

## Oxygenation of the Archean atmosphere: New paleosol constraints from eastern India

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The formation age of Keonjhar paleosol in the Singhbhum Craton of eastern India is interpreted to be between 3.29 Ga and 3.02 Ga. This age data together with documented negative Ce anomaly and heavy rare earth element (HREE) enrichment in the paleosol, besides presence of detrital uraninite and pyrite in the overlying sediments, are interpreted to indicate a transient oxygen-rich atmosphere during the Mesoproterozoic (Mukhopadhyay et al., 2014).

While constraining the formation age of the Keonjhar paleosol is commendable, the inference drawn by the authors about "short-lived oxygenation events" that "are likely to have occurred prior to the GOE" is ambiguous. In this context, I refer to our research, where the amount of redox-sensitive-element like iron retained ( $Fe_R$ ) within many paleosol profiles was estimated, besides quantitatively modelling  $pO_2$  (partial pressure of atmospheric oxygen) variations during the Paleoproterozoic through application of  $Fe^{2+}$  oxidation kinetics to the paleosol data (Murakami et al., 2011). Contrary to the interpretation made by Mukhopadhyay et al., through this discussion, I present fresh analysis to infer that the Mesoproterozoic period was indeed anoxic.

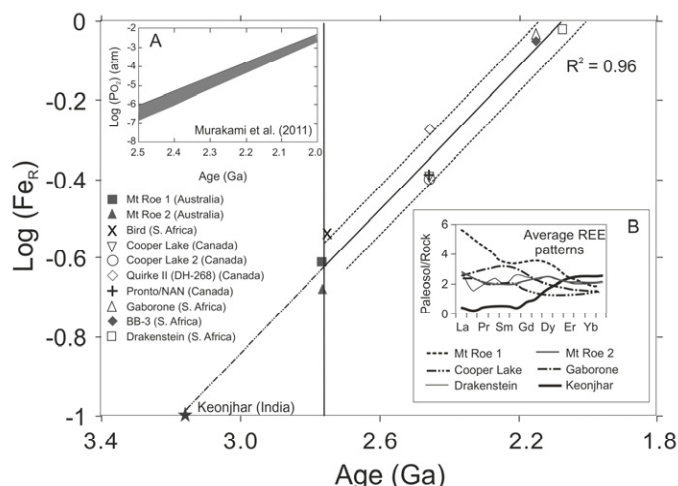
The data published by me (Murakami et al., 2011) is used to construct a reference curve between paleosol age and  $Fe_R$  to achieve the secular variation of iron retention during 2.76–2.0 Ga. To obtain a robust reference curve, some criteria are followed: (1) the selected paleosol profiles must develop on representative parent rocks, (2) if the data pertaining to multiple paleosol profiles developed on the same parent rock are available, their  $Fe_R$  values should be close to each other, and (3) if two or more profiles were developed around the same time at different geographic locations, their  $Fe_R$  values should agree closely.

Figure 1 shows the relationship between paleosol age and  $\log(Fe_R)$ , which exhibits excellent linear correlation ( $R^2 = 0.96$ ). The observed linear behavior mimics the quantitative  $pO_2$  variations of the Paleoproterozoic (see inset A). In order to gain further insight as to how  $Fe_R$  behaved during the Mesoproterozoic period, its value is calculated for the Keonjhar paleosol (data from Bandopadhyay et al., 2010). The estimated  $\log(Fe_R)$  value plots on the extrapolated best fit line (Fig. 1), indicating its preserved nature.

The major inferences of the analysis are as follows:

(1)  $\log(Fe_R)$  versus paleosol age shows gradual increase of iron retention with time (Fig. 1). This plot bears exactly the similar nature when compared with that of quantitative increase in  $pO_2$  variation (Fig. 1A). Thus the iron retention in preserved paleosol profile is a good proxy to ascertain a qualitative measure of the ambient  $pO_2$  during the Archean and Paleoproterozoic periods.

(2) Comparison between the behaviors of  $Fe_R$  and  $pO_2$  with time compels one to conclude that the Keonjhar paleosol from eastern India was developed under oxygen deficient conditions. Further, although short-term fluctuations of both temperature and  $pCO_2$  attendant with global glaciation may result in short-term variations of  $pO_2$  (Murakami et al., 2011), such a possibility for the 3.2-Ga-old Keonjhar paleosol is ruled out, because the oldest known Pongola glaciation took place much later, at ca. 2.9 Ga.



**Figure 1.** Iron retention [ $\log(Fe_R)$ ] in paleosol as a function of time. The best fit regression line (solid) with error bounds (broken) is shown. The dash-dot line beyond the vertical line at ca. 2.76 Ga is extrapolation to the best fit. The Keonjhar paleosol (star) plots on this line, indicating gradual increase of  $Fe_R$  during the entire Mesoproterozoic–Paleoproterozoic period. A: Quantitative  $pO_2$  evolution during the Paleoproterozoic (see Murakami et al., 2011). Secular variations between  $\log(Fe_R)$  and  $\log(pO_2)$  may be compared. Note in B that except for the Keonjhar paleosol, normal enrichment of light rare earth elements (LREEs) relative to heavy REEs (HREEs) in other paleosols is retained. Data and methods can be obtained from the author upon request.

The reduced nature of Keonjhar paleosol presented here is opposite to that inferred by Mukhopadhyay et al. and hence requires further explanation. It is generally observed that LREEs are less mobile than HREEs leading to enrichment in the LREEs relative to the HREEs in the soil samples (Kabata-Pendias, 2000). The consistency observed between  $\log(Fe_R)$  and paleosol age comprising the global data (Fig. 1) do not support the idea that the upper part of the Keonjhar paleosol was eroded. Therefore the average REE pattern of Keonjhar paleosol exhibiting exclusively HREE enrichment (see Fig. 1B) need critical evaluation. The possible imprint of secondary alteration of REE behavior due to metamorphic recrystallization and/or metasomatic changes needs to be eliminated.

### REFERENCES CITED

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