The Archean Atmosphere and Sedimentary Sulfides

Canfield, Habicht, and Thamdrup (Report, "The Archean sulfur cycle and the early history of atmospheric oxygen," 28 Apr., p. 658) conclude from experiments on sulfate-reducing bacteria (SRB) that the early Archean sulfur isotopic record is consistent with low seawater sulfate concentrations and an atmosphere with oxygen at or below 0.4% of present-day levels. If true, arguments supporting global Archean levels of oxygen closer to 1 to 2% of the present level (*1*) or higher (*2*) must be explained or ignored. Furthermore, at localized "oxygen oases" where oxygen levels were supposedly high in an otherwise anoxic world (*3*), high sulfate levels would be expected even if global ocean sulfate levels were low. It then becomes axiomatic that if SRB were operating throughout the oceans, they could not also have been present in early Archean continental or restricted marginal areas of the sea where evaporation raised sulfate levels (*4, 5*). Cameron (*6*) recognized this dilemma, citing 10 references of examples where "sulphate was present in significant concentration in some bodies of water during the early Archaean."

An alternative scenario may help explain the Archean sulfur isotope record: SRB ecosystem role-reversal. Low isotopic fractionations have been observed over a broad range of sulfate reduction rates when SRB use molecular hydrogen as an electron donor [see references (*8, 15*) in Canfield *et al.*'s report]. SRB have a greater affininty for both hydrogen and acetate than do methanogens, with which they compete (*7*). If the first-evolved SRB could not use acetate (the *Desulfovibrio-Desulfotomaculum* types), this would allow Archean methanogens to use this electron donor with only limited competition from SRB. Archean sulfate (and iron) reduction could then have taken place primarily through the use of fermentative hydrogen (hydrogenotrophy). Archean sulfate reduction, if dominated by non-acetate-using SRB, could help explain the observed low sulfur isotopic fractionations (*4*), regardless of the rate of reduction. This would be compatible with both Archean sulfate-rich deposits and the somewhat higher atmospheric oxygen levels needed to support aerobic respiration and a minimal ozone screen (*1*). The later phylogenetic emergence of the acetate-using SRB [*Desulfobacter*, *Desulfobacteriumor*, or the *Desulfococcus* group (*8*)] would signal the beginning of the modern marine ecosystem and the larger sulfur isotopic fractionations one sees from early Proterozoic sediments onward.

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Response

The early Archean isotope record of sedimentary sulfides (*1*) is, from our recent findings described in our *Science* report, consistent with sulfide formation in an environment with low concentrations of ocean sulfate and atmospheric oxygen, or alternatively, by nonbiogenic sources. Towe proposes a unique alternative explanation

where non-acetate-using sulfate-reducing organisms (using H_2 instead) actively reduced sulfate with little isotope fractionation in the presence of abundant sulfate and with high levels of atmospheric oxygen. Consequently, the higher fractionations preserved in the early Proterozoic sulfur isotope record (*1*) resulted from the evolution of acetate-using sulfate-reducing organisms.

We disagree, however, that Towe's scenario can explain the isotope record of sedimentary sulfides. Thus, non-acetate-using sulfate reducers can use a broad spectrum of organic substrates including formate, lactate, ethanol, succinate, fumerate, malate, fructose, dextrose, mannose, glucose, and mucin (*2, 3*). Some of these, like lactate, can be important fermentation products in sediments (*4*), and the metabolism of lactate, as well as many other organic compounds, by non-acetate-using sulfate reducers yields demonstrably high fractionations (*3, 5*). Therefore, we see no reason why an environment dominated by non-acetate-using sulfate reducers should produce negligible fractionations. Furthermore, there is no strong phylogenetic evidence for an evolutionary separation of acetate-using and non-acetate-using sulfate-reducing organisms. Thus, the Archaeal sulfate reducer *Archaeoglobus fulgidus* uses acetate (*6*), as do several species of the Gram-positive sulfate-reducing genus *Desulfotomaculum* (*3*), whereas *Thermodesulfobacterium commune* does not (*7*). All of these have deep phylogenic roots among the sulfate reducers on the basis of molecular sequence comparisons of the sulfite reductase gene and 16*S* ribosomal RNA (*8*).

Modern stromatolites like those shown here from Sharks Bay, Western Australia, are likely homologs to the earliest oxygen-producing ecosystems on Earth.

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Finally, non-acetate-using sulfate reducers metabolizing H_2 as an electron donor have been observed to produce fractionations as great as 16 per mil during sulfate reduction, and fractionations of between 10 and 16 per mil are not uncommon (*5*). Thus, although these fractionations are lower than observed during sulfate reduction with organic compounds, they are too large to be compatible with the early Archean sedimentary sulfur isotope record.

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