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Review

Precambrian supercontinents, glaciations, atmospheric oxygenation, metazoan evolution and an impact that may have changed the second half of Earth history

Grant M. Young*

Department of Earth Sciences, Western University, 1151 Richmond Street N, London, Ontario, Canada N6A 5B7

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A B S T R A C T

In more than 4 Ga of geological evolution, the Earth has twice gone through extreme climatic perturbations, when extensive glaciations occurred, together with alternating warm periods which were accompanied by atmospheric oxygenation. The younger of these two episodes of climatic oscillation preceded the Cambrian "explosion" of metazoan life forms, but similar extreme climatic conditions existed between about 2.4 and 2.2 Ga. Over long time periods, changing solar luminosity and mantle temperatures have played important roles in regulating Earth's climate but both periods of climatic upheaval are associated with supercontinents. Enhanced weathering on the orogenically and thermally buoyed supercontinents would have stripped CO_2 from the atmosphere, initiating a cooling trend that resulted in continental glaciation. Ice cover prevented weathering so that CO_2 built up once more, causing collapse of the ice sheets and ushering in a warm climatic episode. This negative feedback loop provides a plausible explanation for multiple glaciations of the Early and Late Proterozoic, and their intimate association with sedimentary rocks formed in warm climates. Between each glacial cycle nutrients were flushed into world oceans, stimulating photosynthetic activity and causing oxygenation of the atmosphere. Accommodation for many ancient glacial deposits was provided by rifting but escape from the climatic cycle was predicated on break-up of the supercontinent, when flooded continental margins had a moderating influence on weathering. The geochemistry of Neoproterozoic cap carbonates carries a strong hydrothermal signal, suggesting that they precipitated from deep sea waters, overturned and spilled onto continental shelves at the termination of glaciations. Paleoproterozoic (Huronian) carbonates of the Espanola Formation were probably formed as a result of ponding and evaporation in a hydrothermally influenced, restricted rift setting. Why did metazoan evolution not take off after the Great Oxidation Event of the Paleoproterozoic? The answer may lie in the huge scar left by the ~2023 Ma Vredefort impact in South Africa, and in the worldwide organic carbon-rich deposits of the Shunga Event, attesting to the near-extirpation of life and possible radical alteration of the course of Earth history.

1. Introduction

Because it was probably lost to space during the Late Heavy Bombardment (~3.9 Ga), the nature of the early atmosphere is unknown but it was likely rich in H_2 and He. It is widely believed that much of the secondary atmosphere was derived from de-gassing of the Earth's interior so that it is also likely that the early atmosphere was anoxic. Free oxygen is believed to have resulted from photodissociation of water and, more importantly, as a by-product of photosynthetic activity. Oxygen played a crucial role in the evolution of life, both in the opening up of new, highly efficient metabolic pathways and in permitting colonization of shallow waters and land surfaces under the protective cover of the ozone layer (Fischer, 1965). The questions addressed in this paper relate to when and how the Earth's atmosphere changed, its tectonic controls and attendant palaeoclimatic and biological events.

The idea of "continental drift" was first entertained in the 17th century but it was not until quite recently, following documentation of sea floor spreading by Lawrence Morley, and Vine and Matthews (1963), that plate tectonics was widely accepted. An important paper

* Tel.: +1 011 519 473 5692; fax: +1 011 519 661 3198.
E-mail address: gyoung@uwo.ca.

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by Wilson (1966) suggested that the Atlantic Ocean had opened twice, introducing the concept of a supercontinental cycle and its possible role in effecting great climatic perturbations in both Phanerozoic (Fischer, 1984; Worsley et al., 1984) and Proterozoic times (Worsley et al., 1986, 1994; Young, 1991; Bleeker, 2004; Eyles, 2008).

It is widely (but not universally) believed that the transition to an oxygenic atmosphere took place in early Paleoproterozoic times (Cloud, 1968; Roscoe, 1973; Holland, 1999). Roscoe (1973) studied the Huronian Supergroup (~2.45–2.2 Ga) and drew attention to unusual Fe-depleted paleosols, detrital pyrite and uraninite in mineralogically mature fluvial deposits, and an upward transition from drab to red subaerially-deposited sedimentary rocks. These observations placed important constraints on when free oxygen appeared in the atmosphere. Supporting evidence has subsequently been gathered from Paleoproterozoic rocks in many parts of the world and the change in atmospheric composition has come to be known as the Great Oxidation Event (Karhu and Holland, 1996; Bekker et al., 2004) or Lomagundi-Sarioli Event (Melezhik et al., 2005). It was accompanied by strong positive excursions in $\delta^{13}C_{carb}$ (Fig. 1). Since ^{12}C is commonly sequestered by photosynthetic organisms, marked increases in $\delta^{13}C$ values in seawater (which are thought to be captured in precipitates such as carbonates) are taken to indicate periods of enhanced photosynthetic activity and rapid sedimentation, causing removal of ^{12}C from the carbon cycle.

2. Rodinia and the Neoproterozoic climatic cycles

Following the Grenville collisional orogeny and formation of the supercontinent Rodinia, the Earth entered a long period of climatic upheaval. Glacial deposits are extremely widespread (Mawson, 1949; Harland, 1964; Kaufman et al., 1997) and there are significant perturbations in the $\delta^{13}C_{carb}$ curve (Fig. 1). For a recent compilation of Neoproterozoic glacial deposits see Arnaud et al. (2011). The great Neoproterozoic glaciations inspired the phrase, "snowball Earth" (Kirschvink, 1992; Hoffman et al., 1998), which sparked lively discussions regarding its severity. Whatever the outcome of the on-going debate, there can be little doubt that most of today's continents carry evidence of several late Neoproterozoic glacial episodes whose deposits, like those of the first two Paleoproterozoic (Huronian) glaciations, were commonly preserved in rift settings (Young, 1985; Young and Nesbitt, 1985; Eyles and Januszczak, 2004). Both great Proterozoic glacial episodes were initiated following formation of supercontinents (Fig. 2), and introduced extended periods of extreme climatic oscillation. For a recent discussion as to how climates and the evolution of life might have been influenced by the amalgamation and break-up of supercontinents see Santosh (2010).

3. Termination of the Neoproterozoic glaciations

3.1. Cap carbonates

The name "cap carbonate" refers to thin (~3–20 m) buff or pink dolostones and limestones that overlie glacial deposits. They commonly display fine bedding or lamination. Many contain evidence of stromatolitic activity, in the form of broad domes with irregular tube structures oriented approximately normal to regional bedding, regardless of the attitude of the stromatolitic laminations. Most occurrences display a remarkably consistent set of structures including brecciated and veined (sheet-cracked) zones, usually near

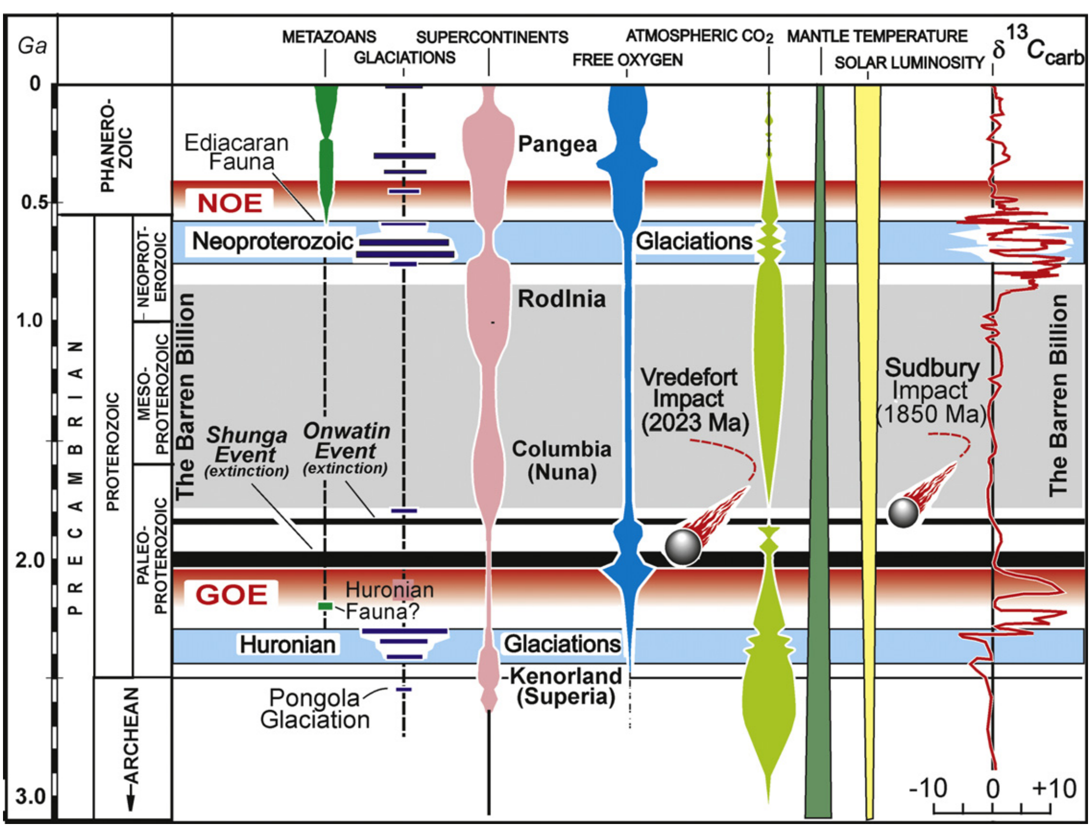

Figure 1. Schematic representation of events discussed in the text. Apart from the right hand column (after Kah et al., 2004; Halverson et al., 2005; Melezhik et al., 2005), the depicted changes are qualitative. Two Precambrian periods of multiple glaciations were followed by accumulation of atmospheric oxygen. Note the two massive impact events that occurred after the Great Oxidation Event (GOE) and caused global extinctions, resulting in accumulation of carbonaceous deposits of the Shunga and Onwatin events. NOE is the Neoproterozoic Oxidation Event (Och and Shields-Zhou, 2011).

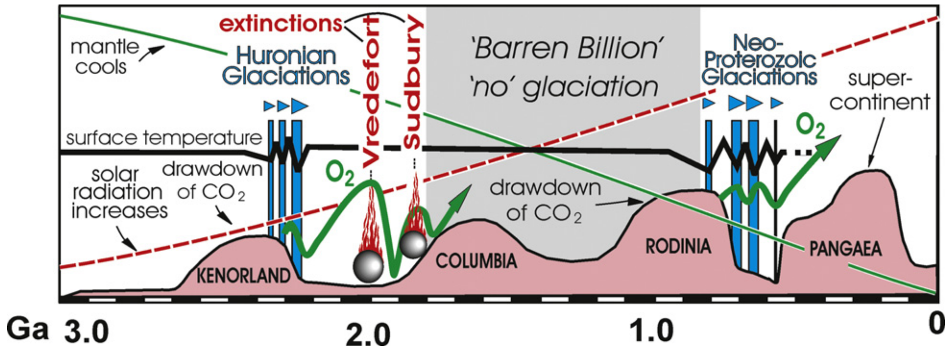

Figure 2. Simplified representation of the proposed relationships between Proterozoic supercontinents and climatic perturbations. Supercontinents (named) are represented by the thick portions of the pink area at the base of the diagram (after Bleeker, 2004). Relative changes in solar luminosity and mantle temperatures are shown by the red and green lines respectively. Thick green arrows show inferred changes in atmospheric oxygen content. Timing of the Vredefort and Sudbury impacts is indicated. See text for explanation and discussion.

the base, laminations and fine bedding, some parallel to regional bedding and some displaying "roll up structures" and pseudo-tepee structures, some of which have been interpreted as large scale ripples formed by giant waves. Some display barium-rich crystal fans thought to have formed by replacement of aragonite deposits that crystallized out of ocean water, suggesting a high degree of saturation.

Among their unusual chemical characteristics, the most widely reported is the occurrence of negative δ^{13}C values, but they also typically display other peculiarities such as high Fe and Mn contents, enrichment in certain trace elements (especially heavy metals), and Post-Archaean Australian Shale (PAAS)-normalized rare earth element (+Yttrium) patterns characterized by depletion in light rare earth elements and positive Eu and Y anomalies, and a lack of negative Ce anomalies. These rocks attracted attention because carbonate rocks, especially dolostones, are generally considered to be associated with warm water conditions whereas the cap carbonates occur immediately above glacial deposits. Cap carbonates are widely distributed in Neoproterozoic successions but are most common in the Marinoan interval (~635 Ma). Since negative δ^{13}C values were discovered in cap carbonates in Australia by Williams (1979), such values have been found in these rocks throughout the world. It was suggested by Bekker et al. (2005) that carbonate rocks of the Paleoproterozoic Espanola Formation and correlative Vagner Formation in Wyoming might be older examples of cap carbonates for they overlie diamictite-bearing formations and have yielded negative δ^{13}C values, the origin of which remains unexplained. Among the suggested theories are that these values are due to near-extirpation of life (Hoffman et al., 1998) but Hoffman (2011) suggested that they might reflect the fractionation of different carbon species as a function of the pH of seawater. It is interesting that δ^{13}C mantle signatures (Deines, 2002) cluster around −5, so that one alternative interpretation is that the values in cap carbonates may have been hydrothermally influenced.

It has been postulated (Kirschvink et al., 2000) that certain formations of the Huronian Supergroup and perhaps other glaciogenic deposits of Paleoproterozoic age in South Africa were formed during an earlier period of world-wide glaciation (snowball Earth conditions). Current theories on the origin of cap carbonates include the following:

(1) It was suggested by Hoffman et al. (1998) and Hoffman (2011) that they formed at the end of global glacial events, when high atmospheric CO_2 caused strong surface weathering that introduced large amounts of dissolved material into world oceans.
(2) Liberation of methane from frozen ground at the end of Neoproterozoic glacial episodes was proposed by Kennedy et al. (2001) and Yang et al. (2003) to explain negative δ^{13}C values and the presence, near the base of many cap carbonate units, of calcite-filled fractures, thought to have formed by gas escape. Hoffman (2011) suggested that the cracks formed by dewatering as water depth decreased.
(3) A stratified ocean, with an upper fresh water layer ("plumeworld"), was proposed by Shields (2005) to explain the formation of cap carbonates.
(4) Overturn of an anoxic deep ocean at the end of glaciations was favoured by Grotzinger and Knoll (1995).
(5) Based on a study of the Nuccaleena Formation in the Flinders Ranges of Australia, Retallack (2011) concluded that this cap carbonate is largely eolian and contains paleosols, indicating subaerial exposure.
(6) A clastic origin for Neoproterozoic cap carbonates was suggested by Fairchild (1993), based on the common occurrence of carbonate clasts in associated diamictites.
(7) A "slow" development of cap carbonates was suggested by Kennedy and Christie-Blick (2011), who presented stratigraphic evidence that ca. 635 Ma cap carbonates of the Amadeus Basin in central Australia represent condensed sections. A similar interpretation was put forward by Font et al. (2010) based on evidence of paleomagnetic reversals in Marinoan cap carbonates of the Mirassol d'Oeste Formation in the Mato Grosso of Brazil. Hoffman (2011) proposed that cap carbonates formed very rapidly, within a few thousand years.
(8) Investigation of major and trace element geochemistry of cap carbonates led Font et al. (2006), Huang et al. (2011) and Meyer et al. (2012) to conclude that they were strongly influenced by hydrothermal processes.

3.2. A cap carbonate deposited on crystalline basement: Antelope Island, Great Salt Lake, Utah

Antelope Island is located at the southeast end of Great Salt Lake in northern Utah, USA. It forms part of the Promontory Range of the Basin and Range Province (Yonkee et al., 2000). Neoproterozoic diamictites there may be correlated to the Mineral Fork Formation (Ojakangas and Matsch, 1980; Christie-Blick, 1983; Young, 2002a). The Neoproterozoic diamictites overlie Archaean(?) to Paleoproterozoic crystalline rocks. This area was chosen to test the hypothesis of Hoffman (2011, and references therein) that, following an inferred global glaciation, broken by the strong build-up of CO_2 in the atmosphere, the first siliciclastic sediments should show evidence of extreme weathering, with a gradual upwards decrease as atmospheric CO_2 returned to less extreme values. The

Chemical Index of Alteration (CIA of Nesbitt and Young, 1982) was used to assess the degree of weathering to which rocks have been subjected. This area was chosen for study because CIA values can be compromised by the presence of carbonates, whereas the glacial (and siliciclastic post-glacial) rocks in this area were presumably derived mainly from crystalline basement.

On Antelope Island diamictites are overlain by a classical cap carbonate, succeeded by a sequence of mudstones. Chemical analyses (unpublished data) were carried out on samples throughout the succession. The results point to low CIA values for the diamictites and, following deposition of the cap carbonates, a gradual upward increase in weathering intensity, similar to that reported at the end of the Paleoproterozoic (Huronian) Gowganda glaciation (Young and Nesbitt, 1999; Fig. 6). These results do not support the idea of extreme $CO_{2(atmos.)}$ values at the end of the glaciations, but rather suggest gradual amelioration of climate accompanied by increased weathering (Fig. 3). Trace element compositions of cap carbonates (including rare earth elements) suggest a hydrothermal influence (see Section 6.1).

3.3. A possible origin for cap carbonates

The combination of field characters, including sharp basal contact and gradational top, large domal stromatolites with tube structures and wave ripples, and geochemical characteristics (precipitation of redox-sensitive elements such as Fe and Mn, PAAS-normalized REE+Y patterns that show depletion in LREE, weak +ve Y anomalies, absence of −ve Eu and Ce anomalies, enrichment in trace elements such as "heavy metals"), together with their world-wide distribution, all point to an origin from hydrothermally-influenced seawater that flooded subsiding continental shelves as it was displaced from the deep ocean by massive amounts of meltwater at the end of the Sturtian (and especially the Marinoan) glaciations. All of the chemical characteristics are satisfied by overturn of a stratified ocean and many not by the run-off weathering theory (or the plumeworld theory). The sticking point for those supporting the overturn model has been the mechanism to effect upwelling of deep ocean waters. At the present day oceanic overturn and oxidation of the deep oceans are mainly brought about by what can be considered as a global oceanic conveyor belt system (Broecker, 1991) which is set in motion by sinking of cold saline waters formed in high latitudes of the Atlantic Ocean where dry winds from Canada cause evaporative concentration of salts (Calvin, 1998). A similar (but much stronger) conveyor system may have developed at the end of the great Neoproterozoic glaciations. It has been proposed that the supercontinent Rodinia straddled the equator. Ocean waters may have been rendered more dense by evaporative concentration of solutes as strong katabatic winds descended from the remaining inland icecaps to the expanding ocean. Extremely high wind velocities were suggested by Allen and Hoffman (2005), based on the common occurrence of unusually large wave ripples in cap carbonates. Upwelling of reduced, metal-charged alkali-rich deep oceanic waters provides a ready explanation for the geochemical characteristics of cap carbonates, although more geochemical data are required. The waters that flooded newly-formed continental shelves were probably initially reducing and highly alkaline but gradually became diluted with post-glacial runoff as fine terrigenous material was introduced and overwhelmed carbonate precipitation. CIA values for mudstones above the cap carbonate at Antelope Island point to a gradual upward increase in weathering intensity, at odds with the decreasing trend predicted from the snowball Earth hypothesis. This finding also requires confirmation from other localities but, as stated above, most Neoproterozoic diamictites are developed above older sedimentary rocks that include abundant carbonates (both limestones and dolostones), so that calculation of CIA values from such rocks is problematic.

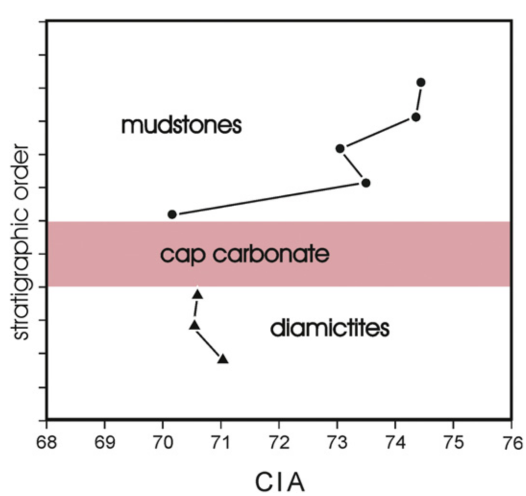

Figure 3. Values for a Chemical Index of Alteration (Nesbitt and Young, 1982) showing that Neoproterozoic diamictite samples from Antelope Island, Great Salt Lake, Utah, have low values, whereas mudstones overlying the cap carbonate show a gradual upward increase in weathering intensity. See text for discussion.

4. Banded iron formations

Most banded iron formations (BIFs) are older than about 1.85 Ga but they make a brief and much less voluminous reappearance in some Neoproterozoic sedimentary successions where they are mostly associated with glacial deposits (Yeo, 1981; Klein and Beukes, 1993; Young, 2002b; Hoffman and Li, 2009). As pointed out by Young (2002b), occurrences of Neoproterozoic iron formation are much fewer than those of glacial deposits of similar age. According to Hoffman and Li (2009; Fig. 6) there are seven Sturtian BIF occurrences (out of 28 listed examples of glacial deposits) and only two of 32 Marinoan glacial occurrences contain iron formations. An iron formation in SE Uruguay has been described by Pecoits et al. (2008) who tentatively assigned a Gaskiers age (ca. 580 Ma) to underlying glacial deposits. They did not consider an open Atlantic-type margin to be an appropriate model for these rocks, suggesting instead that they may have formed in transtensional pull-apart basins that preceded continental collision. It should be noted that Ilyin (2009) listed 20 occurrences of Neoproterozoic iron formations but some of these may be considered as parts of individual basins. As pointed out by Yeo (1981) and Young (2002b), many Neoproterozoic BIFs are preserved in a rift setting and it has been claimed (Basta et al., 2011; Freitas et al., 2011) that some of these lack compelling evidence of contemporaneous glaciation. It is, however, possible that in some active basins tectonic influence on sedimentation was so strong that it masked the original genesis of the sediments. For example glacial deposits may be reworked to the point that the glacial signature is lost (Schermerhorn, 1974; Arnaud and Eyles, 2002). The existence of glacial deposits in some diamictite-bearing Neoproterozoic basins has been denied by Basta et al. (2011), Freitas et al. (2011) and Eyles and Januszczak (2007), who stressed the importance of mass flows and turbidites in their sedimentary fill. These arguments are reminiscent of a debate in the seventies when Schermerhorn (1974) published similar ideas following the recognition of sedimentological criteria for identification of "resedimented" deposits. Different depositional processes can, however, act simultaneously (in this case glaciations and sediment movements related to contemporaneous rift faulting) with one process dominating over and obscuring evidence of the other. Examples of such processes

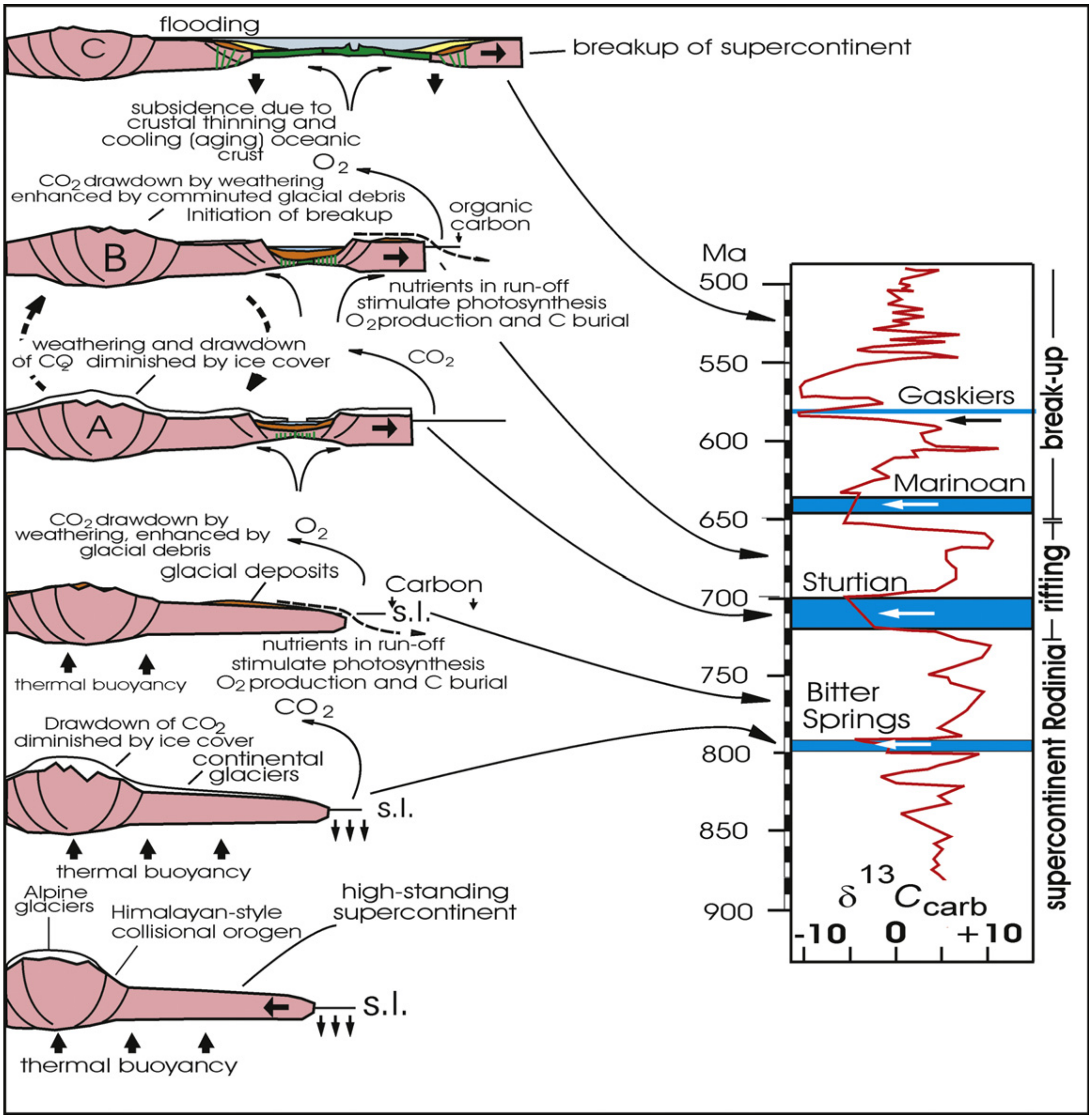

Figure 4. Plate tectonic interpretation of climatic oscillations near the beginning and end of the Proterozoic Eon. Glaciation occurred following amalgamation of a supercontinent but a negative feedback loop led to destruction of ice sheets and to their re-establishment over an extended period of time. Associated changes in ocean chemistry are shown by the pattern of $\delta^{13}C$ values from carbonates at right (after Halverson et al., 2005). The icehouse–greenhouse cycle is repeated (heavy dashed arrows) until the rift–drift transition takes place (condition C). These conditions are envisioned for both Paleo- and Neoproterozoic glacial episodes.

involving the Neoproterozoic Gaskiers glaciations were given by Carto and Eyles (2012).

Two theories have been advanced to explain the Neoproterozoic BIFs. They may be related to hydrothermal activity associated with rift basins, in most (all?) cases accompanied by glaciations, or they may have formed by global overturn of oceans at the end of glaciations, as claimed by Hoffman et al. (1998). Both mechanisms involve oxidation of Fe-charged hydrothermal water but they would have operated on very different scales. The former theory is supported by the sporadic occurrence of iron-formations compared to the world-wide distribution of glaciogenic deposits and cap carbonates, especially those associated with the Marinoan glaciation. An additional problem with the global ocean overturn model is that the iron formations do not always occur above glaciogenic rocks. For example iron formation in the Rapitan Group was precipitated before and contemporaneous with deposition of the thick diamictites of the Shezal Formation, and similar relationships are found in the Kingston Peak and Pocatello Formations in the southern part of the North American Cordillera, and in the Flinders Ranges of South Australia. The intimate association of Sturtian iron-formations with mudstones and diamictites (Yeo, 1981; Klein and Beukes, 1993) and the presence of dropstones in iron formations show that iron (and silica) were being precipitated at the time of glacial deposition, albeit during the retreat phase, and not afterwards as predicted by the snowball Earth hypothesis. The geochemical composition of Neoproterozoic iron formations has been well documented (Yeo, 1981, 1986; Klein and Beukes, 1993; Neale, 1993) and there seems to be general agreement that there is a significant hydrothermal imprint. Rare earth element signatures commonly show depletion of light rare earth elements and positive Eu anomalies of variable magnitude (all relative to PAAS). Neoproterozoic BIFs also commonly display positive Y anomalies. As well as obvious enrichment in Fe and Si, the BIFs are commonly rich in Mn and heavy metals such as Zn, Cu, Mo and Ni. All of these geochemical characteristics suggest hydrothermal influence but they fail to differentiate between an oceanic origin for the parent

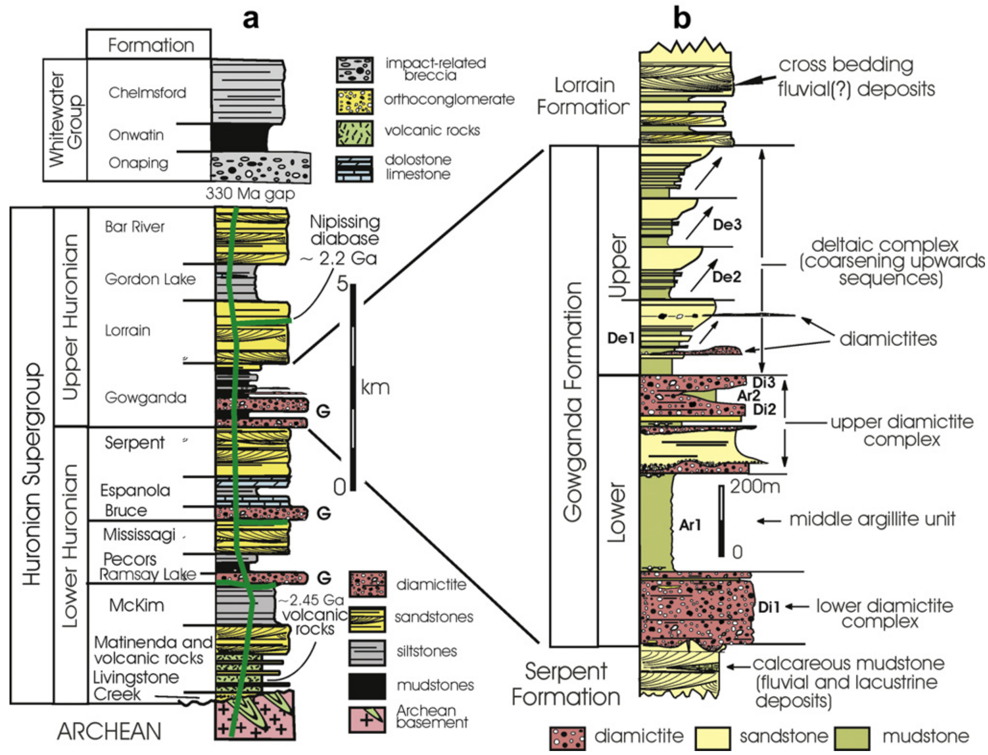

Figure 5. Stratigraphy of Paleoproterozoic supracrustal rocks on the north shore of Lake Huron. a: Generalized stratigraphic succession of the Huronian Supergroup and Whitewater Group. Note the presence of three glaciogenic units (G) and one carbonate-rich unit (Espanola Formation) above diamictite of the Bruce Formation. There is a large hiatus separating the Huronian Supergroup from the Whitewater Group; b: detailed succession of the Gowganda Formation in the southern part of the Huronian outcrop belt (Fig. 6). Note that the upper part of the Gowganda Formation is mostly non-glacial. Abbreviations Di, Ar, De refer to diamictite, argillite, deltaic sequence respectively, as used in Fig. 9.

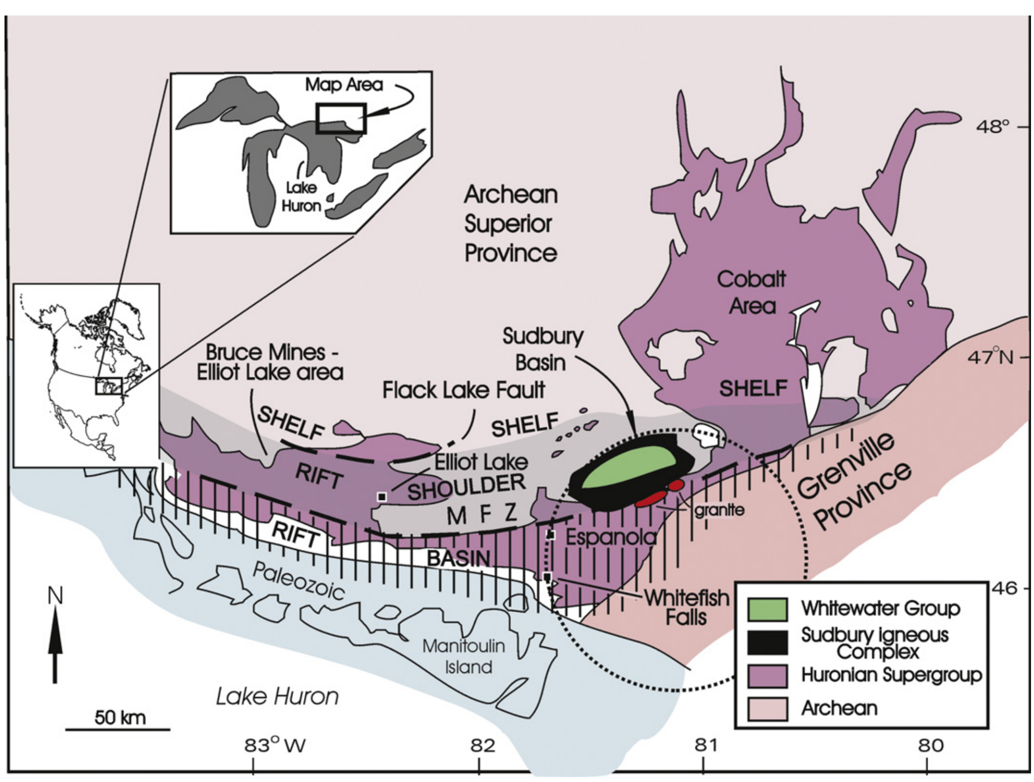

Figure 6. Sketch map to show the distribution and geological context of the Huronian Supergroup on the north shore of Lake Huron. Note that the Supergroup has been divided into three tectono-sedimentary settings, which are related, in part, to major faults. The upper part of the Huronian (beginning with the glaciogenic Gowganda Formation) transgresses onto a wide shelf area to the north. The dotted circle in the vicinity of the Sudbury Basin shows the postulated extent of the scar left by the Sudbury impact.

waters and derivation from a restricted water pool in a hydrothermally influenced rift basin. Field relations such as restricted distribution (relative to widespread development of contemporaneous glaciogenic deposits), major facies changes related to syndepositional faults, and occurrences below and within glaciogenic successions all support the latter depositional setting. Thus the reappearance of banded iron formation in the Sturtian glacial deposits may be due to hydrothermal activity in Red Sea-type rift basins, most of which were affected by glaciations. If cap carbonates are present in these iron formation-bearing sequences they usually occur above the glacial deposits and are commonly weakly developed.

It is noteworthy that BIFs in Alaska (Young, 1982), NW Canada (Eisbacher, 1978; Yeo, 1981, 1986; Klein and Beukes, 1993), Idaho (Fanning and Link, 2004), S. Australia (Whitten, 1970; Young, 1988; Neale, 1993) Egypt (Basta et al., 2011) have a volcanic association, contrary to the statement by Hoffman and Li (2009) that such BIFs are seldom associated with volcanic rocks. The iron formations are commonly intimately intermixed with clastic materials so that many diamictites have an iron-rich matrix. Dropstones occur in some iron formations, indicating that glacial deposition and iron formations were contemporaneous, not sequential. This suggests that Neoproterozoic iron formations are not analogous to cap carbonates. The sporadic distribution, stratigraphic context, facies and thickness variations (Young and Gostin, 1989; their Fig. 16), sedimentary association and geochemical characteristics are in accord with deposition in active rift settings, rather than indicating a global phenomenon, linked to development of a reducing ocean caused by total (or near-total) oceanic ice cover (Kirschvink, 1992; Klein and Beukes, 1993; Hoffman et al., 1998).

It is interesting that no significant iron formations are associated with the termination of the Huronian glaciations, for the presence of the much younger Paleoproterozoic iron formations of the Lake Superior area and elsewhere indicates that the oceans contained abundant iron at the time of Huronian glaciations. This, in turn, suggests that there was no major oceanic overturn following the Huronian glaciations, such as has been suggested as an explanation for some Neoproterozoic BIFs. On the other hand, at a much higher stratigraphic level within the Huronian Supergroup there are some thin siltstones and mudstones in the most southerly outcrops of the Bar River Formation that are decidedly Fe-rich (Young, 1966) and may indicate influx (and oxidation) of some Fe-charged marine waters at a much later time than the termination of the Gowganda glaciation.

5. Kenorland and climatic cycles in the Paleoproterozoic: the Huronian Supergroup and correlatives

Deposition of the Huronian Supergroup followed amalgamation of one of the world's first "supercratons" or supercontinents, named Kenorland by Williams et al. (1991) or Superia (Bleeker, 2004). Is there a relationship between the three Huronian glaciations and that event? Mountain building during continental collisions that generated a supercontinent, and the blanketing effect of such a large area of continental lithosphere on heat escape from the Earth's interior would have led to elevation, and exposure, enhancing both physical and chemical weathering (Fischer, 1984; Young, 1991; Worsley et al., 1994). Withdrawal of CO_2 from the atmosphere by chemical weathering would have led to reduced surface temperatures and, eventually, glaciation. Amalgamation of continental lithosphere diminishes sea-floor spreading activities so that lowered CO_2 emissions would also have contributed to global cooling. Glaciers would, however, have eventually melted because widespread ice cover and lowered surface temperatures inhibit weathering and permit CO_2 buildup, causing a return to a greenhouse state. This important negative feedback loop may provide an explanation for the multiple glaciations at the beginning and end of the Proterozoic Eon (Fig. 4).

How did the planet escape from the cycle of alternating warm and cold periods? According to Young and Nesbitt (1985) deposits of the first two Huronian glaciations were preserved in a rift setting, whereas the youngest (Gowganda Formation) accompanied continental separation. Deglaciation, subsidence of the thinned, fragmented continental crust, and production of young, high-standing oceanic crust led to widespread flooding of continental interiors and deposition of extensive quartz arenites (Young, 1973a). Aggressive post-glacial weathering and increased rainfall, as new seaways invaded the fragmenting supercontinent, enhanced delivery of essential organic nutrients (including P and Fe) to the oceans. Phytoplankton would have flourished, liberating oxygen into the atmosphere (Holland, 2002; Campbell and Allen, 2008). Such activities would have taken place during several interglacial phases (Fig. 4), culminating in the Great Oxidation Event (GOE of Fig. 1). Isotopic evidence for this world-wide event (Karhu and Holland, 1996) was first discovered by Schidlowski et al. (1976) in the form of unusually high positive $\delta^{13}C_{carb}$ values from the Paleoproterozoic Lomagundi carbonate in the former Rhodesia. A link between plate tectonic activity and variations in carbon isotopes in Paleoproterozoic rocks of Western Australia was proposed by Lindsay and Brasier (2002). Similar events characterize the last 300 Ma of the Neoproterozoic Era, but the second oxygenation event was followed by the so-called "Cambrian explosion" of metazoa. The Paleoproterozoic GOE ushered in a very long period that has yielded little evidence of strong climatic or isotopic fluctuations (Fig. 1). There is, however, some evidence that the GOE may have sparked an abortive attempt at higher evolution. Complex structures with symmetrical ornamentation were reported from quartz arenites in the upper part of the Huronian Supergroup (Frarey and McLaren, 1963; Hofmann, 1967) and have been interpreted as possible early metazoans. Because of the extreme age of these structures (2.3–2.2 Ga), this suggestion has generally been dismissed but a satisfactory alternative interpretation has not been forthcoming. Similar structures have been described from correlative quartz arenite units in places as far apart as Wyoming and Finland (e.g. Lauerma and Piispanen, 1967; Kauffman and Steidtmann, 1981). If these events started life on the road to metazoan evolution, why did it turn out to be a dead end? This question is addressed in Section 7 below.

6. Termination of the Paleoproterozoic glaciations

6.1. Paleoproterozoic cap carbonates?

Are cap carbonates unique to the Neoproterozoic? It was suggested by Kirschvink (1992) and Kirschvink et al. (2000) that the Earth may have gone through an early (Paleoproterozoic) phase of extreme glaciations (snowball Earth condition), like those proposed for the Neoproterozoic. Kopp et al. (2005) considered the Paleoproterozoic snowball glaciation to be slightly younger than all of the Huronian glaciations, although the supposedly world-encircling younger glaciation was only reported from South African locations, whereas the Huronian Gowganda Formation has been considered to be much more extensive (Young, 1970, 2004; Ojakangas, 1988).

The Huronian Supergroup of Ontario, Canada, includes three diamictite-bearing glaciogenic formations (Fig. 5). Within the thick (max ~12 km) Huronian succession only one carbonate-rich formation is present – the Espanola Formation, which overlies the Bruce Formation, the second of the three diamictite-rich glacial units. It was suggested by Bekker et al. (2005), mainly on the basis of negative $\delta^{13}C$ values, that the Espanola Formation and an equivalent unit in Wyoming (Young, 1975) may be examples of Paleoproterozoic cap carbonates. Unlike Neoproterozoic cap carbonates the Espanola Formation is thick, ranging from about 150 m in the Elliot Lake area to ~600 m in southern parts of the Huronian outcrop belt. It has a complex stratigraphy and exhibits considerable lateral variability. In the northern part of the Huronian outcrop belt, north of Elliot Lake, the Espanola Formation may be divided into three members (Collins, 1914), a lower limestone, middle siltstone and upper dolomitic unit. In more southerly areas, near Whitefish Falls (Fig. 6), the formation has a much greater siliciclastic content, and the upper dolomitic member is not clearly differentiated (Bernstein and Young, 1990). Descriptions of the stratigraphy and sedimentary structures of the Espanola Formation were given by Eisbacher (1970), Young (1973b) and Bernstein and Young (1990). It is important to note the intimate association between carbonates of the Espanola Formation and siliciclastic rocks (mainly fine grained rocks such as siltstones and fine sandstones) – this differentiates the Espanola Formation from the Neoproterozoic cap carbonates which are interpreted by some (Hoffman et al., 1998; Hoffman, 2011) to have formed rapidly during post-glacial sea level rise that precluded the introduction of siliciclastic materials. There are few modern, complete analyses of rocks of the Espanola Formation but Young (1973b) published some microprobe analyses, showing that the dolomites of the upper part of the Espanola Formation are iron-rich. As part of a regional investigation of the geochemistry of Huronian sedimentary rocks, McLennan (1977) analysed several samples of the Espanola Formation. Some of these results were reported in a subsequent publication (McLennan et al., 1979). In the course of a detailed geochemical study of the overlying sandstone-dominated Serpent Formation Fedo et al. (1997) analysed some carbonate-bearing mudstones that resemble those of the underlying Espanola Formation. In a preliminary attempt to test the comparison between these rocks and Neoproterozoic cap carbonates, some of these geochemical results are re-examined.

As noted by Young (1973b) dolostones of the upper member of the Espanola Formation in the northern part of the Huronian outcrop belt are Fe-rich. This is confirmed by calculating an enrichment factor relative to PAAS (Fig. 7a), using the technique of Font et al. (2006) on the analyses of McLennan (1977). Fig. 7b shows a strong enrichment in Mn in the same member. On the other hand, Na shows strongest enrichment in the lower (limestone) member (Fig. 7c). The upper member of the Espanola Formation is also enriched in Y (Fig. 7d), as are some mudstones of the Serpent Formation. Local development of metamorphic scapolite in the lower part of the Espanola Formation was probably derived from evaporitic minerals (NaCl?).

Rare earth elements (REE) in the Espanola Formation generally show a somewhat flat pattern, resembling PAAS (McLennan et al., 1979) but leachate from a dolomite-rich sample shows hydrothermal influence in the form of strong depletion in LREE. Carbonate-rich samples from the Serpent Formation (Fedo et al., 1997) are also depleted in LREE and have positive Eu and Y anomalies, all characteristic of hydrothermally influenced waters.

Neoproterozoic cap carbonates and the Paleoproterozoic Espanola Formation overlie glaciogenic diamictites and have –ve $\delta^{13}C$ values (Veizer et al., 1992; Bekker et al., 2005). They are commonly enriched in redox-sensitive elements such as Fe and Mn, are depleted in LREE and have positive Eu and Y anomalies – all hydrothermal characteristics. Unlike Neoproterozoic cap carbonates, the Espanola Formation is only locally developed. The Espanola

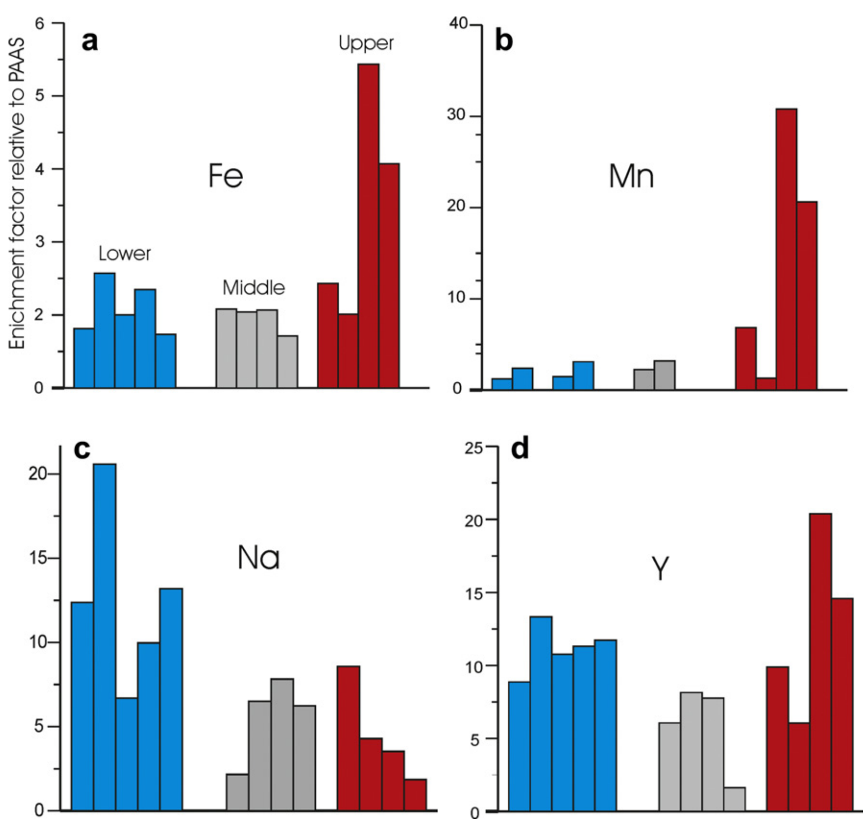

Figure 7. Bar charts showing enrichment factors (relative to PAAS) for some major and trace elements in three members of the Espanola Formation in the Elliot Lake area. a: Fe shows strongest enrichment in the upper (dolomitic) member; b: Mn shows a striking enrichment in the upper member; c: the greatest enrichment in Na is present in the lower (limestone-rich) member; d: Y is most strongly enriched in the upper member. See text for discussion.

Formation is much thicker and has a much higher terrigenous content. Only the upper part is dolomitic, and it is best developed on what has been interpreted as a rift shoulder (Fig. 6). Cap carbonates are dominantly dolomitic. Thus many characteristics of the Espanola Formation differ from those of classical cap carbonates (e.g. Hoffman, 2011) but both offer geochemical evidence of hydrothermal activity.

Hydrothermal influence is most commonly associated with mid-ocean ridges, and such activity probably provides the most plausible explanation for Neoproterozoic cap carbonates (Huang et al., 2011, and references therein). But similar geochemical characteristics are found in some alkaline lakes associated with rift basins (Burke, 1975). The Espanola Formation appears to have been more strongly influenced by local tectonic events (rifting) than by dramatic palaeoclimatic changes. The following section describes some aspects of events at the end of the Gowganda glaciations.

6.2. Mn-rich mudstones

Because the Gowganda Formation is widely accepted to be glaciogenic, there is a tendency for the whole formation to be considered in that light. There is, however, no physical evidence of glacial influence in the upper half of the formation which consists mainly of deltaic deposits. In northerly areas the upper part of the Gowganda Formation is made up of interbedded conglomerates, sandstones and mudstones, or a single coarsening upward cycle (Rainbird and Donaldson, 1988). Thus any consideration of the post-glacial history of the Gowganda Formation in the southern part of the outcrop belt should begin about 500 m below the top of the formation. In the northeastern part of the Huronian outcrop belt it was proposed that the Gowganda Formation should be considered as two separate units that were designated the Coleman and Firstbrook formations (Thomson, 1957), the former containing many glaciogenic diamictites and the latter being mainly fine grained siliciclastic material resulting from progradation of a post-glacial delta system (Rainbird and Donaldson, 1988). A similar two-fold division is appropriate in more southerly regions where they have simply been called lower and upper Gowganda Formation. Recently Sekine et al. (2011) carried out a geochemical investigation of the deltaic deposits of the Firstbrook Formation, reporting enrichment of the basal part in Mn, which they interpreted to indicate the presence of oxygen in the atmosphere at the end of the Gowganda glaciation. The post-glacial part of the Gowganda Formation has a more complex stratigraphy in the southern part of the Huronian outcrop belt, for in the Whitefish Falls area (Junnila and Young, 1995) it consists of several coarsening upward deltaic sequences, as opposed to the single one reported from the Firstbrook Formation in the north. As a follow-up to the study by Sekine et al. (2011) the next section briefly discusses some aspects of the geochemistry of the Gowganda Formation in the Whitefish Falls area.

A fairly comprehensive study of the geochemistry of the Gowganda Formation was published by Young and Nesbitt (1999) and this brief discussion draws on data used for that more wide-ranging account. In the southern part of the Huronian outcrop belt the stratigraphy of the Gowganda Formation is complex, with several diamictite units separated by argillites, sandstones and conglomerates (Fig. 5). Calculation of enrichment factors relative to PAAS, reveals that Mn enrichment is greatest in argillites of the first deltaic unit above the last extensive diamictites. In addition, analyses from a series of samples through the first coarsening upward succession reveal that the most Mn-enriched sample is from near the base (Fig. 8a). The same sample is also somewhat enriched in Fe (Fig. 8b). Enrichment factors using average trace element values from various stratigraphic units in the Gowganda Formation reveal that the strongest enrichments in various "heavy metals", such as Cu, Zn and Cr also occur in the first deltaic unit (Fig. 9). These geochemical characteristics are typical of what has been described from cap carbonates in several localities (Font et al., 2006; Huang et al., 2011; Meyer et al., 2012) and suggest that transgression at the end of the Gowganda glaciation brought Fe- and Mn-rich waters into an oxidizing environment, where they were precipitated, together with heavy metals. In both the northeastern area of the Gowganda Formation (Sekine et al., 2011) and in the southern part, Mn-enriched mudstones follow closely on deposition of the last extensive diamictite. These are the first post-glacial sediments laid down in the transgressing sea, which was subsequently overwhelmed by the advance of a fluvial braid plain and a thick deltaic apron (Rainbird and Donaldson, 1988; Junnila and Young, 1995).

If the Paleoproterozoic glaciations involved a snowball Earth, as suggested by Kirschvink et al. (2000), then extreme weathering conditions should have closely followed the last glacial retreat, which is supposed to have been caused by the buildup of atmospheric CO_2 when weathering was inhibited by global ice cover. Geochemical data from the post-glacial deltaic deposits in the upper Gowganda Formation, however, point to a gradual increase in

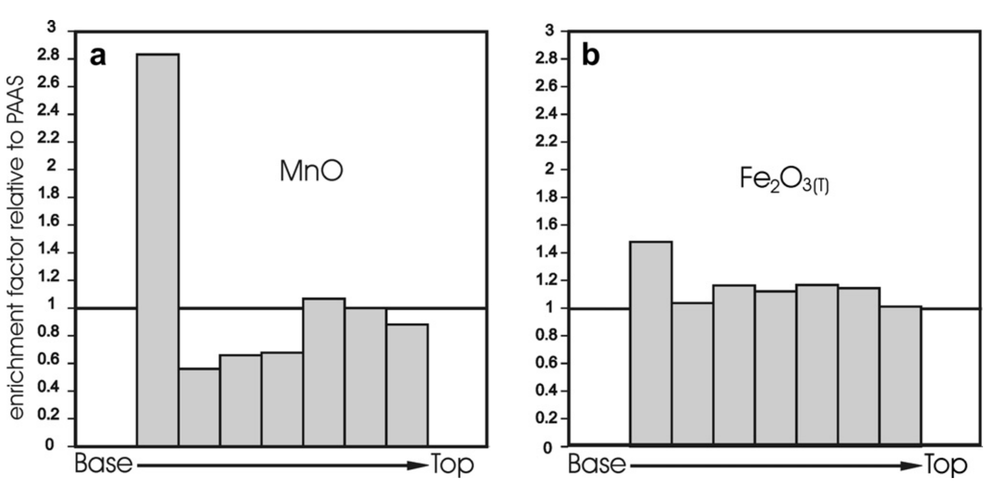

Figure 8. Enrichment factors relative to PAAS for Mn and Fe in fine grained rocks of the first deltaic unit of the Gowganda Formation in the southern part of the Huronian outcrop belt. Note enrichment in Mn and Fe in the lowest samples. Similar enrichment in Mn was noted by Sekine et al. (2011) in the upper part of the Gowganda Formation in the northeastern part of the Huronian outcrop belt (Cobalt area of Fig. 6).

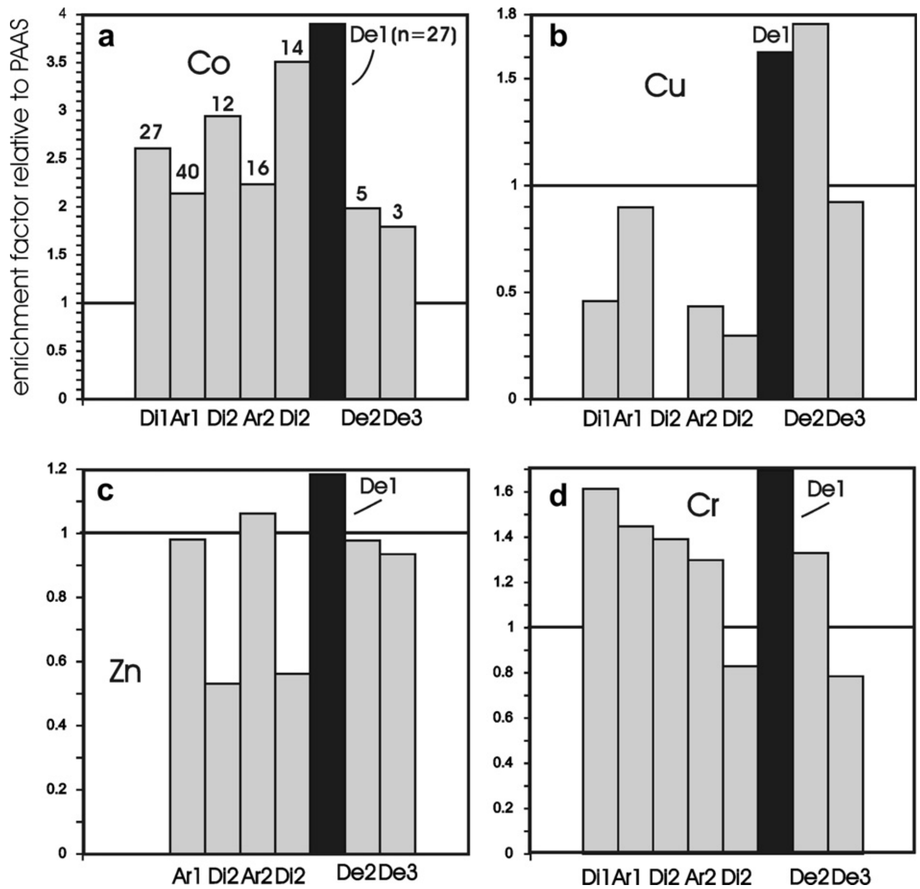

Figure 9. Enrichment factors relative to PAAS for some heavy metals in various subdivisions of the Gowganda Formation in the southern part of the Huronian outcrop belt. Abbreviations at the base of columns are as follows: Di = diamictite, Ar = argillite, De = deltaic unit, as shown on column b of Fig. 5. The values represent the average composition of each unit. The number of analyses represented by each column is shown in part a of the diagram. Note that the first deltaic unit (De1) has high enrichment values.

weathering intensity (increasing CIA values) following deposition of the last diamictites (Young and Nesbitt, 1999; Fig. 6). In addition, analyses of arkosic sandstones in the lower part of the overlying Lorrain Formation (Fig. 5) show that weathering remained relatively moderate until about 1 km above the base (Fig. 10). Thus after deposition of the last extensive glaciogenic sediments, about 1500 m of sediments were laid down before there is chemical and mineralogical evidence of strong weathering. These results are more in keeping with gradual emergence from a more moderate glaciation than that postulated by proponents of a Paleoproterozoic snowball Earth.

7. The Shunga Event and the Vredefort impact

The Shunga Event (Fig. 1) is named from the village of Shunga in NW Russia, where very extensive and thick deposits of carbonaceous material occur in Paleoproterozoic rocks (Melezhik et al., 1999). These unusual rocks are both bedding-parallel and "intrusive" and are thought to have formed, in part, by petrifaction of ancient petroleum deposits (Melezhik et al., 1999). Their C-isotopic signature is taken to indicate an organic origin. The occurrence of similar deposits in various parts of the world (Melezhik et al., 1999) led to its designation as the Shunga Event, although it has no satisfactory explanation (Medvedev et al., 2009). The age of the Shunga Event is placed at about 2.0 Ga. The massive deposit (the type area alone preserves up to 25×10^{10} tonnes of organic carbon in an area of about 9000 km^2) may represent a global extinction event, here suggested to be related to the Vredefort impact (see Moser et al., 2011, and references

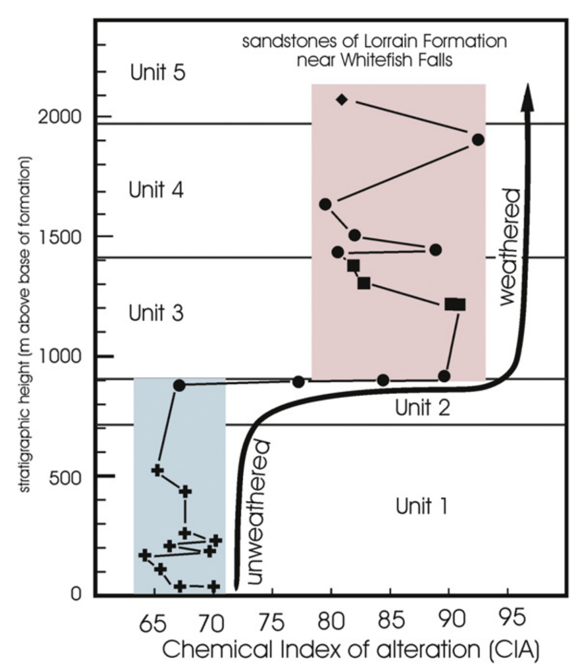

Figure 10. Values for a Chemical Index of Alteration (Nesbitt and Young, 1982) for sandstones from the Lorrain Formation, which overlies the Gowganda Formation (north of Whitedich Falls (Fig. 6)). CIA values remain relatively low for almost 1000 m above the top of the Gowganda, indicating that there was relatively little evidence of weathering immediately after the Gowganda glaciations. See text for discussion.

therein) in South Africa – the largest and oldest confirmed terrestrial impact crater (diameter estimated at ~300 km; age 2023 ± 4 Ma). In south Greenland, on the foreland of the Paleoproterozoic Ketilidian orogen (2130–1848 Ma), Chadwick et al. (2001) discovered sand-sized silicate spherules which they tentatively attributed to the Vredefort impact. Fullerenes have been reported from deposits of the Shunga Event (Buseck et al., 1992), and from those related to the younger (1850 Ma) Sudbury impact (Mossman et al., 2003). Although the significance and even the origin of this unusual form of carbon are not fully understood, its common association with impact events is circumstantial evidence favouring a similar interpretation for the Sudbury and Shunga carbonaceous deposits. The Shunga Event is here interpreted as a major organic extinction, comparable to, but much more severe than, the K-T event. The organic blooms associated with the Great Oxidation Event were abruptly terminated in the aftermath of the Vredefort impact.

The Sudbury impact at about 1850 Ma, excavated a ~250 km-wide crater, and shed debris at least 1000 km to the west (Cannon et al., 2010). The post-impact sedimentary rocks include carbonaceous mudstones and some anthraxolite deposits – possibly representing a second extinction event. Although deposits of shungite, largely consisting of bituminous material thought to be of organic origin (see Melezhik et al., 1999 for history of discovery and definitions) are known from a number of sites around the world, it is interesting that rocks spanning the interval of the Shunga Event are unknown from a large area of North America, where there is a widely developed but unexplained stratigraphic gap – the Great Stratigraphic Gap of Fig. 6. The gap commonly spans the interval separating deposits of rift and passive margin affinity from those of an overlying foreland basin; for example that separating the Huronian Supergroup (~2.44–2.22 Ga) from the Whitewater Group and correlatives to the west (<1.85 Ga). The Sudbury basin, which is considered to be a remnant of the much larger 1.85 Ga Sudbury impact crater (Fig. 6), contains carbon-rich deposits in the form of the Black Onaping and the basal part of the Onwatin Formation, and similar deposits are widespread in areas to the west (Cannon et al., 2010; Fig. 11). Thus it appears that carbon-rich deposits, here attributed to extinction events caused by large impacts, may have a better chance of preservation in areas in the vicinity of the impact than they do in some distant regions. The absence, in large areas of North America, of rocks of comparable age to that of the Shunga Event (the Great Stratigraphic Gap of Fig. 11) may be an antipodal(?) tectonic effect of the huge Vredefort impact, as has been suggested for Mercury, Mars, the Moon and many icy satellites of planets in the solar system (Schultz and Gault, 1975; Watts et al., 1991). According to Gray Hughes et al. (1977) large, basin-forming impacts may cause antipodal vertical ground motions on the order of kilometres. In the Hurwitz basin on the west side of Hudson Bay Aspler et al. (2001) noted a large stratigraphic gap between about 2.1 and 1.9 Ga (without structural discordance) and attributed it to a long period when there was no subsidence. The rocks of the Huronian Supergroup (2.45–2.2 Ga) exhibit a similar long post-depositional hiatus and were not tectonically deformed until the Penokean orogeny at about 1.87 Ga, prior to the Sudbury impact at 1.85 Ga and deposition of the Whitewater Group (Fig. 11). The Vredefort impact occurred at 2.02 Ga, which falls within the lengthy hiatus in the Paleoproterozoic successions in many parts of the Canadian shield. In the absence of accurate continental reconstructions for Paleoproterozoic times such suggestions to explain the Great Stratigraphic Gap are no more than speculations but they are put forward to encourage efforts to obtain more accurate reconstructions of ancient continental masses. It is interesting that carbonaceous deposits associated with the 1.85 Ga Sudbury impact are present in the remnants of the impact site (Sudbury Basin) and up to ~1000 km to the west. In the Sudbury Basin these are fortuitously preserved in a large downfold, whereas the Vredefort impact site has undergone 8–10 km of erosion (Moser et al., 2011) so that any similar deposits would have been lost.

Around the world there followed a long period, between about 1.8 Ga and 800 Ma, sometimes called "the barren billion", that lacks evidence of carbon isotopic excursions (Fig. 1) or glaciations, with the possible exception of sub-glacial meltwater channels and glaciofluvial deposits (ca. 1.8 Ga) described by Williams (2005) from Western Australia.

8. Possible causes of the great Proterozoic glaciations

Why were there two great Proterozoic glacial episodes when there were other supercontinents, such as Columbia or Nuna (Mohanty, 2012; Figs. 1 and 2) which lack such deposits? In Fig. 4 the Proterozoic glacial episodes are shown in the context of the supercontinental cycle but two other critical climatic influences are also shown in Fig. 2 – solar luminosity (increasing with time) and mantle temperatures (decreasing), the latter placing an important control on gaseous emanations related to volcanic activity at oceanic spreading centres and elsewhere. Glacial conditions were introduced only when surface temperatures remained low enough for extended periods of time (including summers) to allow thick accumulations of snow and ice. Because Paleoproterozoic mantle temperatures were probably higher than at present, the Huronian glaciations are thought to have resulted mainly from the combined effects of supercontinentality and weak solar radiation – the "faint young sun". The Neoproterozoic glaciations, on the other hand, took place about 1.4 Ga later, when solar radiation was somewhat greater, so that the diminishing CO_2 content of the atmosphere (due to drawdown by weathering, and cooling of the Earth's interior), together with amalgamation of the great supercontinent, Rodinia, are thought to have led to the climatic upheavals that affected the planet between about 800 and 500 Ma. In spite of amalgamation of the supercontinent Columbia, the great intervening time span of the "barren billion" (Figs. 1 and 2), shows little evidence of significant climatic change or anomalous $\delta^{13}C_{carb}$ values comparable to those at the beginning and end of the Proterozoic. It is suggested (Fig. 2) that throughout most of this long period a balance was maintained among weathering intensity, solar luminosity and mantle temperatures such that, in spite of emergence of a supercontinent, there were no dramatic changes in climate or biological productivity. The Neoproterozoic cycle of extreme climates was terminated when Rodinia began to break apart and a second global oxidation event (the NOE of Och and Shields-Zhou, 2011) occurred in response to proliferation of photosynthetic micro-organisms in the wake of the ice ages. The equable climate of the Cambrian resulted from rising seas that flooded continental shelves, greatly diminishing areas available for subaerial weathering, and increased CO_2 production at newly-forming mid-ocean ridges. It was under such conditions that the Ediacaran fauna appeared and was quickly supplanted by an unprecedented proliferation of metazoan life forms which went on to occupy virtually every niche on and near the surface of the Earth.

Glaciation continued sporadically throughout Phanerozoic time but the Earth appears to have adopted a new climatic pattern, lacking the extreme oscillations of the Proterozoic. The younger continental glaciations were much less extensive and mainly formed at high latitudes. The reasons for this change are not fully understood but the absence of an equator-straddling supercontinent, together with increased solar luminosity may have precluded a return to the dramatic climatic oscillations that marked the beginning and end of the Proterozoic.

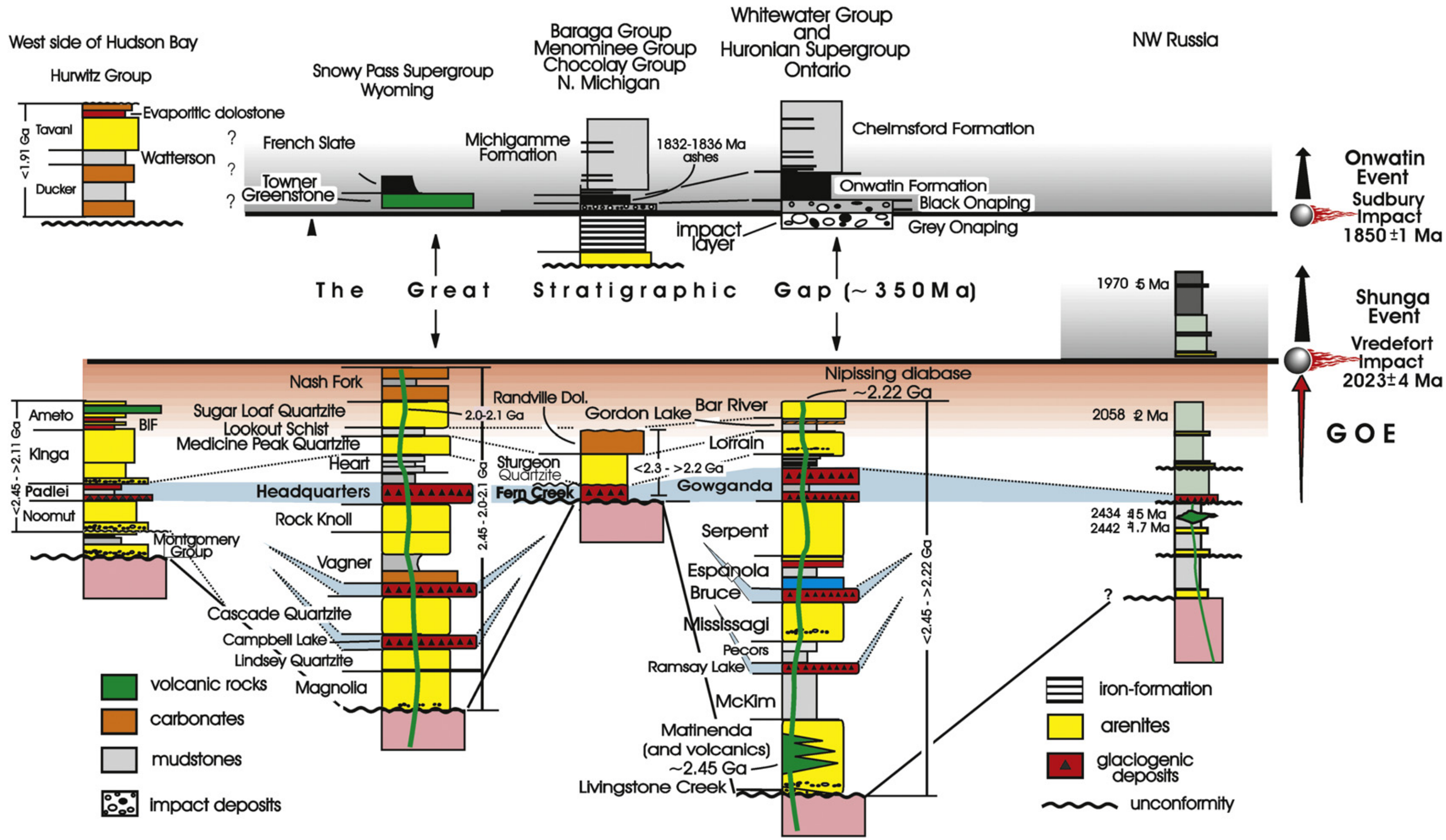

Figure 11. Stratigraphic columns showing Paleoproterozoic successions for a large area stretching from the west side of Hudson Bay to NW Russia. Note the local nature of the first two Huronian glaciations in contrast to the widespread Gowganda Formation and correlatives. The Great Oxidation Event (GOE) was cut short by the Vredefort impact in South Africa, which is considered to be responsible for the Shunga Event, interpreted as a world-wide extinction. A second, slightly smaller impact and succeeding extinction event occurred at 1850 Ga in the Sudbury area of Canada. In many parts of North America there is a very widely developed and long, poorly understood hiatus (up to 350 Ma) that falls into the time period following the Vredefort event (the Great Stratigraphic Gap). The column for NW Russia is based on Melezhik et al. (2010); that from the Hurwitz Group is after Aspler et al. (2001) and the others from Young (2004).

9. Conclusions

Twice during Earth history there was a complex interplay of plate tectonics, greenhouse gases (especially CO_2) and solar radiation that produced a “perfect climatic storm”, resulting in multiple severe glaciations, with intervening warm periods during which increased delivery of elements essential to cyanobacterial metabolism brought about oxygenation of the atmosphere. These events were predicated on orogenic assembly of a large supercontinent at low paleolatitudes, of appropriate size to effect drawdown of sufficient atmospheric CO_2 (by weathering) to initiate glaciation. Because weathering was then inhibited by low temperatures and ice cover, an important negative feedback loop came into play, locking the planet into a long (~ 300 Ma) period of alternating frigid and warm climates. Liberation from the climatic loop was only achieved after fragmentation of the supercontinent, when shallow seas flooded continental interiors, moderating surficial weathering and, together with greenhouse gases released by increased magmatic activity at new ocean ridges, prevented a return to glacial conditions. As the extreme climatic oscillations of the Neoproterozoic drew to a close, flooded continental shelves around the dispersing remnants of the former Rodinia, were colonized by evolving organisms, leading to a metazoan “explosion” in the Cambrian period.

Cap carbonates that overlie Neoproterozoic glacial deposits in many parts of the world are thought to reflect overturn of the deep ocean, following flushing of world oceans with massive amounts of dense, cold, saline melt waters. Carbonates of the Paleoproterozoic (Huronian) Espanola Formation which overlie glacial deposits of the Bruce Formation share some characteristics with Neoproterozoic cap carbonates but their distribution and field character, together with preliminary geochemical data, suggest that they may have formed in a hydrothermally influenced restricted environment associated with rifting of the Huronian Basin. Thus there may have been a reversal of processes between Paleo- and Neoproterozoic times, so that the genesis of Neoproterozoic iron-formations may be more akin to that of Paleoproterozoic carbonates, like the Espanola Formation – both forming in rift-related hydrothermally influenced basins. On the other hand widespread Neoproterozoic cap carbonates may have formed under conditions similar to those that produced Mn- and Fe-rich mudstones, following recession of the Gowganda glaciers – the overturn of deep oceanic waters in response to release of melt waters on a huge scale. More chemical data are needed, especially from Paleoproterozoic rocks, to test these speculations.

The fact that a perfect combination of tectonic processes, solar luminosity and atmospheric composition occurred twice in geological history, each causing alternating icehouse and greenhouse conditions over an extended period of time, raises the intriguing possibility that advanced metazoan evolution could have taken place following the Paleoproterozoic glaciations and the ensuing Great Oxygenation Event. Did two great impacts – the massive Vredefort impact in South Africa at ~2023 Ma and the slightly smaller impact event near Sudbury, Ontario at ~1850 Ma – cause global mass extinctions, each leaving behind a “ smoking gun” in the form of the thick carbon-rich deposits of the Shunga and Onwatin events? Metazoan proliferation and evolution may have been delayed for about 1700 Ma and the course of the ensuing two billion years of Earth history changed by two split-second impacts.

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