Magnesium isotope fractionation during shale weathering in the Shale Hills Critical Zone

Observatory: Accumulation of light Mg isotopes in soils by clay mineral transformation

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Abstract

Magnesium isotopic ratios have been used as a natural tracer to study weathering processes and biogeochemical pathways in surficial environments, but few have focused on the mechanisms that control Mg isotope fractionation during shale weathering. In this study we focus on understanding Mg isotope fractionation in the Shale Hills catchment in central Pennsylvania. Mg isotope ratios were measured systematically in weathering products, along geochemical pathways of Mg during shale weathering: from bedrock to soils and soil pore water on a planar hillslope, and to sediments, stream water, groundwater on a valley floor. Significant variations of Mg isotopic values were observed: $\delta^{26}\text{Mg}$ values (-0.6‰ to -0.1‰) of stream and soil pore waters are about ~ 0.5 ‰ to 1 ‰ lighter than the shale bedrock ($\delta^{26}\text{Mg}$ values of +0.4‰), consistent with previous observations that lighter Mg isotopes are preferentially released to water during silicate weathering. Dissolution of the carbonate mineral ankerite, depleted in the shallow soils but present in bedrock at greater depths, produced higher Mg^{2+} concentrations but lower $\delta^{26}\text{Mg}$ values (-1.1‰) in groundwater, ~ 1.5 ‰ lighter than the bedrock. $\delta^{26}\text{Mg}$ values (+0.2‰ to +0.4‰) of soil samples on the planar hillslope are either similar or up to ~0.2‰ lighter than the bedrock. Hence a heavy Mg isotope reservoir -- complementary to the lighter Mg isotopes in soil pore water and stream water -- is missing from the residual soils on the hillslope. In addition, soil samples show a slight but systematic decreasing trend in $\delta^{26}\text{Mg}$ values with increasing weathering duration toward the surface. We suggest that the accumulation of light Mg isotopes in surface soils at Shale Hills is due to a combined

effect of i) sequestration of isotopically light Mg from soil water during clay dissolution -precipitation reactions; and ii) loss of isotopically heavy particulate Mg in micron-sized particles from the hillslope as suspended sediments. This latter mechanism is somewhat surprising in that most researchers do not consider physical removal of particles to be a likely mechanism of isotopic fractionation. Stream sediments ($\delta^{26}\text{Mg}$ values of +0.3‰ to +0.5‰) accumulated on the valley floor are ~ 0.2 ‰ heavier than the bedrock, and are thus consistent with that mobile particulates are the heavy Mg isotope reservoir.

Our study provides the first field evidence that changes in clay mineralogy lead to accumulation of lighter Mg isotopes in residual bulk soils. This example also demonstrates that transport of isotopically distinct fine particles from clay-rich systems could be a new and important mechanism to drive the Mg isotope compositions of silicate weathering residuals. This mechanism drives fractionation in an opposite direction as might be expected from previous studies, i.e. residual soils are driven to lighter Mg values and sediments become isotopically heavier.

1. Introduction

The geochemical cycle of magnesium (Mg) at the Earth's surface is closely linked to fluctuations of atmospheric CO_2 and long-term climate changes (e.g., Berner et al., 1983; Berner and Berner, 1996; Drever, 1997). As a macronutrient in the soil zone, Mg is also actively recycled through ecosystems (Schlesinger, 1997). It is thus important to study the behavior of Mg during biogeochemical cycling at Earth's surface with different spatial scales. Because of the relatively large mass differences among the Mg isotopes (mass 24, 25, and 26), Mg isotopic ratios ($^{26}\text{Mg}/^{24}\text{Mg}$ and $^{25}\text{Mg}/^{24}\text{Mg}$) have been reported as a useful tracer to elucidate weathering processes and biogeochemical pathways in surficial environments: researchers have investigated Mg isotopes in soils, vegetation, streams, springs, ground waters and ocean waters (e.g., Galy et al., 2002; Young and Galy, 2004; Villiers et al., 2005; Tipper et al., 2006a, b, c; 2008; 2010; 2012; Brenot et al., 2008; Black et al., 2006; 2008; Pogge von Strandmann et al., 2008; Hippler et al., 2009; Bolou-Bi et al., 2010; Li et al., 2010; Liu et al., 2010; Higgins and

Schrag, 2010; Immenhauser et al., 2010; Jacobson et al., 2010; Teng et al., 2010a, b; Ling et al., 2011; Huang et al., 2012, 2013; Liu et al., 2014).

Mg isotope fractionation is a function of lithology, primary mineral dissolution, secondary mineral formation, ion exchange, and uptake into vegetation (e.g., Galy et al., 2002; Villiers et al., 2005; Tipper et al., 2006a, b, c; 2008; 2010; 2012; Brenot et al., 2008; Pogge von Strandmann et al., 2008; 2012; Black et al., 2006; 2008; Ra and Kitagawa, 2007; Bolou-Bi et al., 2010; Wimpenny et al., 2010; Teng et al., 2010b; Wimpenny et al., 2010; Ryu et al., 2011; Huang et al., 2012; Liu et al., 2014). For example, rivers that drain small carbonate watersheds in the Himalayan region have similar Mg isotope compositions as the carbonate bedrock (Tipper et al., 2008). By contrast, rivers that drain silicate bedrock (such as paragneiss) catchments have distinctively lighter Mg isotope ratios compared to the silicate bedrock in the Himalayas (Tipper et al., 2008). In those Himalayan catchments, residual weathering products such as soils were shown to have heavier Mg isotopic compositions as lighter Mg isotopes were preferentially released into the water phase (Tipper et al., 2008). On the other hand, recent laboratory experimental work on basalt dissolution showed that lighter Mg isotopes are preferentially incorporated into newly-formed secondary phases (e.g., chrysotile, a Mg-silicate mineral), leaving the liquid phase enriched in heavy Mg isotopes (Wimpenny et al., 2010). However, a granite dissolution experiment revealed no significant Mg isotope fractionation during granite dissolution when no secondary Mg phases form (Ryu et al., 2011). Fractionation between water and secondary clay minerals is also observed in field studies. A recent study of extremely weathered Neogene tholeiitic basalt in southern China showed that heavy Mg isotopes were preferentially enriched in clay-rich saprolites because the heavy Mg isotopes from the soil waters had adsorbed to kaolin minerals (kaolinite and halloysite) (Huang et al., 2012). Similar adsorption effects on Mg isotope fractions have also been reported by Pogge von Strandmann et al. (2012) for basaltic weathering systems in Iceland.

Mg isotopes are also fractionated during uptake by higher plants as observed in recent experimental work. Roots of rye grass and clover have been shown systematically to be enriched in heavy Mg isotopes relative to their nutrient source (Bolou-Bi et al., 2010). However, lighter Mg isotopes

are preferentially incorporated into chlorophyll molecules during plant growth and thus accumulate in leaves and shoots relative to the roots (e.g., Black et al., 2006; 2008; Ra and Kitagawa, 2007; Bolou-Bi et al., 2010). Thus, at least in some species, roots become isotopically heavy in Mg isotope compositions, and leaves and shoots isotopically light. Bio-recycling of these Mg pools back into soils could therefore affect the distribution of Mg isotopes in soils.

Given the complexity of the Mg isotope fractionation at Earth's surface, more studies under laboratory-controlled or well-constrained field conditions are needed to elucidate the fractionation mechanisms during low temperature biogeochemical processes. Here we focus on Mg isotope fractionation during shale weathering in a temperate watershed in the northeastern USA. Mg isotopes were measured systematically in solid (soil profiles, sediments and bedrock) and liquid weathering products (soil pore waters, groundwaters, and stream waters) from a catchment entirely underlain by gray shale. Shale bedrocks cover almost 25% of the Earth's land surface (Amiotte-Suchet et al., 2003), and weathering of shale has been shown to control global geochemical fluxes of C, P, and Pt-group elements (Petsch et al., 2001; Kolowitz and Berner, 2002; Amiotte-Suchet et al., 2003; Tuttle and Breit, 2009; Tuttle et al., 2009). This study thus sheds light upon the behavior of Mg isotopes in the shale weathering environment and the contribution of this important lithology to the global Mg cycle. More importantly, unlike igneous rocks, conversion of shale to soils involves a series of transformation of clay minerals and this study will help illuminate how these changes in clay mineralogy fractionate Mg isotopes. To our knowledge, this is the first comprehensive case study of Mg isotopic compositions in complementary liquid and solid weathering products in a shale bedrock catchment.

2. Geological Setting

The Susquehanna/Shale Hills Critical Zone Observatory (Shale Hills) was established in 2007 in Huntington County, Pennsylvania (Fig. 1; <http://www.czo.psu.edu/>) to study the coupled chemical, physical, hydrological and biological processes impacting soil formation. This small 8-ha (80000 m²) watershed is located on the northern part of the Appalachian Mountains. Extensive geographic,

geochemistry, hydrological and soil data sets are available at Shale Hills from previous studies (Lynch, 1976; Lynch and Corbett, 1985; Duffy and Cusumano, 1998; Lin, 2006; Lin et al., 2006; Qu and Duffy, 2007; Jin et al., 2010; 2011a, b; Ma et al., 2010; 2011a, b; 2013; West et al., 2011; 2013; Yesavage et al., 2012). As such, Shale Hills provides an ideal field site to study the behavior of Mg isotopes during shale weathering and soil formation. The detailed site information has been provided in Jin et al. (2010) and Ma et al. (2010) and is briefly summarized below.

The catchment has a temperate humid climate, with mean annual temperature of 10 °C and mean annual precipitation of 107 cm (NOAA, 2007). Average local catchment relief is 30 m and a 1st-order stream flows on the central valley floor from east to west (Lynch, 1976; Lin, 2006) (Fig. 1). The catchment is mantled by soils with thickness increasing from ~0.3 m at the ridge top to greater than 3 m in the valley floor and in swales (Fig. 1). The vegetation covering includes deciduous trees (maple, oak, and beech) as well as hemlock and pine (Lin, 2006). Tree density is similar from ridge tops to the valley floor.

The bedrock at Shale Hills, known as the Silurian Rose Hill Formation, is dominated by organic-poor shale (~0.05% total carbon) with rare interbedded limestone and sandstone (Folk, 1960; Lynch, 1976; Lynch and Corbett, 1985). In the carbonate-poor portion, the shale is composed predominantly of illite (58 wt. %), quartz (30 wt. %), vermiculitized chlorite (referred to here as “chlorite”, 11 wt. %), and trace amounts of feldspar (plagioclase and K-feldspar), anatase (TiO₂), pyrite, Fe-oxides (magnetite and hematite) and zircon (Jin et al., 2010; Brantley et al., 2013). The carbonate-rich portion include minerals such as ankerite, which has been observed in a borehole (DC1) at ~20 meters below surface drilled at the northern ridge and from deeper than two meters in 4 boreholes in the valley floor near the entrance to the catchment (Fig. 1). In the carbonate-free Rose Hill shale, Mg is predominantly present in “chlorite” (=chlorite/vermiculite/hydroxyl-interlayered vermiculite) and illite phases (Jin et al., 2010). Carbonates are not present in the soils throughout the catchment, nor in the upper layers of five boreholes drilled in the ridge and valley. The correspondence between carbonate depletion, pyrite oxidation, and the water table at two locations (ridge top and valley floor) lead to the assumption that carbonate removal has been

relatively complete throughout the catchment down to depths (> 6 m) that approximate today's water table and that the reaction fronts for carbonate and pyrite are nested and that they roughly parallel the water table. Brantley et al. (2013) also argued on the basis of C isotopes that precipitation of carbonate may occur at depth (e.g. 7 m deep) under the valley.

Chemical weathering reactions in the Shale Hills soils are dominated by clay transformations: illite and “chlorite” weather to produce vermiculite, hydroxyl-interlayered vermiculite (HIV), and kaolinite (Jin et al., 2010). Mg is readily released into the soil pore waters from dissolution of “chlorite” and illite (Jin et al., 2011b). Assuming the nested reaction front hypothesis (Brantley 2013), ankerite and feldspar dissolve at much greater depths (e.g. 6 to 22 meters deep) (Jin et al., 2010; Brantley et al., 2013). Indeed, the groundwater at Shale Hills has much higher Mg concentrations than most soil porewaters, indicative of ankerite dissolution only at depth below the soil zone (Jin et al., 2011b; Brantley et al., 2013).

U-series isotope activity ratios were measured and modeled to determine the timescales of chemical weathering involved at Shale Hills (Ma et al., 2010; 2013). Along the planar transect on the southern slope that we investigate in the current study (Fig. 1), thin soils (~30 cm) at the ridge top have high soil formation rates ($\sim 45 \pm 12$ m/Myr) (Ma et al., 2010). If we assume that regolith formation and erosion rates are the same, this corresponds to a short residence time for the particles within the soil profile ($\sim 7 \pm 2$ kyr). Consistent with this, West et al. (2013) have reported ^{10}Be measurements of the soil residence time at the ridge top of ~ 9 kyr. In fact, the direct comparison of U-series and ^{10}Be isotope measurements suggested that the regolith formation and erosion rates agree within error for the ridge top site at Shale Hills (Ma et al., 2013; West et al., 2013). Thick soils (~70 cm) at the middle slope and valley floor are consistent with lower soil formation rates ($\sim 17 \pm 14$ m/Myr) and much longer residence times ($\sim 40 \pm 30$ kyr) (Ma et al., 2010). Shale Hills has experienced a significant perturbation from peri-glacial to modern conditions (~ 15 kyr; Gardner et al., 1991) in the geologically recent past. The catchment lies ~ 80 km south of the greatest advance of glacial ice in central Pennsylvania during the last glacial maximum (Braun, 2005).

3. Samples, experimental protocols and analytical methods

Shale weathering and soil formation processes were characterized at selected pedons and catenas at Shale Hills. Major element, rare earth element, U, Fe, and Be isotopic analyses for soil and water samples have been previously reported (e.g., Jin et al., 2010; 2011a, b; Ma et al., 2010; 2011a, b; 2013; West et al., 2011; 2013; Yesavage et al., 2012). We focus here on the Mg isotope compositions of soil profiles along one “planar” transect from the southern slope of the catchment (Fig. 1). Three sites were selected to represent different topographic locations along the hillslope (southern planar ridge top: SPRT; middle slope: SPMS; valley floor: SPVF). A 25 m deep drill core (DC1) on the northern ridge of the catchment provided a sample of what we interpret as unaltered parent material from depth (free of ankerite; Jin et al., 2010). Stream sediments (SS) were also augered at 10 cm intervals until 110 cm below surface for chemical and isotopic analysis at the valley of the stream (Fig.1; Ma et al., 2011b). This 110-cm-deep core of stream sediments (SS) was collected behind a weir built in the 1970s at the center of the valley floor (Fig. 1). The ground surface behind the weir is ~ 30 cm higher than the surface in front of the weir. Hence, we interpret the upper 30cm of this core as the sediments accumulated since the weir was built in the 1970s (modern sediments) while the lower 80 cm of the profile as the older sediments accumulated naturally before the installation of the weir.

Methods of sample collection have been described in detail in previous publications; indeed, the analyses reported here were completed on sample splits from the same samples reported previously (e.g., Jin et al., 2010; 2011a, b; Ma et al., 2010; 2011a, b; West et al., 2011; 2013; Yesavage et al., 2012). These bulk solid samples (2 bedrock, 16 soil samples, and 10 sediment samples) were air-dried and ground to pass through a 100-mesh sieve (<150 μm) before Mg isotope analysis. For each sample, the entire sample, including all rock fragments, sand, silt, and clay subsamples were ground together and analyzed.

Natural water samples (soil pore waters, groundwaters, and stream waters) were also collected from the catchment for Mg isotope analysis (Fig. 1). Soil pore waters were collected by suction lysimeters fabricated with porous cups and PVC tubes (soil water samplers model 1900L from Soil Moisture, Inc.,

40 mm diameter and 1.3 μm maximum pore size). Nests of lysimeters were installed in 2007 at 10 cm depth intervals at the three sites where the soil cores were collected (SPRT, SPMS, and SPVF; Fig. 1). Daily stream and groundwater samples were collected with ISCO auto-samplers (Teledyne Isco, Inc.) at the mouth of the catchment and filtered with 0.45 μm VWR Nylon filters. For all water samples, one aliquot (60 ml) was acidified with ~ 0.3 ml ultrapure nitric acid for dissolved Mg concentrations with inductively coupled plasma optical emission spectrometry (ICP-OES) and Mg isotopes as discussed below. All samples were stored in pre-cleaned HDPE bottles and maintained at about 4 $^{\circ}\text{C}$ until analysis. For this study, 14 soil pore water, 3 stream water and 2 groundwater samples, collected in June (warm and dry summer season) and December (cold and wet winter season) of 2009, were selected to analyze for Mg isotopic compositions. The same water samples have been analyzed and reported for major elements by Jin et al. (2011b).

Magnesium isotopic analyses were measured at the Isotope Laboratory of the University of Arkansas, Fayetteville. Procedures for sample dissolution, column chemistry and instrumental analysis are similar to those reported in previous studies (Yang et al., 2009; Li et al., 2010; Liu et al., 2010; Teng et al., 2010a, b; Teng and Yang, 2014). Briefly, ground solid samples were dissolved in Savillex screw-top beakers in a mixture of concentrated $\text{HF-HNO}_3\text{-HCl}$. For water samples, ~ 50 to 70 g of water were evaporated in Savillex screw-top beakers. Separation of Mg was achieved by cation exchange chromatography with Bio-Rad 200–400 mesh AG50W-X8 resin in 1 N HNO_3 media. Samples containing ~ 50 μg of Mg were loaded on the resin and eluted by 1 N HNO_3 . The Mg yield, based on multiple analyses of pure Mg and synthetic Mg standard solutions, was observed to be $100 \pm 0.2\%$ and the procedure blank was always measured with < 10 ng Mg (Teng et al., 2010a, b; Teng and Yang, 2014). This procedure was repeated in order to obtain a solution with only Mg for mass spectrometry. Two rock and mineral standards (KH- Olivine: Kilbourne Hole, New Mexico and USGS Sco-1 Shale) and one seawater standard were processed with unknown samples for each batch of column chemistry. Magnesium isotopic compositions were analyzed by the standard bracketing method using a Nu Plasma

MC-ICP-MS at the University of Arkansas. Magnesium isotope data are reported in standard δ -notation in per mil relative to DSM3 (Galy et al., 2003):

$$\delta^x Mg = \left\{ \frac{(^x Mg / ^{24} Mg)_{sample}}{(^x Mg / ^{24} Mg)_{DSM3}} - 1 \right\} \times 1000 \quad \text{Eqn. 1}$$

where x refers to mass 25 or 26.

The precision of the measured $^{26}Mg/^{24}Mg$ ratio, based on > 4 repeat runs of the same sample solution during a single analytical session, was observed to be $< \pm 0.04\%$ (2SE) (Teng et al., 2010a). Multiple analyses of IL-Mg-1, a synthetic solution with molar concentration ratios of Mg:Fe:Al:Ca:Na:K:Ti=1:1:1:1:1:1:0.1, yielded $\delta^{26}Mg$ of +0.04 ‰, 0.00 ‰ and -0.02 ‰ (Table 1), within uncertainties of the expected value of $0 \pm 0.04\%$ (2SE). Analysis of seawater standards yielded $\delta^{26}Mg$ of $-0.82 \pm 0.02\%$ and $-0.79 \pm 0.04\%$ (2SE), within uncertainties of the expected value of -0.83 ‰ (Ling et al., 2011 and references therein). Results for rock and mineral standards (KH-olivine, and SCo-1 Shale) analyzed during the course of this study (Table 1) also agree with previously published values (Chang et al., 2003; Galy et al., 2003; Teng et al., 2010a; Young and Galy, 2004; Li et al., 2010). Sample duplicates (DC1-26) show excellent reproducibility of the analytical results ($0.35 \pm 0.03\%$ and $0.35 \pm 0.03\%$, 2SE).

4. Results

Magnesium isotopic compositions of soil, stream sediment and bedrock samples are reported in Table 1. Magnesium isotopic compositions and concentrations for soil pore water, stream water, and groundwater samples are reported in Table 2. Concentrations of major elements (Mg, Al, Fe, and Si) and Zr, cation exchange capacity (CEC), organic matter contents (C and N), and quantitative mineralogy in the soil, sediment, and bedrock samples were previously reported for splits of the same samples by Jin et al. (2010), Andrews et al. (2011) and Ma et al. (2011b) and are compiled in Table 3 for reference.

All Shale Hill samples fall on a mass-dependent fractionation line in a $\delta^{26}Mg$ vs. $\delta^{25}Mg$ diagram within error (Figure 2). The slope of this fractionation line is $\sim 0.509 \pm 0.007$ ($R^2=0.992$), similar to the

average slopes reported in previous studies on terrestrial samples (e.g., Young and Galy, 2004; Teng et al., 2010a; Li et al., 2010). So only $\delta^{26}\text{Mg}$ will be used for future discussion on Mg isotope compositions.

$\delta^{26}\text{Mg}$ values of all Shale Hills samples (soil, water, stream sediment and bedrock) analyzed in this study range from $-1.15 \pm 0.06 \text{ ‰}$ to $+0.50 \pm 0.03 \text{ ‰}$ (2SE). The extents of Mg isotope fractionation are significant for such a small catchment: $\sim 1.7 \text{ ‰}$ for $\delta^{26}\text{Mg}$ values. As a comparison, the compilation of $\delta^{26}\text{Mg}$ values on terrestrial Mg reservoirs shows only $\sim 6 \text{ ‰}$ variation (e.g. Young and Galy, 2004).

The Mg concentrations of DC1 bedrock core samples from 0.3 – 20 m depth fall into a narrow range (average $0.95 \pm 0.09 \text{ wt.}\%$), suggesting that the silicate fraction of the Rose Hill bedrock is relatively homogenous (Jin et al., 2010). Indeed, Mg isotopic compositions ($\delta^{26}\text{Mg}$) in the two analyzed shale bedrock samples (from 4m and 6m depth of the DC1 core) are $0.35 \pm 0.03 \text{ ‰}$ and $0.36 \pm 0.03 \text{ ‰}$, respectively (Table 1; Figure 2), suggesting homogenous Mg isotopic compositions of parent shale. In comparison to the relatively small number of $\delta^{26}\text{Mg}$ data that have been previously reported for shale, our values are similar (post-Archean Australian Shale: -0.27 to 0.49 ‰ ; Li et al., 2010).

Water samples at Shale Hills are characterized by significantly lighter Mg isotopic compositions ($\delta^{26}\text{Mg} = -1.15$ to -0.14 ‰ ; Table 2) relative to the parent shale. Specifically, the $\delta^{26}\text{Mg}$ values in the soil waters, stream and groundwater range from -0.62 to -0.14 ‰ , from -0.54 to -0.47 ‰ , and from -1.05 to -1.15 ‰ , respectively (Table 2). For soil pore water and stream samples that were collected in June and December of 2009 (Table 2), similar Mg isotope values are observed for the same site, with little to no seasonal variations.

Mg concentrations in groundwater samples are $\sim 4 \text{ mg/kg}$ (or ppm) whereas samples of soil porewater from the ridge top (SPRT), mid-slope (SPMS), and valley floor (SPVF) range from 0.5 to 1.8 ppm (Table 2;). The stream water is characterized by Mg concentrations around 2.5 to 2.9 ppm.

The $\delta^{26}\text{Mg}$ values of the soil samples have a narrow range compared to water samples: from 0.22 to 0.37 ‰. Mg in soils is heavier than in the water samples but is similar to or slightly lighter than the bedrock samples (Table 1; Figure 2). Furthermore, soil samples show a systematic decrease in $\delta^{26}\text{Mg}$

values toward the surface in soil profiles at SPMS and SPVF (Fig. 3). Mg concentrations in these soil samples, ranging from 0.36 to 0.92 wt. % (Table 3), are significantly lower than those of the bedrock samples, also decreasing towards the surface (Fig. 3).

The $\delta^{26}\text{Mg}$ values of the stream sediment samples range from 0.28 ‰ to 0.50 ‰ (Table 1). Sediments from 0- 60 cm depth have $\delta^{26}\text{Mg}$ values that are similar to or slightly lighter than the bedrock. In contrast, sediments from 60 to 109 cm depth have $\delta^{26}\text{Mg}$ values heavier than the bedrock (Fig. 4). Mg concentrations in the sediment samples range from 0.50 to 0.62 wt. %, i.e. values that are slightly higher than the soil samples.

5. Discussion

5.1. Magnesium isotope fractionation during shale weathering

When Mg-bearing minerals break down during chemical weathering, Mg can be released into the water phase where it often remains soluble without back-reaction and formation of secondary phases. At Shale Hills, chemical weathering reactions in the soil are dominated by the following clay transformations (Jin et al., 2010):

- (i) Illite $\rightarrow$ vermiculite
- (ii) Chlorite $\rightarrow$ vermiculite
- (iii) Vermiculite $\rightarrow$ hydroxyl interlayered vermiculite (HIV)
- (iv) HIV $\rightarrow$ kaolinite and Fe-oxyhydroxides

In the shale bedrock, Mg mainly resides in clay minerals illite and vermiculitized “chlorite”. Based on the soil pore water and soil chemistry, Jin et al. (2010) estimated for the south planar transect that chlorite dissolution contributes 98% and illite dissolution contributes 2% of the dissolved Mg^{2+} in soil pore waters at Shale Hills.

To correct for relative changes in Mg concentrations due to changes in other elements in the soils, Mg mass transfer coefficients ($\tau_{\text{Zr,Mg}}$) were calculated with Eqn. 2 (Brimhall and Dietrich, 1987; Anderson

et al., 2002). Zr is used here as the reference immobile element during chemical weathering based on previous research at Shale Hills (Zr has been found in Rose Hill shale at Shale Hills only in the highly insoluble mineral zircon; Jin et al., 2010):

$$\tau_{Zr,Mg} = \frac{C_{Mg,w}}{C_{Mg,p}} \cdot \frac{C_{Zr,p}}{C_{Zr,w}} - 1 \quad \text{Eqn. 2.}$$

Here C refers to concentration of Zr or Mg in the weathered soils (w) or in the parent (p) (Table 3).

Positive $\tau_{Zr,Mg}$ values indicate enrichment of Mg relative to parent materials, negative values mean depletion and zero means no gain or loss. Mg mass transfer coefficients ($\tau_{Zr,Mg}$) in all three soil profiles (SPRT, SPMS and SPVF) decrease toward the surface, documenting loss of Mg from the soils (Fig. 5). The mobility of Mg is also documented by higher Mg^{2+} concentrations in soil pore water samples (up to 1.8 ppm; Table 2) than in rainwater at Shale Hills (~0.021 ppm; Jin et al., 2011b).

Mg isotope compositions of soil pore waters are ~0.5 to 1.0 ‰ lighter than the bedrock (Fig. 2), indicating preferential release of lighter Mg isotopes to the aqueous phase when the “chlorite” and illite weather to vermiculite, HIV and then kaolinite in the soils. Similar fractionation factors have been observed between bedrock and natural waters in other silicate weathering systems such as paragneiss and diabase (e.g., Tipper et al., 2006a; Teng et al. 2010b). Soil water exhibits a much larger range of isotope variation, compared to the soils. Many environmental factors may be responsible for this scatter: e.g. (1) addition of Mg from litter leaching may make the shallow soil waters more negative; (2) availability of fresh reactive mineral surfaces and formation of secondary minerals may affect the saturation states and rates of equilibration with respect to different minerals; and (3) adsorption and desorption of Mg^{2+} may control isotope exchange between soil and pore water (e.g. Huang et al., 2012). To interpret the variation of soil water $\delta^{26}Mg$ is beyond the scope of our current study and will require additional investigation.

The groundwaters at ~6 meters depth from the valley are characterized by $\delta^{26}Mg$ isotope compositions ~1.5 ‰ lighter than the bedrock (Fig. 2). Previous work has documented that chemistry of these shallow groundwaters is dominated by dissolution of ankerite, with little contribution from silicate weathering (Brantley et al., 2013). Ankerite, an Fe- and Mn- rich carbonate mineral with a dolomite

structure, was completely depleted from the top 20 m of the DC1 core by weathering at the northern ridge, but ankerite was observed below that depth (Jin et al., 2010). Likewise, carbonate minerals are observed beneath about 2m depth under the valley floor. Ankerite is likely to have very light Mg isotope compositions (e.g. $\delta^{26}\text{Mg} = -3$ to -5 ‰; Young and Galy, 2004). As a consequence of ankerite dissolution, therefore, groundwaters have higher Mg^{2+} concentrations, but lower Mg isotope compositions than soil pore waters (Jin et al., 2010).

The $\delta^{26}\text{Mg}$ values of the stream water (~ -0.5 ‰) overlap with those of the soil pore waters (-0.6 ‰ to -0.1 ‰), consistent with the conclusion that the stream is mainly recharged by down-hillslope flowing soil pore waters that travel along low-permeability interfaces and create intermittently saturated but perched water tables (Jin et al., 2011b). However, the $\delta^{26}\text{Mg}$ values of the stream water are slightly lighter than the average soil pore water composition (Fig. 2), suggesting that the stream may be also receiving a contribution from the local groundwater reservoir. A simple Mg isotope mass balance calculation indicates that the lighter groundwater reservoir ($\delta^{26}\text{Mg}$ end-member value ~ -1.1 ‰) contributes about $\sim 14\%$ of water mass to the stream while the soil pore water ($\delta^{26}\text{Mg}$ end-member value ~ -0.4 ‰, average soil pore water value at the SPVF site which directly recharges to the stream) contributes about $\sim 86\%$.

The observation of lighter $\delta^{26}\text{Mg}$ values in the soil waters than in the bedrock should have led to a complementary heavy Mg isotope reservoir in residual soils, if one considers Mg isotope mass balance for a closed system between soils and pore waters. This is expected especially for Shale Hills where soils have undergone chemical weathering for tens of thousands of years (Ma et al., 2010) and Mg has become significantly depleted in the soils. However, soil samples in the ridge top profile (SPRT) have Mg isotopic compositions similar to the bedrock samples (Table 1; Figure 3) and most soil samples from the middle slope (SPMS) and valley floor (SPVF) profiles are *lighter* than the bedrock. In addition, these soil profiles show a decreasing trend of $\delta^{26}\text{Mg}$ values towards the surface with more intensive loss of Mg. Hence, the current Mg dataset may indicate a heavy Mg isotope reservoir is “missing” from the residual soils on this hillslope (see Section 5.4).

The decreasing trend of $\delta^{26}\text{Mg}$ values in the Shale Hills soil profiles are correlated to the increasing weathering duration of soils towards the surface. The transformation of bedrock to soils starts at a weathering interface at depth. Over time, the weathering interface propagates downward into the bedrock. At Shale Hills, current soil thickness increases from 30 cm at SPRT, to 59 cm at SPMS, and to 67 cm at SPVF along the planar transect. Rates of regolith formation (the weathering advance rate) at these three sites have been determined by using U-series isotope disequilibrium in soils (Ma et al., 2010). The rates decrease systematically with distance from the ridge: $\sim 45 \pm 12$ m/Myr at SPRT, the highest point along the hillslope, to $\sim 18 \pm 12$ m/Myr at SPMS, and $\sim 17 \pm 12$ m/Myr at SPVF. If we assume a simple steady state for these soil profiles at Shale Hills (the weathering advance rate equals the erosion rate and the regolith thickness remains constant over time), the duration of chemical weathering for each soil sample can be estimated by using the regolith production rate reported by Ma et al. (2010) and the total soil depth (Table 3). The total duration of chemical weathering of these three soil profiles increases with distance away from the ridge, from $\sim 7 \pm 2$ kyr for the SPRT, to $\sim 34 \pm 22$ kyr at the SPMS site, to $\sim 40 \pm 28$ kyr at the SPVF site (Table 3, see also Ma et al. 2010).

Large extents of Mg isotope fractionation are observed in the shallow SPMS and SPVF profiles, correlated with longer durations of weathering in the SPMS and SPVF positions (Fig. 3). Young soil samples such as in the SPRT profile and deep SPMS and SPVF profiles show little variations of Mg isotopic compositions compared to the bedrock samples. Hence, the values of $\delta^{26}\text{Mg}$ for these soil samples decrease systematically with their calculated weathering duration (Fig. 6a). This observation suggests preferential accumulation of lighter Mg isotopes and/or depletion of heavy Mg isotopes in older soil samples that have been chemically weathered to a greater extent.

5.2. Possible mechanisms of light magnesium isotope accumulation in shallow soils at Shale Hills

The Mg isotope data shows that soils at Shale Hills (Fig. 2) are depleted in ^{26}Mg relative to parent shale. We evaluate three possible mechanisms to explain such lighter Mg isotopes in shallow soils: 1)

biological recycling of Mg by vegetation adds lighter Mg isotopes to surface soils; 2) Mg-containing carbonates that are characterized by lighter $\delta^{26}\text{Mg}$ values precipitate in surface soils; 3) secondary clay minerals preferentially retain lighter Mg from soil water in shallow soils. As discussed below, we argue that the third explanation, clay mineral transformation, is the most likely mechanism.

5.2.1. Mg recycling by vegetation

Mg is an essential macronutrient for plant growth (Wilkinson et al., 1990; Epstein and Bloom, 2005): dissolved Mg^{2+} ions in soil water are taken up by roots and stored in vegetation for several months to years and then subsequently released back to soils when litter and dead roots decay. These biological processes could potentially fractionate Mg isotopes in soils. For example, plant roots have been shown to preferentially take up heavy Mg isotopes (Boulo-Bi et al., 2010), leading to accumulation of more light Mg isotopes in residual surface soils. Alternatively, plant leaves sometimes have lower Mg isotopic ratios relative to their nutrition sources (e.g., Black et al., 2006; Ra and Kitagawa, 2007; Black et al., 2008; Bolou-Bi et al., 2010). For such a system, lighter Mg isotopes would possibly accumulate in top soils when leaves fall and decay near the land surface.

Although possible, such a mechanism may only play a minor role in the overall Mg mass balance of surface soils at Shale Hills. First, the Shale Hills soils used for this study have been characterized previously by Andrews et al. (2011) for total organic carbon (TOC) and total organic nitrogen (TON): both TOC and TON values increase significantly towards the land surface (Table 3). The highest TOC observed is 2.94 %. Given the Mg concentrations of organic matter (leaf litter: average $1725 \mu\text{g Mg g}^{-1} \text{C}$; Herndon, 2012), only 0.005 wt. % Mg in soils can be associated with organic matter. This value is negligible compared to mineral-derived Mg.

More importantly, if the bio-recycling process introduced a large Mg isotope fractionation for soils relative to bedrock, lighter Mg isotope accumulation would be expected in all the surface soil layers, e.g. in the 0-10 cm depth soils. However, only surface samples at SPMS and SPVF show significantly

lighter Mg isotope compositions (Fig. 3). The lighter Mg isotope signatures are not found in the surface samples at SPRT, which also shows a high concentration of organic matter (Table 3) and would otherwise be expected to show evidence of light Mg isotope accumulation. Thus bio-recycling is unlikely to be the dominant mechanism that causes accumulation of the light Mg isotopes in the soils. However, as we discuss later, this mechanism may be important in explaining the soil water Mg isotope signatures.

5.2.2. Precipitation of carbonate minerals

Carbonate minerals can preferentially incorporate light Mg isotopes when they precipitate (e.g., Galy et al., 2002). Carbonate minerals were only observed in the parent shale bedrock at ~20 meters depth under the ridge or at several meters depth under the valley at Shale Hills; i.e., no carbonates were observed forming in the soils (Jin et al., 2010; Brantley et al., 2013). This is consistent with observations of formation of secondary carbonates in soils worldwide that vary with local climate conditions (Schaetzl and Anderson, 2005). Carbonate precipitation is a dominant process in soils under arid/semi-arid climate (Southard, 2000). It is only observed in humid climates when some layers of a soil pedon are clay-rich and relatively impermeable (Wenner et al., 1961; Schaetzl et al., 1996). At Shale Hills, carbonates were long ago dissolved out of these soils and bedrock layers down to ~20 m under the northern ridge and down to ~6 m under the valley floor. Consistent with this, throughout the catchment, soils uniformly contain < 0.2 wt. % Ca (Jin et al., 2010). Mineralogical analyses have also confirmed that no pedogenic carbonate minerals were observed in these soil profiles (Jin et al., 2010) although secondary calcite has been inferred at ~6 m depth under the valley floor where upwelling of waters may be associated with CO₂ degassing or other processes (Brantley et al., 2013). Such observations are certainly consistent with the presence of very acidic (pH 3-4) and relatively permeable soils at shallow depths throughout Shale Hills (Jin et al., 2010); both conditions strongly favor dissolution instead of precipitation of carbonate minerals in shallow soils. Hence, the hypothesis that lighter Mg isotopes are accumulating in secondary carbonate minerals in the Shale Hills' soils is not supported by the field observations.

5.2.3. Clay mineral transformation

The systematic decrease of $\delta^{26}\text{Mg}$ values with increasing weathering durations in these soils (Fig. 5a) suggests that the Mg isotope fractionation process is directly related to soil formation processes. Both chlorite and illite are 2:1 phyllosilicates. Mg occupies the octahedral sheets in both illite and chlorite, stabilized by strong chemical bonds to oxygen atoms or hydroxyl groups in the structures. However, Mg is also present in chlorite as interlayer sheets, which is bonded slightly more weakly as compared to those within the 2:1 structure. During water-rock interaction, such bonds are broken and chlorite is transformed to vermiculite: some Mg is released into the water (Bock et al., 1994), while some remains in the clay interlayers.

Because of the high layer charge from its 2:1 sheet structure, vermiculite has a high cation exchange capacity (CEC) (Barshad and Kishk, 1969). Furthermore, vermiculite is distinctively different from illite and chlorite in that it has free or hydrated Mg^{2+} in the interlayer region to balance the charge (Fig. 6). The Mg^{2+} interlayer ion in vermiculite is strongly hydrated and readily exchanges with the surrounding solution, e.g., the soil pore water. It is thus highly possible that vermiculite can trap aqueous Mg^{2+} ions with light Mg isotopic compositions from circulating soil waters in its interlayer structure (Fig. 7). The old soils, with high contents of vermiculite and hydroxy-interlayer vermiculite (HIV) (Table 3), hence would likely retain more Mg^{2+} ions from exchange with soil water, and thus would show slightly lighter $\delta^{26}\text{Mg}$ values compared to the younger soils (Fig. 6a). According to this hypothesis, the increasingly low Mg contents and lighter $\delta^{26}\text{Mg}$ values observed at shallower depths in the soils is attributed to the increasing formation of HIV upward in each soil profile as observed in Shale Hills (Jin et al., 2010). Indeed, transformation of illite and chlorite to vermiculite leads to a higher cation exchange capacity (CEC) but a lower Mg content in old soils (Fig. 6b). As a result, exchange of Mg^{2+} ions in the clays with the Mg in the soil water has occurred more extensively with the older soil layers as compared to the younger soils. This is evidenced by the higher CEC/Mg ratios of the older soil layers (Fig. 6c). Fig. 6c uses CEC values reported previously for these same soils (Jin et al., 2010).

Unlike the vermiculite, Mg in chlorite and illite mainly resides in octahedral sheets, and thus is probably not affected by the exchangeable pool. When vermiculite and HIV are converted to kaolinite, all Mg cations in octahedral sites are dissolved and released. This process probably does not induce any further Mg isotope fractionation. So overall, the soils show a relatively small isotope variation even though up to 80% of the Mg was lost from all samples.

5.3. Possible evidence of light Mg isotope accumulation in deep soils at Shale Hills

Both bulk Fe and HCl-extracted Fe for these same soil samples have been observed to become isotopically lighter as weathering proceeds (Yesavage et al., 2012). Similarly, a heavy Fe isotope reservoir is apparently “missing” from the soil samples. Yesavage et al. (2012) proposed that lighter Fe isotopes are preferentially released during rock weathering (either through iron reduction or by ligand-promoted dissolution), but that Fe is re-precipitated back into the soils. Hence lighter Fe isotopes are preferentially retained in soils. Similarly, the deepest SPVF samples showed ($^{234}\text{U}/^{238}\text{U}$) activity ratios greater than 1, whereas other soil samples in these profiles demonstrated ($^{234}\text{U}/^{238}\text{U}$) activity ratios less than 1 (Ma et al., 2010). These high U activity ratios were interpreted to reflect U that was precipitated or adsorbed from soil pore waters that contained U characterized by ($^{234}\text{U}/^{238}\text{U}$)>1. Generally, the input of U to soils has been attributed to co-precipitation or sorption of U in secondary Fe-hydroxides or clay minerals (Ames et al., 1983; Shirvington, 1983; Andersson et al., 1998; Duff et al., 2002; Chabaux et al., 2003a). If precipitation of Fe-oxyhydroxides or clay minerals in the valley floor site also retained lighter Mg isotopes, this process could potentially explain why the deepest two soil samples in the SPVF profile have slightly lighter $\delta^{26}\text{Mg}$ values compared to the parent bedrock and the sample immediately above them (Fig. 3). In other words, it is possible that some of the same processes are affecting the Fe, U, and Mg isotopes.

5.4. A “missing” heavy Mg isotope reservoir in residual soils at Shale Hills

As shown by Jin et al. (2010), depletion profiles are observed for all the major elements Mg, K, Al, Fe, and Si in these soils. These depletion profiles are somewhat unusual because loss of Fe and Al from soils is generally less significant than loss of Mg and K except under very acidic leaching such as in tropical locations (Schlesinger, 1997). Therefore, Jin et al. (2010) suggested that in addition to chemical loss as solute ions, the less soluble Al and Fe were lost predominantly through subsurface transport of fine particles. Jin et al. (2010) further inferred that these particles were larger than 1.3 micron, i.e. the pore size of the suction lysimeters, because very little Fe and Al were observed as solutes in the pore waters in the lysimeters. Given that relatively limited overland flow has been observed in the catchment (Qu and Duffy, 2007), the fine particles are thought to be translocated by intermittently flowing soil waters along the interfaces of the A/B and B/C horizons as well as through vertical macropores (Jin et al., 2011b). Indeed, subsurface particle transport is presumed to be facilitated at Shale Hills because of the clay-rich lithology and because the field conditions are characterized by high infiltration rates, high soil moisture contents, and the presence of macropores (Jin et al., 2010; 2011b). If the lost particles include secondary vermiculite, fine residual illite or chlorite particles that contain the residual Mg after water-rock interactions, these fine particles might be the “missing” heavy Mg isotope reservoir with respect to the residual soils at the hillslope.

To test this, we sampled some of the transported particles that had accumulated in the stream bed. One 110-cm-depth core of stream sediments (SSOW) was collected behind a weir built in the 1970s at the center of the valley floor (Fig. 1). The upper 30cm of this core represents modern sediments accumulated since the 1970s and the lower 80 cm of the profile contains older sediments. Geomorphic observations at Shale Hills have revealed sediment deposits along the axis of the valley floor, reaching ~300 cm thick, suggesting that greater sediment discharges, relative to the transport capacity of the channel, in the recent geological past (West et al., 2013). However, the timescales and rates of sediment accumulation remain uncertain. West et al. (2013) described the stratigraphic features of the channel depositions at the valley floor and suggested that: 1) two charcoal samples dated by C-14 method indicated that the shallow (~40 cm) of natural valley deposits has accumulated over the last ~1000 years, and 2) the deep deposits (e.g.

below ~40 cm depth) are thick and coarse colluvium and consistent with a periglacial origin and transport. Hence, with the exception of the top modern profile, the SSOW profile may present sediments accumulated in the geologically recent past (from 1 kyr to ~15kyr).

Major element data from this sediment core show that the most negative $\tau_{\text{Mg}, \text{Zr}}$ values are observed at ~60 cm depth and $\tau_{\text{Mg}, \text{Zr}}$ values increase gradually upward to the surface as well as downward to ~100 cm depth (Fig. 5). Mg isotopic compositions reveal that the sediments at shallow depths are systematically different from the deep sediments. The top 30 cm depth sediments are accumulated since 1970s and have $\delta^{26}\text{Mg}$ values of +0.28 to +0.34 ‰, slightly lighter or similar to the bedrock values. $\delta^{26}\text{Mg}$ values in these shallow sediments are thus similar to the residual soils, consistent with the previous conclusion that they are modern sediments originated from the current erosion of soils on the hillslope when the weir was built. The deeper sediments from 70-100cm depth have $\delta^{26}\text{Mg}$ values of +0.48 to 0.50 ‰, heavier than the bedrock values. These deeper and putatively older sediments (e.g. up to peri-glacial) are the only samples that we observed that have heavy Mg isotope compositions, i.e., complementary to the soils and waters at Shale Hills. Given this, these transported particles are assumed to be the “missing” heavy Mg isotope reservoir -- in other words, the residual soils have lost fine particles that were transported from hillslope and re-deposited in stream sediments. These observations are also consistent with loss of Mg-rich particles before the 1970s, as the modern sediments from the top 30cm do not show the heavy Mg isotope signature. We hypothesize that the loss of Mg rich particles may have occurred during the periglacial conditions, as freeze-thaw and solifluction were probably extensive in this region ~15 kyr ago and may have enhanced the rates of erosion and transport of fine particles (e.g., Walder and Hallet, 1985; Gardner et al., 1991).

Yesavage et al. (2012) also observed depletion profiles for Fe along the hillslope but a lack of significant enrichment of Fe in both filtered and unfiltered soil pore waters collected by lysimeters. Unfiltered stream waters and pore waters from macro-pores delivering water to the stream bank during high-rain conditions (e.g. summer and fall seasons) had much higher Fe + Al + Si + Ti concentrations

than filtered samples; however, these unfiltered samples only showed slightly higher Mg, K, Na, and Ca concentrations than the filtered samples (Yesavage et al., 2012). Hence, it is unlikely that the inferred Mg rich particles were carried by the macro-pore waters as studied in Yesavage et al. (2012). Such an observation is also consistent with the conclusion that the loss of these particles occurred only in the past, and is not currently observed in the field.

To summarize, the Mg isotope data for soils on the hillslope are consistent with an isotopically heavy Mg reservoir that is currently “missing” from the south planar transect at Shale Hills. We attribute this missing reservoir to loss of particles during shale weathering (Jin et al., 2010). The loss of fine particles might have been transported out of the hillslope in the geological past (e.g. during periglacial period ~15kyr ago) and some may have accumulated in the stream sediments. Our study shows that transport of isotopically distinct fine particles from clay-rich systems could be an important mechanism to drive the Mg isotope compositions of silicate weathering residuals. This mechanism drives fractionation in an opposite direction as might be expected from previous studies, i.e. residual soils are driven to lighter Mg values and sediments become isotopically heavier.

6. Conclusions and Implications

Understanding the behavior of Mg isotope fractionation during chemical weathering has important implications for developing Mg isotopes as tracers in surface environments. To investigate the Mg isotope fractionation during shale weathering, we measured Mg isotopic compositions of solid (soil profiles, stream sediments and bedrock) and water samples (pore, ground-, stream waters) along a well-drained catena on a planar hillslope from the Shale Hills catchment, developed entirely on grey shale under a temperate climate in central Pennsylvania. Fractionation of Mg isotopes during shale weathering is clearly observed at Shale Hills: $\delta^{26}\text{Mg}$ values of stream and soil pore waters are about ~0.5 ‰ to 1 ‰ lighter than the bedrock. This is consistent with previous observations that lighter Mg isotopes are preferentially released to water during silicate mineral weathering (e.g., Tipper et al., 2008). The observation of lighter Mg isotopes in soil waters should lead to a complementary heavy Mg isotope

reservoir in residual weathering products, e.g., the soils at Shale Hills. However, most soil samples also show lighter Mg isotope compositions compared to the bedrock samples, consistent with a heavy Mg isotope reservoir “missing” from the hillslope. This missing reservoir may be partially retained in the watershed in the form of old stream sediments that we observed have complementary heavy $\delta^{26}\text{Mg}$ values. The “missing” Mg is thus inferred to be particulate Mg (> micron size diameter) lost from the hillslope transect but partially retained in the valley floor alluvial sediments.

Soil samples show a clear decreasing trend of $\delta^{26}\text{Mg}$ values upward. This trend is equivalent to increasingly light Mg isotopes with increasing weathering duration. We suggest that the accumulation of lighter Mg isotopes and depletion of heavy Mg isotopes in surface soils at Shale Hills is due to i) mobilization of isotopically light Mg solute during silicate dissolution and re-precipitation as isotopically light vermiculite or HIV; ii) loss of isotopically heavy particulate Mg. Our study provides the first field evidence that changes in clay mineralogy affect the Mg isotope compositions of residual bulk soils during shale weathering, i.e. incorporation of lighter Mg into secondary vermiculite clay. Our study also demonstrates a new and important mechanism – loss of isotopically distinct fine particles -- that could drive the Mg isotope compositions of weathering residuals in an opposite direction as normally expected from silicate weathering, i.e. the residual soils at Shale Hills were driven to lighter Mg values while isotopically heavy sediments were mobilized to the valley floor and out of the catchment. Our study highlights the importance of transport of fine particles in terms of Mg isotope fractionation during shale weathering.

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Figure captions

Figure 1. Sample locations in the Shale Hills catchment (modified after Lin et al. (2006) and Ma et al. (2010; 2011a). Background yellow-brown color indicates regolith thickness and thick yellow lines indicate the outlines of the five previously identified soil series (Lin et al., 2006); grey lines indicate topographic contours (2m interval);. DC1 is the site where 24m of shale drill core was sampled and characterized as parent materials (Jin et al., 2010a). Soil cores SPRT, SPMS, and SPVF comprise a 2D planar transect. Stream sediment samples (SS) were collected behind a sediment fence that was installed in 1970s at the upstream location. Water samples include soil pore waters (sampled from lysimeter nests at the SPRT, SPMS, and SPVF locations), stream waters (sampled at the outlet of the catchment), and groundwaters (sampled from a ~3m deep well close to the stream sample location).

Figure 2. $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of Shale Hills soil, bedrock, and water samples. Duplicated measurements of the seawater standards are also shown. The mass-dependent fractionation line has a

slope of ~ 0.513 ($R^2=0.992$), similar to the average slopes of terrestrial materials reported in previous studies.

Figure 3. Measured $\delta^{26}\text{Mg}$ and Mg concentrations as a function of depth in the soil profiles of SPRT, SPMS, and SPVF. Gray closed circles represent values of two parent shale bedrock samples from the DC1 core at depth of 4 m and 6 m, respectively. The gray bars indicate the range of $\delta^{26}\text{Mg}$ and Mg wt. % in the two bedrock samples. Dashed line indicates the depth to the augering refusal. Error bars in this and subsequent plots represent 2SE.

Figure 4. Measured $\delta^{26}\text{Mg}$ and Mg concentrations as a function of depth in the stream sediment profile (SSOW). The gray bars indicate the range of $\delta^{26}\text{Mg}$ and Mg wt. % in the two bedrock samples. Dashed line indicates the depth to the augering refusal. Error bars in this and subsequent plots represent 2SE.

Figure 5. Mg mass transfer coefficients as a function of depth in the profiles of ridge top (SPRT), middle slope (SPMS), valley floor (SPVF) and stream sediment core (SS) at Shale Hills. Elemental data are from Jin et al. (2010) and Ma et al. (2011b). Error bar indicates the uncertainty of calculated mass transfer coefficients.

Figure 6. Measured $\delta^{26}\text{Mg}$ values, Mg mass transfer coefficients, and total CEC /total Mg ratios as a function of weathering durations for SPRT, SPMS, SPVF and bedrock samples at Shale Hills. Elemental concentrations are from Jin et al. (2010) and Ma et al. (2011b). Total CEC values are from Jin et al. (2010). Weathering durations are calculated from soil depth and regolith production rates determined by U-series disequilibrium in Ma et al. (2010).

Figure 7. A conceptual model showing mineral structures and Mg mobility and exchange for primary Mg-rich minerals illite and chlorite, and secondary Mg-rich mineral vermiculite. Note the different coordinate numbers for Mg ions in these minerals. It is suggested that vermiculite can trap dissolve Mg^{2+} ions with light Mg isotopic compositions from circulating soil waters in its interlayer structure, leading to lower $\delta^{26}\text{Mg}$ values in older soils with high contents of vermiculite and hydroxyl-interlayer vermiculite. The inferred “missing” heavy Mg isotope reservoir is related to the loss of particles (e.g. secondary vermiculite, fine residual illite or chlorite particles) at Shale Hills. Representative $\delta^{26}\text{Mg}$ values from Shale Hills samples are shown.

TABLES

Table 1 Mg isotopic compositions of soil, sediment, bedrock and rock standards.

Sample Name	Type	Location (Longitude/ latitude)	Depth (cm)	$\delta^{26}\text{Mg}$ (‰)	2SE	$\delta^{25}\text{Mg}$ (‰)	2SE
SPRT0010	Soil	SPRT	5	0.33	0.04	0.17	0.03
SPRT1020	Soil	W77.90633°	15	0.33	0.04	0.16	0.03
SPRT2030	Soil	N 40.66386°	25	0.34	0.04	0.18	0.03
SPMS0010	Soil	SPMS	5	0.26	0.04	0.15	0.03
SPMS1020	Soil	W77.90631°	15	0.27	0.04	0.15	0.03
SPMS2030	Soil	N40.66410°	25	0.26	0.04	0.13	0.03
SPMS3040	Soil		35	0.27	0.04	0.15	0.03
SPMS4050	Soil		45	0.33	0.04	0.16	0.03
SPMS5059	Soil		54.5	0.37	0.04	0.19	0.03
SPVF0010	Soil	SPVF	5	0.22	0.03	0.15	0.03
SPVF1020	Soil	W77.90628°	15	0.26	0.03	0.18	0.03
SPVF2030	Soil	N40.66426°	25	0.30	0.03	0.11	0.03
SPVF3040	Soil		35	0.31	0.03	0.15	0.03
SPVF4050	Soil		45	0.33	0.03	0.12	0.03
SPVF5060	Soil		55	0.29	0.03	0.13	0.03
SPVF6067	Soil		63.5	0.30	0.03	0.15	0.03
DC1-8	Bedrock	DC1	115	0.36	0.03	0.21	0.03
DC1-26	Bedrock	W77.90401°	620	0.35	0.03	0.20	0.03
DC1-26	(Duplicate)	N40.66580°		0.35	0.03	0.17	0.03
SSOW0010	Sediment	SSOW	5	0.28	0.03	0.14	0.03
SSOW1020	Sediment	W77.90626°	15	0.34	0.03	0.17	0.03
SSOW2030	Sediment	N40.66424°	25	0.29	0.03	0.14	0.03
SSOW3040	Sediment		35	0.31	0.03	0.17	0.03
SSOW4050	Sediment		45	0.36	0.03	0.18	0.03
SSOW5060	Sediment		55	0.34	0.03	0.18	0.03
SSOW6070	Sediment		65	0.38	0.03	0.20	0.03
SSOW7080	Sediment		75	0.50	0.03	0.28	0.03
SSOW8090	Sediment		85	0.50	0.03	0.22	0.03
SSOW100109	Sediment		105	0.48	0.03	0.23	0.03
KH-olivine	Standard			-0.27	0.03	-0.16	0.03
	Reference value	(Teng et al., 2010a)		-0.27	0.07	-0.14	0.04
Sco-1 Shale	Standard			-0.91	0.04	-0.48	0.03
	Reference value	(Li et al., 2010)		-0.94	0.08	-0.50	0.06

Table 2. Mg isotope compositions and concentrations of soil pore water, stream water, groundwater collected in June and December 2009.

Sample Name	Type	Depth (cm)	$\delta^{26}\text{Mg}$ (‰)	2SE	$\delta^{25}\text{Mg}$ (‰)	2SE	Mg (mg/kg) ¹
SPRT 20	Soil pore water (June)	20	-0.54	0.04	-0.29	0.03	0.55
SPRT 20	Soil pore water (Dec)		-0.59	0.03	-0.32	0.02	
SPRT 30	Soil pore water (June)	30	-0.50	0.04	-0.26	0.03	0.54
SPMS 10	Soil pore water (June)	10	-0.14	0.03	-0.05	0.03	0.82
SPMS 10	Soil pore water (Dec)		-0.20	0.03	-0.08	0.02	
SPMS 20	Soil pore water (June)	20	-0.59	0.04	-0.31	0.03	0.59
SPMS 40	Soil pore water (June)	40	-0.14	0.03	-0.08	0.03	1.8
SPMS 50	Soil pore water (June)	50	-0.24	0.04	-0.15	0.03	1.1
SPVF10	Soil pore water (June)	10	-0.62	0.03	-0.30	0.02	0.86
SPVF 20	Soil pore water (June)	20	-0.48	0.04	-0.25	0.03	1.3
SPVF 30	Soil pore water (June)	30	-0.46	0.04	-0.22	0.03	1.7
SPVF 40	Soil pore water (June)	40	-0.39	0.04	-0.21	0.03	1.6
SPVF 40	Soil pore water (Dec)		-0.42	0.03	-0.20	0.02	
SPVF 60	Soil pore water (June)	60	-0.32	0.04	-0.19	0.03	1.7
LJ09445	Stream (June)	0	-0.54	0.04	-0.27	0.03	2.5
LJ09440	Stream (June)	0	-0.51	0.03	-0.27	0.02	2.9
LJ09998	Stream (Dec)	0	-0.47	0.03	-0.27	0.03	
LJ09508	Groundwater (June)	600	-1.15	0.03	-0.58	0.02	4.0
LJ09515	Groundwater (June)	600	-1.05	0.03	-0.51	0.03	4.0
Seawater standard			-0.82	0.02	-0.44	0.02	
Seawater standard			-0.79	0.04	-0.42	0.03	
Reference value (Ling			-0.84	0.06	-0.42	0.02	

1. The precision for Mg concentrations is better than 3%; Jin et al., 2011

Table 3 Major element concentrations, cation exchange capacity (CEC), organic matter content, weathering duration and mineralogical composition of soil, sediment, and bedrock samples.

Sample Name	Type	Depth	Major chemistry					CEC		Organic matter content		Weathering duration (kyr)	XRD				
			Si	Al	Fe	Mg	Zr	CEC total (meq / kg)	CEC Mg (mmol/kg)	TOC (wt. %)	TON (wt. %)		Quartz %	Illite %	Chlorite %	Fe-Oxides %	Kaolinite %
		(cm)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(mg/k g)										
SPRT0010	Soil	5	27.49	7.2	3.76	0.51	273	43.9	1.61	1.76	0.17	5.6	49.9	29.6	5.5	2.5	2.8
SPRT1020	Soil	15	28.98	7.36	4	0.56	275	38.9	1.66	0.79	0.11	3.4					
SPRT2030	Soil	25	31.13	7.41	4.28	0.59	246	34.3	0.93	0.37	0.08	1.1	55.7	30.1	8.1	2	0.5
SPMS0010	Soil	5	29.96	6.51	2.98	0.43	351	43.1	0.92	1.07	0.12	30.7	55.1	25.4	4.8	2.1	2.7
SPMS1020	Soil	15	32.86	6.93	3.25	0.49	329	35.2	0.98	0.63	0.09	25					
SPMS2030	Soil	25	32.07	7.2	3.6	0.55	295	34.5	1.49	0.34	0.07	19.3	60.7	26.7	6.1	1.9	1.4
SPMS3040	Soil	35	31.6	7.62	3.97	0.62	288	40.5	1.75	0.41	0.07	13.6					
SPMS4050	Soil	45	31.46	8.1	4.26	0.66	277	46.3	2.71	0.22	0.07	8					
SPMS5059	Soil	54.5	30.71	8.63	4.55	0.71	266	39.9	2.61	0.11	0.06	2.6	53.6	35.5	7.1	1.7	0.9
SPVF0010	Soil	5	31.88	5.28	2.5	0.36	349	64.1	9.68	2.94	0.21	36.5	63.3	22.6	3.5	1.9	0.9
SPVF1020	Soil	15	31.83	6.88	3.31	0.52	318	52.3	9.49	0.68	0.09	30.6					
SPVF2030	Soil	25	30.2	8.63	4.08	0.72	258	55.4	10.88	0.45	0.09	24.7					
SPVF3040	Soil	35	28.33	9.05	4.45	0.78	219	62.9	12.25	0.51	0.09	18.8	43.4	47.5	8.3	0.4	0.4
SPVF4050	Soil	45	28.7	9.74	4.79	0.85	208	68.9	13.38	0.24	0.08	12.9					
SPVF5060	Soil	55	27.67	10.21	5.04	0.89	182	71.1	14.18	0.23	0.08	7.1					
SPVF6067	Soil	63.5	26.93	10.32	5.22	0.92	191	70.8	14.07	0.26	0.08	2.1	36.3	54.4	9.3	0	0
DC1-8	Bedrock	115	26.83	11.33	5.44	0.92	179					0					
DC1-26	Bedrock	620	27.25	11.06	5.97	1.05	172	76.4	19.79			0	30.1	60.3	6.9	1.6	0
SSOW0010	Sediment	5	23.52	9.79	4.58	0.57	141										
SSOW1020	Sediment	15	24.41	10.85	5.11	0.62	141										
SSOW2030	Sediment	25	25.39	10.27	5.43	0.57	148										
SSOW3040	Sediment	35	26.32	9.79	5.66	0.53	167										
SSOW4050	Sediment	45	27.49	9.26	6.86	0.53	187										
SSOW5060	Sediment	55	27.11	8.89	7.07	0.5	221										
SSOW6070	Sediment	65	27.35	9.16	6.43	0.55	202										
SSOW7080	Sediment	75	27.07	10.01	6.61	0.62	173										
SSOW8090	Sediment	85	26.46	10.59	6.55	0.61	160										
SSOW90100	Sediment	95	25.9	11.17	5.89	0.59	153										
SSOW100109	Sediment	104.5	26.18	10.85	6.63	0.58	191										

1. Data are from Jin et al. (2010) and Ma et al. (2010, 2011b) CEC: cation exchange capacity; TOC: total organic carbon; TON: total organic nitrogen; the precision for major element concentrations is better than 3%.

FIGURES

Figure 1

Figure 2

Figure 3

Fig 4

Fig. 5

Figure 6

Figure 7