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Strontium isotopes and Rb/Sr tracers in surface soils for locating subsurface lithium pegmatites

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ABSTRACT

Lithium-cesium-tantalum (LCT) pegmatites are a major source of global Li production. They typically occur as dike swarms intruded into metamorphic country rocks. The subsurface locations of these dikes can be difficult to identify from the surface. One common approach is to investigate geochemical anomalies in overlying soils and use these as indicators for the occurrence of subsurface pegmatite dikes. However, even with these methods, economically valuable pegmatites can be difficult to identify, and additional techniques can be beneficial for optimizing geological exploration. Here we present a new methodology for detecting subsurface pegmatites through the analysis of Rb/Sr and strontium isotope ($^{87}Sr/^{86}Sr$) variations in relatively shallow soils overlying LCT pegmatites. During their formation, pegmatites become enriched in Rb and depleted in Sr, resulting in distinctly high Rb/Sr ratios (typically ≫10), and with time, the decay of ^{87}Rb leads to high $^{87}Sr/^{86}Sr$ ratios (typically ≫1.0) far exceeding those of common regional host rocks (typically with Rb/Sr < 10 and $^{87}Sr/^{86}Sr$ < ~0.75). Since soils primarily inherit the $^{87}Sr/^{86}Sr$ values of their underlying parent rocks, we propose using these distinctive geochemical fingerprints in site-specific soil geochemical surveys to detect subsurface LCT pegmatites. We demonstrate the potential and utility of this methodology using surface soils around and overlying buried LCT pegmatites in the Late Paleozoic Tin Spodumene Belt in North Carolina and the Proterozoic Animikie Red Ace in Wisconsin, USA. Soils directly overlying the LCT pegmatites inherit distinctly elevated Rb/Sr (~10–120) and $^{87}Sr/^{86}Sr$ (~1.0–6.8) ratios compared to background soils away from the buried LCT pegmatites ($^{87}Sr/^{86}Sr$ ~0.74–0.77, Rb/Sr ~0.76–3.9), which can be used to identify and reconstruct the location of subsurface LCT pegmatite dikes. The common and uniquely elevated Rb/Sr and $^{87}Sr/^{86}Sr$ signatures of global pegmatites suggest that this method can be widely and globally applied to soils derived from LCT pegmatites.

1. Introduction

Efforts to transition away from fossil fuel-based energy to renewable energy have driven exploration for and extraction of critical raw materials (CRMs) necessary for clean energy technologies (IEA, 2021; Reich and Simon, 2025). Lithium (Li) is an important CRM and a crucial component for batteries used to power electric vehicles, portable devices, and electricity grid storage systems (IEA, 2021). One of the most important sources of Li are hard-rock deposits (>50 % of global Li production) classified as lithium-cesium-tantalum (LCT) pegmatites, known for their unique enrichments of those elements (Bradley et al., 2017; Jaskula, 2024; Moon, 2024). These deposits are distributed globally (Fig. 1A), with current production from deposits in Australia, Canada, China, Zimbabwe, Brazil and Portugal (Jaskula, 2024). Since demand for clean energy technologies and Li is increasing, developing new tools and techniques to aid in exploration for Li deposits is paramount to successfully and sustainably supplying raw materials for the clean energy transition.

LCT pegmatites are typically emplaced as dikes and sills that have intruded into metamorphic host rocks (Bradley et al., 2017; Chappell and White, 2008; Jahns and Tuttle, 1963). They are geochemically and mineralogically unique, resulting from the extreme fractional crystallization of granitic magmas (Černý et al., 1985; Chappell and White, 2008; London, 2016, 2018), or from repeated partial remelting of

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metasediments and granites during orogenic events (Koopmans et al., 2023). These processes result in the removal of relatively compatible elements (e.g. Ca, Sr) that readily incorporate into early-crystallizing magmatic minerals, ultimately resulting in the magmatic enrichment of relatively incompatible elements (e.g. Li, Cs, Ta, Rb), and eventually crystalize to form LCT pegmatite deposits (Bradley et al., 2017; Černý et al., 1985; Chappell and White, 2008; London, 2016). During emplacement of the magma, these processes often result in mineralogical zonation, meaning that pegmatites vary compositionally and have ore-grade sections distinct from "unmineralized" sections of lower economic value (Černý, 1991; Jahns and Tuttle, 1963; London, 2014). Spodumene is often the most important Li-bearing mineral, while petalite and lepidolite can also occur in some deposits (Bradley et al., 2017). These minerals typically co-occur with quartz, K- and Na-feldspars, and micas (Bradley et al., 2017; Jahns and Tuttle, 1963; London, 2014).

Pegmatites typically occur as "swarms" of individual dikes throughout country rock and over large areas (Bradley et al., 2017). For example, hundreds of individual dikes have been found at the Carolina Tin Spodumene Belt (TSB) over an area of ~83 km^2 (Kesler, 1942; Swanson, 2012). Prospecting for pegmatites is difficult given the mineralogical and geochemical variability, the presence of overburden (soils, regolith, plants), and the narrow width of many Li-containing dikes (Balaram and Sawant, 2022; Galeschuk and Vanstone, 2007; Müller et al., 2025; Sirbescu et al., 2025; Steiner, 2019; Sweetapple et al., 2024).

Because soils and their regolith are the weathering products of underlying rocks, soil geochemistry is used to prospect for buried dikes, as soils inherit geochemical signatures from underlying rocks. Previous studies have relied on pathfinder elements such as Li, Cs, Ta, and Rb (Bradley et al., 2017; Galeschuk and Vanstone, 2007; London, 2016; Luecke, 1984; Sirbescu et al., 2025), fractionation-indicator ratios such as K/Rb, and indicator minerals analyzed by portable or laboratory methods (Balaram and Sawant, 2022; Harmon et al., 2025; Sirbescu et al., 2025; Steiner, 2019; Wise et al., 2022a). However, these approaches are challenged by mineralogical variability, sediment overburden (soils and regolith), and the fact that soils are often transported and modified by creep, water, wind, or ice (Galeschuk and Vanstone, 2007). Thus, this study aims to develop new geochemical tracers of pegmatites to be used independently or in tandem with established methods.

A long-recognized feature of LCT pegmatites is their high Rb and low Sr concentrations (and thus high Rb/Sr ratios) as a result of fractionation processes during their formation (Černý et al., 1985; Clark and Černý, 1987), where Sr readily substitutes for Ca (a relatively compatible element) in mineral structures during early stages of fractional

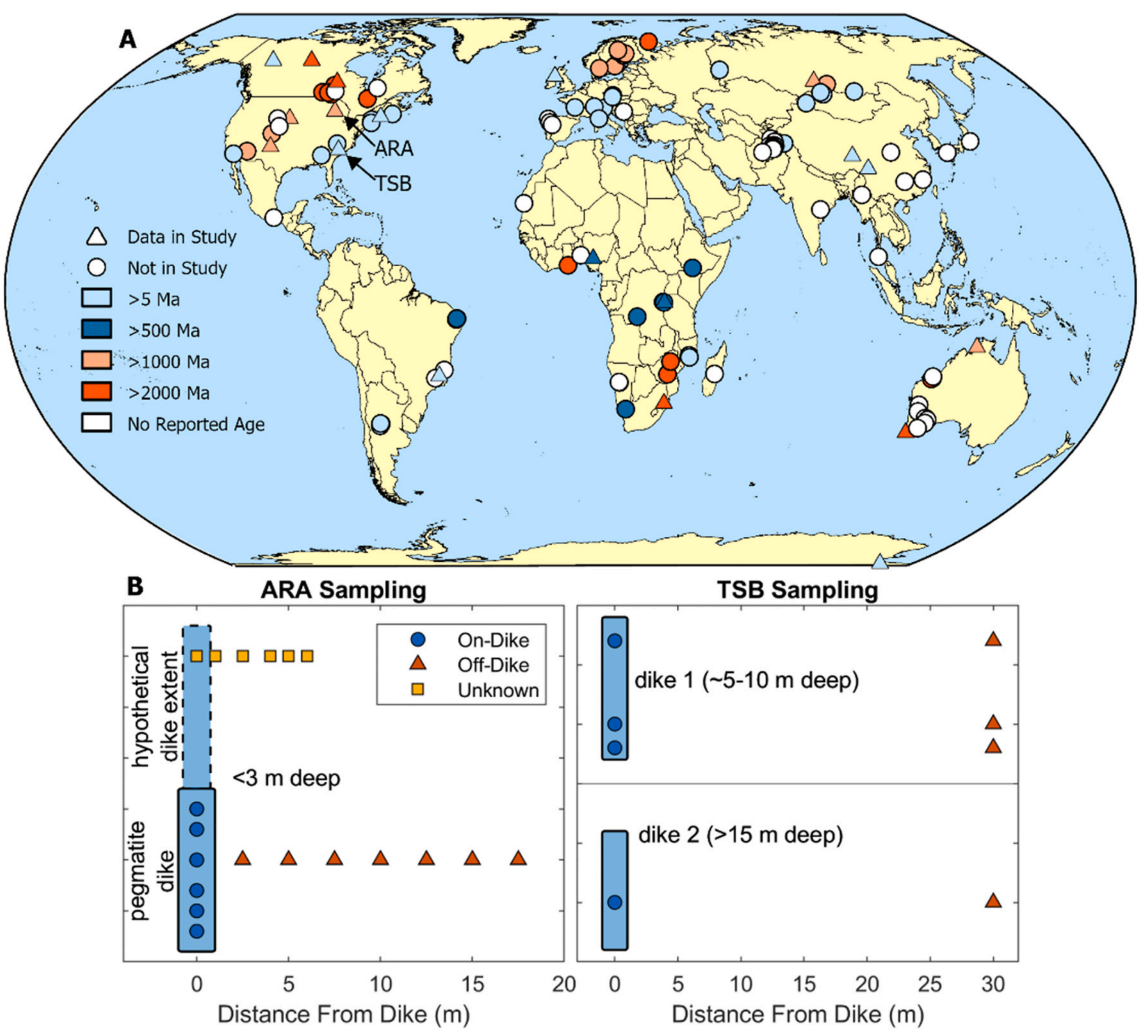

Fig. 1. (A) Map of global pegmatite occurrences as tabulated in Bradley et al. (2017) with reported age (color) whether data were included in the study (triangles vs circles). (B) Schematics of soil sampling maps from the ARA and TSB sites. The blue rectangles with solid outlines represent the known extent of the dike based on outcrops and dashed outlines represents the hypothetical extent of the dike. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

crystallization, while Rb (an incompatible element) remains in the residual melt, eventually substituting for K in pegmatite minerals in late stages of fractional crystallization (Clark and Černý, 1987; Norton, 1973). Because most pegmatites are older than ~300 Ma (McCauley and Bradley, 2014) and ^{87}Rb decays to ^{87}Sr at the long half-life of ~48.8 billion years (Capo et al., 1998), pegmatites are characterized by both high Rb/Sr and high ^{87}Sr/^{86}Sr isotope ratios (Barros et al., 2017; Clark and Černý, 1987; Riley, 1970). Extraordinarily high ^{87}Sr/^{86}Sr ratios, greater than ~100–1000, have been reported in K-rich minerals such as K-feldspars and micas (e.g. lepidolite, muscovite) of pegmatites (Camacho et al., 2012; Clark and Černý, 1987; Makagan et al., 2000; Naumenko-Dèzes et al., 2018; Register, 1979; Trumbull, 1993) and in whole-rock pegmatite samples (~0.75–48.8) (Brookins et al., 1979; Makagan et al., 2000; Matheis and Caen-Vachette, 1983; Register, 1979; Riley, 1970; Rivers, 2022; Williams et al., 2022), reflecting the dominance of radiogenic ^{87}Sr (Clark and Černý, 1987). By comparison, the bulk continental crust is estimated to have an average ^{87}Sr/^{86}Sr ratio of ~0.716–0.738 (Desem et al., 2025; Goldstein and Jacobsen, 1988; McDermott and Hawkesworth, 1990), while most global soils, plants, and natural waters have ^{87}Sr/^{86}Sr ratios between ~0.708 and ~0.711 (Bataille et al., 2020). Since ^{87}Sr/^{86}Sr signatures of soils mimic the composition of their parent lithologies (Capo et al., 1998), we thus hypothesize that the uniquely radiogenic Sr isotope fingerprints of LCT pegmatites are carried into overlying regolith and soils.

Here we investigate Rb/Sr and ^{87}Sr/^{86}Sr ratios in global LCT pegmatites and evaluate whether these signatures are inherited by overlying surface soils that can be used to detect the occurrence of subsurface LCT pegmatites dikes in field sites. We show that the Rb/Sr and ^{87}Sr/^{86}Sr ratios in global LCT pegmatite occurrences are unique and distinguishable from common host rocks, verifying that LCT pegmatites contain a distinct geochemical fingerprint that can identify their occurrence in the subsurface. This is demonstrated through a study of shallow soils overlying two separate LCT pegmatite deposits with contrasting soils, regoliths, and lithology in the United States, including (1) the Paleoproterozoic to Mesoproterozoic (~1800-1400 Ma) (Droubi et al., 2025; Holm et al., 2005; Sirbescu et al., 2025) Animikie Red Ace (ARA) pegmatite in a glaciated and forested landscape in Wisconsin, and (2) the Late Paleozoic (~349 Ma) (Bradley et al., 2017; Rivers, 2022) Tin-Spodumene Belt (TSB) pegmatite in an unglaciated piedmont in North Carolina. Integrating soil data from the two profiles with global LCT pegmatites data, we demonstrate that these geochemical techniques may be globally applicable to Li-rich pegmatite exploration.

2. Materials and methods

2.1. Sample collection and data compilation

Soil and rock samples were collected from two sites, the Animikie Red Ace pegmatite (ARA) in Florence County, Wisconsin, and the Carolina Tin Spodumene Belt (TSB) in North Carolina. Both ARA and TSB are LCT, Group 1 pegmatites (classification of Wise et al. (2022b)), or more specifically, rare-element, lithium-rich (REL-Li) pegmatites (Černý and Ercit, 2005). However, the two pegmatites differ in terms of their mineralogy and degree of fractionation. The ARA can be classified under complex type, lepidolite subtype, formed from highly fractionated magma (Falster et al., 1996; Sirbescu et al., 2025), whereas the TSB is a less fractionated, albite-spodumene type (Černý, 1992; Curry et al., 2025; Swanson, 2012). A brief description of the sample sites is as follows, however more thorough geologic and soil descriptions are elsewhere for the ARA (Sirbescu et al., 2025) and for the TSB (Harmon et al., 2025).

At the ARA, soils were collected from the upper 40 cm, directly over an LCT pegmatite dike (n = 6), these are classified as on-dike, and along a transect perpendicular to and downslope of the dike's footwall (n = 7), up to 17.5 m away, these are classified as off-dike. The dike is < 3 m below the soil surface and is no more than 3 m wide striking approximately north-south and dipping to the west ~50–60° (Liu et al., 2010; Sirbescu et al., 2025). An additional six samples were collected perpendicular to the hypothetical extent of the same dike ~15 m away from the first transect, these are classified as unknown (Fig. 1B). Soil sampling intentionally avoided areas with glacial till, favoring soils formed directly on bedrock (as described in Sirbescu et al. (2025)). Also collected at the ARA were whole-rock samples of LCT pegmatite (n = 3), quartz-schist (n = 3), and a regional granite (n = 1). The soils at the ARA are shallow, undisturbed, relatively immature postglacial soils in a forested setting (Sirbescu et al., 2025).

At the TSB, soil samples were collected from the upper 50 cm, from both directly over a known dike (n = 4), classified as on-dike, and from soils 30 m away from the hanging wall of the dike (n = 4), classified as off-dike (Fig. 1B). Soils were collected from two dike locations, one that is ~5–10 m deep where off-dike samples were collected upslope of the dike and another that is > 15 m deep where off-dike samples were collected downslope of the dike. The dikes are no more than a few meters wide and strike approximately northeast-southwest, steeply dipping to the northeast (Curry et al., 2025; Harmon et al., 2025). Whole rock samples were collected from throughout the TSB as described in Williams et al. (2024) and include the LCT pegmatite (n = 8) and amphibolite gneiss host rocks (n = 5). The soils at the TSB are formed on deep highly weathered profiles in an area with a long history of agricultural land use (Daniels et al., 1999; Harmon et al., 2025).

Mixing curves for soils at the ARA and the TSB were calculated as two endmember mixing models between the mean concentrations or ratios of Rb, Sr, K, Rb/Sr, ^{87}Sr/^{86}Sr, and K/Rb in the whole-rock pegmatites and the background unaltered host rocks. This assumes that the geochemistry of the soils are derived exclusively from these two sources (see sections 4.2 and 4.3).

Geochemical data from whole-rock pegmatites and regional geology across 18 pegmatites districts from 11 countries and Antarctica including Rb and Sr concentrations and ^{87}Sr/^{86}Sr measurements were compiled in Table S1 from the literature (Anderson et al., 2013; Barnes, 2010; Bradley et al., 2017; Brookins et al., 1979; Chalmers et al., 2025; Curry et al., 2025; Falster et al., 1996; Faure and Felder, 1985; Lehmann et al., 2014; Luecke, 1981; Makagan et al., 2000; Maphalala et al., 1989; Maphalala and Trumbull, 1998; Matheis and Caen-Vachette, 1983, 1983; Mueller, 2025; OREAS, 2019; Preinfalk et al., 2002; Register, 1979; Riley, 1970; Rivers, 2022; Walker et al., 1986; Williams et al., 2022, 2024; Yan et al., 2020; Zhou et al., 2025). These include data from the USA (North Carolina, Wisconsin, South Dakota, and New Mexico), Brazil, Ireland, China, Nigeria, Rwanda, Eswatini, Australia, and Canada. The age of each pegmatite deposit was taken either from the reported values in each paper or from the tabulation in Bradley et al. (2017). The compiled dataset (inclusive of new analyses presented here) includes whole-rock analyses of Rb and Sr concentrations in 203 LCT pegmatite samples across 18 pegmatite districts and in 197 related host rock and barren pegmatite samples and of ^{87}Sr/^{86}Sr ratios in 70 LCT pegmatite samples across 10 pegmatite districts and 85 samples of related host rocks and barren pegmatites (Table S1).

For the age distribution model of ^{87}Sr/^{86}Sr, the average Rb/Sr ratio from each deposit was estimated and the maximum and minimum of the deposits taken as endmembers. The initial ^{87}Sr/^{86}Sr was set to the average value of mid ocean ridge basalt (MORB) at 0.702819 (Gale et al., 2013), and the change in ^{87}Sr/^{86}Sr was calculated from the decay of ^{87}Rb to ^{87}Sr based on the measured Rb/Sr ratio and assuming that ^{87}Rb is 27.83 % of total Rb. These assumptions may underestimate whole-rock ^{87}Sr/^{86}Sr because the Rb/Sr ratio includes radiogenic Sr as measured in the modern day and would be lower than the initial Rb/Sr ratio. In addition, the initial ^{87}Sr/^{86}Sr in pegmatites is often more radiogenic than MORB.

2.2. Analytical methods

All solid samples were dried at ~60 °C, crushed, homogenized, and

50 mg was digested in an HNO_3 and HF mixture in Savillex PFA vials. The digestion method has previously been evaluated for soil and pegmatite digestions (Hill et al., 2024a, 2024b; Williams et al., 2024). Elemental concentrations were measured on an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher X-Series II) at Duke University, and the efficacy of digestion and accuracy of the methods was monitored by regular digestion and analysis of soil (NIST SRM 2711a) and rock standards (OREAS 753, USGS G2). For the elements of interest (Li, Cs, Ta, Rb, Sr, K), recoveries were >90 % in the standards.

For Sr-isotopes, ~200–2000 ng of Sr was prepared from digested samples. Sr was purified with Sr-specific resin (particle size 50–100 μm, Eichrom) in PTFE microcolumns (bed volume 150 μL) conditioned and rinsed with HNO_3 and eluted with Milli-Q water (Hill et al., 2024a, 2024b). In several of the pegmatite samples with high Rb concentrations and high Rb/Sr ratios, Rb was not completely removed by the standard column method. These samples were reprocessed first with a fluoride-coprecipitation step following the procedure described in Liu et al. (2020). Briefly, the sample was reacted with HF to precipitate fluorides in which Sr is preferentially enriched while Rb remains in solution. The fluoride precipitates were then redissolved in HCl and H_3BO_3 and evaporated to dryness and the sample was then processed through the standard Sr column method.

Analysis of Sr-isotopes followed standard procedures and was conducted on a ThermoFisher Triton thermal ionization mass spectrometer (TIMS) at Duke University. The purified Sr, in H_3PO_4, was loaded onto single Re filaments with a $TaCl_5$ load solution. The $^{86}Sr/^{88}Sr$ signal was normalized to 0.1194 and the ^{85}Rb signal was monitored to ensure that the ^{87}Rb isobaric interference on ^{87}Sr was negligible and samples were re-run if an ^{85}Rb signal was present. The USGS G2 granite standard was run through the same digestions and Sr separation procedure yielding a value of 0.709762 ± 0.000015 (n = 3) and USGS GSP-2 granodiorite was also run through the fluoride coprecipitation method yielding a value of 0.765069 (n = 1). Repeated analysis of NIST SRM 987 yielded a value of 0.710246 ± 0.000009 (n = 24). All standards were in agreement with accepted values from the GeoReM database (Jochum et al., 2005). We also analyzed two pegmatite standards without published $^{87}Sr/^{86}Sr$ data and provide provisional values; OREAS 753 is an LCT pegmatite standard measured at 2.5941 ± 0.0026 (n = 4) and OREAS 999 is a spodumene standard measured at 3.4097 ± 0.0005 (n = 2). All new data are presented in Table S2.

2.3. Statistical analysis

All statistical analyses were carried out in MATLAB (v 9.13.0). Wilcoxon rank sum tests were employed to determine if two groups have equal means and the statistical significance is reported as a p-value (p). Linear correlations were performed as specified where r^2 represents the correlation coefficient and p indicates significance.

3. Results

3.1. Rb/Sr ratios and Sr-isotopes in global pegmatites and host rocks

Whole-rock analyses of LCT pegmatites have a wide range in Rb/Sr ratios (0.6–4450), while the average value of each pegmatite district ranges from 2.5 to 669 (Fig. 2A, Table S1), reflecting the geochemical

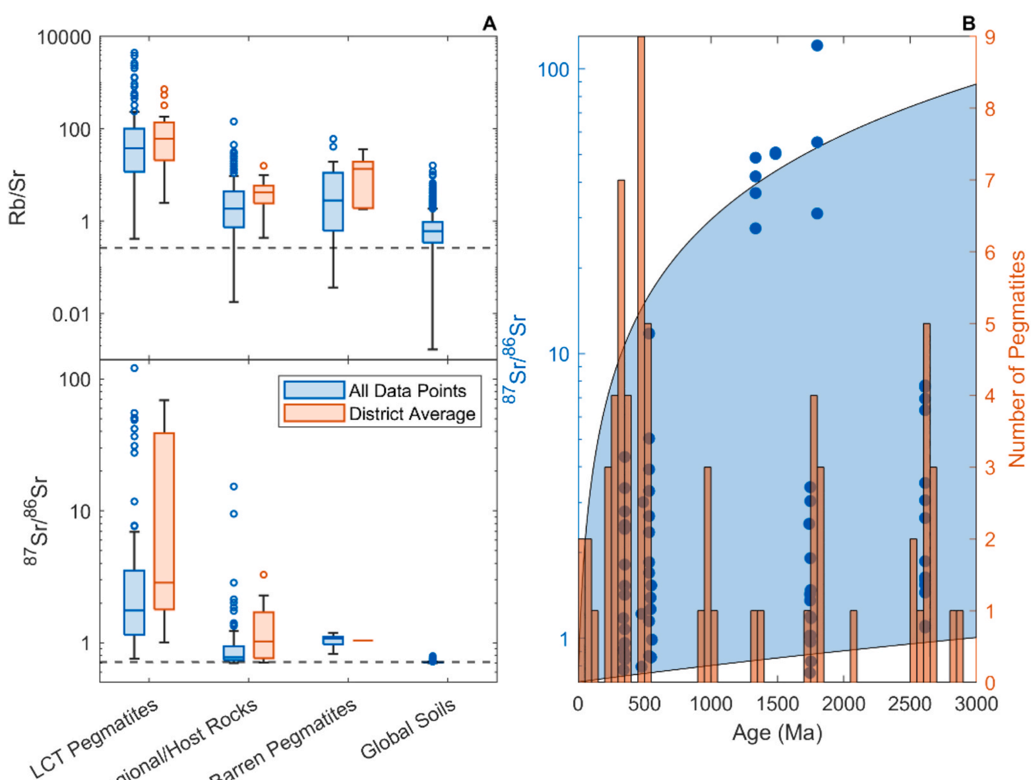

Fig. 2. *(A) Box plots of R/Sr (log scale) and $^{87}Sr/^{86}Sr$ ratios (log scale) in whole-rock LCT pegmatites relative to those of host rocks and other regional rocks, barren pegmatites, and global soils. In all instances, LCT pegmatites typically have much higher ratios of both Rb/Sr and $^{87}Sr/^{86}Sr$ relative to local rocks and soils. Dashed lines represent crustal average values (Desem et al., 2025; Goldstein and Jacobsen, 1988; McDermott and Hawkesworth, 1990; Rudnick and Gao, 2003). (B) The $^{87}Sr/^{86}Sr$ values of individual whole-rock LCT pegmatite samples (blue dots) and the modeled range in whole-rock LCT pegmatites over time (blue shading) relative to a histogram of the age distribution of LCT pegmatites (orange bars) (Bradley et al., 2017; McCauley and Bradley, 2014). The data show the large variations in $^{87}Sr/^{86}Sr$ in pegmatites and that older pegmatites can have much higher values. Data for individual samples generally fall within the range of average estimated values for pegmatite deposits and yet demonstrate that the entire deposits are not homogeneous. The modeled range of $^{87}Sr/^{86}Sr$ values was calculated as described in the methods. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)*

and mineralogical heterogeneity within and between LCT pegmatites. These are consistently higher than local host rocks and barren pegmatites ($p < 0.05$; Fig. 2A), with average values ranging from 0.4 to 35.8. Average $^{87}Sr/^{86}Sr$ values in LCT pegmatites range from ~0.95 to 69, with individual values as high as 121 in the ARA pegmatite measured as part of this study. By comparison, host rocks have $^{87}Sr/^{86}Sr$ ratios ranging between 0.70 and 3.28. While some host rocks show elevated $^{87}Sr/^{86}Sr$ values, the pegmatites at the same site generally plot above the regional background. Given the greater time for ^{87}Rb to decay to ^{87}Sr, older pegmatites can yield much higher $^{87}Sr/^{86}Sr$ ratios (Fig. 2B). Regardless, younger pegmatites, frequently around 300 to 500 Ma, can reasonably be expected to have relatively to extremely elevated average whole-rock $^{87}Sr/^{86}Sr$ ratios as calculated in the age distribution model of $^{87}Sr/^{86}Sr$ (Fig. 2B).

3.2. Soil profiles at ARA and TSB

The parent pegmatites at the ARA are both older and more fractionated and largely composed of K–Rb rich minerals (e.g. lepidolite and K-feldspar) (Falster et al., 1996), resulting in higher Rb/Sr of 521–2050 and $^{87}Sr/^{86}Sr$ of 31.07–121 signatures than at the younger and less fractionated TSB with a lower proportion of K–Rb-rich minerals (e.g. albite, spodumene) (Curry et al., 2025; Swanson, 2012) with Rb/Sr of 7.0–305 and $^{87}Sr/^{86}Sr$ of 0.882–4.337. Additionally, the ARA pegmatite dike is < 3 m deep while the pegmatite dike at the TSB is > 5–15 m deep.

At the ARA site, on-dike soils (n = 6) displayed elevated Li, Cs, Ta, and Rb concentrations (Figs. S1 and S2) that are used for tracers as discussed in Pierangeli et al. (2025) and Sirbescu et al. (2025). The on-dike soils are also characterized by distinctly high Rb/Sr ranging from 10.5 to 119 and $^{87}Sr/^{86}Sr$ ratios ranging from 1.278 to 6.842 (n = 7) (Fig. 3). These ratios decreased with distance from the dike, from 0.879 down to 0.735 (Fig. 3A), consistent with either mixing between pegmatite-derived soils and background soils or derived from the metasomatized host rock in the pegmatite contact aureole which can be enriched in Rb (Sirbescu et al., 2025). Samples collected along a hypothetical dike extension (n = 6) resembled background soils, showing no indication of a buried dike with Rb/Sr between 0.76 and 0.79 and $^{87}Sr/^{86}Sr$ between 0.740 and 0.742. The Rb/Sr and $^{87}Sr/^{86}Sr$ ratios are significantly higher in the on-dike soils than the off-dike soils ($p < 0.01$).

At the TSB site, on-dike soils (n = 4) also exhibited higher Rb/Sr (6.4–47.8) and $^{87}Sr/^{86}Sr$ (0.797–1.366) ratios than off-dike soils (n = 4; $p < 0.05$; Fig. 3) with Rb/Sr between 2.7 and 3.5 and $^{87}Sr/^{86}Sr$ between 0.739 and 0.755. However, differences between on- and off-dike soils were smaller than at ARA. Elemental concentrations of Li, Cs, Ta, and Rb were generally but not consistently higher in on-dike soils (Fig. S2 and described in Harmon et al., 2025).

The K/Rb ratio is an established method for pegmatite exploration, which we also considered in this study. The K/Rb ratio of the on-dike ARA soils ranges from 9.6 to 55, while off-dike soils range from 112 to 376 and the unknown samples from 311 to 336. The on-dike K/Rb ratios at the ARA are significantly ($p < 0.01$) lower than both the off-dike transition zone soils and the unknown samples. At the TSB the K/Rb ratio of on-dike soils ranges from 27 to 78 and off-dike soils from 39 to 100. These on-dike soil K/Rb ratios are not significantly lower than the off-dike soils, which is consistent with the findings of Harmon et al. (2025), where low K/Rb ratios were found in off-dike samples surrounding the known dikes.

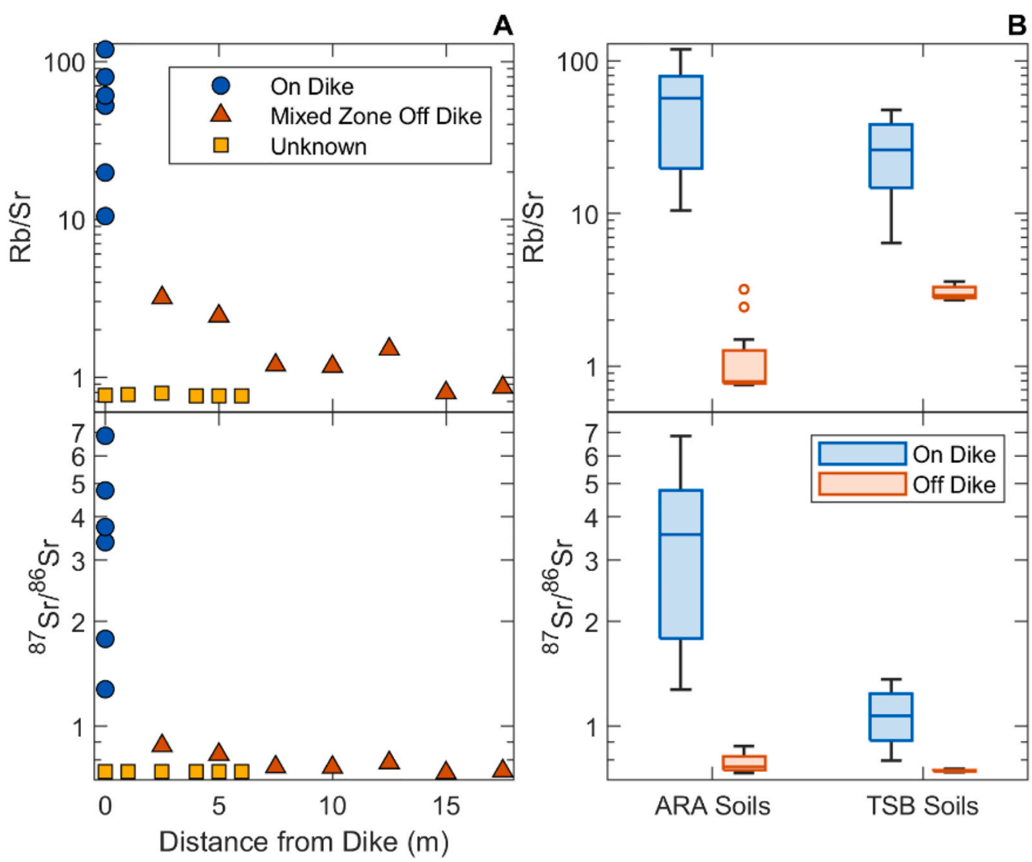

Fig. 3. (A) Rb/Sr and $^{87}Sr/^{86}Sr$ ratios versus distance from ARA pegmatite dike based on a soil transect across the ARA pegmatite. Soils on-dike show distinctly elevated Rb/Sr and $^{87}Sr/^{86}Sr$ ratios while these ratios decrease with distance from the dike, suggesting mixing with distance with background soil. Samples collected over the hypothetical extent of the dike, defined as "unknown" show low Rb/Sr and $^{87}Sr/^{86}Sr$ ratios, similar to soil collected farthest from the dike. (B) Boxplots of Rb/Sr and $^{87}Sr/^{86}Sr$ showing the distinctive higher Rb/Sr and $^{87}Sr/^{86}Sr$ ratios in soils on-dike relative to off-dike at both the ARA and TSB profiles.

4. Discussion

4.1. Distinction between Rb/Sr in pegmatites and host rocks

The Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of LCT pegmatites are generally distinct from the background geology despite some overlap with potentially altered host rocks. Contact aureoles and metasomatic halos can develop during pegmatite emplacement, producing elevated values of Rb/Sr up to ~50 and $^{87}Sr/^{86}Sr$ up to ~15 in host rocks (Falster et al., 1996; Makagan et al., 2000; Preinfalk et al., 2002). However, these effects are typically limited to within ~10 m of dike margins (e.g. Makagon et al., 2000). In contrast, barren pegmatites and host rocks rarely exceed Rb/Sr ratios of 10 and $^{87}Sr/^{86}Sr < 0.75$, reinforcing the diagnostic contrast between LCT pegmatites and surrounding lithologies (Fig. 2A). The age distribution model of $^{87}Sr/^{86}Sr$ (Fig. 2B) also demonstrates that the average $^{87}Sr/^{86}Sr$ value even in younger pegmatites can be uniquely radiogenic, inferring that this diagnostic contrast between pegmatites and surrounding lithologies should be consistent in pegmatites of most ages and degrees of fractionation.

The inorganic fraction of soils inherits the composition of the weathered underlying bedrock, and therefore, distinct isotopic and elemental signatures of pegmatites can be preserved in overlying surface soils (Best et al., 2019; Capo et al., 1998; Dere and Santini, 2024; McQueen, 2012). Consequently, this sharp geochemical contrast between LCT pegmatites and country rock should also be expressed in the compositions of the overlying soils. Large-scale surveys (of the USA and Europe ("GEMAS," 2025; Smith et al., 2011) confirm that global soils have Rb/Sr ratios between 0.0017 and 16, but the majority (90 %) fall between 0.1 and 3 (Fig. 2). A global compilation of soil $^{87}Sr/^{86}Sr$ by Bataille et al. (2020) has shown that $^{87}Sr/^{86}Sr$ ranges between 0.7033 and 0.7911, and of these less than 1 % of the soil samples had $^{87}Sr/^{86}Sr > 0.75$ (Fig. 2). These background ranges are substantially lower than values observed in pegmatites, indicating that soils developed above pegmatite dikes should retain uniquely elevated signatures.

4.2. Assessing Rb/Sr and Sr-isotopes as tracers in soils

In both investigated cases, the geochemical composition of the soil on-dike has elevated Rb/Sr and $^{87}Sr/^{86}Sr$ reflecting the direct connection to the underlying pegmatite (Fig. 3), but with considerable variability. There is no overlap between the Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of the on- and off-dike samples at the ARA and at the TSB, reinforcing our hypothesis that these ratios could be an effective tracer of pegmatite location. Comparing these two sites, the tracers appear to work despite the considerable differences in values and in physical conditions and geologic histories of the sites. For instance, the ARA soils are shallower (<3 m to pegmatite) and postglacial (less than 10,000 year old) meaning that they have a more direct connection to the highly fractionated and highly radiogenic parent pegmatite as compared to the much deeper (>5–15 m to pegmatite) and older soils (at least 1.3–3.1 million years old) (Bacon et al., 2012) at the TSB site with less direct connection to a much less fractionated and less radiogenic pegmatite.

While the Rb/Sr and $^{87}Sr/^{86}Sr$ values of the on-dike soils are elevated, they are still typically below that of the parent pegmatite, suggesting that some of these signatures have been diluted by the background signature of the local host rocks. Fig. 4 shows a calculated two endmember mixing curve between the mean Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of whole-rock pegmatites and the local host rocks, demonstrating that all soil samples fall along or near this hypothetical mixing line at both the ARA and the TSB sites and that the soils are mixtures of the weathered products of these two endmembers. The fraction of the Rb/Sr and $^{87}Sr/^{86}Sr$ signatures derived from the parent pegmatite in on-dike soils at the ARA ranges from ~10 to 50 %, while at the TSB on-dike soils have a much higher fraction ranging from ~60 to 95 % and in some cases overlap with some of the pegmatite values (Fig. 4). Additionally, at the ARA, the mixed zone soils along the transect leading away from the dike also fall along the mixing line and have less than 5 % of the pegmatite signature despite their relatively high Rb/Sr and $^{87}Sr/^{86}Sr$ signatures (Fig. 4). This contrasts with the TSB where the off-dike samples also fall along this mixing line with slightly elevated Rb/Sr and $^{87}Sr/^{86}Sr$ relative to the local host rocks, suggesting that up to ~40–60 % of this soil signature is derived from the pegmatite (Fig. 4). The lower fraction of pegmatite signature in the ARA on-dike soils could reflect the immature and glaciated nature of the soils which would have been physically mixed with the regional geology (Pierangeli et al., 2025), while the apparent mixing zone along the transect leading away

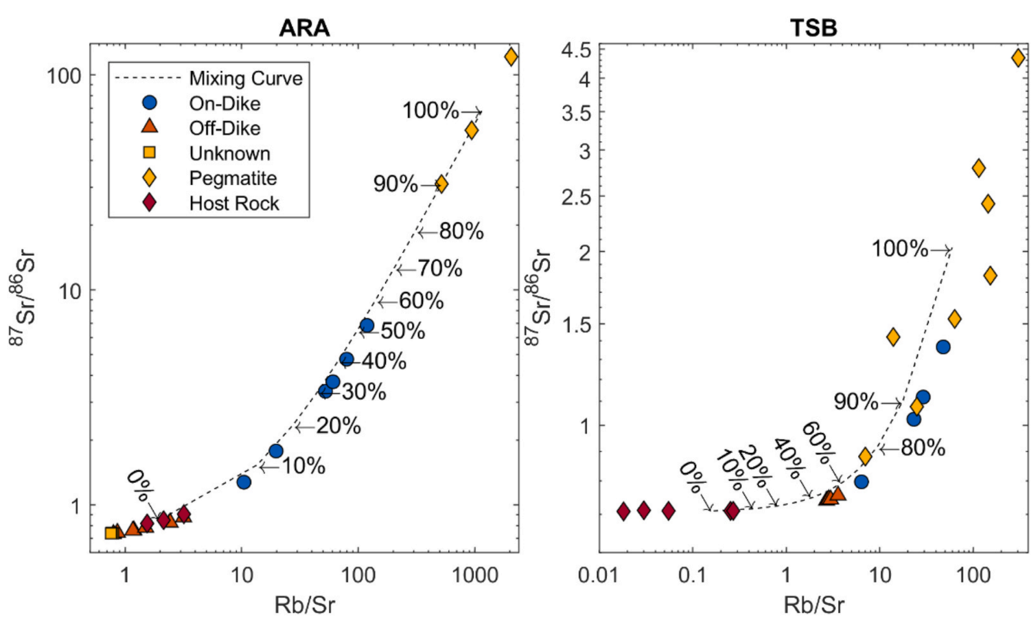

Fig. 4. Calculated mixing curves in soils at the ARA and TSB sites. The endmembers are the mean value of Rb/Sr and $^{87}Sr/^{86}Sr$ in the whole-rock pegmatites and host rocks at each site, thus some samples fall outside the mixing curve. All soil samples fall on or near these mixing curves and the listed percentages are the fraction of pegmatite signature along the curve. At the ARA the relatively low fraction of a pegmatite signature in the on-dike soils is still distinct from those off-dike while at the TSB the on-dike soils retain a much greater fraction of this pegmatite signature and those off-dike also have some influence from the pegmatite.

from the pegmatite may reflect the metasomatic alteration of underlying bedrock adjacent to the ARA, altered during pegmatite emplacement (Liu et al., 2010; Sirbescu et al., 2025), rather than direct mixing with the pegmatite-derived soils. The TSB soils however are much older and the highly weathered products of underlying bedrock (Daniels et al., 1999), which could indicate that these soils are less mobile and less mixed. An alternative explanation could be related to the mineralogy of the TSB pegmatites as they weather to soils, where muscovite, a K–Rb-rich mica common to the TSB pegmatites (Swanson, 2012), is among the least weatherable minerals (Lasaga, 1984), and would have among the highest Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of any mineral in the pegmatite (Clark and Černý, 1987). Thus, a muscovite Rb/Sr and $^{87}Sr/^{86}Sr$ signature could be more prevalent in these highly weathered soils resulting in an apparently elevated pegmatite signature. Similar findings have been observed in granitic soil sequences where the least weatherable minerals control the Rb/Sr and $^{87}Sr/^{86}Sr$ ratios in the oldest soils (Blum and Erel, 1997). The agricultural history of the TSB may have also facilitated greater mixing of the pegmatite signature into the nearby off-dike soils. Nonetheless, there is clearly some mixing between TSB on-dike and off-dike soils as evidenced by the fact that all soil compositions fall along the mixing line. This demonstrates that (1) the elevated Rb/Sr and $^{87}Sr/^{86}Sr$ pegmatite signatures translated to soils can be significantly diluted by background soil values and still be effective indicators for the occurrence of underlying pegmatites; and (2) the pegmatite signature can be widely dispersed in soils around a pegmatite but the on-dike soils still have uniquely elevated values as demonstrated by distinct ratios in the on- relative to off-dike soils at the TSB.

Since pegmatites have elevated Rb/Sr and $^{87}Sr/^{86}Sr$ ratios, thresholds can be set to differentiate between on- and off-dike soils. For example, Rb/Sr ratios greater than 10 and $^{87}Sr/^{86}Sr$ ratios greater than 1.0 at both the ARA and the TSB are only found in on-dike soils. However, some on-dike samples, especially for the deep dike, fall below these thresholds as shown with the TSB soil data (i.e. with Rb/Sr at 6.4 and $^{87}Sr/^{86}Sr$ at 0.797), and are similar to off-dike samples (Fig. 3). Furthermore, the soil transect at the ARA demonstrates that there is a mixing zone between the on-dike soils and the off-dike soils where Rb/Sr and $^{87}Sr/^{86}Sr$ ratios are both below that of the on-dike soils and above that of the background. This would infer that these elevated ratios could reasonably be misconstrued as elevated compared to background levels and therefore suggestive of a subsurface dike. When setting effective general thresholds, a site-specific calibration should be carried out, especially since there is great variability in Rb/Sr and $^{87}Sr/^{86}Sr$ ratios in global pegmatites (section 4.1) and lower thresholds may be more effective with less fractionated or less radiogenic pegmatites. Additionally, Rb/Sr and $^{87}Sr/^{86}Sr$ can be paired together where both high Rb/Sr and high $^{87}Sr/^{86}Sr$ signatures of on-dike soils fall along a strong trend ($r^2 = 0.99$, $p < 0.001$) and over a large range of values, while off-dike soils cluster along the same trend at much lower values (Fig. 4). This is the case at both sites and demonstrates that these tracers can complement each other and may be more successful when paired together.

Additionally, previous work at the TSB has shown that elemental concentrations of K, Rb, and Li in bulk soils are not always elevated in on-dike soils (Harmon et al., 2025). While the sample size at the TSB is small ($n = 4$ on-dike and $n = 4$ off-dike), the distinct nature of Rb/Sr and $^{87}Sr/^{86}Sr$ in pegmatites and on-dike soils presented in this study suggests that they may prove to be more effective than the use of other elemental indicators. At the ARA, however, such elemental indicators in bulk soils were shown to be regularly effective at identifying subsurface pegmatites (Sirbescu et al., 2025), suggesting that Rb/Sr and $^{87}Sr/^{86}Sr$ may be complimentary to such established methods in similar settings to the ARA.

4.3. Comparing Rb/Sr and Sr-isotopes with K/Rb

As demonstrated with the ARA transect, mixing zones (or metasomatic alteration of underlying host rocks) adjacent to pegmatites complicate interpretation by producing transitional signatures with relatively elevated Rb/Sr and $^{87}Sr/^{86}Sr$. Distinguishing on-dike soils from off-dike mixed zones is important for eliminating possible uncertainty regarding the exact location of a subsurface dike. This can be accomplished by setting thresholds or pairing Rb/Sr and $^{87}Sr/^{86}Sr$ as described in section 4.2. However, other tracers such as K/Rb ratios have also been developed and may compliment the tracers presented in this study and might further increase the resolution of on- and off-dike soil determination. The K/Rb tracer has been used to assess the degree of fractionation in LCT pegmatites (i.e., lower K/Rb indicative of high degrees of fractional crystallization) (Černý et al., 1985) and has also been used for pegmatite exploration (e.g. Harmon et al., 2025; Matheis, 1981; Selway, 2005). K/Rb is not always successful as an established tracer for the analysis of thicker or older bulk soils (but may be in soil mica fractions), and low K/Rb expected in bulk soils overlying pegmatites have also been found in off-dike soils surrounding pegmatite dikes of the TSB region (Harmon et al., 2025).

Much like Rb/Sr, K/Rb is indicative of the highly fractionated nature of pegmatites, and adding K/Rb may provide an additional indicator to discriminate between on-dike and off-dike soils. At both sites, the variations of K/Rb with either Rb/Sr or $^{87}Sr/^{86}Sr$ also fall along a mixing line (Fig. 5). At the ARA, pairing the K/Rb ratio and either the Rb/Sr or $^{87}Sr/^{86}Sr$ ratio clearly distinguishes the on-dike and off-dike soils and the relative fraction of the parent pegmatite contributing to these signatures in the on- and off-dike soils is approximately the same as discussed in section 4.2 using only the Rb/Sr and $^{87}Sr/^{86}Sr$ tracers. This demonstrates that at the ARA site there is little difference between pairing Rb/Sr with $^{87}Sr/^{86}Sr$ and pairing those with K/Rb. At the TSB however, this distinction is less clear. Three of the on-dike samples were clearly separated from the off-dike samples, and yet the one on-dike sample from the deepest dike (>15 m deep) has a similar K/Rb ratio to the off-dike samples (Fig. 5). This sample also has relatively elevated Rb/Sr and $^{87}Sr/^{86}Sr$ relative to the off-dike soils and falls above the projected mixing line as well (Fig. 5); possibly caused by dilution of the K/Rb ratio or fractionation of K/Rb during weathering in the deeper soil profile. All together, this would suggest that K/Rb may not always be a sensitive tracer at the TSB, while Rb/Sr and $^{87}Sr/^{86}Sr$ are. While K/Rb may not be as effective as Rb/Sr or $^{87}Sr/^{86}Sr$ tracers, it can still be paired with either and any additional samples should fall along the same mixing line. This means that the fraction of pegmatite material contributing soil geochemistry can be estimated and this could be used as a proxy for determining proximity to an underlying pegmatite dike.

4.4. Implications for global pegmatite exploration

The Rb/Sr and Sr isotope compositions of Li-rich pegmatites are primarily governed by two factors: (1) the degree of magmatic fractionation, which produces relatively to highly elevated Rb/Sr ratios, and (2) the age of intrusion, which determines the extent of ^{87}Rb decay and the resulting radiogenic $^{87}Sr/^{86}Sr$ signature. These dual factors explain the contrasting values observed at the two study sites: the ARA pegmatite is both old (~1800-1400 Ma) (Droubi et al., 2025; Holm et al., 2005; Sirbescu et al., 2025) and highly fractionated (Falster et al., 1996; Sirbescu et al., 2008), yielding very high Rb/Sr and $^{87}Sr/^{86}Sr$ ratios, whereas the younger TSB pegmatite (~349 Ma) (Bradley et al., 2017), derived by partial remelting of metasediments and granite (Curry et al., 2025; Koopmans et al., 2023), displays lower Rb/Sr and less radiogenic $^{87}Sr/^{86}Sr$ values.

At both locations, these geochemical signatures are inherited, from pegmatites, by overlying soils to varying degrees and provide a clear distinction from background off-dike soils that reflect the regional geology. Pairing Rb/Sr and $^{87}Sr/^{86}Sr$ enhances this distinction and may be more robust than using a single tracer (e.g. K/Rb) or elemental variations. Paring these tracers can be used to estimate the relative geochemical effect that the parent pegmatites and host rocks have on

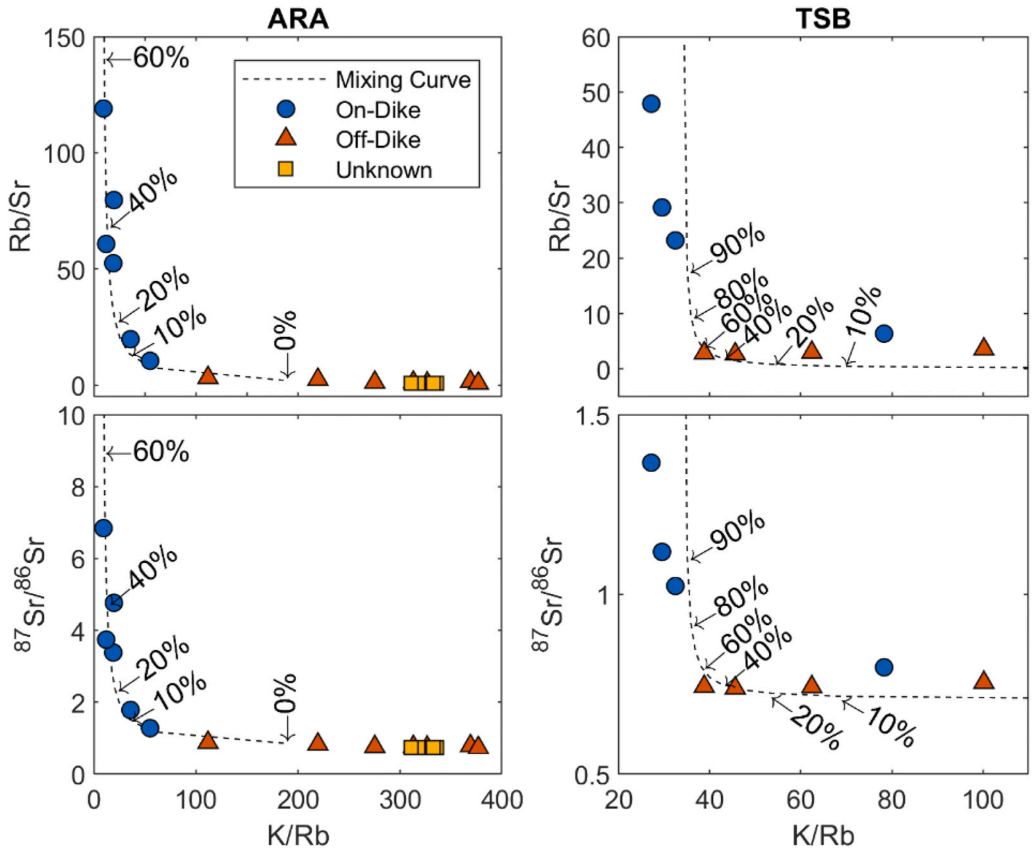

Fig. 5. K/Rb versus Rb/Sr and $^{87}Sr/^{86}Sr$ at ARA and TSB sites. The variations of the different pairs ratios in the soils are consistent with mixing lines between host rocks and. Using K/Rb as an additional tracer separates effectively separates on-dike from off-dike soils at the ARA but is less successful at the TSB. The end members are the same as described in Fig. 3 and use the average value of pegmatite samples and host rocks at each site.

overlying soils, and may be useful for estimating soil proximity to an underlying pegmatite dike. Additionally, all soils at both locations fall along mixing lines between the pegmatite and host rocks and thus many off-dike soils have elevated Rb/Sr and $^{87}Sr/^{86}Sr$ as compared to the background signature (Fig. 4); this relatively elevated signature may be useful during low resolution soil surveys to delineate areas for a higher resolution soil survey. While both Rb/Sr and $^{87}Sr/^{86}Sr$ are effective tracers, their behavior under different weathering regimes may diverge; Sr isotopes, being conservative, are likely to remain more robust than Rb/Sr in soil systems, where Rb/Sr can be fractionated since Rb and Sr behave differently (Blum and Erel, 1997). Future research should consider how and if such fractionation occurs in soils overlying pegmatites and how Rb/Sr and $^{87}Sr/^{86}Sr$ may vary with soil depth. It has also been suggested that soil sampling for exploration should avoid areas of glacial till, as tills represent mixtures of material derived from multiple bedrock sources (Sirbescu et al., 2025). Nevertheless, because the Rb/Sr and $^{87}Sr/^{86}Sr$ signatures of LCT pegmatites are markedly distinct from most regional lithologies, even small contributions of pegmatite material incorporated into overlying glacial-till-derived soils may produce detectable Rb/Sr and $^{87}Sr/^{86}Sr$ anomalies. Since this study focused only on soils developed directly on bedrock, future work should test the applicability of these tracers in soils formed on glacial till and other transported regoliths.

Although this study employed high-precision methods (e.g. TIMS), the large contrasts in values with extreme variations in $^{87}Sr/^{86}Sr$ and large variations in Rb/Sr, suggest that lower resolution and more widely available instruments could also be effective for exploration. For example portable XRF (pXRF) can rapidly measure Rb, Sr, and K in the field (Balaram and Sawant, 2022; Young et al., 2016), enabling in-situ assessment of Rb/Sr and K/Rb, while quadrupole ICP-MS (after Sr column separation) can provide lower-precision yet effective $^{87}Sr/^{86}Sr$ information (Vanhaecke et al., 1999). This potential scalability makes the approach practical for field sites and regional surveys. Pierangeli et al. (2025) recently published a dataset of bulk soils at the ARA and other nearby pegmatites through measurement of Rb, Sr, and K with pXRF. Using this data and plotting K/Rb vs Rb/Sr produces the same results we show here, where elemental data measured by pXRF of all samples fall along a mixing line and low K/Rb and high Rb/Sr consistently correspond to on-dike soils (Fig. S3).

The distinctiveness of Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of LCT pegmatites from around the world relative to nearly all other rocks and soils suggests broad applicability of this method to global LCT pegmatite exploration. Because most pegmatites intrude into similar host lithologies (mica schists or amphibolites in the upper greenschist to amphibolite facies) (Černý, 1992), the general mineralogy of host rocks is expected to be similar and the geochemical contrast between LCT pegmatites and host rocks should be consistent across deposits. Additionally, spodumene is the primary Li-ore mineral in most LCT pegmatite deposits such as the TSB albite-spodumene pegmatites, yet some deposits, including the ARA (lepidolite-subtype), have Li primarily hosted in other minerals such as lepidolite (Bradley et al., 2017) and there can be considerable differences in the Rb/Sr and $^{87}Sr/^{86}Sr$ signatures of these minerals. For example at the Harding pegmatite in New Mexico spodumene and lepidolite co-occur where spodumene, a Li–Al-rich pyroxene, does not appreciably incorporate either Rb or Sr and has Rb/Sr ratios ~14 and $^{87}Sr/^{86}Sr$ ratios ~1.4, while lepidolite, a Li–K–Al-rich mica, readily incorporates Rb but not Sr with extremely high Rb/Sr ratios ~166 and $^{87}Sr/^{86}Sr$ ratios ~199 (Register, 1979). Consequently, LCT pegmatites with primarily lepidolite hosted Li could be even more favorable to the methods presented here and ore zones rich in K-bearing minerals (micas, K-feldspar) may provide even stronger soil signatures than spodumene-dominated zones. Further work is needed to assess how these mineralogical differences are expressed in the composition of the overlying soils.

5. Conclusions

This study demonstrates that globally, whole-rock LCT pegmatites have elevated and unique Rb/Sr (≫10) and $^{87}Sr/^{86}Sr$ (≫1.0) ratios that are distinct from other common rocks and soils (Rb/Sr < 10 and $^{87}Sr/^{86}Sr < 0.75$–1.0), and that these distinct signatures are translated to the compositions of overlying soils (Rb/Sr > 10 and $^{87}Sr/^{86}Sr > 1.0$) due to the weathering of the underlying pegmatite. Our results show that Rb/Sr and $^{87}Sr/^{86}Sr$ variations in surface soils are robust tools for identifying the occurrence of subsurface pegmatites and distinguishing between on-dike and off-dike soils across diverse geological settings. We show that these geochemical methods are applicable in two separate sites with pegmatites formed by different processes (i.e., magnitude of fractional crystallization, mineralogy, and ages of pegmatites), different climate and soil types (i.e., temperate climate with post-glaciation soils in a forested region at the ARA versus subtropical climate with highly weathered soils in an agricultural region at the TSB), and with varied depths to the underlying pegmatites (<3 m at the ARA and >5–15 m at the TSB). This suggests that these are robust geochemical tracers for identifying subsurface Li-rich pegmatites and can be applicable for exploration efforts around the world.

CRediT authorship contribution statement

Grace A. Hall: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gordon D.Z. Williams:** Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mona-Liza C. Sirbescu:** Writing – review & editing, Writing – original draft, Validation, Methodology, Data curation, Conceptualization. **P. Louis Lu:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Gary S. Dwyer:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis. **Daniel D. Richter:** Writing – review & editing, Writing – original draft, Supervision, Resources, Methodology, Funding acquisition. **Avner Vengosh:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2025.106631.

Data availability

All data is available in the paper.

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