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Manganese enrichment in the Gowganda Formation of the Huronian Supergroup: A highly oxidizing shallow-marine environment after the last Huronian glaciation

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ABSTRACT

Oxidative precipitation and authigenic enrichment of the redox sensitive element Mn in sedimentary rocks can serve as a proxy for the release of high levels of O_2 during the Great Oxidization Event (GOE). Here we investigate Mn abundance in sedimentary rocks of the 2.45–2.22 Ga Huronian Supergroup, Canada. We found authigenic Mn enrichments with high Mn/Fe ratios following the appearance of Fe oxides in the Firstbrook Member of the Gowganda Formation of the Huronian Supergroup, which was deposited immediately after the last Huronian glaciation. The Mn-bearing minerals in the Firstbrook Member are spessartine-rich almandine and Mn-bearing chlorite, which are likely to have been formed through post-depositional diagenesis and/or metamorphism using Mn oxides precipitated in the ocean at the time of deposition. When assuming the solution equilibrium between the atmosphere and shallow oceans, oxidative Mn precipitation requires that atmospheric O_2 be higher than ~10^{-2} times the present atmospheric level (PAL). The cumulative Mn amount per unit area in the Firstbrook Member is comparable in magnitude to that in the Mn deposits in the Hotazel Formation of the Transvaal Supergroup, South Africa. Our results suggest an appearance of highly active aerobic biosphere immediately after the last Huronian glaciation, supporting the hypothesis that climatic recovery from the Huronian glaciation accelerated the GOE.

1. Introduction

Multiple lines of evidence support the idea that atmospheric O_2 increased remarkably between 2.5 and 2.0 Ga (termed the Great Oxidation Event (GOE)) (e.g., Anbar et al., 2007; Bekker et al., 2004; Canfield, 2005; Farquhar et al., 2000; Karhu and Holland, 1996; Kirschvink et al., 2000; Papineau et al., 2007; Rye and Holland, 1998). Across this time interval, the O_2 level appears to have increased from less than 10^{-5} of the present atmospheric level (PAL) to more than 10^{-2} PAL (Canfield, 2005; Farquhar et al., 2007; Pavlov and Kasting, 2002). However, the history of the oxygenation in the atmosphere–ocean system during the GOE remains poorly understood. Knowledge on the detailed history of the surface oxygenation during the GOE is important for understanding the evolution of the Earth, because it would provide an insight into the causative mechanism responsible for the rise in O_2 in the atmosphere.

It has long been suggested that the abundance of redox sensitive metals, such as U, Fe, Re, Os, and Mn, preserved in sedimentary rocks and paleosols can provide constraints on the evolution of atmospheric O_2 during the GOE (e.g., Anbar et al., 2007; Canfield, 2005; Holland, 1984; Rye and Holland, 1998). For example, the preservation of detrital uraninite (UO_2) and pyrite (FeS_2) in river deposits older than ~2.3 Ga is clear evidence for the lack of atmospheric oxygen at the time of deposition (e.g., Holland, 1984; Roscoe, 1969). When the O_2 levels rose, U, Re, and Os contained in crustal minerals were dissolved and delivered to the oceans through oxidative weathering (e.g., Canfield, 2005). Additionally, the retention of Fe in paleosols also has been used as an indicator of atmospheric O_2 (e.g., Holland, 1984). In general, under high O_2 conditions, Fe is oxidized and retained in paleosols. The earliest paleosol to show evidence for an oxidizing atmosphere is the 2.2 Ga Hekpoort paleosol of the Transvaal Supergroup, South Africa, although there is considerable disagreement in the O_2 levels proposed for its formation (Beukes et al., 2002; Yang and Holland, 2003).

To further understand the evolution of the atmospheric O_2 levels during the GOE, it is essential to obtain additional geochemical records using other proxies for reconstructing the different levels of

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atmospheric O_2. Because each redox sensitive metal has a different oxidation potential, the comparison of their degrees of enrichment and/or depletion in sedimentary sequences would aid in the reconstruction of atmospheric O_2 levels by providing upper and lower bounds for their oxidization. Given the high oxidation potential of Mn (+490 mV at pH 7; Kopp et al., 2005) among redox sensitive metals, its authigenic enrichment would provide key information on an accumulation of high levels of O_2 at the late stage of the GOE. In contrast to Mo, Re, and Os, Mn is less soluble under oxidizing conditions and precipitates as oxides in the oceans similar to Fe. Previous studies have noted the fact that the Mn-rich members of the 2.2 Ga Hotazel banded-iron Formation in the Transvaal Supergroup, South Africa, imply large quantities of O_2 in the surface zone of the ocean at the time of deposition (Kirschvink et al., 2000; Kopp et al., 2005). The Transvaal Supergroup contains the Makganyene Formation glacial diamictite, which represents a low-latitude global glaciation (i.e., the Paleoproterozoic Snowball glaciation) (Evans et al., 1997; Kirschvink et al., 2000). Because the basal meter of the Hotazel Formation contains dropstones just above the contact with the underlying units over a geographically wide area, Kirschvink et al. (2000) argued that it was the equivalent of the 'Cap Carbonate' for Neoproterozoic glacial units, and marked the termination of the Makganyene glaciation. They interpreted the major precipitation of Mn associated with Fe oxides as the result of a massive release of O_2 into the atmosphere and ocean as a consequence of high levels of biological productivity in the aftermath of the Paleoproterozoic Snowball Earth (Kirschvink et al., 2000). Because the occurrence of major precipitation of Mn has not been reported in other Paleoproterozoic sedimentary sequences, it was uncertain whether such a highly oxidizing shallow-marine environment was global.

In this study, we measure Mn abundance in sedimentary rocks of the Huronian Supergroup, Ontario, Canada, which is known as one of the most continuous successions of the Paleoproterozoic (~2.45–2.22 Ga). This sequence includes three discrete glacial diamictite-units (Fig. 1) (e.g., Young et al., 2001). In this study, we focus on the uppermost glacial diamictite unit of the Gowganda Formation and investigate the redox condition of the atmosphere and ocean at the time of its deposition. Based on the geochemical and geological analyses for the Huronian Supergroup, we discuss the evolution of redox condition of surface environments during the GOE.

2. Geological setting

The Huronian Supergroup crops out along the north shore of Lake Huron (Fig. 1A). Most of the strata are dominated by siliciclastic rocks that are bundled into climatically-controlled trinal cycles, each of which starts with glacial diamictites, followed by mudstones and quartzose sandstones (Fig. 1B) (Young et al., 2001). In the lower part of the Huronian Supergroup (the Matinenda and Pecors formations), mass independent fractionation of sulfur (MIF-S) in sulfides and occurrence of detrital uraninite and pyrite in conglomerates suggest low atmospheric O_2 levels in the atmosphere (e.g., Papineau et al., 2007; Young et al., 2001) (Fig. 2B). In contrast, large fractionations in $\delta^{34}S$ values and near-zero $\Delta^{33}S$ are found in authigenic sulfides from the Espanola and Gordon lake formations (Papineau et al., 2007). In addition, abundant evidence for oxidative continental weathering such as red beds, have been reported in the Lorrain Formation (e.g., Young et al., 2001). These results provide evidence for an oxidizing atmosphere at the time of deposition of the upper part of the Huronian Supergroup (Fig. 1B).

The upper part of the Huronian Supergroup (starting with the Gowganda Formation) is considered as a passive margin succession (Young, 2004; Young et al., 2001). The lower part of the Gowganda Formation (the Coleman Member) consists mainly of matrix-supported diamictite, while the upper part of the Gowganda Formation (the Firstbrook Member) consists of laminated argillite that grades upward into thinly bedded siltstone and fine-grained sandstone and finally into medium- to coarse-grained sandstone of the Lorrain Formation. The depositional environment of the Firstbrook Member is interpreted to be fluvial deltas, based on the presence of a prograding deltaic wedge from prodelta to delta slope (Rainbird and Donaldson, 1988). The quartzose sandstone in the Lorrain Formation would have been formed as a result of intense chemical weathering under hot and humid conditions in the aftermath of the Gowganda glaciation (Long et al., 1999; Sekine et al., 2010).

In contrast to the Makganyene and Hotazel formations in the Transvaal Supergroup deposited at ~2.22 Ga (Cornell et al., 1996; Dorland, 2004), the depositional age of the Gowganda Formation is not constrained by geochronological studies. Thus, it is still controversial whether the Gowganda Formation is correlative with the Makganyene Formation (Bekker et al., 2001, 2006; Hannah et al., 2004; Hilburn et al., 2005; Kopp et al., 2005; Young, 2004). Previous studies that support

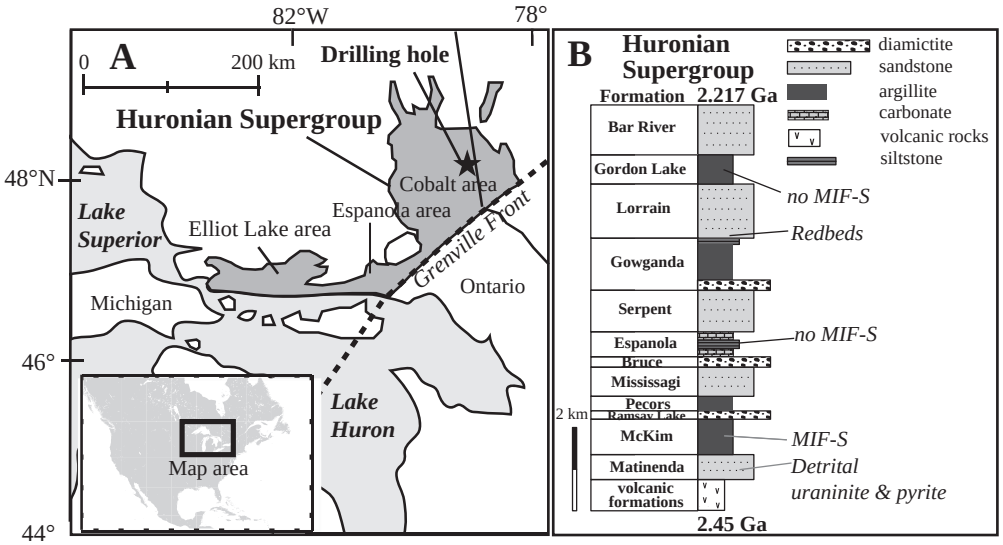

Fig. 1. (A) Location of the Huronian Supergroup and CO0338 drilling hole site. (B) Simplified stratigraphy of the Huronian Supergroup, showing proxy indicators of redox conditions in the atmosphere. The depositional age of the Huronian Supergroup is constrained to between about 2.45 and 2.217 Ga, based on the dating of dyke swarms in basement rocks and the post-Huronian Nipissing diabase, respectively (e.g., Young et al., 2001).

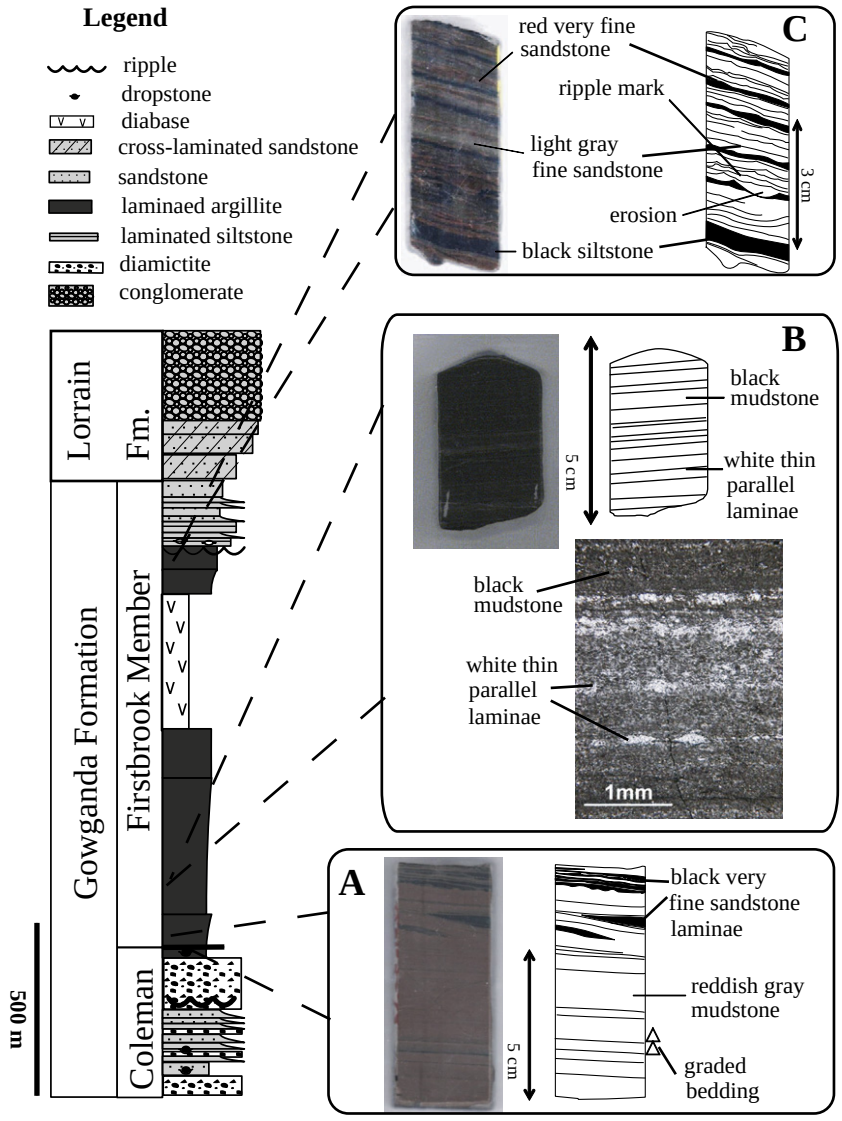

Fig. 2. Stratigraphic column of drillcore CO0338 from the upper part of the Coleman Member of the Gowganda Formation to the basal part of the Lorrain Formation. (A): A picture of reddish laminated argillite, (B) that of gray-green laminated argillite, and (C) gray-green laminated siltstone.

correlation between the Gowganda and Makganyene diamictites were based on chemostratigraphic analyses that were not unique (Bekker et al., 2001, 2005; 2006; Hannah et al., 2004), and assumed a major time gap between the Makganyene and overlying Ongeluk volcanic (despite mapped interfingering between the units, and clasts of the basaltic andesite in the upper units of the diamictite, e.g., Kirschvink et al., 2000). Other supporting evidence includes the presence of soft-sediment textures (pepperites) at the contact of the Gowganda argillite with the intrusions of units interpreted to be the Nipissing diabase (2222 ± 13 Ma) (Young et al., 2004), which is approximately the same age as the Ongeluk/Makganyene (Cornell et al., 1996; Dorland, 2004). This suggests that the depositional age of the Firstbrook Member may be close to that of some parts of the Nipissing diabase. In contrast, others propose that the three Huronian glaciations predate the Makganyene Snowball glaciation, based on the age of the Nipissing diabase (~2.217 Ga) penetrating throughout the Huronian Supergroup (Hilburn et al., 2005; Kopp et al., 2005).

3. Sampling and analyses

Studied samples of the Gowganda Formation were collected from a drillcore (CO0338; stored at Ontario Geological Survey) retrieved from the locality of about 90 km north-west from Cobalt city (48°02′ N, 80°21′ W). The drillcore samples (total core length ~1200 m) span from the Coleman Member of the Gowganda Formation to the basal part of the Lorrain Formation (Fig. 2). The basal part of the Firstbrook Member consists of reddish gray laminated mudstone, which sometimes forms alternations with black very fine sandstone laminae (Fig. 2A). The middle part of the Firstbrook Member consists of black laminated mudstone, where white thin parallel laminae occur in black mudstone (Fig. 2B). The black laminated mudstone gradually changes to black laminated siltstone and cross-laminated sandstone with ripple in the upper part of the Firstbrook Member (Fig. 2C), where red very fine sandstone and light gray fine sandstone form alternations. A more detailed description of the lithostratigraphy of the drillcore can be found in Rainbird and Donaldson (1988).

In addition to the above drillcore samples, we collected rock samples from outcrops and another drillcore (SM0014; stored at Ontario Geological Survey) in order to cover the sedimentary sequences of the Huronian Supergroup. The outcrops for the Bar River, Gordon Lake, Espanola, Bruce, and Ramsay Lake formations are located in the Elliot Lake area in the western part of the Huronian Supergroup (Fig. 1). The samples from the Lorrain, Serpent, and McKim formations are collected from the Espanola area in the

southern part of the Huronian Supergroup distributions (Fig. 1). Detailed locations of the sections are shown in Young et al. (2001) and Auxiliary online materials. The drill site SM0014 was located about 8 km to the north of Elliot Lake city (46°45′99″ N, 82°60′06″ W). The drillcore samples cover the deglaciation periods of both the first and second Huronian glaciations (i.e., the boundary of the Ramsay Lake and Pecors formations, and that of the Bruce and Espanola formations: see Fig. 1). The Ramsay Lake Formation is matrix-supported diamictite, which consists of granitic rounded pebbles and cobbles with dark gray mudstone matrix. The Ramsay Lake Formation is conformably overlain by dark gray laminated mudstone of the basal part of the Pecors Formation. The Bruce Formation contains dropstones of granitic and mafic rocks in a matrix of gray-green sandstone, which changes upward to laminated siltstone in the basal part of the Espanola Formation (Fig. 3B). These sedimentary features reflect the periods of climate recovery from the first and second Huronian glaciations, respectively.

To remove potential contaminants, the surfaces of the rock samples were cut off using a diamond cutter. The samples were then cleaned ultrasonically and powdered with a ball mill. For the samples of diamictite, we carefully removed dropstones and used the matrixes for the analyses. Major elemental and mineralogical compositions of the bulk rock samples were determined using X-ray fluorescence (XRF) analysis (Philips; PW-1480) and a X-ray powder diffraction (XRD) (MAC Science; MXP-3) analysis, respectively, at the University of Tokyo (see Supplementary Table 1 in Auxiliary Material for the XRF results). In order to characterize major minerals and to investigate their occurrence, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and electron microprobe analysis (EPMA) (JEOL; JXA-8900L) were performed for polished thin sections of the samples (see Supplementary Table 2 for the EPMA results).

4. Results

4.1. Mn enrichment in the Gowganda Formation

Fig. 3 shows the stratigraphic variation in Mn abundance in the bulk sedimentary rock samples throughout the Huronian Supergroup. We found remarkable enrichments of Mn abundance (up to 1.7 wt.% MnO) in the Firstbrook Member of the Gowganda Formation. On the other hand, Mn abundances seem to be low in other formations in the Huronian Supergroup. Enrichments of Mn are not found both in the underlying diamictite unit of the Coleman Member and overlying sandstone unit of the Lorrain Formation. Although we did not measure Mn concentrations throughout the Pecors and Espanola formations, the Mn abundances also seem to be low, at least, in the sedimentary rocks deposited immediately after the first and second Huronian glaciations (Fig. 3B and C).

Detailed variations in the abundance of Mn in the samples from the upper part of the Coleman Member to the basal part of the Lorrain

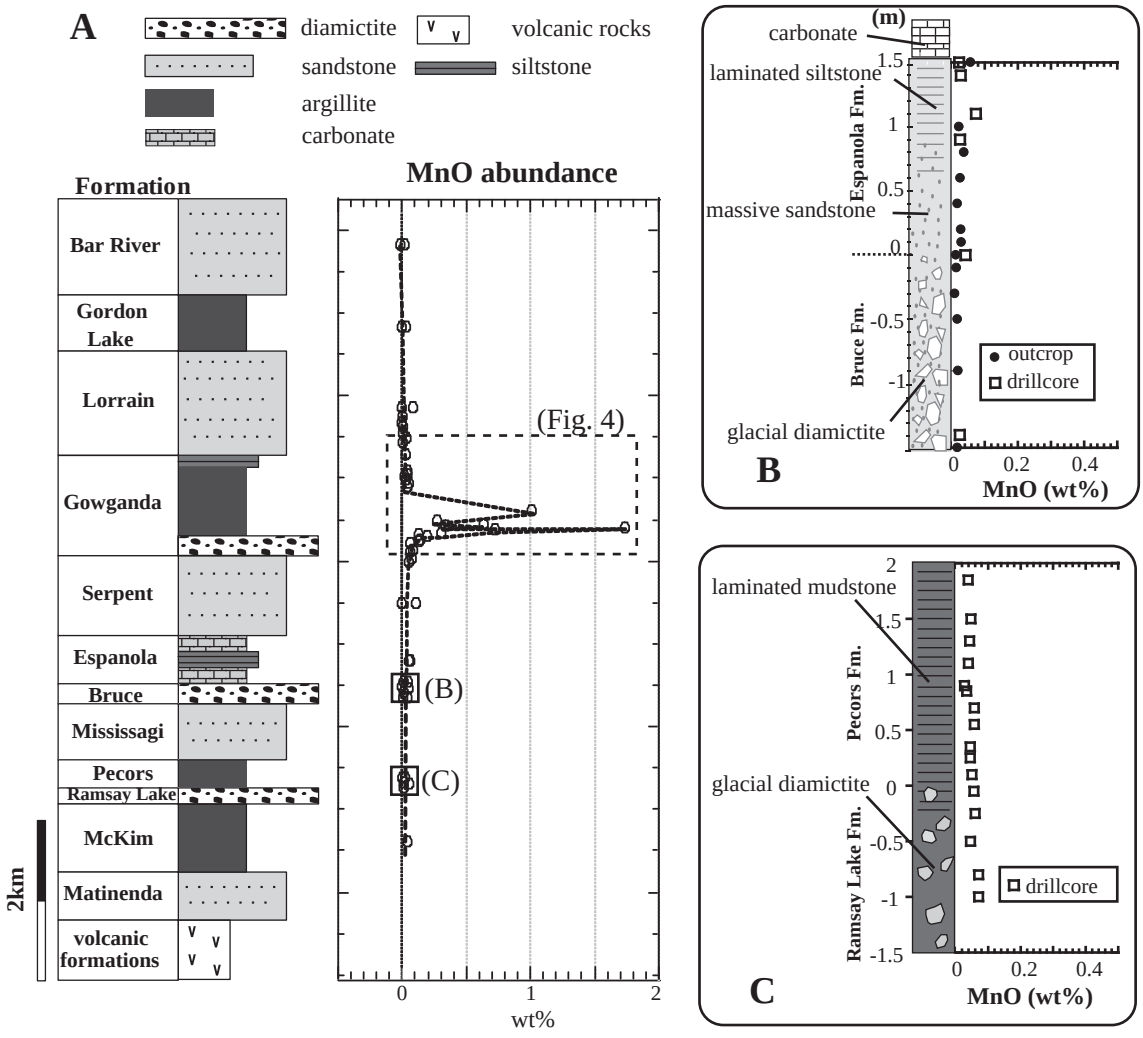

Fig. 3. (A): MnO abundance variation in the sedimentary sequence of the Huronian Supergroup. (B): A close up view of the boundary between the Bruce and Espanola formations. (C): A close up view of the boundary between the Ramsay Lake and Pecors formations. A close up view of the Mn abundance variation in the Gowganda Formation.

Formation are shown in Fig. 4. In the basal part of the Firstbrook Member, Mn abundance gradually increases upward. At 150 m above the boundary between the Coleman and Firstbrook members, Mn abundance reaches about 1.7 wt.%, and then decreases toward the middle part of the Firstbrook Member. The thickness of the interval with higher Mn abundance (> 0.1 wt.% MnO) is about 400 m. The Mn enrichments are also demonstrated by the high Mn/Fe ratios in the sedimentary rocks of the Firstbrook Member (Fig. 4). Reservoirs of detrital components (e.g., oceanic and continental crusts, including Archean upper crusts) typically show a very narrow range of Mn/Fe ratios (i.e., Mn/Fe ~0.016–0.023) (Maynard, 2003). Thus, the high Mn/Fe ratios (Mn/Fe>0.023) at ~100–250 m above the boundary between the Coleman and Firstbrook members cannot be explained by the change in provenance of detrital components. This view of authigenic Mn enrichment is also supported by the high Mn abundance normalized by Al content (i.e., Mn/Al ratio in Fig. 4). Normalization by Al content is commonly used as an indicator of aluminum-silicate fraction of the sediments because of very little ability to move during diagenesis. The XRD analyses show carbonate contents are low to absent in the samples, indicating that the variation in Mn contents cannot be explained by the carbonate dilution effect. These results are suggestive of a significant input of Mn to the sedimentary rocks in the lower part of the Firstbrook Member.

In addition to Mn, the abundance of Fe is relatively high in the lower part of the Firstbrook Member (Fig. 4), which corresponds to the presence of the reddish laminated argillite (Fig. 2). Based on the SEM observations and XRD analyses, the Fe enrichment found in the Firstbrook Member is associated with the appearance of very fine hematite (Fe_2O_3) particles (the size of several μm) scattering in the matrix of the argillite samples. Microscopic observation also reveals that the surfaces of detrital grains, such as quartz and albite, are often coated with hematite. These results are consistent with the previous observations of the appearance of Fe oxides in the Gowganda Formation in the Huronian Supergroup (Young et al., 2004).

4.2. Identification of Mn-bearing minerals

In order to identify Mn-bearing minerals in the Mn-rich rock samples from the Firstbrook Member, we conducted thin section observations and EPMA and SEM analyses. The rock samples enriched in Mn correspond to the gray-green laminated argillite in the stratigraphic column of the Firstbrook Member shown in Fig. 2B. Thin section observations of the rock samples highly enriched in Mn (>1.0 wt.% MnO) show that black mudstone in the gray-green argillite contains detrital fine grains of quartz and albite (~10–20 μm), subhedral to euhedral fine particles (the size of ~5–20 μm) of chlorite and muscovite, and subhedral to euhedral very fine porphyroblasts of almandine (~1–20 μm) (Fig. 5). These minerals are nearly homogeneously distributed in the black mudstone. White thin parallel laminae in the gray-green argillite are mainly composed of very fine detrital quartz grains. Thin section observations also show that the samples with moderate Mn content (0.1–1.0 wt.% MnO) contain spherical clusters of euhedral chlorite with the diameter of ~20–50 μm in the matrix mainly composed of muscovite, quartz, and albite (Fig. 6). In contrast to the samples highly enriched in Mn, almandine cannot be observed in the rock samples with moderate Mn content (Fig. 6). Remineralization of very fine quartz grains due to hydrothermal alterations is sometimes observed in laminae in the gray-green argillite.

Based on the SEM and EPMA analyses, we found two types of Mn-bearing minerals in the samples highly enriched in Mn; one is almandine (~33 wt.% of MnO; hereafter we call spessartine-rich almandine) ($[Mn, Fe]_3Al_2[SiO_4]_3$) and the other is chlorite (~3.0 wt.% of MnO; hereafter we call Mn-bearing chlorite) ($[Fe, Mn, Mg]_5Si_3Al_2O_{10}(OH)_8$) (Fig. 5) (also see Supplementary Table 2 in Auxiliary Material for the data). Given the surface areas of these minerals observed in the thin section, about 65% of Mn in the samples is attributed to spessartine-rich almandine, and the rest is attributed to Mn-bearing chlorite. Because of absence of spessartine-rich almandine, almost all of Mn concentration in the samples with moderate Mn content is attributed from Mn-bearing chlorites (Fig. 6).

Based on the SEM-EPMA analyses and thin section observations, we found that the spessartine-rich almandine and Mn-bearing chlorite in the Firstbrook Member are euhedral (Figs. 5 and 6). The spessartine-rich almandine crystals typically occur as octahedral or partially cracked octahedral with the diameter of ~1–20 μm (Fig. 5). They occasionally include detrital quartz particles in their crystals. The EPMA analyses show that the Mn contents are relatively high at the center of the spessartine-rich almandine crystals and gradually decrease toward the edge showing normal zoning; whereas, the Fe content shows an inverse correlation with the Mn content (Fig. 5 C and D). These results suggest that the spessartine-rich almandine

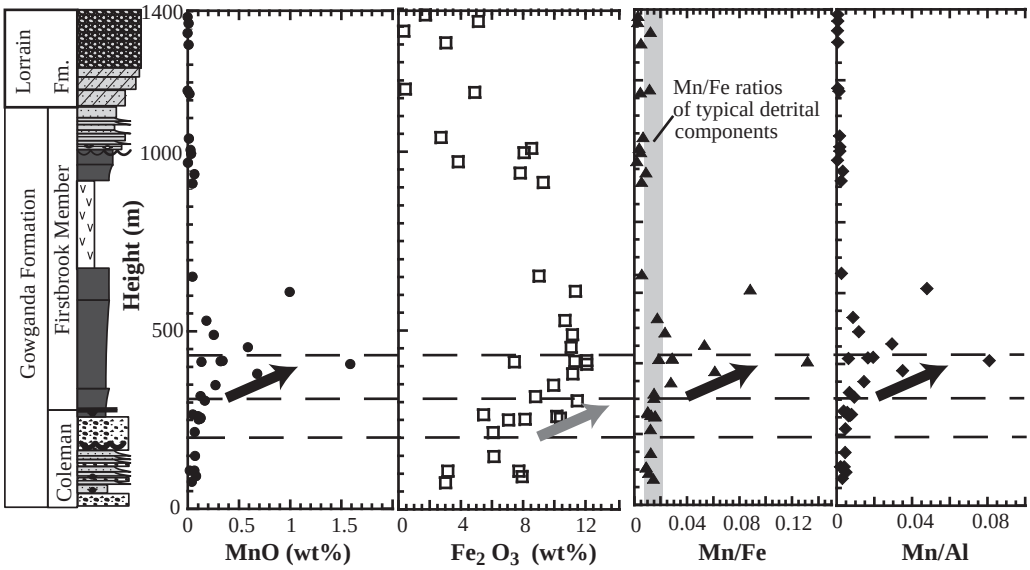

Fig. 4. Geochemical trends of the upper part of the Gowganda Formation and the basal part of the Lorrain Formation, including MnO and Fe_2O_3 abundances and Mn/Fe ratios. The gray area in the figure represents the Mn/Fe ratio of the rock reservoirs on the Earth (e.g., oceanic and continental crusts, including Archean upper crusts) (Maynard, 2003).

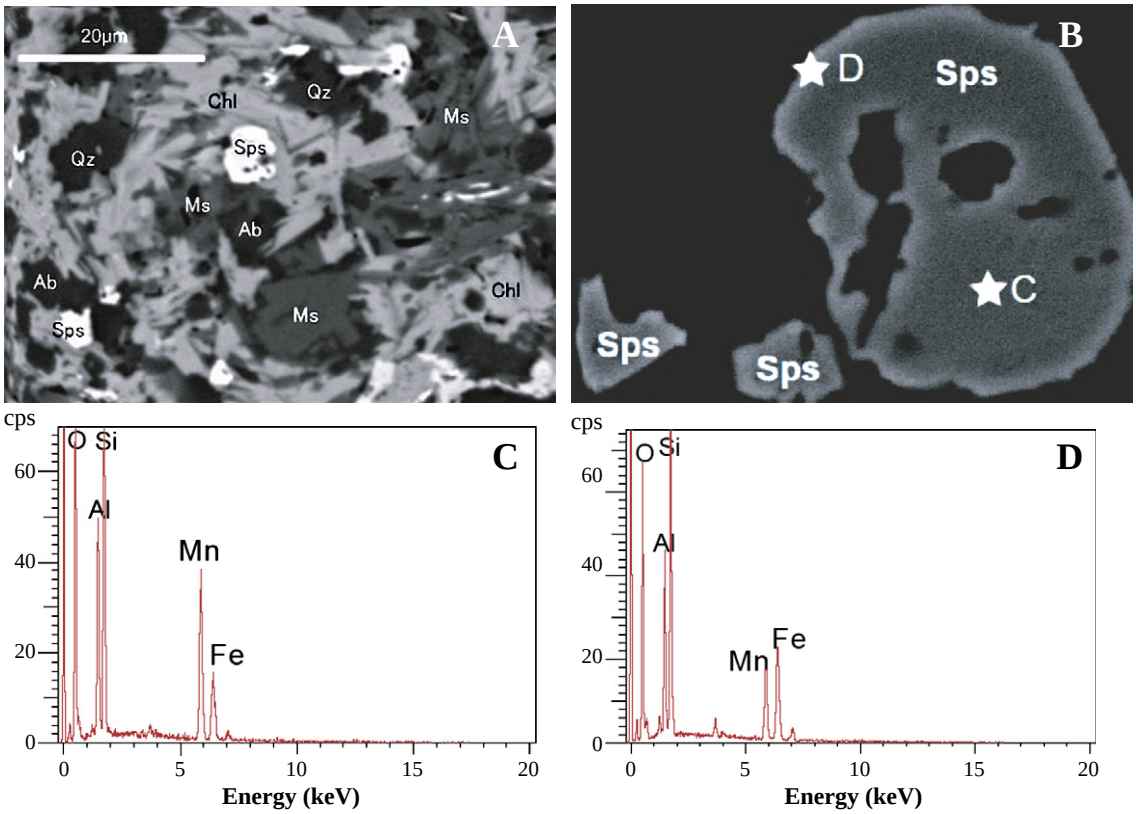

Fig. 5. Scanning electron microscopic (SEM) images of (A) the rock samples highly rich in Mn (>1.0 wt.% MnO) in the Firstbrook Member of the Gowganda Formation (the scale bar is 20 μm) and (B) a close up of a spessartine particles (the size of the image is 10 μm). The symbols of Sps, Chl, Qz, Ab, and Ms represents spessartine, chlorite, quartz, albite, and muscovite, respectively. The stars C and D represent the areas where we obtained EDS spectra. EDS spectra near the center and at the edge of the spessartine-rich almandine particle are shown in (C) and (D), respectively.

crystals have grown with increase in temperature during post-depositional diagenesis and/or metamorphism.

In the samples with moderate Mn content (0.1–1.0 wt.% MnO), Mn-bearing chlorite clusters are elongated parallel to the bedding (Fig. 6), suggesting the diagenetic and/or diagenesis origin of Mn-bearing chlorite. They are abundant in the black mudstone lamina (also see Fig. 2) but are relatively rare in white thin parallel lamina in the rock samples (Fig. 6). In the samples highly enriched in Mn, the Mn-bearing euhedral chlorite is distributed nearly homogeneously in the rock samples.

Given the above observations and mineral assemblages, our results suggest that the spessartine-rich almandine and Mn-bearing chlorite are highly likely to have grown during metamorphism using abundant Mn in the sediments (e.g., Yardley, 1989). Using the chemical compositions of Mn-bearing chlorite and spessartine-rich almandine crystals (Supplementary Table 2), we estimate the pressure and temperature conditions of metamorphism based on the internally-consistent geothermometry in metamorphic rocks (Grambling, 1990). To reproduce the measurements, the metamorphic temperatures are required to be ~300–500 °C (Supplementary Fig. 1). Together with the observations that high-pressure minerals are absent and that the detrital quartz and albite have been retained in the rock samples, the metamorphism would have occurred in the rock samples at the low-pressure (~0.1–0.3 GPa) and low-temperature (~300–350 °C) conditions (e.g., Young, 1976), which might have been occurred by the intrusion of the Nipissing diabase.

Our thin section observations also suggest that the input of Mn in the sediments would not have caused by post-depositional hydrothermal alteration but may have occurred during or immediately after deposition. Thin section observations of the sample with moderate Mn content shows that a micro fault drags detrital laminae containing Mn-bearing chlorite clusters (Fig. 6B). These observations show that the micro fault cut into the sediments before the lithification, suggestive of that although the Mn-bearing minerals were formed by diagenesis and/or metamorphism after the deposition, the enrichment of original Mn had occurred at least before the lithification and diagenesis. Furthermore, we found that a quartz vein cut in the rock sample oblique to the bedding (Fig. 6C), and recrystallization of quartz occurred along the vein. Mn-bearing chlorites are not observed in microcrystalline quartz along the vein. Because the quartz vein also cut the micro fault in the sediments, Mn-bearing chlorite would not have been formed by the quartz vein intrusion and should have existed before the vein intrusion.

5. Discussion

5.1. The mechanism for Mn enrichment

Our petrographical, geochemical, and mineralogical observations of samples from the Mn enrichment and high Mn/Fe ratio horizons (Fig. 4) indicate that the Mn enrichment was due to early post-depositional authigenic processes in the sediment of the basal part of the Firstbrook Member of the Gowganda Formation. According to previous studies (e.g., Maynard, 2003), there are two major mechanisms for authigenic Mn enrichment in sediments. One is an export of dissolved Mn from an anoxic deep ocean and its precipitation in an oxidizing shallow-marine environment (e.g., Kirschvink et al., 2000; Maynard, 2003). The other is Mn leaching from oceanic and continental crusts and its precipitation in sediments through post-depositional hydrothermal activities (e.g., Maynard, 2003). Considering the results of SEM and EPMA analyses and thin section observations of the occurrence of Mn-bearing minerals along laminae

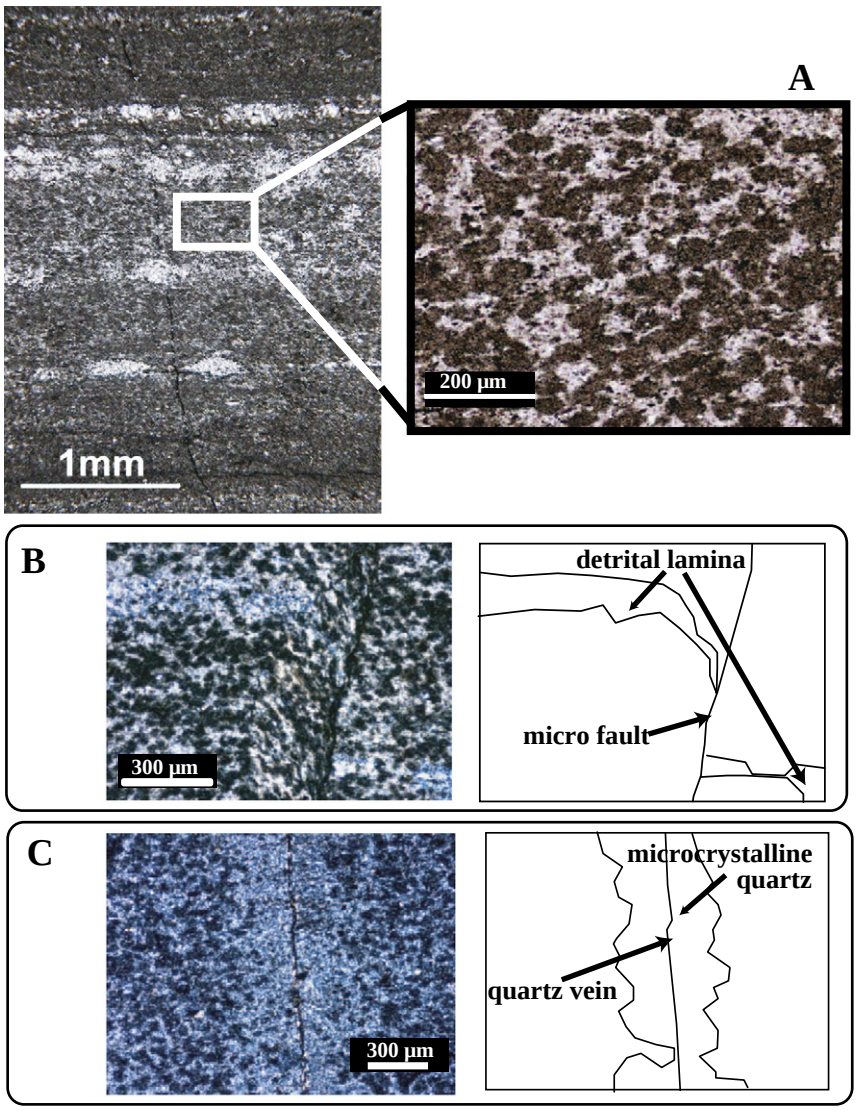

Fig. 6. Optical images of the rock samples moderately rich in Mn (0.1–1.0 wt.% of MnO) from the Firstbrook Member of the Gowganda Formation (open nicols × 5). (A) Mn-bearing chlorite is assembled as dark spherical shape in the thin sections. In (B) and (C), we observe micro faults and quartz veins in the rock samples.

and their absence near the veins (see Section 4.2), the former process is likely to cause the authigenic Mn enrichment in the Firstbrook Member of the Gowganda Formation.

This view is supported by the Fe enrichment in the form of very fine hematite particles in the Firstbrook Member (Fig. 2), suggesting the emergence of oxidizing shallow-marine condition at the time of deposition (Young et al., 2001). Although previous studies suggest the presence of mildly-oxidized surface water at ~2.6–2.5 Ga (e.g., Anbar et al., 2007; Kendall et al., 2010), our findings of the authigenic Mn and Fe enrichment would suggest the emergence of a widespread, highly-oxidized shallow-marine environment immediately after the last Huronian glaciation at ~2.3–2.2 Ga. Because the redox potential of Mn is higher than Fe, Mn precipitation would begin after the oxidization of ferrous Fe in seawater when dissolved O_2 levels increase (Kopp et al., 2005). Accordingly, the appearance of hematite would precede Mn enrichments in sedimentary sequences. In fact, in the Hotazel Formation of the Transvaal Supergroup, the deposition of Fe oxides (banded-iron formations) precedes the major Mn precipitation (Klemm, 2000), supporting authigenic Mn precipitation as a consequence of a massive release of O_2 into the surface zone of an anoxic ocean (Kirschvink et al., 2000). Additionally, Evans et al. (2001) show that fine-grained hematite particles formed early diagenesis are also found in the Hotazel Formation, which are similar to those found in the present study. Our results of the variations in Fe and Mn abundances in the Firstbrook Member (Fig. 2) also show a stratigraphical sequence similar to the Hotazel Formation; i.e., glacial diamictite units, appearances and enrichments of Fe oxides, and authigenic Mn enrichments in ascending order. This may reflect the precipitation of Mn in an oxidizing surface zone of an anoxic ocean.

The absence of Mn enrichments and high Mn/Fe ratios in the sedimentary rocks deposited above the Gowganda Formation (Fig. 3) may reflect reducing or increasing the water depth of redox boundary in the ocean. Precipitation of Mn and high Mn/Fe ratio in sediments usually occur immediately beneath the interface between oxidizing shallow marine and anoxic deep-marine environments in a redox stratified ocean, such as those observed in the present Black Sea (Klemm, 2000). Thus, reducing or increasing the water depth of redox boundary in the ocean would have resulted in lowering the Mn abundance and Mn/Fe ratio in the depositional condition of shallow-marine environment. Considering the continuous presence of red beds (Young et al., 2001) and large fractionations in $\delta^{34}S$ values and near-zero $\Delta^{33}S$ in sulfides in the upper Huronian Supergroup (Papineau et al., 2007), however, the atmosphere and shallow-marine

environments would have remained, at least moderately, oxidizing after the last Huronian glaciation.

5.2. Quantitative comparison with the Mn deposits in the Hotazel formation

The Mn deposits in the Hotazel Formation are known as the world's largest land-based economic reserve of Mn (Cairncross et al., 1997). The previous study proposes that such a large amount of Mn precipitation could have occurred as a consequence of (1) the accumulation of dissolved Mn in the ice-covered oceans during the Paleoproterozoic Snowball glaciation and (2) the subsequent Mn oxidization due to high levels of cyanobacterial activity in the glacial aftermath (Kirschvink et al., 2000). According to the previous observations of the Mn deposits in the Hotazel Formation (the thickness of Mn deposit of ~3–15 m and Mn content of ~40 wt.%) (Tsikos et al., 2003), the cumulative Mn abundance per unit area is estimated to be about 680–1600 g/cm^2.

Despite the lower Mn concentrations of the Firstbrook Member of the Huronian Supergroup (up to 1.7 wt.%) than those of the Hotazel Formation, the much thicker Mn-rich interval in the Firstbrook Member (~400 m) results in the comparable amount of the cumulative Mn abundance to that of the Mn deposits in the Hotazel Formation (~340 g/cm^2; i.e., 20–50% of the Mn abundance). Because the depositional environment of the Firstbrook Member is considered as shallow marine (Rainbird and Donaldson, 1988), the depositional rate would have been high due to discharge of massive detrital components in the glacial aftermath, which may have resulted in dilution of Mn–Fe precipitates and thus prevented formation of Mn–Fe ores in the Firstbrook Member.

5.3. Evolution of the redox state of the atmosphere and ocean during the Huronian glaciations

During the deglaciation, upwelling of sea water would have delivered dissolved Fe and Mn to shallow-marine environments, where phytoplankton blooms might have occurred (Kirschvink et al., 2000). Given the higher oxidation potential of Mn than that of Fe (Kopp et al., 2005), the precipitation of ferrous Fe occurs first during the upwelling, and Mn then precipitates in shallower oceans (Kirschvink et al., 2000). Accepting the previous calculations of the complete oxidization of ferrous Fe in seawater (Holland, 1984; Klemm, 2000), the atmospheric O_2 levels required for the precipitation of Mn are estimated to be more than 10^{-2} PAL, under which marine surface zone of ~200 m should have been oxidized assuming that the water column was close to equilibrium with the atmosphere (e.g., Holland, 1984; Klemm, 2000). The proposed depth of oxidizing marine surface is consistent with the previous estimates of those of the Firstbrook Member (Rainbird and Donaldson, 1988).

In contrast to the last Huronian glaciation, Mn enrichments are not found in the sedimentary rocks deposited immediately after the first and second Huronian glaciations (Fig. 3). In the aftermath of the second Huronian glaciation, nevertheless, there is a large variation in $\delta^{34}S$ and near-zero $\Delta^{33}S$ in sulfides (Papineau et al., 2007). These results suggest that the atmospheric O_2 level at the time interval of deglaciation from the second Huronian glaciation might have been insufficient to lead to the precipitation of Mn ($<10^{-2}$ PAL) in the ocean but became moderately high (~10^{-5}–10^{-2} PAL) enough to cause large fractionations in $\delta^{34}S$ values and near-zero $\Delta^{33}S$ in sulfides. In the interglacial period between the first and second Huronian glaciations, MIF-S in pyrite in the Pecors Formation points to the low atmospheric O_2 ($<10^{-5}$ PAL) (Papineau et al., 2007). Because Mn concentrations and other redox sensitive proxies in the sedimentary rocks are not measured continuously throughout the Huronian Supergroup, we cannot exclude a possibility of spike-like increases in O_2 levels between the available data points at the present stage. However, the comparison of our results of Mn abundance with the previous results of other proxy indicators for the atmospheric O_2 may allow us to speculate a stepwise increase in O_2 in response to the three Huronian glaciations (Fig. 7).

Based on our results and the previous geochemical data, we speculate that the climatic recovery from the Paleoproterozoic glaciations might have accelerated the increase in O_2 by providing large amounts of nutrients to the oceans (Bekker et al., 2005; Kirschvink et al., 2000; Papineau et al., 2007; Sekine et al., 2010). An increase in O_2 in the aftermath of the glaciation then dampens the methane greenhouse, subsequently triggering the next glaciation (Pavlov et al., 2001; Kopp et al., 2005). Again, the climatic recovery from the glaciation would have increased the atmospheric O_2 levels. Such a positive feedback mechanism could be a driving force for the transition to the oxidizing world (i.e., the GOE), which had concurrently occurred with climatic instability recorded as the Huronian glaciations.

5.4. Correlation with the Makganyene Snowball glaciation

The implication of our geochemical data for the global-scale evolution of the surface environments during the GOE depends upon whether the Gowganda Formation correlates with the Makganyene Formation in the Transvaal Supergroup. If they do correlate, our geochemical data suggest that the major precipitation event of Mn and Fe was widespread in the shallow-marine environments in the aftermath of the Paleoproterozoic Snowball glaciation. This in turn means that the Bruce Formation of the Huronian Supergroup would most likely correlate with the glacial diamictite unit of the Rooihoogte/Duitschland Formation in the Transvaal Supergroup. According to our Mn records and the previous MIF-S results (Bekker et al., 2004; Hannah et al., 2004; Papineau et al., 2007), the atmospheric O_2 would have remained intermediate levels (~10^{-5}–10^{-2} PAL) before

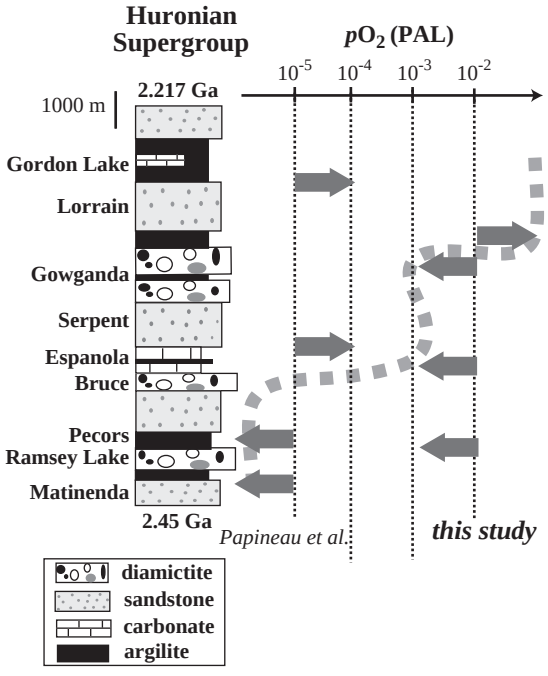

Fig. 7. Schematic diagram of the variation of atmospheric O_2 throughout the Huronian Supergroup (gray dotted line) proposed by geochemical evidences. The Mn enrichment (this study) and mass-independent fractionation (MIF) of sulfur (Papineau et al., 2007) in sediments would reconstruct the atmospheric O_2 levels of 10^{-2} and 10^{-5} PAL, respectively. The arrows represent the constraints on the atmospheric O_2 levels based on the presence or absence of the above geochemical evidences in the sedimentary sequences of the Huronian Supergroup. These results suggest a stepwise increase in O_2 in response to the repeated glacial event during the GOE.

the Paleoproterozoic Snowball glaciation. The highly oxygenated atmosphere and shallow-marine environments would have appeared immediately after the Paleoproterozoic Snowball Earth for the first time in Earth's history.

Alternatively, if the Gowganda glaciation predates the Makganyene Snowball glaciation (Hilburn et al., 2005; Kopp et al., 2005), our observations of the Mn enrichments could reflect the at least local and/or temporal appearance of highly oxygenated environments in the surface ocean and atmosphere (>~10^{-2} PAL) before the Paleoproterozoic Snowball glaciation. If this is the case, our results of the Mn enrichments in the Firstbrook Member might be comparable with the first appearance of no MIF-S found in the lower Timeball Hill Formation of the Transvaal Supergroup (Bekker et al., 2004; Hannah et al., 2004). The appearance of high levels of O_2 in the atmosphere before the Paleoproterozoic Snowball Earth could have resulted in dampening the methane greenhouse effects, possibly triggering the Paleoproterozoic Snowball Earth (Pavlov et al., 2001; Kopp et al., 2005). To investigate the correlation between the Firstbrook Member and Hotazel Formation, more geochronological studies are required for constraining the depositional age of the Gowganda Formation.

6. Summary

We found authigenic Mn enrichments and high Mn/Fe ratios in the lower part of the Firstbrook Member in the Gowganda Formation of the Huronian Supergroup. Based on the results of the SEM and EPMA analyses and thin section observations, the Mn-bearing minerals in the Mn-rich sedimentary rocks are spessartine-rich almandine and Mn-bearing chlorite. Despite the uncertainties on the original Mn-bearing minerals deposited in the sediments and the depositional age of the Gowganda Formation, our study allows us to draw the following conclusions:

1. The observed high concentrations of Mn (up to 1.7 wt.%) with high Mn/Fe ratios (up to 0.13) relative to the levels of typical detrital components indicate the significant inputs of Mn to the black argillite in the lower part of the Firstbrook Member.
2. The thin section observations of the sedimentary rocks show that Mn-bearing minerals (spessartine-rich almandine and Mn-bearing chlorite) occur along laminae in the black argillite and are not related with the occurrence of veins in the samples. These results suggest that although these Mn-bearing minerals were formed by post-depositional metamorphism, the original Mn enrichment is likely to be synsedimentary as a consequence of the precipitation of Mn in the oxidizing shallow-marine environment.
3. Given the cumulative Mn abundance per unit area and the appearance of Fe oxides associated with the Mn enrichments in the Firstbrook Member, the Mn enrichments in the Firstbrook Member are considered as comparable in magnitude with the major Mn and Fe precipitation of the Hotazel Formation of the Transvaal Supergroup.
4. If the Firstbrook Member is stratigraphically correlative with the Hotazel Formation, a release of large quantities of O_2 and subsequent oxidative Mn precipitations may have been widespread in the shallow-marine environments immediately after the Paleoproterozoic Snowball glaciation (Kirschvink et al., 2000).
5. Alternatively, if the Gowganda glaciation predates the Makganyene glaciation, the high levels of atmospheric O_2 would have been developed, at least locally or temporally, before the Paleoproterozoic Snowball Earth event.

Considering the oxidization potential of Mn, the Mn enrichments in the Firstbrook Member suggests that the atmospheric O_2 levels reached ~10^{-2} PAL immediately after the last Huronian glaciation. Based on the discussion that climatic recovery may have accelerated the oxygenation of atmosphere, there could be a positive feedback mechanism among the atmosphere, climate, and biosphere, which might have driven the irreversible transition to the oxidizing world and been responsible for the concurrently-occurred repeated glaciations in the Paleoproterozoic. In the aftermath of the positive feedback between the increase in O_2 and repeated glaciations, the atmospheric O_2 levels would have reached to ~10^{-2} PAL (i.e., the Pasteur point), which allows aerobic microorganisms to adapt from anaerobic respiration to aerobic respiration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2011.05.001.

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