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Sedimentology and geochemistry of the mixed carbonate-siliciclastic Espanola Formation, Paleoproterozoic Huronian Supergroup, Bruce Mines-Elliot Lake Area, Ontario, Canada

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Abstract

The Espanola Formation of the Paleoproterozoic Huronian Supergroup is a mixed carbonate-siliciclastic succession. Detailed sedimentological analysis of the formation in the Bruce Mines-Elliot Lake region reveals 17 sedimentary lithofacies, which comprise three distinct lithofacies associations. The lithofacies associations represent, in ascending order, shoreface, offshore, and nearshore (or lagoon) depositional environments along a wave- and storm-dominated shallow siliciclastic marine shelf. Major, trace, and rare earth element analyses of the siliciclastic component indicate derivation from a mainly granodioritic Archean upper continental crust with some contributions from mafic volcanic and/or sedimentary rocks. The results show that the source rocks were subjected to relatively low to moderate chemical weathering conditions. Stable isotope and elemental analyses of whole-rock limestone samples reveal strongly and consistently negative carbon and oxygen isotopic compositions, generally high Mn and Fe concentrations, and low Sr and Mg concentrations, suggesting post-depositional diagenetic alteration and re-equilibration with hot meteoric waters or infiltrating metamorphic fluids. The carbon and oxygen isotopic compositions are spatially highly variable, indicating local rather than global control, with no clear systematic stratigraphic trends. Petrographic analysis also revealed evidence of intense diagenetic alteration, including recrystallization textures, stylolite structures, widespread dolomitization, and the presence of minerals known to be associated with contact metamorphosed carbonate-rich rocks, such as diopside and scapolite. The Espanola Formation contains evidence of syn-depositional, rift-related seismic activity, including widespread load casts, ball-and-pillow structures, convolute bedding and lamination, dish-and-pillar structures, clastic dykes, and slump structures. With the exception of slump structures and associated slip faces, the majority of these deformation features are restricted to discrete stratigraphic horizons, laterally traceable over 100s of meters, and confined between undisturbed strata of similar lithology. It is proposed that normal fault systems bounding the study area were active during lower Huronian basin subsidence, and may have been the main control on sedimentation.
Keywords

Espanola Formation, Huronian Supergroup, Paleoproterozoic, rift basin, mixed carbonate-siliciclastic, shallow-marine, cap carbonate, geochemistry, stable carbon and oxygen isotopes
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Chapter 1

1 Introduction

1.1 Problem Overview

Rocks of the Huronian Supergroup exposed along the north shore of Lake Huron, Canada, are among the most intensively studied Precambrian rocks, and are considered the type area for Paleoproterozoic rocks of the Canadian Shield (Young, 1984). Preliminary investigations date as far back as 1821 when general geological research and early reconnaissance exploration were initiated, although systematic regional mapping and more specialized research did not begin until the middle of the twentieth century (Junnila, 1987). Such prolonged research has resulted in a considerable volume of Huronian Supergroup literature, which is manifested in the large number of geological reports published by the former Ontario Department of Mines and current Ontario Geological Survey, Ministry of Northern Development and Mines.

Renewed scientific interest in the Huronian Supergroup deposits was primarily inspired by the idea that the succession may contain evidence for an irreversible change in Earth’s atmosphere (i.e., the first appearance of atmospheric oxygen) (Prasad and Roscoe, 1996; Kasting and Ono, 2006; Bekker and Kaufman, 2007). Research was also motivated by the growing interest in Proterozoic glaciations and their global correlation potential, particularly aiming at understanding the cause-and-effect relationships of ancient global glaciation events (Ojakangas, 1988; Hoffman and Schrag, 2002; Evans et al., 1997; Melezhik, 2006). It is thus not surprising that formations of the Huronian Supergroup associated with glacial processes, such as the Gowganda Formation, and ore deposits, such as the Matinenda Formation, have received far more attention than other formations in the sedimentary succession (e.g., Miall, 1983; Mustard and Donaldson, 1987; Young, 1981).

In contrast to glacial-related and economically significant formations, the sedimentology of the Espanola Formation is poorly understood, although its theoretical importance as a potential Paleoproterozoic equivalent of a cap carbonate (continuous layers of carbonate sharply overlying Neoproterozoic glacial deposits) has recently become more widely appreciated (Hoffman et al.,
1998; Kennedy et al., 2001; Bekker et al., 2005). Notwithstanding, it remains unclear whether the cap carbonate comparison is viable. More attention is also being directed to the Espanola Formation because it is the only widespread carbonate-rich unit in an otherwise siliciclastic-dominated succession. Other minor and local carbonate occurrences include a thin (approximately 1.5m) carbonate unit at the contact of the Mississagi and Pecors formations on Haugton Bay (Long, 1973) as well as a very minor part of the Gordon Lake Formation (Hofmann et al., 1980).

A significant challenge in conducting a sedimentary facies analysis of the Espanola Formation is that the discontinuous outcrop exposure over approximately 375 km makes it difficult to trace lateral and vertical facies changes. This challenge is further compounded by an anticipated abundance of lateral facies changes, based on the mixed carbonate-siliciclastic nature of the formation. Rapid facies changes also characterize the formation in regions proximal to fault zones where syn-sedimentary deformation has taken place. Despite this, Bernstein and Young (1990) were able to correlate units across an area 2.2 km wide in the Whitefish Falls area of Ontario, where the rocks are highly deformed and metamorphosed to upper greenschist and locally to amphibolite grade.

1.2 Research Objectives

This study presents the results of the sedimentology, stratigraphy, geochemistry and petrography of the Espanola Formation in the Bruce Mines-Elliot Lake region, Ontario. Rocks in the region have been subjected to subgreenschist grade metamorphism and although folds and faults characterize the area, the folds are predominantly upright and open with gently plunging hinges, and tectonic fabrics are rare (Card, 1978; Bennett, 2006). Although outcrop exposures are discontinuous, the sub-horizontally dipping units allow for detailed sedimentological analysis. The investigation combines the results of different approaches in interpreting the depositional environments for the Espanola Formation, which emphasizes the characteristics of a Paleoproterozoic mixed carbonate-siliciclastic succession that formed in a rift basin during the rift-drift transition. These deposits are usually accompanied by major slope failure and associated soft sediment deformation along with contemporaneous normal faulting (Long, 2004; Young et al., 2001).
This study also aims to determine the types of carbonate minerals (calcite or dolomite), and the nature of their formation, whether primary (formed in situ) or detrital (transported to the site of deposition) based on their textures and composition as determined from thin section analysis and staining techniques. Further compositional analyses are determined from whole rock, major and trace element geochemistry of Espanola Formation siltstones in order to determine the nature of the source rocks (provenance), and the potential that intense chemical weathering occurred during the inferred early stages of Earth’s oxygenation.

The seemingly unusual stratigraphic position of the carbonate-rich Espanola Formation, resting conformably over glaciogenic diamicrites of the Bruce Formation, has attracted the attention of many researchers because it poses a climatic paradox in which an abrupt change from icehouse glacial to greenhouse tropical-like conditions may have taken place (Hoffman and Schrag, 2002). The Espanola Formation, however, is not unique in this respect. Most Neoproterozoic glacial deposits, especially those of Marinoan age, are directly overlain by carbonate deposits (Fairchild, 1993; Kennedy, 1996; Hoffman et al., 1998). The deposits are widely known as cap carbonates, and are characterized by specific sedimentological and isotopic characteristics (Kaufman et al., 1991; Kennedy, 1996). This thesis aims to determine whether the carbonates of the Espanola Formation represent a Paleoproterozoic cap carbonate by comparing carbon and oxygen isotopic results with Neoproterozoic examples as well as those determined from the Espanola Formation by Bekker et al. (2005).

1.3 Geological Setting

The Paleoproterozoic Huronian Supergroup (2.45 – 2.2 Ga; Krogh et al., 1984; Corfu and Andrews, 1986) is exposed along the north shore of Lake Huron and Georgian Bay, Ontario, Canada as a 60 km wide east-west trending belt that extends for approximately 300 km from the city of Sault Ste. Marie in the west to the Ontario-Quebec border in the east (Figure 1.1) (Young and Church, 1966; Long, 1978; Fedo et al., 1997a). The Huronian belt thickens southward, reaching a maximum thickness of approximately 12 km of mostly siliciclastic sedimentary rocks with comparatively very minor carbonates (Young and Nesbitt, 1999; Long, 2004). Subordinate intrusive and extrusive igneous rocks are located near the base of the Huronian succession (Card et al., 1972; Young and Nesbitt, 1999). The Huronian outcrop belt is bounded by rocks of the
Archean Superior Province to the north and west, by lower Paleozoic rocks to the south, and by metamorphic rocks of the Grenville Province to the east (Figure 1.1) (Young et al., 2001). From west to east, the outcrop area of the Huronian Supergroup is subdivided into the Bruce Mines-Elliot Lake, Espanola, and Cobalt areas. Field work for this research was mainly conducted in the northeastern part of the Bruce Mines-Elliot Lake area (Figure 1.1). Although the rocks in the study area have been metamorphosed to lower sub-greenschist grade, the prefix “meta” has been omitted in the remainder of the thesis for simplicity.

1.4 Tectonic Setting

The Huronian Supergroup represents a southward-thickening wedge (Figure 1.2) of mainly sedimentary and minor volcanic rocks that unconformably overlie rocks of the Archean Superior Province to the north. The exact tectonic setting in which the Huronian Supergroup was deposited has been and is still a highly debated topic (Long, 1995, 2004; Young, 1995, 2016). Various tectonic setting models have been proposed, including a rift basin (Meyn, 1973), an aulacogen (Young, 1983), a divergent continental margin (Fralick, 1984), a pull-apart sedimentary basin (Long, 1984), a transtensional extensional basin (Rousell and Long, 1998, Long, 2004), and a passive margin (Bennett et al., 1991).

Structural and stratigraphic studies of the Huronian basin, notably those by Zolnai et al. (1984) and Young and Nesbitt (1985), have strongly suggested that the lower part of the Huronian Supergroup was deposited during Early Proterozoic crustal stretching and contemporaneous rifting and faulting along the southern margin of the Archean Superior Province (Figure 1.2). Young (2014) stressed that the limited areal extent, paucity of marine indicators, thickness changes in units across major faults, and presence of seismic-related structures in the succession below the Gowganda Formation support deposition in a restricted fault-bounded rift basin. The Espanola Formation, which is stratigraphically lower than the Gowganda Formation, was thus deposited during the early rifting stage. The much more extensive upper part of the supergroup, which begins at the base of the Gowganda Formation, was interpreted as representing deposition during a phase of post-rifting regional subsidence of the cratonic margin (i.e., the establishment of a passive continental margin) (Zolnai et al., 1984; Young and Nesbitt, 1985) (Figure 1.2).
The idea that the Huronian Supergroup represents deposition during a transition from continental rifting and ocean opening to passive-margin development was reemphasized and adopted by the majority of more recent workers (e.g., Young et al., 2001; Ojakangas et al., 2001; Young, 2002, 2004, 2016; Long, 2004, 2009; Mungall and Hanley, 2004). The basis for the argument is that the Huronian Supergroup displays attributes that are strikingly comparable to those found in most basins associated with continental rifting, such as associated magmatism, asymmetric basin geometry, wedge-shaped sedimentary packages, and thick sedimentary infills of several kilometers that are usually bounded and influenced by active or reactivated syn-depositional normal faults (Zolnai et al., 1984; Young et al., 2001; Withjack et al., 2002; Allen and Allen, 2005).

In order to explain why the lower half (the rift succession) of the Huronian Supergroup is missing in the adjacent Animikie Basin on the south shore of Lake Superior, Young (2015) suggested that Paleoproterozoic rocks in the Animikie and Huronian basins may have been deposited, respectively, on upper and lower plate segments of a continent that was separated by displacement on a north-dipping detachment fault system (also Young, 2016).

Long (1995) attempted to provide constraints on some of the proposed tectonic setting models by utilizing thickness and paleocurrent trends within the thickest four sequences of predominantly fluvial sandstone in the Huronian Supergoup (Matinenda, Mississagi, Serpent, and Lorrain formations). His constraints were based on the assumption that fluvial systems respond rapidly to tectonic changes, and thus should provide a sensitive record of basin geometry and architecture. Long (1995) found that sandstones within the lower Huronian Supergroup (i.e., below the Gowganda Formation) have fluvial paleoflow patterns that are dominated by transverse and axial components, whereas those of the upper Huronian Supergroup display a rather uniform paleoflow pattern. Accordingly, Long (1995) suggested that the lower Huronian Supergroup represents deposition in an extensional pull-apart basin that was formed on a transform segment of a Paleoproterozoic continental margin as a result of the break-up of the Archean Kenorland supercontinent. Deposition within this basin would have been strongly influenced by steep left-lateral strike-slip faults (e.g., the Murray Fault and the Flack Lake Fault). He proposed that the transition from a rifted strike-slip margin to a passive margin setting, in which the upper
Huronian Supergroup was deposited, probably took place during deposition of the Gowganda Formation (also Rousell and Long, 1998, Long, 2004, 2009; Long et al., 2011).
Figure 1.1: Simplified geological map showing the general location of the study area (black rectangle) and the distribution of the Huronian Supergroup. Note the major structural features in the area, including the Murray fault zone (MFZ), Flack Lake fault (FLF), Sudbury Igneous Complex (SIC), and Creighton (C) and Murray (M) granites. Map modified from Young et al. (2001) and Bekker et al. (2005).
Figure 1.2: Schematic diagram illustrating the configuration of the Huronian basin and the main large-scale structural components that may have exerted influence on the Huronian Supergroup during deposition. Note the restricted nature of the fault-controlled lower units below the Gowganda Formation, compared to the more widespread upper units, reflecting a transition from rift to passive margin development. The volcanic rocks near the base of the Huronian Supergroup are probably related to initial rifting. Diagram reproduced from Young et al. (2001).
1.5 Stratigraphy and Sedimentology of the Huronian Supergroup

The Huronian Supergroup consists formally of four groups, although the two uppermost formations have been informally divided into a separate fifth group by most current workers (Wood, 1973; Rousell and Long, 1998; Long, 2004, Long et al., 2011). In ascending order, the groups are the Elliot Lake, Hough Lake, Quirke Lake, Cobalt, and Flack Lake groups (Figure 1.3). The sedimentary rocks of the three middle groups display a cyclic pattern, arranged into tripartite cycles that are believed to be controlled by glacio-eustacy and/or tectonic uplift and subsidence (Card et al., 1977; Young et al., 2001). Each cycle is represented by basal glacial deposits overlain by fine-grained siltstone/mudstone or carbonate, and capped by thick sandstone (Young and Long, 1976). The glacial deposits include the Ramsay Lake, Bruce, and lower Gowganda formations (Figure 1.3) (Young, 2004; Long, 2004), and their glacial origin is based on some of their associated features, such as striated and grooved underlying rock surfaces, striated and faceted clasts, and laminated fine-grained deposits with dropstones (Lindsey, 1969; Young, 1970). The middle part of each cycle is composed of fine-grained deposits, mainly mudstone (argillite) that has been interpreted as being post-glacial and of deltaic origin (Lindsey, 1969; Young et al., 2001; Bekker et al., 2006). The formations representing these intervals include the Pecors and Espanola formations, and the upper part of the Gowganda Formation (Figure 1.3). The Espanola Formation, however, is distinct in that it is the only carbonate-rich unit within the Huronian Supergroup that follows a glaciogenic interval (Young, 2002). The upper parts of each tripartite cycle are represented by the the Mississagi, Serpent, and Lorrain formations, which are composed of thick, arenaceous deposits. The cross-bedded, mostly medium- to coarse-grained sandstones are interpreted to have been deposited in fluvial, fluvial-deltaic or shallow marine environments (Pienaar, 1963; Palonen, 1973; Long, 1978; Rice, 1986; Young et al., 2001). In order to appreciate the Espanola Formation within a stratigraphic framework, a brief discussion of each of the four Huronian groups is provided in the following section.

1.5.1 Elliot Lake Group

Although poorly exposed, the Livingstone Creek Formation is considered the oldest unit of the Huronian Supergroup and it is exposed only in the western end of the outcrop belt (Bennett et al.,
It consists mainly of fine- to medium-grained, cross-bedded arkosic to subarkosic sandstone with subordinate carbonate and local polymictic conglomerate. The conglomerate contains granitic clasts derived from basement rocks. Uraniferous and pyritic quartz pebble conglomerate characterizes the top of the unit and is interbedded with the lower part of the Thessalon Formation. The presence of uraniferous and pyritic conglomerate, in addition to a paleosol (Gay and Grandstaff, 1980) at the top of the Livingstone Creek Formation, suggests that intense chemical weathering was prevalent at some point after deposition of the group. Nesbitt and Young (1996) and Young et al. (2001) attributed the immature nature of the Livingstone Creek Formation to tectonic uplift rather than climatic factors, suggesting rapid deposition under frigid conditions. The overlying Thessalon Formation is up to 2600 m thick, and is composed of continental mafic and felsic volcanic rocks and volcanogenic sedimentary deposits, which are restricted to the Thessalon area. The formation yielded an age of ca. 2.45 Ga based on U-Pb dating (Krogh et al., 1984; Ketchum et al., 2013). Young et al. (2001) suggested that these volcanic rocks resulted from diachronous volcanism because they are interbedded with rocks of the Matinenda Formation in the eastern and central parts of the Huronian outcrop belt. Interpreted as forming along a developing rift zone, the volcanic strata were subjected to folding and moderate deformation during an episode of compression at about 2.33 Ga (Zolnai et al., 1984), apparently during the closure phase of the rift zone during the Penokean Orogeny (Jolly et al. 1992).

Card et al. (1977) and Debicki (1990) studied the basal Huronian volcanic rocks in the Sudbury area and south of the Cobalt Embayment. Card et al. (1977) divided the rocks into three different formations, which include the Elsie Mountain, Stobie, and Copper Cliff formations. The basal Elsie Mountain Formation consists of 1000 m thick iron-rich, tholeiitic, massive and pillowved basalt flows. Local interflow deposits, mainly flow-top breccia and mudrock, suggest deposition in a deep-water, prodeltaic environment (Long et al., 1999). The approximately 1240 m thick (Debicki, 1990) Stobie Formation contains intermediate volcanic, pyroclastic, and sedimentary rocks. The volcanic flows are massive and pillowved, and interflow laminated siltstone and muddy sandstone are considered prodeltaic in origin (Long, 2009). The Copper Cliff Formation, up to 2600 m thick (Card and Jackson, 1995), is composed mainly of rhyolite flows and pyroclastic deposits (Debicki, 1990).
Figure 1.3: Generalized stratigraphic column of the Huronian Supergroup, with the informal Flack Lake group. Note the uniqueness of the carbonate-rich Espanola Formation among the otherwise siliciclastic-dominated succession. Also note the cyclic repetitions of units within the middle three groups. Subdivisions are according to Robertson (1976). Diagram modified from Long et al. (2011).
The Matinenda Formation rests unconformably on Archean basement, and is best exposed at Denvic Lake and the west part of Tube Lake where it is from 90 to 180 m thick (Robertson, 1976). Bennett (1981) described it as the most commercially significant formation of the Huronian Supergroup because it hosts the major Elliot Lake pyritic paleoplacer uranium ores. The formation consists mainly of uranium-rich quartz pebble conglomerate and arkosic and subarkosic sandstone. The sandstone, as described by Robertson (1976), is medium- to coarse-grained and poorly- to moderately-sorted. Individual bedsets, up to 1 m thick, are generally planar and trough cross-bedded with faint graded bedding. Card and Jackson (1995) and Long et al. (1999) suggested that the Matinenda Formation was deposited as alluvial fans and shallow braided river deposits.

The McKim Formation is the uppermost unit of the Elliot Lake Group, and rests conformably on the Matinenda Formation. It ranges from 1500-1800 m thick near the Elliot Lake area and up to 3000 m thick near Sudbury (Long, 2009). It consists mainly of laminated mudstone interbedded with minor sandstone and siltstone units. Card et al. (1977) identified three lithofacies within the McKim Formation: i) poorly sorted, fine- to coarse-grained muddy sandstone, deposited as turbidites, ii) laminated mudstone interpreted as resulting from prodeltaic suspension deposition (Long, 2009), and iii) fine- to medium-grained, thinly bedded sandstone consistent with turbidity current deposition (Long, 2009).

1.5.2 Hough Lake Group

The Hough Lake Group is composed of the basal Ramsay Lake Formation, the middle Pecors Formation, and the upper Mississagi Formation (Figure 1.3). The Ramsay Lake Formation conformably to disconformably overlies the McKim Formation, and is best exposed along the south side of Ramsey Lake. It is 6 to 9 m thick north of the Murray Fault (Parviainen, 1973; Robertson, 1976), although individual units of the Hough Lake Group thicken south of the Murray Fault. According to Card and Jackson (1995), the thickness is from approximately 10 m in the Elliot Lake area, to up to 180 m south of Kelly Lake (Long, 2009). The Ramsay Lake Formation consists predominantly of massive, clast-rich sandy diamictite with subangular to rounded clasts of pebble to boulder size. The clasts are predominantly composed of granite, volcanic rocks, and quartz, and are set in a muddy (argillaceous), medium- to coarse-grained
sandstone matrix. The formation also contains minor disturbed sandstone and siltstone interbeds. It is widely accepted that the Ramsay Lake Formation is of glacial origin (Young, 1970; Robertson, 1976; Nesbitt and Young, 1982; Young et al., 2001).

The 430-600 m thick Pecors Formation conformably rests on the Ramsay Lake Formation (Card et al., 1977), and mainly consists of thinly laminated mudstone and minor muddy sandstone with sedimentary structures including graded, parallel- and cross-laminated bedding, ripples, and ball-and-pillow structures. The Pecors Formation resembles the McKim Formation both chemically and petrographically (Card and Jackson, 1995; Robertson, 1976) to such a degree that Long (2009) suggested that its position overlying the Ramsay Lake Formation is the only means by which it can be distinguished from the McKim deposits. He also suggested a prodeltaic depositional environment for the Pecors Formation.

The Mississagi Formation conformably overlies the Pecors Formation and reaches a maximum thickness of 3400 m (Long, 1978). It consists of planar and trough cross-bedded, medium- to coarse-grained, arkosic to subarkosic sandstone along with locally preserved conglomerate and mudstone units (Long, 1978, 2009). McDowell (1957) was the first to propose a fluvial origin for the Mississagi Formation, which at that time was part of a unit that also included the Matinenda Formation, and most workers agree with this interpretation (e.g. Young, 1968; Roscoe, 1969; Young, 1973). Long (1978) reconfirmed that the formation was mainly deposited in shallow braided rivers, and Long (2009) also suggested local lacustrine environments in the southern Cobalt plain, based on the recognition of a 120-m thick muddy, fine-grained sandstone unit that is planar and ripple laminated.

1.5.3 Quirke Lake Group

The Quirke Lake Group consists of three units: a lower conglomerate, a middle carbonate-bearing argillaceous unit, and an upper unit of arkosic sandstone, known as the Bruce, Espanola, and Serpent formations, respectively (Figure 1.3). The basal Bruce Formation is mainly composed of poorly sorted, massive to crudely laminated conglomerate (diamictite) with clasts of granite, felsic volcanic, and mafic volcanic rocks set in a matrix of muddy, medium- to coarse-grained sandstone (Long, 2009). The formation thickness is from 10 m to more than 760
m (Parviainen, 1973; Rousell and Long, 1998; Long, 2009). Minor interbeds of mudstone and graded-beded sandstone characterize the upper part of the formation. Diamictites of the Bruce Formation are considered to represent the second glacial interval within the Huronian Supergroup, as a result of their characteristics that are common amongst other proven glacial sedimentary deposits (Bernstein and Young, 1990; Young et al., 2001; Young, 2004).

Carbonate-rich strata of the Espanola Formation conformably overlie the Bruce Formation. According to Bernstein and Young (1990), the Espanola Formation can be divided into a lower limestone member, a middle calcareous siltstone member, and an upper heterolithic member with a total thickness of approximately 560 m. Some workers suggest a mainly deltaic origin for the formation (Junnila and Young, 1995), whereas others suggest partial deposition in lacustrine (Veizer et al., 1992) and tidal environments (Card and Jackson, 1995). Shallow-marine and lacustrine conditions were also inferred by Fedo et al. (1997a), adding that deposition may have taken place in a warm paleoclimate based on stromatolite occurrences reported by Hofmann et al. (1980). Following a detailed study, Bernstein and Young (1990) concluded that the lower two members of the formation may have been deposited under low energy, subtidal shallow marine or lacustrine conditions, and that the upper member may represent deposition in a shallow marine environment with dominant tide and storm processes. A detailed account of the stratigraphy and sedimentology of the Espanola Formation is provided in Chapter 2.

The 250-350 m thick Serpent Formation conformably and gradationally overlies the Espanola Formation (Bernstein and Young, 1990). In the south and west of the Sudbury District, the formation consists of laminated and cross-bedded, medium- to fine-grained feldspathic sandstone (Long, 1976). Northwest of the SIC, however, two members were distinguished within the Serpent Formation (Long, 2009): a lower member composed of massive and crudely bedded conglomerate that grades laterally into planar and trough cross-bedded sandstone, and an upper member of massive sandstone (Long, 2009). The Serpent Formation is distinguished from other sandstone-dominated units of the Huronian Supergroup by its plagioclase-rich composition. This distinctive composition has triggered an intense debate on whether it resulted from changes in provenance, or is simply related to secondary processes such as diagenesis. Fedo et al. (1997a, b) emphasized the role of prevailing paleoclimatic conditions, attributing the abundance of
plagioclase to moderate paleoweathering conditions. This implies deposition during a climatic shift from greenhouse to icehouse conditions because the Serpent Formation overlies the carbonate-rich Espanola Formation and is overlain by the widespread glaciogenic Gowganda Formation.

1.5.4 Cobalt Group

The Cobalt Group is divided into two conformable units: the Gowganda and Lorrain formations (Rousell and Long, 1998, Long, 2004) (Figure 1.3). It unconformably overlies strata of the Hough Lake and Quirke Lake groups (Robertson, 1976), especially in the Bruce Mines and Espanola areas (Young and Nesbitt, 1985). In the Cobalt area, however, rocks of the Cobalt Group rest directly on Archean basement (Long, 2009) where an angular unconformity separates basement rocks from the Gowganda Formation (Mustard and Donaldson, 1987; Young and Church, 1966). Young (1972) linked these unconformities to tectonic reactivation, possibly related to the extension that accompanied a rift to drift transition. It is inferred that formations within the Cobalt Group, as well as Flack Lake Group, were deposited on a newly developed south-facing passive continental margin as the Gowganda and the succeeding formations are much more widespread when compared to the more confined, rift-controlled formations of the lower Huronian Supergroup (Zolnai et al., 1984; Young et al., 2001; Young 2004).

The Gowganda Formation forms the lowermost part of the Cobalt Group, and is considered the basal unit of the upper Huronian succession. It has a maximum thickness of approximately 1500 m (Young and Nesbitt, 1999), and is best exposed in the southern part of the Huronian outcrop belt, particularly on the north limb of the McGregor Bay anticline (Young and Nesbitt, 1985). The formation was informally subdivided into a lower diamicite-bearing unit rich in basement clasts, and an upper sandstone-argillite dominated unit that generally lacks such large clasts (Lindsey, 1969). These two stratigraphic subdivisions have been referred to in most subsequent studies as the lower and upper Gowganda Formation, and were named the Coleman Member and the Firstbrook Member, respectively.

The Coleman Member is 200-500 m or more thick in the Cobalt area (Mustard and Donaldson, 1987) and 200-900 m thick in the McGregor Bay anticline area (Young and Nesbitt, 1985). The
member is composed of a series of thick diamictite units, rich in extra-basinal clasts, followed up-section by laminated argillite units with evidence of at least two major glacial advances in the Southern Province and probably more north of the Murray Fault that are marked by diamictites or progradational cycles (Young, 2015, 2016). The upper part of the Coleman Member is composed of interbedded diamictite, orthoconglomerate, sandstone, and argillite (Lindsey, 1969; Young and Nesbitt, 1999). Young and Nesbitt (1985) conducted a detailed study of the Coleman Member near Whitefish Falls, in which they interpreted the basal diamictite to have been deposited under glacial/glaciomarine conditions accompanied by resedimentation processes, and attributed the associated almost clast-free argillite unit to quiet, deep water conditions that prevailed during recession of the glacier. The authors interpreted the upper diamictites as signifying a readvance of the ice sheet. Deposition under a continental ice sheet was also proposed by Long (2009).

The Firstbrook Member is 380-750 m thick (Junnila and Young, 1995), and consists of thick successions of laminated argillite followed by thinly bedded siltstone and sandstone, that grades upward into medium- to coarse-grained sandstone in the overlying Lorrain Formation (Fletcher and Eyles, 2006). The member also contains interbedded sandstone and mudstone facies. Long (1986) interpreted the Firstbrook Member as being prodeltaic in origin. The same conclusion was drawn by Rainbird and Donaldson (1988), and later confirmed by Junnila and Young (1995).

The Lorrain Formation is one of the thickest and most extensive formations in the Huronian Supergroup, with a total thickness of more than 2000 m (Lowey, 1985; Rainbird and Donaldson, 1988). It conformably overlies the Gowganda Formation (Casshyap, 1971), and is composed of arkosic, subarkosic and supermature quartzose sandstone along with local intervals of conglomerate and mudstone (Lowey, 1985; Long et al., 1999). Young (1973) proposed that the Lorrain Formation can be regionally subdivided into a lower unit of feldspathic sandstone with subordinate amounts of siltstone and mudstone, a middle unit of conglomeratic sandstone, with jasper, chert, and quartz pebbles, and finally an upper unit of white quartzose sandstone (orthoquartzite). The fine- to coarse-grained arkosic sandstone is planar and trough cross-bedded (Rousell and Long, 1998; Long, 2004). Different depositional environments have been proposed for the Lorrain Formation, which include fluvial (Chandler, 1986), beach (Casshyap, 1971), and
marine environments (Pettijohn, 1970; Young, 1973). Taking the enormous thickness of the Lorrain Formation into consideration, it is possible however that all of these proposed depositional environments are represented by its deposits. The supermature Al-rich deposits must have been the result of rigorous chemical weathering under tropical-like conditions, implying a rapid climate amelioration following the Gowganda glaciation (Nesbitt and Young, 1982; Long et al., 1999; Bekker et al., 2005). Williams and Schmidt (1997) conducted a thorough paleomagnetic study of the Gowganda and Lorrain formations in which they suggested deposition at low paleolatitudes for both.

1.5.5 Flack Lake Group

The Flack Lake Group includes the Gordon Lake and overlying Bar River formations (Figure 1.3). Wood (1973) was the first to propose the name Flack Lake Group for these two formations, which had been traditionally included in the Cobalt Group (Roscoe, 1969; Pienaar, 1963; Robertson et al., 1969). Wood (1973) noted that in drill core the contact between the Gordon Lake Formation and the underlying Lorrain Formation was sharp and distinct, and thus he considered it to be disconformable. This stratigraphic subdivision of the upper Huronian was adopted and supported by most subsequent workers (Rousell and Long, 1998; Long, 1995, 2004), mainly on the basis of regional paleocurrent trends determined from fluvial units of the Huronian Supergroup, and also thorough investigations of the tectonostratigraphic evolution of the Huronian basement and basin fill. The inference made by Wood (1973) was supported by McLennan et al. (2000), who used whole rock Sm-Nd and Pb isotopes to evaluate the provenance and post-depositional alteration history of the Huronian fine-grained formations (McKim, Pecors, Gowganda, and Gordon Lake). Their results showed that the Sm-Nd isotopic composition of the lower three formations are uniform and clearly indicative of a provenance dominated by the Archean Superior Province. In contrast, the distinctive Sm-Nd isotopic compositions of the Gordon Lake Formation indicated a broader source, including material with a younger provenance. The Pb isotope data from the same units supported the change in source composition (McLennan et al., 2000, see also Taylor and McLennan, 1995).

The Gordon Lake Formation is from 300 m thick in the northwest, to 760 m thick in the southern part of the Huronian outcrop belt (Chandler, 1988; Card and Jackson, 1995), consistent with the
southward thickening trend of the Huronian Supergroup. The formation consists of interbedded, ripple-laminated, fine-grained quartzose sandstone, siltstone, and laminated mudstone (Long, 2009). Thin beds of coarse-grained sandstone are concentrated in the lower and upper parts of the formation (Chandler, 1988). Wood (1973) was the first to report the occurrence of gypsum and anhydrite nodules in the lower part of the Gordon Lake Formation. These deposits were later interpreted later by Chandler (1986, 1988) to be sabkha-related in origin. Many depositional environments have been suggested for the Gordon Lake Formation, including shallow marine (Robertson, 1976), tidal to supratidal (Frarey, 1977), marine (Rust and Shields, 1987), and deep turbidite (Card, 1978). Hill et al. (2016) reported the presence of microbial induced sedimentary structures in the Gordon Lake Formation and overlying Bar River Formation, supporting the presence of algal mats on a tidally-influenced shoreline.

The roughly 1000 m thick Bar River Formation conformably overlies the Gordon Lake Formation, and is composed almost entirely of mature quartzose sandstone (orthoquartzite) (Rust and Shields, 1987; Young et al., 2001; Long, 2004). Similar to the other thick arenaceous formations of the Huronian Supergroup, the depositional environment of the Bar River Formation has been rigorously debated. It was interpreted as shallow marine (Pettijohn, 1970; Chandler, 1984), nearshore (Card, 1978), and fluvial (Frarey and Roscoe, 1970). Despite the apparent disagreement regarding the depositional settings of thick sandstone units in the Huronian Supergroup, many workers acknowledge that all of the thick sandstone formations (except the Bar River Formation) are at least partially fluvial in origin (e.g., Young, 1973; Long, 1976, 1978; Rainbird and Donaldson, 1988; Rousell and Long, 1998; Long et al., 1999; Young et al., 2001; Long, 2004).

1.6 Local Geology and Access

Investigation of the Espanola Formation in the Bruce Mines-Elliot Lake area was conducted in the summers of 2012 and 2013 (Figure 1.4). Most outcrops were easy to access without any major obstacles except for exposures located on some Quirke Lake islands, which required boat access. The exposures from Elliot Lake to Chiblow Lake were confined to a very narrow band, and the area was heavily vegetated, making it impossible to establish any sections in this region. In addition, urbanization has affected most areas around Blind River and Bruce Mines. A
reasonably thick exposure was, however, found at Cataract Falls, north of Blind River (Figure 1.4). Additional exposures were mapped near Manfred Lake, Roman Island (Quirke Lake), as well as near Parkinson (Figure 1.4). In the Espanola area, two outcrops were mapped at Clear Lake and along the Panache Lake Road (Figure 1.5). One relatively well-preserved outcrop was studied near Bannerman Lake, approximately 2 km southeast of Benny, Ontario in order to gain additional information concerning the form and distribution of stromatolites in the Espanola Formation. In addition to outcrop mapping, five drill cores were logged (totaling approximately 900 m of core), which were provided courtesy of the Ministry of Northern Development and Mines at Sault Ste. Marie. The locations of the drill holes are indicated on Figures 1.6 and Figure 1.7.
**Figure 1.4:** Regional geological map showing locations of studied outcrops of the Espanola Formation within the Bruce Mines-Elliot Lake Area. Note the east-trending Quirke Syncline and the Chiblow Anticline around which most of the exposures were mapped. Other exposures were located at Quirke, Crotch, and Manfred Lakes, and along Hwy 108. Two exposures were mapped at Cataract Lake (1) and near Parkinson (2). Map modified from Long (1977).
Figure 1.5: Geological map showing the area south of Espanola. Stars indicate locations of mapped sections near Clear Lake (1) and along Panache Lake Road (2). No outcrops were found along the shores of the northern part of Apsey Lake.
Figure 1.6: Locations of drill holes 144-1, 150-1, 150-2, 150-4. Map courtesy of the Ministry of Northern Development and Mines.
Figure 1.7: Location of drill hole 138-1 near McCool Lake. Map courtesy of the Ministry of Northern Development and Mines.
Chapter 2

2 Sedimentology of the Espanola Formation

The Espanola Formation forms the middle part of the Quirke Lake Group of the Paleoproterozoic Huronian Supergroup (Figure 1.3). On a regional scale, it conformably and sharply overlies Bruce Formation diamictite, and is conformably overlain by thick, fine- to medium-grained sandstone of the Serpent Formation (Long, 1977). Along the north shore of Lake Huron, the Espanola Formation is recognized in three major areas: Bruce Mines-Elliot Lake, north of Sudbury, and Espanola-Whitefish Falls (Figure 1.1). In accord with the general trend exhibited by other Huronian Supergroup units, the Espanola Formation thickens southward from approximately 150 m north of Elliot Lake, to more than 760 m south of Espanola (Young, 1973).

Several depositional environments have been proposed for the Espanola Formation. Junnila and Young (1995) suggested a mainly prodeltaic origin, as did Young et al. (1977). Other workers proposed partial deposition in lacustrine (Veizer et al., 1992) or tidal marine environments (Card and Jackson, 1995). Shallow marine and lacustrine conditions were also inferred by Fedo et al. (1997a) who suggested that deposition may have taken place in a warm paleoclimate based on stromatolite occurrences reported by Hofmann et al. (1980). Bernstein and Young (1990) concluded that the Espanola Formation may have been deposited subtidally under low-energy conditions, either in a shallow marine or lake setting, following recession of the Bruce glacier(s).

2.1 Previous sedimentological investigations of the Espanola Formation

The Espanola Formation was initially recognized as a single unit called the Bruce Limestone by Winchell (1887). Two additional units were later recognized above the Bruce Limestone by Collins (1914) who called them, in ascending order, the Espanola Greywacke and Espanola Limestone. Quirke (1917) adopted the same threefold subdivision, but considered the three units of Winchell and Collins to be individual formations constituting what he called the Espanola Group. This ranking of the units was, however, downgraded by Collins (1925) who suggested that the lower limestone, middle graywacke, and upper limestone units were members of the
Espanola Formation. This threefold subdivision was adopted and is now used by most workers (e.g. Pienaar, 1963; Card, 1967; Robertson, 1968).

Young (1973) renamed the three members of the Espanola Formation based on textural and compositional grounds. His proposed scheme included a lower limestone member, a middle siltstone member, and an upper dolostone member. Young (1973) acknowledged, however, that whereas all three members were present in the north limb of the Quirke syncline, only the lower limestone member could be recognized in the south limb. In the Whitefish Falls area, a fourth sandstone member was recognized overlying the dolostone member (Young, 1973). The limestone and dolostone members were interpreted to have developed in shallow marine environments, and the middle siltstone member was inferred to have been deposited by turbidity currents in relatively deep water. A fluvial origin was suggested for the sandstone member. Based on these interpretations, Young (1973) suggested that the lower three members of the Espanola Formation may have been diachronously deposited during a marine transgression, following the retreat of the Bruce glacier(s), and that the sandstone member may represent a distal facies that was deposited during subsequent marine regression.

Bernstein (1985) thoroughly investigated the stratigraphy and sedimentology of the Espanola Formation in the Whitefish Falls area. The author informally divided the formation into a lower stratigraphic unit, which includes a lower limestone member and an upper siltstone member, and an upper unit, composed of a lower sandstone member and an upper heterolithic member composed mainly of cross-bedded medium- to coarse-grained subarkosic arenite, interbedded with fine-grained siltstone and mudstone. Based on sedimentary facies analysis, Bernstein (1985) concluded that the limestone and siltstone members were deposited in relatively deep water on an unstable slope, with turbidity currents and/or storm-surge ebb currents being the primary transport mechanisms. In contrast, the sandstone and the heterolithic members of the upper unit were interpreted as having been deposited by large-scale migration of sand bars and sand shoals and by storm-influenced tidal currents, respectively. Bernstein (1985) attributed the deposition of the Espanola Formation to a marine transgression-regression system that was established following termination of the Bruce glaciation, and further inferred that the formation was deposited in an elongate, east-west trending basin, possibly linked to an ocean to the east.
The stratigraphy and sedimentology of the Espanola Formation south of Whitefish Falls was revisited by Bernstein and Young (1990). The authors found that the lower member of the Espanola Formation consisted of both limestone and dolostone, and that the dolostone member, first recognized by Young (1973), was in fact discontinuous. They therefore included the dolostone within the middle siltstone member. Bernstein and Young (1990) acknowledged that the origin of the lower and middle members is enigmatic, but inferred that deposition took place under relatively low energy conditions either in a shallow, subtidal marine environment or in a very large lake. The coarse-grained heterolithic member at the top of the stratigraphy was attributed to deposition in a shallow marine environment influenced by tide and storm processes (Bernstein and Young, 1990). Since the study of Bernstein and Young (1990), there have been no detailed stratigraphic and sedimentological investigations of the Espanola Formation, especially in the Elliot Lake region. In addition, later studies of the Espanola Formation have mainly focused on the isotopic and geochemical aspects of the formation (e.g., Veizer et al., 1992; Bekker et al., 2005).

This chapter aims to describe the sedimentology of the Espanola Formation exposed around the limbs of the Quirke syncline and Chiblow anticline in the Elliot Lake region (Figure 1.4). This detailed sedimentological assessment was based on outcrops and the description and logging of five drill cores totaling approximately 900 m in thickness (Appendix A). The cores came from different locations within the central part of the Quirke Syncline (Figure 2.1). The approach to lithofacies analysis used here is adopted so that each lithofacies represents the products of individual depositional events (c.f. Miall, 1990), is described, and then interpreted in terms of the physical processes that were occurring during transport and deposition. Considering that the characteristics of a depositional environment are determined by a combination of such processes (Reading, 1996), the lithofacies are grouped into lithofacies associations, that should in turn reflect the depositional environment, or environments, of the Espanola Formation. Determining facies sequences or successions, if any, will be considered as well in order to delineate any repetition of processes in response to changes in depositional conditions.
Figure 2.1: Simplified geological map of the Quirke Syncline showing the distribution of the Quirke Lake Group and the major structural elements, mainly normal faults, affecting the area. Stars indicate locations of examined exposures of the Espanola Formation: (1) Manfred Lake; (2) Panel Mine Road; (3) Denison Mine; (4) Island A; (5) Island B; (6) Crotch Lake; (7) Highway 108. Dots represent the locations of the five drill holes.
2.2 Definition of the term facies

The term “facies” in Latin refers to face, figure, appearance, aspect, or look (Teichert, 1958). The term is now widely used in geology, particularly in sedimentary studies. It was first coined and employed by the Swiss geologist A. Gressly (1838), while working in the Alps, to describe rock units that were characterized by similar lithological and paleontological features and to denote their lateral and vertical changes (Selley, 2000). The meaning and usage of the term, however, have been extensively debated since then (e.g., Moore, 1949; Teichert, 1958b; Krumbein and Sloss, 1963). Although a precise definition of the term facies as it is utilized in this research is a necessity, complete discussions and reviews of its origin, meaning and modern sedimentological applications can be found in Teichert (1958b), Anderton (1985), Plint (1995), and Reading (1996).

Middleton (1973) defined the word facies as referring to the sum of the characteristics of a sedimentary unit, including color, geometry, sedimentary structures, grain types and sizes, and biogenic content. Similarly, Tucker (1981) stated: “A facies is a body or packet of sedimentary rock with features that distinguish it from other facies.” With emphasis on its environmental implications, Reading (1996) stated that: “A rock facies is a body of rock with specified characteristics. It may be a single bed, or a group of multiple beds. Ideally, it should be a distinctive rock that formed under certain conditions of sedimentation, reflecting a particular process, set of conditions or environment.” Miall (1990) suggested that a lithofacies, a term first introduced by Krumbein and Sloss (1959), be used when defining a rock unit based solely on its distinctive lithologic characteristics such as composition, grain size, bedding styles, and sedimentary structures, thus drawing a clear distinction between lithofacies and other types of facies such as biofacies and ichnofacies. This research adopts the above stated definitions of facies, and mainly uses the term in a descriptive sense, which is used interchangeably with the term lithofacies, as specified by Miall (1990).

2.3 Sedimentary Lithofacies of the Espanola Formation

Seventeen sedimentary lithofacies were recognized within the Espanola Formation in the study area, based mainly on the physical properties of the rocks, including lithology,
grain size, and sedimentary structures (see Appendix B for a summary table). These lithofacies include:

Lithofacies 1- Interlaminated to interbedded siltstone-carbonate

Lithofacies 2- Massive to faintly laminated carbonate

Lithofacies 3- Wavy laminated sandstone

Lithofacies 4- Massive to faintly parallel-laminated sandstone

Lithofacies 5- Wavy bedded sandstone

Lithofacies 6- Low angle cross-bedded sandstone

Lithofacies 7- Planar interlaminated to interbedded mudstone-siltstone

Lithofacies 8- Wavy laminated to wavy bedded mudstone-siltstone

Lithofacies 9- Grey thickly bedded siltstone

Lithofacies 10- Green thinly laminated siltstone

Lithofacies 11- Interbedded massive and thinly laminated siltstone

Lithofacies 12- Mudstone

Lithofacies 13- Thickly bedded carbonate

Lithofacies 14- Rusty carbonate

Lithofacies 15- Stromatolitic carbonate

Lithofacies 16- Intraformational conglomerate

Lithofacies 17- Intraformational breccia
2.3.1 Lithofacies 1: Interlaminated to interbedded siltstone-carbonate

Strata of lithofacies 1 are from approximately 50 cm to 3 m thick, and consist of interlaminated to interbedded siltstone and carbonate (Figure 2.2). The lithofacies is laterally continuous over several meters, and generally has sharp, non-erosive lower and upper contacts (Figure 2.3). The rocks weather light to dark brown with distinct recessive weathering of the carbonate-rich laminae. On fresh surfaces, carbonate-rich laminae appear white to yellowish gray, and siltstone laminae and beds are very pale green giving the rocks a “zebra-striped” appearance (Figure 2.2). The beds are 2-5 cm thick with wavy upper and lower contacts. Siltstone beds are massive to faintly laminated, whereas carbonate beds are mainly very thinly laminated (Figure 2.2A). Planar lamination is well defined with individual laminae <1-2 mm thick. Massive clusters and radiating crystals of scapolite (1-2 cm in diameter) were identified locally (Figure 2.2B). Lithofacies 1 is intimately associated with lithofacies 2 (Figure 2.3).

In many places lithofacies 1 is highly deformed with widespread faults, 15-20 cm in vertical penetration, and folds that are symmetrical to slightly asymmetrical, with average amplitudes of 5 cm. Distorted beds are bounded by undeformed strata of similar lithology. At Clear Lake near Espanola (location 1; Figure 1.5), a conglomeritic dyke, approximately 0.5 m thick, sharply cuts lithofacies 1 perpendicular to the bedding (Figure 2.4A). The dyke contains clasts of granule to cobble grade. The dyke is internally sorted (description of Eisbacher, 1970) with the coarser clasts concentrated in the centre and finer clasts along the dyke margins (Figure 2.4A). Relatively large scale load structures (approximately 25 cm across) consist of well sorted, coarse-grained carbonate (Figure 2.4B). They have bulbous bases, and overlie mudstone interbeds with irregular contact relationships (Figure 2.4B). Single ball and pillow structures are around 10 cm in diameter, and are internally concentric (Figure 2.4C). Mini joints and faults are also common, penetrating the beds and structures alike but with no evident influence on primary stratification (Figure 2.4). Lithofacies 1 is best exposed on Hwy 108, Clear Lake, Island B and Roman Island (Figures 2.2-2.9).
The interlamination of siltstone and carbonate indicates alternating periods of siliciclastic influx and detrital carbonate accumulation. Planar laminae with non-erosive contacts and the general absence of other primary bedforms suggest low rates of sedimentation by low energy flows under quiet conditions possibly within a restricted environment where strong current and wave activity was minimal (Allen, 1982; Talling et al., 2012; Clerc et al., 2013). The persistent lateral continuity indicates that these depositional conditions were uniform. The wavy and locally erosional contact relationships with bounding units are consistent with relatively high energy conditions, possibly produced by episodic storm-derived waves and currents (McCave, 1985).

The small-scale faults and associated folds are interpreted as synsedimentary because the structures are confined to discrete stratigraphic horizons and are over- and underlain by undisturbed strata of similar lithology (Mazumder et al., 2006; Pillai and Kale, 2011). Deformation may have occurred under unstable conditions, such as a result of overloading, wave-induced stress, gravitational instability, oversteepening of slope, or seismic disturbance (Owen, 1987; Pillai and Kale, 2011; Koç Taşgın, 2011).

Synsedimentary faults have also been associated with differential vertical displacements caused by contemporaneous faulting (Eisbacher, 1970). Similar faults have been described by Pillai and Kale (2011), and have been labeled as intraformational faults. Local slumping and distorted bedding (Figure 2.3B) are consistent with deposition on unstable slopes inclined to gravity-driven, down-slope sediment transport and mobilization (Bussert, 2014). The observed slumping appears coherent (as defined by Dzulynski, 1963) where only minimal mixing of sediment took place, with good preservation of original bedding.

Conglomeratic clastic dikes (and sills) are attributed to local upward fluid escape in the form of liquefied sediment slurries induced by excess pore pressure release (Mills, 1983; Aspler and Donaldson, 1986; Owen, 1996). Based mainly on textural and compositional grounds, conglomeratic clastic dikes of the Espanola Formation have been commonly attributed to forceful injection of pebbly material from the underlying Bruce diamictites (Young, 1968, 1973). They have also been interpreted as being the result of episodic propagation of contemporaneous faults causing mobilization and consequent intrusion of
clastic deposits (Eisbacher, 1970). Thus, together with the widespread occurrence of ball structures, these dykes may indicate deposition and early defromation under tectonically unstable conditions (Young, 1968).

Load and ball-and-pillow structures are attributed to gravitationally unstable density contrasts caused by the apparently rapid and sudden deposition of water saturated coarse-grained, relatively dense, detrital carbonate material over un lithified mud layers (see Mills, 1983; Owen, 1996). Similar structures have been linked to sediment liquefaction brought about by either autogenic or allogenic triggers (Owen and Moretti, 2011). Different potential triggers, including earthquakes, waves and floods, groundwater movement and high sedimentation rate, have been proposed (Obermeier, 1996; Owen et al., 2011).

2.3.2 Lithofacies 2: Massive to faintly laminated carbonate

Lithofacies 2 consists of laterally continuous, massive to faintly laminated carbonate-rich bedsets up to 50 cm thick (Figure 2.5). The rocks appear white on fresh surfaces, and weather to pale yellowish orange and dusky yellowish brown (Figure 2.5). Lithofacies 2 is always found interbedded with lithofacies 1, with sharp linear lower contacts, and sharp undulatory upper contacts (Figure 2.5A). It has a distinct mottled appearance, produced locally by the presence of 3–5 mm size crystals of scapolite. Although lithofacies 2 is predominantly massive, local 1–2 mm thick, resistant, planar siltstone laminae and poorly preserved cross-stratification were observed (Figure 2.5B). The carbonate in lithofacies 2 is typically normally graded and well sorted, and has a granular clastic texture, suggesting a detrital origin, rather than primary precipitation. Rare, 2–4 cm deep tapering-downward shrinkage cracks and mm-scale asymmetrical ripples were identified in profile view (Figure 2.5A). Synsedimentary faults and folds in this lithofacies are similar to those found in lithofacies 1; however, some are confined within single beds.

Lithofacies 2 is well exposed along Hwy 108 where it is closely associated with lithofacies 1 (Figures 2.3, 2.6, 2.7) and on Island B and Roman Island (Figures 2.8, 2.9). At the latter locality, the two lithofacies form an 8 m thick section, consisting of 15-50
cm thick alternating bedsets of grey siltstone and white carbonate. The bedsets are laterally continuous over a few meters, except where affected by normal faults.

**Figure 2.2:** Lithofacies 1: interlaminated to interbedded siltstone-carbonate. (A) Faintly laminated siltstone beds alternating with thinly laminated carbonate-rich layers; note the folding and the zebra-striped appearance. (B) Dark patches of scapolite in lithofacies 1.
Figure 2.3: General outcrop view of lithofacies 1 and lithofacies 2. (A) Alternating beds of grey siltstone and white carbonate. (B) Soft-sediment deformation commonly associated with both lithofacies. Black scale-bar is 0.5 m.
**Figure 2.4:** (A) A thick sedimentary dyke vertically cuts the strata; note the sharp contact and the concentration of coarse-grained components in the core of the dyke. (B) Load structures; note the bulbous bases. (C) Ball and pillow structures. These structures are common in lithofacies 1 at Clear Lake (location 1, Fig. 1.5).
Figure 2.5: Lithofacies 2: massive to faintly laminated carbonate. (A) Sharp-based carbonate bed with undulatory upper contact. Note the tapering-downward shrinkage cracks on the upper part of the bed. (B) Poorly preserved cross-stratification locally found in lithofacies 2. Ruler is 15cm long.
The lithofacies contains evidence of soft-sediment deformation, with carbonate material injected upward into siltstone beds forming flame structures, or carbonate slumped down into silica-rich beds (Figure 2.3B).

Lithofacies 2 is interpreted to have been deposited during alternating sporadic influx of fine-grained siliciclastics and detrital carbonate debris. The detrital carbonate interpretation is supported by the grading and clastic texture of the carbonate beds. This is in agreement with findings of previous petrographic investigations of Espanola carbonates (Young, 1973; Bernstein, 1985; Bernstein and Young, 1990), as well as with the petrographic analysis presented in Chapter 3. These deposits are considered to have been transported and deposited by low- to moderate-energy traction currents, as indicated by the development of faint planar lamination and planar cross-bedding. The latter is generated by the migration of straight-crested dunes (Dalrymple, 1984; Leclair, 2002).

The downwards wedge shaped cracks in lithofacies 2 are probably syneresis cracks originated at the water-sediment interface by expulsion of water from unconsolidated sediments due to compaction or fluctuating salinities (Plummer and Gostin, 1981; Tanner, 2003). Syneresis cracks may form entirely under water without the necessity of subaerial exposure (Plummer and Gostin, 1981; Tanner, 1998; Tanner, 2003). The structures also resemble microbially induced sedimentary structures (MISS), which form by interaction between microbial mats and physical processes such as erosion, transportation, deposition, or deformation (Noffke et al., 2001; Schieber, 2004; Noffke, 2010). Similar MISS have been identified in the Gordon Lake and Bar River formations of the upper Huronian Supergroup (Hill et al., 2016). A definitive interpretation of these wedge-shaped cracks is difficult because of the absence of bedding exposures. The small-scale faults, confined to single beds, are interpreted as resulting from compaction processes on single beds rather than major events affecting the entire succession (Clerc et al., 2013).

Lithofacies consisting of similar mixtures of carbonate and siliciclastic material were interpreted by Mount (1984) to be the result of 4 mechanisms: (1) punctuated mixing, in which sporadic transfer of sediment between siliciclastic and carbonate depositional
environments occurs during high-energy events such as storms, (2) facies mixing, where mixing takes place along the diffuse boundaries between different facies; (3) in situ mixing, where mixing occurs in place as a result of autochthonous generation of carbonate material in a siliciclastic-dominated shelf environment; and (4) source mixing, which involves the supply of carbonate detritus to siliciclastic depositional environments that are proximal to uplifted and exposed carbonate source terranes. The facies mixing mechanism seems to be the most plausible process for the development of the carbonate-siliciclastic commingling observed in lithofacies 1 and lithofacies 2.

2.3.3 Lithofacies 3: Wavy laminated sandstone

Lithofacies 3 consists of planar to wavy laminated fine- to medium-grained sandstone, with subordinate mudstone (Figure 2.10A). Lithofacies 3 is light greenish to light bluish gray on fresh surfaces, and appear pale yellowish orange, yellowish gray, or medium dark gray on weathered surfaces. Bedding surfaces are commonly wavy. Single beds are approximately 10 cm thick with individual laminae measuring 5 mm thick. The strata are laterally continuous over several meters, and are commonly associated with mudstone lithofacies (LF12). The fine-grained component becomes more abundant up-section. At Crotch Lake, the lithofacies contains small, 1.5 cm wide clastic dykes that are composed of material similar to the surrounding layers (Figure 2.10A). Poorly-preserved symmetrical wave ripples and shrinkage cracks were identified on locally exposed bedding surfaces (Figure 2.10B). Lithofacies 3 is best exposed at Crotch Lake (Figure 2.11).

Lithofacies 3 is interpreted as the product of predominant bedload sedimentation by traction currents, with subordinate fallout of suspended load. The combination of these two processes is indicative of highly fluctuating flow energy conditions and waning currents (see Pickett, 2002). This is supported by the common association of lithofacies 3 with the mudstone lithofacies and also by its wavy bedding surfaces. Increasing fine-grained beds up-section strongly indicates a decrease in flow strength. Small clastic dykes can be attributed to small-scale dewatering and upward fluid escape through the sediments (Lowe, 1975). Symmetrical wave ripples form by the action of oscillatory
flows and surface wave activities during sedimentation, and indicate deposition under relatively shallow subaqueous conditions with minimal current influence (Collinson et al., 2006). Polygonal cracks are interpreted as either syneresis cracks or MISS.
Figure 2.6: Stratigraphic section showing the close association of LF1 and LF2. Constructed based on the east exposure of the Espanola Formation on Highway 108 north of Elliot Lake (see Fig. 2.1 for location).
Figure 2.7: Stratigraphic section showing the close association of LF1 and LF2. Constructed based on the west exposure of the Espanola Formation on Highway 108 north of Elliot Lake (see Fig. 2.1 for location).
Figure 2.8: Two closely spaced stratigraphic sections constructed based on exposures of the Espanola Formation at Island B (see Fig. 2.1 for location).
Figure 2.9: Stratigraphic section of the Espanola Formation at Roman Island showing interbedding of siltstone and carbonate (LF1) and massive carbonate (LF2) (see Fig. 2.1 for location).
2.3.4 Lithofacies 4: Massive to faintly parallel-laminated sandstone

Lithofacies 4 consists of massive to faintly parallel-laminated medium- to very coarse-grained sandstone with local quartz granules (Figure 2.12A). The rocks are grayish yellow on fresh surfaces, and appear dusky blue green to moderate brown on weathered surfaces. The bedsets are laterally continuous with an average overall thickness of 0.7 m and bedding surfaces are commonly sharp, and are locally scoured (Figure 2.12B). Although generally massive, the lithofacies locally contains planar parallel lamination (Figure 2.13A), ball and pillow structures (Figure 2.13B), dish and pillar structures (Figure 2.14A), mudstone interbeds, and gutter casts (Figure 2.14B). The majority of these structures have dimensions ranging from 2 to no more than 5 cm. Lithofacies 4 is well exposed at several localities, notably at Denison Mine and Crotch Lake (Figure 2.11).

Lithofacies 4 is interpreted as the result of rapid deposition from high-density turbidity currents accompanied by post-depositional liquidization processes. This interpretation was based on several characteristics, including the generally massive nature of the deposits, the faint planar parallel lamination and the associated soft-sediment deformation structures (see Pickering et al., 1989; Buatois and Mangano, 1994; Miall, 1996). The presence of quartz granules in massive sandstones also indicates rapid deposition from sediment-laden flows (Todd, 1989), and may mark the occurrence of short-lived periods of high-energy wave conditions, such as storm events (Duke and Prave, 1991; Prave et al., 1996). Scoured surfaces result from the flow of high energy turbulent and erosive currents over the surface of sediment that has been just deposited (Hornung et al., 2007). Gutter casts are linear erosional depressions commonly found associated with storm deposits (tempestites) (Myrow, 1992; Chakraborty, 1995; Perez-Lopes, 2001). However, gutter casts have been reported from the base of turbidite beds as well (Whitaker, 1973).
Figure 2.10: Lithofacies 3: wavy laminated sandstone. (A) Alternating planar to slightly wavy laminae of sandstone and mudstone; note the small-scale clastic dyke (black arrow). (B) Weathered symmetrical wave ripples (highlighted with black lines) and shrinkage cracks on the surface. Lens cap measures 5.5 cm wide.
Figure 2.11: Two stratigraphic sections displaying the characteristics of LF3 and LF4 at the Crotch Lake locality (location 6 of Fig. 2.1).
Figure 2.12: Lithofacies 4: Massive to faintly parallel-laminated sandstone. (A) General outcrop view of the lithofacies at Denison Mine. Scale bar is 0.5 m. (B) A local scoured bedding surface (yellow arrow) with a sole mark.
2.3.5 Lithofacies 5: Wavy bedded sandstone

Lithofacies 5 consists of wavy bedded, medium- to coarse-grained sandstone and mudstone (Figure 2.15). The lithofacies is typically 1 to 2.5 m thick and is best exposed at Denison Mine where 2-5 cm thick, wavy sandstone and mudstone beds alternate (Figures 2.15, 2.16). The sandstone beds are white on fresh surfaces and pale yellowish orange on weathered surfaces, whereas mudstone beds are moderate brown on both fresh and weathered surfaces. The beds are laterally continuous over at least 1 m, and bed contacts are mainly gradational with local scouring. Sedimentary structures include small load structures and sand balls that are a 3 mm to 2 cm across, and minor planar cross-lamination. Normal and reverse faults were identified locally (Figure 2.15).

Lithofacies 5 displays the combined attributes of bedload and suspension sedimentation with approximately equal proportions of sand and mud. Gradational bedding contacts normal grading indicate a transition from high-energy flow, responsible for transport and deposition of sand, to low-energy and slack water conditions during which mud settled out of suspension. Fluctuation of flow energy can be induced by tides (Homewood and Allen, 1981) or storms (Strachan, 1986). Local planar cross-lamination was generated by the migration of straight-crested current ripples. The load structures and sand balls are consistent with rapid deposition of higher density sand over lower density mud (Reineck and Singh, 1980; Mills, 1983).

2.3.6 Lithofacies 6: Low angle cross-bedded sandstone

Lithofacies 6 occurs in sets that are 15-70 cm thick, is mainly composed of low angle planar and trough cross-bedded, coarse-grained sandstone, and is locally cross-laminated or massive (Figure 2.17). The rocks are white or light grey on fresh surfaces (Figure 2.17A), and are rusty dark brown where weathered (Figure 2.17B). Lower and upper contacts are mainly sharp and non-erosive, but bases are locally erosive. Although the sandstones are generally very well sorted, local elongate 3–4 cm long carbonate clasts are common where the lithofacies is rusty brown and parallel-laminated, producing flat-pebble intervals. Good exposures of lithofacies 6 are found at the Denison Mine locality.
(Figure 2.18), where it is found associated with the thickly-bedded carbonate lithofacies (LF13) and the massive mudstone lithofacies (LF12).

Lithofacies 6 represents bedload sedimentation by relatively high-energy unidirectional traction current processes. This interpretation is based on the coarse-grained nature of the sandstones and the presence of low angle cross-bedding and local cross-lamination (Allen, 1970; Reineck and Singh, 1980). Planar and trough cross-beds are formed by migration of straight- and sinuous-crested dunes, respectively (Bristow et al., 2000; Leclair, 2002). Low angle cross beds may also indicate traction reworking of sediments by the migration of low-amplitude ripples (Allen, 1982; Paola et al., 1989). Local cross-lamination is attributed to the migration of current ripples, also signifying the involvement of tractional currents (Reineck and Singh, 1980). The local elongate rusty carbonate intraclasts aligned parallel to the lower bedding planes of lithofacies 6 may have been derived from the underlying thickly-bedded carbonate lithofacies by means of erosion and redeposition during storm events (see Shinn, 1983). The occurrence of storm events is also supported by locally erosive bases (Gomez and Astini, 2015).
Figure 2.13: Lithofacies 4: (A) Thin, planar, parallel lamination (some highlighted). The black diagonal line is a post-depositional fracture. (B) Ball and pillow structures.
Figure 2.14: Lithofacies 4: (A) Dish and pillar structures (arrow). (B) Mudstone interbeds and a gutter cast or scour fill (arrow).
Figure 2.15: Lithofacies 5: wavy bedded sandstone. (A) General view of the lithofacies. Hammer shaft is 45 cm. (B) Close-up view showing alternating beds of sandstone (light) and mudstone (dark); note the small-scale normal faults, which are common in this lithofacies.
Figure 2.16: Stratigraphic section from Denison Mine locality showing the relationship between LF1, LF5 and LF9 (location 3 of Fig. 2.1).
Figure 2.17: Lithofacies 6: low angle cross-bedded sandstone. (A) Association with the underlying thickly bedded carbonate lithofacies and the overlying mudstone lithofacies. (B) Well developed low-angle planar cross-lamination. White scale bar is 0.5m.
2.3.7 Lithofacies 7: Planar interlaminated to interbedded mudstone-siltstone

Lithofacies 7 is found in units up to 1.5 m thick, and consists of planar, parallel interlaminated to interbedded very fine- to fine-grained siltstone and mudstone (Figure 2.19). Contacts with associated underlying and overlying lithofacies are sharp to gradational. Individual laminae are a few mm thick, and the bedsets are 2-3 cm thick on average, but reach up to 8 cm locally. Mudstone laminae and bedsets appear grayish blue to dusky blue green on fresh and wethered surfaces, whereas those composed of siltstone are commonly grayish orange on fresh surfaces and moderate orange pink on weathered surfaces. The siltstone bedsets are massive or parallel-laminated, with local small-scale planar cross-lamination, and the mudstone bedsets appear massive (Figure 2.19A). Clastic dykes, up to 8 cm wide, locally cut the strata at angles of 20-30° from the horizontal (Figure 2.19B). The dykes are composed of well sorted, fine- to medium-grained sandstone. The contacts between the dykes and beds are sharp, and several thinly-laminated, commonly upward rotated fragments of the host rock are locally incorporated into the dykes (Figure 2.20). Some of the clastic dykes are affected by near vertical faults with offsets of approximately 3 cm (Figure 2.19B). Lithofacies 7 was found on Highway 108 and at Crotch Lake (Figures 2.6, 2.11, 2.21).

The generally massive, fine grained nature of lithofacies 7 and the absence of erosional features suggest deposition mainly from suspension fall-out in stagnant water under quiet conditions (Buatois and Mangano, 1994; Bussert, 2014). Calm conditions are also indicated by the lack of major synsedimentary deformational structures. However, the presence of faint planar parallel-lamination and local planar cross-lamination within the siltstone laminae indicate tractional grain movement and bedload sedimentation of unidirectional currents (Zakaria, et al., 2013; Clerc et al., 2013). Lithofacies 7, therefore, can be alternatively interpreted as the product of combined suspension and bedload transport.
Figure 2.18: Relationship between four lithofacies of the Espanola Formation at the Denison Mine locality (location 3 of Figure 2.1).
Figure 2.19: Lithofacies 7: planar interlaminated to interbedded mudstone-siltstone. (A) Interlaminated mudstone-siltstone (LF7) overlain by massive to faintly parallel-laminated sandstone (LF4). (B) Interlaminated to interbedded mudstone-siltstone with a clastic dyke cutting the layers at a low angle (arrow). Mechanical pencil and ruler are 15 cm long.
Figure 2.20: A thinly-laminated, upward rotated fragment of the host rock incorporated into a clastic dyke in lithofacies 7.

Two principal mechanisms have been proposed for the development of clastic dykes: sediment deposition into preexisting fractures below (Eyal, 1988; Levi et al., 2006), or upward fluid escape in the form of liquefied sediment slurries induced by excess pore pressure release (Mills, 1983; Owen, 1996). Sandstone dykes within the Espanola Formation have been interpreted as forceful injections of clastic material into cracks along the surfaces of contemporaneous faults, as well as release of excessive pore pressures in unconsolidated sandy material (Eisbacher, 1970; Young, 1973). The clastic dykes found in lithofacies 7 are interpreted as forceful clastic injections from below, either from lower units of the Espanola Formation or from the Bruce Formation, which may or may not be related to contemporaneous faulting. The forceful nature of these intrusions is suggested by their sharp contacts with surrounding strata and the incorporation of fragments that have been rotated upwards. Many of these clastic dykes do not exhibit any vertical displacement, which is usually associated with contemporaneous faulting, as suggested by Eisbacher (1970).
2.3.8 Lithofacies 8: Wavy laminated to wavy bedded mudstone-siltstone

Lithofacies 8 is found in units that are typically <10 cm thick, and consists of wavy laminated to wavy bedded medium- to coarse-grained siltstone and mudstone (Figure 2.22A). Individual laminae range from 2-5 mm thick, and the beds are 2-3 cm thick. Siltstone beds and laminae are pale blue green to moderate blue green on fresh surfaces and moderate pink on weathered surfaces, whereas those composed of mudstone are grayish green on fresh surfaces and pale to dusky yellowish brown on weathered surfaces. Symmetrical wave ripples are the most common sedimentary structures, with amplitudes of 2-3 cm, and wavelengths of <10 cm (Figure 2.22B). Additional sedimentary structures include small-scale sand ripples (<1 cm x 1 cm), sand balls several mm in diameter, rare 4-5 mm long tapering-downward wedge-shaped cracks, and mm-scale cross-lamination (Figure 2.23). Foresets are separated by thin veneers of mudstone (Figure 2.23B). The siltstone beds locally display a fining-upward trend and are covered by mudstone drapes (Figure 2.22B). Upper and lower contacts are sharp, but the lower contacts are locally scoured. Lithofacies 8 is exposed at several localities, including Panel Mine Road, Denison Mine, Manfred Lake, and Panache Lake (Figures 2.21, 2.24).

Lithofacies 8 is the product of alternating suspension and bedload sedimentation. The predominance of coarse siltstones suggests that the traction currents involved were of relatively higher energy than those responsible for deposition of lithofacies 7. The wavy bedding style with well developed symmetrical wave ripples points to the influence of oscillatory flows and surface wave activities (i.e., storms and fair weather) (Collinson et al., 2006). The small-scale cross-lamination observed in some of the siltstone layers is consistent with migrating ripples produced by unidirectional traction currents with low flow velocity (Reineck and Singh, 1980). The gradual fining-upward trends point to progressively waning currents, followed by periods of stagnant water dominated by suspension fall-out of fines, as represented by mud drapes (see Buatois and Mangano, 1994; Longhitano et al., 2012). Although these observations could point to the possible involvement of reversing tidal currents (e.g., Dalrymple, 1992, 2010), no bi-directional
cross-strata or reactivation surfaces were identified in lithofacies 8, pointing strongly towards wave action as the principal depositional process.

Local scours are interpreted as resulting from erosion by bottom currents possibly during episodic storm events (Schieber, 1990; Mulder and Alexander, 2001). Rare wedge-shaped cracks are syneresis cracks or MISS. Sand balls form by gravitationally unstable density contrasts, which is especially common when the strength of the lower bed is reduced by an external trigger (e.g., seismic shaking), causing the overlying sediment to sink into and become embedded in the lower layer (Allen, 1982; Owen, 1987).

2.3.9 Lithofacies 9: Grey thickly-bedded siltstone

Lithofacies 9 forms units approximately 2.5 m thick and consists of thickly bedded medium- to very coarse-grained siltstone (Figure 2.25A). The rocks are black to dark grey or green on fresh surfaces, and weathers to brown. Contacts between the bedsets are sharp to slightly wavy, and individual bedsets are 30-50 cm thick. Sedimentary structures include faint parallel lamination, small-scale current ripple cross-lamination (Figure 2.25B), large-scale (up to 10 cm across) internally concentric ball structures (Figure 2.26A), and distorted bedding (Figure 2.27). Well preserved symmetrical wave ripples were also observed with amplitudes of 2-3 cm and wavelengths of 6 cm (Figure 2.26B). Exposed bedding planes feature ripple marks (Figure 2.28A) and wedge-shaped cracks (Figure 2.28B). Lateral changes in thickness over a few meters were recorded. Lithofacies 9 is best exposed at Panache Lake and Denison Mine (Figure 2.24 and 2.29).
Figure 2.21: Stratigraphic section of the Espanola Formation at Crotch Lake dominated by siliciclastic deposits of LF7, LF8, and LF9. See Figure 2.1 for location.
Figure 2.22: Lithofacies 8: wavy laminated to wavy bedded mudstone-siltstone. (A) Wavy laminated siltstone (yellow to green) and mudstone (grey to brown). (B) Wavy bedded siltstone and mudstone containing wave ripples (arrows).
Figure 2.23: Lithofacies 8: (A) Small-scale sand ripples and sand balls; (B) Cross-lamination.
Figure 2.24: Stratigraphic section of the Espanola Formation at Panache Lake showing the characteristics of LF8, LF9, and LF10 and their associated sedimentary structures.
Figure 2.25: Lithofacies 9: grey thickly-bedded siltstone. (A) General outcrop view. (B) Ripple cross-lamination. Scale-bar is 0.5m. Lens cap diameter is 5.5cm.
Figure 2.26: Lithofacies 9: grey thickly-bedded siltstone. (A) Ball and pillow structure (arrow). (B) Planar cross-laminated symmetrical wave ripples.
Lithofacies 9 was deposited by a combination of bedload and suspended load processes. The medium- to very coarse-grained nature of the siltstone deposits and the planar parallel-lamination and current ripple cross-lamination are consistent with low-energy traction currents. Bressan et al. (2013) suggested that laminated siltstone indicates deposition under fair-weather conditions, which may also account for the sharp bedding contacts. Where the rocks are massive, however, thickly-bedded, coarse-grained siltstone may be attributed to abrupt and rapid settling of silt from suspension that may have been transported by storm-generated flows (Brodzikowski and van Loon, 1991; Bressan et al., 2013). Transportation of these deposits by turbidity currents is unlikely because of the associated abundance of wave ripples. Cross-laminated symmetrical wave ripples are formed by the action of oscillatory flows under relatively shallow subaqueous conditions. Convoluted bedding and ball structures attest to high rates of sedimentation.

Figure 2.27: Distorted bedding found locally in lithofacies 9.
Figure 2.28: Lithofacies 9: grey thickly-bedded siltstone. Wave ripples (A) and shrinkage cracks (B). Lens cap is 5.5 cm wide.
**Figure 2.29:** Stratigraphic section of the Espanola Formation at Denison Mine displaying the characteristics of the grey thickly-bedded siltstones of LF9. See Fig. 2.1 for location.
2.3.10 Lithofacies 10: Green thinly-laminated siltstone

Lithofacies 10 forms units up to 0.5 m thick of fine- to medium-grained, thinly-laminated to thinly-bedded siltstone (Figure 2.30A). The rocks appear light to dark green, and weather dark grey. The lower bedding contacts are sharp, but the upper contacts are gradational and wavy (Figure 2.30B). Individual laminae are a few mm thick, and beds are 10 cm thick on average. Planar parallel-lamination, and planar and trough cross-lamination are the main sedimentary structures. Hummocky cross stratification (HCS), which passes up-section into symmetrical wave ripples was also identified (Figure 2.30). Sand balls from 2-4 cm in diameter are concentrated near the top of the lithofacies. Lithofacies 10 is best exposed at Panache Lake and on Panel Mine Road (Figure 2.24).

Lithofacies 10 is interpreted to have been deposited by traction currents, as suggested by the presence of planar parallel-lamination and planar to trough cross-lamination (Gindre et al., 2012; Zakaria, et al., 2013; Clerc et al., 2013). Planar parallel-lamination forms as a result of low-amplitude (mm high) ripple migration by low- to moderate-energy traction currents (Allen, 1982). It may also be a manifestation of upper plane bed conditions (Bridge and Best, 1997). In contrast, planar and trough cross-laminations are formed by migration of straight and sinuous crested ripples, respectively (Collinson et al., 2006).

Although the fine-grained and laminated nature of lithofacies 10 may also suggest deposition from suspension and subordinate bedload sedimentation by waning low-density turbidity currents (e.g., Buatois and Mangano, 1994), this interpretation is excluded based on the widespread presence of wave ripples as well as the lack of features characteristic of turbidity current deposits, such as normal grading and erosional structures.

Hummocky cross stratification (HCS) is widely considered a structure diagnostic of storm-dominated environments characterized by combined flows (Harms et al., 1975; Dott and Bourgeois, 1982; Plint, 2010; Bayet-Goll et al., 2014). Wave ripples overlying HCS bedsets point to the gradual predominance of oscillatory flows over unidirectional flows (Harms et al., 1975; Collinson et al., 2006). The presence of sand balls also attests
to high sedimentation rates, which are commonly associated with storm-dominated settings (Owen et al., 2011).
Figure 2.30: Lithofacies 10: green thinly-laminated siltstone. (A) A typical storm bed showing a planar parallel lamination (PPL) overlain by hummocky cross stratification (HCS), capped by wave ripples (WR). (B) A storm bed with HCS, note the sharp lower contact.
2.3.11 Lithofacies 11: Interbedded massive and thinly laminated siltstone

Lithofacies 11 is best represented by the 5.2 m thick exposure at Cataract Lake (location 1; Figure 1.4). The lithofacies appears dark brown on fresh surfaces and black on weathered surfaces. It consists predominantly of alternating massive and thinly planar parallel-laminated, fine- to coarse-grained siltstone interbedded with subordinate mudstone and coarse-grained sandstone (Figure 2.31). The massive siltstone beds are less abundant and are from 2-10 cm thick, whereas the thinly laminated siltstone bedsets are from 4-50 cm thick (10 cm on average) (Figure 2.31). Individual laminae are 1-4 mm thick. Contacts between beds and laminae are sharp, but locally erosive. The bedsets are laterally continuous for at least 4 m.

Interbedding of massive and parallel laminated fine- to very coarse-grained siltstone represents deposition by a combination of suspension and bedload sedimentation by low-density turbidity currents (underflows) mainly under low-energy conditions. Similar lithofacies have been interpreted by Clerc et al. (2013) as resulting from predominant suspension settling processes and subordinate low-energy unidirectional currents in the lower flow regime. However, presence of subordinate coarse-grained sandstone and mudstone as well as local erosive contacts suggests periodic fluctuating conditions probably driven by storm-generated flows. In this case, coarse-grained sand is supplied by short-lived influxes during storm events, whereas mud is deposited as background sedimentation during fair weather conditions between storm events (Strachan, 1986; Bussert, 2014).
Figure 2.31: Relatively thick stratigraphic section of the Espanola Formation at Cataract Lake (location 1, Fig. 1.4) composed almost entirely of the interbedded massive and thinly laminated siltstone lithofacies (LF11).
2.3.12 Lithofacies 12: Mudstone

Lithofacies 12 forms units approximately 1 m thick and consists predominantly of mudstone (Figure 2.32). It appears pale yellowish green on fresh surfaces, and looks grayish blue green or dusky yellowish brown on weathered surfaces. This lithofacies is commonly associated with the intraformational conglomerate lithofacies (LF16) (Figure 2.32A), the rusty carbonate lithofacies (LF14), and the thickly bedded carbonate lithofacies (LF13). Upper and lower contacts are planar sharp to wavy erosive. Although the lithofacies appears generally massive to slightly fissile, it locally contains streaks of mm-thick laminae of siltstone and very fine-grained sandstone (Figure 2.32B). Rare 1-2 cm thick chert beds and laminae are also present locally. Lenticular bedding is common in the mudstone lithofacies and is characterized by connected flat and thick coarse-grained sand ripples (Figure 2.33A). The sand ripples are approximately 2 cm high and 5-7 cm long. Single isolated sand lenses of 2-3 cm long appear to float in the mudstone (Figure 2.33B). Wavy bedding is composed of alternating 1-5 cm thick beds of mudstone and fine- to coarse-grained rippled sandstone, with symmetrical wave ripples characterizing the tops of the mudstone layers (Figure 2.34A). The alternating mudstone and sandstone layers are slightly undulating to parallel bedded, and the sandstone ripples are vertically discontinuous (Figure 2.34A). Oscillatory or wave ripples are commonly symmetrical with rounded crests, and have amplitudes of 1-2 cm and wavelengths of 4-5 cm. Wavelengths of up to 8 cm were recorded locally. Some wave ripples are internally cross-laminated with laminae dipping in both directions (Figure 2.34B). Polygonal cracks 1-3 cm wide were recorded on exposed bedding planes (Figure 2.35). Lithofacies 12 is exposed at Manfred Lake, Geneva Lake, and Denison Mine (Figure 2.36).

The high proportion of mudstone suggests that suspension settling from standing water was the major process of sedimentation (Collinson, 1996; Clarke and Parnell, 1999). The association of the mudstone lithofacies with intraformational conglomerates, and the presence of siltstone streaks and fine-grained sandstone laminae, indicates that moderate to extreme fluctuations of flow energy conditions were not uncommon during deposition (see Pickett, 2002). Lenticular and wavy bedding indicate constant alternation of low-energy turbulent flows, during which sand ripples are deposited by waves or tides and
and mud is deposited from suspension during periods of slack water (Reineck and Wunderlich, 1968). The internally cross-laminated ripples with laminae dipping in opposite directions and associated mud drapes observed in this lithofacies strongly support a tidal influence. It is possible, however, that minor storms played a role during sedimentation as well. In this scenario, the deposition of coarse-grained sand ripples may have taken place during storms, and mud deposition represents background sedimentation during fair-weather conditions (Buatois and Mangano, 1994). Symmetrical wave ripples indicate either tide- or storm-generated oscillatory flow, and are thus considered evidence that deposition was, at least partly, within the zone of effective wave action (Banks, 1973; Allen, 1980). Polygonal cracks are interpreted as syneresis in origin, or probably microbiologically induced.

2.3.13 Lithofacies 13: Thickly bedded carbonate

Lithofacies 13 is found in units up to 1.8 m thick and consists of carbonate in beds up to 20 cm thick (Figure 2.37A). The carbonate beds are pale blue on fresh surfaces and moderate orange pink on weathered surfaces. Contacts between the beds are sharp, but non-erosive, and are commonly characterized by increasing mudstone content up-section (Figure 2.37B). Beds of lithofacies 13 have a general massive appearance, but when closely examined, they contain some thin, parallel dark grey siliciclastic layers and interbeds (mainly mudstone). Symmetrical wave ripples contain mudstone drapes between layers, and maintain amplitudes of approximately 4-5 cm and wavelengths of 4 cm (Figure 2.38). Ball and pillow structures are well preserved, with diameters from 2-5 cm (Figure 2.37B). Some local stylolite structures and rusty-weathered clasts (now converted to scapolite) were observed. The stylolites have a relief of a few millimeters, and are characterized by a thin layer of dark clay. Lithofacies 13 can be distinguished from the massive to faintly laminated carbonate lithofacies (lithofacies 2) by its light to slightly dark grey to green color, and by its high carbonate content and coarsely crystalline texture. Lithofacies 13 is best exposed at Denison Mine (Figure 2.18, 2.39), where it represents the thickest carbonate-rich unit in all of the studied sections in the Quirke Lake area.
Figure 2.32: Lithofacies 12: mudstone. (A) General outcrop appearance of the mudstone lithofacies; note its association with the overlying intraformational conglomerate lithofacies (LF16). (B) Parallel laminae of siltstone and very fine-grained sandstone in the mudstone lithofacies. Scale-bar is 0.5m.
Figure 2.33: Lenticular bedding found in lithofacies 12. (A) Connected coarse-grained sand ripples. (B) A single sand lens in mudstone (center).
Figure 2.34: Lithofacies 12: (A) Wavy bedding composed of alternating mudstone and fine- to coarse-grained rippled sandstone; note the symmetrical wave ripples characterizing the tops of the mudstone layers. (B) A close-up view of wave ripples showing internal lamination.
Figure 2.35: Lithofacies 12: Small-scale polygonal cracks on a current-rippled surface. Lens cap measures 5.5 cm wide.
Figure 2.36: Stratigraphic section of the Espanola Formation at Manfred Lake (location 1 of Figure 2.1). The section is dominated by different siliciclastic lithofacies, including the mudstone lithofacies (LF12).
Figure 2.37: Lithofacies 13: thickly bedded carbonate. (A) General outcrop view showing thick, blocky bedsets of carbonate. (B) Ball and pillow structure; note the increasing fine-grained content towards the bedding plane. Scale-bar is 0.5 m.
The coarsely crystalline texture and high carbonate content of lithofacies 13 indicates that the carbonate material was more likely to have been formed by primary inorganic precipitation from a warm, supersaturated, aqueous solution. This is in clear contrast to the detrital origin proposed for carbonates of lithofacies 1 and lithofacies 2. Two factors may have contributed to the carbonate precipitation: high evaporation rates and low siliciclastic supply (Bernstein, 1985). Average thicknesses of carbonate bedsets, and lack of deformation structures and siliciclastic deposits suggest that the optimum conditions for carbonate precipitation were sustained for relatively long periods of time and that the precipitation mainly took place under quiet conditions in a siliciclastic-starved setting. The presence of symmetrical wave ripples indicates that oscillatory flows and surface wave activities were the most dominant physical processes during sedimentation (Allen, 1980). In addition, the associated mudstone drapes and thicker intervening mudstone layers suggest that carbonate depositional episodes were followed by periods of sluggish water dominated by suspension fall-out (Buatois and Mangano, 1994). Alternatively, it is possible that carbonate precipitation was infrequently interrupted by deposition of mud, which was probably supplied by turbidity or storm ebb currents (Bernstein, 1985). Ball and pillow structures indicate liquefaction, which is often triggered by seismic activity (Potter and Pettijohn, 1977; Obermeier, 1996) or the passage of waves, floods, high sedimentation rates and groundwater movement (Owen and Moretti, 2011; Owen et al., 2011). Stylolite development is usually attributed to a burial diagenetic process widely known as pressure solution, which occurs due to gravitational loading by overburden or tectonic forces (Simpson, 1985; Ebner et al., 2010; Koehn et al., 2012).

2.3.14 Lithofacies 14: Rusty carbonate

Lithofacies 14 has a maximum thickness of approximately 0.6 m and is predominantly calcareous. The most characteristic feature of this lithofacies is its distinctive rusty orange to reddish brown weathering appearance (Figure 2.40A); it is light grey on fresh surfaces. The lithofacies is laterally continuous over a few meters, but pinches out locally. Contacts with overlying and underlying lithofacies are straight to wavy. Although commonly massive, the lithofacies is locally deformed, brecciated, or jointed (Figure 2.40B). Poorly preserved stromatolites were found to be associated with the rusty
carbonate lithofacies at Denison Mine locality, first reported in a boulder by Hofmann et al. (1980). Lithofacies 14 is best exposed at Island B, Denison Mine, and Panel Mine Road (Figures 2.18, 2.39, and 2.41).

The rusty carbonate lithofacies is interpreted to have been subaqueously deposited during calm, warm periods characterized by extremely minimized siliciclastic input (e.g. Tucker and Wright, 1990). This is indicated by the absence of siltstone and mudstone interbeds and laminae, which were rather common in the thickly-interbedded siltstone and carbonate lithofacies (lithofacies 1 & 2) and in the thickly bedded carbonate lithofacies (lithofacies 13). This is also supported by the presence of poorly preserved crustose and columnar stromatolites, because microbial mats rarely form stromatolites in siliciclastic-dominated conditions where physical sedimentary processes dominate (Noffke et al., 2002).

**Figure 2.38:** Wave ripples containing mud drapes between layers in lithofacies 13.
Figure 2.39: Stratigraphic section of the Espanola Formation at Denison Mine (location 3 of Figure 2.1). The section is dominated by the thickly bedded carbonate lithofacies (LF13).
Figure 2.40: Lithofacies 14: rusty carbonate. (A) General view of the lithofacies showing its distinctive rusty orange appearance. (B) Very disturbed lamination within the rusty carbonate lithofacies. Scale bar is 0.5 m.
Figure 2.41: Two closely spaced stratigraphic sections of the Espanola Formation exposed on Panel Mine Road (location 2 of Figure 2.1). Note the predominance of the thickly bedded carbonate lithofacies (LF13) as well as the rusty carbonate lithofacies (LF14).
The presence of stromatolites is also an indication that the carbonates are of authigenic, rather than detrital, origin (Hofmann et al., 1980). However, the scarcity of the stromatolites and their poor state of preservation suggest that sedimentation of lithofacies 14 may have been affected by strong stochastic wind and wave-related events (Bowlin et al., 2012). The heavily deformed, disturbed and brecciated nature of this lithofacies all favor of this hypothesis.

2.3.15 Lithofacies 15: Stromatolitic carbonate

Lithofacies 15 is preserved in units up to 6 m thick, and is composed mainly of planar to wavy interlaminated dolomite and limestone (Figure 2.42A). The rocks are from light to dark green and grey on fresh surfaces and weather to yellow, very dark brown, and black. The most characteristic feature of this lithofacies is the presence of moderately-preserved stratiform stromatolites (Figure 2.42B). It is also relatively pure compared with the previously described carbonate-rich lithofacies. Bedsets (biostromes) in this lithofacies are from 6-45 cm thick, consisting of very thinly laminated stromatolites (Figure 2.42). Individual stromatolite laminae range from 1-5 mm thick and have planar to wrinkled laminated forms, consisting of 2-4 cm high anticliforms and synforms. Stromatolite laminae are laterally traceable for just over 1 m. Their lateral discontinuity is commonly due to the widespread presence of faults in lithofacies 15.

Although the stromatolitic carbonate lithofacies is dominated by stratiform stromatolites, columnar forms are also present. These forms include 5 cm wide and 10-15 cm long, discrete and laterally linked hemispheroids (Figure 2.43A) (classification of Logan et al., 1964). In addition, the lithofacies contains mound-like masses of algal laminated sediments, 5 cm thick and 20 cm across (Figure 2.43B). Lithofacies 15 is locally associated with the intraformational conglomerate lithofacies (LF 16), along with some interbeds of parallel laminated mudstone and interlaminated to interbedded siltstone with local small-scale cross-lamination. Secondary calcite and quartz veins were also present.

At Denison Mine, two possible microbially induced sedimentary structures were found associated with lithofacies 15. These are birdseye structures and fenestral fabrics (Figure 2.44). Birdseye structures, also known as small-scale fenestral cavities (Tebbutt et al.,
1965), are very common at the bottom of this unit. Devoid of any fillings, these isolated, spherical to elongate bubble-like voids range from 1-3 mm in diameter, and are horizontally aligned parallel to the bedding planes (Figure 2.44A). Fenestral fabrics are slightly undulating to laminoid structures, and range from 2-8 cm long, 1.5 cm high and up to 3 cm wide (Figure 2.44B). They usually appear as hollow elongated vugs concordant to bedding planes (Figure 2.44B). Some fenestral vugs were found to be completely or partly filled with medium- to fine-grained sandstone embedded in argillaceous matrix, highly resembling lenticular bedding (Figure 2.45). The lithofacies is best exposed at Bannerman Lake, about 60 km northwest of Sudbury (Figure 46).

Lithofacies 15 is interpreted as resulting from in situ subaqueous deposition under mainly quiet, warm and shallow conditions with low siliciclastic supply. This interpretation is based on the carbonate-rich nature of the deposits, as well as the presence of different forms of stromatolitic features (e.g. Tucker and Wright, 1990; Caracciolo et al., 2013). However, conditions of in situ carbonate precipitation may have ceased or been interrupted by intervals of high siliciclastic supply, as indicated by the intercalated parallel laminated mudstone and siltstone layers, which are attributed to suspension fallout and bedload processes, respectively. The stromatolites formed by trapping and binding of minerals by means of growth and metabolic activities of non-skeletal microorganisms such as photosynthetic cyanobacteria (e.g. Grotzinger and Knoll, 1999; Riding and Awramik, 2000; Suarez-Gonzalez et al., 2014). Direct precipitation of minerals via inorganic processes may have also contributed to their development (e.g. Noffke and Awramik, 2013).

Several modes of formation have been proposed for birdseye structures, including spar filling of cavities in and between algal and cyanobacterial mats (Ham, 1952), desiccation and shrinkage of pores in tidal zones (Fischer, 1964), leaching of anhydrite or evaporite molds (Flèugel and Munnecke, 2010), and late diagenetic selective recrystallization (Wolf, 1965). Similar modern structures have been described by Gerdes (2007) and interpreted as being the result of migrating gas from lower organic decay zones towards the surface. Gerdes (2007) also attributed the parallel alignment of such structures to the sealing effect of buried microbial mats. The role of post-burial gas production, due to
organic decay, in the formation of secondary voids has also been highlighted by Noffke et al. (1997). Rising pore water is the mechanism by which gas bubbles are transported upward within the sediment (Flèugel and Munnecke, 2010). Laminoid fenestral fabrics could be the results of alternating wetting and drying of carbonate muds in nearshore environments (Shinn, 1968), shrinking and separation of the surface of microbial mats from adjacent sediments due to drying and desiccation (Logan et al., 1974), and compaction of upward escaping gas bubbles released by organic matter decay (Flèugel and Munnecke, 2010).

2.3.16 Lithofacies 16: Intraformational conglomerate

Lithofacies 16 is composed of clast- to partly matrix-supported intraformational conglomerate with subangular to well-rounded brown to dark reddish brown and rusty orange clasts (Figure 2.47). The clasts are commonly flat, elongated to ellipsoidal and aligned parallel to bedding planes, but in some cases they are vertically arranged, imbricated, randomly distributed or inversely graded (Figure 2.47). The clasts are from 1-10 cm long with 5 cm being the average, and are primarily calcareous in composition. The matrix ranges from light gray calcareous to dark brown argillaceous. Bedding surfaces are erosive (scoured) to highly irregular. Lithofacies 16 tends to be associated with underlying finer-grained (commonly mudstone) lithofacies (Figure 2.47B) and overlying medium- to coarse-grained sandstone lithofacies. Locally, strata of lithofacies 16 pinch and swell for at least 4.8 m, with an average overall thickness of 10 cm. Although it is generally massive, the intraformational conglomerate is rarely found to contain faint planar thin lamination and cross-lamination.

The intraformational conglomerate lithofacies is best exposed at the Panel Mine Road and Denison Mine localities (Figure 2.41 and 2.48), but is noticeably absent from the carbonate exposures at Hwy 108. At Bannerman Lake, this lithofacies is represented by well-laminated, 1-4 cm long unweathered carbonate clasts, along with subordinate siliciclastic debris, in an obvious contrast to the rusty-weathered orange and red clasts that commonly characterize lithofacies 16 elsewhere. Similarly, at Manfred Lake, the intraformational conglomerate lithofacies consists of 1-2 cm long, unweathered carbonate
clasts embedded in a siliciclastic matrix; however, the carbonate clasts at this locality are massive rather than laminated.

The origin of intraformational conglomerate in the Espanola Formation is enigmatic. Robertson (1968), who was the first to label them as intraformational breccia, attributed their development to tectonically-induced disturbances during or shortly following deposition. Allen (1962) described similar intraformational conglomerate from the Lower Old Red Sandstone, and interpreted them as resulting from erosion and redeposition (i.e., reworking) within the depositional basin. Intraformational conglomerates have also been linked to contemporaneous normal faults and clastic intrusions formed in response to differential vertical displacements (Eisbacher, 1970). Young (1973) attributed the origin of most of the conglomerate to downward forceful injections and, similarly, related them to tectonic instability, although he acknowledged that in some cases the conglomerate was independent from any evidence of faulting or intrusion of clastic dykes. Bernstein and Young (1990) described similar conglomerate lithofacies in the Whitefish Falls, and interpreted them as being the result of recurring downslope remobilization events possibly caused by a locally unstable depositional slope. Intraformational conglomerates have also been reported from playa lake sequences and storm influenced carbonate shelves (Long, 2007).
Figure 2.42: Lithofacies 15: stromatolitic carbonate. (A) General view of the laminated stromatolitic carbonate. (B) Stratiform stromatolites (arrow).
Figure 2.43: Lithofacies 15: (A) Discrete and laterally linked columnar stromatolites (arrows); (B) Algal laminated mound-like masses; note the deformed and weathered nature of the exposure.
Figure 2.44: Lithofacies 15: (A) Birdseye structures; (B) Fenestral fabrics.
Figure 2.45: Lithofacies 15: Fenestral fabrics partly filled with medium- to fine-grained sandstone embedded in argillaceous matrix.

It is suggested here that different mechanisms may have contributed to the formation of the intraformational conglomerate lithofacies. Matrix-supported conglomerate with highly variable degrees of sorting and rounding similar to those found at Bannerman Lake and Manfred Lake localities may have been deposited by viscous debris flows (Schultz, 1984). Other features found in these conglomerates such as the chaotic and random distribution of the clasts with no preferred orientation as well as the sharp scoured bases and inverse grading are also commonly associated with highly viscous debris flows (see Bernstein, 1985; Corcoran et al., 1999). The debris flows were apparently subaqueous because the common association of this lithofacies with a better sorted medium- to coarse-grained overlying lithofacies signifies a diluted flow resulting from partial mixing with water (Nichols, 1999). These features collectively suggest that the depositional slope was relatively steep.
Figure 2.46: Stratigraphic section of the Espanola Formation in the Bannerman Lake area. The section is dominated by the stromatolitic carbonate lithofacies (LF15). See text for details.
In contrast, the mainly clast-supported intraformational conglomerates with flat, elongated clasts aligned parallel to bedding planes similar to those found at Dension Mine are interpreted here as resulting from disturbance of newly deposited or partly lithified sediments, which was probably induced by slope instability and/or seismic activities (Bernstein, 1985; Bernstein and Young, 1990). The common presence of internally divided clasts with no offsets strongly supports the idea that their formation was prior to complete lithification. Erosion and redeposition of semiconsolidated carbonate layers during storm events were also proposed as possible mechanisms for the origin of similar intraformational conglomerates (e.g., Shinn, 1983, Pratt, 2010).

2.3.17 Lithofacies 17: Intraformational breccia

Lithofacies 17 consists of a breccia unit up to 3 m thick. The breccia is mainly clast-supported, consisting of chaotically distributed, very angular cobbles and boulders up to 0.6 m in diameter (Figure 2.49). The clasts consist of parallel- and cross-stratified rusty orange weathered dolostone and siltstone in a fine-grained sandstone matrix. Slump breccia in the study area is commonly located proximal to normal faults, and sharply truncates adjacent horizontally-bedded units (Figure 2.49 and Figure 2.50). Lithofacies 17 is spatially scattered, but an ideal example was found in an exposure on Island A (Figure 2.51).

The proposed deformation mechanisms for the development of the intraformational breccia are similar to those suggested for the intraformational conglomerates. These mechanisms include tectonically-induced disturbances during or shortly following deposition (Robertson, 1968), intrusions of clastic material in response to differential vertical displacements associated with active contemporaneous normal faults (Eisbacher, 1970), downward forceful injections related to tectonic instability (Young, 1973), and downslope remobilization of sediments possibly due to unstable depositional slope (Bernstein and Young, 1990). The observation that the intraformational breccia abruptly and sharply truncates adjacent horizontally-bedded units and the fact that the clasts are parallel stratified suggests that their formation has taken place shortly following
Figure 2.47: Lithofacies 16: intraformational conglomerate. (A) General outcrop view showing the association with the underlying mudstone lithofacies (LF12). (B) Rusty, subangular to rounded clasts typically constituting the intraformational conglomerate lithofacies.
Figure 2.48: Stratigraphic section of the Espanola Formation at Denison Mine (location 3 of Figure 2.1) displaying the association of the LF16 with underlying and overlying lithofacies.
Figure 2.49: Lithofacies 17: intraformational breccia. (A) and (B) Note the chaotically distributed, very angular cobbles and boulders, which are composed of parallel- and cross-stratified rusty weathered dolostone and siltstone. Scale bar is 0.5 m; hammer shaft is 45 cm.
**Figure 2.50:** Outcrop drawing showing the intraformational breccia lithofacies (LF17) sharply truncating intraformational conglomerate units at Island B, Quirke Lake (location 5 of Figure 2.1).
Figure 2.51: Stratigraphic section displaying the characteristics of five lithofacies of the Espanola Formation on Island A (location 4 of Figure 2.1). Note the relatively thick intervals of the intraformational breccia lithofacies (LF17).
deposition, at least after partial lithification of the deposits. The proximity of lithofacies 17 to normal faults is interpreted here as an indication of syn-depositional tectonic instability, as initially suggested by Eisbacher (1970).
Chapter 3

3 Petrography of the Espanola Formation

3.1 Previous petrographic investigations

The earliest detailed petrographic analysis of the Espanola Formation was that of Casshyap (1967). He investigated the Espanola Formation exposed in the Espanola-Willisville area, and found that the rocks mainly consist of fine- to coarse-grained calcareous sandstone and siltstone. The majority of the samples contained <10-20% calcite and dolomite in the form of cement; thus, no limestone or dolostone units were recognized in that area. Casshyap (1967) noted that quartz accounted for more than 70% of the detrital fraction, followed by 25% plagioclase feldspar and less abundant microcline and orthoclase feldspar. Phyllite and siltstone rock fragments as well as accessory minerals of metamorphic origin, such as tremolite, diopside, and epidote, constituted the remainder of the samples.

Another important investigation was that of Card et al. (1977) in which the authors studied the stratigraphy, sedimentology and petrology of Huronian Supergroup units, including the Espanola Formation, in the Sudbury-Espanola area. Following the conventional three-member subdivision of the Espanola Formation, Card et al. (1977) found that the lower member is composed of recrystallized limestone and dolostone with approximately 75% calcite and dolomite, 20% quartz and feldspar (K-feldspar and plagioclase), and 5% metamorphic phyllosilicates. Other subordinate, yet common minerals included mica, chlorite, scapolite, and amphiboles, as well as accessory minerals such as iron oxides, sulphides (pyrite and pyrrhotite), apatite, and zircon. The middle siltstone member was mainly composed of phyllosilicates, as well as quartz, feldspars, calcite, and dolomite in variable amounts. Siltstone and shale rock fragments and accessory minerals similar to those found in the lower member were also observed in the middle member (Card et al., 1977). According to Card et al. (1977), samples from the upper part of the formation contained similar mineralogy as the lower two members, albeit in different proportions, and were mostly composed of calcite and dolomite.
Robertson (1976) noted scapolite and amphibole as porphyroblasts in carbonate-rich layers, and biotite, chlorite, and sericite in cleavage zones in siltstones.

Card (1984) conducted a geological investigation of the Espanola-Whitefish Falls area, and reported that the basal limestone member was mainly composed of calcite and dolomite, along with subordinate amounts of detrital quartz, feldspar, biotite, epidote, and chlorite. The siltstone and mudstone, which constitute the majority of the middle siltstone member were composed of varying proportions of quartz, feldspar, calcite, dolomite, mica, chlorite, scapolite, iron oxides, and sulphides. Card (1984) found that the upper dolostone member, which he referred to as the siltstone-limestone member, was quite similar to the lower member, but predominantly contained siliciclastic components, and that the limestone was primarily dolomitic in composition.

Bernstein (1985) provided a brief petrographic description of the Espanola Formation in the McGregor Bay- Bay of Islands area. He reported that the lower limestone member was mainly composed of calcite and dolomite, with greater proportions of terrigenous clastic components, such as silt-sized quartz and feldspars, compared to the equivalent member further north in the Quirke Lake area. Chlorite, muscovite, pyrite, epidote, zircon and apatite were also reported from the lower member. According to Bernstein (1985), the siltstone member petrographically resembled the underlying limestone member, but contained greater amounts of siliciclastic components (mainly quartz and feldspar), as well as siltstone and carbonate rock fragments. Bernstein (1985) did not, however, recognize a mappable dolostone unit in his study area (Bernstein and Young, 1990).

In their guidebook, Robertson and Card (1988) reported that the lower limestone member was recrystallized and transformed into skarn that contained idocrase due to contact metamorphism caused by the intrusion of sill-like bodies of Nipissing gabbro. They also reported biotite, scapolite, amphiboles, diopside, garnet, epidote, wollastonite, and magnetite in the vicinity of Massey and Whitefish Falls.

The only comprehensive, yet brief, petrographic study of the Espanola Formation in the Quirke Lake-Elliot Lake area was that of Young (1973). He found that crystalline calcite is the most common carbonate in the basal limestone member, with virtually no dolomite
content. Fine crystalline pyrite and pyrrhotite as well as ilmenite and magnetite were found disseminated throughout the limestone. Young (1973) reported that the terrigenous material in the limestone member is dominated by quartz and feldspar, especially microcline and Na-plagioclase varieties, along with some sericite crystals. According to this study, the siltstone member is characterized by an increase in silt-sized terrigenous material and the appearance of dolomite, minor calcite and pyrite. Rocks of the overlying dolostone member consisted mainly of primary or early diagenetic dolomite and terrigenous clastics in different proportions. Young (1973) noted that the rocks contain diagenetic calcite, commonly in the form of secondary veins and vugs, as well as iron sulfides. He recognized a positive relationship between the grain size of terrigenous and carbonate material, and that some graded beds were completely composed of carbonate material. Based on these observations, Young (1973) suggested that most of the carbonate in the Espanola Formation was detrital in origin.

A comprehensive petrographic analysis of the Espanola Formation in the area north of Elliot Lake was carried out as part of this research. The aim was to build upon early petrographic observations and to acquire new detailed information pertaining to the chemical and mineralogical compositions of rocks in the study area. Such information is crucial in supporting sedimentological, geochemical, and isotopic interpretations.

### 3.2 Sampling and staining methods

An attempt was made to collect at least one representative outcrop sample from each sedimentological lithofacies. Drill cores were sampled for those lithofacies poorly exposed in the field area. In total, 42 samples were prepared for petrographic analysis. The samples were cleaned, and all weathered surfaces were removed as part of the preparation procedure, except where weathering products were to be examined. Chapter 2 should be consulted for sample locations. A detailed petrographic description of each lithofacies is provided in section 3.3.

In order to confirm the dominant carbonate phase (calcite or dolomite) via visual estimation, a different set of 26 drill core samples were stained using alizarin red S in solution method, following the standard staining techniques of Friedman (1959) and
Dickson (1965). The samples were taken from carbonate-rich intervals of the Espanola Formation, which represent all of the petrographically analyzed lithofacies. A wafer was cut from each core sample, which was then properly cleaned and dried before being etched with a diluted cold hydrochloric acid (HCl) for approximately 2 minutes. The acid solution used in the etching process was prepared by adding 8-10 cc HCl to 100 cc distilled water. Each sample was thoroughly washed with distilled water following etching, and then immersed in alizarin red S solution for 2-3 minutes. The staining solution was prepared by dissolving 0.1 gr of alizarin red in 100 ml 0.2% cold HCl. The 0.2 % HCl involved in the staining solution was prepared by adding 2 ml of HCl to 998 ml of distilled water (e.g., Friedman, 1959). Calcite-dominated samples stained deep red to pinky red, whereas dolomite-dominated samples took no stain. All staining procedures were carried out in the Department of Earth Sciences, Western University. Staining results of all samples are provided in Table 3.1. The results show that calcite is the dominant component of all of the samples, especially those obtained from LF1-LF12, whereas dolomite dominates or coexists with calcite in the majority of the samples from LF13-LF17.

3.3 Petrographic descriptions

3.3.1 LF1: Interlaminated to interbedded siltstone-carbonate lithofacies

Six samples were examined from LF1 (El.14, El.19A, El.19C, El.20, El.41, El.43A). The samples consist of alternating very fine-grained siltstone and carbonate-rich laminae in a clay-size matrix (Figure 3.1a). The matrix-supported siltstone laminae consist of well-sorted, subrounded to rounded detrital grains, which constitute approximately 26% of the samples. The remainder of the samples are composed of ~74% carbonate material. The detrital grains are from 0.0039 mm-0.0625 mm in diameter, and are composed of monocrystalline quartz (92%), mica (3%), opaque minerals (3%), plagioclase (1%), and chert fragments (1%). The samples also contain traces of potassium feldspar and chlorite. Siliciclastic-rich laminae are thinner than carbonate-rich laminae, and are slightly disturbed and contorted (Figure 3.1b).
Carbonate-rich laminae, in contrast, consist of calcite including micrite to fine-grained sparite, with scattered coarse silt-sized quartz grains. Carbonate crystals are generally well sorted, and normal grading was noted in some layers (Figure 3.1c). Some carbonate grains appear well-rounded and are within the same size range of the associated siliciclastic component. These observations suggest that the carbonate content is at least partly detrital in nature. Some carbonate-rich laminae are composed of neomorphic microspar and pseudospar (Figure 3.1d). Their diagenetic origin is indicated by the presence of micrite relicts. One sample clearly shows the neomorphic nature of carbonate minerals; wherein both microspar and pseudospar are present (Figure 3.2a). An important feature of these samples is the presence of scapolite, which replaces coarse pseudospar (Figure 3.1d). The scapolite grains show signs of dissolution and alteration (Figure 3.2b, c), and are commonly altered and replaced by muscovite (Figure 3.2d). Microfractures and faults were also identified.
**Table 3.1:** Staining results of 26 drill core samples from carbonate-rich intervals of the Espanola Formation. X = present, -- = absent

<table>
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<th>Sample</th>
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<th>Lithofacies</th>
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Figure 3.1: Petrographic characteristics of the interlaminated to interbedded siltstone-carbonate lithofacies (LF 1). (A) Alternating very fine-grained siltstone (dark) and carbonate-rich (light) laminae. (B) Disturbed and contorted lamination. (C) Normal grading within a carbonate-rich layer. (D) Carbonate-rich layer composed of coarse carbonate (Cc) pseudospar, which is partly altered to scapolite (Scp).
Figure 3.2: Petrographic characteristics of the interlaminated to interbedded siltstone-carbonate lithofacies (LF 1). (A) Carbonate-rich layer composed of both microspar (Msp) and pseudospar (Psp); note how the latter is partly altered to scapolite (Scp). (B) and (C) Scapolite grains (Scp) showing signs of dissolution and alteration. (D) Scapolite grains highly altered to muscovite.
3.3.2 LF2: Massive to faintly laminated carbonate lithofacies

Four samples were examined from LF2 (El.19, El.39, El.42, El.43B). The samples mainly consist of recrystallized carbonate minerals, primarily calcite, with minor silt-sized detrital grains (Figure 3.3a). The siliciclastic detrital grains constitute approximately 10% of the samples, whereas carbonate minerals account for the remaining 90%. The detrital component is well sorted and is primarily composed of subrounded quartz grains (89%), muscovite (4%), opaque minerals (3%), chlorite (2%), and diopside (1%). Traces of biotite and epidote are also present. The calcite is neomorphic in nature as is evident by its patchy size distribution, inclusion of relicts of carbonate mud (micrite), and its concentration beneath laminations (Figures 3.3a, 3.3b). Some samples consist almost entirely of carbonate minerals in the form of coarse interlocking sparry calcite (sparite) (Figure 3.3c). This is probably the result of recrystallization and obliteration of the original lamination. Widespread, small, dark green diopside crystals were noted (Figure 3.3c). The samples also contain scapolite crystals that are partly dissolved and altered into mica, epidote, and chlorite (Figures 3.3d, 3.4a). Scapolite crystals are rounded, spherical, irregular, or euhedral.

Laminae boundaries are commonly defined by dark, clay-sized siliciclastic material, and are inclined rather than horizontal with some muscovite flakes resting on them. Microfractures are common, along which clay minerals and other alteration products are concentrated (Figure 3.3b). Vugs are randomly distributed and probably formed via dissolution of carbonate (Figure 3.4b).

3.3.3 LF3: Wavy laminated sandstone lithofacies

One sample was examined from LF3 (El.77) and consists of wavy interlaminated medium-grained sandstone, fine-grained siltstone, and mudstone (Figure 3.5a). The sandstone is matrix-supported and is moderately sorted, consisting of 70% detrital grains, 15% clay matrix, and 15% coarse sparite cement (Figure 3.5b). Detrital grains are from 0.0039-0.25 mm in diameter, and are predominantly composed of subangular monocrystalline quartz grains (90%), plagioclase (3%), chlorite (3%), muscovite (2%), and biotite (1%). Traces of K-feldspar, sericite, and iron oxides are also present. Many
feldspars are altered to chlorite and sericite. Some layers within the sample are normally graded. Small-scale infilled microfractures (akin to clastic dykes on a larger scale) were identified with underlying sandy material injected into overlying siltstone and mudstone layers (Figure 3.5c). Minor small-scale ripples were also observed (Figure 3.5d).
Figure 3.3: Petrographic characteristics of the massive to faintly laminated carbonate lithofacies (LF 2). (A) Sample consisting of recrystallized calcite (C), with scattered silt-sized quartz grains (Q). (B) Sample showing the neomorphic nature of the carbonate material where microspar (Msp) and pseudospar (Psp) are present; note the inclusion of carbonate mud (micrite) relicts, (Mc). (C) Sample consisting almost entirely of coarse interlocking sparry calcite crystals (sparite) (C); note the disseminated, small, dark green diopside crystals (Diop). (D) A scapolite crystal altered to or replaced by epidote (Ep) and chlorite (Chl).
**Figure 3.4:** Petrographic characteristics of the massive to faintly laminated carbonate lithofacies (LF 2). (A) A scapolite (Scp) crystal altered to epidote (Ep), chlorite (Chl), and muscovite (Musc). (B) Two vugs (black) resulting from dissolution of carbonate material (C).
Figure 3.5: Petrographic characteristics of the wavy laminated sandstone lithofacies (LF 3). (A) Interlaminated sandstone and siltstone. (B) Sandstone consisting mainly of quartz grains (Q) that are cemented by sparite cement (Cc). (C) Small-scale infilled microfracture (Ss) injecting into overlying siltstone (Slst) and mudstone (Mdst) layers. (D) Small-scale siltstone ripple within sandstone.
3.3.4 LF4: Massive to faintly parallel-laminated sandstone lithofacies

Two samples were examined from the LF4 (El.35, El. 63) and consist of fine- to medium-grained, well-sorted sandstone. The sandstone is mainly grain-supported, and is composed of approximately 84% detrital grains cemented by 14% very fine sparite (Figure 3.6). Detrital grains range from 0.0625-0.25 mm, and are primarily composed of subangular monocrystalline quartz (93%), plagioclase (4%), muscovite (1%), and iron oxides (1%); along with subordinate amounts of microcline, albite, biotite, and pyrite. The samples may have been affected by compaction and pressure solution, as indicated by local concavo-convex contacts and aligned mica flakes between detrital grains (Figure 3.6).

3.3.5 LF5: Wavy bedded sandstone lithofacies

One sample was examined from LF5 (El.12.55). The sample consists of coarse-grained wacke. The matrix-supported sandstone is poorly sorted, and consists of approximately 75% detrital grains and 25% clay-sized matrix material (Figure 3.7a). Detrital grains range in size from 0.0625-1.5 mm, but are mainly around 0.5 mm. They include quartz (85%), rock fragments (10%), plagioclase (2%), microcline (1%), chert (1%), and iron oxides (1%). Quartz grains are subangular to well rounded and locally contain inclusions, and some feldspar grains are altered to clay (Figure 3.7b). The sample is also rich in mudstone, sandstone and chert lithic fragments (Figure 3.7a). No grading was observed.

3.3.6 LF6: Low angle cross-bedded sandstone lithofacies

Two samples were examined from the LF6 (El.4, C154). The samples consist of medium-to coarse-grained, moderately- to well-sorted sandstone. The sandstone contains >97% detrital grains and <2-3% carbonate and silica cement (Figure 3.8). Detrital grains range in size from 0.0625-1 mm and are represented by monocrystalline, subrounded to well rounded quartz (83%), plagioclase (7%), K-feldspar (6%), chert (2%), rock fragments (1%), and traces of mica and iron oxides (Figure 3.8). Alteration of feldspars is widespread in the sample (Figure 3.8b). Lithic fragments are rounded, and are mainly sedimentary, and possibly metamorphic. There is evidence of compaction and pressure-
solution, as indicated by concavo-convex and sutured contacts between quartz grains (Figure 3.8c, d). Quartz overgrowths were also identified (Figure 3.8d).
Figure 3.6: Petrographic characteristics of the massive to faintly parallel-laminated sandstone lithofacies (LF 4). The sandstone is composed mainly of quartz (Q) and plagioclase feldspar (Pf) cemented by carbonate cement (Cc). Note the muscovite flakes (Musc) aligned between quartz grains, suggesting the samples underwent compaction.
Figure 3.7: Petrographic characteristics of the wavy bedded sandstone lithofacies (LF 5). (A) Quartz grains (Q), lithic fragments (Lf), and mudstone matrix (Mm). (B) Quartz grain (Q) containing inclusions and a K-feldspar grain (Kf) that is partially altered to clay.
Figure 3.8: Petrographic characteristics of the low-angle cross-bedded sandstone lithofacies (LF 6). Quartz (Q), plagioclase feldspar (Pf), K-feldspar (Kf), and lithic fragments (Lf) cemented by carbonate cement (Cc). Note the partial alteration of a plagioclase feldspar grain to muscovite (Musc) in (B). Also note the concavo-convex and sutured contacts between quartz grains in (C) and the widespread quartz overgrowths (yellow arrows) in (D).
3.3.7 LF7: Planar interlaminated to interbedded mudstone-siltstone lithofacies

One sample was examined from LF7 (El.12.23). The sample consists of alternating siltstone and mudstone laminae. The siltstone layers contain abundant mudstone, and the mudstone layers contain silt-sized detrital particles (Figure 3.9). The rock is moderately sorted, and is matrix-supported. It consists of approximately 55% detrital grains and 45% clay minerals, which constitute the matrix. Detrital grains are from 0.004 mm-0.0625 mm in diameter, and are composed of monocrystalline quartz (98%), opaque minerals (1%), and traces of feldspar. Laminae contacts are gradational, and the lamination is generally planar horizontal to slightly wavy (Figure 3.9).

3.3.8 LF8: Wavy laminated to wavy bedded mudstone-siltstone lithofacies

One sample was examined from LF8 (El.70); it consists of well-sorted, fine-grained siltstone. The siltstone is matrix- to grain-supported, and is composed of 80% detrital grains, 19% clay matrix, and approximately 1% pore-filling fine sparite. Detrital grains are from 0.03125-0.0625 mm in diameter. Monocrystalline and polycrystalline quartz grains constitute up to 94% of the detrital component, in addition to pyrite (3%), plagioclase (1%), and mudstone lithic fragments (1%). Traces of mica and epidote were also identified, in addition to subordinate chlorite, mainly in the form of vein filling (Figure 3.10a). In-filled microfractures are widespread in the sample, and are composed of very coarse-grained siltstone to fine-grained sandstone (Figure 3.10b). There are also authigenic quartz precipitates, especially around the rims of pyrite grains and along the edges of microfractures (Figure 3.10c). Laminae boundaries are defined by the concentration of fine-grained quartz grains as well as mica and carbonate minerals. The sample is highly affected by veining (Figure 3.10d).

3.3.9 LF9: Grey, thickly-bedded siltstone lithofacies

One sample was examined from the LF9 (El.13). The sample consists of moderately sorted, very coarse-grained siltstone. The siltstone is grain-supported, and is composed of 86% detrital grains and 14% clay minerals disseminated throughout the sample as matrix
material (Figure 3.11). Detrital grains range in size from 0.031-0.125 mm, and are composed of subrounded to rounded monocrystalline quartz (95%), opaque minerals (2%), plagioclase (1%), biotite (1%), and traces of muscovite and chlorite. Laminae boundaries are subtle and gradational.

**Figure 3.9:** Petrographic characteristics of the planar interlaminated to interbedded mudstone-siltstone lithofacies (LF 7). Alternating siltstone and mudstone laminae are arranged into planar parallel lamination. Note the subtle and gradational contacts between laminae.
3.3.10 LF10: Green, thinly-laminated siltstone lithofacies

One sample was examined from the LF10 (El.12.90). The sample consists of alternating thin laminae of mudstone and siltstone (Figure 3.12a). The contacts between laminae are commonly wavy. The sample is matrix-supported, and consists of approximately 30% detrital grains and 70% clay matrix. Detrital grains are concentrated within moderately sorted siltstone layers, and are composed of angular to subrounded monocrystalline quartz (80%), rock fragments (14%), chert (2%), plagioclase (1%), K-feldspar (1%), muscovite (1%), and iron oxides (1%). Rock fragments are composed of siltstone and dolostone (Figure 3.12b).
Figure 3.10: Petrographic characteristics of the wavy laminated to wavy bedded mudstone-siltstone lithofacies (LF 8). (A) Vein filled with chlorite. (B) Microscopic clastic dyke composed of fine-grained quartz grains (Q) cemented by carbonate cement (Cc) with a core of chlorite (Chl). (C) Opaque pyrite grain (Pyr) with an authigenic quartz precipitate (yellow arrow). (D) Veins (yellow arrows) are widespread throughout the sample.
Figure 3.11: Petrographic characteristics of the grey, thickly-bedded siltstone lithofacies (LF 9). It consists of quartz as the main detrital component in a matrix of clay minerals. Note the subtle and gradational laminae boundaries (dashed lines).
Figure 3.12: Petrographic characteristics of the green, thinly-laminated siltstone lithofacies (LF 10). (A) Alternating thin laminae of mudstone and siltstone. (B) Siltstone and dolostone lithic fragments (Lf).
3.3.11 LF11: Interbedded massive and thinly laminated siltstone lithofacies

One sample was examined from the LF11 (El.29). The sample consists of alternating fine-grained siltstone and fine-grained sandstone layers (Figure 3.13a). The sample is grain-supported and well sorted, and is composed of > 75% detrital grains and <25% finely-crystalline dolomite cement. Detrital grains are from 0.0078-0.125 mm in diameter, and are primarily made up of subangular monocristalline quartz grains (91%), plagioclase (6%), opaque minerals (2%), and traces of muscovite and biotite. Siltstone layers are homogeneous, consisting mainly of fine silt-sized quartz with very low carbonate content. The sandstone layers, in contrast, consist of fine sand-sized quartz and feldspars (mainly plagioclase), the latter of which show some alteration to mica. Reverse grading was noted in at least one sandstone layer (Figure 3.13a). In addition, the sandstone layers contain a higher proportion of carbonate material in the form of fine dolomite cement and pore-filling between detrital grains (Figure 3.13b), than the siltstone layers, suggesting that less compaction has taken place. The opaque minerals are mainly iron oxides, and are possibly the products of dolomite oxidation (Figure 3.13c). Few symmetrical wave ripples were noted (Figure 3.13d).

3.3.12 LF12: Mudstone lithofacies

Two samples were examined from the mudstone lithofacies (El.72CL, C50). The samples consist almost entirely of mudstone with subordinate amounts of detrital grains (Figure 3.14). The exact shape and composition of the detrital grains are unresolvable due to their extremely fine-grained nature. Few layers of very fine-grained siltstone are present, which commonly mark laminae boundaries (Figure 3.14a). Outsized quartz grains are scattered throughout the samples, and iron oxides are concentrated along the boundaries between laminae. Faint cross-lamination, and in-filled microfractures were noted. The latter structures intrude into overlying mudstone layers (Figure 3.14b).
Figure 3.13: Petrographic characteristics of the interbedded massive and thinly laminated siltstone lithofacies (LF 11). (A) Alternating fine-grained siltstone and fine-grained sandstone layers; note the reverse grading within sandstone layers. (B) Quartz (Q), plagioclase feldspar (Pf), and pore-filling dolomite (D). (C) Pore-filling dolomite (D) replaced by iron oxides (IrX). (D) Small-scale, symmetrical wave ripples.
**Figure 3.14:** Petrographic characteristics of the mudstone lithofacies (LF 12). (A) Two layers of very fine-grained siltstone (yellow arrows) marking laminae boundaries. (B) A fluid escape structure (silt volcano) intruding into overlying mudstone layers.
3.3.13 LF13: Thickly bedded carbonate lithofacies

Three samples were examined from the LF13 (El.27, El.13.28, El.13.29). The samples consist of carbonate minerals (60%) with fine sand-sized detrital grains (20%) and clay matrix (20%) (Figure 3.15). The detrital grains are from 0.0039-0.25 mm in diameter, and are composed of subrounded to subangular monocrystalline quartz (74%), opaque minerals (19%), muscovite (3%), rock fragments (2%), chert (1%), and traces of plagioclase. The carbonate minerals are fine crystalline calcite or dolomite (Figure 3.15a). Opaque minerals are euhedral (square and hexagonal), and are mostly represented by magnetite and pyrite, some of which are aligned parallel to lamination. Two of the samples contain alternating, mm-thick, pure carbonate and mudstone (micrite) layers (Figure 3.15b, c). The carbonate is in the form of pseudospar. The mudstone layers contain some detrital grains, such as quartz and muscovite, and are affected to some extent by neomorphism and recrystallization. Sedimentary structures within the samples include dewatering structures and stylolites (Figure 3.15d); the latter are defined by the concentration of dark clay-sized material (Figure 3.15d). Weathered surfaces are reddish brown, indicating a high content of iron-bearing carbonate minerals (i.e., dolomite) (Figure 3.15c).

3.3.14 LF14: Rusty carbonate lithofacies

Two thin sections from core samples were examined from LF14 (C95, C173). The samples are composed of matrix-supported calcareous mudstone (Figure 3.16), and consist predominantly of dark carbonate mudstone (95%) with a low content of scattered detrital grains (5%) (Figure 3.16a). Detrital grains range in size from 0.0039-0.0625 mm, and are mainly composed of monocrystalline quartz (96%) in addition to muscovite (1%), biotite (1%), chert (1%), and opaque minerals (1%). Where recognizable, quartz grains are subrounded to angular. Thin parallel lamination is the main sedimentary structure in the samples, and laminae boundaries are defined by increased mudstone content (Figure 3.16a). The samples also contain minor in-filled microfractures that cut through overlying mudstone layers (Figure 3.16b). Normal grading was noted as well.
Figure 3.15: Petrographic characteristics of the thickly bedded carbonate lithofacies (LF 13). (A) Fine crystalline carbonate (Cc) with abundant detrital quartz grains (Q). (B) and (C) Alternating carbonate (light) and mudstone (dark) layers. Note the neomorphic nature of the carbonate material and the weathered surface of the rock (yellow arrow) which is reddish-brown. (D) Stylolite structure defined by the concentration of dark clay-sized material (yellow arrow).
Figure 3.16: Petrographic characteristics of the rusty carbonate lithofacies (LF 14). (A) Dark calcareous mudstone with scattered detrital quartz grains. (B) Sandy infilled microfracture, probably injected from below, cutting through mudstone layers.
3.3.15 LF15: Stromatolitic carbonate lithofacies

Nine samples were examined from LF15 (ST.1A1, ST.1A2, ST.3A, ST.3B, ST.49A, ST.49B, ST.49C, ST.4.1, ST.4.11). The samples consist of thinly-laminated, coarsely-crystalline dolostone (Figure 3.17). The stromatolitic lamination is defined by alternating dark micritic laminae with fine- to coarse crystallized dolostone layers (Figure 3.17a). Some of the micritic laminae contain trapped and bounded detrital, mainly quartz, grains (Figure 3.17b, c, d). Some laminae are slightly folded and disrupted (Figure 3.18a). Detrital grains range in size from 0.03125-0.5 mm, and include, in addition to quartz, traces of muscovite, biotite, epidote, diopside, chlorite, pyrite, and iron oxides. Siltstone and mudstone fragments were also identified, but in minor amounts. Samples from the LF15 contain widespread quartz veins, microfaults, and in-filled microfaults (Figure 3.18b, c). Some of these structures seem to have been widened due to the growth of coarse sparite (or dolomite) that is sandwiched between equant quartz grains (Figure 3.18c, d). This is probably a reflection of the involvement of different stages of deformation, recrystallization and neomorphism. Other evidence indicating different stages of diagenesis include the presence of vugs in a mainly micritic matrix that are filled with very coarse carbonate crystals (Figure 3.19a), and the presence of some micritic carbonate grains that are partially filled with coarse sparite (Figure 3.19b). The samples also contain fenestrae, birdseye structures, and pore spaces that are filled with fine-grained siliciclastics or very coarse sparite and coarse rhomb-shaped dolomite crystals (Figure 3.20a, b, c). Some of these features are totally filled with carbonate crystals (Figure 3.20d, 21a), which locally display signs of strain (Figure 3.21b). Exposure surfaces weather reddish brown which suggests that most of the carbonate minerals are either Fe-rich calcite or iron-bearing dolomite (Figure 3.21c). The neomorphic nature of the carbonate minerals is clearly manifested by their random size distribution (Figure 3.21d).
Figure 3.17: Petrographic characteristics of the stromatolitic carbonate lithofacies (LF 15). The samples consist of alternating fine- to coarse crystalline dolostone layers (D) and dark micritic laminae. Note that some of the micritic laminae contain detrital grains, such as quartz (Q) and lithic fragments (Lf), which were probably trapped and bounded by algal mat growth processes.
Figure 3.18: Petrographic characteristics of the stromatolitic carbonate lithofacies (LF 15). (A) Domal or folded stromatolitic lamination; note the trapped and bounded quartz grains (Q). (B) Micro-faults affecting a recrystallized dolostone (D). (C) In-filled microfracture that was probably originally composed of fine-grained quartz grains (Q), but has been widened due to the growth of coarse carbonate crystals (C). (D) Micro-fault affecting a bedding plane, both of which have been widened by the growth of coarse sparite (or dolomite) crystals (C); the sample is composed of dolomite (D).
Figure 3.19: Petrographic characteristics of the stromatolitic carbonate lithofacies (LF 15). (A) A vug (centre) in a micritic matrix filled with very coarse carbonate crystals (C). (B) Micritic (Mc) carbonate intraclast partly filled with clear coarse sparite (Cc).
Figure 3.20: Petrographic characteristics of the stromatolitic carbonate lithofacies (LF 15). Birdseye structures and pore spaces filled with: (A) detrital fine-grained quartz (Q), (B) and (C) coarse, clear carbonate crystals (C), or (D) coarse, rhomb-shaped dolomite crystals (D).
**Figure 3.21:** Petrographic characteristics of the stromatolitic carbonate lithofacies (LF 15). (A) Fenestrae, some of which are completely filled with coarse carbonate crystals (C). (B) Carbonate crystals (C) filling a horizontal in-filled microfracture (Q). (C) Rusty-weathered surface (yellow arrow). (D) Random size distribution of dolomite crystals (D), suggesting a neomorph origin.
3.3.16 LF16: Intraformational conglomerate lithofacies

Three samples were examined from the LF16 (El.12.3, El.13.13, El.17). The intraformational conglomerate samples are grain- to matrix-supported, and consist of rounded flat pebbles (intraclasts) surrounded by fine-grained detrital matrix (Figure 3.22). The pebbles range in size from 2-25 mm, and are composed of micrite (likely micro dolomite). In contrast, the matrix is composed of moderately sorted detrital grains ranging in size from 0.0156-0.125 mm. The detrital grains are almost entirely made up of subrounded monocrystalline quartz with traces of mica, feldspar, clay minerals, and iron oxides. The matrix also includes coarse rhombohedral dolomite crystals. The most notable features in the samples are small-scale ripples and vugs. The vugs are in-filled with very coarse sparite surrounded by equant and isopachous quartz grains that are probably diagenetic in origin (Figure 3.22c). The samples also display signs of compaction.

3.3.17 LF17: Intraformational breccia lithofacies

Two core samples were examined from the LF17 (C160, C163). The intraformational breccia samples are matrix-supported, and consist of angular pebbles (intraclasts) surrounded by a matrix of poorly sorted sandstone (Figure 3.23a). Similar to the intraformational conglomerates, the pebbles are composed of fine crystalline micrite, which is most likely dolomitic in composition based on staining results of samples obtained from the same unit and the characteristic orange-rusty weathering appearance of these pebbles. The pebbles are from 3-20 mm in apparent diameter. Some pebbles are partly recrystallized into very coarse sparite (Figure 3.23b). Detrital grains forming the matrix are from 0.0039-0.25 mm in diameter, and consist of subrounded to subangular monocrystalline quartz (89%), clay minerals (3%), chert (2%), biotite (2%), muscovite (1%), plagioclase (1%), K-feldspar (1%), and traces of iron oxides. Some of the feldspar grains are clearly altered (Figure 3.23c). The matrix is partly cemented by fine crystalline sparite (Figure 3.23c).
Figure 3.22: Petrographic characteristics of the intraformational conglomerate lithofacies (LF 16). The samples consist of rounded, flat micritic pebbles (intraclasts) in a fine-grained detrital matrix. (A) Under cross polarized light. (B) Under plane polarized light. Note the high degree of roundness of the pebbles. (C) Vug infilled with coarse carbonate (Cc) (black extinct) surrounded by equant and isopachous quartz grains (Q).
Figure 3.23: Petrographic characteristics of the intraformational breccia lithofacies (LF 17). (A) Micritic angular pebbles in a detrital matrix mainly composed of quartz grains. (B) Micrite pebbles (Mc) that are partly recrystallized into very coarse carbonate crystals (Cc). (C) Potassium feldspar grain (Kf) altered to clay minerals (Cl).
Chapter 4

4 Geochemistry of the Espanola Formation

The abundance and distribution of elements, as well as the stable isotopic ratios in sedimentary rocks, were determined in order to understand the influence of specific conditions operating at the time of deposition, such as source composition, weathering, and tectonics. A total of 56 samples were collected from the Espanola Formation in the area north of Elliot Lake, and were prepared for major element, trace element (including REE) and isotope geochemical analyses (Figure 2.1; Table 4.1).

4.1 Methods

Twenty-one very fine- to coarse-grained siltstone and mudstone samples were collected from fresh outcrops, and 10 fine-grained siltstone and mudstone samples were collected from drill core in order to conduct major and trace element analyses (Table 4.1). The samples were relatively unaltered and contained no shearing or veins. The samples were cut using an MK tile saw with a diamond blade, and were crushed using a chipmunk jaw-crusher with steel plates. The crushed samples were pulverized to a 200 mesh size using a tungsten carbide vibratory ring pulverizer. Acetone was used to clean the instruments between samples to prevent contamination. Sample preparation procedures were carried out in the Thin Section and Sample Preparation Laboratory of the Department of Earth Sciences, Western University.

Geochemical analyses were performed at the Geoscience Laboratories of the Ministry of Northern Development and Mines, Sudbury, Ontario. Major elements were determined by first running the samples for loss on ignition (LOI) (100°C under nitrogen atmosphere, 1000°C under oxygen atmosphere) and then applying the fused-disc X-ray fluorescence technique (XRF). Major elements determined include Al₂O₃, CaO, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, and TiO₂. One sample in every 10 was duplicated for quality assurance, and precision and accuracy were better than ±10%, as specified by the Geoscience Laboratories manual. However, there was a low total issue for three samples (C89, C128, and C155) due to the presence of sulfur. Results of the major element
analysis are presented in Table 4.2. Average major oxide compositions for duplicate samples used during XRF analysis of the Espanola Formation samples are provided in Appendix C. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) IMC-100 method was used to determine the concentration of trace and REE. Precision and accuracy were better than ±10%, with some lower detection limits as low as ±0.0001 ppm. The concentrations of the trace and REE are given in Tables 4.3 and 4.4.

A total of 35 rock samples of the Espanola Formation were prepared for stable isotope analysis. The rocks were sampled from carbonate-rich intervals of LF1 and LF2, which belong to the lower lithofacies association (LFA1), and from carbonate-rich intervals of LF13, LF14, and LF15, which are part of the upper lithofacies association (LFA3). Chapter 5 provides more information regarding the basis for the subdivision of the Espanola Formation into three lithofacies associations (LFA1-3), which, in ascending order, represent the lower, the middle, and the upper parts of the formation. The rock samples were collected from two drill cores totaling 260 m thick (Core 138-1 and Core 150-4). A regular sampling interval of 1.5 m was maintained except where siliciclastic-rich units were present. Good preservation of primary fabrics, high textural uniformity, absence of secondary veining, and minimal siliciclastic content were taken into consideration throughout the selection process. The samples were crushed and pulverized in the Thin Section and Sample Preparation Laboratory.

Mineralogy was determined by powder X-ray diffraction (pXRD). Powdered samples were backed and mounted on glass slides, and were scanned using a Rigaku RU-200BVH rotating anode X-ray diffractometer in the Laboratory for Stable Isotope Science (LSIS) at Western University. The diffractometer is equipped with CoKα radiation (λ= 0.1790210 nm), and operates at 45 kV and 160 mA. The scan covered a range of 2 to 82° 20 with a step size of 0.02° and a scanning speed of 10° 20/min. Relative abundances of crystalline minerals in the analyzed samples were estimated using the form-factor corrected background-subtracted peak height of the most intense diffractions of each mineral phase.
Table 4.1: Location and description of samples used for major and trace element analyses

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* See Figure 2.1 for locations of outcrops and drill holes
In order to conduct carbon and oxygen isotopic analyses, approximately 0.05 mg of whole-rock powder of each sample was used to liberate CO$_2$ from the carbonates by reaction with 100% anhydrous phosphoric acid (H$_3$PO$_4$) at 90°C using a Micromass MultiPrep device coupled to a VG Optima dual-inlet, stable isotope ratio mass spectrometer (following the standard mass spectrometer analysis techniques of McCrea, 1950 and Craig, 1953). Reference CO$_2$ was calibrated against NBS-19 and Suprapur standards. To further monitor the accuracy and precision of the method used, NBS-18 and internal laboratory calcite standards (WS-1, Suprapur) were utilized. Replicate analyses during each run of samples yielded a precision better than ±0.1‰ for both δ$^{13}$C and δ$^{18}$O. Determined δ$^{13}$C and δ$^{18}$O compositions for standards and replicates are listed in Appendix D. Results for both oxygen and carbon isotopic ratios are reported in the conventional delta (δ) notation in per mil units (‰) relative to the V-PDB (Vienna Pee Dee Belemnite) international standard (Coplen, 2011) (Table 4.5). Stable isotope compositions were measured in the Laboratory for Stable Isotope Science (LSIS) at Western University, London, Ontario.

As part of the chemical screening for diagenetic alteration of isotopic compositions, elemental concentrations of Ca, Mg, Fe, Mn, and Sr were determined using aqua-regia ICP-AES analysis (Table 4.5). The method is based on incomplete digestion of the samples, meaning that the data produced represent the composition of only the more easily acid-soluble constituents in the samples. Average elemental compositions obtained for duplicate samples and standards used during the aqua-regia ICP-AES analysis of Espanola Formation carbonate samples are listed in Appendix E. The analysis was carried out at the Geoanalysis Laboratory at Western University.
Table 4.2: Major element compositions (as determined by XRF), CIA and CIW values of samples from the Espanola Formation. Bracketed numbers are locations shown in Fig. 2.1; LOI, loss on ignition; CaO*, molar values of CaO in the silicate fraction only; CIA, Chemical Index of Alteration; CIW, Chemical Index of Weathering; ss, sandstone; slst, siltstone; mdst, mudstone.

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Table 4.3: Trace element compositions of samples from the Espanola Formation as determined by ICP-MS. Bracketed numbers are locations of samples shown in Fig. 2.1; ss, sandstone; slst, siltstone; mdst, mudstone.

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4.2 Major element results

Siltstone and mudstone samples from the Espanola Formation contain variable amounts of major element abundances, such as 27-78 wt% SiO$_2$, 0.68-12.41 wt% MgO, and 1.30-4.48 wt% K$_2$O. The amount of CaO ranges from 0.27-20.27 wt%, and increases with decreasing SiO$_2$ (Table 4.2). Accordingly, LOI values tend to be high in samples that contain appreciable CaO. Although the aim was to collect samples from carbonate-free units, the geochemical results indicate that some samples could be classified as calcareous siltstones or mudstones. According to the SandClass system of Herron (1988), the majority of the samples plot in the shale field, with Al$_2$O$_3 >$ SiO$_2$ and K$_2$O > Fe$_2$O$_3$ (Figure 4.1). This classification system was designed to detect subtle differences between compositional classes. Herron (1988) attributed low Fe$_2$O$_3$/K$_2$O ratios to a stable mineral assemblage, and a low SiO$_2$/Al$_2$O$_3$ ratio to a low quartz and high clay component.

![Figure 4.1: Geochemical classification of Espanola Formation samples (fields after Herron, 1988). Note that the majority of the samples plot in the shale field.](image-url)
The samples show positive correlations between Al$_2$O$_3$ and SiO$_2$, TiO$_2$, and K$_2$O, as these oxides are influenced by the silicate fraction (McLennan, 1977), whereas Al$_2$O$_3$ is negatively correlated with CaO and MnO, elements that are controlled by the carbonate fraction (Figure 4.2). This is explained by the substitutions of Sr for Ca, Mn for Ca and Mg, and Fe for Mg in the structures of calcite and dolomite in the Espanola Formation carbonates (Veizer, 1978; McLennan et al., 1979). The substitutions are supported by the positive correlations between Sr and CaO, MnO and MgO, and Fe$_2$O$_3$ and MgO in the samples of this study (Figure 4.3).

The major elements CaO, Al$_2$O$_3$, Na$_2$O and K$_2$O are used to determine the Chemical Index of Alteration (CIA; Nesbitt and Young, 1982). The CIA measures the ratio between the amount of Al$_2$O$_3$ and the sum of the proportions of CaO, Al$_2$O$_3$, Na$_2$O and K$_2$O (Nesbitt and Young, 1982). The CIA values should reflect the degree of chemical weathering that affected the source material, ranging from values of 45-55 for unweathered granites, 75-85 for illite and montmorillonite, and values close to 100 for highly aluminoous clays (Nesbitt and Young, 1982, Young, 2001). Average shales are characterized by CIA values within the range of 70-75 (Fedo et al., 1996). The CIA is calculated as:

$$\text{CIA} = \left[ \frac{\text{Al}_2\text{O}_3}{\left(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}\right)} \right] \times 100$$

Concentrations of major oxides in the equation are calculated in molar proportions, and CaO* represents Ca incorporated in silicate minerals only. An approximate correction to the measured CaO proportions was made in this study to account for the amount of Ca residing in carbonate and phosphate minerals (Table 4.2). The correction method of McLennan (1993) and Sun et al. (2012) was used, wherein CaO* = CaO - 10/3 * P2O5.

The authors suggest that, regardless of the CaO wt%, if the remaining number of moles is found to be less than the molar proportion of Na$_2$O, then it is considered the molar proportion of CaO in the silicate fraction. If the remaining number of moles is greater than the molar proportion of Na$_2$O, then the molar proportion of Na$_2$O is considered the same for the CaO in the silicate fraction. McLennan (1993) applied this method on samples containing up to 12.5 and 21.2 wt% CaO, for which he obtained CaO* values of...
0.0239 and 0.0190, respectively. Similarly, Sun et al. (2012) applied the same method on samples containing up to 7.14 and 8.21 wt% CaO, for which they obtained CaO* values of 0.01 and 0.01, respectively.

CIA values determined for the Espanola Formation samples are from as low as 51 to as high as 80, with an average of approximately 63 (Table 4.2). The majority of the samples, however, yielded CIA values well below that of average shale; these values are from approximately 51 to 69 (Table 4.2). Three samples (EL-13-13, EL-12-82, EL-12-10) have higher CIA values of 72, 76, and 80, respectively, which fall within or above the range of average shale. This is attributed to their relatively higher clay mineral content. One sample (EL-12-70) has an anomalously low CIA value of 40. This is attributed to post depositional enrichment of Na₂O in that sample (4.28 wt. %). The results suggest that the Espanola Formation received detritus from a source that was affected by a relatively low degree of chemical weathering.
Figure 4.2: Scatter diagrams showing positive correlations between Al$_2$O$_3$ and SiO$_2$, TiO$_2$ and K$_2$O, and negative correlations between Al$_2$O$_3$ and CaO and MnO.
Figure 4.3: Scatter diagrams showing positive correlations between (a) Sr and CaO, (b) Fe$_2$O$_3$ and MgO, and (c) MnO and MgO.
The A-CN-K ternary diagram of Nesbitt and Young (1984, 1989) identifies the pathways as the degree of weathering increases. During the initial stages of weathering, the samples mainly plot close and sub-parallel to the $\text{Al}_2\text{O}_3-(\text{CaO}^*+\text{Na}_2\text{O})$ boundary due to the rapid rates of Ca and Na plagioclase removal compared to K-feldspar. As weathering progresses, the samples plot closer to the $\text{Al}_2\text{O}_3-\text{K}_2\text{O}$ join because they still contain considerable amounts of K-feldspar (Nesbitt and Young, 1984). During advanced weathering stages, the weathered residue moves towards the $\text{Al}_2\text{O}_3$ apex due to accumulation of aluminous clay minerals at the expense of K-feldspar (Nesbitt and Young, 1984, 1989). The Espanola Formation samples plot in a steep linear array close and roughly parallel to the $\text{Al}_2\text{O}_3-(\text{CaO}^*+\text{Na}_2\text{O}^+)$ join and far away from the $\text{K}_2\text{O}$ apex (Figure 4.4A). The trend shows no significant deviation from the inferred weathering pathway, which indicates the absence of any marked effects of potassium metasomatism (see Harnois, 1988; Fedo et al., 1995; 1997 a, b).

Several Espanola Formation samples plot below average basalt on the A-CN-K ternary diagram (Figure 4.4A). This is somewhat problematic to interpret, but is most likely due to relative enrichment of $\text{Na}_2\text{O}$ rather than CaO, considering that the latter has been corrected for carbonate minerals. Elevated sodium content may have resulted from metasomatic addition of Na via albitionation of incorporated detrital K-feldspar and plagioclase grains (Fedo et al., 1997). In order to account for this Na metasomatism, Espanola Formation samples were re-plotted on the same A-CN-K ternary diagram after excluding the molar proportions of Na2O (Figure 4.4B). The samples have slightly moved closer to the average shale composition and the $\text{Al}_2\text{O}_3$ apex, a direct result of the removal of Na metasomatism effects. Nonetheless, the majority of Espanola Formation samples still plot below average shale. The high Na content in these samples may also point to derivation from Na-rich Archean tonalite-trondhjemite-granodiorite (TTG) source terrains (e.g., Frost et al., 2006).
Figure 4.4: Espanola Formation samples plotted on the Al₂O₃-(CaO*+Na₂O)-K₂O (or A-CN-K) ternary diagram. A. The linear array displayed by the samples is sub-parallel to the Al₂O₃-(CaO*+Na₂O) join and below the value of average shales, suggesting a lack of intense weathering and K metasomatism. Compositional averages of major minerals and rock types are modified from McLennan et al. (1993). B. Results excluding molar proportions of Na₂O. Note how the samples are closer to the shale composition.
SiO$_2$ contents and K$_2$O/Na$_2$O ratios of bulk sedimentary samples have been used as geochemical parameters in determining tectonic setting (e.g., Bhatia, 1983; Bhatia and Crook, 1986; Huntsman-Mapila et al., 2009). These elements are linked to detrital framework constituents in siliciclastic sedimentary rocks (Roser and Korsch, 1986). Building upon these observations, Roser and Korsch (1986) proposed a K$_2$O/Na$_2$O-SiO$_2$ tectonic discrimination model that encompasses three well defined tectonic setting fields: oceanic island arc (ARC), active continental margin (ACM), and passive margin (PM) (Figure 4.5A). The fields were defined based on data from ancient sedimentary rocks, and were confirmed using modern sands and muds of known tectonic systems. As tectonic settings evolve towards the passive margin type and maturation of sediments increases due to recycling, data points move across the major fields on the diagram (from lower left to upper right). The majority of the Espanola Formation samples plot in the passive margin field (PM), although five samples plot in the active continental margin (ACM), four samples plot in the oceanic island arc field (ARC), and one sample plots between ACM and ARC (Figure 4.5A). This clearly indicates a trend towards a more stable tectonic environment from which the Espanola Formation samples may have been derived.

Similar implications are indicated by the SiO$_2$/Al$_2$O$_3$-K$_2$O/Na$_2$O diagram (e.g., McLennan et al., 1990) (Figure 4.5B). This model adopts the SiO$_2$/Al$_2$O$_3$ ratio as a discrimination parameter because SiO$_2$ and Al$_2$O$_3$ vary antipathetically, resulting in grain size effects becoming more apparent (Roser and Korsch, 1986). The majority of the Espanola Formation samples plot close to the passive margin average, although five samples plot near the active continental margin average, three samples plot around the continental island arc average, and one sample plots close to the oceanic island arc average (Figure 4.5B). This highlights the importance of contributions from sources of relatively stable tectonic settings. However, most of the samples have lower SiO$_2$/Al$_2$O$_3$ ratios than the reference average points (Figure 4.5B), which can be attributed to a grain size effect. Most of the reference averages were determined from turbidite sandstones (Bhatia, 1983), whereas the Espanola Formation samples are mudstones and siltstones. The scattered distribution of the samples parallel to the K$_2$O/Na$_2$O axis indicates slight
variations between the factors affecting composition, including provenance, sedimentary processes, and grain size.

Figure 4.5: Tectonic setting discrimination diagrams for the Espanola formation samples. A. Diagram of Roser and Korsch (1986) includes three fields: passive margin (PM), active continental margin (ACM), and oceanic island arc margin (ARC). Note that the majority of the samples plot in the passive margin field. B. Diagram of McLennan et al. (1990) based on SiO$_2$/Al$_2$O$_3$ and K$_2$O/Na$_2$O ratios. Average data are from Bhatia (1983).
4.3 Trace element results

The trace element data from the Espanola Formation samples show a wide range of abundances (e.g. Sc 3.7-18.5 ppm, Zr 39-292 ppm) that are independent of grain size (Table 4.3). The samples show a generally positive correlation between Al$_2$O$_3$ and Co, Cr, Ga, Ni, Rb, Sc, Th, and Ti (Figure 4.6), which suggests that trace element abundances are primarily controlled by the silicate, rather than carbonate, fraction, as was previously suggested by McLennan (1977), McLennan et al. (1979), and Bernstein, (1985).

![Figure 4.6: Scatter diagrams showing positive correlations between Al$_2$O$_3$ and a set of selected trace elements, including Co, Cr, Ga, Ni, Rb, Sc, Th, and Ti.](image)

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Abundances of the trace elements La, Th, Sc, and Co and their elemental ratios (e.g., Th/Sc, La/Sc, La/Co) are commonly used in provenance studies because of their relatively low mobility during sedimentary processes and metamorphism, as well as their low residence times in sea water (McLennan et al., 1980, 1983; McLennan and Taylor, 1991; Bhatia and Crook, 1986). The La-Th-Sc ternary model was built on the well established positive relationship between felsic igneous rocks and concentrations of La and Th, and between mafic rocks and abundances of Sc in siliciclastic sedimentary rocks derived from them (Wronkiewicz and Condie, 1987; Cullers, 2000). The Espanola Formation samples cluster around the average granodiorite and tonalite-trondhjemite-granodiorite (TTG) compositions with a clear linear trend toward felsic sources (Figure 4.7A). A similar distribution and trend are displayed on the Co/Th and La/Sc ratio plot (Figure 4.7B), which suggests that the Espanola Formation samples were mainly derived or recycled from an exposed upper continental crust of granodioritic and TTG compositions, but with an important contribution from mafic volcanic rocks.

In addition to their utilization in provenance studies, abundances of immobile trace elements, such as La, Th, Sc, and Zr, are used in differentiating the tectonic settings with which siliciclastic deposits are affiliated (e.g., Bhatia and Crook, 1986; Roser and Korsch, 1986; Fatima and Khan, 2012; Wang and Zhou, 2014). Bhatia and Crook (1986) studied the abundance and distribution of these elements in muddy sandstones (wackes) from different well defined tectonic settings of eastern Australia. The authors noted a general systematic increase in La, Th, U, and Zr and a decrease in Sc, Ti and other ferromagnesian elements as provenance shifts in response to changes in tectonic setting from oceanic island arc to continental island arc to active continental margin and finally to passive margin. Bhatia and Crook (1986) concluded that the distribution of these elements is strongly controlled by the nature of tectonic setting, and associated provenance composition, and proposed several models among which La-Th-Sc, Th-Sc-Zr/10, and La/Sc-Ti/Zr are considered the most useful in achieving the optimum differentiation of tectonic settings of sedimentary basins.
The La-Th-Sc ternary model is divided into three fields: A- oceanic island arc; B- continental island arc; and C, D- active and passive continental margins (Figure 4.8A). The majority of Espanola Formation samples plot in the continental island arc field, two samples plot in the active and passive continental margin fields, and five samples plot beyond the designated fields. The samples also display a linear trend pointing towards the La apex, indicating a relatively high La/Sc ratio (average La/Sc= 2.43). Similar results were obtained by using the Th-Sc-Zr/10 ternary model, which provides better discrimination between active and passive continental margin settings (Bhatia and Crook, 1986) (Figure 4.8B). The vast majority of the samples plot in or close to the continental island arc field. The results obtained from both ternary diagrams point to significant siliciclastic contribution from a provenance within a continental island arc tectonic setting. The high linearity of the distribution in the La-Th-Sc model suggests a provenance with mixed felsic-mafic components (e.g., McLennan et al., 1990).

The Zr/Sc-Th/Sc model (McLennan et al., 1993) was utilized in this study in order to evaluate the degree to which the composition of the Espanola Formation samples reflect actual variations in tectonic setting and provenance as opposed to sedimentary processes such weathering and recycling. McLennan et al. (1993) suggested that because Zr is strongly enriched in the heavy mineral zircon, the Zr/Sc ratio is a reliable indicator of zircon enrichment during sedimentary recycling and sorting. In contrast, the Th/Sc ratio is considered a useful index of provenance recycling and igneous chemical differentiation processes. On the Zr/Sc versus Th/Sc diagram, the samples display a trend that follows that of compositional variations (Figure 4.9). This suggests that changes in provenance, rather than sedimentary recycling, are the main factors affecting trace element distribution within Espanola Formation.
Figure 4.8: Tectonic setting discrimination diagrams developed by Bhatia and Crook (1986) based on the relationship between the abundances of A. La-Th-Sc and B. Th-Sc-Zr/10. Note that the majority of Espanola Formation samples plot in the continental island arc field. A- Oceanic island arc; B- Continental island arc; C- Active continental margin; D- Passive margin.
Figure 4.9: Geochemical diagram showing the trend of sedimentary recycling as represented by Zr/Sc vs. the trend of provenance compositional variations as reflected by Th/Sc. Note that the Espanola Formation samples clearly follow the latter trend with no observed influence of sedimentary recycling on this distribution. Diagram after McLennan et al. (1993).

4.4 Rare earth element (REE) results

The distribution patterns and abundances of the REEs are considered effective in determining the composition of source rocks because these elements are minimally affected by chemical and physical modifications during weathering, erosion, transport, diagenesis, and low grade metamorphism (McLennan et al., 1980, 1983; McLennan, 1989; McLennan et al., 2003). For example, the concentration of europium (Eu) compared with samarium (Sm) and gadolinium (Gd) can be used as an index of source rock composition because felsic igneous rocks usually yield negative Eu anomalies compared with mafic igneous rocks, which display little to no Eu anomalies (Cullers, 1994, Cullers, 2000).
The distribution patterns of REEs for the Espanola Formation samples are similar to other average post-Archean clastic rocks, such as the North American Shale Composite (NASC) (Haskin et al., 1968), but overall abundances are lower (Table 4.4). This may be attributed to the dilution effect of the quartz content within these samples (average SiO$_2$ = 52 wt. %; Table 4.2) (e.g., McLennan, 1977). Variations in absolute abundances of REEs have also been attributed to the effects of other sedimentary processes such as weathering and diagenesis, as well as heavy mineral concentration and local differences in source composition (McLennan et al., 1983; 1984). The samples show varied REE abundances with respect to some elements, such as La (15.45-51.43 ppm), Ce (30.17-100.99 ppm), Sm (2.158-9.026 ppm), Gd (1.470-7.961), Dy (1.076-7.029 ppm), and Yb (0.544-3.781 ppm) (Figure 4.10). Compared with chondrite (normalizing values from Haskin et al., 1968), Espanola Formation samples display a steep REE distribution pattern with $\text{La}_{\text{N}}/\text{Yb}_{\text{N}}$ ratios ranging from 3.68 to 20.83 (average = 16.4) (Table 4.4, Figure 4.10). Steep REE patterns with high $\text{La}_{\text{N}}/\text{Yb}_{\text{N}}$ ratios have been associated with strong siliciclastic contribution from felsic source rocks (Corcoran et al., 2013), as chondrite has a primitive composition comparable to basalt and gabbro.

Overall, the Espanola Formation samples display Eu depletions relative to chondrite (Figure 4.10). The average chondrite-normalized Eu depletion for all Espanola Formation samples is $\text{Eu}/\text{Eu}^* = 0.692$; where $\text{Eu}^*$ is the abundance of Eu calculated based on a pattern showing no depletion (e.g., Jakes and Taylor, 1974). This ratio is within the range of typical post-Archean shales (e.g., McLennan et al., 1990). Post-Archean shales are characterized by distinctive and consistent negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.60-0.70$, average = 0.65; McLennan et al., 1990), which are inherited by weathering of exposed granodioritic upper continental crust that formed by partial melting in the lower part of the crust (Jakes and Taylor, 1974; Nance and Taylor, 1976; McLennan et al., 1983b). When partial melting takes place in the lower crust under reducing conditions (a process known also as intracrustal differentiation), the residual plagioclase preferentially retains the reduced $\text{Eu}^{2+}$ because it is very similar in ionic radius and charge to $\text{Sr}^{2+}$. This process generates upper crustal rocks that are characteristically depleted in Eu (Jakes and Taylor,
1974; McLennan, 1989; McLennan et al., 1993). The Eu/Eu* values for the Espanola Formation samples range from 0.50-0.91 (Table 4.4).
Figure 4.10: Chondrite-normalized REE results for the Espanola Formation samples. Normalizing values are from Haskin et al. (1968), with the exception of Dy, which is from Nakamura (1974).
The samples with the highest Eu/Eu* tend to have greater La_N/Yb_N ratios (average of 12.69) compared to the other samples, which can be linked to mafic sources (McLennan et al., 1983). Thus, the variability in Eu/Eu* values may indicate local variations in plagioclase concentrations and/or inefficient mixing of material derived from distinct source rocks (mafic and felsic) (e.g., McLennan et al., 1983; McLennan et al., 1984). Gd_N/Yb_N ratios of the samples vary widely from 0.80-2.81 with an average value of 1.65. This wide variation may indicate contributions from compositionally varied source rocks with minimal and inefficient mixing during sedimentation (e.g., McLennan et al., 1983; McLennan et al., 1984).

4.5 Stable carbon and oxygen isotope geochemistry

The usefulness of stable isotopes stems from the fact that isotopes of an element have different physical and chemical properties arising from their relative mass differences (Hoefs, 2009). These differences in the physicochemical properties of isotopes, in turn, lead them to behave differently during physical, chemical, and biological processes (e.g., crystallization, precipitation, evaporation, diffusion, photosynthesis) (Walther, 2009). Specifically, light and heavy isotopes of an element tend to fractionate to varying degrees between two substances (e.g., seawater and carbonate minerals) or two phases of the same substance (e.g., water and vapor), resulting in small variations in the abundances of the two isotopes in the various compounds (Brownlow, 1979; Hoefs, 2009). The relative isotope abundance, referred to as the isotopic composition, is conventionally expressed as the ratio of the abundance of the heavy to the light isotopes in the sample relative to their ratios in a standard. In studies of carbonate rocks, oxygen and carbon isotopes are the most important (Anderson and Arthur, 1983). International standards V-PDB (Vienna Pee Dee Belemnite) and V-SMOW (Vienna Standard Mean Ocean Water) are currently used to report carbon and oxygen isotope data, respectively (Coplen, 2011).

Considering that the PDB is a marine carbonate, the definition of the isotopic composition implies that marine carbonate rocks deposited in equilibrium with modern-day ocean water have both δ^{13}C and δ^{18}O values of or close to 0‰ on the PDB scale (Sharp, 2007), a reference point against which the magnitude of measured deviations are
tested. It was initially thought that large magnitude departures from these were mainly of diagenetic origin, and that ocean water essentially maintained a constant isotopic composition throughout Earth’s history (e.g., Keith and Weber, 1964; Schidlowski et al., 1975). Later investigations, however, established that there was in fact a secular change in δ¹³C and δ¹�O values of marine carbonates, becoming more negative with increasing age, and that this secular trend was, at least partly, primary in nature; that is, it reflects the isotopic composition of ancient ocean water during carbonate precipitation (e.g., Veizer and Hoefs, 1976; Veizer et al., 1999; Kasting et al., 2006; Prokoph et al., 2008).

If primary in origin, variations in δ¹³C of marine carbonates principally reflect perturbations in the global carbon cycle. Such variations reflect changes in the relative proportions of carbon contributions from the two major carbon reservoirs in the crust: sedimentary inorganic carbonates and organic matter, which are, respectively, characterized by positive (~ 0‰) and negative (~ -25‰) mean δ¹³C values (Hoefs, 2009). Perturbations in the otherwise balanced global carbon cycle are, in turn, linked to global-scale geological and environmental events such as mass extinctions, eustasy, glaciations, productivity, and tectonics (Ripperdan, 2001). Some variations in δ¹³C values of marine carbonates are believed to be depth-dependent caused by the biological pump in the ocean through which fixation of CO₂ onto organic matter during photosynthesis preferentially utilizes ¹²C, resulting in ¹³C enrichment of the surface ocean water. Subsequent oxidation of the reduced organic matter at depth liberates the light carbon isotope, leading to progressive ¹³C depletion with increasing depth through the water column (Freeman, 2001). Carbon isotopes in carbonate rocks are thus mainly used in identifying the possible sources (organic vs. inorganic) and sinks of carbon and in evaluating the relative carbon contributions from the major carbon reservoirs which eventually contribute to our understanding of the biogeochemical carbon cycle and its evolution over time (Des Marais, 2001; Hayes and Waldbauer, 2006). Stable carbon isotopes are also a powerful tool in paleoenvironmental reconstruction and stratigraphic correlation, but only if variations in δ¹³C values are proved to be primary and global rather than local in nature (Alvarenga et al., 2008; Le Guerroué, 2010; Colombié et al., 2011). The most complicating factor in using carbon isotope compositions is diagenesis,
which commonly tends to lower these compositions; this is especially true for Precambrian samples (O’Neil, 1987; Jacobsen and Kaufman, 1999).

The importance of oxygen isotopes in carbonate studies is well established (Anderson and Arthur, 1983). Paleothermometry is one of the earliest and most common applications of the study of oxygen isotopes of carbonate rocks (Ghosh et al., 2006). Urey (1947) suggested that the commonly observed positive $\delta^{18}O$ values of calcium carbonate minerals relative to the more negative values of seawater from which they were formed are temperature-dependant, wherein temperature is the main control on the equilibrium fractionation of oxygen isotopes between seawater and carbonate minerals during precipitation. Oxygen isotopes of marine carbonates can also be used to decipher the isotopic composition of ancient seawater (e.g., Dickson and Coleman, 1980; Marshall and Middleton, 1990). The $\delta^{18}O$ values of carbonate rocks are also a function of the oxygen isotopic composition of the ambient water, which is in turn controlled by environmental factors such as climate, hydraulic system, evaporation, precipitation, altitude, and latitude, among others (Leng and Marshall, 2004). Using oxygen isotopic compositions of carbonate rocks as paleoceanographic and paleoenvironmental proxies is done, however, with the assumption that the rocks were in isotopic equilibrium with the ambient water (e.g., seawater) during precipitation and that post-depositional processes such as diagenesis and metamorphism have not overprinted the primary isotopic signatures (O’Neil, 1987; Jaffrés et al., 2007). Even if the preserved oxygen isotopic compositions were diagenetically overprinted, they may still be useful in evaluating the diagenetic history of the carbonate rock under consideration (Banner and Hanson, 1990; Kaufman and Knoll, 1995).

This study of the isotope geochemistry of Espanola Formation carbonate samples is aimed at (i) detecting any positive or negative stratigraphic variations in $\delta^{13}C$ and $\delta^{18}O$ values; (ii) assessing the magnitude of any deviation of $\delta^{13}C$ and $\delta^{18}O$ of the Espanola Formation from normal values; (iii) evaluating whether the $\delta^{13}C$ and $\delta^{18}O$ values of the samples are of primary or diagenetic origin; and, accordingly, (iv) inferring the prevailing depositional, environmental and/or diagenetic conditions.
4.5.1 Results and interpretations

The results of the pXRD analysis show that virtually all samples contained calcite with an average of approximately 59% for Core 150-4 samples and an average of 54% for Core 138-1 samples (Table 4.5). Out of the 35 samples analyzed, six samples were found to be dolomitic in composition, and were thus excluded. The pXRD analysis also shows that the analyzed samples contain considerable but highly variable amounts of non-carbonate constituents, including quartz (average 23%), mica (7%) and chlorite (6%). Although feldspar was identified in only a few samples, its average in those samples reaches up to approximately 20% (Table 4.5).

4.5.1.1 Drill core 150-4

LFA1 of drill core 150-4 is approximately 40 m thick. It consists mainly of interbedded relatively pure carbonate-rich intervals, from which samples were collected, and thinly-laminated to thinly-bedded muddy to silty carbonate-rich horizons. All samples obtained from LFA1 were limestone, and yielded strongly negative carbon isotopic composition values from −11.0 to −4.9‰ with an average value of −8.7‰. Oxygen isotopic composition values for the same samples are also consistently negative, and range from −10.8 to −8.2 ‰ with an average value of −9.6‰ (Table 4.6). A very poorly defined upper-section enrichment in $^{13}$C and $^{18}$O was noted (Figure 4.11). The samples contain high Fe content (5,064 – 14,935 ppm), slightly high Mn content (341 – 576 ppm), and relatively low Sr concentrations (132 – 264 ppm). Consequently, Fe/Sr is high (20.3 – 91.96), whereas Mn/Sr is low (1.29 – 4.35). The samples appear to be composed of Mg-poor calcite, with an average Mg content of 0.48 % (Table 4.6). This is probably due to the substitution of Fe and Mn for Mg especially in the diagenetic constituents within these samples. In general, such elemental trends coupled with the negative carbon and oxygen isotopic compositions suggest that these samples were subjected to some degree of post-depositional alteration and recrystallization under the influence of meteoric waters or via re-equilibration with hydrothermal fluids and decarbonation reactions during neomorphism or contact metamorphism (Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1990; Kaufman and Knoll, 1995; Horák and Evans, 2011). Petrographic and field observations, such as the highly recrystallized texture of LFA1 carbonates, their
high detrital contents, the presence of diopside and scapolite, and the close association with gabbro dykes favor the latter interpretation.

Table 4.5: Results of X-ray diffraction analysis of 35 carbonate-rich drill core samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcite (%)</th>
<th>Quartz (%)</th>
<th>Mica (%)</th>
<th>Feldspar (%)</th>
<th>Chlorite (%)</th>
<th>Dolomite (%)</th>
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<td>5.5</td>
<td>5.4</td>
<td>1.4</td>
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</table>

Notwithstanding, the lack of correlation between $\delta^{13}C$ and Mn ($R^2 = 0.0166$), Sr ($R^2 = 0.1398$), and Mn/Sr ($R^2 = 0.0410$) (Figure 4.12), and the very weak correlation between $\delta^{18}O$ and Mn ($R^2 = 0.1416$), Sr ($R^2 = 0.4648$) and Mn/Sr ($R^2 = 0.2162$) (Figure 4.13), all indicate that alteration processes were either very minimal or did not greatly affect the
isotopic compositions of these samples. Nevertheless, the strong correlation between δ\(^{13}\)C and δ\(^{18}\)O (R\(^2\) = 0.7759) (Figure 4.14) suggests that some diagenetic alteration took place.

LFA3 in drill core 150-4 is collectively 45 m thick, and is composed of interbedded massive carbonate-rich (mainly dolostone) units alternating with calcareous siltstone and mudstone bedsets. Samples collected from carbonate-rich units of the LFA3 were found to be either dolostone or limestone, using pXRD analysis (see discussion above). Dolostone samples were excluded from further isotopic analysis. All limestone samples of LFA3 yielded negative carbon isotopic values that range from –7.4 to –2.5‰ with an average value of approximately –6‰. The highest δ\(^{13}\)C value was obtained from the very top of the section; otherwise, no clear stratigraphic trend was observed (Figure 4.11). Oxygen isotopic compositions have a wide range, from –20.2 up to –7.2‰, with an average value of –11.7‰ (Table 4.6). General up-section depletion in \(^{18}\)O was noted with the lowest δ\(^{18}\)O value found at the top of the section (Figure 4.11). These samples contain high Fe (4,403 – 10,475 ppm) and very high Mn (582 – 1,480 ppm) concentrations, whereas their Sr content is variable but generally low (31 – 322 ppm). The Mn/Sr ratios are high (4.59 – 18.93), as are the Fe/Sr ratios (13.65 – 299.12) (Table 4.6). Except for sample C-102, there is a clear positive correspondence between these ratios and δ\(^{18}\)O values. The Mg content in the samples is even less than that observed in the LFA1 with an average of 0.37 (Table 4.6). The general increase in Fe, Mn, and Mn/Sr and the decrease in Sr and Mg contents indicate that these samples were probably subjected to higher degrees of post-depositional alteration compared to samples of LFA1. This is supported by the observed stronger correlation between δ\(^{13}\)C and Mn (R\(^2\) = 0.6133), Sr (R\(^2\) = 0.4161), and Mn/Sr (R\(^2\) = 0.8811) (Figure 4.12), and also by the stronger correlation between δ\(^{18}\)O and Mn (R\(^2\) = 0.5361), Sr (R\(^2\) = 0.2853), and Mn/Sr (R\(^2\) = 0.804) (Figure 4.13). Furthermore, the LFA3 samples produce a highly positive correlation between δ\(^{13}\)C and δ\(^{18}\)O (R\(^2\) = 0.8857) (Figure 4.14), which is commonly regarded as an indication of post-depositional isotopic alteration (Veizer, 1983; Banner and Hanson, 1990; Corkeron, 2007; Fairchild and Kennedy, 2007).

As strata of LFA3 represent the uppermost part of the Espanola Formation in core 150-4, it is possible that a prolonged hiatus in sedimentation prior to the deposition of the
overlying Serpent Formation may have exposed these rocks to a greater degree of post-
depositional alteration than that experienced by the LFA1. In addition, the author has
observed widespread normal growth faults and associated slump breccias within the
LFA3 (see Chapter 2 for details). These structures may have provided additional routes
for meteoric and hydrothermal fluids, making them more vulnerable to weathering and
alteration. The presence of rusty weathered units in the LFA3 is consistent with this
interpretation.
Table 4.6: Carbon and oxygen isotope compositions and elemental concentrations of Ca, Mg, Fe, Mn, and Sr for carbonate samples from the Espanola Formation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{13}$C V-PDB</th>
<th>$\delta^{18}$O V-PDB</th>
<th>Ca (%)</th>
<th>Mg (%)</th>
<th>Fe (ppm)</th>
<th>Mn (ppm)</th>
<th>Sr (ppm)</th>
<th>Mn/Sr</th>
<th>Fe/Sr</th>
<th>Thickness (m)</th>
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<td></td>
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Figure 4.11: Generalized stratigraphic column of the Espanola Formation based on Core 150-4 along with measured variations in carbon and oxygen isotopes in carbonate-rich units of LFA1 and LFA3.
Figure 4.12: Cross-plots showing the correlation between carbon isotopic compositions and elemental concentrations of limestone samples from Core 150-4. (A) $\delta^{13}$C vs. Mn; (B) $\delta^{13}$C vs. Sr; (C) $\delta^{13}$C vs. Mn/Sr. Blue triangles denote samples from LFA1. Red triangles denote samples from LFA3.
Figure 4.13: Cross-plots showing the correlation between oxygen isotopic compositions and elemental concentrations of limestone samples from Core 150-4. (A) $\delta^{18}$O vs. Mn; (B) $\delta^{18}$O vs. Sr; (C) $\delta^{18}$O vs. Mn/Sr. Blue triangles represent samples from LFA1. Red triangles represent samples from LFA3.
Figure 4.14: A cross-plot showing the correlation between carbon and oxygen isotopic compositions of limestone samples from Core 150-4. Co-variation of $\delta^{13}\text{C}$ with $\delta^{18}\text{O}$ is a parameter commonly used in geochemical screening for diagenetic alteration of carbonate rocks. The stronger correlation of $\delta^{13}\text{C}$ with $\delta^{18}\text{O}$ in samples of the LFA3 (red triangles) suggests that these rocks were probably subjected to higher degrees of post-depositional alteration compared to those of the LFA1 (blue triangles), See text for further discussion.
4.5.1.2 Drill core 138-1

The 35 m thick LFA1 of drill core 138-1 consists mainly of pure carbonate beds interbedded with thinly laminated mudstone layers of which some are folded and contorted. Contorted bedding and step-faulted layers are the main physical structures in the lithofacies association. Carbon isotopic compositions of the LFA1 display a clear bimodality (Figure 4.15; Table 4.6). The $\delta^{13}C$ values are slightly negative within the lower 14 m of the LFA1 ranging from $-2.7$ to $-1.1\%e$ with an average value of $-1.5\%e$. The values decrease slightly upsection within the lower few meters of the section, but return to values close to the average for the remaining part (Figure 4.15). Although clearly negative, such carbon isotopic compositions resemble those reported from unaltered or slightly altered Proterozoic and Phanerozoic marine carbonates, and are commonly deemed to be well within the normal marine range (e.g., Veizer et al., 1986; Kaufman et al., 1997; Kennedy et al., 1998; Frauenstein et al., 2009). Oxygen isotopic composition values for the same interval are strongly and consistently negative, but vary within a limited range from $-19.7$ to $-18.3\%e$ with an average of $-19.0\%e$ (Table 4.6). Generally, these samples contain very high Fe (5,536 – 20,698 ppm) and Mn contents (644 – 2,786 ppm). Concentration of Sr for these samples is comparatively low (104 – 217 ppm), resulting in variable but generally high Mn/Sr (3.48 – 20.76) and Fe/Sr (25.46 – 198.91) ratios (Table 4.6). These elemental trends are indicative of post-depositional chemical alteration and recrystallization involving meteoric and/or hydrothermal fluids (Brand and Veizer, 1980; Porter et al., 2004; de Alvarenga et al., 2004, 2008). The strongly negative oxygen isotopic compositions observed in these samples (within a range close to $-20\%e$) are particularly suggestive of re-equilibration and isotopic exchange with heated meteoric or infiltrating metamorphic fluids (Valley, 1986; Bekker, 2001; Bekker et al., 2001; Bekker et al., 2005). It is proposed here that such hot fluids were likely introduced during intrusion of the thick Nipissing gabbro that truncates the LFA1 (Figure 4.15). This interpretation is supported by field and petrographic observations which reveal that carbonates of the LFA1 are highly impure (i.e., containing high amounts of quartz and feldspars; Table 4.5), and are recrystallized. The elevated silicate content may have caused these samples to be more prone to decarbonation
reactions (Kaufman and Knoll, 1995). The samples also contain massive and radiating scapolite (1-2 cm in diameter).

The carbon isotopic compositions appear less affected by post-depositional chemical alteration than oxygen isotopic compositions. Different factors may have contributed to this observation, including low water-rock ratios and/or very low concentrations of dissolved carbon in the diagenetic fluids (Banner and Hanson, 1990; Derry et al., 1992; Kaufman and Knoll, 1995; Shields et al., 2002; Font et al., 2006; Jones et al., 2010). If, however, these negative δ¹³C and δ¹⁸O values were considered at least partly original, based on the argument presented below, they may then indicate high inputs of meteoric waters into the system following the recession of the Bruce glaciers (Veizer et al., 1992).

Sample C-114 is considered an outlier within the lower 14 m of the section. It has a relatively lower δ¹³C value of –7.4‰, and has a higher δ¹⁸O value of –9.3‰ compared to the other samples.

Above 15 m and through the end of the LFA1, δ¹³C abruptly shifts to more negative values, from –9.2 to –5.6‰ with an average of –7.6‰. In contrast, δ¹⁸O values become relatively less negative, from – 9.9 to – 8.7‰, with an average value around –9.2‰ (Figure 4.15; Table 4.6). The only exception is sample C-123, which has δ¹³C value of –1.3‰ and δ¹⁸O value of –17.7‰. These samples contain moderate to high concentrations of Fe (1,377 – 9,350 ppm) and Mn (311 – 1,901 ppm). Although Sr content (156 – 233 ppm) is only slightly higher than the samples of the lower part of the LFA1, Mn/Sr (1.41 – 11.22) and Fe/Sr (8.47 – 43.46) ratios are significantly reduced. The decrease in Fe, Mn, Mn/Sr, and Fe/Sr as well as the slightly negative δ¹⁸O may imply a relatively less intense diagenetic alteration of these samples compared to the samples obtained from the lower part of the LFA1. However, the strongly negative δ¹³C values suggest that carbon isotopic compositions were probably susceptible to alteration even under mild diagenetic conditions. Other factors may have also contributed to the low carbon isotopic compositions of the upper part of the LFA1, including the initial mineralogy of the carbonate, the permeability of the rocks, the temperature and composition of the diagenetic fluids, and the fluid-rock ratio (Banner and Hanson, 1990; Valley, 1986).
Despite the apparent disparity between the isotopic compositions of the lower (below 15 m) and the upper parts of the LFA1, the section as a whole shows no correlation between isotopic and elemental compositions. This is evident from the virtually absent correlations between $\delta^{13}$C and Mn ($R^2 = 0.0366$), Sr ($R^2 = 0.0724$), and Mn/Sr ($R^2 = 0.0464$) (Figure 4.16), and also from the very weak correlation between $\delta^{18}$O and Mn ($R^2 = 0.1093$), Sr ($R^2 = 0.143$), and Mn/Sr ($R^2 = 0.1382$) (Figure 4.17). It is possible that the alteration processes that introduced Fe and Mn to these rocks and removed Sr did not significantly alter the isotopic compositions, or, alternatively, the elemental as well as the isotopic compositions of these samples were, at least partly, original. The strong correlation between $\delta^{13}$C and $\delta^{18}$O ($R^2 = 0.8785$) (Figure 4.18) makes the former interpretation more plausible, but the slight upsection depletion, especially within the lower few meters of the section, hints of a contribution from primary processes (e.g., changes in the chemistry of coeval seawater) to the whole-rock carbon isotopic compositions (Fairchild and Kennedy, 2007; Kasemann et al., 2010). It is thus proposed here that while diagenetic processes may have actually overprinted the original isotopic compositions, a remnant of the systematic up-section depletion, a feature commonly associated with Marinoan-aged cap carbonates (e.g., Kennedy et al., 1998), can still be observed in the rocks of the Espanola Formation. Determination of total organic carbon (TOC) and carbon isotopic composition of coexisting organic matter is however needed in order to further confirm the contribution of primary processes. Bekker et al. (2005) reported low TOC content of < 0.2 mg C/g sample for the majority of their samples, which were obtained from the Limestone and Dolostone members (i.e., LFA1 and LFA3, respectively) of the Espanola Formation. The authors also found variable carbon isotope compositions of organic matter with an average value for the fractionation between carbonate and organic phases ($\Delta \delta$) of approximately 20‰. Bekker et al. (2005) suggested that such low TOC content and small differences between carbonate and organic carbon isotopic compositions may have probably been the result of metamorphic alteration of carbon in these samples (see earlier discussion).

The LFA3 in core 138-1 is approximately 80 m thick and contains calcareous fine-grained siltstone interbedded with alternating mud- and carbonate-rich bedsets. Whole-
rock limestone samples collected from the LFA3 yield negative carbon isotopic compositions that vary from –8.9 to –8.0‰. Oxygen isotopic compositions for the same samples vary within a small range from –10.4 to –9.3‰. The contents of Fe (7,408 – 11,513 ppm) and Mn (599 – 1,411 ppm) are high in these samples, whereas Sr content (25 – 158 ppm) is very low. As a result, Mn/Sr (6.7 – 24.6) and, especially, Fe/Sr (59.3 – 463.4) ratios are very high (Table 4.6). The enrichment in Fe and Mn and the depletion in Sr contents as well as the high Mn/Sr and Fe/Sr ratios are indicative of post-depositional chemical alteration and recrystallization (Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1990; Arthur, 2009; Frimmel, 2010; Horák and Evans, 2011). Considering that the isotopic compositions of the LFA3 are very similar to those of the upper part of the LFA1, it is unnecessary to invoke a different alteration mechanism. This interpretation is supported by the variable but generally good correlation between δ¹³C and Mn (R²= 0.2659), Sr (R²= 0.4442), and Mn/Sr (0.9672) (Figure 4.16). Similarly, there is a strong correlation between δ¹⁸O and both Mn (R²= 0.9009) and Sr (R²= 0.7635), although the correlation between δ¹⁸O and Mn/Sr (R²= 0.1542) is very weak (Figure 4.17). Field and petrographic observations, such as the widespread recrystallization and dolomitization, and the presence of features such as rusty weathering, secondary veins, fractures, and stylolites in the LFA3 further support diagenetic alteration (e.g., Kaufman et al., 1991; Kaufman and Knoll, 1995).

The presence of stromatolites in the LFA3 points to the possibility that microbial metabolism of sedimentary organic matter may have also contributed to the lower δ¹³C values of the whole-rock carbonates (Grotzinger and Knoll, 1995; Higgins and Schrag, 2003). There is a lack of correlation between δ¹³C and δ¹⁸O (R²= 0.0482) that may be explained by the small sample population analyzed; only three samples were found to be suited for isotopic analyses.

No clear isotopic variation trends can be established in drill core 138-1 except for the very subtle up-section decrease in both δ¹³C and δ¹⁸O values within the first 7.5 meters of the stratigraphic section. The general absence of stratigraphic trends in relation to carbon and oxygen stable isotopes is probably due to the small sample population and the lack of
a constant sampling interval, both of which were the result of abundant siliciclastic-rich units throughout the LFA1 and LFA3 of the Espanola Formation.
Figure 4.15: Generalized stratigraphic column of the Espanola Formation based on Core 138-1 and measured variations in carbon and oxygen isotopes in the lower LFA1 and the upper LFA3. Note the clear bimodality in the values. Also note the thick gabbro dyke and the virtual absence of LFA2.
Figure 4.16: Cross-plots showing the correlation between carbon isotopic compositions and elemental concentrations of limestone samples from Core 138-1. (A) $\delta^{13}$C vs. Mn; (B) $\delta^{13}$C vs. Sr; (C) $\delta^{13}$C vs. Mn/Sr. Blue triangles represent samples from LFA1. Red triangles represent samples from LFA3.
Figure 4.17: Cross-plots showing the correlation between oxygen isotopic compositions and elemental concentrations of limestone samples from Core 138-1. (A) $\delta^{18}$O vs. Mn; (B) $\delta^{18}$O vs. Sr; (C) $\delta^{18}$O vs. Mn/Sr. Blue triangles denote samples from LFA1. Red triangles denote samples from LFA3.
Figure 4.18: A cross-plot showing the correlation between carbon and oxygen isotopic compositions of limestone samples from Core 138-1. The lack of correlation between $\delta^{13}$C and $\delta^{18}$O exhibited by samples from LFA3 is likely the result of a low sample population. Blue triangles denote samples from LFA1. Red triangles denote samples from LFA3.
Chapter 5

5 Discussion

The following discussion aims to identify the main processes that together controlled the deposition and composition of the Paleoproterozoic Espanola Formation based on the results of lithofacies analysis, petrography and geochemistry. The processes are considered along with the inferred conditions at the time of deposition, especially the stratigraphic relationship between the carbonates and underlying glacial deposits of the Bruce Formation, the inferred rift-related tectonic setting, and the inferred low levels of atmospheric oxygen.

5.1 Depositional environments of the Espanola Formation

The 17 sedimentary lithofacies of the Espanola Formation are grouped into three lithofacies associations (LFA1-3) based on their stratigraphic positions, field relationships, and lithological characteristics. The lithofacies associations represent depositional environments within a wave- and storm-dominated, shallow, siliciclastic marine shelf. In ascending order, these environments include shoreface, offshore, and nearshore or lagoonal settings (Figure 5.1). Modern and ancient mixed carbonate-siliciclastic deposits are common in shallow water settings where both carbonate precipitation and clastic deposition take place (Mount, 1984; Edwards et al., 2003; Lubeseder et al., 2009; Caracciolo et al., 2013; Anan, 2014). There are two end-member types of mixed carbonate-siliciclastic systems: a) shallow water carbonate ramps with occasional siliciclastic input from adjacent land masses located in the hinterland; and b) shallow siliciclastic shelves with patchy carbonate precipitation (Lubeseder et al., 2009). Both systems may be characterized by combinations of the following processes: 1) sporadic transfer of sediment between siliciclastic and carbonate depositional environments during high-energy storm events; 2) lateral interfingering of lithologically and compositionally distinct lithofacies; 3) autochthonous generation of carbonate material in a siliciclastic-dominated shelf environment; and 4) supply of clastic...
carbonates to siliciclastic depositional environments that are proximal to uplifted and exposed carbonate source terranes (Mount, 1984; Caracciolo et al., 2013).

### 5.1.1 LFA1: Upper shoreface lithofacies association

This lithofacies association is equivalent to the lower limestone member of Young (1973), and was identified along Hwy 108 and at Island A and Island B in Quirke Lake (Locations 4, 5, and 7; Figure 2.1). The LFA1 is dominated by interlaminated and interbedded grey siltstone and white carbonate beds (LF1, LF2). Siltstone beds are massive and thinly laminated, whereas carbonate beds are faintly laminated or structureless. The beds are laterally continuous except where affected by normal faults. Basal and upper contacts are sharp to slightly undulatory, and are locally erosional. Siltstone beds are locally discontinuous, leaving the lithofacies association dominated mainly by carbonate-rich intervals. The carbonate beds display characteristic recessive weathering, and locally contain radiating aggregates of scapolite (1-2 cm in diameter), which impart a mottled appearance to the rocks. Sedimentary structures of the LFA1 include well-defined to faintly planar lamination, poorly developed dune scale cross-stratification, rare downward tapering cracks and local asymmetrical ripples. Soft-sediment deformation is common within the LFA1 with carbonate material injected upward or slumped down into siltstone beds, forming flame and load structures. The lithofacies association is also affected by 15-20 cm long synsedimentary faults and symmetrical to slightly asymmetrical synsedimentary folds with average amplitudes of 5 cm. Some of these structures are confined within single bedsets rather than affecting the entire succession. Slumped and distorted beds are locally preserved.

**Interpretation**

The characteristics of LFA1 suggest deposition in an upper shoreface (i.e., upper inner shelf) marine environment dominated by strong and sustained current flows. This is supported by the presence of dune scale cross-stratification, well defined planar lamination, sharp bedding contacts, the cyclic stacking pattern of alternating carbonate and siliciclastic beds, and the general lack of sedimentary structures indicative of wave and storm conditions such as wave ripples and graded bedding. Episodic, short lived
wave- and, possibly, storm-induced current flows may have occasionally prevailed as indicated by local wavy and erosive contact relationships between LF1 and LF2.

Field observations and petrographic analysis (Chapters 2 and 3) show that the carbonate beds of LFA1 have a clastic texture and are normally graded, suggesting a detrital origin of the carbonate material. This is in agreement with previous petrographic investigations of the lower Espanola Formation (Young, 1973; Bernstein, 1985; Bernstein and Young, 1990). This implies that the alternating carbonate-siliciclastic beds of LFA1 may represent deposition by alternating influxes of detrital carbonate debris and fine-grained siliciclastics. Low-grade metamorphism and recrystallization have obliterated most of the primary fabrics and textures of these rocks, allowing local development of scapolite and hindering the identification of the exact origin and formation mechanism of the carbonate material. The limited reworking of LFA1 by currents and waves may be due to early marine carbonate cementation, rather than being an indication of a less agitated depositional environment.

The rare downward tapering cracks may reflect syneresis at the water-sediment interface, involving expulsion of water from unconsolidated sediments during compaction or fluctuating salinities (Tanner, 2003). Alternatively, these structures may be micorobially induced, indicating interaction between microbial mats and physical processes within the depositional environment (Noffke et al., 2001; Noffke, 2010). A definitive interpretation is, however, difficult due to the lack of surface exposures.

5.1.2 LFA2: Lower shoreface to offshore-transition lithofacies association

This lithofacies association is equivalent to the middle siltstone member of Young (1973), and is best exposed in the Denison Mine, Panel Mine Road, Crotch Lake, and Manfred Lake areas (Locations 1, 2, 3, 6; Figure 2.1). Two main features distinguish the LFA2: the predominantly siliciclastic composition and the upward-fining trend, consisting of sandstone at the base followed by a middle portion of mixed siltstone and mudstone, and capped by mudstone. Sandstone units (LF3-LF6) consist of fine- to very coarse-grained sandstone bedsets that range in thickness from a few cm up to 2.5 m. The
sandstone beds are commonly laterally continuous. Lower and upper bedding contacts range from wavy gradational to sharp scoured with quartz granules. Elongated calcareous clasts were also found along some of the basal contacts, producing flat-pebble intervals aligned parallel to the bedding planes. The sandstone beds are generally massive, normally graded, or planar parallel laminated, but they are locally wavy-bedded. Sedimentary structures found in the sandstone lithofacies include planar cross-lamination, planar and trough cross-bedding, ball and pillow structures, dish and pillar structures, mudstone interbeds, and gutter casts. Other structures include poorly preserved symmetrical wave ripple marks and polygonal cracks, and small-scale (few cm long) clastic dykes. Normal and reverse synsedimentary faults were identified locally.

The middle part of LFA2 is composed mainly of a mixture of mudstone, fine- to coarse-grained siltstone, and minor medium-grained sandstone deposits (LF7-LF11). These deposits are arranged in planar and wavy interlaminated to interbedded units with commonly non-erosive, but well defined sharp lower contacts and wavy gradational upper contacts. The units range in thickness from as little as 10 cm to as much as 5.2 m. The most common sedimentary structures in LFA2 include normal grading, planar parallel lamination, low-angle planar to trough current ripple cross-lamination, symmetrical wave ripple cross-lamination (i.e., combined flow ripples), and hummocky cross stratification (HCS). The HCS is predominantly sharp-based and passes upward into wave ripples. Other sedimentary structures include concentric ball and pillow structures, sandstone dykes, convolute bedding, mudstone drapes between cross-laminae, and rare polygonal cracks.

The LFA2 is capped by a mudstone unit (LF12) that is massive to slightly fissile, and is approximately 1 m thick. Individual bedsets range from 10-13 cm thick with intervening mm-thick siltstone and very fine-grained sandstone laminae. Lower and upper bedding contacts are planar sharp to wavy erosive. The most common sedimentary structures in the mudstone unit are wavy and lenticular bedding with connected and isolated sandstone ripples and lenses, combined flow symmetrical wave ripple cross-lamination, and polygonal cracks.
Interpretation

The distribution pattern, lithofacies and sedimentary structures of LFA2 indicate deposition above storm wave base in a mainly wave- and storm-dominated lower shoreface to offshore transition marine environment (i.e., lower inner shelf to mid shelf). The deposition of this lithofacies association was facilitated by higher accommodation and tectonically-driven siliciclastic influx, part of which was probably derived from uplifted continental blocks. The siliciclastics of LFA2 were probably dispersed on the shelf by shore-parallel to shore-oblique storm currents. Wave and storm processes accompanied by weak currents (i.e., combined flows) were particularly important during sedimentation of the lower and middle parts of the LFA2. This is supported by the widespread distribution of features consistent with deposition and reworking under oscillatory flow, including symmetrical wave ripple cross-lamination (combined flow ripples), hummocky cross stratification (HCS), sharp scoured lower bedding contacts with parallel elongated clasts, sole marks and gutter casts. The subangular to subrounded quartz grains and the generally well-sorted nature of the siliciclastics, as revealed by petrographic investigation, all point to deposition under high-energy conditions.

Periods of lower wave energy (i.e., waning oscillation) are indicated by the upward change from HCS into wave ripple lamination and by the mudstone interbeds within mainly massive sandstone units. Tidal currents were an important component of the combined flow during deposition and reworking of the upper part of the LFA2, as indicated by wavy and lenticular beds. This may suggest a shift towards shallower water conditions. Growing tidal influence may also indicate a partially enclosed, as opposed to open, depositional setting (Tucker, 2001; Pratt, 2010). This partial restriction of the basin may have contributed to the precipitation of the overlying carbonate-dominated lithofacies association (LFA3). Nonetheless, the symmetrical wave ripples, which are internally cross-laminated and contain foreset laminae dipping in opposite directions, suggest that wave-generated currents were still the dominant component of the combined flow (de Raaf et al., 1977).
The mudstone in the upper part of LFA2 may have been initially brought in from deeper shelf areas by storm-induced high-energy currents before being reworked by tidal and combined flows. The strongest storm signature within these deposits is the presence of mm-thick siltstone and very fine-grained sandstone laminae within otherwise massive mudstones (Johnson and Baldwin, 1996).

In summary, LFA2 contains features that typically characterize modern shelf storm deposits, including erosive bases and basal lags of elongated clasts derived from underlying units (formed during peak storm flow), hummocky cross stratification (formed by waning storm flow), and combined flow wave ripple cross-lamination and wave rippled top surfaces (indicating fair weather) (Aigner, 1985; Johnson and Baldwin, 1996). The range in bed thickness from 10 cm to 2.5 m is similar to that of modern storm deposits, further supporting deposition in a storm-dominated setting (Johnson and Baldwin, 1996).

5.1.3 LFA3: Nearshore (lagoon) lithofacies association

The LFA3 corresponds to the uppermost dolostone member of Young (1973). It was identified in the Denison Mine and Bannerman Lake areas. The LFA3 consists mainly of grey and rusty-weathered, thickly bedded and wavy laminated stromatolitic dolostone and limestone as well as intervals of intraformational conglomerate and breccia (LF13-LF17). Carbonate beds are laterally continuous with minimal lateral variation in thickness, except where affected by slump breccia. Bedding contacts are sharp, straight to slightly wavy, but non-erosive. Locally, individual beds show an upward increase in mudstone content, whereas others contain parallel laminated mudstone layers. Some carbonate beds also contain wave ripples with mudstone drapes between layers, and stylolite structures.

Several characteristics distinguish carbonates of the LFA3 from those of LFA1. Carbonate units of LFA3 contain thin, wavy laminated stratiform stromatolites, discrete and laterally linked columnar stromatolites, mound-like masses of algal laminated deposits, birds-eye structures, and fenestral fabrics (see Chapter 2 for detailed description). Unlike the stromatolites that were reported from loose blocks in the area by
Hofmann et al. (1980), all of the stromatolitic structures reported in this research were described from outcrops, and are thus regarded as in situ occurrences. LFA3 carbonate has (re)crystallized rather than clastic textures, and contains less siliciclastic content than that of LFA1, as has also been revealed by petrographic analysis (Chapter 3). Rusty-weathered carbonate beds as well as intraformational conglomerate containing rusty carbonate clasts are ubiquitous in LFA3, especially in the lower part of the lithofacies association, features that are lacking in LFA1.

**Interpretation**

The LFA3 represents localized in situ precipitation in a mainly restricted nearshore or lagoonal environment. It is possible that following deposition of the upper part of LFA2, restricted lagoons became more dominant; within which microbial organisms would have thrived, thereby producing the laminated stromatolitic dolostone (e.g., Hofmann et al., 1980; Long, 2007). This interpretation is based on the sedimentary structures observed in LFA3 that are characteristic, in some cases diagnostic, of the inferred depositional setting. These sedimentary structures include relatively well-developed and commonly undisturbed thin, wavy laminated stratiform stromatolites as well as discrete and laterally linked columnar stromatolites, birds-eye structures, and fenestral fabrics (Shinn, 1983b, Tucker and Wright, 1990, Pratt, 1994; Demicco and Hardie, 1994; Reid et al., 2003; Pratt, 2010). The presence of stromatolites suggests that both inorganic and microbially-induced carbonate precipitation mechanisms were involved (Grotzinger and Knoll, 1999; Storrie-Lombardi et al., 2004; Schopf et al., 2007; Mcloughlin et al., 2008). The nearshore environment interpretation is also supported by the presence of intraformational conglomerate intervals consisting of rusty-weathered carbonate flat-pebble intraclasts (e.g. Shinn, 1983a). Although no conclusive evidence of subaerial exposure was documented, the intraformational conglomerate and brecciated intervals may indicate subaerial desiccation and fragmentation of early deposited carbonate crusts followed by erosion and redeposition via storm activity (e.g. Shinn, 1983a, Tucker, 1983; Long, 2007; Gomez and Astini, 2015). However, storm waves may have very limited influence on the depositional environment as indicated by the presence of local and rare wave ripples with mudstone drapes between layers and also by the fact that most of the
stromatolitic forms found in LFA3 are laterally linked. Storm-induced scours around growing microbial mats would instead produce isolated forms (Logan et al., 1964; Pratt, 2010).

Although recent (Holocene) direct precipitation of dolomite is mainly taking place in nearshore peritidal environments (e.g., Mazzullo and Reid, 1988), the generally accepted view is that most ancient dolomite is of diagenetic origin (Tucker and Wright, 1990). Thus, the mainly dolomitic composition of the LFA3 cannot be considered as a reliable paleoenvironmental indicator, especially considering the highly recrystallized nature of these rocks.

5.2 Tectonically-induced sedimentary structures

The Huronian Supergroup was inferred to have been deposited in an extensional basin that evolved from early continental rifting along the southern edge of the Superior Province to drifting and passive-margin development (e.g., Young 1983; Young et al., 2001; Long, 2004). The lower part of the supergroup was interpreted to represent deposition during the rifting phase (Young, 2014). It was suggested in Chapter 1 that this phase of basin development is characterized by active bounding fault systems, which may exert tremendous influence on basin geometry, and, hence, control depositional environments and physical processes acting during sedimentation (Ebinger et al., 2002; Withjack et al., 2002). This tectonic influence should be reflected by a distinctive stratigraphic pattern, sedimentological attributes, and facies distribution of the sedimentary fill within the basin (Gupta and Cowie, 2000).

Influence of active syndepositional normal fault systems on the Huronian basin and its sedimentary succession is well documented on a regional scale; including an asymmetric southward-thickening wedge-shaped geometry in the Quirke Syncline, laterally restricted units within the lower Huronian, and dramatic and significant thickness and facies variations across major faults (Rousell and Long, 1998; Young et al., 2001; Long, 2004; Young, 2014). The study area is bounded by two W-E trending major faults: the Flack Lake Fault and the Murray Fault Zone (Figure 1.1). These faults, along with relative sea level, were the main controls on the stratigraphy and sedimentology of the Espanola
Formation in the study area (Al-Hashim and Corcoran, 2014). For example, the total thickness of the Espanola Formation north of Elliot Lake is approximately 145 m (also Young, 1973), whereas further south across the Murray Fault Zone the formation reaches up to 760 m (Young, 1973; Bernstein and Young, 1990), which suggests active bounding normal faults with differential subsidence rates within the Huronian basin (Bernstein and Young, 1990; Pratt, 1994; 2001; Gomez and Astini, 2015).

The wide variety of soft-sediment deformation structures identified, including load casts, ball-and-pillow structures, convolute bedding and lamination, dish-and-pillar structures, clastic dykes, and slump structures, support syn-sedimentary deformation. Soft sediment deformation structures, especially water-escape structures and normal faults, have also been documented in micro-scale in thin section (see Chapter 3). Field observations indicate that, with the exception of slump structures and associated slip faces, the majority of these deformation features are restricted to discrete stratigraphic horizons, laterally traceable over long distances (100s of meters) and confined between undisturbed strata of similar lithology. This suggests that the structures were caused by liquefaction or fluidization mechanisms, possibly triggered by fault-related seismic activity (i.e., movement along bounding normal faults) during lower Huronian basin subsidence (Al-Hashim and Corcoran, 2014). It is, however, difficult to estimate the relative importance of regional verses local tectonics (e.g., Quirke Lake Fault) during sedimentation of the Espanola Formation because the structural and stratigraphic evolution of rift basins typically involves a complex interaction of different processes acting over varying spatial and temporal scales (e.g., Gawthorpe and Leeder, 2000; Bellingham and White, 2000).

Based on the interpretation of tectonic influence during deposition, the three lithofacies associations may represent different stages of rifted block uplift and basin floor subsidence, both of which may have been locally amplified by isostatic rebound following retreat of the Bruce ice sheet. The first stage represents the very early phase of the transgression that followed withdrawal of the Bruce glacier(s) (Young, 1973) (Stage 1, Figure 5.2), during which shallow water environments were established. LFA1 is believed to have been deposited during this stage. The general lack of soft-sediment deformation structures, except for local slumps and clastic dykes, as well as excellent
preservation of primary sedimentary structures in LFA1 may indicate greater tectonic stability than that of the overlying lithofacies associations. Movement along bounding normal faults and associated seismicity would have been minimal, with no major uplift or subsidence taking place.

The second stage represents the main phase of the transgression, and is characterized by relatively deeper water environments (relative to that of stage 1 and 3) (Stage 2, Figure 5.2). LFA2 is believed to have been deposited during this stage. Relative sea level rise is supported by the fining-upward trend observed in LFA2 (Figure 5.1) (e.g. Sanders and Höfling, 2000). Depositional environments established during stage 2 are inferred to have been tectonically unstable with recurrent movement along bounding normal faults. This inference is based on widespread soft-sediment deformation structures, including ball-and-pillow structures, dish-and-pillar structures, clastic dykes, and convolute bedding (e.g., Obermeier, 1996; Bowman et al., 2004; Levi et al., 2006; Mazumder et al., 2006, Owen et al., 2011; Suter et al., 2011). It is possible that the tectonically unstable conditions coincided with high sedimentation rates and rapid vertical aggradation as supported by the preservation of delicate sedimentary structures such as HCS. The effects of both tectonic instability and high sedimentation rates may have been further amplified by oversteepening of depositional slopes (e.g. Owen et al., 2011).

The final stage represents the early phase of the subsequent regression, and is characterized by the return of a shallow water environment in which LFA3 is believed to have been deposited (Stage 3, Figure 5.2). The in situ precipitation of LFA3 during this stage may have been prompted by two factors: restriction of the basin and limited supply of terrigenous material to the basin. The reduction in terrigenous supply may have resulted from a combination of: i) decreased uplift rates associated with fault inactivity; ii) decreased rates of weathering of uplifted continental blocks due to a change in the climate regime, and iii) submergence of uplifted continental areas due to sea level rise. The concentration of slump breccia and intraformational conglomerate within LFA3 may indicate discrete periods of syn-depositional disturbance caused by earthquakes during fault reactivation. It is possible that stage 3 culminated in the deposition of a heterolithic
unit at the top of the Espanola Formation, which is reported from the Whitefish Falls area further south, but is absent in the study area (Young, 1973; Bernstein and Young, 1990).
Figure 5.1: A composite stratigraphic section of the Espanola Formation showing the different lithofacies and lithofacies associations and their proposed depositional settings.
Figure 5.2: A diagram showing the proposed relationship between the different stages of the transgression that ensued following retreat of the glacier(s) that deposited the Bruce Formation. The inferred lithofacies associations of the Espanola Formation are indicated.
5.3 Stable isotope geochemistry and the concept of cap carbonates

In order to appreciate the significance of the reported isotope geochemical results from the Espanola Formation (Chapter 4), it is important to discuss the concept of cap carbonates, which was originally based on distinct Neoproterozoic carbonate successions (e.g., Plummer 1978; Fairchild and Spiro, 1987; Derry et al., 1992; Kennedy, 1996; Hoffman et al., 1998). The Espanola Formation is similar to many Neoproterozoic cap carbonates in terms of its stratigraphic position and geochemical anomalies. The shared geochemical signatures are discussed in this section.

The Neoproterozoic (1000-542 Ma) sedimentary record holds several indications of extreme environmental and climatic perturbations (Kennedy, et al., 2001; Corsetti and Kauffman, 2003; Ridgwell et al., 2003; Pierrehumbert et al., 2011). Among these indications are the presence of Neoproterozoic glacial deposits on all present-day continents that bear sedimentological and paleomagnetic evidence of at least two episodes of low-latitude, near-sea level glaciations of global or near global scale (Harland, 1964; Schmidt and Williams, 1995; Kennedy, et al., 1998; Sohl et al., 1999; Evans, 2000, 2003; Hoffman and Li, 2009). These widespread glacial deposits are commonly overlain by thin, laterally extensive carbonate deposits, which are widely referred to as cap carbonates or, specifically, cap dolostones (e.g., Kennedy, 1996; Prave, 1999; James et al., 2001; Hoffman and Schrag, 2002; Corsetti et al., 2007; Rose and Maloof, 2010). This intimate stratigraphic association was considered paradoxical because it suggests a rapid shift from glacial (icehouse) to tropical (greenhouse) conditions (Kirschvink, 1992; Hoffman and Schrag, 2002). What complicates matters even further is the fact that most of these cap carbonates are characterized by unusual, large-magnitude isotopic variations; notably, anomalously negative carbon isotopic compositions averaging between 0‰ and approximately −5‰ (Knoll et al., 1986; Kaufman and Knoll, 1995; Halverson et al., 2002, 2005). Some of these cap carbonates are associated with negative δ¹³C anomalies as low as −7‰ (Kaufman et al., 1993; Kennedy et al., 1998; Hoffman et al., 1998).
The possibility that the observed carbon isotopic signals in Neoproterozoic cap carbonates may have originated by processes operating during glaciations and subsequent deglaciations can provide insight into Neoproterozoic environmental changes. This stirred an intense debate revolving around finding the most plausible explanation for the associated cap carbonates and their peculiar sedimentary features and anomalous isotopic compositions. Precisely, a model was sought after by which to explain the mechanism(s) that led to rapid and massive increase in the carbonate alkalinity of the ocean on a global scale (Pierrehumbert et al., 2011). The discussion culminated in the development of several models ranging from extreme, unprecedented environmental changes (e.g., Kirschvink, 1992; Hoffman et al., 1998) to those refuting their paleoenvironmental significance altogether (e.g., Eyles and Januszczak, 2004), with less extreme scenarios in between (e.g., Grotzinger and Knoll, 1995; Kennedy, 1996; Kennedy et al., 2001; Jiang et al., 2003; Shields, 2005).

5.3.1 Proposed models for cap carbonate development and associated negative carbon isotopic anomalies

The Snowball Earth hypothesis (SEH) was first proposed by Kirschvink (1992) to account for the widespread occurrence of Neoproterozoic low-paleolatitude glacial deposits and associated banded iron formations. The hypothesis was later modified and extended by Hoffman et al. (1998) in order to explain the mechanism by which apparently tropical carbonate deposits directly overlie glacial formations, as well as to explain their negative $\delta^{13}C$ excursions. Neoproterozoic cap carbonates commonly display $\delta^{13}C$ values of between $-7\%e$ to $-6\%e$ (James et al., 2001; Giddings and Wallace, 2009), which contrasts with typically calculated values of around $+4.7\%e$ for the sedimentary record of that time period (Knoll et al., 1986; Kaufman et al., 1992; Kaufman and Knoll, 1995; Kennedy et al., 1998; Knoll, 2000).

According to the Snowball Earth hypothesis, the planet experienced several periods of a fully-frozen state during the Neoproterozoic. This state was explained as resulting from a runaway ice-albedo feedback, whereby glacier growth at high latitudes and altitudes was accelerated through the reflection of solar energy by expanding ice sheets, which eventually managed to reach paleo-equatorial latitudes. With a mean global temperature
of \(-50^\circ C\), the model estimated that the ocean was completely and continuously covered with approximately 1 km thick sea ice for an estimated period of 4-30 m.y. (Hoffman et al., 1998; Kirschvink et al., 2000). It was hypothesized that such an extreme global glaciation must have caused marine ecosystems and biological productivity in the surface ocean to collapse and the hydrological cycle to virtually cease for millions to tens of millions of years. It would also strongly reduce the amount of export production and burial rates of organic carbon, causing the carbon isotopic composition of the ocean to reach mantle values of about \(-5\%_e\) (Kump, 1991). The hypothesis envisaged that with the ocean isolated from the atmosphere (i.e., no photosynthesis) and with negligible terrestrial weathering of silicate rocks during glaciation (no major sinks for CO\(_2\)), the atmospheric carbon dioxide emitted by prolonged volcanic activity would gradually build up and reach critical concentrations of up to 350 times the present-day atmospheric level. This ultra-greenhouse climatic condition with high atmospheric pCO\(_2\) (~0.12 bar) would eventually lead to a catastrophic termination of the snowball state by rapidly melting the ice covering the surface of the Earth and raising sea levels. Combined with enhanced continental carbonate and silicate weathering by acidic meteoric waters following deglaciation, the reestablished hyper-active hydrological cycle would deliver high fluxes of carbonate alkalinity to the transgressing post-glacial ocean, causing unusually high levels of seawater carbonate saturation and rapid, widespread deposition of marine carbonates (cap carbonates) over glacial deposits. The high rates of carbonate precipitation may have probably exceeded productivity and organic carbon burial rates, which resulted in \(^{13}\)C depletion of dissolved inorganic carbon (DIC) in the ocean, a geochemical signal inherited by many cap carbonates around the world in the form of negative \(\delta\)\(^{13}\)C values (see also Hoffman and Schrag, 2002). The fact that many of these cap carbonates lack any evidence of glacial influence further attests to the rapid nature of the glacial-deglacial transition (Giddings and Wallace, 2009).

In addition to the high burial rates of carbonate carbon, another influencing factor on carbon isotopic compositions is the rapid hydration and transformation of CO\(_2\) from the atmosphere to the ocean via silicate weathering. The weathering process involves a Rayleigh fractionation of \(+8\%e\) with the atmospheric reservoir becoming progressively
more depleted in $^{13}$C, which explains the observed up-section decrease in $\delta^{13}$C within cap carbonate successions (Kennedy et al., 2001). In contrast, Higgins and Schrag (2003) interpreted the drop in $\delta^{13}$C values in the basal parts of these successions (immediately above glacial deposits) to be an indication of an increase in surface water temperature, which lowers the fractionation between CO$_2$ and carbonate. Higgins and Schrag (2003) also highlighted the important role of kinetic isotope effects associated with rapid carbonate precipitation in the observed drop in $\delta^{13}$C values of cap carbonates. Hoffman et al. (1998) proposed in their SEH model that, eventually, biological productivity would be reestablished, and with it the export production and burial of organic carbon, which is about 27‰ depleted in $^{13}$C relative to carbonate carbon, would resume. These processes, as the authors postulated, is what causes the up-section gradual rebound in $\delta^{13}$C values of cap carbonate sequences and drive them towards more positive preglacial values.

The Snowball Earth hypothesis is, however, not fully accepted because of seemingly conflicting geological observations, including evidence of vigorous hydrological cycle suggesting absence of global freeze-up, lack of evidence of extreme sea level fall, tidal rhytmites suggesting an open ocean, and evidence of wave action indicating an unfrozen sea (Williams and Schmidt, 2000; Young, 2015, 2016).

The gas or methane hydrate destabilization hypothesis of Kennedy et al. (2001) attributes the deposition of Neoproterozoic post-glacial cap carbonates and their strongly negative carbon isotopic excursions to a less drastic environmental disturbance than that proposed by the Snowball Earth hypothesis. Simply, it considers oxidation of methane, which has very low carbon isotopic composition, to be the main source of the excessive carbonate alkalinity in Neoproterozoic post-glacial oceans (also Jiang et al., 2003; Font et al., 2006). The model was built on the assumption that during glaciation and associated sea-level fall, sea-floor organic-rich sediments would become subaerially exposed. The biogenic or thermal degradation of these sediments would produce methane, which would then be sequestered as clathrates or hydrates in terrestrial permafrost of exposed continental shelves and interior basins (Kennedy et al., 2001). The rapid warming and flooding of these shelves and basins during deglaciation would destabilize the gas hydrates, and cold methane seeps would form on the seafloor as a result. Eventually,
microbial sulphate reduction would have oxidized the released methane, producing massive carbonate alkalinity highly depleted in $^{13}$C, which would promote cap carbonate precipitation carrying the same geochemical signature. However, most critics of this hypothesis argue that extremely $^{13}$C depleted values, which are commonly associated with methane seeps (some as low as $-50\%e$, Jiang et al., 2003 and references therein), are not observed in cap carbonates; as well as the question of whether cold methane seeps could quantitatively account for the widespread precipitation of cap carbonates (e.g., Hoffman et al., 2002).

The third prominent hypothesis is the conceptual plumeworld model of Shields (2005). This model was mainly meant to address the global homogeneous distribution of carbonate alkalinity entering seawater following a major glaciation event. The plumeworld model suggests that low latitude deglaciation was extensive and abrupt in nature. This event would yield a low density meltwater plume, which must have extended worldwide, making a physical barrier between the surface and deep ocean reservoirs for thousands of years (Shields, 2005; Rose and Maloof, 2010). In an obvious contrast to the other models that propose abiotic precipitation of cap carbonates from normal salinity seawater, Shields (2005) suggested in his model that cap dolostones formed by microbially-mediated precipitation of carbonate whitings within a low salinity ocean during algal blooms.

Another noteworthy hypothesis includes the upwelling model of Grotzinger and Knoll (1995). These authors suggested that the ocean was physically stratified during late Neoproterozoic glaciations. In such a situation, the surface waters would become enriched in $^{13}$C as organic matter rich in $^{12}$C is exported to the deep, anoxic bottom waters. Alkalinity enriched in $^{12}$C would then form in the deep ocean due to the remineralization of the organic matter by means of bacterial sulfate reduction. Upwelling of the stratified ocean during deglaciation would mix alkalinity-laden deep waters with surface waters, promoting massive precipitation of carbonates anomalously depleted in $^{13}$C (Grotzinger and Knoll, 1995). Kaufman and Knoll (1995) also hinted at the possibility that ventilation of the deep sea following a period of ocean stratification may have contributed to the observed negative excursions in the carbon isotopic record. In
other words, this model implies that alternating positive and negative carbon anomalies in the stratigraphic record should reflect alternating periods of glaciation (ocean stratification) and deglaciation (ocean upwelling and mixing), respectively.

5.3.2 Patterns of stratigraphic variations in carbon isotopic anomalies

Two Neoproterozoic (1000-542 Ma) glacial intervals are recognized on all modern-day continents (e.g., Rose and Maloof, 2010). The older Cryogenian glaciation is known as the Sturtian, whereas the younger is commonly referred to as the Marinoan (Kennedy 1996; Kennedy et al., 1998). Both of these glacial intervals are ubiquitously overlain by cap carbonates that display distinct profiles of negative carbon isotopic anomalies (Kennedy, 1996; Corsetti and Kauffman, 2003). For example, Kennedy et al. (1998) observed that cap carbonates immediately overlying Sturtian glacial intervals are characterized by strongly negative $\delta^{13}C$ values at the base, but become increasingly enriched in $^{13}C$ upsection. In contrast, cap carbonates that overlie Marinoan glacial deposits are commonly characterized by the opposite trend with $\delta^{13}C$ values starting at around 0‰ or slightly negative at the base, and become more depleted in $^{13}C$ (approximately ~5‰) upsection before ultimately shifting towards positive values. Other workers have also reported similar trends (e.g., McKirdy et al. 2001; Higgins and Schrag, 2003; Halverson et al., 2004; Corsetti et al., 2007; Vieira et al., 2007; Pruss et al., 2010; Rose and Maloof, 2010). One explanation for these patterns is that Sturtian cap carbonates are condensed, which means they lack the transgressive systems tracts that host the $\delta^{13}C$ declining-upsection trend (Halverson et al., 2004).

Facies-dependent $\delta^{13}C$ variations are another form of isotopic variation pattern observed in cap carbonates. For example, Giddings and Wallace (2009a) conducted sedimentological and geochemical analyses of a Sturtian cap carbonate sequence in the Adelaide Geosyncline of South Australia, and found that the shallowest facies produces $\delta^{13}C$ values ranging between $-3.6‰$ and $-0.3‰$, whereas the deeper water facies has $\delta^{13}C$ values ranging between $-5.5‰$ and $-3.5‰$. Basinal facies yielded even lighter values with $\delta^{13}C$ ranging between $-6.7‰$ and $-5.7‰$. The authors argued that these $\delta^{13}C$ trends are of primary marine origin based on their regional and stratigraphic consistency.
Giddings and Wallace (2009a) attributed the $\delta^{13}C$-depth relation to the effect of the biological pump in a physically stratified ocean with limited mixing between deep and surface waters (also Giddings and Wallace, 2009b). Kaufman and Knoll (1995) suggested that the gradient of $\delta^{13}C$ values that decreases with depth is the result of oxidation of photosynthetically produced organic matter throughout the water column and to geographic variations in the intensity of upwelling and mixing. Rothman et al. (2003) interpreted such a gradient as being the result of organic matter remineralization because the Neoproterozoic carbon cycle was dominated by a significant pool of dissolved organic matter (also Corsetti et al., 2007). Other workers have also observed the same trend where shallow water cap carbonate facies are enriched in $\delta^{13}C$ compared to their equivalent deep-water facies (see de Alvarenga et al., 2004; Shen et al., 2005; Rieu et al., 2006; Kasemann et al., 2010).

5.3.3 Post-depositional alteration of cap carbonates

Ancient carbonate deposits are susceptible to at least some degree of post-depositional chemical alteration by meteoric- and/or hydrothermal-related diagenesis, recrystallization, dolomitization, and metamorphism (Derry et al., 1992; Jacobsen and Kaufman, 1999; Melezhik et al., 2001; Halverson et al., 2005). This means that these rocks may not retain primary isotopic signatures of the ambient seawater (Frimmel, 2010). Fairchild and Kennedy (2007) suggested that a combination of primary and diagenetic processes may have contributed to the whole-rock carbon isotopic compositions of cap carbonates based on strong covariation between $\delta^{13}C$ and $\delta^{18}O$ values, complete or partial dolomitization, recrystallization, abundant diagenetic cements, and the scatter range in magnitude and value of isotopic signals obtained from stratigraphically equivalent sections. The contribution of primary processes was inferred from the similarity of the $\delta^{13}C$ values between basins, their consistent and global reproducibility, and their systematic decline upsection, reflecting a secular variation of the coeval seawater (also Kasemann et al., 2010).

Kaufman and Knoll (1995) proposed that the major source of alteration of C-isotopic composition of carbonate rocks is the addition of isotopically distinct carbonate phases
via re-equilibration with fluids of different isotopic compositions during recrystallization and neomorphism. Other important sources of alteration include decarbonation reactions during metamorphism which take place only in the presence of silicate minerals (mainly quartz and feldspar) as well as bacterial sulfate reduction and microbial metabolism of sedimentary organic matter; all lead to lower $\delta^{13}$C values of whole-rock carbonate (e.g., Grotzinger and Knoll, 1995; Higgins and Schrag, 2003). Some authors claim that all Neoproterozoic carbon isotope signatures are diagenetically overprinted (e.g., Knauth and Kennedy, 2009). Thus, it is critical to systematically screen carbonate samples under consideration for possible diagenetic alteration and decide whether or not their isotopic signals reliably reflect compositional changes in the chemistry of coeval seawater from which they were precipitated.

Several criteria and tools have been utilized in order to evaluate the extent of chemical alteration of ancient carbonates and their isotopic compositions, including petrologic and geochemical tests of individual carbonate samples. Petrographic tools primarily aim at examining lithological and textural features to screen for diagenetic alteration, such as the degree of fabric preservation and recrystallization, and the ratio between authigenic and detrital components. Stylolites, fractures, veins, and signs of surficial weathering are also indications of alteration or neomorphism (Kaufman et al., 1991; Kaufman and Knoll, 1995). Geochemical approaches, on the other hand, measure abnormal deviations of isotopic and elemental compositions of the carbonate samples under investigation. Concentrations of Mn, Sr, Fe, Mg, and Ca as well as Mn/Sr, Fe/Sr, and Mg/Ca ratios are commonly used in geochemical evaluation of isotopic alteration (Brand and Veizer, 1980; Porter et al., 2004; de Alvarenga et al., 2004, 2008). Chemical alteration and recrystallization of carbonate rocks under the influence of meteoric fluids lead to the removal of primary Sr and the addition of Mn and Fe via substitution into secondary carbonates (Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1990; Arthur, 2009; Frimmel, 2010; Horák and Evans, 2011). This process is also accompanied by the dissolution of primary Mg-rich calcite and reprecipitation of Mg-poor cements, which commonly have lower $\delta^{18}$O values because meteoric, as well as pore fluids are depleted in $^{18}$O relative to seawater (Kaufman et al., 1992; Stoll and Schrag, 2000; Arthur, 2009;
Le Guerroue, 2010). Consequently, any co-variations between these trace element concentrations and ratios and oxygen isotopic compositions with $\delta^{13}$C are regarded as an indication of alteration during water-rock interaction (Banner and Hanson, 1990; Corkeron, 2007).

The diagenetic history of carbonate rocks may, however, be complicated if multiple stages of fluid-rock interaction were involved. Melezhik et al. (2001) also suggested that elemental ratios may be influenced by the initial carbonate composition rather than being solely affected by the degree of post-depositional alteration. Furthermore, Giddings and Wallace (2009 a, b) argued that the use of these diagenetic discriminators (Mn, Sr, Mn/Sr, $\delta^{18}$O), which were originally developed for Phanerozoic carbonates by Veizer (1983), may be challenged if used for Precambrian deposits.

Unlike carbon isotopic excursions, utilization of oxygen isotopic excursions in Precambrian chemostratigraphy is less reliable (Halverson et al., 2010; Jones et al., 2010). The reason is that oxygen isotopic compositions are very sensitive to diagenetic alteration especially via isotopic exchange with meteoric or hydrothermal fluids, which may significantly lower $\delta^{18}$O values of carbonates (Kaufman and Knoll, 1995; Shields et al., 2002; Font et al., 2006). Diagenetic fluids usually have low concentrations of dissolved carbon compared to the high content of carbon in carbonate minerals, meaning that $C$ will be buffered against significant isotopic exchange during alteration, but $O$ will not (Banner and Hanson, 1990; Derry et al., 1992; Jones et al., 2010). This is the rationale behind using crossplots of $\delta^{13}$C and $\delta^{18}$O as a means of screening for alteration via diagenetic fluids; a lack of positive correlation between the two indicates less alteration of $\delta^{13}$C values by diagenetic processes (Veizer, 1983; Kaufman et al, 1992; Frimmel, 2010).

An additional complication in using $\delta^{18}$O in Precambrian chemostratigraphy is the uncertainty surrounding oxygen isotopic composition of ancient oceans (Halverson et al., 2010). Some workers suggest that $\delta^{18}$O composition of seawater has always been buffered by hydrothermal and weathering processes at mid-ocean ridges, and has thus remained invariable over time (e.g., Gregory and Talyor, 1981; Meuhlenbachs, 1986;
1998). Others propose a secular change of oxygen isotopic composition of seawater from negative values of approximately -10‰ V-PDB in the Neoproterozoic to more positive present-day compositions (Wallmann, 2001; Jaffrés et al., 2007). Kaufman and Knoll (1995) accepted values ranging between 0‰ and -5‰ as a good estimate of the primary oxygen isotopic composition of Neoproterozoic seawater. Notwithstanding the lack of consensus, the highly and consistently negative δ¹⁸O (V-PDB) values characterizing Proterozoic cap carbonates are commonly either attributed to the addition of glacial melt water to the surface seawater during post glacial transgression (Veizer et al., 1992; Shields, 2005) or to the effects of post-depositional diagenetic alteration (Bekker, 2001; Bekker et al., 2005).

5.3.4 Chemostratigraphy of the Espanola Formation

Very few studies have evaluated the isotopic composition of carbonate rocks in the Espanola Formation. As part of their investigation of isotopic composition variations of Early Paleoproterozoic seawater, Veizer et al. (1992) studied the isotopic compositions of limestone and dolostone samples from the lower Limestone Member of the Espanola Formation in the vicinity of Elliot Lake. The authors found that the entire sample population was strongly depleted in δ¹⁸O with most values being close to −18‰ PDB. Slight ¹³C depletion was also noted, but in general, δ¹³C values varied consistently within a narrow range of −1.3 ±0.7 PDB. This value was considered by the authors to be within the normal marine range, and is comparable to values reported from other unaltered or least altered Proterozoic and Phanerozoic marine carbonate samples (e.g., Veizer et al., 1986; Kaufman et al., 1997; Kennedy et al., 1998; Frauenstein et al., 2009).

Veizer et al. (1992) tested the possibility that the pronounced ¹⁸O depletion in Espanola carbonates may have resulted from an intense post-depositional alteration of these rocks, but ruled it out based on trace element systematics. For example, it was found that the analyzed samples contain high Sr and low Mn contents. Similarly, using a scatter diagram of δ¹³C vs. Mn, Veizer et al. (1992) found that the δ¹³C values for the same rocks are independent of Mn content, and thus concluded that the observed oxygen and carbon isotopic compositions are not significantly affected by diagenetic processes. The authors
proposed that the strong $^{18}$O depletion and probably the slight depletion in $^{13}$C may have resulted from deposition in an environment with significant influx of meteoric waters (e.g., high latitude/altitude melt waters) during recession of the Bruce glaciers. They stressed that such isotopic compositions are more likely to indicate a non-marine or mixed origin for the Limestone Member of the Espanola Formation in the Elliot Lake area.

In a comparative analysis, Bekker et al. (2005) investigated the similarities between early Paleoproterozoic post-glacial carbonate successions of southern Ontario (Espanola Formation) and Wyoming with isotopically anomalous Neoproterozoic cap carbonates that sharply overlie most Neoproterozoic glacial diamictites (e.g., Kennedy, 1996; Hoffman and Schrag, 2002; Hoffman and Li, 2009). The analyzed Espanola Formation samples were taken from both the lower Limestone and the upper Dolostone members. Their results showed that carbon and oxygen isotope values of these rocks span a wide range, but are consistently negative in all sampled sections. Values for $\delta^{13}$C ranged from $-6.7$ to $-0.8$‰ V-PDB, whereas those for $\delta^{18}$O are significantly depleted, ranging from $-20.5$ to $-11.1$‰.

Bekker et al. (2005) suggested that the pronounced low $\delta^{18}$O values are the result of equilibration with hot diagenetic or metamorphic fluids. The authors argued that the highly recrystallized textures of the analyzed carbonates as well as their elevated $^{87}$Sr/$^{86}$Sr compositions are also in favour of post-depositional alteration. The anomalous negative $\delta^{13}$C values were considered at least partly of primary origin, possibly inherited from dissolved bicarbonate in post-glacial seawater, and were assumed to be globally isochronous markers based on positive correlation with equivalent carbonates from Wyoming and South Africa (Bekker et al., 2001). A metamorphic origin of the negative $\delta^{13}$C values was excluded based on the absence of metamorphic minerals as well as the general lack of correlation between $^{13}$C and $^{18}$O abundances in these rocks. No clear stratigraphic or facies-dependent trends in $\delta^{13}$C values of Espanola carbonates were observed by Bekker et al. (2005).
In line with previous studies, the current research reports highly and consistently negative carbon and oxygen isotopic compositions of whole-rock limestone samples. Several lines of evidence suggest a post-depositional diagenetic overprinting. Generally, the analyzed samples contain high concentrations of Mn and Fe, low concentrations of Sr and Mg, and have high Mn/Sr and Fe/Sr ratios. When coupled with strongly negative $\delta^{18}$O values, such elemental compositions point to re-equilibration and isotopic exchange with hot meteoric waters or infiltrating metamorphic fluids as the prime alteration process. However, correlation between $\delta^{13}$C and Mn, Sr, Mn/Sr, and $\delta^{18}$O reveal that rocks of the Espanola Formation were not affected equally by this process, with samples of the LFA3 showing stronger correlations, and therefore are considered more altered than those of the LFA1. In addition, oxygen isotopic compositions seem to have been more affected by alteration than accompanying carbon compositions because the highest (least altered) $\delta^{18}$O values are still lower than those reported from well-preserved Paleoproterozoic carbonates (Veizer et al., 1992; Melezhik et al., 1997; Bekker, 2001). Independent field and petrographic observations also support the predominance of diagenetic conditions, including highly recrystallized textures and obliteration of original features, dolomitization, high detrital contents, presence of minerals associated with metamorphosed carbonate-rich rocks such as diopside and scapolite, and the association with intrusive gabbro dykes and sills. Rusty-weathered units, normal growth faults, slump breccia, and stylolite structures are particularly common in the LFA3.

Although oxygen isotopic compositions are consistently negative throughout the measured sections, and are believed to have been affected by post-depositional alteration to varying degrees, some carbon isotopic compositions may be at least partly original in nature. This is particularly true for the lower 14 m of Core 138-1 in which carbon isotope values fall well within the normal marine range. In addition, the carbon isotopic compositions are similar to those obtained from correlative, but less altered, carbonates of the Paleoproterozoic Snowy Pass Supergroup of Wyoming (Bekker et al., 1999; Bekker, 2001; Bekker et al., 2005), as well as compositions reported from Neoproterozoic cap carbonates overlying glacial diamictites found worldwide (Kaufman and Knoll, 1995; Hoffman et al., 1998; Kennedy, 1996; Halverson et al., 2005).
Bekker (2001) reported negative carbon isotopic compositions that narrowly range from −3.8 to −1.5‰ V-PDB from the Vagner Formation of the Snowy Pass Supergroup, which is considered correlative to the Espanola Formation based on lithostratigraphic data (Bekker et al., 2003). Oxygen isotopic compositions for the same interval range from −20.9 to −14.5‰ V-PDB. The carbon isotopic compositions, which clearly mimic those of the lowermost part of the LFA1 of Core 138-1, were considered by Bekker (2001) to be of primary origin, thus reflecting secular carbon isotope variations in early Paleoproterozoic seawater, which are in turn the result of environmental changes associated with a global glaciation event (Bekker et al., 2005).

In order to emphasize the global nature of the anomalous negative δ13C values, Bekker et al. (2001) reported similar carbon isotopic compositions from well-preserved carbonates of the early Paleoproterozoic Duitschland Formation, South Africa, which, based on lithostratigraphic and chemostratigraphic attributes, tentatively correlate with carbonates of the Espanola Formation (Bekker, 2001; Bekker et al., 2005). The authors reported negative δ13C values that vary within a narrow range with a minimum value of −3.7‰ V-PDB and δ18O values that are mainly lower than −10‰ V-PDB. Although the oxygen isotopic compositions were attributed to post-depositional alteration, the carbon isotope compositions were considered to be near primary signatures of coeval seawater.

Carbon isotopic compositions reported in this thesis are similar to but generally lower than those commonly observed in Neoproterozoic cap carbonates from Australia, Namibia, Brazil, Svalbard, northwestern Canada, and southern China (e.g., Kaufman et al., 1991; Hoffman et al., 1998; Kennedy, 1996; Kennedy et al., 2001; James et al., 2001; Jiang et al., 2003; Shen et al., 2005; Font et al., 2006; Czerkien, 2007; Vieira et al., 2007; Giddings and Wallace, 2009 a, b; Rose and Maloof, 2010). Despite the similarities, the isotopic compositions from the Espanola Formation samples are considered local rather than oceanic geochemical signatures. This is due to several challenging factors, including the limited areal distribution of the outcrops in the study area as well as the scarcity of cores and well logs; all of which in turn have hindered the construction of a reference sequence stratigraphic framework for the area. In addition, no depth gradient in δ13C could be established nor inferred because the configuration of the depositional basin is
poorly delineated. Establishing the depth-dependant gradient for $\delta^{13}$C would have helped in explaining the differences in isotopic compositions between stratigraphically equivalent units in the two measured sections, especially within the lowermost part of the LFA1. It would also have been helpful in detecting any facies-related isotopic trends. A local origin for the reported isotopic compositions is consistent with the rift setting and semi-restricted depositional basin in which the Espanola Formation was deposited.
Chapter 6

6 Conclusions

The Espanola Formation in the Bruce Mines-Elliot Lake region, Ontario was investigated via lithofacies analysis, petrographic, and geochemical approaches. One of the main objectives of the study was to determine the depositional environments of the Espanola Formation, with special emphasis on features indicative of recurrent syndepositional to early post-depositional, fault-related tectonic activity. The project was also aimed at evaluating the main carbonate minerals (calcite and dolomite) and whether these minerals are primary or detrital in origin, as well as to determine the nature of the tectonic setting, provenance, and the degree of chemical weathering intensity. An attempt was also made to determine whether the carbonate units of the Espanola Formation represent a Paleoproterozoic cap carbonate by means of comparison with Neoproterozoic examples.

Lithofacies and Lithofacies Associations

Seventeen distinct sedimentary lithofacies types were identified within the study area: (LF1) Interlaminated to interbedded siltstone-carbonate, (LF2) Massive to faintly laminated carbonate, (LF3) Wavy laminated sandstone, (LF4) Massive to faintly parallel-laminated sandstone, (LF5) Wavy bedded sandstone, (LF6) Low angle cross-bedded sandstone, (LF7) Planar interlaminated to interbedded mudstone-siltstone, (LF8) Wavy laminated to wavy bedded mudstone-siltstone, (LF9) Grey thickly-bedded siltstone, (LF10) Green thinly-laminated siltstone, (LF11) Interbedded massive and thinly laminated siltstone, (LF12) Mudstone, (LF13) Thickly bedded carbonate, (LF14) Rusty carbonate, (LF15) Stromatolitic carbonate, (LF16) Intraformational conglomerate, and (LF17) Intraformational breccias. These sedimentary lithofacies types were grouped into three lithofacies associations which are, in ascending order: the upper shoreface lithofacies association (LFA1), the lower shoreface to offshore-transition lithofacies association (LFA2), and the nearshore or lagoonal lithofacies association (LFA3).

The LFA1 consists of laterally extensive interlaminated and interbedded siltstone and carbonate layers (LF1 and LF2). Carbonate-rich beds have a clastic texture and are
normally graded, suggesting a detrital origin. Sedimentary structures in the LFA1 include planar lamination, dune scale cross-stratification, rare syneresis or microbially induced cracks, and local asymmetrical ripples. Soft-sediment deformation structures such as conglomeratic clastic dykes, load structures, and slump structures, as well as synsedimentary faults and folds are common in the LFA1. The LFA1 is interpreted to have been deposited in an upper shoreface marine environment dominated by strong and sustained current flow with limited wave influence. Petrographic analysis revealed that samples of the LFA1 consist of alternating siliciclastic and carbonate layers. The siliciclastic component constitutes approximately 10-26% of the samples, and consists mainly of well-sorted, subrounded monocrystalline quartz, in addition to mica, scapolite, opaque minerals, plagioclase, chlorite, diopside, chert fragments, and traces of potassium feldspar and epidote. The carbonate fraction accounts for approximately 74-90% of the samples, and consists predominantly of calcite ranging from micrite to fine-grained sparite. Calcite crystals are generally well-sorted, well-rounded, and normally graded; and are within the same size range of the associated siliciclastic component. Recrystallization is widespread as indicated by neomorphic microspar and pseudospar with micrite relicts.

The LFA2 consists mainly of siliciclastic deposits arranged into basal fine- to very coarse-grained sandstone followed by mixed fine- to coarse-grained siltstone and mudstone and capped by thick mudstone (LF3-LF12). Sedimentary structures include planar parallel lamination, planar and trough cross-lamination and cross-bedding, symmetrical wave ripple cross-lamination (i.e., combined flow ripples), and hummocky cross stratification (HCS). Other primary features include normal grading, gutter casts, symmetrical wave ripple marks, and polygonal cracks. Soft sediment deformation structures are widespread in the LFA2, including concentric ball and pillow structures, dish and pillar structures, sandstone dykes, convolute bedding, and normal and reverse faults. The characteristics of LFA2 suggest deposition above storm wave base in a mainly wave- and storm-dominated lower shoreface to offshore transition zone. The siliciclastic fraction of the LFA2 constitutes approximately 30-84% of the samples with clay matrix and fine sparite cement accounting for the remainder. Subangular to well-rounded
monocrystalline quartz is the dominant type of detrital grain followed in abundance by plagioclase, sedimentary and metamorphic lithic fragments, muscovite, biotite, chlorite, pyrite, potassium feldspar, and traces of albite, epidote, sericite, and opaque minerals. Feldspars are altered into clay minerals or mica, and the samples show signs of compaction and pressure-solution.

The LFA3 consists mainly of laterally continuous thickly bedded and wavy laminated stromatolitic dolostone and limestone (LF13-LF15). Carbonate units contain thin, wavy laminated stratiform stromatolites, discrete and laterally linked columnar stromatolites, mound-like masses of algal laminated deposits, birds-eye structures and fenestral fabrics. LFA3 carbonate has (re)crystallized textures and contains less siliciclastic content than LFA1. Slump breccia, rusty-weathered carbonate beds, and intraformational conglomerate are ubiquitous in the LFA3. The LFA3 is interpreted to have been precipitated in situ in a mainly restricted nearshore or lagoonal environment. Samples from the LFA3 consist mainly of recrystallized and neomorphosed calcite and dolomite, which range in form from micrite to pseudospar to coarsely crystalline sparite and dolomite, constituting approximately 60-95% of the samples. The siliciclastic component is minor and is composed mainly of scattered detrital grains of angular to subrounded monocrystalline quartz along with subordinate amounts of sedimentary rock fragments, muscovite, biotite, plagioclase, and traces of epidote, diopside, chlorite, pyrite, and magnetite.

Collectively, the three lithofacies associations of the Espanola Formation constitute a general fining-upward transgressive sequence that was deposited in a wave- and storm-influenced shallow marine shelf setting over three different stages of a marine transgression following retreat of the Bruce Formation glacier(s).

Tectonic Influence on Sedimentation

Deposition of the Espanola Formation was tectonically influenced. The two major W-E trending fault systems (the Flack Lake Fault and the Murray Fault Zone) present in the study area may have been active during deposition of the Espanola Formation, as indicated by slump structures along slip faces, syn-seidmentary faults and folds, abundant
clastic dykes, and soft-sediment deformation structures. Such characteristics indicate that deformation was synsedimentary tectonism, and probably triggered by fault-related seismic activity during lower Huronian basin subsidence.

**Major and Trace Element Geochemistry**

Geochemically, siltstone and mudstone samples of the Espanola Formation are classified as shales with low Fe$_2$O$_3$/$K_2$O and SiO$_2$/Al$_2$O$_3$ ratios. Chemical Index of Alteration (CIA) values calculated from the Espanola Formation samples range from as little as 51 to as much as 80 with an average of approximately 63, suggesting the source area was subjected to relatively low to moderate chemical weathering conditions. The samples mainly plot in the passive margin field on major element tectonic setting discrimination diagrams. Trace element diagrams reveal that the samples cluster around average granodiorite and Archean tonalite-trondhjemite-granodiorite (TTG) compositions, with a linear distribution pattern. This suggests that the samples were mainly derived or recycled from granodioritic and TTG Archean terrains with some contribution from mafic volcanic and/or Archean sedimentary rocks (consistent with the geology of the Superior Province to the north). The samples plot in the continental island arc tectonic setting on La-Th-Sc and Th-Sc-Zr/10 discrimination diagrams, yet there is no present-day evidence for such systems anywhere near the Huronian basin. The low Zr/Sc ratios combined with moderate Th/Sc ratios indicate that the composition of the Espanola Formation deposits was controlled mainly by compositional variations in source terrane rather than sediment recycling. The REE patterns produced by the samples are LREE enriched compared to chondrite and display small negative Eu anomalies, consistent with a predominant felsic source.

**Stable Isotope Geochemistry**

Stable isotope analysis of limestone samples from the LFA1 reveals that carbon and oxygen isotopic compositions are spatially highly variable, suggesting local rather than global controls, and are consistently and strongly negative. Carbon isotopic compositions range from $-11.0$ to $-4.9‰$ V-PDB in drill core 150-4 and from $-9.2$ to $-1.1‰$ V-PDB in drill core 138-1, whereas oxygen isotopic compositions range from $-10.8$ to $-8.2‰$ V-
PDB and from –19.7 to –8.7‰ V-PDB, respectively. The same samples show generally high Fe, Mn and low Sr concentrations. Coupled with very low δ¹³C and δ¹⁸O values and positive correlation between these values, such elemental characteristics suggest that the carbonate was subjected to post-depositional chemical alteration. Slightly negative δ¹³C values (–2.7 to –1.1‰ V-PDB) with poorly defined trends of upsection depletion, combined with the lack of correlation between isotopic and elemental compositions in some samples hints towards primary processes.

Whole-rock limestone samples from LFA3 yield negative carbon isotopic ratios that range from –7.4 to –2.5‰ V-PDB in drill core 150-4 and from –8.9 to –8.0‰ V-PDB in drill core 138-1, whereas oxygen isotopic compositions vary from –20.2 to –7.2‰ V-PDB and from –10.4 to –9.3‰ V-PDB, respectively. The analyzed samples are characterized by high Fe and Mn contents and low Sr and Mg concentrations. A strong positive correlation between these elemental concentrations and δ¹³C and δ¹⁸O values was noted. In addition, carbon isotopic compositions co-vary strongly with oxygen isotopic compositions. These characteristics are indicative of post-depositional chemical alteration and recrystallization of carbonate minerals. The presence of stromatolites in LFA3 points to the possibility that microbial metabolism of sedimentary organic matter may have also contributed to the lower δ¹³C values.

Cap Carbonate Comparison

Comparisons between the Espanola Formation and Neoproterozoic cap carbonate successions reveal some similarities, including stratigraphic position, anomalously negative carbon isotopic compositions, the transgressive nature of the successions, and widespread sedimentary structures indicative of subtidal deposition within a shelf setting. However, major differences do exist between the Paleoproterozoic and Neoproterozoic successions. The Espanola Formation samples do not display clear stratigraphic or depth-related systematic variations in carbon isotopic compositions and lack many of the sedimentary features that are considered characteristic of typical Neoproterozoic cap carbonates, such as giant wave ripples, tepee structures, and pseudomorphs after aragonite fans. In addition, Neoprproterozoic cap carbonates are commonly laterally
continuous and much thinner than the Espanola Formation, ranging from a few to 27 m thick, and are dominated by dolostone.

The similarities between the Espanola Formation and Neoproterozoic cap carbonates can be attributed to similar shelf depositional environments within rift basin settings, whereas the major differences are mainly a function of local controls confined to the Espanola Formation. These controls include the mainly restricted nature of the depositional environment in which the formation was deposited, as well as the tectonic influence on sedimentation.

**Future Studies**

It is suggested in this thesis that the sedimentology and lithofacies distribution of the Espanola Formation in the Bruce Mines-Elliot Lake region were mainly governed by local tectonic controls rather than global factors. In order to confirm the proposed local controls on deposition of the Espanola Formation, additional sedimentological and geochemical investigations across the entire Huronian outcrop belt are needed. This would also help place the proposed depositional environments for the Espanola Formation in the Bruce Mines-Elliot Lake area within a regional context. In order to overcome the challenge of limited outcrop exposure across the belt, future studies should attempt to utilize more drill core and well log data to construct a reference sequence stratigraphic framework. This would help in delineating the configuration of the depositional basin. A more comprehensive correlation between the Espanola Formation and Neoproterozoic cap carbonates could be facilitated through high density sampling for whole rock and isotopic geochemical analysis, possibly on a cm scale.
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Appendices

Appendix A: Description of drill cores

Drill core # 138-1

Drill core 138-1 has a total thickness of approximately 200 m. The basal part of the core (0-5 m) consists mainly of thinly laminated siltstone and very fine- to medium-grained sandstone. These deposits are massive, poorly sorted especially at the bottom of the section with widespread quartz granules, although a coarsening upward trend was noted. The overlying unit (5-21 m) represents the Limestone Member of Young (1973). It consists of alternating thin mudstone layers and thicker pure carbonate beds. The carbonate-rich beds appear either massive or thinly laminated, whereas the mudstone layers are often parallel thinly-laminated. Intervals of soft-sediment deformation are common throughout the unit with distorted bedding and step-faulting and folding being the main types. The overlying unit (21-32 m) is believed to represent the lower part of the Siltstone Member of Young (1973). It consists of calcareous siltstone and sandstone interbedded with silty and sandy limestone. Deformation is limited in this unit but quartz veins are common. The unit is abruptly truncated by a thick, dark green gabbro unit or dyke (32-98 m). The Siltstone Member reappears following the end of the gabbro (98-162 m). In this interval, it consists mainly of calcareous siltstone and sandstone with subordinate alternating mudstone and carbonate-rich beds. A general upward-coarsening trend was noted; otherwise, the unit is massive except for limited deformation in the form of flame structures and disturbed bedding and faulting. Cross-lamination and a thin flat-pebble conglomerate (possibly a storm bed) have been documented as well.

The uppermost unit (162-177 m) consists of interbedded rusty-weathered and non-rusty carbonate-rich layers. It is possible that this unit corresponds to the Dolostone Member of the Espanola Formation (Young, 1973), and that the rusty coloration is the result of incorporation of high iron content in the dolomite lattice. Some of the rusty beds are fragmented; yielding flat rounded clasts which commonly constitute the intraformational
conglomerate-breccia lithofacies. The drill core is capped by a thick (177-200 m) calcareous siltstone bed that grades up into a calcareous fine-grained sandstone.

Legend

- **Gabbro**
- **Clast-supported Conglomerate**
- **Matrix-supported Conglomerate**
- **Breccia**
- **Sandstone**
- **Siltstone**
- **Muddy**
- **Thin lamination**
- **Coarsening upward**
- **Cross lamination**
- **Fining upward**
- **Quartz veins**
- **Mud ripples**
- **Load structures**
- **Fragmented zone**
- **Contorted bedding**
- **Wave ripples**
- **Load structures**
- **Folding**
- **Faulting**
- **Lenticular bedding**
- **Sand lenses**

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Drill core # 144-1

Drill core 144-1 is approximately 194 m thick. The lower part of the core (0-18 m) overlies the Bruce diamictites, and is composed entirely of interbedded carbonate-rich (limestone) and mudstone. Carbonate-rich beds range in thickness from 20 to 50 cm, whereas mudstone layers are commonly much thinner with sharp to slightly wavy contacts between the two. The unit contains many sedimentary structures, including mud ripples, cross-lamination, and parallel lamination, the latter of which is more common within mudstone beds. Soft-sediment deformation structures are also widespread, including contorted bedding, load casts, and flame structures. No rusty coloration was noted throughout the unit, probably due to the low iron content in the limestones. The overlying unit is a thick (18-38 m) intraformational conglomerate that consists of rounded to subangular rusty carbonate-rich and mudstone clasts. Some of the incorporated clasts are thinly laminated. The conglomerates are matrix-supported, and the matrix ranges in composition from calcareous sandstone to mudstone. The unit abruptly shifts into fine-grained sandstone to coarse-grained siltstone with quartz granules and quartz seams.

A unit composed of thickly interbedded siltstone and mudstone overlies the intraformational conglomerate (38-77 m). Some of the siltstone beds contain rusty and non-rusty thin carbonate-rich layers. The upper part of the unit displays a fining-upward trend, shifting from muddy siltstone to silty mudstone, and becomes dominated by alternating mudstone and carbonate-rich layers with some disturbed bedding and sand lenses. This unit is overlain by a dominantly siliciclastic unit (77-94 m) which consists of poorly sorted fine-grained sandstone with carbonate pebbles followed by a matrix-supported intraformational conglomerate with mud and carbonate clasts contained in a siltstone matrix, which fines upward into poorly sorted very coarse-grained sandstone. It is overlain by an interbedded mudstone and non-rusty carbonate unit which is interrupted by a matrix-supported intraformational conglomerate with some rusty carbonate clasts before reappearing at the top of the unit (94-116 m). This interbedded unit is sharply overlain by a relatively very thick (116-140 m) clast-supported intraformational conglomerate. It contains rusty carbonate clasts, probably derived from the underlying carbonate beds, along with muddy and calcareous silty matrix. Some of the clasts are
thinline laminated, ranging in diameter from few mm up to 7cm. Quartz veins of up to 10 cm wide are widespread in the intraformational conglomerate unit. Following the intraformational conglomerate interval, a unit composed mainly of siltstone with subordinate rusty carbonate interbeds dominates (140-154 m). Up-section, however, this unit gives way to a unit of mainly thick non-rusty carbonate beds with subordinate mudstone layers (154-188 m). This unit may represent the Dolostone Member of the Espanola Formation (see Young, 1973). Similar to Core 138-1, Core 144-4 is capped by calcareous medium- to coarse-grained sandstone (188-194 m).
Drill core # 150-1

This drill core is approximately 167 m. It starts with a lower unit (0-9 m) of mainly carbonate-rich deposits with thin mudstone interbeds. No rusty coloration was observed in this unit, suggesting a primary limestone composition. It is overlain by a unit (9-23 m) of calcareous coarse-grained sandstone followed by intraformational conglomerates containing mud and carbonate clasts. The unit grades upward into a unit (23-62 m) of mainly siltstone and mudstone with few coarse-grained sandstone intervals, displaying fining-upward cycles within them. Pyrite and sand lenses are widespread in this unit. The middle part of the core is composed of a very thick (62-109 m) siliciclastic unit composed predominantly of calcareous siltstone and mudstone with interbeds of coarse-grained sandstone and few rusty carbonate rich layers. The siltstone and mudstone beds contain soft-sediment deformation structures, including contorted bedding, sand balls, and flame structures. Most of the upper part of the core (109-167 m) consists of a massive unit of muddy dolostone which contains intervals of rusty weathering and deformed bedding. It also contains an approximately 5-m-thick matrix-supported intraformational conglomerate bed. The intraformational conglomerate contains flat dolostone pebbles within a matrix of mudstone and siltstone.
Drill core #150-2

Core 150-2 is approximately 205 m thick. The core section commences with a massive gray silty to sandy limestone (i.e., the Limestone Member; Young, 1973) which becomes richer in siliciclastics up-section and grades into calcareous mudstone that coarsens upward into calcareous siltstone and eventually into calcareous poorly sorted pebbly sandstone (0-8 m). The limestone reappears atop the sandstone bed. However, throughout this interval (8- approx. 25 m) the limestone is not massive, but, rather, it is thinly-laminated, and is interbedded with thinly-laminated mudstones. Several deformed and fragmented zones which are possibly reworked or storm beds with disseminated carbonate clasts have been observed in this unit. Small scale folds similar to those described from Highway 108 outcrops are also common (see Chapter 3 for a detailed account). The limestone unit is followed by a unit of mixed siliciclastic components (approximately 25- approx. 36 m). It consists of a lower thinly laminated, calcareous siltstone-sandstone with some deformation and folding, a middle matrix-supported intraformational breccia with rusty, angular clasts embedded in a silty matrix, and an upper poorly sorted pebbly fine-grained sandstone with slump structures. The contact between this sandstone bed and the overlaying very thick (approx. 36- 77 m) intraformational conglomerate-breccia is gradational. The intraformational breccia is matrix-supported, and consists of randomly distributed rusty-weathered carbonate clasts along with minor mudstone and sandstone clasts, ranging in diameter from few mm up to 15 cm. Most of the carbonate clasts and almost all of mudstone clasts are thinly-laminated. The matrix ranges from silt-sized to sand-sized detrital material. Slump structures are the most common features in the intraformational breccia, and, overall, the unit resembles the slump breccia (the mega breccia) which was observed and described from Island A (see Chapter 3 for detailed description of lithofacies). The unit becomes more conglomeratic upwards. The intraformational breccia is overlain by a unit, mainly siliciclastic in composition, which constitutes the main middle part of the core, and likely represents the Siltstone Member of the Espanola Formation (77- 194 m). This extensive interval consists of thickly bedded calcareous coarse-grained siltstone and mudstone both of which contains carbonate-rich interbeds, some of which are rusty-weathered. The
contacts between the siltstone and mudstone beds are gradational. The carbonate interbeds are 2 to several cm thick. The unit contains sporadic few-cm-thick fragmented (reworked) zones with flat fragments arranged parallel to bedding. It also contains reverse grading, small-scale faulting and folding, and soft-sediment deformation structures, including disturbed bedding and flame structures. Symmetrical mud wave ripples as well as mud crack-like structures have been observed as well, but could possibly be associated with soft sediment deformation. The uppermost part of the core (194- approx. 205 m) is mainly composed of pure carbonate beds with some siltstone and mudstone interbeds. The carbonate beds are likely dolomitic in composition as indicated by their orange rusty weathered appearance, suggesting high iron content incorporated in the dolostone. This unit represents the Dolostone Member of the Espanola Formation, according to the subdivision of Young (1073).
Drill core # 150-4

The drill core is approximately 170 m thick. A short gabbro interval (0-7 m) separates the Espanola Formation from the underlying Bruce Formation at the base of the core. The gabbro is overlain by a unit (7-approx. 22 m) composed entirely of calcareous, thinly-laminated fine-grained siltstone and mudstone. This unit shifts gradually into muddy and silty limestone upward. It is overlain by a unit (22-43 m) composed of relatively pure carbonate interbedded with massive and thinly-laminated mudstone. Some of the mudstone layers are disturbed and deformed (i.e., wavy). Generally, the unit displays a decrease in mudstone content upward, but is interrupted near its top by thin intraformational conglomerate and sandy to silty limestone beds. The interbedded limestone-mudstone unit represents the Limestone Member of the Espanola Formation, and is lithologically very similar to the outcrop described at Highway 108. The middle part of the core (43-160 m), which is volumetrically far more significant than the lower and upper parts, is predominantly composed of calcareous siltstone and mudstone. This interval, however, contains frequent non-rusty carbonate-rich interbeds, possibly representing periods of minimized siliciclastic influx. Some of these carbonate layers are rusty and fragmented. Sedimentary structures observed in the siltstone-mudstone unit include symmetrical small-scale waver ripples, ball and pillow structures, load structures, flame structures, and sand lenses. In addition, flaser, wavy and lenticular bedding have all been noted in this unit. Near the top of the unit, the lithology changes from calcareous siltstone/mudstone into muddy/silty carbonate (likely dolomitic in composition) with the most common features being cross-lamination and soft-sediment deformation structures. This is probably a transitional interval between the middle Siltstone Member and the overlaying Dolostone Member. The Dolostone Member (160-approx. 170 m) is represented by mainly massive carbonate-rich beds, some of which are partly rusty and fragmented. This rusty coloration attests to its iron-rich dolomitic composition.
### Appendix B: A summary of the description and interpretation of major sedimentary lithofacies in the Espanola Formation

<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>Lithology</th>
<th>Sedimentary structures</th>
<th>Depositional processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF 1: Interlaminated to interbedded siltstone-carbonate</td>
<td>5 m thick</td>
<td>Planar, parallel lamination.</td>
<td>Deposited by low energy flows under quiet conditions, alternating periods of moderate-minimal siliciclastic input. Episodic high-energy conditions produced by storm waves and currents, and slope instability.</td>
</tr>
<tr>
<td>LF 2: Massive to faintly laminated carbonate</td>
<td>3 m thick</td>
<td>Massive to faint planar lamination. Poorly developed ripple cross-lamination Rate 2-4 cm deep tapering-downward shrinkage cracks. Asymmetrical ripples of mm-scale. Syn-sedimentary faults and folds.</td>
<td>Deposited during alternating influx of fine-grained siliciclastic and detrital carbonate debris. Low-moderate energy, traction currents in shallow waters. Affected by syn-depositional deformation.</td>
</tr>
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<td></td>
<td>Laminae: 5 mm thick. Laterally continuous, 50 cm thick carbonate-rich beds. Sharp basal contacts, upper undulatory contacts. Clastic texture.</td>
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<td></td>
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<tr>
<td>LF 3: Wavy laminated sandstone</td>
<td>10 cm thick</td>
<td>Planar and wavy laminae. Small-scale (1-2 cm wide) clastic dykes. Symmetrical wave ripple marks. 10x10 cm polygonal cracks on exposed bedding surfaces.</td>
<td>Deposition by traction currents and subordinate suspension fallout. Highly fluctuating flow energy conditions, affected by tidal currents.</td>
</tr>
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<td></td>
<td>Fine- to medium-grained sandstone with subordinate mudstone. Laminae: 5 mm thick. Bedding surfaces: wavy, increase in fines up-section.</td>
<td></td>
<td></td>
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<tr>
<td>LF 4: Massive to faintly parallel-laminated sandstone</td>
<td>0.7 m thick</td>
<td>Faint planar parallel lamination. Ball and pillar structures. Dish and pillar structures. Mudstone interbeds and gutter casts. Sedimentary structures 2-5 cm in size.</td>
<td>Rapid deposition from high-density turbidity currents accompanied by post-depositional liquefaction processes. Storm-driven, short-lived periods of high-energy wave conditions and unidirectional flows.</td>
</tr>
<tr>
<td></td>
<td>Medium- to very coarse-grained sandstone with quartz granules. Laterally continuous with sharp, but locally scoured bedding contacts.</td>
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<td>LF 5: Wavy bedded sandstone</td>
<td>2.5 m thick</td>
<td>Wavy bedding. Normal grading. Local planar cross-lamination. Load structures, 3 mm - 2 cm sand balls. Normal and reverse faults several cm long.</td>
<td>Combined bedload and suspension sedimentation under highly fluctuating flow strength and waning currents induced either by tides or storms. Liquefaction processes Syn-depositional faulting Unidirectional traction current processes in a storm-dominated environment.</td>
</tr>
<tr>
<td></td>
<td>Alternating, 2-5 cm thick, medium- to coarse-grained sandstone and mudstone beds. Laterally continuous with gradational bedding contacts.</td>
<td></td>
<td></td>
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<tr>
<td>LF 6: Low angle cross-beded sandstone</td>
<td>15 to 70 cm thick</td>
<td>Cross-lamination. Low angle planar and trough cross-bedding. Erosive bases</td>
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<tr>
<td></td>
<td>Coarse-grained, well sorted sandstone. Flat-pebble conglomerate intervals of rusty, elongated 3-4 cm long carbonate clasts aligned parallel to bedding planes.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LF 7: Planar interlaminated to interbedded mudstone-siltstone</td>
<td>1.5 m thick</td>
<td>Massive. Parallel lamination. Small-scale planar cross-lamination. Clastic sandstone dykes up to 8 cm thick.</td>
<td>Produced by a combination of suspension deposition and unidirectional traction current deposition under quiet conditions.</td>
</tr>
<tr>
<td></td>
<td>Laminae: 2-3 mm thick, beds: 2-3 cm thick. Contacts between beds: non-erosive, sharp-gradational.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LF 8: Wavy laminated to wavy bedded mudstone-siltstone</td>
<td>10 cm thick</td>
<td>Normal grading. Mudstone drapes. Symmetrical wave ripples: amplitudes of 2-3 cm, wavelengths of 10 cm. Sand balls several mm in diameter. Rare 4-5 mm deep, wedge-shaped cracks. Cross-lamination with thin mudstone veneers.</td>
<td>Produced by alternating suspension settling of fines and bedload sedimentation by waning unidirectional tractional currents in a wave-dominated setting.</td>
</tr>
<tr>
<td></td>
<td>Laminae: 2-5 mm thick, beds: 2-3 cm thick. Sharp upper and lower contacts, locally scoured lower contacts.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithofacies</td>
<td>Lithology</td>
<td>Sedimentary structures</td>
<td>Depositional processes</td>
</tr>
<tr>
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</tr>
<tr>
<td>LF 10: Green thinly-laminated siltstone</td>
<td>0.5 m thick Fine- to medium-grained, thinly-laminated to thinly-bedded siltstone. Laminae: few mm thick, beds: 10 cm thick. Bedding surfaces: sharp, but locally erosive, laterally continuous and traceable. Internally sorted conglomeritic dykes up to 0.5 m wide with sharp, straight contacts.</td>
<td>Planar parallel lamination. Low-angle planar to trough cross-lamination. Hummocky cross stratification (HCS). Symmetrical wave ripples.</td>
<td>Bedload deposition by low- to moderate-energy traction currents. Reworking by oscillatory or combined flows in a storm-dominated setting. Rapid deposition accompanied by liquefaction and gravitationally unstable density gradients.</td>
</tr>
<tr>
<td>LF 11: Interbedded massive and thinly laminated siltstone</td>
<td>5.2 m thick Alternating, fine- to coarse-grained siltstone with mudstone and coarse-grained sandstone interbeds. Siltstone beds: 10-50 cm thick, laminae: 1-4 mm thick. Bedding surfaces: sharp, but locally erosive, laterally continuous and traceable.</td>
<td>Massive. Planar parallel lamination. Sand balls of well-sorted, coarse-grained sandstone up to 25 cm in diameter. Ball and pillow structures, 10 cm in diameter, and internally concentric.</td>
<td>Deposition by suspension fall-out of fines and bedload sedimentation by low-density turbidity currents (underflows) mainly under low-energy conditions. Where interbedded with mudstone and coarse-grained sandstone, the lithofacies indicates a combination of suspension and bedload sedimentation under highly fluctuating flow energy conditions driven by storms. Episodic, contemporaneous fault activity.</td>
</tr>
<tr>
<td>LF 12: Mudstone</td>
<td>1 m thick 10-13 cm thick mudstone beds with mm-thick siltstone and very fine-grained sandstone laminae. Lower and upper contacts: planar sharp to wavy erosive.</td>
<td>Massive to slightly fissaile. Lenticular bedding with connected sandstone ripples 2 cm high and 5-7 cm long. Isolated, 2-3 cm sandstone lenses in mudstone. Alternating, 1-5 cm thick beds of mudstone and fine- to coarse-grained rippled sandstone. Internally cross-laminated, symmetrical wave ripples on tops of mudstone layers: amplitudes of 1-2 cm, wavelengths of 4-5 cm. Climbing ripple lamination. Polygenial, 1-3 cm wide cracks.</td>
<td>Represents suspension deposition in calm, low-energy conditions, interrupted by tidal currents and bedload sedimentation. Possible deposition by alternating storm-induced waves and currents and background sedimentation of fines during fair-weather conditions and low siliciclastic supply. Possible interruption of carbonate precipitation by rapid deposition of mud supplied by turbidity or storm currents.</td>
</tr>
<tr>
<td>LF 13: Thickly bedded carbonate</td>
<td>1.8 m thick Thickly bedded and coarsely crystallized light grey carbonate. Beds: 5-20 cm thick. Bed contacts: sharp, non-erosive, characterized by 2-4 cm thick mudstone.</td>
<td>Massive. Local parallel bedding. Symmetrical wave ripples: amplitudes of 4-5 cm, wavelengths of 4 cm Mudstone drapes between layers. Stylolites.</td>
<td>Carbonate precipitation from a warm, supersaturated aqueous solution facilitated by high evaporation rates and low siliciclastic supply. Periods of suspension fall-out of fines. Waning oscillatory flows were the most dominant physical processes during sedimentation. Possible interruption of carbonate precipitation by rapid deposition of mud supplied by turbidity or storm currents.</td>
</tr>
<tr>
<td>LF 14: Rusty carbonate</td>
<td>0.6 m thick Mainly calcareous beds. Weathers rusty orange to reddish brown. Laterally continuous, minimal variation in thickness. Basal and upper contacts: sharp, straight to wavy.</td>
<td>Breccia. Slump structures. Distorted bedding. Poorly preserved stromatolites.</td>
<td>Precipitation of carbonates during calm, warm periods characterized by minimal siliciclastic input and physical processes. Epidodic wind-generated waves and storm activities.</td>
</tr>
<tr>
<td>Lithofacies</td>
<td>Lithology</td>
<td>Sedimentary structures</td>
<td>Depositional processes</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td><strong>LF 15: Stromatolitic carbonate</strong></td>
<td>6 m thick. Dolostone and limestone beds up to 0.5 m thick. Local interbeds of mudstone and siltstone few cm thick</td>
<td>Stratiform and columnar stromatolites. Stratiform beds: 6-45 cm thick, contain very thinly laminated stromatolites; stromatolite laminae: 1-5 mm thick, laterally traceable. Columnar forms: 5 cm wide and 10-15 cm long, discrete and laterally linked hemispheroids; mound-like masses of algal laminated sediments 5 cm thick, 20 cm wide. Birdseye structures are isolated, spherical to elongate voids, 1-3 mm, aligned parallel to bedding planes. Fenestral fabrics: slightly undulating to laminoid, 2-8 cm long, 1-2 cm high, up to 3 cm wide; concordant to bedding planes. Planar and wavy lamination. Small-scale cross-lamination.</td>
<td><em>In situ</em> precipitation of carbonate minerals under quiet, warm and shallow conditions with negligible silicilastic supply. Interrupted by sporadic suspension fallout and bedload sedimentation processes.</td>
</tr>
<tr>
<td><strong>LF 16: Intraformational conglomerate</strong></td>
<td>0.5-1 m thick. Clast-to-matrix-supported with subangular to well-rounded rusty calcareous and dolomitic clasts. Clasts are 5 cm long on average, and are flat elongated to ellipsoidal aligned parallel to bedding planes, but are locally vertically arranged, randomly distributed, inversely graded, or imbricated. Many clasts are internally divided. Matrix ranges from light calcareous to dark argillaceous. Bedding contacts are sharp erosive to highly irregular. Pinches out and swells locally.</td>
<td>Rare faint planar and cross-lamination. Local inverse grading.</td>
<td>Deposited by viscous to diluted subaqueous debris flows on a steep unstable depositional slope. Affected by tectonically unstable conditions with frequent disturbances during or shortly after deposition. Storm-induced erosion and redeposition of newly deposited or partly lithified sediment.</td>
</tr>
<tr>
<td><strong>LF 17 Intraformational breccias</strong></td>
<td>Approximately 3 m thick. Chaotic. Mostly clast-supported. Very angular, cobble to boulder clasts and blocks (up to 0.6 m in dimension) of rusty weathered, parallel and cross-laminated and bedded dolostone along with subordinate siltstone clasts. Light well-sorted fine-grained sandy matrix.</td>
<td>Normal faults. Sharp truncation of adjacent horizontally bedded units.</td>
<td>Gravity-induced slumping due to oversteepening of the depositional slope. Syn-depositional tectonic instability associated with propagation of active contemporaneous normal faults.</td>
</tr>
</tbody>
</table>
Appendix C: Average major oxide compositions for duplicate samples (n=3) used during XRF analysis of the Espanola Formation samples.

<table>
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<th>Lab Sample ID</th>
<th>Client Sample ID</th>
<th>Analyte</th>
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</table>

DUP= laboratory duplicate
Appendix D: δ\(^{13}\)C and δ\(^{18}\)O compositions obtained for standards and duplicate samples used in the mass spectrometer analysis of carbonate samples of the Espanola Formation.

<table>
<thead>
<tr>
<th>Standards</th>
<th>δ(^{13})C V-PDB (‰)</th>
<th>δ(^{18})O V-SMOW (‰)</th>
<th>δ(^{18})O V-PDB (‰)</th>
<th>Accepted Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supra Pur</td>
<td>-35.13</td>
<td>13.34</td>
<td>-17.04</td>
<td>28/13.20</td>
</tr>
<tr>
<td>Supra Pur</td>
<td>-35.34</td>
<td>13.21</td>
<td>-17.17</td>
<td>28/13.20</td>
</tr>
<tr>
<td>Supra Pur</td>
<td>-35.26</td>
<td>13.37</td>
<td>-17.01</td>
<td>28/13.20</td>
</tr>
<tr>
<td>NBS-19</td>
<td>2.01</td>
<td>28.80</td>
<td>-2.04</td>
<td>1.95/28.6</td>
</tr>
<tr>
<td>NBS-19</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>1.95/28.6</td>
</tr>
<tr>
<td>NBS-19</td>
<td>1.29</td>
<td>28.39</td>
<td>-2.44</td>
<td>1.95/28.6</td>
</tr>
<tr>
<td>NBS-19</td>
<td>1.89</td>
<td>28.60</td>
<td>-2.23</td>
<td>1.95/28.6</td>
</tr>
<tr>
<td>NBS-18</td>
<td>-4.71</td>
<td>7.19</td>
<td>-23.00</td>
<td>-5.0/7.2</td>
</tr>
<tr>
<td>NBS-18</td>
<td>-5.00</td>
<td>7.30</td>
<td>-22.90</td>
<td>-5.0/7.2</td>
</tr>
<tr>
<td>NBS-18</td>
<td>-5.06</td>
<td>7.11</td>
<td>-23.08</td>
<td>-5.0/7.2</td>
</tr>
<tr>
<td>WS-1</td>
<td>0.88</td>
<td>26.67</td>
<td>-4.11</td>
<td>0.76/26.23</td>
</tr>
<tr>
<td>WS-1</td>
<td>0.78</td>
<td>26.40</td>
<td>-4.37</td>
<td>0.76/26.23</td>
</tr>
<tr>
<td>WS-1</td>
<td>0.35</td>
<td>26.39</td>
<td>-4.38</td>
<td>0.76/26.23</td>
</tr>
<tr>
<td>LSVEC</td>
<td>-46.37</td>
<td>4.05</td>
<td>-26.05</td>
<td>-46.6</td>
</tr>
<tr>
<td>LSVEC</td>
<td>-46.83</td>
<td>3.04</td>
<td>-27.03</td>
<td>-46.6</td>
</tr>
<tr>
<td>C-112 (DUP)</td>
<td>-2.19</td>
<td>10.44</td>
<td>-19.85</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

DUP = duplicate; n.r. = not reported
Appendix E: Average Ca, Fe, Mg, Mn, and Sr compositions obtained for duplicate samples and standards used during the aqua-regia ICP-AES analysis of Espanola Formation carbonate samples.

<table>
<thead>
<tr>
<th>Duplicates/Standards</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Sr</th>
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<tbody>
<tr>
<td>C-97 DUP</td>
<td>86483</td>
<td>10310</td>
<td>6629</td>
<td>1093</td>
<td>88</td>
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<tr>
<td>C-117 DUP</td>
<td>199096</td>
<td>10403</td>
<td>4355</td>
<td>1084</td>
<td>130</td>
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<tr>
<td>C-130 DUP</td>
<td>114056</td>
<td>9454</td>
<td>4963</td>
<td>1435</td>
<td>153</td>
</tr>
<tr>
<td>AQR Blank</td>
<td>&lt; 0.01</td>
<td>0.02</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>AQR Blank 3</td>
<td>0.02</td>
<td>0.02</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>AQR Blank</td>
<td>&lt; 0.01</td>
<td>0.02</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>AQR EPA-200.3 0.5 ppm</td>
<td>0.53</td>
<td>0.53</td>
<td>0.55</td>
<td>0.57</td>
<td>0.51</td>
</tr>
<tr>
<td>AQR EPA200.4 1 ppm</td>
<td>1.22</td>
<td>0.98</td>
<td>0.94</td>
<td>1.14</td>
<td>0.99</td>
</tr>
<tr>
<td>AQR EPA200.4 1 ppm</td>
<td>1.23</td>
<td>1.06</td>
<td>1.03</td>
<td>1.14</td>
<td>1.00</td>
</tr>
<tr>
<td>AQR EPA-200.6 5 ppm</td>
<td>5.10</td>
<td>5.14</td>
<td>5.02</td>
<td>5.20</td>
<td>5.07</td>
</tr>
<tr>
<td>AQR EPA-200.6 5 ppm</td>
<td>4.96</td>
<td>4.98</td>
<td>5.02</td>
<td>5.15</td>
<td>4.96</td>
</tr>
<tr>
<td>AQR QCS-5</td>
<td>5.05</td>
<td>4.99</td>
<td>4.65</td>
<td>6.07</td>
<td>5.03</td>
</tr>
</tbody>
</table>

DUP= sample duplicate
# Curriculum Vitae

**Name:** Mansour H. Al-Hashim

**Post-secondary Education and Degrees:**

<table>
<thead>
<tr>
<th>University</th>
<th>Location</th>
<th>Years</th>
<th>Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>King Saud University</td>
<td>Riyadh, Saudi Arabia</td>
<td>1998-2001</td>
<td>B.Sc.</td>
</tr>
<tr>
<td>Kansas State University</td>
<td>Manhattan, Kansas, USA</td>
<td>2004-2009</td>
<td>M.Sc.</td>
</tr>
<tr>
<td>The University of Western Ontario</td>
<td>London, Ontario, Canada</td>
<td>2012-2017</td>
<td>Ph.D.</td>
</tr>
</tbody>
</table>

**Related Work Experience**

<table>
<thead>
<tr>
<th>Position</th>
<th>University</th>
<th>Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teaching Assistant</td>
<td>King Saud University</td>
<td>2002-2004</td>
</tr>
<tr>
<td>Lecturer</td>
<td>King Saud University</td>
<td>2009-2011</td>
</tr>
</tbody>
</table>

**Publications:**
