

A new Re-Os age constraint informs the dynamics of the Great Oxidation Event

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ABSTRACT

The early Paleoproterozoic (ca. 2.5–2.2 Ga) represents a critical juncture in Earth history, marking the inception of an oxygenated atmosphere while bearing witness to potentially multiple widespread and severe glaciations. Deciphering the nature of this glacial epoch and its connection with atmospheric oxygenation has, however, proven difficult, hindered by a reliance on disputed stratigraphic correlations given the paucity of direct radiometric age constraints. Nowhere is this more acute than within the South African Transvaal Supergroup: Here, while the loss of oxygen-sensitive mass-independent sulfur isotope fractionation (S-MIF) has been reported from both the Duitschland and Rooihogte formations, divided opinion surrounding the time-equivalence of these units has prompted authors to argue for vastly different oxygenation trajectories. Addressing this debate, we present a depositional Re-Os age (2443 ± 33 Ma) from diamictite samples preserved in drillcore of the upper Duitschland Formation. The 100-million-year separation between the Duitschland Formation and its previously presumed equivalent reveals at least two isolated disappearances of S-MIF, requiring that the Great Oxidation Event was dynamic and proceeded via discrete oxygenation episodes whose structure remains incompletely understood. Importantly, our revised framework aligns the lower Duitschland diamictite with the low-latitude glacigenic Makganyene Formation, supporting hypotheses of widespread regional, and potentially global, early Paleoproterozoic glaciation.

INTRODUCTION

Owing to its extreme oxygen intolerance (Pavlov and Kasting, 2002), the presence of mass-independent sulfur isotope fractionation (S-MIF) within the geological record is taken to reflect the persistence of an oxygen-free atmo-

spheric state for over half of Earth's history. Thereafter, although the broad disappearance of S-MIF is used to constrain the initial accumulation of atmospheric oxygen to 2.5–2.3 Ga, different readings of the S-MIF record have been used to portray vastly different oxygenation trajectories, with researchers arguing for either a unidirectional (Luo et al., 2016; Warke et al., 2020) or an oscillatory oxygenation pathway (Gumsley et al., 2017; Poulton et al., 2021).

Despite being central to both viewpoints, stratigraphic uncertainties within the South African Transvaal Supergroup (Fig. 1) are the root of this divergence. Here, the Duitschland and Rooihogte formations record the disappearance of S-MIF (Fig. 2), which occurred ca. 2316 Ma in the latter (Hannah et al., 2004; Luo et al., 2016). In the absence of direct age constraints from the Duitschland Formation, opinions differ concerning its time equivalence to the Rooihogte Formation, and, while many have correlated these

units (Coetzee, 2001; Luo et al., 2016; Warke and Schröder, 2018; Havsteen et al., 2023; Beukes and Schröder, 2024), others view them as separate entities (Gumsley et al., 2017; Bekker et al., 2020; Poulton et al., 2021; Senger et al., 2023). Thus, radiometric age constraints are necessary to test these stratigraphic models and construct robust regional and global correlations to elucidate the timing and trajectory of atmospheric oxygenation.

Profound changes in atmospheric composition likely influenced the planet's greenhouse gas inventory with concomitant climatic ramifications. Indeed, globally distributed glacial diamictites, some deposited at low latitudes (Evans et al., 1997; Gumsley et al., 2017), imply dramatic climate upheavals and the development of severe, potentially snowball-Earth-like, glaciation(s) during the early Paleoproterozoic (Kirschvink et al., 2000). To determine the extent and synchronicity of these glaciations, absolute age constraints from units hosting glacial deposits, including the Duitschland Formation, are needed to inform a more nuanced understanding of their relationship, if any, with atmospheric oxygenation.

GEOLOGIC BACKGROUND

The Transvaal Supergroup is preserved predominantly within the Griqualand West and Transvaal basins of the Kaapvaal Craton, South Africa (Fig. 1). While analogous chemical sedimentation, conforming to a robust chronostratigraphic framework, defines the lower Transvaal Supergroup (Chuniespoort and lower Ghaap groups), their basin-specific character diverges thereafter (Fig. 2; Beukes, 1983; Nelson et al., 1999; Pickard, 2003). In the Griqualand West Basin, the siliciclastic Koegas Subgroup breaks from chemical sedimentation, being sequentially overlain by the glacigenic Makganyene

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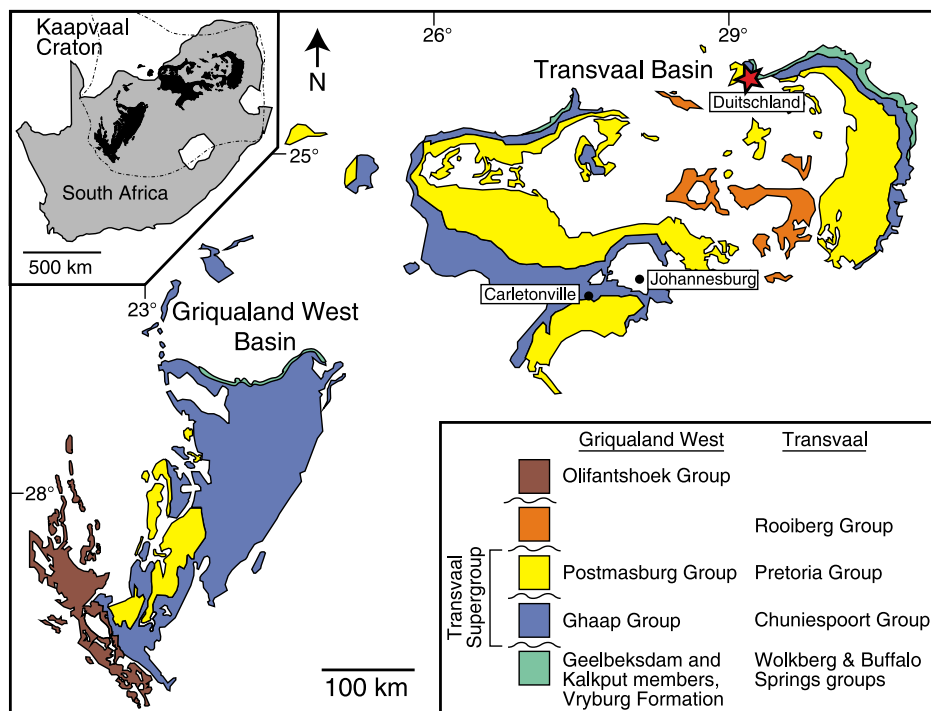


Figure 1. Simplified geology of the Griqualand West and Transvaal basins preserved within the Kaapvaal Craton, South Africa (inset). Core ADL-1 is marked with a star. Modified from Coetzee (2001).

Formation (Evans et al., 1997; Gumsley et al., 2017), the volcanogenic Ongeluk Formation, the Mn- and Fe-rich Hotazel Formation, and carbonates of the Mooidraai Formation. Within the Transvaal Basin, however, the ferruginous Penge Formation grades into the mixed siliciclastic-carbonate Tongwane Formation, which is unconformably overlain by the Duitschland and Timeball Hill formations in the northeast (Fig. 1) and the Rooihoochte and Timeball Hill formations over the remainder of the basin where the Tongwane–Duitschland formations are absent.

While the Rooihoochte–Timeball Hill transition is dated to ca. 2316 Ma in the Carletonville area (Hannah et al., 2004), the Duitschland Formation lacks any direct depositional age constraint. Consequently, the recognition of broad lithological and geochemical similarities between the two units, in combination with their unconformable relationship with the underlying Penge Formation, has prompted some authors to correlate the two units (Coetzee, 2001; Luo et al., 2016; Havsteen et al., 2023; Beukes and Schröder, 2024). In detail, however, while the Duitschland Formation hosts a 30–200-m-thick glaciogenic diamictite near its base (Coetzee, 2001) and is bisected by the mid-Duitschland unconformity (MDU), defined by conglomerates and evidence of syn-depositional faulting (Warke and Schröder, 2018), only locally developed diamictites and conglomerates are seen within the Rooihoochte Formation (Coetzee, 2001; Luo et al., 2016). Furthermore, the Rooihoochte–Timeball Hill contact is gradational,

whereas the Duitschland equivalent is marked by a 20-m-thick chert breccia that may signal a significant hiatus (Coetzee, 2001; Gumsley et al., 2017; see Supplemental Material text¹).

APPROACH AND RESULTS

Aiming to test conflicting viewpoints concerning the timing and trajectory of atmospheric oxygenation, we sampled a fine-grained, locally developed, 0.4-m-thick diamictite interpreted as a gravity flow ~15 m above the MDU for rhenium-osmium (Re-Os) geochronology. Samples containing mudstone and carbonate clasts and matrix were obtained from core ADL-1, drilled at the type locality of the Duitschland Formation (Fig. 1). As detailed in the Supplemental Material, whole-rock diamictite sub-samples from core interval 280.95–280.55 m underwent chemical, mass spectrometry, and data-reduction protocols for Re-Os isotope analysis within the Yale Geochemistry and Geochronology Center. This approach yielded a Model 3 isochron age of 2443 ± 33 Ma with an associated initial $^{187}\text{Os}/^{188}\text{Os}$ (Osi) ratio of 0.15 ± 0.05 , mean square of weighted deviates (MSWD) = 62 (Fig. 3; Table S1). Total uncertainties are

¹Supplemental Material. Detailed analytical methods and sample information, supplemental stratigraphic context, data tables containing all geochronological, petrographic, and whole-rock geochemical data. Please visit <https://doi.org/10.1130/GEOLOGY.S26857663> to access the supplemental material; contact editing@geosociety.org with any questions.

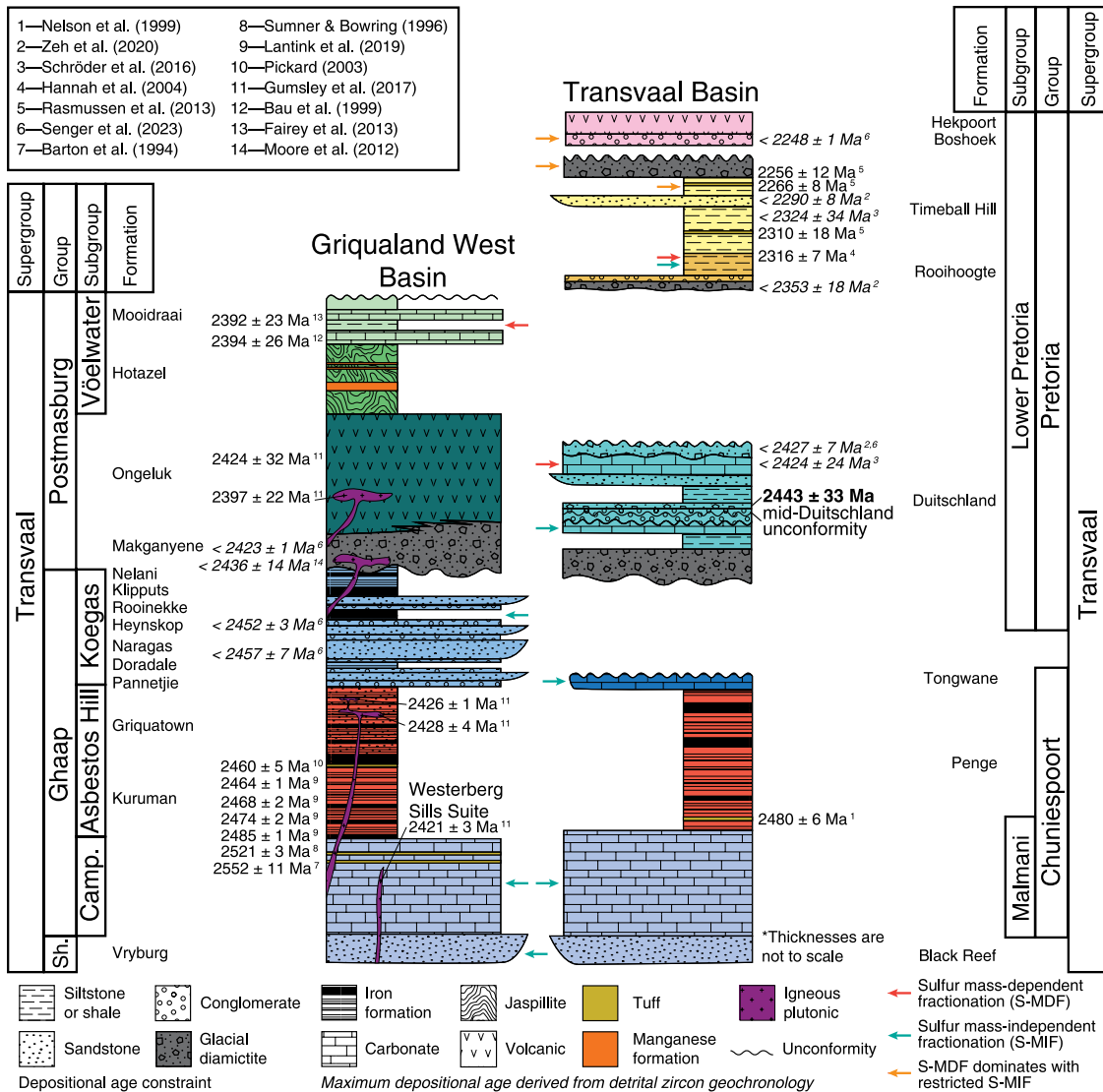
reported at 2σ and include the uncertainty associated with the ^{187}Re decay constant. To verify the hydrogenous origin of Re and Os within the upper Duitschland Formation, major- and trace-element abundance and total organic carbon content determinations were generated at Activation Laboratories, Canada (Table S2).

DISCUSSION

Implications for the Great Oxidation Event

Though other scenarios may be permissible, the weight of the geochemical evidence presented here supports the interpretation that our Re-Os age of 2443 ± 33 Ma constrains deposition of the upper Duitschland Formation to between ca. 2476 and 2410 Ma (see discussion in the Supplemental Material). This new age is consistent with the maximum depositional zircon U–Pb age (Schröder et al., 2016; 2424 ± 24 Ma) and reinterpretation of an existing constraint (Zeh et al., 2020; 2353 ± 18 Ma) by Senger et al. (2023; 2427 ± 7 Ma). The coalescence of these ages invalidates previous correlations (Coetzee, 2001; Luo et al., 2016; Havsteen et al., 2023; Beukes and Schröder, 2024) with the ca. 2316 Ma Rooihoochte Formation (Hannah et al., 2004), identifying the Duitschland Formation as a discrete unconformity-bounded unit (Fig. 2).

Temporal separation of the Duitschland and Rooihoochte formations requires at least two disappearances of S-MIF within the Transvaal Basin, with the first recorded in the lower portion of the upper Duitschland Formation in the Duitschland area (Guo et al., 2009), and the latter occurring ~100 million years later within the upper Rooihoochte Formation in the Carletonville area (Luo et al., 2016). Interestingly, while the isochron-derived Osi (0.15 ± 0.05) overlaps with contemporaneous mantle (0.11 ; Fig. 3), we suggest this value represents a moderate oxidative source of radiogenic Os to the oceans, consistent with co-occurring hydrogenous Re and Os enrichments. Evidence for oxidative weathering combined with multiple losses of S-MIF in the Transvaal Supergroup offers insight into the dynamics of the Great Oxidation Event, requiring multiple sustained oxygenation episodes of sufficient severity to break from the S-MIF-yielding oxygen-free background state that predominated until ca. 2316 Ma (Luo et al., 2016; Izon et al., 2022). Although isolated instances of S-MIF within the overlying Timeball Hill Formation have been used to argue for continued fluctuations in atmospheric oxygen levels until ca. 2250 Ma (Fig. 2; Poulton et al., 2021), subsequent work has failed to identify these instances of S-MIF in the same and adjacent borehole cores (Izon et al., 2022; Uveges et al., 2023). Thus, any post-Rooihoochte oxygen fluctuations must have been ephemeral, representing departures from a more oxygen-replete background state than before ca. 2316 Ma (Uveges et al., 2023). While we await the constraints necessary to fully illuminate the



dynamics of the Great Oxidation Event, it appears that the atmosphere accrued oxygen in an episodic fashion operating on million-year time scales. Defining the timing and tempo of these newly resolved oxygenation episodes remains the critical next step as we test ideas about the cause(s) and consequence(s) of atmospheric oxygenation and their link with glaciation.

Deutschland Formation Correlation with the Griqualand West Basin

Given that the angular unconformity and diverse conglomeratic facies directly underlying the MDU have been ascribed to deposition in a deltaic environment prone to syn-depositional faulting (Warke and Schröder, 2018), the time encompassed by the MDU is likely to be insignificant relative to the precision of our approach (Fig. 3; see Supplemental Material text). Therefore, our 2443 ± 33 Ma age obtained from ~15 m above the MDU provides a close minimum age for the basal Deutschland

glacial diamictite (Bekker et al., 2001; Coetzee, 2001). This age is statistically inseparable from the known maximum and minimum bounds of the glacial Makganyene Formation (Senger et al., 2023; Gumsley et al., 2017), permitting correlation between these two glacial units, while aligning the upper Deutschland Formation and the Vöelwater Subgroup, which is temporally indistinguishable (Fig. 2; Bau et al., 1999; Fairley et al., 2013). Furthermore, recognizing a glacial diamictite in the upper Timeball Hill Formation and equivocal evidence for glacial deposition in the basal Rooihooft Formation (Coetzee, 2001), the Makganyene-Deutschland correlation allows a maximum of three distinct glacial horizons within the Transvaal Supergroup.

Global Correlation of Early Paleoproterozoic Glaciation and Relationship with Oxygenation

Combined sedimentological (Polteau et al., 2006) and paleomagnetic (Evans et al., 1997)

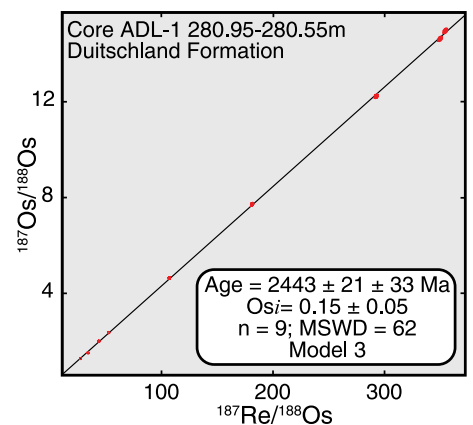


Figure 3. Rhenium-Os isochron from the upper Deutschland Formation (280.95–280.55 m; ADL-1). Plotted ellipses convey 2 σ analytical uncertainties; the larger age uncertainty incorporates uncertainty in the ^{187}Re decay constant (2 σ). Osi—initial $^{187}\text{Os}/^{188}\text{Os}$; MSWD—mean square of weighted deviates.

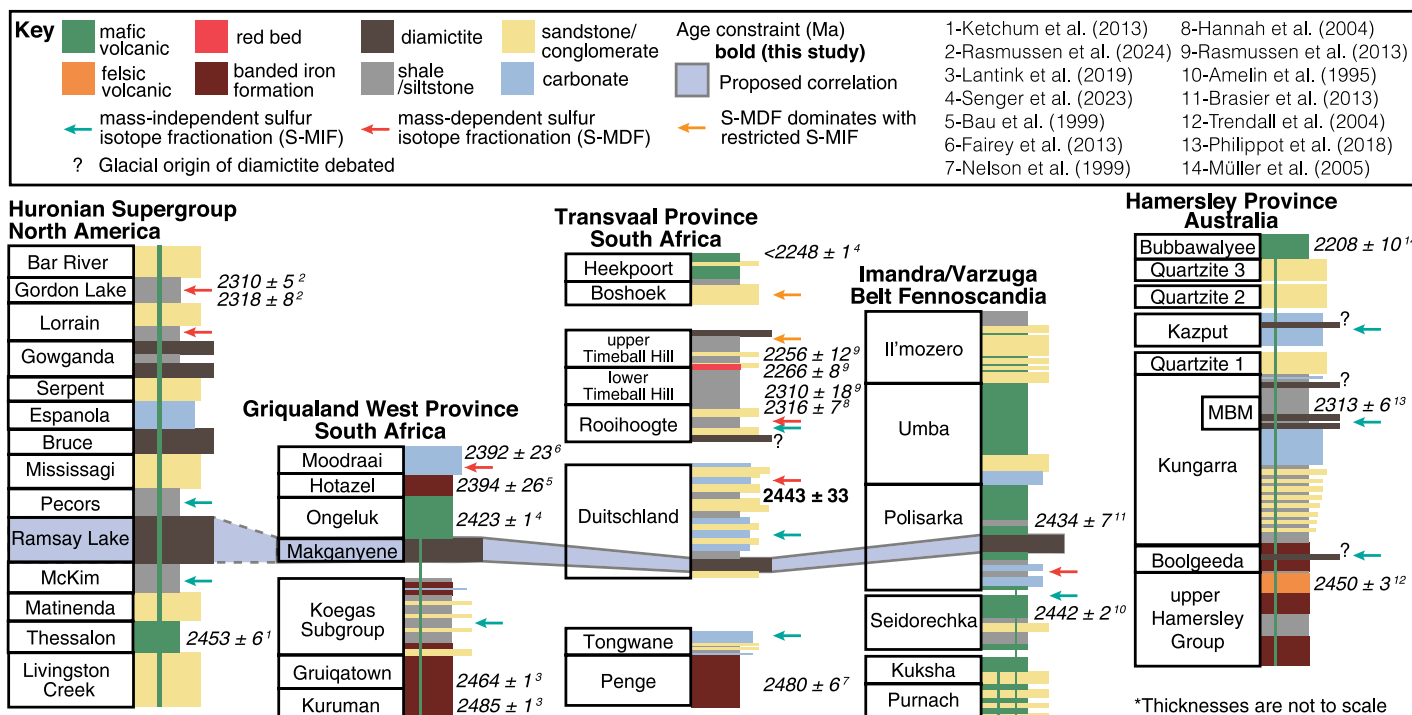


Figure 4. The global chronostratigraphic distribution of, and proposed correlation between, early-Paleoproterozoic-aged diamictite-bearing successions. MBM—Meteorite Bore Member. Modified from Bekker et al. (2020).

evidence characterizes the Makganyene Formation as a marine-influenced, low-latitude, glacial unit. These features, in concert with the global-scale abundance of early Paleoproterozoic glacial diamictites, have prompted many workers to envisage a snowball Earth climatic state during this interval (e.g., Kirschvink et al., 2000). Accordingly, correlation of the lower Duitschland and Makganyene diamictites (Fig. 2) strengthens arguments for widespread glaciation at ca. 2430 Ma.

Further support for widespread glaciation can be found in Fennoscandia (Fig. 4), where the glacial Graywacke-Diamictite Member of the Polisarka Formation, deposited between 2442 ± 2 Ma and 2434 ± 7 Ma, can be correlated with the Makganyene and Duitschland formations (Fig. 4; Amelin et al., 1995; Brasier et al., 2013). Beyond this, however, the picture is less clear. Within the North American Huronian Supergroup, for instance, three diamictite-bearing units were deposited between 2453 ± 6 Ma and 2310 ± 5 Ma (Ketchum et al., 2013; Rasmussen et al., 2024). While the oldest diamictite, the Ramsey Lake Formation, likely correlates with the ca. 2430 Ma South African glacial deposits, the lack of sufficiently precise radiometric ages prevents unequivocal correlation. Given the disputed age (2313 ± 16 Ma or ca. 2430 Ma) of the Meteorite Bore Member, Turee Creek Group (Philippot et al., 2018; Bekker et al., 2020), and contested glacial nature (Martin, 2020; Bekker et al., 2020) of the $<2450 \pm 3$ Ma (Trendall et al., 2004)

diamictite within the underlying Boolgeeda Formation, it is currently unclear how glacial strata from Western Australia correlate globally. Clearly, further geochronologic constraints are required to develop a robust chronostratigraphic framework capable of resolving global-scale glacial dynamics during the early Paleoproterozoic and their potential link to atmospheric oxygenation.

Warke et al. (2020) interpret sulfur mass-dependent fractionation below the Polisarka diamictite as evidence that oxygenation and resultant oxidation of atmospheric methane drove glaciation by reduction of the greenhouse effect (Fig. 4; Pavlov et al., 2000; Claire et al., 2006). In contrast, the persistence of S-MIF above the potentially correlative basal Duitschland diamictite, and subsequent loss across the MDU, favors models in which oxygenation is driven by deglacial weathering (Kirschvink et al., 2000; Gumsley et al., 2017; Poulton et al., 2021). Moreover, documentation of multiple glacial diamictites and losses of S-MIF discounts singular tectonic or evolutionary drivers and instead requires that any causal mechanism for glaciation or oxygenation be dynamic (e.g., Gumsley et al., 2017; Poulton et al., 2021). Additionally, if the Polisarka and lower Duitschland are correlative, the disappearance of S-MIF preceding deposition of the ca. 2430 diamictite in Fennoscandia suggests that reevaluation of equivalent strata in South Africa, the Koegas Subgroup and Tongwane Formation, may provide further insight into the highly dynamic nature of the Great Oxidation Event.

CONCLUSIONS

A new Re-Os isochron age of 2443 ± 33 Ma from a diamictite in the upper Duitschland Formation invalidates previous correlations with the Rooihoogte Formation (Coetzee, 2001; Luo et al., 2016; Havsteen et al., 2023; Beukes and Schröder, 2024). Dissociation of these units by ~ 100 million years requires at least two broad-scale S-MIF losses within the Transvaal Basin (Guo et al., 2009; Luo et al., 2016), implying that atmospheric oxygenation was dynamic and that the Great Oxidation Event comprised multiple, currently ill-defined, oxygenation episodes. Aligning the lower Duitschland diamictite with the glacial Makganyene Formation extends the reach of low-latitude glacial deposits beyond the Griqualand West Basin, emphasizing the broader extent of the ca. 2430 Ma glaciation. In turn, this stratigraphic revision identifies the Ghaap–Postmasburg and Chuniespoort–Pretoria transitions as key intervals to further elucidate the initial causes of these pivotal events in Earth history.

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