# Atmospheric oxygen and carbon dioxide levels in the Precambrian estimated from water-rock-atmosphere interactions

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The evolution of atmosphere has been related to life, ocean chemistry and climate, and investigated intensively using various proxies. Paleosols, ancient weathering profiles, can reflect the partial pressures of atmospheric oxygen and carbon dioxide ($pO_2$ and $pCO_2$, respectively) at the time of weathering, i.e., water-rock-atmosphere interactions. The $pO_2$ and $pCO_2$ levels in the Precambrian, indeed, have been estimated using the chemical compositions of paleosols semi-quantitatively and quantitatively. We have developed new weathering models to quantitatively estimate $pO_2$ and $pCO_2$ levels from Neoarchean-Paleoproterozoic paleosols.

For the estimation of $pCO_2$ levels, one of the weathering models (i) calculates the cation concentrations in porewaters at the time of weathering from those of paleosols, (ii) describes the relationships between $pCO_2$, pH and cation concentrations based on the charge balance between the cations and anions including carbonate species in porewaters, and (iii) finally calculates $pCO_2$ levels at a given temperature constraining pH by thermodynamics of weathering, secondary minerals. We confirmed the validity of the model by applying the model to modern weathering profiles. The estimated $pCO_2$ levels at ~2.8–1.8 Ga are higher than those to maintain the average global surface temperature of the Earth above the freezing point of water only by $CO_2$ itself.

The other weathering model, which considers the steady-state weathering of Fe, calculates the ratio of the precipitated Fe(III)-(oxyhydr)oxides from dissolved Fe(II) to the total dissolved Fe(II) during weathering as a function of $pO_2$. The Fe(II) oxidation rate law required for the model calculation was obtained experimentally. The validity of the model was confirmed by applying the model to laboratory experiments conducted under different $pO_2$ conditions. The model also requires pH of porewater, $pCO_2$, water flow rate and temperature which were estimated separately for each paleosol. The $pO_2$ levels were estimated to be $10^{-6.7}$–$10^{-5.4}$ atm at ~2.46 Ga, $10^{-5.2}$–$10^{-3.2}$ atm at ~2.15 Ga, $10^{-3.9}$–$10^{-1.2}$ atm at ~2.08 Ga and more than $10^{-4.6}$–$10^{-2.5}$ atm at ~1.85 Ga. The estimates of $pO_2$ are well consistent with the constraints given by mass independent/dependent fractionation of sulfur records.