

Alternating Si and Fe deposition caused by temperature fluctuations in Precambrian oceans

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Precambrian banded iron formations provide an extensive archive of pivotal environmental changes and the evolution of biological processes on early Earth. The formations are characterized by bands ranging from micrometre- to metre-scale layers of alternating iron- and silica-rich minerals. However, the nature of the mechanisms of layer formation is unknown. To properly evaluate this archive, the physical, chemical and/or biological triggers for the deposition of both the iron- and silica-rich layers, and crucially their alternate banding, must be identified. Here we use laboratory experiments and geochemical modelling to study the potential for a microbial mechanism in the formation of alternating iron–silica bands. We find that the rate of biogenic iron(III) mineral formation by iron-oxidizing microbes reaches a maximum between 20 and 25 °C. Decreasing or increasing water temperatures slow microbial iron mineral formation while promoting abiotic silica precipitation. We suggest that natural fluctuations in the temperature of the ocean photic zone during the period when banded iron formations were deposited could have led to the primary layering observed in these formations by successive cycles of microbially catalysed iron(III) mineral deposition and abiotic silica precipitation.

Banded iron formations (BIFs) are sedimentary rocks of alternating iron-rich (haematite, magnetite and siderite) and silicate/carbonate (chert, jasper, dolomite and ankerite) layers that were deposited between 3.6 and 2.2 billion years (Gyr) ago^{1,2}. The layers vary from the microscale (micrometres in thickness) that we focus on here, to metre-thick units³. Some deposits, such as in the 2.5-Gyr-old Dales Gorge Member, Hamersley Group, Western Australia, show laterally contiguous layers up to a hundred kilometres in distance¹, suggesting that BIFs were formed uniformly over vast depositional areas tens of thousands of square kilometres in size⁴. The layering in BIFs has been attributed to seasonal or decadal episodic hydrothermal pulsation and/or upwelling of anoxic, Fe-rich waters (roughly 0.02–0.5 mM dissolved Fe(II)) (refs 5,6) into semi-restricted basins already saturated with dissolved silica⁷.

Three main models have been proposed for Fe(II) oxidation and precipitation of the Fe(III) in BIFs. The most widely accepted of these is predicated on the presence of ancient cyanobacteria⁸, the metabolism of which would have produced oxygen that chemically reacted with dissolved Fe(II) and thus precipitated ferric hydroxide, Fe(OH)₃. Although this is the likely mechanism after ~2.5 Gyr ago, a period named the Great Oxidation Event, abundant evidence for an anoxic Archaean era, for example, ref. 9, makes it necessary to consider mechanisms of Fe(III) mineral precipitation in the absence of oxygen. One such anoxic mechanism is ultraviolet-light-driven photo-oxidation of Fe²⁺ and Fe(OH)⁺ (ref. 10). However, a recent study designed to test this mechanism in fluids mimicking the Archaean ocean and containing high concentrations of dissolved Fe(II), silica and HCO₃⁻ demonstrated that the oxidative effects of ultraviolet A or ultraviolet C were negligible¹¹. Similarly, nitrate has been proposed

as an oxidant¹²; detailed studies supporting this mechanism have not yet been conducted. In contrast, another O₂-free oxidation mechanism, the direct microbial precipitation of ferric iron through anoxygenic photosynthesis (photoferrotrophy), is bolstered by the isolation of modern analogue marine and freshwater anoxygenic Fe(II)-oxidizing phototrophs (for example, *Rhodobacter ferrooxidans* sp. strain SW2 (ref. 13), *Chlorobium ferrooxidans* sp. strain KoFox¹⁴, *Rhodovulum iodolum* and *Rhodovulum robiginosum*¹⁵).

Models based on the Fe(II) oxidation rates of these strains under varying environmental conditions demonstrate the plausibility of photoferrotrophy as a means for primary BIF precipitation^{16–18}. Indeed, the ferric iron minerals these strains produce are consistent with the Fe(III) precipitates probably sedimented as primary BIF minerals^{13,19,20}. In particular, photoferrotrophs produce poorly crystalline ferric minerals, which carry a net positive charge¹⁹. Such biogenic minerals are expected to bind to organic carbon (cells), with the net effect being the deposition of cell–mineral aggregates to the sea floor. Once buried, metabolically driven diagenetic reactions and later-stage metamorphism would then transform the aggregates: ferric hydroxide would either dehydrate to haematite (Fe₂O₃) or be reduced to magnetite (Fe₃O₄) and/or siderite (FeCO₃), whereas organic carbon would be oxidized to CO₂. These reactions have been used to explain the lack of organic carbon now present in BIFs²¹, the isotopic composition of the secondary minerals^{22,23}, as well as the main Fe-mineral components of BIFs (ref. 20).

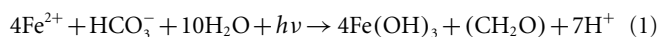
Critical to the argument for ancient photoferrotrophy is evidence of these bacteria in the Archaean, probably as forerunners to oxygenic photosynthesis. First, molecular

phylogenetic analysis of a number of enzymes involved in (bacterio-) chlorophyll biosynthesis suggests that anoxygenic photosynthetic lineages are almost certain to be more deeply rooted than the oxygenic cyanobacterial lineages²⁴. Second, recent studies that indicate anoxygenic phototrophs represent a considerable fraction of biomass in modern stromatolite communities²⁵ and the construction of stromatolite-like structures with the anoxygenic phototroph *Rhodospseudomonas palustris*²⁶ challenge the notion that stromatolites strictly mark cyanobacterial presence in the geologic record. Third, unique biomarkers for anoxygenic phototrophs, remnants of specific light-harvesting pigments, have recently been found in Palaeoproterozoic strata²⁷, offering intriguing evidence for their presence on the ancient Earth. Moreover, 2-methylbacteriohopane-polyol molecules, previously interpreted as exclusive biomarkers for cyanobacteria, have also been identified in significant quantities in modern anoxygenic phototrophic Fe(II)-oxidizers²⁸, making the case for Fe(II)-oxidizing phototrophs at 2.7 Gyr ago just as plausible as that for H₂O-oxidizing cyanobacteria.

Despite the recent advances in linking ancient anoxygenic phototrophic Fe(II) oxidation to BIF precipitation, a satisfactory explanation of how primary iron and silicate mineral can precipitate independently over large areas with some regularity is still lacking in biological models. Here, we put forth the first model showing how cyclic fluctuations in photic-zone seawater temperature link the microbial deposition of Fe(III) hydroxide (through anoxygenic photo-oxidation) to abiotic silica precipitation, and explain how this interplay of biotic and abiotic processes could result in BIF layering.

TEMPERATURE DEPENDENCE OF PHOTOTROPHIC Fe(II) OXIDATION

Several extant strains of anoxygenic Fe(II)-oxidizing phototrophs use light energy to catalyse the oxidation of Fe(II) and the reduction of CO₂, which yields biomass and ferric hydroxide as shown in equation (1).



To determine the potential habitat of anoxygenic phototrophs in the Archaean ocean, we tested the eco-physiological limits of representative strains from each of the three major phylogenetic branches—the purple sulphur bacterium *Thiodictyon* sp. strain F4; the purple non-sulphur bacterium, *Rhodobacter ferrooxidans* sp. strain SW2; and the green sulphur bacterium, *Chlorobium ferrooxidans* sp. strain KoFox. We determined the Fe(II) oxidation rates of these strains under varying conditions of temperature and presence of silica (Fig. 1a,b; Supplementary Information, Fig. S1).

The optimal temperature range of phototrophic Fe(II) oxidation is typical of mesophiles: from 5 to 35°C, with a slow decrease in rate at lower temperatures and a strict upper temperature limit (Fig. 1a). The pattern shown here for strain SW2 is representative of both strains F4 and KoFox (Fig. 2a). The temperature dependence exhibited by our model strains suggests that ancient ocean temperature changes would have significantly affected the extent of phototrophic Fe(II) oxidation, and most importantly, the precipitation and deposition of primary ferric hydroxide.

Archaean ocean temperature is heavily debated, with estimates ranging from 10 to 85°C. Much of the disagreement rests on the interpretation of both O and Si isotope data^{29–34}, as well as on problems related to diagenetic overprinting of ancient rocks. The most recent interpretations, which suggest a temperate Archaean climate of 10–33°C, view the isotope data in terms of known constraints inferred from biological evolution³². Clearly, the

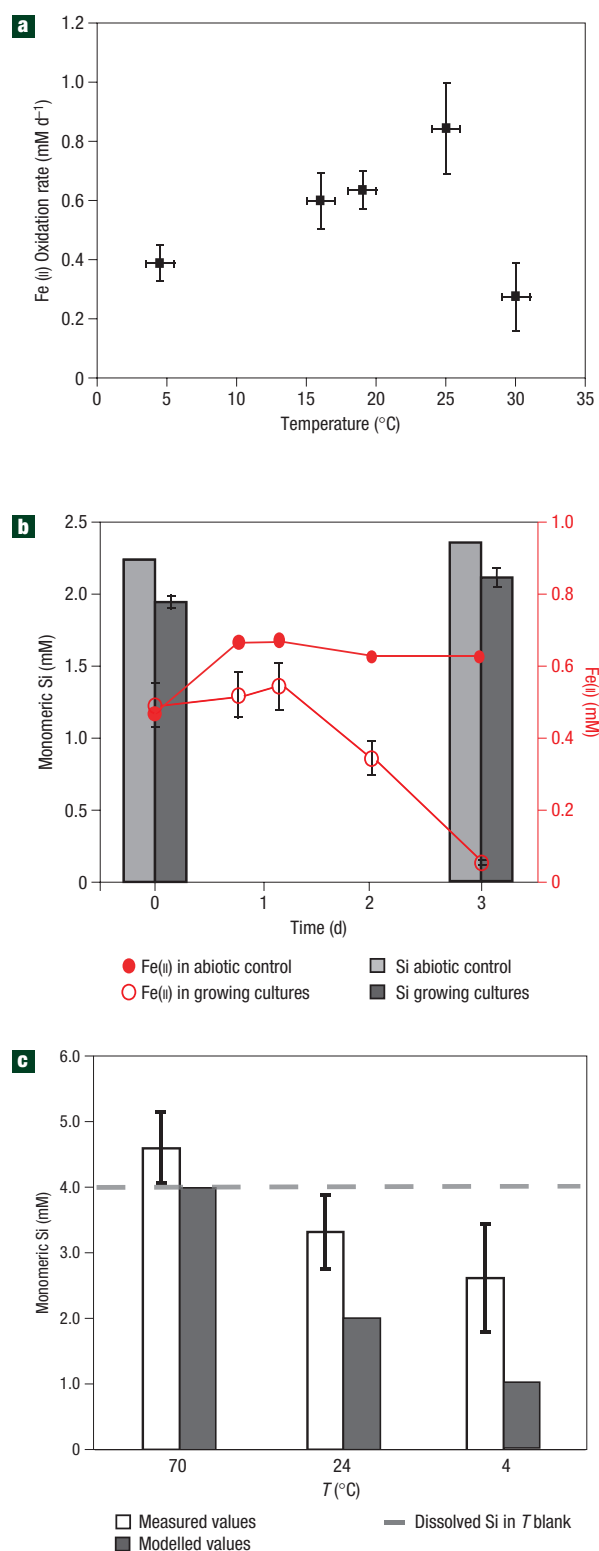


Figure 1 Temperature change drives both the biotic precipitation of Fe(III) minerals and the abiotic precipitation of silica. **a**, Dependence of *Rhodobacter ferrooxidans* sp. strain SW2 Fe(II) oxidation rates on temperature (4 mM dissolved Fe(II); 800 lux). **b**, Microbial oxidation of 0.5 mM Fe(II) by strain SW2 in the presence of 2.0 mM silica, at 75 lux. **c**, Temperature dependence of dissolved silica concentration in non-inoculated medium. Error bars depict standard deviation from the mean (triplicate experiments).

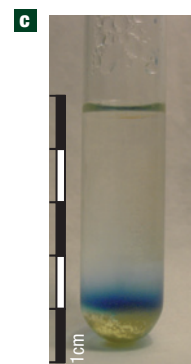
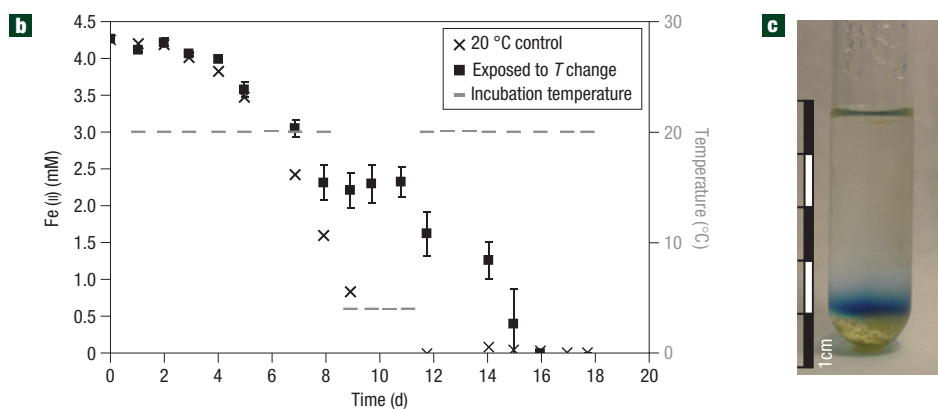
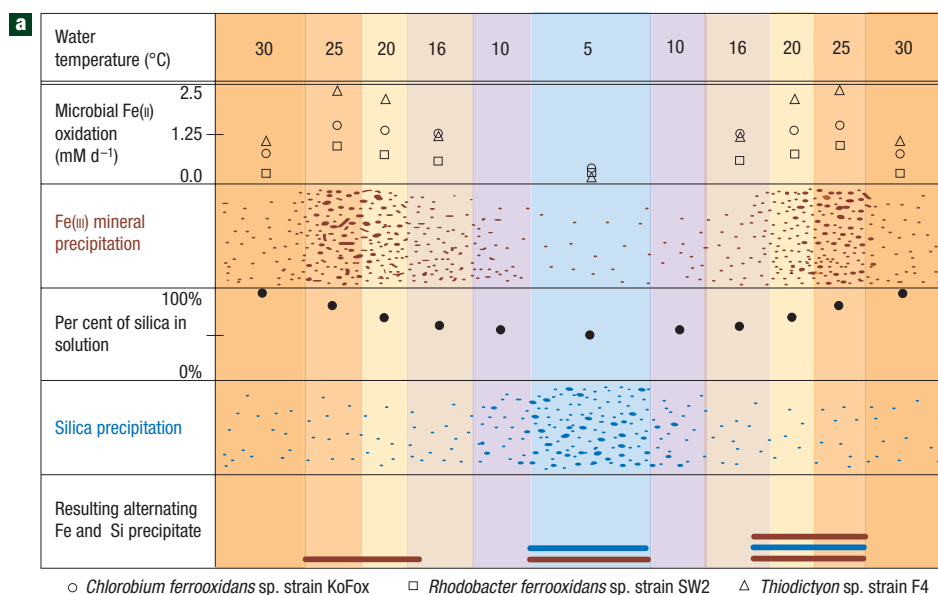


Figure 2 Possible deposition of alternating iron and silicate mineral layers in BIFs as triggered by temperature variations in ocean waters. **a**, Experimentally determined microbial Fe(II) oxidation rates at fluctuating temperature and the resulting Fe(III) mineral precipitation. The effect of temperature fluctuations between 5 and 30 °C on abiotic silica precipitation. **b**, Oxidation of dissolved Fe(II) by strain SW2 at changing temperatures and in a 20 °C control. Error bars depict standard deviation from the mean (triplicate experiments). **c**, Demonstration of microbial Fe(III) mineral precipitation in the presence of silica at 25 °C, and silica precipitation after temperature drop to 4 °C.

mesophilic photoferrotrophs used in this experiment would thrive in such an ocean.

As our study with the extant photoferrotrophs indicated that temperature fluctuations in the water column could control Fe(III) precipitation, we assessed the response of the model strains to extreme temperature fluctuation stress. We tested the Fe(II) oxidation capacity of *Rhodobacter ferrooxidans* sp. strain SW2 throughout a temperature cycle (Fig. 2b; Supplementary Information, Fig. S2). At first, all cultures of strain SW2 were incubated at the temperature optimum of 25 °C and 4 mM dissolved Fe(II). In one experiment, the cultures were transferred to 4 °C for 3 days after the commencement of Fe(II) oxidation. Thereafter, they were returned to 25 °C. At 4 °C, Fe(II) oxidation and Fe(III) mineral precipitation ceased (Fig. 2b). After being returned to 25 °C, bacterially mediated Fe(III) mineral precipitation continued at the same Fe(II) oxidation rate as before the temperature drop. This pattern of growth effectively shows

how such strains could survive a large temperature drop in ocean waters. A second experiment exposed the bacteria to a temperature increase from 24 to 55 °C to mimic what might occur if the depositional waters were subjected to input of hydrothermal fluids from shallow seamount-type systems, as recently proposed by Konhauser *et al.*³⁵. In this experiment, Fe(II) oxidation continued during the temperature increase, but ceased after the bacteria were returned to 25 °C after three days (see Supplementary Information, Fig. S2). This confirmed the results of the temperature-dependence studies (Fig. 1a); the anoxygenic phototrophic Fe(II)-oxidizers known so far cannot survive a prolonged temperature stress up to 55 °C. As no thermophilic photoferrotrophs capable of survival at higher temperatures have been isolated to date, the survival of a photoferrotroph in an Archaean ocean after a temporary large upward temperature shift would depend on its ability to move deeper into cooler parts of the water column. In fact, one of the phototrophic Fe(II)-oxidizers, *Chlorobium ferrooxidans* strain

KoFox, exhibits full Fe(II) oxidation capacity even at very low-light regimes (<50 lux)¹⁸.

CONTROLS ON Si MINERAL DEPOSITION

In an Archaean ocean devoid of silica-secreting eukaryotic species (for example, diatoms, radiolarians), evaporation and/or surface water temperature changes may have been the dominant processes leading to silica supersaturation and abiogenic silica precipitation⁷.

Most BIF depositional models agree that amorphous silica initially precipitated from the water column and later transformed into chert with burial^{7,36}. Of interest to the investigation of BIFs is the behaviour of dissolved silica in cooling Archaean waters. We considered 70 °C as the maximum theoretical temperature from which cooling began^{29,31}. The effect of temperature change on silica solubility both in microbial growth medium and in ocean water was modelled using Geochemist's Workbench 6.0 (Fig. 1c; Supplementary Information, Fig. S3). Abiotic laboratory experiments tested this model in cooling growth medium sampled at 70, 24 and 4 °C (Fig. 1c). As expected, both laboratory experiments and geochemical modelling demonstrated that a drop in temperature triggers the precipitation of silica in a salt solution from 4.6 mM monomeric silica measured in solution at 70 °C, to 3.3 mM at 24 °C and 2.6 mM at 4 °C. Regardless of whether decreasing temperature from 70 to 4 °C or from 24 to 4 °C, silica precipitates from solution (see Supplementary Information, Fig. S3).

LAYERING MODEL OF IRON AND SILICA MINERAL PRECIPITATION

On the basis of previous studies of Fe–silica mineral interactions³⁵, it would be assumed that ferric hydroxide–cell aggregates produced by photoferotrophs would bind any dissolved silica present and remove it from solution. However, experiments carried out in the presence of dissolved silica concentrations relevant for the Archaean ocean (2.0 mM) (ref. 37) showed that biological Fe(II) oxidation rates were unaffected by the presence of silica. Fe(III) minerals even seemed to precipitate separately from silica: *Rhodobacter ferrooxidans* strain SW2 oxidized 0.5 mM dissolved Fe(II) at rates of 0.19 mM Fe(II)/day, both in the absence and presence of 2.0 mM silica, respectively, but the silica remained largely in solution whereas the Fe(II) was oxidized and Fe(III) minerals precipitated (see Fig. 1b, and Supplementary Information, Figs S1,S4). Furthermore, the concentration of dissolved silica in solution at the end of Fe(II) oxidation was significantly lower in batch cultures containing abiotically formed minerals compared with biogenic Fe(III) minerals (see Supplementary Information, Fig. S5A).

Unlike abiotic oxidation experiments of SiO₂-containing solutions of dissolved Fe(II) that confirm the effect of silica sorption to ferric hydroxide in the absence of microbes (see Supplementary Information, Fig. S5B), it is possible that microbially formed ferric hydroxides carry a layer of cell-derived organic matter sorbed to their surfaces that hinders silica binding. Indeed, synchrotron-based X-ray spectroscopy and tomographic imaging of anoxygenic phototroph cultures, which oxidized Fe(II) in the absence and presence of 2.0 mM silica, shows the presence of cell–mineral aggregates at a distance from the amorphous silica (see Supplementary Information, Fig. S6A,B, respectively). Although the mechanism behind this phenomenon is not yet fully understood, it implies that biogenic ferric hydroxide produced by anoxygenic phototrophs is largely decoupled from silica in these systems. This decoupling is important because it suggests a mechanism by which the Fe-rich and silica-rich layers in BIFs were deposited separately, yet triggered by a uniting parameter.

We tested the effects of temperature changes as the uniting parameter of silica and Fe mineral precipitation in Archaean oceans using a combined experimental and modelling approach. Although reconstruction of Precambrian ocean temperature cycles from the BIF rock record is problematic, two lines of evidence suggest that ocean water temperatures fluctuated in the Precambrian period. First, in modern oceans, temperature fluctuations occur with incoming currents, as well as with seasonal variation (see Supplementary Information, Fig. S7). Second, models of the Earth obliquity through time suggest even a minimal tilt of the Earth axis could cause ocean temperature fluctuations³⁸. Given both these calculations of obliquity-driven temperature variations and modern oceans as an analogue, the photic zone of the Archaean BIF basins probably experienced temperature fluctuations of at least ±15 °C due to seasonal/climatic changes or incoming cooler currents³⁹.

Even if just the upper 50 m of the ocean experienced temperature fluctuations, phototrophic Fe(II) oxidation rates, and ferric hydroxide precipitation, would be highest at water temperatures optimal for the growth of the phototrophs (25–30 °C for the model strains) (Figs 1a, 2a). At temperatures above and below this range, precipitation of biogenic aggregates would decrease, and cease completely beyond the metabolic range (Fig. 2a). Owing to the decoupled precipitation of silica and biogenic ferric iron, silica would remain in solution in warm (25–35 °C) waters, whereas microbial Fe(II) oxidation would precipitate Fe(III) minerals. A drop in temperature, however, would trigger the precipitation of amorphous silica, whereas microbial populations would be incapable of oxidizing Fe(II) to Fe(III) to a significant extent (Fig. 2a). The significance of this mechanism is supported by the lack of psychrophilic, anoxygenic Fe(II)-oxidizing isolates so far. The diminished microbial Fe(II) oxidation rates sustained at low temperatures by the known strains could still result in silicate layers containing trace amounts of Fe(III) minerals. In fact, transitions between Fe mineral and silica layering (as described by Garrels⁴⁰) could also be explained by this microbial mechanism.

As temperatures gradually drop from the optimum for microbial Fe(II) oxidation, a broader transition would be formed as rates slowly decrease. We attempted to verify this model by laboratory experiments in which dissolved Fe(II) was oxidized by *Rhodobacter ferrooxidans* sp. strain SW2 in the presence of silica at 25 °C. After the completion of Fe(II) oxidation, the culture was placed at 4 °C for three days and subsequently stained with the silica stain, Molybdenum Blue (Fig. 2c), verifying the production of a silica layer above a Fe(III) mineral layer due to temperature drop. In contrast, as temperatures increase above 35 °C, the transition from the Fe mineral layer formed by microbial Fe(II) oxidation to the silica layer would be abrupt, owing to the strict upper temperature limit of the strains.

As described above, the model strains used in this study do not oxidize Fe(II) at high temperature. However, mesophiles in an Archaean ocean warming to temperatures higher than 35 °C would also produce alternating silica and Fe mineral layering through evaporation within a shallow-water depositional basin⁴⁰ when photoferotrophic mineral precipitation has stopped.

The present study was done with freshwater Fe(II)-oxidizing strains, yet similar oxidation rates observed for marine strains¹⁵ imply that these results are also representative for marine environments. In addition, the present study was carried out with pure strains, and cannot model natural community dynamics. A microbial community of Fe(II)-oxidizing phototrophs would potentially have members that oxidize over a broad temperature range with specific optimal temperatures from each strain. When the ocean temperature deviates from optimum, the

microbes will either decrease their rates of Fe(II) oxidation, or move to a more desirable location in the water column. This dynamic could result in mixed precipitation of Fe/Si, potentially even explaining the fine-scaled variation observed in BIFs.

Although a microbial role in the primary deposition of BIFs has been suggested in past models, we have for the first time described how climatic changes or incoming cooler currents in an Archaean basin inhabited by anoxygenic Fe(II)-oxidizing phototrophs is a uniform trigger that links the initial precipitation of iron and silica minerals, and offers a plausible explanation for the alternating nature of BIF deposits.

METHODS

The model organism *Rhodobacter ferrooxidans* sp. strain SW2 was isolated from a pond in Schaumburger Wald, Hannover region, Germany⁴¹. Bacterial strains were cultivated in anoxic microbial mineral medium modified from Ehrenreich and Widdel⁴¹, composed of 0.6 g l⁻¹ potassium phosphate (KH₂PO₄), 0.3 g l⁻¹ ammonium chloride (NH₄Cl), 0.5 g l⁻¹ magnesium sulphate (MgSO₄·7H₂O) and 0.1 g l⁻¹ calcium carbonate (CaCl₂·2H₂O). To ensure that no Fe minerals were transferred to the experimental cultures with the inoculum, either hydrogen (as H₂/CO₂ 90:10 v/v) or 4 mM acetate was used as an electron donor for pre-experimental cultures. Experimental cultures were supplied with 0.5–4 mM dissolved Fe(II), added as FeCl₂, filtered and buffered at pH 6.8–7.0 following the procedure described previously^{13,19}. Silica was added to the medium already containing dissolved Fe(II) in the form of sodium metasilicate nonahydrate (Na₂O₃Si·9H₂O) to a final concentration of 2 mM monomeric Si (dissolved silica). The inoculum was then immediately added to an initial density of 10⁷ cells ml⁻¹.

Cultures were incubated in triplicate with an abiotic control at 20 °C with a 40 W incandescent light bulb (Philips) light source at light saturation for these strains¹⁸ (800 lux). The cultures were incubated in 25 ml serum bottles, upside down, so that the stopper was at the bottom of the experimental vial. As particular care was taken not to shake the cultures during incubation and sampling, it was possible to sample just from the solution and quantify silica or Fe that had not precipitated.

The rate of Fe(II) oxidation was determined over time using the ferrozine assay⁴², a spectrophotometric test that enables quantification of Fe(II) and total iron in solution. Oxidation rates were determined from the maximum slope of the line plotted as Fe(II) concentration measured over time. A comparison of this simplified zero-order-rate approach with first-order-rate data analysis shows that the zero-order analysis represents a reasonable approximation with only 10–20% lower values than oxidation rates determined by the first-order approach. Therefore, the simpler zero-order approach was used in this study for all further data analysis. The concentration of monomeric silica (dissolved silica) in solution was measured spectrophotometrically based on the molybdosilicate method⁴³.

The abiotic precipitation of silica due to temperature change was first modelled with Geochemist's Workbench Standard 6.0. Using TACT in a simplified approach, the activity coefficient was set to one, which rendered the activity equal to the concentration. The microbial mineral medium solution described above was the solvent considered for these calculations. pH and carbonate buffer was accordingly added to the model calculation. Extra calculations for Archaean ocean water composition yielded qualitatively and quantitatively similar results as calculations for the freshwater medium (see Supplementary Information, Fig. S3). For batch experiments testing the abiotic precipitation of silica due to temperature change, 4 mM silica was added to anoxic microbial mineral medium, prepared as described above⁴¹, and placed at 70 °C. At 70 °C, the solubility of silica is approximately 4 mM, as shown by the geochemical model described above (Geochemist's Workbench). After 24 h, silica remaining in the water column was sampled and monomeric (dissolved) silica quantified with the molybdosilicate method as described above. The procedure was carried out at 24 and 4 °C with 24 h intervals until equilibrium was reached.

To determine whether the strains revive after exposure to temperature changes, cultures were prepared in anoxic microbial mineral medium with dissolved Fe(II) and silica as described above. Fe(II) oxidation was followed throughout the experiment with the ferrozine assay. After the microbial

oxidation of Fe(II) was observed for a number of days, the cultures were moved from 20 °C to 4 °C for a number of days. These cultures were afterwards returned to 20 °C.

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