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The influence of critical zone processes on the Mg isotope budget in a tropical, highly weathered andesitic catchment

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Abstract

In order to assess the effects of critical zone processes on Mg concentrations and isotopic signatures of tropical streams, we studied a well constrained, highly weathered andesitic volcaniclastic catchment in the Luquillo Critical Zone Observatory, Puerto Rico. Our results indicate that dissolved Mg concentrations and isotope ratios in the regolith pore water are mainly controlled by rain input, with weathering inputs being more important at sites with thinner regolith (2.7–0.9 m deep) and at depth (>8 m) on a thick ridgetop regolith (~10 m). In addition to mixing of precipitation and weathering-sourced Mg, an isotopic fractionation process is taking place between dissolved Mg and the regolith, likely during dissolution or recrystallisation of Fe(III)-(hydro)oxides under alternating redox conditions. Bulk regolith is isotopically heavier than both the bedrock and the exchangeable fraction ($\delta^{26}Mg_{\text{regolith-bedrock}} = +0.03$ to $+0.47‰$), consistent with the preferential incorporation of heavy ^{26}Mg into secondary minerals with some exchange of sorbed Mg with isotopically lighter pore water. Magnesium concentrations in the stream show a typical dilution behaviour during a storm event, but the [Mg] – $\delta^{26}Mg$ pattern cannot be explained by mixing of rain and pore water; the data are best explained by a steady-state fractionation model with $\alpha = 1.00115$. During baseflow the stream has $\delta^{26}Mg = +0.01‰$, higher than any of the water samples or the bedrock. *In-situ* analysis of the Mg isotopic composition of bedrock minerals points at the dissolution of Mg-rich chlorite ($\delta^{26}Mg = +0.19‰$) as the most likely source of this isotopically heavy Mg, with mass balance calculations indicating chlorite dissolution is also the main source of Mg to the stream. Overall, our study highlights the importance of atmospheric input of nutrients to the vegetation in tropical areas covered by thick, highly leached regolith, whereas the Mg flux and Mg isotopic signature of watershed exports are dominated by bedrock dissolution delivered to the stream through deeper, usually un-sampled critical zone pathways.

Keywords: Weathering; Mg isotopes; Mg cycle; Critical zone; LCZO; Puerto Rico

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1. INTRODUCTION

Magnesium is an important cation in the global silicate weathering feedback that moderates atmospheric CO_2 over geological time scales (e.g., Berner, 1995; Berner and Berner, 1997; Kump et al., 2000). In contrast to weathering proxies such as Li, which is mainly hosted in silicate minerals and is not involved in biological turnover (Tomascak

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et al., 2016), Mg is present in both silicate and carbonate rocks and is an essential nutrient for all life forms (Schmitt et al., 2012; Bullen, 2014). Because it is a major element in most rocks, waters, and plants, Mg is also less sensitive to the sampling and analytical issues that hamper trace element studies. Furthermore, Mg isotopes (^{24}Mg, ^{25}Mg and ^{26}Mg) are fractionated by chemical weathering (e.g., Teng et al., 2010; Pogge von Strandmann et al., 2012; Liu et al., 2014) and by the uptake by vegetation (e.g., Black et al., 2008; Bolou-Bi et al., 2010, 2012; Tipper et al., 2010, 2012b), thus making them a promising tracer of both the geochemical and biological processes that occur in the weathering environment, which can affect the Mg isotopic composition of the streams. Consequently, a number of recent studies have examined Mg isotope ratios in the *critical zone* (see Bullen, 2014, for a recent review), defined here as the layer of terrestrial Earth extending from the bottom of the weathering zone to the top of the tree canopy. These studies have demonstrated that a range of (bio)geochemical processes can fractionate Mg isotopes, but the relative importance of these processes to Mg isotopic compositions in the critical zone is not well understood despite profound implications for understanding local and global Mg fluxes and cycles through time.

The fractionation of Mg isotopes by primary mineral dissolution has been explained experimentally by two processes: the preferential release of ^{24}Mg (e.g., Wimpenny et al., 2010) and the preferential dissolution of isotopically distinct phases (e.g., Ryu et al., 2011). However, the largest fractionations in silicate watersheds are thought to result from the incorporation of Mg into secondary minerals, with most field-based studies reporting that secondary clays are enriched in ^{26}Mg relative to their parent rock, with a $\Delta^{26}\mathrm{Mg}_{\text{rock-regolith}}$ of +0.5‰ to +1.5‰ (e.g., Teng et al., 2010; Bolou-Bi et al., 2012; Huang et al., 2012; Tipper et al., 2012b; Liu et al., 2014), although Ma et al. (2015) found soils similar or slightly lighter than the shale bedrock. This fractionation is generally expressed as an enrichment in the lighter isotope, ^{24}Mg, in river waters relative to the rocks they drain (e.g., Brenot et al., 2008; Bolou-Bi et al., 2012; Pogge von Strandmann et al., 2012; Tipper at al., 2006, 2008). The mechanism of incorporation of the heavy isotope into clays is an area of active research, with field and experimental evidence suggesting that, apart from incorporation into the structure of the mineral, adsorption–desorption and ion exchange processes at mineral surfaces may also fractionate Mg isotopes in weathering, with the direction and extent of this fractionation still a matter of debate (Jacobson et al., 2010; Tipper et al., 2010, 2012a; Bolou-Bi et al., 2012; Huang et al., 2012; Opfergelt et al., 2012, 2014; Li et al., 2014; Pogge von Strandmann et al., 2012; Wimpenny et al., 2015).

The isotopic effects of Mg sorption onto secondary minerals other than clays, such as oxides and hydroxides, are essentially unknown, with no direct measurements published to date. Nevertheless, several studies have found that sorption onto Al- or Fe-(hydr)oxides in both experimental and natural environments can isotopically fractionate other divalent metals (Cu, Zn, Fe) with a preference for the heavy isotope (e.g., Pokrovsky et al., 2005; Balistrieri et al., 2008; Mikutta et al., 2009). This fractionation can occur even at low pH for Fe(III)-hydroxides (e.g., Violante et al., 2002), indicating Mg isotope fractionation by sorption–desorption into Al-or Fe-(hydr)oxides is possible in highly weathered regoliths, as interpreted by Liu et al. (2014) for the enrichment in ^{26}Mg in bauxites relative to the bedrock.

Fractionation of Mg isotopes by vegetation uptake has been demonstrated in laboratory (Black et al., 2008; Bolou-Bi et al., 2010) and field studies (Tipper et al., 2010, 2012b; Bolou-Bi et al., 2012; Opfergelt et al., 2014), with a general enrichment in ^{26}Mg in plants relative to pore waters or nutrient solutions. A fractionation within the plant is also associated with the translocation of Mg from roots to leaves and with foliage age (Bolou-Bi et al., 2010, 2012). The effect of vegetation uptake has been regarded as a factor controlling the Mg isotopic composition of streams (Bolou-Bi et al., 2010, 2012; Tipper et al., 2012b; Opfergelt et al., 2014), although less important than reactive transport during water–rock or water–soil exchange complex interactions (Bolou-Bi et al., 2012; Tipper et al., 2012b; Opfergelt et al., 2014), which in turn depend on the sources of Mg, the flow paths and the flow rates of water through the critical zone, and on the rates of Mg isotope fractionation, which can only be known at the catchment scale.

The vast majority of field-based studies of Mg isotopes has been focussed on temperate and arctic sites, in spite of the fact that the tropics are disproportionately more important, relative to their land area, in terms of weathering inputs to the oceans, biodiversity and climate change sensitivity (e.g., Stallard and Edmond, 1983; Chapin et al., 2010; Wohl et al., 2012). Equally, Mg isotope systematics during critical zone processes in temperate watersheds cannot be directly extrapolated to the tropics, which are different in a number of ways. One key difference is that the Mg isotope ratios of streams are strongly influenced by seasonality in temperate regions, expressing changes in critical zone processes such as vegetation uptake and water–rock interaction time (e.g., Bolou-Bi et al., 2012; Tipper et al., 2012b), whereas tropical, high precipitation sites have significantly less seasonality. The hydrological functioning of tropical high precipitation catchments also has important peculiarities related to the thick, clay-rich saprolite that often mantles these environments, leading water to flow laterally along high-permeability, near-surface flow paths or via saturation-excess overland flow during intense rain events (Elsenbeer, 2001; Schellekens et al., 2004; Goller et al., 2005; Bonell, 2005; Kurtz et al., 2011). Finally, recent studies on the Caribbean island of Guadeloupe have found that atmospheric inputs can have a strong influence on the δ^{26}Mg of bulk soil (Dessert et al., 2015) and the exchangeable fraction (Opfergelt et al., 2012) of cation-depleted tropical regoliths.

Aiming to fill the gap in Mg isotopic data from the tropics and to generally improve our understanding of the Mg cycle in the critical zone, here we examine the controls on the Mg dynamics, at several temporal and spatial scales, in a well-constrained tropical catchment in the Luquillo Critical Zone Observatory (LCZO), Puerto Rico (Fig. 1). Specifically, we seek to distinguish the biological from the