Investigating the Role of Marine Redox Conditions and Orbital Forcings in an Early Silurian Mass Extinction (Ireviken Event): A Deeper Water Perspective

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INVESTIGATING THE ROLE OF MARINE REDOX CONDITIONS AND ORBITAL FORCINGS IN AN EARLY SILURIAN MASS EXTINCTION (IREVIKEN EVENT):
A DEEPER WATER PERSPECTIVE

By
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A Thesis submitted to the Department of Earth, Ocean and Atmospheric Science in partial fulfillment of the requirements for the degree of Master of Science

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ABSTRACT

The Ireviken carbon isotope excursion (CIE) was a large-magnitude positive shift in δ¹³C values that is recorded in early Silurian (~432 Ma; Llandovery-Wenlock boundary) strata globally. Associated with this CIE is a marine mass extinction, the Ireviken Event (*murchisoni* Event in graptolites), during which approximately 80% of conodont and graptolite fauna went extinct, along with a ~50% reductions in trilobites and brachiopods, as well as a decline in corals, chitinozoans, and acritarchs (organic-walled phytoplankton group). Previous paleoredox studies of carbonate sequences throughout the Ireviken CIE and extinction event intervals have shown evidence for widespread euxinic (anoxic + sulfidic) conditions during this time in the Silurian oceans providing a possible causal mechanism for both of these linked biogeochemical events. This study investigates two localities that preserve deeper marine basinal mudstone/shale sequences to further test this redox-based hypothesis: the Baltic Basin (Latvia) and the Cape Phillips Basin (Bathurst Island, Arctic Canada). A set of local paleoredox proxies for both sites (δ³⁴S_pyr, [Mo, V, Mn], Fe-speciation) are utilized to constrain local marine water column conditions throughout the study interval. Additionally, samples were analyzed from both sections for thallium isotopes (ε²⁰⁵Tl), a global paleoredox proxy for Mn-oxide burial in the oceans. Local paleoredox proxy records (Fe-speciation and [Mn]) indicate both deeper water sections were reducing throughout the Ireviken CIE interval. Pyrite sulfur isotopes from multiple paleocean basins co-vary with previous δ³⁴S_CAS datasets, both records indicate global pyrite burial initiated
at the onset of the Ireviken CIE and continued throughout the peak carbon isotope interval. The new thallium isotope data presented herein suggest the global oceans were more reducing prior to the CIE interval and during the early stages of the marine extinction event, subsequently this interval was followed by a brief oxic event during the rising limb of the CIE and later stages of the extinction event. The thallium isotope data indicate a return to more reducing conditions globally during peak CIE and falling limb values. This study presents new insights and constraints on paleoredox conditions during this interval of the early Silurian suggesting a more complex marine redox history associated with the Ireviken extinction event and CIE. This study also presents a new mathematical model, deriving glacial ice growth from global precipitation, generated from a Milankovitch forcing mechanism which influenced glacial ice sheet growth and 5\textsuperscript{th} order eustatic sea-level fluctuations throughout the Llandovery-Wenlock boundary.
CHAPTER 1

INTRODUCTION

Understanding the mechanisms that generate mass extinction events throughout the Phanerozoic has been a focus for many geochemical investigations over the last three decades. Multiple mass extinctions have occurred throughout Earth’s history and many of these events have direct lithologic and geochemical evidence to suggest the causal mechanisms generating them such as: widespread glaciation, large igneous province (LIP) eruption, meteorite impacts, and marine anoxia. However, the trigger mechanisms for many of these extinction events in the Phanerozoic are still widely debated (i.e., Cretaceous-Paleogene) or unknown due to the lack of direct or proxy evidence in the geologic record. Recently geoscientists have been developing novel geochemical proxies such as, metal isotopes (δ²³⁸U, ε²⁰⁵Tl, δ⁹⁸Mo) and trace element concentrations to combine with traditional stable isotope proxies (δ¹³C, δ³⁴S, δ¹⁸O) to constrain and understand changes in marine oxygen concentrations (i.e., Lu et al., 2018, in press; Scholz, 2018; Owens, 2019). Molecular oxygen is required for a great many multicellular organisms and elemental cycles that affect biological and climatic processes (Anbar and Knoll, 2002).

Throughout the Phanerozoic, oxygen concentrations within the ocean-atmosphere system have fluctuated (Berner et al., 2007; Krause et al., 2018). Oceanic deoxygenation has been regarded as one of several primary causes of mass extinction events (Scholz, 2018; Meyer and Kump, 2008). These O₂ declines have led to multiple ocean anoxic events (OAE’s) within the Mesozoic, as well several that have proposed for the Paleozoic (Jenkyns, 2010; Gill et al., 2011; Owens et al., 2016; Ostrander et al., 2017; Them et al., 2018; Bartlett et al., 2018). Geochemical proxy
evidence has recently indicated that there were major marine oxygen declines associated with 
two major marine extinction events in the Silurian, the Llandovery-Wenlock boundary ‘Ireviken 
Event’ and the mid-Ludfordian ‘Lau Event’ (Bowman et al., 2019; Young et al., 2019).

The Silurian was a geologically brief interval in Earth’s history lasting approximately 25 
million years (McAdams et al., 2019). Life in the Silurian was by in large relegated to marine 
environments where Paleozoic biota and ecosystems were diverse in terms of modes of life 
(planktonic, nektonic, and benthic) and niche space (Sepkoski, 1984). Traditionally, the Silurian 
was thought to be a stable period in Earth’s history with regards to the environment and biota 
(Fischer, 1983; Bassett and Edwards, 1991). However, within the last 20 years, carbon isotope 
and paleontological studies have shown that this is one of the most environmentally volatile 
periods of the Phanerozoic (e.g., Cramer and Saltzman, 2005; Saltzman, 2005; Calner, 2008; 
McAdams et al., 2019; Rose et al., 2019). Many major sea-level oscillations occurred during the 
Silurian, which resulted in alternating carbonate and shale lithofacies within low-latitude shelf 
and epeiric sea settings (e.g., Jeppsson, 1998; Cramer and Saltzman, 2007; Johnson, 2010). At 
least three major (≥ +4 ‰) positive carbon isotope (δ¹³C_<sub>carb</sub>) excursions (CIE’s) are observed 
during the Silurian and are coincident with changes in eustatic sea level and biotic turnover 
events (Saltzman, 2005; Cramer and Saltzman, 2007; Calner, 2008). The Ireviken CIE spans the 
Llandovery-Wenlock boundary (~432 Ma) (Cramer et al., 2015) which has been documented 
from many localities and multiple paleocontinents: Nevada, Oklahoma, Tennessee, Iowa, New 
York, Sweden, Norway, Arctic Canada, Latvia, United Kingdom, Estonia, and Ontario with the
CIE ranging from $+3\%$ to $+5\%$ in magnitude suggesting an increase of organic carbon burial was associated with the Ireviken Event (Cramer et al., 2010).

Previous studies have suggested the Ireviken CIE and extinction event are linked to changes in arid to humid climate-states and changes in ocean circulation patterns, which were caused by changes in sea-level, and expansion/contraction of epeiric seaways in low latitudes leading to an increase in carbon burial in the anoxic deep oceans (Cramer and Saltzman, 2005, 2007). However, this hypothesis does not explain the biotic record of mass extinction nor was there any direct paleoredox evidence to support the inferred changes in marine redox conditions. A recent study from Young et al. (2019) produced some of the first sets of direct redox proxy data to test this hypothesis directly from two carbonate successions where the Ireviken CIE had previously recorded. While their findings do provide the first direct evidence for both local and global increases in marine reducing conditions associated with the Ireviken extinction event and CIE in shallow-water carbonate settings, little is known about the marine redox dynamics recorded within the deeper water shale/mudstone records during this time. This study is the first shale-based multiproxy investigation through Ireviken extinction event and associated CIE from two stratigraphic successions on two separate paleocontinents and ocean basins. A suite of global and local paleoredox proxies ($^{205}\text{Tl}$, [Mo, V, Mn], Fe speciation, $\delta^{34}\text{S}_{\text{pyr}}$) are used to test the hypothesis that widespread oceanic anoxia, and possibly euxinia, was a primary cause of the Ireviken extinction event and led to increased organic carbon burial that resulted in the associated CIE. The study sites analyzed in this work are the Priekule-20 drill core, Latvia from the Baltic Basin and the Twilight Creek outcrop, from Bathurst Island, Canada within the Cape
Phillips Basin. The Ireviken CIE and the extinction event has been previously documented at these sites from two different paleocean basins (Kaljo et al., 1997; Kiipli et al., 2010; Noble et al. 2005, 2012). These datasets will also provide a more comprehensive understanding of the marine redox conditions within these deeper marine environments.
CHAPTER 2

BACKGROUND

2.1. Geologic Setting and Depositional Environments

Both of the study sites were deposited in deep basinal settings on two separate paleocontinents (and palaeohemispheres), adjacent to two different paleocean basins during the Silurian. The Priekule-20 core is located on the southeastern margin of Baltica adjacent to the Rheic ocean and the Twilight Creek section is located on the northwestern margin of Laurentia adjacent to the Panthalassic ocean (Fig. 1). The Priekule-20 drill core was extracted from the southwestern part of modern-day Latvia and represents a deep shelf-basinal depositional facies of the Baltic Basin (Fig. 2; Kiipli et al., 2010). The Priekule-20 drill core has a total thickness of Silurian strata of >450 m and spans in age from Late Ordovician (Katian Stage) through latest Silurian (Pridoli Stage) and is comprised of alternating mudstone and calcareous shale lithologies that have common graptolite fossil occurrences throughout (Kaljo et al., 1997; Ulst, 1979; Kaljo and Nestor, 1990; Kiipli et al., 2010).

In the late Llandovery-early Wenlock interval of the Priekule-20 core (1320 m – 1200 m), stage slices Te3, Te4, Te5, Sh1, Sh2, and Sh3 (sensu Cramer et al., 2011; McAdams et al., 2019) can be placed within the core utilizing detailed graptolite biostratigraphy. The beginning of Telychian 3 stage slice (Te3 - *O. spiralis* graptolite biozone) is between 1320 m – 1315 m based upon the occurrence and last appearance datum (LAD) of *O. spiralis* at 1315 m (Kaljo, personal comm.). The beginning of Telychian 4 stage slice (Te4 – *C. lapworthi* graptolite biozone) is placed between 1315 m – 1307.9 m based upon the LAD of *O. spiralis* at 1315 m and
the FAD of *C. insectus* at 1307.9 m (*C. insectus* is placed at the beginning of Te5 series stage) (Kaljo, personal comm.). The beginning of Telychian 5 stage slice (Te5 – *C. insectus* and *C. centrifugus* graptolite biozone) is placed between 1307.9 m – 1287.2 m based upon the base of *C. insectus* graptolite biozone (1307.9 m) and first appearance datum (FAD) of *C. murchisoni* at 1290.65 m (Kaljo, personal comm.). Sheinwoodian 1 stage slice (Sh1 - *C. murchisoni* and *M. riccartonensis* graptolite biozones) is placed between 1287.5 m and 1265.0 m by (FAD) of *C. murchisoni* at 1287.5 m and lower part of *M. riccartonensis* at ~1280.0 m (Kaljo, personal comm.). The base of Sheinwoodian 2 stage slice (Sh2 - *C. rigidus* and *M. belophorous* graptolite biozones) is placed at ~1280.0 m which includes the remainder of *M. riccartonensis* graptolite biozone and the lower part of *C. rigidus* at 1265.0 m (Cramer et al., 2011). The end of Sh2 is placed at the end of the δ13C_carb excursion at ~1230.0 m (Cramer et al., 2011; McAdams et al., 2019). Sheinwoodian 3 stage slice (Sh3 - *C. rigidus* and *M. belophorous* graptolite biozones) is recorded between ~1230 m – 1200 m by the conclusion of the δ13C_carb excursion to the base of *C. lundgreni* graptolite zone which is not present in this processed portion of the core (Kaljo, personal comm.).

The Twilight Creek section exposes the Cape Phillips Formation (100 km northwest of the modern shelf break) on the northern margin of Bathurst Island, Arctic Canada (Fig. 3). The Cape Phillips Formation was deposited during the Late Ordovician through the early Devonian on the outer margin of northern Laurentia and represents one of the least structurally complicated Silurian successions found in the world (Noble et al., 2005). This section of the Cape Phillips Formation preserves laminated argillaceous lime mudstone interbedded with graptolite-bearing,
calcareous shales that lack bioturbation with only very minor occurrences of brachiopods, cephalopods, ostracods, and trilobites (Noble et al., 2005). The Silurian portion of the Cape Phillips Formation has been interpreted to have been deposited in an open ocean, deep-water setting (Noble et al., 2012).

The lower 90 m of the Twilight Creek section represents strata deposited during the Telychian through Sheinwoodian stages based on detailed graptolite biostratigraphic studies (Noble et al., 2005, 2012). Silurian graptolite biozones allow us to place the following global stage slices within this succession: Te2, Te3, Te4, Te5, Sh1, Sh2, and Sh3. The Telychian 2 stage slice (Te2 – M. crispus graptolite biozone) is placed between 0 m - ~9 m based upon the LAD of M. crispus and the appearance of M. greistonensis. The beginning of Telychian 3 stage slice (Te3 - M. greistonensis graptolite biozone) is placed between ~9 m – ~12 m by the appearance of M. greistonensis and the base of the C. sakmaricus graptolite biozone. The beginning of Telychian 4 stage slice (Te4 - C. sakmaricus graptolite biozone) is placed between ~12 m – 17 m by the appearance of C. sakmaricus and FAD of C. insectus. The beginning of Telychian 5 stage slice (Te5 - C. insectus graptolite zone) is placed between 17 m – 22 m by the LAD of C. insectus and FAD of C. murchisoni. The beginning of Sheinwoodian 1 stage slice (Sh1 - C. murchisoni graptolite biozone) is placed between 22 m - ~25 m by the appearance of C. murchisoni and of C. centrifuges. The beginning of Sheinwoodian 2 stage slice (Sh2 - M. instreenuus and C. kolobus graptolite biozones) is placed between ~25 m - ~57 m by the appearance of M. instreenuus and C. kolobus and conclusion of the δ13C_carb excursion. The beginning of Sheinwoodian 3 stage slice (Sh3 - C. perimi and M. opimus graptolite biozones) is placed between ~57 m - ~90 m by the
return to a post-$\delta^{13}\text{C}_{\text{carb}}$ excursion baseline and appearance of $C. \text{perimi}$ and $M. \text{opimus}$ (Noble et al., 2005; 2012).

2.2. Llandovery-Wenlock Boundary Biotic Records, Sea Level, and Climate

Global paleontological studies spanning the Llandovery–Wenlock boundary record a large decrease in abundance and diversity of marine biota preserved in the carbonate facies (Calner, 2008). Approximately 80% of conodont fauna during this time interval went extinct, known as the ‘Ireviken event’ (Aldridge et al., 1993; Jeppsson 1997; Munnecke et al., 2003). The conodont extinction has been divided into 10 datum levels (extinction steps) that allow strata containing them to be divided into eight conodont biozones indicating that the Ireviken event was a ‘stepwise’ extinction (Munnecke et al., 2003; Cramer et al., 2010). Coinciding with the Ireviken event, was the ‘Murchisoni Event’ event recorded within shale facies and is marked by the first appearance datum (FAD) of $\text{Cyrto} graptus murchisoni$ graptolite, which defines the base of the Wenlock Series, and marks an interval where 80% of graptolite species went extinct (Melchin et al., 1998; Munnecke et al., 2003; Cramer et al., 2010). Globally, graptolite species richness dropped by 50% matching the intensity of the Late Ordovician Mass Extinction (LOME) event (Cooper et al., 2014; Crampton et al., 2016). Fauna such as trilobites, brachiopods, chitinozoans, acritarchs, and scolecodonts were also observed to decrease in abundance and diversity by 50% during this time (Jeppsson, 1990; Munnecke et al., 2003).

Sea level was low during the late Llandovery due to a period of glacial advance over parts of Gondwana (Díaz-Martínez and Grahn, 2007) (Fig. 1), however, global sea level began to
rise into the early Wenlock as ice sheets melted and the climate began to warm (Cramer and Saltzman, 2007). Jeppsson (1990) observed a relationship between lithofacies alternations between clean carbonates and marls/black shales which appear to alternate in cycles throughout the Silurian. These major lithofacies alternations are associated with large-scale conodont faunal turnover events that are now observed globally in the Silurian (Jeppsson, 1998). As reef and platform carbonates expanded they coincided with low diversity and abundance of conodont fauna (Jeppsson, 1990). However, as lithofacies such as marls and lime mudstone were deposited conodont fauna were observed in greater abundance and diversity (Jeppsson, 1998). The change between these marine oceanographic states, represented by changes in lithology, and biodiversity declines in conodont taxa indicate the transition to marine extinction events in conodonts and other shallow-water marine taxa (e.g., Munnecke et al., 2003). To explain these alternations representing extinction events in the Silurian, Jeppsson (1990) developed a model for global oceanic cycles. It was proposed that cooler high latitude and humid low latitude climate episodes (P-episode) interchange with warmer high latitude and dryer low latitude episodes (S-episode) to explain fluctuations in the rate of clay deposition and carbonate production on continental shelves (Jeppsson, 1990). However, due to secular changes in carbon and oxygen isotopes measured in brachiopods representing freshwater input rather than paleoclimate, Bickert et al. (1997) proposed an alternate model that invoked humid- and arid-climate states to account for increased and decreased continental runoff/weathering which influences nutrient influx into the ocean as well as marl deposition. The proposed increase in freshwater influx and nutrients changed circulation patterns which should have influenced carbonate deposition as well.
Ultimately, changes in local-regional salinity were thought to be the major driver of oxygen isotope records across strata deposited on a shallow water Silurian platform on Gotland (Bickert et al., 1997).

2.3. Geochemical Proxy Background

2.3.1. Stable carbon and sulfur isotopes

Biomass that is photosynthetically produced in the surface oceans is isotopically light, being enriched in $^{12}$C, therefore marine organic matter typically has a negative $\delta^{13}$C$_{org}$ value (-25‰ to -30‰) (e.g., Hayes et al., 1999). $\delta^{13}$C values of marine carbonates ($\delta^{13}$C$_{carb}$) passively record stable isotopic values of dissolved inorganic carbon ($\delta^{13}$C$_{DIC}$) which is thought to be globally homogenous on geologic time scales due to the residence time of carbon ($10^5$ yr) being considerably longer than the interocean mixing time ($10^3$ yr). However, $\delta^{13}$C$_{org}$ values are mainly a local proxy because factors such as variations in biological source of preserved marine organic matter, changes in phytoplankton cell geometries, and changes in phytoplankton growth rates have been demonstrated in modern marine environments to significantly influence bulk $\delta^{13}$C$_{org}$ values (e.g., Francois et al., 1993; Hinga et al., 1994; Joachimski et al., 2002; Young et al., 2008). Positive $\delta^{13}$C excursions (i.e., positive CIEs) recorded within sedimentary strata have traditionally been attributed to either increased burial of organic matter and/or preservation of organic matter under reducing marine conditions. Alternatively, due to increases in carbonate weathering associated with sea-level lowstands and exposed carbonate platforms (Kump and
Arthur, 1999; Kump et al., 1999). Carbon isotopes are measured in delta notation ($\delta^{13}C$) with units of per-mil ($\%$) which is defined as:

$$\delta^{13}C = \left[ \left( \frac{^{13}C}{^{12}C_{\text{sample}}} \right) - \left( \frac{^{13}C}{^{12}C_{\text{standard}}} \right) \right] / \left( \frac{^{13}C}{^{12}C_{\text{standard}}} \right) \times 10^3$$

Microbial sulfate reduction (MSR), sulfate oxidation, and sulfur disproportionation are the three significant metabolic processes that impart fractionations upon the stable isotopes of sulfur (e.g., Fike et al., 2015). Hydrogen sulfide ($H_2S$) produced from MSR is isotopically depleted with respect to $^{34}S$, by nearly 70 $\%$ in natural environments (Frye et al., 1991; Sim et al., 2011; Gomes and Hurtgen, 2015). Fractionation of sulfur occurs during microbial sulfate reduction, where the product $H_2S$ is enriched in $^{32}S$ relative to $^{34}S$ resulting in sedimentary pyrite with an isotopically light $\delta^{34}S$ signature (Habicht et al., 1998). Pyrite formation is related to the abundance of hydrogen sulfide ($H_2S$) metabolically produced and the availability of ferric iron ($Fe^{2+}$) in the water column and ocean sediments (e.g., Fike et al., 2015). MSR primarily occurs within the sediments, however when MSR occurs in the water column, the generated sulfide becomes a significant source of biological stress to the local environment as $H_2S$ is toxic to most aerobic organisms (e.g., Vaquer-Sunyer and Duarte, 2010). Sulfur isotopes of sedimentary pyrite ($\delta^{34}S_{\text{pyr}}$) are chiefly used as a local redox proxy because $\delta^{34}S_{\text{pyr}}$ values are dependent upon local water-column redox state, among other local factors such as sulfate concentrations, supply of labial organics, and $Fe^{2+}$ concentrations (Berner, 1985; Lyons, 2009; Fike et al., 2015). Sulfur isotopes are measured in delta notation ($\delta^{34}S$) with units of per-mil ($\%$) which is defined as:

$$\delta^{34}S = \left[ \left( \frac{^{34}S}{^{32}S_{\text{sample}}} \right) - \left( \frac{^{34}S}{^{32}S_{\text{standard}}} \right) \right] / \left( \frac{^{34}S}{^{32}S_{\text{standard}}} \right) \times 10^3$$

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2.3.2. Trace metal geochemistry

Molybdenum, vanadium, and uranium are all conservative tracers in the ocean and are utilized as fingerprint proxies for a variety of reducing aqueous environments and can be utilized as proxies for paleoredox conditions (Algeo and Maynard, 2004; Algeo, 2009; Hardisty et al., 2018; Scholz, 2018). In anoxic conditions, it is generally known that Mo, V, and U are diffused downward in the water column to the seafloor marine sediment by adsorbing onto sinking organic matter (Algeo and Maynard, 2004; Owens et al., 2017; Scholz, 2018). However, studies are still being conducted to further understand the behavior of these trace metals in oxic, anoxic, sub-oxic, and euxinic modern ocean environments (Algeo and Maynard, 2004; Algeo 2009; Scholz, 2018). There are no set standard concentrations of V and U to determine anoxic and euxinic sediments because sedimentation rates vary in different environments, connectivity to the open ocean also varies in different environments, as well as global inventories of trace metals may have varied at different times in Earth history (e.g., Lyons et al., 2009). However, ratios such as Mo/Al, U/Al, V/Al can be implemented to compare the rates of accumulation of these trace metals in the marine sediment (Algeo and Tribovillard, 2009; Scholz, 2018). Comparing ratios of V/Mo and Mo/U as well as other ratios can trace different transitions from ferruginous to sulfidic conditions and vice versa (Scholz, 2018).

Molybdenum (Mo$^{6+}$) in seawater exists as molybdate (MoO$_4^{2-}$) in most seawater concentrations (Algeo and Maynard, 2004). In anoxic conditions MoO$_4^{2-}$ is transferred to the sediment by adsorbing onto sinking organic matter and Mn-hydroxide shuttles (Algeo and Maynard, 2004). Mo$^{6+}$ in molybdate (MoO$_4^{2-}$) can be reduced to Mo$^{5+}$ as MoO$_2^{+}$ through the
sulfate-reducing bacteria decaying organic matter (Algeo and Maynard, 2004). In euxinic environments, Mo is taken up in solid solution by Fe-sulfides reducing Mo$^{6+}$ in molybdate (MoO$_4^{2-}$) to Mo$^{4+}$ in molybdenum sulfide (MoS$_4^{2-}$) (Algeo and Maynard, 2004). If molybdenum concentrations $>$25 ppm are seen in sedimentary rocks, this could be indicative of sediments deposited under a euxinic (anoxic + free hydrogen sulfide) water column, although any enrichments beyond the upper continental crust value of 2ppm of Mo can be due to a variety of factors as discussed above (Algeo, 2009; Lyons et al., 2009; Algeo and Liu, 2020).

Vanadium V$^{5+}$ in oxic seawater primarily exists as vanadate (HVO$_4^{2-}$ and H$_2$VO$_4^-$) (Algeo and Maynard, 2004). In anoxic settings, V$^{5+}$ as vanadate (HVO$_4^{2-}$ and H$_2$VO$_4^-$) reduces to V$^{4+}$ as vanadyl (VO$^{2+}$), hydroxyl species (VO(OH)$_3^-$ or hydroxide (VO(OH)$_2^-$) which is facilitated by the abundance of fluvic and humic acids (Algeo and Maynard, 2004). Vanadium species containing V$^{4+}$ can be incorporated into the sediment by adsorption surface processes or the formation of organometallic ligands. In more reducing settings (euxinic settings), V$^{4+}$ in vanadyl (VO$^{2+}$) or hydroxide species reduces to V$^{3+}$ as vanadium oxide (V$_2$O$_3$) or hydroxide (V(OH)$_3$) due to the presence of H$_2$S (Algeo and Maynard, 2004).

Manganese concentrations [Mn] are also used as a local redox proxy to discern anoxic vs. oxic conditions (Algeo and Maynard, 2004; Owens et al., 2017; Young et al., 2020). In oxic environments, Mn predominantly exists as Mn(III) or Mn(IV) within hydroxides or oxides (MnO$_2$) which is precipitated in the water column or sediment porewaters and buried in particulate form (Algeo and Maynard, 2004; Young et al., 2020). In anoxic environments, Mn diffuses upward and out of the sediment and is dissolved in the water column (Algeo and
Maynard, 2004; Young et al., 2020). Due to the nature of Mn diffusing downwards into the sediment in oxic environments, marine sediments containing Mn concentrations above 850 ppm are considered to have been deposited in highly concentrated oxic environments (Turgeon and Brumsack, 2006).

2.3.3. Iron geochemistry

Iron speciation within Earth’s modern and ancient sediments have shown to be a faithful indicator of local water column and sediment porewater redox conditions (Raisewell et al., 2018; Hardisty et al., 2019). Observing the abundance of concentrations of iron species in the sediment can indicate the extent to which iron is converted to pyrite or other minerals (Raisewell et al., 2018). In anoxic settings there is more highly reactive iron (Fe$_{HR}$) within the water column due to iron reacting to form a suite of sedimentary minerals, including iron sulfides over geologically very short timescales (Raisewell et al., 2018). Fe$_{HR}$ is defined by the sum of Fe present in iron carbonate minerals such as siderite (Fe$_{carb}$), iron oxide minerals such as hematite (Fe$_{ox}$), magnetite (Fe$_{mag}$), and pyrite (Fe$_{py}$): 

$$ Fe_{HR} = Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py} $$

Iron speciation can indicate a local anoxic water column when the highly reactive iron (Fe$_{HR}$) to total iron (Fe$_{T}$) ratio of a sediment sample greater than 0.38, and possibly anoxic between 0.22 to 0.38 (Raisewell et al., 2018). Sediments that have Fe$_{HR}$/Fe$_{T}$ values that fall below 0.22 indicate oxic bottom water conditions. The ability for iron to form pyrite relies heavily on the presence of free hydrogen sulfide within the water column and available iron in the local environment.
(Raisewell et al., 2018). In euxinic settings, the sulfide within the water column and/or sediment pore waters reacts with iron rapidly to form pyrite, therefore, increasing the amount of pyrite associated iron (Fe$_{py}$) in sediments (Raisewell et al., 2018). Euxinic bottom water conditions are inferred from ratios of pyrite iron (Fe$_{py}$) to highly reactive iron (Fe$_{HR}$) that are greater than 0.78, and possibly euxinic between 0.7 to 0.78 (Raisewell et al., 2018; Scholz, 2018).

2.3.4. Thallium isotopes

Measurements of thallium isotopes in marine sediments can be used as records of global changes in Mn-oxide burial if 1) the local marine water column redox conditions in organic-rich sediments are shown to be anoxic to euxinic (based upon Fe speciation and/or trace metal analyses), and 2) if shale/mudstone samples were deposited in a marine environment that is well-connected to the open ocean to ensure global signatures of thallium isotopes are recorded (Owens et al., 2017; Owens, 2019). Thallium isotopic signatures in the geologic record are interpreted as a global ocean proxy for Mn-oxide burial on timescales of a few million years or less (Owens et al., 2017; Ostrander et al., 2017; Them et al., 2018; Bowman et al., 2019; Ostrander et al., 2019; Fan et al., 2020). Since the residence time of thallium is ~18.5 kyr, thallium isotopes are interpreted to be a global proxy due to this residence time being longer than the interocean mixing time of 1-2 kyr (Owens et al., 2017, and references therein). There are two output fluxes which incorporate a fractionation of thallium isotopes in the modern ocean which are 1) uptake of thallium to the sediment adsorption onto Mn-oxides (68% of total Tl burial) and 2) uptake of thallium during alteration of ocean crust (32% of total Tl burial) (Owens et al.,
Thallium isotopic fractionation associated with Mn-oxides ranges from +6 to +12 with an average of +10 whereas the thallium isotopic fractionation associated with ocean crust alteration ranges from -6 to -12 with an average of -7 (Owens et al., 2019 and references therein).

In oxic marine water conditions, Mn-oxides are the first precipitated and buried minerals in sediments based on electron potential (Owens et al., 2017). Fractionation occurs as the heavier (more positive) thallium isotope adsorbs onto the Mn-oxides entering the sediment leaving the water column with the light Tl isotope (Owens et al., 2017). However, during periods of expanded anoxic conditions, it has been proposed that fewer Mn-oxides are preserved and buried globally driving the oceanic thallium isotopic signatures recorded in reducing sediments isotopically heavier (Owens et al., 2017). Therefore, if the global oceans during the Ireviken Event were deoxygenated and the fraction of seafloor anoxia expanded, then a shift towards heavier thallium isotopic values would be predicted in locally reducing sediments spanning the Llandovery-Wenlock boundary interval. Thallium isotopes are measured in epsilon notation ($\epsilon^{205}$Tl) with measured in epsilon units ($\epsilon^{205}$Tl) which is defined as:

$$\epsilon^{205}$Tl = \left(\frac{^{205}$Tl_{sample}}{^{205}$Tl_{NIST997}}\right) \left(\frac{^{205}$Tl_{NIST997}}{^{203}$Tl_{NIST997}}\right) * 10^4$$
CHAPTER 3

METHODS

3.1 Sample Collection and Preparations

The early-middle Silurian portion (~1320 m – 1210 m) of the Priekule-20 drill core (Latvia) was sampled at Tallinn University of Technology, where it is archived at the Institute of Geology. Approximately 78 shale/mudstone samples collected at ~1 m intervals were analyzed for geochemistry. Samples from the Twilight Creek outcrop section were collected and provided by Dr. Paula Noble at the University of Nevada-Reno. Approximately 20 samples were collected at 2 m to 4 m intervals and were previously analyzed for carbon isotopes and TOC wt.% by Noble et al. (2005, 2012). Drill core samples from the Priekule-20 core, Latvia were sonicated in super-pure water (deionized and distilled; 18 MΩ) to remove surficial organic contaminants and drilling muds and then dried, and finally powdered using an agate mortar and pestle. Twilight Creek outcrop samples from Arctic Canada were first trimmed with a diamond-bladed rock saw to remove any weathered surfaces and large recrystallized veins. Then the cut and washed outcrop samples were sonicated in super-pure water to remove any surficial organic contaminants and then dried, and subsequently powdered using an agate mortar and pestle.

3.2. Geochemical Methods

3.2.1. Carbon and sulfur isotopes

For δ^{13}C_{carb} approximately 5 mg of powder were micro-drilled from shale samples from both localities. Then about ~2500 µg of powder was weighed from shale samples using a
microbalance and then placed in an oven overnight at 75°C to remove any excess carbon or organic material that could contaminate the samples. The powdered samples were then reacted with a few ml of H$_3$PO$_4$ for 24 hours at 25°C and CO$_2$ gas obtained from the dissolution of the powdered samples and were measured for stable isotopic analysis using a ThermoFinnigan Delta Plus XP stable isotope mass spectrometer coupled to a Gas Bench II Autocarbonate device at the National High Magnetic Field Laboratory at Florida State University (NHMFL-FSU). The following internal standards were used for calibration of $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O and reported as permil (‰) using the V-PDB (Vienna-Pee Dee Belemnite) scale: ROY-CC (+0.67‰, -12.02‰), MB-CC (-10.5‰, -3.5‰), and PDA (-1.3‰, -5.34‰).

To process samples for $\delta^{13}$C$_{\text{org}}$ ~2 g – 3 g of powder were weighed and dissolved in HCl to remove excess carbonate carbon material. The remaining residue material were rinsed with superpure water (deionized, 18 MΩ) and centrifuged to remove excess acids and then dried overnight in an oven at 70 °C. The dried residues were then homogenized, weighed into tin cups, and analyzed for stable isotopic analysis via combustion at 1020°C using a Carlo Erba Elemental Analyzer coupled to a ThermoFinnigan Delta Plus XP mass spectrometer through a Conflo-III device at the NHMFL-FSU. Internal FSU standards: Acetanilide (-29.2‰), Urea-2 (-8.13‰), and WYSTD (-12.7‰) were calibrated against IAEA standards and are used for calibration and precision of $\delta^{13}$C$_{\text{org}}$ sample data. Ranges for $\delta^{13}$C$_{\text{org}}$ and %C precision are one standard deviation (1σ) between ± 0.2‰ and ± 7‰, respectively. Total organic carbon (TOC) was calculated from the percent carbon (wt. % C) of insoluble material in a sample, determined by the comparison of
voltages for the ion beam intensities of masses 44, 45, and 46 g/mol of CO$_2^+$ between our unknown samples and the known wt.% C of the standard Acetanilide.

The chromium reduction method was utilized to extract sedimentary pyrite following procedures outlined in Bruchert and Pratt (1996) and Canfield et al. (1986). Approximately 0.5 g – 3 g of powdered sample was reacted with a 70:30 mixture of 12 M HCl and 1 M chromium chloride (CrCl$_3$·6H$_2$O) in a purged flask. Flowing N$_2$ gas then transported formed H$_2$S from broken down pyrite (Fe$_2$S) through a 0.1 M Na-citrate solution and into a 0.1 M silver nitrate (AgNO$_3$) solution. H$_2$S then reacted with AgNO$_3$ to form a silver sulfide precipitate (Ag$_2$S). Solid Ag$_2$S precipitate was then filtered, rinsed, and dried onto a 0.22 µm quartz-fiber filter. The dried precipitate was weighed for a [$S_{pyr}$] and [Fe$_{pyr}$] determinations using gravimetry and assuming stoichiometric ratios of 1 FeS$_2$ : 2 Ag$_2$S. $\delta^{34}$S$_{pyr}$ analyses were determined by first homogenizing sample Ag$_2$S powders, then weighing them into tin cups with V$_2$O$_5$ accelerator, and combusting them at 1000°C using a Thermo Isolink Elemental Analyzer coupled to Thermo Delta V IRMS via a Conflo-IV interface at the NHMFL-FSU. Sulfur isotope analysis ($\delta^{34}$S) was reported in delta notation using units of per-mil (‰) relative to VCD-T (Vienna Canyon Diablo Troilite). All samples processed for $\delta^{34}$S were calibrated relative to the standards EMR-CP (+0.9‰), PQM2 (-16‰), ERE (-4.7‰), PQB-D (+40.5‰) and SWP (+20.3‰), precisions are one standard deviation (1σ) between ± 0.2‰.
3.2.2 Trace metal geochemistry and iron speciation

Methods for extracting Molybdenum and Vanadium out of carbonates and black shale samples were adapted from Emerson and Huested (1991) and Hardisty et al. (2018). Approximately 50 mg - 100 mg of powdered sample were placed in quartz vials in an Anton Paar high pressure Asher to remove all organic matter. Sample powders were then weighed out and dissolved in Savillex Teflon beakers using trace metal grade HCl, HNO₃, and HF and heated to ~130 – 160°C for 24–48 hours and then dried down before adding the next round of acids (Hardisty et al., 2018). Trace metal grade H₂O₂ was then added to the sample beakers to oxidize any remaining organic matter in the samples. Once samples were completely dissolved, samples were then dried down and re-dissolved in 2% HNO₃. Trace metal contents (Mo and V) from the undissolved residues were analyzed by an Agilent 7500cs quadrupole inductively coupled plasma mass spectrometer, ICP-MS, at the NHMFL-FSU. To calibrate the trace metal concentrations (ppm) within all unknown samples, USGS geostandards SDO-1 and SGR-1 were also completely dissolved and analyzed for their trace metal contents. If measured SDO-1 and SGR-1 standard trace metal concentrations are within ~10% error of the reported USGS SDO-1 and SGR-1 concentrations, then sample trace metal concentrations were assumed to be credible for analysis and interpretation.

Iron speciation determination on all samples were carried out using methods outlined within Raisewell et al. (2018). Approximately ~100–200 mg of powdered sample was weighed for Fe speciation analysis and placed in a 15 ml centrifuge tube. Samples underwent three separate extractions to obtain Fe associated with carbonate phases, oxide phases, and magnetite
phases. First, 10 ml of 1 M sodium acetate at a pH of 4.5 were added to the samples, and then the sample + solution was placed on a shaker table for 24–48 hours to ensure complete reaction with all sample powder surfaces. Afterward, ~10 ml of centrifuged and reacted reagent was pipetted from samples into new centrifuge tubes and set aside for Fe_{carb} analysis. Then, the remaining original sample was rinsed with super-pure water to remove any previous 1 M sodium acetate reagent. Second, ~10 ml of sodium dithionate at a pH of 4.8 was added to the original sample and then placed on a shaker table for 2 hours. Next, ~10 ml of centrifuged and reacted reagent was pipetted from the original sample and set aside for Fe_{ox} analysis. Then, the remaining original sample was rinsed with superpure water to remove any previous sodium dithionite reagent. Third, 10 ml of ammonium oxalate at a pH of 3.2 was added to the original sample and placed on a shaker table for 6 hours to ensure complete reaction. Afterward, ~10 ml of centrifuged and reacted reagent was pipetted from the original sample and set aside for Fe_{mag} analysis. Total iron (Fe_{T}) contents were determined using the methods described for above trace metal concentrations following standard methods (e.g., Scholz, 2018). Concentrations of Fe (ppm) were determined by an Agilent 7500cs mass spectrometer at the National High Magnetic Field Laboratory. International accepted standard reference samples (SDO-1, SCO-2, and SGR-1) were dissolved simultaneously and were all within the accepted analytical ranges for all reported elements. Results were reported in parts per million (ppm) and analytical precision for standard trace metal concentrations are within ± 5% or better for trace metal species Mo, V, and Mn. Subsequent blanks were measured below the detection limit. The Priekule-20 core trace
metal concentrations and total iron for all unknown samples were scaled by a 33% increase to match with the SDO-1 standard concentrations for Fe and Al.

3.2.3. Thallium isotopes

Thallium was extracted and thallium stable isotopes were analyzed on samples following procedures outlined in Owens et al. (2017). Powdered samples were dissolved using a two-step procedure to obtain complete dissolution. First, 50–100 mg of powdered sediment were treated with 2 M HNO₃ and heated at ~130°C for approximately 12 hours to separate the detrital and authigenic fraction of thallium. Then three cycles of centrifugation, pipetting off the supernatant, and rinsing in super-pure water were conducted to separate the two sample fractions of thallium. After separation of both thallium fractions, 1 ml of HCl was added to the supernatant fraction to dissolve any residual organic matter. Then brominated water was added to the supernatant fraction to be prepared for ion exchange separation. Thallium isotopes were determined by a Thermo Neptune MC-ICP-MS at the NHMFL-FSU. To reconstruct ancient seawater thallium isotope records from marine strata, local water column redox conditions need to be independently established as reducing in order to reconstruct global Mn-oxide burial.
CHAPTER 4

RESULTS

4.1. Baltic Basin – Priekule-20 Core, Latvia

Late Llandovery through early Wenlock geochemical data generated from marlstones and shales within the Priekule-20 core span from 1300 m -1260 m interval (Figure 4). Seventy-six samples were processed for carbonate carbon isotopes. Lower baseline $\delta^{13}$C$_{\text{carb}}$ values are ~0‰ within Te3 (O. spiralis biozone), Te4 (C. lapworthi biozone), and Te5 (C. insectus - C. centrifugus biozones) stage slices. The rising limb of the positive $\delta^{13}$C$_{\text{carb}}$ excursion occurs within Sh1 (C. murchisoni - M. riccartonensis biozones) stage slice. Peak $\delta^{13}$C$_{\text{carb}}$ values of +3‰ are observed at the end of Sh1 (C. murchisoni - M. riccartonensis biozones) through lower Sh2 stage slices (Figure 4A). The falling limb of the $\delta^{13}$C$_{\text{carb}}$ excursion occurs within Sh2 (C. rigidus - M. belophorous biozones) stage slice. Upper baseline $\delta^{13}$C$_{\text{carb}}$ values are ~ −1‰ within Sh3 (C. rigidus - M. belophorous biozones) stage slice.

Organic carbon isotopes (seventy-eight total samples analyzed) show a positive excursion within the Priekule-20 core (Figure 4A). Lower baseline $\delta^{13}$C$_{\text{org}}$ values are ~−29‰ within Te3 (O. spiralis biozone), Te4 (C. lapworthi biozone), and Te5 (C. insectus - C. centrifugus biozones) stage slices. The rising limb of the positive $\delta^{13}$C$_{\text{org}}$ excursion occurs within Sh1 (C. murchisoni - M. riccartonensis biozones) stage slice. Peak $\delta^{13}$C$_{\text{org}}$ values are ~−26‰ appear at the end of Sh1 (C. murchisoni - M. riccartonensis biozones) stage slice (Figure 4A). The falling limb of the $\delta^{13}$C$_{\text{org}}$ excursion occurs within middle-upper Sh2 (C. rigidus - M. belophorous biozones).
biozones) stage slice. Upper baseline δ^{13}C_{org} values are ~31‰ within Sh3 (C. rigidus - M. belophorous biozones) stage slice.

Pyrite sulfur isotopes (thirty-eight total samples analyzed) also show a positive excursion coinciding with the δ^{13}C_{carb} and δ^{13}C_{org} excursions (Figure 4B). Lower baseline δ^{34}S_{pyr} values are ~33‰ within Te3 (O. spiralis biozone), Te4 (C. lapworthi biozone), and Te5 (C. insectus - C. centrifugus biozones) stage slices. The rising limb of the positive δ^{34}S_{pyr} excursion initiates within Te5 (C. insectus - C. centrifugus biozones) and Sh1 (C. murchisoni and M. riccartonensis biozones) stage slices. Peak δ^{34}S_{pyr} values are ~10‰ within Sh2 (C. rigidus and M. belophorous biozones) stage slice occurring after the δ^{13}C_{carb} and δ^{13}C_{org} peak excursion values. The falling limb of the δ^{34}S_{pyr} excursion occurs within the upper part of Sh2 (C. rigidus - M. belophorous biozones) and lower part of Sh3 (C. rigidus - M. belophorous biozones) stage slices. Upper baseline δ^{34}S_{pyr} values range between -18‰ to -15‰ within Sh3 (C. rigidus - M. belophorous biozones) stage slice.

Twenty-three samples were analyzed for ε^{205}Tl, and a negative thallium isotope excursion is observed during the rising limb and initial peak δ^{13}C_{carb} and δ^{13}C_{org} values of the Ireviken CIE (Figure 4D). Lower baseline ε^{205}Tl values are between -3.0 to -2.8 within Te3 (O. spiralis biozone) stage slice. In the overlying Te4 through lower Sh1 stage slices (C. lapworthi–C. murchisoni biozones) ε^{205}Tl values shift slightly lighter to -3.5 to -3.2. Within the upper Sh1 stage slice (M. riccartonensis biozone) ε^{205}Tl values shift sharply negative and fall to values of ~-5.2 within the lowermost part of Sh2 stage slice (C. rigidus - M. belophorous biozones). Subsequently, Tl isotopes begin to rise within the lower-middle Sh2 stage slice reaching ε^{205}Tl
values as heavy as ~ -3.6. Following this interval, Tl isotope values decline again to ~ -4.0 to -4.5 within the upper Sh2 and Sh3 stage slices.

Thirty-nine samples were processed for Fe speciation showing shifts in oxic, anoxic, and euxinic conditions (Figure 5). The following Fe\textsubscript{py}/Fe\textsubscript{HR} results are mentioned in stratigraphic order (Figure 5A). Three Fe\textsubscript{py}/Fe\textsubscript{HR} values are <0.7 between ~0.05 and ~0.62 at the lowermost part of the core within Te3 (O. spiralis biozone) stage slice. One Fe\textsubscript{py}/Fe\textsubscript{HR} value is recorded >0.7 at ~0.72 within Te4 (C. lapworthi biozone) stage slice. Three Fe\textsubscript{py}/Fe\textsubscript{HR} values are between ~0.49 and ~0.66 within Te4 (C. lapworthi biozone) and Te5 (C. insectus - C. centrifugus biozones) stage slices. Two Fe\textsubscript{py}/Fe\textsubscript{HR} values are recorded >0.7 between ~0.70 and ~0.71 within Te5 (C. insectus - C. centrifugus biozones) stage slice. Seven Fe\textsubscript{py}/Fe\textsubscript{HR} values are recorded <0.7 between ~0.53 to ~0.69 within Te4 (C. lapworthi biozone), Te5 (C. insectus - C. centrifugus biozones), and Sh1 (C. murchisoni - M. riccartonensis biozones) stage slices. Fe\textsubscript{py}/Fe\textsubscript{HR} values from Sh1 through Sh3 (C. murchisoni - M. belophorous biozones) stage slices are generally all >0.7 with a few outliers (seven samples) that are < 0.7 within the Sh2 stage slice.

In the Priekule-20 core, Fe\textsubscript{mag}/Fe\textsubscript{HR} ratios were also observed in stratigraphic order (Figure 5B). Most of the Fe\textsubscript{mag}/Fe\textsubscript{HR} data were plotted between values of 0.04 - 0.05 throughout the entire core. However, there were several anomalies including data points recorded at: 0.40 within Te3 (O. spiralis biozone), 0.19 within Te3-Te4 (O. spiralis and C. lapworthi biozones), 0.27 within Te5 (C. insectus - C. centrifugus biozones), 0.09 and 0.12 within Sh2 (C. rigidus - M. belophorous biozones), 0.07 within Sh2 (C. rigidus - M. belophorous biozones), and 0.08 within Sh3 (C. rigidus - M. belophorous biozones) stage slices (Figure 5B).
The following Fe\textsubscript{HR}/Fe\textsubscript{T} results are mentioned in stratigraphic order (Figure 5C). Fifteen samples have Fe\textsubscript{HR}/Fe\textsubscript{T} ratios that are <0.22 fluctuating between ~0.04 - ~0.20 at the lowermost part of the core within the Te3 (\textit{O. spiralis} biozone), Te4 (\textit{C. lapworthi} biozone), Te5 (\textit{C. insectus} - \textit{C. centrifugus} biozones), and Sh1 (\textit{C. murchisoni} - \textit{M. riccartonensis} biozones). Fe\textsubscript{HR}/Fe\textsubscript{T} ratios within the Sh1 through Sh3 (\textit{C. murchisoni} - \textit{M. belophorous} biozones ) stage slices are for the most part >0.22 fluctuating between ~0.22 - ~0.30, with six samples that fall below 0.22 within the upper Sh2 and Sh3 stage slices. All of the Fe\textsubscript{T}/Al values plot over the Average Phanerozoic shale value (~0.53 ± 0.11) fluctuating between ~0.64 - ~0.89 (Figure 5D).

Thirty-nine samples were processed for vanadium concentrations [V, Mo] and are reported in stratigraphic order (Figure 5E-F). Vanadium concentrations within stage slices Te3 through the lower part of Te5 (\textit{O. spiralis} - \textit{C. insectus} biozones) range from 75 to 200 ppm, with only one sample plotting below the average crustal value of vanadium (~100 ppm). Vanadium concentrations fall through Te5 through lower Sh2 stage slices (\textit{C. centrifugus}-\textit{C. rigidus} biozones) ranging from ~ 111 ppm to ~ 50 ppm. Within the middle of Sh2 stage slice [V] increase from ~ 63 ppm to values as high as 208 ppm in the upper Sh2 and Sh3 stage slices.

Molybdenum concentrations from samples within the Te3 through lower Sh2 (\textit{O. spiralis} - \textit{C. rigidus} biozones) stage slices ranged between 0 to 5 ppm (Figure 5F), close to or below the average crustal values of molybdenum (~2 ppm). Within the middle of Sh2 stage slice [Mo] increases from 2.5 ppm to ~11 ppm, and values remain between 2 ppm to 8 ppm throughout the rest of the study interval.
4.2. Cape Phillips Basin – Bathurst Island, Arctic Canada

Pyrite sulfur isotopes (20 total samples were analyzed) also show a positive excursion coinciding with the $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ isotopic excursions (Figure 6B). Lower baseline $\delta^{34}S_{\text{pyr}}$ values are $\sim$-4‰ within the Te5 ($C. \text{insectus}$ biozone) and begin shifting positively within the Sh1 ($C. \text{murchisoni}$ biozone) stage slices. Peak $\delta^{34}S_{\text{pyr}}$ values are $\sim$+24‰ within Sh2 ($C. \text{murchisoni}$ biozone) stage slice occurring after peak $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ excursion values (Figure 6B). The $\delta^{34}S_{\text{pyr}}$ values for the Twilight Creek Section remain high between +10 to +30‰ throughout Sh2 and into Sh3 ($C. \text{perimi} - M. \text{opimus}$ biozones) stage slices.

A negative thallium isotope excursion (16 total samples were analyzed) is observed during the peak $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ isotopic excursions (Figure 6D). An isotopically low $\varepsilon^{205}\text{Tl}$ value of $\sim$-1.8 is recorded within Te2 ($M. \text{crispus}$ biozone) and then values shift slightly positive to $\sim$0.5 within the upper Te4 ($C. \text{sakmaricus}$ biozone) and then back to slightly negative values of -1.4 within Te5 ($C. \text{insectus}$ biozone. Tl isotope values within the Te5 to Sh1 stage slices ($C. \text{insectus} - C. \text{murchisoni}$ biozones) range from -1.4 to -1.8. Then Tl isotope values within late Sh1 and/or early Sh2 ($M. \text{instrenuus} - C. \text{kolobus}$ biozones) stage slice shift negatively from $\sim$-1.3 to $\sim$-3.0. Subsequently, Tl isotopes shift more positively again within the middle of Sh2 ($M. \text{instrenuus} - C. \text{kolobus}$ biozones) to values as heavy as -2.3. Within the overlying Sh3 stage slice ($C. \text{perimi} - M. \text{opimus}$ biozones) $\varepsilon^{205}\text{Tl}$ values shift back to more negative values, $\sim$-3.3, and the uppermost stratigraphic sample value of $\sim$-2.5.

Twenty samples were processed for Fe speciation from the Twilight Creek section (Figure 7). All $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ values recorded from this section fall below <0.7 (Fig. 7A), with the
exception of one sample with the Sh1 (C. murchisoni biozone) stage slice that records a value of 0.7. Most of the Fe_{mag}/Fe_{HR} data were plotted between 0.01 - 0.03 throughout the entire core (Figure 7B). However, there were several anomalies including data points recorded at: 0.04 within Te5 (C. insectus biozone), 0.06 Sh2 (M. instrenuus - C. kolobus biozone), and 0.15 Sh3 (C. perimi - M. opimus biozone) stage slices (Figure 7B). All of the Fe_{HR}/Fe_{T} values recorded from this section are >0.38 ranging between 0.61 and 0.80 (Figure 7C), with the exception of one value of 0.29 in the uppermost Sh2 stage slice (M. instrenuus - C. kolobus biozones). Fe_{T}/Al ratios for this outcrop from Te2 to Sh1 stage slices (M. crispus – C. murchisoni biozones) are recorded at or near the Average Phanerozoic shale value (~0.53 ± 0.11) between ~0.43 and ~0.51. Subsequently in Sh2 stage slice Fe_{T}/Al values increase to 0.59 - ~1.0, and then fall back to at or near the average oxic shale value (~0.53 ± 0.11) between ~0.44 - ~0.54 in the overlying Sh3 (C. perimi - M. opimus biozone).

Twenty samples were processed for vanadium and molybdenum concentrations from the Twilight Creek outcrop (Figure 7E-F). Vanadium concentrations [V] for both the carbonate corrected and carbonate uncorrected values from Te2 through Sh2 (M. crispus- C. kolobus biozones) stage slices predominantly fluctuate below or near the average crustal value of vanadium (~100 ppm) between ~16 ppm – ~83 ppm. Vanadium concentrations recorded within the upper Sh2 (M. instrenuus - C. kolobus biozone) and Sh3 (C. perimi - M. opimus biozone) then increase above the average crustal value of vanadium from ~264 ppm – ~850 ppm.

Molybdenum concentrations [Mo] for both the carbonate corrected and carbonate uncorrected values from Te2 through Te5 (M. crispus- C. insectus biozones) stage slices increase
from ~6 ppm to ~15 ppm. Molybdenum concentrations decrease within Te5 through mid-Sh2 (C. insectus - *M. instrenuus/C. kolobus* biozones) stage slices from 15 ppm down to 6 ppm. [Mo] recorded in the upper Sh2 (*M. instrenuus - C. kolobus* biozone) and Sh3 (*C. perimi - M. opimus* biozone) stage slices increase from ~14 ppm - ~24 ppm.
CHAPTER 5
DISCUSSION

5.1. Local Marine Redox Conditions

5.1.1. Priekule-20 core, Latvia

Fe-speciation is interpreted as a local redox proxy used to decipher anoxic versus oxic conditions, as well as ferruginous versus euxinic conditions, within ancient marine water-columns and sediment porewaters (Raisewell et al., 2018). Ratios of $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ within the Priekule-20 drill core are primarily below the 0.22 possibly anoxic threshold prior to and during the onset of the Ireviken extinction event (Figure 5C). Then $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratios shift heavier ranging between 0.22 and 0.38, throughout most of the rest of the studied interval in this drill core suggesting an increase in local reducing conditions, possibly anoxic, during the peak values through post-excursion baseline interval of Ireviken CIE (Figure 5C). Fe$_{\text{py}}$/Fe$_{\text{HR}}$ ratios within the Priekule-20 drill core oscillate above and below the 0.7 threshold for possibly euxinic bottom water conditions (Figure 5A), suggesting the local water column in this part of the deep shelf of the Baltic Basin was mostly ferruginous throughout the study interval, with a few intervals of possibly euxinic conditions in the Sh1, Sh2, and Sh3 stage slices. Additional support for locally reducing marine water-column can be found in the Fe$_{\text{T}}$/Al values that are significantly enriched beyond the Average Phanerozoic shale value of 0.53 (Figure 5D) suggesting persistent anoxic conditions throughout this study interval in this area of the Baltic Basin (Lyons and Severmann, 2006). The corresponding $\delta^{34}\text{S}_{\text{pyr}}$ values from this core record a $\pm 23\%$ shift and are consistent with other Baltic Basin Llandovery-Wenlock boundary $\delta^{34}\text{S}_{\text{pyr}}$ records documenting large
magnitude $\delta^{34}\text{S}_{\text{pyr}}$ excursions (Rose et al., 2019; Richardson et al., 2019; Young et al., 2020) throughout the Ireviken event and CIE indicating regional increase in pyrite burial (Figure 6).

The new Fe speciation and trace metal geochemical records suggest anoxic to possibly euxinic bottom water conditions were present in this part of the Baltic Basin during the late Llandovery through early Wenlock (Figure 5). Manganese concentrations throughout the Priekule-20 core study interval were all well below the modern marine oxic threshold value of 850 ppm (Figure 4C), suggesting locally reducing bottom water conditions (e.g., Algeo and Maynard, 2004). Vanadium concentrations, a trace metal proxy that requires low-oxygen to anoxic water column conditions to enrich (e.g., Algeo and Maynard, 2004; Reinhard et al., 2013; Owens et al., 2016, 2017), as shown display two intervals of modest enrichments, up to 208 ppm, in these late Llandovery-early Wenlock shales and marls (Figure 5E). There is an interval of drawn down of $[V]$ below average crustal values, in between these enriched zones within this core that corresponds to the rising limb and peak values of the Ireviken CIE (Figs. 4 and 5E). The first vanadium enrichment occurs in the pre-Ireviken event and CIE interval (Te3–middle Te5 stage slice) and a drawdown trend occurs throughout the Ireviken extinction event interval. The second vanadium enrichment interval occurs in falling limb through the post-excursion CIE interval (middle Sh2-Sh3 stage slices). However, Mo contents, which require euxinic conditions to enrich significantly (20 to $>100$ ppm), show only minimal enrichments in the Sh2-Sh3 stage slice interval of enriched vanadium. These muted Mo enrichments combined with Fe speciation evidence for ferruginous to possibly euxinic water column conditions are consistent with modern
non-euxinic marine water columns that have sulfide restricted to the sediment porewaters (Hardisty et al., 2018).

5.1.2. Twilight Creek, Bathurst Island, Arctic Canada

In the Twilight Creek section, ratios of Fe\textsubscript{HR}/Fe\textsubscript{T} (Figure 7C) indicate a locally anoxic marine bottom water conditions before, during, and after the Ireviken Event and CIE, suggesting anoxic conditions were persistent during the late Llandovery-early Wenlock in the Cape Phillips Basin (Figure 7C). The Fe\textsubscript{HR}/Fe\textsubscript{T} ratios from 28 m – 50 m appear to have values greater than 1 (Figure 7C). These anomaly values could be a result of post-depositional pyrite oxidation of the Twilight Creek Outcrop section which may have occurred during section storage due to the considerable amount of time between sampling and Fe extraction (Owens et al., 2016). This post depositional diagenesis could explain the large Fe\textsubscript{HR}/Fe\textsubscript{T} ratios that occur within the middle of the section (Figure 7C). Post pyrite oxidation could result in a “double counting” of the Fe\textsubscript{py} portion of the total Fe\textsubscript{HR} fraction, because Fe\textsubscript{py} would be accounted in the Fe\textsubscript{HR} fraction from the chromium reducible sulfide method as well as the oxidized fraction of Fe\textsubscript{carb} thus yielding larger Fe\textsubscript{HR}/Fe\textsubscript{T} values greater than 1 (Owens et al., 2016). The corresponding Fe\textsubscript{py}/Fe\textsubscript{HR} ratios (Figure 7A) are almost all < 0.7, indicating primarily ferruginous bottom water conditions in this deep shelf setting of the Cape Phillips Basin. The Fe\textsubscript{T}/Al ratios from this section (Figure 7D) within the Ireviken CIE interval trend from values within the Phanerozoic crustal averages (e.g., Raisewell et al., 2008) to values that are notably enriched in iron relative to aluminum. This distinct trend in Fe\textsubscript{T}/Al ratios in this part of the Cape Phillips Basin could suggest an enhanced
Fe transport and trapping by locally euxinic sediment porewater conditions via Fe scavenging through local pyrite formation within the sediments. This is consistent with the corresponding $\delta^{34}$S$_{pyr}$ values from this section that record a $+25\%$ shift indicating a local increase in pyrite burial (Figure 6).

The Fe speciation datasets along with the trace metal records from this section indicate anoxic bottom water conditions with intervals of sulfidic porewaters in this part of the Cape Phillips Basin during the late Llandovery through early Wenlock (Figure 7). Manganese concentrations for the Twilight Creek section are well below the modern marine oxic threshold value of 850 ppm (Figure 4C), indicating locally reducing bottom water conditions (e.g., Algeo and Maynard, 2004). Vanadium concentrations before and during the Ireviken Event and CIE are below the average crustal value (~100 ppm) suggesting less reducing conditions (Figure 7E). However, this is not consistent with the corresponding Fe speciation datasets that indicate persistent anoxic-ferruginous conditions throughout the section during this time. This inconsistency could potentially be due to a drawn down of global trace metal inventories possibly due to an increase in reducing conditions in the global oceans (see global redox section 5.2 below), such drawdowns have been proposed for OAE2 during the Late Cretaceous (Owens et al., 2017). Vanadium concentrations become significantly enriched, values as high as 850 ppm, during the falling limb and post-excursion interval of the Ireviken CIE (late Sh2-Sh3 stage slices), indicating locally anoxic but not necessarily euxinic bottom water conditions (Figure 7E). Corresponding [Mo] in the interval before and during the Ireviken Event and CIE show only minor enrichments, 8–16 ppm. Molybdenum concentrations do show modest enrichments, up to
25 ppm, in the same interval where [V] show significant enrichments. These minor–modest trace metal enrichments and Fe speciation data suggest a similar marine redox environment to that of deep shelf Baltic Basin (see section 5.1.1. above), locally anoxic bottom waters with sulfide restricted to the sediment porewaters.

5.2. Global Marine Redox Conditions

Three major-steps excursions of global ocean redox conditions are proposed based upon interpretations of the new Tl isotope datasets from Latvia and Arctic Canada that span the early Silurian Ireviken extinction event and CIE interval (Figure 8). Furthermore, the new $\delta^{34}S_{pyr}$ profiles from Arctic Canada and Latvia are interpreted as being representative of global changes in pyrite burial rates during this time, as the timing and duration covariance with $\delta^{13}C$ profiles are equivalent to records from carbonate platform settings from multiple sites globally (Richardson et al., 2019; Rose et al., 2019; Young et al., 2019).

In the late Llandovery (Te3-Te5), $\varepsilon^{205}$-Tl records indicate that there were widespread anoxic marine conditions globally during the late Telychian, but corresponding $\delta^{34}S_{CAS}$ data suggest only limited amounts of euxinic seafloor conditions before the Ireviken CIE. Tl isotope records before the Ireviken CIE in the Baltic Basin are heavier (more positive) $\sim$3.0, in Te4 to Te5 stage slices, indicating less global Mn-oxide burial and more widespread anoxic conditions possibly occurring before the Ireviken CIE. Additionally, the Tl isotope record from the Cape Phillips Basin broadly similar to the Baltic Basin records, with heavier (more positive), $\sim$0.5 to -1.3 in Te4 to Te5, also indicating less Mn-oxide burial and more widespread anoxic marine
conditions globally before the Ireviken CIE. The δ³⁴S_CAS records before the Ireviken CIE in the Baltic Basin are stable with little changes ~+25‰ from Viki core, Estonia and ~+30‰ from Gotland, Sweden (Richardson et al., 2019; Rose et al., 2019), indicating little to no change in pyrite burial and thus little change the amount of seafloor euxinic conditions globally. The δ³⁴S_pyr records from Latvia and Arctic Canada, along with other sections mentioned above, broadly mirror this stable interval in the late Llandovery steady baseline in δ³⁴S_CAS records.

During the rising limb of the Ireviken CIE (Sh1-early Sh2), the ε²⁰⁵Tl profiles indicate global marine anoxic conditions decreased. Thallium isotopes trend toward more negative values getting as light as ~-5 in the Baltic Basin, and ~ -3 in the Cape Phillips Basin, indicating an increase in Mn-oxide burial globally during the rising limb of the Ireviken CIE, possibly due to enhanced thermohaline circulation and associated ventilation of marine environments during this time (e.g., Ostrander et al., 2019). Corresponding sulfur δ³⁴S_pyr datasets from the two study sites documented here as well as previously published δ³⁴S_CAS and δ³⁴S_pyr records document a shift towards more positive values (Young et al., 2019). Manganese oxide burial rates were likely increasing globally during this time (shown by the negative ε²⁰⁵Tl excursion), while pyrite burial rates appear to be increasing (shown by the positive δ³⁴S_pyr excursion). The continued increased pyrite formation/burial during this time could be resultant from re-mineralized freshly buried organic carbon within the remaining oxygen minimum zones (OMZs) and other reducing areas within the global oceans. While the negative ε²⁰⁵Tl excursion indicates that reducing seafloor conditions were decreasing globally, but the increasing δ³⁴S_CAS values suggest that within these remaining reducing areas that euxinic conditions were increasing.
Lastly in the early Wenlock (middle-late Sh2) during the falling limb of the Ireviken CIE, thallium isotopes in the Baltic Basin return to heavier (positive) values ~ -3.5, and ~ -2 in the Cape Phillips Basin indicating a return to more widespread reducing conditions throughout the global oceans. The corresponding sulfur $\delta^{34}$S$_{pyr}$ datasets from the two study sites documented here as well as previously published $\delta^{34}$S$_{CAS}$ and $\delta^{34}$S$_{pyr}$ records (Richardson et al., 2019; Rose et al., 2019; Young et al., 2019) document peak values and eventually a return to baseline during this time interval. These sulfur isotope records indicate that as bottom water anoxic conditions expanded globally during this interval euxinic conditions also continued to expand throughout the end of the Ireviken CIE interval.

The negative correlation of the $\delta^{34}$S$_{CAS}$ and $\varepsilon^{205}$Tl signals within the Sh1-early Sh2 stage slices can be explained by the differences in residence times of sulfate and thallium in the oceans as well as the persistent increase in global pyrite burial due to remineralization of freshly buried organic carbon from the Ireviken CIE. Both sulfate (~10^6 yr) and thallium (~18^4 yrs) have larger residence times than the interocean mixing time (10^3 yr) which enables homogenous preservation of both isotope records (Owens et al., 2017; Young et al., 2019). However, because thallium has a shorter residence time than sulfate in the modern global oceans, the isotopic response for $\varepsilon^{205}$Tl occurs more rapidly than changes in the sulfur cycle that are recorded as $\delta^{34}$S$_{CAS}$.

Time estimates for the negative Tl excursion during the early Sheinwoodian are ~ 300-400 kya. This estimate is based upon extrapolation of the U/Pb dating of K-bentonites at the Llandovery-Wenlock boundary (Te5/Sh1; 431.83 ± 0.23 Ma) and at the base of the second stage slice of the Homerian (Ho1/Ho2; 428.45 ± 0.35 Ma) (Cramer et al., 2012; McAdams et al.,
The difference in both of these numerical age dates is about ~2.8 Myr minimum and ~3.96 Myr maximum (McAdams et al., 2019). Assuming that the difference in time between these two age dates is evenly distributed throughout the stage slices contained within, taking half of that amount of time is the approximate duration of the Ireviken CIE, which in this case would have lasted ~1.4 Myr minimum and ~1.98 Myr maximum according to the radiometric dates (McAdams et al., 2019).

5.3. Linkage of Dynamic Marine Redox Conditions to Early Silurian Climate and the Ireviken Extinction Event

The new $\varepsilon^{205}$Tl records from this study and $\delta^{34}$S$_{CAS}$ records from previous studies are interpreted to represent dynamic changes in global redox conditions within the early Silurian oceans throughout the late Llandovery–early Wenlock interval, and may have been a potential causal factor for the major stepwise extinction event documented globally during this time, the Ireviken Event (e.g., Jeppsson, 1998). A proposed mechanism for the dynamic shift towards more oxic, or less reducing conditions, within global marine redox conditions during the Sh1-early Sh2 interval (negative $\varepsilon^{205}$Tl excursion) could be enhanced thermohaline circulation generated from the previously proposed early Sheinwoodian glaciation (Lehnert et al., 2010). In the discussion that follows I focus on this new level of global marine redox dynamics throughout the late Llandovery–early Wenlock interval in the context of coincident changes in the environment/climate, eustatic sea level, and the marine biosphere.
Eustatic sea-level records for the middle Telychian (Te3) indicate a relative highstand in global sea level (Loydell, 1998; Haq and Schutter, 2008; Johnson, 2010). The limited $\varepsilon^{205}$Tl isotope data document the heaviest values in the Priekule-20 core possibly suggesting a greater fraction of the global seafloor was overlain by anoxic bottom waters. However, the limited $\delta^{34}$SCAS records from the Viki core, Estonia (Richardson et al., 2019) through this interval show no major changes suggesting global pyrite burial rates, and thus the extent of euxinic conditions globally did not change during this time. In the middle-late Telychian (Te4) there is sequence stratigraphic evidence for a eustatic sea-level lowstand (Cramer and Saltzman, 2005, 2007; Clay and Desrochers, 2014) that correlates well with evidence for a mid-late Telychian (Te4) glaciation (i.e., abundant glacial tillites found in Bolivia, Peru, Argentina, and other localities in the Amazon Basin) (Diaz-Martinez and Grahn, 2007). Additionally, Sea surface temperature (SST) proxy records (i.e., conodont-phosphate oxygen isotopes; $\delta^{18}$Ophos) from the Baltic Basin show a +0.5 to +1.0‰ shift indicating a cooling event of tropical SSTs (Lehnert et al., 2010; Trotter et al., 2016). The $\varepsilon^{205}$Tl isotope records from this interval record a small but discernable decline suggesting a decrease in anoxic conditions (Figure 4D) in the global oceans, while $\delta^{34}$SCAS records (Richardson et al., 2019) indicate little to no change in the global extent of euxinia in the early Silurian oceans. In the late Telychian (late Te5) sequence stratigraphic evidence and eustatic sea-level records indicate a rise in global sea level (Loydell, 1998; Haq and Schutter, 2008; Johnson, 2010), coinciding with new Tl isotope records that possibly indicate that the anoxic fraction of the seafloor was expanded in the global oceans (Figures 4D and 6D). Additionally, sulfur isotope records ($\delta^{34}$SCAS and $\delta^{34}$S$_{pyr}$) indicate euxinic conditions were
expanding globally (Richardson et al., 2019; Rose et al., 2019; Young et al., 2019). Sea-level and global redox proxy records suggest the initial stages of the Ireviken extinction event, during the late Telychian (late Te5), coincided with transgression and increased anoxic and possibly euxinic conditions globally.

Across the Llandovery-Wenlock boundary (transition between Te5 and Sh1) eustatic sea-level was at a highstand, that was followed by an interval of lowered sea level during the middle of Sh1 (transition between the C. murchisoni and C. riccartonensis biozones) eustatic sea-level (Loydell, 1998; Cramer and Saltzman, 2005, 2007). Sea surface temperature (SST) proxy records (i.e., conodont-phosphate oxygen isotopes; \( \delta^{18}O_{phos} \)) from the Baltic Basin show a \( \sim +1.5\% \) shift, indicating a significant cooling of SSTs in the tropics during peak values of the Ireviken CIE and later stages of the marine extinction interval (Lehnert et al., 2010; Trotter et al., 2016). Additionally, there is evidence of early Wenlock diamictites found in the Eastern Cordillera region of Bolivia (Diaz-Martinez, 2007). The corresponding new Tl isotope records (Baltica and Laurentia) document a large negative excursion, indicating a shift in the global oceans to less reducing/ more oxic marine environments. Climatic cooling and Gondwana glaciation during the Sh1-early Sh2 interval would have been likely associated with more vigorous thermohaline circulation and should have resulted in increases in marine dissolved \( O_2 \) contents, thus ventilating marine settings with suboxic to oxic conditions and promoting more Mn-oxide burial globally. The \( \epsilon^{205}Tl \) records that reducing seafloor conditions were decreasing globally, but the corresponding \( \delta^{34}S_{CAS} \) and \( \delta^{34}S_{pyr} \) records suggest that within these remaining reducing areas that euxinic conditions were increasing. Overall, this interval of lowered sea level, cooler climate,
and more oxic marine conditions corresponds to when extinction rates within corals, ostracods, brachiopods, and acritarchs (marine phytoplankton) were high (Figure 9) (Jeppsson, 1990, 1997; Munnecke et al., 2003; Cramer and Saltzman, 2007; Calner 2008; Young et al., 2019).

Additionally, this interval corresponds to the rising limb and peak values interval of the Ireviken CIE (Figure 4 and 6).

Subsequently during the middle Sheinwoodian (Sh2), eustatic sea-level rose again and Tl isotopes indicate that anoxic conditions expanded globally as carbon isotope values remained high in the global oceans. Additionally, δ^{34}S_{CAS} records through this interval suggest increased euxinic conditions globally in the middle Silurian oceans coinciding with the last stages of the Ireviken extinction event (Figure 9; Jeppsson, 1990, 1997; Melchin et al., 1998; Munnecke et al., 2003; Cramer and Saltzman, 2007; Cooper et al., 2014; Young et al., 2019). During the falling limb of the Ireviken CIE (late Sh2-Sh3) SST proxy records suggest the climate may have warmed, eustatic sea-level was overall higher, while paleoredox proxy records suggest that previously widespread anoxic and euxinic decreased within the global oceans at this time, and overall rates of extinction in the marine biosphere had significantly declined (Jeppsson, 1990, 1997; Bickert et al., 1997; Melchin et al., 1998; Munnecke et al., 2003; Cramer and Saltzman, 2007; Calner 2008; Lehnert et al., 2010; Cooper et al., 2014; Richardson et al. 2019; Rose et al., 2019; Young et al., 2019). Thus, redox changes and migrations of oxygen minimum zone from deep basinal marine settings towards shallower marine settings were linked through eustatic sea-level changes which significantly affected the seafloor extent of reducing conditions locally and globally during this time in the Silurian.
5.4. Milankovitch Cycling and Orbital Forcing

Milankovitch forcing has been a proposed mechanism that needed to be further evaluated to explain the stepwise extinction events during the Silurian (Jeppsson, 1997). However, currently there are no known studies that have addressed this hypothesis directly. In this study, Fe\textsubscript{py}/Fe\textsubscript{HR} and Fe\textsubscript{mag}/Fe\textsubscript{HR} ratios were plotted to indirectly analyze orbital forcing cycles that may have occurred throughout the Llandovery-Wenlock boundary (Figure 5 and Figure 7). Poulton et al. (2015) attributed anti-correlated Fe\textsubscript{py}/Fe\textsubscript{HR} and Fe\textsubscript{ox}/Fe\textsubscript{HR} ratios occurring every ~21 kya to obliquity cycles within a Cretaceous OAE2 sequence in Morocco. Their study analyzed negative anomalies in the Fe\textsubscript{py}/Fe\textsubscript{HR} ratio that are below the 0.7 threshold (Fe\textsubscript{py}/Fe\textsubscript{HR} < 0.7) synchronously with positive anomalies in Fe\textsubscript{ox}/Fe\textsubscript{HR} ratio suggesting local ferruginous conditions were directly caused by an increase ocean input of detrital hematite (Fe\textsubscript{ox}) from the continents via physical weathering (Poulton et al., 2015). However, Poulton et al. (2015) did not provide a cross plot of Fe\textsubscript{py}/Fe\textsubscript{HR} to Fe\textsubscript{ox}/Fe\textsubscript{HR} ratios, nor was an R\textsuperscript{2} value provided to assess what statistical relationship there was between these two datasets. Poulton et al. (2015) proposed that local redox cyclicity observed was attributed to orbital forcing cycles generating oscillating sea-level, which in turn oscillated continental weathering rates of detrital iron oxides (Fe\textsubscript{ox}) into the oceans (Poulton et al., 2015).

The Priekule-20 core shows a similar anti-correlation relationship between Fe\textsubscript{py}/Fe\textsubscript{HR} and Fe\textsubscript{mag}/Fe\textsubscript{HR} ratios with six synchronously identified anti-correlated horizons that appear to represent ~405 kya eccentricity cycles that occur every ~10 m shown before the Ireviken Event, including the rhythmic pulses of the “Red beds” (Figure 10). The ~405 kya eccentricity cycle is
assigned to these Fe\textsubscript{py}/Fe\textsubscript{HR} and Fe\textsubscript{mag}/Fe\textsubscript{HR} anti-correlations due this Milankovitch periodicity matching the estimated timescale of the Ireviken CIE, thallium isotope excursion, and behavior of the Fe\textsubscript{py}/Fe\textsubscript{HR} - Fe\textsubscript{mag}/Fe\textsubscript{HR} anti-correlated anomalies in both palaeohemisphere sections resembling apsidal precession as discussed in this section below (Figures 4 and 5). All the Priekule-20 core Fe\textsubscript{py}/Fe\textsubscript{HR} ratios were cross plotted with Fe\textsubscript{mag}/Fe\textsubscript{HR} ratios and display an \( R^2 \) value of 0.53, a moderate correlation. Excluding the Priekule-20 core values during the Ireviken event, the Fe\textsubscript{py}/Fe\textsubscript{HR} vs. Fe\textsubscript{mag}/Fe\textsubscript{HR} reveal a slightly better correlation, \( R^2 \) value of 0.58. The Fe\textsubscript{py}/Fe\textsubscript{HR} - Fe\textsubscript{mag}/Fe\textsubscript{HR} anomaly at proposed eccentricity cycle-D (early-Te5) is lacking a negative Fe\textsubscript{py}/Fe\textsubscript{HR} anomaly most likely due to a rise in eustatic sea-level at this time migrating the local (and global) euxinic chemocline disabling the negative Fe\textsubscript{py}/Fe\textsubscript{HR} signal (Figures 4 and Figure 10). These oscillating patterns outlined in the Priekule-20 core appear to be very high before the Ireviken Event in stage slices Te3 (\textit{O. spiralis} biozone) (Fe\textsubscript{mag}/Fe\textsubscript{HR} = 0.40), Te4 (\textit{C. lapworthy} and \textit{C. insectus} biozones) (Fe\textsubscript{mag}/Fe\textsubscript{HR} = 0.19), and early Te5 (\textit{C. centrifugus} biozone) (Fe\textsubscript{mag}/Fe\textsubscript{HR} = 0.27) (Figure 5C). Then they become absent during the Ireviken Event in stage slices mid Te5 (\textit{C. centrifugus} biozone) and Sh1 (\textit{C. murchisoni} and \textit{C. riccartonensis} biozones) (Figure 5C). After the event, the oscillating patterns become low/dampened after the event in stage slices Sh2 (\textit{C. rigidus - M. belophorous} biozones) (Fe\textsubscript{mag}/Fe\textsubscript{HR} = 0.12) and Sh3 (\textit{C. rigidus - M. belophorous} biozones) (Fe\textsubscript{mag}/Fe\textsubscript{HR} = 0.04) (Figure 5C). Error bars representing two standard deviations (2\( \sigma \)) are plotted as well to display the reproducibility of the iron speciation data (Figures 5 and 7). The error bars throughout the iron speciation data surpass the reproducibility detection limit (<0) (Figures 5 and 7) However, if one applied the same statistical error bar
analysis to the trace metal data from both basins, the same statistical observations would most likely be seen as well considering the vanadium and molybdenum concentrations before and after the Ireviken event are extremely low (Figures 5 and 7).

During the Ireviken Event, the negative correlation of \( \text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}} - \text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} \) ratios diminish most likely due to one, or a combination of the following reasons: 1) A rise in the 5\(^{th}\) order eustatic sea-level disabling weathering of \( \text{Fe}_{\text{mag}} \) from the continents (Figures 5B and 10) (Cramer and Saltzman, 2007). 2) A transition of eccentricity cycle positioning from the Southern hemisphere (Summer) perihelion position to the Northern hemisphere (Summer) perihelion position transferring eccentricity weathering patterns of \( \text{Fe}_{\text{mag}} \) from the Southern paleogeographic hemisphere to the Northern paleogeographic hemisphere (as discussed in subsections below) (Figure 11). 3) A migration of the euxinic chemocline disabling local pyrite burial (\( \text{Fe}_{\text{py}} \)) initially before the \( \delta^{34}\text{S}_{\text{py}} \) and \( \delta^{13}\text{C}_{\text{carb}} \) excursions due to the rise in the 5\(^{th}\) order eustatic sea-level, followed by an increase of local pyrite burial (\( \text{Fe}_{\text{py}} \)) after the onset of the \( \delta^{34}\text{S}_{\text{py}} \) and \( \delta^{13}\text{C}_{\text{carb}} \) excursions (Figures 4 and 10) (Cramer and Saltzman, 2007). Though the Twilight Creek section does not clearly have the identified anti-correlated synchronous \( \text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}} - \text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} \) ratios seen in the Priekule-20 core, \( \text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}} \) ratios in this section still tend to increase exponentially after the conclusion of the Ireviken Event (Figure 7B).

5.4.1 New proxy proposition for ancient Earth positioning

I propose an anti-correlation relationship of \( \text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}} - \text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} \) ratios observed from two paleogeographic hemispheres provides a new proxy that may pinpoint Earth’s relative
orbital position in three-dimensional geologic time generated by solar tidal/seasonal differences and weathering patterns. Change in tidal bulges on Earth from gravitational forces of the Sun and the Moon have been determined by analyzing changes in eccentricity, semi-major axis (radius) and inclination of orbital patterns (MacDonald, 1964). Today, tidal bulges on Earth can increase tidal discharge, fluvial discharge, and can modulate sediment transport over 1000 km upstream in large low, gradient rivers such as the Mississippi and Fan River deltas (Hoitink and Jay, 2016; Nienhuis et al., 2016; Nienhuis, 2018). River water levels in China oscillate between 2 m - 11 m in height due to a combination of Earth to moon and Earth to Sun astronomical forcing, oscillating between high river heights during the Summer months and low river heights in the Winter months (Hoitink and Jay, 2016). These river height oscillations and enhanced sediment discharges are also highly augmented by monsoonal and hurricane precipitation as well (Hoitink and Jay, 2016; Gambacorta et al., 2018). An example of past evidence of intense sediment transport due to tides occur during the Cretaceous period, which include 10 m thick sections of tidally influenced river deposits found in Utah (Shanley et al., 1992). In addition, high concentrations of low coercivity detrital magnetite and high coercivity detrital hematite have been observed in the rock record from eccentricity maxima causing higher continental runoff during the early Triassic and Cretaceous periods (Wu et al., 2012; Hinnoy et al., 2013; Grabowski et al., 2015).

To explain where the Earth was placed before, during, and after the Ireviken event I have developed some logical pathways which explain the exponentially decreasing relationship in the Fe_{mag}/Fe_{HR} data in the Priekule-20 core (Southern paleogeographic hemisphere). Higher anomaly
ratios of $\text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}}$ occurring in the Priekule-20 core indicates higher rates of seasonal detrital weathering of magnetite (Appendix D) (Figures 5, 10, 11). Increased rates of detrital weathering may result from lower local sea-level and enhanced monsoonal activity, forcing rivers to cut deeper into the Earth’s crust to reach a lower base (sea) level. Lower local sea-level from solar tidal forces and enhanced monsoonal activity in the southern hemisphere is explained by the Earth’s southern paleogeographic hemisphere (Summer) positioned in the Aphelion position due to the decreased force of gravity of the Sun onto the Earth ($F_{\text{Sun on Earth}}$) (Figure 11): 

$$1) \quad F_{\text{Sun on Earth}} = \frac{G \cdot m_{\text{Sun}} \cdot m_{\text{Earth}}}{r^2}$$

Lower anomaly ratios of $\text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}}$ occurring in the Priekule-20 core indicates a recording of lower rates of seasonal detrital weathering of magnetite (Appendix D) (Figures 5, 10, 11). Decreased rates of detrital weathering result from higher local sea-level and decreased monsoonal activity, forcing rivers to shallow and cut back inland to maintain structure and transport water towards a higher base (sea) level. Higher local sea-level from solar tidal forces and decreased monsoonal activity is explained by the Earth’s southern hemisphere (Summer) positioned in the Perihelion position due to the increased force of gravity of the Sun onto the Earth ($F_{\text{Sun on Earth}}$) (Figure 11) (1).

The highest $\text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}}$ ratio occurs at eccentricity cycle (B) Te3 where eustatic sea-level was undergoing highstanding eustatic transgression and regression sequences (Figure 10) (Loydell, 1998; Haq and Schutter, 2008; Johnson, 2010). The $\text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}}$ signal still appears to be preserved during eccentricity cycle (B) Te3 during this time which may suggest seasonal
summer monsoonal precipitation cycles and high seasonal contrast may have more of an impact on local weathering than global eustatic sea-level (Figure 10 and 11). In addition, intensified monsoon activity in the Southern paleogeographic hemisphere would also occur during eccentricity maxima particularly at the eccentricity cycles (A) “Red Bed” (\textit{N. crenulata} biozone) and (B) Te3 (\textit{O. spiralis} biozone) positions due to high seasonal contrasts and intense humidity generation occurring during the Northern paleogeographic hemisphere (Summer) in concert with intensifying rainfall activity and physical/chemical weathering during the wet seasons in the Southern paleogeographic hemisphere (Winter) (i.e. Gambacorta et al., 2018) (Figure 11).

Before the Ireviken Event, the Northern paleogeographic hemisphere (Summer) was most likely in the Perihelion position whereas the Southern paleogeographic hemisphere (Winter) was in the Aphelion position (Appendix D) (Figures 5B, 7B, 11.1). During the Ireviken Event, the Northern paleogeographic hemisphere (Summer) and the Southern paleogeographic hemisphere (Winter) must have been at relatively the same distance to the Sun (Appendix D) (Figures 5B, 7B, 11.2). After the Ireviken Event, the Northern paleogeographic hemisphere (Summer) was most likely in the Aphelion position whereas the southern paleogeographic hemisphere (Winter) was most likely in the Perihelion position (Table 3) (Figures 5B, 7B, 11.3). Enhanced weathering patterns of detrital magnetite and hematite are presumed to be transported predominantly during the Southern hemisphere aphelion position (Winter) and Northern hemisphere aphelion position (Summer) during the ~405 kya eccentricity cycles due to these particular positions consisting of higher temperatures, higher areas of local humidity, higher seasonal contrast, intensified
monsoonal activity, and longer day times which promote the acceleration of chemical and physical weathering (Figure 11) (Hoitink and Jay, 2016; Gambacorta et al., 2018).

5.4.2 New method for calculating the 5th order eustatic sea-level record: The Glacial Charger Model

The “Glacial Charger” model is based upon stratigraphic placement of lithologic, geochemical, and sea-level record data and is used as 1) a platform to calculate changes in eustatic sea-level based upon evaporation/humidity generation from the Northern (~91% - 95% water) paleogeographic hemisphere (Panthalassic Ocean) transformed into glacial ice growth in the Southern paleogeographic hemisphere on the paleocontinent of Gondwana and 2) an update to the Humid-Arid Period model (Figures 1, 10, 11, 12) (Jeppsson, 1990; Bickert et al., 1997; Blakey, 2016). The (A) Upper Telychian “Red Beds” (*N. crenulata* biozone) (1334m -1332 m – Priekule-20 core) are placed at the π/2 eccentrical position due to the “Red Beds” possessing the highest concentration of detrital magnetite (Fe$_{mag}$) at the Llandovery-Wenlock boundary which may have been oxidized into reduced detrital hematite prior to deposition from tidal-influenced-humid-aerobic weathering, suggesting that the eccentricity maxima of the Southern hemisphere (Winter) was placed at the Aphelion position (Figures 10, 11.1, 12A) (Zeigler and Mckerrow, 1975; Channel et al., 1993; Hodych and Buchan 1994; Kiipli et al., 2000; Loydell and Nestor, 2005; Rong et al., 2012; Zhang et al., 2014, 2018; Liu et al., 2016). The hematite grains contained in the Telychian aged “Red Beds” are interpreted to be detrital in origin which are only found in Southern paleogeographic localities thus far such as: Wales, Scotland, Greenland,
Norway, Denmark, Estonia, France, Germany, Czech Republic, Poland, Spain, Austria, Portugal, Italy, Bulgaria, Turkey, South China, Latvia, Saudi Arabia, United States, and Canada. (Ziegler and McKerrow, 1975; El-Khayal, 1987, Hodych and Buchan, 1992; Channel et al., 1993; Kiipli et al., 2000; Sachanski et al., 2010 Rong et al., 2012; Zhang et al., 2014, 2018; Liu et al., 2016).

The (E) mid Sh1 (Ireviken Event) eccentricity cycle is placed at the $\pi$ position due to the observance of both the Priekule-20 core and the Twilight Creek section possessing absent/low Fe$_{\text{mag}}$/Fe$_{\text{HR}}$ anomaly ratios (Figures 10 and 12A). The $\pi$ position represents the (E) mid Sh1 eccentricity cycle where the semi-major axis of the Northern and Southern hemisphere Summer and Winter positions are relatively the same distance away from each other as suggested by the absent Fe$_{\text{mag}}$/Fe$_{\text{HR}}$ ratios in both the Priekule-20 core and TWC sections (Figure 5B, 7B, 11.2, 12A). The three eccentricity cycles occurring before the late Sh1 (Ireviken Event): (B) mid-Te3, (C) early-Te4, and (D) early-Te5 are placed at equal angles (22.5°) between the (A) Upper Telychian “Red Beds” and the (E) mid Sh1 (Ireviken Event) eccentricity cycles (Figures 10 and 12A). The three eccentricity cycles occurring after the Ireviken event: (F) early Sh2, (G) late Sh2, and (H) early Sh3 are placed at equal angles (22.5°) after the (E) late Sh1 (Ireviken Event) eccentricity cycle (Figures 10 and 12A). The missing eccentricity Fe$_{\text{mag}}$/Fe$_{\text{HR}}$ anomaly at (E) late Sh1 (Ireviken Event) is either due to 1) a highstand in the 5th order eustatic sea-level high stand during Sh1 which would minimize detrital weathering rates of continental material or 2) A transition of eccentricity cycle positioning from the Southern hemisphere (Summer) perihelion position to the Northern hemisphere (Summer) perihelion position transferring eccentricity weathering patterns of Fe$_{\text{mag}}$ from the Southern paleogeographic hemisphere to the Northern
paleogeographic hemisphere (Figures 5B, 7B, 10, 11). All semi-axis radii of each of the
eccentricity cycles between the Earth and the Sun are assumed to be constant due to the stability
of the period of eccentricity throughout geologic time and the gravitational interactions between
Earth, Venus, Saturn and Jupiter (Berger et al., 1992; Imbrie et al., 1993; Laskar, 2004;
Gambacorta et al., 2018). In summary, the following time slices are paired with the following
eccentricity positions (Figure 12A):

A) “Red-Beds” (N. crenulata biozone) = π/2 position “Maximum Humidity Area”
B) Mid-Te3 (O. spiralis biozone) = 5π/8 position
C) Early-Te4 = 3π/4 position “Maximum Telychian Glaciation Ice Cap Area”
D) Early-Te5 = 7π/8 position
E) Mid-Sh1 (absent) = π position “Maximum Sheinwoodian Glaciation Ice Cap Area”
F) Early-Sh2 = 9π/8 position “Maximum LSST at cycle (F) Ice Cap Area”
G) Late-Sh2 = 5π/4 position
H) Early-Sh3 = 11π/8 position

To address the concerns for the timing of each of these stage slices previously calibrated
from relative biostratigraphy analysis in relation to numerical age dates from k-bentonites,
McAdams et al. (2019) has recorded three absolute numerical radiometric (U/Pb) age dates
constraining the Llandovery-Wenlock boundary at Te1 stage slice (437.80 ± 0.50 Mya), Te5-Sh1
stage slice (431.83 ± 0.23 Mya), and Ho2 stage slice (428.45 ± 0.35 Mya). It can be said with
great absolute numerical confidence that the time span between the Te1 – (Te5-Sh1) stage slices
is between 6.70 – 5.24 million years and the time span between the (Te5-Sh1) - Ho2 stage slices
is between 3.96 – 2.80 million years (McAdams et al., 2019). However, the numerical time span between each of these absolute numerical age points (k-bentonites) is unknown and not very well constrained (numerically) throughout the Llandovery-Wenlock boundary (McAdams et al., 2019). Therefore, it should not be assumed that numerical time is evenly distributed from relatively calibrated biostratigraphy constraining stage slices because the absolute numerical timing of strata contained between the k-bentonite beds are unknown (McAdams et al., 2019). In the newly calibrated geologic time scale according to Gradstein and Ogg (2004), Milankovitch climatic cycles and astronomical tuning are used as a more credible tool to calibrate geologic time due to the numerically known consistency and periodicity of Milankovitch cycling providing absolute age duration constraints (Milankovitch, 1941). Thus, the eccentricity cycles observed in this study should be analyzed as a more useful tool for numerical calibration of the stage slices constrained within the observed k-bentonites observed throughout the Llandovery-Wenlock boundary. It should be noted that numerical time (1 year) is defined through astronomical observation by observing the time it takes Earth to oscillate around the Sun in one orbital period. Biostratigraphy is a useful tool to relatively date stage slices relative to each other by stratigraphic positioning and correlation of stratigraphic sections/sequences around the world, but one cannot put an absolute numerical age date on a fossil or fossil succession unless there are an adequate amount of absolute numerical age date constraints recorded and observed in time constraining each and every fossil/fossil succession observed in the geologic record.
5.4.3 Glacial Charger Model: calculation of 5th order eustatic sea-level changes

To mathematically calculate the relative ice volume produced during each glaciation resulting in the changes of the 5th order eustatic sea-level record over the Llandovery-Wenlock boundary, an integration of the glacial ice cap area and global humidity area is computed. The relative “Ice area” that is precipitated as snow/glacial ice on the paleo-mega-continent of Gondwana located in the Southern paleogeographic hemisphere is mathematically integrated with the relative “Humidity area” that is evaporated as water vapor from the Panthalassic Ocean located in the Northern paleogeographic hemisphere (Blakey, 2016). To compute the integration of the relative “Humidity area” generated from the Northern paleogeographic hemisphere to each of the relative glacial “Ice areas” produced during each glaciation observed, mathematical functions of “Humidity Area”, “Telychian Ice Cap Area”, “Sheinwoodian Ice Cap Area”, and “LSST at cycle (F) Ice Area” were defined to represent the growth and retreat of global humidity and global glaciations (Figure 12B). These functions are defined upon the time-location of the critical values (crests/maximums) represented by the stratigraphic placement and time intersection of “Red Beds”, glacial tillite records, 5th order eustatic sea-level low stands, and negative thallium excursions at the:

(A) “Red Beds” (*N. crenulata* biozone) \((\pi/2\) position) = “Maximum Humidity Area”

(C) Early Te4 (3\(\pi/4\) position) = “Maximum Telychian Glaciation Ice Cap Area”

(E) Mid Sh1 (Ireviken Event) \((\pi\) position) = “Maximum Sheinwoodian Glaciation Ice Cap Area”

(F) Early Sh2 (9\(\pi/8\) position) = “Maximum LSST at cycle (F) Ice Cap Area”
(Figures 10 and 12) (This study) (Grahn and Caputo, 1992; Caputo, 1998; Cramer and Saltzman, 2007; Johnson (2006); Diaz-Martinez and Grahn, 2007; Loydell, 2007; Page et al., 2007; Lehnert et al., 2010, Munnecke et al. 2010; Ghienne et al., 2013; Clayer and Desrochers, 2014).

The critical value (crest/maximum) of the “Maximum Humidity Area” function is based upon the placement of the (A) Upper Telychian “Red Beds” (N. crenulata biozone) which has a function periodicity of $2\pi$ radians due to the Northern paleogeographic hemisphere perihelion position occurring between 0 and $\pi$ (Figure 12) (Blakey, 2016). The period/time duration of all three glaciation functions are presumed to be $2\pi$ radians as well (Figure 12). This is based upon the assumption that there is a 1:1 relationship between evaporation (Atmospheric Humidity Area generation) and precipitation (Glaciation Ice Area growth) regarding the fact that 86% - 90% of all evaporated water on Earth originates from the oceans and net global evaporation equals net global precipitation according to the USGS (Schmitt, 1995; Huntington, 2006; Gimeno et al., 2012). The functions calibrated based on these above criteria are defined in Figure 12 as:

1) $F(x) = \text{“Atmospheric Humidity Area”}= \sin(x)$
2) $F(x-\pi/4) = \text{“Telychian Ice Area”}= \sin(x-\pi/4)$
3) $F(x) = \text{“Sheinwoodian Ice Area”}= \sin(x-\pi/2) = -\cos(x)$
4) $F(x-5\pi/8) = \text{“LSST at cycle (F) Ice Area”}= \sin(x-5\pi/8)$

The effect of carbon dioxide in the mathematical model is not taken into account due to
1) Currently no present evidence of large igneous province activity or other significant source that would extrude carbon dioxide into the atmosphere throughout the Llandovery-Wenlock boundary. 2) Water vapor itself is a greenhouse gas, which is twice as effective in trapping solar
radiation than carbon dioxide according to NASA and the NOAA (Dessler and Sherwood, 2009; Dessler et al., 2013; Soden and Held, 2005). 3) Water vapor volume evaporated from the global oceans is composed of the same compound that makes up the solid volume of precipitated glacial ice which had also influenced ice growth during the last glacial maximum (Hebbeln et al., 1994).

The double integral between the “Atmospheric Humidity Area” function and each of the three “Glacial Ice Area” functions were computed to show the relative Ice Volume that was produced during the Telychian glaciation, Sheinwoodian glaciation, and LSST at cycle (F) glaciation (Figure 12B). The relative ice volume from the Telychian glaciation, according the integration results, was much larger (~57.2% of total ice) than the ice volume produced during the early-Sheinwoodian glaciation (~27.1% of total ice) and the LSST at cycle (F) glaciation (~15.6%) (Appendices E, F, G) (Figure 12B). The integral computations appear to match the magnitudes of the 5th order eustatic sea-level transgression in Te5, the 5th order eustatic sea-level regression in mid-Sh1, and the 5th order eustatic sea-level transgression-regression sequence during early Sh2 throughout the Llandovery-Wenlock boundary (Figure 10) (Loydell, 1998; Cramer and Saltzman, 2007; Haq and Schutter, 2008; Johnson, 2010).

An interesting phenomena found in this study is the “Sheinwoodian Ice Area” function \[\sin(x - \pi/2) = -\cos(x)\] representing glacial ice precipitation at the Ireviken Event, is mathematically derived from the “Atmospheric Humidity Area” function \[\sin(x)\] representing evaporation (Appendix H) (Figure 12B). This mathematically implies that the rate of change of global precipitation (Glacial ice volume) on Earth directly depends on the relationship of the abundance of evaporated water vapor (humidity generation) from Earth’s global oceans. The
differential relationship between these two functions explain the overall decrease in the 5th order eustatic sea-level lowstands from the Telychian glaciation to the LSST at cycle (F) glaciation throughout the Llandovery-Wenlock boundary (Figure 10) (Cramer and Saltzman, 2007). The Telychian glaciation originated at the π/4 position due to the rate of F(x) = F(x)’ indicating that the rate of global precipitation (Sheinwoodian Ice Area) started to increase whereas the rate of global evaporation (Atmospheric Humidity Area) started to decrease during this time, thus activating the Telychian Glaciation (Figure 12B). Then the peak of the Telychian glaciation occurred at the 3π/4 (Early Te4) position due to the rate of F(x) = F(x)’ suggesting the rate of glacial ice formation (Sheinwoodian Ice Area) started to decrease whereas the rate of global evaporation (Atmospheric Humidity Area) started to increase during this time, thus initiating glacial melt during the early Sheinwoodian and lowstand systems tract (F) glaciations (Figure 12B). At the π/4 position, Ice precipitation (Sheinwoodian Ice Area) accelerated the rate of evaporation (Atmospheric Humidity Area) suggesting a mechanism which caused the massive Telychian glaciation to initiate (Figures 10 and 12B). Then at 3π/4 (Early Te4) position, ice precipitation (Sheinwoodian Ice Area) decelerated positively direction as evaporation (Atmospheric Humidity Area) accelerated negatively suggesting a mechanism to why Telychian melting occurred and why the Sheinwoodian and LSST at cycle (F) glaciations failed to reach the ice volume potential of the Telychian glaciation shown in the 5th order eustatic sea-level curve (Figures 10 and 12) (Loydell, 1998; Cramer and Saltzman, 2007; Haq and Schutter, 2008; Johnson, 2010).
CHAPTER 6

CONCLUSIONS

Both the Priekule-20 core and Twilight Creek outcrop sections are composed of alternating local redox conditions before, during, and after the Ireviken Event. Iron speciation in both sections document predominantly anoxic-ferruginous conditions within the local marine bottom waters. Manganese concentrations in both study sites are below the anoxic threshold of 850 ppm indicating local anoxic conditions were present (Figures 4C and 6C). Vanadium concentrations throughout the Llandovery-Wenlock boundary show locally anoxic conditions before the Ireviken Event, less reducing conditions during the Ireviken Event, and then reducing conditions after the conclusion of the Ireviken Event (Figure 9). Broadscale trends in vanadium concentration trends in both sections may be attributed to a global drawdown in trace metal inventories during this time, however because neither site showed consistently euxinic conditions throughout the study interval therefore more work needs to be done to test this hypothesis. Molybdenum concentrations show a general increase in reducing conditions from the late Llandovery to the early Wenlock in both sections (Figure 9).

During the Ireviken extinction event, carbon and sulfur isotopes show an increase in organic carbon burial, and an increase in pyrite burial (Figure 9) suggesting an increase in widespread reducing conditions in the Silurian oceans over the Llandovery-Wenlock Boundary. Carbonate carbon- and organic carbon- stable isotope records from both Latvia and Arctic Canada tropical deeper water successions show a $+3\%$ to $+5\%$ magnitude positive excursion across the Llandovery-Wenlock boundary interval. Pyrite sulfur isotopes in both sections show a
+23 to +25% positive excursion that covaries with the Ireviken CIE records. The new thallium isotope records (Figure 9) suggest globally expanded anoxic conditions prior to the Ireviken CIE. Subsequently, Tl isotopes in the Priekule-20 core show a negative excursion (-2 magnitude in $\varepsilon^{205}\text{Tl}$) during late Sh1-early Sh2 stage slice interval. Tl isotope records from the same interval in the Twilight Creek section show a negative excursion (-1.7 magnitude $\varepsilon^{205}\text{Tl}$) during late Sh1-early Sh2 stage slice interval. This negative Tl isotope excursion is interpreted as a brief period (~ 300-400 kyr) of marine ventilation/oxygenation during the rising limb of the Ireviken CIE. Thallium isotope records from both sections indicate a return to more reducing conditions during peak and falling limb of the Ireviken CIE.

Tl isotope datasets support the hypothesis of an early Sheinwoodian glacial advance coincident with 1) conodont $\delta^{18}\text{O}_{\text{phos}}$ evidence for cooling during rising limb of the Ireviken CIE, 2) diamictite records in parts of Gondwana, and 3) 5th order eustatic sea-level fluctuations (Loydell, 1998; Cramer and Saltzman, 2007; Diaz-Martinez and Grahn, 2007; Lehnert et al., 2010; Trotter et al., 2016). This new geochemical data from shale-dominated successions reveals evidence for oscillating global marine redox conditions (reducing-oxic-reducing) suggesting more complex redox dynamics may have played a significant role in this stepwise extinction event in the early Silurian. The rapid changes in global marine redox state from more reducing (anoxic/possibly euxinic) to more oxic marine settings may be linked to the later part of the stepwise extinction as major increases in oceanic oxygen levels have been shown to be potentially being toxic for organisms adapted to a lower concentrations of oxygen in marine settings (Colin et al., 2015). However, the increase in marine $\text{O}_2$ levels suggested to occur during
the latter part of the Ireviken extinction event does not explain the initiation of this stepwise extinction event during the late Llandovery. As the initiation of the negative Tl excursion in both sections is recorded after the initiation of the carbon isotope excursions and pyrite sulfur isotope excursions (Figure 4 and Figure 6). Therefore, more research needs to be done on understanding the possible trigger mechanisms and early phases of the Ireviken extinction event.

One potential factor for the initiation of the Ireviken Event is a linkage to rising sea-level during the late Telychian. The 5th order glacio-eustatic sea-level rise was caused by a period where Telychian ice sheets retreated most likely by the deceleration of humidity generation relative to ice precipitation, generating a large transgressional systems track stage in the late Telychian (Te5) and a high systems track stage in the early Sheinwoodian (Sh1) (Cramer and Saltzman, 2007). The change in humidity and ice precipitation generating glacier growth most likely was influenced by Earth’s skewed paleogeography in concert with apsidal precession as suggested in this study (Figures 1 and 12). The result of the Telychian transgression most likely lead to 1) a migration of the global OMZ from deep continental basinal settings to the newly accommodated shallow basinal settings, migrating reducing conditions in new niche spaces as suggested by the reducing Tl isotope values observed before the Ireviken Event and 2) less detrital nutrients such as phosphorous transporting to the oceans as suggested by the dampened \( \text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}} \) and \( \text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} \) ratios, generating oligotrophic conditions in newly formed accommodation space on shallower shelves (Figures 4, 5, 6, 7, 9) (Hallam and Wignal, 1999; Smith et al., 2001; Poulton et al., 2015). Thus, benthic and planktonic organisms during this time may have been required to migrate shoreward to new shallow environments where detrital
nutrients were low in availability and reducing conditions expanded. After newly reducing oxygen environments were introduced onto shallow continental shelves driven by a rise in eustatic sea-level and a rise in the OMZ chemocline, microorganisms may have been forced to undergo sulfate reduction, thus augmenting euxinic conditions and biotic crisis even further (Figure 9). After the sea-level high stand in Sh1, the Sheinwoodian glaciation in mid-Sh1 in concert with a prior absence of respiring organisms and eustatic sea level change, generated the large thallium isotope excursion which could have further influenced the stepwise biotic crisis during the peak Ireviken CIE.
Figure 1: Palaeogeographical map of the Early Silurian displaying both the Priekule core and Arctic Canada sample localities (Blakey, 2012). Red star = Priekule Core (Latvia). Yellow Star = Arctic Canada Outcrop samples.
Figure 2: Modern map of the southern Scandinavian region showing the Priekule-20 drill core located on the western margin of Latvia within the Baltic Basin (Kiipli et al., 2010). Horizontal axis represents East longitude and vertical axis represents North latitude.
Figure 3: Modern map of the Arctic Canada region showing the Twilight Creek (TWC) outcrop located on Bathurst Island within the Cape Phillips Basin (Noble et al., 2012). Horizontal axis represents East longitude and vertical axis represents North latitude.
Figure 4: Stratigraphic column and geochemical data of deep-water grey laminated calcareous shales from the Priekule-20 drill core (Baltic Basin, Latvia). Graptolite biostratigraphy data are from Kiipli et al. (2010 and references therein). A) $\delta^{13}$C$_{carb}$ data & $\delta^{13}$C$_{org}$ data B) $\delta^{34}$S$_{pyr}$ data C) Manganese concentration (carbonate corrected and carbonate uncorrected D) $\varepsilon^{205}$Tl data with error bars ($2\sigma$).
Figure 5: Stratigraphic column and geochemical data of deep-water grey laminsted calcareous shales from the Priekule-20 drill core (Baltic Basin, Latvia). Graptolite biostratigraphy data are from Kiipli et al. (2010 and references therein). A) Fe\textsubscript{py}/Fe\textsubscript{HR} data with error bars (2\(\sigma\)) B) Fe\textsubscript{mag}/Fe\textsubscript{HR} data with error bars (2\(\sigma\)) C) Fe\textsubscript{HR}/Fe\textsubscript{T} data with error bars (2\(\sigma\)) D) Fe/Al data with error bars (2\(\sigma\)) E) Vanadium concentration (carbonate corrected and carbonate uncorrected) F) Molybdenum concentrations (carbonate corrected and carbonate uncorrected).
Figure 6: Stratigraphic column and geochemical data of deep-water black shales and carbonates from the Twilight Creek outcrop section (Cape Phillips Basin, Canada). Graptolite biostratigraphy, $\delta^{13}$C$_{carb}$, and $\delta^{13}$C$_{org}$, data from Noble et al. (2005, 2012 and references therein). A) $\delta^{13}$C$_{carb}$ data & $\delta^{13}$C$_{org}$ data  B) $\delta^{34}$S$_{pyr}$ data  C) Manganese concentration (carbonate corrected and carbonate uncorrected)  D) $\varepsilon^{205}$Tl data with error bars (2$\sigma$).
Figure 7: Stratigraphic column and geochemical data of deep-water black shales and carbonates from the Twilight Creek outcrop section (Cape Phillips Basin, Canada). Graptolite biostratigraphy data from Noble et al. (2005, 2012 and references therein). A) $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ data with error bars ($2\sigma$) (faded points are diagenetically altered) B) $\text{Fe}_{\text{mag}}/\text{Fe}_{\text{HR}}$ $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ data with error bars ($2\sigma$) (faded points are diagenetically altered) C) $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ data with error bars ($2\sigma$) (faded data points are diagenetically altered) D) $\text{Fe}/\text{Al}$ ratios with error bars ($2\sigma$) (faded points are diagenetically altered) E) Vanadium concentration (carbonate corrected and carbonate uncorrected) F) Molybdenum concentrations (carbonate corrected and carbonate uncorrected).
Figure 8: Schematic reconstruction of redox evolution across the Llandovery-Wenlock boundary in the early Silurian showing reducing-oxic-reducing global redox conditions (Young et al., 2019). Yellow region = sulfidic portion of oxygen minimum zone (OMZ) and black region = non-sulfidic portion of OMZ. Lighter blue water color = warmer and less oxygenated waters, darker blue water color = cooler and increased oxygenated waters. Grey stratigraphic column shows approximate paleoocean basin location of Priekule-20 core. A) Increased OMZ and decreased euxinia occurring during the rising limb of the Ireviken carbon isotope excursion (CIE) during Telychian series stage 5 (Te5). B) Decreased OMZ and increasing euxinic conditions during the peak Ireviken CIE during Sheinwoodian series stage 1 (Sh1). C) Increased OMZ and increasing euxinic conditions at the falling limb of the Ireviken CIE during Sheinwoodian series stage 2 (Sh2).
Figure 9: Stratigraphic redox perturbation changes of carbon and sulfur isotopes, ($\delta^{13}C_{\text{carb}}$ from Cramer et al., 2010; Kiipli et al., 2010; Noble et al., 2012; $\delta^{34}S_{\text{CAS}}$ from Young et al., 2019; $\delta^{34}S_{\text{pyr}}$ (this study), I/(Ca+Mg) ratios, (Young et al., 2019: red, Nevada and green, Tennessee) oxygen isotopes ($\delta^{18}O_{\text{apatite}}$ from Lehnert et al., 2010), thallium isotopes ($\varepsilon^{205}\text{Tl}$ from this study), Fe-speciation (this study), and trace metals (this study). Biotic turnover and extinction rates determined stratigraphically (Jeppsson, 1997; Melchin et al., 1998; Munnecke et al., 2003; Calner, 2008; Cooper et al., 2014) during the Ireviken CIE. Global redox conditions are determined by Young et al (2019) and this study. 3rd and 5th order eustatic sea-level curves modified from Cramer and Saltzman (2007).
Timing of Eccentricity Cycles, Thermohaline Circulation, Glaciation, and Sea-Level (Priekule-20 Core)

- **Era Ep. Stg. S.S. Zone**
- **Ranges**
- **Depth (m)**
- **Fe* / Fe**
- **More Total Seasonal Weathering**
- **More Oxidizing**
- **More Reducing**

- **Sh3**
- **Sh2**
- **Sh1**
- **M. cephalotes**
- **C. regulari*/M. cephalotes**
- **C. regulari*/M. cephalotes**

- **Wenlock-Sherwoodian**
- **Silurian**
- **Llandovery-Telychian**

- **1,200**
- **1,220**
- **1,240**
- **1,260**
- **1,280**
- **1,300**
- **1,320** (1,332 m - 1,335 m) (O. spiralis?)
- **1,340**

- **5th Order Eustatic Sea-Level and Glacial Tilt Records**
- **Low**
- **High**

- **~15.6% of Total Ice Volume**
- **~27.1% of Total Ice Volume**
- **~57.2% of Total Ice Volume**

- **1,200**
- **1,220**
- **1,240**
- **1,260**
- **1,280**
- **1,300**
- **1,320** (1,332 m - 1,335 m) (O. crenulata?)

- **1,340**

- **Conclusion**

- **LEGEND**

- **5° w.e. Eustatic Sea Level Curve**
- **Fe* / Fe** peaks representing eccentricity cycles
Figure 10: Timing of Fe\textsubscript{py}/Fe\textsubscript{HR} ratios, Fe\textsubscript{mag}/Fe\textsubscript{HR} ratios (Tidal/Seasonal Weathering), Tl isotopes (Thermohaline Circulation), and 5\textsuperscript{th} order eustatic sea-level curve (Loydell, 1998; Cramer and Saltzman, 2007; Haq and Schutter, 2008; Johnson, 2010), glacial tillite and glaciation records (Grahn and Caputo, 1992; Caputo, 1998; Johnson, 2006, 2010; Diaz-Martinez and Grahn, 2007; Loydell, 2007; Page et al., 2007; Munnecke et al., 2010; Ghienne et al., 2013; Clayer and Desrochers, 2014). The eccentricity cycle anomalies (A-H) that are matched up with glacial tillite records, 5\textsuperscript{th} order sea-level lowstands, and negative thallium isotope perturbations identify as critical maximums for glacial function calibration. Note the first eccentricity cycle (A) “Red Bed” (\textit{N. crenulata}) appearance after the Valgu event occurs in the mid-late Telychian due to intense weathering of Fe-oxides under extreme humid conditions possibly caused by maximum long axis eccentrical radius between the Earth and Sun, representing the “Maximum Humidity Area” function crest point of the “Atmospheric Humidity Area” function. Then the (C) Early-Te4 eccentricity cycle co-occurs with the Telychian Glaciation based upon lowstanding sea-level, glacial tillites, and small negative Tl excursion, representing the “Maximum Telychian Glaciation Ice Cap Area” function crest point of the “Telychian Ice Area” function. The (E) Mid-Sh1 eccentricity cycle co-occurs with the Sheinwoodian Glaciation based upon another lowstand in eustatic sea-level, glacial tillites, and large negative Tl excursion, representing the “Maximum Sheinwoodian Glaciation Ice Cap Area” function crest point of the “Sheinwoodian Ice Area” function. Finally, the (F) Early-Sh2 eccentricity cycle co-occurs with a small sea-level low stand termed “LSST at cycle (F)” based upon a eustatic sea-level lowstand and the latter part of the Tl excursion, representing the “Maximum LSST at Cycle (F) Ice Cap Area” function crest point of the “LSST at cycle (F) Ice Area” function. The Blue, Brown, and Green bars on the 5\textsuperscript{th} order eustatic sea-level curve represent the calculated Ice Volume that was produced during each glaciation throughout the Llandovery-Wenlock boundary, generating the 5\textsuperscript{th} order eustatic sea-level changes. The Ice Volume calculations were generated from the “Glacial Charger” model shown in the figures below.
Figure 11: Schematic showing the relative distance and positioning of the Earth to the Sun in addition to the relative gravitational forces, local sea-level, and seasonal (Monsoonal and Hurricane) weathering patterns determined by Fe\textsubscript{mag}/Fe\textsubscript{HR} patterns before, during, and after the Ireviken Event from the Southern paleogeographic hemisphere (Priekule-20 core) and the Northern paleogeographic hemisphere (Twilight Creek Section (East View)). 1) Relative positioning of the Earth before the Ireviken Event, 2) relative positioning of the Earth during the Ireviken Event, 3) relative positioning of the Earth after the Ireviken Event. A-H are the relative positions of the Sun shown by eccentricity signals found in the Priekule-20 core (Figure 10). A) Relative position of the Earth to the Sun during the deposition of the first appearance of the “Red Bed” (*N. crenulata* biozone) in the middle-upper Telychian (Figure 10). B) Relative position of the Earth to the Sun during the first documented eccentricity cycle in mid-Te3 (“Red bed” *O. spiralis* biozone) (Figure 10). C) Relative position of the Earth to the Sun during the second documented eccentricity cycle in early Te4 (Figure 10). D) Relative position of the Earth to the Sun during the third documented eccentricity cycle in early Te5 (Figure 10). E) Relative position of the Earth to the Sun during Sh1, signal is not documented due to high eustatic sea level during Sh1 (Figure 10). F) Relative position of the Earth to the Sun during the fourth documented eccentricity cycle in early Sh2 (Figure 10). G) Relative position of the Earth to the Sun during the fifth documented eccentricity cycle in late Sh2 (Figure 10). H) Relative position of the Earth to the Sun during the sixth documented eccentricity cycle in early Sh3 (Figure 10). Note that eccentricity positions A-D represent intense evaporation/humidity generation from the Northern paleogeographic hemisphere (Panthalassic Ocean) Summers and more Fe\textsubscript{mag} weathering in the Southern paleogeographic hemisphere Winters due to lower local sea-level, longer Southern hemisphere Winter (wet) season, and potentially more intense monsoonal activity documented in the Priekule-20 core (wet) season. Note that eccentricity positions F-H represent less evaporation/humidity generation from the Southern paleogeographic hemisphere (Rheic Ocean) Winters and more Fe\textsubscript{mag} weathering in the Northern paleogeographic hemisphere Summers due to lower local sea-level, longer Northern hemisphere Summer (wet) season, and potentially more intense hurricane activity documented in the Priekule-20 core and, to an extent, the Twilight Creek Section (Figure 10B and 10).
Figure 12: A) Glacial Charger Model showing the relative distance and positioning of the Earth to the Sun determined by Fe$_{mag}$/Fe$_{HR}$ patterns before, during, and after the Ireviken Event from the Southern paleogeographic hemisphere (Priekule-20 core) and the Northern paleogeographic hemisphere (TWC) (North View). Each eccentricity cycle shown has Earth displayed in the aphelion position with Earth’s rotational axis tilted towards the left where the North symbol is pointing. Black curve represents general dimensionless “Atmospheric Humidity Area” function, blue curve represents general dimensionless “Telychian Ice Area” function, brown curve represents dimensionless “Sheinwoodian Ice Area” function, and green curve represents dimensionless “LSST at cycle (F) Ice Area” function. A) Relative position of the Earth during “Red Bed” (*N. crenulata* biozone) deposition ($\pi/2$), maximum humidity (evaporation) generation area, and where Sheinwoodian ice cap area starts to increase. B) Relative position of the first documented eccentricity cycle during mid Te3 ($5\pi/8$) (Red bed *O. spiralis* biozone) and where LSST at cycle (F) ice cap area begins to increase. C) Relative position of the Earth’s second documented eccentricity cycle during early Te4 ($3\pi/4$) and where Telychian ice cap area reaches its maximum area. D) Relative position of the Earth’s third documented eccentricity cycle during early Te5 ($7\pi/8$). E) Relative position of the Earth’s eccentricity cycle during the Ireviken Event in early Sh1 ($\pi$) where the humidity (evaporation) generation area is at its minimum and where the Sheinwoodian ice cap area reaches its maximum. F) Relative position of the Earth’s fourth documented eccentricity cycle during early Sh2 ($9\pi/8$) and where LSST at cycle (F) ice cap area reaches its maximum area. G) Relative position of the Earth’s fifth documented eccentricity cycle during late Sh2 ($5\pi/4$) where the Telychian ice cap area is at its minimum. H) Relative position of the Earth’s sixth documented eccentricity cycle during early Sh3 ($11\pi/8$). B) Graph showing the function relationships between Atmospheric Humidity Area, Telychian Ice Area, Sheinwoodian Ice Area, and LSST at cycle (F) Ice Area. Shaded regions (integrals) under the curves represent the relative ice and water volumes generated during the Telychian glaciation (57.2% of Total Ice), Sheinwoodian glaciation (27.1% of Total Ice), and LSST at cycle (F) glaciation (15.6 % of Total Ice) (Calculations made in appendices E, F, and G) which appear to match the sea-level changes represented in the 5th order eustatic sea level curve (Figure 10) (Loydell, 1998; Cramer and Saltzman, 2007; Haq and Schutter, 2008; Johnson, 2010). The “Sheinwoodian Ice Area” (Brown curve) function at the Ireviken event is derived from the “Atmospheric Humidity Area” (Black curve) function (Appendix H). The black circles are the points in time where rates of the “Atmospheric Humidity Area” and “Sheinwoodian Ice Area” functions equal each other. At the $\pi/4$ eccentricity cycle, the rate of global evaporation (Atmospheric Humidity Area function) begins to positively decrease, and the rate of global ice precipitation (Sheinwoodian Ice Area function) begins to positively increase suggesting where the “Activation energy point” of the Telychian glaciation starts. At the $3\pi/4$ eccentricity cycle (Early Te4), the rate of global evaporation (Atmospheric Humidity Area function) begins to negatively increase, and the rate of global ice precipitation (Sheinwoodian Ice Area function) begins to positively decrease suggesting where the “Deactivation energy point” of the Telychian glaciation starts/melting begins. The (C) Early-Te4 eccentricity cycle ($3\pi/4$) (*C. lapworthi and
Figure 12 - continued
*C. insectus* biozones) is also the point in time where melting of the Telychian glaciation initiates (Figure 10) (Loydell, 1998; Cramer and Saltzman, 2007; Haq and Schutter, 2008; Johnson, 2010).
APPENDIX B

BALTIC BASIN – LATVIA DATA SET

Table 1: Proxy data generated from the Priekule-20 core including: Depth of core (meters), δ¹³C_{carb} (‰), δ¹⁸O_{carb} (‰), δ¹³C_{org} (‰), TIC – Total Inorganic Carbon (%), TOC – Total Organic Carbon (%), δ³⁴S_{pyr} (‰), Fe_{HR}/Fe_{TOT} (Ratio), Fe_{py}/Fe_{HR} (Ratio), Fe_{mag}/Fe_{HR} (Ratio), Fe/Al (Ratio), ε²⁰⁵Tl (epsilon notation), V (ppm), Mn (ppm), Mo (ppm), U (ppm), Fe_{TOT} (%), V (ppm) (carbonate corrected), Mn (ppm) (carbonate corrected), Mo (ppm) (carbonate corrected), U (ppm) (carbonate corrected).

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<th>Fe_{HR}/Fe_{TOT}</th>
<th>Fe_{mag}/Fe_{HR}</th>
<th>Fe/Al</th>
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Table 1 - continued
## APPENDIX C

### CAPE PHILLIPS BASIN – BATHURST ISLAND, ARCTIC CANADA DATA SET

Table 2: Proxy data generated from the Twilight Creek outcrop section including: Length of outcrop (meters), $\delta^{13}C_{\text{carb}}$ ($\%o$), $\delta^{18}O_{\text{carb}}$ ($\%o$), $\delta^{13}C_{\text{org}}$ ($\%o$), TIC – Total Inorganic Carbon ($\%$), TOC – Total Organic Carbon ($\%$), $\delta^{34}S_{\text{pyr}}$ ($\%o$), Fe$_{\text{HR/Fe_T}}$ (Ratio), Fe$_{\text{py}}$/Fe$_{\text{HR}}$ (Ratio), Fe$_{\text{mag}}$/Fe$_{\text{HR}}$ (Ratio), Fe/Al (Ratio), $\varepsilon^{206}$Ti (epsilon notation), V (ppm), Mn (ppm), Mo (ppm), U (ppm), Fe$_{\text{HR}}$ ($\%$), Fe/Al (carbonate corrected), Mn (ppm) (carbonate corrected), Mo (ppm) (carbonate corrected), U (ppm) (carbonate corrected). Note length of outcrop (meters), $\delta^{13}C_{\text{carb}}$ ($\%o$), $\delta^{18}O_{\text{carb}}$ ($\%o$), $\delta^{13}C_{\text{org}}$ ($\%o$), TIC – Total Inorganic Carbon ($\%$), TOC – Total Organic Carbon ($\%$) were generated previously by Noble et al. (2005).

| Sample Number | Horizon (m) | $\delta^{13}C_{\text{carb}}$ ($\%o$) | $\delta^{18}O_{\text{carb}}$ ($\%o$) | $\delta^{13}C_{\text{org}}$ | $\delta^{34}S_{\text{pyr}}$ ($\%o$) | Fe$_{\text{HR}}$/Fe$_{\text{T}}$ | Fe$_{\text{py}}$/Fe$_{\text{HR}}$ | Fe$_{\text{mag}}$/Fe$_{\text{HR}}$ | Fe/Al | $\varepsilon^{206}$Ti | V (ppm) | Mn (ppm) | Mo (ppm) | U (ppm) | Fe$_{\text{HR}}$ ($\%$) | Mn (ppm) | Mo (ppm) | U (ppm) | Fe$_{\text{HR}}$ ($\%$) | Mn (ppm) | Mo (ppm) | U (ppm) | Fe$_{\text{HR}}$ ($\%$) | Mn (ppm) | Mo (ppm) | U (ppm) | Fe$_{\text{HR}}$ ($\%$) |
|---------------|-------------|--------------------------------------|--------------------------------------|-----------------------------|-----------------------------|--------------------------------|-------------------------------|-------------------------------|---------|------------------|---------|-----------|----------|---------|-----------------|----------|----------|---------|-----------------|----------|----------|---------|-----------------|
| 98TWC         | 6.0         | 1.03                                 | -7.71                                | 29.06                       | 9                           | 1.73                                 | 8.645                         | 0.38894                      | 0.01817 | 0.437                   | 661.5   | 9.901     | 5        | 5         | 0.029                    | 22.79    | 914.8    | 9.5432   | 82.28                  | 1.574    |
| 98TWC         | 10.5        | 0.78                                 | -7.75                                | 29.48                       | 4                           | 1.93                                 | -                             | -                             | -       | -                           | 13.40   | 83.624    | 1269.0   | 21.681                      | 103.55   |
| 98TWC         | 16.0        | 0.03                                 | -7.32                                | 29.36                       | 4                           | 1.68                                 | 9.539                         | 0.7729                      | -       | -                           | 6.26    | 177.4     | 16.18    | 1.583                      | 3.40      |
| 98TWC         | 18.0        | 1.03                                 | -7.07                                | 29.26                       | 4                           | 2.05                                 | 3.941                         | 0.52592                      | 0.02026 | 61.10                    | 1.42    | 71.27     | 5        | 63.66     | 113.67                   | 24.81    | 25.816   | 103.45   | -                     | 1.822    |
| 98TWC         | 20.0        | 1.46                                 | -7.64                                | 28.94                       | 4                           | 2.61                                 | 0.738                         | 0.49901                      | 0.02902 | 0.8001                   | 7.32    | 115.81    | 118.11   | 28.048                      | 99.07     |
| 98TWC         | 22.0        | 1.59                                 | -8.34                                | 28.55                       | 7                           | 3.32                                 | 8.225                         | 0.6326                      | -       | 3.00                    | 0.429   | 713.6     | 11.87    | 1.22       | 61.86                    | 15.45    | 76.267   | -        | -                     | 2.202    |
| 98TWC         | 24.0        | 2.20                                 | -7.59                                | 27.65                       | 0                           | 3.53                                 | 7.344                         | 0.70047                      | 0.01315 | 8.24                     | 1.74    | 62.53     | 6        | 58.64     | 84.99                   | 15.15    | 91.669   | -        | -                     | 2.023    |
| 98TWC         | 28.0        | 2.04                                 | -8.08                                | 26.91                       | 8                           | 1.56                                 | 16.69                         | 1.5151                      | -       | 50.6                    | 0.518   | 747.4     | 13.37    | 2.023                   | 54.541    | 1338     | 15183    | 114.52                      |
| 98TWC         | 32.0        | 2.03                                 | -8.32                                | 27.58                       | 5                           | 1.08                                 | 21.22                         | 1.2101                      | -       | 83.4                    | 2.95    | 62.53     | 6        | 61.86     | 54.541                   | 1338     | 15183    | 114.52   | -                     | 2.023    |
| 98TWC         | 36.0        | 1.96                                 | -8.26                                | 28.02                       | 1                           | 0.79                                 | 15.26                         | 0.16177                      | 0.01352 | 8.24                     | 2.34    | 37.66     | 6        | 57.29     | 60.19                   | 1219     | 156.12   | 105.08   | -                     | 2.023    |
| 98TWC         | 38.0        | 2.48                                 | -8.01                                | 28.18                       | 5                           | 1.26                                 | 13.42                         | 0.1923                      | 0.02245 | 8.24                     | 4.27    | 34.51     | 8        | 55.22     | 63.316                  | 1158     | 167.91   | 101.29   | -                     | 2.023    |
| 98TWC         | 40.0        | 1.34                                 | -8.01                                | 28.18                       | 5                           | 1.26                                 | 13.42                         | 0.1923                      | 0.02245 | 8.24                     | 4.27    | 34.51     | 8        | 55.22     | 63.316                  | 1158     | 167.91   | 101.29   | -                     | 2.023    |
| 98TWC         | 42.0        | 6.85                                 | -                                    |                            |                            |                                      |                                |                               |           |                                      | 9.5432   | 82.28                | -        | -                     | 2.023    |

Note: The table includes proxy data generated from the Twilight Creek outcrop section, with columns for sample number, horizon, isotopic ratios, and chemical concentrations. The data set includes measurements of carbon and oxygen isotopes, Fe/Al ratios, and other geochemical parameters, providing insights into the paleoenvironmental conditions of the area.
| Sample | Horiz. (m) | $\delta^{13}$C | $\delta^{18}$O | $\delta^{18}$O | Fe$_{M}$/Fe$_{T}$ | Fe$_{M}$/Fe$_{T}$ | Femag/Fe$_{T}$ | Fe$_{Al}$/Al | Fe$_{Fe}$/Fe$_{T}$ | Fe$_{Fe}$/Fe$_{M}$ | V (ppm) | V (ppm) | V (ppm) | V (ppm) | Mn (ppm) | Mn (ppm) | Mn (ppm) | Mn (ppm) | Mo (ppm) | Mo (ppm) | Mo (ppm) | Mo (ppm) | U (ppm) | U (ppm) | U (ppm) | U (ppm) |
|--------|------------|---------------|---------------|---------------|----------------|----------------|---------------|--------------|----------------|----------------|---------|---------|---------|---------|-----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 98TWC  | 45         | 0.60          | -8.11         | 28.93         | 2              | 0.82           | 19.06         | 8             | 0.37727       | 0.05861       | 1.2966  | 0.961   | 0.961   | 0.961   | 6         | 27.7    | 8       | 7       | 56.88   | 52.196  | 13.12   | 13.653  | 107.18     |
| 45m    | 45         | 0.60          | -8.11         | 28.93         | 2              | 0.82           | 19.06         | 8             | 0.37727       | 0.05861       | 1.2966  | 0.961   | 0.961   | 0.961   | 6         | 27.7    | 8       | 7       | 56.88   | 52.196  | 13.12   | 13.653  | 107.18     |
| 50m    | 50         | 0.75          | -9.05         | 29.33         | 6              | 1.03           | 17.7          | 1.9592        | 0.09823       | 0.02844       | 8       | 2.29    | 32.3    | 19.60   | 7         | 8       | 59.96   | 2       | 59.477  | 1355    | 14.911  | 110.43  |          |         |
| 98TWC  | 62         | -0.46         | -8.59         | 30.86         | 0              | 1.74           | 27.55         | 5             | 0.53553       | 0.05797       | 3       | 274.4   | 752.6   | 4       | 63.07    | 1       | 412.93  | 1133    | 29.504  | 94.917  |          |         |
| 62m    | 62         | -0.46         | -8.59         | 30.86         | 0              | 1.74           | 27.55         | 5             | 0.53553       | 0.05797       | 3       | 274.4   | 752.6   | 4       | 63.07    | 1       | 412.93  | 1133    | 29.504  | 94.917  |          |         |
| 98TWC  | 66         | -1.13         | -7.43         | 31.37         | 0              | 2.08           | 28.49         | 2             | 0.69221       | 0.14653       | 3.28    | 404.3   | 6       | 24.7    | 67.7    | 1.425   | 590.33  | 1099    | 36.061  | 98.834  |          |         |
| 66m    | 66         | -1.13         | -7.43         | 31.37         | 0              | 2.08           | 28.49         | 2             | 0.69221       | 0.14653       | 3.28    | 404.3   | 6       | 24.7    | 67.7    | 1.425   | 590.33  | 1099    | 36.061  | 98.834  |          |         |
| 98TWC  | 72         | 0.09          | -8.59         | 31.85         | 7              | 2.73           | 31.1          | 9             | 0.62988       | 0.0591       | 4       | 663.2   | 4       | 8      | 66.22   | 5       | 871.99  | 1015    | 26.949  | 87.056  |          |         |
| 98TWC  | 72         | 0.09          | -8.59         | 31.85         | 7              | 2.73           | 31.1          | 9             | 0.62988       | 0.0591       | 4       | 663.2   | 4       | 8      | 66.22   | 5       | 871.99  | 1015    | 26.949  | 87.056  |          |         |
| 98TWC  | 76         | -0.09         | -8.83         | 30.98         | 0              | 2.99           | 23.94         | 2             | 0.65623       | 0.04926       | 8       | 3.23    | 621.7   | 6       | 8       | 58.91   | 1.196   | 731.76  | 800.9   | 20.795  | 69.337  |          |         |
| 80m    | 80         | -0.10         | -9.00         | 31.31         | 4              | 3.56           | 25.22         | 1             | 0.6575        | 0.06899       | 8       | 850.4   | 5       | 4      | 68.63   | 1       | 1096.5  | 982.4   | 29.184  | 88.493  |          |         |
| 98TWC  | 84         | -0.57         | -8.02         | 31.70         | 2              | 1.83           | 29.34         | 1             | 0.55904       | 0.09395       | 0.541   | 2.53    | 446.5   | 1       | 59.67   | 1       | 649.71  | 1100    | 21.799  | 86.829  |          |         |
APPENDIX D

**FE_{mag}/FE_{HR} LOGICAL PATHWAYS**

**Thresholds of determining Earth’s relative positioning and distance from the Sun:**

- Two sections/cores are analyzed simultaneously in geologic time to compare/contrast weathering and gravitational patterns.
- Each section/core spanning the particular geologic event of interest must have been deposited in different paleogeographic hemispheres at the time of deposition.
- Negative anomalies in the Fe\textsubscript{mag}/Fe\textsubscript{HR} ratios below the 0.7 threshold need to be in sync with positive anomalies in Fe\textsubscript{mag}/Fe\textsubscript{HR} ratios.
- Criteria for when the Northern hemisphere’s (Summer) eccentric axis is closest to the Sun (Perihelion):
  1. Highest recorded Fe\textsubscript{mag}/Fe\textsubscript{HR} anomaly ratios recorded in the Northern paleogeographic hemisphere section/core of study synchronous in time (Biostratigraphy) to the,
  2. Lowest recorded Fe\textsubscript{mag}/Fe\textsubscript{HR} anomaly ratios recorded in the Southern paleogeographic hemisphere section/core of study.
- Criteria for when the Northern hemisphere (Summer) and Southern Hemisphere (Winter) are of equal eccentric axis distance away from the Sun is shown by the similar change in Fe\textsubscript{mag}/Fe\textsubscript{HR} anomaly ratios in both hemisphere sections.
- Criteria for when the Southern hemisphere’s (Winter) eccentric axis is closest to the Sun (Perihelion):
  1. Lowest Fe\textsubscript{mag}/Fe\textsubscript{HR} anomaly ratios recorded in the Northern Paleogeographic Hemisphere section/core of study synchronous in time (Biostratigraphy) to the,
  2. Highest recorded Fe\textsubscript{mag}/Fe\textsubscript{HR} anomaly ratios recorded in the Southern Paleogeographic Hemisphere section/core of study.

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Logical pathways showing how relative distance and positioning of the Earth to the Sun can be determined by Fe\textsubscript{mag}/Fe\textsubscript{HR} patterns before and after the Ireviken Event from the Southern paleogeographic hemisphere (Priekule-20 core) and the Northern paleogeographic hemisphere (TWC).
APPENDIX E

CALCULATION OF TELYCHIAN TRANSGRESSION

Equations:
1) Atmospheric Humidity Area = sin(x)
2) Telychian Ice Area = sin(x- (π/4))

*Computation of the point in time where Atmospheric Humidity Area and Telychian Ice Area Curves intersect.*

1) sin(x) = sin(x- (π/4))

*Identity sin(a-b) = sin(a)cos(b) – cos(a)sin(b)*
2) sin(x) = sin(x)cos(π/4) – cos(x)sin(π/4)

3) sin(x) = (1/√2)sin(x) – (1/√2)cos(x)

4) sin(x) = (1/√2)(sin(x) – cos(x))

5) (√2)(sin(x)) = sin(x) – cos(x)

6) (√2)(sin(x)) – sin(x) = – cos(x)

7) 0.4142135(sin(x)) = -cos(x)

8) 0.4142135 = -(cos(x)/sin(x))

*Identity (cos(x)/sin(x)) = (1/tan(x))*
9) 0.4142135 = -(1/tan(x))

10) 0.4142135(tan(x)) = -1

11) tan(x) = -(1/ 0.4142135)

12) tan⁻¹(-(1/ 0.4142135)

x = πn – 3π/8

*n can be any integer (-1,0,1) because there are many solutions (times when both curves intersect), but since we are only dealing with one oscillation (between 0 and π) n = 1*
13) $x = \frac{5\pi}{8}$

* = the point of intersection between the Humidity Area Curve and the Mid-Telychian Ice Cap Area Curve.*

*Computation of the latter half of the integration:*

1) $\int_{5\pi/8}^{\pi} \sin(x) \, dx$

2) $[-\cos(x)] (from \frac{5\pi}{8} \text{ to } \pi)$

3) $\cos(\pi) - (-\cos\left(\frac{5\pi}{8}\right))$

4) $1 - \left((\sqrt{2} - \sqrt{2})/2\right) = \approx 0.6173165$

* = latter half of the integral of the Telychian Ice Volume (between $\frac{5\pi}{8}$ and $\pi$)*

*Computation of the initial half of the integration:*

1) $\int_{\pi/4}^{5\pi/8} \sin\left(x - \frac{\pi}{4}\right) \, dx$

*Apply u-substitution (u = $x - \frac{\pi}{4}$)*

2) $\int_{0}^{3\pi/8} \sin(u) \, du$

3) $-\left[\cos(u)\right] \text{ (from } 0 \text{ to } 3\pi/8)$

4) $-\cos(3\pi/8) - (-\cos(0))$

5) $-((\sqrt{2} - \sqrt{2})/2) + 1 = \approx 0.6173165$

* = initial half of the integral of the Telychian Ice Volume (between $\pi/4$ and $\frac{5\pi}{8}$)*

*Adding both halves of the integral*

$= (1 - ((\sqrt{2} - \sqrt{2})/2)) + -((\sqrt{2} - \sqrt{2})/2) + 1)$

$= \approx 1.2346$

* = Relative dimensionless unit of the Telychian Ice Volume*
APPENDIX F

CALCULATION OF SHEINWOODIAN REGRESSION

Equations:
1) Atmospheric Humidity Area = \sin(x)
2) Sheinwoodian Ice Area = \sin(x - \frac{\pi}{2}) = -\cos(x)

*Computation of the point in time where Atmospheric Humidity Area and Sheinwoodian Ice Area Curves intersect.*

\[\sin(x) = \sin(x - \frac{\pi}{2})\]

*Identity \(\sin(x - \frac{\pi}{2}) = -\cos(x)\)*

\[\sin(x) = -\cos(x)\]

3) \((\sin(x)/\cos(x)) = -1\)

*Identity \(\tan(x) = (\sin(x)/\cos(x))\)*

4) \(\tan(x) = -1\)

5) \(x = n\pi - \frac{\pi}{4}\)

*n can be any integer (-1,0,1) because there are many solutions (times when both curves intersect), but since we are only dealing with one oscillation (between 0 and \(\pi\)) \(n = 1\)*

6) \(x = \frac{3\pi}{4}\)

*This is the point of intersection between the Humidity Area Curve and the Sheinwoodian Ice Area Curve.*

*Computation of the latter half of the integration:*

1) \[
\int_{\frac{\pi}{4}}^{\pi} \sin(x) dx
\]

2) \([-\cos(x)] (from \frac{3\pi}{4} to \pi)\)

3) \(-\cos(\pi) - (-\cos(\frac{3\pi}{4}))\)

4) \(1 - (1/\sqrt{2})\)

* = latter half of the integral of the Sheinwoodian Ice Volume (between \(\frac{3\pi}{4}\) and \(\pi\))*
*Computation of the initial half of the integration:*

\[ 1) = \int_{\pi/2}^{3\pi/4} \sin \left( x - \frac{\pi}{2} \right) dx \]

*Identity \( \sin(x - \frac{\pi}{2}) = -\cos(x) \)*

\[ 2) = \int_{\pi/2}^{3\pi/4} -\cos(x) dx \]

\[ 3) = -1 \int_{\pi/2}^{3\pi/4} \cos(x) dx \]

\[ 4) = -\sin(\pi) \] (from \( \frac{\pi}{2} \) to \( 3\pi/4 \))

\[ 5) = -\sin(3\pi/4) - (-\sin(\pi/2)) \]

\[ 6) = \left( -\frac{1}{\sqrt{2}} \right) + 1 \]

* = half of the integral of the Sheinwoodian Ice Volume (between \( \frac{\pi}{2} \) and \( \frac{3\pi}{4} \))

*Adding both halves of the integral*

\[ 1) = (1 - (1/\sqrt{2})) + ((-1/\sqrt{2}) + 1) \]

\[ = 0.585786 \]

* = Relative dimensionless unit of Sheinwoodian Glaciation Ice Volume*
APPENDIX G

CALCULATION OF SEA LEVEL LOWSTAND SYSTEMS TRACK (LSST) AT ECCENTRICITY CYCLE (F)

Equations:
1) Atmospheric Humidity Area = \sin(x)
2) LSST at cycle (F) Ice Area = \sin(x - \left(\frac{5\pi}{8}\right))

*Computation of the point in time where Atmospheric Humidity Area LSST at cycle (F) Ice Area Curves intersect.*

1) \sin(x) = \sin(x - \left(\frac{5\pi}{8}\right))

*Identity \sin(a-b) = \sin(a)\cos(b) - \cos(a)\sin(b)*

2) \sin(x) = \sin(x)\cos\left(\frac{5\pi}{8}\right) - \cos(x)\sin\left(\frac{5\pi}{8}\right)

3) \sin(x) = \sin(x)(-0.382683) - \cos(x)(0.923879)

4) \sin(x) + (0.382683)(\sin(x)) = -(0.923879)(\cos(x))

5) 1.382683(\sin(x)) = -(0.923879)(\cos(x))

6) \sin(x) = (-0.6681788)(\cos(x))

7) \sin(x)/\cos(x) = -0.6681788

*Identity \sin(x)/\cos(x) = \tan(x)*

8) \tan(x) = -0.6681788

X = n \pi - 0.5890487

*n can be any integer (-1,0,1) because there are many solutions (times when both curves intersect), but since we are only dealing with one oscillation (between 0 and \pi) n = 1*

9) x = 2.552544

*This is the point of intersection between the Atmospheric Humidity Area Curve and the LSST at cycle (F) Ice Area Curve.*

*Computation of the latter half of the integration:*

1) = \int_{2.552524}^{\pi} \sin(x)dx
2) \([-\cos(x)] \ (from \ 2.552524 \ to \ \pi)\)

3) \(-\cos(\pi) - (-\cos(2.552524))\)

4) \(0.168542\)

* = latter half of the integral of the LSST at cycle (F) Volume (between 2.552524 and \(\pi\))

*Computation of the initial half of the integration:*

1) \(\int_{\frac{5\pi}{8}}^{2.552544} \sin \left( x - \frac{5\pi}{8} \right) \, dx\)

*Identity \(\sin(x - \frac{5\pi}{8}) = -\cos\left(\frac{\pi}{8} - x\right)\)*

2) \(\int_{\frac{5\pi}{8}}^{2.552544} -\cos \left(\frac{\pi}{8} - x\right) \, dx\)

3) \(-\int_{\frac{5\pi}{8}}^{2.552544} \cos \left(\frac{\pi}{8} - x\right) \, dx\)

*apply \(u\)-substitution \(u = \frac{\pi}{8} - x\), \(du = -dx\)

4) \(-\int_{-\frac{\pi}{2}}^{-2.15984} \cos (u) \, du\)

*Switch the order of the integration bounds of \(\cos(u)\) so that the upper bound is larger. Multiply the integrand by -1

5) \(-\int_{-2.15984}^{-\frac{\pi}{2}} \cos (u) \, du\)

6) \([-\sin(u)] \ (from \ -2.15984 \ to \ -\frac{\pi}{2})\)

7) \(-\sin(-\frac{\pi}{2}) - (-\sin(-2.15984))\)

8) \(0.168542\)

* = half of the integral of the LSST at cycle (F) Volume (between \(\frac{5\pi}{8}\) and 2.552544)

*Adding both halves of the integral

1) \(0.168542 + 0.168542\)
Relative dimensionless unit of LSST at cycle (F) Glaciation Ice Volume

*Percentages of Total Ice*

Relative dimensionless Ice Volumes
Telychian Relative Ice Volume = ~1.2346
Sheinwoodian Relative Ice Volume = ~0.585786
LSST at cycle (F) Ice Volume = ~0.337084
Total Ice Volume = ~2.15747

*Percentage of Telychian Ice Volume (represents the Telychian transgression rise in Te5)*
\[
\left(\frac{1.2346}{2.15747}\right) \times 100 = \approx 57.2\%
\]

*Percentage of Sheinwoodian Ice Volume (represents the Sheinwoodian regression in late Sh1)*
\[
\left(\frac{0.585786}{2.15747}\right) \times 100 = \approx 27.1\%
\]

*Percentage of LSST at cycle (F) Ice Volume (represents the Sheinwoodian regression in late Sh1)*
\[
\left(\frac{0.337084}{2.15747}\right) \times 100 = \approx 15.6\%
\]
APPENDIX H

MATHEMATICAL PROOF: DERIVATION OF PRECIPITATION (SHEINWOODIAN ICE AREA) FROM EVAPORATION (ATMOSPHERIC HUMIDITY AREA)

Equations:

Atmospheric Humidity Area = \sin(x)
Sheinwoodian Ice Area = \sin(x - \left(\frac{\pi}{2}\right)) = -\cos(x)

1) \frac{d}{dx} (-\cos(x))

*Factor out constants*

2) \frac{\cos(x)}{\cos(x)}

*Using the chain rule*

*From the limit definition of the derivative \frac{d}{dx} (\cos (x)) *

3) \frac{d}{dx} (\cos (x)) = \lim_{h \to 0} (\cos(x + h) - \cos(x))/h

*Apply the cosine angle addition formula to cos(x+h)*

4) = \lim_{h \to 0} (\cos(x)\cos(h) - \sin(x)\sin(h) - \cos(x))/h

*Rearrange in terms of \cos(x) and \sin(x)*

5) = \lim_{h \to 0} (\cos(x) * ((\cos(h) - 1)/h) - \sin(x) * (\frac{\sin(h)}{h}))

*Multiply numerator and denominator of ((\cos(h)-1)/h) by the conjugate term \cos(h)+1 and expand the numerator*

6) = \lim_{h \to 0} (\cos(x) * ((\cos^2(h) - 1)/((\cos(h) + 1)h) - \sin(x) * (\frac{\sin(h)}{h}))

*Apply the Pythagorean identity \sin^2(h) + \cos^2(h) - 1*

7) = \lim_{h \to 0} (-\cos(x) * ((\sin^2(h) /((\cos(h) + 1)h) - \sin(x) * (\frac{\sin(h)}{h})))
*Factor the inside limit*

\[ 8) = \lim_{h \to 0} \left( -\cos(x) \sin(h) / ((\cos(h) + 1) - \sin(x) \cdot \frac{\sin(h)}{h}) \right) \]

*The limit of a product is the product of the limits:*

\[ 9) = \lim_{h \to 0} \left( -\cos(x) \sin(h) / ((\cos(h) + 1) - \sin(x)) \cdot \left( \lim_{h \to 0} \frac{\sin(h)}{h} \right) \right) \]

*By continuity*

\[ 10) = \lim_{h \to 0} \left( -\cos(x) \sin(h) / ((\cos(h) + 1) - \sin(x)) \cdot \left( \lim_{h \to 0} \frac{\sin(h)}{h} \right) \right) \]

*substitute h=0 due to the limit on the left-hand side*

\[ 11) = (-\cos(x) \sin(0) / ((\cos(0) + 1) - \sin(x)) \cdot \left( \lim_{h \to 0} \frac{\sin(h)}{h} \right) \]

\[ 12) = -\sin(x) \cdot \left( \lim_{h \to 0} \frac{\sin(h)}{h} \right) \]

*substitute h=0 due to the limit on the right-hand side*

\[ 13) = (-\sin(x)) \cdot \left( \frac{\sin(0)}{0} \right) \]

*The derivative of -\cos(x) is \sin(x)*

\[ 14) F(x)' = \sin(x) \]
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BIOGRAPHICAL SKETCH

Daniel J. Gouert is a Roman Catholic from Chapel Hill, North Carolina. He obtained his Bachelor’s of Science Degree from Appalachian State University within the Blue Ridge Mountains of Boone, North Carolina in August 2018. He majored in Geology with a concentration in Quantitative Geoscience in addition to a minor in Mathematics. During his freshman year at Appalachian State, Daniel found his love and curiosity for the natural world after a two-week geological backpacking trip on glaciers and basaltic landscapes along the southern coast of Iceland. One year later, Daniel then became interested in pursuing geological research after a fully funded $2,500 summer internship in Angers, France between his sophomore and junior year. He worked with Dutch scientist Dr. Frans J. Jorissen and other French colleagues on modern Benthic Foraminifera within the Bay of Santu and off of the coast of Normandy, France.

After returning home to the States in preluding his junior year, Daniel then worked along a recently hired professor Dr. Cole T. Edwards on strontium isotopes analysis and paleontological analysis on Devonian aged bulk carbonates and conodont microfossils. During his time as an undergraduate researcher junior through senior year, Daniel conducted field work in Nevada and Utah within the Great Basin and Range region fully funded by a paleontological society of America grant and was awarded over $2,000 in combined research funding to present his research at the southeastern Geological Society of America conference in Knoxville, TN. He also was a Teacher Assistant for Introduction to Historical Geology labs. Finally, before he graduated from Appalachian State University, Daniel obtained a $750 scholarship to participate in a field camp in Morocco where he mapped rocks deposited during snowball Earth. He also was on the Dean’s list for four semesters which is awarded to students obtaining a GPA of a 3.45 or higher.

Once his time at Appalachian State University came to an end, Daniel pursued a Master’s of Science Degree in Geology within the hot and humid University of Florida State in Tallahassee, Florida where he worked with Dr. Seth A. Young on geochemical analysis on deep basinal Silurian black shales. His Master’s Degree was fully funded on a Teaching Assistantship,
which consists of a tuition waiver, and a $16,500 per year stipend. While at Florida State University, Daniel participated in an ExxonMobil short course, taught over 80 students in his ESC 1000 Labs, and was awarded a Geological Society of America Grant ($2,159) to fund costs of travel, research and lab equipment. He presented his Masters research project at the Geological Society of America meeting in Phoenix, Arizona.

Daniel is planning to graduate with his Master’s of Science degree in the Fall of 2020 where he concludes his research along with his Academic career. He is now an intern at the Florida Geological Survey.