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Calibration of Sulfate Levels in the Archean Ocean

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The size of the marine sulfate reservoir has grown through Earth's history, reflecting the accumulation of oxygen into the atmosphere. Sulfur isotope fractionation experiments on marine and freshwater sulfate reducers, together with the isotope record, imply that oceanic Archean sulfate concentrations were <200 μM, which is less than one-hundredth of present marine sulfate levels and one-fifth of what was previously thought. Such low sulfate concentrations were maintained by volcanic outgassing of SO_2 gas, and severely suppressed sulfate reduction rates allowed for a carbon cycle dominated by methanogenesis.

It is thought that the Archean Earth had low atmospheric oxygen concentrations (*1*), low oceanic sulfate concentrations (*2*), and elevated atmospheric concentrations of methane, contributing to possible greenhouse warming of Earth's surface (*3*). The biogeochemistries of these elements are linked, in that low atmospheric oxygen levels suppress the oxidative weathering of sulfides and the delivery of sulfate to the oceans, contributing to the low sulfate concentrations (*2*). Low sulfate levels could have inhibited sulfate reduction, enhancing methane production (*2*, *4*).

This reconstruction depends on our ability to extract reliable sulfate concentration information from the isotope record of sulfide and sulfate through time. The isotope record reveals small fractionations of generally <10 per mil (‰) between sulfates and sedimentary sulfides before 2.5 to 2.7 billion years ago (Ga) (*2*). The few available pure culture studies suggest that fractionations become suppressed at a sulfate concentration around 1 mM (*5*, *6*). Current models link reduced fractionations at low sulfate concentration to a limitation of sulfate exchange across the cell membrane (*6*). In this case, most of the sulfate entering the cell becomes reduced, and even with substantial internal enzymatic fractionations, minimal net fractionation is expressed. Sulfate limitation also reduces sulfate reduction rates, with half-saturation constants (k_m) values for marine strains of 70 and 200 μM (*7*, *8*) and for freshwater strains, 5 to 30 μM (*7*). If similar sulfate concentrations limit both fractionation and sulfate reduction rate, then sulfate reducers should maintain substantial fractionation at sulfate concentrations considerably less than 1 mM.

In continuous culture, we explored the fractionations at millimolar and submillimolar sulfate concentrations by *Archaeoglobus fulgidus* grown on lactate at its optimal growth for temperature of 80°C. *A. fulgidus* is an archaeon and was chosen to represent possible early sulfate reducers from hydrothermal settings. We also examined natural populations of sulfate reducers from a coastal marine sediment (natural sulfate concentration, 20 mM) and a freshwater lake sediment (natural sulfate concentration, 300 μM). Freshwater sulfate reducers are especially adapted to low sulfate concentrations (*9*) and could reflect the behavior of possible early low sulfate–adapted organisms, whereas marine sulfate reducers are adapted to high seawater salinities. In the natural population experiments, sediment was incubated at 17°C in a rapidly recirculating flow-through plug reactor (*10*) with lactate (1 mM) as the organic substrate (*11*).

All three different microbial populations produced high fractionations (*11*) of up to 32‰ with 200 μM or greater sulfate (Fig. 1). The average fractionation for sulfate between 200 and 1000 μM was 22.6 ± 10.3‰, which is similar to the average for pure bacterial cultures (*6*) (18 ± 10‰) and natural populations (*6*) (28 ± 6‰) of sulfate reducers utilizing 20 mM or greater sulfate. By contrast, fractionations were consistently less than 6‰ (an average of 0.7 ± 5.2‰) with sulfate concentrations less than 50 μM. Thus, sulfate substantially limited fractionation up to a concentration somewhere between 50 μM and around 200 μM. This is also the concentration range where sulfate limits rates of sulfate reduction (*8*, *9*).

The isotopic composition of sedimentary sulfides will, in addition to the bacterial fractionation, depend on the extent to which sulfides form in a zone of sulfate depletion (*6*,

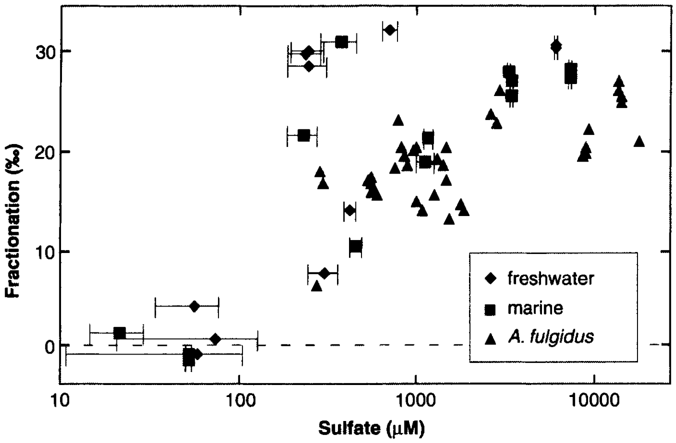

Fig. 1. Isotope fractionation as a function of sulfate concentration for freshwater (diamonds) and marine (squares) natural populations of sulfate reducers and for the hyperthermophile *A. fulgidus* (triangles). For the freshwater and marine populations, horizontal bars plot the range of sulfate concentrations within the reactor, with the higher concentration entering the reactor, and the low concentration exiting the reactor. The symbols are positioned on the bars at the average concentration in the reactor.

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12), and ^{34}S-enriched pore water sulfides may be redistributed by diffusion (*13*). The influence of the sediment environment on the final isotopic composition of sedimentary sulfides depends on sulfate concentration. Therefore, we explored with a diagenetic model how sulfate concentration influences the isotopic composition of sedimentary sulfides (*11*). Sulfides preserve, on average, lower fractionations than the bacterial fractionations (Fig. 2A). Yet, even with 200 μM SO_4^{2-}, a substantial population of sulfides formed, with a δ^{34}S values approaching the bacterial fractionation values (Fig. 2A). Fine-scale single-grain analyses should reveal these ^{34}S-depleted sulfides and the highly ^{34}S-enriched sulfides that were also produced. However, bulk samples and fine-scale laser ablation analysis of sulfides formed before 2.7 Ga do not reveal large fractionations ($\delta^{34}S_{\text{seawater sulfate}} - \delta^{34}S_{\text{pyrite}}$) of 20 to 30‰ (*14*, *15*). An exception is the biologically produced sulfides from the 3.45-billion-year-old North Pole barites of Western Australia, formed in local sulfate-rich evaporitic conditions (*16*).

From our results, low fractionations ($\delta^{34}S_{\text{seawater sulfate}} - \delta^{34}S_{\text{pyrite}}$) of less than 10‰ in the sulfur isotope record before 2.7 Ga were most likely produced by sulfate reducers living in an ocean with less than 200 μM sulfate (*17*). This maximum sulfate concentration is one-fifth that previously thought (*2*, *6*). These low concentrations are consistent with low or negligible oxygen concentrations suppressing the oxidative weathering of sulfide minerals from land (*2*). A locally important source of sulfate could come from the oxidation of hydrothermal sulfide in terrestrial hot springs by anoxygenic photosynthetic bacteria. However, the most important source of sulfate to the oceans was probably volcanic outgassing of SO_2, followed by either direct disproportionation to sulfate and sulfide or conversion to sulfate through gas-phase reactions in the atmosphere. A substantial role for gas-phase sulfur conversions is indicated by the record of minor sulfur isotopes, ^{33}S and ^{36}S, which preserve considerable mass-independent fractionations in the Archean (*18*). These are only known to originate from gas-phase reactions of sulfur compounds in an oxygen-free atmosphere (*19*).

Currently, SO_2 outgasses from volcanoes at a rate of about 1×10^{11} to 3×10^{11} mol year^{-1} (*20*, *21*). Of this, probably about one-half is recycled sedimentary sulfur (*22*), and one-half is from the mantle, producing a mantle flux of sulfate of 0.4×10^{11} to 1.1×10^{11} mol year^{-1}, considering that 75% of the SO_2 is converted to SO_4^{2-} after SO_2 disproportionation (Eq. 1).

$$4SO_2 + 4H_2O \rightarrow H_2S + 3H_2SO_4 \qquad (1)$$

This mantle sulfate flux is between 1/20th and 1/50th of the present-day natural (nonpollutive) river sulfate flux to the oceans of 2×10^{12} mol year^{-1} (*23*) [compare to a similar calculation in (*24*)]. Thus, with Archean volcanic SO_2 degassing rates comparable to those of today, lower sulfate input fluxes would explain lower ocean sulfate concentrations. Rates of volcanic SO_2 degassing could have been higher than they are today. However, more reducing mantle conditions could have substantially reduced the mantle flux of SO_2, thereby reducing the sulfate flux to the oceans, even with a higher degassing rate (*1*). Therefore, extremely low concentrations of sulfate in the Archean were probably maintained by greatly reduced fluxes of sulfate to the oceans.

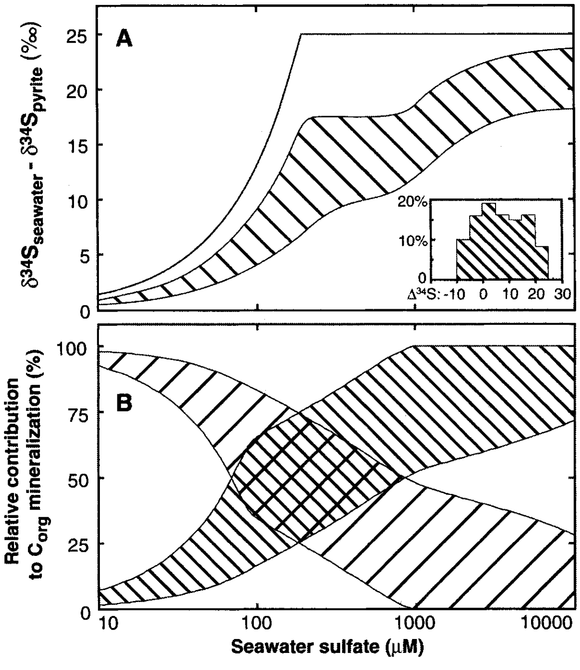

Fig. 2. (**A**) Model results showing how the average isotopic composition of pyrite in sediments is influenced by sulfate concentration. The upper thin line, following our experimental results, shows the biological fractionations imposed on the model, whereas the hatched field shows the isotopic composition of pyrites under average coastal sediment conditions (*11*), with fluxes of reactive organic carbon and sediment particulates of 200 μmol cm^{-2} year^{-1} and 0.1 g cm year^{-1}, respectively (lower line), and 20 μmol cm^{-2} year^{-1} and 0.01 g cm^{-2} year^{-1} (upper line). This range of carbon fluxes reasonably brackets those found in modern sediments ranging from the coastal ocean to the outer slope (*29*). The histogram in the inset shows the frequency with which pyrites at different isotopic compositions are formed with a sulfate concentration of 200 μM and the higher organic carbon flux (200 μmol cm^{-2} year^{-1}). (**B**) The relative importance of sulfate reduction and methanogenesis as a function of sulfate concentration, assuming that only these two processes are involved in organic carbon (C_{org}) mineralization (*11*). The closely spaced hatches represent the relative importance of sulfate reduction for the same high (lower line) and low (upper line) carbon fluxes as used in (A). The loosely spaced hatches represent the relative importance of methanogenesis for high (upper line) and low (lower line) carbon fluxes. At high carbon flux, sulfate reduction is relatively less important, and methanogenesis relatively more important, as compared to the situation at lower carbon flux.

Low concentrations of seawater sulfate would have been unevenly mixed within the global ocean, somewhat analogous to the uneven distribution of oxygen in the modern ocean. The highest concentrations, though still less than 200 μM, would have been in surface waters and possibly in proximity to volcanic terraines. Much lower, or even negligible, concentrations would be expected deeper in the ocean and possibly far away from important source regions, where the supply of sulfate from mixing processes would be diminished by sulfate removal through sulfate reduction.

Evidence from lake sediments suggests that sulfate reduction rates at 200 μM are substantially suppressed compared to rates at 1 mM sulfate, with most of the anaerobic mineralization channeled through methanogenesis (*25*). This database, however, is limited, and we therefore chose to explore with a diagenetic model the relations between sulfate concentration and sulfate reduction rate. We modeled the importance of sulfate reduction in a typical coastal sediment supporting only sulfate reduction and methanogenesis exposed to various concentrations of sulfate in the overlying water. Using the same basic model parameters as in Fig. 2A (*11*), 200 μM sulfate (Fig. 2B) suppressed sulfate reduction by 75% compared to 28 mM sulfate (*26*); and 50 μM sulfate reduced sulfate reduction rates by over 90%. With a reduced carbon flux more typical of outer slope or continental rise sediments (1000 to 3000 m depth), 200 μM sulfate reduces sulfate reduction by 30% compared to 28 mM sulfate (Fig. 2B); and 50 μM sulfate decreases sulfate reduction by about 75%. Our results, therefore, demonstrate that rates of Archean sulfate reduction were reduced compared to those of today (Fig. 2B). This is especially true because 200 μM is a maximum Archean sulfate concentration, and deepwater sediments were likely deposited with much lower sulfate concentrations than those from surface waters, reducing rates of sulfate reduction even further.

From our model results (Fig. 2B), 30 to 70% of the total carbon mineralization goes through methanogenesis at 200 μM sulfate (and even more at lower sulfate concentrations). Although some of the methane would have been reoxidized in the sediment by anaerobic methane oxidation coupled to sulfate reduction (*27*), considerable methane would have escaped (*28*) and could have substantially contributed to the greenhouse warming of the early Earth (*3*, *4*).

Sediment-supported rates of sulfate reduction are highly sensitive to sulfate concentrations from 100 to 1000 μM (Fig. 2B), and the isotope record (*2*, *6*) indicates that sulfate concentrations increased beyond 200 μM starting around 2.4 Ga. The concomitant increase in sulfate reduction rate, both in sediments and in the water column as sulfate became more available, would have reduced methanogenesis substantially, as well as the flux of methane to the atmosphere. This, in concert with a possible rise in atmospheric O_2 providing an increased methane sink, may have led to global cooling and the first known glaciation at around 2.4 Ga (*4*).

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17. Some of the basins from before 2.7 Ga, for which sulfur isotope values are available, may have experienced sulfate concentrations different from those of the global ocean. Lower sulfate concentrations may have been possible if the basin experienced restricted exchange with the ocean, and higher concentrations could have been possible if local sulfate sources were available. The lack of high fractionations, except where high-sulfate environments can be documented (*16*), implies that throughout the wide range of depositional conditions sampled [see data in (*2*)], sulfate concentrations before 2.7 Ga were low. We must conclude that low sulfate concentrations were a persistent feature of marine depositional environments, and we furthermore emphasize that variability in sulfate concentrations within the global ocean was likely.
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Fig. S1
References

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Interannual Variability in the North Atlantic Ocean Carbon Sink

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The North Atlantic is believed to represent the largest ocean sink for atmospheric carbon dioxide in the Northern Hemisphere, yet little is known about its temporal variability. We report an 18-year time series of upper-ocean inorganic carbon observations from the northwestern subtropical North Atlantic near Bermuda that indicates substantial variability in this sink. We deduce that the carbon variability at this site is largely driven by variations in winter mixed-layer depths and by sea surface temperature anomalies. Because these variations tend to occur in a basinwide coordinated pattern associated with the North Atlantic Oscillation, it is plausible that the entire North Atlantic Ocean may vary in concert, resulting in a variability of the strength of the North Atlantic carbon sink of about ±0.3 petagrams of carbon per year (1 petagram = 10^{15} grams) or nearly ±50%. This extrapolation is supported by basin-wide estimates from atmospheric carbon dioxide inversions.

The ocean's contribution to the observed interannual variability of atmospheric carbon dioxide (CO_2) is poorly established. Estimates based on atmospheric measurements of CO_2, oxygen, and stable carbon isotopes indicate that the variability contributed by the oceanic carbon cycle is more than ± 1 Pg C year^{-1} (*1*–*4*). In contrast, estimates based on direct observations of the partial pressure of CO_2 (pCO_2) in surface waters (*5*, *6*) and on modeling studies (*7*, *8*) indicate a contribution of less than ± 0.5 Pg C year^{-1}, mainly associated with tropical Pacific ocean variability caused by El Niño and La Niña (*9*). However, many uncertainties are associated with the modeling studies, and the equatorial Pacific is the only region where interannual variability in oceanic pCO_2 has been directly observed and documented. Given evidence for substantial extratropical variability in sea surface temperature (SST) (*10*) and the ocean's state (*11*), other oceanic regions may contribute substantially to the atmospheric CO_2 variability as well. The North Atlantic Ocean is one of the few regions where enough data are available to investigate interannual to decadal variability in the extratropical ocean carbon cycle. Observationally based estimates (*12*), as well as forward and inverse modeling results (*13*), indicate that this region constitutes the largest ocean sink for atmospheric CO_2 in the Northern Hemisphere, on average taking up about 0.7 ± 0.1 Pg C year^{-1}.

Observations have shown that most of the interannual to decadal climatic variability in the North Atlantic basin occurs in broadly coherent patterns linked to a natural mode of atmospheric pressure variation known as the North Atlantic Oscillation (NAO) (*14*). The

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