

## Estimation for CO<sub>2</sub> levels in the Paleoproterozoic from paleosols

KANZAKI, Yoshiki<sup>1\*</sup>, MURAKAMI, Takashi<sup>1</sup>

<sup>1</sup>Grad. School of Science, Univ. of Tokyo

There remain uncertainties about atmospheric conditions in the early Earth, though numerous researchers have been trying hard to elucidate. The Paleoproterozoic era (especially between 2.5 and 2.0 Ga) has attracted much attentions due to intriguing oxygen rise, multiple global scale glaciation events and co-evolution of early atmosphere and organisms. The concentration of atmospheric CO<sub>2</sub> is a factor that affects the above events and surface temperature, as known as 'faint young sun paradox'. Atmospheric photochemical modeling and paleosols as geological records have given certain constraints on P<sub>CO2</sub> levels, but some of them conflict with one another (e.g., less than 100 PAL (meaning 100 times present atmospheric level) at ~ 2.2Ga (Rye et al., 1995); 7 - 70 PAL at 2.5 - 1.8 Ga (Sheldon, 2006); more than 100 PAL at 2.8Ga (Haqq-Misra et al., 2008)). To estimate the most likely P<sub>CO2</sub> levels in the Paleoproterozoic, paleosols constraints must be re-evaluated.

We used the data of the Cooper Lake paleosol (formed at ~ 2.45Ga, from Utsunomiya et al. (2003)) as this paleosol is diagnosed as well preserved from physical erosion (Murakami et al., 2011). To extract P<sub>CO2</sub> constraints, we firstly estimated ion concentrations in pore water at steady state. Considering the mass balance between solid and water phases, the loss of elements from solid (mol/L (bulk)), which can be obtained from a paleosol, must be the same as the amount transported out from the paleosol by fluid. The amount transported can be expressed by the product of the following parameters; steady state concentrations of ions in water phase (mol/L (water)), transport rate by fluid flow (/yr), porosity of the paleosol at the time of weathering (L (water)/L (bulk)), and total weathering time (yr). Assuming dissolved Si concentration at steady state as 10<sup>-4</sup> - 10<sup>-3</sup> mol/L, Na, Mg, Ca and P concentrations in pore water in a paleosol can be obtained from this mass balance method. As for K concentration, two extreme scenarios were considered, which are no weathering of K scenario and complete weathered K scenario, because K recorded in the Cooper Lake paleosol is affected by K-metasomatism after the paleosol formation. As a next step, we calculated the pHs at which charges of pore waters are maintained, changing P<sub>CO2</sub> from 0.1 PAL to 1000 PAL. Anions considered other than carbonate species included phosphate species, concentrations of which were obtained by mass balance method from the paleosol, and Cl<sup>-</sup> assumed as non buffering anion in the range of < 0.002 M, although Cl<sup>-</sup> concentrations only caused the charge balanced pHs to shift by at most 0.3 in pH unit. As a final step, these charge-balanced waters were checked for saturation state with respect to secondary minerals, and here, kaolinite and smectite were chosen for such minerals. The calculations have revealed that 10 - 1000 PAL of CO<sub>2</sub> are the most likely levels operating at the time of the formation of the Cooper Lake paleosol for the above two extreme scenarios for K. These estimated CO<sub>2</sub> levels are not inconsistent with more than 100 PAL of P<sub>CO2</sub> at 2.8 Ga estimated from atmospheric photochemical modeling (Haqq-Misra et al., 2008).

Keywords: paleosol, weathering, faint young sun paradox, carbon dioxide, Paleoproterozoic