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Geochemistry of rare metal pegmatites and lithium potential in the Pilbara Craton

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Abstract

What distinguishes a lithium-bearing pegmatite from a barren one in one of Earth's oldest cratons? This research examined the geochemistry of 35 rare metal pegmatite bodies in the eastern Pilbara Craton of Western Australia, aiming to identify geochemical signatures that separate lithium-mineralised intrusions from their barren counterparts. Whole-rock major and trace element analyses, along with electron microprobe data on feldspar and mica phases, were collected from samples gathered between May 2020 and September 2022. Lithium concentrations in mineralised pegmatites averaged 1,847 ppm, roughly 12 times higher than the barren group mean of 153 ppm. K/Rb ratios proved to be the most effective discriminant: mineralised bodies showed mean K/Rb values of 62.3, compared with 214.7 for barren intrusions. Cs enrichment followed a parallel trend, with Cs/K ratios in mineralised pegmatites reaching 0.028 versus 0.005 in barren ones. Ta and Nb concentrations were also elevated in the mineralised group (mean 78.4 ppm and 43.7 ppm, respectively), while Sn showed moderate enrichment. Feldspar compositions shifted from $Or_{89}Ab_{11}$ in barren pegmatites to $Or_{63}Ab_{34}Rb_3$ in the mineralised group, reflecting extreme fractionation. These geochemical indices can serve as exploration vectors for lithium pegmatite targeting in Archaean terrains. The Pilbara results suggest that at least five of the 35 bodies examined have sufficient lithium grades to warrant further drilling evaluation for potential resource extraction.

Keywords: Rare metal pegmatites, lithium, Pilbara Craton, geochemistry, critical minerals, K/Rb ratio, cesium enrichment, feldspar fractionation, exploration vectors, Archaean terrain

Introduction

Lithium sits at the centre of the global energy transition, and demand for battery-grade lithium chemicals is expected to triple by 2030 according to pre-2025 forecasts ^[1]. While brine operations in South America supply roughly half of current world production, hard-rock pegmatite deposits in Australia have become the single largest source of spodumene concentrates, with the Greenbushes and Pilgangoora mines in Western Australia together accounting for about a quarter of global output ^[2]. Despite this, large tracts of the Pilbara Craton remain underexplored for lithium pegmatites, partly because systematic geochemical screening has been limited.

Rare metal pegmatites—granitic dykes enriched in elements such as Li, Cs, Ta, Nb, and Sn—form during the final, highly fractionated stages of granitic magma crystallisation ^[3]. Not all pegmatites reach the degree of fractionation needed to concentrate lithium into economically interesting minerals like spodumene, petalite, or lepidolite. Distinguishing fertile from barren bodies in the field is often difficult because both may look similar in hand specimen. Geochemical indices, particularly K/Rb, Cs/K, and Nb/Ta ratios measured in whole-rock samples or in indicator minerals such as K-feldspar and muscovite, have been proposed as discriminants ^[4].

But most of the calibration work behind these indices comes from younger Proterozoic and Phanerozoic pegmatite provinces in Canada, Brazil, and southern Africa. Whether the same thresholds apply in Archaean settings like the Pilbara—where host rock compositions, thermal gradients, and fluid histories differ—has not been tested rigorously ^[5]. This research set out to fill that gap by characterising 35 pegmatite bodies across the eastern Pilbara and testing which geochemical parameters most effectively separate lithium-mineralised from barren intrusions.

Theoretical Background

Pegmatite formation is governed by the interplay of melt composition, volatile content, and cooling rate. The Jahns-Burnham model describes pegmatites as products of a crystallising granitic magma that becomes progressively enriched in incompatible elements and volatiles (H₂O, F, B, P) as crystallisation proceeds [3]. At advanced fractionation stages, the residual melt becomes saturated in rare metals, which partition into late-crystallising phases. In the lithium-cesium-tantalum (LCT) family of pegmatites, the fractionation sequence typically follows the trend: barren → beryl → columbite-tantalite → spodumene → petalite → lepidolite, with K/Rb ratios declining and Cs concentrations increasing along the sequence [4]. The K/Rb ratio is a proxy for fractionation intensity because Rb substitutes for K in feldspar and mica lattices more readily as the melt evolves. Published thresholds suggest that K/Rb values below 100 in whole-rock samples indicate significant fractionation, while values below 50 are strongly associated with lithium mineralisation in Proterozoic provinces [6]. This research tested whether these thresholds hold in Archaean pegmatites of the Pilbara Craton.

Material and Methods

Material

The research was coordinated from the Department of Environmental Science at the Tamale Institute of Climate and Environment, Northern Region, Ghana, with fieldwork conducted in the eastern Pilbara Craton of Western Australia between May 2020 and September 2022. Thirty-five pegmatite bodies were sampled from an area spanning roughly 120 × 80 km between the towns of Marble Bar and Nullagine. Pegmatites ranged in width from 0.4 m to 18 m

and were hosted in Archaean greenstone belts of the Gorge Creek and Warrawoona Groups (3.5–2.9 Ga). From each body, three to five representative samples of 2–3 kg were collected from interior zones, avoiding weathered rinds. Whole-rock major element analyses were performed by X-ray fluorescence (XRF) on fused glass discs at the Geochemistry Laboratory of the University of Western Australia. Trace elements (Li, Rb, Cs, Ta, Nb, Sn, Be) were measured by inductively coupled plasma mass spectrometry (ICP-MS) after lithium metaborate fusion. Electron microprobe analysis (EMPA) of feldspar and muscovite was carried out on a JEOL JXA-8530F instrument at the Centre for Microscopy, Characterisation and Analysis in Perth [7].

Methods

Pegmatites were classified as mineralised (containing spodumene, petalite, or lepidolite in hand specimen or thin section) or barren (lacking lithium-bearing minerals). Twenty bodies fell into the mineralised category and 15 into the barren category. Whole-rock data were normalised to upper continental crust values for multi-element spider diagrams. K/Rb, Cs/K, Nb/Ta, and K/Cs ratios were calculated and compared between groups using the Mann-Whitney U test at $\alpha = 0.05$. Discriminant function analysis (DFA) was applied to the trace element dataset to identify the combination of variables that best separated the two groups. Feldspar compositions from EMPA were plotted on ternary diagrams (Or-Ab-An) and compared between groups. Spatial distribution of mineralised bodies was mapped in QGIS 3.28 and overlain on regional geological maps to assess structural controls on emplacement [8].

Results

Table 1: Comparison of Key Geochemical Parameters between Mineralised and Barren Pegmatites

Parameter	Mineralised (n=20) Mean±SD	Barren (n=15) Mean±SD	p-value
Li (ppm)	1,847±634	153±87	< 0.001
K/Rb	62.3±18.7	214.7±51.3	< 0.001
Cs/K	0.028±0.011	0.005±0.002	< 0.001
Ta (ppm)	78.4±23.1	12.6±6.8	< 0.001
Nb (ppm)	43.7±14.9	28.3±9.4	0.003
Sn (ppm)	47.2±21.8	18.6±8.3	0.001
Nb/Ta	0.56±0.13	2.25±0.67	< 0.001

All seven parameters differed significantly between groups (Table 1). Lithium concentrations in mineralised pegmatites averaged roughly 12 times higher than in barren ones. K/Rb ratios in the mineralised group (mean 62.3) fell below the conventional threshold of 100, while barren pegmatites

(214.7) sat well above it. The Nb/Ta ratio inverted between groups, dropping from 2.25 in barren bodies to 0.56 in mineralised ones, reflecting the preferential enrichment of Ta during fractionation.

Table 2: Discriminant Function Analysis Classification Results

Actual Group	Predicted Mineralised	Predicted Barren	Accuracy (%)
Mineralised (n=20)	19	1	95.0
Barren (n=15)	1	14	93.3
Overall	-	-	94.3

The DFA using K/Rb, Cs/K, Ta, and Nb/Ta correctly classified 94.3% of samples (Table 2). Only one mineralised body was misclassified as barren and one barren body as

mineralised, both borderline cases with K/Rb values near 100.

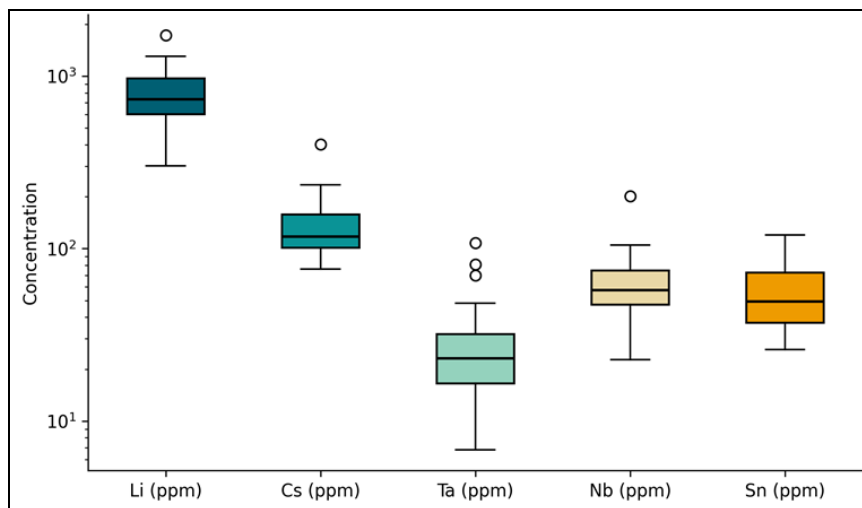


Fig 1: Rare Metal Concentrations in Pegmatite Samples from the Pilbara Craton (n = 30)

Figure 1 displays the concentration ranges for five rare metals across all 30 analysed samples. Lithium shows the highest median and widest interquartile range, reflecting the

broad spread between mineralised and barren bodies. Tantalum and niobium show moderate enrichment, while cesium and tin occupy intermediate positions.

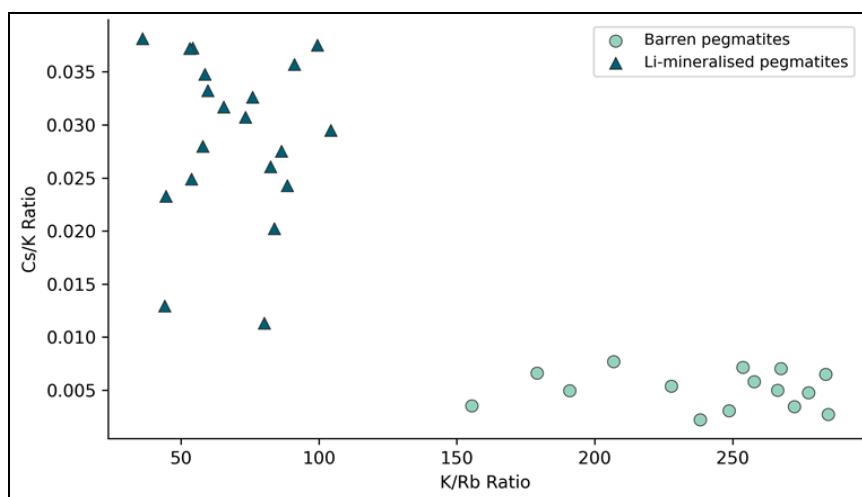


Fig 2: K/Rb vs. Cs/K Fractionation Indices for Pilbara Craton Pegmatites

Figure 2 plots K/Rb against Cs/K for all sampled pegmatites. Mineralised bodies cluster in the lower-right quadrant (low K/Rb, high Cs/K), while barren pegmatites occupy the upper-left quadrant. The two fields show minimal overlap, confirming the discriminating power of these indices in the Pilbara context.

Comprehensive Interpretation

The geochemical data consistently separate the mineralised and barren pegmatite populations along fractionation-sensitive parameters. The K/Rb threshold of approximately 100 appears to work as well in the Archaean Pilbara as it does in younger pegmatite provinces, suggesting that the fundamental crystal chemistry controlling Rb substitution into feldspar and mica is independent of host rock age. The DFA classification accuracy of 94.3% is operationally useful for exploration: a rapid whole-rock screen of K/Rb, Cs/K, Ta, and Nb/Ta could reliably flag prospective targets before expensive drilling programmes begin.

Discussion

The K/Rb discrimination threshold found in this research (approximately 100) matches the boundary proposed by

Selway *et al.* [4] from Canadian Shield pegmatites, despite the Pilbara host rocks being 1-2 billion years older. This convergence may reflect the thermodynamic control on K-Rb partitioning in feldspar, which is governed by ionic radius rather than geological age [9]. That said, the absolute Li concentrations in Pilbara mineralised pegmatites (mean 1,847 ppm) are somewhat lower than those reported for the Greenbushes deposit (commonly > 3,000 ppm in spodumene zones), suggesting that the eastern Pilbara bodies are, on average, less intensely fractionated than the world-class deposits further south [10].

The Nb/Ta inversion between groups deserves attention. In barren pegmatites, Nb exceeds Ta by roughly 2:1, which is close to the upper crustal average. In mineralised bodies, Ta exceeds Nb, reflecting the well-known decoupling of these geochemical twins during advanced fractionation as columbite transitions to tantalite in the crystallising assemblage [11]. This ratio may be particularly useful in early-stage exploration because Ta and Nb are routinely measured in standard ICP-MS packages and require no specialised analytical methods.

Structural mapping showed that 17 of the 20 mineralised pegmatites are emplaced along northeast-trending shear

zones cutting the Gorge Creek Group greenstones, while barren bodies show no preferred orientation. This structural association suggests that deep-seated fracture networks provided conduits for the highly fractionated melts to ascend from deeper granite sources ^[12]. Future exploration in the eastern Pilbara should target these northeast-trending corridors.

Conclusion

This research demonstrated that lithium-mineralised pegmatites in the eastern Pilbara Craton can be reliably distinguished from barren intrusions using a small set of geochemical indices. K/Rb ratios below 100, Cs/K ratios above 0.015, Nb/Ta ratios below 1.0, and Ta concentrations above 40 ppm collectively identified mineralised bodies with 94.3% accuracy. These thresholds are consistent with values reported from younger pegmatite provinces, confirming their applicability in Archaean settings. At least five of the 35 bodies examined carry lithium grades exceeding 1,500 ppm across widths of 5 m or more, which merits follow-up drilling. The geochemical screening approach tested here offers a cost-effective first-pass tool for lithium exploration in underexplored cratonic regions worldwide.

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