

Constraining the thermodynamics and kinetics of reverse weathering reactions and their impact on geologic carbon cycling

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Over geologic timescales, the weathering of igneous minerals to clays and carbonates represents a key sink for atmospheric carbon dioxide (CO₂). Yet, the forward weathering reaction is not completely irreversible in the thermodynamic sense and changing environmental variables – most importantly fluid chemistry – can lead to re-emission of CO₂ to the atmosphere following the initial conversion of igneous minerals to clays and alkalinity. Recent work has yielded enticing evidence of the impact of these reverse weathering reactions on global climate and marine chemistry over Earth's history, but the fundamental geochemical controls on the overall impact of this process are not yet clear. As with all geochemistry, thermodynamic drivers ultimately dictate the direction of both forward and reverse weathering reactions. However, the complicated and diverse chemistry of clay minerals has, until now, limited our ability to evaluate the thermodynamic favorability of (reverse) weathering reactions. Recent innovations in estimating clay mineral thermodynamic properties based on electronegativity techniques [1] now implemented in the PyGCC software package [2] are opening windows into understanding the thermodynamic controls on reverse weathering reactions over geologic timescales. At the same time, kinetic techniques for determining clay mineral precipitation rates at ambient conditions are now enabling enhanced understanding of the rates of low-temperature silicate mineral transformations. In this presentation, we will specifically discuss the differing thermodynamic drivers of reverse weathering in the modern and silica-rich Precambrian oceans as well as the importance of clay mineral weathering as a cation source in natural and engineered basaltic carbon sequestration reactions.

[1] P. Blanc, F. Gherardi, P. Vieillard, N. C. M. Marty, H. Gailhanou, S. Gaboreau, B. Letat, C. Geloni, E. C. Gaucher, B. Madé, Thermodynamics for clay minerals: Calculation tools and application to the case of illite/smectite interstratified minerals. *Appl. Geochemistry* **130** (2021).

[2] A. N. Awolayo, B. M. Tutolo, PyGeochemCalc: A Python package for geochemical thermodynamic calculations from ambient to deep Earth conditions. *Chem. Geol.* **606**, 120984 (2022).