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Geneses and evolutions of iron-bearing minerals in banded iron formations of >3760 to ca. 2200 million-year-old: Constraints from electron microscopic, X-ray diffraction and Mössbauer spectroscopic investigations

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A B S T R A C T

Minerals preserved in banded iron formations (BIFs) are diagenetic and/or metamorphic rather than primary. Knowing their geneses and evolutions are essential for understanding the interactions between the atmosphere, ocean and biosphere in the first two billion years of life history on Earth. Here we use high resolution electron microscopy, X-ray diffraction and Mössbauer spectroscopy to investigate the mineralogy of six BIFs aged from >3760 Ma to ca. 2200 Ma with a variety of genetic conditions. The results reveal that each major iron mineral (magnetite, hematite, carbonate and silicate) has a range of structural and morphological features that represent different geneses and evolutionary histories. Euhedral magnetite crystals with homogeneous internal structures and compositions, 3–5 nm hematite particles aggregated in iron-rich bands and submicrometer-sized euhedral hematite in chert matrix of Fe-Si transitional bands are identified to have transformed from precursors directly precipitated from seawaters. These minerals retain some primary environmental information when BIFs are deposited. The other mineral phases display features of alteration due to multi-redox reactions, hydrothermal or supergene processes, such as crosscutting, mineral replacement or overgrowth, deformation, fracture and porous structures that have overprinted the primary signatures. Such minerals include (1) massive magnetite with fragmentation structures, (2) partly to completely oxidized magnetite crystals, (3) acicular/fibrous hematite in fractures or iron and silica layering, (4) microplaty hematite, (5) hematite oxidized from other Fe(II)-bearing minerals (e.g., magnetite and stilpnomelane), (6) carbonates with heterogeneous chemical compositions, (7) carbonates replacing other minerals (e.g., siderite thin film coating the euhedral magnetite crystals), (8) irregular carbonate cementing other minerals (e.g., magnetite), (9) preferentially orientated fibrous/spindle-like silicates cutting iron- and silica-rich bands and, (10) massive silicate pieces. This study provides detailed mineralogical and petrologic characterizations of BIF minerals that can serve as a reference for future *in situ* geochemical measurements by recent developed techniques.

1. Introduction

Banded iron formations (BIFs) are sedimentary rocks characterized by alternating iron- and silica-rich bands. They were distributed planetary-wide and formed in the first two billion years since life emerged on the Earth (e.g., Klein, 2005; Bekker et al., 2010, 2014). The deposition of BIFs are linked to the Earth's early environmental change and biospheric evolution (e.g., Holland, 1984; Canfield, 1998; Poulton et al., 2004; Kump, 2008; Bekker et al., 2010, 2014). For instance, the Great Oxidation Event (GOE) at 2.45–2.32 Ga is thought to have resulted in a dramatic decline of BIF deposition, although it is still debated whether dissolved Fe(II) in the seawater was removed due to oxidization (Holland, 1984) or sulfidation of the deep ocean (e.g., Canfield, 1998; Poulton et al., 2004). Iron-oxidization bacteria (Widdel et al., 1993; Konhauser et al., 2002; Kappler et al., 2005) and oxygenic photosynthesis have contributed to the precipitation of iron minerals in BIFs (e.g., Konhauser et al., 2002, 2007). Iron-reducing bacteria might have also played important roles at early diagenetic stages (Nealson and Myers, 1990) by enzymatic reduction of Fe (III) and inducing the mineralization of magnetite (e.g., Lovley and Phillips, 1986; Nealson and Myers, 1990; Li et al., 2013c). Therefore, minerals in BIFs may bear information on the marine

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environments and biological processes in the Archean to Paleoproterozoic oceans.

Understanding the geneses and evolutionary histories of minerals enables the full comprehension on data obtained from the minerals in BIFs, and hence, allows accurate interpretations of the contemporary environments and biological processes. However, all minerals now present in BIFs are not primary. Their original features have been obliterated at diagenetic to metamorphic stages (e.g., Bekker et al., 2010, 2014). Major mineral compositions of BIFs are chert/quartz, magnetite, hematite, carbonates (siderite and Fe-dolomite to ankerite series) and a few silicates (e.g., greenalite, stilpnomelane, riebeckite, minnesotaite and grunerite) (e.g., Klein, 2005; Bekker et al., 2010, 2014). Previous studies on the petrology of BIFs were predominantly based on field or conventional optic microscopic observations at relatively low resolutions (e.g., Morris, 1993; Rasmussen et al., 2014). However, as a typical chemical sedimentary rock, BIFs are made of minerals characterized by their submicron to nanometer sizes (Bekker et al., 2010, 2014; Li, 2014). Many petrographic or mineralogical microstructures that may reflect their genetic environments could be overlooked by optic observations (e.g., Li 2014; Sun et al. 2014). This has led to controversial interpretations on the geneses of some minerals (e.g., Trendall and Blockley, 1970; Ayres, 1972; Taitel-Goldman and Singer, 2002; Li et al., 2013c) and arose disputing opinions on iron oxidization and even the necessity of microbes for the deposition of BIFs (e.g., Ahn and Buseck, 1990; Konhauser et al., 2002, 2007; Rasmussen et al., 2013, 2014). For example, hematite in BIFs were once suggested as a secondary mineral with its Fe^{2+}-precursor being oxidized by post-depositional oxic fluids and based on this petrographic observation, the Fe(II)-to-Fe(III) oxidization in the overlying seawaters of BIFs was questioned (Rasmussen et al., 2014). However, recent high-resolution observations on BIFs revealed that at least some hematite (3–5 nm ultrafine particles and submicrometer-sized euhedral crystals) was directly dehydrated from ferric oxyhydroxide precursors, indicating that photosynthetic Fe(II) oxidization indeed occurred in ancient seawaters (Sun et al., 2015).

Toward a better understanding of the geneses and evolutionary histories of minerals in BIF and an accurate interpretation of the depositional environments of BIFs, we present systematic high-resolution electron microscopic, Mössbauer spectroscopic and X-ray diffraction investigations on minerals from BIFs of > 3760 to ca. 2200 million years old. For each major mineral phase several types were recognized in terms of their petrographic features and crystallographic habits. This study could serve as a reference for further investigations that require detailed high resolution petrography, mineralogy and microstructure of BIF.

2. Samples and settings

2.1. Isua BIF (>3760 Ma)

The Isua Supracrustal Belt (ISB) of southern West Greenland is one of the oldest known (~ 3800 Ma) successions of volcanic and sedimentary rocks on Earth. Nutman et al. (1984) and Nutman (1986) divided ISB into nine formations, including a quartz-magnetite-amphibole BIF. The succession was multi-intruded by ultramafic to mafic plutons, repeatedly deformed and metamorphosed to greenschist to amphibolite facies during early Archean to Mesoproterozoic eras. The studied sample was collected from the quartz-magnetite-amphibole BIF, which was tectonically juxtaposed to mafic and ultramafic rocks, and has undergone greenschist to amphibolite facies metamorphisms (e.g., Fedo et al., 2001; Lepland et al., 2002). The Pb-Pb and U-Pb dating for whole rock, magnetite and silicates of the BIF consistently gave a metamorphic age of 3760 ± 70 Ma. The deposition age of the BIF was therefore older than 3760 Ma (Moorbath et al., 1973).

2.2. Abitibi BIF (2728 Ma)

The sample was collected from the chert-jasper-magnetite facies BIF embedded in the uppermost part of the Hunter Mine Group at Abitibi, Canada. Abitibi is the largest Archean greenstone belt in the world (300 km × 700 km). It has been metamorphosed to sub-greenschist to greenschist facies during regional metamorphic events (Powell et al. 1995). The Hunter Mine Group consists of a series of volcanic and sedimentary rocks, which was divided into three evolutionary stages: 2734–2730 Ma lower formational stage; 2732 Ma middle formational stage and 2730–2728 Ma upper formational stage, based on U-Pb and $^{207}Pb/^{206}Pb$ zircon chronology (e.g., Mueller and Mortensen, 2002). The chert-jasper-magnetite facies BIF was derived from hydrothermal fluids during volcanic quiescence, and its age was constrained to 2730–2728 Ma by its host volcanic rock that formed during the upper formational stage (e.g., Chown et al., 2000).

2.3. Wutai BIF (ca. 2500 Ma)

The Wutai BIF was collected from the Wutai Group at the Wutaishan greenstone belt in Shanxi Province, North China. The Wutai Group is divided into three subgroups from lower to upper: Shizui Subgroup, Taihua Subgroup and Gaofan Subgroup. SHRIMP U-Pb and Th-U-Pb dating showed that these three subgroups are very close in age (2530–2515 Ma), and are only tectonically juxtaposed like a lithostratigraphic sequence (e.g., Wilde et al., 2004; Zhang et al., 2012). The studied BIF is embedded in the ultramafic rocks and amphibolites in the lower part of Shizui Subgroup, and has been subjected to folding (Zhang et al., 2012) and amphibolite facies metamorphism (Zhao et al., 1999; Polat et al., 2005).

2.4. Dales Gorge BIF (2480 Ma)

The BIF is from the Dales Gorge Member, Brockman Iron Formation in Hamersley Basin of Western Australia. It is one of the best-preserved iron formations in the world, with a unique lateral stratigraphic and petrographic continuity in a large area (~60,000 km^2). The 50 m thick Whale Shale Member overlays the Dales Gorge BIF and underlays another thick BIF unit named the Joffre Member (e.g., Morris and Horwitz, 1983; Morris, 1993). The Dales Gorge BIF has an age of 2480 Ma (Pickard, 2002) and has been metamorphosed to very low grades by temperatures between 60 and 160 °C (Gole, 1980). It was subdivided into 17 BIF macrobands and 16 S macrobands (Morris and Horwitz, 1983). The BIF macrobands are mainly composed by iron oxides and chert, while the S bands consist of chert, carbonates and silicates (Morris and Horwitz, 1983). The studied sample was collected from one BIF macroband.

2.5. Kuruman BIF (2460 Ma)

The studied sample is an iron oxide facies BIF collected from a drilling core (Simondium-3) of the Kuruman Iron Formation, Transvaal Group, South Africa. The iron oxide facies BIF was deposited during episodic volcanism and dated to 2460 Ma by the SHRIMP U-Pb zircon age of the interbedded tuffaceous rocks (Pickard, 2003). The iron formation overlays a thick sequence of clastic rocks and underlays carbonate and siliciclastic rocks (Altermann and Nelson, 1998). The BIF has undergone low degree metamorphism with a peak metamorphic temperature lower than 170 °C and pressures <1.2 Kbar (Miyano and Beukes, 1984).