Chapter 5
Oxygenation of Early Atmosphere and Potential Stratigraphic Records from India

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Abstract Oxygenation of atmosphere had a profound role in the evolution of life from primitive anoxygenic heterotrophic life forms to oxygenic photoautotrophs and eventually to multicellular organized plant and animal kingdom. Plethora of geological and geochemical evidences particularly the occurrences of pyritiferous- and uraniferous-reduced paleoplacers, distribution of BIF through ages, Fe-depleted reduced paleosols and more importantly the mass-independent multiple sulphur isotope fractionation prior to 2.4 Ga great oxidation event (GOE) collectively suggest an oxygen-deficient atmosphere during the Archean. Recent research from paleosols older than 2.4 Ga and coeval marine sediments using REE-distribution pattern, redox-sensitive trace elements and fractionation of their isotopes indicates more than one attempt of pre-GOE oxygenation. More case studies from well-preserved paleosols and marine sedimentary sinks for trace metals from the Archean would bridge the gap in the record from pre-GOE to GOE oxygenation history. Peninsular India with nearly continuous stratigraphic successions from Paleoarchean to Paleoproterozoic time interval may be potential to study the pre-GOE to GOE transition of the atmosphere.

Keywords Oxygenation · Atmosphere · GOE · Pre-GOE · Paleosol · Peninsular India

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5.1 Introduction

The Earth in its early days was a very different planet from now. The crustal processes, atmosphere, hydrosphere and biosphere were significantly different from the present, and many of the internal and external processes were essentially non-uniformitarian in nature (Cloud 1968, 1972; Canfield 1998; Holland 2006). The atmosphere, in particular, was reducing and is believed to have been constituted by mainly reduced gases, e.g. CO, NH_3, H_2O, H_2, and CH_4 (Shaw 2014). The largely reducing nature of the atmosphere influenced the fundamental metabolic pathways, for example, early microbial life was essentially heterotrophic anaerobic with metabolic pathways free of any involvement of oxygen. The evolution of the atmosphere is of particular importance since the organic evolution and adaptive radiation of different life forms were primarily dependent on the growth of a habitable atmosphere (Brocks et al. 1999; Canfield et al. 2007). The primitive heterotrophic life could transform into modern-day photoautotrophic life forms with the advent of oxygenic metabolic pathway of the aerobic life that occurred only after the oxygen concentration of the atmosphere reached a critical point with many fold increases from the primitive reducing stages (Buick 1992; Knoll 1992, 2003; Knoll and Bauld 1989; Blankenship and Hartman 1998; Anbar and Knoll 2002; Canfield et al. 2007; Farquhar et al. 2011; Cox et al. 2018). The origin and rise of oxygen in the atmosphere is a topic of intense research for over half a century now (Holland 1962, 1994; Berkner and Marshall 1965; Cloud 1972; Garrels et al. 1973; Dimroth and Kimberley 1976; Holland and Beukes 1990; Ohmoto 1996, 1997, 2004; Des Marais 2000; Canfield 2005; Kump 2008; Guo et al. 2009; Bekker 2014; Lyons et al. 2014). Oxygen in the atmosphere is contributed through two primary mechanisms: by the photolysis of water aided by UV-rays and by the photosynthesis of green plants (Kump 2008). The latter process is more effective and is believed to have remained as the main contributor of oxygen in the early atmosphere. There is little doubt that sharp rise in oxygen concentration in the atmosphere could only happen with the advent of photosynthesis at close to the boundary between Neoarchean and Paleoproterozoic time (see for reviews Holland 2006; Bekker 2014). Multiple lines of evidences could narrow down this event of *oxyatmoversion* popularly known as ‘Great Oxygenation Event’ (GOE) (Roscoe 1973) at ~2.4 Ga (e.g. Bekker et al. 2004; Bekker and Holland 2012). However, there is difference in opinion regarding the mode of oxygenation of the early atmosphere, whether it is a single step rise or the GOE was preceded by multiple but transient episodes of oxygen enrichment in the atmosphere (Ohmoto 1997; Holland 1999). Most direct record of atmospheric oxygen concentration is primarily obtained from a few Archean and Paleoproterozoic paleosols (Rye and Holland 1998). The paleosols (Fig. 5.1) provide direct evidences for the presence/absence of significant oxygen in the atmosphere. This chapter summarizes the evidences in favour of sharp rise in GOE from early reducing stage of atmosphere and evidences for pre-GOE episodes of oxygenation. Also, it explores the potential for such studies from the Archean–Paleoproterozoic rock record of the Indian peninsula.

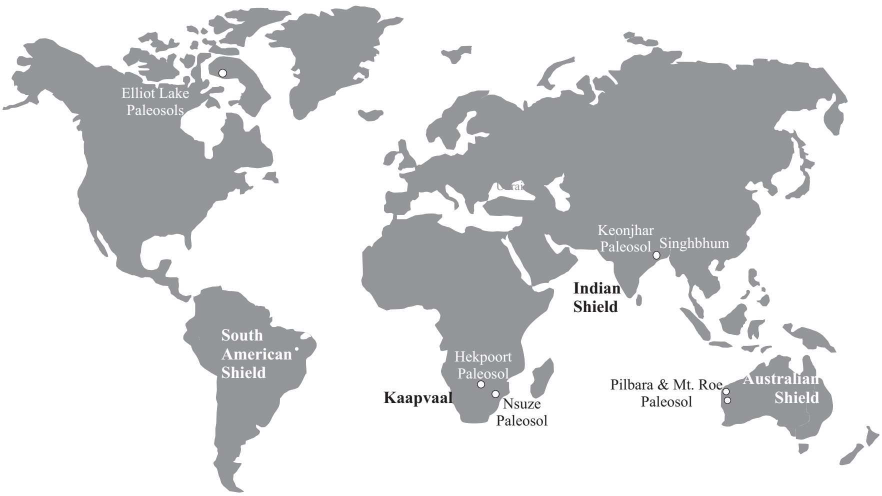

Fig. 5.1 Distribution of some of the well-studied Archean–Paleoproterozoic paleosols world over

5.2 The Reducing Atmosphere

The reducing state of the early atmosphere is supported by the following several evidences (Clemmey and Badham 1982):

Reduced paleoplacers: Many Archean paleoplacer deposits consist of minerals such as pyrite and uraninite as detrital components. The quartz pebble conglomerate (QPC) deposits of the Mesoarchean Mahagiri-Keonjhar Quartzite (Fig. 5.2a) of the Singhbhum craton, eastern India; the similar QPC deposits at the base of the Meso–Neoarchean Bababudan Group of the western Dharwar craton, India; Meso–Neoarchean Witwatersrand auriferous placers in the Kaapvaal craton, South Africa; the Paleoproterozoic Blind River-Elliot Lake detrital uraninite deposits in Canada; and Pilbara block in Western Australia are some of the better known deposits of reduced paleoplacer from pre-GOE time (Roscoe 1957; Gay and Grandstaff 1979; Smith and Minter 1980; Schidlowski 1981; Rasmussen and Buick 1999; Mukhopadhyay et al. 2014, 2016). Uraninites are unstable at oxygen >0.0004 PAL (present atmospheric level) partial pressure of atmosphere (Grandstaff 1974), and at higher oxygen concentration they are oxidized to water-soluble U^{6+} oxides and hence should disappear from detrital sediment load under oxygen atmospheric condition. The presence of detrital uraninite, therefore, constrains the atmospheric oxygen concentration at 10^{-5} PAL during the deposition of such placer deposits (Grandstaff 1974).

Reduced paleosol: Paleosols are the best-preserved direct record of atmospheric oxygen concentration. The main argument for an oxic vs reduced paleosol is the mobilization of Fe in the paleosol profile (Rye and Holland 1998). Fe in the deeper soil profile is released from the bedrock in water-soluble Fe^{2+} state that

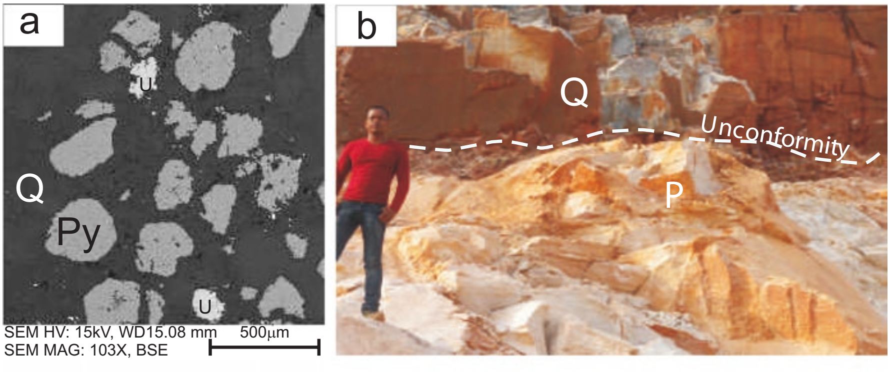

Fig. 5.2 (**a**) SEM backscatter image of auriferous and pyritiferous quartzites from the Mesoarchean Keonjhar Quartzite from Mankharchua area, Singhbhum craton, eastern India. Note rounded pyrite (Py, light grey), quartz (Q, dark background) and uraninite (U, bright) detrital framework grains in the quartzite. (**b**) The Keonjhar paleosol (P) underlying the Keonjhar Quartzite (Q) from the Singhbhum craton, eastern India. The Mesoarchean (>3.1 Ga) paleosol is developed along the unconformity between the Singhbhum Granite (3.2 Ga) basement and the overlying basal QPC-quartzite beds of the Keonjhar Quartzite (after Mukhopadhyay et al. 2014)

travels to the upper part of the profile dissolved in the soil water. In case of soil profile developed in oxic atmosphere, the Fe is oxidized and retained in the topmost part of the profile in the presence of atmospheric oxygen. In reducing atmosphere, the Fe^{2+} escapes the soil profile giving rise to Fe depletion all throughout the profile. The pre-GOE paleosols described from Western Australia, e.g. 2.7 Ga Mount Roe paleosol, exhibit such Fe depletion from bedrock to the top of the profile suggesting that the atmosphere was reducing at the time of formation of this paleosol (Macfarlane et al. 1994).

Secular trend in BIF abundance: Banded iron formations with alternate chert/jasper mesobands/laminae and Fe mineral (oxide/silicate) mesobands/laminae are important constituents of the Archean and Paleoproterozoic successions. The greenstone belts recording deep-water sedimentation during the Eoarchean to Neoarchean times witnessed iron formation deposition in stratified oceans (Dymek and Klein 1988; Beukes and Klein 1992). Iron in the oxygen-starved deeper Archean oceans was largely accumulated in ferrous state. The magnetite-/silicate-rich Fe mesobands of the BIFs in the Archean greenstone belts were explained by precipitation of ferric iron from upwelled oxygenated upper water column of oceans and subsequent microbially induced reduction of ferric oxide (Fe-heterotrophic metabolism) to ferrous oxide/silicate during diagenesis (Beukes and Gutzmer 2008). However, relative abundance of BIF in the rock record witnessed a sharp rise during the early Paleoproterozoic, e.g. Kuruman Iron Formation of the Kaapvaal craton and the Hamersley basin iron formations in the Pilbara craton in Western Australia, Lake Superior deposits in North America and Krivoy Rog in Ukraine. It is believed that with the advent of photosynthesis, at first, the oceans were oxygenated, and the stored ferrous reservoir was oxidized to form huge BIF deposits during the early Paleoproterozoic time. Deposition of such giant BIF successions, on the other hand, exhausted the Fe reserve of the oceans, and hence, BIFs disappeared from later Paleoproterozoic to successions till date excepting for a minor rise soon after the Sturtian snowball event in the Neoproterozoic, e.g. Rapitan Iron Formation in Canada and Urucum BIF in Brazil (Beukes and Klein 1992; Beukes and Gutzmer 2008). The sudden rise of BIF deposition closely coincides with the GOE and indicates oxygenation of Paleoproterozoic oceans that preceded the oxygenation of the atmosphere.

Mass - independent isotopic fractionation: The discovery of mass-independent fractionations in pre-GOE sulphides is perhaps the strongest evidence for oxygen-deficient atmosphere prior to GOE. Sulphur has four natural isotopes: ^{32}S, ^{33}S, ^{34}S and ^{36}S. Fractionation between isotope pairs provides important clues for natural processes, for example, bacterial sulphate reduction, abiotic processes such as hydrothermal/magmatic sulphide/sulphate formation and more importantly the atmospheric sulphur fractionation. The extent of sulphur isotope fractionation is expressed in terms of $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$, where $\delta^{X}S = ((^{x}S/^{32}S)_{sample} - (^{x}S/^{32}S)_{standard})/(^{x}S/^{32}S)_{standard})) \times 1000‰$. The relative fractionation between two isotopes, e.g. ^{33}S and ^{34}S or ^{36}S, is governed by the ratio of mass difference between respective pairs. For example, the mass difference between the numerator and denominator for $^{33}S/^{32}S$ and $^{36}S/^{32}S$ compared to that of $^{34}S/^{32}S$ is 0.515 and 1.91, respectively (Farquhar et al. 2000). Thus $\delta^{33}S = 0.5^{34}S$ and $\delta^{33}S = 1.9^{36}S$ represent relative fractionation between the isotope pairs and, therefore, suggest dependence on the respective mass of the isotopes being fractionated in a *mass-dependent fractionation* process (MDF) (Farquhar et al. 2000; Pavlov and Kasting 2002). The relationship is further presented by another notation $\Delta^{33}S$ $(= 1000 \times ((^{33}S/^{32}S)_{sample} - (^{33}S/^{32}S)_{standard}) - ((^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard})^{0.515})$ and so on, which measures deviation from near-zero low-temperature equilibrium values for sulphur isotope fractionations (Farquhar and Wing 2003). The $\Delta^{33}S$ pyrite samples from sediments of post-GOE ages have values close to zero. In contrast, the samples from pre-GOE sulphides show wide variations from the equilibrium (Farquhar and Wing 2003; Lyons et al. 2014) (Fig. 5.3). The deviation has been explained by non-mass-dependent fraction of sulphur and sulphate aerosols, and such process can only take place in an atmosphere transparent to UV radiations triggering mass-independent fractionation in S_8 species of sulphur (Farquhar et al. 2001). The UV radiation-aided photolysis of sulphur aerosols in the atmosphere would imply deep penetration of UV radiation and hence lack of ozone shield which in turn suggests insufficient oxygen concentration for generating a thick stratospheric ozone shield in the Archean and early Paleoproterozoic Earth prior to GOE.

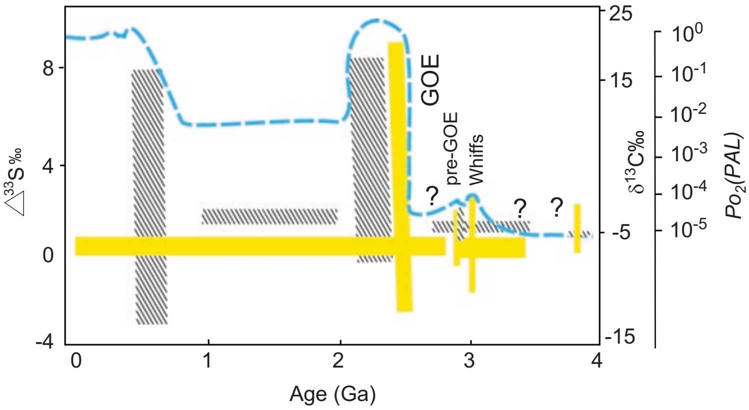

Fig. 5.3 Generalized diagram for the rise of atmospheric oxygen (thick line) (Modified after Holland 2006; Lyons et al. 2014). Note distribution of sulphur isotope (filled rectangles) and carbon isotope compositions (hatched boxes) through ages. Note peaks in the MIF-S signal (deviation from zero value) and positive carbon isotope excursion at around 2.5 Ga (GOE). Also note near-zero or attenuated MIF-S signals and low-magnitude positive carbon isotope excursions in between 2.8 Ga and 3.0 Ga (pre-GOE whiffs)

5.3 The GOE

The great oxidation event or GOE is believed to have witnessed a sharp rise in atmospheric oxygen concentration to more than 10^{-5} PAL at around 2.4 Ga. The major evidence in favour is the disappearance of mass-independent sulphur isotopic fractionation at around 2.5 Ga. The high-resolution S-isotope record from the 2.5 Ga Mount McRae Shale of the Hamersley basin, Western Australia and the stratigraphically equivalent Gamohaan Formation below the Kuruman Iron Formation, South Africa, suggests the onset of the oxidative sulphur cycle on Earth and oxidation of surface ocean at Archean–Proterozoic boundary (Kaufman et al. 2007). However, the precise timing for the GOE remained somewhat debatable and a broad range from 2.2 Ga to 2.45 Ga is considered as the window for the rise in atmospheric oxygen. This time bracket is constrained by the loss of MIF-S signal from around 2.45 Ga and the first appearance of oxic paleosol as recorded in the Hekpoort paleosol in the Transvaal Supergroup, South Africa (Holland and Beukes 1990; Beukes et al. 2002). The Hekpoort paleosol is considered as the earliest candidate for the lateritic soil profile with iron-depleted lower pallid zone to iron-enriched uppermost mottled zone of the paleosol profile (Beukes et al. 2002). Beukes et al. (2002) estimated an age of 2.11 Ga to 2.18 Ga for the development of the Hekpoort lateritic soil profile.

Besides the MIF-S signal and the appearance of the lateritic paleosol in 2.2 Ga rock record, additional evidence for oxygenated atmosphere comes from the carbon isotope excursion of marine sedimentary carbonates. Karhu and Holland (1996) compiled $\delta^{13}C$ values of carbonates and that of organic matters from 2.6 Ga to 1.9 Ga well-preserved successions from North America, South America, Africa and Australia. The huge database brought out a striking secular trend in the carbon isotope compositions from these marine sedimentary carbonates revealing a large positive excursion in $\delta^{13}C$ (10–12‰) during 2.2 Ga and 2.06 Ga time interval (Fig. 5.3). They proposed that the large positive excursion for about 150 million years time span is a result of excess burial of organic carbon in the sediment. The organic carbon burial in turn helped build up oxygen in the atmosphere. Karhu and Holland (1996) further suggested that the large positive excursion would have resulted in 10–12 times increase in oxygen build up to an extent that atmospheric oxygen concentration reached a value >0.03 PAL from value less than 2×10^{-3} PAL between 2.2 and 2.0 Ga. The precise timing of GOE was so far not very well constrained. The scarcity of continuous stratigraphic sequence from the last MIF-S signal and the oldest MDF-S signal in rock successions from the Huronian Supergroup in Canada and the Hamersley and Turee Creek Groups in Western Australia (Papineau et al. 2007; Williford et al. 2011) or the Griqualand West Basin in South Africa (Bekker et al. 2004) leaves a gap of about 100–150 million years between the MIF and MDF records from these successions. Recently, Luo et al. (2016) reduced the stratigraphic gap between MIF-S and MDF-S signals in the Pretoria Group from Transvaal Basin of South Africa to ten million years and constrained the timing of GOE at around 2.33 Ga. The oldest presently known S-MDF signals are found around the Rooihoogte–Timeball Hill Formation boundary in the Pretoria Group of the Transvaal basin in South Africa. Luo et al. (2016) measured multiple sulphur isotopes from drill cores at high stratigraphic resolutions in diagenetic pyrite in a continuous sequence from the lower Timeball Hill down to the upper Rooihoogte Formations which narrowed down the uncertainty in the timing of onset of GOE. They further suggested the duration of the GOE to about 10 million year span from the transition of S-MIF to S-MDF signals within a 5 m thick stratigraphic interval in these drill cores.

5.4 Pre-GOE Whiffs of Oxygenation

In recent times, investigations on a number of pre-GOE Archean paleosols reveal the presence of oxidative weathering before 2.5 Ga. Redox-sensitive trace elements such as Mo, Re, S and U concentration from pre-GOE oceanic sediments and authigenic pyrites, Cr-isotope compositions and REE-fractionation from Mesoarchean paleosols indicate multiple episodes of rise in atmospheric oxygen before the GOE (Anbar et al. 2007; Lyons et al. 2014; Crowe et al. 2013; Mukhopadhyay et al. 2014; Planavsky et al. 2014).

The pre-GOE rise in atmospheric oxygen has been reported from several >2.5 Ga paleosols. The oldest such report is from 3.4 Ga Pilbara paleosol from Western Australia (Johnson et al. 2008). The Pilbara paleosol, first reported as the oldest known paleoweathering surface (Buick et al. 1995), is a deep weathering profile below an angular unconformity between lower >3.5 Ga basic volcanic- and chert-bearing greenstone succession and overlying fluvial to shallow-marine siliciclastic succession of lower greenschist facies metamorphic grade. Johnson (2008) described the paleosol as a typical top-down alteration profile in pyrophyllite (locally chlorite) with hematite (F^{3+})-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). However, unequivocal evidence for Paleoarchean lateritization and the extent of subsequent alteration on the Pilbara paleosol would be important.

The oldest record of Mesoarchean oxic paleosol comes from the Keonjhar paleosol (Fig. 5.2b) developed in the Singhbhum craton in eastern India (Mukhopadhyay et al. 2014). U-Pb zircon data indicate that the pyrophyllite-bearing paleosol was formed between 3.29 Ga and 3.02 Ga. The Keonjhar paleosol drapes the unconformity between the 3.29 Ga component of Singhbhum Granite and overlying siliciclastics of the Keonjhar Quartzite with 3.02 Ga minimum age of detrital zircons. The paleosol profile also shows typical top-down alteration zone with depletion of mobile elements (Na, Ca, Mg, Cs, Zn, Ni) with respect to the basement granitoid that has been interpreted as similar to leached weathering profiles in humid climate. Keonjhar paleosol typically shows Fe and Mn depletion, HREE enrichment and true negative Ce anomaly. Mukhopadhyay et al. (2014) based on these geochemical proxies compared the preserved part of the profile with the pallid zone from the lower part of a lateritic soil profile and suggested that Fe and Mn in reduced state were mobilized to the upper lateritic part and the negative Ce anomaly in the pallid zone primarily resulted from retention of Ce as oxidized Ce^{4+} in the top lateritic part of an oxic soil which is not preserved in studied profiles.

The Nsuze paleosol in the Pongola basin of South Africa is interpreted as oxic paleosol developed during 2.98 Ga to 2.96 Ga (Crowe et al. 2013). The paleoweathering surface developed on top of the basaltic andesites of the Mesoarchean Nsuze Group and below the shallow-marine siliciclastics of the Mozan Group in Pongola Supergroup consists of a chloritic lower part and a thinner sericitic upper part. The altered profile has chemical characteristics similar to soil profile with depletion of mobile elements such as Ca and Na in comparison to immobile elements. Crowe et al. (2013) considered Cr isotope fractionation from the Nsuze paleosol as a reliable indicator for oxidative weathering. Cr^{3+} in soil is oxidized in the presence of manganese oxide to highly soluble Cr^{6+}. The oxidation process also leads to isotopic fractionation between heavy and light isotopes in the oxidized and residual Cr phases. The Cr^{6+} becomes enriched in heavier ^{53}Cr, while the residual Cr^{3+} gets depleted in ^{53}Cr resulting in difference in $\delta^{53}Cr$ ((=$^{53}Cr/^{52}Cr_{sample}/^{53}Cr/^{52}Cr_{standard} - 1$) × 1000‰) values (cf., Frei and Polat 2013). $\delta^{53}Cr$ of the igneous inventory has a near-zero value. The oxidized Cr^{+6}, therefore, attains a positive $\delta^{53}Cr$ value with respect to the igneous inventory, and in contrast, the residual Cr^{3+} remains with low negative $\delta^{53}Cr$ value with respect to the igneous inventory. Crowe et al. (2013) demonstrated that the chloritic weathering profile of the Nsuze paleosol records low negative values suggesting that the Cr^{3+} has been oxidized to +6 state and the soluble Cr^{6+} with heavier isotope went into run off to the oceans. They further demonstrated the enrichment in Cr isotope values from stratigraphically near equivalent chemical sediments of the Ijzermin Iron Formation (IIF) of the Mozan Group. The BIFs in the IIF and the chemical sediments of the Mozan Group are recorded as much as six-time enrichment in heavier isotope with respect to the igneous inventory. Crowe et al. (2013) suggested that the isotopically enriched Cr in the continental run off from the oxidative weathering was deposited in the contemporary marine chemical sediments of the Mozan Group which according to them acted as the sink for the heavier Cr isotope-rich Cr^{6+} derived from the continental run off in an oxic atmospheric weathering condition.

5.5 Discussion

The degree of oxygenation of pre-GOE atmosphere is still a matter of considerable debate. Mainly two opposing schools of thought exist. One school believes that the pre-GOE atmosphere was anoxic with $<10^{-5}$ PAL oxygen concentration (Holland 1994, 1999, 2002, 2006). The opposing view reiterates essentially the same oxygen concentration since at least Eoarchean time (Ohmoto 1997). The controversy mainly arose between the two opposing groups in interpreting the paleosols that have been either interpreted as oxic or reduced paleosols (Holland 2002). The main argument in favour of a reduced paleosol comes from Fe depletion in the 2.7 Ga Mount Roe paleosol in contrast to the Fe-enriched lateritic paleosols of younger times (Rye and Holland 1998; Macfarlane et al. 1994; Yang and Holland 2003). Alternatively, Ohmoto (1996, 1997) proposed that the loss of Fe from the >2.4 Ga paleosol profiles was due to late-stage reductive hydrothermal alteration or alteration by organic acids on an originally oxic Fe-rich paleosol.

Recent research on the >2.4 Ga marine shales and some of the better preserved paleosols using redox-sensitive trace elements (Mo, Cr, S, U), REE and Mo and Cr isotope fractionation suggest the oxygen enrichment at least in between 2.8 Ga and 3.0 Ga (Lyons et al. 2014). Reinhard et al. (2009) suggested that the Mo enrichment in 2.7 to 2.45 Ga Mount McRae Shale in the Hamersley basin is a consequence of the existence of oxidative sulphur cycling well before the GOE. Positive $\delta^{13}C$ excursion and attenuated MIF-S signal are also reported during the time interval of 3.0 Ga to 2.8 Ga (Lyons et al. 2014) (Fig. 5.3). Although the MIF-S signals from rock records older than 2.4 Ga are widely believed as record of very low oxygen concentration of the atmosphere, Ohmoto et al. (2006) showed the absence of such MIF signals from rocks of 2.76 Ga lacustrine sediments and 2.92 Ga marine shales of the Pilbara Craton, Western Australia. Based on which, they suggested that the atmosphere remained oxic since 3.8 Ga with periods of fluctuations during the entire Archean Era and the MIF-S signals are results of increased volcanic outgassing or changes during diagenesis rather than the photochemical reactions with UV radiations. Rosing and Frei (2004) reported higher uranium enrichment in the 3.8 Ga Isua oceanic sediments suggesting the oxidative weathering even during the Eoarchean.

There is a growing consensus that there existed failed attempts of atmospheric oxygenation in the interval between 3.2 Ga and 2.8 Ga before the GOE (e.g. Kump

2008; Philippot et al. 2013; Satkoski et al. 2015). The cause of such increase in oxygen content in the atmosphere is now a major area of research (see for reviews Canfield 2005; Kasting 2013; Zahnle et al. 2013). The supply of oxygen in comparison to the supply of the reduced gases on the Earth's surface is likely to be controlled by both geodynamic and biological processes. At the Archean–Proterozoic boundary, onset of modern-day subduction process in global scale is believed to have triggered release of higher proportion of oxygen from the mantle relative to the reduced species (Kasting et al. 1993; Kump et al. 2000; Barley et al. 2005). Catling et al. (2001) considered that Archean atmosphere with high CH_4 concentration would have promoted oxidation by dissociation. They proposed that dissociation of methane by photochemical reaction at the upper atmosphere would have released reducing species such as H_2 that subsequently escaped the atmosphere. Biological oxygen production by photosynthetic cyanobacteria remains the primary mechanism for the rise in oxygen in the early atmosphere. The beginning of cyanobacterial photosynthesis is debated. Biomarkers such as 2 Me-hopanes that are believed to be produced by cyanobacteria have been reported from 2.7 Ga shales from Western Australia (Brocks et al. 1999). Carbon isotope depletion suggesting incorporation of photosynthetically produced carbon compound has also been reported from carbonates from 2.7 Ga (Hayes et al. 1983, 1992). Older records of cyanobacterial growth have been reported from Barberton Greenstone Belt (3.3 Ga, Byerly et al. 1986) and 3.45 Ga Apex Chert, western Australia (Schopf and Packer 1987; Walter et al. 1980; Schopf 1993). Rosing (1999) reported depleted carbon isotope composition from the 3.8 Ga Isua Greenstone Belt suggesting a possible existence of photosynthesis at the beginning of Eoarchean. The biogeochemical evidences from rocks of 2.7 Ga, therefore, support increased rate of cyanobacterial oxygen production at least 400 million years prior to the GOE.

The limited stratigraphic record from Eoarchean till the Archean–Proterozoic boundary poses a problem for evaluating the role of photoautotrophic oxygen production. The wide gap in stratigraphic record, during the Paleo–Mesoarchean, might induce a bias on the inference on nature of oxygenation of early atmosphere. Therefore, future research should focus on early Archean stratigraphic record with multiple lines of evidences for oxidative weathering cycle in paleosols and spike in reduced species concentration in marine sediment sink, oxidative weathering-induced fractionation of stable isotopes and tracing cyanobacterial bloom from the study of biomarkers.

The Archean cratonic nuclei of the peninsular India comprising stratigraphic record from Paleoarchean to Neoarchean (Radhakrishna and Naqvi 1986; Naqvi 2005) are yet to be explored in detail for evidences on the redox state of early atmosphere and hydrosphere. Granite-greenstone and supracrustal cover sequences record sedimentation in shallow-marine to deep-marine conditions, for example, the oceanic sediments and BIFs in the low-grade Paleoarchean successions of the Iron Ore Group and Mesoarchean cover sequences of the Mahagiri-Keonjhar successions in the Singhbhum craton (Mukhopadhyay et al. 2012, 2014), metasediments and BIFs in the Mesoarchean Sargur Schist belt and the Meso–Neoarchean Bababudan Group and Neoarchean Chitradurga Group in the Dharwar craton

(Chadwick et al. 2000), Meso–Neoarchean Bengpal-Bailadila Groups in the Bastar craton (Roy et al. 2001) (see for reviews Mukhopadhyay et al. 2008; Mukhopadhyay 2019) and a number of metasedimentary enclaves of variable grade of metamorphism in the Aravalli and Bundelkhand cratons. Unconformities at different stratigraphic levels in these successions could be targets for identifying paleosol occurrences. Cratonization of Indian subcontinent since Paleo–Mesoarchean transition to Archean–Proterozoic boundaries envisaged at least two major episodes of granite plutonism, for example, at 3.2 Ga (Singhbhum Granite), 3.0 Ga (Peninsular Gneiss in Dharwar craton) and 3.1 Ga Banded Gneissic Complex (Aravalli craton). These major granitization episodes are also likely to provide continental freeboard for the development of paleosol (e.g. Sreenivas and Srinivasan 1994). The Keonjhar paleosol developed in between 3.2 Ga Singhbhum Granite and 3.0 Ga Keonjhar Quartzite (Mukhopadhyay et al. 2014; see also Bandyopadhyay et al. 2010 for a different stratigraphic interpretation) is one among such rare records of paleosols older than 2.5 Ga on Earth. The Udaipur paleosols (Tulsi-Namla paleosols) (Banerjee 1996; Sreenivas et al. 2001) developed in between the BGC and basal quartzites of the Paleoproterozoic 2.1 Ga Aravalli Supergroup preserves the topmost ferricrete capping of an oxic paleosol developed during 2.5 Ga and 2.1 Ga (Pandit et al. 2008; Wall et al. 2012). Sillimanite-corundum horizon of the Sonapahar sillimanite in Meghalaya, Northeastern India, has been also interpreted as metamorphosed Precambrian bauxite deposit (Golani 1989). Mohanty and Nanda (2016) described 2.4 Ga-reduced paleosol from the base of the Sausar succession in the Central Indian Tectonic Zone. The Indian Precambrian paleosols described so far are developed either on granitoids of >3.1 Ga or on granitoids of 2.5 Ga. With a precision age determination, these paleosols can provide well-constrained information on the redox state of the atmosphere in the pre-GOE and GOE to post-GOE atmospheric transition. Indian Precambrian successions can be important representatives in filling the gaps in stratigraphic records for understanding the evolution of early atmosphere and hydrosphere.

5.6 Conclusions

The Earth's early atmosphere was reducing in nature. Major episode of oxygenation of the atmosphere (GOE) took place at around 2.33 Ga. The GOE is established from the geological evidences such as the disappearance of reduced paleoplacers, appearance of lateritic oxic paleosol, large positive carbon isotope excursion and disappearance of mass independent isotopic fractionation phenomenon. However, there is considerable debate about the oxygen concentration and reduced nature of pre-GOE atmosphere. Trace metal isotopic fractionation for chromium and molybdenum and light REE fractionation from Mesoarchean paleosol support multiple episodes of oxygenation attempt during the Mesoarchean. Further evaluation of stratigraphic record from Paleoarchean to Archean Proterozoic boundary from case studies of low-grade metamorphosed successions, e.g. greenstones and supracrustals from peninsular Indian shield, may be of paramount importance in the study of pre-GOE oxygenation history of the atmosphere.

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