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Using BIF magnetite of the Badampahar greenstone belt, Iron Ore Group, East Indian Shield to reconstruct the water chemistry of a 3.3–3.1 Ga sea during iron oxyhydroxides precipitation

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The rare earth elements and Y (REY) geochemistry is considered to be an important tool to interpret the origin of banded iron formations (BIF) and paleo-ocean chemistry. The interpretations are based on the assumption that there was minimal fractionation of REY during precipitation of iron oxyhydroxide phases in the Precambrian oceans. However, the study of iron precipitation in laboratory and modern marine setting shows that precipitating iron oxyhydroxide phases significantly fractionate REY from solution. The purpose of this work is to inspect the validity of using BIF as a direct proxy for ancient seawater and establish the potentials of REY fractionation into BIF. The BIF magnetite of the 3.3–3.1 Ga Badampahar greenstone belt (BGB) is studied by LA-ICP-MS for trace and REY compositions. Considering the REY fractionation in BIF, the corresponding seawater (3.3–3.1 Ga) REY compositions are reconstructed from the BIF magnetite data using experimental REY partitioning coefficients and compared with modern seawater compositions. The calculated seawater REY patterns (shale normalized) show more pronounced W-type lanthanide tetrad effect relative to modern seawater implying high rate of iron precipitation. The calculated seawater data also show true negative Ce anomalies which indicate that iron was oxidized in presence of free oxygen derived from microbial photosynthesis.

1. Introduction

Banded iron formations (BIF) are Precambrian chemical sedimentary rocks characterized by alternating iron- and silica- rich bands (Trendall and Blockey, 1970). The Y and rare earth elements (REY) chemistry of BIF is considered an important tool to understand their origin and corresponding paleo-ocean chemistry as well as the evolution of early earth's atmosphere, hydrosphere and biosphere (e.g. Fryer, 1977; Danielson et al., 1992; Bau and Dulski, 1996; Planavsky et al., 2010). The shale normalized REY_{SN} patterns of Archean BIF are typically characterized by depleted light rare earth elements ($LREE_{SN}$) relative to heavy rare earth elements ($HREE_{SN}$), positive La_{SN} and Gd_{SN} anomalies and super-chondritic Y/Ho ratios similar to modern seawater, which lead previous researchers to conclude that BIF were originated in a marine setting and record the corresponding seawater chemistry (Bau and Dulski, 1996; Bolhar et al., 2004; Friend et al., 2007; Planavsky et al., 2010; Viehmann et al., 2015). Researchers have made several other significant conclusions regarding BIF genesis such as ocean-redox state determination by Ce_{SN} anomalies and identification of hydrothermal input recognized by Eu_{SN} anomalies and Y/Ho ratios (Fryer, 1977; Danielson et al., 1992; Bau and Dulski, 1996; Smith et al., 2013; Gourcerol et al., 2016).

The REY study of BIF is based on the assumption that REY fractionation was minimal during iron precipitation in the Precambrian seawater (Planavsky et al., 2010; Bekker, 2014; Alibert, 2016). However, the study of iron precipitation in modern oceans and laboratory experiments show a different scenario. In modern marine setting, the hydrogenetic Fe-Mn crusts fractionate REY from seawater, resulting in significant contrast of REY_{SN} patterns with seawater (Bau et al., 1996). Here, REY are significantly fractionated onto precipitating ferric oxyhydroxides by surface complexation (Byrne and Kim, 1990; Bau et al., 1995; Bau, 1999). Laboratory studies on REY fractionation by ferric oxyhydroxides also show that preferential fractionation of LREE relative to HREE and lower partitioning coefficient (K_d) of La, Gd and Y (and Lu) relative to the adjacent elements result in M-type lanthanide tetrad effect in the precipitate and W-type lanthanide tetrad effect in the solution (Masuda et al., 1987; Bau et al., 1996; Bau, 1999). In order to evaluate BIF genesis and paleo-ocean chemistry, it seems to be problematic to use BIF as a direct proxy for ancient seawater. Whether, REY fractionation took place during the precipitation of iron phases in

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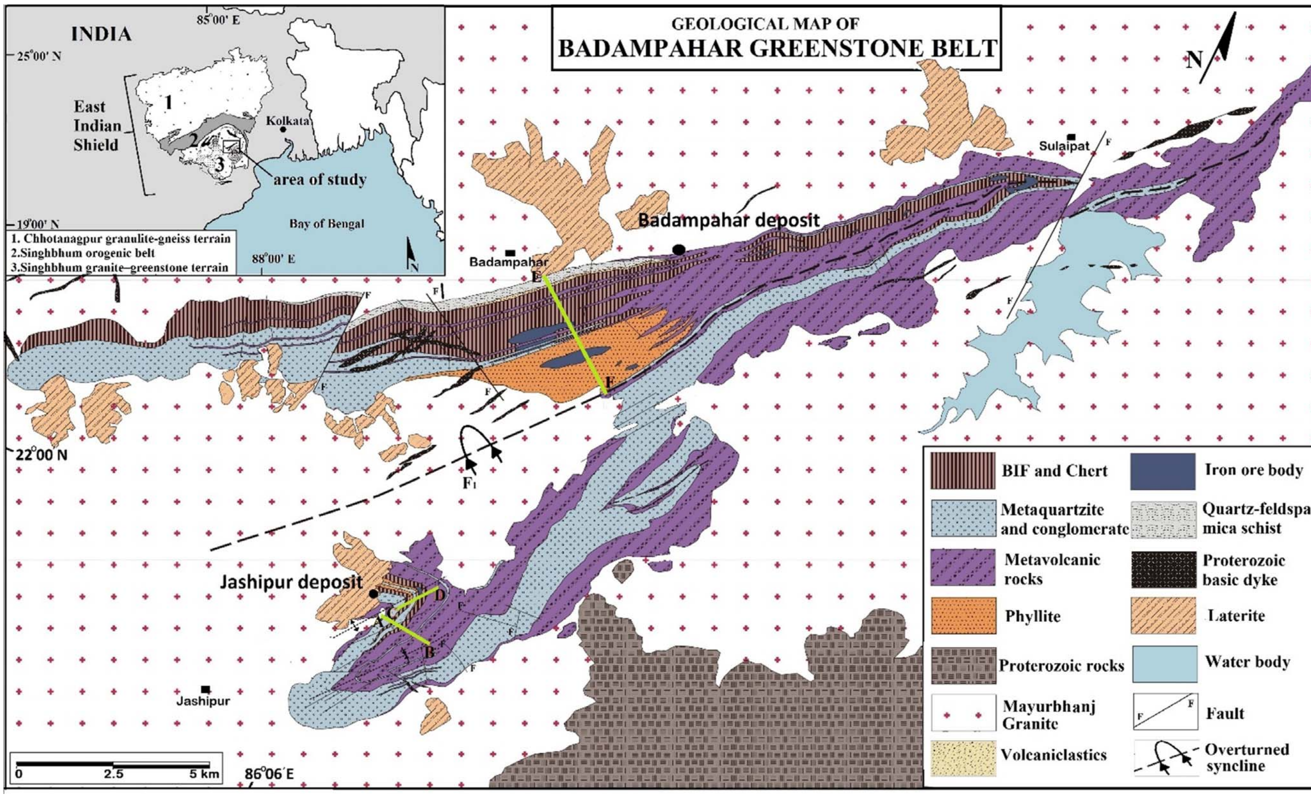

Fig. 1. Geological map of the Badampahar greenstone belt, Iron Ore Group, East Indian Shield.

the Precambrian oceans as it happens in the modern times is a question that still remains open.

The major purpose of this paper is to review the validity of using BIF directly as a proxy for ancient seawater and establish the potentials of REY fractionation into BIF. BIF magnetite of the 3.3–3.1 Ga Badampahar greenstone belt (BGB) is studied by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for trace and REY. Considering the REY partitioning onto precipitating iron phases, the corresponding seawater REY patterns are reconstructed from the studied BIF magnetite and interpreted.

2. Geological background and sampling

2.1. Regional geology

The East Indian Shield comprises the Chhotanagpur granulite-gneiss terrain in the north, the Singhbhum granite–greenstone terrain in the south and the Singhbhum orogenic belt between the aforementioned two terrains (Fig. 1). In the Singhbhum granite-greenstone terrain, three major Archean iron ore belts (Jamda-Koira belt in the west, Gorumahisani-Badampahar belt in the east and Tomka-Daitari belt in the south) surround the granitic craton. The iron ore belts belong to the stratigraphic unit named Iron Ore Group (Saha, 1994). The Jamda-Koira belt and the Tomka-Daitari belt have manganese association with BIF, whereas manganese occurrence is absent in the Gorumahisani-Badampahar belt (Banerji, 1977; Ghosh et al., 2015). The Badampahar greenstone belt (BGB) occurs at the southern part of the Gorumahisani-Badampahar iron ore belt and is surrounded by the Mayurbhanj granite (Fig. 1). The Singhbhum granite Type-A (c. 3328 ± 7 Ma; Misra et al., 1999) occurs as the basement of the BGB rocks and the Mayurbhanj granite (c. 3080 ± 8 Ma and 3092 ± 5 Ma; Misra et al., 1999) intrudes the BGB; the BGB rocks occurring as enclaves within Mayurbhunj granite (Fig. 1). The relative age of the BGB is assumed to be 3.3 Ga to 3.1 Ga. Proterozoic basic dykes (Newer dolerites, Saha, 1994) trending NE-SW and NNW-SSE, also intrude the BGB rocks (Fig. 1).

The BGB comprises BIF and chert intercalated with phyllite, metavolcanic rocks, quartzite, metavolcaniclastics and quartz-feldspar-mica schists (Fig. 2). The BIF interbedded with metavolcano-sedimentary greenstone sequences are of Algoma type. The rocks of the BGB are deformed in multiple stages and metamorphosed in greenschist to lower amphibolite facies (Saha, 1994; Nayak et al., 2011). Detailed structural study reveals at least four major phases of deformation. The first deformation phase (D_1) developed the regional Badampahar isoclinal fold (F_1) plunging 63° towards NNE and foliation S_1. The second deformation (D_2) caused extensive shearing and folding (F_2) with the development of S_2 foliation. S_2 dips from 75° to 85° towards NW. Isoclinal to tight F_2 folds plunge from 25° to 63° towards NE or SW (Fig. 1: near Jashipur). The third deformation phase (D_3) caused open type folds (F_3) plunging from 40° to 75° towards NW. Faults and joints was developed subsequently. Three sets of fault trending NW-SE, E-W and N—S are interpreted from field and satellite imagery. Three sets of penetrative joints are present dipping 80° to 85° towards ESE, 70° to 80° towards SE to SSE and vertical joints trending N-S.

2.2. BIF of the BGB

At the BGB, BIF are present at two different parts of the belt i.e. near Badampahar and near Jashipur (Fig. 1). The BIF of the BGB comprise alternating magnetite- and quartz -rich bands (with occasional presence of ferro-actinolite and magnesio-grunerite) (Fig. 3A, B). The grain size, thickness of the bands and abundance of minerals in bands vary widely. In oriented BIF samples, most magnetite and amphibole (actinolite and grunerite) show elongation parallel to foliation (S_1) indicating their syn-kinematic growth during the first phase of deformation and corresponding metamorphism (Fig. 3B). Sharp mutual boundaries amongst magnetite, quartz and amphiboles represent equilibrium crystallization. Few samples of BIF contain very thick (> 2 cm) alternating magnetite (> 90 modal %) – and quartz-rich bands lacking any amphibole