Iron oxidation and deposition in cyanobacterial mats in a high iron thermal spring

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Chocolate Pots Hot Springs are a collection of iron thermal seeps along the Gibbon River south of Norris Geyser Basin in Yellowstone National Park. The emerging source waters are anoxic, lack sulfide and are high in ferrous iron (50-200 mM). The highest temperature sources are 50-54°C with a pH of 5.3 to 6.0. As the water flows rapidly downhill, it cools, becomes oxygenated, the pH rises, and the Fe^{2+} is oxidized and precipitated as ferrihydrite. The water flows over and through microbial mats composed primarily of cyanobacteria and the filamentous anoxygenic phototroph *Chloroflexus*. The cells were encrusted and permineralized with ferrihydrite

The highest temperature mats are composed of *Synechococcus*, *Cyanothece minerva*, and *Chloroflexus* sp. in varying proportions. Physiological studies performed *in situ* with a voltammetric microelectrode showed that the cyanobacteria were the sole cause of oxygenation of the pore waters. In the light, photosynthetically produced oxygen was responsible for the complete oxidation of all of the Fe^{2+} in the pore waters. In the dark, the pore waters remained anoxic and the iron remained reduced. Maximum oxygen concentration was detected ~0.5 mm below the mat surface. Experiments in which the light regime was shifted from dark to light showed that all the Fe^{2+} was oxidized before oxygen began to accumulate. The rate of this oxidation was 2.03 mM/s. We have also used suspensions of cells prepared from the mats to study the kinetics of iron oxidation per cell under various conditions (see abstract by A. Johnston et al.).

Iron oxidation was also dependent on light intensity and was complete at relatively low levels (80-110 W/m^2). No oxidation of iron occurred in these mats when exposed to near infrared (NIR) radiation only, suggesting that bacteriochlorophyll-containing *Chloroflexus* was not performing anoxygenic photoferrotrophy. Vertical profiles of pH within the mat remained constant between 6 and 6.5 in the light and dark.

Studies of photosynthetic carbon fixation using ^{14}C-bicarbonate in mat suspensions showed that photosynthetic carbon fixation was enhanced in the presence of iron and did not occur under NIR radiation only. The rate increased with increasing full spectrum light intensity.

Contrary to previous observations of cells mineralized by iron oxides, the phototrophs in these mats displayed a high degree of cellular integrity and biosignature fidelity. There was excellent preservation of the photosynthetic membranes which allowed positive identification of the cells as they were permineralized with ferrihydrite.

The presence of cyanobacteria in this high iron anoxic environment provides a model with which to study the oxidation rates of iron when controlled solely by the biological process of oxygenic photosynthesis. It is also an excellent system in which to examine iron biomineralization and biosignature formation by these phototrophs. This is relevant to understanding the physiological potential of cyanobacteria to facilitate iron oxidation in the Precambrian.