Redox States of Archean Surficial Environments

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Redox states of the Archean Eon have been constrained by various lines of evidence, including atmospheric, photochemical, and ecological models, mass-independent fractionations of sulfur isotopes, Fe-depletion of paleosols, and preservation of diagnostic detrital minerals. Although these lines of evidence present seemingly consistent upper limits on $pO_{2,g}$, they are conceptually contradictory about the redox state of Archean surficial environments. Atmospheric, photochemical, and ecological modeling studies agree well with weakly reducing environment under redox states represented by moderate $H_{2,g}$ levels, whereas current interpretations of Fe-depletion in paleosols and the preservation of detrital minerals are based on slow kinetics of oxidative weathering reactions under redox states indicated by low $O_{2,g}$ levels.

In this study, we reconstruct the evolution of $H_{2,g}$ and $O_{2,g}$ during the Archean Eon based on compilation of reported constraints from experiment, geological observation, and modelling studies. We reveal that $pH_{2,g}$ are orders of magnitude higher than $pO_{2,g}$ in the Archean atmosphere. Similar to modern anoxic basins, the redox states of Archean surface environments should be controlled by the more abundant H_2 instead of the very low O_2. Under the redox state indicated by the Archean $pH_{2,g}$ range, Fe^{2+} and reducing Fe(II)-minerals are thermodynamically stable and have no tendency to be oxidized. Weathering in this case should have involved non-redox acidic dissolution of Fe(II)-species or reductive reaction of Fe(III)-species. Fe(II)-depleted paleosols and the preservation of relatively reduced detrital minerals are natural consequences of their thermodynamic stabilities in the Archean Eon's reducing environments rather than slow kinetics of oxidizing reactions. After the appearance of oxygenic photosynthesis, probably in the middle/late Archean, locally oxygenated environments could have existed, while the atmosphere as a whole remained anoxic. The profile of redox states on the Archean surface seems to be a reverse analogue to the modern Earth.