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ORIGINAL ARTICLE

A Review of the Neoproterozoic Global Glaciations and a Biotic Cause of Them

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Abstract
In the Neoproterozoic Era, the Earth experienced two broad intervals of global glaciation, commonly known as Snowball Earth. There was also a rapid diversification of life, with the evolution of most of the eukaryotic lineages. Here, salient evidence for the Neoproterozoic global glaciations, including the carbon isotope record, is reinterpreted, and an alternative explanation for the causes of glaciation is proposed. The proliferation of life could have led to increases in atmospheric O_2 levels and concomitant decreases in CO_2 and CH_4. Coupled biochemical and geochemical changes would have led to global cooling and glaciation. This so-called biotic hypothesis of the Snowball Earth is consistent with the most salient features of the reported evidence and explains the consecutive episodes of global glaciation.

Keywords Snowball Earth · Oxygenic photosynthesis · Neoproterozoic glaciation · Atmospheric gases · Co-evolution of Earth and life

1 Introduction

The ‘Snowball Earth’ hypothesis claims that several global glaciations occurred during the history of our planet and provides a geochemical explanation for how these glaciations ended (Kirschvink 1992; Hoffman et al. 1998; Sohl et al. 1999). This subject has been controversial to the point that several authors have questioned the mere existence of such overall glaciations (Kennedy et al. 2001; Leather et al. 2002; Jiang et al. 2003; Eyles and Januszczak 2004; Fairchild and Kennedy 2007; Chumakov 2008), but the hypothesis has gained acceptance among the scientific community as evidence accumulates.

The first reports of geological evidence for low-latitude glaciation are dated more than 60 years ago (e.g., Harland and Bidgood 1959; Harland 1964). However, the first paleomagnetic evidence (Harland and Bidgood 1959) did not meet today's standards of reliability (Evans 2000).

The first related energy-balance models are due to Budyko (1969), who used a simple model to investigate the effect of ice cover on the global climate. He concluded that if ice sheets reach latitudes beyond ca. 50°, the increased ice-albedo would cause a feedback loop that would lead to the entire planet surface becoming frozen. Subsequently, Faegre (1972) developed a more sophisticated global climate model, which had five solutions. Four of them (including a solution close to our present climate) were unstable to small perturbations. The only stable situation was an ice-covered Earth. Simple energy-balance models rely on radiation and ice-albedo feedback but not on atmospheric composition, which is almost certainly a critical factor in the onset of -and escape from- global glaciation. Nevertheless, the positive ice-albedo feedback also results in global glaciations in much more sophisticated climate simulations that include the atmospheric levels of greenhouse gases (e.g.,Liu et al. 2013; Feulner and Kienert 2014).

Walker et al. (1981) proposed a negative feedback mechanism based on silicate weathering, capable of preventing the so-called ice catastrophe predicted by earlier global climate models. Chemical weathering removes CO_2 from the atmosphere, as exemplified by the reaction of CO_2 dissolved in rainwater with forsterite (Urey 1951):

$$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightleftharpoons 2Mg^{2+} + 4HCO_3^- + H_4SiO_4 \quad (1)$$

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The so-formed bicarbonate is washed into the oceans, where combines with Ca^{2+} and Mg^{2+} to produce carbonate sediments. If the temperature drops, silicate weathering rates will decrease, and CO_2 should accumulate in the atmosphere. The climate forcing of this greenhouse gas would heat the planet again and, ultimately, allow the long term stabilization of Earth's surface temperature.

Eventually, Kirschvink (1992) speculated that a predominance of continents in low latitudes could produce a Snowball Earth due to the higher albedo of continents versus oceans. Global glaciation would lead to the shutdown of chemical weathering, permitting the build-up of volcanic CO_2. Kirschvink (1992) also described how the Earth could escape from a snowball event: the greenhouse effect produced by this long-term accumulation of CO_2 in the atmosphere. Later, Hoffman et al. (1998) developed the hypothesis of Kirschvink (1992) and connected it with carbonate deposition.

Two widespread glacial episodes are customarily recognized in the Neoproterozoic Era: the Sturtian glaciation (717–659 Ma; Rooney et al. 2015) and the Marinoan glaciation (ca. 640–635 Ma; Halverson et al. 2004; Rooney et al. 2015; Crockford et al. 2017; Xing et al. 2018). This major glaciations define the Cryogenian period. Reliable evidence of the glaciations includes globally distributed glacial sediments of diamictites and dropstones at ~ 0.7 Ga (Kirschvink 1992; Hoffman and Schrag 2002; Holland 2006), accompanied with banded iron formations (BIFs, Fig. 1). Fe-enriched cap carbonates were deposited at 0.63 Ga (Hurtgen et al. 2006) immediately after the Marinoan glaciation. Cap carbonate sequences are also found after the Sturtian glaciation (Hoffman and Schrag 2002). Large positive isotopic excursions of ^{34}S found in cap carbonates deposited upon the glacial sediments are consistent with global glaciations (Gorjan et al. 2000; Hurtgen et al. 2002). Thus, thick deposits of cap carbonates are unambiguously related to these glaciations and are thought to be formed by postglacial enhanced weathering by a CO_2 enriched atmosphere (Hoffman et al. 2011). Consistent paleomagnetic data from several continents confirm that ice reached near-equatorial latitudes (Chumakov and Elston 1989; Williams et al. 1995; Sohl et al. 1999; Evans 2003; Macdonald et al. 2010). The durations of these glacial episodes, which lasted for several million years, have been estimated from iridium anomalies and radiometric dates (Bodiselitsch et al. 2005; Macdonald et al. 2010; Rooney et al. 2015; Crockford et al. 2017).

There is extensive evidence for an increase in environmental oxygenation to levels > 10% of present atmospheric level (PAL) roughly at the time of the Neoproterozoic glaciations (Des Marais et al. 1992; Logan et al. 1995; Canfield and Teske 1996; Canfield 1998, 2005; Walter et al. 2000; Holland 2006; Shields-Zhou and Och 2011; Och and Shields-Zhou 2012; Pufahl and Hiatt 2012; Partin et al. 2013; Lyons et al. 2014; Mills et al. 2014; Blamey et al. 2016; Turner and Bekker 2016; Kunzmann et al. 2017). The temporal coincidence of this second oxygenation event (Fig. 2) and the Neoproterozoic Snowball Earth suggests that both events could share a common cause (Walker 2007). On the other hand, Lenton et al. (2014) pointed out that if an increase in continental weathering caused CO_2 drawdown and cooling into the Cryogenian glaciations, this need not have caused a rise in atmospheric oxygen. Nonetheless, such coincidence could also indicate that one of them caused the other. Besides, global glaciations occurred amid important biological innovations (Fig. 2). All these coincidences seem not to be merely fortuitous (Sahoo et al. 2012) but suggest a connection between snowball episodes, oxygen levels and

Fig. 1 Dolomite dropstone embedded in BIF of the Sayunei Formation (Rapitan Group) in the Mackenzie Mountains, Canada; photo by G. A. Gross

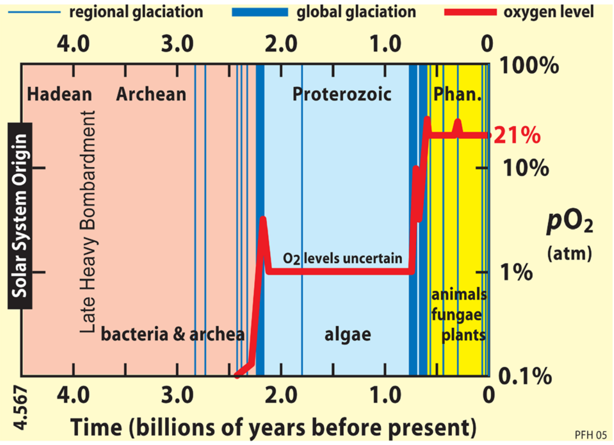


Fig. 2 Schematic approximation of atmospheric oxygen levels through time. Increases in oxygen concentration coincide with global glaciations and biological innovations; by P. F. Hoffman (SnowballEarth.org; retrieved September 2021)

biological activity. Such a scenario would imply significant interactions between the biosphere and the inorganic realms of the Earth.

This work reexamines relevant literature on the Neoproterozoic Era and Snowball Earth. The emerging picture suggests an alternative hypothesis for the prime causes of global glaciations that agrees with the ensemble of established data and allows explaining consecutive snowball events.

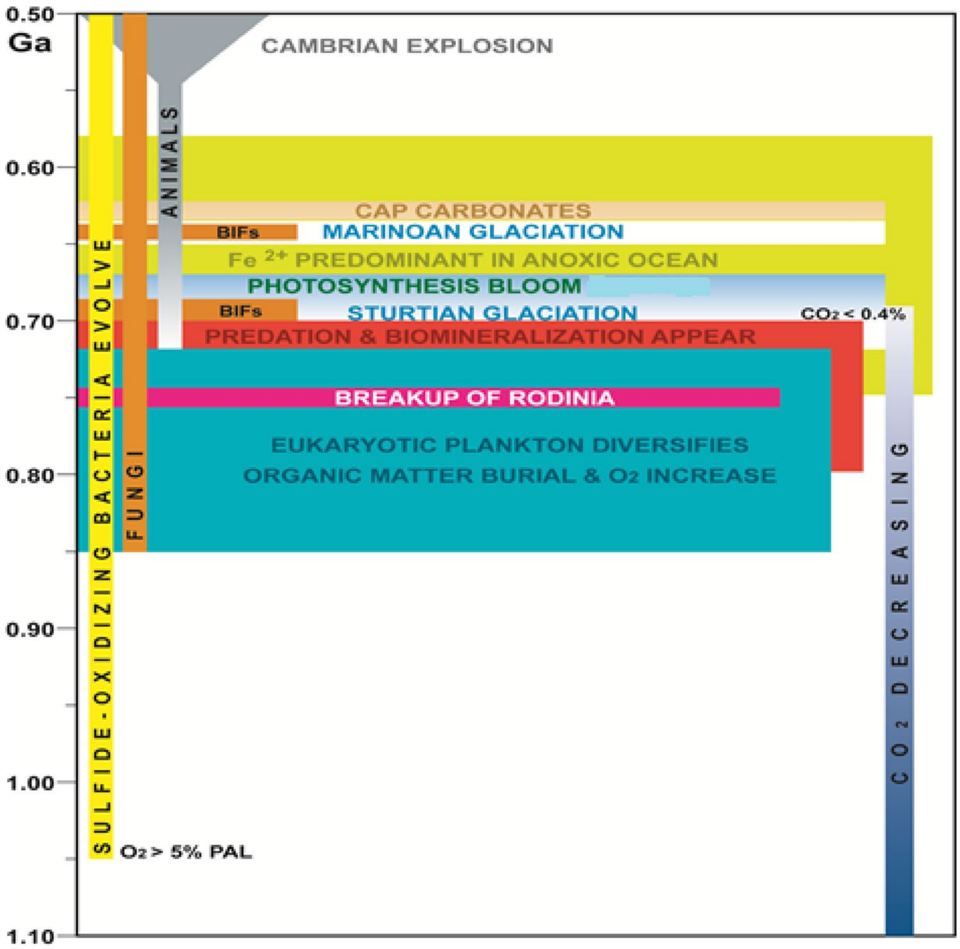
2 Some Controversies on the Neoproterozoic Global Glaciations

The fundamental question in the case of the Neoproterozoic glaciations is: Why were these events so severe that ice extended to near the equator? It has been estimated that solar radiation was 6% lower in the Neoproterozoic than today (Pierrehumbert 2002). Besides, the effect of decreased solar luminosity on the ice extent has been modelled (Crowley and Baum 1993). However, a fainter Sun cannot, by itself, explain global glaciations because luminosity was even lower during earlier periods when no glaciation is recorded (Eyles and Januszczak 2004).

2.1 The Rodinia Rifting and the Weathering Hypothesis

The supercontinent Rodinia rifting occurred approximately at 0.74–0.78 Ga (Figs. 3, 4). This event is commonly cited as a cause of the Sturtian glaciation through unusually high chemical weathering of rift-related magmatic provinces (e.g., Goddéris et al. 2003). One key reason why Rodinia break-up causes such enhanced chemical weathering in models is increased terrestrial rainfall and consequent runoff. Rainfall is generally higher at low latitudes due to rising air in the intertropical convergence zone and increased evaporation related to higher temperatures. The rifting of Rodinia presumably led to CO_2 sequestration due to increased continental weathering of uplifted rift shoulders (Schermerhorn 1983), collisional orogenic belts (Eyles and Januszczak 2004) and new continental margins (Hoffman and Schrag 2002). Faster CO_2 depletion would lead to climate cooling and glaciations. Therefore, this is among the main factors

Fig. 3 Schematic chronology of some significant events discussed in the text



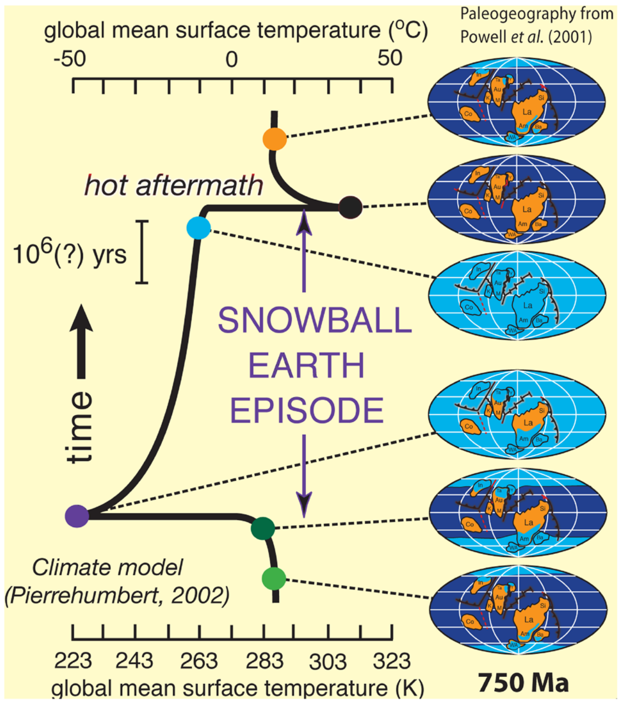


Fig. 4 Evolution of global mean surface temperature in the different phases of a snowball Earth model. Adapted from Hoffman and Schrag (2002)

inferred to have contributed to major Cryogenian glaciations (Walter et al. 2000; Hoffman and Schrag 2002).

Tziperman et al. (2011) argued that if these tectonic arguments are valid, they imply that the Earth should fall into another snowball event shortly after the end of the previous one, given that continental drift is slow (Fig. 4) relative to the carbon cycle feedbacks triggered. However, Mills et al. (2011) concluded that the long gaps (ca. 10^7 years) between global glaciations are explained by weathering rates limited by available silicate. It seems a paradox that silicate weathering can both promote and hinder global glaciations. On one hand, accelerated weathering rates should effectively decrease CO_2 and, therefore, surface temperature. On the other hand, this effect should be compensated by a slower weathering as Earth's surface cools (Walker et al. 1981). Silicate-weathering feedback should prevent the snowball from occurring unless the forcing is applied in less than a few million years, but so fast forcing appears especially difficult in the low-rate silicate weathering scenario of Mills et al. (2011). Furthermore, a silicate-weathering hypothesis for global glaciations works only if the climate was already cold before the onset of weathering (Goddéris et al. 2003). On the other hand, for theories concerning increased weathering following the breakup of Rodinia, there could still be significant weathering in the (relatively warm) tropics in a globally cool climate.

The climate system could suffer short-term perturbations, e.g., by enhanced volcanism, in addition to the long-term cooling trend. In this respect, the possibility of CO_2 sequestration related to the weathering of large igneous provinces (LIP) has been discussed (Goddéris et al. 2003; Rooney et al. 2014; Cox et al. 2016a, b). Cox et al. (2016a; b) propose that elevated rates of continental flood basalt weathering contributed to the initiation of the Sturtian Snowball Earth. Besides, Macdonald and Wordsworth (2017) argue that LIP volcanism might have triggered the Sturtian glaciations via volcanic sulfur aerosol injection into the stratosphere. Please consider, however, that any increase of volcanism encompasses a correspondingly increased release of CO_2. What is more, McKenzie et al. (2016) suggest that reduced continental arc volcanism and CO_2 outgassing correspond with icehouse climates of the Cryogenian. Thus, the role of volcanism on this subject remains controversial.

Even if the palaeogeography could be appropriate for the weathering hypothesis leading to the Sturtian glaciation (Fig. 4), it was significantly different and less suitable for the subsequent Marinoan event (Goddèris et al. 2003; Li et al. 2008). Moreover, the weathering postulate opens the question: Why global glaciations were avoided at other epochs with a lot of continental land in the tropics, both before and after the Neoproterozoic Snowball Earth (e.g., Laurentia approximately 0.58 Ga; Pierrehumbert et al. 2011)? In sum, the weathering mechanism alone seems insufficient to account for the Snowball Earth events (e.g., Maruyama and Santosh 2008), despite it is generally accepted to have contributed to the depletion of atmospheric CO_2 before extreme glaciations.

2.2 Banded Iron Formations

The deposition of BIFs concomitant with Neoproterozoic glaciations (Ilyin 2009) is commonly accepted to result from the reaction of O_2 and Fe^{2+} in the ocean to form deposits of Fe oxyhydroxides, such as $Fe(OH)_3$ (Klein 2005):

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+. \quad (2)$$

This reaction would proceed in the absence of enough dissolved sulfide to scavenge Fe^{2+} to precipitate FeS_2 as pyrite (Hoffman and Schrag 2002). Direct oxidation of Fe^{2+} by bacteria has also been claimed as an alternative pathway to BIFs (Konhauser et al. 2002). Earlier extensive BIFs were deposited during the Paleoproterozoic (Kirschvink et al. 2000; Hoffman and Schrag 2002). Both BIFs and Fe-enriched cap carbonates (Hurtgen et al. 2006) indicate the presence of dissolved Fe^{2+} in the deep ocean at roughly 0.7 Ga. They are generally interpreted as evidence of previous anoxic conditions due to the lack of ocean circulation below an ice sheet that decoupled the atmosphere and the ocean for millions of years (Kirschvink 1992; Klein and Beukes 1993). Iron could be hydrothermally generated at the mid-ocean ridges or leached from the bottom sediments or margin sediments dominated by basaltic detritus (Cox et al. 2016b). Thus, the Snowball Earth hypothesis accounts for the reappearance of BIFs in the geological record after an interruption of more than 1 billion years.

Enhanced biological productivity and burial of biomass when the Neoproterozoic snowball ice melted could have increased oxygen levels (Kirschvink et al. 2000; Walter et al. 2000; Harada et al. 2015). Then, dissolved Fe^{2+} would oxidize to form BIFs when renewed ocean circulation mixed ferruginous deepwater with oxygen-rich surface water (Derry and Jacobsen 1990; Kirschvink 1992; Hoffman and Schrag 2002). This earliest model of Neoproterozoic BIFs formation has been challenged because it predicts their deposition immediately following a snowball event; however, BIFs can contain dropstones (Fig. 1) and occur within or below, rather than above, certain glacial deposits (Williams and Schmidt 2000). A way to fit these observations into the model is to assume that coastal oases remained oxygenated; the BIFs were presumably deposited in these oases (Pierrehumbert et al. 2011).

The number of diverse hypotheses for the initiation of the Cryogenian ice ages is high, perhaps because none of them is good enough so far. This work does not discuss other models, including astronomical forcing, oceanographic effects, the cooling of the Earth and unusual tectonic approaches (Young 1995; Stern et al. 2013). More exotic explanations for these glaciations, such as true polar wander, geomagnetism, or gamma-ray bursts, have also been published (see the review of Maruyama and Santosh 2008). For instance, the galactic model conjectures that gamma-ray explosions create vast amounts of clouds, which would cut off sun rays and freeze the Earth. Another radical concept explains the true polar wander through a quasi-polar dynamo model: the 'switch-on' and 'switch-off' of the Earth's dynamo can lead to the onset and disappearance of the Snowball Earth. However, none of these models has gained common acceptance.

3 The Evolutionary Scenario

The Cambrian explosion was an important milestone of the evolution of eukaryotes, which began hundreds of millions of years before the first large, complex animal body fossils appeared. The main phase of eukaryotic development took place during the middle Neoproterozoic (Porter 2004; Parfrey et al. 2011; Erwin et al. 2011). Marked by increasing oxygen levels, the Neoproterozoic was a turning point for the evolution of multicellular organisms, involving an extraordinary increase in body size up to fully macroscopic life forms (Payne et al. 2009) and the advent of animals (Fig. 3). Both fossils and genetic mutation rates (or molecular clocks) show evidence of the divergence of major eukaryotic clades in that period and a dramatic increase in their abundance and environmental distribution (Knoll 2003; Porter 2004; Knoll et al. 2006; Parfrey et al. 2011). Molecular clocks studies (Heckman et al. 2001) and fossil evidence (Loron et al. 2019) are consistent with the appearance of fungi at 0.85–0.90 Ga (Fig. 3). Diverse methodologies of molecular clocks agree that the first animal families diverged from their single-celled ancestors by ~ 0.80 Ga, and the bilaterian body plan appeared by ~ 0.65 Ga (Sperling and Stockey 2018). A remarkable diversity of eukaryotic species habited in the oceans that surrounded Rodinia (Shields-Zhou and Och 2011).

The pre-Sturtian fossil record and molecular clock studies show the emergence of red and green algae, amoebozoans and rhizarians. Among them are the first known examples of predation and biomineralization (Porter and Knoll 2000; Bengtson, 2002; Porter 2004; Knoll et al. 2006; Lenton et al. 2014; Feulner et al. 2015; Hoffman et al. 2017; Cohen et al. 2017). In particular, a significant biological turnover before the Sturtian glaciation is associated with the appearance of diverse and abundant protozoan fossils and a shift to rising total organic carbon, suggestive of increased primary productivity (Nagy et al. 2009). During the same period, the number of microfossil genera not assigned to a natural group (acritarchs) also increased (Huntley et al. 2006). However, Brocks et al. (2017) examined the fossil record of eukaryotic steroids and concluded that bacteria were the only notable primary producers in the oceans before the Cryogenian period, while algae rose in the time interval between both global glaciations.

Nevertheless, various protistan morphotypes, including vase-shaped microfossils, are found in nonglacial strata of the Tonian Period (Strauss et al. 2014; Riedman et al. 2018) as well as between Sturtian and Marinoan glaciations (Porter and Knoll 2000; Hoffman et al. 2017). Testate eukaryotes before 635 Ma may have enhanced export and burial fraction of organic carbon, leading to increased atmospheric oxygen (Bosak et al. 2011). There is also evidence of possible sponge fossils in pre-Marinoan limestones (Brain et al. 2012), supporting that O_2 levels had already increased to some extent. Although such fossil evidence for Cryogenian animals is not well accepted so far (Antcliffe et al. 2014), biochemical markers of demosponges appear in strata that underlie the Marinoan cap carbonate, too (Love et al. 2009; Brocks et al. 2016). Moreover, molecular clocks and fossils indicate that many clades of eukaryotic algae and heterotrophs (single-celled and multicellular) evolved within the Cryogenian glacial ocean (Canfield et al. 2008; Hoffman et al. 2017).

4 The Second Oxygenation Event

Sulfate concentrations in seawater were lower than modern concentrations during most of the Proterozoic period, as inferred from isotopic differences between sulfates and sulfides and ^{34}S variations in gypsum and anhydrite (Anbar and Knoll 2002; Pavlov et al. 2003). Low sulfate concentrations indicate low rates of pyrite oxidation and, hence, low levels of O_2. Neoproterozoic BIFs are also evidence of low sulfate levels. At significant sulfate concentration, bacterial sulfate reducers would produce sulfide. Sulfide would then precipitate the dissolved iron as pyrite instead of the observed iron oxides. Therefore, levels of O_2 in the atmosphere, although uncertain, were presumably in the order of 1% PAL before the Neoproterozoic (Kump 2008; Lyons et al. 2014; Planavsky et al. 2018). Iron speciation analyses indicate that the deep ocean was oxygen-depleted during the most time of the Neoproterozoic (Canfield et al. 2008; Stolper and Keller 2018). It was consistently rich in Fe^{2+} (Canfield et al. 2008; Guilbaud et al. 2015). Molybdenum concentrations confirm that deep oceans were anoxic until the late Precambrian (Scott et al. 2008). These and other results on redox-sensitive trace metals, such as vanadium and uranium, show that global ocean ventilation did occur after the second rise of atmospheric oxygen (Fig. 2; Och and Shields-Zhou 2012).

Nevertheless, there is growing evidence of progressive surface oxygenation before the Neoproterozoic snowball onset (e.g.,Von Strandmann et al. 2015; Blamey et al. 2016). Rapid deposition of BIFs at ~ 0.75 Ga, before the Sturtian glaciation, suggest that the Neoproterozoic oxygenation was already in progress (Stern et al. 2013). The geochemical behaviour of Cr is sensitive to the redox state of the surface environment because oxidative weathering processes produce Cr(VI). Oxidation of Cr(III) on land is accompanied by an isotopic fractionation, leading to enrichment of the mobile Cr(VI) in the heavier isotope. BIFs associated with the early Sturtian glaciation show growing $\delta^{53}Cr > 0.49\%$, providing independent support for increased surface oxygenation at that time (Frei et al. 2009). Shales provide evidence for the onset of oxidative Cr cycling at ~ 0.80 Ga (Cole et al. 2016). Uranium enrichment data in organic-rich shales also points to a rise in oxygen levels preceding the glaciation (Fig. 3 in Partin et al. 2013). Around 100 Ma before the Sturtian glaciation, high burial rates of organic matter -forced by increased continental weathering and erosion via runoff of nutrients and sediments (Des Marais et al. 1992; Planavsky et al. 2010)- presumably lead to oxygenation, growth of the seawater sulfate reservoir, and deposition for the first time of thick sulfate evaporites (Turner and Bekker 2016). These works match the epoch of the second oxygenation event and the age of development of eukaryotes (Parfrey et al. 2011; Cole et al. 2016). Increasing $\Delta^{34}S$ values exceeded the range achieved by sulfate reduction between 0.80 and 0.70 Ga (Canfield and Teske 1996; Lyons et al. 2014). Canfield and Teske (1996) propose that such a shift in the isotopic composition of sulfides between 1.05 and 0.64 Ga was contemporaneous with the evolution of sulfide-oxidizing bacteria. The sulfur isotopic shift and the apparition of sulfide-oxidizing bacteria could be due to a rise in atmospheric oxygen concentrations to > 5% of PAL (Fig. 3). However, Kunzmann et al. (2017) suggest that sulfide-oxidizing metabolism became globally significant from an ecological point of view after the Marinoan glaciation.

Substantial oxygen levels (up to 40% of PAL; Canfield 1998, 2005; Sperling et al. 2015) both before and after the Cryogenian glaciations could help to explain the existence of dropstones embedded in BIFs (Fig. 1) and other challenging BIFs characteristics (Williams and Schmidt 2000). If the ice had melted in a low oxygen environment, BIFs should appear later, only above dropstones and other glacial deposits (see Hoffman et al. 2011). Moreover, Neoproterozoic BIFs tend to show a high oxidation level, with hematite prevailing over magnetite (Ilyin 2009; Stern et al. 2013), which also suggests substantial oxygen levels. Significant oxygen levels in the Cryogenian are fundamental to the *biotic hypothesis*. So, BIFs with embedded dropstones (Fig. 1) support the new scenario described in the following section.

5 An Alternative Approach: The Biotic Hypothesis

Considering the reviewed evidence on the rise of biomass and oxygen levels before the Cryogenian period, we suggest that one of the main causes of the Neoproterozoic global glaciations was the accumulation of oxygen produced mainly by cyanobacteria and algae. Oxygen consuming processes such as reaction with reduced minerals or ions (e.g., Eq. 2), respiration and biomass oxidation (the reverse of photosynthesis (Smith 1937), Eq. 3):

$$nCO_2 + nH_2O + h\nu \rightarrow C_nH_{2n}O_n + nO_2, \tag{3}$$

oxidation of volcanic gases [e.g., Equation 4 (Goldblatt et al. 2006) and Eq. 5 (Calvert et al. 1978)]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{4}$$

$$2SO_2 + O_2 \rightarrow 2SO_3, \tag{5}$$

or the photochemical production of ozone (Chameides and Walker 1973; Eq. 6):

$$3O_2 + h\nu \rightarrow 2O_3 \tag{6}$$

were unable to counterbalance the high photosynthetic productivity. Even if higher O_2 results in enhanced respiration, creating negative feedback, we suggest that such feedback was insufficient in a scenario where organic matter burial in the sediments was also increasing (Kaufman et al. 1997; Schrag et al. 2002; Knoll 2003; Knoll et al. 2006; Kennedy et al. 2006), as will be detailed below. The increase in oxygen levels led to a decrease in levels of greenhouse gases (predominantly CO_2, but also CH_4), resulting in global cooling.

CO_2 levels decreased because O_2 was the result of photosynthesis (Eq. 3). In general, CO_2 levels in the atmosphere are stabilized by the long-term carbon cycle in a geological timescale, involving exchanges with rocks. However, carbon is rapidly exchanged only between the atmosphere, biota, ocean and soils in the short-term carbon cycle. This cycle can have a severe impact on climate change, as we suffer at present.

CH_4, a greenhouse gas more active than CO_2 on a mol per mol basis, reacted with the rising oxygen (Eq. 4). Albeit the existence of an ozone layer is detrimental to reaction (4), which depends on a photochemical step that produces OH radicals (Goldblatt et al. 2006), CH_4 oxidation in the presence of enough oxygen is fast in geological terms. The lifetime of CH_4 in the modern atmosphere is in the order of only ten years (e.g., Pavlov et al. 2003). Concerning the possible role of CH_4 in the Snowball Earth, Schrag et al. (2002) argued that organic carbon burial could have led to the establishment of an unstable CH_4 greenhouse, the collapse of which could have subsequently triggered an ice age. Conversely, in the biotic hypothesis, the decays in both greenhouse gases, depicted by reactions (3) and (4), were the fundamental causes of a cooler climate and widespread glaciations.

5.1 Related Hypotheses

Although the biotic hypothesis is novel, some ideas reminiscent of it are present in the literature. Pavlov et al. (2003) introduced a model that includes an oxygenation event at the end of the Proterozoic, which would have resulted in a decrease in atmospheric CH_4 sufficient to trigger the Sturtian glaciation. However, this work overestimated the radiative effect of CH_4 (Haqq-Misra et al. 2008). Feulner et al. (2015) proposed that the expansion of eukaryotic algae, which produce a precursor of organic aerosol dimethyl sulfide, raised the emissions of cloud condensation nuclei and may have contributed to the cooling.

Other works (Carver and Vardavas 1994; Lenton and Watson 2004; McMenamin 2004; Tziperman et al. 2011; Le Heron et al. 2013) add credibility to the idea of biologically mediated/enhanced cooling. For instance, Lenton and Watson (2004) suggested that life colonization of the land in the Neoproterozoic involved amplified overall weathering rates. A selective weathering of P would cause a rise in atmospheric O_2, while increased weathering of silicate rocks would cause a decline in CO_2, possibly plunging Earth into a global glaciation. Tziperman et al. (2011) proposed that the main factor was the enhanced export of organic matter from the upper ocean into anoxic deep waters and sediments. There, organic matter undergoes anoxic remineralization via either sulfate- or iron-reducing bacteria. Remineralization can lead to changes in carbonate alkalinity and dissolved inorganic pool. Both changes efficiently lower the atmospheric CO_2 level. Notice that all these concepts, while distinct from the mechanism suggested herein, are compatible with it.

Other hypotheses involving global increases in oxygen levels have also been suggested as drivers of different extensive glaciations, such as the Carboniferous-Permian glaciation (Berner 1998) and the Palaeoproterozoic Snowball Earth (Kopp et al. 2005; Claire et al. 2006; Melezhik 2006).

6 Postglacial Oxygen Levels

Oxygen levels in the atmosphere at the start of a snowball glaciation could persist largely unchanged due to the isolation of the atmosphere from the oceans and land by a global ice sheet and because the hydrological cycle would almost stop. The absence of mass-independent S isotope fractionation ($\delta\,^{33}S \geq 0.3‰$) in Cryogenian sediments is consistent with that scenario (Hoffman et al. 2017). Some O_2 would react with volcanic emissions of reduced gases (e.g., Eq. 5), while some O_2 could be produced presumably after ice melting, due to the decomposition of H_2O_2 previously produced by UV radiation and trapped in the ice (Liang et al. 2006):

$$2H_2O + h\nu \rightarrow H_2O_2 + H_2 \quad (7)$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O. \quad (8)$$

Stepwise increases in atmospheric oxygen (Fig. 2) are explained conventionally via increased primary productivity due to a postglacial nutrient flux to the ocean (Canfield et al. 2007; Planavsky et al. 2010; Sahoo et al. 2012; Laakso and Schrag 2017). For example, Harada et al. (2015) propose that prolonged super-greenhouse conditions and enhanced nutrient input lead to high levels of primary productivity and burial of organic carbon, leading to a sudden (~ 10^4 years) increase in atmospheric O_2. Alternatively, Campbell and Squire (2010) proposed a rapid erosion of Gondwanan 'supermountains' that released a large flux of nutrients into the rivers and oceans. These nutrients triggered an explosion of algae and cyanobacteria that produced a marked increase in the levels of photosynthetic O_2. Concurrently, rapid sedimentation promoted high rates of burial of biogenic pyrite and organic matter. Notice that in this last case, the second oxygenation event, of geo-biologic origin, would be disconnected from both the break-up of Rodinia and global glaciations. Thus, the concurrences depicted in Figs. 2 and 3 as the starting point of the present study would be a mere chance.

Similarly to the increase of oxygen levels just discussed, the advent of notable evolutionary changes—such as the origin and diversification of metazoans—has been attributed to the effects of Cryogenian glaciations via the second oxygenation event (Shields-Zhou and Och 2011; Harada et al. 2015; Hoffman et al. 2017). In opposition, the biotic hypothesis attributes the Cryogenian glaciations to the effects of the evolution of life, as we discuss in the following section.

7 The Role of the Evolution in the Biotic Hypothesis

Even if some eukaryotic clades appeared many millions of years before the onset of global glaciation (Fig. 3), the main factor in the biotic hypothesis is not the moment when they appeared, but the growth of the total biomass with time. We suggest that the size of the carbon reservoir stored as biomass increased significantly in the Tonian Period. Notice that a gradual increase of oxygen along a period of at least 100 million years, inferred from Se isotopes (Von Strandmann et al. 2015), is also consistent with progressive development and proliferation of life. It is noteworthy that, perhaps counter-intuitively, the evolution of animals and fungi also contributed to decrease atmospheric CO_2 levels since virtually all global biomass at any time ultimately comes from CO_2 previously fixed by photosynthesis (Eq. 3). Thus, any increase in total biomass, either dead or alive, buried or not, implies a decrease of this greenhouse gas and the concurrent production of O_2. In the same way, the Devonian rise in atmospheric O_2 has been correlated to the radiations of terrestrial plants and large predatory fish (Dahl et al. 2010). Although the large amounts of carbon stored in the ocean would tend to replenish any CO_2 drawn out of the atmosphere, even a temporary biotic depletion of CO_2 could crucially help reduce the global temperature and trigger global glaciations.

The advent of the first carbonate shells and scales should also contribute to a decrease in CO_2 levels. The first appearance of in vivo sheath calcified cyanobacteria (0.75–0.70 Ga) reflects changes in atmospheric composition, i.e., an increase in pO_2 and a decrease in pCO_2 to below 0.4% (Riding 2006) (see Fig. 3). The efforts of evolving species to adapt to these stressing low CO_2 conditions could have led to a further decrease in global CO_2 levels via enhanced biological gas-concentrating mechanisms. CO_2 levels declined from at least 1.40 to 0.72 Ga (Fig. 4 in Riding 2006), presumably due to silicate-weathering feedback and biological fixation. The Snowball Earth could have been caused merely by CO_2 levels dropping below a critical threshold, which depends on solar luminosity. Silicate-weathering feedback is enough to compensate the Earth's surface temperature for changes in solar radiation. It should prevent per se the snowball bifurcation from occurring unless the forcing is applied rapidly, but the biotic developments summarized here and the related rise of O_2/decrease of greenhouse gases may do the job in a short enough time. In the biotic scenario, CO_2 drawdown would continue after the initial cooling (at least in the tropical regions) until ice sheets eventually reached latitudes low enough to trigger the runaway ice-albedo effect towards global glaciation.

Concerning the biotic hypothesis, it is noteworthy that evolutionary jumps are favoured by stressful environments or by conditions that facilitate the success of new mutations able to survive in the new environment. Afterwards, when moderate conditions return, the novel species thrive and further diversify to replenish all the available ecological niches. Accordingly, a repopulation would occur after each glaciation under new and rapidly changing selective pressures, different from those before the glaciations (Maruyama and Santosh 2008). An analogous scenario appears in the fossil record after several mass extinctions. Remarkably enough, all eukaryote lineages that evolved before the Neoproterozoic glaciations survived them (Porter 2004), i.e., no mass extinction accompanied these exceptional glaciations, which suggest that perhaps the glaciations were incomplete. This suggestion has been called the 'slushball Earth' hypothesis (Hyde et al. 2000; Condon et al. 2002; Rothman et al. 2003; Peltier et al. 2007; Micheels and Montenari 2008; Allen and Etienne 2008). That possibility, first mentioned by Kirschvink (1992), is also a matter of debate (Jenkins et al. 1999; Goddéris and Donnadieu 2008; Hoffman et al. 2008, 2017; Peltier and Liu 2008; Pierrehumbert et al. 2011; Rodehacke et al. 2013).

8 Biotic–Abiotic Interactions and Burial of Organic Carbon

The carbon isotope record provides clues to the Neoproterozoic global carbon cycle. Since the study of Knoll et al. (1986), it is known that Neoproterozoic seawater was characterized by unusually high $\delta^{13}C$, averaging $\geq 5‰$ from 0.82 to 0.72 Ga. The second higher positive $\delta^{13}C$ excursions of marine carbonates in Earth's history occurred during that period (e.g., Holland 2006). Such high values indicate that the proportion of carbon buried as organic matter was significant, which may have allowed O_2 to accumulate in the atmosphere. As a result, Neoproterozoic

O_2 levels increased possibly up to 40% of PAL (Canfield 2005; Shields-Zhou and Och 2011; Och and Shields-Zhou 2012; Lyons et al. 2014; Sperling et al. 2015). High organic carbon burial has been linked to the diversification of eukaryotic plankton (Fig. 3), which altered the dynamics of organic matter production and decomposition (Knoll 2003; Knoll et al. 2006). The flourishing of eukaryotes, including the rise of fungi (Heckman et al. 2001), may have been crucial in setting the stage for the Neoproterozoic Snowball Earth. Fungi recycle organic matter; i.e., they compete with biomass oxidation and contribute to keeping levels of atmospheric CO_2 low.

Lenton et al. (2014) argued that increasing biological complexity in the early Neoproterozoic could have oxygenated the ocean later. Large eukaryotic particles sank quickly through the water column, and the mentioned advent of biomineralization probably contributed to faster sinking fluxes of organic carbon. Enhanced organic burial on the margins of the disintegrating Rodinia, possibly carried down with the first extensive marine precipitation of carbonate snow (Riding 2006), may also have contributed to alter the organic–inorganic carbon cycle (Tziperman et al. 2011). It is noteworthy that the sink of organic carbon to the deep ocean, which was anoxic at that time, was equivalent to its burial since that organic carbon could not be oxidized back to CO_2. That was possibly one of the primary causes of progressive atmospheric oxygenation and depletion of CO_2.

Sustained high $\delta^{13}C$ is compelling evidence for an increase in organic carbon burial (Kaufman et al. 1997; Schrag et al. 2002), and therefore gradual oxygenation before Neoproterozoic global glaciations, as supported by data from organic-rich shale deposits (Partin et al. 2013). Later, frozen oceans caused the hydrologic cycle to shut down and reduced biological productivity, both driving down the ^{13}C composition of seawater (Kaufman et al. 1997; Hoffman et al. 1998; Halverson et al. 2002). That could be the reason why each global glaciation starts with a pronounced negative carbonate ^{13}C excursion.

The fragmentation of Rodinia perhaps triggered other biological mechanisms that contributed to the onset of global glaciation. The ecosystems of shallow seas and lakes on the new continental margins—rich in nutrients and plankton—could have acted as CO_2 sinks due to their rich biological productivity, contributing to global cooling by lowering the greenhouse climate forcing (Shields-Zhou and Och 2011). Similarly, Horton (2015) suggested that P derived from the weathering of large igneous provinces, which occurred during the breakup of Rodinia, fertilized the Neoproterozoic ocean, boosting primary productivity and organic carbon burial rates. That mechanism (along with CO_2 capture by weathering of mafic rocks) perhaps helped to destabilize the climate before glaciation.

9 Why Successive Global Glaciations?

The coupled fluctuations of oxygen and greenhouse gases (reactions (3) and (4)) may be crucial to understand the advent of repeated global glaciations. The seminal work of Kirschvink (1992) pointed out that a global glaciation "would inhibit both silicate weathering and photosynthesis, which are the two major sinks for CO_2 at present […] this would be a rather unstable situation with the potential for fluctuating rapidly between the "ice house" and "greenhouse" states". Consider the ending of the Sturtian glaciation due to a powerful greenhouse effect: the warming climate and the availability of CO_2, sunlight and nutrients in the ocean presumably produced a bloom of life and photosynthetic activity (Fig. 3). In agreement with this scenario, there is evidence of the biogenic origin of cap carbonates (Hoffman et al. 2011). Besides, the renewed hydrological cycle would have led to the chemical weathering of igneous rocks newly exposed to the atmosphere. The increase of total biomass/organic carbon would lead again to some rise in oxygen levels and, along with the renewed weathering, a simultaneous reduction in greenhouse gases to levels low enough to initiate the next snowball episode. We have seen that the time-scale required to enter a new global glaciation in the silicate-weathering scenario is up to ~ 10^7 years (Mills et al. 2011). However, the time-scale to enter the next glaciation is uncertain in the biotic hypothesis because it is a very complex system with feedback loops coupling evolution of species, biological productivity, organic matter burial or oxidation, atmospheric and oceanic compositions, climate forcing, climatic and physical feedbacks on the biosphere, temperature effects on photochemistry, the S and P cycles, etc. Therefore, it is virtually impossible at this time to quantify the primary productivity of the biosphere in the Neoproterozoic. Even the most successful biogeochemical models (e.g.,Claire et al. 2006; Tziperman et al. 2011) are simplified and cannot include all the relevant aspects of the Earth system. A recent attempt to model mid-Proterozoic gross primary productivity (Crockford et al. 2018) delivers rough estimations in the range of 6–41% of pre-anthropogenic levels, merely confirming a concomitant trend of an increasingly more productive biosphere and an increasing atmospheric O_2 (Lyons et al. 2014). Accordingly, the rate of net biospheric O_2 production was roughly 25% of the present rate (Ozaki et al. 2019). Anyhow, for now, we know just enough to develop intriguing hypotheses that explain qualitatively the successive Neoproterozoic Snowball Earth episodes.

The biotic mechanism we have introduced should be tested and developed, and further work is required to substantiate it. Nonetheless, it appears to be consistent with many salient features of the available evidence. Therefore, we consider that it deserves publication so that its merits and flaws can be discussed openly by the scientific community.

Last but not least: Why are global glaciations lacking after the Cryogenian? In addition to the gradual increase in solar luminosity, this fact could be due again to interactions between the biotic and abiotic realms of the Earth. The increase in oxygen levels in the Neoproterozoic enabled the evolution of animals. Animals produce CO_2 by respiration and CH_4 as a byproduct of digestion (in some species). So, animals release greenhouse gases into the atmosphere that help to avoid further global glaciations. Respiration and biomass oxidation (reverse of Eq. 3) hinder any drawdown of CO_2. Notice that, in our contemporary world, these processes recycle organic carbon into CO_2 about as quickly as photosynthesis fixes it. High levels of O_2 (even in the deep ocean) and SO_4^{2-} and the development of bioturbation (Masqué et al. 2002; Tarhan et al. 2018) could help maintain a sufficient concentration of CO_2 via the oxidation of organic matter, i.e., the Phanerozoic world reached a quasi-steady state in total biomass, atmospheric O_2 and greenhouse gases at odds with the dramatic changes in the Neoproterozoic outlined in this work. Although there are alternative hypotheses on this question (Tziperman et al. 2011; Mills et al. 2017), the biotic scenario, if correct, would be a remarkable example of co-evolution by mutual adaptation of Earth and Life.

10 Concluding Remarks

Considerable evolution and proliferation of life in the Neoproterozoic preceded the Snowball Earth and happened in the interglacial periods. The enhanced biological productivity and the accelerated burial and export of biomass boosted oxygen levels with the concomitant drawdown of CO_2 and CH_4. Decreases of such greenhouse gases, coupled with other geochemical changes, appear to be the main driving forces to global glaciation. The evolution of complex life and the corresponding increase of total biomass had a decisive effect on the Neoproterozoic Snowball Earth. The present biotic hypothesis on the causes of the Snowball Earth accommodates the most salient evidence and provides an alternative explanation for successive global glaciations.

The inverse correlation of the described events and the current situation of our planet is manifest. The present-day emissions of CO_2—due to the fast burning of biomass buried during many millions of years (fossil fuels) and deforestation—and of CH_4—mainly due to intensive cattle raising—lead to global warming and climate crisis impacts. In opposition to the development of life in the Neoproterozoic, the biosphere is now suffering the sixth mass extinction. All of these effects have, undoubtedly, anthropogenic causes. One doubts if they will have anthropogenic solutions.

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