

Oxidative forcing of global climate change: A biogeochemical record across the oldest Paleoproterozoic ice age in North America[☆]

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Abstract

Carbon isotope compositions of organic matter in fine-grained siliciclastic units deposited above and below glacial diamictite at the base of the ca. 2.45–2.22 Ga Huronian Supergroup in Ontario, Canada were studied to constrain relationships between profound fluctuations in the exogenic carbon cycle and dramatic climate changes at the beginning of the Proterozoic Eon. In both drill core and outcrop sections the organic matter preserved in proximal lithofacies, dominated by coarse-grained sand and silt, are enriched in ¹³C relative to distal lithofacies, dominated by argillites. In the drill core, sand-dominated lithofacies of the McKim Formation beneath the glacial diamictite of the Ramsay Lake Formation have a narrow range of $\delta^{13}\text{C}$ values (–28.4 to –26.0‰ V-PDB), but organic matter in argillite-dominated lithofacies of the outcrop section ~40 km to the southeast is somewhat more ¹³C-depleted with values ranging from –34.5 to –26.4‰. Similarly, sand-dominated lithofacies of the Pecors Formation above the glacial diamictite in the drill core section with $\delta^{13}\text{C}$ values of ca. –28‰ are notably ¹³C-enriched relative to argillite-dominated lithofacies, which record values as low as –40.5‰. The sand-dominated lithofacies of the Pecors Formation in the outcrop sections have $\delta^{13}\text{C}$ compositions ranging from –34.4 to –27.9‰. The isotopic differences appear to be unrelated to organic carbon abundances, so we suggest that these are controlled by environmental differences in proximal and distal settings. The strong ¹³C-depletion in the organic-lean McKim and Pecors argillites, especially in the drill core section of the Pecors Formation, is consistent with significant biological methane production and oxidative recycling by methanotrophs both before and after the ice age in shallow-water environments stratified with respect to oxygen. The rise of atmospheric oxygen and subsequent enhanced biogeochemical methane cycling in shallow-water settings likely contributed to unstable climate conditions during the Paleoproterozoic glacial epoch.

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1. Introduction

Geochemical and sedimentological evidence suggests that atmospheric oxygen rose at the beginning and the end of the Proterozoic Eon [1–4] in broad association with prolonged glacial epochs. In both intervals, geochemical models have suggested that climate change was linked to

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modulations in the redox state of the atmosphere, perhaps associated with fluctuations in the abundances of methane [5–9], a strong greenhouse gas, and oxidants, like molecular oxygen, formed by photosynthesis or hydrogen escape from the atmosphere [10–12]. For example, the Paleoproterozoic glacial epoch (ca. 2.4–2.2 Ga) – which is characterized by three discrete ice ages in North America – has been linked to oxidation of the atmosphere forcing methane to decline from >1000 ppm down to 10–100 ppm levels [13–15,8,9]. While this model makes a link between the rise of atmospheric oxygen and the glacial epoch, it did not address oscillatory processes that could have resulted in discrete ice ages [16].

Although higher atmospheric methane content is unavoidable in a reducing atmosphere [5], direct evidence for high atmospheric methane content during either Archean Eon or the Paleoproterozoic glacial epoch are lacking insofar as a methane paleobarometer has yet to be developed. Indirect evidence for the methane-rich atmosphere before the rise of atmospheric oxygen includes carbon isotope compositions of organic matter from both marine and terrestrial environments [17,18,31] as well as paleosol data suggesting lower atmospheric CO₂ levels than required by climate models to maintain Earth's surface temperature above freezing at the time of lower solar luminosity [19,13,20]. Available geochemical and geological evidence suggest that atmospheric oxygen started to rise after ca. 2.47 Ga, likely before the oldest Paleoproterozoic ice age [21–24]. Since atmospheric methane content is likely to diminish in the face of rising atmospheric oxygen [13,25,8], it is suggested that methane cycling at that time was enhanced at the redox boundary either within or at the top of the water column.

High relative burial rate of organic carbon was considered as another possible trigger for Paleoproterozoic and Neoproterozoic ice ages [26,27]. Neoproterozoic and, possibly, the last Paleoproterozoic glaciations were indeed preceded by strong positive $\delta^{13}\text{C}$ excursion in seawater composition indicating high relative rates of organic carbon burial. The second Paleoproterozoic glacial event was followed by deposition of a 'cap carbonate' with characteristically negative $\delta^{13}\text{C}$ values, suggesting extreme carbonate alkalinity in the post-glacial shallow-marine environment [27,23]. A cause-and-effect relationship between primary productivity and climate changes was earlier proposed for the Neoproterozoic [26], based on the suggestion that long-term burial of organic carbon decreased atmospheric CO₂ levels resulting in surface refrigeration and increased atmospheric O₂ contents.

Carbon isotope values of organic and inorganic carbon provide constraints on the biogeochemical cycling of carbon. However, carbonates associated with the Paleoproterozoic glacial events are poorly preserved, rare, and thin. Compounding this situation, carbonates directly underlying or overlying the oldest Paleoproterozoic glacial event are unknown and, consequently, carbon isotope composition of the Paleoproterozoic ocean immediately before and after this event remains poorly understood. The available carbon isotope data for carbonates from South Africa, Western Australia, and Brazil, which are either slightly older or younger than the oldest Paleoproterozoic glacial event [27–29] suggest that the carbon isotope composition of seawater through this interval was close to 0‰. These data are inconsistent with a long-term C isotope perturbation either preceding or following the oldest Paleoproterozoic glaciation, but shorter-term excursions associated with this ice age cannot be excluded. While the time periods around 2.7 and 2.1 (Ludikovian–Francevillian) Ga are known as an acme of methanotrophy [30–33], the transition from an anoxic and methane-rich atmosphere to an oxic and CO₂-rich atmosphere at the beginning of the Paleoproterozoic Era may have prompted a similar ecosystem response.

The first objective of this paper is to provide insight into biogeochemical cycling of carbon before and after the oldest Paleoproterozoic glacial event using an organic carbon record, and thus to constrain the carbon isotope composition of contemporaneous seawater. The second objective is to evaluate whether the record of biogeochemical carbon cycling and climate change agrees with the current models for the evolution of atmospheric composition in the Paleoproterozoic Era.

2. Regional setting and stratigraphy

The early Paleoproterozoic Huronian Supergroup outcrops along the north shore of Lake Huron, Ontario, Canada ([34]; see inset in Fig. 1). The Huronian Supergroup is subdivided into four groups by unconformities, the upper three of which are climatically-controlled cycles with glacial diamictites at the base followed by deltaic mudstones or cap carbonate, and overlain by thick fluvial sandstones ([35]; Fig. 2). Radiometric ages for interlayered volcanic rocks and intrusive contacts with the Murray and Creighton granites constrain the age of the basal Huronian between 2.49 and 2.42 Ga [36–38], while the whole Huronian Supergroup is cut by the 2217±1.6 Ma Nipissing sills and dikes [39]. The western part of the Huronian Supergroup that outcrop north of the Murray Fault,

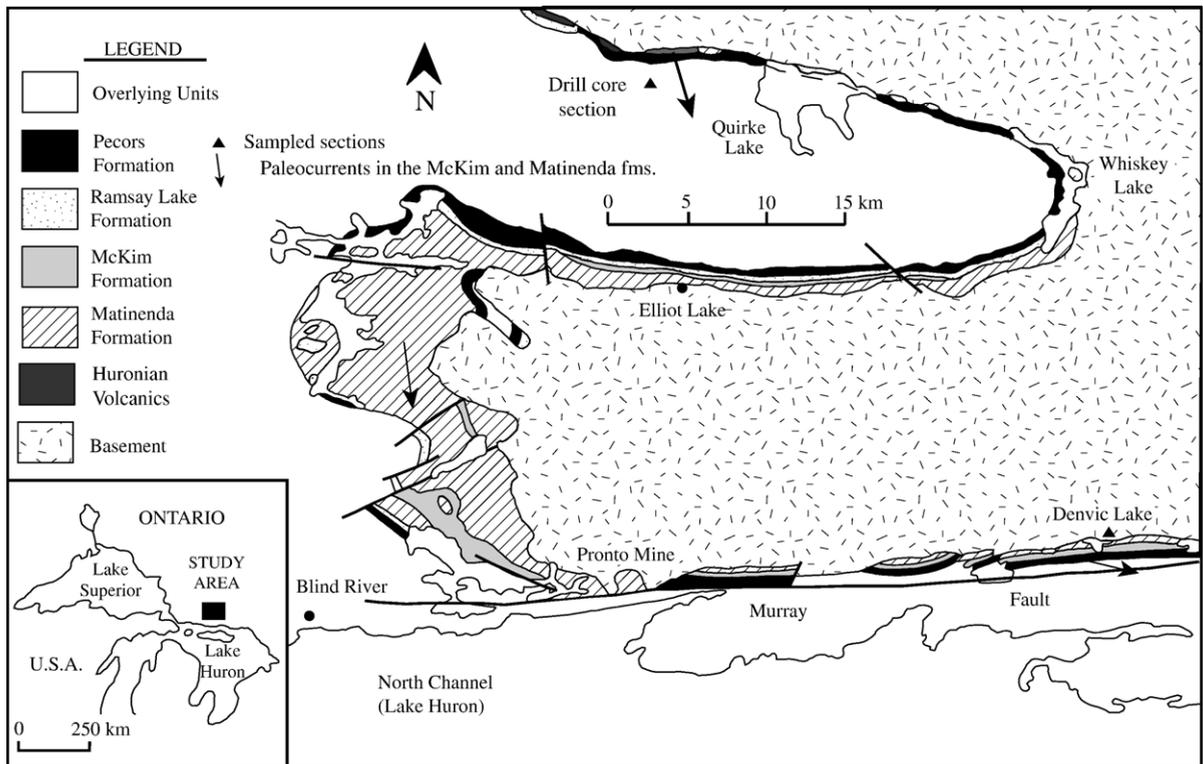


Fig. 1. Simplified map of the study area showing location of the drill core and outcrop sections (modified from [42]). Paleocurrents in the lower part of the Huronian Supergroup indicate paleoslope to the south–southeast.

including our study area, experienced subgreenschist to lower greenschist level of metamorphism [40].

The lower part of the Huronian Supergroup, which rests unconformably on the Archean Superior Province, was deposited in a rift setting possibly connected with an ocean to the east [35,41]. Paleocurrent indicators for the lower Huronian sandstones (Fig. 1), facies analysis, and isopach maps suggest a paleoslope towards the southeast [42]. Locally preserved paleosols at the base of the Huronian Supergroup are reduced [43], while the overlying Livingstone Creek and Matinenda formations contain uraniferous and pyrikerous conglomerates, consistent with low atmospheric pO_2 prior to deposition of the Ramsay Lake diamictite. In addition, both the McKim and underlying Matinenda formations have high CIA (chemical index of alteration) values suggesting warm and humid conditions in their source area [44].

The Upper Huronian Supergroup, starting with the Gowganda Formation, was deposited on a passive margin and contains evidence for an oxygenated atmosphere. The evidence includes red beds of the Upper Gowganda and Lorrain formations [35], the oxidized Ville Marie paleosol below the Lorrain

Formation [45,46], and pseudomorphs after anhydrite and gypsum in the Gordon Lake Formation [47].

The Pecors and McKim formations overlie and underlie, respectively, the oldest of three glacial diamictites of the Huronian Supergroup (Fig. 2). The contact between the Ramsay Lake Formation and the underlying units is conformable in places where the diamictite sits above the McKim Formation and is erosional and unconformable where it overlies the Matinenda Formation or the Archean basement north of Elliot Lake. The unconformable contact is likely related to subglacial erosion. In the Denvic Lake area, there is a coarsening upwards trend at the top of the McKim Formation below the Ramsay Lake Formation interpreted to result from the transition from delta front/prodelta to subaerial delta plain deposits [42]. In contrast, the contact between the Ramsay Lake diamictite and the Pecors Formation appears transitional, insofar as dropstones persist in laminated argillites in the lower part of the Pecors Formation in the Quirke Lake area [48,49]. The upper contact of the Pecors Formation is recognized by a gradual increase in siltstone and sandstone. The McKim and Pecors

formations were deposited on the strand and offshore areas of braided deltas [42].

All fine-grained lithologies of the McKim and Pecors formations were sampled at two to three meter intervals from the Kerr–McGee Corp. 156-1 drill core collared in 1969 in Beange Township (Long. 46°27'56" and Lat. 82°43'15"; Fig. 1) and stored in Sault Ste. Marie by the Ontario Geological Survey. Both the McKim and Pecors formations in this core consist of two upward-shallowing cycles characterized by wave ripples, thin laminations, cross-bedding, and soft-sediment deformation structures (Fig. 3). In addition, sections of the McKim and Pecors formations were measured and sampled

some 40 km to the southeast of the drill core site along the eastern (DA and DB sections; Pecors Formation) and western (DC section; McKim Formation) shores of Denvic Lake (Fig. 1).

In this region, the McKim Formation also consists of two upward-coarsening cycles (Fig. 4). The contact between the Matinenda and McKim formations is sharp but conformable in this area. The latter formation contains rhythmically interlayered thinly laminated argillites, siltstones, and arkosic sandstones with large planar and trough cross-bedding. Argillite and siltstone beds first appear in the cross-bedded Matinenda sandstones 2.5 m below the contact and increase in

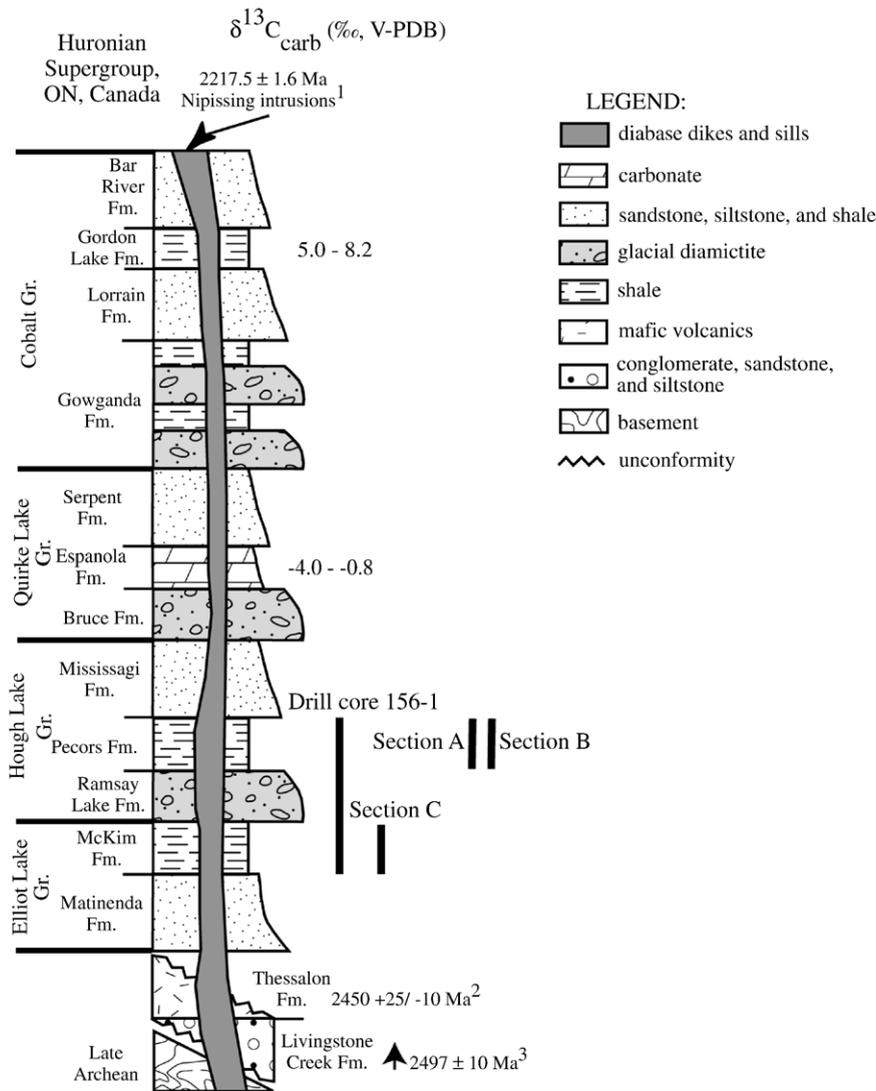


Fig. 2. Stratigraphic column of the Huronian Supergroup in the western part of the outcrop belt, ON, Canada with carbon isotope data for carbonates from [23,82] shown. Vertical bars show stratigraphic intervals covered by the outcrop and drill core sections. References to age constraints: ¹ — [39]; ² — [36]; ³ — [83]. Age with an arrow pointing up indicates detrital zircon age (maximum age of deposition).

thickness upsection. Coarse- to fine-grained massive sandstones of the McKim Formation include 1 to 5 mm thick argillites. Tabular sigmoidal cross-bedding (up to 2 m long and 0.5 m thick) is present in the upper cycle. Cross-bedding indicates a paleocurrent direction to the east. Siltstone interlayered with argillite contains abundant large wave ripples up to 10–15 cm thick. There is ample evidence for soft-sediment deformation including contorted bedding, ball and pillow structures,

slumped blocks, fluidized flow deposits, sandstone dikes, and flat pebble conglomerates with argillite clasts. Taken together, these indicators suggest high rates of sedimentation in an unstable environment. The contact with the Ramsay Lake Formation is sharp and erosional with the argillite overlain by the ~1.5 m thick gray–green sandstone that is in turn overlain by diamictite. The contact between the Ramsay Lake and Pecors formations is gradational based on the first

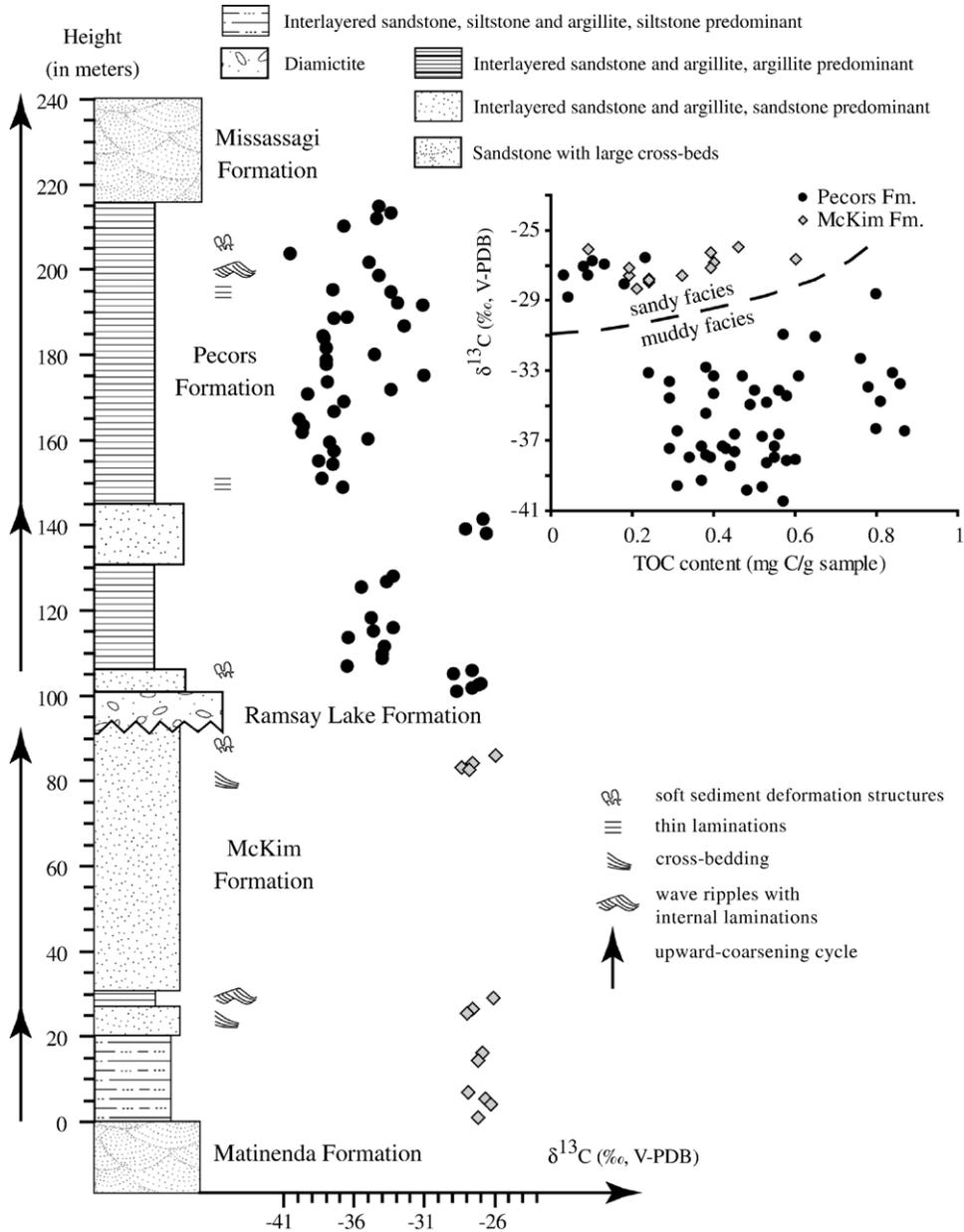


Fig. 3. Stratigraphic column of the McKim and Pecors formations from the Kerr–McGee Corp. drill core 156-1 (Beange Township; Long. 46°27'56" and Lat. 82°43'15"; see Fig. 1 for location) with $\delta^{13}C$ values for organic matter shown. Inset shows the scatter diagram of $\delta^{13}C$ values vs. TOC content and fields for sandy and muddy lithofacies.

appearance of thick argillite and siltstone beds above sandstone with dispersed, up to 10 cm in diameter pebbles of sandstone, argillite, and, rarely, granite. The Pecors Formation in this area also consists of two upward-coarsening cycles with argillites, siltstones with

rare slumped blocks, and fine-grained sandstones. Argillites, siltstones, and arkosic sandstones are commonly interlayered on a small scale and have flaser, wavy, and lenticular bedding. Siltstones have wave ripples that are either linked or solitary, while argillites

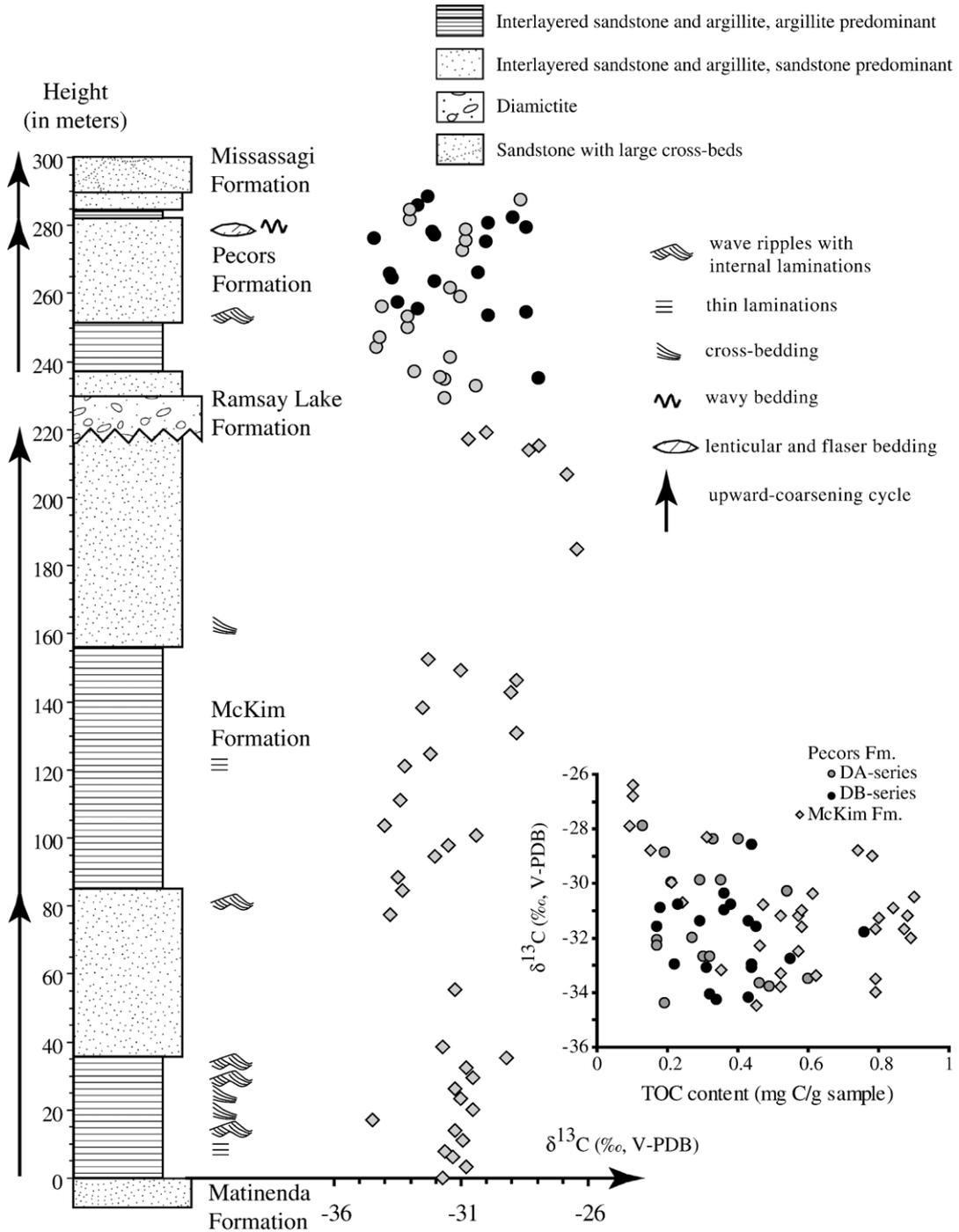


Fig. 4. Compiled stratigraphic column of the McKim and Pecors formations from the outcrop sections in the Denvic Lake area (see Fig. 1 for location) with $\delta^{13}\text{C}$ values for organic matter shown. Inset shows the scatter diagram of $\delta^{13}\text{C}$ values vs. TOC content.

form thinly laminated beds with rare sandstone dikes. Wave ripples in this unit similarly show traction to the east. The formation is overlain by relatively mature Missassagi sandstones with large-scale cross- and planar bedding and upward-fining cycles. The contact between these units is either gradual over the thickness of 1 m or sharp with scours.

Both the McKim and Pecors formations in the drill core and outcrop areas were deposited in a shallow-water environment above wave base. However, in the drill core area the Pecors Formation is significantly thicker than the McKim Formation, while the opposite holds in the outcrop area.

3. Methods

Whole rock powders were prepared and total organic carbon (TOC) was isolated by repeated acidification and centrifugation with concentrated HCl followed by washing with distilled water until the sample reached neutral pH [50]. In some cases, dried samples were mixed with CuO in Vycor tubes, evacuated, sealed, and combusted at 850 °C for 2 h. The volume of CO₂ quantified during cryogenic distillation was used to calculate TOC concentrations. Carbon isotope abundance in extracted and purified CO₂ in ampoules was measured by dual inlet techniques using a variety of gas-source mass spectrometers. In other cases, dried residues were loaded into tin cups and combusted to CO₂ with a Eurovector elemental analyzer on line with a continuous flow GV Isoprime mass spectrometer at the University of Maryland. Uncertainties of TOC abundance and isotope composition were estimated by replicate analyses of organic-rich and organic-poor powders [27]. The organic-rich sample yielded a standard deviation of ±0.26 mgC/g for abundance (5.57 mgC/g average) and ±0.03‰ for carbon isotopic composition (−34.47‰ average); for the organic-poor sample standard deviations were ±0.06 mgC/g (0.18 mgC/g average) and ±1.3‰ (−24.1‰ average) for abundances and carbon isotopic compositions, respectively. Two blanks analyzed in this study contained 0.74 and 1.02 μmoles of CO₂ and had carbon isotope values −20.28 and −20.27‰, respectively.

4. Results

Abundances and carbon isotope values of TOC in core and outcrop samples show a considerable range of stratigraphic variation (Supplementary materials; Table 1). Outcrop samples of the McKim Formation have a significantly higher TOC content (TOC_{av}=0.66 mg C/g sample) with respect to those from the drill core

(TOC_{av}=0.30 mg C/g sample), while drill core samples of the Pecors Formation have similar average TOC content (TOC_{av}=0.46 mg C/g sample) to outcrop samples (TOC_{av}=0.39 mg C/g sample). There is an appreciable difference in δ¹³C values of drill core and outcrop samples. In the drill core (Fig. 3), argillite samples from sand- and silt-dominated lithofacies of the pre-glacial McKim Formation have a small range of δ¹³C values (−28.4 to −26.0‰) similar to that in sand-dominated lithofacies in the lowermost six meters and at the top of the first upward-coarsening cycle of the post-glacial Pecors Formation (−28.9 to −26.6‰, *n*=9). Argillites from the argillite-dominated lithofacies of the Pecors Formation are notably depleted in ¹³C with values as low as −40.5‰. In contrast, samples from the argillite-dominated lithofacies of the McKim Formation from the outcrop section, with a range of δ¹³C values between −34.5 and −26.4‰ (Fig. 4), are depleted in ¹³C relative to drill core samples. Furthermore, outcrop samples of the Pecors Formation are enriched in ¹³C (ranging from −34.4 to −27.9‰) relative to the drill core samples. Carbon isotope compositions of organic matter in the drill core samples of the Pecors Formation (Fig. 3) vary with lithofacies so that coarser-grained sediments from proximal environments are generally enriched in ¹³C relative to distal facies argillites.

5. Discussion

5.1. Preservation of primary carbon isotope composition of TOC

Diagenetic and metamorphic processes result in the breakdown and volatilization of organic molecules thereby altering depositional isotope compositions. These post-depositional processes reduce TOC contents of sediments in association with the preferential loss of ¹²C during thermal degradation [17], typically resulting in more positive δ¹³C compositions of residual organic carbon. The magnitude of this effect has been empirically calibrated against the loss of hydrogen from organic matter such that atomic H/C ratio below 0.2 results in strong ¹³C enrichment [17,51]; however for lower greenschist facies sediments, ¹³C-enrichments associated with such processes are likely to be less than 4‰ [52]. Our results show coherent stratigraphic variations of over twice that magnitude in the McKim and Pecors formations, and further we find no coupled correlation of TOC contents and δ¹³C values in either the drill core or outcrop samples (see insets in Figs. 3 and 4). Organic matter degradation and accompanying ¹³C-enrichment has been observed in proximity to

uranium deposits, which has been ascribed to radiation effects [53,54]. Uranium-bearing conglomerates indeed underlie the McKim Formation in the drill core area. However, argillites of the McKim Formation have carbon isotope values similar to those of average Precambrian and Phanerozoic shales [51,55], while ^{13}C -depleted argillites of the Pecors Formation are stratigraphically further above the uranium-bearing horizon and are not mineralized. Furthermore, radiation-induced fractionation cannot explain ^{13}C -depletion [56]. Given these observations and considering low metamorphic grade of the sediments and absence of carbonates, we conclude that $\delta^{13}\text{C}$ variations mainly reflect primary composition of organic matter.

5.2. Carbon isotope composition of seawater before and after the first Paleoproterozoic glaciation

Lacking marine carbonate, the more straightforward seawater proxy, we attempt to reconstruct seawater composition before and after the Ramsay Lake ice age from carbon isotope composition of organic matter preserved in fine-grained lithologies of the McKim and Pecors formations. As a monitor of change in seawater composition, however, the organic carbon proxy is problematic insofar as compositions and ratios of primary and secondary inputs to temporally equivalent lithofacies (i.e. proximal vs. distal) may be different. Carbon isotope abundances of seawater can be estimated from those of organic matter if the generally observed fractionation between TOC and carbonate in the Proterozoic (28 to 32‰; [57,55] is applied. Such estimates for seawater composition and chemostratigraphic correlations have been attempted for a few siliciclastic-dominated successions [58–60]. Given the likelihood of localized secondary inputs of organic matter, these broad estimates should be viewed with some caution. Nonetheless, the estimates for the McKim and Pecors formations provide no evidence for a significant positive carbon isotope excursion in seawater composition immediately before deposition of the glacial diamictite of the Ramsay Lake Formation, or of a strong negative carbon isotope excursion immediately after. This is consistent with a rather scarce carbon isotope record of carbonates for this time interval [27–29], which records no significant excursions. The only possible exception comes from the Tongwane Formation in South Africa, which unconformably underlies the glacially-influenced Duitschland Formation, and has $\delta^{13}\text{C}$ values up to +3.5‰. On balance, the available data suggest that there was neither excessive burial of organic carbon before the glaciation, nor extreme

carbonate alkalinity flux with negative carbon isotope values into shallow-marine settings in the aftermath of the oldest known Paleoproterozoic ice age.

5.3. Origin of ^{12}C -enrichment in organic matter of the Pecors Formation

Factors that influence the magnitude of carbon isotope fractionation during primary productivity include $p\text{CO}_2$ of surface waters, the ratio of volume to surface area of photoautotrophs, and their growth rate controlled by nutrient supply [55,61,62]. These studies demonstrate limits of possible carbon isotope fractionation during photosynthesis that level off at $\sim 25\%$ at $p\text{CO}_2$ of 10 PAL or greater. Given this constraint and possible isotopic composition of atmospheric CO_2 – based on equilibrium with broadly contemporaneous shallow-marine carbonates – organic carbon $\delta^{13}\text{C}$ values of much less than -35% require secondary inputs of recycled carbon [55]. Average organic carbon compositions of the drill core samples from the Pecors Formation argillite-dominated lithofacies are $-36.0 \pm 2.4\%$, which are lower than the average Phanerozoic (-30%) and Paleoproterozoic (-34%) shale values [55,63]. Similar and even lower carbon isotope values for organic matter have been recorded worldwide at ca. 2.7 Ga [31,64] and between 2.1 and 2.0 Ga [65,66]. These isotope anomalies have been related to the enhanced biogeochemical cycling of methane [31,5,33,67], since methane may be directly converted to biomass with strongly negative $\delta^{13}\text{C}$ compositions by methanotrophic bacteria. Methanotrophs utilize methane and oxidants, sulfate, oxygen, or nitrate/nitrite [31,67,68]. However, it is likely that sulfate was limited in the Huronian Basin at that time. This part of the stratigraphic sequence was deposited in a rift basin with limited access to the global ocean [35], and sulfides are not abundant in these sediments. While multiple S isotope analyses of sulfides in the argillites of the McKim and Pecors formations largely indicate mass dependent fractionations, suggesting that atmospheric oxygen levels were above 10^{-5} PAL [22,69], the range of $\delta^{34}\text{S}$ values is small and thereby consistent with a limited sulfate pool. Anaerobic methane oxidation linked with denitrification is limited to low sulfate environments with exceptionally high nitrate content at the redox boundary [68]. Considering that efficiency of nitrifying bacteria in the Pecors time was likely limited by the low atmospheric oxygen level, this is an unlikely scenario for ^{13}C -depletion in the Pecors Formation.

With the assumption that neither sulfate nor nitrate were important redox couples in the Huronian Basin, dissolved

molecular oxygen was most likely used by methanotrophs to oxidize methane aerobically, which requires minimum levels of CH_4 and O_2 at the redox boundary of 5–10 μM and 12–20 μM , respectively [70,71].

5.4. Redox stratification in the Huronian Basin

If oxygen was supplied from the atmosphere what then was a source of methane in the Huronian Basin? It is conceivable that the sudden release of deep ocean methane clathrates during post-glacial warming (cf. [72,73]) provided the enhanced source of carbon to methanotrophs after the Ramsay Lake ice age. However, the long stratigraphic throw of the strong negative $\delta^{13}\text{C}$ anomaly in the Pecors Formation (over 100 m) argues for a sustained source of methane, rather than a single pulse predicted by the clathrate hypothesis. In the modern oxidized ocean, methanogens produce methane from simple organic compounds within sediments during anoxic diagenesis. Methane migrates continuously upward in sediments and is consumed and oxidized either aerobically with molecular oxygen or anaerobically, coupled with sulfate reduction.

In an atmosphere with low oxygen contents, methane and oxygen could have co-existed and fueled methanotrophic activity at the ocean–atmosphere interface. However, methanotrophic inputs of organic carbon are apparent only in the distal argillite-dominated lithofacies, suggesting that methanotrophs were excluded from oxygenated shallow-water environments. In contrast, organic matter in ca. 2.7 Ga shallow-water deposits has a larger range and more negative $\delta^{13}\text{C}$ compositions with respect to contemporaneous deep-water deposits [64], which is consistent with methanotrophic activity at the ocean–atmosphere interface.

There is a significant difference in $\delta^{13}\text{C}$ values of the drill core and outcrop sections. The distal drill core section of the Pecors Formation is thicker, generally fine-grained, and ^{13}C -depleted relative to the outcrop sections, which are interpreted to have accumulated in more proximal settings. Similarly, the thinner and coarse-grained drill core section of the underlying McKim Formation from proximal settings is ^{13}C enriched relative to the thicker and fine-grained outcrop section from more distal environment. The switch from deep to shallow-water environment in the outcrop sections at Denvic Lake likely

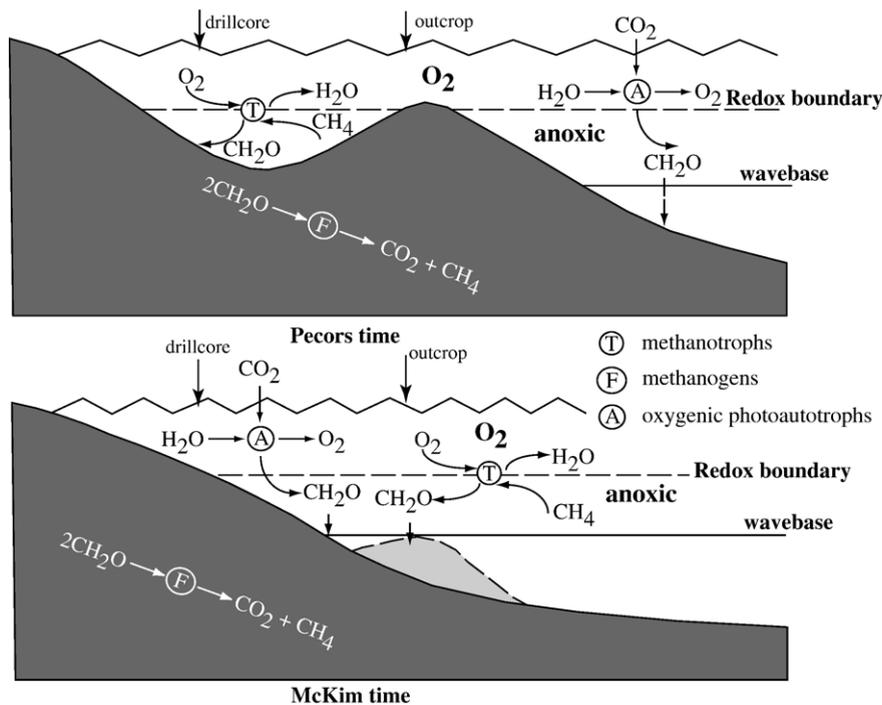


Fig. 5. Model for biogeochemical cycling of carbon in the shallow-water and deeper-water environments of the Huronian Basin during the Pecors and McKim times (modified from [31]). Methanotrophs lived at the redox boundary between oxic and anoxic methane-rich waters. Note that during the McKim time the outcrop section was deposited in the deeper-water setting with respect to the drill core section, while the outcrop sections of the Pecors Formation were deposited after the post-glacial transgression in the shallow-water environment due to the development of the basement high. The rising paleohigh is shown by the light-grey area with dashed border on the lower figure. Position of the outcrop sections with respect to the drill core section is schematic to illustrate changes in basin architecture relevant to the interpretation of the carbon isotope data.

reflects their proximity to a basement high in this area that was actively rising during Pecors time (see Fig. 5; cf. [74,75]). The notable isotopic contrast between lithofacies supports the view that the carbon isotope composition of organic matter was controlled in part by local environmental conditions, in particular, by water depth and contribution of secondary bacterial productivity to the organic carbon pool.

If the source of methane was in the deeper part of the basin, was it biogenic or abiogenic in origin? We accept the biogenic model of methane production. While methane can be produced by hydrothermal processes in the presence of Fe- and Cr-bearing minerals [76,77], there is no evidence for hydrothermal activity or volcanism in the Huronian Basin at that time. The Pecors Formation and the underlying units of the Huronian Basin are very lean in organic carbon, implying that biological methane production and recycling occurred in an organic-poor environment.

Sedimentologic observations of wave ripples with internal cross-laminations in the deeper-water argillites

support the view that both proximal and distal sections were deposited above the wave base. Hence the proposed redox boundary separating methane-rich and anoxic deepwaters and oxic methane-poor shallow-waters was also likely above the wave base (Fig. 5). These observations provide a general view of changing facies and the position of the redox boundary, and hence the focus of methanotrophic inputs in the argillite-dominated environments preserved in both drillcore and outcrop locations.

5.5. Implications for chemical composition of the atmosphere and ocean and climate changes during the Paleoproterozoic glacial epoch

The isotopic results of this study are inconsistent with the view of extreme primary productivity in the aftermath of the oldest Paleoproterozoic ice age (cf. [69]). We recognize no significant enrichment in organic matter content or its isotopic composition – nor are carbonates with highly positive carbon isotope values or phosphates

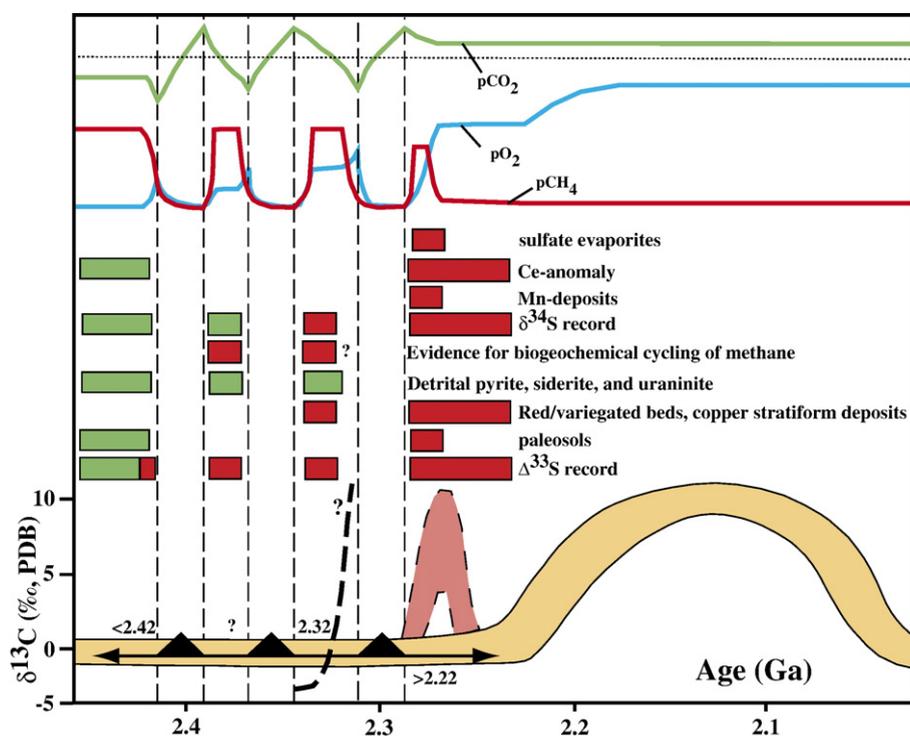


Fig. 6. Schematic presentation of Paleoproterozoic secular carbon isotope variations from Bekker et al. [23] with additional information from Bekker et al. [82] shown in light grey with a dashed border. Black triangles represent three Paleoproterozoic glaciations with their age constraints shown. Indicators of atmospheric and ocean redox state (green — reducing; red — oxidized) relevant to this paper are from Bekker et al. [23]. Atmospheric methane, carbon dioxide, and oxygen levels shown schematically fluctuated during the Paleoproterozoic glacial epoch and induced climate changes (see text for discussion). Dashed line represents atmospheric carbon dioxide level required to maintain greenhouse conditions alone. Positive carbon isotope excursion in the aftermath of the third Huronian glaciation (shown in pink) marks irreversible transition to the oxygenated atmosphere with carbon dioxide acting as a major greenhouse gas thereafter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

present in the Pecos Formation – all of which would be expected under conditions of extreme weathering, continental nutrient flux, productivity, and upwelling. To the contrary, the strong ^{13}C -depletion in organic matter suggests that secondary recycling of limited organic matter by methanogens and methanotrophy were important components of the shallow-water ecosystem in the aftermath of the oldest Huronian ice age. However, shales are rare in association with Paleoproterozoic glacial diamictites, and few of these have been analyzed for carbon isotope compositions. Notably, organic-rich shales of the Rooihogte and Timeball Hill formations sandwiched between two Paleoproterozoic glacial diamictites in South Africa have $\delta^{13}\text{C}$ values as low as -35.6‰ with the ^{13}C -enrichment towards the tops of the upward-shallowing cycles [52,78]. Bekker et al. [27] correlated the glacial diamictites that bracket these units with the second and third glacial diamictites of the Huronian Supergroup, respectively. These data support the view that biogenic methane production and recycling at the shallow-water redox boundary in the ocean may have been sustained throughout the Paleoproterozoic glacial epoch.

Insofar as the Paleoproterozoic glacial epoch has been related to the transition from the anoxic CH_4 -rich atmosphere to an oxic, CO_2 -rich atmosphere (e.g. [13,8,25]), the multiplicity of ice ages is arguably related to oscillations in O_2 and CH_4 production. Kaufman and Bekker [16] and Bekker et al. [23] speculated that fluctuating atmospheric oxygen level during the Paleoproterozoic glacial epoch led to a stepwise increase in carbon dioxide contents of the atmosphere at the expense of methane, which is consistent with the recent results of modeling of atmospheric composition and climate changes during the rise in atmospheric oxygen [8]. ^{13}C -depleted organic matter formed in the aftermath of the oldest Paleoproterozoic glacial event provides the first direct evidence for biogeochemical methane cycling above the wave base in the Huronian Basin during the Paleoproterozoic glacial epoch. It seems likely that some methane produced below the redox boundary escaped to the atmosphere and the consequent balance between biogeochemical methane and oxygen production modulated climatic changes during the Paleoproterozoic glacial epoch.

Our environmental scenario suggests that the rise of atmospheric oxygen prior to the first Huronian glaciation drew down atmospheric methane levels and induced widespread glaciation. Primary productivity would be severely limited beneath ice-covered oceans and atmospheric oxygen and methane levels would be negligible a few million years after the onset of the

glaciation (Fig. 6). On the other hand, atmospheric CO_2 levels would have risen during the ice age given an unabated volcanic flux and limited chemical weathering. Once threshold concentrations of this greenhouse gas were reached, the glaciation would end rapidly and, following climatic amelioration, both oxygenic photosynthesis and methanogenesis would be stimulated by high global average temperatures [79,8]. Atmospheric carbon dioxide concentration may then have declined due to enhanced chemical weathering under extreme greenhouse conditions, whereas atmospheric oxygen and methane levels would have increased with respect to the glacial levels. In the glacial aftermath, renewed primary productivity, anoxic conditions, and extremely warm climate likely enhanced biogenic methane fluxes to the atmosphere. Consequently, surface temperature and fluxes of carbonate alkalinity and nutrients derived from the continents would have declined as atmospheric CO_2 was drawn down by enhanced chemical weathering and biological productivity.

Several scenarios could potentially explain subsequent global cooling leading to the second Huronian ice age. First, as atmospheric CO_2 was falling and atmospheric methane was rising, an organic haze may have formed, which would have deflected sunlight at high altitude [80]. Second, insofar as thermophilic methanogens grow faster than mesophilic and psychrophilic methanogens and most of them have growth optimum above 30 °C , global biological methane production should be directly proportional to ambient temperatures in the range between 2 °C and 85 °C [79]. Thus, biological methane production would be curtailed in the face of falling surface temperature. Third, a decrease in continental weathering would attenuate nutrient fluxes and thereby decrease global net primary productivity, which would in turn affect methane production [81].

It is difficult to presently resolve between these scenarios but each, or a combination of, these factors could be responsible for the subsequent glaciation by increasing concentration of oxygen in the atmosphere at the expense of methane, at a point when atmospheric CO_2 had decreased to concentrations below those required to maintain warm climate.

Some combination of these factors most likely explains the multiplicity of Paleoproterozoic ice ages. The end of the Paleoproterozoic glacial epoch around 2.3 Ga was shortly followed by one or more remarkable positive carbon isotope excursions [3,82] known collectively as the “Lomagundi” event. The release of oxygen during this profound biogeochemical anomaly would have significantly decreased atmospheric methane levels before atmospheric CO_2 fell below the level

required to maintain greenhouse conditions alone. This event most likely marked the irreversible transition to an oxygenated atmosphere with carbon dioxide thereafter acting as the major greenhouse gas throughout the rest of Earth's history with negative feedback between carbon dioxide concentration, continental weathering, and climate.

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2007.04.009](https://doi.org/10.1016/j.epsl.2007.04.009).

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