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A tectonic context for fluctuations in late Paleoproterozoic oxygen content

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ABSTRACT

Nearly all models of Earth's oxygenation converge on the premise that the first notable rise of atmospheric oxygen occurred slightly above the Archean-Proterozoic boundary, with the second notable rise occurring just below the Proterozoic-Phanerozoic boundary. Plate tectonic–driven secular changes found above the Archean-Proterozoic boundary are thought to have been partly or wholly responsible for the initial rise in atmospheric O_2 in the Great Oxidation Event; however, the role of plate tectonics in oxygen levels thereafter is not well defined. Modern plate tectonics undoubtedly play a role in regulating atmospheric O_2 levels. Mountain building, for example, promotes high erosion rates, nutrient delivery to oceans, and efficient biogeochemical cycling of carbon, resulting in the net burial of organic carbon—thought to be the primary regulator of atmospheric O_2 levels on geological time scales. The trajectory of atmospheric O_2 and oceanic redox conditions in the Proterozoic Eon, representing almost 2 b.y. of geological history, shows a dynamic history with global trends that indicate overall high-low-high O_2 levels throughout the Proterozoic Eon, with low-oxygen conditions established by ca. 2.0–1.8 Ga. This contravenes the tenet that major orogenic events (e.g., the Himalaya-scale Trans-Hudson orogen and other coeval orogens that formed the supercontinent Nuna) should yield higher O_2 levels, not lower. The contrast of higher O_2 early in the Paleoproterozoic with lower O_2 later in the Paleoproterozoic is particularly striking, and mechanisms that might have caused this secular change remain unclear. This contribution explores feedbacks related to the tectonic evolution associated with the building of proto-Laurentia and Earth's first supercontinent, Nuna, and how this impacted the trajectory of atmospheric O_2 in the latest Paleoproterozoic Era.

INTRODUCTION

One of the most interesting aspects of the Paleoproterozoic Era is a convergence of evidence pointing to the first permanent oxygenation of the atmosphere (e.g., Lyons et al., 2014, 2021). The oxygen evolution of Earth's atmosphere, from fledgling O_2 "whiffs" in the Archean to O_2 levels high enough to support animal life in latest Proterozoic time, represents a long and complex journey, with the Proterozoic Eon showing the greatest O_2 fluctuations in Earth's history (Fig. 1). The transition from a poorly oxygenated to a permanently oxygenated atmosphere occurred around 2.4 Ga during the so-called Great Oxidation Event

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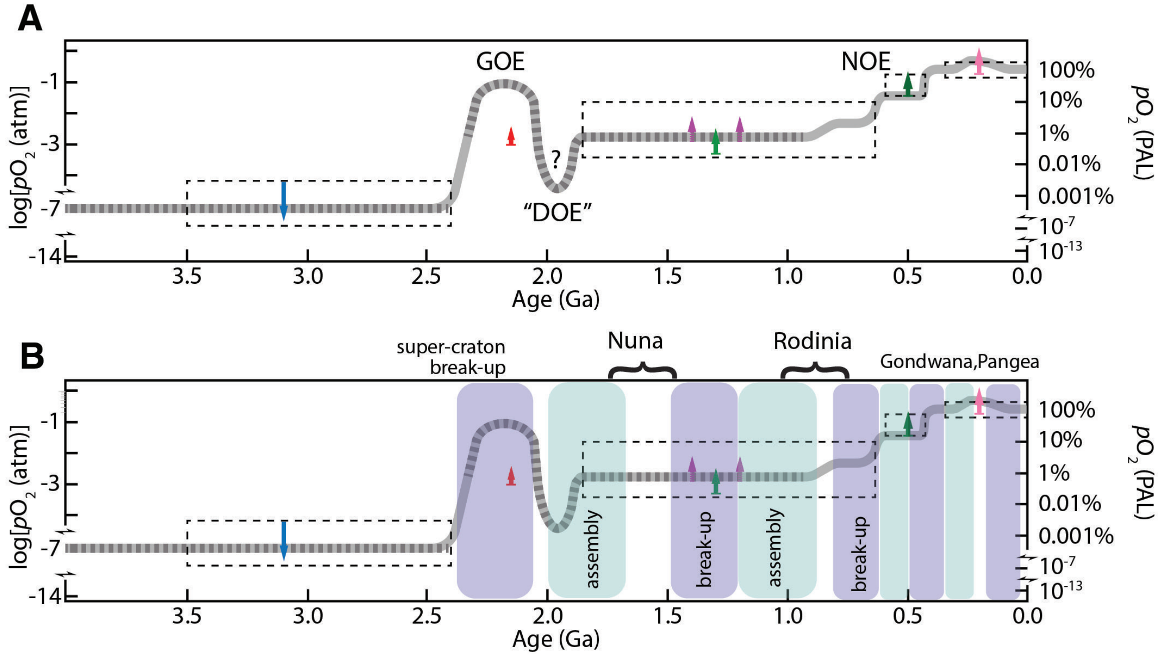

Figure 1. Composite schematic atmospheric O_2 curve throughout Earth's history. (A) The Archean was characterized by low atmospheric oxygen (likely <0.001% present atmospheric level [PAL]) with transient oxidation, whereas the Proterozoic was characterized by a wide range of low (but not Archean-like) to higher levels of atmospheric O_2 (possibly as high as 15%–50% PAL; Bekker and Holland, 2012). The focus of this paper is the Deoxidation Event (DOE) that began after ca. 2.0 Ga. A drop in atmospheric O_2 followed the Great Oxidation Event (GOE) and Lomagundi-Jatuli event (Canfield, 2014; Canfield et al., 2021) and ushered in the low-oxygen conditions of the mid-Proterozoic (e.g., Daines et al., 2017; Planavsky et al., 2018). The absolute O_2 level and dynamics during the Proterozoic overall remain poorly constrained (represented by dashed curve), so a wide range of pO_2 values (represented by dashed boxes) is shown until the Neoproterozoic Oxygenation Event (NOE). Blue, red, green, and pink arrows representing lower or upper bounds of O_2 are from Catling and Zahnle (2020, and references therein); magenta arrows with dashed bottoms representing probable O_2 increases (lacking upper/lower bounds) are from Lyons et al. (2021). Figure is modified from Catling and Zahnle (2020) and Lyons et al. (2021). (B) The assembly and breakup of Earth's supercontinents superimposed on Earth's atmospheric oxygen curve.

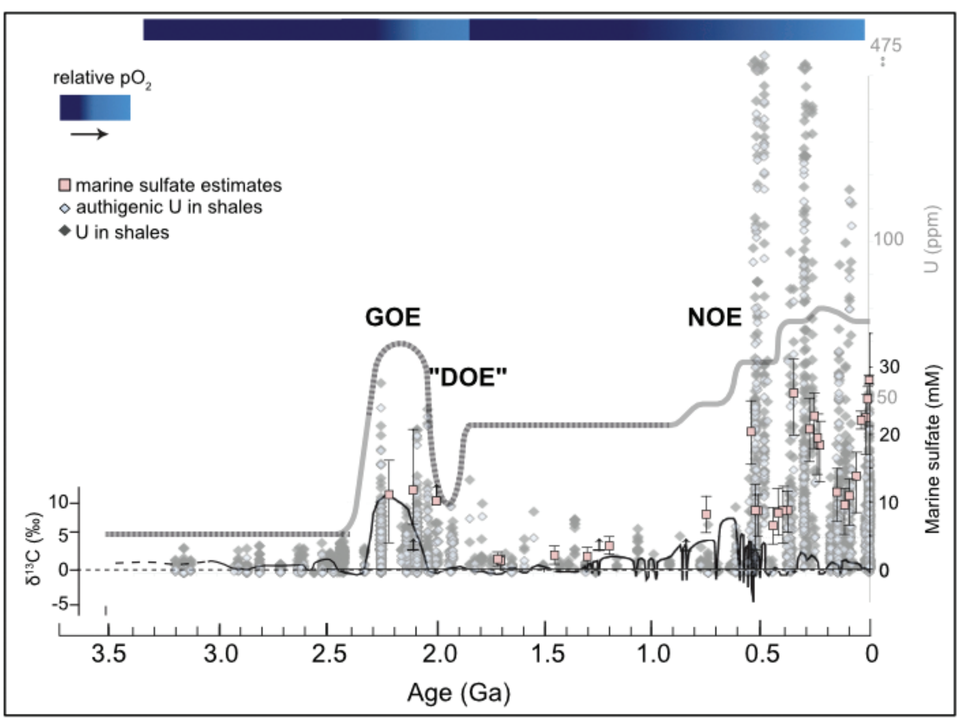

Figure 2. Geochemical and geological evidence of the Great Oxidation Event (GOE), followed by the Deoxidation Event (DOE). Gray curve represents the O_2 curve from Figure 1. Data: Carbon isotope curve (Karhu, 1999); uranium in shales (Partin et al., 2013); oceanic sulfate estimates (Planavsky et al., 2012; Blättler et al., 2018). NOE—Neoproterozoic Oxygenation Event.

(Holland, 2002). This initial rise appears to have been sustained by a second event called the Lomagundi-Jatuli event (Karhu and Holland, 1996), a long-lived positive carbon isotope excursion from ca. 2.22 to 2.06 Ga that is interpreted to reflect an organic carbon burial event resulting from enhanced primary productivity during the Great Oxidation Event (Holland, 2002; Bekker and Holland, 2012). The highest O_2 conditions of the Paleoproterozoic were followed by a transition to lower O_2 levels in the atmosphere-ocean system starting at ca. 2.0 Ga (Planavsky et al., 2012; Partin et al., 2013; Ossa Ossa et al., 2018; Blättler et al., 2018; Mänd et al., 2020), potentially as a consequence of reduced nutrient supply, which would have lowered primary productivity and organic carbon production (Bekker and Holland, 2012; Hodgskiss et al., 2019), or potentially caused by O_2 drawdown from the weathering of organic-rich rocks deposited during the Lomagundi-Jatuli event (Canfield, 2005).

The picture of the most recent oxygen curve (Fig. 1) has come about from a convergence of geochemical evidence over the last decade (e.g., Bekker and Holland, 2012; Planavsky et al., 2012; Partin et al., 2013; Canfield, 2014; Lyons et al., 2014; Blättler et al., 2018), as well as geological evidence, including the reappearance of banded iron formation at ca. 1.9 Ga (e.g., Canfield, 2005), all of which indicate a dramatic change from higher levels of atmospheric O_2 (potentially as high as 15%–50% present atmospheric level [PAL]; Bekker and Holland, 2012) to levels as low as 0.1%–0.01% PAL (Holland, 2007; Canfield, 2014). These dynamic trends contrast with previous models of O_2 rise that assume either a linear or stepwise increase in O_2 levels without a decline in between (e.g., Catling and Claire, 2005; Kump, 2008). The Paleoproterozoic Deoxidation Event—a term introduced here that is defined by a relative decline in O_2 content of the atmosphere-ocean system following the Great Oxidation Event–Lomagundi interval (Figs. 1 and 2)—set the stage for long-term, lower-oxygen conditions in the mid-Proterozoic (1.8–0.8 Ga). Such a flattening of the O_2 curve is generally unexpected given the framework of higher O_2 levels during the first half of the Paleoproterozoic. These unusual Proterozoic O_2 dynamics are unparalleled in Earth's history, and yet no clear geological mechanism explains these trends.

This contribution considers how and why O_2 transitioned from higher levels in the first half of the Paleoproterozoic (Great Oxidation Event–Lomagundi event) to very low levels in the latter half of the Paleoproterozoic starting at ca. 2.0–1.9 Ga (Deoxidation Event), which set the stage for hundreds of millions of years of low-O_2 conditions. Because plate-tectonic processes associated with continent-continent collisions and mountain building should provide positive feedbacks that lead to higher atmospheric O_2 levels, as observed with the supercontinents Rodinia, Gondwana, and Pangea, it is curious that instead, a decline in the O_2 curve coincided with the assembly of the Nuna supercontinent. Similarly, a large igneous province event overlapped with the assembly of Nuna and should have provided nutrients to facilitate enhanced primary productivity, which, coupled with the organic carbon burial potential of the erosion of Himalaya-scale mountain belts, should have resulted in higher atmosphere-ocean O_2 levels, but did not. It is hypothesized here that global plate-tectonic processes were responsible for the oxygenation state of the Proterozoic atmosphere by tipping the scales in favor of sinks that consumed O_2, including oxidative weathering of uplifted rocks during global orogenesis, regional and contact metamorphism during supercontinent assembly, and the flux of reduced gases from volcanism. If correct, future modeling efforts to understand Proterozoic O_2 fluctuations should consider specific tectonic processes that occurred during the assembly of Nuna, for which there is a well-preserved geological record on Laurentia, Baltica, Siberia, India, China, and Antarctica (e.g., Zhao et al., 2002; Evans and Mitchell, 2011; Eglington et al., 2013). The tectonic record of Laurentia might be particularly important because geological evidence has already been used to make the case that modern-style plate tectonics and Himalaya-scale mountain-building events were operative by ca. 1.8 Ga (Corrigan et al., 2009; Weller and St-Onge, 2017). The trial run of global orogenesis under modern-style plate tectonics could have been a detriment to Proterozoic atmosphere-ocean O_2 levels. This chapter summarizes the possible feedback mechanisms related to Paleoproterozoic O_2 fluctuations and specifically attempts to explain the observation that the assembly and evolution of the Nuna supercontinent coincided with the Deoxidation Event in the latest Paleoproterozoic.

Sources and Sinks of Oxygen on Modern and Ancient Earth

Oxygenic photosynthesis is critical to building and maintaining an oxygenated atmosphere and likely developed by ca. 3 Ga (e.g., Planavsky et al., 2014a). Ultimately, all of Earth's O_2 is produced biologically via photosynthesis, where one mole of O_2 is produced along with one mole of organic matter. Today, the O_2 produced by photosynthesis is oxidized back to CO_2 on short time scales, typically within 100 yr. Thus, for geological time scales, the net burial of organic carbon trumps photosynthesis-respiration reactions and becomes the most important mechanism for increasing O_2. Ultimately atmospheric O_2 levels are governed by a mass balance of various fluxes that either liberate oxygen ("source" herein) or consume oxygen ("sink" herein), and the balance among these fluxes ultimately controls atmospheric O_2 levels (e.g., Catling, 2014). In equilibrium, the sources and sinks are equal; in this scenario, atmospheric O_2 remains the same. Thus, atmospheric O_2 only increases when the sources of O_2 exceed the sinks of O_2. The burial of organic carbon is the primary mechanism of increasing atmospheric O_2 (Holland, 1984), as buried organic carbon will not back-react with atmospheric O_2. Only 0.1%–0.2% of the organic carbon is typically buried (Berner, 1982), so most organic carbon produced in modern settings is oxidized and thus becomes an O_2 sink. Today, ~70% of the O_2 in the atmosphere is eventually removed by oxidative continental weathering, while the remaining 30% is consumed by (in decreasing order) metamorphism, subaerial volcanism, seafloor weathering, and submarine volcanism (Catling, 2014). Oxidative continental weathering oxidizes reduced rocks or unconsolidated materials exposed on the continents, including organic carbon, or carbon-, iron-, or sulfide-rich rocks or minerals (e.g., shale, pyrite). Reducing gases (H_2, CO, CH_4, H_2S, and SO_2) released from subaerial volcanism, submarine hydrothermal vents, or via metamorphism that react with O_2 are other important sinks (Catling, 2014). These basic tenets plus the assumption of increased erosion during orogenesis were used to suggest the correlation of supercontinent assembly with increases in atmospheric O_2, which matches well for the amalgamation of Gondwana and Pangea in the Phanerozoic, as well as for the amalgamation of Rodinia in the Proterozoic (Campbell and Allen, 2008).

The prevailing model is that the Great Oxidation Event was not caused by an increase in the source of O_2 (because the flux of organic matter is interpreted to have remained relatively constant after ca. 3.0 Ga; Lyons et al., 2014; Krissansen-Totton et al., 2015), but rather by a dramatic decline in the sinks that consume O_2. A reduction of overall O_2 sinks is linked to various solid-Earth processes, including secular oxidation of the mantle, changes in volcanism, continental freeboard, plate tectonics, and crustal composition. Secular oxidation of the mantle would have decreased the sink of O_2 related to volcanic gases after the Archean (e.g., Holland, 2002; Kadoya et al., 2020). Additionally, submarine volcanism, which emits more reducing gases than subaerial volcanism (Holland, 2002), was dominant in the Archean, whereas subaerial volcanism became increasingly widespread after the Archean-Proterozoic boundary as continents became stable (Kump and Barley, 2007). This shift toward greater distributions of subaerial relative to submarine volcanism, in addition to the gradual transition to a higher ratio of oxidized to reduced species in volcanic and hydrothermal sources, would have decreased the overall sink for O_2 and were likely important factors in causing the Great Oxidation Event (Holland, 2002, 2009; Kasting, 2013; Lee et al., 2016).

Crustal growth and the development of continental freeboard are thought to have built an important framework for organic matter to be buried and oxygen to accumulate and were likely established by ca. 3 Ga (Dhuime et al., 2012; Bada and Korenaga, 2018). Crustal composition was also likely important, and it had begun to transition away from dominantly mafic crust by the Great Oxidation Event (e.g., Smit and Mezger, 2017). The changing composition of the continents from a more mafic to a more felsic composition by ca. 2.5 Ga would have caused a decrease in oxidative efficiency by transitioning away from dominantly iron-rich rocks that consume O_2 when weathered (Lee et al., 2016). As changes in crustal composition likely allowed the Great Oxidation Event to transpire, the Great Oxidation Event itself also had the corollary impact of affecting the composition of the crust (e.g., Bekker and Holland, 2012; Spencer et al., 2019).

Some authors have suggested that solid-Earth processes such as plate tectonics or changes in crustal composition were not required for the Great Oxidation Event. Oxidation of Earth's atmosphere could have resulted from planetary hydrogen escape, combined with oxygenic photosynthesis and subsequent global biogeochemical cycling (Alcott et al., 2019). This model only addresses O_2 increases that would result from biogeochemical cycling, however, and does not address the decline in O_2 that occurred after the Great Oxidation Event. Thus, we must look to other feedbacks to understand Paleoproterozoic O_2 fluctuations. Given the long duration of lower O_2 conditions (Fig. 1), consideration of longer-term plate-tectonic cycles is appropriate.

PROTEROZOIC O_2 FLUCTUATIONS

Archean rocks contain a greater abundance of detrital redox-sensitive minerals (e.g., pyrite, uraninite, siderite) and a greater propensity for mass-independent fractionation of sulfur isotopes than younger rocks (e.g., Johnston, 2011). These characteristics become significantly diminished in the post-Archean geological record. The lack of detrital redox-sensitive minerals after the Archean suggests that the changes that occurred during the Great Oxidation Event were permanent in preventing very low O_2 levels (0.001%–0.01% PAL) from returning (e.g., Johnson et al., 2014). Although often depicted as geologically instantaneous, the Great Oxidation Event transition might have been more protracted than originally thought (cf. Luo et al., 2016; Poulton et al., 2021), but nevertheless it resulted in markedly higher O_2 levels (Fig. 1).

A growing collection of proxy data supports a transition to lower O_2 levels in the atmosphere-ocean system after the Great Oxidation Event–Lomagundi interval that set the stage for long-lived lower O_2 levels during much of the mid-Proterozoic (1.8–0.8 Ga) interval. While uranium isotopes in ca. 1.98 Ga carbonate rocks have been used to show that O_2 in the atmosphere-ocean system remained elevated until ca. 2.0 Ga (Mänd et al., 2020), trends toward lower O_2 levels by ca. 2.0 Ga are consistent with other proxy data, including carbonate-associated sulfate concentrations and uranium concentrations in shales (Fig. 2; Planavsky et al., 2012; Partin et al., 2013), as well as multiproxy stable isotopes (Ossa Ossa et al., 2018) that show a decline in ocean oxygenation between ca. 2.1 Ga and 2.05 Ga. Sulfate evaporite minerals preserved in marine successions show higher seawater sulfate levels during the Lomagundi-Jatuli event (Planavsky et al., 2012) until ca. 2.0 Ga (Blättler et al., 2018), after which lower seawater sulfate levels are interpreted; this is consistent with the loss of sulfate evaporites from the geological record by ca. 1.9 Ga (Pope and Grotzinger, 2003).

Although the mid-Proterozoic interval that followed the Deoxidation Event was generally characterized by low O_2 levels, the uncertainty in the O_2 estimates spans several orders of magnitude and leads to some contradictions (cf. Planavsky et al., 2014b, 2018; Daines et al., 2017). The limitation of proxies in Proterozoic rocks is that they only indirectly indicate atmospheric O_2; they assume a link between oceanic and atmospheric O_2 conditions. It is additionally important to recognize that both spatial and temporal variability existed throughout the

Proterozoic, which can resolve some clashes between proxies indicating higher or lower O_2, e.g., at ca. 1.4 Ga (cf. Daines et al., 2017; Lyons et al., 2021). The mid-Proterozoic interval began with shallow-water ferruginous conditions and the deposition of ca. 1.88–1.84 Ga granular iron formations, placing constraints on atmospheric O_2 in the range of 0.001% to 0.1% PAL (Holland, 2007; Canfield et al., 2021). The persistence of ferruginous conditions in the mid-Proterozoic oceans would have scrubbed phosphorous from ocean waters by the precipitation of iron-phosphate minerals (Derry, 2015), thus limiting primary productivity and organic carbon production. Recent studies suggest that low atmospheric O_2 levels (0.1%–1% PAL) persisted until at least 1.4 Ga (Planavsky et al., 2014b, 2018; Bellefroid et al., 2018) and might have contributed to the delay in the rise of animals (reviewed in Cole et al., 2020). Modeling of organic carbon recycling efficiency suggested a somewhat higher range of 1%–10% PAL for the 1.8–0.8 Ga mid-Proterozoic interval (Daines et al., 2017; Canfield et al., 2021). Geochemical proxies need to be reconciled with the lack of detrital redox-sensitive minerals (e.g., pyrite) in the mid-Proterozoic rock record that would be expected at these very low O_2 levels (e.g., <1% PAL). The next substantial increase in atmospheric O_2 occurred near the end of the Neoproterozoic Era (i.e., ca. 800–600 Ma), which ushered in the rise of animals.

STATUS OF PROTEROZOIC TECTONICS

The emergence of continents by the start of the Proterozoic Eon at 2.5 Ga, as well as the secular cooling of the mantle, undoubtedly played an important role in the evolution of plate-tectonic cycling. Many criteria are used to estimate the timing of the establishment of modern-style plate tectonics on Earth, but one of the simplest ways is to identify the operation of the Wilson cycle (ocean opening via seafloor spreading; ocean closing via subduction and orogenesis), which was in place possibly as early as ca. 3.0 Ga (Shirey and Richardson, 2011), but certainly by the ca. 1.8 Ga Hudsonian orogeny, which records the first well-preserved example (Corrigan et al., 2009; Weller and St-Onge, 2017). Other indicators of the onset of plate tectonics include geological evidence for seafloor spreading (e.g., ophiolite sequences) and evidence for subduction (e.g., ultrahigh-pressure metamorphic rocks), which were in place by ca. 2.0–1.8 Ga (Palin et al., 2020). Whether these features demonstrate a transition by ca. 2.0–1.8 Ga to modern-style plate tectonics with cold, steep, and deep subduction or a mobile lid–type tectonic regime with warm and deep subduction depends on the interpretation of the geological phenomena (Palin et al., 2020, and many references therein). Several geological indicators in Laurentia have been used to support the interpretation of modern-style plate tectonics, including ophiolites, eclogite-facies rocks, and ocean opening and closing of the Pacific-sized Manikewan Ocean, indicative of a Wilson cycle (Scott et al., 1992; Corrigan et al., 2009; Weller and St-Onge, 2017). Importantly, the amalgamation of the Paleoproterozoic–Mesoproterozoic supercontinent Nuna/Columbia occurred by ca. 1.8 Ga and is interpreted to represent Earth's first true supercontinent (e.g., Evans and Mitchell, 2011).

The building of the supercontinent Nuna involved a series of Paleoproterozoic orogenic events in Laurentia, including the Thelon-Taltson, Snowbird, Torngat, Penokean, Wopmay, Rinkian-Nagssugtoqidian, New Quebec, Great Falls, and Trans-Hudson orogens between ca. 2.0 Ga and 1.75 Ga. Other important 1.9–1.8 Ga orogens include the Kola-Karelia, Svecofennian, Volhyn–Central Russian, and Pachelma orogens (Eastern Europe), Akitkan and Central Aldan orogens (Siberia), Transantarctic Mountains orogen, Central Indian tectonic zone, and the Trans–North China orogen, all of which produced mountains with a collective strike length of ~8000 km (Zhao et al., 2002).

The record of Laurentia is particularly important because it contains almost half of the global 2.0–1.8 Ga orogens (Zhao et al., 2002). The Trans-Hudson orogen, the largest and best preserved of these, was the product of an ~4000-km-long continent-continent collisional belt extending from the western United States to Greenland and Scandinavia (Hoffman, 1988; Corrigan et al., 2009). The extent and processes of tectonic events that occurred prior to terminal continent-continent collision show features consistent with modern-style plate tectonics, including indentor tectonics, passive margins, volcanic arcs, and subduction zones (including eclogite-facies rocks) associated with short-duration accretionary orogenies within a larger orogenic system (similar to the Grenville or Appalachian orogens); these features have been reviewed elsewhere in detail (e.g., Hoffman, 1988; Ansdell, 2005; St-Onge et al., 2006, 2009; Corrigan et al., 2009, 2021). Similarities between the Trans-Hudson orogen and the Himalayan orogen (Weller and St-Onge, 2017) demonstrate the scale of this event. Recent work using the Lu content of zircon supports the idea that orogens in the construction of Nuna produced the first Himalaya-scale mountains in Earth's history (Zhu et al., 2022). These data also suggest that such high mountains formed again during Gondwana assembly, but not during the assembly of Rodinia, potentially highlighting a key difference between the two Proterozoic supercontinents.

Nuna's orogenic events culminated in widespread metamorphism. Regional metamorphic facies included both high- and low-pressure metamorphism, in addition to contact metamorphism that resulted from the emplacement of arc- or postcollisional plutons (e.g., Hudsonian granite batholiths; Ansdell, 2005; Corrigan et al., 2009). Eclogite-facies metamorphic rocks, resulting from shallow subduction processes, are documented for the first time in the geological record at ca. 2.1 Ga and peak in abundance around 1.85 Ga, with occurrences in the North China craton, as well as the Trans-Hudson and Nagssugtoqidian orogens (reviewed in Palin et al., 2020). The ubiquity of eclogite-facies metamorphism in the Proterozoic geological record around 1.85 Ga is indicative of widespread subduction associated with the building of Nuna.

Although reconstructions of Nuna differ in continental configuration (cf. Zhao et al., 2002; Eglington et al., 2013), the common thread is the elimination of most continental shelves during assembly. During supercontinent breakup, juvenile oceanic crust that is warmer and more buoyant replaces older and colder oceanic crust, and so younger oceans are expected to be shallower. Broadly, widespread subduction tends to lower eustatic sea level, whereas the opening of ocean basins via seafloor spreading tends to cause sea level to rise (Murphy et al., 2009). Thus, a Wilson cycle or a supercontinent cycle can either lower or raise sea level (e.g., larger ocean basins during breakup; smaller basins during amalgamation). Different processes would have been dominant at different times during the Wilson cycle. Widespread seafloor spreading, passive margin development, and eustatic sea-level rise would have dominated during the development of oceans, like the Pacific-sized Manikewan Ocean, from ca. 2.1 to 1.92 Ga. The closure of these oceans would have involved the subduction of ocean floor and island-arc volcanic rocks and associated accretionary and collisional orogens; for example, the ca. 1.8 Ga Trans-Hudson orogen involved ~90 m.y. of ocean closure. The high erosion rates anticipated to accompany the denudation of mountain chains such as the ca. 1.8 Ga Trans-Hudson orogen continued for ~200 m.y., as recorded by deposition of thick fluvial deposits in the Athabasca Basin, and correlative terrestrial deposits of the Thelon and Hornby Bay basins (e.g., Rainbird and Davis, 2007). These high erosion rates were likely comparable to those observed for the Himalayan mountains today, and the potential for organic carbon burial would have been high. However, a dominance of large-scale terrestrial basins over marine basins might have also impacted organic carbon burial during this time. The breakup of the core of Nuna occurred ca. 1.5–1.25 Ga (Evans and Mitchell, 2011); transient atmospheric O_2 increases at ca. 1.4 Ga and 1.2 Ga are noted in this interval (Fig. 1).

Although large igneous province events have occurred throughout most of Earth's history, they tend to be associated with either mantle plumes or continental breakup (Condie et al., 2015). The biggest spike in the Proterozoic occurred ca. 1.88 Ga (Ernst, 2014) and coincided with supercontinent assembly. Large igneous provinces contain substantial phosphorus and are highly susceptible to chemical weathering (Horton, 2015). Phosphorus is thought to be the limiting nutrient driving primary productivity on geological time scales (Tyrrell, 1999). Because the delivery of phosphorus and other important trace metals (e.g., N, Mo; Anbar and Knoll, 2002) to the oceans is limited by continental weathering, supercontinent cycles influence nutrient delivery to the ocean by exposing and uplifting continental rocks. Importantly, higher CO_2 associated with widespread volcanism, as during a large igneous province event, raises atmospheric temperature and acidifies meteoric waters, and thus would act to enhance weathering and nutrient delivery. So, under typical geological conditions, large igneous province activity leads to enhanced phosphorus delivery, enhanced primary productivity, and enhanced organic carbon burial, providing an ideal recipe for higher atmospheric O_2. However, this is not the case for the period after the ca. 1.88 Ga large igneous province event nor with ca. 2.0–1.8 Ga global orogenesis leading to the supercontinent Nuna.

Thus, the ca. 1.9 Ga Deoxidation Event overlapped with global-scale orogenesis and occurred in step with the transition to modern-style plate tectonics or something broadly similar. The relation, however, between the formation of Nuna and the Deoxidation Event is uncertain. The building of Nuna might be expected to represent a prime time for enhanced delivery of nutrients to the oceans, including phosphorous, and burial of organic carbon (e.g., Campbell and Allen, 2008), yet we see a fall in atmospheric O_2 (Fig. 1).

DISCUSSION

The oxygen status of Earth's surface changed dramatically after the Great Oxidation Event–Lomagundi interval, but the causes are unclear. One consideration is that plate-tectonic processes influenced Proterozoic O_2 cycling because they facilitated feedbacks that consumed or liberated O_2. Plate-tectonic cycles that provide a positive feedback mechanism for increasing O_2 levels include nutrient delivery and efficient biogeochemical cycling of carbon through the erosion of mountains, leading to the burial of organic carbon. High sedimentation rates should lead to a net source of O_2 via enhanced organic matter burial. Campbell and Allen (2008) previously inferred that atmospheric O_2 increases correlated with the amalgamation stage of Nuna; however, the revised Proterozoic O_2 curve calls this relation into question (Fig. 1).

The transition from maximum areal extent of shallow ocean basins with continental shelves during supercontinent breakup to fewer continental shelves associated with deeper ocean basins during supercontinent maxima can help to explain differences in organic carbon burial potential. Fewer continental shelves associated with a long-lived supercontinent (as with Nuna) would also have limited organic carbon burial over hundreds of millions of years—from at least ca. 1.8 Ga to 1.5 Ga. This is partly a function of sea-level changes associated with stages of the supercontinent cycle. The assembly and breakup of supercontinents during the Proterozoic alongside a compilation of the most recent Proterozoic O_2 constraints suggest that supercontinent breakup might be better correlated with O_2 increases (Fig. 1).

Because net O_2 production (by photosynthesis) is partially related to the production of CO_2, volcanic CO_2 emissions exert a control on the rate of burial of organic carbon (e.g., Eguchi et al., 2020). Large amounts of atmospheric CO_2 were emitted from ca. 2.0 to 1.8 Ga, including from mid-ocean-ridge volcanism associated with ocean opening (e.g., the Manikewan Ocean), arc volcanism associated with ocean closing, and subsequent global accretionary and collisional orogenesis (Zhao et al., 2002). For example, contact metamorphism during the emplacement of ca. 1.8 Ga syn- to postcollisional plutons, such as the Hudsonian granite batholiths, and igneous sills associated with the ca. 1.88 Ga Pan-Superior large igneous province event (Heaman et al., 2009; Ernst and Bell, 2010), would have released potentially huge volumes of CO_2 and methane, by analogy with Phanerozoic large igneous province events (Svensen and Jamtveit, 2010). At least some portion of atmospheric CO_2 derived from volcanism and contact metamorphism would be expected to be buried as organic carbon.

Continent-continent collisions in the context of a supercontinent cycle would result in O_2 sinks, including a higher flux of reducing gases (e.g., H_2, CO, SO_2) from crustal oxidation during metamorphism and from volcanism, as well as a greater sink due to oxidative continental weathering, which is a function of uplift and the associated denudation rates. Volcanism and the release of hydrogen from water-bearing magmas, especially prevalent in subduction zones, would also be important because hydrogen is a sink for O_2. These reducing gases from the mantle released to the atmosphere via volcanism or crustal oxidation during metamorphism, especially during supercontinent assembly, could have led to lower O_2 levels.

The overlap of eclogite-facies occurrences with the Deoxidation Event is intriguing. Subduction (and subduction-related arc magmatism) recycles critical elements such as O_2 and S. The thermodynamic conditions and geometry of subduction zones determine the extent of oxidation, where oxidizing fluids are produced more efficiently in cold subduction than in warm subduction through the dehydration of serpentine (Zhang et al., 2021). The dehydration of serpentinite, commonly associated with Pacific-type eclogites, also might provide a link with changing the oxidation state over this time interval.

Continental Weathering Fluxes

Oxidative continental weathering of carbon-, sulfide-, or ferrous iron–bearing rocks is a net O_2 sink (Holland, 2002). The Paleoproterozoic shale record (Fig. 3) shows that ca. 2.1–2.0 Ga shales have elevated organic carbon contents that are similar to Phanerozoic shales. The uplift and oxidative weathering of organic carbon–rich shales that were deposited during the Great Oxidation Event–Lomagundi interval would have been a major sink for O_2 over ~200 m.y., or the length of a rock cycle (Canfield, 2005). The oxidation of organic matter produced during the Great Oxidation Event–Lomagundi interval can be seen in the ca. 1.98 Ga carbon isotopic record (Kump et al., 2011).

Carbon isotopes have guided our canonical knowledge of the relative rates of organic matter production and burial throughout geological time. Thus, our conventional view of the O_2 history of Earth is guided by the carbon isotopic record of marine carbonate rocks (e.g., Karhu and Holland, 1996). The flat carbon isotope record before and after the Lomagundi-Jatuli event (Fig. 2) has been the main driver of the idea that the burial flux of organic carbon relative to inorganic carbon has remained static. For example, Krissansen-Totton et al. (2015) showed almost no change in the average organic carbon burial fraction for the Archean (3.6–2.5 Ga) versus the mid-Proterozoic (1.8–0.8 Ga) records. Conversely, recent work shows that large changes in organic matter burial could be possible without manifesting in the carbon isotope record (Daines et al., 2017; Krissansen-Totton et al., 2021). This is possible because incomplete oxidation of organic matter under lower O_2 conditions and the subsequent subduction of this organic matter pool can potentially decouple the carbon isotope record from organic carbon burial (Krissansen-Totton et al., 2021).

Thus, a factor important to this discussion is the oxidative efficiency of organic carbon under varying levels of pO_2. In a

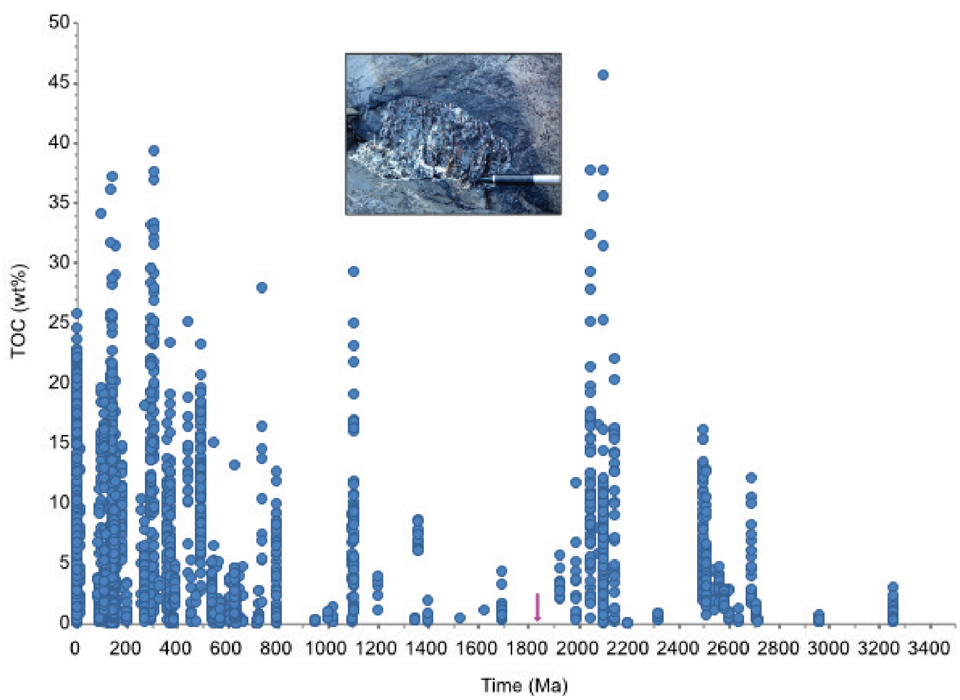

Figure 3. Compilation of total organic carbon (TOC) in shales through time (n = 3197; data are from Partin et al., 2013, and references therein) and photo of refractory organic matter from the ca. 1.83 Ga synorogenic Omarolluk Formation of the Belcher Group (photo by C. Partin); arrow denotes age of the Omarolluk Formation.

completely anoxic atmosphere, the sink of O_2 involving oxidative continental weathering would be expected to be nearly nil. Bolton et al. (2006) and Daines et al. (2017) hypothesized that incomplete oxidation of organic matter due to faster erosion rates, even under modern O_2 levels, results in organic matter being buried in sediments, which should result in an overall increase in O_2. Modeling by Bolton et al. (2006) found that the total organic carbon remaining at the surface has a greater dependence on erosion rate than atmospheric O_2 level. Slow erosion rates (continental average of 4–5 cm/k.y.) do not yield refractory detrital organic carbon in sediments, whereas fast erosion rates (20–50 cm/k.y.) can. Once Nuna was amalgamated and sediment began shedding from large mountains, both fast erosion and low O_2 conditions would have been prevalent at the same time, for at least 200 m.y., as shown by the ca. 1.8–1.6 Ga fluvial sedimentary record (e.g., Rainbird and Davis, 2007). Thus, oxidative weathering of Himalaya-scale mountains created during the formation of Nuna would have moderated Proterozoic atmosphere-ocean O_2 conditions. Despite the fact that oxidative efficiency of organic carbon was sluggish or close to nil, the O_2 curve does not show an increase in O_2 as might be expected. The efficiency of organic matter recycling as a potential O_2 barometer was recently tested by Canfield et al. (2021) for the interval from ca. 1.73 to 0.74 Ga; they found that organic carbon oxidation efficiency was likely similar to that observed today. This suggests that other sinks of O_2 should be explored for understanding Proterozoic O_2 dynamics during this time.

RECOGNIZING THE PALEOPROTEROZOIC "DEOXIDATION EVENT"

Here, some relations between surface conditions and deep Earth processes driven by plate tectonics are explored as a potential driver for the initiation of the Deoxidation Event. Conventional wisdom regarding the supercontinent cycle connects high rates of erosion to greater nutrient delivery to the oceans, resulting in enhanced primary productivity, as well as increased burial of organic carbon and pyrite, which should result in an increase in atmospheric O_2. The organic content of shales (Fig. 3) does not preclude this interpretation (e.g., Krissansen-Totton et al., 2015); however, an increase in organic carbon burial is not manifested in the carbon isotope record (Krissansen-Totton et al., 2021). Fast rates of erosion (20–50 cm/k.y.), manifested in turbidite sequences, are expected to be associated with increased detrital organic carbon in marine sediments that results from incomplete oxidation of organic matter (Bolton et al., 2006). The Bengal Fan of the Himalaya foreland basin is one of the few places where the accumulation of detrital, unoxidized organic matter can be observed today (Galy et al., 2008). Thus, by analogy with the Himalaya-like Trans-Hudson orogen, fast erosion rates would be expected to promote burial of unoxidized organic matter. Many Paleoproterozoic synorogenic foreland/molasse successions at the surface today are of higher metamorphic grade (e.g., Corrigan et al., 2009) and therefore would be unlikely to preserve relict organic matter. Further, higher-metamorphic-grade rocks at the surface indicate uplift and erosion of a large volume of rock that was located at higher crustal levels (and therefore lower metamorphic grades) during early stages of orogenesis, which also imply the loss of recognizable refractory organic matter and its geological record. One rare low-metamorphic-grade example is the prehnite-pumpellyite-facies ca. 2.0–1.8 Ga Belcher Group on the Superior craton in Nunavut, Canada (Jackson, 2013). As would be predicted by fast erosion rates, the synorogenic, rapidly deposited turbidites of the ca. 1.84 Ga Omarolluk Formation of the Belcher Group preserve detrital organic matter (Fig. 3). Voluminous basaltic magmatism, including the ca. 1.88 Ga large igneous province event, would have supplied phosphorous to the oceans, promoting primary productivity and thus organic carbon production. The fast burial rate of this organic carbon would be expected to result in higher atmospheric O_2 levels. Instead, O_2 levels remained low after the termination of ca. 1.8 Ga orogenesis in the formation of Nuna and in the wake of the ca. 1.88 Ga Pan-Superior large igneous province event. Factors that increased atmospheric O_2 potentially included the burial of organic carbon and pyrite during rapid erosion associated with post-supercontinent assembly, as well as the potential for enhanced phosphorous delivery to the oceans from the weathering of the ca. 1.88 Ga large igneous province strata.

Modeling of a reduced flux in organic carbon burial at lower O_2 has been used to explain the transition to lower O_2 conditions by the mid-Proterozoic (Daines et al., 2017). Even in the absence of a loss of O_2 to oxidative continental weathering in this scenario, a net source of O_2 from organic carbon burial is not sufficient to counterbalance typical modern values for volcanic and metamorphic O_2 sinks. Given the uncertainties in these model assumptions, these authors also recognized that it is possible to instead explain a decline in O_2 conditions by attributing a greater proportion to O_2 sinks. Thus, inferences that these sinks had largely declined by ca. 2.5 Ga (e.g., Lee et al., 2016) might be incompatible with the scale of orogenesis associated with the building of Earth's first supercontinent and the potential for large O_2 sinks.

CONCLUSION

A decline in atmosphere-ocean O_2 conditions by ca. 2.0–1.9 Ga is indicated by a broad suite of geological and geochemical evidence, here named the Deoxidation Event. There is a broad consensus that a decline in the ratio of reducing to oxidizing volcanic gases in the early Proterozoic Eon resulted in fewer sinks of O_2, which in turn allowed the Great Oxidation Event to occur (e.g., Holland, 2002; Catling, 2014). In contrast, one possible explanation for the Deoxidation Event is that solid Earth–associated O_2 sinks increased with the onset of enhanced tectonic activity around 2.0–1.8 Ga, when an increased flux of reducing gases from widespread metamorphism and volcanism associated with ocean-continent and continent-continent collisions during the amalgamation of Nuna led to O_2 decrease.

It is proposed here that the near-constant orogenesis occurring during the construction of Earth's first true supercontinent contributed an overall higher flux of reductants from the mantle via volcanism that upset the balance of fledgling post–Great Oxidation Event O_2 conditions in the late Paleoproterozoic. Supercontinent amalgamation is associated with a smaller area of continental margins, decreasing the potential for organic carbon to accumulate and to be buried. Thus, fewer continental shelves coupled with lower sea level after the amalgamation of Nuna could have reduced the capacity of organic matter to accumulate and be buried, thus contributing to decreasing O_2. Major sinks of O_2 during this time included high-grade regional and contact metamorphism during supercontinent assembly, increased flux of reduced gases from arc volcanism during ocean closure, serpentinization of oceanic crust, oxidation of ferrous iron to form extensive iron formations, and oxidative weathering of uplifted rocks during global orogenesis. Weathering of ca. 1.9–1.8 Ga massive-sulfide (Ni-Cu and volcanogenic massive sulfide) deposits that formed during the amalgamation of Nuna (Cawood and Hawkesworth, 2015) would have also been an important sink for O_2 during the Deoxidation Event. At least some portion of huge volumes of atmospheric CO_2 derived from processes such as arc volcanism during global accretionary and collisional orogenesis and large igneous province volcanism would be expected to be buried as organic carbon.

This flux of reductants and their O_2 consumption must have countervailed the large burial flux of organic matter that might be expected to occur with the denudation of global Himalaya-scale mountain chains, and ultimately resulted in the Deoxidation Event. This contrasts with the trend of O_2 conditions during the amalgamation of Rodinia, when O_2 increased, presumably due to fewer O_2 sinks associated with the assembly of Rodinia versus Nuna. Both the number of orogenic events and the scale of mountains produced during the mid-Proterozoic interval (including Rodinia) was smaller by comparison with Nuna or Gondwana (e.g., Zhu et al., 2022), which could potentially explain this difference. Quantification of these sources and sinks in the context of specific Proterozoic tectonic events will clarify their relative importance in determining fluxes that impacted O_2 conditions in a post–Great Oxidation Event world. The role of solid-Earth processes, especially plate tectonics, should not be overlooked when characterizing the dynamic oxygenation path of the Proterozoic atmosphere-ocean system.

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