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High phosphate availability as a possible cause for massive cyanobacterial production of oxygen in the Paleoproterozoic atmosphere

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ABSTRACT

The deposition of major Precambrian phosphorites was restricted to times of global change and atmospheric oxygenation at both ends of the Proterozoic. Phosphorites formed after highly positive carbon isotope excursions in carbonates deposited during the Paleoproterozoic Lomagundi-Jatuli event and the Neoproterozoic Cryogenian and Ediacaran periods. The correlative step-wise rise in atmospheric oxygen over the Proterozoic has been linked to changes in the carbon cycle. However, the postulated relations between carbon isotope events, phosphorites, and atmospheric oxygenation remain unexplained. Paleoproterozoic carbonates of the Aravalli Supergroup, India, preserve evidence for cyanobacterial blooms in the form of tightly packed stromatolitic columns in the world's oldest significant sedimentary phosphate deposit. Restricted basins of the Lower Aravalli Group with stromatolitic phosphorites in Jhamarkotra, Udaipur, Jhabua, and Sallopat exhibit near-zero $\delta^{13}C_{carb}$ values and large ranges of $\delta^{13}C_{org}$ values between -33.3‰ and -10.1‰, indicative of a complex carbon cycle. Because phosphate accumulates primarily in oxic sediments, these eutrophic microbial ecosystems likely developed within the photic zone of the shallow, oxygenated marine realm. This is consistent with deposition during the time of increasingly more oxidizing conditions, after the Great Oxidation Event (GOE). Approximately contemporaneous basins without phosphate deposits from Ghasiar, Karouli, Negadia, Umra, and Babarmal exhibit a range of positive $\delta^{13}C_{carb}$ excursions, some with values up to $+11.2$‰, that suggest high rates of organic carbon burial, and others with moderately high $\delta^{13}C_{carb}$ values around $+6$‰ or $+3$‰, that suggest smaller carbon cycle perturbations. The $\delta^{15}N$ values of all these rocks vary between -0.7‰ and $+3.4$‰, and are consistent with the predominance of nitrogen fixation during cyanobacterial blooms in all basin types. Such low nitrogen isotope values are interpreted to have arisen from the biological response to high phosphate availability. We conclude that increased phosphate availability during and after the Paleoproterozoic Lomagundi-Jatuli event likely caused cyanobacterial blooms and was a key factor in the oxygenation of Earth's atmosphere. Increasing oxygenation of the shallow ocean seafloor favored the removal of excess phosphate as authigenic apatite, thus dampening effects of weathering increases on organic burial and marine $\delta^{13}C_{carb}$ after about 2.0 Ga.

1. Introduction

The oxidation of Earth's atmosphere—the Great Oxidation Event (GOE)—profoundly changed biogeochemical cycles of carbon, nitrogen, and sulfur during the Paleoproterozoic. Although many theories have been proposed to explain the timing and nature of these redox atmospheric changes, none of the models can explain why oxidation occurred at this time, rather than much earlier. These ideas include the production and oceanic delivery of hydrogen peroxide in rain water (Holland et al., 1986) or on ice (Liang et al., 2006), the changing redox state of volcanic gases (Holland, 2002, 2009), the escape of hydrogen to space (Catling et al., 2001), and a late evolution and radiation of cyanobacteria in the Paleoproterozoic (Kopp et al., 2005). However, the increase of reduced submarine volcanism after cratonic stabilization during the Paleoproterozoic might explain the timing of the onset of the GOE (Kump and Barley, 2007). Recently proposed qualitative models, including a methanogen Ni-famine along with progressive mantle cooling through the Archean until

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the onset of the Paleoproterozoic (Konhauser et al., 2009), added other biogeochemical cycles to the problem of the causes of the GOE. Based on organic biomarkers, oxygen-producing cyanobacteria are known to have thrived during the Neoarchean (Waldbauer et al., 2011; Eigenbrode et al., 2008; Eigenbrode and Freeman, 2006a, 2006b). Some biomarker evidence for cyanobacteria during the Archean is debated however (Brocks et al., 1999, 2003; Rasmussen et al., 2008). The existence of oxygenic phototrophy during the Neoarchean and possibly much before (Czaja et al., 2012; Rosing and Frei, 2004; Rosing, 1999) thus require models of atmospheric oxygenation to account for the significantly later timing of the GOE. Unfortunately, none of the above models can explain why atmospheric oxygenation occurred in the Paleoproterozoic, as well as under strikingly similar circumstances of secular changes one billion years later, at the end of the Proterozoic (Shields-Zhou and Och, 2011; Papineau, 2010; DesMarais, 2001). The rise in the terrestrial phosphate flux in the Paleoproterozoic led to an increase in the burial rate of organic carbon and a major transfer of oxygen from the carbon to the sulfur cycle (Konhauser et al., 2011; Bekker and Holland, 2012). The end of the Lomagundi-Jatuli Event (LJE) may have been caused by a decrease in the terrestrial phosphate flux related to sediment weathering (Bekker and Holland, 2012). However, phosphate-rich sediments occur worldwide after the LJE (Papineau, 2010) and it is unclear whether this change in the carbon cycle is the direct result of a change in the phosphorous cycle or of an expansion of aerobic organisms.

Carbon isotope excursions in Paleoproterozoic post-glacial carbonates worldwide (Karhu and Holland, 1996; Buick et al., 1998; Melezhik et al., 1999a; Bekker et al., 2001, Bekker et al., 2006; Maheshwari et al., 2010) are related to the GOE, and collectively referred to as the Lomagundi-Jatuli Event (LJE). In light of the preceding interglacial demise of MIF sulfur isotopes (Papineau et al., 2007; Guo et al., 2009; Williford et al., 2011) from the sedimentary rock record, it is understood that evidence for Paleoproterozoic atmospheric oxygenation are preserved distinctly during the glaciation and post-glacial periods. The GOE is thus chronologically related to the LJE and the preceding glaciations and is defined here to have occurred most significantly between ca. 2.40 (Papineau et al., 2007; Guo et al., 2009; Williford et al., 2011) and 2.06 Ga (Karhu and Holland, 1996; Martin et al., 2011).

It is unclear if oxygen accumulation on Earth's surface stopped or simply slowed down after the GOE. The consequences of the Paleoproterozoic GOE include numerous redox-related unprecedented changes including the widespread deposition of Mn-rich BIFs and manganiferous marine sedimentary rocks (Roy, 2006), the massive oxidation of organic carbon during the Shunga-Francevillian Anomaly (SFA) (Kump et al., 2011), the widespread occurrence of carbonate concretions, the appearance of granular iron formations, and the widespread occurrence of phosphorites and phosphatic marine sediments. Importantly, the latter does not appear to have begun until after the end of the GOE and it has thus been argued that the unprecedented appearance of phosphorites in the late Paleoproterozoic is linked to the GOE by the oxygenation of the shallow oceans that allowed phosphogenesis to occur (Nelson et al., 2010; Pufahl et al., 2010; Papineau, 2010).

Atmospheric oxygen production tied to photosynthetic carbon fixation affects the sulfur and carbon isotopic records indicating increased burial rates of organic carbon, leading to the hypothesis of widespread Paleoproterozoic cyanobacterial blooms fueled by high phosphate availability from increased weathering (Papineau, 2010). Rifting of supercontinents at both ends of the Proterozoic could have been responsible for triggering the series of major glaciations that ultimately culminated in the GOE and possibly also for the Neoproterozoic Oxygenation Event (NOE). Enhanced rates of carbon fixation during oxygenic photosynthesis induced by higher nutrient delivery into seawater, such as phosphate, could have resulted from post-glacial greenhouse conditions, tectonic processes, and accelerated weathering rates. Increased Cr abundance and isotope compositions have been used to infer oxidative weathering of pyrite in crustal rocks during the GOE, which likely led to a decrease in pH of soils (Konhauser et al., 2011). This prediction tested in paleosols formed during the GOE, demonstrated a lower phosphate concentration in these samples than those pre-dating the GOE (Bekker and Holland, 2012).

An increase in seawater phosphate concentration during the GOE has been suggested on the basis of P:Fe ratios in Archean and Paleoproterozoic banded iron formations (BIFs), which represent a phosphate sink (Bjerrum and Canfield, 2002). However, because dissolved silica competes with phosphate adsorption on particulate Fe-oxides (Konhauser et al., 2007), sedimenting ferrihydrite particles would not have been a major sink for phosphate in an Archean ocean saturated with respect to amorphous silica, as is generally believed. In fact, recent compilations of P:Fe molar ratios in BIFs have been used to argue that Neoproterozoic

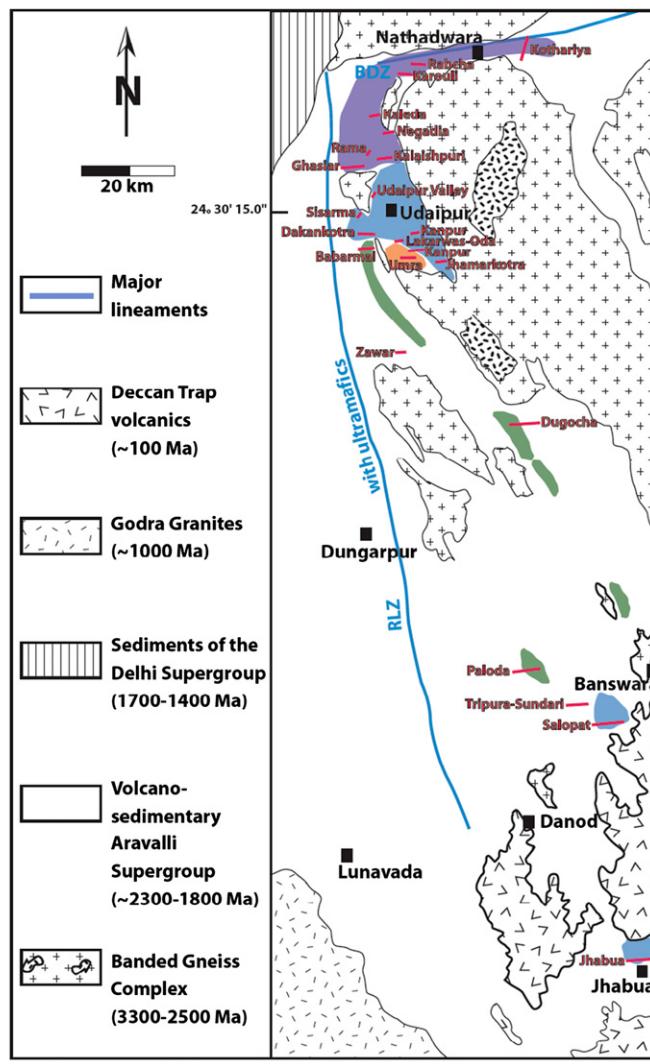

Fig. 1. Simplified regional geologic map of the Aravalli Supergroup in Rajasthan showing in red the sections where samples were collected along with the approximate divisions of four basin types: the PD with near-zero $\delta^{13}C_{carb}$ values (blue), the NPD of the GRK bank shelf with elevated $\delta^{13}C_{carb}$ excursions (purple), and of the Umra isolated basin (orange) and of the calcitic domain at BPB with moderate $\delta^{13}C_{carb}$ excursions (green). BDZ and RLZ are major faults of the Banwaras dislocation zone and the Riakhabedev lineament zone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)