The secular evolution of the reverse weathering sink in the global Li cycle

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The global cycling of Li in the modern ocean is driven primarily by continental chemical weathering and hydrothermal input fluxes, balanced by sinks associated with oceanic crust alteration and the authigenic precipitation of alumino-silicate clays (i.e., "reverse weathering"). Seawater δ^7Li, as constrained by planktonic foraminiferal tests, has evolved significantly over the last 70 Ma, increasing ~9‰ to modern values over the Cenozoic. This increase has been hypothesized to reflect long-term changes in continental weathering [1]. While subsequent modeling efforts suggested that shifts in marine Li sinks could feasibly perturb seawater δ^7Li [2], the mechanism remains unclear.

In this contribution, we propose a novel mechanism for a reverse weathering-driven forcing of seawater δ^7Li. Deep-sea sedimentary pore fluid data suggest that clay authigenesis occurs in carbonate-rich sediments, and that these sediments can represent significant sinks of Li from the global ocean (estimated at a maximum of $<2\cdot10^{10}$ moles Li/a). The Li isotopic data indicate that clay authigenesis occurs at depth in the sedimentary column, while modeling efforts suggest that deep mineral formation (and consequent isotopic fractionation of Li) changes the effective fractionation factor via isotopic distillation. Ultimately, the burial of reactive sediment, ostensibly biogenic silica, has the potential to drive variability in seawater δ^7Li.

We test the sensitivity of seawater δ^7Li to secular trends in global Li diagenetic fluxes using oceanic box models and reactive transport models of the sedimentary section. Deep-sea sedimentary records over the Cenozoic support the hypothesis that the fluxes associated with reverse weathering may have contributed to the observed trends in δ^7Li. Ultimately, the secular variability in the reverse weathering sink has the potential to impact the reconstruction of the continental weathering flux based on δ^7Li proxy records.

[1] Misra and Froelich (2012) *Science* **335**, 818–823. [2] Li and West (2014) *Earth Planet. Sci. Lett.* **401**, 284–293.