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Seasonal variability in silicate weathering signatures recorded by Li isotopes in cave drip-waters

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1 **Highlights**

- 2
- 3 - Time series of soil porewater chemistry from drip-waters in Yorkshire caves
 - 4 - Drip-water lithium isotopes vary spatially and temporally from $\delta^7\text{Li} = +1 \text{ ‰}$ to $+17 \text{ ‰}$
 - 5 - Temporal variability arises from lithium incorporation into secondary phases
 - 6 - Possible controls by seasonal changes in temperature and/or fluid residence time
 - 7 - Seasonal variability should be considered when interpreting paleo-proxy records

8

9 **Key words**

10 chemical weathering; carbon cycle; climate; seasonality; geochemistry; lithium isotopes;

11 porewater; caves

12

13

14

15 **Abstract**

16

17 Silicate weathering is a critical process in Earth's carbon cycle, but the fundamental

18 controls on weathering are poorly understood and its response to future climate change is

19 uncertain. In particular, the potential for changes in seasonality or extreme weather events to

20 control silicate weathering rates or mechanisms has been little studied. Here, we use lithium

21 (Li) isotope measurements in bimonthly sampled drip-waters from two caves in the Yorkshire

22 Dales (U.K.) to assess the response of silicate weathering processes to changes in temperature

23 and hydrology over seasonal timescales. While the caves are contained in limestone bedrock,

24 the drip-water Li isotope signal predominantly reflects silicate weathering of the overlying soils

25 that are dominated by glacial till.

26 Drip-water Li isotope compositions record spatial and temporal variability ranging

27 from $\delta^7\text{Li}$ values of $+1$ to $+17 \text{ ‰}$, with a mean of $+11 \text{ ‰}$. These values are significantly higher

28 than local lithogenic inputs ($\delta^7\text{Li} = -1 \pm 1 \text{ ‰}$), consistent with isotope fractionation during

29 secondary mineral formation. Comparison to temperature, precipitation, drip rates, and drip-

30 water chemistry enables the controls on the Li isotope weathering signatures to be explored,

31 revealing possible roles for both temperature and fluid residence time in setting the balance

32 between primary rock dissolution and secondary mineral formation. Specifically, our Li isotope

33 data are consistent with a scenario in which cooler temperatures and/or longer fluid residence

34 times lead to enhanced secondary mineral formation relative to silicate dissolution.

35 Overall, our results indicate the potential for Li isotope variability over short temporal

36 and spatial scales, which is important to consider when interpreting past changes in weathering

37 processes or fluxes from paleo-records. In addition, the seasonal changes in Li isotopes suggest

38 that weathering processes may be sensitive to seasonality or to extreme weather events, rather

39 than responding only to the mean climate state. With warmer temperatures and more intense

40 rainfall events expected in future, both increased primary rock dissolution and enhanced

41 weathering efficiency (due to reduced secondary mineral formation) could potentially

42 contribute to increased carbon dioxide drawdown by silicate weathering.

43

44

1. Introduction

45

46 Chemical weathering of silicate rocks is a key process that controls Earth's geochemical
47 and carbon cycles, and hence global climate (Walker et al., 1981; Berner et al., 1983), but the
48 strength of the climate-weathering feedback and the timescales it operates over are poorly
49 constrained (e.g. West, 2012; Li et al., 2016; Krissansen-Totton and Catling, 2017). Given the
50 significant uncertainty in how, and how fast, weathering will respond to future climate change,
51 it is essential to obtain a better understanding of the controls on weathering. Lithium (Li)
52 isotopes are a promising tracer for this purpose because they are uniquely sensitive to silicate
53 weathering processes (Dellinger et al., 2015; Pogge von Strandmann et al., 2017a) and
54 insensitive to both carbonate weathering (Kisakürek et al., 2005) and biological effects
55 (Lemarchand et al., 2010; Clergue et al., 2015; Pogge von Strandmann et al., 2016). Lithium
56 isotope records from marine carbonates have been used to constrain globally-integrated
57 changes in weathering fluxes and/or processes in response to climate over multi-kyr to Myr
58 timescales (Hathorne and James, 2006; Misra and Froelich, 2012; Pogge von Strandmann et
59 al., 2017b). In addition, speleothems can record localised changes in weathering processes over
60 tens to thousands of years (Pogge von Strandmann et al., 2017c), while authigenic clay minerals
61 may be another promising archive of paleo-fluid compositions in weathering systems (Clauer
62 et al., 2018). However, chemical weathering could also vary over much shorter timescales
63 (Gislason et al., 2009), in which case both paleo-records and the future global carbon cycle
64 may be sensitive to changes in seasonality or to extreme weather events, rather than responding
65 only to the mean climate state.

66 Lithium isotopes trace weathering processes because rock dissolution is approximately
67 congruent for Li isotopes whereas the formation of secondary minerals such as clays and oxides
68 preferentially removes ^6Li and leaves the weathering solution enriched in ^7Li (Pistiner and
69 Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2010; Dellinger et al., 2015; Pogge von
70 Strandmann et al., 2017a; Hindshaw et al., 2019a). Hence, Li isotopes in soil porewaters or
71 river waters should trace the balance between silicate rock dissolution and secondary mineral
72 formation. Importantly, the formation of secondary clays sequesters some of the cations
73 released during rock dissolution, which can reduce the efficiency of carbon dioxide drawdown
74 during weathering (Pogge von Strandmann and Henderson, 2015). Therefore, Li isotopes
75 potentially provide a tool for quantifying changes in both silicate weathering processes and the
76 efficiency of carbon sequestration by weathering.

77 Measurements of Li isotopes in river waters reflect modern weathering processes at a
78 catchment scale, but 'snapshot' sampling at single points in time has only recently been
79 extended to time series sampling, allowing seasonal changes to be revealed (Liu et al., 2015;
80 Gou et al., 2019; Hindshaw et al., 2019b). In some settings, seasonal variability in Li isotopes
81 could reflect temperature-dependent isotopic fractionation (Gou et al., 2019), but in other cases

82 it hints at a role for fluid residence time in controlling weathering processes (Liu et al., 2015;
83 Hindshaw et al., 2019b). In addition, seasonal variations in river water chemistry may also be
84 influenced by mixing between different fluid reservoirs, such as soil porewaters and deep
85 groundwaters (Tipper et al., 2006; Calmels et al., 2011; Fries et al., 2019; Hindshaw et al.,
86 2019b), rather than necessarily recording fundamental changes in weathering processes. Given
87 also that a large proportion of weathering occurs in soils rather than in rivers, complementary
88 constraints on temporal variability in soil weathering processes are required. However,
89 obtaining soil porewater time series is challenging, so most Li isotope studies on porewaters
90 have only involved snapshot sampling (e.g. Pogge von Strandmann et al., 2012; Steinhoefel et
91 al., 2021) or limited repeat measurements (e.g. Lemarchand et al., 2010; Fries et al., 2019),
92 rather than continuous time series.

93 Here we develop an approach to obtain time series of soil porewater Li isotope
94 compositions using cave drip-waters collected over a two-year period in Pippikin and White
95 Scar caves in the Yorkshire Dales, U.K. The former cave is technically challenging to access,
96 whereas the latter is a show cave that is open to the public. Since the drip-waters are sourced
97 from the overlying soil porewaters before flowing through limestone, these samples contain a
98 record of the temporally evolving weathering fluid chemistry. In theory, silicate weathering
99 and secondary mineral formation in the soils will control the Li isotope compositions of the
100 weathering fluids, with little or no effect from the underlying carbonates (Kisakúrek et al.,
101 2005; Millot et al., 2010b; Pogge von Strandmann et al., 2017a). Therefore, these Li isotope
102 time series enable a first-order quantification of seasonal variability in silicate weathering
103 processes and signatures. In combination with records of temperature, precipitation, drip rates,
104 and drip-water chemistry, we explore the controls on weathering, and specifically assess the
105 possible roles of temperature and fluid residence time in setting the balance between rock
106 dissolution and secondary clay formation. An improved understanding of how chemical
107 weathering processes in soils are recorded by Li isotopes is important for interpreting both
108 modern river data and paleo-records of Li isotope changes, which will feed into a better
109 understanding of how changes in temperature, seasonality, and hydrological processes will
110 impact on the future global carbon cycle.

111

112 **2. Regional setting and samples**

113

114 Drip-water samples were collected from two caves in the Yorkshire Dales, U.K.:
115 Pippikin Pot via its Mistral entrance in the Ease Gill Cavern system (Grid Reference SD 667
116 803), and White Scar Cave beneath Ingleborough (Grid Reference SD 712 745). Descriptions
117 of the caves and their geological setting are given in Waltham and Lowe (2017). They are ~7
118 km apart and both are contained within the Great Scar Limestone of Lower Carboniferous age,
119 which comprises sub-horizontally bedded carbonate with occasional cm- to m-scale shale
120 layers (Waltham, 1970; Waters and Lowe, 2017). Regionally, the limestone is overlain by the

121 Yoredale Group, a cyclic succession of shales, sandstones, and thin limestones, but erosion has
122 completely removed these rocks from the limestone benches overlying the caves (Aitkenhead
123 et al., 2002). Their importance for the present study is that they form the source material for
124 the glacial tills that presently overlie the caves (Mitchell, 1991; Mitchell, 1994; Livingstone et
125 al., 2012). The tills themselves are diamictons, containing predominantly sandstone and
126 limestone clasts in varying proportions, within a poorly-sorted matrix of sand, silt, and clay
127 (Rose, 1991; Murphy et al., 2001). The carbonate content of the matrix is reported to match the
128 proportion of limestone outcropping in the source area (Andrews and King, 1968). An
129 important contrast between the two cave sites is that Pippikin cave is overlain by tills up to 6
130 m thick on which peaty gleyed podsollic soils have developed, whereas the study sites at White
131 Scar Cave lie beneath the side slope of the Chapel-le-Dale valley, on which limestone outcrops
132 protrude through well-drained brown earth soils formed on till patches less than 1 m in
133 thickness.

134 Dye tracing studies at White Scar Cave indicate a timescale of days for the initial
135 breakthrough of tracers from injection points in fractures below the soil cover to drip sites in
136 the cave (Bottrell and Atkinson, 1992). Despite this rapid initial transit, most of the tracer is
137 retained for much longer, with mean residence times of 1 to 2 months (Bottrell and Atkinson,
138 1992). These results indicate that seasonal changes in the trace element chemistry of soil waters
139 (i.e. inputs to the limestone system) can be recorded by sampling cave drip-waters (i.e. outputs).
140 However, the dye tracing also demonstrated that a very small fraction of the tracer was retained
141 in the system for much longer times, and up to six years in one case (Bottrell and Atkinson,
142 1992).

143 The drip-water samples analysed here were collected approximately every two months
144 from August 2016 to November 2018, from two different locations in each cave (see Figs.
145 EA1-2 for maps). Pippikin cave samples A and D (hereafter, Pippikin A and D) were collected
146 from a curtain drip ~200 m from the cave entrance and a ceiling drip ~300 m from the cave
147 entrance. White Scar Cave samples 1 and 3 (White Scar 1 and 3) were collected from a stalactite
148 drip ~400 m from the cave entrance and a collection of drips from a flowstone ~420 m from
149 the cave entrance. At both caves, mean annual surface temperatures are ~8 °C and mean
150 monthly temperatures vary seasonally by ~10 °C, whereas seasonal variations are only ~5 °C
151 inside the cave entrance and < 0.5 °C in the cave interior. Mean annual precipitation totals in
152 the Yorkshire Dales are ~1500 mm (Malham Tarn; Burt and Horton, 2003).

153 Rock and soil samples were also collected from the vicinity of the two caves. Samples
154 from Pippikin cave include: Great Scar Limestone from the cave entrance; an interbedded shale
155 from the nearby Arson Shaft of Ease Gill; Quaternary till from Ease Gill; peaty soil from high
156 ground overlying the cave; and a modern calcareous sediment sample from the floor of the
157 cave. Samples from White Scar Cave include: Great Scar Limestone from near the cave
158 entrance; Yoredale Shale from the overlying hillslopes; and Quaternary till from near the cave
159 entrance.

160

161 **3. Methods**

162

163 **3.1 Sample preparation**

164

165 Drip-water samples were collected in pre-cleaned glass bottles and stored in a fridge.
166 They were filtered in the laboratory at 0.2 μm using a cellulose-acetate filter and syringe to
167 ensure complete removal of fine particles (although visible particle content was minimal) and
168 the filtrate was analysed for Li isotopes and major/trace elements. Unfiltered samples were
169 analysed for oxygen isotopes.

170 All rock and soil samples were dried and crushed with an agate pestle and mortar. In
171 order to aid digestion of the peaty soil and tills, organic carbon was first oxidised using aqua
172 regia. All samples were then subjected to bulk digestion using concentrated HF, HNO₃, and
173 HClO₄ in Teflon beakers on a hotplate at 130 °C, followed by steps in concentrated HNO₃ and
174 6 M HCl. For the Great Scar Limestone samples, leaching was also conducted to separate the
175 carbonate and detrital fractions. The carbonate fraction was extracted by leaching ~100 mg
176 sample in 8 ml 0.1 M HCl for 1 hour (Pogge von Strandmann et al., 2013), enabling an
177 estimated ~40 mg of calcium carbonate to be dissolved. After repeating this leaching step a
178 second time to remove further carbonate, the detrital residue was digested as for the bulk
179 samples, although it should be noted that some minor carbonate likely remained within this
180 operationally-defined residue, so it probably represents a mixed carbonate and silicate signal.
181 In addition, for a subset of the rock and soil samples from Pippikin cave, a Na-acetate leach
182 was used to target the exchangeable fraction, following the method of Tessier et al. (1979) that
183 was recently also applied for measuring Li isotopes (Pogge von Strandmann et al., 2019).
184 Specifically, ~200 mg of sediment was leached in 2 mL 1M Na-acetate, at room temperature
185 and with frequent ultrasonication, followed by centrifugation and collection of the supernatant
186 fluid.

187

188 **3.2 Lithium isotopes**

189

190 Lithium separation followed a standard method of elution in 0.2 M HCl through
191 AG50W X-12 resin, with two column passes through different-sized columns to ensure matrix
192 removal (Pogge von Strandmann et al., 2013). Isotopic measurements were performed on a Nu
193 Plasma 3 MC-ICP-MS at UCL, using a Cetac Aridus 2 desolvation system, ‘super-lithium’
194 cones, and standard-sample bracketing with the IRMM-016 Li standard (Pogge von
195 Strandmann et al., 2019). Samples were measured at least three times within an analytical
196 session, with each measurement integrating ~50 seconds, and the reported values are the mean
197 and standard deviation (2sd) of these values, given in permil after re-normalising to the NIST-
198 8454 LSVEC standard (Table 1). Accuracy and external reproducibility were assessed using

199 seawater and USGS standard BCR-2 (Table EA1a,c), which gave $\delta^7\text{Li}$ values of $+31.3 \pm 0.6$
200 ‰ (2sd, n=28) and $+2.5 \pm 0.3$ ‰ (n=5), respectively, in good agreement with literature data
201 (James and Palmer, 2000; Jeffcoate et al., 2004; Pogge von Strandmann et al., 2011; Liu et al.,
202 2013; Dellinger et al., 2015; Pogge von Strandmann et al., 2019).

203 Because Li isotopes are fractionated during ion chromatography, splits were collected
204 before and after the Li collection interval to assess column yields. Although yields above 99,
205 99.5, or 99.9 % have variously been proposed to indicate good data quality in past studies, it
206 was recently suggested that yields above ~99.8 % are typically required to ensure no resolvable
207 offset between measured and true Li isotope values, at the precision of the current generation
208 of mass spectrometers (Gou et al., 2020). Here, typical yields after two column passes were
209 99.8-100 %. However, for a few samples, yields were in the range of 99.0-99.7 %, in which
210 case a small but resolvable offset in Li isotopes could arise. For the column procedures in our
211 laboratory, we have estimated that a 1 % loss in yield could lead to an offset of 1.7 ‰ for $\delta^7\text{Li}$,
212 based on analyses of seawater samples with differing column yields (Table EA1b). Because
213 we were often sample-limited and not always able to reanalyse samples, for sample
214 measurements where column yields were in the range of 99.0-99.7 %, we retained the Li
215 isotope data but have taken this additional uncertainty into account. Without knowing whether
216 Li was lost from the light or heavy tail, we could not employ a ‘correction’ to our data. Instead,
217 we estimated the maximum possible $\delta^7\text{Li}$ offset based on an empirical linear scaling of 1.7 ‰
218 per 1 % Li loss, and used this value in place of our analytical 2sd uncertainty where it was
219 larger. Such samples are indicated in the version of Table 1 in the Electronic Annex. The typical
220 procedural blank was 0.01-0.04 ng, which was significantly smaller than sample Li amounts
221 (typically 5-10 ng) and did not warrant blank correction.

222

223 **3.3 Major and trace elements**

224

225 Major and trace element concentrations were analysed using a Varian 720 ICP-OES
226 and a Varian 820 ICP-MS. Calibration was based on multi-point calibrations with multi-
227 element solutions. Repeat standard analyses allowed drift to be monitored during analytical
228 runs but no drift correction was applied. Accuracy and precision were assessed by analysis of
229 the international reference standards SLRS-4 (Yeghicheyan et al., 2001; Heimbürger et al.,
230 2013), NW-TMDA, and BCR-2 (Jochum et al., 2016).

231 For water analyses (Table 1, Table EA2), the major and minor elements were analysed
232 by ICP-OES (Ca, Mg, Na, K, Si, Sr), with accuracy within ± 10 %. Minor and trace elements
233 in the waters were analysed by ICP-MS (Li, B, Al, Ti, Mo, Ba, U), with accuracy within ± 4 %,
234 except for B (± 14 %) and U (± 7 %). For rock digests and leaches (Table 2, Table EA3), major
235 and selected minor/trace elements were analysed by ICP-OES (Al, Fe, Ti, Mg, Ca, Na, K, P,
236 Mn, Ba, Sr, Rb, Li), with accuracy within ± 10 % for all elements (Table EA3).

237

238 **3.4 Oxygen isotopes**

239

240 Oxygen isotope compositions of the drip-waters were analysed in the Stable Isotope
241 Laboratory at the University of East Anglia. Subsamples of the water were placed in 1.5 mL
242 vials with septa closures and loaded into the auto-sampler tray of a CDRS instrument (Picarro
243 V 1102-i model). Samples were measured in batches, and each sample was injected and
244 measured 6 times using 2.5 μL of water each time. Together with the samples, two secondary
245 international standards (USGS 64444, USGS 67400) and one internal laboratory standard
246 (NTW – Norwich tap water) were measured, each injected 10 times in order to minimise
247 memory effects. Isotopic compositions were calculated using the calibration line based on the
248 secondary international standards and reported in permil with respect to V-SMOW on the V-
249 SMOW – SLAP scale. The precision of the measurements was 0.1 ‰ for $\delta^{18}\text{O}$ (1sd) (Table 1).

250

251 **3.5 Climate and drip rate monitoring**

252

253 A temperature logger was installed outside the entrance to Pippikin cave to record
254 surface temperatures at 15-minute intervals, from which we calculated monthly average
255 temperatures from September 2016 to December 2018 (Table EA4). Outside of that period, we
256 use temperature data from a nearby weather station in Bingley (Bingley No 2,
257 <https://en.tutiempo.net/climate/united-kingdom.html>), adjusted for the mean difference of 1 °C
258 between these locations. Monthly rainfall totals were measured by a rain gauge located in
259 Ingleton, ~2 km from White Scar Cave and ~8 km from Pippikin cave, from September 2016
260 to November 2018 (Table EA4). Outside of that period, we use precipitation data from the
261 weather station Bingley No 2, adjusted by a factor of 1.4 to account for the higher precipitation
262 totals in the study area. Those monthly rain water samples were also collected and stored for
263 analysis of major/trace elements and Li isotopes (Table EA2). A “Stalagmate” drip logger was
264 installed in Pippikin cave, in the same chamber as the Pippikin D drip-water sampling, to
265 measure drip rates at 15-minute intervals, from which we calculated daily averages and
266 monthly-smoothed data (Table EA5). Instantaneous drip rates were also estimated by manual
267 counting at the individual drip-sites on most occasions that samples were collected (Table 1).

268

269 **4. Results**

270

271 **4.1 Major and trace elements in drip-waters**

272

273 For the complete drip-water dataset, the average major element concentrations are: Ca
274 (1200 $\mu\text{mol/L}$), Na (250 $\mu\text{mol/L}$), Si (69 $\mu\text{mol/L}$), Mg (43 $\mu\text{mol/L}$), K (13 $\mu\text{mol/L}$) (Table 1).
275 The major element chemistry on a Mg-Ca-(Na+K) plot is similar at all sites, being dominated

276 by Ca (mean for each site in the range of 74-84 %), with some Na (13-23 %), and minor Mg
277 (3 %) and K (1 %) (Fig. 1a). These data indicate the dominance of carbonate weathering sources
278 but also require a silicate component, and potentially also some contribution of Na from rain
279 water. On a plot of Mg/Na versus Ca/Na (Fig. 1b), it becomes clear that congruent dissolution
280 followed by mixing between carbonate and silicate sources (or rain water) cannot provide a
281 simple explanation for the data. Instead, these data additionally appear to require either a
282 significant effect from incongruent dissolution, or preferential Mg removal (with or without Ca
283 removal). Such Mg (and Ca) removal could arise through secondary mineral formation, such
284 as clay or calcite precipitation, with the latter clearly evidenced by the formation of stalactites,
285 stalagmites, and flowstones in the caves.

286 For the minor and trace elements, average concentrations are: Sr (900 nmol/L), B (600
287 nmol/L), Al (400 nmol/L), Li (100 nmol/L), Ba (100 nmol/L), Ti (6 nmol/L), Mo (4 nmol/L),
288 U (2 nmol/L) (Table 1). Notably, Li concentrations vary between the sites, being an order of
289 magnitude higher at Pippikin D (mean 450 nmol/L) than at Pippikin A and the White Scar Cave
290 sites (~30 nmol/L). Pippikin D also displays higher Ti, Mo, Ba, and U concentrations, by a
291 factor of around 2 to 3 compared to the other sites, and higher concentrations of certain major
292 elements (Na, K, Mg, and Si are elevated by ~70 %, ~120 %, ~30 %, and ~110 % respectively).
293 Overall, the drip-water Li concentrations are similar to concentrations measured in soil
294 solutions on Guadeloupe (30-100 nmol/L) (Fries et al., 2019), in soil solutions and small
295 streams at the Shale Hills Critical Zone Observatory in the Appalachians (30-120 nmol/L)
296 (Steinboefel et al., 2021), and in spring waters in the Massif Central (10-300 nmol/L) (Négrel
297 et al., 2010). In contrast, they are mostly at the lower end of concentrations measured in major
298 global rivers (~50-800 nmol/L; mean ~200 nmol/L) (Huh et al., 1998).

299 In Figure 2, we plot Mg, Sr, B, and Li concentrations through time, normalised to Na
300 to correct for dilution/concentration effects from rain water inputs or evaporation. At all sites,
301 Mg, Sr, and B co-vary to some extent (Fig. 2a-c), indicating a seasonal signal in the drip-water
302 chemistry. In detail, those temporal patterns indicate generally higher values in summer than
303 in winter, with a lag of around 2 months behind temperature changes (Fig. 2a-c). Such a
304 seasonal pattern is not seen for Li concentrations or Li/Na ratios (Fig. 2d). Instead, Li generally
305 covaries with Na, K, and Si (Fig. 3), although the exact relationship differs between locations,
306 with Li/Na, Li/K, and Li/Si ratios up to an order of magnitude higher at Pippikin D than at the
307 other sites. At Pippikin D, the elevated Li concentrations also correlate with Mg, Ti, Mo, and
308 U concentrations through time (Table 1), whereas a link between Li and these trace elements
309 is not observed at the other sites.

310

311 **4.2 Lithium isotopes in drip-waters**

312

313 There is both spatial and temporal variability in drip-water Li isotope compositions,
314 with a total range in $\delta^7\text{Li}$ values from +1 ‰ to +17 ‰ (Fig. 4). Average $\delta^7\text{Li}$ values were +11.2

315 ± 4.2 ‰ (2sd) for Pippikin A, $+9.0 \pm 2.3$ ‰ for Pippikin D, $+10.3 \pm 7.8$ ‰ for White Scar 1,
316 and $+14.4 \pm 6.2$ ‰ for White Scar 3. As such, typical intra-site variability within each cave
317 was approximately twice as large in White Scar Cave than in Pippikin cave, while mean values
318 in White Scar Cave were ~ 2 ‰ higher than in Pippikin cave (Fig. 4).

319 Temporal variations at an individual site were larger than the spatial variations, with a
320 range in $\delta^7\text{Li}$ values of ~ 7 ‰ at Pippikin A, ~ 5 ‰ at Pippikin D, ~ 13 ‰ at White Scar 1 (~ 8
321 ‰ excluding one low value in December 2017), and ~ 8 ‰ at White Scar 3 (Fig. 4). These
322 variations were often, but not always, coherent through time between sites in the same cave
323 and between the two caves. In particular, all sites recorded a low $\delta^7\text{Li}$ value of $+7$ - 9 ‰ during
324 November 2016, followed by an increase of 4 - 6 ‰ between January and March 2017 (or
325 between March and June 2017 for Pippikin D) (Fig. 4). The Pippikin cave sites then recorded
326 a gradual decrease from summer 2017 through to winter 2017, reaching low $\delta^7\text{Li}$ values during
327 early 2018, before increasing again by summer 2018 (latter increase only recorded at Pippikin
328 A due to low drip rates and a lack of samples from Pippikin D) (Fig. 4a). For White Scar Cave,
329 after reaching high values in March 2017, $\delta^7\text{Li}$ values generally remained elevated, with the
330 exception of a very low value of $+1$ ‰ at White Scar 1 during December 2017, and a return to
331 low values in November 2018 (only recorded at White Scar 3 due to sample unavailability at
332 White Scar 1) (Fig. 4b). Although the pattern is not entirely consistent from year to year, the
333 full dataset records lower $\delta^7\text{Li}$ values during autumn and winter (September-February mean
334 $\sim +9.3$ ‰), with lows particularly in November and December, and higher values during spring
335 and summer (March-August mean $\sim +12.3$ ‰).

336 Drip-waters at Pippikin D generally recorded the lowest Li isotope values (Fig. 4),
337 accompanied by an order of magnitude higher Li concentrations and Li/Na ratios than the other
338 sites (Table 1). The other sites displayed a larger range in Li isotope compositions (Fig. 4),
339 overlapping with Pippikin D but extending to higher values, and a relatively small range in
340 Li/Na ratios (Table 1). At individual sites, there is no clear correlation between Li isotopes and
341 Li/Na ratios, while the links between Li concentrations and other major/trace elements (e.g.
342 Fig. 3) are generally not observed between Li isotopes and major/trace elements.

343

344 **4.3 Lithium isotopes and concentrations in rocks, soils, and rain waters**

345

346 Local rocks, sediments, and soils are characterised by a small range in Li isotopes
347 (Table 2; Fig. 5) and have significantly lower $\delta^7\text{Li}$ values than the cave drip-waters (Fig. 4).
348 The limestone, shale, till, and cave sediments all have $\delta^7\text{Li}$ values in the range of -2 to 0 ‰
349 (Fig. 5a), with good agreement between equivalent samples from the two caves, while the peaty
350 soil from Pippikin cave has a $\delta^7\text{Li}$ value of $+2$ ‰. At Pippikin cave, the bulk limestone has a
351 low Li content (~ 0.3 $\mu\text{g/g}$) that is similar to the Li content of its carbonate fraction (derived
352 from weak HCl leaching), whereas the till, peaty soil, and cave sediment contain ~ 300 times

353 more Li and the shale contains ~8000 times more Li (Fig. 5b). At White Scar Cave, the bulk
354 limestone has a slightly higher Li content (~0.9 $\mu\text{g/g}$) than at Pippikin cave, but its elevated Li
355 content appears to reflect a small silicate component (as revealed by the operationally-defined
356 detrital residue following weak HCl leaching) rather than elevated Li within the carbonate
357 fraction (Fig. 5b). Therefore, the local shale and till at White Scar Cave contain ~200-300 times
358 more Li than the carbonate fraction of the limestone. For both caves, the carbonate fraction of
359 the limestone (derived from weak HCl leaching) has a Li content of ~0.1-0.2 $\mu\text{g/g}$ and an Al/Ca
360 molar ratio of 0.24 mmol/mol, consistent with derivation of the Li isotope signal in that leach
361 from only the carbonate fraction (Pogge von Strandmann et al., 2013; Dellinger et al., 2020).
362 For the shale, till, soil, and cave sediment from the vicinity of Pippikin cave, the exchangeable
363 fraction was extracted using a Na-acetate leach, but is shown to contain a very low Li content,
364 which represents 0.1 % or less of the respective bulk samples (Table 2). Isotopic measurements
365 on those exchangeable fractions gave $\delta^7\text{Li}$ values of ~+5 ‰ for the till and ~+17 ‰ for the soil
366 (Table 2), which are in a similar range to the porewater compositions inferred from the drip-
367 waters (Fig. 4).

368 Measurements of trace elements and Li isotopes on local rain water are also reported
369 (Table EA2), with $\delta^7\text{Li}$ values ranging from 9.2 to 13.9 ‰ between September 2016 and
370 September 2017. However, their mean Li/Na molar ratio of 0.00027 is elevated over values for
371 seawater (from which rain waters in the U.K. are originally derived) by a factor of 5. We
372 therefore suspect that those Li data are affected by contamination, which could arise from dust
373 or anthropogenic sources to rain water (Millet et al., 2010a), and/or from dust or anthropogenic
374 contamination during collection in the rain gauge. The major element data for rain water are
375 consistent with contributions from carbonate and/or silicate dust dissolution (Fig. 1), while
376 anthropogenic contamination is also evident in analyses of contamination-prone elements such
377 as Zn (not shown). We include the rain water data for completeness but, since we cannot rule
378 out dust dissolution or anthropogenic contamination in the rain gauge, we are cautious of
379 interpreting these Li concentration and isotope data as representative of the inputs to the studied
380 cave systems.

381

382 **5. Discussion**

383

384 **5.1 Origin of drip-water Li isotope variations**

385

386 The cave drip-waters record $\delta^7\text{Li}$ values from +1 to +17 ‰ (Table 1, Fig. 4), which
387 could reflect mixing between sources with different Li isotope compositions and/or
388 modification of source compositions due to isotopic fractionation during Li removal processes.
389 Here we address the sources of Li to the drip-waters and the need for Li removal to explain the
390 Li isotope compositions.

391

392 **5.1.1 Rain water contributions**

393 Rain water is usually an insignificant source of Li to soil solutions, ground waters, and
394 river water (e.g. Huh et al., 2001; Lemarchand et al., 2010; Dellinger et al., 2015; HENCHIRI et
395 al., 2016; Gou et al., 2019; Golla et al., 2021). Nevertheless, we consider its possible influence
396 on the cave drip-waters because the drip-waters have Li concentrations that are at the low end
397 of typical riverine Li concentrations (Huh et al., 1998). Rain water in the U.K. is mostly derived
398 from seawater and, since both cave sites are located within ~25 km of the coast, the local rain
399 water can be expected to have a similar Li isotope composition to seawater (e.g. Millot et al.,
400 2010a). We therefore use a seawater endmember (i.e. $\delta^7\text{Li} \sim +31 \text{‰}$, Li/Na molar ratio =
401 0.000055) to assess rain water contributions. This approach specifically accounts only for
402 marine aerosol sources, while excluding potential Li inputs linked to atmospheric dust
403 dissolution (Lemarchand et al., 2010; Millot et al., 2010a; Négrel et al., 2020). Silicate and
404 carbonate minerals contained in fine-grained dust probably partly dissolve in rain water, which
405 could explain both the major element chemistry of the measured rain water samples (Fig. 1)
406 and offsets in their $\delta^7\text{Li}$ values from seawater (Table EA2). However, dust dissolution is also
407 likely to occur within the soil porewaters above the caves, where the deposited dust would have
408 much longer timescales to react. Without sampling of rain waters above the actual cave sites
409 using trace-metal clean methods, these two contributions cannot be separated, and in this study
410 both are grouped within the lithogenic weathering sources (see Section 5.1.2).

411 Drip-water Li/Na ratios are 24 times higher than seawater at Pippikin D and around 2-
412 3 times higher than seawater at the other sites (Table 1). Therefore, marine aerosol inputs can
413 have virtually no influence on the Li budget at Pippikin D and cannot explain the offset in $\delta^7\text{Li}$
414 values between local weathering inputs and drip-waters in that location (Fig. 4). Although
415 Pippikin A has lower Li/Na ratios, the similarity of its mean Li isotope composition and
416 temporal evolution to that of Pippikin D (Fig. 4a) is also inconsistent with a marine aerosol
417 influence. Instead, the relatively low Li/Na ratios in Pippikin A could potentially arise from Li
418 removal during uptake by secondary minerals (Section 5.1.3). The drip-waters from White Scar
419 Cave have similar Li/Na ratios to Pippikin A (Table 1) and are probably also minimally affected
420 by marine aerosol inputs. Because seawater has very low Si concentrations, the close
421 relationship between Li and Si concentrations in the drip-waters (Fig. 3c) also argues against a
422 role for marine aerosols in the Li budget of both caves. For the three sites with low Li
423 concentrations, their Si concentrations are around 8 times higher than in the measured rain
424 water (Table 1, Table EA2), while their Si/Na ratios are around 4 times higher than in the
425 measured rain water and 800 times higher than in seawater. We therefore conclude that marine
426 aerosol sources in rain water are a relatively insignificant source of both Si and Li to the cave
427 drip-waters.

428

429 **5.1.2 Lithogenic weathering sources**

430 The major element chemistry of the drip-waters is broadly consistent with mixing
431 between carbonate and silicate weathering sources, with a greater contribution from carbonates
432 (Fig. 1a). However, the drip-water chemistry also appears to indicate a role for incongruent
433 dissolution and/or the removal of cations (e.g. Mg, Ca) into secondary phases (Fig. 1b), which
434 could comprise clays, oxides, or carbonates. While the Ca budget of the drip-waters is clearly
435 dominated by dissolution of the Great Scar Limestone, the Li content of this limestone is very
436 low and silicate lithologies (e.g. till, shale) are likely to dominate the drip-water Li budget
437 (Table 2, Fig. 5b). A predominant silicate weathering source for Li is supported by the
438 relationships between Li, Na, K, and Si in the drip-waters (Fig. 3), and confirmed by molar
439 Li/Ca ratios, which are 1-2 orders of magnitude higher in the drip-waters (4×10^{-4} for Pippikin
440 D, and $2-3 \times 10^{-5}$ for the other sites) (Table 1) than in carbonate leaches of the Great Scar
441 Limestone ($2-3 \times 10^{-6}$) (Table EA3). Considering a simplified scenario in which Ca in the drip-
442 waters is entirely derived from the carbonate fraction of the limestone, and where Li and Ca
443 behave conservatively, a simple mass balance indicates a contribution of carbonate weathering
444 to the Li budget of $<1\%$ at Pippikin D (i.e. comparison of Li/Ca ratios between the carbonate
445 leach of the Great Scar Limestone and the drip-waters). Repeating this calculation for the other
446 three sites indicates a slightly higher, but still minor, contribution of carbonate weathering to
447 their Li budgets of $\sim 7-10\%$. Note that this calculation ignores removal of Li or Ca from the
448 drip-waters; if there is significant Li removal (relative to Ca), these proportions would be over-
449 estimates of the carbonate weathering contributions. Similar observations have been made for
450 carbonate-dominated river systems, in which minor silicate lithologies almost entirely
451 determine the dissolved Li budget (Kırsakúrek et al., 2005).

452 Among the local silicate sources, we suspect that weathering of the overlying till
453 dominates the Li budget, but we cannot rule out a role for minor shale layers which are reported
454 within Great Scar Limestone (Waltham, 1970) but were not observed to outcrop within either
455 cave in the vicinity of the sampling sites. For Pippikin cave, based on an overlying rock column
456 observed to comprise ~ 40 m limestone ($[\text{Li}] = 0.27 \mu\text{g/g}$) and ~ 6 m till ($[\text{Li}] = 86 \mu\text{g/g}$), a mass
457 balance based on Li concentrations would indicate that the Li budget is made up of $\sim 2\%$ Li
458 contained in the limestone and $\sim 98\%$ in the silicate-dominated till. For White Scar Cave,
459 considering ~ 40 m limestone and ~ 1 m till, $\sim 7\%$ Li is contained in the carbonate fraction of
460 the limestone ($[\text{Li}] = 0.12 \mu\text{g/g}$ based on the carbonate leach) and $\sim 93\%$ in the silicate sources
461 (i.e. till ($[\text{Li}] = 37 \mu\text{g/g}$) and silicate fraction of the limestone ($[\text{Li}] = 0.77 \mu\text{g/g}$ based on
462 difference between bulk limestone and the carbonate leach)). While such first-order estimates
463 of the available Li budget in the lithogenic sources do not address the effects of variable
464 dissolution rates or fluid residence times between rock units, they appear to be in reasonable
465 agreement with our above inferences of carbonate versus silicate contributions based on drip-

466 water and limestone Li/Ca ratios. In addition, both lines of evidence support the potential for
467 proportionally greater silicate weathering contributions at Pippikin cave than White Scar Cave.

468 Regardless of the exact partitioning of Li inputs between different silicate sources, or
469 between silicate and carbonate weathering, the major lithogenic sources span a small range of
470 $\delta^7\text{Li}$ values. Specifically, limestone, shale, till, and cave sediment all have $\delta^7\text{Li}$ values between
471 -2‰ and 0‰ , with peaty soil only slightly higher at $+2\text{‰}$ (Fig. 5a). Therefore, it is not
472 possible to explain either the mean drip-water composition or variability in $\delta^7\text{Li}$ values from
473 $+1\text{‰}$ to $+17\text{‰}$ (Fig. 4) simply by mixing between these sources. We rule out the exchangeable
474 fraction in the tills and soils as a major external input or output of the system because its Li
475 content is so low (Table 1). Furthermore, the observation that the bulk till and peaty soil in the
476 vicinity of Pippikin cave differ by only 3‰ in $\delta^7\text{Li}$ values and have similar Li concentrations
477 (slightly lower in the soil) (Table 2) suggests that organics play no major role in the local Li
478 budget, which is fully consistent with findings in previous studies (e.g. Lemarchand et al.,
479 2010; Clergue et al., 2015).

480

481 *5.1.3 Modification of Li isotopes through uptake by secondary minerals*

482 We demonstrated above that mixing between lithogenic sources is unable to explain the
483 Li isotope compositions of the drip-waters. Therefore, we propose that the input signature of
484 ~ -2 to 0‰ from primary rock dissolution (Fig. 5a) is significantly modified by the preferential
485 removal of ^6Li during secondary mineral formation (e.g. Vigier et al., 2008; Wimpenny et al.,
486 2010; Hindshaw et al., 2019a) or by adsorption onto secondary minerals such as clays or oxides
487 (e.g. Pistiner and Henderson, 2003; Wimpenny et al., 2015; Zhang et al., 2021). Global river
488 water $\delta^7\text{Li}$ compositions are highly variable with a mean of $\sim +23\text{‰}$ (Huh et al., 1998; Pogge
489 von Strandmann et al., 2017a), indicating a typical fractionation of more than 20‰ from their
490 lithogenic weathering inputs. The operation of a similar process here could therefore explain
491 the range of drip-water compositions from $+1\text{‰}$ to $+17\text{‰}$, since it would require fractionation
492 in the range of ~ -2 – 18‰ (mean of $\sim 12\text{‰}$) depending on the degree of Li uptake affecting a
493 given sample.

494 While the formation of secondary minerals and/or the adsorption of Li onto such
495 minerals is implicated, it is difficult to obtain physical evidence for changes in clay
496 precipitation through time because the amount of clay forming is small relative to the total rock
497 volume (Tipper et al., 2012; Pogge von Strandmann et al., 2019; Golla et al., 2021). In addition,
498 there is the possibility that such fine-grained minerals are transported out of the system in sub-
499 surface water flow (Steinboefel et al., 2021). However, the formation of such secondary
500 minerals seems feasible based on thermodynamic calculations in PHREEQC (Parkhurst and
501 Appelo, 1999). Using the measured drip-water chemistry and the mean annual surface
502 temperature of 8°C , these calculations suggest that gibbsite, kaolinite, and Ca-montmorillonite
503 (smectite) are supersaturated, and could therefore form subject to kinetic constraints, while

504 illite is close to saturation and sometimes supersaturated. For the warmest (16 °C) and coolest
505 (1 °C) months of our study interval, and considering a sample with average drip-water
506 chemistry, the saturation state changes from 3.2 to 5.0 for kaolinite, 1.6 to 2.3 for gibbsite, 0.4
507 to 2.6 for Ca-montmorillonite (smectite), and -1.5 to 0.6 for illite. Hence, a number of clay
508 minerals appear to be supersaturated over the entire year, with the extent of supersaturation
509 increasing at lower temperatures. Therefore, clay formation in these settings appears feasible.
510 Temporal increases in $\delta^7\text{Li}$ values also generally correspond to decreasing drip-water Al
511 concentrations, in three out of the four sites (Fig. 6), which could be taken to indicate enhanced
512 removal of Al into secondary minerals such as clays over these intervals.

513 While the above observations appear consistent with a role for clay formation in Li
514 isotope variability, it is important to emphasise that we do not have any direct evidence for clay
515 formation occurring in the system over the timescales of our observations. Therefore, we
516 cannot evaluate the extent to which amorphous precursors rather than crystalline clays may be
517 forming, and we cannot readily distinguish between Li removal by clay precipitation versus Li
518 adsorption onto existing clay minerals (although these two processes are generally associated
519 with different fractionation factors; see Section 5.3). In addition, the formation of other phases
520 such as Fe oxides/oxyhydroxides could also represent a viable sink of light Li isotopes (Pistiner
521 and Henderson, 2003; Steinhoefel et al., 2021).

522

523 **5.2 Controls on temporal variations in Li isotopes**

524

525 Temporal variability in drip-water Li isotopes indicates rapid changes in weathering
526 processes over monthly to seasonal timescales (Fig. 4). As discussed above, the source inputs
527 are uniform in Li isotope composition ($\delta^7\text{Li}$ \sim -2 to 0 ‰; Fig. 5) and secondary mineral
528 formation (or adsorption onto such minerals) is likely required to drive the drip-water Li
529 isotopes to higher values. Therefore, changes through time in the relative balance of silicate
530 rock dissolution versus secondary mineral formation, or in the isotopic fractionation factor
531 during secondary mineral formation, may have been a major driver of drip-water Li isotope
532 variability. In this section, we use records of temperature, precipitation, drip-water chemistry,
533 and drip rates to address the controls on the Li isotope changes and their implications for
534 weathering processes.

535

536 **5.2.1 Temperature-dependent isotope fractionation**

537 The isotopic fractionation of Li between fluids and secondary minerals such as clays is
538 temperature-dependent (Vigier et al., 2008; Li and West, 2014; Dupuis et al., 2017), which
539 leads to the potential for seasonal temperature changes to influence the fluid composition
540 independent of changes in weathering processes (Gou et al., 2019). Although the isotopic
541 fractionation may also depend on the exact mineralogy of the secondary minerals, a similar
542 temperature-dependence has been reported in both laboratory experiments on clays and in

543 natural settings (with presumably mixed assemblages of secondary minerals), with
544 fractionation decreasing by ~ 0.18 ‰ per 1°C of warming over the temperature range of ~ 0 - 30
545 $^\circ\text{C}$ (Li and West, 2014; Gou et al., 2019).

546 Warmer temperatures during summer would be expected to generate less isotopic
547 fractionation, leading to lower (i.e. less fractionated) $\delta^7\text{Li}$ values in the weathering fluids.
548 Assuming that a significant proportion of Li is removed from the fluids by an equilibrium (or
549 batch) process, and additionally making the simplification that seasonal variations of ~ 10 $^\circ\text{C}$
550 in mean monthly surface temperatures (Fig. 7a) are relevant to the depths where weathering is
551 occurring, such an effect could potentially lower peak summer drip-water $\delta^7\text{Li}$ compositions
552 by up to 1.8 ‰ over peak winter values. In contrast, the observations indicate generally higher
553 $\delta^7\text{Li}$ values during summer (Table 1, Fig. 7a). Therefore, temperature-dependent fractionation
554 does not seem able to explain the variation seen in our records. By working in the opposite
555 direction, it could potentially even lead to a more muted Li isotope response in the drip-waters
556 than the true weathering signal. However, applying a temperature correction to each drip-water
557 sample (using the monthly temperature data and otherwise the same assumptions as above)
558 would only increase the magnitude of the seasonal difference in mean drip-water $\delta^7\text{Li}$ values
559 (i.e. March-August minus September-February) from the measured $+3.0$ ‰ to $+3.7$ ‰.
560 Therefore, since temperature variations appear capable of exerting only a minor direct
561 influence on the isotopic fractionation, we do not consider this effect further.

562

563 **5.2.2 Fluid source changes**

564 There is no clear link between precipitation amounts and drip-water Li isotopes (Fig.
565 7c), which is consistent with marine aerosols in rain water providing only a minor source of Li
566 to the drip-waters. However, any rainfall source signal may be delayed during transport through
567 the epikarst (Bottrell and Atkinson, 1992), so we also use stable oxygen isotopes ($\delta^{18}\text{O}$) in the
568 cave drip-waters as a signal of changes in the precipitation source and/or amount (Fairchild
569 and Baker, 2012), while recognising that modification of that signal is possible within the sub-
570 surface (Treble et al., 2013). Regardless of the exact controls on drip-water $\delta^{18}\text{O}$ values, there
571 is also no direct link between the Li isotope changes and the $\delta^{18}\text{O}$ records (Fig. 7d). In
572 particular, during winter 2016 to spring 2017, it is clear that drip-water $\delta^{18}\text{O}$ values shifted
573 towards lower values a few months before the major Li isotope shift occurred (Fig. 7d).
574 Therefore, changing precipitation inputs do not appear to exert a direct control on the drip-
575 water Li isotope records.

576 An alternative fluid source effect could potentially arise indirectly from changes in
577 precipitation, because changes in the water balance could affect fluid pathways and timescales,
578 and therefore change the sources of water influencing a given drip-water site (Bottrell and
579 Atkinson, 1992; McDonald et al., 2007). Since all potential lithogenic input sources have
580 similar Li isotope compositions in both cave settings (Fig. 5a), a switch in fluid pathways that

581 changes the proportions of Li derived from weathering of different lithologies should have no
582 significant effect on drip-water Li isotopes. However, variability in precipitation (and hence
583 effective precipitation) could change the water residence time in the sub-surface and/or lead to
584 mixing between local sub-surface reservoirs with different storage times. The implications of
585 such changes could also differ between different isotopic systems, and we return to this
586 hypothesis in Section 5.2.4.

587

588 **5.2.3 Temperature-dependent weathering kinetics**

589 Seasonal temperature changes could potentially have a major influence on weathering
590 processes, and specifically the weathering congruence (Pogge von Strandmann et al., 2014;
591 Pogge von Strandmann et al., 2017c). Such a situation could arise because increased
592 temperatures may promote faster kinetics for silicate mineral dissolution (Gislason et al., 2009;
593 Eiriksdottir et al., 2013), while decreasing the saturation state and increasing the solubility of
594 non-oxide secondary minerals such as clays (Pokrovski et al., 1998; Stefánsson and Gíslason,
595 2001). Therefore, warm conditions could enhance the dissolution of primary silicate minerals
596 within the till and soil, while hindering modification by secondary mineral formation, leading
597 to low dissolved $\delta^7\text{Li}$ compositions in the drip-waters. As temperature decreases, the extent of
598 oversaturation of kaolinite and Ca-montmorillonite in the cave drip-waters increases (Section
599 5.1.3), while illite may also become slightly oversaturated in the coolest months. Therefore,
600 cooler conditions could reduce the dissolution of silicates, while decreasing the solubility of
601 (non-oxide) secondary minerals thereby increasing their stability (Pokrovski et al., 1998;
602 Stefánsson and Gíslason, 2001), which would enhance Li removal and generate higher $\delta^7\text{Li}$
603 compositions.

604 The observation of generally higher drip-water Li isotope compositions during spring
605 and summer (Fig. 7a) does not initially appear consistent with the above mechanism. However,
606 the most prominent shift from low to high $\delta^7\text{Li}$ values occurred during late winter 2016 to
607 spring 2017 (i.e. November 2016 to April 2017), during an interval when temperatures were
608 low (Fig. 7a). Therefore, while $\delta^7\text{Li}$ values were generally higher during summer, the shifts
609 towards these values typically occurred within the preceding winter. Comparing the mean $\delta^7\text{Li}$
610 values for each cave with an inverted temperature curve could support such a control of
611 temperature on the balance between rock dissolution and clay formation, but with a lag behind
612 atmospheric temperatures of around 3-6 months (Fig. 7b).

613 A lagged response of the weathering signal to changes in surface air temperature might
614 be expected, due to (i) the time needed for temperatures in the weathering system to respond
615 to changes in atmospheric temperatures; (ii) the time needed for changes in weathering
616 reactions (e.g. clay or oxide precipitation, or ion exchange) to occur and progress sufficiently
617 to influence the porewater Li isotopes; and (iii) the time needed for water to flow from the soil
618 porewaters (where most of the silicate weathering is probably occurring) to the cave drip-water

619 sites. The Mg, Sr, and B contents of the drip-waters (and their ratios to Na) also display a
620 seasonal cycle with a lag behind air temperatures, but the lag is only ~2 months (Fig. 2), similar
621 to the lag between air temperatures and drip-water $\delta^{18}\text{O}$ changes (Fig. 7a,d). Elevated Mg, Sr,
622 and B concentrations during summer likely arise from some combination of increases in soil
623 leaching contributions (McDonald et al., 2007) and/or increases in prior calcite precipitation
624 (Fairchild et al., 2000). Hence, these chemical data could be explained by a fast response of
625 such processes to climate in combination with a mean timescale of 1-2 months for water
626 transport to the sampling sites, consistent with previous studies of tracer transport in the White
627 Scar Cave system (Bottrell and Atkinson, 1992).

628 If temperature changes are to be invoked to explain the Li isotope variability, an
629 additional lag of several months appears to be required for Li isotopes compared to those trace
630 element (Mg, Sr, B) and hydrographic ($\delta^{18}\text{O}$) records (Fig. 7). We cannot rule out that some of
631 the secondary mineral formation (or adsorption onto those minerals) may be occurring at depth
632 within limestone pore spaces and fractures, rather than in the till and soils, in which case there
633 may be a significant lag in the seasonal temperature response in the weathering zone compared
634 to the atmosphere (Rau et al., 2015). Alternatively, a slower response time for silicate
635 weathering could arise from the kinetics of secondary mineral nucleation and growth, which
636 for clays may be relatively slow at these temperatures (Hindshaw et al., 2019a), although
637 presumably it would be accelerated if amorphous phases are forming under supersaturated
638 conditions. Since it is challenging to transfer reaction rates between laboratory and field
639 settings, we instead note that field data from a recent study demonstrated that Mg-rich
640 secondary minerals can form and impact upon the major element chemistry of solutions within
641 1–2 months at low temperatures (Oelkers et al., 2019). Therefore, secondary clay formation
642 over seasonal timescales in the soil porewaters and cave drip-waters appears a feasible
643 possibility.

644 Overall, the relationship between changes in atmospheric temperatures and drip-water
645 $\delta^7\text{Li}$ values supports a possible control of silicate weathering kinetics on seasonal changes in
646 Li removal and isotope fractionation, but with lags in the response to temperature of several
647 months (Fig. 7b). However, at present, fluid transport timescales in the system are too poorly
648 constrained to fully evaluate the temperature control on the reactions, while the sampling
649 interval is too similar to the timescales of interest to evaluate the possible cause(s) of the
650 apparently lagged response between different geochemical tracers. In future, higher-resolution
651 sampling could perhaps provide better insight into such processes that are operating and the
652 response time of the weathering system.

653

654 ***5.2.4 Fluid residence time***

655 While temperature changes could play some role in determining the balance between
656 silicate dissolution and clay formation, any such relationship is clearly complex. Instead, or in

657 addition, reactive transport models suggest a control on Li isotopes could arise from changes
658 in fluid residence time in the soils and/or limestone system (Lemarchand et al., 2010; Maher,
659 2010; Wanner et al., 2014; Wanner et al., 2017). Specifically, increases in fluid residence time
660 during dry intervals could enhance secondary clay formation, leading to increased Li removal
661 and higher drip-water $\delta^7\text{Li}$ values, whereas faster transport during wet intervals could hinder
662 secondary clay formation, leading to less fractionated $\delta^7\text{Li}$ values.

663 We test this idea by comparing the Li isotope records from Pippikin A and Pippikin D
664 to instantaneously monitored drip rates during sample collection for Pippikin A (Fig. 8a) and
665 to a monthly-smoothed record of drip rates in the same cave chamber as Pippikin D (Fig. 8b).
666 For Pippikin A, there is a close agreement between instantaneous drip rates and drip-water $\delta^7\text{Li}$
667 values, with higher $\delta^7\text{Li}$ values linked to lower drip rates (Fig. 8a). For Pippikin D, monthly to
668 seasonal shifts towards higher $\delta^7\text{Li}$ values also correspond to intervals with decreasing drip
669 rates, although the link appears stronger with the monthly-smoothed data from the
670 “Stalagmate” drip logger (Fig. 8b) than with the instantaneous measurements (Table 1). For
671 the latter, the drip rates of three samples appear anomalously higher and may not be
672 representative. In addition, an underlying long-term trend from 2016 to 2018 is seen in both
673 the Li isotope and drip rate records from Pippikin cave, with an increase in $\delta^7\text{Li}$ values
674 corresponding to a decline in drip rates (Fig. 8). Based on the assumption that fluid residence
675 time is inversely related to drip rates over such timescales, these data support a clear role for
676 fluid residence time in determining the balance between silicate dissolution and clay formation.

677 In contrast to the observations in Pippikin cave (Fig. 8), we do not resolve a link
678 between instantaneous drip rates and Li isotopes at the White Scar Cave drip sites (Table 1).
679 This observation could suggest that temperature (Fig. 7a,b) rather than fluid residence time is
680 a stronger control in White Scar Cave. However, we are cautious of over-interpreting this
681 observation, because the more continuous nature of the White Scar Cave drips may not provide
682 constraints on the fluid residence time in this system. In addition, we caution that drip rates and
683 fluid pathways can vary significantly, even between adjacent drip sites under identical climate
684 forcing (Bottrell and Atkinson, 1992; Roberts et al., 1999). While such local differences in
685 fluid pathways and residence times between drip-water sites could lead to inter-site and inter-
686 cave variability in Li isotopes (Fig. 4), higher resolution sampling of Li isotopes and drip rates
687 would be needed to directly evaluate this effect. Quantifying the relative contributions of
688 temperature-dependent kinetics and changes in fluid residence times to seasonal changes in
689 weathering processes and Li isotopes is beyond the capability of our present dataset and would
690 appear to be an important future research goal.

691

692 **5.3 Quantification of Li removal into secondary minerals**

693

694 To provide further first-order constraints on weathering processes in these systems, we
695 use the drip-water Li isotope compositions to estimate the proportion of Li that has been
696 removed into secondary minerals. We assume that dissolved Li is dominantly derived from the
697 weathering of silicates in the till and/or shale layers, with a $\delta^7\text{Li}$ composition of $-1 \pm 1 \text{ ‰}$
698 (yellow band in Fig. 5a), and calculate Li removal using an equilibrium (or batch) fractionation
699 model. Such a model has previously been proposed to explain both the weathering of regolith
700 in the Amazon basin (Maffre et al., 2020) and global-scale river chemistry (Pogge von
701 Strandmann et al., 2017a). While recognising that the exact nature of the secondary phases is
702 unconstrained, we follow previous studies in using fractionation factors for secondary clays.
703 The experimentally-determined fractionation between fluid and clays (stevensite and saponite)
704 is $16.6 \pm 1.7 \text{ ‰}$ (2sd) at 20 °C (Hindshaw et al., 2019a), which would translate to $\sim 17\text{-}20 \text{ ‰}$ at
705 the mean annual temperature of our sites (8 °C) (Li and West, 2014; Gou et al., 2019). Hence,
706 the range of fractionation required to explain our drip-water dataset (i.e. $\sim 1\text{-}19 \text{ ‰}$, average ~ 12
707 ‰) can be achieved by clay formation via equilibrium (batch) fractionation.

708 Using a batch model with a fractionation factor ($\alpha_{\text{clay-fluid}}$) of 0.9815 (Li and West, 2014;
709 Gou et al., 2019; Hindshaw et al., 2019a), the average Pippikin cave Li isotope data could be
710 explained by removal of $\sim 60 \%$ of the initial Li, while the average White Scar Cave data could
711 be explained by removal of $\sim 70 \%$. Furthermore, the seasonal shift in Li isotope compositions
712 between November 2016 and April 2017 (Fig. 7b) would imply enhanced Li removal by
713 secondary clay formation during winter, increasing from $\sim 50 \%$ to $\sim 70 \%$ in Pippikin cave and
714 from $\sim 50 \%$ to $\sim 80 \%$ in White Scar Cave. Interestingly, these seasonal changes are comparable
715 in both direction and magnitude to estimates of glacial-interglacial changes from Li isotopes in
716 two speleothems from Israel, where Li removal from the drip-waters was inferred to have
717 increased from $\sim 50 \%$ during warm interglacials to $\sim 70 \%$ during cool glacials (Pogge von
718 Strandmann et al., 2017c). While cautioning against a direct comparison because the
719 speleothem study used a Rayleigh fractionation model (Pogge von Strandmann et al., 2017c),
720 the two studies appear to indicate a broadly similar response of Li removal to temperature
721 changes of $\sim 10^\circ\text{C}$, thereby supporting either a direct or indirect temperature control on
722 weathering processes.

723 Following an approach taken in studies on river waters (e.g. Lemarchand et al., 2010;
724 Liu et al., 2015; Manaka et al., 2017; Pogge von Strandmann et al., 2017a), we also attempt to
725 model the Li isotope evolution in combination with Li/Na ratios. The formation of clays or
726 oxides is expected to remove Li while leaving Na largely unaffected, because Na is generally
727 a mobile major cation (Gislason et al., 1996), such that Li/Na ratios should decrease with
728 increasing secondary mineral formation. As above, we use a Li isotope composition for the
729 initial fluid based on local silicate sources (i.e. till, soils, shale) (Fig. 5) and model isotopic
730 fractionation using a batch model and a fractionation factor of 0.9815 based on clays (Li and
731 West, 2014; Gou et al., 2019; Hindshaw et al., 2019a) (Fig. 9). The general pattern of the data

732 can be explained by such a model, indicating relatively more silicate dissolution at Pippikin D
733 (low $\delta^7\text{Li}$ and high Li/Na) and more clay formation at Pippikin A and the White Scar Cave
734 sites (higher $\delta^7\text{Li}$ and low Li/Na) (Fig. 9a). However, when using the Li/Na ratios of the local
735 silicate sources to constrain the initial fluid composition, the drip-water data fall significantly
736 below the fractionation lines (Fig. 9a). Since the local rocks and till may not weather
737 congruently, and could contain relatively unreactive Li-rich secondary clays that are the
738 product of weathering reactions (e.g. Lemarchand et al., 2010), we also explore a fractionation
739 model starting from the Li/Na ratios of the upper continental crust (Rudnick and Gao, 2003;
740 Teng et al., 2004) (Fig. 9b). This latter approach may better represent the inputs from primary
741 mineral dissolution within the till, and in this case there is a much closer fit to the data, but it
742 is still not possible to simultaneously fit the Pippikin D data and all the data from the other sites
743 with the same model parameters (Fig. 9b). In particular, it is hard to explain the Li isotope data
744 linked to low Li/Na ratios at the other sites, while an even poorer fit would be achieved using
745 a Rayleigh fractionation model (Fig. 9b).

746 The apparent decoupling between Li isotopes and Li concentrations (or Li/Na ratios) in
747 the cave drip-waters (Fig. 9) could indicate the complexity of cave systems in comparison to
748 river systems. Nevertheless, it is important to recognise that rivers also record significant
749 variability, rather than a single universal $\delta^7\text{Li}$ -Li/Na relationship (Millot et al., 2010b; Murphy
750 et al., 2019). One possible complication in caves is that Li could be supplied from local fluid
751 reservoirs with different initial Li/Na ratios, leading to data falling along individual
752 fractionation paths. Another possibility is that the weathering of glacial tills produces a more
753 complex relationship between $\delta^7\text{Li}$ and Li/Na ratios, as proposed for glacially-ground
754 sediments in the Mackenzie River (Millot et al., 2010b). However, neither mechanism would
755 seem that likely to explain the differences between data from Pippikin A and Pippikin D within
756 the same cave system (Fig. 9).

757 A more viable option for decoupling between Li isotopes and Li/Na ratios is a multi-
758 step evolution involving mixing between multiple fluid reservoirs (Fig. 9c). For example, for
759 waters that have evolved to high $\delta^7\text{Li}$ values and low Li/Na ratios, a subsequent mixing event
760 could introduce Li from a less evolved reservoir that has a composition closer to the original
761 source composition (i.e. low $\delta^7\text{Li}$ values and high Li/Na ratios). Such a scenario (red arrow in
762 Fig. 9c) could help explain why some samples from Pippikin A and White Scar Cave fall below
763 the modelled batch fractionation line. This mechanism appears feasible given the evidence for
764 multiple fluid pathways leading to different fluid residence times in the unsaturated zone of
765 White Scar Cave (Bottrell and Atkinson, 1992), but it is hard to fully evaluate because fluid
766 residence times in the soil layers are unconstrained and residence times in the caves likely vary
767 in a complex manner through space and time (Fig. 8).

768 Alternatively, or in addition, changes in Li adsorption onto pre-existing clay minerals
769 could also be occurring, and could be decoupled in space and/or time from secondary clay

770 formation. Indeed, such exchange processes have been proposed to control porewater Mg
771 cycling (Fries et al., 2019), although evidence for an important effect of the exchangeable
772 fraction on Li isotope budgets has so far been mostly lacking (e.g. Pogge von Strandmann et
773 al., 2019). Whereas secondary clay formation involves large isotopic fractionation factors due
774 to structural Li incorporation into the octahedral sites, the removal of Li by ion exchange
775 typically generates less isotopic fractionation, depending on factors such as the clay
776 mineralogy, the specific adsorption site, and the solution chemistry (Pistiner and Henderson,
777 2003; Huh et al., 2004; Wimpenny et al., 2015; Hindshaw et al., 2019a; Pogge von Strandmann
778 et al., 2019; Zhang et al., 2021). In particular, it has been shown that Li isotopic fractionation
779 can be large in the case of adsorption as octahedral inner-sphere complexes (e.g. Zhang et al.,
780 2021), but is virtually absent in the case of outer-sphere complexation of Li with 4-fold
781 coordination in the clay interlayers (e.g. Hindshaw et al., 2019a). Interestingly, the
782 exchangeable fractions in the Pippikin till and soil (Table 2) had fairly similar $\delta^7\text{Li}$ values to
783 the cave drip-waters (Fig. 4), which suggests that any Li removal into such fractions did not
784 involve a large isotopic fractionation. It follows that if Li is removed by both clay precipitation
785 (with a large fractionation) and by adsorption/exchange (with a smaller fractionation), and if
786 those processes operate independently, then Li isotopes and concentrations could become
787 decoupled, enabling data points to fall below the modelled batch fractionation trend (Fig. 9c).
788 Finally, we note that, in the context of a system with at least three potential removal
789 mechanisms for Li (i.e. clay precipitation, interlayer exchange, and oxide formation), and
790 where seasonal or shorter timescales are considered, the inability to fit the data by a single
791 batch or Rayleigh model probably in part reflects non-steady state behaviour (Steinboefel et
792 al., 2021).

793

794 **5.4 Implications for weathering processes**

795

796 While fully quantitative interpretations of the Li isotope data are not possible, this study
797 provides intriguing evidence for temporal changes in the balance between rock dissolution and
798 secondary mineral formation (Figs. 6 and 9). Furthermore, the inferred control exerted by
799 variations in fluid residence time (Fig. 8) is consistent with recent observations of Li isotope
800 behaviour in rivers and soils. For example, studies on river systems with distinct wet and dry
801 seasons have proposed that higher dissolved $\delta^7\text{Li}$ values during times of low flow arise from
802 longer fluid residence times and increased secondary clay formation (Liu et al., 2015; Manaka
803 et al., 2017; Hindshaw et al., 2019b), while a similar control has previously been invoked to
804 explain seasonality in river water Mg isotopes (Tipper et al., 2012). A study from Guadeloupe
805 has also suggested that a decrease in fluid residence time can lead to lower $\delta^7\text{Li}$ values in
806 groundwater, invoking suppressed secondary mineral formation following a heavy rainfall
807 event (Fries et al., 2019). Since the tropical climate, highly weathered andesitic bedrock, and

808 shallow hydrological setting of that study were quite different from the Yorkshire cave setting,
809 the combination of observations from these two contrasting systems appears to indicate a
810 general control of fluid residence time on the weathering system.

811 Studies of river water chemistry can record complex and/or smoothed signals of
812 temporal changes in weathering due to mixing between individual tributaries (e.g. Henchiri et
813 al., 2016) or between different reservoirs (e.g. runoff, soil porewaters, deep groundwater). In
814 contrast, our observations and those of Fries et al. (2019) confirm the potential for rapid
815 temporal variability in weathering processes and weathering signatures within soil porewater
816 and/or shallow groundwater systems. Therefore, monthly to seasonal changes in water-rock
817 interaction within soil porewaters or fractured bedrock may exert a significant control on the
818 Li isotope compositions of the inputs to rivers and hence on riverine compositions. Future
819 studies may explore these processes further using cave drip-waters as a means to generate high-
820 resolution time series of soil porewater Li isotopes in multiple settings and over a range of
821 timescales. Such evidence would inform on both interpretations of the Li isotope proxy, and
822 the potential for rapid changes in chemical weathering processes in response to changes in
823 hydrology or climate.

824 Unlike the effect of fluid residence times, a temperature control on weathering kinetics
825 (Fig. 7b) has not previously been demonstrated using Li isotopes in large river systems.
826 However, research on small local systems may better allow the response of weathering to
827 temperature changes to be isolated, without overprinting from changes in mixing and transport.
828 Studies on soil chronosequences (Ryu et al., 2014) and speleothems (Pogge von Strandmann
829 et al., 2017c) have both suggested that warmer temperatures can lead to more congruent
830 weathering with less secondary clay formation, while cooler conditions allow more retention
831 of cations and Li in secondary minerals, which is supported by thermodynamic data (Pokrovski
832 et al., 1998). By identifying a link between seasonal temperature variations and the extent of
833 Li removal from soil porewaters, particularly in samples from White Scar Cave, our results
834 appear to support those studies, and further suggest they may be extended over seasonal or
835 shorter timescales. However, our interpretations of the drip-water data are limited by a lack of
836 constraints on subsurface fluid pathways and residence times, and there are several mechanisms
837 that could potentially generate a lagged response in the Li isotope signature relative to climate
838 forcing. In addition, the specific mechanisms (precipitation, adsorption, or cation exchange)
839 and mineralogy (clays, amorphous phases, or oxides) influencing our Li isotope data also
840 remain uncertain, and therefore we urge some caution in how such data are interpreted over
841 these shorter timescales.

842 Finally, we emphasise that temporal changes in secondary clay formation would
843 translate into changes in weathering efficiency that could influence carbon dioxide drawdown.
844 Specifically, intervals with colder temperatures and/or longer subsurface fluid residence times
845 might lead to proportionally more secondary clay formation, reducing the efficiency of carbon
846 sequestration by weathering. The opposite situation could arise during intervals with warmer

847 temperatures and/or shorter fluid residence times, since more congruent weathering (i.e.
848 increased primary mineral dissolution relative to secondary clay formation) could lead to more
849 efficient carbon drawdown. Therefore, rather than simply responding to the mean global
850 climate state, it appears that future weathering changes could be sensitive to variability in local
851 hydrographic conditions linked to an increased prevalence of extreme weather events such as
852 storms (Möller et al., 2016) and droughts (Samaniego et al., 2018). In such a scenario, both
853 increased primary rock dissolution and enhanced weathering efficiency (due to reduced
854 secondary mineral formation), in combination, might be expected to contribute to increased
855 carbon dioxide drawdown by silicate weathering. However, quantifying the regional or global
856 scale weathering response to such changes will require improved constraints on the controls on
857 weathering processes, and on how they are recorded by systems such as Li isotopes as a
858 function of secondary mineralogy, over a range of spatial and temporal scales. Since the Li
859 isotope signal in cave drip-waters reflects silicate weathering in the overlying soils,
860 speleothems from well-constrained systems could provide a useful archive of the local response
861 of Li isotopes, and potentially silicate weathering processes, to climate changes over longer
862 timescales.

863

864 **6. Conclusions**

865

866 Monitoring of drip-water Li isotopes in two Yorkshire caves reveals complex spatial
867 and temporal variability that suggests a link between climate forcing and weathering processes
868 in soil porewaters on monthly to seasonal timescales. Specifically, our data demonstrate that
869 temperature and fluid residence time appear to exert controls on drip-water $\delta^7\text{Li}$ values, likely
870 reflecting changes in the extent of Li removal into secondary minerals. Because of the differing
871 controls on primary mineral dissolution and secondary mineral formation, cooler temperatures
872 and/or longer fluid residence times may lead to enhanced secondary mineral formation relative
873 to rock dissolution, leading to higher drip-water $\delta^7\text{Li}$ values. If the secondary minerals are
874 clays, this scenario could represent a significant reduction in weathering efficiency, because
875 secondary clay formation reduces the efficiency of carbon dioxide drawdown from silicate
876 weathering. However, at present, we cannot rule out alternative controls from adsorption or
877 exchange of Li with existing mineral surfaces, or a contribution from oxides rather than clays;
878 in these latter cases, the impact on weathering efficiency would likely be smaller.

879 Our results have two broader implications. First, the variability in Li isotopes over short
880 temporal and spatial scales should be considered when interpreting paleo-records of Li isotopes
881 in terms of changes in weathering processes or intensity. Second, our Li isotope evidence
882 suggests that both past and future weathering changes may be sensitive to seasonality or to
883 extreme weather events that influence the local hydrological cycle, rather than responding only
884 to the mean global climate state. More intense rainfall events in future might be expected to
885 lead to both increased primary rock dissolution and enhanced weathering efficiency (due to

886 reduced clay formation), thereby increasing carbon dioxide drawdown by silicate weathering,
887 but such a hypothesis is presently speculative and needs to be tested with further experimental
888 data and field data from a wider range of settings.

889

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891

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897

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899

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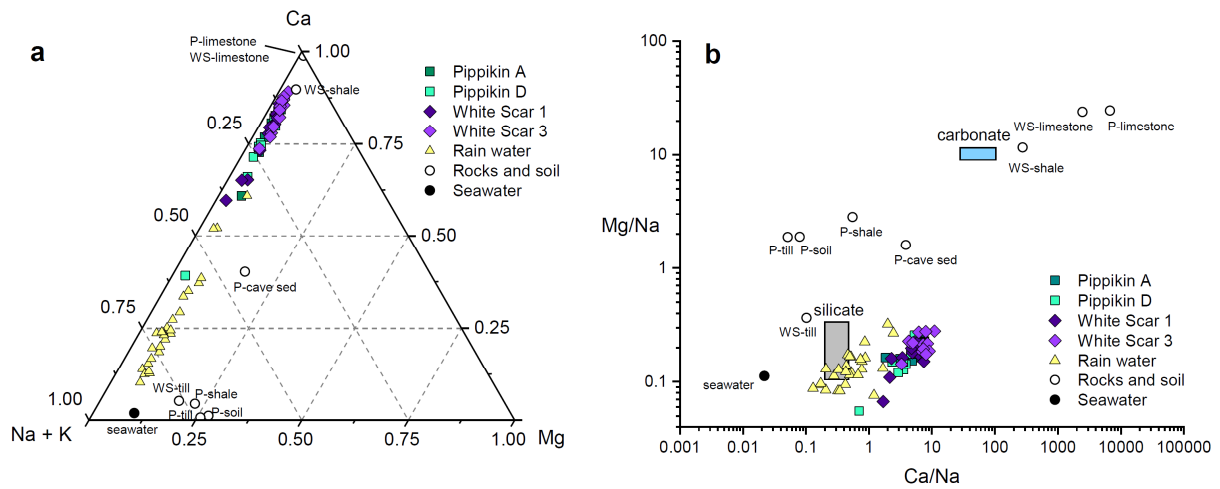
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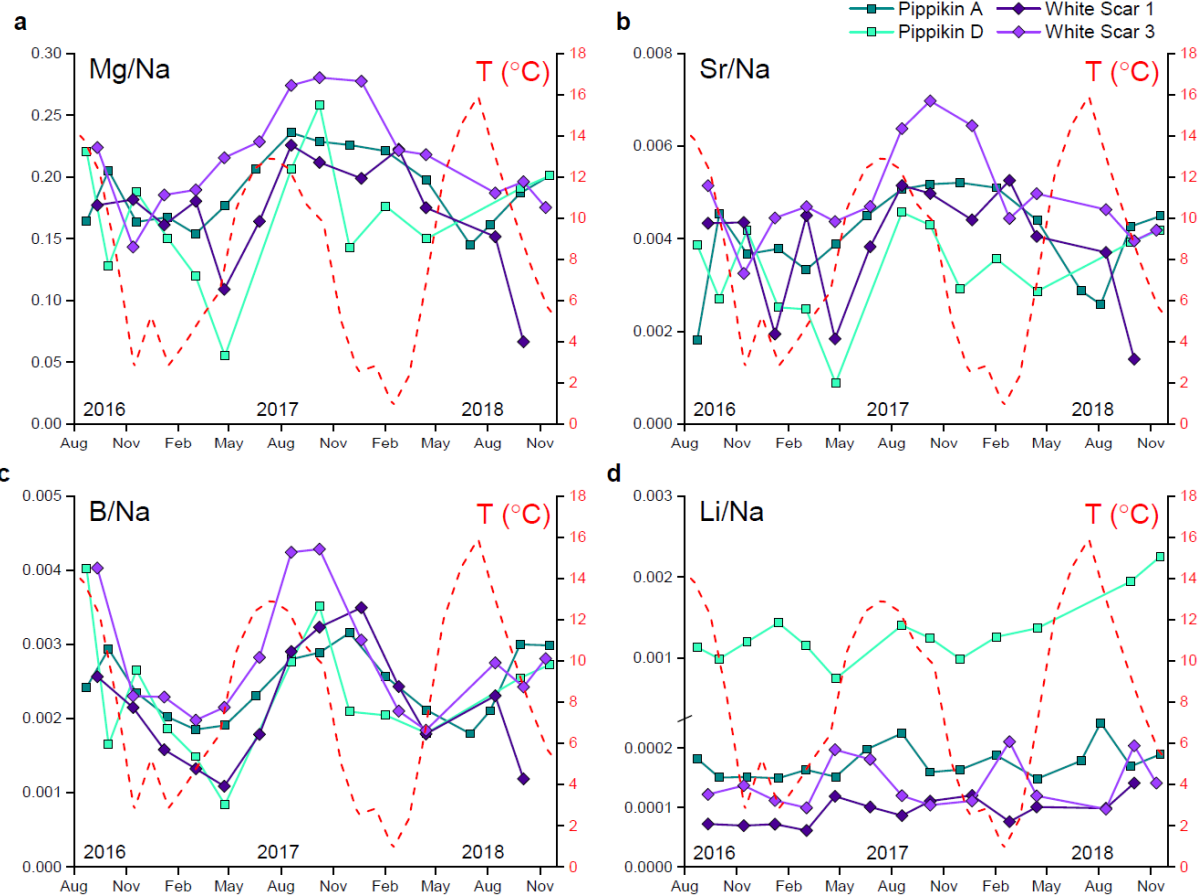
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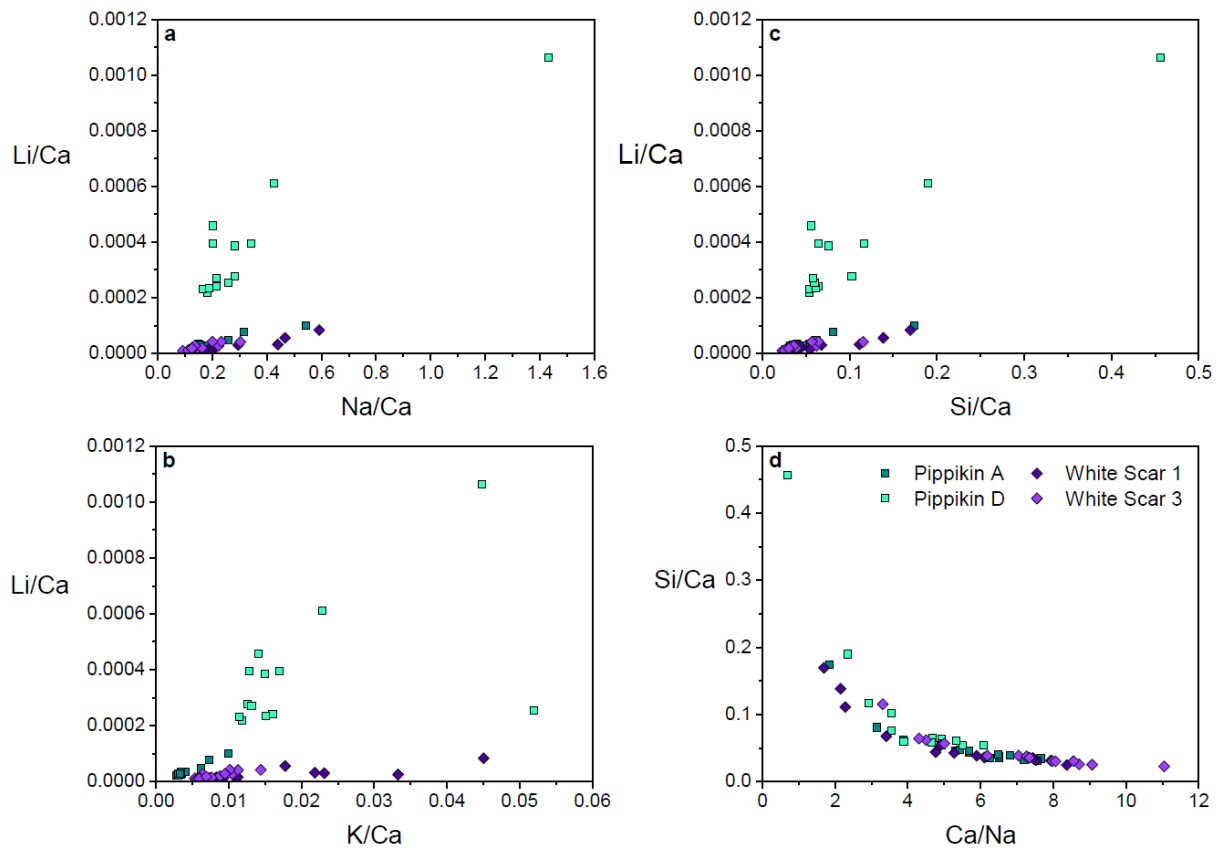
Fig. 1: Major element chemistry of the cave drip-waters and rain waters, compared to local lithogenic sources and seawater. (a) Ternary plot of Ca-Mg-(Na+K) molar proportions. (b) Molar ratios of Mg/Na versus Ca/Na. See Table 2 for full sample details of the local rocks and soils. Prefixes ‘P’ and ‘WS’ indicate samples from the vicinity of Pippikin cave and White Scar Cave, respectively. Note that the representative global silicate and carbonate endmembers in panel (b) indicate typical values based on river chemistry (Gaillardet et al., 1999) rather than the full range of potential variation in source rocks.

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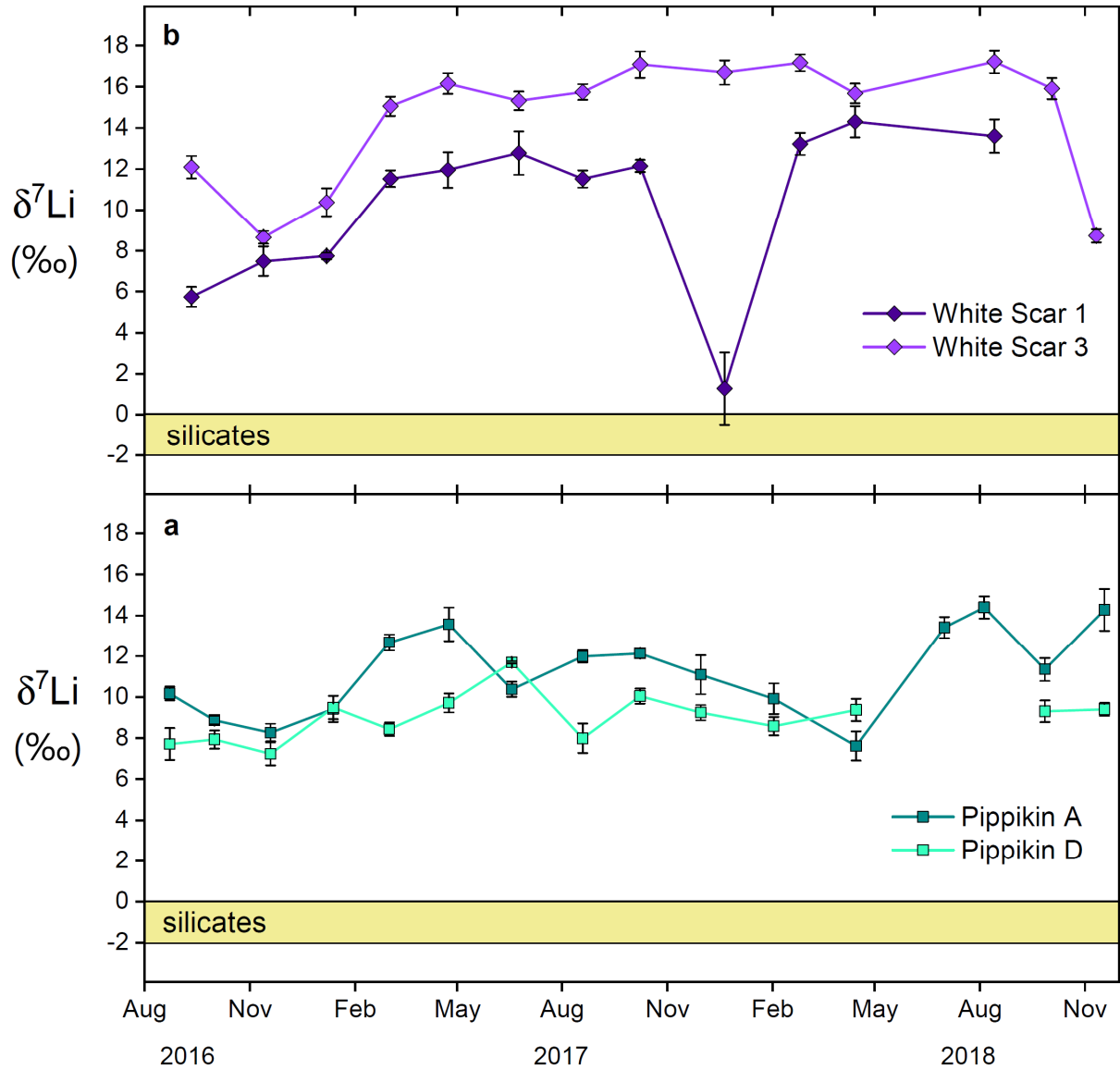
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Fig. 2: Time series of drip-water chemistry plotted as molar ratios: (a) Mg/Na, (b) Sr/Na, (c) B/Na, (d) Li/Na. Red dashed line indicates monthly surface air temperatures outside Pippikin cave.



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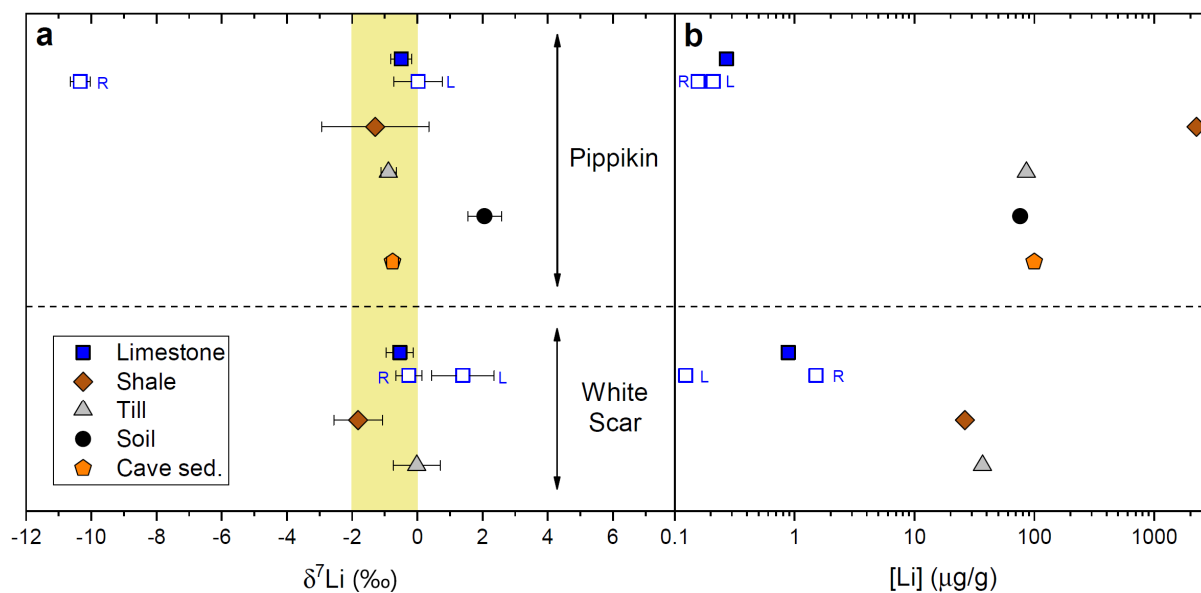
Fig. 3: Cross plots of drip-water Li/Ca molar ratios against (a) Na/Ca, (b) K/Ca, and (c) Si/Ca, and (d) cross plot of Si/Ca against Ca/Na, indicating mixing between silicate and carbonate endmembers.



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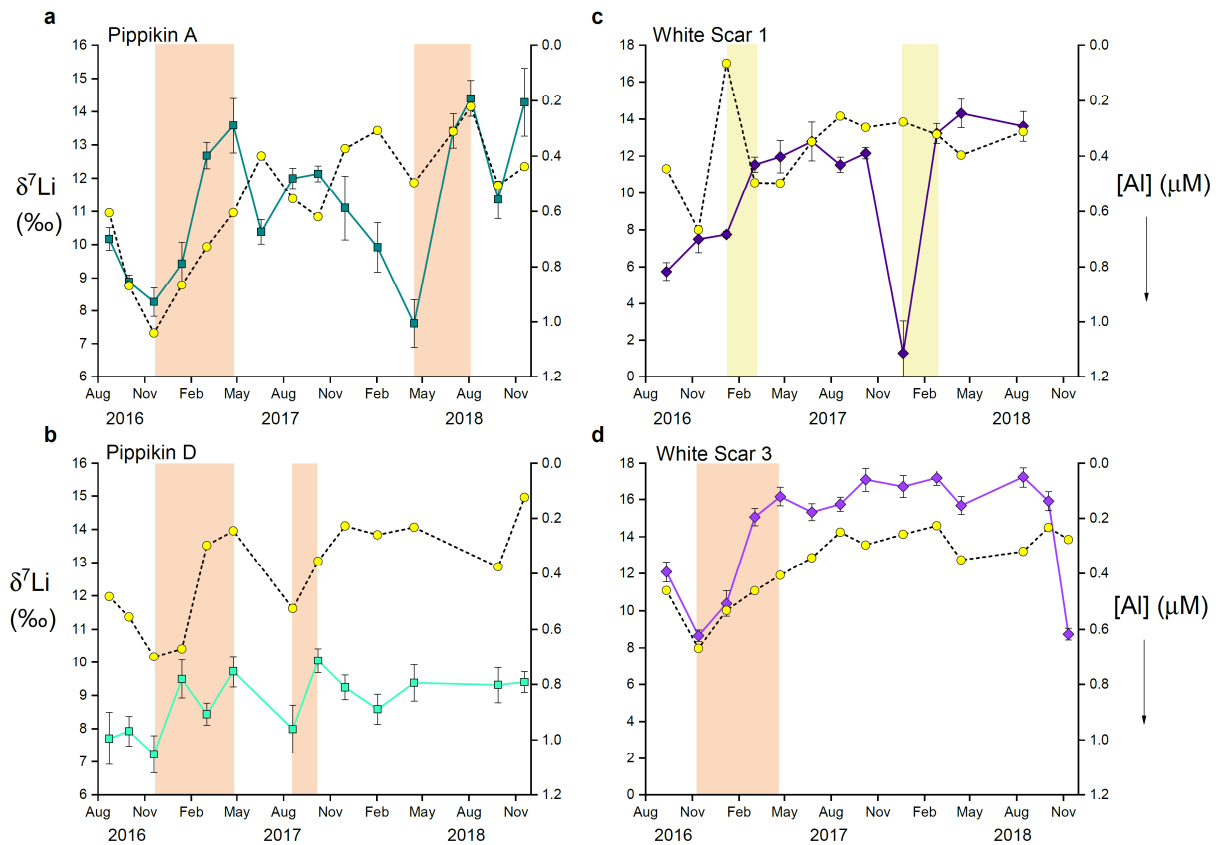
Fig. 4: Time series of drip-water Li isotopes for (a) Pippikin cave, and (b) White Scar Cave. Yellow bar indicates the Li isotope composition of local silicate sources (see Fig. 5a). Error bars for drip-water data represent 2sd (see Table 1).

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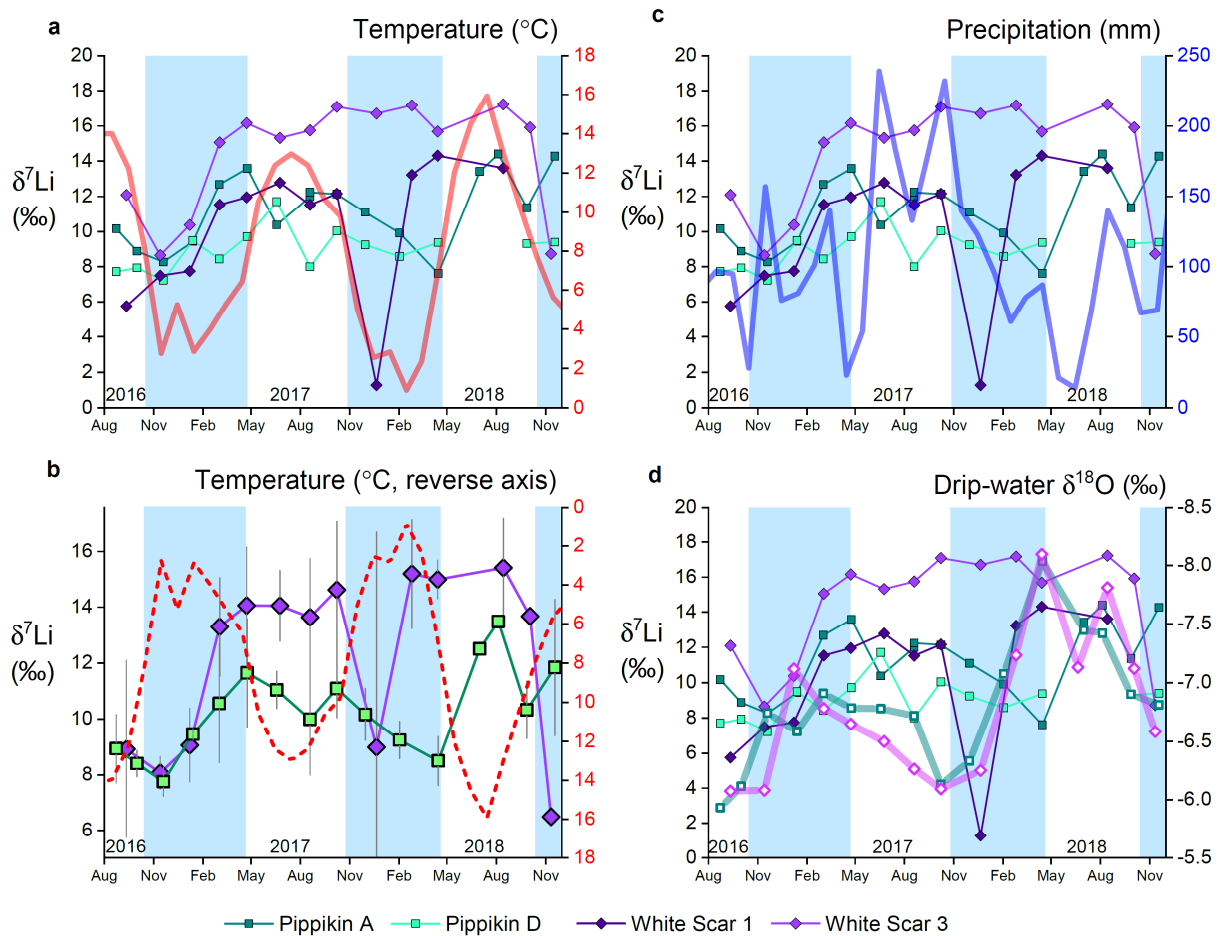
Fig. 5: Composition of local rocks, sediments, tills, and soils at Pippikin cave and White Scar Cave (see Table 2 and text for sample details): (a) Li isotopes, (b) Li concentrations (on a logarithmic scale). Open blue squares represent leachates (L) and residues (R) of the limestone. In panel (a), the yellow bar highlights the Li isotope range of all bulk samples (excluding the peaty soil). Error bars for Li isotopes represent 2sd.



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Fig. 6: Temporal variability in Li isotopes (coloured symbols and solid lines) and Al concentrations (yellow circles and dashed black lines) at each of the four sites: (a) Pippikin A; (b) Pippikin D; (c) White Scar 1; (d) White Scar 3. Note that the Li isotope data are on separate y-axes for Pippikin cave and White Scar Cave, whereas the Al data are on the same (reversed) y-axis for all sites. Orange bars indicate the main intervals when Li isotopes shifted towards higher values accompanied by decreasing Al concentrations, while yellow bars indicate shifts towards higher Li isotope values at White Scar 1 that were not accompanied by obvious changes in Al concentrations.

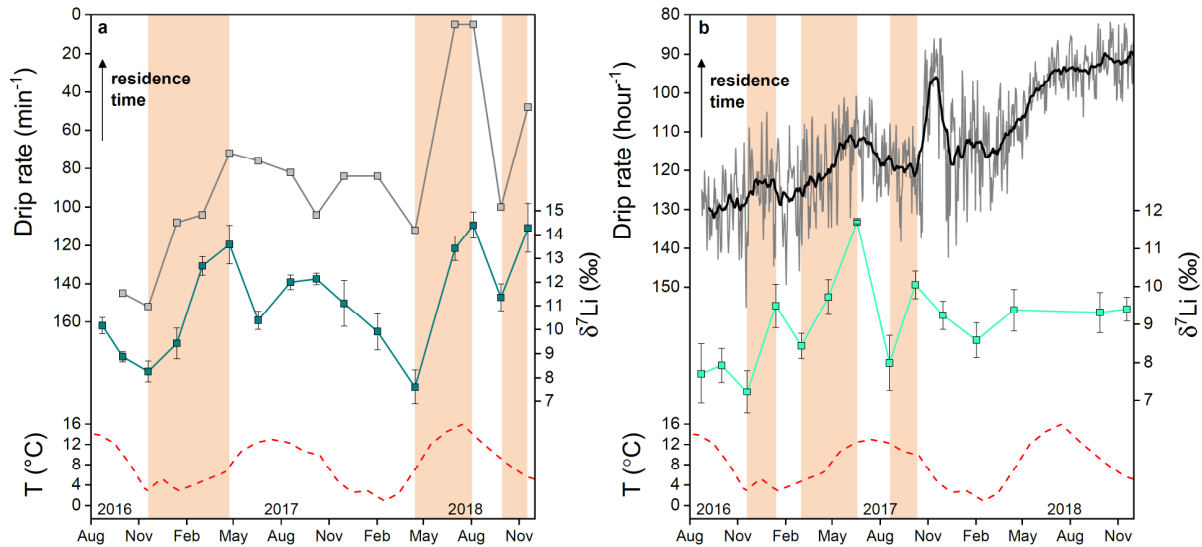
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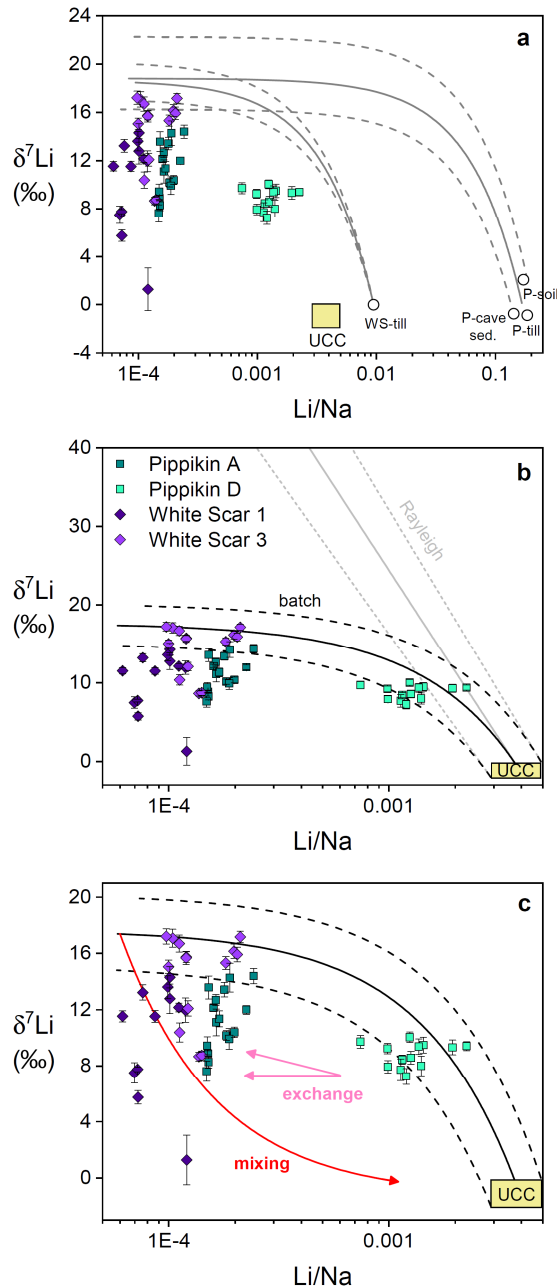
Fig. 7: Time series of drip-water $\delta^7\text{Li}$ values (symbols and lines) compared to (a) monthly surface air temperature outside Pippikin cave (red line); (b) temperature as in panel (a) but on a reverse axis (red dashed line); (c) monthly precipitation (blue line); and (d) drip-water $\delta^{18}\text{O}$ (thick green line, Pippikin cave; thick purple line, White Scar Cave; plotted values are the mean of the two drip sites for each cave; note inverted axis). In panel (b), the $\delta^7\text{Li}$ values are the mean of the two drip sites in each cave (green symbols and line, Pippikin cave; purple symbols and line, White Scar Cave), with the vertical bars indicating the range of measured values rather than representing error bars. Note that where $\delta^7\text{Li}$ data exist for only one of the two sites in a given cave, the measured value is adjusted by half the mean $\delta^7\text{Li}$ offset between the two sites to account for inter-site variability. In all panels, blue bars highlight cold intervals with below average monthly air temperatures.

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Fig. 8: Time series from (a) Pippikin A and (b) Pippikin D of drip rates (note inverted axes), drip-water Li isotopes, and monthly surface air temperatures (measured outside Pippikin cave). Drip rates in (a) are from instantaneous measurements during drip-water sampling. Drip rates in (b) are from the nearby “Stalagmate” drip logger rather than the drip site itself (grey line, daily drip rates; black line, monthly-smoothed). Note the differing units for drip rates between panels (a) and (b). Orange bars indicate intervals when Li isotopes shifted towards higher values, which were generally accompanied by lower drip rates that are inferred to reflect longer fluid residence times (indicated by arrows).



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1260 **Fig. 9:** Cross plots of drip-water $\delta^7\text{Li}$ values against Li/Na molar ratios, compared to modelled fluid evolution
1261 during secondary clay removal. (a) Batch (equilibrium) fractionation curves from an initial fluid with the
1262 composition of local till at White Scar Cave, or with the mean composition of local till, soil, and cave sediment
1263 at Pippikin cave (see Table 2 for sample details; prefixes ‘P’ and ‘WS’ indicate Pippikin and White Scar,
1264 respectively). (b) Batch (equilibrium) fractionation curve (black) and Rayleigh fractionation curve (grey) based
1265 on an initial fluid derived from a silicate source with $\delta^7\text{Li} = -1 \pm 1$ ‰ (Fig. 5a) and Li/Na ratio of the upper
1266 continental crust (UCC) (0.0029-0.0049) (Rudnick and Gao, 2003; Teng et al., 2004). (c) Multi-step evolution
1267 including batch fractionation as in (b) followed by either mixing with a silicate-derived fluid source or
1268 adsorption/exchange with secondary clay minerals. For all panels, the fractionation factor $\alpha_{\text{clay-fluid}}$ is 0.9815
1269 (range of 0.983-0.980), based on temperature-adjusted experimental data for clays (Li and West, 2014; Gou et
1270 al., 2019; Hindshaw et al., 2019a). Solid lines indicate the most likely fluid evolution, while dashed lines
1271 indicate upper and lower bounds based on those parameter ranges. In panel (c), the “mixing” arrow models a
1272 starting point on the batch fractionation curve at $\text{Li/Na} = 0.00006$ (i.e. matching the lowest recorded drip-water
1273 Li/Na value) followed by mixing with a silicate-derived fluid source ($\delta^7\text{Li} = -1$ ‰ and $\text{Li/Na} = 0.0039$), while
1274 the “exchange” arrows schematically indicate adsorption/exchange with clay minerals involving a smaller
1275 magnitude of fractionation or no fractionation (see text). Note logarithmic x-axes for all panels and the different
1276 x-axis scale for panel (a).

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Tables

Table 1: Analyses of cave drip-waters for drip rates, oxygen isotopes, major and trace elements, and Li isotopes

Location	Date	Drip rate min ⁻¹	$\delta^{18}\text{O}$ ‰	Ca $\mu\text{mol/L}$	Mg $\mu\text{mol/L}$	Na $\mu\text{mol/L}$	K $\mu\text{mol/L}$	Si $\mu\text{mol/L}$	Sr nmol/L	B nmol/L	Al nmol/L	Ti nmol/L	Mo nmol/L	Ba nmol/L	U nmol/L	Li nmol/L	Li/Na molar	$\delta^7\text{Li}$ ‰	2sd ‰
Pip A	23-Aug-16	-	-6.33	487	43.5	265	4.9	84.7	483	640	610	4.6	3.4	48.2	1.4	48	0.00018	10.2	0.3
Pip A	01-Oct-16	145	-5.86	1140	44.0	214	4.0	51.7	973	630	870	6.7	2.2	172	2.3	32	0.00015	8.9	0.2
Pip A	19-Nov-16	152	-6.40	1140	34.4	211	3.8	53.3	773	500	1040	6.2	3.5	86.5	2.6	32	0.00015	8.3	0.4
Pip A	13-Jan-17	108	-7.21	1100	32.4	193	3.7	48.0	731	390	870	7.5	3.8	78.5	2.5	29	0.00015	9.4	0.6
Pip A	03-Mar-17	104	-6.98	1010	31.7	206	4.0	54.6	685	380	730	7.8	3.7	81.7	2.3	34	0.00016	12.7	0.4
Pip A	24-Apr-17	72	-6.65	1010	31.3	177	3.5	46.5	688	340	600	5.3	3.6	76.6	2.2	27	0.00015	13.6	0.8
Pip A	18-Jun-17	76	-6.73	1220	38.8	188	4.2	42.8	845	430	400	3.4	3.0	136	2.0	37	0.00020	10.4	0.4
Pip A	19-Aug-17	82	-6.62	1350	46.6	198	4.7	53.0	1000	550	550	3.2	2.6	180	2.3	44	0.00023	12.0	0.3
Pip A	19-Aug-17	replicate ^a	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.2	0.6
Pip A	08-Oct-17	104	-6.26	1410	42.1	184	3.9	48.4	952	530	620	3.9	2.7	111	2.6	29	0.00016	12.1	0.2
Pip A	30-Nov-17	84	-5.94	1140	34.0	151	3.1	34.9	784	480	370	3.5	2.3	83.5	2.2	25	0.00016	11.1	1.0
Pip A	02-Feb-18	84	-7.17	1070	32.8	149	3.4	34.5	757	380	310	3.2	3.0	454	2.2	28	0.00019	9.9	0.7
Pip A	15-Apr-18	112	-8.47	1060	32.0	162	3.3	39.2	714	340	500	3.6	3.0	121	2.0	24	0.00015	7.6	0.7
Pip A	01-Jul-18	<5	-7.45	963	36.1	249	6.0	60.1	717	450	310	3.1	3.5	106	1.7	45	0.00018	13.4	0.5
Pip A	05-Aug-18	<5	-7.51	760	38.8	241	5.6	61.2	622	510	220	4.6	4.1	147	1.6	59	0.00024	14.4	0.5
Pip A	27-Sep-18	100	-6.59	1060	31.6	169	3.2	37.3	723	510	510	2.8	2.8	95.6	1.9	29	0.00017	11.4	0.6
Pip A	18-Nov-18	48	-6.36	1020	31.7	158	3.4	41.4	707	470	440	4.6	3.2	152	2.1	30	0.00019	14.3	1.0
Pip D	23-Aug-16	64	-5.53	827	39.0	177	13.3	53.4	682	710	480	8.0	2.8	83.3	1.4	200	0.00113	7.7	0.8
Pip D	01-Oct-16	10	-6.37	1450	52.2	408	18.3	149	1110	670	560	11.6	6.5	197	2.9	403	0.00099	7.9	0.4
Pip D	19-Nov-16	68	-7.08	1060	36.3	193	12.6	57.3	807	510	700	6.9	3.9	161	1.8	231	0.00120	7.2	0.6
Pip D	13-Jan-17	9	-5.96	863	55.4	368	19.8	164	927	690	670	12.3	8.7	126	2.8	527	0.00143	9.5	0.6
Pip D	03-Mar-17	8	-6.84	1110	45.5	379	18.8	129	938	560	300	11.0	9.1	162	2.6	435	0.00115	8.4	0.3
Pip D	24-Apr-17	6	-6.92	774	61.3	1110	34.7	353	984	930	250	20.8	13.3	111	2.9	823	0.00074	9.7	0.5
Pip D	18-Jun-17	6	-6.83	-	-	-	-	-	-	-	-	-	-	-	-	-	-	11.7	0.1
Pip D	19-Aug-17	12	-6.82	1540	52.3	254	17.7	82.8	1160	700	530	8.5	5.2	190	2.9	356	0.00140	8.0	0.7
Pip D	08-Oct-17	48	-6.00	961	46.5	180	14.5	58.8	774	630	355	4.7	3.2	141	1.7	224	0.00125	10.1	0.4
Pip D	30-Nov-17	8	-6.73	1370	50.3	352	71.2	81.6	1030	740	230	10.8	7.9	240	2.8	347	0.00099	9.2	0.4
Pip D	02-Feb-18	10	-6.98	1340	50.8	288	17.7	78.2	1030	590	260	13.3	7.9	157	3.1	363	0.00126	8.6	0.5
Pip D	15-Apr-18	6	-7.60	1350	57.0	380	20.2	102	1090	690	230	14.4	9.6	174	3.2	520	0.00137	9.4	0.5
Pip D	01-Jul-18	no drip	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pip D	05-Aug-18	-	-7.33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pip D	27-Sep-18	7	-7.21	1620	62.7	329	20.9	103	1290	840	380	16.2	8.7	243	3.8	639	0.00194	9.3	0.5
Pip D	18-Nov-18	6	-7.27	1630	66.4	330	23.0	91.4	1390	900	130	17.6	9.5	263	4.3	745	0.00225	9.4	0.3
WS 1	11-Sep-16	-	-6.22	1560	45.4	256	12.8	56.2	1110	660	450	2.8	1.0	46.2	1.2	19	0.00007	5.7	0.5
WS 1	13-Nov-16	-	-6.08	1070	39.7	218	11.7	58.1	949	470	670	3.2	0.9	36.6	1.2	15	0.00007	7.5	0.7
WS 1	07-Jan-17	continuous	-7.01	488	34.5	214	10.6	54.2	417	340	70	3.0	0.8	15.8	0.6	15	0.00007	7.7	0.2
WS 1	04-Mar-17	continuous	-6.84	1670	35.9	199	11.4	41.0	896	260	500	3.2	0.7	38.1	1.3	12	0.00006	11.5	0.4
WS 1	23-Apr-17	70	-6.64	666	33.9	310	11.8	92.2	571	340	500	3.7	1.5	30.0	1.3	37	0.00012	12.0	0.9
WS 1	24-Jun-17	54	-6.57	864	41.6	254	20.0	58.4	971	450	350	3.0	1.1	46.0	1.1	26	0.00010	12.8	1.0
WS 1	19-Aug-17	continuous	-6.24	1230	52.5	233	13.8	52.6	1200	680	260	2.6	0.7	51.4	1.2	20	0.00009	11.5	0.4
WS 1	08-Oct-17	continuous	-6.09	1780	50.1	236	14.8	57.1	1180	760	300	3.5	1.8	60.6	1.4	26	0.00011	12.2	0.3
WS 1	21-Dec-17	212	-6.23	1060	44.1	222	35.1	46.3	977	780	280	3.4	45.2	128	1.3	27	0.00012	1.3	1.8

WS 1	25-Feb-18	-	-7.11	1020	38.6	173	9.4	39.2	912	420	320	3.0	1.2	34.8	1.5	13	0.00008	13.2	0.5
WS 1	14-Apr-18	continuous	-8.26	1750	38.7	221	12.9	54.8	894	400	400	4.0	1.2	57.2	1.3	22	0.00010	14.3	0.8
WS 1	20-Jun-18	98	-7.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WS 1	14-Aug-18	-	-7.81	1640	33.4	220	13.7	57.2	815	510	310	4.9	1.0	43.6	1.1	22	0.00010	13.6	0.8
WS 1	03-Oct-18	34	-7.03	923	36.4	545	41.6	156	766	650	330	3.7	2.5	150	1.2	77	0.00014	-	-
WS 1	11-Nov-18	84	-6.63	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WS 3	11-Sep-16	-	-5.93	1010	50.2	224	10.6	62.6	1150	900	460	3.0	1.3	67.2	1.0	27	0.00012	12.1	0.5
WS 3	13-Nov-16	-	-6.08	924	40.0	279	10.4	107	908	640	670	5.1	2.1	46.0	1.3	38	0.00014	8.7	0.3
WS 3	07-Jan-17	continuous	-7.22	1450	38.1	205	9.3	56.1	912	470	530	4.1	1.5	51.0	1.1	23	0.00011	10.4	0.7
WS 3	04-Mar-17	continuous	-6.72	1660	36.2	191	8.9	42.9	895	380	460	4.1	1.0	37.5	1.1	19	0.00010	15.1	0.5
WS 3	23-Apr-17	130	-6.66	1550	46.1	214	9.9	58.6	936	460	410	4.7	1.6	125	1.4	42	0.00020	16.2	0.5
WS 3	24-Jun-17	93	-6.43	941	50.0	219	13.6	60.3	1030	620	340	3.0	1.4	172	1.2	40	0.00018	15.3	0.5
WS 3	19-Aug-17	continuous	-6.29	1270	56.3	206	11.2	49.2	1310	870	250	3.1	1.0	60.1	1.2	25	0.00012	15.7	0.4
WS 3	08-Oct-17	continuous	-	2030	51.4	184	11.5	45.9	1280	790	300	3.2	1.6	57.9	1.2	19	0.00010	17.1	0.6
WS 3	21-Dec-17	continuous	-6.27	1270	44.0	159	9.7	38.7	1020	490	260	3.8	1.1	43.9	1.1	18	0.00011	16.7	0.6
WS 3	25-Feb-18	-	-7.36	1010	44.8	202	10.3	57.2	898	430	230	5.5	1.8	77.6	1.4	43	0.00021	17.2	0.4
WS 3	14-Apr-18	continuous	-7.92	1620	41.4	190	9.6	49.6	943	350	350	5.6	2.0	58.6	1.3	23	0.00012	15.7	0.5
WS 3	20-Jun-18	130	-7.21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WS 3	14-Aug-18	-	-7.81	1590	32.8	175	9.4	39.9	812	480	320	5.4	1.3	48.4	1.0	17	0.00010	17.2	0.5
WS 3	03-Oct-18	46	-7.21	1540	41.1	209	14.6	55.0	828	510	230	4.5	1.8	166	1.3	43	0.00020	15.9	0.5
WS 3	11-Nov-18	continuous	-6.54	1460	31.7	181	10.1	44.0	758	510	280	3.9	1.6	197	1.0	26	0.00014	8.7	0.3

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1282 (-) : not determined.

1283 ^a : full Li isotope replicate, including filtration, elemental separation, and mass spectrometry.

1284 Lithium isotope standards yield $\delta^7\text{Li} = +31.3 \pm 0.6$ (2sd, n=24) for seawater and $\delta^7\text{Li} = +2.5 \pm 0.3$ (n=5) for BCR-2.

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Table 2: Characterisation of local rocks, tills, and soil for Li isotopes, Li concentrations, and selected elemental ratios

Cave	Sample	$\delta^7\text{Li}$ ‰	2sd ‰	[Li] µg/g	Li/Na mol/mol	Al/Ca mmol/mol
Pippikin	Great Scar Limestone - bulk	-0.5	0.3	<i>0.27</i>	0.02	0.58
Pippikin	Great Scar Limestone - carbonate leach	0.0	0.7	<i>0.21</i>	0.02	0.24
Pippikin	Great Scar Limestone - residue	-10.3	0.3	<i>0.16</i>	0.02	0.78
Pippikin	interbedded shale, Arson Shaft, Ease Gill - bulk	-1.3	1.6	2260	3.40	141000
Pippikin	interbedded shale, Arson Shaft, Ease Gill - exchangeable	16.7	1.2	<i>0.79</i>	-	-
Pippikin	Quaternary till, Ease Gill - bulk	-0.9	0.2	86	0.19	619000
Pippikin	Quaternary till, Ease Gill - exchangeable	5.3	0.7	<i>0.03</i>	-	-
Pippikin	peaty soil, overlying Pippikin cave - bulk	2.1	0.5	76	0.17	447000
Pippikin	peaty soil, overlying Pippikin cave - exchangeable	16.7	0.3	<i>0.08</i>	-	-
Pippikin	cave sediment, floor of Pippikin cave - bulk	-0.8	0.2	100	0.14	5650
Pippikin	cave sediment, floor of Pippikin cave - exchangeable	-5.0	0.7	<i>0.10</i>	-	-
White Scar	Great Scar Limestone - bulk	-0.5	0.4	<i>0.89</i>	0.03	2.58
White Scar	Great Scar Limestone - carbonate leach	1.4	1.0	<i>0.12</i>	0.01	0.24
White Scar	Great Scar Limestone - residue	-0.3	0.4	<i>1.51</i>	0.10	10.5
White Scar	Yoredale Shale - bulk	-1.8	0.7	26	0.22	244
White Scar	Quaternary till - bulk	0.0	0.7	37	0.01	32400

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For all the limestone data and all exchangeable fractions, Li concentrations are estimates based on the signal intensity from MC-ICP-MS (shown in italics).
All other elemental data are from ICP-OES (see Table EA3 for full elemental analyses).
(-): not determined.

Table EA1: Lithium isotope measurements of standards

Table EA1a: Seawater standards

Standard	$\delta^7\text{Li}$ ‰	2sd ‰	Li in splits %
Seawater	31.3	0.2	0.2
Seawater	31.4	0.6	0.1
Seawater	31.1	0.3	0.0
Seawater	31.0	0.3	0.0
Seawater	30.9	0.4	0.1
Seawater	32.2	0.1	0.1
Seawater	31.3	0.5	0.0
Seawater	31.4	0.4	0.0
Seawater	31.4	0.8	0.1
Seawater	31.4	0.5	0.1
Seawater	31.5	0.6	0.2
Seawater	31.5	0.6	0.1
Seawater	31.2	0.5	-
Seawater	31.5	0.4	0.4
Seawater	31.6	0.3	0.2
Seawater	31.3	0.1	0.7
Seawater	31.3	0.4	0.2
Seawater	31.5	0.3	0.2
Seawater	31.2	0.4	0.6
Seawater	30.8	0.2	0.1
Seawater	31.2	0.5	0.1
Seawater	31.8	0.2	0.1
Seawater	31.4	0.6	0.0
Seawater	31.5	0.6	0.0
Seawater	31.3	0.6	0.0
Seawater	31.1	0.5	0.1
Seawater	31.4	0.8	0.0
Seawater	31.0	0.4	0.1
Seawater mean, 2sd	31.3	0.6	

Table EA1b: Seawater standards with variable column yields

Standard	$\delta^7\text{Li}$ ‰	2sd ‰	Li in splits %	$\delta^7\text{Li}$ offset ‰	$\delta^7\text{Li}$ offset / % Li in splits
Seawater - variable yield	32.1	0.5	0.4	0.8	2.0
Seawater - variable yield	35.6	0.7	2.3	4.3	1.9
Seawater - variable yield	42.4	0.8	8.2	11.1	1.4
Mean $\delta^7\text{Li}$ offset (‰) / % Li in splits					1.7

Table EA1c: BCR2 standards

Standard	$\delta^7\text{Li}$ ‰	2sd ‰
BCR2	2.6	0.1
BCR2	2.7	0.2
BCR2	2.4	0.3
BCR2	2.5	0.1
BCR2	2.5	0.4
BCR2 mean, 2sd	2.5	0.3

(-): not determined.

Table EA2: Rain water trace element concentrations and Li isotopes

Date	Ca μmol/L	Mg μmol/L	Na μmol/L	K μmol/L	Si μmol/L	Sr nmol/L	B nmol/L	Al nmol/L	Ti nmol/L	Mo nmol/L	Ba nmol/L	Li nmol/L	Li/Na mol/mol	δ ⁷ Li ‰	2sd ^a ‰	2sd ^b ‰	Yield ^c
Sep-16	37	15.1	133	82.9	10.2	37	400	125	8.2	3.4	16.9	20	0.00015	12.5	1.1	1.1	
Oct-16	125	21.0	162	48.9	12.5	97	550	157	8.3	3.5	19.0	30	0.00019	13.1	0.8	0.8	
Nov-16	19	4.4	36	5.5	9.6	17	30	93.0	3.0	1.0	6.5	12	0.00032	11.4	0.5	0.5	
Dec-16	29	16.1	172	18.5	8.1	33	150	64.0	4.2	1.2	8.5	33	0.00019	11.2	0.7	0.7	
Jan-17	19	12.5	143	7.2	1.7	28	150	17.1	2.2	1.0	5.5	23	0.00016	13.4	0.3	0.3	
Feb-17	17	6.9	81	4.5	11.9	20	bdl	123	2.8	0.7	14.7	22	0.00027	9.2	0.3	0.6	*
Mar-17	22	5.7	68	16.3	1.2	19	60	18.7	2.3	0.5	5.4	18	0.00026	-	-	-	
Apr-17	79	15.5	102	16.7	3.5	62	150	113	4.9	1.0	44.9	27	0.00027	9.4	0.8	0.8	
May-17	81	6.4	49	19.7	8.5	47	180	96.8	2.6	2.4	12.5	19	0.00040	12.2	0.9	0.9	
Jun-17	23	5.4	47	17.1	2.5	14	80	52.3	2.5	0.7	4.9	15	0.00032	13.9	0.3	0.4	*
Jul-17	32	12.2	70	78.9	12.1	19	820	139	5.9	5.6	4.0	19	0.00027	11.1	0.1	0.1	
Aug-17	28	8.9	64	26.4	11.2	17	370	102	5.5	2.1	8.7	15	0.00024	12.7	1.2	1.2	
Sep-17	40	12.8	77	41.5	5.2	29	270	87.6	4.3	1.0	12.7	33	0.00043	12.7	0.4	0.5	*
Oct-17	35	21.6	166	49.7	3.4	34	370	39.7	3.4	1.4	11.9	24	0.00015	-	-	-	
Nov-17	33	12.7	98	31.7	5.0	22	190	145	5.0	2.1	8.2	23	0.00024	-	-	-	
Dec-17	69	19.8	161	33.7	13.4	48	270	84.5	7.5	0.6	31.3	35	0.00022	-	-	-	
Jan-18	34	19.4	200	5.1	4.9	40	140	104	4.0	0.9	12.6	32	0.00016	-	-	-	
Feb-18	50	11.2	119	4.2	15.1	42	40	47.0	2.7	0.7	30.2	23	0.00019	-	-	-	
Mar-18	55	13.1	158	4.7	4.8	51	bdl	65.0	2.4	0.9	15.6	22	0.00014	-	-	-	
Apr-18	77	4.9	64	2.3	8.0	49	bdl	53.7	1.9	0.8	19.1	15	0.00023	-	-	-	
May-18	235	25.9	96	29.1	11.9	211	330	129	5.1	1.1	111	52	0.00054	-	-	-	
Jun-18	104	19.4	119	28.3	7.8	74	300	91.6	3.0	1.2	47.6	85	0.00072	-	-	-	
Jul-18	71	18.6	82	135	2.8	47	650	268	4.5	0.9	21.5	22	0.00027	-	-	-	
Aug-18	145	23.4	72	191	5.8	77	1420	449	11.1	0.8	20.7	23	0.00032	-	-	-	
Sep-18	95	16.3	141	149	6.3	54	1250	420	9.5	2.0	32.7	24	0.00017	-	-	-	
Oct-18	41	8.8	55	65.0	2.9	32	990	313	4.2	0.2	139	12	0.00022	-	-	-	
Nov-18	70	23.7	141	115	4.0	85	1180	522	7.3	0.3	302	33	0.00024	-	-	-	

bdl: below detection limit.

(-): not determined.

a: 2sd based on multiple analyses within analytical run.

b: 2sd used for plotting (the larger value of the analytical 2sd or 1.7‰/% Li in cut; see Table EA1b).

c: for samples marked by *, the column yield was between 99.0 and 99.8 % and a modified 2sd was used to account for uncertainty due to Li loss

Lithium isotope standards yield δ⁷Li = +31.3 ± 0.6 (2sd, n=24) for seawater and δ⁷Li = +2.5 ± 0.3 (n=5) for BCR-2.

Table EA3: Characterisation of local rocks and soils, including elemental composition data

Cave	Sample	$\delta^7\text{Li}$ ‰	2sd ‰	[Li] µg/g	Li/Na mol/mol	Al/Ca mmol/mol	Al mg/g	Fe mg/g	Ti mg/g	Mg mg/g	Ca mg/g	Na mg/g	K mg/g	P µg/g	Mn µg/g	Ba µg/g	Sr µg/g	Rb µg/g	Li µg/g
Pippikin	Great Scar Limestone - bulk	-0.5	0.3	<i>0.27</i>	0.02	0.58	0.19	0.20	0.010	1.07	482	0.04	0.07	90	38	2.9	174	bdl	<i>0.27</i>
Pippikin	Great Scar Limestone - carbonate leach	0.0	0.7	<i>0.21</i>	0.02	0.24	0.07	0.06	bdl	1.06	435	0.04	bdl	120	43	2.9	170	bdl	<i>0.21</i>
Pippikin	Great Scar Limestone - residue	-10.3	0.3	<i>0.16</i>	0.02	0.78	0.13	0.17	0.006	0.69	249	0.02	0.02	bdl	22	1.4	104	bdl	<i>0.16</i>
Pippikin	interbedded shale, Arson Shaft, Ease Gill	-1.3	1.6	2260	3.40	141000	201	20.5	8.31	6.57	2.12	2.20	30.2	120	45	469	95.3	160	2260
Pippikin	Quaternary till, Ease Gill	-0.9	0.2	86	0.19	619000	57.7	28.4	3.49	3.05	0.14	1.53	11.3	230	352	139	49.2	70	86
Pippikin	peaty soil, overlying Pippikin cave	2.1	0.5	76	0.17	447000	61.7	17.3	3.65	2.93	0.21	1.47	9.70	100	28	117	53.5	62	76
Pippikin	cave sediment, floor of Pippikin cave	-0.8	0.2	100	0.14	5650	59.5	31.6	4.24	3.91	15.6	2.31	12.5	580	802	276	78.9	71	100
White Scar	Great Scar Limestone - bulk	-0.5	0.4	<i>0.89</i>	0.03	2.58	0.73	0.39	0.037	2.50	420	0.10	0.35	bdl	133	5.1	267	bdl	<i>0.89</i>
White Scar	Great Scar Limestone - carbonate leach	1.4	1.0	<i>0.12</i>	0.01	0.24	0.06	0.10	bdl	1.93	343	0.06	0.02	bdl	114	2.2	202	bdl	<i>0.12</i>
White Scar	Great Scar Limestone - residue	-0.3	0.4	<i>1.51</i>	0.10	10.5	1.32	0.58	0.097	1.62	187	0.05	0.44	bdl	76	5.8	129	bdl	<i>1.51</i>
White Scar	Yoredale Shale	-1.8	0.7	26	0.22	244	30.9	17.6	1.51	4.76	188	0.39	12.4	140	458	109	219	47	26
White Scar	Quaternary till	0.0	0.7	37	0.01	32400	50.4	31.5	3.28	5.01	2.31	13.0	11.0	550	879	378	88.0	60	37
BCR-2							71.3	93.2	13.2	19.5	47.7	23.0	14.9	1450	1410	683	325	41	8.7
Accuracy (%)							0%	-3%	-3%	-10%	-6%	-1%	1%	-8%	-7%	0%	-4%	-10%	-5%

bdl = below detection limit (at solution concentration analysed).

For the limestones (including leaches and residues), Li concentrations are based on the signal intensity from MC-ICP-MS (shown in italics).

For all other samples, Li concentrations are from ICP-OES.

All other elemental concentrations are from ICP-OES.

Accuracy for BCR-2 is assessed as the difference between measured and reference values (Jochum et al., 2016).

Reference:

Jochum K.P., Weis U., Schwager B., Stoll B., Wilson S.A., Haug G.H., Andreae M.O., Enzweiler J. (2016) Geostandards and Geoanalytical Research 40, 333-350.

Table EA4: Monthly precipitation and mean monthly temperature

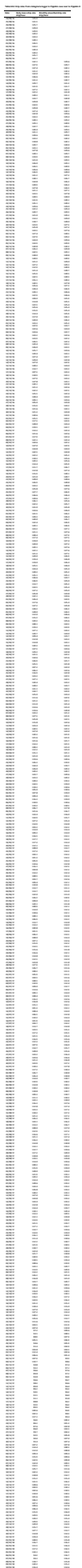
Month	Precipitation ^a mm	Temperature ^b °C	Notes
Apr-16	<i>104</i>	<i>4</i>	c,d
May-16	<i>90</i>	<i>9</i>	c,d
Jun-16	<i>102</i>	<i>12</i>	c,d
Jul-16	<i>83</i>	<i>14</i>	c,d
Aug-16	<i>97</i>	<i>14</i>	c,d
Sep-16	95	12.22	
Oct-16	28	8.14	
Nov-16	157	2.76	
Dec-16	76	5.24	
Jan-17	81	2.86	
Feb-17	101	3.99	
Mar-17	140	5.23	
Apr-17	23	6.44	
May-17	54	10.53	
Jun-17	239	12.39	
Jul-17	183	12.97	
Aug-17	133	12.39	
Sep-17	182	10.65	
Oct-17	232	9.79	
Nov-17	140	5.04	
Dec-17	123	2.54	
Jan-18	96	2.83	
Feb-18	61	0.9	
Mar-18	78	2.36	
Apr-18	87	7.01	
May-18	21	12.02	
Jun-18	14	14.54	
Jul-18	68	15.93	
Aug-18	140	12.93	
Sep-18	114	10.23	
Oct-18	67	7.74	
Nov-18	69	5.62	
Dec-18	<i>177</i>	<i>4.74</i>	c

a: Monthly precipitation totals measured in Ingleton (except data in italics from Bingley).

b: Mean monthly temperatures measured outside the entrance to Pippikin cave (except data in italics from Bingley).

c: Monthly precipitation estimated from nearby weather station in Bingley (Bingley No 2, <https://en.tutiempo.net/climate/united-kingdom.html>), adjusted by a factor of 1.4 to account for the higher precipitation totals in the study area.

d: Mean monthly temperature estimated from nearby weather station in Bingley (Bingley No 2, <https://en.tutiempo.net/climate/united-kingdom.html>), adjusted by 1 °C to account for the lower temperatures in the study area.



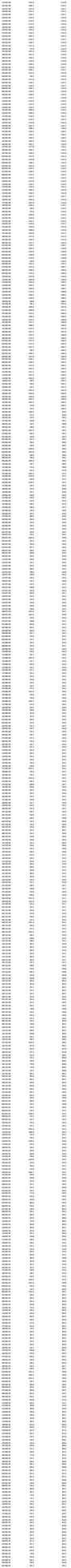


Figure EA2: Cave survey of White Scar Cave, showing drip-water sampling locations White Scar 1 and 3
 Reproduced from: Waltham A.C. (1977) White Scar Cave. *Transactions of the British Cave Research Association* 4 (3), 345-353.

WHITE SCAR CAVE

Ingleton Yorkshire

