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Onset of coupled atmosphere-ocean oxygenation ~2.3 billion years ago

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The initial rise of molecular oxygen (O_2) shortly after the Archean-Proterozoic transition 2.5 billion years (Ga) ago was more complex than the single step-change once envisioned. Sulfur mass-independent fractionation (S-MIF) records suggest that the rise of atmospheric O_2 was oscillatory, with multiple returns to an anoxic state until perhaps 2.2 Ga ago[1,2,3]. Yet, few constraints exist for contemporaneous marine oxygenation dynamics, precluding a holistic understanding of planetary oxygenation. Here we report thallium (Tl) isotope ratio and redox-sensitive element (RSE) data for marine shales from the Transvaal Supergroup, South Africa. Synchronous with S-MIF evidence of atmospheric oxygenation in the same shales[3], we find lower authigenic $^{205}Tl/^{203}Tl$ ratios indicative of widespread manganese (Mn) oxide burial on an oxygenated seafloor and higher RSE abundances consistent with expanded oxygenated waters. Both signatures disappear when S isotope data evidence brief returns to an anoxic atmospheric state. Our data connect recently identified atmospheric O_2 dynamics on early Earth with the marine realm, marking a turning point in Earth's redox history away from heterogeneous and highly localized "oasis"-style oxygenation.

The timing and tempo of the initial rise of molecular oxygen (O_2) on Earth, commonly referred to as the "Great Oxidation Event" (GOE), remains a topic of intense debate[4]. This debate is fueled in large measure by the links connecting O_2 to life. Large-scale O_2 production requires oxygenic photosynthesis, and so by understanding the GOE we come to better understand one of life's earliest and most profound impacts on our planet. The GOE forever changed the evolutionary trajectory of life on Earth, eventually setting the stage for the evolution and rise of animal life.

The evidence commonly referred to as a 'smoking gun' for the GOE is the disappearance of sulfur mass-independent isotope fractionation (S-MIF) from Earth's ancient sedimentary record[5]. Generation of S-MIF is mediated by photochemical reactions that occur in the absence of a stratospheric ozone (O_3) layer, and therefore requires an atmosphere with negligible amounts of the O_2 from which O_3 derives. One-dimensional photochemical models that simulate S-MIF production and preservation estimate a partial pressure of O_2 (pO_2) below 10^{-6} (0.0001%) of the present atmospheric level (PAL), what essentially amounts to trace levels of O_2[6,7].

Early datasets suggested that S-MIF sharply and irreversibly disappeared from Earth's sedimentary record 2.3 Ga ago[8,9]. This rapid disappearance is captured most clearly in sedimentary rocks from the Transvaal Supergroup from South Africa, specifically those spanning the boundary between the Rooihoogte and Timeball Hill formations. Taken at face value, these S isotope data seemed to indicate a singular and rapid atmospheric O_2 rise lasting ~1–10 million years[9]. More recent datasets have, however, uncovered multiple episodes of S-MIF disappearance and reappearance in the overlying strata[3] (Figure 1A). Similar S-MIF dynamics are found in sedimentary deposits from Western Australia[1] and Fennoscandia[2]. The minutia of these expanded datasets remains a topic of continued investigation[10,11]. Nevertheless, their most straightforward explanation remains an oscillatory initial rise of O_2 in Earth's atmosphere, lasting a few hundred million years[3,12].

While much progress has recently been made in our understanding of atmospheric O_2 dynamics across the GOE, our understanding of coeval marine O_2 dynamics has not kept pace. Before the GOE, evidence of local O_2 accumulation is found at times and places in the surface ocean – in so-called "oxygen oases" – alongside S-MIF evidence of a persistently anoxic atmosphere[13,14]. Following the disappearance of S-MIF, oceanic and atmospheric oxygenation have generally fluctuated in tandem, with changes to one directly affecting the other (albeit with some incongruency controlled by marine biogeochemical cycling, for example during Mesozoic Oceanic Anoxic Events[4]). The importance of this transition away from oasesstyle oxygenation is of major importance, as it marks the first development of a stably oxygenated global surface ocean[15]. But the timing of this transition is currently unknown.

We attempt to track this oxygenation transition using sedimentary thallium (Tl) isotope ratios (reported as $\varepsilon^{205}Tl = (^{205/203}Tl_{sample} \div {}^{205/203}Tl_{NIST-997} - 1) \times 10{,}000$). Thallium isotopes can track ancient ocean oxygenation by reconstructing past changes in seafloor manganese (Mn) oxide burial, a process that requires O_2-bearing bottom waters[16]. A uniquely large positive isotope fractionation effect is imparted on Tl during sorption to Mn oxides (up to $\alpha = 1.0021$, where $\alpha = (^{205}Tl/^{203}Tl)_{solid}/(^{205}Tl/^{203}Tl)_{solution}$), in particular hydrogenous Mn oxides that precipitate directly from oxygenated seawater and that are constituted primarily of hexagonal birnessite[17,18]. Modern seawater is enriched in the lighter-mass Tl isotope because of widespread seafloor Mn oxide burial on today's well-oxygenated seafloor (seawater $\varepsilon^{205}Tl = -6$ compared to the modern seawater input value of $\varepsilon^{205}Tl \approx -2$ [ref 19]). The seawater $\varepsilon^{205}Tl$ value is today, and was likewise probably also in Earth's past, transferred to sulfide minerals (e.g., pyrite) in sediments formed under reducing conditions (defined here as lacking sedimentary Mn oxide burial, for example in fully anoxic sediments or sediments with a shallow porewater oxygen penetration depth[20,21,22]). These sulfide minerals can be targeted with acid-leaching techniques (see Methods) and their "authigenic" Tl isotopic composition ($\varepsilon^{205}Tl_A$) can then be used as a direct estimate for the ancient seawater $\varepsilon^{205}Tl$ value[20,23].

We complement our isotopic data with sedimentary redox-sensitive element (RSE) enrichments. We focus on two RSEs: molybdenum (Mo) and uranium (U). Oxidative weathering serves as the primary input mechanism of Mo and U to modern seawater[24,25]. During this process, Mo and U are oxidized, liberated from the upper continental crust, and delivered to oceans as the soluble molybdate oxyanion (MoO_4^{2-}) and uranyl carbonate complex ($UO_2[CO_3]_3^{4-}$). These species are stable over a very long timeframe in today's well oxygenated ocean, evident by their calculated residence times of ~440 kyr for Mo[25] and ~400 kyr for U[26]. At multiple times in Earth's past, the spread of anoxic seawater dramatically decreased the solubility, and hence concentrations, of Mo and U in the global ocean. The removal efficiency of these elements is so high under anoxic conditions (anoxic and sulfidic conditions in the case of Mo[27]) that substantial reservoir drawdown is even possible under high rates of supply via oxidative weathering (e.g., during Mesozoic Oceanic Anoxic Events, when pO_2 was comparable to today[28]). Thus, seawater Mo and U reservoir sizes are modulated by changes in both oxidative weathering and global marine redox, but changes to the latter can outcompete the former. Evidence of large seawater Mo and U reservoirs is strong evidence of oxygenated oceans, especially during the Precambrian when lower pO_2 led to substantially decreased rates of oxidative weathering[4].

We apply our paleoceanographic tools to organic-rich shales from the ~2.31 to 2.22 Ga Rooihoogte and Timeball Hill formations preserved in drill core EBA-2 (Fig. 1; see Methods). The EBA-2 drill core captures the abrupt disappearance of S-MIF in the uppermost Rooihoogte Formation once thought to signify the transition to a permanently oxygenated atmosphere (~1,340 m drill-core depth[8,9]; see Fig. 1A/G). This S-MIF disappearance occurred prior to 2,316 ± 7 Ma according to a Re-Os age derived from overlying shales[29]. The EBA-2 drill core also captures the more recently identified S-MIF dynamics extending into the Timeball Hill Formation indicating a protracted, oscillatory GOE (extending upward to ~800 m core depth[3]; Fig. 1A). These S-MIF dynamics extend beyond 2,256 ± 6 Ma according to U-Pb ages derived from tuff beds located in the uppermost part of this formation[30].

Previously reported data suggested that some EBA-2 samples were deposited under the locally reducing conditions ideal for seawater ε^{205}Tl capture[3,31]. Across the Rooihoogte-Timeball Hill boundary, and concurrent with multiple S-MIF oscillations, many samples show an elevated proportion of highly reactive to total Fe (Fe_{HR}*/$Fe_T \geq 0.38$; where Fe_{HR}* includes a correction for loss of highly reactive Fe to clay minerals during early diagenesis[3]) and high total organic carbon (TOC) contents (Fig. 1). These combined signatures indicate sedimentation beneath at least locally anoxic bottom waters[32]. The new RSE data also support this interpretation. Elevated Mo and U enrichment factors (EFs; calculated relative to bulk upper continental crust[33] as Metal EF = $(\text{Metal/Al})_{\text{sample}} \div (\text{Metal/Al})_{\text{crust}}$) across the Rooihoogte-Timeball Hill boundary (Fig. 2D/E, 2J/K) indicate efficient RSE removal, and hence also require anoxic bottom waters (anoxic and sulfidic in the case of Mo[27]). This interval captures the most pronounced S-MIF fluctuations present in the EBA-2 drill core, thus providing particularly strong evidence for fluctuating atmospheric oxygen levels. Samples from the Timeball Hill Formation above ~1,300 m drill core depth were often deposited under locally oxic conditions according to Fe speciation data (Fig. 1B) and these samples are thus unlikely to always be reliable seawater ε^{205}Tl archives[3]. However, certain samples above ~1,300 m, including some that carry a S-MIF signature indicative of a return to atmospheric anoxia[3], do have elevated Fe_{HR}*/Fe_T ratios and slightly elevated U EF values, supporting anoxic water column conditions conducive to seawater ε^{205}Tl capture.

Coherent trends emerge between our paleoceanographic tools and the multiple S isotope data reported for the same samples (Fig. 3A-3C). Lower-than-crustal $\varepsilon^{205}Tl_A$ values, down to –5.1 ± 0.2, are found exclusively in samples without a clear S-MIF signature (i.e., where $\Delta^{33}S = 0.0 \pm 0.3‰$[10]; Fig. 3A). Strong Mo and U EFs, as high as Mo EF = 384 and U EF = 46, are also commonly found in these same samples (Fig. 3B-3C), although fewer samples have elevated Mo EF due to the additional requirement for elevated water column sulfide concentrations[27]. The opposite trends, higher $\varepsilon^{205}Tl_A$ values and lower Mo and U EFs, are found in S-MIF-bearing samples, including those that document short-lived intervals of atmospheric anoxia in the upper part of the succession (i.e., above ~1,300 m).

The geochemical coherence found across the Rooihoogte-Timeball Hill formation boundary supports a coupled relationship between atmospheric and oceanic oxygenation, rather than a decoupled oxygen 'oasis' scenario. Lower $\varepsilon^{205}Tl_A$ values indicate widespread burial of Mn oxides beneath O_2-bearing bottom waters on the seafloor at the same time S-MIF loss indicates atmospheric oxygenation. This inference is corroborated by the coeval Mo and U enrichments, which require some combination of widespread oxygenated seawaters and intensified oxidative weathering on land. By contrast, higher $\varepsilon^{205}Tl_A$ values indicate little to no seafloor Mn oxide burial at the same time S-MIF signals indicate a return to an anoxic atmospheric state. This is again corroborated by the RSE data, which require some combination of expanded anoxia on the seafloor and less intense oxidative weathering on land to account for the generally much smaller enrichments.

Alternative means for driving low sedimentary $\varepsilon^{205}Tl_A$ values do exist, but none of them appear applicable in this case. It is possible that biomass may preferentially incorporate the lighter-mass Tl isotope, and if so sediments that receive a large proportion of their Tl from biomass could have low $\varepsilon^{205}Tl$ values[22]. More work is warranted on the topic, but this scenario seems unlikely based on currently available Tl isotope data; no modern marine sediments studied to this point possess low $\varepsilon^{205}Tl_A$ values that can be convincingly linked to delivery of Tl via biomass[21,22]. Previous work has established that the EBA-2 drill-core was deposited near an ancient redoxcline[31], and therefore the general sample-to-sample $\varepsilon^{205}Tl_A$ scatter found near the Rooihoogte-Timeball Hill formation boundary (Fig. 1L) could also be linked to local redox changes (e.g., redox changes that promote Mn oxide formation and dissolution). Changes in terrigenous influx seem an unlikely explanation for the observed trends, as is also the case for the multiple S isotope variations[10], because this material would be expected to have a $\varepsilon^{205}Tl$ value more or less similar to average upper continental crust, with $\varepsilon^{205}Tl \approx -2$.

Low inferred seawater $\varepsilon^{205}Tl$ values near the Rooihoogte-Timeball Hill formation boundary suggest sufficient bottom water O_2 accumulation for widespread burial of Mn oxides. Uncertainties surrounding the flux per areal unit of Tl removal into the different types of marine sediments deposited during the GOE, or what the different sediment types even were, preclude quantitative estimations of the areal extent of seafloor oxygenation[34]. Additional uncertainties associated with ancient ocean mixing timescales and seawater Tl residence times complicate assumptions of a globally homogenous seawater Tl reservoir. Nonetheless, it stands to reason that a low seawater ε^{205}Tl value, and by extension also the oxic area of seafloor Mn oxide burial required to promote it, was at least regional in extent, and potentially occurred over a significant portion of the global seafloor. The dissolved seawater Mn reservoir before the GOE was very large, perhaps four orders of magnitude larger than today[35], because reduced Mn(II) is more soluble than its oxidized Mn(III/IV) counterparts and would have been the predominant stable form of Mn in an overwhelmingly anoxic global ocean. Hence, in the relatively small areas of the Paleoproterozoic shallow ocean that were persistently oxygenated, Mn oxide burial rates could have been very high, exerting substantial leverage on seawater ε^{205}Tl values. Consistent with this prediction, the world's largest sedimentary Mn deposit, the ~2.4 Ga old Hotazel Formation in South Africa[36], is also found at a time of inferred atmospheric O_2 instability prior to the end of the GOE[12].

Anaerobic Mn-oxidation pathways are sometimes invoked as an alternative means for explaining evidence of Mn-oxide precipitation prior to the GOE. The two most commonly invoked pathways are anoxygenic photosynthesis (via Mn-oxidizing phototrophs[37,38]) and abiotic photo-oxidation (via UV-light[39]). Crucially, both pathways are light-dependent and would thus have been relegated exclusively to the photic zone. Even if formed in this manner, Mn oxides would be very unlikely to survive transit through anoxic waters below the photic zone, let alone long-term burial in sediments with persistently anoxic pore waters[34]. Thallium would be released back into the water column during the reductive dissolution process, preventing a net isotope fractionation effect[22].

An absence of low $\varepsilon^{205}Tl_A$ values above ~1,300 m core depth in the Timeball Hill Formation is notable and seems to indicate less prolific Mn oxide burial on the seafloor over this extended period. Muted Mn oxide burial does not necessarily imply less widespread oxygenated bottom waters. Rather, a diminished dissolved seawater Mn(II) reservoir was more likely to blame (illustrated in Fig. 3). Surface ocean oxygenation was generally more stable after S-MIF loss ~2.3 Ga ago[15], equating to a larger area of seafloor capable of burying Mn oxides. However, burial in each individual environment would now be limited by lowered Mn(II) availability. If this hypothesis is correct, then ~2.3 Ga could mark a dramatic turning point for the global marine Mn cycle.

Earth surface redox ~2.3 Ga ago was clearly different from the preceding time interval; pO_2 was higher and fluctuated in concert with at least regional changes in ocean oxygenation. Evidence of regional seawater oxygenation is found ~2.5 Ga ago and before, but always alongside S-MIF evidence of a functionally anoxic atmosphere[14]. Two particularly prominent transient "whiffs" of oxygen are identified in the late Archean sedimentary record ~2.65 Ga and ~2.50 Ga ago. The younger ~2.50 Ga old event was particularly strong according to, amongst other data, Mo EF values as high as 82 and ε^{205}Tl values as low as –4.3 in organic-rich shales from the Mount McRae Shale, Western Australia[34,40]. And yet, S-MIF remained a persistent, uninterrupted feature of the sedimentary record across this event[41]. Compare these signals to those recovered from the Rooihoogte and Timeball Hill formations (Fig. 2). Higher Mo EF values, up to 384, indicate more intense oxidative weathering on land (note however that an expanded area of emerged, weatherable land[42] could also have contributed to this Mo EF increase). Higher U EF values, up to 46, are even more compelling. Unlike Mo, U is not strongly enriched in shales formed during the ~2.50 Ga whiff event (U EF values are less than 3[42]). The lack of U enrichment in the older shales is probably due to the higher oxidation requirements of uraninite (UO_2), the primary crustal U host, relative to sulfides, the primary crustal Mo host[44]. In other words, the partial pressure of O_2 in Earth's atmosphere ~2.50 Ga ago was sufficiently high to promote widespread oxidative sulfide weathering on land, but not high enough to promote widespread oxidative UO_2 weathering. This apparently changed by ~2.3 Ga ago according to our dataset.

The GOE signifies a tipping point in Earth's O_2 mass-balance[35,45]. For the first time on a global scale, net production of O_2 during oxygenic photosynthesis outpaced O_2 destruction by reducing minerals exposed at Earth's surface and reducing gases released from its interior. At first, production did not dramatically outpace destruction. This allowed for brief reversals in the relationship, for example when oscillatory changes in biogenic fluxes of reduced gases led to transient increases in the rate of O_2 destruction[46]. These reversals affected both the atmospheric and oceanic realm according to our new data. Only much later, after what seems to have been a few hundred-million-years after initial S-MIF loss, did O_2 sources sufficiently outpace O_2 sinks to forever oxygenate our planet[3]. Oxygenation was progressive and manifested early on only as transient events. These events increased in strength with time leading up to the tipping point, as O_2 mass-balance progressively shifted in favor of accumulation. Empirical evidence supports this claim, with oxygenation episodes of seemingly increasing magnitude identified at ~2.65 Ga, ~2.50 Ga, and now ~2.32 Ga ago.

References

1. Philippot, P., Avila, J.N., Killingsworth, B.A., Tessalina, S., Baton, F., Caquineau, T., Muller, E., Pecoits, E., Cartigny, P., Lalonde, S.V., Ireland, T.R., Thomazo, C., Van Kranendonk, M.J., Busigny, V., 2018. Globally asynchronous sulphur isotope singals require re-definition of the Great Oxidation Event. Nature Communications 9, 2245.

2. Warke, M.R., Rocco, T.D., Zerkle, A.L., Lepland, A., Prave, A.R., Martin, A.P., Ueno, Y., Condon, D.J., Claire, M.W., 2020. The Great Oxidation Event preceded a Paleoproterozoic "snowball Earth". Proceedings of the National Academy of Sciences 117, 13314-13320.
3. Poulton, S.W., Bekker, A., Cumming, V.M., Zerkle, A.L., Canfield, D.E., Johnston, D.T., 2021. A 200-million-year delay in permanent atmospheric oxygenation. Nature 592, 232-236.
4. Lyons, T.W., Reinhard, C.T., Planavsky, N.J., 2014. The rise of oxygen in Earth's early ocean and atmosphere. Nature 506, 3017-315.
5. Farquhar, J., Bao, H., Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur cycle. Science 289, 756-758.
6. Pavlov, A.A., Kasting, J.F., 2002. Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. Astrobiology 2, 27-41.
7. Catling, D.C., Zahnle, K.J., 2020. The Archean atmosphere. Science Advances 6, eaax1420.
8. Bekker, A., Holland, H.D., Wang, P.-L., Rumble III, D., Stein, H.J., Hannah, J.L., Coetzee, L.L., Beukes, N.J., 2004. Dating the rise of atmospheric oxygen. Nature 427, 117-120.
9. Luo, G., Ono, S., Beukes, N.J., Wang, D.T., Xie, S., Summons, R.E., 2016. Rapid oxygenation of Earth's atmosphere 2.33 billion years ago. Science Advances 2, e1600134.
10. Izon, G., Luo, G., Uveges, B.T., Beukes, N., Kitajima, K., Ono, S., Valley, J.W., Ma, X., Summons, R.E., 2022. Bulk and grain-scale minor sulfur isotope data reveal complexities in the dynamics of Earth's oxygenation. Proceedings of the National Academy of Sciences 119, e2025606119.
11. Uveges, B.T., Izon, G., Ono, S., Beukes, N.J., Summons, R.E., 2023. Reconciling discrepant minor sulfur isotope records of the Great Oxidation Event. Nature Communications 14, 279.
12. Gumsley, A.P., Chamberlain, K.R., Bleeker, W., Söderlund, U., De Kock, M.O., Larsson, E.R., Bekker, A., 2017. Timing and tempo of the Great Oxidation Event. Proceedings of the National Academy of Sciences 114, 1811-1816.
13. Olson, S.L., Kump, L.R., Kasting, J.F., 2013. Quantifying the areal extent and dissolved oxygen concentrations of Archean oxygen oases. Chemical Geology 362, 35-43.
14. Ostrander, C.M., Johnson, A.C., Anbar, A.D., 2021. Earth's first redox revolution. Annual Review of Earth and Planetary Sciences 49, 337-366.
15. Reinhard, C.T., Planavsky, N.J., 2022. The history of ocean oxygenation. Annual Review of Marine Science 14, 331-353.
16. Calvert, S.E., Pedersen, T.F., 1996. Sedimentary geochemistry of manganese: implications for the environment of formation of manganiferous black shales. Economic Geology 91, 36-47.

17. Rehkämper, M., Frank, M., Hein, J.R., Porcelli, D., Halliday, A., Ingri, J., Liebetrau, V., 2002. Thallium isotope variations in seawater and hydrogenetic, diagenetic, and hydrothermal ferromanganese deposits. Earth and Planetary Science Letters 197, 65-81.
18. Phillips, R.F., Wang, Y., Klein, F., Farfan, G., Ostrander, C.M., Gadol, H., Hansel, C.M., Nielsen, S.G., 2023. The role of manganese oxide mineralogy in thallium isotopic fractionation upon sorption. Geochimica et Cosmochimica Acta 356, 83-92.
19. Nielsen, S.G., Rehkämper, M., Prytulak, J., 2017. Investigation and application of thallium isotope fractionation. Reviews in Mineralogy and Geochemistry 82, 759-798.
20. Owens, J.D., Nielsen, S.G., Horner, T.J., Ostrander, C.M., Peterson, L.C., 2017. Thallium-isotopic compositions of euxinic sediments as a proxy for global manganese-oxide burial. Geochimica et Cosmochimica Acta 213, 291-307.
21. Wang, Y., Lu, W., Costa, K.M., Nielsen, S.G., 2022. Beyond anoxia: Exploring sedimentary thallium isotopes in paleo-redox reconstructions from a new core top collection. Geochimica et Cosmochimica Acta 333, 347-361.
22. Ostrander, C.M., Nielsen, S.G., Gadol, H.J., Villarroel, L., Wankel, S.D., Horner, T.J., Blusztajn, J., Hansel, C.M., 2023. Thallium isotope cycling between waters, particles, and sediments across a redox gradient. Geochimica et Cosmochimica Acta 348, 397-409.
23. Nielsen, S.G., Goff, M., Hesselbo, S.P., Jenkyns, H.C., LaRowe, D.E., Lee, C.A., 2011. Thallium isotopes in early diagenetic pyrite – A paleoredox proxy? Geochimica et Cosmochimica Acta 75, 6690-6704.
24. Dunk, R.M., Mills, R.A., Jenkins, W.J., 2002. A reevaluation of the oceanic uranium budget for the Holocene. Chemical Geology 190, 45-67.
25. Miller, C.A., Peucker-Ehrenbrink, B., Walker, B.D., Marcantonio, F., 2011. Re-assessing the surface cycling of molybdenum and rhenium. Geochimica et Cosmochimica Acta 75, 7146-7179.
26. Ku, T.-L., Mathieu, G.G., Knauss, K.G., 1977. Uranium in open ocean: concentration and isotopic composition. Deep Sea Research 24, 1005-1017.
27. Erickson, B.E., Helz, G.R., 2000. Molybdenum (VI) speciation in sulfidic waters: stability and lability of thiomolybdates. Geochimica et Cosmochimica Acta 64, 1149-1158.
28. Hetzel, A., Böttcher, M.E., Wortmann, U.G., Brumsack, H.-J., 2009. Paleo-redox conditions during OAE-2 reflected in Demerara Rise sediment geochemistry (ODP Leg 207). Palaeogeography, Palaeoclimatology, Palaeoecology 273, 302-328.
29. Hannah, J.L., Bekker, A., Stein, H.J., Markey, R.J., Holland, H.D., 2004. Primitive Os and 2316 Ma age for marine shale: implications for Paleoproterozoic glacial events and the rise of atmospheric oxygen. Earth and Planetary Science Letters 225, 43-52.

30. Rasmussen, B., Bekker, A., Fletcher, I.R., 2013. Correlation of Paleoproterozoic glaciations based on U-Pb zircon ages for tuff beds in the Transvaal and Huronian Supergroups. Earth and Planetary Science Letters 382, 173-180.
31. Zerkle, A.L., Poulton, S.W., Newton, R.J., Mettam, C., Claire, M.W., Bekker, A., Junium, C.K., 2017. Onset of the aerobic nitrogen cycle during the Great Oxidation Event. Nature 542, 465-467.
32. Raiswell, R., Hardisty, D.S., Lyons, T.W., Canfield, D.E., Owens, J.D., Planavsky, N.J., Poulton, S.W., 2018. The iron paleoredox proxies: a guide to the pitfalls, problems and proper practice. American Journal of Science 318, 491-526.
33. Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. In *The Crust*, v.3 (ed. R.L. Rudnick). Elsevier, 1-64.
34. Ostrander, C.M., Nielsen, S.G., Owens, J.D., Kendall, B., Gordon, G.W., Romaniello, S.J., Anbar, A.D., 2019. Fully oxygenated water columns over continental shelves before the Great Oxidation Event. Nature Geoscience 12, 186-191.
35. Holland, H.D., 1978. *The Chemistry of the Atmosphere and Oceans.* 351 pp., John Wiley. New York.
36. Kirschvink, J.L., Gaidos, E.J., Bertani, L.E., Beukes, N.J., Gutzmer, J., Maepa, L.N., Steinberger, R.E., 2000. Paleoproterozoic snowball Earth: Extreme climatic and geochemical global change and its biological consequences. Proceedings of the National Academy of Sciences 97, 1400-1405.
37. Johnson, J.E., Webb, S.M., Thomas, K., Ono, S., Kirschvink, J.L., Fischer, W.W., 2013. Manganese-oxidizing photosynthesis before the rise of cyanobacteria. Proceedings of the National Academy of Sciences 110, 11238, 11243.
38. Daye, M., Klepac-Ceraj, V., Pajusalu, M., Rowland, S., Farrell-Sherman, A., Beukes, N., Tamura, N., Fournier, G., Bosak, T., 2019. Light-driven anaerobic microbial oxidation of manganese. Nature 576, 311-314.
39. Liu, W., Hao, J., Elzinga, E.J., Piotrowiak, P., Nanda, V., Yee, N., Falkowski, P.G., 2020. Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. Proceedings of the National Academy of Sciences 117, 22698-22704.
40. Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., Kaufman, A.J., Gordon, G.W., Scott, C., Garvin, J., Buick, R., 2007. A whiff of oxygen before the great oxidation event? Science 317, 1903-1906.
41. Kaufman, A.J., Johnston, D.T., Farquhar, J., Masterson, A.L., Lyons, T.W., Bates, S., Anbar, A.D., Arnold, G.L., Garvin, J., Buick, R., 2007. Late Archean biospheric oxygenation and atmospheric evolution. Science 317, 1900-1903.

42. Bindeman, I.N., Zakharov, D.O., Palandri, J., Greber, N.D., Dauphas, N., Retallack, G.J., Hofmann, A., Lackey, J.S., Bekker, A., 2018. Rapid emergence of subaerial landmasses and onset of a modern hydrologic cycle 2.5 billion years ago. Nature 557, 545-548.
43. Kendall, B., Brennecka, G.A., Weyer, S., Anbar, A.D., 2013. Uranium isotope fractionation suggests oxidative uranium mobilization at 2.50 Ga. Chemical Geology 362, 105-114.
44. Sverjensky, D.A., Lee, N., 2010. The great oxidation event and mineral diversification. Elements 6, 31-36.
45. Catling, D., 2014. The Great Oxidation Event transition. In *Treatise on Geochemistry*, ed. Holland, H.D., Turekian, K.K., pp. 177-195. Oxford, UK. Elsevier, 2nd edition.
46. Wogan, N.F., Catling, D.C., Zahnle, K., Claire, M.W., 2022. Rapid timescale for an oxic transition during the Great Oxidation Event and the instability of low atmospheric O2. Proceedings of the National Academy of Sciences 119, e2205618119.
47. Nielsen, S.G., Rehkämper, M., Porcelli, D., Andersson, P., Halliday, A.N., Swarzenski, P.W., Latkoczy, C., Günther, D., 2005. Thallium isotope composition of the upper continental crust and rivers – an investigation of the continental sources of dissolved marine thallium. Geochimica et Cosmochimica Acta 69, 2007-2019.
48. Reinhard, C.T., Raiswell, R., Scott, C., Anbar, A.D., Lyons, T.W., 2009. A late Archean sulfidic sea stimulated by early oxidative weathering of the continents. Science 326, 713-716.

Figure captions

Figure 1: Geochemistry of the EBA-2 drill core from South Africa. (A,G) Oscillations in atmospheric O_2 between ~2.32 Ga and ~2.22 Ga ago are captured by fluctuating S-MIF ($\Delta^{33}S$) signals that extend into the upper Timeball Hill Formation[3,9]. Note that some of these samples do not have accompanying Fe speciation or trace metal data (signified with + datapoints). **(B,H)** Elevated Fe_{HR}/Fe_T ratios and **(C,I)** TOC abundances suggest that these sedimentary rocks were deposited beneath an anoxic water column near the Rooihoogte-Timeball Hill boundary; above this boundary, muted values suggest formation beneath an oxygenated water column[3,31]. All datapoints are colored according to the local redox conditions suggested by their respective Fe speciation data (see legend in panel B). New **(D,J)** Mo and **(E,K)** U enrichment factor data support these local redox constraints (see the text). These redox-sensitive element data, together with **(F,L)** new $\varepsilon^{205}Tl_A$ data, provide novel information about marine redox conditions during the GOE. Data are compiled from this and previous studies[3,9,31]. Error bars in panels F and L are in 2SD and are either equal to the individual sample's reproducibility or the USGS shale SCo-1 reproducibility, whichever is greater. Stratigraphic column is modified from previous work[3]. The depositional age in the lower panel is based on shale Re-Os geochronology[29]. The gray-shaded area in the $\Delta^{33}S$ data panel signifies the typical mass-

dependent fractionation range of 0.0 ± 0.3‰[10]. The brown-shaded area in the ε^{205}Tl panel signifies the estimated average for upper continental crust[47]. R. = Rooihoogte Formation and R.D. = Rietfontein Diamictite.

Figure 2: Geochemical comparison of Paleoproterozoic shales targeted in this study versus older Archean shales that evidence an early "whiff" of O_2. The more pronounced shifts in the younger shales **(A–C)** track paired oscillations in atmospheric and marine O_2, whereas the muted trends in the older shales **(D–F)** – all of which bear S-MIF signals – track isolated oxygen oases. Data are from drill cores EBA-2 and ABDP9 and are compiled from this and previous studies[3,34,40,41,43]. The gray shaded area refers to unfractionated Δ^{33}S values of 0.0 ± 0.3‰[10]. The brown-shaded area signifies the estimated average ε^{205}Tl value for upper continental crust[48]. Datapoints are colored based on local redox conditions, as identified by Fe_{HR}/Fe_T[3,31,48] (see Fig. 1 legend).

Figure 3: Conceptual schematic of hypothesized changes to the dissolved seawater Mn(II) reservoir and seafloor Mn oxide burial as a result of oscillatory oxygenation during the GOE. Consequent effects on sedimentary S and Tl isotope trends are also included.

Materials and Methods

The Rooihoogte and Timeball Hill formations in drill core EBA-2

Samples targeted in this study come from the EBA-2 core (26.4700ºS, 27.5883ºE) drilled near Carltonville in South Africa (Kloof Goldfields Property, Eastern Boundary Area). Many of the same drill core depths were targeted in previous work[3,31]. The studied interval comprises the Rooihoogte and Timeball Hill formations, and the succession has been subjected to only lower greenschist facies regional metamorphism[49]. The upper part of the Rooihoogte Formation predominantly consists of mudstone and black shale that coarsens upwards into siltstone, with a thin chert breccia at the top[49]. The Timeball Hill Formation comprises two upward coarsening sequences where the lower part of both sequences is composed of highly carbonaceous black mudstone[50]. The mudstones in each sequence become less carbonaceous up-section, and are interbedded with dark-grey to grey siltstones. The mudstones and black shales of the upper Rooihoogte and Timeball Hill formations were deposited in a pro-delta setting, which is generally thought to have had open connection to the ocean to the southwest[49,51,52,53]. The upper sequence of the Timeball Hill Formation is capped by a glacial diamictite and conglomerate of the Reitfontein Member[50].

Thallium isotope ratios

Samples were prepared for Tl isotope ratio analysis in the NIRVANA Laboratory at Woods Hole Oceanographic Institution (WHOI). Roughly 200 mg of finely powdered material from each targeted EBA-2 drill core depth was transferred to a pre-cleaned perfluoroalkoxy alkane (PFA) vial (Savillex) and subjected to an overnight 2 M HNO_3 leach shown in previous work to successfully isolate authigenic (seawater-derived) Tl from detrital (terrigenous-derived) Tl[20,23,54]. Once leached, samples were centrifuged, the supernatant pipetted into a new pre-cleaned PFA vial, and digested to completion on hot plates using a series of concentrated acid mixtures. To avoid digesting any detrital Tl inadvertently transferred after centrifugation, HF was not used at any point during digestion (only HNO_3, HCl, and H_2O_2). Before Tl isotope analysis, samples were purified from matrix elements via a two-step ion-exchange chromatography[55,56].

Thallium isotope ratio measurements were performed following procedures outlined in previous work[55,56] and using a Thermo Finnigan Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) located at the WHOI Plasma Mass Spectrometry Facility. A desolvating nebulizer system was used during sample introduction (Aridus II) and measurements were performed in low-resolution mode using sample-standard bracketing and external normalization to NIST SRM 981 Pb. NIST SRM 997 was used as the bracketing standard; all ε^{205}Tl data are calculated relative to this standard. Because each sample was doped with a known quantity of NIST SRM 981 Pb, authigenic Tl concentrations could be calculated during MC-ICPMS analysis using measured $^{205}Tl/^{208}Pb$ ratios. Samples and standards were analyzed at a concentration of ~7 ng/g Tl, which typically yielded an ion current around 80 pA on m/z 205 (10^{11} Ω resistor). All samples were analyzed in duplicate. The average and maximum 2 standard deviation (SD) reproducibility of these duplicate measurements was 0.3 and 0.8 ε units. One USGS shale SCo-1 standard was leached, purified, and analyzed with each sediment sample set to monitor accuracy. This standard yielded a $\varepsilon^{205}Tl_A$ value of -2.9 ± 0.3; 2SD ($n = 4$), which is indistinguishable from values reported in previous work ($\varepsilon^{205}Tl_A = -2.9 \pm 0.1$; 2SD[54]). Reported errors are always in 2SD and either equal to the individual sample's reproducibility or the USGS shale SCo-1 reproducibility, whichever is greater.

Molybdenum and uranium abundances

Redox-sensitive element concentration data were generated using a Thermo Fisher Scientific iCAP Q ICP-MS located at the WHOI Plasma Mass Spectrometry Facility. Concentrations were calculated via reference to ion beam intensities obtained from a five-point calibration curve constructed from serial dilutions of a gravimetrically prepared multi-element standard. Indium (In) was added to each sample before measurement as an internal standard to monitor and correct for signal drift. Concentration measurements conducted using the same methods and instrument are shown to be accurate and precise to within ±5–10% based on agreement with replicates and published USGS reference material values[57].

References cited only in the Materials and Methods

49. Coetzee, L.L., 2001. Genetic stratigraphy of the Paleoproterozoic Pretoria Group in the Western Transvaal. M.Sc. Thesis, Rand Afrikaans University, 212 pp.
50. Coetzee, L.L., Beukes, N.J., Gutzmer, J., Kakegawa, T., 2006. Links of organic carbon cycling and burial to depositional depth and establishment of a snowball Earth at 2.3 Ga. Evidence from the Timeball Hill Formation, Transvaal Supergroup, South Africa. South African Journal of Geology 109, 109-122.
51. Visser, J.N.J., 1972. The Timeball Hill Formation at Pretoria—a prograding shore-line deposit. Annual Geological Survey of Pretoria 9, 115-118.
52. Eriksson, K.A., 1973. The Timeball Hill Formation—a fossil delta. Journal of Sedimentary Research 43, 1046-1053.
53. Eriksson, P.G., Reczko, B.F.F., 1998. Contourites associated with pelagic mudrocks and distal delta-fed turbidites in the Lower Proterozoic Timeball Hill Formation epeiric basin (Transvaal Supergroup), South Africa. Sedimentary Geology 120, 319-335.
54. Ostrander, C.M., Owens, J.D., Nielsen, S.G., 2017. Constraining the rate of oceanic deoxygenation leading up to a Cretaceous Oceanic Anoxic Event (OAE-2: ~94 Ma). Science Advances 3, e1701020.
55. Rehkämper, M., Halliday, A.N., 1999. The precise measurement of Tl isotopic compositions by MC-ICPMS: application to the analysis of geological materials and meteorites. Geochimica et Cosmochimica Acta 63, 935-944.
56. Nielsen, S.G., Rehkämper, M., Baker, J., Halliday, A.N., 2004. The precise and accurate determination of thallium isotope compositions and concentrations for water samples by MC-ICPMS. Chemical Geology 204, 109-124.
57. Shu, Y., Nielsen, S.G., Zeng, Z., Shinjo, R., Blusztajn, J., Wang, X., Chen, S., 2017. Tracing subducted sediment inputs to the Ryukyu arc-Okinawa Trough system: Evidence from thallium isotopes. Geochimica et Cosmochimica Acta 217, 462-491.

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Author Contributions

C.M.O. and S.G.N. conceptualized the study, in collaboration with A.W.H. and A.B.. A.B. and S.W.P. collected and provided the samples. C.M.O., A.W.H., Y.S., and K.P.O. prepared the samples for geochemical analysis. C.M.O. and Y.S. performed isotopic analysis. C.M.O. drafted the initial manuscript. A.W.H., A.B., S.W.P., and S.G.N. helped C.M.O. revise the manuscript before submission and during revision.

Competing Interests

The authors declare no competing interests.

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Data Availability Statement

All data reported in the present study are available through Mendeley Data at DOI: 10.17632/89gjpt9zxv.1