

Review

# Tools and Workflows for Grassroots Li–Cs–Ta (LCT) Pegmatite Exploration

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**Abstract:** The increasing demand for green technology and battery metals necessitates a review of geological exploration techniques for Li–Cs–Ta (LCT) pegmatites, which is applicable to the work of mining companies. This paper reviews the main controls of LCT pegmatite genesis relevant to mineral exploration programs and presents a workflow of grassroots exploration techniques, supported by examples from central Europe and Africa. Geological exploration commonly begins with information gathering, desktop studies and Geographic Information System (GIS) data reviews. Following the identification of prospective regional areas, initial targets are verified in the field by geological mapping and geochemical sampling. Detailed mineralogical analysis and geochemical sampling of rock, soil and stream sediments represent the most important tools for providing vectors to LCT pegmatites, since the interpretation of mineralogical phases, deportment and liberation characteristics along with geochemical K/Rb, Nb/Ta and Zr/Hf metallogenic markers can detect highly evolved rocks enriched in incompatible elements of economic interest. The importance of JORC (Joint Ore Reserves Committee) 2012 guidelines with regards to obtaining geological, mineralogical and drilling data is discussed and contextualised, with the requirement of treating LCT pegmatites as industrial mineral deposits.

**Keywords:** LCT; pegmatite; lithium; exploration; targeting

## 1. Introduction

Over the last four decades research into rare metal Li–Cs–Ta (LCT) pegmatite mineralisation has predominantly focused on the understanding of late-stage magmatic fractionation and hydrothermal alteration processes enriching incompatible elements of potential economic interest in felsic peraluminous melts. In particular, the mineralogy and geochemistry of LCT pegmatites have been studied in great detail and are presented in case studies from Canada and the US [1–4], Ireland [5,6], the European Variscides [7–12], the Sveconorwegian orogeny [13,14], Central-East Africa [15–18] and Australasia [19–22]. These case studies have resulted in the definition of tectonic, mineralogical and geochemical factors controlling the location of mineralisation and zonation within the roof of peraluminous S-type granite plutons, pegmatitic offshoots into metasedimentary country rock or anatectic melts with no established link to S-type granites.

On the other hand, from an economic and industrial perspective, only a limited number of case studies are available, describing relevant mineral exploration techniques which are directly applicable to the daily business of mining and exploration companies. In the recent past, aspects of mineral exploration techniques applied to LCT pegmatite mineralisation have been published, covering (i) hyperspectral remote sensing [23], (ii) whole-rock geochemistry [1,24–26], (iii) stream sediment geochemistry [27–29], (iv) soil geochemistry [30], and (v) best practice reporting of LCT pegmatite exploration results according to the JORC (Australian Joint Ore Reserves Committee) standard [31]. In the current literature, a unified approach for industrial grassroots LCT pegmatite exploration is

largely lacking. Therefore, this paper attempts to fill this gap by providing a workflow for early stage target generation, identification and testing of LCT pegmatites.

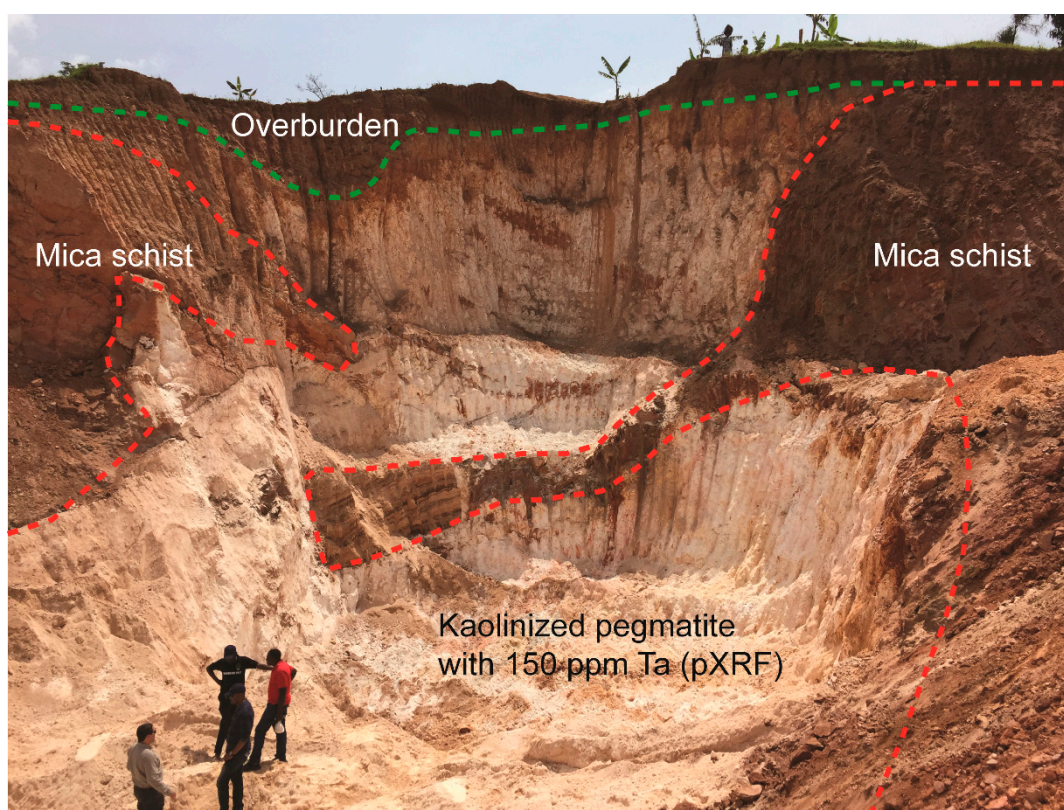
## 2. An Overview of LCT Pegmatites and Implications for Mineral Exploration

In light of the recent green technologies and battery metals “boom”, rare element LCT pegmatites form an important aspect of sustainable Li, Cs and “coltan” (Nb–Ta) supplies (approx. 40% of the global Li production), and are therefore explored for and mined globally [10,32,33]. Major pegmatite occurrences, such as Tanco (Canada) and Greenbushes (Australia) contain important resources of these metals and new deposits are currently explored for around the world. Available literature on the nature and genesis of pegmatite mineralisation is vast and often disputed, and will be reviewed to highlight the formation, occurrence, composition, zoning, and rare metal enrichment of pegmatites, with a view to identifying physical and chemical properties relevant to mineral exploration and mining.

### 2.1. Definition and Classification

London (2008) [34] defines a pegmatite as an igneous rock of predominantly granitic composition, which is distinguished from other igneous rocks by (1) the extremely coarse and systematically variable size of its crystals, typically increasing by a  $\sim 10^2$  from margins to centre, or (2) by an abundance of crystals with skeletal, graphic or other strongly directional growth habits, or (3) by a prominent spatial zonation of mineral assemblages, including monomineralic zones. Pegmatites have traditionally been linked to a parental granite [1,3] and can either occur in close proximity to the latter or as off-shoot dyke swarms up to 20 m wide and several kilometres long in metasedimentary country rocks (Figure 1). However, pegmatites with a missing apparent parental granite are common [3], and it is suspected that the source granite occurs at depth [30]. On the other hand, studies published in the 2010s on the anatectic origin of granitic pegmatites in Europe and North America demonstrate that there are “thousands of pegmatites without parental granites” [13], i.e., pegmatite fields can be unrelated to a source granite and instead form by partial melting and anatexis of crustal material [4,13,14,35–39], or energy and melt circulation along deep lithospheric fault zones [40]. In the current literature, there are numerous descriptions of pegmatite sub-classifications, but to date there is no universally accepted model explaining the diverse features and genesis of granitic pegmatites [39]. An exhaustive discussion and critical evaluation of historic pegmatite classifications was published by Müller et al. (2018) [41] and currently represents a significant summary of pegmatite classification studies. From an economic point of view rare-metal pegmatites, as opposed to barren pegmatites, contain beryl, lithium aluminosilicates, phosphates and rare metal oxides [42]. Černý and Ercit (2005) [43] and Černý et al. (2012) [44] use mineralogical, geochemical and structural (zonation) criteria along with necessary knowledge of P-T conditions to broadly divide rare-element pegmatites into two geochemical groups or families, taking into account the composition and volume of source material from which the granitic melt is originated: Nb-Y-F (NYF) and LCT enriched pegmatites, which can be further divided into an array of sub-classes and sub-types. NYF pegmatites are sourced by alkaline A-type granites originating from the melting of lower continental crust and mantle, whilst LCT pegmatites are commonly related to the partial melting of subducted continental crust consisting of metamorphosed sediments, leading to the emplacement of peraluminous S-type granites [44]. Although this classification is widely accepted in the literature, a number of aspects, such as the necessity for consideration of the tectonic histories and settings of the pegmatites, are disputed. For example, Dill (2015) [10] describes the spatial association of Variscan NYF and LCT pegmatites at Pleystein and Hagendorf (Germany), respectively, which would imply two drastically different geodynamic settings across a distance of several kilometres. Studies of pegmatite occurrences in the Sveconorwegian orogen have shown that NYF pegmatites do not only form in anorogenic (A-type magmatism) settings, but also in compressional or extensional orogenic settings unrelated to plutonic magmatism [13]. Additional shortcomings of the Černý and Ercit classification [43] are the dependence on the crystallisation depth and pressure, which is commonly difficult to obtain, and a possible lack of characteristic REE and F-minerals in pegmatites, which

do not allow to fit pegmatites into the NYF classification [41]. Rare-element pegmatites that were formed in a pluton-unrelated setting can therefore lack the characteristic F (“NY” instead of “NYF”) or Li (“CT” instead of “LCT”) signature [13]. These aspects question the validity of the currently accepted classification. Müller et al. (2018) [41] advocate for a revised classification of pegmatites relying on measurable criteria, such as (1) indicative minerals and mineral assemblages of primary magmatic origin, (2) quantitative mineralogy and geochemistry of quartz, garnet, topaz, beryl and columbite-group minerals, (3) pegmatite structure (zonation and graphic quartz-feldspar intergrowths) and (4) crystallisation age. Despite the ongoing discussion on pegmatite classification, this paper will focus exclusively on economically relevant and sought-after pegmatites with LCT signature and their associated mineralisation and exploration potential.



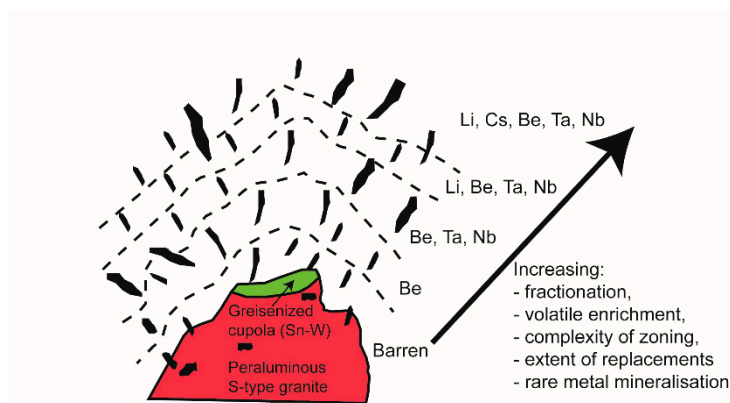
**Figure 1.** Typical exposure of Li–Cs–Ta (LCT) pegmatite in the Ruhanga area, Rwanda. This pegmatite is currently (in 2018) exploited for columbite-tantalite mineralisation. The pegmatite body is 15–20 m wide and has a lateral extension of at least 2.5 km. Complete kaolinisation of feldspars, resulting in an unzoned appearance, characterise most Rwandan pegmatites. This creates issues with slope stability [45], but allows simple artisanal open-cast excavation of the orebody to a depth of 30 m. Note the rafts of biotite schist in the weathered pegmatite illustrating the assimilation of country rock material, which can have a detrimental influence on ore grade and dilution, and therefore needs to be appropriately modelled.

## 2.2. Formation, Rare Metal Enrichment, and Geodynamic Setting

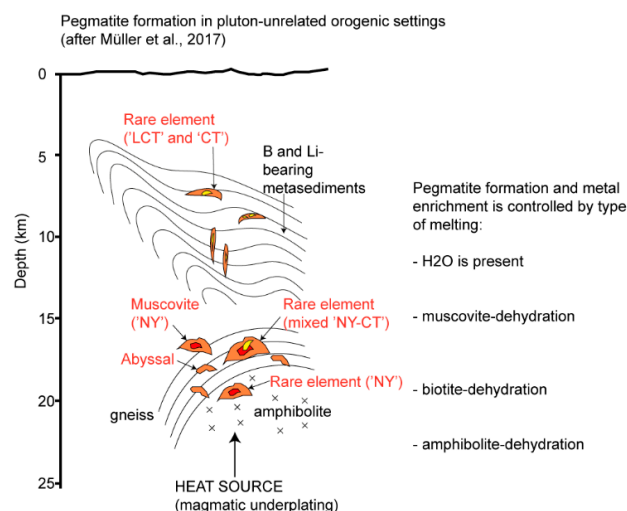
Pegmatite-forming melts are produced by (1) fractional crystallisation of granitic magma plutons (Figure 2), and (2) partial melting of crustal or mantle rocks involving the presence of fluids [46]. In the first scenario, siliceous melt is separated from parental granites by filter pressing and intrudes into metasedimentary country rocks, where the melt crystallises and forms unzoned or zoned pegmatites [10]. The concentration of fluxing elements, such as F, B, P, Li and H<sub>2</sub>O, reduces the viscosity and solidus temperature of the melt, but increases the solubility of large-ion-lithophile elements (LILE) and high-field-strength elements (HSFE) [3]. Depending on temperature, LILE precipitate



and form minerals when fluxing elements are removed from the melt by chemical quenching [2]. However, fractional crystallisation is not regarded as the sole factor of pegmatite formation and element mobility in peraluminous melts. Firstly, several studies suggest that felsic pegmatites can be derived by partial melting and anatexis rather than fractional crystallisation of a parent granite (Figure 3) [13,39,41]. This is particularly evident in the pegmatite fields of Mt. Mica [4] and Southern Norway [14,47] where geophysical gravity surveys, radiometric dating, isotopes, whole-rock and mineral chemistry indicate that pegmatites are unrelated to nearby S-type granite plutons. Secondly, there is evidence that sub-solidus hydrothermal alteration, specifically the transition between pure magmatic fractionation and hydrothermal alteration, plays a significant role in localising economically significant mineralisation of Sn, W, Li, Cs, Ta and Nb [7]. Whole-rock geochemical data presented in Ballouard et al. (2016) [7] demonstrated that K/Rb, Nb/Ta and Zr/Hf ratios represent valuable geochemical and metallogenic markers for this magmatic–hydrothermal transition zone.  $K/Rb < 150$ ,  $Nb/Ta < 5$  and  $Zr/Hf < 18$  define pegmatitic–hydrothermal evolution characterised by increased substitution of K with Rb in micas and feldspars, fractionation of Nb over Ta due to hydrothermal sub-solidus reactions enriching Ta in F-rich residual melts and leading to secondary muscovitisation [48], and increasing Kd values of Hf in zircon [8,49]. The removal of Li (petalite or spodumene) and Li-F (lepidolite) minerals from the silicate melt, along with the diffusion of these fluxing elements into adjacent host rocks, will lead to a sudden drop in Ta solubility and the subsequent precipitation of columbite-tantalite group minerals. Therefore, the Nb/Ta ratio decreases with increasing fractionation, and Nb-Ta mineral phases evolve from manganocolumbite to manganotantalite [26]. In this context, binary plots of K/Rb vs. Li, Cs, or Ta and K/Rb vs. Nb/Ta or Zr/Hf present a useful tool to visualise magmatic fractionation and hydrothermal alteration processes and to determine the most fractionated/prospective samples. Whilst these petrogenetic ratios were initially developed on the mineral chemistry of muscovites and other host silicates, the concept has meanwhile been successfully implemented in mineral exploration campaigns [26,28,29,45], underlining the significance of litho-geochemistry in applied aspects of peraluminous rare metal granite and pegmatite exploration.



**Figure 2.** Traditional model of regional zonation and rare metal enrichment of pegmatites and pegmatite fields related to S-type granite plutons implying that zoned pegmatite fields are related to and have a similar age as a nearby granite intrusion (modified from [26]). This model is currently challenged by a number of authors who outline evidence for an anatectic origin of pegmatite melts, e.g., [4,13,36,37,47]. Whilst pegmatite fields can be zoned, the zonation is in some cases not spatially related to a pluton, but to individual pods of pegmatitic melt.



**Figure 3.** Simplified model of anatectic pegmatites formed in orogenic settings characterised by a distinct lack of nearby granite plutons (modified from [13]).

LCT pegmatites are related to orogenic belts, typically involving high-grade metamorphic terrains and reworked or exhumed deep continental crust. Examples are found around the world, such as Palaeoproterozoic granulite belts of northern Scotland [50], Archean–Proterozoic greenstone belts of Canada, Africa and Australia [10,20,22], and Phanerozoic mountain belts, particularly the European Variscides (also termed the Hercynian Fold Belt), and its extension along the Alleghanian Orogen into the New England province of North America [10]. Previous regional studies have demonstrated that LCT pegmatites predominantly occur in continent–continent collision zones [51], whilst Sn and W deposits can be decoupled and occur in post-orogenic extension and continental arc settings [12]. Based on European pegmatite occurrences, Dill (2015) [10] divided the geodynamic setting of rare metal pegmatites into primary “Variscan” and reworked “Alpine” types, whilst “Andean” and “Island Arc” type pegmatites are considered barren. The fertility of LCT pegmatites is determined by the presence of (i) intensely chemically weathered, and therefore Li-, Cs-, Sn- and W-enriched sedimentary protolith, accumulating along continental margins as a result of sedimentary and tectonic processes, and (ii) an orogenic and mantle-derived heat source during subduction and melting processes resulting in the preferential formation of Sn, W and LCT mineralisation across major suture zones [12]. In essence this means that, from a geodynamic perspective, prospective LCT pegmatites are found and should be explored for in areas that underwent crustal growth and reworking of voluminous metasedimentary source material which, coupled with a heat source, mobilised the ore elements from the source rock to form peraluminous melts. The awareness and supporting data for applicable geodynamic settings, mineralisation system architecture, fluid and metal sources, pathways, reservoirs and traps have been available for several decades, however the integration of these factors into a mineral systems model originally defined by Wyborn et al. (1994) [52] has not been taken into account until recently. Using examples from Archean rare metal pegmatites of the Archean Yilgarn and Pilbara cratons of Western Australia, Sweetapple (2017) [21] demonstrated that integrating (a) sources (precursor granitoids generated by partial melting of Archean trondjemite–tonalite–granodiorite rocks), (b) host rocks (mafic or ultramafic rocks in greenstone belts), (c) fluid flow sources, reservoirs, and heat drivers (younger granites) and (d) melt and fluid pathways (foliations associated with regional shear and fault zones, fractures generated in host rock due to magmatic overpressure) can be implemented at craton to deposit scale exploration targeting.

### 2.3. Composition, Grade/Tonnage and Geometry

The bulk composition of pegmatites contains subequal proportions of quartz, alkali feldspar, and plagioclase, comprising greater than 80% of the rock, and therefore plots in the granite field of the

Quartz, Alkali feldspar, Plagioclase, Feldspathoid (QAPF) diagram [3]. However, the composition is inherently poorly understood due to issues with sampling heterogeneous, coarse-grained geological bodies. The Tanco pegmatite at Bernic Lake, Manitoba, is probably one of the best studied economic pegmatites and is classified as granitic considering a combined quartz, plagioclase and alkali feldspar abundance of 82% [53]. Dill (2015) [10] provides bulk geochemical data for pegmatitic rocks of the Hagendorf–Pleystein Pegmatite Province (Germany), supporting the overall granitic composition of pegmatites. LCT pegmatites are generally devoid of magnetic or conductive minerals and consequently lack a density, gamma-ray and magnetic contrast to metasedimentary host rocks [54]. Of interest to the mineral exploration geologist are pegmatites that contain abundant and economic quantities of lithium aluminosilicates and phosphates, pollucite, beryl and Sn–Nb–Ta–REE oxides. In the case of the Leinster rare-element pegmatite belt in Ireland, spodumene pegmatites contain spodumene (10–40%), albite (25–35%), quartz (15–20%), Li-muscovite (10–15%), spessartine garnet (5%), and <5% K-feldspar, apatite, cassiterite and sphalerite [5]. Similar compositions are observed in other economic deposits, such as King Mountain (US), Wolfsberg (Austria) and Kaustinen (Finland). However, only a minor fraction of pegmatites in any given district are enriched in these elements and minerals, whilst the majority of pegmatites contains these elements at minor (<5%) or accessory (<1%) levels [34].

Ore grades in rare-element pegmatites are commonly irregularly distributed [31]. Bradley et al. (2017) [55] present comparative data of major, economic LCT pegmatites and demonstrate that economic pegmatites should generally contain minimum grades of 1 wt. %  $\text{Li}_2\text{O}$  and 0.1 wt. %  $\text{Ta}_2\text{O}_5$  at tonnages of 7 Mt and 0.01 Mt, respectively. Importantly, this study implies that pure world-class Li pegmatites are less abundant (10 used for the study) than Ta deposits (35 used in the study). Pegmatites can take the shape of flat-lying or variably dipping dikes, sills, pods, tabular and lenticular-shaped bodies. In a study of the Evje-Iveland pegmatite field (southern Norway), Snook (2013) [47] outlined the dimensions of zoned, anatectic pegmatites in amphibolites and other metasedimentary country rocks, commonly taking the shape of pods and lenses with a thickness of 4 to 15 m and a strike length of 10 to 50 m. In contrast, the Mt. Mica pegmatite (US) is thought to consist of batches of anatectic melt which accumulated and coalesced into a larger volume [4]. On the other hand, the Kaustinen pegmatites (Finland) consist of a flat-lying dike swarm with a length of 450 m and a maximum individual dike width of 10 m [56]. The pegmatite dikes of the giant Greenbushes deposit (Australia) are up to 3 km long, 40 to 250 m wide, 400 m deep and variably dip 40–50° [20]. This means that grade and tonnage of economic metals in rare-element pegmatites can be variable. Consequently, distinguishing barren from fertile or rare element pegmatites, and importantly outlining economic grades and tonnages using mineralogical and geochemical techniques is a key aspect in commercial pegmatite exploration.

#### 2.4. Regional and Internal Zoning

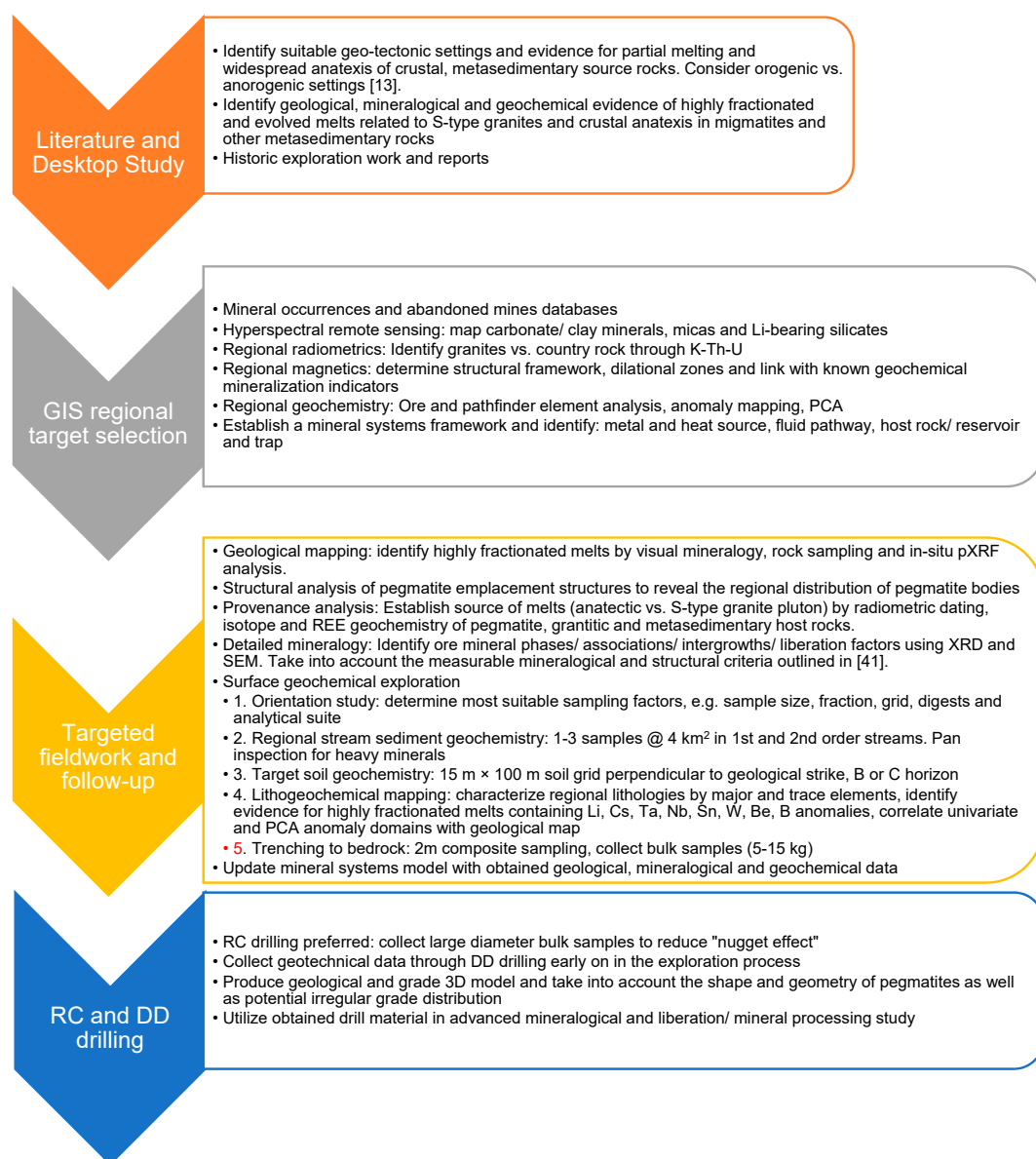
Pegmatites are typically characterised by regional and internal zonation patterns, manifested by distinctive mineralogical and geochemical signatures, which are routinely used in geological and geochemical exploration programs [1,26]. In pegmatite swarms and groups, zonation as a function of cooling, chemical fractionation and hydrothermal alteration can be observed with increasing distance from the granitic source, forming a sequential appearance of exotic minerals [3,34]. Figure 2 shows an idealised sequence of barren proximal to Be–, Be–Nb–Ta, Li–Be–Ta–Nb and Li–Cs–Be–Ta–Nb–enriched pegmatites related to S-type granite plutons. This outward sequence of mineral and element zonation patterns has been challenged by a number of authors who outline evidence for an anatectic origin of pegmatite melts [4,13,14]. Whilst pegmatite fields can be zoned, the zonation is in some cases not spatially related to a pluton, but to individual pods of pegmatitic melt in metasedimentary country rock which were likely to be affected by secondary hydrothermal alteration processes [47]. Internally, the structure of pegmatites is variable and can take the form of either zoned or unzoned patterns. London (2018) [3] provides a detailed account of internal zonation patterns which will be summarised here. Unzoned pegmatites are located within or adjacent to granite cupolas and are characterised by their isotropic rock fabric and coarse grain size (several cm or larger) in relation to plutonic rocks.

Plagioclase and quartz are anhedral and of uniform size, whereas K-feldspar is porphyritic and exhibits skeletal or graphic granite intergrowths. Unzoned pegmatites can form economic sources of quartz, feldspar, spodumene and mica. On the other hand, the internal fabric of zoned pegmatites depends on the habit and orientation of crystals, as well as the spatial segregation of minerals by zonal mineral assemblages. Zoned pegmatites comprise border, wall, intermediate, and core zones which have unique mineralogical and geochemical properties. Border zones comprise 1–3 cm-wide cooling margins of fine-grained and granophyric granitic rock at the contact with the host rock. The typical mineralogy comprises plagioclase-quartz-muscovite, with accessory tourmaline, beryl, garnet, cassiterite and columbite. The wall zone consists of inward-orientated K-feldspar, micas, beryl, and tourmaline, with considerably larger crystal sizes. The intermediate zone follows inward from the wall zones and is principally formed of more abundant monophase K-feldspar, quartz, muscovite, sodic plagioclase and lithium aluminosilicates. The centre or core of zoned pegmatites is pure quartz. Historically, it was assumed that the quartz core formed during the last stage of the pegmatite crystallisation process. However, experiments by London and Morgan (2017) [57] demonstrated that in Li-rich melts, albite, and lepidolite can follow the crystallisation of pure quartz. From a practical perspective, the recognition of regional and internal pegmatite zonation is a fundamental task during geological and geochemical sampling and fieldwork.

### 3. Suggested Grassroots Exploration Strategy

#### 3.1. Literature and Desktop Study

Grassroots exploration programs commonly commence with a detailed literature review of regional geology, mineralisation occurrences, and styles (Figure 4). Exploration geologists unfamiliar with LCT and Sn(–W) mineralisation are advised to become familiar with general pegmatite geology and mineralogy, in order to develop an understanding of element associations, fractionation patterns, orebody geometry and grade–tonnage relationships [2,3,10,34]. Furthermore, a desktop study should aim to identify evidence of suitable regional geo-tectonic settings involving deep crustal reworking and exhumation processes, leading to partial melting of crustal, metasedimentary source rocks, such as along the European Variscan belt [12]. In particular, consideration should be put on different orogenic and anorogenic settings and the presence of anatectic melts [13]. Supporting evidence in the form of exhumed granulites, migmatites and two-mica peraluminous granites with accessory minerals, for example tourmaline and fluorite indicating the presence of B and F fluxing elements, can be obtained from regional geological maps and databases. For example, Dill (2015) [10] provides an exhaustive list of pegmatite sites and mineralogy, which is useful and applicable to generating conceptual exploration targets. National geological survey departments provide summary reports of historic company exploration work and represent a valuable resource. For example, the Finnish Geological Survey carried out investigative work into the occurrence of LCT pegmatites in the Kaustinen Province and other permissive tracts, and published geological, geophysical and mineralogical data in support of a growing local mining industry [56,58]. Similarly, the Ontario Geological Survey regularly produces multi-commodity exploration reports covering summaries of recommended areas prospective for LCT mineralisation [59].



**Figure 4.** Workflow for early-stage LCT pegmatite target generation, definition and testing.

### 3.2. Review of GIS Public Domain Datasets and Regional Target Selection

A literature and desktop study is followed by a review of public domain GIS data and leads to regional target selection. Mineral occurrences and abandoned mine GIS databases support the spatial delineation of ore and pathfinder minerals, along with formerly productive mines, and so represent a tool to delineate prospective mineral belts. Hyperspectral remote sensing data obtained from Landsat, ASTER and Sentinel-2 satellite missions work particularly well in arid environments characterised by a limited abundance of vegetation to delineate granitic intrusions, hydrothermal alunite and clay minerals, and Li-bearing silicate minerals (spodumene and petalite), using RGB band combinations, ratios and selective principal component analysis [23,60]. In a case study from the Fregeneda-Almendra region in Spain and Portugal Cardoso-Fernandes et al. (2019) [23] utilized and developed a variety of spectral signatures to identify currently excavated LCT pegmatites through hydrothermal alteration halo mapping and direct identification of Li-bearing minerals. In this context, the importance of thermal bands in the discrimination of Li-bearing pegmatites using remote sensing data was demonstrated, as silicate minerals (spodumene and petalite) have distinctive emission bands in the thermal spectrum. The most applicable band combinations and ratios for the determination



of areas enriched in Li minerals were determined as RGB 2113 and 7/6 (ASTER); RGB 3211 and 3/5 (Landsat-8); RGB 216 and 2/4 (Landsat-5); RGB 3212 and 3/8 (Sentinel-2). In the same study, selective PCA of two-band subsets (e.g., bands 1 and 3 for ASTER) highlighted Li-bearing areas as the subset used two target bands and two principal components only, and therefore reduced the overall noise of the dataset.

Regional airborne radiometric surveys are another applicable tool for identifying granite intrusions and stocks, i.e., the metal and heat source of the mineralisation system, through analysis of K–Th–U spectrometer data [61,62]. Airborne radiometric and magnetic surveys are usually conducted simultaneously and, whilst LCT pegmatites often do not contain magnetic or conductive sulphide minerals [54,56], magnetic surveys allow geologists to establish structural control on granite emplacement and link regional shear, fault, and dilational zones to known mineral and geochemical anomalies, therefore establishing a fluid migration pathway and potential mineralisation traps.

Regional geochemistry datasets outline the enrichment of incompatible and pathfinder elements (Sn, W, Nb, Ta, Li, K, Cs, Rb, Zr, Hf, Cu, Be and B) in rock, soil and stream sediment data. However, historically, most governmental geological surveys have employed aqua regia digests as part of their analytical procedures [63]. This choice significantly decreases the ability to dissolve silicate and oxide minerals, such as cassiterite, petalite, spodumene, columbite, tantalite and zircon. Therefore, concentrations of incompatible and pathfinder elements might be significantly lower in aqua regia digested samples, thereby restricting the usability of these datasets in rare element pegmatite exploration [64]. Conversely, other governmental surveys in Ireland employed non-digested pressed pellet X-ray fluorescence (XRF) analyses [65], which have clear advantages as the analytical technique is able to measure most major rock-forming elements, as well as Ta, Nb, Zr and Hf, but excluding Li. Nevertheless, XRF techniques still prove to be valid exploration tools, particularly when pathfinder elements and K/Rb, Nb/Ta and Zr/Hf ratios are analysed [28]. However, depending on the quality and age of datasets, not all desirable pathfinder elements will be available. Regional geochemical data can be employed to conduct univariate anomaly mapping [66] and dimension reduction techniques (principal component analysis), in order to identify relevant incompatible and pathfinder element associations and subsequently link the results with geological maps and published literature. For example, the assessment of the 1980s regional rock geochemical analyses provided by the French Bureau de Recherches Géologiques et Minières (BRGM) led to the initial delineation of a 200 km<sup>2</sup> extensive W and LCT exploration target area in the central and northern Vosges Mountains [29].

### 3.3. Targeted Fieldwork, Sampling, Mineralogy and Follow-Up

Once targets and elements of a mineralisation system have been identified by desktop and data studies, investigations should focus on field visits and a detailed description of the geological setting. Geological mapping, structural analysis of pegmatite emplacement structures, litho-geochemical analysis and radiometric age dating aim to (1) reveal the regional distribution of pegmatite bodies and (2) locate and confirm evidence for highly fractionated and evolved melts, located in the cupolas of granite stocks, pegmatitic off-shoots into country rock [10] or anatectic melts unrelated to S-type granites [4,36,67]. In other words, at this early stage, the provenance of the pegmatitic melts should be determined in order to link the overall geotectonic (crustal depth) setting with pegmatite occurrences and metal sources leading to a better understanding of the spatial dimensions and chemical composition (“LCT” vs. “CT” in orogenic/ pluton-unrelated settings) of expected pegmatite fields [13]. Supportive mineralogical evidence for fractionated melts are the visual presence of abundant muscovite and cassiterite, along with tourmaline, topaz, and fluorite, which act as fluxing indicators [9,68]. Geochemical analysis of rock samples collected during mapping campaigns aims to provide concentrations of fractionation pathfinder elements and evidence for a genetic relationship of the pegmatite with either a metasedimentary-sourced S-type granite pluton or anataxis-derived migmatite. The analysis of bulk pegmatite composition, in particular, is often challenging due to the very large grain size and zonation encountered. As a result, representative bulk grab or hand

drill samples of either exploration trenches or active development benches or stopes need to be collected across the pegmatite from the hanging-wall contact to the foot-wall contact with pulverised sub-samples mixed and analysed as one representative sample [4]. Despite potential accuracy issues, varying detection limits for W and Ta, and the absence of Li and Cs analyses, in-situ portable XRF (pXRF) analysis of Sn, W, Ta and K/Rb proves to be a valid primary geochemical investigation technique for determining the enrichment of ore elements [69], whilst REE, B, Li, Sn and Ta determined by fusion ICP (Inductively Coupled Plasma) and DCP (Direct Current Plasma) spectroscopy is required for the reliable determination of overall grade, source material and provenance [4].

Numerous case studies underline the significance of automated mineralogical techniques in the rare metal granite and pegmatite exploration process [27,70–73]. Rapid identification of ore mineral associations, intergrowths, and liberation factors is achieved by the use of UV light for identifying Li silicates, scanning electron microscopy (SEM), electron microprobe analysis (EPMA), automated SEM-EDS mineralogy (QEMSCAN<sup>®</sup> or Mineralogic<sup>®</sup>), laser induced breakdown spectroscopy (LIBS), Raman spectroscopy and X-ray diffraction (XRD) analysis. Li-bearing minerals, such as spodumene, eucryptite, lepidolite, zinnwaldite or petalite, are particularly challenging to identify visually and to distinguish from common rock-forming silicate minerals, therefore emphasising the importance of mineralogical techniques. XRD techniques provide information on ore grade Nb–Ta oxides, and Li-bearing silicate minerals, whilst QEMSCAN<sup>®</sup>, SEM and EPMA techniques can quantify the purity/contamination of the ore by deleterious elements (F, Fe and P) and determine potential recovery and processing methods, such as conventional flotation, gravity, or magnetic separation technologies [31]. As part of the EU Horizon 2020 Flexible and Mobile Economic processing technologies (FAME) project, Simons et al. (2018) [74] developed a new method for characterisation of Li minerals using SEM/QEMSCAN<sup>®</sup>-based automated mineralogy. This approach is based on distinct Al:Si ratios, and the absence of other major elements, but also used a sample that has been optically validated for the minerals of interests to act as a reference, in granite-related pegmatites and greisens, such as spodumene, petalite, beryl and zinnwaldite. Whilst spodumene and petalite were successfully identified on samples from Li-prospects at Cínovec (Czech Republic), Gonçalo (Portugal) and the Kaustinen pegmatite field (Finland), using characteristic Al:Si ratios of 1:2 and 1:4, respectively, Li micas could not be uniquely identified from Li-absent micas as the micas did not show any distinct chemical difference other than the Li which is not detectable by automated SEM-EDS mineralogy. For this reason, bespoke characterisation and QEMSCAN<sup>®</sup> calibration/ database development for each individual prospect is required.

Geochemical sampling and analysis of soil, till and stream sediments has proven to be a very effective method for localising metal anomalies in geological materials affected by secondary dispersion processes [75,76]. Considering the exploration for LCT pegmatite deposits, a preliminary orientation study will determine the most suitable sample location, weight, size fraction, grid and analytical requirements. Previous pXRF orientation studies of stream sediments have demonstrated that optimum field sample weights are 0.5–1.5 kg and that the silt to very fine sand grain size fraction (<75 µm) yields the best signal to noise ratio [29]. In contrast, soil surveys may necessitate the collection of the coarser sand fraction (>600 µm) to achieve optimum chemical analysis results [64]. The obvious difference in the choice of grain size fractions is a result of secondary dispersion processes, where comminution of heavy mineral grains, such as cassiterite or columbite-tantalite, is less pronounced in residual soils than in active streams. The presence of target metals in silicate minerals requires the utilisation of either pressed pellet XRF or strong chemical digests before subsequent ICP-MS analysis. A total sodium-peroxide fusion has proven effective in targeted granite and pegmatite exploration [45], whilst near-total four acid digest (HCl, HNO<sub>3</sub>, HF and HClO<sub>4</sub>) is useful in regional multi-commodity and granite-pegmatite geochemical surveys [29]. Partial aqua regia (HNO<sub>3</sub> and HCl at a 1:3 molar ratio) digests lack the ability to attack silicate and heavy mineral grains and are consequently of limited use [64]. One to three stream sediment samples per 4 km<sup>2</sup>, collected in first and second order streams in mountainous terrain, along with panning and visual inspection of a heavy mineral concentrate, proved

sufficient to recognise and narrow down mineralised zones within a prospective granite [29]. Black heavy mineral aggregates, comprising ilmenite, rutile, and containing inclusions of columbite-(Fe) and pyrochlore group minerals, were successfully used to outline pegmatite mineralisation in southeast Germany [27]. Detailed targeted geochemistry of residual B horizon soils (40 cm depth), with a sample grid spacing of 15 m × 100 m and perpendicular to geological strike led to the delineation of Sn, Cs and W anomalies related to vein mineralisation in slates and meta-siltstones along the southern flank of the Carnmenellis granite of Cornwall, United Kingdom [64]. Concentrations of Li (20–170 ppm), Cs (0.64–15.7 ppm), Ta (0.2–4.4 ppm), and Sn (2–6 ppm) represent a positive soil anomaly over the LCT pegmatite field of the Little Nahani Pegmatite Group, eastern Yukon Territory, Canada [77]. In the Ruhanga area of Rwanda, large muscovite flakes, present in the B-horizon of residual, deeply weathered tropical soils overlying pegmatite swarms, were analysed by pXRF, and returned very low values of  $4 < K/Rb < 4.8$  and Ta values ranging from 150–450 ppm, implying highly fractionated peraluminous bedrock (Figure 5) [45]. Meanwhile, soils overlying adjacent unmineralised biotite schists are characterised by  $270 < K/Rb < 320$ . Exploration in glacial drift terrain, however, will require the collection of bottom-of-till C horizon samples, in order to minimise the effects of glacial dispersion on lithochemical signatures [76]. Conversely, weak-leach enzyme leaches (selective leach extraction which employs an enzyme reaction to preferentially dissolve amorphous manganese dioxides) on transported B horizon soils have been successfully tested in Ontario and Manitoba, and supported the generation of exploration targets [24,30].



**Figure 5.** Portable XRF (pXRF) equipment is a valuable screening tool in grassroots LCT pegmatite exploration. At Ruhanga (Rwanda), B horizon soils overlying kaolinised LCT pegmatite contained large flakes of muscovite. Analysis by pXRF provided K/Rb values of 4.8, indicating highly fractionated bedrock and therefore a possible target [45].

Whilst the Canadian case studies utilised a univariate anomaly detection approach, lithochemical fingerprinting of regional and highly fractionated target lithologies using immobile major and trace elements, K/Rb, Nb/Ta, and Zr/Hf ratios, along with Li, W and Sn analyses, demonstrated that mineralisation processes and systems can be delineated in areas with soil cover and other geological media affected by secondary dispersion processes [29,45]. Applying geochemical and metallogenic markers to stream sediment analyses, for example, facilitated the mapping of Sn, W, Li and Ta anomalies



in hydrothermally-altered granite source material characterised by  $70 < K/Rb < 225$  and  $Nb/Ta < 5$ . Furthermore, depending on the size of the sample grid, the lithochemical classification process can lead to the production of regional lithochemical maps [28], which can potentially improve existing governmental datasets and streamline exploration in greenfields exploration programs. Local targets outlined by geological mapping and geochemical surveys are subsequently explored by channel sampling or trenching the bedrock [24], followed by detailed mapping and composite bulk sampling, in order to account for the potential irregular distribution of ore elements and minerals. Importantly, selective sampling of the pegmatite ore body should not be carried out, as isolated and thin, high grade veins of limited width or length are unlikely to be of economic interest [31]. The “nugget effect” conundrum implies that mapping and sampling should aim to identify multiple pegmatites or pegmatite swarms, providing sufficient tonnage over the course of mine life.

Similar to outcrop observations, visual mineralogy, pegmatite zonation and structural orientation data are important attributes exploration geologists need to recognise, describe and record in databases. New geological, mineralogical and geochemical data and evidence obtained from field exploration are used to continuously update the mineralisation system model previously established for the area of investigation.

### 3.4. Drilling

After exploration targets have been identified through desktop studies, geochemical and geological fieldwork, and sampling, prospective targets will have to be drill tested in order to obtain information about key geological factors rendering a LCT pegmatite economic, i.e., orebody geometry (lateral and vertical extension, dilution through country rock rafts, Figure 1), grade, and tonnage in order to produce a geological and grade 3D model. Reverse circulation (RC) drilling is the preferred method as, unlike traditional diamond core (DD) drilling, this technique facilitates the recovery of large diameter bulk samples and therefore minimises the “nugget effect”, often experienced with narrow-vein tin mineralisation and large pegmatitic minerals [31]. However, DD holes allow geotechnical parameters to be collected early in an exploration campaign. Operating in steep, mountainous terrain such as Rwanda, particularly requires information about geomechanical properties (RQD, RMR and Q-factors, hydrogeological parameters), to ensure safe mine and excavation designs during the mine operation phase [45]. The geometry of pegmatites is of particular importance as the shape and orientation of the pegmatite body will determine not only the best exploratory drillhole orientation and resulting intersection with the pegmatite body, but also inform on potential mining methods. Whilst the sub-horizontal pegmatite body of the Tanco deposit (Canada) requires room and pillar underground mining operation below Bernic Lake [53], the 40–50° inclined Greenbushes pegmatite is currently excavated using a large open pit operation following the pegmatite along the strike and dip of the Donnybrook-Bridgetown shear zone [20]. Furthermore, clause 49 in the JORC guidelines [78] essentially requires LCT pegmatites to be treated as industrial mineral deposits. For this reason, drillhole samples are required to undergo chemical and mineralogical analysis for determination of lithium product grades ( $Li_2O$  or  $Li_2CO_3$ ), along with a specification of the nature of lithium minerals present in the deposit [31].

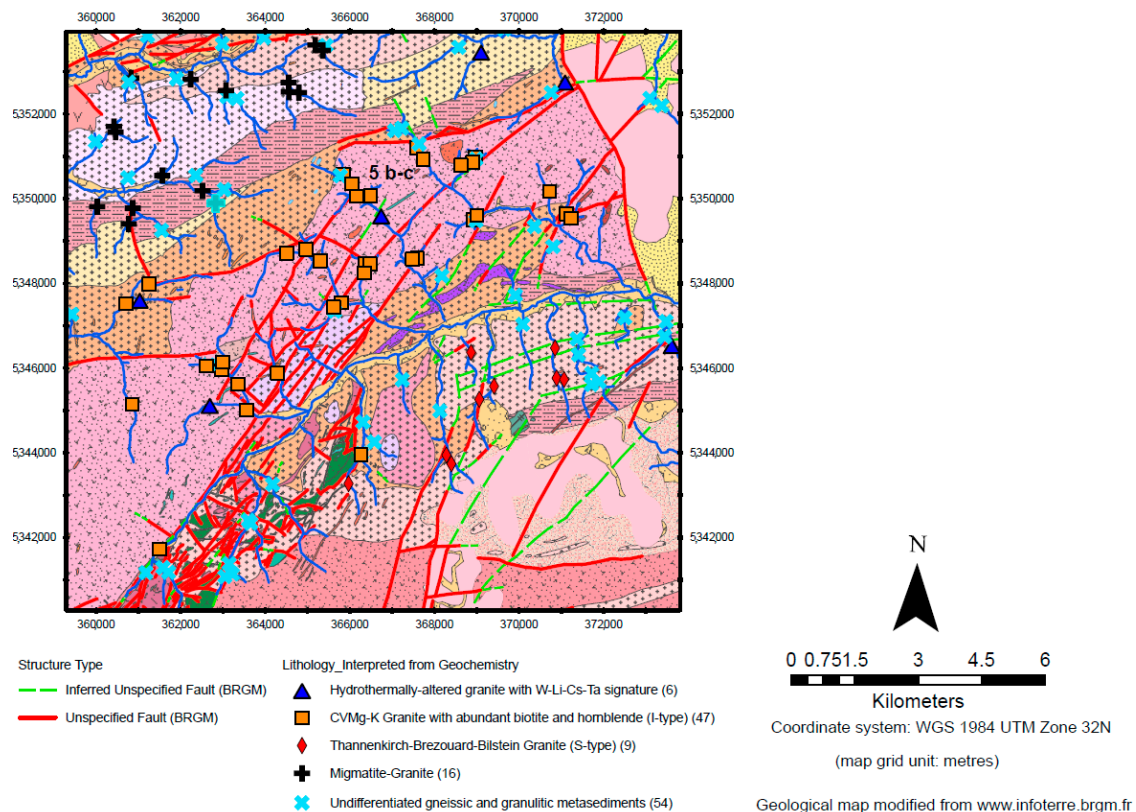
## 4. Case Studies of LCT Pegmatite Exploration

Two previously published examples highlighting key aspects of LCT pegmatite exploration (Figure 4) will be presented in the following two sections. The first case study describes conceptual target generation and a geochemical exploration survey in the Vosges Mountains (France) [29], whilst the second case study principally outlines the outcomes of an exploration programme involving geochemistry, geophysics and petrology leading to the discovery of economic LCT pegmatites at Kaustinen (Finland) [56,58].



#### 4.1. Conceptual Target Generation, Field Mapping and Petrogenetic Exploration Indicators

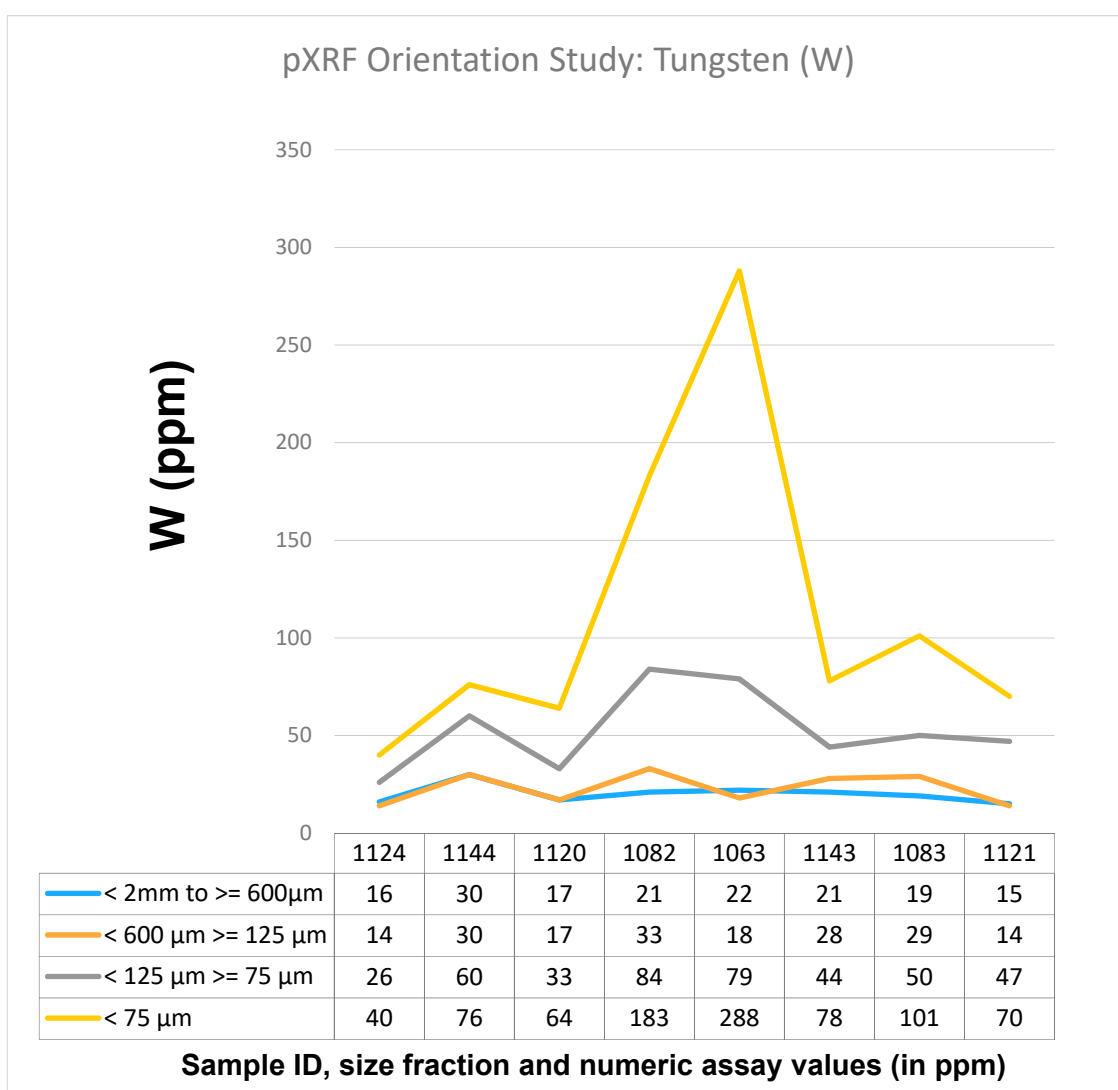
The increasing interest and upswing of the battery metals industry during the mid-2010s led to a screening study of underexplored, and potentially prospective, Variscan terrains in Central Europe [29]. An initial review of French Geological Survey (BRGM) data [79] identified W anomalies of >50 ppm in I-type granites of the central, highly metamorphosed, domain of the Variscan Vosges Mountains as a potential exploration area for Sn–W and Li–Cs–Ta mineralisation. Even though the area around Sainte-Marie-aux-Mines (Figure 6) is known to host post-Variscan base metal deposits in highly metamorphosed gneisses, no granite-related mineralisation systems were previously described.



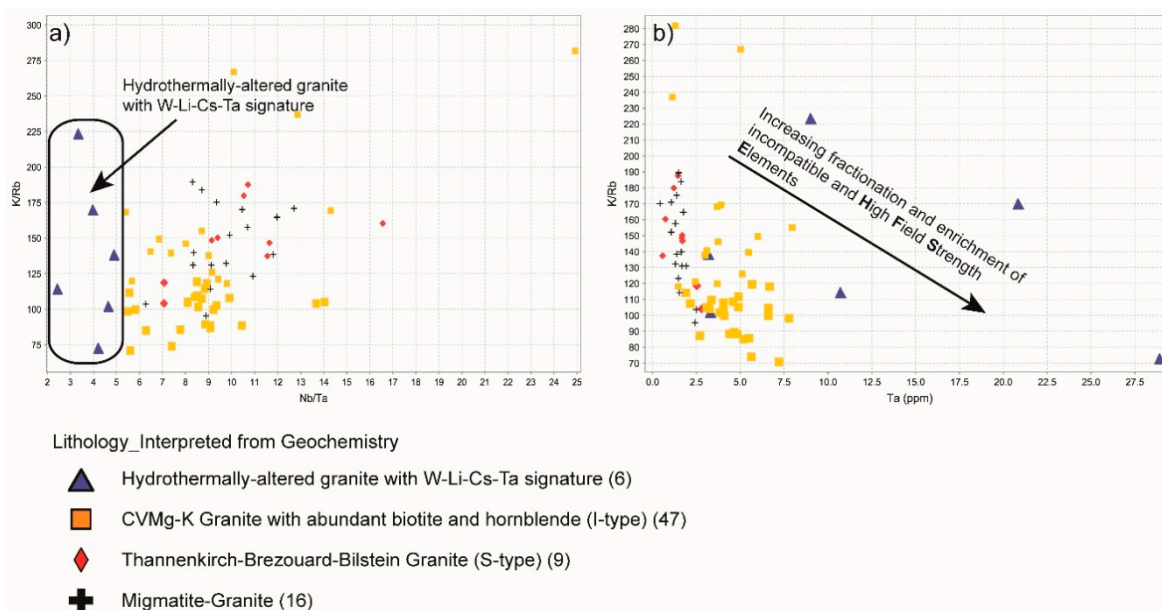
**Figure 6.** Lithologies interpreted from stream sediment geochemistry on modified Bureau de Recherches Géologiques et Minières (BRGM) geological map and structures, modified from Steiner (2019) [29] and BRGM (2019) [79]. The illustrated area covers the SW–NE trending Central Vosges Mg–K (CVMg–K granite), surrounded by highly metamorphic rocks of Paleozoic age. Observed leucogranitic and pegmatitic rocks with visible muscovite and tourmaline (location indicated as 5 b–c) along with interpreted “hydrothermally-altered granites with W–Li–Cs–Ta signature” are principally located along SW–NE orientated fault systems in the CVMg–K granite.

Following this desktop review, a decision was made to investigate the area in closer detail in order to prove whether the historic anomalies are (1) isolated occurrences, (2) related to the seemingly ubiquitous I-type (Central Vosges Mg–K) granite and (3) part of a potentially larger late-stage magmatic–hydrothermal mineralisation system. Initial reconnaissance work consisted of scout mapping of an approx. 200 km<sup>2</sup> area, supported by regional stream sediment sampling of first and second order streams. A pXRF screening and orientation study conducted on a selected number of sieved and homogenised stream sediment samples determined the –75µm fraction to be the optimum sample medium as the fraction returned the highest values for W, Cu and Ta (Figure 7). Additional multi-commodity targeted four acid digest followed by ICP-MS analysis resulted in the confirmation of pXRF results and the delineation of distinct Li (830 ppm), Ta (28.9 ppm) and W (578 ppm) anomalies in the host granite. In particular, the analysis of petrogenetic ratios, i.e. Nb/Ta < 5, 36 < Zr/Hf < 39 and

70 < K/Rb < 225 (Figure 8), revealed the presence of apparently strongly fractionated granite material in streams forming the topographic expression of large-scale shear zones and faults. Detailed mapping of these zones led to the discovery of distinct muscovite-tourmaline bearing leucogranites near previous W and Li anomalies in otherwise mantle-derived I-type granite host rock, implying that the stream sediment anomalies are presumably related to a secondary melting and fractionation event producing highly evolved felsic rocks. Ongoing unpublished research using SEM and QEMSCAN techniques investigate the mineralogy of both stream sediment samples and leucogranites with the aim to determine economic department of target elements in minerals. This case study shows that conceptual target generation using regional geological knowledge and historic data from national geological surveys can assist the identification of preliminary target areas. Furthermore, geological mapping and observations along with regional multi-element geochemistry and the utilisation of petrogenetic ratios can successfully narrow down target areas and reveal zones of increased magmatic fractionation and hydrothermal alteration, that may potentially be prospective for Li, Ta and W mineralisation.



**Figure 7.** Results of an orientation study [29] carried out using portable pXRF equipment in order to determine the most suitable grain size fraction for the present stream sediment sampling campaign.

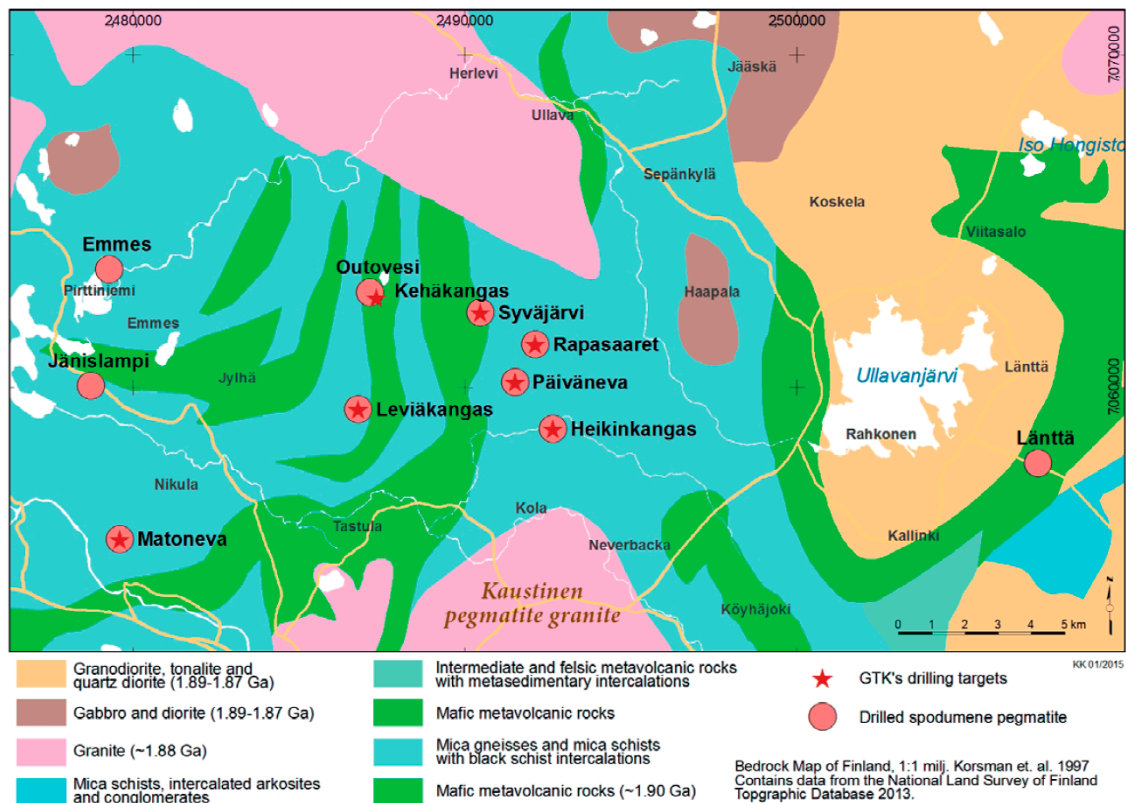


**Figure 8.** Examples from a stream sediment study [29] illustrating the use of (a) K/Rb vs. Nb/Ta and (b) K/Rb vs. Ta bivariate plots to determine highly fractionated granitic lithologies enriched in incompatible elements. In the central Vosges Mountains (France), peraluminous melts affected by hydrothermal alteration are thought to occur within a larger I-type granite province. In stream sediment samples, hydrothermally-altered granites are characterised by  $70 < K/Rb < 225$  and  $Nb/Ta < 5$ .

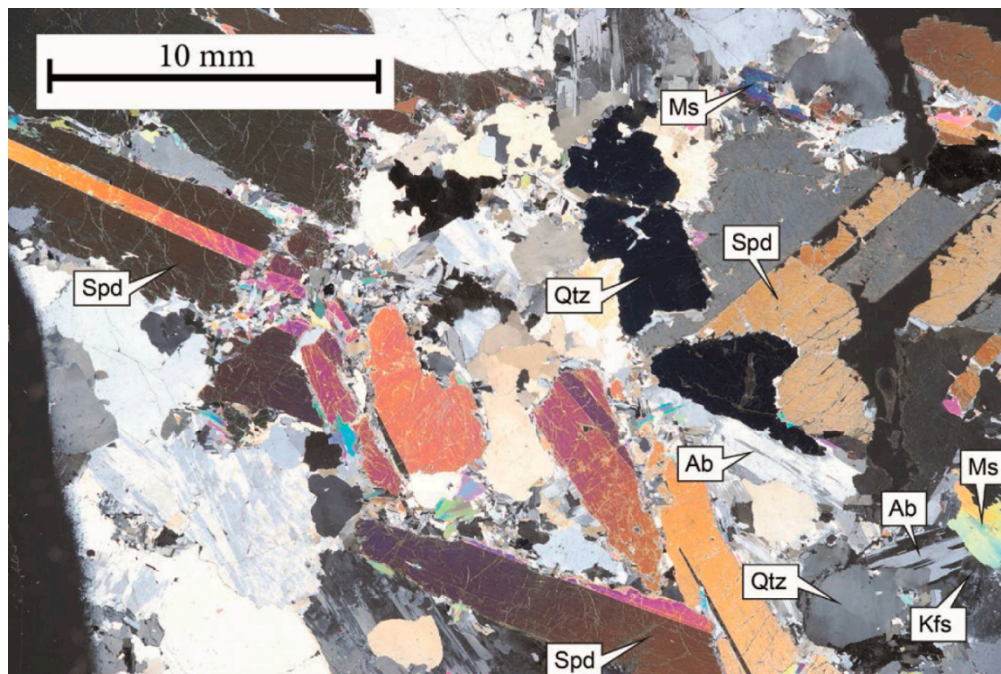
#### 4.2. Till Geochemistry, Geophysical Surveys and Petrology

The Kaustinen LCT pegmatite field, consisting of a number of exploration areas, is one of the most prospective rare element pegmatite terrains in Western Finland [58], located in the Pohjanmaa (Ostrobothnia) Schist belt (Figure 9). The area was explored by the Finnish Geological Survey (GTK) for more than a decade since the early 2000s [29]. After the governmental exploration phase had finished in 2013 the deposit contained 1.3 Mt with 1.08 wt. %  $Li_2O$ . The deposit is currently owned and developed by Keliber Oy, a Finnish industrial minerals company. The Kaustinen pegmatite swarms cross-cut intercalated Paleoproterozoic mica schists and metavolcanic host rocks and form relatively flat-lying, tabular bodies with dimensions of up to  $500\text{ m} \times 20\text{ m}$  [80]. The pegmatite swarms are thought to be related to the nearby Kaustinen “pegmatite” granite. Pegmatites are mildly zoned and generally contain albite, quartz, K-Feldspar, spodumene and muscovite along with accessory amounts of Nb–Ta oxides, cassiterite and tourmaline (Figure 10). Initial exploration by the GTK in the 2000s involved a follow-up of a 1950s spodumene pegmatite boulder discovery, surface mapping, glacial boulder tracing, and bottom-of-till geochemical sampling along  $50\text{ m} \times 50\text{ m}$  grids and selected lines with a 15 m sample spacing. The distinct occurrences of spodumene pegmatite rocks in glacial boulder fans along with Li anomalies of up to 5770 ppm in till led to the definition of linear trends and exploration targets in metasedimentary and meta volcanic country rocks (Figure 11). Subsequently, 15.5 line km of gravity and  $4.4\text{ km}^2$  of gravity and magnetic ground geophysical surveys were conducted in order to determine a potential geophysical signature of the pegmatites. The results, however, did not confirm a geophysical signature of the pegmatites as the petrophysical properties of pegmatites and metasedimentary and metavolcanic host rocks are similar (Figure 12). Drill targets were therefore principally generated by geological observations and geochemical surveys. A later GTK drilling programme comprised a combined 155 RC and DD drillholes (17 km), geochemical multi-element assaying using XRF, acid and fusion techniques coupled with ICP-MS. Detailed logging of drill core allowed to outline the dimensions of the Kaustinen pegmatites. In addition, the application of optical petrography (Figure 10) and SEM on visible mineralisation intersections in core resulted in a detailed understanding of pegmatite mineralogy and zonation.



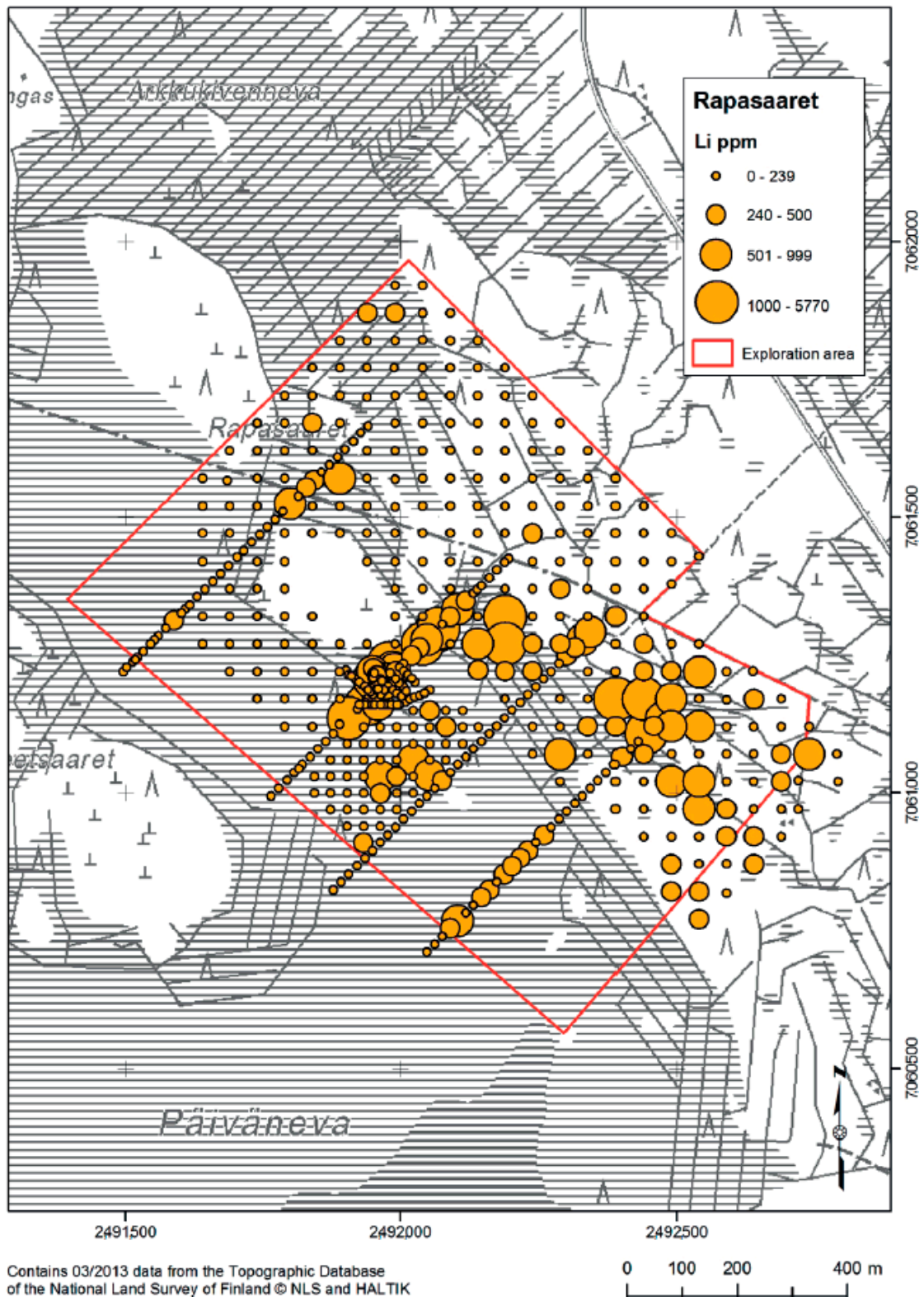


**Figure 9.** The Kaustinen Li pegmatite province, western Finland, showing the locations of the drilled spodumene pegmatites between 2004 and 2012. From Ahtola et al. (2015) [56].

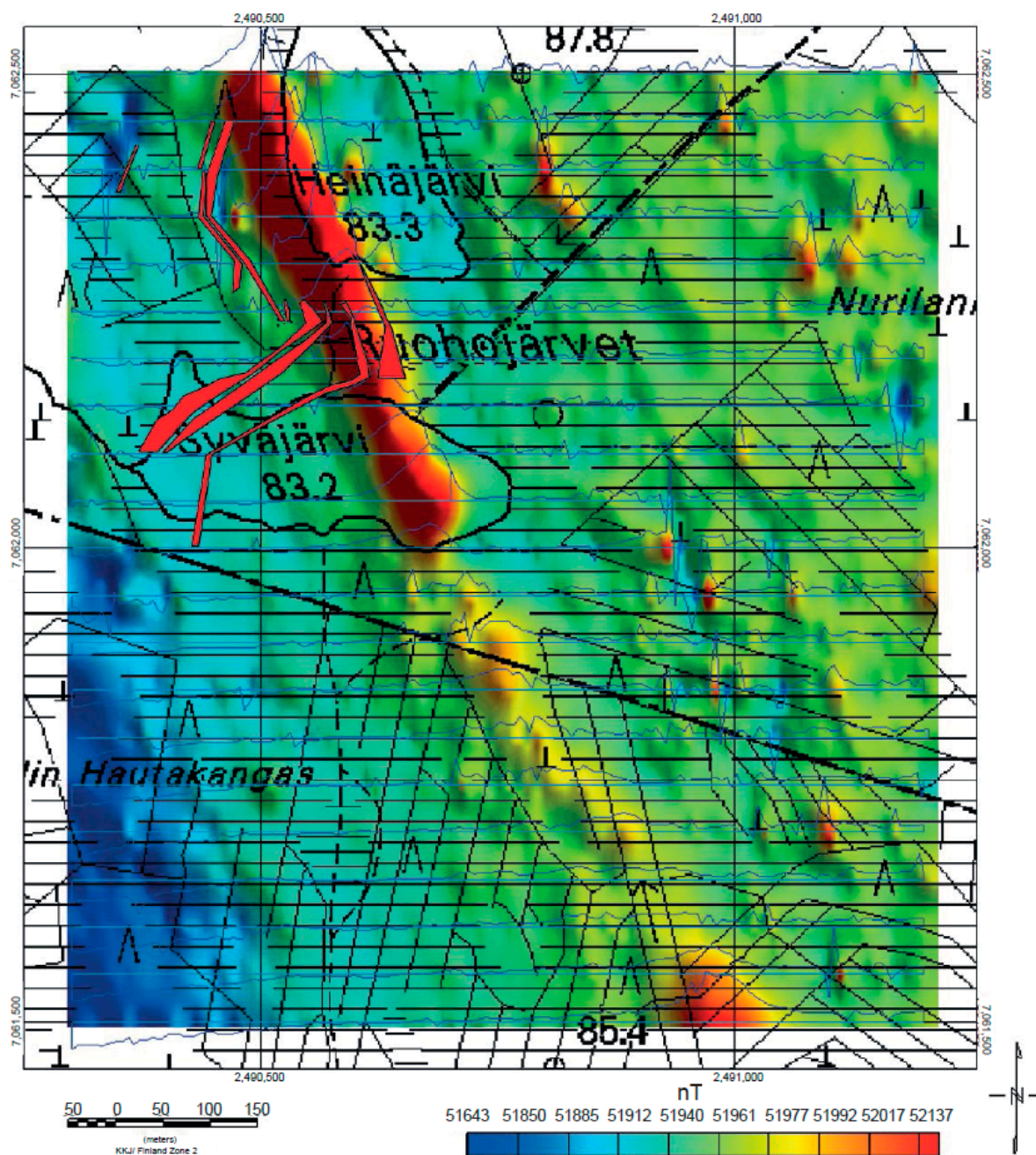


**Figure 10.** Thin section of spodumene pegmatite from drill core in the Leviäkangas exploration area, Kaustinen Li pegmatite province. Mineral abbreviations: Spd (Spodumene), Qtz (Quartz), Kfs (Potassium feldspar), Ab (Albite), Ms (Muscovite). From Ahtola et al. (2015) [56].





**Figure 11.** Map of the till sampling grid (from Ahtola et al. (2015) [56]) with plotted Li anomalies (in ppm) in the Rapasaaret target area, Kaustinen Li pegmatite province. The highest Li values (>1000 ppm) indicate the presence of Li pegmatite. Note: this study has not applied petrogenetic fractionation ratios as exploration vectors.



**Figure 12.** Ground magnetic map of the Syväjärvi exploration area, Kaustinen Li pegmatite Province. Modified from Ahtola et al. (2015) [56]. The blue lines show the magnetic profiles, whereas the red polygons mark the spodumene pegmatite. The positive magnetic anomaly (red colour) is caused by intermediate volcanic rocks. Basemap © National Land Survey of Finland, license number MML/VIR/TIPA/217/10.

In summary, the Kaustinen case study clearly demonstrates that the most reliable techniques for LCT pegmatite exploration are detailed geological field observations, along with geochemical and drilling surveys and mineralogical studies leading to the delineation of pegmatite geometry, zonation and chemical composition.

## 5. Conclusions

Petrological and mineralogical aspects of LCT pegmatite-related mineralisation have been extensively studied over the last four decades, leading to a detailed understanding of tectonic

and geochemical controls on pegmatite emplacement and ore genesis. This paper highlights a field trialled early-stage, grassroots exploration workflow applicable to the scope and aims of a mineral exploration company. Desktop literature and GIS studies form the starting point of an exploration campaign and provide a synthesis of historical information, data, regional prospectivity along with the identification of LCT mineralisation system elements. In a follow-up field campaign, geological outcrop and trench mapping, as well as detailed mineralogy and geochemical rock, soil and stream sediment sampling campaigns, are designed to continuously delineate and test areas of increased prospectivity, which are eventually drill tested in order to obtain additional information on orebody dimensions, grade, tonnage, and geomechanical properties. In light of clause 49 of the JORC reporting guidelines, the importance of determining ore mineral species requires the implementation of mineralogical methods at all stages of a LCT pegmatite exploration campaign.

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