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6 **Variations of Mg isotope geochemistry in soils over a Hawaiian 4 Myr chronosequence**
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45 **ABSTRACT**

46 Magnesium (Mg) isotopes fractionate during rock/mineral weathering and leaching,
47 secondary mineral neoformation, adsorption/desorption, and plant-related Mg recycling, but the
48 mechanisms and extent of fractionation are not well understood. Here, we report the fate of Mg
49 and its isotopes during weathering and soil development in the Hawaiian Islands by sampling
50 soils of varying age (0.3, 20, 150, 1,400, and 4,100 ka) in undisturbed humid rainforests.
51 Magnesium concentrations in bulk soils are variable with depth and age, ranging from 0.07 to
52 8.79 wt.%, and significant Mg depletions (up to 99%) relative to parent basalts are visible after
53 20 ka. Bulk soils display a large age-dependent range of $\delta^{26}\text{Mg}$ values ranging from -0.60 to
54 $+0.26\%$. A sequential leaching scheme showed that labile Mg is depleted whereas residual Mg is
55 enriched in isotopically heavy Mg. The two youngest soils (0.3 ka) display $\delta^{26}\text{Mg}$ value similar
56 to basalt for both labile or residual Mg, indicating either that basalt weathering causes little Mg
57 isotope fractionation or that $\delta^{26}\text{Mg}$ value is overwhelmed by the primary minerals during 0.3 ka.
58 However, in the older soils (≥ 20 ka), the $\delta^{26}\text{Mg}$ values of both labile and residual Mg vary non-
59 linearly as a function of time, with an increase in the difference between them. These variations
60 are explained by both plant-related Mg recycling and progressive mineral transformations,
61 evolving from short-range-order (SRO) minerals (allophane and ferrihydrite) to more crystalline
62 products (goethite, gibbsite and kaolin minerals). Indeed, plant-related Mg recycling causes the
63 enrichment of light Mg isotopes in the labile Mg, while crystalline secondary phases incorporate
64 more and more heavy Mg isotopes with time. These results reconcile experimental and field
65 studies and highlight a weathering control of Mg isotopes delivered to the oceans.

66

67 **Keywords:** Magnesium isotopes; Secondary minerals; Isotope fractionation; Basalt weathering;
68 Soil; Hawaii

69 1. INTRODUCTION

70 The release of cations, especially calcium (Ca) and magnesium (Mg), from silicate rocks
71 during chemical weathering is one of the most important processes controlling long-term climate
72 change, seawater chemistry and nutrient cycling in soils (Berner et al., 1983; de Villiers and
73 Nelson, 1999; Berner, 2004). Basalt weathering is important in terms of global carbon cycle
74 because it accounts for about 35% of the global CO₂ sink associated with silicate weathering
75 while basalt covers less than 5% of the overall continental area (Dessert et al., 2003). In parallel,
76 basalt weathering exports considerable amount of major and trace elements, and nutrients to the
77 ocean via river transport (Dessert et al., 2001, 2003).

78 In this context, non-traditional stable isotopes, such as lithium, calcium, and magnesium
79 isotopes, can be used to trace silicate weathering and reconstructing paleo-climate (e.g., Tipper et
80 al., 2006, 2008a; Vigier et al., 2009; Misra and Froelich, 2012; Pogge von Strandmann et al.,
81 2008, 2012, 2013; Ryu et al., 2014). However additional work is needed to provide clear
82 linkages between fractionation processes occurring in natural Earth surface systems and those
83 deduced from experimental studies. Many studies indicate that significant Mg isotope
84 fractionation occurs during rock/mineral dissolution, secondary mineral neof ormation,
85 adsorption/desorption, plant uptake/decomposition and recycling (e.g., Tipper et al., 2006,
86 2008a; Black et al, 2008; Pogge von Strandmann et al., 2008; Teng et al., 2010; Wimpenny et al.,
87 2010, 2014; Ryu et al., 2011, 2016; Bolou-Bi et al., 2010, 2012; Huang et al., 2012; Lee et al.,
88 2014; Liu et al., 2014; Opfergelt et al., 2014; Gao et al., 2018). However, reported directions of
89 Mg isotope fractionation appear contradictory. For example, dissolution experiments show that
90 light Mg isotopes are preferentially released during primary olivine dissolution (Wimpenny et
91 al., 2010), even as other studies indicate little apparent Mg isotope fractionation between solution

92 and primary phases (Ryu et al., 2016). Also some experimental studies indicate small but
93 significant isotope fractionation during preferential incorporation of light Mg isotopes into
94 secondary minerals, such as chrysotile, brucite, saponite and stevensite (Wimpenny et al., 2010;
95 Li et al., 2014; Hindshaw et al., 2020). In contrast, other phases, such as brucite, kerolite and
96 lizardite have shown preferential incorporation of heavy Mg isotopes (Wimpenny et al., 2014;
97 Ryu et al., 2016). Likewise, field studies have reported both enrichment in light and heavy Mg
98 isotopes in soil minerals. Some studies suggest that secondary minerals have heavy Mg isotope
99 compositions due to either the preferential incorporation of heavy Mg isotopes into mineral
100 lattice, or the adsorption of heavy Mg isotopes onto mineral surface/interlayer (Tipper et al.,
101 2006; Teng et al., 2010; Huang et al., 2012; Opefergelt et al., 2012; Liu et al., 2014; Gao et al.,
102 2018), but the opposite was also shown (Pogge von Strandmann et al., 2008). An experimental
103 study by Hindshaw et al. (2020) suggests that the direction of Mg isotope fractionation depends
104 on the difference in the Mg–O bond length between a crystal lattice and solution. Although the
105 number of experimental studies has increased, few investigations have focused on natural
106 weathering profiles drawn from clear geological and ecological contexts. As a consequence, we
107 lack clarity on Mg isotope fractionation during key soil forming processes.

108 Here, we examine processes responsible for Mg isotope fractionation in basaltic soils
109 collected along a well-known humid-environment chronosequence in the Hawaiian Islands (e.g.
110 Vitousek et al. 1997; Vitousek, 2004; Chadwick et al., 1999, 2009; Chorover et al., 2004;
111 Wiegand et al., 2005; Ziegler et al., 2005; Pett-Ridge et al., 2007). This chronosequence allows
112 us to better understand the fate of Mg and its isotopes from the initial stages of basalt leaching to
113 the slow accumulation of metastable secondary minerals and their eventual reorganization into
114 relatively inert secondary crystalline phases (secondary mineral formation). We also assess the

115 role of atmospheric deposition and vegetation assimilation and release of Mg. This study
116 provides new insights into understanding the behavior of Mg isotopes during basalt weathering
117 and secondary mineral transformation as a function of age as well as the biogeochemical cycle of
118 Mg closely related to the long-term CO₂ cycle.

119

120 **2. MATERIALS AND METHODS**

121 *2.1. Study area*

122 Detailed descriptions of the study area are given in previous studies (Crews et al., 1995;
123 Vitousek et al., 1997; Vitousek, 2004; Ryu et al., 2014). In short, the Hawaiian chronosequence
124 considered here varies in age from 0.3 ka to 4100 ka and has been referred to as the “Long-
125 Substrate Age Gradient (LSAG)” (Vitousek et al., 1997). All six sites where the profiles have
126 developed in lava mixed with tephra with substrate ages of 0.3, 20, 150, 1400, and 4100 ka are
127 near 1200 m elevation, receive 2500 mm annual rainfall, and have a mean annual temperature of
128 15°C. The soils and climate support rain forests composed of primarily of *Metrosideros*
129 *polymorpha* and *Cibotium spp* (Vitousek, 2004). The two youngest sites (0.3 ka; Thurston (Th)
130 and Ola’a (Ol)) are in Keanakakoi tephra derived from phreatomagmatic eruptions of tholeiitic
131 composition at the summit of Kilauea (McPhie et al., 1990; Fiske et al., 2009), while the older
132 sites (≥ 20 ka) are composed of alkali basalt, such as hawaiiite, mugearite, and their associated
133 tephra (MacDonald et al., 1983; Wright and Heltz, 1986; Wolfe and Morris, 1996). All soils are
134 located on primary shield volcano surfaces, where physical erosion and groundwater influences
135 are minimal. Although the two youngest soils are Andisols dominated by primary basaltic
136 material (glass, plagioclase, augite, olivine, magnetite, and ilmenite), primary volcanic minerals
137 and volcanic glass are absent and are replaced by non-crystalline secondary minerals in soils 20

138 ka and older (Kurtz et al., 2001). The two intermediate-age soils, 20 ka and 150 ka, are highly
139 weathered Andisols composed of chemically active metastable secondary minerals such as
140 ferrihydrite, allophane, and immogolite. The two oldest sites, 1400 ka and 4100 ka, are highly
141 weathered Ultisols and Oxisols dominated by relatively inert crystalline Al- and Fe-oxides and
142 kaolin minerals (Chadwick et al., 1999; Vitousek et al., 1997; Pett-Ridge et al., 2007).
143 Furthermore, although quartz and mica in Hawaiian soils are derived uniquely from continental
144 dust sources (Kurtz et al., 2001), only small amounts of mica may be found in the older soil
145 profiles (Ziegler et al., 2005) because dust undergoes chemical weathering in the soil
146 environment older than 150 ka, with mica weathering faster than quartz (Kurtz et al., 2001).

147

148 *2.2. Sampling and sequential leaching*

149 Soils studied here are the same as those investigated in a companion Li isotope study
150 (Ryu et al., 2014). Samples were collected from hand-dug pits to about 1 m depth except for the
151 youngest soil; Thurston (Th) is about 40 cm deep and overlies unweathered pahoehoe lava, and
152 Ola'a (Ol) is about 70 cm deep and overlies a buried soil on the ~1 ka old Kulanaokuaiki tephra
153 (Fiske et al., 2009; Fig. S1).

154 In order to distinguish the Mg isotopic composition of different Mg fractions (i.e., labile
155 versus residual Mg) in the soil samples and two USGS reference materials (BHVO-2 and BIR-
156 1), we conducted a three-step leaching and digestion; (1) MilliQ water leach (water leachate), (2)
157 1 M ammonium chloride (NH₄Cl) leach (NH₄Cl leachate), (3) 4 M acetic acid (HAc) leach (HAc
158 leachate), and (4) complete digestion of the silicate residue (residue).

159 Steps (1) to (3) define the “labile” Mg, which means the Mg released or exchanged
160 relatively easily when the soil sample is in contact with soil solution. It includes the Mg from the

161 macroporosity (water leachate), the ion-exchangeable Mg (NH₄Cl leachate), and the less
162 leachable Mg in carbonates and/or Fe-oxyhydroxides/silicate lattice (HAc leachate; Jacobson and
163 Blum, 2000; Chan and Hein, 2007; Wimpenny et al., 2014).

164 Step (4) defines the “residual” Mg, which means the Mg mainly associated with the
165 silicate minerals but also (nano)crystalline Fe- and Al-phases.

166

167 *2.3 Sample preparation and elemental analysis*

168 About 1.0 g of the soil samples was reacted with 10 mL of MilliQ water for 6 h using a
169 Thermo Scientific Vari-MixTM Test Tube Rocker. The mixture was centrifuged, and the
170 supernatant was passed through a 0.45 µm polypropylene syringe filter, dried, and re-dissolved
171 in 5% HNO₃. The residue was then reacted with 10 mL of 1 M NH₄Cl for 6 h (pH = 7) prior to
172 repeating the same procedures above. Thereafter, the residue was reacted with 10 mL of 4 M
173 HAc for 6 h (pH = 2) and repeated the same procedures above. Finally, the residue was dried and
174 a 0.1 g sub-sample was powdered and completely digested in a 5:3 mixture of HF and HNO₃.
175 Bulk soil samples crushed in a shatter box equipped with a tungsten carbide grinding container
176 were also completely digested in a 5:3 mixture of HF and HNO₃. All HF-digested samples were
177 dried, refluxed several times in 6.0 M HCl to remove fluorides, and re-dissolved in 5% HNO₃.
178 Cation and trace element concentrations were measured using a Perkin Elmer Optima 8300 ICP-
179 AES and a Thermo Elemental X-7 ICP-MS, respectively at the Korea Basic Science Institute
180 (KBSI). Repeated analyses of USGS rock standard powders (BCR-2, BHVO-2, and BIR-1)
181 yielded external reproducibilities better than ±5%.

182

183 *2.4 Magnesium isotope analysis*

184 Magnesium was separated from matrix elements using an AG-50W-X8 resin (200–400
185 mesh). After loading the sample, matrix elements were eluted with 5 mL of 0.15 M HF, followed
186 by 10 mL of the mixture of 0.5 M HCl and 95% acetone, and 8 mL of 1 M HNO₃ before
187 collecting Mg in 12 mL of 1 M HNO₃. Magnesium isotope ratios were measured using a
188 Neptune MC-ICP-MS upgraded with a large dry interface pump at the KBSI. Samples were
189 introduced using a quartz dual cyclonic spray chamber and analyzed with a standard-sample-
190 standard bracketing method. Sample intensities were matched to within 10% of the intensity of
191 the standard. Using the Jet sample cone and X-skimmer cone, the sensitivity was ~100 V/ppm on
192 mass 24 at a typical uptake rate of 100 μL/min. Prior to isotopic analysis, each sample was
193 checked for yield and the concentration of matrix elements (Al, Ca, Fe, K, Mn, Na, and Ti).
194 Yields were about 100% and the matrix concentration did not exceed 1% of the Mg
195 concentrations. The total procedural blanks were negligible with less than 3 ng of Mg. All
196 ²⁶Mg/²⁴Mg and ²⁵Mg/²⁴Mg ratios are reported in delta notation relative to DSM-3, where $\delta^x\text{Mg} =$
197 $[(^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM-3}} - 1] \times 1000$ and $x = 25$ or 26 . Samples were analyzed in
198 replicate ($n = 3 - 4$), where uncertainties are reported as two standard deviations (2σ). The long-
199 term Mg isotope measurements of three reference materials (DSM-3, CAM-1, and SRM980)
200 yielded $\delta^{26}\text{Mg}$ values of $-0.01 \pm 0.06\text{‰}$ (2σ , $n = 408$), $-2.62 \pm 0.06\text{‰}$ (2σ , $n = 404$), and $-4.32 \pm$
201 0.09‰ (2σ , $n = 249$), respectively, in good agreement with reported values (Table S1; e.g., Galy
202 et al., 2001, 2003; Tipper et al., 2008b; Huang et al., 2009; Lee et al., 2014). The chemical
203 purification, and the precision and accuracy of Mg isotope measurements have been validated
204 using the USGS powder and IAPSO seawater reference materials. BHVO-2 yielded a $\delta^{26}\text{Mg}$
205 value of $-0.20 \pm 0.07\text{‰}$ (2σ , $n = 3$), BIR-1 yielded a $\delta^{26}\text{Mg}$ value of $-0.17 \pm 0.08\text{‰}$ (2σ , $n = 4$),

206 and IAPSO yielded a $\delta^{26}\text{Mg}$ value of $-0.83 \pm 0.04\%$ (2σ , $n = 36$), consistent with reported values
207 (Table S1; Teng, 2017 and references therein).

208

209 2.5. Calculations of Mg gain or loss

210 The relative gain ($\tau_{j,w} > 0$) or loss ($\tau_{j,w} < 0$) of Mg with depth at each weathering profile
211 was estimated as follows (Brimhall and Dietrich, 1987; Chadwick et al., 1990):

$$212 \quad \tau_{j,w} = \frac{C_{j,w} \times C_{i,p}}{C_{j,p} \times C_{i,w}} - 1, \quad (1)$$

213 where C is the concentration of an element, w and p refer to the weathered and parent materials,
214 respectively, and i and j refer to the immobile and mobile elements, respectively. Kurtz et al.
215 (2000) performed comprehensive analyses of a wide range of trace metals in Hawaiian soils and
216 found that that Nb and Ta are the least mobile elements in these soils compared to traditionally
217 known immobile elements, such as Th, Zr and Al. Thus, for these calculations, we used Nb as
218 the index element.

219 The depth-integrated τ_{Mg} allows us to calculate the total loss or gain of Mg and other
220 elements over the timescale of each profile as follows:

$$221 \quad \tau_{int} = \frac{\sum(\tau_h \cdot \rho_h \cdot z_h)}{\sum(\rho_h \cdot z_h)}, \quad (2)$$

222 where τ_h is the $\tau_{j,w}$ value of each horizon (h ; Eq. (1)), z_h is horizon thickness, and ρ_h is horizon
223 density taken from Pett-Ridge et al. (2007).

224

225 2.6. Quantifying relative contribution of each Mg source

226 Previous work has shown that with age basalt weathering becomes relatively less
 227 important to the soil budget and atmospheric inputs become more important, in particular for Sr
 228 and Nd (Vitousek et al., 1997; Kurtz et al., 2001; Chadwick et al., 2009). However, a recent
 229 study also showed that atmospheric input is not a primary control of Li isotopic compositions in
 230 the Hawaiian soils (Ryu et al., 2014). It is possible to estimate the relative contribution from the
 231 various Mg sources for each studied soil profile, as has been done for U and Li (Pett-Ridge et al.,
 232 2007; Ryu et al., 2014). The Mg contribution from Asian dust can be estimated because the
 233 elemental composition of the dust in Hawaii has remained relatively invariant during the past
 234 4100 ka (Kyte et al., 1993). Thus,

$$235 \quad Mg_{dust} = C_{dust}^{Mg} \cdot F_{dust} \cdot t, \quad (3)$$

236 where C_{dust}^{Mg} is the average Mg concentration in either upper continental crust (UCC; [Mg] = 1.5
 237 wt.%; Rudnick and Gao, 2014) or in loess ([Mg] = 0.58 wt.%; Li et al., 2010), F_{dust} is the average
 238 long-term dust deposition rate for Hawaii (30 mg/cm²/ka for the younger soils (<20 ka) and 125
 239 mg/cm²/ka for the older soils (≥20 ka); Kurtz et al., 2001), and t is the age of the soil site.

240 Similarly, the atmospheric Mg input linked to rainwater can be calculated as follows:

$$241 \quad Mg_{rainwater} = C_{rainwater}^{Mg} \cdot MAP \cdot t, \quad (4)$$

242 where $C_{rainwater}^{Mg}$ is the Mg concentration in Hawaiian rain (5.83×10^{-2} μg/cm³ at Thurston (Hawai'i)
 243 and 1.43×10^{-1} μg/cm³ at Kokee (Kauai); Carrillo et al., 2002) and MAP is the Mean Annual
 244 Precipitation (2500 mm/yr). Since the sites exhibit minimal physical erosion, the overall
 245 weathering thickness should be directly linked to their age (e.g., Pett-Ridge et al., 2007). In this
 246 context, the quantity of Mg released from the parent basalt can be estimated as follows:

$$247 \quad Mg_{basalt} = C_{basalt}^{Mg} \cdot z_t \cdot S_c \cdot \rho_{basalt}, \quad (5)$$

248 where C_{basalt}^{Mg} is the Mg concentration in basalt (6.1 wt.% in tholeiitic basalt for the two youngest
 249 sites, and 3.3, 2.2, 6.1 and 4.9 wt.% in alkali basalt for the older sites, respectively; Ziegler et al.,
 250 2005), z_t is the total regolith thickness (m), ρ_{basalt} is the average density of basalt including void
 251 and infilled vesiculated tephra (1.25 g/cm³; Chadwick et al., 2003), and S_c is the collapse factor.
 252 Total regolith thickness is difficult to determine even in cases where a backhoe or drill is
 253 available because of local variability related to void spaces and hydrological permeability
 254 (Goodfellow et al., 2013). We calculated values representing soil horizons to 1-m depth.

255 Eqs. (3) – (5) allow us to calculate the total Mg in the regolith, which is the sum of Mg
 256 released from the parent basalt, with Mg added from dust and rainwater along the course of the
 257 regolith development as follows:

$$258 \quad Mg_{total} = Mg_{basalt} + Mg_{dust} + Mg_{rainwater} \quad (6)$$

259 It is possible to compare Mg_{total} corresponding to the regolith residence time, to the Mg
 260 currently present in the regolith, $Mg_{present}$ (i.e. depth-integrated Mg mass per unit area). The
 261 difference between these two parameters allows the total Mg exported by the profile Mg_{loss} to be
 262 evaluated as follows:

$$263 \quad Mg_{present} = \sum_h (\rho_h \cdot z_h \cdot C_h^{Mg}) \quad (7)$$

$$264 \quad Mg_{loss} (\%) = \left[Mg_{present} / (Mg_{basalt} + Mg_{dust} + Mg_{rainwater}) - 1 \right] \times 100, \quad (8)$$

265 where C_h^{Mg} is the Mg concentration in the each soil horizon. All results are given in Table S3.

266

267 3. RESULTS

268 3.1. Mg concentrations and Mg isotope compositions in bulk soils

269 Tables 1 and 2 present all Mg isotope data, along with elemental geochemistry reported
270 in Ryu et al. (2014). Magnesium concentrations ([Mg]) of the bulk soil are variable with depth
271 and age, ranging from 0.07 to 8.79 wt.% (Fig. 1). At the 0.3 ka sites (Th and Ol), [Mg] in the
272 organic-rich surface horizons is 0.52 and 1.08 wt.%, respectively, and abruptly increases to about
273 6.2 wt.% for the deeper horizons, similar to tholeiitic basalt (6.1 wt.%; Ziegler et al., 2005). At
274 the 20 ka site, [Mg] is relatively low for the upper horizons (0.14 wt.% on average; 0–27 cm)
275 and gradually increases to 1.66 wt.% in the deeper horizons (1.66 wt.%; 94–110 cm), which is
276 much lower than that of alkali basalt (2.3 wt.%; Chadwick et al., 2003). At the three oldest sites
277 (150, 1400, and 4100 ka), [Mg] is quite low, ranging from 0.07 to 0.71 wt.%, with an average of
278 0.25 ± 0.33 wt.% (2σ , $n=36$).

279 The $\delta^{26}\text{Mg}$ values of bulk soil samples span a significant range, from -0.60 to $+0.26\text{‰}$
280 ($-0.16 \pm 0.36\text{‰}$, 2σ , $n=36$; Table 1 and Fig. 2). The youngest sites (0.3 ka; Th and Ol) exhibit
281 little variation in $\delta^{26}\text{Mg}$ ($-0.27 \pm 0.09\text{‰}$, 2σ , $n=13$), in good agreement with reported $\delta^{26}\text{Mg}$ for
282 the Hawaiian basalts ($-0.26 \pm 0.06\text{‰}$, 2σ , $n=11$; Zhong et al., 2017) and for fresh oceanic basalts
283 more generally ($-0.26 \pm 0.07\text{‰}$, 2σ , $n=110$; Teng et al., 2010). At the 20 ka site, $\delta^{26}\text{Mg}$ values
284 range from -0.44‰ for the organic-rich surface sample to -0.15‰ for the subsurface samples
285 with an average of $-0.26 \pm 0.26\text{‰}$ (2σ , $n=4$). At the 150 ka site, $\delta^{26}\text{Mg}$ values range from -0.60‰
286 for the organic-rich surface sample to -0.01‰ for the subsurface samples with an average of
287 $-0.12 \pm 0.47\text{‰}$ (2σ , $n=6$). At the 1400 ka site, $\delta^{26}\text{Mg}$ value is the lowest at the organic-rich
288 surface (-0.55‰), and increases up to 0.26‰ for the subsurface samples with an average of
289 $-0.04 \pm 0.54\text{‰}$ (2σ , $n=6$). At the oldest site (4100 ka), $\delta^{26}\text{Mg}$ values are relatively consistent,
290 ranging from -0.11 to $+0.05\text{‰}$, with an average $-0.05 \pm 0.13\text{‰}$ (2σ , $n=6$), regardless of depth.

291

292 *3.2. Mg isotope compositions in sequential leachates and residue*

293 In the various leachates, Mg displays a wide range of $\delta^{26}\text{Mg}$ values, from -1.01 to
294 $+0.06\text{‰}$ ($-0.37\pm 0.53\text{‰}$, 2σ , $n=58$; Table 2 and Fig. 2). The water and NH_4Cl leachates have
295 similar $\delta^{26}\text{Mg}$ values, within uncertainty, of $-0.37\pm 0.53\text{‰}$ (2σ , $n=23$) and $-0.28\pm 0.49\text{‰}$ (2σ ,
296 $n=14$), respectively. The HAc leachate displays relatively lighter $\delta^{26}\text{Mg}$ values of $-0.42\pm 0.53\text{‰}$
297 (2σ , $n=21$). The residual Mg, With the exception of the organic-rich surface samples, residual
298 Mg at the sites older than 20 ka, showed much heavier $\delta^{26}\text{Mg}$ values of $+0.02\pm 0.48\text{‰}$ (2σ , $n=25$)
299 (Table 2). We define a “labile” pool as the sum of Mg released during the water, NH_4Cl and HAc
300 leaches, which shows that the two youngest sites (0.3 ka; Th and Ol), display a labile Mg with an
301 average $\delta^{26}\text{Mg}$ value of $-0.18\pm 0.13\text{‰}$, (2σ , $n=31$). The residues (‘residual’ Mg) show an average
302 $\delta^{26}\text{Mg}$ value of $-0.23\pm 0.05\text{‰}$ (2σ , $n=11$) that is consistent with Hawaiian basalt within
303 uncertainties.

304 In contrast, at the 20 ka site, the ‘labile’ Mg in the organic-rich surface sample becomes
305 depleted in heavy Mg isotopes ($-0.49\pm 0.23\text{‰}$, 2σ , $n=3$) compared to the residual Mg (-0.07‰ ,
306 $n=1$). In the subsurface samples of the same site, both labile and residual Mg display similar
307 $\delta^{26}\text{Mg}$ values of $-0.01\pm 0.21\text{‰}$ (2σ , $n=2$) and $-0.03\pm 0.08\text{‰}$ (2σ , $n=3$), respectively.

308 Interestingly, at the sites older than 20 ka, the labile Mg from the organic-rich surface
309 samples display much lighter $\delta^{26}\text{Mg}$ values ($-0.59\pm 0.31\text{‰}$, 2σ , $n=15$) compared to basalts. For
310 the subsurface samples at the sites older than 150 ka, the residual Mg becomes enriched in heavy
311 Mg isotopes ($+0.24\pm 0.24\text{‰}$, 2σ , $n=13$) compared to the labile Mg ($-0.59\pm 0.31\text{‰}$, 2σ , $n=15$).

312

313 **4. DISCUSSION**

314 *4.1. Variations of Mg concentrations in soils*

315 Figure 1 shows the depth variations of [Mg] in all soil profiles. In the organic-rich surface
316 horizons, τ_{Mg} decreases from -18% to -99% with age, indicating progressive loss of Mg during
317 pedogenesis. In the two youngest soils, the organic-rich surface is already depleted by up to 29%
318 in Mg compared to parent basalt. This could be partly explained by the dilution by soil organic
319 matter (SOM) due to the high SOM content of the 0–3 cm depth sample (56 wt.%) (Ziegler et al.,
320 2005). Another possibility is that Mg released from basalt leaching and/or from decomposition of
321 plant would move deeper into the profile or be lost because Mg is highly mobile and water-
322 soluble. Below 12 cm depth in the two youngest soils (0.3 ka), τ_{Mg} turns into positive, indicating
323 the enrichment relative to the surface and the relative gain of Mg compared to basalt. This
324 feature is likely the result of the surface Mg moving deeper into the profile. At the sites older
325 than 0.3 ka, τ_{Mg} abruptly decreased near -100% compared to the 0.3 ka sites due to the
326 significant consumption of primary minerals by 20 ka (Vitousek et al., 1997). In contrast, both
327 [Al] and [Fe] increase with depth as well as age (Fig. 1) due to residual enrichment and
328 redistributions. These metals are more strongly retained during progressive mineral
329 transformations starting with the synthesis of metastable SRO minerals and followed by their
330 transformation into relatively inert secondary minerals. Although SRO minerals (e.g., allophane,
331 imogolite and ferrihydrite) and sesquioxides (hematite and goethite) replaced primary minerals
332 during the first 20 ka (Chorover et al., 1999) with large specific surface areas of 600 m²/g (Hall
333 et al., 1985) and 120 m²/g (Schwertmann and Taylor, 1989), respectively, only a little Mg was
334 trapped within aggregates formed by association of SRO and organic matter (Opfergelt et al.,
335 2014). At the three older sites (150, 1400 and 4100 ka), τ_{Mg} is close to -100% at all depths
336 although the contents of poorly crystalline total (gibbsite and poorly crystalline kaolin minerals)

337 and kaolin minerals (kaolinite and halloysite) significantly increase (Ziegler et al., 2005).
338 Overall, most of Mg released from basalt leaching was lost (up to 100%) in the soils older than
339 0.3 ka and only a small amount of the remaining Mg was either trapped within aggregates
340 formed by association of secondary phases and organic matter (Opfergelt et al., 2014) or
341 incorporated into the octahedral sites of secondary phases.

342 Depth-integrated τ_{Mg} (τ_{int}^{Mg}) values allow us to investigate the variations of Mg along the
343 LSAG (Fig. 3). As previously described in Ryu et al. (2014), τ_{int} for alkali elements (Na and K)
344 are negative at all sites and the older soils (≥ 20 ka) display average τ_{int} of close to -100% ,
345 indicating that both Na and K are completely lost after 20 ka (Vitousek et al., 1997). In contrast,
346 τ_{int} for alkaline earth elements (Sr and Mg) are positive at the two youngest sites (0.3 ka).
347 Interestingly, at the 20 ka site τ_{int}^{Mg} is relatively high compared to Na, K, and Sr, similar to τ_{int}^{Li}
348 (Ryu et al., 2014). This relatively high τ_{int}^{Mg} relative to Na, K and Sr at the 20 ka could be due to
349 the fact that the surface 25 cm was deposited by renewed eruptions about 5 ka at the 20 ka site
350 (Chadwick et al., 2009) and/or to the lower mobility of Mg (compared to alkali elements) during
351 mineral leaching. For the older sites (≥ 150 ka), τ_{int}^{Mg} is close to -100% , indicating that secondary
352 phases do not retain Mg during neoformation, in contrast to Li which was significantly retained
353 by crystalline phases (e.g., kaolin minerals; Ryu et al., 2014). Previous studies showed that
354 gibbsite and kaolinite contain small amount of Mg (typically $< \sim 0.02$ wt.%) (Peskleway et al.,
355 2003; Mermut and Cano, 2001).

356 Previous works have shown that with age basalt leaching becomes relatively less
357 important to the soil budget for several elements, such as Sr and Si, and atmospheric inputs (dust
358 and rainwater) become more important (Kurtz et al., 2001; Ziegler et al., 2005; Chadwick et al.,

359 2009). However, a recent Li isotope study showed that the relative proportion of each Li source
360 (basalt, dust and precipitation) is 80–100%, 6–20%, and 0.8%, respectively (Ryu et al., 2014),
361 indicating a major contribution of basalt weathering to the Li budget that is significantly retained
362 in secondary phases, in particular in kaolin minerals (kaolinite and halloysite). Using Eqs. (3) –
363 (8) above, we calculated the contribution of each Mg source to the soil Mg budget and Mg loss
364 (Fig. S2 and Table S3). The results show that the parent basalt provided between 78% and 100%
365 of Mg_{total} and dust becomes significant from 150 ka (6%) and reached at maximum 22% of
366 Mg_{total} at 4100 ka. It is interesting to note that although the impact of dust input on the Sr budget
367 is significant at 150 ka (Stewart et al., 2001), it is not the case in the Mg budget because dust is
368 highly depleted in Mg compared to basalt (Kurtz et al., 2001), and because most of Mg at the
369 older sites (≥ 20 ka) are lost due to weathering, dissolution and leaching by soil waters (Table
370 S3).

371

372 4.2. Magnesium isotopic compositions of 'labile' Mg

373 A sequential leaching of USGS reference materials (BHVO-2 and BIR-1) showed that
374 water leachate yielded lighter $\delta^{26}Mg$ values compared to the other leachates, indicating water-
375 soluble Mg is depleted in heavy Mg isotopes (Table S1). However, as shown in section 3.2,
376 Hawaiian soil samples showed that the water and NH_4Cl leachates have similar $\delta^{26}Mg$ values, of
377 which the 0.3 ka site samples have $\delta^{26}Mg$ values of $-0.20 \pm 0.11\text{‰}$ (2σ , $n=9$) and $-0.11 \pm 0.11\text{‰}$
378 (2σ , $n=7$), respectively. Although it is difficult to compare them to soil samples older than 20 ka
379 due to a limited data, both leachates also show similar $\delta^{26}Mg$ values within uncertainties (Table
380 2). This result is consistent with previous work showing that water and exchangeable fractions
381 have similar isotopic compositions for Ca, Sr, and Ba isotope systems (Bullen and Chadwick,

382 2016). Thus, the water and NH₄Cl leachates together are hereafter referred to ‘exchangeable
383 Mg’. Previous studies have shown that exchangeable Mg in volcanic soils (Opfergelt et al.,
384 2014), clay minerals (Wimpenny et al., 2014) and paddy soils (Gao et al., 2018) leached by
385 either NH₄Ac or NH₄Cl are depleted in heavy Mg isotopes compared to bulk samples, suggesting
386 that the isotopic composition of exchangeable Mg is likely to reflect either the fluid phases in
387 which the sample last equilibrated (Wimpenny et al., 2014; Gao et al., 2018) or the mixture of
388 different Mg sources (sea spray and organic matter) as well as the possible effects of sorption
389 (Opfergelt et al., 2014). However, exchangeable Mg in the Hawaiian soil samples are enriched in
390 either heavy Mg isotopes at the 0.3 ka sites or depleted at the sites older than 20 ka. We will
391 discuss the processes controlling the isotopic composition of exchangeable Mg in a later section.

392 The HAc leachates have Mg isotopic composition either similar to or a bit more depleted
393 in heavy Mg isotopes compared to exchangeable Mg, of which the 0.3 ka site samples have
394 $\delta^{26}\text{Mg}$ value of $-0.18 \pm 0.09\text{‰}$ (2σ , $n=9$) and the samples at the older sites (≥ 20 ka) have $\delta^{26}\text{Mg}$
395 value of $-0.67 \pm 0.35\text{‰}$ (2σ , $n=9$). However, a previous study found that the HAc leachates from
396 clay minerals were relatively enriched in heavy Mg isotopes (Wimpenny et al., 2014), suggesting
397 that while the HAc leach mostly accounts for either ion-exchangeable Mg, it may also remove
398 other easily leachable phases (carbonates or Fe-oxyhydroxides; Jacobson and Blum, 2000; Chan
399 and Hein, 2007) or cause some breakdown of the mineral lattice (Jacobson and Blum, 2000).
400 Because the Hawaiian soils we sampled contain no pedogenic carbonates (Vitousek et al., 1997;
401 Chadwick et al., 2009; Ziegler et al., 2005), the Mg isotopic composition of the HAc leachates
402 would reflect less labile, more strongly bound Mg onto either surface complexes of secondary
403 phase (SRO) and soil organic matter (SOM) and/or Fe-oxyhydroxides. We will discuss the
404 processes controlling the isotopic composition of Mg from HAc leachates in a later section.

405

406 *4.2.1. Behavior of Mg isotopes in the organic-rich surface soil*

407 Although simple mass balance indicates that the contribution of basalt weathering to the
408 soil Mg budget is dominant, the contribution of other sources, such as dust, rainwater and plants,
409 on Mg isotopic compositions in the surface samples (O horizon; < 6 cm except for 20 ka site)
410 could be significant because [Mg] is quite depleted (Fig. 1). Figure 4a shows Mg isotope
411 variations in the organic-rich surface soil as a function of age. The $\delta^{26}\text{Mg}$ values of 'labile' Mg
412 (released by water, NH_4Cl and HAc leach, as explained in section 2.2) in the surface samples
413 range from $-0.88 \pm 0.24\text{‰}$ (2σ , $n=3$) at the 150 ka site to $-0.23 \pm 0.13\text{‰}$ (2σ , $n=6$) at the 0.3 ka
414 sites. The HAc leachates display much lighter $\delta^{26}\text{Mg}$ values at the sites older than 0.3 ka (Table
415 2). Although the 'labile' Mg is depleted in light Mg isotopes, previous studies have shown that
416 labile Mg can be isotopically depleted (Opfergelt et al., 2012; Wimpenny et al., 2014) or
417 enriched in heavy Mg isotopes (Huang et al., 2012; Pogge Von Strandmann et al., 2012). At the
418 0.3 ka sites, $\delta^{26}\text{Mg}$ values of all labile Mg are similar to that of Hawaiian basalt within errors.
419 Because Mg is an essential nutrient for plant growth, plants play an important role of its
420 recycling in the soil system, especially at the surface, as plants take up and release Mg during the
421 growth and decay, respectively. Both the organic-rich surface soils and labile fractions showed
422 an enrichment of K relative to Na, when compared to K/Na ratios of basalt (0.24-0.39; Ziegler et
423 al., 2005) and rainfall (0.05-0.18; Bern et al., 2015), suggesting that vegetation is transporting
424 biologically important elements to the surface (since Hawaiian plants have highly enriched K/Na
425 ratios (Trostle, 2014)). Plants preferentially accumulate heavy Mg isotopes in their tissues,
426 resulting in soil water depleted in heavy Mg isotopes (Black et al., 2008; Bolou-Bi et al., 2010,
427 2012). Since we did not detect Mg isotope fractionation of the 'labile' Mg in the O horizon at the

428 two youngest sites, we suspect that biological fractionation is being masked by the high Mg
429 supply from congruent basalt weathering. In addition, these young soils only a small amount of
430 the primary minerals have transformed to secondary clays (e.g., Chorover et al., 2004; Ziegler et
431 al., 2005); as a consequence, the residual Mg displays a $\delta^{26}\text{Mg}$ value of $-0.20\pm 0.01\text{‰}$ (2σ , $n=2$)
432 similar to Hawaiian basalt.

433 At the older sites (>0.3 ka), $\delta^{26}\text{Mg}$ values of labile Mg in the organic-rich surface samples
434 decrease from $-0.49\pm 0.23\text{‰}$ (2σ , $n=3$) to $-0.70\pm 0.24\text{‰}$ (2σ , $n=2$) with age (Fig. 4a). The HAc
435 leachates display lower $\delta^{26}\text{Mg}$ values than both water and NH_4Cl leachates (i.e., exchangeable
436 Mg). This suggests that less labile Mg strongly bound onto either the complexes of secondary
437 phase and soil organic matter (SOM) and/or Fe-oxyhydroxides is depleted in heavy Mg isotopes.
438 At the sites older than 20 ka, $\delta^{26}\text{Mg}$ values of the 'labile' Mg is variable, of which water-soluble
439 Mg yields $\delta^{26}\text{Mg}$ values similar to that of seawater ($-0.83\pm 0.09\text{‰}$, 2σ ; Ling et al., 2011). This
440 suggests substantial contribution of dilute rainwater Mg to this labile pool. Nonetheless, we
441 could not exclude the effect of plant biocycling of Mg because both plant uptake and secondary
442 mineral formation causes soil water to be depleted in isotopically heavy Mg. On the other hand,
443 $\delta^{26}\text{Mg}$ values of residual Mg in the surface samples are quite variable, ranging from -0.44 to
444 $+0.19\text{‰}$. All these surface samples mainly contain SOM with little secondary phases (Table S2;
445 Ziegler et al., 2005). Previous studies have shown that the top 5 cm of the soil profiles exhibit a
446 shift toward more negative $\delta^{30}\text{Si}$ values due to plant-related Si uptake and phytolith precipitation
447 (recycled biogenic silica) in the topsoil (Derry et al., 2005; Ziegler et al., 2005). Likewise, a shift
448 toward more positive $\delta^{26}\text{Mg}$ values in the organic-rich surface samples is likely to be plant-
449 related Mg uptake and litterfall decomposition. Indeed, previous studies have shown that plants
450 (e.g., particularly roots (Bolou-Bi et al., 2012) and aboveground vegetation (Trostle, 2014)) can

451 be enriched in heavy Mg isotopes. However, more investigations are needed to confirm it in the
452 case of these Hawaiian ecosystems.

453

454 *4.2.2. The impact of vegetation on the labile Mg*

455 At the two youngest sites, the 'labile' Mg of the subsurface soils display $\delta^{26}\text{Mg}$ values
456 ranging from -0.29 to -0.02‰ , with an average of $-0.17 \pm 0.12\text{‰}$ (2σ , $n=25$). Furthermore, the
457 water, NH_4Cl and HAc leachates have similar average $\delta^{26}\text{Mg}$ values of -0.20‰ , -0.11‰ , and
458 -0.18‰ , respectively (Table 2). The fact that all the leachates are close to the Hawaiian basalts
459 is likely due to the large concentration of Mg supplied by congruent basalt weathering, which
460 buffers the effect of Mg isotope fractionation by plants. An alternative is that the degree of Mg
461 isotope fractionation by Hawaiian plants may not be as large as what is known for
462 granite/sandstone-grown plants (Bolou-Bi et al., 2012), but we consider this explanation unlikely
463 because hydroponic experimental approaches and adsorption on organics also demonstrated
464 strong isotope fractionations (up to $+1.66\text{‰}$; Bolou-Bi et al., 2010, 2012; Black et al., 2008).

465 At the 20 ka site, water leachates of two subsurface samples have average $\delta^{26}\text{Mg}$ value of
466 $-0.01 \pm 0.21\text{‰}$ (2σ , $n=2$), ranging from -0.08 to $+0.06\text{‰}$. This indicates that the solution (i.e.,
467 soil water) is enriched in isotopically heavy Mg compared to Hawaiian basalt or rainwater (Fig. 4
468 and Table 2) and therefore a simple mixing of these two sources (basalt dissolution and rain)
469 cannot explain the isotopic values. In contrast, it has been shown that litterfall supplies organic
470 matter that is a key constituent of the soil exchange complex and thus a potential sink for Mg
471 (Bolou-Bi et al., 2010, 2012; Opfergelt et al., 2014). Therefore, these results suggest that, since
472 litter decomposition could significantly affect the Mg biogeochemical cycle, it could also explain

473 the shift towards heavy $\delta^{26}\text{Mg}$ of the exchangeable or labile fraction (Bolou-Bi et al., 2012;
474 Opfergelt et al., 2014).

475 At the older sites ($\geq 20\text{ka}$), despite limited data, Mg isotope variations of the labile pool
476 are similar to the ones observed in the O horizon, as discussed above (Fig. 4). The $\delta^{26}\text{Mg}$ values
477 of the 'labile' Mg range from -0.89 to $+0.06\text{‰}$, with an average of $-0.52 \pm 0.49\text{‰}$ (2σ , $n=17$;
478 Table 2). The water and NH_4Cl leachates (exchangeable Mg) have average $\delta^{26}\text{Mg}$ value of
479 $-0.45 \pm 0.56\text{‰}$ (2σ , $n=10$), slightly heavier than the HAc leachate ($-0.63 \pm 0.28\text{‰}$, 2σ , $n=7$). This
480 is much heavier than local rainwater and therefore these variations can also be partly attributed to
481 downward migration of dissolved organic matter and the plant-related Mg redistribution (Figs. 4
482 and 5), as evidenced in previous studies (e.g. Marin-Spiotta et al., 2011; Kramer et al., 2012;
483 Bullen and Chadwick, 2016). Furthermore, it cannot be explained by the mixing between local
484 rainwater and congruent dissolution of basalt because primary minerals were completely
485 consumed before 20 ka (Vitousek et al., 1997; Kennedy et al., 1998). It is possible that Mg
486 isotope variations of the labile Mg at the older sites ($\geq 20\text{ka}$) may reflect the plant-related Mg
487 recycling of different tissues of plants with different Mg isotopic compositions (Bolou-Bi et al.,
488 2012). Indeed, plants drawing upon high levels of available nutrients in fertile sites (young- to
489 intermediate-aged sites) produce tissues with relatively high nutrient concentration and
490 decompose more rapidly than those from infertile sites (older sites; Vitousek et al., 1997); This
491 was shown for Ca isotopes (Wiegand et al., 2005). Further investigations are needed to quantify
492 more precisely Mg isotope fractionation by biological Mg recycling in the soil system, but this
493 study indicates that when the concentration of Mg is relatively low due to little basalt weathering
494 input, the isotopic composition of labile Mg is more likely to be influenced by plant-related Mg
495 recycling rather than local rainwater.

496

497 *4.3. Different behavior of Mg isotopes in the residual Mg*

498 Contrary to labile Mg, most of residual Mg plotted outside of a mixing plot, indicating
499 other processes, such as basalt weathering and secondary phase formation, may control their Mg
500 isotopic compositions (Fig. 5). In following sections, we discuss the mechanisms involved in
501 setting the isotopic signal in the residual Mg.

502

503 *4.3.1. Basalt weathering*

504 We don't fully understand the controls on Mg isotope fractionation during weathering.
505 Two experimental studies have concluded that silicate dissolution causes dissolved phases to
506 have different Mg isotope composition compared to parent mineral/rock due to either isotope
507 fractionation or conservative mixing (Wimpenny et al., 2010; Ryu et al., 2011, 2016). For the
508 Hawaiian LSAG sites, other isotope systems, such as Si and Li isotopes (Ziegler et al., 2005;
509 Ryu et al., 2014), have revealed that basalt leaching does not fractionate those isotopes at the 0.3
510 ka sites. Therefore, the behavior of Mg isotopes at the two youngest sites provide a baseline for
511 evaluating Mg isotope fractionation during progressive basalt dissolution. For subsurface
512 samples at the 0.3 ka sites, the differences in $\delta^{26}\text{Mg}$ values between all labile Mg and bulk basalt
513 ($\Delta^{26}\text{Mg}_{\text{labile Mg-basalt}}$) range from -0.02 to $+0.25\text{‰}$, with an average of $+0.10 \pm 0.15\text{‰}$ (2σ , $n=13$) at
514 the Th site and of $+0.10 \pm 0.09\text{‰}$ (2σ , $n=12$) at the Ol site (Table 2 and Fig. 4b). Likewise,
515 $\Delta^{26}\text{Mg}_{\text{residual Mg-basalt}}$ ranges from 0.00 to $+0.07\text{‰}$, with an average of $+0.04 \pm 0.04\text{‰}$ (2σ , $n=5$) at
516 the Th site and of $+0.04 \pm 0.06\text{‰}$ (2σ , $n=4$) at the Ol site. Although labile Mg has a slightly heavy
517 $\delta^{26}\text{Mg}$ value compared to bulk basalt, all results highlight that basalt weathering does not
518 fractionate Mg isotopes. Secondary mineral phases in these soils (up to 18 wt.% of SRO minerals

519 and 13 wt.% of poorly crystalline; Ziegler et al., 2005) have little effect on Mg isotopic
520 compositions of both labile and residual Mg, which seem to be set by the basalt isotopic
521 signature. In short, no difference in $\delta^{26}\text{Mg}$ values between soil and basalt at the two youngest
522 sites confirms that Mg isotope fractionation is negligible during basalt weathering under natural
523 conditions. Fractionation processes are imposed by soil and ecosystem processes acting on the
524 Mg once it is released from rock minerals.

525

526 *4.3.2. Secondary mineral formation*

527 As elements are being leached from basalt, the remaining element configurations become
528 more stable: soil minerals evolve first to SRO minerals (e.g., allophane and ferrihydrite),
529 sesquioxides (hematite and goethite), and then to crystalline products, such as goethite, gibbsite
530 and kaolin minerals (Vitousek et al., 1997; Chorover et al. 2004; Ziegler et al., 2005). To date,
531 although many experimental and field studies have investigated Mg isotope fractionation during
532 secondary mineral formation, the reported directions are not yet clear (e.g., Wimpenny et al.,
533 2010, 2014; Huang et al., 2012; Liu et al., 2014; Opfergelt et al., 2014; Ryu et al., 2016; Gao et
534 al., 2018; Hindshaw et al., 2020). As detailed below, our results for the Hawaiian soils are
535 consistent with enrichments in heavy isotopes during secondary phases formation.

536 First, at the 20 ka site, the soils contain mostly SOM, chemically active SRO minerals
537 (allophane and ferrihydrite) and sesquioxide phases (goethite and hematite), in which SRO
538 minerals combined with SOM could adsorb labile Mg onto their surfaces (Chorover et al., 2004),
539 implying that the complexes of SRO minerals combined with SOM control the Mg retention
540 capacity on the soil exchange complex. As discussed in section 4.4.2, the two water leachates
541 significantly enriched in heavy Mg isotopes ($-0.01 \pm 0.21\%$, 2σ , $n=2$) compared to Hawaiian

542 basalt or rainwater likely reflect plant recycling. However, we cannot exclude the possibility that
543 Mg isotope fractionation occurred during adsorption onto oxides – we did not conduct Mg
544 isotope sorption experiments to evaluate that possibility. Furthermore, residual Mg in the
545 subsurface samples at the 20 ka site showed much heavier $\delta^{26}\text{Mg}$ values of $-0.03 \pm 0.08\text{‰}$ (2σ ,
546 $n=3$) compared to bulk basalt (Figs. 2c & 4b and Table 2). Although Opfergelt et al. (2014)
547 suggested that Mg cannot be easily incorporated into the octahedral sites of SRO minerals
548 (allophane), other studies showed that Mg in the SRO extraction through the treatment with
549 oxalate in the dry soils on Kohala displayed much heavier $\delta^{26}\text{Mg}$ values compared to Hawaiian
550 basalt (Trostle, 2014) and that $\delta^{26}\text{Mg}$ in bauxites correlates with gibbsite abundance (Liu et al.,
551 2014), indicating that either nanocrystalline (SRO) and/or crystalline Fe- and Al-phases (i.e.
552 goethite/hematite and gibbsite) may be responsible for enriched heavy Mg isotopes in residual
553 Mg. Changes in bond lengths and vibrational frequencies in the octahedral sheets affect isotope
554 fractionation (Wang et al., 2017) as the crystal structure distorts to accommodate an ion with a
555 different charge and/or radius (Laurora et al., 2011; Michalski et al., 2015). Therefore, during the
556 substitution of octahedrally coordinated Fe by Mg in goethite/hematite, the bond length from
557 substituting elements can be approximated as the sum of the ionic radii of the cation and of the 6-
558 fold coordination O^{2-} anion (Shannon, 1976) even if bond lengths are not always accurately
559 known. For example, because the ionic radii of octahedral Mg^{2+} (0.72 Å) and Fe^{3+} (0.645 Å) are
560 slightly different (Shannon, 1976), the average Mg–O bond length in goethite (~ 2.095 Å) is
561 longer than the average Fe–O bond length (~ 2.02 Å; Changela et al., 2012) through cation
562 substitution, which is also longer than the average Mg–O bond length in water (~ 2.07 Å; Carugo
563 et al., 1993; Bock et al., 1994; Pavlov et al., 1998). Likewise, gibbsite has two-thirds of its
564 octahedral sites filled with Al^{3+} and one-third unoccupied, allowing small cations (e.g., Li, Mg,

565 Ni and Co) to fit into the unoccupied octahedral voids without significant deformation of the
566 layer (Isupov, 1999). As we discussed above, the intercalated Mg–O length in gibbsite (2.105 Å)
567 is longer than the Al–O length in gibbsite (1.92 Å; Ladeira et al., 2001) or the average Mg–O
568 bond length in water (2.072 Å) without substantial bond contraction (Isupov, 1999). Although
569 several studies proposed a general trend relating Mg–O bond length to the direction of Mg
570 isotope fractionation (e.g., Liu et al., 2014; Gao et al., 2018; Hindshaw et al., 2020), there does
571 not appear to be a strong correlation between average Mg–O bond length and Mg isotope
572 fractionation in octahedral coordination (Schauble, 2011). Therefore, the fact that residual Mg is
573 enriched in heavy Mg isotopes is more likely to attributed to nanocrystalline (SRO) Fe– and Al–
574 phases rather than gibbsite although this would certainly deserve to be verified experimentally.

575 Contrary to the 20 ka site, the 150 ka soils at depth of < 30 cm contain large amounts of
576 Qtz and mica (depth-integrated $\tau_{\text{int}} = 15$ wt.%; Ziegler et al., 2005), indicating significant impact
577 of dust input. The impact for Mg may be smaller because a) basalts have high initial Mg contents
578 and b) the isotopic contrast between radiogenic continental Sr and basaltic Sr is greater than
579 between dust and basalt sources which have similar $\delta^{26}\text{Mg}$ values. If Asian dust has strongly
580 influenced samples, the soil samples should reflect Mg isotopic composition of Asian dust (Fig.
581 5). Previous studies indicated that the average composition of Asian dust delivered to Hawaii has
582 not varied over the last 4 million years spanning the Hawaii chronosequence (Kyte et al., 1993),
583 and that modern Asian dust largely reflects the average composition of upper continental crust
584 (UCC; Zieman et al., 1995). Furthermore, the fact that the difference in a weighted average
585 $\delta^{26}\text{Mg}$ between the UCC (–0.22‰; Li et al., 2010) and 20 sedimentary composites from eastern
586 China (–0.16‰; Li et al., 2010) is within the analytical error of $\pm 0.1\%$ (2σ) indicates that Mg
587 isotopic composition of Asian dust reflects that of UCC. Nonetheless, residual Mg in the

588 subsurface samples yield a $\delta^{26}\text{Mg}$ value of $+0.18\pm 0.18\%$ (2σ , $n=4$) much heavier than both
589 Hawaiian basalt and UCC (Figs. 2d & 4b). Instead, the subsurface soils also contain greater
590 amounts of chemically active SRO minerals, Fe- and Al-crystalline compounds, and poorly
591 crystalline kaolin minerals (Chadwick et al., 2003; Chorover et al., 2004; Ziegler et al., 2005). As
592 discussed above, the incorporation of Mg into both SRO and Fe- and Al-crystalline phases
593 causes residual Mg to be enriched in heavy Mg isotopes at the 150 ka site as well.

594 At the 1400 ka site, the subsurface soil samples mainly contain SRO minerals and
595 crystalline phases (i.e., gibbsite and kaolinite/halloysite; Chorover et al., 2004; Ziegler et al.,
596 2005). For the subsurface soil samples, the residual Mg showed $\delta^{26}\text{Mg}$ values ranging from
597 $+0.27$ to $+0.46\%$, with an average of $+0.38\pm 0.18\%$ (2σ , $n=4$), much heavier than basalts and
598 other younger sites (Figs. 2e & 4b). This implies that the incorporation of Mg into the octahedral
599 sites of crystalline secondary minerals (i.e., kaolinite/halloysite) plays a key role, and that this
600 process favors an isotope fractionation towards heavy Mg isotopes (Fig. 5b). As discussed above,
601 Mg could be incorporated into the octahedral sites of kaolinite/halloysite substituting for Al
602 because kaolinite/halloysite is a 1:1 continuous layered silicate composed of an octahedral layer
603 coordinated to a tetrahedral layer similar to lizardite (Ryu et al., 2016). Considering the Al-O
604 length in kaolinite (~ 1.91 Å; Bish, 1993), the incorporated Mg-O length in kaolinite (~ 2.095 Å)
605 is longer than the average Mg-O length in water (~ 2.07 Å; Carugo et al., 1993; Bock et al.,
606 1994; Pavlov et al., 1998) due to the ionic radii of Mg^{2+} (0.72 Å) and Al^{3+} (0.535 Å; Shannon,
607 1976). However, experimental study showed that the residual kaolinite is enriched in heavy Mg
608 isotopes compared to bulk kaolinite ($+1.63\%$; Wimpenny et al., 2014), implying that it is
609 difficult to relate Mg-O bond length to the direction of Mg isotope fractionation when the
610 difference in bond length between two phases is small, and that the direction of Mg isotope

611 fractionation could be dependent on local field conditions (Hindshaw et al., 2020). In short,
612 positive $\delta^{26}\text{Mg}$ values of residual Mg in soil at the 1400 ka site likely reflect additional Mg
613 isotope fractionation caused by kaolinite/halloysite formation.

614 At the oldest-aged site (4100 ka), the subsurface soil samples mainly contain Al- and Fe-
615 crystalline compounds and crystalline kaolin minerals (i.e. goethite/hematite, gibbsite, and
616 kaolinite/halloysite) (Chorover et al., 2004; Ziegler et al., 2005). For the subsurface soil samples,
617 the residual Mg showed heavy $\delta^{26}\text{Mg}$ values ranging from +0.13 to +0.26‰, with an average of
618 $+0.18 \pm 0.10\%$ (2σ , $n=5$), evidencing that crystalline secondary phases (i.e. goethite, gibbsite and
619 kaolinite/halloysite) preferentially incorporate heavy Mg isotopes into their octahedral sites,
620 causing Mg isotope fractionation (Figs. 2f & 4b). Previous Li isotope study suggested that
621 warmer and wetter conditions in the Pliocene enhance more congruent release of Li isotopes
622 during periods of more intensive weathering of the basaltic rocks (Ryu et al., 2014). Likewise,
623 this process may explain the 4100 ka soils have relatively lighter $\delta^{26}\text{Mg}$ compared to the 1400 ka
624 soils. Otherwise, gibbsite may lead to larger Mg isotope fractionation rather than kaolinite
625 because 1400 ka soils contain more gibbsite than 4100 ka soils (Ziegler et al., 2005), but this
626 remains to be rigorously demonstrated.

627 Overall, based on our dataset, $\delta^{26}\text{Mg}$ values at sites older than 20 ka would be controlled
628 mainly by Mg isotope fractionation through crystallographical evolution from Fe- and Al-
629 crystalline compounds (i.e., goethite/hematite and gibbsite) to kaolin minerals (kaolinite and
630 halloysite). Although it is not possible to quantitatively estimate the degree of Mg isotope
631 fractionation during basalt weathering and secondary minerals transformations in the Hawaiian
632 chronosequence, it appears that crystalline secondary phases preferentially incorporate heavy Mg
633 isotopes during their transformations, confirming the close relation between the Mg–O bond

634 length and the direction of Mg isotope fractionation (Hindshaw et al., 2020). Furthermore, the
635 results indicate that the degree of Mg isotope fractionation is mainly attributed to secondary
636 mineral transformations as a function of soil age.

637

638 *4.4. Comparison with other studies*

639 The LSAG has been very well-studied in several isotope systems, such as Ca, Si, Li
640 isotopes (Wiegand et al., 2005; Ziegler et al., 2005; Ryu et al., 2014; Bullen and Chadwick,
641 2016) in order to decipher biogeochemical processes involved in the terrestrial element cycle,
642 and highlight the role of basalt weathering and secondary mineral transformation. In particular,
643 Wiegand et al. (2005) examined $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Ca isotopes along the LSAG to see how
644 different alkaline earth elements behave, highlighting the effects of both marine aerosol and plant
645 cycling on Ca isotopes. As shown for [Mg] and its isotopic composition of labile Mg in this
646 study, they indicated that both exchangeable and total Ca pool decrease with age and that Ca
647 isotopes in soil exchangeable pool are influenced by the mixture of marine aerosol and plant-
648 related Ca cycling. Likewise, Bullen and Chadwick (2016) analyzed Ba, Ca and Sr stable
649 isotopes along the Kohala climosequence and found that biocycling of these ions created a
650 negative fractionation that was maintained on the near-surface exchange complex, although with
651 differing affinities – Ba was most strongly held and Ca least strongly held against leaching.
652 Overall, stable isotope systems of alkaline earth elements can be powerful proxies for
653 deciphering their biogeochemical cycles.

654 As a relevant study, Trostle et al. (2014) investigated Mg isotopes at an arid (~30 cm
655 MAP) soil chronosequence on the Island of Hawaii and highlighted the contribution of
656 pedogenic carbonate to light Mg isotopes in soils. Furthermore, they suggested that the evolution

657 of the soil mineralogy and morphology during progressive soil development results in significant
658 changes in Mg isotopes through time, which is consistent with our study. Although there is little
659 effect of pedogenic carbonates on the isotopic composition of Mg in this study, both studies
660 indicate that basalt weathering and secondary mineral transformation plays an important role of
661 Mg isotopic compositions in soil system with little effect of Asian dust, incorporating heavy Mg
662 isotopes into secondary phases. However, when compare the Mg isotope study conducted in
663 Iceland (Opfergelt et al., 2014) to our study that both are basaltic soil but different climate, there
664 are clear discrepancies between them. Opfergelt et al. (2014) showed that both exchangeable Mg
665 and clay fractions are depleted in heavy Mg isotopes compared to basalt although bulk soils are
666 isotopically similar to the parent basalt, highlighting the importance of Mg retention on the soil
667 exchange complex and the contribution of sea spray and vegetation (Fig. 5). While the soil
668 exchange complex is a key factor controlling Mg isotopes in both soil systems, in Iceland cold
669 conditions lead to slower weathering rates and development of crystalline secondary phases,
670 whereas in Hawaii there is fast secondary mineral transformation that enhances incorporation of
671 isotopically heavy Mg into crystalline secondary phases.

672

673 **5. CONCLUSIONS**

674 The Hawaiian Islands LSAG chronosequence allows us to better understand Mg isotope
675 fractionation during progressive basalt weathering and open-system biogeochemical
676 transformations in soil. Given the large concentration of Mg in basalts, the effect of atmospheric
677 deposition to the soil Mg budget for all the sites is small. The major fractionations to Mg
678 isotopes in soils are strong plant-related changes to labile Mg, although there may be some effect
679 due to rainwater input and bond-length selectivities during incorporation of Mg into secondary

680 Al- and Fe-oxyhydroxides. The variations of Mg isotopes in residual Mg mostly reveal Mg
681 isotope fractionation during secondary mineral formation favoring heavy Mg isotopes. Two
682 youngest soils (0.3 ka; Th and Ol) display $\delta^{26}\text{Mg}$ values consistent with Hawaiian basalt,
683 regardless of labile and residual Mg, indicating that basalt weathering results in little or no Mg
684 isotope fractionation over 0.3 ka. However, residual Mg in the intermediate- and oldest-soils (\geq
685 20 ka) display more variable but much enriched $\delta^{26}\text{Mg}$ values compatible with the known
686 mineralogical and crystallographical evolution of these profiles, suggesting that secondary
687 mineral transformation is a key process controlling Mg isotope fractionation. Overall, Mg
688 isotope variations in labile and residual Mg of soils in Hawaiian LSAG are determined by the
689 effects of plant-related Mg recycling and incorporation of heavy Mg isotopes into
690 (nano)crystalline secondary phases.

691

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934 **FIGURE CAPTIONS**

935 **Figure 1.** Elemental concentrations and the elemental gain ($\tau_{j,w} > 0$) or loss ($\tau_{j,w} < 0$) versus
936 depth. (a)-(c) Concentrations of Mg, Al and Fe in each soil profile. (d)-(f) τ_{Mg} is
937 calculated using Eq. (1). All [Mg], [Al], [Fe] and [Nb] data in parent basalts are from
938 Ziegler et al. (2005). (see text for more details).

939 **Figure 2.** Magnesium isotope compositions versus depth. The black and blue lines represent
940 average $\delta^{26}\text{Mg}$ values of -0.26‰ (Hawaiian basalts; Zhong et al., 2017) and -0.83‰
941 (seawater; Ling et al., 2011), respectively.

942 **Figure 3.** Depth-integrated parameters versus age. (a) The Mg gain or loss (τ_{Mg}), (b) $\delta^{26}\text{Mg}$, (c)-
943 (f) Mineralogical compositions (Ziegler et al., 2005). The black line in (b) represents
944 average $\delta^{26}\text{Mg}$ value of -0.26‰ in Hawaiian basalts (Zhong et al., 2017). Error bars are
945 smaller than the symbols.

946 **Figure 4.** Magnesium isotopic compositions in the labile and residual Mg as a function of age.
947 (a) Organic-rich surface soils and (b) Subsurface soils. The colored-lines represent
948 seawater (blue; -0.83‰ ; Ling et al., 2011), basalt (black; -0.26‰ ; Zhong et al., 2017),
949 plant (green; -0.07‰ ; Trostle, 2014) and SOM (brown; $+0.06\text{‰}$; Trostle, 2014),
950 respectively.

951 **Figure 5.** $\delta^{26}\text{Mg}$ values versus $1/[\text{Mg}]$ ($\text{wt.}\%^{-1}$) for the labile and residual Mg in all soil samples
952 measured in this study. Asian dust $\delta^{26}\text{Mg}$ is assumed to be equal to the upper continental
953 crust (UCC) $\delta^{26}\text{Mg}$ (-0.22‰ ; Li et al., 2010) with [Mg] of 1.5 wt.% (Rudnick and Gao,
954 2014). Plant $\delta^{26}\text{Mg}$ is $-0.07 \pm 0.26\text{‰}$ (2σ , $n=4$; Trostle, 2014) with [Mg] of 0.15 ± 0.12
955 wt.% (2σ , $n=4$; Trostle, 2014), SOM $\delta^{26}\text{Mg}$ is $+0.06 \pm 0.48\text{‰}$ (2σ , $n=4$; Trostle, 2014)

956 with [Mg] of 0.03 ± 0.02 wt.% (2σ , $n=4$; Trostle, 2014), rainwater $\delta^{26}\text{Mg}$ is assumed to be
957 equal to seawater $\delta^{26}\text{Mg}$ (-0.83‰ ; Ling et al., 2011) with [Mg] of 0.09 ± 0.11 ppm (2σ ,
958 $n=6$; Carrillo et al., 2002), and Hawaiian basalts $\delta^{26}\text{Mg}$ is $-0.26 \pm 0.06\text{‰}$ (2σ , $n=11$;
959 Zhong et al., 2017) with [Mg] of 4.7 ± 1.6 wt.% (2σ , $n=10$; Zhong et al., 2017). The grey
960 shaded field marks the mixing zone between each considered end-member. Error bars for
961 soil samples are smaller than the symbols. Data for a cross symbol are from Opfergelt et
962 al. (2014). Symbols are the same as in Fig. 2.

963

964 **Figure S1.** Map of the Hawaiian Islands showing the sampling locations and their substrate ages
965 (Modified from Crews et al., 1995).

966 **Figure S2.** Fraction of each end-member (basalt, dust and rainwater) relative to the total Mg (%)
967 versus age. Error bars represent 1σ , propagated using the range of [Mg] for each end-
968 member (see text for more details).

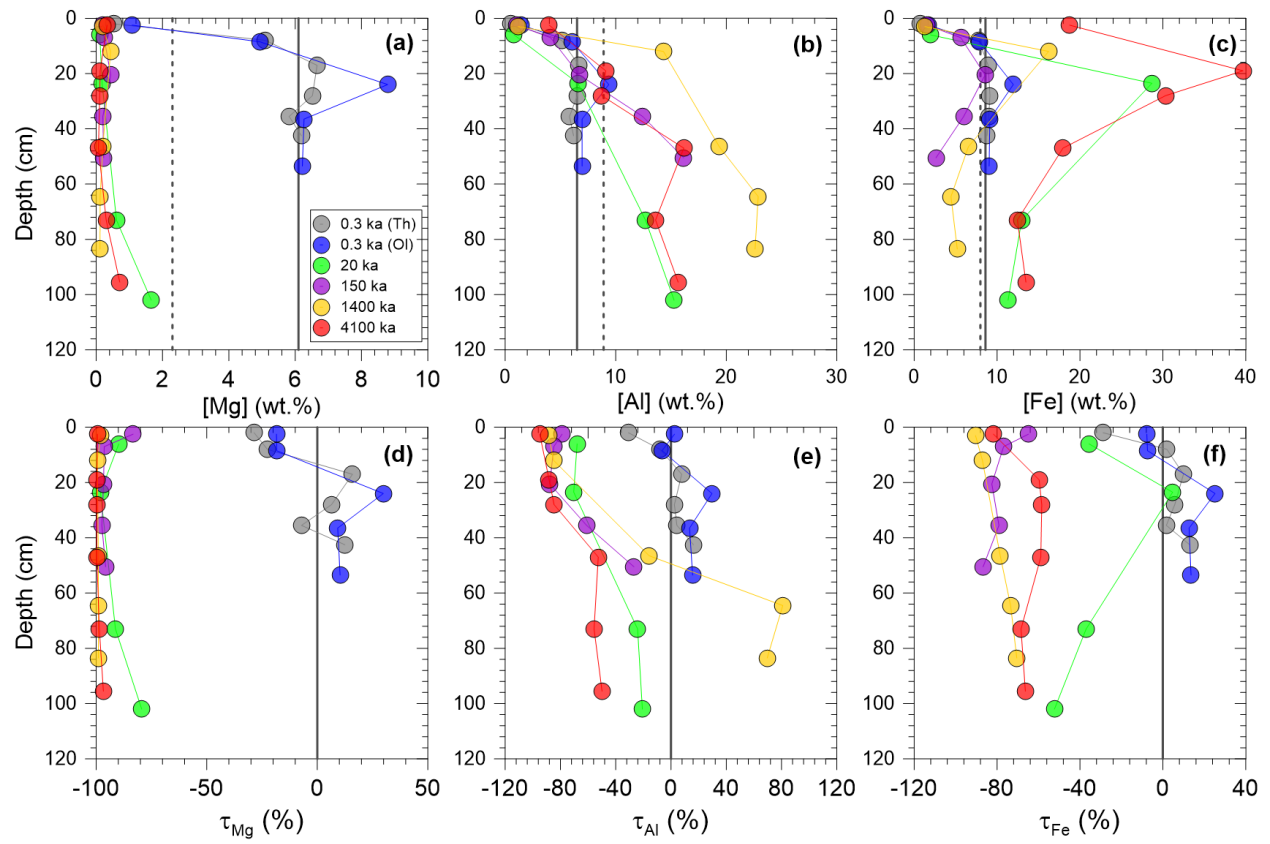


Fig. 1. Ryu *et al.*

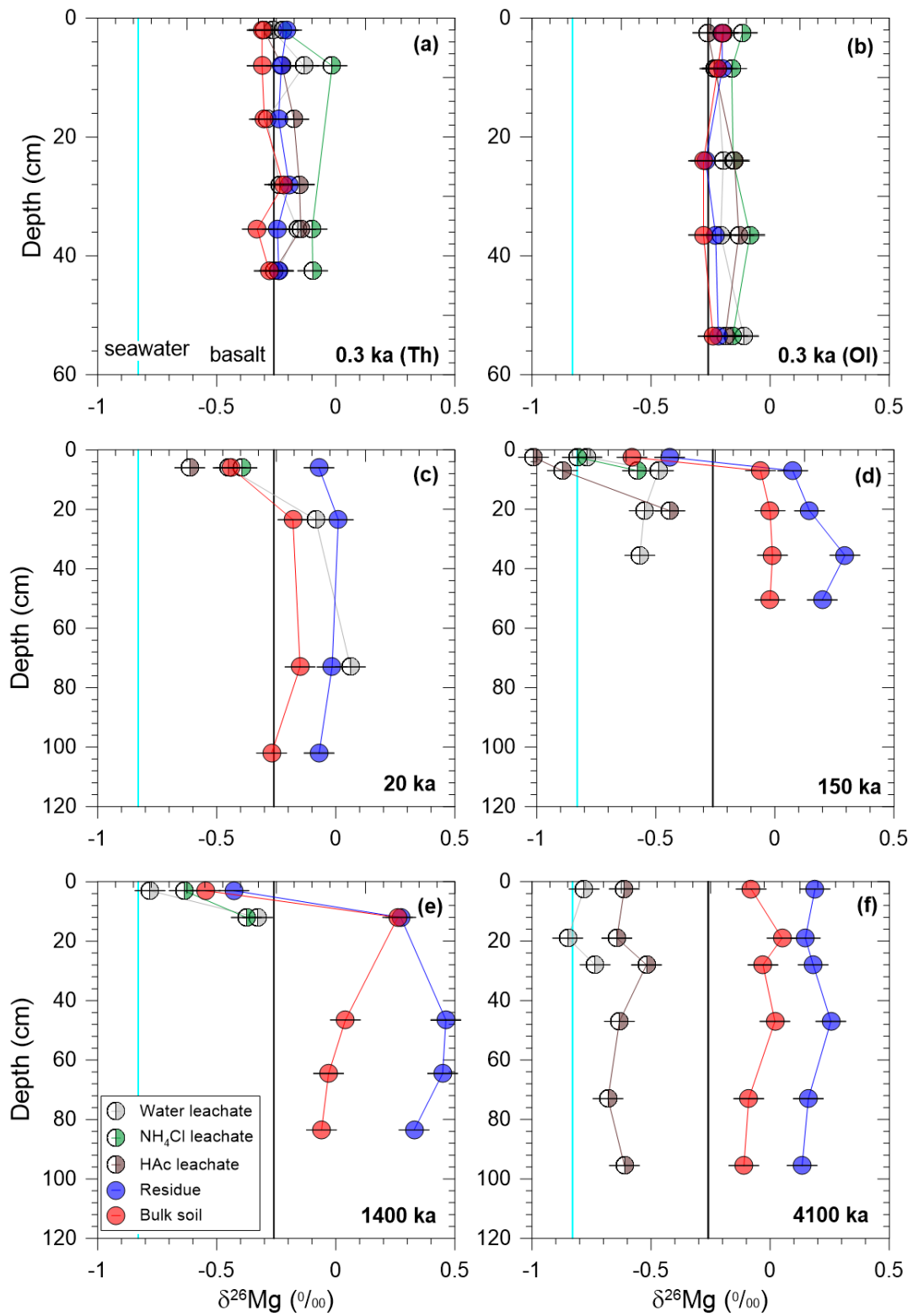


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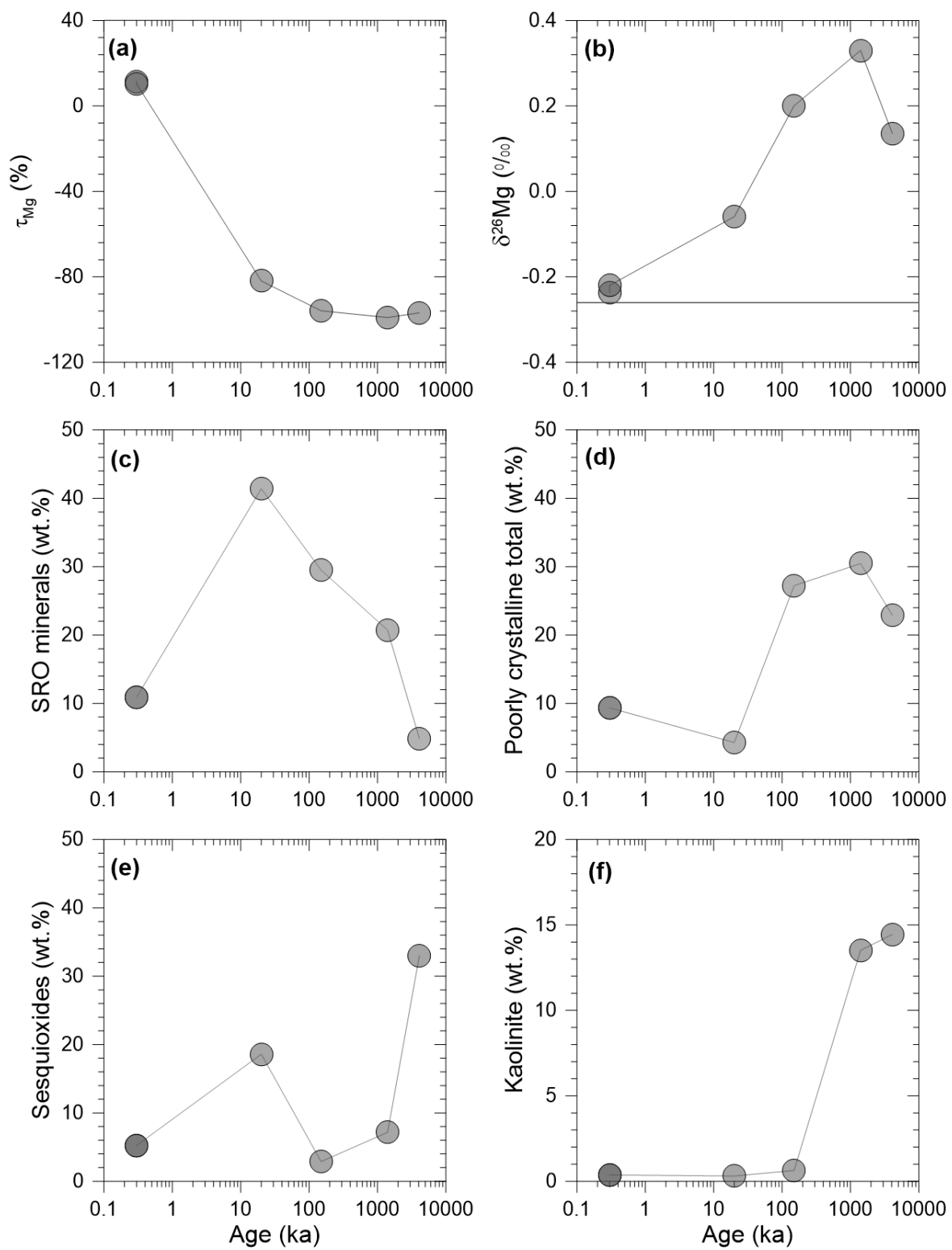


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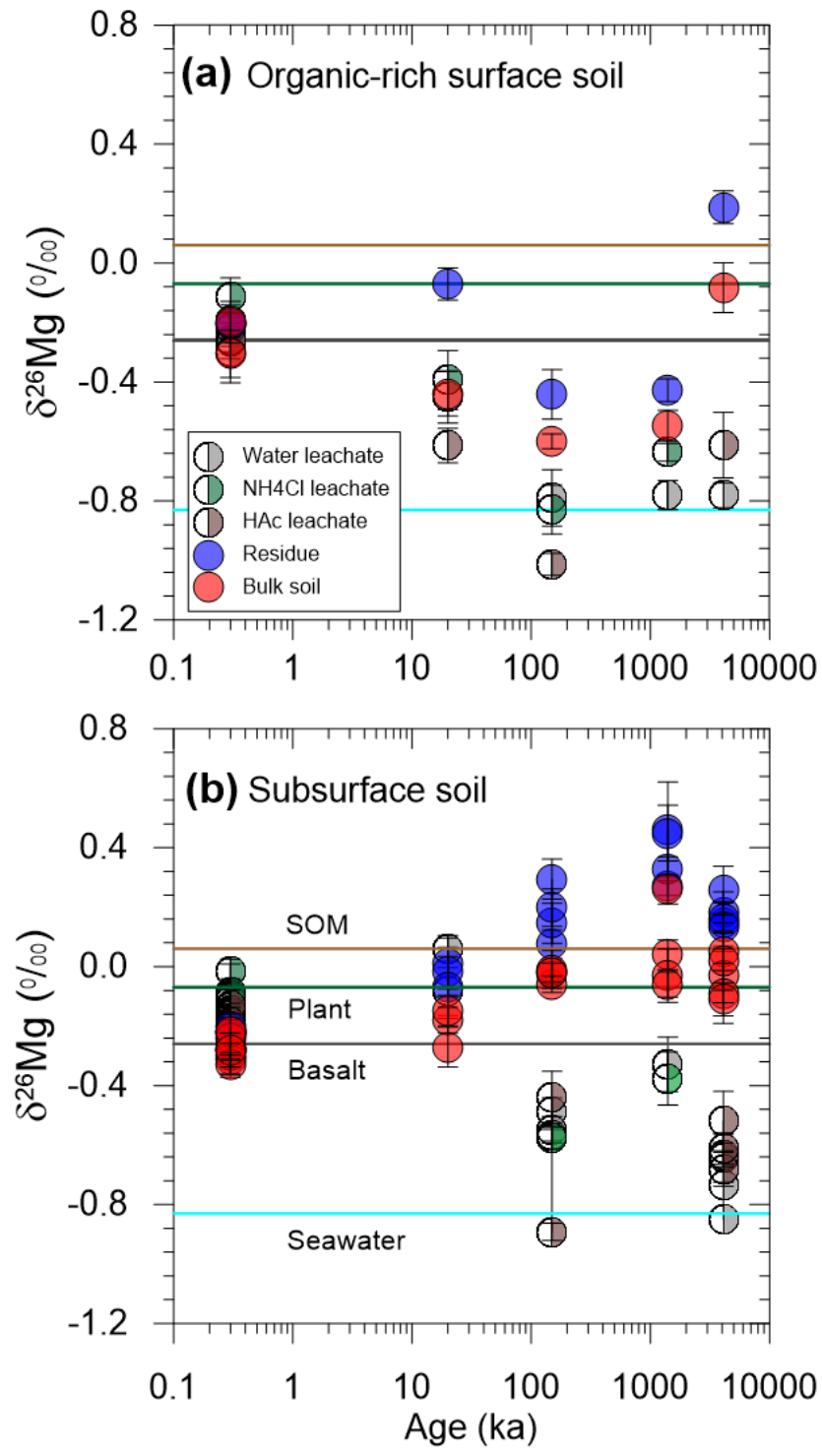


Fig. 4. Ryu *et al.*

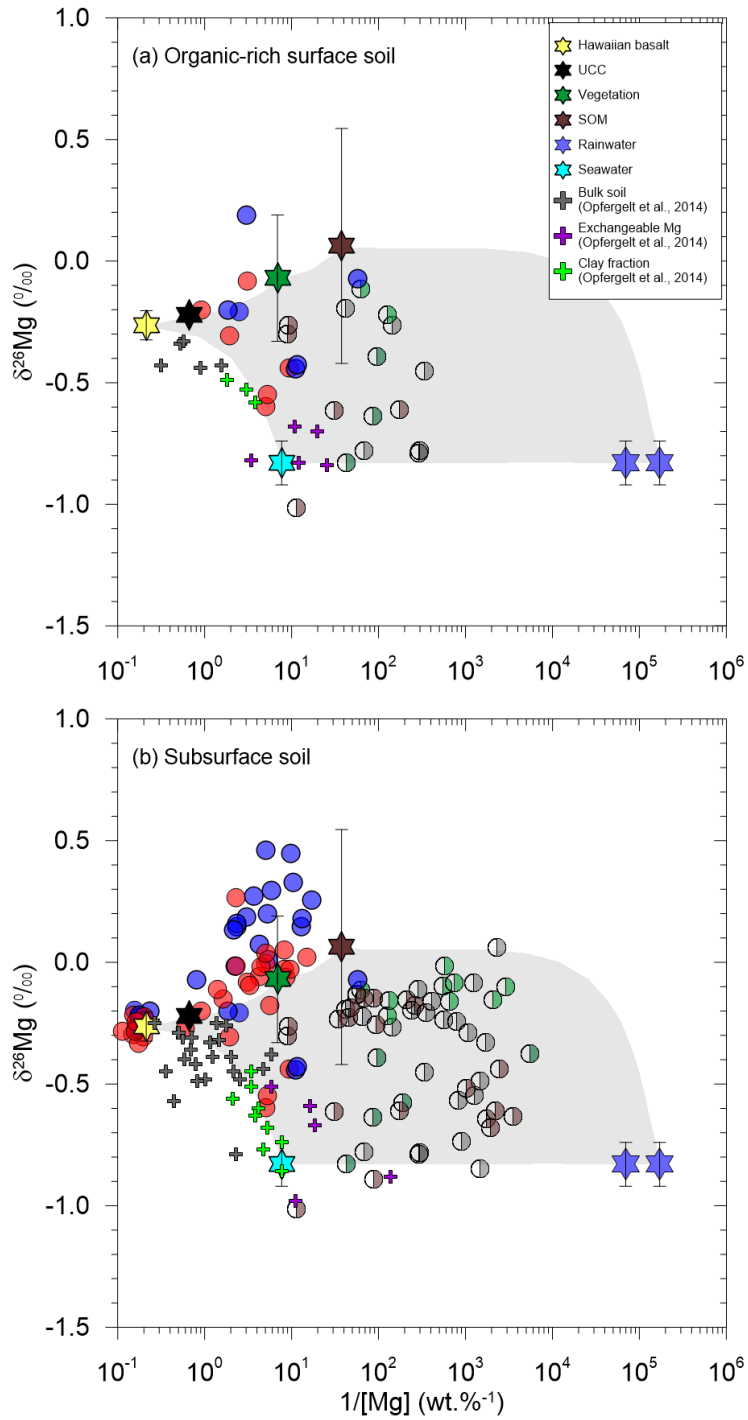


Fig. 5. Ryu *et al.*

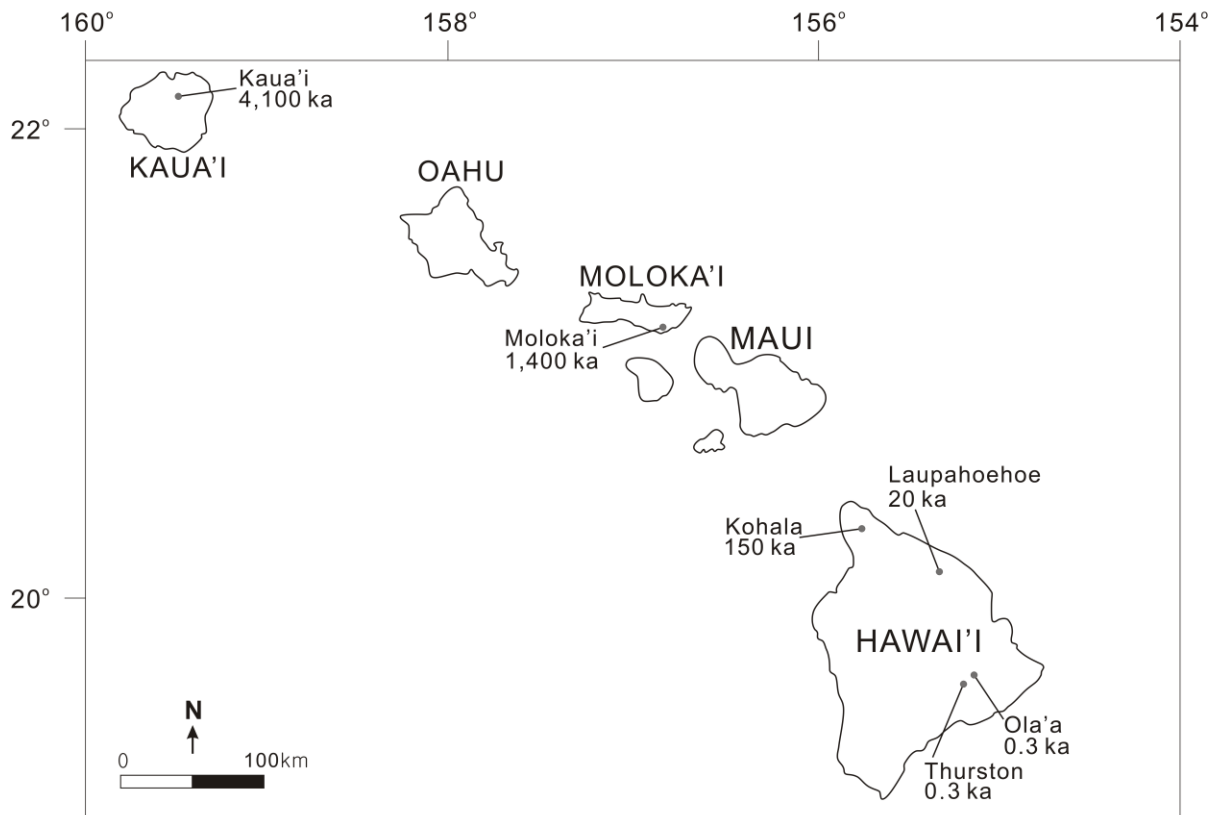


Fig. S1. Ryu *et al.*

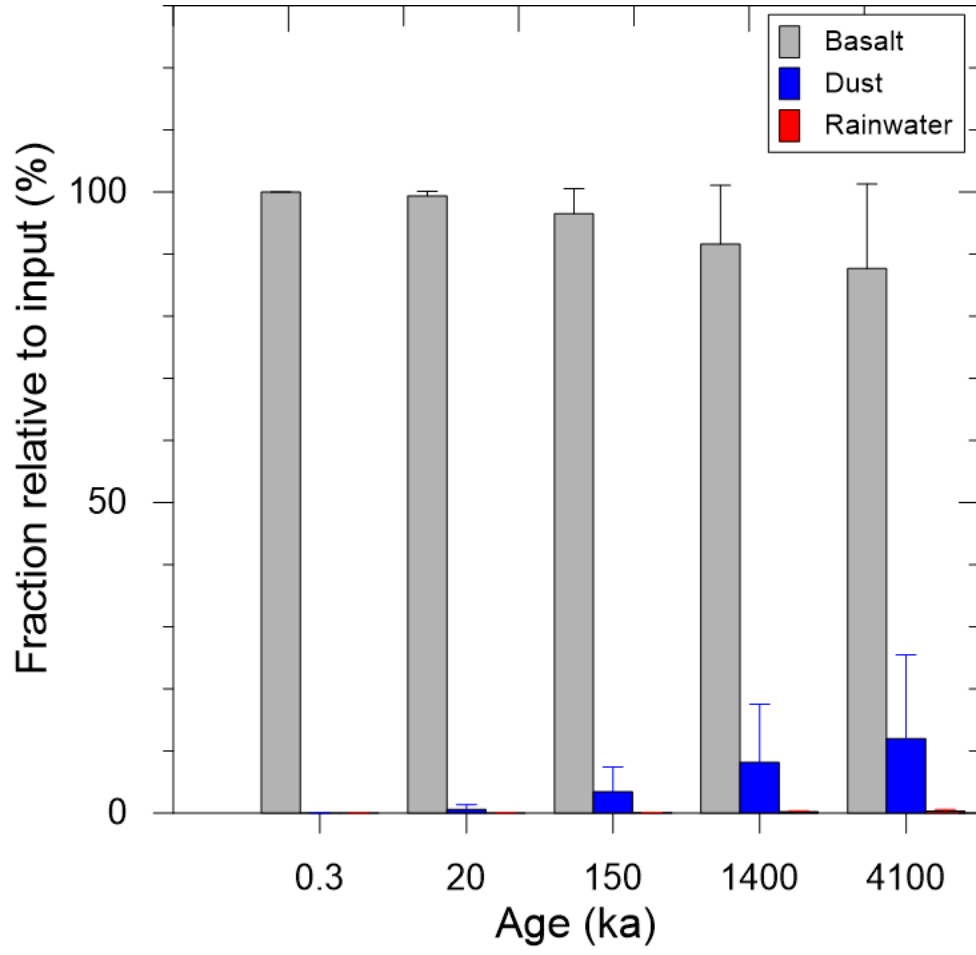


Fig. S2. Ryu *et al.*