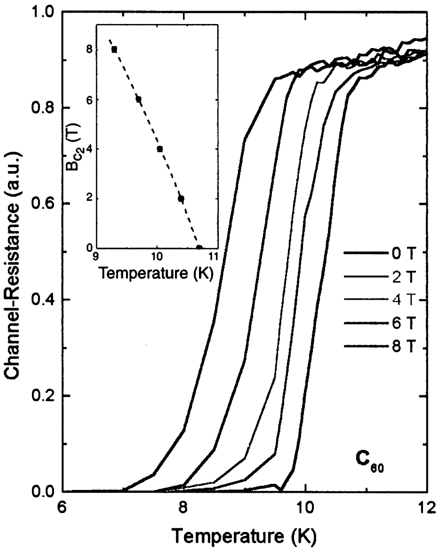

Fig. 5. Transition to the superconducting state for different magnetic fields applied perpendicular to the channel. The variation of the upper critical magnetic field H_{c2} with temperature is shown in the inset (slope ≈ −5 T/K).

same type as in A_3C_{60}. The filling of the band is controlled by the applied gate voltage, and because of the strong electron-phonon interaction in this material, the channel region becomes superconducting below 11 K.

The possibility of investigating superconductivity as function of electron (or hole) density in a simple FET device opens up various opportunities to find superconductivity in new classes of materials, especially organic semiconductors. In addition to being able to implement the longstanding idea of an ultimate field-induced switch (insulator-superconductor transformation), this technique also opens up new ways to substantially modify the electronic state in molecular crystals.

References and Notes

1. J. E. Lilienfeld, U.S. Patent 1,745,175 (1926).
2. M. M. Atalla, E. Tennenbaum, E. J. Scheiber, *Bell Syst. Tech. J.* **28**, 749 (1959).
3. R. E. Glover and M. D. Sherill, *Phys. Rev. Lett.* **5**, 248 (1960).
4. J. Mannhart, J. Ströbel, J. G. Bednorz, Ch. Gerber, *Appl. Phys. Lett.* **62**, 630 (1993).
5. J. Mannhart, J. G. Bednorz, K. A. Müller, D. G. Schlom, J. Ströbel, *J. Alloys Compd.* **195**, 519 (1993).
6. M. S. Dresselhaus, G. Dresselhaus, R. Saito, in *Physical Properties of High Temperature Superconductors IV*, D. M. Ginsberg, Ed. (World Scientific, Singapore, 1994), pp. 471–565; A. P. Ramirez, *Supercond. Rev.* **1**, 1 (1994).
7. A. F. Hebard *et al.*, *Nature* **350**, 600 (1991).
8. J. H. Schön, S. Berg, Ch. Kloc, B. Batlogg, *Science* **287**, 1022 (2000).
9. Ch. Kloc, P. G. Simpkins, T. Siegrist, R. A. Laudise, *J. Cryst. Growth* **182**, 416 (1997).
10. J. H. Schön, Ch. Kloc, R. A. Laudise, B. Batlogg, *Phys. Rev. B* **58**, 12952 (1998).
11. E. Frankevich, Y. Maruyama, H. Ogata, *Chem. Phys. Lett.* **214**, 39 (1993).
12. R. C. Haddon *et al.*, *Appl. Phys. Lett.* **67**, 121 (1995).
13. S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
14. T. Yildirim *et al.*, *Phys. Rev. Lett.* **77**, 167 (1996).
15. It has been observed that the charge transfer across a copper/C_{60} interface also occurs only at the topmost layer of C_{60} [A. F. Hebard, R. R. Ruel, C. B. Eom, *Phys. Rev. B* **54**, 14052 (1996)].
16. C. M. Varma, J. Zaanen, K. Raghavachari, *Science* **254**, 989 (1991).
17. M. A. Schlüter, M. Lannoo, M. Needls, G. A. Baraff, D. Tomanek, *Phys. Rev. Lett.* **68**, 526 (1992).

18. J.H.S. gratefully acknowledges financial support b the Deutsche Forschungsgemeinschaft. We thank I Bucher for the use of equipment and H. Y. Hwan D. W. Murphy, H. Störmer, and C. M. Varma fo helpful discussions.

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The Archean Sulfur Cycle and the Early History of Atmospheric Oxygen

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The isotope record of sedimentary sulfides can help resolve the history of oxygen accumulation into the atmosphere. We measured sulfur isotopic fractionation during microbial sulfate reduction up to 88°C and show how sulfate reduction rate influences the preservation of biological fractionations in sediments. The sedimentary sulfur isotope record suggests low concentrations of seawater sulfate and atmospheric oxygen in the early Archean (3.4 to 2.8 billion years ago). The accumulation of oxygen and sulfate began later, in the early Proterozoic (2.5 to 0.54 billion years ago).

Life has dramatically modified the surface chemistry of Earth. A most conspicuous expression of this is the accumulation of oxygen, a product of oxygenic photosynthesis by plants and cyanobacteria, into the atmosphere and oceans. Atmospheric oxygen promotes the oxidative weathering of rocks on land, forming oxidized species such as iron oxides and soluble sulfate (*1*). As a result, the accumulation of sulfate into the oceans (the concentration is presently 28 mM) and the formation of iron oxides during weathering on land are two substantial geochemical expressions of oxygen accumulation into the atmosphere (*1*, *2*). Still, considerable controversy and debate surround when atmospheric oxygen first began to accumulate. In one scenario, atmospheric oxygen reached present-day levels by the earliest Archean [3.8 billion years ago (Ga)] and has persisted in high concentrations ever since (*3*). In another scenario, atmospheric oxygen first began to accumulate much later, around 2.2 to 2.3 Ga in the early Proterozoic (*2*). Present-day levels may not have been reached until sometime in the Neoproterozoic, 0.54 to 1.0 Ga (*4*).

The history of seawater sulfate concentrations is germane to differentiating between these two models for atmospheric oxygen accumulation. Low concentrations of seawater sulfate into the early Archean would be consistent with, and provide evidence for, low early Archean concentrations of atmospheric oxygen (*5*). Inferences as to the history of seawater sulfate accumulation ar based, primarily, on interpretations of th sulfur isotope record of ancient sedimentar sulfide minerals. This record shows sedimentary sulfides between 3.4 and 2.8 Ga wit isotopic compositions of ±5 per mil (‰ around a contemporaneous seawater sulfat isotopic composition [$\delta^{34}S$ (*6*)] of 2 to 3% (*7*). The principal feature of this record is th small isotope difference between seawate sulfate and sedimentary sulfides.

The interpretation of this record is based o our understanding of the factors controlling isotope fractionation during sulfate reduction b sulfate-reducing bacteria. These bacteria are responsible for most of the sulfide formed i modern marine sediments. There is a tendenc for pure cultures of sulfate-reducing bacteria t fractionate less as specific rates (rate per cell) o sulfate reduction increase (*8*). Increasing temperature can lead to higher specific rates fo individual species of sulfate reducers, anc therefore, lower fractionations might be expected at higher temperatures. Thus, minimally fractionated early Archean sedimentary sulfide may have formed at rapid rates of sulfate reduction in a warm, sulfate-rich (10 to 28 mM) ocea (*3*, *9*), providing support for high early Archea atmospheric oxygen concentrations (*3*, *9*).

This ocean model requires extensions o relations between specific rates of sulfate reduction, temperature, and isotope fractionation beyond current observations. Thus, fo *Desulfovibrio desulfuricans*, the most studie sulfate-reducing bacterium, fractionations o 10 to 26‰ are observed at 40° to 45°C, th upper temperature limit for the survival of th organism, where specific rates of sulfate reduc

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tion are also the highest (*8*). These fractionations are too large to explain the small fractionations preserved in the early Archean isotope record (*7*). Therefore, we explored the relation between temperature and isotope fractionation for natural populations of sulfate-reducing bacteria metabolizing at temperatures >45°C. For these experiments, we used sediment collected by the deep-sea submersible *Alvin* from an active hydrothermal vent area in the Guaymas Basin, Gulf of California (*10*). At the sampling location, sediment temperatures increased from 2.8°C at the sediment surface to 100°C by 15- to 20-cm depth. Sediment was sectioned into depth intervals with measured in situ temperatures of 50° to 60°C and 70° to 90°C. Sediment sections were subsequently incubated, intact, in flow-through reactors with lactate, ethanol, or acetate as substrates for sulfate-reducing bacteria and with sulfate concentrations of 2, 5, and 28 mM (*11*). Incubations were conducted at temperatures within the in situ range for each section, with organic substrates supplied both in excess (nonlimiting) and in concentrations limiting sulfate reduction rate.

We report the highest temperatures to which isotope fractionation during sulfate reduction has been measured and see fractionations of 13 to 28‰, at temperatures up to 85°C (Fig. 1A) (*12*). These high fractionations were independent of sulfate concentration between 2 and 28 mM and were observed both when organic substrate was limiting in concentration, suppressing microbial activity, and when it was nonlimiting. Specific rates of sulfate reduction could not be measured in these experiments, although the highest specific rates would be expected when organic matter was nonlimiting. Indeed, we measured the highest volume-based rates under these conditions (Fig. 1B). Our natural population fractionation results provide no support for reduced fractionations at temperatures above 40° to 45°C (*13*).

Although we could not measure specific rates of sulfate reduction in our experiments, pure cultures of sulfate-reducing bacteria metabolizing between −1.7° and 80°C, including organisms with different temperature adaptations (*14*) (Fig. 2), show little systematic variation in specific rates of sulfate reduction with temperature. There appear to be upper limits on specific rates of sulfate reduction in nature, and these limits should constrain the extent to which high specific rates can limit isotope fractionation. Thus, although correlations between specific rate of sulfate reduction, temperature, and fractionation might hold for individual organisms (*15*), these correlations cannot be projected beyond the temperature range of the organism.

High rates of sedimentary sulfate reduction (rate per volume of sediment) are a key feature of the warm, sulfate-rich, early Archean ocean model, resulting in complete sulfate depletion near the sediment-water interface and produc-

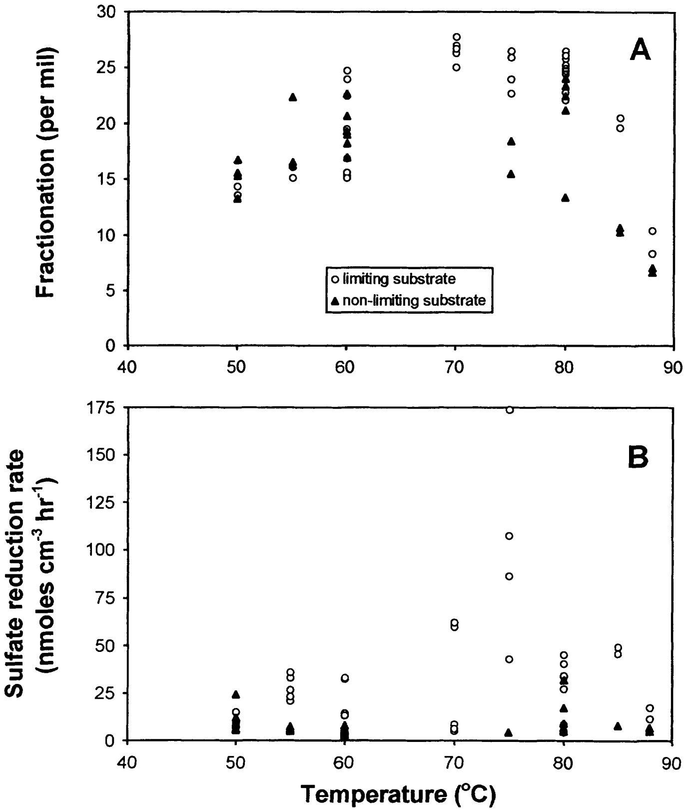

Fig. 1. (**A**) Isotope fractionation is shown during sulfate reduction by mixed populations of sulfate-reducing bacteria metabolizing on ethanol, lactate, and acetate, under both limiting and nonlimiting substrate conditions with artificial seawater containing 2, 5, and 28 mM sulfate. Under limiting substrate conditions, all, or nearly all, of the substrate was used within the flow-through reactor. Under nonlimiting conditions, only a portion of the substrate was used, and considerable excess substrate exited the reactor. Isotope fractionation was calculated relative to the isotopic composition of the input sulfate, with a small correction for sulfate depletion within the reactor with a Rayleigh distillation model. No systematic differences in fractionation were observed between the substrates used or with sulfate between 2 and 28 mM, and, therefore, these data have not been indicated separately [data are available at *Science* Online (*29*)]. (**B**) Rates of sulfate reduction within the flow-through reactors are shown. Rates were measured with both limiting and nonlimiting substrate and are shown separately.

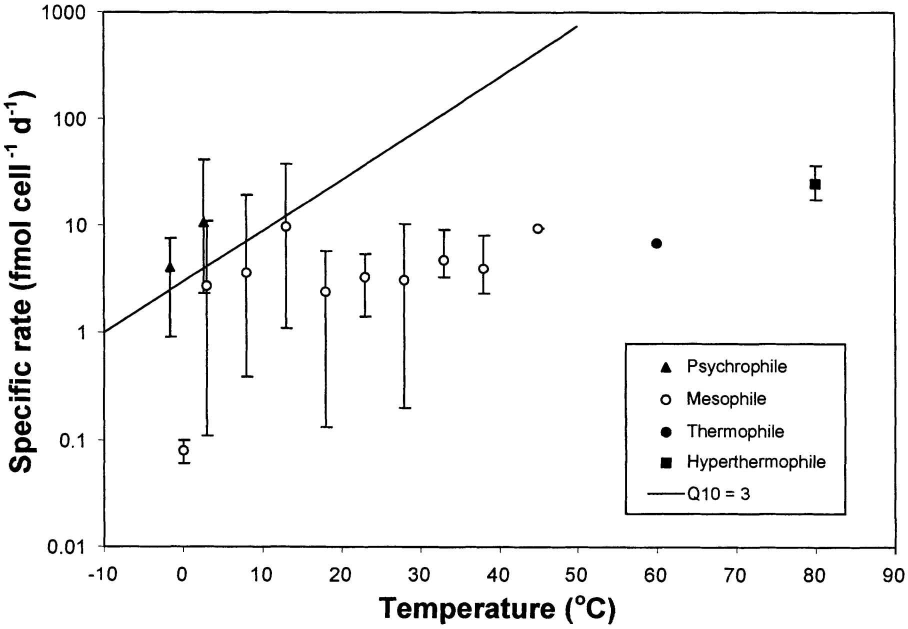

Fig. 2. Specific rates of sulfate reduction (rate per cell) are compiled here for a wide range of sulfate-reducing bacteria with different temperature adaptations (*14*). Specific rates were binned into 5°C intervals. Vertical lines indicate the full range of measured rates, and the average rate is provided by the symbol. Experiments reporting specific rates were conducted under both optimal and suboptimal conditions for bacterial growth. Therefore, the range of specific rates encountered here may reasonably reflect the range of specific rates that might be encountered in nature. Data come from (*8, 30, 31*). The specific rates reported at 80°C were determined in chemostat experiments on the Archaeal sulfate reducer *Archaeoglobus fulgidus* as part of this study. Shown for comparison is the increase in specific rates predicted if organisms responded across different temperature adaptations with a $Q_{10} = 3$, a value typical for sulfate-reducing bacteria (*14*).

ing a sediment closed to sulfate exchange (*3*, *9*). A closed system could explain the generally small 2 to 3‰ differences between the average isotopic composition of sulfides, and of contemporaneous seawater sulfate, in early Archean sediments (*16*). We used a diffusion-reaction diagenetic model to explore the relation between sulfate reduction rates and sulfate depletion in an hypothetical early Archean sediment. We assumed a flux of metabolizable organic carbon (0.5 mmol cm^{-2} year^{-1}) and sediment deposition rate (0.1 cm year^{-1}) comparable to active modern shelf sediments (*17*) and a sulfate concentration of 28 mM, the same as today. The model (*18*) was started with sulfate reduction rates comparable to active modern shelf sediments and produced a sulfate profile also similar to modern shelf sediments (Fig. 3A). With increasing rates of sulfate reduction, more rapid depletion of organic matter occurs near the sediment surface and, consequently, leads to more vigorous near-surface sulfate consumption (Fig. 3, B and C). The result is less active sulfate reduction and minimal sulfate depletion deeper in the sediment.

The organic carbon flux was doubled, retaining the high intrinsic organic matter reactivity in Fig. 3C, and still, even with these higher sulfate reduction rates (Fig. 3D) (*19*), only limited sulfate depletion was observed. The highest rates of sulfate reduction explored here (30 mol liter^{-1} year^{-1}; Fig. 3D) are higher than any modern measurements and are comparable to proposed early Archean rates (10 to 100 mol liter^{-1} year^{-1}) (*3*, *9*). We show here, however, that such high rates are associated with rapid organic matter consumption and, therefore, attenuate quickly with sediment depth. Importantly, and counter to predictions, increasing rates of sulfate reduction do not result in closed-system behavior.

Overall, rapid rates of sulfate reduction, with abundant sulfate and at elevated temperatures up to 85°C, should produce sedimentary sulfides depleted in ^{34}S by about 13 to 28‰ compared with seawater sulfate. We have previously shown that modern microbial mats, supporting very high rates of sulfate reduction (up to 15 mol liter^{-1} year^{-1}), produce sulfide depleted in ^{34}S by 20 to 40‰ at temperatures from 10° to 30°C (*20*). These high fractionations are preserved as pyrite in the mats (*21*). Therefore, at high and low temperatures, high fractionations are expected during sulfate reduction with abundant sulfate. The minimally fractionated early Archean sedimentary sulfides are most consistent with either sulfate reduction at low sulfate concentrations of <1 mM (*22*), where isotope fractionation during sulfate reduction is greatly reduced (*23*), or a nonbiogenic source of sulfide, if sulfate-reducing bacteria had not yet evolved. As sulfate-reducing bacteria likely evolved before cyanobacteria (*24*), a low oxygen atmosphere is consistent with both of these scenarios.

By 2.75 Ga, sedimentary sulfides with δ^{34}S values as low as -18‰ are found (*25*, *26*). Although some of these sulfides are volcanogenic (*25*), in other instances, a bacteriagenic source is possible (*26*). By 2.75 Ga, therefore, sulfate reduction may have been well established, but only locally expressed [probably in restricted sulfate-rich environments (*25*)], as evidenced by the general lack of ^{34}S-depleted sulfides in organic matter–containing shales of this age (*25*). By 2.2 to 2.3 Ga, ^{34}S-depleted sulfides of certain biological origin and reflecting generally abundant seawater sulfate concentrations of 1 mM or greater become a continuous feature of the geologic record (*7*, *27*). Independent lines of geochemical evidence point to the first accumulation of oxygen into the atmosphere around this time (*2*).

Organic biomarker (*28*) and organic carbon stable isotope evidence (*7*) support the evolution of oxygenic photosynthesis by 2.7 Ga. There existed on Earth, therefore, a protracted period of at least 400 to 500 million years, from >2.7 Ga to 2.2 to 2.3 Ga, where biological oxygen production resulted in little net oxidation of Earth's surface. It appears that the evolution of metabolic innovations such as oxygenic photosynthesis and sulfate reduction is separated in time from their geochemical expression. This separation in time complicates our attempts to pace the timing of metabolic evolution and underscores the importance of elucidating the poorly understood biogeochemical mechanisms regulating Earth's surface chemistry.

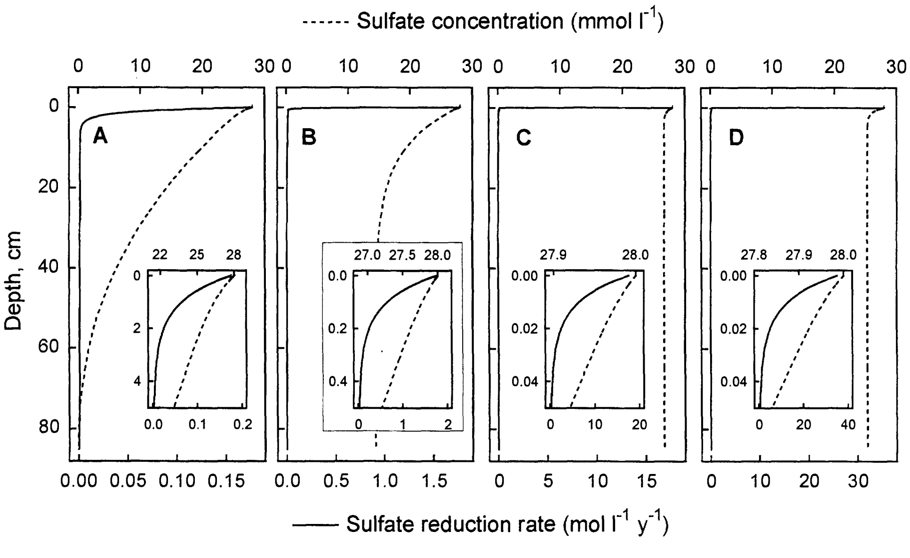

Fig. 3. Modeled depth distributions of sulfate reduction rate and sulfate concentration are shown for a hypothetical early Archean sediment. In the first three cases (**A** to **C**), the same flux of metabolizable carbon (0.5 mmol cm^{-2} year^{-1}) to the sediment surface is used, comparable to active modern shelf sediments (see text). This flux of organic carbon is equivalent to a reactive carbon concentration of 10 weight % (wt %) (about 25% organic matter) at the sediment deposition rate (0.1 cm year^{-1}) used in our calculations. Rates of sulfate reduction are increased (A to C) in one order of magnitude steps by increasing the reactivity of the organic carbon decomposing [the value of the rate constant k_i (*18*)]. For (A), $k_1 = 0.1$ year^{-1} and $k_2 = 0.001$ year^{-1}; for (B), $k_1 = 1.0$ year^{-1} and $k_2 = 0.01$ year^{-1}; and for (C), $k_1 = 10$ year^{-1} and $k_2 = 0.1$ year^{-1}. In the final case (**D**), the flux of metabolizable carbon (and concentration of reactive carbon; 20 wt %) is doubled from the other three examples, whereas the same high rate constants used in case (C) are retained. The insets provide an expanded view of the upper portions of the sediment column.

References and Notes

1. R. M. Garrels and E. A. Perry, in *The Sea*, E. D. Goldberg, Ed. (Wiley-Interscience, New York, 1974), pp. 303–316.
2. H. D. Holland, in *Early Life on Earth*, S. Bengtson, Ed. (Columbia Univ. Press, New York, 1995), pp. 237–244; *Geochem. News* **100**, 20 (1999).
3. H. Ohmoto, T. Kakegawa, D. R. Lowe, *Science* **262**, 555 (1993); H. Ohmoto, *Geochem. News* **93**, 12 (1997).
4. L. V. Berkner and L. C. Marshall, *J. Atmos. Res.* **22**, 225 (1965); A. H. Knoll, in *Origin and Early Evolution to the Metazoa*, J. H. Lipps and D. W. Signor, Eds. (Plenum, New York, 1992), pp. 53–84; D. E. Canfield and A. Teske, *Nature* **382**, 127 (1996).
5. Levels of atmospheric oxygen exert a primary control on the input rate of sulfate to the oceans; sulfide will be recycled and not oxidized during weathering if oxygen is sufficiently low [B. Rasmussen and R. Buick, *Geology* **27**, 115 (1999)]. The oxygen level necessary for substantial pyrite (FeS_2) weathering to sulfate can be approximated from the kinetics of the reaction between pyrite and oxygen [M. A. Williamson and J. D. Rimstidt, *Geochim. Cosmochim. Acta* **58**, 5443 (1994)]. About 5000 years are required to oxidize a 100-μm pyrite grain in an aqueous solution of low ionic strength, pH of 5 (the calculation is not very sensitive to pH), 25°C, and with 1 μM of oxygen. Soils typically range from 3000 to 100,000 years in age [W. H. Schlesinger, *Nature* **348**, 232 (1990); P. W. Birklund, *Pedology, Weathering, and Geomorphological Research* (Oxford Univ. Press, Oxford, 1974)]. Therefore, with 1 μM oxygen, sufficient time should be available during weathering for substantial pyrite oxidation, leading to the accumulation of sulfate into the oceans. An oxygen concentration of 1 μM is about 0.4% of the present-day, air-saturated concentration of 260 μM at 25°C in fresh water.
6. δ^{34}S refers to the isotopic composition of sulfur species

expressed as ‰ (parts per thousand) deviation from the Canyon Diablo Troilite (CDT) standard and given by $10^3[(^{34}S/^{32}S)_{sam} - (^{34}S/^{32}S)_{CDT}]/(^{34}S/^{32}S)_{CDT}$.

7. J. M. Hayes, in *Earth's Earliest Biosphere, Its Origin and Evolution*, J. W. Schopf, Ed. (Princeton Univ. Press, Princeton, NJ, 1983), pp. 291–301; D. E. Canfield, *Nature* **396**, 450 (1998).
8. I. R. Kaplan and S. C. Rittenberg, *J. Gen. Microbiol.* **34**, 195 (1964); L. A. Chambers, P. A. Trudinger, J. W. Smith, M. S. Burns, *Can. J. Microbiol.* **21**, 1602 (1975).
9. H. Ohmoto and R. P. Felder, *Nature* **328**, 244 (1987); T. Kakegawa, H. Kawai, H. Ohmoto, *Geochim. Cosmochim. Acta* **62**, 3205 (1998).
10. J. B. Corliss *et al.*, *Science* **203**, 1073 (1979).
11. A. N. Roychoudhury, E. Viollier, P. Van Cappellen, *Appl. Geochem.* **13**, 269 (1998).
12. At 88°C, a large decrease in fractionation was observed with both limiting and nonlimiting substrate (Fig. 1A). This decrease was accompanied by a decrease in sulfate reduction rate (Fig. 1B), and we speculate that this high temperature approached the upper limit for growth by the sulfate-reducing population. Reduced fractionations are sometimes observed when organisms metabolize considerably outside of their optimal growth range (*8*), perhaps as a result of physiological stress on the organism.
13. The actual isotopic composition of Guaymas Basin sedimentary sulfides has yet to be reported, but a substantial mantle-derived hydrothermal source of sulfide could overprint biological fractionations from sulfate reduction [J. M. Peter and W. C. Shanks III, *Geochim. Cosmochim. Acta* **56**, 1025 (1992)].
14. On the basis of the temperature of maximum growth rate, organisms may be broadly classified into four major groups. Psychrophiles are organisms with growth optima below 20°C, and some may grow below the freezing point of water [R. M. Atlas and R. Bartha, *Microbial Ecology: Fundamentals and Applications* (Addison Wesley Longman, Menlo Park, CA, 1998), pp. 281–331]. Mesophiles have growth optima in the range of 20° to 45°C, thermophiles have their growth optima between 45° and 75°C, and hyperthermophiles have growth optima from 80° to 115°C (thus far, higher temperatures for metabolism are not known). For all organisms, growth rates are reduced at temperatures on either side of the optimal growth temperature. The highest specific rates of metabolism are generally found above the growth optima and, in some cases, even at temperatures above those where growth occurs (*30*). Continued metabolism at high rates above the maximum temperature for growth will result in mortality of the population. For sulfate-reducing bacteria metabolizing below the temperature of maximum specific rate, a 10°C increase in temperature causes an increase in rate of, typically, two to four times [J. T. Westrich and R. A. Berner, *Geomicrobiol. J.* **6**, 99 (1988)]. This rate of increase is known as the Q_{10}.
15. Factors other than specific rate of sulfate reduction can also influence isotope fractionation, including electron donor [H_2 produces reduced fractionations compared with organic substrates (*8*)] and physiological state of the organism (*12*). Furthermore, interspecies differences in isotope fractionation are possible, but as yet poorly explored.
16. The isotopic composition of sulfide in a closed system will match the isotopic composition of the original sulfate after sulfate depletion, regardless of the fractionation.
17. J. J. Middelburg, K. Soetaert, P. M. J. Herman, *Deep Sea Res. I* **44**, 327 (1997).
18. Our model assumes two types of organic carbon depositing to the sediment surface at equal concentrations and decomposing by sulfate reduction with first-order kinetics: $dC_i/dt = -k_iC_i$. In this expression, C_i represents the concentration of organic carbon of one type, t is time, and k_i is the intrinsic rate constant defining the reactivity of the organic carbon. We assume that the reactivity (k_i) of each of the two organic carbon fractions varies by two orders of magnitude, consistent with sediment observations [C. Rabouille, J.-F. Gaillard, J.-C. Relexans, P. Tréguer, M.-A Vincendeau, *Limnol. Oceanogr.* **43**, 420 (1998)]. We changed rates of sulfate reduction by changing the k_i values and solved the model analytically ("Modified Berner" model of B. P. Boudreau and J. T. Westrich [*Geochim. Cosmochim Acta* **48**, 2503 (1984)]).
19. Considerably higher fluxes of organic carbon to early Archean sediments would have required higher ocean nutrient concentrations and more active nutrient cycling, leading to much higher rates of photosynthetic primary production. We are unaware of any data supporting such high rates of carbon production and remineralization in the early Archean.
20. K. S. Habicht and D. E. Canfield, *Nature* **382**, 342 (1996).
21. ———, *Geochim. Cosmochim. Acta* **61**, 5351 (1997). High fractionations (25 to 30‰) are also preserved in rapidly depositing continental margin sediments experiencing relatively rapid rates of sulfate reduction (up to 0.5 mol liter^{-1} year^{-1}) and with sulfate depletion at the shallow depth of 10 to 20 cm [J. P. Chanton, C. S. Martens, M. B. Goldhaber, *Geochim. Cosmochim. Acta* **51**, 1201 (1987); J. Val Klump and C. S. Martens, *Geochim. Cosmochim. Acta* **51**, 1161 (1987)].
22. A sulfate level of around 2.0 mM has been suggested for 3.2-Ga seawater from the analysis of fluid inclusions within quartz veinlets and vugs dispersed within ironstone pods believed to be precipitated in a sea floor hydrothermal vent setting [C. E. J. de Ronde, D. M. deR. Channer, K. Faure, C. J. Bray, E. T. C. Spooner, *Geochim Cosmochim. Acta* **61**, 4025 (1997)]. Although this is a low concentration compared with modern seawater, our results support even lower Archean seawater sulfate concentrations.
23. A. G. Harrison and H. G. Thode, *Trans. Faraday Soc.* **53**, 84 (1958).
24. Phylogenies constructed from sequence comparisons of the 16S ribosomal RNA molecule show thermophilic sulfate-reducing bacteria of the genus *Thermodesulfobacterium* branching more deeply within the Bacterial domain than the lineage housing Cyanobacteria [E. Stackebrandt, D. A. Stahl, R. Devereux, in *Sulfate-Reducing Bacteria*, L. L. Barton, Ed. (Plenum, New York, 1995), pp. 49–87; N. R. Pace, *Science* **276**, 734 (1997)]. This observation supports an early evolution of sulfate-reducing bacteria, predating the evolution of oxygen-producing Cyanobacteria.
25. E. M. Cameron and K. Hattori, *Chem. Geol.* **65**, 341 (1987).
26. A. M. Goodwin, J. Monster, H. G. Thode, *Econ. Geol.* **71**, 870 (1976); H. G. Thode and A. M. Goodwin, *Precambrian Res.* **20**, 337 (1983).
27. A. H. Knoll and D. E. Canfield, in *Isotope Paleobiology and Paleoecology*, R. N. Norris and R. M. Corfield, Eds. (Paleontological Society, Pittsburgh, PA, 1998), pp. 212–243; D. E. Canfield and R. Raiswell, *Am. J. Sci.* **299**, 697 (1999); E. M. Cameron, *Nature* **296**, 145 (1982).
28. J. J. Brocks, G. A. Logan, R. Buick, R. E. Summons, *Science* **285**, 1033 (1999).
29. Supplemental data are available at www.sciencemag.org/feature/data/1048533.shl.
30. C. Knoblauch, B. B. Jørgensen, J. Harder, *Appl. Environ. Microbiol.* **65**, 4230 (1999).
31. M. E. Böttcher, S. M. Sievert, J. Kuever, *Arch. Microbiol.* **172**, 125 (1999).

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Heightened Odds of Large Earthquakes Near Istanbul: An Interaction-Based Probability Calculation

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We calculate the probability of strong shaking in Istanbul, an urban center of 10 million people, from the description of earthquakes on the North Anatolian fault system in the Marmara Sea during the past 500 years and test the resulting catalog against the frequency of damage in Istanbul during the preceding millennium. Departing from current practice, we include the time-dependent effect of stress transferred by the 1999 moment magnitude $\mathbf{M} = 7.4$ Izmit earthquake to faults nearer to Istanbul. We find a 62 ± 15% probability (one standard deviation) of strong shaking during the next 30 years and 32 ± 12% during the next decade.

The 17 August 1999 $\mathbf{M} = 7.1$ Izmit and 12 November 1999 $\mathbf{M} = 7.1$ Düzce earthquakes killed 18,000 people, destroyed 15,400 buildings, and caused $10 billion to $25 billion in damage. But the Izmit event is only the most recent in a largely westward progression of seven large earthquakes along the North Anatolian fault since 1939. Just northwest of the region strongly shaken in 1999 lies Istanbul, a rapidly growing city which has been heavily damaged by earthquakes 12 times during the past 15 centuries. Here, we calculate the probability of future earthquake shaking in Istanbul, using new concepts of earthquake interaction, in which the long-term renewal of stress on faults is perturbed by transfer of stress from nearby events.

Stress triggering has been invoked to explain the 60-year sequence of earthquakes rupturing

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