

Sinclair: Australia's First Caesium Deposit: Discovery and Exploration Implications

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INTRODUCTION

The Sinclair caesium deposit, discovered in 2016, delineated in 2017 and developed in 2018, is Australia's first mining operation to commercially extract the caesium-rich mineral, pollucite, and represents a globally important discovery. As commonly noted (e.g., Trueman *et al.*, 2020), known economic caesium deposits are extremely rare with only three known mining operations having reported commercial quantities of pollucite; Bernic Lake Mine (Manitoba, Canada), Bikita Mine (Zimbabwe), and the Sinclair Mine (Western Australia).

The formation of pollucite only occurs in extremely differentiated, complex lithium-caesium-tantalum (LCT) pegmatites and given their size and rarity, caesium-rich deposits globally are either challenging to explore for or failed to form during the emplacement of the LCT pegmatite. The discovery and development of the Sinclair caesium mine, described in detail by Batt *et al.* (2020) has provided a rare opportunity to examine an extremely differentiated, complex LCT pegmatite with applied technologies to provide insight for future exploration and discoveries of economic caesium deposits.

DISCOVERY

The announcement of a significant caesium (Cs) intersection (6 m at 25.7% Cs₂O) associated with lithium-caesium-tantalum (LCT) pegmatites on the Pioneer Dome was reported by Pioneer Resources Ltd. on 17th October 2016 (Pioneer Resources Ltd. 2016a). Follow-up drilling delineated a cluster of pollucite lenses, named the Sinclair Caesium Deposit (Sinclair), with an initial Mineral Resource Estimate of 10,500 tonnes of the caesium ore, pollucite with a grade of 17.1% Cs₂O (Pioneer Resources Ltd. 2017). The commencement of mining operations was reported on 13th September 2018 (Pioneer Resources Ltd. 2018), less than 2 years from discovery.

Pollucite [(Cs,Na)₂(Al₂Si₄O₁₂) 2H₂O] is a rare mineral with a high value attributed to its high caesium content (~29.66% Cs₂O), which forms in extremely differentiated LCT pegmatite systems. Global supply is very constrained and world resource estimations are unavailable (USGS 2020). Caesium chemicals are sold in limited quantities under confidential contracts so a true market price is unavailable.

Caesium is used in the production of photoelectric cells, energy conversion devices, such as fuel cells, magneto-hydrodynamic generators, and polymer solar cells; however its main use is in the manufacture of caesium formate brine, a heavy liquid (1.8 to 2.4 g/cm³) used in high-pressure, high-temperature well drilling for oil and gas.

LOCATION AND GEOLOGICAL SETTING

The Sinclair caesium deposit is located 35 km north-northwest of Norseman in Western Australia (Fig. 1a). The mine is located within the Archaean-aged Yilgarn Craton of Western Australia, within the Coolgardie Domain of the Norseman – Wiluna Greenstone Belt, which contains several significant spodumene deposits, including Mt Marion and Bald Hill.

The Pioneer Dome is defined by a granitoid core that has intruded older Archaean-aged gneiss (Fifty Mile Tank Gneiss) and a greenstone sequence. The greenstone sequence comprises a mafic suite (black shale, ultramafic and mafic volcanics, and gabbro intrusions), which in turn has been stratigraphically overlain by a thick sedimentary sequence (Fig. 1b). Pegmatite bodies have preferentially intruded into the greenstone sequence. The Pioneer Dome and surrounding lithoscape has been metamorphosed to greenschist and lower-amphibolite facies and has been multiply deformed resulting in isoclinal folding (Griffin 1989).

At least 13 clusters of pegmatites, including LCT pegmatites, have been identified along a 20 km strike length on the eastern flank of the Pioneer Dome (Fig. 1c). The East Pioneer pegmatite corridor comprises a narrow (<1 km wide) mafic suite of rocks trending roughly north-south, faulted up against the Fifty Mile Tank Gneiss. This corridor is dominated by strong north-south cleavages and pegmatite dykes occur in both the gneiss and greenstones (Griffin 1990). To date the only available age determination is of the Fifty Mile Tank Gneiss dated at $\geq 2664 \pm 5$ Ma (Nelson 1997).

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The pegmatite wall zones typically consist of quartz, K and Na feldspars, and muscovite, while core zone minerals include biotite, lepidolite, petalite, pollucite (where present), tourmaline, and beryl. Less deformed pegmatites consistently cut more deformed pegmatites, which suggest that there were several episodes of pegmatite intrusion.

EXPLORATION METHODOLOGY

Targeting spodumene-bearing pegmatites, conventional grid soil (-80 mesh) samples were collected over mapped pegmatite clusters within the mafic-ultramafic stratigraphy of the East Pioneer “Goldilocks” pegmatite corridor. Initial results obtained from standard geochemical analysis of soils by 4-acid digest confirmed the presence of coincident Li, Nb, and Rb anomalies over PEG06 and PEG09, with the latter body having lepidolite in surface float (Pioneer Resources Limited 2016c).

All subsequent soil samples were initially analysed by field-portable X-ray Fluorescence Spectrometry (pXRF) instrumentation. This technology is commonly used in mineral exploration to provide instantaneous assessment of key element concentration, but is unable to resolve the concentrations of elements lighter than sodium, which has an atomic number of 11. Lithium (with an atomic number of 3) is thus not directly detectable by pXRF instruments. To address this limitation, correlation of observed Li content with a co-existing suite of 5 elements (Rb, Nb, Ta, Ga, and Cs) resolvable by pXRF in the initial round of geochemical results was used to derive an experimental algorithm (Li-Index) to estimate Li content by proxy. Where initial pXRF analysis returned an elevated Li-Index value, results were validated by conventional four-acid digest. Evaluation of the Li-Index against standard geochemical assays for lithium in these validation tests demonstrated a similar spatial distribution (Figure 2) with a correlation coefficient $r^2 > 0.84$ (Brand & Brand 2017).

Data for over 7,200 soil samples were used to identify nine high priority targets including PEG008a, host to the Sinclair and 15 mid-rank targets within the 13 pegmatite clusters.

Following rock chip sampling and field mapping of PEG008a (Fig. 3), commencement of an inaugural 5000m RC drilling program in mid-2016 (Pioneer Resources Limited 2016b) identified both high grade lithium and caesium (Pioneer Resources Limited 2016a) with PDRC015 (6 m at 27.7% Cs₂O from a depth of 47 m) being the discovery hole for the Sinclair Zone Caesium Deposit.

During the delineation and development of the Sinclair Mine, in addition to conventional four-acid digest ICP-MS and fusion XRF assays, a range of both readily available and innovative technologies were applied in defining the deposit character including portable Raman spectroscopy (pRaman), short-wavelength infrared spectroscopy (SWIR), Fourier-transform infrared spectroscopy (FT-IR), portable XRF (pXRF), and micro-XRF (μXRF). The application of these technologies proved invaluable during the development of Sinclair as with a small resource of the pollucite and consequent short mining operational cycles, rapid assay turn-around and mineral confirmation was of paramount importance.

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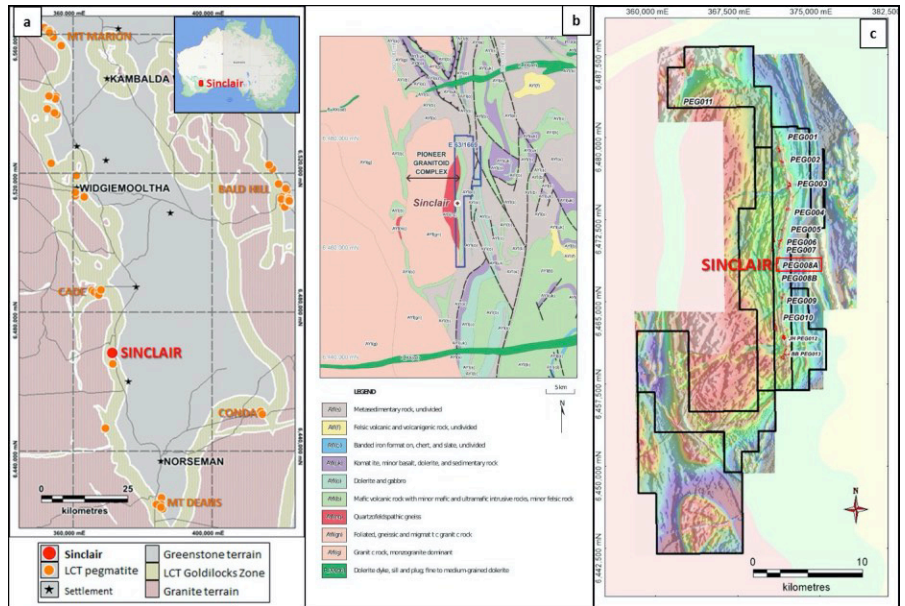
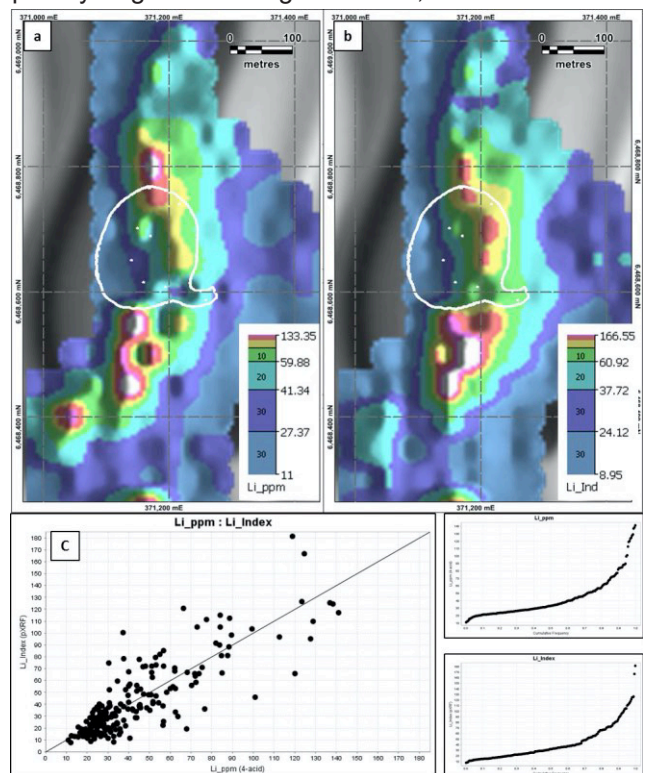


Figure 1. (a) Regional location map of the Sinclair deposit showing the granite-greenstone terrane and the known LCT-pegmatite occurrence located within the greenstone “Goldilocks Zone”, (b) Regional geology of the Pioneer District, after Myers et al. (1998), (c) Distribution of Pioneer Dome pegmatite clusters.

Figure 2. Image of lithium in soils over PEG008a (a) 4-acid digest ICP-MS, (b) pXRF Li-index with the Sinclair pit outline (white) for spatial context, (c) element probability plots and correlation ($r^2 = 0.84$) between Li and pXRF Li-Index.



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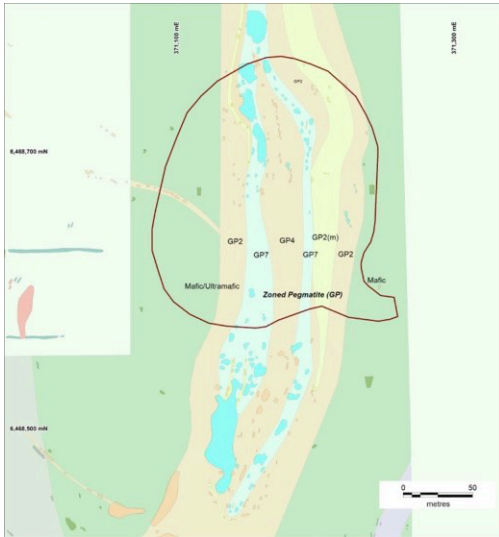


Figure 3. Detailed 1:1,000 mapping of PEG008 completed by Pioneer Resources Ltd. subsequent to the discovery of the Sinclair resource. Outline of final Sinclair pit rim shown by solid maroon line for spatial context. GP2, Pegmatite Wall Zone; GP4, Pegmatite Intermediate Zone (Microcline); GP7, Pegmatite Core Quartz Zone.

Grade control sampling during mine development was undertaken using a matrix-match Cs calibration on a countertop Bruker CTX XRF instrument. This instrument provided a comprehensive and virtually immediate geochemical monitoring capacity for sampled materials, which were confirmed by fusion XRF data post mining (Brand *et al.* 2019a).

To aid in the identification and mapping of mineralogical zones at Sinclair and in the surrounding Pioneer Dome LCT pegmatites, pRaman application was developed based on a spectral library of LCT-minerals prepared from the Sinclair system. Tested against 8,000 pRaman and FT-IR spectra collected from RC and diamond drill core and an additional about 2,000 grade control samples covering the economically important lower economic Li and Cs zones in the Sinclair Caesium Mine, this field-portable spectral methodology was able to provide rapid and robust identification of the key mineralogy

present in the LCT pegmatite systems, including routine differentiation of pollucite and the key lithium silicates, eucryptite and petalite (Fig. 4), and reliable identification of the dominant components and corresponding mineralogical zonation of samples from the Sinclair system (Brand *et al.* 2019b).

Integrated results from pXRF and pRaman analysis of the Sinclair pegmatite are able to define the central core, being discrete pollucite pods (GP8), the flanking high-purity quartz (GP7), and discrete lepidolite (GP9) with the intermediate albite (cleavelandite), zinnwaldite, petalite, and eucryptite zone (GP6) occurring further outboard (Perring & Brand 2019).

SINCLAIR LCT PEGMATITE *Pegmatite litho-geochemistry*

Benchmarked against known LCT pegmatite systems, the host pegmatite of Sinclair shows a unique chemistry of elevated Cs:K ratio, which is very distinct when compared with to petalite dominant and spodumene dominant pegmatite systems, reflecting its extreme fractionation (Fig. 5).

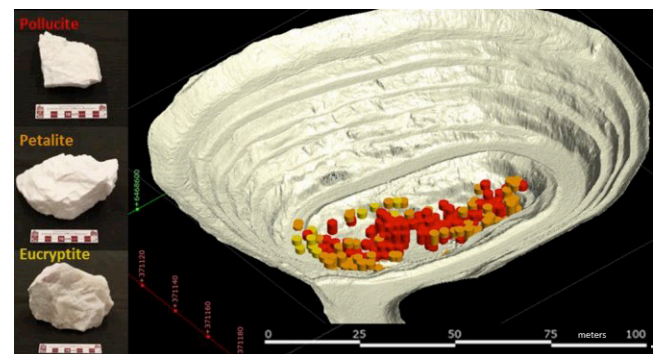


Figure 4. Distribution of pollucite (red), petalite (orange), and eucryptite (yellow) within the Sinclair Pit identified by pRaman spectroscopy during mine development.

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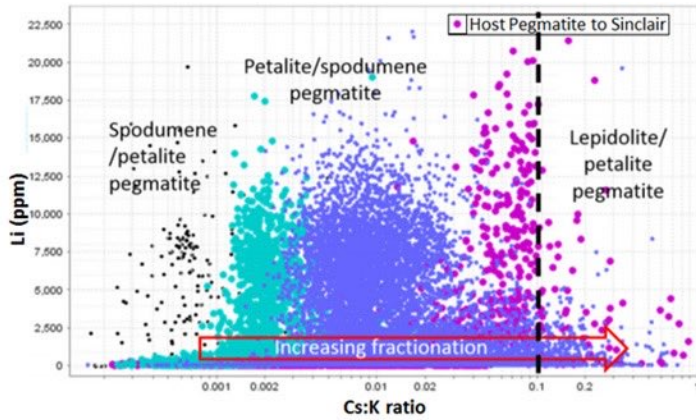


Figure 5. Plot of Cs:K ratio vs Li from three LCT pegmatites showing the extreme fractionation undertaken at Sinclair (purple).

As documented in literature (e.g. Černý *et al.* 1981), the K:Rb ratio is an efficient vector to map out the fractionation of an LCT pegmatite system. Plotting the Sinclair deposit data on to a Cs vs K:Rb scatter plot (after Breaks *et al.* 2003) graphically depicts the fractionation trend of the pegmatite (Fig. 6a) and the intimate relationship of Cs and Li. This is further emphasized by plotting the pegmatite zones from the discovery hole (PDR015) on a Cs vs K:Rb scatterplot (Fig. 6b).

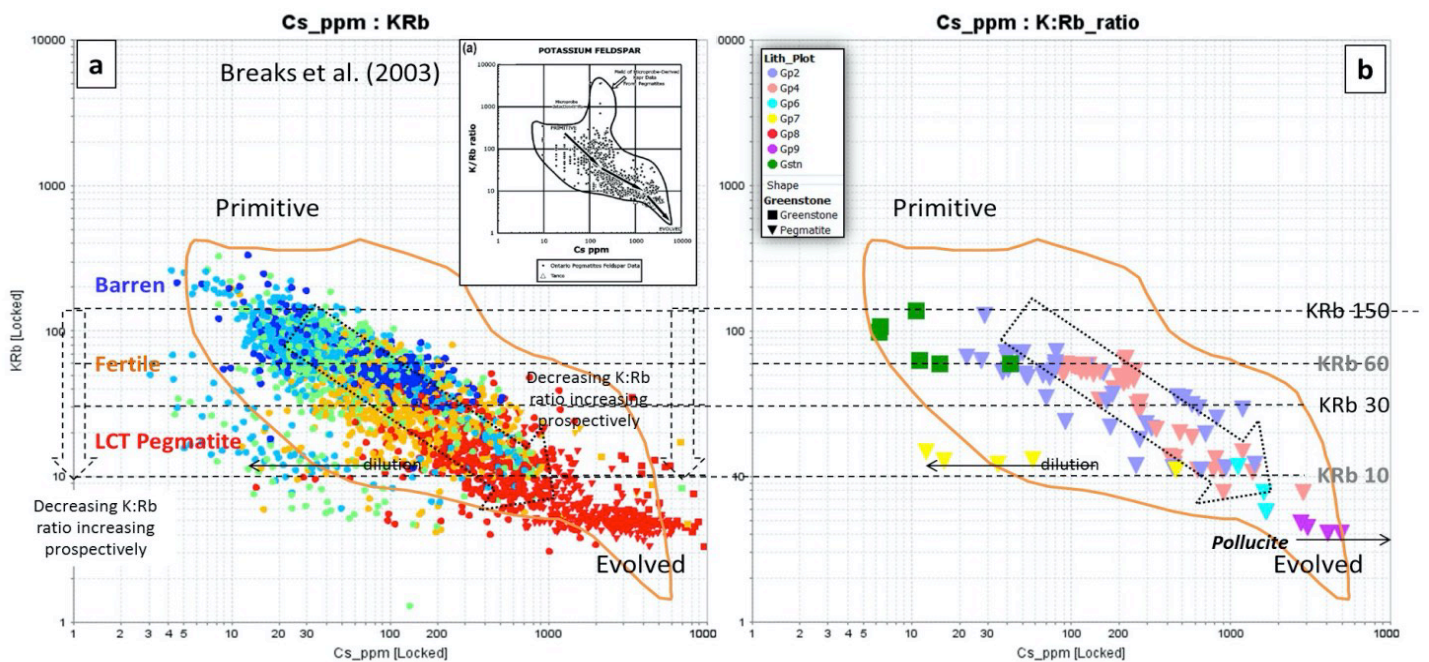


Figure 6. Plot of Cs vs K:Rb scatter plot showing general fractionation trends modified after Breaks *et al.* (2003) (insert); (a) all Sinclair drill data coloured by lithium (blue low, red elevated), (b) discovery hole, PDR015 coloured by pegmatite zones (pollucite plots to the right of the diagram).

Down-hole plots of PDR015 shows both the footwall (GP2) and hanging wall (GP4) having decreasing K:Rb ratio through their respective zones into the core of the mineralized pegmatite hosting pollucite – lepidolite (Fig. 7). Both Cs and Rb are significantly elevated within the GP4 - hanging wall and GP2 – footwall. Although there is a statistical relationship between these two elements, they are hosted by different mineral phases; Rb is hosted in microcline whereas the Cs forms a primary dispersion front associated with Mn (Potter & Brand 2019).

Geology and mineralogy

Common with the Bernic Lake and Bikita deposits, the Sinclair deposit’s host LCT pegmatite consists of an outer pegmatite wall zone that is coarse grained, and dominated by plagioclase feldspar, muscovite, and quartz with accessory garnet, tourmaline, and beryl and an inner core zone composed of, in decreasing order, quartz, albite (cleavelandite), lepidolite, pollucite, petalite, zinnwaldite, eucryptite, beryl, amblygonite, and topaz. The core zone is ‘capped’ by a thick (~35-40m) monomineralic potassium feldspar zone (Fig. 8).

The pollucite mineralisation (GP8) is monomineralic, similar to the Bernic Lake deposit (London 2018), and forms small (~2-10m) discreet pods (Figure 9) spatially associated with albite (cleavelandite), lepidolite (GP9), petalite (GP5), and quartz (GP7). To date petalite (and eucryptite) are the key Li-silicate minerals present at Sinclair with only very rare instances of spodumene detected, unlike pollucite zones described from Tanco (Stilling *et al.* 2006) and Bikita (Dittrich *et al.* 2018).

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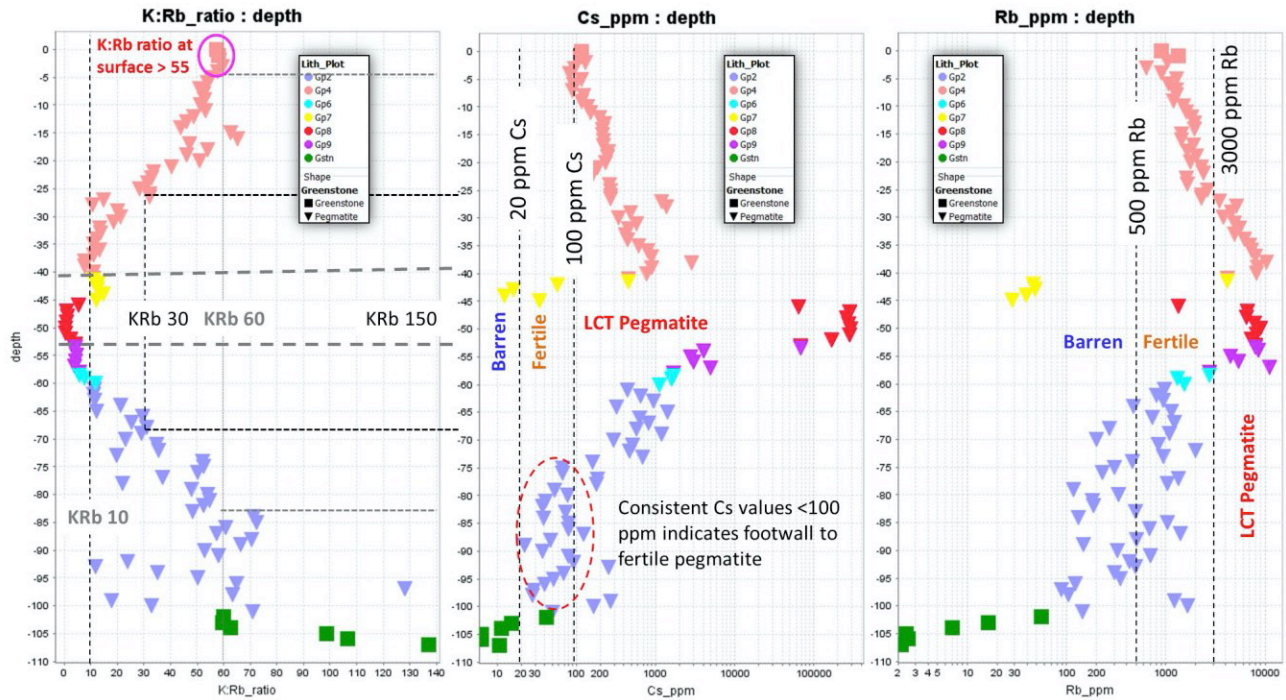


Figure 7. Down hole plots (depth in metres, m) from the discovery hole (PDRC015) showing decreasing K:Rb trend into the pegmatite core associated with increasing Cs and Rb concentrations.

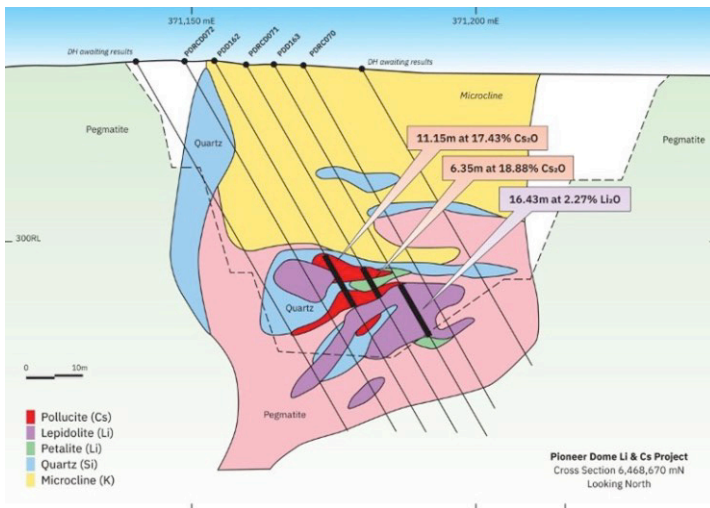


Figure 8. Geological cross section of Sinclair at 6468670m N with diagrammatic pit outline.

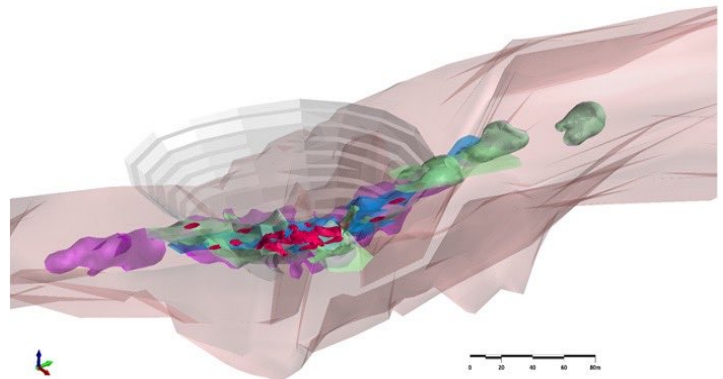


Figure 9. 3D model of selected mineralized domains within PEG008 prior to mining of the Sinclair Pollucite Zone. Pegmatite host body shown by peach-coloured envelope, with Core Pollucite Zone (GP8) shown in red, Core Petalite Zone (GP5) in green, Core Lepidolite Zone (GP9) in purple, and Core Quartz Zone (GP7) in blue. Final pit wireframe overlain for spatial context.

Chemical and mineral zonation in the pegmatite core

During the development of the Sinclair Mine, the use of the CTX pXRF instrument provided a comprehensive geochemical dataset and the pRaman, used to identify lithium silicate minerals (e.g., petalite, eucryptite), provided a comprehensive mineral data set.

Integrating the results, Figures 10a & 10b show a central core of discrete Cs pods (pollucite) associated with Si flanks (quartz) zoned by elevated Rb (lepidolite and microcline) with an outer flank of Mn (Zinnwaldite) and Ca (cleavelandite). Figure 10c, a long section through the deposit, shows the pollucite zone is capped by the overlying monomineralic potassium feldspar zone with basal Rb enrichment. Phosphorous-rich zones map out amblygonite, which has developed beneath the lepidolite (Rb) and appears to be breached by Cs (pollucite) potentially indicating deeper pods or a feeder conduit.

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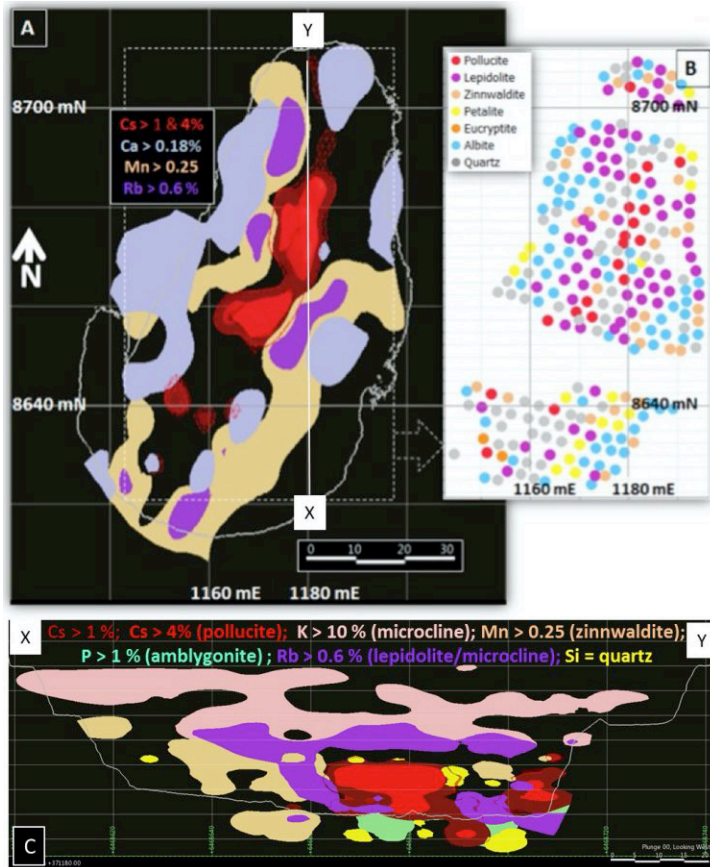


Figure 10. Chemical and mineral zonation in the pegmatite core; (a) plan section of Sinclair at 295 m RL showing selected element concentration analyzed by pXRF, and (b) dominant mineral phase identified by pRaman spectroscopy, (c) long section of Sinclair at 1180 mE showing the zonation and monomineralic microcline cap enriched in Rb at its base.

Pegmatite weathering

Published data on pegmatite weathering, associated regolith development and landscape evolution is rare to non-existent; this is a sizable knowledge gap when exploring for LCT pegmatites in deeply weathered terrains such as the Yilgarn Craton.

During the development of the Sinclair Deposit, zones of weathered pollucite were encountered, typically associated with contacts and structures along which groundwater had penetrated. Weathered material collected during mining was investigated using X-ray diffractometry (XRD) and μ XRF. The breakdown product of pollucite formed an inner white and outer pink phase (Fig. 11) both were confirmed by CSIRO as montmorillonite. The μ XRF mapping shows the catastrophic loss (leaching) of Cs at the weathering interface with manganese associated with pink montmorillonite. Lepidolite veinlets remain unaltered, enriched in Rb and K. Had all the pollucite been converted to montmorillonite clay, an array of pods or miarolitic (clay filled) cavities (London 2018) would have formed along the Sinclair center line.

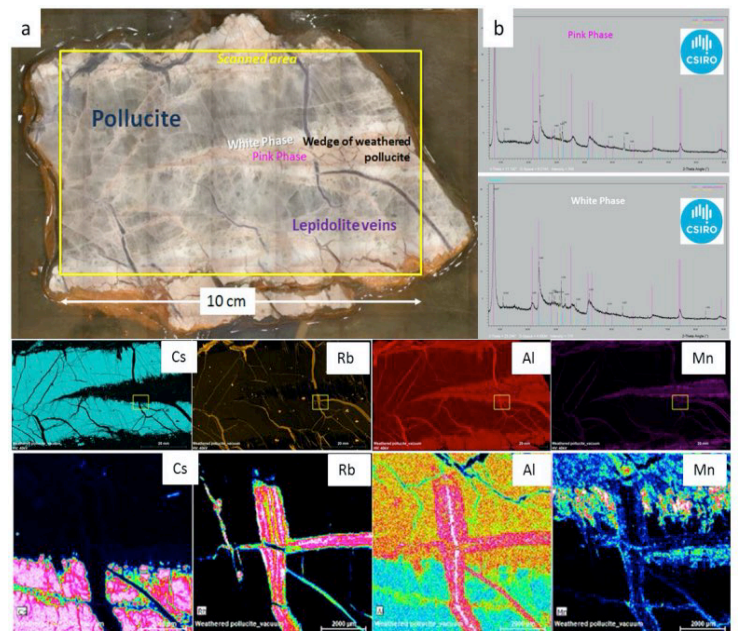


Figure 11. (a) weathering pollucite set in resin with XRD traces showing the montmorillonite as the weathered phases (b) μ XRF element maps (Cs, Rb, Al, Mn) of the entire sample and zoomed in element concentration maps of Cs showing the weathering front and the catastrophic loss of Cs, Rb mapping out the lepidolite veinlets, Al mapping out the lepidolite vein, and montmorillonite and Mn front giving the pink colour to the montmorillonite.

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DISCUSSION AND EXPLORATION IMPLICATIONS

Initially routine soil sampling analyzed by conventional 4-acid digestion ICP-MS resulted in the development of the Li-Index pXRF calibration that enabled rapid screening of samples in the field to identify priority drill targets. Drilling of these targets resulted in the discovery of Cs at Sinclair. This discovery has provided an opportunity to investigate and thus improve our understanding of this style of mineralization utilizing extensive exploration and mining data sets to develop models for future discoveries.

The Sinclair surface soil results are low order (max Cs, 100 ppm; max Li, 141 ppm) producing a coherent and robust anomaly extending for over 450m (Cs > 20 ppm; Li > 50 ppm) and are offset to the up-dip projection of the known mineralization (Figure 12).

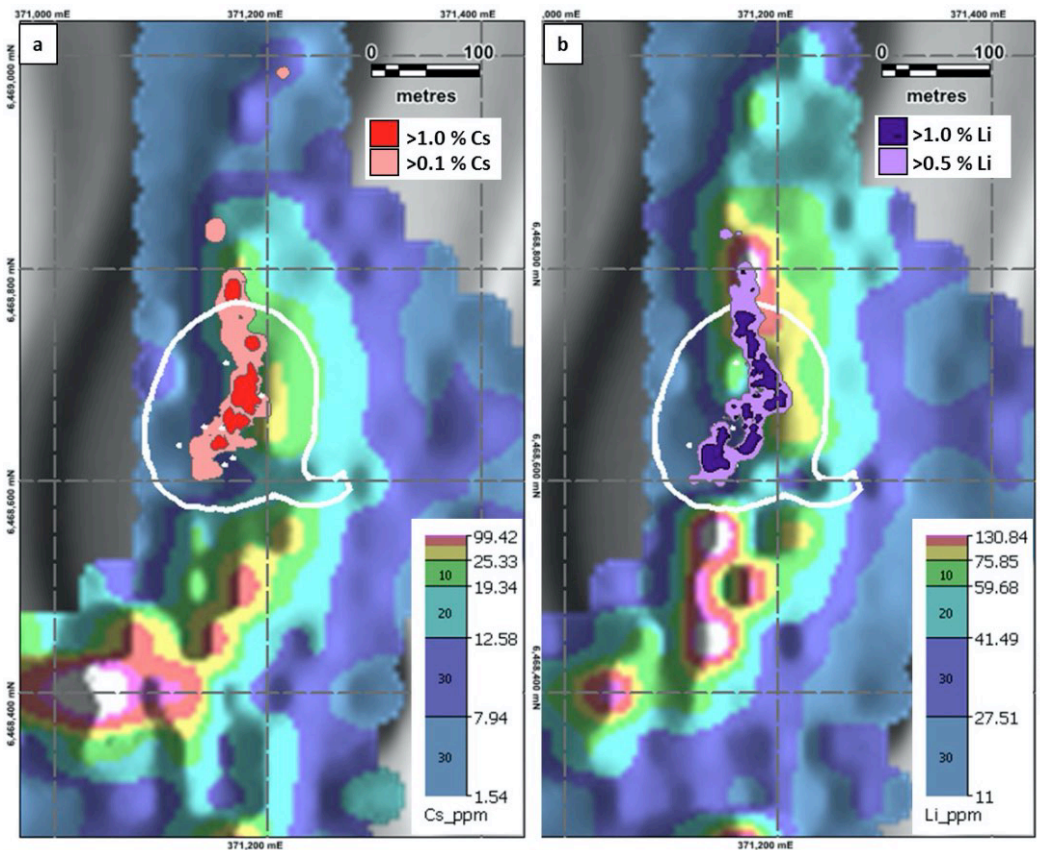


Figure 12. Image of surface soil response (4-acid/ICP-MS) and projection of the drill results (4-acid/ICP-MS) (a) caesium, (b) lithium with the Sinclair pit outline (white) for spatial context.

Litho geochemistry enabled a precise understanding of which pegmatite zone was intersected and enhanced vectoring into the pegmatite core identifying “near misses”, such as Rb enrichment in the outer zones. Although not undertaken, the leaching of Cs from pollucite during weathering would suggest water sampling could be utilized on a regional and local scale.

During the delineation of the resource a significant effort was undertaken to develop other field portable, rapid analytical systems (e.g., pRaman) that aided the development of the resource and will contribute to future exploration. Collaboration between Pioneer Resources and Portable Spectral Services (previously Portable XRF Services) to develop and calibrate field portable systems provided fit-for-purpose, “real time”, and inexpensive chemical and mineralogical data which became invaluable during the short mining cycle of Sinclair. Following the mining of Sinclair, regional exploration continued utilizing the pRaman and Li-Index pXRF calibration resulting in the identification of the spodumene in Dome North (Pioneer Resources Limited 2019) and the discovery of Cade Spodumene Deposit containing 11.2 Mt at 1.21% Li₂O (Essential Metals 2020).

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