

LETTERS

Sulphur isotope evidence for an oxic Archaean atmosphere

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The presence of mass-independently fractionated sulphur isotopes (MIF-S) in many sedimentary rocks older than ~2.4 billion years (Gyr), and the absence of MIF-S in younger rocks, has been considered the best evidence for a dramatic change from an anoxic to oxic atmosphere around 2.4 Gyr ago^{1–9}. This is because the only mechanism known to produce MIF-S has been ultraviolet photolysis of volcanic sulphur dioxide gas in an oxygen-poor atmosphere. Here we report the absence of MIF-S throughout ~100-m sections of 2.76-Gyr-old lake sediments and 2.92-Gyr-old marine shales in the Pilbara Craton, Western Australia. We propose three possible interpretations of the MIF-S geologic record: (1) the level of atmospheric oxygen fluctuated greatly during the Archaean era; (2) the atmosphere has remained oxic since ~3.8 Gyr ago, and MIF-S in sedimentary rocks represents times and regions of violent volcanic eruptions that ejected large volumes of sulphur dioxide into the stratosphere; or (3) MIF-S in rocks was mostly created by non-photochemical reactions during sediment diagenesis, and thus is not linked to atmospheric chemistry.

The abundance ratios of the stable isotopes of sulphur (³²S, ³³S, ³⁴S and ³⁶S) in a material *i* are typically expressed as the deviations from those in troilite (FeS) in Cañon Diablo meteorite, such as $\delta^{33}\text{S}_i(\text{‰}) = [({}^{33}\text{S}/{}^{32}\text{S})_i / ({}^{33}\text{S}/{}^{32}\text{S})_{\text{VCDT}} - 1] \times 1,000$, where VCDT is the international sulphur isotope standard. The $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values of most Earth materials typically fall on the terrestrial fractionation line¹⁰: $\delta^{33}\text{S} = 0.515 \times \delta^{34}\text{S}$. Such relationships occur because the magnitude of isotope fractionation during most (bio)chemical reactions depends primarily on differences in isotope mass, which is termed mass-dependent fractionation. Deviation from the terrestrial fractionation line is commonly expressed as: $\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}$. A $\Delta^{33}\text{S}$ range of $0 \pm 0.2\text{‰}$ has been suggested for mass-dependent fractionation^{5,11}; $\Delta^{33}\text{S}$ values outside this range reflect MIF-S.

Previous researchers^{1,5–9} have suggested a general trend with geologic time in $\Delta^{33}\text{S}$ values of sedimentary rocks (Fig. 1): Stage I (>2.4 Gyr), distinct MIF-S ($\Delta^{33}\text{S} = -2\text{‰}$ to $+8\text{‰}$); Stage II (~2.4 to ~2.0 Gyr), small or no MIF-S ($\Delta^{33}\text{S} = 0 \pm 0.5\text{‰}$); and Stage III (<2.0 Gyr), no MIF-S ($\Delta^{33}\text{S} = 0 \pm 0.2\text{‰}$). By irradiating SO₂ gas with an ultraviolet laser (wavelength $\lambda = 193$ nm) in the absence of O₂, Farquhar *et al.*³ produced S⁰ (elemental sulphur) with large positive $\Delta^{33}\text{S}$ values ($+65 \pm 5\text{‰}$) and SO₄^{2–} with large negative $\Delta^{33}\text{S}$ values ($-17 \pm 5\text{‰}$). From photochemical modelling, the maximum atmospheric *p*_{O₂} value to create MIF-S by ultraviolet photolysis of SO₂ was estimated to be ~10^{–2} present atmospheric level (PAL)^{3,5} or ~10^{–5} PAL (ref. 4). From these data sets, recent investigators^{1–9} have concluded that the following major changes occurred ~2.4 Gyr ago: (1) the atmosphere dramatically changed from anoxic (*p*_{O₂} < 10^{–5} PAL) to oxic (*p*_{O₂} > 10^{–5} or >10^{–2} PAL); (2) input of atmospheric S⁰ to the oceans ceased because of the

complete conversion of volcanic SO₂ to SO₄^{2–} in an oxic atmosphere; and (3) oceanic SO₄^{2–} concentration began to rise due to the increased oxidative weathering of pyrite.

In some Archaean (>2.5 Gyr) sedimentary rocks, very small $\Delta^{33}\text{S}$ values (within $0 \pm 0.2\text{‰}$) have been recognized^{1,5–8}. However, their significance cannot be fully evaluated without mineralogical and geochemical information to determine whether sulphur compounds recorded the isotopic signatures of the contemporaneous atmosphere or those of subsurface environments. Here we present the results of isotopic, mineralogical and geochemical investigations of modern weathering-free drill cores recently recovered by the Archaean Biosphere Drilling Project from two major Archaean sedimentary formations in the Pilbara Craton: the world's oldest lake sediments (the 2.76-Gyr-old Hardey Formation) and one of the oldest marine shales (the 2.92-Gyr-old Mosquito Creek Formation; Fig. 2). The Archaean Biosphere Drilling Project, geologic settings of the drill sites, and the methods and results of analyses are described in the Supplementary Information.

Sulphur occurs in our samples almost exclusively as pyrite (FeS₂) crystals, though not as detrital grains from the weathering of igneous rocks or sulphide-rich ore bodies, nor had they formed from hydrothermal fluids during and/or after sediment deposition. The morphology and modes of occurrence of pyrites in the Archaean shales are very similar to those in Devonian black shales, which suggests they grew from Fe-S precursors that formed from H₂S in the overlying water bodies and/or in sediment pore waters during sediment accumulation and diagenesis. Most (if not all) of the H₂S was probably generated by the reduction of aqueous SO₄^{2–} by sulphate-reducing bacteria.

Essentially all pyrites in Phanerozoic sediments were formed by sulphate-reducing bacteria that used the SO₄^{2–} and organic matter in water, which explains the general correlations between the concentrations of sulphide-S in sediments and SO₄^{2–} in water^{12,13}. For example, SO₄^{2–} concentration averages 28 mM in modern oceans and ~1 mM in freshwater lakes, which results in differing sulphide-S concentrations (~0.2 wt% versus ~0.05 wt%) and S-to-C weight ratios (~0.37 versus ~0.07) between average normal marine sediments (those deposited under oxygenated sea water) and average lake sediments. Because H₂S concentration in a euxinic water body is much higher than in an open sea, sediments deposited in such conditions generally have much higher pyrite contents (S = ~0.5 to ~10 wt%) and variable S/C ratios.

The S-to-C concentration relationships of the 2.76-Gyr lake sediments (Hardey Formation) are very similar to modern sediments in low-SO₄^{2–} lakes, as are those of the 2.92-Gyr-old marine shales (Mosquito Creek Formation) to modern sediments in euxinic seas (Fig. 3). This implies that the SO₄^{2–} concentrations of the 2.92-Gyr-old Mosquito Creek Sea were comparable to modern euxinic seas

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(~20 to ~30 mM)^{12,13} but much higher than modern lakes, and that sulphate-reducing bacteria were actively producing H₂S that resulted in pyrite formation. This suggestion contrasts with a current popular Archaean sulphur cycle model^{1-9,14} that postulates very-low-SO₄²⁻ oceans (<1/100 of the present level) and minimal sulphate-reducing bacteria activity. From the δ³⁴S values of pyrites (Supplementary Tables), we estimate the δ³⁴S_{SO₄} values were ≥ +2‰ for the 2.76-Gyr-old lake and ≥ +8‰ for the 2.92-Gyr-old sea, and the kinetic isotopic fractionation of ³⁴S/³²S accompanying sulphate reduction Δ_{SO₄-H₂S} = δ³⁴S_{SO₄} - δ³⁴S_{H₂S} was ≥ 5‰ in the lake and ≥ 7‰ in the sea.

Because the background concentrations of aqueous sulphur species in the Archaean Hardey Lake were probably much less than those in the Mosquito Creek Sea, we expected to recognize easily the contributions of atmospheric sulphur to the surface waters and to detect larger Δ³³S variations in the Hardey (lacustrine) samples. However, this was not so. The δ³⁴S and Δ³³S values of the 18 lacustrine samples range only from -2.73‰ to +1.74‰ and -0.21‰ to +0.25‰, respectively (Figs 1 and 4). With an analytical uncertainty of ±0.05‰ for Δ³³S, we suggest that all these samples fall within the mass-dependent fractionation range. The δ³⁴S and Δ³³S values of 24 marine shale samples show slightly larger variations, from +1.40‰ to +7.7‰ and -0.51‰ to +0.18‰, respectively; all but five samples fall within the mass-dependent fractionation range. Typical sedimentation rates for shales are ~1 to ~10 cm per

1,000 years (ref. 15), so our data suggest that during the ~1- to ~10-Myr period required to accumulate the ~100-m section of non-marine Hardey (or marine Mosquito Creek) shales, the surface waters did not receive measurable contributions of atmospheric S⁰ or SO₄²⁻ with MIF-S signatures.

Large MIF-S values were previously recognized in sedimentary rocks 2.47–2.72 Gyr and 3.2–3.8 Gyr in age (Fig. 1). Farquhar and Wing⁵ concluded that ~0.5% to ~10% of the sulphur used in pyrite formation during Stage I (>~2.4 Gyr) came from atmospheric S⁰, while the remainder (>90%) came from the bacterial sulphate reduction of sea water SO₄²⁻, which was mostly supplied by the oxidative weathering of pyrite on land. They also suggested the Δ³³S values of Stage II (~2.4 to ~2.0 Gyr) sediments indicated an atmospheric p_{O₂} > 10⁻⁵ (or >10⁻²) PAL, which prevented new additions of atmospheric S⁰ and SO₄²⁻ with large MIF-S signatures to the oceanic SO₄²⁻ reservoir. The small MIF-S in Stage II sediments may have resulted from the weathering of older land sediments with MIF-S signatures into the oceans⁵. Previously, Δ³³S analyses were not reported on sedimentary rocks of a well-defined age between ~2.72 Gyr and ~3.0 Gyr. The Δ³³S values of the 2.76-Gyr-old Hardey and 2.92-Gyr-old Mosquito Creek formations are essentially the same as for Stage II pyrites (Fig. 1). Therefore, a scenario similar to that for Stage II sediments may be applicable to these formations. This would imply that atmospheric p_{O₂} levels fluctuated greatly (a ‘yo-yo atmosphere’) during the Archaean, possibly from anoxic

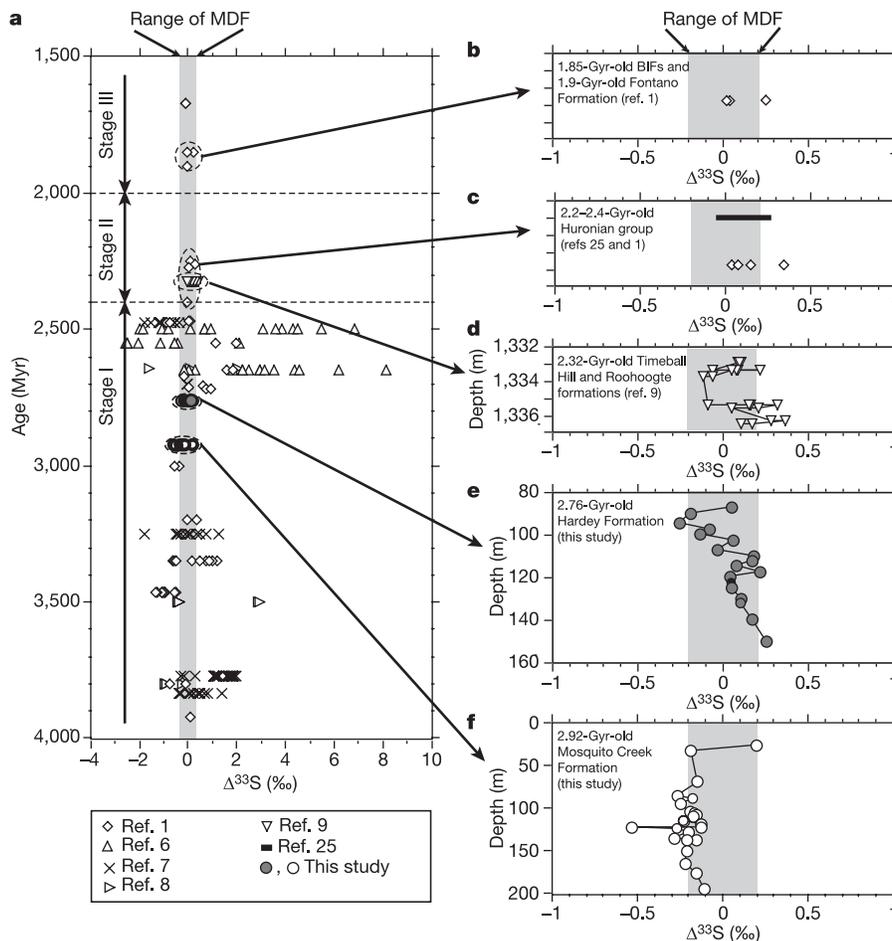


Figure 1 | MIF-S record. Δ³³S values of sulphur-bearing compounds (mostly pyrite and/or barite) in pre-1.6-Gyr-old sedimentary rocks. Each point represents one analysis. Δ³³S values outside the shaded range (Δ³³S = 0 ± 0.2‰) may contain MIF-S atoms. **a**, A summary of data from the literature and this study. Sources of data and methods of analysis: refs 1, 6 and 25, SF₆ method using bulk rock/sulphide sulphur converted Ag₂S; refs 8 and 9,

spot analyses of pyrite crystals using SF₆ method; ref. 7, spot analyses of single sulphide grains by secondary ion mass spectrometry. The divisions of stages I–III are from ref. 5. **b–f**, Plots of Δ³³S values versus the stratigraphic positions of samples. The 1.85-Gyr-old BIFs in **b** refer to the Biwabik and Gunflint banded iron formations. The thick bar in **c** is the range of isotope values from ref. 25.

Age	Group	Formation	Myr	
Proterozoic	Hammersley group	Boolgeeda Iron	2,410	
		Woongara volcanics	2,449	
		Weeli Wollie	2,454	
		Brockman Iron	2,470	
		Mt McRae shale & Mt Sylvania	~2,500	
		Wittenoon	2,542	
		Carawine dolomite	2,590	
		Marra Mamba Iron	2,593	
		Jeerinah	2,630	
		Maddina	2,690	
Archaean	Mount Bruce supergroup	Fortescue group	Tumbiana	2,717
			Kylena	2,740
			Hardey	2,760
			Mt Roe basalt	2,775
			Mosquito Creek	2,905
		Nulagine	Coondamar	>2,926
			Pilbara supergroup	>3,000

Figure 2 | Stratigraphy of the Pilbara Craton. Stratigraphic column with ages comprising sedimentary volcanic rocks in the Pilbara-Hammersley districts, Western Australia^{26–28}. The five sedimentary formations (Mt McRae shale, Carawine, Jeerinah, Hardey and Mosquito Creek) subjected to sulphur isotope investigations by ref. 6 (dotted border) and this study (solid border) are outlined.

(<10⁻⁵ PAL) before ~3.0 Gyr, to oxic (>10⁻⁵ or >10⁻² PAL) between ~3.0 and ~2.75 Gyr, to anoxic between ~2.75 and ~2.4 Gyr, back to oxic after ~2.4 Gyr. The recent discovery of molecular fossils of cyanobacteria and eukarya in 3.2-Gyr-old sediments from the Pilbara Craton¹⁶ supports such a scenario, because it suggests the possible development of an oxic atmosphere before ~2.5 Gyr ago. Future research on different geologic formations may suggest the atmospheric *p*_{O₂} level fluctuated even more frequently and rapidly during the Archaean.

Alternatively, the $\Delta^{33}\text{S}$ record of sedimentary rocks (Fig. 1) may suggest that the atmosphere has remained oxic since ~3.8 Gyr ago, and that MIF-S signatures represent times and regions of violent volcanic eruptions that ejected large volumes of SO₂ to the stratosphere, where it would be above the ozone shield and hence subject to ultraviolet photolysis. The discovery of significant MIF-S signatures ($\Delta^{33}\text{S} = +0.67\text{‰}$ and -0.50‰) in volcanic ashes associated with the recent violent eruptions of Mt Pinatubo and another unknown volcano, and the absence of MIF-S in ashes associated with minor eruptions¹⁷, supports this interpretation. In fact, the 2.5-Gyr-old McRae and 2.7-Gyr-old Jeerinah shales, which exhibit large MIF-S signatures (Figs 1 and 4), contain abundant volcanogenic sediments¹⁸. The frequent occurrence of Archaean rocks with large MIF-S, but the decreasing magnitude of MIF-S in younger rocks, may be because Earth's interior was hotter and volcanic activity was much more intensive and extensive during the Archaean, as indicated by the abundance of Archaean komatiites, layered intrusions, granitoids and mantle plumes^{19,20}. In fact, the Archaean volcanic flux of SO₂ is estimated to be three to four times higher than today²¹.

The above arguments were made under the fundamental assumption

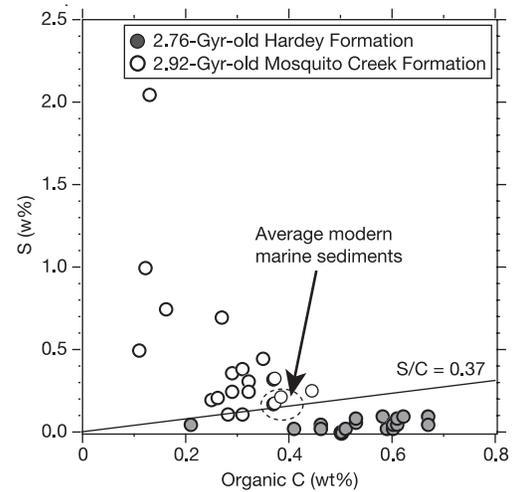


Figure 3 | S and organic C. S concentration versus organic C concentration for the studied samples, compared to average modern marine sediments^{12,13}.

tion that the only mechanism to create MIF-S signatures is the atmospheric photochemical reaction of volcanic SO₂. However, this assumption must be evaluated for the following reasons: (1) a serious discrepancy exists between photochemical experimental results and geologic measurements. Ultraviolet photolysis of SO₂ generates S⁰ with very large negative $\delta^{34}\text{S}$ ($-60 \pm 20\text{‰}$) and positive $\Delta^{33}\text{S}$ ($+65 \pm 5\text{‰}$) values³, while Ono *et al.*⁶ suggested that pyrite with the most positive $\delta^{34}\text{S}$ ($\sim +10\text{‰}$) and positive $\Delta^{33}\text{S}$ ($\sim +8\text{‰}$) values in the McRae and Jeerinah shales represented atmospheric S⁰ (Fig. 4). If so, the transformation of S⁰ with negative $\delta^{34}\text{S}$ (experimentally produced S⁰) to pyrite-S with positive $\delta^{34}\text{S}$ would have required an unidentified non-photochemical reaction in water and/or sediments that caused very large negative MIF-S effects ($\Delta^{33}\text{S} = \sim -70\text{‰}$). (2) By recognizing a significant difference in temperature dependence of the equilibrium fractionation factors for the ³³S–³²S and ³⁴S–³²S exchanges between S₂ and H₂S gases, Deines²² has shown that the $\Delta^{33}\text{S}$ values of S₂ and H₂S may range from infinitely large positive to infinitely large negative values at

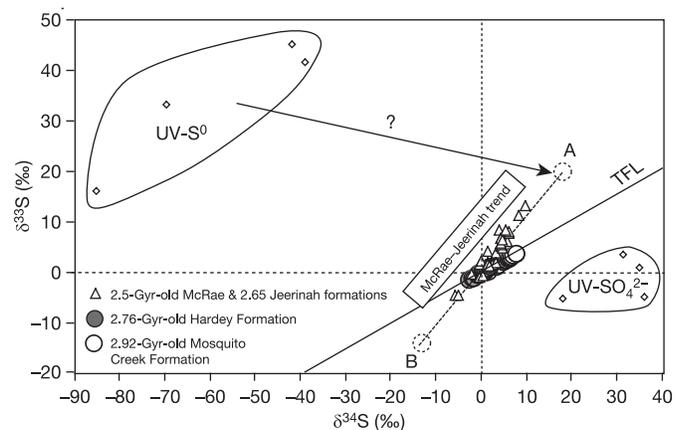


Figure 4 | $\delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ relationships. $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values of the 2.76-Gyr-old Hardey and 2.92-Gyr-old Mosquito Creek formations (this study) are compared to those of the 2.65-Gyr-old Jeerinah and the 2.5-Gyr-old Mt McRae shale formations⁶, and those of S⁰ (UV-S) and SO₄²⁻ (UV-SO₄²⁻) produced by ultraviolet photolysis of SO₂ (ref. 3). Ono *et al.*⁶ interpreted the McRae-Jeerinah trend as the result of mixing two types of pyrite, one that formed from atmospheric S⁰ (A) and another from atmospheric SO₄²⁻ (B). However, the transformation of UV-S⁰ to atmospheric S⁰ (A) requires a non-photochemical reaction with large negative MIF-S effects (see text).

temperature $T \approx 71.5^\circ\text{C}$. (3) Watanabe *et al.*²³ were able to generate H_2S with distinct MIF-S signatures ($\Delta^{33}\text{S} = 0.30\text{--}0.45\text{‰}$) through the thermochemical reduction of SO_4^{2-} by amino acids at $T \approx 170^\circ\text{C}$. Combining these data with the Rayleigh and/or recycling sulphate-sulphide processes, they explained much larger $\Delta^{33}\text{S}$ values in sedimentary rocks. (4) Ono *et al.*²⁴ discovered distinct MIF-S signatures ($\Delta^{33}\text{S} = 0.27\text{--}0.34\text{‰}$) in pyrite crystals from a fossilized Jurassic ammonite (~ 150 Myr in age) that must have formed by the bacterial or thermochemical reduction of porewater SO_4^{2-} , by using organic matter in the ammonite during sediment diagenesis.

Therefore, it may be premature to assume that all MIF-S in rocks indicate an anoxic atmosphere. A more complete record of $\Delta^{33}\text{S}$ in Archaean and younger rocks, which includes the geologic, mineralogical and geochemical context, along with laboratory experiments on the fractionations of multiple sulphur isotopes during a variety of non-photochemical reactions, is required to relate the $\Delta^{33}\text{S}$ rock record to the atmospheric, thermal, and biological history of the Earth.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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