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Late Archean Biospheric Oxygenation and Atmospheric Evolution

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High-resolution geochemical analyses of organic-rich shale and carbonate through the 2500 million-year-old Mount McRae Shale in the Hamersley Basin of northwestern Australia record changes in both the oxidation state of the surface ocean and the atmospheric composition. The Mount McRae record of sulfur isotopes captures the widespread and possibly permanent activation of the oxidative sulfur cycle for perhaps the first time in Earth's history. The correlation of the time-series sulfur isotope signals in northwestern Australia with equivalent strata from South Africa suggests that changes in the exogenic sulfur cycle recorded in marine sediments were global in scope and were linked to atmospheric evolution. The data suggest that oxygenation of the surface ocean preceded pervasive and persistent atmospheric oxygenation by 50 million years or more.

The history of Earth-surface oxygenation is written in the geological record of redox-sensitive elements preserved in ancient sediments. The discovery of large non-mass-dependent (NMD) S isotope anomalies in Archean and the earliest Paleoproterozoic sediments are believed to record changes in atmospheric O₂ levels, as these result from photochemical reactions in a low O₂ atmosphere (1–4). To document temporal changes in the magnitude of these isotope excursions, we focused on high stratigraphic resolution analyses of organic-rich shale and carbonate from a recently drilled scientific core (5) through the ~2500 million-year-old Mount McRae Shale of northwestern Australia. Previous studies of the Mount McRae Shale identified abundant 2- α methyl hopanoids (6), produced by cyanobacteria that most likely generated O₂, as well as eukaryotic sterols (7), which are biomolecules that require O₂ for their synthesis (8). We investigated the time-series history of elemental and isotope variations through the succession and interpreted the upper half of the formation as capturing the oxygenation of the terminal Archean surface ocean and biosphere, a result further supported by a companion trace-metals study (9).

In the present study, a modified online combustion method (5, 10) for rapid analysis of whole-rock S and a high-precision fluorination technique for analysis of chemically extracted sulfide S were applied to samples from the core. We used unprecedented, high-resolution records ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$) in concert with

stratigraphic variations in elemental abundances [weight percent (wt %) C and S] and ¹³C compositions of carbonate and organic matter to address the cause(s) of fluctuation in NMD effects preserved in these ancient sediments. These results were compared to a previous study of the Mount McRae Shale (11) and to new S isotope data from the stratigraphically equivalent Gamohaan and Kuruman Iron formations in South Africa (12–14) to evaluate the spatial extent of the interpreted events.

The Mount McRae Shale core intersects laminated and well-preserved sediments that accumulated in a marine environment below the wave base. A regional sequence analysis (15) indicates the presence of two depositional cycles; each sequence starts in carbonate or siliciclastic turbidite or breccia and deepens upwards to either pelagic shale or banded iron-formation (Fig. 1). The succession has experienced only mild regional metamorphism (prehnite-pumpellyite facies to <300°C) and minimal deformation (gentle folding to dips <5°) (16). Radiometric age constraints place the Mount McRae Shale very near the Archean/Proterozoic boundary (~2500 million years old) (9) and just before the disappearance of large NMD effects that are inferred to mark the rise in atmospheric O₂ (1–3, 17).

Geochemical data from the Mount McRae Shale (Fig. 1) suggest a tight coupling between environmental and biological signals, with a substantial transition recorded at ~153 m in the core. Acid leaching of extractable iron from Mount McRae samples indicates that siderite dominates in the lower half of the formation, which is consistent with the absence of O₂ in deeper depositional environments. On the other hand, calcite is a primary carbonate phase in the upper Mount McRae Shale, indicating the general absence of soluble iron in the shallow water column at this time. Carbonate and total organic C $\delta^{13}\text{C}$ values increase progressively up the core. Total organic C and total S values are high throughout the Mount McRae Shale but

are notably enriched above the mineralogic transition in the interval between 135 and 153 m, where up to 16 wt % C and S are observed. In the interval between 130 and 135 m, visual evidence of pyrite nodules, laminations, and graded beds suggests some degree of sulfide remobilization, which may help to explain the sharp drop in total S abundance in the homogeneous-shale host rock.

The high-resolution S isotope record reveals considerable stratigraphic variation in $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ (18), including substantial bed-to-bed oscillations. In evaluating the time-series S isotope data, the Mount McRae Shale can be divided (19) into a lower unit (>153 m), where $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ show positive correlation, and an upper unit (<153 m), where $\delta^{34}\text{S}$ values become increasingly negative. Of particular interest is the interval above 130 m, where positive $\Delta^{33}\text{S}$ values are coupled with negative $\delta^{34}\text{S}$ values; this S isotope relation may record an important environmental and biological event near the Archean/Proterozoic boundary.

The lower half of the Mount McRae Shale from the Archean Biosphere Drilling Project (ABDP)-9 core is interpreted to have accumulated in a deep, anoxic environment insofar as sediments are dominated by sideritic shale and banded iron-formation (13, 14). The positive correlation between $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ in the lower Mount McRae Shale has been interpreted as either a primary atmospheric array (11) or mixing between atmospherically derived NMD S with mass-dependent terrestrial inputs. This mixing may well explain the long-term and bed-to-bed variability in S isotope compositions (Figs. 1 and 2B). It is difficult to independently assess the quantitative contribution of terrestrial inputs [with $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ ~ 0 per mil (‰)] relative to NMD inputs. However, nonzero values of $\Delta^{33}\text{S}$ (either positive or negative) must ultimately be linked to fluxes of sulfate and elemental S from the atmosphere. We interpret the dominance of positive $\Delta^{33}\text{S}$ through this stratigraphic interval as indicating the preferential incorporation of reduced NMD S (atmospheric elemental S) into marine sediments, probably facilitated by microbial elemental S reduction. This microbial process is capable of transferring the $\Delta^{33}\text{S}$ to pyrite, while imparting little to no additional isotopic fractionation in $\delta^{34}\text{S}$. Ono *et al.* (11) previously explained variations in NMD signatures within the Mount McRae strata by physical and biological mixing of these atmospheric sources. The isotopic similarity (in $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$) between their core and ours, presently 300 km apart, points to a basin-scale phenomenon linked through atmospheric inputs (20). However, rapid bed-to-bed (or even within bed) variability and small differences in the magnitude of the positive $\Delta^{33}\text{S}$ excursion probably reflect local controls related to variable mixing of S from distinct surface reservoirs, including the deep and shallow ocean as well as terrestrial environments.

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As noted above, the upper half of the Mount McRae Shale, which is dominated by turbidites of carbonate and shale that accumulated below the storm wave base, is characterized by sulfides with negative $\delta^{34}\text{S}$ values coupled with positive $\Delta^{33}\text{S}$ values (Figs. 1 and 2A). The $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values of these sulfides imply microbial sulfate reduction with larger isotopic fractionations, which may reflect sulfate reduction in the water column (21), possibly coupled with rising sulfate concentrations (22). This interpretation is consistent with the high organic C contents in sediments above 153 m in the core, which are plausibly linked to high rates of primary productivity that released oxidants into the shallow marine environment. On the other hand, the positive $\Delta^{33}\text{S}$ values reflect incorporation of reduced photolytic S. To account for these two features, we propose that the S isotope signatures in the upper Mount McRae Shale reflect the establishment of a widespread and possibly permanent oxidative S cycle, perhaps for the first time in Earth's history, in a water column that was stratified with respect to oxygen (23).

In the late Archean oceans, O_2 would accumulate in highly productive regions along con-

tinental margins and perhaps to a lesser degree in distal settings, where nutrient levels were high enough to stimulate oxygenic photosynthesis. Possible explanations to account for the isotopic observations above 153 m include elemental S reducers capable of producing large ^{34}S depletions (an unlikely scenario given the small redox change associated with this metabolic pathway) or the activation of microbial disproportionation reactions (24). Because the former are currently unknown and the latter are not clearly evident until the mid-Proterozoic (25), we suggest an alternative solution related to increases in O_2 initiated during the productivity event recorded in the core above 153 m. Inorganic S oxidation generally requires high levels of dissolved O_2 , whereas microbial S oxidation, which is thought to be ancient in origin, would proceed at lower (or absent) O_2 concentrations but still would require an electron acceptor to drive phototrophic oxidation. In either case, the magnitude of isotopic fractionation associated with oxidation is small (26) and unlikely to account for the negative $\delta^{34}\text{S}$ values of sulfides in the upper Mount McRae sediments. Thus, we propose that the

sulfate formed through oxidation (with positive $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$) was re-reduced by microbial sulfate reduction to form sulfides depleted in $\delta^{34}\text{S}$ but retaining positive NMD $\Delta^{33}\text{S}$ values (Figs. 1 and 2A).

The organic C and S spike between 153 and 135 m corresponds to an interval where both $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values are typically negative (19). Although broadly binned with the upper Mount McRae Shale interval, these sediments provide important environmental constraints on a source of S (with a negative $\Delta^{33}\text{S}$ composition) and the mechanism for its sink into sediments. Low Archean atmospheric O_2 levels would generally limit oxidative weathering, the principal source of sulfate to the modern oceans. With rising atmospheric O_2 levels, however, some metals and associated S from terrestrial sources may have been released to the shallow marine environment (9), but contributions from juvenile S ($\Delta^{33}\text{S} = 0$) or preexisting sedimentary sources ($\Delta^{33}\text{S} > 0$) cannot account for the negative $\Delta^{33}\text{S}$ value of the S from this interval. Thus, a major source of sulfate to the Archean ocean at this time would have been atmospheric in origin and would have carried a negative $\Delta^{33}\text{S}$ signature

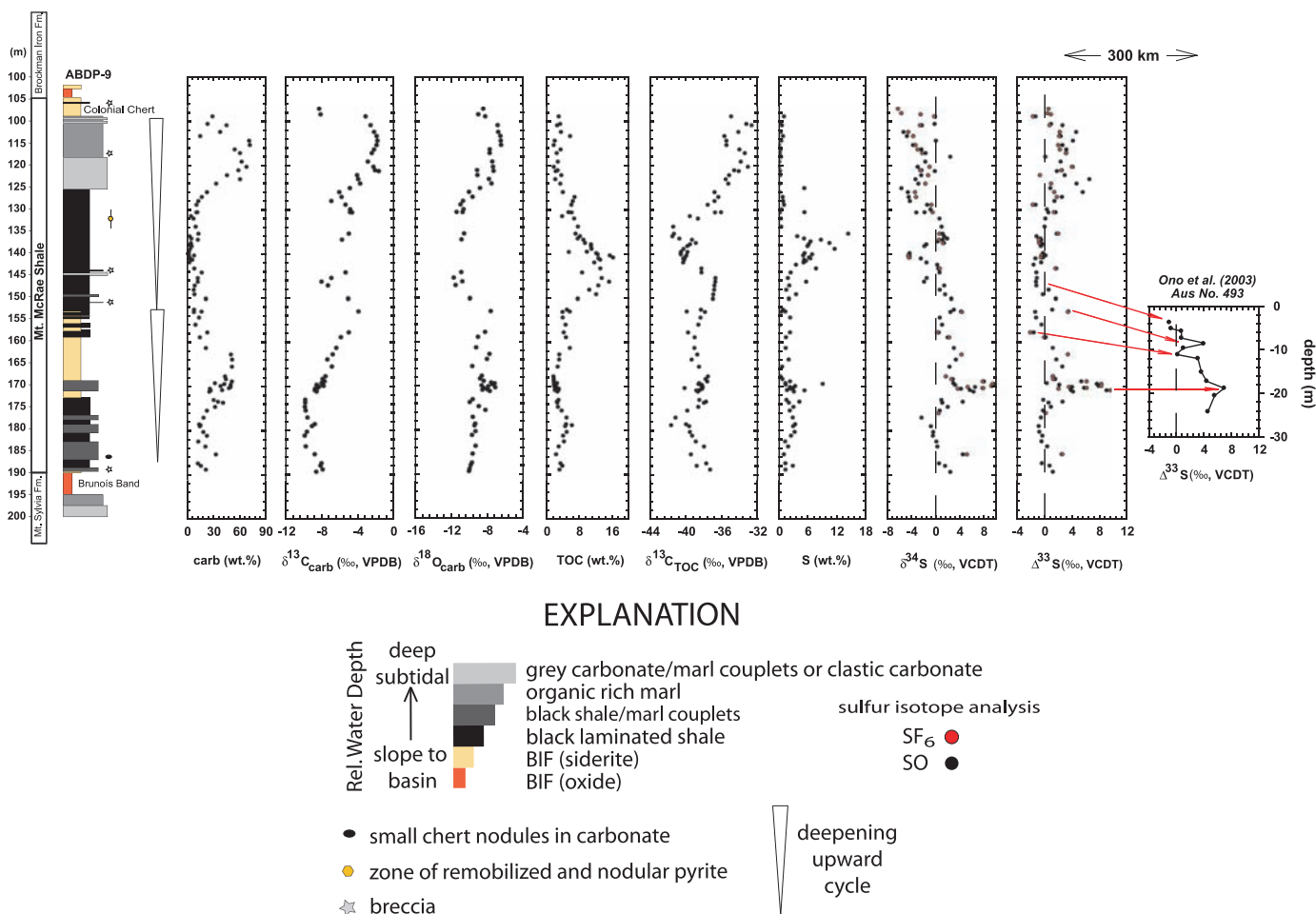


Fig. 1. Lithologic and time-series elemental (C and S) and isotopic ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, and $\Delta^{33}\text{S}$) trends in the ~2500 million-year-old Mount McRae Shale. Sequence subdivisions are based on (15). Trends in $\Delta^{33}\text{S}$ in the lower

Mount McRae Shale are correlated with equivalents in a separate core drilled some 300 km away from the core in this study (11). VPDB, Vienna Pee Dee belemnite; TOC, total organic C; VCDT, Vienna Canyon Diablo Troilite.

(1, 4). In keeping with previous arguments for Archean seawater sulfate (27), we interpret deep- and open-ocean seawater sulfate as having a negative $\Delta^{33}\text{S}$ composition and acting as the major source of S in the pyritic interval above 153 m. Sulfate in the anoxic deep ocean was nonetheless likely to have been low (potentially $<200\ \mu\text{M}$) (22) and possibly even lower on the continental shelves. However, we suggest that enhanced microbial sulfate reduction, stimulated by high rates of organic C burial in the presence of abundant reactive iron, would serve as an effective long-term sulfate sink and conceivably result in the concentration of open-ocean S (with negative $\Delta^{33}\text{S}$) into the sediments (28).

Further insight into the Archean S cycle, specifically atmospheric evolution, is gained through the evaluation of the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ relation. Whereas mass-dependent processes fractionate ^{33}S and ^{36}S in systematic ways ($\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -7$) (29, 30), NMD photochemical experiments (2, 31) suggest a wavelength dependence to the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ relation, and with a few exceptions, observations from the Archean record generally follow

$\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -1$. This value is broadly consistent with measurements of sulfides from a wide range of Archean sediments (1, 32). Additionally, the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ relation may characterize NMD contributions to surface environments even when the absolute magnitude of $\Delta^{33}\text{S}$ is small (33, 34). The high-resolution ^{36}S analysis of the Mount McRae Shale reveals measurable differences for $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ within the succession (Fig. 2, C and D), further supporting the stratigraphic distinctions outlined above. The resolvable difference between the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ relation in the upper and lower Mount McRae Shale indicates a change in atmospheric composition, because according to current knowledge, such shifts can only be caused by changing photochemical reactions involving S-bearing gases (35).

If the change in atmospheric composition suggested above is real, we expect the signal to be widespread in nature. To test this prediction, we have undertaken S isotope analyses of samples from the broadly equivalent Transvaal Basin in South Africa. The studied South African core intersects the Gamohaan and Kuruman Iron Formations (5, 12, 13, 36), which record sim-

ilar lithologic transitions to those observed in northwestern Australia. Although it is possible that these two successions (now over 8000 km apart) accumulated along the margins of a contiguous ocean basin, palinspastic reconstruction (37) of the two subbasins on the basis of existing outcrop area suggests that the core locations were at least 1000 km apart when the sediments accumulated.

The similarity in S isotope records between the South African and Australian sediments is pronounced (Fig. 2). The correlation between these widely separated basins strongly supports the spatially pervasive character of $\Delta^{33}\text{S}$ (and $\Delta^{36}\text{S}$) production, implying a degree of lateral atmospheric homogeneity. The $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ of the lower portion of the South African core matches that of the lower Mount McRae Shale, whereas the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ from the upper portion is quite similar to that of the upper Mount McRae sediments. The consistency of the $\delta^{34}\text{S}$ versus $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$ relations between the Australian and South African cores indicates that the S isotope variations reflect widespread and probably global variations in the Archean S cycle. The origin of the profound $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ anomaly at ~ 170 m in the Mount McRae core and its equivalent in South Africa is unknown, but it is probably related to a pulsed flux of atmospheric inputs to surface environments that was captured over long distances in similar depositional settings. Whereas the transition captured at ~ 153 m might reflect changes in the atmospheric O_2 budget, it is also possible that changes in the abundance of other atmospheric species (CO_2 and CH_4) may be responsible for differences in the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ relations. However, the independent trace-metal evidence (9) and lower stability of methane under oxidizing conditions point to an increasingly important role for O_2 in surface environments.

We interpret our data from Western Australia and South Africa to suggest a progressive oxygenation of the Archean biosphere. This conclusion is in accord with the trace-metal data (9), which similarly suggest the onset of oxidizing processes. Combined, these time-series records of mineralogic, elemental, and S isotopic change provide clues to coupled changes in the redox state of the shallow ocean (largely before the atmosphere became oxygenated) in relation to biological innovation before the Archean/Proterozoic boundary, including the oldest evidence for an active and globally distributed oxidative S cycle.

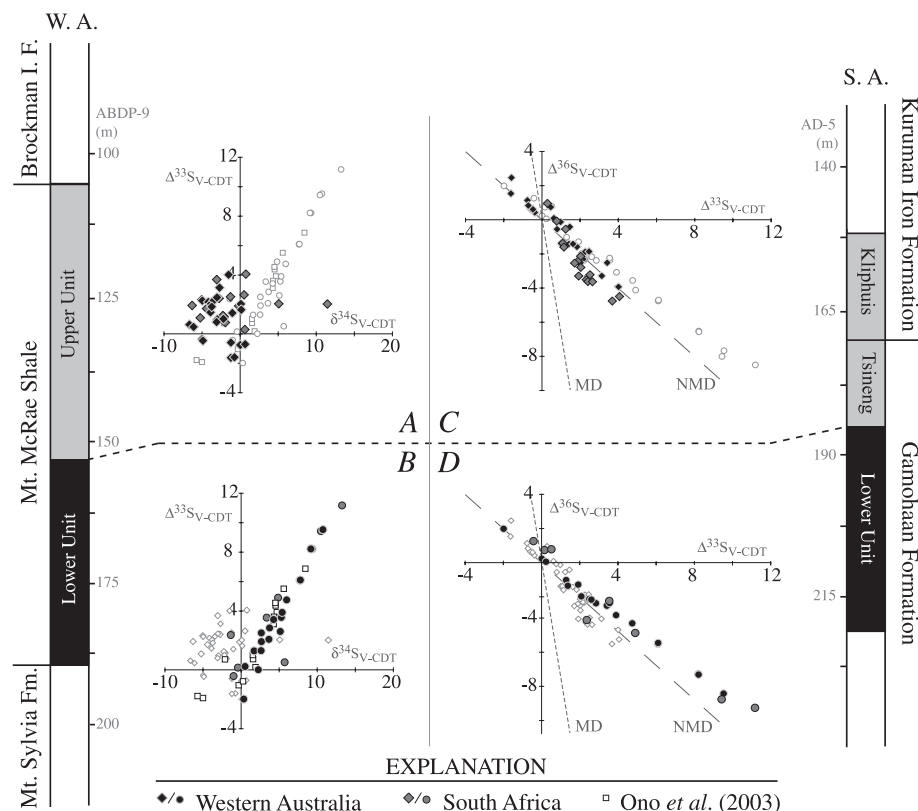


Fig. 2. Triple isotope plots [$\delta^{34}\text{S}$ versus $\Delta^{33}\text{S}$ in (A) and (B) and $\Delta^{33}\text{S}$ versus $\Delta^{36}\text{S}$ in (C) and (D)] for the Mount McRae Shale in Western Australia (W. A.) and the equivalent Gamohaan and Kuruman formations in South Africa (S. A.). Data from both cores are divided into upper [(A) and (C)] and lower [(B) and (D)] intervals. All data outside the target stratigraphic interval is shown in light gray for comparison. The anomalous S isotope compositions recorded in (A) are interpreted as reflecting oxidizing conditions. Mass-dependent fractionations of ^{33}S and ^{36}S resulted in an array with a slope of ~ -6.85 (30, 32) [labeled as MD in (C) and (D)], whereas data from this study fit the general Archean slope of ~ -1 (2). The $\Delta^{33}\text{S}$ versus $\Delta^{36}\text{S}$ relation between the correlated upper and lower intervals is statistically different, pointing to the evolution of atmospheric composition in the late Archean Eon. I. F., iron formation.

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 - All bulk samples were analyzed by the sulfur monoxide method in triplicate, and the reported values are averages of these measurements. Uncertainties are better than 0.3‰ for both $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values, which is comparable with uncertainties based on multiple standard measurements during each analytical session. For SF_6 analyses, uncertainties are 0.14, 0.008, and 0.20‰ for $\delta^{33}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$, respectively.
 - Monte Carlo resampling of data suggests that the two intervals carry a unique isotopic mean. In the lower half, we calculated means of $\delta^{34}\text{S} = 3.04 (\pm 0.50)$ and $\Delta^{33}\text{S} = 1.98 (\pm 0.44)$. In the upper half, including the organic and pyrite-rich horizon, the data indicate means of $\delta^{34}\text{S} = -1.41 (\pm 0.34)$ and $\Delta^{33}\text{S} = 1.10 (\pm 0.29)$. Considered alone, data from the pyritic interval between 153 and 135 m indicate means of $\delta^{34}\text{S} = -0.80 (\pm 0.47)$ and $\Delta^{33}\text{S} = -0.54 (\pm 0.17)$.
 - Atmospheric photochemistry is presently the only known mechanism that can account for the nonzero $\Delta^{33}\text{S}$ data and their relationship to $\Delta^{36}\text{S}$ values in the Archean record (1–4, 17). The principal source of S in the Archean atmosphere was volcanic (although biogenic sources may have also existed). Gas-phase photochemistry involving sulfur dioxide or sulfur monoxide has been shown in closed-cell photochemical experiments (2) to result in NMD sulfate (SO_4^{2-} ; with negative, and in some cases positive, $\Delta^{33}\text{S}$ values) and elemental S (S_8 , with positive $\Delta^{33}\text{S}$ values). These reactions are sensitive to the wavelength of available ultraviolet radiation, and this parameter depends on, among other things, atmospheric O_2 concentrations. The transfer pathways of S from the atmosphere to Earth's surface also depend on O_2 concentration. An atmospheric model (4) constrains an upper limit of $<10^{-5}$ of present atmospheric levels of O_2 for the transfer of nonzero $\Delta^{33}\text{S}$ (and $\Delta^{36}\text{S}$) containing SO_4^{2-} and S_8 to Earth's surface; at a higher partial pressure of O_2 , the two S reservoirs homogenize in the atmosphere, and the photochemical signal is not preserved.
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 - A Monte Carlo resampling of the entire Mount McRae data set ($\Delta^{33}\text{S} = 1.25 \pm 0.17$), which mirrors that of the entire Archean (27), points to a negative $\Delta^{33}\text{S}$ reservoir of the Archean S cycle largely lost from the geological record. Evidence from banded iron-formations, volcanic massive sulfide deposits, and other sea-floor environments may ultimately provide tests for a sulfate concentration gradient in the Archean ocean and solve the mystery of the missing negative $\Delta^{33}\text{S}$ reservoir. Ultimately, the balance of sources and sinks maintained generally low sulfate concentrations that allowed for spatial isotopic heterogeneities.
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 - Mass-dependent recycling has not been used to substantially alter the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ relation of Archean samples, but recycling by processes associated with the establishment of an oxidative S cycle in the surface ocean may also account for some of the variation due to the different (\sim –7) $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slopes.
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SOM Text
Figs. S1 to S4
Tables S1 and S2
References

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A Whiff of Oxygen Before the Great Oxidation Event?

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High-resolution chemostratigraphy reveals an episode of enrichment of the redox-sensitive transition metals molybdenum and rhenium in the late Archean Mount McRae Shale in Western Australia. Correlations with organic carbon indicate that these metals were derived from contemporaneous seawater. Rhenium/osmium geochronology demonstrates that the enrichment is a primary sedimentary feature dating to 2501 ± 8 million years ago (Ma). Molybdenum and rhenium were probably supplied to Archean oceans by oxidative weathering of crustal sulfide minerals. These findings point to the presence of small amounts of O_2 in the environment more than 50 million years before the start of the Great Oxidation Event.

Many lines of evidence point to a rapid rise in the partial pressure of atmospheric O_2 (P_{O_2}) from $<10^{-5}$ times the present atmospheric level (PAL) between 2.45 and 2.22 billion years ago (Ga) (1, 2), a transition often referred to as the Great Oxidation Event (GOE).

The GOE could have been an immediate consequence of the evolution of oxygenic photosynthesis (3). Alternatively, O_2 biogenesis may be ancient (4). If so, the GOE was a consequence of an abiotic shift in the balance of oxidants and reductants at Earth's surface (5–8). This debate can

be addressed by looking for evidence of localized or short-lived concentrations of O_2 before 2.45 Ga.

The abundances of some transition elements in sedimentary rocks are sensitive to the availability of O_2 (9). In particular, in the modern oxygenated environment, molybdenum (Mo) exists in rivers and oceans primarily as the unreactive molybdate ion (MoO_4^{2-}). Oxidative weathering of Mo-bearing sulfide minerals in crustal rocks leads to the accumulation of Mo in the oceans, where it is the most abundant transition element (at a concentration of ~ 105 nM) (10, 11). The abundance of Mo in the oceans is reflected in

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