Re-Evaluating the Late Devonian Mass Extinction:

A Geochemical Investigation of the Relationship between Carbon Isotope Fluctuations, Faunal Turnover, and Paleoenvironmental Change Recorded in Upper Devonian Carbonates of the Lennard Shelf, Western Australia

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Abstract

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Chair of the Supervisory Committee:

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The primary goal of this dissertation is to increase understanding of the so-called Late Devonian mass extinction through the use of stable isotope geochemistry. Despite decades of research, the timing, cause(s), and extent of the events surrounding this devastating interval in Earth history remain poorly understood. One of the best places to study the Devonian period is the Lennard Shelf in the Canning Basin of Western Australia. This region contains extensive, well-preserved exposures of Middle and Upper Devonian (Givetian, Frasnian, and Famennian) carbonate reefal platforms and slopes that are ideal for geochemical analyses. A significant amount of information could be learned about the Late Devonian mass extinction in the Canning Basin if we had a detailed chronostratigraphic framework of platform to basin strata and a better understanding of the paleoenvironmental conditions during the Upper Devonian. This research aims to use stable isotope chemostratigraphy to help build a high resolution chronostratigraphy

and examine any environmental changes leading up to and following the F-F boundary that may have contributed to Devonian extinction events in the Canning Basin.

This dissertation is divided into two parts; the first concerns my research on the Late Devonian mass extinction while the second is ancillary and documents my astrobiology research rotation. Part 1 contains introductory and concluding remarks as well as three chapters written as scientific manuscripts that have been, or will soon be, submitted for journal publication. The first of these three chapters examines the local and global controls on carbon isotope chemostratigraphy in the Lennard Shelf system to validate the use of secular variations as a chronostratigraphic tool for regional and global correlations. The next chapter provides a detailed, expanded view of the F-F boundary and constrains the pattern of carbon isotope perturbations across said boundary at the intra-zonal scale. The third scientific chapter broadens focus from the F-F to the entirely of the Upper Devonian and presents the first carbon isotope composite curve from Western Australia that is used to test the global nature (timing and extent) of Late Devonian events and examine the relationship between carbon isotope fluctuations, faunal turnover, and changes in the paleoenvironment (sea level, climate, ocean chemistry, paleogeography). Results from Part 1 not only have implications for re-evaluating one of the "Big Five" mass extinctions in the Phanerozoic, but are also relevant to studies in astrobiology and have additional applications in the oil and gas industry. The final chapter of my dissertation, which is in Part 2, concerns interdisciplinary, astrobiology work done during summer quarter, 2014, that was devoted to analyzing the relationship between astronomy and geology circa 1770-1810. This chapter is included in my dissertation as partial fulfillment of my dual-title astrobiology degree.

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Beer -- the substance from which great memories are made,
lasting friendships are forged, and dissertation research imagined.

This dedication is split two ways, much like a good black and tan:

To my parents, Colleen and Tim, for instilling in me a sense of appreciation for social libations,
and for inciting in me an insatiable curiosity about the world around (and under) me.

To one of my oldest friends, Joey Hawkins,
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INTRODUCTION

Extinction is a natural and inevitable part of evolution; it makes way for new species, and it also reminds us that life is vulnerable. My desire to study extinction events, and the evolution of Earth's surface environments and the residing biota, stemmed from my early interests in astrobiology and paleontology. I liked the interdisciplinary nature of astrobiology and was intrigued by the idea of using the fossil record to better understand the evolution of life on earth so that we might be able to predict the trajectory of life elsewhere in the universe.

One of the most important discoveries about the history of animal life on Earth is that it was affected by five "major" mass extinctions, wherein major refers to the widespread extent and severity of biodiversity loss (at least a 50% extinction of species). In temporal order, these crises were the end Ordovician, Late Devonian, end Permian, end Triassic, and end Cretaceous mass extinctions (Raup and Sepkoski, 1982). The triggering mechanism(s) for all but the end Cretaceous event remain heavily debated, but proposed hypotheses include both extraterrestrial and earth-bound phenomena including bolide impact, climate change, ocean anoxia, and flood basalt volcanism.

Regardless of the cause, globally devastating events and widespread environmental changes are not unique to Earth; evidence for large bolide impacts has been observed on other planets within and outside of our solar system and the study of extrasolar planets has revealed seasonal climate variability that may impact the habitability of a planet (Jones, 2008). Gaining a better understanding of mass extinctions on our own planet, particularly their causes and effects, we astrobiologists can search more knowledgeably for possible life that may have endured similar catastrophes on Earth-like planets orbiting other stars.

The discovery that at least one of the “Big Five” was caused, to significant extent, by large body impact and was of short temporal duration (namely the asteroid that wiped out the dinosaurs and about half of all other species 65 million years ago, e.g. Alvarez et al., 1980; Schulte et al., 2010), has commonly led to the inference that the other four mass extinctions were also of short duration (< 1my in duration prior to onset of recovery) and that they were global. To validate these assumptions, a detailed examination of each individual mass extinction is required. This dissertation focuses on re-evaluating just one of the “Big Five,” the so-called Late Devonian mass extinction that purportedly occurred ~375 million years ago at the Frasnian-Famennian (F-F) boundary (Figure I.1); but more specifically on the assessment of the complex changes (geochemical, biological, paleoenvironmental) during the long-term led up and recovery of this event (>20 Ma interval of time spanning the Frasnian and Famennian, and perhaps even the Givetian), and how these changes were expressed in the carbon isotope record. This extinction is neither the most catastrophic nor the best known, but it is perhaps the most controversial as not even the major facts are agreed upon yet (Van Valen, 1984), the protracted nature is heavily debated, and the conditions surrounding the Late Devonian world remain poorly understood.

The Late Devonian mass extinction was unusual in that it carried a distinct ecological signature, including preferential losses of low-latitude, shallow-water organisms (Copper, 1986), with the most severe decline in diversity occurring within the geologic period rather than at the end of it (McGhee, 1996). Although nominally culminating at the F-F boundary, there is increasing support that the extinction was also complicated and long lasting. For instance, Bambach et al. (2004) showed that biodiversity began declining during the end of the Middle Devonian and continued to decline through the end of the Late Devonian. This relatively long duration of species loss suggests either a gradual extinction or pulses of many short-term extinction events.

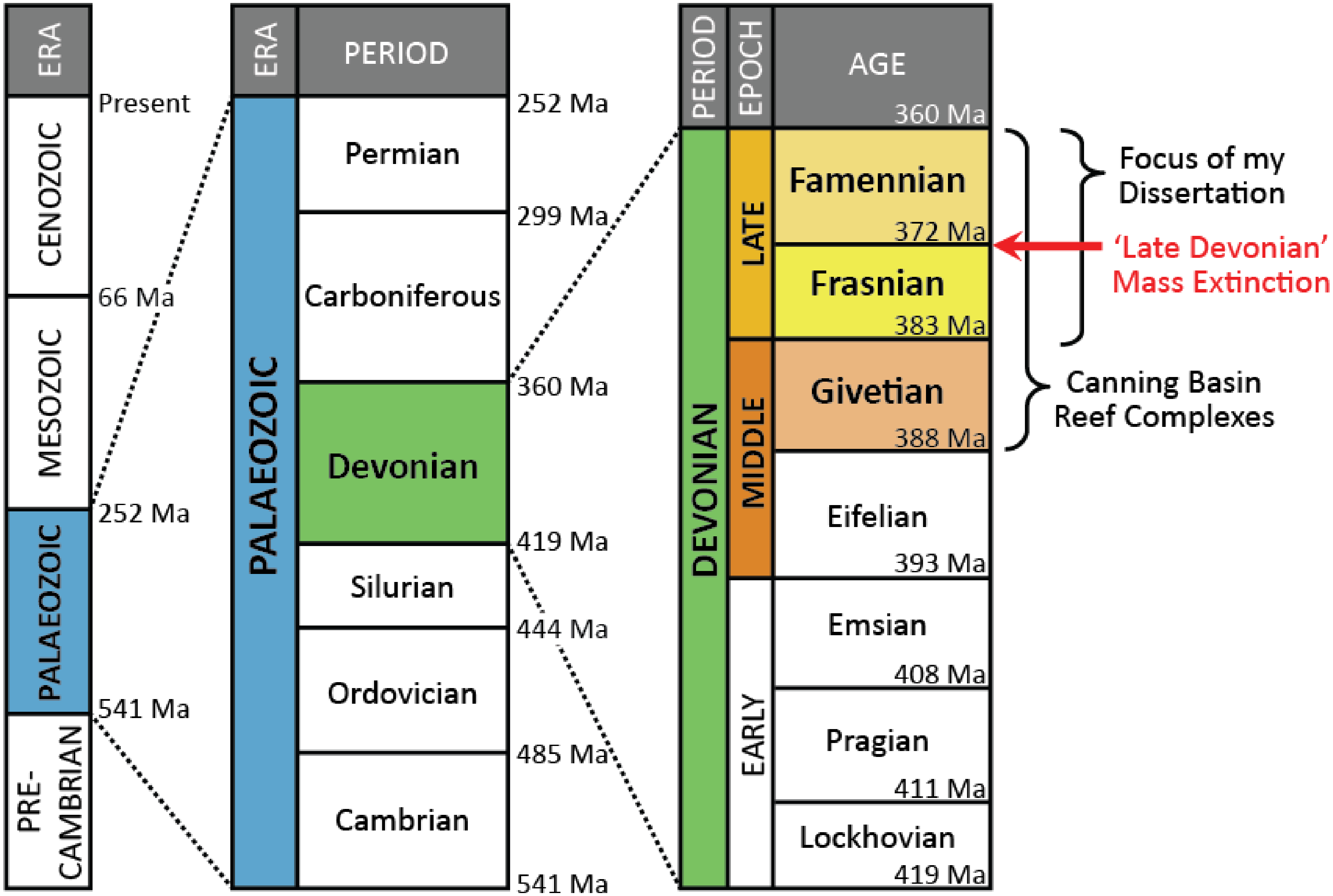

Figure I.1: Geologic timescale highlighting the subdivision of the Devonian period and the time interval most relevant to this dissertation. Numerical ages (Ma = millions of years before present) from the International Commission on Stratigraphy (Cohen et al., 2013).

Current paleontological, lithological, and geochemical data seem to lend support for the step-wise extinction hypothesis. For example, patterns of diversity loss during this time, at least for conodonts, brachiopods, and ammonoids, show several distinct intervals of elevated extinction rates (Bayer and McGhee, 1986). Middle - Late Devonian strata in Europe record a series of anoxic events, as evidenced by black shale deposits, and carbon isotope perturbations leading up the F-F boundary; the most notable of these are the *falsiovalis* event near the Givetian-Frasnian (G-F) boundary, the *punctata* event in the Middle Frasnian, and the Lower and Upper Kellwasser events in the Upper Frasnian. However, conflicting and poorly constrained isotope records (e.g. Wang et al., 1991; Zheng et al., 1993; Joachimski et al., 2002; Racki et al., 2004; Yans et al., 2007) and the absence of organic-rich deposits in some localities (e.g. Joachimski and Buggisch, 1993; Bond et al., 2004), has led to considerable debate over the global nature and paleoenvironmental factors responsible for these potential precursor extinction events.

Hypothesized causes for the Late Devonian mass extinction currently include ocean anoxia (e.g. Joachimski and Buggisch, 1993), sea-level change (Johnson, 1974), bolide impact (e.g. Nicoll and Playford, 1993), ocean-wide eutrophication (e.g. Algeo and Scheckler, 1998), global warming (Thompson and Newton, 1988), and global cooling related to glaciation (Caputo and Crowell, 1985), to paleogeography (Copper, 1986), and/or to a decline in atmospheric CO_2 levels due to an increase in land plant biomass (Algeo et al., 1995). Multiple-causality scenarios that integrate several mechanisms through biogeochemical-climatic feedbacks have also been proposed (Buggisch, 1991). Much of the evidence, however, remains equivocal, and no hypothesis accounts well for the protracted, step-wise nature and systematic selectivity of the Late Devonian mass extinction.

One of the best places to study the Devonian period is the Lennard Shelf in the Canning Basin of Western Australia (Figure I.2). This region contains one of the best-preserved examples of a fossil barrier reef system known from the Phanerozoic (Figure I.3). In spite of 350 km of excellent exposures and a long history of investigation, to date no instance of Late Devonian shallow water anoxia has been described from this system (Playford, 1980). This lack of organic-rich material, coupled with the paleo-position of the Lennard Shelf on the widely distant and poorly studied supercontinent of Gondwana, makes this region ideal for testing the global nature of Late Devonian events (Figure I.2). Initially, my plan was to examine the Late Devonian mass extinction from a paleontological perspective; however, the focus of my dissertation changed unexpectedly as I was introduced to the study of stable-isotope geochemistry in my first year of graduate school. Since this transition, I've been relying on stable isotopes of carbon and oxygen as investigative tools rather than fossil material.

All who have, or are currently working on the Lennard Shelf recognize the need for a high resolution chronostratigraphic framework if questions concerning paleoenvironmental changes and faunal extinctions of Canning Basin biota are to be answered. Such frameworks not only facilitate robust regional correlations and the comparison of age-equivalent stratigraphy in different settings worldwide, but also enable unprecedented interpretation and analysis for a clearer understanding of the timing and extent of the events surrounding Devonian extinction events. The goal of this dissertation is to re-evaluate the Late Devonian mass extinction through the lens of stable isotope chemostratigraphy; $\delta^{13}C$ profiles will be used to help construct a high resolution chronostratigraphy and understand environmental conditions leading up to and following the F-F boundary in the Lennard Shelf (Figure I.4). It is the contention of this dissertation that Frasnian and Famennian (and perhaps Givetian) events were part of a longer-

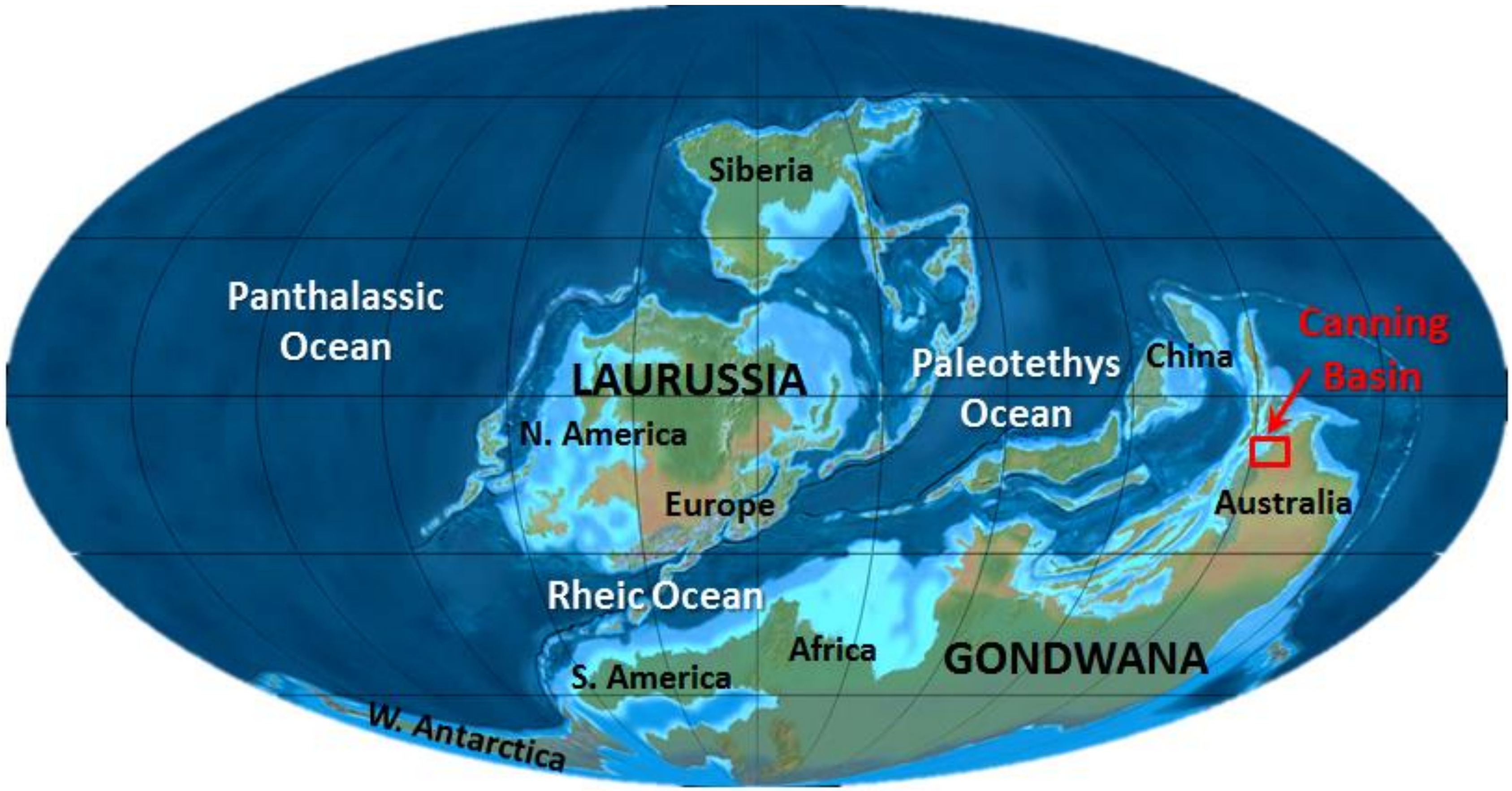

Figure I.2: Reconstructed paleogeography of the Late Devonian (Blakey, 2008). Red box shows the approximate location of the field area for this dissertation research; the Lennard Shelf carbonate reefal-platform system in the Canning Basin of Western Australia.

Figure I.3: Aerial photograph of Late Devonian reefal outcrops along the Lennard Shelf in the Canning Basin of Western Australia. This particular image shows Windjana Gorge National Park (photo courtesy of Peter Ward).

Figure I.4: The Frasnian-Famennian Boundary in Windjana Gorge National Park (photo courtesy of Tom Tobin). Fr. = Frasnian, Fam. = Famennian.

scale pattern of environmental change with the F-F mass extinction as but one of several biotic turnovers.

The generation of chronostratigraphic frameworks, however, can be difficult to develop if using only one stratigraphic technique. In the Canning Basin, past attempts using traditional sequence stratigraphic concepts have been compromised by the presence of depositional hiatuses and unconformities of unknown lateral and temporal extent, especially in platform-top settings (Playford, 1980; George and Chow, 1999). Depositional heterogeneity, such as lateral facies variability in slope settings, also hinders sequence stratigraphic correlations. Biostratigraphy in the Canning Basin has relied heavily on conodonts and ammonoids, which occur in the distal, deeper water facies but are rare to absent within the platform strata. Such local endemism reduces biostratigraphic usefulness and hence the need for other chronostratigraphic markers such as magnetostratigraphy and stable isotope chemostratigraphy.

To address some of these issues, this work was completed as part of a larger, multi-disciplinary effort. The Canning Basin Chronostratigraphy Project (Figure I.5) was developed with the aim of constructing a well-constrained, high resolution chronostratigraphic framework across shelf-to-basin depositional environments through the integration of several stratigraphic techniques; these included carbon isotope chemostratigraphy, conodont biostratigraphy, magnetostratigraphy, sequence stratigraphy, and trace element chemostratigraphy (Playton et al., 2013). Participating members included a variety of academics from various institutions (University of Western Australia, California Institute of Technology, Curtin University, University of Greenwich, University of Washington), researches from the Geological Survey of Western Australia and Chemostrat Incorporated, and industry professionals from Chevron Energy Technology Company in the United States and Australia. Fieldwork for this project was

Figure I.5: Personnel of the Canning Basin Chronostratigraphy Project during the 2009 field season (photo courtesy of Tom Tobin).

primarily carried out in the Lennard Shelf between June and August, from 2007 to 2011. I was fortunate that I was able to work with and learn from a wide variety of individuals on this interdisciplinary project, this allowed me to broaden my scope of knowledge and also contributed to my professional development.

Results from this dissertation will not only improve our geological understanding of Upper Devonian carbonates in the Canning Basin of Western Australia, but they are also relevant to astrobiology and industry research. For example, the goals of this dissertation parallel those of the 2008 Astrobiology Roadmap (Des Marais et al., 2008), specifically Goals 4 and 6. For example, this work aims to better understand how long-term and episodic changes in ocean chemistry, and to a lesser extent climate, have influenced the evolution of an ancient reef system. Results from this dissertation work will not only provide insights into the environmental conditions of this Devonian ecosystem, but may also serve as a guide for understanding current, and perhaps future, environmental changes that might impact the evolutionary trajectory of life on Earth. From an industry point of view, this research can help guide the search for new sources of hydrocarbons. The integrated chronostratigraphic framework, for example, has implications for developing better subsurface model frameworks and improving reservoir characterization in complex depositional settings. The quality control workflow developed and described in Chapter 1 can be applied to carbonate slope and basin reservoirs that exhibit such complexity, like the Carboniferous fields of Kazakhstan (e.g. Tengiz and Karachaganak Fields; Kuznetsov, 1997) and the Permian fields of west Texas (e.g. Wolfcamp reservoirs; Montgomery, 1996), using core and cuttings.

In the following paragraphs I will briefly explain the context and background of each of the chapters in my dissertation. While the work in total contributes to our understanding of the Late

Devonian mass extinction, it also raises new questions that should be addressed, some of which I touch on in the concluding section and some of which I hope to work towards answering in my research as my career continues.

The first of these chapters (Chapter 1; Hillbun et al., in revision) focuses primarily on methodology, as well as on validating the use of carbon isotope chemostratigraphy, which has proven to be a powerful tool for identifying, correlating and understanding major biotic crises (Magaritz, 1989; Holser, 1997; Prokoph and Veizer, 1999; Chen et al., 2002; Kump and Arthur, 1999). However, the usefulness of isotopic trends for correlation and paleoenvironmental interpretation relies on the preservation of primary marine $\delta^{13}C$ values and can therefore be challenged by a number of local controls on isotope fractionation (e.g. Patterson and Walter 1994; Holmden et al. 1998; Swart and Eberli 2005; Katz et al. 2007). A thorough diagenetic investigation of the samples, including petrographic analysis of thin sections and the microdrilling of individual carbonate components, is typical to ensure preservation potential. Upon realizing the scale of the Canning Basin Chronostratigraphy Project, however, with over 7000 samples in the dataset, I sought a more time and cost efficient approach. Chapter 1 (Hillbun et al., in revision) describes the streamlined workflow developed to analyze and quality control isotope analyses so that secular variations could be reliably used for correlation and interpretation. We validated the workflow by generating a chemostratigraphic correlation framework for the Lennard Shelf that was corroborated by integrated conodont biostratigraphy and magnetostratigraphy.

I then compared chemostratigraphic profiles from the Lennard Shelf to carbon isotope profiles from coeval sections elsewhere in the world. For the most part, the isotope records were morphologically similar and chronostratigraphically correlative, but, the timing of maximum values associated with the Upper Kellwasser excursion was different than expected. Rather than being coincident with the F-F boundary, our results showed that the excursion peak actually occurs distinctly below it. In Chapter 2, I discuss possible explanations for this discrepancy and the imposing implications for each (Hillbun et al., in prep.a). But our preferred hypothesis invokes a difference in biostratigraphic resolution and/or a scenario in which the major environmental and biotic stressors on the global marine carbon pool leading up to the Upper Kellwasser event horizon may have diminished before the F-F boundary itself. As a result, isotopic records in more restricted, shallow marine basins, such as those in Europe and North America, may have been experiencing a lag effect due to isolation of the dissolved inorganic carbon pool. We also incorporate some trace element data into Chapter 2 in attempts to better understand the mechanism(s) responsible for the major isotope perturbations.

In the third chapter, we broaden our focus from the F-F boundary to the entirety of the Upper Devonian subsystem (Hillbun et al., in prep.b). The majority of research on the Late Devonian mass extinction revolves primarily around the F-F boundary interval, with considerably less work done in the Lower-Middle Frasnian and Middle-Upper Famennian. In the Caning Basin, and in all of Gondwana in fact, there has been no geochemical investigation on strata outside the F-F interval, let alone spanning the entire Upper Devonian. Our goal for Chapter 3 was to produce the first carbon isotope composite curve for the Upper Devonian in the Lennard Shelf. While we were able capture all of the Frasnian, however, our curve extends only into the uppermost *marginifera* Zone in the Famennian because younger outcrop was not available to us. A high density sampling strategy combined with conodont biostratigraphy allowed us to better constrain the timing of some of the excursions, as reported from Laurussia (e.g. Buggisch and Joachimski, 2006), and to resolve higher frequency, shorter-term events that typically go unrecognized. Five major and five minor positive $\delta^{13}C$ excursions have been identified that can be used to aid stratigraphic correlations. Despite the lack of associated black shale deposits, the major excursions are interpreted to be of global significance as they exhibit comparable patterns and are correlative with geochemical events in other parts of the world. The minor excursions, described for the first time from the Lennard Shelf, appear to be at least regional phenomena, but further investigation is required to determine their global nature. This work allows us to test the global extent of Late Devonian events and to examine the relationship between excursions in the carbon isotope record and coincident faunal extinctions and changes in the paleoenvironment such as the transition from greenhouse to icehouse climatic conditions, the proliferation of land plants, an increase in continental runoff due to active mountain building events, the repeated rising and falling of sea level, and related changes in ocean chemistry and circulation. This work also has broader implications for understanding the significance of some of the biotic events as precursor/minor extinctions leading up to the F-F boundary.

This dissertation, like much scientific research, has also led to further questions. In the concluding section of Part 1, I elaborate on some of the implications of this dissertation as a whole. I also touch on results from this work that are unfortunately not included in this dissertation due to the interest of time, but will be published shortly after I graduate. I further explore avenues of future research to test some of the proposed hypotheses or reconcile potentially contradictory data.

Chapter 4 in Part 2 of my dissertation analyzes the relationship between astronomy and geology circa 1770-1810. This chapter is disconnected from my primary PhD research on Lennard Shelf carbonates and the Late Devonian mass extinction in Part 1, but I've included it in my thesis for a number of reasons. First, it contains a summary of my astrobiology research rotation project that was completed as a requirement of my dual-title PhD in Earth and Space Sciences and astrobiology. Second, my interest in astrobiology sparked my infatuation with mass extinction events and was a primary driving factor that motivated me to peruse graduate research; without astrobiology, this thesis may not have become a reality. And finally, my experience with the astrobiology community at UW, including that of my research rotation, taught me the importance of interdisciplinary research, trained me to communicate my science with people outside of my field, and ultimately has helped to shape the scientist I have become.

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CHAPTER I

Global and Local Controls on Carbon Isotope Fractionation in Upper Devonian Carbonates from the Lennard Shelf, Western Australia: A Streamlined Approach for Generating Primary Marine Secular Curves for Regional Correlation

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ABSTRACT

High resolution carbon isotope chemostratigraphy, achieved through high density sampling, can aid stratigraphic correlations in heterogeneous carbonate slope-to-basin systems. However, making such correlations can be challenged by diagenetic processes which modify or reset primary marine isotope values and destroy original stratigraphic trends. Current methods for precluding compromised isotope values and generating reliable secular curves are time consuming and expensive, especially for large, stratigraphically extensive datasets. To address this issue, ~2700 carbon isotope values derived from Upper Devonian carbonates along the Lennard Shelf in the Canning Basin of Western Australia were used to develop a workflow for quality control of bulk-rock data that includes microdrilled component analysis, petrography, and empirical facies relationships, but does not require thin sections and component sampling for every sample. Although some diagenetically altered samples make it through the process and some well-preserved samples are removed, this approach has produced reliable secular curves from bulk-rock data which are suitable for regional and even global correlations. Importantly, the results from this work also show that different depositional environments along the Lennard Shelf (platform - slope) variably affect the preservation of primary marine isotope values and thus their utility as a stratigraphic correlation tool.

INTRODUCTION

Carbon isotope chemostratigraphy has been widely used as a correlation tool for chronostratigraphic studies of all ages around the world (Vahrenkamp, 1996; Menegatti et al., 1998; Montañez et al., 2000; Saltzman, 2002; Morrow et al., 2009). Robust correlations are based on the tested hypothesis that secular variations in carbon isotope values from inorganic marine carbonates reflect changes in ocean chemistry on a global scale (Kump and Arthur, 1999). The use of carbon isotopes as a successful correlation tool is contingent upon the analysis of well-preserved material and preservation of the primary marine signal. However, numerous chemical, physical, and biological processes can modify or reset primary marine isotope values and destroy original stratigraphic trends (e.g. Patterson and Walter 1994; Holmden et al. 1998; Swart and Eberli 2005; Katz et al. 2007). To preclude diagenetically altered samples and derive the primary marine isotope values necessary for generating robust secular curves, a few different methods have been developed. Arguably the best method involves petrographically analyzing and microdrilling well-preserved, individual carbonate components from each sample. However, even calcitic, non-luminescent layers of brachiopod shell material, which was once regarded as the “gold standard” for evaluation of primary marine values (Popp et al., 1986; Veizer et al., 1986), is not always reliable due to vital effects unique to each species (Grossman et al., 1993; Selleck and Koff, 2008). Moreover, this approach is laborious, time consuming and costly.

In attempts to alleviate some of the latter issues, many recent studies have focused on the use of isotope analyses from bulk-rock samples rather than from microdrilled carbonate components. Past studies, both Devonian in age (e.g. Buggisch and Joachimski 2006) and not (e.g. Katz et al. 2007), have shown that bulk-rock samples have a high potential for preserving primary marine carbon-isotope values as long as any stabilization and recrystallization have taken place in a post-depositional system closed to changes in the carbon pool. In an open system like the meteoric diagenetic environment, CO_2 or re-mineralized carbon derived from external sources (such as soil gas CO_2 or weathered organic shales) can alter the original isotopic composition, causing a superposition of local and global signals (Gross, 1964; Allan and Matthews, 1982; Śliwiński et al., 2011). Because decoupling these signals is a fundamental problem, which has consequently led many away from the use of bulk-rock material in stable isotope studies, time and resources must still be invested into a thorough diagenetic evaluation.

Because of the time-intensive and costly approaches for generating reliable carbon isotope profiles, previous chemostratigraphy studies generally have either limited resolution (Veizer et al., 1986) or stratigraphic coverage (Stephens and Sumner, 2003). In contrast, our dataset from the Lennard Shelf carbonate system in the Canning Basin of northwestern Australia (Figure 1.1) has a high sampling density (1-2 samples/m) that extends over extensive stratigraphic intervals (45 m to 700 m sections). This provides better control for examining depositional controls on diagenetic processes and understanding how these processes are manifested in our sections. This is important not only for assessing the preservation of carbon-isotope values and generating secular curves, but also for developing a more efficient approach to decoupling the marine signal from diagenetic overprints.

This paper does not describe a new method for carbon isotope analysis but rather proposes a new approach, using the previously described methods, for application to a large dataset and/or a project limited in sample material (i.e. core and cuttings). As an alternative to evaluating each and every sample, we offer a more practical quality-control workflow for bulk-rock samples that uses discriminative criteria, such as mineralogy, bulk-rock constituents, and predictable trends in the isotope values, to pick out diagenetic overprints based on only an appropriate subset of the

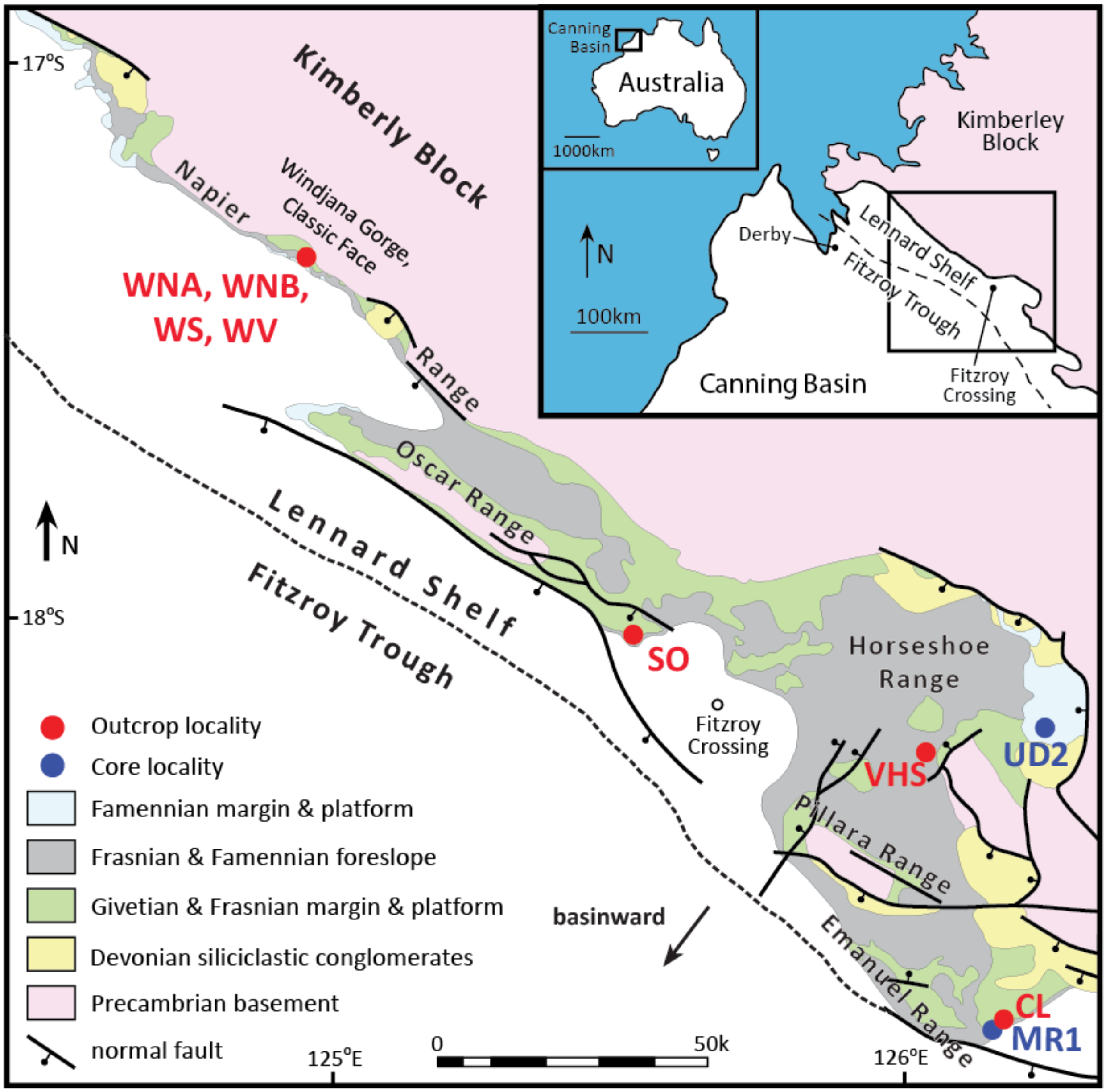

Figure 1.1: Map of Upper Devonian reefal platform and slope outcrop exposures along the Lennard Shelf in the Canning Basin of Western Australia. Map shows generalized geologic information and structural features as well as sample localities (Modified after Playford et al. 2009). See Table 1.1 for non-abbreviated locality names.

samples. Individually, each criterion is arguably unreliable as a means to evaluate the isotopic composition of seawater. The aim of this study, however, is to collectively use the criteria as diagenetic indicators/predictors in an effort to efficiently remove potentially altered isotope values and minimize stratigraphic overprints. While it is true that evaluating every sample is the most accurate method, as supported by decades of isotope research, it is tedious, expensive, and too time consuming to apply to every sample, especially in isotopic studies with relatively large datasets (>1000 samples).

This new approach was developed in response to an extensive, multidisciplinary project in the Canning Basin, Western Australia, that aims to develop a high resolution chronostratigraphy for the region through the integration of carbon isotopes, conodont biostratigraphy, sequence stratigraphy, and magnetostratigraphy; the individual and integrated datasets are forthcoming and will not be discussed in detail here. As part of this larger study, 17 sections (>3900 m of stratigraphy) were stratigraphically investigated and >7000 oriented hand samples and one-inch-diameter (2.5 cm) core plugs were collected for the various aforementioned analyses. Sample collection was at sub-meter stratigraphic spacing (59 cm avg., 16 cm min., 95 cm max.), with the aim of capturing facies changes where possible. In instances where samples were collected from breccia, blocks and allochems were avoided and the matrix or marine cement targeted instead to ensure that isotopic analyses were representative of the sedimentation event, and not the timing of sedimentation prior to material transport.

For this paper, nine stratigraphically-overlapping, Frasnian-Famennian aged sections were chosen from the larger dataset (Figure 1.2). Those selected are geographically spread over ~250 km of outcrop exposures and represent a variety of paleogeographic settings from open-ocean, isolated platforms and protruding reef spines to more restricted, land-attached shelf settings.

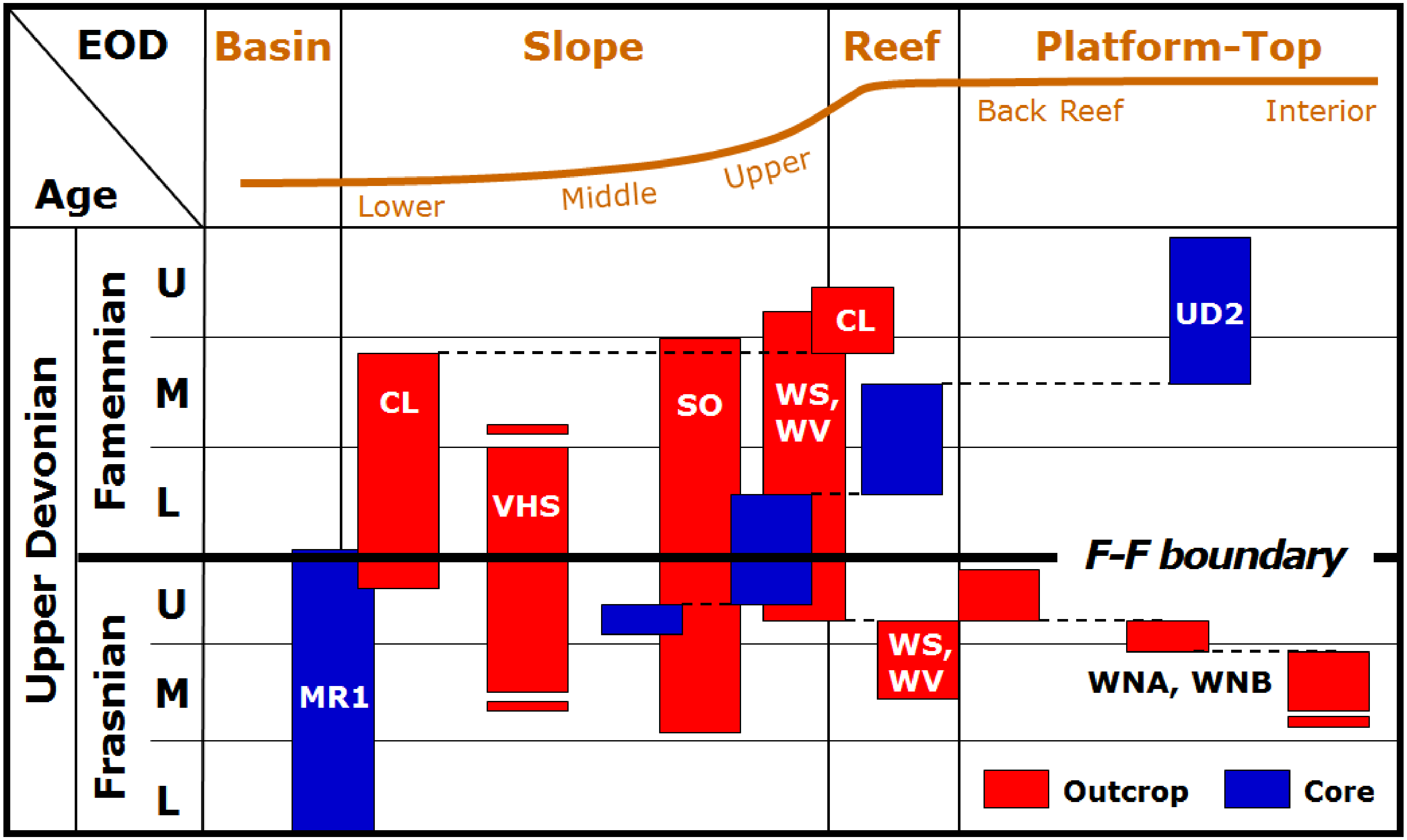

Figure 1.2: Sample coverage showing the relative ages and depositional environments of the nine sections sampled for this study (modified after Playton et al., 2013). The geographic locations and relative spatial distribution of these sections are shown in Figure 1.1. See Table 1.1 for non-abbreviated locality names.

Further details regarding the sections, including age, stratigraphic thickness, and depositional environment are in Table 1. Herein we discuss the discriminative criteria that were identified and then applied in the workflow. Diagenetic trends and depositional controls crucial to this process are also discussed, along with the limitations of the new approach and the use of the resulting isotope profiles for correlation purposes.

The scope of this study does not include chemostratigraphic interpretations, but rather focuses on the following objectives:

1) Develop discriminative criteria for the quality control of a large bulk-rock dataset by identifying depositional facies relationships with carbon-isotope fractionation trends from only a sub-set of samples. Discriminative criteria will be based on predictable isotope trends as well as microdrilled component analyses, petrography, and empirical facies relationships, but not thin sections and component sampling for every sample.

2) Demonstrate that said workflow is successful by using it to construct stratigraphically extensive, high resolution carbon isotope curves for different depositional environments along the Lennard Shelf that can be used for regional and potentially global correlations.

GEOLOGIC SETTING

The Canning Basin is a large (500,000 km^2) sedimentary basin located in northern Western Australia (Figure 1.1) between the Kimberley and Pilbara cratons (Veevers and Wells, 1961; Hocking et al., 1994; Tyler and Hocking, 2001). The Lennard Shelf region along the northern margin of the Canning Basin contains a world class outcrop example of a reefal carbonate shelf-to-basin system which has become known colloquially as the “Devonian Great Barrier Reef.”

The outcropping limestones are Middle to Late Devonian in age (Givetian, Frasnian, and Famennian), extend over an area ~350km long and ~50km wide, and have an estimated maximum thickness of at least 2500 m (Playford and Lowry, 1966). This carbonate system is relatively well-preserved (Hurley 1986; Kerans et al. 1986) and has undergone little metamorphic or structural deformation (Begg, 1987; Drummond et al., 1991; Dörling et al., 1995)(Wallace et al., 2002), making it an ideal locality for isotopic studies. Decades of research have been devoted to understanding the many aspects of this Upper Devonian carbonate system, including the stratigraphic architecture and sequence development (Guppy et al., 1958a; Read, 1973; Playford et al., 1989; George et al., 1997; Ward, 1999), depositional processes and controls (Playford, 1984; Playford, 2002; Playton, 2008; George et al., 2009; Playton et al., 2010), and the biostratigraphic framework (Ziegler and Sandberg, 1990; Becker et al., 1993; Becker and House, 1997; Klapper, 2007). A comprehensive summary of most of this work can be found in Playford et al., (2009).

A variety of depositional environments, from the platform to the basin, are exposed along the Lennard Shelf and have been described in detail by (Playford, 1980). In this paper, the platform-top setting refers to Playford's, (1980) platform-interior, back-reef, and reef-flat facies while the slope setting has been sub-divided here to include lower-, middle-, and upper-slope facies; these new designations correspond to the author's reefal-slope- and fore-reef slope subfacies. Microbial textures occur in almost all depositional settings, although they are most common and abundant in reef-flat through upper-slope facies in Famennian aged strata of the Lennard Shelf system.

Previous geochemical studies in the Canning Basin showed that portions of the Lennard Shelf have been subjected to a series of diagenetic events that produced local chemical changes in the marine carbon reservoir which may have resulted in syn- and post-depositional alteration of primary marine carbon isotope values (Kerans, 1985; Kerans et al., 1986; Hurley and Lohmann, 1989; Wallace et al., 1991). During the Middle and Late Devonian, numerous fluctuations in sea level resulted in repeated exposure of sediments to the meteoric environment, making them more susceptible to dissolution and recrystallization by fluids depleted in ^{13}C. This is especially true for platform-top sections which are more prone to exposure during marine regressions than relatively deeper-water slope sections. After reef growth ceased in the Late Devonian, the carbonate system was covered by siliciclastic-rich, shallow-marine facies of the Fairfield Group (Druce and Radke, 1979) and was subsequently subjected to localized dolomitization and Mississippi-Valley-Type (MVT) mineralization during early burial diagenesis (Wallace et al., 2002). In an effort to minimize the potential influence of MVT-type burial fluids on the preservation of isotope values, our investigated sections were chosen away from ore deposits.

During the Middle Carboniferous- Early Permian, the Fairfield Group was eroded over much of the inner Lennard Shelf, presumably by glaciation (Playford, 2002), resulting in subaerial exposure and karstification of the reef complexes. In the Permian and Mesozoic, the system was buried for a second time, only to be exhumed and karstified again during Cenozoic uplift (Forman and Wales, 1981; Embleton, 1984). Meteoric diagenesis during this period of exposure resulted in dedolomitization and calcite recrystallization. In terms of isotopic preservation and resetting, episodic burial- and meteoric diagenesis can result in a progressive trend towards lower $\delta^{18}O$ values (Wallace et al., 1991). However, this is not always the case for $\delta^{13}C$ values; because diagenetic fluids in carbonate rocks generally contain comparatively little secondary or transported carbon, $\delta^{13}C$ values are relatively stable and have a higher preservation potential than $\delta^{18}O$ values (Machel and Mountjoy, 1986).

METHODS

Laboratory Methods

To achieve high-resolution isotope records and increase time and cost efficiency considering the number of samples, carbon and oxygen isotope analyses were primarily performed on whole-rock samples. Over 2700 samples were powdered for "bulk" rock analyses at the Stable Isotope Research Facility at the University of Washington (Table 1.1; Appendix 1.1). In this paper, the term "bulk" refers to samples that were powdered using a hand-held Woodtek drill, a method which has a relatively coarser drilling resolution compared to a computerized microdrill, but is significantly more time efficient. The analytical precision of both $\delta^{13}C_{carb}$ and $\delta^{18}O$ analyses based on sample replicates and laboratory standards is $\leq \pm 0.1$ ‰. Data were corrected using laboratory standards and are reported here in standard delta notation relative to VPDB (Vienna PeeDee Belemnite). The bulk-rock methodology of Stephens and Sumner (2003) was followed for all isotopic analyses with the exception of the following modifications:

1. Approximately 250 petrographic "thick sections" (70-100 μm) were made from a facies-representative subset of the samples. To assess preservation and the effects of diagenesis on facies assemblages, the thick sections were petrographically analyzed under transmitted light and cathodoluminescence (CL) using a Technosyn cold cathodoluminescence microscope.

   After diagenetic screening, individual components (such as skeletal material, non-skeletal grains, micritic mud, and various generations of cement) from a variety of facies were drilled from the thick sections using a high precision, fully automated Merchantek micromill. A representative "bulk" sample was also taken from each thick section for comparison. Marine cements (primarily fibrous and microcrystalline) and other matrix components were

Table 1.1: Sample dataset showing stratigraphic thickness, age, depositional environment, number of samples collected, total isotopic analyses completed, and number of bulk rock analyses with a quality control (QC) value less than or equal to 1.5, for each section and core measured. *denotes cores, all others are outcrop transects. See Figure 1.1 for section and core locations.

Section/Core Name	Thickness (m)	Age	Depositional Environment	Samples Collected	Isotopic Analyses	
					Total	QC $\leq$ 1.5
South Oscars (SO)	584.4	M Fras - U Fam	middle - upper slope	639	780	530
Horse Spring (VHS)	102.0	M Fras - M Fam	lower - middle slope	292	297	243
Casey Falls (CL)	419.0	U Fras - U Fam	lower - upper slope	589	498	416
Windjana North A (WNA)	143.0	M - U Fras	platform interior - reef flat	282	309	74
Windjana North B (WNB)	171.3	M - U Fras	platform interior	359	336	164
Windjana Slope (WS)	258.5	M Fras - L Fam	middle slope - reef flat	261	140	88
Windjana Valley (WV)	510.0	M Fras - U Fam	middle - upper slope	510	283	238
McWhae Ridge* (MR1)	42.1	L Fras - L Fam	lower slope/basin	155	154	148
UD2*	703.0	M Fras - U Fam	middle slope - platform-top	712	332	248
Totals	**2933.3**	**L Fras - U Fam**	**platform interior - basin**	**3799**	**3129**	**2149**

preferentially targeted for the initial bulk-analyses because results from previous studies (Kerans et al. 1986; Stephens and Sumner 2003) have shown them to be good approximations of Devonian sea-water values. All remaining samples (those without accompanying thick sections, ~2400) were polished and powdered for bulk-rock isotope analyses.

2. An additional quality control (QC) step was developed and applied to assess the effects of diagenesis on samples without accompanying microdrilled data to extract diagenetically modified isotope values from the bulk-rock dataset.

Quality Control Workflow

The quality control "step" was actually an iterative process in which six discriminative criteria were developed during the course of this study (Table 1.2). The discriminative criteria were collectively used to rank samples on a scale of 1-3; where 1 represents well preserved primary marine material, 2 represents intermediate and only slightly diagenetically modified material, and 3 signifies a higher degree of diagenetic modification and thus the highest potential for reset $\delta^{13}C$ values. While a sample may initially be assigned more than one QC value, due to the application of multiple discriminate criteria, the final QC ranking was determined by the highest (worst) value; this allowed for a conservative evaluation of the data. Initial criteria included instrument standard deviations of $\delta^{13}C$ values, lithology/mineralogy, and primary texture preservation. Later results from the petrography, analysis of microdrilled carbonate components, and bulk-rock analyses were used to create additional discriminative criteria. In essence, these criteria acted as a basic, yet refined, standard for filtering a large (in excess of ~500 samples) bulk-rock dataset in a time- and cost-efficient manner.

Table 1.2: Quality control (QC) scheme developed in this study. Table shows criteria used to assign QC values to isotope data. For each sample, criteria were ranked from 1-3 (1=best preserved), the final QC value for the sample was determined by the criterion with the highest (worst) value. Based on this classification, samples with a QC value of 2 or 3 were omitted.

Criteria \ QC Value	Best Preserved 1	1.5	2	Least Preserved 3
1. Instrument Stdev.	≤ 0.05	0.051 - 0.099		≥ 0.1
2. Lithology/Mineralogy	Limestone (calcite)	Mixed limestone-siliciclastic, Siliciclastic	Mixed limestone-dolomite, appearance of iron-pyrite	Dolomite, Mixed dolomite-siliciclastic, Volcanic (basement)
3. Bulk Rock Constituents	Dominantly marine cement and/or other matrix components	Abundant skeletal grains/ shell material		Abundant blocky calcite
4. Cathodoluminescence (where applicable)	Non-dully luminescent	Dull - low luminescence	Moderate luminescence	Brightly luminescent (homogeneous, zoned, banded, clotted)
5. Bulk $\delta^{13}C$ (‰) value	≥ 0‰	< 0‰ AND assoc. with exposure surfaces	< 0‰ AND assoc. w/ microbial facies or boundstone textures	< 0‰, (unless assoc. w/ microbial facies or exposure surfaces)
6. Bulk $\delta^{18}O$ (‰) value	≥ -6.0‰		Between -6 and -7‰	< -7.0‰

We are hesitant to provide step-by-step instructions, and instead provide a generalized workflow, because the criteria developed in this study are unique to the Lennard Shelf and may not be applicable to other localities, of similar or varying age, due to differing depositional conditions and burial histories. However, the QC process described in this study can be tailored for use with any large isotopic dataset by modifying existing criteria and/or developing new criteria.

Using only a subset of the samples, which are representative of the different depositional facies, one must first determine which carbonate components are the most reliable for preserving primary marine signatures and which are the most susceptible to diagenetic alteration. This is most commonly done using a combination of petrography, cathodoluminescence, and microdrilled isotope data. Next, predictive trends, features, or distributions that are closely associated with either the well-preserved samples or the diagenetically modified samples must be identified. These trends can then be used to direct bulk-sample drilling towards certain components, within any study, to increase the probability of obtaining a marine signal useful for correlation. Once the samples have been drilled and analyzed following the learned guidelines, the bulk-rock data can then be evaluated for diagenetic trends, such as facies specific covariations in carbon and oxygen values (Hurley and Lohmann, 1989), and also for depositional (facies) controls on isotopic fractionation. Observed tendencies are useful for establishing cut-off values and discriminative criteria that can be extrapolated to the entire dataset in attempts to decouple the global marine signal from local overprints. Due to the iterative nature of developing the QC process, we will present the petrographic and microdrilled component analyses first, followed by the learned guidelines for bulk-rock drilling, the results of the bulk-rock analyses, the development of the discriminative criteria, and then the findings and application of the QC workflow.

Integration and Correlation

Isotopic profiles were constructed for each measured section using data with a QC rating of 1.5 or better. To provide additional constraints and stratigraphic context, the carbon isotope data were integrated with conodont biostratigraphy (Roelofs et al., 2015), magnetostratigraphy (Hansma et al., 2015), and sequence stratigraphy (Playton et al., 2013). Combining these methods reduced correlation uncertainty and was important for assessing the influence of local controls, such as depositional setting and facies, on the preservation of primary marine values. While the entire integrated dataset is not presented in this paper, Figure 1.3 shows an example of the multiple data types existing for each section.

PETROLOGY AND MICRODRILLING ANALYSES

Isotopic data from the microdrilled samples were analyzed in conjunction with transmitted light petrography and cathodoluminescence and are presented here for comparison between slope- and platform-top facies. Within each of these facies, only the most abundant carbonate components were targeted and have been divided into four groups; (1) biogenic components, (2) marine cements (only fibrous and equant-isopachous varieties), (3) matrix components, and (4) blocky calcites (various generations of equant calcite cement).

Biogenic Components

The biogenic components sampled include echinoderms, brachiopods and various stromatoporoid genera. In general, these components are relatively abundant but can be facies specific and distributed unevenly throughout the sections in which they do appear. Echinoderms are well preserved and non-luminescent, recording some of the highest isotopic values (+1 to +4 ‰ for $\delta^{13}C$ values, -3.5 to -5 ‰ for $\delta^{18}O$ values) regardless of depositional setting (Table 3).

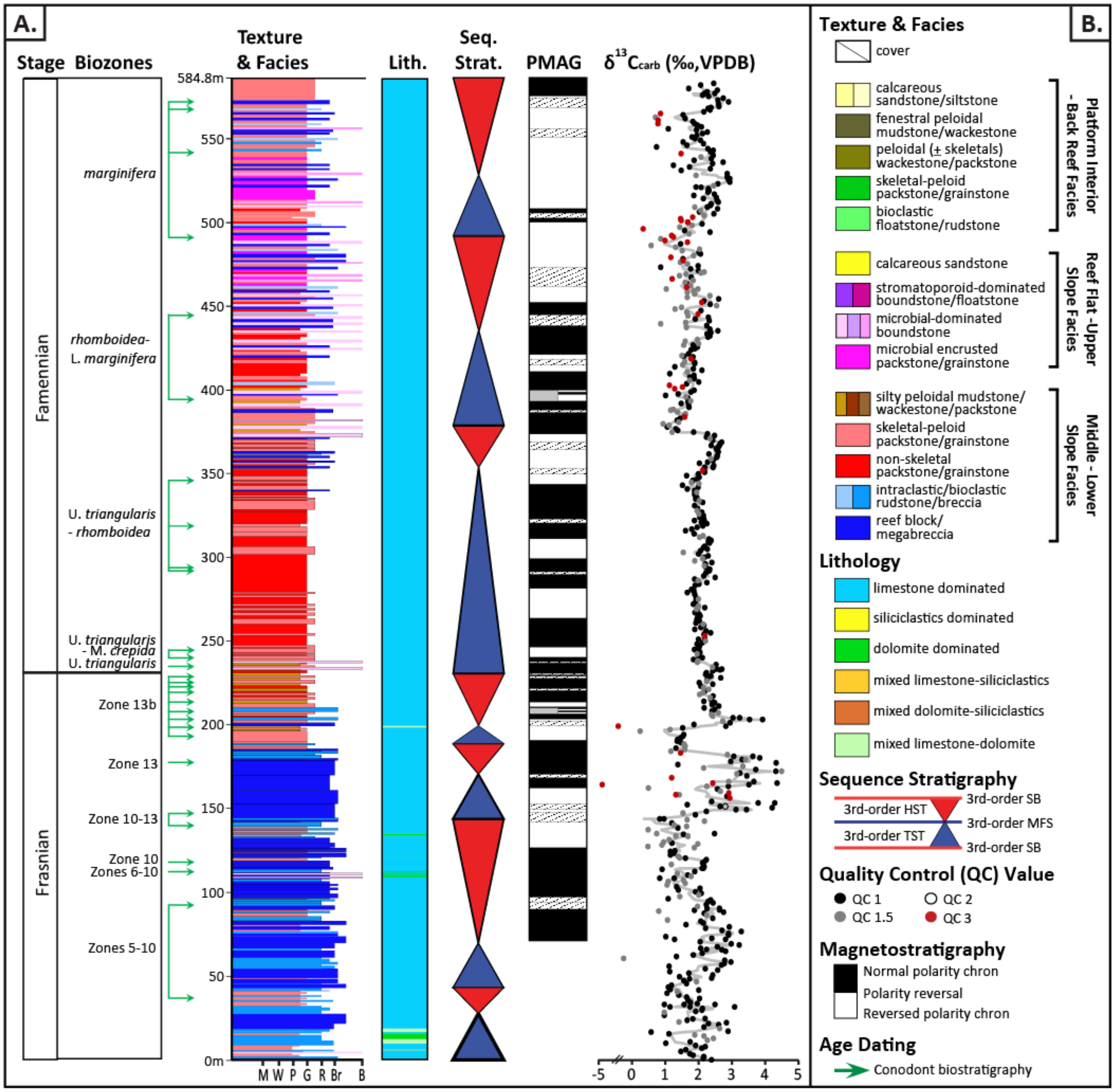

Figure 1.3: Example of a measured section showing the various types of data collected and utilized for stratigraphic analyses. For each section, all available data, including conodont biostratigraphy (Roelofs et al., 2015), paleomagnetic reversals (Hansma et al., 2015)), interpreted sequence stratigraphy (Playton et al., 2013), lithostratigraphy, details about texture and facies assemblages (M = mudstone, W = wackestones, P = packstone, G = grainstone, R = rudstones, Br = breccia, B = boundstone) and carbon isotope chemostratigraphy, were integrated to improve stratigraphic correlations. B) Legend applicable to Figures 3A, 9A, and 12. For the sequence stratigraphy, HST = highstand systems tract, TST = transgressive systems tract, LST = lowstand systems tract, SB = sequence boundary, MFS = maximum flooding surface.

Brachiopods are also typically non-luminescent, while stromatoporoids (*Actinostroma, Stachyodes and Amphipora*) exhibit a range of luminescence intensities when observed under CL. Unlike echinoderms, both stromatoporoids and brachiopods are variably recrystallized and exhibit an isotopic trend (in both carbon and oxygen) towards more negative values.

Marine Cements

Early marine cements are widespread and well preserved (texturally and chemically) in lower, middle and upper slope facies (Figure 1.4A and B). In thin section we see that bladed and scalenohedral varieties are present, but fibrous cements are more abundant and voluminous. Because of their relative abundance, fibrous cements are most likely to be captured, at least in part, when drilling bulk-rock samples and were therefore the main focus of the marine cement microdrilling. In all platform-top facies, well preserved marine cements are rare, especially fibrous varieties. Identifying and micro-sampling these cements is challenging due to the variable degrees of recrystallization and diagenesis. Rather than fibrous cements, equant-isopachous cements were primarily targeted in the platform because they were relatively more abundant, easily identifiable, exhibited non- or dull- luminescence, and required little difficulty in microdrilling. Isotopic values obtained from fibrous- and equant-isopachous cements are relatively invariant for carbon, but show variations in shift magnitude with respect to oxygen (Figure 1.5). The variation in oxygen is greater in platform-top facies (>4 ‰) than slope facies (~2.5 ‰). In all depositional facies sampled, bulk-rock analyses closely approximate the $\delta^{13}C$ values of microdrilled cements (Figure 1.6).

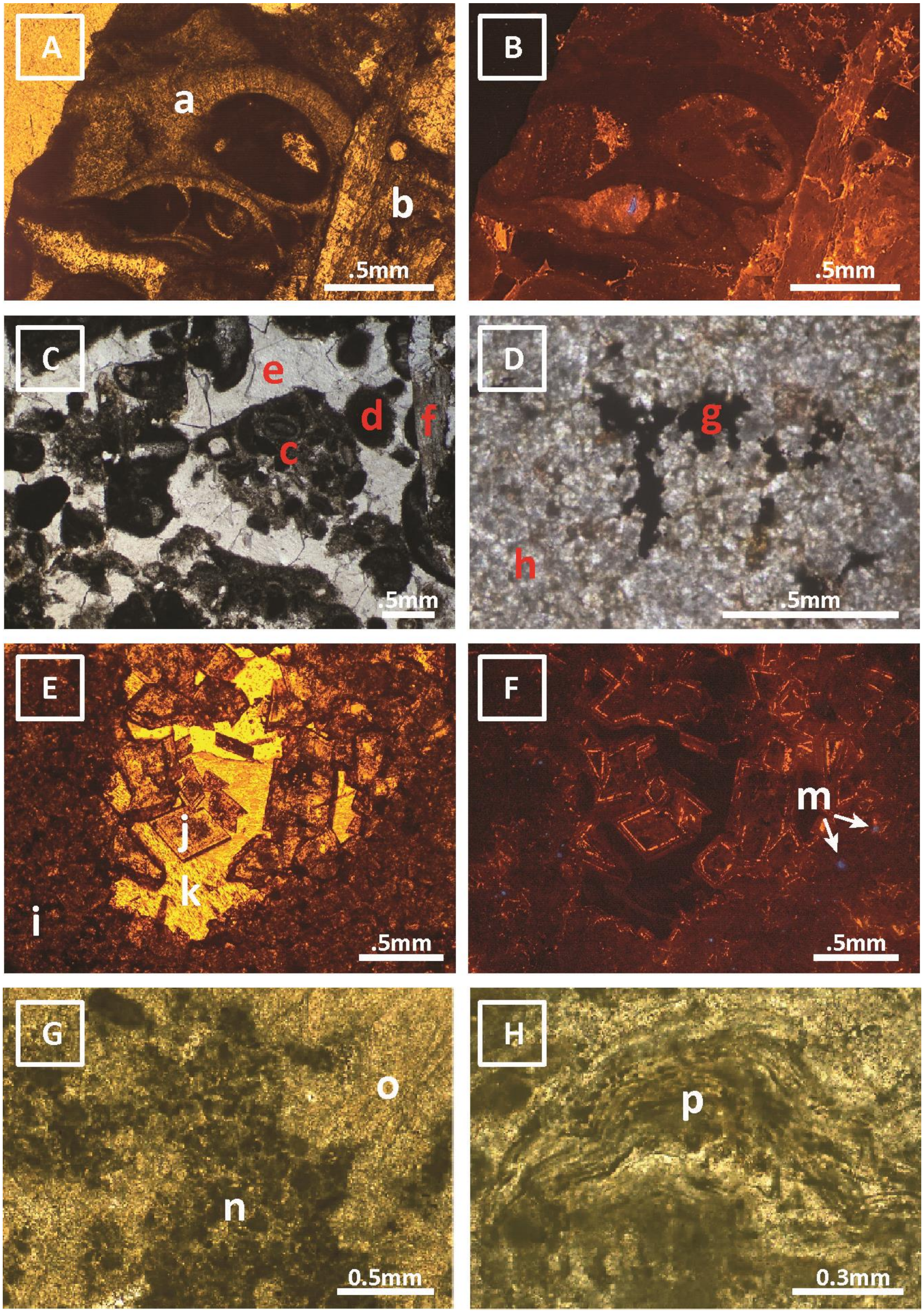

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Figure 1.4: Thick section photomicrographs illustrating characteristic features in lower-middle slope (A-C), platform-top (D-F), and upper slope-reef margin (G-H) settings. A. Skeletal-peloidal grainstone (plane-polarized light) showing allochems cemented by well preserved and non-luminescent fibrous cement (a). Later stylolites (b) cross-cut primary depositional fabrics but do not appear to chemically alter (luminescence) the early marine cements. South Oscar transect, sample 210. B. Same area in micrograph A under cathodoluminescence. C. Skeletal-peloidal grainstone showing composite (c) and isolate (d) grains cemented by synsedimentary blocky calcite (e) and cross-cut by a later stylolite (f); note limited grain to grain contact in the sample (plane-polarized light). South Oscar transect, sample 210. D. Example of pyrite (g) as it commonly occurs in matrix replacing dolomite (h) in platform-top settings. Light brown areas adjacent to the pyrite are iron oxides, also a common constituent in the platform (plane-polarized light). Windjana North B transect, sample 38. E. Photomicrograph of a dissolution cavity. Replacement dolomite in the matrix forms the wall of the cavity (i), but is overlain by zoned dolomite cement (j) and non-luminescent blocky calcite type 2 (k). Windjana North B transect, sample 38. F. Same area in micrograph E under cathodoluminescence. Note presence of luminescing (blue) siliciclastics material in the platform (m). G. Microbial encrusted boundstone facies (plane-polarized light) dominated by microbial growth (n) and well preserved fibrous cements (o). Casey Falls transect, sample 297. H. Another type of microbe (p), this one more filamentous, common in encrusted boundstone facies (plane-polarized light). Casey Falls transect, sample 313.

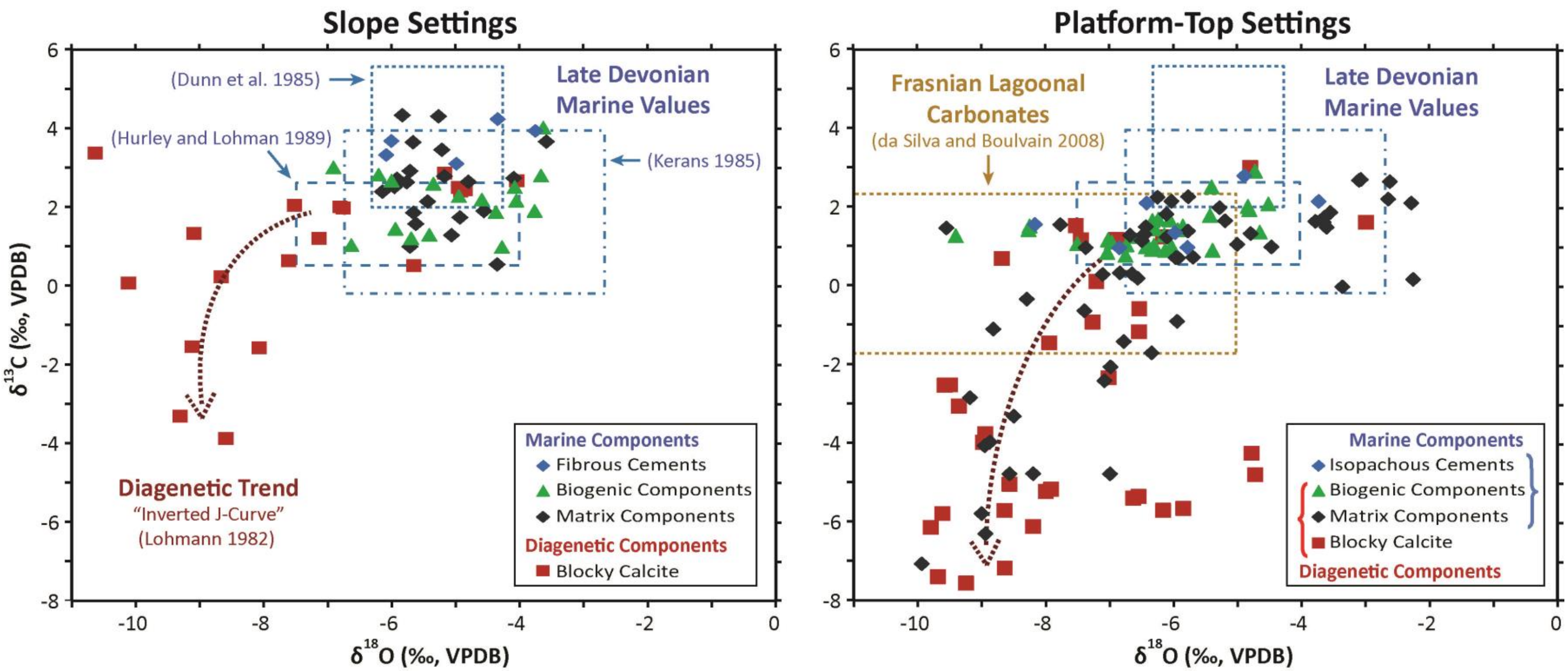


Figure 1.5: Comparative isotope cross-plots of microdrilled data for various carbonate components in slope and platform settings. Plotted for reference on both diagrams are the ranges of isotope values (blue boxes) typical for Late Devonian marine cements and brachiopods in the Canning Basin (Kerans 1985; Hurley and Lohmann 1989) and Europe (Dunn et al. 1985). For platform-top settings, the isotopic range of shallow water, lagoonal carbonates is also plotted (da Silva and Boulvain 2008). See Table 3 for more specific information about the types of biogenic, matrix, and blocky calcite components sampled.

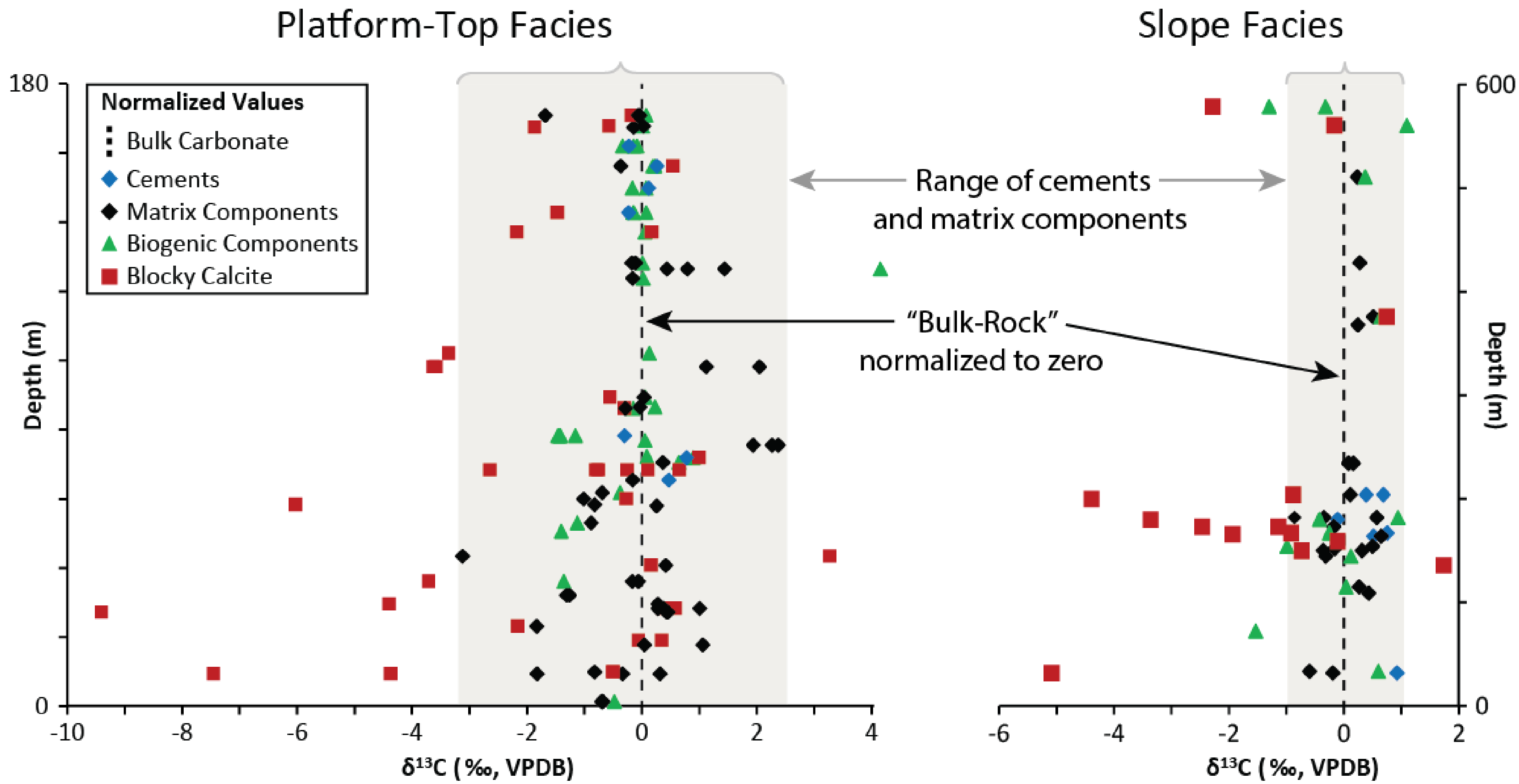


Figure 1.6: Microdrilled carbonate components normalized to their respective (coeval) bulk-rock values. Shaded grey areas show the range of deviation from bulk-values for cements and other matrix components. Effectively, these ranges represent confidence intervals and thus provide a baseline for making robust correlations.

Matrix Components

Inorganic matrix components (micritic sediments, microcrystalline cements, non-skeletal grains, syntaxial overgrowths, stylolites, and fenestrae) are variably preserved and exhibit significantly different isotopic distributions depending on the environment of deposition (Figure 1.5). In slope sediments, matrix components are typically well-cemented and exhibit dull background luminescence, unless they are in close proximity to fractures or stylolites. In such cases, matrix components may exhibit moderate or bright luminescence. Isotopic values of matrix components in slope facies, which range from +0.5 to +4.3 ‰ for carbon and -3.6 to -7.6 ‰ for oxygen, are consistent with published Devonian data for similar matrix elements (Kerans, 1985; Veizer et al., 1986; da Silva and Boulvain, 2008). No systematic variation in isotope values was observed with regard to chemical and textural preservation (luminescence). In platform-top facies, the matrix components exhibit the largest spread in carbon (between +2.7 and -7.1 ‰) and oxygen (between -2.3 and -9.9 ‰) isotope values. Within this distribution, six groups were characterized primarily based on lithology (calcite vs. dolomite) and cathodoluminescence, and to a lesser degree, isotopic values (Figure 1.7, Table 1.3).

Blocky Calcite Cements

Blocky calcite cements are observed in both slope- and platform-top facies but are relatively more abundant in the latter. Petrographically, different generations of blocky calcite are almost indistinguishable, but in isotope cross-plot space and when viewed under CL, five groups of blocky calcite can be distinguished (Figure 1.8). Of these, all occur in slope facies and at least four in platform-top facies. These are (I) non-luminescent blocky calcite type I, (II) non-luminescent blocky calcite type II, (III) moderate-brightly luminescent blocky calcite,

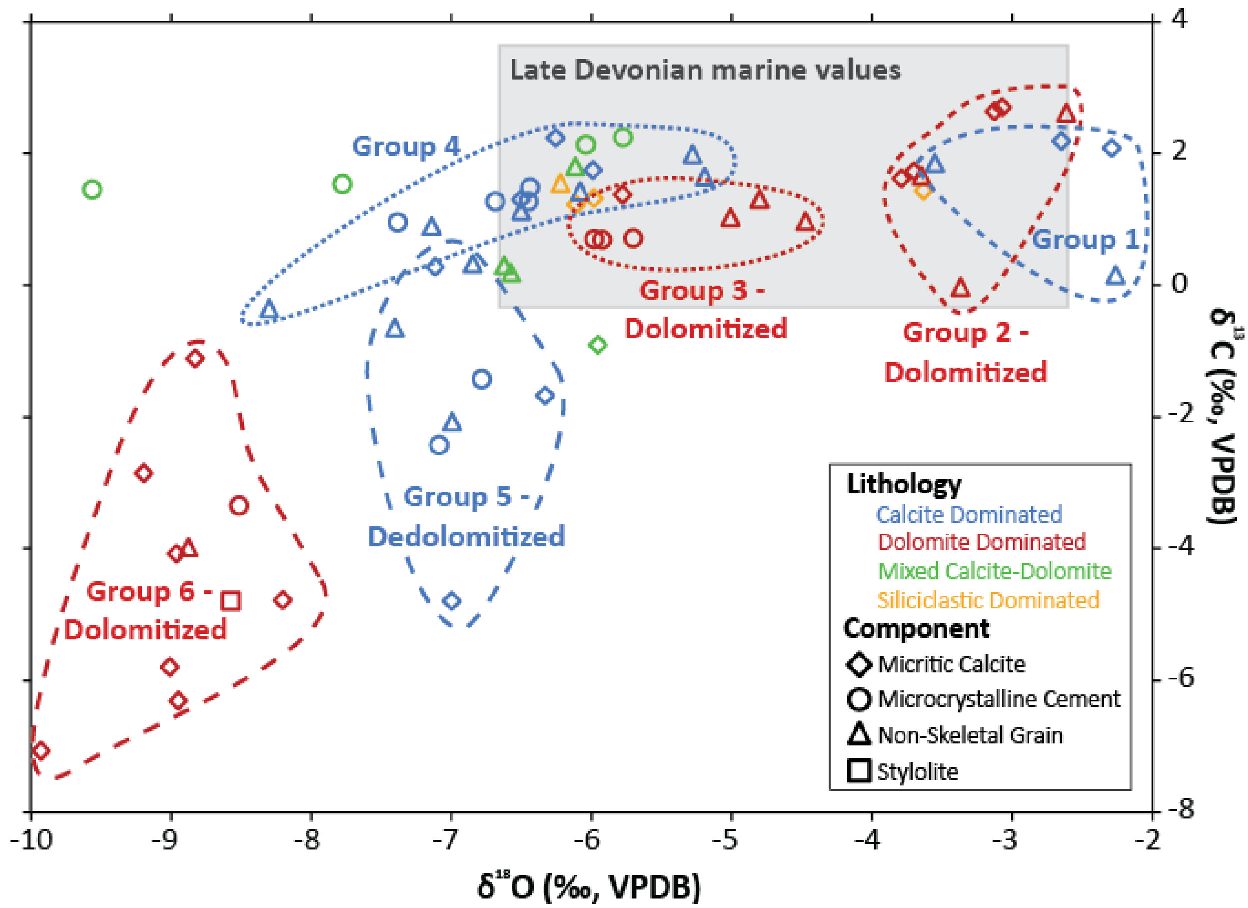


Figure 1.7: Isotope cross-plot of microdrilled platform-top matrix components. Groupings are based primarily on lithology (calcite or dolomite) and cathodoluminescence. Specific details about these different groups can be found in Table 4. The grey box, which is also in Figure 1.8, illustrates the previously reported range of values for well-preserved, Late Devonian marine cements from the Lennard Shelf, Western Australia (Kerans 1985).

Table 1.3: Petrographic characteristics and isotopic data for the six groups of platform-top matrix components seen in Figure 1.7.

Platform-top Matrix	Dominant Mineralogy	Cathodo-luminescence	$\delta^{13}C_{carb}$ (‰)			$\delta^{18}O_{carb}$ (‰)		
			Avg.	**Stdev.**	**Range**	**Avg.**	**Stdev.**	**Range**
Group 1	Calcite	Non-Dull	+1.6	1.0	+1.0 to +2.2	-2.7	0.6	-3.6 to -2.3
Group 2	Dolomite	Non-Dull	+1.8	1.0	-0.3 to +2.7	-3.3	0.4	-3.8 to -2.6
Group 3	Dolomite	Dull-Bright	+1.0	0.3	+0.7 to +1.4	-5.4	0.6	-6.0 to -4.5
Group 4	Calcite	Moderate-Bright	+1.3	0.6	-0.3 to +2.2	-6.5	0.8	-8.3 to -5.2
Group 5	Calcite (with dedolomite)	Non-Bright	-1.6	1.6	-4.8 to -0.3	-6.8	0.4	-7.1 to -5.9
Group 6	Dolomite	Non-Dull	-4.4	1.7	-7.1 to -1.1	-8.9	0.5	-9.9 to -8.2

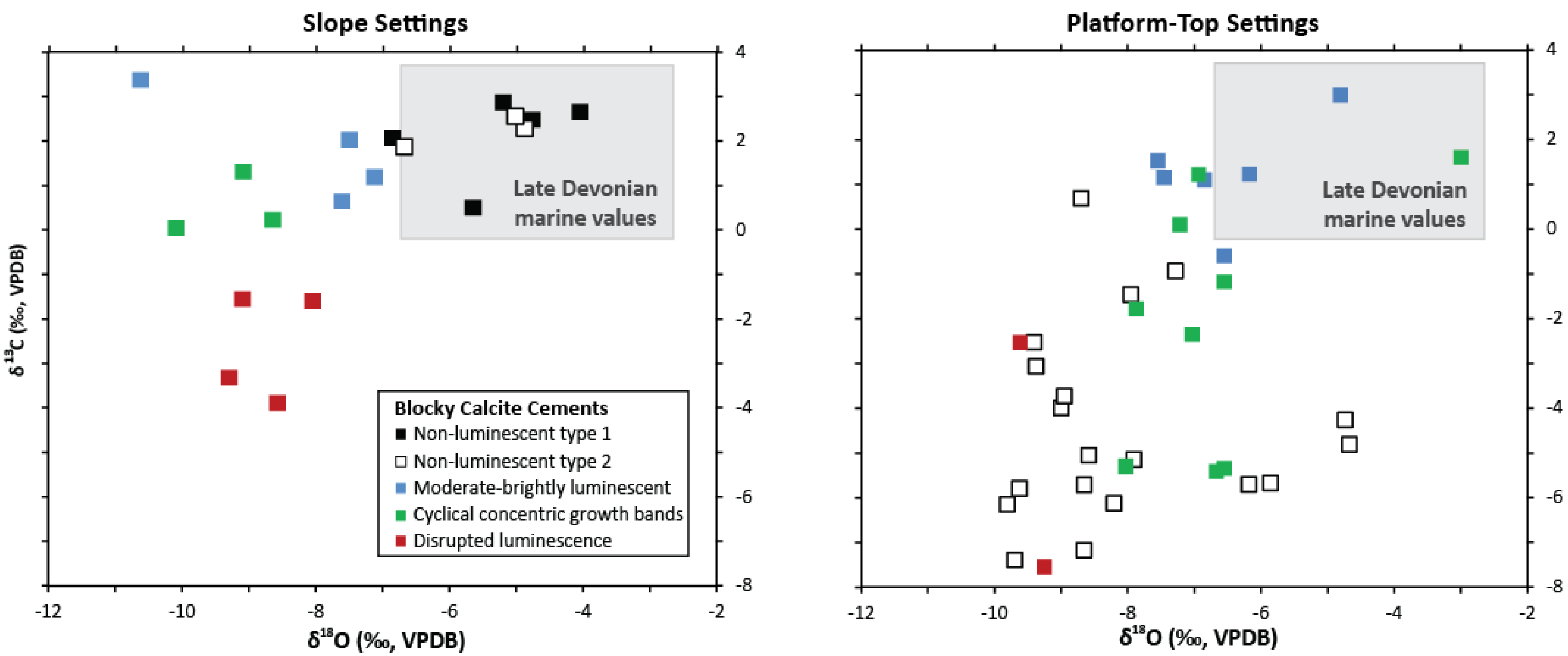


Figure 1.8: Isotope cross-plots of data from microdrilled samples for various generations of blocky calcite cement in slope and platform-top settings.

(IV) blocky calcite with thin, cyclical, brightly luminescent concentric growth zones herein referred to as banded blocky calcite, and (V) blocky calcite with a disrupted luminescence. None of the blocky calcite sampled was determined to be ferroan (based on staining).

Of particular interest to this study was the identification of two generations of clear, nonferroan, non-luminescent blocky calcite (types I and II). Data from microdrilled samples for these two generations exhibit positive isotopic values comparable to that of Devonian sea water (Figure 1.8). While blocky calcite type II primarily fills in cavities and fractures that cross-cut primary depositional fabric, type I occludes inter-granular porosity (Figure 1.4C) and is commonly cross-cut by later veins, fractures, and stylolites. No compaction or deformation is observed between grains that have been cemented by blocky calcite type I and grain-to-grain contact is minimal. The moderately to brightly luminescent, banded, and disrupted varieties of blocky calcite (types III – V) tend to have more negative carbon and oxygen isotope values than the non-luminescent blocky calcite varieties (Figure 1.8) and occur almost exclusively in cavities and fractures. On average, the $\delta^{13}C$ values of these generations deviate substantially from their respective bulk-rock analyses (Figure 1.6). Mean average values for all blocky calcite groups can be found in Table 1.4.

Trends in the Microdrilled Sample Data

In microdrilled samples from both platform-top and slope facies, $\delta^{13}C$ and $\delta^{18}O$ values delineate a similar concave, downward-curving trend (Figure 1.5), also known in the literature as an "inverted J-curve” (Lohmann, 1982). However, the distribution of the various components that compose the curve is different for each depositional setting. In slope facies, biogenic and matrix components as well as fibrous cements plot solely in the positive portion of the trend,

Table 1.4: Carbon and oxygen isotope data (average values, standard deviations, and observed ranges) for microdrilled carbonate components by depositional setting. N/A=only 1 sample was drilled.

Microdrilled Carbonate Componants	Slope Settings						Platform Settings					
	$\delta^{13}C_{carb}$ (‰)			$\delta^{18}O_{carb}$ (‰)			$\delta^{13}C_{carb}$ (‰)			$\delta^{18}O_{carb}$ (‰)		
	Avg.	Stdev.	Range	Avg.	Stdev.	Range	Avg.	Stdev.	Range	Avg.	Stdev.	Range
Biogenic Components												
Echinoerms	+2.5	0.9	+1.0 to +4.0	-4.8	1.1	-6.9 to -3.6	+2.1	N/A	+2.1	-4.5	N/A	-4.5
Brachiopods	+1.5	0.5	+1.2 to +1.9	-5.0	0.9	-4.4 to -5.7	+1.0	0.9	-0.5 to +2.4	-6.9	1.4	-5.1 to -9.4
Actinostroma	+1.7	0.7	+1.0 to +2.8	-5.1	1.3	-6.6 to -3.7	+1.7	0.2	+1.5 to +1.9	-5.5	0.6	-4.8 to -6.3
Stachyodes	+2.8	0.4	+2.6 to +3.1	-5.6	0.4	-5.9 to -5.3	+1.2	0.3	+1.0 to +1.6	-6.5	0.3	-6.3 to -7.0
Amphipora	-	-	-	-	-	-	+1.2	1.1	-1.1 to +2.9	-6.3	1.1	-4.7 to -8.3
Unknown Skeletal Fragments	+2.8	N/A	+2.8	-6.2	N/A	-6.2	-0.2	0.1	-0.2 to - 0.1	-6.9	0.1	-6.9 to -7.0
Marine Cements												
Fibrous Cements	+3.6	0.5	+3.1 to +4.2	-5.0	1.0	-6.1 to -3.7	+1.3	N/A	+1.3	-4.4	N/A	-4.4
Recrystalized Fibrous Cements	+2.8	N/A	+2.8	-7.2	N/A	-7.2	-	-	-	-	-	-
Isopachous Cements	-	-	-	-	-	-	+1.7	0.7	+0.9 to +2.8	-6	1.6	-4.9 to -6.9
Matrix Components												
Micritic Calcite	+2.7	0.8	+1.6 to +4.3	-5.7	0.5	-7.6 to -4.8	-0.6	3.1	-7.1 to +2.7	-6.1	2.3	-2.3 to -9.9
Microcrystalline Cement	+2.1	0.4	+1.7 to +2.5	-5.7	0.5	-6.1 to -4.9	+0.5	1.7	-3.3 to +2.2	-6.9	1.1	-5.7 to -9.6
Non-Skeletal Grains	+2.4	1.5	+0.5 to +4.3	-5.4	0.5	-5.8 to -4.3	+0.6	1.5	-4.0 to +2.6	-5.6	1.8	-2.3 to -8.9
Syntaxial Overgrowths	+2.8	0.9	+1.9 to +3.7	-4.1	0.5	-4.6 to -3.6	-	-	-	-	-	-
Stylolites	-	-	-	-	-	-	-4.8	N/A	-4.8	-4.8	N/A	-8.6
Fenestrae	-	-	-	-	-	-	+2.1	N/A	+2.1	-4.4	N/A	-4.4
Blocly Calcites												
Non-Luminescent Type 1	+2.1	0.9	+0.5 to +2.9	-5.3	1.0	-6.8 to -4.0	-	-	-	-	-	-
Non-Luminescent Type 2	+2.3	0.3	+2.0 to +2.5	-5.5	1.0	-6.8 to -4.9	-4.4	2.2	-7.4 to +0.7	-8.1	1.6	-4.7 to -9.8
Moderate-Brightly Luminescer	+1.8	1.2	+0.6 to +3.4	-8.2	1.6	-10.6 to -7.1	+1.2	1.1	+3.0 to -0.6	-6.6	1.0	-4.8 to -7.5
Banded	+0.5	0.7	+0.1 to +1.3	-9.3	0.7	-10.1 to -8.6	-2.0	2.8	-5.4 to +1.6	-6.6	1.5	-3.0 to -8.0
Disrupted	-2.6	1.2	-3.9 to -1.6	-8.8	0.6	-9.3 to -8.1	-5.0	3.5	-7.6 to -2.5	-9.4	0.2	-9.3 to -9.6

whereas blocky calcites plot along the entire curve. Because blocky calcite is the only component that plots significantly outside the range of previously reported Devonian sea-water values, avoidance of blocky calcite during hand drilling of slope sediments will increase the likelihood that bulk-rock analyses will provide a close approximation of primary marine values. In platform-top facies, both the blocky calcites and the matrix components plot along the entire curve. This overlapping distribution of carbonate components in platform-top facies challenges the separation of primary marine isotope values from those that have been modified, particularly as it relates to targeted bulk-rock drilling.

Dolomitization

Dolomitization and the occurrence of dolomite crystals in the Lennard Shelf is almost exclusively restricted to platform-top environments (Hurley, 1986; Wallace et al., 1991), specifically back-reef and platform-interior facies. The degree of dolomitization decreases basinward such that middle- to lower-slope facies contain almost no dolomite. Both a replacement phase and a cementation phase of dolomitization are observed (Figure 1.4D-F), but we focus only on the former because it is volumetrically more abundant, relatively widespread (both stratigraphically and within individual platform-top samples), and primarily replaces finer-grained components within the matrix. The replacement dolomite occurs as isolated crystals, or as a pervasive mosaic of crystals, that are small in size (10-200 μm) and subhedral to anhedral in shape. Under cathodoluminescence, dolomite rhombs are either non luminescent or have an inner, non-to-dully luminescent core surrounded by a thin, brightly luminescent rim (Figure 1.4F). In some instances, two generations of replacement dolomite, each exhibiting a different cathodoluminescent pattern, exist within the same sample.

What is important to note is that replacement dolomitization does not predictably preserve or modify primary marine isotope values. In some instances, isotopic data from dolomitized samples are within Devonian sea-water estimates (Figure 1.7, Group 2), while in other cases, components are either relatively depleted in oxygen alone (Figure 1.7, Group 3) or are significantly reset for both carbon and oxygen (Figure 1.7, Group 6). Even when coupled with CL analysis, non- to dully-luminescent components within a dolomitized matrix record some of the highest (Figure 1.7, Group 2) and lowest (Figure 1.7, Group 6) isotopic values (Table 1.3). In general, non-to-dully luminescent components that maintain their original calcite mineralogy and have not been subjected to replacement dolomitization tend to preserve primary marine values (Figure 1.7, Group 1; Figure 1.5, slope facies matrix components). However, calcite recrystallization can variably modify both carbon and oxygen values (Figure 1.7, Groups 4 and 5). Upon petrographic inspection, it was discovered that the non-dolomitized matrix samples with the most negative $\delta^{13}C$ values (Figure 1.7, Groups 5) contain dedolomite, or calcite that originated from dolomite.

A potentially meaningful relationship was also observed between negative carbon isotope values, dolomitization, and reduced iron (Fe^{2+}). Petrographic inspection revealed an abundance of reduced iron (Fe^{2+}), in the form of pyrite (Figure 1.4D), only in platform sediments. Where pyrite was observed in thin section, replacement dolomite was always observed as well. The reverse was not always the case, i.e., where replacement dolomite was observed, pyrite was not always observed. However, in all samples lacking observable evidence for dolomitization (i.e. no dolomite crystals or crystal molds), pyrite was also not observed. Interestingly, dolomitized platform-top samples with negative carbon isotope values (Figure 1.7, group 6) almost always contained pyrite, while the dolomitized samples with positive isotope values (Figure 1.7, groups 2 and 3) only contained pyrite some of the time.

GUIDELINES FOR BULK-ROCK SAMPLING

The following section summarizes the pertinent diagenetic trends used as guidelines for bulk-rock drilling of samples without accompanying thin sections. Marine cements, micrite, and non-skeletal grains were preferentially targeted for bulk-rock sampling because 1) they are relatively well-distributed throughout all sections, allowing for a higher resolution isotope record compared to one derived primarily from skeletal material (i.e. brachiopods and echinoderms) that can be facies specific, 2) they commonly occur in close proximity to one another, minimizing the amount of unwanted material sampled as a result of the hand-drilling method, and 3) in slope facies, their (microdrilled) isotope values are similar to the proposed marine/eogenetic signature for the Upper Devonian (Hurley and Lohmann, 1989) and are consistent with Paleozoic sea-water values (Veizer et al. 1999).

Biogenic components were preferentially avoided during bulk-drilling because of their restricted distribution and observed recrystallization trends Figure 1.5). The recrystallization was diverse and not predictable within the context of this study; it was observed in multiple facies, in different depositional environments, and to various degrees even within a single sample. Blocky calcites (equant calcite cements) were also avoided because they commonly recorded diagenetic isotope values (Figure 1.7). Avoidance was easy in samples from platform-top facies because blocky calcites were present almost exclusively in fractures, cavities, and dissolved grains. In slope facies, however, blocky calcite was present not only in fractures and cavities, but also between grains and in interstitial spaces. The latter cases were difficult to differentiate during bulk-drilling.

BULK-ROCK ANALYSIS RESULTS

Upper Devonian carbonates from the Lennard shelf record both primary-marine and diagenetic bulk-rock $\delta^{13}C$ values. The latter notwithstanding, comparison of our microdrilled- and bulk-rock analyses verified the use of bulk-rock samples from the Lennard Shelf as proxies for marine seawater $\delta^{13}C$ values. Petrographic analysis coupled with isotopic cross-plots of bulk-rock values for carbon and oxygen revealed that the preservation of primary marine isotope values and thus the utility of chemostratigraphy as a stratigraphic correlation tool were dependent on the depositional environments within the Lennard Shelf, specifically the types of diagenetic processes experienced by each setting. To clearly illustrate the observed depositional controls, the bulk-rock isotope data have been divided into three depositional groups; platform-top, reef-flat to upper-slope, and middle- to lower-slope.

Platform-Top

Bulk-rock analyses of shallow-water sediments, specifically those from back-reef and platform interior facies, are not suitable for assessing the primary isotopic composition of seawater because of extensive alterations. An isotopic cross-plot of the bulk-rock data shows a large negative spread with respect to both carbon and oxygen values (Figure 1.9); a trend similar to the one observed in the microdrilled-sample dataset (Figure 1.5). Detailed measured sections through platform-top settings document multiple subaerial exposure surfaces, evidenced by dissolution cavities, tidal-flat facies, caliche, and karstified surfaces. Petrographic analysis reveals substantial dissolution and recrystallization, as well as an abundance of siliciclastics, dolomite rhombohedra, fractures, stylolites and blocky calcite cement (Figure 1.4D-F). Unsurprisingly, platform-top sections and related isotope profiles contain the highest percentage of isotopically altered values (Figure 1.10A, Table 1).

Upper Slope and Reef Flat

A facies specific overprint on isotopic values from upper-slope and reef-flat sediments challenges correlations in these settings (Figure 1.10A). While only ~20 % of the upper-slope and reef-flat data lie outside the range of previously accepted values for Devonian marine carbonates (Figure 1.9), ~85 % of these outliers are associated with encrusting microbial boundstone facies (Figure 1.4G-H). Within the boundstone deposits, a significant negative trend is present (relative to assumed marine values), but in carbon only, with bulk $\delta^{13}C$ values as low as -5.3 ‰. Similarly depleted $\delta^{13}C$ values associated with microbial carbonates have been observed in modern marine settings (Andres et al., 2006) as well as Devonian sections in Canada (J. Day, *personal communication*). Bulk-rock isotope values from upper-slope and reef-flat sediments that are not associated with microbial boundstone facies and are textually well-preserved exhibit $\delta^{13}C$ values that are comparable with interpreted primary marine values reported from Late Devonian carbonates in the Canning Basin (Kerans, 1985).

Lower- and Middle Slope

In lower- and middle-slope settings, where well preserved limestone is abundant and microbial boundstone less common, bulk-rock isotope data can be used to generate high-confidence carbon isotope profiles with robust and easily identifiable secular trends (Figure 1.10A). Thin sections reveal excellent preservation of original textures and an abundance of non-luminescing carbonate components (Figure 1.4A-C). An isotopic cross-plot of the bulk-rock data (Figure 1.9) shows no

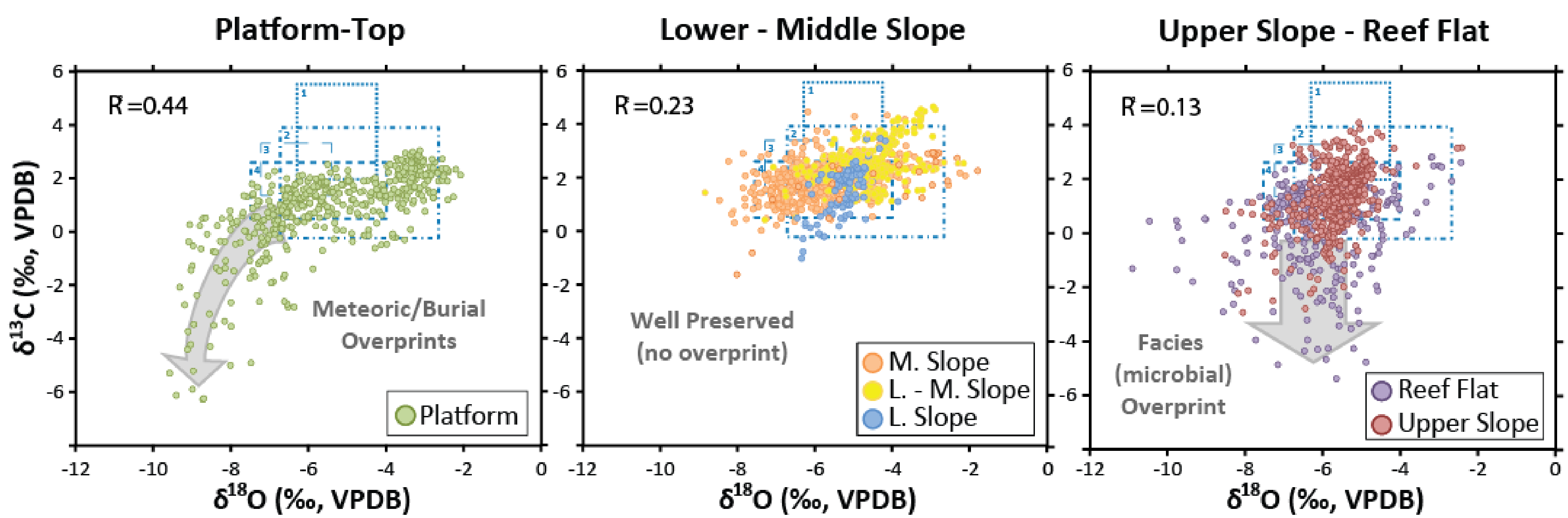


Figure 1.9: Isotope cross-plots representing bulk rock $\delta^{13}C$ and $\delta^{18}O$ values from different depositional environments. Dashed blue boxes show the range fields of previously measured Upper Devonian open-marine cements from Europe (box 1, Dunn et al. 1985), the Lennard Shelf in Western Australia (box 2, Kerans 1985; box 4, Hurley and Lohmann, 1989), and North America (box 3, Walls et al. 1979). Grey arrows highlight general trends in the data. Figure 1.10A shows how the observable trends in each depositional environment manifest in an isotopic profile.

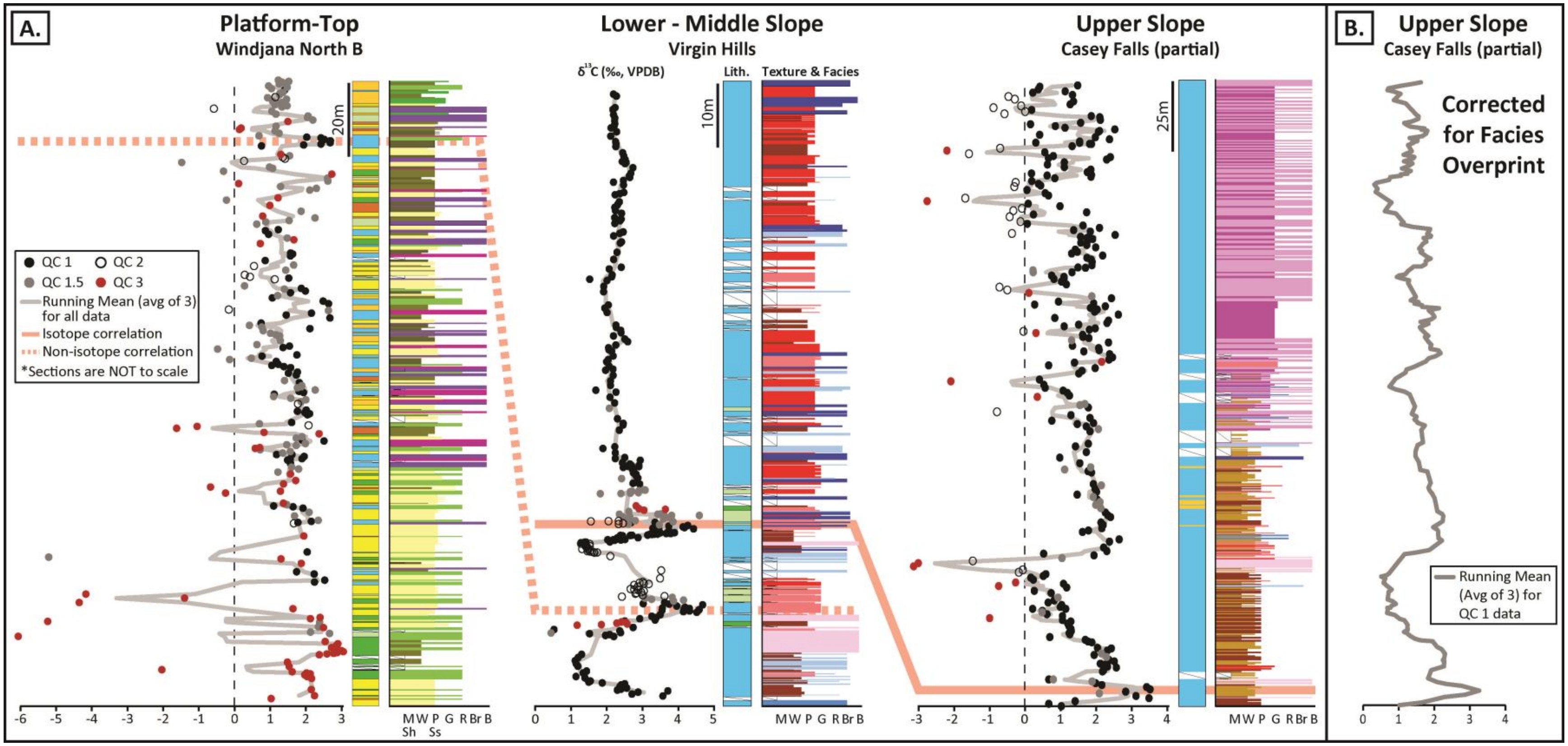


Figure 1.10: A. Representative bulk-rock isotope profiles for different depositional environments compared to their respective measured sections. Running means calculated using all data (quality control values 1-3). Note the relative isotopic noise and abundance of negative $\delta^{13}C$ values in the platform and upper-slope compared to the lower- and middle-slope. In the upper-slope, the more negative values are associated with microbial boundstones (light pink color in the texture and facie scheme). Correlations are constrained using conodont biostratigraphy and magnetostratigraphy. B. Upper-slope section from Casey Falls corrected for facies overprint. Running mean calculated using data with quality control values of 1.5 or better.

clear statistical covariance between carbon and oxygen (R^2= 0.23) and lacks other trends typically associated with significant diagenetic alteration (Hurley and Lohmann, 1989). The majority of our lower- and middle-slope data are within the range of estimates for well-preserved Devonian carbonate components believed to be precipitated in equilibrium with seawater as shown in Figure 1.9 (Dunn et al., 1985; Kerans, 1985; Hurley and Lohmann, 1989).

DISCRIMINATIVE CRITERIA (Table 1.2)

Below, we summarize the six discriminative criteria used for separating out primary marine isotope values in our large bulk-rock dataset.

Criterion #1: Instrumental Standard Deviation

The instrumental standard deviation associated with each carbon isotope value, as opposed to the standard deviation of replicate carbon analyses, was the first criterion used to assess preservation potential. Data with instrumental standard deviations ≥0.1 were assigned a QC value of 3 because high values represent instrument instability and/or other analytical abnormalities during a given sample measurement. This criterion is not dependent on local controls and can therefore be applied to any study.

Criterion #2: Lithology/Mineralogy

Samples with a predominantly calcite mineralogy, as determined from thin section or hand sample analysis, were initially given a QC value of 1 because well-preserved calcite has a high probability of preserving original isotopic signatures (Machel and Mountjoy, 1986; Holser, 1997). For platform-top data, lithology was not consistently helpful as a discriminative criterion because both calcite- and dolomite-dominated samples recorded primary marine values as well as modified values. Samples subjected to dolomitization were assigned higher QC values (2 or 3) because isotopic values associated with dolomite were unpredictably reset (Figure 1.7).

Criterion #3: Bulk-Rock Constituents

Petrographic analysis was used to identify carbonate constituents that revealed a pattern or tendency towards preservation or alteration that could, in turn, be used as a predictive tool. For example, an abundance of marine cement, micrite, and/or non-skeletal grains was used as an indicator (during hand sample analysis) of potentially unaltered samples because non-biogenic components generally recorded marine-like isotope values (Figure 1.5). Despite the observed recrystallization trends, samples dominated by skeletal material were ranked as a 1.5 because the biogenic components were preferentially avoided during bulk-drilling and were commonly associated with abundant fibrous cements and/or matrix components.

The presence of blocky calcite was used to assign a QC value of 3 because where we observed abundant amounts in hand samples (specifically in cavities and fractures), bulk-rock values deviated substantially from their respective microdrilled components and showed a range of isotopically reset values for different generations (Figure 1.6). Unfortunately for the majority of samples, we were unable to use the occurrence of blocky calcite type 1 to identify potentially preserved material because we were unable to differentiate it from the other types of blocky calcite without CL analysis. The occurrence of pyrite was used as conservative discriminative criterion, specifically in platform-top sediments, because it removed all negative $\delta^{13}C$ values and only some positive $\delta^{13}C$ values associated with dolomitization. Depending on the size of the pyrite, however, this criterion was generally applicable only to samples with thin sections.

Criterion #4: Cathodoluminescence

Due to the nature of this study, discrimination based on CL character was applicable for a limited number of samples only, i.e. those with accompanying thin sections. In such cases, samples dominated by moderately or brightly luminescent components were ranked as a 3 because they tended to record more negative isotopic values consistent with meteoric and/or burial diagenesis.

Criterion #5: $\delta^{13}C$ Values

The facies-dependent overprint observed in upper-slope- and reef-flat settings was used initially to develop criterion #5 in the QC process; $\delta^{13}C$ values less than 0 ‰ and associated with microbial boundstone facies were assigned a higher QC value because of their observed tendency for recording isotopic depletion (Figure 1.9). Previously reported range estimates of marine cements, brachiopods, and matrix components from well-preserved Devonian sections (Walls et al., 1979; Dunn et al., 1985; Kerans, 1985; Hurley and Lohmann, 1989), were additionally implemented as a more robust guide for distinguishing primary-marine values; data that fell outside of these reported ranges, generally in the negative direction, were interpreted to have been modified, to some degree, by diagenetic processes. One exception to this criterion was made for negative $\delta^{13}C$ values associated with exposure surfaces. These data are not interpreted to reflect primary marine values, but, they receive a QC value of 1.5 because they're potentially useful for regional scale correlations and remain useful in that respect.

Criterion #6: $\delta^{18}O$ Values

Similar to criterion #5, previously reported $\delta^{18}O$ values (-6.7 to -2.7 ‰) of Late Devonian marine cements from the Canning Basin (Kerans, 1985), were used as a guide for interpreting alteration. We were able to better constrain this -6.7 ‰ cut-off value based on the isotopic results of the microdrilled samples; given that almost all $\delta^{18}O$ values of matrix components and fibrous-cements from well-preserved middle- and lower slope facies are ≥ -6.0 ‰ (Figure 1.5), bulk-rock $\delta^{18}O$ values less than this are interpreted to reflect diagenetic modification. As such, this lower limit for oxygen was used as culling criterion; specifically, $\delta^{18}O$ values ≥ -6.0 ‰ in the bulk-rock data were given a QC value of 1, while $\delta^{18}O$ values ≤ -6.0 ‰ were assigned a higher value (2 or 3).

APPLICATION AND RESULTS OF THE QC WORKFLOW

Our quality control workflow ranked about 70% of the bulk-rock analyses as either a 1 or 1.5 on the QC scale (Table 1.1); these interpreted primary marine values were used to construct isotopic profiles for each measured section. The remaining ~30% (the QC 2 and 3 data) were predicted to reflect some degree of isotopic alteration and subsequently removed from the dataset. The QC process is not without limitations, however; some diagenetically altered samples inevitably made it through the selectin process while some well-preserved samples were removed. Due to the occurrence of dedolomite in calcite-dominated hand samples, some dedolomitized samples recording altered $\delta^{13}C$ values were likely classified as QC 1 (well-preserved) data inadvertently. Without making a thin section of all the samples designated as having a calcite lithology, we cannot ensure that all dedolomitized/recrystallized samples will be removed from the dataset during the QC process. As a result, secular curves produced from the QC data may exhibit some negative noise (e.g. Figure 1.10A). Conversely, some samples recording primary marine isotope values were wrongfully excluded during the QC process, such as those containing the seemingly unaltered (isotopically) generation of dolomite (Figure 1.7, Group 2) or blocky calcite (Figure 1.8, type 1). In instances when well-preserved samples were mistakenly assigned higher QC values (2 and 3) and removed from the dataset, isotopic profiles constructed from the remaining data do not appear to be significantly affected, likely as a result of our high sampling density.

While this process is not without error, the QC approach was successful when applied to samples from reef-margin- and slope facies (Figure 1.11). In these settings, where stratigraphic stacking patterns are less understood than the shallow water platform, and depositional heterogeneity hinders our ability to recognize and correlate systems tracts, quality controlled bulk-rock isotope data proved to be useful for making regional correlations and building an integrated chronostratigraphic framework for Lennard Shelf carbonates that correlates ~16 million years of stratigraphy, along 200 km of outcrop, and across depositional environments (Figure 1.12). In upper-slope and reef-flat sediments in particular, the QC workflow removed negative $\delta^{13}C$ values associated with microbial boundstone facies (Figure 1.10A) which allowed secular trends to be better exposed (Figure 1.10B).

The best constrained tie-points for the correlation framework are derived from three large (average amplitude of +2 to +3 ‰), positive carbon isotope excursions observed in slope sections (Figure 1.12). Isotope excursion 1 is observed in three measured sections and is biostratigraphically constrained within conodont Zones 6 and 11. Isotope excursion 2 is identifiable in at least four, possibly five, sections, and is biostratigraphically constrained within Zones 12 and 13A (Montagne Noire conodont zonation, Klapper, 1989; Girard et al., 2005). Isotope excursion 3 occurs in seven sections and is present within Zones 13B and 13C. The latter two excursions (2 and 3) have also been recognized previously in coeval Lennard Shelf sections (Joachimski et al., 2002; Stephens and Sumner, 2003; George et al., 2014).

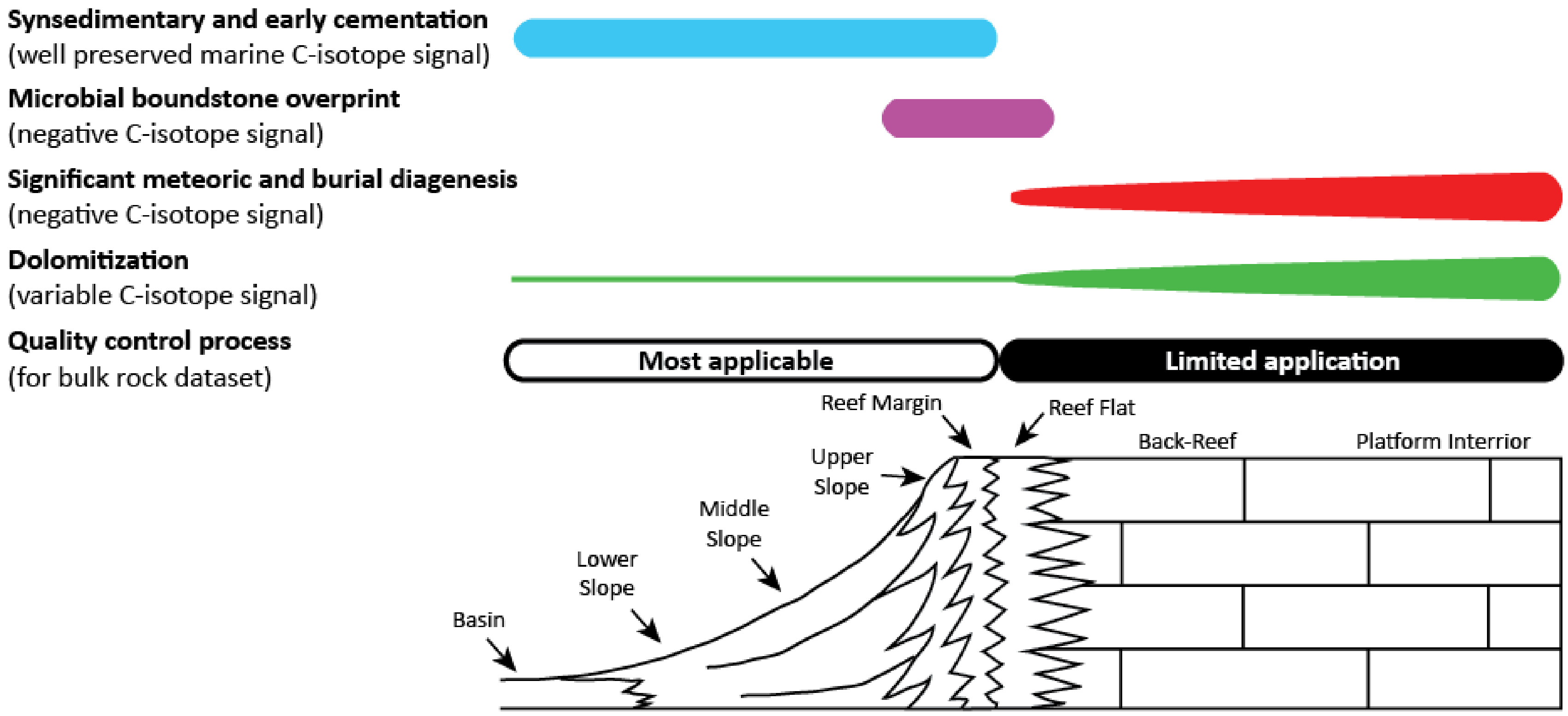
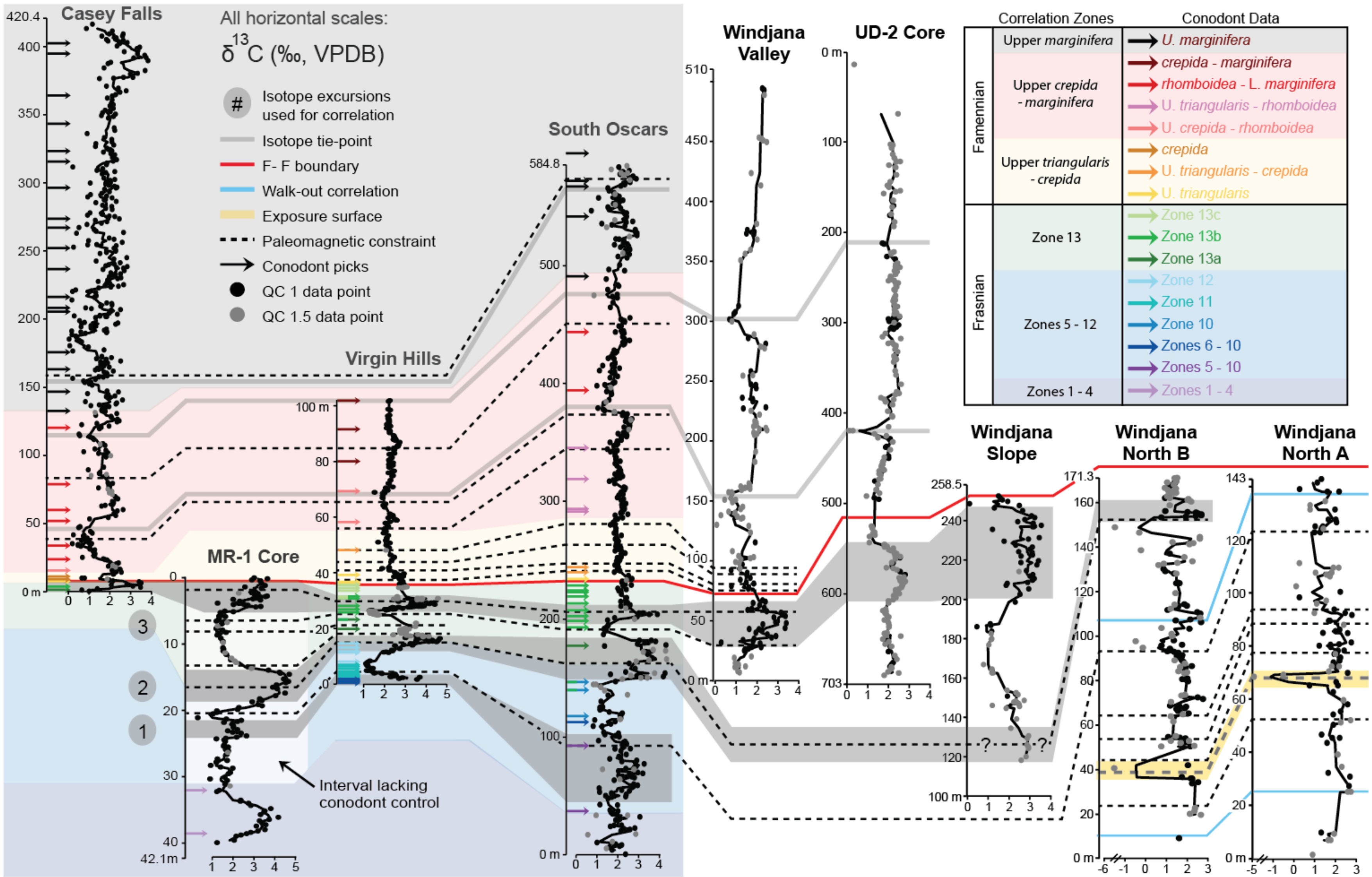


Figure 1.11: Summary diagram showing the distribution of depositional controls that influence the preservation of primary marine carbon isotope values. Applicability of the quality control process is also provided for each depositional environment.



See figure caption on next page.

Figure 1.12: Chemostratigraphic framework for Lennard Shelf carbonates showing the integration of bulk-rock isotope data (QC values ≤ 1.5) with conodont biostratigraphy (Roelofs et al., 2015) and paleomagnetic constraints (Hansma et al., 2015). Isotopic profiles are arranged by depositional environment such that water-depth shallows to the right. Conodont data were used to create correlation biozones, but uncertainty exists in their upper and lower limits.

Three additional isotopic tie-points, all of which are corroborated by the integrated datasets, are defined using negative trends in the bulk-rock secular curves. These isotopic excursions and tie-points are especially useful in areas lacking other constraints, such as the Windjana Valley transect and the UD-2 core, as they allow for the correlation of sections that may not have been incorporated into the framework otherwise.

Although the scope of this study is not global in nature, the $\delta^{13}C$ trends documented in this study are similar to- and correlative with carbon isotope excursions reported from sections throughout Europe and North America (Joachimski and Buggisch, 1993; Joachimski et al., 2002; Buggisch and Joachimski, 2006; Yans et al., 2007; Morrow et al., 2009; Śliwiński et al., 2011); at least two positive shifts, and possibly as many as five, can be recognized, including the two associated with the Upper and Lower Kellwasser horizons and related extinction events in Europe which are attributed to organic carbon burial (Figure 1.13). As such, these secular variations can be used as proxies for global oceanic changes in the inorganic carbon-pool as well as for regional, and eventually global, chronostratigraphic correlation as long as discriminate standards are followed.

The quality control process developed in this study has, however, proven unsuccessful for correcting the diagenetic overprints observed in platform-top facies. Targeted bulk-rock drilling was not always fruitful in these settings because individual components were variably

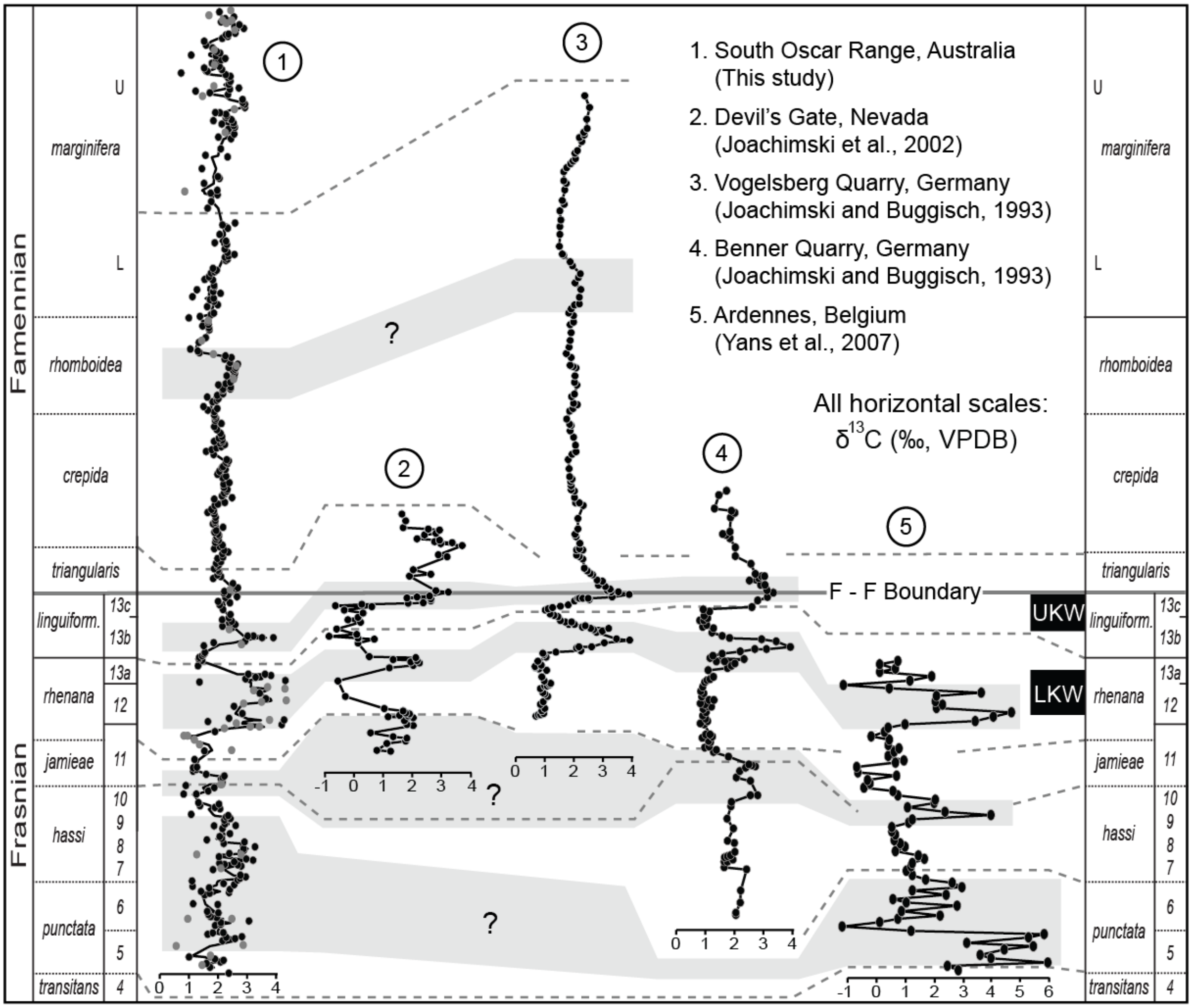


Figure 1.13: Comparison of quality controlled bulk-rock isotope data (South Oscar section, this study) with Upper Devonian $\delta^{13}C$ profiles from Europe and North America. Grey shaded bars highlight excursions of similar age (based on available conodont biostratigraphy from each study).

recrystallized and isotopically reset in an unpredictable manner. Although blocky calcites were preferentially avoided, platform-top bulk-rock isotope data contain an abundance of isotopically reset values (Figures 1.9 and 1.10A). Despite the removal of QC 2 and 3 data, recognition of secular trends in platform-top facies remains hindered by considerable scatter as well as by numerous negative excursions delineated by only one or two data points (Figure 1.10A).

However, correlations within the platform-top are still possible using the isotopically compromised data, albeit on a local scale only, if the tie-points are negative excursions of similar magnitude that co-occur within an interval of meteoric exposure. One such correlation was made between two of our transects across Frasnian platform-top facies; both sections exhibit a large negative excursion in $\delta^{13}C$ values (7 ‰ negative excursion to -5 ‰ average values) that co-varies with a negative excursion of similar magnitude in the $\delta^{18}O$ values. While the negative carbon and oxygen excursions used as isotopic pinning-points do not reflect primary marine values, their correlation was supported by the paleomagnetic data, and to a lesser extent, a ground-truthed, walk-out outcrop correlation. Future work attempting to improve correlations in similar, diagenetically-unpredictable settings are encouraged to analyze samples using traditional, detailed methods, i.e. all samples should be thin sectioned, screened for diagenetic alteration, and then microdrilled.

Some caution should be taken when interpreting isotope excursions and secular trends in processed isotope data. Determination of which isotope excursions and secular trends are robust enough for correlation can be established by comparing the microdrilled isotope data to the respective bulk-data (Figure 1.6). For example, $\delta^{13}C$ values for the inorganically precipitated components (excluding blocky calcites) from slope facies show the least variation from bulk-rock values; on average less than +0.8 ‰. On the contrary, similar inorganic components derived from platform-top facies deviate from bulk-rock values by variable amounts, with matrix components deviating by as much as 3 ‰. We suggest then that bulk-rock isotope excursions and secular trends with a magnitude greater than +0.8 ‰ (± 0.2 ‰) are reliable for correlation, while excursions and trends with a magnitude less than +0.8 ‰ (± 0.2 ‰) are unreliable. In platform-top facies, we considered bulk-rock isotope excursions and secular trends with a magnitude less than +3 ‰ (± 0.5 ‰) unreliable for correlation, and thus we made almost no isotopic correlations between platform sections.

DISCUSSION

Meteoric and Burial Diagenesis of Platform-Top Facies

In general, bulk-rock and microdrilled samples from the platform-top tend to have more negative $\delta^{13}C$ values than samples from contemporaneous, deeper-water sediments (Table 1.3, Figure 1.11). Similar patterns have been documented in both modern (Lloyd, 1964) and Paleozoic sediments (Holmden et al., 1998; Immenhauser et al., 2002; da Silva and Boulvain, 2008) and are commonly attributed to the long residence time of water in restricted platform-top settings (Patterson and Walter, 1994), mixing of meteoric fluids or terrestrial runoff depleted in ^{13}C (Immenhauser et al., 2003; Panchuk et al., 2006), or various post-depositional diagenetic events. While all of these hypotheses are plausible, water mass "aging" atop the narrow shelf setting seems to be the least likely as the Canning Basin had open circulation with seawater during the Devonian period (Carpenter et al., 1991), and negative carbon isotope values are recorded in both restricted and non-restricted platform-top facies. Diagenetic alteration via fluid-rock interactions (such as those commonly associated with meteoric and burial environments) is a more probable mechanism for isotopic resetting in light of the isotopic analyses from this study and results from previous work on Lennard Shelf carbonates (Hurley and Lohmann, 1989; Wallace et al., 1991). The susceptibility of platform-top sediments to diagenetic alteration is likely due to platform-top facies having (1) a high susceptibility to subaerial and thus meteoric exposure, and (2) relatively higher porosities and permeability than well-cemented slope facies in the Lennard Shelf, which provide pathways for fluid migration and increase potential reactive surface area (Bishop, 2008).

Isotopic correlations in platform-top sections have often been hindered by the effects of syn- and/or post-depositional diagenesis (Holmden et al., 1998; da Silva and Boulvain, 2008), but some studies have found success in extracting and correlating what are believed to be marine isotopic signatures from platform-top facies. In the Lennard Shelf system, Stephens and Sumner (2003) regionally correlated isotopic profiles, using positive excursions, measured from back-reef facies with coeval deeper water sections. In the Ardennes (Belgium), isotopic analyses of shallow shelf carbonates (bank through reef facies) allowed for the recognition of a large positive $\delta^{13}C$ excursion that permitted correlations on a more global scale to sections in the Czech Republic, Poland, and China (Yans et al., 2007) To minimize the diagenetic overprints that are common in platform-top environments, these previous studies thin sectioned and petrographically screened all samples and then either microdrilled individual components from each sample, or used a combination of microdrilled and bulk-rock analyses. It is also possible that the sections measured in these earlier studies are better preserved than those in our study.

Dolomitization of Platform-Top Facies

Isotopic analysis of platform-top matrix components reveals that samples were subjected to at least two post-depositional diagenetic events; dolomitization and a later phase of recrystallization that resulted in dedolomitization of some platform sediments. This is consistent with the burial history of the Lennard Shelf presented by (Wallace et al., 1991). The occurrence of dolomitized platform samples with marine-like carbon isotope ratios suggests that the early phase of dolomitization did not significantly affect primary marine $\delta^{13}C$ values. Findings by (Land, 1980) and (Tucker, 2001), support that dolomitization associated with burial tends to leave carbon isotope ratios unaltered. Moreover, similarly high $\delta^{13}C$ values have been reported from dolomites in other localities along the Lennard shelf (Wallace, 1990) and in the southern part of the Canning Basin (Kerans, 1985; Wallace et al., 1991). However, it is unclear why some of the samples were more susceptible to later diagenetic events than others (i.e. why some of the dolomitized samples preserve marine-like $\delta^{13}C$ values while others record negative $\delta^{13}C$ values).

Permeability (Kerans, 1985) and crystal/grain size (Bullen and Sibley, 1984) have been suggested as controlling factors for dolomitization. The presence of iron (Fe^{2+}) may also be a key component or a companion to dolomite formation, at least in the Canning Basin carbonate system. Previous studies have suggested that the presence of reduced iron has a catalytic effect on the precipitation of dolomite (Carpenter, 1980; Gaines, 1980; Morrow, 1982). More recently, organic matter degradation by sulfate-reducing bacteria has been shown to promote dolomite precipitation which results in the precipitation of pyrite and the release of iron to the pore water by reduction of Fe oxides (Compton, 1992). This most recent hypothesis may best explain the observed trends in the isotope values of the dolomitized samples. Effectively, primary marine carbon values may have initially been preserved in all dolomitized samples due to a decrease in porosity (associated with the replacement dolomite) which made samples less susceptible to even later diagenetic fluids. In samples containing abundant iron, organic degradation by sulfate-reducing bacteria could account for the pyrite formation and concomitant decrease in $\delta^{13}C$ values due to the addition of isotopically light carbon from the organic material.

Microbial Influence on Reef-Flat and Upper-Slope Facies

The negative fractionation (up to -5 ‰) observed in the microbial encrusted boundstone facies from reef-flat and upper- slope settings suggests that these facies are either more prone to meteoric alteration than other facies, or that this is a primary facies derived signal in which calcite was precipitated out of equilibrium with seawater due to a preferential incorporation of ^{12}C into microbial boundstone. It is unlikely that the observed negative values are simply due to the decay of organic carbon during burial because 1) the isotopic depletion is facies specific, 2) our samples, as well as typical Upper Devonian slope sediments from the Lennard Shelf (Playford et al., 2009), contain very little organic material, and 3) microbial boundstones are cemented very early, most of them synsedimentary, and the fibrous and microcrystalline cements observed in thin section appear to be pristinely preserved (e.g. Figure 1.4G and H).

In consideration of the petrography and isotopic results, a facies overprint due primarily to microbial activity seems most plausible for the upper-slope encrusted boundstone facies as there is little evidence of alteration by meteoric fluids with low $\delta^{13}C$ values; the boundstone facies are textually and chemically (based on cathodoluminescence) well-preserved and show no evidence for subaerial exposure or meteoric dissolution. Considering the $\delta^{18}O$ values, encrusted boundstone facies in the upper-slope are more positive than those in the reef-flat and fall within the published range of well-preserved carbonate components from similar aged sections elsewhere in the world (Figure 1.9). In the reef-flat, $\delta^{18}O$ values of microbial boundstone samples are highly heterogeneous. Given that reef-flat settings are relatively proximate to the shoreline, especially in the narrow Lennard Shelf setting, and typically experience shallower water depths than upper-slope settings, a combination of meteoric diagenesis and microbial activity likely influenced the isotopic evolution of reef-flat carbonates.

Isotopic studies on modern microbes may provide an explanation for the depleted $\delta^{13}C$ values observed in the microbial encrusted boundstone facies of Lennard Shelf carbonates. Andres et al., (2006), sampled modern stromatolites in the Bahamas and found that the microbial carbonates were 1 to 2‰ more negative than the surrounding sediments. The authors attributed the isotopic depletion to rapid respiration rates, arguing that the microbes created a localized dissolved inorganic carbon (DIC) pool separate from the marine DIC pool. Unlike the modern stromatolites which impart a -1 to -2‰ fractionation effect, the magnitude of isotopic depletion for carbon is highly variable in the Devonian-aged microbial carbonates from the Lennard Shelf. This variability has many possible causes, including but not limited to variations in seasonal temperature, ocean chemistry (specifically pH and CO_3^{2-}), carbonate precipitation rate, photosynthesis rate, and metabolic processes (Sumner, 2001). It is also possible that the exchange of DIC between the surface of the stromatoporoid and the surrounding seawater occurs at an inconsistent rate, resulting in a variable effect of the local microbial-made DIC pool. Alternatively, negative $\delta^{13}C$ values of the microbial carbonates may have been dampened to various degrees during the drilling process, due to sample mixing with cements and other components that typically have more positive $\delta^{13}C$ values. It remains unclear which factor or combination of factors is responsible for the observed negative $\delta^{13}C$ values in the microbial carbonates.

Elsewhere in the world, microbial carbonates have been shown to induce significant negative shifts in carbon isotope ratios, up to 5 or 6‰, relative to assumed marine values in the whole-rock carbonates (J. Day, *personal communication*). In these Middle Devonian aged sediments in Alberta, Canada, intervals of isotopic depletion were associated with deep-water, anaerobic microbial carbonates. In the Lennard Shelf system, microbial-dominated facies in deep water settings (lower- and middle-slope) do not appear to exhibit the facies overprint that is common in upper-slope and reef-flat settings (Figure 1.10A). This suggests that the microbes living in shallower water depths, at least in Lennard Shelf system, fractionate carbon differently than the microbes living in relatively deeper water further down the slope. If we assume this to be true, then the fractionation effect is a function of water depth, which in turn can be related to light availability and photosynthesis.

Increased Preservation of Isotope Values in Middle and Lower Slope Facies

Lower- and middle-slope facies have been interpreted to record primary marine isotope values useful for correlation (Figure 1.11). Previous isotopic studies on Lennard Shelf carbonates have reported similar findings for relatively deep-water facies (Stephens and Sumner, 2003; George et al., 2014), and have been successful in correlating those strata to Upper Devonian carbon isotope curves from Europe and North America (Joachimski et al., 2002). However, this is not always the case for similar aged sections elsewhere in the world. In Kazakhstan, for example, the carbonate slopes of the Tengiz platform system have been significantly modified by burial diagenesis in both near-surface and deep-burial environments (Collins et al., 2006). As a result, the slope deposits at Tengiz are highly fractured, partially dolomitized, and have been exposed to a variety of post-depositional fluids that have the potential to reset isotopic values.

The preservation of slope sediments from the Lennard Shelf, and subsequently the preservation of marine isotope values, is attributed, at least in part, to a synsedimentary phase of blocky calcite cement. Two generations of nonferroan, non-luminescent blocky calcite were identified in this study, however, previous work only recognized one phase of this cement and interpreted it as post-depositional; in the section present in Geikie Gorge, formation of the nonferroan, non-luminescent blocky calcite was attributed to meteoric waters (Wallace et al., 1991), while in the

South Oscar Range, formation was attributed to later burial fluids (Hurley and Lohmann, 1989). In our study, only one phase of the nonferroan, non-luminescent blocky calcite has been interpreted as post-depositional (Figure 1.8, type 2), the other (type 1) most likely precipitated early, in equilibrium with seawater rather than from later fluids, based on isotopic and petrographic analyses. This synsedimentary phase is of particular importance because it is abundant and acts to preclude primary porosity and permeability, in turn making slope facies less susceptible to later fluid migration and diagenetic process that might alter carbon isotope values.

CONCLUSIONS

To generate high-resolution carbon isotope profiles, useful for stratigraphic correlation, in a time- and cost-efficient manner, we developed an approach for quality control of bulk-rock data that allows for management of 1000s of samples. The approach is a set of discriminative criteria that enables separation of primary marine values from those that have been diagenetically compromised. This approach is applicable to- and serves both academic and industry purposes and has implications for use with core and cuttings since thin sections and component analysis are sometimes unavailable options.

Results from this study have shown that different depositional environments along the Lennard Shelf affect, to various degrees, the preservation of the global marine carbon isotope signal. Platform-top facies generally record diagenetic modification that is unpredictable, rendering the QC approach ineffective. An isotopic overprint on microbial encrusted boundstone in reef-flat- and upper-slope facies challenges stratigraphic correlations unless the bulk-rock data are corrected for the overprint. Bulk-rock samples from middle- and lower-slope settings were typically well-preserved and recorded primary marine isotope values; the increased preservation is at least in part due to a synsedimentary phase of blocky calcite cement.

The application of the QC workflow to data generated from reef-margin and slope settings has successfully produced isotopic profiles from the bulk-rock data which exhibit secular trends and excursions that are recognizable in multiple sections (both outcrop and core) along 200 km of discontinuous outcrop on the Lennard Shelf (Figure 1.12). These trends, which were used as correlation pinning-points for the construction of a chronostratigraphic framework, are certainly primary as they are recognized from transects representing various depositional settings and different paleogeographic environments and can be correlated to sections elsewhere in the world (Figure 1.13). This regional framework has global, chronostratigraphic implications (Hillbun et al., 2016) since secular variations in $\delta^{13}C$ values reflect changes in carbon cycling and ocean chemistry on a global scale (Magaritz, 1989; Kump and Arthur, 1999).

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CHAPTER II

Upper Kellwasser Carbon Isotope Excursion Pre-Dates the F-F Boundary in the Upper Devonian Lennard Shelf Carbonate System, Canning Basin, Western Australia

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ABSTRACT

Here we report four high-resolution carbon isotope records in addition to trace element data for the Frasnian-Famennian (F-F) boundary interval in the Lennard Shelf carbonate system of the Canning Basin, Western Australia. This region lacks the characteristic black shale horizons associated with the global Late Devonian Kellwasser extinction events, yet still exhibits a trend in carbon isotope character similar to what has been reported from elsewhere in the world (two positive $\delta^{13}C$ excursions with ~3-4‰ amplitudes). Enrichments in select trace element ratios suggest that both excursions are related to periods of oxygen deprivation and perhaps increased biological productivity. Given the continuous and stratigraphically expanded nature of Lennard Shelf sections, together with high density sampling constrained by both conodont biostratigraphy and magnetostratigraphy, we observe that the Upper Kellwasser isotope excursion (maximum $\delta^{13}C$ values) and associated trace element enrichments occur distinctly lower than the F-F boundary level. These results have implications for the paleoenvironmental conditions leading up to the Late Devonian Mass Extinction in terms of ocean chemistry and circulation patterns. This dataset allows for a rare, detailed look at the temporal relationship between the Kellwasser events and the F-F boundary and constrains the pattern of carbon isotope perturbations at the intra-zonal scale.

INTRODUCTION

The Late Devonian Mass Extinction (LDME) is recognized as one the five greatest biotic crises of the Phanerozoic (Sepkoski, 1986). Decades of research on numerous European localities has led to the understanding that there are actually two separate extinction pulses known as the Upper and Lower Kellwasser events in the *linguiformis* (or Montagne Noire Zones 13b and 13c of Klapper, 1989) and *rhenana* (Montagne Noire Zones 12 and 13a) conodont Zones, respectively, of the late Frasnian. These horizons are characterized by significant faunal turnover, positive carbon isotope excursions (average amplitude of about +3‰), and the deposition of black shales and bituminous limestones (e.g. McGhee, 1996), and are thought to reflect widespread anoxic conditions (Feist, 1985; Buggisch, 1991; Wendt and Belka, 1991; Hallam and Wignall, 1999) during pulses of sea level transgression (Johnson et al., 1985; Sandberg et al., 1988; Buggisch, 1991; Sandberg et al., 2002).

However, the timing of the carbon isotope excursion associated with the Upper Kellwasser deposits and extinctions in Europe (herein referred to as the Upper Kellwasser excursion) is not well constrained and the cause(s) poorly understood. The majority of Late Devonian geochemical studies document Upper Kellwasser excursion maxima at or slightly higher than the F-F boundary (e.g. Joachimski et al., 2002; Xu et al., 2003; Buggisch and Joachimski, 2006; George et al., 2014). As a result, they inadvertently lump the succession of related geo- and bio-events together and give the illusion that the Upper Kellwasser excursion and F-F boundary are time-equivalent. This can be particularly problematic when attempting to make chronostratigraphic correlations or to determine causal mechanisms.

Exacerbating these problems are the conflicting isotope records that have been reported for this time period, with some workers noting either the absence of isotopic excursions (Geldsetzer et al., 1987), or the occurrence of negative excursions (Wang et al., 1991;Goodfellow et al., 1988), or the absence of organic-rich deposits (e.g. Joachimski and Buggisch, 1993; Bond et al., 2004). These discrepancies have generated debate over the role of global anoxia as a potential kill mechanism. Paleo-redox data for this time interval are also contradictory: whereas the trace element analyses from most studies have given credence to oceanic anoxia (e.g. Riquier et al., 2006), others infer oxic conditions (e.g. George et al., 2014). Furthermore, in many localities around the world, F-F boundary sections are highly condensed (e.g. Joachimski et al., 2002), or incomplete due to unconformities and depositional hiatuses related to the sharp marine regression in the uppermost Frasnian (Johnson et al., 1985; Sandberg et al., 1988; Geldsetzer et al., 1993; Muchez et al., 1996; Stephens and Sumner, 2003), and/or limited in terms of sampling density or biostratigraphic control at the intra-biozonal scale (e.g. Bratton et al., 1999; Stephens and Sumner, 2003; van Geldern et al., 2006).

This contribution reports new data from the northern margin of Gondwana in order to constrain the timing of the Upper Kellwasser excursion and to better understand the causal mechanism(s) relating to the Kellwasser events. Here we present four detailed carbon-isotope profiles, constrained at the intra-zonal level by high-resolution conodont biostratigraphy and magnetostratigraphy. We obtained our data from measured outcrop sections through organic-poor facies in variable slope environments of the Lennard Shelf mixed carbonate-siliciclastic system, Canning Basin, Western Australia (Figure 2.1). In this region, middle-slope breccia-grainstone and upper-slope boundstone settings appear to be stratigraphically expanded relative to many other global localities. In Europe, for example, Conodont Zone 13 (Figure 2.2) is generally < 2m-thick (Buggisch and Joachimski, 2006), whereas in this study the same interval of time is represented by > 20 m of stratigraphy. As such, our sections provide a continuous, more expanded view of upper Frasnian to lower Famennian strata and allow for a more detailed examination of the Upper Kellwasser excursion as it relates to the timing of the F-F boundary. The stable isotope data, with some accompanying trace element analyses, also provide insight into changes in the global carbon pool and redox conditions of the ocean during this time.

AREA DESCRIPTIONS, METHODS & MATERIALS STUDIED

During the Middle Devonian, subsidence and rifting of the Canning Basin (e.g. Veevers and Wells, 1961; Kennard et al., 1994) led to the prolific growth of carbonate reefs along the shallow terraces of the Lennard Shelf. Today, over 350 km of Middle to Late Devonian carbonates are exposed in the northern part of the basin and have been subjected to decades of stratigraphic, paleontological, and geochemical research (Guppy et al., 1958b; Playford and Lowry, 1966; Druce, 1976; Playford, 1980; Becker and House, 1997; George et al., 1997; Stephens and Sumner, 2003; Nothdurft et al., 2004; and others). During the interval of time most relevant to this study, namely the Late Frasnian and Early Famennian, the reefal platform and slope system exhibited progradational growth morphology and experienced episodic collapse events that transported large amounts of material down-slope (Playford, 1980; Sandberg et al., 2002; Playton, 2008). An abrupt fall in sea level coincident with the F-F boundary resulted in the sub-aerial exposure and erosion of platform-top facies while sedimentation continued uninterrupted on the slope and in the basin. As such, deeper water settings were preferentially targeted in this study because of their potential for stratigraphic completeness.

Four stratigraphic sections from sites spanning 200 km across the Lennard Shelf outcrop belt were investigated in detail for facies and stratigraphy, and sampled for carbon isotope- and trace element geochemistry, biostratigraphy, and magneto-stratigraphy (Figure 2.1). Samples include plugs (2.5 cm diameter, 10 cm length) and hand specimens, and were collected at a spacing of 16 – 95 cm (1 sample/59 cm on average) from three relatively thick (ca. 50-250 m), middle- and upper-slope sections (Table 2.1) in the southeastern part of the Oscar Range (SO; 17°54.983′S, 125°17.9′E), from the Virgin Hills formation in the Horse Springs Range (VHS; 18°12.133′S, 126°01.483′E), and north of Windjana Gorge (WV; 17°23.767′S, 124°56.767′E) in the Napier

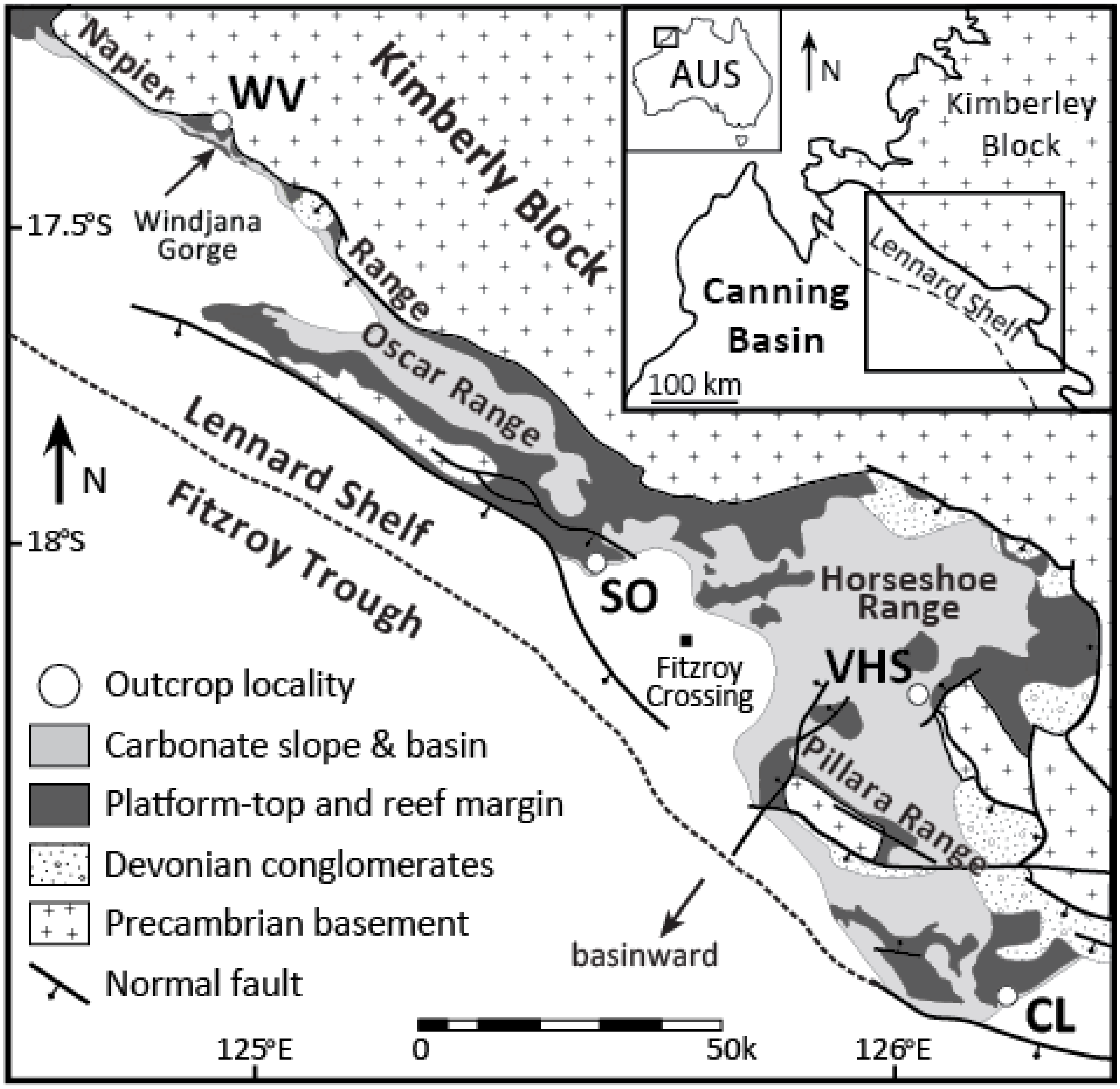

Figure 2.1: Map of field area (modified after Playford et. al., 2009). Samples for this study were collected from four outcrops along the Lennard Shelf in Western Australia; Casey Falls (CL), Horse Springs (VHS), South Oscar Range (SO), and the Windjana Gorge area (WV). Insets show the location of the Lennard Shelf carbonate system in relation to the Canning Basin and Australia.

Table 2.1: Depositional characteristics and isotopic data associated with Kellwasser equivalent excursions 1 and 2. Amplitude and maximum $\delta^{13}C$ values are reported relative to VPDB. Data for excursion 1 at WV and CL are not available because neither section extended into the age appropriate strata. See Figure 2.1 for non-abbreviated locality names.

Section	Paleogeographic Setting	Depositional Environment	Excursion 1 (L.KW equivalent)			Excursion 2 (U.KW equivalent)		
			Associated Facies	Amp.	Max.	Associated Facies	Amp.	Max.
SO	isolated, open marine	middle - upper slope	skeletal-rich megabreccia	+3.4‰	+4.4‰	platform-derived packstone/grainstone, breccia	+2.5‰	+3.9‰
VHS	land attached, broad embayment	middle slope	skeletal-peloidal packstone/ grainstone, microbial-dominated boundstone	+3.5‰	+4.7‰	platform-derived grainstone, megabreccia, wackestone	+3.2‰	+4.6‰
WV	land attached	upper slope	Not Available			massively bedded microbial boundstone, megabreccia	+2.5‰	+3.4‰
CL	land attached, reef spine	lower slope	Not Available			silt-dominated wackestone/packstone	+2.8‰	+3.5‰

Range. For comparison purposes, samples from one relatively condensed transect through silt-dominated lower-slope deposits at Casey Falls in the Lawford Range (CL; 18°43.983′S, 126°5.119′E) were also obtained. Specimens for geochemical and isotopic analysis were typically taken from >5 cm below the modern surface (i.e., deepest portion of plug sample). Sampling of breccias excluded blocks and allochems, instead targeting the matrix and marine cements, to ensure that geochemical analyses were representative of the time of deposition and that paleomagnetic analyses were conducted on presumably unrotated material.

Integrated magnetostratigraphy and conodont biostratigraphy provided the primary temporal constraints for the geochemical analyses (see Appendix 2.1 for a detailed list of all biostratigraphic data used in this dissertation). The paleomagnetic reversal records were derived from previously published datasets analyzed at the University of Western Australia; data for VHS and SO were reported by Hansma et al. (2015) and WV was evaluated by Tohver et al. (in prep.). Paleomagnetic data for CL were not incorporated into this study--due to the relatively condensed nature of this section, magnetostratigraphic correlations were ambiguous. Samples obtained for conodont analysis were collected from all sections but were only age diagnostic for the SO, VHS, and CL sections (Hansma et al., 2015; Roelofs et al., 2015). For additional constraint, an independent conodont study (Klapper, 2007) conducted at the VHS site was incorporated into our work.

For carbon isotopes, 350 samples were analyzed at the Stable Isotope Research Facility at the University of Washington; 82 are presented from the SO section, 169 from VHS, 66 from WV, and 33 from CL. Hillbun et al. (see Chapter 1) evaluated all samples for diagenetic alteration and showed that bulk-rock analyses record primary marine $\delta^{13}C$ values useful for regional and global correlations. Samples that were previously identified as potentially dolomitized, recrystallized, or otherwise altered were not included in this study. Following the bulk-rock methodology of Stephens and Sumner (2003), and the quality control workflow of Hillbun et al. (Chapter 1), sample cores were polished and then drilled using a hand-held Woodtek drill with a diamond coated bit. All sample powders were reacted with phosphoric acid at 70°C in an automated Kiel device with the resulting CO_2 gas analyzed by a ThermoFinnigan MAT253 mass spectrometer. The analytical precision of $\delta^{13}C_{carb}$ and $\delta^{18}O$ analyses based on sample replicates and laboratory standards is ≤ ±0.1 ‰. Data were corrected using laboratory standards and are reported here in standard delta notation relative to VPDB.

Trace element analyses for the SO section were carried out by Chemostrat, Inc. (Appendix 2.2). Each sample was ground to a powder in a ball mill, and following Li-metaborate fusion, was analyzed using inductively coupled plasma optical emission spectrometry and mass spectrometry (ICP-OES MS). The methods of fusion and analysis are those described in Jarvis and Jarvis, (1995). These analytical methods result in data for both major- and trace elements, reported as oxide percent by weight and parts per million by weight (ppm), respectively. Precision for the major element data was generally better than 2 % and ca. 3 % for the high-abundance trace element data derived by ICP-OES. The remaining trace elements determined from the ICP-MS were generally less precise, with analytical error of ca. 5%. Analytical error is ±1% for major and ±3–7 ppm for trace elements depending on abundance. Expanded uncertainty values (95% confidence) that incorporate all likely errors within a statistical framework derived from 11 batches of 5 certified reference materials (CRMs), each prepared in duplicate, are typically 5–7% (relative) for major elements and 7–12 % (relative) for trace elements.

RESULTS

Bio- and Magnetostratigraphic Constraints on the F-F Boundary

To determine the location of the F-F boundary, the widely used standard conodont zonations of the Frasnian (Montagne Noire succession, Klapper, 1989; Girard et al., 2005) and Famennian (Ziegler and Sandberg, 1990) are applicable to our sections in the Lennard Shelf (Figure 2.2). As defined at the boundary-stratotype section in Montagne Noire, France (House et al., 2000), the lower boundary of the *triangularis* Zone, and base of the Famennian Stage, is marked by the lowest occurrence of Palmatolepis *subperlobata*. In our VHS section the interval between the Lower *triangularis* Zone and the uppermost part of Frasnian Zone 13 (i.e. the margin of error around the stratigraphic position of the F-F) is only 20 cm; in the SO section it is less than 4.3 m, and in CL it is no more than 5.7 m. At VHS and SO, the F-F boundary is arbitrarily placed at the stratigraphic midpoint between the latest known Frasnian (35.75 m and 228.7 m, respectively) and earliest known Famennian (35.95 m and 233 m, respectively) strata (Figure 2.2). At CL, the boundary is less biostratigraphically constrained but is currently placed just below the lowest observed occurrence of P. *subperlobata*, at the base of the first microbial boundstone (at 7.5 m).

Magnetostratigraphic correlation of WV with previously examined records from VHS and SO (Hansma et al., 2015) revealed seven major magnetozones for the interval of time studied (Frasnian conodont Zone 11 to Famennian *crepida* Zone) (Figure 2.2). Four periods of mixed, dominantly reversed polarity and three periods of normal polarity have been recognized, and the F-F boundary has been identified within the N7 normal chron. In the WV section, where biostratigraphic control is lacking, the boundary is constrained within the N7 chron, an interval that is ~10 m thick; the F-F boundary is arbitrarily placed at the center point of this chron (Figure 2.2).

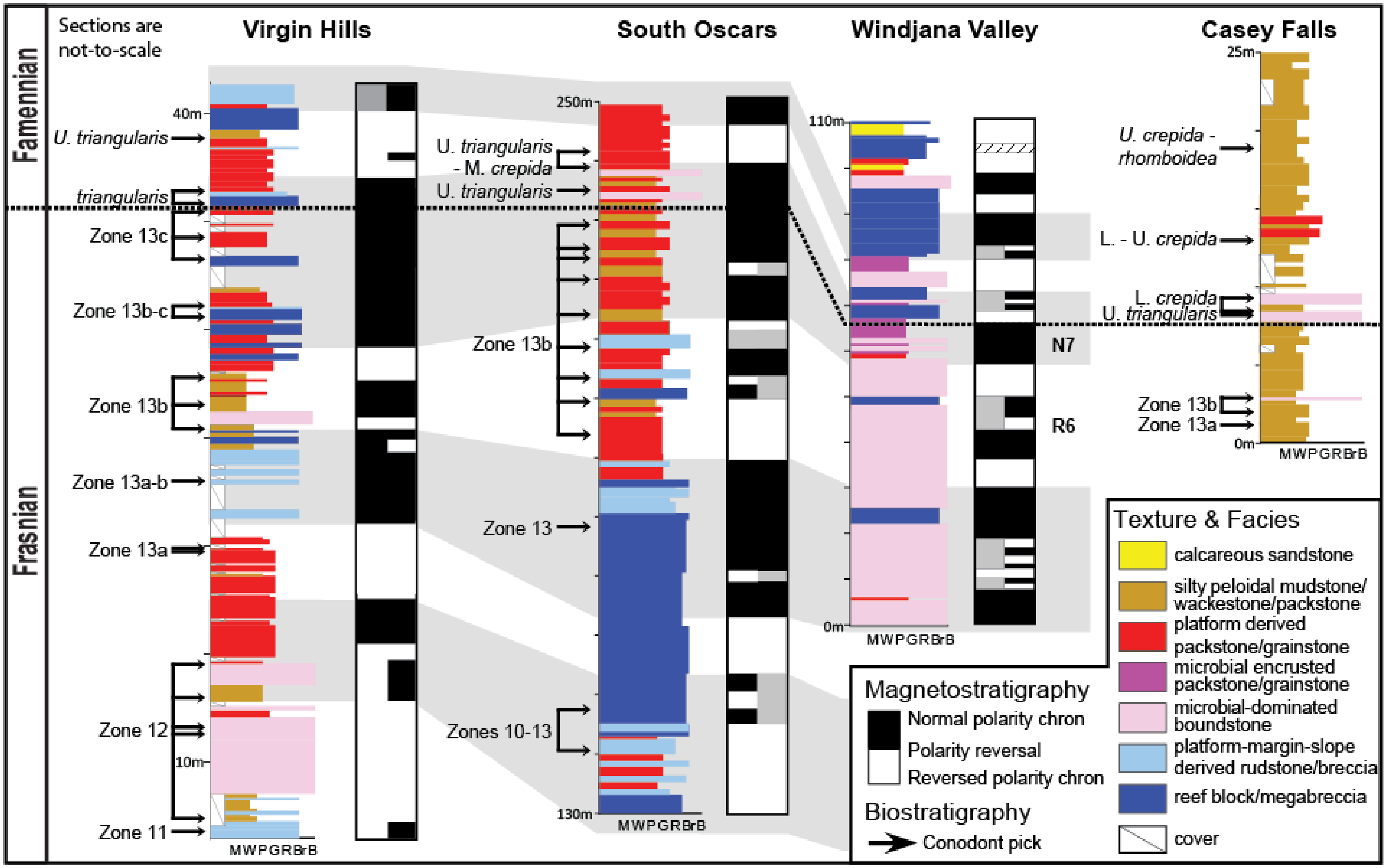

Figure 2.2: Measured sections showing bio- and magneto-stratigraphic control used for correlation and to constrain the position of the F-F boundary. Paleomagnetic reversal records (partials) are from Hansma et al., (2015) and Tohver et al., (in prep). Grey shading shows correlation of normal (and mixed-normal) polarity chrons. M=mudstone, W=wackestone, P=packstone, G=grainstone, R=rudstone, Br=breccia, B=bound/bafflestone.

Carbon Isotope Stratigraphy

High-resolution carbon isotope stratigraphy reveals two major positive excursions stratigraphically lower than the F-F boundary. The timing and amplitude of these perturbations are comparable between sections, despite differences in facies, depositional environments, and paleogeographic settings (Table 2.1). Furthermore, petrographic analysis of selected samples reveals excellent preservation of original fabrics, relatively minor amounts of calcite recrystallization, and the absence of dolomitization, suggesting that the isotopic composition of the original seawater is represented (Chapter 1).

Excursion 1 (Figure 2.3) is stratigraphically lower than excursion 2 and is observed in only two sections. In SO, an increase in $\delta^{13}C$ values from +1‰ to +4.4‰ (max value) is measured from megabreccia deposits and constrained within conodont Zones 10 and 13. In the VHS section, isotope values recorded in thick grainstone beds increase from +1.2‰ to +4.7‰ (max value) within Zones 12 and 13a. While excursion 1 exhibits similar amplitudes and maximum values in both sections, the interval of elevated values in SO is noticeably expanded stratigraphically downsection relative to VHS. Based on conodont biostratigraphy, excursion 1 can be correlated with the deposition of the Lower Kellwasser Horizon in Europe (e.g. Buggisch and Joachimski 2006), and we interpret it to be time-equivalent to the Lower Kellwasser excursion reported from localities around the world (Joachimski et al., 2002; Xu et al., 2003; Stephens and Sumner, 2003; George et al., 2014; and others).

Excursion 2 is documented in all four localities (Figure 2.3). In both SO and VHS, $\delta^{13}C$ values increase from +1.4 ‰ and +1.3 ‰ (baseline values) to +3.9 ‰ and +4.6 ‰ (max. values), respectively, within conodont Zone 13b. Isotopic data from WV show a positive shift (~+0.9‰ baseline values to +3.4‰ max values) occurring wholly within the R8 chron, which is

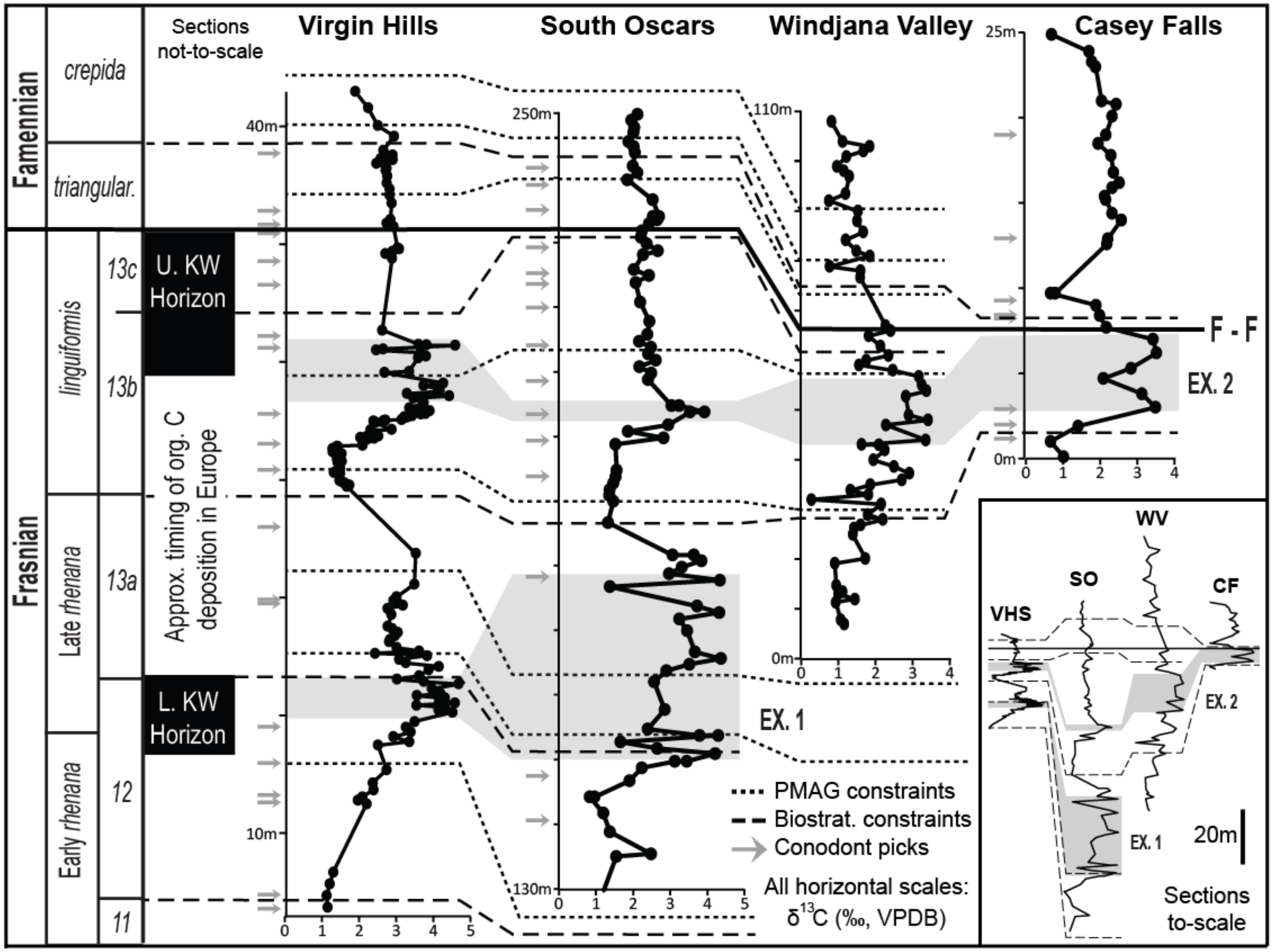

Figure 2.3: Comparison of isotopic profiles across the F-F boundary in the Lennard Shelf carbonate system. Grey highlighting of maximum δ^{13}C values shows the stratigraphic positions of excursions (Ex.) 1 and 2 relative to the standard (Ziegler and Sandberg, 1990) and Montagne Noire (Klapper, 1989) conodont zonations. Position of the F-F boundary is constrained by bio- and magneto-stratigraphic data (see Figure 2.2 for magnetostratigraphic correlation). Inset shows isotopic profiles to-scale; dashed lines show biostratigraphic correlations and the solid line = the Frasnian-Famennian (F-F) boundary.

constrained within conodont Zone 13b, and possibly 13a, based on magnetostratigraphic correlation. Although resolution of conodont biostratigraphic control is less precise in the condensed CL section, the data are similar; $\delta^{13}C$ values from silt-dominated, lower slope facies begin to increase in Zone 13b (and possibly the very uppermost part of Zone 13a) from +0.7 ‰ (baseline values), and reach maximum values (+3.5 ‰) just below the first appearance of *Pa. subperlobata*.

In all sections, increasing $\delta^{13}C$ values associated with excursion 2 can be roughly correlated with the onset of deposition of the Upper Kellwasser horizon in Europe during Zone 13b (Figure 2.3). However, maximum isotope values associated with the Lennard Shelf excursion begin to decline towards more baseline values during the upper Frasnian, before the F-F boundary and the cessation of Upper Kellwasser shale deposits in Europe. In VHS, SO, and WV in particular, the F-F is clearly not associated with a positive shift in $\delta^{13}C$ values. The transition from the uppermost Frasnian into the *triangularis* Zone of the lower Famennian is marked by slightly elevated $\delta^{13}C$ values relative to Frasnian baseline values of +1 to +1.5‰. This slow recovery trend, albeit typically observed only in the *triangularis* Zone, is characteristic of European isotope records (e.g. Buggisch and Joachimski, 2006). Given the temporal constraints provided by the bio- and magnetostratigraphy data, we interpret excursion 2 as the Upper Kellwasser excursion, but, it pre-dates conventional timing. Rather than maximum $\delta^{13}C$ values being coincident with or closely adjacent to the F-F boundary, they occur distinctly lower, in upper Frasnian strata.

Trace Elements as Tests for Anoxia and Productivity

Based on the work of previous studies (e.g. Adams and Weaver, 1958; Jones and Manning, 1994; Algeo and Maynard, 2004; Rimmer, 2004) trace element ratios of U/Th and V/Cr are used to evaluate the state of marine oxygen levels. Because uranium and vanadium are commonly concentrated in sediments deposited under reducing conditions (Shaw et al., 1990; Emerson and Huested, 1991), comparing them with non-redox sensitive elements that are typically found in the detrital fraction (Th and Cr) can provide insight into changes in paleo-oxygenation. Typical range estimates for oxic, dysoxic, and anoxic water conditions have been suggested for U/Th and V/Cr ratios (Jones and Manning, 1994) and are employed here for reference. Given these threshold values, both paleo-redox proxies indicate low-oxygen levels (Figure 2.4) which correspond to the $\delta^{13}C$ excursions associated with both Kellwasser events noted in this study (Figure 2.3). For the Upper Kellwasser in particular, it appears that V/Cr values remain elevated for a longer period of time relative to U/Th.

Elemental ratios of Cu/Al and Ni/Al are reported for their use as reliable indicators of changes in paleo-bioproductivity (e.g. Piper and Perkins, 2004; Riquier et al., 2006; Perkins et al., 2008), particularly in the absence of preserved organic-rich material. While a variety of trace elements behave as micronutrients in oxic marine environments and are deposited in association with the organic carbon flux from surface primary productivity, both nickel and copper may be retained within their host sediments even if the organics are partially or completely re-mineralized after deposition (Tribovillard et al., 2006). In our study, the measured ratios of Cu/Al and Ni/Al exhibit less obvious trends than the ratios of U/Th and V/Cr; there is considerable scatter associated with the Lower Kellwasser interval in both proxies, but the elevated values are correlative with the isotopic excursion. For the Upper Kellwasser, relative enrichments in Ni/Al and Cu/Al are observed near and above maximum $\delta^{13}C$ values, respectively.

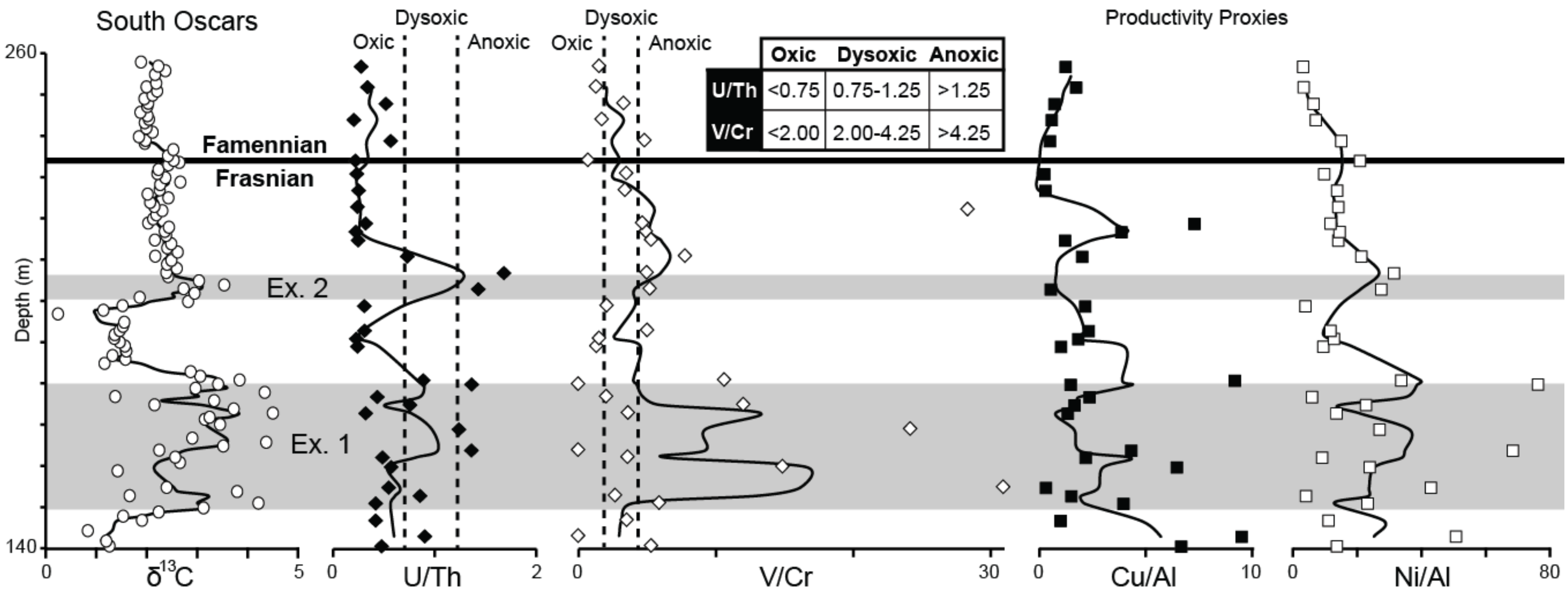

Figure 2.4: Chemostratigraphic profiles of elemental ratios used as qualitative proxies for paleoredox conditions and bioproductivity. Shaded areas represent the stratigraphic position of maximum carbon isotope values associated with the Lower and Upper Kellwasser excursions (Ex. 1 and 2, respectively; Ex. = excursion). Trace element ratio thresholds for oxic, dysoxic, and anoxic water conditions from Jones and Manning (1994).

DISCUSSION

Discrepancy in Timing

The interval of time surrounding the Frasnian-Famennian (F-F) boundary is generally marked by two positive carbon-isotope excursions (~3 ‰ average amplitude) in the marine carbonate record that correspond to the well-studied, organic-rich Kellwasser horizons and associated extinction events first described from sections in Central Europe and Morocco (McGhee et al., 1986; Buggisch, 1991; Joachimski and Buggisch, 1993; Joachimski et al., 1994; Joachimski et al., 2002). Despite the lack of similarly aged organic-rich deposits in the Lennard Shelf system, we report a European-like trend in carbon isotope values from four different measured sections. While the absence of black shales and bituminous limestones from this time interval in Western Australia has created some doubt over the global nature of the two Kellwasser events, our geochemical results are consistent with the hypothesis that the Kellwasser events are indeed world-wide phenomena, and the trace element data support a period of at least dysoxia (if not anoxia) associated with the events. Our evidence for a $\delta^{13}C$ excursion associated with the Lower Kellwasser event within Zones 12 and 13a is consistent across datasets in this study and corroborates the record from other sections in Australia (Stephens and Sumner, 2003; George et al., 2014) and Europe (e.g. Buggisch and Joachimski, 2006). However, our chronostratigraphically constrained record of the Upper Kellwasser excursion, particularly the timing of maximum $\delta^{13}C$ values, suggests that the geochemical event is distinct from and pre-dates the F-F boundary, in contrast with other workers' findings (Figure 2.5).

There are four possible ways to reconcile our data with the global data set. First, the data may reflect local phenomena or paleoenvironmental conditions unique to the Lennard Shelf and thus have no global implications.

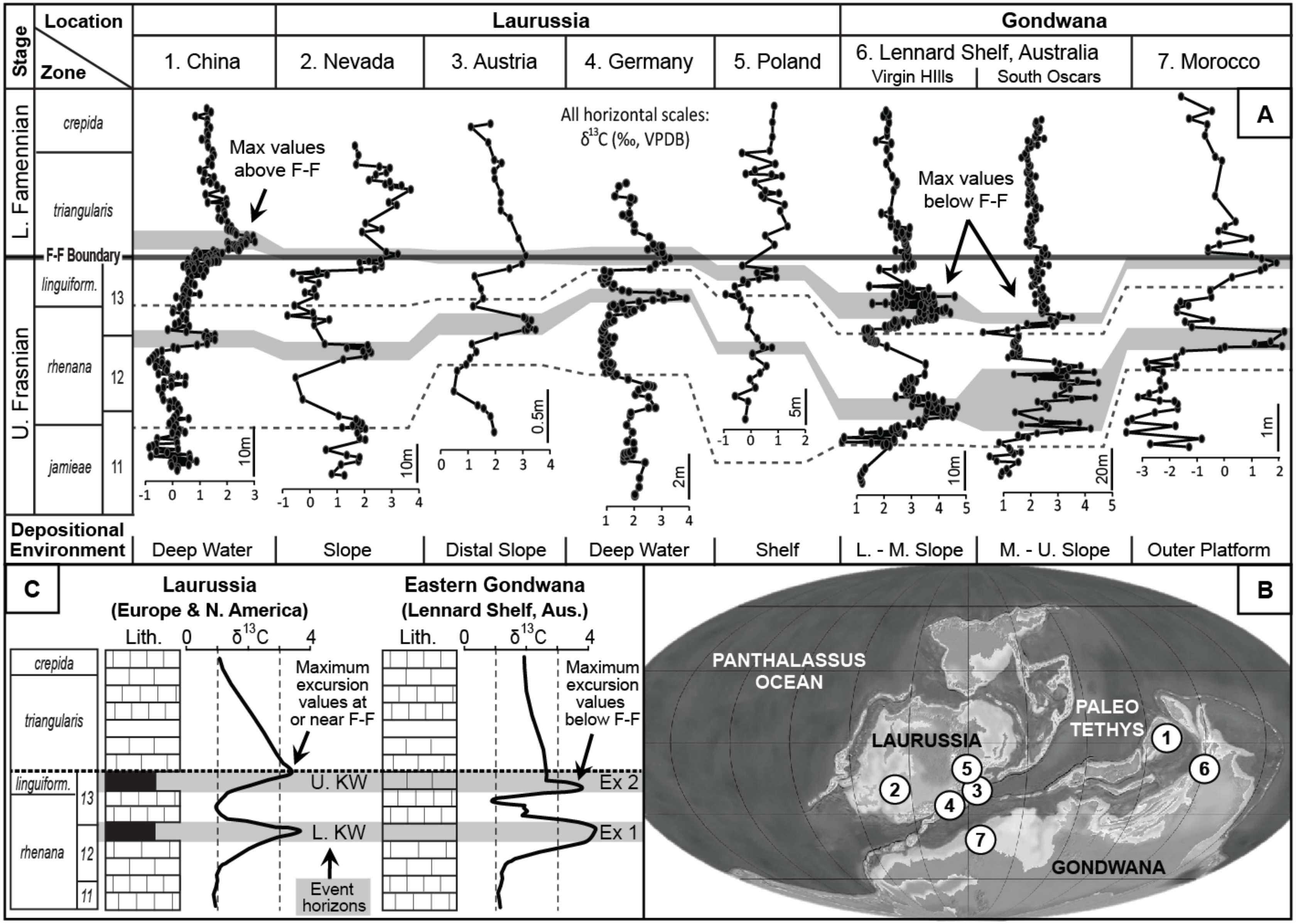

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Figure 2.5: A. Comparison of $\delta^{13}C$ maxima for the Upper- and Lower Kellwasser geochemical events from Guilin, China (Xu et al., 2003), Devils Gate, Nevada (Joachimski et al., 2002), Wolayer Glacier, Austria (Buggisch and Joachimski, 2006), Benner Quarry, Germany (Joachimski and Buggisch, 1993), Kowala, Poland (Joachimski et al., 2002), the Lennard Shelf, Western Australia (this study), and Bou Ounebdou, Morocco (Joachimski et al., 2002). The depositional environment for each section has been indicated and biostratigraphic constraints drawn in accordance with the original data. B. Paleo reconstruction of the Late Devonian (Blakey, 2008) showing locations of the various $\delta^{13}C$ records. C. Generalized lithologic- and isotopic trends across the F-F boundary for sections in Laurussia and Eastern Gondwana (modified from Joachimski and Buggisch, 1993).

Second, a discrepancy in timing could be due either to a diachronous appearance of upper Frasnian conodont faunas or to differences in biostratigraphic resolution, possibly related to variable sampling densities. Third, these Lennard Shelf sections may represent a rarely preserved, expanded interval of the F-F transition that is not present elsewhere possibly because of highly condensed facies assemblages or unrecognized depositional hiatuses. Lastly, differences in paleogeography and ocean circulation between different study areas may account for the variation in the timing of isotopic excursions, reflecting differences in riverine input or restricted circulation in intracratonic basins, for example.

The first hypothesis, that of highly localized $\delta^{13}C$ patterns, is at odds with the broad and replicable patterns in $\delta^{13}C$ values recognized from the Lennard Shelf, in this study and others (Joachimski et al., 2002; Stephens and Sumner, 2003; George et al., 2014), which are similar in shape and amplitude to the well-studied excursions associated with the Kellwassers and equivalent horizons documented throughout Europe (e.g. Buggisch and Joachimski, 2006), North Africa (Joachimski et al., 2002), North America (e.g. Wang et al., 1996), and China (Xu et al., 2003). The refined timing of the Upper Kellwasser excursion is consistent between multiple sections of our study, regardless of differing slope facies and paleogeographic settings. Sections in Kowala, Poland and Bou Ounebdou, Morocco (Joachimski et al., 2002) also reported similar findings of elevated $\delta^{13}C$ values below the F-F boundary. However, these authors argued that the expected stratigraphic continuations of the excursions were muted by recrystallization during the anaerobic oxidation of organic matter. The lack of correlative organic-rich sediments in our Lennard Shelf sections precludes this as a possible explanation for our results.

In addition to studies in the Canning Basin, the occurrence of positive excursions without accompanying anoxic sediments has been documented at the Wolayer Glatcher site in Austria (Joachimski and Buggisch, 1993) and in Nevada, USA (Joachimski et al., 2002). These authors' assessment that the anomalies in $\delta^{13}C$ reflect global changes in the total dissolved marine carbon reservoir, as opposed to local anoxia, is corroborated by our findings from Western Australia. A similar argument has been made for the isotopic data associated with the Oceanic Anoxic Events in the Cretaceous Period; that is, the deposition of black shales and sub-oxic conditions were regional but their effects on the marine $\delta^{13}C$ record were global (e.g. Tsikos et al., 2004; Wagreich, 2009). We therefore conclude that the Lennard Shelf isotope record is a viable marine proxy that documents the extensive burial of organic carbon in other sedimentary basins around the world (North America, Europe, China, and North Africa).

The second hypothesis invoking the diachronous appearance of conodonts is considered unlikely. Extensive work in the Canning Basin has established that the Lennard Shelf conodont succession is comparable and time equivalent to the standard conodont zonations used globally for the upper Frasnian and lower Famennian with no discrepancies between first and last appearance data of key species (Glenister and Klapper, 1966; Druce, 1976; Ziegler and Sandberg, 1990; Klapper et al., 1993; Klapper, 1989, 2007). Bioturbation was also ruled out as a possible explanation for the observed discrepancy because the isotope excursion believed to represent the Upper Kellwasser event was found to occur as much as 20 meters or more below the F-F boundary (SO), a depth too great to reasonably account for any biological displacement of material.

In terms of sampling density and resolution, our study has very good constraints around the F-F boundary, and where we lack conodont control, magnetostratigraphy aids our correlations. However, isotopic studies commonly differ, sometimes significantly, in their biostratigraphic resolution. In the Canning Basin, for example, conodont samples were collected at a density of >1 sample per meter from the Virgin Hills section at Horse Springs (Klapper, 2007), allowing for the distinction of individual Montagne Noire conodont zones, including each subdivision of Zone 13 (a, b, and c). In contrast, zonal resolution for the isotopic record at Dingo Gap (George et al., 1997, cited in Stephens and Sumner, 2003) was not achieved; the low sample-density average (1 sample each ca. 5 meters) created an apparent compression of the isotopic excursions (Figure 2.6). This problem of low resolution is exacerbated by the tendency for authors to cite prior work in place of providing the actual biostratigraphic data (e.g. Wang et al., 1996; Joachimski et al., 2002; Xu et al., 2003; Stephens and Sumner, 2003), rendering chronostratigraphic comparisons at the zonal level difficult to assess.

This problem of uneven sampling density is especially true for the Lennard Shelf where isotopic profiles for the Late Frasnian and Early Famennian appear to differ slightly from one another in the timing of their excursions (Figure 2.6). For example, a recent study of a basinal core near our VHS section reported a large positive excursion, interpreted to represent the Upper Kellwasser, as occurring entirely above the F-F boundary in the *triangularis Z*one (George et al., 2014). The authors also documented another two $\delta^{13}C$ anomalies just below the boundary, constrained by a limited number of samples, two samples over 20 meters spanning Frasnian conodont Zones 6 to 13 and three samples from conodont Zone 13. The constraints for these two lower excursions

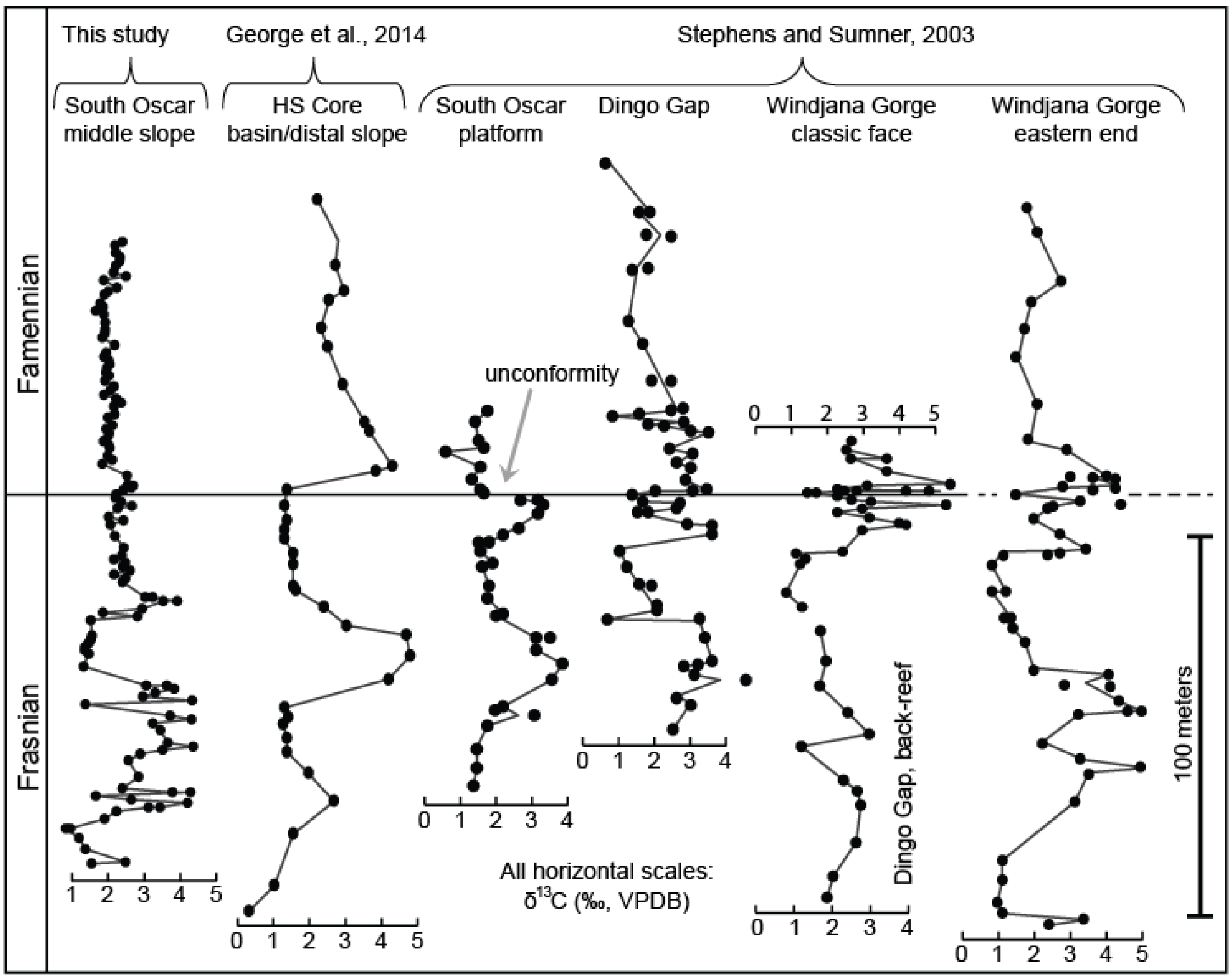

Figure 2.6: Comparison of carbon isotope profiles, and relative timing of $\delta^{13}C$ excursions (maximum values), from various studies in the Lennard Shelf carbonate system (Stephens and Sumner, 2003; George et al., 2014; this study).

suggest a correlation with our reported excursions, and thus represent the Lower and Upper Kellwasser events, respectively. None of our studied sections record the Famennian excursion reported by George et al. (2014).

The other prominent C-isotope study of the F-F interval in the Canning Basin (Stephens and Sumner, 2003) also showed two positive isotope excursions at Dingo Gap; one occurring below the boundary and the other straddling it (Figure 2.6). George et al. (2014) interpreted the broad upper excursion, which had two distinct peaks, as representing both Kellwasser events. However, the conodont resolution for Dingo Gap is not sufficiently detailed to determine with any certainty the zones in which the excursions actually occur. At this time it remains unclear if differences in biostratigraphic resolution within the Canning Basin, and potentially elsewhere, can account for the observed discrepancy in timing.

The third and fourth scenarios presented are the most plausible as they are most consistent with- and easily explained by our results. In three of our measured sections the isotopic expression of the Upper Kellwasser was observed in continuous succession in grainstone, breccia, and massive boundstone from middle- and upper-slope settings where depositional dips were relatively steep (up to 30˚) and sedimentation rates presumably greater (Playton, 2008; Hansma et al., 2015). A combination of expanded stratigraphy and high-density sampling demonstrates that the timing of maximum values associated with the Upper Kellwasser excursion is different than previously documented (Figures 2.2 and 2.3). Our results from the distal-slope sediments (CL section) differ from the other three in that the section is highly condensed (conodont Zone 13b to *Crepida* Zone is <10m thick) and exhibits maximum $\delta^{13}C$ values at or near the F-F boundary, typifying the problems created by condensed sections. We attribute these differences primarily to low sedimentation rates. While the presence of an end-Frasnian depositional hiatus or unconformity may also render isotopic records incomplete, there is no definitive evidence for this in our section. In the case of the South Oscar section studied by Stephens and Sumner (2003), a positive $\delta^{13}C$ excursion with maximum values below the F-F boundary was observed in platform-top settings, but its potential extent remains unknown due to a documented unconformity. In any case, the isotopic pattern observed at CL is more comparable to those reported from sections in Europe and Morocco (Figure 2.5), possibly because the isotopic data associated with the Upper Kellwasser event in these regions are commonly derived from similarly condensed facies or incomplete sections.

In contrast to results from most geochemical studies during the Late Devonian, the low oxygen conditions recorded by the trace element data at SO do not appear to persist up to the F-F boundary; like the $\delta^{13}C$ data, they occur entirely within Frasnian conodont Zone 13b (Figure 2.4). This finding is comparable to findings from the Great Basin in North America where anoxic conditions also pre-dated the F-F (Bratton et al., 1999). Evidence from the fossil record suggests that the most severe pulse of the Late Devonian mass extinction likewise occurred before the boundary (McGhee, 1996); many groups became extinct before the end of the Frasnian (brachiopods, Dutro, 1981) at the base of the Upper Kellwasser horizon including trilobites (e.g. Feist, 1991), goniatites (Becker and House, 1994), ostracods (Casier, 1987; Olempska, 2002), and rugose corals (Ma and Bai, 2002). In the Canning Basin there also was a dramatic loss of conodont biodiversity at the end of conodont Zone 13b (Klapper, 2009) and a regional extinction of all ammonoid genera at the onset of 13c (Becker and House, 2009). Assuming that the global carbon pool indicates a return to less stressful conditions after the Upper Kellwasser and associated extinction events, but prior to the F-F boundary, the geological record from settings with more restricted water circulation would have experienced a lag in the recovery of $\delta^{13}C$

values to baseline values. Effectively, this lag would persist until early Famennian times due to the sequestration of some localities from the global marine carbon reservoir. On a basin scale, however, the lag in isotopic values would be contemporaneous and thus $\delta^{13}C$ trends would remain useful, at least as a regional correlation tool.

The paleogeography of the Late Devonian (Figure 2.5) indicates varying potential for isolation of some regions from the marine carbon reservoir. For example, almost all European, North American, and North African sections were located in shallow, epicontinental settings at this time. Ongoing convergence between Laurussia and Gondwana forced the closing of the Rheic Ocean and constricted the southwestern part of the Paleotethys seaway (Keppie and Ramos, 1999; Stampfli et al., 2002; Torsvik et al., 2012). Shallow water settings in the affected regions became increasingly susceptible to the effects of the end-Frasnian regression, and also experienced an increased influx of continentally-derived material from weathering and erosion associated with active orogenies (e.g. Dalziel et al., 1994). Logically, carbonate sedimentation and reef development in these regions would have been heavily influenced by local sources of dissolved inorganic carbon (DIC) and the development of low oxygen conditions in such relatively restricted settings. Comparatively, the Canning Basin had fewer external controls; the Lennard Shelf carbonate system experienced open circulation with sea water during the Late Devonian (Carpenter et al., 1991), and there were no active mountain building events in Western Australia during that time span (Plumb, 1979; Forman and Wales, 1981). Consequently, it’s unlikely that our observed discrepancy in timing of the Upper Kellwasser was a product of regional scale variations in the DIC pool. Moreover, carbonate deposition, as it pertains to reef growth, may have been more prolific in the Canning Basin because periods of more stressful paleoenvironmental conditions were likely shorter lived.

Possible Excursion Mechanisms

The black shales and bituminous limestones characteristic of the Kellwasser horizons in Europe are commonly interpreted to have been deposited under reducing oceanic conditions during intervals of substantial carbon burial (Wilde and Berry, 1984; Joachimski and Buggisch, 1993; Becker and House, 1994; Wignall, 1994; Algeo et al., 1995). The geochemical results from this Lennard Shelf study are consistent with such a scenario. The pattern of trace elements in the SO section does not support persistent or pervasive anoxia, but the U/Th and V/Cr patterns do indicate stressed, reducing oceanic conditions concurrent with both excursions. The record of low oxygen conditions is clearer for the Upper Kellwasser interval with the more diffuse pattern from the Lower Kellwasser suggesting more intermittent periods of oxygen restriction. While middle-slope settings may reflect water oxygenation by deep currents, the megabreccia-dominated slope facies from which the Lower Kellwasser was analyzed likely indicate reefal collapse and re-deposition of platform-derived material, which may reflect more oxic conditions, within an overall anoxic environment (lower) on the slope.

Reduced oxygen levels in the SO section may be related to the prevalence of bottom-water anoxia in the deepest parts of the global ocean (e.g. Goodfellow et al., 1989)**.** Decades of research have shown that the Frasnian stage is coincident with a globally warm climate, the proliferation of land plants, and eustatic sea-level rise punctuated by transgressive-regressive cycles--conditions that are favorable to episodic ocean stratification and the formation of anoxia in deep-water settings (Brass et al., 1982; Johnson et al., 1985; Wilde and Berry, 1986; Tyson and Pearson, 1991; Algeo et al., 1995; Hallam and Wignall, 1999; Averbuch et al., 2005). Short-term transgressive pulses have been shown to correlate with the two Kellwasser excursions in both Europe (Johnson et al., 1996; Buggisch and Joachimski, 2006) and the Canning Basin

(Stephens and Sumner, 2003). These transgressive episodes would result in a landward migration of oxygen-depleted waters from bathyal settings into shallower environments such as the Lennard Shelf System.

These findings that support anoxia contradict the conclusions of George et al. (2014), who described the positive excursions in the Lennard Shelf as occurring in “oxic facies.” These authors hypothesized that the $\delta^{13}C$ anomalies could be attributed to an increase in biological productivity due to enhanced nutrient influxes from continental weathering during times of lowered relative sea level. While our geochemical results support a relative increase in marine productivity during the Upper Kellwasser interval, and perhaps to a lesser extent for the Lower Kellwasser, it seems unlikely that (regional) enhanced land-derived nutrient loading was the driving factor. Relatively distal sections, such as those on the lower slope and in the basin (i.e., section VHS of this study; George et al., 2014) are not typically affected by terrestrial influx; productivity blooms are commonly restricted to near-shore environments where the influence of continentally derived material is greatest (Riquier et al., 2006). The lack of active orogenies in Western Australia at this time further decreases the likelihood of extensive nutrient transport. A more probable explanation for the observed trace element pattern, at least for the Upper Kellwasser, is that localized phosphorous renewal under deep-water anoxic conditions led to eutrophication (Ingall and Jahnke, 1997), resulting in the expansion of oxygen-deprived water into shallower depositional settings. This hypothesis was similarly suggested for the Upper Kellwasser in the Harz Mountains of Germany by Riquier et al. (2006).

In the event that terrestrially sourced productivity was the primary driver of paleoenvironmental change and isotopic excursions recorded in the Lennard Shelf System, we would expect to see some vestige of the organic byproducts, particularly in sections (SO, WV) that have high sedimentations rates conducive to the preservation of organic matter (e.g. Muller and Suess, 1979; Sageman and Lyons, 2003) and which represent relatively proximal settings compared to the basinal core studied by George et al. (2014). However, no such organic-rich material was detected. The wholesale decomposition of organic material is unlikely, given that all isotopic profiles documented from the Lennard Shelf display no evidence of a ^{12}C influx from organic carbon remineralization (this study; Joachimski et al. 2002; Stephens and Sumner 2003; George et al. 2014).

CONCLUSION

This work presents an integrated view from the northern margin of Gondwana, constraining the pattern of carbon-isotope perturbations across the Frasnian-Famennian transition at the intra-zonal scale. The Lennard Shelf isotope record has been interpreted as a viable marine proxy that reflects global oceanic conditions and the burial of organic carbon in sedimentary basins elsewhere. Minor differences in the chemostratigraphic profiles notwithstanding, studies of the Canning Basin indicate depleted $\delta^{13}C$ values at or below the F-F boundary (Figure 2.6). We propose that the relative depletion reflects a sudden decline in primary productivity at the end of the Frasnian, much like negative excursions observed at other mass extinction boundaries (e.g. Zachos et al., 1989; Holser, 1997; Galli et al., 2005; Stanley, 2010).

Despite the absence of lithological evidence for the well-known Kellwasser events, two positive $\delta^{13}C$ excursions have been identified from four Lennard shelf outcrops that are comparable in amplitude to Late Devonian sections around the world. Well-constrained biostratigraphy and magnetostratigraphy in the three stratigraphically expanded sections helped to constrain the Upper Kellwasser carbon isotope excursion (maximum values) to MN Zone 13b and thus differentiate it in time from the F-F boundary. These results suggest that major environmental and biotic stressors on the global marine carbon pool leading up to a mass extinction may have diminished before the F-F boundary itself. As a result, isotopic records with prolonged excursions into the Famennian may be experiencing a lag effect due to isolation of the DIC pool in more restricted, shallow-marine basins. These results demonstrate that isotopic data alone are insufficient to determine the position of a major mass extinction boundary in geological time. However, integrated datasets, such as the one presented in this study, demonstrate that $\delta^{13}C$ excursions, at least within a basin, can be used as chronostratigraphic markers and thus have utility for correlation.

Geochemical data for the Upper Kellwasser interval are most consistent with the interpretation that a globally warm climate and eustatic highs during the Late Devonian led to the formation of bottom-water anoxia in deep ocean basins that periodically spread into shallower settings on the Lennard Shelf via transgressive pulses and/or the development of eutrophic conditions due to phosphorous regeneration. These conditions are arguably widespread, but the Lennard Shelf is unique in that it records the global signal (geochemically) without accompanying lithological evidence (i.e. black shales). A similar scenario for the Lower Kellwasser is postulated although the role of eutrophication remains to be determined; as such, further trace element analyses are needed.

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CHAPTER III

High-Resolution Carbon Isotope Chemostratigraphy of Upper Devonian Carbonates from the Lennard Shelf, Canning Basin, Western Australia

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ABSTRACT

Until recently, carbon isotope chemostratigraphy for the Devonian was best known from studies throughout Europe, and to a lesser extent, from North America. Here we present the first carbon isotope composite curve for the Upper Devonian (Frasnian Zone 1 to the Famennian *marginifera* Zone) in Western Australia, derived from the reefal platform and basin system located along the northern edge of the Lennard Shelf in the Canning Basin, Western Australia. A high-density sampling strategy combined with conodont biostratigraphy allowed us to better constrain the timing of isotopic excursions and resolve higher frequency, shorter-term events that are typically unrecognized.

In this study five major and five minor positive $\delta^{13}C$ excursions have been identified that can be used to aid stratigraphic correlations. Despite the lack of associated black shale deposits, the major excursions are interpreted to be of global significance as they exhibit comparable patterns and are correlative with geochemical events in other parts of the world; namely the *falsiovalis*, *punctata*, Lower Kellwasser, Upper Kellwasser, and Condroz/Enkeberg events. The minor excursions, described for the first time from the Lennard Shelf, appear to be at least regional (shelf-wide) phenomena, but further investigation is required to determine their global nature. This work has implications for understanding global changes in ocean chemistry and for examining the relationship between coeval isotope excursions, extinctions, and paleoenvironmental events.

INTRODUCTION

Late Devonian (Frasnian and Famennian) strata record a dynamic interval in Earth history and have subsequently been a major focus of stratigraphic and geochemical study (Geldsetzer et al., 1993; Joachimski & Buggisch, 1993; Playford et al., 1984; Wang et al., 1996; Joachimski et al., 2002). Although this period of time is best known for the mass extinction at the Frasnian-Famennian (F-F) stage boundary, the rock and fossil records of the Upper Devonian document a series of what are postulated to be global chronostratigraphic events; most relevant to this study are the *falsiovalis* event at the base of the Frasnian, the *punctata* event in the middle Frasnian, the Kellwasser events in the upper Frasnian, and the Condroz and Enkeberg events in the middle Famennian (House, 2002). In general, these events are coincident with major faunal turnover, perturbations to the marine geochemical record, changes in global climate, sea level fluctuations, changeovers from stressed to normal marine oceanic conditions, and the widespread deposition of black shale horizons (Sandberg et al., 1988; Goodfellow et al., 1989; Buggisch, 1991; Joachimski and Buggisch, 1993; Walliser, 1996; Wang et al., 1996; Bratton et al., 1999). However, the absence of organic-rich material in several coeval sections (e.g. Poland, Austria, and Australia) has made it difficult to recognize these events in outcrop and has led to increasing doubt over their global nature. Moreover, most of what we do know comes from studies throughout Europe and in North America, localities on only one of two Devonian paleo-supercontinents (Laurussia) (Figure 3.1). Despite decades of research in these regions, the nature and extent of Late Devonian events remain unsettled.

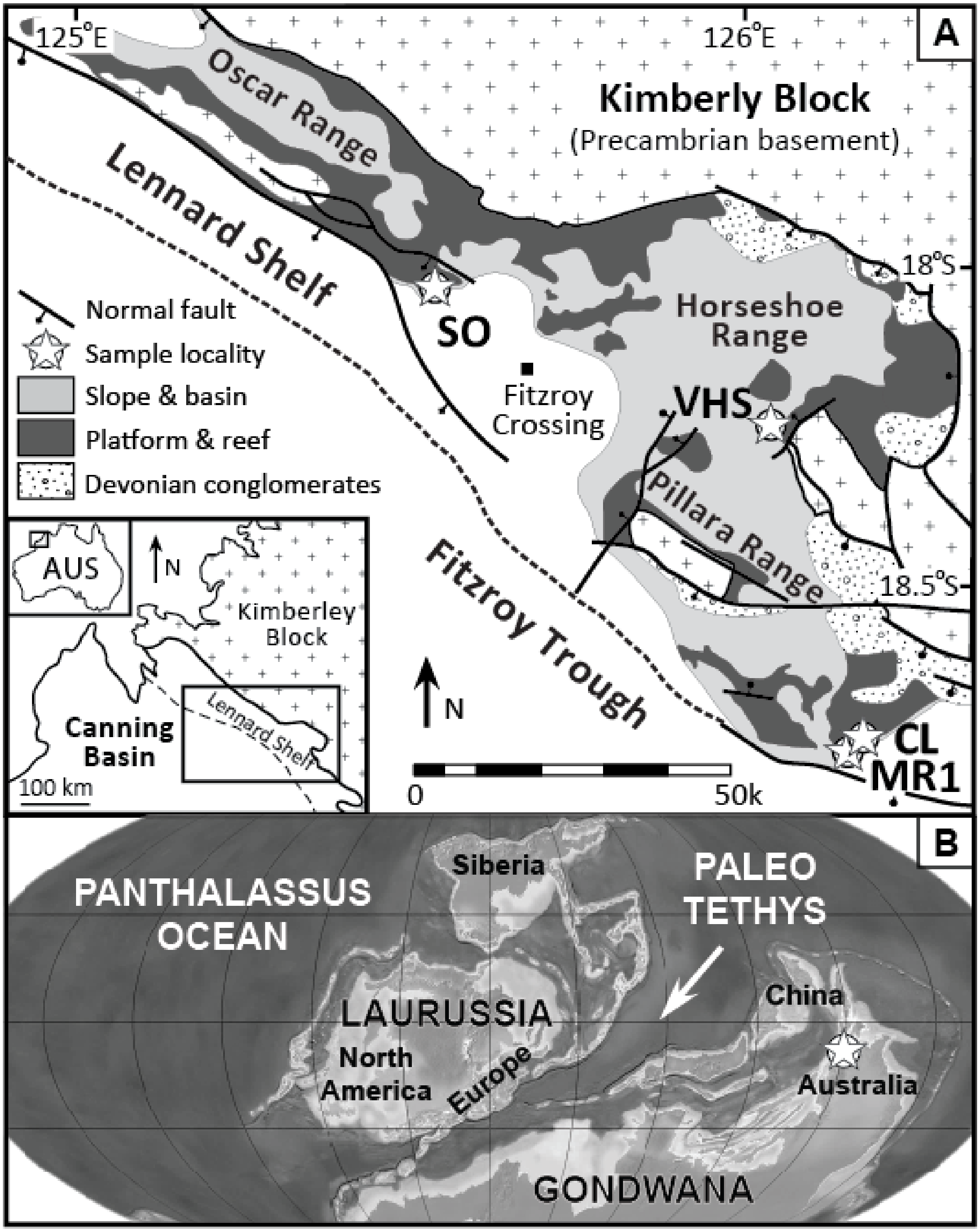

Figure 3.1: A) Map of the Devonian carbonate system along the Lennard Shelf in the Canning Basin, Western Australia, showing sample localities (modified after Playford et al. 2009). SO = South Oscar section, VHS = Virgin Hills section, CL = Casey Falls section, MR1 = McWhae Ridge core. B) Plate reconstruction of the Late Devonian (modified after Blakey, 2008).

Arguably one of the best ways to test global extent is to compare datasets from geographically separated sedimentary basins, particularly those on different continents and separated by large oceanic basins (Racki, 2005). Our study area, along the northern margin of the Canning Basin in Western Australia, is well-suited for investigating the extent of Late Devonian events because it was once part of the paleo-supercontinent Gondwana (Figure 3.1). The goal of this research is to use high-resolution secular trends in $\delta^{13}C$ values derived from slope settings in the Lennard Shelf carbonate system to construct the first composite carbon isotope curve for Upper Devonian (Frasnian and Famennian) strata in the Canning Basin. Using this new record, we will test the global extent of Late Devonian events by comparing our isotopic results with those reported by studies around the world. The high-resolution nature of the composite curve also allows us to better constrain the timing of isotope excursions and examine their potential relationships with changes in the paleoenvironment including sea level, climate, ocean circulation, and faunal turnover. We chose to employ carbon isotope chemostratigraphy because it has been proven to be a powerful tool for making regional and global correlations (e.g. Vahrenkamp, 1996; Menegatti et al., 1998; Montañez et al., 2000; Saltzman, 2002), for interpreting changes in the paleo-environment (Magaritz, 1989; Holser, 1997; Prokoph and Veizer, 1999; Chen et al., 2002; Immenhauser et al., 2003) and for identifying major biotic crises (Kump and Arthur, 1999).

The State of Devonian Carbon Isotope Research

In Laurussia, where stratigraphically extensive and composite secular curves for the Frasnian and Famennian have been reported, some results are inconsistent and/or have a relatively low temporal resolution that does not allow for the recognition of isotopic perturbations at or below the zonal level (Racki, 2005). Two of the most comprehensive composite curves currently available--one derived from whole-rock analyses of samples from sections in central and southern Europe, the other from brachiopod calcite collected from areas in Europe, N. America, China, and Russia--do not recognize the *punctata* event within Frasnian conodont Zones 4-6 (van Geldern et al., 2006; Buggisch and Joachimski, 2006). The character of the excursion also remains under debate as the studies that do recognize the event differ in their reported magnitudes and directions (e.g. Racki et al., 2004; Yans et al., 2007). The duration and stratigraphic position of the older *falsiovalis* excursion is also not well constrained (van Geldern et al., 2006; Buggisch and Joachimski, 2006), raising questions about its potential connection with the deposition of black shales and dysoxic conditions in the lower Frasnian (Buggisch, 1972; Belka and Wendt, 1992; House, 2002; Lüning et al., 2004; Buggisch and Joachimski, 2006) or with events at the Givetian-Frasnian (G-F) boundary such as the start of a major transgression and the extinction of many invertebrate fauna (House, 1985; Walliser, 1985; Ebert, 1993). Furthermore, isotopic studies from around the world continue to differ in their timing of the Upper Kellwasser excursion, placing maximum values below-, or coincident with-, or above the F-F boundary (Joachimski et al., 2002; Xu et al., 2003; Buggisch and Joachimski, 2006; George et al., 2014; Chapter 2, Hillbun et al., in prep. a). Even more uncertain is the nature of the positive excursion associated with the Condroz and/or Enkeberg bio-events, with relatively less known about its extent since it has only been reported from two sections in Germany (Buggisch and Joachimski, 2006). Clearly, much remains to be answered about the timing, extent, and relative significance of events in the Late Devonian.

Prior to this study, carbon isotope chemostratigraphy of Upper Devonian strata from the Lennard Shelf in the Canning Basin was in its infancy; $\delta^{13}C$ records are known only from a few studies, almost all of which are limited to the interval of time directly surrounding the F-F boundary (Joachimski et al., 2002; Stephens and Sumner, 2003; George et al., 2014). The pioneering work by Stephens and Sumner (2003) showed that carbon isotope values based on bulk-rock carbonates exhibit primary marine signatures and are reliable for intra-basinal correlations. However, samples for their study were taken approximately once every 10 meters, with higher density sampling only at the F-F boundary. A second, higher resolution (~1 sample per 20 cm) study analyzed deep-water strata at McWhae Ridge and Casey Falls, and using these results Joachimski et al. (2002) correlated Lennard Shelf strata to Upper Devonian carbon isotope curves from Europe and North America. However, the sections at both of these localities focus only on the F-F boundary and are relatively thin, neither one in excess of 10 m. Until now, a continuous, high-resolution carbon isotope record has yet to be produced for the Upper Devonian in the Lennard Shelf system.

In this paper, we reconstruct the carbon isotope history of Upper Devonian strata (Frasnian Zone 1 to Famennian *marginifera* Zone) in the Lennard Shelf and present the first composite curve for Gondwana. High-resolution chemostratigraphy, constrained primarily by biostratigraphy, has allowed us to expand upon previous work, particularly in the Canning Basin, in both time and detail. First, this study broadens focus from the F-F boundary to the entirety of the Frasnian and most of the Famennian, allowing us to better examine isotopic trends preceding and following one of the most devastating mass extinctions in Earth history. Second, our high-density sampling strategy allows us to better define the nature and stratigraphic position of isotopic excursions, as well as to resolve shorter-term events that often go unrecognized. Our composite $\delta^{13}C$ curve will be compared with coeval isotope records from sections throughout Laurussia. The results will be discussed in relation to the deposition of organic carbon, to previously documented extinction horizons, to global changes in sea level (Johnson et al., 1985), to ocean circulation and the global carbon cycle, and to a lesser extent, to paleo-continental configuration.

INVESTIGATED SECTIONS

Four stratigraphically overlapping sections were investigated from the Lennard Shelf in the Canning Basin (Figures 3.1 and 3.2). During the Late Devonian, these sections were part of a reefal platform and slope system located about 15° south of the equator on eastern Gondwana (Playford et al., 2009). Today, the exhumed network of outcrops extends approximately 350 km along the northern margin of the Canning Basin and exposes well-preserved sections ideal for detailed chemostratigraphic studies. The investigated sections reflect deposits from a range of slope environments (upper, middle, and lower) in various paleogeographic settings (Table 3.1). Slope deposits were specifically chosen for this study because they are relatively well-preserved, are ideal for conodont biostratigraphy, and have been shown to record primary marine $\delta^{13}C$ values useful for both regional and global correlations (Chapter 1, Hillbun et al., in revision).

The 585 m-thick South Oscar (SO) section (Figures 3.1 and 3.2) in the southeastern part of the Oscar Range is relatively expanded and contains middle-to-upper slope deposits. The base of the section is no older than Frasnian Montagne Noire (MN) Zone 5, while the top of the section is no younger than the Famennian *marginifera* Zone (Table 3.1). The F-F boundary appears to be conformable and has been arbitrarily placed (in this study) at the stratigraphic midpoint between the latest known Frasnian strata at 228.7 m and earliest known Famennian strata at 233 m.

The Virgin Hills (VHS) section (Figures 3.1 and 3.2) was measured in the Horse Springs Range and contains ~102 m of lower-to-middle slope deposits that are relatively condensed compared to the SO section. VHS ranges from MN Zone 6 to within the *crepida-marginifera* Zones (Table 3.1) and is conformably underlain by three meters of strata not sampled in this study, recording MN Zones 1 through 5 (Klapper, 2007). The F-F boundary also appears to be conformable and

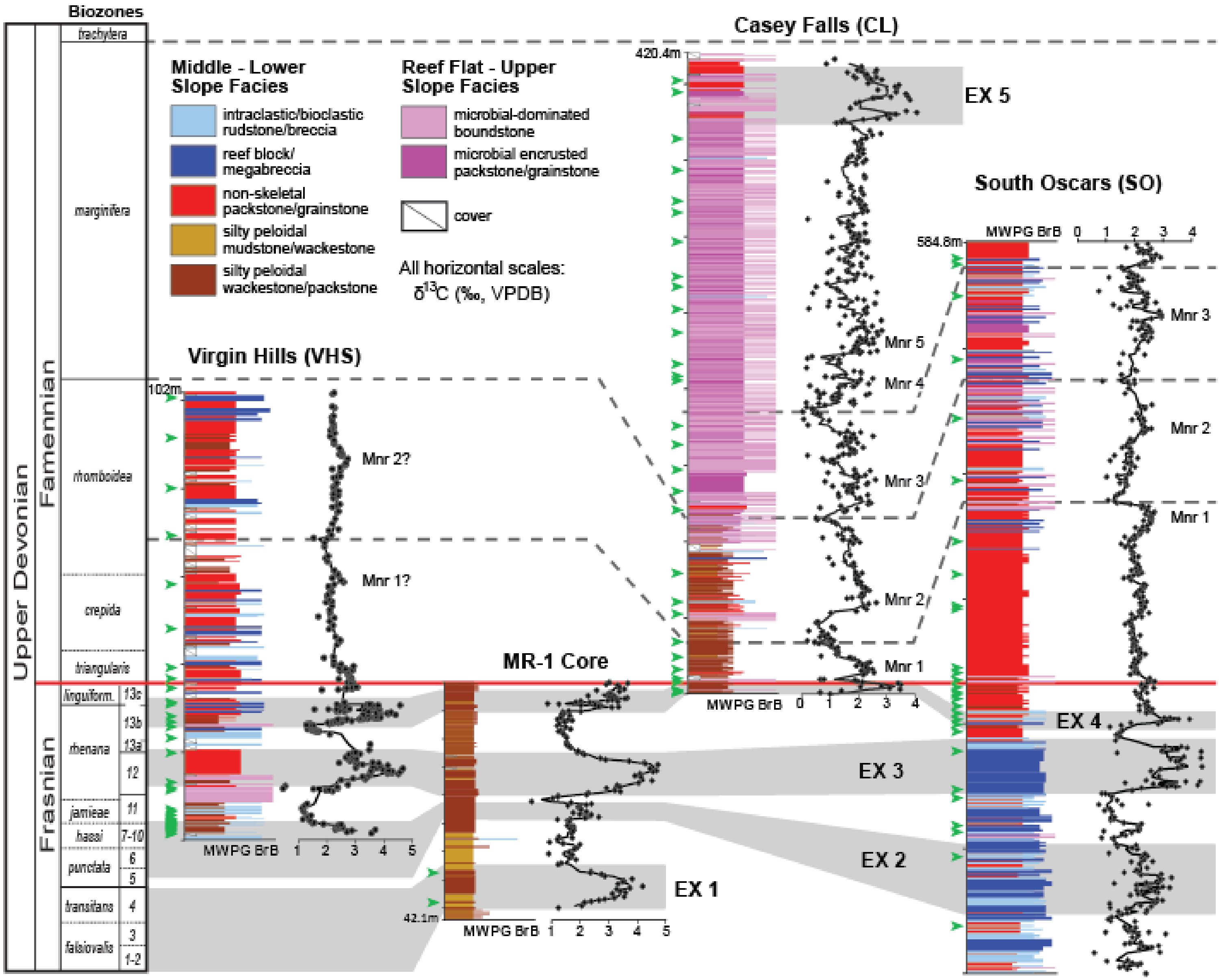

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Figure 3.2: Correlation of $\delta^{13}C$ values measured on bulk-rock carbonates from slope sections in the Lennard Shelf system. Data shown represent only the interpreted primary marine values that were used to construct the Upper Devonian composite curve (Figure 3.3). Gray shaded bars highlight major excursions, dashed gray lines show additional isotope tie-points constrained by biostratigraphy (green arrows show conodont picks) and corroborated by magnetostratigraphy (Hansma et al., 2015). For stratigraphic sections: M = mudstone, W = wackestones, P = packstone, G = grainstone, R = rudstones, Br = megabreccia, and B = boundstone.

Table 3.1: Sample dataset showing stratigraphic thickness, relative conodont age (see Figure 3.2), paleogeographic setting, depositional environment (EOD), number of samples collected, and total isotopic analyses completed for each section and core measured (*denotes cores, all others are outcrop transects). The number of analyses interpreted to reflect primary marine values and the number of diagenetically modified values are also shown. The latter were removed from the analyzed dataset. See Figure 3.1 caption for non-abbreviated section names.

Locality	**Thickness**	**Relative Age**		**Paleogeographic Setting**	**EOD**	**Samples Collected**	**Isotopic Analyses**		
		Section base	**Section top**				**Total**	**Preserved**	**Altered**
SO	584.4 m	Within Zones 5-10	upper *marginifera*	isolated, open marine	middle - upper slope	639	616	412	204
VHS	102 m	Zone 6	within *crepida* - *marginifera*	land attached, broad embayment	lower - middle slope	292	296	255	41
CL	419 m	Zone 13a	upper *marginifera*	land attached, reef spine	lower - upper slope	589	461	379	82
MR1*	42.1 m	Within Zones 1-4	*triangularis*	land attached, reef spine	lower slope/basin	155	153	146	7

constrained within a 20-cm interval by the last appearance of Frasnian fauna at 35.75 m and the first appearance of Famennian fauna at 35.95 m.

The 420 m-thick Casey Falls (CL) section (Figures 3.1 and 3.2) was measured at the southern end of the Lawford Range and extends from MN Zone 13a to the *marginifera* Zone (Table 3.1). The base of the section contains highly condensed lower-slope deposits while the upper part of the section is characterized by upper-slope facies dominated by encrusted microbial boundstone. The F-F boundary at CL has relatively less biostratigraphic control; it is constrained to within a 5.7-m interval and has been placed at the 7.5-m mark, just below the lowest observed occurrence of P. *subperlobata* and at the base of the first microbial boundstone.

A continuous 42 m-thick drill core (MR1) (Figures 3.1 and 3.2) through distal slope deposits was taken from the west side of McWhae Ridge at the southern end of the South Lawford Range (Playford, 1980). Similar to the base of the CL section, MR1 is highly condensed. The core is interpreted to contain deposits from the latest Givetian to the latest Frasnian or earliest Famennian (Table 3.1). The first three meters of the core are interpreted to be latest Givetian in age based on biomarker analysis (Tulpani et al., in review), and conodonts indicating MN Zones 1-4 were collected just above this. A ground-truthed walk-out correlation and integrated paleomagnetic data (E. Tohver, *personal communication*) suggest that the F-F boundary is located within the upper few meters of the core.

METHODS

Field and Laboratory Methods

The investigated sections (Figure 3.2), measuring a total of ~1150 m, were described in detail for stratigraphic evaluation. For isotopic analyses ($\delta^{13}C_{carb}$ and $\delta^{18}O$), hand samples and drilled core plugs (one-inch-wide, 2.5 cm) were collected from outcrop sections (SO, VHS, CL) and a Minex portable drill was used to continuously collect core (1.32"/32.5mm diameter) from the MR1 locality. Sample collection occurred at sub-meter to meter stratigraphic spacing, with the aim of capturing facies changes where possible. A total of 1526 isotopic analyses, performed at the Stable Isotope Research Facility at the University of Washington, derive from bulk-rock analysis of targeted marine cements, micrite, and non-skeletal grains following the methodology of Stephens and Sumner (2003). The analytical precision of $\delta^{13}C_{carb}$ and $\delta^{18}O$ analyses based on sample replicates and laboratory standards is $\leq \pm 0.1$ ‰. Data were corrected using laboratory standards and are reported here in standard delta notation relative to VPDB.

Constructing the Composite Curve

In an effort to construct the most accurate composite curve (Figure 3.3), 334 isotopic analyses were removed from the dataset because they fell outside the range of previously reported values for Devonian sea water and marine cements (Walls et al., 1979; Dunn et al., 1985; Kerans, 1985; Hurley and Lohmann, 1989) and/or were derived from less well-preserved samples interpreted to have a high probability of diagenetically modified values (see Chapter 1). Correlation of the resulting four isotope records was constrained by conodont biostratigraphy and corroborated by prior magnetostratigraphic work (Hansma et al., 2015) (Figure 3.2). Following the approach laid out by Buggisch and Joachimski (2006), each isotope datum was then assigned an absolute age date based on biozone boundaries, and the nonparametric locally weighted regression method "Locfit" (Loader, 1997, 1999) was applied to the data. We used the 2013 timescale from the International Commission of Stratigraphy (Cohen et al., 2013) to assign the most recent age dates to the conodont biozone boundaries.

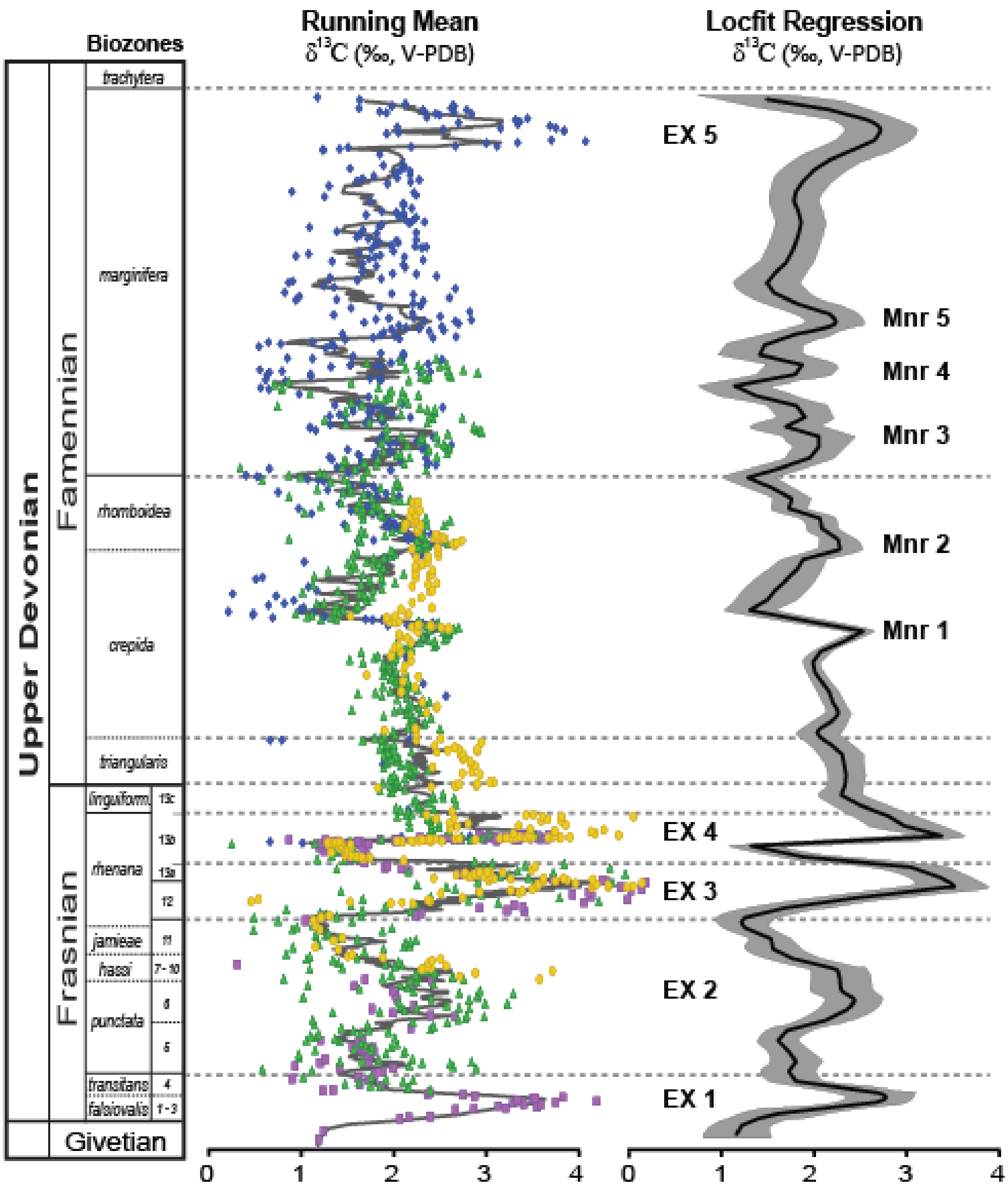

Figure 3.3: Compilation of Upper Devonian $\delta^{13}C$ values from well-preserved bulk-rock samples; blue diamonds - CL samples; green triangles - SO samples; yellow circles – VHS samples; purple squares – MR1 samples. All data were used to calculate running mean and locfit (with 99% confidence interval) curves. See Figure 3.2 for explanation of biostratigraphic zones.

The largest uncertainties in the composite curve are attributed to 1) the interpolation between isotope datums with robust age determinations, which is based on sediment thickness and facies assuming constant and continuous deposition, and 2) the accuracy of the age assignments to the top and bottom of each section. Furthermore, it should be noted that an accurate comparison between the Lennard Shelf secular curve and coeval isotope records globally may be hindered by differences in sampling density, sedimentation rates, the occurrence of diastems, and biostratigraphic resolution.

RESULTS

The composite $\delta^{13}C$ record for the Lennard Shelf recognizes five major and five minor positive isotope excursions in the Upper Devonian (Figure 3.3; Table 3.2), none of which are coincident with the deposition of black shale horizons in our sections. Based on conodont biostratigraphy the five major isotope excursions are constrained within MN Zones 1-4 (*falsiovalis-transitans*), 5-10 (*punctata-hassi*), 11-13a (*jamieae*-late *rhenana*), 13b-13c (*linguiformis*), and the upper *marginifera* biozone, respectively. The five smaller, yet still distinct, isotope excursions occur within the upper *crepida* to *marginifera* Zones in the Famennian. Two of the major excursions (Figure 3.2, excursions 2 and 5) and all minor excursions are described for the first time from the Lennard Shelf. The five major excursions are interpreted to be of global significance as they are observable in other parts of the world and are chronostratigraphically correlative based on our biostratigraphic constraints (Figure 3.4). The minor excursions appear to be at least regional phenomena as their correlation in the Lennard Shelf system is supported by conodont biostratigraphy and magnetostratigraphy; further investigation is required to determine their global nature, if any.

Table 3.2: Comparison of carbon isotope data (Amp = amplitude, Max = maximum value) for the five major excursions reported in this study. $\delta^{13}C$ values are relative to VPDB. N/A = not available.

Section	Excursion 1		Excursion 2		Excursion 3		Excursion 4		Excursion 5	
	Amp.	Max.	Amp.	Max.	Amp.	Max.	Amp.	Max.	Amp.	Max.
MR1	+3‰	+4.2‰	+1.1‰	+2.7‰	+3.7‰	+4.7‰	+2‰	+3.6‰	N/A	
SO	N/A		+2.1‰	+3.3‰	+3.4‰	+4.4‰	+2.5‰	+3.9‰	N/A	
VHS	N/A		+2‰	+3.7‰	+3.5‰	+4.7‰	+3.2‰	+4.6‰	N/A	
CL	N/A		N/A		N/A		+2.8‰	+3.5‰	+2.8‰	+4‰

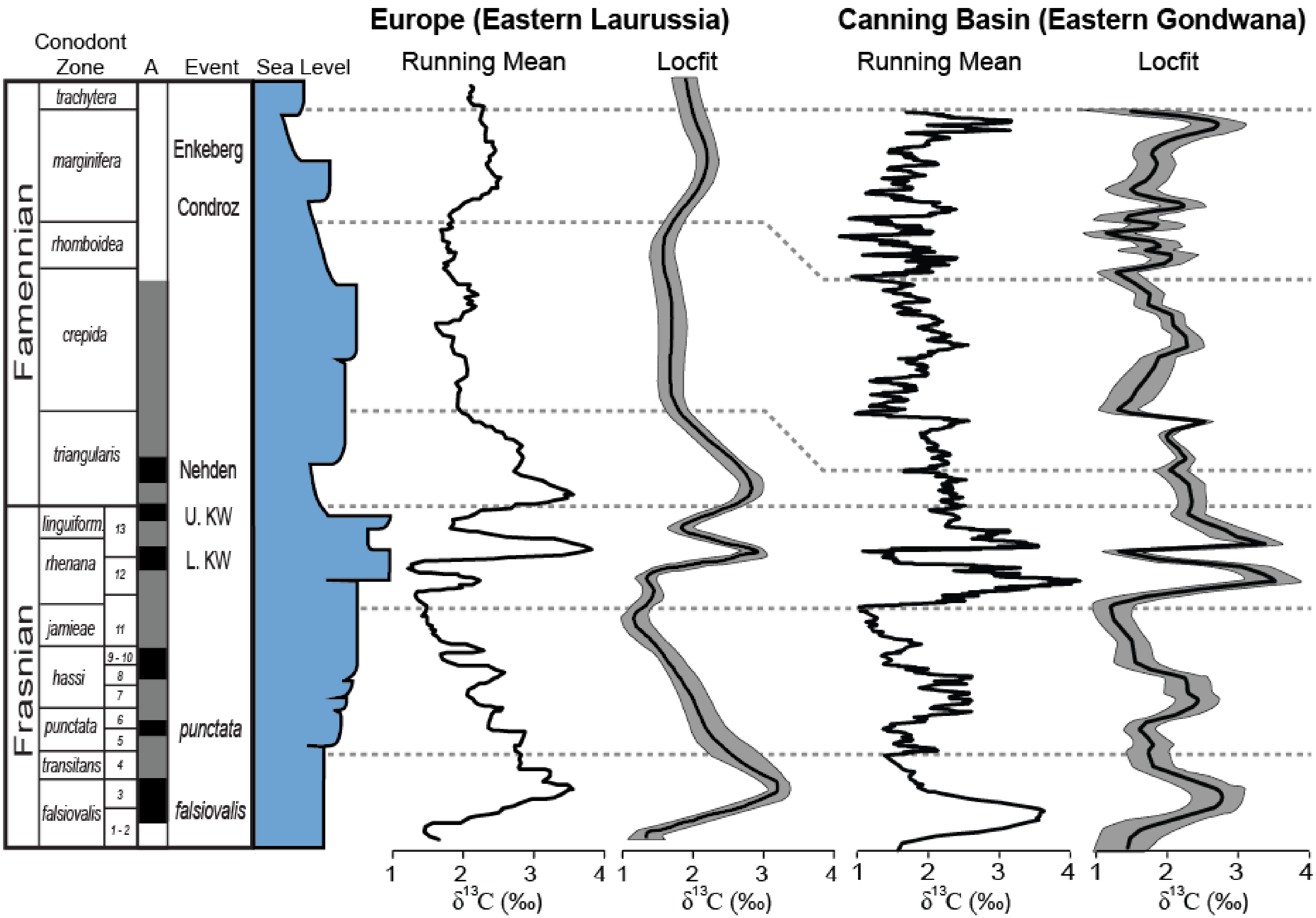

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Figure 3.4: Comparison of European and Lennard Shelf composite $\delta^{13}C$ curves for the Upper Devonian (modified after Buggisch and Joachimski, 2006, to include results from this study); with major biotic events (House, 2002), changes in sea-level (Johnson et al., 1995, 1996), and occurrences of black shale deposits in Europe/North Africa and Laurentia (A) (Buggisch and Joachimski, 2006). Isotope values are relative to VPDB.

Excursion 1: upper Givetian - lower Frasnian

Carbon isotope data for the uppermost Givetian and lower Frasnian are known from the distal slope deposits of MR1. Near the base of this core (Figure 3.2), a major positive excursion (EX 1; Figure 3.3), with an amplitude of +3 ‰ and max values as high as +4.2 ‰ (Table 3.2), occurs in a skeletal-poor, silty peloidal wackestone facies. Conodont biostratigraphy constrains EX 1 to within MN Zones 1-4. While we can't exclude the possibility that sample values may have begun to increase as early as the latest part of the Givetian, the return from maximum to baseline values occurs before the end of conodont Zone 4.

Excursion 2: middle Frasnian

The second major positive excursion (EX 2; Figure 3.3) is documented in the middle Frasnian from three sections (SO, VHS, MR1), all with baseline $\delta^{13}C$ values between +1 ‰ and +1.5 ‰. In SO, EX 2 occurs within breccia-dominated middle-slope deposits, has an amplitude of +2.1 ‰ (Table 3.2), and is constrained to within Zones 5-10. In siltstone-dominated lower slope deposits at the very base of VHS, only the downward limb of EX 2 is present; it is constrained to within Zones 6-10 and has an amplitude of at least +2 ‰, with peak values at least as high as +3.7 ‰. In MR1, a positive excursion (+2.7 ‰ max values) is observed in similar silt-dominated facies. Although conodont control is lacking for this interval of the core, the excursion is interpreted to be EX 2 because age constraints at the top and bottom of the core allow for paleomagnetic correlation (E. Tohver, *personal communication*) and isotopic comparison (Figure 3.3) with the other sections.

Excursion 3: upper Frasnian

Excursion 3 (EX 3; Figure 3.3) is documented from the lower part of the upper Frasnian, with data available for SO, VHS, and MR1 (Figure 3.2). Average baseline values are between +1 ‰ and +1.5 ‰ for all sections, but sharply increase to maximum values up to +4.5 ‰ in SO and +4.7 ‰ in VHS. This excursion was observed in MR1, based on magnetostratigraphic correlation (E. Tohver, *personal communication*) and isotopic comparison within available conodont constraints, with similar peak values and slightly larger amplitude (Table 3.2). Conodont data indicate that EX 3 in SO and VHS is within Zones 12 and 13a and is therefore time correlative to the Lower Kellwasser horizon in Europe (Buggisch, 1972; Schindler, 1990; Walliser, 1996) and the associated excursion documented in other datasets from around the world (e.g. Joachimski and Buggisch, 1993; Joachimski et al., 2002; Xu et al., 2003; Buggisch and Joachimski, 2006).

Excursion 4: uppermost Frasnian (and possibly lowermost Famennian)

All four sections exhibit a major positive isotope excursion (EX 4; Figures 3.2 and 3.3) in the uppermost Frasnian. In both SO and VHS, EX 4 is entirely within the Frasnian, below the F-F boundary (Chapter 2, Hillbun et al., in prep. a); $\delta^{13}C$ values increase from baseline (+1.3 ‰ in SO and +1.5 ‰ in VHS) to maximum values (+3.5 ‰ in SO and +4.4 ‰ in VHS) within Zone 13b (Table 3.2), and possibly Zone 13c in VHS. For both sections, elevated values begin to decrease while still in the upper Frasnian and continue to decline toward more baseline levels (+2 ‰) across the F-F boundary and into the *triangularis* Zone of the lower Famennian. In other words, there does not appear to be a positive excursion coincident with the F-F boundary in either the SO or VHS sections (Figure 3.2).

In the more condensed CL and MR1 sections (Figure 3.2), EX 4 has slightly lower maximum values (Table 3.2). While the excursion starts in Zone 13b, maximum values appear to occur at or near the F-F boundary and remain elevated into the *triangularis* Zone (Figure 3.2). However, we are unable to distinguish if EX 4 is distinct from, or time equivalent to, the F-F boundary because the upper part of the MR1 core is not well constrained (biostratigraphically) and the Frasnian Pa. *linguiformis* fauna at CL is separated from the overlying Famennian Pa. *triangularis* fauna by a 5.7 m interval lacking a conodont record. In all sections (CL, MR1, SO, VHS), only the beginning of EX 4 is biostratigraphically correlative to the Upper Kellwasser horizon in Europe (Buggisch, 1972; Schindler, 1990; Walliser, 1996) and associated isotopic datasets (e.g. Joachimski et al., 2002) (Figure 3.4).

Excursion 5: middle Famennian

Excursion 5 (EX 5) (Figure 3.3) consists of two large, but relatively short-lived positive perturbations that are observed in microbial boundstone at the top of the CL section (Figure 3.2) and are constrained biostratigraphically to the upper part of the *marginifera* Zone. The first excursion has an amplitude of +2.8 ‰ (+4 ‰ max values) and is directly overlain by a slightly smaller excursion with +2 ‰ amplitude (+3.7 ‰ peak values). It remains speculative whether EX 5 is one excursion containing a few potentially altered values, or two distinct excursions that are relatively short-lived. Correlation with the European isotope record suggests that EX 5 is one excursion containing a few potentially altered values, or two distinct excursions that are relatively short-lived.

Minor Excursions: lower – middle Famennian

Five minor positive excursions (Mnr 1 – Mnr 5; Figures 3.2 and 3.3), with amplitudes between +1 ‰ and +2.4 ‰, are present within lower-middle Famennian strata; Mnr 1 and Mnr 2 are within the upper *crepida to rhomboidea* Zones while Mnr 3, 4 and 5 are within the *marginifera* Zone. With the exception of Mnr 1, the minor excursions are associated, in part, with microbial boundstone facies. The minor excursions are most easily recognized in the SO and CL sections (Figure 3.2) where they are particularly useful for regional-scale correlations when combined with biostratigraphic and/or magnetostratigraphic control. In the VHS section (Figure 3.2), Mnr 1 and Mnr 2 are arguably absent, although for purposes of constructing the composite curve, two considerably smaller (+0.6 ‰ and +0.5 ‰ amplitudes), similar-aged isotope trends were selected for correlation.

Diagenesis

A number of physical, chemical, and biological processes have been shown to modify primary marine isotope values in carbonate rocks. This alteration is especially true in interior-seaway and platform-top settings that are frequently subjected to sea level fluctuations. In short, the factors that commonly contribute to isotopic variability include, but are not limited to, depositional environment, variable water circulation as it relates to restriction and water mass ‘aging’, meteoric exposure, changes in biological productivity, climate, evaporation, and changing ocean circulation patterns (e.g. Lloyd, 1964; Patterson and Walter, 1994; Holmden et al., 1998; Immenhauser et al., 2003; Swart and Eberli, 2005; Panchuk et al., 2006; Katz et al., 2007). However, samples collected from relatively deeper paleo-water depths in basins that experienced open marine circulation (Carpenter, 1991), such as those in this study (Chapter 1), are arguably less susceptible to the local controls inherent to shallow-water environments and to more restricted settings. Moreover, the fluctuations of $\delta^{13}C$ values in Canning Basin slope strata reported in this and previous studies (Joachimski et al., 2002; Stephens and Sumner, 2003; George et al., 2014) record secular variations in seawater $\delta^{13}C$ documenting their potential as a global chronostratigraphic tool.

Based on previous Lennard-Shelf isotope studies (Joachimski et al., 2002; Stephens and Sumner, 2003; Hillbun et al., in revision; Chapter 1, this dissertation), it is our understanding that bulk-rock values from well-preserved slope sections have a high potential to preserve a primary marine signal for inorganic carbon. Additionally, the petrology, luminescence, and $\delta^{18}O$ values from a sub-set of the samples lend support to the notion that the broad isotopic trends observed in our $\delta^{13}C$ records are primary features (Chapter 1). Petrographically, original textures are generally preserved and show no evidence of significant recrystallization. Early marine cements and micrite are primarily non-luminescent, and cross plots of $\delta^{13}C$ and $\delta^{18}O$ (Figure 3.5) lack the typical trends (Lohmann, 1982) associated with diagenetic alteration. Moreover, the observed isotopic excursions are recognizable in multiple sections along the Lennard Shelf, regardless of facies and paleogeographic setting (Figure 3.2). Thus, trends are almost certainly original.

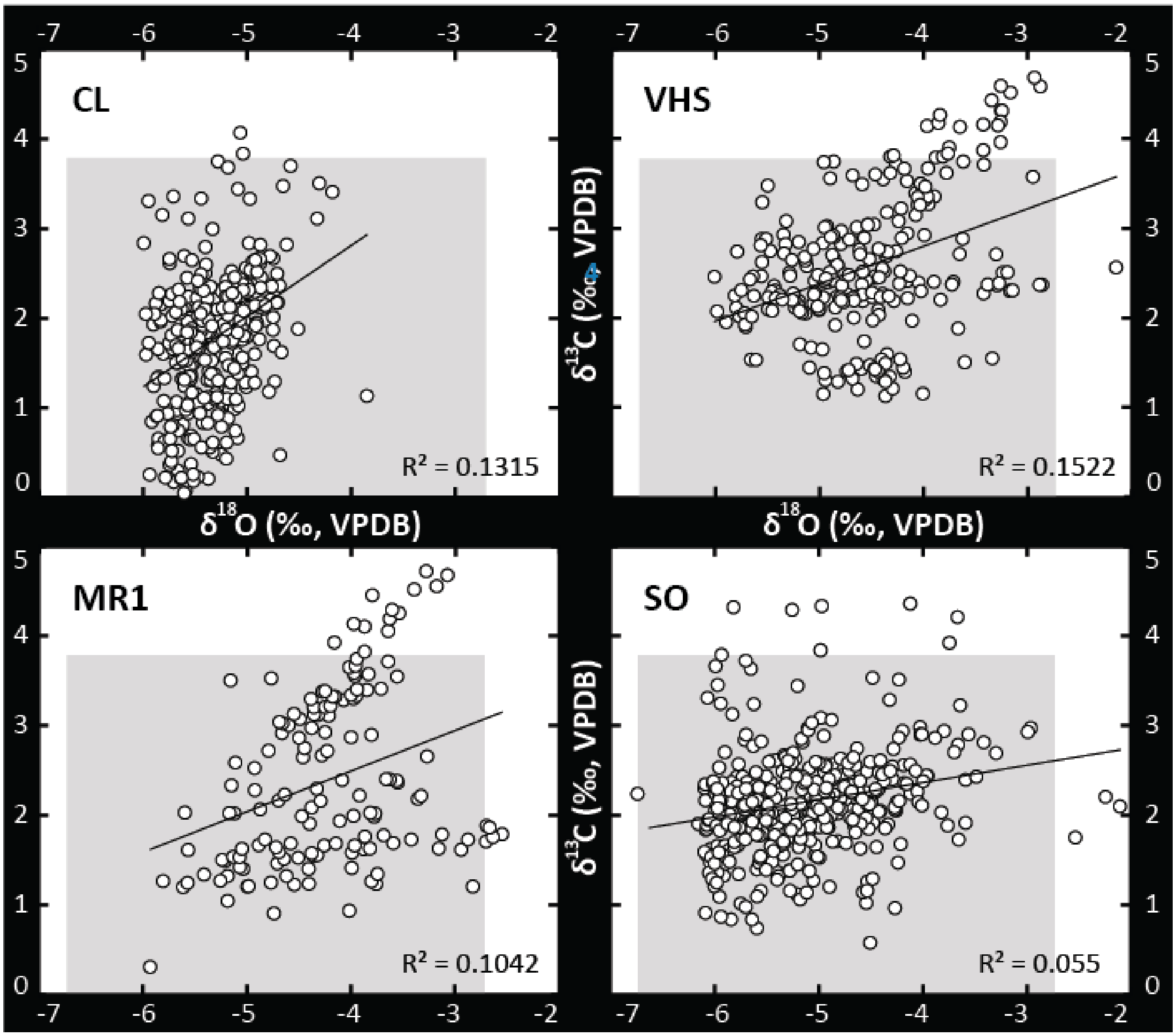

Figure 3.5: Isotope cross-plots representing bulk rock $\delta^{13}C$ and $\delta^{18}O$ values for each sample locality. Grey boxes show the approximate range of previously measured open-marine cements from the Upper Devonian in the Lennard Shelf system (Playford et al., 1984; Kerans, 1985; Hurley and Lohmann, 1989).

DISCUSSION

Correlation and Comparison of Excursions, Events and Horizons

The European composite curve by Buggisch and Joachimski, (2006) combined with high-resolution isotope data from North America (e.g. Joachimski et al., 2002; Holmden et al., 2006; Morrow et al., 2009) represent the best constrained $\delta^{13}C$ curves for the Upper Devonian in Laurussia, which can be biostratigraphically tied to a number of events (extinctions, widespread black shales, and sea level fluctuations) (Figure 3.4). The major positive carbon isotope excursions documented from these studies are interpreted to reflect substantial burial of organic carbon and the subsequent sequestration of ^{12}C from the marine dissolved inorganic carbon (DIC) pool (Wilde and Berry, 1984; Joachimski and Buggisch, 1993; Becker and House, 1994; Wignall, 1994; Algeo et al., 1995). Despite the absence of black shales in the Canning Basin sections, the carbon isotope records are comparable to the time-equivalent curves produced from the distant basins in Laurussia (Figure 3.4). This positive correlation indicates that Lennard shelf strata represent a more-or-less continuous record and that the isotopic profiles reflect primary marine values and thus changes in global carbon cycling in the ocean. Where the curves differ, the discrepancies can be largely explained by differences in sampling density and by variable local controls on the marine carbon reservoir including the presence of organic material. The curve from the Lennard Shelf has arguably more structure, which proved useful for regional correlations, and better resolution, which has helped refine the timing of some events in this study. Regional correlation of the isotope excursions with previous stratigraphic and paleontological work in the Canning Basin also provides insight on the potential roles of sea level and faunal turnover.

Major excursion 1 (EX 1) is similar in time and magnitude as the *falsiovalis* geochemical event reported by Buggisch and Joachimski (2006), but the duration represented by our sections is considerably shorter. Rather than extending into the middle Frasnian, our biostratigraphic data now constrain the return to baseline values to be in the lower Frasnian (no higher than the top of Zone 4). EX 1 also does not appear to be related to geo- or bio-events at the G-F boundary, at least in the Lennard Shelf system, but instead reflects events that occurred just afterwards in the early part of the Frasnian. For example, during deposition of strata assigned to Zone 1 (Figure 3.2), the first major sea level transgression (Elliot ridge back-stepping event) in the Canning Basin occurred (Playford et al., 2009), and there was an abrupt decline in coral faunas (Brownlaw, 2000), as well as the deposition more distally of basinal black shale deposits (Gogo Formation) interpreted to have been deposited under hypoxic conditions (Playford et al., 2009). Due to the long-ranging nature of lower Frasnian conodonts in the Canning Basin, however, further age constraint of the *falsiovalis* event, that is, limiting it possibly to Zone 1, needs to come from sections elsewhere.

We interpret excursion 2 as the *punctata* event, which has been reported relatively recently from the *transitas* to *punctata* Zones (MN Zones 4-6) in sections from Belgium (Yans et al., 2007), Poland (Racki et al., 2004; Pisarzowska et al., 2006), China (Zheng and Liu, 1997; Ma et al., 2008), western Canada (Holmden et al., 2006), and Nevada, USA (Morrow et al., 2009). The absence of this event in some other studies may be due to its transient nature (0.5–1.0 Ma duration) and thus to low sampling density (e.g. van Geldern et al., 2006) or to depositional hiatuses and stratigraphic gaps related to erosional bottom currents (Huneke, 2006). Where the *punctata* event has been recognized, however, various excursion magnitudes (1 ‰ to 6 ‰) and directions (Yans et al., 2007; da Silva et al., 2010) have been reported, and the event’s connection with a faunal extinction heavily debated (Day, 1996 and House, 2002 vs. Yans et al., 2007). Our results, in conjunction with prior paleontological work that shows a number of Lennard Shelf goniatites, corals, and key conodont species going extinct at the end of Zone 5 and within Zone 6, are most comparable with studies of slope deposits in China that document a positive excursion, on the order of 2.5 ‰, that is coincident with significant faunal turnover (Ma et al., 2006; Ma et al., 2008). A few localities in North America report similar biotic events, but the shallow, restricted nature of the basins results in amplified excursion magnitudes (Day, 1996; House, 2002; Śliwiński et al., 2011). The cause of the *punctata* excursion and associated biotic events ultimately remains unknown, but in Western Australia, they may be related to a major transgression (the Wagon Pass event) that occurred at the Zones 5-6 boundary. On a more global scale it's possible that the Alamo bolide impact, evidenced by the Alamo breccia deposited along the western margin of Laurussia (presently Nevada) during the *punctata* Zone (Sandberg et al., 2002), may have been a driving mechanism, but it remains speculative at this time. We also can't rule out the possibility that EX 2 post-dates the *punctata* event such that it is unique to the Lennard Shelf isotope record or is related to the positive excursion within the *hassi* and *jamieae* conodont Zones documented from Benner Quarry in Germany (Buggisch and Joachimski, 2006).

Excursion 3 is correlative to previously reported isotope shifts from the Lennard Shelf (Joachimski et al., 2002; Stephens and Sumner, 2003; George et al., 2014) and to the Lower Kellwasser horizon and associated extinctions and sea level changes documented throughout Laurussia (McGhee et al., 1986; Joachimski and Buggisch, 1993; Joachimski et al., 1994; and others) (Figure 3.4). In the Lennard Shelf system, the onset of EX 3 is also correlative with a third-order transgression (Classic Face event) and directly follows a major decline in corals along with the loss of several conodont species (Brownlaw, 2000; Playford et al., 2009). Ex 3 is, however, slightly larger in magnitude than those in Europe, south China, and North America, possibly because of the lack of black shales in our sections, which precludes the possibility of organic carbon remineralization and subsequent isotopic depletion.

The Upper Kellwasser event, correlated here to EX 4, has been a major focus of Paleozoic study because of its association with the Late Devonian Mass Extinction (e.g. Playford et al., 1984; Joachimski and Buggisch, 1993; Geldsetzer et al., 1993; McGhee, 1996; Wang et al., 1996; Joachimski et al., 2002; Bond and Wignall, 2008). Most studies have reported the excursion as being coincident with the F-F boundary and having peak $\delta^{13}C$ values through the lower part of the *triangularis* Zone (lower Famennian); those results that differed have been attributed to diagenesis and/or carbon remineralization (Joachimski and Buggisch, 1993; Joachimski et al., 2002; Buggisch and Joachimski, 2006). However, well-preserved isotope values from our study suggest that the Upper Kellwasser geochemical event and the F-F boundary are not coincident. The base of EX 4 in this study is correlative to the base of the Upper Kellwasser black shale horizon in Europe, but the drop in peak values is distinctly below the F-F boundary, before deposition of the Upper Kellwasser horizon ceases; in the SO section, for example, the excursion maxima occurs >25 m below the boundary. Although $\delta^{13}C$ values are still elevated above baseline values across the F-F, they are associated with a declining trend. The discrepancy in timing may be related to depositional hiatuses around the boundary (Stephens and Sumner, 2003), but more likely to variability in biostratigraphic control or to a lag in the isotopic response of more restricted basins (see Chapter 2, Hillbun et al., in prep. a, for full discussion). The revised timing, as suggested here, is supported by a multitude of faunal extinctions, both in Laurussia and the Lennard Shelf, that occur below the F-F boundary, specifically at or near the base of the Upper Kellwasser horizon (Dutro, 1981; Casier, 1987; Schindler, 1990; Feist, 1991;

Becker and House, 1994; McGhee, 1996; Walliser, 1996; Ma and Bai, 2002; Olempska, 2002; Becker and House, 2009; Klapper, 2009).

Comparison with the Buggisch and Joachimski (2006) curve reveals that EX 5 in the *marginifera* Zone (Figure 3.3) may be correlative to the positive isotopic shift roughly associated with the Condroz and/or Enkeberg bio-events as recognized by House (1985), Becker (1993), and Walliser (1996) (Figure 3.4). The apparent two-peak morphology of EX 5 lends support to the idea that the excursion is representative of two distinct extinction events. However, it is also plausible that EX 5 is a single excursion given that the negative values between the two peaks correspond with microbially dominated upper-slope facies. This correspondence could suggest that microbial communities were locally influencing the DIC pool and coincidentally causing a decrease in δ^{13}C values at the midpoint of the excursion (Andres et al., 2006; Hillbun et al., in revision, Chapter 1). In either case, EX 5 is almost certainly coincident with at least one episode of biotic turnover because a number of regional-scale extinctions in Canning Basin goniatites are observed throughout the *marginifera* Zone, including the more widespread and globally recognized extinction of *pseudoclymeniidae* in the upper part of the Zone (see Appendix 2 in Playford et al., 2009).

Given the magnitude of EX 5, which is considerably greater in this study than those initially reported by Buggisch and Joachimski (2006) from time equivalent sections in Germany, the excursion merits future investigation as it may be more important than previously thought. In the Lennard Shelf, for example, EX 5 may be related to the final collapse of reefal systems near the end of Famennian. While the global decimation of reef communities elsewhere in the world is generally tied to the Hangenberg event at the end of the Devonian (Walliser, 1996), the demise of reefs in Western Australia happens earlier, within the *expansa* and *praesulcata* Zones

(Playford et al., 2009), and may therefore have a connection with the events that directly precede it (i.e. EX 5).

In the Lennard Shelf composite curve there are many minor excursions, on the order of 1-2 ‰, of relatively short duration during the Famennian, suggesting some instability in either the local or global DIC pools of the ocean. On a regional scale these transient shifts, which may be related to local changes in primary productivity, add structure to the isotopic curve which is particularly useful for intra-basinal correlations. The global extent and application of these minor perturbations remain to be tested, but their repetitive and evenly spaced nature suggests that they might be Milankovitch controlled, possibly by the eccentricity cycle. Given the onset of the end-Famennian (Middle *praesulcata* Zone) ice age (Streel, 1986, 1992) it's not unreasonable to assume that changes in sea level may have been influential. During greenhouse times, Milankovitch cycles are relatively difficult to observe, but with the gradual increase in southern hemisphere glaciation during the Famennian (Caputo, 1985; Caputo and Crowell, 1985), changes in sea level, such as those tied to the growing and shirking of polar ice caps, become more prominent (Montañez et al., 2007). Although there is no obvious sedimentological evidence for short-term transgressive-regressive cycles in the microbial boundstone where the excursions occur, minor changes in sea level at thermocline depth could affect microbial growth which in turn could affect the local DIC pool.

Possible Excursion Mechanisms

Differences in expression of Late Devonian events (isotopic and geologic) may be explained by differing paleogeographies, specifically as it relates to the paleo-position of distant basins in Laurussia and Gondwana. The Devonian was a time of active tectonism associated with the convergence of supercontinents and the subsequent constriction of the Paleo Tethys seaway, the rise of mountain belts in Europe and North America, and ultimately the formation of shallow interior seaways and intra-shelf basins (Ziegler, 1989; Scotese and McKerrow, 1990; Golonka, 2002; Ford and Golonka, 2003). These changes likely had an effect on ocean circulation and climate patterns, which in turn led to the restriction of many sedimentary basins.

Varying degrees of communication between shallower, more restricted water masses and the global marine DIC pool could account for the observed differences in excursion magnitudes and durations between studies, as well as for the heterogeneous deposition of black shales in some areas. For example, during times of stress leading up to any one of the observed major perturbations in the marine $\delta^{13}C$ record, it is reasonable to suggest that the global ocean was experiencing only dysoxic conditions whereas the more restricted basins, such as those in Laurussia, may have been closer to anoxic. In the latter case, there is greater preservation potential for organic material, and the reduced circulation could result in the amplification of isotopic values. Such a scenario may explain the data reported for the *punctata* event in North America where black shales are prevalent and $\delta^{13}C$ values are as high as +6 ‰. During periods of recovery, when the global ocean started to become more oxygenated, it's conceivable that the restricted basins remained poorly ventilated, at least for some lag period. This could explain the prolonged changes in $\delta^{13}C$ values associated with the *falsiovalis* and Upper Kellwasser excursions documented from localities in Laurussia.

Despite differences in expression, the major isotopic signals reported from the Upper Devonian in Laurussia are observed from sedimentary basins on both paleo-supercontinents, including those in which almost no black shales have been deposited. Observed disturbances in the carbon isotope record may therefore reflect the heterogeneous accumulation of organic carbon in more restricted basins (only) such as those in Laurussia, or it's possible that burial was more widespread, albeit confined to undocumented deeper-water settings and/or subjected to later erosion in some areas. In any case, the organic material that was being deposited was great enough to influence the global signal such that sections in Western Australia appear to record the carbon sequestration that was happening elsewhere.

The correspondence of positive $\delta^{13}C$ excursions in the Lennard Shelf system to black-shale horizons in other parts of the world suggests the prevalence of low oxygen conditions and supports anoxia as a primary causal mechanism. The lack of organic rich deposits in our Lennard Shelf study and elsewhere does not refute this hypothesis but rather supports the excursions as indicators of global changes in ocean chemistry. Moreover, it's possible that our sampling localities represent environments sufficiently high on the slope to remain oxygenated despite sub-oxic conditions persisting in deeper depositional settings (e.g. Playford et al., 2009). It therefore remains plausible that Late Devonian ocean chemistry reflects carbon burial under low oxygen conditions on a global scale, but that the associated anoxia was confined to deep-ocean bottom waters or more restricted basins. It also remains unclear if the positive excursions can alternatively or in addition be attributed to increasing primarily productivity, as suggested by Algeo et al. (1995), and/or climatic cooling (Caputo and Crowell, 1985; Copper, 1986), as both can have a global impact; as such, a more detailed examination is required to determine their potential roles.

The relationship between carbon isotope excursions and changes in sea level is also poorly understood. In the Lennard Shelf system, carbon isotope data (this study) reveal a mechanistic link between positive trending $\delta^{13}C$ values and periods of transgression, similar to what has been documented from Mississippian limestones of the Madison Formation (Katz et al., 2007). However, perturbations in Late Devonian $\delta^{13}C$ records from elsewhere in the world have been correlated to almost all stages of sea level fluctuation (e.g. Johnson et al., 1985; Sandberg et al., 1988; Buggisch, 1972,1991; Johnson et al., 1996). These inconsistencies between studies are attributed (at least in part) to the difficulty in discerning between global eustasy and local controls on sea level. For example, while the global ocean may be rising in response to the thermal expansion of water, individual sedimentary basins may also be experiencing regional sea-level fluctuations due to tectonic uplift and/or subsidence. This is particularly true in the Canning Basin where Late Devonian faulting has been proposed as a driver of regional transgression (e.g. Hardie et al., 1991; Read et al., 1991). While a tectonic control on sea level cyclicity cannot be ruled out, it is unlikely given it would have to act regularly over the length of the Lennard Shelf (~500 km) by episodic subsidence due to faulting on a small vertical scale (<10 m) (Playford et al., 2009).

CONCLUSION

Integrated carbon isotope chemostratigraphy and biostratigraphy of the Lennard Shelf provides the first composite $\delta^{13}C$ curve for the Upper Devonian in Western Australia. Five major and five minor positive $\delta^{13}C$ excursions have been identified that permit robust correlations on a regional scale. Further correlation of the five major excursions with similar-aged sections in Europe, Canada, the United States, North Africa, and China validates (at least) the major excursions as global geochemical events. Unlike many of the positive excursions documented from elsewhere in the world, none of the excursions recorded here from the Canning Basin coincides locally with black shales or otherwise organic rich strata.

A high-density sampling strategy allowed for the first recognition of the *punctata* and Enkeberg and/or Condroz geochemical events in the Lennard Shelf system. Well constrained conodont biostratigraphy, together with continuous and stratigraphically expanded sections, revealed that the Upper Kellwasser excursion occurs distinctly lower than the F-F boundary in the Canning Basin, and also helped to refine the timing of the relatively older *falsiovalis* excursion.

The composite carbon isotope curve presented here is currently the only Upper Devonian record from the paleo-supercontinent of Gondwana. Moving forward, a standardized composite isotope record for the Devonian representing both supercontinents is greatly needed. To construct such a curve, more high resolution records are required, especially from localities within Gondwana. A composite curve would help resolve issues regarding timing, isotopic character, and the relative role of global and local controls

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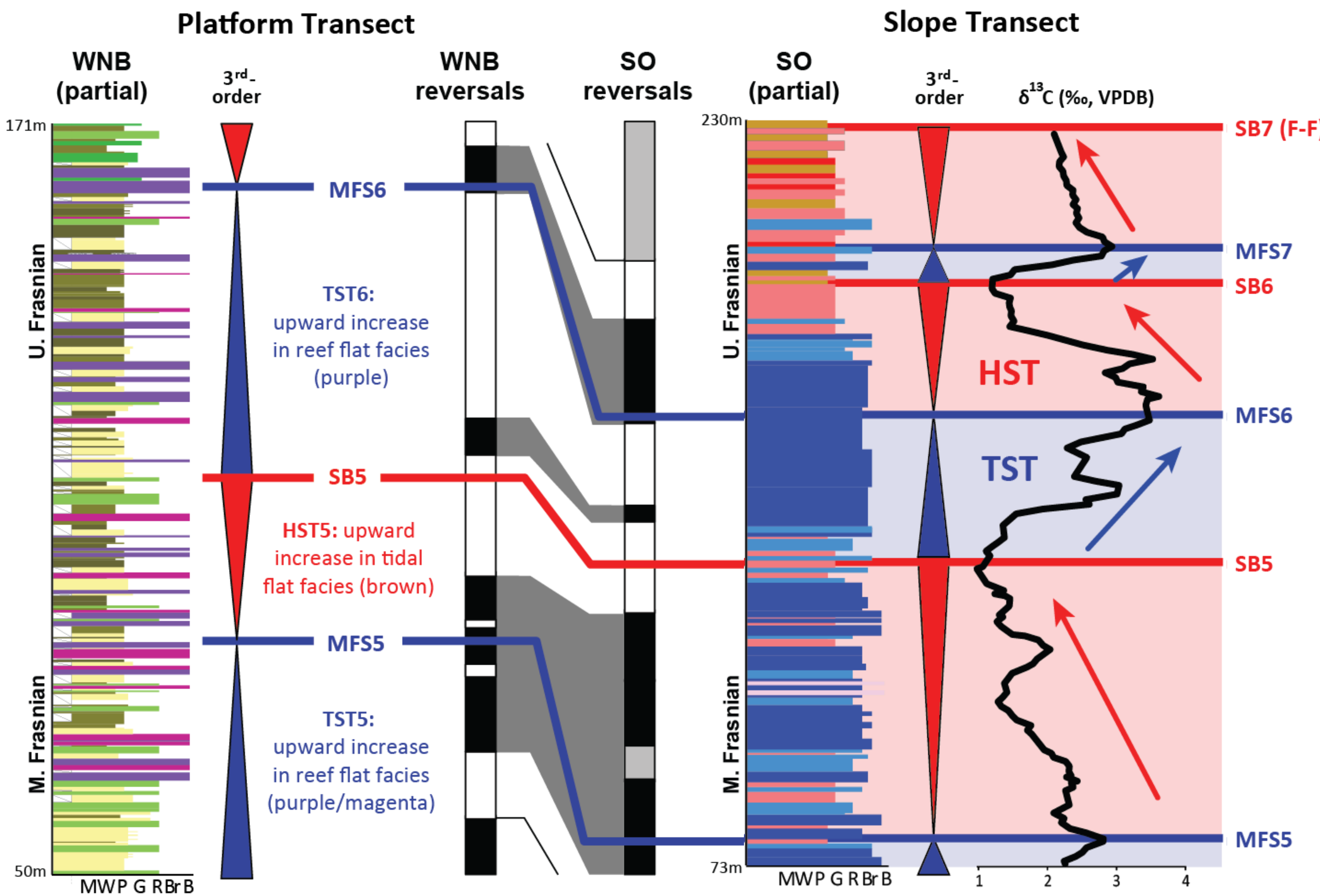
PART 1 CONCLUSION

Carbon isotope chemostratigraphy of the Lennard Shelf has proved to be a reliable tool for developing integrated chronostratigraphic frameworks and for making both regional- and global-scale correlations (Chapter 1). In turn, these results have helped to constrain the timing and pattern of carbon isotope profiles across the Frasnian and Famennian stages of the Upper Devonian and demonstrate that isotopic data alone are insufficient to determine the position of a major mass extinction boundary in geological time (Chapters 2 and 3). Major isotope perturbations appear to be correlated with independently documented paleobiological disturbances and considerable changes in (at least) relative sea level (Chapter 3). The linkage between the repeated rise and fall of sea level to faunal turnover in the fossil record is agreeable with studies that suggest sea level change as one of the major causes of extinction due to habitat reduction and loss (e.g. Walliser, 1996). Minor differences in isotopic expression notwithstanding, results from the Lennard shelf are also consistent with these bio-, geo-, chemical events being global phenomena.

The integration of carbon isotopes with limited trace element data has shed light on the nature of paleoenvironmental conditions, on the northeastern margin of Gondwana, during the events of the Late Devonian. Despite the absence of organic-rich material or black shale deposits, the Lennard Shelf appears to have experienced at least periodic low-oxygen conditions across depositional environments, although not to the extent commonly seen in more restricted basins elsewhere (e.g. Joachimski et al., 2001; Bond et al., 2004; Averbuch et al., 2005; Śliwiński et al., 2011). Geochemical data is most consistent with bottom-water anoxia originating in deep basinal settings and then periodically spreading to shallower depths in the Lennard Shelf via transgressive pulses and/or the development of eutrophic conditions due to phosphorous regeneration. However, forthcoming trace element analyses on additional sections may expand upon or complicate this picture. While it should be stressed that the Canning Basin was only a small region of the Late Devonian world and not a sufficient area for drawing global conclusions, these results provide field-based, geochemical ground truth to the ocean anoxia kill mechanism that has been previously hypothesized for Late Devonian extinction events (Becker, 1993; Joachimski and Buggisch, 1993; Bratton et al., 1999; Lüning et al., 2004).

The integration of the isotopes with the litho-, bio-, and magnetostratigraphy provided a sequence stratigraphic framework in which to evaluate the isotopes within. In doing so, we found a meaningful relationship between sea level, specifically third order systems tracts, and trends observed in $\delta^{13}C$ values from complex slope settings (Figure C.1). This relationship, in which $\delta^{13}C$ values showed an upward positive trend (increasing $\delta^{13}C$ values) during transgressive systems tracts and an upward negative trend (decreasing $\delta^{13}C$ values) during highstand systems tracts, was observed in multiple slope sections with platform-top control. This consistent pattern, which suggests a systematic link between the carbon isotope record (the DIC pool), carbon burial/primary productivity, and sea level (Katz et al., 2007), allowed us to use the isotope trends as proxies for identifying slope systems tracts. As a result, we were not only able to make high resolution correlations through heterogeneous slope sections with higher confidence, but also establish the 1st Famennian sequence stratigraphic framework for the Canning Basin (see Playton et al., 2013). A paper that details how the trends in $\delta^{13}C$ values may be used as a predictive sequence stratigraphic tool in areas with limited correlation constraints is forthcoming and will appear as part of an SEPM special publication later this year (2015).



See next page for figure caption.

Figure C.1: Relationship between third-order systems tracts and carbon isotope excursions in the Lennard Shelf system (reproduced with permission from T. Playton). This figure shows typical stacking patterns in a platform-top transect and the interpreted sequence stratigraphy (red and blue triangles) along with the carbon isotope chemostratigraphy of a correlative slope transect. Using the paleomagnetic reversal record, which was well-preserved in both depositional settings, the platform-derived sequence stratigraphy was extrapolated into the slope. Examination of the isotope data within the sequence stratigraphic framework revealed a predictive trend—increasing $\delta^{13}C$ values associated with transgressive systems tracts and negative trending $\delta^{13}C$ values with highstand systems tracts.

The results of this dissertation as a whole support a multi-part extinction hypothesis that warrants a re-evaluation of the so-called Late Devonian mass extinction. While many studies have linked the mass extinction to a relatively narrow interval of time, of perhaps ~1 million years from the beginning of the Lower Kellwasser in conodont Zone 12 to the top of the Upper Kellwasser horizon at the F-F boundary, our results argue for a series of extinctions over the course of ~10 or more million years.

Comparison of integrated bio-, magneto- and chemostratigraphic data with paleontological records from the Lennard Shelf reveals the occurrence of four major carbon isotope excursions in the Frasnian that are coincident with distinct marine species extinctions, at least one of which was not previously known from the Devonian of Australia; from oldest to youngest, these events are the *falsiovalis*, *punctata*, and the two Kellwassers. The fossil and geochemical records across these events suggests that what has been termed the Late Devonian mass extinction is really composed of four separate extinctions occurring over a greater than ten million year interval of time. These results would seemingly remove the Late Devonian mass extinction as one of the "Big Five." In fact, in the nature of carbon cycling, global sedimentation styles (e.g. the heterogeneous deposition of black shales), and faunal turnover, this interval of time most closely resembles the middle to late Cretaceous world, where multiple periods of oceanic anoxic events produced unstable carbon isotope records and temporally separated, minor mass extinctions including the Cenomanian-Turonian boundary event (e.g. Kauffman and Hart, 1996).

When Raup and Sepkoski, (1982) first delineated the "Big Five," they noted that the Late Devonian mass extinction did not appear as a statistically significant event because family extinctions were distributed over two stages (the Frasnian and Givetian). They were uncertain if this "smearing of extinctions" over an approximately 15 million time interval was a reflection of sampling error and resolution, or if it was a real phenomenon reflecting an unusual long-term, episodic extinction event. Our findings would seem to lend support for the latter.

There is still a considerable amount of research that needs to be completed on the Late Devonian mass extinction and on mass extinctions in general. But given the need for- and benefit of well-constrained, high resolution datasets (Chapter 2 and 3), researching new localities, or revisiting sections with new ideas applied to existing data, will allow for a better understanding not only of the extent and duration of the minor mass extinctions documented from the Lennard shelf, but also their relative importance.

Potential for Future Work

Qualitatively, we tested the accuracy of the quality control (QC) workflow and evaluated the appropriateness of excluding QC2 and 3 data by comparing the resulting bulk-rock isotope profiles with previously published datasets from around the world (Chapter 1). However, a more quantitative assessment of the QC process and its success rate would be useful for individuals deciding on the applicability of this approach to their dataset. In an initial attempt at this, 95%

confidence intervals were calculated for each isotopic profile and the QC 2 and 3 data that fell outside of this range counted and compared to the number of QC 1 data that also fell outside the range. But comparing the data to itself proved insufficient as it relied on circular logic. It is now apparent that a true assessment of the QC workflow would require that each sample be thin sectioned and petrographically analyzed to independently check the appropriateness of original QC value assignments.

If we assume our aforementioned multi-part extinction hypothesis for the Late Devonian to be true, then more exciting and pressing areas of future work would revolve around testing the significance of earlier Givetian events, and in particular, determining the role, if any, of an end-Givetian or Givetian-Frasnian event. Similar to lower and middle Frasnian events, many F-F mass extinction studies also ignore the biological and geochemical changes taking place during the end of Givetian stage. In the Canning Basin, for example, there has been almost no geochemistry work endeavored on Givetian strata. Elsewhere in the world, however, the interval of time leading up the G-F boundary is characterized by a negative excursion followed by a positive one in $\delta^{13}C_{carb}$ values and widespread black shale horizons (Buggisch and Joachimski, 2006). Based on current paleontological collections, the G-F transition showed a sharp decline in tabulate corals and other reef organisms that may have been historically and quite erroneously underestimated in terms of the degree of biodiversity loss (Bayer and McGhee, 1986; Scrutton, 1997; Copper, *personal communicatio*n).

An initial investigation of an excavated quarry, near the Pillara Mine outside of Fitzroy Crossing, lends support to a significant precursor extinction event in the Givetian. In fact, the Pillara Road Quarry (PRQ) section reveals for the first time the presence of organic-rich deposits in shallow marine facies that are interpreted to have been deposited in low-oxygen conditions in the

Canning Basin of Australia. Secular trends in various isotope profiles ($\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and $\delta^{34}S$) and the discovery of various biomarkers including crocetane (K. Grice, *personal communication*), supports this interpretation and further argues for anoxia and possibly euxinia. The organic-rich intervals contain the highest total organic carbon (TOC) yet found in the Canning Basin (Playford et al., 2009) and are in many cases coincident with what appear to be "death assemblages" of corals and stromatoporoids. Preliminary paleontological work indicates that PRQ is Givetian in age, and not Frasnian as many had expected. However, further biostratigraphic work is essential to confirm this determination; until then, the age remains an area of considerable debate and thus does its relative significance as either a precursor extinction or minor mass extinction event. Moreover, conflicting evidence including the observed occurrence of type IV kerogen (K. Grice, *personal communication*) and pyrite need to be addressed before causal mechanisms can be suggested and compared with what has been proposed for similar studies elsewhere (e.g. Walliser, 1996; Buggisch and Joachimski, 2006).

It would help considerably if we had data from similar-aged sections in the Caning Basin with which to compare the PRQ data. While two possibilities do exist, namely the transect measured at Guppy Hills (PGH) and the HD14 core, the isotopic profiles from these localities are insufficient for robust correlation due to diagenetic overprinting, and in the case of the HD14 core, a substantial number of missing samples as well. The absence of available biostratigraphic data for all three sections and the relatively short nature of PRQ further challenge correlations at any scale. I did collect approximately 100 coral specimens, as well as some brachiopod and gastropod samples, in an attempt to construct a biostratigraphic range chart but I was unsuccessful in my attempt due to the limited amount of time I had for this task. Future work could continue this effort but thin section analysis is required for the coral identifications.

Assuming the Givetian age assignment of PRQ, PGH, and HD14 are correct, the ability to chronostratigraphically correlate these sections, or others of the same age in the Lennard Shelf, and integrate them into the chronostratigraphic framework (Chapter 1) is arguably one of the most important tasks for future research endeavors. This would extend our coverage of Canning Basin carbonates from the Late Devonian into the upper part of the Middle Devonian, the results of which have intriguing implications for expanding upon our revised Devonian extinction hypothesis.

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PART 2

CHAPTER VI

Exploring the Connections between Astronomer William Herschel (circa 1800) and His Contemporary Natural Historians, the "Geologists"

ABSTRACT

William Herschel (1738-1822) was the dominant astronomer of his day and one of the best observers the world has ever seen. With thousands of observations made through his personally constructed telescopes, Herschel discovered the planet Uranus and made fundamental contributions to measuring our place in the Milky Way galaxy, cataloging thousands of nebulae and star clusters in an effort to understand stellar evolution and the structure of the universe (or the "construction of the heavens" as he called it) . While considerable attention has been given to Herschel's observations and astronomical accomplishments, much less is known about the influence of other scientific disciplines on his ideas. During his life interdisciplinary work was not just encouraged (as in astrobiology today) but was customary; astronomers, biologists, mathematicians, physicians, etc. were all part of a single community of natural philosophers that studied and communicated across today's scientific disciplines. This paper focuses on the history of astronomy and geology circa 1770-1810, specifically investigating the connections between William Herschel's research and the work of his contemporary natural historians, the "geologists."

ASTROBIOLOGY RELEVANCE AND RATIONALE

Interdisciplinary research is one of the basic principles of Astrobiology. In upholding this principle, the interdisciplinary merit of this work is two-fold. First, the scope of this work was interdisciplinary; the primary goals of the project were to (1) better understand the influence that collaborations across diverse scientific disciplines had on the work of astronomer William Herschel, (2) gain new insight into how the scientific community interacted ~200 years ago, and (3) explore specifically how astronomy and geology fed off one another during the 18th century, particularly how their interplay may have played a role in advancing science at the time. Second, as a geochemist and soft-rock geologist, this project allowed me to think and work outside of my traditional disciplinary boundaries, which in turn, helped to broaden my knowledge in both astronomy and the history of science. As a result of this project, I was able to gain a new perspective on what science is, what science has been in the past, and how science has transformed throughout history.

It is our hope that the results and insights gained from this project will also benefit a future astrobiology endeavor, specifically a comprehensive biography of William Herschel, which is currently being written by Dr. Sullivan. Unlike existing biographies that focus solely on the astronomical achievements of Herschel, this new book aims to incorporate the many aspects of Herschel's life outside of astronomy, including his ideas on extraterrestrial life, his earlier career as a musician, his technological achievements in the realm of telescopes, and (hopefully) his influential relationships with geologists and other natural historians.

INTRODUCTION

Two centuries ago (circa 1770-1810), when interdisciplinary work was not just encouraged but was customary, scientists and intellectuals alike (astronomers, biologists, mathematicians, doctors, etc.) were all part of a single community of natural philosophers that studied and communicated across now-traditional scientific disciplines (Rudwick, 2005). This is evidenced by the interdisciplinary sources cited within their published papers in the *Philosophical Transactions of the Royal Society*. It is sometimes unclear, however, how much influence collaboration had on the notable research and discoveries of that era. If scientists had worked separately in their respective disciplines, would the course of historic advancements proceeded along the same timeline? Herein we focus specifically on the innovative ideas and contributions of astronomer William Herschel (1738-1822), and the relevant work of his contemporary natural historians, primarily those working in the realm of earth sciences. The purpose of this paper is to explore possible linkages that argue in favor of interdisciplinary collaborations and/or intellectual exchange between Herschel and 18th century earth scientists (referred to throughout this paper as geologists).

Sir William Herschel (Figure 4.1), the most renowned astronomer of his time, was at the forefront of observational research; his work essentially doubled the scales at which his contemporary astronomers were working, both spatially and temporally. For example, while his colleagues were focusing on cataloging stars in specific regions of the sky and illustrating their locations on 2-dimensional spheres, Herschel's interests were three-dimensional, what he called "deep space," and on a more galactic scale such that he estimated the distance of countless stars from the Earth, created a map of the Milky Way galaxy, and attempted to understand the structure of the universe (Hoskin, 2012). Temporally, Herschel recognized that the universe must

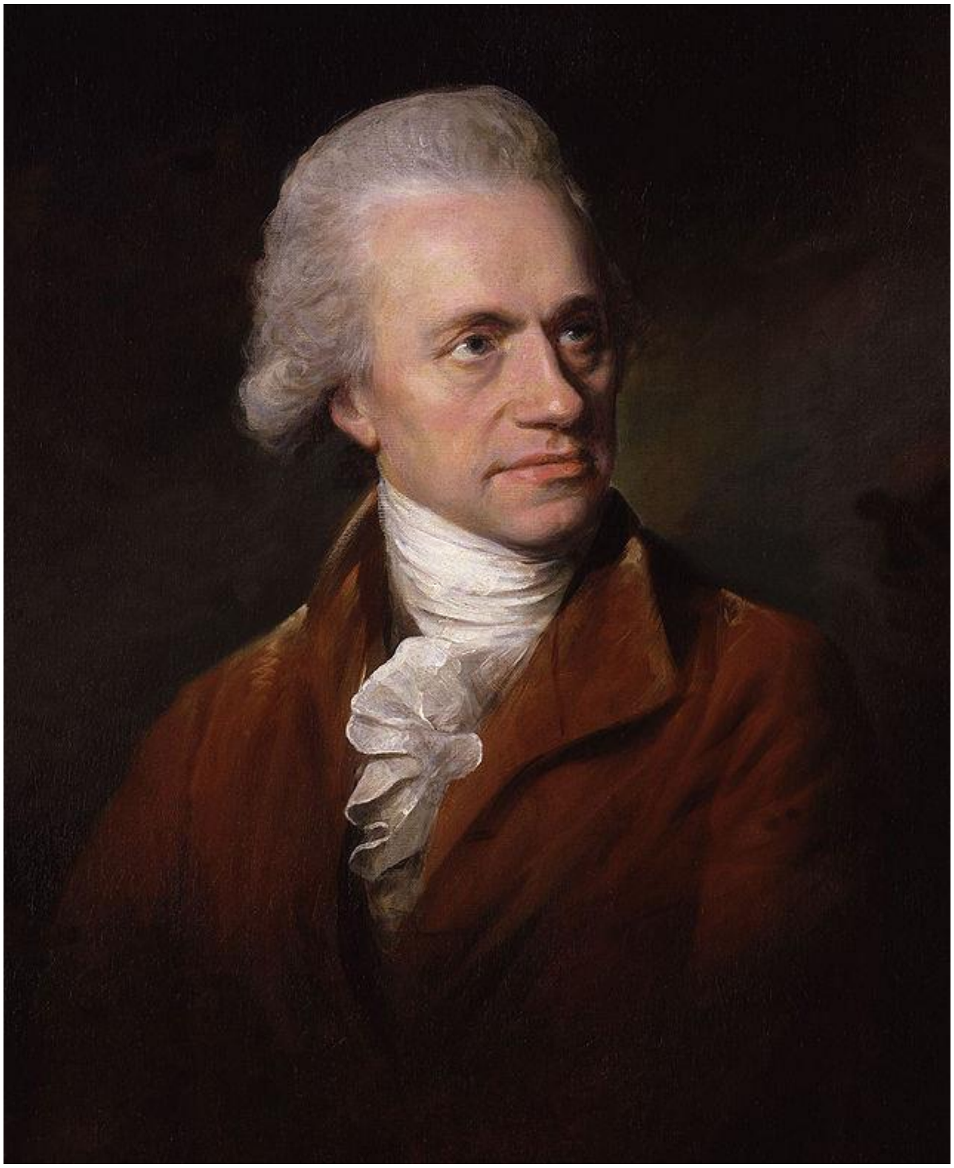

Figure 4.1: Portrait of William Herschel "painted in oil on canvas in 1785 by Lemuel Francis Abbott" (Hoskin, 2011: p.146).

be much older than previously thought because his idea of "deep space" also implied "deep time" (i.e. he believed that brightness correlated to distance, which meant that very faint stars were hundreds of thousands, or perhaps millions, of light years away. In seeing the light given off from those distant stars, one is essentially seeing the light as it existed hundreds of thousands, or millions, of years ago[1]). This led Herschel to theorize about stellar evolution; because gravity was the only force one could think as acting on such a large scale, he postulated that widely scattered stars would eventually condense into more tightly packed clusters given they had a considerable amount of time to do so.

Herschel's then-new ideas about deep space, deep time, and stellar evolution (gradual change) parallel those of his contemporary natural historians, especially those studying the structure and processes of the Earth. Just as Herschel was expanding the spatial scope of his work, "geologists" were beginning to transition from studying more regional scale processes and surficial deposits to formulating theories on a more global and three-dimensional scale, such as those about the interior structure of the Earth. German geologist Abraham Werner (1749-1817), for example, looked at the succession of rocks in the mountains of Saxony and showed that they were not positioned at random, but follow each other in a certain definite order. He then proposed that the Earth was comprised of multiple layers, or formations, each one successively younger (Laudan, 1994). Similar to the ideas of gradual change and deep time, James Hutton (1726-1797) theorized that the Earth initially formed by the gradual solidification of a molten mass and that continents were continually being eroded and then reformed by the same processes

[1] "… A telescope with a power of penetrating into space, like my 40- feet one, has also, as it may be called, a power of penetrating into time passed… when we see an object of the calculated distance at which one of these very remote nebulae may still be perceived, the rays of light which convey it image to the eye, must have been more than nineteen hundred and ten thousand, that is, almost two millions of years on their way; and that, consequently, so many years ago, this object must already have had an existence in the sidereal heavens, in order to send out those rays by which we now perceive it." *Phil. Trans*. 1802, 92, pp. 498-499.

that have been operating throughout Earth's history (Bailey, 1967; Dean 1992). This led him to the conclusion that the Earth must be significantly older than the 6000 year age inferred from the Bible. Like Herschel, natural historians in the realm of geology, were also transcending the spatial and temporal scales of earlier times, albeit in their own respective field of study.

Herschel also had an interest in the mountains he observed on the moon[2], many of which he believed to be active volcanos, despite numerous opposing views in the astronomy community. This fascination with lunar volcanos is yet another example of Herschel's paralleling interests with 18th century geologists; but rather than the moon, many natural historians were puzzled by- and subsequently focused on studying the eruptive volcanos that existed on earth. This similarity, and those mentioned in the previous paragraphs, begs the question "was it simply a coincidence? Or was there inspiration behind the innovative research and ideas of Sir William Herschel?"

GOALS AND APPROACH

The overarching goal of this project is to investigate potential connections between the work of Astronomer William Herschel and that of his contemporary natural historians. Using a combination of primary (manuscripts, personal correspondences, visitor logs, and library records) and secondary (scientific and biographical literature) sources, we hope to gain a better understanding of the influence geologists may have had on the notable research and discoveries of Herschel in the late 18th and early 19th centuries.

To achieve this goal, this paper focuses on the following six objectives:

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[2] Herschel's first paper that was communicated to the R.S. and published in *Phil. Trans*. was "Astronomical Observations Relating to the Mountains of the Moon" (1780, 70, 507-526). In 1787, Herschel published "An Account of Three Volcanos in the Moon" (77, 229-232).

Objective 1: Create a timeline of relevant events and publications to trace the origination and development of Herschel's notable ideas, especially those relating to the construction of the heavens, deep space, deep time, and stellar evolution.

Approach 1: Using primarily Hoskin's *Discoverers of the Universe* (2011), Laudan's *From Mineralogy to Geology* (1994), and various publications from the *Philosophical Transactions of the Royal Society of London (*1760-1815), I constructed a chronological timeline of significant events in Herschel's life and the scientific community circa ~1760 -1815. I have also included the dates of his relevant astronomy papers as well as any potentially influential geology publications. Additional attention was paid to if, and when, he mentioned or made reference to any geology related ideas, terminology, or individuals.

Objective 2: To identify potential candidates that may have contributed to or helped shape Herschel's work, generate a list of natural historians with geology related research that not only pre-dates Herschel's ideas concerning the construction of the heavens (i.e. deep space, deep time, and/or stellar evolution), but also has similar themes.

Approach 2: Natural historians, those with earth science related research similar to- and pre-dating much of Herschel's research, were identified using Mather's and Mason's *A Source Book in Geology* (1970), Rudwick's *Bursting the Limits of Time*(2005), and Laudan's *From Mineralogy to Geology* (1994). Emphasis was placed on 18th century geologists, although 16th and 17th century geologist were also investigated.

Objective 3: In pursuit of a mechanism for intellectual exchange, identify natural historians (primarily those with geological interests) that directly communicated- and potentially had scientific discussions with Herschel, either through written correspondence or in person.

Approach 3: Using the Herschel Archive from the Royal Astronomical Society, all known correspondents with 5 or more letters were selected and organized by profession (Appendix 4.2). In a few instances, known geologists with less than 5 letters were also included. *The Complete Dictionary of Scientific Biography* (2008) and the electronic databases at the University of Washington Library were used to determine the profession and in some instances, research interests, of the individuals selected. In a few rare cases in which the aforementioned two sources were unable to provide information, Google was used as a final resort. All letters from individuals identified as having some connection with geology were then read and examined for potential connections with Herschel's research. To identify natural historians that may have visited- or communicated in person with Herschel, I used the Herschel visitor log for the time that they lived at Datchet, Old Windsor, and Slough. Hoskin's *Discoverers of the Universe* book (2011) also provided chronological information about various meetings and encounters that Herschel had with geologists.

Objective 4: In further pursuit of a mechanism for intellectual exchange, make a list of natural historians with geological related research that was published in Phil. Trans. during, or leading up to, Williams's tenure with the Royal Society of London as he may have read the papers or perhaps even heard them read orally at the meetings.

Approach 4: I scanned through all publications in *Phil. Trans*., starting in 1760 and ending in 1785 (when William published his second paper on the construction of the heavens), and made a listing of the papers, and their corresponding authors, that were within the realm of earth science. I further examined papers that appeared to be related to- or have some connection with the ideas and themes presented in Herschel's work.

Objective 5: Determine if Herschel references or gives credit to natural historians/philosophers in his publications concerning the construction of the heavens.

Approach 5: I read Herschel's six papers in *Phil. Trans.* on the construction of the heavens (a list of these papers is provided in Appendix 4.6) and documented all footnote citations and in-text references made to individuals other than himself or his own work. From this list, I determined if mention or credit was given to any natural historians or geology related research.

Objective 6: Analyze any linkages that exist between Herschel and the natural historians identified during the workflow of goals 2 through 5, and determine their significance.

Approach 6: I cross referenced the lists of natural historians that (1) have relevant work in the realm of geology (objective 2, Appendix 4.1), (2) have corresponded with or visited Herschel (objective 3, Appendices 4.2 and 4.3), (3) have authored geology related articles in *Phil. Trans*. (objective 4, Appendix 4.4), and (4) have been referenced by Herschel in one of his papers (objective 5, Appendix 4.6). I then generated a list of leading candidates with Herschelian connections (Appendix 4.7) by selecting the individuals which appeared on multiple lists. I also checked a sub-set of the Herschel library[3], as recorded by Isabella Herschel and edited by Sydney Ross (2001), to see if it contained publications by any of the potential candidates. In instances where I found a correlation, I also noted any special annotations, such as hand written comments, made by the author or by Herschel. I then proceeded to rank the leading candidates, in order of their potential influence, by evaluating the strengths and weaknesses of available evidence.

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[3] Dr. Woodruff Sullivan III compiled an approximate listing of William Herschel's library from Isabella Herschel's catalogue (edited by Sydney Ross, 2001) of John and Williams combined libraries.

To set the stage for this paper, we will first provide a brief overview of the "scientific community" in the 18th century and discuss the then-current state of astronomy and conceptual foundations of "geology".

BACKGROUND

Conceptual Foundations of Geology

During Herschel's time, the scientific community was not made up of the typical scientists we think of today, but rather of educated individuals from a wide range of professions (including doctors, lawyers, ministers, etc…) that partook in research as only a peripheral activity to their main, income providing job[4]. While a few individuals were employed by the government or universities and did receive salaries for doing research, the wages paid were often inadequate without other sources of income (McCormmach, 2012). The research endeavors within the community were highly varied, and any one individual might be interested in such topics ranging from chemistry and physics to human physiology and animal husbandry.

Scientists, regardless of their research interests, were commonly referred to as either natural historians or natural philosophers[5]; although in many instances, both titles applied. Those interested in studying the materials, processes, and history of the earth, were more specifically considered mineralogists. This is because the term "mineral" (and thus mineralogist) had a much broader definition than the one today. Before the 19th century, any non-living, naturally occurring solid object (and sometimes fluid), was considered a mineral. It was not until the last

[4] It should be noted that in a few instances individuals had independent wealth that afforded them the pleasure of conducting research whenever they desired.

[5] Natural historians focused on systematic descriptions and the classification of living and non-living entities while natural philosophers used math and physics to detect causal relationships and natural laws underlying living and non-livings things (Rudwick, 2005).

quarter of the 18th century that the study of mineralogy was subdivided into more discrete categories similar to the modern scope of geology[6] (Laudan, 1994). While the distinction of geology as a specialized discipline did not come about until 1807[7], we refer to mineralogists as "geologists" in this paper for the purpose of familiarity.

For geologists during the 17th and 18th centuries, as well as other natural historians, it was common knowledge that the surface of the earth was made of four different classes of minerals; metals, earths and stones, salts, and sulfurs (or bitumens or inflamables). This classification was based on how the minerals reacted to heat and water, the two elements believed to be the major agents of geological change. According to Laudan (1994), "the mineral classes played a pivotal role in theories about the earth's structure or history…mineralogists had to explain why the earth's crust was differentiated into these classes; on the other hand, they used the mineral classes to explain the gross features of the crust - its rocks, and ultimately its physical geography - and to reconstruct earth's history."

In theorizing about the earth's structure and history, scientists in the late 17th and early 18th century had to fit their ideas within a coherent framework that was consistent with available information about present and past conditions. Because travel during this time was exceptionally difficult and most parts of the Earth's surface had yet to be described in any detail, or even studied at all, natural historians relied primarily on the current state of geological knowledge (that of minerals as previously discussed), and on Scripture, which most considered an empirical record of earth's past conditions (Porter, 1977; Laudan, 1994). And while the interpretation of

[6] In 1774, Abraham Werner divided the broad study of mineralogy into three specialties; mineral geography (the study of the distribution or rocks and minerals), oryctognosy (the identification and classification of minerals), and geognosy (the study of the formation and history of rocks and minerals), Laudan, 1994.
[7] According to Rudwick (1985), the founding of the Geological Society of London in 1807 marks the beginning of geology as a specialized scientific discipline.

the Bible varied from individual to individual, most natural historians agreed upon a few keys facts: (1) the earth had once been fluid[8], (2) during the Creation, God made land and separated it from the ocean[9], (3) after the origin of man, a large flood[10] covered the surface of the earth and killed almost all life upon it, and (4) the earth was ~6000 years old[11]. Given these beliefs, natural historians differed in their views concerning the origin and nature of the Flood, its role in shaping the surface of the earth, and the approach they took in attempting to explain it all[12].

By the late 18th century, natural historians started to place less emphasis on the biblical story of creation and instead relied on experiments and field observations. It was this transition that led many to openly theorize about the age of the earth, believed to be much older than previously thought, and its formation process (Laudan, 1994). For example, French naturalist Georges-Louis Leclerc, Comte de Buffon, proposed the idea that the earth started as a hot, molten ball that originated as part of the sun, but was torn away and then slowly cooled over time. From a series of experiments, in which he allowed spheres of different sizes and materials to gradually cool, he calculated the minimum amount of time that must have passed since the formation of the earth[13];

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[8] "The earth was without form and void, and darkness was upon the face of the deep; and the Spirit of God was moving over the face of the waters" *(Genesis* 1:2*).*

[9] In *Genesis* (1:6-7), God said "Let there be a firmament in the midst of the waters, and let it separate the waters from the waters." Then "God made the firmament and separated the waters which were under the firmament from the waters which were above the firmament."

[10] This was in reference to the Genesis flood narrative (*Genesis* chapters 6-9). "The flood continued forty days upon the earth…And the waters prevailed so mightily upon the earth that all the high mountains under the whole heaven were covered...And all flesh died that moved upon the earth, birds, cattle, beasts, all swarming creatures that swarm upon the earth, and every man; everything on the dry land in whose nostrils was the breath of life died. And the waters prevailed upon the earth a hundred and fifty days" (*Genesis* 7:17-24).

[11] The ~6000 year age estimate for the earth is based on the succession of genealogy in the Old Testament. One of the most popular chronologies was published by Archbishop James Ussher in 1650.

[12] For example, Thomas Burnet called upon Cartesian physics to explain the biblical earth by natural causes in *The Sacred History of the Earth* (London, 1684), while John Ray applied physical principles in discussing the creation and flood, (in *Three Physico-Theological Discourses*, London, 1693, 1713).

[13] He also calculated the elapsed time since the formation of the planets and various satellites in our solar system (Rudwick, 2005).

and he arrived at a number much greater than the biblical 6000 years[14]. From meticulous observations of erosion and sedimentation, Scottish naturalist James Hutton believed that earth processes continued in a never-ending cycle (Dean, 1992) and further concluded "... that it had required an indefinite space of time to have produced the land which now appears... so that, with respect to human observation, this world has neither a beginning nor an end" (*Theory of the Earth*, 1788, pp. 27-28). While their estimates varied, other natural historians shared similar views that the earth was considerably old, including individuals such as Horace Benedict de Saussure (1740-1799), John Playfair (1748-1819), and Abraham Werner (1750-1817) (Gillispie et al., 2008).

Minerals, volcanos, earthquakes, and strata were also 'hot topics' in early geology. Mineralogy became increasingly popular in Europe in the late 18th century following the economic hardship of the Seven Years' War (1754-1763) and the ensuing industrial revolution (Porter, 1977; McCormmach, 2012); schools of mining not only provided employment opportunities for geologists but also education in the natural sciences. Volcanos were of interest most likely because of their close proximity to people who often settled near volcanic areas because of the abundance of nutrient-rich soils (McCormmach, 2012). As a consequence of living near volcanos, earthquakes were a common occurrence, which naturally aroused curiosity (and sometimes fear) and led people to surmise about their origin and nature. Strata, or layers of sedimentary rocks, were particularly interesting because their composition, thickness, lateral extent, and structural characteristics (faulting or folding) could provide information about past geological events, processes, and environments of deposition (Mather and Mason, 1970; Laudan, 1994). In 1695, English naturalist John Woodward proposed that "all terrestrial matter is

[14] In *Epochs of the history of the Earth* (1779), he estimated the age of the earth to be roughly 75,000 years.

naturally in layers or strata" and that these strata could be seen all over the world[15]. Some twenty years later, Englishman John Stachey drew perhaps the first geological cross-section of strata in the subsurface[16] and then in 1727 he compiled the first table of British strata. The term 'strata' appears repeatedly throughout 18th century geology literature and was frequently used by natural historians such as James Hall, William Hamilton, Robert Hooke, James Hutton, John Michell, and John Playfair (Mather and Mason, 1970). Interestingly, the term 'strata' also appears continuously in Herschel's first two papers on the construction of the heavens.

The Current State of Astronomy

During the 18th century, astronomers focused primarily on solar system bodies (the sun and moon, other planets and their satellites, and comets), regarding "fixed stars" as nothing more than the constant backdrop of the universe (Brush, 1996). Because of its relative closeness to the earth, astronomers naturally knew more about the sun than the other fixed stars. It was believed that all heavenly bodies obeyed the law of gravity, the same force that was known to govern all objects on earth. Working under this assumption (which we know today to be correct), astronomers spent most of their time calculating the sizes, masses, periods, and orbits of nearby celestial bodies as well as working out the distance of the sun from the earth. Few people started thinking beyond the solar system; in fact, almost all research during this time was concerned with understanding entities in the physical universe for their usefulness as navigation tools (McCormmach, 2012).

Comparatively, much less was known about the stars and nebular objects that lay at greater distances from the earth. It was known that stars were different from one another, in color and

[15] *Essay toward a Natural History of the Earth*, (London 1695).
[16] "Observations on the strata in the Somersetshire coal fields," *Phil Trans.* 1719, 360, 972-973.

apparent brightness, and that some stars were more variable than others (changing, fading, disappearing, and moving relative to one another). However, many questions remained about the size, distance, and distribution of stars and nebulae in space; the latter two are of particular interest to this paper as they provide context for understanding the evolution of Herschel's work.

For the few astronomers concerned with the universe outside the solar system, determining the distance to the stars was one of the most important tasks in sidereal astronomy (McCormmach, 2012). During this time, there were two methods of determining the distance to stars; that of parallax, which measures the change in the apparent position of a star when viewed from different lines of sight, and photometry, which uses comparative brightness to estimate distances[17]. While the method of parallax was more widely attempted, it was extremely difficult given that the distances of stars were so great and the precision of telescopes too limited. Photometry was not without its own limitations[18], but it gained popularity throughout the 18th century as better instruments and methods for comparing light were developed; and it was this method that Herschel employed in his research endeavors (Hoskin, 2011).

The noticeable distribution of stars in the night sky also fascinated those interested in sidereal astronomy; and of particular intrigue was the large, dimly glowing band that arched across the night sky. Thomas Wright believed that the stars were "promiscuously distributed" throughout space until his observations of the Milky Way led him to argue that the stars were actually scattered "in some regular order[19]." Drawing from Wright's book, German philosopher

[17] A star's distance was assumed to be inversely proportional to its apparent brightness (Brush, 1996).
[18] During the 17th and early 18th centuries, the distances of stars, as determined by their magnitudes, was highly uncertain. This is because the scale of magnitude used to classify stars lacked rigor; a star's magnitude was judged by the eye and could therefore vary significantly from person to person, and on observational conditions (McCormmach, 2012).
[19] *Original Theory or New Hypothesis of the Universe,* (1750). While Herschel had a copy of Wright's book, it remains unclear if he read it (Hoskin, 2011, p.100).

Emmanuel Kant used logic (and not observations) to formulate his own theory about the organization of stars in our galaxy, proposing a rotating disc model[20]. These early ideas about non-random star arrangements were further supported by the later work of the astronomer and geologist John Michell, who used statistics to demonstrate that more stars occur in pairs or groups than a random distribution could account for (Michell, 1767). It was not until 1784 that Herschel reported similar observations of the Milky Way, noting that stars were concentrated in certain parts of the sky, "….arranged into strata, which seem to run a great length." While there were many hypotheses concerning the arrangement of stars in the universe[21], Herschel was the first to study the heavens in a systematic way. And "…in addressing the stars in their entirety…," backed by his meticulous star counts, he "pioneered a new kind of scientific study," paving the way for future astronomers (McCormmach, 2012: pp.152-153).

RESULTS AND DISCUSSION

1. Development of Herschelian ideas (objective 1, see Appendix 4.8 for more specific dates)

William Herschel was born in Germany on November 15th, 1738. As a young boy, he attended the garrison school in Hanover and was further educated at home in the art of music by his father Issak Herschel, a military musician. Following the family tradition, 14-year-old Herschel joined his father and brother in the regimental band of the Hanoverian Guards as an oboist and violinist. In 1759, Herschel left the battlefield in Germany for safety in England, where he started his professional life as a music teacher before becoming an accomplished organist and conductor (Hoskin, 2011).

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[20] *A Naturalistic Hypothesis of Earth Origin* (1755). It's believed that Herschel was not aware of this work by Kant as the book had limited circulation due to bankruptcy of the bookseller (Hoskin, 2011, p.100).

[21] In 1761, astronomer Johann Heinrich Lambert, also contributed ideas about the Milky Way, suggesting it was a flattened universe. But the influence on Herschel is doubtful as Herschel did not acquire Lambert's book until 1799 (Hoskin, 2011, p.100).

It wasn't until his mid-30s that he began to turn his eyes and attention to the heavens above. His early interests undoubtedly shaped by the first few books he purchased related to astronomy and mathematics, namely James Ferguson's *Astronomy* (1756) and Robert Smith's *Opticks* (1738) and *Harmonics* (1749). Borrowing a telescope, he made his first observations of Saturn and the Orion nebula, for the latter of which he made a sketch and noted that its shape differed from the one in Smith's *Opticks.* In an effort to build his own telescope for further viewing, he began learning how to grind and polish speculum mirrors[22]; a skill that he would master and that would eventually enable him to make the most powerful telescopes of his time. As Herschel's interest in astronomy grew throughout his career, so did the size of his telescopes; however the primary purpose(s) behind his desire to build bigger and better observational instruments remains speculative[23].

Early in his astronomy career, Herschel had an advantage over all other observers because of the size and quality of his telescopes. As previously discussed, one of the greatest unknowns in stellar astronomy was the distance to neighboring stars. According to Hoskin (2011), Herschel was aware of Galileo's idea to use double stars to measure stellar distances, and so with his superior telescopes, he began searching the sky for double stars. By the end of 1781, he had catalogued no fewer than 269 double stars, 227 of which were new discoveries.

Also that year, he became the first person in recorded history to discover a planet, namely Uranus; in doing so, he doubled the scale of the solar system as Uranus was found to be orbiting

[22] In the 17th and 18th centuries, speculum metal (an ally produced most commonly from mixing copper and tin, although other metals were occasionally added) was used for making mirrors in reflecting telescopes because when compared to other metals used for mirrors during that era (i.e. bronze), it had a highly reflective surface when polished and tarnished less easily. It was not until the mid- 19th century that the superior silvered glass mirrors we use today were invented (King, 1955).

[23] It's been suggested that testing his early theory on nebulosity (that all nebulae are actually clusters of distant, unresolvable stars) and searching for intelligent life elsewhere in the universe, were among the primary motivational factors (Hoskin, 2011: p.216).

the sun far beyond Saturn (Hoskin, 2011, pp.49 - 51). Herschel's unprecedented discovery also made him famous throughout Europe, procured his fellowship in the Royal Society, and even gained him patronage from the King of England. In response to Herschel naming his planet "Georgium Sidus," King George III appointed him astronomer to the court, and in doing so, allowed him to give up his musical profession to peruse a full-time career in astronomy (Hoskin, 2011, pp.57 - 66).

It was not until 1783 that Herschel stated to spend less time on double stars and instead devote his energy to examining nebulae and star clusters. While it's been suggested that his observations of the Andromeda nebula piqued his interest in the subject[24], it's uncertain what sparked his transition away from double stars. As proposed by Hoskin, (2011, pp.82 - 86), Caroline Herschel's discovery of two new nebulae on Feb. 26th, 1783, may have provided Herschel with the inspiration to change research directions. Perhaps the ease with which his sister, a novice, made the discoveries illuminated the range of opportunities available to him in this relatively new field.

From his years of observations of nebulae and star clusters, Herschel began thinking about the structure of the universe, or the "construction of the heavens" as he called it. As an aside, this desire to comprehend the entirety of the universe was matched only by some geologists, those who worked towards a global understanding of the earth. Throughout his career, Herschel wrote seven papers investigating this topic, although the first two, which were published in 1784 and 1785, contain the most compelling connections with geology. In the first paper[25], Herschel

[24] In reference to his observations of the Andromeda nebula on August 6, 1780, Herschel wrote "To be observed. All the nebulas, their stars counted, and the form delineated," (Hoskin, 2011).
[25] "Account of Some Observations Tending to Investigate the Construction of the Heavens*," Phil. Trans.,* 1784, 74, 437-451.

focused on the Milky Way, describing its structure using geology related terminology, which he admitted to "borrow[ing]…from the natural historians." For example, he described the Milky Way as a large sidereal stratum composed of "a number of stars arranged between two parallel planes, indefinitely extended every way, but at a given considerable distance from each other," with a smaller, secondary stratum that branches out[26]. He also noted that one's position in any one stratum determines the perspective with which one sees the stars and the galaxy[27]. And similar to the geological ideas about a stratum of rock, Herschel believed that a stratum of stars may vary in size (lateral extent), thickness, position, and number of constituents (being minerals in geology and stars in astronomy). In the second paper[28], Herschel used a statistically based method he referred to as "star-gaging" to measure the size and shape of the Milky Way and construct a cross-sectional map of the galaxy (Figure 4.2).

During the late 1780's, Herschel continued to catalog thousands of nebulae and star clusters, reporting his results and their implications in his third construction of the heavens paper in 1789. After the completion of this manuscript, however, some of his ideas on the subject began to change, namely his thoughts on the extent of the Milky Way and those about nebulosity. In mapping the structure of the galaxy, his star gaging method was based on two assumptions, one of which was that his telescope (at the time, his 20 ft. telescope which had an 18.5 in. reflector), could see the furthest stars at the end of the galaxy. But with the construction of his newer and larger 40 ft. telescope in 1789 (which had a 48 in. reflector), he was able to see stars beyond

[26] "…the Milky Way, which, according to this hypothesis, is no other than the appearance of the projection of the stars contained in this stratum and its secondary branch." *Phil. Trans*., 1784, 74, p.445.

[27] "…the great stratum, called the Milky Way,… an eye placed somewhere within it will see all the stars in the direction of the planes of the stratum projected into a great circle, which will appear lucid on account of the accumulation of the stars; while the rest of the heavens, at the sides, will only seem to be scattered over the constellations, more or less crowded, according to the distance of the planes or number of stars contained in the thickness or sides of the stratum." *Phil. Trans*., 1784, 74, p. 443.

[28] "On the Construction of the Heavens*," Phil. Trans.*, 1785, 75, 213-266.

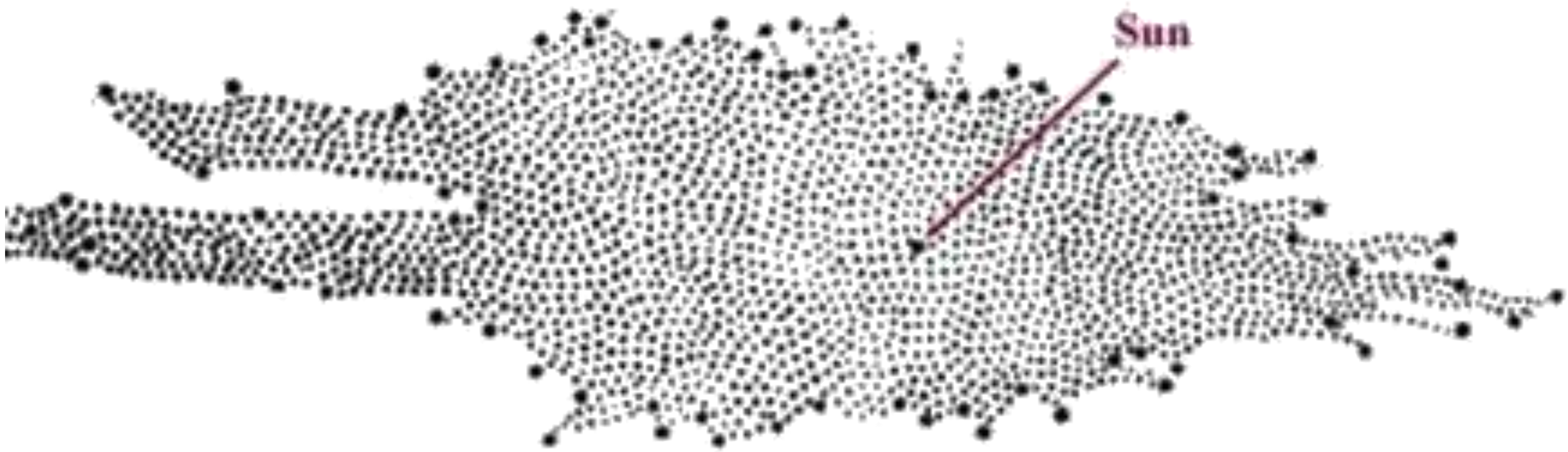

Figure 4.2: William Herschel's cross-section of the Milky Way Galaxy that was published in 1785 in the Philosophical Transactions of the Royal Society.

what he initially believed to be the edge of the Milky Way, leading him to conclude that his assumption was invalid. Then in 1790, an observation of true nebulosity (a cloudy atmosphere of nebulous material that not only surrounds the star but also occurs at a similar distance), led him to reject his hypothesis that all nebulae were actually distant clusters of unresolvable stars.

With these new realizations and continued observations, Herschel started to theorize about star formation. And in his last few papers concerning the construction of the heavens, he argued that the arrangement and organization of celestial bodies is constantly changing. These early ideas of a cyclical, evolutionary process were the foundation for what we know today as the theory of stellar evolution (Hoskin, 2011). Herschel proposed that stars formed slowly over great lengths of time as widely scattered luminous matter gradually moved closer and closer to each other until they condensed into clouds and then eventually stars. In turn, these stars would then attract one another to form clusters, which would continue to condense until finally a gravitational collapse would cause the whole process to start over again. Similar to these ideas, geologists such as James Hutton were formulating the basic principles behind what is known today as uniformitarianism, a theory which states that earth processes, such as the formation and weathering of rocks, occur slowly and gradually over long periods of time, eventually repeating themselves in an endless cycle.

In addition to the geological themes discussed in relation to the construction of the heavens papers, several other parallels can be drawn between the work of Herschel and that of contemporary natural historians. The first inclination of Herschel's potential research connection with geology started with his early observations of mountains on the moon. It was this topic that would help introduce Herschel to the broader scientific community in England, as it was the subject of his first paper submitted to and published by the Royal Society[29]. Further observations of the moon led Herschel to believe that some of the mountains may actually be volcanos, similar to the ones observed on earth; in 1787, he witnessed bursts of light on the moon which he attributed to volcanic eruptions[30], and then in 1792, he claimed to have seen at least 150 "bright, red, luminous points" on the moon as it was being eclipsed[31]. In his log book, he surmised that these red points were indeed volcanos[32]. There was additional support for Herschel's claims, and even his ideas[33], such as the independent account by William Wilkins in 1794 of a "light, like a star …in the dark part of the Moon[34]" (*Phil. Trans*., 84, 429-440).

In 1797, while on vacation with his family in Bath, Herschel took a direct interest in geology; he was intrigued by some fossil shells that he had found, particularly with their peculiar location high above the ocean in which marine organisms are known to live. With his brother Alexander, he took a day trip outside of Bath to the nearby mountains in attempts to find more of the marine fossils. Based on his geological observations, Herschel made notes about his ideas on how the fossils got to their present location; specifically he thought about changes in sea level,

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[29] It was actually one of two papers by Herschel that were submitted to the R.S. by William Watson. The paper of interest is "Astronomical Observations Relating to the Mountains of the Moon*," Phil. Trans*., 1780, 70, 507-526.

[30] In "An Account of Three Volcanos in the Moon," *Phil. Trans*., 1787, 77, 229-232.

[31] The observations were made on October 22, 1790 and later published in *Phil. Trans*., 1792, 82, 23-27.

[32] In the paper, Herschel does not refer to the red dots as volcanos, rather he states that "we know too little of the surface of the moon to venture at a surmise of the cause from whence the great brightness, similarity, and remarkable colour of these points could arise." This quote, and the in-text quote, from p.27 of the 1792 paper (see reference in footnote 31).

[33] During a solar eclipse in 1778, Spanish admiral Don Antonio de Ulloa reported seeing a red "luminous point [that] was towards the North-west part of the moon's disk" and commented that it was "remarkable, that no other luminous speck was perceived in the disk besides this." Ulloa believed that what he had seen was the sun shining through a deep cleft on the edge of the Moon. Upon reading this account, Italian physicist Giambatista Beccaria (1716 – 1781) argued against this, suggesting that what Ulloa had actually seen was a volcanic eruption on the Moon. Beccaria further claimed that two of his young relatives had seen a similar spot of light on the moon during a total lunar eclipse in 1772 (Home, 1972). The quote by Ulloa is from p. 115 in "Observations on the Total (with Duration) and Annular Eclipse of the Sun, Taken on the 24th of June, 1778, on Board the Espagne, Being the Admiral's Ship of the Fleet of New Spain, in the Passage from the Azores towards Cape St. Vincent's." Phil. Trans., 1779, 69, **105**-119.

[34] The observations by Wilkins were made on March 7th, 1794.

sedimentation, uplift, erosion, and how these processes must repeat themselves in order to explain the observed location of the fossils (Hoskin, 2011: p.159). This train of thought mirrored that of Hutton's, particularly with respect to his widely-known ideas concerning uniformitarianism and *The Theory of the Earth (1788)*.

One last similarity between the geologists and Herschel is the concept of deep time. As discussed in the geological background section, natural historians of this time were continually pushing back their estimates for the age of the earth. We first see direct evidence of Herschel suggesting an ancient universe in his 1802 paper, in which he stated "a telescope with a power of penetrating into space…has also, as it might be called, a power of penetrating into time past[35]." Given that light travels at a constant, finite speed, he estimated that the earth must be at least 2 million years old as he could see light coming from stars that he predicted were about 2 million light-years away. While Herschel may have come to this conclusion about time much earlier in his career, there is currently no concrete evidence suggesting if, or when, it may have happened.

2. Prominent Natural Historians with Herschelian Related Ideas (objective 2)

Twenty-two natural historians have been identified as having geology related research that may have influenced Herschel's descriptions of sidereal strata, his drive for understanding the entire universe, his fascination with lunar mountains and volcanos, and/or his novel ideas concerning stellar evolution and deep time (the full list of individuals can be found in Appendix 4.1). Of these, fifteen of the geologists commonly use the term strata in describing the structure of the earth, fourteen focus on research endeavors and theories that encompass the entirety of the earth, six study mountains and/or volcanos, six believe in slow, cyclical processes of change, and six

[35] See footnote 1.

are concerned with estimating the age of the earth beyond biblical convention[36]. The geologists with the greatest number of these paralleling research themes are Horace Benedict de Saussure (1740-1799), James Hutton (1726-1797), John Playfair (1748-1819), George Louis Leclerc, Comte de Buffon (1707-1788), and John Michell (1724-1793).

Benedict de Saussure was a widely traveled alpine geologist from Geneva. Like Herschel, he was well-known for his tireless efforts and countless observations, often in formidable conditions (Gillispie et al., 2008). And just as Herschel saw star clusters and nebulae as the keys to understanding the construction of the heavens, Saussure saw mountains as the keys to understanding the structure of the earth; and so he sought to observe and study as many as he could. Saussure's alpine research (on the inclination of strata, the nature of fossils and rocks, and the processes associated with erosion), led him to the conclusion that the planet was vastly older than generally thought, and his ideas eventually formed the basis of Darwin's theory of evolution (Mather and Mason, 1970).

Similar to Herschel's innovative ideas on star formation which helped to establish the theory of stellar evolution, Hutton's argument that processes associated with sedimentation are cyclical in operation founded the general principles that some fifty years later came to be known as uniformitarianism. Hutton believed that earth processes are not only cyclical, but that they had been repeated an indeterminate number of times in the past; and because he could find no evidence to suggest that processes such as sedimentation and erosion might cease, he assumed that they would continue indefinitely (Bailey, 1967; Dean, 1992). And just as Herschel extrapolated from his data theories applicable to star formation in the entire universe, Hutton claimed that the theory supported by his results in Brittan could be extended to all parts of the

[36] Interestingly, 6 of the 22 also had some research in astronomy.

globe; to support his claim, Hutton later provided additional observations and cited other published accounts of similar phenomena and materials occurring around the world (Bailey, 1967).

Scottish geologist John Playfair shared the same views as his good friend Hutton, so much so that he worked to further develop and popularize the ideas in his own book. Interestingly, or perhaps coincidentally, Playfair gave a copy of his *Illustrations of the Huttonian Theory,* (1802), to Herschel[37]. While Playfair's book and Hutton's original articles were not published[38] until after Herschel formulated the ideas for his first two 'construction of the heavens' papers, it's still possible that he may have been influenced by the revolutionary work of these two geologists as the main concepts were supposedly conceived some twenty years earlier[39].

French naturalist Comte de Buffon was not only interested in studying the history of the earth, but like Herschel he was also fascinated with understanding the universe beyond our world. Among other things, Buffon was also a cosmologist, and he hypothesized that a large comet had collided with the sun, ejecting material into space that eventually became the planets and satellites of solar system (Mather and Mason, 1970). From extensive cooling experiements predicated on the idea that solar system bodies were intially molten, Buffon calculated that it took over 75,000 years for the earth to solidfy and reach present-day conditions[40]. In studying the sedimentation (formation) and erosion of strata, however, he realized that much more time was required; in fact, he thought that "the more we extend time, the closer we shall be to the truth"

[37] As determined from the appearance (and special inscription made by the author) in Herschel's library, see footnote 3.
[38] Hutton published an abstract with the ideas in 1785, but the full article did not appear until 1788.
[39] According to his good friend Joseph Black, in a letter to Princess Dashkow; see W. Ramsay, *Life and Letters of Joseph Black, M.D.* (London, 1918), 117–125.
[40] *Histoire et théorie de la terre (*1749); *The collision hypothesis of Earth origin* (1776).

(*Époques de la nature*, 1779, p. 40). Similar to Herschel's view that the earth must be at least 2,000,000 years old, Buffon suggested a period of as long as 3,000,000 years[41].

Englishman John Michell started his career as a geologist interested in the structure of the earth, but with time, he became an astronomer interested in the structure of the heavens. In his early years, Michell studied earthquakes and meticulously described strata[42] in the near-surface layers of the earth. But just as Herschel was expanding the scale of his work, looking past the solar system and into the universe beyond, Michell was increasing the depth of his work, literally, as he began studying the earth's interior. Contrary to the beliefs of most other geologists during this time that volcanos were superficial phenomena of no profound geological significance, Michell argued that earthquakes and volcanic eruptions had deep-rooted causes far below the earth and were permanent and fundamental geological processes (Michell, 1760). He was interested in developing a method for determining the distance to the origin of earthquakes and the depth at which they occurred. As Michell transitioned to astronomy, he was likewise concerned with determining distances, although this time to the stars. In 1767[43], he described and advocated a more practical method for measuring stellar distance known as photometry, which estimated distance by quantitatively comparing the brightness of stars; it was this method that Herschel later employed in his own work.

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[41] The three million year estimate only appears in an unpublished draft of the manuscript. He abandoned this longer time scale and only published his original calculation of 75,000 years due to his fear of being misunderstood by his readers (Gillispie et al., 2008).

[42] According to McCormmach, (2012), Michell was interested in their composition, thickness, arrangement, horizontal continuity, vertical diversity, spatial distribution, inclination, and structural features (bending, fracturing and internal laminae).

[43] "An Inquiry into the Probable Parallax"

3. The Spread of Ideas through Communication (objective 3, see appendices 2 and 3)

Correspondence and visits were important channels for the sharing of ideas and scientific discussions during this time, primarily because the technology for other forms of communication was either absent or limited. Letters and visits were especially influential for Herschel because he traveled relatively little and attended very few Royal Society meetings (Hoskin, 2011), the latter of which not only encouraged, but promoted scientific exchange.

According to William's and Caroline's visitor log book, Herschel entertained a number of visitors during his time as astronomer to the court, eight of whom were natural historians. In almost all instances, however, nothing is known about the interaction or intellectual exchange during the visits. One exception, however, is the stopover by French volcanologist, Barthelemi Faujas De Saint-Fond (1741-1819), on the night of August 15th, 1784. In his travel notes[44], Faujas recounted many of the details from his visit, including Herschel's thoughts about the moon which were "so extraordinary that they should be ridiculed if they had not originated from a man of such merit and exactitude." Herschel had shared with Faujas his ideas about volcanos forming on the moon, based on his repeated observations[45] of "a very remarkable conical peak [on the moon], which imperceptibly grew larger" in only a few days, and which had two distinct streams flowing down the sides, suggesting a "true volcanic eruption."

In a letter to Herschel[46], dated May 14th, 1788, Faujas recalled his visit at Datchet and further discussed lunar volcanos. Since Faujas had studied volcanos on earth, he has some ideas in regards to Herschel's observations and thoughts about volcanos on the moon. Faujas wrote, "I

[44] While Faujas' visit with the Herschel's was later published in his book *Voyage en Angleterre, en Écosse, et aux Îles Hébrides*, vol. 1 (Paris, 1797), an earlier manuscript of Faujas' was analyzed by Dollfus, (1987) and found to include some additional and differing information.
[45] Starting on the 4th of May, 1783, and continuing throughout the month.
[46] RAS (W.1/13.F5). The letter was translated from French to English by Dr. Woodruff Sullivan III.

am not embarrassed to consider the moon by analogy as another real Earth", “we must presume that the moon is a world like ours,” and “it's conceivable that there could be subterranean fire there that would produce visible effects” (such as the light seen by Herschel). He went on further in his comparison, suggesting that there could well be a small, undetected atmosphere on the moon due to volcanic outgassing, and that despite the moon’s current condition (solid and cold), it may have been different, perhaps more earth-like, in the past; there could have been a thicker atmosphere and there may have been a central heat source that could have warmed the surface, permitting conditions necessary for habitation. Unfortunately, it’s unknown how Herschel reacted to these ideas about lunar geology and the implications for extraterrestrial life as there is no return letter, or other response, to Faujas.

In addition to the aforementioned letter by Faujas, there are 1181 other letters (995 incoming and 186outgoing[47]) in the Herschel Archive at the Royal Astronomical Society. Of these, 108 were identified as coming from, or going to, natural historians; however, none of these letters contained any geology relevant material, save for the one from Faujas. The discussion of lunar volcanos, in Faujas’ letter and to a lesser extent during his visit at Datchet, is the only direct evidence we have of a natural historian directly communicating with Herschel regarding geological ideas. While it’s conceivable that other letters between Herschel and geologists may have once existed but have since been lost, it seems unlikely given that Herschel devoted relatively little time to writing letters and was particularly neglectful in responding to those written by his friends and family (Hoskin, 2011).

[47] The Herschel Archive has only 184 outgoing letters, however, the existence of two more outgoing correspondences is known from the content of a letter written from Herschel to Michell (W.1/13.M101).

4. The Spread of Ideas through Publications (objective 4, see appendices 4 and 5)

In further pursuit of a mechanism for intellectual exchange, journal publications, and all books in his library for that matter, were used to glean insight on potential influential people. Published scientific literature was an extremely important source of knowledge for Herschel because he received no formal education beyond grade school; he was largely self-taught, driven by his curiosity and desire to learn. As a thorough reader of the *Philosophical Transactions of the Royal Society*, Herschel likely read many of the geology-related articles that appeared, and on occasion perhaps heard them read orally at meetings or even met with the authors.

It was determined that 63 natural historians authored, or co-authored, a total of 75 geology related articles in *Phil. Trans.* from 1760 to 1785[48]. The majority of these authors (62 of the 64) only published one or two articles, but Peter Collinson (1694 – 1768) communicated three and William Hamilton (1731 - 1803) authored a staggering ten! While Collinson was notable among natural historians in London and abroad, and often acted as a middleman for international exchange of ideas (Gillispie et al., 2008), it's unlikely that his articles had much influence on Herschel's astronomy research as they primarily focused on fossil teeth and shells found in North America. However, it's conceivable that these papers may have sparked interest and/or later geology-related ideas when Herschel observed marine fossils while on vacation with his family in Bath.

On the other hand, the sheer number of papers communicated by Hamilton at Royal Society meetings and later published in *Phil. Trans.* argues the likelihood that Herschel was, at the very

[48] Herschel also authored a geology related article during this time (*Phil. Trans.*, 1780, 70, 507-526), but it was not taken into account for these results.

least, aware of the author and his extensive work on volcanos and volcanic eruptions[49]. It is also probable that Herschel read the compilation of Hamilton's work[50], *Campi Phlegraei (1776),* as it was widely owned and sought after in the scientific community; its popularity primarily owing to the 54 superbly detailed and hand-colored illustrations that accompanied the book (Thüsen, 1999; Wood, 2006). Here I suggest the possibility that Hamilton was more than just a familiar name to Herschel, but rather a potential source of inspiration. But to make this connection, we first need a brief introduction to the state of knowledge concerning volcanos, on the moon and earth, in the 18th century.

For most of the century, the origin of various topographic features on the moon received little inquiry, from either astronomers or natural historians[51]. Publications about lunar structures would simply report their existence, and in some instances provide estimates for their heights, but offered no further discussion as to their origin (Home, 1972: p.1); as such, mountains on the moon were just that, mountains, not volcanos. This was perhaps due to the rarity and primitive state of knowledge about volcanos. It was not until the latter part of the 18th century that individuals throughout Europe became concerned with volcanos (either out of curiosity or fear) due to the notable increase in eruptions during this time (Sigurdsson, 1999); Mount Vesuvius in Italy had entered one of its cyclical periods of intense activity and there were particularly severe blasts from both Mount Etna in Sicily and Laki volcano in Iceland, the latter of which released

[49] Today, Hamilton is perhaps best-known as the husband of Emma Hamilton, mistress of Admiral Lord Nelson (Constantine, 2001).

[50] In 1776, Hamilton's *Phil. Trans*. articles were bound together into a single volume, *Campi Phlegraei.* Under Hamilton's direction, the lavish illustrations were drawn to ensure accuracy and then hand-colored by artist Pietro Fabris (Thüsen, 1999).

[51] Home (1972, p.9) "searched in vain in a large number of treatises on astronomy and/or natural philosophy [as well as various encyclopedias] spanning the entire eighteenth century, for a recognition that the origin of the lunar surface features was even a subject worthy of discussion."

poisonous gases that were carried by the Gulf Stream over to Europe[52]. As a result, volcanology progressively developed in the scientific community and the advent of Neptunism[53] and Plutonism[54] further motivated research and heated debates; the Neptunists argued that volcanos had no geological significance because they were superficial phenomena resulting from localized combustion, while the Plutonists, which saw heat as the most important agent in the history of the planet, maintained that volcanos were based on a heat source deep in the Earth's interior and therefore represented central phenomena in the structure and workings of the Earth (Laudan, 1994).

Hamilton's extensive field research while working as a British diplomat in Naples (1764 – 1800) led him to side with the views of the Plutonists (Figure 4.3), believing that volcanic activity had occurred in cycles throughout history and therefore must have contributed substantially to the formation of the Earth's surface (Constantine, 2001). Hamilton's observations of Vesuvius and Etna convinced him to reject the long-standing view that mountains were consumed by volcanos burning within them. He argued instead that volcanism was a constructive force, such that "mountains are produced by volcanos, and not volcanos by mountains."[55] And while Hamilton was aware of the dangers inherent to volcanic activity, his papers and illustrations often emphasized many of the positive aspects, such as their benefits to civilization; he advocated that

[52] Severe eruptions of Mount Vesuvius occurred in 1760, 1767, 1779, and 1794; Mount Etna in 1766 and 1787; Laki volcano in 1783 (Sigurdsson, 1999).

[53] Neptunism, proposed by German geologist Abraham Werner in the 1780's, theorized the formation of the earth as an entirely linear process. It hypothesized an early planet covered by water; but eventually the ocean receded and dissolved minerals precipitated from solution to form the soil rocks and land we see today (Laudan, 1994).

[54] Plutonism was the opposing theory to Neptunism. Although no one person is given credit, James Hutton was among the primary founders and supporters during the 1780's. The theory gave great importance to the interior heat of earth, which was well known from mines, and hypothesized that earth formed by solidification of a molten mass. The earth's heat, along with the force of gravity, was thought to be the driving mechanisms responsible for all natural processes on earth (i.e. sedimentation and erosion). It was also believed that these processes were cyclical and indefinite in operation (Laudan, 1994).

[55] *Observations of Mount Vesuvius, Mount Etna, and other Volcanos,* 1774, p.52.

Figure 4.3: A dramatic scene of advancing lava flows from the eruption of December 1760 to January 1761, Plate XII in Hamilton's *Campi Phlegraei (vol. 2, 1776)*. Hamilton used the original caption of this image to argue against those who believed that the source of a volcanoes heat (and fire) was always near the summit. A digital copy of Hamilton's *Campi Phlegraei*, and the accompanying illustrations (including Figures 4.3 to 4.8), can be found in the special collections of Honnold Mudd Library, (http://ccdl.libraries.claremont.edu/col/cpo).

volcanos provide nutrient-rich soil for farming (Figures 4.4 and 4.5), stones for paving and building materials (Figure 4.6), an aesthetically pleasing view (Figure 4.7), and a landscape favorable to permanent water sources (Constantine, 2001; Wood, 2006).

While it remains speculative if Hamilton's lifelong pursuit of studying volcanos on earth ever led him to theorize about the possibility of volcanos on the moon, it is known that his work directly influenced others interested in the subject; of particular interest are German scientists George Lichtenberg (1742 - 1799) and Franz Aepinus (1724 - 1802). In Lichtenberg's 1778 paper on the moon[56], the author explicitly acknowledged Hamilton's work on Vesuvius as he thought it helped to shape his "…belief that the inequalities of the surface of the Moon were of volcanic origin". For the amateur astronomer Aepinus, it was Hamilton's book[57] that provided inspiration; in comparing his own observations of the moon's surface with the terrestrial volcanic structures illustrated in *Campi Phlegraei,* Aepinus proposed that lunar craters had been formed by past volcanic eruptions and that lunar rays were evidence of past lava flows coming from the largest volcanos. Although Aepinus sent a translated copy of his paper to Hamilton[58], his ideas never gained him much recognition among his contemporary astronomers[59] or natural historians (Home, 1972).

[56] "Ein Paar Neuigkeiten vom Monde."*Göttinger Taschen-Calender for 1779*. Published 1778, pp. 25 - 30. Translation and interpretation of the paper taken from Home, 1972.
[57] *Campi Phlegraei (1776), received by* Aepinus in 1778.
[58] "Ueber den Bau der Mondfläche, und den vulcanischen Ursprung ihrer Ungleichheiten." *Schriften der Berlinischen Gesellschaft naturforschender.* 1781, pp.1 - 40. The paper was sent by Aepinus to Hamilton in 1782 (Homes, 1972).
[59] It's intriguing to think about the possibility of Herschel reading Aepinus', or even Lichtenberg's papers given that they were published in German.

Figure 4.4: A view of Naples from the sea shore, Plate IV in *Campi Phlegraei (vol. 2, 1776)*. The farmers and cattle in the foreground emphasize one of the many positive aspects of living in a volcanic region, the abundance of nutrient-rich soil.

Figure 4.5: Lake Agnano, Plate XVIII in *Campi Phlegraei (vol. 2, 1776)*.. Hamilton described this lake as being “evidently the crater of an ancient volcano.” More farmland is pictured in the fore- and background of the figure. Hamilton further noted that the lake provided a constant source of water for the farmers and that in certain regions “steam baths,” which were warmed by the internal heat of the earth, could be found.

Figure 4.6: "Section of a part of the cone of the Mountain of Somma," Plate XV in *Campi Phlegraei (vol. 2, 1776)*. In Hamilton's description of the illustration, he pointed out the "strata of erupted material [are] exactly similar to those of Vesuvius." He also noted that the "quarry supplies stone, for the purposes of building and paving."

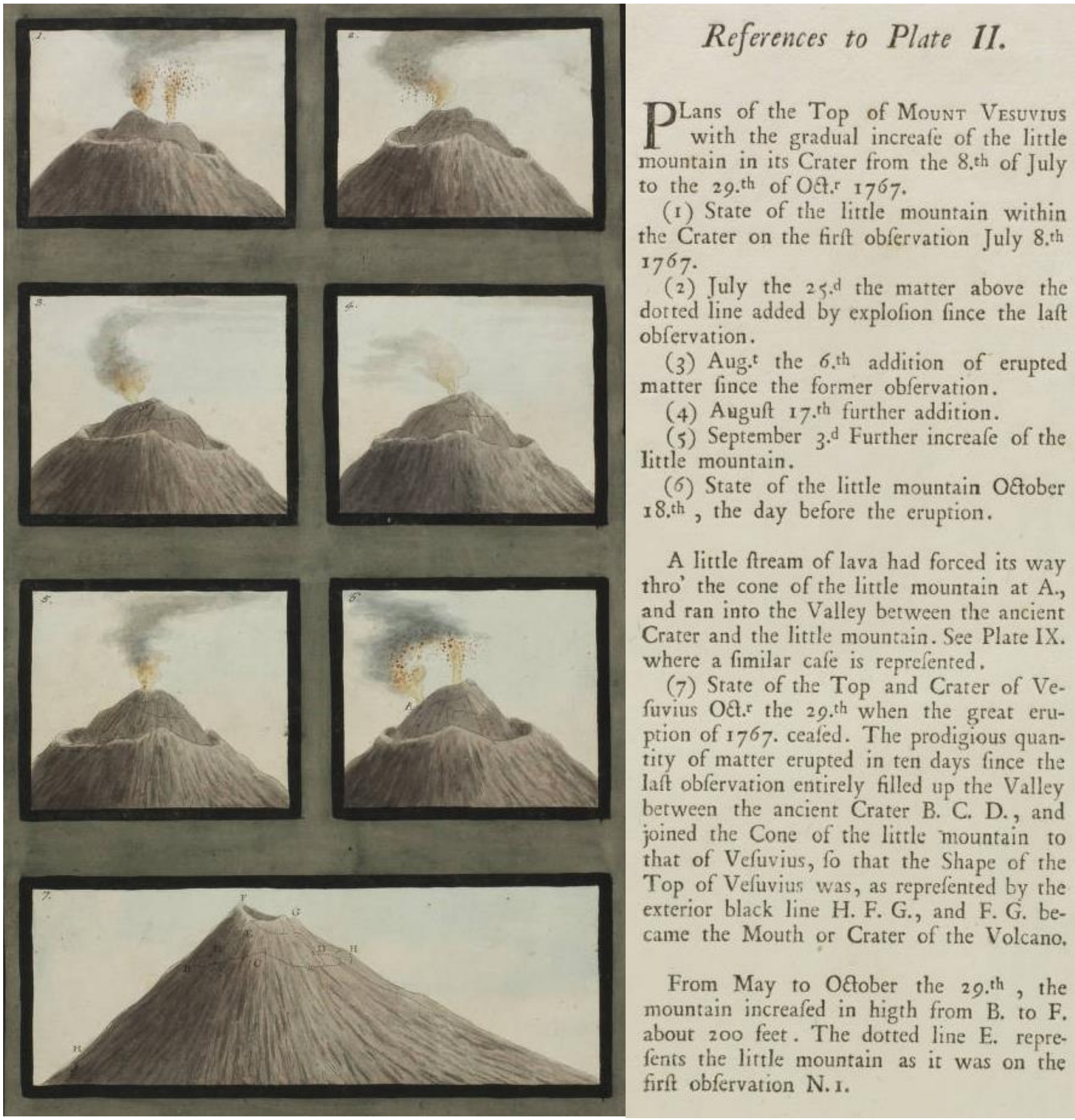
Figure 4.7: A view of Campi Phlegraei, Plate III in *Campi Phlegraei (vol. 2, 1776).* This figure shows the peaceful co-existence of Naples and Mount Vesuvius. The traffic on the road, the boats in the bay, and the citizens on the shore-front illustrate the role of the volcano as part of the city's daily life.

Like Lichtenberg and Aepinus, Hamilton may have similarly had an influence on Herschel's thoughts concerning volcanos on the moon, specifically the progression of his ideas from "Mountains on the Moon" in 1780 to erupting "Volcanos in the Moon" in 1787. It was perhaps not just his observations of "eruptions of fire, or luminous matter[60]" coming from the mountains on the moon that were influential, but current literature and discussions with colleagues and visitors[61] may have also played a significant role, especially in persuading him to publically claim active volcanism on the moon. It's hard to imagine it's a coincidence that Herschel's interest in lunar mountains began during the popularization of volcanology in the late 18th century, not to mention shortly after the publication of Hamilton's well-known compilation of papers on the subject. Even more intriguing is the fact that Hamilton visited Herschel twice during this time (see Appendix 4.3). And just as Hamilton had reported seeing Vesuvius growing hundreds of feet in height before his very eyes (Figure 4.8), Herschel too claimed to have observed the formation of a volcano in only a few nights, albeit with his telescope and on the moon.

Herschel's speculation about the likelihood of habitable conditions on the moon also incites curiosity about the source of his reasoning. In a letter to astronomer Nevil Maskelyne on June 12th, 1780 (Royal Astronomical Society Archive), Herschel argued that "there is a provision of light and heat [on the moon]: also, in all appearance a soil proper for habitation full as good as ours, if not perhaps better – who can say that it is not extremely probable, nay beyond doubt, that there must be inhabitants on the moon of some kind or other?" Is the source of heat Herschel

[60] Quote from "Volcanos on the Moon," (1780, p.230).

[61] Faujas recalls his observations and discussions with Herschel concerning lunar volcanos in his book (see footnote 45) and in his written letters to Herschel (see footnote 47). In 1786, there is a record from a diary entry by Fanny Burney, on December 30th, 1786, which reports a visit to Herschel: "The moon… has already afforded him two volcanos" (*The Herschel Chronicle* by Constance A. Lubbock, 1933, p. 170, Cambridge).



References to Plate II.

PLans of the Top of MOUNT VESUVIUS with the gradual increaſe of the little mountain in its Crater from the 8.th of July to the 29.th of Oct.r 1767.

(1) State of the little mountain within the Crater on the firſt obſervation July 8.th 1767.

(2) July the 25.d the matter above the dotted line added by exploſion ſince the laſt obſervation.

(3) Aug.t the 6.th addition of erupted matter ſince the former obſervation.

(4) Auguſt 17.th further addition.

(5) September 3.d Further increaſe of the little mountain.

(6) State of the little mountain October 18.th, the day before the eruption.

A little ſtream of lava had forced its way thro' the cone of the little mountain at A., and ran into the Valley between the ancient Crater and the little mountain. See Plate IX. where a ſimilar caſe is repreſented.

(7) State of the Top and Crater of Veſuvius Oct.r the 29.th when the great eruption of 1767. ceaſed. The prodigious quantity of matter erupted in ten days ſince the laſt obſervation entirely filled up the Valley between the ancient Crater B. C. D., and joined the Cone of the little mountain to that of Veſuvius, ſo that the Shape of the Top of Veſuvius was, as repreſented by the exterior black line H. F. G., and F. G. became the Mouth or Crater of the Volcano.

From May to October the 29.th, the mountain increaſed in higth from B. to F. about 200 feet. The dotted line E. repreſents the little mountain as it was on the firſt obſervation N. 1.

Figure 4.8: Mount Vesuvius, Plate II in in *Campi Phlegraei (vol. 2, 1776)*. This figure shows a time series of illustrations depicting the rapid growth of Vesuvius, as observed by Hamilton, from July 8^{th}, 1767 to October 29th, 1767.

referred to only coming from the sun, or is this an allusion to volcanos and the interior heat source they imply? In his mention of soil, how does Herschel know it's suitable for life and that it's similar to the soil on earth? Is it possible that these ideas stemmed from Hamilton's unique advocation that volcanos provide numerous benefits to humans, one of which was fertile soil? While there are numerous parallels that can be drawn[62] between Herschel's papers on lunar volcanos and Hamilton's work on terrestrial volcanos, speculation remains over the mechanism of intellectual exchange between the two as the one known written correspondence provides no relevant clues and there is no record of what was discussed during their visits.

5. Giving Credit Where Credit is due (objective 5, see Appendix 4.6)

While examining Herschel's in-text and footnote citations within his seven papers concerning the construction of the heavens, it was noted that very few individuals or literary sources were acknowledged. He did commonly reference his own papers, as well as a number of star atlases such as Messier's catalog of nebulae and star clusters (see Appendix 4.6), but it remains unclear if the novel ideas he presented were truly his own, or if they were shaped by the influence of others.

In his first paper concerning the structure of the Milky Way[63] Herschel gave credit to the natural historians for the terminology he used in describing the "interior construction of the heavens, and its various nebulous and sidereal strata (p.438)." In fact, he "borrow[ed this] term from the natural historians" repeatedly throughout his papers. In discussing his results and their

[62] Although not directly relevant to this argument, the impact of Hamilton's work on the development of early volcanology mirrors the importance of Herschel's work as the starting point in selenology (the scientific study of the formation and composition of the Moon's crust).
[63] "Account of Some Observations," 1784.

implications for understanding the "natural causes" of star clusters[64], he emphasized the need to go beyond the "bare enumeration of phenomena" in the observable universe; he warranted this extrapolation of data by asking "why should we [astronomers] be less inquisitive than the natural philosopher, who sometimes, even from an inconsiderable number of specimens…is enabled to present us with the history of its life, progress, and decay (p.214)?" But more than justifying his interpretations or using geology-related vocabulary, did Herschel also "borrow" any ideas from the natural historians?

While no direct evidence has been found linking the geology-related ideas of a natural historian with those presented in Herschel's work, its perhaps noteworthy that John Michell, an astronomer AND geologist, was the only individual to explicitly be given credit for his intellectual contributions (concerning the construction of the heavens, see Appendix 4.6). Unlike all other references, which simply provided a title or name of an individual, Herschel also devoted a few sentences to explaining Michell's pertinent findings. For example, in describing the structure of the Milky Way and the "remarkable collection of many hundreds of nebulae (p.255)" in his 1785 paper[65], Herschel acknowledged Michell's ideas about stellar systems[66], specifically his claim that "the stars…gathered together into groups" and his "elegant proof of this on the computation of probabilities." In a succeeding paper[67], Herschel again referenced Michell's "Probable Parallax" (1767) paper and his calculation that "the odds are near 5,000,000 to 1 that no fixed stars…scattered at random in the whole heavens, would be within so small a distance from each other as the Pleiades are (p.215)." Although not explicitly stated, it is my interpretation that Herschel cited Michell's proof of the Pleiades to show that the Milky Way as a

[64] In a "Catalogue of a Second Thousand of New Nebulae and Clusters of Stars," 1789.
[65] "On the Construction of the Heavens," 1785
[66] Those presented in Michell's 1767 paper, "An Inquiry into the Probable Parallax."
[67] See footnote 64.

whole was similarly a non-random distribution of stars. But Herschel went beyond Michell's work and claimed that within the galaxy, stars were uniformly distributed. He then developed a star gaging approach that allowed him to explore the finer-scale details within the Milky Way and ultimately hypothesize about the structure of our galaxy.

In addition to the construction of the heavens papers, Michell was acknowledged in some of Herschel's earlier publications. In his 1782 paper "On the Parallax of the fixed stars" (*Phil. Trans*., 72, 82 - 111), for example, Herschel embraced Michell's suggestion that "another kind of hitherto unknown parallax" may "account for some part of the [proper] motions already observed in some of the principal stars (p.103)." In response to criticisms he received concerning assumptions he made in the paper[68], Herschel again used Michell as his ally, selecting several quotations from Michell's paper to show that his contemporary shared many of the same ideas[69]. A year later, in his paper[70] on the proper motion of the sun and the solar system, Herschel wrote that "Mr. Michell's admirable idea of the stars being collected in the systems… appears to be extremely well-founded, and is every day more confirmed by my observations." The numerous references made to Michell in his papers and correspondences[71] indicate that Herschel was intimately aware of Michell's research and its relevance to his own. And although all the examples provided are in relation to Michell's work in astronomy, the fact that he is repeatedly cited (not to mention is the only individual to receive significant acknowledgment in Herschel's

[68] He received criticism for his claims that (1) stars were about the same size as the sun and (2) that the distance of fixed stars was proportional to their magnitude (in a letter from Neville Maskelyne, on behalf of the Royal Society Committee on Papers, to Herschel on April 19, 1782. RAS, W.1/13, M.18.).
[69] In a letter from Herschel to Nevil Maskelyne, written on April 28th, 1782.
[70] "On the Proper Motion of the Sun and Solar System; with an Account of Several Changes that Happen Among the Fixed Stars Since the Time of Mr. Flamsteed" *Phil. Trans.*, 1783, 73, 247-283.
[71] Michell was mentioned in several other correspondences to and from Herschel, see for example those mentioned in McCormmach, 2012: pp. 154 – 156.

papers on the Milky Way), suggests that William was likely aware of, if not also influenced by Michell's earlier work in geology.

6. The Most Probable Influential Geologists (objective 6, see Appendix 4.7)

In consideration of the results that have been discussed and the data that is contained in the appendices, three natural historians stand out as the most likely candidates to have influenced the ideas and/or work of William Herschel: William Hamilton (Figure 4.9), Barthelemi Faujas de Saint-Fond (Figure 4.10), and John Michell. A full list of leading candidates, ranked by their perceived importance, can be found in Appendix 4.7.

Faujas was identified as one of the most probable influential geologists because of his extensive research on volcanos, an interest shared by Herschel, and the evidence for their direct communication (in person and written) concerning the moon - its volcanos and atmosphere, and their relative importance for creating habitable conditions analogous to earth[72]. However, the timing of the aforementioned exchanges of information generates some doubt over Faujas' influence. For example, Faujas' geology-relevant letter in 1788 post-dated all of Herschel's publications concerning volcanos on the moon. Moreover, Faujas' first meeting with Herschel at the Royal Society in early August of 1784, his one known visit to Datchet on August 15th, 1784, and his two letters written in 1786 and 1788, also supersede Herschel's first publication on the construction of the heavens, suggesting that he had little influence on the original ideas presented therein. However, we do have evidence that Faujas communicated with Herschel on the night of August 15th, 1784 (see Results, section 3). Despite the fact that the written account of Faujas visit was not published until 1799, it's clear that the two talked about volcanoes before Herschel

[72] Royal Astronomical Society, Herschel Archive (W.1/13.F.5). Also, see Appendix 4.9.

Figure 4.9: Sir William Hamilton, portrait by George Romney (image from the Library of Congress).

Figure 4.10: French geologist and world traveller Barthelemi Faujas de Saint-Fond (image from the Library of Congress).

published his second paper on lunar volcanoes in 1787. Moreover, Faujas traveled extensively and visited many of the world's leading natural historians, such as the Comte de Buffon, James Hutton, Joseph Black, and William Hamilton[73]. The ideas of Faujas may have been communicated indirectly to Herschel through others; or vice-a-versa, Faujas may have passed along the ideas of his contemporaries during his later discussions with Herschel.

In comparison to Faujas, the evidence in favor of Hamilton as a source of inspiration is perhaps slightly more persuasive. Hamilton's research concerning volcanos and strata (see section 2 in Results) may have been more known to Herschel considering Hamilton's impressive publication record in *Phil. Trans.* and the popularity of his uniquely illustrated *Campi Phlegraei (*see section 4 in Results). Given their membership together in the Royal Society, as well as Hamilton's known excursions to London (at least in 1771-72, 1783-84, and 1791; Barrett, 1983) and their occasional visits with one another (as recorded in the Herschel's' visitors book), the likelihood of intellectual exchange between Hamilton and Herschel was also greater when compared to Faujas (who primarily resided in France, a country often socially isolated from England due to intermittent periods of War between the two countries). Lastly, Hamilton shared Herschel's passion for music; he was a violinist and often provided musical entertainment for his family and friends (Gillispie et al., 2008). Unfortunately there is no record of Herschel attending one of his soirees, or even evidence that Herschel knew about Hamilton's musical interests, but the mere fact that the two shared yet another facet of their lives strengthens their possible connection to one another.

[73] Faujas de Saint-Fond. *Travels in England, Scotland, and the Hebrides: Undertaken for the Purpose of Examining the State of the Arts, the Sciences, Natural History and Manners, in Great Britain: ...* in Two Volumes with Plates, translated from French. London: Printed for James Ridgway, 1799.

While no written correspondence is recorded in the Herschel Archive, one letter between Hamilton and Herschel does exist[74]. In short, the letter expressed Herschel's interest in observing the planets from Naples and his desire to know if Hamilton would speak to the King of Naples on his behalf. An analysis of the letter has argued that the formal third-person style of the writing indicates that the men were not personally acquainted (Barrett, 1983); however, I believe a contrary case can be made based on the other circumstantial details. According to the letter, Herschel "called on" Hamilton, likely at his place of residence given that the letter did not have an address, contained no postal markings, and was written without a date (perhaps because it was intended to be seen the same day). If the two men were not personally acquainted, why would Herschel have had the letter hand-delivered (personally or otherwise) rather than sent directly to the King through the mail? And why choose Hamilton at all – unless Herschel was at least somewhat familiar with him. Perhaps Herschel trusted Hamilton for some unknown reason and/or was aware of his position in Naples and his social status with the King. Either way, Herschel surely had a good reason for entrusting his letter to Hamilton as it was meant for royalty and had significant ramifications for Herschel if positively received. In retrospect, the better question to have asked would have been - why would Herschel not want Hamilton to deliver his letter?

The content of the letter was not only important for its insinuation of a personal connection, but also because it highlighted Herschel's interest in undertaking an extensive observational study in Naples, the city where Hamilton primarily resided. Before this letter, historians tended to think of Herschel as an astronomer tied to his home in England. But Herschel's request to study abroad begs the question - why Naples? Barrett (1983) posed some scenarios, including possible desires

[74] Unfortunately the date of the letter is unknown, but circumstantial evidence suggests that it was written between May and September of 1791, when Hamilton took leave in London (Barrett, 1983).

to visit a warmer climate or the well-known Italian astronomer Giuseppe Piazzi. But how inconceivable would it be to imagine that Herschel may have also chosen Naples because of Hamilton's presence there, because the two shared common interests and wanted to work on understanding lunar volcanos? Perhaps a stretch, but at least no evidence exists to refute the idea.

However, the most compelling case that can be made regarding the connection between Herschel and a natural historian is for the astronomer and geologist John Michell. While there is no "smoking gun," the evidence is highly suggestive that much of Herschel's work is indebted to Michell's contributions in astronomy and geology, almost all of which pre-date Herschel's notable ideas. Five significant parallels can be drawn between these two pioneers in sidereal astronomy: (1) their interest in stellar statistics, (2) their desire for improved instruments, (3) their use of stellar photometry, (4) their use of the word strata to describe global/universal structures (discussed in Results section 2), and (5) their love of music.

Herschel's ideas concerning the construction of the heavens were shaped by Michell's work in stellar statistics, and perhaps to a lesser extent by his advocation for stellar photometry and improved telescopes. In determining the structure of the Milky Way, Herschel's star gaging approach for data collection relied on two important assumptions: (1) that stars were distributed uniformly throughout the Milky Way and were not located beyond the boundaries of the system, and (2) that his telescope could see to the ends of the galaxy and resolve all stars within its limits. On a broad scale (as previously suggested in section 5 of the results), the first assumption may have been predicated on Michell's mathematical proof that a random distribution of stars was statistically improbable.[75] In other words, Herschel may have viewed the Milky Way galaxy as a

[75] Michell surmised that the observed clustering of stars was either a result of an "original act by the creator" or some general law such as gravity.

non-random grouping of stars such that one could determine the limits of the system purely by determining the distance at which stars were no longer part of the grouping. However, it is equally plausible that Michell's statistical proof, coupled with Herschel's later observations of numerous star clusters, actually led William to question his initial assumption of uniformity. In 1817, Herschel stated that "with regard to these gages, which on a supposition of an equality of scattering were looked upon as gages of distances, I have now to remark that, although a greater number of stars in the field of view is generally an indication of their greater distance from us, these gages, in fact, relate more immediately to the scattering of stars…"[76] The second assumption, which Herschel also later realized to be false, was initially given credence based on the superior quality of his telescopes. With the advent of his 40 foot instrument, he recognized that a larger aperture allowed him to see new stars that were previously unresolvable. He then concluded that "…the utmost stretch of the space-penetrating power of the 20 feet telescope could not fathom the profundity of the milky way…"[77]

Like Herschel, Michell devoted much of his astronomy career to designing and building better telescopes[78]. But while most other astronomers were concerned with the development of more precise instruments for measuring parallax, Michell argued instead for larger telescopes, ones bigger than any yet built. He believed that an increase in size was more beneficial because it would increase the number of visible stars in the sky, allow for the resolution of nebulae into star clusters, and provide more accurate information about gradations in star brightness, which in turn would enable astronomers to make better estimates of the distances and magnitudes of stars in

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[76] "Astronomical Observations and Experiments Tending to Investigate the Local Arrangement of the Celestial Bodies in Space and to Determine the Extent and Condition of the Milky Way" Phil. Trans., 1817, 107, 302-331.
[77] See footnote 76.
[78] Michell was drawn to inventing new measuring instruments and improving research methods, in both geology and astronomy. He is credited with inventing the "astrophotometer," a device that allowed him to better compare degrees of brightness from one star to another (McCormmach, 2012).

the solar system (McCormmach, 2012). While Michell made many attempts to make such telescopes, it was Herschel that ultimately succeeded in making Michell's vision a reality. Whether or not he was motivated by Michell's arguments[79], Herschel dedicated much of his time to making bigger and better telescopes because he believed them a necessity to observe stellar phenomena, such as double stars, and he required them for his "construction of the Milky Way."[80]

To create his map of the galaxy, Herschel relied on his powerful telescopes to estimate distances to the stars. But because no one had yet successfully measured a stellar parallax Herschel employed stellar photometry. Michell's "Probable Parallax" (1767) paper, which Herschel read and cited on multiple occasions, may well have provided the rationale; as previously discussed (Results, section 2), Michell strongly advocated that stellar photometry offered astronomers a more practical way to estimate stellar distances.

Outside of astronomy, Michell and Herschel shared yet another common interest, a love for music in a life of science. Although he was not as well-known or distinguished as Herschel, Michell was a skilled violinist. And according to one of his great-grandsons, he held musical soirees at his home in Thornhill (Bux, 1871, as cited by McCormmach, 2012: pp.197 – 198). It was also suggested that Herschel, among many others in the scientific community, attended these parties and may have even joined in on several occasions. It's also conceivable that Herschel may have had musical discussions with Michell given Michell's collaboration with Robert Smith and his contribution to *Harmonics*, a book that Herschel was impressed with (McCormmach, 2012: p.197).

[79] Michell's plea for bigger telescopes was in his 1767 publication on the "Probable Parallax," a paper which Herschel read and cited.
[80] In a letter from Herschel to Christian Mayer on October 8th, 1782, (RAS, W.1/1,59-61) and a letter from Herschel to de Lalande on May 23rd, 1783, (RAS, W1/1.).

Although the majority of the evidence points to Michell as the primary source of inspiration for Herschel, considering Michell's work pre-dates many Herschelian ideas, the influence may not have been a one-way street. Their shared interests went further than the distribution of stars; it also concerned the nature of stars. For example, there is a connection between Michell's later publication "On the Means of Discovering the Distance"[81] (1784) and Herschel's many observations of double stars (McCormmach, 2012: pp. 204-208). On May 26th, 1783, Michell sent a letter to Henry Cavendish containing a copy of his *Phil. Trans.* manuscript (1784, 74, 35-57) to be communicate to the Royal Society. In the paper, he claimed that the method of determining the "distance, magnitude, and weight" of certain stars had originally occurred to him many years before (~1773), but he chose not to further investigate the idea because he doubted the possibility of observing the double stars necessary to make his claim. It was not until Herschel published his "Catalogue of Double Stars" in 1782 (*Phil. Trans.*, 72, 112-162) that he regained the hope of pursing his method[82]. Michell was impressed by Herschel's work and believed it was "a most valuable present to the astronomical world…a very wonderful progress in this branch of astronomy, in which almost nothing of any consequence had been done by anyone before him."[83] Michell was grateful for Herschel's work as it provided him with a "vast number of double stars," many of which were "properly circumstanced" for the continuation of his research[84]. He further noted that (p.56) that "…it is not improbable, that a few years may inform us, that some of the great number of double, triple stars, &c. which have been observed

[81] "On the Means of Discovering the Distance, Magnitude, &c. of the Fixed Stars, in Consequence of the Diminution of the Velocity of Their Light, in Case Such a Diminution Should be Found to Take Place in any of Them, and Such Other Data Should be Procured from Observations, as Would be Farther Necessary for That Purpose. Phil. Trans., 1784, 74, 35-57; by John Michell, in a letter to Henry Cavendish on May 26th.

[82] On July 2nd, 1783, Michell told Cavendish that "it was not till after I heard of Mr. Herschel's discovery of so many double stars, when I was last in London (for I had hardly heard anything of it before) that I began to think, that possibly the diminution of the velocity of light might now begin to be the foundation of some observations" (from a reprint of the letter in McCormmach, 2012: p. 364).

[83] "Means of Discovering the Distance" p.36, (see footnote 81 for full citation).

[84] Letter from Michell to Cavendish, July 2nd, 1783, in McCormmach, 2012: p.365.

by Mr. Herschel, are systems of bodies revolving about each other." Not surprisingly, Herschel validated Michell's prediction nearly two decades later (1803 and 1804) when he demonstrated that many of his double stars were actually binary companions "… intimately held together by the bond of mutual attraction."

In terms of a mechanism for intellectual exchange, Michell's *Phil. Trans.* papers provide the most concrete and direct evidence, but written correspondence between the two (Appendix 4.2), albeit focused primarily on astronomy and the construction of telescopes, also suggests that scientific dialog was common. And even though we only have one documented record of Michell and Herschel meeting in person[85], it can be argued from their numerous shared interests and mutual respect for one another that they met many times and likely influenced each other. In one pertinent example, Michell wrote to Henry Cavendish and said that "Mr. Herschel's idea of the Solar System being in motion, I think not at all improbable, but I apprehend it will require a great many more observations, than we are yet in possession of." But even more important was Michell's recognition that "It would indeed be very desirable, if this matter could be made out pretty clearly, as it might then afford us the means of discovering some time or other a secular parallax, as I have hinted on a former occasion[86], and by that means give us another step towards discovering the real distance to the stars." This passage highlights Michell's recognition of Herschel's work, the results of which he noted would be extremely valuable to "us" (astronomers

[85] Herschel also made at least two visits to Michell's home in Thornhill, one before his death and one after. The first visit of record was on July 13th, 1792, when Herschel's was on his way home after a seven-week trip to Scotland (as recorded in a journal entry by Herschel, RAS W.7/15.1- pp.136, i73). The second known trip was during the summer of 1793; Herschel visited Michell's residence after his death and bought one of Michell's speculum mirrors (with a 29" diameter) from his son-in-law for 30 pounds, despite his criticism that it was not of superior quality or craftsmanship (the critique of the speculum can be found in W.7/14/i17-18, also see Hoskin, 2011: p.159). No additional accounts of personal visits are known.

[86] In Michell's "Probable Parallax" paper (1767), he wrote that the observed change in the position of stars "may be owing either to the real motion of the stars themselves, or to that of the Sun, or partly to the one, and partly to the other" (pp.252-253).

in general, I assume). In realizing the importance of each other's' work[87], the motivation to engage in meaningful scientific discussion would have been strong.

CONCLUSION

This rotation project is the first in-depth exploration of the linkages between astronomer William Herschel and contemporary natural historians[88]. During the 18th century remarkable advancements were being made in both geology and astronomy, and the Royal Society was at the nexus of these two threads, both intellectually and socially. My analysis of personal correspondences, visitor logs, articles in *Philosophical Transactions,* and secondary scientific and biographical literature revealed that there was indeed a connection between Herschel's research and the work of several notable geologists including William Hamilton, Barthelemi Faujas de Saint-Fond, and John Michell. Unfortunately there is no smoking gun that points directly to these geologists, but I did find evidence that there was significant influence.

While this project focuses only on the arguments in favor of geologists directly influencing the ideas of Herschel, other possible explanations do exist. For example, it's conceivable that Herschel's innovative theories and ideas were entirely his own, formed independently of any other person or research endeavor. But it's also likely that others played some role; the earlier suggestive ideas of Kant, Wright, and Lambert, for instance, may have influenced Herschel's

[87] Herschel's acknowledgement of Michell's work is evident in his references, which are of significant importance considering the overall lack of citations made my Herschel; Michell's appreciation of Herschel's work in known primarily from letters (McCormmach, 2012).

[88] McCormmach (2012) did write an entire biography on the astronomer and geologist John Michell. It is his view that Michell's ideas and innovative research were largely underappreciated both by his contemporaries and the modern scientific community. The book cites many intriguing facts and letters that draw parallels between Michell's work and that of several notable natural historians, but interestingly the author does not take the next step to make claims about Michell's likely influence on the research of his contemporaries, the geologists or otherwise.

work on the structure of the Milky Way.[89] Further research examining the possible linkages between Herschel and contemporary biologists, such as Erasmus Darwin, may also reveal additional motivational sources, especially in relation to his research on stellar evolution and deep time. But until further connections can be found in support of these alternative hypotheses, I argue that geology played a more important role than anyone has ever appreciated.

FUTURE WORK

There were several interesting ideas and tangential topics that surfaced during the course of this project. While they were not pursued due to time constraints, future rotation projects or those interested in Herschel and connections with his contemporary natural historians, could follow-up on these ideas at a later date.

1. Herschelian connections relating to heat and infrared light

Later in his career, Herschel became interested in heat and infrared light. In fact, he published several papers in Phil. Trans. on these subjects; four papers were presented in 1800 (vol. 90, p.255-283; p.284-292; p.293-326; p.437-538) and two more in 1801 (vol. 91, p.265-318; p.354-362). While researching significant natural historians with geological research, it was discovered that several of these individuals also made notable contributions related to heat and light. It is therefore possible that these natural historians may have had some influence on Herschel's later work, or vice-a-versa. For example, James Hutton theorized the existence of invisible light in his book "*Philosophy of Light, Heat,* and *Fire" (*1794), after conducting a series of rudimentary experiments. He also noted that more sophisticated experiments would be needed to further understand and prove his idea. James Hall, a Scottish geologist and chemist, experimented

[89] See footnotes 19 - 21.

extensively with various rocks and showed that they were produced by intense heat and slow cooling. Comte de Buffon, a French naturalist, wrote a paper on the heat of the earth and conducted a series of experiments to estimate the age of the earth. Future endeavors could look for additional ties.

2. Herschelian connections with "biologists" relating to evolution

Although Herschel's research on stellar evolution was discussed in relation to geological ideas about gradual change through time and cyclical earth processes such as uplift and erosion, a potential connection also exists with biologists and their theories on plant and animal evolution. One contemporary of Herschel's was Erasmus Darwin (1731-1802), a well-known physician (and grandfather of Charles Darwin) who wrote poems about the relatedness of all forms of life on earth and described a theory of evolution not unlike the theory we know[90].

3. How unusual was Herschel's lack of citations?

As previously mentioned, Herschel gave intellectual credit to very few individuals or literary sources within his seven papers concerning the contruction of the heavens. It reamins unclear if the scarcity of citations was due to Herschel's lack of formal education, was something typical of 18th century publications, or can be attributed to something else entirely. A future study could compare the number of references that Herschel made in his papers to that of his contemporary astronomers who were university educated.

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[90] "Would it be too bold to imagine, that in the great length of time, since the earth began to exist, perhaps millions of ages before the commencement of the history of mankind, would it be too bold to imagine, that all warm-blooded animals have arisen from one living filament, which the great first cause endued with animality, with the power of acquiring new parts, attended with new propensities, directed by irritations, sensations, volitions, and associations; and thus possessing the faculty of continuing to improve by its own inherent activity, and of delivering down those improvements by generation to its posterity, world without end!" From E. **Darwin's** *Zoonomia, or the laws of organic life (1st ed., 1794.* 2nd ed. London: J Johnson, 1796. 3rd ed, 1801).

4. Scientific Clubs

In the 18th century, scientific clubs were popular among the educated, at least in England and Scotland, but presumably elsewhere as well. These clubs facilitated scientific exchange as they provided an informal setting for conversation and debate. Members could share their research and look to friends and colleagues for insight or new ideas. Most clubs met before formal meetings or over dinner, such as the Club of the Royal Philosophers and "the Monday Club" in London (McCormmach, 2012: p.105). In Scotland, the Oyster Club was a weekly social gathering among friends that often attracted out-of-town visitors and savants (John Rae, 1895: pp.334 - 338, 416 - 419). Unfortunately it is unknown if Herschel was a member of any such clubs; but if he was, these scientific gatherings may have played an important role in shaping his research and/or ideas.

5. Herschel, an astrobiologist at heart?

From the begining of Herschel's astronomy career, he believed that life undoubtedly existed elsewhere in the universe[91]. His early paper on lunar mountains[92] even contained a detailed seciton on the inhabitants of the moon, whom he called lunarians; however, it was excluded from the article at the behest of the Astronomer Royal, Nevil Maskelyne[93]. It has also been speculated that the search for intelligent life and extrasolar habitable conditions were among the primary factors motivating him to build bigger and better telescopes (Hoskin, 2011: p.216). Further

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[91] "It may, perhaps, be esteemed to be a mere matter of curiosity to search after the height of the lunar mountains. I grant that there are more necessary and more useful objects of inquiry in the science of astronomy; but when we consider that the knowledge of the construction of the moon leads us insensibly to several consequences, which might not appear at first; such as the great probability, not to say almost absolute certainty, of her being inhabited, we shall soon agree, that these researches are far from being trifling." In "Astronomical Observations Relating to the Mountains of the Moon*," P*hil. Trans. 1780, vol. 70, p. 507-508.

[92] See footnote 29 for paper citation.

[93] The removed section appears in the original letter written from Herschel to Maskelyne on June 12th, 1780 (Royal Society Archives).

exploration of Herschel's interests in extraterrestrial life would lend itself to an intriguing astrobiology research rotation project.

6. Geologists and the making of telescopes

Mineralogy was popular in Europe during the 18th century owing to the increased demand for building materials following the economic hardship of the Seven Years' War (1754-1763) and the ensuing industrial revolution (Porter, 1977; McCormmach, 2012). Many articles in *Phil. Trans.* concerned themselves with the examination of various minerals and ores. Further connections may be made between Herschel and the Mineralogists regarding building materials, particularly those useful in the construction of telescopes and speculum mirrors.

CONCLUDING REMARKS

In reflecting on the project, I can say that I have truly enjoyed the rotation, much more than I initially anticipated. At the start, I was hesitant because I had very little experience in conducting research within the realm of science history, but I realized that my lack of knowledge in the subject was to be expected given the nature of the Astrobiology research rotation. It was challenging at first, given the language differences associated with old English and the unfamiliar types of data I had to work with (letters, visitor logs, travel diaries, etc…). But the project provided me with new perspectives on how to approach different types of problems and how to make the most of datasets that are anything but complete.

To my surprise, learning about the history of astronomy and geology in the 18th century really appealed to me; most of the literature on the subject was enjoyable to read, especially outside during the summer, and I began to appreciate the freedom that the project allowed me. While I was initially skeptical that I would be able to find the evidence I needed to make compelling arguments, I was soon surprised (and eventually a little overwhelmed perhaps) by the number and variety of connections I was able to make between Herschel and his contemporary natural historians; and in light of the results, I view this project as a success.

It should also be noted that the rotation evolved over the course of several months. As I continued to dig deeper into the literature and discuss my findings with Woody, the scope of the project transformed in ways that were not anticipated by either myself or Dr. Sullivan. For example, when we first started looking for geologists whose worked paralleled that of Herschel's, we focused on the natural historians that were primarily interested in strata as Herschel's construction of the heavens papers commonly used the term as a descriptive adjectives. But eventually many more linkages between Herschel and the natural historians were made, namely their similar interests in cyclical processes (stellar evolution), deep time, and global/universal phenomena. After cross-referencing all the different sources of data that were compiled, it was noted that none of the highest ranked candidates (Appendix 4.7) were particularly concerned with deep time (or extending geological time). However, a new connection was discovered relating to volcanos and their counterparts on the moon. It was similarly surprising when we discovered that John Michell was not just an astronomer, as Woody had initially thought, but also a renowned geologist, one with many more connections to Herschel than originally anticipated. Additional parallels between Herschel's ideas and those of the natural historians were revealed throughout the course of the project, but in the interest of time many of them were not pursued further.

My favorite part of the rotation has been working with Dr. Woody Sullivan, his enthusiasm for and dedication to the subject made this experience not just educational but also fun. I am grateful for his continued help and guidance throughout the project, and especially for the valuable feedback he provided with regard to this paper. The only aspect of the project that I would change would be the writing component; while I think this paper is a good representation of my work, will allow for future reflection on this experience, and will hopefully be of assistance to Dr. Sullivan while writing his own book, I did not anticipate the amount of time it would require. If I had the luxury of doing the project over again, I think I would spend more time exploring the other potential connections we identified (such as those outlined in the future work section), and would provide my results in either a relatively informal report or a short paper accompanied by a longer appendices.

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APPENDICES

APPENDIX 1.1

Summary of Lennard Shelf $\delta^{13}C_{carb}$ and $\delta^{18}O$ Data

See electronic attachment (excel file) for a summary of the bulk-rock and microdrilled carbon and oxygen isotope data analyzed in this dissertation (see Chapter 1 for a detailed description of the methods). Data are arranged by section, then by quality control value, and finally by stratigraphic height (in meters).

APPENDIX 2.1

Conodont Biostratigraphy

The standard Montagne Noire (MN) succession by Klapper (1989) and subsequently modified 15-fold zonation by Girard *et al*. (2005) is used to define the Frasnian Conodont Zones (CZ) in the Upper Devonian. Famennian Conodont Zones are based on the zonation by Ziegler and Sandberg (1990). The conodont biostratigraphy used in this dissertation is primarily based on the work of Kate Trinajstic and Brett Roelofs at the University of Western Australia (Roelofs et al., 2015). Additional data for the Frasnian portion of the Horse Springs section (VHS) was taken from previously published work in the same locality (Klapper, 2007).

South Oscar Section (SOC)

Sample I.D.	Meters (m)	Species	Age	Comments
SOC 3	2.8	Barren		
SOC 9	8.7	Barren		
SOC 41	38.8	*Pa. punctata*	Zones 5 - 10	Possibly Zones 5-9 (Klapper, 2009)
SOC 80	75.7	Barren		
SOC 100	93	*Icriodus alternatus*	Zones 5-10	
SOC 120	112.8	*An. Gigas, Polygnathus normalis?*	Zones 6 - 10	Zone 6 based on Klapper, 2009.
SOC 124	117	*An. gigas, Pa. proversa, Pa. kireevae, Pa. plana.*	Zone 10	
SOC 150	140.6	Barren	Zones 10-13	
SOC 157	147.8	*Hindeodella sp.*	Zones 10 -13?	Undiagnostic
SOC 185	177.8	*Pa. bogartensis*	Zone 13	
SOC 200	192.8	*Pa. beckeri, Pa. winchelli, Pa. boogaardi, Pa. juntianensis, Pa. klugi, Pa. linguiformis, Pa. nicholli, Pa. rhenana, An. Buckeyensis.*	Zone 13b	
SOC 205	198.8	*Pa. boogaardi*	Zone 13b	
SOC 210.5	203.3	*Pa. buckeyensis, Pa. boogaardi*	Zone 13b	
SOC 215	208.8	*Icriodus alternatus*	Zone 13b	

SOC 219.7	213.6		Zone 13b	
SOC 225	218.8	*Pa. winchelli*	Zone 13b	
SOC 228.5	221.3	*Pa. winchelli, Pa. linguiformis, Pa. nicolli*	Zone 13b	
SOC 230	223.8	*Pa. linguiformis*	Zone 13b	
SOC 235	228.7	*Pa. linguiformis*	Zone 13b	
SOC 240	233	*Pa. tenuipunctata, Pa. glabra sp. Pa. subperlobata, P. minuta minuta*	Upper *triangularis*	Age based on upper limit of subperlobata in the Canning Basin
SOC 245	238.8	*Pa. glabra, Pa triangularis, Pa. minuta minuta*	U. *triangularis* – Mid *credpida*	
SOC 250	243.9	*Icridous alternatus, Pa. triangularis, Pa. minuta minuta, Pa. subperlobata*	U. *triangularis* – Mid *credpida*	
SOC 259	91	*Pa. minuta minuta*	U. *triangularis* – *rhomboidea*	
SOC 300	293.8	*Pa. subperlobata, Pa. minuta minuta*	U. *triangularis* – *rhomboidea*	
SOC 324	318.9	*Pa. minta minuta*	U. *triangularis* – *rhomboidea*	
SOC 350	345	*Pa. minuta minuta*	U. *triangularis* – *rhomboidea*	
SOC 400	393.8	*Pa. glabra glabra, Pa glabra pectinata. Pa. minuta minuta, Po. confluens*	*rhomboidea* – L. *marginifera*	
SOC 450	443.5	*Pa. glabra pectinata*	*rhomboidea* – L. *marginifera*	
SOC 500	491.5	*Sc. velifera, Pa. minuta minuta*	U. *marginifera*	
SOC 550	541.5	Icriodus, *Polygnathus* sp. *Pa. glabra pectinata*	U. *marginifera*	
SOC 575	566.5	*Polygnathus* sp.	U. *marginifera*	
SOC 580	570.7	Barren	U. *marginifera*	
SOC 600	App. 590	*Pa. minuta minuta, Pa. gracillus gracillus*	U. *marginifera*	

Horse Springs Section (VHS)

Sample I.D.	Meters (m)	Conodont Species	Age	Comments
	0 - 0.64		Zone 6	Data from Klapper, 2007
	0.64 - 0.93		Zone 7	
	0.93 - 1.05		Zone 8	
	1.05 - 1.30		Zone 8-9	
	1.5 - 1.8		Zone 10	
VHS 300	1.6	*An. curvata, Pa. punctata, Pa. hassi*	Zone 10	Productive sample
VHS 301	1.9	*Pa. punctate*	Zone 10	Productive sample
	2 - 2.1		Zone 10 top	Klapper, 2007
VHS 302	2.2	*An. gigas, Pa. hassi*	Zone 11	Moderate abundances
VHS 303	2.4	*An. gigas, Pa. hassi, Pa. kiriveevae*	Zone 11	
VHS 305	2.7		Zone 11	
VHS 307	2.9	*An. gigas, Pa. hassi,*	Zone 11	
VHS 308	3.15	*An. buckeyensis , An. gigas, Pa. hassi, icriodus.*	Zone 11	High abundances.
VHS 310	3.55	*An. gigas, Pa. hassi, Pa. kiriveevae, Pa. feisti.*	Zone 11	
VHS 311	3.7	*An. gigas, An. buckeyensis, Pa. hassi, Pa. feisti.*	Zone 11	Highly productive.
VHS 312	3.85	*An. gigas, An. buckeyensis, Pa. hassi, Pa. feisti.*	Zone 11	High abundances
VHS 314	4.5		Zone 11	
VHS 315	4.75		Zone 11	
VHS 317	5.6	*Pa. feisti, An. gigas, An. buckeyensis, Pa. hassi,*	Zone 11	Highly productive.
VHS 318	6.4	*An. Gigas*	Zone 11	Highly productive.
VHS 319	6.8	*Palamto, An. gigas, An. Buckeyensis*	Zone 11	High productivity.
	7.2		Zone 12 base	Klapper, 2007
VHS 2	11.35	*Pa. hassi, Pa. mulleri, Pa. juntianensis*	Zone 12	
VHS 4	11.65	*Pa. hassi, Pa. mulleri, Pa. juntianensis*	Zone 12	
VHS 010	13	*An. buckeyensis, Pa. bogartensis*	Zone 12	
	14.6		Zone 12 top	Klapper, 2007
VHS 56-57	19.85-20	*An. curvata, Pa. bogartensis, Pa. winchelli, Po. Decorosa*	Zone 13a	

VHS 060	23.2	*An. curvata, Pa. bogartensis, Pa. boogaardi, Pa. winchelli, Pa. klugi, Pa. rhenana*	Zone 13a or 13b	
VHS 072	25.75	*An. buckeyensis, Pa. beckeri, Pa. boogaardi, Pa. winchelli, Pa. kulgi, Pa. juntianensis, Pa. linguiformis, Pa. niccolli, Pa. punctate, Pa. kireevae*	Zone 13b	
VHS 89	26.7	*An. Iodes*	Zone 13b	
VHS 114	28	*Pa. juntianensis*	Zone 13b	
VHS 115	28.05	*Pa. juntianensis*	Zone 13b	
VHS 144	30.9	*Ancyrodella sp.*	Zone 13b-c	
VHS 147	31.35	*Pa. bogartensis*	Zone 13b-c	
	32.1		Zone 13b top	Klapper, 2007
	33.6		Zone 13c base	Klapper, 2007
VHS 158	34.6	*Pa. bogartensis, Po. Brevilamina*	Zone 13c	
	35.75		Zone 13c top	Klapper, 2007
	35.95		*triangularis* Base	Klapper, 2007
VHS 165	36.65	*I. alternatus, Pa. triangularis, Po. Brevilamina*	*triangularis*	Likely L. *triangularis*
VHS 179	39.2	*Pa. subperlobata, Pa. delicatula platys, Po. Brevilamina*	*Upper triangularis*	
VHS 189	48	*Pa. perlobata, Pa. minuta minuta, Pa. regularis*	*Upper triangularis - crepida*	
VHS 205	58.2	*Pa. perlobata, Pa. minuta minuta, Pa. quadrantinodosalobata*	*crepida - rhomboidea*	
VHS 221	69.2	*Pa. perlobata, Pa. minuta minuta, Pa. quadrantinodosa-lobata, Pa. glabra pectinata*	*crepida - rhomboidea*	
VHS 237	79.9	*Pa. minuta minuta, Pa. glabra pectinata*	*crepida - marginifera*	
VHS 259	91	*Pa. minuta minuta, Pa. glabra pectinata*	*crepida - marginifera*	
VHS 273	101.8	*Pa. minuta minuta, Pa. glabra pectinata, Pa. glabra elongate, Pa gracillus gracillus*	*crepida - marginifera*	

Casey Falls Section (CL)

Sample I.D.	Meters (m)	Species	Age	Comments
CL1	1	*An aff.ioides. Pa. winchelli*	Zone 13a	
CL1.5	1.5	*Pa. juntianensis, pa. klugi, An. Sp.*	Zone 13b	
CL2.2	2.2	*An aff.ioides, Pa juntianensis, Pa.boogartensis,*	Zone 13b	
CL 5	5	Barren		No sign of anything
CL7.9	7.9	*Pa. trinagularis, Pa superlobata, Pa. regularis, Pa. minuta minuta*	Late *triangularis*	
CL8	8	*Apatognathus sp*	Lower *crepida*	Frutaxites bed
CL9	9	*Pa. superlobata, Pa. tenuipunctata, Po. Brevilamina, I. alternatus*	Lower *crepida*	
CL12.4	12.4	*Pa. tenuipunctata, Pa. minuta minuta*	Lower to upper *crepida*	
CL18.3	18.3	*Pa. minuta minuta,, Pa. glabra pectinata Pa. glabra glabra*	Upper crepida - rhomboidea	
CL31	31	*Pa. minuta minuta, Pa. glabra pectinata, Po. glabra glabra P. confluens*	*rhomboidea* - lower *marginifera*	
CL45	45	*Pa. minuta minuta Pa. glabra pectinata*	*rhomboidea* - lower *marginifera*	
CL67	67	*Pa. minuta minuta, Pa. glabra pectinata*	*rhomboidea* - lower *marginifera*	
CL73	73	*Pa. glabra pectinata, Pa minuta minuta*	*rhomboidea* - lower *marginifera*	
CL92	92	*Pa. minuta minuta, Pa. glabra pectinata*	*rhomboidea* - lower *marginifera*	
CL127.5	120.85	*Pa. glabra pectinata, Thrinacodus, protocrodus, ctenacanthus, phoebodus*	*rhomboidea* - lower *marginifera*	

CL141	132.1	*Sc. velifera*	U. *marginifera*	
CL151	138.4	Undiagnostic	U. *marginifera*	
CL161.5	146.05	*Sc. velifera*	U. *marginifera*	
CL183.5	162.73	*Pa. minuta minuta, Pa. glabra pectinata Sc. velifera*	U. *marginifera*	
CL201	175.6	*Pa. minuta minuta*	U. *marginifera*	
CL244	205	Undiagnostic	U. *marginifera*	
CL249	208.1	Undiagnostic	U. *marginifera*	
CL260	215.9	*Pa. minuta minuta*	U. *marginifera*	
CL287	236.3	*Pa. helmsi, Po. Species*	U. *marginifera*	
CL304	252.7	*Pa. helmsi, Po. Normalis*	U. *marginifera*	
CL318	265.8	*polygnathus*	U. *marginifera*	
CL324	272.4		U. *marginifera*	
CL349	*295.2*	*Pa. shindwolfi*	U. *marginifera*	
CL372	315.9	*Pa. helmsi, Sc. velifera*	U. *marginifera*	
CL380	323.4	*Pa. helmsi, Sc. Velifera*	U. *marginifera*	
CL395	341.9	*Pa. helmsi, Sc. Velifera, Po.sp*	U. *marginifera*	
CL414.5	362.8	Undiagnostic	U. *marginifera*	
CL443	394.7	polygnathids	U. *marginifera*	
CL450	402.3	Undiagnostic	U. *marginifera*	
CL471		*Pa. helmsi*	U. *marginifera*	Above section

McWhae Ridge Core (MR1)

Sample I.D.	**Meters (m)**	**Species**	**Age**	**Comments**
MR1 90-91	21.14 - 21.32	Ozarkodinia sp., Ctenacanthus sp.	Undiagnostic	
MR1 114	26.15	Barren	Undiagnostic	
MR1 135	34.02 - 34.04	Polygnathus *assymetricus*	Zones 1-4	species renamed mesotaxis ovalis?
MR1 153-154	39.73 - 39.88	Polyganthus *assymetricus*	Zones 1-4	

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APPENDIX 2.2

Select Major- and Trace Element Data for the South Oscar Section

Both major- and trace element analyses for the South Oscar section were carried out by Chemostrat, Inc. and are reported as oxide percent by weight and parts per million by weight (ppm), respectively. Not all results are shown--only those elements relevant to the scope of Chapter 2 are listed.

Sample #	Depth (m)	Al_2O_3 (wt %)	U (ppm)	Th (ppm)	V (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	U/Th	V/Cr	Cu/Al	Ni/Al
150	140.6	0.32	0.26	0.54	5.70	1.08	2.12	4.42	0.47	5.29	6.67	13.87
152	143.0	0.08	0.14	0.15	1.56	0.00	0.80	4.25	0.90	0.00	9.51	50.84
156	146.8	0.37	0.28	0.67	5.26	1.49	0.37	4.17	0.42	3.53	0.98	11.20
160	151.0	0.21	0.14	0.34	4.98	0.85	0.82	4.84	0.42	5.88	3.95	23.40
162	152.8	1.25	1.91	2.24	11.66	4.36	1.86	5.26	0.85	2.68	1.49	4.22
164	154.8	0.09	0.11	0.21	3.33	0.11	0.03	3.94	0.54	30.91	0.30	43.04
168	159.8	0.18	0.15	0.27	0.46	0.03	1.14	4.26	0.57	14.84	6.46	24.07
170	162.1	0.59	0.42	0.88	5.87	1.63	1.27	5.39	0.48	3.60	2.17	9.19
172	163.8	0.05	0.11	0.08	0.16	0.00	0.20	3.11	1.36	0.00	4.32	68.48
176	168.9	0.15	0.28	0.23	4.15	0.17	0.00	3.99	1.24	24.12	0.00	27.05
180	172.8	0.43	0.23	0.73	5.85	1.62	0.57	5.94	0.32	3.61	1.32	13.70
182	174.8	0.16	0.20	0.27	1.57	0.13	0.27	3.71	0.75	12.00	1.64	22.90
184	176.8	0.69	0.76	1.77	5.75	2.83	1.63	4.22	0.43	2.03	2.36	6.10
187	179.8	0.05	0.08	0.06	1.33	0.00	0.07	3.76	1.36	0.00	1.46	76.34
196	180.8	0.15	0.21	0.24	4.28	0.40	1.34	4.91	0.88	10.63	9.20	33.80
192	189.0	0.48	0.22	0.95	1.80	1.36	0.48	4.64	0.24	1.33	1.01	9.64
194	190.9	0.36	0.16	0.70	1.47	0.96	0.66	4.72	0.23	1.53	1.81	12.95
200	192.8	0.42	0.31	1.00	5.30	1.05	0.96	4.96	0.31	5.03	2.31	11.90
205	198.8	1.51	1.29	4.25	9.65	4.63	3.25	6.02	0.30	2.08	2.15	3.98
209	202.9	0.18	0.51	0.36	3.15	0.60	0.10	5.04	1.43	5.21	0.52	27.58
213	206.8	0.14	0.59	0.35	0.75	0.15	0.00	4.52	1.68	4.99	0.00	31.63
217	210.8	0.22	0.38	0.52	4.65	0.60	0.44	4.74	0.73	7.76	2.01	21.48
221	214.7	0.25	0.16	0.67	3.94	0.74	0.30	3.52	0.24	5.31	1.20	14.26
223	216.8	0.30	0.14	0.62	5.83	1.19	1.14	4.35	0.22	4.92	3.85	14.70
225	218.8	0.39	0.30	0.95	4.91	1.05	2.87	4.66	0.32	4.67	7.29	11.84
229	222.8	0.28	0.17	0.72	4.98	0.18	0.00	4.01	0.24	28.30	0.00	14.28
233	226.8	0.30	0.16	0.64	3.92	1.16	0.08	4.22	0.25	3.39	0.26	13.90
237	230.8	0.41	0.19	0.82	4.33	1.24	0.09	4.06	0.23	3.49	0.21	9.93
241	234.0	0.18	0.08	0.38	0.18	0.25	0.00	3.71	0.22	0.71	0.00	21.01
245	238.8	0.30	0.48	0.86	3.15	0.65	0.14	4.55	0.56	4.82	0.48	15.17
250	243.9	0.58	0.24	1.18	2.64	1.53	0.33	4.17	0.20	1.73	0.56	7.22
254	247.8	0.79	0.88	1.70	6.01	1.83	0.55	5.22	0.52	3.28	0.69	6.59
258	251.8	1.82	1.20	3.56	8.19	6.39	3.12	6.29	0.34	1.28	1.71	3.44
262	256.8	1.75	0.97	3.55	8.75	5.80	2.15	5.80	0.27	1.51	1.23	3.31
266	260.8	0.29	0.26	0.64	1.45	0.80	0.87	4.18	0.41	1.82	3.02	14.52

APPENDIX 4.1

Prominent Natural Historians

This list is comprised of prominent natural historians with earth science related research that is both similar to- and pre-dates Herschel's research. Emphasis was placed on 18th century geologists, although 16th and 17th century geologist were also investigated. This list was made independent of the other appendices (i.e. the list of Herschel's correspondents and visitors was not referenced when generating this list). Instead, *A Source Book in Geology* (Mather and Mason, 1970), *Bursting the Limits of Time* (Rudwick, 2005), and *From Mineralogy to Geology* (Laudan, 1994) were used to identify prominent natural historians that may have influenced Herschel. Note that this list is in alphabetical order and contains both predecessors and contemporaries of William Herschel.

- ABBE SOULAVIE, Jean Louis Giraud (1752-1813)
  - French churchman, author and natural philospher
  - Research on determining the chronological seuqence of rocks (1781)
- BRONGNIART, Alexandre (1770-1847)
  - French geologist (stratigrapher) and professor of natural history
  - Showed slow, cyclical deposition of sedimentary rocks in the Paris Basin (1808)
  - Developed biostratigrpahy (along with Cuvier)
- COMTE DE BUFFON, Geroge Louis Leclerc (1707-1788)
  - French Naturalist interested in chemistry, biology, mineralogy, astronomy, physics
  - Was among the first to create an autonomous science, free of any theological influence
  - Juxtaposes a plutonian cosmogony and a neptunian theory of the earth (1749)
  - Emphasized the importance of natural history and the great length of geological time
  - Estimated age of earth to be 75,000 yrs based on his experiments on cooling
  - Publicaiotns on both the origin and hisotry of the earth (1776 and 1779)
  - emphasized the importance of natural history and the great length of geological time
- CUVIER, Georges (1769-1832)
  - *French zoologist, paleontologist, geologist, comparative anatomist*
  - Established basic principles of biostratigraphy with A. Brongniart
  - *Theory of the Earth* (1813)
  - Proposed that new species were created after periodic catastrophic floods (extcintions)

- DELUC, Jean Andre (1727-1817)
  - *French geologist, meteorologist, physicist, theologist*
  - Published on the history of the solar system before the birth of the sun
  - Research goal was to reconcile Genesis and geology
- ENGLEFIELD, Sir Henry Charles (1752-1822)
  - English antiquary, chemist, mathmetician, astronomer, geologist
  - Made scientific contributions to the Royal society, Linnean Society, Royal Institution, Society of Antiquaries, and to Nicholson's Journal and Tilloch's Philosophical Magazine
  - His geolgoy interests focused on volcanology and earthqaukes.
- FAUJAS DE SAINT-FOND, Barthelemi (1741-1819)
  - French geologist (volcanologist) and world traveller
  - Studied the forms, structure, composition and superposition of rocks
  - Realized the importance of measuing stratigraphic sections in the subsurface
  - Developed a theory about the origin of volcanoes (1778)
- HALL, Sir James (1761-1832)
  - Scottish geologist and chemist
  - Published papers on the chemical composition and consolidation of strata
- HAMILTON, Willaim (1731-1803)
  - Scottish diplomat, antiquarian, archaeologist and geologist
  - Observation based field work primarily on volcanos
- HOOKE, Robert (1635-1703)
  - English physicist and mathematician known for his work on earthquakes
  - Believed in the cycle of continents (uplifting and sinking)
  - Theorized that earthquakes change the level of strata, (1705)
- HUTTON, James (1726-1797)
  - *Scottish geologist, naturalist,* chemical manufacturer and agriculturalist
  - Originated the theory of uniformitaianism
  - *Theory of the Earth*: ideas formed ~1767, abstract 1785, article 1788, book 1795
  - Argued that sedimentation is cyclical and has been/will be repeated over time
  - Claimed his theory could be extended to all parts of the world
  - Believed the earth must have formed more than 6000 yrs ago
  - Proposed the existence of invisible light (*Philosophy of Light, Heat*, and *Fire,* 1794)
- LAVOISIER, Antoine Laurent (1743-1794)
  - French chemist, *physiologist, geologist, economist,* **founder of modern chemistry**
  - *Littoral and pelagic beds* (1793), about the phenomina and process of sorting
- LLOYD, John (1750-1815)
  - British naturalist, interested in earthquakes and mineralogy
- MAILLET, Benoit de (1656-1738)
  - French *geologist and oceanographer*
  - Theorized an eternal universe, one undergoing slow development by natural processes
  - Heavenly bodies were believed to be eternally renovated
  - Believed the Earth was at least two billion years old

- MICHELL, John (1724-93)
  - English Astronomer and professor of geology
  - Believed the earth was composed of regular and uniform strata (1760)
- PALLAS, Peter Simon (1741-1811)
  - German zoologist, botanist, natural historian
  - Studied *Mountains of various ages* (1771)
  - Was a member of an expedition to observe the transit of Venus (1769)
  - Discovered pallasite, a new type of stony-iron meteorite (1772)
- PLAYFAIR, John (1748-1819)
  - Scottish geologist, mathematician, physicist, astronomer
  - Developed and popularized Hutton's ideas on the *Theory of the Earth* (1802)
  - Introduced several significant geological terms (ex. geological cycle, igneous origin)
- SAUSSURE, Horace Benedicte de (1740-1799)
  - Swiss aristocrat, physicist, professor of philosophy at Geneva, founder of alpinism
  - Saw mountains as the key to understanding the theory of the earth
  - Research focued on the inclination of strata, fossils, rocks and minerals in the Alps
  - His work with rocks, erosion, and fossils lead him to the idea that the earth was much older than generally thought
  - He was an early user of the term "geology" - see *Voyages* (1779)
- STENSEN, Nicolaus (1638-1687)
  - Danish physician, churchman, naturalist, and professor of anatomy
  - One of the founders of stratigraphy, e**stablished the law of superposition**
- STRACHEY, John (1671-1743)
  - English naturalist
  - One of the first attempts at drawing a geological cross-section (1719)
- WERNER, Abraham (1750-1817)
  - German geologist, Father of the Neptunist theory
  - Interested in geologic succession, stratigraphy, and the classification of rocks and other geologic data according to the period of formation
  - Believed the earth was older than 6000yrs, "perhaps 1,000,000 years" old
- WOODWARD, John (1665-1722)
  - English naturalist, antiquarian, geologist and professor of physics in London
  - Research focuses on the natural history of the earth (1695, 1723)
  - Proposed that all the materials of the earth are naturally arranged in horizonal strata, based on field observations
  - Aimed to "get a complete and satisfactory information of the whole mineral kingdom"
  - He published and focused on making global observations (1696)

APPENDIX 4.2

Correspondents of William Herschel

This list was generated using the Herschel Archive at the Royal Astronomical Society and has been organized by profession, and then alphabetically by last name. All correspondences from geologists and natural philosophers were included; in all other categories, however, only correspondenets with four or more letters were included. *The Complete Dictionary of Scientific Biography* (2008) and the electironic databases at the University of Washingotn Library were used to determine the primary profession of the correspondants; in a few rare cases, Google was used to determine research interests. Following each name is the number of correspondences known to exist.

"GEOLOGISTS" (natural historians within the realm of geologic study)

- BANKS, Sir Joseph (1743-1820), 75 letters from 1781-1816
- DELUC, Jean Andre (1727-1817), 8 letters from 1784-1809
- ENGLEFIELD, Sir Henry Charles (1752-1822), 17 letters from 1787-1800
- FAUJAS DE SAINT-FOND, Barthelemi (1741-1819), 2 letters from 1786-1788
- HAMILTON, Sir William (1731-1803), 1 letter in 1791[94]
- LLOYD, John (1750-1815), 1 letter in 1796
- MICHELL, John (1724-1793), 5[95] letters in 1781

OTHER NATURAL HISTORIANS

- BLAGDEN, Sir Charles (1748-1820), 41 letters
- BREWSTER, Sir David (1781-1868), 7 letters
- HUTTON, Charles (1737-1823), 6 letters
- KOMARZEWSKI, Jan Chrzciciel (1748-1809), 22 letters
- LICHTENBERG, Georg Christoph (1742-99), 10 letters
- MANN, Abbe Theodore Augustin (1735-1809), 2 letters
- MARUM, Martin van (1750-1837), 4 letters
- MORE, Samuel (1724-99), 1 letter
- PRIESTLEY, Joseph (1733-1804), 1 letter
- RASPE, Rudolf Eric (1737-94), 1 letter

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[94] Not recorded in the RAS Herschel archive (letter known from Barrett (1983).

[95] The Herschel Archives has only 3 of these letters; one of the letters was addressed directly to Herschel, the other two were addressed to W. Watson for Herschel. The whereabouts of the remaining two letters remain unknown; there existence is known only from the content of the letter Michell wrote directly to Herschel.

- WATSON, Sir William (1715-87), 1 letter
- WATSON, Sir William (1744-1824), 89 letters

ASTRONOMERS

- AUBERT, Alexander (1730-1805), 33 letters
- BODE, Johann Elert (1747-1826), 24 letters
- CASSINI, Jean-Dominique de, Comte de Thury (1748-1845), 12 letters
- BRUEHL, Hans Moritz, Graf von (1736-1809), 24 letters
- GROOMBRIDGE, Stephen (1755-1832), 11 letters
- HAHN, Friedrich von, Graf(1741-1805), 10 letters
- HAMILTON, J. W. A. (dates unknown), 4 letters
- HORNSBY, Thomas (1733-1810), 10 letters
- MENDOZA Y RIOS, Jose de (1763-1816), 6 letters
- LALANDE, Joseph-Jerome Le Francais de (1732-1807), 40 letters
- LAPLACE, Pierre Simon, Marquis de (1749-1827), 7 letters
- MASKELYNE, Nevil (1732-1811), 70 letters
- MECHAIN, Pierre-Francois-Andre (1744-1804), 11 letters
- MESSIER, Charles (1730-1817), 4 letters
- PIAZZI, Giuseppe (1746-1826), 9 letters
- PICTET, Marc-August. (1752-1825), 5 letters
- PIGOTT, Edward (1753-1825), 20 letters
- POND, John (1767-1836), 8 letters
- ROBERTSON, Abraham (1751-1826), 9 letters
- SCHROETER, Johann Hieronymus (1745 – 1816), 36 letters
- SEYFFER, Karl Felix (1762-1822), 6 letters
- THOELDEN, A. F. (unknwn dates), 9 letters
- VINCE, Samuel (1749-1821), 18 letters
- WILSON, Patrick (1743-1811), 101 letters
- WOLLASTON, Francis (1731-1815), 22 letters
- ZACH, Franz Xaver, Freiherr von (1754-1832), 14 letters

MUSICIANS

- BURNEY, Charles (1726-1814), 8 letters
- LINLEY, Ozias Thurston (1766-1831), 4 letters

FAMILY

- HERSCHEL, Caroline Lucretia (1750-1848), 43 letters
- HERSCHEL, Johann Alexander (1745-1821), 6 letters
- HERSCHEL, Sir John Frederick William (1792-1871), 4 letters
- HERSCHEL, Lady Mary, 6 letters

MISCELLANEOUS

- BEST, George (1759 – 1818), 5 letters
- BONAPARTE, Lucien, Prince de Canino (1775-1841), 7 letters
- BOULTON, Matthew (1728-1809), 5 letters
- BOYER, Alexis, Baron (1757-1833), 7 letters
- ERSKINE, David Steuart, eleventh Earl of Buchan (1742-1829), 4 letters
- GREATHEED, Bertie (1759-1826), 6 letters
- MAGELLAN, Jean-Hyacinthe de (1722-90), 5 letters
- PLANTA, Joseph (1744-1827), 15 letters

UNKNOWN

- DAUNEY, Alexander (1828- abt 1912?), 5 letters
- WLOEMEN, Gottlob Theobald, (unknown dates), 7 letters

APPENDIX 4.3

Natural Historians that Visited William Herschel

This is a list of the known natural historians that visited Herschel at Datchet (August 1782 - June 1785), Old Windsor (June 1785 - March 1786), or Slough (March 1786 - August 1822), between 1783 and 1792, as recorded in one of three observatory logs books[96]. Note that from 1783 to 1787 specific dates (day and month) for each visit are not recorded; it is unknown if the visitors are listed from memory in random order or if they were recorded in chronological order of their appearance. Starting on August 3, 1787, William recorded the day, month, and year of visitors until September 26, 1792.

- Joseph Banks
  - 3 visits: 1783-1784; 1783-1787; March 4, 1788
- Joseph Priestly
  - 2 visits: 1783-1787; April 10, 1792
- William Hamilton[97]
  - 4 visits: 1783-1787; August 6, 1787; May 19, 1788; August 27, 1791
- Henry Englefield
  - 2 visits: 1783-1787; December 11, 1788
- John Playfair
  - 1 visit: August 20, 1788
- Jean Andre DeLuc
  - 2 visits: May 24, 1789; June 20, 1789
- John Lloyd[98]
  - 1 visit: June 6, 1789
- Robert Hall[99]
  - 1 visit: June 26, 1791

[96] The observatory log book of visitors used in this study was a scanned copy of the original, provided by the courtesy of Dr. Woodruff Sullivan III; the original is on display at the William Herschel museum in the United Kingdom. There are two known additional visitor logs; the first records visitors from October 4th, 1793 to April, 1798 (with two additional entries from 1798 - 1822), and the second records visitors starting on January 5th, 1791 and ending in June, 1822. Interestingly, the record of visitors during the overlapping period of the two logs is not identical, although it is somewhat consistent.

[97] Only the 1783-87 and 1991 visits are known with confidence as the visitor log documents "Sir William Hamilton." The other two visits, in 1787 and 1788, were made by a "Mr. Hamilton," which may or may not refer to Sir William Hamilton.

[98] The visitor was recorded as "Edw Llyod" in Caroline's visitor log.

[99] The visitor was recorded as "Mr. and Mrs. Hall."

APPENDIX 4.4

Authors with Geology Related Articles in *Phil. Trans*. from 1760-1785

This is a list of natural historians with publications in *Phil. Trans*. that are within the realm of earth science. The query started with volume 51 in 1759/1760, several years before Herschel started studying astronomy, and ended with volume 75 in 1785, when Herschel published his 2nd paper on the Construction of the Heavens. Authors in bold had articles that appeared to be related to- or have some connection with the ideas and themes presented in Herschel's work. The authors are listed in alphabetical order by last name. Following each name is the number of articles they published in Phil. Trans. during the specified time range (denoted as A:#), as well as the number of existing correspondences they had with Herschel (L:#).

1. Stanesby Alchorne – A:1, L:0
2. **James Anderson – A:2, L:0**
3. **Joseph Banks – A:2, L:75**
4. Daines Barrington – A:1, L:0
5. John Beccaria – A:1, L:0
6. **William Bowles – A:1, L:0**
7. William Brakenridge – A:1, L:0
8. **Peter Collinson – A:3, L:0**
9. Emanuel Mendes da Costa – L:2, L:0
10. George Croghan – A:1, L:0
11. **Alexander Dalrymple – A:1, L:0**
12. Edward Delaval – A:1, L:0
13. **Mathew Dobson – A:1, L:0**
14. **Henry C. Englefield – A:1, L:17**
15. George Fordyce – A:2, L:0
16. **Dr. Fothergill – A:1, L:0**
17. Edward Gulston – A:1, L:0
18. **William Hamilton – A:10, L:1**
19. Thomas Heberden – A:1, L:0
20. William Heberden – A:1, L:0
21. **William Herschel – A:1, L:N/A**
22. William Hirst – A:1, L:0
23. Henry Horne – A:1, L:0
24. William Hunter – A:1, L:0
25. **Charles Hutton – A:2, L:6**
26. **Francesco Ippolito – A:1, L:0**
27. James Keir – A:1, L:0
28. Edward King – A:2, L:0
29. **John Lloyd – A:2, L:1**
30. **Robert Mackinlay – A:1, L:0**
31. **Theod Aug. Mann – A:1, L:2**
32. Nevil Maskelyne – A:1, L:70
33. **John Michell – A:1, L:5**
34. Jeremiah Milles – A:2, L:0
35. Mr. Molloy – A:1, L:0
36. Donald Monro – A:1, L:0

37. Edward Wortley Montagu – A:1, L:0

38. Henry More – A:1, L:0

39. Robert More – A:1, L:0

40. Samuel More – A:1, L:1

41. Michael Morris – A:1, L:0

42. Charles Morton – A:2, L:0

43. Turberville Needham - A:1, L:0

44. Petr. Simon Pallas – A:1, L:0

45. Thomas Pennant – A:1, L:0

46. Joshua Platt – A:1, L:0

47. Joseph Priestley – A:1, L:1

48. Rudolf Eric Raspe – A:1, L:1

49. James Rennell – A:1, L:0

50. Right Reverend Richard – A:1, L:0

51. Patrick Russell – A:1, L:0

52. John Rutty – A:1, L:0

53. George Shuckburgh – A:1, L:0

54. Francis Haskins Eyles Stiles – A:2, L:0

55. John Strange – A:2, L:0

56. Mr. Verelst – A:1, L:0

57. Adam Walker – A:1, L:0

58. Dr. Watson – A:2, L:89

59. Thomas West – A:1, L:0

60. Mons. Weymarn – A:1, L:0

61. Benjamin Wilson – A:1, L:2

62. William Withering – A:2, L:0

63. Peter Woulfe – A:2, L:0

64. George Yonge – A:1, L:0

APPENDIX 4.5

Geology Related Articles in the Philosophical Transactions of the Royal Society

The query was made for articles between 1759/1760 and 1785. 76 Articles were found to be related to earth sciences. 28 articles, denoted with ➢, were identified as being potentially significant papers in terms of their relation to Herschel's work.

Vol. 51, 1759 - 1760

- John Rutty
  Thoughts on the Different Impregnation of Mineral Waters; More Particularly concerning the Existence of Sulphur in Some of Them, p.275-282
- William Brakenridge
  Concerning the Sections of a Solid, Hitherto Not Considered by Geometers, p.446-457
- Patrick Russell
  An Account of the Late Earthquakes in Syria, p.529-534
- Jeremiah Milles
  Remarks on the Bovey Coal, p.534-553
- ➢ John Michell
  Conjectures concerning the Cause, and Observations upon the Phaenomena of Earthquakes; Particularly of That Great Earthquake of the First of November, 1755, Which Proved So Fatal to the City of Lisbon, and Whose Effects Were Felt As Far As Africa, and More or Less throughout Almost All Europe, p.566-634.
- Turberville Needham
  An Account of a Late Discovery of Asbestos in France, p.837-838
- Jer. Milles
  A Further Account of Some Experiments Made on the Bovey Coal, p.941-944

Vol. 52, 1761 - 1762

- ➢ Francis Haskins Eyles Stiles
  An Account of an Eruption of Mount Vesuvius, p.39-40
- ➢ Francis Haskins Eyles Stiles
  Another Account of the Same Eruption of Mount Vesuvius, p.41-44
- ➢ Robert Mackinlay
  Concerning the Late Eruption of Mount Vesuvius, and the Discovery of an Antient Statue of Venus at Rome, p.44-45
- Right Reverend Richard
  An Account of a Production of Nature at Dunbar in Scotland, Like That of the Giants-Causeway in Ireland, p.98-99

- Emanuel Mendez da Costa
  An Account of Some Productions of Nature in Scotland Resembling the Giants-Causeway in Ireland, p.103-104
- Robert More
  An Account of the Earthquake at Lisbon, 31st March 1761, p.141-142
- Mr. Molloy
  Another Account of the Same Earthquake, p.142-143
- Thomas Heberden
  An Account of the Earthquake Felt in the Island of Madeira, p.155-156
- Benjamin Wilson
  Observations upon Some Gems Similar to the Tourmalin, p.443-447
- Henry More
  Observations on the Tides in the Straits of Gibraltar, p.447-453
- John Beccaria
  An Account of the Double Refractions in Crystals, p.486-490
- Nevil Maskelyne
  Observations on the Tides in the Island of St. Helena, p.586-606

Vol. 53, 1763

- Henry Horne
  Observations on Sand Iron, p.48-61
- Mons. Weymarn
  An Account of an Earthquake in Siberia, p.201-210
- Edward Gulston
  An Account of an Earthquake at Chattigaon, p.251-256
- William Hirst
  An Account of an Earthquake in the East Indies, of Two Eclipses of the Sun and Moon, Observed at Calcutta, p.256-262
- Mr. Verelst
  An Account of the Earthquakes That Have Been Felt in the Province of Islamabad, with the Damages Attending Them, from the 2d to the 19th of April, 1762, p.265-269

Vol. 54, 1764

- Joshua Platt
  An Attempt to Account for the Origin and the Formation of the Extraneous Fossil Commonly Called the Belemnite, p.38-52

Vol. 55, 1765

- Edward Delaval
  Experiments and Observations on the Agreement between the Specific Gravities of the Several Metals, and Their Colours When United to Glass, as Well as Those of Their Other Proportions, p.10-38
- In a Letter to the Rev. Samuel Chandler
  An Account of an Earthquake Felt at Lisbon, December 26, 1764, p.43-44
- W. Heberden
  Some Account of a Salt Found on the Pic of Teneriffe, p.57-60

Vol. 56, 1766

- William Bowles and P. Collinson
  Some Observations on the Country and Mines of Spain and Germany, with an Account of the Formation of the Emery Stone, p.229-236
- Emanuel Mendes da Costa
  Supplement to the Account of the Discovery of Native Tin, p.305-306

Vol. 57, 1767

- Edward King
  An Attempt to Account for the Formation of Spars and Crystals, p.58-64
- William Hamilton
  Containing an Account of the Last Eruption of Mount Vesuvius, p.192-200
- Alexander Dalrymple and C. Morton
  On the Formation of Islands, p.394-397
- Edward Wortley Montagu
  Containing Some New Observations on What is Called Pompey's Pillar, in Egypt, p.438-442
- Peter Collinson and George Croghan
  An Account of Some Very Large Fossil Teeth, Found in North America, p.464-467
- Peter Collinson
  Sequel to the Foregoing Account of the Large Fossil Teeth, p.468-469

Vol. 58, 1768

- William Hamilton
  An Account of the Eruption of Mount Vesuvius, in 1767, p.1-14

Vol. 59, 1769

- William Hamilton
  Containing Some Farther Particulars on Mount Vesuvius, and Other Volcanos in the Neighbourhood, p.18-22

Vol. 60, 1770

- R. Watson
  Experiments and Observations on Various Phaenomena Attending the Solution of Salts, p.325-354

Vol. 61, 1771

- William Hamilton
  Remarks upon the Nature of the Soil of Naples, and Its Neighbourhood, p.1-47
- Donald Monro
  An Account of a Pure Native Crystalised Natron, or Fossil Alkaline Salt, Which is Found in the Country of Tripoli in Barbary, p.567-573
- R. E. Raspe
  Containing a Short Account of Some Basalt Hills in Hassia, p.580-583

Vol. 62, 1772

None

Vol. 63, 1773

- Adam Walker

  Containing an Account of the Cavern of Dunmore Park, Near Kilkenny, in Ireland, p.16-19
- Michael Morris

  A Short Account of Some Specimens of Native Lead Found in a Mine of Monmouthshire, p.20-21
- Charles Morton and William Withering

  Experiments upon the Different Kinds of Marle Found in Staffordshire, p.161
- Daines Barrington

  Some Account of a Fossil Lately Found Near Christ-Church, in Hampshire, p.171-172

Vol. 64, 1774

- Mathew Dobson and Dr. Fothergill

  A Description of a Petrified Stratum, Formed from the Waters of Matlock, in Derbyshire, p.124-127

Vol. 65, 1775

- John Strange

  An Account of Two Giants Causeways, or Groups of Prismatic Basaltine Columns, and Other Curious Vulcanic Concretions, in the Venetian State in Italy; with Some Remarks on the Characters of These and Other Similar Bodies, and on the Physical Geography of the Countries in Which They are Found, p.5-47
- John Strange

  An Account of a Curious Giant's Causeway, or Group of Angular Columns, Newly Discovered in the Euganean Hills, Near Padua, in Italy, p.418-423

Vol. 66, 1776

- Peter Simon Pallas

  Account of the Iron Ore Lately Found in Siberia, p.523-529
- James Keir

  On the Crystallizations Observed on Glass, p.530-542
- Peter Woulfe

  Experiments Made in Order to Ascertain The Nature of Some Mineral Substances; And, in Particular, To See How Far the Acids of Sea-Salt and of Vitriol Contribute to Mineralize Metallic and Other Substances, p.605-623

Vol. 67, 1777

- Thomas West

  An Account of a Volcanic Hill Near Inverness, p.385-387
- George Shuckburgh

  Observations Made in Savoy, in Order to Ascertain the Height of Mountains by means of the Barometer; Being an Examination of Mr. De Luc's Rules Delivered in His Recherches Sur les Modifications de l'Atmosphere, p.513-905

Vol. 68, 1778

- William Hamilton
  Giving an Account of Certain Traces of Volcanos on the Banks of the Rhine, p.68 1-6
- Mr. Anderson and William Hamilton
  An Account of a Large Stone Near Cape Town. In a letter on Having Seen Pieces of the Said Stone, p.102-106
- Thomas Henry
  An Account of the Earthquake Which Was Felt at Manchester and Other Places, on the 14th Day of September, 1777, p.221-231
- Charles Hutton
  An Account of the Calculations Made from the Survey and Measures Taken at Schehallien, in Order to Ascertain the Mean Density of the Earth, p.689-788

Vol. 69, 1779

- Peter Woulfe
  Experiments on Some Mineral Substances, p.11-34
- Edward King
  Account of a Petrefaction Found on the Coast of East Lothian, p.35-50
- George Fordyce, Stanesby Alchorne, and William Hunter
  An Examination of Various Ores in the Museum of Dr. William Hunter, p.527-536
- Theod Aug. Mann and Joseph Banks
  A Treatise on Rivers and Canals, p.555-656

Vol. 70, 1780

- Charles Hutton
  Calculations to Determine at What Point in the Side of a Hill Its Attraction Will Be the Greatest, p.1-14
- George Fordyce
  A New Method of Assaying Copper Ores, p.30-41
- William Hamilton
  An Account of an Eruption of Mount Vesuvius, Which Happened in August, 1779, p.42-84
- Mr. Herschel and Dr. Watson
  Astronomical Observations Relating to the Mountains of the Moon, p.507-526

Vol. 71, 1781

- James Rennell and Joseph Banks
  An Account of the Ganges and Burrampooter Rivers, p.87-114
- Thomas Pennant
  An Account of Several Earthquakes Felt in Wales, p.193-194
- John Lloyd
  Account of an Earthquake at Hafodunos Near Denbigh, p.331-333
- Henry C. Englefield
  Account of the Appearance of the Soil at Opening a Well at Hanby in Lincolnshire, p.345-346

Vol. 72, 1782

- William Hamilton and Samuel More

  An Account of Some Scoria from Iron Works, Which Resemble the Vitrified Filaments Described by Sir William Hamilton, p.50-52
- William Withering and Joseph Priestley

  An Analysis of Two Mineral Substances, viz. the Rowleyrag-Stone and the Toad-Stone, p.327-336

Vol. 73, 1783

- John Lloyd

  Account of an Earthquake, p.104-105
- William Hamilton

  An Account of the Earthquakes Which Happened in Italy, from February to May 1783, p.169-208
- Francesco Ippolito and William Hamilton

  Account of the Earthquake Which Happened in Calabria, March 28, 1783, p.209-vii

Vol. 74, 1784

None

Vol. 75, 1785

- James Anderson and George Yonge

  An Account of Morne Garou, a Mountain in the Island of St. Vincent, with a Description of the Volcano on Its Summit, p.16-31

APPENDIX 4.6

In-Text Citations Made by W. Herschel

For the purpose of this exercise, any reference Herschel made to individuals or previous publications, including his own, were considered a "citation." Citations were only counted for Herschel's seven papers concerning the construction of the heavens. The page numbers listed after each citation indicate the location of the reference as it appears in Herschel's paper. All six articles were published in *Philosophical Transactions of the Royal Society of London;* the year, volume, and page numbers can be found following the titles below. The symbol ➢ denotes a citation of possible significance.

1. *Account of Some Observations Tending to Investigate the Construction of the Heavens*, 1784, 74, 437-451.
    - ▪ "natural historians," p.438
    - ▪ *Connaissance des temps*, p.439, 440, 441, 449
    - ▪ Messier and Mechain (mentioned jointly), p.441, 450
    - ▪ Messier, p.441
    - ▪ De La Lande, p.446
    - ▪ His "former paper on the subject of the solar motion," p.448

2. *On the Construction of the Heavens*, 1785, 75, 213-266.
    - ▪ Sir Isaac Newton, p.215
    - ▪ His 1784 paper on the *Account of Some Observations…*, p.219
    - ▪ Flamsteed, p.220, 264
    - ➢ John Michell, p.255
    - ▪ *Connaissance des temps, p.256, 257, 261, 261, 262, 263*
    - ▪ Caroline Herschel, p.262

3. *Catalogue of a Second Thousand of New Nebulae and Clusters of Stars; With a Few Introductory Remarks on the Construction of the Heavens*, 1789, 79, 212-255.
    - ▪ "natural philosopher" (uses them in a simile), p.214
    - ➢ John Michell (in-text citation and footnote), p.215
    - ▪ His 1785 paper *On the Construction of the Heavens*, p.219
    - ▪ His mathematical papers from the Bath Philosophical Society (1780 and 1781), p.221
    - ▪ De La Caille's catalogue, p.255
    - ▪ Mr. Wollaston's catalogue, p.255

4. *Catalogue of 500 New Nebulae, Nebulous Stars, Planetary Nebulae, and Clusters of Stars; With Remarks on the Construction of the Heavens,* 1802, 92, 477-528.

   - His article *On the Power of Penetrating into Space by Telescopes* (1800), p.483,498
   - Flamsteed, De La Caille, Bradley, Mayer (in reference to a star, ζ Aquarii), p.484
   - Huygens, *Systema Saturnium*, p.499

5. *Astronomical Observations Relating to the Construction of the Heavens, Arranged for the Purpose of a Critical Examination, the Result of Which Appears to Throw Some New Light upon the Organization of the Celestial Bodies*, 1811, 101, 269-336.

   - *Connaissance des temps* (referring to nebula), p.269, 271, 272, 278, 279, 281, 285, 290, 297, 304-307, 309, 311-314, 320
   - His own catalogues of stars and nebula published in past Phil. Trans., p.271, 273
   - Huyghens (in relation to the discovery of Orion), p.279, 323, 324
   - Mr. Bode's Atlas Coelestis, p.292

6. *Astronomical Observations and Experiments Tending to Investigate the Local Arrangement of the Celestial Bodies in Space, and to Determine the Extent and Condition of the Milky Way*, 1817, 107, 302-331.

   - Mr. Bode's "catalogue of stars," p.306
   - His article on *Experiments for Ascertaining How Far Telescopes Will Enable Us to Determine Very Small Angles* (1805), p.312
   - His "Paper read before the Royal Society, November 21, 1799" (pertaining to the method for calculating telescope power), p.318
   - His article *On the Power of Penetrating into Space by Telescopes* (1800), p.319
   - His article *On the Construction of the Heavens* (1785), p.325

7. *Astronomical Observations and Experiments, Selected for the Purpose of Ascertaining the Relative Distances of Clusters of Stars, and of Investigating How Far the Power of Our Telescopes May Be Expected to Reach into Space, When Directed to Ambiguous Celestial Objects,* 1818, 108, 429-470.

   - *Connaissance des temps* – implicitly when discussing all of the Messier clusters
   - "The great sidereal stratum of the milky way," p.453

APPENDIX 4.7

Leading Candidates with Herschelian Connections

This record was generated by cross-referencing appendices 4.1- 4.4 (prominent natural historians with relevant work in the realm of geology, correspondents of Herschel, natural historians that visited the Herschels, and authors of geology related articles in *Phil. Trans*. from 1760-1785), and then selecting those individuals which appear on multiple lists. Candidates were further ranked by perceived importance/influence, on a scale of 1 to 3 (with a 1 denoting candidates with the highest potential for influence, and a 3 representing candidates with limited or uncertain influence potential), which was determined by the relative strengths and weaknesses of available evidence for personal connection and/or similar research ideas. Within each rank, candidates are organized in alphabetical order. The single strongest (pro) and weakest (con) arguments are listed first and in bold font, followed by other pertinent information listed in order of perceived importance. Note that the Herschel library[100] was also checked for publications by the candidates; if no mention of the library is made, nothing was found for that particular individual.

Unless otherwise noted, bibliographic information is primarily sourced from the *Complete Dictionary of Scientific Biography* (Gillispie et al., 2008) and to a lesser extent from *A Source Book in Geology, 1400-1900* (Mather and Mason, 1970). Evidence of correspondence is from the Herschel Archive at the Royal Astronomical Society. Evidence of home visits, while the Herschel's lived at Datchet (Aug. 1782 - Jun. 1785), Old Windsor (Jun. 1785 - Mar. 1786), and Slough (Mar. 1786 - Aug. 1822), is from the Herschel's visitor log (see Appendix 4.3). R.S. = Royal Society of London, *Phil. Trans. = Philosophical Transactions of the Royal Society*.

[100] An approximation of William Herschel's library was made by Dr. Woodruff Sullivan III, using *The Catalogue of the Herschel Library: Being a Catalogue of the Books Owned by Sir William Herschel, Kt. and by His Son Sir John F.w. Herschel, Bart*. Troy, NY: Printed for the editor, 2001, by Isabella Herschel and Sydney Ross (Ed.).

(1) Highest Ranked Candidates:

- FAUJAS DE SAINT-FOND, Barthelemi (1741-1819)
  Pro: Direct evidence of a geologist giving Herschel ideas about the moon, its atmosphere, and it's volcanos (and their relative importance for creating habitable conditions)[101]
    - **In the only letter found among Herschels' correspondances (within this study) to be geology related**

  Con: Faujas's one known visit (1784) and two letters (1786 and 1788) post-date Herschel's first paper on the construction of the heavens
  Pro: Communicated and met with Herschel
    - 2 letters, spent one night observing with Herschel at Dachet, met him at the R.S.[102]

  Con: No record of Herschel responding to any of Faujas's letters
  Pro: Studied the forms, structure, composition, and superposition of rocks and volcanos
  Pro: His geolgoical research was based on observsations and had a global focus
  Pro: Realized the importance of measuing stratigraphic sections in the subsurface
  Pro: World traveler, meets with various astronomers and geologists
    - Met James Hutton and Joseph Black in Edinburgh, October 1784 (Rae, 1895)

  Pro: had a close relationship with Buffon (initiated in 1776)

- HAMILTON, Willaim (1731-1803)
  Pro: Well-known natural historian that frequently published on geology related material in *Phil. Trans.* (from at least 1770-1785)
  Con: No direct evidence of communication via letters
  Pro: May have influenced Herschel's 1787 paper concerning volcanos on the moon
    - Observation based field work primarily on volcanos, to a lesser extent on earthquakes

  Pro: Visited Herschel at least 4 times (1783-1791) and presumably met at R.S. meetings
  Pro: Hamilton was a violinist and gave musical entertainments

- MICHELL, John (1724-93)
  Pro: Michell's work is similar to, but pre-dates, the major contributions made by Herschel
    - **His work on stellar statistics was the basis for Herschel's Milky Way diagram**
    - **Described and promoted stellar photometry, the method of determining the distance from earth to a star by measuring it's brightness**
    - **Advocated the need for larger telescopes in astronomy**
    - **Early paper on the earth being composed of regular and uniform strata (1760)**

  Con: He published very few papers and was often given little or no credit for his work[103]
  Pro: Herschel cites Michell in 2 of his contruction of the heavens papers
    - Michell was the only individual given any significant mention in his papers

  Pro: At least 5 correspondances known between Michell and Herschel
  Con: Letters were entirely about telescope construction and 1 had a very negative tone
  Pro: Blagden mentions Michell's contribution to *Construciton of the Heavens* in a letter

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[101] Royal Astronomical Society, Herschel Archive (W.1/13.F.5). Also, see Appendix 4.9.
[102] Faujas de Saint-Fond. *Travels in England, Scotland, and the Hebrides: Undertaken for the Purpose of Examining the State of the Arts, the Sciences, Natural History and Manners, in Great Britain: ... in Two Volumes with Plates. Translated from the French of B. Faujas Saint-Fond*. London: Printed for James Ridgway, 1799.
[103] McCormmach, R. (2012).*Weighing the World: The Reverend John Michell of Thornhill*. Dordrecht: Springer.

Con: Lived in a rural area outside London, made infrequent visits to friends and RS meetings
Pro: Both an astronomer and geologist
Pro: Was a violinist and "held musical soirees in his home in Thornhill, to which men of science such as Cavendish, Priestly, Herschel, and Joseph Black occasionally came[104]"

(2) Intermediate Ranked Candidates:

- COMTE DE BUFFON, Geroge Louis Leclerc (1707-1788)
  Pro: Well-known scientist, interested in the origin and hisotry of the earth (1776 and 1779 publications), that emphasized the the great length of geological time
  Con: No direct connection with Herschel
  Pro: Laid the groundwork for many fundimental ideas in geology
  Pro: Had both geology and astronomy related publicaitons
  Pro: Was among the first to create an autonomous science, free of any theological influence

- DELUC, Jean Andre (1727-1817)
  Pro: A friend of Herschel's that communicated and visited with him often
  - 8 letters, 2 visits to Herschel's home, a dinner invitation[105], member of the R.S.
  Con: Letters did not indicate any intellectual exchange of ideas
  Pro: Published on the history of the solar system before the birth of the sun
  Pro: He reviewed one of Herschel's papers[106]
  Con: His research goal was to reconcile Genesis and geology
  Con: He opposed Hutton's ideas on erosion, believed it was not an ongoing process

- HALL, Sir James (1761-1832)
  Pro: Hall's work on heat may have influenced Herschel's later work on the same subject
  - Herschel had a copy of Hall's 1812 publicaiton on heat in his library
  Con: No evidence found suggesting any correspondence via letters
  Pro: Interested in the chemical composition and consolidation of strata
  Pro: President of the Royal Society of Edinburgh and friend of James Hutton
  Pro: May have visited Herschel at his home in Slough (1791)
  Pro: Met weekly with James Hutton, John Playfair, and other natural historians, as part of the Oyster Club, to share and disucuss scientific ideas (Rae, 1895)

- HUTTON, James (1726-1797)
  Pro: Hutton's geological research has numerous parallels with Herschel's work
  - Interested in deep time of the earth (he theorized an eternal earth)
  - Believed in gradual change and cyclical processes on the earth
  - His research had a global perspective
  Con: No evidence found suggesting any correspondence or meeting
  Pro: Ideas about the *Theory of the Earth* formed circa 1767[107]
  Con: Ideas not published until 1785, 1788, and 1795

[104] Bux, K. "Sir William Herschel" *English Mechanic and World of Science.* 13 (1871): 309-310.
[105] Royal Astronomical Society, Herschel Archive (W.1/13.L.61).
[106] Royal Astronomical Society, Herschel Archive (W.1/ 13.L.67).
[107] Ramsay, W. and F. Donnan. (1918). *The Life and Letters of Joseph Black, M.D*. London: Constable, p.117-125.

Pro: Hutton gave Herschel a copy of *Theory of the Earth*
Pro: May have influenced Herschel's work on invisible (infared) light
- Hutton proposed the existence of invisible light in 1794 which Herschel later confirmed with more advanced experiments

Pro: Met weekly with Sir James Hall, John Playfair, and other natural historians, as part of the Oyster Club, to share and disucuss scientific ideas (Rae, 1895).

- MAILLET, Benoit de (1656-1738)

  Pro: Numerous parallels with Herschel's work
  - **Theorized an eternal universe (with eternally renovated heavenly bodies) undergoing slow development by natural processes at random**
  - **Interested in deep time of the earth (estiamted ~2Ga)**
  - **Analysed present-day marine mechanisms to explain the geological past (following essentially uniformitarian principles)**
  - **Presented one of the first systematic theories of general transformism**

  Con: No direct evidence for mechanisms of intellectual exchange
  Pro: His ideas influenced many leading naturalists such as Buffon and Cuvier
  Pro: Made numerous geological observations during his extensive travels

- PLAYFAIR, John (1748-1819)

  Pro: Developed and popularized Hutton's ideas on the *Theory of the Earth* in his book *Illustrations of the Huttonian Theory,* which he gave a copy of to Herschel
  - **William made pencil notes in some of the margins**

  Con: Playfair's book popularizing Hutton was not publihed until 1802
  Pro: Visited Herschel at Slough in 1788, were at Greenwich observtory together in 1782
  Con: No evidence found suggesting correspondence via letters
  Pro: He introduced several geological terms to the scientific community (i.e. geological cycle, igneous origin)
  Pro: Lectured on physics and astronomy at the University of Edinburgh
  Pro: Met weekly with James Hutton, Sir James Hall, and other natural historians, as part of the Oyster Club, to share and disucuss scientific ideas (Rae, 1895)

<u>(3) Lowest Ranked Candidates:</u>

- BANKS, Sir Joseph (1743-1820)

  Pro: Frequent communication and visits with Herschel (and various other natural historians)
  - **President of the Royal society, 75 documented correspondances with Herschel, at least 3 visits to Herschel's home**

  Con: Bank's correspondances are primarily about Royal Society buisness
  Pro: **Scientific promoter whose adult life was directed toward the advancement of science**
  Con: Most of Bank's research, which was mostly biology related, was never published

- ENGLEFIELD, Sir Henry Charles (1752-1822)

  Pro: Frequent communication and visits with Herschel
  - **17 letters, at least 2 visits to Herschel's home, member of the Royal Society**

Con: No direct evidence of intelliectual exchange; communication appears to be one-sided and letters were not geology related, but rather about astronomical observations

Pro: Both an astronomer and geologist with astronomical publications in 1781 and 1784

Con: No geology related publicaitons until 1816

Con: His geology research focused primarily on the Isle of Wight

- WERNER, Abraham (1750-1817)

  Pro: Interested in geologic succession based on deep time (Earth was thought to be ~1 Ma)

  Con: Contributions to geology were rarely published; spread largely by word of mouth

  - Any influence (if at all) was likely indirect, through his disciples

  Con: No evidence found suggesting correspondence or meeting

  Pro: Classified all geological data, separated rock classification from that of minerals

- WOODWARD, John (1665-1722)

  Pro: His research focused on the history of the earth and it's strata (1695, 1723)

  Con: No evidence for intellectual exchange or passage of ideas

  Pro: Published and focused on making global observations (1696)

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Mather, K. and S. Mason. *A Source Book in Geology, 1400-1900*. Cambridge: Harvard University Press, 1970.

Rae, John. Life of Adam Smith. London: Macmillan and Co., 1895. p. 334-338, 416-419.

APPENDIX 4.8

Timeline of Relevant Events in William Herschel's Life

This is a chronological timeline of events and publications relating to the life of William Herschel (circa ~1760 -1815) that are relevant to the origination and development of Herschel's notable ideas, especially those relating to the construction of the heavens. Also included are potentially influential events and scientific publications related to earth science. This timeline was constructed using Hoskin's *Discoverers of the Universe* (2011), Laudan's *From Mineralogy to Geology* (1994), and various publications from the *Philosophical Transactions of the Royal Society of London (*1760-1815).

1760
February 28 - Michell's paper concerning the earth with "regular and uniform strata" was read for the first time at the R.S.

1767
May 7 - Michell's paper about *An Inquiry into the Probable Parallax* was first read at the R.S.

1770
- W.H. purchased Robert Smith's *Optiks*

1773
Spring - W.H. started becoming interested in astronomy
May 10 - W.H. purchased a copy of James Ferguson's book, *Astronomy*
September 27 - W.H. learned how to grind and polish mirrors
Late October - W.H. casted discs for 2 ft. and 5 ½ ft. reflectors

1774
March 1 - W.H. opened his first observing book and examined Saturn and the Orion nebula
March 4 - W.H. observed and sketched the Orion nebula and noted that its shape differed from Huygens sketch in Robert Smith's *Optiks.*

1776
May - W.H. was working on a 10 ft. reflector with a 9 in. diameter mirror
May 28 - W.H. viewed the moon with his new 10 ft. telescope and noted no evidence of Ferguson's lunarians, but he could detect "growing substances"
July 30 - W.H. viewed an eclipse of the moon with his new 20 ft. reflector (w/ 12 in. diameter mirror)

- Comte de Buffon publishes *The collision hypothesis of Earth origin*.

1777

- D.H taught W.H. how natural historians gather and classify large numbers of specimens.

1778

November - W.H. polished the "most capital speculum" for his 7 ft. telescope, which gave him an advantage over all other observers because of its size and quality

December 15 - W.H. noted the shape of Orion's nebula had altered slightly

1779

- Comte de Buffon publishes *Epochs of the history of the Earth*.

August 17 - W.H. began devoting his time to examining the sky and looking for double stars.

October - W.H. again observes the Orion nebula and again notes alteration

December 31 - W.H. was invited to join the Bath Philosophical Society

1780

May 11 – W.H.'s paper *"Astronomical Observations Relating to the Mountains of the Moon" was read aloud at the Royal Society*

June 12 – W.H. sends Maskelyne a letter about inhabitants on the moon[108]

August 6 - W.H. examined the Andromeda nebula.

1781

January - W.H. began construction of a gigantic telescope, with a 4 ft. reflector mirror, that would be four times greater in diameter than his current telescope

March 13 - W.H. discovered Uranus

December 7 - W.H. elected to the Royal Society and given a copy of Messier's Catalog of Nebulae and Star Clusters by his good friend William Watson

End of - W.H. had catalogued no fewer than 269 double stars, 227 of which were new discoveries

1782

March - Aubert confirmed W.H.s claim that Polaris was a double star

May 19 - W.H. gave his last public musical performance

May 25 - W.H. met King George

May 29 - W.H.'s telescope was found to be superior to any at the Royal Observatory[109]

June 8 - W.H. determined that his telescopes were superior, perhaps "the best telescopes that were ever made"[110]

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[108] In a letter to Maskelyne, W.H. states that "…there is almost an absolute certainty of the Moon's being inhabited… For instance, seeing that our earth is inhabited and comparing the moon with this planet: finding that in such a satellite there is a provision of light and heat: also, in all appearance a soil proper for habitation full as good as ours, if not perhaps better – who can say that it is not extremely probable, nay beyond doubt, that there must be inhabitants on the Moon of some kind or other?" (pp. 522 - 526 of *Phil. Trans.*, 1780, 70, 507-526).

[109] W.H. took his reflector to the Greenwich Observatory for appraisal by the astronomer Royale and then visited the Kings Observatory at Kew for inspection.

June 15 - W.H. met with Maskelyne, Aubert, Playfair, Shepherd, and Arnold at the Greenwich Observatory
July 2 - W.H. was invited to Windsor Castle, by the King, to show heavenly bodies to the Royal family
July – W.H. wrote an article for *Phil. Trans.* naming his planet "Georgium Sidus" after the King
July - W.H. became appointed astronomer to the court, which in turn allowed him to renounce his musical profession and devote his time and full attention to astronomy
August – W.H. moves to his new home at Datchet, in England
August 20 - W.H.s 20 ft. telescope was operational at his home in Datchet
September 7 - W.H. discovered the Saturn nebula
Autumn - W.H. began training his sister C.H. in astronomy

1783
February 26 – C.H. discovers two new nebula[111]
March 4 - W.H.'s research changed directions; from double stars to nebulas and star clusters[112]
May 8 - W.H. attended a Royal Society
Spring - T. Collinson suggested that W.H. try to refract the rays of the star with a prism and his telescope
May 21 - W.H. compared the spectra of Mu and Alpha Cephei[113]
October - W.H. constructed a new, larger, 20 ft. telescope with an 18 in. mirror.
October 28 - W.H. unknowingly validated the theory that red light travels the fastest based on his observation of Jupiter's third moon during an eclipse[114]
November – In response to a suggestion about watching from when his planet passes in front of a star, W.H. writes that God had made planets for intelligent beings and thus there would be an atmosphere on Uranus that would blur any reddening effect

1784
April - W.H. published his first paper on the construction of the heavens in *Phil. Trans.*
June 17 - W.H.'s first *Construction of the Heavens* paper was read at the R.S.
June 22 - W.H. abandoned his idea of "true nebulosity" after coming across the Omega nebula
August 15 - W.H. was visited by French geologist, Faujas Saint-Fond
End of the year - W.H. sent the Royal Society a second catalog of 434 double stars
End of the year - 1785 - W.H. began to ask himself a range of original scientific questions[115]

1785
February 3 - W.H.'s second paper concerning the construction of the heavens was read at the R.S.

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[110] This was determined after he compared his telescopes to those at the Greenwich Observatory on June 1, 1782 and to his friends Aubert's, on June 8, 1782.
[111] Only one of the nebulas she discovered was new, the other was actually already known by Messier but it was recorded in a later edition of *Connoissance de Temps,* which the Herschel's did not have.
[112] Hoskins believes that Caroline's discoveries of nebula on Feb. 26th of the same year, inspired W.H.'s change in research directions.
[113] According to Hoskins, in doing so, he inaugurated the pre-history of astrophysics.
[114] This theory was originally postulated by Marquis's de Courtirron in 1752.
[115] According to Hoskin (2011), the questions regarded the solar system, planets, stars, light, etc…

March 7 - James Hutton's "Abstract Concerning the System of the Earth" made public at the R.S. of Edinburgh
April 4 – Second reading of Hutton's abstract at the R.S. of Edinburgh
June - W.H. moves to a house in Old Windsor

1786
March - W.H. moves to Slough, where he remains until his death in 1822
April 27 - W.H. "Catalogue of One Thousand New Nebulae and Clusters of Stars" was read at the R.S.

1787
April 26 - W.H.s paper on "An Account of Three Volcanos in the Moon" was read at the R.S.

1788
May 8 - W.H. married the widow Mary Pitt
May 14 - French geologist Faujas de Saint-Fond sends W.H. a letter about volcanos and potential life on the moon

- James Hutton's "Theory of the Earth" published[116]
- John Playfair visited Herschel at Slough

1789
June 11 – W.H.'s third paper on the construction of the heavens was read at the R.S.
August 28 – first observations made with the newly built 40 ft. telescope

1790
October 22 - W.H. observed ~150 "bright, red, luminous points" on the moon believed to be volcanoes[117]
November 13 – Observed "true nebulosity" (cloudy atmosphere surrounding a star), leading him to abandon his current theory that all nebulae are star clusters

1794
March 7 - W. Wilkins independently observes "…light, like a star, seen in the dark park of the moon…[118]"

1795

- James Hutton's 1788 article was expanded to a two-volume work entitled *Theory of the Earth*

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[116] "Theory of the Earth; or an Investigation of the Laws observable in the Composition, Dissolution, and Restoration of Land upon the Globe" in *Transactions of the Royal Society of Edinburgh*, vol. I, Part II, pp. 209–304, plates I and II. The paper concludes; "The result, therefore, of our present enquiry is, that we find no vestige of a beginning,- no prospect of an end."
[117] Only in his log book does W.H. call the dots "volcanos."
[118] Published in *Phil. Trans*. 1794, pp. 429-440 and read to the R.S. on July 10, 1774.

1797
August – W.H. took an interest in geology (fossils) while on a family vacation in Bath

1798
April - W.H.'s curiosity for stellar spectra was revived.

1802

- W.H. had added no fewer than 2510 nebula and clusters to the hundred or so listed by Messier
- John Playfair published *Illustrations of the Huttonian Theory of the Earth*

July 1 - W.H.s forth paper related to the construction of the heavens was read at the R.S.

1805 - 1806

- W.H. published a paper in *Phil. Trans.* in which he estimated the actual speed at which the sun, stars, and planets were moving

1807

- Geological Society of London founded

1811
June 20 - W.H.'s fifth paper related to the construction of the heavens was read at the R.S.

1814

- End of W.H.'s observation career

1817
June 19 - W.H.'s sixth, and last, paper related to the construction of the heavens was read at the R.S.

1822

August 25 - W.H. dies at his home in Slough

APPENDIX 4.9

Partial Translation of Herschel's Correspondence from Faujas de Saint-Fond

French volcanologist, Barthelemi Faujas de Saint-Fond, (1741-1819) , spent a night observing with Herschel in August (15th and 16th), 1784, and later sent him two letters; the first in 1786, recalling the "entire night" he had with Herschel and the skillfull instructions on observing techniques he received, and the second letter, in 1788, about lunar volcanos and life on the moon. The letters, which come from the Herschel Archive at the Royal Astronomical Society (W.1/13.F4 and 13.F5), were written in French but have been translated into English by Dr. Woodruff Sullivan III. Below is a partial translation of the 1788 letter, with topics of interest to this paper in bold. Notes about the content of the untranslated parts of the letter are also provided for context.

<u>1788 letter from Faujas to Herschel (W.1/13.F5)</u>

- [Faujas never explicitly mentions Herschel's paper on lunar volcanos[119], which was published in the previous year, although clearly his reading of it in *Phil. Trans.* must have prompted him to write this letter].

- Having not heard from William, Faujas is wondering if his previous letter and the print[120] he had sent made it. He asks that William please reply.

- Faujas complains about the pettiness of French astronomers, how he admires Herschel, and asks for more specific information on the 40ft telescope.

- Since Faujas has studied volcanos on earth, he has some ideas in regards to Herschel's ideas about volcanos on the moon.

- Faujas recalls that Herschel told him (during his visit to Datchet) about the new lunar feature [May 1783] that appeared in the same spot where Herschel had days before seen a bright light.

- Faujas wants to know about the two <u>faint</u> volcanos that Herschel saw; were they located in the region that Hevelius called *Mons Porphyrites*?

[119] "An Account of Three Volcanos in the Moon*,"* 1787, 77.

[120] 21 months after his visit, Faujas sent W.H. a letter and print of the moon based on a "rare engraving" of Cassini's observations.

- Faujas writes, **"I am not embarrassed to consider the moon by analogy as another real [*veritable*] Earth"**, **and it's conceivable that there could be subterranean fire there that would produce visible effects.**

- “without the atmospheric air of Earth, the dephlogisticated air or vital air [oxygen] of the moon could combine with several salt substances and metallic limes that perhaps are part of the water [solutes in the lunar liquid water - the maria]; the same are part of saltpeter...permitted in vitriolic [sulfuric] acid factories in chambers deprived of atmospheric air...”

- “...conflagration of inflammable bodies, and if the water is similarly made of vital air [oxygen] and inflammable air [hydrogen], as one finds at the XXX, the water can decompose and supply the inflammable material that is the heart of fire.”

- Faujas has had long and frequent conversations on this topic with the illustrious naturalist Buffon, who is a good friend, and Buffon agrees with the possibility of Faujas’ views, but with one embarrassing objection, namely the same as the astronomers' objection: the absolute lack of a lunar atmosphere.

- But Faujas makes two points: (1) **there could well be a <u>small</u> [undetected] atmosphere on the moon**, and (2) **despite Buffon's idea that the moon is now "absolutely congealed" [solid and cold], nevertheless it was different in the past when the central heat warmed the ground and gave life to all the animals and plants (as on earth) and the surface became suitable [habitable] again.**

- "Now what is the atmosphere if not exhalations of various air-particles [*aeriformes*] that emanate from bodies due to heat, electricity, fermentation, decomposition of liquids and solids, etc." [leaunes?] known now as fixed air [nitrogen], alkaline air [ammonia], inflammable air [hydrogen], vital air [oxygen] or *air pur* [pure air?], dephlogisticated air or vital air [oxygen], etc.”

- Likewise water is held in solution in the air - although by nature it is heavy, it floats in the atmosphere because it acquires a lightness that allows it to rise into the upper regions. There are perhaps some bodies in nature that can be vaporized since even gold itself, when exposed to a burning mirror [solar reflector], smokes, is volatilized, and starts to gild at a certain distance from silver foil. Several of these vapors are *cohersible* [??], while others remain eternally "suspended" [meaning several can convert back to a solid and others never can?]

- Thus if by some large accident our earth suddenly experienced a degree of solidification that penetrated to its center, susceptible vapors would condense and acquire weight [density?] by the meeting of molecules or by new combinations, and would fall on the earth, but the electrical fluid (whose effects are manifest in what we call the vacuum)j, inflammable air (the lightest of the emanations), uncombined vital air, and several other unknown elastic fluids would not always form an atmosphere around the terrestrial body. **This atmosphere, deprived of all the *cohersible* [??] molecules, would in truth be extremely diaphanous and its transparency could make it imperceptible, but it would still exist.**

- "This is perhaps the state of the moon, but in all cases the vital air combines with minerals, with salts, and with a bunch of ground [surface] substances, which could permit the burning of combustible bodies. Without the benefit of atmospheric air volcanos can thus vigorously burn. On a *terre* [world] that doesn't have the same atmosphere (although it would be difficult to form an idea of a world that would be entirely so deprived), and for the objects that we cannot reach [travel to], **we must never abandon the thread of analogy - we must presume that the moon is a world like ours."**

- Forgive me for digressing on all this when you are better than all the others to shed light [on these matters] not by theory [as Faujas has described], but by "good observations made with as much Wisdom as Genius."

The End