Geoscience Frontiers 7 (2016) 927–936

Contents lists available at ScienceDirect

China University of Geosciences (Beijing)

Geoscience Frontiers

journal homepage: www.elsevier.com/locate/gsf

Research paper

Spectral characteristics of banded iron formations in Singhbhum craton, eastern India: Implications for hematite deposits on Mars

Mahima Singh [a], Jayant Singhal [a], K. Arun Prasad [a], V.J. Rajesh [a,*], Dwijesh Ray [b], Priyadarshi Sahoo [c]

[a] Department of Earth and Space Science, Indian Institute of Space Science and Technology, Valiamala P.O., Thiruvananthapuram 695 547, India
[b] Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India
[c] Geological Survey of India, State Unit: Odisha, Nuipalli, Bhubaneswar 751 012, India

A R T I C L E I N F O

Article history:
Received 2 August 2015
Received in revised form
6 November 2015
Accepted 10 November 2015
Available online 30 November 2015

Keywords:
Banded iron formation
Singhbhum craton
VIS/NIR spectroscopy
Raman spectroscopy
Terrestrial analog
Mars

A B S T R A C T

Banded iron formations (BIFs) are major rock units having hematite layers intermittent with silica rich layers and formed by sedimentary processes during late Archean to mid Proterozoic time. In terrestrial environment, hematite deposits are mainly found associated with banded iron formations. The BIFs in Lake Superior (Canada) and Carajas (Brazil) have been studied by planetary scientists to trace the evolution of hematite deposits on Mars. Hematite deposits are extensively identified in Meridiani region on Mars. Many hypotheses have been proposed to decipher the mechanism for the formation of these deposits. On the basis of geomorphological and mineralogical studies, aqueous environment of deposition is found to be the most supportive mechanism for its secondary iron rich deposits. In the present study, we examined the spectral characteristics of banded iron formations of Joda and Daitari located in Singhbhum craton in eastern India to check its potentiality as an analog to the aqueous/marine environment on Mars. The prominent banding feature of banded iron formations is in the range of few millimeters to few centimeters in thickness. Fe rich bands are darker (gray) in color compared to the light reddish jaspilitic chert bands. Thin quartz veins (<4 mm) are occasionally observed in the hand-specimens of banded iron formations. Spectral investigations have been conducted in VIS/NIR region of electromagnetic spectrum in the laboratory conditions. Optimum absorption bands identified include 0.65, 0.86, 1.4 and 1.9 μm, in which 0.56 and 0.86 μm absorption bands are due to ferric iron and 1.4 and 1.9 μm bands are due to OH/H_2O. To validate the mineralogical results obtained from VIS/NIR spectral radiometry, laser Raman and Fourier transform infrared spectroscopic techniques were utilized and the results were found to be similar. Goethite-hematite association in banded iron formation in Singhbhum craton suggests dehydration activity, which has altered the primary iron oxide phases into the secondary iron oxide phases. The optimum bands identified for the minerals using various spectroscopic techniques can be used as reference for similar mineral deposits on any remote area on Earth or on other hydrated planetary surfaces like Mars.

1. Introduction

Banded iron formations (hereafter BIFs), reported over all continents in association with Precambrian greenstone belts, are defined as chemical sedimentary rocks with alternate layers (varying thickness) of iron oxides (magnetite and/or hematite) and silica (jasper, quartz and chert) (Cloud, 1973; Gross, 1980; Melnik, 1982; Klein, 2005; Polat and Frei, 2005 and references therein). They are formed mainly by sedimentation processes in which water plays a major role in deposition during the time span of Archean to Proterozoic epochs (Klein, 2005). The formation processes (seasonal/microbial?) of various layers and the mechanisms for oxidizing Fe (possibly microbial) are still highly debated (Posth et al., 2008). Deposition of BIFs in ocean basins are the result of oxidation of reduced Fe, either generated through continents or by hydrothermal fluids. BIFs have also found their significance as a major rock unit to explain related sea water chemistry and the

* Corresponding author. Tel.: +91 471 256 8522.
E-mail addresses: rajeshvj@iist.ac.in, rajeshvj2000@gmail.com (V.J. Rajesh).
Peer-review under responsibility of China University of Geosciences (Beijing).

http://dx.doi.org/10.1016/j.gsf.2015.11.003
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evolution of lithosphere-biosphere-atmosphere in terrestrial conditions (Klein and Beukes, 1989; Derry and Jacobsen, 1990; Kaufman and Knoll, 1995; Rao and Naqvi, 1995; Johnson et al., 2003, 2008; Trendall and Blockley, 2004). Systematic chemical studies of representative iron phases from BIFs provide significant information about thermal regime of host basin, the redox conditions of deep ocean water and the source of Fe and other elements (Holland, 1973; Klein and Ladeira, 2004; Bhattacharya et al., 2007; Frei and Polat, 2007; Pecoits et al., 2009). These parameters make BIFs a good proxy to be considered for planetary studies. Presence of BIFs has been speculated on Mars based on the identification of extensive layered hematite and hydrothermal silica rich deposits (Christensen et al., 2000, 2001; Squyres et al., 2008; Ruff et al., 2011; Bost et al., 2013). Crowley et al. (2008) studied the diversity of spectral signatures of terrestrial BIFs in detail and proposed the implications for the identification of similar type of deposits on Mars. The well preserved sedimentary structures with least deformation, unmetamorphosed deposit (except few local thermal metamorphic effects) and extensively mined areas to get samples devoid of any atmospheric effects are some of the features of BIFs which make them suitable candidates for terrestrial analogs for the interpretation of the regional evolution of hematite deposits and paleoenvironments on Mars (Christensen et al., 2000, 2001; Hynek et al., 2002; Ormö et al., 2004; Glotch and Christensen, 2005). Several studies have been carried out with the BIF samples of Lake Superior (Canada) and Carajas (Brazil) to interpret the formation conditions of regional hematite deposits on Mars (Christensen et al., 2000, 2001; Fallacaro and Calvin, 2006; Bridges et al., 2011). Spectral signatures along with preliminary geochemical results of these BIFs have been utilized to interpret the sites as potential Martian analog sites. The BIFs of these two areas along with BIFs from Coppin Gap Greenstone Belt, Pilbara craton, Australia, were listed in the International Space Analog Rockstore (Bost et al., 2013).

Mars surface has been marked with the widespread layered hematite deposits and other FeO-OH polymorphs (Fe-oxides and Fe-(oxy-)-hydroxides), mainly in Meridiani Planum, Aram Chaos, and Valles Marineris regions (Christensen et al., 2000, 2001, 2004). Layered hematite deposits of Meridiani Planum on Mars are proposed to be of sedimentary origin due to absence of any volcanogenic geomorphic features such as lava flows and fissures. Many authors have discussed the formation mechanism of the layered hematite deposits, but climatic conditions during their formation are yet to be studied in detail. Bridges et al. (2008) proposed that Carajas BIFs, formed as a supracrustal sequence at lower temperature (Dalstra and Guedes, 2004) are suitable to interpret the ancient marine environments on Mars and the spectral data in VIS-NIR-SWIR-TIR region would aid in identifying similar deposits on Mars. Therefore, detailed characterization of different BIFs in terrestrial environments will sequentially improve the superiority of our understanding for identifying mineralogical composition of the planet and its evolutionary history. Though, there are several occurrences of banded iron formations in India (Radhakrishna and Naqvi, 1986), studies considering them as analog sites are not yet initiated (Singh et al., 2015). Banded iron formation of Singhbhum craton in eastern India has long been discussed as geochemically similar to Lake Superior type BIFs. These BIFs are comparable to those BIFs in Carajas (Brazil), Finland and Australia (Majumder et al., 1982). This study provides the results from VIS/NIR radiometry, back scattered image interpretation, laser Raman and ATR-FTIR (Attenuated total reflectance-Fourier transform infrared) spectroscopy which helped constrain spectral aspects of BIF of Singhbuhm craton and it will add the information to our understanding about the regions with similar mineralogy in extraterrestrial conditions. Laboratory VIS/NIR radiometry and laser Raman measurements of these rocks will contribute in better detection of similar rock types on Mars. On this context, the study of Precambrian BIFs in relation to Martian hematite deposits could be significant to have a better understanding on the paleoenvironmental conditions. The optimum bands identified for hematite and goethite can be used as a reference for unidentified similar mineral deposits for future extraterrestrial missions.

2. Regional geology, sample description and analytical methods

The Singhbhum-Odisha craton forms a triangular crustal block, bounded by Chotanagpur gneissic complex to the North, eastern Ghat Granulite belt to the South and the Bastar craton to the West and by recent alluvium to the East (Saha and Ray, 1984, 1994; Mahadevan, 2002; Misra, 2006). This craton consists mainly of granitoid rocks, metasedimentary (Iron Ore Group), meta-volcanic schists and granites (Mahalik, 1987; Saha, 1994; Mazumder, 2005; Misra, 2006; Mukhopadhyay et al., 2006). The BIFs of north Orissa are extensively developed supracrustals encircling the Singhbhum granite complex and various views have been proposed on the evolution of these supracrustals and their relation to the granite intrusives (Fig. 1). Jones (1934), Dunn (1940) and Saha (1994) believed that all the BIFs were formed as a single assemblage during the Archean underlain and/or intruded by the different phases of Singhbhum granites. According to Saha (1994), the age of formation could be between 3.3 and 3.1 Ga. Iyengar and Banerjee (1971), Banerji (1974, 1975, 1980) and Iyengar and Murthy (1982) classified BIFs into two distinct age groups; older (Gorumahisani group) and younger (Noamundi group). Prasad Rao et al. (1964) and Acharya (1976, 1984) has categorized the BIFs into three distinct stratigraphic formations, the oldest around Pallahara and Gorumahisani, the intermediate at Daitari and the youngest at the Joda-Koida region. The youngest one contains rich deposits of iron and manganese ores and forms a horse-shoe shaped synclinal structure (Jones, 1934). Relatively younger metasedimentary deposits of banded iron formations of Joda and Daitari region have two types of mineral assemblages: first, banded hematite jasper and second, banded hematite quartzite. These BIFs are conspicuous by the presence of alternate bands composed predominantly of iron oxide and silica. Secondary hematite formed after metamorphism, is generally found in the form of bladed crystals, specular variety called specularite whereas silica is of cryptocrystalline type, admixed with iron oxide dust and granules in jasper to mega quartz. The extensive volcano-sedimentary sequences in the Simlipal and Keonjhar plateaus are considered equivalent to the Dhanjoris and younger to BIFs by Saha and his associates, while others (Prasad Rao et al., 1964; Iyengar and Banerjee, 1971; Banerji, 1974) found them sandwiched between BIFs. The extensive lava flows designated as Malangtoli Lava, occur between Malangtoli and Pallahara, and underlie the undeformed Kolhan sequence of the area (Saha, 1994). The age of volcanics and the volcano-sedimentary sequences in the North Odisha craton is early Proterozoic (Saha, 1994). The age of the sequence volcanic–BIF–ultramafic in Singhbhum craton is estimated to be 3.51 Ga (Mukhopadhyay et al., 2008).

The spatial view of the study areas, Joda from Noamundi-Jamda belt and Daitari from Tumka-Daitari belt is clear from Fig. 2a,b. The field observations confirm the presence of BIF (Fig. 3a), conglomerate (Fig. 3b) and massive chert (Fig. 3c) occurrences in the areas. Systematic sampling was done during the field work for further laboratory analyses. The samples collected from the study areas, Joda and Daitari, in Odisha have been characterized by VIS/NIR, Raman and FTIR techniques. Freshly cut surfaces were used for VIS/NIR spectra acquisition. Hyper spectral signatures (VIS/NIR) of the

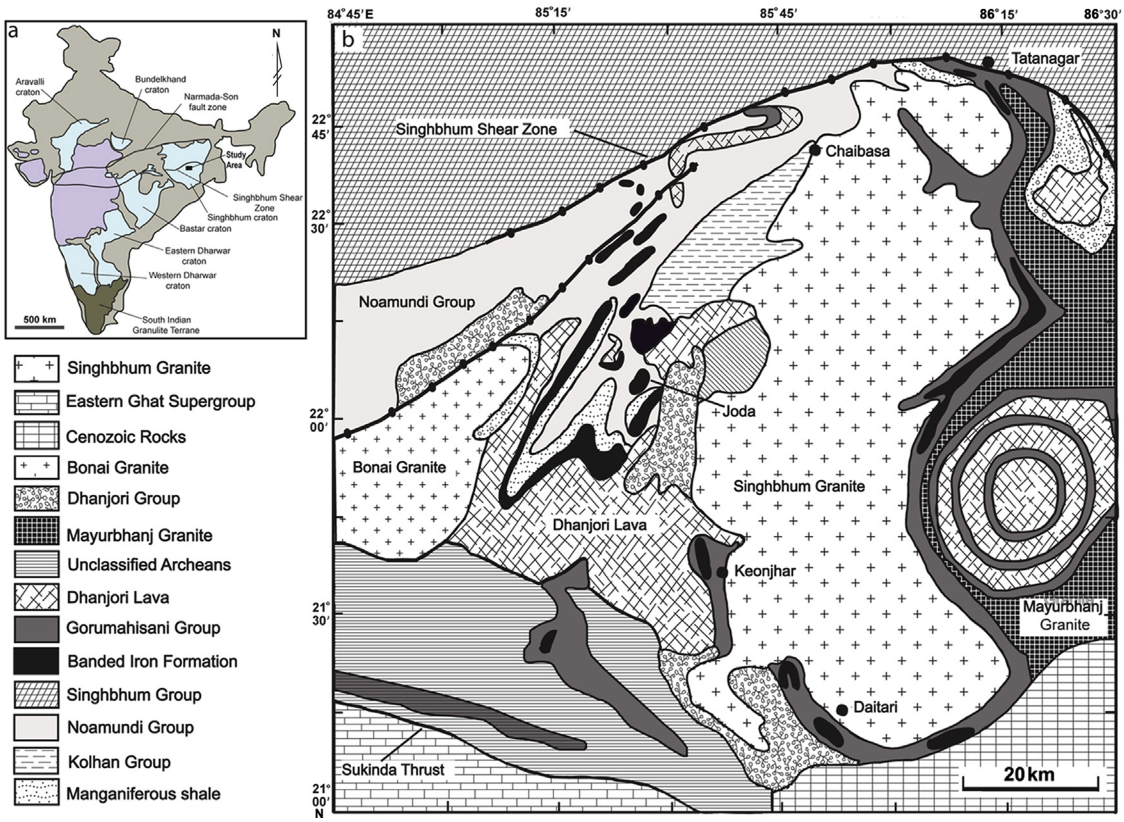

Figure 1. (a) Generalized tectonic map of India (modified after French et al., 2008). (b) Generalized geological map of iron ore deposits, Singhbhum Craton, Odisha, India (modified after Roy and Venkatesh, 2009).

BIF samples (hand-specimen and powders of 500 μm) were collected using ASD FieldSpec® 3 spectroradiometer in the wavelength range of 350 to 2500 nm. The fiber optic cable along with the gun holding it was mounted on the tripod at nadir position. Spectral signatures were collected in a controlled laboratory dark room environment. In another tripod, a tungsten filament halogen lamp with the wavelength range of 400 to 2500 nm was used as artificial light source for spectral data collection. Spectralon®, the standard white reference panel was used for measurement of irradiance for each set of measurement. The collected spectra were processed and then matched with the reference spectra available in USGS (United States Geological Survey) spectral library to confirm the minerals present in the samples. Spectral Feature Fitting (SFF) and Spectral Angle Mapper (SAM) techniques have been used to match the unknown spectra from the Joda and Daitari region of Odisha to the standard reference from USGS spectral library.

The polished thin sections were studied for petrography and further analyzed using SX-100 Electron Microprobe Analysis

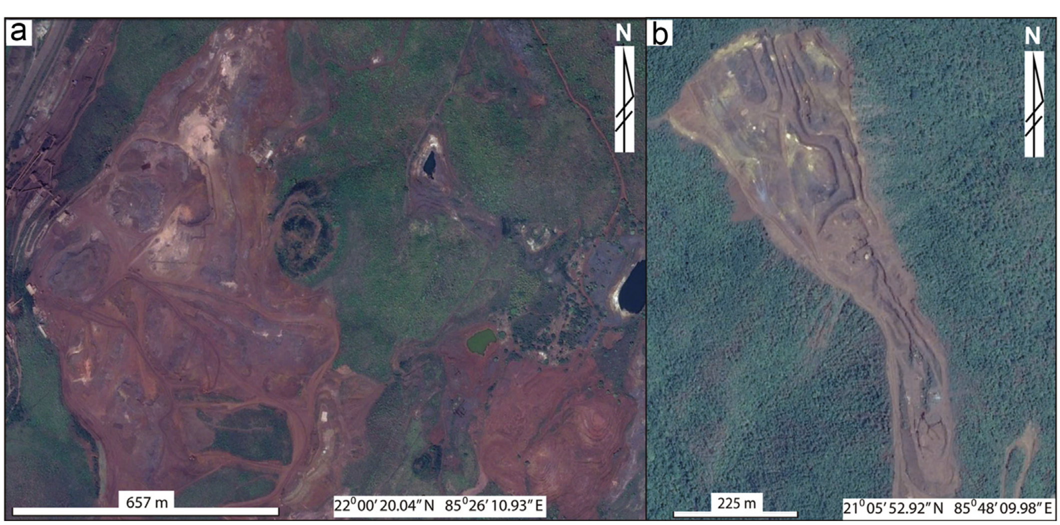

Figure 2. (a, b) Stepped landscape feature exposed on the surface, and developed due to mining in Joda and Daitari respectively as obtained from Google Earth.

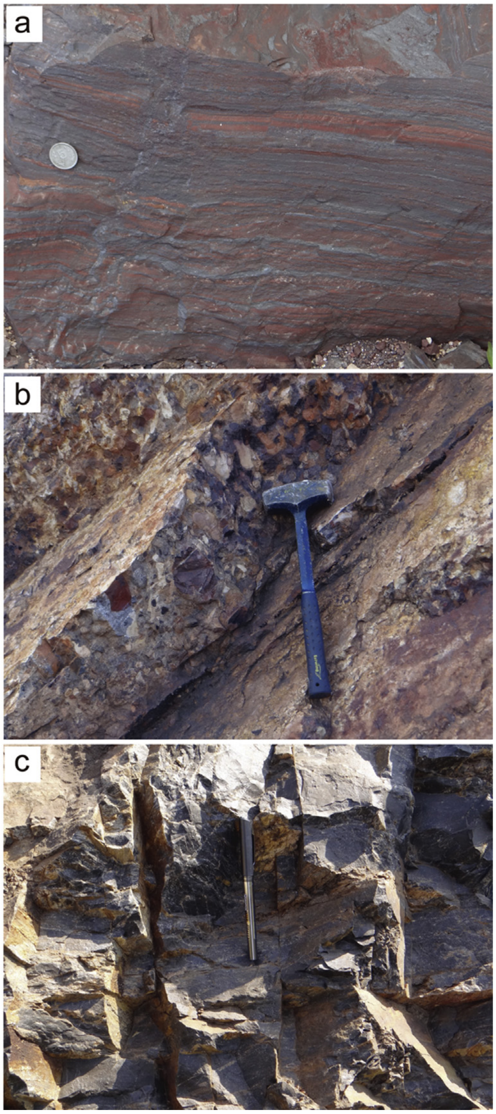

Figure 3. Field photographs illustrating (a) gray hematite and reddish jaspilitic chert, typical in banded iron formation, (b) conglomerate having iron rich matrix and boulders of chert/jasper and (c) black massive chert.

housed in Physical Research Laboratory, Ahmedabad, India. The analytical conditions were: current of 30 nA and voltage of 15 kV for hematite, magnetite, specularite and jaspilitic chert, and a current of 10 nA and voltage of 12 kV for chamosite. Silicate and oxide standards were used for calibration of the samples.

Laser Raman Spectroscopic analysis of BIF samples was conducted on a Laser Raman spectrometer at Indian Institute of Science (IISc), Bangalore, India. Laser Raman spectrometer at IISc equipped with a SPEX double monochromator, an intensified CCD and 2 ns pulsed ND-YAG lasers with frequency doubled output was used for analysis.

The infrared spectroscopic data was obtained by means of a Fourier Transform Infrared spectrometer with an attenuated total reflectance accessory (FTIR-ATR) housed at Indian Institute of Space Science and Technology (IIST), Thiruvananthapuram, India. The spectra were collected with the PerkinElmer's Infrared (FTIR & IR) spectrometer using fine powders of samples. The powders were pressed at 55 to 60 kb. The infrared (IR) spectra were recorded immediately after the separation of the sample powder from the bulk sample. Spectra were collected in 700 to 4000 cm^{-1} range with an optical resolution of 0.5 cm^{-1} and wavelength precision of 0.01 cm^{-1} at 220 V, 50 Hz power supply. A baseline correction was made before interpretation of the data.

3. Results

3.1. VIS/NIR Spectra

The spectral characteristics of the samples were studied to specify the characteristic absorption bands for different minerals in BIFs. It has been observed that the spectra of the samples (Hem_J011 and Goe_J017) from Joda and Daitari, Odisha are found to match with the spectra of hematite and goethite minerals of USGS spectral library (mineral ID Hem_FE2602 and GWS220) (Fig. 4a). The spectra of the sample Hem_J011 shows the characteristic absorption features at 0.65 (weak) and 0.86 μm (strong) which are basically due to strong iron-oxygen charge transfer absorption and electronic band related to crystal field transitions in ferric iron respectively (Thangavelu et al., 2011). The representative spectrum of hematite is devoid of any absorption after 1 to 2.5 μm, but has a moderate increase in the reflectance in the region. Sample Goe_J017 has shown the spectral signature with typical absorption bands at 0.65 (weak), 0.86 (strong), 1.4 (strong) and 1.9 μm (strong), in which 0.65 and 0.86 μm are due to strong iron-oxygen charge transfer absorption and electronic band related to crystal field transitions in ferric iron, and 1.4 and 1.9 μm are due H_2O and OH/H_2O respectively. Presence of hydrous absorption bands in VIS-NIR spectra confirms the existence of goethite in these samples.

The spectra of samples Hem_J011 and Goe_J017 have been compared with the CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) spectral library spectra of 4 samples (Hem_F1CC17B, Hem_CAGR04, Goe_C1GO01 and Goe_C1JB047) for the assessment of the differences/similarities in the spectral signatures (Fig. 4b). A careful investigation on the spectral signatures of hematite from present study (Hem_J011) and spectral library spectrum (Hem_F1CC17B and Hem_CAGR04) revealed that the spectral signatures of Hem_J011 and Hem_CAGR04 are similar with a minor variation in the absorption pattern in 0.5–0.8 μm wavelength regions. This difference in the absorption pattern can

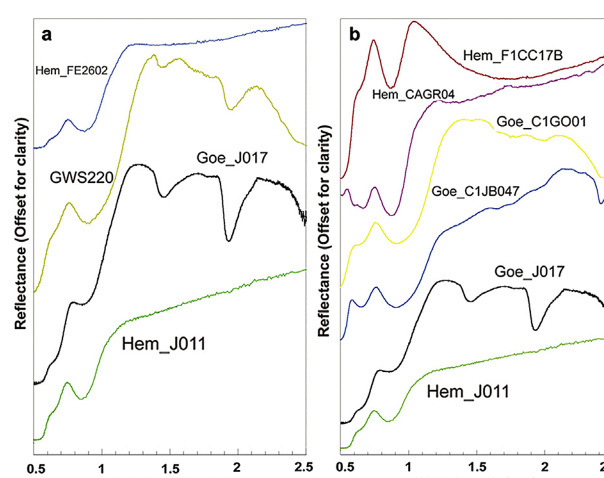

Figure 4. (a) VIS/NIR laboratory spectra of the samples Hem_J011 and Goe_J017 of Odisha BIFs along with the USGS spectral library spectra with the sample names Hem_FE2602 and GWS220 (Source: http://speclab.cr.usgs.gov/spectral). (b) VIS/NIR laboratory spectra of BIF samples Hem_J011 and Goe_J017 along with the CRISM spectral library spectra (with the sample names Hem_F1CC17B, Hem_CAGR04, Goe_C1GO01 and Goe_C1JB047).

be attributed to the compositional variations of iron oxides in the samples. Apart from this variation in the spectrum in this region, there are no other visible differences in both the spectra. CRISM spectral library spectrum of the sample Hem_F1CC17B shows similar absorption pattern to the sample Hem_J011 spectrum in the 0.5 to 1 μm wavelength region whereas a prominent difference is being observed in 1 to 2.5 μm region. The difference is a huge sag centered at around 1.6 μm in the spectral library spectrum Hem_F1CC17B, whereas no such feature is observed in the spectrum of hematite present in the sample Hem-J011 from the study area. Spectral signature of Goe_C1GO01 and Goe_C1JB047 from CRISM spectral library are found to be matching well with the spectrum of Goe_J017 from the study area. The representative spectra show absorption bands at 0.65 (weak), 0.86 (strong), 1.4 (weak for CRISM spectral library spectra and strong for samples from present study) and 1.9 μm (weak for CRISM spectral library spectra and strong for samples from present study), and these absorption bands assignment is same as in the earlier described text. Additionally, CRISM spectral library spectra of Goe_C1GO01 and Goe_C1JB047 show weak and narrow absorption at 2.4 μm, which is typical to the OH bond in water. Summary of the absorption bands detected in the samples from present study, USGS mineral spectral library and CRISM spectral library are given in Table 1.

3.2. Petrographic studies

Mineralogical studies of Joda and Daitari BIFs revealed that they consist of hematite, magnetite, specularite and jaspilitic chert. Alternate bands of hematite and jaspilitic chert have been observed (Fig. 5). Contacts between the microbands of hematite and jaspilitic chert are usually sharp, with more transition towards low hematite (Fig. 5a,b). Hematite microbands are comparatively thick, mainly consist of hematite grains (in high proportion), and large grains of magnetite and specularite. Jaspilitic chert band comprises mainly quartz grains with some large distorted grains of hematite. Quartz veins of varying thickness are present intruding alternate bands of hematite and jaspilitic quartz (Fig. 5b). Chamosite, a hydrous aluminum silicate of iron, is also present in very small amounts.

The iron-rich layer is mainly composed of hematite grains with different textures. Massive anhedral aggregates of hematite and xenomorphic hematite crystals are common (Fig. 6a,b). Sporadic distribution of relatively larger hematite grains is conspicuous. Quartz veins are also marked with the presence of hematite crystals (Fig. 6c). Mostly, platy specularite aggregates are found associated with the jaspilitic chert microbands rather than hematite rich layer (Fig. 6d). Chamosite is found associated with platy specularites. Specularite, also called gray hematite, is mainly found in the form of platy crystals in the groundmass of fine grained hematite. A very small amount of magnetite is present in the hematite rich layers. Jaspilitic chert occurs inter-bedded with Fe-rich microbands.

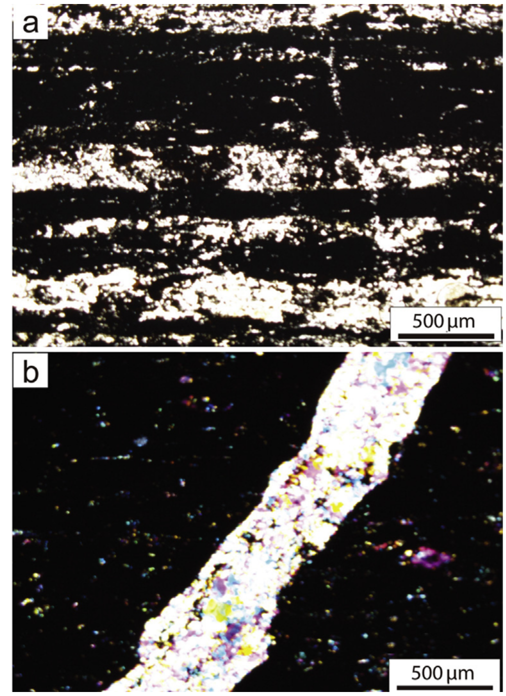

Figure 5. (a) Photomicrographs of finely laminated BIFs where iron-'rich' microbands are defined by hematite and/magnetite, interbedded with occasional pure chert micro layers and (b) prominent microbands of hematite and interbedded light colored chert along with the micro-intrusion of quartz vein.

3.3. Laser Raman spectra

Laser Raman spectra of characteristic minerals are presented in Fig. 7. The main phases identified using laser Raman spectroscopic technique include quartz and hematite; observed Raman peaks at 142, 209, 353, 469 and 1160 cm^{-1} correspond to quartz (Fig. 7a–c) and 224, 291 and 1315 cm^{-1} correspond to hematite (Fig. 7d,e) in accordance with the literature (Shebanova and Lazor, 2003). Raman spectral quality depends mainly on grain size; therefore it is necessary to take into consideration the crystallinity/grain size of the samples. Hematite, the main crystalline mineral in oxide group is considered as a strong Raman scatterer, gives strong peaks in 210–294 cm^{-1} region, mainly due to translational movements of Fe. Apart from these Raman peaks of hematite, one moderate peak has also been observed at 1315 cm^{-1} (Fig. 7f). Presence of goethite is clear in the samples with the VIS-NIR analysis, but no prominent peaks are observed in the Raman spectra, a broad peak is observed in the form of a doublet at 386–412 cm^{-1} in which 386 cm^{-1} peak corresponds to goethite (Fig. 7c,d). Magnetite is recognized as a minor phase and identified by the typical Raman peak at 670 cm^{-1} (Fig. 7f).

Table 1
Summary of the absorption bands identified in the samples from BIFs in Singhbhum craton, USGS mineral spectral library and CRISM spectral library. X indicates that these absorption bands were observed in the spectral signature.

Identity	Study area		USGS spectral library		CRISM spectral library				Assignments
Sample name	Hem_J011	Goe_J017	Hem_FE2602	GWS220	Hem_F1CC17B	Hem_CAGR04	Goe_C1GO01	Goe_C1JB047	
0.65 μm	X	X	X	X	X	X	X	X	Ferric ion
0.86 μm	X	X	X	X	X	X	X	X	Ferric ion
1.4 μm		X		X				X	H_2O
1.9 μm		X		X			X	X	OH/H_2O
2 μm					X				Pyroxenes
2.4 μm							X	X	OH/H_2O

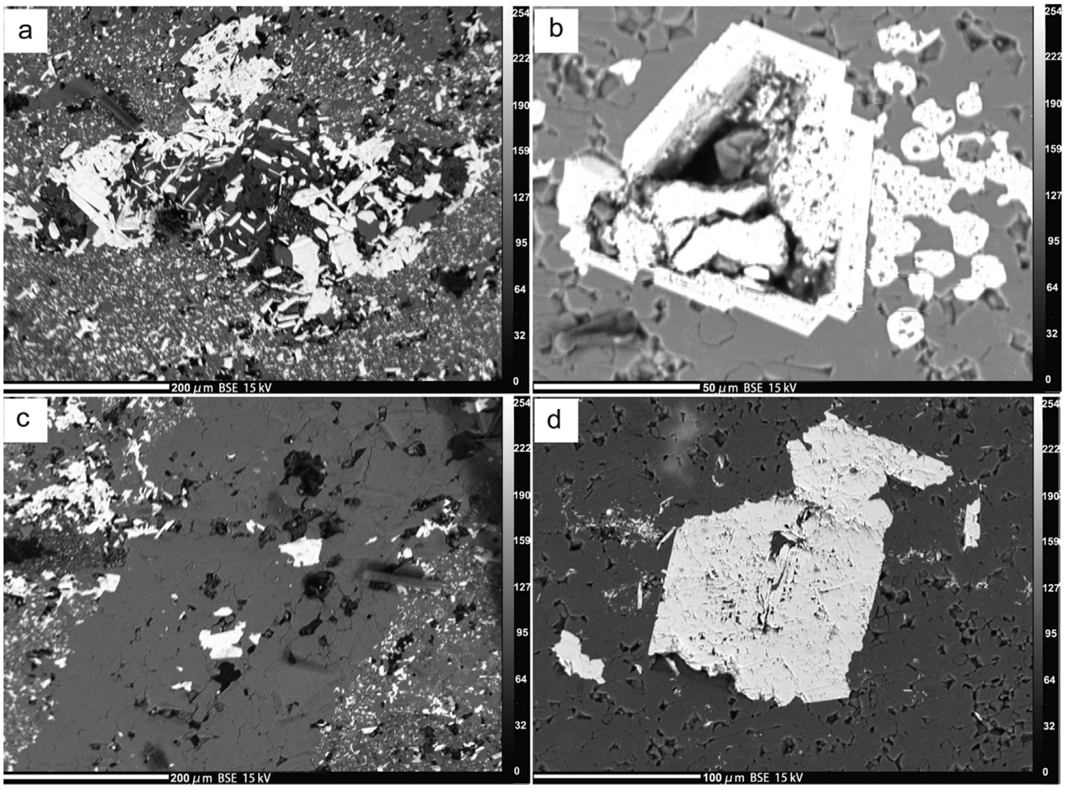

Figure 6. Back scattered electron images illustrating various textures of studied BIFs: (a) finely crystallized laths of hematite, (b) cryptocrystalline specularite, (c) quartz vein with hematitic inclusions and (d) a single large grain of specularite.

3.4. ATR-FTIR spectra

The average of 6 collected spectra using ATR-FTIR analyses is presented in Fig. 8 where most intense vibrations fall in the wavelength region 700 to 1800 cm^{-1}. The most intense vibrations in the wavelength range 900–1130 cm^{-1} are attributed to hematite and quartz (Brinatti et al., 2010). Relatively mild vibrations in the region of 1200 of 1800 cm^{-1} are due to hydroxyl bending in the sample (Ruan et al., 2002). Apart from these intense vibrations, the wavelength region 2800 to 3000 cm^{-1} is marked by mild vibrations which are attributed to hydroxyl stretching. The problem observed here is that minor mineral phases (goethite, quartz) are masked by the major mineral phase (hematite) when the sample is crushed and mixed, and hence these phases cannot be detected in the spectra due to a relatively high detection threshold inherent to this kind of technique. However, ATR-FTIR analysis is a very sensitive technique to the hydrogen bonding and water vibrations (Rull et al., 2007; Nakamoto, 2009), thus being used for the determination of hydrous phases in natural mineral/rock samples. The water vibration has been confirmed by the observed 3600 cm^{-1} vibration in the spectra. The results point to the hydration of outcrops by percolating water in the aerial to sub-aerial environment.

A summary of various mineral phases detected by different techniques is listed in Table 2.

4. Discussion

Most significant aspect of iron phases is that, they occur in a variety of geological settings, beginning from modern iron rich environments such as Rio Tinto to older ones such as BIFs and their comparison may help in generating the feasible models for the early formation of primary iron phases and the initiation of hematite formation on Mars. Joda and Daitari iron ore mines consist of stratigraphic layering or bands of hematite and quartz (mainly jasper and/or chert) of sedimentary nature. VIS/NIR results show characteristic spectral signatures of BIFs with absorption bands at 0.65, 0.86, 1.4 and 1.9 μm by which the presence of hematite and goethite can be easily confirmed (Fig. 4a,b). Apart from these Fe-oxide spectral signatures in terrestrial BIFs, silicate minerals (mainly quartz polymorphs) could also be identified in thermal infrared region (8–14 μm) of electromagnetic spectrum (Bridges et al., 2011). The reflectance maxima caused by silicon-oxygen stretching vibrations in quartz is a distinctive sharply pointed shape related to the polycrystalline grain fabrics and thin iron oxide coating (Crowley et al., 2008). Specularite in Singhbhum craton BIFs is the secondary mineral phase similar to goethite, and has been generated from magnetite (Beura and Satpathy, 2012). Initiatives to use laser Raman spectroscopy for planetary studies has already been taken up as it has several advantages over other types of spectroscopic techniques (Hirschfeld, 1974; Wang et al., 1995; Sharma et al., 2002). Raman analysis provides sharp spectral features for minerals and/mixtures. Hence, it is most likely to be employed in interplanetary missions to detect spectral features of various minerals in a particular region. The laser Raman and ATR-FTIR spectra obtained for the BIF samples of Singhbhum craton demonstrates the presence of oxide and silicate minerals such as hematite and quartz (Figs. 7 and 8). Based on the ATR-FTIR spectral results (moderate peak at 3600 cm^{-1}), it is clear that hydrated phases of iron oxide are present. VIS/NIR spectra also confirm the hydrous phase of iron oxide, i.e. goethite, based on the identified absorption bands at 1.4 and 1.9 μm. Mössbauer spectroscopic results are also reported for the native iron samples collected from the Precambrian Chaibasa shales, Singhbhum craton, eastern India (Chandra et al., 2010).

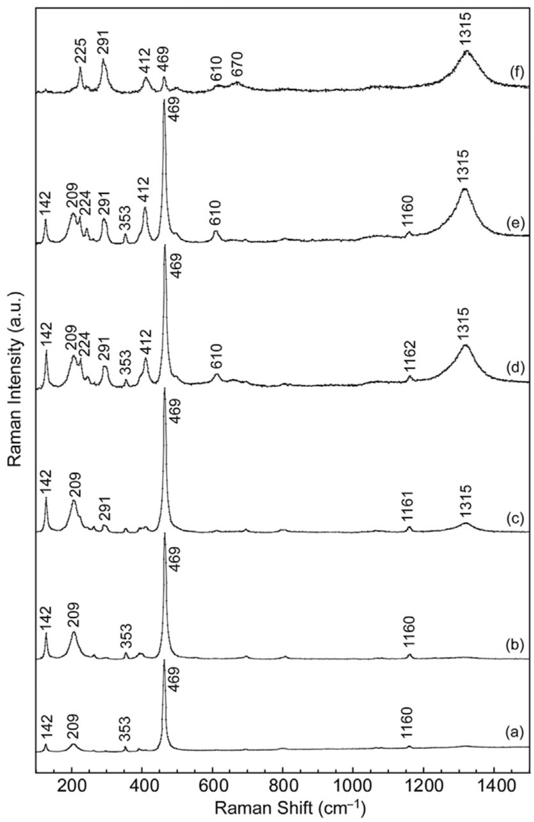

Figure 7. Raman spectra of the major mineral phases in BIFs: (a) and (b) the characteristic peaks of quartz, (c) a minor peak of hematite, (d) and (e) characteristic peaks for hematite and quartz, and (f) the characteristic peak for hematite as a major component and magnetite and quartz as minor components.

Iron being sensitive to environmental conditions due to variable oxidation states could form different minerals in response to the existing environmental conditions such as Eh, pH and concentrations of certain active species like CO_2, SiO_2, S etc. In terrestrial conditions, hematite occupies a wider field of stability with high Eh (>0.6) and high pH (>4) in Precambrian BIFs (including Odisha

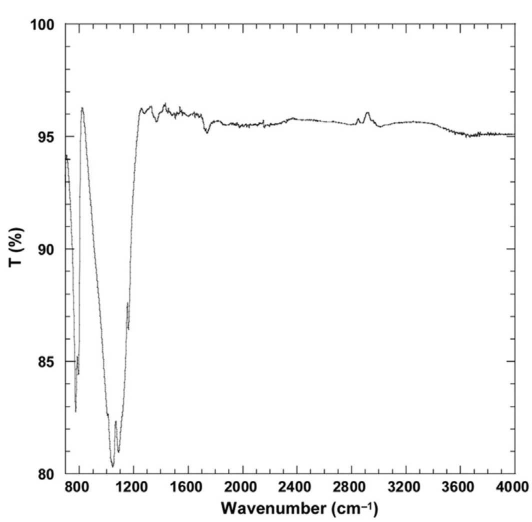

Figure 8. ATR-FTIR Infrared Spectra from studied BIFs (average spectra of 6 analyses performed with BIFs sample powders).

Table 2
Summary of the minerals detected in the samples using different techniques. X indicates that these species were uniquely identified with the technique, while O indicates that there is a weak and inconclusive, though compatible, feature. I indicates that no feature was observed.

Detected mineral species	Odisha BIF			
	VIS-NIR	BSE	Raman	ATR-FTIR
Hematite	X	X	X	X
Goethite	X	O	X	X
Specularite	I	X	O	O
Magnetite	I	X	X	O
Quartz	I	X	X	X
Chamosite	I	X	I	I

BIFs) and its formation is subjected to the activity of CO_2, S and SiO_2 and therefore, always associated with silicates, carbonates and sulphides (Garrels and Christ, 1965; Stanton, 1972). The common belief on the formation of BIFs in terrestrial conditions is through direct precipitation from low temperature aqueous solutions in response to changes in environmental conditions (Eh/pH) or different diagenetic alterations of precipitated ferric-hydroxides, but it has also been reported that the BIF mineralogy is the outcome of metamorphic processes (Mücke and Annor, 1993). On Mars, lepidocrocite in addition to goethite is possibly precipitated from low temperature aqueous solutions in basaltic regolith (Posey-Dowty et al., 1986; King and McSween, 2005). After the formation of iron phases in conditions of a warmer and H_2O-CO_2 rich atmospheres, hematite was formed from these previously formed Fe-oxide phases (Gooding, 1978; Burns and Fisher, 1990, 1993). Therefore, the mechanisms for the formation of hematite from other iron phases on both planetary surfaces are proposed to be similar (Burns, 1988; King and McSween, 2005).

The geomorphological and mineralogical evidences revealed early Mars has hosted diverse environments dominated by water masses (Carr, 1981, 1996; Banin et al., 1992; Longhi et al., 1992; Morris et al., 2006) and these circumstances has raised the possibility of occurrence of BIFs on Mars, which is not yet confirmed. Analysis of thermal emissivity spectrometer (TES) data has proved the occurrences of coarse-grained crystalline hematite (Christensen et al., 2000, 2001), with no evidences of cherty silica in Meridiani region on Mars. Considering the absence of any cherty silica deposit in association with hematite deposits, the Rio Tinto system deposits have been studied in detail as an analog to ancient environment on Mars in a regional scale. The Tinto River Basin, an extreme acidic environment, has water enriched in ferric iron and sulphates and these acidic waters produce sediments rich in ferric iron dominated by sulfate and oxyhydroxide associations, in which silicates are absent (Fernández-Remolar et al., 2004). Further, the mineralogical assemblage identified includes hematite deposits along with other silicate minerals and sulfate salts (Squyres et al., 2004, 2008; Clark et al., 2005). Identification of silicate phases in hematite rich regions increases the possibility for the detection of deposits comparable to terrestrial BIFs. Infra-red analyses of terrestrial platy gray hematites support an aqueous origin for iron oxides on Mars surface (Lane et al., 2002). Genesis of layered hematite in Meridiani region has been proposed to be formed though the precipitation of insoluble hydrous ferric oxide during the oxygenation of the upper layers of the sea, and further through burial metamorphism (Christensen et al., 2000; Lane et al., 2000, 2002; Fernández Remolar et al., 2002, 2004). Considering the extent of hematite outcrops in Mars, the environment that hosted BIFs have been proposed to be analog to the environments in which Martian hematite could have been formed (Catling and Moore, 2000, 2003). From the analog point of view, the mineralogy

Table 3
Comparative account of the different features of BIFs in Singhbhum craton to that of earlier studied Martian analog sites like Lake Superior and Carajas (Brazil) and Mars.

Features	BIF	Lake Superior BIF	Carajas BIF (Brazil)
Hyperspectral characterization	Absorption band at 650–850 nm corresponding to Fe content in hematite	Absorption band at 650–850 nm corresponding to Fe content in hematite	Deep absorption band at 880 nm
Metamorphism/ deformation	Unmetamorphosed except for localized thermal metamorphism effect (Majumder et al., 1982)	More metamorphosed state as a whole deposit	Supracrustals sequence with little deformation (Bridges et al., 2011)
Research as analog to Mars	Early environments of different regions and implications to formation of specularite on Mars (present study)	Spectral observations to locate the BIFs on Mars (Fallacaro and Calvin, 2003)	Ancient water processes (Bridges et al., 2011)

detected in Odisha BIFs show similarities to those obtained from Mars, especially hematite rich Meridiani region on Mars. Mineralogy of Singhbhum craton BIFs detected by several techniques includes Fe oxide phases (hematite, goethite, magnetite and specularite) and silicate phases (chert/jasper/quartz). The optimum absorption bands identified by VIS-NIR radiometry for hematite and goethite could be used as a reference for future interplanetary mineralogical orbital explorations along with the USGS and CRISM spectral libraries. In the Martian scenario, the reflectance spectra could be used to locate BIFs/a similar deposit, as it is very much likely that they would be present at regional scale (Bridges et al., 2008). Specularite, a secondary iron oxide in the study area was formed from the earlier iron phases (possibly from magnetite). We envisage a similar mechanism for the formation of extensive specularite/platy hematite deposits on Mars. Therefore, Singhbhum craton BIFs provide planetary geoscientists with an excellent analog for water driven processes that resulted in the generation of specularite on Earth and Mars. A comparative account of the results from Singhbhum craton BIFs to other proposed analog BIFs sites namely Lake Superior BIFs and Brazilian Carajas BIFs is given in Table 3.

BIFs are chemical sediments, typically thinly bedded or laminated, whose principal chemistry comprises anonymously high content of Fe, commonly but not inevitably containing silica rich layers, mainly chert (Klein and Beukes, 1992, 1989). The very first evidence of ancient life on Earth has been found associated with the Gunflint Iron Formation, which contains a variety of filamentous to coccoidal forms of microorganisms (Barghoorn and Tyler, 1965; Awramik and Barghoorn, 1977; Strother and Tobin, 1987). Filamentous and coccoidal microorganisms of Gunflint Iron Formation has been investigated by many scientists and has been found that some of the filamentous microfossils were mineralized by hematite (Allen et al., 2001; Schelble et al., 2004; De Gregorio and Sharp, 2006). Several microfossils have been detected in chert, including Gunflint Chert (Barghoorn and Tyler, 1965), Dressler Formation (Van Kranendonk, 2006) and Apex Chert (Schopf, 1993). The precipitation of silica forms an ideal environment for the preservation of microfossils in geologically significant periods (Preston and Genge, 2010), because it provides a harder substrate which is less prone to reworking and removal of biomolecules. Rhyne chert has been studied for its silicified microorganisms by Preston and Genge (2010) and proposed that if life had ever existed on Mars, microorganisms would have likely been silicified by Martian hot spring deposit with regards to the similar early evolution of Earth and Mars. Black chert deposits of iron ore group of Singhbhum craton can also add valuable information and help in identifying similar characters. Black chert that is associated with BIFs in Singhbhum craton has been proved as a potential host revealing several clues on the palaeobiogical evolution of our early Earth (Barghoorn and Tyler, 1965; Schopf, 1993; Van Kranendonk, 2006).

Bridges et al. (2011) proposed that where spectra indicate bands of hematite and jaspilitic quartz, without discernable clays, and where this pattern extends from the millimeter to meter scale and is laterally continuous, it is highly likely BIFs are present. On Mars, these signatures should be observable at the regional scale from orbiters and at outcrop scale from rovers (Bridges et al., 2011). Other important aspect to be analyzed is that BIFs have a strong magnetic signature. NASA's Mars Global Surveyor (MGS) mission found strong magnetic lineations in the planet's ancient crust that exceed terrestrial values by an order of magnitude, indicating the presence of an intense ancient Martian magnetic field (Connerney et al., 1999). The magnetized material might be ancient lava flows or magmatic intrusions, although a contribution from Martian BIFs cannot be discounted (Bridges et al., 2011). The search for the banded iron formation on Mars would be an outstanding breakthrough to get the insights into the geological past of the planet. The hematite deposits therefore, could be treated as potential target rocks for probing ancient microbial and hydration processes. The terrestrial BIFs have recorded primitive aqueous habitable environments where early forms of life such as stromatolites have been reported (Cloud, 1965, 1972; Hartmann, 1984; Konhauser et al., 2002, 2003). The planetary geosciences community consider BIFs as potential Martian analogs for hematite deposition (Fallacaro and Calvin, 2003; Bridges et al., 2011).

5. Conclusions

This study on geological and spectral characteristics of BIFs in Singhbhum craton will help to have a better understanding on the paleo-environmental conditions of formation of iron deposits on Mars. Spectroscopic studies could aid in differentiating the iron ore deposits on Mars and also help in the relative enrichment of Fe content in different deposits. Laser Raman and ATR-FTIR spectroscopic techniques are proved to be very significant in analyzing different mineral mixtures, whereas it is difficult to identify each mineral species in a mixture through VIS/NIR radiometry. Chert/quartz, an integral part of BIFs could not be identified in VIS/NIR analysis, but it is easily distinguishable by laser Raman and ATR-FTIR spectroscopic techniques. We hope that this geologic and spectral study of BIFs will help during the testing and calibration phase of the on-going and future missions to Mars.

Acknowledgments

This work was financially supported by Indian Institute of Space Science and Technology (IIST), Thiruvananthapuram. The first author acknowledges IIST Thiruvananthapuram for a Junior Research Fellowship. Constructive comments by Co Editor-in-Chief, Prof. M. Santosh, and anonymous reviewers significantly improved the manuscript. We would like to thank Dr. Gnanapazham (Department of Earth and Space Sciences, IIST) and Dr. Sajeev Krishnan (Centre for Earth Sciences, IISc, Bangalore) for fruitful discussions and analytical facilities.

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