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Old Fort Point Formation: Neoproterozoic Negative $\delta^{13}\text{C}$ Excursion Recorded in a Deep-Water
Carbonate Succession

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Geological Sciences

by

Jordan Nicole Lanni

September 2017

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ABSTRACT OF THE THESIS

Old Fort Point Formation: Neoproterozoic Negative $\delta^{13}\text{C}$ Excursion Recorded in a Deep-Water Carbonate Succession

by

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Master of Science, Graduate Program in Geological Sciences
University of California, Riverside, September 2017
Dr. Andrey Bekker, Chairperson

The Precambrian recorded dramatic atmospheric and geochemical fluctuations, such as the “Snowball Earth,” the most severe glaciation in geologic history, and the Earth’s most significant negative carbon isotope excursion, the Shuram Excursion, which has been identified in multiple, globally-disparate locations. The excursion recorded a rapid negative $\delta^{13}\text{C}$ shift to approximately -12‰ and recovery over hundreds of meters in some units, which are predominantly shallow-marine carbonates. The excursion’s poor age constraints currently imply a maximum duration of some forty million years, between 635 Ma and approximately 591 Ma. This requires a large input of carbon-12 over a significant period of geologic time, and while debate exists over whether it is primary or diagenetic in origin, evidence now leans in favor of a primary origin. This study presents $\delta^{13}\text{C}$ data from a deep-water turbiditic carbonate in the Canadian Rockies that has produced a precise Re-Os date of 607.8 ± 4.7 Ma (Kendall, et al., 2004), known as the Old Fort Point Formation. Significantly, this unit records a $\delta^{13}\text{C}$ excursion of -11.5‰ below the stratigraphic level that yielded the Re-Os date. The distinctive $\delta^{13}\text{C}$ record implies that it is correlative to the Shuram Excursion, and moves the Shuram Excursion farther back than previously thought. The presence of multiple excursions between the Shuram Excursion and the

Precambrian-Cambrian boundary indicate that the carbon cycle was in a dynamic state following the meltdown of the Marinoan glaciation. The OFPF helps to constrain the Shuram Excursion, but further work is needed to determine if current stratigraphic correlations based on the assumption of a single large negative excursion in the Ediacaran are correct, or multiple and short-lived carbon isotope excursions are typical for the early part of the Ediacaran and have been mis-correlated in the absence of absolute age constraints.

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Introduction

The Neoproterozoic geologic record reflects significant changes in the geochemical, biological, and tectonic realms. Increasing oxygenation paired with the rise of metazoans and the initiation and termination of the most severe glaciations (“Snowball Earth” scale) in geologic history created the stage for significant shifts in biogeochemical cycles of elements such as carbon. The Snowball Earth conditions were followed by deposition of cap carbonates, whose geochemical signatures of approximately -5‰ $\delta^{13}\text{C}$ indicates that burial of organic matter was significantly suppressed during that time (Hoffman, et al., 1998). Nearer the close of the Ediacaran, the Shuram Excursion recorded $\delta^{13}\text{C}$ values as negative as -12‰ , in some cases persisting over hundreds of meters, and could have lasted millions of years (Burns & Matter, 1993). Geochronology is the key to better understanding the Shuram Excursion, as with few radiogenic dates the duration and cause of the Shuram Excursion are uncertain. The Shuram Excursion is constrained to have occurred after the Marinoan glaciation, that terminated sometime around 635 Ma, and before ca. 591 Ma in South China, which leaves a temporal gap with an approximate duration of 45 Myr (Zhu, et al., 2013). This potentially long duration has raised controversy over the nature of the Neoproterozoic carbon cycle and whether it is a diagenetic overprint or a record of the primary seawater values. While it records covariation between carbon and oxygen, which is a signature of diagenesis, similar, highly negative $\delta^{13}\text{C}$ records are observed in roughly equivalent units on multiple continents. This indicates that the Shuram Excursion indeed records primary seawater composition (Grotzinger, et al., 2011). Other lines of evidence – Ca and Mg isotopes, $\delta^{13}\text{C}_{\text{org}}$ values as low as -40‰ in long-chain *n*-alkanes and mid-chain monomethyl alkanes, and high Sr concentrations from the record of the Excursion in Australia – tip the scales toward a primary signal (Husson, et al., 2015; Lee, et al., 2015). This suggests that the carbon cycle behaved very differently following the Marinoan glaciation alongside the emergence of increasingly more complex Ediacaran animals and rising oxygen levels in the atmosphere-ocean system (Fike, et al., 2006). Better constraining the Shuram Excursion is important to understanding what caused such extreme perturbations to the carbon

cycle with its duration, magnitude, and the inferred range of accompanied redox changes (from pervasive oxygenation to expansion of anoxia) unparalleled in Earth's history

In this study, sedimentological and geochemical data is presented from a deep-water siltstone-carbonate succession in the Rocky Mountains of Alberta, Canada, known as the Old Fort Point Formation (OFPF). The middle member of the formation, a black shale, has been dated at 607.8 ± 4.7 Ma (Kendall, et al., 2004), providing the sole geochronological data point from the entire southern Canadian Cordillera. Stable isotopic analyses reveal a highly negative $\delta^{13}\text{C}$ excursion with a nadir of -11.5‰ resembling the profile of the Shuram Excursion observed elsewhere in other basins. Unlike in other Shuram Excursion units, however, carbon and oxygen isotopes of the OFPF do not covary. They also contain high Sr concentrations and low Mn/Sr ratios. The excursion in the OFPF carbonates occurs below shales that were sampled to obtain the Re-Os date. Together, the evidence presented in this study indicates that this formation recorded the Shuram Excursion and provides a precise time-constraint for the excursion, pushing it back farther than previously estimated. Combined with the ca. 591 Ma age from South China (Zhu, et al., 2013), this could indicate that the excursion did not last as long as previously estimated, or that there are multiple excursions that have erroneously been correlated as isochronous.

This thesis will first present a review of major events of the late Neoproterozoic throughout the Ediacaran, focusing on the Marinoan glaciation and the Shuram Excursion, in addition to a short big-picture introduction to the Windermere Supergroup, of which the OFPF is a part (Chapter 2). Chapter 3 will cover an introduction on past research on the OFPF, though the details of conclusions on this research will be discussed later. The methods will be presented in chapter 4, covering the field work conducted, methods used to conduct stable isotope analyses, to obtain minor and trace element concentrations, how total inorganic carbon (TIC%) was calculated, and petrography. Carbon and oxygen isotope results will be discussed in chapter 5, along with detailed geological field observations, petrographic analyses of samples chosen for trace element concentrations, and the trace element results of that study. Geochemical results are also presented

in tables in appendices C, D, and E. Chapter 6 will present a detailed discussion regarding the evidence for a deep-water deposition, the preservation of the $\delta^{13}\text{C}$ signal, how the OFPF now relates to current stratigraphic correlations in Canada, how the OFPF compares to the Marinoan cap carbonates and the carbonates of the Shuram Excursion, and what the OFPF's Re-Os date means for the Shuram Excursion and knowledge of the larger Neoproterozoic world. Finally, the author's conclusions will be presented in chapter 7.

To sum, with poor biostratigraphic control in the Precambrian, stratigraphy relies on a handful of geochronological dates and, predominantly, chemostratigraphy. This limitation has caused controversy over the durations of significant environmental perturbations such as glaciations and perturbations in the global carbon cycle. In the case of the Shuram Excursion, the potentially long-lived excursion raises concerns over our understanding of the contemporary carbon cycle. Better geochronological constraints will help to shape the interpretations of this event. This study builds upon prior research to suggest that a carbonate succession in Canada records the Shuram Excursion while also providing a Re-Os date that pushes the Excursion farther back than previously estimated.

Chapter 2: Background

This chapter will present concise reviews of the carbon cycle, the Neoproterozoic period, the sedimentology and geochemistry of the Marinoan cap carbonates, the geochemistry of the Shuram Excursion, and a brief overview of the Windermere Supergroup. The carbon cycle has been intensely studied for decades and it is beyond the scope of this work to provide an in-depth review of most of the complex nature of the carbon cycle. Thus, the scope will be limited to the goal of this thesis: establishing the fundamentals of excursions and diagenesis. For more in-depth reviews of the carbon cycle, please see Schidlowski & Aharon, 1992, Hayes & Waldbauer, 2006, Halverson, et al., 2005, and Kump, 1991 and references within those works for more detailed information.

2.1 The Carbon Cycle and Carbon Isotope Excursions

On Earth, the total size of the carbon reservoir is estimated to be over 75 million gigatons. Evidence for carbon's biogeochemical cycle has been observed in rocks containing the earliest evidence of life. Carbon is also integral to the precipitation of one of the most abundant shallow-crustal mineral groups, the carbonates. It has a residence time in the ocean of approximately 100,000 years, with the dominant carbon species in seawater today being bicarbonate (HCO_3^-) (Falkowski, et al., 2000; Schidlowski & Aharon, 1992). It is a critical recorder of shifts in the geochemical and biological realms through time. The two most stable isotopes of carbon are ^{12}C and ^{13}C . The ratio between ^{12}C and ^{13}C is expressed in delta notation in the following equation, as the proportion of ^{13}C to ^{12}C in the sample relative to the proportion of ^{13}C to ^{12}C in the standard,

$$\delta^{13}\text{C} (\text{‰}) = \left(\frac{(^{13}\text{C}/^{12}\text{C} \text{ of sample})}{(^{13}\text{C}/^{12}\text{C} \text{ of standard})} - 1 \right) \times 1000 \quad \text{Eq. 1}$$

where $\delta^{13}\text{C}$ values are reported relative in per mil ‰ relative to the Vienna Pee Dee Belemnite (VPBD). An abundance of carbon-12 results in delta values being “light” or below 0‰, and an abundance of carbon-13 results in delta values being “heavy” or above 0‰.

Since the dawn of life, the carbon cycle and the $\delta^{13}\text{C}$ record of carbonates have been influenced by the balance of biological uptake of carbon and precipitation of carbonate rocks. Sources of carbon in the atmosphere and ocean include volcanic outputs, metamorphic decarbonations, and degassing at mid-ocean ridges, which contribute carbon with $\delta^{13}\text{C}$ value of -5‰ to the atmosphere and ocean (Figure 1). The weathering of carbon-rich rocks on the continents also contributes carbon to the ocean via riverine inputs, which inherit the $\delta^{13}\text{C}$ values of the weathered carbonates. Weathering of continental silicates consumes CO_2 , but the largest and most influential carbon sinks lie in the ocean, where two significant reservoirs of carbon exist: that of dissolved organic carbon (DOC), and that of dissolved inorganic carbon (DIC) (Kump & Arthur, 1999). The surface seawater $\delta^{13}\text{C}$ value is in constant equilibrium with the atmosphere, and $\delta^{13}\text{C}$ becomes increasingly lighter with depth in the oceans due to remineralization of organic matter as it sinks. Carbon-fixers, utilizing the Calvin cycle of photosynthesis and carbon reduction, strongly prefer the lighter carbon isotope and exert a pronounced fractionation of -20 to -30‰ (Schidlowski & Aharon, 1992). This process ultimately buries significant volumes of organic carbon on the seafloor with a corresponding amount of oxygen released to the atmosphere and surface environments in the process. Carbonate precipitation imparts negligible fractionation, and consequently, carbonate rocks preserve the $\delta^{13}\text{C}$ value of seawater, allowing us to constrain the secular trend in the seawater $\delta^{13}\text{C}$ value.

Though DOC is strongly enriched in ^{12}C , inorganic carbon (with approximately -5‰ value now) constitutes a significantly larger reservoir in the ocean ($10,000 \times 10^{12}$ moles C compared to $40,000 \times 10^{12}$ moles C respectively), and when these reservoirs were balanced over most of Earth's history, the seawater $\delta^{13}\text{C}$ signal was approximately 0‰ (Schidlowski & Aharon, 1992; Kump & Arthur, 1999). While carbonate $\delta^{13}\text{C}$ composition through time has been anchored at approximately 0‰, imbalances have produced carbon isotopic excursions, where excesses in ^{13}C (positive excursions) or ^{12}C (negative excursions) indicate significant changes in the biogeochemical carbon cycle (Veizer & Hoefs, 1976; Schidlowski & Aharon, 1992). Excursions are ultimately tied to the

oxidizing power of the atmosphere-ocean system, where periods of decreased oxidation of organic matter and its increased burial rates result in positive excursions, while periods of increased oxidation of organic matter and its decreased burial rates produce negative excursions (Kump & Arthur, 1999; Schidlowski & Aharon, 1992). Combined with other redox-sensitive elements such as sulfur and iron, it is possible to approximate the causes of excursions and global redox conditions through time. The Precambrian is associated with increasingly negative $\delta^{34}\text{S}$ values of sedimentary sulfides (Halverson, et al., 2010), indicating rising oxygen levels sufficient to oxidize pyrite on the continents to produce sulfate and deliver it to the ocean and restrict formation of sedimentary sulfides to local environments with anoxic water column or pore water conditions. The end of deposition of banded iron formations occurred in the Precambrian as well, as the oceans became more oxidized (Young, 2013). In the Neoproterozoic, the $\delta^{13}\text{C}$ trend reflected increasing oxygen levels via positive isotope excursions.

Examples of carbon isotope excursions in the Precambrian include the “Lomagundi Event,” a Paleoproterozoic highly positive $\delta^{13}\text{C}$ excursion thought to be global. It is observed on multiple continents and spans up to tens of kilometers of stratigraphic thickness, and has been tied to the Great Oxidation Event and explained via models such as enhanced organic carbon burial or more acidic continental weathering delivering nutrients to the ocean and driving primary productivity (Bekker & Holland, 2012). Following the “Boring Billion” of the Mesoproterozoic, the early Neoproterozoic period recorded the Bitter Springs Anomaly reported in Australia and Svalbard, below the Sturtian glaciation (Halverson, et al., 2005). The Bitter Springs Anomaly has been linked to true polar wander events (Klaebe, et al., 2016; Halverson, et al., 2007; Maloof, et al., 2006). The Trezona Anomaly preceded the Marinoan glaciation, and has been explained as resulting from various diagenetic processes or by a signal of changes in the seawater $\delta^{13}\text{C}$ signal (Rose, et al., 2012). The Trezona Anomaly was followed by the Marinoan glaciation, where cap carbonates overlying tillites recorded negative $\delta^{13}\text{C}$ values of around -5‰, indicating suppressed biological activity and low burial rates of organic matter. The $\delta^{13}\text{C}$ recovered to a short stratigraphic interval

of positive $\delta^{13}\text{C}$ values, but this was followed by the most negative carbon isotope excursion in geologic history, known as the Shuram Excursion, where $\delta^{13}\text{C}$ values reached -12‰ (Burns & Matter, 1993). The Shuram Excursion remains enigmatic due to its occurrence over significant stratigraphic thicknesses in some units.

In an ideal world where diagenesis and metamorphism left no $\delta^{13}\text{C}$ overprint, the $\delta^{13}\text{C}$ values of carbonates would reflect the primary seawater value. Realistically, however, diagenesis and metamorphism disturbs the $\delta^{13}\text{C}$ record and results in negative $\delta^{13}\text{C}$ values (Banner & Hanson, 1990; Valley, 1986). As carbon generally has a low concentration compared to oxygen in diagenetic waters, carbon is generally more resistant to isotopic resetting. However, carbon can be significantly altered in the sediment via biological processes that release ^{12}C , such as via authigenic carbonate production. Authigenic carbonate is produced at or below the sediment-water interface in low oxygen conditions, where bacteria oxidize organic matter and reduce sulfate, which oversaturates the pore water with respect to carbonate, increases the pore water alkalinity, and typically drives $\delta^{13}\text{C}$ negative (Schrag, et al., 2013). Authigenic carbonate has been proposed as a primary driver behind the Shuram Excursion by potentially playing a larger role in the Precambrian carbon cycle than in the Phanerozoic (Macdonald, et al., 2013). This process can diagenetically drive $\delta^{13}\text{C}$ values negative, and consequently a positive correlation between carbon and oxygen isotope values generally indicates diagenetic alteration (Allan & Matthews, 1982; Banner & Hanson, 1990; Veizer & Hoefs, 1976). Various screens have been developed to ascertain degrees of alteration that depend on the ratios of elements that are enriched in seawater compared to those enriched in meteoric fluids (Kaufman & Knoll, 1995). These include carbon and oxygen isotope covariation, Mn/Sr ratios, covariation between organic and carbonate carbon isotope values, cathodoluminescence, and comparison of $\delta^{13}\text{C}$ profiles from multiple sections (Knoll, et al., 1986; Narbonne, et al., 1994).

Carbonate rocks (principally calcite and aragonite) are fundamentally comprised of calcium (Ca^{2+}) and carbonate (CO_3^{2-}), but minor and trace elements are common constituents. These

elements include magnesium, manganese, strontium, rubidium, and various metals such as iron, chromium, copper, and zinc. These elements are taken up during precipitation either by replacing the Ca or equivalently-sized ion in defects within the crystal lattice structure. Additionally, these concentrations can be vulnerable to diagenesis. Trace element concentrations can shed light on the diagenetic history of a carbonate rock. Seawater and meteoric waters carry different groups of trace elements. The process of recrystallization leads to the enrichment or depletion of elements in a carbonate rock. For example, the concentration of strontium is high and manganese is low in seawater, but in basinal fluids the opposite is true. Ultimately, diagenesis is a local effect and carbonate rocks that have been heavily altered should show distinct local variations in their isotope values as well as major and trace element concentrations (Kaufman & Knoll, 1995).

In sum, carbon has played an important role in the geochemical and biological realms throughout Earth's history. Life prefers the lighter carbon isotope, leaving ^{13}C -enrichment in carbonate rocks. The ratio between these two values ($\delta^{13}\text{C}$) reveals key information about the fluxes of carbon sinks in the past. Carbon is vulnerable to resetting in carbon-rich fluids, which drives $\delta^{13}\text{C}$ negative and provides a key indicator of diagenesis. While life in the Phanerozoic formed a significant sink of carbon, primary production was reduced in the Precambrian and, as such, the biogeochemical carbon cycle was more volatile. The Neoproterozoic carbon cycle was transitional in the modern biogeochemical carbon cycle, and the oxidation state of the atmospheric and biological realms were transitional as well.

2.2 Neoproterozoic Era

The Neoproterozoic Era (1000 – 541 Ma) was a dynamic period in Earth's history following the "boring billion" of the Mesoproterozoic. The era is divided into the Tonian (1000 – 720 Ma), Cryogenian (720 – 635 Ma), and Ediacaran periods (635 – 541 Ma) (Cohen, et al., 2016). It was a time of significant changes in the climate, atmosphere and ocean chemistry, evolution of life, and plate tectonics (Knoll, et al., 1986; Meert & Lieberman, 2008; Hoffman, et al., 1998). Neoproterozoic rocks recorded two long-lived global glaciations, the Sturtian and Marinoan glaciations (Hoffman &

Li, 2009; Fairchild & Kennedy, 2007). A shorter-lived, regional glaciation, the Gaskiers glaciation, occurred in the middle of the Ediacaran. By the end of the era, the deep ocean became more thoroughly oxygenated (Fike, et al., 2006; Lyons, et al., 2014; Love, et al., 2009; Turner & Bekker, 2016). Along with other geobiologically important elements, the seawater carbon isotopic signature was in flux, where it was temporarily driven to negative values following the Snowball Earth glaciations, and subsequently driven to even more negative values in what is known as the Shuram Excursion (Condon, et al., 2005; Narbonne, et al., 2012; Grotzinger, et al., 2011; Condon, et al., 2005). See Figure 2.

Though evidence of sponges takes primitive animal life to as early as the Cryogenian, the late Ediacaran period saw the radiation of more complex animals, known as the Ediacaran biota, that have been observed globally (Glaessner & Wade, 1966; Droser & Gehling, 2008; Hofmann, et al., 1990). Finally, the Neoproterozoic supercontinent Rodinia began to rift around 750 Ma, drawing down CO₂ levels via silicate weathering and rapidly decreasing global temperatures, plunging the surface conditions into a “Snowball Earth.” The breakup of the supercontinent, Rodinia, was accompanied by the distinctive, steady rise of the ⁸⁷Sr/⁸⁶Sr global seawater signature (Young, 2013; Santosh, 2010; Halverson, et al., 2007).

Due to the low-resolution biostratigraphy in the Precambrian, chemostratigraphy and geochronology have assumed the major roles in helping to refine the stratigraphy. Ediacaran chemostratigraphy relies heavily on carbon and strontium isotope ratios, which exhibit distinctive excursions and trends allowing correlation across the globe. Where suitable rocks are available, geochronology is even more reliable and its application is more widespread. For example, tightly-constrained dates on multiple Marinoan-aged rocks have converged on a termination of the glaciation at around 635 Ma (Rooney, et al., 2015). In other cases, the lack of geochronology has complicated and obscured interpretations, such as in the case of the Shuram Excursion (Bowring, et al., 2007).

For over one hundred years, geologists have sought to solve a paradox of the global distribution of glaciogenic diamictites (tillites) deposited at low latitudes in the latter-half of the Neoproterozoic (Eyles & Januszczak, 2004). The climatic and geophysical conditions required to deposit such rocks were culled under the umbrella term “snowball Earth” by Joe Kirschvink in his seminal paper in 1992. He proposed that a large portion of continental landmass was in the middle and low latitudes, thus raising the albedo of the equatorial zone and driving down global temperatures. The globe became seized by a runaway albedo affect, plunging it into a severe “snowball” phase. It would be difficult to retreat from it, due ice and snow cover creating a high albedo. Under ice-cover the CO₂ sink of continental silicate weathering would be shut-down. Volcanic activity would continue, however, and CO₂ levels would build in the atmosphere. This would raise global temperatures until the albedo effect was overcome and the glaciers would rapidly retreat (Kirschvink, 1992; Hoffman & Schrag, 2002). There were multiple “snowball Earths” at both ends of the Proterozoic, but the Neoproterozoic glaciations formed the foundation of Kirschvink’s hypothesis. These are known today as the older Sturtian (717-660 Ma) and the younger Marinoan glaciation (terminating 635 Ma) (Rooney, et al., 2015). These glaciations were named for the glaciogenic successions in central South Australia, in the Adelaide Rift Complex of the Flinders Ranges (Glaessner & Parkin, 1957; Dunn, et al., 1971). Today these two names identify stratigraphically equivalent glacial deposits around the world.

2.3 Marinoan glaciation

A distinctive feature of Snowball stratigraphy is the presence of “cap carbonates,” regionally widespread, thin limestone or dolostone deposits overlying Marinoan- and Sturtian-aged tillites. Globally distributed, they bear unique but similar sedimentological characteristics and indicate warm-water deposition (Williams, 1975; Corsetti & Lorentz, 2006). Unique sedimentary textures include metre-scale wave ripples (“mega-ripples”), sheet-crack cements, barite crystal fans, tube structures, and aragonite-pseudomorph crystal fans (Allen & Hoffman, 2005; James, et al., 2001; Hoffman & Macdonald, 2010; Kennedy, 1996; Cloud, 1974; Corsetti, et al., 2013). These

features have not been seen in the geologic record since that time. Cap carbonates are geochemically unique as well, recording a typical carbon isotopic excursion nadir of -5‰ , near the value of mantle carbon, or carbon from volcanic CO_2 input (Halverson, et al., 2005). Since carbonate solubility increases as water temperature decreases, and as modern carbonates are most common at low latitudes, the precipitation of cap carbonates over tillites indicates that the shallow-marine waters had warmed rapidly and sufficiently following glaciation. This juxtaposition has created a climate paradox with no clear answer yet. The sudden alkalinity flux to the ocean following deglaciation is often called upon for the precipitation of these carbonates (Hoffman & Schrag, 2002).

Palaeomagnetic evidence supports the low-latitude position of land masses during the Snowball Earth phase (Evans, 2000). Geochronology has proved useful in establishing the timeline of the Neoproterozoic glaciations. Though the Snowball Earth hypothesis is surviving a test of time and supported by long-standing observations, it is not without controversy. A detailed examination of the various questions raised by the Snowball Earth hypothesis is beyond the scope of this work. Numerous recent summaries have been published and it is not the author's goal to draw a conclusion on the veracity of the arguments presented in those works. Please see Hoffman & Schrag, 2002, Fairchild & Kennedy, 2007, Corsetti & Lorentz, 2006, and Eyles & Januszczyk, 2004 and the references therein for a more complete examination of the Snowball Earth hypothesis.

2.4 Shuram Excursion

The marine biogeochemical realm was in flux following the rapid deglaciation of the Marinoan glaciers. Though multiple carbon isotope excursions occurred over the whole of the Proterozoic, the post-Marinoan Shuram Excursion is the most dramatic shift ever recorded (Grotzinger, et al., 2011). The excursion is named for the carbonate Shuram Formation of the Huqf Supergroup, in the Sultanate of Oman, where the excursion reaches a nadir of nearly -12‰ $\delta^{13}\text{C}$ with a gradual return over hundreds of metres, implying a duration of millions of years (Figure 4) (Burns & Matter, 1993). In comparison, Phanerozoic excursions have durations of hundreds of

thousands of years and values typically do not fall below mantle carbon values of -5‰ $\delta^{13}\text{C}$ (Saltzman & Thomas, 2012; Bristow & Kennedy, 2008).

The excursion is observed in several other localities (Grotzinger, et al., 2011), such as the Wonoka Formation in Australia, the Doushantuo Formation in South China and the Johnnie Oolite in Death Valley, California (Condon, et al., 2005; Kaufman, et al., 2007; Calver, 2000). Possible Shuram Excursion localities have been observed elsewhere (section 6.5) (Melezhik, et al., 2007; Pokrovsky, et al., 2006; Prave, et al., 2009; Ries, et al., 2009; Loyd, et al., 2012). See Figure 3.

The rocks of the Shuram Excursion were deposited in relatively shallow mixed carbonate-siliciclastic marine environments, at or above storm-wave-base. Sedimentary features are not unusual: they include grainstones, hummocky cross-stratification, and ripples. All sequences were deposited above but not in contact with Marinoan tillites. Stratigraphically the Shuram Formation is the most complete of the four. Both the Johnnie Formation and the Wonoka Formation are characterised by deeply-incised submarine canyons overlying the isotope excursion (Bergman, et al., 2011; Giddings, et al., 2010). The Doushantuo Formation is condensed and the excursion is truncated by a sequence boundary (Grotzinger, et al., 2011; Condon, et al., 2005). None of the localities have undergone any significant metamorphism, and the Australian and Oman sections are considered unmetamorphosed.

The carbonate isotopic profile is the most salient feature of the Shuram Excursion. All localities recorded the carbon isotopic values that lighten rapidly toward nearly -12‰ $\delta^{13}\text{C}$ and gradually recover to 0‰ $\delta^{13}\text{C}$ over hundreds of meters. The excursion exhibits little point-to-point variation across each locality and, notably, the excursion is similar in magnitude and morphology across the globally widespread locations. In all localities, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ covary whereas $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ are decoupled. Concentrations of carbonate-associated sulfate (CAS), Sr and Mn are elevated and variable (Derry, 2010; Loyd, et al., 2012).

Radiometric data is sparse. Constraining the excursion has relied on a combination of stratigraphic correlations, basin analysis, and paleontology when available. All localities overly Marinoan-aged tillite-cap-carbonate packages; they underlie Ediacaran bioassemblages within close stratigraphic proximity, containing species such as *Cloudina* and *Namacalathus* which are constrained to appear between 550-543 Ma and at ~548 Ma, respectively (Grotzinger, et al., 2000; Penny, et al., 2014). The Shuram Formation has an estimated depositional age of 601 ± 8 Ma, which is derived from sedimentation and subsidence rates (Le Guerroué, et al., 2006). The Wonoka itself has yielded no radiometric data, but its minimum age is constrained by the Bonney Sandstone dated at 556 ± 24 Ma from a single zircon grain, a range of 50 to 80 Myr (Le Guerroué & Cozzi, 2010; Ireland, et al., 1998). The Johnnie Oolite has been correlated with Neoproterozoic rocks in Utah deposited before 580 Ma (Kaufman, et al., 2007). In the Doushantuo Formation, the termination of the Shuram Excursion has been dated at 591.1 ± 5.3 Ma (Zhu, et al., 2013). Thus, the excursion's duration is crudely constrained to a maximum of roughly 45 million years.

The unique carbon isotopic signature combined with geochronological limitations have raised concerns over the Excursion's diagenetic history and its relationship to the larger Precambrian geochemical world. Those who argue for a secondary origin cite the covariance of carbon and oxygen isotopes, which is an indicator of diagenesis (Derry, 2010). Diagenetic carbon isotope excursions have been recorded in Pliocene-aged carbonates from the Great Bahama Bank (Swart & Kennedy, 2011). However, carbon isotope profiles produced by diagenesis are characterized by the lightest values nearest to the subaerially-exposed surface, with values becoming progressively heavier with depth (Allan & Matthews, 1982). The opposite trend is seen in the Shuram excursion. Proponents of the diagenesis explanation argue that a long-lived primary Excursion would require a large oxidant source when the Earth's atmosphere and oceans were predominantly reducing, and for which there is little geological evidence of such a source (Bristow & Kennedy, 2008).

Diagenesis fails to explain how a carbon isotope excursion with a distinctive shift, morphology, and thickness is recorded on multiple cratons. Additionally, diagenesis fails to explain how we have not seen more “Shuram Excursions” since. There are varying explanations for a primary origin. These include the rapid oxidation of fossil organic matter from the weathering of older organic-rich rocks, the oxidation of a vast dissolved organic matter (DOM) seawater reservoir, methane oxidation – among others (Rothman, et al., 2003; Fike, et al., 2006; Kaufman, et al., 2007; Bjerrum & Canfield, 2011). There is evidence to support a primary origin. Calcium and magnesium isotope studies on the Wonoka Formation indicate that the carbon isotopic values are primary (Husson, et al., 2015). An absence of diagnostic secondary textures and the presence of primary textures as well have been observed in the Wonoka Formation (Haines, 1990). CAS values in the Johnnie Oolite indicate a period of rapid environmental oxidation producing elevated, varying sulfate concentrations and possibly producing the extreme negative shift in carbon isotope values, while oxygen and sulfur isotopes indicate minor diagenetic effects (Kaufman, et al., 2007).

Analysing the numerous arguments for both a diagenetic signal and a primary signal of the Shuram Excursion is beyond the scope of this work. Instead the reader is directed toward more thorough reviews of the topic such as Grotzinger, et al., 2011 and Derry, 2010 and the references therein. The controversy will likely continue until more geochronological data helps to constrain the duration. If primary, the excursion presents implications for our understanding of the evolution of the atmosphere and for the subsequent Ediacaran explosion and the evolution of life on Earth.

2.5 Windermere Supergroup

The Neoproterozoic Windermere Supergroup comprises many of the highest peaks of the central Rocky Mountains of Canada, exposed in dramatic thrust sheets formed during Phanerozoic orogenic events (Figure 5) (Eisbacher, 1981; Price, 2009; Brown & Read, 1983). Windermere rocks were uplifted and carved by recent glacial activity, forming the rugged terrain as we know it today. The Windermere Supergroup forms a narrow sinuous belt extending from Alaska to Mexico (Ross, et al., 1995). In Canada, it is estimated to crop out across 35,000 km² (Ross & Murphy, 1988). The

supergroup is a shallowing-up succession of predominantly siliciclastic rocks deposited along the eastern Laurentian margin. It has an estimated thickness of 9km and is thought to have been deposited between 736 – 569 Ma (Ross & Murphy, 1988; Ross, 1991; Eisbacher, 1981; Ross & Arnott, 2004; Stewart, 1972). It is composed of three thick successions: the basal Toby Diamictite, the Horsethief Creek Group (which roughly encompasses the Miette Group and the Kaza Group in other localities), and the lower portion of the Caribou Group (Ross & Murphy, 1988).

The Windermere Supergroup was deposited in two phases coincident with the rifting of the supercontinent Rodinia. The Toby Diamictite recorded the initial rifting phase, and the Horsethief Creek and Caribou Groups recorded the second, tectonically-quiet phase (Young, 1992; Stewart, 1972; Ross, 1991). The siliciclastics of the Horsethief Creek Group has long been interpreted as turbiditic (Terlaky, et al., 2015). See Figure 24 for more detailed regional correlations.

Chapter 3: Geologic Background

3.1 Old Fort Point Formation

In upper Windermere Supergroup stratigraphy, there is a distinctively-coloured triad of units long referred to as “the Marker” (Walcott, 1910; Aitken, 1969; Ross & Murphy, 1988). The Marker is dominated by green and purple shales with minor pink carbonate-green siltstone couplets, coarse blue limestone breccia, and a chaotic conglomerate of coarse carbonate clasts. It was named the Old Fort Point Formation, after the prominent Old Fort Point landmark in Jasper, Alberta, composed of the turbidites of this formation (Charlesworth & Remington, 1960; Aitken, 1969). The Old Fort Point Formation (henceforth OFPF) has been divided into three members: the basal Temple Lake Member, the Geikie Siding Member, and the upper Whitehorn Mountain Member (Smith, 2009). Very significantly, the middle Geikie Siding Member, a black shale, has yielded a Re-Os age of 607.8 ± 4.7 Ma (Kendall, et al., 2004).

The lower OFPF has been interpreted as deep-water slope deposits, between the bathyal to abyssal plain bathymetric depths (section 6.1) (Smith, 2009). The middle of the OFPF is a shale

and is interpreted as a sea level high stand. In later OFPF time, the basin shallowed and these deep-water rocks were subjected to submarine canyon incision. The erosion is so significant in some areas that the basal rocks have been removed.

Recent geochemical work was conducted on the carbonate sections of the OFPF, revealing a pronounced $\delta^{13}\text{C}$ nadir of around -11.5‰ (Smith, 2009), and a profile similar to the Shuram Excursion. Despite the lighter isotopic signal, along with the Re-Os age and a lack of contact with any tillite, it was interpreted as an anomalously depleted, very young Marinoan cap-carbonate (Kendall, et al., 2004; Smith, 2009). The handful of complications that this interpretation posed were briefly acknowledged but were not satisfactorily addressed. In the Northwest Territories of Canada, shallow-marine carbonates once correlated to the OFPF are older than 632.3 ± 5.9 Ma (Rooney, et al., 2015). This poses a challenge to long-standing stratigraphic correlations with the OFPF. See section 6.3 for further discussion.

Chapter 4: Methods

4.1 Field work

Field work was conducted over the month of August 2014 in the Jasper and Lake Louise, Alberta regions. Two sections were measured in Jasper: 1) site 16W, along Highway 16 or Yellowhead Pass Highway, and 2) site Pyrite Point/PP which is southeast of the Old Fort Point landmark along the Athabasca River. At site 16W, approximately 174m of section were measured and 134 carbonate samples were collected. At site PP, approximately 82m of section was measured and 33 samples were collected. Samples were chosen based on field recognition of carbonate mineralogy and testing fresh surfaces with dilute hydrochloric acid. Fresh samples were chosen to minimize weathering effects.

In Lake Louise, locations were only scouted. An outcrop of the black shale of the Geikie Siding Member, and the coarse carbonate conglomerate of the Whitehorn Mountain Member were observed. Samples were collected but not logged.

4.2 Geochemical analyses

Three forms of analyses were conducted on samples in this study. Stable isotopic analyses for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were conducted to compare the rocks' profiles to those of the Snowball Earth cap carbonates and those of the Shuram Excursion. Major and trace element concentrations were conducted to reveal any significant alteration and to compare it to the literature on Ediacaran carbonates. 11% of the total samples were chosen for petrographic analyses to determine degree of recrystallization and mineralogy.

Samples were cut with a diamond saw blade perpendicular to bedding and polished with silicon carbide sandpaper. Microdrilling locations were chosen based on low silt content, using a hand lens and microscope. The carbonate facies were microdrilled with Kingsley North, Inc. diamond drills in sizes 1.00mm and 1.25mm.

Polished sample slabs were stained to determine the bulk rock's mineralogical nature. The staining procedure employed 2% hydrochloric acid, Alizarin red S and potassium ferricyanide (Dickson, 1965). Siliciclastic materials either did not stain, or stained pale grey green. Red and purple-red dye results were interpreted as calcite or ferrous carbonate respectively, while blue and teal dye results were interpreted as dolomite. Results are listed in Table 4.

4.3 Stable isotope analyses: $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

Sample powders were weighed within a range of 225 μg to 275 μg . The powder was dissolved with five syringe drops of pure phosphoric acid (H_3PO_4) and warmed for twenty-four hours at 80°C on the Finnigan Gas Bench, connected to the Bekker Group's Thermo Delta V continuous flow mass spectrometer. Standards NBS-18 and NBS-19, in-house standards UCRM1, UCRDOLO, and established standards UCD and NBS-88-B were used (geochemical signatures and references listed in Table 1). These were chosen to represent calcite and dolomite with a range of carbon and oxygen isotopic values. The standards were weighed at 250 μg each. UCD was chosen for the standard linearity, while all six standards were repeated every ten samples. 10% of the samples were replicated.

Standard	$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}$ (VSMOW)	Mineralogy	Reference
UCD	2.0900	-1.9100	Calcite	Lab bottle
UCRM1	-42.9760	-17.0870	Calcite	Lab logbook
UCRDOLO	-2.9740	-6.5160	Dolomite	Lab logbook
NIST SMR 88b	2.0520	-6.3790	Dolomite	Lab logbook
NBS18	-5.0100	-23.0100	Limestone	Lab logbook
NBS19	1.9500	-2.2000	Carbonatite	Lab logbook

Table 1: Geochemical signatures and references for carbonate standards used in this study. (Friedman, et al., 1982)

4.4 Major and trace elemental concentrations

Major and trace element concentration work was conducted on the induced couple plasma mass spectrometer in the Biogeochemistry Lab of the University of California Riverside. Sample powders were weighed to within a range of 55 to 67 milligrams. The powders were dissolved with trace metal grade 4M hydrochloric acid. The vials were placed in a centrifuge and the separated liquids were decanted. The solutions were diluted one hundred-fold with 2% nitric acid. The standard solution was comprised of Ca, Mg, Mn, Fe, Sr, Rb, Zn, Cu, Co, and Cd. These stock elements were combined into one flask of 2% nitric acid and six standard splits were taken, in a series of decreasing proportion of stock-to-nitric acid. These standards were tested first as a quality check. The detection limits for the elements in the standard solution are listed in Table 2. The samples were run on the ICP-MS and the raw data was first back-corrected to parts per million and then corrected for total inorganic carbon.

Element	Conc. (ppm)	Element	Conc. (ppm)	Element	Conc. (ppm)
Ca	100	Mg	5	Cr	2
Zn	10	Cd	2	Fe	1
Sr	10	Cu	2	Mn	1

Table 2: Detection limits in ppm for major and trace elements for the ICP-MS.

4.5 Total inorganic carbon

The total inorganic carbon contents were determined two ways: first using the peak area and sample mass data from the stable isotopic analyses on the mass spectrometer and the second using calcium and magnesium concentrations from the ICP-MS. The mass spectrometer peak method was as follows.

$$\frac{(\text{sample peak area}) \times (\text{standard mass})}{(\text{sample mass}) \times (\text{standard peak area})} = \text{total inorganic carbon (\%)} \quad (1)$$

For each sample, the mass spectrometer measures a total of fifteen peaks – the first four and the last peak are CO₂ gas, and the remaining nine are sample peaks. The first sample peak was omitted as it is more volatile and inconsistent. Instead the second sample peak (or the sixth overall peak) of each sample and standard was chosen for peak area. The correction was calculated as in (1). Standard UCD was the most consistent standard in each run for calcite. The standard UCRDOLO was used to correct samples listed as dolomite in Table 4.

The second method used calcium and magnesium values measured on the ICP-MS. For calcite, it required the number of moles of Ca in both a pure sample and the actual sample, mass of Ca in a pure sample, and the mass of Ca in the actual sample. Dolomite requires the inclusion of magnesium as well. The equations below illustrate the method.

First, we calculated the number of moles of calcite by dividing the sample powder mass by the molecular mass of calcite, and for dolomite the sample powder mass was divided by the molecular mass of dolomite (2(3).

$$\frac{\text{sample powder (g)}}{\text{molecular mass of calcite } (\frac{\text{g}}{\text{mol}})} = \text{moles of calcite (mol)} \quad (2)$$

$$\frac{\text{sample powder (g)}}{\text{molecular mass of dolomite } (\frac{\text{g}}{\text{mol}})} = \text{moles of dolomite (mol)} \quad (3)$$

The mass of Ca in a pure calcite sample was calculated by multiplying the moles of calcite by the molar weight of Ca. The combined masses of Ca and of Mg in a pure dolomite were calculated by multiplying the moles of dolomite by the sum of the molar masses of Ca and Mg (4(5).

$$\text{moles of calcite (mol)} \times \text{molar mass of Ca} \left(\frac{g}{mol} \right) = \text{mass of Ca in pure calcite (g)} \quad (4)$$

$$\begin{aligned} \text{moles of dolomite (mol)} \times \left((\text{Ca molar mass} + \text{Mg molar mass}) \left(\frac{g}{mol} \right) \right) \\ = \text{mass of Ca and Mg in pure dolomite (g)} \end{aligned} \quad (5)$$

The mass of each measured Ca and measured Mg in the sample was calculated by multiplying the mass of the sample powder by the measured elemental content in ppm and dividing by 1,000,000 (eq. (6)(7)).

$$\frac{\text{sample powder (g)} \times \text{measured Ca (ppm)}}{1,000,000} = \text{mass of measured Ca (g)} \quad (6)$$

$$\frac{\text{sample powder (g)} \times \text{measured Mg (ppm)}}{1,000,000} = \text{mass of measured Mg (g)} \quad (7)$$

Finally, as every sample contained both calcium and magnesium, the fraction total inorganic carbon (TIC) each sample was calculated by dividing the sum of the mass of Ca and Mg measured in the sample by the sum of the mass of Ca and Mg in pure dolomite.

$$\frac{\text{mass of measured Ca} + \text{Mg (g)}}{\text{mass of Ca} + \text{Mg in pure sample (g)}} = \text{fraction TIC of sample (\%)} \quad (8)$$

The results for both methods are listed in Table 6. In seventeen of the samples the two methods' results varied significantly. This is attributed to inherent error in weighing powders for the mass spectrometer, in which static cling from the wax paper results micron-scale loss of powder and discrepancies between the measured weight on the

balance and the volume of powder that is deposited in the plastic vial. Additionally, not all the powder settles to the bottom of the vial due to static cling. This results in less mass being dissolved than originally weighed. Dolomite or calcite correction was decided based on the staining results and further confirmed by Mg wt%, both of which are listed in Table 4.

4.6 Petrography

Thin sections were prepared by sanding smooth one side of a cut hand sample and attaching it with a thin layer of epoxy to a thin section glass slide approximately 1mm in thickness. The attached rocks were then cut and sanded down to an approximate sample thickness of 30µm and analyzed for mineralogy.

Chapter 5: Results

5.1 Geological descriptions of sampled sections

5.1.1 Site 16W located at Yellowhead Pass Highway 16

Site 16W is located at N 52°52.356' and W 118°17.48', some 13km west of Jasper along the Miette River and Highway 16, known as Yellowhead Pass (Figure 7). The outcrop is a succession of couplets of carbonate-siltstone layers, with colours ranging from pink to green to purple-grey, followed by a thick section of monotonous purple and green siltstones, and capped by a thick section of cream and pink carbonate alternating with green silty layers (see Figure 8). Except for the blue limestone breccia, sedimentary structures are rare; those that are present are limited to low-amplitude ripples and wavy laminations, a few scour marks, and planar laminations. Occasional silt or sand lenses occur within limestone beds. These will be discussed in more detail below.

Though the overall measured section was structurally simple, folds are present in the lower half of the section. Charlesworth et al., 1967 observed complex structural deformation in the OFPF. He ultimately concluded that the entire formation was less competent than the surrounding coarser-grained siliciclastics and formed the core of a complex anticlinorium. In this study folds were observed, but the author is confident that this section's stratigraphic integrity was not compromised by the deformation.

The measured section can be broken down into five individual sub-sections or "units," (see Figure 8) There are three distinct carbonate sections: Unit 1, Unit 3, and Unit 5. Unit 2 and 4 consist of siltstones, shales, and limestone breccia.

Unit 1 is about 7.5 m thick and is characterised by interbedded grey-pink limestone greater than 1cm in thickness and grey siltstones about 0.5cm thick with occasional cream sandstone lenses about 1cm thick. Gradually limestones become dominant with pink, orange, cream and green beds greater than 1cm in thickness. Higher in the unit, sandstone greater than 1cm in

thickness begins to interbed with limestone; scour marks occur along boundaries. Near the top of unit 1, sandstone dominates with limestone lenses. Pyrite cubes less than 4mm were observed near the top of the unit and along limestone-sandstone boundaries. There is one instance of very minor folding at the top of the unit.

Unit 2 is a stratigraphically thick (92m) sequence of monotonous siltstones. This Unit was not studied in detail. For the upper two-thirds of the outcrop, fresh faces of siltstones are purple, while fresh faces from the lower third are green siltstones. The purple siltstones weather to grey-purple and green siltstones weather to any one of grey, buff, yellow, or brown. There are occasional ripple marks and minor structural deformation. Over the five uppermost meters of the unit, rare limestone lenses are observed, below siltstones interbed with purple limestone. Unit 2 has a gradational transition into unit 3.

Unit 3, the "Middle Carbonate," is about 8.25m thick. Unit 3 is comprised of pink and yellow limestone beds about 1 cm thick alternating with silty green layers. This bed is folded and the middle of the unit forms the fold core. Pyrite cubes about 1mm in size are also observed in the middle of the section.

Unit 4 is 32m thick and is distinct from the surrounding limestones. Slates comprise the approximately 15m meters section at the base; they are folded, possibly faulted and are crumbly, chalky, and dark orange. There is a sharp boundary with about 1-m thick breccia having a dark-blue limestone matrix and black limestones clasts. The breccia is poorly sorted with clasts ranging in sizes from a few millimetres to several centimetres. Limestone transitions sharply into buff-weathered slates with dark grey fresh faces. Thin (1-4mm thick) sandy intervals occur regularly within the slates. Sedimentary structures are primarily planar laminations with occasional cross-bedding. These resemble the slates at the bottom of bed 4, but less deformed. The same dark blue limestone breccia returns, and bed 4 is truncated sharply by what appears to be a fault.

Unit 5, the “Upper Carbonate,” is 36m thick and is characterised by dominantly limestone with silty or sandy interbeds. In the first few metres, there are two stratigraphically short (a few metres each) sections of deformed slate resembling the slate from unit 4, but these were omitted from Figure 8 for simplicity. The unit 5 limestones are yellow and pink for the lower 11m of section, with typically thin silty interbeds, but sandy interbeds were also observed. These sandy interbeds ranged in thickness from .5cm to 2cm and display wavy laminations and scour marks along the sandstone-limestone boundaries. Limestone beds range from 0.5cm to 4cm in thickness. Above the lower 11m, for the next 5m-thick interval, the limestones are red and greater than 1cm thick, and the silty beds are green and about 1cm thick. The silty beds have slightly wavy laminations. At this stratigraphic level, that the siltstones become purple and thicken up to 12cm and the red limestones thin to under 4cm. The siltstones have occasional planar laminations, but overall are cross-bedded. The limestones displayed no obvious sedimentary features. In the uppermost 12m of section, the limestones become dominant again. In the last few meters, sandstone alternates with limestone until limestone disappears.

5.1.2 Site PP

Site Pyrite Point (PP) is located approximately 2 km south east of the Old Fort Point. It is an outcrop of turbiditic siltstones grading into limestones, forming a narrow ridge that drops precipitously into the Athabasca River. An 82m section was measured and 33 samples were collected. See Figure 9.

The siltstones are grey and thinly-bedded, with beds approximately 3mm thick (see Figure 9). Sedimentary structures are rare. There are occasional thin carbonate lenses. The siltstone-carbonate contacts are characterized by scour marks and ripples, and the carbonates are brown or pink. Upsection, carbonate layers become common until siltstones transition completely into dominantly cream and pink carbonates alternating with thin green silty layers. Sedimentary features in the carbonate layers are limited to ripples and planar laminations.

5.2 Stable isotope analyses

Results are listed in Table 5. In both sites, the carbon profile is similar and distinctive. In site Pyrite Point, the section begins with carbon isotopic values at -11‰ and becoming steadily heavier over 80m up-section, where the section ends at -8‰ . Site 16W is characterized by three overall trends in the carbon isotopic values. In the lower 16W, the isotopic values begin at -11‰ and the values rapidly over 7m. Roughly 90m of siltstones interrupt the profile. Carbonates resume in the middle 16W, with another excursion to about -10.5‰ . Again, the values rapidly enrich over a few metres and then hover around -8‰ . Siltstones again interrupt the carbonates. In the upper 16W, carbon isotopic values hover between -8‰ and -9‰ for some 25m before becoming progressively lighter up section to a nadir of approximately -10.5‰ . In the section's final metres the values return to -8‰ .

While carbon varies widely, oxygen displays a narrow range of values throughout both sections. At Pyrite Point, the values begin at -14.5‰ and gradually lighten to -15‰ , but overall do not respond to changes in carbon isotopic values. At 16W most of the values are around -16‰ , with occasional and isotopically limited variations. Unlike Pyrite Point, there is no gradual trend towards either lighter or heavier values.

Data was collected over three runs, using both calcite and dolomite standards. Standard UCD was chosen for the linearity standard. Analytical precision for UCD for all runs was 74.603 ± 3.098 , while the analytical precision for UCRDOLO was 83.245 ± 2.68 .

5.3 Major and minor elemental concentrations

Results are listed in Table 6 and in Figure 16Figure 23. Mg weight % calculations for samples reveal that four are high-magnesium calcite, with the maximum weight % in sample 16W082 with 43 wt% Mg. In the carbonate samples, Mg is typically less than 5000ppm. In the dolomitic samples, it ranges between 60 000 and 125 000ppm. Ca ranges between approximately

220 000 and 970 000 ppm, but hovers just under 400 000ppm over all. Rb and Zn were below detection limits except for the dolomitic samples. Cu in most samples is below 10 ppm, but spikes into the double digits and occasionally in the hundreds, with a dolomite sample recording 157 ppm. Cd is below 5 ppm in all samples. Sr ranges between 200 and over 600ppm. Mn ranges between 1000 – 2000 ppm. Fe is consistently below 10 000 ppm, except for two samples that are nearly 70 000ppm and 90 000 ppm each.

Exceptional concentrations of several elements typically occur in dolomitic samples. Naturally Mg is enriched, but also Cr, Mn, Fe, Zn, and Rb are enriched. Conversely, most of the dolomite samples are depleted in Sr, Cd, and Cu.

Compared to these results, the OFPF records generally low concentrations except for Sr and in dolomitic samples. Dolomitic samples recorded Cr between 3.4 and 39.4ppm, Cu between 4.2 and 168.1, Zn between 3.4 and 106.3ppm, Rb up to 65.9ppm, and Fe between 7959 and 83739ppm. In this same set of elements, calcite records Cr up to 18ppm, Cu up to 138ppm, Zn up to 4.9ppm, and Rb up to 4.2ppm. Cd, Mn, and Sr concentrations in calcite are comparable to dolomite.

5.4 Petrography and sample analysis

Petrography focused on samples analyzed on the ICP-MS to determine mineralogy and to put minor and trace elemental data in the proper context. Samples with significant amounts of siliciclastic content were eliminated from the ICP-MS analyses pool. Siliciclastic percentages were determined via a petrographic microscope. Samples share several characteristics:

- Siliciclastic content ranges from 10 to 50%
- Siliciclastic minerals include muscovite, quartz, albite, and chlorite.
- Pyrite and either fine-grained pyrite or iron-oxides are common
- Few if any sedimentary structures are observed outside of occasional mm-scale graded beds

- Non-vein calcite is typically fine-grained spar
- Veins are calcite, rarely dolomite or quartz

16W-005 is comprised of alternating layers of silt and carbonate. Carbonate layers are mostly fine-grained sparry calcite, and recrystallization has obscured grain boundaries. Siliciclastic content is approximately 35 – 50% of rock, with quartz and muscovite common. Veins filled with clays or iron oxides are present. Pyrite is common. Silty layers grade from mostly silt to a higher proportion of carbonate over a few mms. No sedimentary structures were observed.

16W-009 is comprised of fine-grained sparry calcite with interspersed beds of silt, where the texture indicates two mm-scale fining-up sequences of siliciclastic to carbonate. Siliciclastic minerals observed include muscovite, chlorite, albite, and quartz. Iron oxides are also present. Muscovite occurs both as detrital (fine, broken grains deposited parallel to bedding) and metamorphic (euhedral and suspended in carbonate). The rock is approximately 20-40% siliciclastics. No sedimentary structures were observed. In the hand sample, there are mm-scale flame structures of silt into carbonate. Reduction spots are observed, including on one flame structure.

16W-013's base is characterised by a structure resembling a "slump" with parallel bedding laminations where μm -scale pyrite grains are concentrated along the base of each lamination. The rest of the sample is comprised of carbonate and silt layers. Pyrite is common in siliciclastics and rare in carbonates. The carbonate is also observed in the silt layers, and is generally fine-grained. Siliciclastics comprise no more than approximately 20% of the rock. Refer to Figure 28.

16W-018: predominantly fine-grained sparry calcite with perhaps 20% siliciclastic content. Siliciclastics include muscovite, chlorite, and quartz. Veins filled with clays are present, as is pyrite but it is uncommon. Veins composed of coarse sparry calcite and rare dolomite (determined by dyeing results), and are concentrated in gently open folds in the sample. Fine-grained iron-oxides occur around the sparry veins. Wispy beds of muscovite are interspersed throughout the calcite.

16W-019. Comprised of approximately 20% siliciclastics, it is a carbonate with thin silty layers. Veins are filled with clays; iron-oxides are common. Siliciclastics include muscovite, albite, and quartz. No sedimentary structures are observed.

16W-024 is a predominantly fine-sparry calcite with minor siliciclastics, perhaps <15%. Mm-scale pyrite is surrounded by coarser calcite and muscovite grains. There are very thin veins of either dolomite and or clays. No sedimentary structures except planar laminations. Refer to Figure 29.

16W-030: carbonate with approximately 50% siliciclastics. Carbonate has been recrystallized and no pyrite is observed. Quartz, muscovite and albite are common.

16W-031: carbonate with approximately 45% siliciclastics. Siliciclastic grains are finer-grained than in 16W-030, and there are more areas of cleaner carbonate. Clay and calcite veins observed.

16W-034 has one layer of clean carbonate (very few siliciclastics) but the rest of the sample is siltier, in the form of silt layers, silty carbonate and clay-filled stylolites. Veins cutting perpendicular to bedding are filled with euhedral carbonate. Carbonate layers have less than 20% siliciclastics.

16W-038 has undergone significant recrystallization (>50%) and mm-scale calcite veins cut through the original texture. Siliciclastics comprised approximately 50% of the rock. There are few fine-grained and clean carbonate layers. Refer to Figure 30 **Error! Reference source not found..**

16W-041: potentially graded bedding of silt to fine-grained carbonate. Sample contains approximately less than 40% siliciclastics, mostly quartz with some muscovite and chlorite. Mm-scale calcite veins cut across bedding. Coarse pyrite is observed.

16W-043 is comprised of sparry calcite with some siliciclastics (mostly muscovite) with approximately 40% siliciclastics in some areas of the sample, but estimate is less than that for most of the sample. Recrystallized, mm-scale calcite veins cut parallel to bedding. Euhedral pyrite observed.

16W-051 is comprised of mostly fine-grained calcite with few siliciclastics grains, with siliciclastic content potentially as low as 10%. The few observed are muscovite. No sedimentary structures are observed. There is a distinctive “knife-edge” boundary between recrystallized coarser-grained spar and fine-grained spar. Stylolites have formed along this boundary and are filled with iron oxides and clays. Fine-grained pyrite is common. Calcite veins cut perpendicular to bedding. Refer to Figure 31.

16W-055 is dominantly carbonate with approximately 20% siliciclastics, which includes muscovite, chlorite, potentially actinolite, and quartz. Pyrite is common in siliciclastic layers. Carbonate texture is characterised by interlayered beds of fine-grained and coarser-grained carbonate. Refer to Figure 32.

16W-058 is dominantly calcite with approximately less than 15% siliciclastics, those being muscovite, and quartz, and iron oxides. The sample has been recrystallized in varying random patches of coarse sparry calcite, but fine-grained spar is also present. There is a distinctive layer of rust-colored calcite parallel to bedding, likely stained with iron oxides, with no noticeable change in grain size or mineralogy. Numerous calcite veins cut across the sample.

16W-062 is comprised of calcite with approximately 30% siliciclastics. More than half of it has been recrystallized.

16W-066 is a partially recrystallized calcite. Siliciclastic content ranges between 20 to 50%, those observed being muscovite, quartz, albite, and chlorite. Pyrite is not present. There are many calcite and clay veins.

16W-107 is comprised of alternating beds of calcite and siliciclastics. Siliciclastic content is approximately <30% and grains dispersed throughout the calcite. Chlorite, muscovite, and quartz are observed. The calcite has been partially recrystallized, and the recrystallized layers exhibit mild foliation.

Chapter 6: Discussion

6.1 Depositional Setting of the Old Fort Point Formation (OFPF)

The OFPF has been a point of scientific interest for over one hundred years, as it is a widespread and distinctive “marker” that can be used to determine stratigraphic position (Figure 24) (Aitken, 1969; Walcott, 1910). The OFPF’s colourful shales and siltstone-carbonate couplets are underlain and overlain by arkosic sandstones of other Windermere Supergroup units (Charlesworth, 1967; Mountjoy & Price, 1985). Decades of field work across the Canadian Rockies have led to the interpretation that the OFPF represents a phase of deep-water turbiditic deposition forming a sub-marine fan along the eastern Laurentian passive margin (Poulton & Simony, 1980; Pell & Simony, 1987; Ross & Murphy, 1988; Ross, et al., 1995; Kendall, et al., 2004; Smith, 2009; Terlaky, et al., 2015; Arnott & Hein, 1986). This deep-water submarine fan-to-basin interpretation is based on: 1) abundant Bouma sequences, various low-energy sedimentary structures, and carbonate-siltstone couplets transitioning to a sequence boundary of erosive sub-marine canyon channel-fill deposits; 2) anoxic conditions resulting negative $\delta^{34}\text{S}$ pyrite throughout the OFPF; 3) geometry of the sedimentary basin with the expected deeper-water depositional settings west of the OFPF, and conformable nature of the Windermere stratigraphy; 4) regionally extensive nature of the OFPF Marker; and 5) sedimentologic similarity to other carbonate-siliciclastic sequences interpreted as deep-water deposits.

The OFPF is a transgressive-highstand shallowing-up sequence of turbidites and carbonate-siltstone couplets culminating in an organic-rich black shale; the lower and middle OFPF is locally eroded by submarine-canyon incision characterised by channel-fill deposits and breccia of the upper OFPF member. Carbonate-siltstone couplets characterize the lower OFPF (Figure 8; the “lower carbonate” and “middle carbonate” of this study); their outcrop is regionally extensive and indicating deposition of mixed siliciclastics and carbonates over a substantial area (Smith, 2009). The carbonates and the siltstones bear few sedimentary structures; those that are observed are traction structures consistent with low-density turbidite flows (this study and Smith, 2009).

Turbidite sequence B-E characterized this depositional phase, while sequence A-D is typical of the Upper Conglomerate Member; together these indicate deposition in a sub-marine fan setting (Ross, et al., 1995; Poulton & Simony, 1980). The phase of sub-marine canyon incision corresponds to the upper member of the OFPF; it cuts deep into the lower members. The channel fill deposits are characterized by mass slumping, conglomerates, diamictite containing lower OFPF clasts, chaotic coarse-grained breccia, poorly-sorted coarse-to-fine-grained sandstones, and mudstones (Poulton & Simony, 1980; Arnott & Hein, 1986; Smith, 2009 and this study). This phase is thought to have been caused in part by regional uplift accompanied by syn-depositional extensional faulting. The upper member is consistent with upper fan deposition indicating a shift in proximity to the source of the fan (Walker, 1984). At the end of deposition of the Windermere Supergroup, the extensional faulting ceased so that carbonate platforms recorded by the Byng Formation could develop. Detailed and thorough research has been conducted on the turbidites of the Windermere Supergroup and it is not this study's intention to either challenge the long-standing interpretation or provide an in-depth review of the evidence for turbiditic deposition. The reader is directed toward detailed studies on basin structure, sedimentology, and depositional setting across the southern Canadian Cordillera, such as Terlaky, et al., 2015, Ross & Arnott, 2004, Poulton & Simony, 1980, Pell & Simony, 1987, Smith, 2009 and references within these publications for more information.

The OFPF has been interpreted as being deposited on the basinal slope to abyssal plain (Ross, 1991; Ross & Arnott, 2004; Smith, 2009). This interpretation is based on: 1) the turbidites that are exposed over a large area and have not been disturbed or reworked by wave action; 2) the Windermere basinal sequence of 3-5km is conformable, except for the local incision of the upper OFPF into the lower OFPF; and 3) $\delta^{34}\text{S}$ data suggests that the OFPF was possibly deposited under fluctuating redox conditions and is a proximal correlative of deeper-water organic-rich black shales and limestones to the west. The lateral continuity of the OFPF carbonate-turbidite "marker," traceable throughout the southern Canadian Cordillera, requires a long-lived basin of sufficient size and depth to allow the deposition of such sediments that were not affected by higher-energy erosion

and deposition. The post-rift phase of the Laurentian passive margin allows for such a basin, and syn-depositional faulting indicates that throughout the depositional phase of the Miette Group and correlatives, extension helped to generate accommodation space in such a large basin. The Windermere sediments are thinnest at their eastern boundary and thickest at their western boundary, forming a distinctive wedge facing to the west and indicating extensive basinal deposition (Gabrielse, 1972). While preservation bias is a factor due to sub-Cambrian erosion, with perhaps as much as 4 km of sediments removed in the east, the basinal geometry is a product of increasingly thicker and deeper-water correlatives further west and not simply a product of removal (Gabrielse, 1972; Ross & Murphy, 1988). The entire southern Windermere Supergroup sequence, from the Toby diamictite to the Byng carbonate ramp at the end of the Ediacaran, records a continuous deposition with only minor and limited interruptions during the upper OFPF time. Finally, Ross et al., 1995 correlated the Kaza Marker in the west to the OFPF in the east. They suggested that both represent a deep-water turbiditic phase based on similar sedimentological features but the Kaza Marker was deposited under constantly anoxic conditions at a greater basinal depth as reflected by organic matter-rich shales and limestones, while the OFPF was deposited slightly higher on the basinal slope under fluctuating redox conditions, evidenced by both pyritic and hematitic rich shales, in addition to relatively organic matter-lean carbonates and an organic matter-rich shale of the Middle Member (Ross & Murphy, 1988; Ross, et al., 1995; Smith, 2009).

Fluctuating redox conditions are supported by pyrite sulfur isotopes. Pyrite is common throughout the OFPF carbonates and black shales, and often distributed along thin silty layers between carbonate beds (this study; Smith, 2009; Ross, et al., 1995). These crystals are often euhedral and several mms across, but have been recrystallized (Ross, et al., 1995; Smith, 2009). Ross et al., 1995 reported a dramatic $\delta^{34}\text{S}$ shift from approximately 5‰ at the base of the OFPF to -20‰ at the next studied sample 50m above the base. This shift gradually recovers to 0‰ over the course of 70m (Figure 25). These values were interpreted as primary seawater values, since sulfur isotopes in pyrite tend to resist metamorphic resetting, and thus representative of biological sulfate

reduction under unlimited seawater sulfate in the Neoproterozoic deep-water ocean (Ross, et al., 1995). Smith 2009 studied $\delta^{34}\text{S}$ values of samples exposed to lower metamorphic grade than those in Ross' 1995 study; Smith reported recrystallization based on isotopic homogeneity in the pyrite crystals and stratigraphic trends similar to Ross' study.

Paleocurrent data indicates that the sediments had an eastern provenance (Ross, 1991). The carbonates were reworked from a carbonate platform that was removed via the erosion that ultimately formed the sub-Cambrian unconformity separating Windermere from Cambrian rocks (Ross & Murphy, 1988; Smith, 2009).

Finally, though no two depositional environments are identical, it could be helpful to compare depositional basins to find similarities and differences that help to aid in interpreting paleoenvironments. The OFPF is sedimentologically similar to other carbonate-siliciclastic sequences interpreted as deep-water slope-to-base deposits. The Ordovician Cow Head Breccia of Newfoundland, Canada has been interpreted as deposited on a slope under contourite-dominated and minor turbidite processes along the proto-Atlantic continental margin. This is based on deep-water fauna assemblages of eyeless trilobites and deep-water ichnofacies, continuous thin-bedded limestones, green siltstones, marls, radiolarian cherts, mass-flow deposits, and slumps (Hubert, et al., 1977). The Cambrian Frederick Limestone of Maryland, US has been interpreted as a shallowing-up upper-slope deposited along a passive margin based on abundant, thinly laminated argillaceous limestone containing complete Bouma sequences grading from sparse planar laminated to cross-laminated and graded beds, thick-bedded detrital limestone breccia and slumps with clasts of coarse-grained sandstones and oolitic limestones and minor interbedded mudstones (Reinhardt, 1977). The Cambrian Hales Limestone of Nevada, US is interpreted as a deep-water, submarine fan deposited along an open-ocean margin based on dark-grey limestone with fine-grained texture, low-energy mm-scale planar laminations, diagenetic pyrite, gravity-flow and slump deposits, a lack of wave-induced sedimentary structures, and distinct shallow-water and deep-water trilobite assemblages (Cook & Taylor, 1977; Tucker & Wright, 1990). Though the OFPF

characteristics and processes are not necessarily identical to these (owing partly to a Precambrian environment), they all share fundamental characteristics such as thin-bedded alternating fine-grained limestone and siliciclastics, turbidity processes, and breccia. The OFPF shares characteristics unique to each location, such as green siltstones (Cow Head Breccia), pyrite (Hales Limestone), and mass-slumping (Frederick Limestone). A deep-water interpretation is consistent with the characteristics observed in other mixed limestone-siliciclastics environments interpreted as deep-water deposits.

Given the evidence presented here, this study agrees with the current depositional and geochemical interpretations that others have reached over the last thirty years, that the Old Fort Point Formation represents a deep-water submarine fan complex operating under primarily turbiditic processes resedimenting shallow-water carbonate and siliciclastics in basin under fluctuating redox conditions along the Laurentian passive margin.

6.2 Metamorphism, diagenesis, and the integrity of the isotopic values

Diagenesis and metamorphism pose challenges to creating a global $\delta^{13}\text{C}$ picture based on ancient rocks. Multiple lithological and geochemical analyses have been developed to screen carbonate samples for diagenetic alteration, such as petrographic analysis, the relationship between carbon and oxygen isotopic values, stratigraphic patterns that repeated at multiple sites, covariation between organic and carbonate carbon isotope values, radiogenic isotopes such as $^{87}\text{Sr}/^{86}\text{Sr}$, ratios of minor and trace element concentrations, comparing stable isotopic values of individual minerals, and cathodoluminescence, among others (Veizer, 1983; Narbonne, et al., 1994; Knoll, et al., 1986). The $\delta^{13}\text{C}$ values are interpreted as primary if expected patterns used for diagenetic screening are not observed such as covariation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, high Mn/Sr, low Sr, and variable $\delta^{13}\text{C}$ profiles on a basin-scale.

Petrographic evidence for moderate alteration is observed, as illustrated in appendix B. Textures include patches of both fine-grained spar alternating with patches of recrystallized coarse spar. Few sedimentary features are observed, in part due to partial recrystallization of many

samples. Later veining has cut across bedding and introduced calcite and dolomite, sometimes associated with quartz. Non-carbonate grains include muscovite (both detrital and metamorphic), quartz, chlorite, albite, iron oxides, and pyrite. Fine-grained pyrite is attributed to early diagenetic processes, but the less common coarse euhedral grains are attributed to later diagenetic fluid flow. This is based on the presence of coarse calcite and euhedral metamorphic muscovite surrounding coarse pyrite cubes. Stylolites are common in samples originating in folds and these have introduced clay minerals; often recrystallized coarse calcite is observed surrounding these clay-filled stylolites. However, fine-grained phases are observed, usually in association with very fine-grained pyrite but not siliciclastics.

Diagenesis drives both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ more negative, resulting in a covariation between the two isotopic profiles (Banner & Hanson, 1990). In the OFPF, all but the middle 16W exhibit negative correlation between carbon and oxygen isotope values (Figure 12). For all localities, however, the R^2 is less than 0.05, due to the data's wide spread of carbon values but narrow range of oxygen values. Samples were also plotted according to their general mineral group, either "dolomite" or "calcite," where "calcite" includes the ferroan carbonates (determined from dyeing) (Figure 13). $\delta^{13}\text{C}$ values across the two groups are similar. However, dolomite has a strong positive correlation between oxygen and carbon, with an R^2 of 0.5. The calcite group has a weakly negative correlation with an R^2 of 0.04. The positive correlation indicates that the dolomite samples have undergone more significant diagenetic alteration than calcites, consistent with the replacement nature of dolomite.

Beyond carbon and oxygen, dolostone samples exhibit patterns in minor and trace elements distinct from limestone samples (Figure 16 to Figure 17). Of the total 46 samples, 5 (10%) were HMG limestone and the remaining 41 (90%) were limestone. In regard to the HMG limestone samples, Cd, Mn, and Sr concentrations indistinguishable from limestones. Cr and Cu are moderately enriched, while Zn, Rb, and Fe are greatly enriched. Fe is as high as 90,000 ppm (compared to the limestone group's approximately 9000 ppm). As for limestone, the samples

display lower concentrations for all minor and trace elements except Sr where all limestones are more enriched than HMG limestones. The minor and trace element enrichments in HMG limestones suggests that they were altered by diagenetic and metamorphic fluids rich in Cr, Cu, Zn, Rb, and Fe while the limestones avoided such extreme alterations.

As Mn is enriched in meteoric waters and Sr is expelled from the crystal lattice during recrystallization, low values of Mn/Sr are considered good indicators that the $\delta^{13}\text{C}$ values observed are primary, with Mn/Sr < 10 the threshold for isotopic resetting (Kaufman & Knoll, 1995). Mn/Sr is under 10 across both sites, with most samples under 4 (Figure 15). When Sr is plotted against $\delta^{13}\text{C}$, two populations are observed: a smaller set of samples between 450ppm and 600ppm and most of the samples between 450ppm and 250ppm (Figure 14). The samples with the highest Sr concentrations also correspond to the most depleted carbon isotopic values and suggests that the most depleted values are preserved primary values. High Sr is also indicative of an aragonite precursor carbonate. This is consistent with recrystallized aragonite seafloor fans observed in Marinoan-aged cap carbonates and Shuram Excursion carbonates, as well as postulated aragonite seas in the Precambrian (Hardie, 2003; Corsetti & Kaufman, 2003; James, et al., 2001; Melezhik, et al., 2009; Pruss, et al., 2008).

The profile and magnitude of the $\delta^{13}\text{C}$ profiles argue against diagenesis. In both localities of this study the carbonates record $\delta^{13}\text{C}$ profiles of similar morphologies and magnitudes. Both site 16W and site PP begin at approximately -11‰ and recover towards approximately -7.5‰ up-section. Site 16W records three distinct excursions of comparable magnitude. Site PP's stratigraphically brief carbonate bears one excursion. In $\delta^{13}\text{C}$ profiles altered by near-surface diagenesis, such as those referred to in the Great Bahama Bank, the profile is reversed: the profiles begin with the most negative $\delta^{13}\text{C}$ values near the sub-aerially exposed surface and become progressively more positive with depth (Swart & Kennedy, 2011). Highly negative $\delta^{13}\text{C}$ values can result from the oxidation of methane (as low as -70‰), and methane clathrate destabilization has been suggested as a precursor to the Marinoan glaciation and post-glacial meltdown (Schrag,

2002). Carbonates under the influence of methane oxidation display locally variable $\delta^{13}\text{C}$ values ranging from negative to positive (Bekker, et al., 2016). The $\delta^{13}\text{C}$ profiles in this study exhibit a smooth, coherent recovery from more negative to more positive values in multiple localities, inconsistent with expected patterns of methane diagenesis. This pattern was also observed in a more regionally extensive study (Smith, 2009).

The OFPF has undergone structural deformation caused by extensive regional thrust faulting; the sites chosen for this study experienced less severe deformation than locations to the west. Site PP has not been deformed, but simple folding is observed in site 16W and veining is common in samples obtained from those folds. However, the stable isotopic trends indicate that the stratigraphy has been preserved. Regionally, the Windermere Supergroup has been exposed to Mesozoic greenschist metamorphism (Charlesworth, 1967). Metamorphic grade reaches greenschist-amphibolite west in the Columbia Mountain ranges and low greenschist grade in the east. The metamorphic grade of the rocks from this study's localities have undergone less severe metamorphism than locations further west (Kendall, et al., 2004; Smith, 2009; Parker, 2009). Though metamorphism tends to drive $\delta^{13}\text{C}$ values down via decarbonation, the low-to-moderate greenschist grade observed in the OFPF has not obscured the primary stable isotopic values (Smith, 2009; Valley, 1986). Additionally, Neoproterozoic rocks of much higher metamorphic grade have been interpreted to record a primary seawater value (Melezhik, et al., 2007; Prave, et al., 2009).

The OFPF records $\delta^{13}\text{C}$ values comparable to other globally distributed Neoproterozoic carbonates (section 6.4). This combined with evidences provided here indicate that the $\delta^{13}\text{C}$ of the samples in this study is likely a primary record of Neoproterozoic seawater values.

6.3 Geochronological constraints and Implications of Stratigraphic Correlations

Constructing 540 million years of Phanerozoic history is a relatively simple task: robust paleontological and geochronological records help to constrain geochemical trends to build a coherent record. The opposite is true of the Precambrian. Due to poor geochronological and

paleontological controls, stratigraphic correlations are typically based on geochemical trends such as carbon, oxygen, strontium, and sulfur isotopes. These trends are paired with lithological patterns, depositional geometrical models, sequence stratigraphy, and supplemented with any available paleontology and radiogenic data. In this way correlations across modern-day continents are possible. The most profound shifts in Earth's atmospheric and marine realms are observed in the Precambrian, their timing is not as precisely bracketed as their Phanerozoic counterparts. Significant shifts last potentially tens of millions of years, far beyond similar events in the Phanerozoic or durations predicted by geochemical models (Derry, 2010).

In the Windermere Supergroup, the handful of radiogenic dates were obtained primarily from the northern Canadian Cordillera. Accurate stratigraphic correlations across the central Rocky Mountains have been difficult to achieve. In general, the Windermere Supergroup possesses few bioassemblages. A few that have been observed are the Ediacaran assemblages found in the Twitya Formation in the Mackenzie Mountains, and *Namacalathus-Cloudina* assemblages found in the upper Miette Group of British Columbia (Narbonne, et al., 1994; Hofmann, et al., 1991; Hofmann & Mountjoy, 2001; Hofmann & Mountjoy, 2010; Hofmann, et al., 1990). As siliciclastic rock dominates the sequence, few units are suitable for radiometric dating. Consequently, the loose stratigraphic constraints have resulted in inconsistent stratigraphic divisions and diverse local nomenclature across the Canadian Cordillera. Due to the OFPF's unique carbonate lithology, it has been correlated to both Sturtian- and Marinoan-aged carbonates elsewhere in Canada (Smith, 2009).

In the Mackenzie Mountains, the Sturtian glaciation's maximum and minimum depositional ages are constrained by the Rapitan Group's age of 716.5 ± 0.2 Ma (^{206}Pb - ^{238}U zircon) and the Twitya Formation dated at 662.4 ± 3.9 Ma (Re-Os), respectively (Rooney, et al., 2014; Macdonald, et al., 2010). The Marinoan glaciation's termination is constrained by one Re-Os date, 632.3 ± 5.9 Ma from the Sheepbed Formation overlying the Icebrook diamictite with its cap-carbonate, the Teepee Dolomite (Figure 6) (Rooney, et al., 2015). The Twitya Formation, a deep-water shale, was

correlated to the OFPF based on potentially compatible stratigraphic position (Eisbacher, 1981). Recently, the Twitya Formation has been dated at 662.4 ± 3.9 Ma (Rooney, et al., 2014). Additionally, the OFPF carbonates have been correlated with the Teepee Dolomite (Ross, et al., 1995). This is based on clasts with dolostone crystal rosettes resembling the Teepee Dolomite within the upper OFPF.

Clasts similar to the Teepee Dolomite in the OFPF led to the interpretation that it is also the deep-water equivalent to the Vreeland Diamictite of Mt. Vreeland (Figure 6) (McMechan, 2000; Smith, et al., 2013). There is no “marker” in the Vreeland region, and south of Vreeland the OFPF is not in contact with diamictite. The upper OFPF records a significant erosional period that cuts into the base of the formation locally, and is characterised by a coarse breccia fill (section 6.1) (Smith, 2009). Likely these dolomite clasts were removed from an older, topographically higher source that was necessarily lithified prior to erosion. Additionally, the Teepee Dolomite’s minimum $\delta^{13}\text{C}$ value is -7‰ and carbonates of the OFPF reach $\delta^{13}\text{C}$ of -11.5‰ (this study and Narbonne, et al., 1994).

The Twitya Formation and the Sheepbed Formation ages are incompatible with the age of the OFPF. The OFPF has been dated at 607.8 ± 4.8 Ma (Kendall, et al., 2004), resulting in an age difference between the OFPF and the Twitya Formation of about fifty million years. The ages of the OFPF and the Marinoan Sheepbed result in an age difference of more than 24 Ma. The correlation of the OFPF with either the Twitya Formation or the Teepee Dolomite is thus likely incorrect. Additionally, due to the remote area, no geochronological or geochemical work has been conducted in the Monkman Pass/Mt. Vreeland region and any correlation with the OFPF is based on poor stratigraphic constraints.

A possible locality recording the Shuram Excursion is the Gametrail Formation in the Mackenzie Mountains in Canada, where a Shuram-like trend with a $\delta^{13}\text{C}$ nadir of -8‰ was observed (Macdonald, et al., 2013). Additionally, it bears the typical covariation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values but unlike other Shuram localities, the excursion is seen in both the carbonate and the organic carbon.

The Gametrail Formation is an approximately 320 m thick upward-shallowing dolostone succession of ribbon carbonates deposited on the slope to the west of platform carbonates (Aitken, 1991). Stratigraphically, it is not in contact with the Marinoan diamictite or cap-carbonate. The OFPF's $\delta^{13}\text{C}$ trend is morphologically similar and could be correlated. Paleontologically, the Gametrail Formation underlies and overlies Ediacaran fossils while the FAD for fossils overlying the OFPF is approximately 1.3 km higher, potentially placing it temporally higher than the OFPF, depending on sedimentation rate (Hofmann & Mountjoy, 2010). The OFPF's deep-water nature could explain the stratigraphic difference, but overall the stratigraphy between the two regions is not similar and correlating the two successions is not simple. The limited exposure of Neoproterozoic stratigraphy in the Monkman Pass/Mt Vreeland area (geographically midway between the Mackenzie Mountains and the southern Rocky Mountains) is not easily correlated to either locale. It is possible that the Chowika Limestone is a Shuram correlative based on stratigraphic position but geochemical analyses would need to be conducted before that correlation can be made.

Based on age and geochemical constraints presented here, the OFPF cannot be correlated to any Marinoan-aged diamictite or cap-carbonate, and was likely deposited during the post-Marinoan time. As discussed in sections 6.3 and 5.4, geochemically it can be correlated to Shuram Excursion units around the globe, but those units have been assigned younger depositional ages.

6.4 Comparing the Marinoan Cap-carbonates, the Shuram Excursion, and the OFPF

The OFPF has been correlated to Sturtian glacial units, but geochronologic data now renders the correlations not likely to be correct and thus the Sturtian time interval will not be considered in the following discussion (Rooney, et al., 2014). Geochronology and geochemistry now suggests that the OFPF was deposited in post-Marinoan time, but a comparison between the OFPF and Marinoan cap carbonates is still relevant. The OFPF can be interpreted as recording the Shuram Excursion based on the following characteristics: 1) $\delta^{13}\text{C}$ profile comparable to the carbon isotope trends in other units known to record the Shuram Excursion, 2) $\delta^{34}\text{S}$ trend similar to $\delta^{34}\text{S}$ profiles in the Shuram Excursion carbonates, 3) deposition during a transgressive-highstand

sequence, 4) the presence of submarine canyons in the Johnnie Formation, the Wonoka Formation, and the OFPF, and 5) comparable age between the OFPF, the Shuram Formation, and the Doushantuo Formation.

Marinoan cap carbonates bear unique geochemical and sedimentological properties (Corsetti & Lorentz, 2006). Typical $\delta^{13}\text{C}$ values do not fall below -5 or -6‰, the canonical mantle carbon isotopic value (Halverson, et al., 2005). Cap carbonate $\delta^{18}\text{O}$ values co-vary with $\delta^{13}\text{C}$ and exhibit a spread between approximately -14 and -8‰; these values are more depleted than non-Snowball Earth carbonates and this depletion is attributed to the input of isotopically light post-glacial meltwater (Halverson, et al., 2010; Jiang, et al., 2007). The Shuram Excursion records a significant $\delta^{13}\text{C}$ excursion of -12‰, though this nadir varies by location with some potential Shuram locations recording a $\delta^{13}\text{C}$ nadir of approximately -9‰. Plotting $\delta^{13}\text{C}$ values against $\delta^{18}\text{O}$ values for the Shuram Excursion carbonates reveals a positive correlation ($r^2 = 0.62$) (Derry, 2010). This diagenetic signature is considered as one of the Shuram Excursion's defining features, yet it occurs within similar $\delta^{13}\text{C}$ profiles separated by hundreds of kilometers. The excursion gradually recovers over a few hundred meters to 0‰ (Calver, 2000; Burns & Matter, 1993). Contrastingly, all but one of the OFPF's $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ sections exhibit a negative instead of positive correlation with low R^2 values (see section 6.2). The $\delta^{13}\text{C}$ values exhibit a wide spread (up to 4‰) compared to a narrow range of $\delta^{18}\text{O}$ (approximately 1‰). Thus, the OFPF records a negative carbon isotopic excursion similar in magnitude and morphology to the Shuram Excursion but with isotopic relationships suggesting that the $\delta^{13}\text{C}$ values are primary.

Middle Neoproterozoic $\delta^{34}\text{S}_{\text{SO}_4}$ values hovered around 20‰, but Australian and Namibian Marinoan cap carbonates record negative $\delta^{34}\text{S}_{\text{pyr}}$ values during cap-carbonate deposition, followed by recovery (Hurtgen, et al., 2002; Fike, et al., 2006; Halverson & Hurtgen, 2007). In Oman, the Hadash cap-carbonate records positive $\delta^{34}\text{S}$ values for both sulfate and pyrite (Fike, et al., 2006). The Doushantuo cap carbonate $\delta^{34}\text{S}$ values do not fluctuate significantly (Huang, et al., 2013). During the Shuram Excursion in all localities, both $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{pyr}}$ exhibit parallel falls

(Grotzinger, et al., 2011). Within the Shuram Formation itself, $\delta^{34}\text{S}_{\text{SO}_4}$ records a decrease from 28‰ (coincident with the beginning of the $\delta^{13}\text{C}$ downturn) to approximately 20‰ before switching to the gradually rising trend above the Shuram Formation (Fike, et al., 2006; Osburn, et al., 2015). The Doushantuo Formation records similar negative $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{pyr}}$ trends in the Shuram-equivalent section (Xiao, et al., 2012). The Clemente Oolite in Mexico records a negative $\delta^{34}\text{S}_{\text{SO}_4}$ trend, gradually changing to more positive values. The Johnnie Oolite of Death Valley records a value of approximately 27‰, prior to the carbon isotope excursion, followed by a pronounced decline to 17‰ near the top of the excursion (Kaufman, et al., 2007). The $\delta^{34}\text{S}_{\text{pyr}}$ values from the stratigraphic level immediately underlying the OFPF are approximately 15‰ but starting at the base of the OFPF $\delta^{34}\text{S}_{\text{pyr}}$ values decrease, culminating at -31‰ in the black shale. $\delta^{34}\text{S}_{\text{pyr}}$ values then gradually trend towards through values the OFPF (Smith, 2009; Ross, et al., 1995). This was interpreted as an indication of anoxic depositional condition with unlimited sulfate availability (Smith, 2009).

$^{87}\text{Sr}/^{86}\text{Sr}$ in the whole Neoproterozoic generally increases from approximately 0.7055 in the Tonian to nearly 0.7090 near the Ediacaran-Cambrian boundary (Macdonald, et al., 2013). Marinoan glacigenic rocks are associated with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7070 (Narbonne, et al., 1994). On the other hand, carbonates recording the Shuram Excursion are noted for their high Sr concentrations even in high metamorphic grade, and for bearing $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values as high as 0.7090 (Melezhik, et al., 2007; Burns & Matter, 1993). The strontium concentrations in the Shuram Formation and the Wonoka Formation are in the 400 ppm and 500-1100 ppm range, respectively (Burns, et al., 1994; Foden, et al., 2001). The Doushantuo Formation records Sr concentrations between 400 and 700 ppm (Huang, et al., 2011). The OFPF records Sr concentrations between 250 and 600 ppm, which is consistent with both Marinoan and Shuram Excursion carbonate rocks (Table 3).

Other than strontium concentrations, trace element data for the Marinoan cap-carbonates and carbonates of the Shuram Excursion is limited. A few studied locations include China, Canada,

and Australia. The OFPF records relatively low concentrations of elements except for Sr, but these are still comparable to the Marinoan and the Shuram Excursion carbonates (Table 3). Dolomite samples are significantly enriched in Zn, Cr, Cd, Fe, and Rb compared to calcite samples (section 6.1; Figure 16 Figure 23), which is attributed to diagenetic fluids during dolomitization.

Sequence	Mn (ppm)	Fe (ppm)	Cr (ppm)	Cd (ppm)	Zn (ppm)	Sr (ppm)
Marinoan cap-carbonates	1067 - 5071	2746 - 9093	< 100	0.078 – 2.02	11.3 - 381	283 - 528
Shuram Excursion carbonates	995 - 600	3000 - 9000	20 - 112	< 1	≤ 400	201 - 1420
OPPF	3779	83739	≤ 39	≤ 4.6	≤ 106	242 - 559
OPPF average	1564	7923	4.95	1.9	4	360

Table 3: sampling of trace element concentration ranges for Marinoan cap carbonates, Shuram Excursion carbonates, and the OFPF. Sources: (Huang, et al., 2011; Miller, et al., 2017; Kunzmann, et al., 2013; John, et al., 2017; Calver, 2000; Burns, et al., 1994; Foden, et al., 2001)

The termination of the Marinoan glaciation is well-constrained now to approximately 635 Ma (Rooney, et al., 2015), whereas the Shuram Excursion is poorly constrained with a possible range of 44 Ma from the Shuram and the Doushantuo Formations. For comparison, the OFPF has been dated by the Re-Os method on shales at 607.8 ± 4.7 Ma (Kendall, et al., 2004). This presents the first precise constraint on the duration of the Shuram Excursion and is discussed in detail in section 6.5.

Carbonates of the Shuram Excursion and the Marinoan cap-carbonates were deposited during transgression, but cap-carbonates are deep-water deposits while Shuram Excursion carbonates were deposited above storm-wave-base (Burns & Matter, 1993; Calver, 2000; Prave, et al., 2009; Loyd, et al., 2015; James, et al., 2001; Preiss, 2000; Corsetti & Lorentz, 2006). The

OFPF is a deep-water turbiditic sequence deposited during a transgressive-to-highstand phase, capped by the middle member black shale. A distinctive feature of the Johnnie Formation and the Wonoka Formation is the presence of deeply-incised submarine canyons (Clapham & Corsetti, 2005; Giddings, et al., 2010). In the Nopah Range of Death Valley, the Rainstorm Member of the Johnnie Formation (which records the Shuram Excursion) is characterised by submarine canyon incision to a maximum depth of 120 m with canyon-fill deposits (Clapham & Corsetti, 2005). The incision and canyon fill are associated with along-strike extensional syn-depositional faulting indicating a tectonic instead of glacial driver. The Wonoka Formation is similarly cut by submarine canyon incision to a maximum depth of nearly 2 km (Giddings, et al., 2010). These canyons' origins are enigmatic and have been variously attributed to salt diapirism, sub-aerial exposure, a Mediterranean-style closed basin formed by either tectonic uplift or evaporation, sub-marine formation, and open-marine tectonic uplift (Christie-Blick, et al., 1990). The Death Valley canyons have been correlated to post-Marinoan incised valleys in Idaho and Utah and have been linked to regional uplift along the Laurentian coastline during the early Paleozoic (Levy, et al., 1994). In the OFPF, regionally-extensive submarine canyons are a distinctive feature, where erosion was so severe that cut into the lower two members of the OFPF and removed several hundred meters of rock sequence (Smith, 2009; Arnott & Hein, 1986). This canyon incision has been attributed to regional tectonic uplift across the southern Canadian Cordillera, which shifted the depositional regime in the Windermere basin from deep-water to shallowing-upward deposition (Smith, 2009).

Based on sedimentologic and stratigraphic similarities, it has been proposed that the Neoproterozoic Australian and Canadian sequences had been once connected prior to the breakup of Rodinia (Stewart, 1972; Young, 1992). Indeed, the west-facing coastline of Laurentia is interpreted as open-marine, since the western margin of the Windermere basin has not been located (Ross, 1991). Though the terminal Ediacaran Risky Formation was correlated to the Wonoka Formation in Australia (Young, 1992), geochemical and geochronological studies negate this correlation. As the Gametrail Formation has recently been identified to record the Shuram

Excursion (Macdonald, et al., 2013), the Wonoka Formation should instead be correlative to the Gametrail Formation. The OFPF, though correlated to Marinoan cap-carbonates, has yielded geochemical and geochronological data that implies a younger deposition and Shuram-equivalent interpretation. Like in Death Valley, post-Windermere Supergroup deposition recorded the early Paleozoic uplift (Devlin & Bond, 1988). The submarine canyons of the Johnnie Formation, Wonoka Formation, and OFPF, combined with the underlying and distinct $\delta^{13}\text{C}$ excursion, indicate that all three are correlative.

In summary, the OFPF's geochemical, geochronological, and stratigraphic features negate a correlation with Marinoan-aged cap carbonates. Instead, the OFPF represents a primary, deep-water record of the Shuram Excursion. Its precise age helps to constrain the age of the Shuram Excursion, which currently is poorly dated.

6.5 The OFPF and the nature of the Shuram Excursion

The Shuram Excursion's $\delta^{13}\text{C}$ profile requires unique explanations for either primary or diagenetic processes. Though the Shuram Excursion possesses "diagnostic" diagenetic features such as carbon and oxygen isotopic co-variation, the evidence overwhelmingly points to a primary origin: consistent carbon isotope excursions across multiple sites in one region and across the globe; elevated CAS concentrations, which indicate good preservation, as diagenesis tends to decrease CAS concentrations; in Oman, $\delta^{13}\text{C}_{\text{org}}$ values as low as -40‰ have been observed in long-chain *n*-alkanes and mid-chain monomethyl alkanes, which indicates a preserved record of a significant organic carbon perturbation; and finally, high Sr concentrations and Ca isotopes from the Wonoka Formation in Australia coincide with the most negative $\delta^{13}\text{C}$ values from that region (Lee, et al., 2015; Husson, et al., 2015; Fike, et al., 2006; Grotzinger, et al., 2011). As diagenetic alteration models inadequately explain these observations, the Shuram Excursion appears to record a significant shift in Earth's carbon cycle significantly later than the Marinoan meltdown.

The Shuram Excursion is observed in four localities: Oman, Australia, California, and China (Burns & Matter, 1993; Calver, 2000; Jiang, et al., 2007; Bergman, et al., 2011). Additional localities

have been reported. the Clemente Oolite of Mexico records a depletion to -10‰ and has been correlated to the Johnnie Formation in Death Valley (Loyd, et al., 2015). Carbonates from the Neoproterozoic Zhuya Group in Siberia record a $\delta^{13}\text{C}$ excursion lighter than -10‰ (Pokrovskii, et al., 2006). The Kauriyala Formation in India records a negative $\delta^{13}\text{C}$ excursion similar to the Shuram Excursion (Kaufman, et al., 2006). The Gametrail Formation in Canada, the Girdsta Formation in Scotland, and the Sugetbrak Formation in China all record carbon isotope excursions of up to -8 or -9‰ (Macdonald, et al., 2013; Prave, et al., 2009; He, et al., 2007). The Leivset Marble in Scandinavia and the Girdsta Formation have been interpreted as high-grade metamorphic records of the Shuram Excursion (Melezhik, et al., 2007; Prave, et al., 2009). The upper Johnnie and Wonoka Formations are characterized by submarine canyon incision, where the Wonoka excursion is truncated by incision (section 6.4). Variations in the Shuram Excursion can be attributed to local conditions (such as sedimentation rates, organic matter concentrations, and redox conditions), as was observed in the Shuram Excursion phase of the Doushantuo Formation where spatial heterogeneity is recorded between the studied sections (Li, et al., 2017).

Various explanations for a primary origin of the Shuram Excursion have been put forth. Oxidation of a large DOC (dissolved organic carbon) reservoir could explain the rapid carbonate depletion that is not observed in organic carbon (Rothman, et al., 2003; Fike, et al., 2006). Sedimentary methane hydrate destabilization was suggested as a way to introduce significant volumes of reduced carbon into the marine carbon cycle without completely consuming the available oxidant budget (Bjerrum & Canfield, 2011). Johnston et al., 2012 suggested weathering of organic-rich shales on the continent or migration of local hydrocarbon reserves as another source of isotopically light carbon, along with alternative oxidants such as SO_4 instead of O_2 , which would preserve the fragile O_2 levels in the marine and atmospheric realms. Finally, lateral heterogeneities in the Shuram Excursion recorded in the Doushantuo Formation led to the suggestion of a three-tiered stratified ocean model in which the upper oxic and lower euxinic levels would record positive $\delta^{13}\text{C}$ values while an intermediate euxinic level would record negative $\delta^{13}\text{C}$ values (Ader, et al.,

2009). Any model explaining the Shuram Excursion should explain the lack of covariation between carbonate and organic carbon, the excursion's record over hundreds of meters of carbonate, and the similarity between global, disparate locations. Determining the excursion's duration has been hampered by poor geochronological constraints. As discussed in section 6.4, the excursion is currently constrained between Marinoan cap carbonates (though via subsidence and depositional rates, the Shuram Formation was estimated to have an average age of 601 ± 8 Ma) and a Re-Os date of 591.1 ± 5.3 Ma in China (Le Guerroué, et al., 2006; An, et al., 2015). The potentially long duration has generated controversy and a long duration, if it is long, should be explained by models. Though the Shuram Excursion is still enigmatic, global, pulsed oxidation of dissolved carbon-12 would be consistent with increasing oxidation of the atmosphere and ocean, which is supported by the $\delta^{34}\text{S}$ record, metazoan evolution, and trace element concentrations such as Mo and U (Lyons, et al., 2014). Ultimately it is beyond the scope of this work to conclusively determine the most appropriate explanation of the Shuram Excursion.

Our knowledge of the carbon cycle in the late Ediacaran is dependent on the deposition and preservation of carbonates. Though the Shuram Excursion is the most negative excursion, it is not the only excursion leading up to the Ediacaran boundary. In Death Valley, three excursions are observed after the Shuram Excursion, recording a series of -8‰, -5‰, and -2‰ $\delta^{13}\text{C}$ excursions up-section (Verdel, et al., 2011). In India, the Kauriyala Formation records multiple $\delta^{13}\text{C}$ excursions, notably one reaching -8‰ and another -5‰ $\delta^{13}\text{C}$, following the Shuram Excursion there (Kaufman, et al., 2006). In the Mackenzie Mountains, the terminal-Ediacaran Risky Formation records an excursion of approximately -4‰ after the excursion in the Gametrail Formation (Macdonald, et al., 2013). In Sonora, Mexico, an excursion of -5‰ is recorded at the Ediacaran-Cambrian boundary (Lloyd, et al., 2015). Much of the Ediacaran following the Shuram excursion in the Doushantuo Formation is truncated by a sequence boundary and so any record of multiple excursions there has been lost (Condon, et al., 2005). The Wonoka Formation records a single excursion, but like in Canada, the sequence is dominantly siliciclastic (Calver, 2000). Additionally, the Wonoka

Formation has been deeply incised by submarine canyons (Christie-Blick, et al., 1990). Similarly, the Sugetbrak Formation in China is dominantly siliciclastic and records only the Shuram Excursion and a -2‰ $\delta^{13}\text{C}$ excursion at the Ediacaran-Cambrian boundary (He, et al., 2007). Finally, the Shuram Formation records a rapidly fluctuating carbon record after the excursion and leading up to the Cambrian boundary, owing to the greater proportion of carbonate deposition preserving a stratigraphically complete Ediacaran carbon record in that region (Burns & Matter, 1993). Site 16W of the OFPF records three excursion, two of which record similar magnitude and morphology. While the Shuram Excursion's unique characteristics point to a significant perturbation in the carbon pool, the current low-resolution geochronology prevents further interpretation of whether the Shuram Excursion is a single isochronous event or a diachronous response to regional changes such as tectonics, climate, redox conditions, etc.

Carbonates recording the Shuram Excursion have not yielded any geochronological data, resulting in a controversy over its duration. Current age constraints restrict the excursion's duration to some 44 Ma years (An, et al., 2015; Le Guerroué, et al., 2006). The Shuram Excursion in South China has been dated to have ended by 591.1 ± 5.3 Ma (Zhu, et al., 2013). The Shuram Formation's estimated average age is 601 ± 8 Ma based on subsidence and sedimentation rates in Oman, but geochronologically it overlies Marinoan cap-carbonates (Le Guerroué, et al., 2006). The OFPF's Re-Os date of 607.8 ± 4.7 Ma is the first precise date from within the excursion itself, and approximately 17 Ma exist between the OFPF and the estimated age of the Doushantuo Formation. If this date is correct, the OFPF represents the earliest record of the Shuram Excursion, placing it after the deposition of Marinoan cap carbonates and before the Gaskiers glaciation suggested to have occurred between 580-579 Ma (Pu, et al., 2016). The vast span of time between the OFPF and the Doushantuo Formation indicates that either future geochronological dating will push the Shuram Excursion in China back even further or the Shuram Excursion possibly represents multiple excursions deposited in a diachronous event. See Figure 26 and Figure 27.

The Shuram Excursion's record is also limited by distinctive incision in several units. Submarine canyon incision in the OFPF, the Wonoka Formation, and the Johnnie Formation, along with the unconformity above the Doushantuo Formation could indicate regional tectonic uplift terminating the excursion in Australia, the South China craton, and along the western Laurentian coastline (Young, 1992; Condon, et al., 2005; Arnott & Hein, 1986; Clapham & Corsetti, 2005).

In summary, the Shuram Excursion remains an enigma. Multiple explanations have been suggested, but evidence today points to a primary origin of a significant perturbation in the carbon isotope record. It suffers from poor age constraints, but the OFPF's precise age during the excursion provides the oldest suggested record of the excursion, and implies that it could be a diachronous event. Several Shuram Excursion units around the globe, particularly those in Australia, China, Death Valley, and Canada, recorded a dramatic sea level drop in the form of a significant sequence boundary or deeply incised submarine canyons. These basins could have been affected by regionally restricted tectonic changes.

6.6 Connecting the OFPF to the larger Neoproterozoic world

The OFPF provides insight into the Ediacaran world following the most severe glaciations in geologic history (Kirschvink, 1992). The Ediacaran period experienced dramatic fluctuations in the $\delta^{13}\text{C}$ values of seawater, witnessed emergence of increasingly complex metazoan life; sulfur isotopes indicate rising seawater sulfate concentrations and an increasingly oxygenated ocean and atmosphere (Lyons, et al., 2014; Fike, et al., 2006). Following the Shuram Excursion, the seawater $\delta^{13}\text{C}_{\text{carb}}$ values fluctuate contemporaneously with the appearance of body and trace fossils around the globe (Narbonne, et al., 2012).

Past $\delta^{34}\text{S}_{\text{pyr}}$ studies conducted on the OFPF indicate the presence of unlimited sulfate as well as rising sulfate through the Ediacaran period alongside increasing oxygenation of the atmosphere and oceans (Smith, 2009; Ross, et al., 1995). This is consistent with the $\delta^{34}\text{S}$ trends in other units recording the Shuram Excursion.

As discussed in detail in section 6.5, the OFPF's precise Re-Os age of 607.8 ± 4.7 Ma provides the one precise geochronological data point for the southern Canadian Cordillera (Kendall, et al., 2004). It also places the most extreme negative carbon isotopic excursion before the Gaskiers glaciation, contrary to popular estimation (Fike, et al., 2006; Grotzinger, et al., 2011; Halverson, et al., 2005). The OFPF's $\delta^{13}\text{C}$ signal is preserved in deep-water carbonates likely comprised of redeposited sediments from shallower waters. The OFPF's carbon profile, through nearly 200 m of carbonate in some locations, represents a contemporaneous seawater carbon isotopic signal. Though diagenesis and metamorphism have influenced the oxygen isotopes in the OFPF, other lines of evidence support a primary $\delta^{13}\text{C}$ record of the Shuram Excursion (section 6.2), where the lack of covariation in carbon and oxygen isotopes (a trait of the Shuram Excursion) puts to rest the suggestion that an extreme carbon isotopic depletion is simply a diagenetic overprint. Additionally, Smith 2009 observed a co-variation between carbonate and organic carbon isotopes, which is considered a primary characteristic. The lack of such a covariation is yet another trait of the Shuram Excursion (Grotzinger, et al., 2011). The variations between the numerous units recording the carbon isotope excursion can likely be attributed to local conditions such as sedimentation rate, burial rate of organic matter, and redox conditions.

6.7 Future work

Future work on the OFPF should focus on studying carbonate-associated sulfate (CAS) isotopes and concentrations to quantify late-Ediacaran seawater sulfate. The Shuram Excursion records elevated CAS concentrations and this would provide another line of support for the OFPF's correlation. Though redox-sensitive trace elements are of generally low concentrations in the OFPF, the stratigraphic extent of redox conditions can be better constrained with trace element isotopic ratios. Finally, the Shuram Excursion records high $^{87}\text{Sr}/^{86}\text{Sr}$ values, and if other Shuram Excursion localities are significantly younger than the OFPF, we should expect lower $^{87}\text{Sr}/^{86}\text{Sr}$ values for the OFPF. Determining the $^{87}\text{Sr}/^{86}\text{Sr}$ values for the OFPF will help to shed light on whether the Shuram Excursion is a single or multiple events.

Chapter 7: Conclusions

The Ediacaran period was marked by dramatic fluctuations in the atmospheric realm, including the most severe glacial period, which deposited great thicknesses of tillite and subsequent isotopically-light cap-carbonates (around -5‰ $\delta^{13}\text{C}$) around the globe. Later, the largest negative carbon isotopic shift in geologic history occurred, known as the Shuram Excursion. It is observed in carbonates from multiple continents (e.g., Oman, South China, Australia, NW Canada, and Death Valley, California) and recorded a dramatic shift of -12‰ followed by a gradual recovery over hundreds of meters (Burns & Matter, 1993; Calver, 2000; Macdonald, et al., 2013). Controversy surrounds its nature but evidence points to a primary origin of the excursion. Multiple explanations for the excursion have been suggested, which are predominantly variations on the reduction of a significant input of organic carbon. The excursion has raised concerns over our understanding of the Neoproterozoic carbon cycle, its relationship to Ediacaran biota, and the increasingly oxygenated Ediacaran atmosphere and ocean (Fike, et al., 2006).

In the Windermere Supergroup of the Canadian Rockies, the Old Fort Point Formation (OFPF) is a laterally-continuous carbonate-black shale marker observed throughout the southern Canadian Cordillera, and has long been used to determine stratigraphic position (Aitken, 1969). The shales, siltstones, and carbonates represent a phase of deep-water turbidite deposition on the basin slope to abyssal plain, where shallow-water carbonate sediments were redeposited from higher on the slope. Turbidite deposition was followed by an extensive phase of sub-marine canyon incision (section 6.1). The OFPF has been correlated to Sturtian- and Marinoan-aged glacigenic units based on stratigraphic position and sedimentological characteristics, though it is not in stratigraphic contact with glacially-influenced units. Though geochronological data from the Windermere Supergroup has been sparse until recently, a precise Re-Os date of 607.8 ± 4.7 Ma (Kendall, et al., 2004) has helped to shed light on earlier proposed correlations. As the Marinoan glaciation is now considered to have terminated around 635 Ma (Rooney, et al., 2015), the OFPF's age conflicts with current correlations. Additionally, data presented here have revealed that the

OFPF records a highly negative carbon isotope excursion, with values as negative as -11.5‰ at the base and gradually recovering upsection. The signal is interpreted as primary based on various geochemical screens such as lack of co-variation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, similar isotopic trends in multiple locations, Mn/Sr mostly < 4, and high Sr concentrations (section 6.2).

The OFPF's precise date and $\delta^{13}\text{C}$ profile indicate that it is a record of the Shuram Excursion (section 6.4). This correlation provides a possible maximum depositional age for the Shuram Excursion and pushes the excursion's age further back in the Ediacaran period. As the top of the Shuram Excursion recorded in the Doushantuo Formation has been dated at 591.1 ± 5.3 Ma (Zhu, et al., 2013), the OFPF's date suggests that the Shuram Excursion was possibly a diachronous event. Additional units recording the Shuram Excursion have been identified, and multiple post-Shuram excursions have been observed in single sections (section 6.5). The Shuram Excursion in Australia and Death Valley is associated with deep submarine canyon incision, and in South China it is truncated by an unconformity (Condon, et al., 2005; Clapham & Corsetti, 2005; Giddings, et al., 2010). As the OFPF is also associated with canyon incision, the four locations may have been subjected to regional tectonic uplift that did not occur in other localities. It would also put to rest the controversy regarding a diagenetic or primary origin, as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the OFPF do not co-vary (section 6.5).

Carbon isotopes, sulfur isotopes, and paleontology all indicate that following the Marinoan glaciation the Ediacaran period recorded an increasingly oxygenated atmosphere and ocean leading up to the Ediacaran biota and Cambrian Explosion. The Shuram Excursion has presented challenges to our understanding of the Neoproterozoic carbon cycle, due to its highly negative signal and its potentially long duration. The record of the OFPF provides a step forward in constraining the Shuram Excursion and enriching our understanding of Earth's biogeochemically most volatile time period.

Appendices

Appendix A: Figures

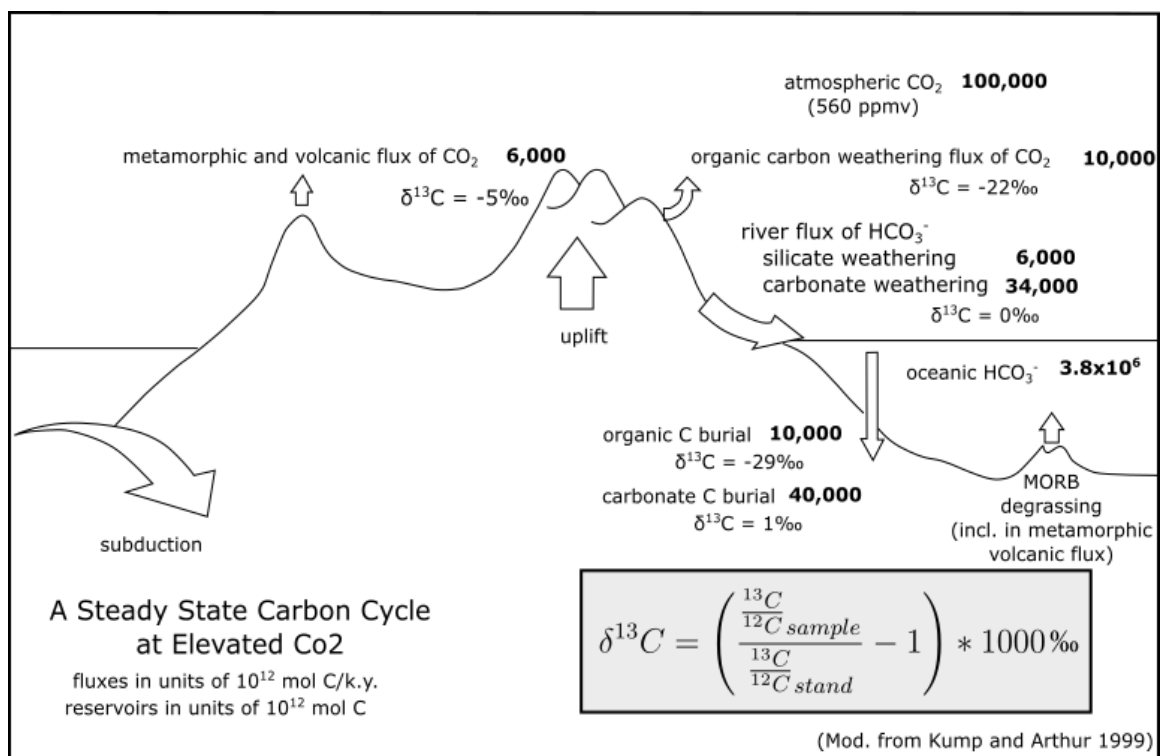


Figure 1: The Carbon cycle's sinks and sources, the volumes and isotopic signatures of each.

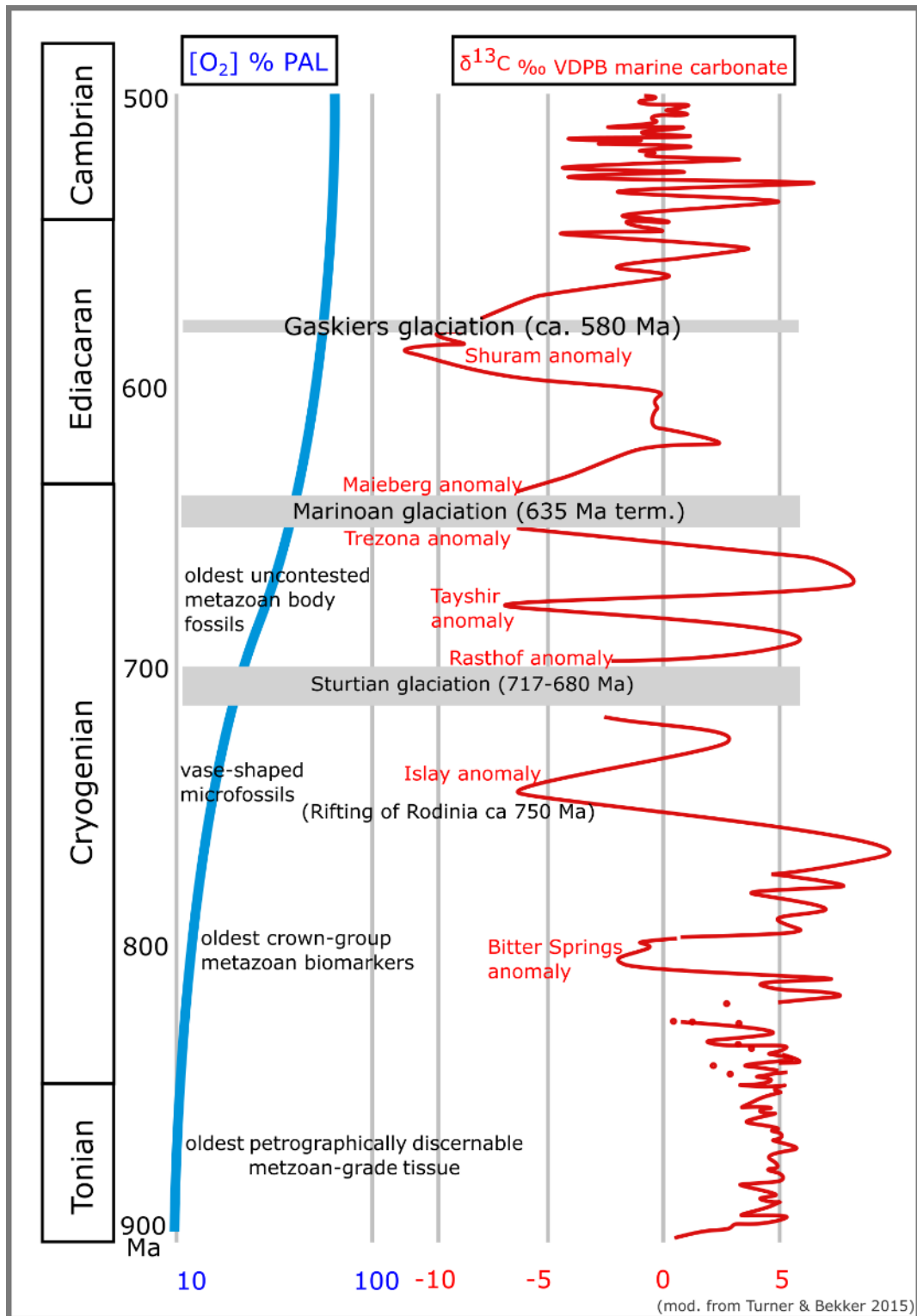


Figure 2: Oxygen and carbon trends of the Neoproterozoic. Mod. Turner & Bekker 2015

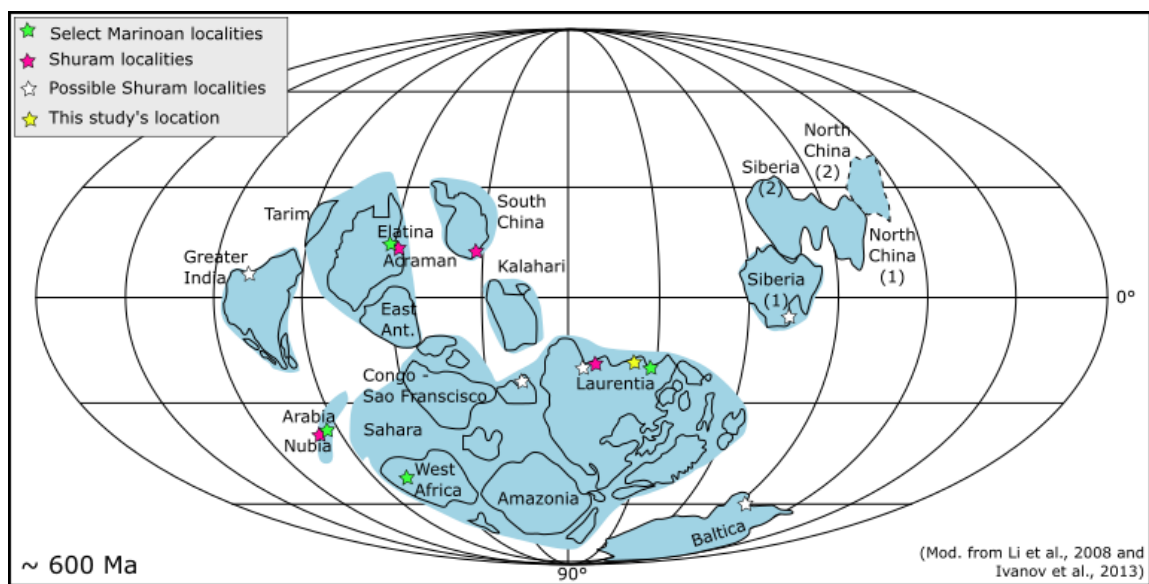


Figure 3: Reconstruction of late Neoproterozoic continents at approximately 600 Ma.

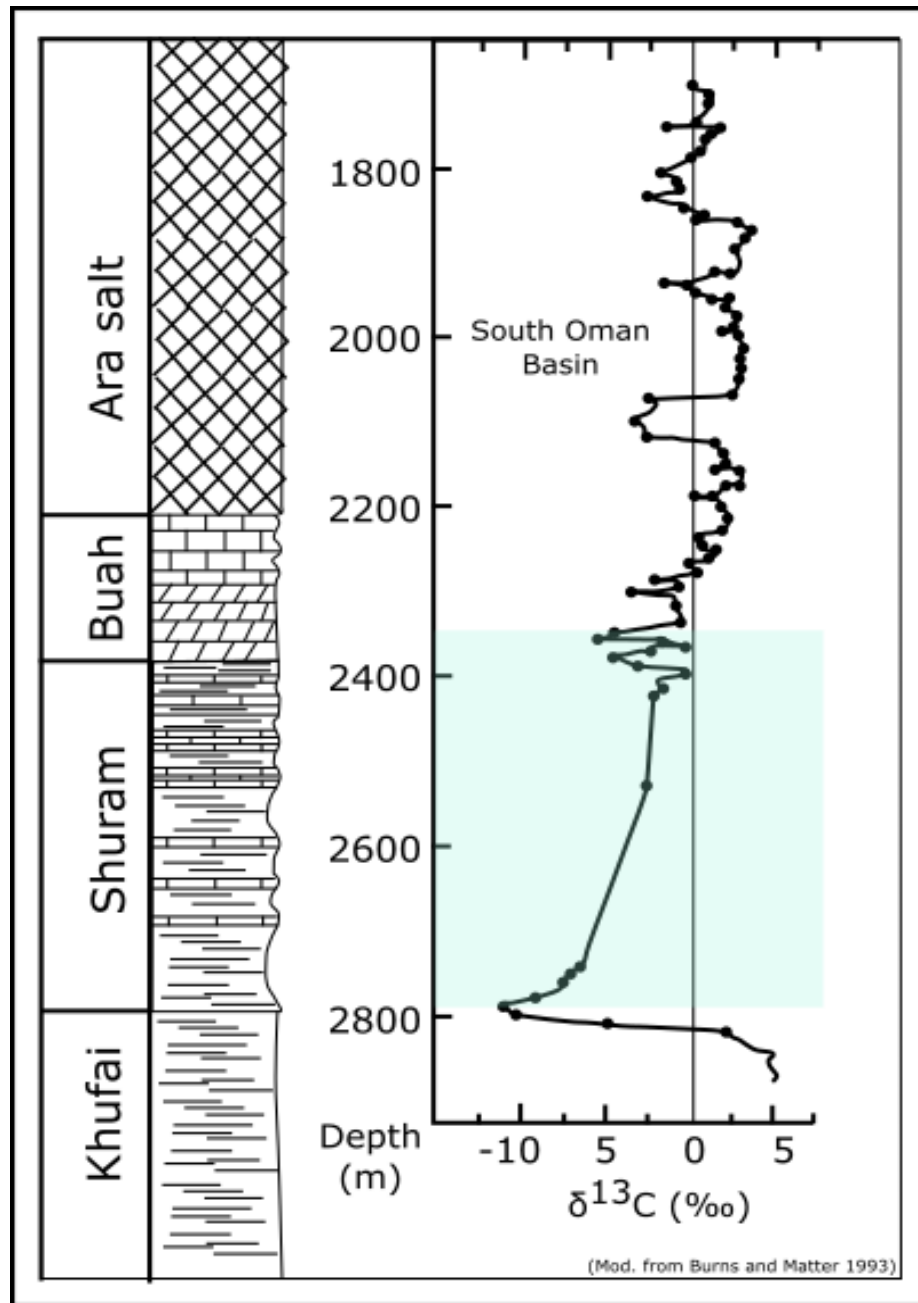


Figure 4: Carbon isotopic profile of the Shuram Formation

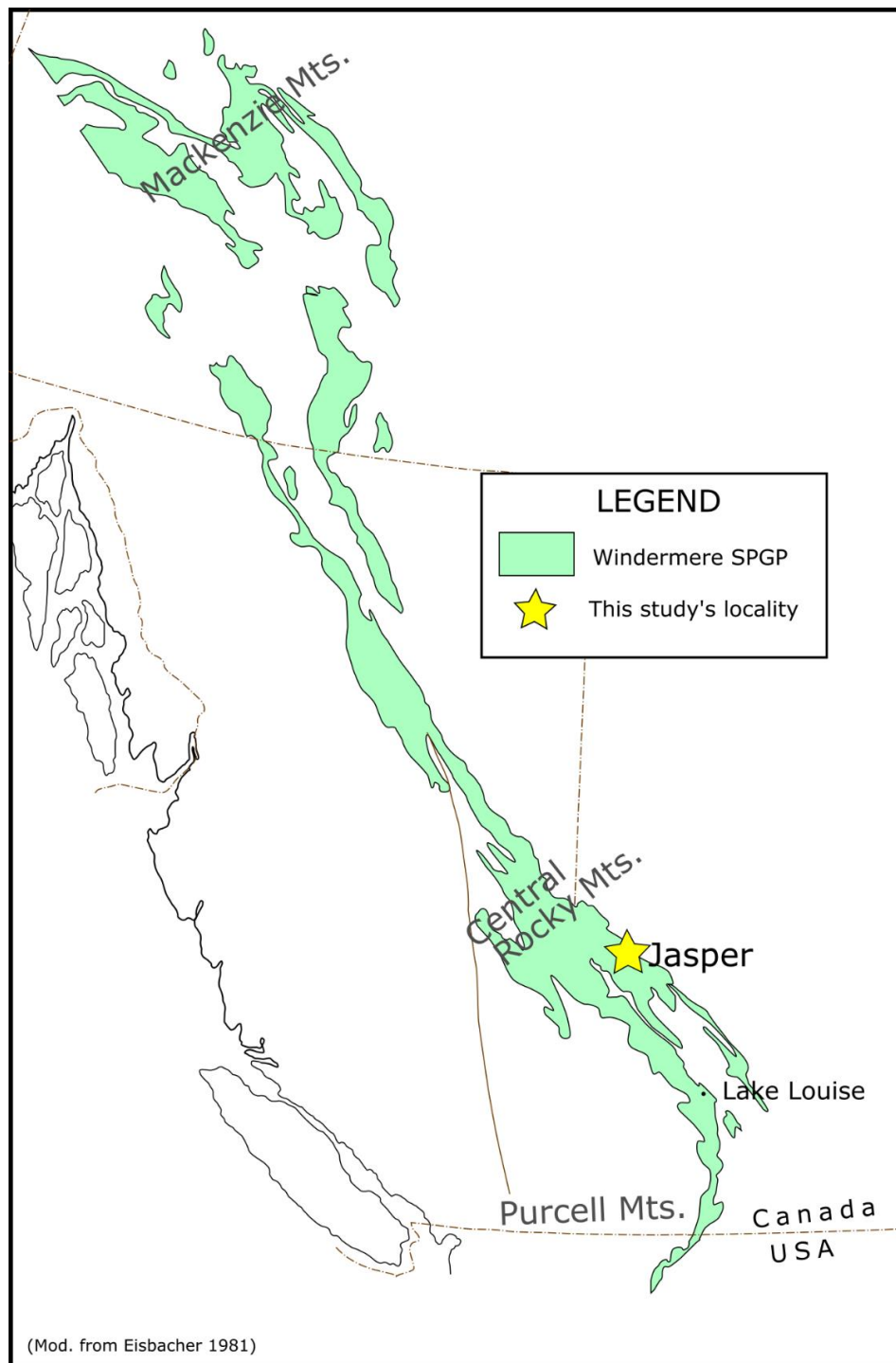


Figure 5: Simplified regional of the Proterozoic in the Central Rockies and the Mackenzie Mountains.

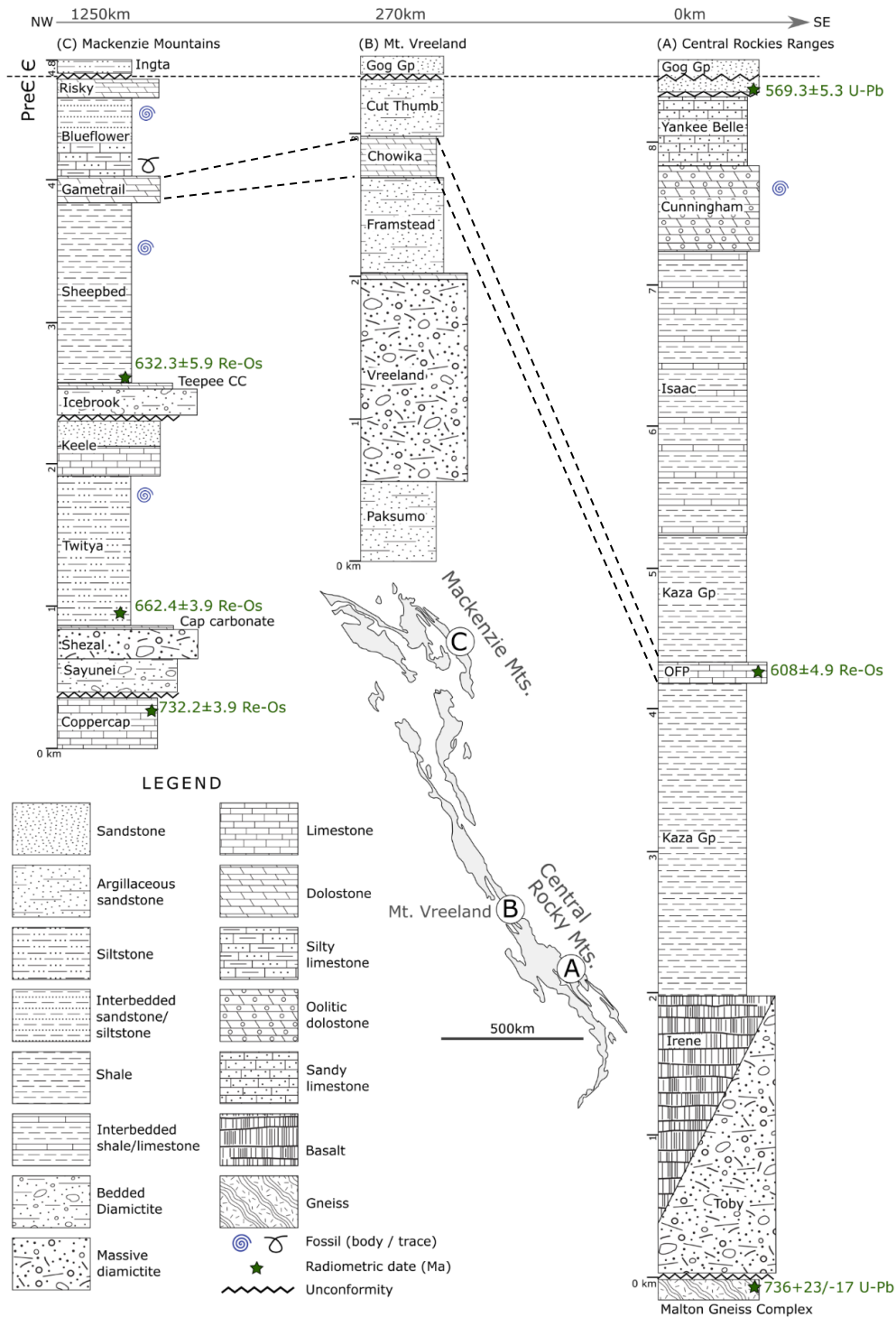


Figure 6: Simplified stratigraphic columns of three localities correlated to one another based on stratigraphic position: the OFP with the Vreeland diamictite and the Teepee or the Twitya. Stratigraphy modified from (Ross, et al., 1995; McMechan, 2000; James, et al., 2001). Dashed lines indicate potential correlation. Paleontological data from (Hofmann, et al., 1990; Hofmann & Mountjoy, 2010). Radiometric data from (Kendall, et al., 2004; Rooney, et al., 2014; Rooney, et al., 2015; McDonough & Parrish, 1991; Colpron, et al., 2002)

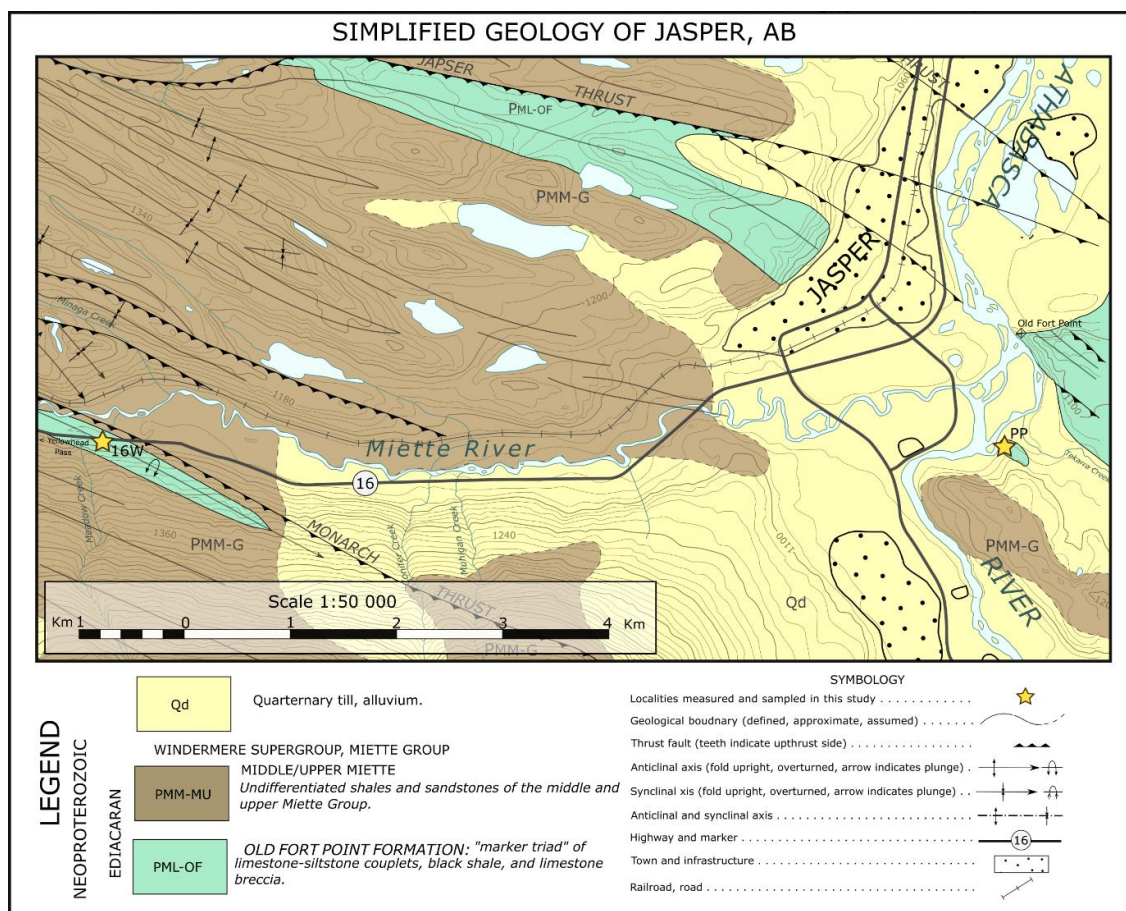


Figure 7: Map of the geology of the Jasper region. This study's localities denoted by yellow stars.

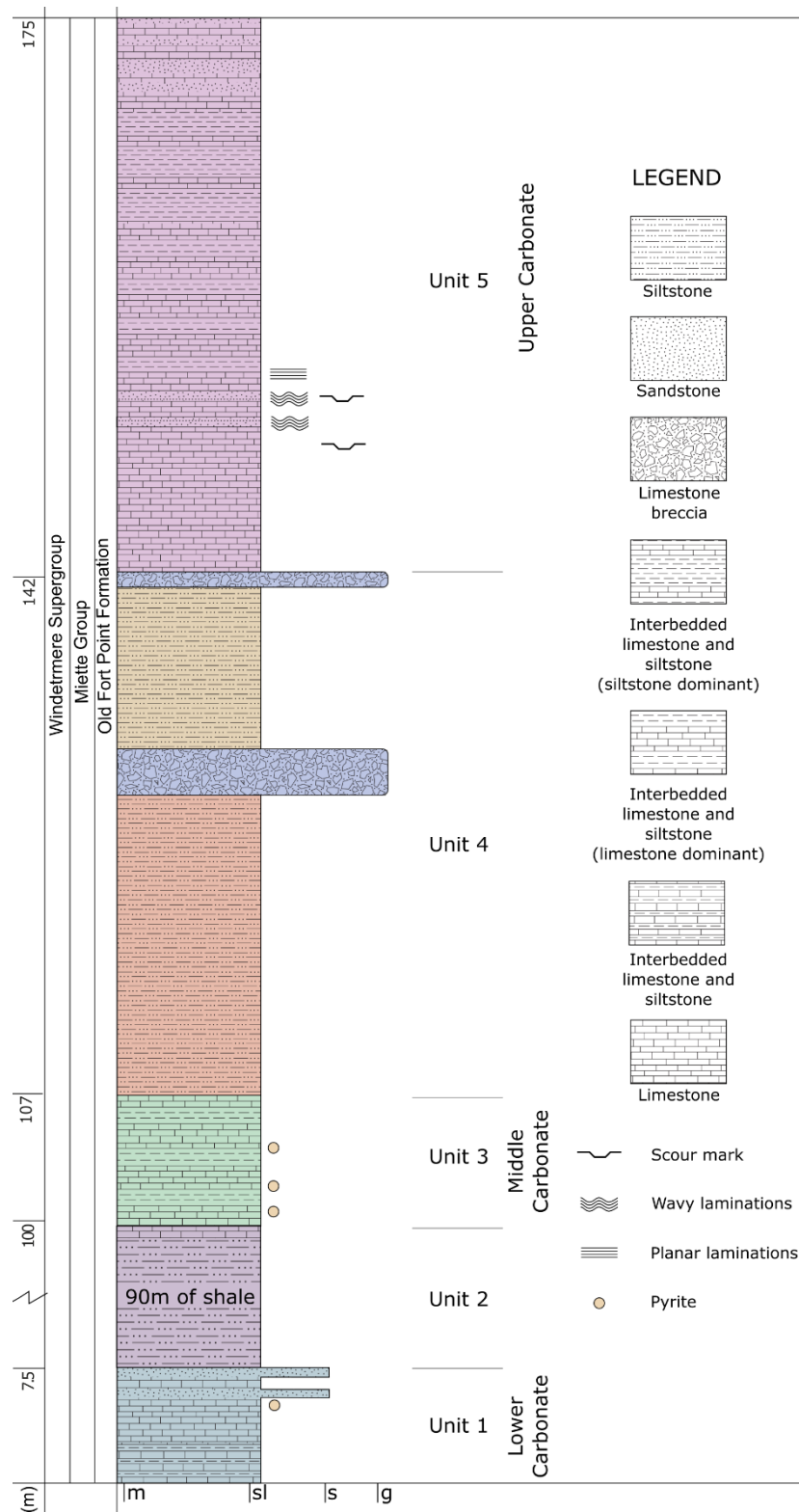


Figure 8: Stratigraphic column for site 16W.

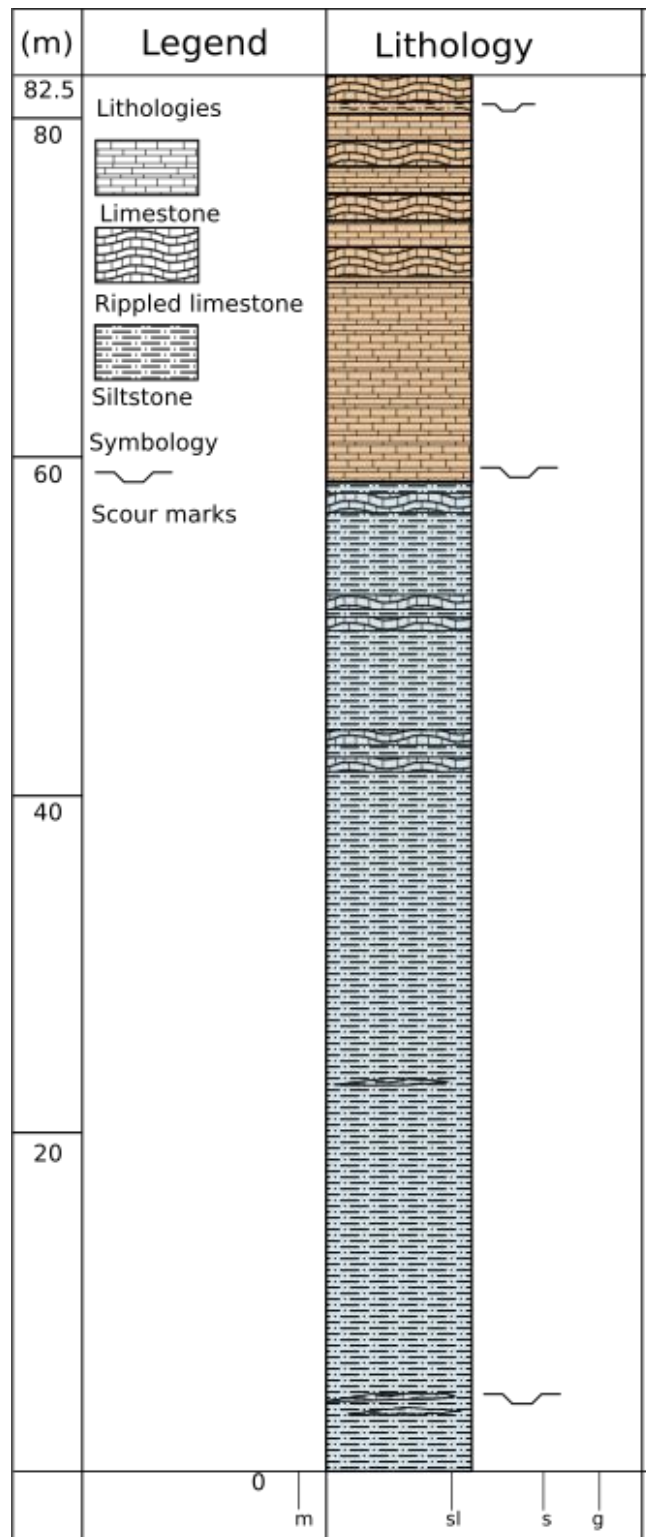


Figure 9: Stratigraphic column for site Pyrite Point ("PP").

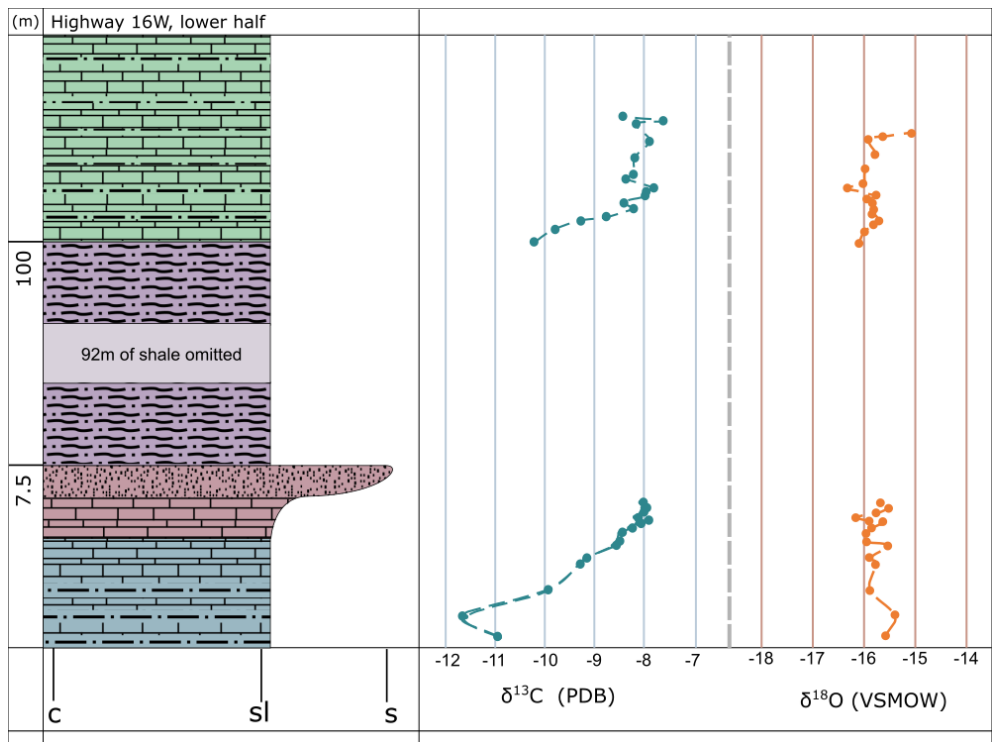
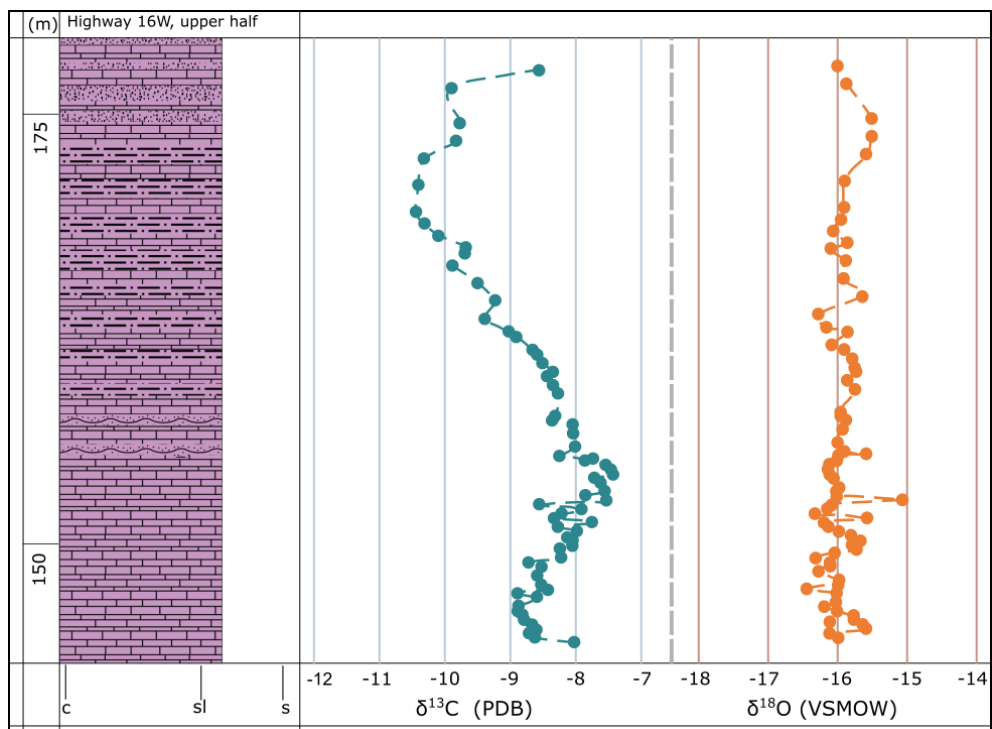


Figure 10: $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for site 16W.

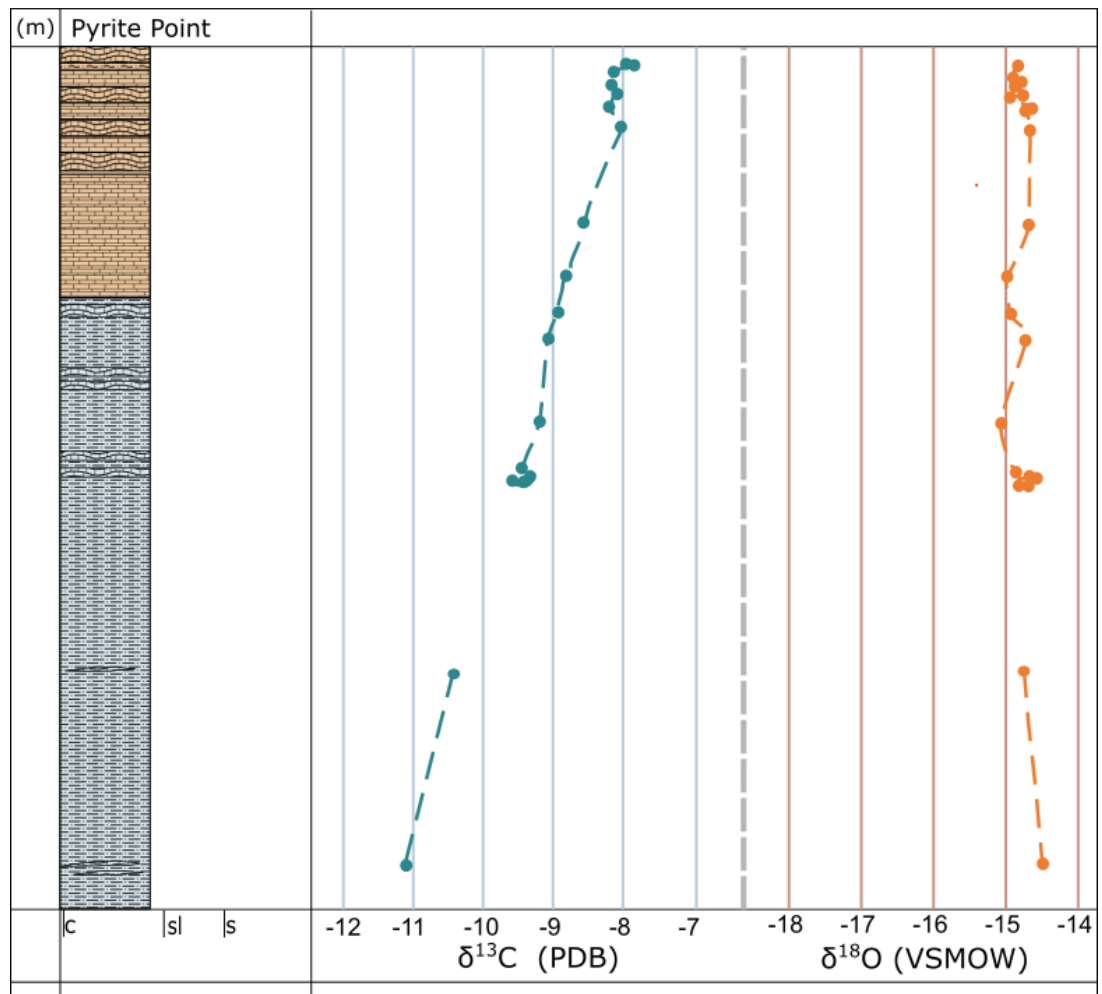


Figure 11: $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for site PP.

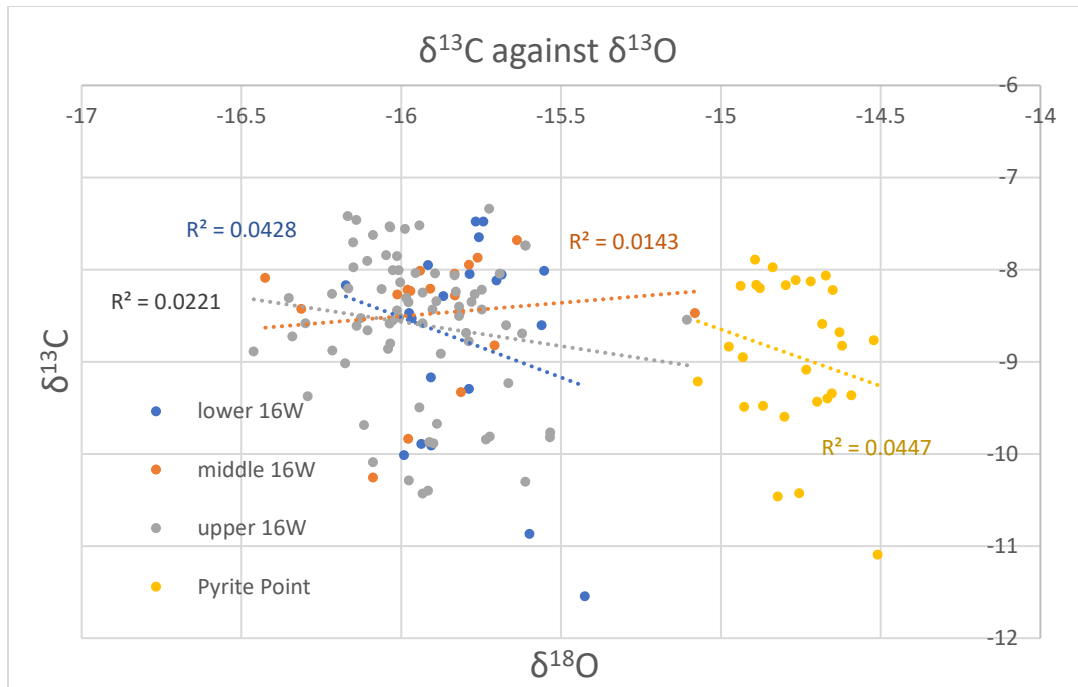


Figure 12: $\delta^{13}\text{C}$ plotted relative to $\delta^{13}\text{O}$ with correlation relationships and R^2 values. Black/grey: upper 16W; orange: middle 16W; blue: lower 16W; yellow: Pyrite Point

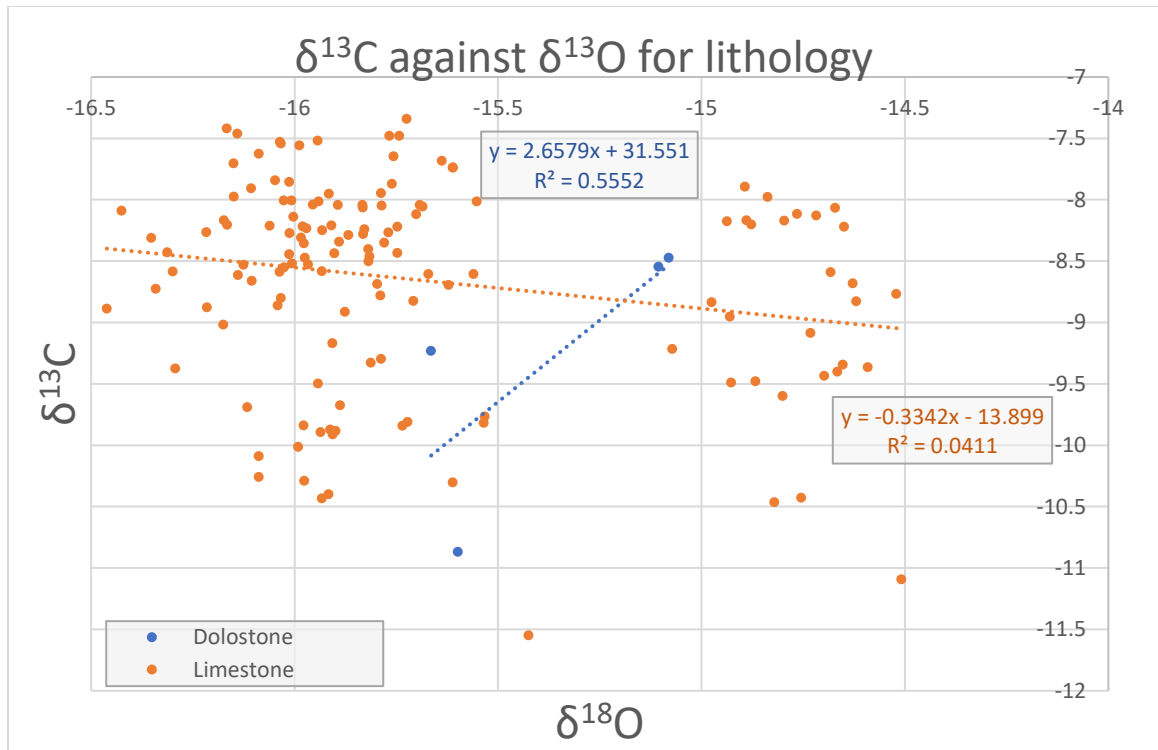


Figure 13: δ¹³C plotted against δ¹⁸O according to dominant lithology. Orange: limestone; blue: dolostone. Best-fit lines with R² and slope equation for each group in appropriate colours.

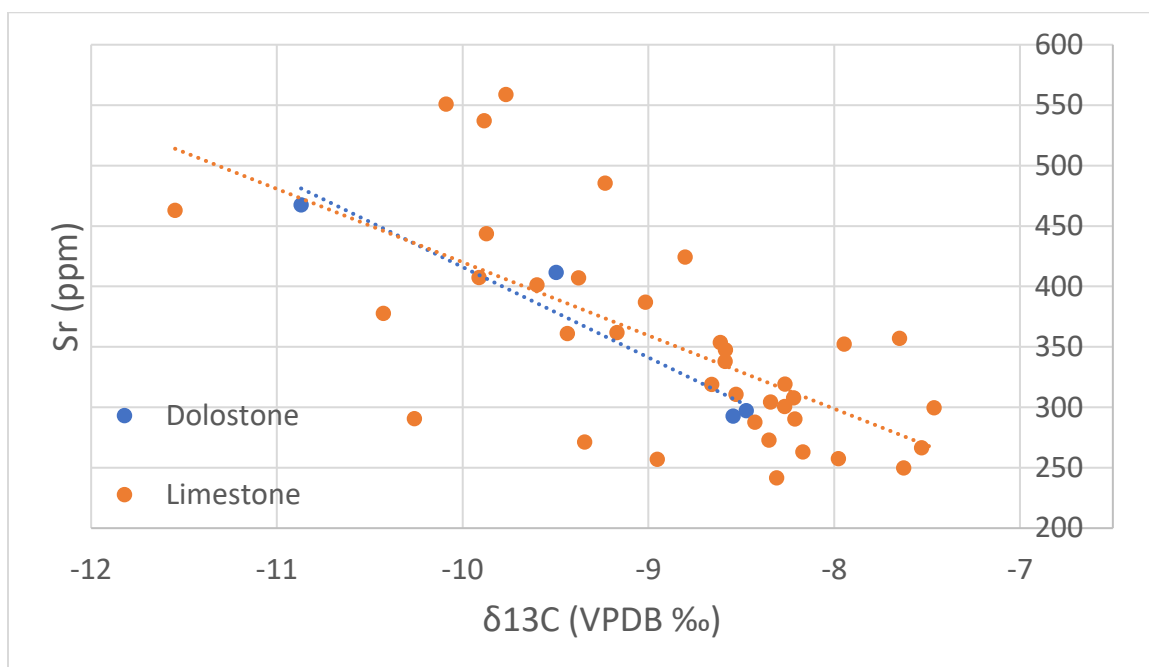


Figure 14: Sr concentrations plotted against carbon isotopic values, with dolomite and calcite populations. Both for mineralogies, Sr decreases with increasing ^{13}C enrichment.

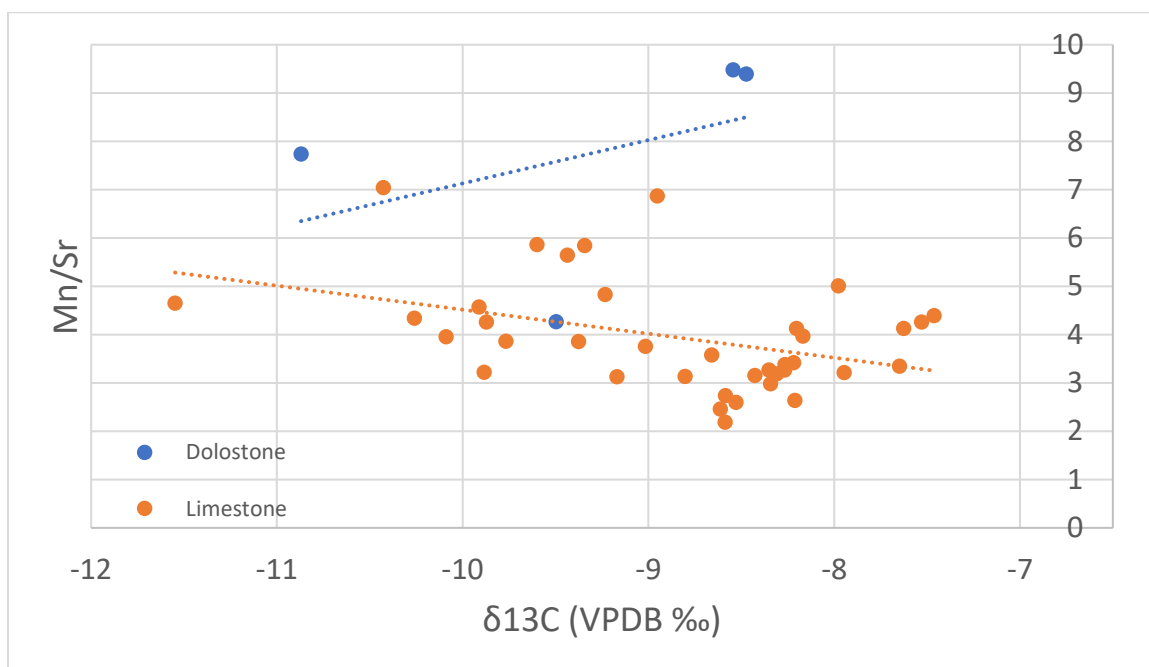


Figure 15: Graph depicting Mn/Sr plotted $\delta^{13}\text{C}$ values.

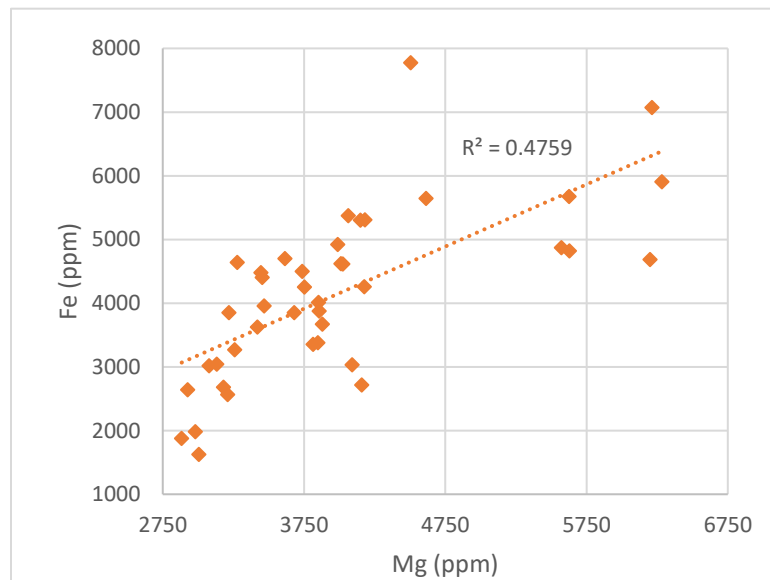
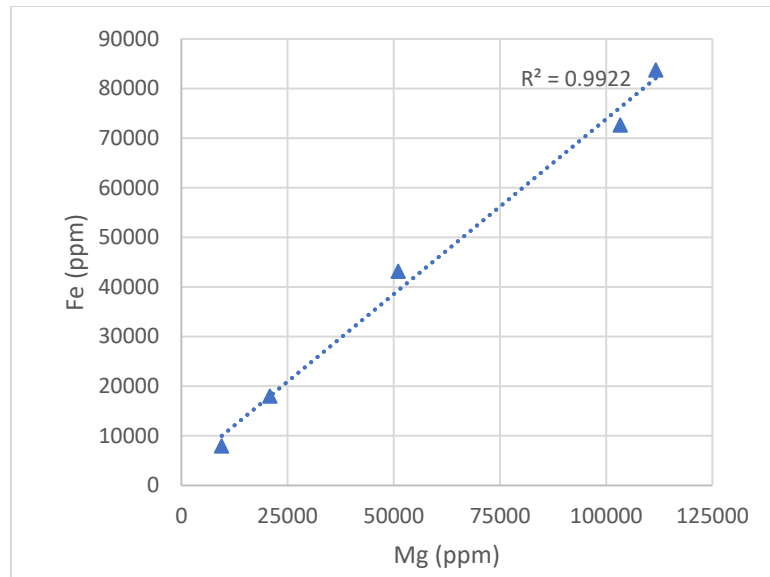


Figure 16: Fe vs Mg for dolostone (top) and limestone (bottom)

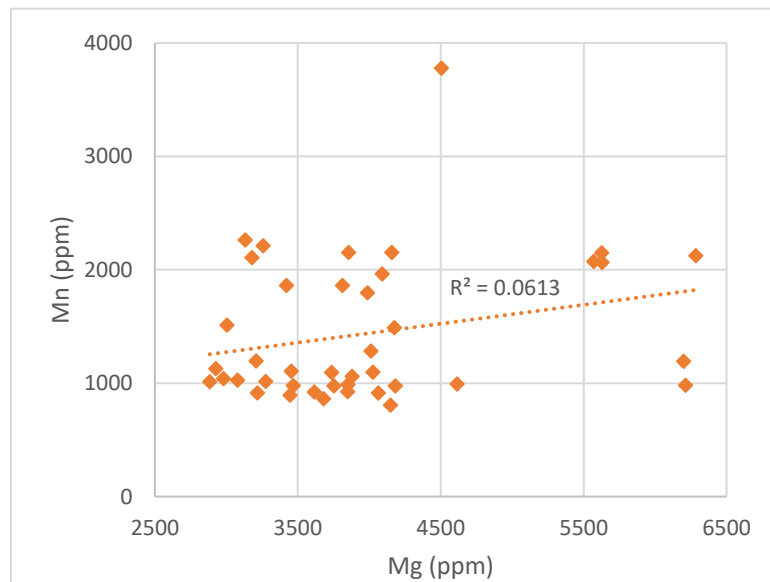
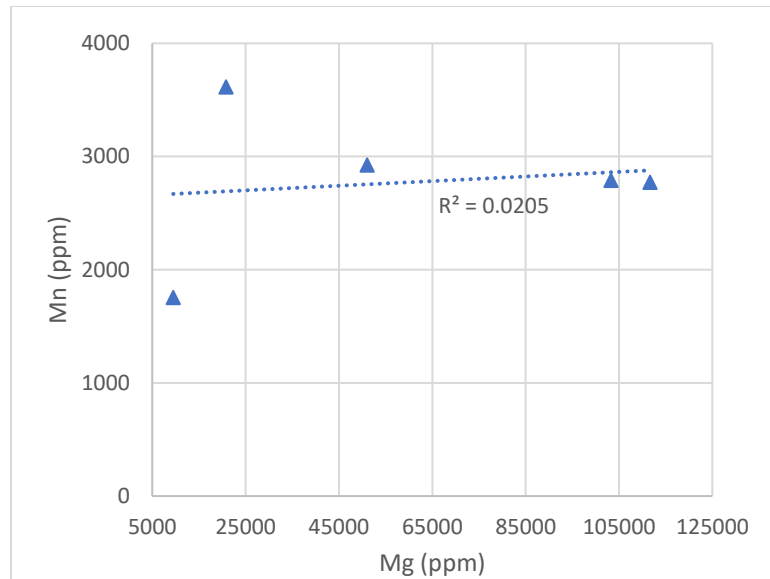


Figure 17: Mn vs Mg for dolostone (top) and limestone (bottom).

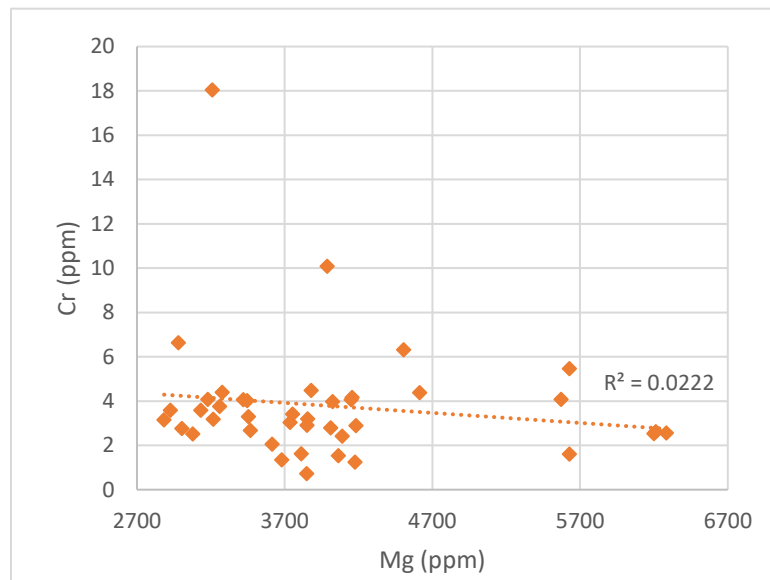
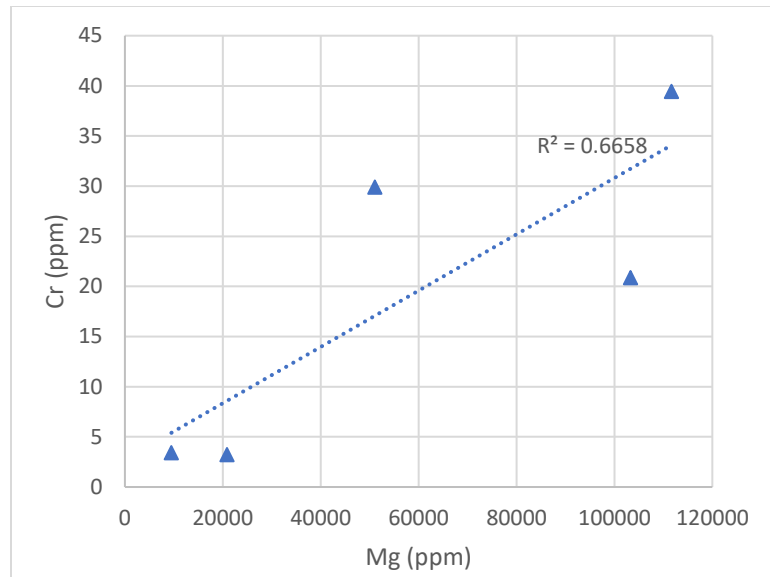


Figure 18: Cr vs Mg for dolostone (top) and limestone (bottom)

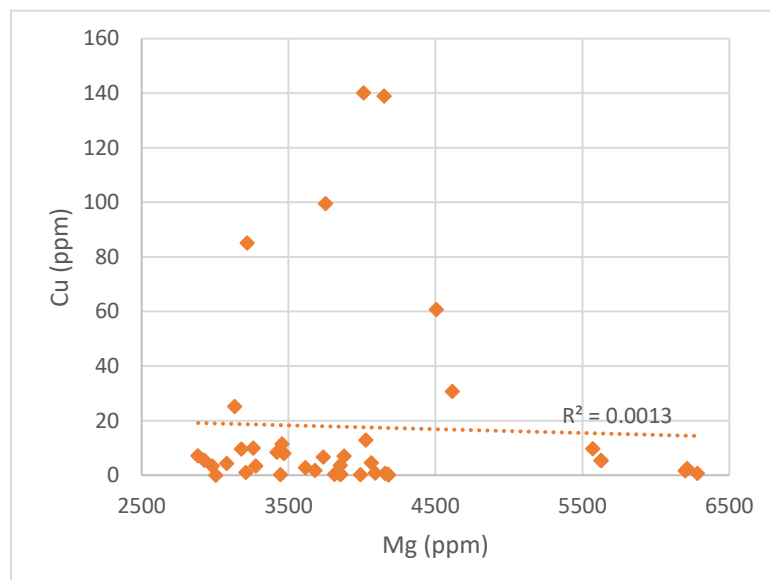
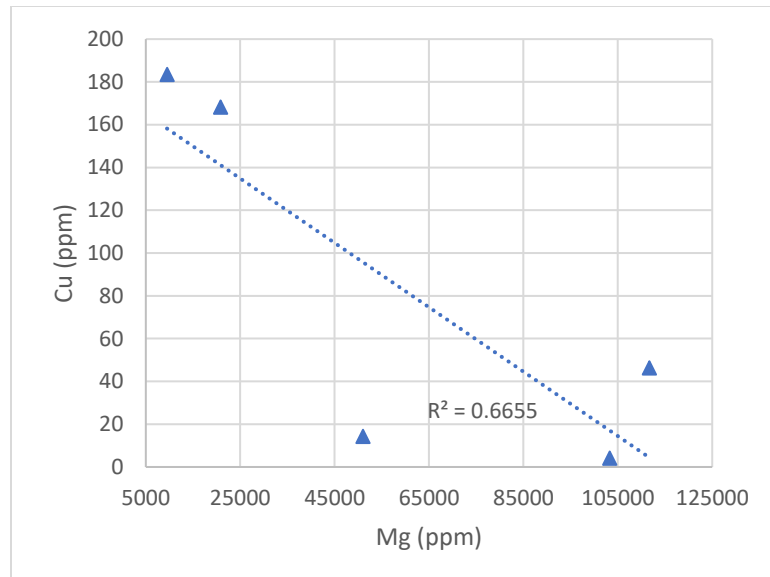


Figure 19: Cu vs Mg for dolostone (top) and limestone (bottom).

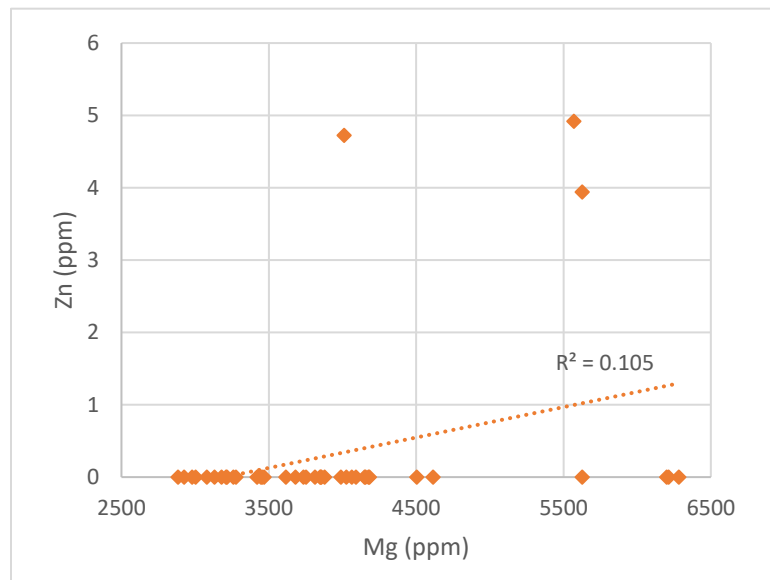
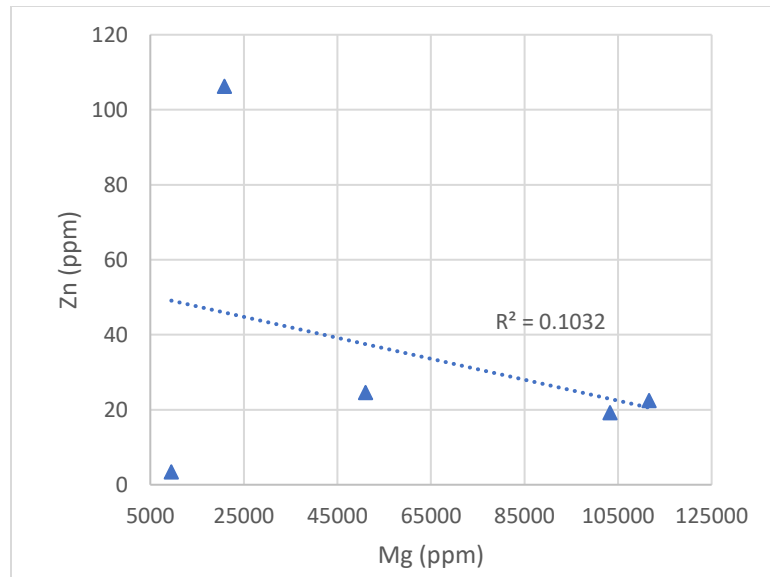


Figure 20: Zn vs Mg for dolostone (top) and limestone (bottom).

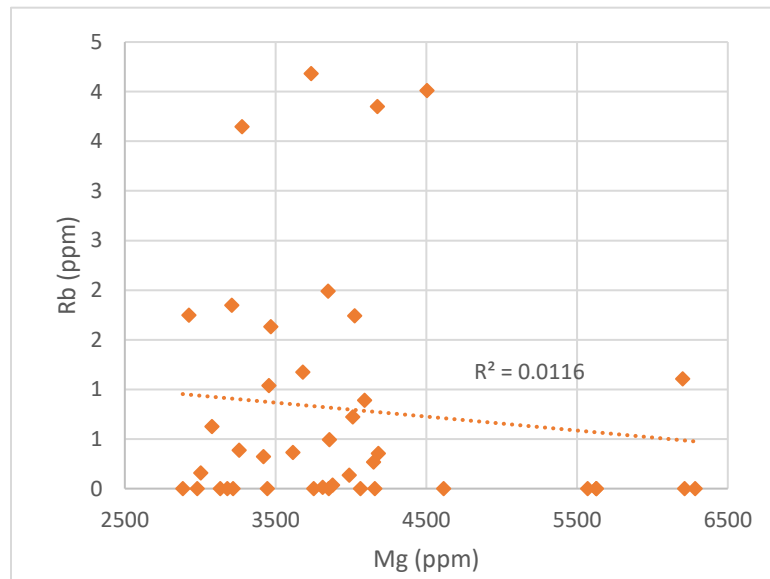
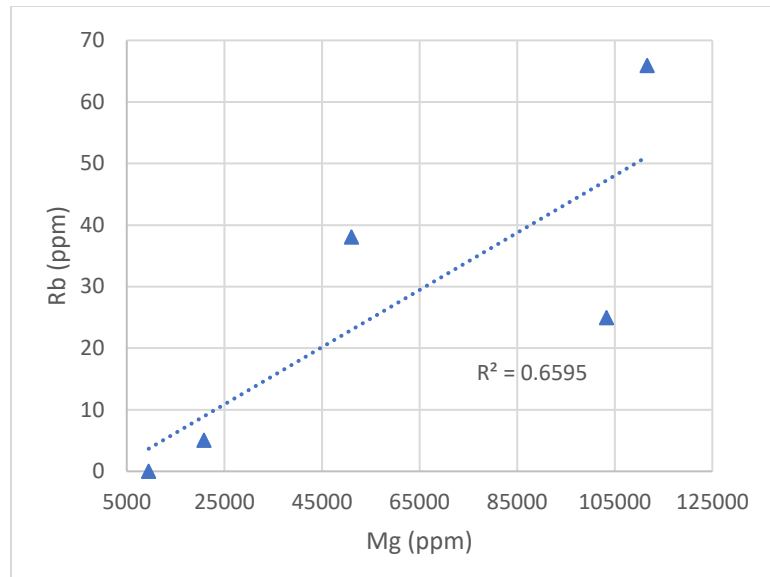


Figure 21: Rb vs Mg for dolostone (top) and limestone (bottom).

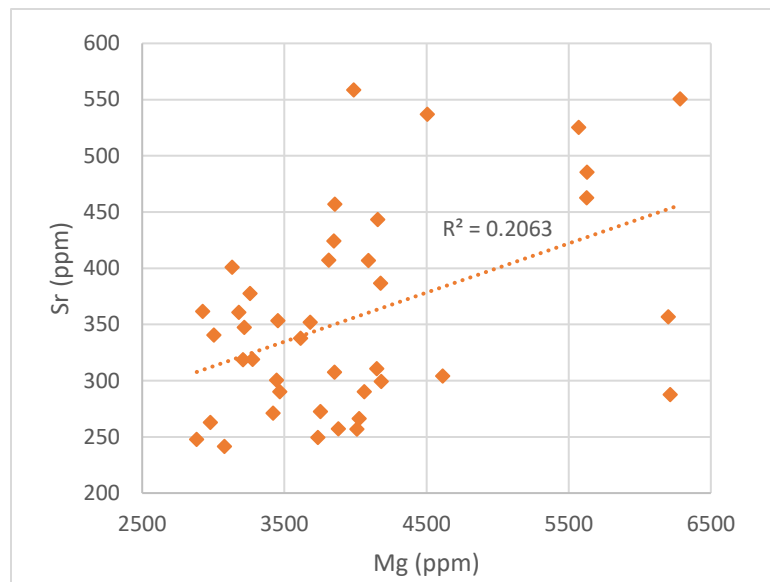
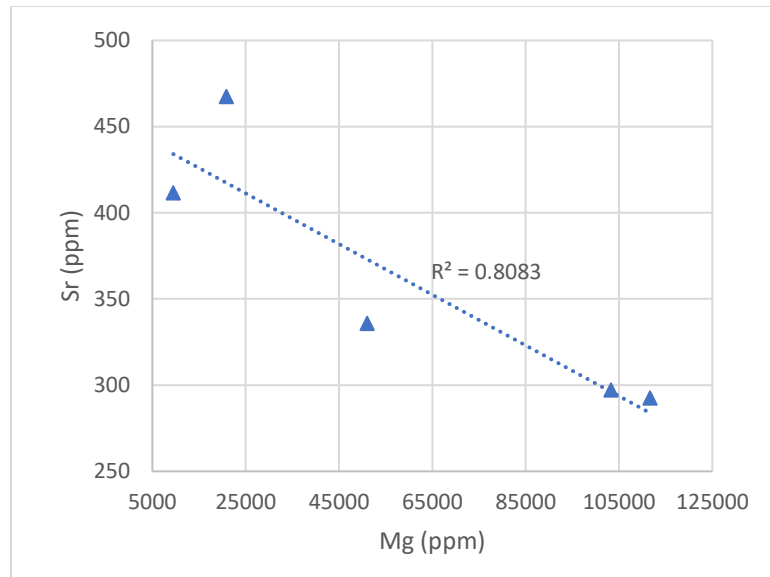


Figure 22: Sr vs Mg for dolostone (top) and limestone (bottom).

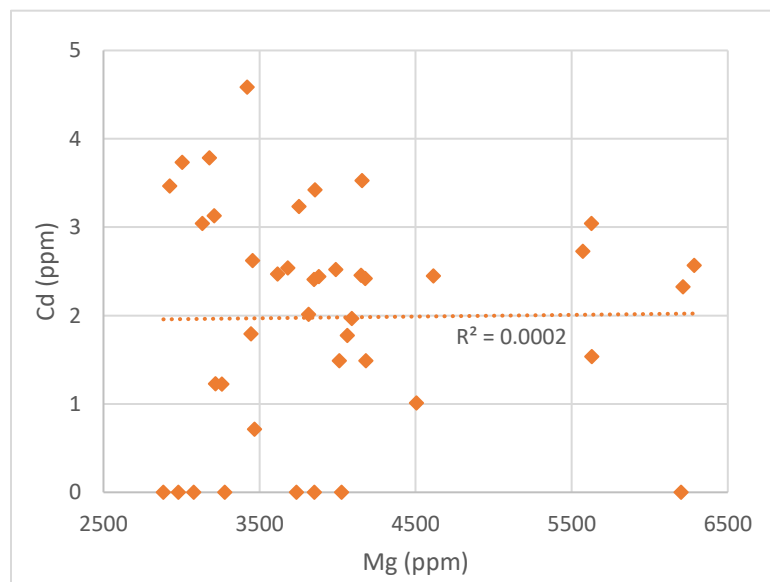
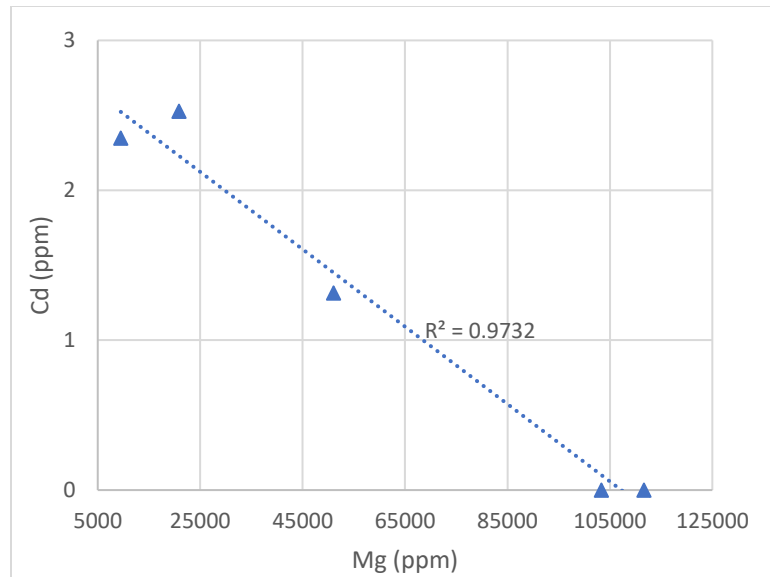


Figure 23: Cd vs Mg for dolostone (top) and limestone (bottom).

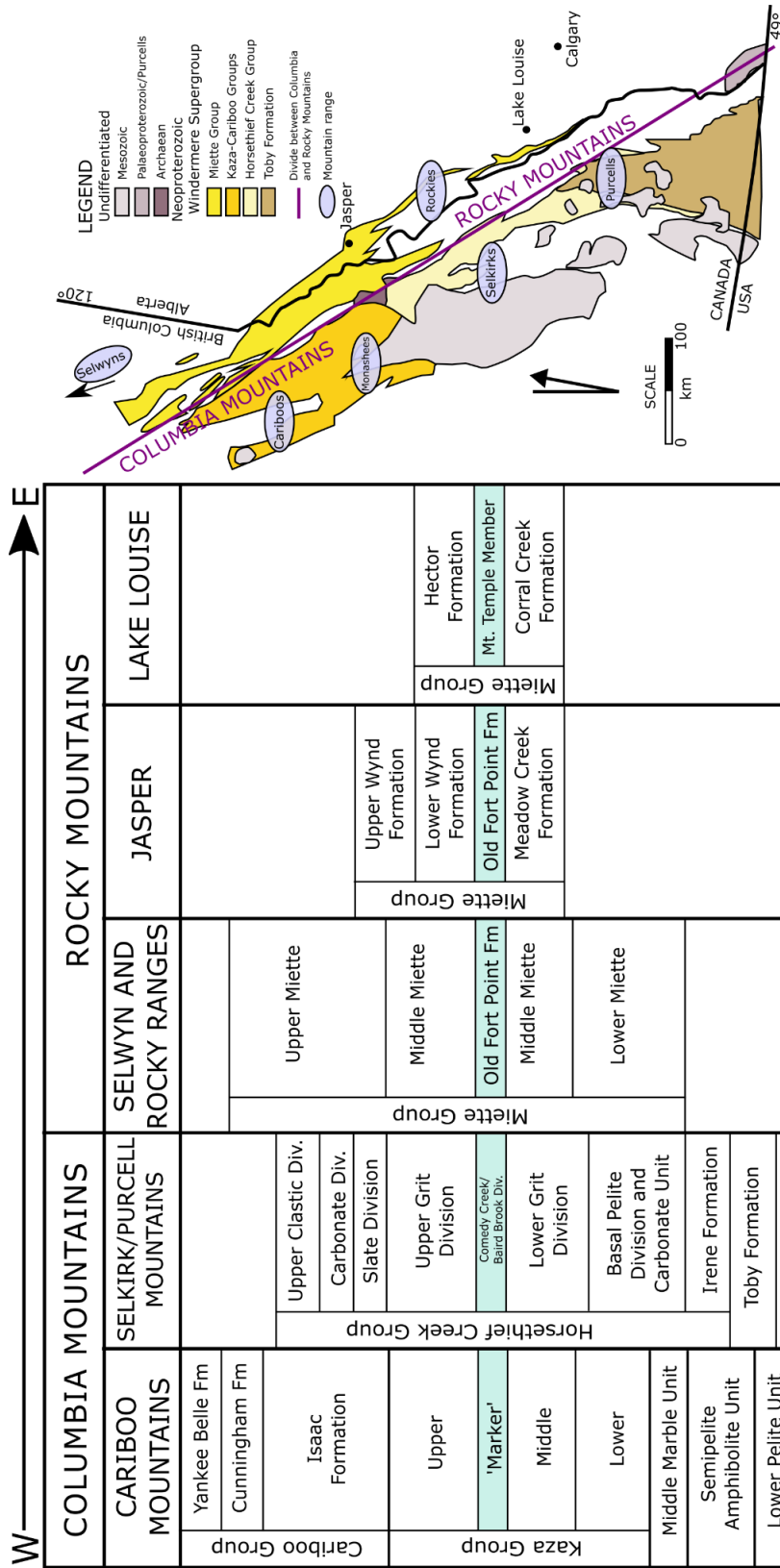


Figure 24: Windermere Supergroup stratigraphy; OFPF and correlatives in teal. Mod. Smith 2009

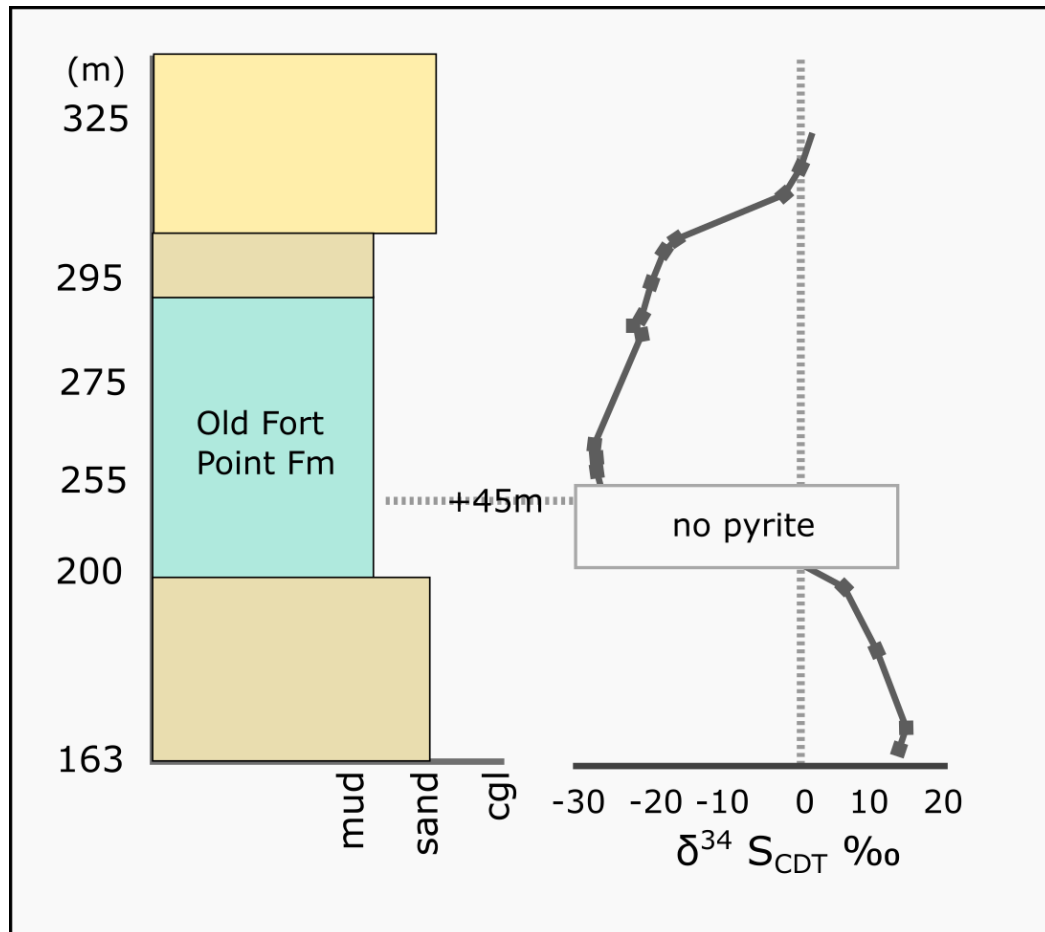


Figure 25: OFPF sulfate curve after Ross et al., 1995. Tan-colour polygons are non-OPPF units.

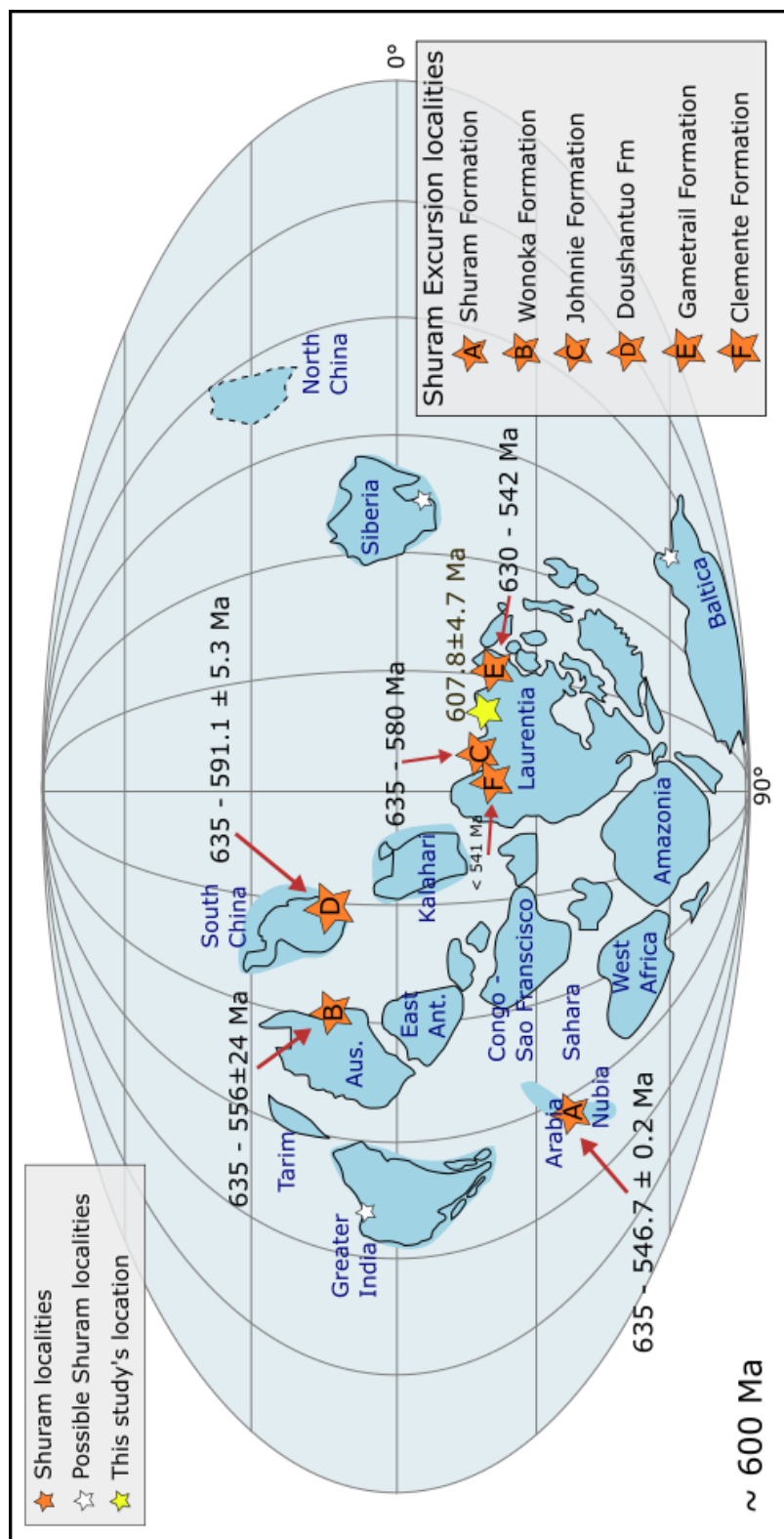


Figure 26: Continental reconstructions circa 600 Ma, modified from Li et al., 2008. Geochronological constraints from Kendall et al., 2004; Zhu et al., 2013; Macdonald et al., 2013; Bowring et al., 2007; Bergmann et al., 2011; Le Guerroué 2010

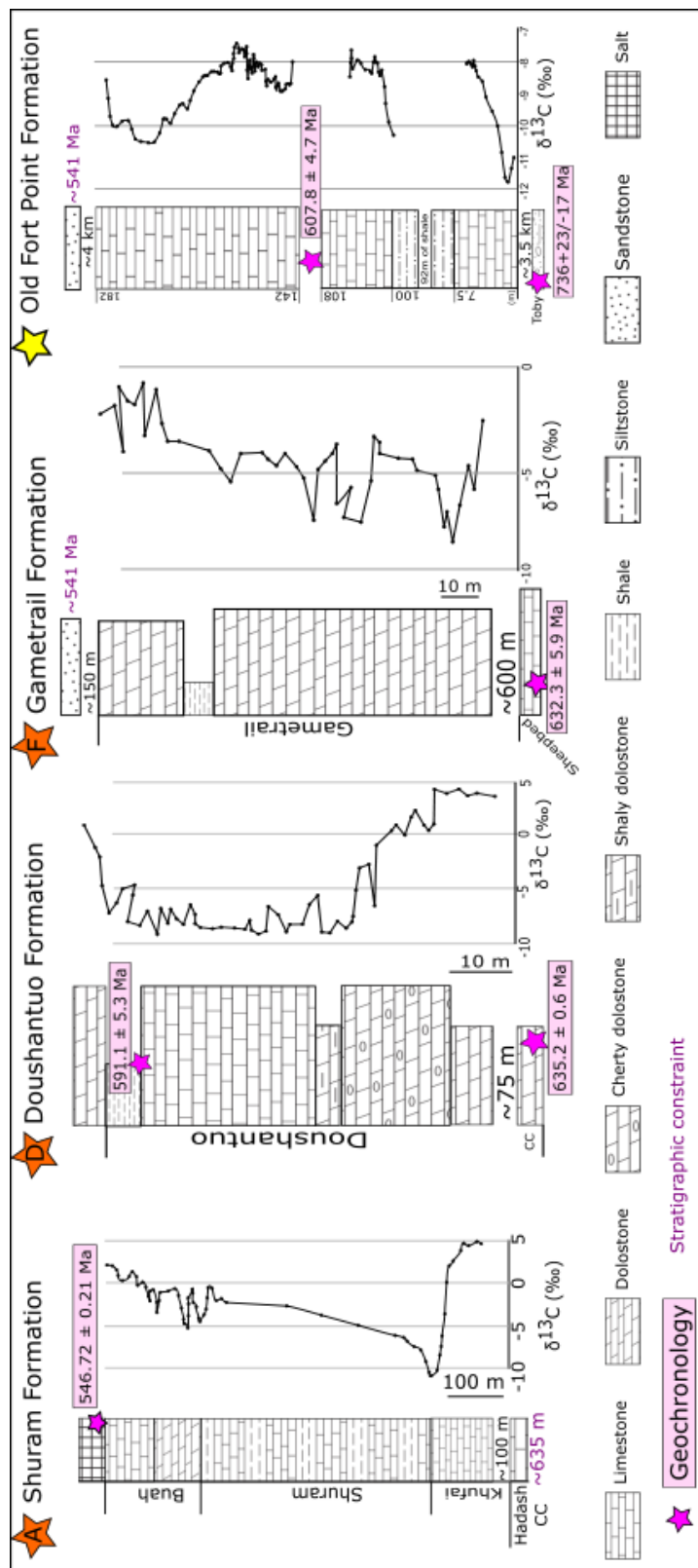


Figure 27: Stratigraphic columns for units recording the Shuram Excursion that have geochronological age constraints. Constraints from Kendall et al., 2004; Zhu et al., 2013; Macdonald et al., 2013; Bowring et al., 2007.

Appendix B: Petrography

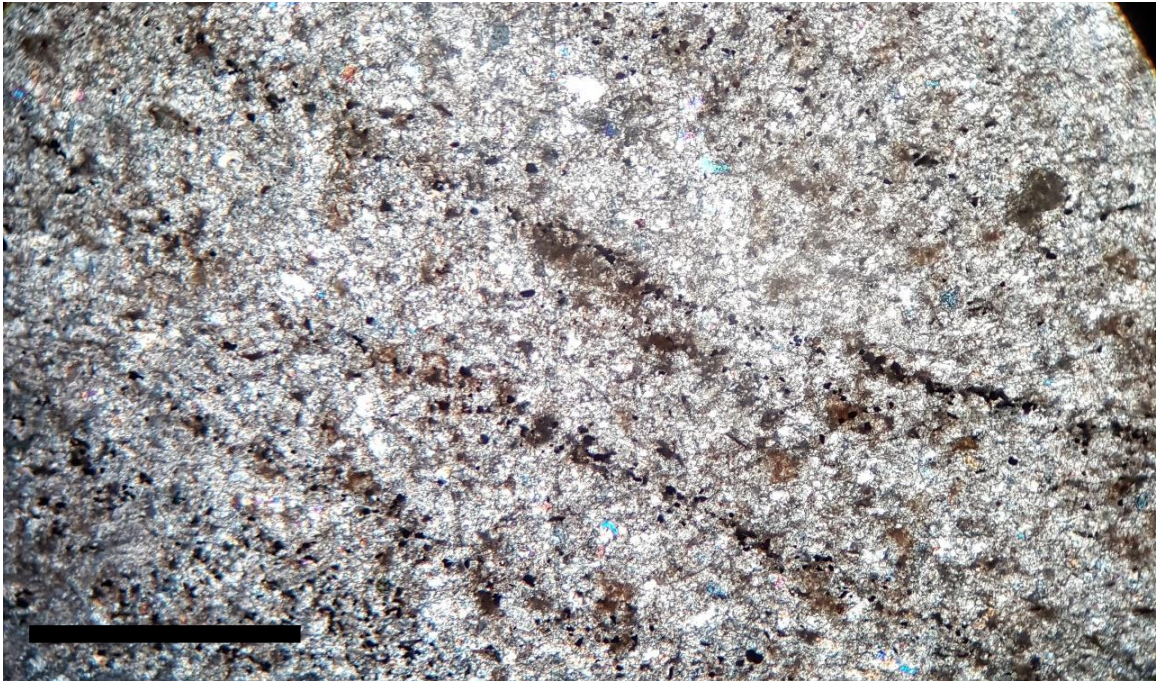


Figure 28: Microphoto of sample 16W-013. Parallel laminations with μm -scale pyrite along the bottom. Bar represents 1mm.

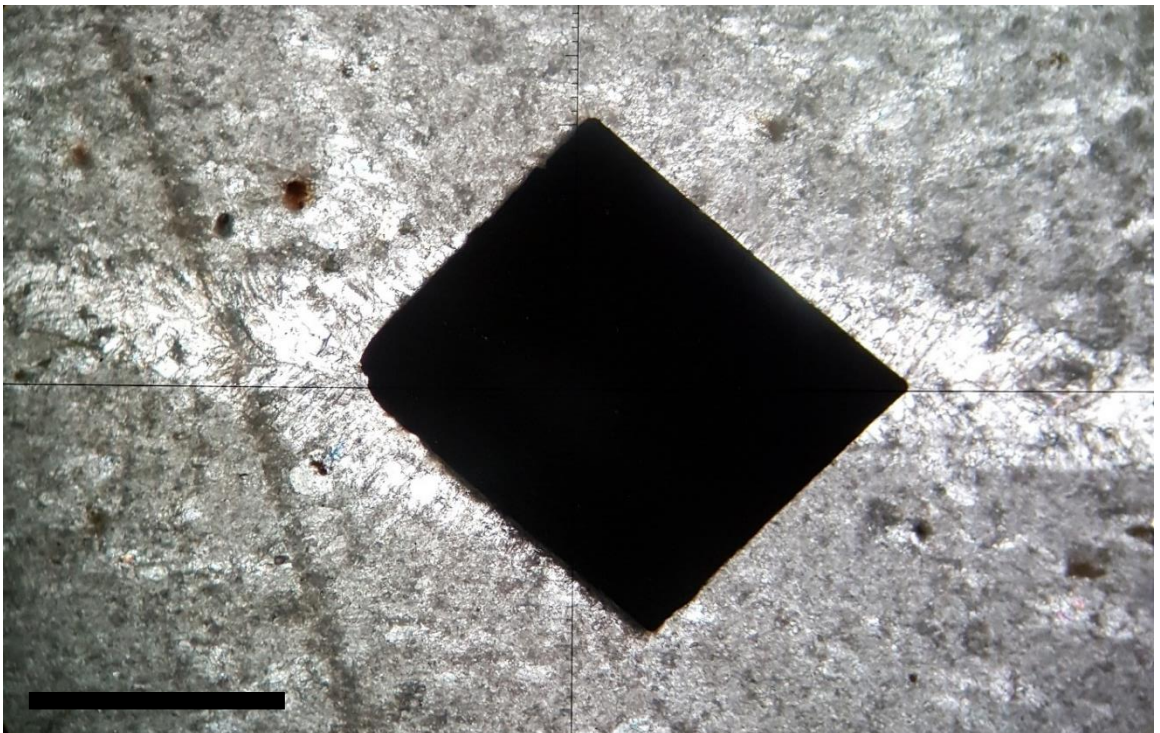


Figure 29: Microphoto of sample 16W-024. Pyrite surrounded by calcite spar. Bar represents 1mm.

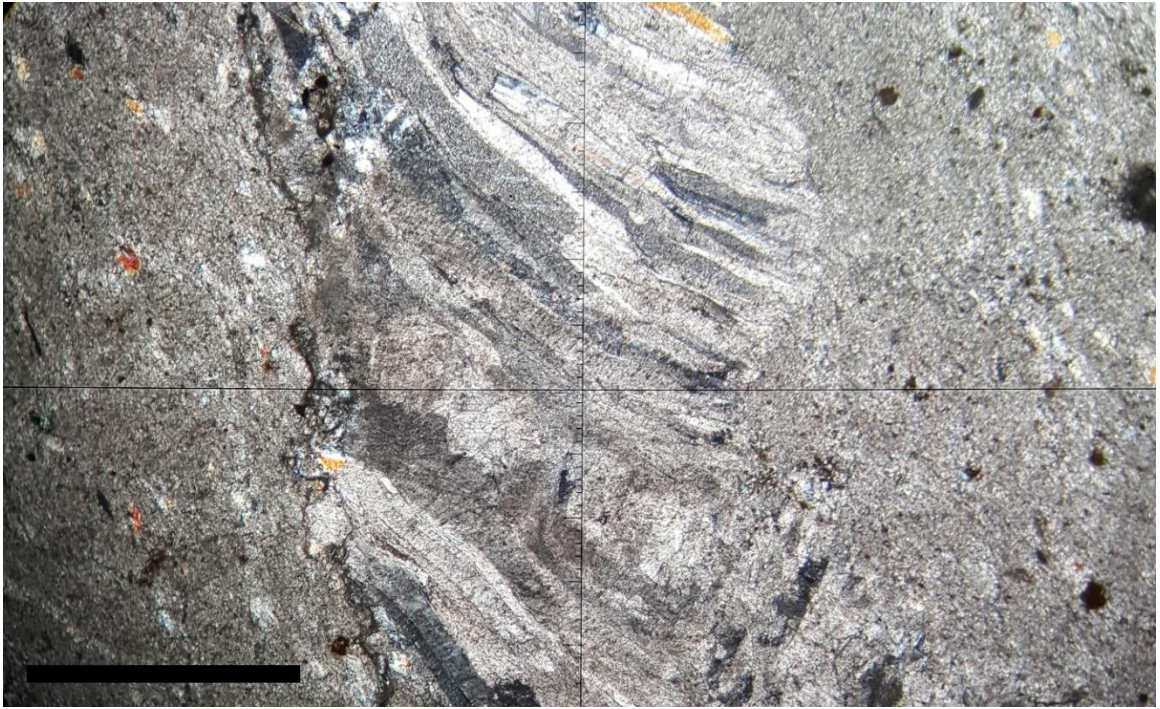


Figure 30: Microphoto of 16W-038. Example of exceptional recrystallization (not typical of sample pool). Bar represents 1mm.

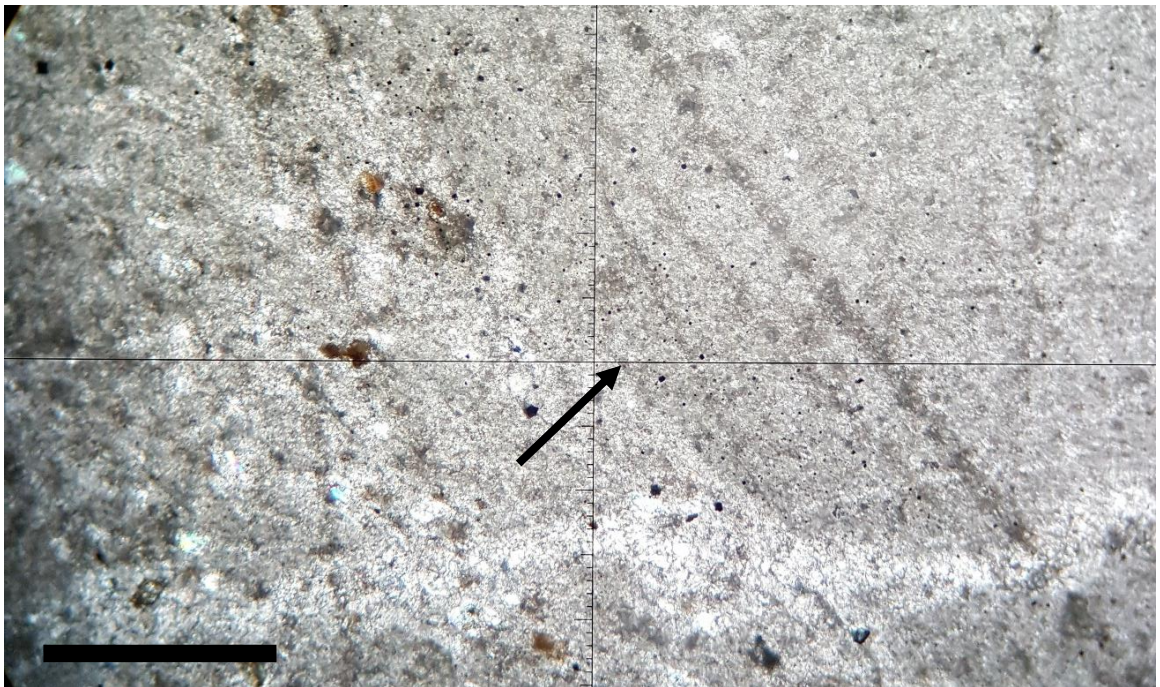


Figure 31: Microphoto of 16W-051. Black arrow: boundary between coarser- and finer-grained calcite. Bar represents 1mm.

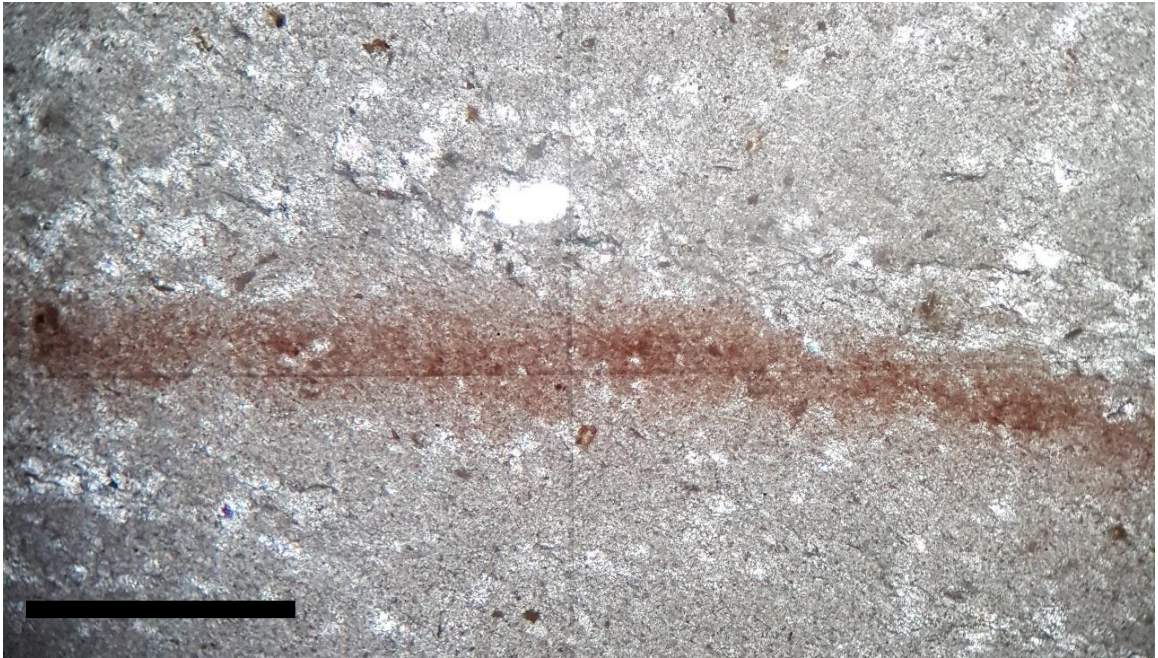


Figure 32: Microphoto of sample 16W-055 depicting distinctive ruddy limestone layer. Bar represents 1mm.

Appendix C: List of all samples

Sample ID	Mineralogy	Depth (m)	Site
16W-001	Calcite	0	16W
16W-005	Calcite	1	16W
16W-007	Calcite	2.25	16W
16W-009	Calcite	3.5	16W
16W-010	Calcite	3.5	16W
16W-013	Calcite	3.8	16W
16W-014	Calcite	4.4	16W
16W-016	Calcite	4.6	16W
16W-017	Calcite	4.6	16W
16W-018	Calcite	5	16W
16W-019	Calcite	5.25	16W
16W-020	Calcite	5.5	16W
16W-021	Calcite	5.6	16W
16W-022	Calcite	5.8	16W
16W-024	Calcite	5.8	16W
16W-025	Calcite	6	16W
16W-026	Calcite	6.25	16W
16W-027	Calcite	6.5	16W
16W-028	Calcite	6.5	16W
16W-029	Calcite	6.5	16W
16W-030	Calcite	98.75	16W
16W-031	Calcite	98.75	16W
16W-032	Calcite	99.5	16W
16W-034	Calcite	100	16W

16W-035	Calcite	100	16W
16W-036	Calcite	100.25	16W
16W-037	Calcite	100.75	16W
16W-038	Calcite	101.1	16W
16W-039	Calcite	101.5	16W
16W-040	Calcite	101.75	16W
16W-041	Calcite	102	16W
16W-043	Calcite	102.5	16W
16W-044	Calcite	102.8	16W
16W-045	Calcite	103.8	16W
16W-046	Calcite	103.8	16W
16W-047	Calcite	104.8	16W
16W-050	Calcite	105.8	16W
16W-051	Calcite	106	16W
16W-052	Dolomite	106.25	16W
16W-053	Calcite	142.25	16W
16W-054	Calcite	142.5	16W
16W-055	Calcite	142.75	16W
16W-056	Calcite	143	16W
16W-057	Calcite	143.25	16W
16W-058	Calcite	143.5	16W
16W-059	Calcite	143.75	16W
16W-060	Calcite	144	16W
16W-061	Calcite	144.25	16W
16W-063	Calcite	144.75	16W
16W-064	Calcite	145	16W

16W-065	Calcite	145.25	16W
16W-066	Calcite	145.5	16W
16W-067	Calcite	146	16W
16W-068	Calcite	146.5	16W
16W-069	Calcite	146.75	16W
16W-070	Calcite	147	16W
16W-071	Calcite	147.25	16W
16W-072	Calcite	147.5	16W
16W-073	Calcite	147.75	16W
16W-074	Calcite	148	16W
16W-075	Calcite	148.25	16W
16W-076	Calcite	148.5	16W
16W-077	Calcite	148.75	16W
16W-078	Calcite	149	16W
16W-079	Calcite	149.25	16W
16W-080	Calcite	149.5	16W
16W-081	Calcite	149.75	16W
16W-082	Dolomite	150	16W
16W-083	Calcite	150.25	16W
16W-084	Calcite	150.5	16W
16W-085	Calcite	150.75	16W
16W-087	Calcite	151.25	16W
16W-088	Calcite	151.5	16W
16W-089	Calcite	151.75	16W
16W-090	Calcite	152	16W
16W-091	Calcite	152.25	16W

16W-092	Calcite	152.5	16W
16W-093	Calcite	152.6	16W
16W-094	Calcite	152.75	16W
16W-095	Calcite	153.25	16W
16W-097	Calcite	154	16W
16W-098	Calcite	154.5	16W
16W-099	Calcite	154.75	16W
16W-100	Calcite	155	16W
16W-101	Calcite	156.25	16W
16W-102	Calcite	156.75	16W
16W-103	Calcite	157.25	16W
16W-104	Calcite	157.5	16W
16W-105	Calcite	158	16W
16W-106	Calcite	158.5	16W
16W-107	Calcite	158.75	16W
16W-108	Calcite	159.5	16W
16W-109	Calcite	159.75	16W
16W-110	Calcite	160.5	16W
16W-113	Calcite	161.5	16W
16W-115	Calcite	162.5	16W
16W-117	Calcite	163.5	16W
16W-120	Calcite	164.2	16W
16W-121	Calcite	164.5	16W
16W-123	Calcite	165.2	16W
16W-125	Calcite	165.8	16W
16W-127	Calcite	166.5	16W

16W-128	Calcite	168	16W
16W-130	Calcite	169.5	16W
16W-131	Calcite	170.5	16W
16W-132	Calcite	171.5	16W
16W-133	Calcite	173.5	16W
16W-134	Calcite	174.5	16W
PP-001	Calcite	4.5	Pyrite Point
PP-003	Calcite	22.25	Pyrite Point
PP-005	Calcite		Pyrite Point
PP-006	Calcite	43	Pyrite Point
PP-007	Calcite	43	Pyrite Point
PP-008	Calcite	43.5	Pyrite Point
PP-009	Calcite	43.5	Pyrite Point
PP-010	Calcite	44	Pyrite Point
PP-013	Calcite	48.75	Pyrite Point
PP-015	Calcite	56.5	Pyrite Point
PP-016	Calcite	59	Pyrite Point
PP-019	Calcite	62.5	Pyrite Point
PP-020	Calcite	62.5	Pyrite Point
PP-021	Calcite	67.5	Pyrite Point
PP-022	Calcite	76.5	Pyrite Point
PP-032	Calcite	78.5	Pyrite Point
PP-031	Calcite	78.5	Pyrite Point
PP-029	Calcite	79.5	Pyrite Point
PP-030	Calcite	79.5	Pyrite Point
PP-028	Calcite	80.5	Pyrite Point

PP-026	Calcite	81	Pyrite Point
PP-025	Calcite	81.5	Pyrite Point
PP-023	Calcite	82.5	Pyrite Point
PP-024	Calcite	82.5	Pyrite Point

Table 4: List of all samples.

Appendix D: Stable isotopic analyses

Sample ID	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
16W-001	-10.86994076	-15.59835229
16W-005	-9.139314536	-15.80633342
16W-007	-11.54811547	-15.42507539
16W-009	-9.911215901	-15.90612499
16W-010	-8.898514271	-15.7021942
16W-013	-9.296096337	-15.78724013
16W-014	-9.169980041	-15.90678554
16W-016	-8.606169149	-15.56026469
16W-017	-8.527823908	-15.96684175
16W-018	-8.396048376	-15.53559314
16W-019	-8.473086586	-15.97443174
16W-020	-8.28732585	-15.86784123
16W-021	-8.118223538	-15.70112011
16W-022	-7.950881517	-15.9153245
16W-024	-8.168984813	-16.17329217
16W-025	-7.895894471	-15.79064162
16W-026	-8.048024243	-15.78573093
16W-027	-8.014933776	-15.55225228
16W-028	-8.055257945	-15.68508693
16W-029	-7.476498026	-15.48483833
16W-030	-7.64772389	-15.75621114
16W-031	-10.10485585	-15.73221454
16W-032	-10.2593506	-16.08753292
16W-034	-9.837975034	-15.97797175

16W-035	-9.329307954	-15.812275
16W-036	-9.194291444	-15.77031006
16W-037	-8.823796169	-15.70786514
16W-038	-8.281280584	-15.8315449
16W-039	-8.463734911	-15.81542893
16W-040	-8.043990881	-15.83307411
16W-041	-8.015506101	-15.94040106
16W-043	-7.870995226	-15.76040415
16W-044	-8.427582805	-16.31254411
16W-045	-8.272506288	-16.01232563
16W-046	-8.218483225	-15.97978363
16W-047	-8.234268228	-15.9706396
16W-050	-7.94725553	-15.78764479
16W-051	-8.209678953	-15.9087912
16W-052	-7.682189348	-15.63761139
16W-053	-8.473872047	-15.08038338
16W-054	-8.005468354	-16.00769973
16W-055	-8.6131907	-16.13887807
16W-056	-8.693810706	-15.62104019
16W-057	-8.605477867	-15.67118301
16W-058	-8.686583336	-15.79701178
16W-059	-8.77979675	-15.78897639
16W-060	-8.802231963	-16.03357985
16W-061	-8.861813206	-16.04095553
16W-063	-8.587979893	-16.03631795
16W-064	-8.888017939	-16.46160243

16W-065	-8.443519177	-16.01316873
16W-066	-8.520812553	-16.00623669
16W-067	-8.585340661	-16.29949408
16W-068	-8.529487306	-16.12563853
16W-069	-8.725214916	-16.34061269
16W-070	-8.211428545	-16.06090156
16W-071	-8.219179776	-15.74746182
16W-072	-8.241004438	-15.82827877
16W-073	-8.044182392	-15.69172798
16W-074	-8.06296338	-15.83228551
16W-075	-8.140305128	-16.00236997
16W-076	-7.975995449	-16.14873748
16W-077	-8.265508252	-16.21647796
16W-078	-7.738372486	-15.61068821
16W-079	-8.310621639	-16.35154705
16W-080	-8.205104798	-16.16538438
16W-081	-7.906419174	-16.10620024
16W-082	-8.544907354	-15.10553666
16W-083	-7.530439726	-16.03568257
16W-084	-7.842414477	-16.04735764
16W-085	-7.557519056	-15.98748975
16W-087	-7.625566659	-16.08773013
16W-088	-7.70531646	-16.14984255
16W-089	-7.420400468	-16.16656762
16W-090	-7.462960749	-16.1400489
16W-091	-7.543099409	-16.03337199

16W-092	-7.855703968	-16.01291277
16W-093	-7.739086242	-15.61136756
16W-094	-8.24997903	-15.93229422
16W-095	-8.005409304	-16.02605833
16W-097	-8.039161135	-15.95473097
16W-098	-8.041914901	-15.89368043
16W-099	-8.355808755	-15.9764774
16W-100	-8.309342389	-15.98365561
16W-101	-8.267448924	-15.76915251
16W-102	-8.34241398	-15.88992216
16W-103	-8.435184699	-15.74741328
16W-104	-8.351250642	-15.77975413
16W-105	-8.502894812	-15.81825431
16W-106	-8.583498845	-15.93273734
16W-107	-8.659912847	-16.105354
16W-108	-8.913039946	-15.87604978
16W-109	-9.016753568	-16.174638
16W-110	-9.375706655	-16.29259597
16W-113	-9.233038265	-15.66438402
16W-115	-9.497470067	-15.94246387
16W-117	-9.872068141	-15.91216005
16W-120	-9.68931033	-16.11619881
16W-121	-9.675363704	-15.88817591
16W-123	-10.08981138	-16.08755403
16W-125	-10.29022887	-15.97584278
16W-127	-10.43328513	-15.93249778

16W-128	-10.40026785	-15.91603444
16W-130	-10.30190681	-15.61102975
16W-131	-9.818899419	-15.53443449
16W-132	-9.766493048	-15.53277857
16W-133	-9.884644654	-15.89889838
16W-134	-8.55168127	-16.02586879
PP-001	-11.09382469	-14.50879786
PP-003	-10.42707084	-14.75439989
PP-005	-10.46427636	-14.82083637
PP-006	-9.599319998	-14.8006224
PP-007	-9.436269652	-14.69768019
PP-008	-9.36537486	-14.59091431
PP-009	-9.343693797	-14.6524302
PP-010	-9.479670608	-14.86738542
PP-013	-9.216137386	-15.07136489
PP-015	-9.086890061	-14.73192858
PP-016	-8.952239063	-14.93041593
PP-019	-8.835600964	-14.97464349
PP-020	-8.682472472	-14.62830039
PP-021	-8.590020052	-14.68242506
PP-022	-8.065996137	-14.67111636
PP-032	-8.221230733	-14.64950153
PP-031	-8.128411057	-14.71804479
PP-029	-8.175889876	-14.93737304
PP-030	-8.116500176	-14.76497985
PP-028	-8.202276507	-14.87707178

PP-026	-8.17134895	-14.79598106
PP-025	-8.168367984	-14.88878631
PP-023	-7.976941943	-14.83764378
PP-024	-7.893538259	-14.89288204
16W-063-R1	-8.403596328	-15.8183404
16W-063-R2	-8.436042756	-15.90195969
16W-087-R1	-7.519338319	-15.94319916
16W-087-R2	-7.341343771	-15.72435022
16W-121-R1	-9.8117	-15.7222
16W-121-R2	-9.8429	-15.7346
PP-008-R1	-9.4895	-14.9265
PP-008-R2	-9.4016	-14.6659
PP-020-R1	-8.8267	-14.6198
PP-020-R2	-8.7671	-14.5214

Table 5: Stable isotope analyses for this study.

Appendix E: Elemental concentrations

Sample	Mg wt%	Mg	Ca	Cr	Mn	Fe	Cu	Zn	Rb	Sr	Cd
16W001	6.02	20837	348160	3.2	3615	18026	168.1	112.8	BDL	467	3.0
16W004	1.06	3856	391574	3.2	2153	3876	0.4	0.0	BDL	457	2.8
16W005	1.56	5627	365561	1.6	2151	5678	5.4	0.0	BDL	463	2.6
16W007	1.05	3813	387243	1.6	1862	3355	0.3	0.0	BDL	407	2.7
16W009	0.83	3004	388110	2.8	1512	1625	0.0	0.0	BDL	341	2.9
16W013	0.81	2925	389877	3.6	1130	2644	5.5	0.0	BDL	362	2.8
16W016	1.15	4149	389823	4.1	807	5304	138.9	0.0	BDL	311	2.0
16W022	0.82	2980	388914	6.6	1042	1986	3.4	0.0	BDL	263	0.0
16W024	0.79	2884	390032	3.2	1014	1878	7.2	0.0	BDL	248	0.0
16W029	1.71	6200	390302	2.5	1193	4686	1.6	0.0	BDL	357	0.0
16W043	1.12	4063	389892	1.5	916	5376	4.6	0.0	BDL	290	1.4
16W045	1.65	6213	407918	2.6	982	7076	2.5	0.0	BDL	288	1.7
16W047	1.08	3852	386747	2.9	989	4011	3.7	0.0	BDL	308	0.0
16W052	39.29	103316	264420	20.9	2789	72672	4.2	17.2	0.2	297	0.0
16W054	1.02	3681	390404	1.3	864	3854	1.8	0.0	BDL	352	2.0
16W059	0.95	3455	391528	3.3	1108	4404	11.4	0.0	BDL	354	2.4
16W063	1.11	3849	374445	0.7	926	3383	0.4	0.0	BDL	424	2.1
16W067	1.01	3615	385750	2.1	924	4701	2.8	0.0	BDL	338	2.1
16W070	0.89	3217	390256	3.2	916	3853	85.2	0.0	BDL	347	1.1
16W077	0.95	3468	394514	2.7	979	3957	8.0	0.0	BDL	290	BDL
16W079	0.89	3277	399400	4.4	1016	4640	3.4	0.0	BDL	319	0.0
16W082	43.02	111657	262692	39.4	2772	83739	46.3	40.7	31.8	293	0.0
16W083	0.84	3079	394418	2.5	1028	3017	4.4	0.0	BDL	242	0.0
16W087	1.08	4025	408350	4.0	1098	4615	12.9	0.0	BDL	266	0.0
16W090	1.02	3736	396621	3.0	1095	4502	6.7	0.0	BDL	250	0.0

16W101	1.15	4182	391622	2.9	978	5310	0.1	0.0	BDL	299	1.6
16W102	0.94	3446	398635	4.0	895	4482	0.3	0.0	BDL	301	1.8
16W104	1.23	4614	406117	4.4	993	5645	30.8	0.0	BDL	304	2.3
16W107	1.02	3753	397163	3.4	976	4253	99.6	0.0	BDL	273	2.2
16W109	0.88	3209	394612	18.1	1196	2567	1.1	0.0	BDL	319	2.5
16W110	1.14	4176	397335	1.3	1491	4259	0.3	0.0	BDL	387	2.8
16W113	2.65	9496	378513	3.4	1754	7959	183.5	0.0	BDL	412	2.6
16W115	1.12	4090	393874	2.4	1964	3032	0.8	0.0	BDL	407	2.9
16W117	1.54	5628	371288	5.5	2066	4823	5.4	0.0	BDL	485	2.6
16W119	1.13	4158	396915	4.2	2154	2716	0.7	0.0	BDL	444	2.9
16W123	1.50	5571	373936	4.1	2075	4871	9.7	0.0	BDL	525	2.3
16W132	1.72	6284	368352	2.6	2125	5907	0.8	0.0	BDL	551	2.3
16W133	1.08	3988	373752	10.1	1799	4923	0.3	0.0	BDL	559	2.3
PP003	1.22	4505	375076	6.3	3780	7775	60.8	0.0	BDL	537	1.9
PP006	0.87	3259	404523	3.8	2212	3271	10.0	0.0	BDL	378	2.4
PP007	0.83	3133	406911	3.6	2264	3045	25.2	0.0	BDL	401	2.4
PP009	0.85	3180	401098	4.1	2108	2682	9.6	0.0	BDL	361	2.7
PP016	0.91	3421	405894	4.1	1862	3627	8.5	0.0	BDL	271	2.7
PP023	1.07	4011	403742	2.8	1285	4622	140.2	7.3	BDL	257	1.6
PP028	1.04	3879	402830	4.5	1062	3672	7.0	0.0	BDL	257	2.0
PP033	15.61	51034	329485	29.9	2925	43143	14.3	17.0	12.8	336	0.8

Table 6: All elements analyzed on the ICP-MS, with TIC(%) and Mg wt%. All elements reported in parts per million (ppm)

Sample	Mg	Ca	Cr	Mn	Fe	Cu	Zn	Rb	Sr	Cd
16W001	4.01	0.64	36.63	0.6	3.43	1.61	2.75	8.89	0.81	1.43
16W004	1.77	0.29	70.21	1.16	1.79	0.48	2.74	0.84	0.65	0.34
16W005	9.7	1.08	98.45	2.66	2.26	1.01	4.76	1.27	1.03	1.02
16W007	4.17	0.18	52.97	2.27	1.11	1.15	2.59	1.3	0.91	1.64
16W009	3.88	0.78	49.57	0.82	1.14	0.98	3.64	0.68	1.75	2.33
16W013	4.87	0.9	18.04	2.84	2.35	1.14	2.38	0.92	0.67	2.49
16W016	7.27	0.65	8.68	1.37	1.61	1.47	2.74	0.21	1.1	1.1
16W022	1.83	1.43	10.17	1.5	0.79	0.93	0.38	0.88	0.87	0.98
16W024	1.5	0.41	67.06	2.17	2.07	1.81	1.8	0.49	0.36	0.45
16W029	2.59	1.84	50.71	3.02	1.48	1.4	11.49	0.72	2.23	0.76
16W043	1.93	0.79	19.51	1.18	2.41	0.97	2.43	0.75	0.78	2.6
16W045	6.62	0.89	27.6	1.58	1.5	0.72	1.59	0.23	0.8	1.41
16W047	7.99	0.68	84.98	1.98	1.1	0.75	1.22	0.44	1.26	0.7
16W052	6.02	0.63	25.66	2.74	1.2	1.37	24.06	>100	0.35	0.37
16W054	1.46	0.45	38.52	0.81	2.1	0.18	1.84	0.84	0.93	0.51
16W059	4.62	1.18	32.87	2.55	3.95	1.5	11.66	1.74	1.05	0.47
16W063	3.16	0.78	51.54	1.31	1.62	0.9	2.06	1.22	0.98	1.37
16W067	8.76	1.18	36.77	0.65	0.48	0.67	1.42	0.61	0.88	2.55
16W070	5.62	0.66	22.03	1.11	2.32	2.66	2.03	0.75	0.56	1.53
16W077	5.09	0.47	8.79	0.68	0.84	1.81	0.8	0.79	0.92	0.99
16W079	4.79	0.57	49.78	0.48	0.47	0.93	0.54	2.43	0.31	0.92
16W082	3.63	1	12.26	1.1	0.22	1.45	11.29	5.61	0.75	1.28
16W083	4.9	0.89	40.96	0.66	0.88	0.87	1.98	0.48	0.91	0.75
16W087	2.66	0.4	67.09	2.02	1.15	2.3	2.92	1.97	1.15	0.96
16W090	3.55	0.23	39.03	2.65	2.4	3.17	2.49	1.18	0.76	0.69
16W101	1.18	0.69	52.1	1.06	0.42	0.57	2.42	1.77	0.81	3.41

16W102	8.09	1.6	21.15	0.53	2.07	1.01	1.9	0.86	0.7	1.16
16W104	7.59	1.46	39.17	2.09	1.12	1.29	4.91	0.97	1.17	0.55
16W107	9.05	0.38	25.39	0.78	1.38	2.04	3.88	0.6	0.86	0.82
16W109	5.98	0.15	40.77	0.89	1.6	0.91	1.26	1.59	0.93	1.56
16W110	4.01	0.46	62.42	0.24	0.78	0.51	1.69	0.78	1.04	1.67
16W113	6.79	1.04	21.19	1.62	1.27	2.53	13.55	0.84	1.14	2.59
16W115	4.18	1.35	48.75	3.31	1	0.63	0.56	0.29	1.02	1.1
16W117	6.23	1.02	22.19	0.68	0.58	1.08	18.37	0.84	0.83	1.59
16W119	4.92	0.53	29.46	1.32	1.48	0.18	1.91	0.11	1.52	6.12
16W123	6.33	0.7	40.03	0.65	0.14	1.56	17.09	0.23	1.05	2.58
16W132	2.74	0.52	38.25	0.85	1.85	1.72	9.95	0.58	0.13	0.87
16W133	5.64	1.37	22.67	0.63	0.46	0.48	1.39	1.61	1.09	0.97
PP003	5.61	1.83	34.22	0.83	2.52	2.05	1.08	2.3	1.41	1.81
PP006	6.71	0.73	7.61	0.96	1.04	0.94	1.22	0.27	1.66	2.28
PP007	1.93	0.27	22.73	1.06	1.71	1.87	1.32	0.96	0.54	1.74
PP009	6.88	0.49	48.85	0.44	1.88	1.36	0.68	0.97	1.49	0.7
PP016	5.66	0.86	21.32	1.55	3	1.13	3.3	1.34	0.26	1.2
PP023	7.09	1.66	19.01	2.75	1.9	2.61	17.1	0.61	1.74	1.55
PP028	10.48	0.62	27.36	1.81	2.2	0.61	5.02	0.2	0.99	0.86
PP033	11.09	0.76	14.49	1.27	0.25	0.58	7.4	4.21	0.67	0.44
Average	5.22	0.815	36.50	1.41	1.50	1.25	4.77	1.27	0.95	1.41

Table 7: Relative standard deviations (RSDs) reported for each element analyzed on the ICP-MS for major, minor, and trace element analyses.

Sample	TIC %	TIC % (MS)	Mn/Sr	Rb/Sr
16W001	0.42	0.425	7.73	0.01
16W004	0.65	0.563	4.71	0.00
16W005	0.56	0.483	4.65	BLD
16W007	0.66	0.577	4.57	0.00
16W009	0.79	0.687	4.44	0.00
16W013	0.76	0.659	3.12	0.00
16W016	0.77	0.666	2.60	0.00
16W022	0.81	0.705	3.97	BLD
16W024	0.82	0.711	4.09	BLD
16W029	0.77	0.664	3.34	0.00
16W031	0.77	0.463	4.34	BLD
16W043	0.71	0.672	3.15	BLD
16W045	0.81	0.616	3.41	BLD
16W047	0.32	0.706	3.21	BLD
16W052	0.82	0.327	9.39	0.08
16W054	0.75	0.715	2.45	0.00
16W059	0.75	0.650	3.13	0.00
16W063	0.80	0.652	2.18	0.00
16W067	0.81	0.695	2.74	0.00
16W070	0.78	0.708	2.64	BLD
16W077	0.71	0.680	3.38	0.01
16W079	0.22	0.619	3.18	0.01
16W082	0.86	0.226	9.48	0.23
16W083	0.72	0.748	4.26	0.00
16W087	0.77	0.627	4.12	0.01

16W090	0.77	0.671	4.39	0.02
16W101	0.76	0.671	3.26	0.00
16W102	0.73	0.661	2.98	BLD
16W104	0.79	0.629	3.26	BLD
16W107	0.78	0.688	3.58	BLD
16W109	0.72	0.678	3.75	0.01
16W110	0.69	0.621	3.86	0.01
16W113	0.71	0.586	4.26	BLD
16W115	0.67	0.614	4.83	0.00
16W117	0.73	0.580	4.26	BLD
16W119	0.60	0.637	4.86	BLD
16W123	0.65	0.516	3.95	BLD
16W132	0.62	0.559	3.86	BLD
16W133	0.52	0.537	3.22	0.00
PP003	0.74	0.455	7.04	0.01
PP006	0.73	0.645	5.86	0.00
PP007	0.77	0.634	5.64	BLD
PP009	0.76	0.672	5.84	BLD
PP016	0.83	0.662	6.87	0.00
PP023	0.80	0.724	5.00	0.00
PP028	0.34	0.691	4.13	0.00
PP033		0.343	8.71	0.11

Table 8: Mn/Sr, Rb/Sr for all samples run on the ICP-MS.

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