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## Controls on the Mg cycle in the tropics: insights from a case study at the Luquillo Critical Zone Observatory

María Chapela Lara<sup>a,\*</sup>, Heather L. Buss<sup>a</sup>, Philip A.E. Pogge von Strandmann<sup>b</sup>, Céline Dessert<sup>c</sup>, Jérôme Gaillardet<sup>c</sup>

<sup>a</sup>*Bristol Isotope Group, School of Earth Sciences, University of Bristol, Bristol BS8 1RJ, UK*

<sup>b</sup>*Institute of Earth and Planetary Sciences, University College London and Birkbeck, University of London, London WC1E 6BT, UK*

<sup>c</sup>*Institut de Physique du Globe de Paris, 75252 Paris Cedex 05 France*

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### Abstract

To better constrain the mechanisms controlling short-term Mg dynamics in the tropics, we sampled critical zone compartments of a catchment covered by thick, highly weathered regolith. Our Mg and  $\delta^{26}\text{Mg}$  data indicate that rain is a main source of Mg throughout the regolith, and we do not observe Mg isotope offsets in vegetation/surficial pore water. In addition to rain and weathering inputs, a heavy isotope excursion at ~1 m depth indicates a fractionation process, likely sorption-desorption or clay dissolution. Stream water  $\delta^{26}\text{Mg}$  reflects inputs from rain and a heavy source, likely differential weathering along deep bedrock fractures.

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### 1. Introduction

The dual role of Mg in the Earth's surface, both as a nutrient and as a constituent of rocks, makes it a promising tracer of geochemical and biological feedbacks in the critical zone. However, most studies have taken place in temperate sites, despite the fact that the tropics are proportionally more important in terms of weathering inputs to the oceans, biodiversity and climate change sensitivity<sup>1,2</sup>. Here we examine controls on the short-term Mg dynamics of a small, andesitic volcanoclastic catchment (Bisley 1) that is part of the Luquillo Critical Zone Observatory (LCZO), in the mountains of Puerto Rico.

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\* Corresponding author. Tel.: +44 117954 5432  
E-mail address: [M.ChapelaLara@bristol.ac.uk](mailto:M.ChapelaLara@bristol.ac.uk)

Our approach was to analyse the elemental and Mg isotopic composition of critical zone compartments, focusing first on a 9.7 m deep regolith on the top of a ridge, where 1D vertical water movement can be assumed, and then on three other sites along a topo-sequence towards the Bisley 1 stream (Fig.1a). Each site is equipped with nested suction lysimeters at different depths, from which we collected pore water on two occasions (January 2008 and November 2009). We complement these data with analyses of the dominant tree-type in the ecosystem (Tabonuco, *Dacryodes excelsa*), bedrock at a drilled borehole<sup>3</sup>, openfall precipitation, and stream water at base flow and during a storm event (6 July 2011, Fig. 2a). Prior to Mg isotope measurements we processed the samples through cation exchange resin to obtain a pure Mg solution<sup>4</sup>. Values are expressed using the usual delta notation in permil, as deviations from the DSM3 standard<sup>5</sup>.

## 2. Results

This regolith is acidic (pH 3 to 4) and highly leached, containing only kaolinite (50% to 82%), microcrystalline quartz (12% to 29%) and oxides (2.5% to 7%) above 8 m depth in the deepest site (Site 1, Fig. 1a). Accumulations (mm's thick) of Mn-oxides are occasionally visible. Although the weathering profile is fully developed (most cations are totally lost), a number of elements are locally enriched at ~1 m depth (e.g. Fe, Ni, Cr and P), where there is also a 10% decrease in kaolinite content and a 20% increase in bulk density.

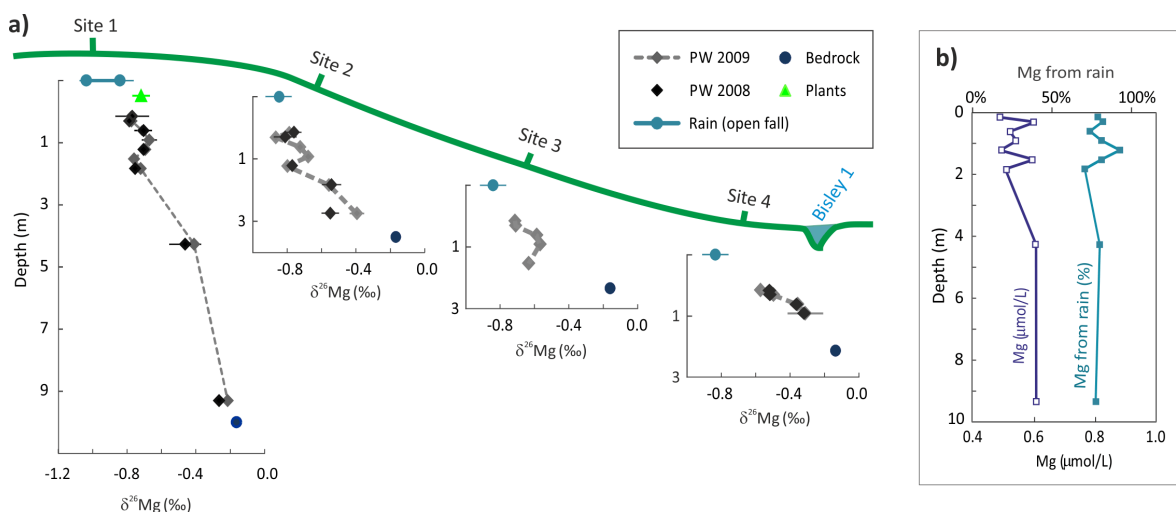


Fig. 1. a)  $\delta^{26}\text{Mg}$  in pore water (PW) in sites along a topo-sequence in the Bisley 1 catchment (topography not to scale). Error bars are 2SD and the Y axes are depth in meters.  $\delta^{26}\text{Mg}$  values of bedrock, vegetation and rain are shown for reference (depth arbitrary). b) Pore water contains up to about 0.6  $\mu\text{M}$  Mg of which 71 to 93% is attributed to rain input at Site 1.

Mg isotope data are summarized in Figs. 1 and 2. Tabonuco bark  $\delta^{26}\text{Mg}$  (-0.72‰) falls within the range of published vegetation values, but is lighter than most field samples<sup>6-8</sup>. Precipitation (openfall) values (-1.04‰ and -0.89‰) are slightly lighter than sea water. The Mg isotope composition of the un-weathered bedrock (-0.17‰) is within range of published data for silicate rocks<sup>8</sup>. Pore water  $\delta^{26}\text{Mg}$  in the deepest site increases with depth, from -0.78‰ at 0.15 m to -0.22‰ at 9.3 m (Site 1, Fig.1a). Within this trend there is a heavy excursion at 0.9 m depth, where  $\delta^{26}\text{Mg}=-0.67‰$ . A similar trend is seen in the other sites along the slope, except in the riparian zone, which does not show the heavy excursion (Site 4, Fig.1a).

The Mg concentrations and  $\delta^{26}\text{Mg}$  during a storm event are linearly correlated in stream water ( $r^2=0.98$ , Fig 2b). The highest Mg concentrations (45.7  $\mu\text{M}$ ) and highest  $\delta^{26}\text{Mg}$  values (0.01‰) are recorded during the low water stages, and the lowest Mg contents (10.6  $\mu\text{M}$ ) and lowest  $\delta^{26}\text{Mg}$  (-0.71‰) at high stages (Fig 2a).

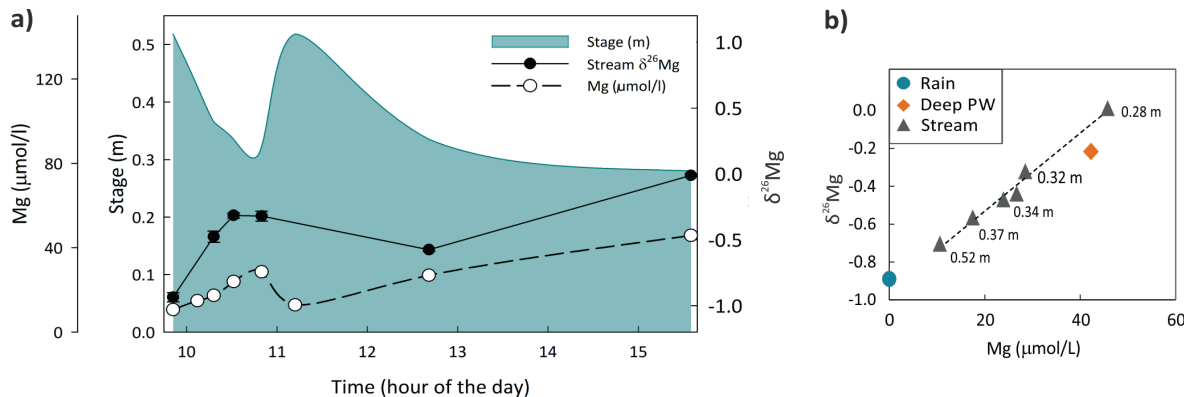


Fig. 2. a) Magnesium composition of the Bisley 1 stream during a storm event, represented by the water level (stage). Error bars are 2SD. b)  $[Mg]$  vs  $\delta^{26}Mg$  plot of the same storm event (stage given next to symbols), suggesting there are Mg inputs from sources other than rain and pore water (PW) to the stream. Deep pore water (PW) is from Site 1.

### 3. Discussion

#### 3.1 Controls on Mg dynamics in deep regolith

An important effect of vegetation on solution  $\delta^{26}Mg$  has been reported from field and laboratory studies, with plants preferentially taking up the heavier isotope<sup>9</sup>, but we do not find values distinct from rain within the rooting zone in Site 1 (Fig. 1a). This may be due to recycling of plant litter Mg, counteracting isotope fractionation during plant growth, or due to surface waters being constantly replenished by rainfall. The possible role of dust inputs to surface pore waters remains to be assessed, but low  $\delta^{26}Mg$  values at shallow samples suggest it is relatively low (assuming dust with a silicate origin). This feature is apparent in data from both sampling dates, as is the trend from light to heavy Mg isotope ratios with increasing depth, suggesting that the mechanisms controlling Mg are the same over annual time scales (Fig. 1a).

The general pattern in  $\delta^{26}Mg$  is consistent with predominance of rain at the surface and bedrock weathering at the base of the profile (Fig. 1a). However, we calculated the fraction of Mg sourced from rain ( $([Mg]/[Cl]_{rain})(Cl_{pw})/Mg_{pw}$ )<sup>9</sup> and found that it accounts for 71% to 93% of the Mg throughout the profile, and reaches its maximum at ~1 m depth (Fig. 1b). This is very close in space to the  $\delta^{26}Mg$  anomaly, suggesting that a fractionation process, rather than a change in the proportion of mixing end-members, is involved in this heavy excursion (because rainfall is isotopically light). There are no primary Mg-containing minerals left above 8 m depth, thus constraining the possibilities to one or a combination of two mechanisms: 1) preferential sorption of  $^{24}Mg$  or desorption of  $^{26}Mg$  into/from secondary minerals, suggested by the heavy excursion in Mg isotope ratios coinciding in depth with a change in redox indicators (data not shown); or 2) dissolution of  $^{26}Mg$ -enriched clays (here, impure kaolinite and/or minor illite), indicated by a lower clay abundance at ~1 m depth.

#### 3.2 Are these controls the same at the catchment level?

The sites on the hillslope may be expected to show differences in Mg dynamics as compared with the ridge top site due to lateral flow, erosion, less litter accumulation or deeper rooting. However, the  $\delta^{26}Mg$  pattern is broadly the same for all of the sites (Fig. 1a), including the heavy excursion at ~1 m depth, indicating that the controls discussed in the previous section are somewhat independent of topographic position. Although the depth profiles are similar along the topo-sequence,  $\delta^{26}Mg$  in the shallow samples is higher down slope. Whereas pore water at 0.15 m depth in Site 2 has  $\delta^{26}Mg = -0.79\%$ , which is very similar to the ridge top (Site 1 =  $-0.78\%$  at 0.15 m),  $\delta^{26}Mg$  at that depth in Site 3 =  $-0.72\%$  and at Site 4 =  $-0.59\%$ , possibly because these profiles are shallower and receive a larger proportion of dissolved Mg from weathering relative to rain. Site 4 is the shallowest and may not have weathered enough to develop the heavy anomaly; its Mg inputs could be further complicated by its location on the floodplain.

As expected, rain input dominates stream water  $\delta^{26}\text{Mg}$  during the peaks of the storm, with successively larger amounts of a  $^{26}\text{Mg}$ -rich component as the storm approaches base flow (Fig. 2a). This component, that must be heavier than bulk bedrock and pore water (Fig. 2b), could be the dissolution of  $^{26}\text{Mg}$  rich minerals by water flowing through deep paths within fractured bedrock<sup>3,10</sup> upstream of the sampling site. This calls attention to the need for a better understanding of deep critical zone processes, which are important for nutrient budgets when surficial pools are exhausted by extreme weathering.

#### 4. Conclusions

Mg and  $\delta^{26}\text{Mg}$  data from a deep, highly weathered regolith indicate that most of this element comes from rain, even at the regolith-bedrock interface, highlighting the importance of atmospheric inputs to nutrient budgets in tropical sites. The rapid replenishment of surface pore water may also result in a decoupling from the effects of vegetation, as no Mg isotope fractionation between vegetation and surface waters is observed. In addition to isotopic mixing of rain and bedrock inputs, at ~1 m depth, a secondary weathering-related fractionation process produces a heavy excursion in Mg isotope ratios, likely due to Mg sorption-desorption from secondary minerals or clay dissolution. These features are conspicuous along a topo-sequence, suggesting that the same controls on Mg function at the catchment level, despite important differences in topography and regolith depth. The stream Mg composition reflects dominant inputs from rain and an unknown heavy component, likely sourced from deep fracture zones.

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