

Riverine Mg isotope ratios reflect deep critical zone weathering in a tropical andesitic catchment

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Isotopic ratios can be useful tracers of riverine solute sources, weathering mechanisms and transport processes in the critical zone. In a highly weathered, marine-bedded, andesitic, metavolcaniclastic catchment in the Luquillo Critical Zone Observatory (Puerto Rico, USA), we determined that [Mg] and $\delta^{26}\text{Mg}$ in regolith pore waters mainly reflect rain input, with increasing weathering inputs with depth. The effect of vegetation uptake on the pore water $\delta^{26}\text{Mg}$ is negligible. Pore water Mg is primarily a mixture of precipitation and weathering-sourced Mg, but an isotopic fractionation occurs during dissolution-recrystallization of Fe(III)-(hydro)oxides under alternating redox conditions near the soil-saprolite interface. Bulk regolith Mg is isotopically heavier than bedrock Mg, consistent with the preferential incorporation of heavy ^{26}Mg into secondary minerals.

Stream [Mg] shows typical dilution behaviour during a storm event, but the relationship between [Mg] and $\delta^{26}\text{Mg}$ is consistent with steady state fractionation ($\alpha=1.00115$). During base flow, stream water Mg is isotopically heavier than regolith pore water or bedrock. *In-situ* (LA-MC-ICPMS) $\delta^{26}\text{Mg}$ analysis of the bedrock minerals indicates dissolution of Mg-rich chlorite ($\delta^{26}\text{Mg} = +0.19\text{‰}$), deep in the critical zone at rock-saprolite interfaces and in fractured bedrock, as the likely source of this isotopically heavy Mg; mass balance calculations indicate it is also the main source of Mg to the stream. This result highlights the importance of weathering processes that occur 10s of meters below the rooting zone, to watershed exports. Conversely, shallow processes (e.g., vegetation-induced weathering) have little to no impact on the production and export of weathering-sourced solutes.