Effects of cation exchange processes on the isotopic composition of $\delta^{26/24}$Mg , $\delta^{25/24}$Mg , $\delta^{88/86}$Sr and ^{87}Sr/^{86}Sr at the freshwater-seawater interface.

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Cation exchange reactions involve the rapid "swapping" of dissolved cations with cations weakly-bound to the surfaces of common environmental adsorbents, such as clay minerals. Quantifying the controls of cation exchange reactions is vital for understanding aquifers, the soil environment, nutrient fluxes in estuaries, and, crucially, how these processes impact our calculations of the long- and short-term carbon cycle [1]. In particular, large changes in the concentration and composition of dissolved cations at the freshwater-seawater interface drive cation exchange reactions that can influence dissolved cation inputs into the ocean [2].

Despite the widespread importance of cation exchange reactions in the critical zone, a few key outstanding questions remain. 1) What is the role of cation exchange in controlling the fractionation of novel stable isotope systems (Mg/Sr/Li), especially at the freshwater-saltwater interface, and 2) what are the reaction kinetics and equilibrium states of the cation exchange reactions.

Here, we use a novel application of stable isotopic tracers; $\delta^{26/24}$Mg and $\delta^{88/86}$Sr to determine the isotopic fractionation factors for Mg and Sr. The extent of chemical equilibration in the experiments is assessed using novel 'three-isotope' methods: employing $\delta^{25/24}$Mg (with the addition of a ^{25}Mg spike), as well as ^{87}Sr/^{86}Sr ratios. We have quantified the exchange of Mg-Sr-Ca-Na cation in carefully controlled laboratory experiments between natural waters (river waters and seawaters) and common environmental adsorbents (clay minerals such as smectite and kaolinite), determining the compositional dependence of the exchange equilibrium constants (Ca, Na, Mg, Sr) and stable isotope fractionation factors (Mg and Sr).

[1] Tipper et al. (2021), *PNAS* 118, 1 e2016430118
[2] Sayles and Mangelsdorf (1979), *GCA* 41, 7 951-960