

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

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A Comment by Das Sharma (2015) accepts our assertion (Mukhopadhyay et al., 2014) that a thick (>8 m) pyrophyllite-quartz horizon in the Singhbhum Craton of eastern India represents a Mesoarchean paleosol (the Keonjhar Paleosol), but disputes the notion that the presence of a negative cerium (Ce) anomaly signifies its development during a transient Mesoarchean atmospheric oxygenation event. Das Sharma suggests this and other geochemical features are due to “metamorphic recrystallization or metasomatic changes.” We welcome the opportunity to further discuss the Keonjhar Paleosol and address the concerns raised.

Several geochemical proxies have previously been proposed to yield information on the redox state of the atmosphere and oceans. Recognition of the redox-sensitive behaviour of iron (Fe) in paleosols has led to the distinction of oxidized paleosols where Fe₂O₃ is retained and paleosols that formed in a reducing environment where FeO is lost (e.g., Rye and Holland, 1998). The main argument of Das Sharma against the Keonjhar Paleosol having been formed during a transient Mesoarchean atmospheric oxygenation event arises from the observation that it has lower Fe concentrations compared to the granitic parent rock, signifying that it formed in a reducing environment. Crucially, what Das Sharma seems to have missed is that we stated, “the Keonjhar Paleosol now preserved below the sandstone likely represents the pallid alteration zone of the lower part of a lateritic soil profile marked by the characteristic Fe and Mn depletion, HREE enrichment, and a negative Ce anomaly.” Non-retention of Fe in the Keonjhar Paleosol is clearly presented and discussed in our original paper, and is in agreement with lower Mn/Ti and U/Th ratios and generally higher V/Ti ratios in the paleosol compared to the unaltered parent granite. HREE enrichment may be related to leaching from HREE-rich refractory phases, or preferential sorption of HREE on kaolinite (Coppin et al., 2002). The presence of a negative Ce anomaly in the paleosol is a feature that can only be explained by retention of Ce as cerianite [Ce^(IV)O₂] in the upper part of the original soil profile; hence, meaning this upper part formed in contact with an oxidizing atmosphere. The original upper part of the Keonjhar Paleosol was likely removed prior to or during deposition of the unconformably overlying succession of detrital pyrite and uraninite-bearing quartzarenites and conglomerates. The presence of these redox-sensitive detrital minerals is significant in that not only do they illustrate the sediments were deposited in relatively oxygen-poor waters, their preservation argues against large-scale circulation of post-depositional oxidizing fluids. If HREE enrichment and negative Ce anomalies in the Keonjhar Paleosol were indeed due to later metamorphic or metasomatic processes involving oxygen-rich fluids, it is difficult to envisage a mechanism by which REE would be selectively remobilized without affecting Fe, U, and V, all of which suggest a reducing environment. Not only are detrital uraninite and pyrite preserved in the overlying quartzarenites, but cerianite has not been observed. Furthermore, pyrophyllite is only stable up to low metamorphic grades. For these combined reasons,

we maintain the geochemical features preserved within the Keonjhar Paleosol are original features from the time of its development in the Mesoarchean, prior to unconformable deposition of the clastic sediments.

A plot of Fe retention (Fe_R) in selected paleosols for three broad time slices (Mesoarchean, Neoproterozoic, and Paleoproterozoic) is used by Das Sharma (2015, figure 1) to infer a gradual increase in *p*O₂ from Mesoarchean to Paleoproterozoic times. In this diagram, the Keonjhar Paleosol is said to define a linear correlation with the other featured paleosols, which, according to Das Sharma, signifies that *p*O₂ has gradually risen from the Mesoarchean into the Paleoproterozoic. Not only does Das Sharma incorrectly plot the Keonjhar Paleosol at ca. 3.2 Ga (it is more likely to have developed at ca. 3.02 Ga), we question the validity of attempting to reconstruct ca. 1.1 b.y. of atmospheric evolution based on three clusters of data points and an extrapolation to an incorrectly presented age for the Keonjhar Paleosol. Moreover, Das Sharma does not attempt to discuss a growing body of evidence from different cratons and using different geochemical/isotopic proxies which support transient Mesoarchean oxygenation of the atmosphere and shallow waters (e.g., Crowe et al., 2013; Planavsky et al., 2014). The notion of a gradual increase in atmospheric oxygen from the Neoproterozoic into the Paleoproterozoic severely conflicts with a wealth of geochemical and geological evidence in favor of significant Neoproterozoic to Paleoproterozoic atmospheric oxygen fluctuations, and a dramatic rise in atmospheric oxygen between ca. 2.5 Ga and 2.3 Ga during the Great Oxidation Event (e.g., Lyons et al., 2014, and references therein).

The topic of oxygenation of Earth’s atmosphere and oceans is one that has been debated for many years. In order to move this debate forward, it is necessary to consider a wide range of proxies and, importantly, it is vital to understand the geological context of the samples analyzed in as far as is possible. Earth’s contemporary atmosphere is not spatially or temporally homogeneous (e.g., variations in natural methane production rates; Nisbet et al., 2014). This inherent heterogeneity is perhaps worth bearing in mind when trying to elucidate the abundance of molecular oxygen in Earth’s atmosphere in deep time.

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