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A 200 million year delay in permanent atmospheric oxygenation

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The rise of atmospheric oxygen fundamentally changed the chemistry of surficial environments and the nature of Earth's habitability[1]. Early atmospheric oxygenation occurred over a protracted period of extreme climatic instability marked by multiple global glaciations[2,3], with the initial rise of oxygen to above 10^{-5} of the present atmospheric level (PAL) constrained to ~2.43 billion years ago (Ga)[4,5]. Subsequent fluctuations in atmospheric oxygen levels have, however, been reported until ~2.32 Ga[4], which currently denotes the perceived timing of irreversible oxygenation of the atmosphere[6,7]. Here, we report a high-resolution reconstruction of atmospheric and local oceanic redox conditions across the final two glaciations of the early Paleoproterozoic Era, as documented by marine sediments from the Transvaal Supergroup, South Africa. Based on multiple sulfur isotope and Fe-S-C systematics, we demonstrate continued oscillations in atmospheric oxygen levels after ~2.32 Ga, linked to major perturbations in ocean redox chemistry and climate. Oxygen levels thus fluctuated across the 10^{-5} PAL threshold for ~200 million years, with permanent atmospheric oxygenation finally arriving with the Lomagundi carbon isotope excursion at ~2.22 Ga, some 100 million years later than currently estimated.

The transition to a permanently oxygenated atmosphere underpins the concept of the Great Oxidation Event (GOE) and represents a pivotal period in Earth history that ultimately led to the Earth's current state of habitability[1,8]. While multiple independent lines of evidence document a significant rise in atmospheric oxygen during the GOE[1,8], the most definitive tool for tracking atmospheric oxygenation comes from the preservation (and subsequent loss) of mass-independent fractionation of multiple sulfur isotopes (MIF-S) in marine sedimentary rocks[9,10]. The onset of the GOE is constrained to ~2.43 Ga based on the initial loss of the MIF-S isotope signal[4,5]. However, the permanent loss of the MIF-S isotope signal, representing the transition from a functionally anoxic to an oxic atmosphere with pO_2 sustained above $>10^{-5}$ of the present atmospheric level (PAL)[11], has been timed to ~2.32 Ga[6,7].

The GOE is associated with extreme climatic instability, with the latest stratigraphic reconstructions advocating four distinct glaciations (Extended Data Fig. 1), where the oldest three are found at low-latitudes and thus represent possible 'Snowball' Earth intervals[3]. While atmospheric oxygenation has traditionally been viewed as a singular, irreversible event[12-14], emerging evidence supports significant instability in atmospheric oxygen concentrations across the GOE[2,4] (see Methods). Fluctuations in atmospheric composition are often linked to greenhouse gas concentrations and the development of glacial conditions, specifically via the oxidation of atmospheric methane[2,13,15-18]. Indeed, after the initial loss of the MIF-S signal in the lead up to the first Paleoproterozoic glaciation[5], there is compelling evidence for a return and subsequent loss of MIF-S after the second glaciation in the Duitschland Formation of the Transvaal Supergroup, South Africa[19]. This is followed by a return to MIF-S in the aftermath of the third glaciation in the Eastern Transvaal Basin, before the signal is again lost in the upper Rooihoogte Formation[6,7] (Fig. 1), representing the widely accepted permanent oxygenation of the atmosphere. The final Paleoproterozoic glaciation occurs ~60-100 million years after this purported permanent rise of atmospheric oxygen (Fig. 1), and thus currently stands alone in appearing to lack a direct link to oxygen fluctuations across the 10^{-5} PAL threshold.

To test this history of Earth-system oxygenation and associated climate change, we provide a high-resolution reconstruction of atmospheric and local oceanic redox conditions through the later stage of the GOE, with analyses based on multiple sulfur isotope and Fe-S-C systematics (see Methods for a full description of the geologic setting, analytical techniques and additional data discussion, and Supplementary Information for all data). We focus on well-preserved drill cores (EBA-1 and EBA-2) that intersected shallow-marine strata, with drill core EBA-1 likely documenting a slightly shallower-water depth relative to EBA-2. The succession comprises the Rooihoogte Formation (deposited shortly after the third Paleoproterozoic glaciation), two upward-shallowing sequences (separated by a depositional break of ~40-50 million years) of the overlying Timeball Hill Formation (which hosts the Reitfontein Diamictite at the top, representing the final Paleoproterozoic glaciation), and the overlying Boshoek Formation (Fig. 1).

Our multiple sulfur isotope analyses document large $\Delta^{33}S$ anomalies indicative of a functionally anoxic atmosphere ($<10^{-5}$ PAL) in interval A of the upper Rooihoogte Formation (Fig. 2; Extended Data Fig. 2). Through interval B of the upper Rooihoogte Formation, the $\Delta^{33}S$ results are consistent with existing data showing mass-dependent fractionation of multiple sulfur isotopes (MDF-S) and hence higher atmospheric oxygen levels[7]. A return to MIF-S in interval C indicates a subsequent drop in atmospheric oxygen levels[7], but the $\Delta^{33}S$ anomaly is then lost across the Rooihoogte-Timeball Hill formation boundary (Fig. 2; Extended Data Fig. 2), marking the previously accepted permanent rise of atmospheric oxygen to $>10^{-5}$ PAL[6,7] (Fig. 1). Our more extensive dataset, however, captures a return to large MIF-S across several overlying intervals of the Timeball Hill Formation, including the run-up and aftermath of the Reitfontein glaciation (Figs. 2 and 3).

While our data record a large range in MIF-S values (up to ~9‰ in the Rooihoogte Formation, and up to ~3‰ through the Timeball Hill Formation and Reitfontein Diamictite), smaller MIF-S anomalies observed in some early Paleoproterozoic sedimentary successions have been linked to recycling of older Archean sulfides[5,26-28]. However, consistent with previous studies of the Rooihoogte and Timeball Hill formations[6,7], we interpret our MIF-S data to dominantly reflect a primary atmospheric signal. Specifically, an early diagenetic origin has been convincingly demonstrated for sulfide minerals in the EBA drill cores[7] (see Extended Data Fig. 3 for additional support), and there is no evidence for a hydrothermal contribution to the Δ^{33}S signal (see Methods). Moreover, the MIF-S signals we document are consistent with expectations based on a dominant primary, contemporaneous source of sulfide rather than recycling of weathered sedimentary pyrite. Here, we note that following a return to low atmospheric oxygen ($<10^{-5}$ PAL), the expectation would be for the sediments to record a dominant MIF-S signal, with a possible minor overprint from remnant seawater sulfate carrying a mass-dependent sulfur isotope signal (MDF-S) from earlier oxygenation. If we first adopt the conservative approach where Δ^{33}S values of 0.0 ± 0.3‰ document mass-dependent fractionation of sulfur isotopes (MDF-S), as is broadly consistent with post-GOE variability (Fig. 3A), samples with Δ^{33}S >0.3‰, including those above the Rooihoogte-Timeball Hill formation boundary, plot close to the Archean Reference Array (ARA) for Δ^{36}S/Δ^{33}S (Fig. 3B; Extended Data Fig. 4) supporting a dominant, primary atmospheric signal[7,22,23]. These MIF-S signals are fundamentally different to the deviation from both the ARA and the post-GOE reference line evident for many early Paleoproterozoic samples for which MIF-S recycling has been invoked[5,27,28] (Extended Data Fig. 5).

By contrast, our samples within the Δ^{33}S = 0.0 ± 0.3‰ range plot close to the Δ^{33}S/δ^{34}S and Δ^{36}S/Δ^{33}S post-GOE reference lines representing sulfides deposited under an oxygenated atmosphere (Fig. 3). Some of these samples plot in the field where the post-GOE reference lines and the Archean Reference Array (ARA) overlap (Fig. 3), and hence could have been deposited under anoxic atmospheric conditions. This may account for the shallower Δ^{36}S/Δ^{33}S slope (-3.2 ± 1.3; Extended Data Fig. 5) evident for our MDF-S data, relative to the post-GOE reference slope (-7.2 ± 1.4). However, a contribution from recycled MIF-S, which would be an expectation following atmospheric oxygenation and subsequent oxidation of pyrite, is also a possibility.

Our MDF-S data are also consistent with the presence of Earth's earliest seawater sulfate evaporites in the Gordon Lake Formation of the Huronian Supergroup, and in the underlying upper Duitschland Formation[29,30], which are coeval to the Rooihoogte and lower Timeball Hill formations. These evaporite data record MDF-S signals[31], implying a well-mixed seawater sulfate inventory of substantial size that did not carry a significant MIF-S signal (see Methods). Thus, while it is theoretically possible for samples that plot along the ARA to have originated from recycling, fluctuating levels of atmospheric oxygen provide the most parsimonious explanation for the distinct S isotope trends evident in our data. Therefore, in contrast to previous inferences[6,7], oxygen concentrations did not permanently cross the 10^{-5} PAL threshold after the third Paleoproterozoic glaciation at ~2.32 Ga.

While multiple sulfur isotopes serve as a binary signal for atmospheric O_2 (MDF-S>10^{-5} PAL<MIF-S), Fe-S-C systematics allow reconstruction of the local shallow-water redox response to climate dynamics and changes in atmospheric oxygen levels, in a setting that is considered to have been connected to the open ocean[25]. The synthesis of the $\Delta^{33}S$ and Fe-S-C datasets comprises a timeline that begins with a likely substantial influx of glacially derived nutrients during deposition of the Rooihoogte Formation, as also documented for the aftermath of Neoproterozoic 'Snowball' Earth glaciations[32]. This nutrient input stimulated primary production, total organic carbon (TOC) burial, and hence local oxygen production, leading to the development of oxic conditions (denoted by Fe_{HR}/Fe_T^* <0.38 and/or Fe/Al <0.66) in very shallow waters, as documented throughout the Rooihoogte Formation in drill core EBA-1 (Fig. 2; Extended Data Fig. 2). However, consistent with the perspective of shallow-ocean 'oxygen oases' in the run-up to permanent atmospheric oxygenation[33-35], the flux of oxygen was not sufficient to fully oxygenate the atmosphere, and thus MIF-S persists in interval A of the upper Rooihoogte Formation.

A very shallow oxycline is suggested by fluctuations between oxic, ferruginous (anoxic, Fe-bearing; denoted by Fe_{HR}/Fe_T^* >0.38 and/or Fe/Al >0.66, with Fe_{py}/Fe_{HR}^* <0.7) and possibly even euxinic (anoxic, sulfidic; denoted by Fe_{HR}/Fe_T^* >0.38 and/or Fe/Al >0.66, with Fe_{py}/Fe_{HR}^* >0.8) conditions in the slightly deeper-water drill core EBA-2 through interval A and in the lower part of interval B of the upper Rooihoogte Formation. Continued oxygen production then appears to have transiently oxygenated the atmosphere during deposition of interval B of the upper Rooihoogte Formation (Figs. 2 and 3). Oxidative weathering at this time would have increased the influx of sulfate to the oceans, leading to the observed expansion in sedimentary $\delta^{34}S$ values. Elevated sulfate levels, combined with abundant TOC, then led to the transient development of euxinia at the top of interval B in the upper Rooihoogte Formation (drill core EBA-2, Fig. 2).

There was then a return to reducing atmospheric conditions during deposition of interval C of the Rooihoogte Formation. This coincides with high $\delta^{34}S$ values at the base of interval C, consistent with lower seawater sulfate concentrations due to a decrease in oxidative weathering, which promoted a return to ferruginous water-column conditions (Fig. 2). Across the Rooihoogte-Timeball Hill formation boundary, there was a second significant pulse of atmospheric oxygenation. This pulse again increased the continental weathering flux of sulfate and biogenic pyrite formation (as indicated by the major increase in the range of $\delta^{34}S$ values and elevated Fe_{py}/Fe_{HR}), before transiting to oxic seawater conditions in the lower part of the Timeball Hill Formation (Fig. 2).

The water column redox dynamics through the Rooihoogte and basal Timeball Hill formations thus reflect the combined influence of glacial melting and fluctuations in atmospheric oxygen documented by our multiple sulfur isotope data. Longer timescale fluctuations in oxygenation are nevertheless apparent throughout the remainder of the succession. While oxic shallow waters persisted through the lower sequence of the Timeball Hill Formation (interval D; Fig. 2), oxygen production was apparently not sufficient to maintain an oxygenated atmosphere, as the MIF-S signature returns at this stratigraphic level (Fig. 3). This deoxygenation was relatively short-lived, however, as a return to MDF-S indicates that the 10^{-5} PAL threshold was again exceeded in the upper part of the lower Timeball Hill Formation sequence (Fig. 3). The upper Timeball Hill Formation (interval E) initially shows evidence for fluctuations between oxic and ferruginous depositional conditions in a relatively deeper-water setting, while the atmosphere transitioned from a dominantly reducing to oxidizing state (Figs. 2 and 3). The oxycline then shallowed, resulting in persistent shallow-water ferruginous anoxia and a reducing atmosphere towards the top of the upper Timeball Hill Formation. This anoxic atmosphere-ocean state persisted through the Reitfontein Diamictite and the lower part of the overlying Boshoek Formation (Fig. 3), with the exception of terrestrial to shallow-marine quartzites that document oxic water-column conditions at the base of the Boshoek Formation (Fig. 2).

While local marine redox data should be viewed with caution when making global inferences, our data appear to support a long-lived, dynamic interplay between the biogeochemistry of shallow waters and fluctuations in atmospheric oxygenation. We next explore links between shallow-water redox conditions, and atmospheric O_2, CO_2 and CH_4, to assess potential drivers of the final Paleoproterozoic glaciation. As with the Neoproterozoic ‘Snowball’ Earth glaciations, escape from glaciation at the base of the Rooihoogte-Timeball Hill succession was likely initiated by a syn-glacial volcanic build-up of CO_2, leading to intense greenhouse conditions[2,36]. Modelling suggests that chemical weathering took >10^7 years to reduce atmospheric CO_2 concentrations to background levels in the aftermath of Neoproterozoic glaciations[37]. Elevated CO_2 as a means to end the third Paleoproterozoic glaciation is supported by the highly chemically weathered nature of the sediments of the lower Timeball Hill Formation, as indicated by high values for the chemical index of alteration (CIA) weathering proxy (Fig. 3c)[25].

In keeping with an atmospheric state prone to oscillations across the 10^{-5} PAL pO_2 level, our data suggest that a shallow oxycline was typical of open-marine environments throughout this period, and indeed, anoxia likely extended throughout the water column in certain (e.g., upwelling) regions of the ocean[34], promoting a high global marine methane efflux to the atmosphere. In this context, with the exception of the immediate aftermath of the second Paleoproterozoic glaciation, carbonate C isotopes record fluctuating, but positive, values across this time period (Fig. 4). Thus, the low organic carbon isotope values ($\delta^{13}C_{org}$) observed in relatively deeper-water parts of the succession[25] are highly fractionated (Fig. 3), supporting a significant contribution from the oxidation of ^{13}C-depleted methane. We thus propose that during deposition of the upper Timeball Hill Formation, which began after a 40-50 million year hiatus[3], elevated post-glacial atmospheric CO_2 would have long been drawn down through silicate weathering[37], and hence methane dynamics likely played a more critical role than CO_2 in triggering the fourth Paleoproterozoic glaciation.

Indeed, during deposition of the upper part of interval E, less intense chemical weathering is supported by a clear overall decrease in the CIA weathering proxy broadly coincident with atmospheric oxygenation (Fig. 3), which is consistent with a cooling climate initiated by oxidation of atmospheric methane. A decrease in chemical weathering would also have diminished the oceanic influx of nutrients, thereby decreasing productivity, TOC burial, and hence oxygen production, thus driving the atmosphere-ocean system back to an anoxic state prior to the onset of the final Paleoproterozoic glaciation (Fig. 3). Low productivity then continued to limit organic matter production and burial, thus maintaining atmospheric oxygen concentrations at a low level throughout the glaciation.

Our new sulfur isotope data demonstrate that the Rooihoogte-Timeball Hill formation boundary does not record the permanent crossover of the 10^{-5} PAL atmospheric oxygen level, and thus revises the widely accepted ~2.32 Ga age for the permanent oxygenation of Earth's atmosphere. Indeed, a compilation of sulfur isotope data (Fig. 4) demonstrates fluctuations in atmospheric oxygen levels across the entire Paleoproterozoic glacial epoch (~2.43-2.22 Ga), and suggests that the Lomagundi carbon isotope excursion at ~2.22 Ga was the tipping point for permanent atmospheric oxygenation, which occurred more than 100 million years later than previously thought. Thus, we redefine the GOE as the Great Oxidation Episode, a transitory period that lasted more than 200 million years, during which atmospheric redox oscillations straddled the 10^{-5} PAL threshold, progressively increasing beyond it to influence higher atmospheric oxygen threshold indicators such as oxidised paleosols, continental red beds, a disappearance of redox-sensitive minerals in placer deposits, and the first appearance of shallow-water sulfate evaporite deposits[8,39] (Fig. 4). The permanent termination of this transitional period is supported by evidence for elevated atmospheric O_2 levels during the Lomagundi Event, and possibly an 'overshoot' to oxygen concentrations not seen again until the terminal Neoproterozoic[39].

The final Paleoproterozoic glaciation is not known in other key successions (see Methods), and the latest paleogeographic reconstructions place the Transvaal Basin at mid-to-high latitudes during emplacement of the Hekpoort Formation[40], which immediately overlies the Boshoek Formation (Fig. 1). This suggests that while the final Paleoproterozoic glaciation was driven by atmosphere-ocean redox dynamics, it may also represent a waning in the severity of the climatic response to oxygenation as the Earth became progressively poised at an overall higher oxygenation state across each glaciation of the GOE[2]. It thus appears that the delayed rise in permanent atmospheric oxygenation that we document ushered in a new period of climatic and biogeochemical stability that persisted until the 'Snowball' Earth glaciations of the late Neoproterozoic, some 1.5 billion years later.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at…

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Main Figure Legends:

Fig. 1. Simplified Paleoproterozoic stratigraphy of the Eastern Transvaal Basin, South Africa, showing the studied interval. Constraints on atmospheric oxygen are provided by mass-independent (MIF-S) and mass-dependent (MDF-S) sulfur isotope fractionations[6,7,19].

Fig. 2. Geochemical and isotopic profiles for drill cores EBA-1 and EBA-2. Note the scale changes for stratigraphic depth (to aid clarity) for the Reitfontein Diamictite and Boshoek Formation in drill core EBA-1, and for the Reitfontein Diamictite and Rooihoogte Formation in drill core EBA-2. Dashed line on Fe/Al plots represents the boundary (0.66) for distinguishing oxic and anoxic water-column conditions[20]. Dashed lines on $Fe_{HR}/Fe_{T}*$ plots represent the boundaries for distinguishing oxic (<0.22) and anoxic (>0.38) water column conditions[21]. Dashed lines on $Fe_{py}/Fe_{HR}*$ plots represent the boundaries for distinguishing euxinic (>0.8) and ferruginous (<0.7) water column conditions, which are only applicable for samples deposited from an anoxic water column (shown as closed circles). $Fe_{HR}/Fe_{T}*$ and $Fe_{py}/Fe_{HR}*$ ratios are corrected for transformation of unsulfidized Fe_{HR} to Fe-rich clays during diagenesis (see Methods). Horizontal dashed lines divide the succession into informal intervals (A–E) to aid interpretational clarity. TOC = total organic carbon.

Fig. 3. Multiple-sulfur isotope systematics and summary of atmospheric and oceanic redox conditions. A. $\Delta^{33}S/\delta^{34}S$ plot showing the similarity between post-GOE data and samples with $\Delta^{33}S$

< 0.3‰ from the present study, as well as the clear distinction with respect to samples with $\Delta^{33}S$ > 0.3‰, which straddle the Archean Reference Array (ARA)[22,23]. Inset shows a magnification at the origin, where dashed lines represent the 95% confidence interval for MDF-S data. B. $\Delta^{36}S/\Delta^{33}S$ plot showing the close similarity between the data of the current study and the post-GOE[24] and Archean Reference Arrays. Inset shows a magnification at the origin for the data from the current study. C. Stratigraphic summary of $\Delta^{33}S$ composition, chemical index of alteration (CIA), organic C ($\delta^{13}C_{org}$) isotope composition[25], and atmospheric and oceanic redox evolution (normalized to the thickness of individual units in drill cores EBA-1 and EBA-2, after correction for thickness of diabase intrusions). Grey arrow on the CIA plot summarises the overall trajectory of the data.

Fig. 4. Compilation of $\Delta^{33}S$ data and simplified carbonate C isotope ($\delta^{13}C$) trends for the 2.5-2.0 Ga time interval. Red circles represent data from the current study; black circles represent a compilation of published data[7,24]. Blue bars represent the four glacial intervals. $\delta^{13}C$ curve is modified after ref [38], with the dashed line highlighting the portion that is poorly defined. Geological indicators for the redox state of the atmosphere-ocean system are from refs [30,39].

METHODS

Geological setting

Diamond drill cores EBA-1 (26.4669ºS, 27.5875ºE) and EBA-2 (26.4700ºS, 27.5883ºE) were drilled near Carltonville in South Africa (Kloof Goldfields Property, Eastern Boundary Area), and intersected well-preserved, early Paleoproterozoic strata of the Transvaal Supergoup. The studied interval comprises the Rooihoogte and Timeball Hill formations in both cores, in addition to the overlying Boshoek Formation in EBA-1 (Fig. 2). The two cores were drilled in close proximity (<1 km apart) on a paleohigh in the Potchefstroom Synclinorium (Extended Data Fig. 6), and the succession has been subjected to only lower greenschist facies regional metamorphism[49].

The Rooihoogte Formation is divided into upper and lower members, with the boundary at 1196.9 m in EBA-1 and 1345.6 m in EBA-2. The lower Rooihoogte Formation (not sampled for this study) comprises the Giant Chert Breccia Member, which is an *in situ* karst breccia, consisting of brecciated dolostone and chert with some black shale[7]. Above the Giant Chert Breccia Member is the Bevetts Member (not sampled for this study), which formed during transgression onto the erosional surface, resulting in deposition of a sheet-like basal conglomerate or poorly sorted reworked chert breccia with some black shale[7]. Elsewhere in the region, a glacial diamictite then occurs[49], but this lithology is not present in cores EBA-1 and EBA-2, likely due to erosion at the sequence boundary with the upper Rooihoogte Formation[7]. The upper Rooihoogte Formation in drill cores EBA-1 and EBA-2 dominantly consists of mudstone and black shale that coarsen upwards into siltstone, with a thin chert breccia at the top[49].

The Timeball Hill Formation comprises two upward coarsening sequences[25]. The lower part of both sequences is composed of highly carbonaceous black mudstone[49]. The mudstones in each sequence become less carbonaceous up-section, and are interbedded with dark-grey to grey siltstone. The lower mudstone-siltstone unit grades upwards into the Galsrand Member, which is a fine- to medium-grained quartzite succession with oolitic ironstone beds[49]. The mudstones and black shales of the upper Rooihoogte and Timeball Hill formations were deposited in a prodelta basin setting, which is generally thought to have had open connection to the ocean to the southwest[49-52]. Based on the increased thickness and more oxygenated depositional setting (see below) of the Rooihoogte Formation in core EBA-1 relative to core EBA-2, it is likely that the latter was deposited in a somewhat deeper-water setting.

The lower sequence of the Timeball Hill Formation is interpreted to have formed by progradation of deltaic complexes, ranging from deep-water, prodelta black mudstone at the base, through delta front mudstone and siltstone, to shallow-water delta plain sands and oolitic ironstone of the Galsrand Member[25]. The Galsrand Member is considered to have been deposited in a warm, well-oxygenated setting, based on the occurrence of hematite and the highly chemically weathered nature of the sediments, as indicated by the chemical index of alteration (CIA) weathering proxy[25]. In core EBA-1, a small zone of groundwater or hydrothermal alteration from ~624 to 639 m depth has been documented[25,49]. We report two samples from this zone, one of which was measured for multiple sulfur isotopes. However, this sample (at 637 m; Supplementary Information Table S3) documents a mass dependent sulfur isotope fractionation (MDF-S), similar to surrounding samples, suggesting minimal post-diagenetic alteration of its isotopic signal.

The upper sequence of the Timeball Hill Formation is capped by diamictite and conglomerate of the Reitfontein Member. The Reitfontein diamictite is composed of angular to sub-rounded clasts in a matrix of mudstone and siltstone[25]. In outcrop, faceted and bull-nosed glacially striated pebbles have been observed, leading to its interpretation as a glacial deposit[49,50]. This glacial diamictite is considered correlative to a diamictite in the Ditlhojana Shale in the Bushveld structural basin[53], which is an extension of the Transvaal structural basin into Botswana to the west, as well as a diamictite in the Tlaameng Formation in the Kanye structural basin ~50 km to the west of the Bushveld structural basin[3]. However, based on current global correlations[41], this glacial horizon in southern Africa is not recognized in other sedimentary successions (Extended Data Fig. 1). The contact between the diamictite and the underlying shale/siltstone is gradational, and the matrix of the diamictite reflects continued deposition of shale and siltstone[49]. For the present study, sampling of the Reitfontein Member focussed on the matrix, rather than clasts. The Reitfontein Member is overlain by the Boshoek Formation, the lower part of which occurs in core EBA-1. The lower Boshoek Formation starts with a poorly sorted, chert-pebble conglomerate that fines upwards into shale and siltstone[49].

The conglomerate is considered to represent reworking of the Reitfontein diamictite during major regression, with the overlying black shale representing renewed marine transgression[49].

U-Pb dating[3] of the lower Timeball Hill Formation gave ages of 2309 ± 10 Ma and 2307 ± 8 Ma (Extended Data Fig. 1), which are consistent with a minimum isochron age of 2316 ± 7 Ma based on Re–Os dating of syngenetic to early diagenetic pyrite across the Rooihoogte-Timeball Hill formation boundary[54]. U-Pb dating[3] of two tuff beds at 709.5 m and 711.6 m in the upper sequence of the Timeball Hill Formation in core EBA-1, gave ages of 2256 ± 6 Ma and 2266 ± 4 Ma, suggesting a hiatus of about 40-50 million years between deposition of the lower and upper sequences.

Global correlations

The global correlation of Paleoproterozoic glacial successions deposited during the Great Oxidation Event (GOE) has undergone major revision over recent years, in part based on improved constraints from radiometric dating. As shown in Extended Data Fig. 1, four discrete glaciations are currently advocated between ~2.46 and 2.22 Ga[3,4,41]. The Duitschland Formation of the Transvaal sub-basin has previously been correlated with the Rooihoogte Formation[49], a correlation that is still preferred by some authors[7]. However, the glacial diamictite that occurs at the base of the lower Duitschland Formation has also been correlated with the second glaciation of the Huronian succession in North America, based on carbon isotope chemostratigraphy and lithostratigraphy[30,55]. This is supported by the youngest detrital zircon age of 2424 ± 24 Ma for the Duitschland Formation[56], considerably pre-dating age constraints for the Rooihoogte and lower Timeball Hill formations (Extended Data Fig. 1), which contains detrital and volcanic zircons with 2310 ± 9 and 2308 ± 8 Ma ages[3,56]. We stress here, however, that the main conclusions of the current work are not contingent on the precise nature of the correlation between the Duitschland Formation and the Rooihoote/Timeball Hill/Boshoek formation succession.

The Makganyene Formation of the Griqualand West sub-basin also contains a glacial diamictite, which was previously correlated with the Reitfontein diamictite[3,49]. However, improved age constraints[4] confirm that the Makganyene Formation is instead correlative with the first glaciation of the Huronian succession[41,57] (Extended Data Fig. 1). The Turee Creek Basin of the Pilbara Craton, Western Australia, is another succession of critical importance for understanding the dynamics of the GOE[27]. The succession has previously been regarded to span the entirety of the GOE, from ~2.45 Ga to 2.2 Ga, incorporating two, or possibly three, glaciations[58,59]. However, in addition to diagenetic pyrite, detrital pyrite is present in all sandstones, conglomerates and debrites deposited throughout the succession[27,41], which implies low levels of atmospheric oxygen during transport and deposition. Based on a detailed reappraisal of the sequence stratigraphy, geochronology and carbon isotope chemostratigraphy of the Turee Creek Basin, it has been suggested that the Turee Creek Group is more restricted in its time span, and instead broadly correlates with the first glacial cycle of the Paleoproterozoic[41] (Extended Data Fig. 1).

Existing constraints on atmospheric oxygenation

Multiple sulfur isotope data have been reported[6] for a limited suite of samples from the Rooihoogte Formation and base of the Timeball Hill Formation in core EBA-2. These data document a MDF-S signal, which has widely been accepted as marking the onset of permanent atmospheric oxygenation at ~2.32 Ga. More recently, higher resolution multiple sulfur isotope data through three drill cores (including EBA-2) that intersected the Rooihoogte Formation and the base of the Timeball Hill Formation have been reported[7]. These data show a rapid transition from a large mass-independent sulfur isotope signal (MIF-S) of up to +8‰, through a thin transitional zone (3-4 m) where the lower part records a small $\Delta^{33}S$ range (<0.5‰) and the upper part documents larger $\Delta^{33}S$ (0.5 to 2‰) shifts, to near-zero $\Delta^{33}S$ (<0.3‰) values in the uppermost Rooihoogte and lowermost Timeball Hill formations. This implies that this episode of oxygenation occurred rapidly, over a 1 to 10 million-year time interval[7]. In contrast to the current study, no previous study has reported multiple sulfur isotope data above the bottom 4 m of the >500-m-thick Timeball Hill Formation, and no previous study has integrated oceanic redox data with multiple sulfur isotope systematics through any part of the succession.

Multiple sulfur isotope data have previously been published for other successions recording the Paleoproterozoic glacial period (as summarised in terms of MIF-S and MDF-S for four key areas in Extended Data Fig. 1). In particular, the Duitschland Formation documents a loss of MIF-S[19], which, based on updated correlations, suggests probable oscillations in atmospheric oxygen in rocks older than those of the current study[4]. A record of possible fluctuations in atmospheric oxygen has also been reported based on sedimentary sulfides deposited in the Turee Creek Basin (Hamersley Province) of Western Australia[27]. In this case, small-magnitude MIF-S signals (generally <1.5‰) persist throughout, punctuated by short intervals with sulfides having MDF-S. These signals have been attributed to the weathering of sulfides with pre-existing MIF-S, combined with short time intervals of atmospheric oxygenation[27]. This suggestion is supported by a combined sulfur and oxygen isotope study of barite from the Kazput Formation[28], which was deposited in the upper part of the Turee Creek Group (Fig. S2). However, as discussed above, the precise correlation of this succession to other key GOE localities is controversial. Thus, the significance of the Turee Creek

Group in relation to our high resolution study of the final stages of the GOE, as recorded by the Pretoria Group, is unclear.

Multiple S isotope data have also been reported for rocks deposited on the Fennoscandian Shield, northwest Russia[5]. This places the onset of the GOE, as denoted by a MIF-S to MDF-S transition, close to 2,434 ± 6.6 Ma in age. It has also been demonstrated that small, but resolvable, MIF-S signals occur throughout the Huronian Supergroup of Canada, which potentially arises due to a variety of reasons, including homogenization by regional metamorphism, sulfur recycling, or dilution of MIF-S by magmatic fluids[43]. Given the uncertainties outlined above, the well-preserved Paleoproterozoic succession of the Carltonville region of South Africa, as analysed in the present study, offers a prime opportunity to explore the dynamics of the GOE as it approached its critical, concluding stage.

Geochemical analyses

Total organic carbon (TOC) was determined on a C-S Leco CS230 Analyzer after treatment with 50% HCl to remove carbonate phases. Accuracy (>98%) was ensured relative to Leco certified standards 501-506, and replicate extractions gave a RSD of <5%. Total Fe and Al were determined on ashed samples via a HF-HNO_3-$HClO_4$ extraction, with HBO_3 used to ensure full solubilization of Al. Solutions were analysed by ICP-OES with >98% recovery relative to international sediment standard PACS-2, and with RSDs of <5%.

Iron speciation analysis was conducted via a well-established sequential extraction procedure[60], with acid-volatile sulphides (Fe_{AVS}) and pyrite Fe (Fe_{py}) quantified gravimetrically via a two-step chromous chloride distillation[61]. The sequential extraction protocol extracts different operationally defined Fe pools, including carbonates such as siderite (Fe_{carb}), ferric oxides such as goethite and hematite (Fe_{ox}), and magnetite (Fe_{mag}). These phases define an Fe pool which is considered 'highly reactive' (Fe_{HR}) during sedimentation and diagenesis[62], determined as the sum of $Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}$. A boiling HCl extraction was also performed[63] to determine an Fe pool (consisting largely of sheet-silicate Fe) that is poorly reactive during diagenesis[64] (Fe_{PRS}), but which includes Fe-rich clay minerals that may have been formed from non-sulfidized Fe_{HR} during diagenesis[65,66]. Iron solutions were analysed via AAS, and replicate extractions gave RSDs of <5% for all Fe phases[67]. Geochemical data are reported in Supplementary Information.

We report 261 new $\Delta^{33}S$ analyses (207 via SO_2, and 54 via SF_6, which also provides $\Delta^{36}S$ data). Sulfur isotope measurements were performed on Ag_2S precipitates from the two-step chromous chloride distillation, using three measurement techniques. Samples in Supplementary Information Tables S3 and S4 that report only $\delta^{34}S$ compositions were determined via EA-IRMS by Iso-Analytical

Ltd, with repeat analyses of internal barium sulfate standards IA-R036 and IAEA-SO-5 giving values of 20.75 ± 0.20‰ (n = 34; accepted value = 20.74‰) and 0.37 ± 0.34‰ (n = 28; accepted value = 0.50‰), respectively. Samples in Supplementary Information Tables S3 and S4 that report $\delta^{34}S_{SO2}$ and $\Delta^{33}S_{SO2}$ compositions were analysed using an EA attached to a ThermoScientific Delta V Plus configured in continuous flow mode. Correction via SF_6 calibrated standards[68] leads to an integrated $\delta^{34}S$ variability of 0.1‰, and $\Delta^{33}S$ variability of 0.07‰. Samples in Supplementary Information Tables S3 and S4 that report $\delta^{34}S_{SF6}$, $\Delta^{33}S_{SF6}$ and $\Delta^{36}S_{SF6}$ were analysed by conventional fluorination methods (SF_6). Compositions measured with the latter method provide an additional check on $\Delta^{33}S_{SO2}$ data, but also allow for higher precision $\Delta^{33}S$ and $\Delta^{36}S$. Here, Ag_2S was fluorinated with F_2, and the product SF_6 was cleaned prior to measurement on a dual-inlet MAT 253. The long-term precision is 0.2‰, 0.008‰ and 0.20‰ for $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$, respectively.

Constraints on a primary versus secondary origin for MIF-S

A primary syngenetic or diagenetic origin for sulfide minerals in the EBA-1 and EBA-2 cores has been extensively demonstrated[6,7]. A unique feature of our dataset is that we can place petrographic observations of mineral morphology within the context of both the redox history of the samples and their multiple sulfur isotope signature. In Extended Data Fig. 3, photomicrographs from scanning electron microscopy (analyses were performed on a Tescan VEGA3 XM Scanning Electron Microscope with an Oxford Instruments X-max 150 EDS detector) provide support for a syngenetic or diagenetic origin for pyrite in all samples (Extended Data Figs. 3a, b, d, e, f), as well as support for a syngenetic origin for a portion of the Fe-oxide minerals deposited under ferruginous conditions (Extended Data Fig. 3c). We found no evidence for rounded or externally corroded (as a result of weathering) detrital pyrite grains. Instead, pyrite is euhedral, occurring either in isolation (Extended Data Fig. 3a), or as disseminated grains (Extended Data Fig. 3b) or clusters (Extended Data Figs. 3b, f), and we stress that these morphologies were a feature of samples with significant MIF-S. Pyrite-rich samples deposited under euxinic water column conditions (as determined via Fe speciation) showed evidence of primary pyrite with secondary overgrowths (Extended Data Fig. 3e), which is entirely consistent with initial precipitation from a euxinic water column, followed by overgrowths produced during early diagenesis. Similarly, in ferruginous samples we observed euhedral Fe-oxide clusters with clay laminations bending around the clusters, and with the clay matrix within the clusters (Extended Data Fig. 3c), supporting precipitation and settling of Fe-(oxyhydr)oxide minerals from a ferruginous water column.

While these observations suggest that our sulfur isotope data are not compromised by the inclusion of detrital pyrite carrying a remnant MIF-S signal, an additional factor concerns the possibility that the sulfate delivered to the basin originated from oxidative weathering of pyrite with a pre-existing MIF-S signal[26-28]. As previously argued[7], there are several lines of evidence against a significant remnant MIF-S signal. First, all euxinic samples carry a MDF-S signal, consistent with the requirement for a high influx of sulfate produced via oxidative weathering. This suggests that the rocks being weathered in the provenance area did not carry a strong MIF-S signal. In addition, the succession was deposited in a large open-marine basin, which was several hundred kilometres wide[41,69,70]. This suggests that, particularly if the atmosphere had remained oxic, the sulfate reservoir size should have been large enough to buffer against a weathering-derived MIF-S signal[7]. Indeed, the Gordon Lake Formation of the Huronian Supergroup, which hosts tuffs of the same age as the lower Timeball Hill Formation[3], contains shallow-marine sulfate evaporites[30,71,72]. This indicates that the seawater sulfate reservoir had reached a sufficient size to allow for the formation of such deposits, and these lack MIF-S and have moderately positive δ^{34}S values, reflecting the isotopic composition of seawater sulfate[30,71,72]. Similarly, sulfate evaporites in the underlying upper Duitschland Formation (Fig. S2) also lack MIF-S and have moderately positive δ^{34}S values[72]. Although it is likely that the seawater sulfate reservoir fluctuated in size during the early stage of the GOE, the critical point is that it was episodically large when the atmosphere was oxygenated, and at these times it did not carry a remnant MIF-S signal. Conversely, a smaller seawater sulfate reservoir is entirely consistent with intervals of atmospheric anoxia. In addition, we note that the occurrence of MIF-S signatures is not random, but instead occurs in clusters at similar stratigraphic levels in both cores (Fig. 3). Taken together, these considerations suggest that it is highly unlikely that the MIF-S signals document a random record of a remnant weathering signal derived from a poorly mixed marine sulfate reservoir under oxygenated atmospheric conditions.

Furthermore, as discussed in the main text, perhaps the most compelling evidence for a primary origin for the sulfur isotope composition lies in the observation that samples with mass-dependent and mass-independent fractionations fall close to the Δ^{33}S/δ^{34}S and Δ^{36}S/Δ^{33}S reference arrays (Fig. 3), which are considered to reflect an atmospheric composition for post-GOE and Archean sulfides, respectively[22-24]. In Extended Data Fig. 4, we use orthogonal data regression (ODR) to quantify the uncertainty in the determination of Δ^{36}S/Δ^{33}S slopes[5]. ORD incorporates uncertainties in both the abscissa and ordinate, and is thus preferable to linear regression, which only takes into account errors in the vertical coordinate when determining the best fit slope. This analysis clearly documents the differing trajectories of the two data-sets, including for MIF-S-bearing samples deposited above the

Rooihoogte-Timeball Hill formation boundary, providing strong support for primary fluctuations in atmospheric oxygen across the 10^{-5} PAL threshold.

By contrast, during oxidative weathering of older continental sulfides with a pre-existing MIF-S signal, mixing of the resultant sulfate riverine influx with mass-dependent sulfate produced under oxygenated atmospheric conditions, would produce isotopic signals that deviate considerably from the post-GOE and Archean reference arrays. This is evident in published data[5,27,28] where a MIF-S influence from recycling has been invoked (Extended Data Fig. 5). Pyrite and barite multiple S isotope analyses from the Turee Creek Group, as well as pyrite analyses from Fennoscandia, show considerable scatter, and while some of the data plot close to either the post-GOE $\Delta^{36}S/\Delta^{33}S$ reference line or the Archean Reference Array (ARA), a large proportion of samples straddle between these reference lines. In particular, many of the Hamersley Province samples plot in the slope range of -1.0 to -1.5. This range has been considered to represent perturbations to the standard ARA due to temporally restricted episodes of either enhanced methane-derived organic haze[24,44,45] or volcanic sulphur input[46]. Oxidative weathering of sulfide minerals carrying this specific signal could therefore be responsible for data that fall in the -1.0 to -1.5 range[28]. However, this signal is also consistent with mixing between recycled MIF-S and MDF-S produced in an oxygenated atmosphere. Indeed, several samples plot outside this range, which may imply that such mixing was a prominent factor in the generation of these isotopic signals. Nevertheless, regardless of the precise pathway for generation of the sulfur isotope signals, deviation from the Archean and post-GOE reference lines for a significant proportion of the Hamersley Province and Fennoscandia data supports a recycled MIF-S component[5,27,28], or mixed MIF-S and MDF-S components, which might be expected for samples deposited during the earlier stages of the GOE.

A final consideration concerns the possibility that the MIF-S signals above the Rooihoogte Formation represent hydrothermal alteration by fluids carrying a MIF-S signal derived from older rocks deeper in the succession. However, these drill cores are exceptionally well-preserved and there is little evidence for fluid flow of this type[49]. We also note that such fluid flow would often be expected to result in precipitation of a variety of metal monosulfides, in addition to pyrite. Indeed, there are very low concentrations of metal monosulfides present in a very few samples (reported as Fe_{AVS} in Supplementary Information Tables S1 and S2). However, where there was sufficient sulfide extracted, these samples were analysed for their sulfur isotope compositions and in all cases, the metal monosulfides carry a MDF-S signal, conclusively confirming that the MIF-S signals originate from syngenetic or diagenetic pyrite.

Assessment of ocean redox conditions

Geochemical redox data for cores EBA-1 and EBA-2 are shown in Extended Data Figs. 7 and 8. While local redox data may be affected by a variety of factors, including sea level fluctuations and tectonics, the local response of the ocean to extreme perturbations induced by major periods of global deglaciation can provide valuable insight into ocean-atmosphere interactions. To assess whether samples were deposited from an oxic or anoxic water column we utilise Fe speciation and Fe/Al ratios. In terms of Fe/Al ratios, the succession documents a complex history, with some samples showing values above the upper threshold[20] for identifying water column anoxia (0.66), and others having ratios below this value. In terms of Fe speciation, oxic conditions are indicated when Fe_{HR}/Fe_T ratios are <0.22, while Fe_{HR}/Fe_T ratios exceeding 0.38 arise from additional water-column precipitation of Fe_{HR} minerals under anoxic conditions. Fe_{HR}/Fe_T ratios between 0.22 and 0.38 are considered equivocal[21], and may be a consequence of either rapid background sedimentation under anoxic conditions (e.g., turbidite deposition), or transfer of non-sulfidized Fe_{HR} minerals to poorly reactive sheet-silicates (Fe_{PRS}) during diagenesis and burial metamorphism, which is particularly common in anoxic, non-sulfidic sediments[65,66]. For samples deposited from anoxic bottom waters, the Fe_{py}/Fe_{HR} ratio is used to discriminate between ferruginous ($Fe_{HR}/Fe_T > 0.38$; $Fe_{py}/Fe_{HR} < 0.7$) and euxinic water column conditions[21] ($Fe_{HR}/Fe_T > 0.38$; $Fe_{py}/Fe_{HR} > 0.8$).

Many of the samples with Fe/Al >0.66 (indicating deposition from an anoxic water-column) have Fe_{HR}/Fe_T ratios that fall within the equivocal zone, and to assess potential loss of Fe_{HR} via transfer to Fe-rich clay minerals, which does not affect Fe/Al ratios, we thus consider Fe_{PRS} concentrations[65,66]. Phanerozoic sediments deposited from an oxic water column[48] have average Fe_{PRS} concentrations of 1.80 ± 0.85 wt%, and average Fe_{PRS}/Al ratios of 0.21. Many of our samples plot above this ratio (Extended Data Figs. 7 and 8), and also have significantly higher Fe_{PRS} concentrations (Supplementary Information Tables S1 and S2), suggesting extensive transfer of Fe_{HR} to Fe_{PRS}. We provide a conservative assessment of possible loss of Fe_{HR} (for samples with $Fe_{PRS}/Al > 0.21$) by calculating a corrected depositional Fe_{HR}^* concentration:

$$Fe_{HR}^*/Al = (Fe_{HR}/Al)_{meas} + ((Fe_{PRS}/Al)_{meas} - (Fe_{PRS}/Al)_{PAS})$$

where *meas* represents the measured ratio, and *PAS* represents average oxic Phanerozoic shale. Based on these revised Fe_{HR}^* contents, we calculate corrected Fe_{HR}/Fe_T^* and Fe_{py}/Fe_{HR}^* ratios (Extended Data Figs. 7 and 8). This approach provides a considerably improved assessment of water-column redox conditions during deposition of cores EBA-1 and EBA-2, and while our approach does not alter our overall conclusions, it results in 80-90% consistency in terms of redox agreement between Fe_{HR}/Fe_T^* and Fe/Al ratios for both cores, strongly supporting the use of these ratios as proxies for the redox state of the water column.

Data availability statement: All data generated or analysed during this study are included in this published article (and its Supplementary Information files).

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Additional information

Supplementary information is available for this paper at

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Extended Data Figure Captions:

Extended Data Fig. 1 Generalised stratigraphic correlation between the Transvaal/Griqualand (South Africa), Hamersley (Pilbara, Western Australia) and Huronian (Ontario, Canada) successions (modified after ref [41]). The exact stratigraphic position of the loss of MIF-S in the Huronian Basin is uncertain[42,43] and hence not shown.

Extended Data Fig. 2 Geochemical data for the lower part of the Pretoria Group. Dashed lines on Fe_{HR}/Fe_T* plots represent the boundaries for distinguishing oxic and anoxic deposition, and on Fe_{py}/Fe_{HR}* plots represent the boundaries for distinguishing ferruginous and euxinic water-column conditions[21]. Dashed lines on $\Delta^{33}S$ plots are at -0.3‰ and +0.3‰.

Extended Data Fig. 3 Scanning electron microscope images of pyrite and Fe-oxide morphologies. A. EBA-2, Rooihoogte Fm., 1346.2 m. Sample deposited under oxic conditions, $\Delta^{33}S$ = +2.16‰; B. EBA-1, Rooihoogte Fm., 1168 m. Sample deposited under oxic conditions, $\Delta^{33}S$ = +1.77‰; C. EBA-1, Timeball Hill Fm., 1137 m. Sample deposited under ferruginous conditions, $\Delta^{33}S$ = +1.44‰; D. EBA-2, Rooihoogte Fm., 1335.6 m. Sample deposited under ferruginous conditions, $\Delta^{33}S$ = +0.25‰; E. EBA-2, Rooihoogte Fm., 1338.3 m. Sample deposited under euxinic conditions, $\Delta^{33}S$ = +0.17‰; F. EBA-1, Timeball Hill Fm., 706 m. Water column redox state not analysed, $\Delta^{33}S$ = +1.61‰.

Extended Data Fig. 4 Sulphur isotope trends for Rooihoogte-Timeball Hill formation samples. A. Orthogonal data regression for samples with MIF-S ($\Delta^{33}S$ >0.3‰), showing calculated $\Delta^{36}S/\Delta^{33}S$ slope (blue line) and 3σ confidence interval (shaded blue area). Samples from above the Rooihoogte Formation are distinguished as open blue circles. B. Orthogonal data regression for MDF-S samples ($\Delta^{33}S = 0 \pm 0.3$‰), showing calculated $\Delta^{36}S/\Delta^{33}S$ slope (red line) and 3σ confidence interval (shaded red area).

Extended Data Fig. 5 Sulphur isotope data from Fennoscandia[5] and Western Australia[27,28]. ARA = Archean Reference Array[22,23]; R-TH = Rooihoogte/Timeball Hill/Boshoek formations. Blue dashed lines represent the range for the ARA (-0.9 ± 0.1). Perturbed slope range represents maximum deviation from the standard ARA due to the temporal effects of either enhanced methane-derived organic haze[24,44,45] or volcanic sulphur input[46].

Extended Data Fig. 6 Simplified geologic map of the Transvaal Supergroup outcrop area (modified after ref [47]).

Extended Data Fig. 7 Ocean redox data for EBA-1. Dashed line on Fe/Al plot represents the upper boundary for distinguishing anoxia[20], and on the Fe_{PRS}/Al plot represents the Phanerozoic average[48].

Dashed lines on Fe_{HR}/Fe_T and Fe_{HR}/Fe_T* plots distinguish oxic and anoxic deposition[21]. Dashed lines on Fe_{PRS} plot represent the average Phanerozic range (1.80 ± 0.85 wt%; ref [48]).

Extended Data Fig. 8 Ocean redox data for EBA-2. Dashed line on Fe/Al plot represents the upper boundary for distinguishing anoxia[20], and on the Fe_{PRS}/Al plot represents the Phanerozoic average[48]. Dashed lines on Fe_{HR}/Fe_T and Fe_{HR}/Fe_T* plots distinguish oxic and anoxic deposition[21]. Dashed lines on Fe_{PRS} plot represent the average Phanerozic range (1.80 ± 0.85 wt%; ref [48]).