The Great Oxidation Event preceded a Paleoproterozoic “snowball Earth”

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Edited by Mark Thiemens, University of California San Diego, La Jolla, CA, and approved April 28, 2020 (received for review February 18, 2020)

The inability to resolve the exact temporal relationship between two pivotal events in Earth history, the Paleoproterozoic Great Oxidation Event (GOE) and the first “snowball Earth” global glaciation, has precluded assessing causality between changing atmospheric composition and ancient climate change. Here we present temporally resolved quadruple sulfur isotope measurements (δ33S, Δ32S, and Δ36S) from the Paleoproterozoic Seidorechka and Polisarka Sedimentary Formations on the Fennoscandian Shield, northwest Russia, that address this issue. Sulfides in the former preserve evidence of mass-independent fractionation of sulfur isotopes (S-MIF) falling within uncertainty of the Archean reference array with a Δ33S/Δ32S slope of −1.8 and have small negative Δ32S values, whereas in the latter mass-dependent fractionation of sulfur isotopes (S-MDF) is evident, with a Δ36S/Δ33S slope of −8.8. These trends, combined with geochronological constraints, place the S-MIF/S-MDF transition, the key indicator of the GOE, between 2,501.5 ± 1.7 Ma and 2,434 ± 6.6 Ma. These are the tightest temporal and stratigraphic constraints yet for the S-MIF/S-MDF transition and show that its timing in Fennoscandia is consistent with the S-MIF/S-MDF transition in North America and South Africa. Further, the glaciogenic part of the Polisarka Formation occurs 60 m above the sedimentary succession containing S-MDF signals. Hence, our findings confirm unambiguously that the S-MIF/S-MDF transition preceded the Paleoproterozoic snowball Earth. Resolution of this temporal relationship constrains cause-and-effect drivers of Earth’s oxygenation, specifically ruling out conceptual models in which global glaciation precedes or causes the evolution of oxygenic photosynthesis.

quadraple sulfur isotopes | mass independent fractionation | Great Oxidation Event | snowball Earth

The early Paleoproterozoic transition from mass-independently fractionated sulfur isotopes (S-MIF) to mass-dependent fractionation (S-MDF; i.e., where Δ33S and Δ36S ≈ 0) is now recognized as a key proxy identifying a unidirectional and global rise in atmospheric oxygen (1), the Great Oxidation Event (GOE; ref. 2). In broad temporal proximity with the S-MIF/S-MDF transition were periods of severe glaciation, including at least one “snowball Earth” event (3, 4). However, assessing causality (if any) between, and enhancing understanding about, changing atmospheric chemistry and ancient climate change leading to glaciations is hindered by the poorly constrained timing of the S-MIF/S-MDF transition with respect to glacial deposits, a problem which is compounded by spurious intercratonic stratigraphic correlations (4–6). As a consequence, a variety of hypotheses, with disparate ordering of key Earth system events, have been advanced including planetary oxygenation being tied to secular changes in planetary degassing following an early evolution of oxygenic photosynthesis (7, 8), the evolution of oxygenic photosynthesis directly triggering a Paleoproterozoic snowball Earth glaciation (4), and/or chemical weathering following deglaciation leading to the GOE (9, 10). Additionally, complicating interpretations of the significance of the S-MIF/S-MDF transition is the “crustal memory effect” hypothesis (11), namely, the reduction in Δ33S magnitude and prevalence of positive Δ33S values in the early Paleoproterozoic could reflect oxidative weathering and erosion with subsequent incorporation of Archean S-MIF signals into younger sediments (11, 12). This has led some workers to suggest that the S-MIF/S-MDF transition in the rock record could lag the atmospheric transition by as much as 10 to 200 Ma (11, 13). Such a scenario undermines using the S-MIF/S-MDF transition as a chemostratigraphic correlation surface (14) and a unique time marker of planetary oxygenation (13, 15, 16), as well as obscuring causality between planetary oxygenation and glaciation (4, 9).

We present a temporally constrained Δ33S, Δ32S, and Δ34S dataset from the Seidorechka and Polisarka Sedimentary Formations of the Imandra/Varzuga Greenstone Belt in the northwest Russian portion (Kola Peninsula) of the Fennoscandian Shield (SI Appendix, Fig. S1). Our data enable us to constrain the nature of S-MIF recycling within the basin, determine the timing of the S-MIF/S-MDF transition, and confirm that the GOE preceded the Paleoproterozoic snowball Earth event.

Significance

The causality between the Paleoproterozoic Great Oxidation Event (GOE) and a global “snowball Earth” glaciation has remained unresolved due to an inability to determine their relative timing. We present quadruple sulfur isotope data from northwest Russia which constrain the GOE between 2,501 and 2,434 Ma. These are the tightest temporal and stratigraphic constraints ever presented for the GOE and show that the GOE predated Paleoproterozoic glaciation in Russia and snowball Earth deposits in South Africa. Our results preclude hypotheses of Earth’s oxygenation in which global glaciation precedes or causes the evolution of oxygenic photosynthesis.

Author contributions: M.R.W., T.D.R., A.L.Z., A.L., A.R.P., A.P.M., D.J.C., and M.W.C. designed research; M.R.W., T.D.R., A.L.Z., and M.W.C. performed research; M.R.W., T.D.R., A.L.Z., Y.U., and M.W.C. contributed new reagents/analytic tools; M.R.W., T.D.R., A.L.Z., and M.W.C. analyzed data; M.R.W. wrote the paper; and T.D.R., A.L.Z., A.L., A.R.P., and M.W.C. contributed to writing the paper.

The authors declare no competing interest.

This article is a PNAS Direct Submission.

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Data deposition: The data and methods supporting this article can be accessed on the University of St Andrews Research Portal (DOI: 10.17630/2faeb51f-7353-4fbc-abdd-cbc7991fc446).

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2003090117/-/DCSupplemental.

First published June 1, 2020.
Geological Setting and Chronological Constraints

The Imandra–Varzuga Greenstone Belt consists of a suite of Paleoproterozoic sedimentary and volcanic rocks that rest unconformably on a mostly Neoarchean gneissic basement (SI Appendix, Fig. S1). Key intervals of the succession were targeted for coring as part of the International Continental Scientific Drilling Program’s Fennoscandian Arctic Russia - Drilling Early Earth Project (FAR-DEEP; ref. 17).

FAR-DEEP drillcore 1A recovered the Seidorechka Sedimentary Formation, a 120-m-thick succession of shallow-marine shale, siltstone, and minor limestone and sandstone that is divided into five lithostratigraphic members: Sandstone-Siltstone member, Dolostone member, Quartzite member, Limestone-Shale member, and Shale member (Fig. 1 and ref. 17). The formation overlies a pervasive zone of calcitization and sericitization developed on the underlying Kuksha Volcanic Formation that is interpreted as a paleoweathering crust (18). The Seidorechka Sedimentary Formation is overlain by the Seidorechka Volcanic Formation. Both the Kuksha and Seidorechka volcanic rocks are mostly basalts but contain minor dacitic and rhyolitic units.

The 129-m-thick Polisarka Sedimentary Formation was recovered in FAR-DEEP drillcore 3A and sharply overlies the Seidorechka Volcanic Formation. The Polisarka Sedimentary Formation is divided into a lower Limestone member and an upper glaciogenic Greywacke-Diamictite member (17, 19); various basaltic, andesitic, and komatiitic lava flows and ultramafic intrusions punctuate the succession (Fig. 1). The Limestone member is comprised of rhythmic interlayers of shale, marl, and limestone interpreted as having been deposited in a low-energy subtidal setting (17). Dropstones have been reported in the Limestone member (17) but bedding-parallel foliation which flattens and rotates clasts renders this interpretation contestable (19). The formation is overlain by komatiitic lava flows of the Polisarka Volcanic Formation (Fig. 1 and ref. 17).

The maximum depositional age of the Imandra/Varzuga sedimentary succession is constrained by isotopic dilution thermal ionization mass spectrometry (ID-TIMS) U-Pb zircon ages of 2,501.5 ± 1.7 Ma and 2,504.4 ± 1.5 Ma for the Neoarchean Pana Tundra and Monche plutons (20). The Seidorechka Volcanic Formation has a baddeleyite age of 2,442 ± 1.7 Ma and the spatially associated Imandra lopolith has a zircon age of 2,441 ± 1.6 Ma (both U-Pb ID-TIMS; ref. 20), whereas zircon grains from a metahydracite in the upper part of the formation are 2,448 ± 8 Ma in age (21). A 2,429 ± 6.6-Ma cross-cutting plagio-quartz dacitic metaporphirite (U-Pb zircon SHRIMP; ref. 22) provides a minimum age for the Seidorechka Volcanic Formation. The Polisarka Volcanic Formation has yielded ID-TIMS zircon ages of 2,434 ± 6.6 Ma (19). Combined these constraints indicate that the Seidorechka Sedimentary Formation was deposited between 2,501.5 ± 1.7 Ma and 2,441 ± 1.6 Ma and the Polisarka Sedimentary Formation between 2,441 ± 1.6 Ma and 2,434 ± 6.6 Ma.

Results

Seidorechka Sedimentary Formation. Values of δ⁳⁴S range from −14.6 to +1.6‰ with a mean value of −6.8‰ (1σ = 3.8‰; n = 24) and show stratigraphic variation. Between 186 and 121 m, δ⁳⁴S values systematically increase upward (Fig. 1). Above 112 m (Shale member), δ⁳⁴S values are negative and do not show any stratigraphic trend. Δ⁳³S values vary from −0.43 to +0.25‰ for the Seidorechka succession (SI Appendix, Table S1) but are almost entirely negative with a mean value of −0.14‰ (1σ = 0.14‰; n = 24). Δ⁳⁶S values range from −0.61 to 1.65‰ with a mean value of 0.16‰ (1σ = 0.52‰; n = 23).

Within the Seidorechka Sedimentary Formation there is no clear stratigraphic trend for Δ⁳³S values (Fig. 1). However, the Quartzite member has more negative and variable Δ⁳⁴S values (−0.43 to −0.29‰). Δ⁳⁶S values in the lower portion of the core are positive but above ~140 m they become negative. Δ⁳⁶S values are highest in the Quartzite member and portions of the overlying Limestone-Shale member. There is a weak positive correlation between δ⁳⁴S and Δ⁳³S values in this formation (see Fig. 3).

Linear regression of a cross-plot of Δ³⁶S and Δ³³S values from the Seidorechka Sedimentary Formation yields a slope of −1.8 (24) but shallowly inclined if the Quartzite member is excluded. The calculation of Δ³⁶S/Δ³³S slopes by linear regression ignores the abscissa’s (Δ³³S) uncertainty and cannot determine an uncertainty on the slope value itself; hence, we performed an orthogonal regression analysis, resulting in a Δ³⁶S/Δ³³S slope of −1.86 ± 0.47 (1σ). Within uncertainty, the data fall along the “Archean reference array” (ARA; Fig. 2B). Mass-dependent fractionation processes can produce small-magnitude Δ³³S and Δ³⁶S, which yield Δ³⁶S/Δ³³S slopes ranging from −6 through –12 (23). Orthogonal regression analysis thus also allows us to state that the sulfur within the Seidorechka Sedimentary Formation demonstrates mass independence within an 8σ confidence interval.

Polisarka Sedimentary Formation. The Limestone member and Greywacke-Diamictite member archive distinctly different S isotope patterns (Figs. 1 and 24). In the Limestone member, δ⁳⁴S values range from −26.6 to −10.2‰ (mean = −16.6‰; 1σ = 5.4‰; n = 10; SI Appendix, Table S2). Strongly negative δ⁳⁴S values are observed within a 14-m-thick interval (~186 to 200 m) of limestone and shale. In contrast, the diamictite δ⁳⁴S values range from −0.8 to 0.0‰ (mean = −0.5‰; 1σ = 0.3‰; n = 5). Δ⁳⁴S values of the greywacke and dolarenite samples from ~115 and ~125 m transition from negative δ⁳⁴S values in the underlying Limestone member to near zero δ⁳⁴S values in the diamictite. Within this ~10 m interval, δ⁳⁴S values increase from −8.5 to −1.6‰.

Within the majority of the Limestone member (depths >170 m) Δ⁳⁴S values are low and positive, ranging from +0.03 to +0.05‰ (mean = +0.02; 1σ = 0.01‰; n = 14) and Δ³⁶S values are positive, ranging from +0.21 to +0.75‰ (mean = +0.45; 1σ = 0.16‰; n = 14). One dolarenite sample from the uppermost Limestone member (~124 m) has a negative Δ³⁴S value of −0.38 that is similar to Seidorechka values.

Samples from the Limestone member (~170 m) plot tightly along a steep, mass-dependent Δ³⁶S/Δ³³S slope of ~8.8, as determined by the standard methodology of linear regression (Fig. 24). Orthogonal regression analysis including the analytical uncertainties in the Δ³³S predicts a much steeper slope of −61.7 ± 53.5 (1σ). While our data fit criteria in which best-fit orthogonal slopes are known to overpredict (SI Appendix, Methods), the analysis reveals that our data could be fit by a wide variety of slopes, including positive (as indicated by wide blue band in Fig. 2C). A distinctly mass-dependent slope of −8.2 is obtained as a one SD from the best orthogonal fit, complementing the slope of ~8.8 from linear regression. The possibility remains that our data were obtained from a distribution of samples with mass-independent properties, but we have demonstrated that such a sampling would have been a statistical aberration exceeding 1σ. We consider this possibility highly unlikely given that the consistently low Δ³³S values and expanded negative δ⁳⁴S range (Fig. 3) have the more parsimonious explanation of mass-conservation effects stemming from mass-dependent microbial processing (24).

Within the Greywacke-Diamictite member Δ³⁴S values are negative, ranging from −1.06 to −0.39‰ (mean = −0.60‰; 1σ = 0.59‰; n = 5) and Δ³⁶S values are low and consistently positive, ranging from +0.01 to +0.03‰ (mean = +0.02; 1σ = 0.01‰; n = 14). The Δ³⁴S/Δ³³S values of the Greywacke-Diamictite member do not show any correlation but broadly cluster at the positive Δ³⁴S and negative Δ³⁶S range of values measured from the Seidorechka Sedimentary Formation and align the latter’s Δ³⁴S/Δ³³S slope (Fig. 24). The dolarenite sample (~124 m) of the
Limestone member plots in the negative $\Delta^{33}S$, positive $\Delta^{36}S$ quadrant and aligns strongly with the Seidorechka dataset (Fig. 2A). Polisarka samples fail to show any systematic correlation between the width of $\delta^{34}S$ values (≈26‰) and the narrow range in $\Delta^{33}S$ values (<0.1‰; Fig. 3).

Discussion

Disappearance of S-MIF in Fennoscandia. Where $\Delta^{33}S$ carries a low-magnitude S-MIF signal, covariations in $\Delta^{36}S$ and $\Delta^{33}S$ are examined to ascertain whether an atmospheric S-MIF signature is preserved (25). Neoarchean and early Paleoproterozoic successions possess $\Delta^{36}S/\Delta^{33}S$ slopes of between −0.9 and −1.6 which define the ARA (26–30). Low-magnitude $\Delta^{36}S$ and $\Delta^{33}S$ values make calculation of $\Delta^{36}S/\Delta^{33}S$ slopes more uncertain (29). Our orthogonal regression analysis shows that the $\Delta^{36}S/\Delta^{33}S$ slope of the Seidorechka succession is consistent with the ARA (Fig. 3A and B), indicating atmospheric production of S-MIF in the absence of ozone. In contrast, the steep $\Delta^{36}S/\Delta^{33}S$ slope of −8.8 for the Limestone member of the Polisarka Sedimentary Formation is inconsistent with the preservation of an atmospheric S-MIF signal (Fig. 2A). Whereas a positive relationship exists between $\Delta^{33}S$ vs. $\delta^{34}S$ in the Seidorechka Sedimentary Formation, in the Polisarka Sedimentary Formation very low $\Delta^{33}S$ values are associated with a wide scatter of negative $\delta^{34}S$ values (Fig. 4).

The near-zero $\Delta^{33}S$ values and $\Delta^{36}S/\Delta^{33}S$ characteristics of the Greywacke-Diamictite member, and a lone dolarenite sample from the Limestone member, fall within the $\Delta^{36}S/\Delta^{33}S$ slope typifying the Seidorechka succession (Figs. 2A and 3C). This...
apparent return of S-MIF coincides with facies that record increased detrital input by glacigenic and/or higher-energy processes (e.g., dolarenite). Critically, there is direct correspondence between S isotope values and lithofacies: the intervals of "normal" or "background" sedimentation do not show S-MIF, whereas those of enhanced sediment flux (e.g., diamictite) do. The most parsimonious interpretation of this pattern is that the enhanced flux obscured the S-MDF signal by bringing into the basin detritus carrying a recycled S-MIF signal.

Our findings are clear: the \( \Delta^{36}S/\Delta^{33}S \) and \( \Delta^{33}S/\delta^{34}S \) trends in the lower Polisarka Sedimentary Formation require that the S-MIF/S-MDF transition, often invoked as the key GOE indicator, occurred within a 70-My window bracketed by \( \sim 2,501 \) Ma and \( \sim 2,434 \) Ma. However, the duration was likely much less as three unconformities occur within that time window: 1) The basement-sediment contact is a major nonconformity marked by an erosive-based conglomerate unit comprised of basement-derived clasts, 2) a thick (as much as 10 m) paleoweathering crust separates the Seidorechka Sedimentary Formation from the underlying Kuksha volcanic rocks, and 3) the base of the quartzite unit in the middle of the Seidorechka Sedimentary Formation defines an angular unconformity. Further, the glacigenic diamictite and associated units of the Polisarka succession occur 60 m above sedimentary units containing S-MDF signals. This confirms that the S-MIF/S-MDF transition predates the glaciation but precludes a precise estimate of the time interval between disappearance of S-MIF and the glaciation.

It is not possible to test whether the S-MIF signal reappears above the diamictite as the glacial unit is overlain by Polisarka Volcanic Formation (Fig. 1). The volcanic units are in turn overlain by the Umba Sedimentary Formation but, as the latter preserves the Lomagundi–Jatuli positive carbonate isotope excursion, it likely dates to \( \sim 2,200 \) to \( 2,060 \) Ma (17) and irreversible disappearance of the S-MIF signal has been demonstrated by this period (31).

Crustal Recycling of S-MIF Signals. The recurrence of S-MIF in the glacial Greywacke-Diamictite member implies that S-MIF recycling can temporarily overwhelm a background mass-dependent signal as highlighted by the "crustal memory effect" hypothesis. However, the near-zero \( \Delta^{33}S \) values and S-MDF \( \Delta^{36}S/\Delta^{33}S \) characteristics of the

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**Fig. 2.** (A) Cross-plot of \( \Delta^{33}S \) and \( \Delta^{36}S \) values from both the Polisarka (squares) and Seidorechka (circles) successions with marker color as assigned in Fig. 1 and shown in the key. Slope values were calculated using linear regression. Error bars are as listed in SI Appendix, Tables S1 and S2. (B) Orthogonal regression plot of all facies from the Seidorechka Sedimentary Formation (gray circles) showing calculated \( \Delta^{36}S/\Delta^{33}S \) slope (blue line) and 3σ confidence interval (shaded blue area). (C) Orthogonal regression plot of the Limestone member (Polisarka Sedimentary Formation; dark blue squares) showing calculated \( \Delta^{36}S/\Delta^{33}S \) slope (gray line) and 3σ confidence interval (shaded blue area).

**Fig. 3.** Cross-plot of \( \Delta^{33}S \) and \( \delta^{34}S \) values from both the Polisarka (red squares) and Seidorechka (blue circles) successions. Error bars displayed are as listed in SI Appendix, Tables S1 and S2.
Is the S-MIFS/MDF Transition Globally Asynchronous? Constraining the precise timing of the S-MIFS/MDF transition has been frustrated by a lack of robust absolute age constraints. However, improved stratigraphic correlations between western Australia, Fennoscandia, North America, and southern Africa have emerged (13, 16, 31–33). In the discussion below we summarize these and compare them to the constraints now established for Fennoscandia (Fig. 4).

The laterally correlative Duitschland and Rooihoogte Formations (Transvaal Basin, South Africa) archive the S-MIFS/MDF transition (16, 34–36). The Duitschland Formation has an upper S-MDF–bearing portion and lower S-MIF–bearing portion that are separated by a major regional unconformity of unknown duration (36). The lower portion was deposited between 2,480 and 2,310 Ma (37, 38). The upper portion is younger than 2,424 Ma but could be closer to ~2,310 Ma in age based on dating of the conformably overlying successions (31, 38, 39). Geochronological data for the Griqualand West Basin (Fig. 4) are sparse but the first appearance of a mass-dependent signal is in the Mooi德拉 Formation based on five samples that define a Δ34S/Δ33S slope of ~12 (34), implying that the S-MIFS/MDF transition had occurred by ~2,390 Ma (40, 41).

In western Australia, the S-MIFS/MDF transition is ambiguous. In the Boolgeeda Iron Formation (Hamersley Group, western Australia) an S-MDF signal is first recorded after 2,450 Ma (13, 33), which is broadly coeval with the Fennoscandian S-MIFS/MDF transition, but is succeeded by S-MIF signals. Siltstones at the top of the Boolgeeda Iron Formation contain pyrite with cores and rim compositions consistent with sulfate reduction of a sulfate reservoir with a recycled S-MIF component (13). Such values could be consistent with the crustal memory effect and could have occurred within 10^5 to 10^7 y of the S-MIFS/MDF transition. However, other sulfur isotope studies of the Boolgeeda Iron Formation have contrasting Δ33S and Δ34S values, including negative Δ33S values that would be inconsistent with the crustal memory effect and indicative of a reducing atmosphere (42). In the overlying Turee Creek Group (~2,312 ± 22 Ma) two intervals record positive Δ33S values and Δ34S/Δ33S values that fall on the ARA (13). However, both intervals either consist of clastic and glaciogenic sedimentary rocks or were deposited in an environment that experienced significant detrital input (43). Thus, the S-MIF signals recorded in both intervals could reflect similar, localized crustal recycling processes as previously inferred (13). Such overprinting likely reflects discrete periods of enhanced sediment influx, such as during periods of...
deglaciation, rather than prolonged and continuous (10^8 yr) operation of the crustal memory effect.

The S-MIF/S-MDF transition in the Huronian Supergroup on the Superior Craton (North America) is constrained to between the extrusion of the Copper Cliff Rhyolite at 2,452.5 ± 6.2 Ma and ~2,308 Ma (Fig. 4 and refs. 31, 44, and 45), though this has been disputed (46). Given the thickness of strata and presence of major stratigraphic unconformities between the S-MIF-bearing Pecors Formation and S-MDF-bearing Espanola Formation, the S-MIF/S-MDF transition is likely considerably older than ~2,308 Ma.

In summary, and notwithstanding the potential for enhanced sediment flux to mask the timing of the S-MIF/S-MDF transition, the current age constraints indicate that the transition is broadly synchronous across North America, South Africa, and Fennoscandia. The transition in western Australia remains uncertain and could be obscured by crustal recycling processes.

The GOE Preceded a Paleoproterozoic Snowball Earth. In the Griqualand West Basin, the glacialic Makganyene Formation is intercalated with the volcanic Ongeluk Formation, which was extruded in the low latitudes, suggesting the Makganyene glaciation was intercalated with the volcanic Ongeluk Formation, which was glacigenic. In the Makganyene West Basin, the glacigenic Makganyene Formation is certain and could be obscured by crustal recycling processes.

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The Seidorechka Sedimentary Formation in Fennoscandia preserves small negative Δ3S/Δ34S values and aligns along a Δ35S/Δ34S slope that is consistent with the ARA and an atmospheric S-MIF signal. Overlying sediments from the Polisarka Sedimentary Formation preserve near-zero Δ34S values and lie along a steep Δ35S/Δ34S slope that is consistent with S-MDF. This observation constrains the timing of the S-MIF/S-MDF transition, and therefore the establishment of an oxidizing atmosphere on Earth, to between ~2,501 and ~2,434 Ma. Critically, this transition occurred sometime prior to the ca. 2,428- to 2,423-Ma snowball Earth glaciation given that the glacialic part of the Polisarka Formation occurs ~60 m above S-MDF–bearing strata of the Polisarka Sedimentary Formation. This is the tightest temporal constraint yet imposed on the GOE and the agreement between the Fennoscandian and South African sulfur isotope records shows that the S-MIF/S-MDF transition preceded a Paleoproterozoic snowball Earth event.

Methods

Samples and Protocol. FAR-DEEP drill-cores 1A and 3A were sampled using known procedures (52). Core samples (rock types listed in SI Appendix, Tables S1 and S2) were cut, crushed, and prepared for isotopic analysis using previous described techniques (29, 30) which are described fully in the SI Appendix. Δ34S values were measured on SO2 gas at the University of St Andrews, Scotland, using a Thermo IsoLink Elemental Analyzer coupled to MAT 253 mass spectrometer in continuous-flow mode. The analytical uncertainty for δ34S is better than 0.3‰ (1σ). Minor sulfur isotope analyses (Δ33S, Δ35S) were performed on SF6 gas at the University of St Andrews using offline SF6 generation and a second, dedicated Thermo MAT253 mass spectrometer in dual-inlet mode. SF6 gas was generated by fast-heating Ag2S to 590 °C in the presence of a solid fluorinating agent, CoF3, using an updated Curie point pyrolysis method (53) detailed in SI Appendix. Δ34S values were calculated as Δ34S = 1,000 * (∑[ln(32S/34S)/1,000 + 1] − 0.515 * ln(34S/33S)/1,000 + 1)) and Δ35S values were calculated as Δ35S = 1,000 * [ln((35S/32S)/1,000 + 1) − 1.9 * ln((36S/32S)/1,000 + 1)]. Analytical uncertainty was determined from repeated analysis of IAEA-S1 between March 2019 and January 2020 (n = 64), yielding Δ34S and Δ35S values of 0.116 ± 0.015‰ and ~0.572 ± 0.177‰ (mean ± 1σ), respectively. In addition to linear regression, orthogonal data regression (ODR) was used to incorporate uncertainties in both the abscissa and ordinate and quantifies the uncertainty in the determination of Δ34S/Δ33S slopes.

Materials and Data Availability. All information pertaining to the experimental protocol and ODR analysis is fully detailed in SI Appendix. All raw isotopic data and sample metadata are reported in SI Appendix, Tables S1 and S2, and all IAEA-S1 standard data are shown in SI Appendix, Fig. S2 and listed in full in Dataset S1. The data and methods supporting this article can be accessed on the University of St Andrews Research Portal (54).

ACKNOWLEDGMENTS. We thank M. Mesli for assistance during core sampling, Yanan Shen and an anonymous reviewer whose comments greatly improved the manuscript, and the St Andrews MIF in Atmospheres group for useful discussions. This project has received funding from the European Research Council under the European Union’s Horizon 2020 research and innovation programme (Grant 678812 to M.W.C.).
2. H. D. Holland, The oxygenation of the atmosphere and oceans. Philos. Trans. R. So- c. Lond. B Biol. Sci. 361, 903–915 (2006).

3. D. A. Evans, N. J. Beukes, J. L. Kirshcnic, Low-latitude glaciation in the Palae- oproterozoic era. Nature 386, 262–266 (1997).

4. R. E. Kopp, J. L. Kirshcni, I. A. Hiliburn, C. Z. Naz, The Paleoproterozoic snowball Earth: A climate disaster triggered by the evolution of oxygenic photosynthesis. Proc. Natl. Acad. Sci. U.S.A. 102, 11131–11136 (2005).

5. S. J. Wang, R. L. Rust, R. M. Gaschnig, H. Wang, L. E. Wasylenki, Methanogenesis sustained by sulfide weathering during the great oxidation event. Nat. Geosci. 12, 296–300 (2019).

6. T. A. Laakso, D. P. Schrag, Methane in the precambrian atmosphere. Earth Planet. Sci. Lett. 522, 48–54 (2019).

7. M. W. Claire, D. C. Catling, K. J. Zahnle, Biogeochemical modelling of the rise in atmo- spheric oxygen. Geobiology 4, 239–269 (2006).

8. H. D. Holland, Why the atmosphere became oxygenated: A proposal. Geochim. Cosmochim. Acta 73, 5241–5255 (2009).

9. J. L. Kirshcni et al., Paleoproterozoic snowball earth: Extreme climatic and geo- chemical global change and its biological consequences. Proc. Natl. Acad. Sci. U.S.A. 97, 1400–1405 (2000).

10. T. A. Laakso, D. P. Schrag, A theory of atmospheric oxygen. Geobiology 15, 366–384 (2017).

11. C. T. Reinhard, N. J. Planavsky, T. W. Lyons, Long-term sedimentary recycling of rare sulphur isotope anomalies. Nature 497, 100–103 (2013).

12. J. Farquhar, B. A. Wing, Multiple sulfur isotopes and the evolution of the atmosphere. Earth Planet. Sci. Lett. 213, 1–13 (2003).

13. P. Philippot et al., Globally asynchronic sulphur atmospheric isotope signals require re-definition of the Great Oxidation Event. Nat. Commun. 9, 2245 (2018).

14. P. F. Hoffman, The great oxidation and a siderian snowball Earth: MIF-S based cor- relation of Paleoproterozoic glacial epochs. Chem. Geol. 362, 143–156 (2013).

15. B. A. Killingsworth et al., Constraining the rise of oxygen with oxygen isotopes. Nat. Commun. 10, 4924 (2019).

16. A. P. Gumseley et al., Timing and tempo of the great oxidation event. Proc. Natl. Acad. Sci. U.S.A. 114, 18118–18127 (2017).

17. V. A. Melezhik et al., “6.1. the imandra/Varzuga Greenbelt” in Reading the Archive of Earth’s Oxygenation, V. A. Melezhik, Ed. (Springer, 2013), Vol. 2, pp. 505–590.

18. S. Soomer et al., High-CO 2, acidic and oxygen-starved weathering at the Fenno- scandinian Shield at the Archean-Proterozoic transition. Precambrian Res. 327, 68–80 (2019).

19. A. T. Brasier et al., Earth’s earliest global glaciation? Carbonate geochemistry and geochronology of the Polisarka Sedimentary formation, Kola Peninsula, Russia. Precambrian Res. 235, 278–294 (2013).

20. Y. V. Amelin, L. M. Heaman, V. S. Semenov, U-Pb geochronology of layered mafic intrusions in the eastern Baltic Shield: Implications for the timing and duration of Paleoproterozoic continental rifting. Precambrian Res. 75, 31–46 (1995).

21. V. V. Chashchin, T. B. Bayanova, N. V. Levkovich, Volcanopladimatic association of the early-stage evolution of the Imandra-Varzuga rift zone, Kola Peninsula, Russia: Geological, petrogeochemical, and isotope-geochronological data. Petrology 16, 279–298 (2008).

22. A. B. Vreski, E. S. Bogomolov, T. F. Zinger, S. A. Sergeev, Polychronic sources and multiple sulfur isotopes and the evolution of the atmosphere. Earth Planet. Sci. Lett. 213, 1–13 (2003).

23. B. A. Killingsworth et al., “6.1. the imandra/Varzuga Greenbelt” in Reading the Archive of Earth’s Oxygenation, V. A. Melezhik, Ed. (Springer, 2013), Vol. 2, pp. 505–590.

24. S. Soomer et al., High-CO 2, acidic and oxygen-starved weathering at the Fenno- scandinian Shield at the Archean-Proterozoic transition. Precambrian Res. 327, 68–80 (2019).

25. T. A. Reinhard, M. A. Grenfell, Multiple sulfur isotopes. Precambrian Res. 334, 289–329 (2015).

26. K. K. Kettunen, L. M. Heaman, G. Bennett, D. I. Hughes, Age, petrogenesis and tec- tonic setting of the Teshsali volcanic rocks, Huronian Supergroup, Canada. Precambrian Res. 233, 144–172 (2013).

27. H. Cui et al., Searching for the great oxidation event in North America: A reappraisal of the Huronian Supergroup by SIMS sulfur four-isotope analysis. Astrobiology 18, 519–538 (2018).

28. T. C. Kampmann, A. P. Gumseley, M. O. de Kock, U. Soderlund, U-Pb geochronology and paleomagnetism of the Westerberg Sill suite, Kaapvaal Craton - support for a coherent Kaapvaal-Pilbara block (Vaalbara) into the Paleoproterozoic? Precambrian Res. 269, 58–72 (2015).

29. J. Farquhar, D. T. Johnston, B. A. Wing. Implications of conservation of mass effects on mass-independent isotopic fractionations: Influence of network structure on sulfur isotope phase space of dissimilatory sulfate reduction. Geochim. Cosmochim. Acta 71, 5862–5875 (2007).

30. J. Farquhar et al., Isotopic evidence for Mesoproterozoic anoxia and changing atmo- spheric sulphur chemistry. Nature 449, 706–709 (2007).

31. S. Ono et al., New insights into Archean sulfur cycle from mass-independent sulfur isotope records from the Hamersley Basin, Australia. Earth Planet. Sci. Lett. 213, 15–30 (2003).

32. S. Ono, A. J. Kaufman, J. Farquhar, D. Y. Sumner, N. J. Beukes, Lithofacies control on multiple-sulfur isotope records and Neoarchean sulfur cycles. Precambrian Res. 169, 58–67 (2009).

33. A. L. Zerkle, M. W. Claire, S. D. Domagal-Goldman, J. Farquhar, S. W. Poulton, A bi- stable organic-rich atmosphere on the Neoarchean Earth. Nat. Geosci. 5, 359–363 (2012).

34. G. Izen et al., Multiple oscillations in Neoarchean atmospheric chemistry. Earth Planet. Sci. Lett. 431, 264–273 (2015).

35. G. Izen et al., Biological regulation of atmospheric chemistry en route to planetary oxygenation. Proc. Natl. Acad. Sci. U.S.A. 114, 2571–2579 (2017).

36. J. Farquhar et al., “5.1 FAR-DEEP core archive and database” in Reading the Archive of Earth’s Oxygenation, V. A. Melezhik, Ed. (Springer, 2013), Vol. 2, pp. 493–502.

37. Y. Ueno, S. Aoyama, Y. Endo, F. Matsu’ura, J. Foriel, Rapid quadruple sulfur isotope analysis at the sub-micromole level by a flash heating with CoF 3. Chem. Geol. 419, 29–35 (2015).

38. M. R. Warke et al., The Great Oxidation Event preceded a Paleoproterozoic snowball Earth (dataset). St Andrews Research Portal. https://doi.org/10.17630/eaeb5f1-7353-4fbc-abb4-cbce7991c44b. Deposited 14 April 2020.