

Extending the record of the Lomagundi–Jatuli carbon isotope excursion in the Labrador Trough, Canada

Malcolm S.W. Hodgskiss, Kelsey G. Lamothe, Galen P. Halverson, and Erik A. Sperling

Abstract: The Labrador Trough in northern Québec and Labrador is a 900 km long Rhyacian–Orosirian orogenic belt containing mixed sedimentary–volcanic successions. Despite having been studied intensively since the 1940s, relatively few chemostratigraphic studies have been conducted. To improve our understanding of the Labrador Trough in the context of Earth history, and better constrain the local record of the Lomagundi–Jatuli carbon isotope excursion, high-resolution sampling and carbon isotope analyses of the Le Fer and Denault formations were conducted. Carbonate carbon isotopes ($\delta^{13}\text{C}$) in the Le Fer Formation record a large range in values from -4.4% to $+6.9\%$. This large range is likely attributable to a combination of post-depositional alteration and variable abundance of authigenic carbonate minerals; elemental ratios suggest that the most ^{13}C -enriched samples reflect the composition of the water column at the time of deposition. Cumulatively, these data suggest that the Lomagundi–Jatuli Excursion was ongoing during deposition of the Le Fer Formation, approximately 2 km higher in the stratigraphy than previously recognised. However, the possibility of a post-Lomagundi–Jatuli Excursion carbon isotope event cannot conclusively be ruled out. The directly overlying Denault Formation records a range in $\delta^{13}\text{C}$ values, from -0.5% to $+4.3\%$, suggesting that it was deposited after the conclusion of the Lomagundi–Jatuli Excursion and that the contact between the Le Fer and Denault formations occurred sometime during the transition out of the Lomagundi–Jatuli Excursion, ca. 2106 to 2057 Ma.

Key words: Lomagundi Excursion, Lomagundi–Jatuli Excursion, Labrador Trough, Le Fer Formation, Denault Formation, carbon isotopes.

Résumé : La fosse du Labrador, dans le nord du Québec et au Labrador, est une ceinture orogénique rhyacienne–orosirienne de 900 km de long renfermant des séquences sédimentaires–volcaniques mixtes. Bien qu'elle ait fait l'objet de nombreuses études depuis les années 1940, relativement peu d'études chémostratigraphiques s'y sont intéressées. Afin d'améliorer la compréhension de la fosse du Labrador dans le contexte de l'histoire de la Terre et de mieux délimiter le registre local de l'excursion Lomagundi–Jatuli des isotopes du carbone, un échantillonnage de haute résolution et des analyses des isotopes du carbone des Formations de Le Fer et de Denault ont été effectués. Les isotopes du carbone ($\delta^{13}\text{C}$) de carbonates dans la Formation de Le Fer présentent une grande fourchette de valeurs allant de $-4,4\%$ à $+6,9\%$, vraisemblablement attribuable à une combinaison d'altération post-dépôt et d'abondance variable de carbonates authigènes; les rapports élémentaires donnent à penser que les échantillons les plus enrichis en ^{13}C reflètent la composition de la colonne d'eau au moment du dépôt. Collectivement, ces données indiqueraient que l'excursion Lomagundi–Jatuli était en cours durant le dépôt de la Formation de Le Fer, ce qui la place environ 2 km plus haut dans la colonne stratigraphique que sa position reconnue auparavant. La possibilité d'un évènement enregistré par les isotopes de carbone qui serait postérieur à l'excursion Lomagundi–Jatuli ne peut toutefois être exclue avec certitude. La Formation de Denault immédiatement au-dessus présente une fourchette de valeurs de $\delta^{13}\text{C}$ allant de $-0,5\%$ à $+4,3\%$, ce qui indiquerait qu'elle a été déposée après la fin de l'excursion Lomagundi–Jatuli et que le contact entre les Formations de Le Fer et de Denault s'est produit durant la transition au sortir de l'excursion Lomagundi–Jatuli, vers 2106 Ma à 2057 Ma. [Traduit par la Rédaction]

Mots-clés : excursion Lomagundi, excursion Lomagundi–Jatuli, fosse du Labrador, Formation de Le Fer, Formation de Denault, isotopes du carbone.

Introduction

The ca. 2.2–1.8 Ga Labrador Trough (Fig. 1) has been studied nearly continuously since the 1940s, yet its geochronology and tectonic history remain poorly constrained, in large part due to poor exposure in a region with dense pine forest, lakes, and swamps. Many formational contacts are unexposed and the difficulty in generating a stratigraphic framework for the region is compounded by significant west–east variability in lithologies (Figs. 1 and 2) and metamorphic grade (from subgreenschist to

amphibolite and granulite facies), as well as complex structural geology (with large-scale folding cut by a series of imbricated thrust faults; Dimroth 1978). Nevertheless, the Labrador Trough is of significant geologic interest because it is a large (>900 km long) region with an intricate tectonic history that records the breakup of the eastern Superior Craton margin and the assembly of Nuna (Hoffman 1988). It is also host to significant iron ore deposits, which cumulatively represent the majority of iron ore production in Canada (Neal 2000), as well as other mineral deposits of economic interest (e.g., copper-nickel-platinum group elements, ura-

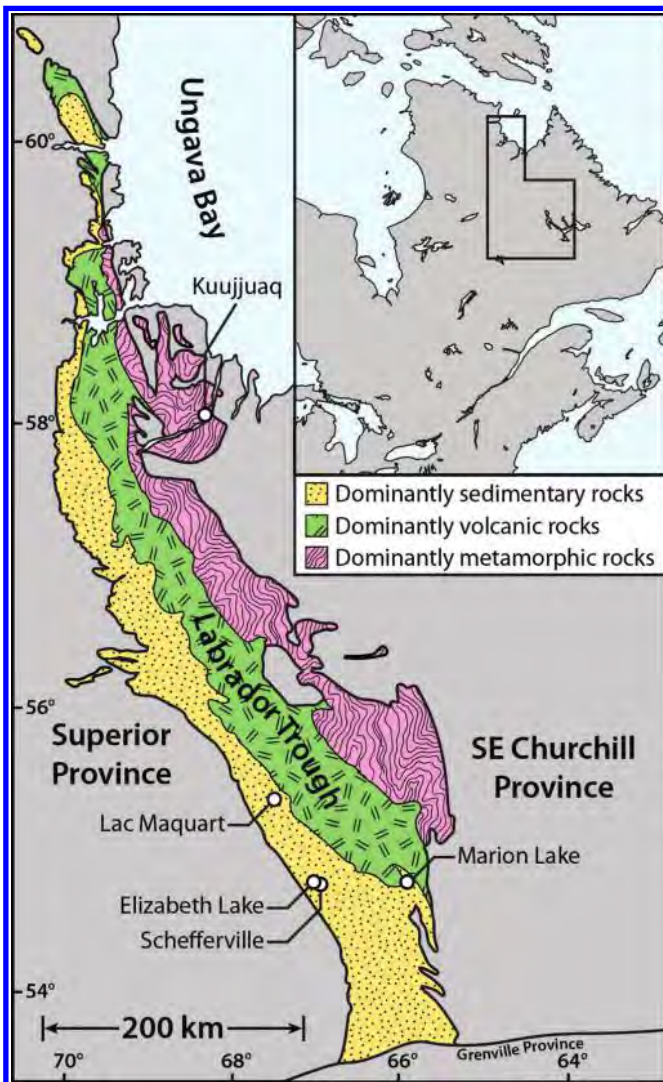
Received 24 October 2019. Accepted 25 February 2020.

M.S.W. Hodgskiss and E.A. Sperling. Department of Geological Sciences, Stanford University, 450 Serra Mall, Stanford, CA 94305, USA.
K.G. Lamothe* and G.P. Halverson. Department of Earth and Planetary Sciences, McGill University, 3450 Rue University, Montréal, QC H3A 0E8, Canada.
Corresponding author: Malcolm Hodgskiss (email: msw@stanford.edu).

*Present address: School of Earth Sciences, University of Melbourne, 253 Elgin Street, Carlton, VIC 3053, Australia.

Copyright remains with the author(s) or their institution(s). Permission for reuse (free in most cases) can be obtained from [RightsLink](https://www.copyright.com).

Fig. 1. Map of the Labrador Trough and location within Canada, showing localities visited for this study, as well as dominant lithologies. Base map and lithological data from Dimroth (1978) and Clark and Wares (2005), created in Adobe Illustrator CC 2017. [Colour online.]



nium, and sulphides, among others; Clark and Wares 2005). The Labrador Trough has been the subject of studies that have examined the carbon isotope composition of the stratigraphy, diagenetic fluids, Paleoproterozoic ocean chemistry, and redox state (Schrijver et al. 1986; Rosenbaum et al. 1995; Melezhik et al. 1997; Kuznetsov et al. 2003; Bekker et al. 2009; Raye et al. 2015; Kipp et al. 2017). Overall, the Labrador Trough represents a long and complex record of Paleoproterozoic Earth history, including early plate tectonics, the assembly of Laurentia, and dynamics of the global carbon cycle. To better understand the Labrador Trough in the context of the evolving Paleoproterozoic Earth system and the Lomagundi–Jatuli carbon isotope excursion, we conducted a carbon isotope chemostratigraphic study of the lower Labrador Trough succession.

The Lomagundi–Jatuli Excursion

The Lomagundi–Jatuli Excursion (LJE) is the largest positive carbon isotope excursion in Earth history, both in terms of duration and magnitude. It is recorded in Paleoproterozoic sedimentary successions around the world, including the Labrador Trough (Melezhik et al. 1997, 1999). The LJE is generally distinguished by highly elevated $\delta^{13}\text{C}$ values (+5‰ to +10‰; e.g., Karhu and Holland

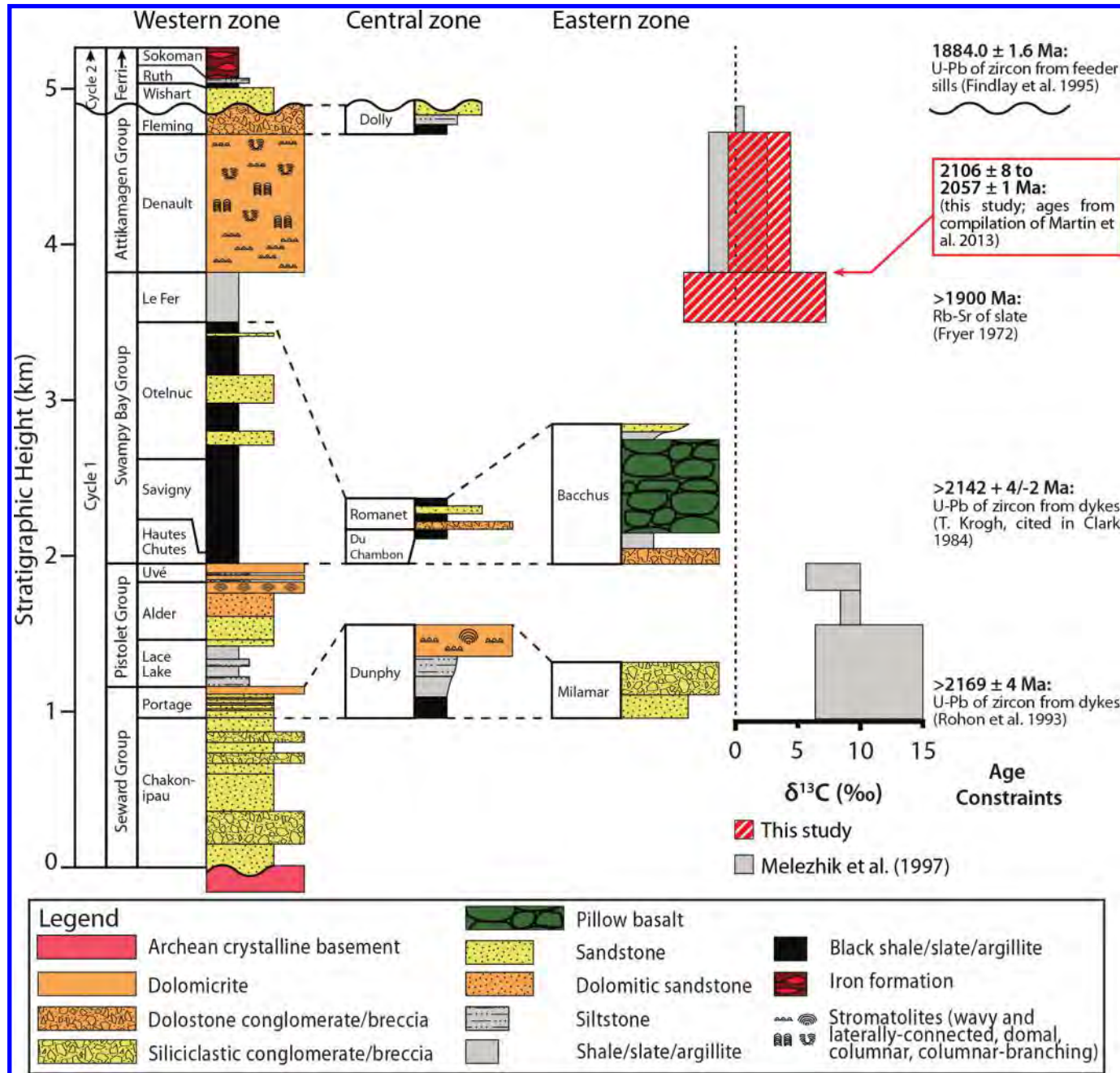
1996; Melezhik and Fallick 2010; Maheshwari et al. 2010), although it has also been noted that there is extreme variability in $\delta^{13}\text{C}$ between regions, and in some cases, within a single stratigraphic section (Melezhik et al. 1999; Hayes and Waldbauer 2006; Bekker et al. 2003), with some areas reaching extraordinary values of +28‰ (Bekker et al. 2003). The LJE is canonically interpreted to represent the burial of a high amount of organic carbon relative to carbonate carbon, with the corresponding production of excess oxygen (Karhu and Holland 1996), although both the significance and underlying causes for generating such ^{13}C -rich carbonates remains debated (e.g., Hayes and Waldbauer 2006; Schrag et al. 2013; Bachan and Kump 2015; Miyazaki et al. 2018). It has been suggested that the LJE came to an end as a result of a decrease in nutrient supply, especially phosphorus, to the global ocean (Bekker and Holland 2012). Triple-oxygen isotope data from sulphate minerals suggest that the end of the LJE did coincide with a decline of at least 80% in primary biospheric productivity (Hodgskiss et al. 2019a). Although the LJE is found globally, it has surprisingly large age uncertainties. Based on global age constraints and assuming a synchronous initiation and termination of the LJE, onset occurred ca. 2306 ± 9 to 2221 ± 5 Ma and termination occurred ca. 2106 ± 8 to 2057 ± 1 Ma (Karhu and Holland 1996; Martin et al. 2013).

In many successions that record the end of the LJE, the uppermost ^{13}C -enriched carbonates underlie (or are interbedded with) highly organic-rich, typically fine-grained clastic sedimentary rocks. In Fennoscandia, the Tulomozero Formation (with $\delta^{13}\text{C}$ from +5.5‰ to +17.1‰; Melezhik et al. 1999) is overlain by highly organic-rich shale and bituminous rocks of the Zaonega Formation, with total organic carbon (TOC) up to 98 wt.% (Melezhik et al. 2004). The Francevillian F Formation in Gabon contains ^{13}C -enriched carbonate (with $\delta^{13}\text{C}$ from -3.3‰ to +9.7‰) overlain by organic-rich shales up to 22.5 wt.% TOC (Ossa et al. 2018). This stratigraphic relationship is replicated in the Snowy Pass Supergroup, Wyoming, USA. (Bekker et al. 2003), Union Island Group, Northwest Territories, Canada (Kipp et al. 2017; Magad-Weiss 2019; A.V.S. Hood and P.F. Hoffman, personal communications, 2019), and elsewhere. These organic-rich deposits, along with associated interbedded carbonates bearing very negative carbonate $\delta^{13}\text{C}$ values, record what some have interpreted to be a global negative carbon isotope excursion (with carbonate $\delta^{13}\text{C}$ reaching approximately -14‰). This so-called “Shunga Excursion” has been observed in both Fennoscandia and Gabon (Kump et al. 2011), but data increasingly imply that these values record a combination of local and diagenetic factors such as a methanogenesis and post-depositional alteration (Qu et al. 2012; Weber and Gauthier-Lafaye 2013; Črne et al. 2014; Kreitsmann et al. 2019).

Geological context

The stratigraphy of the Labrador Trough, formally comprising the Kaniapiskau Supergroup, is divided into numerous groups (Seward, Pistolet, Swampy Bay, Attikamagen, and others) and three informal depositional “cycles” bounded by unconformities. Cycle 1, the lowest, directly overlies Archean granites and gneisses and is the subject of this study. It consists of the Seward Group, composed of fine- to coarse-grained siliciclastic sedimentary rocks and basalt (Chakonipau Formation), with mixed carbonate-siliciclastic formations (Portage, Dunphy, and Milamar formations; Dimroth 1978). The overlying Pistolet Group transitions from fine-grained siliciclastic lithologies at the base (Lace Lake Formation) to mixed carbonate-siliciclastic (Alder Formation) and finally a carbonate-dominated succession at the top (Uvé Formation; Dimroth 1978). The Swampy Bay Group is dominated by fine-grained clastic sedimentary rocks in the western (Hautes Chutes, Savigny, and Otelnuic formations) and central Labrador Trough (Romanet and Du Chambon formations), but it is dominated by basalt in the eastern region (Bacchus Formation; Dimroth 1978). At the top of the Swampy Bay Group is the poorly

Fig. 2. Highly simplified stratigraphy of Cycle 1 and lower Cycle 2 in the Labrador Trough (Dimroth 1978). $\delta^{13}\text{C}$ data from Melezhik et al. (1997; grey boxes) show extreme ^{13}C -enrichment in carbonate sedimentary rocks of the Portage, Dunphy, Alder, and Uvé formations, consistent with deposition during the Lomagundi–Jatuli Excursion (LJE). New $\delta^{13}\text{C}$ data from this study (red striped boxes) show that the LJE continues during deposition of the Le Fer Formation, and concludes at or very near the Le Fer/Denault contact. The Denault and Fleming formations then record $\delta^{13}\text{C}$ values near 0‰. Age constraints from within the Labrador Trough shown at right (Fryer 1972; T. Krogh, cited in Clark 1984; Rohon et al. 1993; Findlay et al. 1995; Martin et al. 2013; refer to main text for details). The new age constraint on the Le Fer – Denault contact presented here (2106 ± 8 to 2057 ± 1 Ma; based on global correlations from Martin et al. 2013) suggests that the erosional unconformity between Cycles 1 and 2 represents a significant hiatus, perhaps >100 Myr. Ferri., Ferriman Group. [Colour online.]

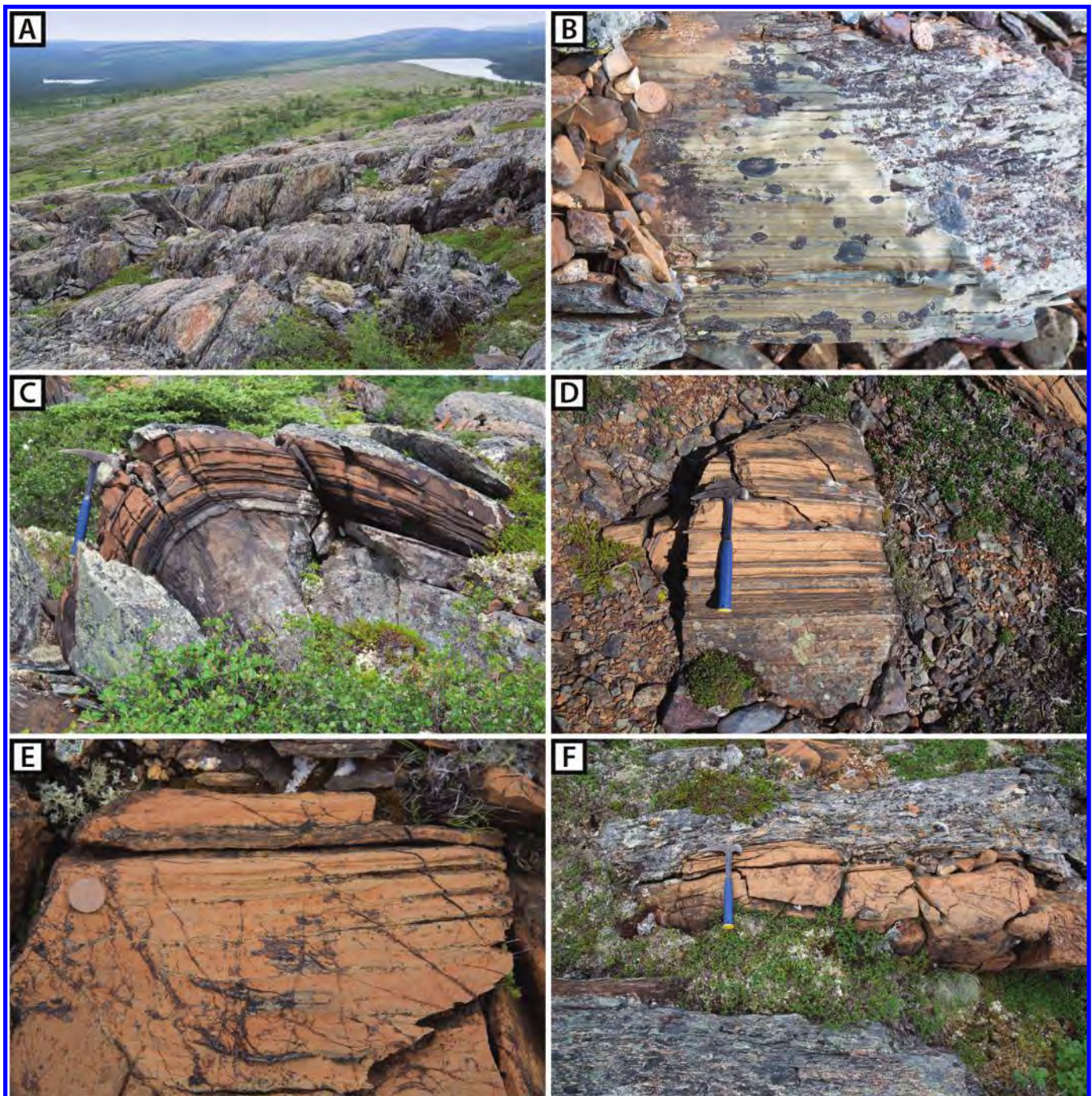


exposed, dominantly siliciclastic Le Fer Formation (Fig. 3). The overlying Denault Formation (lower Attikamagen Group; Fig. 4) is composed largely of dolostone. Stratigraphy overlying the Denault Formation consists of chert breccia (Fleming Formation) and fine-grained sandstone, siltstone, and mudstone (Dolly Formation; Dimroth 1978). The top of Cycle 1 is marked by a low angle erosional unconformity (Fig. 2).

Cycle 1 is interpreted as recording the formation of an intracratonic rift basin and the subsequent development of a passive

margin (Clark and Wares 2005). The deposition of immature, continental rift sandstone and conglomerate is recorded by the Chakonipau Formation (lower Seward Group), which is in turn overlain by the passive margin sandstone and carbonate of the correlative Portage, Dunphy, and Milamar formations (upper Seward Group), as well as the overlying Pistolet Group. The passive margin was subsequently drowned, concomitant with deposition of the Swampy Bay Group, which is dominated by fine-grained clastic sediments and basalt (Clark and Wares 2005;

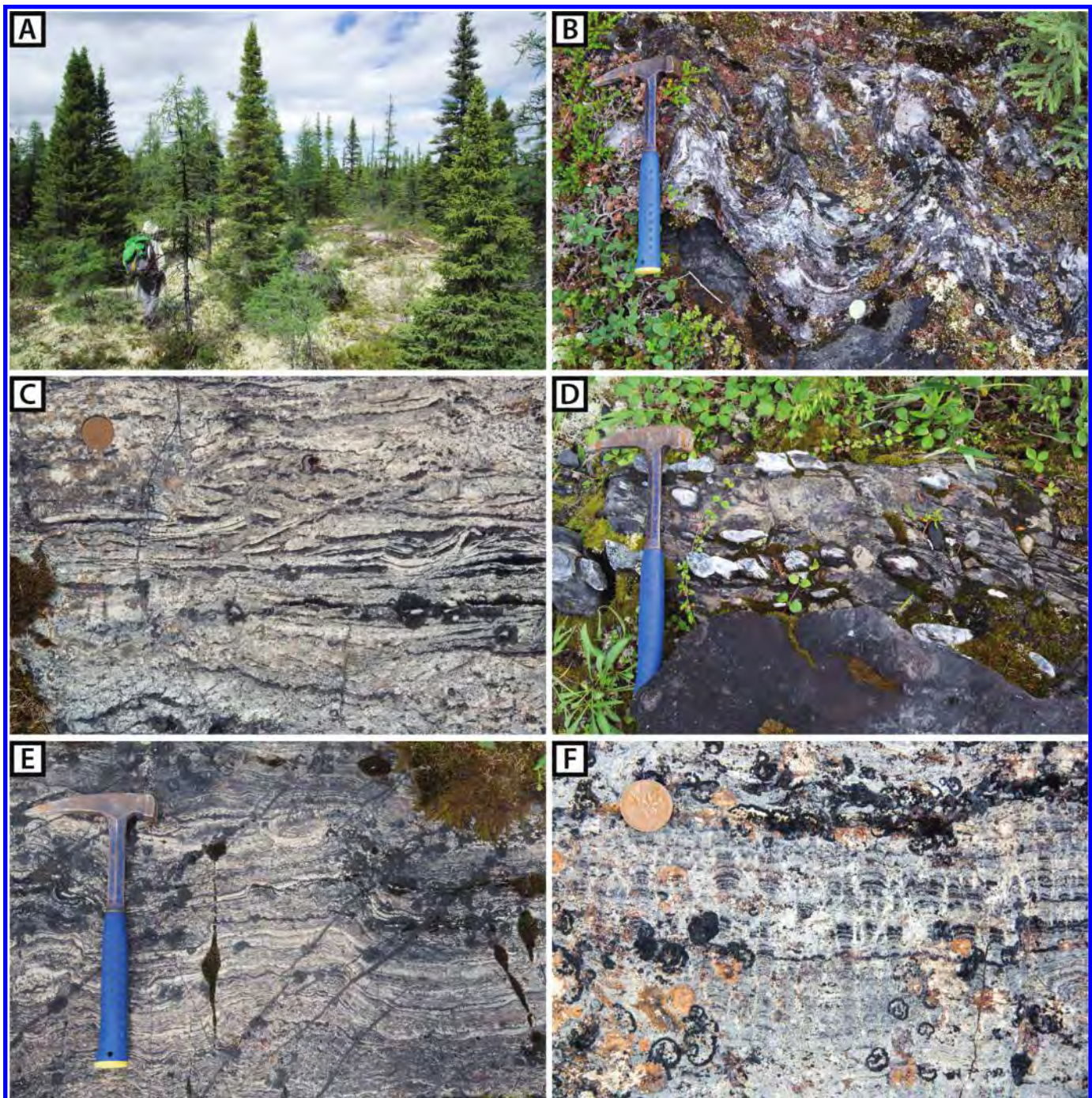
Fig. 3. Representative photographs of the Le Fer Formation at Lac Maquart, the type locality (Dimroth 1978). (A) View south toward Lac Maquart (top right). (B) Laminated silty shale that comprises the vast majority of the Le Fer Formation. Canadian penny for scale (diameter of 19 mm). (C) Folded dolomiticrite and silty shale beds. Hammer for scale. (D) Well-laminated and bedded dolomiticrite with thin interbeds of silty shale. Hammer for scale. (E) Crudely laminated dolomiticrite. Penny for scale. (F) Crudely laminated lens of dolomiticrite in silty shale. Hammer for scale. [Colour online.]



Bekker et al. 2009). The Le Fer and Denault formations of the overlying Attikamagen Group are the focus of this study. The Le Fer Formation is composed of variably red, green, and grey silty shale, commonly with tabular laminations (Dimroth 1971, 1978). Very minor beds of fine- to medium-grained sandstone, as well as variably shaley dolomiticrite beds and lenses ranging in thickness from <10 cm to several metres, constitute a very small portion of the formation. Dimroth (1971, 1978) interpreted the Le Fer Formation to have been deposited below the fair-weather wave base,

potentially in a prodelta setting. The overlying Denault Formation is composed dominantly of dolograstone, stromatolitic dolostone, and microbialaminite, with lesser amounts of dolomitic breccia and conglomerate, and minor fine sandstone and mudstone (Dimroth 1971, 1978; Zentmyer et al. 2011). The Denault Formation is interpreted to have been deposited on an eastward-dipping carbonate ramp, with some localities representing potential offshore highs (Zentmyer et al. 2011). Hoffman and Grotzinger (1989) documented a stromatolite reef complex in the

Fig. 4. Representative photographs of the Denault Formation at Marion Lake. (A) Representative exposure of the Denault Formation at Marion Lake, which is considerably worse than the near 100% exposure reported for this locality by Donaldson (1963). (B) Conophyton stromatolites. Hammer for scale. (C) Tabular intraclast breccia. Canadian penny for scale (diameter of 19 mm). (D) Scattered chert nodules, some of which occur preferentially along stratigraphic horizons. Hammer for scale. (E) Microbialaminite and bioherms. Hammer for scale. (F) Minidigitate stromatolites, likely the result of chemical precipitation of carbonate minerals (Hofmann and Jackson 1987). Canadian penny for scale. [Colour online.]



laterally equivalent Abner Formation in the northern Labrador Trough, ~300 km north–northwest of the area studied here. Deposition of the Denault Formation (and Abner Formation) is interpreted to represent the reestablishment and progradation of a carbonate platform sequence (Clark and Wares 2005).

Direct depositional ages are sparse in the Labrador Trough. Zircons from a granophyre dyke intruding the Chakonipau Formation (lowest Cycle 1) yield a U–Pb isotope dilution thermal ionization mass spectrometry (ID–TIMS) age of 2169 ± 2 Ma (Rohon

et al. 1993). Zircons extracted from a rhyolite dyke intruding the Bacchus Formation were dated at 2142 ± 4 – 2 Ma (T. Krogh, cited in Clark 1984). Rb–Sr dating of slate in the Le Fer Formation provided an age of ca. 1900 Ma (Fryer 1972). Deposition of Cycle 2 is constrained to have commenced by 1884.0 ± 1.6 Ma (Findlay et al. 1995) based on U–Pb zircon analyses of ages from gabbro sills that are interpreted as feeder sills to basalt within the Menihok Formation (lower Cycle 2). More recently, Henrique-Pinto et al. (2017) applied detrital zircon geochronology to the Kaniapiskau Supergroup, but

all ages were >2500 Ma — significantly older than depositional age constraints.

Carbon isotope chemostratigraphy of the Labrador Trough

Existing carbonate $\delta^{13}\text{C}$ data (Schrijver et al. 1986; Rosenbaum et al. 1995; Melezhik et al. 1997) for the Labrador Trough are limited and lacking the sampling density of modern studies (e.g., Bekker et al. 2003). Melezhik et al. (1997) measured the $\delta^{13}\text{C}$ composition of major carbonate units through Cycle 1 and observed a stepwise decrease in $\delta^{13}\text{C}$ near the top of the cycle (Fig. 2). Most $\delta^{13}\text{C}$ analyses from Cycle 1 record extreme ^{13}C -enrichment: the Dunphy Formation (+14.5‰ to +15.4‰; $N = 4$), Portage Formation (+6.1‰; $N = 1$), Pistolet Group (+8.8‰ to +11.2‰; $N = 5$; formations unspecified), Alder Formation (+8.7‰ to +10.2‰; $N = 4$), and Uvé Formation (+5.3‰ to +10.4‰; $N = 9$) are all consistent with deposition during the LJE. These very positive $\delta^{13}\text{C}$ values are followed by a significant decrease, as recorded in the Denault Formation and laterally equivalent Abner Formation (−2.0‰ to +3.2‰; $N = 24$), and finally the Fleming Formation (−0.6‰; $N = 1$). The return to $\delta^{13}\text{C}$ values near 0‰ in the Denault, Abner, and Fleming formations suggests that they were deposited following the end of the LJE.

The $\delta^{13}\text{C}$ variations reported by Melezhik et al. (1997) raise the question of where the end-LJE lies within the stratigraphy of the Labrador Trough, given that much of these data are insufficiently stratigraphically resolved to evaluate any long-term trends in $\delta^{13}\text{C}$. Nonetheless, the significant decrease in $\delta^{13}\text{C}$ would suggest that the end of the LJE occurs somewhere between the Uvé Formation and the stratigraphically higher Denault Formation (and laterally equivalent Abner Formation). Unfortunately, this interval is dominated by fine-grained siliciclastic sedimentary rocks, hindering high-resolution sampling of carbonate rocks across this portion of the stratigraphy (Fig. 2). We targeted the Le Fer Formation, which has been reported to contain very minor beds and lenses of dolomicrite, shaley dolomite, and dolomitic shale, as well as the carbonate-dominated Denault Formation that directly overlies it to better constrain the variations in $\delta^{13}\text{C}$ across this critical interval.

Given that in many LJE successions, extremely ^{13}C -enriched carbonates are followed by deposition of high-TOC sedimentary rocks prior to the return to baseline $\delta^{13}\text{C}$ values near 0‰, it seems probable that the sedimentary record in the Labrador Trough should be analogous. Specifically, it predicts that in the Labrador Trough, the LJE terminated before (or perhaps during) deposition of the Hautes Chutes Formation, which contains up to 15 wt.% TOC (Kipp et al. 2017). It follows that carbonate lithologies in the Le Fer Formation would therefore record $\delta^{13}\text{C}$ values near 0‰, similar to the overlying Denault Formation, which has been documented to record $\delta^{13}\text{C}$ values between −2.0‰ and +3.2‰ (Melezhik et al. 1997). However, this hypothesis requires a globally synchronous termination of the LJE and would be complicated by the occurrence of any post-LJE positive carbon isotope excursions. One possible excursion has been identified in the 2.03 Ga “Woolly Dolomite” (where 57 m of carbonate sedimentary rocks record $\delta^{13}\text{C}$ values up to +8.4‰; Bekker et al. 2016), although it is unclear if these values reflect a global excursion.

Methods

Samples were cut using a diamond saw to remove weathered portions, then drilled on fresh surfaces, taking care to avoid fractured or coarsely recrystallised regions. The resulting powders were used for all subsequent analyses.

Carbon and oxygen isotope analyses were carried out in the Stable Isotope Laboratory at McGill University, Montréal, Québec, Canada, using a Nu Instruments (Wrexham, UK) Perspective iso-

tope ratio mass spectrometer coupled to a Nu Carb sample preparation device. Repeat analyses of standard reference materials yielded 2σ uncertainties of $\pm 0.1\%$ and $\pm 0.2\%$ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively. All $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements are reported relative to Vienna Pee Dee Belemnite (V-PDB).

Major, minor, and trace element abundance measurements were performed at l’Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, France. To dissolve only the carbonate fraction (i.e., excluding clays and silicates), a weak dissolution procedure was used (Rongemaille et al. 2011). Approximately 20 mg of powder was dissolved in 0.5 mL 5% acetic acid overnight at room temperature. Measurements were performed on a Thermo Scientific (Waltham, Massachusetts, USA) ELEMENT XR high-resolution inductively coupled plasma mass spectrometer. Repeat analyses of the CAL-S standard reference material yielded 1σ uncertainties of $\leq 9\%$ for Ca, Mg, Mn, and Sr, and 12% for Fe. Refer to Hodgskiss et al. (2019b) for detailed methods.

Results

Stratigraphy

Le Fer Formation

The Le Fer Formation was studied at Lac Maquart (Figs. 1, 5), the type locality defined by Dimroth (1978). The sections, where exposed, are composed almost entirely of green-grey silty shale. Due to the extremely homogenous nature of the Le Fer Formation, combined with poorly visible laminations in outcrop, it is difficult to conclusively identify all folds and deformation; thicknesses are therefore regarded as approximate. One partial section was measured spanning approximately 1050 m, as well as four smaller, partial sections (Fig. 5). Very minor fine sandstone beds, and beds and lenses of dolomicrite, shaley dolomite, and dolomitic shale, occurred throughout the section, with carbonate lithologies being laterally discontinuous over tens to hundreds of metres (Fig. 3).

Denault Formation

The Denault Formation was studied at Marion Lake and an unnamed lake near Elizabeth Lake (Figs. 1, 6). The stratigraphic section at Marion Lake measured 653 m thick and was composed largely of dolograstone, stromatolitic dolostone, and microbially laminated dolostone (Fig. 4). Chert nodules occur irregularly. The stratigraphic section measured near Elizabeth Lake was approximately 228 m thick and dominated by massive dolomicrite with rare current ripples and minor dolograstone. Neither the lower nor upper contacts were exposed at either location.

Carbon and oxygen isotopes

A total of 210 samples were analysed from five partial sections of the Le Fer Formation, and two partial sections of the Denault Formation. Refer to Supplementary Information¹ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

Le Fer Formation

Measured values of $\delta^{13}\text{C}$ vary considerably within the Le Fer Formation, even over very short stratigraphic intervals. Samples range between −4.4‰ and +6.9‰, with variation of several permil over tens of centimetres (and within the same bed), and almost 5‰ over just 10 m (Figs. 5 and 7). $\delta^{18}\text{O}$ values generally range from −10.2‰ to −5.1‰.

Denault Formation

In contrast to the Le Fer Formation, $\delta^{13}\text{C}$ measurements of the Denault Formation are relatively coherent and record a comparatively small range of −0.5‰ to +4.3‰. Variations are smooth and exhibit a trend of decreasing $\delta^{13}\text{C}$ values up-section (Figs. 6 and 7). $\delta^{18}\text{O}$ values generally range from −7.2‰ to −3.9‰.

¹Supplementary data are available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/cjes-2019-0198>.

Fig. 5. Stratigraphy and $\delta^{13}\text{C}$ chemostratigraphy of the Le Fer Formation at Lac Maquart. (A) Drone photomosaic of the Le Fer Formation, showing locations of measured sections. Note that the grey-orange expanse in the top half of the image is orange-grey soil, not exposed Le Fer Formation. (B) Partial sections of the Le Fer Formation that range in thickness from almost 1050 m (ML1804) to just over 20 m (ML1808). The formation is dominated by grey-green silty shale, with only very minor amounts of dolomiticrite, silty dolomiticrite, and sandstone. $\delta^{13}\text{C}$ varies considerably over very short stratigraphic distances, with variations up to 5‰ over approximately 12 metres. $\delta^{13}\text{C}$ can also vary by several permil over tens of centimetres within the same bed, like other areas that have undergone significant post-depositional alteration (e.g., Kreitsmann et al. 2019). The most positive sample reaches +6.9‰, consistent with deposition during the Lomagundi–Jatuli Excursion. Note that vertical scale varies between some sections. In section ML1803, the Wishart Formation (Wish) is erosively unconformable with the underlying Le Fer Formation. The Le Fer Formation continues after some 37 m of Wishart Formation, with the contact being an inferred fault (the contact is not exposed). [Colour online.]

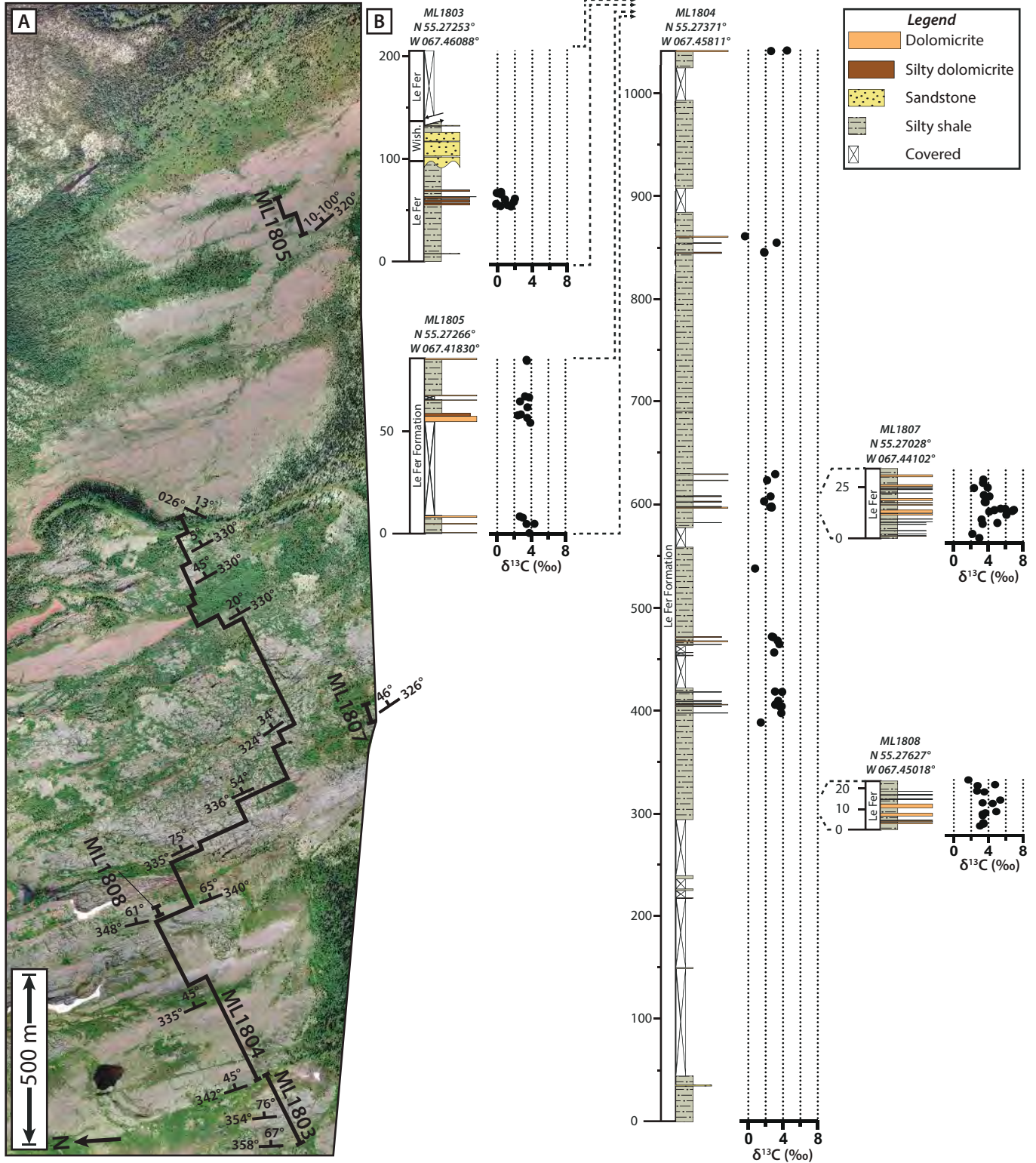


Fig. 6. Partial stratigraphic sections of the Denault Formation near Elizabeth Lake and Marion Lake. The section at Elizabeth Lake consists largely of featureless dolomicrite, whereas Marion Lake consists of abundant dolograinstone and microbialaminite, with a significant diversity of stromatolite morphologies. $\delta^{13}\text{C}$ at Elizabeth Lake increases slightly from +3.0‰ to +3.7‰ (with an outlier of +4.3‰ near the base), before decreasing to +1.8‰ at the top of the section. At Marion Lake, $\delta^{13}\text{C}$ values rise from near +1.0‰ at the base of the section to +1.5‰, before declining to +0.5‰. Refer to main text for detailed discussion of correlation between these stratigraphic sections. [Colour online.]

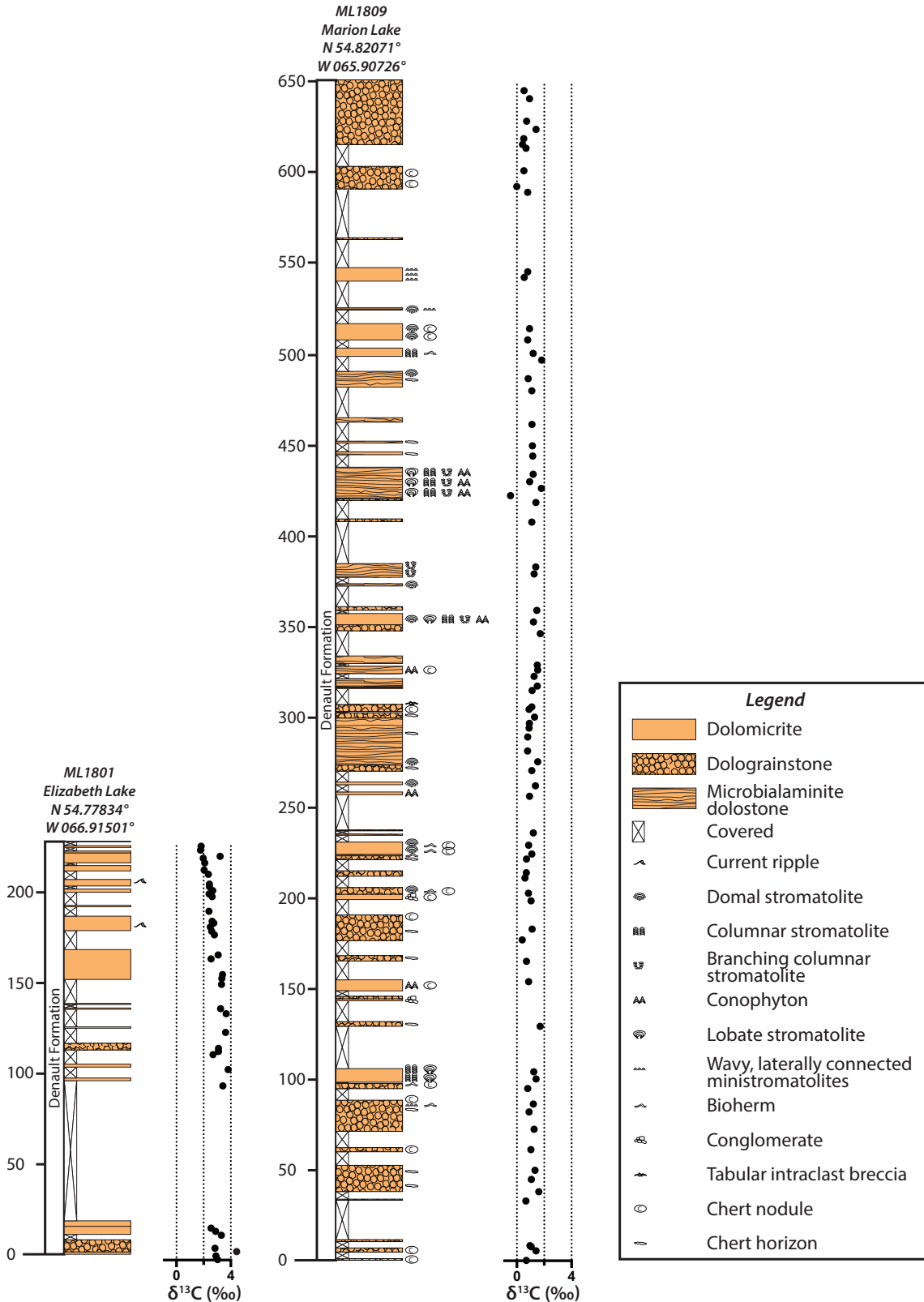
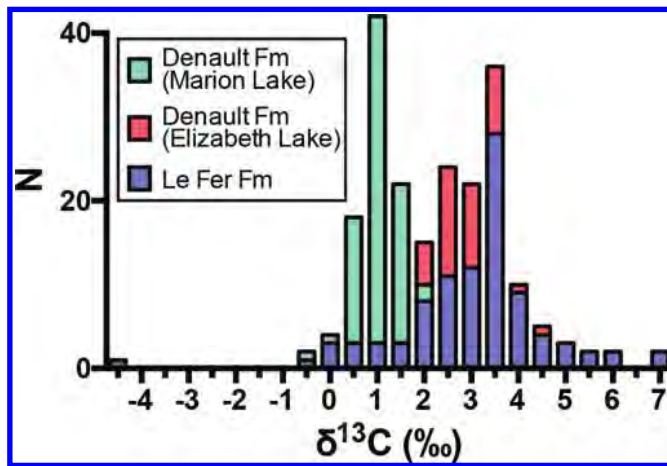


Fig. 7. Histogram of $\delta^{13}\text{C}$ results for the Le Fer and Denault formations (box width of 0.5‰). The Le Fer Formation is considerably more variable than the Denault Formation, with a peak at +3.5‰, and values reaching up to +6.9‰. The Denault Formation is strongly bimodal, with samples from Elizabeth Lake being significantly more ^{13}C -enriched than samples from Marion Lake. [Colour online.]



Major, minor, and trace element concentrations

A subset of 69 samples from the Le Fer and Denault formations were measured for major, minor, and trace element concentrations. A total of 33 samples from the Le Fer Formation were selected to capture the general range of $\delta^{13}\text{C}$ values, with an emphasis on the most ^{13}C -rich samples. A total of 36 samples from the Denault Formation provide a stratigraphic resolution of approximately 20–30 metres. Refer to Supplementary Information¹ for elemental abundance values.

Le Fer Formation

In the Le Fer Formation, calcium concentrations range from 1.6 to 14.8 wt.%, and magnesium concentrations range from 0.8 to 8.2 wt.%. The ranges for manganese, strontium, and iron concentrations are 940 to 11 500 ppm, 45 to 400 ppm, and 0.8 to 3.6 wt.%, respectively. Magnesium-calcium ratios (Mg/Ca) range from 0.72 to 0.98 (mol/mol), and manganese-strontium ratios (Mn/Sr; mol/mol) ratios range from 13.8 to 196. Finally, Fe/(Ca+Mg+Fe) ratios range from 0.023 to 0.20 (mol/mol).

Denault Formation

In the Denault Formation, calcium concentrations range from 6.9 to 15.4 wt.%, and magnesium concentrations range from 4.3 to 9.8 wt.%. The ranges for manganese, strontium, and iron concentrations are 150 to 3000 ppm, 23 to 87 ppm, and 0.05 to 1.9 wt.%, respectively. Mg/Ca ranges from 0.94 to 1.12, Mn/Sr ranges from 6.2 to 92.6, and Fe/(Ca+Mg+Fe) ranges from 0.0015 to 0.086.

Discussion

Primary versus secondary isotopic signatures

As with any ancient carbonate sedimentary rock sequence, it is important to consider how the measured geochemical signatures may have been modified by post-depositional processes. This is particularly true for the Le Fer Formation, in which samples have generally low carbonate contents, and are therefore not ideal chemostratigraphic targets. To characterise how isotopic signatures have been altered, we used elemental abundances and ratios (Mg/Ca, Mn/Sr, Ca+Mg, Fe/(Ca+Mg+Fe)), as well as isotope ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$). Increasing Mg/Ca values are indicative of dolomitisation and are accompanied by increasing $\delta^{18}\text{O}$ values when that dolomitisation occurs early (Land 1980). Increasing Mn/Sr values are indicative of increased meteoric alteration and burial diagenesis, both of which will decrease $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Brand and

Veizer 1980, 1981). An approximation of the carbonate content can be made using Ca+Mg, reflecting the combination of calcite and dolomite (and perhaps magnesite). Samples with lower Ca+Mg values would be less carbonate-buffered and, therefore, more susceptible to diagenetic processes. Further, the bulk-rock chemistry of a sample with only a small amount of “primary carbonate” would be more sensitive to change from the formation of authigenic or diagenetic carbonate than a sample with a very large amount of “primary carbonate”. If the authigenic carbonate has a carbon source with a negative $\delta^{13}\text{C}$ composition, such as organic matter, then decreasing Ca+Mg should accompany lower $\delta^{13}\text{C}$ values. The formation of authigenic carbonates will result in increasing Fe/(Ca+Mg+Fe) values and decreasing Mg/Ca, both of which correspond to decreasing $\delta^{13}\text{C}$ values (Brand and Veizer 1980). Finally, comparison of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is useful for broadly evaluating diagenesis and open system behaviour: if there is a strong positive relationship, the samples with the highest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values should generally reflect most “primary” seawater values (Brand and Veizer 1981).

Le Fer Formation

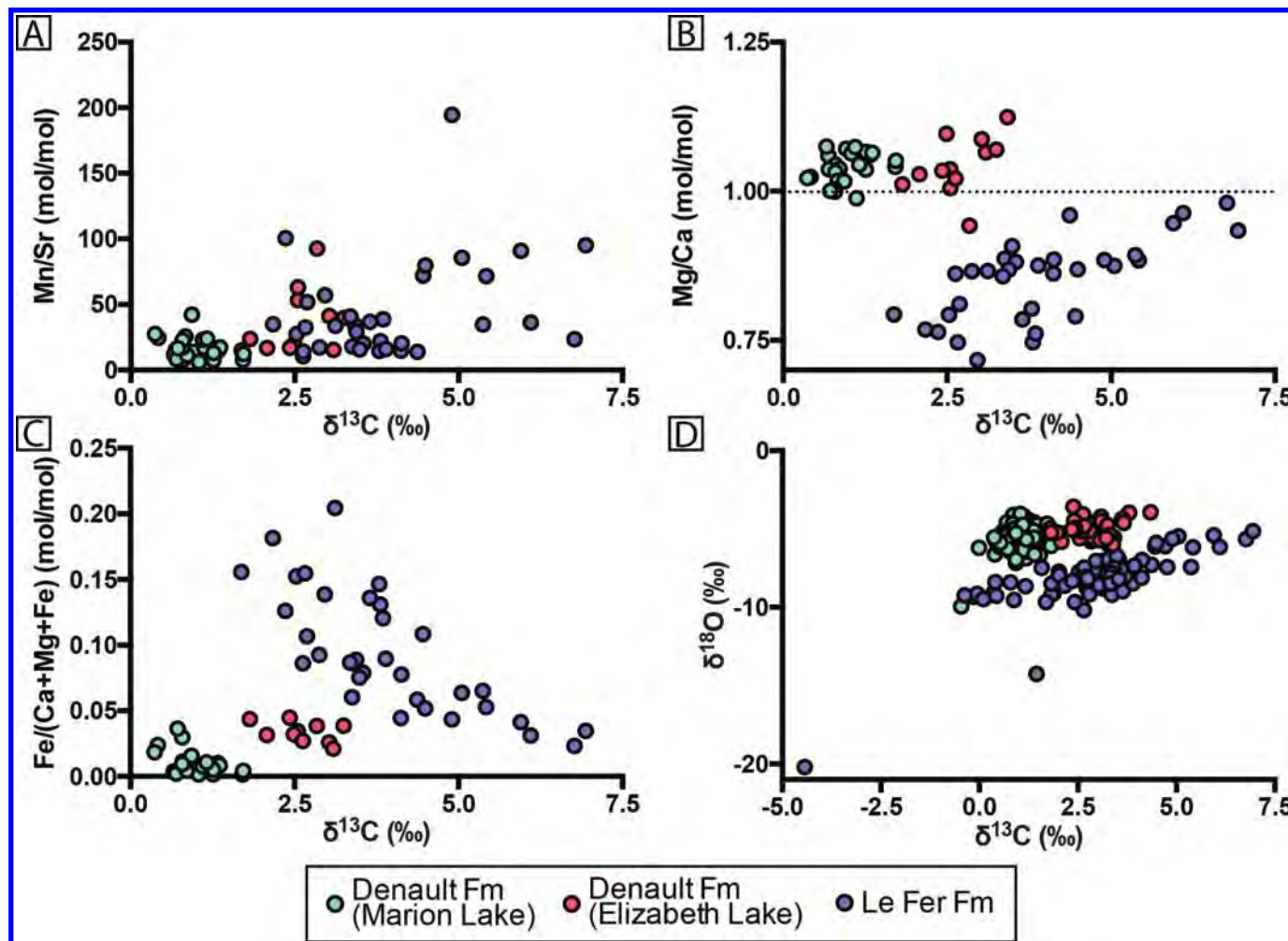
In the Le Fer Formation, $\delta^{18}\text{O}$ values have only a very weak positive correlation with traditional proxies for dolomitisation and diagenesis, with R^2 values of 0.24 and 0.36 for Mg/Ca and Mn/Sr, respectively. However, $\delta^{18}\text{O}$ has a strong, positive relationship with $\delta^{13}\text{C}$ ($R^2 = 0.69$), consistent with open system behaviour and modification of isotopic values (Fig. 8D). Although $\delta^{13}\text{C}$ values correlate better with Mg/Ca ($R^2 = 0.48$), Mn/Sr ratios have a very weak relationship ($R^2 = 0.12$). $\delta^{13}\text{C}$ has a weak positive relationship ($R^2 = 0.44$) with Ca+Mg, consistent with some amount of authigenic carbonate shifting bulk $\delta^{13}\text{C}$ toward less positive values. $\delta^{13}\text{C}$ has a negative relationship with Fe/(Ca+Mg+Fe), with an R^2 of 0.57, again suggesting that the formation of authigenic carbonate minerals shifted bulk-rock $\delta^{13}\text{C}$ toward less positive values. Extrapolating to an Fe content of near zero (i.e., with only very minor authigenic carbonate, as in the Denault Formation) would suggest primary $\delta^{13}\text{C}$ values near +7.4‰. The strong relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($R^2 = 0.69$) is consistent with secondary alteration of bulk isotopic signatures. Although metamorphism generally results in more negative $\delta^{13}\text{C}$ values (Valley 1986), the subgreenschist facies of the Le Fer Formation samples studied here (Dimroth 1978) makes metamorphic reactions an unlikely factor for significant $\delta^{13}\text{C}$ modification.

Considering the relatively strong relationships between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ and Fe/(Ca+Mg+Fe) (Figs. 8C, 8D), we interpret the most positive $\delta^{13}\text{C}$ values in the Le Fer Formation to reflect the most “primary” isotopic signatures. It is likely that the carbonate lithologies in the Le Fer Formation underwent intense diagenetic alteration in part because they are in a formation consisting almost entirely of silty shale and are therefore not carbonate-buffered. The bulk-rock $\delta^{13}\text{C}$ values may be further offset from “primary” values by a variable contribution from ^{13}C -depleted authigenic carbonate minerals.

Denault Formation

The correlation between diagenetic proxies and $\delta^{13}\text{C}$ values is considerably weaker in the Denault Formation. Mg/Ca and Mn/Sr ratios have R^2 values of 0.09 and 0.13, respectively, when compared with $\delta^{13}\text{C}$ (Figs. 8A, 8B). Similarly, $\delta^{18}\text{O}$ has only a very weak relationship with $\delta^{13}\text{C}$, with an R^2 of 0.11 (Fig. 8D). The relationship between $\delta^{13}\text{C}$ and Mg/Ca and Mn/Sr is also weak, with R^2 values of 0.05 and 0.22, respectively. There is no relationship between $\delta^{13}\text{C}$ and Ca+Mg ($R^2 = 0.00$), suggesting that changes in bulk-rock $\delta^{13}\text{C}$ as a consequence of being poorly carbonate-buffered are negligible, consistent with the Denault Formation being dominantly carbonate. $\delta^{13}\text{C}$ has an R^2 of 0.44 when compared with Fe/(Ca+Mg+Fe) (Fig. 8C), but the relationship is opposite of what would be expected during the formation of authigenic carbonates. Even when

Fig. 8. Comparison of diagenetic proxies against $\delta^{13}\text{C}$ values for the Le Fer and Denault formations. (A) Mn/Sr does not correlate with $\delta^{13}\text{C}$ in either formation, although the Le Fer Formation exhibits higher Mn/Sr values, consistent with increased meteoric and burial diagenesis. (B) The Le Fer Formation exhibits a positive relationship ($R^2 = 0.48$) between Mg/Ca and $\delta^{13}\text{C}$, consistent with the formation of authigenic carbonate minerals bearing less positive $\delta^{13}\text{C}$ values (e.g., Kreitmann et al. 2019). In contrast, both sections of the Denault Formation exhibit Mg/Ca values near or slightly above 1, consistent with being composed of dolomite and perhaps some amount of magnesite. (C) The Le Fer Formation exhibits a relatively strong negative relationship between $\text{Fe}/(\text{Ca}+\text{Mg}+\text{Fe})$ and $\delta^{13}\text{C}$ ($R^2 = 0.57$), again consistent with the formation of Fe-bearing authigenic minerals, resulting in less positive $\delta^{13}\text{C}$ values. The Denault Formation exhibits a relationship between $\text{Fe}/(\text{Ca}+\text{Mg}+\text{Fe})$ and $\delta^{13}\text{C}$ ($R^2 = 0.44$), although the positive slope is opposite to what would be expected if the formation of authigenic minerals was changing bulk-rock $\delta^{13}\text{C}$ values. (D) The Le Fer Formation exhibits a strong positive relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ($R^2 = 0.69$), consistent with relatively open system behaviour and modification of “primary” isotopic signatures. The Denault Formation, in contrast, exhibits no such relationship ($R^2 = 0.11$). [Colour online.]



the sections at Elizabeth Lake and Marion Lake are considered separately, the relationships between $\text{Fe}/(\text{Ca}+\text{Mg}+\text{Fe})$ and $\delta^{13}\text{C}$ are still very weak (0.09 and 0.20, respectively). Ultimately, we conclude that although $\delta^{18}\text{O}$ values of the Denault Formation likely experienced considerable post-depositional alteration, the $\delta^{13}\text{C}$ values were not altered by these secondary processes and likely reflect conditions during formation and deposition of the original carbonate sediment. This improved preservation of geochemical signatures in the Denault Formation, when compared with the Le Fer Formation, can be attributed to being composed nearly entirely of carbonate lithologies.

Carbon isotope chemostratigraphy

Possible drivers of ^{13}C -enrichment in the Le Fer Formation

The $\delta^{13}\text{C}$ values measured in the Labrador Trough are notably positive, with the most positive values overlapping with published LJE values (e.g., Karhu and Holland 1996). To determine if

these samples can be assigned to the LJE, we explore possible scenarios for their ^{13}C -enrichment.

Methanogenesis is one possible mechanism to consider for the very positive $\delta^{13}\text{C}$ values measured in the Le Fer Formation (up to +6.9‰). The degradation of organic matter results in the production of ^{13}C -poor methane and ^{13}C -rich carbon dioxide (Irwin et al. 1977). Dissolution of this carbon dioxide in water shifts the $\delta^{13}\text{C}$ of the local dissolved inorganic carbonate (DIC) reservoir toward higher values (+15‰ to +30‰). Methane, although insoluble in water, can undergo anaerobic oxidation that drives local DIC toward very negative values (−60‰; e.g., Birgel et al. 2006; Naehr et al. 2007). Studies of modern methane seep environments have documented large variations in $\delta^{13}\text{C}$ values, with ranges as large as −60‰ to +30‰ at a single site (Naehr et al. 2007). The range of $\delta^{13}\text{C}$ values in the Le Fer Formation (−4.4‰ to +6.9‰), is relatively small in comparison to that of methane seeps. Further, methanogenesis requires a source of organic carbon to degrade. Although

TOC contents were not measured on the Le Fer Formation, the grey-green appearance at the locality measured (and red to grey elsewhere; Dimroth 1978) are consistent with very low TOC contents, making significant methanogenesis within Le Fer Formation sediments unlikely.

In modern carbonate platforms, such as the Bahamas, water mass restriction can result in the precipitation of carbonate sediments with $\delta^{13}\text{C}$ values several permil higher than that of marine DIC (Patterson and Walter 1994), a trend that has similarly been recognised in ancient carbonate platforms (e.g., Halverson et al. 2005). Although having only a single section through the Le Fer Formation prohibits identification of any similar isotopic gradient, we note that the Le Fer Formation is interpreted to have been deposited below the fair-weather wave base (Dimroth 1971, 1978), with the relatively deep depositional environment suggesting that local water mass restriction is unlikely to have played a significant role in shifting $\delta^{13}\text{C}$ toward higher values.

Diagenesis, the formation of authigenic carbonate minerals, nor metamorphic reactions are likely causes for these positive $\delta^{13}\text{C}$ values, given that all three processes would shift the isotopic composition toward more negative values.

It would, therefore, appear unlikely that the most positive $\delta^{13}\text{C}$ values in the Le Fer Formation can be attributed to methanogenesis, water mass restriction, diagenesis, authigenic carbonate formation, or metamorphism. Overall, these data are consistent with the Le Fer Formation recording precipitation from ^{13}C -rich seawater. Although the large scatter in Le Fer Formation $\delta^{13}\text{C}$ values (likely due to diagenesis and the formation of authigenic carbonate minerals) prohibits the interpretation of changes in $\delta^{13}\text{C}$ with respect to stratigraphic height or secular changes in the Earth system, the highest $\delta^{13}\text{C}$ values are broadly consistent with the $\delta^{13}\text{C}$ record of the LJE (e.g., Karhu and Holland 1996; Melezhik et al. 1997, 1999; Bekker et al. 2003; Martin et al. 2013).

Extreme ^{13}C -enrichment does not necessarily require deposition that is coeval with the LJE, and the possibility of post-LJE extreme ^{13}C -enrichment(s) complicates correlation. As one example, a potential post-LJE positive $\delta^{13}\text{C}$ excursion has been recognised in the ca. 2030 Ma “Woolly Dolomite” in Australia (Bekker et al. 2016), occurring over 57 m of stratigraphy and lasting perhaps 2 Myr. Although the poor age constraints for the Le Fer Formation cannot be used to rule out correlation with the “Woolly Dolomite”, we note that no $\delta^{13}\text{C}$ excursions have yet been correlated with the “Woolly Dolomite”. Given that there is ample evidence for a widespread record of elevated carbonate $\delta^{13}\text{C}$ values during the LJE (e.g., Karhu and Holland 1996; Martin et al. 2013) we interpret the Le Fer Formation as being coeval with the LJE, while allowing that it may instead record a post-LJE excursion.

Bimodality of Denault Formation $\delta^{13}\text{C}$

In contrast to the Le Fer Formation, the Denault Formation records isotopic signatures with a higher fidelity and coherent variations, allowing for comparison between sections. The $\delta^{13}\text{C}$ values of the two sections measured at Elizabeth Lake (+1.8‰ to +4.3‰) and Marion Lake (−0.5‰ to +1.8‰) are highly bimodal, with only minor overlap (Fig. 7). We identify four possible scenarios for explaining this bimodal signature: (I) Differing degrees of diagenetic alteration, authigenic carbonate formation, and metamorphism between sampling sites; (II) varying degrees of water mass restriction; (III) incomplete stratigraphic sections that capture distinct parts of secular variation in marine DIC $\delta^{13}\text{C}$; and (IV) variations in seawater- versus sediment-buffered early diagenesis.

It is unlikely that diagenetic alteration (scenario I) can explain the bimodal distribution of $\delta^{13}\text{C}$ values because the proxies do not indicate significant diagenesis or a significant contribution of authigenic carbonate. Further, even if the minor differences in the severity of diagenesis could explain the differences in $\delta^{13}\text{C}$ between stratigraphic sections, the trends are opposite to what would be predicted. That is, the site that generally appears to have

undergone more intense diagenesis (Elizabeth Lake) actually records more positive $\delta^{13}\text{C}$ values than Marion Lake. Varying metamorphic grade is an alternate mechanism for the bimodality, given that Marion Lake is ~65 km east of Elizabeth Lake, and isograds in the Labrador Trough strike north–northeast (increasing toward the east). Although Elizabeth Lake is in the subgreenschist facies region, Marion Lake is in the greenschist facies region, and so the comparatively low $\delta^{13}\text{C}$ values at Marion Lake could be the result of metamorphic decarbonation. However, Donaldson (1966, p. 58) noted that carbonate rocks at Marion Lake “show little more than slight recrystallisation,” suggesting that increasing metamorphic grade alone could not control the $\delta^{13}\text{C}$ variation, especially given that coherent variations are preserved. Regarding scenario II, it has been observed that the restriction of water masses can result in “offset” $\delta^{13}\text{C}$ values with respect to the open ocean, driving the $\delta^{13}\text{C}$ of restricted DIC toward both more negative or positive values (Patterson and Walter 1994; Holmden et al. 1998; Halverson et al. 2005). Zentmyer et al. (2011) interpreted the Denault Formation at Marion Lake as having been deposited on an offshore topographic high (perhaps related to tectonism), whereas at Elizabeth Lake it was deposited in an inner- to mid-ramp setting. If water mass restriction was the primary factor for the bimodality of $\delta^{13}\text{C}$ values between these two stratigraphic sections, it could shift values toward being more positive or negative, making it difficult to identify with only two stratigraphic sections. Zentmyer et al. (2011) noted the occurrence of small (generally <20 μm) gypsum pseudomorphs, suggesting that the Denault Formation records evaporitic and restricted conditions, and may explain the more positive $\delta^{13}\text{C}$ values at Elizabeth Lake (the more proximal locality). Given that both stratigraphic sections are incomplete and a temporal correlation cannot be made, it is also possible that they were deposited at different times with little/no temporal overlap, in which case the $\delta^{13}\text{C}$ values need not be directly correlatable (scenario III).

The significance of early diagenesis of carbonate sediments, particularly with respect to being seawater- versus sediment-buffered (scenario IV), is increasingly recognised as an important variable in modification of primary $\delta^{13}\text{C}$ values in highly fractionated shallow waters with carbonate deposition (Higgins et al. 2018; Ahm et al. 2018; Hoffman and Lamothe 2019). On platform margins, carbonate sediments commonly undergo seawater-buffered early diagenesis, in which the compositions of the resulting diagenetic minerals are controlled mainly by the composition of the diagenetic fluid, seawater. Ultimately, this drives $\delta^{13}\text{C}$ values toward marine DIC. Conversely, platform–interior sediments undergo sediment-buffered early diagenesis, in which the compositions of diagenetic minerals are controlled mainly by the initial sediments, allowing for the preservation of $\delta^{13}\text{C}$ values distinct from marine DIC (if there has been significant fractionation of the water from which carbonates precipitated, relative to seawater; Ahm et al. 2018). In such a scenario, the offshore high (Marion Lake) would likely undergo seawater-buffered early diagenesis, resulting in $\delta^{13}\text{C}$ values closer to marine DIC (and generally nearer to 0‰). Conversely, the inner- to mid-ramp (Elizabeth Lake) may have undergone more sediment-buffered early diagenesis, allowing for preservation of more positive $\delta^{13}\text{C}$ values. Unfortunately, it is impossible to distinguish between scenarios II, III, and IV with the current data set, and all remain possibilities for explaining the observed bimodality of Denault Formation $\delta^{13}\text{C}$ values. Nonetheless, the Denault Formation records $\delta^{13}\text{C}$ values that are unambiguously indicative of being deposited following the end of the LJE.

Extending the record of the LJE in the Labrador Trough

The occurrence of very positive $\delta^{13}\text{C}$ values in the Le Fer Formation provides the first evidence for a continuation of the LJE above the Uvé Formation. Given that the Le Fer Formation is approximately 2 km stratigraphically higher than the Uvé Formation, this represents a significant extension of the LJE in the Labrador

Trough, albeit through an interval that is dominated by fine-grained clastic sedimentary rocks. Contrary to what was predicted based on the lithologic patterns of other end-LJE successions, the end-LJE in the Labrador Trough did not coincide with deposition of the organic-rich Hautes Chutes Formation, but, in fact, occurred much higher in the stratigraphy.

Despite intense research efforts to apply radiometric dating in the Labrador Trough, direct depositional ages remain sparse. However, the revised placement of the end-LJE within the Kaniapiskau Supergroup to somewhere near the Le Fer – Denault contact permits application of age constraints obtained elsewhere on the LJE. These data imply that the Le Fer Formation could be either older or younger than the youngest ^{13}C -rich LJE carbonates (2106 ± 8 Ma), but is older than the oldest post-LJE carbonates (2057 ± 1 Ma; reviewed by Martin et al. 2013). Conversely, the absence of the LJE in the directly overlying Denault Formation implies deposition after ca. 2106 ± 8 to 2057 ± 1 Ma. These inferred age correlations are much older than previous age interpretations, which had placed the Denault Formation closer in age to the overlying ca. 1880 Ma Ferriman Group (Wardle et al. 2002; Clark et al. 2006; Zentmyer et al. 2011). If correct, and assuming no major depositional hiatus between the Denault Formation and the Fleming/Dolly formations (Fig. 2; Birkett 1991), this revision to the age of the upper part of Cycle 1 implies that the previously recognised unconformity separating Cycles 1 and 2 may encompass $\gg 100$ Myr.

Despite these significantly revised stratigraphic constraints on the end-LJE within the Labrador Trough, any further regional refinement may prove very difficult. In addition to the poor outcrop of the Le Fer Formation, interpretation of secular variations in $\delta^{13}\text{C}$ is hindered by the scarcity of carbonate lithologies in this unit and the high likelihood of variably modified isotopic signatures. We also emphasise that the interpretation of high $\delta^{13}\text{C}$ during deposition of the Le Fer Formation recording the LJE is based on just a handful of samples out of the 95 analysed. If a lower threshold of +5‰ was applied, only 7% of samples record the LJE; only 3% of samples exceed a +6‰ threshold, and no samples exceed a +7‰ threshold. In contrast, the interpretation that the Denault formed post-LJE appears robust, given that none of the 115 analyses exceed +5‰, and only one exceeds +4‰. In addition to the maximum values, the median $\delta^{13}\text{C}$ value of the Le Fer Formation is also significantly higher than the Denault (Mann-Whitney test, $U = 2143$, $p = 6.5 \times 10^{-14}$). Collectively, these results underscore the importance of collecting many samples at a high-resolution, especially when the formation contains only a very small proportion of carbonate lithologies.

The revision to $\delta^{13}\text{C}$ chemostratigraphy in the Labrador Trough presented here is also important for studies attempting to better constrain the termination of the LJE. Given that the end-LJE is approximately 2 km higher in the stratigraphy than previously recognised, the very organic-rich shale and slate that occurs between the Uvé and Le Fer formations (i.e., Hautes Chutes, Savigny, Otelnuc, Du Chambon, and Romanet formations) are candidates for providing rhenium–osmium (Re–Os) age constraints on the LJE. Similarly, black shale has been reported in the upper Denault Formation (Zentmyer et al. 2011), providing a Re–Os target deposited more shortly after the end of the LJE than previously recognised.

If the Le Fer Formation records a post-LJE carbon isotope excursion that is analogous (although not necessarily correlative) with the “Woolly Dolomite” excursion rather than the LJE, it was likely deposited before ca. 2.02 Ga, given that no significant positive excursions have been identified in the ca. 2.02–1.88 Ga $\delta^{13}\text{C}$ record (Hodgskiss et al. 2019b). This scenario would suggest deposition of the Le Fer Formation between 2106 ± 8 (age of the youngest known LJE carbonate sedimentary rocks; Martin et al. 2013) and 2018.5 ± 1.0 Ma (age of basal Belcher Group, with carbonate $\delta^{13}\text{C} < 3.7\%$; Hodgskiss et al. 2019b). Given that the Bacchus Formation is $>2142 \pm 4/-2$ Ma, this scenario raises the possibility of an addi-

tional significant depositional hiatus within the Labrador Trough, of as little as ~ 30 Myr ($2142 \pm 4/-2$ Ma to 2106 Ma) to perhaps more than 120 Myr ($>2142 \pm 4/-2$ Ma to 2018.5 ± 1.0 Ma). Such a hiatus within Cycle 1 of the Labrador Trough has previously been suggested by Bekker et al. (2009), potentially as the result of a major tectonic reorganisation. This scenario is still compatible with a significant depositional hiatus >100 Myr between Cycles 1 and 2, depending on depositional duration of the Denault and Fleming/Dolly formations.

Conclusion

The application of carbon isotope chemostratigraphy to the Le Fer Formation indicates that the LJE may extend much higher (~ 2 km) in the stratigraphy than previously recognised. Although the very positive $\delta^{13}\text{C}$ values in the Le Fer Formation cannot be used to concretely eliminate the possibility that the Le Fer Formation records a post-LJE carbon isotope excursion (such as the “Woolly Dolomite” in Australia) rather than the LJE itself, the sole locality of the former versus the numerous localities of the latter would strongly suggest the Le Fer Formation records deposition during the LJE. The Denault Formation records post-LJE values, as suggested by Melezhik et al. (1997). The two stratigraphic sections measured in the Denault Formation record bimodal $\delta^{13}\text{C}$ values. These differences may reflect asynchronous deposition between the two sections, varying $\delta^{13}\text{C}$ of DIC due to water mass restriction, or different modes of early diagenesis. The Le Fer – Denault contact formed during or near the end-LJE transition, suggesting that the previously identified (e.g., Clark and Wares 2005) major depositional hiatus between Cycles 1 and 2 may exceed 100 Myr in duration. If the Le Fer Formation were to record a post-LJE $\delta^{13}\text{C}$ excursion, it would suggest a depositional hiatus of at least ~ 30 Myr, to perhaps more than 120 Myr, within Cycle 1. This application of carbon isotope chemostratigraphy has yielded valuable insights on the evolution of the Labrador Trough and helped to develop a better understanding of this complex sedimentary archive in the greater context of the evolving Earth system. It also highlights the need for, and importance of, an improved global carbon isotope chemostratigraphic framework during this interval, as well as the direct radiometric age constraints in the Labrador Trough.

Acknowledgements

We thank A. Bekker and an anonymous reviewer for detailed and constructive comments on the manuscript. Air Saguenay provided extremely professional, friendly, and reliable float plane support during fieldwork. S.V. Lalonde is thanked for assistance with elemental analyses, and the Kativik Regional Government is thanked for providing permission to carry out this work. M.S.W.H. is grateful for Natural Sciences and Engineering Research Council of Canada Postgraduate Scholarships – Doctoral (NSERC PGS-D) funding and a Stanford University McGee Grant. E.A.S. acknowledges an Ocean Sciences Research Fellowship from the Alfred P. Sloan Foundation for support.

References

- Ahm, A.S.C., Bjerrum, C.J., Blättler, C.L., Swart, P.K., and Higgins, J.A. 2018. Quantifying early marine diagenesis in shallow-water carbonate sediments. *Geochimica et Cosmochimica Acta*, **236**: 140–159. doi:10.1016/j.gca.2018.02.042.
- Bachan, A., and Kump, L.R. 2015. The rise of oxygen and siderite oxidation during the Lomagundi Event. *Proceedings of the National Academy of Sciences*, **112**: 6562–6567. doi:10.1073/pnas.1422319112.
- Bekker, A., and Holland, H.D. 2012. Oxygen overshoot and recovery during the early Paleoproterozoic. *Earth and Planetary Science Letters*, **317**: 295–304. doi:10.1016/j.epsl.2011.12.012.
- Bekker, A., Karhu, J.A., Eriksson, K.A., and Kaufman, A.J. 2003. Chemostratigraphy of Paleoproterozoic carbonate successions of the Wyoming Craton: tectonic forcing of biogeochemical change? *Precambrian Research*, **120**: 279–325. doi:10.1016/S0301-9268(02)00164-X.

- Bekker, A., Davis, D., and Wing, B.A. 2009. Chemostratigraphy and geochronology of the Kaniapiskau Supergroup, Labrador Trough indicate a major tectonic reorganization event hidden in the first cycle. Geological Association of Canada - Mineralogical Association of Canada, Program with Abstracts, Abstract ID: U21D-09.
- Bekker, A., Krapež, B., Müller, S.G., and Karhu, J.A. 2016. A short-term, post-Lomagundi positive C isotope excursion at c. 2.03 Ga recorded by the Woolly Dolomite, Western Australia. *Journal of the Geological Society*, **173**: 689–700. doi:10.1144/jgs2015-152.
- Birgel, D., Peckmann, J., Klautzsch, S., Thiel, V., and Reitner, J. 2006. Anaerobic and Aerobic Oxidation of Methane at Late Cretaceous Seeps in the Western Interior Seaway, USA. *Geomicrobiology Journal*, **23**: 565–577. doi:10.1080/01490450600897369.
- Birkett, T.C. 1991. Origin of the Lower Proterozoic Fleming Chert-Breccia, Newfoundland, Labrador-Quebec. Geological Survey of Canada, paper 91-12.
- Brand, U., and Veizer, J. 1980. Chemical diagenesis of a multicomponent carbonate system – 1: trace elements. *Journal of Sedimentary Research*, **50**: 1219–1236. doi:10.1306/212F7BB7-2B24-11D7-8648000102C1865D.
- Brand, U., and Veizer, J. 1981. Chemical diagenesis of a multicomponent carbonate system – 2: Stable isotopes. *Journal of Sedimentary Research*, **51**: 987–997. doi:10.1306/212F7BB7-2B24-11D7-8648000102C1865D.
- Clark, T. 1984. Géologie de la région du lac Cambrien, territoire du Nouveau-Québec. Ministère de l'Énergie et des Ressources du Québec, ET 83-02.
- Clark, T., and Wares, R. 2005. Lithotectonic and Metallogenic Synthesis of the New Québec Orogen (Labrador Trough). *Géologie Québec*, Ministère des Ressources Naturelles et de la Faune Report MM 2005-1.
- Clark, T., Leclair, A., Pufahl, P.K. 2006. Lithostatigraphic Reconnaissance in the Schefferville Area (NTS 2315) and Geological and Metallogenic Studies in the Zeni Lake Area (NTS 2316). *Géologie Québec*, Ministère des Ressources Naturelles et de la Faune Report 2006–7.
- Črne, A.E., Melezhik, V.A., Lepland, A., Fallick, A.E., Prave, A.R., and Brasier, A.T. 2014. Petrography and geochemistry of carbonate rocks of the Paleoproterozoic Zaonega Formation, Russia: documentation of ¹³C-depleted non-primary calcite. *Precambrian Research*, **240**: 79–93. doi:10.1016/j.precamres.2013.10.005.
- Dimroth, E. 1971. The Attikamagen-Ferriman Transition in Part of the Central Labrador Trough. *Canadian Journal of Earth Sciences*, **8**: 1432–1454. doi:10.1139/e71-132.
- Dimroth, E. 1978. Région de la Fosse du Labrador (54°30' and 56°30'). Ministère des Ressources naturelles du Québec, RG 193.
- Donaldson, J.A. 1963. Stromatolites in the Denault Formation, Marion Lake, Coast of Labrador, Newfoundland. Geological Survey of Canada Bulletin 102.
- Donaldson, J.A. 1966. Marion Lake map-area, Quebec–Newfoundland (23 I/13). Geological Survey of Canada Memoir 338, 85 pp.
- Findlay, J.M., Parrish, R.R., Birkett, T.C., and Watanabe, D.H. 1995. U-Pb ages from the Nimish Formation and Montagnais glomeroporphyritic gabbro of the central New Québec Orogen, Canada. *Canadian Journal of Earth Sciences*, **32**: 1208–1220. doi:10.1139/e95-099.
- Fryer, B.J. 1972. Age determinations in the Circum-Ungava Geosyncline and the evolution of Precambrian banded iron formations. *Canadian Journal of Earth Sciences*, **9**: 652–663. doi:10.1139/e72-055.
- Halverson, G.P., Hoffman, P.F., Schrag, D.P., Maloof, A.C., and Rice, A.H.N. 2005. Toward a Neoproterozoic composite carbon-isotope record. *GSA Bulletin*, **117**: 1181–1207. doi:10.1130/B25630.1.
- Hayes, J.M., and Waldbauer, J.R. 2006. The carbon cycle and associated redox processes through time. *Philosophical Transactions of the Royal Society B: Biological Sciences*, **361**: 931–950. doi:10.1098/rstb.2006.1840. PMID:16754608.
- Henrique-Pinto, R., Guilmette, C., Bilodeau, C., and McNicoll, V. 2017. Evidence for transition from a continental forearc to a collisional pro-foreland basin in the eastern Trans-Hudson Orogen: detrital zircon provenance analysis in the Labrador Trough, Canada. *Precambrian Research*, **296**: 181–194. doi:10.1016/j.precamres.2017.04.035.
- Higgins, J.A., Blättler, C.L., Lundstrom, E.A., Santiago-Ramos, D.P., Akhtar, A.A., Ahm, A.C., et al. 2018. Mineralogy, early marine diagenesis, and the chemistry of shallow-water carbonate sediments. *Geochimica et Cosmochimica Acta*, **220**: 512–534. doi:10.1016/j.gca.2017.09.046.
- Hodgskiss, M.S., Crockford, P.W., Peng, Y., Wing, B.A., and Horner, T.J. 2019a. A productivity collapse to end Earth's Great Oxidation. *Proceedings of the National Academy of Sciences*, **116**: 17207–17212. doi:10.1073/pnas.1900325116.
- Hodgskiss, M.S., Dagnaud, O.M., Frost, J.L., Halverson, G.P., Schmitz, M.D., Swanson-Hysell, N.L., and Sperling, E.A. 2019b. New insights on the Orosirian carbon cycle, early Cyanobacteria, and the assembly of Laurentia from the Paleoproterozoic Belcher Group. *Earth and Planetary Science Letters*, **520**: 141–152. doi:10.1016/j.epsl.2019.05.023.
- Hoffman, P.F. 1988. United plates of America, the birth of a craton: early Proterozoic assembly and growth of Laurentia. *Annual Review of Earth and Planetary Sciences*, **16**: 543–603. doi:10.1146/annurev.16.050188.002551.
- Hoffman, P.F., and Grotzinger, J.P. 1989. Abner/Denault reef complex (2.1 Ga), Labrador Trough, N.E. Quebec. In *Reefs, Canada and adjacent area*. Edited by H.H.J. Geldsetzer, N.P. James, and G.E. Tebbutt. Canadian Society of Petroleum Geologists, Memoir 13, pp. 49–54.
- Hoffman, P.F., and Lamothe, K.G. 2019. Seawater-buffered diagenesis, destruction of carbon isotope excursions, and the composition of DIC in Neoproterozoic oceans. *Proceedings of the National Academy of Sciences*, **116**: 18874–18879. doi:10.1073/pnas.1909570116.
- Hofmann, H.J., and Jackson, G.D. 1987. Proterozoic minstromatolites with radial-fibrous fabric. *Sedimentology*, **34**: 963–971. doi:10.1111/j.1365-3091.1987.tb00586.x.
- Holmden, C., Creaser, R.A., Muehlenbachs, K.L.S.A., Leslie, S.A., and Bergstrom, S.M. 1998. Isotopic evidence for geochemical decoupling between ancient epeiric seas and bordering oceans: implications for secular curves. *Geology*, **26**: 567–570. doi:10.1130/0091-7613(1998)026<0567:IEFGDB>2.3.CO;2.
- Irwin, H., Curtis, C., and Coleman, M. 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature*, **269**: 208–213. doi:10.1038/269209a0.
- Karhu, J.A., and Holland, H.D. 1996. Carbon isotopes and the rise of atmospheric oxygen. *Geology*, **24**: 867–870. doi:10.1130/0091-7613(1996)024<0867:CIATRO>2.3.CO;2.
- Kipp, M.A., Stüeken, E.E., Bekker, A., and Buick, R. 2017. Selenium isotopes record extensive marine suboxia during the Great Oxidation Event. *Proceedings of the National Academy of Sciences*, **114**: 875–880. doi:10.1073/pnas.1615867114.
- Kreitsmann, T., Kivilaivir, M., Lepland, A., Paiste, K., Paiste, P., Prave, A.R., et al. 2019. Hydrothermal dedolomitisation of carbonate rocks of the Paleoproterozoic Zaonega Formation, NW Russia—Implications for the preservation of primary C isotope signals. *Chemical Geology*, **512**: 43–57. doi:10.1016/j.chemgeo.2019.03.002.
- Kump, L.R., Junium, C., Arthur, M.A., Brasier, A., Fallick, A., Melezhik, V., et al. 2011. Isotopic evidence for massive oxidation of organic matter following the Great Oxidation Event. *Science*, **334**: 1694–1696. doi:10.1126/science.1213999. PMID:22144465.
- Kuznetsov, A.B., Melezhik, V.A., Gorokhov, I.M., Melnikov, N.N., and Fallick, A.E. 2003. Sr Isotope Composition in Paleoproterozoic Carbonates Extremely Enriched in ¹³C: kaniapiskau Supergroup, the Labrador Trough of the Canadian Shield. *Stratigraphy and Geological Correlation*, **11**: 209–219.
- Land, L.S. 1980. The isotopic and trace element geochemistry of dolomite: the state of the art. *SEPM Special Publications No. 28*, pp. 87–110.
- Magad-Weiss, L.K. 2019. The Union Island Group of the Great Slave Lake, NWT, Canada: a Perspective on the Aftermath of the Lomagundi Carbon Isotope Excursion. M.Sc. thesis, Department of Earth Sciences, University of California, Riverside, Calif.
- Maheshwari, A., Sial, A.N., Gaucher, C., Bossi, J., Bekker, A., Ferreira, V.P., and Romano, A.W. 2010. Global nature of the Paleoproterozoic Lomagundi carbon isotope excursion: a review of occurrences in Brazil, India, and Uruguay. *Precambrian Research*, **182**: 274–299. doi:10.1016/j.precamres.2010.06.017.
- Martin, A.P., Condon, D.J., Prave, A.R., and Lepland, A. 2013. A review of temporal constraints for the Palaeoproterozoic large, positive carbonate carbon isotope excursion (the Lomagundi-Jatuli Event). *Earth-Science Reviews*, **127**: 242–261. doi:10.1016/j.earscirev.2013.10.006.
- Melezhik, V.A., and Fallick, A.E. 2010. On the Lomagundi-Jatuli carbon isotopic event: the evidence from the Kalix Greenstone Belt, Sweden. *Precambrian Research*, **179**: 165–190. doi:10.1016/j.precamres.2010.03.002.
- Melezhik, V., Fallick, A., and Clark, T. 1997. Two billion year old isotopically heavy carbon: evidence from the Labrador Trough, Canada. *Canadian Journal of Earth Sciences*, **34**: 271–285. doi:10.1139/e17-025.
- Melezhik, V.A., Fallick, A.E., Medvedev, P.V., and Makarikhin, V.V. 1999. Extreme ¹³C_{carb} enrichment in ca. 2.0 Ga magnesite-stromatolite-dolomite-red beds' association in a global context: a case for the world-wide signal enhanced by a local environment. *Earth-Science Reviews*, **48**: 71–120. doi:10.1016/S0012-8252(99)00044-6.
- Melezhik, V.A., Filippov, M.M., and Romashkin, A.E. 2004. A giant Palaeoproterozoic deposit of shungite in NW Russia: genesis and practical applications. *Ore Geology Reviews*, **24**: 135–154. doi:10.1016/j.oregeorev.2003.08.003.
- Miyazaki, Y., Planavsky, N.J., Bolton, E.W., and Reinhard, C.T. 2018. Making sense of massive carbon isotope excursions with an inverse carbon cycle model. *Journal of Geophysical Research: Biogeosciences*, **123**: 2485–2496. doi:10.1029/2018JG004416.
- Naehr, T.H., Eichhubl, P., Orphan, V.J., Hovland, M., Paull, C.K., Ussler, W., et al. 2007. Authigenic carbonate formation at hydrocarbon seeps in continental margin sediments: a comparative study. *Deep Sea Research Part II: Topical Studies in Oceanography*, **54**: 1268–1291. doi:10.1016/j.dsr2.2007.04.010.
- Neal, H.E. 2000. Iron deposits of the Labrador Trough. *Exploration and Mining Geology*, **9**: 113–121. doi:10.2113/0909113.
- Ossa, F.O., Eickmann, B., Hofmann, A., Planavsky, N.J., Asael, D., Pambo, F., and Bekker, A. 2018. Two-step deoxygenation at the end of the Paleoproterozoic Lomagundi Event. *Earth and Planetary Science Letters*, **486**: 70–83. doi:10.1016/j.epsl.2018.01.009.
- Patterson, W.P., and Walter, L.M. 1994. Depletion of ¹³C in seawater ΣCO₂ on modern carbonate platforms: significance for the carbon isotopic record of carbonates. *Geology*, **22**: 885–888. doi:10.1130/0091-7613(1994)022<0885:DOICSC>2.3.CO;2.
- Qu, Y., Črne, A.E., Lepland, A., and Van Zuilen, M.A. 2012. Methanotrophy in a Paleoproterozoic oil field ecosystem, Zaonega Formation, Karelia, Russia. *Geobiology*, **10**: 467–478. doi:10.1111/gbi.12007. PMID:23009699.
- Raye, U., Pufahl, P.K., Kyser, T.K., Ricard, E., and Hiatt, E.E. 2015. The role of sedimentology, oceanography, and alteration on the δ⁵⁶Fe value of the

- Sokoman Iron Formation, Labrador Trough, Canada. *Geochimica et Cosmochimica Acta*, **164**: 205–220. doi:[10.1016/j.gca.2015.05.020](https://doi.org/10.1016/j.gca.2015.05.020).
- Rohon, M.L., Vialette, Y., Clark, T., Roger, G., Ohnenstetter, D., and Vidal, P. 1993. Apehbian mafic–ultramafic magmatism in the Labrador Trough (New Quebec): its age and the nature of its mantle source. *Canadian Journal of Earth Sciences*, **30**: 1582–1593. doi:[10.1139/e93-136](https://doi.org/10.1139/e93-136).
- Rongemaille, E., Bayon, G., Pierre, C., Bollinger, C., Chu, N.C., Fouquet, Y., et al. 2011. Rare earth elements in cold seep carbonates from the Niger delta. *Chemical Geology*, **286**: 196–206. doi:[10.1016/j.chemgeo.2011.05.001](https://doi.org/10.1016/j.chemgeo.2011.05.001).
- Rosenbaum, J.M., Cuney, M., and Sheppard, S.M.F. 1995. ¹³C-rich dolomites from Quebec. Paleoclimate Signal? *In Terra Abstracts*, Meeting of European Union (EUG-8), Strasbourg, France, pp. 329–330.
- Schrag, D.P., Higgins, J.A., Macdonald, F.A., and Johnston, D.T. 2013. Authigenic carbonate and the history of the global carbon cycle. *Science*, **339**: 540–543. doi:[10.1126/science.1229578](https://doi.org/10.1126/science.1229578). PMID:[23372007](https://pubmed.ncbi.nlm.nih.gov/23372007/).
- Schrijver, K., Bertrand, R., Chagnon, A., Tassé, N., and Chevé, S.R. 1986. Fluids in cupriferous dolostones and dolomite veins, Proterozoic Dunphy Formation, Labrador Trough. *Canadian Journal of Earth Sciences*, **23**: 1709–1723. doi:[10.1139/e86-158](https://doi.org/10.1139/e86-158).
- Valley, J.W. 1986. Stable isotope geochemistry of metamorphic rocks. *Reviews in Mineralogy and Geochemistry*, **16**: 445–489.
- Wardle, R.J., James, D.T., Scott, D.J., and Hall, J. 2002. The southeastern Churchill Province: synthesis of a Paleoproterozoic transpressional orogen. *Canadian Journal of Earth Sciences*, **39**: 639–663. doi:[10.1139/e02-004](https://doi.org/10.1139/e02-004).
- Weber, F., and Gauthier-Lafaye, F. 2013. No proof from carbon isotopes in the Francevillian (Gabon) and Onega (Fennoscandian shield) basins of a global oxidation event at 1980–2090 Ma following the Great Oxidation Event (GOE). *C.R. Geosci.* **345**: 28–35. doi:[10.1016/j.crte.2012.12.003](https://doi.org/10.1016/j.crte.2012.12.003).
- Zentmyer, R.A., Pufahl, P.K., James, N.P., and Hiatt, E.E. 2011. Dolomitization on an evaporitic Paleoproterozoic ramp: widespread synsedimentary dolomite in the Denault Formation, Labrador Trough, Canada. *Sedimentary Geology*, **238**: 116–131. doi:[10.1016/j.sedgeo.2011.04.007](https://doi.org/10.1016/j.sedgeo.2011.04.007).