INTRODUCTION

Banded iron formations (BIFs) host the world’s largest iron ore deposits, and they formed predominantly through the deposition of ferric iron [Fe(III)] from ferruginous oceans during the Archean Eon (1, 2). Most models for BIF deposition invoke photosynthesis in the oxidation of ferrous iron from seawater to induce its subsequent precipitation and deposition as mixed valence iron (oxyhydr)oxides and carbonate phases (3–6) [see (7) and (8) for alternative models]. BIFs thus likely record the activity of Earth’s early photosynthetic biosphere (3). Two modes of photosynthesis have been implicated in Fe(II) oxidation—canonical oxygentic photosynthesis by the ancestors of modern cyanobacteria (3) and iron-dependent anoxygenic photosynthesis (4, 5), referred to as photoferrotrophy. Photoferrotrophic bacteria grow using light and Fe(II) to fix CO₂ into biomass and produce Fe(III) as a metabolic by-product (4, 5). In the presence of silica, photoferrotroph cell surfaces repel iron (oxyhydr)oxides. In silica-rich Precambrian seawater, this repulsion would have separated biomass from ferric iron and would lead to large-scale deposition of BIFs in anoxic settings. Excess biomass not deposited with BIF would have deposited in coastal sediments, formed organic-rich shales, and fueled microbial methanogenesis. As a result, the deposition of BIFs by photoferrotrophs would have contributed fluxes of methane to the atmosphere and thus helped to stabilize Earth’s climate under a dim early Sun.
using modern photosynthetic bacteria with revised theoretical estimates of Fe(II) fluxes to the Archean ocean and box modeling of coupled carbon and iron cycling to show that photosynthetic Fe(II) oxidation could have sustained large-scale, organic-poor BIF deposition in ocean upwelling systems over hundreds of millions of years.

### RESULTS AND DISCUSSION

#### Separation of biomass and Fe(III)

To explore the fate of biomass and Fe(III) during photosynthetic Fe(II) oxidation, we conducted experiments using *Chlorobium phaeoferrooxidans* strain KB01—a photoferrotrophic bacterium that was isolated from the water column of ferruginous Kabuno Bay, a sub-basin of Lake Kivu in East Africa (21). We also conducted experiments with *Chlorobium ferrooxidans* strain KoFox, a sediment-dwelling photoferrotroph that tends to associate with Fe(III) (oxyhydr)oxides without becoming encrusted (23, 29), as well as a model marine oxyphototrophic cyanobacterium of the genus *Synechococcus*. Strain KB01 is the only known photoferrotroph from a pelagic environment (21), and pelagic photoferrotrophs, including those that would have populated Precambrian ferruginous oceans, face a special challenge—they must maintain their position within sunlit waters despite the precipitation of heavy Fe(III) (oxyhydr)oxides without becoming encrusted (23, 29), as well as a model marine oxyphototrophic cyanobacterium of the genus *Synechococcus*. Strain KB01 cells had near neutral surface charges (fig. S4), whereas cells of strain KoFox had strongly negative surface charges (fig. S4), whereas cells of strain KoFox had near neutral surface charges (fig. S4), whereas cells of strain KoFox demonstrated that cell-mineral association was diminished relative to the silica-free experiments, with 72 ± 7% of strain KoFox cells remaining suspended (Fig. 2A and fig. S5A). We also grew both strains KB01 and KoFox in their standard growth medium containing 4 mM phosphate and no silica, which led to little cell-mineral association for strain KB01 (Fig. 2A) and modest association for strain KoFox (fig. S5A). Detailed electron microscopy revealed that the surfaces of KB01 cells were entirely free from Fe(III) (oxyhydr)oxide precipitates (Fig. 3), whereas strain KoFox tended to form multicellular aggregates that variably associated with the mineral precipitates (fig. S3A). Strain KB01, and to a somewhat lesser extent strain KoFox, thus avoids encrustation with Fe in low-P, high-Si waters, as well as in standard growth media with high phosphate, remaining suspended despite Fe(III) (oxyhydr)oxide precipitation.

We also subjected *Synechococcus* cells to Fe-Si-rich growth conditions in a similar fashion (Fig. 2A and fig. S5A). *Synechococcus* associated to a greater extent with the Fe(III) (oxyhydr)oxide products of Fe(II) oxidation than did the photoferrotrophs under these conditions. Such an association was expected, despite the presence of silica, given that oxygen effuses from *Synechococcus* cells, reacts rapidly with Fe(II), and causes precipitation of Fe(III) (oxyhydr)oxides on the cell surfaces—an association likely maintained due to binding of organic ligands, as observed in many previous environmental and laboratory studies (32, 34, 35). Photoferrotrophs adapted to pelagic lifestyles thus appear most capable of avoiding co-sedimentation with Fe(III) and remain buoyant with the potential for separation of biomass from Fe(III) at larger scales in the environment.

#### Mechanisms of cell-mineral separation

Surface charge often influences cell-mineral association, or lack thereof, and as solution P:Fe or Si:Fe ratios increased, the surface charge on the Fe(III) (oxyhydr)oxides formed became more negative (Fig. 2B) due to the incorporation of P or Si anions into the oxyhydroxide structure (33). Conversely, Fe(II) oxyhydroxide particles were positively charged under low P or Si conditions, which is consistent with observations of positively charged Fe(III) precipitates in many environments (31). Strain KB01 cells had strongly negative surface charges (fig. S4), whereas cells of strain KoFox had near neutral surface charges (fig. S4), similar to some microaerophilic Fe(II) oxidizers (36). This difference in surface charge between strains KB01 and KoFox reflects different cell surface chemistries (table S2), notably an abundance of anionic surface functional groups on strain KoFox with different acid-base behavior than strain KB01 (Supplementary Materials and fig. S3). Benthic microorganisms, such as strain KoFox, commonly produce surface
Thompson et al., Sci. Adv. 2019; 5 : eaav2869     27 November 2019

SCIENCE ADVANCES | RESEARCH ARTICLE

Fig. 2. Cell surface characteristics for strain KB01 and the relationship between ferric iron surface charge and medium anions. Fractions of planktonic (blue) versus sedimented (red) cells (A) for photoferrotrophic strain KB01 under varying geochemical conditions: 400 μM Fe(II) with low P (3 μM) [unmarked]; 400 μM Fe(II), low P (3 μM), with 0.6 mM Si [A]; 400 μM Fe(II), low P (3 μM), with 1.0 mM Si [B]; 400 μM Fe(II), low P (3 μM), with 1.5 mM Si [C]; and 10 mM Fe(II) with 4.4 mM P [D]. C. ferrooxidans and Synechococcus are also shown under the [C] conditions. Rhodobacter strain SW2 is shown under the [D] conditions. The zeta potential (B), in millivolts, of the ferric iron precipitates is depicted with an increasing ratio of Si or P to Fe, where the error bars are all within the data points. Last, for the extended DVLO modeling for strain KB01 (C), the main graph depicts the interaction energies of the three forces (AB, Lewis acid base; LW, Lifshitz–van der Waals; EL, electrostatic) and the total (TOT) for those forces from 3 to 5 nm, while the inset depicts the forces from 0 to 5 nm.

Fig. 3. Scanning electron microscopy and transmission electron microscopy image of strain KB01. Scanning electron photomicrograph (A) and transmission electron photomicrograph (B) of C. phaeoferrooxidans strain KB01 revealing various internal and external cell structures as well as a lack of encrustation (A and B) and a rare association with Fe(III) precipitates (A).

layers rich in anionic functional groups to facilitate attachment to solid substrates (37), and these anionic surface functional groups tend to strongly bind Fe(III), effectively neutralizing surface charge (fig. S4). The role of Fe(III) in controlling surface charge on strain KoFox was confirmed by rinsing KoFox cells with reducing agents (sodium dithionite) that liberated Fe(III) and caused a shift in the surface charge to more negative values (fig. S4). These same rinses had little effect on cells of KB01 (fig. S4), confirming the role of surface chemistry and Fe(III) binding in controlling association of cells to Fe(III) (oxyhydr)oxides. The direct role of cell surface charges in dictating mineral association and co-sedimentation is also evident from the strong inverse relationship (fig. SSB) between mineral surface charges and cell-mineral separation.

To assess the biophysical mechanisms that control cell-mineral associations, we determined interfacial properties of the cell and Fe(III) oxyhydroxide surfaces and conducted extended Derjaguin-Landau-Verwey-Overbeek (DVLO) modeling to quantify the forces that develop between these surfaces (Supplementary Materials) (36, 38). DVLO modeling uses measurements of physical surface properties to calculate interfacial forces as a function of distance between surfaces. Our model results revealed that the negative surface charge on strain KB01 led to electrostatic repulsion between its surface and negatively charged Fe(III) (oxyhydr)oxides (Fig. 2C). The more neutral charge on strain KoFox, conversely, led to a weak electrostatic attraction (fig. S5C). Lewis acid-base and Lifshitz–van der Waals forces were much weaker than the electrostatic forces, but we note that the acid-base properties of strain KB01 lead to repulsion of Fe(III) (oxyhydr)oxides, even without electrostatic effects. Surface charge, therefore, controls cell-mineral association, and ultimately like-charged surfaces cause the physical separation of strain KB01 and, by extension, other pelagic photoferrotrophs from their Fe(III) oxyhydroxide by-products. These findings have important implications for BIF deposition and the coupling of carbon and iron cycles in the Archean Eon. We note that while strain KB01 is a derived member of the phylum Chlorobi, its cell surface chemistry is typical for Gram-negative bacteria (30, 39), and our results are thus likely extensible to its ancestors and most other Gram-negative bacteria, with the exception of benthic organisms, like strain KoFox, that have unusual modifications to their cell surfaces. Stem group, pelagic photoferrotrophs in Archean oceans, therefore, most likely had cell surface chemistries and interacted with Fe(III) (oxyhydr)oxides much like strain KB01.

Revised Precambrian Fe budgets
Before proceeding to model coupled carbon and iron cycling, we sought to reconcile the possible material fluxes of Fe(II) to the oceans and those needed to sustain BIF deposition (26, 40). These material fluxes serve as boundary conditions for our models and help tether our results to the geologic record. Peak BIF deposition rates imply an Fe burial flux of 45 mol m⁻² year⁻¹ over areas greater than 10¹¹ m², or ~4.5 Tmol Fe year⁻¹ (5), and at steady state, Fe(II) must
be actively resupplied to the oceans at this rate through a combination of hydrothermal venting and continental and seafloor weathering. Previous estimates of modern hydrothermal Fe fluxes of ~2 Tmol year\(^{-1}\) (Supplementary Materials), on their own, are insufficient to support steady-state BIF deposition (table S3) (1, 26, 40). These estimates were based on the product of hydrothermal fluid flow and Fe(II) concentrations measured in circulating on- and off-axis fluids (41). Global Fe fluxes, however, would have been much different in the Archean Eon because of enhanced hydrothermal activity (40, 42), smaller continents (43), reduced seawater sulfate (42, 44), weathering of Earth’s crust at low oxygen (18, 45, 46), and pervasively anoxic oceans.

Hydrothermal fluid fluxes to the oceans have been calculated from a variety of geochemical and physical data resulting in a wide range of estimates for these fluxes in the literature. A recent compilation from a number of sources (47), however, provides a synthesis of both on- and off-axis fluid flow as well as a modeled distribution of these values that yields averages (modes) of \(5 \times 10^{13}\) and \(1.5 \times 10^{16}\) kg year\(^{-1}\), respectively (47). These values are greater than values considered in previous estimates of modern hydrothermal Fe(II) budgets, implying that modern Fe(II) fluxes to the oceans were underestimated (41). Archean hydrothermal fluid flow was, furthermore, likely higher than today due to greater heat loss from the Archean lithosphere (26, 48). Following previous work (26), we thus scaled the updated estimates for modern fluid flow by the ratio of past to modern lithospheric heat loss (Supplementary Materials). This yields estimates for hydrothermal fluid flow at 2.5 Ga of \(1 \pm 0.6 \times 10^{13}\) and \(4 \pm 0.6 \times 10^{16}\) kg year\(^{-1}\) for on- and off-axis venting, respectively (table S3). Crucially, these revised estimates for fluid flow increase the possible Fe(II) fluxes to both the modern and Archean oceans.

The concentration of Fe(II) in modern on-axis hydrothermal fluids is \(\sim 6\) mmol kg\(^{-1}\) (41), but this depends on the chemistry of seawater that circulates through seafloor basalts. Notably, high concentrations of sulfate (28 mM) in modern seawater lead to production of hydrogen sulfide in anoxic hydrothermal fluids, and this hydrogen sulfide reacts with Fe(II) to form iron-sulfide minerals that limit the concentration of Fe(II) in effluxing fluids (42). Sulfate concentrations in Archean seawater were much lower than today due, in part, to the lack of oxidative pyrite weathering on the continents (44). Models of hydrothermal fluid chemistry, therefore, predict that Fe(II) concentrations in high-temperature hydrothermal fluids were 10-fold higher when seawater was sulfate free versus the modern 28 mM (42), implying that high-temperature vent fluids in the Archean Eon could have had up to 60 mmol kg\(^{-1}\) Fe(II). Combining such a high-temperature hydrothermal Fe(II) concentration (42) with revised on-axis hydrothermal fluid flow results in Fe(II) fluxes of \(8 \pm 3\) Tmol year\(^{-1}\) at 2.5 Ga (table S3), and these are similar to, but smaller than, other recent estimates (49). The effect of seawater sulfate concentrations on the Fe(II) concentration in lower-temperature, off-axis hydrothermal fluids appears less pronounced, and so we conservatively consider off-axis hydrothermal Fe(II) concentrations equivalent to today (~0.75 mmol kg\(^{-1}\)) (42). This results in possible off-axis Fe(II) fluxes of up to \(30 \pm 5\) Tmol year\(^{-1}\) (table S3). Combining these new estimates for on- and off-axis Fe(II) fluxes, we redefine upper possible limits on hydrothermal Fe(II) delivery to the oceans at 2.5 Ga as \(\sim 40\) Tmol year\(^{-1}\) (table S3).

In addition to the Fe(II) fluxes from hydrothermal venting, modern continental weathering also contributes Fe to the oceans. We thus assessed the potential delivery flux of continental Fe(II) to Archean oceans, taking into consideration the low oxygen atmosphere (45) and smaller continent sizes (43), resulting in a total Fe(II) weathering flux of 5 Tmol year\(^{-1}\) to the oceans (Supplementary Materials). Summing continental weathering and hydrothermal Fe(II) fluxes yields an upper possible global Fe(II) flux of \(\sim 45\) Tmol year\(^{-1}\) to the oceans 2.5 Ga (table S3). This is more than sufficient to deposit BIF at 4.5 Tmol year\(^{-1}\) and is supplied mostly through previously unconsidered off-axis hydrothermal venting. These revised Fe(II) fluxes place upper boundaries on the magnitude of global coupled carbon and iron cycling, which we explore below using biogeochemical box models.

### Modeling Archean marine iron and carbon cycles

We assume that biological production in our model is driven by photoferrotrrophy, and while oxygenic photosynthesis could have been active from the Mesoarchean (46, 50), its contribution to primary production may have been small before the GOE due to competition with photoferrotrrophs (15, 51). Nevertheless, discriminating between modes of photosynthesis would have no real effect on our model outcomes because oxygen produced would react with Fe(II), yielding the same 4:1 stoichiometry between iron oxidation and carbon fixation as in photoferrotrrophy. Biomass degradation in our model was first channeled through heterotrophic Fe(III) reduction and then, given the near absence of sulfate in the Archean ocean (44), microbial methanogenesis (22, 44). We implicitly assumed that both Fe(III) reduction and methanogenesis are preceded by the breakdown of organic matter through hydrolysis, glycolysis, and fermentation. Rates of organic matter breakdown were parameterized on the basis of observations from modern anoxic marine basins (52, 53). However, we note that, unlike today, the biological pump in the Archean oceans would have operated without ballastting from fecal pellets. Biological production and nutrient cycling in the modern oceans can be divided into three broad oceanographic provinces—open ocean, coastal zone, and upwelling regions (52). In detail, the distribution and biological activity of these provinces depend on ocean circulation patterns, continental configurations, and nutrient supply, but in the absence of robust constraints on these parameters for the Archean oceans, we assumed that the relative contributions of similar such provinces to biological production scale with continental area and were otherwise similar to the modern. We thus distributed total biological production across these three provinces according to their relative productivities in the modern ocean (52) and scaled continental area from 0 to 100% of the modern (Fig. 4 and Supplementary Materials).

Our results revealed that upwelling provinces support Fe(II) oxidation and Fe(III) oxyhydroxide sedimentation at rates sufficient to deposit even the largest BIFs, such as those of the Hamersley Basin in Western Australia (Fig. 5, Table 1, and Supplementary Materials). Notably, Fe(III) (oxyhydr)oxides, with a relatively high density (3.8 g cm\(^{-3}\)) and a tendency to aggregate to larger particle sizes (54), had an average settling velocity of \(2 \times 10^{4}\) m year\(^{-1}\). This led to their deposition within a maximum of 40 km from their locus of initial precipitation, assuming a 150-m-deep water column and current velocities less than 650 m year\(^{-1}\) (fig. S6 and table S4) (52, 55). Furthermore, this localized deposition occurred despite the strong horizontal current velocities that are characteristic of upwelling provinces (52, 55). In stark contrast, the average settling velocity of biomass not associated with Fe(III) (oxyhydr)oxides was 0.35 m year\(^{-1}\), and biomass can thus be transported at distances more than 6000 km—greater than...
Dissolved Fe(II) concentrations in the deep ocean, and rates of upwelling (Fig. 5). These variables can be constrained to likely ranges based on material fluxes recorded in sedimentary rocks (1, 28, 40), bounds for global cycling (1, 28, 40), and tempered analogies to modern systems (21, 56)—model outputs within these ranges are delineated by the shaded area in Fig. 5. Deep ocean Fe(II) concentrations are constrained to <70 µM, similar to earlier estimates of 50 µM based on siderite and calcite solubility (28), because higher Fe(II) concentrations led to global Fe(II) oxidation rates that exceed the revised maximum global Fe(II) supplies and recycling combined (table S3). Even at these relatively low Fe(II) concentrations (20 to 70 µM), upwelling provinces could have supported area-specific rates of BIF deposition of up to 54 mol m⁻² year⁻¹ over areas greater than 10¹² m² (Table 1), as needed to deposit the largest of the Archean BIFs (5). Notably, with decreased cell-mineral association, increased continent size, increased deep-water Fe(II) concentrations, and increased upwelling rates, Fe(II) consumption could have eventually outpaced even upper limits for Fe(II) supply, and this would have led to depletion of deep ocean Fe(II). Within the most likely parameter space, rates of global primary production through photoferritrophy would have been less than 1% of modern primary production (Table 1) and, in the absence of oxygen and sulfate, most of this...
biomass would have been remineralized through Fe(III) reduction and methanogenesis in the open ocean, with the remainder buried in sediments (Table 1). Global primary production is limited by P availability over geological time and marine primary production scales with P concentrations in the oceans (57). Reconstruction of P concentrations in the Archean oceans implied 0.04 to 0.13 μM (15), which is ~1 to 4% of the modern and sufficient to support our estimates for primary production. Notably, up to 45% of all remineralized carbon was channeled through methanogenesis, and the fraction of remineralization through methanogenesis increased with decreased cell-mineral association, increased continent size, increased deepwater Fe(II) concentrations, and increased upwelling rates (Fig. 5 and Table 1). Variations in all of these processes thus likely influenced global rates of iron deposition and methane production and could have contributed to the development of differing BIF facies.

The model prediction that methanogenesis would have played a key role in carbon degradation in Archean ferruginous oceans is also supported by other Earth system models (49) and observations from modern ferruginous basins. In Kabuno Bay, East Africa, for example, carbon produced through photoferrotrophy is remineralized through methanogenesis (21), leading to an export of ferric iron from the euphotic zone even under extremely quiescent physical conditions. Likewise, despite abundant Fe(III) (oxyhydr)oxides, as much as 50% of the carbon degradation in ferruginous Lake Matano is channeled through methanogenesis, rather than Fe(III) reduction (56). Empirical observations thus point generally to carbon and iron cycling under ferruginous conditions that ultimately leads to methane production even in the absence of the large-scale advective processes that operate in the oceans. When integrated into a box model of the Archean marine iron and carbon cycles, our observations of cell-Fe(III) oxyhydroxide separation during photoferrotrophy quantitatively describe an Archean biosphere that: (i) accounts for the Fe(III) deposition rates needed to form BIFs; (ii) explains the fate of biomass and its absence from BIFs; and (iii) provides a strong source of methane to the biosphere.

This model demonstrates that, within the geologically constrained parameter space, global rates of methanogenesis can easily reach 3.2 Tmol year$^{-1}$ (Table 1), and with the near absence of oxygen and sulfate to fuel methane oxidation, most of this methane would be delivered to the atmosphere (58). On the basis of new solutions (49) to photochemical models (59), this biospheric methane flux (3.2 Tmol year$^{-1}$) would support a 10 ppmv (parts per million by volume) methane atmosphere under our benchmark scenario, with a possible range of between 1 and 20 ppmv across the likely model parameter space (Table 1). While these methane concentrations alone are unlikely to support a warm climate, positive feedbacks with other concurrent modes of photosynthesis, like H$_2$-based anoxygenic photosynthesis, markedly increase both biospheric methane fluxes to the atmosphere and atmospheric methane concentrations (49).

Our observations of extant photoferrotrophs, revised global Fe budgets, and models of coupled C and Fe cycling thus support an upside-down Archean biosphere, similar to that originally proposed by Walker (19), in which the deposition of BIFs leads to a methane-rich atmosphere. Our results further imply that cell-Fe(III) separation augments marine methane production through the breakdown of photoferrotrophic biomass and mechanistically ties biospheric methane fluxes to the deposition of BIF. The role this plays in atmospheric chemistry and greenhouse warming should be tested through further biogeochemical-photochemical modeling efforts.

### METHODS

Photoferrotrophic strains and cyanobacteria were grown in basal media (21) and in alternative media (Supplementary Materials and table S1) until late exponential phase. Subsamples of both Fe(II)/Fe(III) and pigments were used to track the growth kinetics and to assess the in vitro cellular association to Fe(III). The surface properties of each strain and their metabolic Fe(III) by-products were assessed by measuring their surface potential using the Particle Metrix ZetaView. The acid-base properties of cell surfaces were determined through titrations. Cell surface contact angles were measured for DVLO modeling in three different liquids—water, glycerol, and diiodomethane (36, 38). Electron microscopies [scanning electron microscopy (SEM) and transmission electron microscopy (TEM)] were used to image cell-mineral interactions (Supplementary Materials). The particle sizes of the Fe(III) (oxyhydr)oxides produced by the photoferrotrophic strains were measured using a Mastersizer 2000 particle size analyzer, and these were then used to model the impact of horizontal ocean
current velocities on the settling time of both Fe(III) particles and cellular biomass (Supplementary Materials, fig. S6, and table S4). The box model of the Archean marine carbon and iron cycles was designed with three boxes (each representing an oceanic province) to capture variability in fluxes through each box (Supplementary Materials, Figs. 4 and 5, fig. S8, and Table 1).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/11/eaav2869/DC1

**Supplementary Materials and Methods**

Section S1. Cell surface features and acid-base chemistry

Section S2. Cell-surface interaction and extended DVLO modeling

Section S3. Iron concentration and supply

Section S4. Physical separation of ferric iron oxyhydroxides and cellular biomass in an ocean setting

Section S5. Box model of Archean marine carbon and iron cycles

Section S6. Organic carbon burial and diagenesis

Table S1. Range of concentrations in the growth media used throughout experiments.

Table S2. Cell surface characteristics and cell-mineral interaction modeling.

Table S3. Modern and Archean Fe fluxes

Table S4. Different scenarios of the physical separation model, with each case using a different water velocity.

Table S5. Data compilations for Fig. 1 and fig. S1.

Fig. S1. The redox state of iron in BIF through time where the red bars indicate the siderite-rich BIFs.

Fig. S2. Growth curve for *C.phaeopellicoides* strain KB01.

Fig. S3. Additional SEM and TEM images of strains KB01 and KoFox under two conditions.

Fig. S4. Surface charge of strains KB01 and KoFox.

Fig. S5. Additional cell surface characteristics for strain KoFox.

Fig. S6. Modeling the settling velocity of carbon and iron using a range of horizontal current velocities.

Fig. S7. Modeled weight % organic carbon in the coastal and open ocean sediments.

Fig. S8. Iron and carbon box model sensitivity results.

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View/request a protocol for this paper from *Bio-protocol*.

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