Clue on ocean redox condition from trace element and rare earth element (REE) composition of iron formation and carbonate rocks from the late Paleoproterozoic Morar Formation, Gwalior Group, central India

Pritam P. PAUL*, Partha Pratim CHAKRABORTY**, Fumito SHIRAISHI***,†, Kaushik DAS***,†, Atsushi KAMEI‡ and Sourabh BHATTACHARYA§

*Manav Rachna International Institute of Research and Studies, Faridabad-121004, India
**Department of Geology, University of Delhi, Delhi-110007, India
***Department of Earth and Planetary Systems Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan
†Hiroshima Institute of Plate Convergence Region Research, Higashi-Hiroshima 739-8526, Japan
‡Department of Geosciences, Shimane University, Shimane 690-0823, Japan
§Earth, Ocean and climate sciences, Indian Institute of Technology, Bhubaneswar 752050, India

Trace element and rare earth element (REE) composition of iron formation and carbonate rocks from the Morar Formation, Gwalior Group, central India provides valuable information on the redox condition of late Paleoproterozoic Ocean. Facies types of iron formation suggest deposition in various oceanic environments ranging from shoreface–beach to subtidal shelf settings, whereas carbonates belong to shallow and deep subtidal settings. La/Nd values between 0.57 and 25, MREE enrichment and small negative (0.69) to positive (1.46) Ce anomaly in iron formation suggest a stratified character for the Gwalior Sea with development of shallow transitional redoxcline. Whereas deep sea is interpreted as near anoxic and ferruginous, the shallow sea was not very high in dissolved oxygen (DO2) either. A suboxic to mild oxic shallow sea condition (DO2 ≥ 0.2 µM) is interpreted allowing Mn (II) oxidation and Ce sequestration. Carbonates, however, do not register any geochemical signature of redoxcline possibly because of the depositional setting either close to or below the redoxcline.

Keywords: Trace element, REE, Redoxcline, Morar Formation, Gwalior Group, Paleoproterozoic

INTRODUCTION

The Proterozoic Eon (2500-541 Ma, Gradstein et al., 2012) encompasses more than 40% of the Earth’s history and represents a unique time period. The non-reversible changes that the planet witnessed in the time period include amalgamation and breakup of supercontinents with growing importance of Phanerozoic-style plate tectonics (Nelson et al., 1999), dramatic oceanic and atmospheric changes on global scale (Hoffman et al., 1998), biological evolution leading to the advent of multicellular life (Knoll, 1994), and major changes in the upper crustal composition (Taylor and McLennan, 1997). None of these changes followed uniform and steady character, and especially Paleoproterozoic (2500-1800 Ma) and late Neoproterozoic (800-541 Ma) time period witnessed major biological, tectonic, climatic, and atmospheric changes. The billion-year interval (1800-800 Ma) mostly encompassing the Mesoproterozoic time is marked by tectonic, climatic, and evolutionary stability (Holland, 2006; Mukherjee et al., 2018). Nevertheless, amongst the above-mentioned breakthrough changes, the most debated one is oxygenation of Proterozoic atmosphere and hydrosphere, since it is intimately tied up with appearance and proliferation of life. It is generally believed that atmospheric O2 partial pressure (P02) rose modestly for the first time (from <0.001 to >0.1% of present atmospheric level; PAL) at the Great Oxidation Event (GOE, 2.45Ga; Brocks et al., 1999) and further waited patiently for about two billion years to rise to a
higher level in Neoproterozoic Oxygenation event (NOE; Shields-Zhou and Och, 2011). The idea, however, is contested in recent studies by Lyons et al. (2014) and Mukhopadhyay et al. (2014), wherein evidence for oxygenic photosynthesis and whiffs of rising atmospheric oxygen is put forward well before the GOE. In fact, dynamic scenarios that have emerged in recent studies include possibility of a much higher \( P_{O_2} \) in early stage of the GOE, which is followed by a deep plunge to a lower level (\(<0.1\%\) PAL) in next billion years until it rose again at the NOE (1000–541 Ma; Planavsky et al., 2015).

More dynamic and debated oxygenation history has been proposed for the Proterozoic hydrosphere. While many researchers (Canfield, 1998; Scott et al., 2008; Reinhard et al., 2013 and many others) support stratified ocean model with near oxic surface water and euxinic and/or ferruginous deep water in late Paleoproterozoic and Mesoproterozoic, the other view (Planavsky et al., 2014; Tang et al., 2016) advocates relatively low oxygen concentration (\(<0.2\ \mu\text{mol/l}\) in shallow seawater till mid-Proterozoic (~ 1.54 Ga). Oxygenation of deep-ocean is also controversial. From disappearance of iron formation in rock record, Holland (1984) and Holland and Beukes (1990) contemplated beginning of deep ocean oxygenation at ~ 1.8 Ga, which did not get support from studies on biomarkers of sulphur bacteria (Brocks et al., 2005) and Mo, Sr, Cr, and S isotope compositions in black shales (Arnold et al., 2004) and pyrites (Canfield, 1998, 2004; Poulton et al., 2004). Low trace element and phosphorus (P) concentrations in marine black shales allowed researchers to believe a continuation of the sulphidic-anoxic deep ocean throughout the Mesoproterozoic and parts of the Neoproterozoic until the \( P_{O_2} \) approached modern levels after ~ 1 Ga. A third view (Slack et al., 2007; Tang et al., 2016) claims suboxic condition with low concentrations of dissolved \( O_2 \) but no \( H_2S \) in the deep ocean based on \( REE \) and redox-sensitive Ce signature in hydrothermal silica-iron oxide sediments in open marine volcanogenic massive sulfide deposits.

All these studies considered rare earth element data, particularly Ce anomalies, as a robust proxy for shallow-marine redox condition. In fact, \( REE \) composition of iron formation and non-skeletal carbonates potentially preserve original oceanic signature, if the water-rock ratio between diagenetic-hydrothermal–metamorphic fluids and sedimentary rocks is low (Bau and Duski, 1996; Planavsky et al., 2010). Also, Ce is considered a unique redox proxy because in addition to its trivalent oxidation state, like other \( REEs \), it also exists in tetravalent oxidation state depending on the environmental oxidation condition. However, post-depositional reductive dissolution of iron oxide can significantly mobilize LREE including Ce to pore water and result in disturbance of the \( REE \) signature.

With this understanding, a number of recent studies have focused on iron formations as proxy for the emergence of oxygen in the Earth system: its initial production by at least 2.7 Ga (Kendall et al., 2010), its spread through the atmosphere between 2.45 and 2.32 Ga, the GOE (Farquhar et al., 2011), and a plunge in next billion years (mid-Proterozoic, 1.8–0.8 Ga; Reinhard et al., 2013; Tang et al., 2016). In this contribution, we use the geochemical proxy such as Ce anomaly, \( REE + Y \) and trace element signatures from iron formations and non-skeletal carbonates from the Gwalior basin, central India to throw light on possible ocean redox structure during the late Paleoproterozoic time.

**GEOLOGICAL SETTING**

**Basin geology**

Unconformably overlying the Bundelkhand gneiss in central India, rocks of the Gwalior Group (maximum thickness ~ 1.8 km) are exposed over an area of 2400 km\(^2\) (Ramakrishnan and Vaidyanadhan, 2010) (Figs. 1a and 1b). The Gwalior Group is subdivided into two formations; lower Par Formation and upper Morar Formation, the boundary between the two is marked by the presence of a meters-thick volcanic and volcanoclastic unit (Fig. 1c). The siliciclastic Par Formation, restricted all along the southern margin of the basin, is made up of medium to coarse-grained sandstones, fanglomerate/conglomerate, heterolithic sandstone-shale-carbonaceous shale; sandstones, by far, represent the largest volumetric proportion. From geochemical characters of clastics from the Par Formation, Absar et al. (2009) inferred severe weathering in the immediate basement of the basin. Formally overlying the Par Formation, rocks of the Morar Formation (maximum thickness ~ 800 m) represent dominant parts of the outcrop area of the Gwalior basin and composed mainly of iron formation and limestone with subordinate fine-grained argillaceous sediments, viz., ferruginous shale, black siliceous shale, and kaolinitic clay.

**Geochronological framework**

Two phases of dykes within the Bundelkhand Granite Massif, basement for the Gwalior basin, are dated as of 2150 and 2000 Ma through \(^{40}\text{Ar}^{39}\text{Ar}\) systematics (Ramakrishnan and Vaidyanadhan, 2010) and \( 1830 \pm 200 \) Ma (Rb-Sr isochron; Ramakrishnan and Vaidyanadhan, 2010) and \( 1854 \pm 7 \) Ma (U-Pb zircon concor-
The lower age limit for the Gwalior Group is constrained at 1.83 Ga (cf. Dubey, 1930). Absar et al. (2009, 2010) attempted dating of carbonates within the Morar Formation with Pb–Pb systematics and recorded ages of 1914 ± 120 Ma and 1866 ± 250 Ma. Recently, Paul (2017) has generated Sm–Nd mineral isochron age of 1787 ± 60 Ma from a basaltic sill that separates the Par and the Morar Formation. Taking into consideration the radiometric ages of basement mafic dyke and recalculating the Rb–Sr dates from the intrabasinal mafic rocks, Absar et al. (2009) bracketed the Gwalior depositional history between 2000 and 1791 Ma.

SEDIMENTARY FACIES

Iron formation

Limited availability of outcrop caused serious constraint on the field-based characterization of iron formation. Outcrops are dominantly isolated and exposed as railway/road cuttings and quarry sections. Six different facies types identified based on bed geometry, primary sedimentary structures, lithological affinity (chert–carbonate–shale-associated), and mineralogy (hematite/magnetite/Fe–chlorite). Figure 2 illustrates facies types and interpretation of paleogeographic settings that vary from shoreface–beach to subtidal distal shelf setting. Facies types MBF–1 and 2 record depositions in the wave-dominated shallow marine setting ranging from the beach–upper shoreface to distal shoreface. Plane-laminated tabular ferruginous sandstones with low-angle truncation in facies MBF–1 (Fig. 3a) resemble high energy sheet flow sandstones described from upper shoreface–beach setting (Clifton, 2006), whereas muddy and wave ripple laminated (Fig. 3b) lenticular sandstones of MBF–2 bear signatures for distal shoreface within fair-weather conditions.
wave base. The occurrence of wave ripples with wave-length: amplitude ratio of 8.5:1 and chevron cross-stratification in facies MBF–2 bear indication for the operation of fair weather oscillatory flow (Sarkar et al., 1996; Chakraborty and Paul, 2008). In either of these facies types, iron can be noticed both in an autochthonous and reworked form. Quartz and hematite constitute dominant mineralogy for both MBF–1 and 2 with subordinate magnesioferrite in MBF–1 and rare alumino-phosphate, i.e. berlinite in MBF–2.

The occurrence of hummocky cross-stratification (HCS) and gutter (Figs. 3c and 3d) suggests storm-induced sedimentation in facies MBF–3. Absence of any signature indicating fair weather reworking suggests depositional environment between fair weather and storm wave base, possibly in inner shelf setting. The presence of microbial (stromatolitic) structures in facies MBF–4 (Figs. 3e and 3f) suggests the intertidal to the supratidal environment. However, absence of any signature indicating emergence and desiccation, viz. mud crack rules out supratidal origin; instead, the occurrence of small domal stromatolite columns with wavy laminations within inter-columnar spaces bear indication for the low-energy shallow subtidal setting. Iron phases in facies MBF–3 and 4 are represented dominantly by hematite with magnetite with magnesioferrite in subordinate volume. The occurrence of clay phases like montmorillonite also noticed in some samples.

The highest percentage of Fe compared to other facies types distinguishes the laminated chert-carbonate-iron formation facies (MBF–5) from other facies types. The hallmark character for this facies is repetitive and regular alternations of mm- to centimeters-thick jasper and iron-rich layers laterally persisting for 100s of meter without any appreciable change in thickness (Fig. 3g). Hematite, magnesioferrite, and goethite with negligible quartz characterizes this facies. Significant lateral persistence of laminae without any outcrop-scale disruption and very low quartz content suggest low-energy distal depositional setting like the subtidal mid-shelf setting below the storm wave base. The occurrence of magnesioferrite \([\text{Mg(Fe}^{3+}\text{)}_2\text{O}_4]\), a spinel group mineral that forms a solid solution with magnetite, in a significant amount implies more anoxic condition for this facies than previously described facies types. Facies MBF–6 is characterized by alternation with fissile splintery shale and without any current or wave structure and represents the most distal setting with the highest bathymetry of the Morar Sea. Magnetite with subordinate hematite constitutes iron phases in this facies.
Figure 3. (a) Plane-laminated tabular sandstones in MBF-1. (b) Wave rippled (arrowed) siltstones in MBF-2. (c) Gutter (arrowed) and (d) hummocky cross-stratification (arrowed) in MBF-3. (e) Microbial carbonate in MBF-4 (f) with presence of small domal growth. (g) Alternation of thick and thin layers of jasper and Fe-rich band in MBF-5.
The Fe-rich bands of iron formation, in general, are submicron to centimeter–scale in thickness. Fe mineral phases associated with carbonate and chert (facies MBF-3, 4, and 5) are dominantly hematite and subordinately magnetite, while those alternated with shale (facies MBF-5 and 6) are Fe oxide/hydroxide recrystallized to hematite (cf. Chakraborty et al., 2015). At cases, Fe-rich bands entirely comprise of euhedral to subhedral crystals of martite, pseudomorph of magnetite (Fig. 4a) and hematite grains exhibit skeletal texture (Fig. 4c). The skeletal structure of hematite is potentially formed at the late diagenetic stage by oxidation of residual iron carbonates that might have escaped early silicification (Lascelles and Tsiokos, 2015). In addition, a few samples of massive iron formation have micro–fractures filled with goethite (colloform nature) (Fig. 4b). Fe-rich bands are sometimes disrupted by cross-cutting veins of calcite and chert (Fig. 4d).

**Carbonate**

Carbonates within the Morar Formation occur at two discrete stratigraphic levels, viz. i) at basal part of the Formation (Bela-ki-Bauri section); either as microbial limestones with occasional domal growth in alternation with volcanioclastics or as discrete lenticular limestone beds in alternation with dark grey shale and ii) at middle part of the Formation (Utila section); centimeter– to decimeter–thick tabular beds of massive or plane–laminated micritic limestone in alternation with light–grey limy shale (Figs. 5a, 5b, and 5c).

Limestones of these sections are dominantly micritic/ sucrosic in grain size (Figs. 5a and 5b) and calcitic in mineralogy. Mosaics of sparry calcite are present in patches or within late–stage veins (Fig. 6c); the maximum spar size measured is ~ 1000 µm. Dolomite grains, wherever present, are in the form of individual rhomb and volumetrically never exceed >6% in any of the observed thin sections. Only rarely, incipient replacement of micritic groundmass by cryptocrystalline silica (Fig. 6d) is noticed. Carbonates of the Bela-ki-Bauri section are sometimes mixed with volcanioclastics and basaltic melt resulting in replacement of micritic groundmass (Figs. 6e and 6f). The occurrence of pyrite within the micritic groundmass can be noticed in patches (Fig. 6g).

**MATERIAL AND METHODS**

Iron formations (37 samples) and carbonates (29 samples) were cleaned with Milli–Q water and powder to >200 mesh size. Whole–rock geochemical analyses for major and trace elements were carried out by the X–ray fluorescence (XRF) technique using Rigaku ZXS systems equipped at the Hiroshima University, Japan. At the Hiroshima University, X–ray generated by a 3kW Rh–W dual anode tube was radiated on fused bead samples. The detailed routine procedure is illustrated in Saha et al. (2016). The analytical precision (1σ) of major elements measured in XRF ranges between 0.001 and 0.14 wt%, whereas that for minor elements ranges between 0.68 and 2.39 ppm, as outlined in Kanazawa et al. (2001). Rare earth compositions of the carbonate samples were meas-
ured at the Wadia Institute of Himalayan Geology (WIHG), India using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP–AES JOBIN YVON JY–70). The details are in Das et al. (2009). On the other hand, REE compositions of iron formation samples were analyzed using Inductively Coupled Plasma Mass Spectrometer (ICPMS) at Shimane University, Japan. The analyzing procedure was as described by Kamei (2016).

Although REEs are commonly trivalent (+3), Ce and Eu can also occur in +4 and +2 states in addition to +3 state depending on the redox condition of their carrying fluid (Alibo and Nozaki, 1999; Hohl et al., 2015). Variations in shale (Post–Archean Australian Shale; Nance and Taylor, 1976)-normalized (SN) REE pattern commonly expressed either as anomalies from the pattern (i.e., for Ce and Eu) or as the elemental ratio (e.g., Yb(SN)/Pr(SN) etc.). However, care has to be taken in assessing true negative Ce(SN) anomalies from apparent Ce anomalies, which may arise because of La overabundance in seawater. To resolve the issue, Bau and Dulski (1996) took the help of an additional chemical parameter i.e., Pr/Pr*. In absence of any chemical reason in seawater that may result in Nd or Pr anomalies, the presence of a true Ce anomaly should lead to Pr/Pr* ≠ 1 (Bau and Dulski, 1996; Fei Ling et al., 2013). Keeping this in view, the present study calculated Ce/Ce* = Ce(SN)/[Pr(SN)2/Nd(SN)], Pr/Pr* = Pr(SN)/[0.5Ce(SN) + 0.5Nd(SN)], La/La* = La(SN)/[3Pr(N) – 2Nd(N)], and Gd/Gd* = Gd(SN)/[0.33 Sm(N) + 0.67Tb(N)] by following previous studies (Bau and Dulski, 1996; Lawrence et al., 2006; Ling et al., 2013; Tong et al., 2016).

RESULTS

Iron formation

Out of 37 iron formation samples from different facies types, 13 samples were analyzed for major and trace elements and REE, while the rest of the samples were analyzed only for REE (Tables 1 and 2). Jasper samples recorded constantly high SiO₂ (92.25–99.02%) and relatively low Fe₂O₃ (3.27–7.09%), while SiO₂ content showed a wider range (40.49–83.61%) and higher Fe₂O₃ (13.88–57.44%) in Fe-rich band samples. Except for two samples (BIF–Gw–1 and BIF–Gw–32), iron formation samples showed low concentrations of lithophile (Al, Ti, Zr, Th, and Sc) elements (3.62–44.05 wt%; av. 20.69 wt%), ∑REE (15.26–96.21 ppm), and Th (0.09–4.59 ppm) and co-variations between Ce/Ce*, Pr(SN)/Yb(SN), and Y/Ho ratios with Th concentration were insig-
Figure 6. Micritic (a) and sucrosic (b) carbonate. (c) Late-stage vein filled with sparry calcite. (d) Micritic carbonate groundmass replaced by cryptocrystalline silica in the Utilla section. (e) Extensive replacement of carbonate by volcanics, carbonates found only in patches. (f) Lapille within the micritic/tuffaceous groundmass. (g) Pyrite within sucrosic groundmass (arrowed).
These features are the characteristics of low clastic input (Planavsky et al., 2010; Tang et al., 2016). Irrespective of facies types, MnO concentration is uniformly low (0.03–0.11%) and MnO/Fe2O3 ratios range from 9 × 10⁻⁴ to 1 × 10⁻², which is lower than those recorded from hydrothermal iron hydroxide deposits of modern oxygenated oceans (e.g., Mid Atlantic Ridge precipitates; German et al., 1991, 1995; Slack et al., 2007).

The concentration of chalcophile elements, viz. Ni and Cu are uniformly low in both jasper and Fe-rich band; in most of the samples their concentrations are <50 and <20 ppm, respectively. Also, P2O5 content is low in both jasper and Fe-rich band samples (varying from 0.01–0.61%; av. 0.096%). The concentrations of Sc and Zr are 0.26–1.85 ppm and 0.56–35.85 ppm, respectively.

Shale-normalized REE data show a sub-parallel REE pattern with marginal LREE enrichment (Table 2 and Fig. 7e). Except for a few samples, Y/Ho ratios show relatively high values (33–50), which is close to the modern seawater values (~40–80; Nozaki et al., 1997). Only a couple of samples (BIF–Gw–5, BIF–Gw–6, BIF–Gw–14, and BIF–Gw–16) records Y/Ho values of 23.55–28.61, which is close to shale or crustal value (~27; Nozaki et al., 1997) (Table 2). Leaving aside samples with high La (marked by '*' in Table 2), La/La* and Gd/Gd* values mostly show positive anomalies (i.e., values larger than 1). Several samples show La/La* and Gd/Gd* values larger than 1.2 (grey area in Fig. 7f), which is the characteristics of modern and Archean seawater (cf. Viehmann et al., 2015). Iron formation samples (irrespective of jasper or Fe-rich band) record a wide variation in Ce anomaly ranging from marginally negative to small positive, i.e., 0.59–1.46 (Figs. 7e and 9a).
| REE/Gppm | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Yb | Ho | Er | Tm | Y | Yb* | La/La* | Gd/Gd* | Pr/Pr* | Ce/Ce* | Eu/Eu* | Y/Ho | Yb(SN)/Pr(SN) | Pr(SN)/Yb(SN) |
|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----------|-----------|---------|---------|---------|-------|-----------------|-----------------|
|          |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |          |           |         |         |         |       |                 |                 |
|          |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |          |           |         |         |         |       |                 |                 |
|          |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |          |           |         |         |         |       |                 |                 |
|          |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |          |           |         |         |         |       |                 |                 |

* Values not considered for further calculation, ** not analysed.

Table 2. REE + Y (trace elements) data and elemental ratios from Morar iron formation samples.

P.P. Paul, P.P. Chakraborty, F. Shiraishi, K. Das, A. Kamei and S. Bhattacharya.
Carbonates

29 carbonate samples (18 from the Bela–ki–Bauri section and 11 from the Utila section) are analyzed for REE. Table 3 presents the REE data. ∑REE values range from 33.35 to 226.46 ppm; whereas ∑REE for Bela–ki–Bauri samples ranges from 39.62 to 226.46 ppm and that of the Utila section are low and fall in a narrow range (33.35–71.16 ppm). Shale–normalized REE data (Figs. 8d and 8e) reveals a nearly smooth pattern with a clear signature of MREE (Sm to Ho) enrichment. The degree of MREE enrichment is calculated from La(SN)/Sm(SN) and La(SN)/Dy(SN) ratios: La(SN)/Sm(SN) ratios are 0.45–1.07 at the Bela–ki–Bauri section and 0.65–0.97 at the Utila section, while La(SN)/Dy(SN) ratios are 0.25–0.99 at Bela–ki–Bauri section and 0.51–1.01 at the Utila section.

Redox reconstruction of hydrosphere from carbonate REE data demands assessment for any effect of diageneisis, dolomitization or detrital contamination. Although it is believed that diageneisis does not alter REE pattern of carbonates in a large way (Webb et al., 2009), Ce enrichment, Eu depletion, and decrease in Dy(SN)/Sm(SN) ratio potentially occur during diageneric alteration (Ling et al., 2013). Cross–plots of Ce/Ce* with Eu/Eu*, Dy(SN)/Sm(SN), and ∑REE (Figs. 8a–8c) do not show any significant correlation (r² values 0.197, 0.029, and 0.045, respectively), suggesting insignificant diageneric effect in the REE patterns of studied carbonate samples (Shields and Stille, 2001).

Shale–normalized REE patterns of carbonates record small positive Ce anomaly of variable degrees (Fig. 9b); the magnitudes of anomaly are 1.03–1.19 at the Utila section and 1.08–1.18 at the Bela–ki–Bauri section. Most Gwalior carbonate samples show La(SN)/Nd(SN) values >1 (Table 3) and MREE–enrichment. It is noteworthy that carbonate samples uniformly record small positive Ce anomaly unlike the modern and Archean seawater (strong negative or absence of Ce anomaly; Derry and Jacobsen, 1990; Planavsky et al., 2014).

Three samples with substantial silica replacement (Fig. 6e) show a somewhat different trend: they are characterized by high ∑REE (Fig. 8c) and La/Sm, La/Dy, La/\Nd, etc.
| Sample | Utiila section | Bela ki Bauiri section |
|--------|---------------|-----------------------|
| L-0/12-01-13 | 12.75 | 13.01 |
| L-1/12-01-13 | 6.85 | 24.77 |
| L-2/12-01-13 | 12.06 | 10.21 |
| L-3/12-01-13 | 11.84 | 26.5 |
| L-4/12-01-13 | 8.38 | 17.64 |
| L-5/12-01-13 | 12.3 | 15.9 |
| L-6/12-01-13 | 8.23 | 17.34 |
| L-7/12-01-13 | 8.28 | 19.1 |
| L-8/12-01-13 | 12.26 | 29.05 |
| L-9/12-01-13 | 10.17 | 20.94 |
| L-10/12-01-13 | 14.53 | 30.77 |
| L-11/12-01-13 | 8.18 | 16.95 |

La/Nd(SN), La/Sm(SN), Dy/Sm(SN), Dp/Pr* Ce/Ce*, Eu/Eu* from carbonate samples.
Nd values ≥1. To consider the possible influence of siliciclastic on REE, these data are excluded from later discussion.

**DISCUSSION**

Fe-oxides at circum-neutral pH record REE patterns of seawater, whereas Mn oxides preferentially scavenge Ce and HREE and hence, register enrichment of those elements with respect to seawater (De Carlo et al., 2000; Ohta and Kawabe, 2001). Modern oxygenated seawater records strong negative Ce anomaly but no such anomaly is recorded when the seawater is anoxic (German and Elderfield, 1990; Byrne and Sholkovitz, 1996). In fact, the absence of any Ce anomaly in Archean and early Paleoproterozoic iron formations suggests the reducing character of basins. Both small negative (Derry and Jacobsen, 1990; Bolhar et al., 2005) and consistent small positive Ce anomalies (Slack et al., 2007) are recorded from late Paleoproterozoic hematitic iron formations. However, it is generally believed that ~1.9 Ga iron formations, deposited after the initial rise of atmospheric oxygen (GOE), commonly show positive Ce anomalies (Planavsky et al., 2010).

Marginal negative to small positive Ce anomaly in iron formation (0.69–1.46) bears strong indication towards mildly oxidizing to reducing condition. Whereas negative Ce anomalies point towards an oxidizing condition in the shallow sea, positive Ce anomalies indicate that there was redox cycling of Ce in the subtidal environment of the Gwalior Sea. A stratified water column with a transitional redox zone must have existed so that Ce(IV) scav-
enged by Mn–Fe oxides, organic matters and clay minerals in oxic-suboxic shallow sea went through reductive dissolution below the redoxcline, resulting in accumulation of reduced Ce(III) (Byrne and Sholkovitz, 1996; Slack et al., 2007). Chemical proxies like very low MnO concentration (0.03–0.11%), low to very low MnO/Fe2O3 ratio and a variable light to heavy REE (Pr/SN/Yb/SN) ratio including samples (12 out of 33 total samples analyzed; Table 2) recording values ≥ 1 point towards reductive Mn–Fe oxide dissolution across the redox boundary (De Carlo and Green, 2002; Tang et al., 2016). A possible modern analog may be the Black Sea where small negative to positive Ce anomaly is interpreted as a result of the stratified water column in terms of concentration of oxygen, H2S, dissolved and particulate Mn (Germán et al., 1991). The rare presence of sulfide in association with iron formation and dominant hematite mineralogy rules out anoxic, sulfidic condition around 1.84 Ga (German et al., 1991). Recent studies using sulfur isotope composition and model for rate–dependent sulfur isotope change in marine carbonate-associated sulfides (CAS) Kah et al. (2004) calculated marine sulfate levels only 5 to 15% of modern values for more than 1 Ga after initial oxidation of Earth’s biosphere. A suboxic to the near anoxic condition that is equally compatible to account for most of the geochemical results may be a more acceptable alternative global deep ocean model (Arnold et al., 2004; Slack et al., 2007; Singh et al., 2018). Sulfidic condition possibly remained restricted within intracratonic basins and shallow shelves those had limited communication with the global ocean (Slack et al., 2007).

Geochemical signatures from carbonates are not found in full agreement with geochemical proxies from BIF. Alkali most pre ~ 1.54 Ga carbonates (Planavsky et al., 2010; Tang et al., 2016; Bellefroid et al., 2018), Gwalior carbonates, irrespective of facies type, record absence of negative Ce anomaly (1.03–1.19) and suggest minimum Ce redox cycling. Geochemical signatures in support of the presence of a redoxcline could not be found from carbonates. It is pertinent to mention here that from sedimentological evidence it is interpreted that carbonates in the Morar sea were deposited at shallow (Bela-kí) or deep (Utila) subtidal setting, which may be either close to the redoxcline or below it. La/Nd values >1 and uniform positive Ce anomaly in carbonates bears indication of consistent low concentration of dissolved O2 in Gwalior deep sea.

Since carbonates are not the efficient carrier of redox-sensitive elements during deposition (Tang et al., 2016) and the negative Ce anomaly in BIF remains well evident, it may be argued that the Morar coastline was mildly oxidizing only where the dissolved concentration of O2 raised above 0.2 μM favoring Mn(II) oxidation. A subtle drop in DO2 (<0.2 μM) across the redoxcline resulted in Gwalior deepwater suboxic to near anoxic and ferruginous. This is consistent with previous studies (Poulton et al., 2010; Luo et al., 2014; Zhang et al., 2018) that suggest a very low surface water oxygenation in late Paleoproterozoic and early Mesoproterozoic oceans.

CONCLUSIONS

1. REE + Y signature including small negative to positive Ce anomaly in BIF bears indication for a stratified water column in late Paleoproterozoic Gwalior sea with mildly oxidizing shallow water and reducing ferruginous deep sea. Absence of sulfide in association with BIF and dominant hematite mineral-
ogy rule out the sulfidic condition and instead allowed the proposition of suboxic to near anoxic condition with $P_{O_2} < 0.2 \mu M$ in Gwalior deep sea.

2. The dissolved concentration of oxygen (DO$_2$) was not so high in the shallow water of the Gwalior Sea either. The shallow Gwalior sea possibly was of mildly oxidizing/suboxic nature that could allow limited Mn(II) oxidation and Ce sequestration. Redoxcline was shallow and the absence of any significant negative Ce anomaly does not support a well-oxygenated condition even in shallow Gwalior coastline.

3. Gwalior carbonates do not record any signature for redoxcline. Carbonates in Gwalior basin belong to either shallow subtidal or deeper shelf below wave base depositional setting and record La/Nd values >1, MREE enrichment and uniform positive Ce anomaly.

ACKNOWLEDGMENTS

We thankfully acknowledge financial supports from the University Grants Commission in the form of a major Project and National Post-Doctoral Fellowship (SERB no. PDF/2017/000320) award to the first author. Thanks also due to Dr. Subhojit Saha for assisting in the field.

REFERENCES

Absar, N., Raza, M., Roy, M., Naqvi, S.M. and Roy, A.K. (2009) Composition and weathering conditions of Paleoproterozoic upper crust of Bundelkhand Craton, Central India: Records from geochemistry of clastic sediments of 1.9 Ga Gwalior Group. Precambrian Research, 168, 313–329.

Absar, N., Raja, M., Roy, M., Pandey, B.K., et al. (2010) Pr, Sr, and Isotopic systematics of chemical sedimentation of Paleoproterozoic Gwalior Group, Bundelkhand Craton, Central India: Implication for age and provenance. Exploration and Research for Atomic Minerals, 20, 73–96.

Alibo, D.S. and Nozaki, Y. (1999) Rare earth elements in seawater: particle association, shale-normalization, and Ce oxidation. Geochimica et Cosmochimica Acta, 63, 363–372.

Arnold, G.L., Anbar, A.D., Barling, J. and Lyons, T.W. (2004) Molybdenum isotope evidence for widespread anoxia in Mid-Proterozoic oceans. Science, 304, 87–90.

Bau, M. and Dulski, P. (1996) Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron formations, Transvaal Supergroup, South Africa. Precambrian Research, 79, 37–55.

Bellefroid, E.J., Hood, A.V.S., Hoffman, P.F., Thomas, M.D., et al. (2018) Constraints on Paleoproterozoic atmospheric oxygen levels. Proceedings of the National Academy of Sciences, 115, 8104–8109.

Bolhar, R., Van Kranendonk, M.J. and Kamber, B.S. (2005) A trace element study of siderite-jasper banded iron formation in the 3.45 Ga Warrawoona Group, Pilbara Craton formation from hydrothermal fluids and shallow seawater. Precambrian Research, 137, 93–114.

Brooks, J.J., Logan, G.A., Buick, R. and Summers, R.E. (1999) Archean molecular fossils and the early rise of eukaryots. Science, 285, 1033–1036.

Brooks, J.J., Love, G.D., Summers, R.E., Knoll, A.H., et al. (2005) Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. Nature, 437, 68–70.

Byrne, R.H. and Sholkovitz, E.R. (1996) Marine chemistry and geochemistry of the lanthanides. In Handbook on the Physics and Chemistry of Rare Earths (Geijsbeek, K.A., Jr. and Eyring, L. Eds.). Elsevicer, Amsterdam, 497–593.

Canfield, D.E. (1998) A new model for Proterozoic ocean chemistry. Nature, 396, 450–453.

Canfield, D.E. (2004) The evolution of the earth-surface sulphur reservoir. American Journal of Science, 304, 839–61.

Chakraborty, P.P. and Paul, S. (2008) Forced regressive wedges on a Neoproterozoic siliciclastic shelf: Chandrapur Group, central India. Precambrian Research, 162, 227–247.

Chakraborty, P.P., Pant, N.C. and Paul, P.P. (2015) Controls on sedimentation in Indian Palaeoproterozoic basins: clues from the Gwalior and Bijawar basins, central India. In Precambrian Basins of India: Stratigraphy and Tectonic Context (Majumder, R. and Eriksson, P.G. Eds.), pp. 352, Geological Society London, Memoirs, 67–83.

Clifton, H.E. (2006) A re-examination of facies models for clastic shorelines. In Facies Models Revisited (Posamentier, H.W. and Walker, R.G. Eds.). SEPM special publication, 84, Tulsa, Oklahoma, USA, 293–337.

Dai, Y.D., Song, H.M. and Shen, J.Y. (2004) Fossil bacteria in Xuanlong iron ore deposits of Hebei Province. Science China (Earth Science), 47, 347–356.

Das, K., Yokoyama, K., Chakraborty, P.P. and Sarkar, A. (2009) Basal tuffs and Contemporaneity of Chhatisgarh and Kharai basins based on new dates and geochemistry. Journal of Geology, 117, 88–102.

Deb, M., Thorpe, R. and Kristic, D. (2002) Hindoli Group of Rocks in the Eastern Fringe of the Aravalli-Delhi Orogenic Belt-Archean Secondary Greenstone Belt or Proterozoic Supracrustals? Gondwana Research, 5, 879–883.

De Carlo, E.H., Wen, X.Y. and Irving, M. (2000) The influence of redox reactions on the uptake of dissolved Ce by suspended Fe and Mn oxide particles. Aquatic Geochemistry, 3, 357–389.

De Carlo, E.H. and Green, W.J. (2002) Rare earth elements in the water column of Lake Vanda, McMurdo dry valley, Antarctica. Geochimica et Cosmochimica Acta, 65, 1231–1234.

Derry, L.A. and Jacobsen, S.B. (1990) The chemical evolution of Precambrian seawater: Evidence from REEs in banded iron formation. Geochimica et Cosmochimica Acta, 54, 2965–2977.

Dubey, V.S. (1930) Helium Ratios of the basic rocks of Gwalior series. Nature, 126.

Edwards, K.J., Rogers, D.R., Wirsns, C.O. and McCollom, T.M. (2003) Isolation and characterization of novel psychrophilic, neutrophilic, Fe-oxidizing, chemolithoautotrophic α and γ-Proteobacteria from the deep sea. Applied and Environmental Microbiology, 69, 2906–2913.

Farquhar, J., Zerkle, A.L. and Bekker, A. (2011) Geological constraints on the origin of oxygenic photosynthesis. Photosynthesis Research, 107, 11–36.

German, C.R. and Elderfield, H. (1990) Application of the Ce
anomaly as a paleoredox indicator: the ground rules. Paleoceanography, 5, 823-833.

German, C.R., Holliday, B.P. and Elderfield, H. (1991) Redox cycling of rare earth elements in the suboxic zone of the Black Sea. Geochimica et Cosmochimica Acta, 55, 3553-3588.

German, C.R., Masuzawa, T., Greaves, M.J., Elderfield, H. and Edmond, J.M. (1995) Dissolved rare-earth elements in the Southern Ocean: cerium oxidation and the influence of hydrosphere. Geochimica et Cosmochimica Acta, 59, 1551-1558.

Gradstein, F.M., Ogg, J.G., Schmitz, M.D. and Ogg, G.M. (2012) The Geological Time Scale. (4th edition). Elsevier, Amsterdam.

Hoffman, P.F., Kaufman, A.J., Halverson, G.P. and Schrag, D.P. (1998) A Neoproterozoic snowball Earth. Science, 281, 1342-1346.

Hohl, S.V., Becker, H., Herzlieb, S. and Guo, Q. (2015) Multi-proxy constraints on alteration and primary compositions of Ediacaran deep-water carbonate rocks, Yangtze Platform, South China. Geochimica et Cosmochimica Acta, 163, 262-278.

Holland, H.D. (1984) The Chemical Evolution of the Atmosphere and Oceans. Princeton University Press.

Holland, H.D. (2006) The oxygenation of the atmosphere and oceans. Philosophical Transactions of the Royal Society, B 361, 903-915.

Holland, H.D. and Beukes, N.J. (1990) A paleoweathering profile from Griqualand West, South Africa: evidence for a dramatic rise in atmospheric oxygen between 2.2 and 1.9 by bp. American Journal of Science, 290-A, 1-34.

Kah, L.C., Lyons, T.W. and Frank, T.D. (2004) Low marine sulfate and protracted oxygenation of the Proterozoic biosphere. Nature, 431, 834-838.

Kamei, A. (2016) Determination of trace elements abundance in the Yangtze Gorges area, South China: implications for oxygenation of ocean shallow seawater. Precambrian Research, 225, 110-127.

Liu, X.M., Kah, L.C., Knoll, A.H., Cui, H., et al. (2016) Tracing Earth's O₂ evolution using Zn/Fe ratios in marine carbonates. Geochemical Perspective Letters, 2, 24-34.

Luo, G.M., Junium, C.K., Kump, L.R., Huang, J.H., et al. (2014) Shallow stratification prevailed for ~1700 to ~1300 Ma ocean: evidence from organic carbon isotopes in the North China Craton. Earth Planetary Science Letter, 400, 219-232.

Lyons, T.W., Reinhard, C.T. and Planavsky, N.J. (2014) The rise of oxygen in Earth’s early ocean and atmosphere. Nature, 506, 307-315.

Mallikharjuna Rao, J., Poornachandra Rao, G.V.S., Widdowson, M. and Kelley, S.P. (2005) Evolution of Proterozoic mafic dyke swarms of the Bundelkhand granite massif, central India. Current Science, 88, 502-506.

Mukherjee, I., Large, R.R., Corkrey, R. and Danyushevsky, L.V. (2018) The Boring Billion, a slingshot for complex life on Earth. Scientific Reports, 8:4432, 1-7.

Mukhopadhyay, J., Crowley, Q.G., Ghosh, S., Ghosh, G., et al. (2014) Oxygenation of the Archean atmosphere: New paleosol constraints from eastern India. Geology, 42, 923-926.

Nance, W.B. and Taylor, S.R. (1976) Rare-Earth Element Patterns and Crustal Evolution-1. Australian Post-Archean Sedimentary-Rocks. Geochimica et Cosmochimica Acta, 40, 1539-1551.

Nelson, D.R., Trendall, A.F. and Altermann, W. (1999) Chronological correlations between the Pilbara and Kaapvaal cratons. Precambrian Research, 97, 165-189.

Nozaki, Y., Zhang, J. and Amakawa, H. (1997) The fractionation between Y and Ho in the marine environment. Earth Planetary Science Letter, 148, 329-340.

Obta, A. and Kawai, I. (2001) REE (III) adsorption onto Mn dioxide (δ-MnO₂) and Fe oxyhydroxide: Ce (III) oxidation by δ-MnO₂. Geochimica et Cosmochimica Acta, 65, 695-703.

Paul, P.P. (2017) Autogenetic and Allogenic controls on late Paleoproterozoic continental and marine sedimentation: clues from Gwalior rift basin, Central India. pp. 254, Ph.D. thesis, University of Delhi, Delhi, India.

Planavsky, N.J., Bekker, A., Rouxel, O.J., Kamber, B., et al. (2010) Rare earth element and yttrium compositions of Archean and Paleoproterozoic Fe formations revisited: New perspectives on the significance and mechanisms of deposition. Geochimica et Cosmochimica Acta, 74, 6387-6405.

Planavsky, N.J., Reinhard, C.T., Wang, X.L., Thomson, D., et al. (2014) Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. Science, 346, 635-638.

Planavsky, N.J., Tarhan, L.G., Belfroid, E.J., Evans, D.A.D., et al. (2015) Late Proterozoic transitions in climate, oxygen, and tectonics, and the rise of complex life. In Earth-Life Transitions: Paleoecology in the Context of Earth System Evolution (Polly, P.D., Head, J.J. and Fox, D.L. Eds.). The Paleontological Society Papers, Volume 21, 47-82.

Poulton, S.W., Fralick, P.W. and Canfield, D.E. (2004) The transition to a sulphidic ocean similar to 1.84 billion years ago. Nature, 431, 173-177.

Poulton, S.W., Fralick, P.W. and Canfield, D.E. (2010) Spatial variability in oceanic redox structure 286-1.8 billion years ago. Nature Geoscience, 3, 486-490.

Ramakrishnan, M., and Vaidyanadhan, R. (2010) Geology of India. pp. 556, Geological Society of India 1, Bangalore.

Reinhard, C.T., Planavsky, N.J., Robbins, L.J., Partin, C.A., et al. (2013) Proterozoic ocean redox and biogeochemical stasis. Proceedings National Academy Science U.S.A., 110, 5357-5362.

Roy, A.K., Absar, N., Kumar, S., Sharma, R., et al. (2005) Some observation on lithostratigraphy and uranium potential of Gwalior Group of rocks, Gwalior District, MP. Proceedings
of International Conference on Precambrian Crustal growth and Tectonism. Bundelkhand University, Jhansi, 299–301.

Saha, S., Das, K., Hidaka, H., Kimura, K., et al. (2016) Detrital zircon geochronology (U–Pb SHRIMP and LA-ICPMS) from the Ampani Basin, Central India: Implication for provenance and Mesoproterozoic tectonics at East Indian cratonic margin. Precambrian Research, 281, 363–383.

Sarkar, A., Chakraborty, P.P., Mishra, B., Bera, M.K., et al. (2010) Mesoproterozoic sulphidic ocean, delayed oxygenation and evolution of early life: sulphur isotope clues from Indian Proterozoic basins. Geological Magazine, 147, 206-218.

Sarkar, S., Chakraborty, P.P. and Bose, P.K. (1996) Proterozoic Lakheri Limestone, Central India: facies, paleogeography and physiography. In Recent Advances in Vindhyan Geology (Bhattacharya, A. Ed). Memoir Geological Society of India, 36, 5-25.

Scott, C., Lyons, T.W., Bekker, A., Shen, Y., et al. (2008) Tracing the stepwise oxygenation of the Proterozoic ocean. Nature, 452, 456–459.

Schippers, A., Neretin, L.N., Lavik, G., Leipe, T. and Pollehne, F. (2005) Manganese (II) oxidation driven by lateral oxygen intrusions in the western Black Sea. Geochimica et Cosmochimica Acta, 69, 2241-2252.

Shields, G. and Stille, P. (2001) Diagenetic constraints on the use of cerium anomalies as palaeoseawater redox proxies: an isotopic and REE study of Cambrian phosphorites. Chemical Geology 175, 29-48.

Shields-Zhou, G.A. and Och, L. (2011) The Neoproterozoic oxygenation event: geochemical evidence and biological consequences. GSA Today, 21, 4-11.

Singh, A.K., Chakraborty, P.P. and Sarkar, S. (2018) Redox structure of Vindhyan hydrosphere: clues from total organic carbon, transition metal (Mo, Cr) concentrations and stable isotope (δ13C) chemistry. Current Science, 115, 1334–1341.

Slack, J.F., Grenne, T., Bekker, A., Rouxel, O.J. and Lindberg, P.A. (2007) Suboxic deep seawater in the late Paleoproterozoic: Evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA. Earth and Planetary Science Letters, 255, 243–256.

Tang, D., Shia, X., Wang, X. and Jiang, G. (2016) Extremely low oxygen concentration in mid-Proterozoic shallow seawaters. Precambrian Research, 276, 145-157.

Tang, D.J., Shi, X.Y., Liu, D.B., Lin, V.T., et al. (2015) Terminal Paleoproterozoic ooidal ironstone from North China: a sedimentary response to the initial breakup of Columbia supercontinent. Earth Science Journal, China University Geoscience, 40, 290-304.

Taylor, S.R. and McLennan, S.M. (1997) The origin and evolution of Earth’s continental crust. Journal of Australian Geology and Geophysics, 17, 52-62.

Viehmann, S., Baua, M., Hoffmann, J.E. and Münker, C., (2015) Geochemistry of the Krivoy Rog Banded Iron Formation, Ukraine, and the impact of peak episodes of increased global magmatic activity on the trace element composition of Precambrian seawater. Precambrian Research, 270, 165-180.

Webb, G.E., Northdurft, L.D., Kamber, B.S., Kloprogge, J.T. and Zhao, J.-X. (2009) Rare earth elements geochemistry of scleractinian coral skeleton during meteoric diagenesis: a sequence through neomorphism of aragonite to calcite. Journal of International Association of Sedimentologists, 56, 1433-1463.

Zhang, K., Zhu, X., Wood, R.A., Shi, Y., et al. (2018) Oxygenation of the Mesoproterozoic ocean and the evolution of complex eukaryotes. Nature Geoscience, 11, 345-350.

Manuscript received October 11, 2019
Manuscript accepted January 26, 2020
Manuscript handled by Jun-ichi Ando