The influence of lithology on Mg cycling in highly weathered catchments: insights from dMg isotopes at the Luquillo CZO

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As weathering advances, the main source of inorganic nutrients to soils changes from bedrock weathering to atmospheric inputs. Similarly, plants are expected to cycle nutrients more tightly as soils become more leached. These two concurrent processes can lead to a decoupling between shallow and deep biogeochemical cycles in terms of the predominant source of inorganic nutrients (atmospheric input at the surface, weathering at depth) and of the processes that control their cycling. To investigate the influence of lithology on this potential decoupling at the late stages of weathering, we used Mg isotopes to trace the cycle of inorganic nutrients in two catchments covered by highly-leached regolith at the Luquillo Critical Zone Observatory, Puerto Rico. We focused on two deep (~9 m) ridgetop profiles that have comparable internal (degree of weathering, topography) and external (vegetation, climate) characteristics, but differ in their underlying bedrock (andesitic-volcaniclastic and granitic). We identified a shallow-deep decoupling of Mg sources to the regolith at annual to kyr time scales (porewater, bulk regolith) over both lithologies, consistent with the anticipated predominance of atmospheric inputs at late stages of weathering. However, unexpectedly, we see little effect of vegetation uptake on the Mg isotope composition of the rooting zone, despite large recycling factors calculated from Mg concentrations. At the catchment scale, the shallow-deep decoupling of Mg sources affects the Mg isotope signature of the stream in the volcaniclastic catchment, reflecting the input of solutes derived from deep silicate weathering during baseflow (Chapela Lara et al., 2017, GCA). In contrast, the $\delta^{26}Mg$ signature of the stream at the granitic catchment reflects a mixture of porewater and rain. Altogether, our work indicates that the chemical and physical (fracturing style and particle size) differences between the two parent rocks are erased in the upper 2 m of the regolith, as expected, but affect the Mg isotope budget through most of the regolith profiles and in the streams that drain them.