Protection of phototrophic iron(II)-oxidizing bacteria from UV irradiation by biogenic iron(III) minerals: Implications for early Archean banded iron formation

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ABSTRACT

On the Archean Earth (4.0–2.5 Ga) the lack of a protective ozone layer meant that harmful ultraviolet radiation (UVR) reached the surface almost unattenuated. For survival, primitive photosynthetic bacteria would have required strategies preventing UV-induced damage to their DNA. At that time, a fraction of the planktonic cells were likely anoxygenic photosynthesizers that oxidized dissolved Fe(II) to Fe(III) during their metabolism. The result of their metabolism was most likely the ferric mineral precursors for the deposition of banded iron formations. Although Fe(III) (oxyhydr)oxide minerals absorb UV radiation while still transmitting higher wavelengths, it is unknown whether minerals produced by Fe(II) oxidizers could have acted as an in situ UVR sunscreen. Here we demonstrate that the anoxygenic phototrophic Fe(II) oxidizers *Rhodopseudomonas palustris* strain TIE-1 and *Rhodobacter ferrooxidans* strain SW2 form nanometer-sized grains of ferrihydrite that are loosely attached to the cell surfaces. These biogenic Fe(III) minerals were shown to protect the bacteria from UV-C irradiation, while cells grown in the absence of Fe(II) displayed diminished cell viability as a consequence of damage to their DNA. Importantly, this study implies that primitive Fe(II)-oxidizing bacteria would have been able to produce their own UV screen, enabling them to live in the shallow photic zone of ancient oceans.

INTRODUCTION

It is widely accepted that photosynthetic bacteria could have played a crucial role in Fe(II) oxidation and the precipitation of banded iron formations (BIFs) during the late Archean–early Paleoproterozoic (2.7–2.4 Ga) (Posth et al., 2013). It is less clear whether bacteria similarly caused the deposition of the oldest BIF at ca. 3.85 Ga (Mloszewska et al., 2012). Current constraints place the existence of cyanobacteria in the oceans by 3.0 Ga (Crowe et al., 2013; Planavsky et al., 2014), and perhaps even earlier (Stüeken et al., 2015). As an alternative to O_2-producing cyanobacteria, in particular during Eoarchean (4.0–3.6 Ga) and Paleoarchean (3.6–3.2 Ga) BIF deposition for which no direct evidence for the participation of cyanobacteria exists, anoxygenic photosynthetic bacteria, so-called photoferrotrophs, could have contributed to Fe(III) mineral deposition (Craddock and Dauphas, 2011; Czaja et al., 2013; Kappler et al., 2005; Pecoits et al., 2015). These bacteria use Fe(II) as electron donor and light as energy source, producing biomass and Fe(III) minerals (Widdel et al., 1993). Their presence in the early Archean has recently been supported by studies suggesting that cyanobacteria would have been phosphorous starved (Jones et al., 2015) and that ferruginous seawater would have been toxic to cyanobacteria (Swanner et al., 2015a); both would have favored photoferrotrophy and explain BIF deposition at that time.

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In the absence of an ozone (O_3) layer, plankton would have been subject to higher levels of ultraviolet radiation (UVR), in particular UV-C (100–280 nm) (Cockell, 2000). Because DNA strongly absorbs at 254 nm, UV-C causes DNA strand breakage (Sinha and Häder, 2002) and the formation of photoproducts, such as cyclobutane pyrimidine dimers (CPD), that inhibit transcription and replication of the chromosome and cause mutations (Pfeifer, 1997). Hence, in order to survive, these early plankton must have used strategies to contend with detrimental UVR by developing protective pigments (Dillon and Castenholz, 1999) and UV damage repair systems (Häder and Sinha, 2005; Sinha and Häder, 2002). However, it is also possible that before these biological responses evolved, primitive plankton produced an external sunscreen from the solutes readily available to them (Bishop et al., 2006; Cleaves and Miller, 1998; Cockell, 2000; Phoenix et al., 2001). Due to the micrometer size of cells, such an effective external screen could consist of nanoparticular mineral particles that were available in proximity to the cell's surface.

Archean oceans were characterized by high concentrations of dissolved Fe(II) (Holland, 1973). In the presence of UVR or photosynthetically active radiation (PAR; 400–1000 nm), Fe(II) would have been abiologically (Cairns-Smith, 1978) or biologically oxidized (Posth et al., 2013), leading to the formation of Fe(III) (oxyhydr)oxides such as ferrihydrite, $Fe(OH)_3$. Ferrihydrite is an effective absorber of UV light (<400 nm), while higher wavelengths are reflected, scattered, and transmitted and are thus still available for photosynthesis (Bishop et al., 2006; Phoenix et al., 2001). Therefore, it is possible that ancient photoferrotrophs would have been able to produce their own inorganic UV shield in form of Fe(III) minerals (Bishop et al., 2006; Pierson et al., 1993). Here we determined to what extent the phototrophic Fe(II) oxidizers *Rhodopseudomonas palustris* strain TIE-1 and *Rhodobacter ferrooxidans* strain SW2 are protected from UVR in the presence and absence of Fe(III) minerals.

MATERIALS AND METHODS

UV treatment was carried out in an anoxic chamber where a UV lamp (8 W, S/L; Herolab, Germany) was used to irradiate the bacterial cultures with 254 nm UV-C. Cultures grown without (no UV shield present) or with 4 or 8 mM Fe(II) [biogenic Fe(III) minerals present as UV shield], respectively, were split to ensure same cell numbers and health state in both non-treated and UV-treated cultures. Cultures were poured into sterile petri dishes to a liquid layer thickness of <0.3 cm, and UV-C radiation (254 nm) was applied from the top for varying time spans. Non-irradiated controls were treated the same, but covered with aluminum foil to avoid UVR. The irradiated and non-irradiated cultures were then used either to inoculate new Fe(II)-free or Fe(II)-containing medium, to perform growth experiments, or for DNA damage analysis. Full details of growth conditions, analytical methods, and enzyme-linked immunosorbent assay (ELISA) for DNA damage determination in the form of CPD photoproducts are provided in the GSA Data Repository[1].

RESULTS AND DISCUSSION

Photoferrotrophic Biomineralization

Neutrophilic Fe(II)-oxidizing bacteria produce Fe(III) minerals that bind at negatively charged nucleation sites, e.g., extracellular polymeric substances or the cell wall. For phototrophic Fe(II)-oxidizing bacteria, it was previ-

[1]GSA Data Repository item 2015355, methods, is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

ously shown that most strains are able to prevent precipitation of Fe(III) minerals on their cell surfaces, but that the cells are closely associated with the minerals (Hegler et al., 2010; Schädler et al., 2009; Wu et al., 2014). Our study shows that cells of the phototrophic Fe(II)-oxidizing strain *Rhodobacter ferrooxidans* SW2 are in close proximity to the produced nanoparticular minerals, although the cell surfaces remain mostly free from precipitates (Fig. 1). A similar loose association of cells with Fe(III) minerals was shown for *Rhodopseudomonas palustris* TIE-1 (Jiao et al., 2005). Characterization of the minerals produced during Fe(II) oxidation by X-ray diffraction (XRD) analysis revealed poorly crystalline ferrihydrite as the dominating mineral (Jiao et al., 2005), but also nanoparticular goethite and lepidocrocite (Posth et al., 2010).

Cell Viability after UV-C Irradiation

To evaluate the potential protective effect of these biogenic minerals formed by photoferrotrophs against UVR, bacterial growth on acetate determined by means of the optical density (OD) at 600 nm was compared for cultures inoculated with UV-treated and non-UV-treated cultures grown with or without Fe(II), i.e., in the presence or absence of a UV shield. *Rhodobacter ferrooxidans* SW2 showed no increase in $OD_{600\,nm}$, i.e., no growth, within 10 d, in cultures containing an inoculum from a culture grown without Fe(II) and treated with UV light for 5 or 10 min. This suggests that the UV treatment killed or inactivated most cells in the cultures that were used as inoculum. By contrast, acetate cultures inoculated with non-UV-treated inoculum from an acetate culture showed a mean absorption of 0.789 after 6 d (Fig. 2A). Similarly, a culture inoculated with inoculum from a healthy, non-UV-treated Fe(II)-grown culture grew with acetate to a mean $OD_{600\,nm}$ of 0.797 after 6 d. Surprisingly, cultures inoculated with inoculum from a UV-treated Fe(II)-grown culture showed high OD values of 0.773 (inoculum with 5 min UV treatment) and 0.688 (inoculum with 10 min UV treatment) (Fig. 2B), clearly suggesting that the Fe(III) minerals present during UV treatment protected the cells from damage because the growth was similar to that obtained in cultures inoculated with non-UV-treated samples.

Cultures of *Rhodopseudomonas palustris* TIE-1 showed the same trend in OD as the cultures of *Rhodobacter ferrooxidans* SW2. Cultures inoculated with a non-UV-treated inoculum from a culture that was grown without Fe(II) reached an OD of 1.541 after 3 d. In contrast, cultures inoculated with UV-treated cells grown without Fe(II) (no UV screen) showed no change in OD after 10 d of incubation, suggesting much less, if any, viable cells (Fig. 2C). Similar to SW2, TIE-1 cultures inoculated with samples from Fe(II)-grown cultures were able to grow to an $OD_{600\,nm}$ of 1.502 after 4 d (inoculum from non-UV-treated culture), 1.342 (inoculum with 5 min UV treatment), and 1.487 (inoculum with 10 min UV) after 6 d (Fig. 2D). These results show that Fe(III) minerals present during UV treatment function as screen against harmful UVR and protect the cells from damage.

Damage of Cell DNA during UV-C Irradiation

In addition to monitoring OD in cultures inoculated with UV-treated cells, we also quantified the direct effect of UVR on DNA (Fig. 3) by determining relative CPD production. UV-induced damage to the DNA was indicated by

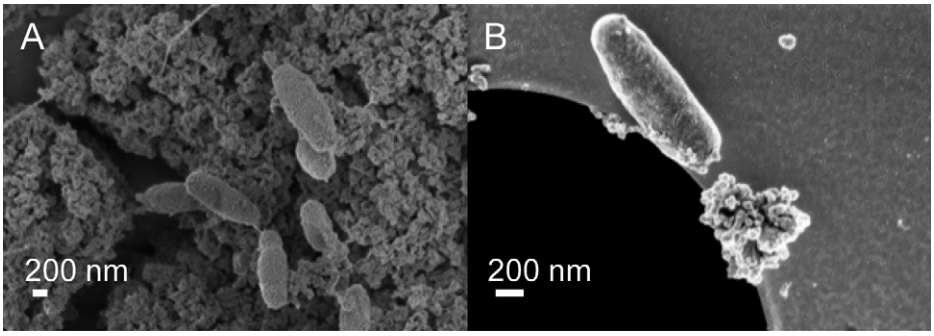

Figure 1. Scanning electron micrographs of phototrophic Fe(II)-oxidizing bacterium *Rhodobacter ferrooxidans* strain SW2 grown in presence of 4 mM Fe(II). Samples were taken at late exponential growth phase when almost all Fe(II) was oxidized and biogenic Fe(III) minerals were formed. Cells are loosely associated with Fe(III) minerals. Images were taken with in-lens detectors at acceleration voltages of 1 kV (A) or 2 kV (B).

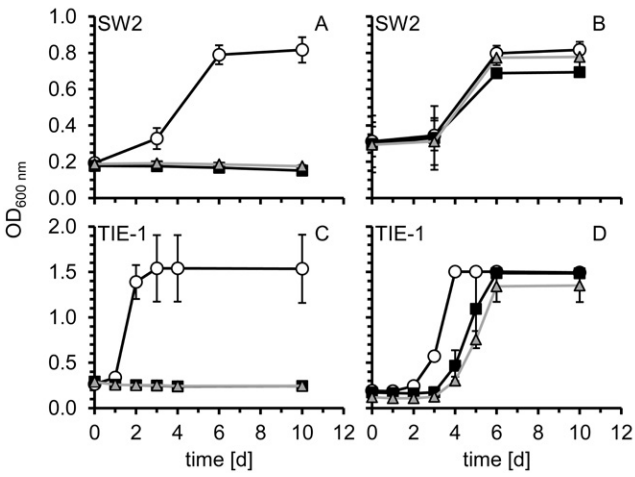

Figure 2. Influence of UV treatment on growth of photoferrotrophic strains of bacteria *Rhodobacter ferrooxidans* SW2 and *Rhodopseudomonas palustris* TIE-1. Growth was quantified with acetate as electron donor by measuring optical density (OD) at 600 nm in cultures that were inoculated with inoculum from cultures that were UV treated. Graphs show data for cultures inoculated from cultures grown without Fe(II) (A, C) or with Fe(II) (B, D) (biogenic minerals present) with non-UV-treated controls (open circles), UV treated for 5 min (filled triangles), and UV treated for 10 min (filled squares). Error bars indicate standard deviation calculated from two to three parallels.

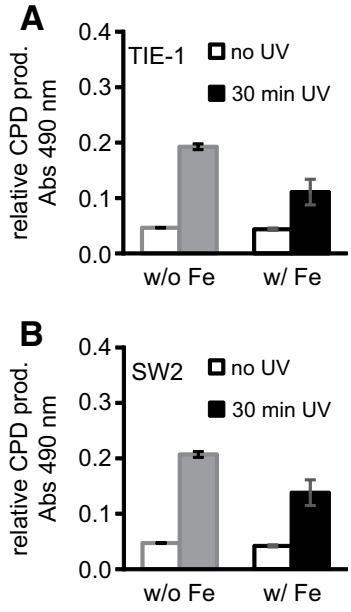

Figure 3. Influence of UV treatment on DNA damage quantified as cyclobutane pyrimidine dimer photoproducts (CPD prod.) for photoferrotrophic strains of bacteria *Rhodopseudomonas palustris* TIE-1 (A) and *Rhodobacter ferrooxidans* SW2 (B). Relative production of CPD in DNA extracts of cultures grown without Fe(II) (gray) or with Fe(II) (black) and with (filled bars) or without (open bars) 30 min of UV treatment is shown. Error bars indicate standard deviation calculated from triplicate measurements.

an increase in CPD in DNA for both photoferrotrophic strains. In both Fe(II)-oxidizing cultures, the Fe(III) minerals provided a protective effect of the DNA. Specifically, absorption values at 490 nm in the ELISA assay with DNA extracted for non-UV-treated *Rhodopseudomonas palustris* TIE-1 cultures were 0.046 ± 0.002 when grown without Fe(II) and 0.044 ± 0.001 when grown with Fe(II). This suggests no effect by the Fe(II) itself on the DNA (Fig. 3A). By comparison, in DNA extracts from UV-treated cultures, values of 0.193 ± 0.023 [grown without Fe(II)] and 0.111 ± 0.004 [grown with Fe(II)] were observed, suggesting more DNA damage by UVR in the absence of the Fe(III) minerals. Similar effects were observed for *Rhodobacter ferrooxidans* SW2: for non-UV-treated cultures, absorption values of 0.047 ± 0.002 [no Fe(II)] and 0.042 ± 0.001 [with Fe(II)] were determined. After UV treatment, the values increased to 0.207 ± 0.010 [no Fe(II)] and 0.138 ± 0.004 [with Fe(II)] (Fig. 3B).

IMPLICATIONS FOR PHOTOFERROTROPHS ON EARLY EARTH

A number of arguments have recently been made in support of photoferrotrophy being responsible for the precipitation of BIFs before the evolution of cyanobacteria (Crowe et al., 2013; Planavsky et al., 2014). This includes studies that have suggested that Fe(II) UV photooxidation (Konhauser et al., 2007) and oxidation by hydrogen peroxide (Pecoits et al., 2015) were unlikely to have been significant compared to photoferrotrophy; iron isotope studies that have suggested that the values in the 3.8 Ga Isua supracrustal belt (Greenland) were best explained by biological oxidation (Craddock and Dauphas, 2011; Czaja et al., 2013; Swanner et al., 2015b); molecular studies that have suggested an early evolutionary role of anoxygenic phototrophs (Xiong et al., 2000), possibly with Fe(II) as one of the first available electron donors (Olson, 2001) that could have been used even in the presence of high dissolved H_2 (Croal et al., 2009); and modeling studies that have suggested that photoferrotrophs would have fared better than cyanobacteria given early seawater chemistry (Kappler et al., 2005; Jones et al., 2015).

However, without stratospheric ozone, UVR was attenuated much less than today [UVR fluxes estimated for the late Archean ocean from Cockell (2000, his figure 3a) to be ~0.01 µmol photons/(m^2 s nm) for 254 nm in 1 m depth, while for modern oceans it is calculated (see the Data Repository) to be 5.0×10^{-4} µmol photons/(m^2 s nm)]. It was suggested that at 5 m depth, the potential DNA damage may have been two orders of magnitude higher than in present-day oceans, and an order of magnitude higher at 15 m depth (Cockell, 2000). Exposure to hazardous UVR would have been a substantial burden and especially affected life in shallow water or microbial mats. The question then is: Did microbes inhabit the uppermost oceans during the Eoarchean and Paleoarchean? Certainly the presence of purported stromatolites in the 3.49 Ga Dresser Formation, northwestern Australia (Walter et al., 1980), and the presence of carbonaceous matter with carbon isotopes consistent with autotrophy in the 3.42 Ga Buck Reef Chert in the Barberton greenstone belt, South Africa (Tice and Lowe, 2004), suggest that phototrophs did indeed inhabit the upper euphotic zone early in Earth's history.

To survive in proximity to the ocean's surface where solar radiation enabled photosynthesis and where nearness to land provided better access to nutrients, microbes would have used different strategies to avoid or decrease UV-induced damage. Although modern planktonic organisms are equipped with protective cellular components, e.g., pigments (Garcia-Pichel, 1994), and they possess UV repair mechanisms, for example photoreactivation by the enzyme photolyase or nucleotide excision repair (Häder and Sinha, 2005; Sinha and Häder, 2002), it is unclear whether these mechanisms were in place during the early Archean. The influence of indirect effects of UV radiation that are mostly mediated by means of production of reactive oxygen species (ROS) that react with proteins, lipids, and DNA and subsequently induce oxidative damage that leads to increased membrane porosity (Chamberlain and Moss, 1987; Pattison and Davies, 2006) in anoxic Archean oceans is difficult to estimate as well. Inorganic substances might have protected microorganisms from UVR, e.g., iron, silica, or sulfur (Bishop et al., 2006; Gómez et al., 2007; Phoenix et al., 2001; Pierson et al., 1993), and in environments where Fe(II) was abundant, the production of Fe(III) minerals may have constituted an early survival strategy. Properties of such Fe(III) minerals include the absorption of light in the low UV range (<400 nm), although visible light (~390–700 nm) is still transmitted. Depending on the mineral structure and identity, the transmission of light in the blue and violet range (400–500 nm) varies (Bishop et al., 2006). Nanoparticular Fe(III) minerals which are produced by phototrophic Fe(II)-oxidizing bacteria enable good penetration of a broader wavelength range of visible and near-infrared light (Bishop et al., 2006). Accessory pigments, for instance carotenoids, absorb light between 400 nm and 550 nm. Protein complexes containing chlorophyll *a* and *b* (used in oxygenic photosynthesis) show absorption maxima at ~400–480 nm and ~650–700 nm, respectively. However, solar radiation used by protein complexes containing bacteriochlorophylls that are involved in anoxygenic photosynthesis ranges from 715 to 1035 nm (Fuchs et al., 2006). Hence, Fe(III) minerals produced by Fe(II)-oxidizing bacteria absorb radiation exactly in those wavelength ranges that cause damage to DNA (<320 nm) while still transmitting radiation that is necessary for photosynthesis (~400–550 and 620–1100 nm).

Our findings suggest that ancient Fe(II)-oxidizing microorganisms would have grown by Fe(II) oxidation and at the same time produced their own effective UV shield in form of Fe(III) minerals. In our experiments, the UVR intensity was ~0.31 µmol photons/(m^2 s nm) for 254 nm (for calculation see the Data Repository) and thus ~30× higher than estimated for a depth of 1 m in the Archean ocean (see calculation above), and we also used 4–8 mM Fe concentrations that were probably higher than concentrations in the ancient ocean (up to 0.5 mM; Morris, 1993). Therefore, the actual extent of UV shielding at lower Fe concentrations in the ancient ocean is difficult to predict. This is true in particular because not only Fe(II) concentrations but also continuous flux of Fe(II) from hydrothermal sources has to be considered. Ultimately, in order to function as an effective UV shield, it is necessary that the flux of Fe(II) and the precipitation of Fe(III) minerals in proximity to the cells is sufficiently rapid to shield the bulk of the microbial community from damaging radiation.

Nevertheless, we show here that this Fe mineral UV shield can protect microorganisms from UV-induced damage, particularly on the DNA level, as seen in the decrease in CPD production in the presence of biogenic Fe(III) minerals. This decrease in CPD would still allow mutations in DNA of microorganisms, but to a much lesser extent. As mutation is one of the main drivers of evolution (Sagan, 1973), the lower CPD load in the protected microorganisms would have still enabled UV-induced early evolution, however possibly with less lethal outcomes.

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Protection of phototrophic iron(II)-oxidizing bacteria from UV irradiation by biogenic iron(III) minerals: Implications for early Archean banded iron formation

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