1 **The lithium and magnesium isotope signature of olivine dissolution in soil**

2 **experiments**

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20 **Abstract**

21   This study presents lithium and magnesium isotope ratios of soils and

22 their drainage waters from a well-characterised weathering experiment with

23 two soil cores, one with olivine added to the surface layer, and the other a

24 control core. The experimental design mimics olivine addition to soils for CO_2

25 sequestration and/or crop fertilisation, as well as natural surface addition of

1

26   reactive minerals such as during volcanic deposition. More generally, this study

27   presents an opportunity to better understand how isotopic fractionation records

28   weathering processes. At the start of the experiment, waters draining both cores

29   have similar Mg isotope composition to the soil exchangeable pool. The

30   composition in the two cores evolve in different directions as olivine dissolution

31   progresses. Mass balance calculations show that the water $\delta^{26}Mg$ value is

32   controlled by congruent dissolution of carbonate and silicates (the latter in the

33   olivine core only), plus an isotopically fractionated exchangeable pool. For Li,

34   waters exiting the base of the cores initially have the same isotope composition,

35   but then diverge as olivine dissolution progresses. For both Mg and Li, the

36   transport down-core is significantly retarded and fractionated by exchange with

37   the exchangeable pool. This observation has implications for the monitoring of

38   enhanced weathering using trace elements or isotopes, because dissolution rates

39   and fluxes will be underestimated during the time when the exchangeable pool

40   evolves towards a new equilibrium.

41

42   *Keywords:*

43   *Chemical weathering; lithium; magnesium; stable isotopes; weathering rate; soil*

44   *core experiments*

45

46   **1. Introduction**

47   Chemical weathering of continental silicate rocks supplies alkalinity and

48   cations that drive carbonate formation and provides nutrients to the ocean to

49   fuel primary productivity and organic carbon burial (Berner, 2003; Ebelmen,

50   1845). Because these are the primary processes removing CO_2 from the

51   atmosphere on timescales $>10^5$ years, weathering is a key process driving

52   climate change over geologic time (Berner et al., 1983; Colbourn et al., 2015;

53   Godderis et al., 2013). A climate-driven feedback may make silicate weathering a

54   dominant climate-moderating process, helping to explain the long-term stability

55   of Earth's climate (Walker et al., 1981). However, the strength of this feedback is

56   disputed, in part because supply of weatherable material (high activity primary

57   silicates) also exerts an important control on weathering fluxes (Goudie and

58   Viles, 2012; Pogge von Strandmann et al., 2017a; Pogge von Strandmann et al.,

59   2017c; Raymo et al., 1988; West et al., 2005).

60   Despite considerable research, the fundamental processes controlling

61   weathering, and ultimately the evolution of atmospheric pCO_2, are still poorly

62   known. Understanding the relative roles of climate vs. material supply in

63   determining weathering fluxes is challenging because the weathering

64   mechanisms that operate at soil profile scales remain difficult to resolve.

65   Moreover, it has proven difficult to relate soil-scale processes to those that

66   operate at catchment and global scales, given the heterogeneities in supply of

67   fresh primary rock, mineral saturation, pH, mineral surface area, reactivity and

68   temperature in natural environments (e.g., Gislason et al., 2009; Maher and

69   Chamberlain, 2014; Stallard and Edmond, 1983; Stefansson and Gislason, 2001;

70   West et al., 2005). Laboratory experiments provide insight into mineral

71   weathering rates and their dependence on many of these parameters, but rates

72   calculated from laboratory experiments are generally several orders of

73   magnitude higher than those observed in natural environments (White and

74   Brantley, 2003), suggesting that the underlying mechanisms may also differ. To

75 address this discrepancy, experiments emulating the inherently complex

76 processes operating in the natural environment are necessary.

77   The uncertainty in understanding weathering rates in natural systems has

78 further implications for understanding the potential for "enhanced weathering"

79 as a strategy for removing anthropogenic CO_2 from the atmosphere (Andrews

80 and Taylor, 2019; Schuiling and Krijgsman, 2006; Taylor et al., 2020). Proposals

81 for enhanced weathering include spreading finely-ground silicate and carbonate

82 minerals on land surfaces (Hartmann et al., 2013; Koehler et al., 2010; Renforth,

83 2012; Schuiling and Krijgsman, 2006), in coastal environments (Hangx and

84 Spiers, 2009; Schuiling and de Boer, 2010), and in the ocean (Koehler et al., 2013;

85 Renforth et al., 2013). In each case, the aim is to increase the amount of mineral

86 dissolution and associated CO_2 drawdown. However, without precise knowledge

87 of weathering rates, it is not yet possible to determine whether enhanced

88 weathering would be a net sink of CO_2, given the energy required for rock

89 grinding and transportation (Moosdorf et al., 2014; Renforth, 2012).

90   A relatively new development in the study of weathering is the use of

91 "non-traditional" stable isotopes. A number of these systems are fractionated by

92 weathering processes and therefore have the potential to trace weathering, and

93 even determine weathering fluxes. These tools could offer significant advantages

94 over approaches that require several simultaneous measurements (e.g. multiple

95 elemental concentrations, runoff rates, surface area, etc.). Magnesium isotopes

96 ($\delta^{26}Mg$) are such a potential tracer of weathering processes, useful because Mg is

97 a direct part of the long-term carbon cycle (Berner et al., 1983). Magnesium is

98 present in both silicate and carbonate rocks, and these components typically

99 have significantly different isotope ratios (Huang et al., 2013; Li et al., 2010;

4

100 Saenger and Wang, 2014). This difference means that the $\delta^{26}Mg$ of rivers is

101 controlled both by lithology and by additional, smaller fractionation during

102 uptake of mostly heavy Mg during formation of secondary minerals (Liu et al.,

103 2014; Opfergelt et al., 2014; Opfergelt et al., 2012; Pogge von Strandmann et al.,

104 2008; Pogge von Strandmann et al., 2012; Ryu et al., 2016; Tipper et al., 2010;

105 Tipper et al., 2008; Tipper et al., 2006b; Wimpenny et al., 2011; Wimpenny et al.,

106 2014).

107   Lithium isotopes (δ^7Li) also show promise as an isotopic tracer of

108 weathering, unusual in being dominantly controlled by silicate weathering. The

109 Li isotope ratio is unaffected by plant uptake and primary productivity

110 (Lemarchand et al., 2010; Pogge von Strandmann et al., 2016), and negligibly

111 influenced by weathering of carbonates, even in carbonate-dominated

112 catchments (Kisakürek et al., 2005; Millot et al., 2010; Pogge von Strandmann et

113 al., 2017b). The δ^7Li of silicate rocks comprises a narrow range ($\delta^7Li_{continental\ crust}$

114 $\sim 0.6 \pm 0.6\text{‰}$ (Sauzéat et al., 2015), $\delta^7Li_{basalt} \sim 3–5\text{‰}$ (Elliott et al., 2006))

115 relative to that in rivers (2–43‰, global mean $\sim$23‰ (Dellinger et al., 2015;

116 Huh et al., 1998; Murphy et al., 2019; Pogge von Strandmann et al., 2006)). The

117 high variability in rivers is caused by preferential uptake of ^6Li into secondary

118 minerals formed during weathering, driving residual waters isotopically heavy

119 (Huh et al., 2001; Huh et al., 1998; Kisakürek et al., 2005; Lemarchand et al.,

120 2010; Liu et al., 2015; Millot et al., 2010; Pistiner and Henderson, 2003; Pogge

121 von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Pogge von

122 Strandmann and Henderson, 2015; Pogge von Strandmann et al., 2014; Vigier et

123 al., 2009; Wimpenny et al., 2015; Wimpenny et al., 2010). Dissolved Li isotope

124 ratios are therefore controlled by the ratio of primary mineral dissolution

125   (supplying low, rock-like, δ^7Li to solution), relative to secondary mineral

126   formation (preferentially removing ^{6}Li and therefore leading to high dissolved

127   δ^7Li). This balance means that dissolved Li isotopes trace what is often referred

128   to as the congruency of silicate weathering (where congruent weathering

129   features a high ratio of primary mineral dissolution to secondary mineral

130   formation) (Bouchez et al., 2013; Dellinger et al., 2015; Misra and Froelich, 2012;

131   Pogge von Strandmann et al., 2010; Pogge von Strandmann and Henderson,

132   2015).

133   In this study, we examine Mg and Li isotope ratios from a well-

134   characterised soil weathering experiment (Renforth et al., 2015). The aims of

135   this study are (i) to better understand the processes that affect dissolved Li and

136   Mg isotope compositions, (ii) to assess whether these isotopic tracers are useful

137   for determining weathering processes and rates, including in enhanced

138   weathering applications, and (iii) to compare isotopic methods with a more

139   conventional approach to calculating weathering rates using elemental

140   concentrations and ratios (Renforth et al., 2015).

141

142   **2. Experimental approach**

143   As a step towards bringing the inherently complex weathering

144   environment into controlled laboratory conditions, 1 m long soil cores were

145   taken from agricultural land. These cores are described in detail in Renforth et

146   al., 2015. Briefly, three cores were extracted from the same location, in North

147   Oxfordshire, UK. The bedrock in the region is Jurassic limestone and mudstone,

148   and the soils are generally calcareous. The cores span the ploughed layer

149   (~10cm), the underlying B and C horizons, and parent rock material at the

150   bottom of the cores. One core was used to examine the bulk soil composition.

151   The other two were used as column reactors, with a modified Hoagland nutrient

152   solution (~200 µg g^{-1} K, N, 30 µg g^{-1} P, 37 ng g^{-1} Ca, 30 ng g^{-1} S; 0.2ng g^{-1} Li, 69 ng

153   g^{-1} Mg,) dripped into the top of each soil column at 15 ml h^{-1} for 133 days at a

154   constant temperature of 19°C. The Hoagland solution was used to mimic the

155   effect of fertiliser added to an agricultural setting. The observed residence time

156   of water in each column was approximately 3 days (observed as the continuing

157   drip time once influent water was shut off), similar to the residence time

158   expected based on the flow rate and measured porosity, of 3.3 days. The influent

159   solution was mixed in four separate, but identical, sequential batches. Effluent

160   waters exited the base of each column continuously, and were sampled

161   periodically for chemical analysis. Effluent pH exhibited no trends with time (7.5

162   ± 0.2 for the control core and 7.2 ± 0.2 for the olivine core (Renforth et al.,

163   2015)). To minimise evaporative loss, source beakers, collection beakers, and the

164   soil columns were capped, with solution removed or introduced via tubing.

165   Water samples were collected periodically from the base of each soil column.

166   To mimic weathering of fresh silicate, 100 g of crushed olivine was stirred

167   into the top of one of the cores ("olivine core") at the start of the 133-day

168   experiment, while nothing was added to the control core, although the top was

169   also stirred (Fig. 1). The olivine grain size was determined by dry sieving (78%

170   had a particle diameter of >125µm; for full grain size characterisation see

171   Renforth et al., 2015). The olivine grain surface area was measured by BET,

172   giving 3.04 ± 0.03 m^2 g^{-1}. Our experimental approach, of sudden addition of a

173   mineral to the soil surface, mimics other sudden-addition scenarios, such as

174 deposition of volcanic ash deposits or intentional mineral addition to consume

175 CO_2 by enhanced weathering.

176   The study of Renforth et al. (2015) determined the dissolution rate of the

177 ground olivine added to soils, based on effluent major element concentrations

178 such as Mg and Si. That study also determined a mineral surface-area-dependent

179 weathering rate for such "enhanced" experiments.

180

181 **3. Methods**

182   Major element concentrations in bulk soils and olivine powder were

183 determined by XRF (Renforth et al., 2015). For isotope separation, material was

184 dissolved in concentrated $HF-HNO_3-HClO_4$ at elevated temperature in PFA

185 beakers on hotplates, followed by evaporation to dryness and sequential heated

186 re-dissolution first in concentrated HNO_3 and then in 6M HCl. Exchangeable and

187 carbonate fractions were also sampled using a sequential extraction technique

188 (Tessier et al., 1979): the exchangeable fraction was extracted with 1M Na

189 acetate (pH 8.2), while the carbonate fraction was dissolved with Na acetate

190 buffered to pH5 with acetic acid. The effluent solutions collected from the

191 bottom of the soil columns were passed through 0.2 μm membrane Whatmann

192 cellulose nitrate filters before analysis (Renforth et al., 2015).

193   For Mg isotopes, ~0.4–1μg of Mg was purified through a two-stage cation

194 exchange procedure (Pogge von Strandmann et al., 2011; Pogge von Strandmann

195 et al., 2019c) and analysed relative to the standard DSM-3 on a Thermo Neptune

196 MC-ICP-MS at the Bristol Isotope Group (Pogge von Strandmann et al., 2012).

197 Seawater and BCR-2 were also analysed following identical purification

198 procedures, giving long-term (during 10 years of analyses) values of $\delta^{26}Mg$ = -

199   0.83 ± 0.05‰ (n = 33; chemistry = 27, where "chemistry" refers to standards

200   processed through full procedural chemistry as used for samples, and

201   uncertainty is 2sd) and -0.25 ± 0.05‰ (n = 18; chemistry = 16), respectively, in

202   keeping with other studies, as reported in prior compilations (Foster et al., 2010;

203   Pogge von Strandmann et al., 2011; Shalev et al., 2018; Teng et al., 2015).

204   For Li isotope analysis, sufficient drip water was evaporated to attain

205   20ng of Li. Lithium was separated using a two-stage cation exchange technique,

206   described in detail elsewhere (Pogge von Strandmann and Henderson, 2015),

207   and analysed on a Nu Instruments HR MC-ICP-MS (high resolution multi-

208   collector inductively coupled plasma mass spectrometer) at Oxford University.

209   Results are given as ‰ deviation from the standard L-SVEC. To assess accuracy

210   and precision, seawater and USGS standards BCR-2 (basalt) and SGR-1 (shale)

211   were analysed, giving δ^7Li = 31.3 ± 0.6‰ (n = 50, chemistry = 50), 2.7 ± 0.4‰ (n

212   = 4, chemistry = 4) and 3.6 ± 0.4‰ (n = 3, chemistry = 3), respectively, which are

213   in agreement with other studies (Dellinger et al., 2015; Phan et al., 2016; Pogge

214   von Strandmann et al., 2019a; Pogge von Strandmann et al., 2012).

215

216   **4. Results**

217   *4.1 Mg isotopes*

218   The MgO content of the olivine was 47.7 wt%, with a $\delta^{26}Mg$ of -0.23 ± 0.06

219   ‰, identical to mantle-derived olivine (Pogge von Strandmann et al., 2011). In

220   contrast, the bulk soils had around 0.50 ± 0.03 wt% MgO and a $\delta^{26}Mg$ of -0.44‰

221   (Table 1). Around 0.5% of the initial bulk soil Mg was in the exchangeable

222   fraction, based on the Na-acetate leach. Exchangeable Mg was isotopically light (-

223   1.54 to -2.48‰; Fig. 2B). The carbonate fraction (comprising ~16% of the total

224　soil Mg) was isotopically even lighter (δ^{26}Mg = -3.24 to -3.31‰), in the range of

225　previously measured carbonate rocks (~-4 to -1‰) (Saenger and Wang, 2014;

226　Tipper et al., 2006b). Residual soils (i.e. after removal of exchangeable and

227　carbonate fractions), accounting for the remaining ~84% of total Mg (likely

228　contained in clay minerals), had δ^{26}Mg values indistinguishable from those of the

229　initial bulk soil. Towards the base of the soil column, bulk soil had δ^{26}Mg values

230　similar to primary silicates (~-0.2‰), which likely made up the initial

231　composition of the silicate portion of the soil.

232　　　　Magnesium was not deliberately added to the influent solution, although a

233　background concentration of 69 ng ml^{-1} was measured. The drip waters from the

234　control column started at ~7 µg ml^{-1} Mg and gradually decreased to 4.5 µg ml^{-1}

235　over time (Fig. 3C; Table 2). Effluent-water concentrations from the olivine core

236　were between 1 and 5 µg g^{-1} higher. The decrease in overall Mg concentrations

237　with time in effluent waters from both cores is discussed in Renforth et al.

238　(2015) and is attributed to carbonate and exchangeable complexes adjusting to

239　the composition of the artificial drip waters (e.g., adjustment of the exchangeable

240　complex to a different influent composition compared to natural rain

241　experienced in the field). Renforth et al. (2015) used the difference in [Mg]

242　between the olivine treatment and the control to derive olivine dissolution rates.

243　The drip water δ^{26}Mg from both columns started at approximately the same

244　value (-2‰), and the two solutions became resolvably distinct from each other

245　after ~17 days. The waters from the control core then became isotopically

246　lighter almost linearly with time, with a final value of -2.73‰ (Fig. 3D). In

247　contrast, the olivine core drip waters were almost unchanged over time,

248   resulting in a difference between the two columns ($\Delta^{26}Mg_{olivine\text{-}control}$) of 1‰ by

249   the end of the experiment.

250

251   *4.2 Li isotopes*

252   The Li concentration of the olivine was 1.2 μg g^{-1}, with a δ^7Li of 2.7 ±

253   0.3‰, identical to the mantle (Lai et al., 2015; Marschall et al., 2017). The Li

254   concentration of the bulk soils was fairly low (1–3 μg g^{-1}) compared to the upper

255   continental crust (30.5 ± 3.6 μg g^{-1}) or silicate-rich soils (1.1–130 μg g^{-1})

256   (Lemarchand et al., 2010; Pogge von Strandmann et al., 2012; Sauzéat et al.,

257   2015). The δ^7Li of the soils ranged between -0.7 and 2.1‰ (Fig. 2A; Table 1),

258   largely within the reported range for the continental crust (0.6 ± 0.6‰) (Sauzéat

259   et al., 2015).

260   Approximately 0.5% (0.2–0.7%) of bulk soil Li was in the exchangeable

261   fraction (Na acetate leach – Table 1), similar to Mg. The δ^7Li of this exchangeable

262   fraction varied between -5.9 and +6.6‰ (Fig. 2A). The Li concentrations in the

263   carbonate leach were below detection limits (<0.01 ng/g); thus ≈99.5% of the Li

264   was in silicate fractions.

265   The Li concentration in the effluent drip waters was 1.1 ± 0.3 ng g^{-1} in the

266   control column and 1.3 ± 0.2 ng g^{-1} in the olivine column (Fig. 3A; Table 2). A

267   total of ~9.6 μg Li was added to the columns from the original input solution

268   during the entire experiment, representing 16–18% of the concentration in the

269   effluent solutions. The δ^7Li of the influent water was 12.3 ± 0.4‰. In

270   comparison, the mass of Li in the control column's exchangeable fraction (see

271   below for calculation) was ~57 μg Li, six times more than the added Li.

272   The effluent δ^7Li started out in both cores at similar values ($\sim$13‰). The

273   effluent water composition stayed at approximately 12‰ in both cores for the

274   first $\sim$20 days of the experiment (Fig. 3B), after which the control core waters

275   increased to a maximum of 24.2‰ by 54 days, and then remained relatively

276   constant. In contrast, the olivine core effluent's δ^7Li was lower and did not

277   increase beyond 16.6‰, resulting in a difference between the two columns

278   (Δ^7Li$_{olivine-control}$) of -7 to -10‰ by the end of the experiment.

279

280   *4.3 Mass balance*

281   A mass balance of elemental influx and output can be constructed, based

282   on several assumptions. The first is that the input-corrected effluent flux of Ca

283   from the control column is solely due to the dissolution of carbonates within the

284   core. This was shown by Renforth et al. (2015), who report a linear correlation

285   between [Ca] and total inorganic carbon in the bulk solid-phase of the cores. We

286   also assume that the input-corrected effluent flux of Si from the control column is

287   due to dissolution of silicates (clays, given a lack of primary silicates) within the

288   core. We use the measured x/Ca and x/Si (where x is either Mg or Li) ratios of

289   the leached and residual silicate and carbonate fractions to determine the mass

290   of Mg and Li in the core and in particular, the proportion that each phase

291   contributes to the material exiting the core in the effluent solutions. We assume

292   that all effluent Li and Mg that remains after correcting for input, silicate and

293   carbonate dissolution stems from the soil's exchangeable fraction:

294     $X_{exch} = X_{influent} - X_{effluent} - X_{silicate} - X_{carbonate}$ Eqn. 1

295     $X_{exch} = X_{influent} - X_{effluent} - \left[\left(\frac{X}{Si} \right)_{clay} \times Si \right] - \left[\left(\frac{X}{Ca} \right)_{carb} \times Ca \right]$ Eqn. 2

296 where X is the flux (in µg) of Li or Mg; 'Si' and 'Ca' are the fluxes of Si and Mg;

297 exch, clay and carb are the exchangeable, clay and carbonate fraction,

298 respectively. Then, based on the assumption that the cores are identical, we can

299 further determine the amount of Li and Mg that stems from the dissolution of

300 olivine in the olivine core:

301 $$X_{exch} = X_{influent} - X_{effluent} - X_{silicate} - X_{carbonate} - X_{olivine} \qquad \text{Eqn. 3}$$

302 We emphasise that this mass balance calculation is not determining the

303 partitioning of Mg or Li between the different solid phases within the soil, but

304 between the contributors of Mg and Li to effluent solution. The uncertainties of

305 this mass balance stem from analytical uncertainty on the concentration

306 measurements, which then propagate, so that the larger mass balance

307 contributors (e.g. carbonate for Mg) have a larger influence on the ultimate error.

308 Error propagation of the analytical uncertainties yield ±~6% relative error on

309 the mass balance.

310

5. Discussion

312 *5.1 Elemental mass balances*

313 5.1.1 Magnesium

314   The mass balance of the effluent from the control core after 5 days from

315 the start of the experiments shows that ~55% of the Mg stems from carbonate

316 dissolution and ~42% from the exchangeable fraction (so these two sources

317 make up >97% of the total eluted Mg) (Fig. 4). Less than 0.5% is initially from the

318 dissolution of clay. By the end of the experiment, over 4 months later, the

319 proportion from carbonate dissolution has increased to 65% at the expense of

320 the contribution from the exchangeable fraction (Fig. 4).

321   In the olivine column, after 5 days from the start of the experiment olivine

322   dissolution contributes ~19% of the dissolved Mg. By the end of the experiment,

323   olivine is the largest supplier of Mg (~45%), greater than Mg from carbonates or

324   the exchangeable fraction (Fig. 4).

325

326   5.1.2 Lithium

327   The lithium mass balance of the effluent from the control core after 5 days

328   is dominated by Li from the exchangeable pool (>84%), while clay only

329   contributes ~1.5% and carbonates 0.05% (with the remaining ~14% coming

330   from Li in the initial input solution). The fractions of Li from each source remain

331   largely unchanged during the course of the experiment (~85% from the

332   exchangeable fraction by the end) (Fig 5).

333   In the olivine core, after 5 days only 5% of the effluent's Li is sourced from

334   olivine dissolution, while by the end of the experiment ~10% is from the olivine,

335   with the remainder still dominated by exchangeable Li. The lack of Li in the soil

336   carbonates motivates the use of Li as a silicate weathering tracer, independent of

337   carbonate sources (Gou et al., 2019; Kisakürek et al., 2005), but also shows that

338   in these soil solutions both primary and secondary silicates provide less Li than

339   the exchangeable pool. The results also show that Mg and Li can be decoupled

340   during weathering, even though Li substitutes for Mg in both primary and

341   secondary silicates (Hindshaw et al., 2019).

342

343   *5.2 Magnesium isotopes*

344   5.2.1 Mg isotopes in the soils

345   The selective leaches of the different phases at different depths of the soil

346   show that the carbonates are isotopically light (∼-3.3‰), the silicates are

347   isotopically heavy (∼0‰), and the exchangeable fraction has an intermediate

348   composition (∼-1.8‰), as also observed by other soil and carbonate studies

349   (Chapela Lara et al., 2017; Opfergelt et al., 2014; Saenger and Wang, 2014; Tipper

350   et al., 2006b). There is comparatively little isotopic variation with depth in any of

351   the phases (Fig 2), although the δ^{26}Mg of the exchangeable fraction increases by

352   ∼0.6‰ with depth.

353

354   5.2.2 Control core behaviour during the experiment

355   For the first 17 days of the experiment, the δ^{26}Mg of the control core's

356   effluent solution stayed approximately constant (and similar to that of the olivine

357   core, discussed below). The significant effect on the Mg mass balance of the

358   exchangeable fraction (42%) suggests that the initial effluent must be strongly

359   affected by the composition and nature of this fraction. It is likely that ion

360   exchange retarded the downward transport of the Mg added to the influent

361   solution, while the change in solution chemistry led to release of previously

362   adsorbed Mg. If, as is likely, the [Mg] in the influent solutions was not in

363   equilibrium with the exchangeable pool (because the [Mg] is likely lower than

364   that in the original pore waters, as well as potentially due to changes in pH,

365   temperature, etc.), Mg was released from the exchangeable pool, and the Mg

366   concentration of the effluent solution decreased with time (Fig. 3C), resulting in a

367   decrease in the proportion of exchangeable Mg provided to solution with time

368   (Fig. 4). Thus, because of the retardation by ion exchange, the duration of the

369   downward movement in the core of Mg is not three days (the water residence

15

370   time), but around 17 days, a feature discussed further in the context of Li

371   isotopes below.

372   Following this initial period of time, the δ^{26}Mg of the control core's

373   effluent solution started to decrease almost linearly to a final value of -2.73‰

374   (Fig. 3D), without reaching any obvious isotopic steady-state. The mass balance

375   shows that this decrease is largely due to increasing contribution from the

376   dissolution of (isotopically light) carbonates with time.

377   Based on a standard isotopic mass balance equation (identical in

378   assumptions to that described in Section 4.3) it is possible to calculate the

379   isotope ratio of Mg coming from the exchangeable pool at the start of the

380   experiment.

381    $$\delta_{effluent} = (f\delta)_{influent} + (f\delta)_{exch} + (f\delta)_{sil} + (f\delta)_{carb} \qquad \text{Eqn. 4}$$

382   where f is the Mg mass fraction each phase makes up of the total, and δ is the

383   isotope ratio. The calculated isotopic composition can then be compared to the

384   isotope ratio of the leached exchangeable fraction, and any difference will be due

385   to fractionation caused by isotopic exchange. We find that the δ^{26}Mg exiting the

386   exchangeable pool is approximately -1‰, exhibiting a fractionation factor of

387   ~0.56‰ from the lowest exchangeable fraction. This amount of isotope

388   fractionation is similar to that reported from exchange experiments (Wimpenny

389   et al., 2014) and observed in soil profiles (Tipper et al., 2010) and basaltic

390   groundwaters (Oelkers et al., 2019), suggesting that, while most of the Mg is

391   sourced from carbonate dissolution (65% by the end of the experiment), the

392   observed isotope ratio in the effluent is due to mixing between light Mg from the

393   carbonate and fractionated Mg from the exchangeable pool (which contributes

394   ~32% of Mg).

16

395

5.2.3. Olivine core behaviour

As described above, the δ^{26}Mg of the control and the olivine core were identical for the first 17 days of the experiment, due to retardation of the Mg signal by ion exchange as fluids travelled down the soil column. Once the chemical signal of added (fractionated) Mg reached the bottom of the core, δ^{26}Mg in the effluent from the olivine core increased relative to that from the control core (Fig. 3), and by the end of the experiment was ~1‰ higher than that of the control core. The elemental mass balance shows that this increase was due to addition of isotopically heavy Mg from olivine dissolution.

The impact of olivine dissolution vs. the combination of carbonate and exchangeable Mg is demonstrated by plotting δ^{26}Mg as a function of Mg/Ca ratios (Fig. 6). The olivine core clearly has higher Mg/Ca ratios and higher δ^{26}Mg values, indicating addition of high-Mg, isotopically heavy material — as expected for olivine.

Renforth et al. (2015) derived an olivine dissolution rate for these core experiments by comparing the Mg flux from both cores. Here, we observe a significant ($p < 0.05$) relationship between Δ^{26}Mg$_{olivine-control}$ (i.e., the difference between the two cores that reflects the specific effect of olivine dissolution on the dissolved Mg isotope composition) and the olivine dissolution rate calculated from Mg fluxes (Renforth et al., 2015) (Fig. 8B). Although there is some scatter (largely because Δ^{26}Mg increases linearly with time, while Δ[Mg] does not), the amount of isotopic difference between the effluent of the two cores increases both with time and with the olivine dissolution rate. This is to be expected if the only tangible difference between the two cores is the dissolution of the added

17

420   (isotopically heavy) olivine. However, we note that the absolute amount and

421   rates of dissolving olivine inferred both from the mass balance and from the

422   isotope ratios are likely lower than the true values, due to retardation by the

423   exchangeable pool, and hence olivine-derived Mg taking longer than expected to

424   exit the core to be analysed.

425   From an overall weathering perspective, the data from these core

426   experiments indicate that lithology (i.e. silicates vs. carbonates) exerts a

427   significant control on Mg isotopes, in agreement with other studies (Li et al.,

428   2010; Pogge von Strandmann et al., 2019b; Teng et al., 2010; Tipper et al., 2008;

429   Tipper et al., 2006a; Tipper et al., 2006b). Retardation by ion exchange provides

430   an additional element of complication: on long, natural weathering, timescales,

431   Mg isotopes appear to be a useful tracer of weathering lithology, and potentially

432   also silicate weathering characteristics. However, on the timescales of this

433   experiment, and indeed any weathering or enhanced weathering experiment

434   where results are necessary within a relatively short period, ion exchange may

435   mean that observed effects in drainage solutions do not necessarily reflect the

436   total dissolution reactions taking place.

437

438   *5.3 Lithium isotopes*

439   5.3.1 Soil characteristics

440   The bulk rock δ^7Li values in the soil core are fairly constant with depth (-

441   0.7 to +2.1‰). Studies on the δ^7Li of bulk soils in different settings show

442   everything from little variation with depth (Huh et al., 2004; Lemarchand et al.,

443   2010; Pistiner and Henderson, 2003), isotope ratios becoming lighter with depth

444   (Clergue et al., 2015; Huh et al., 2004; Liu et al., 2013; Tsai et al., 2014) and

445   isotope ratios becoming heavier with depth (Kisakurek et al., 2004; Liu et al.,

446   2013; Pogge von Strandmann et al., 2012). Explanations for this behaviour range

447   from mixing of detrital material (e.g. Tsai et al., 2014) to fractionation during

448   formation of secondary minerals and depletion of Li during weathering (e.g.

449   Clergue et al., 2015). Here, the largely invariant δ^7Li values with depth suggest

450   that, in terms of the silicates that control the bulk soil Li composition, there is

451   little depth-variation in this profile.

452   To our knowledge, no study has yet examined how the exchangeable pool

453   behaves in a soil profile, but broadly similar processes likely apply. In our first

454   such profile, exchangeable δ^7Li reaches a peak of 12.6‰ at 30cm depth and then

455   decreases to -6‰ at 80cm depth (Fig. 2). For most of the profile, the

456   exchangeable pool is isotopically heavier than the bulk soil.

457   Overall, the exchangeable pool will have been exchanging Li with pore

458   waters, with an isotope fractionation on the order of 10–20‰ towards lighter

459   values (Pogge von Strandmann et al., 2019a; Hindshaw et al., 2019), as also

460   calculated by mass balance below. This process should theoretically drive both

461   pore waters and the exchangeable pool isotopically heavy with time (and depth).

462   While this process appears to be occurring down to 30cm, below this depth the

463   exchangeable pool becomes increasingly lighter and less concentrated, resulting

464   in a positive co-variation between δ^7Li and [Li] in the exchangeable pool (Fig. 7).

465   The reason for this trend is not entirely clear: a low Li concentration likely also

466   reflects a low [Li] in the pore waters, which would then be expected to have a

467   higher δ^7Li composition as material is removed and fractionated (Clergue et al.,

468   2015; Pogge von Strandmann et al., 2017b), imparting high δ^7Li to the

469   exchangeable pool. It is possible that exchange is slower deeper in the profile, as

470   the proportion of primary carbonates increase, but the data do not allow us to

471   definitively identify the mechanism.

472   While the exchangeable fraction only makes up ~0.5% of the Li in the

473   bulk soil, and is therefore not important for the bulk soil δ^7Li composition, it has

474   a considerably larger influence on the Li composition of the effluent solutions

475   (Fig. 5).

476

477   5.3.2 Control core behaviour

478   As described in Section 5.1, the behaviour of effluent Li in the control core

479   is entirely dominated by Li from the exchangeable pool (84.1% at the start of the

480   experiment, and 84.7% by the end of the experiment).

481   The control and olivine cores exhibit identical δ^7Li behaviour for the first

482   ~20 days (as opposed for ~17 days for Mg) of the experiment with a δ^7Li value

483   of ~12‰ (Fig. 3B). Given the exchangeable fraction's dominance, the initial

484   effluent's δ^7Li should be directly related to the δ^7Li of the exchangeable fraction

485   at the bottom of the soil core. The solution composition is ~18‰ higher than the

486   deepest exchangeable fraction, generally higher than previously reported

487   fractionation during sorption of Li onto secondary minerals of 0–12‰, while

488   structural Li tends to have fractionation factors >21‰ (Hindshaw et al., 2019;

489   Millot and Girard, 2007; Pistiner and Henderson, 2003; Pogge von Strandmann et

490   al., 2019a; Pogge von Strandmann et al., 2020). It may therefore be the case that

491   the final fractionation is not only occurring between the deepest exchangeable

492   fraction, but also layers further up the soil column with higher δ^7Li. The

493   concentration-weighted average of the exchangeable fraction in the entire soil

494   column is ~8‰, giving a fractionation factor of ~4‰, within the reported range

495   for exchangeable Li. Alternatively or in addition, the isotopic composition may be

496   influenced by incorporation of Li into structural sites, with higher fractionation

497   factors.

498   During the experiment, the control core's effluent δ^7Li increases rapidly to

499   20‰ and eventually stabilises at ~23‰. There is no evidence that the

500   secondary mineralogy changed during this time, based on broadly constant

501   mineral saturation states (kaolinite SI = 6.5 ± 0.6 (Renforth et al., 2015)).

502   Instead, this behaviour is likely due to retardation by ion exchange (Davidson

503   and Dickson, 1986; Johnson and DePaolo, 1997; Krishnaswami et al., 1982;

504   Porcelli and Swarzenski, 2003), as the newly added dissolved Li moves down the

505   core, similar to that observed for Mg. The [Li] in the influent solution is out of

506   equilibrium with the exchangeable fraction (due to differences in composition,

507   pH, temperature from the natural soil waters), so it liberates Li from the

508   exchangeable pool. In other words, the change in δ^7Li after 20 days is due to the

509   addition of influent material affecting the exchangeable pool. A similar isotopic

510   mass balance as described above for Mg shows that the δ^7Li of material coming

511   from the exchangeable pool is ~12.7‰, hence exhibiting a fractionation factor of

512   ~18‰ from the lowest exchangeable fraction (similar to that inferred from the

513   initial solutions). This heavy Li moves down the core, but because of retardation,

514   the duration of this movement is not three days (the water residence time), but

515   the observed ~20 days. This also means that the effluent isotope ratio will

516   continue to evolve, as the lighter isotopes retained in the exchangeable fraction

517   eventually also moves down the core and into the effluent. The retardation factor

518   R for Li in the exchangeable fraction, assuming perhaps over-simplistically, a

519   linear form of the Langmuir isotherm, is:

520     $R = 1 + \frac{q}{c}$ Eqn. 5

521   where q is the adsorbed ions and C the ions in effluent solution. This yields an R

522   value of 1.85 for the final experimental sample for Li. In comparison, the R value

523   for Mg is 1.32. Using a seepage velocity of 0.31 m/day (Fig. 1), this gives an

524   exchangeable Li transport rate of 0.17 m/day for Li and 0.23 m/day for Mg.

525   Theoretically, this means that it would take ~19 days for the heavy Li and ~14

526   days for the Mg to make it into the effluent solution. This is slightly shorter than

527   the observed breakthrough time, but we note that the time resolution of the

528   sampling is low, and the above calculations are based on constant Darcy

529   velocities and porosities through the core. Importantly, the different retardation

530   factors for Li and Mg explain why the apparent breakthrough times are different

531   for the two elements. Such behaviour will further decouple Li and Mg isotopes.

532   The sorption partition coefficient can also be calculated from the

533   retardation factor, according to (Krishnaswami et al., 1982):

534     $K = \frac{q}{c}$ Eqn. 6

535   where K is a dimensionless distribution coefficient. This is related to the 'normal'

536   partition coefficient K_d by the equation:

537     $K = K_d \left(\frac{\rho(1-n)}{n} \right)$ Eqn. 7

538   By this calculation, the sorption partition coefficient is ~0.093 for Li, and ~0.037

539   for Mg. In other words, in this setting, Li sorbs ~2.6 times more readily than Mg,

540   explaining the slightly longer retardation time for Li.

541

542   5.3.3 Olivine core behaviour

543   As described above, the d7Li of the effluent from the olivine core diverges

544   from that of the control core beginning after ~20 days, ending up 7‰ lower (Fig.

545   3B). The retardation of the downward-flowing added Li (with associated isotopic

546   fractionation) by the exchangeable pool functions identically in both the control

547   and olivine core. However, in the olivine core, the addition of heavy Li from the

548   exchangeable fraction is to an extent counterbalanced by addition of light Li from

549   dissolution of the olivine (δ^7Li = 2.7‰).

550   The initial isotope fractionation between soil and effluent, or between

551   olivine and effluent (average soil and olivine having virtually identical δ^7Li: 2.3

552   vs. 2.7‰, respectively), was Δ^7Li$_{soil-solution}$ = ~-10‰ at the start of the

553   experiment. After 20 days, the effluent from the olivine core has a δ^7Li value that

554   increases, leading to Δ^7Li$_{soil-solution}$ = -14‰ by the end of the experiment,

555   compared to -21‰ in the control core (Fig. 3B). This difference suggests that

556   olivine dissolution is not promoting relatively greater Li uptake by the

557   exchangeable pool or by secondary minerals, which would drive δ^7Li higher than

558   the control core. This amount of fractionation can be compared with the

559   dissolution-precipitation batch-reactor olivine experiments conducted by

560   Wimpenny et al. (2010a). A similar degree of isotopic fractionation between the

561   initial olivine and final solution is observed in both experiments, even though

562   Wimpenny et al. (2010a) did not conduct their experiments in soil. They

563   concluded that this fractionation was due to chrysotile ($Mg_3(Si_2O_5)(OH)_4$)

564   precipitation. In our study's soil experiments, however, chrysotile is always

565   significantly undersaturated (average saturation index ~ -9), and instead the

566   exchangeable pool appears to dominate Li behaviour.

567   The $\Delta^7Li_{olivine-control}$ values correlate with the olivine weathering rate

568   calculated from the difference in Mg flux between the two cores (Renforth et al.,

569   2015) (Fig. 8A; r^2 = 0.72). This correlation is consistent with a first-order control

570   on the dissolved δ^7Li from primary mineral dissolution rates; that is to say, the

571   more olivine dissolves, the more it contributes relatively unfractionated δ^7Li,

572   thus decreasing the solution δ^7Li relative to the control core. The observed

573   correlation is also consistent with an identical amount of adsorption (or

574   secondary mineral formation) in both cores, meaning that the only additional

575   control on the olivine core's effluent δ^7Li is olivine dissolution.

576   The core experiments also provide a test of the generally accepted

577   controls on Li isotopes. The prevailing model is that dissolved Li isotopes are

578   determined by weathering congruency, which is the ratio of primary mineral

579   dissolution to secondary mineral formation. In the core experiments, the

580   addition of primary silicates (olivine) drove solution δ^7Li to lower values,

581   implying more congruent weathering. Further, the large effect of the

582   exchangeable pool on Li in these experiments (>80%) contrasts to experiments

583   where relatively fresh basalt was reacted with water with almost no initial pool

584   of clay minerals (Pogge von Strandmann et al., 2019a). In those experiments, the

585   exchangeable fraction only comprised 12–16% of the total Li, with the rest due

586   to clay mineral neoformation. This difference highlights the long timescales

587   required to precipitate significant amounts of secondary minerals. In other

588   words, by importing pre-formed soils into the laboratory (rather than only fresh

589   rocks), these soil core experiments have very different characteristics from

590   experiments with olivine alone. The strong affinity of Li for exchangeable sites

591   means that, while it provides important information on weathering on natural

24

592   timescales, on relatively short timescales (e.g., associated with enhanced

593   weathering), ion exchange may mean that dissolution effects are harder to

594   observe.

595

596   *5.4 Comparison of Li and Mg isotopes*

597   Overall, there is a negative co-variation between $\Delta^{26}Mg$ and Δ^7Li (Fig. 9).

598   Hence, despite the decoupling of the behaviour of Li and Mg due to the difference

599   in effect the exchangeable pool exerts, in terms of artificial addition of olivine,

600   both isotope systems exhibit a similar response. What this means is that in these

601   through-flow experiments, the experimental duration was not long enough for

602   significant secondary mineral formation to occur. In contrast, secondary mineral

603   formation did occur within this length of time in closed system experiments

604   (Pogge von Strandmann et al., 2019a). If secondary mineral formation were to

605   occur, it would be expected that it would be different in the olivine core

606   compared to the control core, due to the addition of dissolved cations (Gíslason

607   et al., 1996).

608   In terms of natural weathering, therefore, these experiments can shed

609   some light on "incipient weathering", which in weathering studies represents the

610   initial or very early part of the weathering reaction, although it has never been

611   clear to what extent it encompasses sorption or secondary mineral formation

612   (Navarre-Sitchler et al., 2015). Incipient weathering has been used to explain

613   several different observations in Li isotope space (Kisakurek et al., 2004; Millot

614   et al., 2010; Rudnick et al., 2004; Ryu et al., 2014), including driving the dissolved

615   phase both isotopically heavy (Millot et al., 2010) and leaving the isotope ratios

616   of soils virtually unaltered (Ryu et al., 2014). In the case of these experiments,

617   initial weathering of fresh material ('incipient weathering") clearly drives the

618   dissolved load towards the composition of the primary weathering material,

619   with fractionation by secondary minerals having minimal additional effect.

620   In terms of enhanced weathering, these experiments show that, while

621   olivine dissolution (and hence CO_2 drawdown) will occur during the initial

622   phases, the ultimate effect of enhancing weathering (i.e. including the increase in

623   the formation of secondary weathering products) still largely remains unknown,

624   and will require multi-year experiments to examine and quantify.

625

626   **6. Conclusions**

627   A well-characterised experiment in a soil core was used to assess the

628   controls on lithium and magnesium isotope ratios during weathering. Olivine

629   was added to the top of one core and compared to a control core without olivine

630   For both Mg and Li, the exchangeable pool of sorbed elements on mineral

631   surfaces in the soil exerted a significant role on the effluent composition,

632   retarding the transport of chemical signals down the core by around 17–20 days.

633   Ion exchange occurred in response to changing pore-water chemistry and

634   imposed an isotope fractionation on effluent waters at the base of the core. This

635   will also result in a significant amount of time before effluent isotope ratios

636   finally reach a full steady-state, when the retarded, fractionated signal finally

637   breaks through.

638   Input of Mg to the effluent solution were largely from dissolution of

639   carbonate plus dissolution of silicate in the olivine core, which drove the $\delta^{26}Mg$ of

640   the olivine core towards higher (more olivine-like) values with time. Mg isotopes

641   were thus largely controlled by the congruent dissolution of different lithologies,

modified in the short-term by isotopic fractionation associated with sorption onto the exchangeable fraction (of ~0.5‰, similar to natural studies). This observation supports the idea of using Mg isotopes as a lithological tracer, though interpretation of such Mg isotope signals will be complex on timescales where the exchangeable pool in the soil is adjusting to change.

The Li isotopic fractionation between the lowest part of the core's exchangeable pool and that in fluids in the core is ~18‰, and is 4‰ between the solution and the total core's concentration-weighted exchangeable fraction, similar to that observed in natural systems for exchangeable Li. Addition of olivine and its subsequent dissolution drove the solution δ^7Li lower (towards that of olivine) with time, showing that addition of primary silicate increases weathering congruency (at least on the timescale of a few months).

The use of these isotope systems in enhanced weathering situations does not necessarily add information that could not be accessed by trace element concentrations, at least when it comes to determining dissolution rates (and hence CO_2 drawdown rates). Both isotope systems have, however, revealed that the exchangeable pool significantly retards the transport of elements derived from the dissolution of added silicates, when those silicates are added to a pre-existing soil complex. Hence, using either isotope ratios or trace elements to examine and quantify enhanced weathering will be significantly complicated by the exchangeable pool, because any dissolution signal can take a significant amount of time to recognisably arrive at a monitoring station. This will then likely cause an initial underestimation of the added silicate dissolution rates and fluxes, unless the monitoring duration extends to the total equilibration time. In terms of natural weathering signals, the long averaging time for seawater

667 records means this process will not matter. However, for archives of less

668 integrated processes (e.g. speleothems), this process may be important.

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980   Table 1. Li and Mg concentration and isotope ratios of the bulk soils, and their

981   exchangeable and carbonate fractions (based on Na-acetate and acetic acid

982   buffered with Na-acetate leaches, respectively).

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985   Table 2. Li and Mg concentrations and isotope ratios of the effluent solutions.

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990   Figure 1. Schematic of the experimental setup. The plough layer depth was 0.2m

991   (figure modified from Renforth et al., 2015).

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994   Figure 2. A) Li isotope profiles for bulk soils and exchangeable leaches. B) Bulk

995   soil, exchangeable and carbonate δ^{26}Mg with soil depth. Analytical uncertainty is

996   smaller than the symbol sizes.

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999   Figure 3. Effluent concentrations and isotope ratios. (A) Li concentrations; (B) Li

1000   isotope ratios, with the dashed line representing the composition of the olivine,

1001   and the shaded area the composition of the bulk soils. (C) Mg concentrations

1002   from Renforth et al. (2015); (D) Mg isotope ratios, with the dashed lines

1003   representing the composition of the added olivine and leached carbonate

1004   fractions, as labelled, while the shaded areas represent the bulk soils and

1005   exchangeable soil Mg fractions. The error bars represent the 2sd analytical

1006   uncertainty, unless smaller than the symbols.

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1009   Figure 4. Mg mass balance for the initial and final effluent solutions.

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1012   Figure 5. Li mass balance for the initial and final effluent solutions.

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1015   Figure 6. Mg isotopes as a function of the Mg/Ca ratio of the effluent solutions.

1016   The olivine core's effluent is clearly affected by a Mg-rich and isotopically heavy

1017   phase.

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1020   Figure 7. The Li concentration and isotope ratio of the exchangeable pool in the

1021   soil column.

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1024   Figure 8. A) Correlation between the Li isotope difference between the cores and

1025   the olivine dissolution rate (determined from Mg concentrations; Renforth et al.,

1026   2015). A logarithmic fit is shown because if the fit were linear, fractionation due

1027   to weathering could increase indefinitely. B) Relationship between the Mg

1028   isotope difference between the drip waters from both cores and the olivine

1029   weathering rate determined from Mg concentrations. The error bars represent

1030   the 2sd propagated uncertainty.

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1033   Figure 9. The isotopic difference between the control and olivine cores for both

1034   Li and Mg isotopes plotted relative to each other.

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