

A lithium isotopic perspective of basalt weathering: Cycling of Li and its mobility relative to Ca and Mg

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Abstract

Lithium isotope composition ($\delta^7\text{Li}$) has been extensively utilized to trace silicate weathering. Although the direction and magnitude of Li isotope fractionation during Li adsorption onto secondary minerals are well understood, the relative importance of Li partitioning via its adsorption vis-à-vis structural incorporation into clay minerals on overall Li isotope fractionation remains poorly constrained. In this study, we investigate the bulk, exchangeable and oxyhydroxide phases of two basaltic weathering profiles to assess the processes regulating Li distribution and its isotope fractionation. The decrease in $\delta^7\text{Li}$ values toward the top of the weathering profiles, coupled with increases in Li/Al, Fe/Al, and Mn/Al ratios, indicates role of clay minerals and Fe-Mn oxyhydroxides in the preferential adsorption and/or structural incorporation of ^6Li . In one of the profiles, processes of sorption and desorption of Li are driven by pH variations. Mass balance calculations demonstrate that crystal-bound Li in clay minerals dominates the total Li budget of the weathered basalts and therefore drive the depth-dependent variation in $\delta^7\text{Li}$ within the weathering profiles.

The estimates of $\delta^7\text{Li}$ in weathering solutions show excellent agreement between two independent approaches. The estimated solution $\delta^7\text{Li}$ values are about 8.1-12.6‰ higher than that of the parent basalts and fall within the range of $\delta^7\text{Li}$ offsets observed between the rocks and solutions in river and groundwater systems in basaltic catchments. We establish empirical relationships between $\delta^7\text{Li}$, mobility of Li relative to Ca and Mg, and the chemical index of alteration (CIA) in weathering profiles. These relationships provide a framework for reliable prediction of $\delta^7\text{Li}$ and Li mobility relative to Ca and Mg during basaltic weathering. Additionally, by integrating published values of $\delta^7\text{Li}$ and CIA in river sediments, we demonstrate that $\delta^7\text{Li}$ values of river sediments can be predicted from their CIA. The results and findings of this study have important implications for the utility of Li isotope composition as a tracer of silicate weathering intensity and the relative mobilities of Li, Ca and Mg.

56 **Keywords**

57 Basaltic weathering; Lithium isotope; Adsorption; Desorption; pH; Relative mobility

58 **1. Introduction**

59 Chemical weathering of silicate rocks acts as a sink of atmospheric CO₂ over the geological time
60 scale (Walker et al., 1981; Raymo et al., 1988; Amiotte Suchet et al., 2003). Among aerially exposed
61 silicate rocks, basalts represent only ~9% (Rad et al., 2007), whereas their chemical weathering accounts
62 for 30-35% of global CO₂ consumption and contributes to 23-30% of the global dissolved load to sea
63 water (Gaillardet et al., 1999; Dessert et al., 2003; Rad et al., 2007). Lithium and its isotopes have been
64 extensively utilized to study continental silicate weathering (Huh et al., 2001; Dellinger et al., 2015; Pogge
65 von Strandmann and Henderson, 2015) because of several unique features: (i) Li has a relatively uniform
66 crustal distribution in both concentration and isotope space, (ii) it is dominantly hosted in silicate minerals
67 and thus continental weathering flux of Li and its isotopic composition are insensitive to weathering of
68 carbonate rocks, (iii) due to its large relative mass difference, significant isotopic fractionation is
69 observable during incongruent weathering (Pistiner and Henderson, 2003; Rudnick et al., 2004; Misra and
70 Froelich, 2012; Gou et al., 2019). In addition, Li does not participate in biological processes (Pogge von
71 Strandmann et al., 2016). While Li isotopic ratios serve as robust tracers of continental silicate weathering,
72 there is a limited understanding of how Li covaries with Ca and Mg during continental weathering. The
73 mechanistic and quantitative understanding of continental fluxes of two major alkaline earth elements (Ca
74 and Mg) is important because of their intricate involvement in carbon cycle, where their respective
75 carbonate minerals act as the final sink of atmospheric CO₂ over geological time scale (Raymo and
76 Ruddiman, 1992; Gaillardet et al., 1997; Amiotte Suchet et al., 2003; Dessert et al., 2003).

77 Lithium, the lightest alkali element, is fluid mobile and has two stable isotopes (⁶Li, ⁷Li), which
78 have large relative mass difference of ~16%. Thus, significant mass dependent fractionation of Li isotopes

occurs during low temperature water-rock interactions (Chan et al., 1992; Pistiner and Henderson, 2003; Rudnick et al., 2004). The primary cause of Li isotopic fractionation during incongruent weathering has been attributed to equilibrium partitioning of Li between secondary minerals and conjugate fluids (Huh et al., 1998; Pistiner and Henderson, 2003; Vigier et al., 2008). During silicate weathering ^6Li is preferentially scavenged by the secondary weathering products such as clay minerals and Fe-Mn oxyhydroxides (Chan et al., 1992; Pistiner and Henderson, 2003), whereas the fluid phases are enriched in ^7Li compared to the secondary solid phases. This phenomenon is attributed to tetrahedral coordination of Li^+ with four water molecules ($[\text{Li}(\text{H}_2\text{O})_4]^+$), where the weaker hydration bond of $^6\text{Li}-\text{H}_2\text{O}$ compared to $^7\text{Li}-\text{H}_2\text{O}$ bond (Yamaji et al., 2001; Wimpenny et al., 2015) results in preferential dehydration of ^6Li leading to its incorporation into octahedral sites of secondary phases (Pistiner and Henderson, 2003; Wimpenny et al., 2010a; Hindshaw et al., 2019). The impact of pH on Li isotopic fractionation has been explored but remains inconclusive (Li and Liu, 2020; Pogge von Strandmann et al., 2012; Zhu et al., 2023). There is no consensus on the direction of Li isotope fractionation with pH variation. For example, Zhu et al. (2023) proposed preferential desorption of ^6Li at decreasing pH, whereas Li and Liu (2020) documented desorption of ^7Li under similar conditions. Published body of work on weathering profiles (Lemarchand et al., 2010; Ryu et al., 2014; Chapela Lara et al., 2022) have demonstrated that a decrease in pH in the upper part of the profiles results in the dissolution of secondary phases, leading to a preferential loss of ^6Li from clay minerals. A few studies also report kinetic fractionation of Li isotopes during low temperature water-rock interactions (Teng et al., 2010). The study of Pistiner and Henderson (2003) demonstrates that the degree of Li isotope fractionation is dependent on the types of secondary minerals, which in turn is influenced by the intensity of weathering.

Investigation of weathering profiles developed on basaltic rocks have demonstrated that the Li isotope composition of profiles is influenced by secondary mineral formation, external inputs such as the

102 deposition of marine aerosols and eolian dust, and diffusion of Li across the paleo-water table (Huh et al.,
103 2004; Kısakurek et al., 2004; Rudnick et al., 2004; Teng et al., 2010; Tong et al., 2021; Xiong et al., 2022).
104 Although the magnitude and direction of Li isotopic fractionation during weathering is well understood,
105 there is limited knowledge on the specific processes and their relative importance in regulating $\delta^7\text{Li}$ of
106 weathered rocks (Teng et al., 2010). For example, the relative importance of Li adsorption onto clay
107 mineral surfaces vis-a-vis its incorporation into the lattice of neo-formed minerals is poorly understood
108 (Pogge von Strandmann et al., 2010; Wimpenny et al., 2015; Tong et al., 2021; Zhang et al., 2021; Cai et
109 al., 2024; Zhu et al., 2023). Decoupling these processes is crucial for utilizing Li as a tracer of water-
110 particle interaction during silicate weathering and to develop constraints on fluvial $\delta^7\text{Li}$ systematics, which
111 helps us elucidate past and present weathering rates.

112 We present and discuss Li isotope data of two weathering profiles developed on basaltic rocks of
113 Rajmahal Volcanic Province (RVP) in India. Based on trace element and Li isotope composition of the
114 bulk material and adsorbed fractions of the weathering profiles, we demonstrate that Li isotopes undergo
115 intense cycling after weathering via sorption-desorption processes. Additionally, we evaluate the mobility
116 of Li relative to Ca and Mg during chemical weathering as a function of chemical index of alteration.
117 Utilizing our results and published body of work, we compare relative mobility of Li, Ca and Mg during
118 basalt weathering under variable climate regimes. Furthermore, utilizing published data for riverine
119 suspended particulate matter (SPM), we demonstrate that $\delta^7\text{Li}$ values of SPM can be predicted from
120 their CIA. We also determine Li isotopic composition of weathering solutions using two independent
121 approaches and observe excellent agreement between these calculations.

122 **2. The study area**

123 The Rajmahal Volcanic Province (RVP) is located in central eastern part of India (Fig. 1). The
124 eroded remnants of RVP cover an area of approximately 4300 km² (Ghose et al., 2017). Rajmahal basalts

are mostly exposed in the Rajmahal hills located in the state of Jharkhand. These basalts are made up of multiple volcanic lava flows with a maximum reported thickness of 600 m. These volcanic eruptions are related to the Kerguelen hotspot activity (Baksi, 2022). The rocks are primarily tholeiitic basalts and basaltic andesites, with minor abundances of trachyandesites, andesites, dacites, and rhyolites. The mineral constituents of these basalts are labradoritic plagioclase, pigeonitic-augitic pyroxene, opaque minerals and primary glass (Mukherjee, 1971). The mineral proportions vary, with plagioclase constituting 19–56%, pyroxene 18–47%, and opaque minerals 1–10% of the bulk composition (Mukherjee, 1971).

Rajmahal basalts are dated at 118 ± 2 Myr (Baksi, 2022). The Rajmahal trap basalts were subjected to intense chemical weathering from late Cretaceous to early Paleogene during northward equatorial drift of Indian plate. In peninsular India, the intense chemical weathering along the east-west oriented belt plausibly favored the formation of weathering profiles across the Rajmahal Basalt Traps during the Eocene and Oligocene (Bardossy, 1981). The region currently experiences a humid to sub-humid climate, and receives an annual rainfall of about 1500 mm mostly via southwest monsoon. About 80% of annual rainfall occurs during June to September. The study area is characterized by seasonal rivers flowing from west to east (Fig. 1), many first-order streams, and small tributaries that drain the basaltic terrain, resulting in a characteristic dendritic drainage pattern. The major rivers flowing through this region are the Bansloi, Brahmani and Gumani (Fig. 1).

3. Materials and methods

Two weathering profiles, namely the Dalahi ($24^{\circ} 23.12' N$, $87^{\circ} 28.76' E$; Fig. 1) and Pakuria ($24^{\circ} 18.26' N$, $87^{\circ} 45.30' E$; Fig. 1), developed on Rajmahal basalts were collected from the southern part of the RVP in Jharkhand, India. Detailed descriptions of these profiles have been given in Sharma et al. (2025). Briefly, the total exposed thickness of the Dalahi and Pakuria profile is ~ 400 cm and 10 m,

respectively. Both the profiles exhibited gradual upward transitions from basalts to weathered material, followed by a progressively more weathered horizons comprising ferricrete nodules. Our earlier work, based on immobile element ratios, showed that both weathering profiles are well preserved and developed *in-situ* (Sharma et al., 2025). The procedures for glass beads preparation for major elements analysis, sample digestion, and extraction of exchangeable and oxyhydroxide phases are detailed in our earlier publication (Sharma et al., 2025) and briefly summarized in the supplementary material (Section S1).

3.1. Clay-sized fraction

To separate the clay-sized fractions, the residues left after extraction of exchangeable and oxyhydroxide phases (Section 3.2) were treated with a mixture of 30% H₂O₂ and 0.02N HNO₃ to remove the organic fractions (Gupta and Chen, 1975). Thereafter, the clay-sized fractions were separated by centrifugation (Bouchez et al., 2021; Pryor et al., 2024), and their masses were used to calculate clay-sized fractions. The analytical reproducibility, evaluated by replicate determinations, was better than $\pm 4\%$.

3.2. Measurements

The details of measurements of major elements (Al, Ca, Mg, Si, Na, K, Fe, and Mn) and trace elements (Th and Cs) concentrations in bulk samples, as well as Mn concentrations in exchangeable and oxyhydroxide phases are available in Sharma et al. (2025) and briefly summarized in the supplementary material (Section S2). The new data generated in this study include Li concentrations in bulk, concentrations of Li, Ba, Al and Cs in exchangeable and oxyhydroxide phases, and $\delta^7\text{Li}$ values in bulk rocks and weathered materials.

The bulk Li concentrations were determined by analyzing the acid-digested solutions by a quadrupole ICP-MS (ThermoScientific® X Series 2) at IISER Kolkata following multi-element external calibration and internal standard (In) addition. The measurement accuracy was better than $\pm 7\%$ as determined from analysis of multiple certified reference standards like BHVO-2 (Hawaiian Basalt), GSP-

171 2 (Granodiorite), and JSD-3 (Stream sediment) (Table S1). The analytical reproducibility, based on
172 replicate analyses, was within $\pm 2\%$.

173 The concentrations of Li, Cs, Ba, and Al in the exchangeable and oxyhydroxide fractions were
174 determined using a quadrupole ICP-MS (ThermoScientific® X Series 2) at IISER Kolkata following multi-
175 element external calibration and internal standard (In) addition. The measurement accuracy, based on
176 analysis of certified reference standard BHVO-2 and NIST-traceable standard IV-Stock 8 (Inorganic
177 Ventures®), was better than $\pm 3\%$ for Li and Ba, and $\pm 7\%$ for Al and Cs (Table S2). Analytical
178 reproducibility, evaluated based on replicate analyses, was within $\pm 8\%$ for all elements in both the
179 exchangeable and oxyhydroxide phases.

180 **3.2.1. Li purification and $\delta^7\text{Li}$ analysis**

181 Lithium was purified following the method outlined by Bohlin et al. (2018). The Savillex® PFA
182 columns with an inner diameter of 4 mm and a height of 25 cm were packed with 3 mL of Bio-Rad® AG
183 MP-50 cation exchange resin (100–200 μm mesh size). The resin was cleaned with 10N HCl, followed
184 by Milli-Q water wash. The resin was allowed to resettle by gravity, ensuring a uniform resin bed. The
185 column was then conditioned with 9 mL of 0.7N HCl. Samples solutions containing 1-2 ng of Li were
186 loaded onto the resin in 200 μL of 0.7N HCl. The columns were washed with 3 mL of 0.5N HF, followed
187 by 8 mL of 0.7N HCl. Lithium was then eluted using 13 mL of 0.7N HCl. To ensure complete recovery
188 and account for any potential tailing of the Li peak, 1 mL fractions were collected both before and after
189 the Li cut. The purified Li-aliquots were collected in acid-cleaned Savillex® vials and dried overnight on
190 a hotplate at 80°C . After drying, the samples were refluxed for 24 hours with 200 μL of concentrated
191 HNO_3 to dissolve residual organic matter, if any. After refluxing, the solutions were evaporated to dryness
192 and re-dissolved in 200 μL of 2% HNO_3 prior to isotope analysis. All acids (HNO_3 , HCl, and HF) used
193 for column chromatography and Li isotope analysis were purified by double distillation using a Savillex®

194 DST-4000 sub-boiling distillation unit in a ISO Class 5 (Class 1000) laminar flow clean bench, placed
195 within an ISO Class 7 (Class 10000) cleanroom.

196 Lithium isotope ratio was determined using a single collector triple quadrupole ICP-MS (Agilent®
197 8900) at IISc Bangalore (Juzer et al., 2022). Instrumental mass bias was corrected using external
198 normalization following the standard sample bracketing (SSB) protocol (Bohlin et al., 2018) with Li
199 concentration matching of all samples with NIST-L-SVEC-8545 standard. Samples were analyzed at [Li]
200 of 0.8 ppb using a block of 75 cycles, with integration time of 2.6 seconds for ^6Li and 0.2 seconds for ^7Li .
201 Measurements were done in duplicate, and both isotopes were determined in pulse mode. The results are
202 reported as $\delta^7\text{Li}$ (‰), calculated using the formula $[(^7\text{Li}/^6\text{Li})_{\text{Sample}}/(^7\text{Li}/^6\text{Li})_{\text{Standard}} - 1] \times 1000$ ‰, with
203 NIST-L-SVEC-8545 as the reference standard. The measured $\delta^7\text{Li}$ of the rock standards BCR-2 and
204 BHVO-2 were 3.30 ± 0.58 ‰ (2σ ; $n=2$) and 4.44 ± 0.96 ‰ (2σ ; $n=2$), respectively. These values are
205 analytically indistinguishable from published values of BCR-2: 3.19 ± 0.39 ‰ and BHVO-2: 4.58 ± 0.38 ‰
206 (Zhu et al., 2019). Purification and analysis of seawater yielded a $\delta^7\text{Li}$ value of 31.26 ± 0.82 ‰ (2σ ; $n=3$)
207 which is in good agreement with the published values of 31.27 ± 0.4 ‰ (Bohlin et al., 2018; Juzer et al.,
208 2022). The measured $\delta^7\text{Li}$ value for the secondary Li standard (6Li-N-SRM) is -8.27 ± 0.40 ‰ (2σ ; $n=3$),
209 which is within the range of published values of -8.18 ± 0.39 ‰ (Bohlin et al., 2018). Analysis of samples
210 in replicates provides the mean external reproducibility of the measured $\delta^7\text{Li}$ to be ± 0.24 ‰ (2σ , $n=4$).

211 4. Results

212 The concentrations of major and trace elements in the weathered materials and parent basalts are
213 listed in Table 1. The density and pH data are listed in Table 1. The concentrations of Ca, Na and Mg
214 decrease (Table 1), while the concentrations of Al, Fe and Mn increase toward the top of the profiles
215 (Table 1).

216 The elemental loss during the chemical weathering was determined relative to the parent basalt by
 217 normalizing concentrations of an element to that of the immobile element Th (Nesbitt, 1979):

$$218 \quad [m]_{\text{lost}} \% = \left[1 - \left(\frac{\left(\frac{C_{m,w}}{C_{i,w}} \right)}{\left(\frac{C_{m,p}}{C_{i,p}} \right)} \right) \right] \times 100 \quad (1)$$

219 where C is concentration of a mobile (m) or immobile (i) element in the weathered materials (w)
 220 or parent (p) basalts. Thorium (Th) is used as an immobile element because it behaves conservatively
 221 during the weathering of basalt (Ma et al., 2007), and show minimal contribution from aeolian dust sources
 222 in these weathering profiles (Sharma et al., 2025). An elemental gain or loss relative to the parent rock
 223 composition is implied if $[m]_{\text{lost}} \% < 0$ or > 0 , respectively. The upward increase in $[Li]_{\text{lost}} \%$ in both
 224 profiles, associated with the increasing CIA values (Fig. 2), suggests Li loss due to weathering of primary
 225 minerals. However, in the Dalahi profile, the $[Li]_{\text{lost}} \%$ exhibits an upward decrease starting at ~110 cm,
 226 indicating significant Li enrichment in the top section.

227 4.1. Lithium concentrations and $\delta^7\text{Li}$ values in weathering profiles

228 In the unaltered basalts (parent), Li concentrations range from 5.4 to 6.3 $\mu\text{g/g}$, and $\delta^7\text{Li}$ values vary
 229 from 6.1 to 8.1‰ (Table 1). These $[Li]$ values are identical to published data for basalts (Huh et al., 2004;
 230 Liu et al., 2013; Xiong et al., 2022), whereas the $\delta^7\text{Li}$ values of the Rajmahal basalts are similar to the
 231 upper limits of $\delta^7\text{Li}$ values reported for the Hawaiian basalts (4‰–6‰; Pistiner and Henderson, 2003;
 232 Huh et al., 2004), Hainan basalts (0.7‰–5.3‰; Xiong et al., 2022), but higher than those in the Deccan
 233 basalts (2.5‰; Kisakurek et al., 2004). In weathered materials of the two studied profiles, $[Li]$ and $\delta^7\text{Li}$
 234 values vary significantly, ranging from 4.1 to 14.4 $\mu\text{g/g}$ and 0.5 to 6.9‰, respectively (Table 1). The
 235 higher $[Li]$ was observed in the upper sections of both the profiles followed by a gradual downward
 236 decrease (Table 1). In Dalahi profile, the $\delta^7\text{Li}$ value increases downward from 2.1‰ at the top up to a

value of 5.1‰ at ~80 cm depth. In the section deeper than 80 cm, $\delta^7\text{Li}$ values decrease to a value of 0.9‰ at ~130 cm depth (Table 1; Fig. 2). Further below, $\delta^7\text{Li}$ values increase downward up to the parent rock values. In Pakuria profile, the $\delta^7\text{Li}$ value decreases from 3.1‰ at the top to 0.5‰ at 165 cm, followed by an increasing downward variation up to the basaltic values.

4.2. Elemental composition of leachable phases

The concentrations of major and trace elements in the exchangeable and oxyhydroxide phases are listed in Table 2. The concentrations of Li, Mn, and Al are higher in the oxyhydroxide fractions than in the exchangeable fractions, whereas concentrations of Ba exhibit an opposite trend (Table 2). The cumulative elemental concentrations of both exchangeable and oxyhydroxide fractions are considered here as representative of the adsorbed ($[\]_{\text{ads}}$) fraction. In Dalahi profile, $[\text{Li}]_{\text{ads}}$ increases upward up to 60 cm, before decreasing towards the top (Table 2), whereas in the Pakuria profile, $[\text{Li}]_{\text{ads}}$ shows an upwardly increasing trend (Table 2). Significant positive correlations of $[\text{Li}/\text{Al}]_{\text{ads}}$ and $[\text{Ba}/\text{Al}]_{\text{ads}}$ with $[\text{Mn}/\text{Al}]_{\text{ads}}$ and $[\text{Cs}/\text{Al}]_{\text{ads}}$ (Fig. S1) indicate that $[\text{Li}]_{\text{ads}}$ and $[\text{Ba}]_{\text{ads}}$ are associated with clay minerals and Mn oxyhydroxides in both the profiles. These observations are consistent with the knowledge that clay minerals and oxyhydroxides are efficient in adsorbing both Li and Ba (Eylem et al., 1990; Chan and Hein, 2007; Pogge von Strandmann et al., 2023; Sajih et al., 2014; Cai et al., 2024; Zhu et al., 2023).

5. Discussion

5.1. Potential Li and $\delta^7\text{Li}$ contribution from aeolian dust

The preservation and *in-situ* nature of the Dalahi and Pakuria profiles were evaluated by Sharma et al. (2025) through detailed analyses of major and trace element compositions. Based on the variation of Nb and Zr, Sharma et al. (2025) estimated that aeolian dust accounts for up to ~5% and ~7% of total mass in the Dalahi and Pakuria profiles, respectively. The mass flux of Li derived from dust ($F_{\text{Li}}^{\text{dust}}$) in each

sample was calculated following the approach of Kurtz et al. (2001), using the mass fraction of dust (f_d) estimated based on the Nb–Zr pair (Sharma et al., 2025) and the Li concentration of the UCC (20 $\mu\text{g/g}$; Taylor and McLennan, 1985) as the dust endmember ($C_{\text{Li}}^{\text{dust}}$):

$$F_{\text{Li}}^{\text{dust}}(\text{mg}/\text{cm}^2) = \sum f_d \times C_{\text{Li}}^{\text{dust}} \times \rho_i \times \Delta t_i \times 10^{-3} \quad (2)$$

where ρ_i is the density of a section i (g/cm^3) with a thickness Δt_i (cm). The estimated mass flux of Li derived from aeolian dust are 0.13 mg/cm^2 and 0.26 mg/cm^2 in the Dalahi and Pakuria profile, respectively. The mass flux of Li released from the weathering of basalt is calculated using the method outlined by Ryu et al. (2014):

$$F_{\text{Li}}^{\text{basalt}}(\text{mg}/\text{cm}^2) = C_{\text{Li}}^{\text{p}} \times Z_t \times S_c \times \rho_p \times 10^{-3} \quad (3)$$

where C_{Li}^{p} is the Li concentration in the parent basalts (5.39-6.26 $\mu\text{g/g}$, Table 1). The profile thickness (Z_t) is 376 cm in Dalahi and 1000 cm in Pakuria profile (Table 3). The collapse factor (S_c) is defined as the ratio of Th in topmost weathered material to basalt and is used to correct for mass loss or gain during weathering (2.54-2.84, Table 3). The basalt density (ρ_p) is 2.26 and 2.58 g/cm^3 for the Dalahi and Pakuria profile (Table 1), respectively. The calculated mass flux of Li ($F_{\text{Li}}^{\text{basalt}}$) ranges from 11.65 mg/cm^2 and 45.76 mg/cm^2 in the Dalahi and Pakuria profile, respectively. This suggest that the Li mass flux derived from dust is insignificant, accounting for <0.6% in the Pakuria and <1.2% in Dalahi profile (Table 3).

The impact of dust on the bulk $\delta^7\text{Li}$ of weathered materials was evaluated by using a two-component mixing model:

$$\delta^7\text{Li}^{\text{expected}} = \delta^7\text{Li}^{\text{dust}} f_{\text{Li}}^{\text{dust}} + \delta^7\text{Li}^{\text{P}} (1 - f_{\text{Li}}^{\text{dust}}) \quad (4)$$

Using the fraction of Li derived from dust ($f_{\text{Li}}^{\text{dust}}$; Table 3) and the $\delta^7\text{Li}$ composition of the UCC (0.6‰; Sauzeat et al., 2015) as the dust endmember ($\delta^7\text{Li}^{\text{dust}}$), we show that dust input can lower $\delta^7\text{Li}$ values

relative to the parent basalt ($\Delta\delta^7\text{Li}^{\text{P} - \text{expected}}$) by up to 0.04‰ in Pakuria and 0.06‰ in Dalahi profile. Therefore, the dust-induced decrease in $\delta^7\text{Li}$ values is insignificant, given that the $\delta^7\text{Li}$ differences between parent basalt (P) and weathered materials ($\Delta\delta^7\text{Li}^{\text{P} - \text{bulk}}$) are up to 5.3‰ in Dalahi and 7.7‰ in Pakuria profile. However, if the Saharan dust compositions ($[\text{Li}]=18.5 \mu\text{g/g}$; $\delta^7\text{Li}=-0.7\text{‰}$, Clergue et al., 2015) are used, the dust-induced decrease in $\delta^7\text{Li}$ values relative to the parent basalt is 0.05‰ in Pakuria and 0.07‰ in Dalahi profile. Our exercise demonstrates that dust derived Li has an insignificant impact on $[\text{Li}]$ and $\delta^7\text{Li}$ in the profiles, irrespective of the end member dust compositions used in calculations.

5.2. Cycling of Li during progressive weathering: relative role of adsorption vs. structural incorporation

The loss of major cations due to the breakdown of minerals during chemical weathering is evident from the upward decreasing trends in Ca/Al , Na/Al , Si/Al and Mg/Al ratios for both the profiles (Fig. 2). The evidence for progressive weathering of minerals also comes from increasing trends in the chemical index of alteration (CIA) in the upward direction for both profiles (Fig. 2). The upward increase of $[\text{Li}]_{\text{lost}}$ % in both profiles, associated with the increasing CIA values (Fig. 2), suggests a loss of Li due to weathering of primary minerals. These observations suggest that the increase in weathering intensity in the upper sections of profiles is characterized by a greater degree of elemental loss from primary minerals such as plagioclase and pyroxene. However, in Dalahi profile, $[\text{Li}]_{\text{lost}}$ % exhibits an upward decrease starting at ~110 cm, implying addition of Li. Additionally, Li/Al , Fe/Al and Mn/Al ratios exhibit increasing upward trends, supporting the notion of Li addition to the profile through secondary phases such as clay minerals and Fe-Mn oxyhydroxides (Fig. 2). The Li addition can result from any one or a combination of the following processes: (i) adsorption of Li onto the surfaces of clay minerals and Fe-Mn oxyhydroxides, and (ii) Li incorporation into the crystal structure of neo-formed clay minerals. Lithium

is known to be adsorbed onto secondary phases, which is also evident from observed moderate to high positive correlations of Li/Al with Mn/Al, Al/Si and Fe/Al in the weathering profiles (Fig. 3a-c), indicating its adsorption onto clay minerals and Fe-Mn oxyhydroxide phases. Furthermore, Li/Al ratios demonstrate strong positive correlation with Cs/Al, thus providing further evidence for Li sorption in the profiles (Fig. 3d). Because of its large size, Cs is strongly adsorbed onto clay minerals (Nesbitt et al., 1980; Kabata-Pendias and Pendias, 2001) and therefore is used here as an index of adsorption (Sharma et al., 2025). However, the compositions of leachable phases (exchangeable and oxyhydroxides) show that adsorbed Li accounts for only <5% of the bulk Li. Moreover, the upward increase in Al/Si ratios and clay-sized fractions (Tables 1 and 2) raises the possibility that clay minerals also incorporate a substantial amount of Li into their crystal structure. We test this possibility using mass balance calculations (Section S3, supplementary information), which demonstrate that a majority of Li in the bulk phases is hosted within the crystal structures of the neo-formed clay minerals ($[Li]_{\text{crystal-bound}}$), accounting for up to ~85-90% of total Li (Section S3 and Table S3). These results are consistent with the study of Pogge von Strandmann et al. (2019), which demonstrated that up to 84–88% of Li is incorporated into the crystal lattice of newly formed clay minerals, with a minor fraction being adsorbed onto mineral surfaces.

The calculated crystal-bound molar Al/Si ratios of clay minerals vary from 0.41 to 0.84 (Section S3; Table S3) in the studied profiles, and increase toward the top of the profiles with an increase in weathering intensity (Table S3, Fig. S2a). This upward increase in Al/Si ratio indicates progressive desilication and formation of Al-rich clay minerals such as kaolinite (Delvigne et al., 2016; Frings et al., 2021). The range of calculated Al/Si ratios corresponds to mixed assemblages of clay minerals consisting of montmorillonite (Al/Si: 0.33 to 0.50, Rozalen et al., 2009; Khalifa et al., 2020), illite (Al/Si: 0.79, Khalifa et al., 2020), and kaolinite (Al/Si: 0.92 to 0.95, Frings et al., 2021). Furthermore, the positive correlation between molar Al/Si ratio and $[Li]_{\text{crystal-bound}}$ (Fig. S2b) suggests that, clay minerals such as

325 kaolinite formed during progressive weathering drive enhanced incorporation of Li into their crystal
326 structures.

327 **5.3. Variation of $\delta^7\text{Li}$ and influence of post-weathering processes**

328 In the upper layers of the profiles, $\delta^7\text{Li}$ values exhibit considerable fluctuations and are lower than
329 the basaltic $\delta^7\text{Li}$ values (Fig. 2). Additionally, $\delta^7\text{Li}$ values show weak to significant positive correlations
330 with CIA, Mg/Al, Ca/Al and Na/Al ratios (Fig. S3). As Li isotopes do not fractionate during dissolution
331 (weathering) of silicate minerals (Pistiner and Henderson, 2003; Huh et al., 2004), the $\delta^7\text{Li}$ variation is
332 likely driven by post-weathering processes. As discussed earlier, sorptive enrichment of Li is evident in
333 the upper sections of both profiles. The lower $\delta^7\text{Li}$ values in the upper sections of the profiles are driven
334 by either adsorption of Li or its incorporation into structure of neo-formed clay minerals (Pistiner and
335 Henderson, 2003; Lemarchand et al., 2010; Hindshaw et al., 2019; Li and Liu, 2020; Chapela Lara et al.,
336 2022) or both. Further evidence for the role of secondary minerals come from inverse correlations of $\delta^7\text{Li}$
337 with Al/Si, Cs/Al ratios and adsorbed Mn concentrations ($[\text{Mn}]_{\text{ads}}$) (Fig. 4). These observations together
338 support the hypothesis that post weathering processes of basalts play a crucial role in regulating the $\delta^7\text{Li}$
339 values in weathering profiles, as observed elsewhere for basaltic weathering (Huh et al., 2004; Kısakurek
340 et al., 2004; Tong et al., 2021; Xiong et al., 2022).

341 **5.4. The effect of pH on geochemical cycling of Li and its isotopic composition**

342 The degree of Li loss ($[\text{Li}]_{\text{lost}}\%$) varies considerably with depth and exhibits general upward
343 increasing trends in both profiles (Fig. 2). However, as discussed earlier, in the upper ~110 cm of the
344 Dalahi profile, $[\text{Li}]_{\text{lost}}\%$ is characterized by an upwardly decreasing trend (Fig. 2), indicative of enrichment
345 of Li. This observation, together with a ~2-fold increase in the Al/Si ratio and increase in clay-sized
346 fraction (%) in the upward direction (Tables 1 and 2) in this section of the upper Dalahi profile, is

supportive of incorporation of substantial amount of Li into crystal structure of the clay minerals (Section S3). The $\delta^7\text{Li}$ values in both profiles decrease from the bottom to the top (Fig. 2), except in the upper 130 cm of the Dalahi profile, where its fluctuations define a boomerang-shaped pattern. Furthermore, the $\delta^7\text{Li}$ values in this profile increase downward within the depth interval of 32-80 cm followed by a downward decrease up to a depth of 130 cm. These patterns indicate that heavier Li (^7Li) desorbed from upper horizon of the profile is transported downward by ^7Li rich pore water and is subsequently re-adsorbed by the underlying horizon. Given that ^7Li is preferentially released during desorption, this process can account for at least a part of the observed $\delta^7\text{Li}$ increase up to a depth of 130 cm in the Dalahi profile.

The distribution of Li and fractionation of its isotopes in weathering profiles are known to be modulated by variation of pH (Lemarchand et al., 2010; Zhu et al., 2023; Chapela Lara et al., 2022). Experimental studies show that Li is partitioned between interlayer and octahedral sites of clay minerals, with octahedral sites preferentially being enriched in ^6Li (Wimpenny et al., 2015; Hindshaw et al., 2019). The distribution of Li isotopes between interlayer and octahedral sites can cause a difference of $\sim 20\%$ in $\delta^7\text{Li}$ (Williams and Hervig, 2005; Vigier et al., 2008). In basaltic weathering profile, $\delta^7\text{Li}$ of exchangeable phase has been reported to be up to $\sim 20\%$ heavier than that of residual phase (Tong et al., 2021). Published body of work on clay minerals shows that a decrease in pH of equilibrating solution promotes the release of Li from exchangeable sites (Hao et al., 2021). However, the exact mechanism(s) responsible for the pH-driven Li isotope fractionation remains enigmatic. The striking similarity between the upward decreasing trends of $\delta^7\text{Li}$, $[\text{Li}]_{\text{ads}}$ and pH in the upper ~ 80 cm of the Dalahi profile (Fig. 5) is suggestive of $\delta^7\text{Li}$ variation in this section through pH dependent processes. Specifically, our data indicates desorption of Li at lower pH in the upper ~ 80 cm of profile, leading to preferential release of ^7Li from interlayer sites. This inference is in line with the observations of (i) up to $\sim 28\%$ higher $\delta^7\text{Li}$ values of the exchangeable phases than that of crystal-bound Li in clay minerals in a weathering profile developed on

370 paragneiss (Cai et al., 2024) and (ii) preferential leaching of ^7Li from interlayer sites of clay minerals
371 during granite weathering, resulting in ^6Li enrichment of residual Li in weathered materials (Zhang et al.,
372 2021). Our hypothesis of pH dependent desorption of Li is further supported by experimental studies that
373 demonstrate preferential desorption of ^7Li when pH of the reacting solution was decreased from 8.5 to 4.3
374 (Li and Liu, 2020).

375 The desorption of Li in upper ~80 cm of the Dalahi profile is likely driven by the adsorption of Al,
376 as evident from an increase of $[\text{Al}]_{\text{ads}}$ towards top of the profile with a decrease in soil pH (Fig. 5).
377 Published body of work has reported that Al^{3+} becomes the dominant cation in the interlayer sites of the
378 clay minerals as soil pH decreases (Jin et al., 2010). Furthermore, the pH-dependent desorption of Li from
379 the upper section also finds support from a positive correlation of $[\text{Ba}]_{\text{ads}}$ with $[\text{Li}]_{\text{ads}}$ in lower part of the
380 profile and a $[\text{Ba}]_{\text{ads}} - [\text{Li}]_{\text{ads}}$ negative correlation in upper part of the Dalahi profile (Fig. 6). Here, we use
381 Ba as a pH-independent tracer, as its adsorption-desorption is known to be insignificantly impacted by pH
382 variations (Eylem et al., 1990; Zhang et al 2001). The adsorption of Ba is evident in significant positive
383 correlations of $[\text{Ba}]_{\text{ads}}$ and clay-sized fractions with Al/Si ratio (Fig. 6), suggesting that degree of Ba
384 adsorption increases with the abundance of clay minerals. Furthermore, the positive correlation of
385 $[\text{Li}]_{\text{crystal-bound}}$ with $[\text{Li}]_{\text{ads}}$ in the lower section below ~80 cm and the negative correlation in upper section
386 (Fig. 6). These observations together support the idea that in upper section, Li is getting desorbed, while
387 it is added to the crystal structures as evident from upward increasing trend of $[\text{Li}]_{\text{crystal-bound}}$ enriched in
388 ^6Li (Table S3). Furthermore, $[\text{Li}/\text{Al}]_{\text{ads}}$ ratios show a positive correlation with pH, whereas $[\text{Li}/\text{Al}]_{\text{crystal-}}$
389 bound ratios do not exhibit such a correlation (Fig. S4). This observation is in line with the knowledge that
390 Li adsorption onto or its desorption from clays surfaces is influenced by pH (Park et al., 2015; Prodromou,
391 2016; Li and Liu, 2020), while incorporation of Li into the crystal structure of clay minerals is independent
392 of pH variation (Hoyer et al., 2015).

393 It is noteworthy that our inference of Li desorption in the upper section is not evident from the
 394 decreasing trend of bulk Li/Al in downward direction (Fig. 1), although the observed $\delta^7\text{Li}$ variation is
 395 consistent with this interpretation. This apparent discrepancy can be reconciled with the analytical
 396 resolution of concentration determination, which limits our ability to delineate these trends. On the
 397 contrary, the change of $\delta^7\text{Li}$ associated with desorption can be discerned because of higher analytical
 398 precision of $\delta^7\text{Li}$ and significant $\delta^7\text{Li}$ differences between the adsorbed and $[\text{Li}]_{\text{crystal-bound}}$ in neo-formed
 399 clay minerals (up to ~28‰; Tong et al., 2021; Cai et al., 2024). It is noteworthy that a strong negative
 400 correlation is observed between $\Delta\delta^7\text{Li}_{\text{bulk-crystal bound}}$ and the fraction of crystal-bound Li ($f_{\text{Li}}^{\text{crystal-bound}}$) in
 401 clay minerals (Fig. S5), suggesting that with an increase in the fraction of $[\text{Li}]_{\text{crystal-bound}}$, the $\Delta\delta^7\text{Li}_{\text{bulk-crystal}}$
 402 _{bound} decreases (See Section S4 for $\delta^7\text{Li}_{\text{crystal-bound}}$ calculations, Fig. S5). These results further underline the
 403 importance of crystal-bound Li in influencing the bulk $\delta^7\text{Li}$ values in weathered basalts.

404 Our inference of Li desorption and the resultant decrease in $\delta^7\text{Li}$ values within the top 80 cm layer
 405 of the Dalahi profile is consistent with signatures of re-adsorbed Li in the layer below, as evident from an
 406 increasing trend in upward direction (130-80 cm) of $[\text{Li}]_{\text{ads}}\%$, $\delta^7\text{Li}$ values, and pH (Fig. 4). The
 407 observations shown in Fig. 4 indicate that below the zone of Li desorption, ^7Li -enriched porewater
 408 migrates downward that drives re-adsorption of Li at higher pH. This is expected because, the degree of
 409 Li adsorption increases at higher pH (Park et al., 2015; Prodromou, 2016; Li and Liu, 2020). Thus, our
 410 interpretation of pH-dependent Li desorption and re-sorption are consistent with the established behavior
 411 of Li in surficial aqueous environments.

412 **5.5. Modeling Li isotopic fractionation**

413 As discussed above, the general decreasing trends in $\delta^7\text{Li}$ values observed in both profiles are
 414 dominantly driven by the preferential incorporation of ^6Li into the structure of clay minerals (Pistiner and

415 Henderson, 2003; Hindshaw et al., 2019; Li and Liu, 2020). The Rayleigh fractionation model has been
 416 previously applied to explain the $\delta^7\text{Li}$ variations in weathering profiles (Rudnick et al., 2004; Liu et al.,
 417 2013). However, because Li transport in weathering profiles occurs primarily via ionic diffusion rather
 418 than via advection, $\delta^7\text{Li}$ variations can be accurately explained using a batch fractionation model (Teng et
 419 al., 2010; Bouchez et al., 2013; Clergue et al., 2015; Negrel and Millot, 2019). We incorporate batch
 420 fractionation model (Bouchez et al., 2013; Clergue et al., 2015; Negrel and Millot, 2019) into a two-step
 421 scenario to predict the evolution of $\delta^7\text{Li}$ values in two weathering profiles. The first step involves the
 422 release of Li during dissolution of the parent rock without any isotopic fractionation (Pistiner and
 423 Henderson, 2003). The second step involves the preferential incorporation of ^6Li from solution into the
 424 crystal-structure of clay minerals. This process has an apparent fractionation factor of α [$\alpha_{\text{solid-solution}} =$
 425 $(^7\text{Li}/^6\text{Li})_{\text{solid}}/(^7\text{Li}/^6\text{Li})_{\text{solution}}$] usually less than 1. We assume isotopic equilibrium between the solution and
 426 the secondary phases during Li incorporation. Therefore,

$$427 \quad \delta^7\text{Li}_w = \frac{\alpha_{\text{solid-solution}} \times \delta^7\text{Li}_p + 1000 f_{\text{Li}} \times (\alpha_{\text{solid-solution}} - 1)}{\alpha_{\text{solid-solution}} (1 - f_{\text{Li}}) + f_{\text{Li}}} \quad (5)$$

428 where w and p refer to weathered materials and parent basalt, respectively. The fraction of Li incorporated
 429 into secondary phases ($1 - f_{\text{Li}}$) can be determined, relative to the immobile element Th, as the following:

$$430 \quad 1 - f_{\text{Li}} = \frac{\left(\frac{\text{Li}}{\text{Th}}\right)_w}{\left(\frac{\text{Li}}{\text{Th}}\right)_p} \quad (6)$$

431 The optimal fractionation factors for the profiles were determined based on the best fit of the model
 432 data with the measured $\delta^7\text{Li}$ values. The optimal fractionation factors ($\alpha_{\text{solid-solution}}$) range from 0.980 to
 433 0.998 and 0.971 to 0.994 for Dalahi and Pakuria profile (Fig. 7), respectively. These $\alpha_{\text{solid-solution}}$ values are

434 consistent with those either determined experimentally ($\alpha_{\text{solid-solution}} = 0.972\text{-}0.999$; Wimpenny et al., 2015
 435 and references therein), or obtained from field studies ($\alpha_{\text{solid-solution}} = 0.970\text{-}0.989$; Millot et al., 2010;
 436 Tipper et al., 2012; Dellinger et al., 2015; Clergue et al., 2015; Negrel and Millot, 2019). The large range
 437 in optimal $\alpha_{\text{solid-solution}}$ (Fig. 7) suggests that the evolution of $\delta^7\text{Li}$ in the weathering profiles is most likely
 438 influenced by the nature of secondary minerals (See section 5.2), given that the magnitude of Li isotope
 439 fractionation varies significantly with the type of secondary phase (Vigier, 2008; Wimpenny et al., 2015).
 440 For example, Wimpenny et al. (2015) reported a $\alpha_{\text{solid-solution}}$ value of 0.984 for Li incorporation into
 441 structure of gibbsite, whereas Vigier (2008) reported $\alpha_{\text{solid-solution}}$ values of 0.979-0.988 for Li incorporation
 442 into the smectite structure. Our calculations indicate that batch fractionation model can effectively explain
 443 the range of $\delta^7\text{Li}$ values in the entire weathered sections in both the Dalahi and Pakuria profiles, except
 444 for four samples (RJS-3, RJS-4, RJS-5, and RJS-6) in the upper part of the Dalahi profile. As discussed
 445 earlier in section 5.4, the $\delta^7\text{Li}$ signatures of these samples are influenced by Li desorption.

446 **5.6. Calculation of Li isotopic composition of weathering solutions**

447 The Li isotopic composition of weathering solutions reflects the extent of water-rock interaction,
 448 the magnitude and direction of Li isotopic fractionation, thereby provide an understanding of Li mobility.
 449 Since Li is partitioned between the fluid and solid phases during and after weathering, the $\delta^7\text{Li}$ of the
 450 solution provides insights into the relative contributions of primary mineral dissolution, secondary mineral
 451 formation, and adsorption/desorption processes. Here, we determine the $\delta^7\text{Li}$ value of solutions, based on
 452 the premise that Li behaves conservatively during weathering and thus the total Li distributed between the
 453 weathering solution and the weathered material is equivalent to parent rock. Therefore, the following
 454 relationship can be written:

$$455 \quad f_{\text{Li}}^{\text{sol}} + f_{\text{Li}}^{\text{profile}} = 1 \quad (7)$$

$$\delta^7\text{Li}_p = (f_{\text{Li}}^{\text{sol}} \times \delta^7\text{Li}_{\text{sol}}) + (f_{\text{Li}}^{\text{profile}} \times \delta^7\text{Li}_{\text{profile}}) \quad (8)$$

where the $\delta^7\text{Li}_p$, $\delta^7\text{Li}_{\text{sol}}$ and $\delta^7\text{Li}_{\text{profile}}$ represent average $\delta^7\text{Li}$ of fresh basalt (parent), solution and weathering profile, respectively, f represents the fraction of Li in solution ($f_{\text{Li}}^{\text{sol}}$) or in weathering profile ($f_{\text{Li}}^{\text{profile}}$) relative to parent rock. Therefore,

$$\delta^7\text{Li}_{\text{sol}} = \left[\frac{\delta^7\text{Li}_p - (f_{\text{Li}}^{\text{profile}} \times \delta^7\text{Li}_{\text{profile}})}{(1 - f_{\text{Li}}^{\text{profile}})} \right] \quad (9)$$

The fraction of Li in the whole profile can be estimated from the mass balance of Li:

$$f_{\text{Li}}^{\text{profile}} = \frac{\left(\sum_{i=1}^n [\text{Li}]_i \times \Delta t_i \times \rho_i \right) / \left(\sum_{i=1}^n [\text{Th}]_i \times \Delta t_i \times \rho_i \right)}{\left(\frac{\text{Li}}{\text{Th}} \right)_p} \quad (10)$$

where ρ_i and Δt_i represent the density and thickness of any sampling section (i), respectively. Similarly, depth integrated $\delta^7\text{Li}_{\text{profile}}$ of the whole profile can be calculated as:

$$\delta^7\text{Li}_{\text{profile}} = \frac{\sum_{i=1}^n \delta^7\text{Li}_i \times [\text{Li}]_i \times \Delta t_i \times \rho_i}{\sum_{i=1}^n [\text{Li}]_i \times \Delta t_i \times \rho_i} \quad (11)$$

The $\delta^7\text{Li}_{\text{sol}}$ calculated based on eq. 9 are $14.9 \pm 2.1\%$ and $20.8 \pm 4.4\%$ for the Dalahi and Pakuria profiles, respectively. The $\delta^7\text{Li}_{\text{sol}}$ can be independently determined using the fractionation factor (α) used earlier in the batch fractionation model.

$$\delta^7\text{Li}_{\text{sol}} = (1 - \alpha_{\text{solution-solid}}) \times 1000 + \delta^7\text{Li}_p \quad (12)$$

Using the average values of α (0.991 ± 0.007 for the Dalahi and 0.985 ± 0.008 for Pakuria profiles, Fig. 7) and $\delta^7\text{Li}_p$ (6.13% - 8.14% ; Table 1) in the eq. 12, the $\delta^7\text{Li}_{\text{sol}}$ is calculated to be 15.1% for the Dalahi profile and 23.1% for the Pakuria profile. The $\delta^7\text{Li}_{\text{sol}}$ calculated based on two independent approaches are indistinguishable from each other considering errors of determination. The $\Delta\delta^7\text{Li}_{\text{parent-sol}}$ for two profiles

474 (-8.1 to -12.6‰) fall between the $\Delta\delta^7\text{Li}_{\text{parent-sol}}$ values reported for groundwaters (-5.6 to -20.3‰) and
475 rivers (-7.7 to -29.5‰) draining the basaltic catchments (Fig. S6; Pogge von Strandmann et al., 2006; Liu
476 et al., 2015), providing further confidence in our determination of $\delta^7\text{Li}_{\text{sol}}$ values.

477 **5.7. Mobility of Li relative to Ca and Mg during basalt weathering**

478 The variation of global atmospheric CO_2 levels over the geological time scale depends on the
479 mechanism and rates of silicate weathering (Raymo and Ruddiman, 1992; Gaillardet et al., 1997; Amiotte
480 Suchet et al., 2003; Dessert et al., 2003; Misra and Froelich, 2012). Lithium isotope composition of rivers
481 is considered a reliable tracer of silicate weathering, as dissolved Li is primally sourced from weathering
482 of silicate minerals (Dellinger et al. 2015; Gou et al. 2019, Pogge von Strandmann et al., 2020). For
483 meaningful utilization of $[\text{Li}]$ and $\delta^7\text{Li}$ as tracers of silicate weathering, it is important to establish the
484 relationships between Li and Ca (Mg) during weathering, given that the precipitation of both Ca and Mg
485 as carbonate minerals in seawater impacts the long-term CO_2 budget of the atmosphere. Thus, mobility of
486 Li relative to Ca and Mg during weathering has been of interest in recent studies (Pogge von Strandmann
487 et al., 2016; 2017a; 2019; 2020). The relative mobility of Li compared to Ca and Mg is reported in studies
488 based on river water compositions (Dellinger et al., 2015; Pogge von Strandmann et al., 2016; 2017b;
489 2020); however, relative behaviour of these elements during weathering remains unaddressed. The
490 formation of clay minerals and oxyhydroxides during weathering and transport can sequester substantial
491 amount of Ca, and Mg, thereby affecting the efficiency of silicate weathering in drawing down the CO_2
492 (Dellinger et al., 2015; Pogge von Strandmann et al., 2017a; Pogge von Strandmann et al., 2019; Tipper
493 et al., 2021). The observed trend of Li/Al ratios in the weathering profiles contrast with those of Ca/Al,
494 and Mg/Al ratios (Fig. 2), implying that the dissolution, mobility, and precipitation of Li differ from that
495 of Mg and Ca. A measure of mobility of Li relative to Ca and Mg in the weathering profiles can be
496 quantitatively understood from the following relative mobility parameter:

$$\left(\frac{\text{Li}}{\text{X}}\right)_{\text{RM}} = \frac{\left(\frac{\text{Li}}{\text{X}}\right)_{\text{profile}}}{\left(\frac{\text{Li}}{\text{X}}\right)_{\text{parent}}} \quad (13)$$

where X stands for Ca or Mg, and RM for relative mobility. A $\left(\frac{\text{Li}}{\text{X}}\right)_{\text{RM}}$ value of 1 indicates mobility of Li identical to that of Ca or Mg during weathering, whereas a value of less than 1 results from preferential release of Li over Ca or Mg. Substantial incorporation and scavenging of Li by secondary minerals would inhibit Li mobility, thus resulting in $\left(\frac{\text{Li}}{\text{X}}\right)_{\text{RM}} > 1$.

In the studied profiles, $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ values are in the range of 5.62–11.79 and 3.99–10.64, respectively (Table 2), suggesting decreased relative mobility of Li. In both studied profiles, the observed positive correlations of CIA with $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ (Fig. 8) suggest that as weathering intensity increases, higher abundances of clay minerals result in greater removal of Li from solution and thereby reducing its mobility relative to Ca and Mg. This interpretation is supported by the observed positive correlation of $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ with clay-sized fractions (Fig. S7).

As expected, significant inverse correlations are observed for $\delta^7\text{Li}$ with both $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ (Fig. 8), indicating lower $\delta^7\text{Li}$ values with increasing removal of Li from the solution. At incipient weathering, the release of Li, Ca and Mg appear to be less incongruent, as evident from $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ values closer to 1, possibly because of lower abundance of secondary minerals and decreased scavenging of Li from the fluids, leading to higher $\delta^7\text{Li}$ values in the saprolites.

We also determined the relative mobility parameters and $\delta^7\text{Li}$ values for each of the complete profiles using mass balance approach (See section S5). Based on the weathering profile data for the depth

515 intervals studied (Fig. 8), the empirical relationships of $\delta^7\text{Li}$ with $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$, $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ and CIA, and of
 516 $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ with CIA (Fig. 8 and Fig. S3a) were derived from regression of the data (Table S4).
 517 We demonstrate that $\delta^7\text{Li}$ of the whole weathering profiles (See eq. 11), obtained from mass balance
 518 calculations are consistent, within the errors of estimations, with those obtained from the empirical
 519 relationships based on regression analyses of $\delta^7\text{Li} - \left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$, $\delta^7\text{Li} - \left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$, $\delta^7\text{Li} - \text{CIA}$, $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}} - \text{CIA}$ and
 520 $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}} - \text{CIA}$ data (See Table S4). Therefore, this exercise shows that $\delta^7\text{Li}$ values and relative mobility
 521 parameters $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ can be predicted using the CIA values of weathered materials, at least
 522 for basaltic weathering in the RVP.

523 Published data allow us to evaluate the relative mobilities of Li, Ca and Mg in weathering profiles
 524 developed on basaltic rocks under diverse climatic regimes and spanning a wide range of weathering
 525 intensities (Kisakurek et al., 2004; Li et al., 2020; Tong et al., 2021; Xiong et al., 2022). Our compilation
 526 indicates that $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ values vary by three to four orders of magnitude (Fig. S8). While weak
 527 to moderate inverse correlations are observed in the Bidar and Zhanjiang profile data, the trends differ
 528 notably for weathered basalts from the Hawaii and Hainan Islands. The data for the Hawaiian samples do
 529 not exhibit inverse correlations in $\delta^7\text{Li} - \left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ space, with significant differences observed between
 530 weathering under dry and humid conditions. This is mainly due to higher $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ values observed in
 531 weathered basalts in humid conditions. In the Hainan islands, the $\delta^7\text{Li}$ values of highly weathered basalts
 532 do not exhibit well defined covariation trends with either $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ or $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$. When the relative mobility
 533 parameters are plotted against CIA (Fig. S9), strong positive correlations are observed as expected, except
 534 for highly weathered basalts. At high weathering intensities ($\text{CIA} > 90$), the relative mobility parameters

show significant higher variability within a narrow range of CIA values. Therefore, in the plots of $\delta^7\text{Li}$ vs. $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\delta^7\text{Li}$ vs. $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$, highly weathered samples exhibit steeper variation trends compared to moderately weathered samples. Hawaiian basalts weathered under humid conditions exhibit higher $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ values, which form a cluster when plotted against CIA. Therefore, our compilation of global data on weathered basalts does not demonstrate consistent covariation between $\delta^7\text{Li}$ and relative mobility parameters. This observation highlights the need for further studies to develop better understanding of processes regulating the relative mobilities of Li, Ca and Mg, particularly under conditions of intense chemical weathering.

We now assess if the $\delta^7\text{Li}$ -CIA variation trends observed in this study also apply to the riverine suspended particulate matter (SPM). This exercise aims at evaluating whether $\delta^7\text{Li}$ can be reliably predicted from the empirical $\delta^7\text{Li}$ -CIA relationship. Our compilation of global riverine SPM data demonstrates significant positive covariation trends (Fig. 9), with a few outliers. Notably, the data from two profiles of this study align well the general variation trends observed in the riverine SPM dataset, although, as expected, the SPM data exhibit more scatter. Considering that the major element compositions and $\delta^7\text{Li}$ of the riverine SPM are subject to significant solute-particle interactions, grain size variations and mineralogy during fluvial transport (Dellinger et al., 2014; Ma et al., 2020; Tipper et al., 2021), the general $\delta^7\text{Li}$ -CIA correlation trend observed for the riverine SPM and weathered basalts is particularly striking. Based on this correlation, we propose that $\delta^7\text{Li}$ values can be predicted from CIA values within the range of $\pm 0.01\text{‰}$ to $\pm 3.45\text{‰}$, with prediction accuracy improving at higher CIA values. Existing studies, however, are insufficient to assess whether this approach can be reliably extended to riverine sediments across space and time. Nonetheless, our observations and compilation of global data provide a useful framework for estimating $\delta^7\text{Li}$ values of sediments directly from CIA values. We

557 acknowledge that such an empirical approach is simplistic and may be refined through future research. To
558 establish $\delta^7\text{Li}$ as an effective tracer of silicate weathering, a more comprehensive understanding of Li
559 behaviour during fluid-particle interactions is required through further Li isotopic studies on weathering
560 profiles, river waters and sediments. Such investigations are essential to gain insights into Li mobility
561 relative to other cations and its influence on $\delta^7\text{Li}$ signatures in both modern and ancient records.

562 **6. Conclusions**

563 In this study, we investigated two well-characterized basaltic weathering profiles in the Rajmahal
564 Volcanic Province. Our interpretation framework combined findings from this study, outputs from mass
565 balance and isotope fractionation models and global datasets from weathering profiles and river sediments
566 in basaltic catchments. The findings and assessments of this study highlight following key features:

- 567 **i.** Adsorption of Li onto secondary minerals of weathered basalts, accounting for a minor fraction of
568 total Li, results in a preferential uptake of ^6Li .
- 569 **ii.** However, Li incorporation into clay-structures – consistent with a batch fractionation model –
570 dominates the total Li budget of the weathered basalts. The combined processes of adsorption,
571 desorption and structural incorporation of Li govern the depth-dependent variation in $\delta^7\text{Li}$ within
572 the weathering profiles.
- 573 **iii.** The estimates of $\delta^7\text{Li}$ of weathering solutions show excellent agreement between two independent
574 approaches.
- 575 **iv.** The empirical relations between $\delta^7\text{Li}$, relative mobility indices $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ and CIA, in
576 weathering profiles can be used to reliably predict the $\delta^7\text{Li}$ and relative mobility indices for the
577 entire weathering profiles.

578 **v.** We demonstrate for the first time that $\delta^7\text{Li}$ of riverine sediments can be predicted from CIA values.
579 This framework would significantly advance efforts to establish $\delta^7\text{Li}$ as a robust tracer of silicate
580 weathering intensity and relative mobilities of Li, Ca and Mg in both modern and ancient records.

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CRediT authorship contribution statement

Anup Kumar Sharma: Conceptualization, Investigation, Writing - Original Draft, Project administration, Methodology, Validation, Formal analysis. **Tarun Kumar Dalai:** Conceptualization, Investigation, Writing - Original Draft, Writing - Review & Editing, Resources, Supervision, Project administration, Funding acquisition, Methodology, Validation, Formal analysis. **Sambuddha Misra:** Investigation, Writing - Review & Editing, Resources, Methodology, Validation, Data Curation, Formal analysis. **Prem Chand Kisku:** Resources, Data Curation, Validation, Formal analysis. **Jitendra Kumar Pattanaik:** Resources, Data Curation, Validation, Formal analysis.

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Appendix A. Supplementary Material

Supplementary material includes the following:

Section S1. Processing of samples

Section S2: Previously published data

Section S3: Estimation of crystal-bound Li concentration in neo-formed clay minerals

Section S4: Calculation of $\delta^7\text{Li}_{\text{crystal-bound}}$

Section S5: Calculation of CIA and mobility of Li relative to Ca and Mg for whole profiles

Figures: Fig. S1 to Fig. S10.

Tables: Table S1 to Table S4.

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Figures

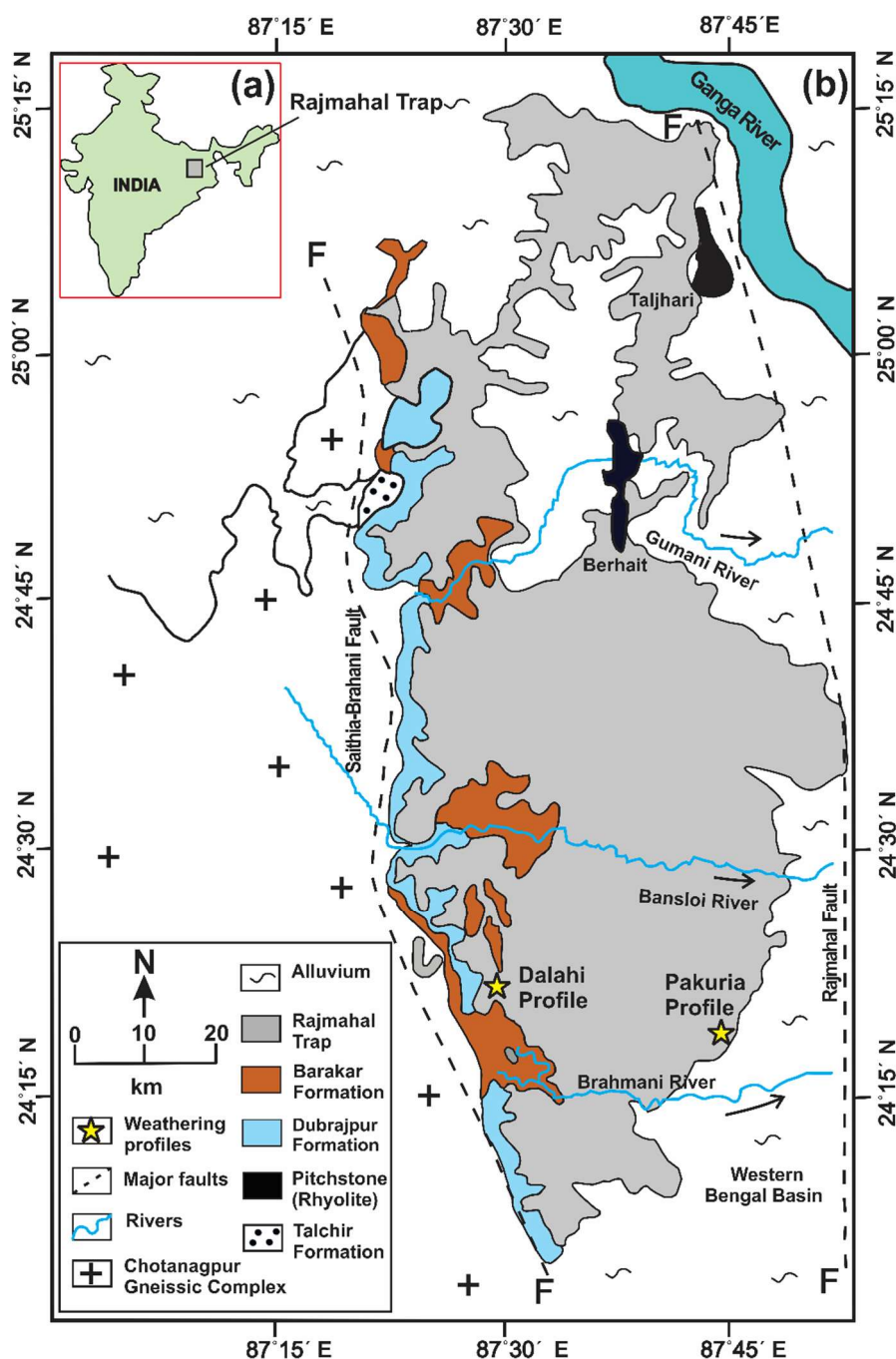


Fig. 1. The Rajmahal Volcanic Province (RVP) and the study area. **(a)** The areal extent of the trap basalts of the RVP in India. **(b)** Geological map of the RVP (modified after Ghose et al., 2017), showing the distribution of trap basalts and the locations of the studied weathering profiles (red stars). The map also shows the Gondwana Supergroup formations (Dubrajpur, Barakar and Talchir) and Chotanagpur granite-gneiss terrain.

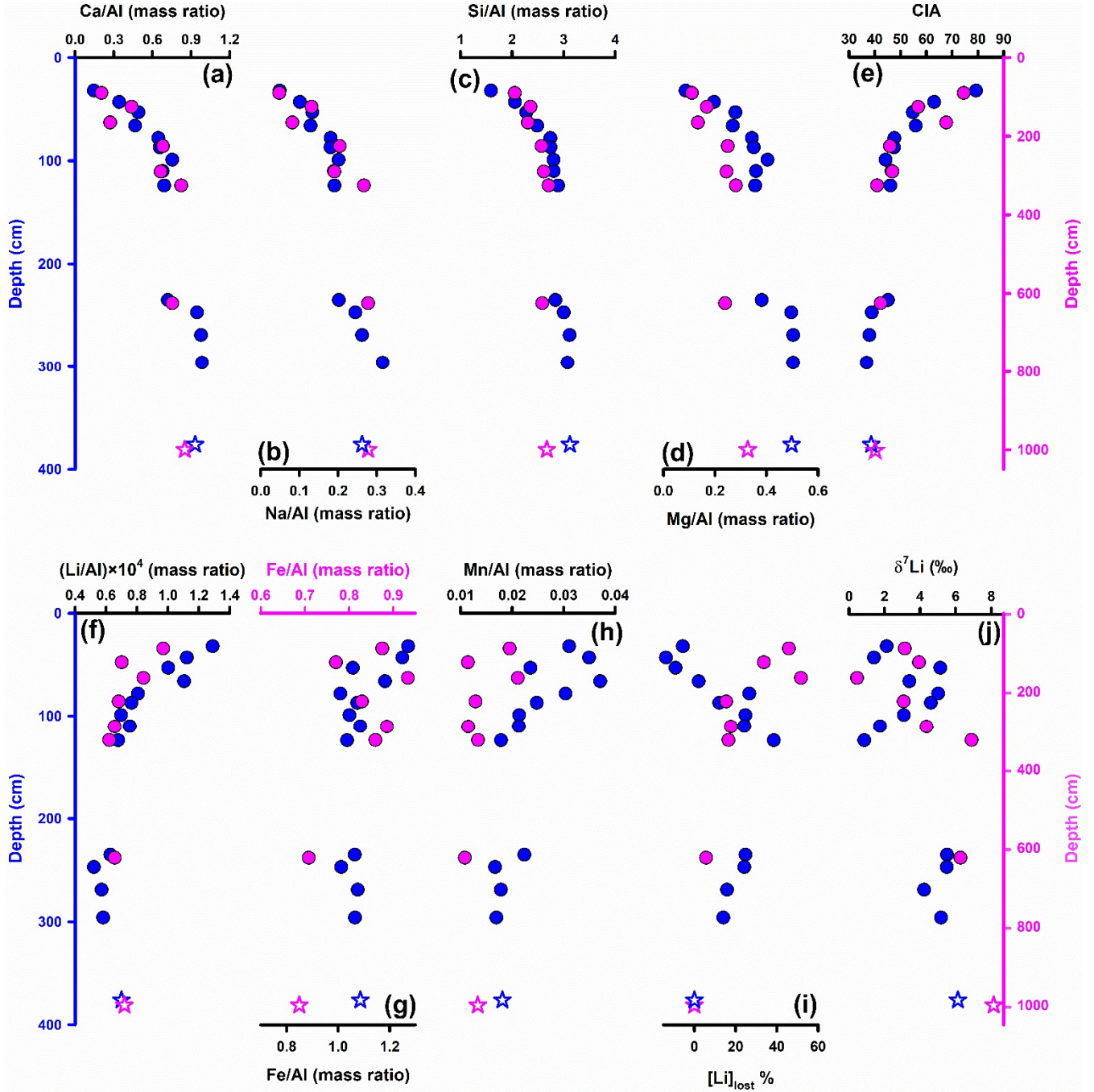


Fig. 2. Depth variation of Ca/Al, Na/Al, Si/Al, Mg/Al, CIA, Li/Al, Fe/Al, Mn/Al, $[\text{Li}]_{\text{lost}}\%$ and $\delta^7\text{Li}$ in the Dalahi (blue) and Pakuria profile (pink). Stars represent the parent basalt compositions. The upward decrease in the ratios of Ca/Al (a), Na/Al (b), Si/Al (c), and Mg/Al (d), combined with the upward increase in the CIA (e), suggest progressive loss of elements due to chemical weathering. The upward increasing variations in the Li/Al (f), Fe/Al (g) and Mn/Al (h) suggest enrichment of Li in the upper profiles is driven by sorption processes. The $[\text{Li}]_{\text{lost}}\%$ (i) increases upward with increase in CIA (e), except in the upper ~110 cm of the Dalahi profile, where $[\text{Li}]_{\text{lost}}\%$ shows a decreasing trend. Upward-decreasing trends of $\delta^7\text{Li}$ (j) are evident in both the profiles except in the upper sections, where $\delta^7\text{Li}$ values increase before decreasing (See discussion in subsection 5.2). Note different scales of Fe/Al ratio and depth for two profiles.

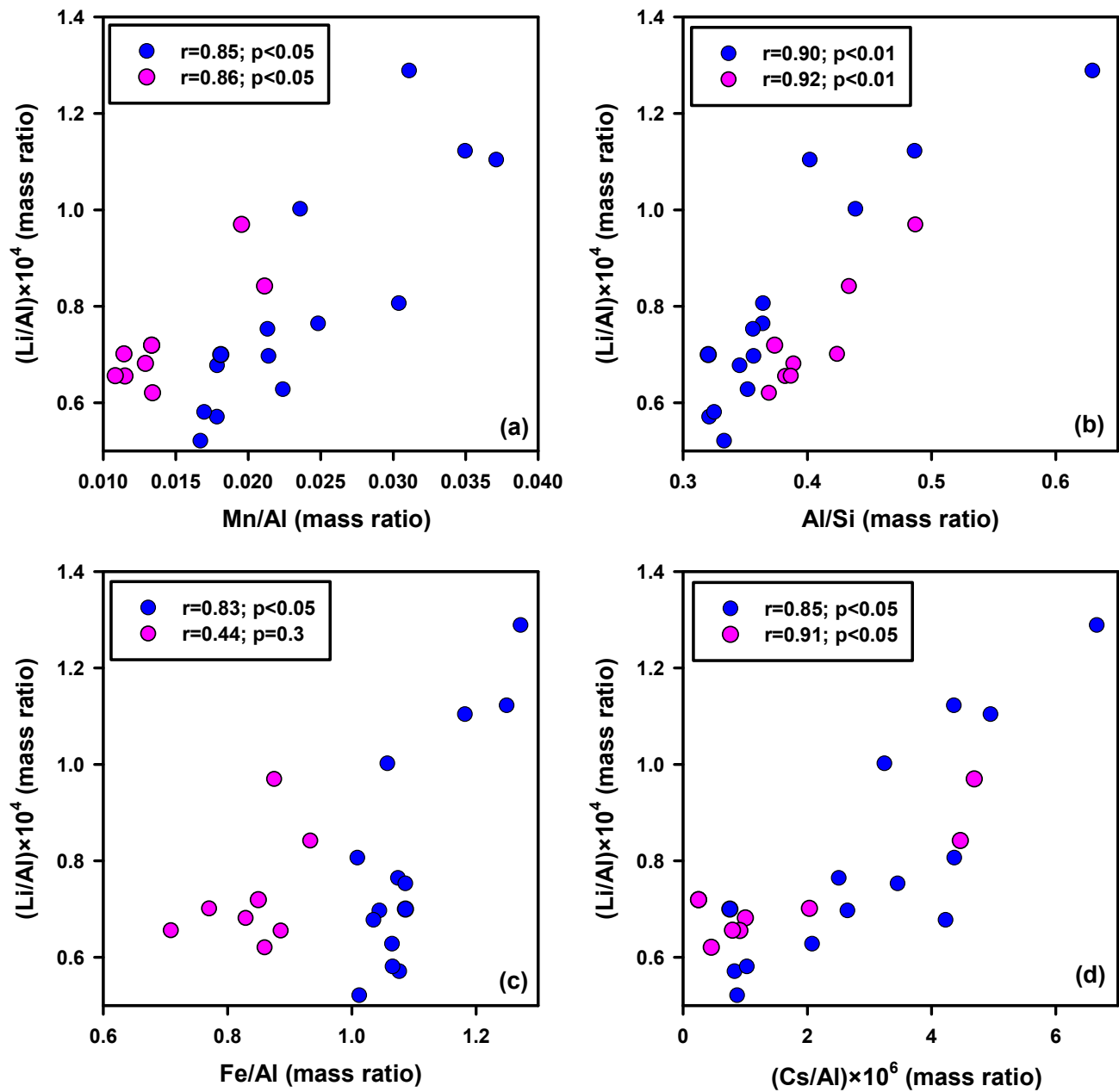


Fig. 3. Significant positive correlations are evident for Li/Al ratio with Mn/Al (a), Al/Si (b), Fe/Al (c) and Cs/Al (d) ratios, with the exception of a weak positive correlation between the Li/Al and Fe/Al in Pakuria Profile. These observations are suggestive of association of Li with clay minerals and oxyhydroxides.

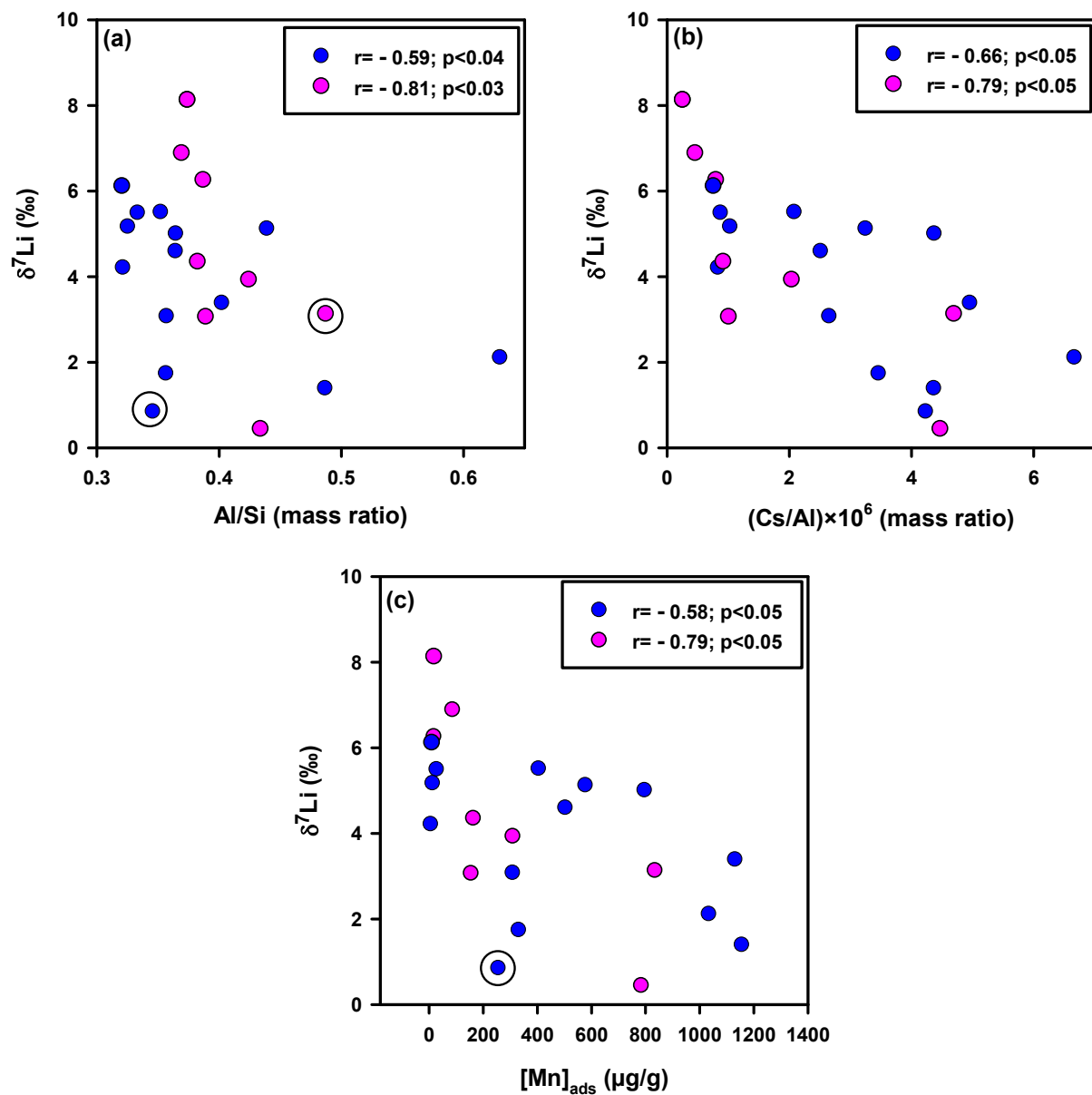


Fig. 4. The observed significant inverse correlation of $\delta^7\text{Li}$ with Al/Si (a), Cs/Al (b) and $[\text{Mn}]_{\text{ads}}$ (c), suggests that the sorption of Li (see Fig. 3) contributes to the lower $\delta^7\text{Li}$ values in the profiles. The outliers (circled) are excluded from regression analysis. Dalahi profile (blue), Pakuria profile (pink).

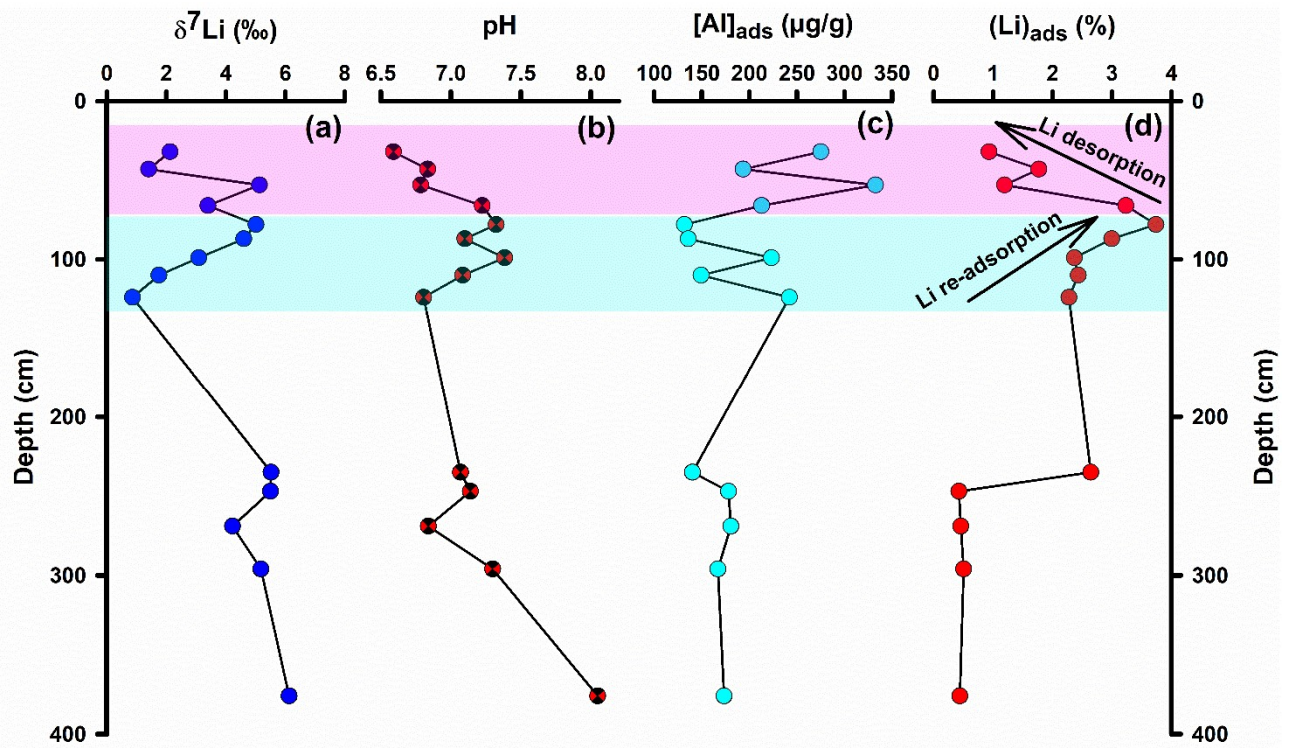
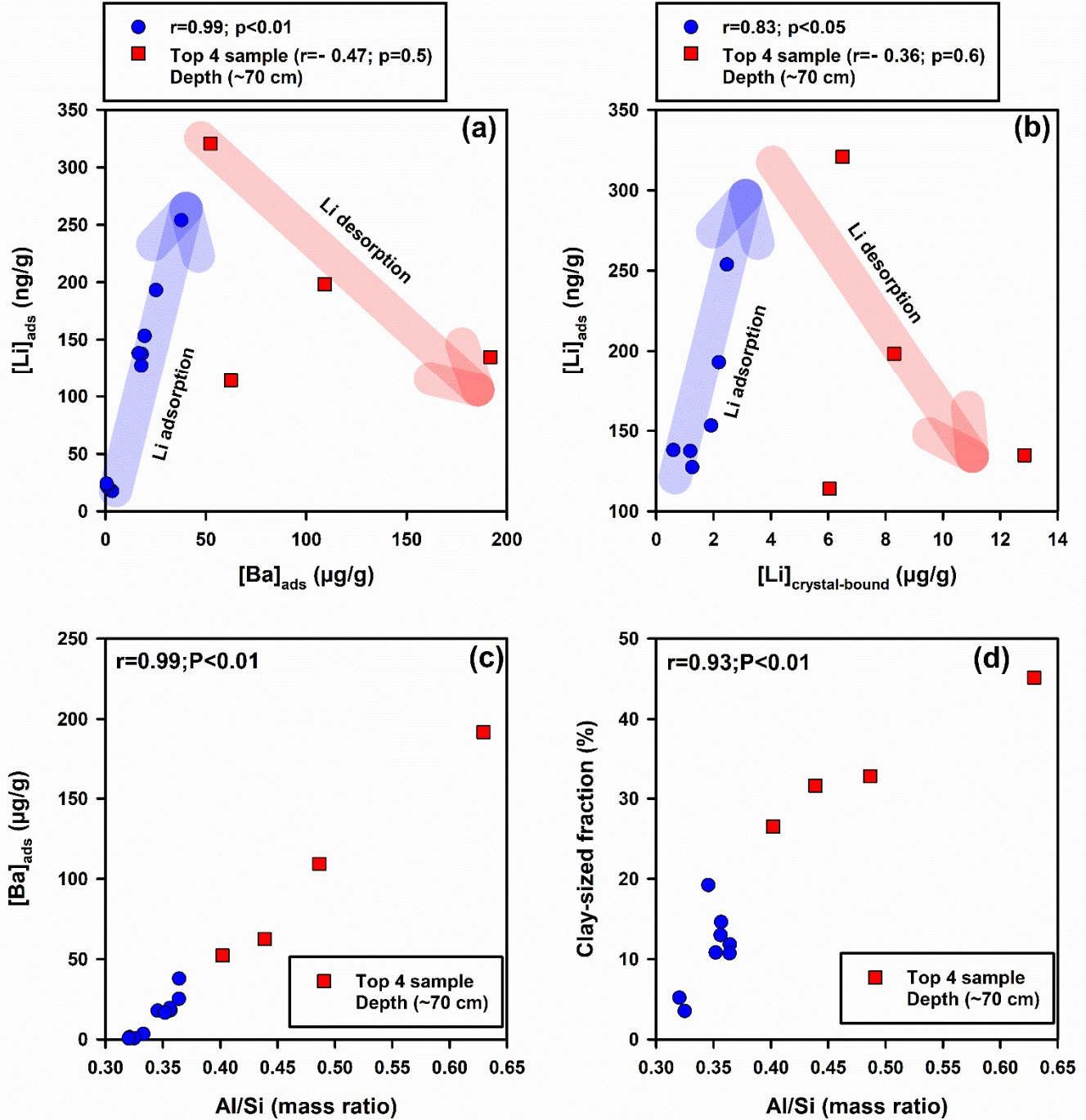


Fig. 5. Depth variation of $\delta^7\text{Li}$, pH, $[\text{Al}]_{\text{ads}}$ and $\text{Li}_{\text{ads}}\%$ in the Dalahi profile. The horizons colored in light-pink and light-cyan represent zones of desorption and re-adsorption of Li as inferred in this study (detailed discussion in Section 5.4).



974

975 **Fig. 6.** Significant positive correlations of $[Li]_{ads}$ with $[Ba]_{ads}$ (a) and $[Li]_{crystal-bound}$ (b) are observed in the
 976 lower section, whereas weak negative correlations are evident in the upper section of the Dalahi profile.
 977 Note that degree of Ba adsorption keeps increasing with abundances of clay minerals, as evident from a
 978 positive correlation of $[Ba]_{ads}$ and clay-sized fractions with Al/Si (c, d) ratio in the profile. Together, these
 979 observations are suggestive of Li adsorption in the profile, except in the upper horizon where its desorption
 980 is evident. The arrows colored in light-blue and light-red represent the direction of increasing adsorption
 981 and desorption of Li, respectively.

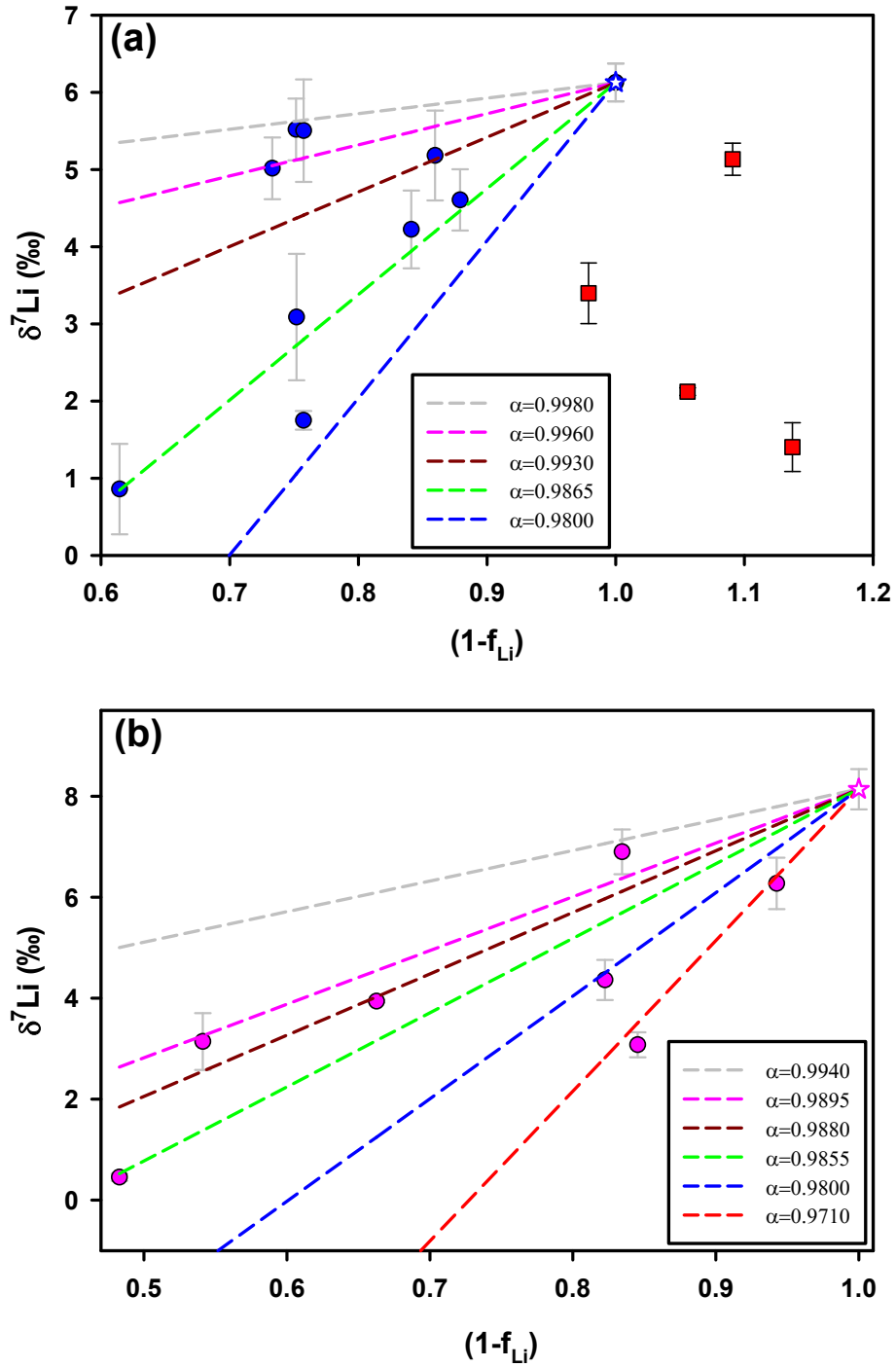
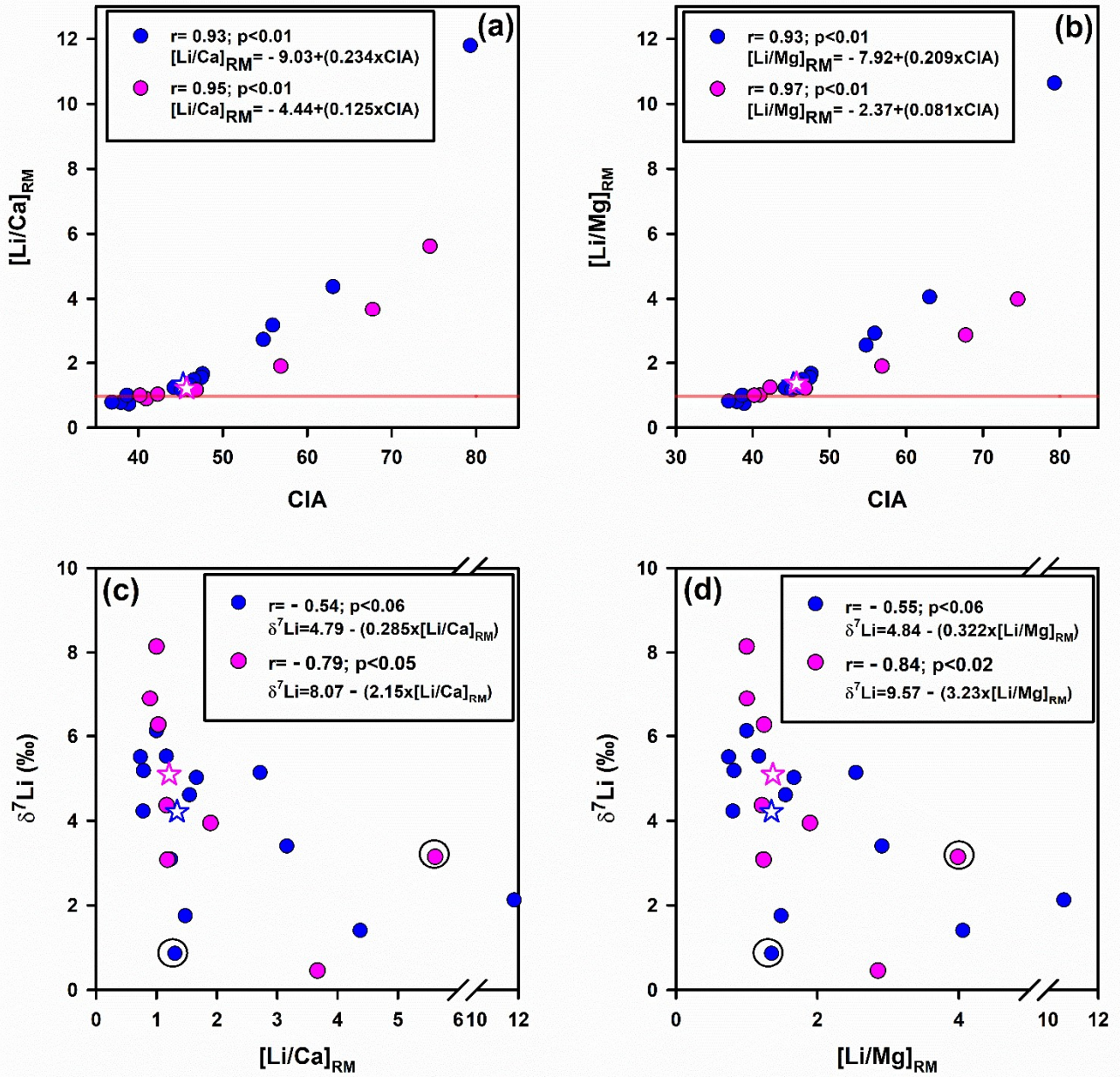
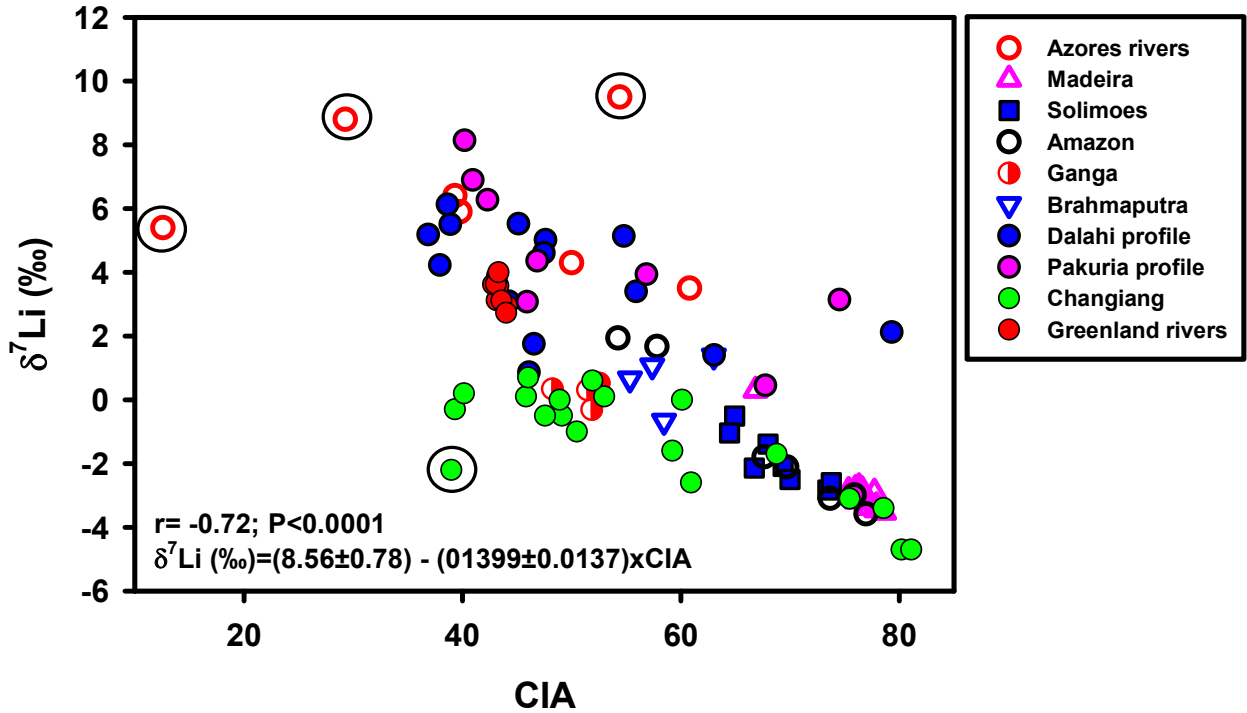


Fig. 7. $\delta^7\text{Li}$ of weathered basalts as a function of proportion of Li incorporated into secondary phases ($1-f_{\text{Li}}$) in Dalahi (a) and Pakuria profile (b). Straight lines represent the evolution of $\delta^7\text{Li}$ predicted by the batch fractionation model (see section 5.5). The circles represent the measured $\delta^7\text{Li}$ as a function of calculated ($1-f_{\text{Li}}$) values. The four samples (square) in the upper section of the Dalahi profile are outside the model prediction because of inferred desorption of Li (see section 5.4, Fig. 6). Stars represent the parent basalt $\delta^7\text{Li}$.



989

990 **Fig. 8.** Variation of $\left(\frac{Li}{Ca}\right)_{RM}$ (a) and $\left(\frac{Li}{Mg}\right)_{RM}$ (b) as a function of CIA in the studied profiles. The variation
 991 of δ^7Li with $\left(\frac{Li}{Ca}\right)_{RM}$ (c) and $\left(\frac{Li}{Mg}\right)_{RM}$ (d) are also shown. The stars represent the whole-profile values,
 992 determined based on mass balance calculations (section 5.7). The outliers (open-circled) are excluded from
 993 regression analysis. Dalahi profile (blue), Pakuria profile (pink).



994 **Fig. 9.** Variation of $\delta^7\text{Li}$ with CIA in riverine suspended particulate matter (SPM) and weathering profiles
 995 of this study. A few outliers (circled) are excluded from regression analysis. $\delta^7\text{Li}$ data sources: Azores rivers
 996 (Pogge von Strandmann et al., 2010), Madeira (Dellinger et al., 2014), Solimoes (Dellinger et al., 2014),
 997 Amazon (Dellinger et al., 2014), Ganga (Dellinger et al., 2014), Brahmaputra (Dellinger et al., 2014),
 998 Changjiang (Wang et al., 2015), and Greenland rivers (Wimpenny et al., 2010b). CIA values of SPM were
 999 calculated using major element oxides data from Pogge von Strandmann et al. (2010) for the Azores rivers,
 1000 Bouchez et al. (2011) for the Maderia, Solimoes and Amazon, Lupker et al. (2013) for the Ganga and
 1001 Brahmaputra, Chetelat et al. (2009) for the Changjiang, and Wimpenny et al. (2010b) for the Greenland
 1002 rivers. CIA values are calculated as $[\text{Al}_2\text{O}_3 \times 100 / (\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{CaO} + \text{Na}_2\text{O})]$, where oxides are in molar
 1003 proportions (Nesbitt and Young, 1982).

Tables

Table 1. Major and trace element concentrations, and Li isotopic composition of the weathered and parent basalts.

Sample code	Depth (cm)	pH	Density (g/cm ³)	Al	Ca	Fe	Mg	Na	K	Si	Mn	Al/Si	CIA	Li	Th	Cs	δ ⁷ Li (‰)	2σ ^a
				wt. %								mass ratio		μg/g				
Dalahi profile (DP)																		
RJS 3	32	6.59	1.30	11.2	1.63	14.3	0.96	0.55	0.12	17.8	0.35	0.63	79	14.45	2.14	0.75	2.12	0.05
RJS 4	43	6.84	1.66	9.97	3.40	12.5	1.96	1.01	0.12	20.5	0.35	0.49	63	11.19	1.54	0.43	1.40	0.32
RJS 5	53	6.79	2.08	9.53	4.67	10.1	2.67	1.27	0.12	21.7	0.22	0.44	55	9.55	1.37	0.31	5.14	0.21
RJS 6	66	7.23	1.97	8.98	4.17	10.6	2.42	1.16	0.15	22.3	0.33	0.40	56	9.91	1.58	0.44	3.40	0.39
RJS 7	78	7.33	2.11	8.41	5.43	8.48	2.89	1.52	0.22	23.1	0.26	0.36	48	6.78	1.45	0.37	5.02	0.59
RJS 8	87	7.10	1.97	8.43	5.53	9.05	2.95	1.52	0.13	23.1	0.21	0.36	47	6.44	1.15	0.21	4.61	0.40
RJS 9	99	7.39	2.14	8.33	6.27	8.69	3.36	1.68	0.13	23.3	0.18	0.36	44	5.80	1.21	0.22	3.09	0.40
RJS 10	110	7.09	2.20	8.35	5.67	9.07	3.00	1.58	0.15	23.5	0.18	0.36	47	6.29	1.30	0.29	1.75	0.82
RJS 11	124	6.81	2.11	8.25	5.70	8.53	2.94	1.57	0.19	23.9	0.15	0.35	46	5.59	1.42	0.35	0.86	0.12
RJS 12	235	7.07	2.08	8.30	5.97	8.84	3.17	1.68	0.14	23.6	0.19	0.35	45	5.21	1.09	0.17	5.52	0.66
RJS 13	247	7.14	2.25	7.89	7.45	7.98	3.91	1.93	0.14	23.7	0.13	0.33	39	4.11	0.85	0.07	5.51	0.50
RJS 14	269	6.84	2.25	7.82	7.63	8.41	3.94	2.05	0.17	24.4	0.14	0.32	38	4.46	0.83	0.06	4.23	0.58
RJS 15	296	7.30	2.25	7.76	7.64	8.27	3.91	2.45	0.20	23.9	0.13	0.32	37	4.51	0.82	0.08	5.18	0.40
RJS 16 (parent)	376	8.05	2.26	7.70	7.17	8.37	3.83	2.02	0.32	24.0	0.14	0.32	39	5.39	0.84	0.06	6.13	0.24
Pakuria profile (PP)																		
PB1	90	7.30	1.65	9.91	2.02	8.67	1.10	0.47	0.16	20.4	0.19	0.49	75	9.61	24.0	0.46	3.14	0.07
PB2	125	7.46	2.10	9.49	4.15	7.31	1.60	1.25	0.22	22.4	0.11	0.42	57	6.65	13.0	0.19	3.94	0.56
PB3	165	7.22	1.70	9.17	2.49	8.55	1.23	0.75	0.20	21.1	0.19	0.43	68	7.72	18.4	0.41	0.45	0.03
PB4	225	7.44	2.20	9.00	6.13	7.46	2.25	1.84	0.28	23.2	0.12	0.39	46	6.13	12.0	0.09	3.08	0.40
PB5	290	7.36	2.10	8.76	5.81	7.76	2.15	1.67	0.22	22.9	0.10	0.38	47	5.74	12.7	0.08	4.36	0.44
PERN	325	7.63	2.30	8.67	7.14	7.46	2.44	2.31	0.27	23.5	0.12	0.37	41	5.38	11.9	0.04	6.90	0.25
PFAA	625	8.09	2.61	9.30	7.00	6.59	2.23	2.58	0.34	24.0	0.10	0.39	42	6.10	12.3	0.07	6.27	0.51
PFB1 (parent)	1000	8.42	2.58	8.71	7.40	7.40	2.85	2.42	0.22	23.3	0.12	0.37	40	6.26	11.9	0.02	8.14	0.40

Depth, pH, density, major element, Th and Cs concentrations, and CIA values are from Sharma et al. (2025).

^b 2σ represents the external 2 standard deviation of duplicate measurements for each sample (See subsection 3.2.1).

Table 2. Major and trace element concentrations in the exchangeable and oxyhydroxide phases, and clay-sized fractions in the profiles. The relative mobility parameters are also listed.

Sample code	Depth (cm)	Clay-sized fraction (%)	Exchangeable					Oxyhydroxides					$\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}^a$	$\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}^a$
			Mn	Al	Ba	Li	Cs	Mn	Al	Ba	Li	Cs		
			μg/g			ng/g		μg/g			ng/g			
Dalahi profile (DP)														
RJS 3	32	45.2	40.8	4.99	175	5.73	183	992	270	17.16	129	7.37	11.79	10.64
RJS 4	43	32.8	16.2	3.50	89.6	6.83	95.6	1138	190	19.60	191	5.12	4.38	4.06
RJS 5	53	31.6	26.1	4.34	52.4	9.10	94.0	550	328	10.05	105	5.65	2.72	2.55
RJS 6	66	26.5	14.0	1.62	34.6	17.8	122.1	1115	211	17.59	303	7.57	3.16	2.91
RJS 7	78	11.8	8.34	0.99	24.2	19.4	104.8	787	131	13.55	234	5.12	1.66	1.67
RJS 8	87	10.7	15.0	1.41	19.7	24.7	67.54	487	134	5.46	168	3.09	1.55	1.55
RJS 9	99	14.6	9.66	6.91	14.6	27.8	75.57	298	216	3.46	110	3.58	1.23	1.23
RJS 10	110	13.0	20.9	1.81	16.3	26.4	79.16	309	147	3.18	127	3.15	1.48	1.49
RJS 11	124	19.2	22.9	1.83	15.4	37.1	123.7	232	240	2.41	90.2	6.48	1.30	1.35
RJS 12	235	10.8	15.2	6.57	12.5	24.4	69.3	388	134	4.04	114	2.92	1.16	1.17
RJS 13	247	nm	6.38	11.3	2.84	6.98	30.1	19.7	167	0.44	10.6	1.88	0.73	0.75
RJS 14	269	nm	1.50	6.25	1.07	8.19	14.6	3.15	174	0.20	12.4	1.64	0.78	0.81
RJS 15	296	3.53	2.75	11.6	0.47	10.4	27.0	8.51	155	0.13	12.5	2.47	0.79	0.82
RJS 16 (parent)	376	5.18	1.80	10.6	0.44	9.05	19.2	6.91	163	0.11	14.9	1.98	1.00	1.00
Pakuria profile (PP)														
PB1	90	20.5	4.57	2.55	73.37	15.6	41.9	829	116	12.6	160	2.63	5.62	3.99
PB2	125	13.6	9.75	2.49	36.24	16.5	57.0	298	155	1.56	44.1	1.76	1.89	1.90
PB3	165	15.1	2.98	5.82	30.24	29.3	70.0	780	81.9	10.28	125	3.27	3.67	2.86
PB4	225	4.42	6.84	2.78	16.15	10.1	33.6	147	206	0.60	17.4	0.88	1.18	1.24
PB5	290	5.55	5.71	7.30	15.00	9.85	34.2	156	239	0.60	19.3	1.21	1.17	1.22
PERN	325	nm	2.46	15.1	5.74	5.11	16.8	82.8	190	0.92	9.74	0.84	0.89	1.00
PFAA	625	5.22	0.87	25.4	4.62	5.31	28.0	15.1	274	0.49	9.87	1.50	1.03	1.25
PFB1 (parent)	1000	nm	6.11	14.9	0.37	29.2	5.03	10.4	178	0.06	23.3	0.59	1.00	1.00

nm: not measured

^aSee eq. 13 for determination of $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$.

The Mn concentrations in the exchangeable and oxyhydroxide phases are from Sharma et al. (2025).

Table 3. Results of the calculated mass flux of Li derived from parent basalts and aeolian dust source.

Profile Name	Profile thickness (cm)	Collapse factor (Sc)	F_{Li}^{basalt} ^a (mg/cm ²)	F_{Li}^{dust} ^b (mg/cm ²)	$(f_{Li}^{dust})^c$ ×100 (%)
Dalahi profile (DP)	376	2.54	11.65	0.13	1.12
Pakuria profile (PP)	1000	2.84	45.76	0.26	0.58

^a F_{Li}^{basalt} is calculated using eq. 3.

^b F_{Li}^{dust} is calculated using eq. 2.

^c f_{Li}^{dust} is calculated as: $f_{Li}^{dust} = \frac{F_{Li}^{dust}}{F_{Li}^{basalt}}$.

Supplementary information for

A lithium isotopic perspective of basalt weathering: Cycling of Li and its mobility relative to Ca and Mg

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The Supplementary information include:

1. **Section S1.** Processing of samples
2. **Section S2:** Previously published data
3. **Section S3:** Estimation of crystal-bound elemental concentration in neo-formed clay minerals
4. **Section S4:** Calculation of $\delta^7\text{Li}_{\text{crystal-bound}}$
5. **Section S5:** Calculation of CIA and mobility of Li relative to Ca and Mg for whole profiles
6. **Figures:** Fig. S1 to Fig. S10.
7. **Tables:** Table S1 to Table S4.

1037 **Section S1. Processing of samples**

1038 **S1.1 Preparation of glass beads for determination of major elements concentration by XRF**

1039 Major element concentrations were determined by analyzing the fusion beads (glass beads). The
1040 powdered samples were accurately weighed and mixed with a flux of 65% lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$)
1041 and 35% lithium metaborate (LiBO_2) in a 1:10 ratio, and a few grains of lithium bromide were added to
1042 the mixture. The mixtures were transferred into platinum crucibles and melted at 1250°C . The melts were
1043 poured into pre-heated platinum moulds to form the fusion beads. The beads were removed and stored in
1044 desiccator for at least twenty-four hours before analysis.

1045 **S1.2 Sample dissolution**

1046 About 100 mg of accurately weighed dry sample powders were combusted at 550°C in a muffle
1047 furnace for ~5 hours to oxidize the organic matter. The ashed samples were quantitatively dissolved in a
1048 mixture of HNO_3 , HCl and HF in a 1:3:2 volume ratio in a pre-cleaned PFA vial (Savillex[®]). The digested
1049 samples were subsequently evaporated to dryness at sub-boiling temperature ($\sim 80^\circ\text{C}$) and then
1050 gravimetrically re-dissolved in ~60 g of 5% HNO_3 . Procedural blanks, sample replicates and certified
1051 reference standards were processed with every batch of digestion. The HNO_3 and HCl used for sample
1052 processing were double distilled (DD) in a Savillex[®] DST-1000 sub-boiling distillation unit, whereas the
1053 ultrapure grade HF was procured commercially.

1054 **S1.3 Sequential extraction**

1055 The exchangeable and amorphous Fe-Mn oxyhydroxide phases were extracted following the
1056 established methods (Gupta and Chen, 1975; Chen et al., 2012) detailed in Sharma et al. (2025). Briefly,
1057 the extraction of exchangeable phases involved leaching of ~3 g of powdered sample in pre-cleaned 50
1058 mL centrifuge tube with 40 mL of 1N ammonium acetate (Sigma Aldrich, > 99.99 % purity) buffered at
1059 pH 7 with superpure ammonium hydroxide (Carlo Erba). These mixtures were shaken on a reciprocating

shaker overnight at 400 rpm and were subsequently centrifuged at 5000 rpm. The supernatants were decanted into pre-cleaned Savillex[®] beakers. The residues were washed three times with Milli-Q water (18.2 M Ω -cm) and washings were collected and mixed with the supernatant. The leachates were dried and gravimetrically re-dissolved in 5% HNO₃ prior to analysis. For extraction of oxyhydroxide phases, the residues left after the extraction of exchangeable phases were treated with 40 mL of 0.005N hydroxylamine hydrochloride (HH; 99.999% purity); 1.5% acetic acid ($\geq$ 99.99% purity) and 0.03N ethylenediaminetetraacetic acid (EDTA; 99.995% purity) solution, buffered at pH 4 with sodium hydroxide. The mixtures were shaken for one hour on a reciprocating shaker at 400 rpm, and then processed as outlined above for exchangeable fractions.

Section S2. Previously published data

Major element concentrations were determined using glass beads by a Bruker[®] Tiger S-8 WD-X-Ray Spectrometer. Analytical accuracy was evaluated through repeated analyses of certified reference standards NIST 2711a (soil), SDC-1 (mica schist), and MESS-3 (marine sediment), and was better than $\pm$ 8% ($\sim$ 0.3-7% for Al, $\sim$ 2-4% for Ca, $\sim$ 4-6% for Mg, $\sim$ 0.6-6% for Si, $\sim$ 3-5% for Na, $\sim$ 0.6-3% for K, $\sim$ 1-8% for Fe and $\sim$ 0.3-4% for Mn). Based on the analysis of samples in replicates, the analytical reproducibility was within $\pm$ 5%.

The concentrations of Th and Cs were measured by a triple quadrupole inductively coupled plasma mass spectrometer (QQQ-ICP-MS; Agilent[®] 8900) at IISc, Bangalore. Based on the analysis of certified reference standards BCR-2 (basalt), BHVO-2 (basalt), and GSP-2 (granodiorite), the measurement accuracy was better than $\pm$ 4 ($\sim$ 3 for Cs and $\sim$ 1-3.5% for Th). Analytical reproducibility, determined from replicate analyses of samples, was within $\pm$ 3%.

The concentrations of Mn in the exchangeable and oxyhydroxide fractions were determined using a quadrupole ICP-MS (ThermoScientific® X Series 2) at IISER Kolkata. Based on the analysis of certified reference standard BHVO-2 and NIST-traceable standard IV-Stock 8 (Inorganic Ventures®), the measurement accuracy was ~0.5-2.7%. Analytical reproducibility, based on replicate analyses, was within ±7% for both phases.

Section S3. Estimation of crystal-bound Li concentration in neo-formed clay minerals

We deconvolute and quantify elemental budgets of three distinct pools of weathered materials; (i) adsorbed (interlayer sites; $[X]_{\text{ads}}$), (ii) crystal-bound (crystal structure of neo-formed minerals; $[X]_{\text{crystal-bound}}$), and (iii) residual silicate minerals ($[X]_{\text{Res}}$), representing the unweathered or primary minerals. Clay minerals incorporate trace elements into two primary sites: the octahedral site (or crystal-bound) and the interlayer site (adsorbed). Thus total (bulk) elemental concentration within the weathering profile can be written in terms of the contribution from the above three components as:

$$[X]_{\text{total}} = [X]_{\text{Res}} + [X]_{\text{crystal-bound}} + [X]_{\text{ads}} \quad \text{S1}$$

where $[X]_{\text{Res}}$, $[X]_{\text{crystal-bound}}$ and $[X]_{\text{ads}}$ represent elemental concentration in the residual silicate minerals, crystal structure of clay minerals and adsorbed phases (exchangeable + oxyhydroxides), respectively, per unit mass of bulk phase. We calculate $[X]$ in the residual silicate minerals as:

$$[X]_{\text{Res}} = \left(\frac{X}{\text{Na}} \right)_{\text{parent}} \times [\text{Na}]_{\text{sample}} \quad \text{S2}$$

where, X represents element Li, Si or Al. As Na is a mobile element and insignificantly participates in solid-solution interaction after weathering (Gislason et al., 1996; Millot et al., 2010; Pogge von

Strandmann et al., 2017), all Na remaining in the weathered material is assumed to be residual. Therefore, we use the $\left(\frac{X}{Na}\right)_{\text{parent}}$ ratio of fresh basalts to estimate $[X]_{\text{Res}}$.

We determine elemental concentrations in the adsorbed phases by combining concentrations in the exchangeable and oxyhydroxide phases. Using the elemental concentrations of the adsorbed and residual silicate phases, per unit mass of bulk phase in eq. S1, the crystal-bound elemental concentration are calculated. These calculations show that up to ~85% and ~90% of the total Li in the Pakuria and Dalahi profiles (Table S3), respectively, is incorporated into the crystal structure of neo-formed minerals. The strong positive correlations between $[Li]_{\text{crystal-bound}}$ and the clay-sized fractions and a near-zero y-intercept of the regression line (Fig. S10) further corroborate the reliability of our approach of estimation of Li incorporated into the crystal structure of clay minerals.

To calculate the amount of Si incorporated into the crystal structure of newly formed clay minerals, we assumed that after weathering the released Si is partitioned into: (i) the crystal structure of newly formed clay minerals, (ii) dissolved phases ($[Si]_{\text{ads}}=0$; Middelburg et al., 1988; Frings et al., 2021) and (iii) residual silicate minerals. Therefore, $[Si]_{\text{crystal-bound}}$ can be calculated using equations S1 and S2.

Section S4. Calculation of $\delta^7Li_{\text{crystal-bound}}$

We determine the δ^7Li value of crystal-bound Li ($\delta^7Li_{\text{crystal bound}}$) in neo-formed clay minerals, based on the premise that bulk Li is distributed between the residual silicate minerals, adsorbed and crystal-bound phases in secondary minerals. Therefore, the following relationship can be written:

$$\delta^7Li_{\text{bulk}} = f_{\text{Res}}\delta^7Li_{\text{Res}} + f_{\text{crystal-bound}}\delta^7Li_{\text{crystal-bound}} + f_{\text{ads}}\delta^7Li_{\text{ads}} \quad \text{S3}$$

where the subscripts bulk, Res, crystal-bound, and ads represent bulk, residual silicate minerals, crystal-bound, and adsorbed phases, respectively, and f represents the fraction of Li relative to bulk Li.

1121 The release of Li during dissolution of the parent rock is known to cause negligible Li isotope fractionation
 1122 (Pistiner and Henderson, 2003). Therefore,

$$1123 \quad \delta^7\text{Li}_{\text{Res}} = \delta^7\text{Li}_{\text{parent}} \quad \text{S4}$$

1124 By substituting eq. S4 into eq. S3, we get:

$$1125 \quad \delta^7\text{Li}_{\text{bulk}} = f_{\text{Res}}\delta^7\text{Li}_{\text{parent}} + f_{\text{crystal-bound}}\delta^7\text{Li}_{\text{crystal-bound}} + f_{\text{ads}}\delta^7\text{Li}_{\text{ads}} \quad \text{S5}$$

1126 Previous studies have reported that the $\delta^7\text{Li}$ of the adsorbed phases is up to 28‰ higher than that
 1127 of crystal-bound Li in neo-formed minerals (Tong et al., 2021; Cai et al., 2024). Therefore, the relationship
 1128 between $\delta^7\text{Li}$ of the crystal-bound and adsorbed phases can be expressed as:

$$1129 \quad \delta^7\text{Li}_{\text{ads}} = \delta^7\text{Li}_{\text{crystal-bound}} + 28\text{‰} \quad \text{S6}$$

1130 Substituting eq. S6 into eq. S5 and rearranging gives:

$$1131 \quad \delta^7\text{Li}_{\text{crystal-bound}} = \frac{(\delta^7\text{Li}_{\text{bulk}} - f_{\text{Res}}\delta^7\text{Li}_{\text{parent}} - 28f_{\text{ads}})}{(f_{\text{crystal-bound}} + f_{\text{ads}})} \quad \text{S7}$$

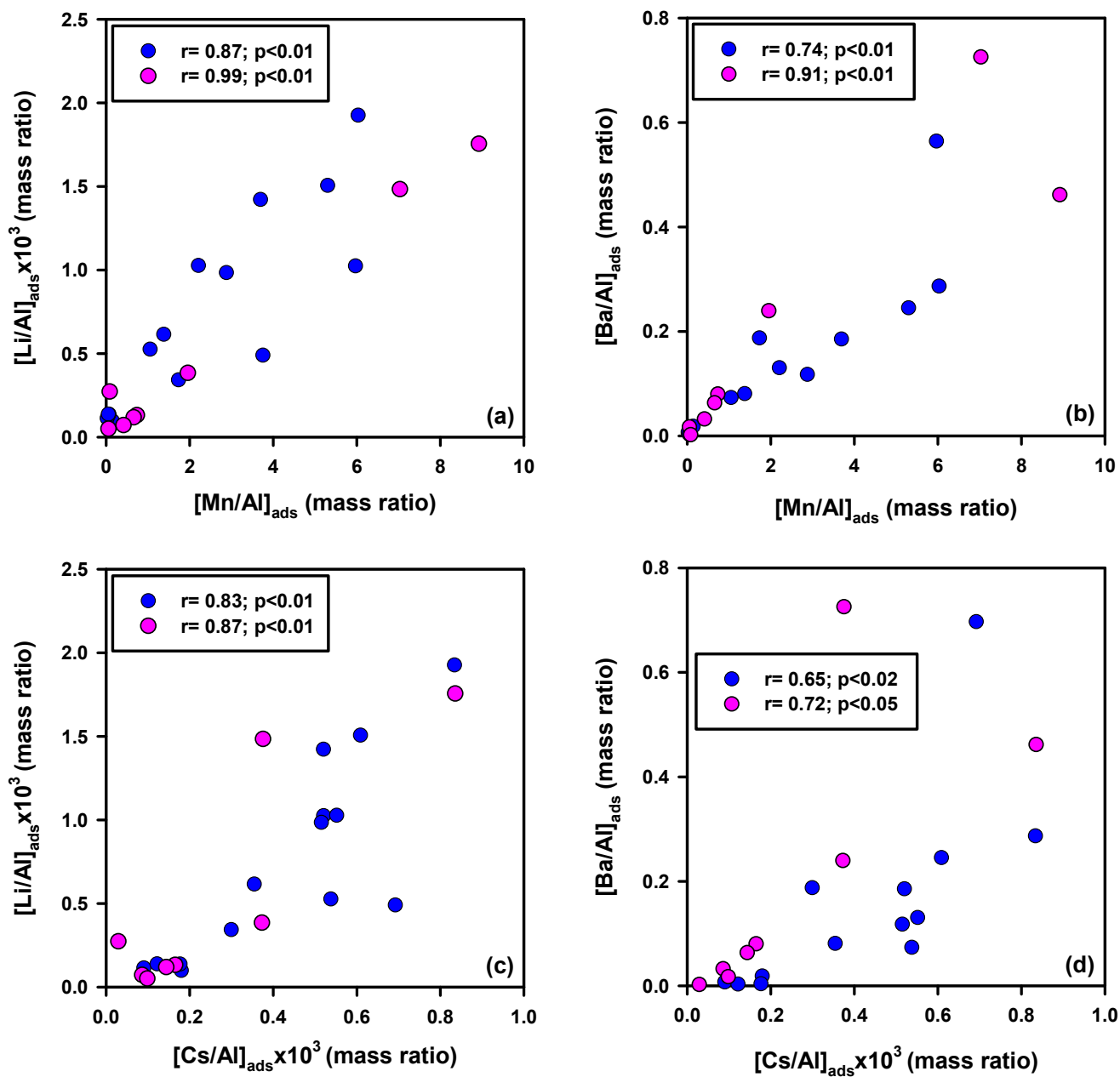
1132 Section S5. Calculation of CIA and mobility of Li relative to Ca and Mg for whole profiles

1133 The proportion of an element (X) in a weathering profile relative to the parent rock is calculated
 1134 utilizing the depth integrated mass balance of the whole profile (See eq. 10). The mobility of Li relative
 1135 to Ca and Mg can be written as:

$$1136 \quad \left(\frac{\text{Li}}{\text{X}}\right)_{\text{RM}} = \frac{f_{\text{profile}}^{\text{Li}}}{f_{\text{profile}}^{\text{X}}} = \frac{\left[\frac{(\sum_{i=1}^n [\text{Li}]_i \times \Delta t_i \times \rho_i)}{(\sum_{i=1}^n [\text{Th}]_i \times \Delta t_i \times \rho_i)} \right]}{\left[\frac{(\sum_{i=1}^n [\text{X}]_i \times \Delta t_i \times \rho_i)}{(\sum_{i=1}^n [\text{Th}]_i \times \Delta t_i \times \rho_i)} \right]} \quad \text{S8}$$

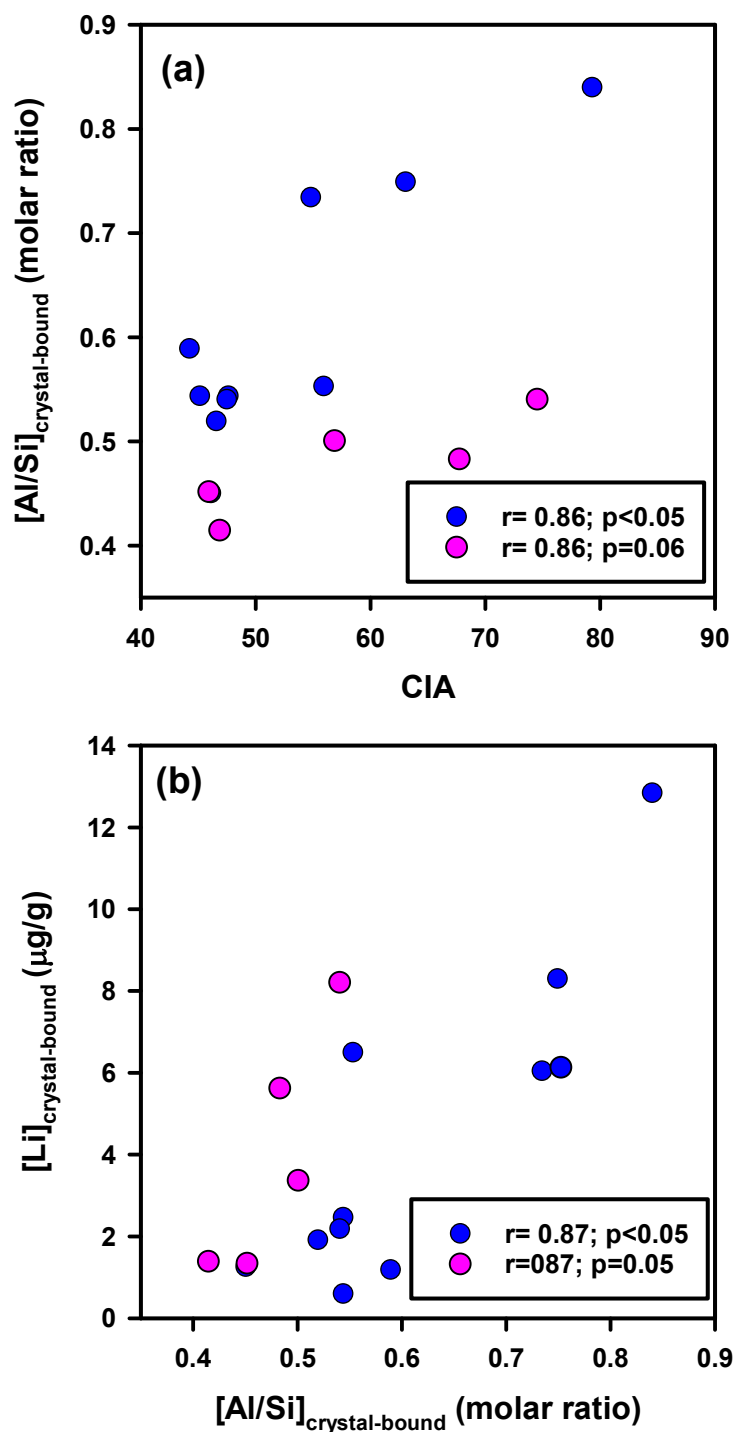
where ρ_i and Δt_i represent the density and thickness of any sampling section (i), respectively, and X is the elemental concentration of Ca or Mg. Based the eq. S8, the mobility of Li relative to Ca and Mg, is calculated to be 1.34 and 1.35 for the Dalahi profile, and 1.21 and 1.37 for the Pakuria profile, respectively. Using eq. 11 (details in the section 5.6 of main text), we calculated the depth-integrated $\delta^7\text{Li}$ values of the whole profiles to be 4.21‰ for the Dalahi profile and 5.07‰ for the Pakuria profile. These $\delta^7\text{Li}$ values of the weathered material are 1.92‰ and 3.07‰ lower than those of the parent material in the Dalahi and Pakuria profiles, respectively. Using eq. 10, we calculated the fraction of each element/oxide in the weathering profile relative to the parent rock. To determine the depth integrated CIA value for the whole profile, we calculated concentrations of Al_2O_3 , CaO , Na_2O , and K_2O for the whole profile. This was done by multiplying the element fractions in the weathering profile relative to the parent rock by the elemental concentrations of the parent rock. The CIA values were then calculated using the molar proportions of these oxides as (Nesbitt and Young, 1982):

$$\text{CIA} = \left[\frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \right] \times 100 \quad \text{S9}$$

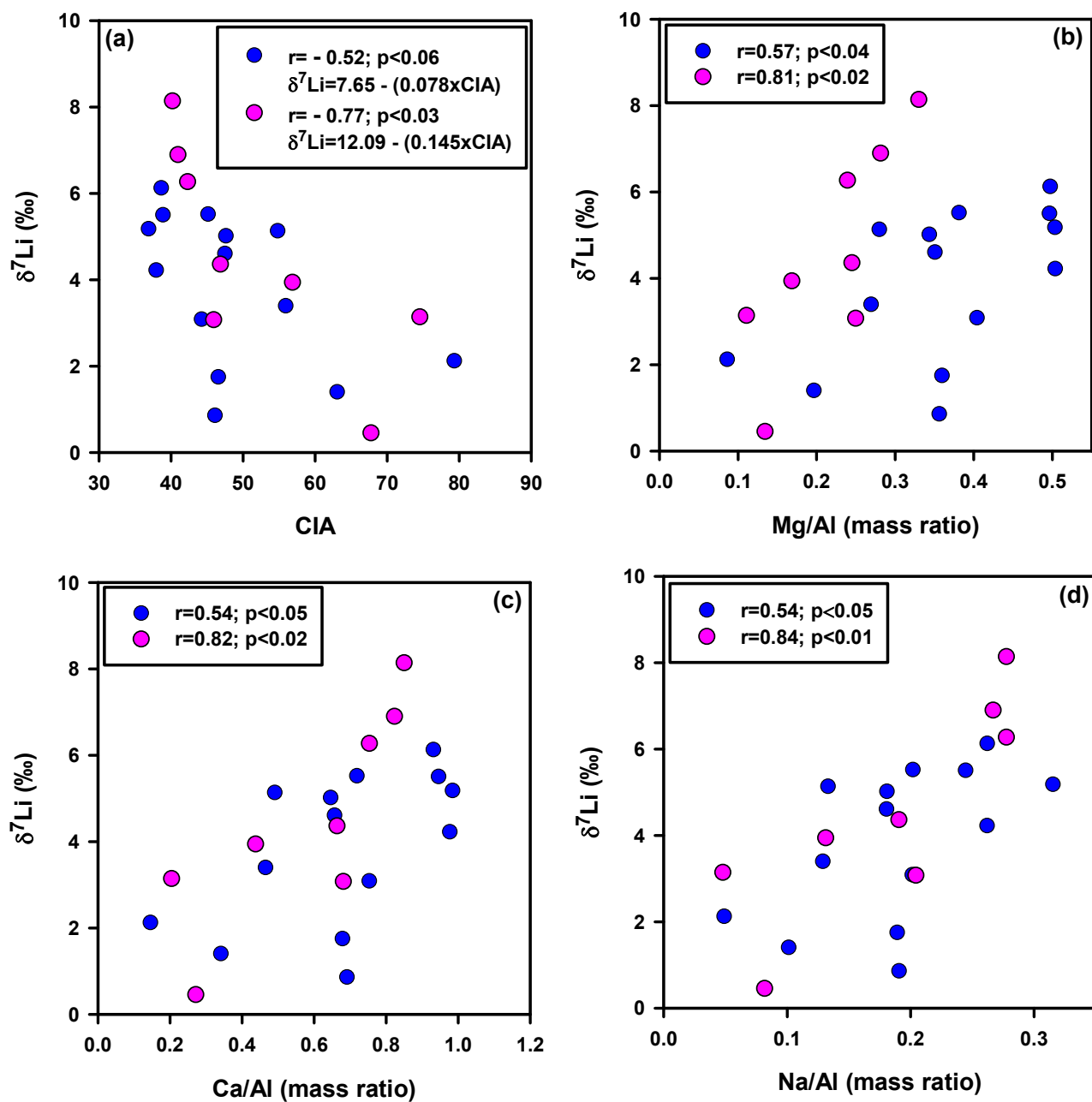


1150

1151 **Fig. S1.** Significant positive correlations of $[Li/Al]_{ads}$ (a, c) and $[Ba/Al]_{ads}$ (b, d) with $[Mn/Al]_{ads}$ and
 1152 $[Cs/Al]_{ads}$ in the Dalahi (blue) and Pakuria (pink) profiles.



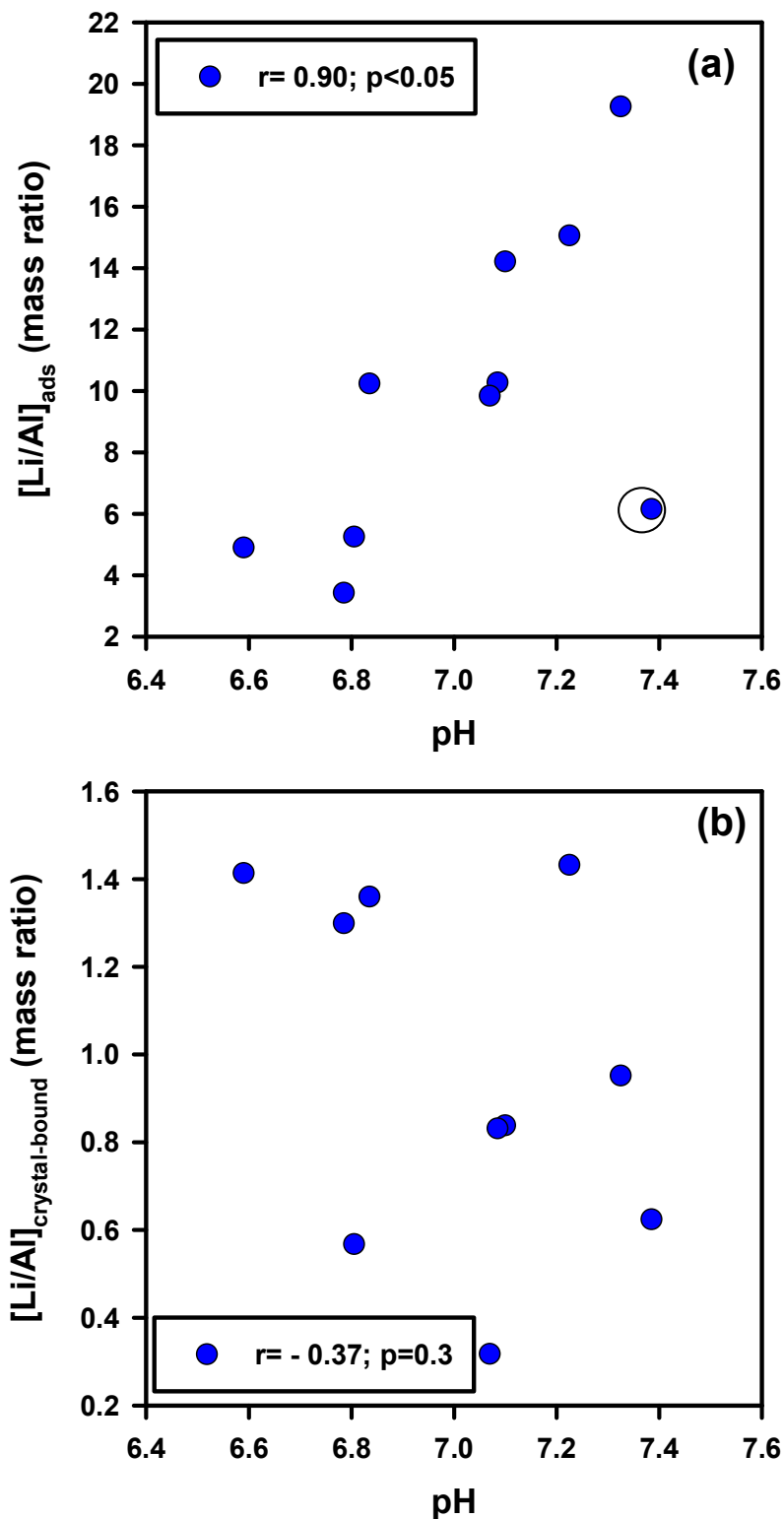
1153 **Fig. S2.** The positive correlation of $[\text{Al/Si}]_{\text{crystal-bound}}$ with CIA **(a)** and $[\text{Li}]_{\text{crystal-bound}}$ **(b)** in the Dalahi (blue)
 1154 and Pakuria profile (pink). See Section S3 and Table S3 for details on the calculation of crystal-bound
 1155 elemental concentrations in newly formed clay minerals. Note: four fresh basalt samples from the Dalahi
 1156 and three from Pakuria profiles, with CIA values ≤ 42 , are excluded in these plots (See Table S3 for
 1157 details).



1158

1159 **Fig. S3.** The $\delta^7\text{Li}$ values of weathered material as a function of CIA (a), Mg/Al (b), Ca/Al (c) and Na/Al
 1160 (d) in the Dalahi (blue) and Pakuria profile (pink).

1161



1162 **Fig. S4.** The $[\text{Li}/\text{Al}]_{\text{ads}}$ show a positive correlation with pH, whereas $[\text{Li}/\text{Al}]_{\text{crystal-bound}}$ show no systematic
 1163 trend with pH in the Dalahi profile. The outlier (circled) is excluded from regression analysis. Note: four
 1164 fresh basalt samples are excluded from panel **b** (see Table S3 for details).

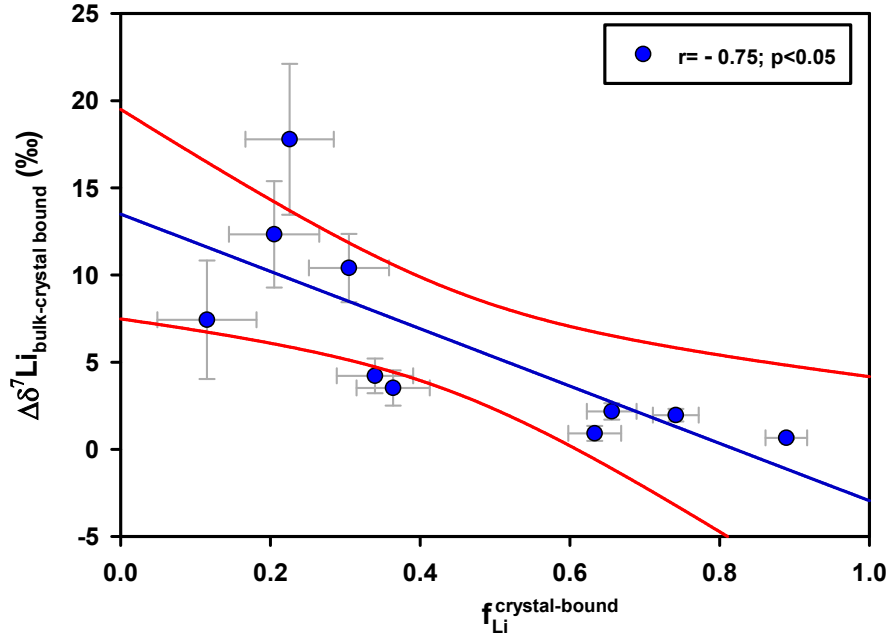


Fig. S5. Variation of $\Delta\delta^7\text{Li}_{\text{bulk-crystal bound}}$ as a function of fraction of Li in the crystal structure (Section S4) of neo-formed clay minerals in the Dalahi profile. Note: four fresh basalt samples with chemical index of alteration (CIA) values ≤ 39 (Table 1) are excluded in this plot (See Table S3 for details). The line of regression (blue) and 95% confidence intervals (red) are also shown.

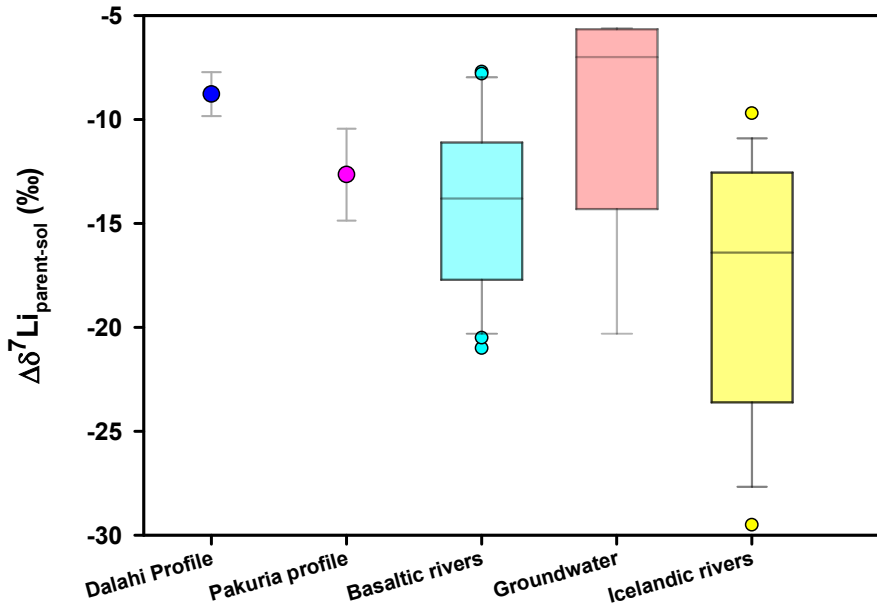
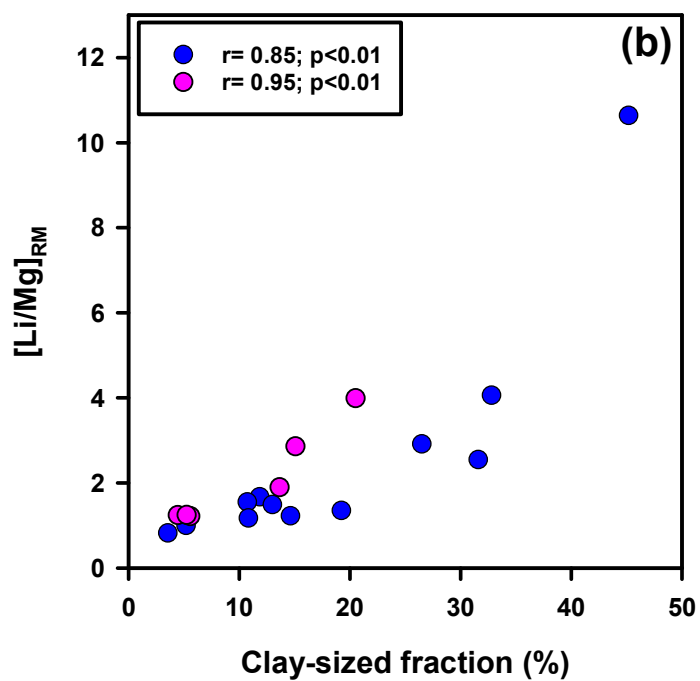
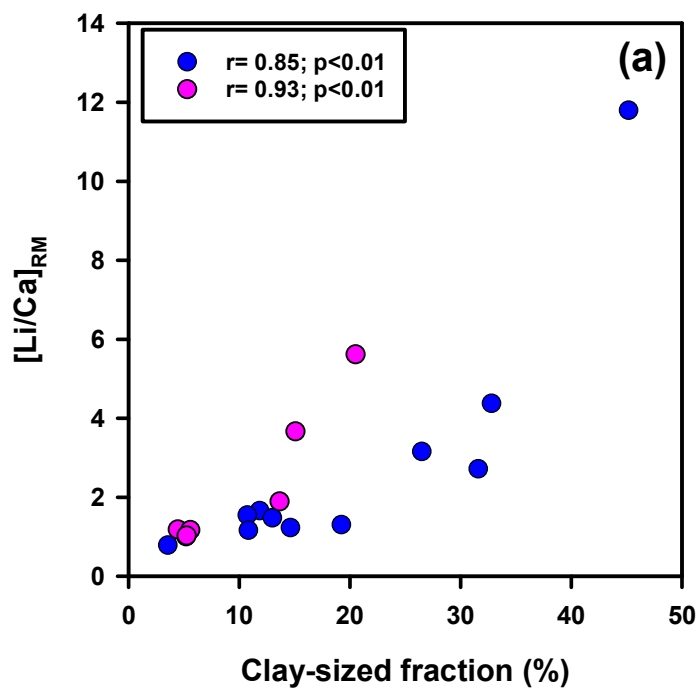
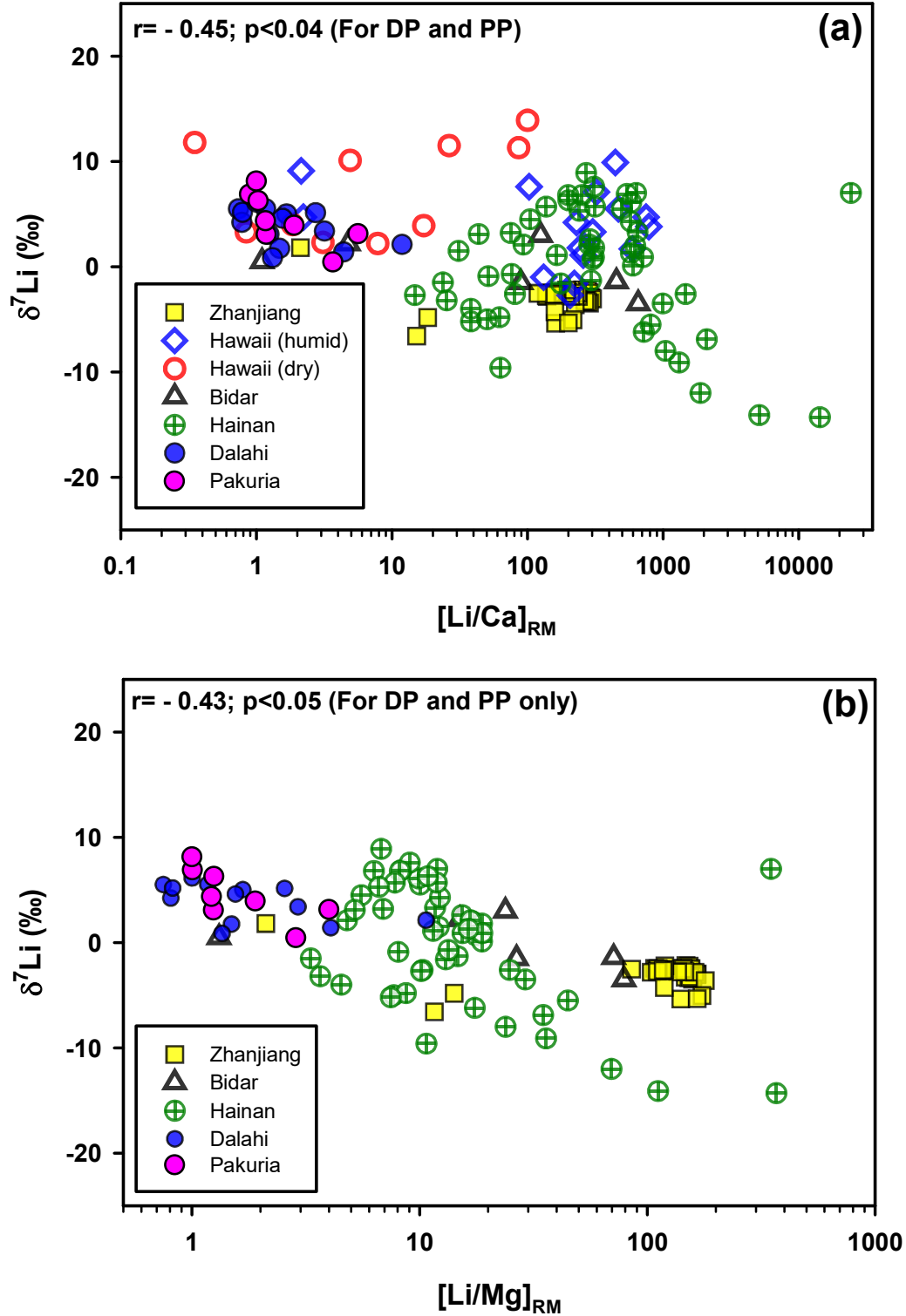


Fig. S6. Comparison of $\Delta\delta^7\text{Li}_{\text{parent-sol}}$ values in two weathering profiles of this study with $\Delta\delta^7\text{Li}_{\text{parent-sol}}$ values reported for present-day groundwater (Liu et al., 2015) and river water draining basaltic catchments (Pogge von Strandmann et al., 2006; Liu et al., 2015). Our calculated $\Delta\delta^7\text{Li}_{\text{parent-sol}}$ values are bracketed by those determined in the basaltic catchments. The parent $\delta^7\text{Li}$ value for Iceland basalt was taken from Marschall et al. (2024).



1174

1175 **Fig. S7.** Significant positive correlations of $\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{RM}}$ (a) and $\left(\frac{\text{Li}}{\text{Mg}}\right)_{\text{RM}}$ (b) with clay-sized fraction (%) in the Dalahi
 1176 (blue) and Pakuria (pink) profile.



1177 **Fig. S8.** $\delta^7\text{Li}$ of weathered basalts as a function of the mobility of Li relative to Ca (a) and Mg (b) in the Dalahi,
 1178 Pakuria, Hainan, Bidar, Hawaii and Zhanjiang profiles. Data sources: Zhanjiang (Tong et al., 2021), Hawaii (Li et
 1179 al., 2020), Bidar (Kisakurek et al., 2004) and Hainan (Xiong et al., 2022). Note that $[\text{Li}/\text{Mg}]_{\text{RM}}$ values for Hawaiian
 1180 weathered basalts could not be determined as Mg data is not available.

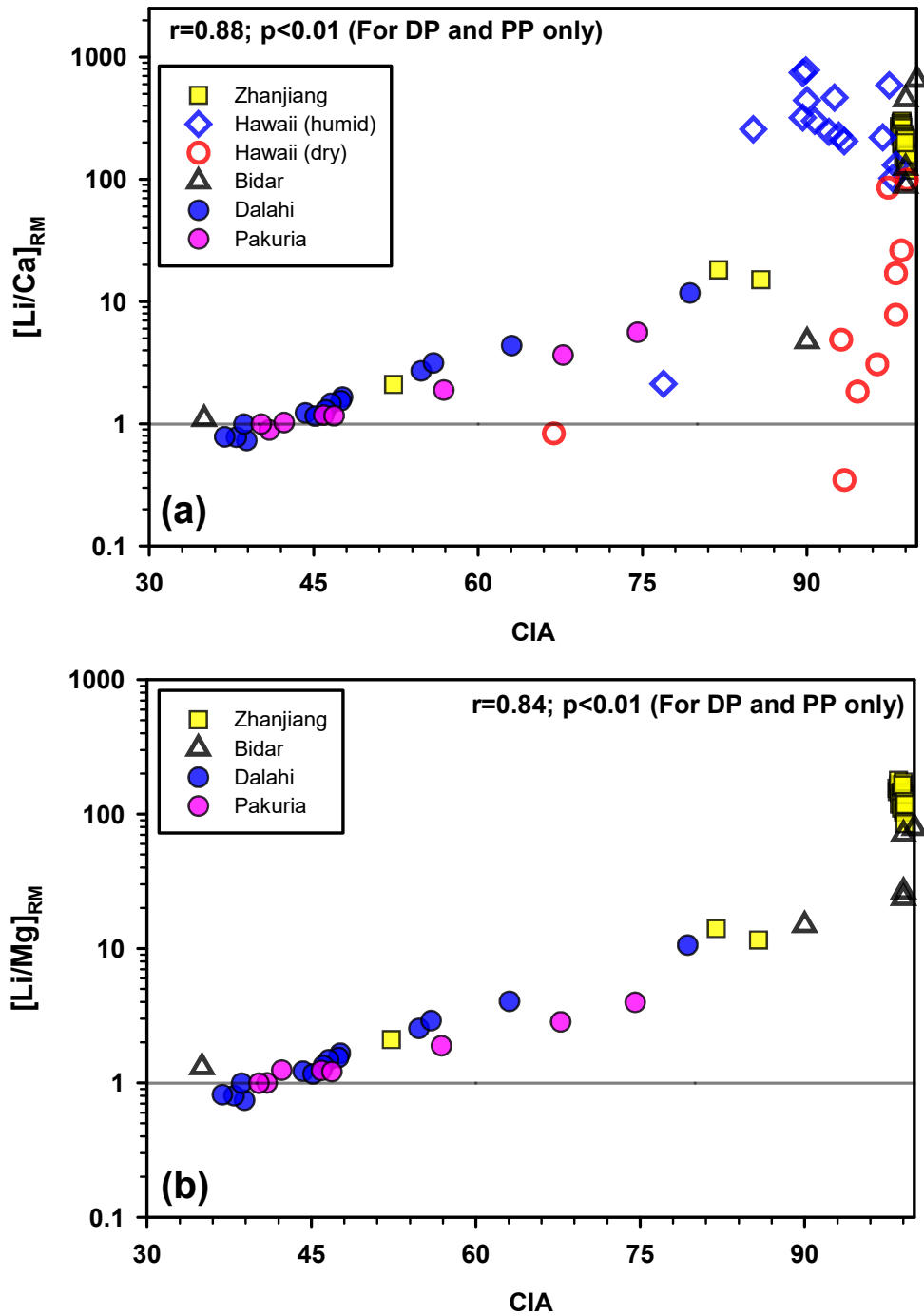


Fig. S9. Variation of relative mobility parameters vs. CIA in the weathered basalts in the Dalahi, Pakuria, Bidar, Hawaii and Zhanjiang profiles. The positive correlation of the mobility of Li relative to Ca (a) and Mg (b) with CIA suggests that as weathering intensity increases, Li becomes less mobile compared to Ca and Mg. The variation trends exhibit steeper slopes at CIA values >90. The horizontal lines represent identical mobility of Li relative to Ca and Mg. Data sources: Zhangjiang (Tong et al., 2021), Hawaii (Li et al., 2020); Hainan (Xiong et al., 2022) and Bidar (Kisakurek et al., 2004). Note that $[Li/Mg]_{RM}$ values for Hawaiian weathered basalts could not be determined as Mg data is not available.

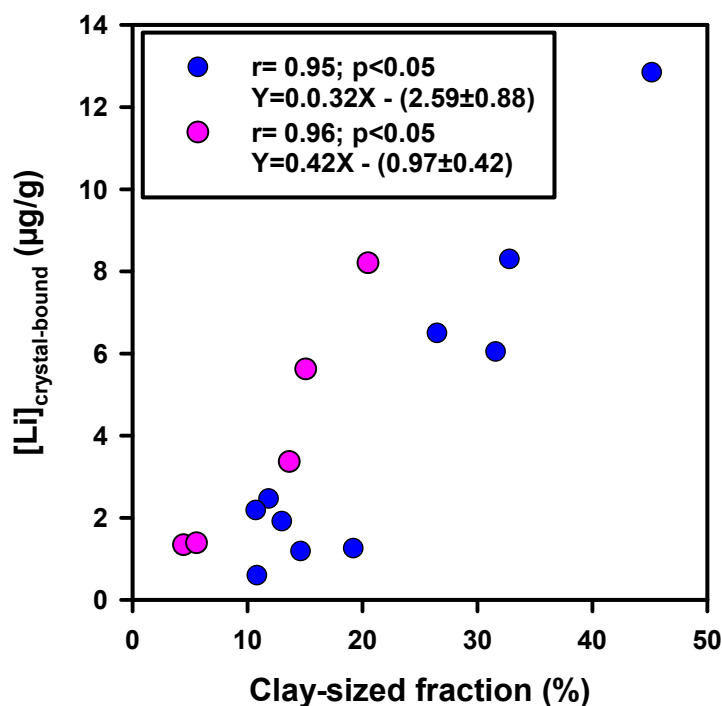


Fig. S10. The strong positive correlation between $[Li]_{\text{crystal-bound}}$ and clay-sized fraction (%) in the Dalahi (blue) and Pakuria (pink) profile. Note: four fresh basalt samples from the Dalahi and three from Pakuria profiles are excluded in this plot (see Table S3 for details).

Table S1. The concentrations of Li in the certified reference standards during analysis of bulk samples.

Elements ($\mu\text{g/g}$)	Reference standard	Certified Value	Measured value	Accuracy (%)	n
Li	BHVO-2	5	4.9 $\pm$ 0.5	1.5	3
Li	JSD-3	151	161.3 $\pm$ 1.2	-6.8	3
Li	GSP-2	36 $\pm$ 1	35.5	1.3	1

Table S2. Major and trace element concentrations in the reference standards during analysis of exchangeable and oxyhydroxide phases.

Elements ($\mu\text{g/g}$)	Reference standard	Certified/Reported Value	Measured value	Accuracy (%)	n
Li	BHVO-2	5	4.87 $\pm$ 0.03	2.6	3
Li	IV-Stock 8	100.1 $\pm$ 0.4	100.5 $\pm$ 2.5	-0.5	4
Al	BHVO-2	7.16 $\pm$ 0.08	6.71 $\pm$ 0.58	6.3	3
Al	IV-Stock 8	100.1 $\pm$ 0.4	99.1 $\pm$ 5.2	0.9	3
Ba	BHVO-2	130 $\pm$ 13	128 $\pm$ 8	1.3	3
Ba	IV-Stock 8	100.1 $\pm$ 0.4	97.9 $\pm$ 7.1	2.1	4
Cs*	BHVO-2	0.0996 $\pm$ 0.002	0.093 $\pm$ 0.005	6.6	3

*Reported values from Jochum et al. (2015).

1197 **Table S3.** Calculated concentrations of Li, Al and Si in neo formed clay minerals and its fraction relative
 1198 to bulk phase and molar $[Al/Si]_{\text{crystal-bound}}$ ratios.

Sample Code	Depth (cm)	[Li]crystal-bound	[Al]crystal-bound	[Si]crystal-bound	[Al/Si]crystal-bound (molar ratio) ^a	$f_{Li}^{crystal-bound} \times 100$ (%) ^b
		μg/g	wt. %	wt. %		
Dalahi profile (DP)						
RJS-3	32	12.8	9.09	11.3	0.84	89
RJS-4	43	8.30	6.10	8.48	0.75	74
RJS-5	53	6.04	4.65	6.60	0.73	63
RJS-6	66	6.50	4.54	8.54	0.55	66
RJS-7	78	2.47	2.59	4.96	0.54	36
RJS-8	87	2.19	2.61	5.03	0.54	34
RJS-9	99	1.19	1.90	3.37	0.59	20
RJS-10	110	1.92	2.31	4.62	0.52	30
RJS-11	124	1.26	2.22	5.13	0.45	23
RJS-12	235	0.60	1.89	3.62	0.54	12
RJS-13	247	nc	nc	nc	nc	nc
RJS-14	269	nc	nc	nc	nc	nc
RJS-15	296	nc	nc	nc	nc	nc
RJS-16	376	nc	nc	nc	nc	nc
Pakuria Profile (PP)						
B1	90	8.21	8.19	15.8	0.54	85
PB2	125	3.37	4.98	10.4	0.50	51
PB3	165	5.62	6.46	13.9	0.48	73
PB4	225	1.34	2.35	5.43	0.45	22
PB5	290	1.39	2.72	6.83	0.41	24
PERN	325	nc	nc	nc	nc	nc
PFAA	625	nc	nc	nc	nc	nc
PFB1	1000	nc	nc	nc	nc	nc

1199 See section S3 for the calculations of $[Li]_{\text{crystal-bound}}$, $[Al]_{\text{crystal-bound}}$ and $[Si]_{\text{crystal-bound}}$.

1200 ^aMolar $[Al/Si]_{\text{crystal-bound}}$ ratio = $([Al]_{\text{crystal-bound}}/[Si]_{\text{crystal-bound}}) \times 1.04$.

1201 ^b $f_{Li}^{\text{crystal-bound}}$ is calculated as: $f_{Li}^{\text{crystal-bound}} = \frac{[Li]_{\text{crystal-bound}}}{[Li]_{\text{bulk}}}$.

1202 nc: not calculated for four fresh basalt samples from the Dalahi (RJS-13, 14, 15 and 16) and three from the Pakuria
 1203 profile (PFB1, PFAA and PERN) as their CIA values are identical to those of the parent basalts (Table 1),
 1204 considering the uncertainty of estimates (Sharma et al., 2025).

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Table S4. Comparison of $\delta^7\text{Li}$, $[\text{Li}/\text{Ca}]_{\text{RM}}$ and $[\text{Li}/\text{Mg}]_{\text{RM}}$ values obtained for the whole profile by mass balance calculations with those determined from regression parameters of depth-profile data.

Whole profile mass balance Input value ^a	Depth-profile data regression equation ^b	Predicted value ^c	Whole profile mass balance Calculated value ^a
Dalahi profile			
$[\text{Li}/\text{Ca}]_{\text{RM}} = 1.34$	$\delta^7\text{Li} = (4.79 - 0.285 \times [\text{Li}/\text{Ca}]_{\text{RM}}) \text{‰}$	$\delta^7\text{Li} = 4.4 \text{‰}$	$\delta^7\text{Li} = 4.2 \text{‰}$
$[\text{Li}/\text{Mg}]_{\text{RM}} = 1.35$	$\delta^7\text{Li} = (4.84 - 0.322 \times [\text{Li}/\text{Mg}]_{\text{RM}}) \text{‰}$	$\delta^7\text{Li} = 4.4 \text{‰}$	$\delta^7\text{Li} = 4.2 \text{‰}$
CIA = 45.30	$\delta^7\text{Li} = (7.65 - 0.078 \times \text{CIA}) \text{‰}$	$\delta^7\text{Li} = 4.1 \text{‰}$	$\delta^7\text{Li} = 4.2 \text{‰}$
CIA = 45.30	$[\text{Li}/\text{Ca}]_{\text{RM}} = (-9.03 + 0.234 \times \text{CIA})$	$[\text{Li}/\text{Ca}]_{\text{RM}} = 1.57$	$[\text{Li}/\text{Ca}]_{\text{RM}} = 1.34$
CIA = 45.30	$[\text{Li}/\text{Mg}]_{\text{RM}} = (-7.92 + 0.209 \times \text{CIA})$	$[\text{Li}/\text{Mg}]_{\text{RM}} = 1.54$	$[\text{Li}/\text{Mg}]_{\text{RM}} = 1.35$
Pakuria Profile			
$[\text{Li}/\text{Ca}]_{\text{RM}} = 1.21$	$\delta^7\text{Li} = (8.07 - 2.15 \times [\text{Li}/\text{Ca}]_{\text{RM}}) \text{‰}$	$\delta^7\text{Li} = 5.5 \text{‰}$	$\delta^7\text{Li} = 5.1 \text{‰}$
$[\text{Li}/\text{Mg}]_{\text{RM}} = 1.37$	$\delta^7\text{Li} = (9.57 - 3.23 \times [\text{Li}/\text{Mg}]_{\text{RM}}) \text{‰}$	$\delta^7\text{Li} = 5.1 \text{‰}$	$\delta^7\text{Li} = 5.1 \text{‰}$
CIA = 45.71	$\delta^7\text{Li} = (12.09 - (0.145 \times \text{CIA}) \text{‰}$	$\delta^7\text{Li} = 5.5 \text{‰}$	$\delta^7\text{Li} = 5.1 \text{‰}$
CIA = 45.71	$[\text{Li}/\text{Ca}]_{\text{RM}} = (-4.44 + 0.125 \times \text{CIA})$	$[\text{Li}/\text{Ca}]_{\text{RM}} = 1.27$	$[\text{Li}/\text{Ca}]_{\text{RM}} = 1.21$
CIA = 45.71	$[\text{Li}/\text{Mg}]_{\text{RM}} = (-2.37 + 0.081 \times \text{CIA})$	$[\text{Li}/\text{Mg}]_{\text{RM}} = 1.33$	$[\text{Li}/\text{Mg}]_{\text{RM}} = 1.37$

^a Calculated from whole profile mass balance approach (See section S5).

^b Regression equations are derived from the data shown in figures 8 and S3a.

^c Predicted values of $\delta^7\text{Li}$ were based on the input values of $[\text{Li}/\text{Ca}]_{\text{RM}}$, $[\text{Li}/\text{Mg}]_{\text{RM}}$ or CIA in the regression equations obtained from depth-profile data. Predicted values of $[\text{Li}/\text{Ca}]_{\text{RM}}$ or $[\text{Li}/\text{Mg}]_{\text{RM}}$ values were derived by using input values of CIA in the regression equations obtained from depth-profile data.

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