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 to 0.9 m deep) and at depth (> 8 m) on a thick ridgetop regolith (~10 m). Vegetation uptake has a limited effect on surficial pore water $\delta^{26}Mg$ (average $\delta^{26}Mg_{pw-rain} = + 0.20‰$). 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 recrystallization of Fe(III)-(hydro)oxides under alternating redox conditions. Bulk regolith is isotopically heavier than both the bedrock and the exchangeable fraction ($\delta^{26}Mg_{regolith-bedrock} = + 0.03$ to $+ 0.47‰$), consistent with the preferential incorporation of

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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 δ^{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 (δ^{26}Mg $= + 0.19‰$) as the most likely source of this isotopically heavy Mg, with mass balance calculations indicating it 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 fluxes and Mg isotopic signature of watershed exports are dominated by bedrock dissolution delivered to the stream through deeper, usually un-sampled critical zone pathways.

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., 2010). In contrast to weathering proxies such as Li, which is mainly hosted in silicate minerals and is not involved in biological turnover (Lemarchand et al., 2010), Mg is present in both silicate and carbonate rocks and is an essential nutrient for all life forms. 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. Liu et al., 2014; Pogge von Strandmann et al., 2012; Teng et al., 2010) and by the uptake by vegetation (e.g. Black et al., 2008; Bolou-Bi et al., 2012; Bolou-Bi et al., 2010; Tipper et al., 2010; Tipper et al., 2012b), thus making it 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 Schmitt et al., 2012, 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 by two processes: preferential release of ^{24}Mg (e.g., Wimpenny et al., 2010) and 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 $\Delta^{26}Mg_{rock-regolith}$ of + 0.5‰ to + 1.5‰ (e.g., Bolou-Bi et al., 2012; Liu et al., 2014; Tipper et al. 2012b), whereas pore fluids are isotopically light. 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., Bolou-Bi, 2012; Brenot et al., 2008; Pogge von Strandmann et al., 2012; Tipper at al., 2006, 2008; Teng et al., 2010). 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 silicate weathering environments (Bolou-Bi et al., 2012; Huang et al., 2012; Jacobson et al., 2010; Li et al., 2014; Opfergelt et al., 2012, 2014; Pogge von Strandmann et al., 2012; Tipper et al., 2010, 2012a; 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., Balistrieri et al. 2008, Pokrovsky 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-(hyro)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 (Bolou-Bi et al., 2012; Tipper et al., 2010; Tipper et al., 2012a; Opfergelt et al., 2013), with a general enrichment in ^{26}Mg in plants relative to pore waters or nutrient solutions. There is also a fractionation within the plant 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., 2012a; Opfergelt et al., 2013), although less important than reactive transport during water-rock or water-soil exchange complex interactions (Bolou-Bi et al., 2012; Tipper et al., 2012a; Opfergelt et al., 2013), 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., Chapin et al., 2010; Stallard and Edmond, 1983; Wohl et al., 2012). At the same time, 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., 2012a), 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

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environments, leading water to flow laterally along high-permeability, near-surface flowpaths 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 in 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 geochemical components of the Mg cycle and to quantify their relative contributions to the Mg solute fluxes in the watershed. We hypothesize that the largest input to the whole critical zone Mg budget is the dissolution of bedrock minerals, and that dissolution-precipitation during weathering controls the δ^{26}Mg of the deep critical zone over all the time scales studied. In the regolith, we hypothesize that Mg fluxes and δ^{26}Mg values over short time scales (days to decades) are strongly affected by cycling by vegetation within the rooting zone, but are more influenced by dissolution of atmospheric dust over intermediate time scales (decades to kyrs). In the stream, we expect the δ^{26}Mg signature to reflect rain and shallow pore water during storm events and deeper critical zone sources during baseflow.

To test these hypotheses, we measured the Mg concentrations and Mg isotopic ratios of precipitation; stream water during baseflow and storm flow; bedrock; vegetation; and depth profiles of pore water (at different topographic positions), bulk regolith and exchangeable Mg. We compare the relative influence of different Mg sources, fractionation processes and timescales on the Mg isotope signature of stream water at baseflow and storm flow.

2. FIELD SETTING

Environmental data has been gathered in the Luquillo Mountains of north-eastern Puerto Rico for 20+ years by the US Forest Service International Institute of Tropical Forestry (IITF), the US Geological Survey's Water Energy and Biogeochemical Budgets (WEBB) project, and the NSF Long Term Ecological Research (LTER) program. Building on this history, the NSF Luquillo Critical Zone Observatory (LCZO) was founded in 2006. The LCZO therefore provides one of the best instrumented and contextualised sites in the world in which to study tropical critical zone processes. For this study we focus on a small volcaniclastic catchment (Bisley 1) that is part of the Rio Mameyes watershed that drains north into the Atlantic Ocean (Fig. 1). This catchment is underlain by Cretaceous, marine-deposited, quartz-poor meta-volcaniclastic rocks of the Fajardo Formation (Jolly et al., 1998), which is dominated by thick-bedded tuff breccias with andesitic clasts, interbedded with coarse grained tuff, tuffaceous sandstone and cherty siltstone (Briggs, 1973). The bedrock was altered during diagenesis and hydrothermal metamorphism, during which the fine grained groundmass was devitrified, sericitized and chloritized; phenocrysts of biotite, plagioclase and augite were replaced by chlorite and actinolite (Buss et al., 2013; Table 1).

The warm and humid climate of the Luquillo Mountains (Table 1) has favoured intense and rapid weathering (e.g., White et al., 1998; Dosseto et al., 2012), producing a mantle of regolith that can reach at least 37 m deep in the Bisley 1 catchment (Buss et al., 2013). Here we define all the weathered material developed over the bedrock as regolith (including saprolite and soil). The primary minerals of the volcaniclastic bedrock weather mostly *in situ* to microcrystalline disordered kaolinite and halloysite, illite, and Fe- and Al-oxides (Huffaker, 2002; Dosseto et al., 2012; Buss et al., in rev.; Porder et al., 2015; Table 1). Occasional accumulations of Mn-oxides are visible in the saprolite as mm-thick layers. The deepest regolith also contains about $7 - 12$ wt% chlorite and $2 - 4$ wt% feldspars (Table 1, S3; Buss and White, 2012; Buss et al., in rev.). This saprolite produces clay-rich but moderately well-drained ultisols (Scatena, 1989; Johnston, 1992) that are mantled by a thin layer of leaf litter in most areas.

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We focused our work on a regolith depth profile from a ridgetop site (B1S1 in Fig. 1), classified as a Typic Haplohumult (Yi-Balan et al., 2014; Huffaker, 2002), for which major element chemistry, mineralogy, microbiology and physical properties have been presented in Buss et al. (in rev.) and Liermann et al. (2014). This regolith is highly leached, containing only secondary minerals and quartz above 8 m depth (Liermann et al., 2014) and, in contrast to the usual trends with depth (e.g., Brantley and Lebedeva, 2011), many parameters show a discontinuity at ~1 m depth. For instance, bulk density is expected to increase steadily with depth (Brady and Weil, 2007), but here it increases from 0.9 m to 1.5 m depth (Buss et al., in rev.). Similarly, water contents are high throughout the profile (35 to 25 vol.%), but the minimum is reached from 0.9 m to 1.5 m depth (Buss et al., in rev.). The regolith is moderately to strongly acidic at all depths (average pH =3.6; Liermann et al., 2014). A full soil pit description by horizon at this site can be found in Yi-Balan et al. (2014), who report two layers with redoximorphic features (mottling, red and gley layers) indicative of alternating redox conditions, most marked between 1.0 and 1.4 m depth.

3. METHODS

3.1 Sample collection

We obtained splits of regolith from four cores augered during the installation of pore water samplers along a slope transect (Figs. 1, 4; Buss et al., in rev.), from the top of a ridge (B1S1) to the riparian zone of Bisley 1 stream (B1S4, Figs. 1, 4), and from two bedrock cores drilled on the nearby road (Fig. 1; Buss et al., 2013). We selected a thin section from one of these cores for analysis of the Mg isotopic composition of individual minerals in the bedrock (sample B1W2 at 6.4 m depth in Buss et al., 2013; Table S1).

To investigate the Mg cycle at different time scales we analysed the Mg isotopic composition of the regolith at the ridgetop site in three different reservoirs. 1) Pore water, which reflects processes at the scale of water residence time in the regolith (~2 y, Buss et al., in rev.); 2) the exchangeable fraction (NH$_4$-acetate extract, method in Buss et al., in rev.), reflecting Mg sorbed onto minerals and

approximating longer-term bioavailability; and 3) the bulk solid, reflecting processes over the time scale of regolith development (~30 ky; Dosseto et al., 2012).

The temporal variability of Mg concentrations in pore water, sampled from suction lysimeters, is discussed in Buss et al. (in rev.). We sampled lysimeters for Mg isotope analysis in November 2009. Samples were filtered to 0.45 μm (SFCA-membrane, Cole-Parmer) into acid-washed HDPE bottles following procedures used by the USGS at this site (e.g., Murphy and Stallard, 2012a). Preliminary Mg isotope analyses were conducted at the *Institute de Physique du Globe de Paris* on pore waters collected from three of the four sites in January 2008 (Chapela-Lara et al., 2014), and are presented here for comparison.

Stream water samples were collected during a storm event in June 2011 at the gaged outlet of the catchment, and major and some trace elements were analysed by ICP-AES. Openfall precipitation was collected above the canopy at the head of the catchment (Fig. 1). To calculate Mg fluxes at the catchment level we used the LTER online data base for daily stream discharge from 2000 to 2005, daily rain discharge from 2000 to 2011 (Gonzalez, 2011a,b,), and weekly chemical composition of the stream and precipitation from 2000 to 2010 (McDowell, 2010, 2012).

Plant leaves and bark samples were collected at the ridgetop site (B1S1) by the USGS, oven dried and powdered. Here we present only the results of the bark of the predominant species, Tabonuco tree (*Dacryodes excelsa*), which accounts for 45.7% of the aboveground biomass in this catchment (Scatena, 1993).

3.2 Elemental and isotopic analysis

The elemental composition of the plant samples was measured by ICP-OES at the Central Analytical Laboratory in the Department of Crop and Soil Science, Oregon State University. Major and trace elements in pore water, bulk regolith, ammonium-acetate extractable cations, and bedrock samples were analysed by the USGS by ICP-MS after multi-acid digestion, or by SGS Laboratories (Toronto,

Ontario, Canada) by ICP-AES after lithium metaborate fusion digestion; much of this data was presented in Buss et al. (2013; in rev.) but Nb data and additional samples are presented here (Table S1). Splits of those samples (plant, regolith and bedrock samples) and rock standards were digested in an ultra-pure concentrated acid mixture (HF, HCl, HNO_3) for Mg isotope analysis.

We purified all samples using the cation exchange chemistry procedure detailed in Pogge von Strandmann et al. (2011). Briefly, an amount of sample containing ~1 μg Mg was dried, treated with $HNO_3+H_2O_2$ to remove any organic matter, re-dissolved in 2M HNO_3, and passed through two sets of chromatographic columns filled with Biorad AG50W X12 cation exchange resin. Because of high Ti/Mg ratios, bulk regolith samples underwent an additional purification step to remove Ti, whose ions cause interferences when measuring Mg isotopes in low resolution mode of the MC-ICP-MS. For this we used an additional set of columns with 0.25 mL of TRU-Spec resin and 7M HNO_3 as the eluent (Pogge von Strandmann et al., 2012). We measured the Mg isotope ratios on a Thermo Neptune multi-collector ICP-MS at the Bristol Isotope Group laboratory, using the standard-sample bracketing technique (DSM3 standard), with a concentration within ± 10% of that of the sample. Results were normalized using the common delta notation in per mil (Galy et al., 2003):

$$\delta^x Mg\ (‰) = \left(\frac{\left[\frac{^xMg}{^{24}Mg} \right]_{sample}}{\left[\frac{^xMg}{^{24}Mg} \right]_{standard}} - 1 \right) \times 1000 \tag{1}$$

where x can be 24 or 25. We monitored the long term precision of our measurements with the Mg Cambridge-1 standard (CAM-1), which yielded $\delta^{26}Mg = -2.56 \pm 0.10$ ‰ (2sd, n = 54) over a period of two years, and our pore water sample B1S1 ($\delta^{26}Mg = -0.77 \pm 0.04$ ‰, 2sd, n = 14). The accuracy and external precision of our whole chemical+analytical procedure were assessed by analysing seawater ($\delta^{26}Mg = -0.85 \pm 0.07$ ‰, n = 13, within analytical uncertainty of the value measured by Foster et al., 2010) and USGS rock standards BHVO-2 and BCR-2 (Table 2).

The Mg-bearing minerals (pyroxene, amphibole and chlorite) in the thin section selected for *in situ* Mg isotope analyses (B1W2-2-2) were identified and quantified by elemental mapping using EDX analysis (Thermo 10 mm^2 silicon drift detector), coupled with backscatter electron (BSE)

imaging on a scanning electron microscope (SEM, Hitachi S-3500N) at the University of Bristol. The elemental compositions of these minerals were then determined using WDS electron probe microanalysis (EPMA, Cameca SX100; Table S2).

The micro-scale Mg isotope composition of individual minerals and their Mg and Al concentrations were determined by UV femtosecond laser ablation coupled to a Thermo Neptune MC-ICP-MS (fs LA-MC-ICP-MS, Fem2) in the Earth Surface Geochemistry laboratory at GFZ Potsdam. Instrumentation, data acquisition and evaluation procedures are described in detail in Schuessler and von Blanckenburg (2014). Laser ablation was performed on individual minerals grains with a spatial resolution at each analysis location of less than 100 x 100 µm surface area with less than 10 µm crater depth. The laser beam, with a diameter of ~25 µm, was scanned across the mineral surface to adapt to the irregular shape of the grains with repetition rates between 20 to 40 Hz. The high mass resolution mode of the MC-ICP-MS was used for Mg isotope ratio measurements, which had already been successfully applied during laser ablation MC-ICP-MS to resolve isobaric interferences ($^{52}Cr^{2+}$ on $^{26}Mg^+$, $^{50}Ti^{2+}$ and $^{50}Cr^{2+}$ on $^{25}Mg^+$, or $^{48}Ca^{2+}$ and $^{48}Ti^{2+}$ on $^{24}Mg^+$; Oeser et al., 2014). Mass bias correction was performed using the komatiite glass GOR132-G as bracketing standard. Using a $\delta^{26}Mg$ value for GOR132-G of -0.17 ‰ relative to DSM-3 (Oeser et al., 2014), we converted results to δ-values relative to DSM-3 (Tables3 and S5). Si was used as internal standard element (IS, determined independently, Table S1) for determination of Mg and Al concentrations with an uncertainty estimated to be better than 5%.

The uncertainty of the fsLA-MC-ICP-MS method for Mg isotope ratios is estimated to be better than ±0.12‰ (2sd) for $\delta^{25}Mg$ and ±0.25‰ (2sd) for $\delta^{26}Mg$, respectively, based on repeat measurements on reference materials during four analytical sessions (Table S3). This uncertainty encompasses differences in the analyses of BHVO-2G between analytical sessions (Fig. S1), induced by instrument performance and tuning. At the current level of experience in this novel application, we report a rather conservative estimate on the laser ablation Mg isotope measurement uncertainty of $\pm$ 0.25‰ (2sd), which is nevertheless sufficient to interpret the measured mineral $\delta^{26}Mg$ data within the scope of this study. The measurements of BHVO-2G basaltic glass (average $\delta^{26}Mg = -0.17 \pm 0.25$‰,

2sd, n = 26) agree within uncertainties to published values from bulk rock analyses and the recommended value for this reference material (-0.20 ± 0.07‰; Teng et al., 2015; Fig. S1, Table S3). Moreover, to test the method on the specific chemical matrix composition of the investigated samples in this study, we measured a glass made from bulk sample powders B1W-2-2-2 and B1W-2-6-2 by flux free fusion using an Ir strip (Stoll et al., 2008) using fsLA-MC-ICP-MS, which gave Mg isotope values in good agreement (within analytical uncertainty of ± 0.25‰ in $\delta^{26}Mg$) with the bulk Mg isotope values of the same sample powder analysed by solution MC-ICP-MS after acid-digestion and Mg column chemistry purification (Table 3, Fig. S1).

4. RESULTS

4.1 Mg loss and degree of weathering of the regolith

Most cations are lost from the regolith between 1 m and 8 m depth (Buss et al., in rev.), including Mg (Fig. 2c). The cation exchange capacity (CEC) of this regolith is very low, from 0.5 cmol$_c$ kg^{-1} at 0.6 m depth, to a maximum of 2.7 cmol$_c$ kg^{-1} at the deepest sample (Buss et al., in rev.). Consequently Mg concentrations in this fraction are also low, from 1.47 to 10.1 mmol kg^{-1} (Fig. 2b), and constitute only between 1% and 5% of the bulk Mg. Dissolved Mg in pore water is also very low and does not show a clear trend with depth (Fig. 2a), in contrast to the longer-term pools, which increase progressively with depth below 1.2 m depth (Figs. 2b,c).

To estimate the fraction of Mg remaining in the regolith after weathering has proceeded (f_{Mg}), we used the average composition of the bedrock samples (Table S1) as the starting parent material, and we chose Nb as the index element because it is comparatively immobile in tropical settings (e.g. Kurtz et al., 2000; Ma et al., 2007). The results describe a Mg-poor regolith characterised by a depletion profile from 9.7 m to 1.2 m depth (f_{Mg} from 0.14 to 0.01), that becomes slightly more enriched in Mg above 1.2 m depth (f_{Mg} = 0.1 at the surface, Fig. 3a).

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To measure the overall degree of alteration of the regolith we used the Parker Index of Weathering (WIP), regarded as the most appropriate alteration index for heterogeneous parent rocks and highly weathered regolith, because it includes only the most mobile oxides and allows for Al mobility. This index is calculated from molar concentration proportions as (Price and Velbel, 2003):

$$\text{WIP} = 100 \cdot \left[\frac{2Na_2O}{0.35} + \frac{MgO}{0.9} + \frac{2K_2O}{0.25} + \frac{CaO}{0.7} \right] \qquad (2)$$

where a fresh rock can have WIP >100 and a totally weathered sample would have WIP = 0. The regolith at the ridgetop site (B1S1) is the most weathered of the four; the two located on slopes (B1S2 and B1S3) achieve similar alteration to the ridgetop site, but over much less depth (Fig. 3b). The thinnest profile, at the riparian site (B1S4), is the least altered at depth and has the largest variation in WIP, going from values typical of fresh rock (~300) to a WIP of 37 over less than a meter of depth (Fig. 3b).

4.2 Mg and δ^{26}Mg of water and vegetation

Magnesium in openfall ranged between 2 and 150 μM L^{-1} from 2000 to 2010 (Table S4). Mg in pore water ranged between 4.9 μM to 37.3 μM L^{-1} during 2008, with the highest values in the valley site B1S4 (Table S5; Buss et al., in rev.). Mg concentration in pore water is most variable in surficial samples (varying by up to 9.7 μM L^{-1} on the ridgetop site), and comparatively stable below 4 m depth (Fig. 4). This variation does not otherwise follow a clear pattern with depth but, on average, the lowest values are in the uppermost samples and the highest below 4 m depth (Fig. 4; Buss et al., in rev.). Compared with the longer-term pools represented by the exchangeable fraction and the bulk regolith, Mg is the most variable in the short-term pool represented by pore water (Fig. 2a).

The Mg isotope composition of all samples is summarised in Fig. S1 and Table 2. The measured δ^{26}Mg values of local openfall precipitation ($-$ 1.10‰ to $-$ 0.92‰) are within uncertainty or slightly lower than seawater δ^{26}Mg ($-$ 0.85 $\pm$ 0.07‰). Tabonuco bark (the dominant species in this ecosystem), has δ^{26}Mg = $-$ 0.72‰, within the range of published vegetation values but lighter than

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most plants collected in the field (Schmitt et al., 2012, and references therein). Pore water $\delta^{26}Mg$ in the ridgetop profile (B1S1) shows a clear trend with depth (r = 0.96), increasing from − 0.78‰ at the surface (0.15 m) to − 0.22‰ at 9.3 m depth (Fig. 5). Within this trend there is a heavy excursion from 0.6 to 1.2 m depth, whith $\delta^{26}Mg$ reaching a local maximum of − 0.67‰ at 0.9 m depth (Table 2, Fig. 5). A similar pattern is apparent in the other profiles, and three of them also record a heavy excursion in $\delta^{26}Mg$ at ~ 1 m depth (Fig. 6). These features are present in samples collected both in 2008 and in 2009 (Chapela-Lara et al., 2014; shown for the ridgetop site in Fig. 6).

Magnesium concentrations in the stream during the storm event varied between 10.6 μM L^{-1} and 45.7 μM L^{-1}, similar to values reported by Schellekens et al. (2004) in the neighbouring Bisley 2 catchment during storm flow and baseflow, respectively. The $\delta^{26}Mg$ values ranged from + 0.01‰ to − 0.74‰, lower than the bedrock and the bulk regolith except for the end of the event when the stream returned to a low level stage (Fig. 7). Mg isotope ratios and [Mg] in the stream samples are linearly correlated ($r^2 = 0.98$), with the highest [Mg] and heaviest $\delta^{26}Mg$ values (+ 0.01‰) during the low flow stage and the lowest [Mg] and lightest $\delta^{26}Mg$ (− 0.74‰) during high stage (Fig. 7).

4.3 Mg isotopic composition of the bulk regolith and the exchangeable fraction

The $\delta^{26}Mg$ values of bulk regolith in the ridgetop site show a gradual enrichment in the heavy isotope as weathering proceeds, from values close to the bedrock at the deepest sample ($\delta^{26}Mg = -0.07‰$, Fig. 5) to a maximum of + 0.37‰ at 1.8 m depth (Fig. 5); from 1.8 m to the shallowest sample (0.6 m depth) $\delta^{26}Mg$ decreases.

The $\delta^{26}Mg$ of the exchangeable fraction of the regolith is the least variable of the three pools studied (pore water, exchangeable, bulk), with similar values to the bedrock from 9.3 m up to 6 m depth. However it does show an decreasiong $\delta^{26}Mg$ trend above 3 m depth, reaching $\delta^{26}Mg = -0.47‰$ at the shallowest sample (0.6 m, Fig. 5). The difference in $\delta^{26}Mg$ between the three pools studied increases towards the surface of the profile (Fig. 5). For example, the measured $\delta^{26}Mg_{regolith - pw}$ is + 0.72‰ on average, but as low as + 0.15‰ at 9.7 m depth and as high as + 1.09‰ at 0.6 m depth. Pore

water and the exchangeable fraction have similar $\delta^{26}Mg$ values ($\Delta^{26}Mg_{exch - pw}$ from + 0.07‰ to + 0.37‰, Fig. 5).

4.4 Mg isotopic composition of the bedrock

The Mg isotope composition of the andesitic un-weathered bedrock (− 0.17‰ to − 0.05‰) is within the range of recommended values for intermediate igneous rock standards (Teng et al., 2015). Mg-rich chlorite, the most abundant Mg-bearing phase in the bedrock (20.4 wt%, Buss et al., 2013), has an average $\delta^{26}Mg$ of +0.19 ± 0.20‰ (2sd, n=9) as determined by laser ablation MC-ICP-MS (Fig. 8, Table 3). This is considerably heavier than the value published by Ryu et al. (2011) from mineral separates of granite (− 1.82 ± 0.07‰), or by Pogge von Strandmann et al., 2015, from metamorphic chlorite at the slab-mantle interface (− 1.03 to + 0.02‰), although lighter samples from that study were altered by diffusion. The other Mg-bearing phases present in the rock, pyroxene and amphibole, have average $\delta^{26}Mg$ values of − 0.16 ± 0.24‰ and − 0.33 ± 0.36‰, respectively (Fig. 8, Table 3), similar to published values for mineral separates of Fe-Mg silicates measured after bulk dissolution (hornblende = − 0.32 ± 0.09‰, and biotite = − 0.29 ± 0.08‰, Ryu et al., 2011; olivine= − 0.27 ± 0.07‰, Teng et al., 2015).

Using the abundances and Mg concentrations of chlorite (Buss et al., 2013), pyroxene and amphibole (Table S2), which are the three significant Mg-bearing minerals in the rock, together with their Mg isotope compositions (Table 3), we calculated a bulk rock [Mg] of 4.41 wt.% and an average $\delta^{26}Mg$ of − 0.05‰, in reasonable agreement with the average measured values for the bulk bedrock (3.30 wt% Mg, Buss et al., 2013; $\delta^{26}Mg$ = − 0.10‰, this work).

5. DISCUSSION

5.1 Controls on the Mg and δ^{26}Mg of pore waters

5.1.1 Atmospheric inputs

To estimate the contribution of rain to pore water Mg we applied the common chlorine balance method to the ridgetop site (White et al., 2009; Buss et al., in rev.), using the average [Mg] and [Cl] of pore water (Table S4), and the average [Mg] and [Cl] in openfall from 2006 to 2008. We estimate that rain-sourced Mg constitutes between 71% and 93% of total Mg in pore water, resulting in very low (1.1 to 7.7 μM L^{-1}) rain-corrected Mg concentrations (*Mg**; Fig. 4). The maximum rain input is reached at 1.2 m depth and not in the most surficial samples as we expected. Furthermore, Mg concentrations (either raw or rain-corrected) do not show a clear trend with depth (Fig. 4), as opposed to the expected pattern of predominance of rain at the surface and a gradual increase of weathering inputs towards the base of the profile. No concentration effect of evapotranspiration at the surface of the profile can be appreciated either because of the abundant precipitation throughout the year in this site (Gioda et al., 2013).

In contrast to Mg concentrations, δ^{26}Mg values do show a clear trend with depth (r = + 0.96), with values close to those of rain near the surface and heavier values, close to those of bedrock, at depth (Fig. 5), as has been reported in pore water at other sites (Bolou-Bi et al., 2012; Tipper et al., 2010). However, our pore water data do not plot along a straight line in δ^{26}Mg vs. 1/Mg space (not shown) as would be expected for a two end-member mixing, indicating that a fractionation process is likely contributing to the Mg isotopic ratios of this profile, which is further discussed in Section 5.1.3. The heavy excursion at ~ 1 m depth cannot be explained by a difference in rain inputs either: at this depth samples have the highest rain inputs (Fig. 4), which would shift δ^{26}Mg towards rain-like values (− 0.97‰), the opposite of what we observe (Fig. 5).

Another source of atmospheric Mg input to the catchment could be Saharan dust, which has been found to be a significant source of nutrients to the Luquillo Mountains (e.g., Pett-Ridge et al.,

2009). However, Stallard (2001) did not observe a significant contribution of Mg in the desert-dust component of a 13 year study of precipitation at El Verde (8.2 km from our study site), consistent with our data not showing an enrichment in Mg in pore water near the surface of the regolith (Figs. 2a, 4). The ultimate reason for the lack of dust-derived Mg in rain and pore water may be the fact that Saharan dust that reaches Puerto Rico is composed of relatively insoluble secondary clays (more than 85% illite, kaolinite and montmorillonite; Reid et al., 2003), which are most likely to contribute to the Mg solid load rather than the dissolved load of the catchment as has been observed on the Caribbean island of Bermuda (Herwitz et al., 1996). Indeed, there is an enrichment of Mg in bulk regolith above 1.5 m depth (Figs. 2c, 3a) paired with a shift in $\delta^{26}Mg$ towards silicate-like values (Fig. 5), whereas such features are not apparent in the most surficial pore water samples (Fig. 5). Atmospheric inputs to the bulk regolith are also evidenced by a small increase in the chemical alteration index above 1.2 m depth (Fig. 3b, Table S1), a feature that was also reported by Dosseto et al. (2012) at another ridgetop profile in this catchment.

5.1.2 Vegetation uptake

Because the soil in this site is strongly depleted in Mg, and tropical vegetation tends to have tight nutrient cycles close to the surface, we expected to find a strong fractionation effect of vegetation uptake over surficial pore water $\delta^{26}Mg$. Surprisingly, pore water samples within the rooting zone (0.0 to 0.6 m depth) have $\delta^{26}Mg$ similar to rain within our external uncertainty (0.07‰), with $\Delta^{26}Mg_{pw-rain}$ of $+0.20‰$ on average (Fig. 5, S2), lower than previously published studies that commonly show a difference close to $+0.25‰$ (e.g., Black et al., 2008; Bolou-Bi et al., 2010, 2012; Tipper et al., 2010, 2012;), but that can be as high as $+1.05‰$ (Bolou-Bi et al., 2010). The Tabonuco tree sample has $\delta^{26}Mg = -0.72‰$, very similar to the surface pore water value of $-0.77‰$, which is consistent with a lack of Mg isotope fractionation by plant uptake. However, we recognise that the largest fractionation of Mg isotopes is expected to occur at the root level (Bolou-Bi et al., 2010), which we did not analyse, and to a lesser extent during intra-plant translocation (Black et al., 2008; Bolou-Bi et al., 2010, 2012).

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Therefore, although the small differences in $\delta^{26}Mg$ between pore water, rain and vegetation are suggestive of vegetation uptake having little effect on the isotopic composition of the soil over the pore water residence time in this environment, more extensive vegetation analyses to required.

5.1.3 Fractionating geochemical reactions within the regolith

Our calculations indicate that rain is the main source of Mg to pore water (Fig. 4), but the general trend in $\delta^{26}Mg$ with depth requires dissolution of bedrock (Figs. 5, 6, Section 5.1.1). In addition, the $\delta^{26}Mg$ vs. 1/Mg pattern and the $\delta^{26}Mg$ excursion at ~ 1 m depth (Fig. 5) require a fractionation mechanism. Because the effect of vegetation uptake on pore water $\delta^{26}Mg$ is of subordinate importance below the rooting zone (0.6 m), this fractionation is likely due to geochemical reactions within the regolith. There are no primary Mg-containing minerals left above 8 m depth of the regolith profile (Table S3, Buss et al., in rev.), which limits the plausible geochemical fractionation processes to 1) the precipitation or dissolution of secondary minerals, or 2) the sorption or desorption of Mg onto/from secondary minerals (clays, gibbsite, goethite, or other (hydr)oxides of Fe, Mn or Al).

The higher $\delta^{26}Mg$ of bulk regolith relative to the bedrock and pore water (Fig. 5, S2) is consistent with secondary minerals preferentially incorporating the heavier ^{26}Mg isotope, in agreement with most studies of $\delta^{26}Mg$ in the weathering environment (e.g. Bolou-Bi et al., 2012; Huang et al., 2012; Liu et al., 2014; Teng et al., 2010; Tipper et al., 2010). Furthermore, the lower $\delta^{26}Mg$ of the exchangeable fraction relative to the bulk regolith (Figs. 5, S2) is in agreement with recent experimental results that indicate that Mg adsorbed into interlayer spaces and charged surface sites is relatively enriched in light ^{24}Mg compared to the residual clay (Wimpenny et al., 2014). Nonetheless, the mineralogy of the regolith is dominated by kaolinite and other 1:1 clays (Table 1, S3), which can hold little Mg within its mineral lattice or at exchangeable sites, and we do not find a correlation between clay contents and $\delta^{26}Mg$ in any of the regolith pools studied.

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The bulk regolith $\delta^{26}Mg$ approximately increases as the contents of Fe(III)-(hydr)oxides also increase (r = + 0.62; Fig. 9a), whereas $\delta^{26}Mg$ in the exchangeable fraction decreases (r = − 0.70; Fig. 9b). These opposite trends suggests that the isotopically heavy Mg may preferentially be tightly bound within the Fe(III) − (hydr)oxide grains while isotopically light Mg forms readily exchangeable surface complexes. During periods of reducing conditions, Fe(III)-(hydr)oxides dissolve (Liptzin and Silver, 2009), which would preferentially release ^{26}Mg into the pore water. The coincidence in space of redoximorphic features indicative of temporarily reducing conditions (1.0 to 1.4 m depth; Yi-Balan et al., 2014), an increase in ferrous iron (Liermann et al., 2014), and the heavy excursion in pore water $\delta^{26}Mg$ at ~1 m depth support this explanation.

Another explanation for our observations can be that the Fe from soils in this catchment is composed predominately of short-range-order Fe phases (Peretyazhko and Sposito, 2005), which are subjected to extensive atom exchange and re-crystallisation processes (Tishchenko et al. 2015). These 'ripening' processes are known to expel trace metals from co-precipitated iron phases (e.g. Pedersen et al., 2005; Frierdich et al., 2012) and could be expelling Mg to the more labile surface complexes as crystallinity increases, as suggested by a general increase in exchangeable Mg as total Fe increases (r = + 0.60; Fig. 9c) and crystalline Fe(III)−(hydr)oxides decrease (r = − 0.72; Fig. 9d). This combined process would preferentially release the heavy isotope, as suggested by the inverse correlation between Fe(III)−(hydr)oxides and $\delta^{26}Mg$ in the exchangeable fraction (Fig. 9b). This process could also account for the heavy excursion in pore water $\delta^{26}Mg$ at ~ 1 m depth, because oscillating redox conditions have been shown to enhance the crystallisation of Fe(III)-(hydr)oxides phases (Thompson et al., 2009).

Microbial metabolism might be yet another mechanism for Mg isotope fractionation within the regolith, as Mg is the most common divalent metal in living cells (e. g. Fagerbakke et al., 1999; Heldal et al., 2012), and the fractionation of Mg isotopes by microbial weathering has been demonstrated for forsterite dissolution (Oelkers et al., 2015), although other studies report negligible fractionation during Mg uptake by cyanobacteria (Mavromatis et al., 2012; Shirikova et al., 2013). In

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our regolith the abundance of microbial cells (Liermann et al., 2014) is correlated with $\delta^{26}Mg$ in pore water (r = − 0.70; Fig. 9f), suggesting bacteria might be preferentially taking up the heavy isotope. If this were the case, we can speculate that the fluctuating redox conditions from 1.0 to 1.4 m depth may cause periodic die-offs of microbial populations, releasing heavy ^{26}Mg into the pore water, which is consistent with a sharp decrease in cell numbers at 1.1 m depth (Liermann et al., 2014) and with the heavy anomaly in pore water $\delta^{26}Mg$ (Fig. 5).

5.1.4 Topography

Pore water $\delta^{26}Mg$ increases with depth at all four sites and the heavy excursion at ~1 m depth is present in three of them (Fig. 6), indicating that the controls on the pore water $\delta^{26}Mg$ discussed in the previous sections are relatively independent of topographic position. Nonetheless, sites on the hillslopes (B1S2, B1S3) may be expected to show differences in Mg dynamics as compared with the ridgetop site (B1S1) due to, for example, slopes having less infiltration of rain water and less water-rock contact time, exposure of fresher (more Mg-rich) material by erosion, or less Mg input from decomposition of accumulated litter. Likewise, the Mg isotopic composition of the valley site (B1S4) could be further complicated by litter accumulation and long reducing periods when flooded by the stream. Indeed, the slope and the valley sites have higher $\delta^{26}Mg$ values and higher Mg concentrations than the ridgetop site (Fig. 6): whereas pore water at B1S2 has $\delta^{26}Mg$ = − 0.79‰, similar to the ridgetop site (− 0.78‰), $\delta^{26}Mg$ at the lower slope (B1S3) and valley (B1S4) sites are − 0.72‰ and − 0.59‰, respectively. The relative enrichment in both total Mg and ^{26}Mg at these sites as compared to the ridgetop is consistent with larger weathering inputs from their less weathered regolith (lower WIP, Fig. 3b, Table S1) and shallower bedrock (Fig. 6).

5.2 Controls on the Mg and $\delta^{26}Mg$ of the stream

5.2.1 Mixing, fractionation and the source of baseflow Mg

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Magnesium in the stream shows a typical dilution behavior, with the highest concentration during baseflow, becoming progressively lower as the storm proceeds. Mg isotope ratios seem to follow a similar dilution trend, with the heaviest values during baseflow (Fig. 7), so we expected the Mg isotopic composition of the stream to reflect mixing between baseflow Mg sources (deep pore water, ground water) and storm water sources (direct rainfall, runoff, and shallow pore water). However, Mg concentration and $\delta^{26}Mg$ in the stream are strongly, linearly correlated ($r^2 = 0.98$) during the entire storm event (Figs. 10, 11), not following the expected pattern of binary mixing that would produce a hyperbola in a $\delta^{26}Mg$ vs. [Mg] space (Langmuir et al., 1987). Likewise, there is a good correlation between $\delta^{26}Mg$ and ln[Mg] ($r^2 = 0.92$, not shown). These clear $\delta^{26}Mg - Mg$ trends suggest that, although dilution by storm sources may be controlling the stream [Mg] during the storm event, it is isotopic fractionation that is driving the $\delta^{26}Mg$ signature, in agreement with previous works that show fractionation due to weathering-related processes is the predominant factor controlling $\delta^{26}Mg$ in small rivers (Tipper et al., 2006, 2008).

Apart from following a linear trend in a $\delta^{26}Mg$ vs Mg space, to account for the observed data any fractionation processes (± mixing with storm water sources) must fulfil two conditions: 1) start from an initial reservoir with an isotopic composition that is at least as enriched in ^{26}Mg as the baseflow ($\delta^{26}Mg = + 0.01‰$); and 2) be capable of modifying the stream $\delta^{26}Mg - Mg$ at the time-scale of the duration of the storm event (~ 6 h; Table 2).

Baseflow source

Our findings support a source of water to the stream deeper than any of the sampled pore waters, which have maximum $\delta^{26}Mg$ value of $- 0.22‰$ (Table 2; Figs. 6, S2). This implies that there are sources other than rain and pore water contributing to the Mg budget of the stream, in agreement with indirect evidence form previous studies at the Bisley catchments using S isotopes.

Among our sampled Mg-bearing reservoirs only chlorite (Fig. 8) or the bulk regolith above 8.2 m depth (Fig. 5) have the necessary heavy Mg isotope composition, but the dissolution rates of these silicates, in the order of kyrs (e.g. White and Buss, xxx), would make them irrelevant for a short storm event. Nevertheless, baseflow in this catchment is sustained throughout the whole year, thus reflecting water delivered through deeper pathways with residence times larger than the fast-flow pathways that predominate during storm events. Chlorite contains ~22 times more Mg than the bulk regolith in molar proportions, is the most abundant Mg-bearing phase in the bedrock (Tables 1, S2), and is more susceptible to dissolution than the kaolinite-rich, Mg-poor regolith at Earth's surface conditions. Therefore, chlorite is the most likely phase determining the isotopically heavy Mg signature of the stream during baseflow.

Fractionation processes

Rayleigh fractionation models are widely used to describe stable isotope ratios in rivers and calculate fractionation factors associated with weathering reactions perhaps add some refs here?. Their general assumption is that the element of interest is being leached out from the catchment, with a preferential loss of one of its isotopes. The best known example of a Rayleigh-like system in weathering is the dissolution of a mineral without precipitation of a secondary phase, which we develop in the supplementary material, and summarise in Figure 10a. However, while we argue chlorite dissolution is the best candidate for the initial reservoir of any fractionation or mixing process, to sustain that chlorite dissolution can control the Mg and δ^{26}Mg of the stream in the hourly time scale of the storm event is problematic.

Alternatively, the linear trend on δ^{26}Mg vs [Mg] in the stream (Figs. 10, 11) can be modelled using a mass balance approach (Bouchez et al., 2013; Dellinger et al., 2015), considering the small catchment as an open, flow-through system in which Mg is released to solution by one reaction while it is removed by another (e. g., incorporation into secondary minerals). Whereas chlorite dissolution and Mg uptake by secondary mineral precipitation are both unlikely to control the stream chemistry at

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the time-scale of a single storm event, ion exchange and sorption-desorption have reactions rates rapid enough to occur even over 30 minute time-scales and, in fact, several researchers have proposed ion-exchange is a first order control on stream chemistry (e.g Berner et al., 1998; Clow and Mast, 2010; Cerling et al., 1989). Therefore, although we do not have enough evidence to conclusively resolve if sorption or ion exchange are the predominant way of Mg isotope fractionation, we contend these are the only plausible mechanisms capable of fractionating Mg isotopes at the required hourly time-scale. The Bisley streams are usually poor in suspended sediments, but they increase to measurable concentrations during storm events (XX to YYY%, refs.) providing a likely substrate for temporary Mg sorption and Mg isotopic fractionation in the stream.

At steady state, all Mg inputs and outputs, as well as their isotopic compositions, are balanced and the Mg isotope composition of the stream can be modelled as:

$$\delta^{26}Mg_{stream} = \delta^{26}Mg_i - \Delta_{i,s}\left(1 - f_{Mg}\right) \tag{3}$$

where all the variables are the same as in Eq. (3). Our data are well explain by this model (Fig. 10b), with separation factors between 0.95 and 1.35, and the best fit for $\Delta_{i,s} = +1.15$. According to this model, the Mg fraction of the heavy source (f_{Mg}) represents between 80% (baseflow) and 20% (peak of the storm) of the dissolved Mg in the stream. Substituting f_{Mg} into Eq. (3) we estimate a separation factor of $\Delta_{i,s} = +1.15$‰ (Fig. 10b), larger than predicted by the Rayleigh fractionation model ($\Delta_{i,s} = +0.55$ to $+0.95$‰, Fig. 10a). The $\delta^{26}Mg$ of deep pore water falls within the same fractionation line as the stream (Fig. 10b), suggesting both have inputs from the chlorite weathering.

5.2.2 Flow paths and sources of Mg to the stream

Possible sources of water to the stream are direct rainfall, overland flow, throughflow within the regolith, flow at the regolith-bedrock interface and groundwater. As was discussed in the previous section, the $\delta^{26}Mg$ of baseflow reflects the input of sources deeper than any of our sampled pore water, likely flow through bedrock fractures or at the bedrock-regolith interface. Nonetheless, pore

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water may influence the δ^{26}Mg signature of the stream during other stages of storm events, as has been found from water composition mixing models and hydrometric studies (Schellekens et al., 2004). The δ^{26}Mg signature of this contribution would depend on the depth of the pathways followed by water before reaching the stream, as indicated by our data along the topographic profile, which show differing δ^{26}Mg in pore water over a relatively short distance (Fig. 6, Section 5.4.1). To test this idea we performed a simple mass balance, assuming that our pore water profiles are representative of the pore water composition by landscape unit in the whole catchment (B1S1= ridges, B1S2 = slopes and B1S4 = valleys):

$$\delta^{26}Mg_{PW} = f_r \cdot \delta^{26}Mg_r + f_s \cdot \delta^{26}Mg_s + f_v \cdot \delta^{26}Mg_v \qquad (6)$$

where δ^{26}Mg$_{PW}$ is the overall Mg isotopic composition of pore water in the catchment, and *fs, fr, fv* are the fraction of Mg that comes from pore water in the slopes, the ridges, and valleys, respectively. The Bisley 1 catchment comprises 55% slopes, 23% ridges and 22% valleys (map not shown), from which we can estimate the pore water fractions coming from each landscape unit as:

$$f_i = \frac{A_i \cdot Mg_i \cdot z_i \cdot \theta_i}{(A_r \cdot Mg_r \cdot z_r \cdot \theta_r) + (A_s \cdot Mg_s \cdot z_s \cdot \theta_s) + (A_v \cdot Mg_v \cdot z_v \cdot \theta_v)} \qquad (7)$$

where f_i is the fraction of Mg coming from pore water in each unit, θ_i is the water content of the regolith, z_i is the depth of the regolith, Mg_i is a depth-weighted Mg concentration of pore water, and A_i is the area fraction of the catchment covered by each unit (Table 4) for $i =$ ridges (r), slopes (s) or valleys (v). We assume that all the regolith in the catchment has the same water content at any given time, 28%, which is the mean value of the published values for this site (Buss et al., in rev.; Liermann et al., 2014).

Most of the flow during storm events in the Bisley catchments has been inferred to occur through macropores in the top 20 cm of the regolith (Schellekens, 2004; McDowell, 1992), which we will call subsurface shallow flow (SSF). Water following this pathway is the main contributor to the peaks of the storm in terms of chemical composition (Schellekens et al., 2004), so we used the mass balance Eqs. (7) and (8) to investigate if this is the case also for Mg isotopes and obtained [Mg] =

34.8 μM L^{-1} and δ^{26}Mg = − 0.70‰ (Table 4), similar to the δ^{26}Mg of the stream at the peaks of the storm (− 0.74‰) but with a Mg concentration closer to baseflow (45.8 μM L^{-1}). This apparent contradiction is probably due to the fact that riparian zones in this site are often saturated (Stallard, 2012). Indeed, if we exclude the valley site (B1S4) from the calculations, we obtain [Mg] = 21.6 μM L^{-1} and δ^{26}Mg$_{SSF}$= − 0.78‰, within error of the δ^{26}Mg of the stream at the peak of the storm and a more reasonable Mg concentration, suggesting that SSF possibly bypasses pore water in the valleys, which have the heaviest δ^{26}Mg at the surface samples (− 0.55‰) of all sites. Field observations support this argument, as quick flow springs form gullies at slope positions before reaching the valleys (e.g., Schellekens et al., 2004).

Using the same equations for pore water throughout the whole regolith, without the assumption of a constant depth of water flow, we obtain a similar [Mg] than for SSF but higher δ^{26}Mg (− 0.44‰; Table 4). Table 4 also illustrates that whereas in terms of area the slopes are by far the predominant physiographic unit in the catchment, in terms of Mg fractions ridges are more important due to their deeper regolith and thus higher capacity to store water. Figure 11 shows that if pore water Mg from the whole catchment became well mixed before reaching the stream, it would contribute to the stream during the intermediate stages of the storm; if it remained differentiated by following different pathways to the stream, the ridges would contribute during the intermediate stages and the slopes during the high stages of the storm. The valleys does not seem to contribute to the stream at any stage (Fig. 11).

5.3 Mg mass balance of the catchment and weathering rates

Our estimation of the size of the different Mg pools and fluxes in this catchment are summarised in Table 5. Most of them are in agreement with previously published values (McDowell, 1998; Porder et al., 2015), except the regolith pools, which are somewhat higher due to the fact that other studies only

consider the top meter whereas we considered the entire augerable regolith. Among the relatively mobile pools, the exchangeable fraction is by far the largest, followed by the vegetation (Table 5).

Export of nutrients from watersheds as solid, rather than dissolved, phase may represent an additional source or sink of Mg and fractionate isotopes during ion exchange with the dissolved load in a stream (e.g. Dellinger et al., 2014; Tipper et al., 2012b; Bouchez et al., 2013). We did not sample such solid phase components (suspended solids, coarse particulate organic matter, and bed sediment), in our study, but the suspended sediment concentrations are very low in the volcaniclastic watersheds of the LCZO, and most dissolved constituents including Mg are derived from bedrock weathering or atmospheric deposition (Stallard and Murphy, 2014). The flux of coarse particulate organic matter (i.e., leaves, wood and other plant material) represents only 0.00242 kg ha^{-1} yr^{-1} of [Mg] flux out of the Bisley catchments (Heartsill Scalley et al., 2012), which is negligible compared to the 60 kg ha^{-1} yr^{-1} solute [Mg] flux (McDowell, 1998). Streambed sediments are also unlikely to contribute significant Mg, as the streams in the volcaniclastic catchments of the LCZO are characteristically lined with bedrock, boulders or cobbles, with little bed sediment (Murphy et al., 2012). Finally, ionic exchange in the stream is unlikely to be an important process for Mg fractionation because the sediments are dominated by 1:1 type clays (Buss and White 2012; Dosseto et al., 2012), which have very low cation exchange capacity.

After all these considerations, a mass balance for Mg in the whole catchment, assuming there are no water outputs other than the stream, can be written as:

$$Q_p + Q_L + Q_{BR} + Q_{dust} = Q_v + Q \tag{8}$$

where Q_p is bulk precipitation, Q_L is litter decomposition, Q_{BR} is the dissolution of the bedrock, Q_{dust} is the dust solid load not included in the openfall samples, Q_v is uptake by vegetation and Q is the stream export. We consider litter decomposition and vegetation uptake to be in steady state, and thus Eq. (8) is simplified to:

$$Q_p + Q_{BR} + Q_{dust} = Q \tag{9}$$

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Substituting the values of Q_p and Q from Table 5 into Eq. (9) and solving for Q_{BR}, we can estimate a flux of 35 kg ha^{-1} yr^{-1} (or 1440 mol ha^{-1} yr^{-1}) of Mg from bedrock dissolution, making it the largest input to the stream (Table 5) as has been found in larger streams within the LZCO (Stallard and Murphy, 2012, and references therein). This result highlights the importance of deeper, usually un-sampled, critical zone pathways for Mg fluxes in areas covered by thick, highly leached regolith.

The fact that the [Mg] in pore water and the exchangeable fraction within the rooting zone are dominated by rain inputs (Section 5.1), whereas the [Mg] in the stream is dominated by bedrock dissolution coming from deeper pathways (Section 5.2), is consistent with a decoupling between the water that is taken up by the vegetation, and the water that reaches the streams (McDonell, 2014; Evaristo et al. 2015), although the source of Mg seems to be even deeper than suggested by $\delta^{18}O$ and δ^2H studies (Evaristo et al., 2016).

Using the abundance of chlorite in the bedrock (Buss et al., 2013), its Mg content (Table S2), and assuming all Mg-bearing minerals are dissolving either congruently or have non-Mg bearing clays as the product (e.g. kaolinite), we can use the bedrock dissolution Mg flux (Table 5) to estimate that chlorite dissolves roughly at 19 kg ha^{-1} yr^{-1} (763 mol ha^{-1} yr^{-1}) in this catchment. This rate is an order of magnitude faster than the highest published watershed-scale dissolution rates for other ferromagnesian silicates (biotite = 26 mol ha^{-1} yr^{-1}, Mast et al., 1990; hornblende = 24 mol ha^{-1} yr^{-1}, Williams et al., 1993), illustrating how the fast weathering rates of tropical catchments as compared with temperate ones (e.g. Dosseto et al., 2012) leads to its strong influence on the Mg fluxes to the streams and to the oceans.

5.4 Implications for the Mg isotope exports from tropical catchments

Our results indicate that in areas covered by thick, highly leached regolith, the flux of Mg through deeper pathways in the critical zone could be comparatively more important than through shallower pathways, even if they are minor in terms of water fluxes. However, the differences in pore water

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$\delta^{26}Mg$ along the slope transect show that there is also a differentiation related to the degree of weathering, even within the same catchment (Fig. 6). These observations and the few studies other studies including pore water, bulk regolith and stream $\delta^{26}Mg$ data in silicate catchments, indicate that the Mg isotope composition of pore water exported to the streams will evolve over kyr time scales, from the stage when rock has just been exposed to chemical weathering (Tipper et al., 2012), and fast-reacting minerals are still available (Trostle et al., 2014; Dessert et al., 2015), to the extreme weathering stage where atmospheric inputs, changes in redox conditions within the regolith, and hydrological factors become comparatively more important (e.g., our B1S1 site; Dessert et al., 2015; Liu et al., 2014). We clearly need more studies to refine our interpretation, especially at intermediate weathering stages, but rough patterns can be already be noted in Figure 12. For example, the Mg isotopic composition of streams and rivers remains basically constant above ~75% chemical depletion (CIA) of the regolith, despite continuing increase in the regolith $\delta^{26}Mg$ values (Fig.12).

Acknowledging that weathering stages can coexist within the same catchment and are not necessarily exclusive, we put forward the following conceptual model to summarise the evolution of the Mg isotopic composition of silicate catchments (Fig. 12):

1) Incipient weathering stage (fractured bedrock or thin, young soils): The regolith has a Mg isotopic composition very similar to the bedrock. Dissolution of primary minerals is the main control on the $\delta^{26}Mg$ signature of the streams, which thus can be heavier or lighter than the bedrock.

2) Advanced weathering stage (bedrock-saprolite interfaces on fully developed profiles): Regolith mineralogy is dominated by 2:1 secondary clays, oxides, and some remaining primary minerals, and has Mg isotope ratios heavier than the bedrock. The streams have lower $\delta^{26}Mg$ than the bedrock they drain due to secondary minerals preferentially holding ^{26}Mg, but they can reflect the dissolution of primary minerals during baseflow.

3) Extreme weathering stage (deep, highly weathered regolith): The regolith has a very low cation exchange capacity (CEC), because it is comprised mostly of 1:1 clays and Fe, Mn, Al

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(hydr)oxides below their point of zero charge. As a result, the bulk regolith has a high $\delta^{26}Mg$, but little influence on the $\delta^{26}Mg$ of the streams. The $\delta^{26}Mg$ signature of the streams is thus very similar to the previous stage, with a $\delta^{26}Mg$ signature similar or slightly higher than the bedrock during baseflow and $\delta^{26}Mg$ fluctuations reflecting mostly varying rain inputs.

Ultimately, the $\delta^{26}Mg$ of the streams will depend on which parts of the bedrock and the regolith interact with water, which in turn depends on the physical, rather than geochemical, properties of the catchment. Our study thus highlights the need for a good understanding of the local geo-hydrological setting to narrow the geochemical hypotheses, while also illustrates how geochemical observations ($\delta^{26}Mg$ in this case) can in turn give insight into the water pathways and on the subsurface architecture of the critical zone.

6. CONCLUSIONS

To better understand the effects of critical zone processes on Mg concentrations and the Mg isotopic signature of streams in tropical catchments, we studied a well constrained, highly weathered volcaniclastic catchment in the Luquillo Critical Zone Observatory, Puerto Rico. As hypothesized, the general depth trend of pore water $\delta^{26}Mg$ is consistent with rain inputs at the surface and bedrock weathering at the base of the profile, despite the fact that it is not clearly expressed in rain-corrected Mg concentrations. Contrary to what we expected, most Mg in pore water is sourced from rain, highlighting the importance of atmospheric inputs to nutrient budgets in tropical sites. However, binary mixing between rainfall and weathering end-members is insufficient to explain the relationship between [Mg] and $\delta^{26}Mg$ in pore waters, indicating that a fractionation process is also taking place, interpreted to be the preferential retention of heavy ^{26}Mg in secondary minerals. A separate fractionation process is evidenced by a ~ 0.11‰ shift in $\delta^{26}Mg$ towards heavier values at ~ 1 m depth, coinciding with redoximorphic features and a correlation between [Mg] and $\delta^{26}Mg$ in the bulk regolith and the exchangeable fraction with Fe(III)-(hydr)oxide contents; we interpret this isotopic

excursion to represent the release of isotopically heavy Mg from Fe(III)-(hydr)oxides during periodic reducing conditions.

Given that the soil is strongly depleted in Mg, and that tropical vegetation tends to have tight nutrient cycles close to the surface, another surprising result of our study is that the effect of vegetation uptake is of subordinate importance for the surficial pore water δ^{26}Mg. Instead, we conclude that rain water infiltration and geochemical reactions within the regolith control the short-term Mg isotope behaviour within the regolith.

The relative importance of the Mg-controlling processes in shallow samples differs over the time scales studied. Whereas [Mg] and δ^{26}Mg data in pore water and the exchangeable fraction indicate that rain is the predominant source of Mg in the surface up to approximately decadal time scales, at the longer time scale represented by the bulk regolith the dominant Mg source to the shallow critical zone is dust. Bedrock weathering is the predominant source of Mg at the deeper samples over all the time scales.

Pore water depth profiles along a topo-sequence show the same trend from lower to higher δ^{26}Mg and [Mg] contents with increasing depth, but shallower, less-weathered sites have higher [Mg] and δ^{26}Mg than the ridgetop site. We used these values to estimate the composition of pore water from the whole catchment exported to the stream under varying flow path scenarios. These calculations suggest that flow paths largely bypass the pore water in the valley regolith, whereas shallow flow may contribute to the stream during the peaks of storm events, and pore water from the ridges and the slopes may contribute to the stream at intermediate and high stages of storm events, respectively.

During baseflow, the stream is isotopically heavier than any of the pore water sampled or the bedrock, indicating that there are sources other than rain, bulk bedrock dissolution and pore water contributing to the Mg budget of the stream. *In situ* analysis of the δ^{26}Mg of the bedrock minerals allowed us to identify chlorite dissolution as the most plausible isotopically heavy source of Mg to the stream. This calls attention to the need for a better understanding of deep critical zone processes,

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which are comparatively more important for watershed chemical budgets when surficial pools are exhausted by extreme weathering.

Altogether, our study highlights the importance of atmospheric inputs of nutrients to tropical ecosystems (rain on the short time scale and dust on the longer time scale), whereas the dissolution of primary minerals is the most relevant factor for the Mg fluxes and the Mg isotope signature of the streams, even at the advanced weathering stage of this catchment.

Acknowledgments

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