

High Resolution Chemostratigraphy and Cyclostratigraphy of Lower Silurian Neritic Carbonates from Anticosti Island, Quebec, Canada.

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Abstract

The storm-dominated paleotropical carbonate succession exposed on Anticosti Island in Eastern Canada represents one of the most complete, thickest, and well-preserved successions in the world spanning the O/S Boundary. This study develops a new high resolution integrated lithostratigraphic, cyclostratigraphic, and chemostratigraphic framework for the upper Hirnantian to lower Telychian (Upper Ordovician to lower Silurian) succession on Anticosti, by examining ~450 m of strata from a recent stratigraphic drill core (Martin La Mer), supplemented by ~120 m of outcrop, all from the south-central part of the island. Four facies assemblages and three time-specific facies were identified in this succession and can be organized into three orders of superimposed transgressive-regressive cycles. New high resolution isotopic curves were produced by sampling well-preserved bulk micrite at a resolution of 0.5-1.0 m per sample; in total 443 samples were taken from core and 168 from outcrop, corresponding to the Ellis Bay, Becscie, Merrimack, Gun River, Menier, Jupiter and Chicotte formations. Four distinct positive carbon isotope excursions are recognized in the study interval; the upper Hirnantian (+5‰), Lower Aeronian (+2‰), Upper Aeronian (+6‰), and Valgu (+3.5‰) excursions. These $\delta^{13}\text{C}$ excursions accompany lithology, and sea level changes and are likely driven by transitions between humid and arid climate states coupled with ocean changes. Multi-ordered $\delta^{18}\text{O}$ trends are recognized to occur in association with $\delta^{13}\text{C}$ trends; long-term and intermediate scale $\delta^{18}\text{O}$ fluctuations are likely controlled by glacio-eustasy and Silurian climate fluctuations, while high-frequency fluctuations may record an astronomical forcing signal.

Résumé

La succession carbonatée, exposée sur l'île d'Anticosti dans l'est du Canada, représente l'une des successions les plus complètes, les plus épaisses et les mieux préservées au monde à la frontière de l'Ordovicien et du Silurien (O/S). Cette succession est principalement représentée par des dépôts carbonatés sous forte influence de tempêtes dans un ancien milieu marin tropical peu profond. La présente étude présente un tout nouveau cadre stratigraphique de haute-résolution intégrant lithostratigraphie, cyclostratigraphie et chimiostratigraphie et datant de la fin de l'Hirnantien à la fin du Télychien (Ordovicien supérieur au Silurien inférieur). L'étude porte sur ~450 m de strates sédimentaires d'une récente carotte de forage (Martin La Mer), complétée par ~120 m d'affleurement, se trouvant dans la partie centre-sud de l'île. Quatre grands assemblages de faciès et trois faciès plus restreints dans le temps ont été identifiés dans cette succession et peuvent être organisés en trois ordres de cycles transgressifs-régressifs superposés. De nouvelles courbes isotopiques à haute résolution ont été produites en échantillonnant de la micrite en vrac, mais bien conservée à une résolution de 0,5-1,0 m par échantillon ; au total, 443 échantillons ont été prélevés dans des carottes et 168 dans des affleurements, correspondant aux formations d'Ellis Bay, Becscie, Merrimack, Gun River, Menier, Jupiter et Chicotte. Quatre excursions positives d'isotopes en carbone sont reconnues dans l'intervalle d'étude : les excursions de l'Hirnantien supérieur (+5‰), l'Aéronien inférieur (+2‰), l'Aéronien supérieur (+6‰) et du Valgu (+3.5‰). Les excursions $\delta^{13}\text{C}$ s'accompagnent par des changements lithologiques et relatifs du niveau de la mer et sont probablement dues à des changements climatiques humides à arides, ainsi qu'à des changements océaniques. Les tendances multiordres en $\delta^{18}\text{O}$ sont aussi reconnues en

association avec les tendances en $\delta^{13}\text{C}$; les fluctuations à long terme et à échelle intermédiaire en $\delta^{18}\text{O}$ sont probablement contrôlées par les fluctuations glacio-eustatiques siluriennes, tandis que les fluctuations à haute fréquence auraient enregistré un signal par forçage astronomique.

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Chapter 1: Introduction

1.1 Prologue

The Ordovician and Silurian periods were a critical time in Earth's history as they were marked by immense changes in both climate and biodiversity. Three major biotic events occurred during this interval; the Great Ordovician Biodiversification Event (GOBE), the end-Ordovician Mass Extinction (the second largest of the "big five" mass extinctions), and the early Silurian post-extinction recovery (Munnecke *et al.*, 2010; Cooper *et al.*, 2012; Melchin *et al.*, 2012). Climatically the Ordovician and Silurian periods occur within an extended greenhouse interval that was interrupted by the Early Palaeozoic Icehouse (EPI), a ~30 m.y. cool interval characterized by the widespread glaciation of Gondwana (Frakes *et al.*, 1992; Page *et al.*, 2007; Munnecke *et al.*, 2010). Seven glacial maxima occur within the EPI, four in the Late Ordovician and three in the Llandovery, the largest of which occurred in the late Hirnantian (Munnecke *et al.*, 2010). The Silurian Period itself was incredibly volatile and was punctuated by multiple short-lived climatic events, strong sea level fluctuations, and oceanic turnovers, all of which are commonly associated with moderate scale extinctions and perturbations of the global carbon cycle (Calner, 2008; Munnecke *et al.*, 2010; Melchin *et al.*, 2012). Associated with these extinctions are several major positive isotopic carbon excursions which coincide with or are preceded by biotic turnovers (Munnecke *et al.*, 2010; Cramer *et al.*, 2011). The precise causes of these excursions are highly debated and include changes in organic productivity (e.g. Branchley, *et al.*, 1994; Kump and Arthur, 1999), increased carbonate weathering during sea-level lowstands (e.g. Saltzman, 2002; Melchin and Holmden, 2006a), and climate driven changes in

oceanic circulation patterns (e.g. Bickert *et al.*, 1997; Munnecke *et al.*, 2003). Regardless of the exact mechanism of these excursions, they provide a distinct geochemical signature useful for local, regional, and global scale correlations with other Silurian strata. Until recently most Silurian research has focussed on the Wenlock, Ludlow, and Pridoli (middle to upper Silurian); consequently, the Llandovery (lower Silurian) remains understudied (Munnecke *et al.*, 2010; Cramer *et al.*, 2011). The ~900 m thick exposed succession (~550 m of Llandovery strata) on Anticosti Island in Eastern Canada is one of the most complete, thickest, and well-preserved successions in the world spanning the Ordovician-Silurian boundary, and provides an excellent opportunity to study this critical, yet poorly understood, Epoch of the Silurian.

1.2 Current Study and Objectives

The current study on Anticosti Island focusses on the uppermost Hirnantian and the Llandovery (Rhuddanian to early-Telychian) succession recovered from a recent stratigraphic drill core, and outcrops from costal exposures and river cuts on the southwestern part of the Island. The main objectives of this study are to: 1) create a high-resolution integrated lithostratigraphic, chemostratigraphic, and cyclostratigraphic framework for the studied succession; 2) test for the presence of positive carbon and oxygen isotopic excursions as well as assess the preservation of the primary marine isotope signature; 3) investigate and assess the cause and effect relationship between multi-ordered sea level fluctuations, lithology changes, and carbon and oxygen isotopic excursions.

1.3 Previous Work on the Lower Silurian of Anticosti

Richardson (1857) was the first to map the geology of Anticosti Island, dividing the exposed strata into six units listed alphabetically from A-F. These six units were later refined to seven, and formally named the English Head, Charleton, Ellis Bay, Becscie River, Gun River, Jupiter River and Chicotte formations (Schuchert and Twenhofel, 1910). Twenhofel (1928) produced the first geological map and revised the stratigraphy of the island, renaming the Charleton Formation the Vauréal, and the Becscie River the Becscie Formation. Further revisions to formation thicknesses and contacts were made by Bolton (1961, 1972, 1975) and Petryk (1979, 1981b), and an updated map was produced by Petryk (1981a). Revisions to the stratigraphy of Petryk (1981b) has led to the addition of two formations; the shaly upper beds of the Becscie Formation were reclassified as the Merrimack Formation (Copper and Long, 1989), and the two lowermost members of the Jupiter Formation were formally redefined as the Menier Formation (Copper and Jin, 2012). Other recent stratigraphic revisions include Copper *et al.* (2012), Copper *et al.* (2013), and Copper and Jin (2014, 2015) detailing the exposed succession, as well as Bédard *et al.* (2014) and McLaughlin *et al.* (2016) detailing the subsurface succession. The most recent geologic map is based on Desrochers and Gauthier (2009).

Sedimentological studies of the Silurian succession include Long (2007), which summarizes the sedimentology, stratigraphy, and subsidence history of the entire exposed succession on Anticosti. Sami and Desrochers (1992) details the sedimentology and depositional history of the Becscie and Merrimack formations; and Desrochers (2006), Desrochers *et al.*

(2007), Clayer and Desrochers (2014), and James *et al.* (2015), each detail aspects of the sedimentology, depositional history, and stratigraphic architecture of the Chicotte Formation.

Nearly all work on the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphy of Anticosti has been focussed around the Ordovician-Silurian boundary (see summary in Mauviel and Desrochers, 2016). To date only Azmy *et al.* (1998), Munnecke and Männik (2009) and Daoust (2017) present chemostratigraphic curves focussed on portions of the Silurian Anticosti succession.

1.4 Methodology

This study combines subsurface data from the stratigraphic drill core Martin la Mer (NAD 83 zone 20, 514835E, 5459001N), and field samples collected at eight locations in the southwest region of the island; sample locations include Triplesia Creek, Cape Jupiter, Cape Ottawa, the Jumpers, and the cliffs along Brick River (Fig. 1.1). A variety of field and laboratory techniques were used for this study, including core and petrographic observation, cyclostratigraphic analysis, stable isotope geochemistry, and trace element geochemistry.

1.4.1 Core and Petrographic Observations

Detailed logging of the Martin la Mer core was completed at the Ministère de l'Énergie et des Ressources Naturelles (MERN) warehouse in Québec City. Standard core logging techniques were used to describe lithologic facies in terms of composition, depositional textures and fabrics, sedimentary structures, and intensity of bioturbation. Observations were made across a ~450 m core interval comprising the upper Ellis Bay, Becscie, Merrimack, Gun River, Menier, and Jupiter formations. A set of nine representative samples were selected for

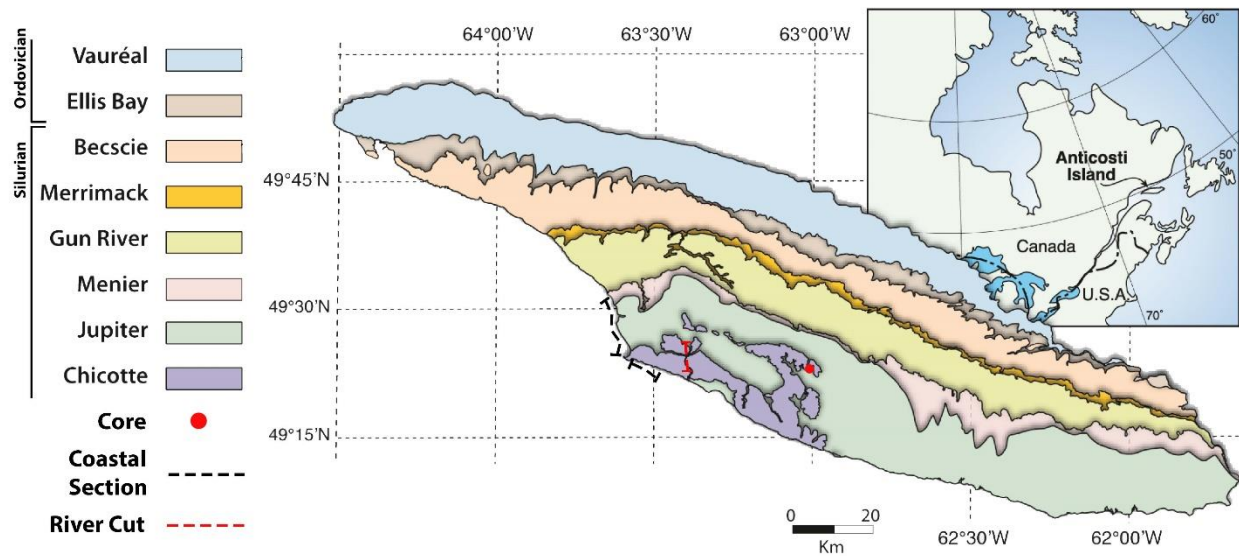


Figure 1.1: Geologic map of Anticosti Island. General location of studied outcrops and the MLM core are indicated on the map. (based on Desrochers and Gauthier, 2009; modified after James *et al.*, 2015)

detailed description and divided in half using a rock saw. One half of each sample was polished, varnished, and photographed, while the other half was prepared for thin section analysis.

1.4.2 Cyclostratigraphic Analysis

The studied succession was subdivided into metre-scale Transgressive/Regressive (TR) cycles (*sensu* Embry, 2009) using various erosion and deposition surfaces or zones present in the core. Facies shifts observed within metre-scale TR cycles can be used to identify lower order TR cycles at the decameter scale.

1.4.3 Stable Isotope Analysis

A bulk rock sampling procedure was used to produce a continuous high-resolution chemostratigraphic record that is independent of brachiopod distribution in the studied succession. In total 627 samples, 184 from outcrop and 443 from core, were collected for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis; the finest available micritic (occasionally peloidal) material from each sample was selected and drilled using a handheld drill and titanium drill bit. In outcrop approximately 100 m of the Jupiter Formation and 30 m of the Chicotte Formation were sampled at a 0.5-1.0 m resolution. In core, samples were collected at a 1 m resolution across approximately 450 m of strata, including the upper Ellis Bay (45 m), Becscie (114 m), Merrimack (12 m), Gun River (114 m), Menier (38 m), and Jupiter (126 m) formations. Sample analysis was performed at the G.G. Hatch Stable Isotope Laboratory at the University of Ottawa on a Thermo Finnigan Gas Bench II and Delta XP mass spectrometer, with an analytical precision of $\pm 0.1\text{‰}$. Results are reported in per mil (‰) and measured against the Vienna Pee Dee Belemnite (VPDB) standard.

1.4.4 Trace Element Geochemistry

In order to assess the preservation of the primary marine isotope signature and evaluate for possible diagenetic alteration, a subset of 45 samples from core and 5 from outcrop was selected and analyzed for trace element geochemistry. Analysis was performed at the University of Ottawa Geochemistry Laboratory on a Varian (Agilent) Vista-Pro Inductively Coupled Plasma Emission Spectrometer (ICP-ES) equipped with a CCD detector. Results are reported in parts per million (ppm) with detection limits of 0.016 ppm and 0.034 ppm for Mn and Sr respectively.

Chapter 2: Geological Setting

2.1 Regional Geology

Anticosti Island is located in the Gulf of St. Lawrence in eastern Canada, roughly 30 km south of the North Shore of Quebec, and 75 km northeast of the Gaspé Peninsula. The island is 222 km in length and 55 km at its widest point. The exceptionally thick (~900 m) mixed carbonate-siliciclastic section exposed on Anticosti represents one of the most complete and well-preserved successions spanning the Ordovician-Silurian boundary in the world (Barnes, 1988; Long, 2007; Ghienne *et al.*, 2014).

The Anticosti Basin initially developed as a passive margin succession following rifting that occurred in the Neoproterozoic to Early Cambrian along the eastern margin of Laurentia (Malo, 2004; Allen *et al.*, 2009). In the Middle Ordovician, this passive margin was transformed into a foreland basin following the partial closure of the Iapetus Ocean during the Taconic orogeny (Lavoie, 2008). Subsidence rates in this foreland basin were locally tectonically controlled reaching a peak of 17.9 cm/ka in the Katian, before thrust loading decreased subsidence to 0.96 cm/ka in the Hirnantian, and 0.8 cm/ka in the early Aeronian (Long, 2007). A period of renewed thrusting occurred in the mid-Aeronian increasing subsidence rates to 3 cm/ka, before subsequently decreasing to 0.2 cm/ka in the Telychian (Long, 2007).

During the late Ordovician and early Silurian, the Anticosti Basin was located at a palaeolatitude of 15° S to 20° S (Fig. 2.1), within the peri-equatorial tropical hurricane belt of the Iapetus Ocean (Nestor *et al.*, 2010; Scotese, 2014). Deposition was storm dominated and located along the submerged margin of Laurentia on a southwestward dipping carbonate ramp

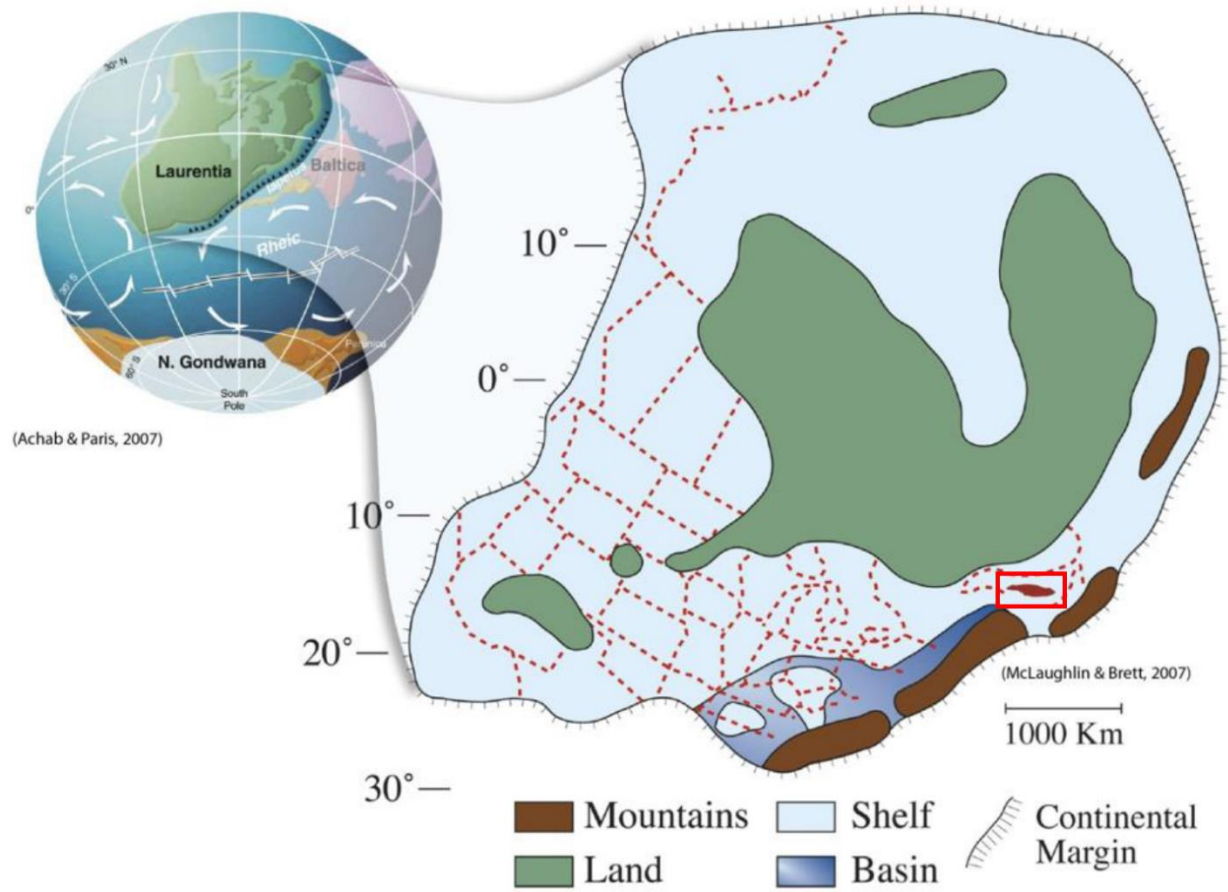


Figure 2.1: Palaeogeographic map of Laurentia during the Late Ordovician. Note the location of Anticosti Island highlighted by the red box (modified from Achab and Paris, 2007; McLaughlin and Brett, 2007).

within a shallow epeiric sea (Long, 2007; Desrochers *et al.*, 2010). Facies change laterally across the island, from mixed siliciclastic-carbonate facies in the eastern section to carbonate dominated facies of the central and western sections; this east-west depositional trend represents the transition from a siliciclastic influenced proximal nearshore environment, to a carbonate dominated offshore environment (Long, 2007; Desrochers *et al.*, 2010).

Through the combination of a stable sediment supply in an actively subsiding basin, a nearly complete and exceptionally thick succession accumulated within the Anticosti Basin (e.g. Sandbian to Katian = ~1600 m, Hirnantian = ~100 m, Rhuddanian to mid-Telychian = ~500 m), and is one or two orders thicker than other age equivalent shallow water carbonate sections (Ghienne *et al.*, 2014). Several major discontinuities are present at the basin margin sections (east end of Anticosti Island), but few can be traced westward into the thickest basin centre sections (Desrochers *et al.*, 2010).

2.2 Regional Stratigraphy

The exposed succession on Anticosti Island has been divided into eight formations (Fig. 2.2), with three additional formations recognized in the subsurface (References *Ibid.*; Desrochers *et al.*, 2012; McLaughlin *et al.*, 2016). In ascending order, the exposed units include the Ordovician Vauréal and Ellis Bay formations, and the Silurian Becscie, Merrimack, Gun River, Menier, Jupiter, and Chicotte formations; the Ordovician Romaine, Mingan, and Macasty formations are only present in the subsurface (Desrochers *et al.*, 2012). Exposed strata are generally composed of interbedded micrites, calcarenites, grainstones, and calcareous mudstones, with mixed carbonate-siliciclastic sandstones present at the east end of the island

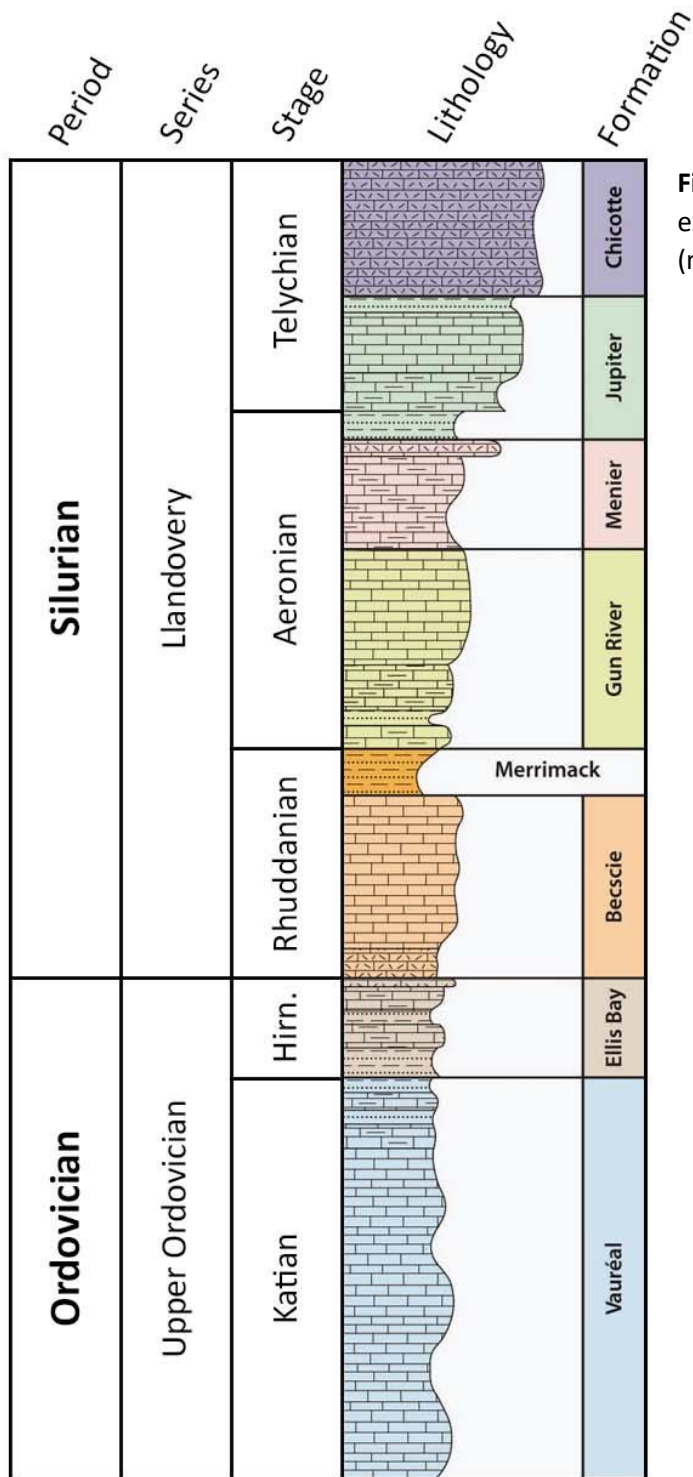


Figure 2.2: General stratigraphy of the exposed succession of Anticosti Island (modified from James *et al.*, 2015).

Legend

	calcareous shale with limestone		encrinite limestone and bioherms
	limestone with calcareous shale		limestone

Hirn. = Hirnantian

(Long, 2007; Desrochers and Gauthier, 2009). Notable lithologic expectations include the reefal buildups of the Hirnantian Laframboise Member of the Ellis Bay Formation, and the crinoidal limestones, bryozoan mud mounds and coral-stromatoporoid bioherms and biostromes comprising the Telychian Chicotte Formation (Brunton and Copper, 1994; Desrochers, 2006; Copper *et al.*, 2013).

The exposed strata on Anticosti Island are relatively tectonically undisturbed, but locally affected by minor faults and fracture networks interpreted to represent far field strain related to the Appalachian orogen (Bordet *et al.*, 2010; Pinet *et al.*, 2015). In the subsurface, several high angle normal faults have been identified through seismic interpretation, affecting Ordovician strata up to the Vauréal Formation (Bordet *et al.*, 2010; Duchesne *et al.*, 2016). South of Anticosti Island in the offshore portion of the basin, a 40 km wide fold and fault belt has developed sub-parallel to the Gaspé Peninsula (Pinet *et al.*, 2012). This region, which is characterized by broad open synclines, narrow anticlines, and northwest striking faults, was formed mainly during the Middle Devonian Acadian orogeny (Pinet *et al.*, 2012).

2.3 Biostratigraphy of the Lower Silurian of Anticosti Island

Anticosti Island contains Silurian strata ranging from earliest-Rhuddanian to mid-Telychian in age (Fig. 2.3). The strata are age constrained by conodonts (Uyeno and Barnes, 1981, 1983; Zhang and Barnes, 2002, 2004; Munnecke and Männik, 2009), while chitinozoan biostratigraphy is largely focused on the Upper Ordovician and Rhuddanian succession (Achab, 1981; Soufiane and Achab, 2000; Achab *et al.*, 2011; Achab *et al.*, 2013). Graptolites, a key Silurian index fossil, are sparsely distributed in the Anticosti succession making precise

Figure 2.3: A summary of relevant biozones of Anticosti Island. Biozonations of conodonts, graptolites, chitinozoans, and pentamerid brachiopods from Anticosti are plotted relative to the standard global graptolite biozonation. Abbreviations: Ord = Ordovician, U.Ord = Upper Ordovician, Hirn. = Hirnantian, UEB = Upper Ellis Bay, MMK = Merrimack.

GLOBAL				LOCAL				
Period	Series	Stage	Standard Graptolite Biozonation (Cramer et al., 2011)	Lithostratigraphy		Biostratigraphy		
				Formation	Conodonts (Zhang and Barnes, 2002; Munneke and Männik, 2009)	Chitinozoans (Achab, 1981; Soufiane and Achab, 2000; Achab et al., 2011)	Brachiopods (Jin and Copper, 2000)	Graptolites (Riva and Petryk, 1981; Melchin, 2008)
Silurian	Llandovery	Telychian	<i>Oktavites spiralis</i>	Chicotte	<i>Pterospirifer</i> <i>amorphognathoides</i> <i>angulatus</i>		<i>P. subrectus</i> – <i>C. gaspeensis</i> CZ	
			<i>Monoclimacis crenulate</i>		<i>Pterospirifer</i> <i>eopennatus</i> ssp. n. 2			
			<i>Monoclimacis griestoniensis</i>		<i>Pterospirifer</i> <i>eopennatus</i> ssp. n. 1			
			<i>Streptograptus crispus</i>					
		Aeronian	<i>Spirograptus turriculatus</i>	Jupiter	<i>Ozarkodina aldrigei</i>	<i>Conochitina</i> sp. (= <i>dolioliformis</i>)	<i>Stricklandia planirostrata</i> AZ	Various <i>Normalograptus</i> Sp.
			<i>Spirograptus guerichi</i>			<i>Clathrochitina?</i> sp. 2		
			<i>Simulograptus sedgwickii</i>	Menier	<i>Ozarkodina clavula</i>	<i>B. proboscifera</i>	<i>P. palaformiz</i> – <i>S. gwelani</i> CZ	
			<i>Lituigraptus convolutes</i>				<i>Kulumbella xacta</i> TRZ	
			<i>Pristiograptus leptotheca</i> <i>Monograptus argenteus</i>	Gun River		<i>A. ramosaspina</i>		
			<i>Demirostrites peninatus</i> <i>Demirostrites triangulatus</i>					
				MMK	<i>Ozarkodina strena</i>	<i>C. electa</i>	<i>Virgiana mayvillensis</i> TRZ	
			<i>Coronograptus cyphus</i>		<i>Oulodus jeannae</i>			
			<i>Cystograptus vesiculosus</i>	Becschie	<i>Oulodus panuarensis</i>	<i>B. postrobusta</i>	<i>Virgiana barrandei</i> TRZ	
			<i>Parakidograptus acuminatus</i>			<i>C. post- oncina</i>		
			<i>Akidograptus ascensus</i>		<i>Ozarkodina hassi</i>	<i>P. nodifera</i>	<i>Viridita lenticularis</i> TRZ	
			<i>Neodiversograptus persculptus</i>			<i>A. ellisbayensis</i>		
Ord.	U. Ord	Hirn.		UEB	<i>Fauna 13</i> (<i>G. ensifer</i>)	No Chitinozoans <i>S. taugourdeui</i>		<i>N. parvulus</i> <i>N. abbreviatus</i>

biostratigraphic correlations difficult (Melchin, 2008). Shelly fauna (including brachiopods and corals) has been heavily studied and remain useful for temporal correlations (Copper and Long, 1989; Jin and Copper, 2000; Copper *et al.*, 2012; Copper *et al.*, 2013; Copper and Jin, 2012, 2014, 2015).

The Ellis Bay Formation and the lowermost 1-2 m of the Becscie Formation are Hirnantian in age (Achab *et al.*, 2013; Copper *et al.*, 2013). The majority of the Becscie Formation is early Rhuddanian in age (Copper and Jin, 2014), but the chitinozoan *A. ellisbayensis* recovered from the basal beds of the Becscie is Hirnantian (Achab *et al.*, 2013); the Merrimack Formation is late Rhuddanian in age (Copper and Long, 1989). The first appearance of the conodont *Oulodus jeannae* occurs within the lower Gun River formation, indicating the Merrimack-Gun River formational boundary coincides with the Rhuddanian-Aeronian stage boundary (Zhang and Barnes, 2002). The *C. electa* and *A. ramosasina* chitinozoan zones from the Gun River Formation (Soufiane and Achab, 2000) match the Baltic Raikülla stage, the regional equivalent of the Aeronian (Copper *et al.*, 2012). Soufiane and Achab (2000) assigned a late Rhuddanian age to the Gun River Formation, however, numerous other studies demonstrated that the Gun River Formation is Aeronian in age (e.g. Jin and Copper, 2000; Zhang and Barnes, 2002; Copper *et al.*, 2012; Copper and Jin, 2014). The Menier and lowermost Jupiter formations are late Aeronian in age, with the Aeronian-Telychian boundary occurring within the Jupiter Formation (Copper and Jin, 2012, 2015). The Aeronian-Telychian boundary is roughly coincident with the Richardson-Cybèle member boundary as suggested by the presence of the graptolite *Stimulograptus sedgwickii* within the Richardson Member (Riva and Petryk, 1981; Copper and Jin, 2015). The contact between the Jupiter and Chicotte formations

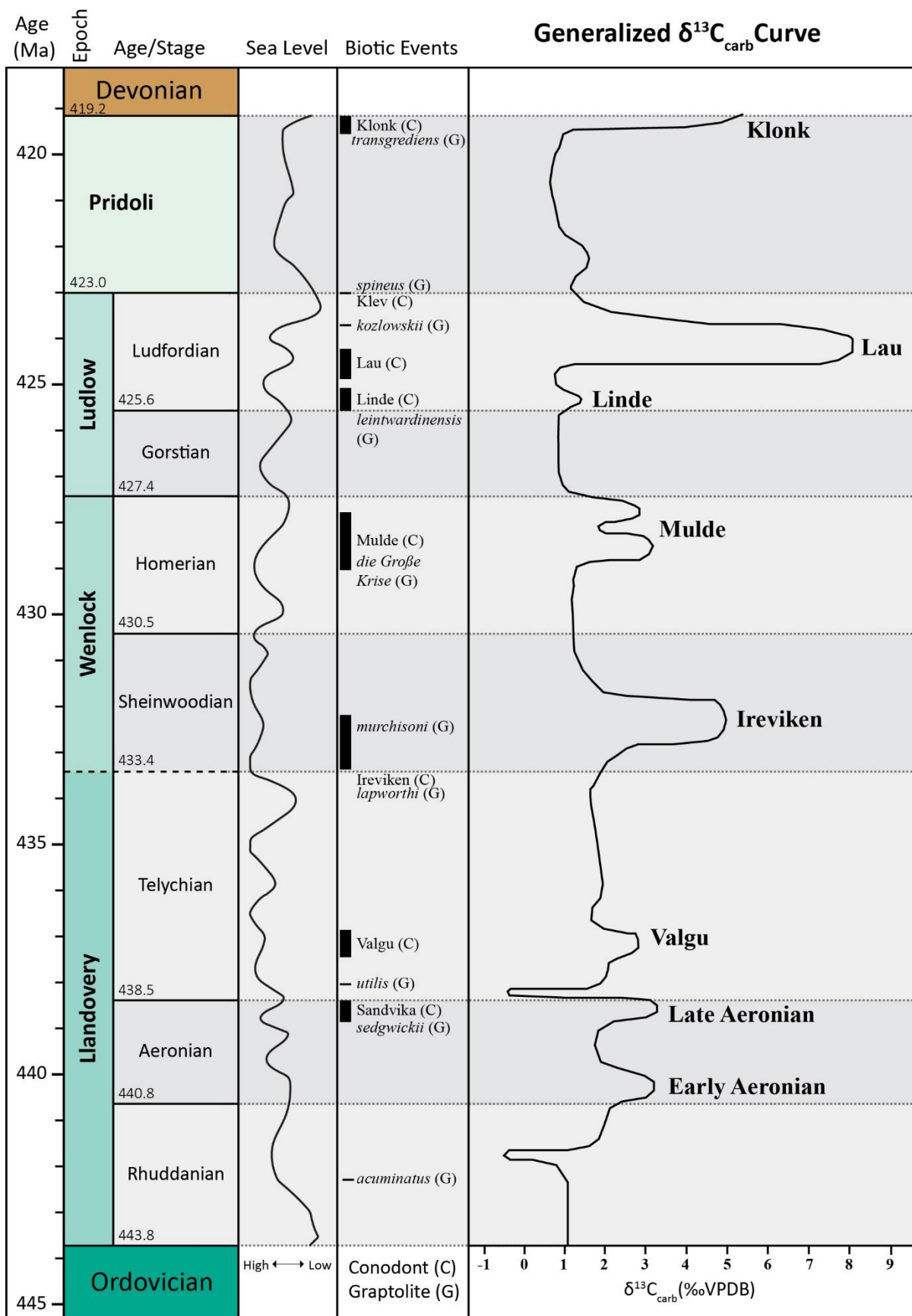
corresponds to the first appearance of the conodont *P. eopennatus*, indicating a mid-Telychian age for the uppermost Jupiter and Chicotte formations (Munnecke and Männik, 2009).

2.4 The Silurian Isotopic Carbon Record

The Silurian is one of the shortest periods of the Phanerozoic (duration of ~24 Myr) yet contains some of the most frequent and significant fluctuations in the isotopic carbon record (Munnecke *et al.*, 2010; Cramer *et al.*, 2011). Eight major positive $\delta^{13}\text{C}$ excursions are recognized in the Silurian, occurring in the early Aeronian, late Aeronian, early Telychian, early Sheinwoodian, mid Homerian, lowermost and mid Ludfordian, and the late Pridoli (Fig. 2.4). The magnitude of these $\delta^{13}\text{C}$ excursions are extremely large when compared to excursions of the Mesozoic and Cenozoic; the Ludfordian (or Lau) excursion is the largest post-Cambrian $\delta^{13}\text{C}$ excursion recorded in the Phanerozoic with maximum documented values of up to 12‰ (Calner, 2008; Munnecke *et al.*, 2010; Melchin *et al.*, 2012). Excursions typically occur in association with lithological changes such as periods of expanded reef growth, or the increased deposition of argillaceous sediments (Munnecke *et al.*, 2010). The development of oncolites, stromatolites, and other microbial facies are common, and notably occur in association with the peaks of the Ireviken, Mulde, and Lau excursions (Munnecke *et al.*, 2003; Calner, 2008; Munnecke *et al.*, 2010). Excluding the early Aeronian, all Silurian $\delta^{13}\text{C}$ excursions are associated with moderate scale biotic extinctions, especially affecting conodonts and graptolites (Melchin *et al.*, 2012).

The isotopic carbon record of the Llandovery and the three positive $\delta^{13}\text{C}$ excursions recorded during this epoch (early Aeronian, late Aeronian, and Valgu excursions) are largely

Figure 2.4: Generalized Silurian isotopic carbon record. The sea level curve is based on Haq and Schutter (2008), conodont and graptolite bioevents are modified after Melchin et al. (2012), and the $\delta^{13}\text{C}$ curve and placement of excursions is based on Cramer et al. (2011).



understudied when compared to the excursions of the Wenlock-Ludlow interval (Cramer *et al.*, 2011). As a result, the causes, duration, and global occurrence of these excursions are only known in a general sense. Chemostratigraphic curves produced from shallow water and deep water strata, recorded in either $\delta^{13}\text{C}_{\text{carb}}$ or $\delta^{13}\text{C}_{\text{org}}$, from various localities and palaeobasins are compiled in Figures 5.3 and 5.4 and are compared in Chapter 5.3. Many of these curves only document one or two excursions, while some document none; raising concerns about the stratigraphic completeness. Only strata from subsurface Wisconsin (McLaughlin *et al.*, 2013) and the Moose River Basin (Bancroft *et al.*, 2015) sequentially record early Aeronian, late Aeronian, and Valgu excursions.

Chapter 3: Cyclostratigraphy

3.1 Introduction

An integrated lithostratigraphic and cyclostratigraphic analysis on 446 m of upper Hirnantian to lower Telychian strata from the recent Martin La Mer (MLM) stratigraphic core is presented below. First, the major depositional facies are briefly described and interpreted. Second, the repetitive nature of these facies is examined to identify multi-scaled stratigraphic trends and their stratigraphic architecture.

3.2 Facies Description and Interpretation

Numerous sedimentological outcrop based studies cover portions of the upper Hirnantian to lower Telychian succession on Anticosti (Sami and Desrochers, 1992; Long, 2007; Farley, 2008; Desrochers *et al.*, 2010; Copper and Jin, 2012, 2014, 2015; Copper *et al.*, 2012; Copper *et al.*, 2013; Ghienne *et al.*, 2014; Mauviel, 2016), with (Daoust, 2017) integrating outcrop with subsurface data from the La Loutre #1 drill core. Facies descriptions from these previous studies were used and applied to the subsurface material from the MLM core.

In this study, a common assemblage of rock types was identified throughout the core, mainly consisting of a variety of calcisiltites, calcarenites, rudstones, lime mudstones, and calcareous shales. These rock types represent distinct depositional facies, where sediments were deposited below fairweather wave base on a mid to outer carbonate ramp under the influence of frequent storm events (Aigner, 1985). Storm deposition is evidenced by the frequently hummocky and swaley cross-stratified (HCS and SCS) calcisiltite/calcarenite beds with sharp, locally scoured basal contacts. HCS and SCS form under oscillatory-dominated

combined flow during storms (Dumas and Arnott, 2006). These storm beds, called tempestites, are locally interbedded by more argillaceous strata that were deposited during fairweather times. Two end member types of tempestites can be distinguished; medium to thick bedded, grain-dominated proximal tempestites, and thin bedded, mud-dominated distal tempestites.

Due to the large volume of core examined, it would be impractical to measure and record each individual bed, or to describe and interpret individual facies in detail. Instead facies were grouped into facies assemblages based on the relative abundance of grain-dominated versus mud-dominated beds, bed thicknesses, and relative abundance of calcareous shale. Four general facies assemblages (FA) were identified (Table 1); FA 1- calcareous shale (Fig. 3.1a, 3.2a), FA 2- mud dominated tempestites (Fig. 3.1b, 3.3a), FA 3- mixed muddy/grainy tempestites (Fig. 3.1c, 3.2b,c,d), and FA 4- grain dominated tempestites (Fig. 3.1d, 3.2a,b,c); corresponding to fairweather deposition, and distal, intermediate, and proximal tempestites respectively. Additionally, three time-specific facies (TSF) were identified (Table 1); TSF 1- interbedded argillaceous lime mudstone and calcareous shale (Fig. 3.3b), TSF 2- dense lime mudstone (Fig. 3.3c), and TSF 3- reef limestone (Fig. 3.4). Each TSF has a limited stratigraphic occurrence within the core but is lithologically distinct, occluding it from being grouped into a facies assemblage. Present in all facies is a diverse biotic assemblage dominated by open marine stenohaline taxa including crinoids, brachiopods, molluscs, bryozoans, trilobites, tabulate corals, rugose corals, and stromatoporoids.

Table 1: Facies descriptions and interpretations from the Martin La Mer Core.

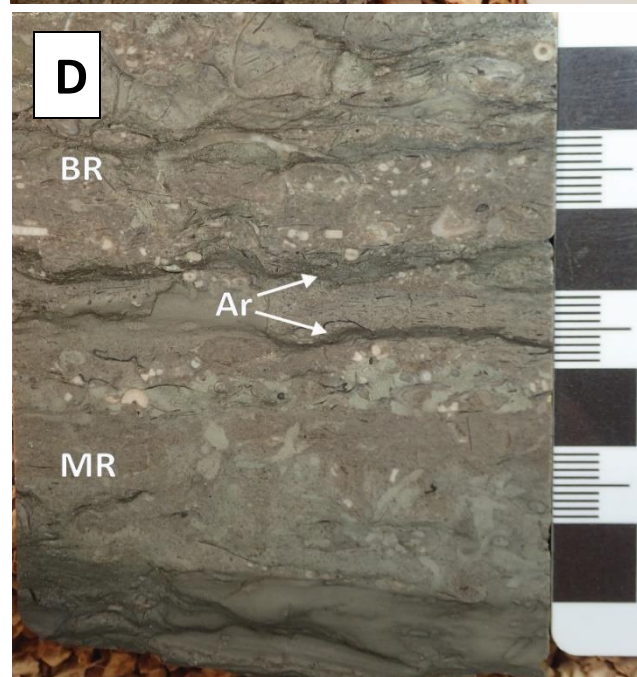
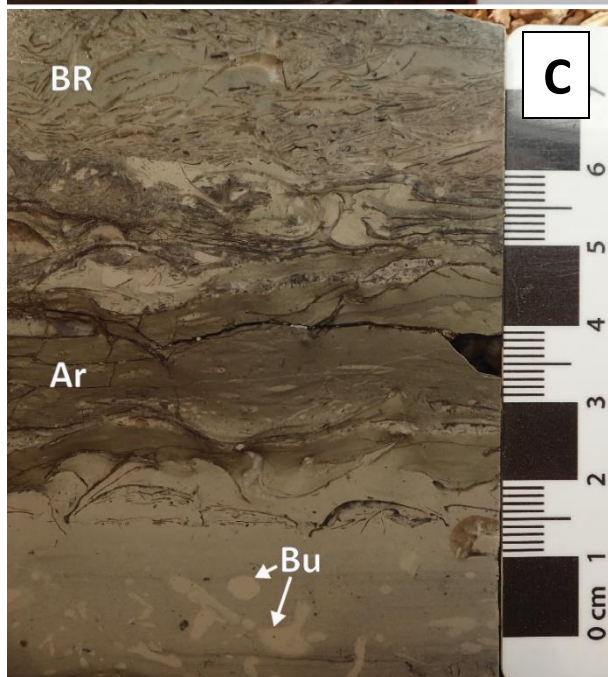
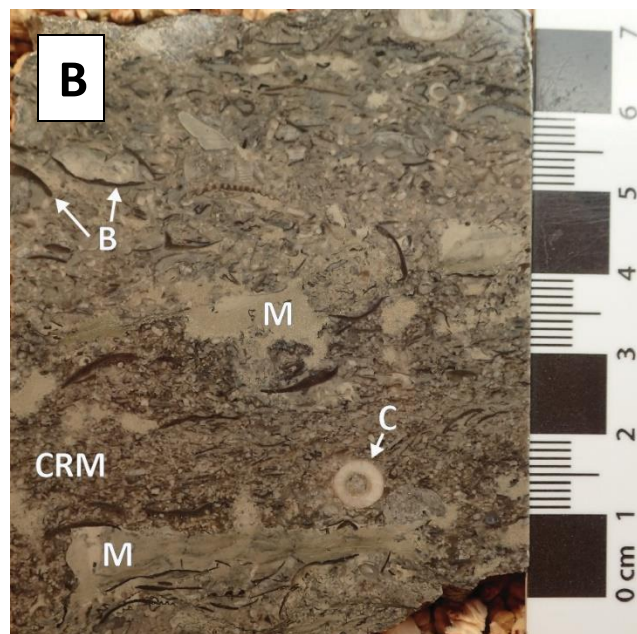
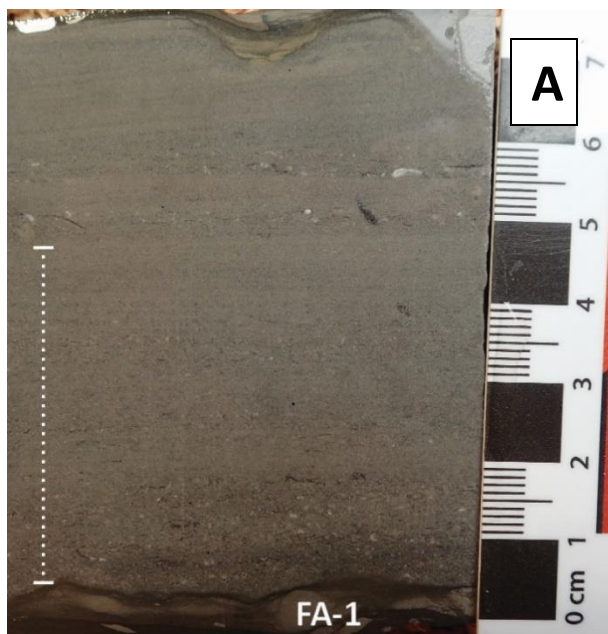
Facies Assemblage	Description	Interpretation
FA 1- Calcareous shale	Massive to fissile dark grey calcareous shale, interbedded with all facies. Variable thickness, from thin laminations (<1mm thick) to thin beds (<5 cm thick), rarely up to ~10 cm thick. Variably bioturbated; thicker beds tend to be more bioturbated. Minimal bioclasts present, and generally increase in abundance upsection.	Fair weather deposition in mid to outer ramp setting. May also be influenced by climatic fluctuations.
FA 2- Mud dominated tempestites	Nodular to thin bedded lime mudstone to wackestone with common interbeds of calcareous shale, and uncommon interbeds of thin calcisiltite/calcareenite. Lime mudstones are massive to laminated and variably bioturbated; with increasing bioturbation thin lime mudstone beds become discontinuous and nodular in appearance. Mudstone beds contain minimal bioclasts but increase in abundance upsection where they become a mix of mudstone and wackestone. Calcisiltite/calcareenite interbeds are laminated, contain abraded bioclasts, and have sharp basal contacts.	Distal tempestites deposited in a lower mid ramp to outer ramp environment.
FA 3- Mixed muddy and grainy tempestites	An intermediate facies assemblage between FA 2 and FA 4. Comprises a mix of HCS/SCS calcisiltite/calcareenite and massive to laminated lime mudstone/wackestone in approximately even abundance; common interbeds of calcareous shale. Thin interbeds of bioclastic or intraclast rudstone are present, typically in association with HCS/SCS beds.	A mix of HCS/SCS and muddy tempestites deposited in a mid-ramp setting.
FA 4- Grainy dominated tempestites	Dominated by medium to thick bedded HCS/SCS calcisiltite/calcareenite with thin interbeds of calcareous shale, and uncommon interbeds of thin bedded, laminated lime mudstone. HCS/SCS beds have sharp basal contacts, commonly have normally graded bases, and consist of well sorted abraded bioclasts and peloids; amalgamation of HCS/SCS beds is common. Beds of bioclastic or intraclast rudstones with sharp erosional basal contacts are common throughout; rudstone beds typically occur in association with HCS/SCS beds.	Proximal tempestites deposited in an upper mid ramp to lowermost inner ramp setting.

Time Specific Facies	Description	Interpretation
TSF 1- Interbedded argillaceous lime mudstone and calcareous shale	Interbedded argillaceous lime mudstone and calcareous shale, with conformable sharp contacts between individual beds. Argillaceous lime mudstone beds are massive and moderately to highly bioturbated, whereas calcareous shale beds are typically highly fissile, and non bioturbated; both contain a minor amount of bioclasts. Thin interbeds of crinoid rich bioclastic calcisiltite/calcareenite with sharp basal contacts are present throughout, in both mudstone and shale beds.	Occurs before upper Aeronian excursion, and the minor unnamed excursion. Influx of shale may reflect climactic changes.
TSF 2- Dense lime mudstone	Mix of dense, massive lime mudstone and laminated argillaceous mudstone; uncommon interbeds of calcareous shale, and rare interbeds of very thinly bedded (<1 cm thick) calcisiltite/calcareenite. Bioturbation is present in both massive and argillaceous beds, but more abundant in massive limestone beds. Contacts between massive lime mudstone and argillaceous beds are gradational to sharp; minor amounts of bioclasts are present throughout but are more abundant in argillaceous beds.	Coincides with both Aeronian excursions; Deposited in a lower mid ramp to outer ramp setting?
TSF 3- Reef Limestone		
3A- Calcimicrobial-coral bioherms	Stratigraphic reefs interfingering with thin-bedded muddy limestones and calcareous shales. Reef cores comprise amalgamated boundstone layers separated by shale; reef builders in order of importance include; calcimicrobes, tabulate corals, bryozoans, and stromatoporoids. Bioherms are capped by a regionally extensive erosional surface and draped by basal Becscie strata (description after Desrochers, <i>et al.</i> 2010). In the Martin La Mer core, only the shale-free, cross-stratified reef flank facies and a thin basal oncolitic rudstone are observed.	Inner mid-ramp patch reef development.
3B- Coral-stromatoporoid bioherms	Patch reefs dominated by tabulate corals, rugose corals, and stromatoporoid; other significant biota include encrusting cyanobacteria, crinoids, brachiopods, and green algae. Inter-reef strata comprise crinoid dominated packstones to grainstones (description after Copper and Jin, 2012). In the Martin La Mer core, this facies comprises inter-reef strata dominated by crinoids, brachiopods, coral fragments, and other abraded bioclasts; small in-situ corals and stromatoporoids are present locally and encrusted by cyanobacteria. Thin interbeds of calcareous shale are present throughout.	Inner mid-ramp patch reef development.



Figure 3.1: Core photos of facies assemblages 1-4. Note how dark shale content decreases with successive photos. All core photos have the same scale (1.5 m from bottom to top). A) FA 1 Calcareous shale. Dark grey calcareous shale interbedded with light grey nodular limestone (FA 2). B) FA 2 mud dominated tempestites. In the core here, thin bedded lime mudstones overlie nodular lime mudstone. Note the dark grey beds and thin laminations of calcareous shale (FA 1) throughout. C) FA 3 mixed muddy and grainy tempestites. Core comprises a mix of thin bedded lime mudstone, HCS calcisiltite/calcareenite, and bioclastic rudstone, with minor interbeds of calcareous shale (FA 1). D) FA 4 grainy dominated tempestites. Core comprises medium to thick bedded HCS/SCS calcisiltite/calcareenite with abundant rudstone interbeds, and minor calcareous shale (FA 1) interbeds.

Figure 3.2: Note that all core photographs are oriented perpendicular to bedding. A) Medium bedded HCS calcisiltite/calcarenite from FA 4 overlying FA 1. Note the subtle normal grading and laminations highlighted by the dotted line. B) Bioclastic rudstone associated with FA 3 and FA 4. Large crinoid (C), brachiopod (B), and mudstone (M) fragments sit within a finer crinoid rich matrix (CRM). C) Brachiopod rich bioclastic rudstone (BR) associated with FA 3 and FA 4 overlying argillaceous lime mudstone (Ar). Note the burrowing (Bu) within the clean lime mudstone at the bottom of the picture. D) Interbedded mud rich (MR) and bioclast rich (BR) tempestites from FA 3. Individual beds are separated by thin argillaceous laminations (Ar).



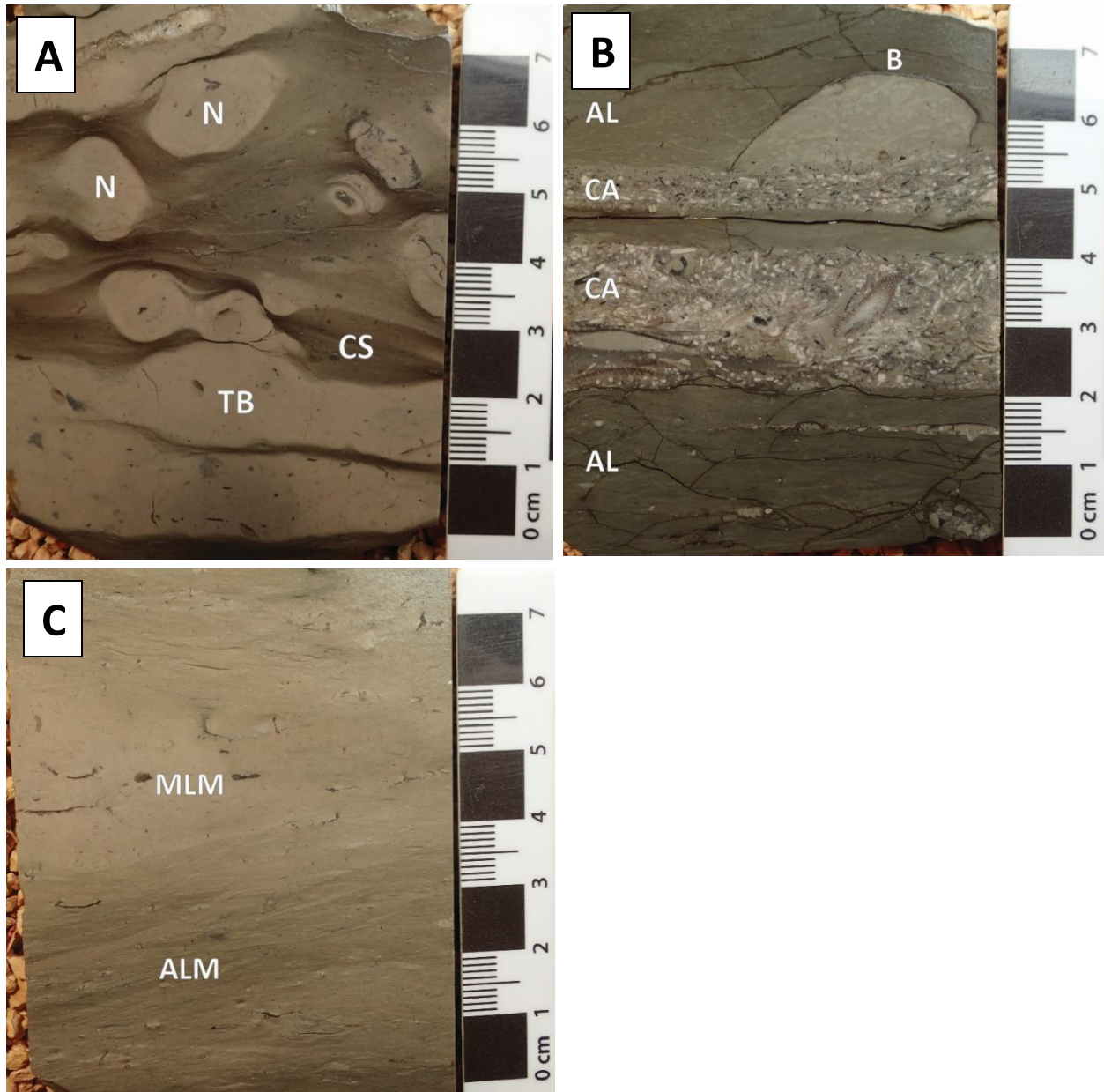


Figure 3.3: A) FA 2 mud dominated tempestites with calcareous shale (CS) interbeds. Note the difference in continuity between thin bedded lime mudstones (TB) and the nodular lime mudstones (N). B) TSF 1 interbedded argillaceous lime mudstone and calcareous shale. Argillaceous lime mudstone (AL) beds are punctuated by thin bedded bioclastic calcarenite (CA) interbeds, with an intact brachiopod (B) shell half at the top. Note the clean bioturbated lime mudstone deposited beneath the brachiopod shell. C) TSF 2 dense lime mudstone. Clean massive lime mudstone (MLM) beds are interbedded with laminated argillaceous lime mudstone (ALM) beds. Shell fragments and other bioclasts are dispersed throughout the core.



Figure 3.4: TSF 3 reef limestone. A) TSF 3a calcimicrobial-coral bioherms. A large stromatoporoid (S) and rugose coral (R) are intergrown with light grey calcimicrobes (C) within a muddy matrix. Note photo is from the La Loutre #1 core examined by Daoust (2017). B) TSF 3b coral-stromatoporoid bioherms. A large stromatoporoid (ST) encrusted with a dark grey microbial buildup (M) forms the framework of the reef. Rugose corals (R) and a large brachiopod (B) are also present within the bioclast rich matrix.

3.3 Stratigraphic Trends and Architecture

Various stratigraphic tools were used to delineate relative sea level changes within the upper Hirnantian to lower Telychian succession of the MLM core including: variations in grain size, changes in bed thickness, gradual versus abrupt facies changes, and relative abundance of shale. In outcrop, the recognition of stratigraphic motifs is easier because of differential weathering (*sensu* Mauviel, 2016; Daoust, 2017), a “natural enhancement” not observed on the pristine unweathered surface of core material. As a result, the identification of thinner or short-lived cycles is more difficult, and not always possible in the core.

Facies patterns reflecting sea level changes were identified at three thickness scales (Fig. 3.5): low-order (>75 m), intermediate-order (10-25 m), and high-order (2-10 m). These multi-scaled facies trends were interpreted to represent multi-ordered transgressive regressive (T-R) cycles (*sensu* Embry, 2009). Each T-R cycle can be divided into two system tracts; a shallowing upwards regressive system tract (RST) and a deepening upwards transgressive system tract (TST). Each RST is bounded by a maximum flooding zone or surface (MFZ) at its base, and a maximum regressive surface or zone (MRS) at its top, whereas each TST is bounded by a MRS at its base and a MFZ at its top. An individual TST is characterized by finer grained, typically shale rich, thicker bedded strata, while a RST is characterized by coarser grained, typically shale poor, thinner bedded strata.

Three and a half low-order cycles were identified in the studied succession with thicknesses of 75, 115, and 150 m respectively, as well as a final ~110 m thick regression. These low-order T-R cycles thicken upsection and comprise multiple shallowing upwards and

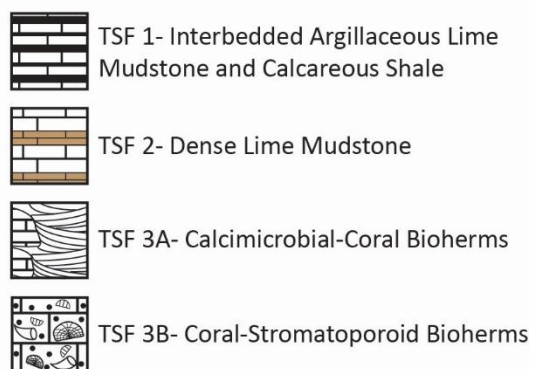
deepening upwards sequences that, when considered as a whole, appear to display an overall shallowing upwards trend. Low-order cycles can be subdivided into at least 28 intermediate-order T-R cycles; with 6-8 intermediate-order cycles present in each low-order cycle. Intermediate-order cycles range between 10-25 m in thickness, and generally thicken upsection. An average of 3-5 high-order cycles are present in intermediate-order cycles; with individual high-order cycles varying between 2-10 m in thickness. High-order cycles were only identified in the upper half of the studied succession (0-233 m), at least partially facilitated by a larger core diameter.

Figure 3.5: Legend and stratigraphic logs of the Martin La Mer core highlighting lithostratigraphy, cyclostratigraphy, members, and formations.

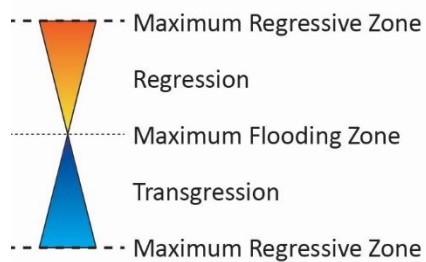
Facies Assemblages

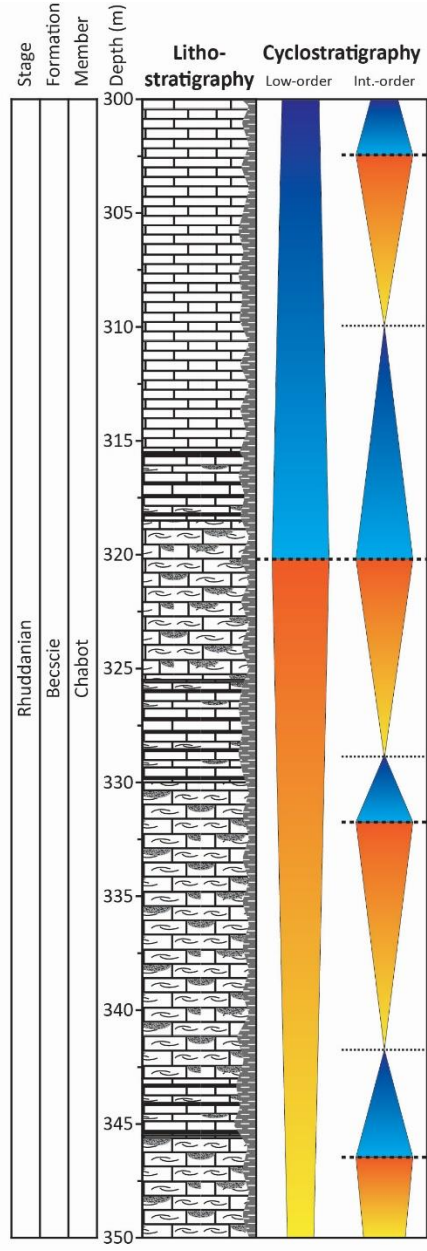
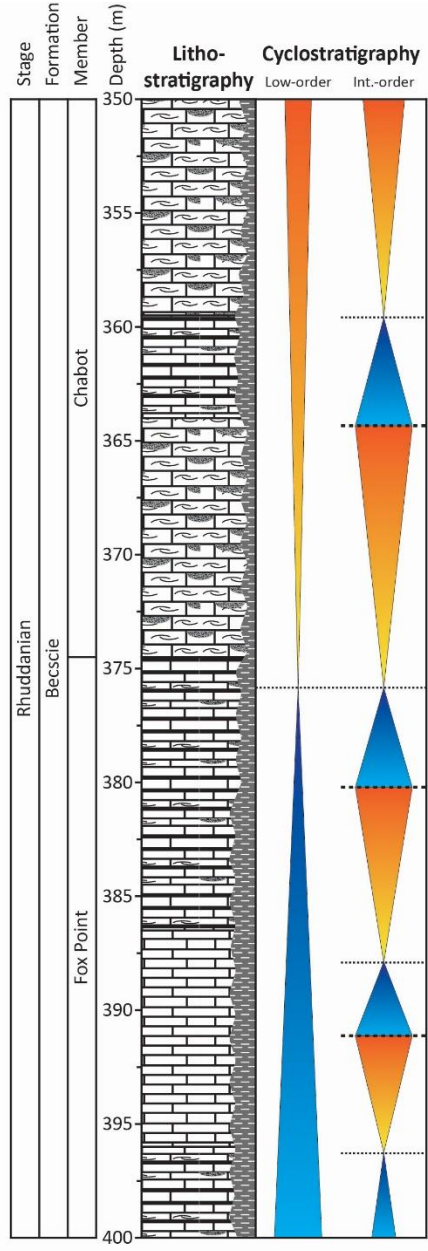
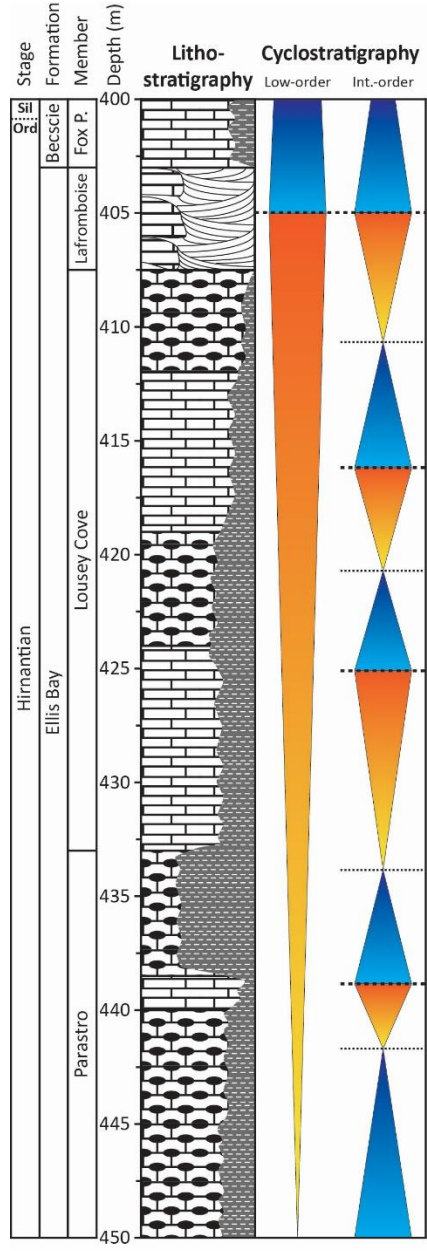


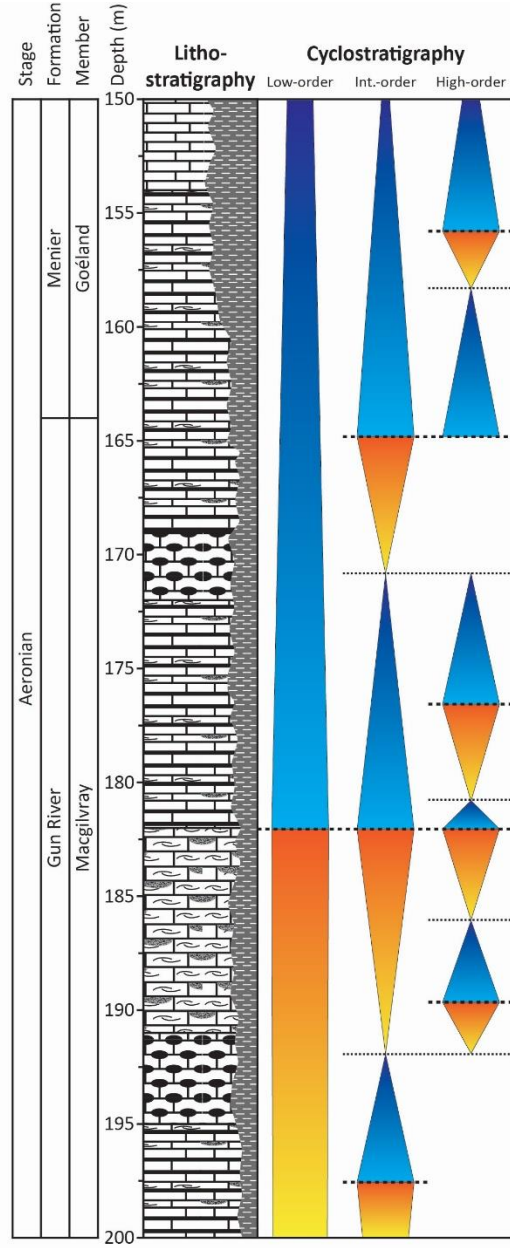
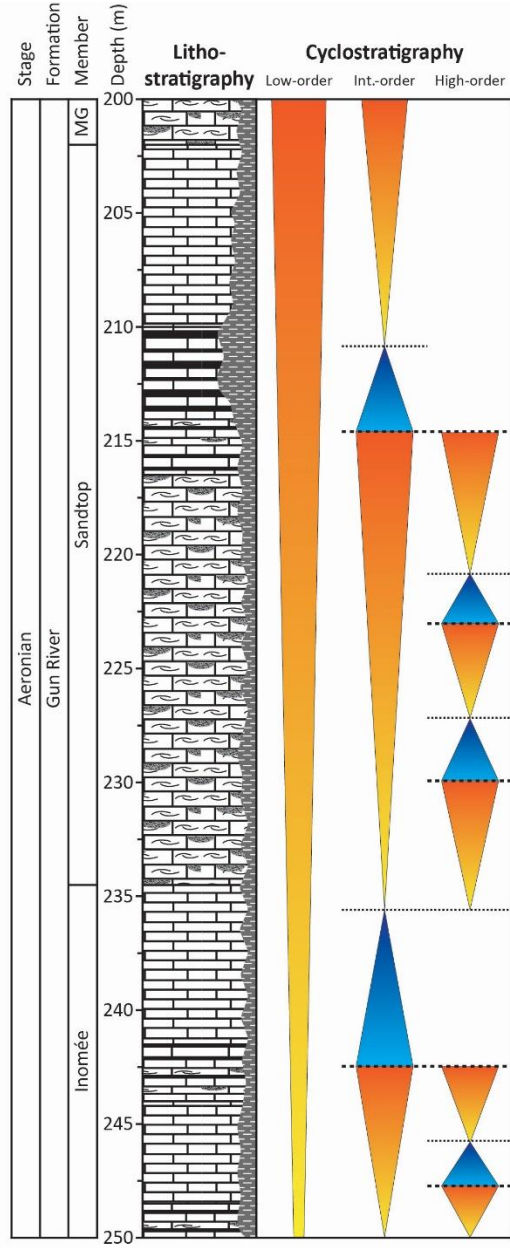
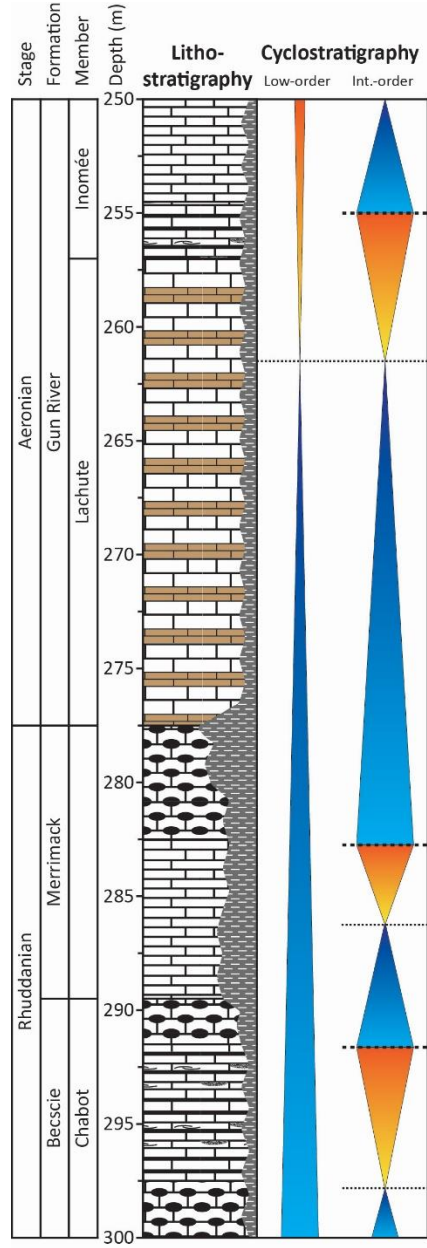
Time Specific Facies

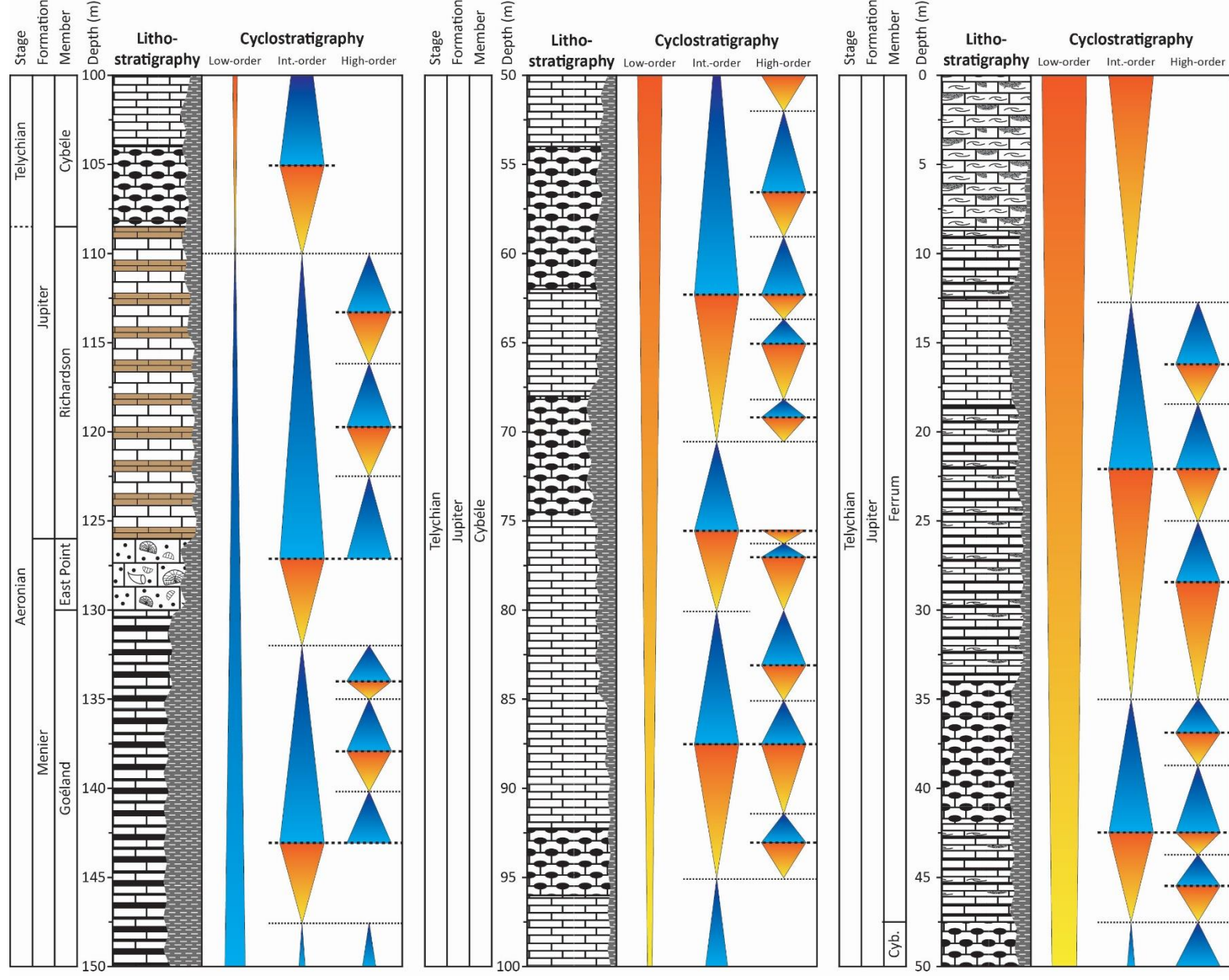


Cyclostratigraphy









Chapter 4: Chemostratigraphy

4.1 Introduction

The high resolution $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves produced in this study comprise a total of 443 data points from the MLM drill core, supplemented by 168 data points from three outcrop sections in the south-central part of Anticosti Island. Four positive $\delta^{13}\text{C}$ excursions can be recognized in the studied succession; the upper Hirnantian isotopic carbon excursion (Upper HICE), the Lower and Upper Aeronian isotopic carbon excursions (Lower AICE and Upper AICE respectively), and the Valgu Excursion. The Upper HICE and Lower AICE were only recorded in the core, the Upper AICE was recorded both in core and outcrop, and the Valgu Excursion was recorded twice in outcrop.

4.2 Outcrop Data

4.2.1 *Upper Aeronian Excursion*

The Upper AICE is recorded in outcrop within the Jupiter Formation in a composite section where samples were collected at Triplesia Creek, Cape Jupiter, and Cape Ottawa (Fig. 4.1). From the base of the section, $\delta^{13}\text{C}$ values rise rapidly from $\sim 1\text{‰}$ in the shale rich Goéland Member and peak at $\sim 4.5\text{‰}$ across the entire Richardson Member (approximately 35 m). At the lower contact of the Cybèle Member, $\delta^{13}\text{C}$ values return to a pre-excursion level of $\sim 1\text{‰}$. Values for $\delta^{18}\text{O}$ are irregular in the lower half of the curve, but a general trend can be recognized in the composite section. The $\delta^{18}\text{O}$ curve displays an increase from -5‰ at the base reaching a peak of -4.5‰ between 30 and 35 m, followed by a gradual decrease to -5.5‰ at ~ 47 m.

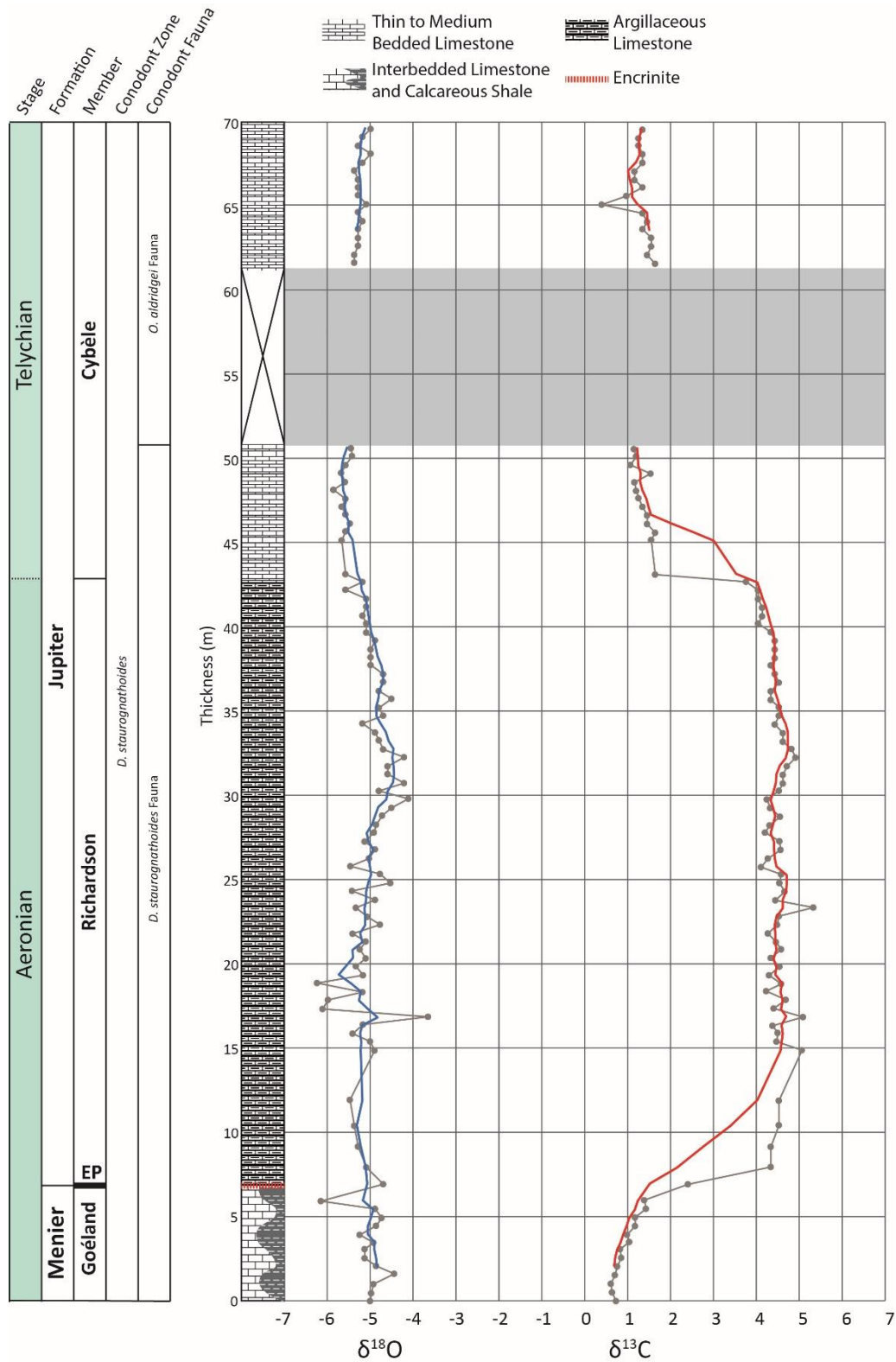


Figure 4.1: Composite section of the Upper Aeronian isotopic carbon excursion in outcrop. Coloured lines are a running average (n=5); EP = East Point Formation; Conodont data is from Uyeno and Barnes (1983). See text for explanation.

4.2.2 Valgu Excursion

In this study, the Valgu Excursion is recorded from a composite section within the Chicotte Formation (Fig. 4.2) consisting of samples collected at the Jumpers and two localities along Brick River. Although the Valgu Excursion is not encountered in the core, the peak of the excursion (~30-40 m) was recorded twice in outcrop; at the Jumpers and at one of the localities along Brick River.

At the base of these sections, the upper Jupiter strata display $\delta^{13}\text{C}$ values near $\sim 0\text{‰}$, with a slight positive shift upwards. A negative shift in $\delta^{13}\text{C}$ values (peaking at -2‰) is present within the shale rich Pavillon Member, immediately preceding the Valgu Excursion. The Valgu Excursion starts at, or near, the base of the Chicotte Formation; initially reaching its peak values of $\sim 3.5\text{‰}$ but still maintaining relatively enriched values of $\sim 2.5\text{‰}$ for the rest of the accessible Chicotte section. A minor trend in $\delta^{18}\text{O}$ appears to be present. From the base of the curve, a slight positive shift can be observed with $\delta^{18}\text{O}$ values peaking at approximately -5‰ in the Pavillon and upper Ferrum members of the Jupiter Formation. Following the peak of the Valgu Excursion, $\delta^{18}\text{O}$ values are progressively depleted, from -5‰ in the lower Chicotte Formation to -6‰ at the top of the accessible outcrop.

4.3 Integrated Hirnantian to Telychian Curve

When the MLM core and outcrop data spanning the Valgu Excursion are integrated, a nearly continuous chemostratigraphic curve is now accessible, and ranges from the upper Hirnantian to Telychian in age (Fig. 4.3). This integrated curve comprises ~ 500 data points

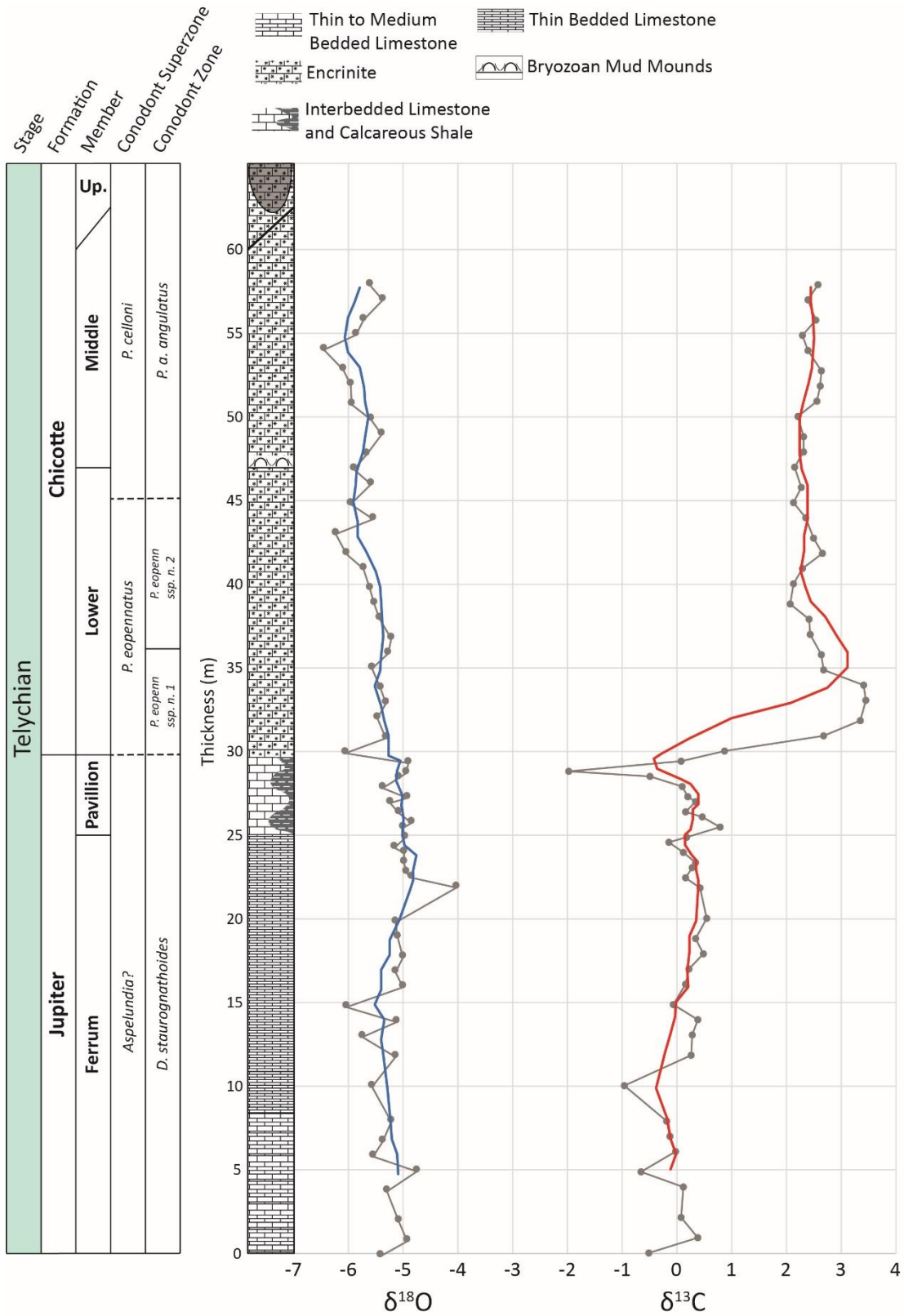


Figure 4.2: Composite section of the Valgu Excursion in outcrop. Coloured lines are a running average (n=5). Conodont data is from Munneke and Männik (2009). See text for explanation.

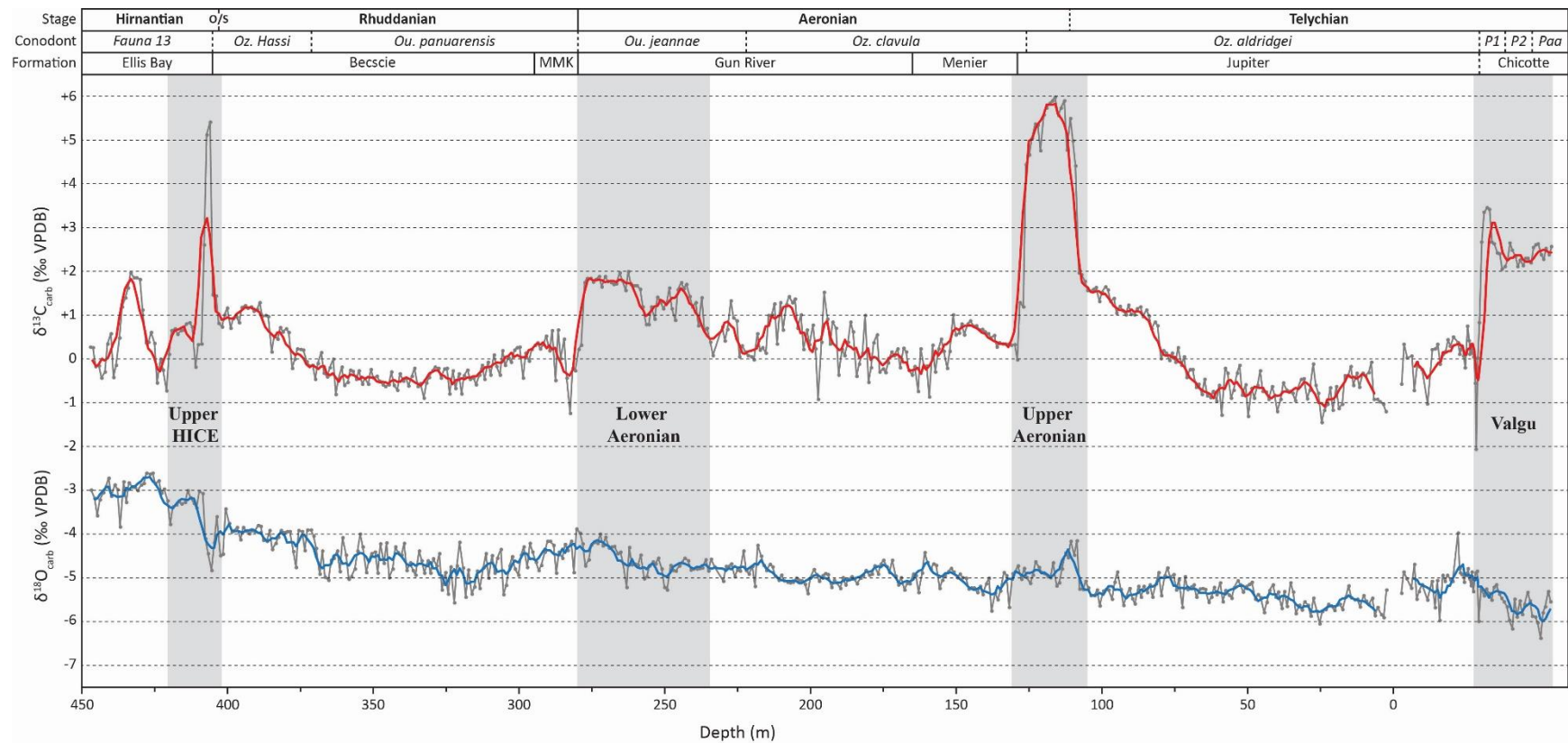


Figure 4.3: Composite chemostratigraphic curve of the upper Hirnantian to Telychian succession. Most of the data is from the MLM core (0–450 m). Data covering the Valgu Excursion is from outcrop (see Figure 4.2). Coloured lines are a running average ($n=5$); see Text for detailed explanation. Conodont data from Zhang and Barnes (2002) and Munnecke and Männik (2009).

Abbreviations: MMK = Merrimack Formation; P1 = *Pterospathodus eopennatus* ssp. n. 1; P2 = *Pterospathodus eopennatus* ssp. n. 2; Paa = *Pterospathodus amorphognathoides angulatus*.

sampling ~500 m of strata spanning seven formations, with only a small gap (<10 m) separating individual data sets.

Long term $\delta^{13}\text{C}$ trends, short term $\delta^{13}\text{C}$ fluctuations, and three distinct positive isotopic carbon excursions can be recognized in the MLM core (Fig. 4.3). The Upper HICE occurs within the uppermost Ellis Bay Formation (within the Lafromboise Member) and reaches a peak of +5‰ between 405 and 406 m depth. The Lower AICE consists of two peaks sustained over a ~40 m interval within the lower Gun River Formation and has maximum $\delta^{13}\text{C}$ values of +1.9‰. A primary peak occurs between 277 and 257 m and is separated from a second peak between 254 and 237 m by a minor negative shift in $\delta^{13}\text{C}$ values. The Upper AICE reaches a maximum $\delta^{13}\text{C}$ peak of +6‰ and is present between 127 and 108 m depth within the Richardson Member of the Jupiter Formation. High-frequency ($\pm 0.5\%$) fluctuations in $\delta^{13}\text{C}$ values can be observed throughout the curve between individual excursions. Between the HICE and Lower AICE as well as between the Upper AICE and Valgu excursions, $\delta^{13}\text{C}$ values display an arcuate trend gradually decreasing and then gradually increasing in magnitude. Between the Lower AICE and Upper AICE $\delta^{13}\text{C}$ fluctuations are more volatile, and a minor unnamed $\delta^{13}\text{C}$ excursion (approximately +1‰) is present between 215-198 m depth; although less defined, an arcuate trend in $\delta^{13}\text{C}$ values is observable between the Aeronian excursions. Additionally, notably preceding each of the three Silurian excursions is a brief negative dip in $\delta^{13}\text{C}$ values.

Three scales of $\delta^{18}\text{O}$ trends can be recognized within the studied succession. A long-term decline in $\delta^{18}\text{O}$ values can be observed across the entire curve, from -3‰ in the Ellis Bay Formation, to nearly -6‰ in the uppermost Chicotte Formation. Superimposed on this long-term shift, at least five intermediate scale trends are present including; 1) a negative shift (-3‰

to -5‰) from 446 to 320 m depth, 2) a positive shift (-5‰ to -4‰) from 320 to 260 m depth, 3) a negative shift (-4‰ to -5.5‰) from 260 to 140 m depth, 4) a positive shift (-5.5‰ to -4.5‰) from 140 to 110 m depth, and 5) a final negative shift (-4.5‰ to -6‰) from 110 m to the top of the core. High-frequency fluctuations (0.5-1.0‰) in $\delta^{18}\text{O}$ values are present throughout the succession but are most pronounced within the Becscie Formation. Additionally, preceding and/or coinciding with each of the Silurian isotopic carbon excursions a positive shift in $\delta^{18}\text{O}$ values can be observed.

4.4 Trace Element Analysis and $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ Cross Plots

Trace element geochemistry was performed to test for diagenetic alteration on 45 samples from the MLM core and 5 samples from outcrop spanning the Valgu Excursion. A cross-plot of Sr and Mn yields an R^2 value of 0.0362, indicating no significant correlation between parameters (Fig. 4.4).

Cross-plots of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the MLM core (Fig. 4.5) and from outcrop data spanning the Upper Aeronian (Fig. 4.6) and the Valgu excursions (Fig. 4.7) reveal R^2 values of 0.0244, 0.0989, and 0.3093 respectively, indicating little to no correlation between parameters.

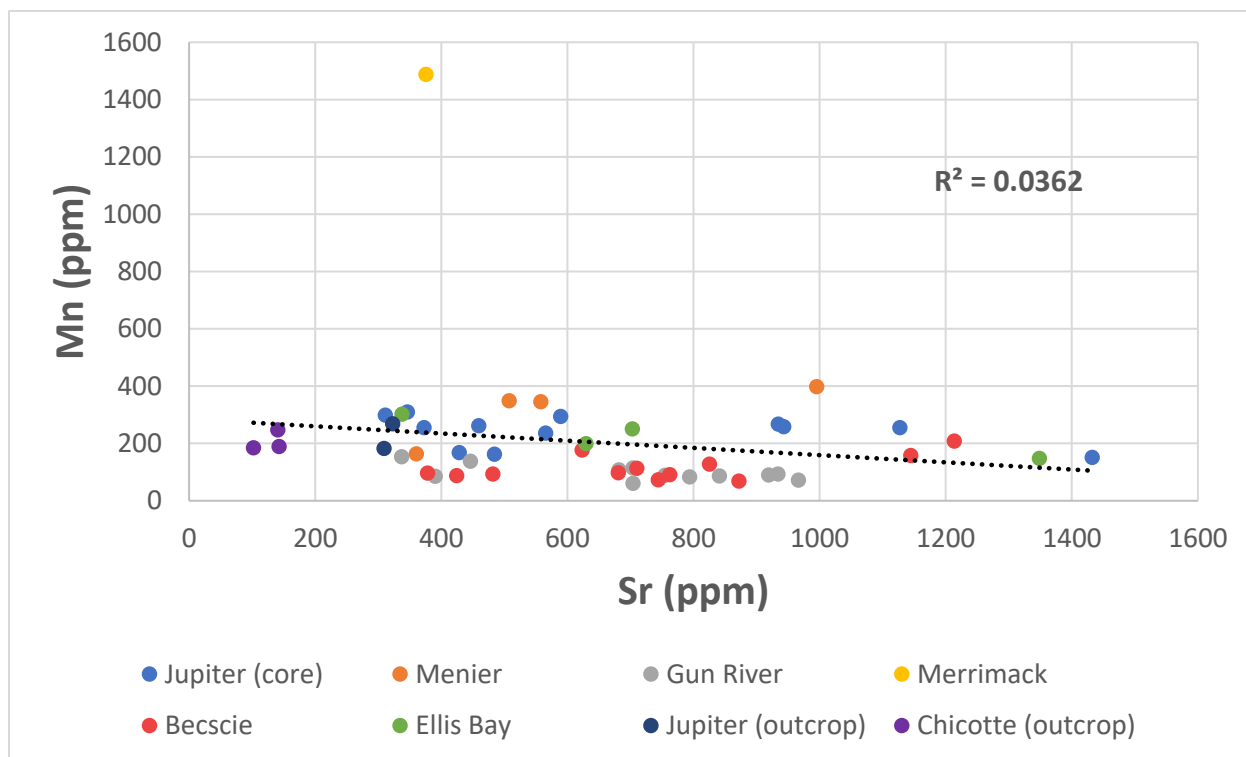


Figure 4.4: Cross-plot of Mn and Sr for core and outcrop samples. Data points are divided by formation.

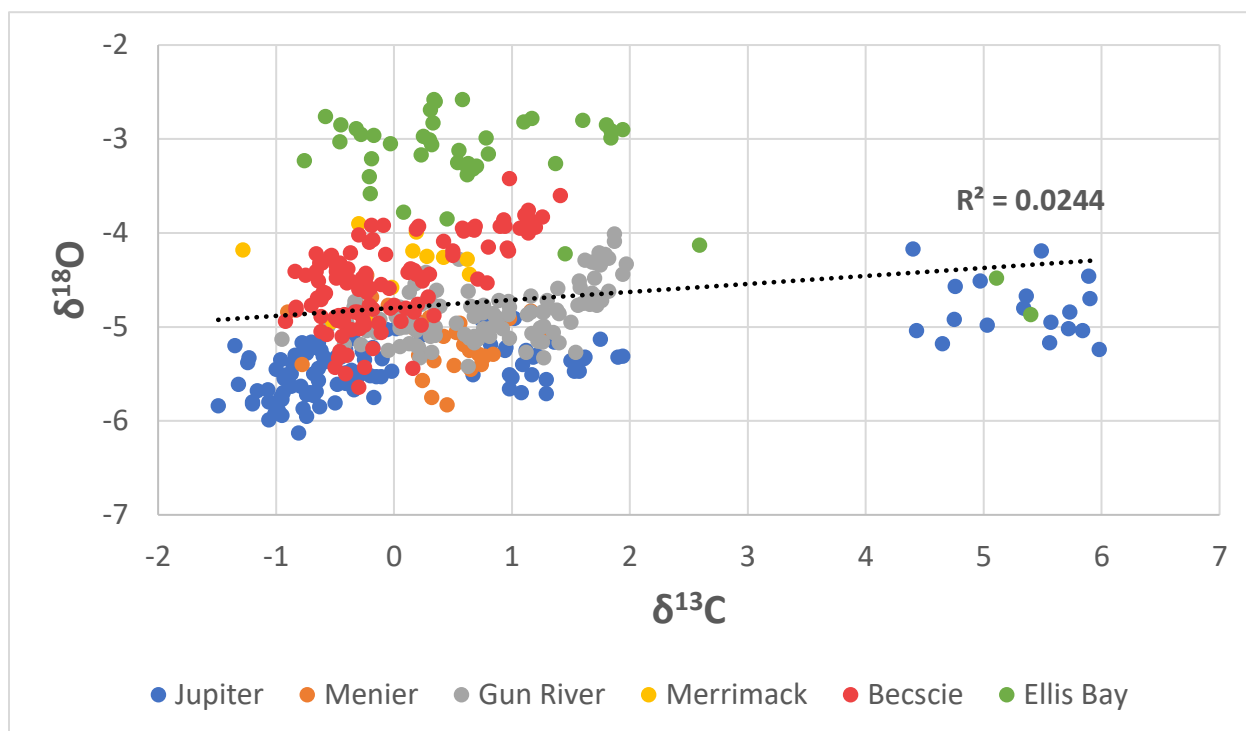


Figure 4.5: Cross-plots of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the MLM core. Data points are divided by formation.

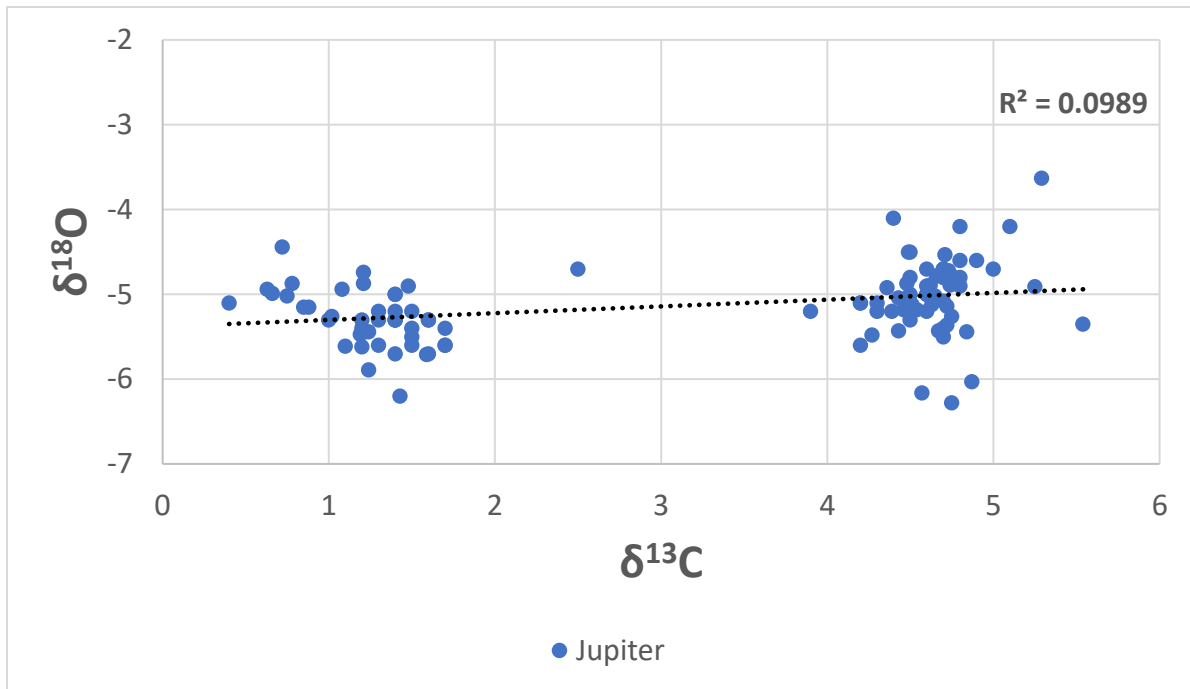


Figure 4.6: Cross-plots of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the Upper Aeronian Excursion in outcrop. Data points only span the Jupiter Formation.

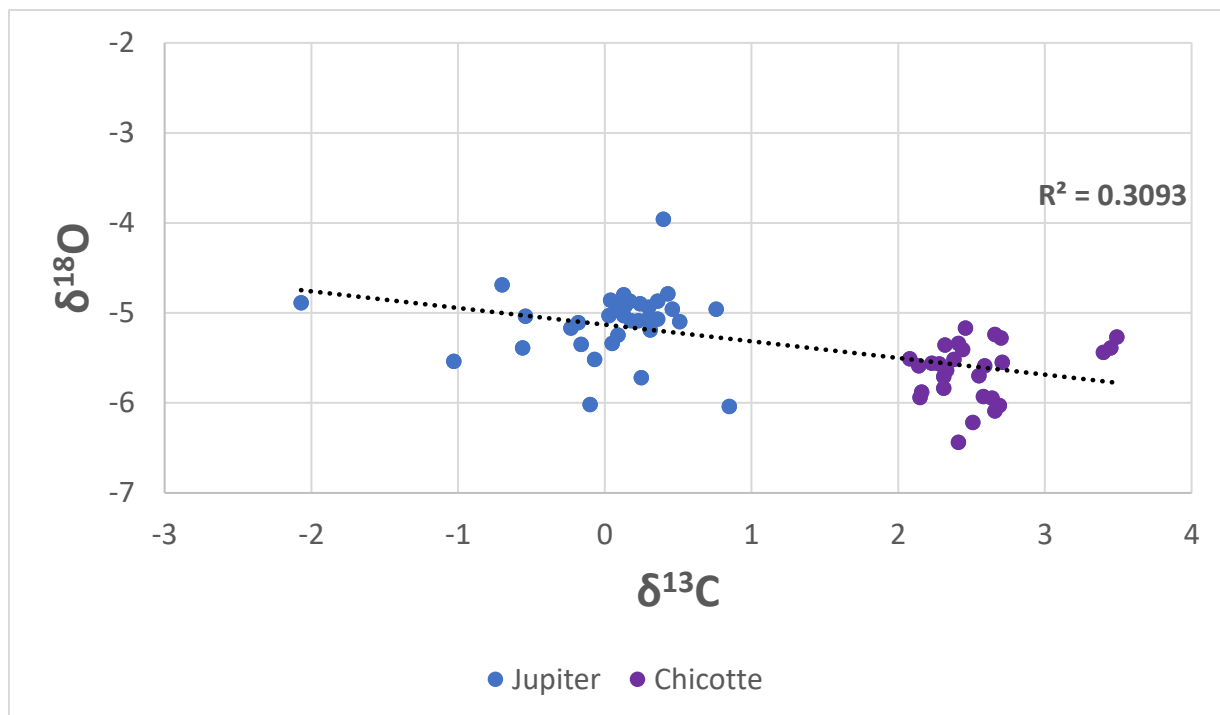


Figure 4.7: Cross-plots of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the Valgu Excursion in outcrop. Data points are divided by formation.

Chapter 5: Discussion

5.1 Chemostratigraphy

5.1.1 Preservation of the Isotopic Signal

In this study, fine micritic matrix was preferentially sampled for geochemical analysis and the preservation of the original isotopic signals were screened a number of ways. In core examination fine, primary sedimentary structures are well preserved, and no obvious diagenetic or neomorphic fabrics were identified. Furthermore, burrows and other biogenic structures are uncompacted and retain original fabrics, indicating cementation and lithification occurred early during burial. Petrographic examination of the Anticosti succession (*sensu* Mauviel, 2016; Daoust, 2017) confirms the matrix comprises aphanocrystalline calcite ($< 10\ \mu\text{m}$) and exhibits no neomorphic fabrics; furthermore, when thin sections were stained with Alizarin Red S and Potassium Ferricyanide, they stained pink suggesting little to no burial diagenesis (cf. Dickson, 1966). Conodont elements recovered from throughout the Silurian succession yield alteration indices of 1, indicating burial temperatures never exceeded $50^{\circ}\text{--}80^{\circ}\text{C}$, and that diagenetic stabilization likely occurred at shallow depths (cf. Uyeno and Barnes, 1983; Munnecke and Männik, 2009). Geochemical studies of various macrofossils indicate all major groups are well preserved and not diagenetically altered (e.g. Azmy *et al.*, 1998; Finnegan *et al.*, 2011), and visual examination of brachiopods and other shelly fauna indicate exquisite preservation as fine structures and internal layering are intact (Jin and Copper, 2000; among others). Additionally, the segments of the chemostratigraphic curves produced in this study (Fig. 4.3) exhibit similar patterns to coeval segments seen in other Anticosti studies (Azmy *et al.*,

1998; Munnecke and Männik, 2009; Mauviel and Desrochers, 2016; Daoust, 2017), and the four positive $\delta^{13}\text{C}$ excursions identified in the Hirnantian to Telychian succession are in agreement with global $\delta^{13}\text{C}$ curves established from multiple palaeocontinents (Ordovician- Bergström *et al.*, 2009; Silurian- Cramer *et al.*, 2011).

The covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in marine carbonates is often associated with diagenetic alteration (Lohmann, 1988; Marshall, 1992). Cross plots of isotopic data from this study (Figs. 4.5-4.7) yield R^2 values of 0.0244, 0.0989, and 0.3093 respectively, indicating no significant correlation. A subset of stable isotope samples was analysed for trace element geochemistry, particularly Mn and Sr, as their covariance is commonly attributed to diagenesis. A Mn/Sr cross plot (Fig. 4.4) displays a R^2 value of 0.0362, indicating a lack of correlation. The absence of significant correlation in both $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ and Mn vs. Sr suggests that the micritic samples used in this study were neither significantly affected by meteoric nor burial diagenesis but their induration was rather facilitated by an early cementation at, or near, the sea floor in a relatively closed marine system.

5.1.2 Upper Aeronian Excursion: Core vs Outcrop

When the $\delta^{13}\text{C}$ signal of the Upper AICE in core (average of 5.3‰) and outcrop (average of 4.6‰) are compared (Figs. 4.1 and 4.3), a magnitude difference of ~0.7‰ is observed. The core and outcrop localities are roughly 50 km apart, placing the outcrop on a relatively deeper, more basinward portion of the palaeoramp during deposition. Basinward isotopic gradients in $\delta^{13}\text{C}$ are well documented in the modern ocean (Patterson and Walter, 1994), and have been recorded in the geologic record (e.g. Panchuk *et al.*, 2005; Saltzman and Edwards, 2017); in

most cases a basinward increase in $\delta^{13}\text{C}$ values is observed, where the lowest $\delta^{13}\text{C}$ values are recorded near shore, increasing toward the open ocean. For example, in the modern setting, open ocean waters around the Great Bahama Bank record $\delta^{13}\text{C}$ values up to 4‰ heavier than the terrestrially influenced near shore waters of the Florida Bay (Patterson and Walter, 1994); in Mohawkian aged strata (Late Ordovician), coeval sediments across the Eastern United States document an isotopic gradient of ~4.5‰, where $\delta^{13}\text{C}$ values of -2.0‰ are recorded near the palaeoshore, and values up to +2.5‰ are recorded towards the basin centre (Panchuk *et al.*, 2005). Anticosti Island, however, appears to record a basinward decrease in $\delta^{13}\text{C}$ values. Basinward $\delta^{13}\text{C}$ decreases have been documented to occur during multiple Silurian positive isotopic carbon excursions and may be attributed to the development of a local isotopic gradient through enhanced carbonate weathering (Loydell, 2007). During a sea level lowstand, a greater area of carbonate rock would become exposed and subsequently weathered; this would in turn increase the amount of carbonate sediment in the riverine outflow and deliver a greater proportion of $\delta^{13}\text{C}$ enriched sediment to the ocean (Kump *et al.*, 1999; Melchin and Holmden, 2006a). Most of this $\delta^{13}\text{C}$ enriched sediment would be deposited relatively close to shore, and as a result shallower near shore carbonates will record a slightly enriched $\delta^{13}\text{C}$ signal when compared to those deposited in a more distal deeper water setting (Melchin and Holmden, 2006a). In addition to a basinward $\delta^{13}\text{C}$ gradient, a depth gradient is present in the ocean due to biological productivity. Photosynthesis only occurs in the photic zone, where the lighter ^{12}C is preferentially incorporated into organic matter, thus enriching surface waters in ^{13}C ; as organic matter sinks, this isotopically light carbon is delivered to the deep ocean, and through decomposition is reincorporated into the water column (Raven and Falkowski, 1999).

This process known as the “biological pump” creates an isotopic gradient where $\delta^{13}\text{C}$ values become more negative with increasing depth; the actual magnitude of this gradient, however, would be controlled by the primary productivity of the surface waters (Raven and Falkowski, 1999).

Ultimately the processes that cause isotopic gradients occur on a larger basinal scale (100's to 1000's of km), while the core and outcrop localities in this study are relatively proximal to each other, and both represent neritic carbonates. Determining the precise cause of the magnitude difference observed for the Upper AICE is out of the scope of this current study, but some consideration is pointing to the carbonate weathering hypothesis. Melchin and Holmden (2006b) predicted that a large positive $\delta^{13}\text{C}$ excursion should occur in the shelfal carbonates of Estonia and on Anticosti Island, stating, “a strong positive excursion (likely $>3\text{‰}$) should be seen in strata of the lower *S. sedgwickii* Zone in a carbonate platform setting that has continuous sedimentation and sampling through this interval.” Strata of this age are not preserved in Estonia due to an unconformity (Kaljo and Martma, 2000), but on Anticosti the Upper AICE does indeed have a large magnitude and occurs within the *S. sedgwickii* graptolite zone.

5.2 Controlling Factors on Silurian $\delta^{13}\text{C}$ Excursions

The suspected factors driving the positive $\delta^{13}\text{C}$ excursions during the Silurian will be presented below. Then, the integrated lithostratigraphic, cyclostratigraphic, and chemostratigraphic data from this study will be presented and discussed in the next section.

5.2.1 Facies and Sea Level Changes

Silurian positive $\delta^{13}\text{C}$ excursions coincide with significant sea level fluctuations and distinct facies changes. The onset of most excursions is commonly marked by a relative sea level fall and the development of an unconformity (Munnecke *et al.*, 2010). A well-recorded pattern of sea level change can be seen for the Ireviken, Mulde, and Lau excursions on the Swedish island of Gotland; a regression precedes each of these excursions, but peak $\delta^{13}\text{C}$ values are recorded during subsequent transgressions and highstands (Calner, 2008). In some cases, the precise timing between sea level changes and $\delta^{13}\text{C}$ excursions is, however, poorly constrained as different methods have been used to construct Silurian sea level curves (sequence stratigraphy, palaeocommunity analysis, $\delta^{18}\text{O}$ signal, tectonic subsidence); thus, many published sea level curves show conflicting patterns (Munnecke *et al.*, 2010).

The Silurian can be divided into eight periods of expanded reef growth and prolific carbonate production, each alternating with periods of widespread deposition of argillaceous sediments and diminished carbonate production (Brunton *et al.*, 1998; Munnecke *et al.*, 2003). The deposition of shale and argillaceous limestone precedes most $\delta^{13}\text{C}$ excursions, and the excursions occur during the periods of expanded carbonate production (Munnecke *et al.*, 2003; Cramer and Saltzman, 2007). Additionally, microbial carbonates such as oncolites and stromatolites, are commonly associated with $\delta^{13}\text{C}$ excursions (Munnecke *et al.*, 2010); microbial facies are most abundant during are the maximum recorded $\delta^{13}\text{C}$ values of the Ireviken, Mulde, and Lau excursions (Munnecke *et al.*, 2003; Calner, 2008). On Anticosti Island, the HICE is recorded within the microbial carbonate rich strata the upper Hirnantian Lafromboise reefs;

here the HICE is marked by a basal oncolite layer, and peak $\delta^{13}\text{C}$ values are concurrent with widespread calcimicrobial-metazoan buildups (Desrochers *et al.*, 2010).

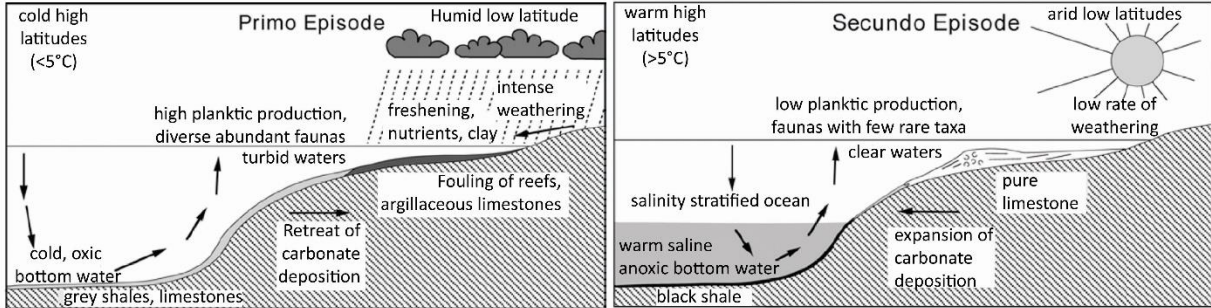
5.2.2 Biotic Events

Nearly all Silurian positive $\delta^{13}\text{C}$ excursions are associated with moderate scale biotic extinction events, especially affecting conodonts, graptolites, and trilobites (Munnecke *et al.*, 2010). Furthermore, hemipelagic organisms are more greatly affected than those living in shallower environments, suggesting the driving cause of an extinction began in the deep ocean and then expanded into shallow waters (Munnecke *et al.*, 2003). In the stratigraphic record the first extinction datum precedes the onset of an excursion, peak $\delta^{13}\text{C}$ values are typically observed within the interval of lowest biodiversity, and decreasing $\delta^{13}\text{C}$ values (or a return to background $\delta^{13}\text{C}$ levels) coincides with the recovery of biotic diversity (Calner, 2008). Positive $\delta^{13}\text{C}$ excursions and biotic events are likely not driving causes for one another, but instead are both effects of global scale climatic or oceanic events (Munnecke *et al.*, 2010).

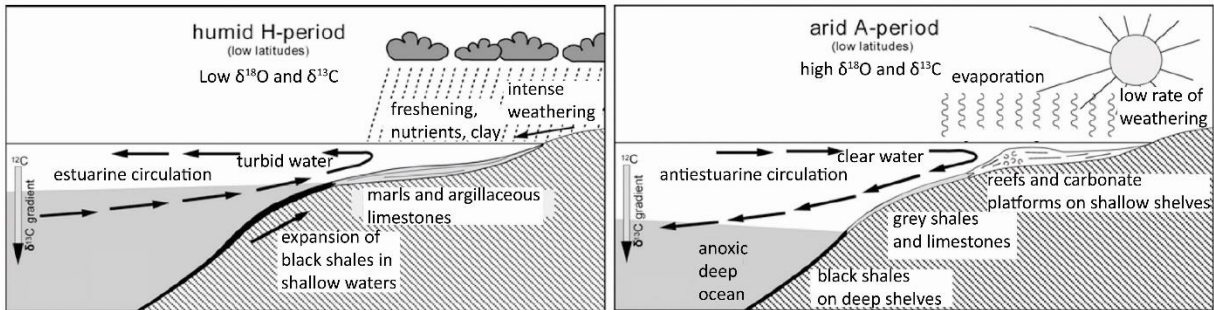
5.2.3 Climate Events and Volcanism

The climate of the Silurian was incredibly dynamic and characterized by frequent and significant change. The period begins with the Early Palaeozoic Icehouse, where three glacial maxima occur in the Llandovery, before transitioning to an extended greenhouse interval that lasted until the Mississippian (Frakes *et al.*, 1992; Page *et al.*, 2007; Munnecke *et al.*, 2010). First identified by Jeppsson (1990) through the investigation of temporal changes in lithology and conodont faunas in Gotland, the Silurian can be further divided into alternating climate states; Primo Episodes, or humid climate states, and Secudno Episodes, or arid climate states (Fig. 5.1).

Jeppsson (1990)



Bickert et al. (1997)



Cramer and Saltzman (2007)

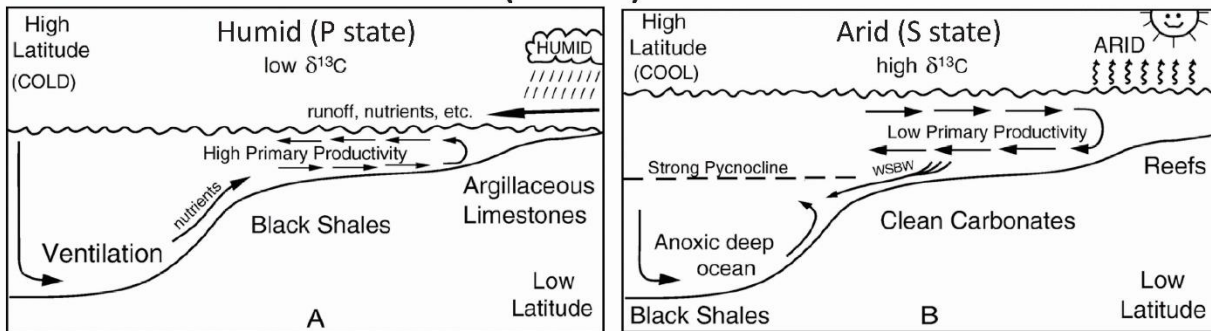


Figure 5.1: Comparison of Silurian climate models. Jeppsson (1990) proposed the first model, which was later modified by Bickert *et al.*, (1997); the Cramer and Saltzman model combines aspects from both the Jeppsson and Bickert models. See text for explanation. Note the Jeppsson and Bickert model diagrams are modified from Calner (2008).

The Jeppsson (1990) model fails to explain isotopic fluctuations in the Silurian and was later modified by Bickert *et al.* (1997) to account for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ excursions related to climate cycles (Fig. 5.1). In the Bickert model the Silurian time interval is divided into alternating humid and arid climate states, comparable to the Primo and Secundo episodes of Jeppsson (1990). The driving forces behind climate cycles and the details and precise application of these climate models are highly debated topics, and out of the scope of the current study; however, humid and arid climate states leave distinct lithological and geochemical fingerprints that are identifiable in the rock record. During humid climate states (Fig. 5.1) sea level is typically lower, continental weathering is expedited, and argillaceous limestones and shales are deposited in shallow waters with depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures (Bickert *et al.*, 1997; Brunton *et al.*, 1998; Cramer and Saltzman, 2005, 2007). Conversely, arid states (Fig. 5.1) are characterized by a higher sea level, depressed continental weathering, the expansion of carbonate platforms with widespread reef growth, and the deposition of clean carbonates with elevated $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signals (Bickert *et al.*, 1997; Brunton *et al.*, 1998; Cramer and Saltzman, 2005, 2007).

K-bentonites (volcanic ash beds) can be recognized throughout the Silurian, but in the Llandovery, volcanism was most active in the late Aeronian and early Telychian (cf. Huff, 2016). Concentrations of ash beds occur within the *S. sedgwickii* graptolite zone in Nova Scotia (Bergström *et al.*, 1997), the Appalachian Basin (Bergström *et al.*, 1998a), and at Dob's Lin in Scotland (Bergström *et al.*, 1998b); it is worth noting that this is the chronostratigraphic interval that contains the Upper AICE. Additionally, a significant (up to 115 cm thick) and regionally extensive ash bed known as the Osmundsberg K-bentonite bed, has been identified in stratigraphic sections throughout Baltoscandia and the British Isles (Bergström *et al.*, 1998b;

Inanli *et al.*, 2009); the Osmundsberg K-bentonite bed, which occurs in the *Sp. turriculatus* graptolite zone (early Telychian, between the Upper AICE and Valgu excursions), has not yet been traced to North America (Inanli *et al.*, 2009). In addition to impacting climate, volcanism releases isotopically light carbon into the atmosphere; negative $\delta^{13}\text{C}$ excursions may occur, but these excursions will be very short-lived (< 200 ky) and better recorded in the organic carbon ($\delta^{13}\text{C}_{\text{org}}$) record than the inorganic carbon ($\delta^{13}\text{C}_{\text{carb}}$) record (Kump and Arthur, 1999).

5.2.4 Oceanic State

Changes in oceanic state accompany the fluctuations between humid and arid climatic states in the Silurian (Fig. 5.1). Humid periods are characterized by estuarine circulation in shallow waters, and an oxygenated deep ocean, while arid periods are characterized by anti-estuarine circulation and stratified, anoxic bottom waters (Bickert *et al.*, 1997). Increased precipitation during humid periods increase riverine runoff, reducing salinity in shallow waters, and driving estuarine circulation patterns (Bickert *et al.*, 1997). Estuarine circulation results in the upwelling of nutrient rich bottom waters, and the subsequent ventilation of the deep ocean; this nutrient increase promotes primary productivity resulting in the deposition of organic rich shales in shallow waters (Bickert *et al.*, 1997; Cramer and Saltzman, 2005, 2007). During arid periods, evaporation was more prevalent in shallow waters, increasing salinity and driving anti-estuarine circulation patterns (Bickert *et al.*, 1997). This results in the downwelling of warm, saline, oxygenated surface waters to the deep ocean; when warm surface water reaches the cooler waters of the deep ocean, a pycnocline develops, preventing ventilation and creating an anoxic deep ocean (Bickert *et al.*, 1997; Cramer and Saltzman, 2005, 2007). Primary productivity is inhibited and $\delta^{13}\text{C}$ depleted organic matter is sequestered to the anoxic deep

ocean, resulting in a positive $\delta^{13}\text{C}$ excursion in shallow waters (Cramer and Saltzman, 2005, 2007).

5.2.5 Isotopic Signals

The Silurian $\delta^{13}\text{C}$ record is unique in Earth's history in both the frequency and magnitude of positive $\delta^{13}\text{C}$ excursions. Seven major positive $\delta^{13}\text{C}$ excursions occur within ~24 my during the Silurian, including three excursions (the Lower and Upper AICE and the Valgu) occurring within ~5 my during the Llandovery (Cramer *et al.*, 2011). No other geological Period had so many significant $\delta^{13}\text{C}$ excursions over a short time interval. The onset and termination of the Silurian $\delta^{13}\text{C}$ excursions typically display rapid climbing and declining limbs of their $\delta^{13}\text{C}$ values. The amplitude of these excursions is exceptionally large when compared to other Phanerozoic excursions, with three excursions (early Sheinwoodian Ireviken, late Ludfordian Lau, and late Pridoli Klonk excursions; see Fig. 2.4) recording $\delta^{13}\text{C}$ values exceeding 5‰. The late Ludfordian Lau excursion is the largest documented positive carbon excursion in the Phanerozoic, with $\delta^{13}\text{C}$ values averaging +8‰ globally and reaching peak values of up to +12‰ in Australia (Calner, 2008; Munnecke *et al.*, 2010; Melchin *et al.*, 2012).

The $\delta^{18}\text{O}$ record parallels the $\delta^{13}\text{C}$ record for most of the Silurian, and most positive $\delta^{13}\text{C}$ excursion are accompanied by a positive $\delta^{18}\text{O}$ excursion; thus, the factors that drive $\delta^{13}\text{C}$ trends and excursions are believed to also drive the $\delta^{18}\text{O}$ record (Munnecke *et al.*, 2003; Munnecke *et al.*, 2010). The Anticosti $\delta^{18}\text{O}$ signal and possible factors affecting it will be discussed in more detail in Chapter 5.4.

5.2.6 The Llandovery of Anticosti: Integrated Dataset

The integrated lithostratigraphic, cyclostratigraphic, and chemostratigraphic data from the MLM core display common trends that can be used to decipher the driving forces behind these enigmatic Silurian isotopic excursions (Fig. 5.2). First, the peaks of both $\delta^{13}\text{C}$ excursions occur within relatively clean limestones (TSF 2- dense lime mudstone), while underlying strata are shale rich; this lithology change is abrupt and coincides with the rising limb of each excursion. Second, both $\delta^{13}\text{C}$ excursions reach peak magnitudes near the maximum flooding zone of a low-order transgression and are preceded by an intermediate-order regression; additionally, a slight negative dip in $\delta^{13}\text{C}$ values is recorded in conjunction with this regression. Finally, a minor $\delta^{18}\text{O}$ excursion (increase of $\sim 1\text{‰}$) accompanies both $\delta^{13}\text{C}$ excursions. These lithology changes, sea level fluctuations, and isotopic signatures are interpreted to represent an arid climate state, and the Lower and Upper AICE are, hereby, interpreted to each have developed due to the transition from a humid to an arid climate state (cf. Bickert *et al.*, 1997; Cramer and Saltzman, 2005, 2007). However, the causes of these climate cycles are unclear (Munnecke *et al.*, 2010), and the determination of the mechanism that causes the $\delta^{13}\text{C}$ excursion is out of the scope of this study.

Figure 5.2: Integrated litho-, cyclo-, and chemostratigraphy of the MLM core. Excursions are highlighted in the chemostratigraphy column; as discussed in Chapter 4.3, the Lower AICE appears to comprise two smaller peaks.

Facies Assemblages



FA 1- Calcareous Shale



Lenticular Beds
FA 2- Mud Dominated Tempestites
Nodular Beds



FA 3- Mixed Muddy and Grainy Tempestites



FA 4- Grainy Dominated Tempestites

Time Specific Facies



TSF 1- Interbedded Argillaceous Lime
Mudstone and Calcareous Shale



TSF 2- Dense Lime Mudstone

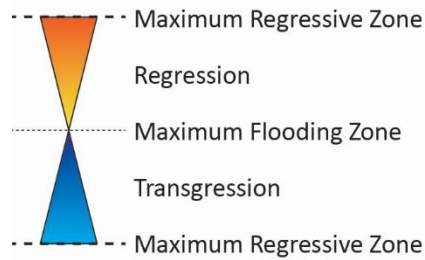


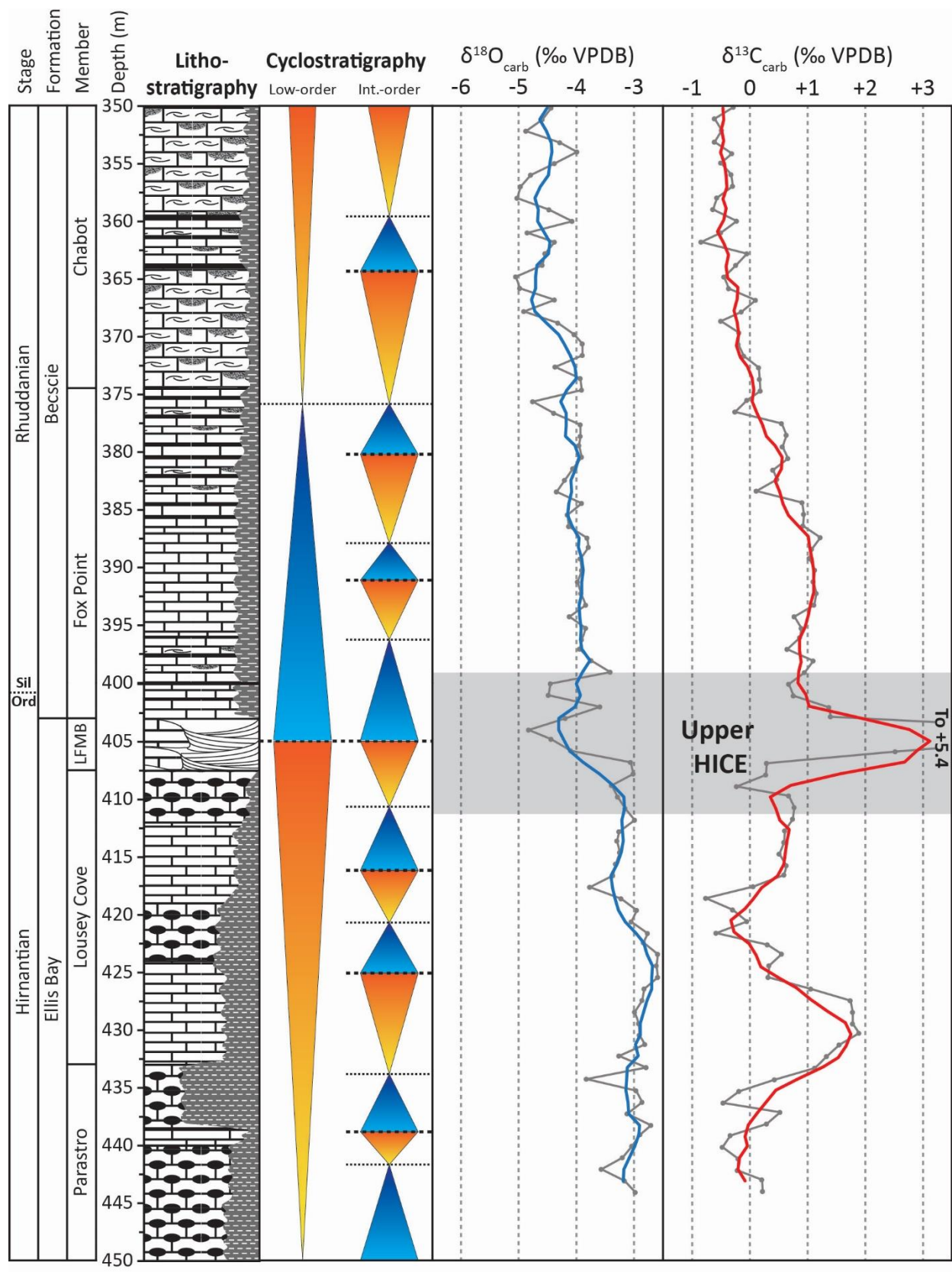
TSF 3A- Calcimicrobial-Coral Bioherms

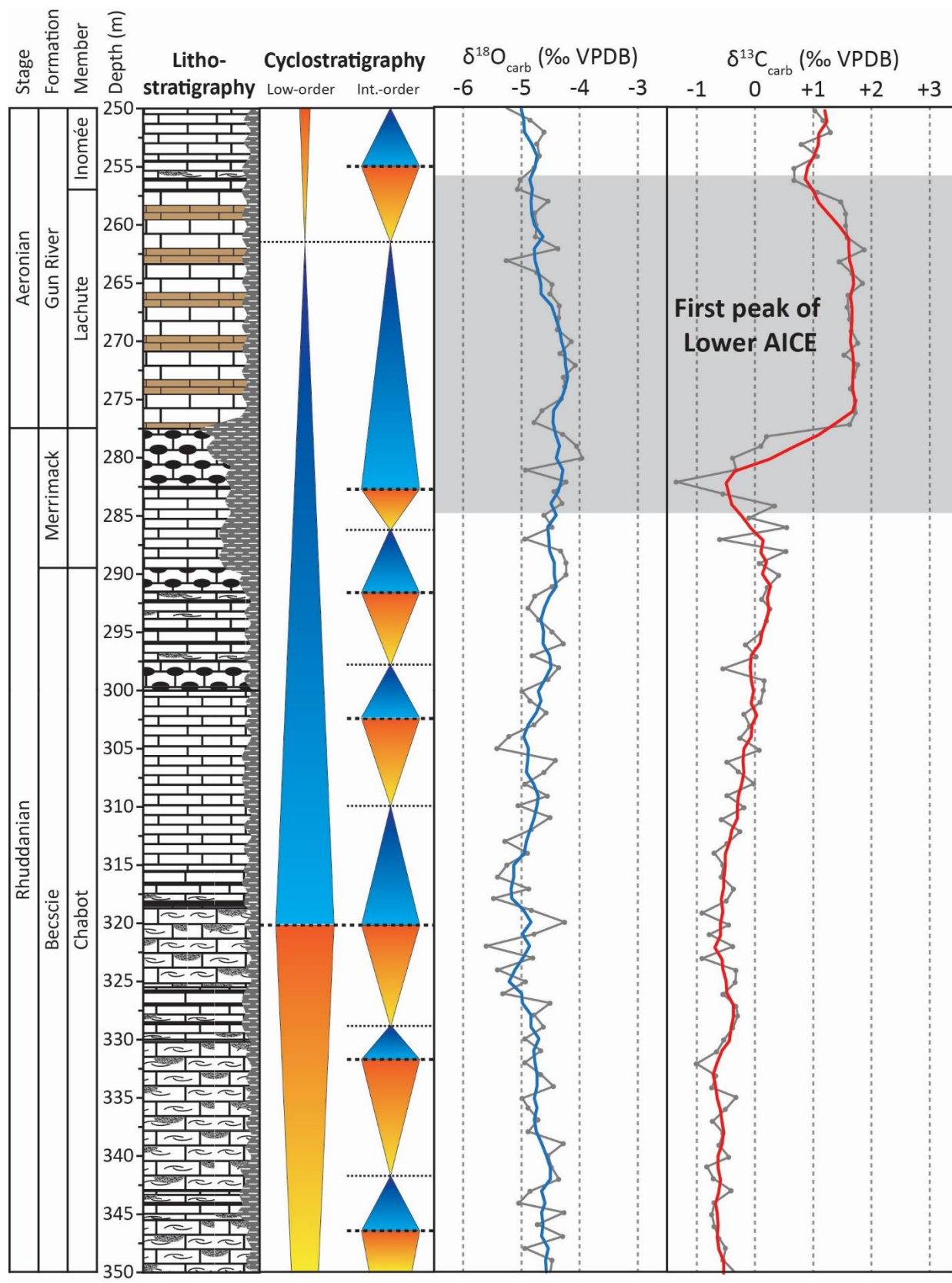


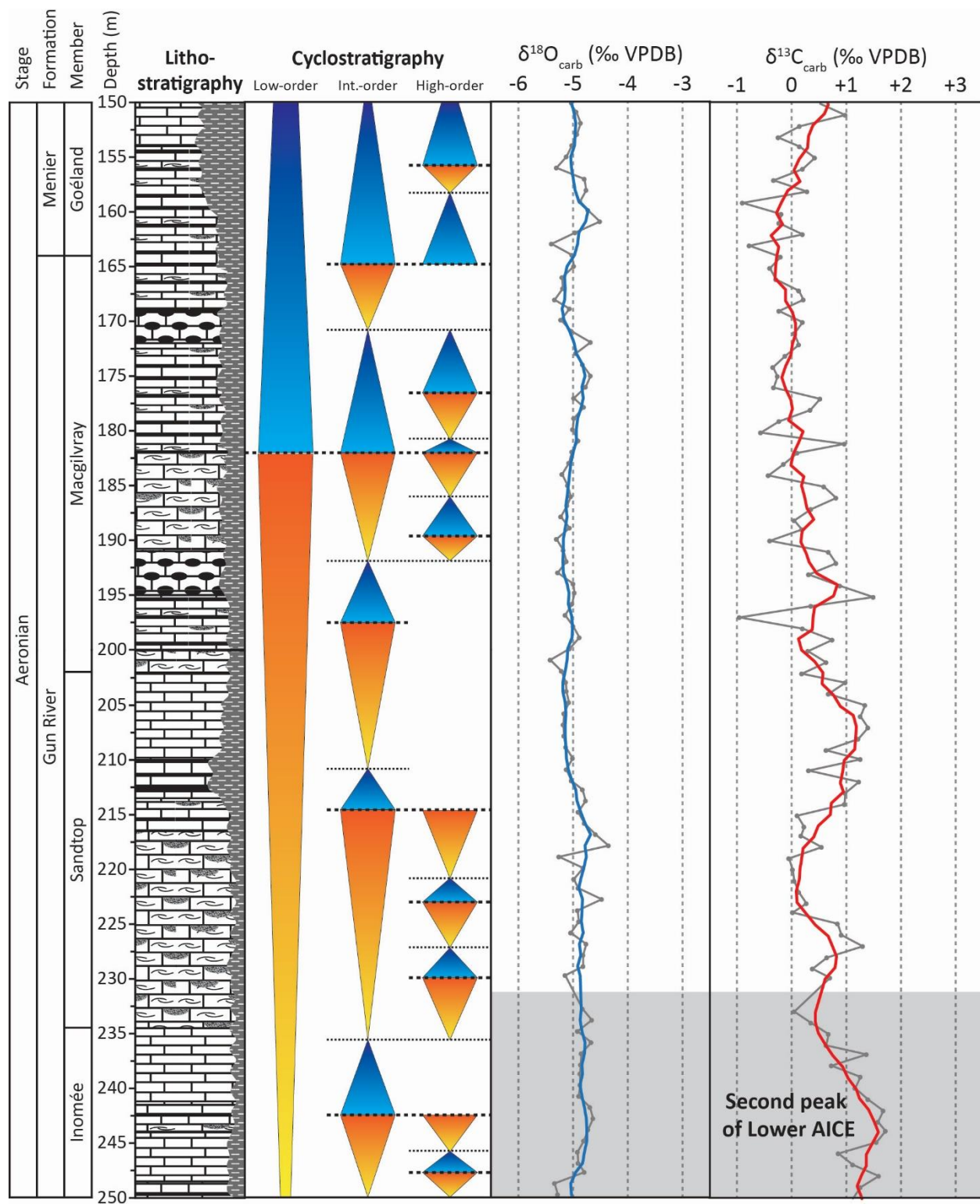
TSF 3B- Coral-Stromatoporoid Bioherms

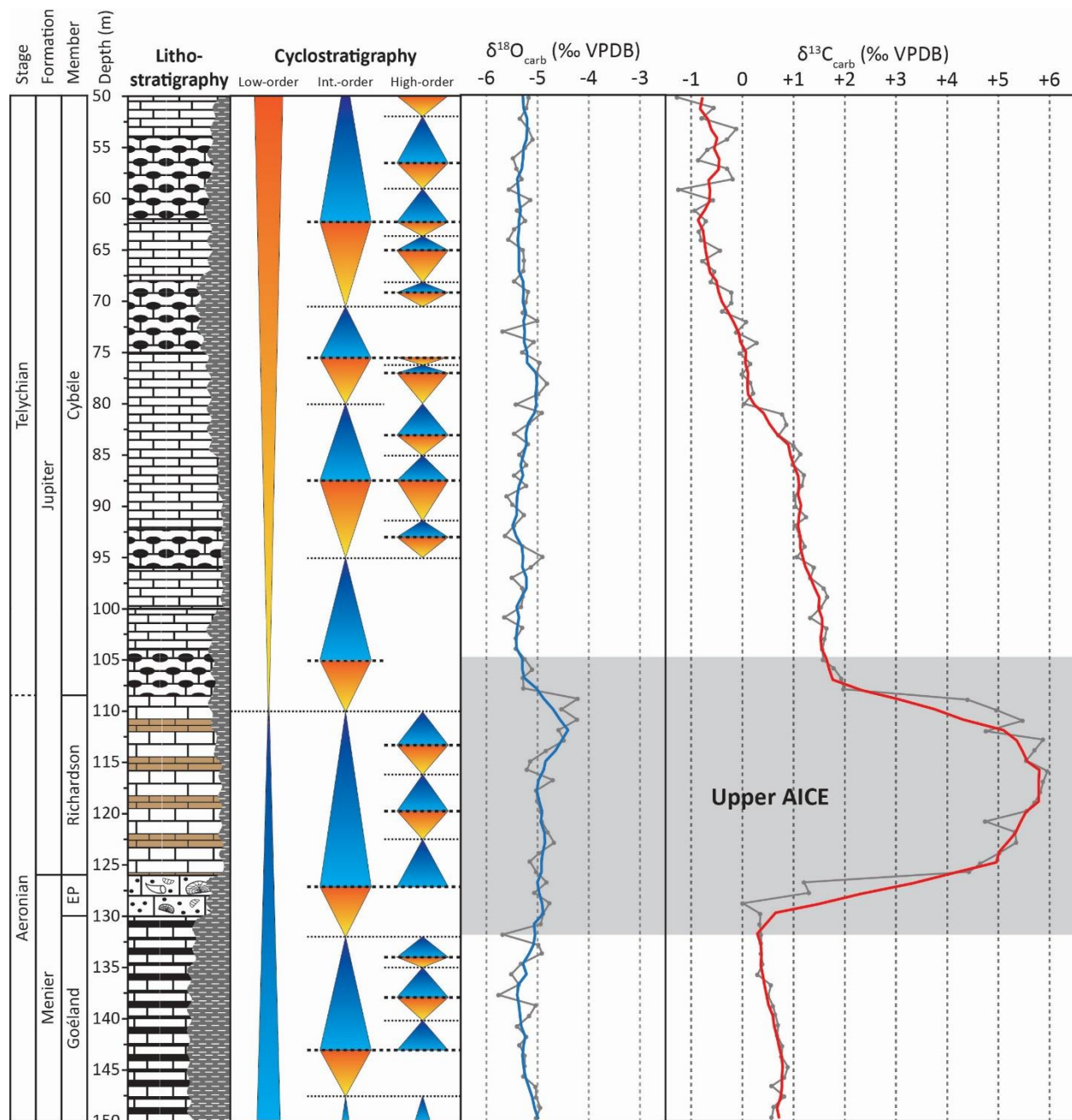
Cyclostratigraphy

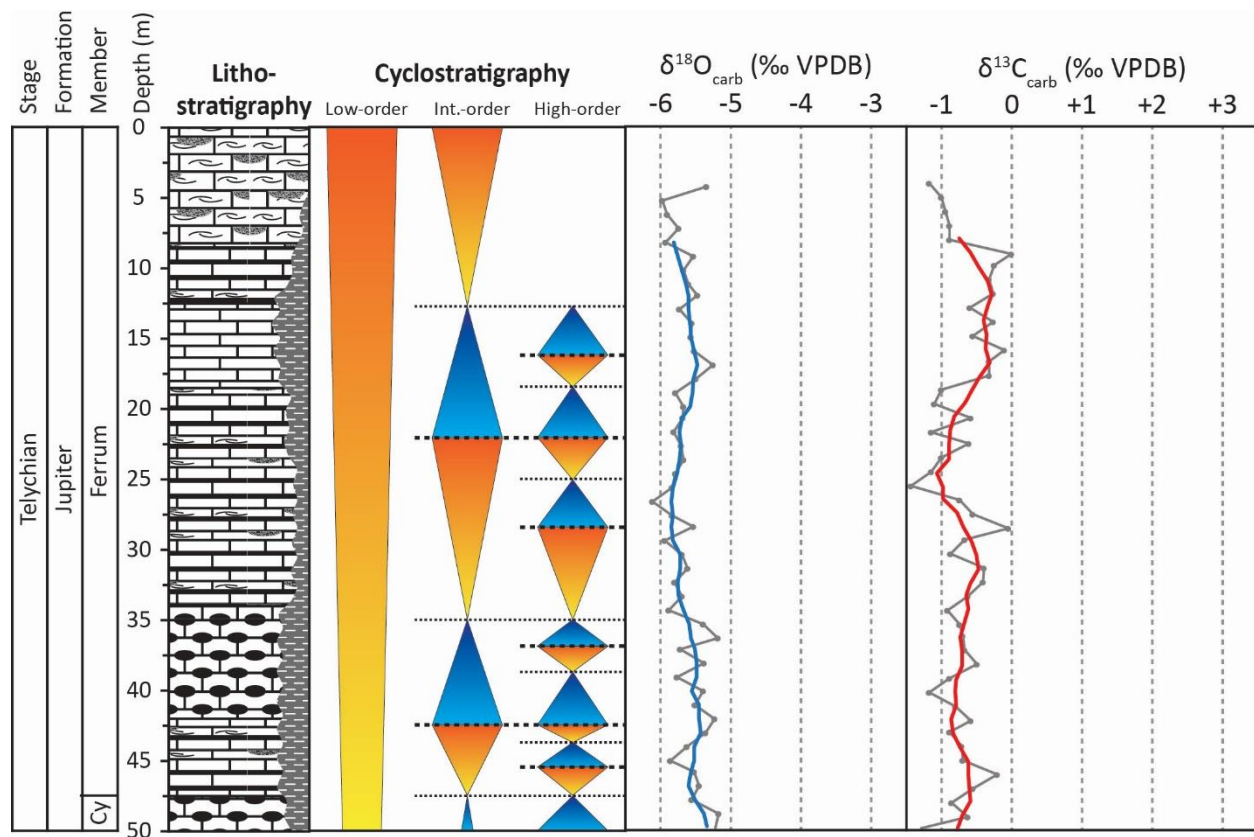












5.3 Global Chronostratigraphic Correlations during the Llandovery

Positive $\delta^{13}\text{C}$ excursions provide a distinct geochemical signature with immense potential for local, regional, and global scale stratigraphic correlations; these excursions alone, however, cannot be used for accurate temporal correlations. Through the integration of graptolite and conodont biostratigraphy with carbon isotope chemostratigraphy, a global chronostratigraphic framework has been established for the Silurian (Cramer *et al.*, 2011). This globally recognized chronostratigraphic framework allows for both stratigraphic and temporal correlation between carbonate strata worldwide that record $\delta^{13}\text{C}$ excursions.

Numerous $\delta^{13}\text{C}$ curves have been produced for the Llandovery from shallow water and deep water strata, recorded in either $\delta^{13}\text{C}_{\text{carb}}$ or $\delta^{13}\text{C}_{\text{org}}$, and from various localities and palaeobasins (Fig. 5.3). Many of these curves only document one or two $\delta^{13}\text{C}$ excursions, while some document none (Fig. 5.4); only two curves document all three Llandovery excursions (Fig. 5.4, curves 4 and 6). The $\delta^{13}\text{C}$ curve produced in this study (Figs. 4.3 and 5.4) from the Anticosti succession documents four consecutive $\delta^{13}\text{C}$ excursions; the upper Hirnantian isotopic carbon excursion (Upper HICE), the Lower and Upper Aeronian isotopic carbon excursions (Lower AICE and Upper AICE respectively), and the Valgu Excursion. In the following section the composite $\delta^{13}\text{C}$ curve from this study (Fig. 4.3) will be compared to previously published Llandovery $\delta^{13}\text{C}$ curves (Fig. 5.4). The Ordovician portion of the $\delta^{13}\text{C}$ curve is not the focus of this study and will only be briefly discussed here; for a more detailed discussion refer to Mauviel and Desrochers (2016).

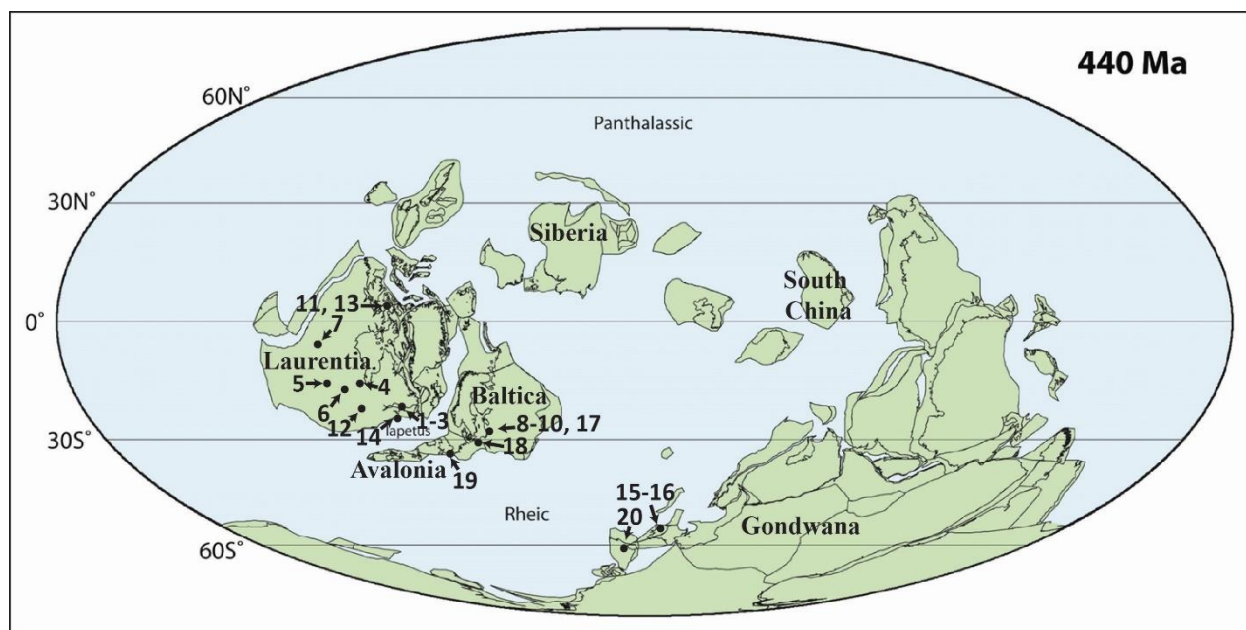
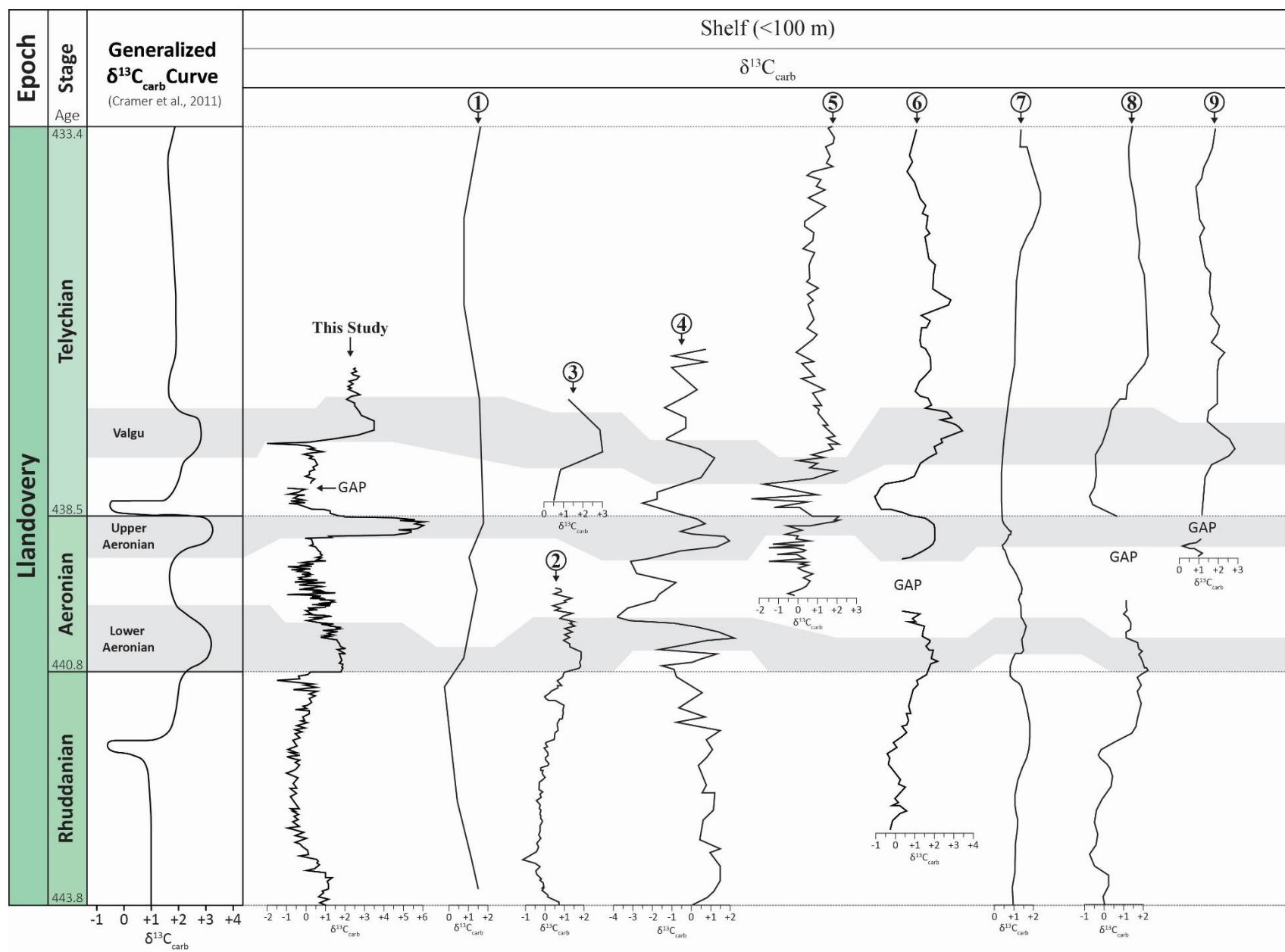
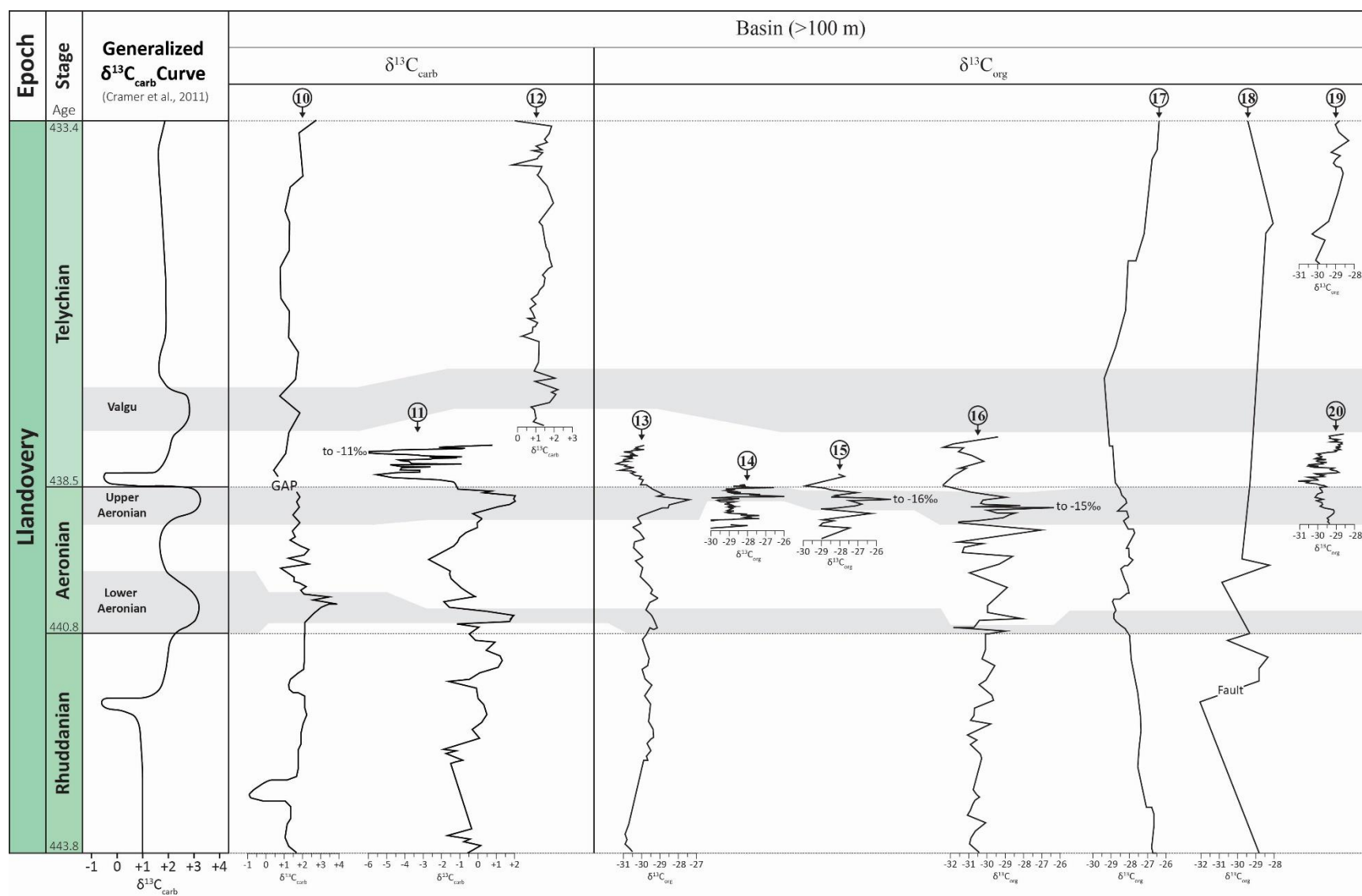


Figure 5.3: Global distribution of chemostratigraphic curves from figure 5.4 during the Rhuddanian. See figure 5.4 for sources (modified after Torsvik and Cocks, 2013).

Figure 5.4 (next two pages): Previously published isotopic carbon chemostratigraphic curves covering the Llandovery. All curves are rescaled vertically according to time, and horizontally according to magnitude. Sources for curves (section thickness is in brackets): 1: Azmy *et al.*, (1998), Anticosti Island (550 m); 2: Daoust (2017), Anticosti Island (250 m); 3: Munnecke and Männik (2009), Anticosti Island (30 m); 4: Bancroft *et al.*, (2015), Moose River Basin (150 m); 5: McAdams *et al.*, (2017), Iowa Basin (40 m); 6: McLaughlin *et al.*, (2013), Subsurface Wisconsin (150 m); 7: Gouldey *et al.*, (2010), Nevada (300 m); 8: Kaljo and Martma (2000), Estonia, Kirikukula Core (105 m); 9: Kaljo *et al.*, (2003), Estonia, Viki Core (80 m); 10: Kaljo *et al.*, (2003), Estonia, Ruhnu Core (250 m); 11: Melchin and Holmden (2006b), Canadian Arctic (110 m); 12: McLaughlin *et al.*, (2012), Appalachian Basin (40 m); 13: Melchin and Holmden (2006b), Canadian Arctic (110 m); 14: Melchin *et al.*, (2015), Nova Scotia (150 m); 15: Štorch and Frýda (2012), Prague Synform (9 m); 16: Frýda and Štorch (2014), Prague Synform, (16 m); 17: Gouldey *et al.*, (2010), Estonia, Ilka Core (240 m); 18: Sullivan *et al.*, (2018), Poland, Zwierzyniec-1 Core (30 m); 19: Loydell and Frýda (2007), Wales, (75 m); 20: Loydell *et al.*, (2015), Spain (12 m).





In the Hirnantian upper Ellis Bay Formation, a slight increase in $\delta^{13}\text{C}$ values is recorded in the Lousy Cove Member, and the Upper HICE is largely constrained to the Lafromboise Member (Fig. 4.3); the Upper HICE is similar in magnitude to previous outcrop based studies of Anticosti Island (see Figure 4 in Mauviel and Desrochers, 2016), and in the La Loutre #1 core (Daoust, 2017). Although it should be noted that the Upper HICE is stratigraphically thinner in this study, likely due to the drill core piercing the Lafromboise inter-reef facies rather than the thicker reef cores. The Ellis Bay Formation is capped by a regional scale erosional surface, which exposed resistant reef cores and partially removed inter-reef facies and reef flank strata, presumably removing part of the Upper HICE in the MLM core (cf. Desrochers *et al.*, 2010).

No positive $\delta^{13}\text{C}$ excursions are present in the Rhuddanian, and most curves record minor short term $\delta^{13}\text{C}$ fluctuations superimposed on a long term arcuate trend (Fig. 5.4). A distinct negative $\delta^{13}\text{C}$ excursion present on the generalized global $\delta^{13}\text{C}$ curve is absent in many sections, and only appears to be recorded in subsurface Wisconsin (Fig. 5.4, curve #6), Estonia (Fig. 5.4, curve #8 and 10), and in the Canadian Arctic (Fig. 5.4, curve #11). On Anticosti Island a negative $\delta^{13}\text{C}$ excursion is recorded within the Merrimack Formation immediately preceding the Rhuddanian-Aeronian boundary (Fig. 5.4, this study and curves 1 and 2).

The Lower AICE was previously documented in $\delta^{13}\text{C}_{\text{carb}}$ from shallow water facies (Fig. 5.4, curves 2, 4, 6 and 8) on Anticosti Island (Daoust, 2017), in the Moose River Basin (Bancroft *et al.*, 2015), in subsurface Wisconsin (McLaughlin *et al.*, 2013), and in Estonia (Kaljo and Martma, 2000), as well as in $\delta^{13}\text{C}_{\text{carb}}$ from deep water facies (Fig. 5.4, curves 10 and 11) in Estonia (Kaljo *et al.*, 2003) and the Canadian Arctic (Melchin and Holmden, 2006b). The stratigraphic motif and magnitude of the excursion are comparable in all of these curves, with

each recording an increase of roughly 1.5-2‰ from background $\delta^{13}\text{C}$ values; however, the magnitude is slightly higher in the Moose River Basin (Fig. 5.4, curve #4) and slightly lower in the Kirikukula core in Estonia (Fig. 5.4, curve #8). Additionally, the Lower AICE was recorded from deep water facies in $\delta^{13}\text{C}_{\text{org}}$ (Fig. 5.4, curves 13 and 16), in the Canadian Arctic (Melchin and Holmden, 2006b) and the Czech Republic (Frýda and Štorch 2014), where both curves record a peak excursion of roughly -28.5‰, or an increase of ~1‰ from background $\delta^{13}\text{C}$ values. On Anticosti Island, the Lower AICE recorded in this study (from the MLM core) is comparable in magnitude and stratigraphic occurrence to the excursion in the La Loutre #1 core (Daoust, 2017). In both cores the Lower AICE has a peak magnitude of approximately +2‰, occurs within the lowermost Gun River Formation, and is preceded by a negative spike in $\delta^{13}\text{C}$ values within the Merrimack Formation, but the excursion appears to be better defined in the MLM core. In the MLM core, the excursion is ~40 m thick and is characterized by an initial “blocky” peak separated from a secondary peak by a slight negative shift in $\delta^{13}\text{C}$ values (Fig. 5.4). In the La Loutre #1 core the initial “blocky” peak is present, but the upper boundary of the excursion is not obvious and is characterized by a series of smaller peaks (Fig. 5.4, curve #2); depending on where the upper boundary is placed, the excursion may be between 20 to 45 m thick in this core.

Although not officially recognized, the minor $\delta^{13}\text{C}$ excursion (approximately +1‰) present between 215-198 m depth (Fig. 4.3) in the MLM core may be recorded in other published $\delta^{13}\text{C}$ curves (Fig. 5.5). Minor excursions with similar magnitudes and located at similar stratigraphic levels (relative to the Lower and/or Upper AICE) are present at ~25m depth in the La Loutre #1 core on Anticosti Island (cf. Daoust, 2017), within the Ekwan River Formation in the

Moose River Basin (cf. Bancroft *et al.*, 2015), at ~520 m depth in the Ruhnu core in Estonia (cf. Kaljo *et al.*, 2003), and within the Lower Hopkinton Formation of the Iowa Basin, where a minor excursion was recognized by Waid and Cramer (2017). However, this correlation remains speculative as accurate correlation of this minor excursion is impossible without precise biostratigraphic control.

As the Upper AICE coincides with the *S. sedgwickii* graptolite zone, the excursion has been recorded in numerous studies in $\delta^{13}\text{C}_{\text{org}}$ from deep water graptolitic shales (Fig. 5.4, curves 13-16); in the Canadian Arctic (Melchin and Holmden, 2006b), Nova Scotia (Melchin *et al.*, 2015), and in the Czech Republic (Štorch and Frýda, 2012; Frýda and Štorch, 2014) the excursion has a peak magnitude at roughly -26‰; increasing ~4‰ from background values. Additionally the Upper AICE has been recorded in $\delta^{13}\text{C}_{\text{carb}}$ from shallow water facies (Fig. 5.4, curves 4-6) in the Moose River Basin (Bancroft *et al.*, 2015), the Iowa Basin (McAdams *et al.*, 2017; Waid and Cramer, 2017), and subsurface Wisconsin (McLaughlin *et al.*, 2013), as well as deep water facies (Fig. 5.4, curve #11) in the Canadian Arctic (Melchin and Holmden, 2006b); each of these curves record peak $\delta^{13}\text{C}$ values of +2‰ to +3‰, with a maximum increase of ~4‰ from background $\delta^{13}\text{C}$ values. In this study, the Upper AICE reaches peak $\delta^{13}\text{C}$ values of nearly +6‰ (or an increase of ~5.5‰ from background values). Not only is this the first time the Upper AICE has been recorded on Anticosti Island, but this the highest magnitude ever documented for the Upper AICE across all palaeocontinents. Despite the magnitude differences, the Upper AICE in this study has a similar stratigraphic motif to other published $\delta^{13}\text{C}$ curves. In all sections the onset and end of the excursion are relatively abrupt and following the end of the excursion a

protracted period of low $\delta^{13}\text{C}$ values extends into the early Telychian (Fig. 5.4, curves, 4-6, 11, 13-16).

The Valgu Excursion was previously documented in $\delta^{13}\text{C}_{\text{carb}}$ from shallow water facies on Anticosti Island (Munnecke and Männik, 2009), the Moose River Basin (Bancroft *et al.*, 2015), the Iowa Basin (McAdams *et al.*, 2017; Waid and Cramer, 2017), and subsurface Wisconsin (McLaughlin *et al.*, 2013), deep water facies in the Appalachian Basin (McLaughlin *et al.*, 2012; Sullivan *et al.*, 2016), and in both shallow and deep water facies in Estonia (Kaljo *et al.*, 2003; Munnecke and Männik, 2009); see Figure 5.4, curves 3-6, 9, 10, 12. Most of these curves record peak values similar in magnitude to this study, where $\delta^{13}\text{C}$ increases roughly +3‰ from background values; curves from Estonia (Fig. 5.4, #9 and 10) and the Appalachian Basin (Fig. 5.4, #12) record a slightly lower magnitude, and only increase +2‰ from background $\delta^{13}\text{C}$ values. Curves produced from Estonia also demonstrate intrabasin variability as the Valgu Excursion is absent in the Kirikukula core (Fig. 5.4, curve #8) but is present in multiple other cores (Fig. 5.4; Viki core, curve #9; Ruhnu core, curve #10). On Anticosti Island, the Valgu Excursion as recorded in this study is similar in magnitude and stratigraphic occurrence to the curve from Munnecke and Männik (2009). In both, the Valgu excursion occurs within the lower to middle Chicotte Formation and reaches peak values of 3-3.5‰ (Fig. 5.4, this study and curve #3), but the $\delta^{13}\text{C}$ curve from this study has a greatly improved sampling resolution.

Sequential Aeronian (Lower and Upper AICE) and Valgu excursions are only documented in the Wisconsin subsurface (McLaughlin *et al.*, 2013), the Moose River Basin (Bancroft *et al.*, 2015), and Anticosti Island (this study). The Llandovery portion of the Wisconsin and Moose River Basin $\delta^{13}\text{C}$ curves each cover ~150 m of strata, while the Anticosti curve covers ~450 m of

strata. Lithologically, both the Wisconsin and Moose River Basin sections comprise pervasively dolomitized strata; while the $\delta^{13}\text{C}$ signal is robust and not significantly altered during diagenesis, the $\delta^{18}\text{O}$ signal is susceptible to alteration and thus the $\delta^{18}\text{O}$ values in both these sections has likely been reset (cf. Banner and Hanson, 1990). Conversely, the Anticosti succession is minimally affected by meteoric and burial diagenesis and appears to record relatively pristine $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signals (see Chapter 5.1). Additionally, both the Wisconsin and Moose River Basin sections are somewhat condensed, and the Wisconsin section contains multiple significant depositional hiatuses; the Anticosti succession contains no significant regional unconformity, and the gap in data in Figure 4.3 reflects an unsampled stratigraphic interval between core and outcrop. The Lower Silurian of Anticosti Island appears to contain the thickest, most complete, and best-preserved successions of the Llandovery $\delta^{13}\text{C}$ record in the world. A carbonate succession as expanded and pristine as Anticosti provides a unique and invaluable resource for future study of the isotopic carbon record, and for the investigation into the causes and effects of major $\delta^{13}\text{C}$ excursions.

5.4 The Anticosti $\delta^{18}\text{O}$ Signal

As discussed in Chapter 4.3, three scales of $\delta^{18}\text{O}$ trends can be recognized within the studied succession; a long-term decline from -3‰ in the Ellis Bay Formation to -6‰ in the Chicotte Formation, intermediate-scale fluctuations with magnitudes of 1.0-2.5‰, and high-frequency fluctuations recording complex but repetitive shifts 0.5-1.0‰ in magnitude (Fig. 4.3).

The $\delta^{18}\text{O}$ signal is primarily affected by temperature, global ice volume, and salinity, and is commonly used to track glacial and interglacial periods; preferential evaporation and

accumulation of isotopically lighter ^{16}O in ice sheets will result in higher $\delta^{18}\text{O}$ signals being recorded during glacial advance, and lower $\delta^{18}\text{O}$ signals during glacial retreat (Grossman, 2012). The long-term decline and intermediate-scale fluctuations in $\delta^{18}\text{O}$ values in the Anticosti record (Fig. 4.3) likely reflect the protracted glaciation of Gondwana during the Late Ordovician and early Silurian. Glaciation peaked in the Hirnantian (Munnecke *et al.*, 2010), and glacial tillites identified in the Amazonas, Parnaíba, and Peru-Bolivia basins in South America, record additional periods of glacial advance in the early Aeronian, late Aeronian, and late Telychian (Caputo, 1998; Díaz-Martínez and Grahn, 2007). Additionally, climate fluctuations would influence the long-term and intermediate-scale trends in the $\delta^{18}\text{O}$ record. Enhanced evaporation during an arid period would preferentially remove ^{16}O and increase sea water salinity, resulting in a more enriched $\delta^{18}\text{O}$ signal (Bickert *et al.*, 1997). Conversely, during a humid period enhanced precipitation would deliver ^{16}O into the system and decrease sea water salinity, resulting in a lower $\delta^{18}\text{O}$ signal (Bickert *et al.*, 1997). High-frequency fluctuations are more difficult to interpret but are similar in magnitude and cyclic pattern to the Pleistocene $\delta^{18}\text{O}$ curve, which records glacioeustatic changes influenced by astronomical forcing (Lisiecki and Raymo, 2005). In previous studies of Anticosti, high-frequency $\delta^{18}\text{O}$ fluctuations loosely correlate with metre-scale transgressive-regressive cycles and correlate well with decametre-scale transgressive-regressive cycles, reinforcing the interpretation of astronomical forcing as a driving factor of cyclicity (*sensu* Mauviel, 2016; Daoust, 2017). A finer sampling interval (50 cm or less) was, however, required to interpret the smaller metre-scale transgressive-regressive cycles; thus, no clear correlation between high-frequency $\delta^{18}\text{O}$ fluctuations and palaeobathymetric interpretations deduced from our facies analysis could be made.

Chapter 6: Conclusion

In this study an integrated lithostratigraphic, cyclostratigraphic, and chemostratigraphic analysis was completed for the upper Hirnantian to lower Telychian succession of Anticosti Island. A portion (446 m) of a recent stratigraphic drill core and ~120 m of outcrop from three sections in the south-central part of the island were investigated, corresponding to the Ellis Bay, Becscie, Merrimack, Gun River, Menier, and Jupiter formations in core and the Jupiter and Chicotte formations in outcrop.

A common assemblage of rock types was identified across the upper Hirnantian to lower Telychian portion of the Martin La Mer core, representing deposition below fairweather wave base on a mid to outer carbonate ramp under the influence of frequent storm events. These common rock types were grouped into four facies assemblages (FA) and three time-specific facies (TSF); FA 1- calcareous shale, FA 2- mud dominated tempestites, FA 3- mixed muddy/grainy tempestites, FA 4- grain dominated tempestites, TSF 1- interbedded argillaceous lime mudstone and calcareous shale, TSF 2- dense lime mudstone, and TSF 3- reef limestone. Three orders of transgressive-regressive cycles were identified in the studied succession; low-order (>75 m), intermediate-order (10-25 m), and high-order (2-10 m). Three and a half low-order cycles were identified, with 6-8 intermediate-order cycles present in each low-order cycle, and an average of 3-5 high-order cycles present in each intermediate-order cycle.

The high resolution $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves produced in this study comprise a total of 443 data points from the Martin La Mer core, supplemented by 168 data points from outcrop. Four positive $\delta^{13}\text{C}$ excursions can be recognized in the studied succession; the upper Hirnantian

isotopic carbon excursion (+5‰), the Lower Aeronian isotopic carbon excursion (+2‰), the Upper Aeronian isotopic carbon excursions (+6‰), and the Valgu Excursion (+3.5‰); the Hirnantian and Lower Aeronian excursions were recorded in core, the Upper Aeronian was recorded in core and outcrop, and the Valgu Excursion was recorded at two localities in outcrop. Three superimposed scales of $\delta^{18}\text{O}$ trends were recognized; a long-term decline from -3‰ to -6‰ across the entire succession, intermediate-scale fluctuations with magnitudes of 1.0-2.5‰, and high-frequency fluctuations recording cyclical shifts 0.5-1.0‰ in magnitude. Changes in lithology, sea level, and isotopic signals lead to the interpretation that Silurian climate cycles are the driving force behind positive $\delta^{13}\text{C}$ excursions in the Llandovery, where the excursions occur following the transition from a humid to an arid climate state. The causes of these climate fluctuations and the precise mechanism of the excursions however, remain enigmatic. Long-term and intermediate-scale trends in $\delta^{18}\text{O}$ values are likely controlled by glacial advance and retreat in the Late Ordovician and early Silurian, with a secondary influence of changing climate state; high-frequency fluctuations are more difficult to interpret but may record an astronomical forcing signal.

Anticosti Island appears to contain the thickest, most complete, and best-preserved successions of the upper Hirnantian and Llandovery isotopic carbon record in the world. Most coeval successions contain significant depositional hiatuses or are diagenetically altered, and no other section in the world records sequential Hirnantian, Lower Aeronian, Upper Aeronian, and Valgu excursions. Additionally, with peak values of +6‰, Anticosti Island records the highest magnitude ever documented for the Upper Aeronian excursion. Historically the Llandovery remains the least understood and most understudied epoch of the Silurian, but in recent years

this trend is changing. Many other Llandovery studies only focus on one aspect of stratigraphy (i.e. only detailing conodont biostratigraphy or only discussing $\delta^{13}\text{C}$ chemostratigraphy); this is one of the first studies to integrate high resolution chemostratigraphy into a lithostratigraphic and cyclostratigraphic framework. This new high resolution integrated stratigraphic framework will be invaluable for future work on the Llandovery, including investigation into the causes of climate fluctuations, the driving forces behind positive $\delta^{13}\text{C}$ excursions, and the development of novel isotope systems.

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Appendices:

Appendix A: Stable isotope data from outcrops.

Brick Canyon							
Sample	From Datum		$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Latitude	Longitude	GPS Note
	(m)	Formation	(‰)	(‰)			
BC-001	0	Jupiter	0.87	-5.32	49 22 32.5N	63 24 1.3W	
BC-002	1	Chicotte	2.7	-5.28			
BC-003	2	Chicotte	3.4	-5.44			
BC-004	3	Chicotte	3.49	-5.27			
BC-005	4	Chicotte	3.45	-5.39			
BC-006	5	Chicotte	2.71	-5.55			
BC-007	6	Chicotte	2.66	-5.24			
BC-008	7	Chicotte	2.46	-5.17			
BC-009	8	Chicotte	2.44	-5.41			
BC-010	9	Chicotte	2.08	-5.51			
BC-011	10	Chicotte	2.14	-5.59			
BC-012	11	Chicotte	2.31	-5.71			
BC-013	12	Chicotte	2.69	-6.03			
BC-014	13	Chicotte	2.51	-6.22			
BC-015	14	Chicotte	2.38	-5.52			
BC-016	15	Chicotte	2.15	-5.94			
BC-017	16	Chicotte	2.28	-5.57			
BC-018	17	Chicotte	2.16	-5.88			
BC-019	18	Chicotte	2.33	-5.64			
BC-020	19	Chicotte	2.32	-5.36			
BC-021	20	Chicotte	2.23	-5.56			
BC-022	21	Chicotte	2.58	-5.93			
BC-023	22	Chicotte	2.64	-5.95			
BC-024	23	Chicotte	2.66	-6.09			
BC-025	24	Chicotte	2.41	-6.44			
BC-026	25	Chicotte	2.31	-5.84			
BC-027	26	Chicotte	2.55	-5.7			
BC-028	27	Chicotte	2.41	-5.34			
BC-029	28	Chicotte	2.59	-5.59			

Brick River							
Sample	From Datum (m)	Formation	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Latitude	Longitude	GPS Note
BR-001	0	Jupiter	-0.56	-5.39	49 23 46.0N	63 24 3.8W	
BR-002	1	Jupiter	0.36	-4.87			

BR-003	2	Jupiter	0.03	-5.03
BR-004	4	Jupiter	0.09	-5.25
BR-005	5	Jupiter	-0.7	-4.69
BR-006	6	Jupiter	-0.07	-5.52
BR-007B	7	Jupiter	-0.16	-5.35
BR-008	8	Jupiter	-0.23	-5.17
BR-009	10	Jupiter	-1.03	-5.54
BR-010	12	Jupiter	0.23	-5.09
BR-011	13	Jupiter	0.25	-5.72
BR-012	14	Jupiter	0.36	-5.07
BR-013	15	Jupiter	-0.1	-6.02
BR-014	16	Jupiter	0.12	-4.95
BR-015	17	Jupiter	0.18	-5.09
BR-016	18	Jupiter	0.46	-4.96
BR-017	19	Jupiter	0.3	-5.06
BR-018	20	Jupiter	0.51	-5.1

The Jumpers

Sample	From Datum (m)	Formation	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Latitude	Longitude	GPS Note
JM-001	0	Jupiter	0.4	-3.96	49 22 46.6N	63 31 38.6W	Start point
JM-002	0.5	Jupiter	0.13	-4.8			
JM-003	1	Jupiter	0.24	-4.9			
JM-004	1.5	Jupiter	0.3	-4.94			
JM-005	2	Jupiter	0.09	-4.93			
JM-006	2.5	Jupiter	-0.18	-5.11			
JM-007	3	Jupiter	0.14	-4.92			
JM-008	3.5	Jupiter	0.76	-4.96			
JM-009	4	Jupiter	0.43	-4.79			
JM-010	4.5	Jupiter	0.13	-5.03			
JM-011	5	Jupiter	0.31	-5.19			
JM-012	5.5	Jupiter	0.17	-4.87			
JM-013	6	Jupiter	0.05	-5.34			
JM-014	6.5	Jupiter	-0.54	-5.04			
JM-015	7	Jupiter	-3.01	-4.96			
JM-016	7.5	Jupiter	0.04	-4.86			
JM-017	8	Jupiter	0.85	-6.04			
JM-018	8.5	Chicotte	2.8	-5.17			
JM-019	9	Chicotte	3.21	-5.01			
JM-020	9.5	Chicotte	3.19	-5.01			
JM-021	10	Chicotte	2.57	-5.09			
JM-022	10.5	Chicotte	2.42	-5.24			

JM-023	11	Chicotte	2.23	-5.39			
JM-024A	11.5	Chicotte	2.19	-5.59			
JM-025	12	Chicotte	1.9	-5.28			
JM-026	12.5	Chicotte	1.8	-5.3			
JM-027	13	Chicotte	1.9	-5.2	49 22 50.8N	63 32 6.9W	End point

Cape Jupiter

Sample	From Datum (m)	Formation	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Latitude	Longitude	GPS Note
GU-001	0	Jupiter	5.25	-4.91	49 29 38.9N	63 37 8.4W	Site 1
GU-002	0.5	Jupiter	4.65	-5.02			
GU-003	1	Jupiter	4.67	-5.43			
GU-004	1.5	Jupiter	4.54	-5.18			
GU-005	2	Jupiter	5.29	-3.63			
GU-006	2.5	Jupiter	4.57	-6.16			
GU-007	3	Jupiter	4.87	-6.03			
GU-008	3.5	Jupiter	4.39	-5.2			
GU-009	4	Jupiter	4.75	-6.28			
GU-010	4.5	Jupiter	4.46	-5.18			
GU-011	5	Jupiter	4.72	-5.36			
GU-012	5.5	Jupiter	4.51	-5.12			
GU-013	6	Jupiter	4.75	-5.26			
GU-014	6.5	Jupiter	4.63	-5.12			
GU-015	7	Jupiter	4.43	-5.43			
GU-016	7.5	Jupiter	4.66	-4.78	49 29 43.9N	63 37 12.0W	Site 2
GU-017	8	Jupiter	4.7	-5.08			
GU-018	8.5	Jupiter	5.54	-5.35			
GU-019	9	Jupiter	4.62	-4.89			
GU-020	9.5	Jupiter	4.84	-5.44			
GU-021	10	Jupiter	4.71	-4.53			
GU-022	10.5	Jupiter	4.75	-4.78			
GU-023	11	Jupiter	4.27	-5.48			
GU-024	11.5	Jupiter	4.43	-5.04			
GU-025	12	Jupiter	4.74	-4.89			
GU-026	12.5	Jupiter	4.72	-5.14			
GU-027	13	Jupiter	4.36	-4.92			
GU-028	13.5	Jupiter	4.48	-4.87			
GU-029	14	Jupiter	4.73	-4.72			
GU-030	14.5	Jupiter	4.49	-4.5			
GU-031	15	Jupiter	4.4	-4.1			
GU-032	15.5	Jupiter	4.7	-4.8			
GU-033	16	Jupiter	4.8	-4.2			

GU-034	16.5	Jupiter	4.8	-4.6
GU-035	17	Jupiter	4.9	-4.6
GU-036	17.5	Jupiter	5.1	-4.2
GU-037	18	Jupiter	5	-4.7
GU-038	18.5	Jupiter	4.8	-4.8
GU-039	19	Jupiter	4.8	-4.9
GU-040	19.5	Jupiter	4.6	-5.2
GU-041	20	Jupiter	4.7	-4.7
GU-042	20.5	Jupiter	4.7	-4.8
GU-043	21	Jupiter	4.5	-4.5
GU-044	21.5	Jupiter	4.5	-4.8
GU-045	22	Jupiter	4.7	-4.7
GU-046	22.5	Jupiter	4.6	-4.7
GU-047	23	Jupiter	4.5	-5
GU-048	23.5	Jupiter	4.6	-5
GU-049	24	Jupiter	4.6	-5
GU-050	24.5	Jupiter	4.6	-4.9
GU-051	25	Jupiter	4.5	-5.1
GU-052	25.5	Jupiter	4.2	-5.1
GU-053	26	Jupiter	4.3	-5.2
GU-054	26.5	Jupiter	4.3	-5.1
GU-055	27	Jupiter	4.2	-5.1
GU-056	27.5	Jupiter	4.2	-5.6
GU-057	28	Jupiter	3.9	-5.2
GU-058	28.5	Jupiter	1.7	-5.6

Rocky Tide between Cape Jupiter and Triplesia Creek

Sample	From Datum (m)	Formation	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Latitude	Longitude	GPS Note
RT-001	N/A	Jupiter	2.5	-4.7	49 30 2.6N	63 37 45.7W	
RT-002	N/A	Jupiter	4.5	-5.1	49 29 59.4N	63 37 41.1W	
RT-003	N/A	Jupiter	4.5	-5.3	49 29 57.2N	63 37 36.8W	
RT-004	N/A	Jupiter	4.7	-5.4	49 29 53.3N	63 37 27.7W	
RT-005	N/A	Jupiter	4.7	-5.5	49 29 47.6N	63 37 17.5W	

Triplesia Creek

Sample	From Datum (m)	Formation	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Latitude	Longitude	GPS Note
JUP-001	0	Menier	1.43	-6.2	49 30 24.4N	63 37 52.5W	Site 1
JUP-002B	0.5	Menier	1.48	-4.9			
JUP-003	1	Menier	1.21	-4.74			
JUP-004	1.5	Menier	1.21	-4.87			

JUP-005	2	Menier	1.02	-5.26			
JUP-006	2.5	Menier	1.08	-4.94			
JUP-007	2.9	Menier	0.85	-5.15			
JUP-008	3.4	Menier	0.88	-5.15			
JUP-009	3.9	Menier	0.78	-4.87			
JUP-010	4.4	Menier	0.72	-4.44			
JUP-011	5.05	Menier	0.63	-4.94			
JUP-012	0	Menier	0.76	-5.14	49 30 26.0N	63 37 56.4W	Site 2
JUP-013	0.5	Menier	0.7	-4.6			
JUP-014	1	Menier	0.64	-4.84			
JUP-015	1.5	Menier	0.54	-4.68			
JUP-016	2	Menier	0.66	-4.99			
JUP-017	2.5	Menier	0.75	-5.02			

Cape Ottawa Site A

Sample	From Datum (m)	Formation	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Latitude	Longitude	GPS Note
COA-001	0	Jupiter	1.6	-5.7	49 28 12.1N	63 36 43.7W	
COA-002	0.5	Jupiter	1.7	-5.6			
COA-003	1	Jupiter	1.5	-5.5			
COA-005	1.5	Jupiter	1.5	-5.6			
COA-006	2	Jupiter	1.4	-5.7			
COA-007	2.5	Jupiter	1.3	-5.6			
COA-008	3	Jupiter	1.24	-5.89			
COA-009	3.5	Jupiter	1.2	-5.62			
COA-010	4	Jupiter	1.59	-5.71			
COA-011	4.5	Jupiter	1.1	-5.61			
COA-012	5	Jupiter	1.24	-5.44			
COA-013	5.5	Jupiter	1.19	-5.47			

Cape Ottawa Site B

Sample	From Datum (m)	Formation	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Latitude	Longitude	GPS Note
COB-001	0	Jupiter	1.7	-5.4	49 27 27.3N	63 37 4.9W	
COB-002	0.5	Jupiter	1.5	-5.4			
COB-003	1	Jupiter	1.6	-5.3			
COB-004	1.5	Jupiter	1.6	-5.3			
COB-005	2	Jupiter	1.4	-5.3			
COB-006	2.5	Jupiter	1.5	-5.2			
COB-007	3	Jupiter	1.4	-5.3			
COB-008	3.5	Jupiter	0.4	-5.1			
COB-009	4	Jupiter	1	-5.3			

COB-010	4.5	Jupiter	1.4	-5.3
COB-011	5	Jupiter	1.2	-5.3
COB-012	5.5	Jupiter	1.2	-5.4
COB-013	6	Jupiter	1.4	-5.2
COB-014	6.5	Jupiter	1.4	-5
COB-015	7	Jupiter	1.3	-5.3
COB-016	7.5	Jupiter	1.3	-5.2
COB-017	8	Jupiter	1.4	-5

Appendix B: Stable isotope data from the Martin La Mer core.

Sample	Depth (m)	Formation	Member	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
MLM-003	3	Jupiter	Ferrum	-1.23	-5.33
MLM-004	4	Jupiter	Ferrum	-1.06	-5.99
MLM-005	5	Jupiter	Ferrum	-1.01	-5.92
MLM-006	6	Jupiter	Ferrum	-0.96	-5.75
MLM-007	7	Jupiter	Ferrum	-0.95	-5.94
MLM-008	8	Jupiter	Ferrum	-0.11	-5.53
MLM-009	9	Jupiter	Ferrum	-0.34	-5.67
MLM-010	10	Jupiter	Ferrum	-0.41	-5.6
MLM-011	11	Jupiter	Ferrum	-0.36	-5.47
MLM-012	12	Jupiter	Ferrum	-0.68	-5.73
MLM-013	13	Jupiter	Ferrum	-0.35	-5.55
MLM-014	14	Jupiter	Ferrum	-0.64	-5.57
MLM-015	15	Jupiter	Ferrum	-0.2	-5.52
MLM-016	16	Jupiter	Ferrum	-0.41	-5.24
MLM-017	17	Jupiter	Ferrum	-0.41	-5.49
MLM-018	18	Jupiter	Ferrum	-1.06	-5.8
MLM-019	19	Jupiter	Ferrum	-1.16	-5.68
MLM-020	20	Jupiter	Ferrum	-0.66	-5.69
MLM-021	21	Jupiter	Ferrum	-1.2	-5.82
MLM-022	22	Jupiter	Ferrum	-0.69	-5.71
MLM-023	23	Jupiter	Ferrum	-1.07	-5.67
MLM-024	24	Jupiter	Ferrum	-1.2	-5.8
MLM-025	25	Jupiter	Ferrum	-1.49	-5.84
MLM-026	26	Jupiter	Ferrum	-0.81	-6.13
MLM-027	27	Jupiter	Ferrum	-0.63	-5.85
MLM-028	28	Jupiter	Ferrum	-0.15	-5.53
MLM-029	29	Jupiter	Ferrum	-0.74	-5.95
MLM-030	30	Jupiter	Ferrum	-0.94	-5.7
MLM-031	31	Jupiter	Ferrum	-0.48	-5.61
MLM-032	32	Jupiter	Ferrum	-0.5	-5.81
MLM-033	33	Jupiter	Ferrum	-0.71	-5.7
MLM-034	34	Jupiter	Ferrum	-0.98	-5.89
MLM-035	35	Jupiter	Ferrum	-0.82	-5.38
MLM-036	36	Jupiter	Ferrum	-0.78	-5.17
MLM-037	37	Jupiter	Ferrum	-0.74	-5.72
MLM-038	38	Jupiter	Ferrum	-0.58	-5.37
MLM-039	39	Jupiter	Ferrum	-0.95	-5.77
MLM-040	40	Jupiter	Ferrum	-1.24	-5.38
MLM-041	41	Jupiter	Ferrum	-0.87	-5.5
MLM-042	42	Jupiter	Ferrum	-0.66	-5.22

MLM-043	43	Jupiter	Ferrum	-0.96	-5.35
MLM-044	44	Jupiter	Ferrum	-0.79	-5.63
MLM-045	45	Jupiter	Ferrum	-0.77	-5.87
MLM-046	46	Jupiter	Ferrum	-0.3	-5.52
MLM-047	47	Jupiter	Ferrum	-0.64	-5.44
MLM-048	48	Jupiter	Cybèle	-0.93	-5.55
MLM-049	49	Jupiter	Cybèle	-0.7	-5.16
MLM-050	50	Jupiter	Cybèle	-1.35	-5.2
MLM-051	51	Jupiter	Cybèle	-0.62	-5.25
MLM-052	52	Jupiter	Cybèle	-0.86	-5.39
MLM-053	53	Jupiter	Cybèle	-0.18	-5.22
MLM-054	54	Jupiter	Cybèle	-0.35	-5.12
MLM-055	55	Jupiter	Cybèle	-0.74	-5.28
MLM-056	56	Jupiter	Cybèle	-0.93	-5.53
MLM-057	57	Jupiter	Cybèle	-0.36	-5.46
MLM-058	58	Jupiter	Cybèle	-0.25	-5.35
MLM-059	59	Jupiter	Cybèle	-1.32	-5.61
MLM-060	60	Jupiter	Cybèle	-0.64	-5.17
MLM-061	61	Jupiter	Cybèle	-1	-5.45
MLM-062	62	Jupiter	Cybèle	-0.77	-5.28
MLM-063	63	Jupiter	Cybèle	-0.91	-5.51
MLM-064	64	Jupiter	Cybèle	-0.87	-5.63
MLM-065	65	Jupiter	Cybèle	-0.49	-5.32
MLM-066	66	Jupiter	Cybèle	-0.84	-5.3
MLM-067	67	Jupiter	Cybèle	-0.6	-5.31
MLM-068	68	Jupiter	Cybèle	-0.68	-5.5
MLM-069	69	Jupiter	Cybèle	-0.27	-5.21
MLM-070	70	Jupiter	Cybèle	-0.27	-5.26
MLM-071	71	Jupiter	Cybèle	-0.45	-5.32
MLM-072	72	Jupiter	Cybèle	0.02	-5.02
MLM-073	73	Jupiter	Cybèle	-0.17	-5.75
MLM-074	74	Jupiter	Cybèle	0.23	-5.09
MLM-075	75	Jupiter	Cybèle	-0.1	-5.34
MLM-076	76	Jupiter	Cybèle	0.1	-4.97
MLM-077	77	Jupiter	Cybèle	-0.06	-5.03
MLM-078	78	Jupiter	Cybèle	0.1	-4.82
MLM-079	79	Jupiter	Cybèle	0.16	-5
MLM-080	80	Jupiter	Cybèle	-0.02	-5.47
MLM-081	81	Jupiter	Cybèle	0.74	-4.92
MLM-082	82	Jupiter	Cybèle	0.82	-5.19
MLM-083	83	Jupiter	Cybèle	0.67	-5.51
MLM-084	84	Jupiter	Cybèle	0.95	-5.22
MLM-085	85	Jupiter	Cybèle	1.09	-5.4

MLM-086	86	Jupiter	Cybèle	0.94	-5.25
MLM-087	87	Jupiter	Cybèle	1.17	-5.51
MLM-088	88	Jupiter	Cybèle	1.12	-5.25
MLM-089	89	Jupiter	Cybèle	0.98	-5.66
MLM-090	90	Jupiter	Cybèle	1	-5.54
MLM-091	91	Jupiter	Cybèle	1.21	-5.3
MLM-092	92	Jupiter	Cybèle	0.98	-5.51
MLM-093	93	Jupiter	Cybèle	1.08	-5.7
MLM-094	94	Jupiter	Cybèle	1.18	-5.32
MLM-095	95	Jupiter	Cybèle	1.02	-4.91
MLM-096	96	Jupiter	Cybèle	1.36	-5.16
MLM-097	97	Jupiter	Cybèle	1.29	-5.56
MLM-098	98	Jupiter	Cybèle	1.56	-5.33
MLM-099	99	Jupiter	Cybèle	1.62	-5.32
MLM-100	100	Jupiter	Cybèle	1.5	-5.36
MLM-101	101	Jupiter	Cybèle	1.29	-5.71
MLM-102	102	Jupiter	Cybèle	1.61	-5.34
MLM-103	103	Jupiter	Cybèle	1.57	-5.47
MLM-104	104	Jupiter	Cybèle	1.53	-5.47
MLM-105	105	Jupiter	Cybèle	1.54	-5.29
MLM-106	106	Jupiter	Cybèle	1.75	-5.13
MLM-107	107	Jupiter	Cybèle	1.9	-5.32
MLM-108	108	Jupiter	Cybèle	1.94	-5.31
MLM-109	109	Jupiter	Richardson	4.4	-4.17
MLM-110	110	Jupiter	Richardson	4.97	-4.51
MLM-111	111	Jupiter	Richardson	5.49	-4.19
MLM-112	112	Jupiter	Richardson	4.76	-4.57
MLM-113	113	Jupiter	Richardson	5.89	-4.46
MLM-114	114	Jupiter	Richardson	5.73	-4.84
MLM-115	115	Jupiter	Richardson	5.56	-5.17
MLM-116	116	Jupiter	Richardson	5.98	-5.24
MLM-117	117	Jupiter	Richardson	5.9	-4.7
MLM-118	118	Jupiter	Richardson	5.84	-5.04
MLM-119	119	Jupiter	Richardson	5.72	-5.02
MLM-120	120	Jupiter	Richardson	5.57	-4.95
MLM-121	121	Jupiter	Richardson	4.75	-4.92
MLM-122	122	Jupiter	Richardson	5.34	-4.8
MLM-123	123	Jupiter	Richardson	5.36	-4.67
MLM-124	124	Jupiter	Richardson	5.03	-4.98
MLM-125	125	Jupiter	Richardson	4.65	-5.18
MLM-126	126	Jupiter	Richardson	4.43	-5.04
MLM-127	127	Menier	East Point	1.16	-4.83
MLM-128	128	Menier	East Point	1.27	-5.08

MLM-129	129	Menier	East Point	-0.05	-4.77
MLM-130	130	Menier	Goéland	0.3	-4.9
MLM-131	131	Menier	Goéland	0.29	-4.95
MLM-132	132	Menier	Goéland	0.32	-5.75
MLM-133	133	Menier	Goéland	0.32	-5
MLM-134	134	Menier	Goéland	0.32	-4.92
MLM-135	135	Menier	Goéland	0.34	-5.36
MLM-136	136	Menier	Goéland	0.24	-5.57
MLM-137	137	Menier	Goéland	0.51	-5.41
MLM-138	138	Menier	Goéland	0.45	-5.83
MLM-139	139	Menier	Goéland	0.55	-5.06
MLM-140	140	Menier	Goéland	0.59	-5.19
MLM-141	141	Menier	Goéland	0.65	-5.45
MLM-142	142	Menier	Goéland	0.64	-5.25
MLM-143	143	Menier	Goéland	0.74	-5.4
MLM-144	144	Menier	Goéland	0.72	-5.29
MLM-145	145	Menier	Goéland	0.84	-5.29
MLM-146	146	Menier	Goéland	0.77	-5.31
MLM-147	147	Menier	Goéland	0.53	-5.06
MLM-148	148	Menier	Goéland	0.78	-5.05
MLM-149	149	Menier	Goéland	0.56	-4.96
MLM-150	150	Menier	Goéland	0.53	-5.05
MLM-151	151	Menier	Goéland	0.98	-4.91
MLM-152	152	Menier	Goéland	0.15	-4.83
MLM-153A	153	Menier	Goéland	-0.24	-4.9
MLM-154	154	Menier	Goéland	0.15	-5
MLM-155	155	Menier	Goéland	0.42	-5.1
MLM-156	156	Menier	Goéland	0.21	-5.3
MLM-157	157	Menier	Goéland	-0.32	-4.75
MLM-158	158	Menier	Goéland	0.28	-4.72
MLM-159	159	Menier	Goéland	-0.9	-4.84
MLM-160	160	Menier	Goéland	-0.19	-4.68
MLM-161	161	Menier	Goéland	-0.23	-4.45
MLM-162	162	Menier	Goéland	0.2	-4.94
MLM-163	163	Menier	Goéland	-0.78	-5.4
MLM-164	164	Menier	Goéland	-0.2	-5
MLM-165	165	Gun River	Macgilvray	-0.4	-4.96
MLM-166	166	Gun River	Macgilvray	-0.28	-5.19
MLM-167	167	Gun River	Macgilvray	0.13	-5.18
MLM-168	168	Gun River	Macgilvray	0.22	-5.33
MLM-169	169	Gun River	Macgilvray	-0.23	-5.04
MLM-170	170	Gun River	Macgilvray	0.21	-5.22
MLM-171	171	Gun River	Macgilvray	0.05	-5.01

MLM-172	172	Gun River	Macgilvray	0.13	-4.63
MLM-173	173	Gun River	Macgilvray	-0.12	-4.92
MLM-174	174	Gun River	Macgilvray	-0.34	-4.79
MLM-175	175	Gun River	Macgilvray	-0.26	-4.63
MLM-176	176	Gun River	Macgilvray	-0.33	-4.73
MLM-177	177	Gun River	Macgilvray	0.53	-4.96
MLM-178	178	Gun River	Macgilvray	0.34	-4.77
MLM-179	179	Gun River	Macgilvray	-0.23	-4.96
MLM-180	180	Gun River	Macgilvray	-0.56	-4.99
MLM-181	181	Gun River	Macgilvray	0.97	-4.87
MLM-182	182	Gun River	Macgilvray	0.1	-5
MLM-183	183	Gun River	Macgilvray	-0.15	-5.06
MLM-184	184	Gun River	Macgilvray	-0.42	-5.19
MLM-185	185	Gun River	Macgilvray	0.6	-5.08
MLM-186	186	Gun River	Macgilvray	0.81	-5.02
MLM-187	187	Gun River	Macgilvray	0.35	-5.09
MLM-188	188	Gun River	Macgilvray	0.05	-5.21
MLM-189	189	Gun River	Macgilvray	0.19	-5.04
MLM-190	190	Gun River	Macgilvray	-0.4	-5.3
MLM-191	191	Gun River	Macgilvray	0.68	-5.17
MLM-192	192	Gun River	Macgilvray	0.81	-5.1
MLM-193	193	Gun River	Macgilvray	0.32	-5.27
MLM-194	194	Gun River	Macgilvray	0.88	-4.97
MLM-195	195	Gun River	Macgilvray	1.5	-4.95
MLM-196	196	Gun River	Macgilvray	0.35	-5
MLM-197	197	Gun River	Macgilvray	-0.95	-5.13
MLM-198	198	Gun River	Macgilvray	0.21	-4.97
MLM-199	199	Gun River	Macgilvray	0.75	-4.85
MLM-200	200	Gun River	Macgilvray	0.3	-5.04
MLM-201	201	Gun River	Sandtop	0.63	-5.42
MLM-202	202	Gun River	Sandtop	0.19	-5.2
MLM-203	203	Gun River	Sandtop	0.98	-5.12
MLM-204	204	Gun River	Sandtop	0.68	-5.1
MLM-205	205	Gun River	Sandtop	1.35	-5.06
MLM-206	206	Gun River	Sandtop	1.26	-5.16
MLM-207	207	Gun River	Sandtop	1.4	-5.17
MLM-208	208	Gun River	Sandtop	1.22	-5.15
MLM-209	209	Gun River	Sandtop	0.64	-5.12
MLM-210	210	Gun River	Sandtop	1.27	-4.99
MLM-211	211	Gun River	Sandtop	0.31	-5.1
MLM-212	212	Gun River	Sandtop	1.24	-5.01
MLM-213	213	Gun River	Sandtop	0.98	-4.79
MLM-214	214	Gun River	Sandtop	0.97	-4.73

MLM-215	215	Gun River	Sandtop	0.11	-4.87
MLM-216	216	Gun River	Sandtop	0.23	-4.76
MLM-217	217	Gun River	Sandtop	0.18	-4.54
MLM-218	218	Gun River	Sandtop	0.55	-4.28
MLM-219	219	Gun River	Sandtop	-0.05	-5.25
MLM-220	220	Gun River	Sandtop	0.02	-4.78
MLM-221	221	Gun River	Sandtop	0.05	-4.96
MLM-222	222	Gun River	Sandtop	0.13	-4.88
MLM-223	223	Gun River	Sandtop	0.27	-4.42
MLM-224	224	Gun River	Sandtop	0.02	-4.89
MLM-225	225	Gun River	Sandtop	0.84	-4.86
MLM-226	226	Gun River	Sandtop	0.92	-5.02
MLM-227	227	Gun River	Sandtop	1.3	-4.72
MLM-228	228	Gun River	Sandtop	0.65	-4.78
MLM-229	229	Gun River	Sandtop	0.39	-4.78
MLM-230	230	Gun River	Sandtop	0.71	-5.13
MLM-233	233	Gun River	Sandtop	0.05	-4.79
MLM-234	234	Gun River	Innommée	0.36	-4.61
MLM-235	235	Gun River	Innommée	0.68	-4.89
MLM-236	236	Gun River	Innommée	0.63	-4.62
MLM-237	237	Gun River	Innommée	1.38	-4.82
MLM-238	238	Gun River	Innommée	0.74	-4.83
MLM-239	239	Gun River	Innommée	1.26	-4.84
MLM-240	240	Gun River	Innommée	1.16	-4.84
MLM-241	241	Gun River	Innommée	1.4	-4.86
MLM-242	242	Gun River	Innommée	1.68	-4.64
MLM-243	243	Gun River	Innommée	1.58	-4.58
MLM-244	244	Gun River	Innommée	1.72	-4.68
MLM-245	245	Gun River	Innommée	1.56	-4.77
MLM-246	246	Gun River	Innommée	0.86	-4.89
MLM-247	247	Gun River	Innommée	1.13	-4.87
MLM-248	248	Gun River	Innommée	1.6	-4.75
MLM-249	249	Gun River	Innommée	1.27	-5.33
MLM-250	250	Gun River	Innommée	1.12	-5.27
MLM-251	251	Gun River	Innommée	1.27	-4.84
MLM-252	252	Gun River	Innommée	1.39	-4.59
MLM-253	253	Gun River	Innommée	0.89	-4.72
MLM-254	254	Gun River	Innommée	1.16	-4.67
MLM-255	255	Gun River	Innommée	0.76	-4.77
MLM-256	256	Gun River	Innommée	0.76	-5.02
MLM-257	257	Gun River	Innommée	1.17	-5.07
MLM-258	258	Gun River	Lachute	1.57	-4.51
MLM-259	259	Gun River	Lachute	1.66	-4.76

MLM-260	260	Gun River	Lachute	1.65	-4.73
MLM-261	261	Gun River	Lachute	1.68	-4.74
MLM-262	262	Gun River	Lachute	1.97	-4.33
MLM-263A	263	Gun River	Lachute	1.54	-5.27
MLM-264	264	Gun River	Lachute	1.76	-4.72
MLM-265	265	Gun River	Lachute	1.94	-4.44
MLM-266	266	Gun River	Lachute	1.7	-4.48
MLM-267	267	Gun River	Lachute	1.68	-4.31
MLM-268	268	Gun River	Lachute	1.72	-4.32
MLM-269	269	Gun River	Lachute	1.75	-4.34
MLM-270	270	Gun River	Lachute	1.87	-4.09
MLM-271	271	Gun River	Lachute	1.62	-4.29
MLM-272	272	Gun River	Lachute	1.87	-4.01
MLM-273	273	Gun River	Lachute	1.79	-4.23
MLM-274	274	Gun River	Lachute	1.74	-4.21
MLM-275	275	Gun River	Lachute	1.82	-4.27
MLM-276	276	Gun River	Lachute	1.82	-4.62
MLM-277	277	Gun River	Lachute	1.72	-4.77
MLM-278	278	Merrimack	N/A	0.28	-4.25
MLM-279	279	Merrimack	N/A	0.19	-3.99
MLM-280	280	Merrimack	N/A	-0.3	-3.9
MLM-281	281	Merrimack	N/A	-0.24	-4.93
MLM-282	282	Merrimack	N/A	-1.28	-4.18
MLM-283	283	Merrimack	N/A	-0.47	-4.4
MLM-284	284	Merrimack	N/A	0.42	-4.26
MLM-285	285	Merrimack	N/A	-0.02	-4.58
MLM-286	286	Merrimack	N/A	0.64	-4.44
MLM-287	287	Merrimack	N/A	-0.52	-4.94
MLM-288	288	Merrimack	N/A	0.62	-4.28
MLM-289	289	Merrimack	N/A	0.16	-4.19
MLM-290	290	Becscie	Chabot	0.5	-4.19
MLM-291	291	Becscie	Chabot	0.3	-4.44
MLM-292	292	Becscie	Chabot	0.2	-4.76
MLM-293	293	Becscie	Chabot	0.34	-4.88
MLM-294	294	Becscie	Chabot	0.29	-4.68
MLM-295	295	Becscie	Chabot	0.19	-4.44
MLM-296	296	Becscie	Chabot	-0.07	-4.23
MLM-297	297	Becscie	Chabot	0.1	-4.8
MLM-298	298	Becscie	Chabot	-0.46	-4.32
MLM-299	299	Becscie	Chabot	0.24	-4.51
MLM-300	300	Becscie	Chabot	0.23	-4.98
MLM-301	301	Becscie	Chabot	0.17	-4.84
MLM-302	302	Becscie	Chabot	-0.11	-4.55

MLM-303	303	Becscie	Chabot	0	-4.77
MLM-304	304	Becscie	Chabot	-0.18	-5.23
MLM-305	305	Becscie	Chabot	0.16	-5.44
MLM-306	306	Becscie	Chabot	-0.39	-4.38
MLM-307	307	Becscie	Chabot	-0.2	-4.59
MLM-308	308	Becscie	Chabot	0.06	-4.94
MLM-309	309	Becscie	Chabot	-0.4	-4.53
MLM-310	310	Becscie	Chabot	-0.11	-5.06
MLM-311	311	Becscie	Chabot	-0.49	-4.48
MLM-312	312	Becscie	Chabot	-0.18	-4.81
MLM-313	313	Becscie	Chabot	-0.4	-5.3
MLM-314	314	Becscie	Chabot	-0.62	-4.89
MLM-315	315	Becscie	Chabot	-0.46	-5.26
MLM-316	316	Becscie	Chabot	-0.5	-5.43
MLM-317	317	Becscie	Chabot	-0.29	-4.86
MLM-318	318	Becscie	Chabot	-0.41	-5.5
MLM-319	319	Becscie	Chabot	-0.83	-4.82
MLM-320	320	Becscie	Chabot	-0.37	-4.21
MLM-321	321	Becscie	Chabot	-0.7	-4.77
MLM-322	322	Becscie	Chabot	-0.3	-5.64
MLM-323	323	Becscie	Chabot	-0.83	-4.79
MLM-324	324	Becscie	Chabot	-0.25	-5.43
MLM-325	325	Becscie	Chabot	-0.26	-4.93
MLM-326	326	Becscie	Chabot	-0.47	-5.33
MLM-327	327	Becscie	Chabot	-0.24	-4.48
MLM-328	328	Becscie	Chabot	-0.21	-4.77
MLM-329	329	Becscie	Chabot	-0.3	-4.6
MLM-330	330	Becscie	Chabot	-0.45	-4.94
MLM-331	331	Becscie	Chabot	-0.58	-4.64
MLM-332	332	Becscie	Chabot	-0.92	-4.94
MLM-333	333	Becscie	Chabot	-0.59	-4.65
MLM-334	334	Becscie	Chabot	-0.66	-4.41
MLM-335	335	Becscie	Chabot	-0.25	-4.98
MLM-336	336	Becscie	Chabot	-0.42	-4.87
MLM-337	337	Becscie	Chabot	-0.65	-4.69
MLM-338	338	Becscie	Chabot	-0.47	-4.88
MLM-339	339	Becscie	Chabot	-0.53	-4.24
MLM-340	340	Becscie	Chabot	-0.37	-4.51
MLM-341	341	Becscie	Chabot	-0.75	-4.45
MLM-342	342	Becscie	Chabot	-0.63	-4.32
MLM-343	343	Becscie	Chabot	-0.33	-4.84
MLM-344	344	Becscie	Chabot	-0.62	-5.05
MLM-345	345	Becscie	Chabot	-0.66	-4.22

MLM-346	346	Becscie	Chabot	-0.62	-4.71
MLM-347	347	Becscie	Chabot	-0.54	-4.25
MLM-348	348	Becscie	Chabot	-0.43	-4.94
MLM-349	349	Becscie	Chabot	-0.47	-4.44
MLM-350	350	Becscie	Chabot	-0.27	-4.48
MLM-351	351	Becscie	Chabot	-0.6	-4.63
MLM-352	352	Becscie	Chabot	-0.48	-4.93
MLM-353	353	Becscie	Chabot	-0.61	-4.32
MLM-354	354	Becscie	Chabot	-0.3	-4.02
MLM-355	355	Becscie	Chabot	-0.49	-4.41
MLM-356	356	Becscie	Chabot	-0.31	-4.84
MLM-357	357	Becscie	Chabot	-0.29	-5.02
MLM-358	358	Becscie	Chabot	-0.57	-5.08
MLM-359	359	Becscie	Chabot	-0.64	-4.51
MLM-360	360	Becscie	Chabot	-0.21	-4.1
MLM-361	361	Becscie	Chabot	-0.5	-4.9
MLM-362	362	Becscie	Chabot	-0.84	-4.41
MLM-363	363	Becscie	Chabot	-0.04	-4.59
MLM-364	364	Becscie	Chabot	-0.23	-4.63
MLM-365	365	Becscie	Chabot	-0.44	-5.1
MLM-366	366	Becscie	Chabot	-0.36	-5.03
MLM-367	367	Becscie	Chabot	0.12	-4.42
MLM-368	368	Becscie	Chabot	-0.13	-4.96
MLM-369	369	Becscie	Chabot	-0.49	-4.35
MLM-370	370	Becscie	Chabot	-0.18	-4.07
MLM-371	371	Becscie	Chabot	-0.19	-3.92
MLM-372	372	Becscie	Chabot	-0.09	-3.92
MLM-373	373	Becscie	Chabot	0.17	-4.4
MLM-374	374	Becscie	Chabot	0.19	-3.96
MLM-375	375	Becscie	Fox Point	0.21	-3.93
MLM-376	376	Becscie	Fox Point	-0.03	-4.8
MLM-377	377	Becscie	Fox Point	-0.24	-4.43
MLM-378	378	Becscie	Fox Point	0.58	-3.95
MLM-379	379	Becscie	Fox Point	0.66	-3.96
MLM-380	380	Becscie	Fox Point	0.59	-3.98
MLM-381	381	Becscie	Fox Point	0.69	-3.93
MLM-382	382	Becscie	Fox Point	0.42	-4.09
MLM-383	383	Becscie	Fox Point	0.5	-4.24
MLM-384	384	Becscie	Fox Point	0.14	-4.38
MLM-385	385	Becscie	Fox Point	0.94	-3.93
MLM-386	386	Becscie	Fox Point	0.97	-4.19
MLM-387	387	Becscie	Fox Point	0.96	-4.16
MLM-388	388	Becscie	Fox Point	1.26	-3.83

MLM-389	389	Becscie	Fox Point	1.11	-3.81
MLM-390	390	Becscie	Fox Point	1.07	-3.95
MLM-391	391	Becscie	Fox Point	1.17	-3.93
MLM-392	392	Becscie	Fox Point	1.14	-4
MLM-393	393	Becscie	Fox Point	1.2	-3.94
MLM-394	394	Becscie	Fox Point	1.15	-3.86
MLM-395	395	Becscie	Fox Point	0.8	-4.15
MLM-396	396	Becscie	Fox Point	0.93	-3.86
MLM-397	397	Becscie	Fox Point	0.9	-3.93
MLM-398	398	Becscie	Fox Point	0.68	-3.97
MLM-399	399	Becscie	Fox Point	1.14	-3.76
MLM-400	400	Becscie	Fox Point	0.98	-3.42
MLM-401	401	Becscie	Fox Point	0.71	-4.49
MLM-402	402	Becscie	Fox Point	0.79	-4.53
MLM-403	403	Becscie	Fox Point	1.41	-3.6
MLM-404	404	Ellis Bay	Laframboise	1.45	-4.22
MLM-405	405	Ellis Bay	Laframboise	5.4	-4.87
MLM-406	406	Ellis Bay	Laframboise	5.11	-4.48
MLM-407	407	Ellis Bay	Lousey Cove	2.59	-4.13
MLM-408	408	Ellis Bay	Lousey Cove	0.32	-3.06
MLM-409	409	Ellis Bay	Lousey Cove	0.3	-3.01
MLM-410	410	Ellis Bay	Lousey Cove	-0.21	-3.4
MLM-411	411	Ellis Bay	Lousey Cove	0.7	-3.29
MLM-412	412	Ellis Bay	Lousey Cove	0.8	-3.16
MLM-413	413	Ellis Bay	Lousey Cove	0.78	-2.99
MLM-414	414	Ellis Bay	Lousey Cove	0.63	-3.26
MLM-415	415	Ellis Bay	Lousey Cove	0.62	-3.3
MLM-416	416	Ellis Bay	Lousey Cove	0.54	-3.25
MLM-417	417	Ellis Bay	Lousey Cove	0.67	-3.32
MLM-418	418	Ellis Bay	Lousey Cove	0.62	-3.38
MLM-419	419	Ellis Bay	Lousey Cove	0.08	-3.78
MLM-420	420	Ellis Bay	Lousey Cove	-0.76	-3.23
MLM-421	421	Ellis Bay	Lousey Cove	-0.28	-2.95
MLM-422	422	Ellis Bay	Lousey Cove	-0.03	-3.05
MLM-423	423	Ellis Bay	Lousey Cove	-0.58	-2.76
MLM-424	424	Ellis Bay	Lousey Cove	0.33	-2.83
MLM-425	425	Ellis Bay	Lousey Cove	0.58	-2.58
MLM-426	426	Ellis Bay	Lousey Cove	0.35	-2.6
MLM-427	427	Ellis Bay	Lousey Cove	0.34	-2.58
MLM-428	428	Ellis Bay	Lousey Cove	1.1	-2.82
MLM-429	429	Ellis Bay	Lousey Cove	1.8	-2.85
MLM-430	430	Ellis Bay	Lousey Cove	1.84	-2.99
MLM-431	431	Ellis Bay	Lousey Cove	1.84	-2.91

MLM-432	432	Ellis Bay	Lousey Cove	1.94	-2.9
MLM-433	433	Ellis Bay	Lousey Cove	1.6	-2.8
MLM-434A	434	Ellis Bay	Parastro	1.37	-3.26
MLM-435	435	Ellis Bay	Parastro	1.17	-2.78
MLM-436	436	Ellis Bay	Parastro	0.45	-3.85
MLM-437	437	Ellis Bay	Parastro	-0.17	-2.96
MLM-438	438	Ellis Bay	Parastro	-0.45	-2.85
MLM-439	439	Ellis Bay	Parastro	0.55	-3.12
MLM-440	440	Ellis Bay	Parastro	0.31	-2.69
MLM-441	441	Ellis Bay	Parastro	-0.32	-2.89
MLM-442	442	Ellis Bay	Parastro	-0.46	-3.03
MLM-443	443	Ellis Bay	Parastro	-0.19	-3.21
MLM-444	444	Ellis Bay	Parastro	-0.2	-3.58
MLM-445	445	Ellis Bay	Parastro	0.23	-3.17
MLM-446	446	Ellis Bay	Parastro	0.25	-2.97

Appendix C: Mn and Sr trace element data from core and outcrop.

Martin La Mer Data			
Sample	Formation	Mn (ppm)	Sr (ppm)
MLM-008	Jupiter	168.60	428.62
MLM-018	Jupiter	310.40	346.23
MLM-028	Jupiter	162.72	484.03
MLM-040	Jupiter	298.83	311.11
MLM-050	Jupiter	255.34	372.67
MLM-060	Jupiter	261.83	459.42
MLM-070	Jupiter	294.03	589.57
MLM-082	Jupiter	268.03	934.32
MLM-092	Jupiter	259.01	943.28
MLM-102	Jupiter	255.68	1127.49
MLM-112	Jupiter	236.06	565.66
MLM-123	Jupiter	151.71	1432.42
MLM-130	Menier	345.67	557.95
MLM-140	Menier	397.78	995.22
MLM-151	Menier	349.14	507.74
MLM-162	Menier	163.40	360.58
MLM-172	Gun River	153.77	337.17
MLM-181	Gun River	108.24	681.44
MLM-190	Gun River	114.85	704.25
MLM-197	Gun River	137.82	446.32
MLM-207	Gun River	89.24	754.65
MLM-218	Gun River	85.39	390.58
MLM-227	Gun River	60.84	703.78
MLM-238	Gun River	86.63	840.96
MLM-248	Gun River	89.79	919.29
MLM-256	Gun River	83.58	793.90
MLM-265	Gun River	72.18	966.63
MLM-275	Gun River	93.07	933.69
MLM-282	Merrimack	1488.35	375.69
MLM-292	Becscie	177.26	623.09
MLM-302	Becscie	91.37	762.38
MLM-312	Becscie	93.77	481.96
MLM-322	Becscie	72.99	744.09
MLM-332	Becscie	96.73	377.98
MLM-342	Becscie	69.08	871.99
MLM-352	Becscie	97.58	680.47
MLM-362	Becscie	88.22	424.48
MLM-372	Becscie	113.90	710.16

MLM-382	Becscie	127.77	825.34
MLM-392	Becscie	157.63	1144.46
MLM-402	Becscie	208.30	1213.32
MLM-412	Ellis Bay	199.22	629.45
MLM-422	Ellis Bay	302.28	337.39
MLM-432	Ellis Bay	147.68	1348.62
MLM-442	Ellis Bay	250.66	702.83

Outcrop Data

Sample	Formation	Mn (ppm)	Sr (ppm)
BC-004	Chicotte	189.07	142.93
BC-016	Chicotte	185.27	102.21
BC-026	Chicotte	246.90	140.85
BR-009	Jupiter	268.36	322.93
BR-017	Jupiter	182.57	309.18