



The formation of magnetite in the early Archean oceans



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ABSTRACT

Banded iron formations (BIFs) are iron- and silica-rich chemical sedimentary rocks that were deposited throughout much of the Precambrian. The biological oxidation of dissolved Fe(II) led to the precipitation of a ferric oxyhydroxide phase, such as ferrihydrite, in the marine photic zone. Upon burial, ferrihydrite was either transformed into hematite through dehydration or it was reduced to magnetite via biological or abiogenic Fe(III) reduction coupled to the oxidation of buried microbial biomass. However, it has always been intriguing as to why the oldest BIFs are characteristically magnetite-rich, while BIFs formed after the Neoproterozoic are dominated by hematite. Here, we propose that some magnetite in early Archean BIF could have precipitated directly from seawater through the reaction of settling ferrihydrite and hot, Fe(II)-rich hydrothermal fluids that existed in the deeper waters. We conducted experiments that showed the reaction of Fe(II) with biogenic ferric iron mats under strict anoxic conditions lead to the formation of a metastable green rust phase that within hours transformed into magnetite. Our model further posits that with the progressive cooling and oxidation of the Earth's oceans, the above reaction shuts off, and magnetite was subsequently restricted to reactions associated with diagenesis and metamorphism.

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1. Introduction

Banded iron formations (BIFs) are one of the most important sedimentary archives for understanding Precambrian ocean chemistry and the evolution of the marine biosphere (e.g., Bekker et al., 2010, 2014). Two types of BIF have been recognized with respect to their depositional setting. Algoma-type BIF are stratigraphically linked to submarine-emplaced volcanic rocks in greenstone belts and, in some cases, with volcanogenic massive sulfide deposits (Ohmoto, 2003). They range in age from Eoarchean to early Paleoproterozoic, which possibly reflects the absence of large, stable cratons at that time (Isley and Abbott, 1999). Superior-type BIF, which becoming common in the late Archean to Paleoproterozoic, were deposited in the near-shore continental-shelf environments, and are typically interbedded with carbonates, quartz arenite, and black shale, but with only minor amounts of volcanic rocks (Klein, 2005). Unlike most Algoma-type BIF, which rarely extend for more than 10 km along strike and are usually not more than 50 m thick, the Superior-type BIF can be extremely laterally extensive, with original extents estimated in some cases to be over 100,000 km² (Morris, 1993; Isley and Abbott, 1999). Superior-type

BIF first appear in the late Archean, when construction of large continents first began. From ca. 2.6 to ca. 2.4 Ga, global mafic magmatism culminated in the deposition of giant Superior-type BIF in South Africa, Australia, Brazil, Russia, and Ukraine (Isley and Abbott, 1999).

BIF are dominated by silica (~40–50%) and iron oxides (~20–40%). The mineralogy of the least metamorphosed BIF consists of chert (SiO₂), magnetite (Fe₃O₄), hematite (Fe₂O₃), siderite (FeCO₃) and various iron-silicate minerals, such as greenalite ((Fe)₃Si₂O₅(OH)₄): the presence of both ferric and ferrous minerals gives BIF an average oxidation state of Fe^{2.4+} (Klein, 2005). It is generally agreed that none of the minerals in BIF are primary, but that instead, the minerals reflect both diagenetic and metamorphic overprinting. For instance, hematite is believed to be a dehydrated product of a ferric hydroxide precursor, such as ferrihydrite, precipitated in the photic zone via enzymatic oxidation (Kappler et al., 2005) or oxidation by O₂ derived from oxygenic cyanobacteria (Planavsky et al., 2014). This view was recently supported by Sun et al. (2015) who conducted high resolution transmission electron microscopy (TEM) and selected area electron diffraction (SAED) of fine mineral structures in BIF from the 2.73 Ga Abitibi greenstone belt in northwestern Canada and the 2.46 Ga Kuruman Iron Formation in South Africa to ascertain the timing and paragenesis of hematite. Sun et al. (2015) interpreted that the 3–5 nm ultrafine hematite crystals in the hematite bands and those submicrometer

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(sub)ehedral hematite crystals randomly distributed in the chert matrix of transitional zones between iron oxide- and chert-rich bands were directly dehydrated from a precursor ferric hydroxide phase.

In terms of magnetite, a number of petrographic studies have described the mineral as being of sedimentary origin. For instance, Krapež et al. (2003) reported several forms of diagenetic magnetite, including (1) disseminated grains within but obscuring sedimentary laminae, (2) laminated beds that clearly truncated sedimentary layering, (3) layer-discordant veins, and (4) cleavage fills. Ewers and Morris (1981) even suggested that most magnetite in the BIF of the 2.48 Ga Dales Gorge Formation of Western Australia was secondary by showing overgrowth of a fine-grained ferric hydroxide precursor. Recently, Li et al. (2013) proposed a model to account for magnetite formation in BIFs that included a three-stage sequence, beginning with the biomineralization of magnetite by dissimilatory Fe(III) reduction (DIR) of an initial ferric iron-rich sediment coupled to the oxidation of dead phytoplankton biomass, followed by magnetite crystal aging, and ultimately pressure-temperature induced abiotic growth of the biogenic magnetite during metamorphism.

Five lines of evidence are in agreement with the notion that magnetite formation during diagenesis was initially driven by DIR. First, extant hyperthermophilic *Bacteria* and *Archaea* branch deeply in the universal phylogenetic tree (i.e., they represent an ancient metabolism) and can reduce Fe(III). Second, highly negative $\delta^{56}\text{Fe}$ values in magnetite-rich BIF samples as old as 2.9 Ga have been observed and are comparable to the negative fractionations measured in experimental culture with DIR bacteria (e.g., Johnson et al., 2008). Third, Li et al. (2011) conducted detailed crystallochemical analysis of magnetite from the Dales Gorge Member BIF and reported magnetite with a lattice constant and $\text{Fe}^{2+}/\text{Fe}^{3+}$ stoichiometry very similar to those produced by DIR bacteria including *Geobacter*, *Shewanella* and *Thermoanaerobacter*. Fourth, biogenic magnetite crystals have very pure chemical compositions, which is regarded as one of the major criteria for assigning a biogenic origin to magnetite (Li et al., 2011) – magnetite in BIF can also have a pure end-member composition (Gole, 1981). Fifth, recent experimental low-grade alteration of biogenic magnetite demonstrated how the fine-grained magnetite produced via DIR (a few hundred nm or smaller in size) can grow in size to nearly 1 micron upon reaction of ferrihydrite and microbial biomass under simulated low-grade metamorphic conditions (Li et al., 2013).

Despite the wide acceptance of a secondary origin for magnetite in BIF, it has always been puzzling why BIFs from the early Archean are predominantly composed of magnetite. For instance, the ~ 3.7 Ga BIFs from the Isua Supracrustal Belt (ISB) in Western Greenland (Frei and Polat, 2007; Czaja et al., 2013), 3.05–2.95 Ga Mount Gibson BIF in Western Australia (Lascelles, 2006), and 2.98 Ga West Rand Group of the Witwatersrand Supergroup, South Africa (Smith et al., 2013) contain mostly magnetite as the iron oxide phase. Gross (1986) reported that the early BIFs (prior to 2.6 Ga) have higher $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios in the oxide facies than those in the late stage, indicating a relatively high amount of magnetite in the early deposited BIFs. It is observed that the Archean BIFs are characterized by not only high abundance of magnetite, but also their high grade metamorphic grades (Klein, 2005). For example, the BIF of ISB is of amphibole metamorphic grade and with almost 100% magnetite as its oxide phase, but Fe-isotopic compositions of both stratigraphic bands and magnetite crystals within bands show features not influenced by metamorphic fluids (Frei and Polat, 2007; Czaja et al., 2013). By contrast, BIFs deposited after 2.6 Ga show a dramatic increase in hematite content. For instance, the 2.48 Ga Dales Gorge Formation (Li et al., 2011) and the 1.9–1.8 Ga Frere Formation in Western Australia (Klein, 2005) are mostly composed of hematite, as are the

many Neoproterozoic BIFs (Klein, 2005). On a related note, Gole (1981) showed that under the same grade of metamorphic alteration, $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the magnetite-rich BIF is not higher than that of coexisting shale with high content of organic matter, implying later diagenetic or metamorphic processes might not be able to produce substantial amount of magnetite in BIFs. In terms of organic carbon content in BIF, it is extremely low and there is also no significant variation through time (Klein, 2005), suggesting that there was unlikely to have been more biomass production in the early Archean oceans than thereafter. In other words, the excess magnetite might not be a reflection of more organic carbon burial or enhanced DIR. Moreover, because negative $\delta^{56}\text{Fe}$ values are not found in the sedimentary record prior to around 2.9 Ga, Johnson et al. (2008) suggested that DIR did not have a large impact on the marine sedimentary record before that time.

Based on oxygen isotopic thermometry and silicon isotopic compositions in early Archean cherts, it has been estimated that seawater temperature could have been as high as 55–85 °C (Knauth, 2005). Therefore, it is possible that the higher magnetite content in Archean Algoma-type BIF might be due to the reaction of hot, Fe(II)-rich seawater with primary ferric hydroxides; the latter formed via photosynthetic Fe(II) oxidation – photoferrotochy – because to date this is the most accepted model in the absence of free oxygen (see Kappler et al., 2005; Konhauser et al., 2007; Pecoits et al., 2015). In other words, the key ingredients for the early formation of magnetite in the hot seawater rich with Fe(II) and ferric hydroxide precipitation were available in that window of time, but as the mean ocean temperature cooled and as the ocean water column became gradually oxygenated on the shelf, hydrothermal fluids cooled upon mixing, and ultimately the mechanism for magnetite formation ceased to exist. Certainly the REE patterns in Algoma-type BIFs, specifically the shale normalized europium (Eu) anomalies, have been central in showing that Archean BIFs record a strong influence of high-temperature hydrothermal fluids on the seawater dissolved REE (e.g., Jacobsen and Pimentel-Klose, 1988; Derry and Jacobsen, 1990; Isley and Abbott, 1999; Smith et al., 2013). In contrast, the REE patterns of BIFs precipitated in the Paleoproterozoic demonstrate waning hydrothermal input at that time (Derry and Jacobsen, 1990).

In this study we experimentally test the hypothesis that in the early Archean ocean, the episodic reaction of hot Fe(II)-rich hydrothermal fluids with biogenic ferric hydroxide led to the precipitation of magnetite. We reacted microbial induced ferric oxyhydroxides precipitates with dissolved Fe(II) under strictly anaerobic conditions and found the formation of magnetite, with green rust (GR) as the intermediate phase at temperatures in excess of 50 °C.

2. Sample and methods

2.1. Sample preparation

In this study we used ferrihydrite mats produced by *Gallionella* and *Leptothrix* from the Low Pond of Aberdeen Country Park, Hong Kong. Although these mats do not contain photoferrotochy species as predicted for the Eoarchean oceans, ferrihydrite has been proved to be the only ferric oxyhydroxide in the Fe(II)-oxidizing mat (Lv et al., 2016). The low organic matter in those ferric iron biomats was suggested to be comparable to the biological precipitation of ferric oxyhydroxide precursors from the ferruginous ocean (Kappler et al., 2005; Swanner et al., 2015). By using this ferrihydrite mat, we could also test the possible role biomass might have played in the conversion of ferrihydrite to more stable iron oxides at higher temperatures in the Archean ferruginous waters.

The ferrihydrite mats of *Gallionella*–*Leptothrix* were returned to the laboratory and suspended in 0.05 M HEPES (2-[4-(2-hydr-

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