A number of Precambrian sedimentary basins of the Indian subcontinent offer scope for tracking early oxygenation history of atmosphere and hydrosphere. Available studies, though certainly not exhaustive, record signatures of pre-great oxygenation event (GOE) whiffs of atmospheric oxygenation between 3.29 and 3.02 Ga. Besides, available geochemical signatures from Precambrian sedimentary rocks (BIF, sulfides, sulfates, argillaceous sediments and phosphorites) suggest a generally sub-oxic shallow marine and bipartite oxic-sulfidic condition in late Paleoproterozoic and Mesoproterozoic time, respectively. In this backdrop, occurrence of phosphorites in several late Paleoproterozoic basins possibly indicates formation of local oxygen oasis in presence of cyanobacterial community. From heavy to very heavy $\delta^{34}$S values in sulfides (pyrite) present in a number of Mesoproterozoic basins and Mo, Mo/TOC values from argillaceous intervals of the Vindhyan Supergroup, it is inferred that the deep hydrosphere was, in general, anoxic and, at times, euxinic.

Introduction

The Proterozoic Eon (2500–541 Ma before present, Gradstein et al., 2012) encompasses more than 40% of the Earth history and represents an unique time period that witnessed amalgamation and breakup of supercontinents (Dalziel, 1997) with growing importance of Phanerozoic-style plate tectonics (Nelson, 1998; 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 e.g., Paleoproterozoic (2500 - 1800 Ma) and late Neoproterozoic (800 -541 Ma) witnessed major biological, tectonic, climatic and atmospheric changes. The billion year interval (1800 - 800 Ma) mostly encompassing the Mesoproterozoic time on the other hand is marked by tectonic, climatic and evolutionary stability (Reddy and Evans, 2009; Mukherjee et al., 2018). Nevertheless, amongst 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 despite the early appearance of cyanobacteria and initiation of oxygenic photosynthesis well before the Great Oxidation Event (GOE) (Farquhar et al., 2011), the early atmosphere remained reducing in nature with reduced gases e.g., CO, NH$_3$, H$_2$O, H$_2$, CH$_4$, CO$_2$ and N$_2$ as main constituents (Shaw, 2014; Kanzaki and Murakami, 2015). A combination of processes viz. a switch from dominant submarine to subaerial volcanism, gradual oxidation of continents and concomitant decrease in reduced metamorphic gases, a decline in nickel availability and deposition of banded iron formation caused change in the fluxes of oxidants and reductants to the Earth’s surface to promote photosynthesis (Kasting, 2013) and led to the rise of O$_2$ at the GOE (2.4 to 2.3 Ga ago). The idea that concentration of O$_2$ in the atmosphere rose modestly for the first time (i.e <0.001% to >0.1% of Present Atmospheric Level, PAL) at the GOE and further waited patiently for about two billion years to rise to a higher level in Neoproterozoic Oxygenation event (NOE; Och and Shields-Zhou,2012) is contested in recent studies by Lyons et al., (2014); Crowe et al., (2013) and Mukhopadhyay et al., 2014), wherein evidences for whiffs of rise in atmospheric oxygen are put forward well before the GOE. In fact, dynamic scenarios that have emerged in recent studies include possibility of a much larger $p$O$_2$ early on at the GOE, which is followed by a deep plunge to a lower level (<<0.1% PAL) in next billion year...
Figure 1. Generalized geological map of peninsular India (star marks indicate discussed sections; a) detail geological map and lithostratigraphy (with available geochronology data) for the Vindhyan basin, Aravalli basin and Gwalior basin; b) detail geological map and lithostratigraphy (with available geochronology data) for the Singhbhum craton, Sausar craton, Shillong plateau, Cuddapah basin and Chhattisgarh basin.
until it raised again at the NOE (1000-541 my before present) under the combined influence of: i) intense chemical weathering of early Neoproterozoic continental landmass assembled near paleo-equator, ii) weathering of Large Igneous Provinces (LIPs) and enhanced supply of phosphorus (P) in ocean iii) organic bloom in ocean triggered by enhance availability of phosphorus vis-à-vis increased carbon burial (Planavsky et al., 2015).

More dynamic and debated oxygenation history has been proposed for the Proterozoic hydrosphere. While a strong school (Canfield, 1998; Scott et al., 2008; Planavsky et al., 2011; Reinhard et al., 2013 and many others) believes in 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 µm/litre) in shallow seawater till mid-Proterozoic (~1.54 Ga). Opinions vary widely for oxygenation of deep-ocean as well. From disappearance of iron formation (BIF) in rock record, Holland, (1984), Holland & Beukes (1990) contemplated beginning of deep ocean oxygenation at c. 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 pyritites (Canfield, 1998, 2004; Poulton et al., 2004). Low trace element and phosphorous (P) concentrations in marine black shales allowed workers to believe continuation of the sulphidic-anoxic deep ocean throughout the Mesoproterozoic and parts of the Neoproterozoic until the pO2 approached modern levels after c. 1 Ga. A third view (Slack et al., 2007) claims sub-oxic condition with low concentrations of dissolved O2 but no H2S 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. These studies considered Rare Earth Elements and Yttrium (REE + Y) data, particularly cerium (Ce) anomalies, as robust proxy for shallow-marine redox condition. In fact, 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. While in anoxic hydrosphere of Archean and Paleoproterozoic, the lack of trivalent Ce oxidation and absence of deep-ocean ferromanganese oxides led to high (positive) Ce concentration, in modern oxygenated deep-ocean oxidation of Ce to tetravalent state and availability of ferromanganese oxide (nodule and crust) result in negative Ce anomaly in sea water.

The Peninsular India, an ensemble constituting Archean cratonic nuclei, orogenetic belts, intrusive rocks and cover of extrusive volcanic and sedimentary rocks, records c. 3.0 Ga of Precambrian history (3.5-0.5 Ga; Fig. 1) and is considered a unique archive preserving the yet unexplored Precambrian events. Available geochronological data suggests cratonization of continental blocks viz. Aravalli-Bundelkhand, Eastern and Western Dharwar, Bastar and Singhbhum and their amalgamation in Peninsular India at about 2.5 to 2.6 Ga (Meert et al., 2010). On the cratonic basement, sedimentary basins evolved between late Archean and late Neoproterozoic, locally straddling the Precambrian-Cambrian boundary. Amongst them, most important are the unmetamorphosed and nearly undeformed Proterozoic cratonic basins, classically referred to as ‘Purana Basins’ in Indian stratigraphy. An attempt has been made to classify these basins (Meert et al., 2010; Meert and Pandit, 2015; Basu and Bickford, 2015) under three tiers viz. Paleo- to Mesoproterozoic, early Neoproterozoic and late Neoproterozoic, spanning an age range between 2 Ga and 542 Ma (Fig. 1). Availability of paleosol, chemical sediments e.g. carbonates, phosphorites, iron formations and sulfides (pyrite), sulfates (barite) etc. as integral parts of deformed late Archean and undeformed, unmetamorphosed Proterozoic basin fill packages have facilitated study of atmosphere and hydrosphere oxygenation history preserved in Indian geological records. Aim of present contribution is to collate and summarize available information from Precambrian basins of the Indian subcontinent.

**Atmospheric oxygenation record**

Paleosols are the best preserved direct record of atmospheric oxygen concentration (Rye and Holland, 1998). The study of Precambrian paleosol is seriously constrained by the extent and state of preservation. When a paleosol suffered significant erosion after weathering, false conclusions could be drawn from it (e.g., Rye and Holland 1998; Beukes et al., 2002; Murakami et al., 2011). However, better preserved records from the Archean-Paleoproterozoic paleosols allow the distinction between the oxic and reduced paleosols based on mobilization of soluble Fe2+ in the reduced paleosol profile (Rye and Holland, 1998) (e.g., 2.7 Ga Mount Roe paleosol, Macfarlane et al., 1994). The Fe2+ on the other hand is retained in the form of Fe3+ in the upper part of the profile as laterite capping in case of the oxic paleosols (e.g., Hekpoort Paleosol, Beukes et al., 2002). The pre-GOE rise in atmospheric oxygenation has been reported from several >2.5 Ga paleosols (e.g. Hokkalampi Paleosol from North Karelia, Finland: Marmo, 1992). The oldest such report comes from the ~3.4 Ga Pilbara paleosol from Western Australia (Johnson et al., 2008). Johnson et al. (2008) described the paleosol as a typical top down alteration profile in pyrophyllite (locally chloride) with hematite (F3+)-rich alteration zone at the upper part similar to lateritic profile of the 2.2 Ga Hekpoort paleosol from the Transvaal basin South Africa (Beukes et al. 2002). Mukhopadhyay et al. (2014) reported pre-GOE oxygenation from the ~3.0 Ga old Koonjar Paleosol in the Singhbhum craton, India. Pre-GOE oxygenation was also suggested by Crowe et al. (2013) from the 2.98 Ga to 2.96 Nsuze paleosol in the Pongola basin South Africa. However, recent studies report uncertainties on such interpretation (e.g. Kasting, 2013; Kanzaki and Murakami, 2015; Rybacki et al., 2016). Other evidences come from: reduced paleo placers from Archean deposits consisting of minerals such as pyrite and uraninite as detrital components (e.g., Grandstaff, 1974; Smith and Minter, 1980; Rasmussen and Buick 1999; Mukhopadhyay et al., 2012; 2016), secular trend in BIF abundance (Dymek and Klein, 1988; Beukes and Klein, 1992) and mass independent isotopic fractionation (MIF) in pre-GOE sulfides (Farquhar and Wing, 2013; Lyons et al., 2014). Luo et al. (2016), based on the model of Goldblatt et al. (2006), suggested that the great oxidation event or GOE witnessed a sharp rise in atmospheric oxygen concentration to more than 10 ^{3} P aL at around 2.33 Ga. A recent update of the model (Daines and Lenton, 2016) argued that a high level of atmospheric methane is necessary for the rapid rise of oxygen, which may or may not be the case in the early Paleoproterozoic (e.g., Zahlten et al., 2006; Olson et al., 2016). Major evidence in favour of oxygenation is the disappearance of mass-independent sulphur isotopic fractionation at around 2.5 Ga (Kaufman et al., 2007).
Indian Record

Oxygen in atmosphere from Paleosols and fluvial deposits

From paleosols of the Singhbhum, Aravalli and Bastar Cratons and Meghalaya plateau:

Reducing nature of early atmosphere is recorded in the uraniferous quartz pebble conglomerate (QPC) deposits from Mesoarchean Mahagiri-Keonjhar-Mankaharchua quartzites (Mukhopadhyay et al., 2014, 2016) and basal parts of the Meso-Neoarchean Dhanjori succession in the Singhbhum craton and the similar QPC deposits at the base of the Mesoarchean Bababudan Group of the western Dharwar craton (Srinivasan and Ojakangas, 1986). Precambrian paleosols are reported from the Singhbhum craton (Bandyopadhyay et al., 2010; Mukhopadhyay et al., 2014), Aravalli craton (Banerjee, 1996; Sreenivas et al., 2001), Central Indian Tectonic Zone (CITZ) (Mohanty and Nanda, 2016), Eastern Ghats (Dash et al., 1987; Sreenivas and Srinivasan, 1994) and Sonapahar sillimanite in Meghalaya, Northeastern India (Golani, 1989). Among these the first three occurrences have been studied in detail.

The Keonjhar Paleosol ranks among the oldest paleosols in the world (Fig. 2). The pre-GOE Mesoarchean oxic paleosol is developed over the 3.2 Ga Singhbhum Granite from the Singhbhum craton in eastern India (Mukhopadhyay et al., 2014). U-Pb zircon data suggest that the Keonjhar Paleosol was developed between 3.29 Ga and 3.02 Ga. The top part of the paleosol is not preserved. Mukhopadhyay et al. (2014) described typical top-down alteration zone with depletion of mobile elements (Na, Ca, Mg, Cs, Zn, Ni) with respect to the basement granitoid. They also noted Fe-Mn depletion, HREE enrichment and true negative Ce-anomaly from the preserved profile of the Keonjhar Paleosol. The reduced paleoplacers of uraniferous-pyritiferous QPCs of the overlying Keonjhar-Mahagiri Quartzite (Mukhopadhyay et al., 2016) suggest the return of the reducing atmosphere and support whiffs of oxygenation of early atmosphere prior to GOE (Fig. 2).

The Udaipur paleosol (Tulsi-Namla paleosol) (Banerjee, 1996; Sreenivas et al., 2001) developed in between the BGC and basal quartzite of the Paleoproterozoic Aravalli Supergroup preserves the topmost ferricrete capping of an oxic paleosol supposedly developed during 2.5 Ga and 2.1 Ga (Banerjee, 1996; Pandit et al., 2008; Wall et al., 2012; Fig. 1a, 2). However, from 1709±8 Ma age of a single detrital zircon grain from the Delwara Formation and 1.9–1.7 Ga detrital zircon ages from the Jamarkotra Formation, McKenzie et al. (2013) questioned the early Paleoproterozoic age of the paleosol. The paleosol is exposed at the base of the Debari quartzite all over the Girwa (Udaipur) valley and has been metamorphosed in greenschist facies. The Udaipur paleosol at Tulsi-Namla section

Figure 2. A summary diagram showing current status on understanding of atmosphere and hydrosphere oxygenation and signatures from Indian Precambrian basins.
includes the most complete section with lower saprolite zone, followed upward by white mica zone capped by red ferricrete (Pandit et al., 2008; Wall et al., 2012). Pandit et al., (2008) described five zones within Tulsi-Namla paleosol. The Udaipur paleosol with complete profile of a typical laterite is comparable to the Hekpoort paleosol of South Africa (Beukes et al., 2002). However, Sreenivas et al. (2001) did not observe any ferricrete horizon in the profile they studied and they reported that the paleosol had been metamorphosed to kyanite grade that subsequently broke down to mica.

Mohanty and Nanda (2016) described ~2.4 Ga paleosol from the base of the Sausar succession in the Central Indian Tectonic Zone (Fig. 1b). The paleosol horizon overlies the Tirodi Gneiss (~2500 Ma) in Central India. These authors reported that the paleosol is depleted in HREE and shows flat Ce and Eu anomalies, low ΣREE, and high (La/Yb)γ. Based on these proxies they suggested a reducing atmospheric condition during the formation of the paleosol. Based on available geochronologic data from the Sausar Group and Tirodi Gneiss, Mohanty and Nanda (2016) suggested the age of the paleosol to be in between 2.48 Ga and 2.45 Ga. This age bracket is consistent with the reducing nature of atmosphere before the GOE at 2.33 Ga (Luo et al., 2016).

Silimanite-Corundum horizon of the Sonapahar silimanite in Meghalaya, Northeastern India has been also interpreted as metamorphosed Precambrian bauxite deposit (Golani, 1989; Fig. 1b). From major and trace element data, Dash et al. (1987) interpreted quartz-sillimanite-garnet bearing khondalites in Orissa as deeply weathered soil profile metamorphosed in upper amphibolite-granulite grade. Sreenivas and Srinivasan (1994) reviewed chemical compositions of more than 300 metapelites and khondalites from Dharwar craton, Aravalli craton and Eastern Ghats. They are of the opinion that most of the khondalites are metamorphosed paleosols, a view echoed long ago by Pascoe (1950).

The Indian Precambrian paleosols described so far are developed either on granitoids of >3.1 Ga or on granitoids of ~2.5 Ga. With precise age determination these paleosols can provide well-constrained information on the evolution of oxygen in the atmosphere.

Redox structure of hydrosphere

*From basins of Bundelkhand, Bastar and Dharwar cratons*

Redox-sensitive chemical sedimentary rocks like iron formations, syngenetic pyrite deposits and authigenic sediments like carbonates and phosphorites along with sediments showing Nd, Sr isotopic composition and REE distribution pattern of the ambient sea water provide authentic information about the Proterozoic hydrosphere including its oxidation state. Despite such a large scope of deciphering the paleohydroscopic condition, limited work has been done in India and studies remained largely restricted to a few basin fills. These include ~1.7 Ga old phosphorite deposit from the Aravalli craton (McKenzie et al., 2013), ~1.45 Ga old iron formation from the Gwalior basin of the Bundelkhand craton, sulfides (pyrite) from the Vindhyan and Chhatisgarh basins of Bundelkhand and Bastar cratons and sulphates (barite) from the Cuddapah basin of the Dharwar craton (Fig. 1a,b). The stratigraphic units include phosphorite in the middle part of the Aravalli Supergroup, Rajasthan; ferruginous, aluminous phosphorites in the Bijawar Group, Banded Iron Formation (BIF) from the Morar Formation of the Gwalior Group; authigenic pyrite deposits from the Bijoygarh Shale Formation of the Vindhyan Supergroup; Chharmuria Limestone Formation of the Chhatisgarh Supergroup in the central India. Barite-pyrite deposit from the Cumbum Shale Formation of the Cuddapah Supergroup is also included. Geochemical proxy element analysis from the argillaceous intervals of the Vindhyan Supergroup (Singh et al., 2018) indicating hydrosphere redox structure also reported.

**Basin wide Chronology**

Mafic dykes in the Bundelkhand granite dated by Rb-Sr and K-Ar methods suggest 1775-1790 Ma and 1800 Ma ages for these rocks (cf. Ramakrishnan and Vaidyanadhan, 2008; Pradhan et al., 2012). Absar et al. (2005, 2008, 2010) dated carbonate rocks and banded iron formations (BIF) from the upper part of the Morar Formation, Gwalior basin with Pb–Pb isotopic technique (1914±120 Ma and 1866±250 Ma). In recent time, Paul (2017) dated volcanic rocks present at the transition zone between the Par Formation and Morar Formation using Sm-Nd systematic (1787 ± 60 Ma). This age data helped in constraining late Paleoproterozoic depositional age of the sediments of the Gwalior basin including the Morar Formation.

Pb–Pb dates of stromatolitic limestones from the Kajrahat and Rohtas Formations of the Vindhyan Supergroup are 1627±76 Ma (Banerjee and Russell, 1993), 1721 ± 90 Ma (Sarangi et al., 2004; Ray, 2006), 1601 ± 130 Ma (Ray et al., 2003) and 1599 ± 48 Ma (Sarangi et al., 2004). The zircon U–Pb dates (both conventional and SHRIMP techniques) of 1630.7 ± 0.4 Ma (Ray et al., 2002) and 1628 ± 0.8 Ma (Rasmussen et al., 2002) of the Porcellanite Formation, occurring between the Kajrahat and Rohtas Formations of the Semri Group of the Lower Vindhyan are consistent with the Pb–Pb dates determined independently. A bedded tuff present within the Rampur Shale Formation of the Lower Vindhyan is also dated as 1599 ± 8 Ma by U-Pb methods. Palaeomagnetic studies and a LA-ICPMS U–Pb detrital zircon age of 1020 Ma from the Upper Bhandar sandstone (Malone et al., 2008) brackets the upper limit of the Vindhyan Supergroup. Hence, the syn-sedimentary pyrites in the Bijoygarh Shale, discussed in this paper, suggest a Mesoproterozoic age of 1.6 Ga and 1.0 G.

Das et al. (2009) calculated ~ 1455 ± 47 Ma age (EPMA U–Th–Pb dates of monazite grains from bedded tuff) for the basal part of the Chhatisgarh succession. The U–Pb SHRIMP date on zircon from the tuff layers in the uppermost Tarenza Shale provides an age range of 990–1020 Ma (Patranabis Deb et al., 2007). Bounded between two well-dated horizons, the pyritiferous Chharmuria Limestone undoubtedly indicates a Mesoproterozoic age.

The lower part of the Cuddapah basin provides ages between 1817 ± 24 Ma (Rb–Sr date of the Pulivendla mafic sill emplaced into the Tadpatri shales: Bhaskar Rao et al., 1995) and 1756 ± 29 Ma (Pb–Pb date of uranium bearing stromatolitic dolomite from the Vempalle and Tadpatri Formations (Zachariah et al., 1999). The 40Ar–39Ar age of 1418 ±8 Ma of lamproite dyke intrusion within the Cumbum shale (Chalapathi Rao et al. 1999) marks the termination of the Cuddapah sedimentation. Although both Rb–Sr and Ar–Ar ages are prone to resetting, the age ranges suggest that both the pyrite and barite samples of the Cumbum shale, studied by Sarkar et al. (2009), belong to Mesoproterozoic age between 1.8 Ga and 1.4 Ga.
**Signature from Iron Formation of the Morar Group, Gwalior basin**

The Rare Earth Element (REE) distribution patterns shown by the iron formations have been extensively used to interpret chemistry of the ocean basins. This is because many temporal trends in the REE datasets reflect fluctuations in the marine redox conditions. With this understanding, Paul (2017) carried out REE analyses of BIF from late Paleoproterozoic Morar Formation of the Gwalior Group, central India. Small negative to positive Ce anomaly observed within Gwalior BIFs (Fig. 3) is comparable with Ce anomalies reported from sulfidic waters of the Black Sea. However, rare presence of sulfide minerals in association of the dominant hematite mineralogy of BIF helped Paul (2017) to rule out the possibility of anoxic, sulfidic environment in then deeper-waters of the Gwalior sea. Instead, a sub-oxic condition (dissolved O₂ below ~0.2 μmol/liter and no dissolved sulfide) is inferred that allowed neither Mn oxidation nor Ce sequestration. The sub-oxic ocean model also got support from i) unequivocal La/Nd value of >1, ii) MREE enrichment similar to modern open oceans and marginal seas, and iii) small negative to positive Ce anomalies in Gwalior BIF. This pattern is not like Archean anoxic oceans (without any anomaly) or modern oxygenated marine water (with strong negative Ce anomaly). A clear dominance of positive Eu anomaly in the Proterozoic ocean model also got support from ii) unequivocal La/Nd value of >1, i) MREE enrichment similar to modern open oceans and marginal seas, and iii) small negative to positive Ce anomalies in Gwalior BIF. This pattern is not like Archean anoxic oceans (without any anomaly) or modern oxygenated marine water (with strong negative Ce anomaly). A clear dominance of positive Eu anomaly in Post-Archean Australian Shale (PAAS) normalized REE pattern of Gwalior BIF bears clear signature of higher temperature and reduced hydrothermal solution influence in shallow subtidal waters of the Gwalior Sea. These differences become obvious when compared with modern sea floor iron oxyhydroxide precipitates from reduced high temperature hydrothermal fluids. This interpretation has to be seen in the context of mass balance estimates for REEs in the oceans based on Nd isotopic composition and on Eu anomalies. Derry and Jacobsen (1990) have shown large variations in the REE distribution patterns in similar sediments and inferred the non-conservative behavior of Eu during mixing of hydrothermal waters with ambient water.

**Signatures from sulfides and sulfates**

The fractionation of sulphur between sulfate (SO$_4^{2-}$) and sulfide (H$_2$S) species in oceans is driven by bacterial sulphate reduction (BSR). Sulfide produced by BSR is either recycled as sulfate or combines with available iron to form pyrite (FeS$_2$). Burial of sedimentary pyrites (and organic carbon) eventually controls oxygen in an ocean–atmosphere system (Berner, 1984; Bottrell and Newton, 2006). BSR preferentially fractionates $^{32}$S in sulfides, making the remaining sulfates enriched in $^{34}$S. Since the amount of reduction depends both on the redox state at the sediment–water interface and the supply of sulfate in the water column, the sulphur isotope compositions ($\delta^{34}S$) of sedimentary sulfides are used as potential tracer of ocean chemistry. With this understanding, Sarkar et al. (2010) determined $\delta^{34}S$ values for authigenic pyrites from the Bijoygarh Shale of Vindhyan Super Group, Charnurina Limestone of Chhattisgarh Super Group, Cumbum Shale and Narji Limestone of Cuddapah Super Group and barite from the Pullampet Formation (Mangampeta mine) of the Cuddapah Super Group (Fig. 1).

Moderate to very heavy $\delta^{34}S$ values are recorded from pyrites in these basins with values ranging from 8.1 to 38.8‰. In fact, a depletion of $\delta^{34}S$ values generated from pyrites collected from Vindhyan and Chhattisgarh basins (Sinha et al. 2001; Guha, 1971; Sarkar et al., 2010) reveals mean $\delta^{34}S$ values of Chhattisgarh and Vindhyan pyrites as 26.3 ± 0.9‰ (n = 12) and 25.5 ± 8.7‰ (n = 42), respectively. Limited data from syn-sedimentary Cuddapah pyrites show a mean $\delta^{34}S$ value of 28.3 ± 11.8‰ (n = 6). When all available data are considered, pyrites from the Vindhyan and Chhattisgarh basins record $^{34}S$ enrichment, ranging between 4.5‰ and 40.7‰, irrespective of the nature of pyrite (framboidal, euhedral or laminated). No pyrite from these basins has registered moderate to extreme negative $\delta^{34}S$ values as observed in most sedimentary pyrites of Phanerzoic age (Strauss, 1999; Canfield & Raiswell, 1999; Canfield, 2004 and references therein). The $\delta^{34}S$ values as high as ~40‰ are closer to or even higher than the known $\delta^{34}S$ value of Proterozoic marine sulfates (Strauss, 1997; Kah et al., 2001; Gellatly and Lyons, 2005). $\delta^{34}S$ values from marine sulfate i.e the Cuddapah barite show a narrow range i.e 41.8 to 45.5‰ (cf. Clark et al., 2004) with a mean value of +42.3‰ (Sarkar et al., 2010). These values are not only enriched by about 10–15‰ more than the contemporary (Mesoproterozoic) marine sulfate (Kah et al., 2001, 2004; Gellatly and Lyons, 2005), but also have exceptionally small variation compared to other Proterozoic barite deposits of the world (Clark et al., 2004; Strauss, 1999; Kah et al., 2001; Kah et al., 2004; Gellatly & Lyons, 2005). The maximum pyrite $\delta^{34}S$ value of ~40‰ is not very different from this sulphate value.

From geochemical model involving kinetic isotope effect during the SO$_4^{2-}$↔S$^2-$ reduction and SO$_2$↔H$_2$S ratio of different geochemical systems that are either open or closed with respect to SO$_2$, H$_2$S, Sarkar et al. (2010) concluded that very high $\delta^{34}S$ values (>35 ‰) in both Chhattisgarh and Cuddapah basins are result of pyrite removal/ burial at a rate much faster than the rate of sulfate reduction (cf. Ohmoto & Rye, 1979; Strauss & Schieber, 1990). The data provide evidence in support of a hypothesized global Proterozoic sulfidic anoxic ocean where very low concentrations of marine sulfate, bacterially reduced in closed systems, produced $\delta^{34}S$ values in pyrites similar to or even heavier than marine sulfate. The comparatively lower $\delta^{34}S$ values in Vindhyan pyrites is interpreted as result of semi-confined marine depositional environment where SO$_2$ flux was still higher (though limited) compared to the other two basins.
**Signature from argillaceous sedimentary rocks**

Singh et al. (2018) carried out redox-sensitive elements (Mo, Cr) and primary organic productivity (total organic carbon; TOC) analysis from argillaceous intervals of the Vindhyan succession to provide clue on redox conditions in the Proterozoic ocean. Their analytical data suggested that the hydrosphere during Vindhyan sedimentation developed euxinic deep water only during deposition of Arangi, Rampur and Bijoygarh black shale. They called the condition as anoxic but certainly not completely euxinic during the deposition of Koldaha and Rewa shale. Low concentration of Mo and Cr within the argillaceous intervals helped these authors to conclude that the Vindhyan Sea behaved as a moderate Mo, depleted Cr reservoir. The consistent low concentration of Cr within the Vindhyan shales is attributed to insignificant terrestrial supply of Cr (Cr (VI)) due to very low oxygen concentration in the contemporary atmosphere.

**Signature from phosphatic rocks**

Precambrian phosphorites are believed to have commonly formed in the shallow marine setting through phosphogenesis i.e as authigenic precipitates having the mineralogy of francolite or carbonate fluorapatite (Banerjee et al., 1980). Francolite shows extensive substitution of its components and is expressed as \( \text{Ca}_{1-3} \text{Na}_{0.1} \text{Mg}_{0.5} (\text{PO}_4)_{1.8} (\text{CO}_3)_{0.2} (\text{SO}_4)_{0.1} F_2 \). Processes like authigenesis; hydrodynamic reworking in the shallow marine realm and organic activity in the sunlit shallow shores produce phosphate rich layers, frequently associated with the cyanobacterial mats. Phosphorus is removed from the nutrient rich surface waters by cyanobacteria and authigenically converted to carbonate fluorapatite through mediation of a series of microbially induced reactions in the bottom and pore waters (Schidlowski et al., 1985; Banerjee and Klemm, 1985, Banerjee et al.1986). The pore waters tend to become supersaturated with respect to calcium phosphate leading to precipitation of carbonate fluorapatite in fairly anoxic environment, virtually cut off from the oxic waters of the basin. Chert and black shales are common associated rocks in such depositional settings. Recently, it was observed (Reinhart et al., 2013) that despite more limited extent of euxinia that was provided the organic matter and created anoxia) was heavily influenced from the arenite units underlying the phosphate deposit. One such example is India’s largest phosphorite deposit in the Aravalli belongs to the tail end of the oxygenation event which continued into the early phase of the boring billion and therefore does not strictly coincide with the GOE as postulated earlier (Papineau, 2010, Pufahl, 2010). It possibly indicates relatively oxygenated (suboxic?) shallow marine condition through late Paleoproterozoic to early Mesoproterozoic as documented by intimate association of non-pelletal, dense authigenic phosphorite formed through the cyanobacterial interventions. Occurrence of phosphatic laminae and beds in the Rohtas and Kajratah limestones of Vindhyan basin in the Son valley, Gangolihat Dolomite in the Kumaun Himalaya, Chelma area of the Cuddapah Supergroup and Charmuria Formation in the Chhattisgarh Supergroup (Banerjee, 1985) justify this contention. Also, Fe-rich aluminous phosphorites of putative Paleoproterozoic age occurring in the Bijawars of central India (Banerjee et al, 1982) is modeled in terms of extensive weathering related origin. Such shallow marine phosphorites and weathering profile related phosphorites are in stark contrast to upwelling related Phanerozoic phosphorites formed in the deeper part of shelf. This difference most likely reflects the dissimilarity in the oxygenation state of the sea floor (Nelson et al., 2010, Reinhart et al. 2013) between the Proterozoic and Phanerozoic times.

**Discussion**

From convergence of geochemical evidence, it is suggested that the unidirectional and significant oxygenation of the Earth surface occurred in two major steps; first step at 2.33 Ga (Luo et al., 2016) and the second step between 800 Ma and 541 Ma (Scott et al., 2008; Tang et al., 2016). The time period encompassing late Paleoproterozoic and Mesoproterozoic, remains the most intriguing time slot and is debated period in the Earth history principally because of i) first appearance of eukaryotes, though in low diversity (Blumenberg et al., 2012; Reinhard et al., 2013) and ii) claim of very low oxygen concentration in shallow seawaters (Tang et al., 2016). Within this broad framework, reports on whiffs of oxygenation keep coming from Archean records. Indian geology is no exception; the 3.29 – 3.02 Ga old Keonjhar paleosol in the Singhbhum craton holds signature of Paleo- and Meso-Archean oxygenation whiffs. Short-lived character of these whiffs and return of reduced atmospheric conditions can be envisaged from occurrence of reduced uraniferous-pyritiferous paleoplacers in arenites overlying the Keonjhar paleosol or report of 2.48-2.45 Ga old reduced paleosol from the Sauras succession. The Sonapahar sillimanite has not been studied in detail.

Available geochemical results from marine sedimentary pile, both carbonates and argillites belonging to late Paleoproterozoic-Mesoproterozoic basins all over the Indian sub-continent are not sufficiently exhaustive to provide definitive answers to various mysteries of the redox conditions in the hydrosphere. While BIFs from late Paleoproterozoic Morar Formation register a suboxic marine condition from unequivocal La/Nd value >1, MREE enrichment and small negative to positive Ce anomaly, moderate to very heavy δ14S values from sulfides (pyrite), close to or even higher than the reported δ34S value of Proterozoic marine sulfate (barite), present in Mesoproterozoic Bijoygarh Shale of the Vindhyan Supergroup and Charmuria Limestone of the Chhattisgarh Supergroup support the sulfidic and anoxic deep ocean model, similar to the ‘Canfield Ocean’ model (Logan et al., 1995; Hurtgen et al., 2002; Canfield, 2004). Argillaceous sediments from the Vindhyan Supergroup, analyzed for redox-sensitive elements and total organic carbon (TOC), support the anoxic deep ocean model throughout the Mesoproterozoic. The
study, however, refuted the idea of persistent euxinic deep ocean model. Considering sulfidic condition as the major cause behind persistent ocean euxicity, Singh et al. (2018) inferred that low Mo and low Mo/TOC values in the argillaceous intervals are signals for dominant non-sulfidic deep ocean condition in course of Vindhyan sedimentation history. In contrast, a relatively oxygenated shallow marine condition possibly prevailed through late Paleoproterozoic and Mesoproterozoic times as suggested from close association of non-pelletal, dense, authigenic, phosphorites with cyanobacterial colony in many late Paleoproterozoic – early Mesoproterozoic Indian basins. This conjecture is likely to be over-simplification of the complex depositional processes in the backdrop of recent chromium isotope study on shallow marine ironstones (Planavsky et al., 2014) that estimates below 0.2 µM dissolved oxygen (i.e 0.1% of PAL) in mid-Proterozoic shallow marine environment.

The discussion here highlights the fact that the Proterozoic chemical sedimentary rocks in the Indian subcontinent need to be studied in more details for making definitive interpretations of the past atmosphere and hydrosphere and make significant contribution to our understanding of the onset of oxygenation event in the Earth history.

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