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Is the Lomagundi Event present on the Rae craton? A case study from the Murmac Bay Group

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Abstract: Shortly after the initial rise of atmospheric oxygen in the Paleoproterozoic Era, a major perturbation occurred in the global carbon cycle, which is manifested as a long-lived positive carbon isotope excursion recorded in ~2.22 to 2.06 Ga carbonate rocks, known as the Lomagundi Event. Beyond its significance for evolving seawater composition, this geochemical event can be used as an indirect age marker in Paleoproterozoic sedimentary successions. Documenting further occurrences of this event in other Paleoproterozoic carbonate rocks confirms that the event was global and reflects ambient seawater composition. This event, however, has only been documented in two successions in Canada, despite the ubiquity of Paleoproterozoic-aged rocks on the Canadian Shield. Our study focuses on metacarbonate rocks from the Paleoproterozoic-aged Murmac Bay Group on the southwestern margin of the Rae craton in northern Saskatchewan. Measured $\delta^{13}\text{C}$ values (up to 7.8‰) fall within the range of the Lomagundi Event, but most values are relatively low, suggesting CO_2 loss (decarbonation) altered the $\delta^{13}\text{C}$ values. Stable carbon isotope data coupled with major element geochemical data allowed us to account for the degree to which the values have changed due to metamorphic CO_2 loss. We also compare $\delta^{13}\text{C}$ values from micro-drilled (dolomite and calcite phases) to whole-rock $\delta^{13}\text{C}$ values from the same samples to characterize the $\delta^{13}\text{C}$ composition of pre-metamorphic carbonate minerals. Both measured and corrected $\delta^{13}\text{C}$ values place the Murmac Bay Group metacarbonates within

23 the range of values that characterize the Lomagundi Event and indicate, for the first time,
24 the presence of the Lomagundi Event on the Rae craton.

25

26 Key words: Paleoproterozoic, carbonates, Lomagundi Event, carbon isotopes, Canadian
27 Shield

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Introduction

Several Paleoproterozoic-aged marine carbonate successions deposited between ~2.22 and 2.06 Ga record anomalously high $\delta^{13}\text{C}$ values ranging from 4‰ to 16‰ (e.g., Schidlowski et al. 1975; Karhu and Holland 1996; Melezhik et al. 1999; Planavsky et al. 2012; Martin et al. 2013). This event is known as the Lomagundi positive carbon isotope excursion, or Lomagundi Event, after its discovery in the Lomagundi Group of Zimbabwe (Melezhik et al. 2005). These highly positive $\delta^{13}\text{C}$ values found within Paleoproterozoic carbonate rocks have been attributed to an organic carbon burial event that resulted in a large influx of atmospheric oxygen (Karhu and Holland 1996) that post-dates the onset of the Great Oxidation Event (Lyons et al. 2014). The Lomagundi Event has been documented in more than 22 locations worldwide, contributing to the idea that the Lomagundi Event records a significant perturbation to the global carbon cycle (Karhu and Holland 1996; Maheshwari et al. 2010a; Martin et al. 2013). However, some metasedimentary successions of this age experienced higher grades of metamorphism, especially in widespread 1.9 to 1.7 Ga orogens, which likely depleted carbonate $\delta^{13}\text{C}$ values. Therefore, identifying the Lomagundi Event in these successions presents a challenge, but higher metamorphic grade rocks have the potential to show that the geographical extent of the Lomagundi Event is larger than currently known. Previous studies have shown that near-to primary $\delta^{13}\text{C}$ values can be retained in amphibolite and even granulite facies metacarbonate rocks (e.g., Bol et al. 1995). Finding evidence of a positive carbon isotope excursion in higher-grade rocks is promising since metamorphism tends to drive $\delta^{13}\text{C}$ values lighter, therefore measurement of carbon isotope values in metamorphosed carbonates has the potential to identify high $\delta^{13}\text{C}$ values indicative of the

Lomagundi Event. To our knowledge, the Lomagundi Event has only been documented in two amphibolite-grade carbonate successions previously (Melezhik et al. 2003; Master et al. 2013). This validates the possibility that the Lomagundi Event can be preserved in higher metamorphic grade rocks. Thus, if the Lomagundi Event is truly global in extent and recording seawater composition, all marine carbonate successions deposited in this time interval should show a record of the event.

The Lomagundi Event has not yet been described from a Paleoproterozoic succession on the Rae craton. The Murmac Bay Group (MBG) is a Paleoproterozoic-aged metasedimentary succession located on the southwestern margin of the Rae craton in northern Saskatchewan, Canada. Current age constraints suggest that the entire MBG was deposited sometime after 2.33 Ga and before 1.94 Ga, the latter of which records the onset of metamorphism to the amphibolite facies (Ashton et al. 2013; Bethune et al. 2013). Importantly, the available age constraints overlap the time interval of the Lomagundi Event. The lower MBG succession includes metacarbonate rocks, which provide an opportunity to test for the presence or absence of the Lomagundi Event. Finding highly positive $\delta^{13}\text{C}$ values indicative of the Lomagundi Event would support the interpretation that the MBG was deposited in a marine environment (Ashton et al. 2013), as well as provide new age constraints on carbonate deposition.

We present new stable isotopic data ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values) in addition to major element geochemistry to test for the presence or absence of the Lomagundi Event in MBG metacarbonate rocks. We also address the impact of CO_2 loss (decarbonation) from metamorphic mineral transformations within the MBG metacarbonate rocks on their isotopic compositions.

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75 **Geological Setting**

76 The Paleoproterozoic-aged MBG was deposited near the margin of the
77 southwestern Rae craton on the Beaverlodge Domain, and is presently exposed on the
78 northern edge of Lake Athabasca in northwest Saskatchewan, Canada (Figure 1). Much
79 of the northern Canadian Shield is underlain by the Rae craton, which is bounded to the
80 southeast by the Hearne craton and separated by the Snowbird tectonic zone (Figure 1).
81 These two Archean cratons comprise the larger western Churchill province in northern
82 Canada. The northwestern margin of the Rae craton is bounded by the Proterozoic-aged
83 Taltson magmatic zone (Hoffman, 1988; Ashton et al. 2013) that separates the Rae craton
84 from the Archean Slave craton. The southwestern Rae craton is composed largely of 3.0
85 to 2.6 Ga basement rocks, with a number of granitic intrusive suites at 2.5 – 2.46 Ga, 2.33
86 – 2.29 Ga, and 1.93 – 1.91 Ga (Ashton et al. 2013).

87 The MBG is a multiply-deformed metasedimentary succession with at least two
88 recognized events of deformation, the Talston (1.94 - 1.93 Ga) and the Snowbird orogens
89 (1.91 – 1.90 Ga) (Hartlaub et al. 2004; Ashton et al. 2013; Bethune et al. 2013). The
90 Beaverlodge Domain was intruded by granitic rocks that were associated with the Taltson
91 Orogeny, during which the MBG was metamorphosed to amphibolite to granulite facies
92 between 1.94 to 1.91 Ga (Figure 1; Ashton et al. 2013; Bethune et al. 2013). The MBG
93 lies unconformably on top of Archean basement rocks, some of which have been dated,
94 including the ~3.0 Ga Elliot Bay and Cornwall Bay granites (Hartlaub et al. 2004;
95 Bethune et al. 2013). The dominant lithologies of the MBG are quartzite, basalt,
96 psammite, and pelite, with thin units of banded iron formation and carbonate (Hartlaub et

al. 2004; Ashton et al. 2013) (Figure 2). The lower MBG is composed of a locally occurring polymictic conglomerate that lies unconformably on top of Archean basement rocks. The conglomerate is interbedded within quartzite, which varies locally in thickness (5 to 500m) (Hartlaub et al. 2004). Small scale planar cross bedding and larger scale (meter-scale) trough cross bedding features have been preserved within the quartzite (Hartlaub et al. 2004). Evidence of these locally preserved features suggests that the quartzites might have been deposited in a high-energy fluvial or shoreline environment (Hartlaub et al. 2004). The dolostone that forms the basis of this study occurs within the quartzite unit and varies from two to tens of meters in tectonostratigraphic thickness (Hartlaub et al. 2004) occurring sometimes as isolated pockets within the quartzite (Ashton et al. 2000). The quartzite-dolomite package is overlain by a banded iron formation that consists of cm-thick alternating quartz and magnetite-hematite rich layers, followed by a medium- to fine-grained amphibolite (Hartlaub et al. 2004). The upper MBG consists of a thick package of aluminous psammopelite and pelite that is stratigraphically above and locally interlayered with both the quartzite and the amphibolite (Hartlaub et al. 2004).

Methods

Petrographic, geochemical, and isotopic analysis was performed on metacarbonate rocks of the MBG to test for the presence of the Lomagundi Event. Samples 6-2, 6-2A, and the sample series 9-1 to 9-9 were collected in the field, near Beaverlodge Lake and Goldfields (Figure 1), respectively, within a known stratigraphic context, whereas samples 4700- 0050, -6100, 4709-6001, and 4701- 3075A are from the

Saskatchewan Geological Survey archives. Samples were cut into slabs and polished prior to micro-drilling; micro-drilling targeted the calcite and dolomite phases present. A subset of carbonate samples was crushed for whole-rock isotopic and geochemical analysis. Standard carbonate staining techniques were used to determine carbonate mineralogy, which utilized a mixture of Alizarin red-S and potassium ferricyanide (Dickson 1965; Hitzman 1999). Petrographic analysis was done on both stained and unstained thin sections. Isotopic ratios of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from both micro-drilled and whole-rock samples were measured at the University of Saskatchewan Isotope Laboratory at the University of Saskatchewan. Samples were initially roasted in a vacuum oven at 200°C for 1 hour to remove water and volatile organic contaminants that can alter isotopic values. Samples were analyzed using a Finnigan Kiel-IV carbonate preparation device directly coupled to the dual inlet of a Finnigan MAT 253 isotope ratio mass spectrometer at the Saskatchewan Isotope Laboratory. Carbonate samples (20-50 micrograms) were reacted at 70°C with 3 drops of anhydrous phosphoric acid for 420 seconds. The CO_2 evolved was cryogenically purified before analysis. Isotope ratios are corrected for acid fractionation and ^{17}O contribution using the Craig correction, and reported in per mil (‰) notation relative to the Vienna-Pee Dee Belemnite (V-PDB) scale. Data is directly calibrated against the international standard NBS-19 that has $\delta^{13}\text{C} = 1.95\text{‰}$ (V-PDB) and $\delta^{18}\text{O} = -2.2\text{‰}$ (V-PDB) values. Precision and accuracy are monitored through routine analysis of NBS-19 and in-house check standards calibrated against NBS-19. Analytical error and reproducibility of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are 0.05‰ and 0.11‰, respectively ($n = 25$). Dolomite $\delta^{18}\text{O}$ values are calculated using the following

fractionation factors at 70° C: calcite = 1.008698 (Swart et al. 1991) dolomite = 1.009926 (Rosenbaum and Sheppard 1986).

Whole-rock major element geochemical analysis was conducted at Activation Labs in Ontario (their 4C - XRF Fusion package), specifically for MgO, CO₂, CaO, MnO, SiO₂, and Fe₂O₃, according to the heavy absorber fusion technique of Norrish and Hutton (1969). Loss on ignition (LOI) of H₂O⁺, CO₂, S, and other volatiles, is determined from the weight loss once the sample has been roasted at 1050° C for 2 hours. The fusion disk is created from the mixing of 0.5 g equivalent of the roasted sample with a 6.5 g combination of lithium metaborate and lithium tetraborate with a releasing agent of lithium bromide. Samples were analyzed on a Panalytical Axios Advanced wavelength dispersive XRF. The detection limit is about 0.01 wt% for most elements.

The CO₂ analysis was conducted at Activation labs (their 4F – CO₂ infrared (IR) package). Samples (0.2 g) were thermally decomposed in a pure nitrogen environment at 1000°C, using an ELTRA CW-800, directly releasing CO₂. H₂O is removed from the system before the detection of CO₂. IR energy is then absorbed by the CO₂ at a precise wavelength. IR calibration is achieved using pure calcium carbonate standard (USZ 25-2006). This method has a detection limit of 0.01%.

Results

The $\delta^{13}\text{C}$ values for the micro-drilled samples show a wide range (9‰), with a minimum value of -1.2‰, a maximum value of +7.8‰, and an average value of +1.1‰. Associated $\delta^{18}\text{O}$ values show a range of 7‰, with a maximum value of +18.0‰ and a minimum value of -10.9‰ with an average value of -15.5‰. By contrast, the whole-rock

$\delta^{13}\text{C}$ show lower values overall: -4.1‰ (minimum), 5.3‰ (maximum), and 0.1‰ (average), but a similar range of values (9.4‰). The associated $\delta^{18}\text{O}$ values show a range of 4.4‰ and a minimum of -18.4‰ and maximum of -14.0‰, with an average value of -16.3‰ (Table 1). Petrographic analysis shows that the major mineral composition of the samples varies between ferroan and non-ferroan dolomite $\pm$ tremolite (Table 2; Figure 3). However, calcite and quartz are present in some samples, as is magnetite (trace). Where present, the quartz typically shows a xenotopic mosaic texture or is present as an overgrowth on the dolomite. Results from whole-rock geochemical analysis show MgO/CaO ratios that are similar or slightly below that of stoichiometric dolomite (0.71; Table 3). Whole-rock geochemical data was coupled with whole-rock $\delta^{13}\text{C}$ values to assess the impact of CO_2 loss (decarbonation) that occurred through metamorphism. We use Rayleigh fractionation calculations to estimate the post-burial alteration of whole-rock $\delta^{13}\text{C}$ values that occurred through decarbonation (Table 3).

Discussion

Petrographic analysis and mineral paragenesis

Though the MBG carbonates now contain dolomite, calcite, and tremolite as the dominant mineralogical assemblage, the pre-metamorphic mineralogy was likely dominated by dolomite (Figure 3A). The presence of tremolite requires that dolomite was a large component of the pre-metamorphic carbonate mineralogy, in order to account for the Mg requirement of the tremolite present within the samples. The following equation is the most likely reaction for the formation of tremolite (Winkler 1979; Melezhik et al. 2003): $5 \text{ dolomite} + 8 \text{ quartz} + 1 \text{ H}_2\text{O} \rightarrow 1 \text{ tremolite} + 3 \text{ calcite} + 7 \text{ CO}_2$

The presence of twinned calcite crystals indicates the metamorphic recrystallization of calcite (Figure 3B). Though calcite is likely present in both pre-metamorphic and metamorphic phases, this could not be distinguished petrographically. Tremolite overgrowth of the calcite is observed in thin section (Figure 3B), as well as pitting that can indicate the presence of alkaline rich fluids interacting with the preexisting calcite. Melezhik et al. (2003) and Črne et al. (2014) demonstrated the importance of targeting pre-metamorphic carbonate minerals (typically dolomite) via micro-drilling, which reflects the best approximation of primary $\delta^{13}\text{C}$ values. In epidote-amphibolite facies dolostones, post-metamorphic calcite was shown to record lighter $\delta^{13}\text{C}$ values as compared to pre-metamorphic calcite (Melezhik et al. 2003). Given this framework, we targeted both dolomite and calcite phases via micro-drilling as part of our isotopic analysis to test for primary and secondary isotopic signals. Accordingly, our micro-drilled dolomite samples record the highest $\delta^{13}\text{C}$ values, while micro-drilled calcite yielded lower values (Table 1). In one case, the $\delta^{13}\text{C}$ value of micro-drilled calcite is identical to the whole-rock isotopic value of 1.1‰ (Table 1, Figure 4A), which is consistent with the presence of metamorphic calcite in the sample.

Assessment of isotopic values

Previously documented Lomagundi Event $\delta^{13}\text{C}$ values range from +4.6‰ to +16.6‰ (e.g., Baker and Fallick 1989a; Baker and Fallick 1989b; Karhu 1993; Karhu and Holland 1996; Melezhik et al. 1997; Bekker et al. 2003; Bekker et al. 2006; Tang et al. 2011). By contrast, some of the $\delta^{13}\text{C}$ values from the MBG (Table 3) fall within this range, but show lower than average values overall. The micro-drilled and whole-rock

average $\delta^{13}\text{C}$ values are +1.1‰ and +0.1‰ respectively, which are lower than the global Lomagundi Event average value (+4.7‰) (Maheshwari et al. 2010). However, due to the higher metamorphic grade of our samples, the lower values can be attributed to decarbonation processes, including the transformation of pre-metamorphic carbonate minerals to tremolite. Regardless of metamorphic grade, our two highest measured values (5.3‰ whole-rock and 7.8‰ micro-drilled) do fall within the established range of Lomagundi Event values. In the following, we consider the extent to which the MBG metacarbonates experienced CO_2 loss and conclude that the measured $\delta^{13}\text{C}$ values likely underestimate the primary values by a minimum of 4‰. Therefore the majority of our corrected values are consistent with other worldwide Lomagundi Event values.

In order to estimate the extent to which $\delta^{13}\text{C}$ values decreased from their initial values, we looked at two possible models—Rayleigh and batch distillation. By assuming the rock devolatilized within a closed system, the $\delta^{13}\text{C}$ will vary directly with the degree of devolatilization in accordance with mass balance. However, the more likely case is a continuous decarbonation reaction, where there is an ongoing exchange and removal of small amounts of fluid (Valley 1986), therefore we use the following equation, the Rayleigh fractionation model: $\delta^f = \delta^i + 10^3(F^{\alpha-1}-1)$, where F is the mole fraction of carbon that remains in the rock after volatilization, α is the isotopic fractionation factor, and lastly, δ^i and δ^f are the initial and final isotopic values of the rock in standard per mil notation. Rayleigh fractionation approximates the effects of decarbonation within an impure (quartz-bearing) dolomitic rock better than the alternative batch model. This is supported by our samples, 70% of which have an F value greater than 0.6. The shift in the isotopic values of our samples are best described by the Rayleigh model, since F

values are above a threshold value (>0.6) are considered align best with Rayleigh fractionation (Valley 1986).

The remaining CO_2 within the samples (F) can be determined from the measured amounts of CO_2 , CaO , and MgO of each sample by assuming that the samples were either dolomite or calcite, depending on their CaO/MgO ratio (Table 3). Dolomite samples were identified based on the MgO/CaO ratio of stoichiometric dolomite (0.72) and all other samples were assumed to be calcite. By assuming that our highest $\delta^{13}\text{C}$ value ($+7.8\text{‰}$) represents the closest-to-primary $\delta^{13}\text{C}$ value (δ^i), we calculate the fractionation factor, α , and $\Delta^{13}\text{C}_{(\text{CO}_2-\text{carb})}$ and estimate the degree to which our $\delta^{13}\text{C}$ values have been reset. Our results show that a group of the whole-rock samples have $\delta^{13}\text{C}$ values that were shifted to lighter values by $\sim 4\text{‰}$, while other samples gave unreasonable values (Table 3). In conjunction with these calculations the extent to which our samples experienced decarbonation correlates with the Si content of the sample, that is, samples with greater Si contents show a higher degree of decarbonation (lower F values) (Figure 4B) due to Si as the limiting reagent in the reaction of dolomite to tremolite (Valley 1986).

The formation of tremolite, present in most of our samples, provides a mechanism for this CO_2 loss and the subsequent alteration of initial $\delta^{13}\text{C}$ values. However, there is a large and unrealistic range of values for α ($0.579 - 1.484$) and $\Delta^{13}\text{C}_{(\text{CO}_2-\text{carb})}$ values if only dolomite is considered as the dominant pre-metamorphic mineralogy. For samples that are found within similar metamorphic facies it is unlikely to have the $\Delta^{13}\text{C}_{(\text{CO}_2-\text{carb})}$ values differ so greatly without an additional source of carbon (cf. Melezhik et al. 2003). The other possible reason for such a varied $\Delta^{13}\text{C}_{(\text{CO}_2-\text{carb})}$ is that the Rayleigh calculation

in this case is based solely on the assumption that the targeted phases were either dolomite or calcite, as opposed to being a mix of the two.

Although the cause of the long-lived positive carbon isotope excursion of the Lomagundi Event is not well-constrained, it is thought to be the result of a large organic carbon burial event (cf. Karhu and Holland 1996; Hayes and Waldbauer 2006). One alternative explanation to produce ^{13}C -enriched values in carbonate is the formation of late diagenetic dolomite in the presence of methanogenesis (Yudovich et al. 1991; Dix et al. 1995). Assessing the possibility of diagenetic, specifically methanogenic, dolomite in our samples is not straightforward due to the large degree of metamorphic recrystallization. Though we cannot completely exclude the possibility of methanogenic dolomite formation, we consider this possibility to be less likely given the age constraints of our samples (falling within the Lomagundi Event interval) and recent datasets that provide insight into the predicted consequences of an anomalous organic carbon burial event, as discussed below.

The carbon isotopic record of Lomagundi-aged carbonates was originally interpreted to represent a massive organic carbon burial event that led to a marked increase in atmospheric oxygen content (e.g., Karhu and Holland 1996). Since then, multiple independent lines of evidence have confirmed that the Lomagundi Event interval does indeed reflect high oxygen conditions (Bekker and Holland 2012), including elevated concentrations of redox-sensitive trace elements (e.g., Scott et al. 2008; Sahoo et al. 2012; Partin et al. 2013) and sulfate in the oceans (Planavsky et al. 2012; Scott et al. 2014), as well as the presence of sulfate evaporite deposits (Schröder et al. 2008). Further evidence from organic carbon isotopes records a massive oxidation of organic matter

after the Lomagundi Event (Kump et al. 2011), consistent with the idea of organic carbon burial driving the positive carbon isotope excursion. Although local processes, including diagenesis, likely have a bearing on the carbon isotopic value of Paleoproterozoic carbonates, the overwhelming majority of evidence points to an organic carbon burial event that led to markedly higher atmospheric oxygen levels. Since the burial of organic carbon is the most important regulator of atmospheric oxygen levels (e.g., Canfield 2005; Holland 2006) and organic carbon burial can explain highly positive carbon isotope values, we consider this to be the most parsimonious explanation for the carbon isotope values recorded during the Lomagundi Event.

Implications of documenting a new Lomagundi Event occurrence

The results of our study indicate that the MBG records high $\delta^{13}\text{C}$ values (up to +7.8‰) that fall within the documented range of $\delta^{13}\text{C}$ values for the Lomagundi Event. The present age constraints for MBG metacarbonates support this, since deposition occurred sometime after 2.33 Ga (Ashton et al. 2013), suggesting the Lomagundi Event might be recorded. The range in values from both micro-drilled and whole-rock analyzed samples of MBG metacarbonates indicates that they are within the range of values observed in the Lomagundi Event worldwide (Table 4). Therefore, this conclusion provides a new (indirect) depositional age constraint for the MBG metacarbonates to be sometime between ~2.22 and 2.06 Ga. Considering the relatively thin nature of the MBG metacarbonates (Figure 2), it is unlikely that our samples capture the entire Lomagundi Event interval. Instead, the lower MBG was deposited sometime during this interval and captured seawater values.

Conclusions

Based on carbon and oxygen isotope trends and whole-rock geochemical results of MBG metacarbonate rocks, we infer that $\delta^{13}\text{C}$ values in the micro-drilled samples of dolomite record closest to primary carbon isotopic values. The lightest $\delta^{13}\text{C}$ values can be explained by decarbonation reactions and Rayleigh fractionation. The extent of decarbonation, as indicated by F values, scales with the Si content of impure metacarbonate samples. Therefore, the impure metacarbonate rocks lost more CO_2 , shifting their $\delta^{13}\text{C}$ values to lower values. The high $\delta^{13}\text{C}$ values ($\leq +7.8\text{‰}$) found in the MBG suggest that the Lomagundi Event is recorded in the Murmac Bay metacarbonates, therefore constraining the timing of deposition to be between ~ 2.22 and 2.06 Ga. Although the Lomagundi Event has been described from other cratons within Laurentia (e.g., Superior and Wyoming cratons), our study presents the first evidence that the Lomagundi Event was recorded in a succession deposited on the Rae craton and is the first described from western Canada.

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Tables.

Table 1. Measured carbon and oxygen isotope values for both whole rock and micro-drilled metacarbonate samples. Precision for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is 0.05‰ and 0.11‰, respectively.

Table 2. Mineral assemblages of select metacarbonate samples based on stained thin section petrography.

Table 3. Chemical composition of whole-rock metacarbonate samples (MgO , CaO , CO_2 , and $\delta^{13}\text{C}$) and calculated values of the amount of decarbonation (F), $\Delta^{13}\text{C}_{(\text{CO}_2-\text{carb})}$, and therefore shifted carbon isotopic values.

Table 4. Compilation of select highly positive $\delta^{13}\text{C}$ values representing the Lomagundi Event from Maheshwari et al. (2010), and the maximum and minimum values for our MBG samples.

Figure Captions.

Figure 1. Upper: Craton map of the western Churchill province (Rae and Hearne cratons) and Slave craton, highlighting Paleoproterozoic successions of the southern Rae craton (Ashton and Hartlaub 2008). Lower: Geological map of the Murmac Bay Group (Ashton et al. 2007) and surrounding area including sample locations in this study.

Figure 2. A generalized tectonostratigraphic column of the Murmac Bay Group (see Geological Setting for details), with carbon isotope values from this study plotted in stratigraphic context.

Figure 3. A. Photomicrograph (in cross-polar) showing the typical appearance of twinned dolomite within the MBG metacarbonate rocks. **B.** Photomicrograph showing the typical appearance of the tremolite overgrowth (bladed rhombs) of the metamorphosed calcite. Calcite also shows twinning, consistent with metamorphic recrystallization.

Figure 4. A. Cross-plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ for both whole-rock and micro-drilled samples. **B.** Cross-plot of Si content vs. the F value for each whole-rock metacarbonate sample, showing the linear relationship between increased loss of carbon (lower F values) and higher Si content.

A generalized tectonostratigraphic column of the Murmac Bay Group (see Geological Setting for details), with carbon isotope values from this study plotted in stratigraphic context.
215x233mm (300 x 300 DPI)

Table 1.

Sample #	$\delta^{13}\text{C}$ (‰, V-PDB)	$\delta^{18}\text{O}$ (‰, V-PDB)	Sample type
6-2	-0.5	-18.4	whole rock
6-2A	1.7	-16.1	whole rock
9-1	-0.7	-16.8	whole rock
9-3	-2.0	-17.8	whole rock
9-8	-0.1	-16.7	whole rock
9-9	1.1	-15.5	whole rock
0050	-0.2	-14.5	whole rock
3075	5.3	-14.0	whole rock
6001	-0.1	-16.0	whole rock
6110	-4.1	-18.3	whole rock
6336	0.6	-15.3	whole rock
			Microdrilled mineral
6-2	-1.2	-13.7	Dolomite
6-2A	7.8	-10.9	Dolomite
9-1	0.6	-16.3	Calcite
9-3	-0.9	-18.0	Calcite
9-6	0.8	-15.6	Calcite
9-7	-0.1	-17.6	Calcite
9-8	0.4	-17.2	Calcite
9-9	1.1	-15.1	Calcite

Sample #	Calcite	Ferroan Calcite	Dolomite	Ferroan Dolomite	Tremolite	Magnetite	Quartz
6-2A	X				X		
6-2			X		X		X
9-1			X		X		
9-3		X		X	X	X	
9-4	X	X	X		X		
9-6			X			X	
9-7	X	X					
9-8			X		X	X	
9-9			X			X	X

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Table 3.

Sample #	wt%			$\delta^{13}\text{Cf}$	mol%					F	α	$\Delta^{13}\text{C}$ (CO ₂ - carb)	MgO/CaO	Mineralogy
	MgO	CaO	CO ₂		MgO	CaO	CO ₂	CO ₂ necessary	CO ₂ Lost					
6-2	14.59	14.08	1.64	-1.2	362	251	37	613	576	0.06	1.003	3	1.04	Dolomite
6-2A	22.62	16.33	6.69	1.7	561	291	152	852	700	0.18	1.004	4	1.39	Dolomite
6110	2.85	1.65	0.46	-4.1	71	29	10	100	90	0.10	1.005	5	1.73	Dolomite
9-3	15.53	25.16	18.4	-0.9	385	449	418	834	416	0.50	1.01	12	0.62	Dolomite
9-1	16.66	28.02	34.90	0.6	413	500	793	500	-293	0.63	1.00	-1	0.59	Calcite
9-8	15.73	28.63	34.60	0.4	390	511	786	511	-276	0.65	1.00	-1	0.55	Calcite
9-9	17.43	29.44	43.60	1.1	432	525	991	525	-466	0.53	1.00	-2	0.59	Calcite
0050	20.11	29.13	43.60	-0.2	499	519	991	519	-471	0.52	1.00	0	0.69	Calcite
3075	20.61	30.25	43.50	5.3	511	539	988	539	-449	0.55	0.99	-9	0.68	Calcite
6336	0.27	29.99	44.60	0.6	7	535	1013	535	-479	0.53	1.00	-1	0.66	Calcite
6001	19.9	51.40	41.40	-0.1	494	917	941	917	-24	0.97	1.00	4	0.01	Calcite

Table 4.

Location	Lithology	$\delta^{13}\text{C}$ Min.	$\delta^{13}\text{C}$ Max.
North America			
Murmac Bay Group	Dolostone		
Micro-drilled		-1.2	7.8
Whole-rock		-4.1	5.3
Africa			
Mcheka Formation	Dolostone	2.6	13.6
Norah Formation	Dolostone	5.6	16.6
Francevillian Series	Dolostone	2.6	6.3
Gumbu Group	Limestone	4.7	7
Duitschland Formation	Dolostone	-2.0	10.1
Ruwenzori Mountains	Dolostone	1.4	11.3
Sengoma-Silverton	Dolostone and Limestone	8.3	11.2
Lucknow Formation	Dolostone	8.7	10.4
Australia			
Bubble Well Member, Juderina Formation	Dolostone	5.7	8.8
India			
Jhamarkotra Formation	Dolostone	5.4	11.2
South America			
Cercadinho Formation	Dolostone	3.3	5.4
Fecho do Funil Formation	Dolostone	5.6	7.4
Rio Itapicuru Greenstone Belt	Dolostone	5.5	9
Itabuna-Salvador-Curaca orogen	Dolostone	2.2	6.9
Guarinos greenstone belts	Dolostone	-0.7	14.5
Rio de la Plata craton	Dolostone	-5.6	11.6