Redox state of the Neoarchean Earth environment

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A Titan-like organic haze has been hypothesized for Earth's atmosphere prior to widespread surface oxygenation ~2.45 billion years ago (Ga). We present a high-resolution record of quadruple sulfur isotopes, carbon isotopes, and Fe speciation from the ~2.65-2.5 Ga Ghaap Group, South Africa, which suggest a linkage between organic haze and the biogeochemical cycling of carbon, sulfur, oxygen, and iron on the Archean Earth. These sediments provide evidence for oxygen production in microbial mats and localized oxygenation of surface waters. However, this oxygen production occurred under a reduced atmosphere which existed in multiple distinct redox states that correlate to changes in carbon and sulfur isotopes. The data are corroborated by photochemical model results that suggest bi-stable transitions between organic haze and haze-free atmospheric conditions in the Archean. These geochemical correlations also extend to other datasets, indicating that variations in the character of anomalous sulfur fractionation could provide insight into the role of carbon-bearing species in the reducing Archean atmosphere.

The Campbellrand-Malmani carbonate platform of the ~2.65-2.5 billion years old (Ga) Ghaap Group (Transvaal Supergroup, South Africa) is one of the oldest carbonate platforms on Earth. Molybdenum concentrations and isotopes, Re/Mo ratios, and N isotope systematics all suggest biological production of O₂ in surface waters during deposition of the upper part of the succession at ~2.5 Ga. This suggestion of significant O₂ production prior to Earth's first Great Oxidation Event is supported by nutrient and trace metal systematics in coeval successions from other areas. However, production of O₂ apparently did not lead to a pervasive rise in atmospheric oxygen levels.

Here, we focus on the lower part of the Ghaap Group, spanning the top of the Boomplaas Formation through the lower part of the Upper Nauga Formation (Fig. 1). Our samples come
from drillcore GKF01, and represent deposition primarily below wave base in a slope
environment, with cyclic units of microbialites passing upwards into slope carbonates. Radiometric age constraints place the base of the core at $\sim 2.65 \pm 0.08$ Ga and the top of the measured section (within the Upper Nauga) at $\sim 2.5$ Ga. The succession is exceptionally well-preserved, having experienced only gentle tectonic warping and sub-greenschist facies metamorphism.

**Oxygenation of the Neoarchean oceans**

Fe speciation analyses reflect water column redox conditions at the time of deposition, and show significant variations throughout the section (Fig. 1; Table S1). Many samples have elevated ratios of highly reactive Fe ($Fe_{carbonates} + Fe_{oxides} + Fe_{magnete} + Fe_{pyrite}$) to total Fe ($Fe_{HR}/Fe_T > 0.38$), indicating deposition from an anoxic water column. For those samples exhibiting high $Fe_{HR}/Fe_T$, the ratios of pyrite to highly reactive Fe ($Fe_{Pyr}/Fe_{HR}$) generally fall below 0.7-0.8, suggesting that when the bottom waters were anoxic, ferruginous (Fe(II)-rich) rather than euxinic (sulfide-rich) conditions were dominant. Other samples representing shallow water deposition (microbialites of the Monteville Fm) or transported shallow-water deposits (the Lokammona), fall close to the average oxic Phanerozoic signal, suggesting formation from an oxic water column. The low $Fe_{HR}/Fe_T$ ratios and correlative facies assemblages imply that cyanobacterial $O_2$ production in microbial mats resulted in oxygenation of shallow surface waters as early as $\sim 2.65$ Ga.

Cyanobacterial oxygen production is further supported by trends in $\delta^{34}S$ and $\Delta^{33}S$. Sulfur isotope values for the majority of the section fall on or near a linear trend in $\delta^{34}S$ versus $\Delta^{33}S$ that has been described in Archean samples ($\Delta^{13}S = 0.9 \times \delta^{34}S$) (Fig. 2A). This trend is interpreted to reflect mixing between sulfides formed from two primary atmospheric sources carrying
opposite sulfur mass independent fractionation (S-MIF) signals – e.g., an oxidized source (sulfate) with negative $\Delta^{33S}$ and a zero valent source (S$_0$) with positive $\Delta^{33S}$. Samples associated with microbial mats of the upper Monteville and the Lower Nauga have positive $\Delta^{33S}$ values that plot parallel to the primary Archean array, but are enriched in $^{34S}$ by $\sim$3 to 7%o (Fig. 2A). This trend could not result from changes in sulfate reduction fractionations alone, as this scenario would only rotate the array. We suggest this association reflects formation of pyrite from a residual pool of sulfide generated within the microbial mats that was partially oxidized via $O_2$ near the mat surface, enriching the sulfide in $^{34S}$ (see Supplementary Information, SI, for further discussion).

Redox state of the Neoarchean atmosphere

Covariations in $\Delta^{33S}$, $\Delta^{36S}$, and carbon isotope data reveal an important connection between the Neoarchean sulfur and carbon cycles. Quadruple sulfur isotope values vary considerably upcore (Fig. 1; Table S2), but all show S-MIF signals reflecting photochemical production in an atmosphere devoid of significant $O_2$ Samples from the Boomplaas and Lokammona Formations form a linear array in $\Delta^{33S}$ versus $\Delta^{36S}$, with a slope in $\Delta^{36S}/\Delta^{33S}$ of approximately $-0.96$ (Fig. 2B). This slope is close to the reference line defined by previous measurements of Archean sulfide and sulfate minerals ($\sim$0.9), and is also interpreted to reflect mixing of sulfur from two or more atmospheric sources. In several distinct intervals within the overlying section, the samples preserve $\Delta^{33S}$ and $\Delta^{36S}$ values that form arrays rotating in a clockwise manner, forming steeper slopes in $\Delta^{36S}/\Delta^{33S}$, approaching -1.5 (Fig. 2B). The data preserve a continuum of $\Delta^{36S}/\Delta^{33S}$ slopes between $\sim$0.9 and -1.5, and extend to highly positive $\Delta^{33S}$ regardless of $\Delta^{36S}/\Delta^{33S}$. Biological sulfur cycling can produce scatter in the $\Delta^{36S}$ intercept, since sulfate reduction can affect $\Delta^{36S}$ much more than $\Delta^{33S}$ (Fig. S1). However, a rotation of
the arrays to different $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slopes instead implies a change in the nature of the primary S-MIF signature, either due to a change in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ for a single atmospheric signal, or due to variable amounts of mixing between two or more atmospheric sources with different $\Delta^{36}\text{S}/\Delta^{33}\text{S}$.

Samples with the greatest deviation in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ occur in three distinct zones, at around 1400 m, 1100 m, and 800 m depth in the core. These zones correspond to intervals exhibiting highly $^{13}\text{C}$-depleted organic matter, falling to $\delta^{13}\text{C}_{\text{org}}$ values lower than -40‰ (Fig. 1; Fig. S2). Negative excursions in $\delta^{13}\text{C}_{\text{org}}$ are typically interpreted to reflect higher CH$_4$ fluxes and an increased contribution of methanotrophic biomass to sedimentary organic matter. A significant amount of methane oxidation (methanotrophy) in the modern oceans occurs anaerobically; however, Fe$_{\text{HR}}$/Fe$_T$ ratios near Phanerozoic oxic values in some of the $\delta^{13}\text{C}_{\text{org}}$-depleted samples suggest that methanotrophy could also have proceeded via O$_2$ (Fig. 1).

A closer examination of previously published Neoarchean sulfur isotope data reveals similar correlations between changes in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope and $\delta^{13}\text{C}_{\text{org}}$ in ~2.5 Ga sections in South Africa (the Gamohaan Formation) and in Western Australia (the Mount McRae Shale) (Fig. S3). Samples forming an array with $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ of -1.5 have also been reported for the ~2.73 Ga Tumbiana Formation of the Fortescue Group of Western Australia, which preserves a large global negative $\delta^{12}\text{C}_{\text{org}}$ excursion down to -60‰. We suggest that the correlation between negative $\delta^{13}\text{C}_{\text{org}}$ excursions and $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ anomalies in two sections and over ~200 million years implies a global connection between methane and variations in atmospheric S-MIF signals.

**Modeling the Neoarchean atmosphere and hypotheses for S-MIF production**

Interpreting the magnitude of S-MIF in the geologic record requires knowledge of the production, transformation, and mass partitioning of atmospheric sulfur, as well as subsequent biogeochemical pathways to sedimentation. Recently measured absorption spectra for $^{32}\text{SO}_2$. 


SO$_2$, and SO$_2$ help constrain S-MIF production by SO$_2$ photolysis and imply that changing concentrations of UV absorbers$^{23}$ (such as organic haze$^{20,24}$ formed at high atmospheric CH$_4$:CO$_2$) might influence the S-MIF signature. S-MIF from SO$_2$ photolysis could also be supplemented by other mass-independent kinetic isotope effects$^{25-27}$, in reactions such as SO photolysis, S+S$_2$ $\rightarrow$ S$_3$, CS$_2$ photolysis$^{28,29}$, or the production/destruction of excited-state SO$_2$.

Generation of significant S-MIF via any reaction other than SO$_2$ photolysis remains hypothetical but worthy of future research given that multiple source reactions might help explain the data$^{22}$. S-MIF, once created, partitions into all atmospheric sulfur species, and requires the simultaneous presence of two (or more) atmospheric exit channels for preservation$^{17}$. Furthermore, these exit channels vary as a function of atmospheric methane, oxygen, and sulfur concentrations$^{14,30}$, and biogeochemical processes could further transform the signal prior to preservation in sedimentary environments$^{31}$.

To evaluate these possible alternatives, we ran 1-D early Earth photochemical models where we increased CH$_4$ concentrations until an organic haze formed. The model utilized here advances similar studies$^{14,32}$ by analyzing hazy atmospheres after the evolution of oxygenic photosynthesis. Furthermore, we consider the effect of fractal aggregate scattering by hydrocarbon aerosols$^{33}$, and contrast with traditional Mie scattering results. We use these models to explore how optical depth, reaction pathways, and sulfur exit channels vary as a function of CH$_4$ concentration, and tie these atmospheric properties to candidate mechanisms for the observed changes in $\Delta^{36}$S/$\Delta^{33}$S. Figures 3 and S8 show two sets of photochemical model simulations, both varying CH$_4$ concentrations from 1 to 50,000 ppm, while holding CO$_2$ concentrations at 1% and ground-level O$_2$ concentrations at 10 ppb. The two simulations differ only in their hydrocarbon particle scattering physics (see SI for a discussion of boundary
conditions, particle formation and scattering). For both fractal and Mie scattering cases, higher CH₄ resulted in increasingly reduced atmospheres, as evidenced by decreasing OH concentrations (Fig. 3A; S8A). Despite large volcanic SO₂ and H₂S fluxes, none of our model atmospheres accumulated large enough concentrations of SO₂ or OCS to affect S-MIF (see SI for additional discussion). The dominant contributors to opacity between 180 and 220 nm in our haze-free models were CO₂ absorption and Rayleigh scattering. Prior to haze formation, most photons longward of 200 nm reached the Earth surface.

Even when CH₄ is too low to promote haze formation (CH₄:CO₂ < 0.1), changes to CH₄ concentrations altered the redox chemistry and impacted S-MIF exit channels. Enhanced CH₄ concentrations alone do not affect S-MIF, as the CH₄ absorption spectrum does not overlap the vibrational bands of SO₂ that give rise to S-MIF. Instead, increases in CH₄ provided the reducing capacity to polymerize elemental sulfur, thus promoting aerosol S₈ as an exit channel. Simultaneously, SO₂ replaced sulfate as the most oxidized exit channel (Fig. 3C; S8C), implicating the SO₂/S₈ couple as carriers of opposite-sign S-MIF. Reaction rates for S₈ polymerization, excited state SO₂ formation and SO₂ photolysis all increased with increasing CH₄ concentrations (Fig. 3B; S8B). If any of these reactions produces significant S-MIF, they could modify the signal produced by SO₂ photolysis. Regardless of mechanism, we suggest this haze free regime is the origin of the 0.9 Archean ‘reference’ slope in Δ^{36}S/Δ^{33}S.

At CH₄:CO₂ > 0.1, a hydrocarbon haze dramatically altered our model atmospheres. The broadband absorption by this haze caused a drastic reduction in photochemical reactions, and specifically a slowdown of the S cycle. In the fractal scattering case, SO₂ photolysis rates slowed by nearly two orders of magnitude (Fig 3B), as photons shortward of 220 nm were scattered by the stratospheric haze. By contrast, SO₂ photoexcitation to \(^1\)SO₂ (210-327 nm) and \(^3\)SO₂ (337-
remained prevalent. There are two potential sources of S-MIF variation in this regime: a changing ratio of \( \text{SO}_2 \) photolysis to photoexcitation, and opacity effects arising from fewer total photons. Other pathways involving multiple S atoms, such as \( S_3 \) polymerization or \( \text{SO-SO} \) dimer formation, became unfeasible in the photon-starved \( \text{CH}_4:\text{CO}_2 > 0.1 \) environment.

For \( 0.1 < \text{CH}_4:\text{CO}_2 < 0.2 \), haze-induced shielding led to counter-intuitive decreases in the \( \text{CH}_4 \) fluxes needed to support increasing \( \text{CH}_4 \) concentrations. As atmospheric \( \text{CH}_4 \) rose the haze thickened, decreasing both \( \text{CH}_4 \) photolysis and the formation of radicals that destroy \( \text{CH}_4 \). The haze therefore diminished the photochemical sinks for \( \text{CH}_4 \) such that larger concentrations could be maintained at lower \( \text{CH}_4 \) source fluxes. This would have made atmospheres with \( 0.1 < \text{CH}_4:\text{CO}_2 < 0.2 \) unstable. If a biosphere produced enough \( \text{CH}_4 \) to reach \( \text{CH}_4:\text{CO}_2 > 0.1 \), a positive feedback would have ensued, increasing \( \text{CH}_4 \) concentrations until \( \text{CH}_4:\text{CO}_2 \approx 0.2 \), at which point further increases in \( \text{CH}_4 \) concentrations would have required biologically unfeasible \( \text{CH}_4 \) fluxes (see details in SI).

In both simulations, atmospheres with \( \text{CH}_4:\text{CO}_2 > 0.2 \) are unsustainable. If organic particles scatter light according to Mie theory, a thick haze could be prevented by a Gaian climate/\( \text{CH}_4 \) feedback\(^{24} \) on global glaciations\(^{34} \). If organic particles behave like fractal scatterers, a thick haze would have formed a UV shield effective enough to shut down photochemical haze production (see Fig. 3B and SI). In either case, we can place an upper limit of \(-0.2\) on the atmospheric \( \text{CH}_4:\text{CO}_2 \) ratio.

In summary, there are two accessible, stable regimes in our photochemical simulations: \( \text{CH}_4:\text{CO}_2 < 0.1 \), and \( \text{CH}_4:\text{CO}_2 \approx 0.2 \). In the first of these regimes, \( \text{SO}_2 \) photolysis was a major source of S-MIF, although other potential S-MIF reactions proceeded rapidly enough to be quantitatively relevant. The exit channels varied as a function of atmospheric redox state, and the
magnitude of S-MIF in a given exit species would be expected to vary inversely with the relative mass fraction. In the second regime, the atmospheric S cycle operated slowly due to haze-induced opacity that significantly decreased photolysis rates in the lower atmosphere. SO$_2$ photolysis remained a likely source of S-MIF, and the lower photon availability could have led to significant SO$_2$ isotopologue absorption effects. S-MIF from symmetry-dependent de-excitation of SO$_2$ also had the potential to be an important source of S-MIF in this regime. SO$_2$ became the dominant exit channel, so its S-MIF signature should trend to 0 by mass balance considerations, with correspondingly higher S-MIF magnitudes in the minor (by mass) exit channels. Transition between the first and second regimes could therefore induce changes in S-MIF source magnitudes, coupled with changes in the reservoirs by which S-MIF exits the atmosphere. If low $\delta^{13}$C$_{org}$ reflects periods of enhanced methane flux, a bi-stable atmospheric transition from haze-free (CH$_4$:CO$_2$ < 0.1) to thin haze (CH$_4$:CO$_2$ = 0.2) could explain the $\Delta^{36}$S/$\Delta^{33}$S slope changes in ancient sediments.

Consideration of these models along with the high-resolution geochemical dataset presented here points to a Neoarchean depositional environment that includes: (1) microbial mat ecosystems similar to modern mats, with intensive internal recycling of sulfur; (2) cyanobacterial oxygen production and shallow water oxygenation as early as ~2.65 Ga; and (3) a link between methanotrophy and S-MIF producing atmospheric chemistry, indicating a reducing atmosphere with multiple episodes of organic haze formation during periods of enhanced biological CH$_4$ production. These records provide crucial evidence for the biogeochemical production and fate of oxidants and reductants in the oceans and atmosphere during the critical period in Earth history immediately pre-dating the first major rise in atmospheric oxygen.
Methods

Pyrite sulfur isotope compositions were determined on Ag$_2$S precipitates from distillation with chromous chloride. Quadruple S isotope measurements were performed at the University of Maryland, following the techniques described in Domagal-Goldman et al.\textsuperscript{24}, and reported as $\delta^{34}$S

$$\Delta^{32}S = (^{33}S/^{32}S)_{\text{sample}}/(^{33}S/^{32}S)_{\text{V-CDT}} - 1.$$

Analytical uncertainties on S isotope measurements, estimated from long-term reproducibility of Ag$_2$S fluorinations, are 0.14, 0.008, and 0.20 (1σ) for $\delta^{34}$S, $\Delta^{33}$S, and $\Delta^{36}$S, respectively. Iron speciation was determined at Newcastle University via the sequential extraction techniques of Poulton et al.\textsuperscript{12,13}. Replicate extractions give an RSD of <5% for all extraction steps. Total organic carbon (TOC) was measured on a Leco analyzer after treatment with dilute 20% HCl to remove carbonate phases. Organic C isotopes were measured on acid-treated samples by EA-IRMS, reported as $\delta^{13}$C = (($_{13}$C/$_{12}$C)$_{\text{sample}}$/$_{13}$C/$_{12}$C)$_{\text{VPDB}} - 1$ (‰). Replicate analyses ($n = 6$) of an internal standard ($\delta^{13}$C$_{\text{org}} = -26.43$‰) gave an average value of $-26.43 \pm 0.06$‰ (1σ) during the sample run.

The 1-D photochemical model derives from Zhanle et al.\textsuperscript{30}, but contains the organic carbon species and chemistry from Domagal-Goldman et al.\textsuperscript{24}, as well as their $\delta$ two-stream radiative transfer scheme. The model simultaneously solves photochemical production and loss for 74 species undergoing 392 reactions, including transport by eddy and molecular diffusion over a 100 km grid with 0.5 km grid spacing. We adopt the temperature, eddy diffusion, and water vapor profiles from Domagal-Goldman et al.\textsuperscript{24}, leaving all other parameterizations (rainout, lightning, diffusion-limited hydrogen escape, etc.) unchanged. The modern solar flux is
used, although sensitivity tests were run approximating the spectral character of the sun at 2.5 Ga. Further details, including boundary conditions, are given in the Supplementary Information.

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Author Contributions
A.L.Z. performed sulfur isotope analyses and spearheaded the study, M.W.C. and S.D. D-G. developed and ran the atmospheric models, S.W.P. collected the samples and performed Fe speciation analyses. All authors contributed to data interpretation and manuscript preparation.

Competing Financial Interests
The authors declare no competing financial interests.

References


**Figure Legends**

346 Figure 1. Lithologic and geochemical data for the bottom part of core GKF01, through ~2.65 to 2.5 Ga sediments of the Ghaap Group (lithologies from Schröder *et al.*). Data include pyrite sulfur isotope values (δ³⁴S, Δ³³S, Δ³⁶S, and Δ³⁶S/Δ³³Sₚᵥ, calculated as the absolute value of the deviation from a Δ³⁶S/Δ³³S slope defined by the Boomplaas and Lokammona Formations), carbon isotopes of organic carbon (δ¹³Corg), and Fe speciation data (Tables S2 and S3). Symbols are defined in Figure 2. Grey circles are from Ono *et al.*³⁵, grey squares are from Kendall *et al.*³⁴, and grey diamonds are from Fischer *et al.*³⁶.

353 Figure 2. Cross-plots for quadruple sulfur isotopes from the GKF01 section. A. δ³⁴S versus Δ³³S values. The dotted line is the Archean reference line (Δ³³S = 0.89 × δ³⁴S)¹⁴. B. Δ³³S versus Δ³⁶S...
values. The solid line represents a reference array with \( \Delta^{36}\text{S}/\Delta^{33}\text{S} \) slope of -0.9, and the dotted line represents an array with a slope of -1.5.

Figure 3. Photochemical model results for fractal particles. Models were run with CO\(_2\) fixed at 1% and ground-level CH\(_4\) mixing ratios from 1\( \times 10^{-6} \) to 0.05, displayed as CH\(_4\):CO\(_2\) ratios.

Shaded regions indicate unconverged solutions. A. Mixing ratios (solid lines, left axis) and fluxes (dashed lines, right axis). B. Photochemical reaction rates relative to the rate at CH\(_4\):CO\(_2\) = 10\(^{-4}\) (non-red lines, left axis). Effective optical depth at 200 nm (solid) and 550 nm (dashed) (red lines, right axis). C. Sulfur exit channels shown as fraction of total sulfur leaving the atmosphere. The dotted line is the sum of exit channels shown.
Figure 1. Zerkle et al.
Figure 2. Zerkle et al.
Figure 3. Zerkle et al.