Relationships between the silicate weathering feedback, pCO₂ and equilibrium solute concentrations

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Recent studies have suggested that thermodynamic limitations on riverine solute fluxes exert a first-order control on global chemical weathering rates. As such, these limitations may play a prominent role in the regulation of atmospheric greenhouse gases over geologic timescales by constraining the maximum weathering flux under any given climatic and lithologic boundary condition. In this study, we develop a theoretical scaling relationship between equilibrium solute concentrations and pCO₂ based on reaction stoichiometry between primary mineral dissolution and secondary mineral precipitation and the equilibrium constants. We then test this theoretical scaling relationship against reactive transport simulations of chemical weathering profiles spanning the plagioclase solid solution series under open- and closed-system weathering conditions. Under open-system conditions, equilibrium bicarbonate concentrations vary as a power law function of pCO₂ ($y = kx^n$) where both k and n increase with increasing plagioclase Ca:Na based on reaction stoichiometry and equilibrium constants. Under closed system conditions, bicarbonate concentrations vary linearly with pCO₂ at low values and approach open system scaling at high pCO₂. Finally, we discuss the implications of these results for the role of vascular land plant evolution in driving the strength of the silicate weathering negative feedback in terms of both *(1)* setting steady-state pCO₂ for a given volcanic degassing rate; and *(2)* sensitivity of the climate system to long-term changes in degassing rates and/or transient carbon cycle perturbations.