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Manganese oxides, Earth surface oxygenation, and the rise of oxygenic photosynthesis

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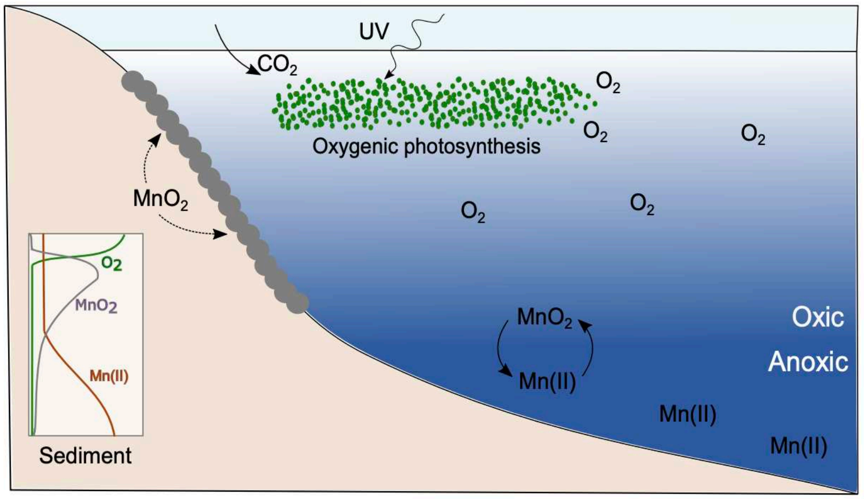
Abstract

Oxygenic photosynthesis is arguably the most important biological innovation in Earth's history, facilitating the transition to a habitable planet for complex life. Dating the emergence of oxygenic photosynthesis, however, has proven difficult with estimates spanning a billion years. Sedimentary manganese (Mn) enrichments represent a potentially important line of evidence given the high redox potentials necessary to oxidize Mn in natural environments. However, this view has been challenged by abiotic and anaerobic Mn oxidation pathways that decouple Mn enrichments from oxygenation. With these in mind, we review Mn oxidation pathways and Mn enrichments and evaluate their relation to Earth’s oxygenation. We argue that despite possible alternative pathways, shallow oxygenated seawater is a prerequisite for generating and, importantly, preserving significant sedimentary Mn enrichments (and associated geochemical signals). This implies that Mn enrichments indeed track Earth’s oxygenation and oxygenic photosynthesis emerged 100s of millions of years prior to irreversible atmospheric oxygenation.

1. Introduction

Manganese (Mn) has played a critical role in shaping our knowledge of Earth’s protracted oxygenation, in large part due to its inherent sensitivity to changes in ambient redox conditions and propensity to undergo phase transitions during biogeochemical cycling (Fig. 1). Some of the strongest evidence for oxygen (O_2) in the environment prior to the Great Oxidation Event (GOE), which began before ca. 2.43 Ga (Gumsley et al., 2017; Bekker et al., 2020, 2021), is the presence of massive $\delta^{13}C$-depleted Mn(II) carbonates in association with iron formations and iron-rich mudstones that are believed to have been formed through Mn(IV) reduction (e.g., Planavsky et al., 2014; Smith and Beukes, 2023; Smith et al., 2023). Similarly, isotopic fractionations (e.g., Cr, Mo, and Fe) that are driven by the presence of Mn(IV) oxides (Crowe et al., 2013; Frei et al., 2009; Planavsky et al., 2014; Wang et al., 2022) provide indirect evidence for ambient, local O_2 at least ~500 Myrs prior to the onset of the GOE (Warke et al., 2020). Some of these isotopic signals (e.g., Cr) may have been generated by more recent weathering (Albut et al., 2018; Heard et al., 2021), highlighting the need for additional robust proxies. For many years the Kalahari Mn deposit in the Hotazel Formation, South Africa, which hosts massive Mn-ore deposits, was viewed as unequivocal evidence for pervasive environmental oxygenation (e.g., Johnson et al., 2013; Tsikos et al., 2010) thus anchoring the GOE to the date of Mn deposition in the Hotazel Formation. A recent study on the mafic volcanic rocks of the underlying Ongeluk Formation places the age of the Hotazel Formation closer to 2.4 Ga (Gumsley et al., 2017). Linking deposition of the Hotazel Formation to the GOE serves as an example of how knowledge regarding the connections between ambient environmental conditions, the biosphere, and the formation of Mn deposits has the potential to inform our understanding regarding Earth’s oxidation.

a) Mn cycle: oxic model



b) Mn cycle: anoxic model

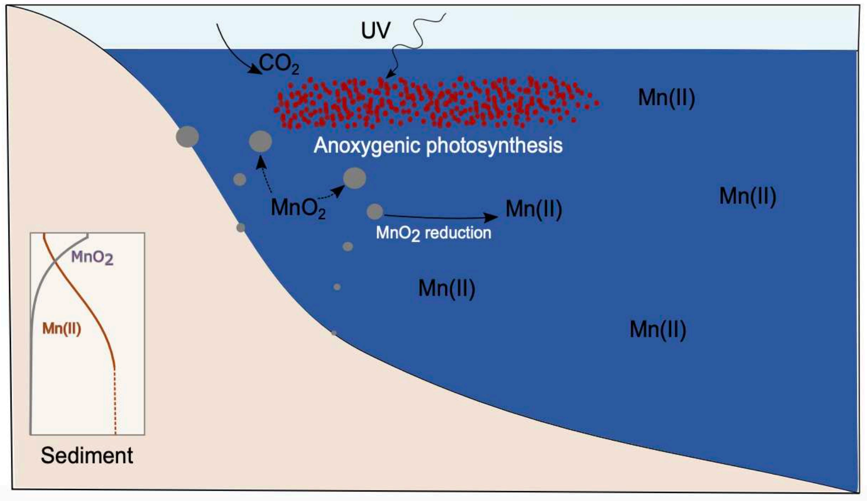


Figure 1. Schematic illustration of the manganese cycle. (A) Manganese cycling under oxic conditions, where O_2 produced by cyanobacteria in the photic zone leads to the deposition of Mn(IV) oxides. (B) Anoxic manganese cycling, where Mn(II) is oxidized by either anoxygenic photosynthetic bacteria or UV photooxidation. Inset in both models is the expected pore water chemistry profile, with a higher preservation potential for Mn(IV) oxides in A.

While the evidence is increasingly pointing to the emergence of oxygenic photosynthesis sometime in the Archean, by the onset of the Paleoproterozoic, evidence for free oxygen in Earth's surface environments becomes less controversial. For instance, enrichments in redox-sensitive elements (RSE) such as rhenium and molybdenum, which require oxidative weathering for their generation, have been documented in the 2.5 Ga Mt. McRae Shale, Western Australia (Anbar et al., 2007). These RSE enrichments appear to be robust, reflecting primary signals, as supported by an unperturbed Re-Os age of 2495 ± 14 Ma, indicating that the system has been not altered or reset by post-depositional processes (Kendall et al., 2015). Yet, even signals such as this, which appear to be generally well constrained remain the subject of debate and ongoing investigation. For instance, Slotznick et al. (2022) presented sedimentological observations in combination with synchrotron x-ray spectroscopy images and sulfur isotope data to argue for fluid migration and subsequent oxidative weathering in the generation of RSE enrichments in the 2.5 Ga Mt. McRae Shale. Such debate highlights the lack of consensus in reconstructing the history of Earth's oxygenation and the room for additional work.

The most convincing geochemical evidence for the presence of O_2 in the environment remains the disappearance of sulfur mass-independent fractionations (S-MIF) (Farquhar et al., 2011, 2000). However, S-MIF is an atmospheric signal, and O_2 produced in the oceans was likely scavenged by marine and atmospheric sinks – reduced species – prior to the onset of the GOE. The disappearance of S-MIF occurred during the GOE, when O_2 in the atmosphere may have risen to a substantial fraction of the 21% in today's atmosphere during the Lomagundi-Jatuli Event, before returning to low to intermediate levels during the Proterozoic (Catling and Zahnle, 2020; Lyons et al., 2014; Planavsky et al., 2018). The exact timing and structure of the GOE remain an area of active discussion (G. Chen et al., 2022; Poulton et al., 2021). For instance, it is possible that O_2 levels remained elevated until at least 2.0 Ga given RSE enrichments and positively fractionated $\delta^{238}U$ recorded in the Zaonega Formation, NW Russia (Mänd et al., 2020; see Ossa Ossa et al. (2022) for an alternative view). Other recent studies have suggested that the disappearance of MIF may have begun before the ca. 2.45-2.43 Ga (Warke et al., 2020; Bekker et al., 2020, 2021), that S-MIF signals are asynchronous between depositional basins (Philippot et al., 2018), and that O_2 may have oscillated for several hundred million years prior to the establishment of permanent atmospheric oxygenation (Bekker et al., 2020, 2021; Poulton et al., 2021). The complexity in the structure behind the rise of atmospheric O_2 and uncertainty in timing of the emergence of oxygenic photosynthesis as a metabolism capable of shaping Earth's surface environment, therefore, requires the integration of both geologic and geochemical lines of evidence.

The canonical view of large-scale Mn deposits and associated geochemical signals, including molybdenum and chromium isotope compositions and Mn/Fe ratios driven by oxidation (Crowe et al., 2013; Frei et al., 2009; Planavsky et al., 2014; Wang et al., 2022), is that they provide evidence for Archean O_2. However, there is a growing number of studies that introduce uncertainty in this paradigm. For instance, it has been suggested that Mn(II) could have been oxidized through a direct, anoxygenic photosynthetic pathway (Olson, 1970; Johnson et al., 2013) or by ultraviolet light (Liu et al., 2020), rather than by O_2 within seawater or atmosphere. To this end, recent culturing experiments have provided support for an oxygen-independent microbial pathway (Daye et al., 2019) and highlighted the potential importance of chemosynthetic Mn oxidation where electrons from Mn are coupled to carbon fixation (Yu and Leadbetter, 2020). Further challenging the requirement for O_2 in generating sedimentary Mn enrichments is recent work, suggesting that Mn(II)-enriched carbonates in the Transvaal Supergroup are the result of Mn^{2+} replacement of high-magnesium calcite precursors (Siahi et al., 2020), although this interpretation would be largely at odds with both carbon (Beukes et al., 1990; Fischer et al., 2009; although see also Tsikos et al., 2022) and iron isotopes (Johnson et al., 2008), which strongly support the diagenetic reduction of Fe and Mn during carbonate formation.

A recent increase in arguments for alternative Mn oxidation pathways that could account for the generation of substantial Mn accumulations in the absence of O_2 – anoxygenic photosynthetic pathways, photooxidation, or the direct nucleation of Mn carbonates within the water column – has spawned a new generation of discussion about the canonical interpretation of large Mn deposits. These alternative pathways for generating Mn accumulations, if fully validated ans shown to be quantitatively significant, could in principle shift our framework for viewing Mn deposits and oxygen prior to the GOE. As these new perspectives have implications for generating Mn oxides as well as carbonates, it is necessary to fully evaluate their implications for interpreting the Archean to Paleoproterozoic environment and rise of oxygenic photosynthesis. Here we review the various pathways for Mn oxidation in the environment, the conditions necessary for the preservation of Mn enrichments and the evidence for the deposition of Mn(III,IV) oxides throughout Earth's history. Furthermore, we synthesize this information in the context of a fundamental question – *Do substantial Mn carbonate deposits and associated isotopic signals prior to the Great Oxidation Event provide unambiguous evidence for the presence of free* O_2 *in Earth's surface environments?* We argue that the presence of shallow oxygenated seawater is a necessity for their deposition, and as such implies that the presence of significant Mn enrichments tracks the oxygenation of Earth's surface environments through time. Knowledge of the oxidative and reductive cycling of Mn on Earth, therefore, has critical implications for interpreting the geologic record of Earth's protracted oxygenation.

2. Marine Mn cycling, present, and past

As the twelfth most abundant element in Earth's crust, Mn plays an important role in the biogeochemical cycling of carbon, iron, sulfur, and many trace elements. While a wide range of oxidation states for Mn is known (-3 to +7), the most common oxidation states found in nature are +2, +3, and +4; with +2 corresponding to the reduced soluble form, and +3 and +4 being the less soluble oxidized forms. The main source of oxidized Mn in the modern oceans is riverine flux with only a minor contribution from glaciers and wind-born dust (Poulton and Raiswell, 2002). Sources for Mn(II), on the other hand, include hydrothermal vents and sedimentary, biologically catalyzed Mn(III, IV) oxide reduction coupled to organic matter oxidation, with the latter being the most important source for dissolved Mn (Burdige, 1993).

Despite its low concentration in the modern oxygenated ocean, dissolved Mn(II) is necessary for carbon fixation and biomass generation in the euphotic zone, thus playing a critical role in photosynthesis (Sunda and Huntsman, 1988). While most biologically utilized Mn is recycled in the surface ocean through repeated uptake by photosynthetic organisms and the release through organic matter degradation by heterotrophic organisms, a fraction will reach the seafloor through incorporation into marine organic aggregates. In addition to biological incorporation, soluble Mn(II) can be removed from the water column through oxidation. In the modern ocean with abundant dissolved O_2, the oxidation of Mn(II) is documented in a wide range of marine settings, facilitated by Mn(II)-oxidizing microorganisms (Sunda and Huntsman, 1988). Although it has only recently been shown that Mn(II)-oxidizing microorganisms may conserve energy from the reaction (Yu and Leadbetter, 2020), many bacteria and fungi are known to mediate Mn(II) oxidation, using molecular oxygen or superoxide without energy conservation (Hansel, 2017; Nealson, 2006; Sunda and Huntsman, 1994, 1988; Tebo et al., 2005). Mn(IV) oxides have the ability to influence the availability of trace elements in the ocean including iron, cobalt, nickel, and zinc, and radionuclides, like thorium and protactinium, by particle scavenging. Mn(IV) oxides, thereby, exercise a strong control on the availability and cycling of many bio-essential and particle-reactive trace elements in the ocean (Hayes et al., 2015; Jeandel et al., 2015; Means et al., 1978; Murray, 1975; Tonkin et al., 2004; Yamagata and Iwashima, 1963).

Mn(IV) oxide particles sink to the ocean floor, and if oxygen has been consumed by heterotrophic bacteria, Mn(IV) is respired to Mn(II) coupled to organic matter oxidation, a process known as dissimilatory Mn reduction (DMR). While the general view is that the final product of DMR is Mn(II), some studies report the production of soluble or ligand-complexed Mn^{3+} (e.g., (Ehrlich, 1987; Jones et al., 2020). The Mn(II) produced during DMR is released into porewater or an anoxic water column, along with inorganic carbon, or may be organically complexed (Elderfield, 1981). Most of the Mn(II) produced by DMR during diagenesis is transported upward into the overlying oxic sediments, where through the reaction with oxygen, it is converted back into Mn(IV) oxides, with only a minor fraction escaping re-oxidation and reaching bottom waters as aqueous Mn(II) (Sundby, 1977; Thamdrup et al., 1994). It is also likely that some oxidized Mn escapes the sediment. The degree to which Mn(II) is fluxed from the sediment pile into the overlying bottom water depends on the availability of benthic O_2. The diffusive flux of Mn(II) can be enhanced through increased organic matter delivery, a higher export flux of Mn(IV) oxides, or the limited availability of alternative terminal electron acceptors for organic matter oxidation such as nitrate (Burdige, 1993), which leads to increased Mn(IV) oxide reduction.

Unlike the modern oxygenated oceans, where widespread oxidation of Mn limits the concentration of Mn(II) available to the nanomolar (10^{-9} M) range, the pervasively anoxic oceans of the early Earth would have allowed the accumulation of dissolved Mn(II) to tens or even hundreds of micromolar (10^{-6} M). Such conditions are similar to modern anoxic freshwaters, where DMR below the chemocline may result in an appreciable pool of dissolved Mn^{2+}. Notably, Brownie Lake, a modern permanently stratified anoxic iron-rich lake in Minnesota, shows a strong Mn gradient across the redox boundary in the water column with the concentration of dissolved

Mn(II) exceeding 100 μM, about five orders of magnitude higher than that observed in modern oxygenated oceans (Lambrecht et al., 2018). Similarly, the anoxic, sulfide-rich water of the Black Sea shows Mn^{2+} concentrations of up to 10 μM, suggesting a wide range for Mn(II) is possible in anoxic settings. While factors such as differences in the flux of Mn particles and rate of Mn(IV) reduction can explain such a wide range of Mn(II) concentrations in modern anoxic settings, the formation of Mn(II) sulfide minerals (e.g., alabandite and rambergite) under the sulfide-rich conditions of the Black Sea could provide a possible explanation that accounts for the lower concentration of Mn(II) in the water column than was observed by Lewis and Landing (1991). Support for such a mechanism can be drawn from reported authigenic Mn(II) sulfide minerals in the Landsort Deep in the Baltic Sea (Lepland and Stevens, 1998). Unlike iron sulfide minerals that are commonly reported and observed in a wide range of modern anoxic settings, the formation of Mn(II) sulfide minerals is less common and appears to occur in environments where the concentration of sulfide is high. For instance, synchrotron-based microprobe techniques on anoxic, sulfide-rich sediments in Fayetteville Green Lake, New York, suggest the presence of Mn(II) sulfide below the chemocline, where the concentration of sulfide reaches up to several mM (Herndon et al., 2018). There is no evidence for significant Mn(II) sulfide formation in the Archean oceans, and pervasively iron-rich and low-sulfate conditions, as indicated by numerous geochemical proxies, suggest a minor, if any, role for Mn(II) sulfide minerals in the Archean marine Mn cycle.

Another potentially important sink for reduced Mn(II) under anoxic conditions is the formation of Mn(II) carbonates. While observations from modern anoxic settings suggest that most Mn(II) produced by DMR would diffuse upward and react with oxygen to form Mn(IV) oxides at the oxic-anoxic boundary (Jones et al., 2011), a maximum of Mn(II) may form just below the boundary due to vigorous Mn(IV) oxide reduction (Herndon et al., 2018). Microbial sulfate reduction at this boundary, which produces bicarbonate via concomitant organic matter oxidation, can lead to supersaturation of pure Mn carbonates (e.g., rhodochrosite, pseudo-kutnahorite) (Jones et al., 2011). These steps are well demonstrated in Lake Matano, Indonesia, where more than 90% of the Mn(II) produced through DMR is re-oxidized, with <10 % exported as solid Mn(II) species (Jones et al., 2011). Manganese(II) carbonates have also been observed in the anoxic, iron-rich Brownie Lake in Minnesota, suggesting that formation may occur at the oxic-anoxic boundary, where the concentration of O_2 is below 5 μM (Wittkop et al., 2020). Specifically, at the chemoclines of both Brownie Lake and Lake Matano, where the concentration of O_2 falls below 5 μM, the high carbonate alkalinity pool, resulting from organic matter breakdown, in combination with elevated Mn(II) from the reduction of Mn(IV), leads to the supersaturation of Mn carbonates. While the generation of small Mn(II) carbonates deposits may be possible, it is important to note that the development of Mn(II) carbonates in these sediments requires the oxidative cycling of Mn(II) to Mn oxides, and subsequent formation of Mn carbonates during diagenesis.

3. Chemical pathways for Mn(II) oxidation

In the modern oceans, the microbially mediated oxidation of Mn(II) by molecular O_2 is the most dominant pathway for the production of Mn(IV) oxides (e.g., Tebo et al., 2005); however, Mn(IV) oxides may be produced without the involvement of O_2 through various abiotic and biotic pathways. While knowledge of potential Mn(II) oxidation pathways is key to models of biogeochemical Mn cycling under various environmental conditions, it is also critical to interpreting the record of Mn deposits that pre-date the rise of oxygen. Prior to the GOE, molecular O_2, the most potent Mn(II) oxidant, was nearly absent in the coupled ocean-atmosphere system, except for in productive surface waters where O_2 oases were likely present (Olson et al., 2013). In this section, we review the possible biotic and abiotic pathways for Mn(II) oxidation and discuss the viability of each pathway in explaining the pre-GOE Mn records (Fig. 2).

3.1 Biotic oxidation of Mn(II)

Biological oxidation of Mn(II) with O_2 by multi-copper oxidase enzymes in bacteria and related laccase enzymes in fungi has long been recognized despite the lack of energetic benefit to the organisms (Hansel, 2017) (Fig. 2a and b). Recently, a bacterium was shown to conserve energy from O_2-independent chemolithoautotrophic growth by oxidizing Mn(II), with electron transfer possibly mediated through terminal oxidases (Yu and Leadbetter, 2020). Relevant to marine environments is the oxidation of Mn(II) by superoxide, which is produced from O_2 reduction by animal haem peroxidases in bacteria and fungi (Hansel et al., 2012; Learman et al., 2011). Superoxide-mediated Mn oxide formation has recently been demonstrated for phototrophs (Chaput et al., 2019), although superoxide production is also ubiquitous in the deep ocean (Diaz et al., 2013).

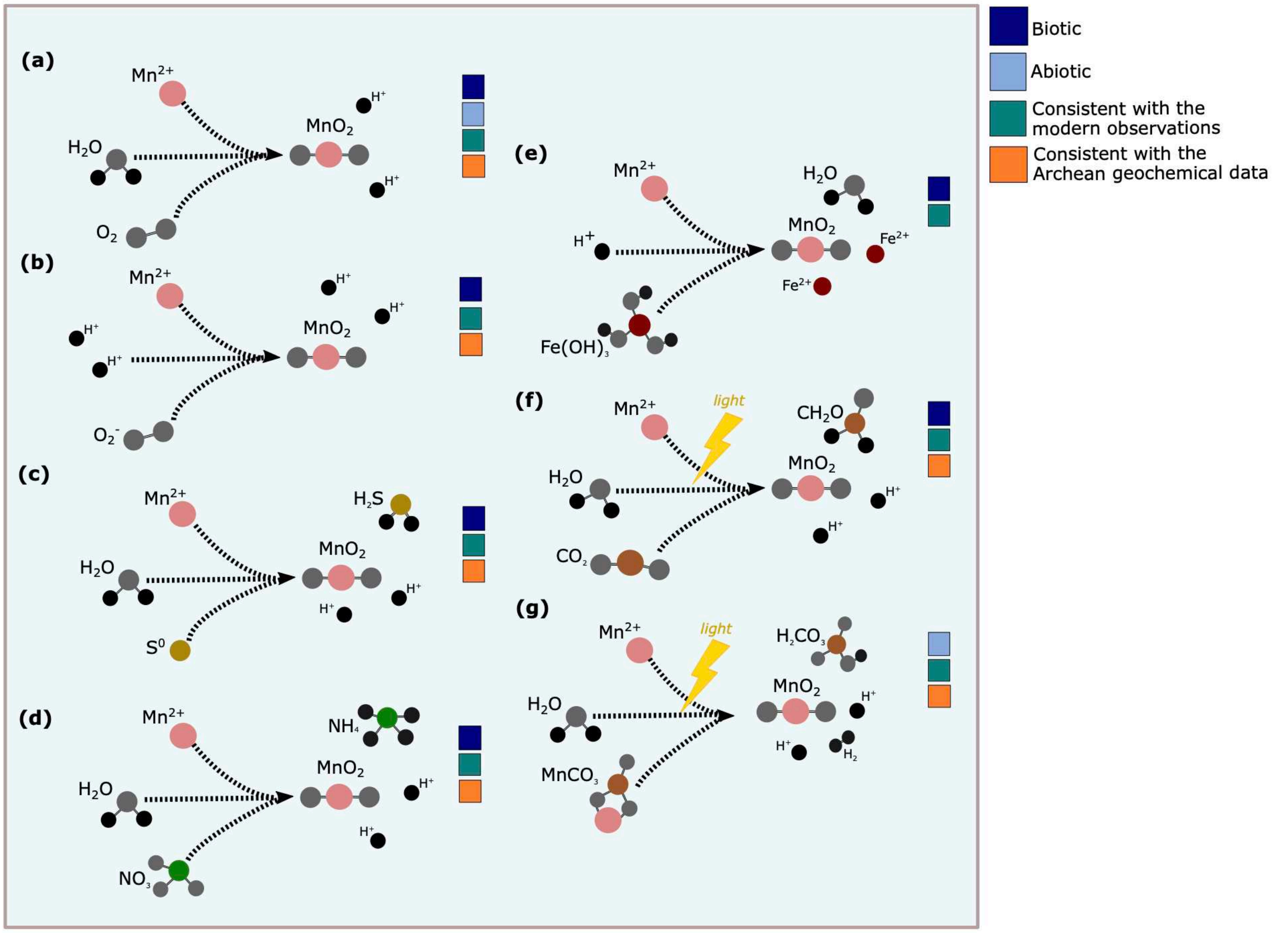


Figure 2. Possible pathways for dissolved manganese (Mn(II)) oxidation include oxidation of manganese by (a) oxygen, (b) superoxide (c) oxidized sulfur (e.g., S^0), (d) nitrate (NO_3), (e) ferric iron (Fe(III)), (f) anoxygenic phototrophy, (g) photooxidation. While there are multiple pathways for the oxidation of Mn(II) in the modern oceans, under Archean, iron-rich conditions, oxidation of manganese is most likely to occur biologically through the presence of molecular oxygen (a) or abiotically through photooxidation of Mn(II) carbonates (e.g., rhodochrosite) (g).

Perhaps the most prominent environmental signal for Mn(II) oxidation with molecular O_2 is the observation of a peak in particulate Mn concentrations at the oxic-anoxic boundary in modern redox-stratified settings (e.g., Jones et al., 2011). This peak is a direct result of the reaction of Mn(II), produced through DMR, that is transferred through molecular or turbulent diffusion to overlying oxygenated waters or porewaters, where it reacts with oxygen and generates a peak in the Mn-oxide depth profile. While a wide range of organisms facilitate the transformation of Mn(II) to Mn(IV) oxides using O_2, the biochemical and genetic details of this oxidation pathway are yet to be fully resolved.

When O_2 is absent, oxidation of Mn(II) may occur using other oxidants. For instance, by culturing biofilms recovered from a modern anoxic meromictic sulfide-rich lake, a recent study reported the formation of Mn(III, IV) oxides under anoxic conditions (Daye et al., 2019). Alternative oxidants for the formation of Mn(III,IV) oxides under such conditions remain uncertain. However, the absence of conspicuous, thermodynamically feasible oxidants in the culture medium, as well as the known capacity for sulfur metabolism and moderately high-potential photosynthetic reaction centers in the cultured microorganisms (e.g., green sulfur bacterium *Chlorobium sp*.), indirectly suggest the possible involvement of S-species in oxidizing Mn(II) (Fig. 2c). Based on their results, it is possible that Mn(II) oxidation could have been coupled with the reduction of elemental sulfur under anoxic sulfur-rich conditions:

$$CO_2 + 2H_2S + \text{light} \longrightarrow CH_2O + 2S^0_{(s)} + H_2O \qquad (1)$$

$$Mn^{2+} + S^0_{(s)} + 2H_2O \longrightarrow MnO_{2(s)} + HS^- + 3H^+ \qquad (2)$$

where the first reaction produces elemental sulfur via anoxygenic photosynthesis using hydrogen sulfide as the electron donor (the canonical metabolism of green sulfur bacteria), and the second reaction couples Mn(II) oxidation to elemental sulfur reduction (Van Cappellen et al., 1998; Henkel et al., 2019; Katsev et al., 2004). Such a pathway implies that the anoxic formation of Mn(III, IV) is possible through coupling with sulfide-based anoxygenic photosynthesis. Energetically, the second reaction is only favorable under circumneutral to mildly alkaline pH conditions and at low concentrations of sulfide. This metabolic pathway would require appreciable sulfide, likely generated through sulfate reduction, to be subsequently oxidized to elemental sulfur. However, at the same time, sulfide concentrations would need to remain below a critical threshold.

To assess the thermodynamic favourability of the formation of Mn oxides by the reaction of Mn(II) and elemental sulfur (reaction 2), we conducted a simple Gibbs Free Energy calculation (ΔG). The value of ΔG was calculated for high (100 μM) and low sulfide conditions (10 μM). To better bracket the range of environmental conditions under which this pathway can be energetically favorable, we employed a stochastic approach in which concentrations of different species were randomly selected from a range of values and the most probable range of ΔG values at different sulfide levels was obtained. The calculation was done for two different Mn oxide minerals of pyrolusite and birnessite. The ranges of Mn(II) and pH were assumed to be between 100 to 500 μM and 6 to 7, respectively, consistent with the suggested range of Mn(II) and pH in the Archean oceans (Halevy and Bachan, 2017; Jones et al., 2011). As shown in Fig. 3, thermodynamic considerations suggest that at sub-mM concentrations of Mn(II), the formation of Mn oxides is only possible if sulfide levels are below 100 μM. This sulfide range (and pH) is consistent with culture-based experiments with green sulfur bacteria and provides an explanation for the apparent anaerobic Mn(II) oxidation (Daye et al., 2019). Notably, there was an absence of Mn(III,IV) oxide mineral production in experiments with 1 μM Mn(II) or 1 mM sulfide (Daye et al., 2019).

Observations from the modern sulfide-rich Black Sea provide further support for interactions between Mn(II) and sulfur cycling under sulfidic conditions. In this case, high concentrations of hydrogen sulfide have been shown to couple with the reduction of Mn oxides, producing oxidized sulfur species (e.g., SO_4, S_2O_3) and Mn(II) (Henkel et al., 2019). This situation differs from the above mechanism where elemental sulfur oxidized Mn(II), as the high sulfide is contributing to the formation of Mn-sulfides following Mn oxide reduction (e.g., Kiratli and Ergin, 1996; Herndon et al., 2018).. Results from modern sulfide-rich freshwaters also indicate that oxidation of sulfide by Mn(IV) oxide can result in the production of sulfate and Mn(II), and the sulfate produced through this pathway can be used to oxidize the biologically produced methane in the anoxic water column (Su et al., 2020).

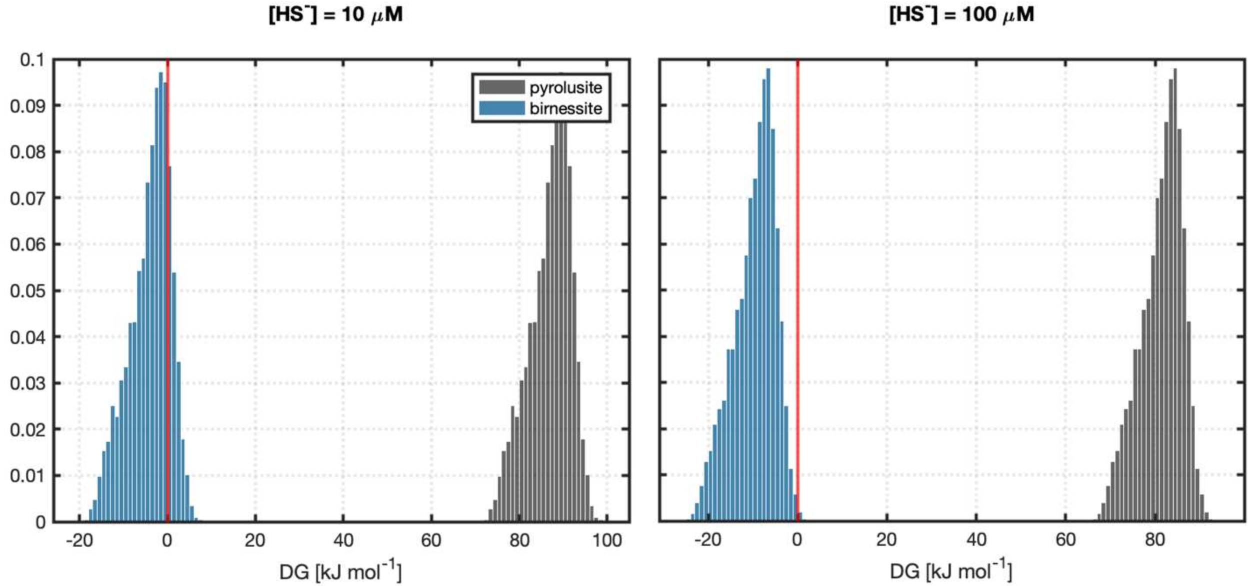


Figure 3. Gibbs-free energy estimation for the favourability of the sulfur-dependent Mn oxidation pathways at two different sulfide concentrations in seawater. Our estimation indicates that sulfur-dependent Mn oxidation is only favorable when seawater sulfide concentration is below 100 μM.

Another possible biologically mediated pathway to produce Mn oxides is through anoxygenic photosynthesis (non-O_2-producing photosynthesis) (Fig. 2f). Like ferrous iron (Fe^{2+}), anoxygenic phototrophs can theoretically oxidize Mn(II) while reducing CO_2 to biomass (Fischer et al., 2015; Olson, 1970). The formation of Fe(III) (oxyhydr)oxides by anoxygenic photosynthesis is well documented in the modern, anoxic, ferruginous freshwater systems, with implications for the formation of iron formations in the late Archean and Paleoproterozoic (Crowe et al., 2008; Ehrenreich and Widdel, 1994; Swanner et al., 2020). In contrast, the significance of photosynthetically mediated Mn(II) oxidation in modern settings remains unknown. However, recent observations from optical (UV-visible) and X-ray absorption spectroscopy have shown that through photosystem II (PSII) the light-dependent oxidation of Mn(II) can lead to the formation of a birnessite-type Mn(III, IV) oxide, providing experimental support for the possibility of ancient Mn oxidation photosystems (Chernev et al., 2020). Yet, despite these recent efforts to identify a microbe capable of photosynthetic Mn^{2+} oxidation, this metabolism has not yet been demonstrated in an extant microbial lineage.

Other potential electron acceptors for the oxidation of Mn(II) under anoxic conditions are iron oxides (e.g., $Fe(OH)_3$) and nitrate (NO_3) (Fig. 2d & 2e). The possible pathway for Mn(II) oxidation using Fe(III) is described by (Davison, 1993):

$$2\ Fe(OH)_3(s) + Mn^{2+} + 2\ H^+ \longrightarrow 2\ Fe^{2+} + MnO_2(s) + 4\ H_2O. \qquad (3)$$

This pathway may be thermodynamically feasible under mildly acidic conditions, where the concentration of dissolved ambient iron is extremely low. However, the potential for Mn oxidation with iron oxides as the electron acceptor under anoxic conditions in natural systems remains poorly constrained. Conversely, the reverse reaction – the oxidation of dissolved Fe^{2+} with MnO_2 – is possible, and well-known, under a wide range of environmental conditions (Davison, 1993; Schaefer et al., 2017). This reverse reaction is likely to be quantitatively more important and plays a critical role in separating Mn and Fe in aqueous systems. The importance of the reverse reaction is supported by observations in the geological record such as in the Sinqeni Formation (Smith and Beukes, 2023) and the Hotazel Formation (see Fig. 2 in Gutzmer and Beukes, 1995), where Mn enrichment only occurs once Fe becomes depleted, implying that any remaining Fe^{2+} reacts with any formed $Mn^{3+/4+}$, keeping it in solution until the Fe is mostly removed.

Nitrate is another thermodynamically feasible electron acceptor for the oxidation of Mn(II). Evidence for NO_3^--driven oxidation of Mn(II) is scarce in modern aqueous systems, but it may occur through the following pathways:

$$4\ Mn^{2+} + NO_3^- + 5\ H_2O \longrightarrow 4\ MnO_{2(s)} + NH_4^+ + 6\ H^+ \qquad (4)$$

$$4\ Mn^{2+} + NO_3^- + 5\ H_2O \longrightarrow NH_3 + 4\ MnO_{2(s)} + 7\ H^+\ . \qquad (5)$$

Apparent evidence for Mn(II) oxidation with nitrate as the electron acceptor can be found from the observation of Mn(IV) oxide production in sediments in which O_2 is nearly absent and there is no apparent spatial overlap between Mn(II) and O_2 in 1D depth profiles, with nitrate being the only other abundant oxidant for dissolved Mn(II) in that region of the sediment column (Boudreau et al., 1998; Jung et al., 2017; Luff and Moll, 2004). Thermodynamically, this reaction is only favorable under relatively alkaline conditions and with a high concentration of NO_3^-. Based on incubation experiments under anoxic conditions, the reduction of MnO_2 increased NO_3^- production when the MnO_2 level is high (Hulth et al., 1999). Direct tests, however, provided no evidence for Mn-dependent NH_4^+ oxidation, even in Mn oxide-rich sediments or with exogenous Mn(III) (Crowe et al., 2012).

3.2 Abiotic oxidation of Mn(II)

Production of Mn(III/IV) oxides can occur without biological involvement, although rates of abiotic oxidation reactions tend to be much slower than those characteristic of biotic pathways. The biotic oxidation of Mn by molecular O_2 is reported to be many times more rapid than the abiotic pathway (e.g., Diem and Stumm, 1984), although there is a strong pH dependence below pH 9. The sluggish kinetics of abiotic oxidation of Mn(II) can be offset by organic and inorganic catalysts, as well as reactive oxygen species. Specifically, the abiotic oxidation of Mn(II) can potentially be catalyzed by molecular O_2 or through complexation with organic compounds (e.g., ligands) (Nico et al., 2002; Duckworth and Sposito, 2005) or by Mn oxide mineral surfaces (Diem and Stumm, 1984; Davies and Morgan, 1989; Junta and Hochella, 1994). For instance, experimental studies show the possibility of abiotic oxidation of Mn(II) to amorphous Mn(III, IV) on the surface of magnetite (Fe_3O_4) and hematite (Fe_2O_3) (Ren et al. 2013). Experimental studies suggest that abiotic oxidation of Mn(II) that involves mineral surfaces can be kinetically competitive relative to the biologically-mediated oxidation of Mn(II) (e.g., Ren et al. 2013). Reactive oxygen species, on the other hand, can have both positive and negative impacts on the oxidation rate of Mn(II). For instance, superoxide (O_2^-) can result in an enhancement in the abiotic oxidation of Mn(II) while hydrogen peroxide (H_2O_2) can act as a reductant for Mn oxides (Godwin et al. 2020).

Light is another important catalyst for the abiotic oxidation of Mn(II) (Anbar and Holland, 1992; Jung et al. 2017; Liu et al., 2020) (Fig. 2g). For instance, experimental studies suggest that in the presence of light, oxidation of Mn(II) to Mn(IV) catalyzed by the superoxide radical, generated from photolysis of nitrate, can have rather fast kinetics (Jung et al. 2017). This photochemical pathway results in the formation of birnessite (Jung et al. 2017). Light energy available in the photic zone of the ocean can oxidize Mn(II) without requiring oxidants such as O_2

and elemental sulfur or high-potential photosynthetic reaction centers (Liu et al., 2020). The idea of Mn(II) and Fe(II) photooxidation is not new (Cairns-Smith, 1978), and recent experimental findings indicate that the abiotic photooxidation of rhodochrosite ($MnCO_3$) under anoxic conditions can produce manganite (Mn(III)OOH) and H_2 gas (Liu et al., 2020). Similarly, Mn(II) can be oxidized through photocatalytic reactions with superoxide radicals produced by the photolysis of nitrate (Jung et al., 2017) or on the surfaces of iron and titanium oxides (Jung et al., 2021b, 2021a). The overall pathway for such photooxidation is:

$$2\mathrm{Mn(II)CO_3} + 4\mathrm{H_2O} \xrightarrow{hv} 2\mathrm{Mn(III)OOH} + \mathrm{H_2} + 2\mathrm{HCO_3^-} + 2\mathrm{H^+}. \qquad (6)$$

The reaction described by Liu et al. (2020) is the proposed mechanism most relevant to the early oceans and proceeds at an incident wavelength of around 230 nm. This suggests a possible role for this pathway in forming Mn oxides in very shallow-water environments since the light in such UV wavelengths is strongly attenuated with depth. The plausibility of this mechanism, however, is low as rhodochrosite would not likely have accumulated to sufficiently high concentration in the photic zone of the Archean ocean (Lyons et al., 2020). Furthermore, complex solution chemistries that are closer in salinity to that of seawater have been shown to inhibit photooxidation of Fe^{2+} (e.g., Konhauser et al., 2007), suggesting that to some degree shielding by the water column may prevent widespread UV photooxidation of reduced, aqueous species.

3.3 Insights into possible Mn(II) oxidation pathways on the Archean Earth: A synthesis

Despite a wide range of possibilities for the oxidation of Mn(II) in modern oxic and anoxic settings, there are only a few biotic pathways for Mn(II) oxidation that are relevant for Archean oceans because low concentrations of Mn(II) oxidants and high concentrations of labile Mn reductants (like Fe^{2+}) would have limited Mn(II) oxidation in the absence of O_2. Assuming no O_2 involvement in the production of Archean Mn(II) oxides, the next available oxidants under anoxic conditions would have been oxidized sulfur (e.g., elemental sulfur), nitrate, and iron oxides. However, all these remain, at best, poorly supported as important Mn oxidants based on observations in modern environments and would likely have been of minor abundance in the 3.0 billion-year-old oceans. The sulfur-dependent oxidation of Mn(II), as discussed above, would likely require a high concentration of elemental sulfur. Under extremely low-sulfate conditions of the Archean oceans (Crowe et al., 2014; Habicht et al., 2002; Halevy, 2013), biologically mediated formation of elemental sulfur was likley insignificant; however, photochemical production of elemental sulfur in the atmosphere could have been an important source of the elemental sulfur to the oceans. It is nevertheless unclear if the flux of photochemically produced elemental sulfur to the surface ocean would have been large enough to result in pervasive oxidation of Mn(II), implying a limited role for elemental sulfur in the formation of Mn oxides. To this end, we note that pre-GOE sedimentary Mn-enrichments are generally lacking in sulphide minerals (Smith and Beukes, 2023; Smith et al., 2023), which would be expected to form as a byproduct of the oxidation of Mn^{2+} by elemental S through the concomitant generation of reduced sulphur (see reaction 2).

Archean nitrogen isotope records suggest an insignificant role of nitrate in the global nitrogen cycle before the GOE, implying an unimportant role, if any, in facilitating Mn(II) oxidation in anoxic waters (Mettam et al., 2019; Zerkle et al., 2017; Zerkle and Mikhail, 2017). We note that for a 2.9 Ga granular iron formation, nitrate within the water column was viewed as a potentially important oxidant for organic carbon (Smith et al., 2017). Perhaps more importantly, however, by 2.5 Ga there is evidence for the accumulation of nitrate in local environments within the Mt. McRae shale in western Australia and the Campbellrand-Malmani platform from South Africa (e.g., Garvin et al., 2009; Godfrey and Falkowski, 2009; Busigny et al., 2013). Under Archean ferruginous (Fe(II)-rich) conditions, the accumulation of Mn oxide through iron oxide reduction was also unlikely, even if iron oxides were being widely produced through photoferrotrophy, because preservation of Mn oxides would be hampered by the ambient Fe(II) in the Archean ocean (i.e., reversed reaction 3 that leads to the separation of Mn and Fe in aqueous systems) (Jones et al., 2011) (more on this below).

By analogy to the O_2-replete modern ocean, the most likely pathway for quantitatively important Archean Mn(II) oxidation would have been via molecular O_2 or superoxide produced through photosynthesis in the surface ocean. These oxidants would have reacted with available Mn(II) transported from anoxic deep waters in a manner similar to that observed in modern anoxic waters and sediments (Jones et al., 2011). Any operation of this pathway during the Archean implies the rise of oxygenic photosynthesis and at least local O_2 accumulation before the rise of atmospheric oxygen associated with the GOE. This possibly is consistent with Archean geochemical proxy records including fractionated Cr and Mo isotopes at roughly three billion years ago (Crowe et al., 2013; Planavsky et al., 2014).

Archean Mn oxides could have been produced abiotically through photooxidation. There are two main factors to consider with respect to the occurrence and importance of Mn(II) photooxidation (Liu et al., 2020) under Archean conditions: light intensity and the presence of rhodochrosite ($MnCO_3$). Photons of the required wavelengths (~230 nm) for extensive Mn(II) photooxidation were likely for the Archean oceans and continents, although solar luminosity was at about 80% of its modern value and so the light intensity incident to the outer atmosphere would have been weaker. We note, however, that radiation incident to the surface oceans would also have depended on atmospheric composition. Results from modern permanently stratified freshwater systems, as the best analogs for the chemistry of Archean oceans, point to the possibility of appreciable rhodochrosite ($MnCO_3$) formation in anoxic waters (Herndon et al., 2018; Wittkop et al., 2020). As noted above, the reduction of Mn oxides in the water column could have led to elevated dissolved Mn(II) and localized $MnCO_3$ supersaturation. Importantly, photooxidation of Mn(II) in rhodochrosite results in the production of H_2, and the H_2 released through this process could have fueled ancient microbial metabolisms and aided in Earth's surface oxygenation through hydrogen escape (Liu et al., 2020). However, two key questions remain concerning the potential role of Mn photooxidation: (i) its potential quantitative importance and (ii) the efficiency of this reaction at higher, marine salinities. Specifically, it has been questioned whether rhodochrosite would have accumulated to appreciable concentrations in the photic zone of the Archean ocean, as precipitates should have settled through the water column quickly (Lyons et al., 2020). Further, experimental work on the photooxidation of Fe by UV light has shown that photooxidation becomes negligible under solution chemistries like those expected for the Archean ocean (Konhauser et al., 2007). Notably, Mn photooxidation has only been demonstrated under relatively simple solution chemistry (Liu et al., 2020), and it remains to be seen whether this process could have occurred under conditions more representative of the Archean oceans.

4. Preservation of Mn oxides during the Archean

Regardless of the possible biotic and abiotic pathways for the production of Mn(III, IV) oxides, preservation of Mn oxides in the sedimentary rock record (delivery to the seafloor and subsequent burial) likely required a lack of Mn reductants in overlying waters. In anoxic, iron-rich Archean oceans, the reduction of Mn oxides coupled with the oxidation of organic matter and Fe^{2+} would likely have caused the dissolution of the Mn oxides before they reached the seafloor. Once on the seafloor, organic matter oxidation proceeds through a cascade of electron acceptors according to their availability and free energy yields (Froelich et al., 1979). For the preservation of Mn oxides, conditions within the sediment pile would have required that O_2 or nitrate act as the primary terminal electron acceptors during organic matter oxidation, both of which require O_2. Comparing the timescale for Mn oxide export from the water column to the kinetics of the reactions for organic- and Fe-driven Mn reduction can offer some insights into the extent of Mn oxide preservation under ferruginous Archean conditions. An important implication for paleoenvironmental interpretations is that even if Mn(IV) oxides are formed in the absence of O_2 through abiotic pathways, their delivery to the sediments would almost certainly necessitate O_2 within the water column in order to achieve export to the seafloor.

To provide an estimate of the Mn oxide preservation potential, we consider a simple calculation to estimate the settling time through the Archean ocean water column. We conservatively assume the settling velocity of Mn(IV) oxide particles to be on the order of 10 m d^{-1} (which is more than twice what is observed in the modern anoxic, iron-rich lakes (e.g., Jones et al., 2011) and depth to be around 100 meters, typical for the surface mixed-layer in the modern oceans. This leads to a settling rate for Mn oxides through a 100 m Achaean ocean water column that would have been on the order of 0.1 d^{-1}. Effective preservation of Mn oxides would only occur if the deposition rate would outcompete the destruction rate of Mn(IV) oxide through the reduction of Mn oxides by organic matter and Fe(II) oxidation. Reported rate constants for Mn reduction with organic matter are between 1 to 5 d^{-1} (e.g., Jones et al., 2011; Stumm and Morgan, 1996). These values are about an order of magnitude higher than the rate constant for the deposition of Mn oxides, suggesting that Mn oxides would have been reduced in an anoxic water column prior to burial in the sediment. Considering a depth of 10 meters for the water column, the deposition rate can be comparable to the reduction of Mn oxides by organic matter, implying that some Mn oxides may escape reduction and reach the seafloor, at depths less than 10 meters. This simple calculation, however, does not account for the reduction of Mn by Fe(II). Assuming a conservative estimate for Archean seawater Fe(II) concentration on the order of 10 μM (Konhauser et al., 2017), the rate constant of Mn reduction by Fe(II) would be on the order of 10 d^{-1} (Van Cappellen and Wang, 1996), which suggests that Mn reduction would outpace Mn oxide deposition in a water column with a depth of 10 m under anoxic and ferruginous conditions.

Observations from modern ferruginous lakes provide further insight into the potential for the preservation of Mn oxides under anoxic conditions similar to those of Archean oceans. For example, in Lake Matano, Indonesia, an almost complete reduction of Mn oxides in the water column was observed (Jones et al., 2011). Results from synchrotron-based X-ray fluorescence and X-ray spectroscopic analyses of bottom sediments and sinking particles in Lake Matano indicate a highly efficient reduction of Mn oxide under anoxic conditions, with almost no Mn oxide export to sediments underlying anoxic waters (Jones et al., 2011). These observations further indicate that the depth of Mn oxide penetration into anoxic waters is less than 2 meters, and below this depth, the oxides are reduced via oxidation of organic matter, Fe(II), H_2S, and possibly CH_4 (Jones et al., 2011). While the presence of sulfide may limit the relevance to the Archean, the ancient oceans were replete in Fe(II) whose oxidation in shallow waters would have led to enhanced Mn oxide reduction. Notably, the penetration depth depends on the settling velocity of Mn oxide particles as well as reductant concentrations. Fe(II) concentrations are expected to have been similar in the Archean oceans (Crowe et al., 2008). Further, Mn oxide settling velocities would have depended on particle size and density, as well as the extent of aggregation. In the absence of information on settling velocities in the Archean oceans, we assume that they were similar to those in modern Lake Matano. Manganese oxide penetration depths may thus have been similar in the Archean oceans, implying that under anoxic ferruginous conditions, Mn oxides would only be preserved in extremely shallow waters. This interpretation is inconsistent with suggestions of Mn oxide deposition and enrichments in sediments below wave base (>150 meters; Boggs, 1995) in the Archean-Paleoproterozoic rock record (Ostrander et al., 2019), suggesting the importance of some O_2-containing surface waters.

For instance, Mn-rich carbonates of the Hotazel Formation offer strong evidence for the diagenetic reduction of an Mn(III, IV) precursor within the sediment pile, and these were deposited below the wave base. Taken together, the above approximation of Mn oxide settling, along with the observations from the modern ferruginous lakes, suggests that while traces of Mn oxide might be potentially produced in the absence of environmental O_2, their export to sediments and preservation requires sufficiently oxidizing conditions and O_2 in order to limit the accumulation of Fe(II), which would reduce Mn oxides. The presence of O_2 would also preclude water column Mn oxide reduction by organic matter, which happens only under very low O_2 levels or anoxia. We note that in extreme cases, where sediment accumulation is very rapid, Mn oxides may be buried before they are reduced, which may complicate diagenetic pathways. Given the free energy yields of possible terminal electron acceptors, the accumulation of O_2 or nitrate, which itself requires O_2, would be required to consume organic matter and limit the reductive dissolution of Mn oxides.

The inferred preservation of Mn oxides all the way to the seafloor and isotopically light carbon in Mn-carbonates assumed to form during diagenesis thus likely required deposition from a Fe(II)-free, at least mildly oxygenated Archean water column. Collectively, these arguments yield some of our earliest geochemical evidence for O_2 accumulation in the surface ocean (Planavsky et al., 2014; Ossa Ossa et al., 2019) and thus the early occurrence of biological O_2 production during photosynthesis.

While the organic matter is generally viewed as leading to the reduction of Mn(IV) through DMR, it is also possible that some degree of association of Mn with the organic matter may insulate Mn oxides from reduction. For example, organic complexes may stabilize Mn(III) in porewaters, accounting for an appreciable fraction of the dissolved Mn pool (Madison et al., 2013). The majority of this Mn(III) is generated by the oxidation of Mn(II) by O_2 when upwardly diffusing Mn(II) reaches oxic porewaters; however, a small amount of this Mn(III) may also be attributed to Mn(IV) reduction (Madison et al., 2013). Similarly, organic matter coatings have been shown to insulate Fe(III) oxyhydroxides from reductive dissolution during diagenesis over prolonged timescales (e.g., Lalonde et al., 2012). Whether or not a similar mechanism could also stabilize Mn(III,IV) oxides remains an open question worth exploring given the similarities in the chemistry of Fe and Mn, however such relationships do not seem to enhance Mn oxide preservation in modern settings.

5. Mn oxides in the rock record

The distribution of manganese oxides has been variously used in efforts to reconstruct Earth's redox state (Fig. 4), both through temporal changes in their abundance and their relationships to other geochemical proxies. Often, the temporal trend in sedimentary Mn deposits is juxtaposed against the banded iron formation (BIF) record (Bekker et al., 2014; Maynard, 2010). While the record of Mn ores through time is in many ways decoupled from that of BIF, principally by the presence of Mn ore deposits in the Phanerozoic, there are instances where a clear positive relationship between Mn and Fe abundances is preserved, such as in the Sinqeni, Koegas, and Hotazel formations in South Africa (Smith, 2018). The decoupling of the Mn ores and BIFs, however, is not purely secular. For instance, Bekker et al. (2003) noted that Mn deposits developed following the Lomagundi excursion, but not BIFs. In part, the decoupling may be ascribed to the differential redox potentials of Fe and Mn, which is reflected in oxidation of Fe(II) prior to Mn(II) (Krauskopf, 1957) and the limited preservation potential for Mn oxides in the presence of Fe(II) as discussed above. Unlike for iron formations where the Phanerozoic record is principally ironstones, there are a number of large Phanerozoic Mn deposits (Fig. 4C). Moreover, the cessation of BIF deposition has been variously attributed to oxygenation, waning iron fluxes to the ocean, and/or the increasing importance of sulfide in the Proterozoic oceans (Bekker et al., 2014; Canfield, 1998; Holland, 1984; Konhauser et al., 2017). It has also been pointed out that large Mn ore deposits are both stratigraphically and geographically constrained relative to the widespread BIFs of the Archean and Paleoproterozoic (Maynard, 2010).

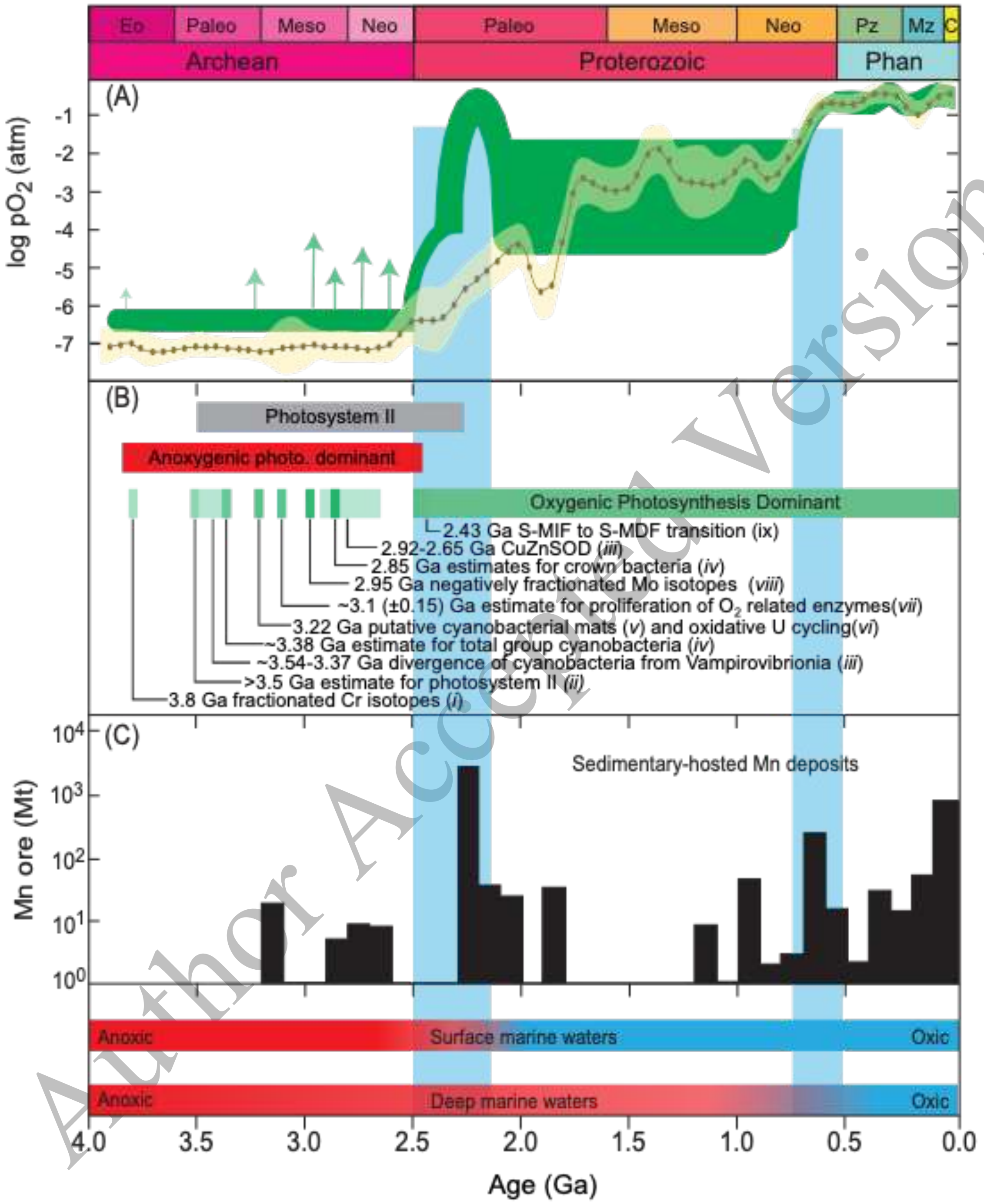

Eo
Paleo
Meso
Neo
Paleo
Meso
Neo
Pz
Mz
C
Archean
Proterozoic
Phan
(A)
log pO_2 (atm)
-1
-2
-3
-4
-5
-6
-7
(B)
Photosystem II
Anoxygenic photo. dominant
Oxygenic Photosynthesis Dominant
2.43 Ga S-MIF to S-MDF transition (ix)
2.92-2.65 Ga CuZnSOD (*iii*)
2.85 Ga estimates for crown bacteria (*iv*)
2.95 Ga negatively fractionated Mo isotopes (*viii*)
~3.1 (±0.15) Ga estimate for proliferation of O_2 related enzymes(*vii*)
3.22 Ga putative cyanobacterial mats (*v*) and oxidative U cycling(*vi*)
~3.38 Ga estimate for total group cyanobacteria (*iv*)
~3.54-3.37 Ga divergence of cyanobacteria from Vampirovibrionia (*iii*)
>3.5 Ga estimate for photosystem II (*ii*)
3.8 Ga fractionated Cr isotopes (*i*)
(C)
Sedimentary-hosted Mn deposits
Mn ore (Mt)
10^4
10^3
10^2
10^1
10^0
Anoxic
Surface marine waters
Oxic
Anoxic
Deep marine waters
Oxic
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Age (Ga)

Figure 4. (A) Models for the trajectory of oxygenation of Earth's surface environments from the Archean through to the modern, adapted from Lyons et al., (2014) (green) and G. Chen et al., (2022) (yellow), including 'whiffs of oxygen' dating back to 3.8 Ga. (B) Age constraints on the evolution of oxygenic photosynthesis, the appearance of photosystem II, and the dominance of anoxygenic photosynthesis from (i) Frei et al., (2016); (ii) Cardona et al., (2018); (iii) Boden et al., (2021); (iv) Fournier et al., (2021); (v) Homann (2019), (vi) Satkoski et al., (2015); (vii) Jabłońska and Tawfik (2021); (viii) Planavsky et al., (2014); and (ix) Warke et al., (2020) and Bekker et al., (2020, 2021). (C) The distribution of sedimentary Mn deposits through time adapted from (Maynard, 2010). (D) The redox state of shallow- and deep-marine waters after Alcott et al., (2019).

Given both the continued formation of Mn deposits into the Phanerozoic and changes in the tempo and locus of BIF deposition following the GOE, including a general decline in BIF deposition from the Paleoproterozoic to Mesoproterozoic, it was argued that the progressive oxygenation of Earth's surface environments did not exert a strong control on the abundance or distribution of Mn deposits through time (Maynard, 2010). However, it should be noted that the early Proterozoic Mn reserves in the Kalahari Mn Field, South Africa, are by far the largest (Beukes et al., 2016), they thus represent a massive Mn depositional event associated with the GOE.

Before examining the linkages between Mn formations and O_2 (Fig. 4), we briefly examine the temporal relationship of South African Mn enrichments leading up to the GOE. The Neoarchean to Paleoproterozoic Transvaal Supergroup of South Africa is preserved in three sub-basins — the Griqualand West, Transvaal, and Kanye — and displays a succession spanning the GOE (Eriksson et al., 2006; Smith and Beukes, 2016). The Griqualand West sub-basin contains the Campbellrand Subgroup, a thick succession of dolomitic carbonates overlain by several hundred meters of BIF of the Kuruman and Griquatown formations of the Asbesheuwels Subgroup (Beukes, 1984). Volcanic ash beds below the Kuruman iron formation yield U-Pb dates of 2521 ±

3 Ma (Sumner and Bowring, 1996), consistent with a maximum depositional age of 2460 ± 5 Ma for the Kuruman Formation (Pickard, 2003). New high-precision U-Pb ages generated for the Kuruman Formation through chemical-abrasion isotope-dilution thermal ionization mass spectrometry (CA-ID-TIMS) place the base of the Kuruman Formation at 2484.6±0.34 Ma and the top at 2464.0 ± 1.3 Ma (Lantink et al., 2019). Overlying the Asbesheuwels Subgroup is the Koegas Subgroup, which, in turn, is overlain by the Makganyene glacial diamictites and the volcanics of the Ongeluk Formation (Tsikos and Moore, 1997). Overlying the Ongeluk Formation is the Hotazel Formation, which hosts the extensive Kalahari Manganese Field (Gutzmer and Beukes, 1995; Tsikos et al., 2010), and is overlain by the Mooidraai Formation (Gutzmer and Beukes, 1995; Kunzmann et al., 2014; Tsikos et al., 2010). Initial U-Pb age estimates place the Ongeluk Formation at 2222 ± 13 Ma (Cornell et al., 1996), while Mooidraai Formation carbonates yield Pb-Pb and U-Pb dates of 2394 ± 26 and 2392 ± 13 Ma, respectively (Bau et al., 1999; Fairey et al., 2013). Recent Re-Os dating of the Nelani Formation of the Koegas Subgroup yields a depositional age of 2479 ± 22 Ma (Kendall et al., 2013), and U-Pb dating of Ongeluk Formation volcanics yields an age of 2426 ± 3 Ma (Gumsley et al., 2017). The importance of understanding the age of these deposits and their relation to the oxygenation of the Achaean to Paleoproterozoic atmosphere and Earth systems evolution is underscored by recent efforts to correlate the Kaapval craton with their equivalents in the Pilbara Craton of Western Australia (see Bekker et al., 2020, 2021; although see Phillipot et al., 2020, for discussion).

The Koegas Subgroup, similar to the Hotazel Formation, contains Mn-enriched intervals (Schröder et al., 2011). X-ray absorption spectroscopy reveals that Mn enrichments are generally restricted to iron formations and concentrated in Mn-bearing carbonates displaying diagenetic textures (Johnson et al., 2013). Schröder et al. (2011) determined that the terrigenous mudstone and iron formation facies contain Mn concentrations ranging from 0.1 to 11.6 wt% and 0.3 to 16.6 wt%, respectively.

While it has been suggested that the progressive oxygenation of Earth's surface environments may not strongly control Mn deposition, there are still intriguing parallels between the temporal trends in the Mn oxide and BIF records, most notably a peak in the abundance of Mn deposited at 2.4-2.0 Ga (Fig. 4C), which is dominated by the Kalahari Manganese Field of South Africa, and the general absence of Mesoproterozoic Mn deposits. Although we note the recent documentation of two pulses of Mn deposition at ~1.45 Ga and 1.11 Ga recorded in the Ullawarra Formation and Collier and Manganese groups in Western Australia, respectively, that coincide with hypothesized periods of oxygenation in the Mesoproterozoic (Spinks et al., 2023). The Kalahari Manganese Field represents a substantial reserve of Mn, with approximately 8 billion tons with Mn contents varying between 20-48% (Gutzmer and Beukes, 1996, 1995; Tsikos et al., 2003). The extensive Kalahari Manganese Field is hosted in the Hotazel Formation, which also contains several intervals of BIF and has levels of both high-grade Mn oxides and low-grade Mn ores characterized by the presence of braunite (Mn(III) silicate), as well as Mn carbonates (Fig. 5). The depleted $\delta^{13}C$ values for these carbonates suggest oxidation of organic carbon during carbonate formation (Tsikos et al., 2003). In hydrothermally altered high-grade ores, a wider array of Mn oxides is observable. Previously, the Kalahari Manganese Field was dated to about ~2.22 Ga and assumed to coincide with the GOE (Bau and Alexander, 2006). An updated Paleoproterozoic geochronology of the Kaapval craton has demonstrated that the Hotazel Formation, and by extension the Kalahari Manganese Field, is much closer to 2.4 Ga in age (Gumsley et al., 2017).This raises the significant likelihood that the Mn enrichments in the Koegas

Subgroup and the Kalahari Manganese Field are in some manner related specifically to the early onset of the GOE that likely extended over hundreds of millions of years (Poulton et al., 2021).

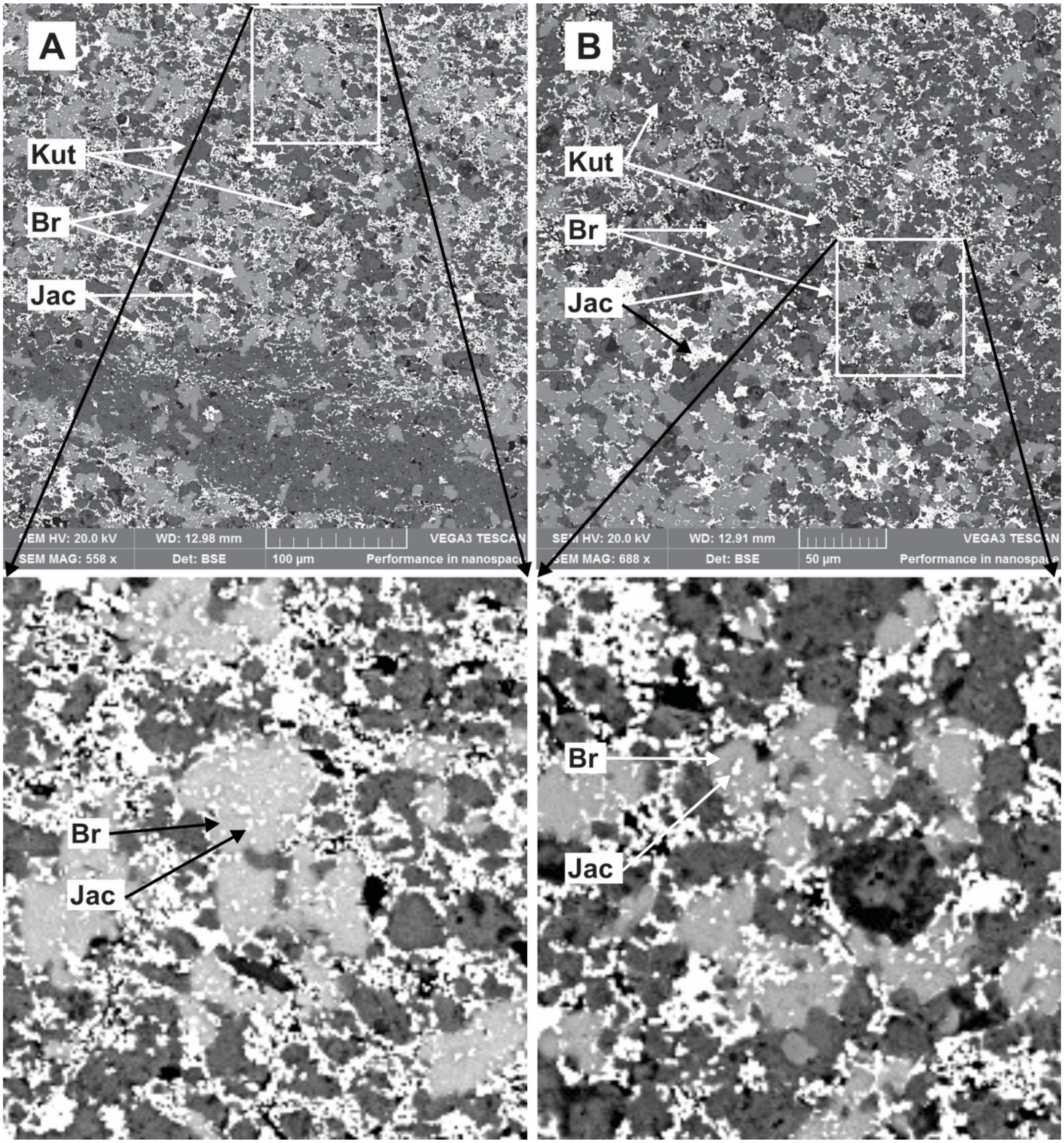


Figure 5. Backscatter electron image under scanning electron microscope showing manganese mineral occurrences in the lower (A) and upper (B) Mn intervals of the ~2.4 Ga Hotazel Formation, Transvaal Supergroup, South Africa. It appears that jacobsite (Jac; $(Mn,Mg)Fe_2O_4$) is the earliest phase as it is overgrown by or included in by braunite (Br; $Mn^{2+}Mn^{3+}_6(SiO_4)O_8$). Similarly,

kutnohorite (Kut; $CaMn^{2+}(CO_3)_2$) is interstitial to or overgrows the braunite. Given the close associations, these diagenetic mineral phases with reduced to mixed valence Mn, likely grew in close succession to one another if not near contemporaneously. Samples were collected from a core drilled on the Middelplaats farm, in the south-central Main Kalahari Deposit of the Kalahari Manganese Field. Photo credit: Dillan Fitton.

As noted above, the Hotazel Formation in South Africa is one of the world's largest Mn deposits and has been canonically linked to the onset of the Great Oxidation Event (GOE). As such, the linkages between the Hotazel Formation and the rise of oxygen, require further consideration. As detailed above recent geochronology constraints that have improved our knowledge of the Hotazel Formation's age include Re-Os dating of shales in the Koegas Subgroup (Kendall et al., 2013), and U-Pb dating of Ongeluk Formation volcanics (Gumsley et al., 2017), placing its deposition close to 2.4 Ga deposition shortly after the onset of the GOE.

The Hotazel Formation represents the youngest episode of iron formation deposition in the Transvaal Supergroup and contains extensive Mn deposits. Borehole data has revealed four units of BIF interlayered with three Mn layers consisting of braunite and Mn carbonates (Tsikos and Moore, 1997). To date, the braunite in the Hotazel Formation is the oldest occurrence of preserved oxidized Mn in the rock record. Older successions are characterized by Mn carbonates, which may reflect the effects of Mn reduction. The lower beds of the Hotazel Formation are characterized by oxide-dominated facies, whereas the middle and upper facies are dominated by silicate and carbonate minerals (Tsikos and Moore, 1997). Negative Ce anomalies, indicative of oxygenic conditions, have been documented in the lower Mn-rich beds of the Hotazel Formation (Fig. 6) (Schier et al., 2020). These are the oldest confirmed negative Ce anomalies documented from unaltered drill core (Fig. 6), providing strong evidence for a primary oxygenic signal associated with Mn deposition, and demonstrating that in the Transvaal Supergroup it appears that increasing Mn concentrations coincide with the onset and progression of the GOE.

The relative abundances of sedimentary Mn and Fe provide further information on depositional redox states and by extension the presence or absence of O_2 (Wang et al., 2022). For instance, low Fe/Mn ratios in 2.95 Ga BIF from the Sinqeni Formation indicate enrichment of Mn relative to Fe and coincide with depleted Mo isotopes that require the adsorption of light Mo onto Mn oxides (Planavsky et al., 2014). This relationship would indicate that the contemporaneous seawater was at least mildly oxygenated, with limited free Fe(II). Other lines of independent evidence support this conclusion. For example, in the Sinqeni Formation, the interval with the highest Mn enrichment is also characterized by the lightest Fe isotope values (Planavsky et al.,

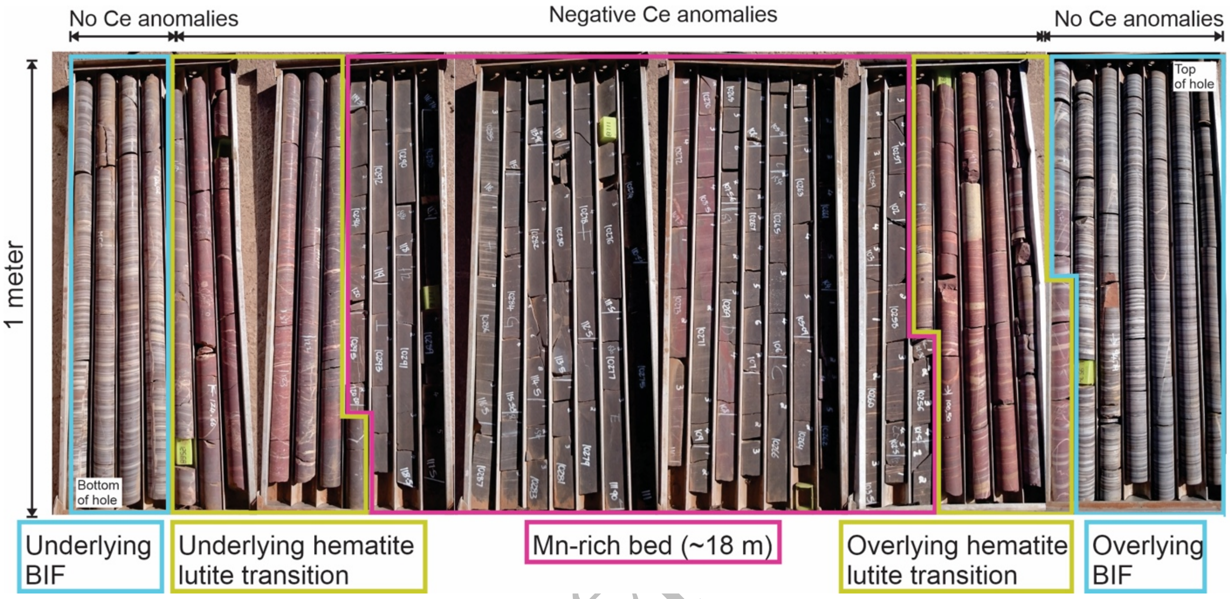


Figure 6. A combination of photographs of drill core intersecting the lower Hotazel Formation at Middelplaats Farm in the southern Kalahari Manganese Field, South Africa. Illustrated are the first (lowermost) banded iron formations to the left, the lower manganese bed in the middle, and the second banded iron formation to the right, along with the transitional hematite lutite beds below and above the lower manganese bed. Cerium anomalies, first reported by Schier et al. (2020), only occur in the hematite lutite and manganese beds.

2014; Albut et al., 2019; Heard et al., 2021). Similarly, Wang et al. (2022) documented substantial shifts in the δ^{56}Fe values and Mn/Fe ratios of ~2.5–2.4 Ga iron formations in both western Australia and South Africa, which likely reflect changing marine redox conditions across large portions of the continental margins. Specifically, as δ^{56}Fe values in these iron formations become more negative towards ~2.4 Ga, Mn/Fe ratios become higher, and a negative correlation between Mn/Fe ratios and δ^{56}Fe values is observed for all iron formation samples across this interval (Wang et al., 2022). This is the product of gradually increasing seawater O_2 levels, where light Fe isotope values develop when the oxidation of Fe at the chemocline is not quantitative (e.g., Rouxel et al., 2005; Busigny et al., 2014; Hiebert et al., 2018). This possibility would suggest that Mn oxide deposition was most intense once water column Fe oxidation removed most Fe(II), allowing Mn oxide export to underlying sediments without extensive reduction by Fe(II).

As mentioned, there are a number of Phanerozoic Mn ore deposits that may contradict a purely oxidative control on the deposition of Mn deposits through time, at least from a first-order perspective, although the oceans may have remained anoxic at depth until well into the Paleozoic (Dahl et al., 2010; Lu et al., 2018; Sperling et al., 2015; Stolper and Keller, 2018). For instance, the Late Devonian Xialei Mn deposit in the Yougiang basin, South China block, is lower Famennian in age (~372 -358.9 Ma) (Yan et al., 2020). Manganese (II) carbonates and silicates in the Xialei Mn deposit petrographically pre-date the formation of pyrite, a result of Mn(IV) being a higher energy yielding a terminal electron acceptor compared to sulfate, and were likely deposited as Mn(IV)-oxides before undergoing diagenesis and subsequent hydrothermal alteration (Yan et al., 2020). This process is effectively analogous to that proposed for the Mn shuttle in the Archean to Paleoproterozoic coinciding with BIFs deposition where oxidized Mn(IV) deposited to the sediment undergo reduction during early diagenesis. Importantly, the Mn enrichments are coupled to Mn(IV) oxide deposition. This episode of Mn oxide deposition may have been promoted by the establishment of anoxic conditions during the Fammennian (Late Devonian), allowing a build-up of appreciable dissolved Mn(II), similar to the Archean oceans prior to the GOE. This may also be interpreted as reflecting the oxygenation of the prior anoxic Paleozoic ocean and the ultimate establishment of well-oxygenated oceans (Dahl et al., 2010; Lu et al., 2018; Sperling et al., 2015; Stolper and Keller, 2018). Similarly, residual Mn(III)-bearing oxides and mixed valence Mn-silicates have been documented in both the Xialei Mn deposit and Permian Zunyi Mn deposit in South China, suggestive of primary Mn(IV) oxide reduction (Yan et al., 2022). Finally, recent parallels between petrographic microstructures observed in the Carboniferous Kalaatehe Formation and experimental incubations where Mn(IV) oxide reduction promotes Mn(II)-carbonate formation have also been documented, providing further support for the role of DMR in the formation of these massive ore deposits (Huang et al., 2022).

Two settings that may support the development of Mn deposits that warrant further consideration are O_2 minimum zones and euxinic settings (Maynard, 2010). Both of these environments may lead to the development of sedimentary Mn deposits, and both are intrinsically linked to primary production in the biosphere. Oxygen-minimum zones and euxinia develop on continental shelves and in restricted basins, respectively, due to high levels of primary productivity and flux of organic carbon to the seafloor. Here, we focus on the Carboniferous Zhaosu and Malkansu Mn deposits in China, as they offer interesting analogues to the Mn enrichments associated with O_2 minimum zones and euxinia, respectively (Dong et al., 2022, 2023). Both deposits are dominated by Mn(II)-carbonate minerals and multiple independent lines of evidence (e.g., Ce anomalies, C and Mo isotopes) indicate that the Mn(II)-carbonate ores were formed during diagenesis via the coupled oxidation of organic matter and reduction of Mn(IV)-oxides deposited from an oxygenated water column. Specifically, the Malkansu Mn ore beds are hosted within laminated, organic-rich mudstones (i.e., black shales) reflective of a relatively deep-water depositional environment. Further, Fe speciation, coupled with a high abundance of small framboidal pyrites (mean diameter ~5 μm), indicates that these black shales were deposited in euxinic (H_2S-bearing) bottom waters. Combined, the Mn-ore intervals document the sharp oxygenation of euxinic bottom waters, a process that might be induced by the periodic incursions of oxic seawater associated with eustatic sea level rises (Dong et al., 2023). By contrast, the Zhaosu Mn carbonate deposit occurs within a marine transgressive siliciclastic-carbonate succession. Given the associated limestones with strongly negative Ce anomalies, an oxic-suboxic stratified water column (most likely an O_2 minimum zone) might have characterized the Zhaosu basin during Mn deposition (Dong et al., 2022). In both scenarios, Mn mineralization is driven by the presence of an anoxic (or euxinic) water body underlying shallower oxic waters. While O_2 may not have been the primary driver of Mn mineralization in these systems, the biosphere and O_2 certainly played a role in generating the hydrographic conditions necessary for the development of these sedimentary Mn deposits.

In Fayetteville Green Lake, New York (Herndon et al., 2018), and Brownie Lake, Minnesota (Wittkop et al., 2020), primary Mn(II)-rich carbonates have been reported to form in reducing waters below a chemocline. In both cases, Mn was associated with a carbonate sediment phase, while Fe was more typically associated with sulfides. Additionally, in the Otter Lake, Michigan, Mn enrichments in carbonates have also been documented (Wittkop et al., 2014). However, these are present dominantly as manganoan siderites, which may point to previously ferruginous conditions within the Otter Lake (Swanner et al., 2020). Consistent with these observations, recent work has argued that Mn enrichments in the Griquatown and Kuruman iron formations are the result of calcite precipitation and subsequent diagenetic replacement by ankerite and siderite (Siahi et al., 2020). Note that Carboniferous Mn-carbonate ores in the Longtou Deposit, China, preserved as rhodochrosite, manganoan calcite, and braunite laminae, have similarly been suggested to form via direct Mn-carbonate precipitation, driven by the influx of Mn-rich water masses, which led to the supersaturation and precipitation of Mn carbonates (F. Chen et al., 2022). The precipitation of the Longtou Mn-carbonate ores is in part attributed to the onset of anoxia driven by the upwelling of a hydrothermal water mass. This model for the Longtou Deposit is supported by seawater-like $\delta^{13}C$ values in the carbonates that suggest a primary formation pathway rather than DMR. These recent studies demonstrate the potential for formation of Mn carbonates within the water column and may have significant implications for Archean to Paleoproterozoic Mn deposits (Tsikos et al., 2022). In several cases, however, including Fayetteville Green Lake and Brownie Lake, the precipitation of Mn carbonate depends on a strong redoxcline being present and the decoupling of Fe and Mn by sulfur. This promotes the generation of high Mn/Fe ratios within the water column. In Brownie Lake, for instance, this is achieved through a combination of sulfur cycling and iron oxidation by either photoferrotrophs or microaerophilic iron-oxidizing bacteria and results in Mn(II) concentrations in excess of 100 μM (Wittkop et al., 2020). This observation may indicate that to some degree, oxidizing conditions or at least biological Fe oxidation are necessary for generating the conditions required for the precipitation of primary Mn carbonates. Whether or not these various models for primary Mn carbonates can be applied across the Archean to Paleoproterozoic record remains an avenue for future work. In any event, each of these scenarios points to some combination of O_2, biology, and hydrographic processes generating the conditions necessary for the formation of appreciable Mn enrichments.

5. Archean oxygenation and the GOE: Genomic, geochemical, and Mn oxide evidence

While the presence of Mn oxides, or their diagenetic derivatives, has often been used as evidence of oxygenation of at least portions of the environment in the Archean, reconstructing the protracted history of oxygenation (Fig. 4) is challenging. This is compounded by imprecise and often divergent molecular clock estimates for the rise of oxygenic photosynthesis in bacteria and either trace or cryptic geochemical signals. Divergent estimates for the rise of oxygenic photosynthetic lineages span a range of over a billion years (Fig. 4B), with estimates of 2.6–2.5 Ga based on the divergence between the Oxyphotobacteria and its sister lineage Melainabacteria (Shih et al., 2016) and ~2.3 Ga based on the divergence of stem cyanobacteria molecular clocks constrained by horizontal gene transfer (Magnabosco et al., 2018). Recent work, however, pushes the emergence of oxygenic photosynthesis back even further to the early Archean, perhaps >3.5 Ga, based on molecular clock estimates for the emergence of photosystem II, which is necessary to split water in photosynthetic pathways (Cardona et al., 2018). More recently, improved models imply the emergence of cyanobacteria in the early Archean with oxygenic photosynthesis arising in the Mesoarchean, hundreds of millions of years before the GOE (Fournier et al., 2021). The origin of oxygenic photosynthesis broadly corresponded with the emergence of stem group lineages of cyanobacteria and was followed by an interval of diversification that is the time equivalent to the GOE. Similarly, a recent phylogenomic study on oxygen-producing and -utilizing enzymes suggests a rapid proliferation of these enzymes around 3.1 Ga (Jabłońska and Tawfik, 2021). Taken together, and in light of the most recent analyses, molecular biological evidence points to photosynthetic oxygen production well before the GOE, thus supporting models for Archean sedimentary Mn seafloor delivery and even enrichment based on the export of Mn oxides from at least mildly oxygenated, relatively shallow-water columns.

There has also been a focus on using a diverse suite of geochemical tracers to reconstruct Earth's oxygenation history (Fig. 4A) (see Catling and Zahnle (2020) and Lyons et al., (2021, 2014) for reviews). A more recent effort to reconstruct the history of Earth's oxygenation (Fig. 4A) has utilized machine learning approaches to estimating O_2 levels based on mafic igneous geochemistry data, producing a remarkably similar history to that based on traditional sedimentary proxies (G. Chen et al., 2022). Studies that have used sedimentary proxies have identified possible indications of O_2 within the water column and atmosphere from as early as 3.8 to 3.7 Ga based on positive chromium isotope ratios (δ^{53}Cr) and elevated U/Th ratios in BIF samples from the Isua Greenstone Belt (Frei et al., 2016). Positive δ^{53}Cr signals have also been observed in contemporaneous 3.0 Ga paleosols and BIFs, which similarly imply free O_2 in Earth's surface environments in the Mesoarchean (Crowe et al., 2013). However, the 3.0 Ga δ^{53}Cr compositions in BIFs have recently been challenged, with indications that recent oxidative weathering of outcrop rocks may have contributed to the positive δ^{53}Cr compositions in BIFs (Albut et al., 2018; Heard et al., 2021). Critically, the large-scale generation of positively fractionated δ^{53}Cr likely requires the presence of Mn oxides in continental weathering environments, as originally thought (Frei et al., 2009) or may be generated during the rapid oxidation of Mn(II) and Cr(III) within the water column (Miletto et al., 2021). In a similar fashion, Ce anomalies from outcrop samples of iron formation of the 3.22 Ga Moodies Formation have recently been shown to reflect REE mobility during more recent weathering (Bonnand et al., 2020), highlighting the potential dangers of later overprints. Additional evidence for Archean O_2 comes from oxidative uranium cycling (Satkoski et al., 2015) based on U-Th-Pb analyses of the 3.2 Ga Manzimnyama BIF, Fig Tree Group, South

Africa; putative cyanobacterial mats identified in the 3.22 Moodies Group, South Africa (Homann, 2019; Homann et al., 2018, 2015); elevated Mn/Fe ratios and a significant negative correlations between Mn/Fe ratios and δ^{56}Fe values are observed in the ~3.22 Ga Moodies BIF and other BIFs and exhalites (Hiebert et al., 2018; Wang et al., 2022) and Mn/Fe ratios and δ^{98}Mo in the ~2.95 Ga Sinqeni BIF (Planavsky et al., 2014) in South Africa; coupled S and Fe isotope values in pyrites from shallow-water stromatolitic dolostones of the 3.0 Ga Nsuze Group in South Africa (Eickmann et al., 2018); and the possibility that nitrate was available as an oxidant for organic carbon remineralization in the ~2.9 Ga Nconga Formation in southern Africa (Smith et al., 2017). A recent, detailed study of the Ijzermijn Iron Formation Bed part of the ~2.95 Ga Sinqeni Formation (Smith and Beukes, 2023) provides further evidence for environmental oxidation consistent with previous work on Mo isotopes on this formation (Albut et al., 2019; Planavsky et al., 2014). Geochemical differences between localities along the paleo-shoreline and those more distal are documented, with proximal settings being characterized by features such as C isotope depletion in carbonates and higher MnO abundances (Smith and Beukes, 2023). These spatial relations indicate that there was Mn(II) oxidation by O_2 and deposition of Mn oxides in proximal settings, followed by subsequent diagenesis; for this to occur, Fe(II) had to have been removed by oxidation in more distal settings (Smith and Beukes, 2023).

Given the above discussion of Mn oxides in the rock record and this brief history of Earth's oxygenation, we can now attempt to answer the question: *Does the history of Mn oxides support the protracted oxidation of Earth's surface environments in the build-up to the GOE?* An inverse correlation between Mn oxides and molybdenum isotopes (δ^{98}Mo) is generated through the negative fractionation of Mo during adsorption to Mn oxides, such that negative δ^{98}Mo values are observed in samples of iron formations with the lowest Fe/Mn ratios. This relationship has been observed in the 2.95 Ga Sinqeni Formation, suggesting that Mn oxide export and sedimentation delivered fractionated Mo to the sediments at the time of deposition (Planavsky et al., 2014). Despite studies such as these, however, the early history of oxygenation on Earth remains the focus of continued work. One challenging aspect is that many iron formations lack sedimentary structures, implying that deposition occurred below the wave base (e.g., Beukes and Gutzmer, 2008; Smith et al., 2013). This observation places deposition below ~100-150 m, and to some degree disconnects their deposition from the shallow oxidizing water expected at this point in Earth's history. Yet, Mn enrichments in the iron formations of the Witwatersrand Supergroup (Smith et al., 2013), the Sinqeni Formation (Albut et al., 2019; Planavsky et al., 2014; Ossa Ossa et al., 2019), and the Koegas and Hotazel formations (Wang et al., 2022) would require a substantial flux of Mn at depths below 150 m, given the lack of sedimentary structures, and by extension at least low levels of O_2 in the water column. Given the necessity for shallow waters with ambient O_2 in preserving sedimentary Mn oxide enrichments and the rise of Mn deposits preserved in the lead-up to the GOE, it is reasonable to conclude that large sedimentary Mn enrichments are linked, at least indirectly, to the presence of O_2 in the environment.

6. Conclusions

While Mn enrichments in ancient sedimentary successions are traditionally thought to reflect Earth's surface oxygenation, new observations suggest other possibilities. The potential for microbial anaerobic Mn oxidation in extant organisms and the demonstration of UV photooxidation insinuate that O_2-independent modes of Mn enrichment may have the potential to explain sedimentary Mn enrichments prior to the onset of oxygenic photosynthesis. However, although support for such pathways in laboratory settings is growing, combined consideration of the well-known environmental geochemistry of Mn and ancient depositional conditions strongly implies that such anoxic pathways had little potential to drive large-scale Mn oxide deposition in the Archean. For example, anaerobic microbial oxidation has only been achieved in a sulphidic medium (Daye et al., 2019). That sulphide should result in appreciable iron? sulphide formation and deposition. However, such occurrences are not, for example, observed in the Witswatersrand-Mozaan succession (Smith et al., 2023) and Pongola Supergroup (Smith and Beukes, 2023; Smith et al., 2023). The same deficiencies apply to the Hotazel Formation, which contains little to no sulphide minerals. Moreover, these anaerobic pathways would be unable to account for the associated geochemical proxy records, including trace element and isotopic signals (e.g., Cr, Mo) that support environmental oxygenation in pre-GOE successions. Similarly, abiotic nucleation of Mn carbonates is challenging to reconcile with existing interpretations of depleted C isotope data that point toward dissimilatory reduction of Mn oxides. Moreover, abiotic oxidation of Mn(II) through photooxidation driven by UV light is unlikely in Archean marine settings. The low likelihood of photooxidation is suggested by the expected lack of rhodochrosite in the Archean surface ocean, the locus of photooxidation, and because seawater salinities are likely to limit the effectiveness of this pathway, as has been demonstrated previously for Fe. Given these considerations, it is likely that anoxic pathways were only minor contributors to the development of appreciable Mn enrichments.

Overall, the presence of Mn enrichments, along with other geochemical proxies for oxidizing conditions such as heavy Cr or light Mo isotopic compositions or enriched RSE abundances in shales, likely reflect oxygenated water columns. Importantly, regardless of the specific mechanism of oxidation, water column O_2 is almost certainly necessary to support Mn oxide transport to the seafloor. In keeping with this view, the close association between increasing environmental oxidation in the Paleoproterozoic and Mn enrichment in sediments of the Transvaal Supergroup, notably the Hotazel Formation, suggests a causal relationship. Indeed, based on geochemical considerations, such as the ability of Fe(II) to reduce Mn(IV) oxides in the water column, it becomes apparent that preservation of large Mn enrichments almost certainly requires some degree of environmental oxygenation. Overall, this suggests that the presence of sedimentary Mn enrichments prior to the GOE requires bottom water O_2 or a redoxcline that sits near the seawater-sediment interface and would allow the export of Mn oxides. Such a model is consistent with the enrichment of Mn in Phanerozoic systems, which require oxygenated waters overlying either euxinic basins or O_2 minimum zones.

Based on the available data, we conclude that presence of Mn oxides before the rise of atmospheric O_2 and as early as 3.0 Ga is a direct result of the emergence of oxygenic photosynthesis and the onset of oxidative cycling of elements. Such a conclusion is entirely in line with recent molecular clocks that predict oxygenic photosynthesis by the Mesoarchean. Therefore, we contend that in combination with other geochemical proxies, the record of Mn enrichments in the Archean to Paleoproterozoic strongly reflects the incipient oxygenation of Earth's surface environments.

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Author contributions

LJR and MF conceived the study. All authors contributed to the discussion of ideas and writing the manuscript.

Competing Interests

The authors declare no competing interests.

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