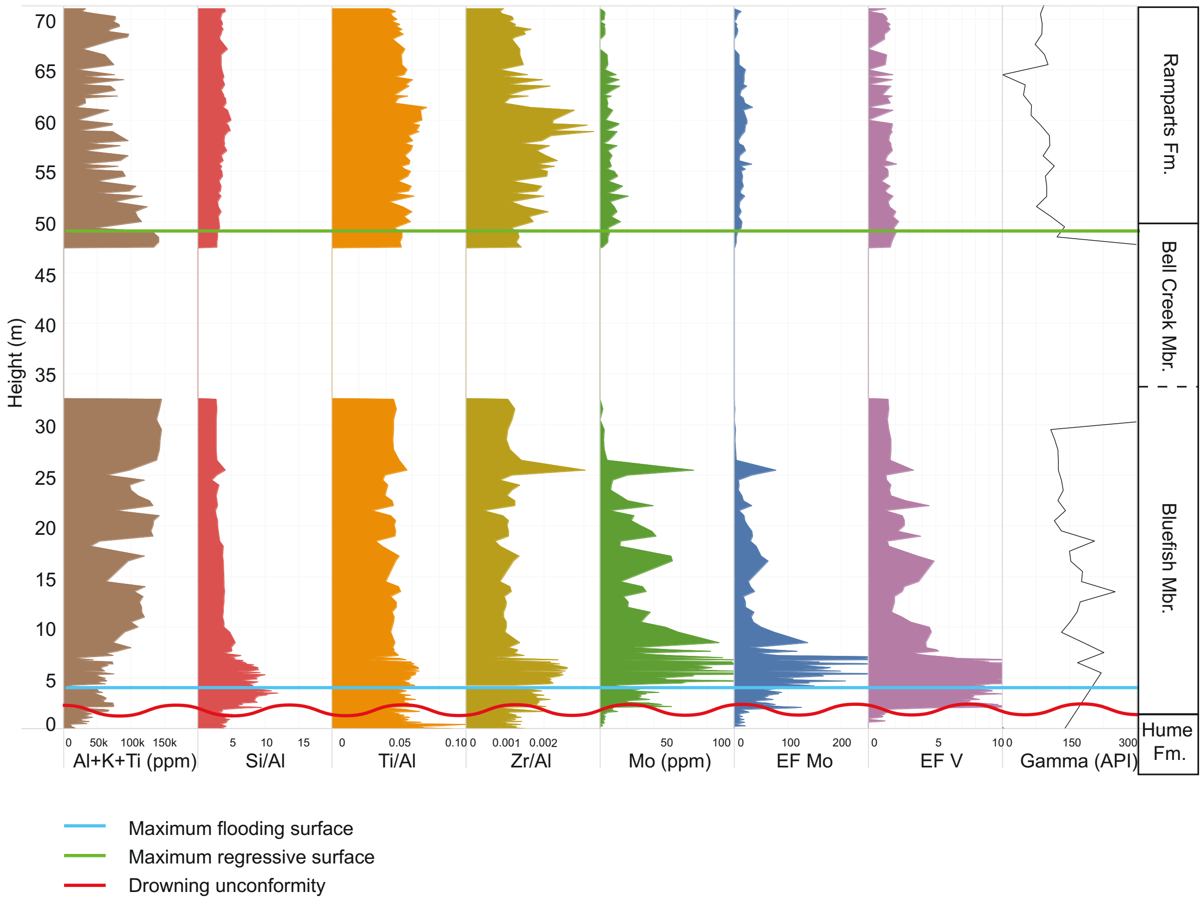

Figure 2.11 Plots of pXRF and gamma data from the Mountain River outcrop. Plots from left to right are the concentration of detrital inputs (Al, K and Ti), the ratio of Si/Al, the ratio of Ti/Al, the ratio of Zr/Al, the concentration of Mo, the Mo enrichment factor, the V enrichment factor and a gamma ray plot. These geochemical proxies are used to interpret a drowning unconformity at 2 m, a maximum flooding surface (MFS) and 5 m and a maximum regressive surface (MRS) at 50 m.

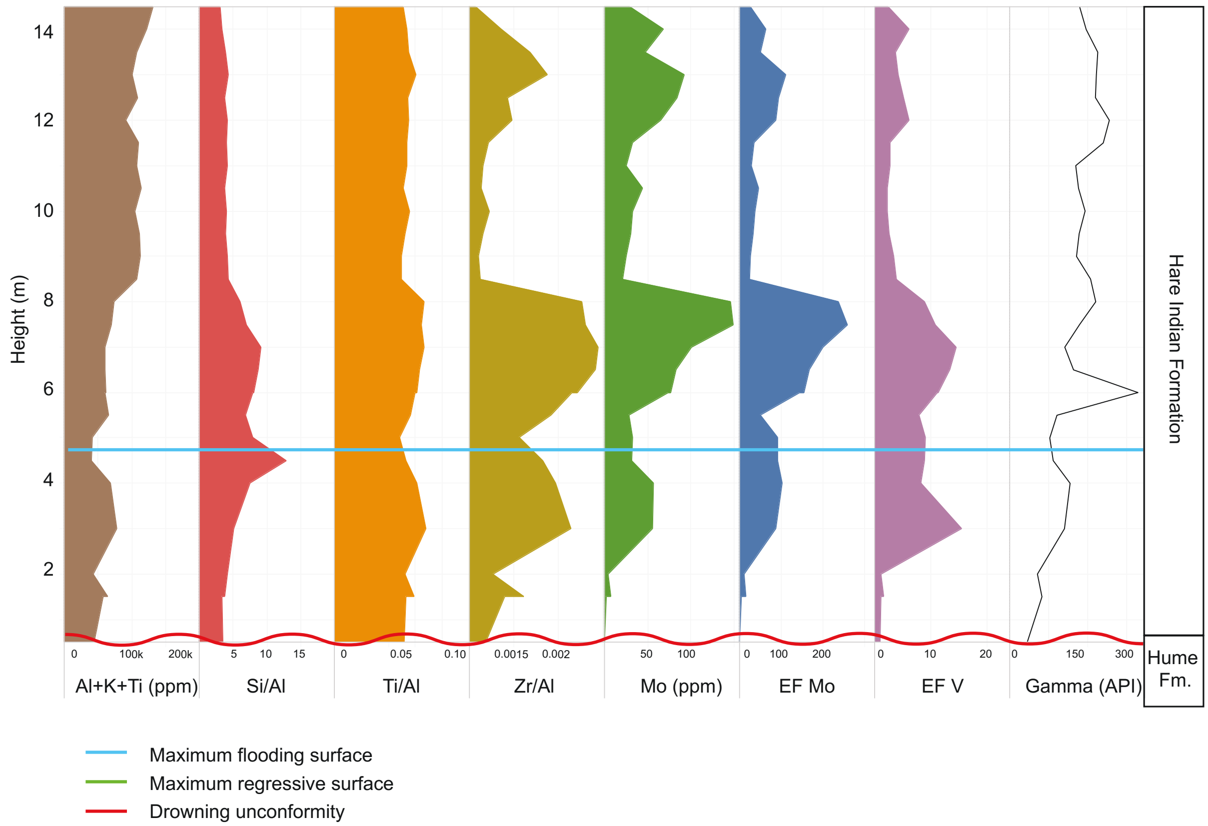

Figure 2.12 Plots of pXRF and gamma data from the West Powell Creek outcrop. Plots from left to right are the concentration of detrital inputs (Al, K and Ti), the ratio of Si/Al, the ratio of Ti/Al, the ratio of Zr/Al, the concentration of Mo, the Mo enrichment factor, the V enrichment factor and a gamma ray plot. These geochemical proxies are used to interpret a drowning unconformity at the base of section and a maximum flooding surface (MFS) and 4.5 m.

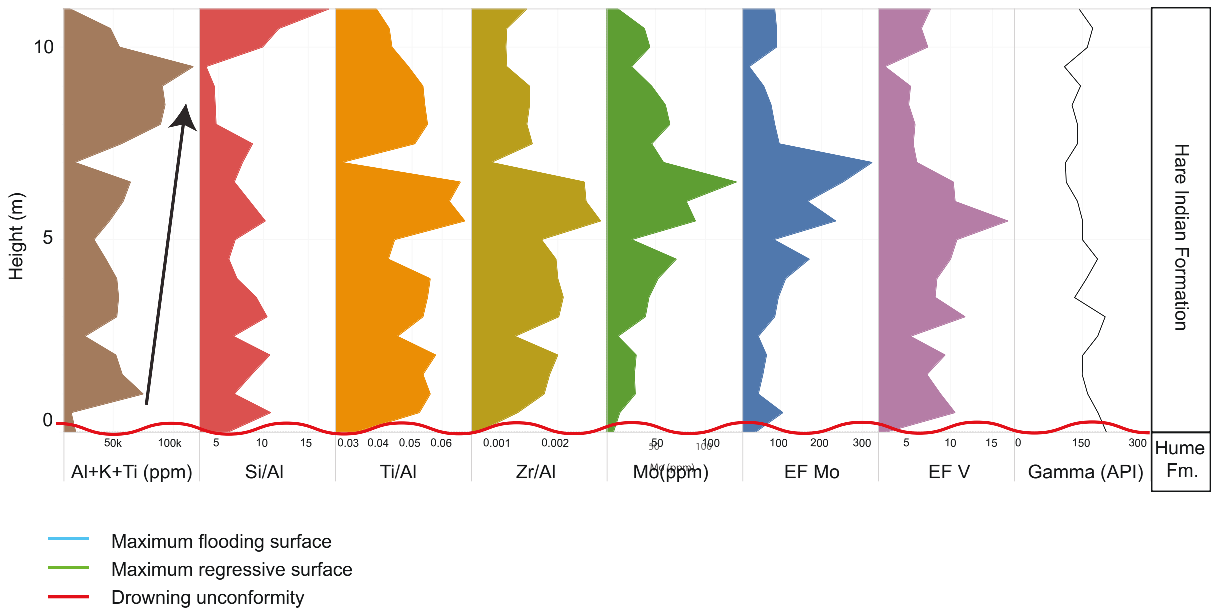

Figure 2.13 Plots of pXRF and gamma data from the Dodo River outcrop. Plots from left to right are the concentration of detrital inputs (Al, K and Ti), the ratio of Si/Al, the ratio of Ti/Al, the ratio of Zr/Al, the concentration of Mo, the Mo enrichment factor, the V enrichment factor and a gamma ray plot. These geochemical proxies are used to interpret a drowning unconformity at the base of section. Trends suggest increasing terrigenous input moving up section.

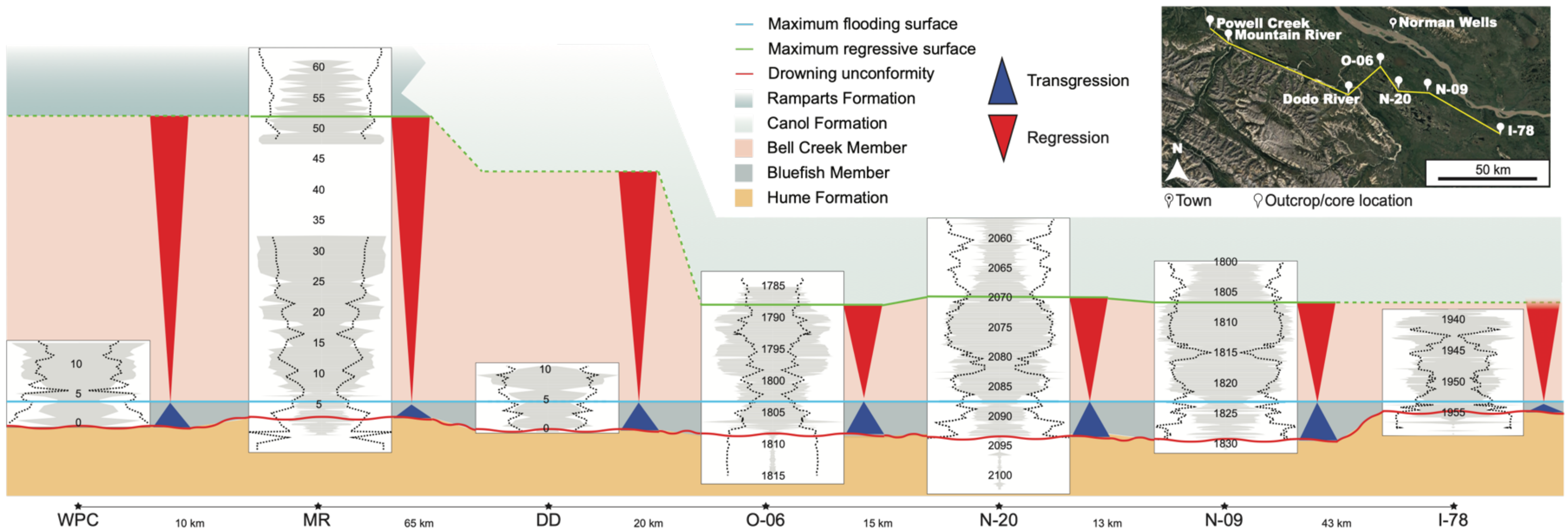

Figure 2.14 Sequence stratigraphic correlation running northwest to southeast through the Central Mackenzie Valley of the Hare Indian Formation at the West Powell Creek outcrop (WPC), Mountain River outcrop (MR), Dodo River outcrop (DD), the ConocoPhillips Loon Creek O-06 core (O-06), the ConocoPhillips Mirror Lake N-20 core (N-20), the Husky Little Bear N-09 core (N-09, and the MGM Shell East Mackay I-78 core (I-78). For each location, the grey shaded area represents the terrigenous input elements (Al+K+Ti) plotted as a butterfly plot where the centre of the plot represents zero. The overlain dotted line is a butterfly plot of a gamma ray profile. Using a maximum flooding surface as a datum, transgressive-regressive cycles are correlated between localities.

Table 2.1 Sequence stratigraphic nomenclature and observed chemostratigraphic expression used in this study. Modified from LaGrange et al. (2020).

Term	Definition	Chemostratigraphic Expression
Maximum flooding surface (MFS)	Transgression of the shoreline ends and regression of the shoreline begins	- Minimum terrigenous input, - Possible spike in Si/Al ratio - Redox sensitive metals enriched (in unrestricted marine shelf settings)
Maximum regressive surface (MRS)	Normal regression of the shoreline ends and transgression of the shoreline begins	- Maximum terrigenous input - Redox sensitive metals may or may not be enriched (in unrestricted marine shelf settings)
Transgressive systems tract (TST)	Deposited when the rate of sea-level rise outpaces the rate of shoreline sediment supply	- Decreasing terrigenous input - Si/Al may increase - Redox sensitive trace elements increase (in unrestricted settings)
Regressive systems tract (RST)	Deposition during shoreline regression including deposition during forced regression and normal regression	- Increasing terrigenous input - Si/Al may decrease - Redox sensitive elements decrease (in unrestricted settings)

3 Lithological facies and chemofacies analysis of the Hare Indian Formation, Mackenzie Mountains and Central Mackenzie Valley, Northwest Territories, Canada

3.1 Introduction

Facies, a term first developed by Amanz Gressly (1838), uses objective physical, chemical and biological descriptions to distinguish rocks with similar properties (Cross and Homewood, 1997; Wang and Carr, 2012). Facies are interpreted as the product of genetic processes in specific depositional environments, and can change laterally and vertically, which allows for the association of facies with certain environments. Lithofacies is a continuation of this classification scheme, coined by Eberzin in 1940, focusing on the lithological characteristics of the rock (Krumbein, 1948; Teichert, 1958; Wang and Carr, 2012). A further continuation is microfacies, introduced by Brown (1943), which uses petrographic analysis. Microfacies are particularly useful in fine-grained successions, where physical structures may be smaller-scale features. The classification scheme is applied to mudstones using physical and biological observations at the thin section scale (Schieber, 1989; Schieber, 1994).

Chemical facies, or chemofacies, similarly, are stratigraphic units with a unique chemical signature related to the environmental conditions under which they were deposited (Pearce et al, 1999; Reátegui *et al.*, 2005). Traditional facies analysis relies on lithology or fossil distribution in order to describe facies and their associated interpretations. In cases where lithology or the types of fossils present are more homogeneous, macroscopic fossils may be absent, or mineralogical variability is limited, it can be difficult to differentiate facies or make valuable interpretations. Classification schemes like microfacies and chemofacies are used in order to overcome these challenges.

Chemofacies analysis is helpful in understanding paleoenvironmental conditions, paleoproductivity, and sequence stratigraphy in rocks where that may otherwise prove challenging. Element distribution facilitates these interpretations as elements may be enriched under certain conditions, may be associated with particular minerals or mineral groups, and may be associated with terrigenous material rather than marine material (Tribovillard *et al.*, 2006; Turner *et al.*, 2016). In particular, this approach is popular in fine-grained successions where traditional methods relying on characteristics like grain size might not be suitable (*e.g.* Jenkyns and Clayton, 1997; North *et al.*, 2005; Pearce *et al.*, 2005; Hildred *et al.*, 2010; Ratcliffe *et al.*, 2015; Nyhuis *et al.*, 2016; Playter *et al.*, 2018). Describing facies based on geochemical data also removes some of the subjective nature of facies description at the macro- or micro-scale.

Studies have used isotope, inductively coupled plasma mass spectrometry (ICP-MS), and portable X-ray fluorescence (pXRF) data in order to delineate chemofacies in successions. Montero-Serrano *et al.*, (2010) applied constrained cluster analysis to X-ray diffraction (XRD) and inductively coupled plasma optical emission spectrometry (ICP-OES) data to distinguish facies. Reátegui *et al.*, (2005) also used constrained cluster analysis with ICP-OES data. Other studies have used factor analysis, principal component analysis, and hierarchical cluster analysis (*e.g.* Rowe *et al.*, 2017; Playter *et al.*, 2018).

Here, different types of facies analysis are applied to the Hare Indian Formation and compared to each other. Sedimentological facies (e.g. lithofacies and microfacies) are compared at the macro and micro scale, along with geochemical facies, in pursuit of the interpretation of the depositional environment, as well as to provide insights into paleoproductivity. Lithofacies, microfacies, and chemofacies are compared in order to determine which manner of facies analysis might be most useful in certain instances. This is accomplished by combining data from core, thin sections, and pXRF.

3.2 Geological Background

The Hare Indian Formation is a mudstone unit located in the Mackenzie Mountains and Central Mackenzie Valley of the Northwest Territories. It is Givetian (Middle Devonian) in age and is the oldest formation in the Horn River Group (Figure 3.1). The Hare Indian Formation is underlain by the Hume Formation, and overlain by the Ramparts Formation and the Canol Formation, depending on the location. It is split into two members: the basal Bluefish Member and the overlying Bell Creek Member (Pyle and Gal, 2016). The Horn River Group is a mixed clastic and carbonate succession deposited on the shelf and slope of the Northern Canadian Mainland Sedimentary Basin, on a divergent passive margin near the palaeoequator (Pugh, 1983; Morrow and Geldsetzer, 1988; Morrel, 1995; Morrow, 2012). During the Middle Devonian, a clastic wedge began prograding westward over the stable Mackenzie Platform, depositing the Hare Indian Formation (Pugh, 1983; Al-aasm *et al.*, 1993).

Previous studies have presented lithofacies schemes for the Hare Indian Formation. In general, the Hare Indian Formation is divided into three discernible lithofacies: 1) an organic-rich, black, laminated shale with fossils, that is mainly present in the lower Bluefish Member; 2) a thicker green or grey shale with thin interbedded limestones and silt; and 3) a darker grey shale also with some silt and limestone (Muir *et al.*, 1985; Pyle and Gal, 2016).

3.3 Methods

Three cores were logged in detail: the ConocoPhillips Loon Creek O-06 core, the ConocoPhillips Mirror Lake N-20 core, and the Husky Little Bear N-09 core (Figure 3.2). A facies scheme was developed for sedimentological macroscopic observations. These features include physical sedimentary structures (parallel laminae, for example), changes in mineralogy (presence of pyrite, for example), changes in fissility, pronounced colour change, discernible grain size changes, and fossil presence.

Agglomerative hierarchical cluster analysis was applied to the compositional dataset that was collected using a portable energy-dispersive X-ray fluorescence (pXRF) analyser, to characterise chemofacies.

Energy-dispersive X-ray fluorescence is a non-destructive method of collecting compositional data at high resolutions. A Thermo Scientific Niton XL3t portable XRF analyser is used to collect the data analysed here. Slabbed core is thoroughly cleaned and measured every 10 centimetres and at depths of interest (*i.e.* nodules, major mineralogical changes). The analyser stimulates a sample using X-rays and then detects and measures the X-rays emitted from the sample. Every sample is measured for 180 seconds using helium purging in order to decrease the level of detection. Data is reported for 34 elements in parts per million. The analyser is calibrated by Thermo Scientific with a proprietary algorithm. Every ten measurements, a certified reference material, the USGS Brush Creek Shale and a 99.995% silica blank are measured to ensure the accuracy and precision of the data.

Agglomerative hierarchical cluster analysis (AHC) was run using XLSTAT using Ward's method and the Euclidean distance of dissimilarity (Addinsoft, 2020). The elements used in this analysis are Si, Al, K, Ca, Ti, V, Fe, Zr, Mo, and Mg. These elements were chosen because they make up a high fraction of the bulk geochemistry of the samples, and are useful geochemical proxies in distinguishing paleoenvironment, provenance, paleoredox conditions, clay fraction and mineralogy (Pearce *et al.*, 2005; Ratcliffe *et al.*, 2010; Playter *et al.*, 2018).

Lithofacies and geochemical facies are compared to microfacies from Biddle *et al.*, (in review). Therein, samples from the Horn River Group were analysed petrographically for sedimentology and ichnology. Their dataset comprised in part thin sections from the same cores used in this study. Core-scale facies, chemofacies and microfacies are compared here as a means of using various methods to interpret the paleodepositional environment under which the Hare Indian Formation was deposited.

3.4 Results

3.4.1 Lithofacies

The Hare Indian is split into five distinct core lithofacies (F1-F5) (Figure 3.3). These facies are based principally on the presence of carbonate minerals and fossils, fissility, and colour. The most prevalent macroscopic sedimentary structure, continuous or discontinuous laminae, are also considered. These facies are F1) an intercalated limestone/dolostone and dark grey mudstone, F2) brownish-black mudstone with rare carbonate laminae and cm-scale limestone/dolostone beds, F3) medium grey calcareous mudstone, F4) medium grey homogeneous-appearing mudstone and F5) Light and medium grey calcareous fossiliferous mudstone. Their characteristics are summarised in Table 3.1.

3.4.2 Chemofacies

Agglomerative hierarchical clustering of pXRF data from the N-09, N-20 and O-06 cores resulted in 5 distinct clusters, here called chemofacies (C1-C5). The differences in elemental distribution are summarised in Table 3.2. Representative depths in the core corresponding to each chemofacies are shown in Figure 3.4.

Chemofacies 2, 4 and 5 (C2, C4, C5) appear quite similar, and quite homogeneous, dark grey with rare laminae and rare pyrite (Figure 3.4, B, D, E). Chemofacies 3 (C3) is often carbonate-rich with common laminae and appears more distinct (Figure 3.4, C). Chemofacies 1 (C1) sometimes resembles C2, C4 and C5, but sometimes has common laminae or may appear quite carbonate-rich (Figure 3.4). Chemofacies 1 is also less well defined in that it has less clear elemental relationships than other chemofacies. Where other chemofacies are high or low in certain elements, C1 is moderate in most elements and low in calcium and molybdenum.

3.4.3 Microfacies

The microfacies scheme used in this paper is adapted from Biddle *et al.*, (in review). There are four microfacies (MF2, MF4, MF7 and MF8) that appear in the Hare Indian Formation, as well as cone-in-cone structure calcite. Representative examples of these microfacies are shown in Figure 3.5. Their characteristics are summarised in Table 3.3. This model organised microfacies in terms of mineralogy, texture, and bioturbation intensity, and then interpreted sedimentary mechanism and proximity to the paleoshoreline (Biddle *et al.*, in review).

3.4.4 Comparison of Facies Distribution

A visual comparison of the lithofacies, microfacies and chemofacies occurrences by depth is provided in Figure 3.6 for the Husky Little Bear N-09 core, Figure 3.7 for the ConocoPhillips Loon Creek O-06 core, and Figure 3.8 for the ConocoPhillips Mirror

Lake N-20 core. In addition, the incidence of lithofacies to chemofacies, as well as chemofacies to lithofacies is shown as a contingency table in Figure 3.9, as well as by core location in Figure 3.10. The incidence of microfacies to lithofacies is also shown in Figure 3.11.

Visual inspection suggests that C3 and F3 often occur at the same depths, though typically in the lower half of the core. Chemofacies 3 and F3 are both carbonate-rich facies. Chemofacies 3 is high in calcium, and F3 is a calcareous mudstone. Of C3 occurrences, 43.2% coincide with F3 and of F3 occurrences, 39.6% coincide with C3 (Figure 3.9). Facies 5 also commonly occurs with calcium rich C3 75.0% of the time. F5, a carbonate-rich mudstone with carbonate fossils throughout, is only present at the base of the Hare Indian Formation of the O-06 core and is absent in the other two cores.

Facies 2 is the most common, making up 54.9% of the cores, and relates strongly with all chemofacies. Facies 4 and C4 coincide often, with 71.3% of F4 assigned as C4, though the reverse is lower at 53.8%. In the breakdown of occurrence by core, lithofacies and chemofacies correlate more reliably in the N-09 and N-20 core, while in the O-06 core, C1 makes up the majority of the core, comprising 80% of F1, 76.9% of F2, 20% of F3 and 61.9% of F4. Chemofacies 1 is defined by moderate amounts of most elements analysed, and low amounts of calcium and molybdenum.

The majority of thin sections are identified as MF7 (45% of thin sections in the Hare Indian Formation) or MF8 (21% of thin sections in the Hare Indian Formation). Microfacies 7, the fossiliferous discontinuous to continuous wavy parallel argillaceous mudstone coincides 69% of the time with F2, again likely because F2 is so prevalent. Facies 2 does contain some tentaculitids, often pyritized, but they are not always observable at core scale. MF8, the intraclast-rich discontinuous planar parallel argillaceous mudstone coincides 50% of the time with F2 and 50% of the time with F4. The features used to distinguish MF8 (intraclasts, detrital silt, graded bedding, and microfossils) are not observed at the core scale. Facies 4 appears quite homogeneous, as does F2, apart from rare carbonate laminae. Microfacies 2, the homogeneous appearing dolomitized argillaceous mudstone is the next most abundant microfacies (17%). It coincides with F2 (20%), F3 (40%) and F4 (40%). F2 and F3 are both quite homogeneous-appearing, and F3 contains common carbonate laminae, which are quite likely dolomitic in some instances, and calcitic in others. Microfacies 4, the rarely bioturbated discontinuous wavy parallel silt-bearing mudstone is only identified in two thin sections, both of which coincide with F2. Lastly, there are three thin sections of cone-in-cone structures, a diagenetic feature (Kowal-Linka, 2010). These coincide with F2 (33%) and F3 (67%).

3.5 Discussion

The Hare Indian Formation is classified using different types of facies: lithofacies, microfacies and chemofacies. Each classification scheme is used to draw different conclusions about the depositional processes, rock composition, and/or paleoredox conditions. The different facies schemes are compared and contrasted, with the aim of finding overlap in their interpretations.

Lithofacies, microfacies and chemofacies do correspond at some depths. The obvious features (*e.g.* carbonate-rich horizons) are easily identified in each facies type, whereas subtler features (*e.g.* increased clay content) are more readily detected by a particular classification method (*e.g.* chemofacies).

3.5.1 Lithofacies

The Husky Little Bear N-09 core and the ConocoPhillips Mirror Lake N-20 core show similar distributions of lithofacies. Both are dominated by alternating F1, F2 and F3 from the base of the core until the middle. The upper halves of the cores are mainly F4. The ConocoPhillips Loon Creek O-06 core is quite different from the other two cores. The base of the O-06 core is the only example of F5, the carbonate-rich fossiliferous mudstone present at the transition between the Hume Formation and the Hare Indian Formation. This may be due to the proximity of the O-06 core to the Kee Scarp Reef, located at Norman Wells.

Beyond paleo-shoreline or reef proximity, it is relatively difficult to make interpretations based on lithofacies alone. Compositionally heterogeneous samples and microscopic physical sedimentary structures often appear homogeneous at the core scale. Additionally, mudstones may appear homogeneous, but often vary horizontally and vertically (Lazar *et al.*, 2015). Suspension settling, sediment-gravity flows, storm reworking and contour currents are all mechanisms associated with mudstone deposition (Stow and Lovell, 1979; Potter et al, 1980; Macquaker *et al.*, 2010; Schieber *et al.*, 2010). However, the products of these mechanisms are not readily observable at the core scale. This requires the use of thin sections, rather than core scale facies.

Lithofacies are also unreliable in assessing the composition of the rock. Here, the differentiating characteristics between lithofacies include fissility, which is sometimes used as a proxy for clay versus silica content, and colour; neither of which are consistent characteristics when considering composition. Fissility is the product of the alignment of phyllosilicate minerals, made more prominent by weathering (Aplin and Macquaker, 2011). When compared to chemofacies, these indicators don't always align with what the pXRF data would suggest.

Observable differences in fine-grained lithofacies are colour, fissility, obvious mineralogy changes and macrofossils. These features do not correlate well with chemofacies or microfacies distinctions. Some features, like the presence of F5 at the base of the O-06 section provide clues that the section was deposited more proximally to the Kee Scarp Reefs, but in general, the interpretations that can be made using mudstone lithofacies are limited.

3.5.2 Chemofacies

The Husky Little Bear N-09 and the ConocoPhillips Mirror Lake N-20 cores both primarily consist of C4, while in the ConocoPhillips Loon Creek O-06 core, C1 is the most prevalent chemofacies. Chemofacies 4 is characterised by a high proportion of elements relating to clay minerals, redox-sensitive metals and Si. Conversely, C1 is characterised by moderate amounts of these elements, but particularly low Ca and Mo. This may be interpreted as decreased clastic dilution, compared to the other cores (Bohacs *et al.*, 2005).

In core, chemofacies occurrences do not necessarily correspond to observably different visual characteristics. Chemofacies 4 and C5 appear very similar in core (Figure 3.4, D and E), though C4 is higher in clay minerals and C5 is higher in Si. Chemofacies 1 and C3 also appear similar (Figure 3.4, A and C), though C1 is low in Ca, and C3 is high in Ca.

Characteristics like increased silica, high clay fraction, or elevated redox-sensitive trace metal concentrations may be easier to identify and correlate in fine-grained successions using chemofacies than other classification systems. Microfacies may provide a more detailed interpretation of small-scale depositional conditions, but methods like pXRF make collecting a large amount of high-resolution geochemical data relatively inexpensive and efficient, allowing for a more continuous examination of the changes in element ratios throughout the core. A potential drawback is that including too many elements may result in an abundance of chemofacies, making the results difficult to interpret (Pearce *et al.*, 2005; Ratcliffe *et al.*, 2015; Playter *et al.*, 2018).

Another limitation associated with chemofacies is the data collection methods involved. For example, pXRF analysis has lower detection limits for lighter elements than other analytical methods like ICP-MS or bench top wavelength dispersive X-ray fluorescence (Rowe *et al.*, 2017). In addition, the accuracy of pXRF is primarily determined by the user's or manufacturer's calibration (Lynch *et al.*, 2016). This can affect the application of the data, for instance some analyses benefit from having quantitative data, others from trends in data. However, analyses like ICP-MS are costlier, destructive techniques, which may limit the resolution of the study.

3.5.3 Microfacies

Microfacies are an important component of the interpretation of physicochemical depositional conditions. Using the small-scale physical sedimentary structures, bioturbation, and diagenetic features identifiable in thin section to make interpretations that are not possible to make from the core scale, or from geochemistry alone.

The microfacies presented here support deposition by sediment-gravity flows under poorly oxygenated bottom waters (MF2), plug-like flows and low density turbidity flows associated with poorly oxygenated bottom waters (MF4), surge or surge-like turbidity currents and/or debrites in relatively oxygenated bottom waters with intense storm reworking (MF7), and persistent plug-like flows in a proximal setting (MF8) (Biddle *et al.*, in review). In general, these interpretations support the idea that the Hare Indian Formation experienced a period of regression followed by transgression (Chapter 2). Again, this is different in the O-06 core, where thin section interpretations would suggest that the location was quite proximal (relatively shallow) throughout deposition, apart from a sample at 1800 m, which is assigned as MF2, a more distally associated microfacies.

The relationship between microfacies and other types of facies is less clear. One reason for this is a paucity of pXRF data at depths where thin sections were previously taken (pXRF taken at 10 cm intervals, thin sections taken at visual depths of interest). However, there are lithological core facies corresponding to pXRF measurments.

The study of fine-grained succession should include a variety of methods to best understand paleoenvironmental and physicochemical depositional conditions.

3.6 Conclusion

In summary, microfacies suggest a deposition occurred first distally, then more proximally and was controlled by plug-like flows, turbidity currents and debrites. Chemofacies help differentiate calcareous and dolomitized depths from more siliceous depths, and clay-rich depths. These results can also help understand locales that may be more proximal or distal. Lithological facies are useful in quickly differentiating carbonate minerals and in some cases more proximal facies, like F5.

These results help understand the uses of each of these classification schemes. Microfacies are important in a fine-grained succession in understanding the mechanisms responsible for deposition. Chemofacies can further inform the fine-scale distributions of elements and minerals in fine-grained successions. These insights can be used to discuss paleoenvironmental conditions. Lithological facies are most useful in fine-grained successions in making preliminary inferences, and possibly in deciding where to sample, but are not the most useful in making interpretations better suited to a petrographic study or geochemical investigation. In fine-grained successions like the Hare Indian Formation, the best course of action is to use multiple classification schemes in order to best understand the paleoenvironmental and physicochemical conditions.

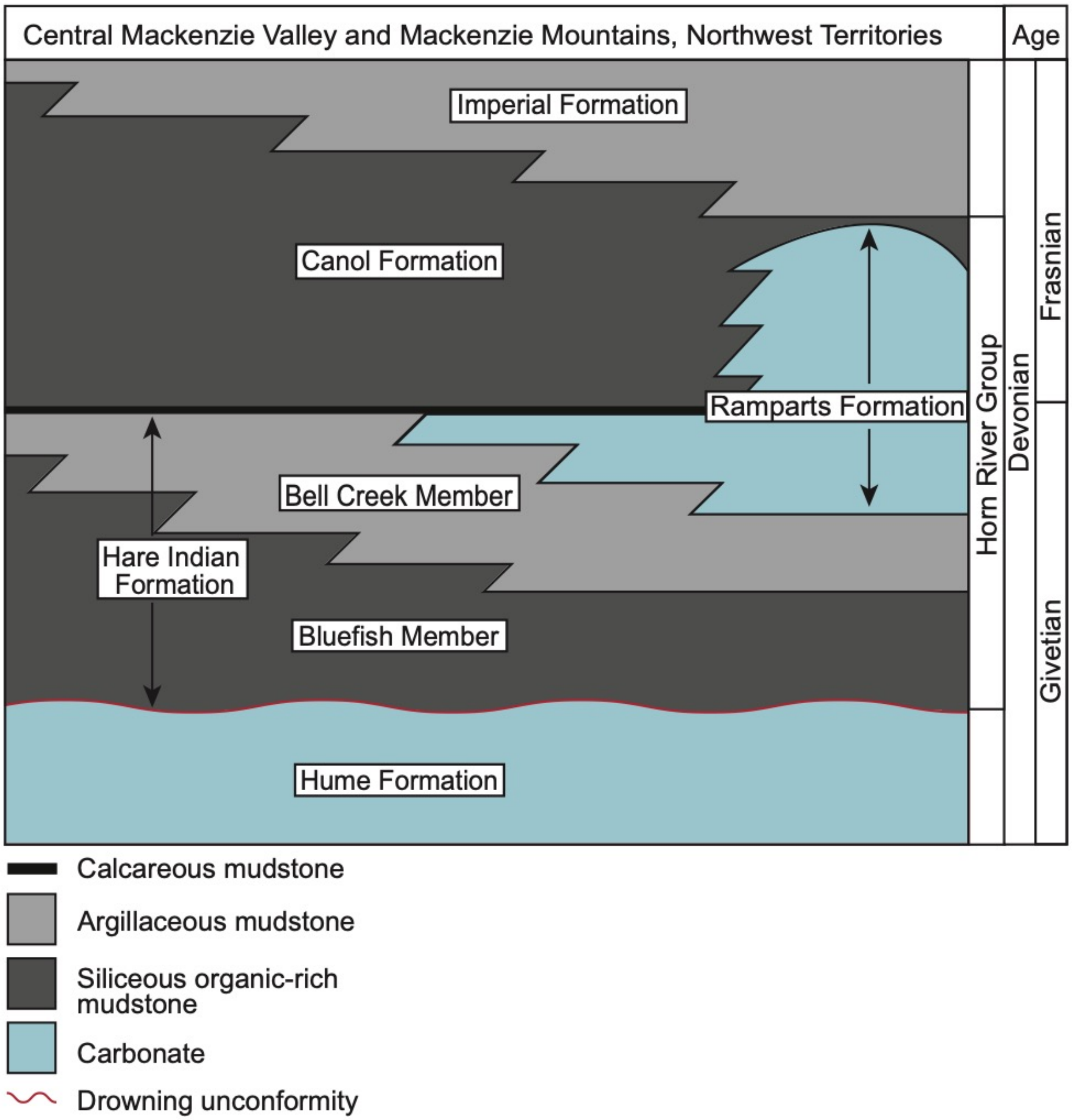

Figure 3.1 Schematic stratigraphic column of the Middle to Late Devonian Horn River Group in the Central Mackenzie Valley and Mackenzie Mountains, Northwest Territories, Canada. Modified from LaGrange et al., (2019).

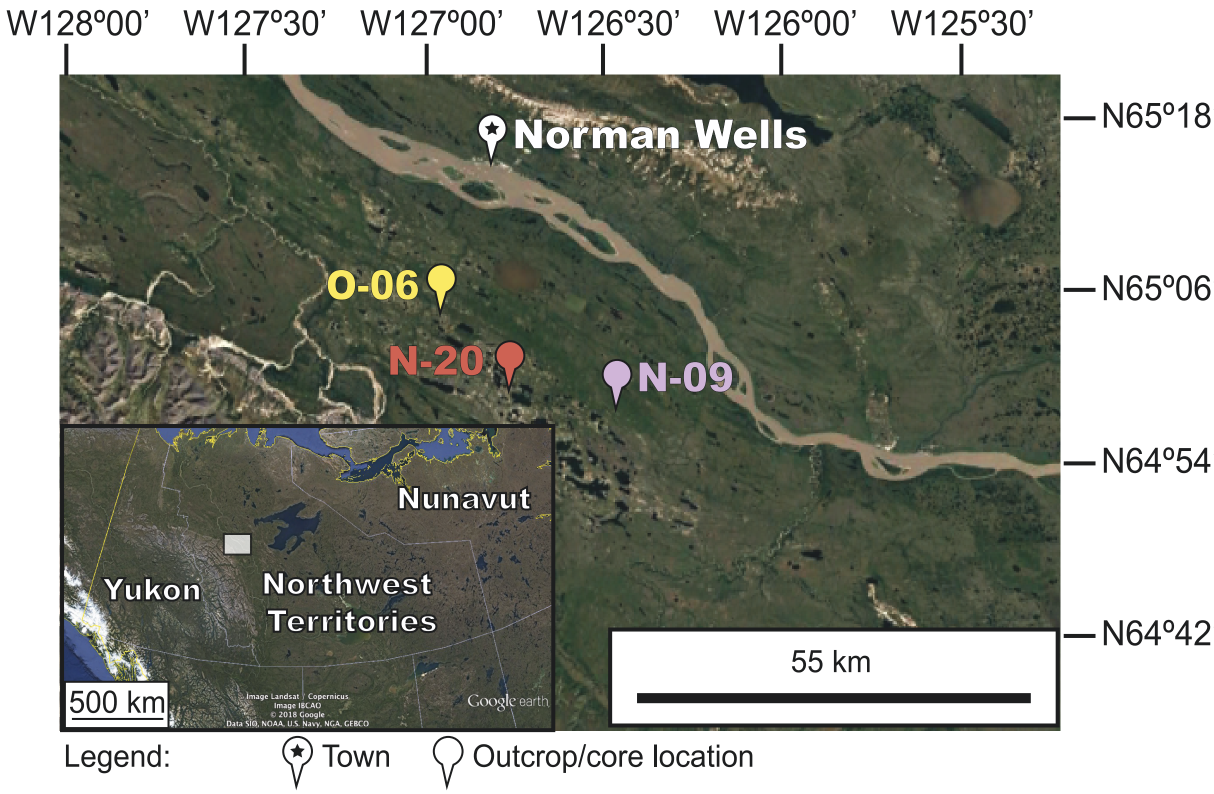

Figure 3.2 Map of the study area showing the location of the three cores considered in this study relative to Norman Wells, Northwest Territories, Canada. Images are modified from GoogleEarth.

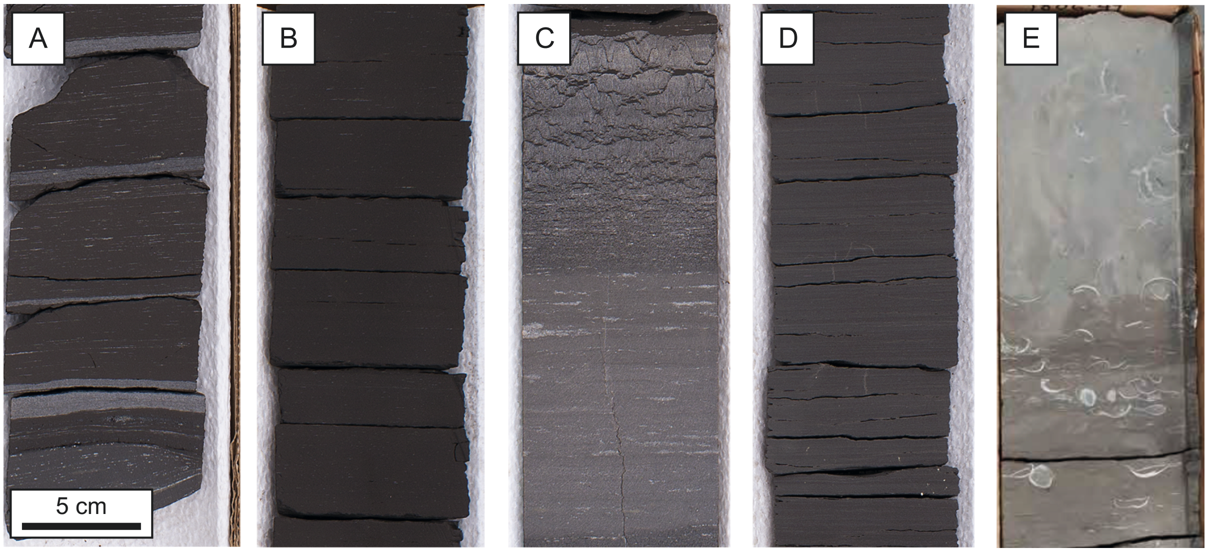

Figure 3.3 Representative examples of the five lithological core facies described. (A) Core facies 1 (F1) is shown, an intercalated limestone/dolostone and dark grey mudstone. The example is taken from the Husky Little Bear N-09 core at 1828.34 m. (B) Core facies 2 (F2) is shown, a brownish black mudstone with rare carbonate laminae and centimetre scale limestone/dolostone beds. The example is taken from the Husky Little Bear N-09 core at 1822.72 m. (C) Core facies 3 (F3) is shown, a medium grey calcareous mudstone. The example is taken from the Husky Little Bear N-09 core at 1826.48 m. (D) Core facies 4 (F4) is shown, a medium grey homogeneous-appearing mudstone. The example is taken from Husky Little Bear N-09 core at 1811.05 m. (E) Core facies 5 (F5) is shown, a light and medium grey calcareous and fossiliferous mudstone. The example is taken from the ConocoPhillips Loon Creek O-06 core at 1806.47 m.

Table 3.1 Descriptions of the five lithofacies described from the three cores in this study.

Facies Name	Occurrence and Contacts	Sedimentology and Accessories	Fossils
F1: Intercalated limestone/dolostone and dark grey mudstone	· Present mainly at the base of the Hare Indian Formation · Contacts are sharp	· Continuous and discontinuous planar parallel calcite/dolomite laminae and cm-scale beds intercalated with dark grey planar parallel laminated mudstone · Low fissility	· Tentaculitids in laminae
F2: Brownish black mudstone with rare carbonate laminae and cm-scale limestone/dolostone beds	· Dominant throughout lower Hare Indian Formation · Contacts are mainly gradual, some sharp with F3 and F4	· Rare limestone/dolostone laminae or cm-scale beds · Some calcite/dolomite and/or pyrite nodules · Low - moderate fissility · Planar parallel laminae common, often continuous, rarely discontinuous · May appear homogenous	· Pyritized tentaculitids rare observed on bedding planes
F3: Medium grey calcareous mudstone	· More prominent in the Bluefish Member · Contacts are quite sharp	· Abundant wavy discontinuous non-parallel laminae, continuous and discontinuous planar laminae · Graded bedding is common · Low fissility · Often has beds of cone-in-cone calcite structures	· Abundant tentaculitids, occasional shell fragments or ammonoids
F4: Medium grey homogenous appearing mudstone	· More prominent in the Bell Creek Member · Contacts are gradual	· Rare calcareous laminae · Homogenous appearing · Rare pyrite nodules · Moderately fissile	· None Observed
F5: Light and medium grey calcareous fossiliferous mudstone	· Present at the base of the Bluefish Member · Gradual contact with underlying Hume Formation and overlying facies	· Alternating medium grey mudstone and light grey calcareous mudstone · Wavy laminae · Low fissility	· Abundant disarticulated bivalve shells and shell fragments

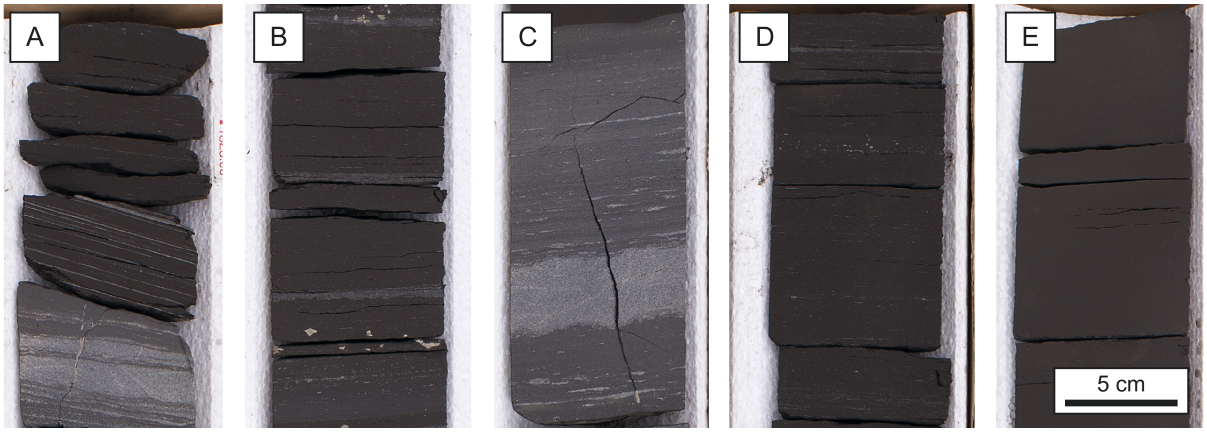

Figure 3.4 Representative examples of how five chemofacies calculated using agglomerative hierarchical clustering of pXRF data appear in core. All examples have been taken from the Husky Little Bear N-09 core. (A) Chemofacies 1 (C1) is characterised by low amounts of calcium and molybdenum, and moderate amounts of other tested elements. This sample is taken from 1828.7 m. (B) Chemofacies 2 (C2) is characterised by high iron and magnesium, and low molybdenum. This sample is taken from 1824.4 m. (C) Chemofacies 3 (C3) is characterised by high calcium, and low silicon, aluminum, potassium, titanium, vanadium, iron, zirconium and molybdenum. This sample is taken from 1828.3 m. (D) Chemofacies 4 (C4) is characterised by high silicon, aluminum, potassium, titanium, vanadium, zirconium and molybdenum. This sample is taken from 1825.3 m. (E) Chemofacies 5 (C5) is characterised as having the highest silicon, and particularly low magnesium. This sample is taken from 1822.04 m.

Table 3.2 Descriptions of the characteristics of chemofacies determined by AHC using pXRF data on the three cores considered.

Facies Name	Description	Interpretation
C1	· Low **Ca** and **Mo**	· Decreased clastic dilution
C2	· High **Fe** and **Mg** · Low **Mo**	· Dolomitzation has occurred
C3	· High **Ca** · Low **Si**, **Al**, **K**, **Ti**, **V**, **Fe**, **Zr**, and **Mo**	· Presence of calcite
C4	· High **Si, Al, K, Ti, V, Zr**, and **Mo**	· High clay fraction and influence of redox-sensitive elements
C5	· High **Si** · Low **Mg**	· High silica

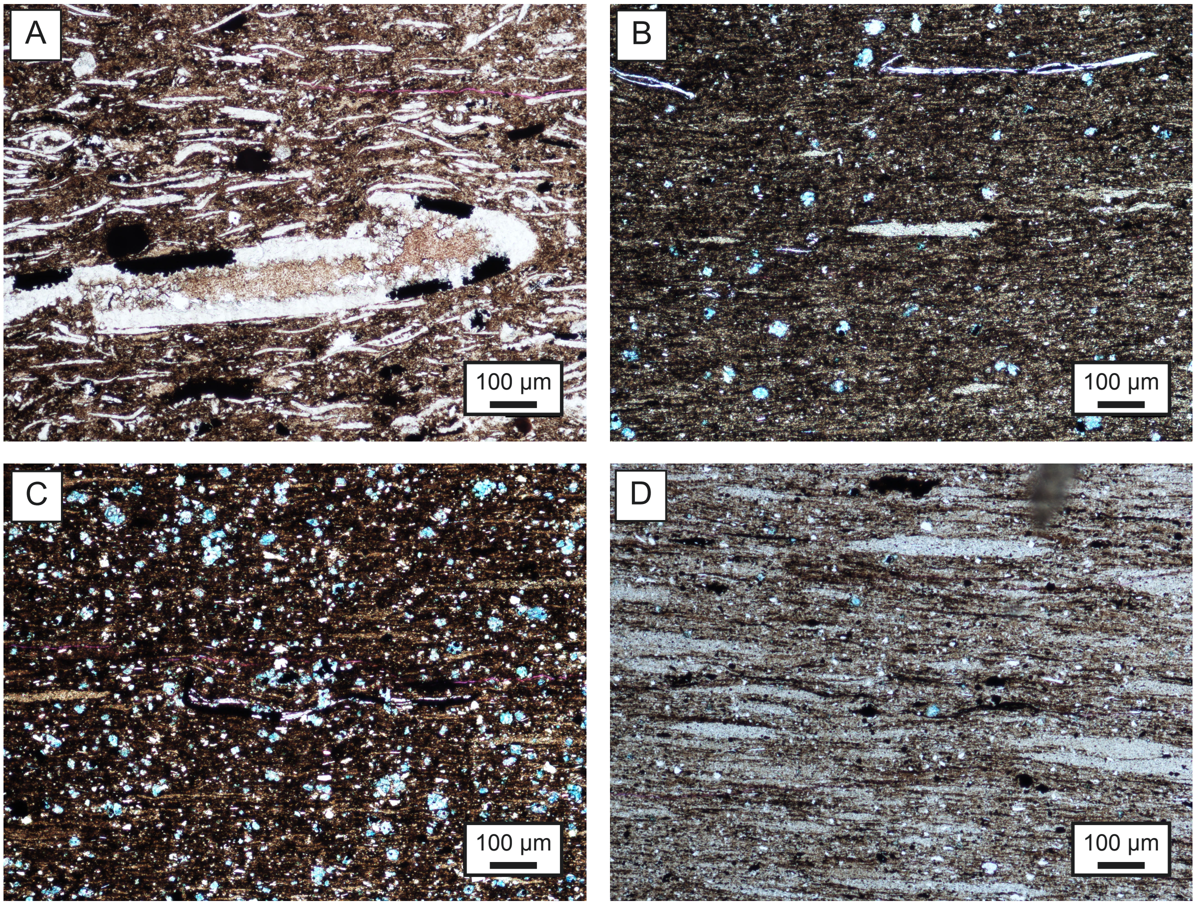

Figure 3.5 Representative examples of the four microfacies present in the Hare Indian Formation. All sample are taken from the Husky Little Bear N-09 core. (A) Microfacies 7 (MF7) is the fossiliferous mudstone. This sample is taken from 1823.52 m. (B) Microfacies 4 (MF4) is the discontinuous, wavy parallel silt bearing mudstone. This sample is taken from 1820 m. (C) Microfacies 2 (MF2) is the homogeneous appearing dolomitized argillaceous mudstone. This sample is taken from 1814.67 m. (D) Microfacies 8 (MF8) is the intraclast-rich discontinuous planar parallel argillaceous mudstone. This sample is taken from 1812.42 m (Modified from Biddle et al., in press).

Table 3.3 Characteristics of the microfacies considered from these core thin sections. Modified from Biddle et al., (in press).

Microfacies Name	TOC% Range	Description	Interpretation
MF2 : Homogenous-looking dolomitized argillaceous fMs	2.2 - 4.7	· >20% early diagenetic dolomite, most commonly ferroan rhombic dolomite · <5% detrital silt · Sedimentary structures and bioturbation cannot be identified due to pervasive dolomitization · Rare tentaculitid fossils	Rare low density turbidity flows with long residence times, associated poorly oxygenated sediment pore waters
MF4: Rarely bioturbated discontinuous wavy parallel silt bearing fMs	2.9 - 6.8	· 5 - 30% detrital silt · Unlaminated to weakly plane parallel laminated · Absent to common intraclasts · Rare microbial mats · BI: < 10% · Body fossils: conodonts, agglutinated foraminifera, radiolarians, tentaculitids · Common diagenetic dolomite and calcite	A mix of plug-like flows and low density turbidity flows with poorly oxygenated sediment pore waters
MF7: Fossiliferous discontinuous to continuous wavy parallel argillaceous fMs	5.3 - 7.7	· 10 - 100% tentaculitid fossils · Shells are generally intact, some are fragmented · Fossils are sporadic throughout (matrix supported) and/or concentrated along isolated bedding planes (grain supported) · Contain bioclastic graded bedding (coarse fossil beds fining upwards to detrital clay beds) · BI: 0 - 20% · Diagenetic dolomitization and pyritization	Hemipelagic suspension settling of calcareous microfossils with intermittant low density turbidites and rare high intensity storm generated bottom currents
MF8: Intraclast-rich discontinuous planar parallel argillaceous fMs	3.3 - 4.2	· >30% intraclasts · 0 - 30% detrital silt · Graded bedding, thin distal turbidites, and rare soft sediment deformation · BI: 0 - 20% · Body fossils: conodonts, radiolarians	Bedload traction transport under persistent bottom water currents
Cone-in-cone structures	N/A	N/A	N/A

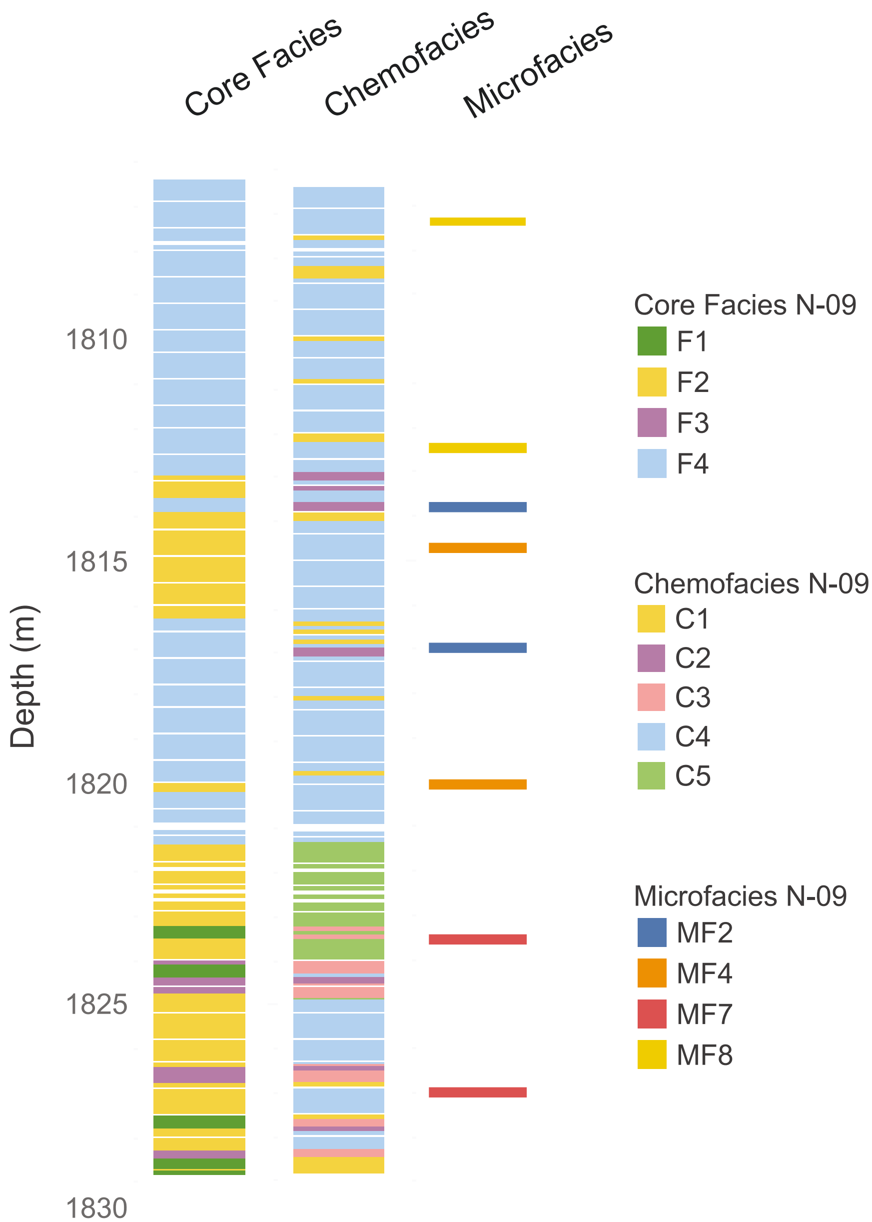

Figure 3.6 Comparison of lithological core facies, chemofacies and microfacies in relation to depth for the Husky Little Bear N-09 core.

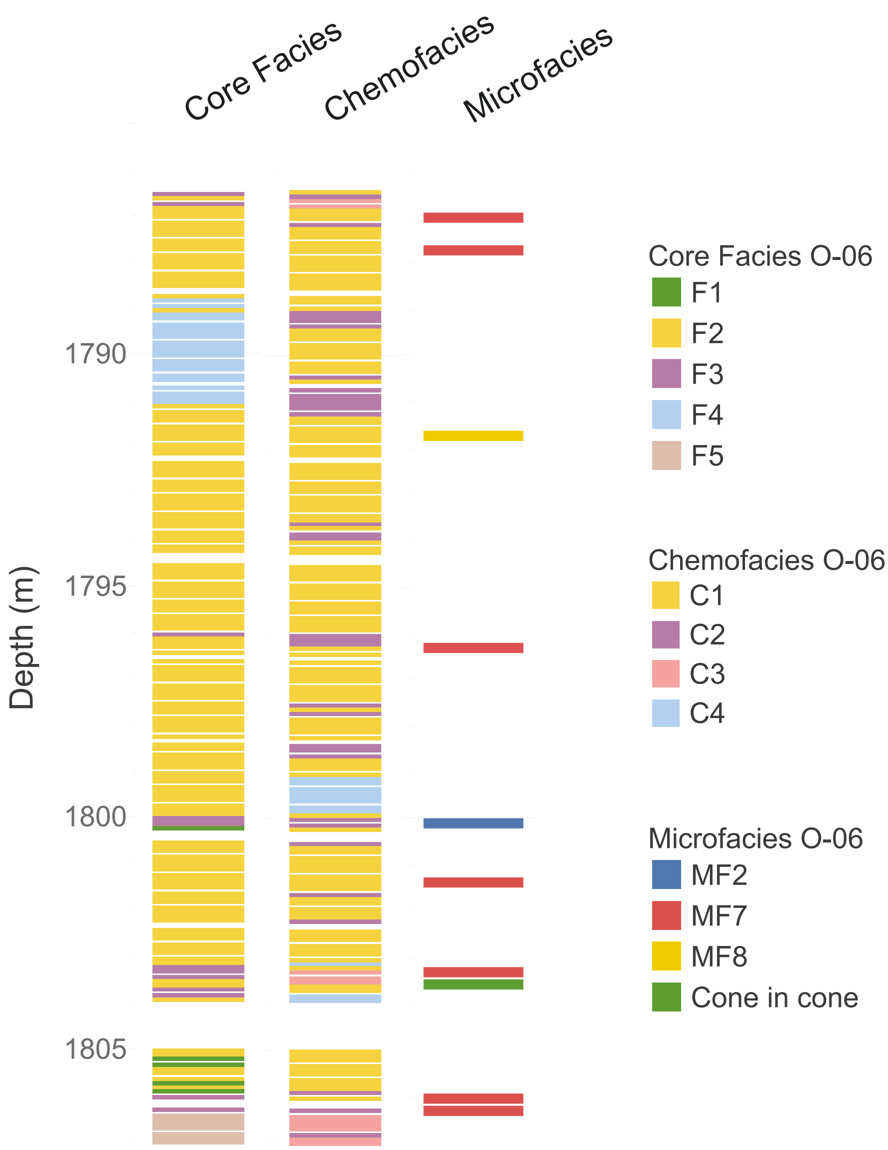

Figure 3.7 - Comparison of lithological core facies, chemofacies and microfacies in relation to depth for the ConocoPhillips Loon Creek O-06 core.

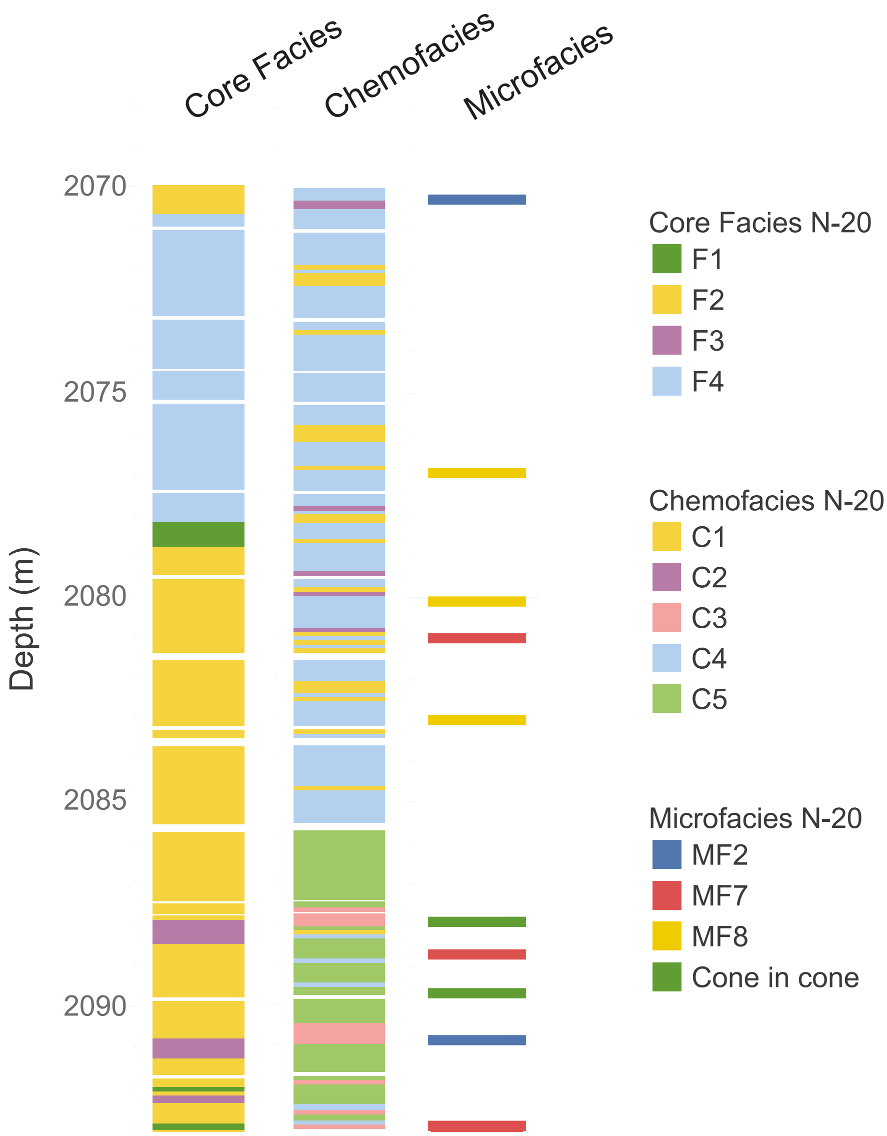

Figure 3.8 Comparison of lithological core facies, chemofacies and microfacies in relation to depth for the ConocoPhillips Mirror Lake N-20 core.

	% of Total Core	F1	F2	F3	F4	F5
C1	0.276	0.056	0.691	0.028	0.219	0.000
C2	0.081	0.019	0.481	0.135	0.327	0.038
C3	0.068	0.159	0.273	0.432	0.000	0.136
C4	0.443	0.024	0.430	0.007	0.538	0.000
C5	0.130	0.048	0.845	0.095	0.012	0.000

	% of Total Core	C1	C2	C3	C4	C5
F1	0.046	0.355	0.032	0.226	0.226	0.129
F2	0.549	0.335	0.068	0.033	0.335	0.193
F3	0.072	0.083	0.146	0.396	0.042	0.167
F4	0.323	0.181	0.079	0.005	0.713	0.005
F5	0.012	0.000	0.250	0.750	0.000	0.000

0.000 1.000

Figure 3.9 Incidence heat map showing the rate at which chemofacies occur with lithofacies and the rate at which lithofacies occur with chemofacies.

N-09	% of Total Core	F1	F2	F3	F4	F5
C1	0.093	0.261	0.130	0.043	0.565	0.000
C2	0.049	0.000	0.167	0.250	0.667	0.000
C3	0.085	0.333	0.095	0.571	0.000	0.000
C4	0.615	0.007	0.362	0.000	0.632	0.000
C5	0.126	0.097	0.839	0.032	0.032	0.000
N-20						
C1	0.105	0.042	0.417	0.042	0.500	0.000
C2	0.031	0.000	0.857	0.000	0.143	0.000
C3	0.052	0.000	0.667	0.333	0.000	0.000
C4	0.537	0.049	0.472	0.008	0.472	0.000
C5	0.231	0.019	0.868	0.132	0.000	0.000
O-06						
C1	0.703	0.031	0.846	0.023	0.100	0.000
C2	0.173	0.031	0.531	0.125	0.250	0.063
C3	0.059	0.000	0.182	0.273	0.000	0.545
C4	0.059	0.000	0.909	0.091	0.000	0.000
C5	0.000	0.000	0.000	0.000	0.000	0.000

N-09	% of Total Core	C1	C2	C3	C4	C5
F1	0.065	0.313	0.000	0.438	0.063	0.188
F2	0.368	0.033	0.022	0.022	0.604	0.286
F3	0.069	0.059	0.176	0.706	0.000	0.059
F4	0.498	0.114	0.065	0.000	0.780	0.008
F5	0.000	0.000	0.000	0.000	0.000	0.000
N-20						
F1	0.039	0.111	0.000	0.000	0.667	0.111
F2	0.581	0.075	0.045	0.060	0.436	0.338
F3	0.070	0.063	0.000	0.250	0.063	0.438
F4	0.310	0.169	0.014	0.000	0.817	0.000
F5	0.000	0.000	0.000	0.000	0.000	0.000
O-06						
F1	0.026	0.800	0.200	0.000	0.000	0.000
F2	0.737	0.769	0.119	0.014	0.070	0.000
F3	0.077	0.200	0.267	0.200	0.067	0.000
F4	0.108	0.619	0.381	0.000	0.000	0.000
F5	0.041	0.000	0.250	0.750	0.000	0.000

0.000 1.000

Figure 3.10 Incidence heat map showing the rate at which chemofacies occur with lithofacies and the rate at which lithofacies occur with chemofacies broken down by core location.

Microfacies	% of Thin Sections	F1	F2	F3	F4	F5
MF2	0.17	0.00	0.20	0.40	0.40	0.00
MF4	0.07	0.00	1.00	0.00	0.00	0.00
MF7	0.45	0.08	0.69	0.08	0.00	0.00
MF8	0.21	0.00	0.50	0.00	0.50	0.00
Cone-in-cone	0.10	0.00	0.33	0.67	0.00	0.00

Figure 3.11 Incidence heat map of microfacies in relation to core lithofacies.

4 Conclusions

In this study, the sedimentology and sequence stratigraphy of the Hare Indian Formation are examined using geochemical proxies and multiple facies classification schemes. The results of these analyses further refine the depositional environment, paleoredox conditions, sediment transport mechanism and relative sea level fluctuations.

4.1 Chemostratigraphy

Chemostratigraphic analysis results suggest there are two systems tracts recorded in the Hare Indian Formation: a TST and an RST. Redox-sensitive trace metals like Mo and V are enriched throughout the formation. In conjunction with microbioturbation analysis, these results support the interpretation of intermittent euxinia throughout the deposition of the Hare Indian Formation (Biddle *et al.*, in review). Silica peaks in the Bluefish Member suggest increased biogenic silica either from reduced sediment dilution or increased productivity. The applications of this work include more detailed regional mapping as well as core to outcrop correlations.

4.2 Facies analysis

The conclusions of the lithofacies, chemofacies and microfacies analyses suggest that each approach supports interpretations of the depositional environment. Lithofacies may not always be a suitable or practical choice as characteristics like grain size and small-scale physical sedimentary structures may impede interpretations. Lithofacies may be useful as a starting point, in considering where to sample, for example. In order to assess fine-scale features, petrographic analysis and microfacies classification yields more detailed interpretations of the sediment transport mechanisms involved in deposition. For further analyses, chemofacies may be useful. Specifically, pXRF can be useful in taking high-resolution, non-destructive measurements that may not always be possible with other methods. Chemofacies may be used to infer mineralogical changes at a finer scale or support paleoredox interpretations.

4.3 Future work

The methods used in this study could be improved in several ways. Additional core or outcrop locations, especially complete sections of the Hare Indian Formation, though the recessive nature of the Bell Creek Member make this challenging. In addition, more cases of the Hare Indian Formation where the Ramparts Formation is present would strengthen this framework. Additionally, isotopic analysis (C, N, and Mo) could clarify the controls on biogenic silica in the Bluefish Member (reduced clastic dilution or increased productivity) as well as confirm paleoredox conditions. Lastly, having both consistently spaced thin sections as well as depths of interest would strengthen interpretation comparisons across facies schemes.

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