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Effects of bioturbation on carbon and sulfur cycling across the Ediacaran–Cambrian transition at the GSSP in Newfoundland, Canada

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Abstract: The initiation of widespread penetrative bioturbation in the earliest Phanerozoic is regarded as such a significant geobiological event that the boundary between Ediacaran and Cambrian strata is defined by the appearance of diagnostic trace fossils. While ichnofabric analyses have yielded differing interpretations of the impact of Fortunian bioturbation, the disruption of sediments previously sealed by microbial mats is likely to have affected at least local changes in carbon and sulfur cycling. To assess the geochemical effects of penetrative bioturbation, we conducted a high resolution chemostratigraphic analysis of the siliciclastic-dominated basal Cambrian Global Stratotype Section and Point (GSSP; Chapel Island Formation, Newfoundland, Canada). A positive δ13C excursion in organic matter starts at the Ediacaran–Cambrian boundary and returns to stably depleted values near the top of member 2, while the δ34S of carbonate carbon increases from strongly depleted values toward seawater values beginning near the top of member 2. Pyrite sulfur coincidently undergoes significant δ34S depletion at the Ediacaran–Cambrian boundary. These isotope anomalies most likely reflect progressive ventilation and oxygenation of shallow sediments as a consequence of bioturbation. In this interpretation, sediment ventilation in the earliest Cambrian may have spurred a temporary increase in microbial sulfate reduction and benthic sulfur cycling under low-oxygen conditions. In the late Fortunian, local carbon cycling appears to have stabilized as reductants were depleted and more oxygenated conditions predominated in the shallow substrate. Overall, these data attest to the geochemical significance of the initiation of sediment ventilation by animals at the dawn of the Phanerozoic.

Résumé : Le début de la bioturbation pénétrante répandue au tout début du Phanérozoïque est un événement géobiologique jugé si important que la limite entre les strates édiacariennes et cambriennes est définie par l’apparition d’ichnofossiles diagnostiques. Si les analyses d’ichnofabriques ont produit des interprétations divergentes de l’incidence de la bioturbation fortunienne, la perturbation de sédiments préalablement scellés par des tapis microbiens a vraisemblablement entraîné des modifications locales, à tout le moins, des cycles du carbone et du soufre. Afin d’évaluer les effets géochimiques de la bioturbation pénétrante, nous avons réalisé une analyse chimiostratigraphique de haute résolution du point stratotypique mondial (PSM) à dominante silicoclastique de la base du Cambrien (Formation de Chapel Island, Terre-Neuve, Canada). Une excision positive du δ13C dans la matière organique commence à la limite Édiacarien–Cambrien et revient à des valeurs uniformément appauvries près du sommet du membre 2, alors que, à partir des environs du sommet du membre 2, le δ34S de carbonates passe de valeurs fortement appauvries à des valeurs qui tendent vers celles de l’eau de mer. Le soufre pyritique présente un appauvrissement conccurrent significatif en δ34S à la limite Édiacarien–Cambrien. Ces anomalies isotopiques reflètent fort probablement l’aération et l’oxygénation progressives de sédiments peu profonds des suites de la bioturbation. Selon cette interprétation, l’aération de sédiments au tout début du Cambrien pourrait avoir provoqué une augmentation provisoire de la sulfatoréduction microbienne et une accélération du cycle du soufre benthique dans des conditions pauvres en oxygène. Au Fortunien tardif, le cycle du carbone à l’échelle locale semble s’être stabilisé avec l’épuisement des réducteurs et la prédominance de conditions plus oxygénées dans le substrat peu profond. Collectivement, ces données témoignent de l’importance géochimique du début de l’aération des sédiments par les animaux à l’aube du Phanérozoïque. [Traduit par la Rédaction]

1. Introduction

The Ediacaran–Cambrian transition represents a first-order fundamental change in Earth system history. It records an unprecedented increase in the diversity and disparity of soft-bodied and shelly faunas representative of modern animal phyla (Erwin et al., 2011; Erwin and Valentine, 2013), preserved in remarkable assemblages of trace and biomineralized body fossils. Some of these animals were capable of penetrating the widespread microbial mats that had characterized the Ediacaran Period (McIlroy and Logan, 1999; Carbone and Narbonne, 2014; Buatois et al., 2014).

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Three temporally overlapping revolutions in the infauna (Mángano and Buatois 2017), the Cambrian Information Revolution (Plotnick et al. 2010), the Agronomic Revolution (Seilacher and Pflüger 1994; Seilacher 1999), and the Cambrian Substrate Revolution (Bottjer et al. 2000) may have provided greater opportunities for early animals by expanding habitable ecosystems (McIlroy and Logan 1999; Knoll and Bambach 2000). Ecosystem expansion via bioturbation might explain the macro-evolutionary lag between the diagenesis and the Cambrian Stage 2. To test the hypothesis that penetrative bioturbation on sediments: it features a thick, homogeneous, and fine-grained siliciclastic succession of well-preserved sedimentary rocks that document the progressive increase in size, complexity, and diversity of trace fossils from the terminal Ediacaran to Cambrian Stage 2. To test the hypothesis that penetrative bioturbation altered the benthic biogeochemistry of this basin, we analyzed a high-resolution stratigraphic collection of CIF mudstones and siltstones tied to existing detailed sedimentary and ichnofabric architectures for their carbon and sulfur abundance and isotopic compositions.

2. Geological background

2.1. Geological history

The Chapel Island Formation (Hutchinson 1962) is situated along the western end of the Burin Peninsula, which is located in southeastern Newfoundland, Canada (Fig. 1). It is part of the Avalon Terrane, an island arc that developed off the northern margin of Gondwana and later accreted to Laurentia. U–Pb dating of andesites suggests that the volcanic arc developed between 635 and 570 Ma, and that Avalonia either rifted from Gondwana between 585 and 540 Ma, or that a topographic barrier arose and diverted Gondwana drainage basins away from the Avalonian margin (Murphy et al. 2004). Paleogeographic reconstruction places Avalonia at a high latitude in the Ediacaran and Cambrian (Landing et al. 2013b). The terrane and its shelf sediments later accreted to Laurentia by overthrusting during the Acadian Orogeny in Devonian time (Bradley 1983).

2.2. Lithostratigraphy and depositional facies

Sedimentary successions similar to the CIF occur discontinuously at the base of Cambrian successions in Avalonian Newfoundland, Nova Scotia, and New Brunswick (Geyer and Landing 2016). In Newfoundland, the CIF is subdivided into five informal members based on outcrops at Grand Bank Head (GBH), Fortune Head (FH), and Little Dantzic Cove (LDC) (Bengtson and Fletcher 1983). The lower four members together constitute the Quaco Road Member formally defined in New Brunswick, while member 5 is equivalent to the Mystery Lake Member (Landing 1996). On the Burin Peninsula of Newfoundland, the 1 km thick CIF primarily comprises fine-grained siliciclastic sediments deposited in storm-dominated, shallow marine and deltaic environments ranging in depth from intertidal to just below storm wave-base (Myrow 1992; Myrow and Hiscott 1993). Nodules of ferroan dolomite occur sporadically throughout the succession (Brasier et al. 1992; Strauss et al. 1992), but bedded limestones are restricted to a few decimetre-thick beds in member 4 (Myrow and Landing 1992).

At GBH the red-bed dominated Rencontre Formation grades conformably into CIF member 1, which includes red and green sandstones interspersed with siltstones and shales. Lenticular, channel-fill sandstone beds, desiccation and syn-erisis cracks, mud intraclasts, current ripples, and erosional features are present throughout the member, suggesting peritidal marginal marine environments. The upper half of the member contains fewer red sandstones and more dark gray shales and siltstones; this facies has been interpreted to reflect deposition near a low-energy, muddy, micro- to mesotidal coastal plain (Myrow and Hiscott 1993). These gray-black mudstones continue to the top of the GBH section and into the basal 4 m of the FH section. They are overlain by informal member 2, which is 430 m thick and consists of homogeneous grey and green siltstones and mudstones with thin, storm-deposited sandstone interbeds. Deposition of member 2 occurred predominantly between wave-base and storm wave-base in muddy deltaic and shelf environments (Myroy and Hiscott 1993). The basal Cambrian GSSP is located 2.4 m above the base of member 2 (Narbonne et al. 1987; Landing 1994; Brasier et al. 1994). The LDC section contains the upper 135 m of member 3, comprising thinly laminated silver-green siltstones that were deposited in a distal shelf setting below storm wave-base, and member 4 (85 m), which consists of low energy inner-shelf mudstone with thin peritidal carbonate caps that contain abundant small shelly fossils (SSFs; Myrow and Landing 1992; Myrow and Hiscott 1993). The member 4–5 boundary is a disconformity that reflects basin reorganization and progradation of a thick sandstone succession.

2.3. Biostratigraphy

Uppermost Ediacaran deposits (in informal member 1 and the basal 2.4 m of member 2; Narbonne et al. 1987) contain impressions of Ediacarian soft-bodied fossils such as Harlaniella and...
Palaeopascichnus (Fig. 2a); the latter is an index fossil for the upper Ediacaran worldwide (Antcliffe et al. 2011). Simple trace fossils, principally millimetre-diameter burrows Planolites and Helminthoidichnites (Fig. 2f), range throughout the studied section and probably represent horizontal grazing traces within the microbial mats (Buatois et al. 2014). Specimens of the organic-walled tube Sabellitides cambriensis (Fig. 2b) range from below the GSSP to the top of the CIF.

Isolated specimens of Treptichnus and Gyrolithes occur in the uppermost few metres of the Ediacaran (Gehling et al. 2001; Laing et al. 2018), but the first abundant small-scale penetrative burrows of Treptichnus (Figs. 2g and 2h), Gyrolithes (Fig. 2i), and arthropod scratch marks (Fig. 2m) first appear in the Treptichnus pedum Zone, which marks the basal strata of the Cambrian System (Crimes and Anderson 1985; Narbonne et al. 1987; Herringshaw et al. 2017). All of the taxa of the Treptichnus pedum Zone continue upwards into younger strata. Overlying strata of the Rusophycus avallonensis Zone (from 130 m above the GSSP to the top of the succession) contain a diverse trace fossil assemblage that indicates further sediment disruption. The R. avallonensis Zone contains more than 20 taxa, including the sinuous to meandering horizontal feeding burrow Psammichnites (Figs. 2e and 2k), the trilobite resting burrow Rusophycus (Fig. 2j), and the spreiten feeding burrow Teichichnus (Fig. 2f). Specimens of Rusophycus from the CIF are currently regarded as the world’s oldest unequivocal evidence for the high-level crown-groups Ecdysozoa, Lobopodia, and Arthropoda (Benton et al. 2015; Wolfe et al. 2016).

Mudstones near the top of member 3 record the first appearances of the early-micro-molluscs Watsonella crosbyi and Aldanella attleborensis (Fig. 2c). These fossils define the base of the Watsonella crosbyi Zone, which is currently under consideration for the base of Cambrian Stage 2 of the Terreneuvian Series (Fig. 3a). Member 3 also contains specimens of Platysolenites cooperi (McIlroy et al. 2001). Peritidal limestones in member 4 contain a Ladathecia wackestone and new SSF species, including: Igorella ungulata, Coleoloides typicalis, Tikistheca korobovi, Fomitichella infundabuliformis, Lapworthoida ludvigensis, Allatheca deckeri, and Protohertzina (?) canadia (Landing et al. 1989, 2013a; McIlroy and Szaniawski 2000). The preservation of this diverse assemblage in limestone event beds might be considered as recording the onset of the Cambrian Explosion, but may equally or better be regarded as an artifact of faunal migration or taphonomic bias (Landing 1993, 2013a; Droser et al. 1999; Maloof et al. 2010).

3. Methods

A systematic collection of 180 stratigraphic samples from the wave-cut GBH, FH, and LDC exposures of grey and green mudstones and siltstones through informal members 1 through 4 of the CIF was analyzed for the abundance and isotopic composition of carbonate, total organic carbon (TOC), and pyrite sulfur. We present our integrated stratigraphy relative to the height and depth in metres above and below the GSSP datum, respectively. A complete description of the methods employed in geochemical analyses is included in Appendix A.

3.1. Sampling strategy

The stratigraphic interval analyzed in this study ranges from near the base of informal member 1 to the top of member 4, covering a stratigraphic interval that is analogous to the Quaco Road Member formally defined in New Brunswick (Landing 1996). Member 5 was not sampled because it overlies a sequence boundary and features relatively coarse-grained lithologies. Sampling for carbon and sulfur analysis was limited to fine-grained green to grey colored lithologies (mudstones, shales, and siltstones), and to the thin limestone beds in member 4. Sandstones and red bed intervals (e.g., 99–155 m above GSSP) were excluded from sampling insofar as oxidized and coarse-grained lithologies are less likely to preserve organic matter and pyrite. Samples were not selected from fault surfaces or areas of fault gouge. One carbonate nodule (GBH 01.55C) was tested for organic matter abundance and isotopic composition.

The exposure of member 1 along the coast at GBH is characterized by steeply inclined beds of alternating red, green, and grey to black mudstone. These outcrops are stratigraphically continuous, with the exception of three narrow normal faulted intervals with minor stratigraphic offsets. Where strata are continuous, we measured exact stratigraphic positions relative to our datum; in faulted zones the assigned positions reflect distance perpendicular to dip and have not been corrected across fault surfaces. Therefore, we primarily compare the aggregate carbon and sulfur values of member 1 to values from demonstrably Cambrian strata.
Fig. 2. Key soft-bodied fossils (a, b), small shelly fossils (c, d), and trace fossils (e–m) from the Chapel Island Formation at Fortune Head (a, b, c, i–m), Grand Bank Head (f–h), and Little Dantzic Cove (c, d). Stratigraphic ranges are those in the Chapel Island Formation, and are given relative to the basal Cambrian Global Stratotype Section and Point (GSSP). Scale bars represent 1 cm. (a) Palaeopascichnus delicatus Fedonkin, a soft-bodied Ediacara-type fossil impression, range from −80 to −0.2 m; (b) Sabellidites cambriensis Yanishevsky, an organic-walled small shelly fossil, range from −20 m to the top of the succession; (c) Aldanella attleborensis (Shaler and Foerste), pyrite steinkern of an originally aragonitic micromollusc, range from +550 m to the top of the succession (Watsonella crosbyi Zone); (d) Ladatheca cylindrica (Grabať), crushed conch of an originally aragonitic hyolith, range from member 3 or uppermost member 2 to the top of the succession (Ladatheca cylindrica and Watsonella crosbyi Zones); (e) Psammichnites gigas Torell, a feeding burrow, range from +130 m to above the top of the succession (Rusophycus avalonensis Zone); (f) Helminthoidichnites tenuis, a simple horizontal burrow that is common from −6 m to above the top of the succession (long-ranging taxon occurring in all trace fossil zones); (g, h) Treptichnus pedum (Seilacher), horizontal feeding burrow with vertical probes, range from −6 m to above the top of the succession (Treptichnus pedum and Rusophycus avalonensis Zones); (i) Gyrolithes polonica Fedonkin, vertical spiral burrow, range from +0.5 to +400 m (Treptichnus pedum and Rusophycus avalonensis Zones); (j) Rusophycus avalonensis Crimes and Anderson, trilobite resting burrow, range from +130 m to above the top of the succession (Rusophycus avalonensis Zone); (k) Psammichnites, regularly meandering grazing burrow, range from +325 to +410 m (Rusophycus avalonensis Zone); (l) Teichichnus rectus Seilacher, a horizontal, spreiten, feeding burrow, range from +280 to above the top of the succession (Rusophycus avalonensis Zone); (m) Arthropod scratch marks, range from +2 m to above the top of the succession (Treptichnus pedum and Rusophycus avalonensis Zones). [Colour online.]
but we have not interpreted the internal chemostratigraphy of member 1. The FH and LDC exposures are continuous and faults along the shoreline outcrops have been mapped in detail; samples collected from those sections are directly keyed to stratigraphic positions determined in an earlier sedimentological study of the CIF (Narbonne et al. 1987).

4. Results

Elemental and isotope abundances of all analyzed CIF samples along with their lithologic associations are reported in the supplementary data (Table S12), and are systematically discussed below. Based on the geochemical trends, we bin the data into three distinct intervals (see A, B, and C in Figs. 3, 4, 6, and 7). For all sampled facies, including the peritidal limestones, TOC abundances range from 0.05% to 0.24% (Fig. 3b), and sulfur abundances from <0.05% to 1.36% (Fig. 3f). Carbonate abundances in the mudstones range from 3.6% to 42.2% (Fig. 3d). After stoichiometric conversion, carbonate carbon constitutes 94.2 ± 2.7% of total carbon when averaged for all samples in the succession. There is an increase in carbonate abundance between Intervals A and B, rang-

Fig. 4. Stratigraphic Intervals A, B, and C are defined by a positive excursion in organic carbon isotopes. Chemostratigraphic trends through the Chapel Island Formation (CIF) are expressed here in box and whisker plots. The left and right sides of each box correspond to the lower and upper quartile, respectively, of the data bin. The line in the middle of each box represents the median value of the bin. Whiskers on the left and right of each box represent the total range of values in the bin. Diagonal notches on each box represent the comparison interval at 5% significance for each median, where the notch width (w) is set by the function $w = q_3 - q_1$, where $q_1$ is the lower quartile, and $q_3$ is the upper quartile, and $n$ is the number of points in the bin. If two comparison intervals do not overlap between two bins, there is a 95% probability that the median values of those bins are significantly different.

Organic $^{13}$C abundances ($\delta^{13}$C$_{org}$) in Ediacaran strata (member 1 and the basal 2.4 m of member 2; i.e., Interval A) range narrowly, with a mean $\delta^{13}$C$_{org}$ of $-28.1 \pm 1.3$‰ VPDB (1σ reported for all standard deviations). Within 1 m of the Ediacaran–Cambrian boundary, however, there is a $^{13}$C enrichment in organic carbon that is sustained over the overlying 378 m of section (i.e., Interval B; Figs. 3c and 4a). A 10-point running average line applied to the organic carbon isotope data changes slope at 0.3 m above the GSSP datum. In the $\delta^{13}$C$_{org}$ excursion interval, the range of $\delta^{13}$C$_{org}$ values is larger than except for a decrease from Interval B to Interval C, from a mean of 0.10% (median = 0.09%) to 0.08% (median = 0.07%).

Returns to stable pre-excursion values at a height of 378 m above the GSSP.

Conversely, the time-series carbon isotope composition of the carbonate fraction ($\delta^{13}$C$_{carb}$) reveals an antithetic negative $\delta^{13}$C shift of $-2$‰ also starting at the base of the Fortunian Stage (Fig. 3e). These carbonates are strongly depleted in $^{13}$C, reaching a stable minimum near $-27$‰ VPDB in the lower $R$. avalonensis Zone, some 150 to 300 m above the GSSP. Above ~300 m, $\delta^{13}$C$_{carb}$ values in mudstone samples begin to increase, reaching values in the range of $-10$‰ to $-20$‰ VPDB at the top of the measured succession. A local maximum of $\delta^{13}$C$_{carb}$ is superimposed on this positive trend and peaks at 565.5 m above the GSSP with a value of $-6.85$‰ VPDB.

There is a $-60$‰ range in $\delta^{34}$S$_{pyr}$ values through the measured interval (Fig. 3g), with a broad (albeit noisy) trend toward lower $34^{S}$ abundances up section. A 10-point moving average line applied to the $\delta^{34}$S$_{pyr}$ data set reaches a maximum and begins to decline between 10 and 20 m below the GSSP, but the slope of the line steepens sharply less than 1 m above the GSSP datum. The decline in $\delta^{34}$S$_{pyr}$ is coupled with a net decrease in pyrite abundances (Fig. 4f), including a largely sulfur-barren interval (~0.05% mass for all but one sample) from 200 to 400 m above the GSSP in upper member 2 (Fig. 3f). However, a scatter plot of $\delta^{34}$S$_{pyr}$ versus sulfur abundance for individual samples does not indicate correlation between $\delta^{34}$S$_{pyr}$ and sulfur abundance ($R^2 = 0.0678$; Fig. 5c). Although $\delta^{34}$S$_{pyr}$ values in members 3 and 4 are generally depleted,
Fig. 5. Scatter plots comparing isotopic signatures to elemental abundance. (a) $\delta^{13}$C of organic carbon (per mil relative to Vienna Pee Dee Belemnite) versus mass percent total organic carbon (TOC) of bulk rock; (b) $\delta^{13}$C of carbonate carbon (per mil relative to Vienna Pee Dee Belemnite) versus mass percent carbonate of bulk rock; (c) $\delta^{34}$S of pyrite sulfur (per mil relative to Vienna Canyon Diablo Troilite) versus mass percent sulfur of bulk rock.

there is a local maximum in $\delta^{34}$S$_{pyr}$ that peaks 2.9 m above the FAD of Watsonella crosbyi at a value of 7.52‰ VCDT.

A Gaussian mixture model was used to sort the data from the scatter plot of $\delta^{13}$C$_{org}$ versus $\delta^{34}$S$_{pyr}$ into three bins (Fig. 6). The resulting clusters are nearly identical to Intervals A, B, and C, which are stratigraphically defined by the initiation and termination of the organic carbon isotope excursion (see Section 5.2.). Five out of 69 points receive divergent classifications between the model-generated set and the stratigraphically bounded set, of which only one point, 10.69 m above the GSSP (i.e., FH 10.69), is situated near an interval boundary.

5. Discussion

5.1. Controlling factors of the isotopic variations

5.1.1. Paleoabathymetry and lithology

Organic carbon isotope variations in the CIF have been attributed to paleoabathymetric variations between peritidal and distal shelf settings (Strauss et al. 1992). However, the interval that begins 378 m above the GSSP features uniform $\delta^{13}$C$_{org}$ values despite paleoabathymetric deepening from middle (upper member 2) to distal (member 3) shelf environments, followed by shallowing to inner shelf and peritidal (member 4) settings regardless of the sampling locality (Fig. 3c). These observations indicate that water column depth did not exert a strong influence on $\delta^{13}$C$_{org}$ compositions. The organic and carbonate carbon isotope trends continue between FH and LDC without discernible offsets. On the other hand, the increase in sulfur abundance from upper FH to lower LDC is most likely a facies effect because the sediments of the LDC section were deposited in a more distal shelf setting than those in the FH section (Myrow 1992). Even though the overall trend of sulfur isotope depletion is clear between all three exposures (Fig. 4c), the facies dependence of sulfur abundance makes it difficult to attempt more refined interpretations of the sulfur isotope chemostatigraphy.

To minimize isotopic shifts that may have occurred as a result of lithologic changes, sampling was restricted to green and gray shale–mudstone–siltstone intervals, as well as the limestone beds of member 4. Although the member 1–2 boundary marks a lithologic transition from gray-black peritidal shale to green-gray, thinly laminated subtidal siltstone, the organic isotope excursion initiates 0.3 m above the GSSP—i.e., 2.7 m above the base of member 2—as indicated by a 10-point moving average line (Fig. 3c). Additionally, the abrupt termination of the organic isotope excursion occurs in homogeneous mudstones of upper member 2, nearly 40 m below the top of the FH section, and the stabilized $\delta^{13}$C$_{org}$ signal of Interval C persists through mudstone, siltstone, and peritidal limestone facies.

5.1.2. Thermal alteration

X-ray diffraction analysis of illites from the CIF indicates maximum burial temperatures of 140–200 °C (Strauss et al. 1992). Generally consistent with this estimate, kerogen and microfossil colors lie in the range of 3–5 on the Thermal Alteration Index (Tissot and Welte 1984), suggesting maximum heating between 150 and 250 °C. This temperature range falls into the zeolite or prehnite–pumpellyite metamorphic facies (Strauss et al. 1992). Insofar as these chemostatigraphic signals are preserved in rapidly accumulating, monotonous, fine-grained silicilastic facies and the metamorphic grade of the succession is low, it is unlikely that thermal effects (Hayes et al. 1983) were the cause of the carbon isotope excursions or the low overall TOC and high carbonate abundance in the CIF mudstones. It is also important to note that although the carbonate fraction of the mudstones is clearly not reflective of an oceanic alkalinity signal, the peritidal limestones in member 4 record $\delta^{13}$C$_{carb}$ values of $-3.1\%$, $-1.2\%$, and $0.6\%$ VPDB (Strauss et al. 1992), suggesting minimal thermal alteration.

Loss of organic carbon via thermal alteration can enrich refractory carbon by $\sim6\%$ for every 10-fold decrease in carbon abundance (Hayes et al. 1983); however, mean and median TOC (wt%) in the CIF remain nearly uniform over the sampled intervals despite wide variance (Figs. 3b and 4d), and there is no apparent correlation between TOC (wt%) and $\delta^{13}$C$_{org}$ values (Fig. 5a). Furthermore, low average TOC abundances and wide variance in TOC (wt%) have not affected the $\delta^{13}$C$_{org}$ signal. This is evident from comparing Interval B to Interval C; both have similar amounts of variance in TOC (wt%), but Interval C has substantially less variance in $\delta^{13}$C$_{org}$ (Fig. 4).

It is evident that the low TOC (wt%) values in the CIF do not result from thermal diagenesis; instead, we suggest that they reflect microbial remineralization and the production of authigenic carbonate. This is corroborated by depleted values of $\delta^{13}$C$_{carb}$ in mudstone cements through most of the sampled interval that give way to unaltered seawater $\delta^{13}$C$_{carb}$ values in the peritidal limestone beds. The observation that the carbon and sulfur anomalies coincide with paleontological evidence for penetrative bioturbation also suggests that the measured geochemical changes resulted from sediment ventilation by earliest Cambrian animals, with the additional possibility of changes in water column carbon cycling. Thus, while the isotope chemostatigraphy of the CIF might not offer a reliable imprint of primary oceanic signals, it does likely reflect changes in the exchange of fluids and gases across the sediment–water interface and the biological reworking.
of sedimentary organic matter associated with penetrative bioturbation. In short, we interpret the $\delta^{13}C_{\text{org}}$, $\delta^{13}C_{\text{carb}}$, and $\delta^{34}S_{\text{pyr}}$ signals as indicators of sedimentary ventilation by animals and the microbial response to changes in the oxidation state and sulfate abundance of pore waters (Fig. 7).

5.2. Biogeochemical reconstruction: Intervals A, B, and C

5.2.1. Interval A (Terminal Ediacaran)

Ediacaran strata of the CIF are distinguished by a combination of enriched pyrite sulfur isotopes and depleted organic carbon isotopes (Fig. 6). Carbonate carbon isotopes are strongly depleted and are probably the authigenic products of anaerobic microbial respiration. These isotopic signals were generated in part by the sedimentary sealing that characterized the Ediacaran sea floor. Matground biofilms inhibited diffusion of seawater alkalinity and sulfate into the sediments, as well as the diffusion of methane and sulfide out of them. Additionally, the burial flux of organic carbon may have been degraded and refractory as a result of inefficient export and long residence times in the water column (McIlroy and Logan 1999). Matgrounds would have attenuated oxidative processes in the sediments. Cambrian-style bioturbation probably increased solute exchange between seawater and pore water, especially if bioturbating animals established advective flow pathways in pore water via bio-irrigation (Herringshaw et al. 2017).

A temporal buildup of sulfate in the Chapel Island basin is suggested by the 60‰ decrease of $\delta^{34}S$ abundances of pyrite in the mudstone samples from the base to the top of the measured section. We attribute this large shift to progressively greater degrees of sulfur isotope fractionation during open system MSR (Sim et al. 2011; Zhereleznitskaya et al. 2014), made possible through the ventilation of sediments. Ventilation spurred the conversion of H$_2$S to sulfate or intermediate sulfur compounds by way of chemolithotrophic sulfide oxidation. Reoxidative sulfur cycling in shallow sediments had become globally significant by the early Ediacaran (Kunzmann et al. 2017), and even in low-oxygen bottom waters, bioturbation would have intensified reoxidative sulfur cycling via

5.2.2. Interval B (Early Fortunian)

Although some Ediacaran organisms may have supplied oxygen to the sediments beneath their own bodies via simple diffusion (Dufour and McIlroy 2016), evidence for more vigorous sediment ventilation by animals starts at the base of the Treptichnus pedum Zone defining the Ediacaran–Cambrian boundary (Narbonne et al. 1987; Bottjer et al. 2000; Herringshaw et al. 2017). This mode of bioturbation may have been a response to an increase of organic matter export from the water column to the sediments due to the efficient packaging into fecal pellets associated with the advent of coelomate animals (Logan et al. 1995; McIlroy and Logan 1999), or to the evolution of larger phytoplankton in response to increased zooplankton predation (Butterfield 2009). Coelomate-grade animals may also have sought shelter from predation in the sediments. Cambrian-style bioturbation probably increased solute exchange between seawater and pore water, especially if bioturbating animals established advective flow pathways in pore water via bio-irrigation (Herringshaw et al. 2017).
Fig. 7. Schematic diagram of interpreted geochemical effects of bioturbation through the Chapel Island Formation, based on interpretation of carbon and sulfur chemostratigraphy. Intervals A, B, and C are defined by the positive excursion in organic carbon isotopes. (a) The late Ediacaran regime featured slow particle settling, limited diffusion of sulfate into sediments, and microbial reworking of relatively degraded organic matter. (b) The early Fortunian featured more rapid particle sinking and penetrative bioturbation. In a regime of more rapid sulfur cycling and lower benthic oxygen, microbial sulfur reduction (MSR) increased. (c) By the late Fortunian, more thorough sediment ventilation by bioturbating animals resulted in more complete oxygenation of the shallow substrate as its reservoir of reduced compounds was depleted. Aerobic respiration replaced anaerobic respiration as the dominant mode of benthic microbial heterotrophy, which, in concert with increased seawater mixing, led to the decline of isotopically depleted authigenic carbonates in mudstone cements.

bacterial sulfur disproportionation. As long as oxygen was a limiting reagent, MSR in shallow sediments would have increased in a regime of more rapid sulfur cycling. As implied by the sulfur-barren interval at FH (Fig. 3f), progressive substrate oxygenation ultimately depleted shallow sediments of sulfides, after which MSR reactions were pushed deeper into the substrate and lost their prominent role in remineralization reactions. Reactive transport modeling also demonstrates that bio-irrigation tends to flush sulfur compounds out of sediments, which offers further explanation for the low pyrite abundance through much of member 2 (van de Velde and Meysman 2016).

Carbon isotope variations in Interval B may also result from MSR reactions in a regime of intensified sulfur cycling. The positive Δ13Corg excursion in refractory organic carbon from basal Cambrian strata of the CIF is an unusual feature; the only other documentation of a potential positive excursion in organic carbon in basal Cambrian strata is from a similar silicilastic-dominated succession on the East European Platform (Strauss et al. 1997). We hypothesize that the organic carbon isotope excursion documented in the CIF resulted from enhanced burial of labile organic matter. This would occur as a result of benthic oxygen decline, which could have resulted from increasingly efficient export of organic matter (McIlroy and Logan 1999; Butterfield 2009), or from a decline in primary production spurred by more efficient phosphorous burial through bioturbation (Boyle et al. 2014). In either case, bottom water deoxygenation would confer an advantage to anaerobic respiration in the shallow substrate. Consumption of organic matter by MSR is slower and less quantitative than aerobic respiration, and the anaerobic process notably increases pore water alkalinity (LaRowe and van Cappellen 2011). In eitheroxic or anoxic sediments, refractory organic compounds tend to be enriched in 13C by 3‰–4‰ relative to their more labile counterparts (McArthur et al. 1992; Böttcher et al. 1998; Freudenthal et al. 2001). With these observations in mind, Interval B is viewed as a period of low-oxygen conditions in which MSR generated strongly 13C-depleted carbonates and left behind refractory organic matter enriched in 13C (Fig. 7). As a whole, this biogeochemical scenario would explain the increase in carbonate abundance and Δ13Corg values along with the decrease in δ34S, %S, and δ34S values above the Ediacaran–Cambrian boundary. In short, a combination of oxygen depletion in bottom waters and increased sedimentary sulfur cycling—both potentially spurred by bioturbation—can account for the isotopic shifts in carbon and sulfur seen in Interval B.

5.2.3. Interval C (Late Fortunian and Early Stage 2)

The Δ13Corg signal returns to pre-excursion values 378 m above the GSSP. We propose that this reflects a stabilization of local carbon and oxygen cycling, at which point MSR was outcompeted by metabolically more efficient aerobic respiration in shallow sediments (Fig. 7). This is attested by the end of the Δ13Corg excursion, the decrease in TOC (wt%), and the progressive increase in δ34S. The shift toward aerobic respiration in the shallow substrate would have hindered benthic production of authigenic carbonate, thus driving Δ13Ccarb toward more positive values as MSR was forced into deeper sediments. Greater infiltration of seawater alkalinity into ventilated sediments likewise would have driven an increase in Δ34S. Reorganization of the local carbon cycle in the late Fortunian might be related to water column oxygenation, which likely increased during this interval (Chen et al. 2015). Near the top of the analyzed section at LDC, diagnostic SSFs of Cambrian Stage 2 appear in mudstone and carbonate facies. In this interval, mudstone Δ13Ccarb compositions rise toward seawater values, which are preserved in the near 0‰ values of the bedded limestones (Brasier et al. 1992; Strauss et al. 1992). This shift in Δ13Ccarb is in line with model results that imply that Phanerozoic stabilization of the carbon isotope record, including the decline of authigenic carbonate formation, may have resulted from bioturbation (Boyle et al. 2018). Values of Δ13Corg remain stably depleted through most of Interval C, while pyrite sulfur isotope abundances are variable but strongly depleted in 34S relative to underlying strata.

5.2.4. Summary of biogeochemical interpretations

Our Interval zonation is defined by the stratigraphic boundaries of the positive excursion in Δ13Corg. In our interpretation, Interval A (~128 to 0 m) reflects an Ediacaran regime of sealed substrates...
and negligible solute exchange with seawater, with deposition of refractory organic carbon and Rayleigh distillation of sulfur isotopes. Interval B (0 to 378 m) reflects initial sediment ventilation by bioturbating animals, probably concurrent with low-oxygen conditions. MSR would be expected to increase if bioturbation initially lowered water column pO2 (Boyle et al. 2014), or if more efficient export productivity shifted oxygen demand toward the seafloor (McIlroy and Logan 1999). In either case, penetrative bioturbation and bio-irrigation would have promoted the oxidative sulfur cycle in sediments, which would explain the precipitous drop in δ34S values above the GSSP (Canfield and Farquhar 2009). Inefficient consumption of organic matter by MSR (LaRowe et al. 2001) would have led to burial of more refractory organic carbon, which would account for the positive excursion in δ13Corg compositions (Freudenthal et al. 2001). Interval B ended as the oxygen buildup depleted reductants from the shallow substrate, forcing MSR deeper into the sediments. Interval C (378 to 626 m) in turn likely featured ventilation and oxygenation of sediments along with more efficient aerobic respiration of the benthic detrital flux. Notably, oxygenation of the shallow substrate as suggested by this biogeochemical model was followed by the local first appearance of bio-mineralizing organisms of Cambrian affinity.

5.3. Sediment disruption versus sediment ventilation
Previous studies of the CIE have shown an abrupt appearance of penetrative burrows near the base of member 2 (Narbonne et al. 1987; Gehling et al. 2001; Laing et al. 2018) with increased depth of burrowing and intensity of bioturbation upward through the formation (McIlroy and Logan 1999; Gougeon et al. 2018). Our geochemical data suggest that this earliest Cambrian infaunal activity was sufficient to affect geochemical cycling on at least a localized scale. Furthermore, a regime of limited sediment disruption does not preclude infaunal generation of the isotopic changes documented in the CIE, especially in light of the fact that bio-irrigation (Herringshaw et al. 2017) and agrichnia (i.e., the stimulation of microbial growth in burrows via accelerated redox cycling; Laing et al. 2018), are attributed to key fossils of the Treptichnus pedum Zone within the CIE. These behaviors would have increased rates of physical and biogeochemical cycling, even in the absence of more physically disruptive behaviors such as sediment bulldozing. Additionally, lateral permeability within upper matground sediments tends to be significantly higher than permeability across the matground–water interface, allowing for lateral fluid transport within matground sediments (Wieland et al. 2001).

This raises an important question about the relationship between physical disruption of sediments and chemical cycling in sediments: how abruptly did rates of chemical cycling and remineralization respond to incipient penetrative bioturbation, and how sensitive were these rates to varying modes of burrowing behavior? The reactive transport model of van de Velde and Meysman (2016) distinguishes bio-mixing (i.e., advection of sediment), which increases rates of MSR by forcing labile organic carbon down into sediments, from bio-irrigation (i.e., advection of fluid), which efficiently flushes sulfur from the sediments into the water column, thereby depleting the pore water sulfide reservoir. Notably, the model also demonstrates that incipient, low-intensity bio-mixing rapidly increases the rate of MSR, which then levels off as the sediments are more intensely stirred. These results are consistent with the isotopic imprint of strengthening MSR in Interval B followed by weakening MSR in Interval C, as attested by δ13Corg and δ34Sorg trends. Additionally, the sulfide flushing effect of bio-irrigation may explain the large pyrite–barren interval in member 2.

Our understanding of the effects of bio-mixing and bio-irrigation on Cambrian geochemistry will benefit from reconciling and refining the parameters of different numerical models, especially if model outputs are used to constrain divergent responses, feedback processes, or reservoir sizes that act as inputs for a second generation of models. For example, the sulfur-based box model of Canfield and Farquhar (2009), also adapted by Tarhan et al. (2015), includes a coefficient (α) for the fraction of MSR-generated sulfide that escapes burial (in this case as a result of bio-irrigation or the lack of ferrous iron to produce pyrite), as well as an exponent (γ) that modulates the response of MSR to increases in oceanic sulfate concentration:

\[ \frac{\text{SO}_2\text{O}_{\text{Ocean}}}{\text{F}_{\text{in}} - E} = \frac{1}{\alpha \text{OC}} \]

where \( F_{\text{in}} \) is the flux of sulfur into the ocean, \( E \) is the flux of sulfur into evaporites, \( \alpha \) is a constant of proportionality, and \( \text{OC} \) is the average sedimentary concentration of labile organic matter. The exponent γ would equal unity if the rate of MSR increased as a linear function of oceanic sulfate concentration, but the diminishing concentration of labile organic matter in deeper sediments typically limits MSR rates even as sulfate penetration increases, thus reducing the value of γ.

In their models, both Canfield and Farquhar (2009) and Tarhan et al. (2015) lower the value of x to represent the overall influence of bioturbation, but hold y constant through each simulation. The reactive transport model of van de Velde and Meysman (2016), however, implies that both x and y are sensitive to the mode of bioturbation. These authors suggest that bio-mixing increases y by advecting labile carbon downward from surface sediments, while bio-irrigiation decreases y by oxygenating sedimentary pore waters and thereby limiting the activity of sulfate reducers despite greater sulfate penetration. Both modes of bioturbation are expected to decrease values of x, but bio-irrigiation decreases it more effectively via sulfide flushing. In short, by lowering both x and y, bio-irrigiation would have been responsible for a larger flux of sulfur to the water column than bio-mixing, and it may have induced significant chemical fluxes even if bio-mixing was not pervasive. Of course, sulfur fluxes would have been sensitive to other changes such as depth variations of the sedimentary redoxcline, changes in microbial ecology, and the oxygenation of the water column; nonetheless, the geochemical profile of the CIE indicates that bio-irrigiation may have been a significant factor in establishing early Cambrian fluxes of sulfur between the sediment and the water column.

6. Conclusions
To investigate the biogeochemical effects of penetrative bioturbation across the Ediacaran–Cambrian boundary, we conducted a chemostatigraphic analysis of the elemental and isotopic abundances of carbon and sulfur at the Ediacaran–Cambrian GSSP (Chapel Island Formation, Newfoundland). Trends in δ13C_carb, δ13C_org, and δ34S_pyr from Ediacaran to Cambrian strata suggest that penetrative burrowing at the GSSP coincided with geochemical changes in the water column and (or) in sediments. Isotopic depletion in pyrite sulfur above the GSSP suggests that burrowing increased the availability of sulfate to the sediments through progressive ventilation that stimulated the oxidative sulfur cycle. This reordering of the benthic sulfur cycle may have played a role in the increase of marine sulfate concentrations, particularly if bio-irrigation was a common trace-making habit.

We argue that the δ13C_org excursion and the accompanying increase in carbonate abundance documented in the lower Fortunian strata of the CIE reflect increased rates of MSR under transient low-oxygen benthic conditions. A decline in bottom water pO2 in the earliest Cambrian could have resulted from more efficient biological pumping, although it is possible that bioturbation itself may have lowered water column pO2 by burying phosphorus and inhibiting primary production. A decline in bottom water pO2 in concert with an increased supply of sulfate and labile organic
matter would have spurred an increase in shallow sedimentary MSR, which in turn may have generated the organic carbon isotope excursion that terminates in upper Fortunian strata. The end of the organic carbon isotope excursion implies stabilization of carbon and oxygen cycling in the shallow substrate, potentially related to a balance between the production, export, and remineralization of organic matter and (or) to a stabilization of water column pO2. Meanwhile, the δ13Ccarb profile exhibits a strong authigenic imprint that weakens considerably up section, suggesting an increase of seawater mixing and a decline in the activity of MSR by the late Fortunian. In short, the isotopic signals in the CIF indicate ventilation and ultimately oxygenation of the shallow substrate, followed by the appearance of bomineralized Cambrian fossils. Our findings suggest that bioturbation induced geochemical changes in the earliest Cambrian sediments of Newfoundland, and that oxygenation of the shallow substrate was at least a localized precursor to the appearance of bomineralizing animals of Cambrian affinity.

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References


Platysolenites from the Placentian of southeastern Newfoundland. Lethaia, 23(2): 179–182.


trap and separated by a gas chromatography (GC) column prior to elemental and isotopic analysis. Two urea standards (\(\text{CH}_4\text{N}_2\text{O}:\text{CH}_2\text{N}_2\text{O}\); 20% C abundance with \(\delta^{13}\text{C} = -29.39\%\)) were measured between every 10 samples to monitor the accuracy and precision of measurements. Organic carbon isotope measurements are reported as \(\%\) deviations (±0.1‰, 1σ) from the Vienna Pee Dee Belemnite (VPDB) standard, and abundances are reported as TOC (wt%) (weight percent total organic carbon) relative to the pre-acidified mass of sample powder. TOC abundances were calculated by first determining the TOC (wt%) of acidified residues with

\[
(A1) \quad \%\text{TOC}_{\text{residue}} = \left[ \frac{20.0}{\%\text{C}_{\text{avg.urea}}} \right] \%\text{TOC}_{\text{measured}}
\]

where 20.0 is the known mass percentage of carbon in urea; \(\%\text{C}_{\text{avg.urea}}\) is the mean mass percentage of carbon measured in the batch urea samples; and \(\%\text{TOC}_{\text{measured}}\) is the uncorrected mass percentage of carbon measured in an acidified sample. The TOC (wt%) of bulk rock was then calculated by factoring in the fraction of bulk powder lost during acidification:

\[
(A2) \quad \%\text{TOC}_{\text{bulk}} = \%\text{TOC}_{\text{residue}} \left[ 1 - \frac{\%\text{CO}_3}{100} \right]
\]

where \(\%\text{CO}_3\) is the mass percentage of carbonate in the bulk sample as determined by acidification. Determining percent carbonate via acidification can yield inaccurate results if the rock contains an appreciable amount of salts, but there is no indication that the CIF was deposited in an evaporative facies. Corrected standard deviations (\(\sigma_{\text{corr}}\)) for \%\text{TOC}_{\text{bulk}} were calculated with

\[
(A3) \quad \sigma_{\text{corr}} = \left[ \frac{\%\text{TOC}_{\text{bulk}}}{20.0} \right] \sigma_{\text{urea}}
\]

where 20.0 is the mass percentage of carbon in urea and \(\sigma_{\text{urea}}\) is the standard deviation of all measured carbon mass percentages of the urea standards in a batch.

For sulfur analyses, ∼0.3 mg of \(\text{V}_2\text{O}_5\) was added to 1–8 mg of powdered residues to ensure quantitative combustion at 1030 °C in a different quartz combustion column filled with high purity copper wire. To determine the accuracy and precision of sulfur measurements, two NBS-127 barite standards (\(\text{BaSO}_4\); 12.74% S with \(\delta^{34}\text{S} = +20.3\%\)) and two IAEA-S-1 standards (\(\text{Ag}_2\text{S}\); 12.94% S with \(\delta^{34}\text{S} = -0.3\%\)) were measured between each set of 10 samples. Sulfur isotope data are expressed with the \(\delta^{34}\text{S}\) notation as per mil (‰) deviations (±0.3‰, 1σ) from the Vienna Canyon Diablo Troilite (VCDT) international standard. For total sulfur (TS) abundance of the samples, a calculation similar to those used for TOC (see above) using measured NBS-127 sulfur abundances and carbonate percentages determined by acidification was used to correct sample values.

Attempts at \(\text{CO}_2\) generation via phosphoric acid digestion of minor and trace mudstone carbonate with our on-line system were hindered by incomplete reactions. This was probably due to the presence of trace siderite, ankerite, or other insoluble late diagenetic carbonates in the CIF mudstones. These minerals resist dissolution in phosphoric acid at standard temperatures and reaction times. X-ray diffraction analyses of several representative mudstone samples did not yield carbonate mineral abundances because of interference from the high abundance of silicates. Therefore, in lieu of acid digestion, total carbon abundance and isotope compositions of non-acidified bulk sample powders were measured by combustion in the same manner as acidified residues. The bulk sample powders were analyzed along with a house standard carbonate (JTB-1; 12.0% C abundance with \(\delta^{13}\text{C} = -1.78\%\)) using the combustion system. Carbonate \(\delta^{13}\text{C}\) values (\(\delta^{13}\text{C}_{\text{carb}}\)) were then calculated from \(\delta^{13}\text{C}_{\text{org}}\) and \(\delta^{12}\text{C}_{\text{bulk}}\) values using the mass balance equation

\[
(A4) \quad \delta^{12}\text{C}_{\text{carb}} = \left[ \%\text{TOC}_{\text{bulk}} + (\%\text{CO}_3 \times 0.120) \right] \times \delta^{12}\text{C}_{\text{bulk}} - (\%\text{TOC}_{\text{bulk}} \times \delta^{13}\text{C}_{\text{org}}) \times \frac{\%\text{CO}_3}{0.120}
\]

where \(\delta^{13}\text{C}_{\text{carb}}\) is the \(\delta\)-value of total carbon in a non-acidified sample; \(\delta^{13}\text{C}_{\text{org}}\) is the \(\delta\)-value of the organic carbon in the sample; and 0.120 is the molar fraction of carbon in calcium carbonate. Carbonate carbon isotope measurements are reported as \(\%\) deviations from the Vienna Pee Dee Belemnite (VPDB) standard. Error values (1σ) for \(\delta^{13}\text{C}_{\text{carb}}\) measurements range from 0.2% to 0.5% (Table S1, Supplementary Material); these values derive from error analyses of the JTB-1 carbonate standards combusted for each batch of \(\delta^{13}\text{C}_{\text{bulk}}\) analyses. Assuming the CIF carbonate fraction includes trace siderite, ankerite, or other late diagenetic carbonates, we evaluated whether the presence of these minerals would have an effect on \(\delta^{13}\text{C}_{\text{carb}}\) values determined by mass balance calculations. For example, changing the molar fraction term to 0.104 (i.e., assuming that 100% of carbonate minerals are siderite) would change resulting values of \(\delta^{13}\text{C}_{\text{carb}}\) by only 0.02 ± 0.03‰. It is further possible that a fraction of very fine clay material was lost from the samples during acidification and leaching, which would introduce error into the \(\%\text{CO}_3\) term in Eqs. (A2) and (A4). However, even if it is assumed that each sample lost 3% of its bulk mass to silicate dissolution, the resulting reduction in \(\%\text{CO}_3\) would change the calculated \(\delta^{13}\text{C}_{\text{carb}}\) values by a mean of only 0.17‰ (median of 0.08‰); in all but nine samples, the absolute value of the error would be less than 0.5‰.