

# Shedding light on manganese cycling in the early oceans

Timothy W. Lyons<sup>a,1</sup>, Charles W. Diamond<sup>a</sup>, and Kurt O. Konhauser<sup>b</sup>

Agreement is often in short supply within the community of researchers asking questions about Earth's earliest history. One exception, however, is the near-consensus view that oxygen ( $O_2$ ) was mostly absent from the atmosphere and oceans before about 2.4 to 2.3 Ga—the so-called Great Oxidation Event (GOE). It is also widely accepted that the cycles for iron (Fe) and manganese (Mn) in the early oceans are essential themes in our still nascent understanding of the earliest chapters of life's coevolution with its host environments at Earth's surface. Yet, despite this community accord over the importance of Fe and Mn, we still know very little about the principal pathways of oxidation for these metals and the implications for early  $O_2$ . There are three fundamental possibilities: 1) biologically mediated reactions in the presence of even small amounts of  $O_2$ , 2) anoxygenic photosynthesis with Fe(II) or Mn(II) as electron donors yielding oxidized forms of those metals as by-products, and 3) sunlight-catalyzed photochemical oxidation by ultraviolet (UV) radiation without contributions from life or  $O_2$ . The latter is perhaps the least appreciated among these three, even though abiotic reactions likely had elevated importance in early oceans as life was finding its first footholds. Liu et al. (1) refocus attention on the photochemical possibility by exploring the details of photooxidation of Mn(II) in the mineral rhodochrosite ( $MnCO_3$ ; Fig. 1) in a series of elegant experiments and by examining the implications of their results in terms of oceanic and atmospheric chemistry during the Archean Eon (4.0 to 2.5 Ga).

The idea of photooxidation of Mn and Fe in the early oceans is not new. Cairns-Smith (2), among others, pushed the concept for oxidation of dissolved  $Fe^{2+}$  to explain the ubiquity of oxidized Fe(III) present in oxide minerals such as hematite ( $Fe_2O_3$ ) in the voluminous Fe-rich deposits of Archean age. Anbar and Holland (3) followed by suggesting equally important photochemistry for Mn. They then took their experimental results for photooxidation a step further by intimating that the Fe oxides of Archean iron formations



**Fig. 1. Gem-quality crystalline rhodochrosite ( $MnCO_3$ )—an eye-catching version of the far more mundane small mineral grains that may have settled through the early oceans and accumulated on the seafloor. As the grains settled and accumulated, UV radiation may have oxidized the mineral-bound Mn(II), resulting in Mn oxides and release of  $H_2$  to the mostly  $O_2$ -lean atmosphere and biosphere. Image credit: The Arkenstone, iRocks.com.**

might have derived from reactions between photooxidized Mn and the abundant dissolved  $Fe^{2+}$  in the  $O_2$ -free (anoxic) Archean oceans. Importantly, researchers were then, as they are now, speculating creatively on alternatives to  $O_2$ -driven oxidation because  $O_2$  was in short supply in the Archean oceans and atmosphere, yet oxidized minerals often were not.

Fast-forward a decade from the paper of Anbar and Holland (3), however, and photooxidation as a significant pathway for Fe(II) was challenged in view of the interfering effects that are intrinsic to the complex chemistry of seawater—in contrast to the simplified backdrops of experimental simulations. These interferences, linked to the many dissolved components

<sup>a</sup>Department of Earth & Planetary Sciences, University of California, Riverside, CA 92521; and <sup>b</sup>Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton, AB T6G 2E3, Canada

Author contributions: T.W.L., C.W.D., and K.O.K. wrote the paper.

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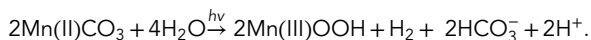
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<sup>1</sup>To whom correspondence may be addressed. Email: [timothy.lyons@ucr.edu](mailto:timothy.lyons@ucr.edu).

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of seawater, can mute the impacts of photochemistry on Fe cycling. In doing so, Konhauser et al. (4) shifted the conversation toward anoxygenic photosynthesis for Fe(II), also known as photoferroto-phy and widely observed in the modern world (5), to explain the abundant Fe oxides in Archean iron formations (6). Whether intentional or not, photooxidation as a significant process during the Archean Eon was moved to the back burner for the last two decades, leaving Mn cycling largely unexplained because an anoxygenic photosynthetic mechanism for Mn(II)—analogous to that for Fe(II)—was not known despite decades of searching (more on this below).

Liu et al. (1), to their credit, turn the light back on for photooxidation. In doing so, they focus on rhodochrosite rather than dissolved (reduced)  $Mn^{2+}$  in seawater, citing interactions involving the  $Fe^{2+}$  abounding in the same waters that limit  $Mn^{2+}$  oxidation. Determining the relative roles of mineral-bound Mn(II) in rhodochrosite versus dissolved  $Mn^{2+}$  in the photochemistry of the Archean oceans certainly remains on the must-do list of additional research. Nevertheless, the authors demonstrate convincingly that oxidation of Mn(II) in rhodochrosite can be efficient, particularly in the UV range expected from an early sun with limited atmospheric attenuation of the solar flux in the near absence of  $O_2$  and thus UV-shielding ozone ( $O_3$ ). The authors then imagine the  $H_2$  resulting from this process could have helped fuel microbial metabolisms and contributed to the progressive oxidation of Earth's surface through escape of  $H_2$  to space. The key considerations are well captured in the related net reaction:



For simplicity, we refer to oxidized Mn mineral products [the Mn(III)OOH precursor and subsequent phases formed over time] as “Mn oxides.”

This is a good place to remind the reader about the central position Mn oxide formation has played in discussions about Earth's initial oxygenation. First, let us ignore quantitatively significant abiotic photooxidation of Mn. Whether right or wrong, most authors do. If we then assume the absence of an anoxygenic photosynthetic mechanism for Mn (also a common practice), we are left with Mn oxide formation via  $O_2$  as a smoking gun for early oxygenation of the ocean-atmosphere system. This fingerprint very often calls upon proxies for the original Mn oxides—whether formed on land or in the oceans—because the primary oxides are often no longer preserved in ancient rocks. Prominent examples among those proxies include the chromium (Cr) isotope system and its applications as an  $O_2$  paleobarometer, which tie ultimately to the assumption that Cr(III) is oxidized in soils to Cr(VI) by Mn oxides that form in predictable ways that can be linked to quantifiable abundances of  $O_2$  in the atmosphere (7–9).

Similarly, formation and deposition of Mn oxides and their interactions with molybdenum (Mo), which scale at least semi-quantitatively with the presence of  $O_2$  in the oceans, have presumably driven Mo isotope variability in seawater over time (10). In fact, some of the oldest putative evidence for biological  $O_2$  production by cyanobacteria at ca. 3.0 Ga lies with Mo isotope data interpreted to reflect original fractionations via adsorption onto Mn oxides (11). Those oxides are thought to have formed in the presence of  $O_2$  in the surface waters of those prehistoric oceans. Likewise, interactions with Mn oxides assumed to form via  $O_2$ -driven oxidation are presumed to have dictated the thallium (Tl) isotope composition of the oceans over geologic time (12). It is

not necessary to be an expert in this field to imagine the after-shocks that could reverberate at scientific conferences and in the literature if appreciable Mn(II) oxidation no longer demands substantial  $O_2$ , as Liu et al. (1) suggest.

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The Archean is a distant chapter in Earth history. Not surprisingly, its secrets are not exposed easily, and the plot thickens with each step forward. Liu et al. (1), for example, remind us that Mn oxides could form abiotically through photooxidation in the absence of  $O_2$ , which could in theory drive the Cr, Mo, and Tl isotope trends seen in ancient sediments that are interpreted to reflect the presence of  $O_2$ . What's more, Daye et al. (13) recently argued for an anoxygenic photosynthetic explanation for Mn(II) oxidation, also calling into question novel metal isotope data as definitive windows to the presence and abundance of ancient  $O_2$  (see also ref. 14). In this light, future studies must focus on the fate of Mn oxides formed in ancestral oceans—regardless of the mechanisms of Mn oxidation. An essential question, for example, is whether the signals of those oxides, such as diagnostic metal isotope data, would be transferred to the sediments and thus the geologic record in the absence of  $O_2$ —rather than rapidly dissolving in the anoxic waters.

Liu et al. (1) give us a lot to think about. We might take issue, for example, with the assertion that rhodochrosite was an important mineral in Archean oceans. There is not much evidence supporting this claim. In fact, the reports are sparse other than those limited to the time around the GOE immediately following the Archean. Those relatively younger occurrences are attributed to oxide formation in the newly emerging presence of  $O_2$  and conversion to rhodochrosite in the sediments through microbial reactions that reduce Mn oxides while oxidizing organic matter. In the process, related alkalinity increases would elevate rhodochrosite saturation in pore waters. In other words, this would be rhodochrosite formed and buried in the absence of light and thus photochemistry. Consistent with this possibility, carbon isotope data for past rhodochrosite accumulations are typically attributed to microbial breakdown of organic matter in the dark sediments. If correct, the rhodochrosite did not form in the water column or on the seafloor where it could have been exposed to light.

Liu et al. (1) note examples of rhodochrosite formation in stratified water columns of modern lakes, but their relevance to ancient oceans could be questioned given the general paucity of Archean rhodochrosite occurrences. Also, rhodochrosite that might have formed in the water column could have settled rapidly within and below the photic zone—that is, beneath the uppermost layers where sunlight penetrates in sufficient amounts to drive these UV-dependent reactions. Further, concerns about the Cr isotope proxy must ask whether extensive Mn photochemistry is likely below the surface in soil horizons on land. Overall, and importantly, we are left wondering whether rhodochrosite-related reactions, although possible and even likely, were ever a significant contributor to the Archean Mn cycle.

There is still so much unknown about the initial oxygenation of the oceans and atmosphere. It is true that loss of mass independent

fractionation of sulfur at the GOE is a clear, generally unquestioned signal for the initial rise of O<sub>2</sub> in the atmosphere. Yet, many studies suggest that biologically produced O<sub>2</sub> could have accumulated to appreciable levels as vast “oases” in the surface oceans (15) or beneath microbial mats (16). These features could have facilitated Mn(II) oxidation long before its accumulation in the atmosphere at the GOE and in the deep oceans likely much later (17–19). Again, the plot thickens.

Notwithstanding the remaining questions, studies like that of Liu et al. (1) are vital. Through wonderfully robust experimentation,

they remind us that Mn cycling is diverse in its processes and products and that the preserved mineralogical, elemental, and isotopic manifestations of those twists and turns may not always be among our most compelling windows to the timeline of Earth’s earliest oxygenation. In the process, and despite any quibbles, the case has been made that photooxidation of Mn, and Fe by inference, must be placed firmly back on the table as we iterate toward a view of our early history that can be embraced for its open-mindedness and interdisciplinarity—and for the fluid, forward-looking, and constructive discourse that results.

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