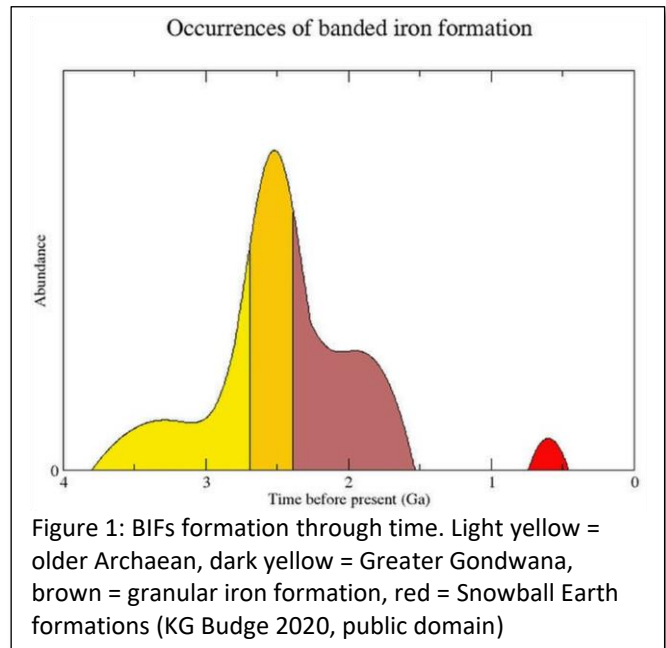




What are Banded Iron Formations (BIFs)?

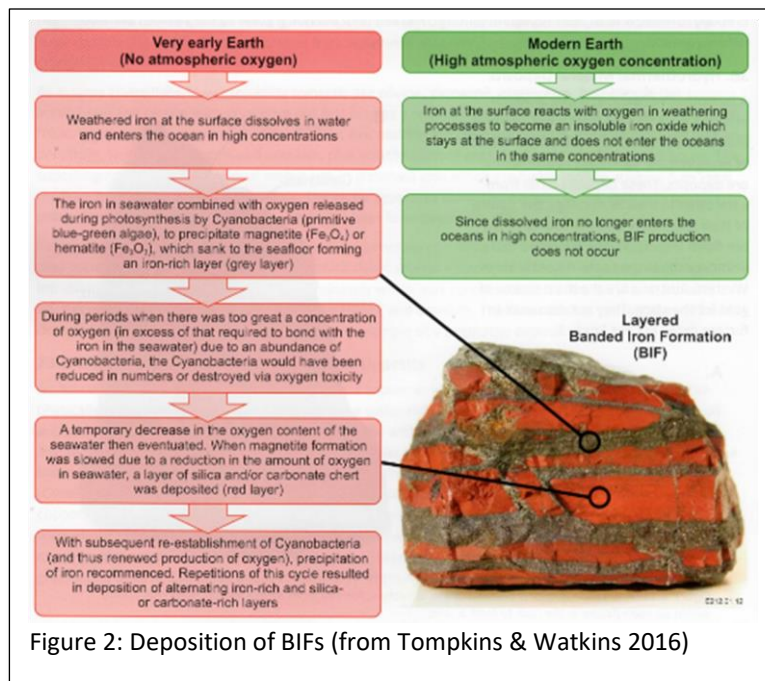
Banded iron formations are large accumulations of iron rich sedimentary rocks that were deposited in shallow marine troughs or basins. Iron rich bands are composed of hematite (Fe_2O_3), magnetite (Fe_3O_4), siderite (FeCO_3) or pyrite (FeS_2). The iron poor bands contain chert (fine-grained quartz) with lesser amounts of iron oxide.

Deposits are tens of kilometres long, several kilometres wide and 150 – 600 metres thick. Large Australian BIFs are found in Proterozoic rocks of the Pilbara craton and Archaean rocks of the Yilgarn craton in Western Australia.



The established explanation – cyanobacteria producing oxygen (from Cloud 1973)

Cloud's (1973) explanation of BIFs as evidence of oxygenic photosynthesis has been taught for at least 20 years in Earth and Environmental Science classes. This idea explains how a major evolutionary innovation in the biosphere changed the geosphere, hydrosphere and atmosphere.





Problems with the established explanation

- BIFs are very old rocks that have been altered since deposition.
- Oxidation of iron does not require oxygen.
- There are many types of photosynthesis (only one produces oxygen).
- New evidence suggests BIFs were created by photoferrotrophy or abiotic processes.

BIFs are very old and have been altered

In the billions of years since their deposition, BIFs have experienced physical and chemical changes as they formed sedimentary rock (diagenesis), as fluid flowed through the layers and as heat caused metamorphism. Thus, it is difficult to find crystals of the original minerals that formed BIFs.

The BIFs that are mined economically are generally 60% - 70% iron and contain no evidence of chert bands. These formations weather extremely rapidly. The exposed BIFs in Western Australia are highly weathered and have been re-cemented with silica from evaporating groundwater. The chert-free BIFs are thought to have lost their silicates very early during diagenesis.

Nodules of chert are used to study the original BIF minerals because chert is nonporous and resists fluid flow. Some researchers proposed that hematite particles found in chert represent the original minerals. They consider magnetite and siderite to be products of diagenesis.

Recent electron microscopy studies indicate that greenalite (iron silicate) is the primary mineral of BIFs. After deposition of the original greenalite, magnetite formed during metamorphism, replacing the original iron silicates and carbonates. The heat of metamorphism can cause this replacement. Less heat is required if water is present (generally from the flow of water through sediment layers).

Oxidation of iron does not require oxygen

In the modern atmosphere and hydrosphere, iron oxide forms easily in the presence of water and oxygen. This is the familiar process of rusting. However, oxidation is a chemical process that involves the loss of electrons. Electron loss can occur without the involvement of oxygen. There are many lineages of Bacteria and Archaea that can use iron as an electron donor, thus oxidising iron. These microbes include the purple and green sulfur bacteria.

Many types of photosynthesis

Photosynthesis uses a light-harvesting pigment to absorb specific wavelengths of light and convert this into chemical energy. Light energy is used to remove an electron from the pigment. This electron is picked up by other molecules and used to power cellular metabolism. The electron lost from the pigment must be replaced.

Oxygenic photosynthesis replaces the pigment electron with an electron produced by splitting a water molecule. This produces oxygen as a byproduct. Oxygenic photosynthesis is used by plants, eukaryotic algae and cyanobacteria.

Resourced by





The most ancient forms of photosynthesis did not produce oxygen. Anoxygenic photosynthesis is still used by a diverse range of Bacteria and Archaea living in lakes, hot springs and soil. Oxygen is not produced as a byproduct because water is not the electron donor. Electron donors for anoxygenic photosynthesis include:

- Hydrogen sulfide (H_2S)
- Elemental sulfur
- Hydrogen (H_2)
- Ferrous iron (Fe^{2+})
- Nitrite (NO_2^-)

Hydrothermal vents and volcanoes would have directly or indirectly supplied these substances. Canfield et al (2006) calculated that an iron-based ecosystem would be the most productive of the anaerobic photosynthetic options. The estimates for iron-based primary production are the best match with observed carbon isotope ratios used to estimate primary production in the Early Archaean. Modern oxygenic ecosystems are 10 times more productive.

Alternate explanations for the formation of BIFs

There are two main explanations for BIFs.

Photoferrotrophy

Photoferrotrophy is an ancient process where Bacteria and Archaea use ferrous ions (Fe^{2+}) for energy (some Bacteria fix inorganic carbon). The byproducts are ferric hydroxide, greenalite and siderite. Some photoferrotrophic bacteria use iron to create magnetite (the main iron oxide in BIFs) within their cells.

Photoferrotrophy is thought to be the first form of photosynthesis, dominating in the Archaean oceans which had high ferrous iron, low sulfide and no oxygen. The formation of BIFs based on photoferrotrophy is shown in Figure 3.

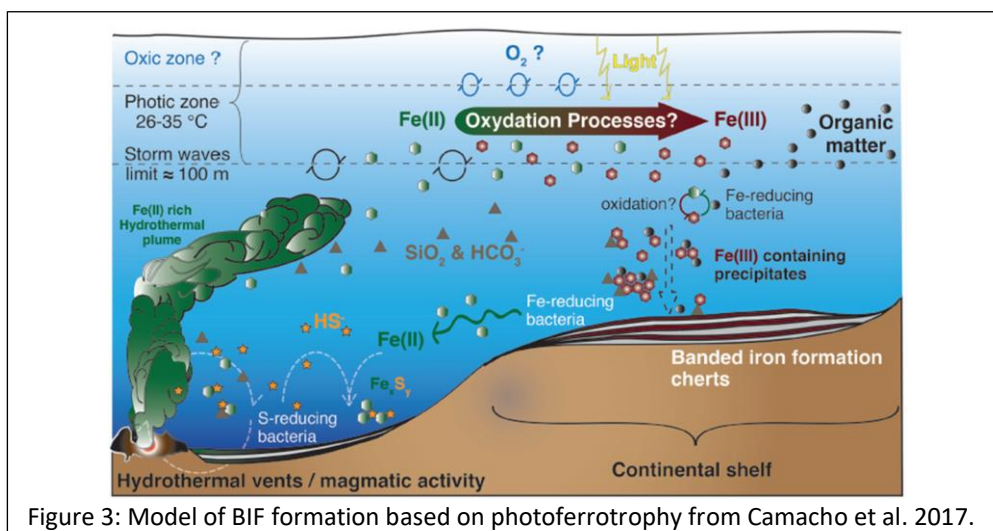


Figure 3: Model of BIF formation based on photoferrotrophy from Camacho et al. 2017.

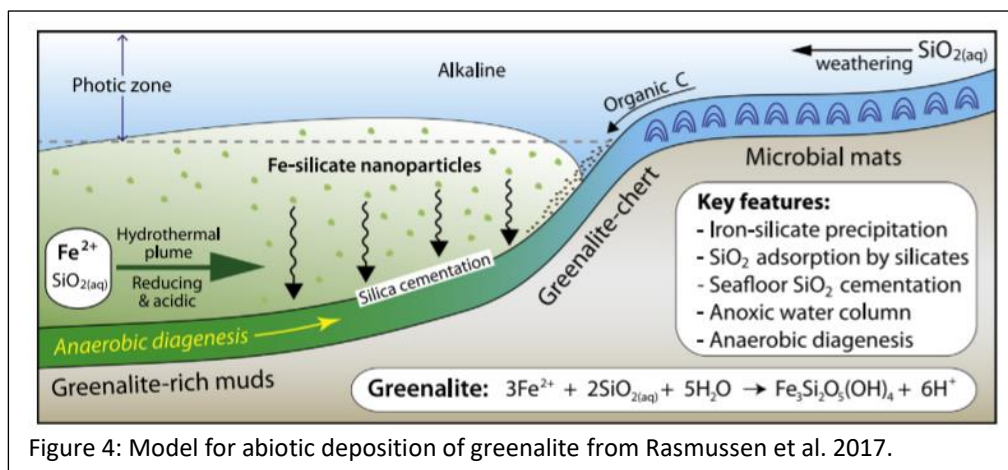


Sulfide levels rose in the Proterozoic, at which time the photoferrothrophic model of BIF formation would have no longer been dominant. In sulfur-rich environments, iron forms iron sulfides and sulfide-driven forms of photosynthesis would have dominated primary production. Genetic evidence suggests that oxygenic photosynthesis arose approximately 2.3 billion years ago, around the time of the Great Oxidation Event and during the last phase of BIF deposition (brown in Figure 1).

Critics of photoferrothrophic and photosynthetic models of BIF formation point to the lack of organic carbon in BIFs. This can be explained if other microbes degraded the organic matter, but perhaps there is a simpler explanation – abiotic processes.

Abiotic processes

Electron microscopy of BIF-hosted cherts indicates that greenalite $[(\text{Fe}^{2+}, \text{Fe}^{3+})_{2-3}\text{Si}_2\text{O}_5\text{OH}_4]$ is the original iron containing mineral in BIFs. The composition of the iron in the greenalite suggests that greenalite formed from abiotic processes that were dependent on pH (Figure 4). Photoferrothrophy produces Fe^{3+} as a product, but the greenalites found in BIF cherts are 80% - 90% Fe^{2+} .



Those who champion the abiotic deposition of BIFs concede that bacteria could have been involved in the process. However, an abiotic process is the simplest explanation with the least steps.

Conclusion

Over the two billion years of their deposition, it is likely that there were several processes involved in the formation of banded iron. Changes in ocean chemistry and the evolution of life determined the relative importance of these processes. Photoferrothrophy, abiotic greenalite deposition and (later) oxygenic photosynthesis are all likely to have had a role at different times.

After deposition, the iron minerals in BIFs were altered through geological and chemical processes. Removal of silicates occurred early in diagenesis as fluids were removed from the deposits. Heat led to the formation of magnetite during metamorphic processes.



References:

- Camacho A, Walter XA, Picazo A, Zopfi J (2017). Photoferrotrophy: remains of an ancient photosynthesis in modern environments. *Frontiers in Microbiology* **8**: 323. doi: 10.3389/fmicb.2017.00323 (Open Access)
- Canfield DE, Rosing MT, Bjerrum C (2006). Early anaerobic metabolisms. *Philosophical Transactions of the Royal Society B* **361**: 1819-1836. doi: 10.1098/rstb.2006.1906 (Open Access)
- Cloud P (1973). Paleoecological significance of the banded Iron formation. *Economic Geology* **68**(7):1135-1143.
- Griffin BM, Schott J, Schink B (2007). Nitrite, an electron donor for anoxygenic photosynthesis. *Science* **316**: 1870.
- Hanada S (2016). Anoxygenic photosynthesis – a photochemical reaction that does not contribute to oxygen reproduction. *Microbes and Environments* **31**(1): 1-3. doi: 10.1264/jsme2.ME33101rh (Open Access)
- Johnson JE, Muhling JR, Cosmidis J, Rasmussen B, Templeton AS (2018). Low-Fe(II) Greenalite was a primary mineral from Neoproterozoic oceans. *Geophysical Research Letters* **45**: 3182-3192. doi: 10.1002/2017GL076311 (Open Access)
- Lascelles DF (2012). Banded iron formation to high-grade iron ore: a critical review of supergene enrichment models. *Australian Journal of Earth Sciences* **59**(8): 1105-1125.
- Rasmussen B, Muhling JR (2018). Making magnetite late again: evidence for widespread magnetite growth by thermal decomposition of siderite in Hamersley banded iron formations. *Precambrian Research* **306**: 64-93.
- Rasmussen B, Muhling JR, Suvorova S, Krapež B (2017). Greenalite precipitation linked to the deposition of banded iron formations downslope from a late Archean carbonate platform. *Precambrian Research* **290**: 49-62.
- Soo RM, Hemp J, Parks DH, Fischer WW, Hugenholz P (2017). On the origins of oxygenic photosynthesis and aerobic respiration in Cyanobacteria. *Science* **355**: 1436-1440.
- Strbak O, Dobrota D (2019). Archean Iron based metabolism analysis and the photoferrotrophy-driven hypothesis of microbial magnetotaxis origin. *Geomicrobiology Journal* **36**(3): 278-290.
- Tomkins DE, Watkins JM (eds.) (2016). *Exploring Earth and Environmental Science Year 12, 2nd Edition*. Earth Science Western Australia: Perth.