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## Introduction

- Banded Iron Formations (BIF; Fig.1) are chemical sediments rich in iron and silica that formed as a result of the oxidation of Fe(II) to Fe(III), by either free oxygen, or anoxygenic photoferrotrophic microbes (Garrels et al., 1973).
- BIF are critical proxies for studying Archean to Paleoproterozoic ocean chemistry and Early earth processes.
- On the early Earth, in the absence of oxygen, oxidation of Fe(II) was carried out by anoxygenic photoferrotrophs. These are anaerobic microbes that use light and Fe(II) to produce their own energy.
- Around the time of the Great Oxidation Event (GOE), aerobic cyanobacteria became more dominant and likely became the driving mechanism behind the oxidation of Fe(II) in Paleoproterozoic oceans (Kasting 1992).
- Once Fe(III) was oxidized it would have begun to precipitate as a Fe(III) oxyhydroxide, forming aggregates with cyanobacteria and silica. This led to the formation of dense, heavy clusters that increased the settling rate of all three substances.
- Once at the seafloor, organic carbon from the cyanobacteria became compacted into the BIF precursor sediments and was readily available for consumption by heterotrophic seafloor microbial communities.

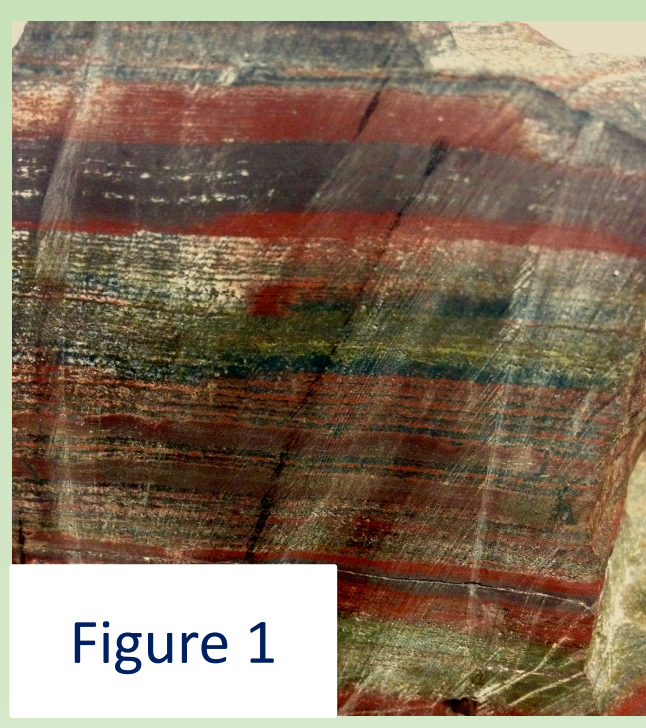


Figure 1

This investigation examines:

- (i) The settling rate of Fe(III), silica, and cyanobacterial aggregates.
- (ii) The amount of organic carbon (cyanobacteria) and iron that settles.
- (iii) The effect that cyanobacteria have on the settling rate of Fe(III).

## Methods

- Liquid cultures of the cyanobacterium *Synechococcus* strain PCC 7002 (Fig.2) were initiated by streaking colonies from petri-dishes (Fig.3) and adding them to 50 mL of A+ media altered to be EDTA deficient and 1 mL of vitamin B12.
- The bacteria was then placed in a 30°C incubator for one week.
- After one week, cultures were transferred into a 500 mL volumetric flask where EDTA deficient A+ media was added to 300mL (Fig.4).



Figure 2



Figure 3

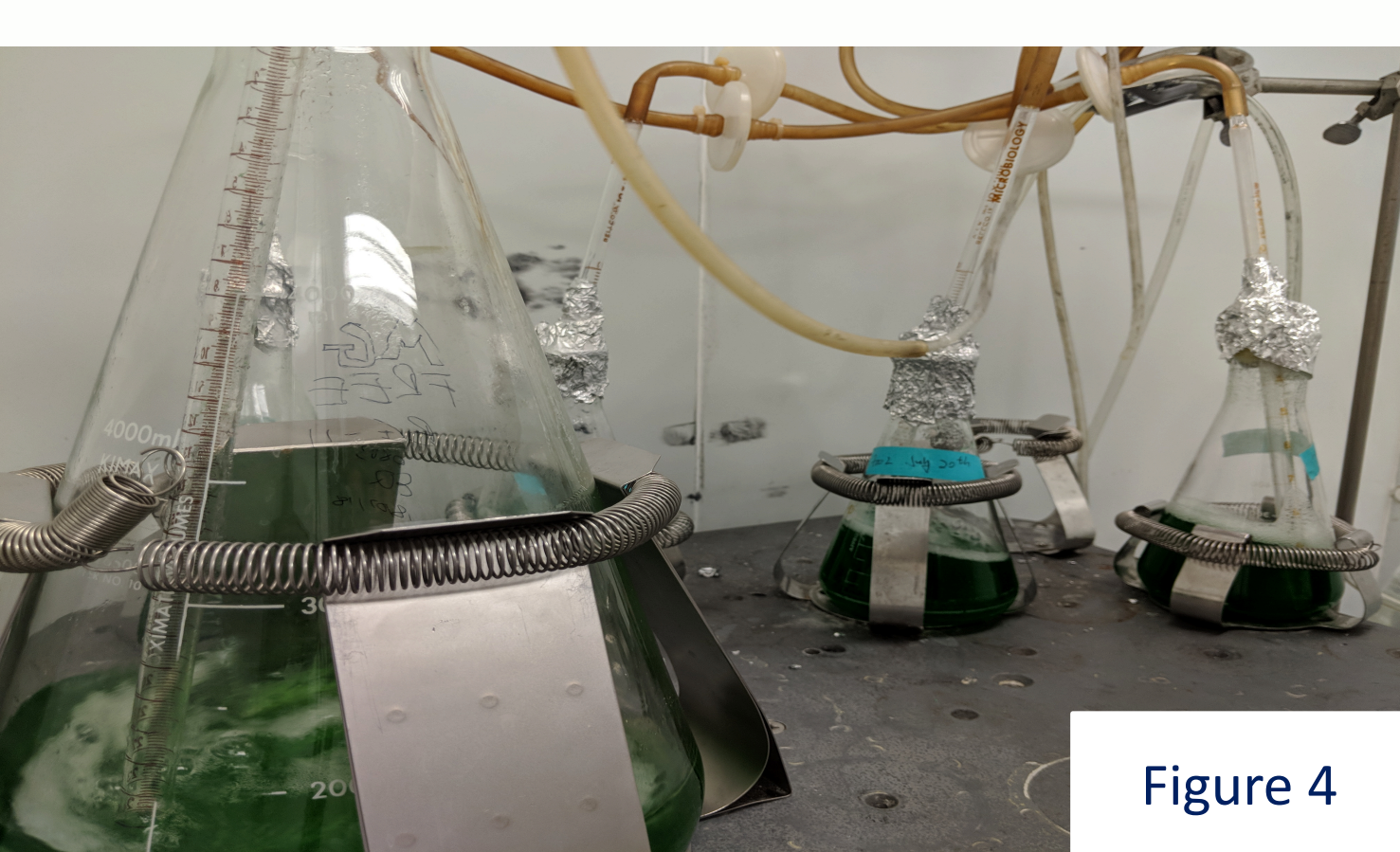


Figure 4

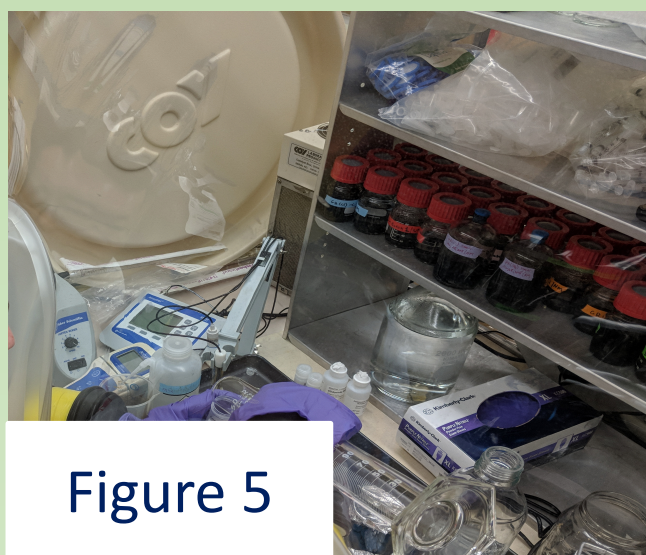


Figure 5

- Anaerobic solutions of FeCl<sub>2</sub>·4H<sub>2</sub>O and Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O were created (Fig.5) using nitrogen purged 18.2mΩ-cm ultrapure water (Fig.6)

- Optical density was measured using A UV-VIS spectrophotometer by transferring 1 mL of liquid culture into a cuvette followed by the reading absorbance at λ=750nm.

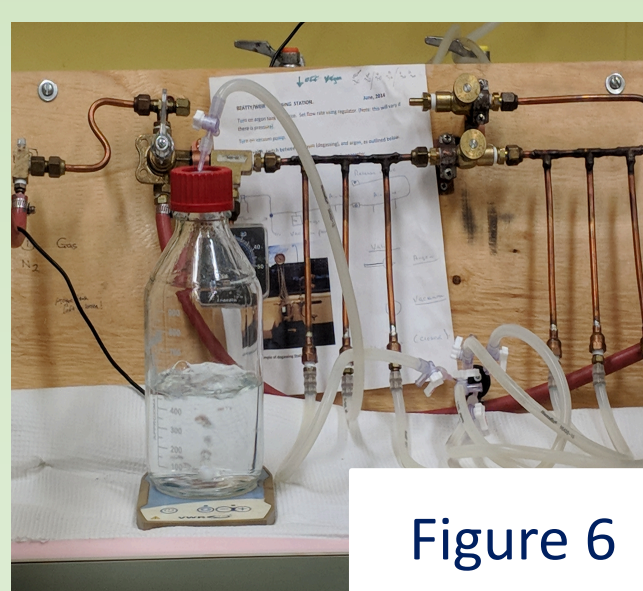


Figure 6

- The flocculation tank was prepared by adding ultrapure water, NaCl, liquid culture, and the FeCl<sub>2</sub>·4H<sub>2</sub>O and Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O solutions (Fig.7).

- Once the metal solutions were added, aggregates began to form and sink to the bottom of the tank.



Figure 7

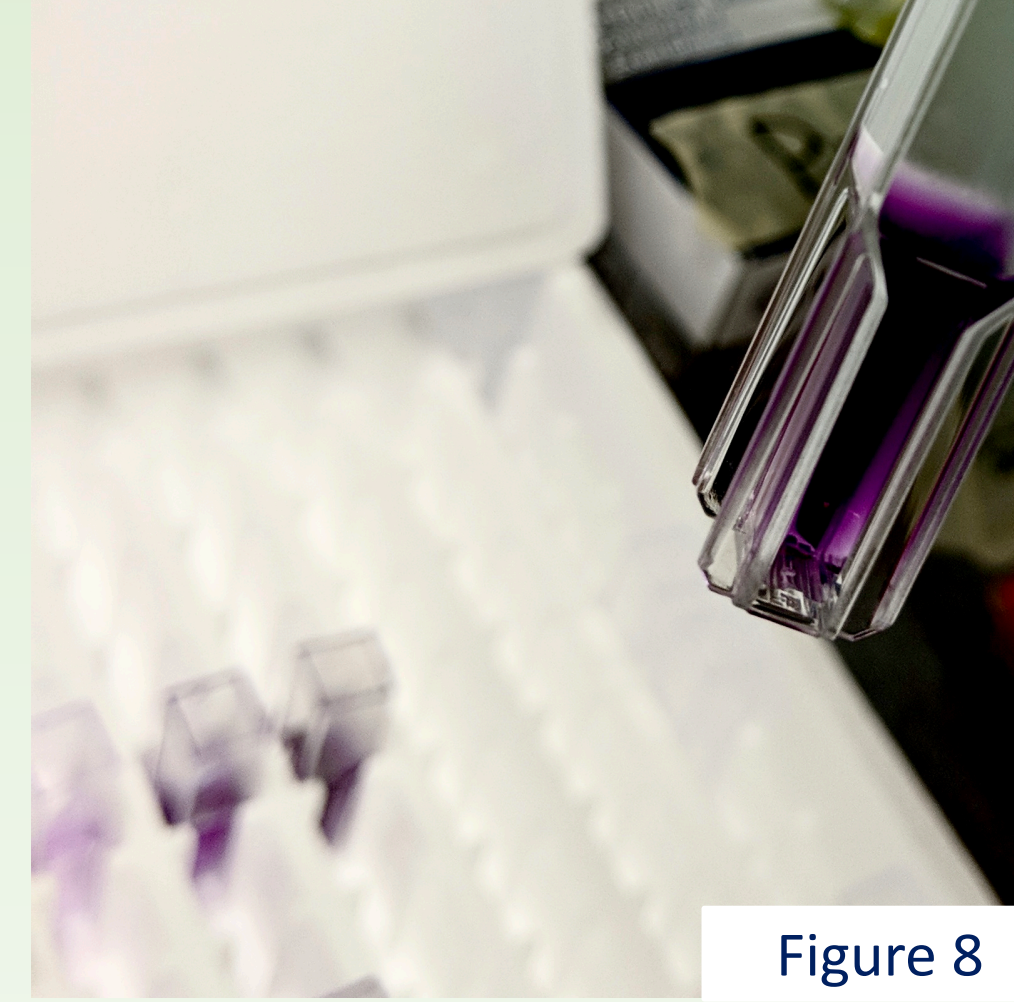


Figure 8

- Fe(II) and Fe(III) concentrations were determined using the ferrozine method, which forms purple complexes with Fe(II) (Fig.8; Violier et al, 2000)
- Different concentrations of Fe(II) result in varied shades of purple (i.e. the darker the purple, the higher the Fe(II) concentration).

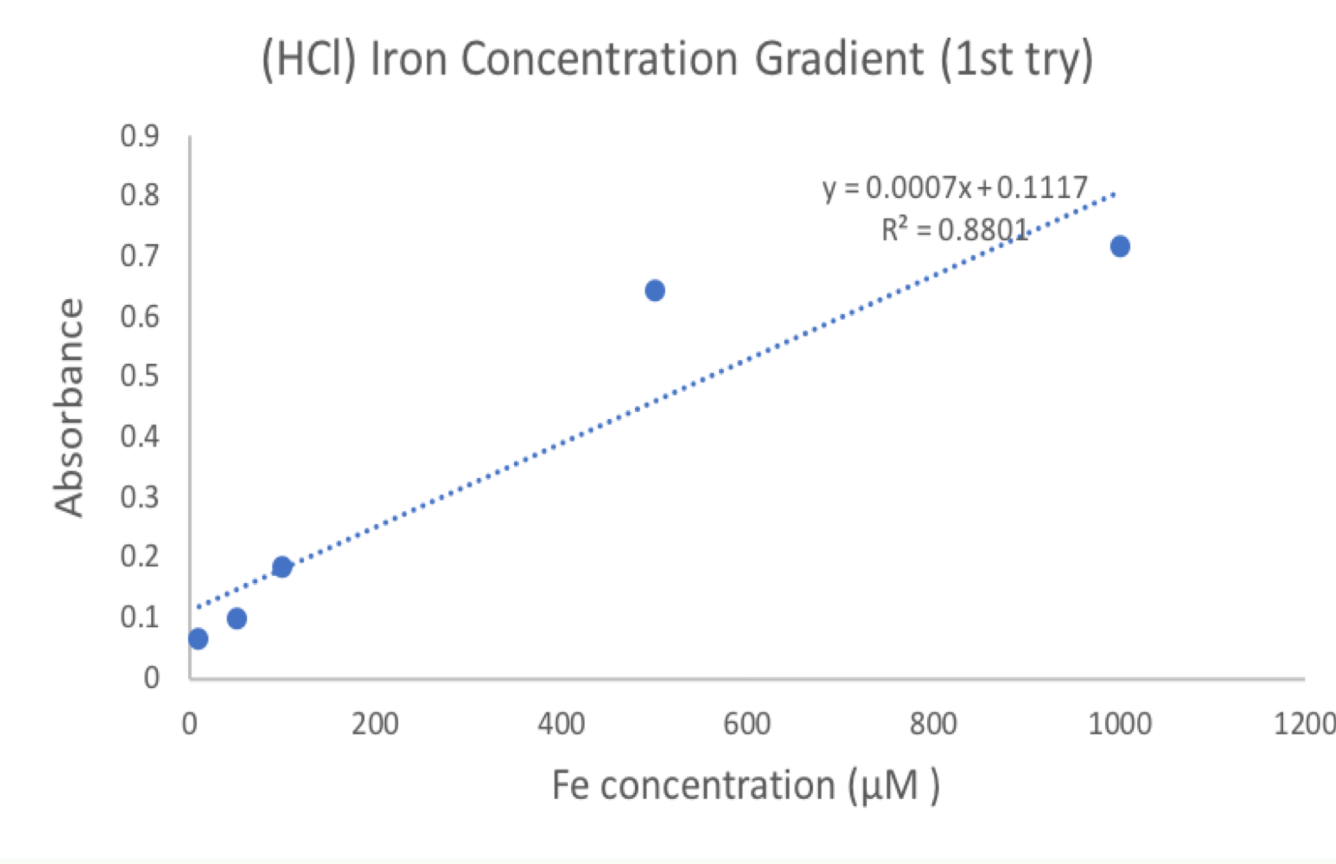


Figure 9. The standard curve of the Fe(II).

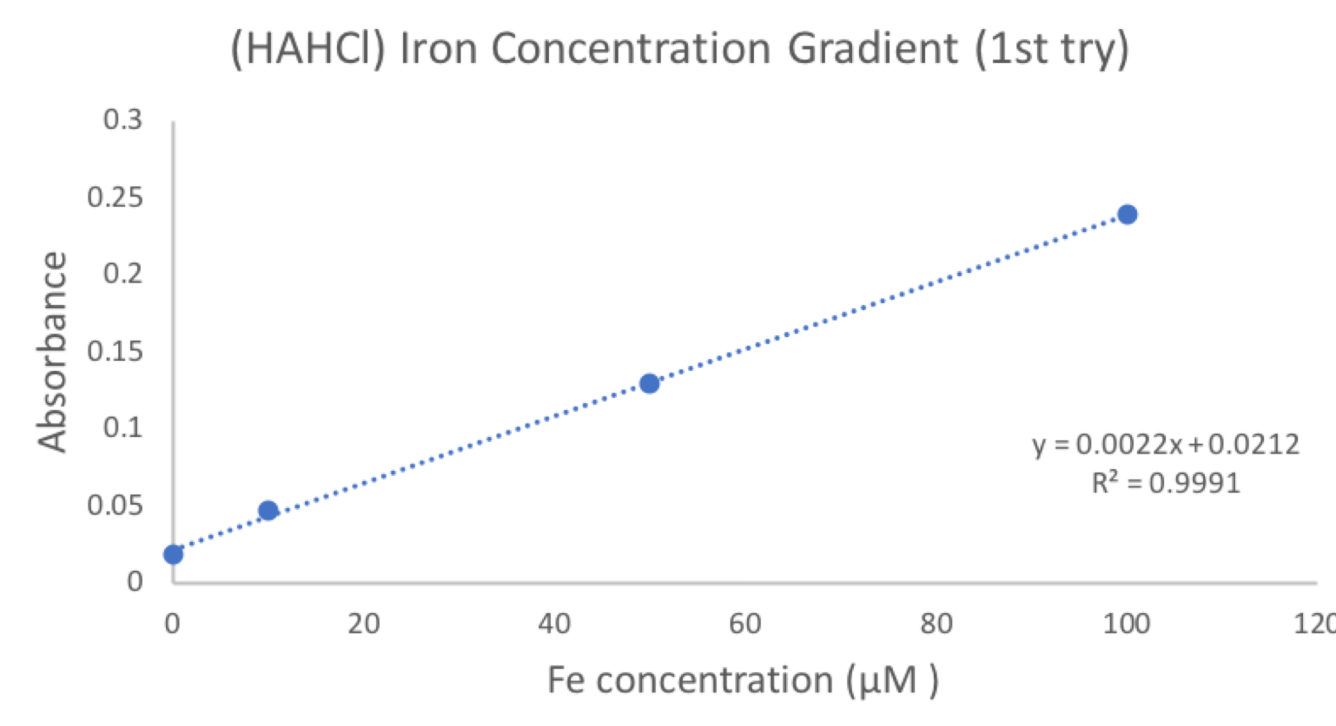


Figure 10. Standard curve for total Fe concentration.

- Fe(II) concentration is determined by adding HCl and ferrozine to sample and measuring the absorbance.
- Total Fe concentration (Fe(II)+Fe(III)) is measured by adding hydroxylamine hydrochloride to sample and remeasuring the absorbance.
- Sample absorbance is then compared to the standard curve and the Fe concentration is determined.

## Results

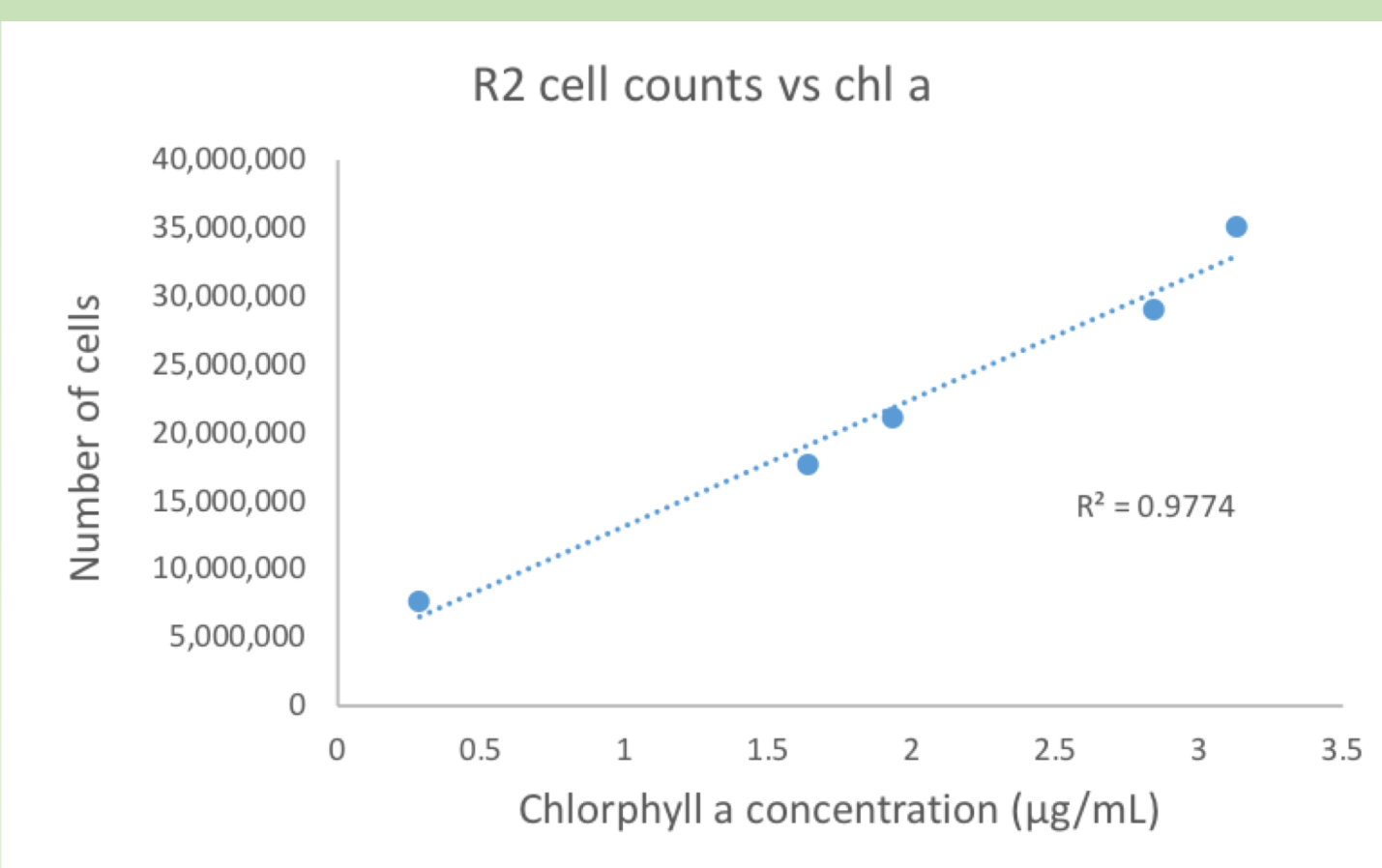


Figure 11. Calibration curve for the number of cyanobacteria cells and the chlorophyll a concentration (μg/mL).

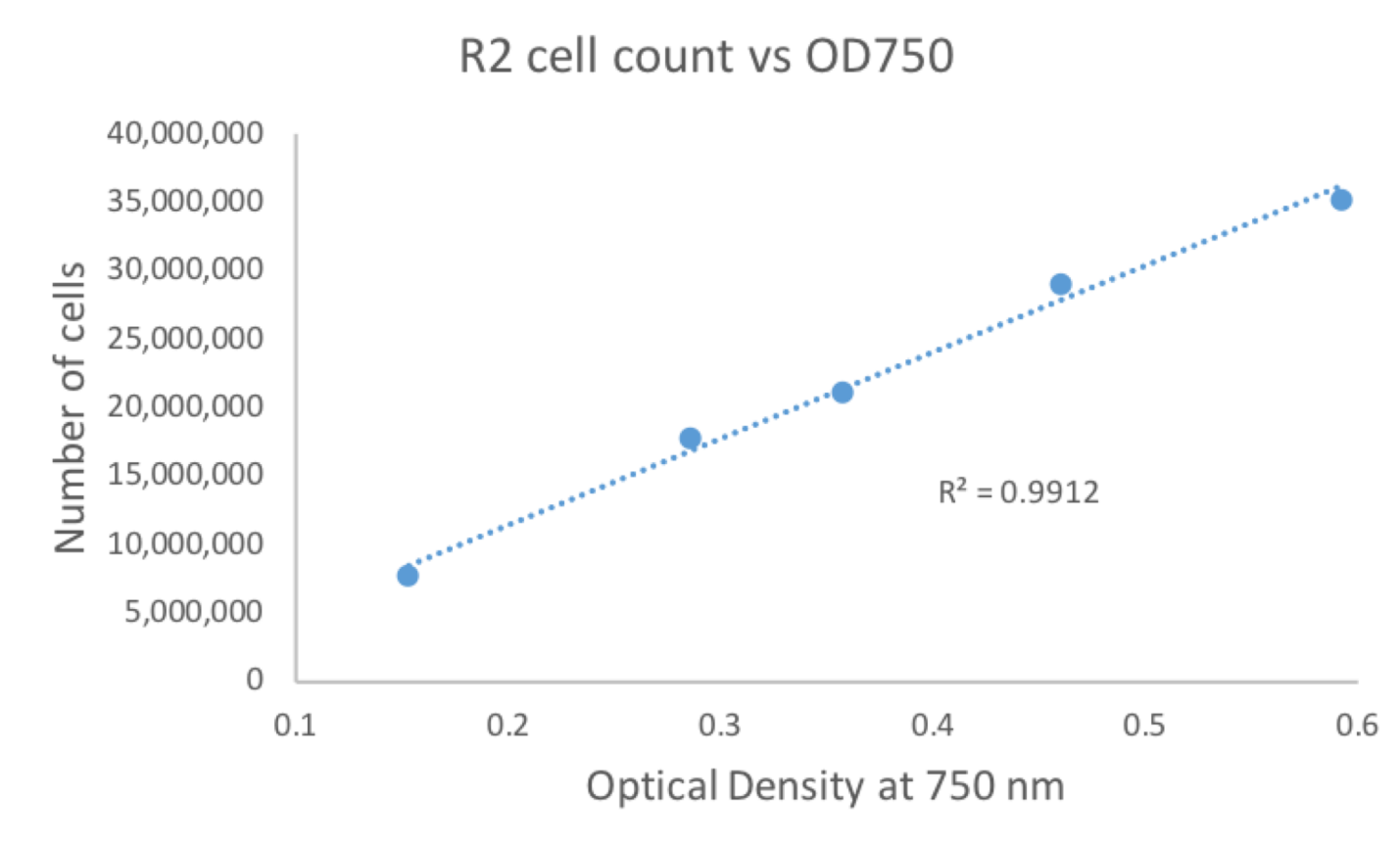


Figure 12. Relationship between the number of cyanobacteria cells in and the OD at a wavelength of 750nm.

- The cells left in suspension was calculated from the the of the graph: R2 Cell Count VS Chl a (chlorophyll a):  
$$\text{Cells} = 9,295,753 * [\text{chl a}] + 3,874,344$$
$$9,295,753 * [0.76288] + 3,874,344 = 10,965,879 \text{ cells}$$
- The number of cells before the experiment began was calculated from the equation of the graph: R2 Cell Count VS OD 750:  
$$\text{Cells} = 62,968,360 * \text{OD} - 1,127,973$$
$$62,968,360 * 0.582 - 1,127,973 = 35,519,613 \text{ cells}$$

### Cells Settled:

$$\text{Cells}_{\text{settled}} = \text{Cells}_{\text{initial}} - \text{Cells}_{\text{final}}$$
$$35,519,613 - 10,965,879 = 24,553,734 \text{ cells}$$

### Amount of Iron Settled:

$$[\text{Fe}]_{\text{settled}} = [\text{Fe}]_{\text{initial}} - [\text{Fe}]_{\text{final}}$$
$$1800\mu\text{M} - 3.09\mu\text{M} = 1796.91\mu\text{M}$$

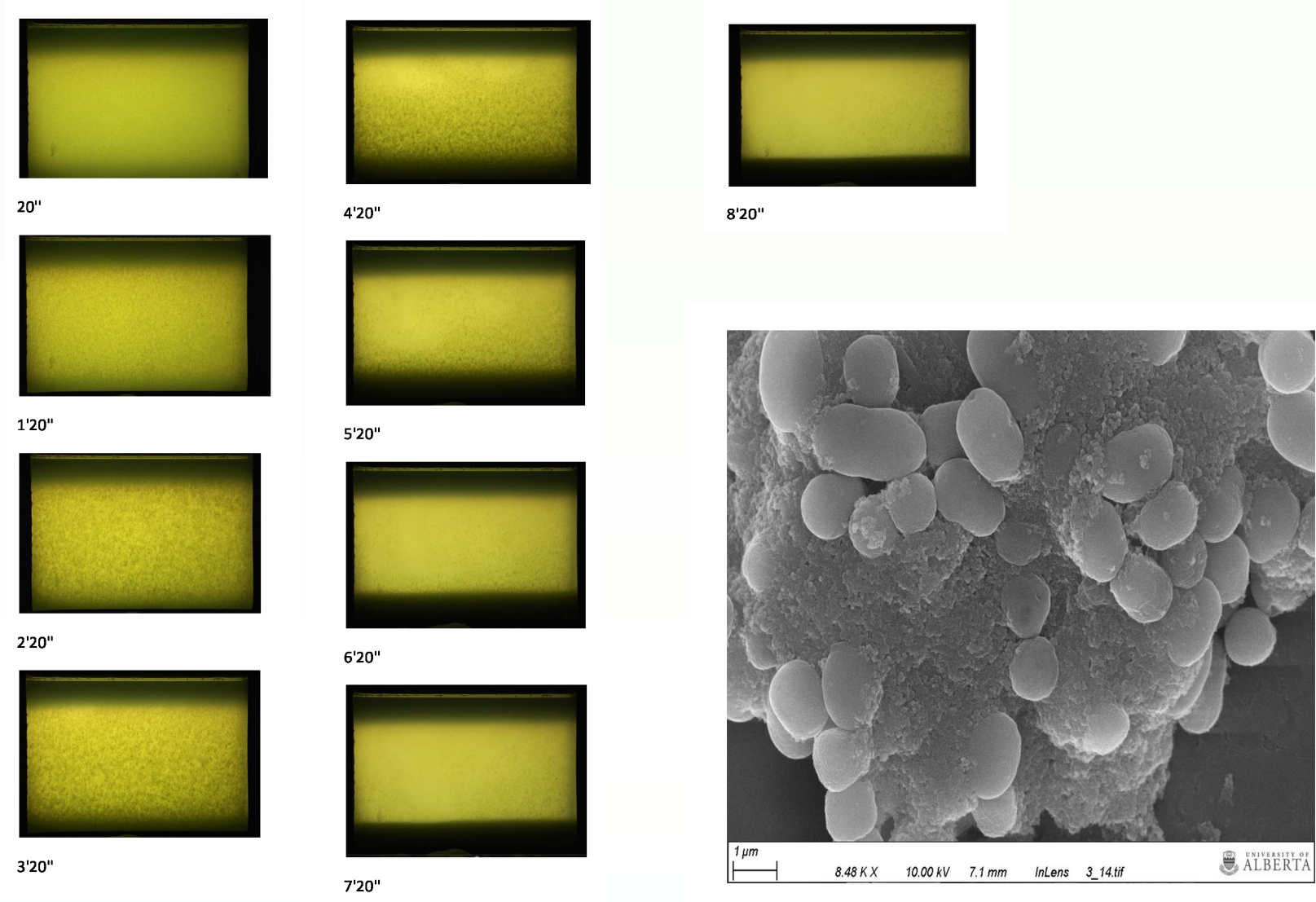


Figure 13. Settlement over ten minutes where the height of the tank water is 10cm.

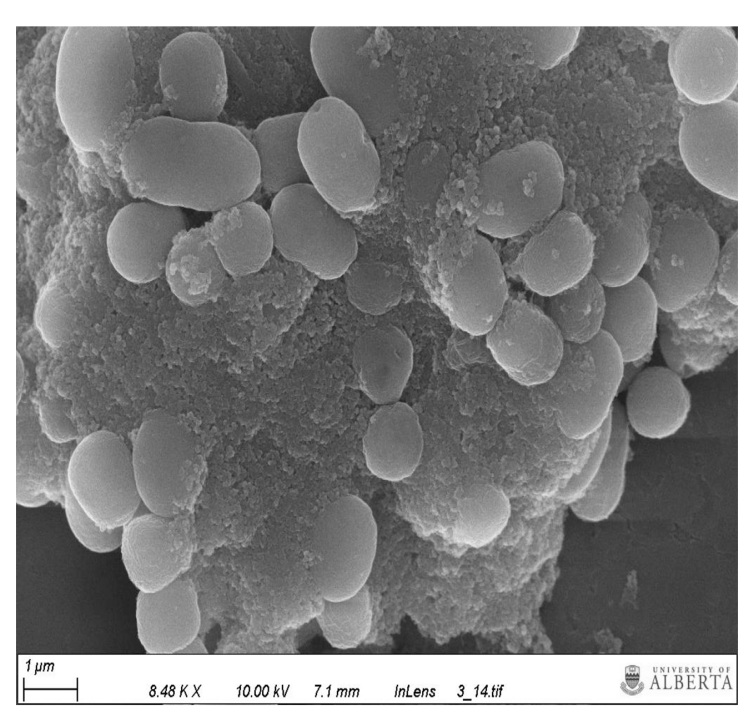


Figure 14. SEM of cyanobacteria, Fe, and silica aggregates.

## Control Experiment

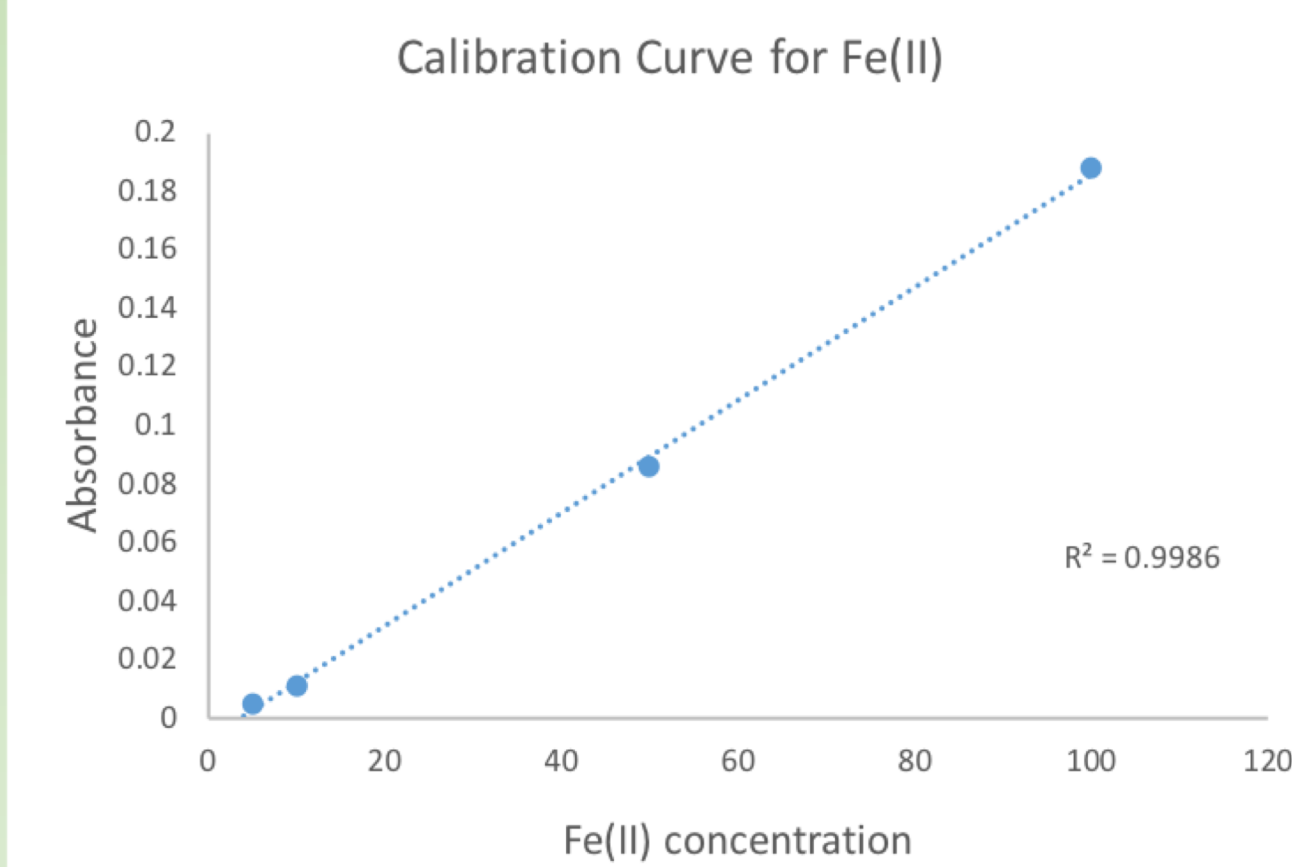


Figure 15. Standard curve for Fe(II) concentration.

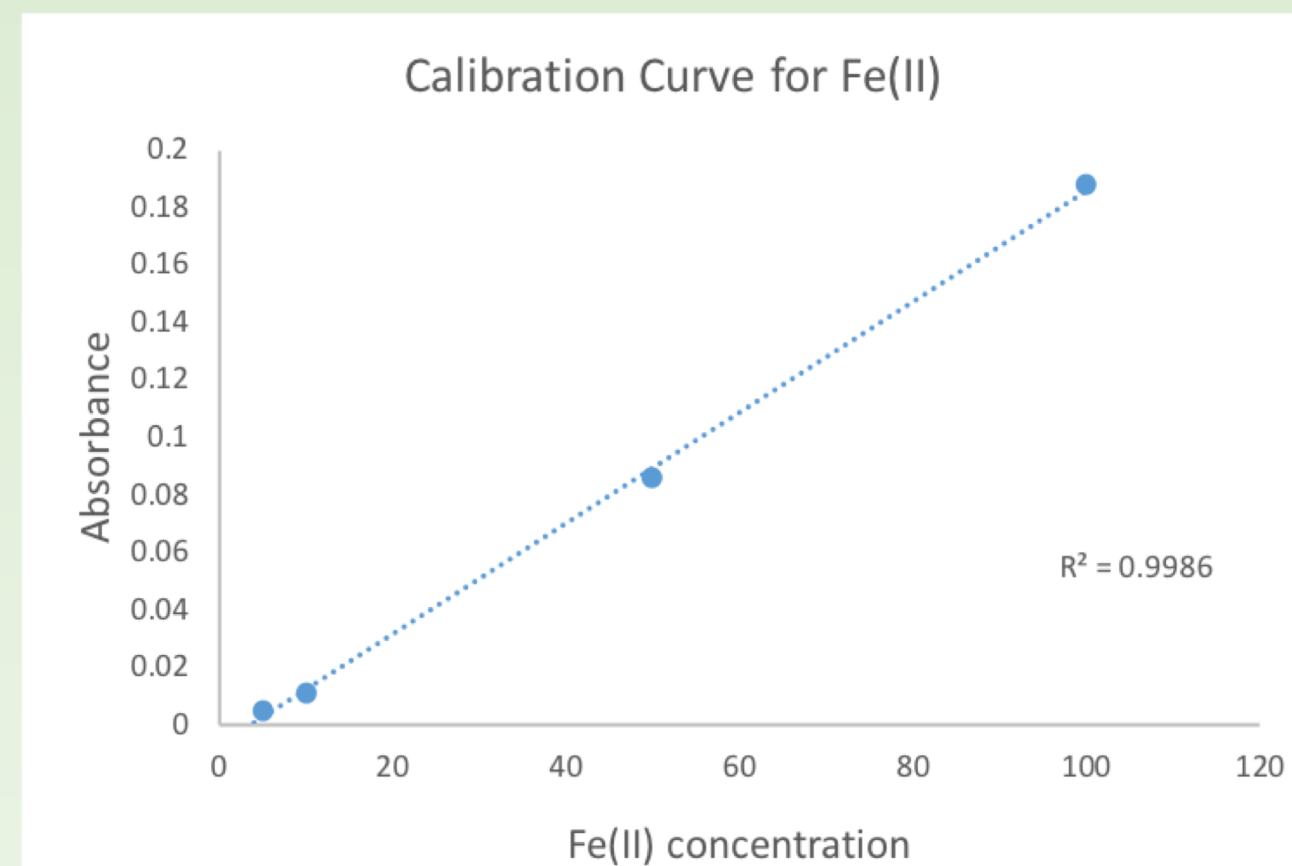


Figure 16. standard curve for total Fe concentration.

### Amount of Iron Settled:

$$[\text{Fe}]_{\text{settled}} = [\text{Fe}]_{\text{initial}} - [\text{Fe}]_{\text{final}}$$
$$142.789 \mu\text{M} - 11.158 \mu\text{M} = 131.632 \mu\text{M}$$

## Conclusions

- From the results, it is clear that more than 2/3 of the bacteria settled, suggesting that many ancient cyanobacteria may have been deposited during the formation of BIFs.
- Because of the large amount of bacteria that sank, the experiment also suggests that there was enough organic carbon to support heterotrophic communities, as cyanobacteria would have been an abundant food source in the sediments.
- With regards to Fe, as over 99% in solution sank to the bottom of the tank in such a short amount of time, it appears that cyanobacteria did in fact help oxidize Fe(II) to Fe(III) while increasing the settling rate. This would have been highly favourable to the formation of BIF deposits.

## References

- Viollier, E., Inglett, P.W., Hunter, K., Roychoudhury, A.N. and Van Cappellen, P., 2000. The ferrozine method revisited: Fe(II) / Fe(III) determination in natural waters. Appl. Geochem, 15: 785-790.
- Garrels RM, Perry EA Jr, Mackenzie FT. 1973. Genesis of Precambrian iron-formations and the development of atmospheric oxygen. Econ. Geol. 68:1173–79.
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