

Fractionation of K isotopes in coastal groundwater systems: Implications for the global K cycle and oceanic isotope budgets

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The coastal groundwater system plays a pivotal role in the global hydrological and biogeochemical cycles, with groundwater-derived solutes (e.g., nitrogen, phosphorus) estimated to be equivalent to that of the river input into the ocean^[1-2], thereby influencing the chemical composition of oceans. To date, little is known about potassium (K) fate in coastal aquifers and the impact of submarine groundwater discharge (SGD) on seawater $\delta^{41}\text{K}$ values, which are $\sim 0.55\text{‰}$ enriched in $\delta^{41}\text{K}$ relative to the bulk silicate Earth. Here, we present the K isotope and hydrochemical data of recharging river water, as well as unconfined and confined groundwater in the coastal region of Jiangsu province, China. The K isotope signatures revealed distinct fractionation mechanisms, with $\delta^{41}\text{K}$ values exhibiting an overall increase in unconfined aquifers (-0.41‰ to 0.78‰) and confined aquifers (-0.14‰ to 1.37‰). Specifically, chemical weathering and clay adsorption processes collectively govern the K concentrations and $\delta^{41}\text{K}$ values of non-seawater-influenced groundwater. In contrast, in seawater-influenced groundwater, the formation of clay minerals that sequester K from aquifers results in an elevation of $\delta^{41}\text{K}$ values to 0.78‰ – 1.37‰ , as increased ionic strength inhibit K adsorption onto clays. Thus, a clay incorporation-induced K isotopic fractionation factor ($\alpha=0.9997$ to 0.9999) was derived using the Rayleigh fractionation model. Utilizing a K mass-balance model in conjunction with Monte Carlo simulations, we evaluated the response of seawater $\delta^{41}\text{K}$ values to SGD. Our results indicate that the $\delta^{41}\text{K}$ value of seawater increases by more than 0.3‰ when the K flux from SGD is comparable to the riverine input. This study highlights the role of SGD in the global K cycle and the oceanic isotopic budget, with important implications for the temporal evolution of seawater K isotope values.

[1] Goldschmidt, Rodellas V, Garcia-Orellana J, Masqué P, Feldman M, Weinstein Y (2015), *Proceedings of the National Academy of Sciences* 112, 3926-3930.

[2] Goldschmidt, Santos IR, Chen X, Lecher AL, Sawyer AH, Moosdorf N, Rodellas V, Tamborski J, Cho H-M, Dimova N, Sugimoto R, Bonaglia S, Li H, Hajati M-C, Li L (2021), *Nature Reviews Earth & Environment* 2, 307-323.