2021

Stream Sediment Geochemistry and Automated Mineralogy as Exploration Tools for LCT-Pegmatite and Granite-related Mineralisation

CASE STUDIES FROM THE LEINSTER GRANITE (IRELAND) AND THE VOSGES MOUNTAINS (FRANCE)

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Submitted by Benedikt Maximilian Steiner to the University of Exeter as a thesis for the degree of Doctor of Philosophy by Publication in Geology, 2 March 2021.

I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Signature: B. Steiner

Abstract

This PhD thesis consists of four original papers and a synthesis chapter investigating the applicability of geochemical pathfinders and automated mineralogical analysis to regional (1 sample per 4 km^2) stream sediment surveys. In the context of exploration for rare metal granite and Li-Cs-Ta (LCT) pegmatites, the principal aim of this study was to examine and establish the essential links between geological, geochemical and mineralogical factors and to develop robust tools for commercial stream sediment geochemistry- and mineralogy-based exploration targeting.

The concept of applying granite and pegmatite mineralisation-related pathfinder elements and ratios to stream sediments, developed originally for mineral (K-feldspar, mica, Nb-Ta oxides) and bulk litho-geochemical exploration using outcrop and drill core samples, was tested in a case study using the Geological Survey of Ireland (GSI) stream sediment dataset for the Leinster Granite and adjacent Caradocian Volcanic Belt. Firstly, this study has demonstrated that incompatible (K/Rb) and immobile (Nb/Ta, Zr/Hf) trace element ratios, along with ore-forming elements (Li, Cs, Ta, Nb, Sn, W), provide useful pathfinders in exploration at 1:500,000 scale. Secondly, they can be used to delineate catchment areas within the Leinster Granite that bear evidence of increased magmatic fractionation and hydrothermal alteration characteristic of LCT pegmatite mineralisation. Prospective catchments have been identified in areas with known mineralisation (e.g., eastern flank of the Leinster Granite in the Blackstairs and Northern Units) and where none had been previously detected (e.g., Borris-Fennagh area). Distinctive values of K/Rb (<150), Nb/Ta (<7), Zr/Hf (28-47 ppm), Cs (12-47 ppm, Ta <7.5 ppm, W <10 ppm and Sn up to 50 ppm in

samples located in the Blackstairs, Tullow and Northern units of the Leinster Granite, imply that fractional crystallisation and magmatic-hydrothermal alteration locally altered the chemistry of the Leinster granite and led to enrichment of incompatible elements, most importantly Li, Ta, and Sn.

Additional examination of the applicability of geochemical pathfinder ratios for rare metal granite and LCT pegmatite exploration was conducted on nearly 200 stream sediment samples from the Northern and Central regions of the Vosges Mountains, NE France. The Vosges Mountains, which represent a Variscan basement complex on the western flank of the Rhine Graben, are relatively underexplored in terms of mineralisation, with the last regional mineral reconnaissance campaign conducted in the early 1980s. A similar approach was used to that for the Leinster Granite, to produce: (1) a geochemical classification of principal regional lithological units; (2) an assessment of magmatic fractionation and hydrothermal alteration processes in underlying rocks; and (3) the delineation of new exploration targets in the Grosse Goutte, Hergauchamps, Grand Rombach, Agigoutte and Barembach areas. In addition, the combination of detailed geological observations in the catchment areas, as well as the application of automated mineralogy using QEMSCAN®, improved the characterisation of signatures in stream sediments related to magmatic-hydrothermal mineralisation. This included the identification of mineral associations characteristic of tourmaline-muscovite-chlorite (greisen) alteration and the presence of cassiterite, wolframite, ilmenorutile and columbite minerals. These mineral associations suggest the presence of critical metal mineralisation associated with late-stage hydrothermal alteration affecting S- and hybrid I-S-type source granites, along major regional lineaments and shear zones of the Vosges Mountains.

Overall, the results of this study demonstrate that the application of geochemical magmatic fractionation pathfinder elements and ratios can be used in surface geological materials affected by secondary dispersion, if the catchment geology and mineralogy is taken into account and integrated into the geochemical interpretation. The knowledge gained from this research was summarised in a review paper providing a synthesis of LCT pegmatite genesis (Steiner, 2019a), development of applicable exploration techniques (Steiner, 2018, 2019b; Steiner et al., 2019), a catchment-prospectivity map for the Sainte Marie-aux-Mines area (Steiner, 2019b), and a systematic ‘cookbook’ approach to commercial exploration targeting and related investigations (Steiner 2019a).

Acknowledgements

This PhD study has been supported by the Camborne School of Mines, University of Exeter, principally by providing laboratory facilities to analyse the numerous stream sediments collected in the Vosges Mountains. Gavyn Rollinson and Sharon Uren were instrumental in facilitating the analytical work, for which I am very grateful for. The University of Exeter also financially supported the publication of two open access papers in *Minerals* which helped to make the papers available for the wider public to access and download.

I have been fortunate to be supervised by Prof. Jens Andersen and Prof. Ben Williamson, both experts in the field of igneous petrology and economic geology. I would like to express my sincere gratitude for their support and very helpful comments and guidance during the project. Their comments and suggestions significantly improved aspects of the papers and the synthesis chapter.

I would like to thank Nicolas Finlayson (2017), John Condron, Oisín Coffey and Matt Burford (2018) for their support during the two stream sediment sampling campaigns in the Vosges. Without their help, the 200 stream sediments would certainly not have been collected within two weeks.

I would also like to thank Dr James Barnet for his long-term moral support and trusted friendship. Not only was he involved in the first reconnaissance visit to the Sainte Marie-aux-Mines area on a cold day in December 2016, but he also helped with cross checking the scientific English of my manuscripts. Since then we have written two summary review papers on Eastern Siberia together.

I am thankful for the support I received from my fiancée, Mariola, who encouraged me to carry out this project despite the additional long hours and weeks spent away from home.

Finally, I want to express my thanks to my family, who supported me by providing access to our countryside chalet in the Vosges, continuously wondering what I was doing up in the mountains and why hundreds of muddy sample bags were lined up in a neatly manicured garden.

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i. List of original publications

This PhD thesis is mainly composed of the following four publications:

Paper 1:

Steiner, B.M. 2018. Using Tellus stream sediment geochemistry to fingerprint regional geology and mineralisation systems in Southeast Ireland. *Irish Journal of Earth Sciences*, 36, 45-61.

Paper 2:

Steiner, B.M. 2019. W and Li-Cs-Ta geochemical signatures in I-type granites - A case study from the Vosges Mountains, NE France. *Journal of Geochemical Exploration*, 197, 238-250.

Paper 3:

Steiner, B., Rollinson, G.K., Condron, J.M. 2019. An Exploration Study of the Kagenfels and Natzwiller Granites, Northern Vosges Mountains, France: A Combined Approach of Stream Sediment Geochemistry and Automated Mineralogy. *Minerals*, 9(12), 750-779.

Paper 4:

Steiner, B. 2019. Tools and Workflows for Grassroots Li-Cs-Ta (LCT) Pegmatite Exploration. *Minerals*, 9(8), 399-422.

Declaration of PhD candidate contribution to the published papers and thesis: Benedikt Steiner was the corresponding author for each of the above listed papers, and has been responsible for the compilation and edits to the manuscripts. His contributions, as sole author, to Papers 1, 2 and 4 were 100%. His contribution to Paper 3 was 90%, mainly in data acquisition, interpretation and production of the paper. Dr Gavyn Rollinson contributed 5% through conducting the QEMSCAN® analyses and providing the raw data which were subsequently interpreted by Benedikt Steiner. John Condron contributed the remaining 5% by helping to collect stream sediments in the Natzweiler area.

ii. Background and motivation for the study

The roots of this study can be traced back to 2010-11, when I worked as an exploration geologist on the Rössing uranium exploration site in Namibia and was tasked with investigating the mineralisation potential of ‘alaskites’ (leucogranites) and pegmatites. Whilst conducting a number of conceptual desktop studies, and being relatively ‘fresh’ and ‘green’ in the mining industry, I was not able to locate published and peer reviewed case studies for Li-Cs-Ta (LCT) pegmatite exploration. Similarly, I could not find any all-encompassing reviews of pegmatite exploration techniques beyond the commonly practised litho- and mineral geochemistry approaches. As most commercial regional mineral exploration programmes make use of soil and stream sediment sampling, and no studies have been published using these techniques, an early idea developed to conduct research on the usability of stream sediment geochemistry for defining pathfinder vectors to LCT pegmatite mineralisation. The aim was therefore to extend commonly accepted and practised approaches in mineral- and litho-geochemistry to secondary dispersed surficial material.

For this reason, my first aim was to conduct a proof-of-concept study using an available public domain dataset from SE Ireland (Paper 1), and to subsequently apply the knowledge and experience gained to a relatively underexplored region in Europe, the Variscan Vosges Mountains in France (Papers 2 and 3). Having regularly visited the Vosges for family holidays over the last 25 years, I was reasonably familiar with local geographical and geological aspects. Given the rather underexplored nature of mineral deposits in the area, with the last regional exploration programme conducted in the early 1980s, the opportunity arose to make a significant contribution to further the understanding of Variscan mineralisation styles in the Vosges. The research also provided an opportunity to test and verify exploration techniques for LCT pegmatites and other granite-related mineralisation in a greenfields exploration setting. The experience and knowledge that were generated in the preparation of Papers 1-3 were used to produce the all-encompassing review of LCT pegmatite exploration study (Paper 4) that I had begun thinking about during long field days in the Namib Desert nearly 10 years earlier.

The groundwork for this PhD study was conducted between 2017 and 2019, including the acquisition and interpretation of field data during two field seasons, as well as the compilation and submission of manuscripts to scientific journals.

1. Introduction

1.1. Scope and significance of the study

The growing demand for technology and battery metals in the 2010s has led to an increased drive in exploration for critical and rare metal granite and LCT (Li-Cs-Ta) pegmatites, as evidenced from a surge in the number of junior companies and governmental agencies exploring for these commodities worldwide. This development was fuelled by increasing lithium prices until 2018 (Figure 1), whereas the current commodity price is more volatile and affected by oversupply concerns. Until the early 2000s, pegmatites, and specifically LCT pegmatites, were considered to be of academic interest only and were rarely exploited commercially. This perception changed in the 2010s when governments began to regularly update lists of metals critical to their economic development (European Commission, 2017). Global production of commodities from LCT pegmatites is dominated by the Tanco Mine in Manitoba and the Greenbushes Mine in Western Australia. Most other operations are relatively small scale dominated by artisanal and illegal coltan mining in Central Africa (Linnen et al., 2012). The main uses of Li, Cs and Ta metals are in the ceramic, industrial minerals and electronic industries (Graedel et al., 2014; Dessemond et al., 2019).

1.1.1. Occurrence and distribution of critical and rare metals

Critical metals such as Li, Nb, Ta, Sn and W can be found in potentially prospective concentrations in a variety of geological settings ranging from sedimentary depositional environments (Li deposits in playas, continental and geothermal brines) to granites and pegmatites (Gourcerol et al., 2019; Brooks, 2020). Mineralisation in orogenic terranes is generally associated with highly fractionated (felsic) magmatic systems and secondary hydrothermal alteration

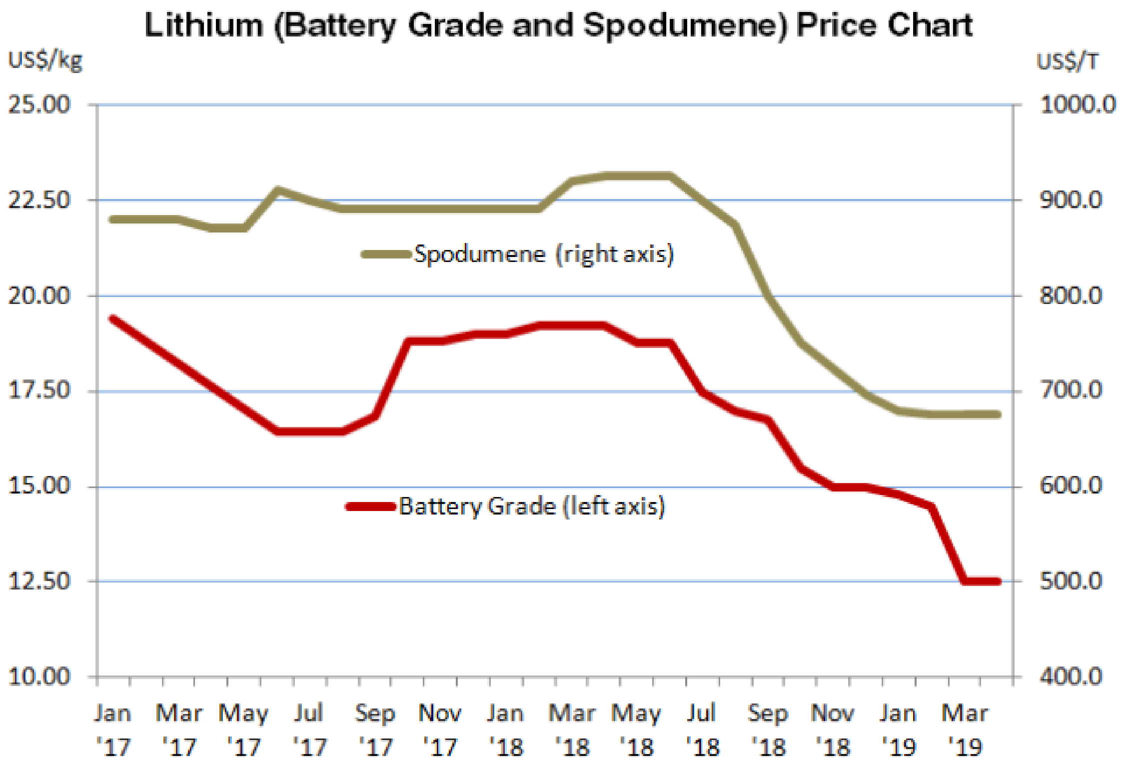

Figure 1. Price of spodumene and battery grade lithium per tonne from January 2017 to March 2019 (Consensus Economics Inc., 2019).

affecting primary granitic rocks and pegmatites (London, 2018; Kaeter et al., 2018, 2021a; Ballouard et al., 2020; Barros et al., 2020). Critical metal mineralisation is therefore mainly related to the formation of rare metal granites, LCT and NYF pegmatites and greisens, although minor occurrences are associated with quartz-montebrasite hydrothermal veins and tosudite mineralisation in gold deposits (Gourcerol et al., 2019). Rare metal granites are felsic, peralkaline, metaluminous and peraluminous intrusive rocks, forming in extensional, orogenic and anorogenic settings that host magmatic disseminated mineralisation (Cerný and Ercit, 2005). Metaluminous to peraluminous, medium and high phosphorous rare metal granites generally have the highest critical metal endowment and consequently are prospective for exploration. LCT and NYF (Nb-Y-F) pegmatites are coarse-grained and/or aplitic igneous rocks of granitic composition, which form in comparable geotectonic settings to rare metal granites. The economic enrichment of Li, Cs, Ta and Sn is more pronounced in LCT pegmatites commonly encountered in orogenic and anorogenic settings (Cerný and Ercit, 2005; Linnen et al., 2012), whereas mixed LCT and NYF pegmatite mineralisation was recently described in orogenic settings, such as in the Czech part of the Moldanubian Zone (Novák et al., 2012), and the Damaran Belt in Namibia (Ashworth et al., 2018, 2020). Greisen deposits mainly form as a result of high-temperature hydrothermal (vein-related) alteration of the upper and marginal portions of peraluminous rare metal and metaluminous granites and pegmatites and their host rocks (Štemprok et al., 2005). Their mineralogy is characterised by a porous assemblage of muscovite and quartz, often with additional Li micas (e.g. lepidolite, zinnwaldite), amblygonite-montebrasite, cassiterite and wolframite mineralisation.

Rare metal granites and pegmatites have been described and researched around the World, with a particular focus on North American and European examples as well as the well-known rare metal granite and pegmatite districts of Central-East Africa (Hulsbosch et al., 2013, 2017; Melcher et al., 2017). In the European Variscan belt, Li, Cs, Ta, Nb, Sn, W and other critical metals are mainly associated with Carboniferous–Permian peraluminous granites of Cornwall (Simons et al., 2016, 2017), the Erzgebirge and Bohemian Massif (Thomas and Tischendorf, 1987; Štemprok et al., 2005; Breiter, 2012; Breiter et al., 2007, 2017), French Massif Central (Cuney et al., 1992; Marignac and Cuney, 1999), Spain and Portugal (Charoy and Noronha, 1991; Roda-Robles et al., 2009; 2016; Marignac et al., 2020). Li mineralisation in the Variscan Belt is mainly within greisen-altered peraluminous granites, largely as Li-micas such as lepidolite, zinnwaldite and trilithionite (Gourcerol et al., 2019) and less often as spodumene. In contrast, Li mineralisation in the Iberian Variscan Belt, the Moldanubian Zone of the Czech Republic and the Caledonian Leinster Granite is often related to LCT pegmatites as primary spodumene and/or Li-mica and petalite, along with a characteristic accessory assemblage containing Ta(-Nb), Sn and W minerals. The pegmatites do not necessarily demonstrate a comagmatic evolution and relationship with nearby S-type granites, as demonstrated in the Leinster Province (Barros and Menuge, 2016). The presence of these distinctive metallogenic trends does not only have implications for prospectivity analysis and regional exploration, mainly in the selection of target areas, prospective lithologies and bedrock occurrences, but also affects downstream mineral processing applications as spodumene extraction and processing workflows are currently better understood and more advanced than for micas (Dessemond et al., 2019; Wikedzi et al., 2020). Therefore, the ability to recognise not only the enrichment of Li, Nb, Ta, Sn and W in magmatic-hydrothermal systems, but also the spatial distribution of prospective host rocks and related exploration techniques, is of significance to support the delineation of new mineral deposits and the (re-) evaluation of mineralisation trends and districts.

The aim of this PhD study was to provide a comprehensive review of regional exploration techniques (stream sediment sampling) for Li, Nb, Ta, Sn and W deposits and, from this, to carry out practical case studies in variably explored European metallogenic provinces.

1.1.2. A summary of the processes leading to the enrichment of critical metals in granites and pegmatites

Rare metal mineralisation in granites and LCT pegmatites is attributed to global tectonic processes affecting the deposition and subsequent reworking of an enriched sedimentary protolith during major regional orogenic events. Romer and Kroner (2016) outline three major controls on rare metal prospectivity at the scale of metallogenic belts, such as the European Variscides: 1) Intense chemical weathering in tectonically stable and low topographic areas which results in residual enrichment of Li, K, Rb, Cs, Sn, and W in siliciclastic sediments, which are 2) subsequently transported and deposited at continental margins; and 3) a heat source is required to drive magmatic-hydrothermal systems related to anatexis and felsic peraluminous magmatism. Such a heat source could include internal heating in orogenically-thickened crust leading to muscovite and K-feldspar melting, mantle heat advection in subduction settings, exhumation of ultra-high temperature (UHT) metamorphic rocks, or the presence of mantle-derived melts in (post-orogenic) extensional rift settings. All three controls were identified in the Leinster Granite Province (Luecke, 1981; Barros and Menuge, 2016) and the central and northern Vosges Mountains (Tabaud et al., 2014, 2015), increasing their conceptual prospectivity for rare metal granite and LCT pegmatite deposits from a regional geological and metallogenic point of view.

It is commonly accepted that peraluminous, high phosphorous rare metal and muscovite granites have the strongest enrichment in Ta, Sn and Li (Gourcerol et al., 2019). However, a purely peraluminous magmatic composition is not necessarily required to account for elevated levels of rare metals in granites and pegmatites. In an extensive data review and modelling study, Ballouard et al. (2020) demonstrated that Nb and Ta can also show elevated concentrations in enriched and contaminated mantle-derived alkaline (‘A2-type granite’), as well as more primitive ‘A1-type’, granites in anorogenic extensional and rift settings. In the context of subduction-related magmatic processes, the authors discuss the role of source rock composition, magmatic-hydrothermal evolution and rare metal enrichment in granites: Peraluminous muscovite granites form during initial partial melting of pelitic sediments and mica-rich igneous rocks in the lower-middle crust during syn- and late-collisional tectonic events. Partial melting under muscovite breakdown conditions will result in a residue that is enriched in biotite and ilmenite. In contrast, A2-type granitoids form by secondary high-temperature partial melting of these biotite- and ilmenite-rich, residual intermediate to felsic crustal rocks. High-temperature metamorphism produces F-rich biotite and leads to increased solubility of zircon, monazite and Fe-Ti oxide minerals in silicate melts. Consequently, this can produce a melt enriched in F, HFSE and REE, and characterised by relatively high Nb/Ta values as Nb is more compatible in biotite and ilmenite than Ta (Stepanov and Hermann, 2013).

Anatexis of meta-sedimentary protoliths can produce granite- and pegmatite-forming melts that are not necessarily linked to a source granite at depth (Goodenough et al., 2014; Barros and Menuge, 2016; Müller et al., 2016; Simmons et al., 2016). In a recent study of barren and LCT pegmatites of the Harris Granulite Belt (Scotland), Shaw et al. (2016) demonstrated that the composition of pegmatites may be more strongly controlled by the chemistry of the protolith than by magmatic processes such as fractional crystallisation. Consequently, variations in rare metal concentrations and petrogenetic indicator ratios in resulting rocks will depend on both protolith composition and mineralogy, and the levels and nature of contamination and fractionation during orogenic events. The authors suggested that source-rock melting took place at depth, within the Harris Granulite Belt, where small lenses of magma were trapped and then underwent fractionation to more fluid-rich compositions. These moved upwards through the crust to form highly evolved, and predominantly unzoned pegmatitic pods at the current erosion level.

The characteristic presence of Nb, Ta, HFSE and LILE in evolved peraluminous, muscovite-rich granites and late-stage pegmatites is explained by primary magmatic fractionation of minerals enriched in incompatible elements, followed by pervasive magmatic-hydrothermal alteration (Linnen et al., 2012; London, 2018). The latter is thought to involve F-rich hydrothermal fluids that selectively mobilised HFSE by complexation with F, Li, B and Cl. From detailed mineralogical studies on LCT pegmatites from Ireland and Rwanda, it has been suggested that sub-solidus hydrothermal processes may involve highly reactive F-rich fluids escaping along fractures and grain boundaries (Hulsbosch et al., 2013; Kaeter et al., 2018, 2021a; Barros et al., 2020). These would be capable of resorbing primary spodumene, K-feldspar, columbite, tantalite and mica to produce highly reactive Li-, K-, Ta-, Sn- and Nb-bearing fluids for the formation of albite-muscovite-greisen assemblages containing secondary cassiterite, microlite, lepidolite, muscovite, and also columbite group minerals (CGM) which have increasingly Ta-rich compositions towards their margins. In addition, HFSE and Sn could be transported into surrounding country rocks to form Sn and W vein deposits (Kaeter et al., 2021a).

In summary, Li, Nb, Ta and Sn mineralisation encountered in rare metal granites and pegmatites is the result of a complex interplay of source rock geochemistry, as well as magmatic, hydrothermal and structural processes. Specifically, LCT pegmatite mineralisation is produced by fluids emanating from granitic melts which were emplaced via prominent structural weaknesses, potentially forming a transition between granite-hosted mineralisation and late orogenic Sn-W vein deposits at shallower crustal levels, proximal and distal to known granite plutons or small batches of anatectic melt (Romer and Kroner, 2016; Shaw et al., 2016; Kaeter et al., 2021a). Exploration targeting should consequently consider the global setting of rare metal mineralisation during the orogenic and anorogenic evolution of continental crust. These concepts potentially create exploration scenarios in previously underexplored regional geodynamic settings, such as Archean and Proterozoic greenstone or granulite belts.

The three case studies presented herein provide examples of exploration initiatives to locate mineralisation, and predict its nature, in predominantly granite-dominated geological environments that show, in the case of the Leinster Granite and Vosges Mountains, clear geochemical and mineralogical signatures of magmatic fractionation and hydrothermal alteration. The relatively underexplored Vosges Mountains are characterised by a complex and protracted history of chemically distinct Variscan granite intrusions which are enriched in rare metals attributed to late-stage hydrothermal overprinting. However, whilst no major known pegmatites have previously been delineated previously in the Vosges, evidence for their existence is from the presence of coarse quartz-feldspar pegmatitic boulders identified during exploration work in 2017 and 2018. These boulders might, along with geochemical and mineralogical data, provide geological evidence for the transition to and emplacement of rare metal-enriched melts along defined structural corridors, representing a transition from granite to pegmatite emplacement and magmatic fractionation to hydrothermal alteration.

1.1.3. Common geochemical techniques used in the study of granite and pegmatite deposits

To date, most published academic papers have focussed on the genesis of granites and LCT pegmatites, along with the related enrichment of critical metals of possible economic interest (e.g. Černý, 1989; London, 2008; Simmons and Webber, 2008; Dill, 2015; London 2018). These studies generally used tried and tested combinations of geological and mineralogical observations, along with geochemical information in the form of mineral chemistry and whole-rock litho-geochemistry (Möller and Morteani, 1987; Selway et al., 2005).

Historically, there has been a significant research focus on explaining the occurrence of exotic minerals as a function of magmatic fractionation, hydrothermal fluid generation, and expulsion of fluids from the cupola of large S-type granite batholiths into metasedimentary country rocks (London, 2018). As previously explained, however, such pegmatites can also have an anatectic origin (Müller et al., 2017; Simmons et al., 2016).

To explain magmatic fractionation and enrichment of incompatible elements in late-stage magmas and magmatic-hydrothermal fluids, economic geologists use characteristic geochemical pathfinder elements and ratios such as Li, Sn, W, Be, K/Rb, Nb/Ta and Zr/Hf. These are usually obtained from mineral chemistry (e.g., mica and feldspar) or whole-rock (outcrop chip and drill core samples) geochemical data (Möller and Morteani, 1987; Selway et al., 2005; Ballouard et al., 2016). A decreasing K/Rb ratio, particularly below 150, reflects substitution of K by Rb in micas and K-feldspar during the evolution of granititic melts and pegmatite-hydrothermal systems, particularly when hydrothermal alteration processes result in metasomatic formation of K-rich minerals (Shaw, 1968). Nb/Ta values of <5 imply an increase in hydrothermal sub-solidus reactions, enriching more soluble Ta in F-rich residual melts and leading to more intense fractionation of Nb over Ta and secondary muscovitisation (Linnen and Keppler, 1997; Ballouard et al., 2020). The Zr/Hf ratio describes the fertility of evolving metaluminous and particularly peraluminous melts, as zircon is the primary reservoir for both Zr and Hf and preferentially incorporates Zr into the crystal structure (Lowery Claiborne et al., 2006). In peraluminous melts zircon strongly fractionates Zr from Hf, therefore, crystallisation of zircon controls Zr/Hf resulting in low Zr/Hf in residual melts (Fujimaki, 1986; Linnen and Keppler, 2002; Breiter et al., 2017; Gardiner et al., 2017).

Applied and routine mineral exploration campaigns rarely use mineral chemistry data, unless, at a later stage, there is a significant academic interest in researching the genesis of a pegmatite body. More commonly, early-stage greenfields prospecting and exploration campaigns make use of residual or transported geological materials which have undergone secondary dispersion, such as soils, stream sediments and glacial till, to define exploration targets under cover or at a distance from the sampling location (Moon et al., 2005). To date, however, there have been few academic studies on secondary dispersion materials to see if they record and can be used to locate the source of rare metal granite and LCT pegmatite signatures or, more generally, geochemical signatures resulting from late stage magmatic-hydrothermal processes in felsic melts. This study therefore sought to address this gap by undertaking three case studies where such geochemical and mineralogical signatures are evident in stream sediment samples. These were in explored (Leinster Granite, Ireland) and underexplored terrains (Vosges Mountains, France). The objective was to increase the generation of data and knowledge for these areas to improve their overall ‘attraction’ for researchers, explorationists and commercial investors.

1.2. Aims and objectives of the study

The aim of this study was to develop improved geochemical and mineralogical tools to explore for granite and pegmatite-related deposits which host critical and rare metal mineralisation, and from this to answer the following questions:

1.) *Can rare metal granite and LCT pegmatite geochemical pathfinder elements and ratios, previously established in mineral and litho-geochemical studies, be used in routine stream sediment geochemical surveys?*

This was addressed by applying and interpreting pathfinder ratios, such as K/Rb, Nb/Ta and Zr/Hf, along with ore forming elements, to the Geological Survey of Ireland (GSI) stream sediment dataset. This dataset covers the Leinster Granite and surrounding Irish Caledonides, an area known to host greisen vein W and LCT pegmatite mineralisation. The learnings and outcomes of the Leinster study were subsequently applied to a newly acquired dataset for an area in the Variscan Vosges Mountains, which has no previously known pegmatite or granite-related mineralisation.

2.) *How can automated mineralogical analysis be integrated into an existing stream sediment survey, and what additional value does this technique provide in the study of granite- and pegmatite-related mineralisation?*

This was tackled by selecting a number of stream sediment samples, collected as part of a Vosges Mountains exploration campaign by the author, that are rich in incompatible trace and ore elements. These samples were analysed using QEMSCAN® automated mineralogical analysis. The objective was to identify source mineral associations responsible for geochemical signatures in the stream sediment samples. The results of this investigation were used to assess the effectiveness of QEMSCAN® for routine mineralogical analysis of <75 µm stream sediment samples and to determine the exploration value of this approach for rare metal granites and LCT pegmatites. Furthermore, a flow chart of stream sediment sampling procedures was developed to guide the use of geochemical and mineralogical techniques in routine sampling surveys.

3.) *From existing understanding of European granite- and pegmatite-related critical and rare metal deposits, such as in SW England and the Erzgebirge,* *can targets be identified in underexplored areas such as the Vosges Mountains of NE France?*

This was addressed in a desktop study on the occurrence and regional geology of Variscan granites in the Vosges Mountains, and subsequently by conducting a regional reconnaissance stream sediment sampling campaign in the identified granite complexes. The latter required the collection of samples that could be analysed for both geochemistry and mineralogy. This approach provided data to better understand granite petrogenesis and geochemistry and to assess the enrichment processes of rare metals in granites.

4.) *What would a science-driven commercial mineral exploration approach to LCT pegmatite exploration look like, and what aspects would need to be considered on a routine basis?*

This was addressed by researching the wider topic and significance of LCT pegmatites, by compiling a summary review paper on their exploration and genetic models, and by developing a scientific and commercially sound exploration strategy.

1.3. Research and thesis structure

Research carried out as part of this PhD study was conducted between 2017 and 2019, involving two field seasons along with extended data processing, synthesis and interpretation using ArcGIS® and ioGAS™ software packages. Manuscripts were submitted to the Irish Journal of Earth Sciences, Journal of Geochemical Exploration and Minerals for consideration. After the required reviews and modifications, the manuscripts were accepted for publication.

The research was therefore structured on a topical paper by paper basis, even though the main periods of work spent on the different aspects of the thesis largely overlapped. The sequence of research and publication outputs followed the intended thesis structure. Firstly, the concept of applying pathfinder elements and ratios to stream sediments was tested in a known mineralisation district (Paper 1). This was followed by data acquisition, processing and interpretation in an underexplored district (Papers 2 and 3), and finally, by completing a summary review paper on LCT pegmatite exploration (Paper 4). It should be noted that Paper 4 was published three months before Paper 3 and therefore does not incorporate some of the results of Paper 3.

The remainder of the thesis consists of a methodology synthesis chapter, which describes the techniques used in the study, a discussion chapter, which places the four papers into the wider context of related science, followed by the four original, peer-reviewed papers published in 2018 and 2019.

2. Geological setting of the study areas

This thesis comprises of four papers that are primarily based on three geographic areas in Ireland and France. Paper 1 covers an area of 7544 km^2 on the south-eastern tip of Ireland, including counties Wicklow, Wexford, and parts of Kildare, Carlow, Kilkenny and Waterford. The study area is characterised by a relatively flat topography with sparse geological outcrops which limited fieldwork to exposures of individual outcrops and stream drainage channels. Much of the area is covered in Quaternary glacial landforms such as meltwater channel deposits, hummocky sand and gravel, moraines, eskers and drumlins, formed during periods of asynchronous and asymmetric glacial growth and retreat from 27–15 ka BP (Greenwood and Clark, 2009; Clark et al., 2012, 2018; Ó Cofaigh et al., 2012;). Evidence of NW-SE to N-S and NE-SW trending glacial landforms in the form of glacial till, subglacial lineations, glacially streamlined bedrock and crag and tails features were recorded in the Wicklow and Blackstairs Mountains, and in the central part of Wexford County, respectively (Fealy et al., 2009; Geological Survey of Ireland, 2013; BRITICE, 2017). These features record a phased advance and retreat of the Irish Ice Cap and Irish Sea Ice Stream, respectively, during the Last Glacial Maximum. A total of 1851 archive and re-analysed GSI samples from the Leinster Granite and Irish Caledonides were used for this study. The Caledonian age (~400 Ma) Leinster Granite, which has a surface area of ~1500 km2, was emplaced into Lower to Middle Ordovician metasediments of the Ribband Group (Roycroft, 1989). It is described as a two-mica, two-feldspar, peraluminous, S-type granodiorite consisting of five main units: the Northern Unit, Upper Liffey Unit, Lugnaquilla Unit, Tullow Lowlands Unit and Blackstairs Unit (Sweetman, 1987). LCT mineralisation is present within pegmatites that intersect the main Leinster Granite, particularly along the eastern flank of the intrusion (Luecke, 1981; O'Connor and Reimann, 1993). They are believed to have formed either by extreme fractionation of the magmas which produced the Leinster Granite or had a different, more REE-rich source (Barros and Menuge, 2016).

Papers 2 and 3 cover two separate areas of Variscan basement in the Vosges Mountains, NE France. Paper 2 focuses on the larger Sainte Marie-aux-Mines area, which is part of the central Vosges domain, while Paper 3 covers the northern Vosges Mountains. Both areas are forested and have a steep, largely uninhabited, mountainous topography with first to third order streams that drain into the deeply incised Lièpvre (Paper 2) and Bruche (Paper 3) river valleys. Due to the widespread and dense forestation of the mountain ranges and dense undergrowth, outcrop is usually sparse and limited to the steep flanks of first to third order drainage channels. The regolith in both study areas comprises poorly developed residual cambisols with limited evidence of soil horizon development (Institut National de la Recherche Agronomique, 2018), which are used for agriculture along the Lièpvre and Bruche valleys. A local ice cap covered the Vosges Mountains during the last glacial maximum (Würmian/Weichselian Stage) and a variety of fluvioglacial and aeolian landforms have been recognised, particularly in the central-southwestern Vosges and along the western and eastern flanks of the mountain range (Mercier and Jeser, 2004; Mercier, 2014). Evidence of glacial sediment or till was neither shown on BRGM maps (BRGM, 2021), nor encountered during fieldwork in the topographically higher parts of the study areas.

The northern Vosges Mountains, surrounding the Champ du Feu Massif near Natzwiller, host I- and S-type magmatic rocks which are thought to have formed in association with the subduction of Rhenohercynian oceanic crust underneath Saxothuringian continental crust (Elsass et al., 2008; Tabaud et al., 2014).

The Sainte-Marie-aux-Mines shear zone, located in the central Vosges Mountains, hosts calc-alkaline, I-type 'actinolite granites', referred to in this thesis and elsewhere as the 'Central Vosges Mg-K granites' ('CVMg-K'). These are thought to have formed from mantle-derived partial melts at 337.2 ± 1.8 Ma (Tabaud et al., 2015). Younger, S-type 'Western Central Vosges' granites (W-CVG) formed at 321.6 ± 2.8 Ma following anatexis of granulites and gneisses. Paper 2 investigates the larger Sainte-Marie-aux-Mines area (Figure 3), which is part of the central Vosges domain. Paper 3 focuses on the northern Vosges Mountains and the suite of I- and S-type granite intrusions of the Champ du Feu Massif (Figure 4).

In the Vosges Mountains, similar to the Cornubian Orefield and the Erzgebirge, Lower Palaeozoic metasedimentary rocks were intruded by Carboniferous Variscan S-type granites, leading to a number of syn- and post-magmatic mineralisation events. These peraluminous two-mica granites, and to a lesser degree, peripheral pre-Variscan metamorphic rocks, are rich in Sn, W, Li, Ta, Nb, Mo, Cu, Fe, Mn and U (Fluck and Weil, 1976; Dekoninck et al., 2017). The metals are vein-hosted and often occur within structurally-controlled granitic cupolas, comparable to other Variscan basement complexes (Cuney et al., 1990).

Apart from a regional reconnaissance campaign in the early 1980s, which described the distribution of Sn, W and Cu in the Vosges Mountains (Leduc, 1984), Li-Ta-Nb geochemical signatures have not been described in the Natzwiller or Sainte Marie-aux-Mines study areas. Therefore, the present study represents a significant contribution to the knowledge of metal endowment in the Vosges Mountains.

3. Methodology synthesis

The thesis comprises four papers that are based on both desktop data processing and interpretation workflows, as well as primary data acquisition involving fieldwork and laboratory analyses. This section summarises the different approaches and workflows that were employed during the course of the project.

3.1. Fieldwork

Fieldwork in the Vosges Mountains comprised two ten-day field stints in the Sainte Marie-aux-Mines (Paper 2) and Natzwiller (Paper 3) areas. The aim of the fieldwork was to obtain an independent and comprehensive geochemical dataset by sampling first and second-order streams at a low sampling density of 1 sample per 2–4 km^2, reflecting commonly practised regional reconnaissance sampling approaches by governmental geological surveys and exploration companies. The sample locations were selected to test distinctive structural and geochemical trends identified from previous BRGM investigations (Leclerc, 1984), as well as to characterise the different intrusive units across the northern and central Vosges.

Stream sediment samples were collected from stream traps, such as in the lee of large boulders or on point bars. They were sieved in the field to retain the <2 mm fraction which was placed into plastic bags. The sediment was allowed to settle in the bag before excess water was poured back into the stream. The resulting material yielded average weights of 500 g per sample. The sample bags were zip-tied and labelled with sample ID, coordinates and elevation information. In addition, heavy mineral concentrates were obtained from each sampling location by manual panning. These were used to visually identify the presence of indicator minerals such as cassiterite, to provide visual confirmation of the source mineralogy producing geochemical anomalies in stream sediments. However, the HMCs were not analysed for trace element geochemistry. After each sampling location, the equipment was thoroughly cleaned to prevent cross-contamination.

A detailed list of stream sample attribute data (colour, grain and mesh size, anthropogenic contamination, trap type, etc.) was recorded on an iPad using ESRI's 'Collector for ArcGIS' app (Version 19.0, ESRI, Redlands, CA, USA). Daily data quality checks and synchronisation with a master database ensured that the data quality was consistent throughout the sampling campaign.

Detailed observations and comparisons of drainage sediment composition, outcropping adjacent lithologies and heavy minerals present in pans were noted, supporting the subsequent mineralogical classification of samples. Linking observations of stream sediments and adjacent outcrops with subsequent mineralogical analysis confirmed that stream sediments were largely unweathered. They therefore accurately represent the overall bedrock geology of respective catchment areas and can be used for further representative geochemical interpretation workflows.

3.2. Geochemistry and mineralogy

Papers 1–3 contain extensive descriptions of stream sediment geochemistry and related interpretation of numerical data. Whilst Paper 1 is entirely based on a publicly available dataset published by the Geological Survey of Ireland (GSI), Papers 2 and 3 contain new data generated as part of this project. In addition, Paper 3 provides new mineralogical data from automated mineralogical analysis of selected stream sediment samples. A detailed account and a critical review of the geochemical and mineralogical techniques used as part of this PhD project, along with the quality control (QC) procedures, are compiled in Appendix A.

3.3. Data interpretation

The workflow of geochemical data interpretation included the use of univariate and multivariate statistics and lithological mapping. The results from the univariate statistical analysis were compiled as summary tables in Papers 2 and 3, comprising information on minimum, maximum, mean, median, 5th, 10th, 25th, 30th, 60th, 75th, 80th, 90th, 95th, 98th, and 99th percentiles. Multivariate analysis in Paper 3 comprised of principal component analysis (PCA) using a $\log_{10}$ transformation and B, Be, Cu, Li, Nb, Rb, Sn, Ta, Th, Ti, W and Zr as input variables. PCA involved the reduction of 12 input dimensions into two-dimensional variable-sample analysis (RQ) plots. In RQ plots, samples plot as points and variables as vectors, with the length of the vectors proportional to the variability of the two displayed principal components. RQ plots offer the possibility to determine element relationships for the principal components bearing the highest variance in the dataset.

Initial classification of lithological units using multi-element geochemistry was achieved by delineating population clusters in bivariate geochemical plots and PCA RQ plots. Each sample point was assigned a lithology depending on a characteristic trace element signature, obtained mainly from historic petrological studies but also AusIMM litho-geochemical tables (Mazzuchelli, 2011) and the FOREGS Geochemical Database (Salminen et al., 2005). These lithologies were then refined using geological observations in upstream catchment areas and float, to better represent subtle nuances in geochemical composition.

By assigning a single source lithology to each stream sediment sample, the assumption was made that at the scale of available geological maps and survey planning (e.g., 1:50k in the Vosges, 1:500k at Leinster), each stream sediment sample will carry a trace element signature characteristic of each previously mapped lithological polygon. This assumption therefore allowed for a rapid delineation of a corresponding litho-geochemical signature on a regional basis. It was clear, however, that at the comparably much smaller scale of individual drainages, lithological variations may be more distinct and influenced by local primary and secondary geochemical dispersion processes. The local effects of lithological variations (Section 5.2.) were mitigated by detailed inspections of the coarse reject stream sediment sample (>2 mm) and nearby outcrops. These observations were recorded in the sampling database, which was subsequently used to inform the geochemical interpretation of bivariate and PCA plots. For example, highly fractionated lithologies in the CVMg-K granite were determined using K/Rb ratios of <150, Nb/Ta ratios of <5 (Selway et al., 2005; Ballouard et al., 2016) and characteristic enrichment patterns of W, Li, Ta, supported by the observation of leucogranite float in river channels. Due to the generally steep topography, dense woodland and soil cover, resulting in a patchy distribution of geological outcrops mainly restricted to stream channels (Section 1.3.), a reliable estimation of average bedrock composition for each catchment area weighted by percentage area of the different bedrocks in the catchment was not made. In the author’s opinion, this approach would require a detailed drainage-scale bedrock geological map. Such a map is beyond the scope of this project and the availability of geological outcrops in the study area.

A similar approach of using immobile trace element data to fingerprint lithological, alteration and mineralisation processes in rock, drill core and soil samples has been practised for a number of years by Australian geochemists. Readers are referred to Halley (2020) for a comprehensive review of the workflow.

3.4. A critical reflection of the overall research methodology

The initial project concept, planning and realisation was based on previous experience in soil and stream sampling, in particular using workflows and standard operating procedures (e.g., BGS G-BASE manual) in an industrial context. The project involved a desktop and literature study of the Vosges Mountains using spatial data (BRGM, 2021) and relevant geological publications, conceptual regional target generation, along with an initial field visit to Sainte-Marie-aux-Mines to acquire a set of orientation samples. A significant addition to previously employed workflows during the orientation study and subsequent sampling programmes included use of the ESRI Collector for GIS app, which became mainstream in 2015 after several years of research and development by major commercial GIS software developers. Use of the GIS app sped up the process of sample collection and data management. The time required for sample collection decreased from ~30–35 minutes using traditional paper-based means of data capture to ~20–25 minutes using the app. This increased the number of samples collected and processed each day by four to five samples and resulted in a higher overall sampling productivity.

During the first sampling campaign in the central Vosges (Paper 2), field observations and topographic maps indicated that nearly all samples taken from first and partly second order streams were located within 500 m or less from the actual stream source (i.e., given the steep topography, the stream sediment samples were not transported far from their bedrock parent). This was further confirmed by detailed inspection of the >2 mm fraction obtained during the sampling process, along with bedrock lithologies mapped in exposed stream beds and surrounding outcrops further upstream. Whilst the verification of drainage lithologies is a common procedure and was previously practised by the author in an industrial setting, it became clear that more evidence was required to confirm the representativity of stream sediments in a drainage basin, in order to improve the interpretation of the geochemistry and corresponding source mineralogy of individual samples.

Following a discussion and reflection on the employed sampling techniques with Dr. Gavyn Rollinson, a decision was made to improve the reliability of geochemical interpretation by conducting automated mineralogical analysis of both stream sediments and surrounding corresponding outcrop samples. Automated mineralogy has only seen very limited use in stream sediment studies to date (e.g., Mackay et al., 2016), but selective indicator mineral chemistry studies at Leinster are in progress (Kaeter et al., 2021b). In addition, the technique is resource intensive and costly (approximately £500 per sample) and, unless a large financial budget is available, can usually only be applied to a selected number of samples. Therefore, geochemical analysis of key pathfinder elements and ratios delineating prospective drainages in Paper 3 was employed in the first instance to select appropriate samples for further mineralogical investigation.

The sample grain size used for automated mineralogical analysis was equivalent to the optimum grain size (<75 µm), determined in an orientation study (Paper 2) and used during geochemical analysis, which is less influenced by hydraulic effects and therefore better represents the drainage and catchment (Fletcher, 1997). This approach consequently allowed a direct comparison between mineralogy and geochemistry. Whilst the mineralogy of coarser grain size fractions, i.e., fine (177 µm) to coarse (1 mm) sands, could be determined during an orientation study to aid the determination of indicator minerals, using different grain size fractions in geochemical and mineralogical samples would possibly not provide an accurate reflection of the source mineralogy causing a geochemical anomaly, if the presence of geochemical anomalies is limited to a specific grain size fraction (e.g., the silt and clay size fraction (<75 µm). However, these considerations should be assessed on a project-by-project basis, as part of an orientation study testing the geochemical and mineralogical response of common screen sizes. From a practical and financial point of view, the use of existing geochemical analyses to determine samples for further mineralogical analysis would certainly support a streamlined mineralogical testing campaign, avoiding random mineralogical testing of stream sediment samples.

The combination of mineralogy and whole stream sediment geochemical data proved to be very valuable and informative, confirming both the source mineralogy causing the geochemical anomaly and possible alteration assemblages, providing evidence for late-stage hydrothermal alteration and mineralisation processes. Consequently, the study conducted as part of Paper 3 proved the scientific and commercial scope of improving the understanding of drainage-scale geological and mineralogical processes in the study area. In addition, along with the characterisation of local geological and mineralogical processes, the application of advanced multivariate statistics to geochemical interpretation and unsupervised classification (Principal Component Analysis) techniques supported the assignment of lithological attributes to individual stream sediment samples.

In addition, whilst the use of an industry-standard four acid digest along with a comprehensive multi-element analytical suite (Halley, 2020) successfully outlined the presence of regional geochemical anomalies in stream sediments (Papers 2 and 3), a more aggressive sample decomposition, such as sodium peroxide fusion, could be employed to allow for a comprehensive and targeted analysis of resistate minerals and elements, such as zircon, cassiterite and tantalite.

In summary, the stream sediment surveys in the Vosges Mountains proved that stream sediments should generally not only be interpreted using univariate statistical tools, as routinely employed during industrial surveys, but also incorporate knowledge generated from both geological and mineralogical investigations of drainages, their source rocks and possible dispersion patterns, and multivariate geochemical interpretation techniques supported by mineralogical analysis.

4. Summary of the research papers

The four published papers together provide a case for the routine analysis of stream sediment geochemical as well as mineralogical data during exploration, particularly when assessing regional (>200 km^2) areas identified from the delineation of conceptual targets during Phase 1 desktop studies. The research carried out bridges the gap between routine uni- and multivariate metal association and anomaly assessment workflows, and further genetic interpretations which aim to establish and explain the lithological control of mineralisation in rare metal granite and pegmatite source rocks. The Leinster Granite and Vosges Mountains represent two such areas which are prospective for critical metal mineralisation in Europe. In the Leinster area (Paper 1), litho-geochemical fingerprinting and the application of petrogenetic indicator ratios to stream sediment data proved the presence of drainages prospective for LCT pegmatites and greisen W mineralisation along the eastern flank of the Leinster Batholith and the East Carlow Deformation Zone (Luecke, 1981; O'Connor and Reimann, 1993). In the Vosges (Papers 2 and 3), the use of stream sediment geochemical pathfinder techniques, supported by data from automated mineralogical analysis, provided evidence for genetic processes responsible for previously unknown lithologically- and structurally-controlled Li, Nb, Ta, Sn and W mineralisation in a variety of metaluminous to peraluminous Variscan granites.

In addition, this research has highlighted the need for a closer evaluation of the multi-faceted processes leading to: 1) the occurrence of critical metal anomalies in stream sediments; and 2) the mineralisation processes in rare metal granites. Therefore, the following section will provide a reflection and synthesis of the generated new knowledge and results of the research. The acquired data, geological and geographical observations in the Vosges will be used as a starting point for determining the types of geochemical and mineralogical evidence needed for locating and characterising critical metal mineralisation in media affected by secondary dispersion. This has led to the development of a refined approach to stream sediment sampling, and an improved understanding of the metallogenic setting of a selected area of the European Variscan Belt. The developed workflow and considerations will be particularly beneficial in remote and poorly mapped areas where geochemical and mineralogical surveys can add additional value to support the definition of stratigraphy, lithologies and anomalous metal abundances.

5. Synthesis and discussion

5.1. The use of stream sediment geochemistry and automated mineralogy as reconnaissance targeting tools

Stream sediment geochemistry has long been recognised as a valuable investigation tool in the prospecting, exploration and mining of mineral deposits (Moon et al., 2005; Moon, 2021). Stream sediments are routinely collected by governmental geological surveys, research departments and industry for areas of specific metallogenic interest (e.g., data in SE Ireland used in Paper 1; O'Connor and Reimann, 1993: Knights and Heath, 2016) or entire countries (e.g., in the 1970s a United Nations Development Programme collected tens of thousands of stream sediments across Rwanda; Ivanov, 1979).

Stream sediment geochemistry is relatively well understood being dependant on catchment geology, physical sedimentation processes and element mobility. It is usually evaluated using statistical means to investigate secondary dispersion and the occurrence and distribution of metal anomalies (Hawkes, 1976; Hale and Plant, 1994; Moon et al., 2005). Over the last four decades, a large number of research papers have been published using data from stream sediments as a tool in orientation studies (e.g., Fletcher, 1997), for catchment analysis (e.g., Hale and Plant, 1994), geochemical anomaly and mineral prospectivity mapping (e.g., Carranza, 2008), and microchemistry of mineral grains (e.g., Chapman et al., 2000a, 2000b; Mackay et al., 2016).

In the author’s experience, however, most regional stream geochemical datasets are not fully used and analysed in terms of pathfinder and trace element geochemistry, particularly by industry. Limited studies have been published on the use of trace element geochemistry for regional lithological mapping, particularly in terms of LCT pegmatite and granite-related mineralisation. Kirkwood et al. (2016) analysed such information to extract lithostratigraphic information from G-BASE stream sediment datasets, proving that variations in geochemistry correspond to mapped variations in the bedrock geology of SW England. In Northern Ireland, Earls (2016) applied a combination of governmental Tellus geophysical, soil and stream geochemical data to improve the understanding of bedrock hosts for gold mineralisation. Only recently have researchers published routine interpretation workflows for multi-element geochemical datasets applicable to rock (drill core and outcrop) and soil materials, but not stream sediments (Halley, 2020).

The geochemical and mineralogical work conducted as part of this PhD study demonstrated that an understanding of local and regional bedrock geology, as well as associated sedimentological and secondary dispersion processes, is essential for the interpretation of geochemical and mineralogical data obtained from routine stream sediment surveys, carried out by governmental geological surveys and industry. For example, the possible variability in bedrock lithologies, accessory mineral content and secondary dispersion processes can potentially influence geochemical signatures and ratios. The drainage bedrock geology of the Vosges study areas is reasonably well understood and controlled by carrying out routine inspections of coarse drainage sediment, rock float and outcrops, supported by selected automated mineralogical analyses, ultimately leading to a better understanding of multivariate geochemical responses and signatures.

However, other greenfield areas might be: 1) covered by transported overburden such as extensive glacial till in the northern Hemisphere, potentially introducing erroneous geochemical signatures into stream sediments; 2) affected by sedimentary, including winnowing, processes at regional and catchment basin scale; 3) characterised by complex lithological compositions in drainages; and 4) inadequately placed into context in terms of bedrock geology.

Sedimentary processes at catchment basin scale and their influence on the appropriate choice of sample representativity and fraction, in the context of the acquired Vosges samples, warrant further discussion. Stream channels are usually coupled to the valley slopes at the catchment basin scale, i.e. weathering or erosion processes provide the channels with sediment from local sources, whereby the sediment represents all parts of the catchment equally (Fletcher, 1997). On the contrary, decoupling of streams from their source areas occurs where the catchment sizes increase, particularly in lower topographic areas characterised by wide flood plains. In these areas, streams flow through and erode their own alluvial deposits, which are not necessarily sourced from the surrounding mountain slopes. As a result, the stream sediment does not represent all parts of the drainage and catchment equally. In the Vosges, field observations and the use of topographic base maps indicated that nearly all samples were taken from first and partly second order streams located within 500 m or less from their sources. As a result of the topography and absence of flood plains, the stream sediment samples were eroded from a proximal bedrock parent.

Winnowing (i.e., the selective removal of fine or coarse grains from the stream bed through sedimentary processes) is a common mechanism influencing stream sediment geochemistry on a regional-, catchment- and stream bed-scale.

Lapworth et al. (2012) provide a case study of Nigerian (dry) stream sediments affected by Saharan Harmattan winds depositing wind-blown sands and removing fine-grained clays, leading to a zircon-rich residual stream sediment which will essentially affect bulk sample composition. In European temperate environments, at catchment- and stream bed-scale, winnowing processes can result in the enrichment of heavy minerals, such as cassiterite or zircon, in fine-grained (<100 µm) stream sediment at both high- and low-energy sites, due to the potential removal of finer less dense grains. Nevertheless, the collection of fine-grained stream sediments is generally commonplace, as heavy minerals are less influenced by hydraulic effects and better represent the drainage and catchment geology (Fletcher, 1997). In the central Vosges, a number of samples contained anomalous Zr concentrations of up to ~36,000 ppm. These concentrations could be explained by winnowing but are more likely to be the result of an enrichment of heavy minerals in well-developed stream traps, as fine clays and silts were abundant upon visual inspection of the samples.

Stream sediment composition can be influenced by soil erosion resulting from agricultural contamination and associated influx of abundant fine-grained material into streams. This scenario has particularly been observed in tropical regions, where coarser sediment fractions and HMCs should be routinely analysed (Paopongsawan and Fletcher, 1993). Samples in the Vosges were collected from undisturbed forested areas, where no soil erosion was observed.

Seasonal effects influencing the abundance and transport of indicator minerals are particularly evident in the tropics and in higher altitude mountainous areas, where ice melting or seasonal rainfall lead to variable fluvial dynamics. In the Vosges, samples were obtained just after winter in early-mid spring, when indicator mineral abundance is likely to be higher compared to the drier summer months. For this reason, the geochemical and mineralogical interpretation of stream sediments should be informed by processes affecting drainage geology and secondary dispersion. Whilst this is not always a straightforward process, particularly when dealing with historical data that was inherited or acquired from other sources, or when working in fast-paced industrial environments affected by limited time and budgets, an effort should be made to investigate the sedimentological controls on stream sediment geochemistry and mineralogy.

In light of the applicability and use of stream sediment surveys by governmental agencies and industry, clear guidelines are required that allow geologists of all knowledge and experience levels to understand and follow, but also critically question and evaluate, standardised workflows and observations in the field. Several widely used methodological sampling guidelines are publicly available. For example, the G-BASE survey guidelines were developed by the BGS (Johnson, 2005) and are used as part of international geochemical baseline mapping projects (Lapworth et al., 2012). However, whilst the G-BASE guidelines clearly describe sampling logistics, sample acquisition, processing and QC protocols, a workflow for assessing the link between drainage geology, geochemistry and mineralogy carried out during orientation and routine sampling surveys is not presented.

The learnings of this PhD study were summarised into a concise A4 landscape workflow (Figure 2), which aims to provide geoscientists with a starting point to consider the variety of aspects relevant to the collection and subsequent interpretation of stream sediment geochemical and mineralogical data. Whilst workflows are developed to standardise fieldwork, workflows should be adjusted to relevant and applicable geographical and geological scenarios. For example, Figure 2 refers to rare metal granite and pegmatite deposit signatures, but different secondary dispersion processes and geochemical signatures might be characteristic of other deposit types and geological and geographical environments.

The proposed workflow follows a cognitive learning and feedback loop-based structure of UNDERSTAND – PLAN – TEST – EVALUATE AND REFLECT. Before logistics-intensive stream sediment surveys are commenced, an orientation study (Hale and Plant, 1992; Fletcher, 1997) is required to UNDERSTAND the spatial distribution of watersheds, sedimentological and lithological controls on stream sediment geochemistry. The results of the orientation study can be used to evaluate the feasibility of stream sediment sampling in the project area and to provide initial background, threshold and anomalous metal concentration ranges and mineral assemblages in the area. Orientation studies should be carried out in drainages and watersheds delineated by GIS and regional geological analysis. They should be supported by geological mapping, portable XRF (pXRF) analysis, heavy mineral concentrate (HMC) sampling and trial automated mineralogical analysis, in order to provide a first insight into local geological variations and mineralogical responses of various screen sizes and sample volumes. A particular focus should be placed on the recognition of accessory minerals indicative of the presence of different bedrocks and mineralisation types, such as greisens, spessartine and columbite-tantalite-bearing granites, and pegmatites.

In a subsequent step, explorationists should use the outcomes of their orientation study to PLAN the details of the actual stream sediment survey. Considering administrative, logistical and geological requirements, sampling strategies and protocols must be compiled. This could be achieved by adapting the G-BASE procedures (Johnson, 2005) to the project scope and ensuring training is delivered to project staff, highlighting the importance of understanding the key link between sample acquisition, geochemistry, mineralogical assemblage and lithological control. In addition, the planning phase should consider specific database architecture and input values adapted to likely occurring rocks and minerals identified during a previous orientation study.

The TEST phase comprises the actual stream sediment survey, whereas detailed observations are conducted of present outcrops, coarse stream sediment material and HMCs in order to better understand the catchment geology and likely geochemical and mineralogical responses during later sample analysis and interpretation. As the extent of the sampling campaign will be much larger than during an initial orientation study, particular attention should be paid to possible mixing of stream sediment source rocks and secondary dispersion processes that might possibly impact pathfinder geochemical and mineralogical signatures, such as winnowing.

Following sample collection, geologists should EVALUATE AND REFLECT on the acquired dataset. Geochemical data usually undergoes data cleaning, QAQC, levelling (e.g., Z-score), uni- and multivariate statistical analysis and lithological ‘fingerprinting’, taking into account the continuously improved geological knowledge acquired from the previous work steps. Mineralogical (Paper 3) and microchemical analysis of HMC or accessory minerals of petrogenetic relevance (Chapman et al., 2000a; Dill et al., 2014; Kaeter et al., 2020) should be further considered to integrate mineralisation, lithological and secondary dispersion processes in watersheds.

	AIMS	OBJECTIVES	REMARKS
UNDERSTAND	1. Evaluate feasibility of SS sampling in project area 2. Conduct GIS watershed analysis 3. Explain geochemical variations in area	• Conduct test/ orientation study in selected drainages using historic data/ initial understanding of the area/DEM • Use pXRF to determine ideal size fraction for geochemical response • Use trial automated mineralogy, determine usability of mineralogical information of proposed screen size • Collect heavy mineral concentrates (HMC) for additional visual mineralogy and analysis • Link geochemistry to local geological variations, sedimentology and mineralogical response	• In terms of granite/ LCT pegmatite targets ensure that structural control is understood as well as variations of local granitic facies and possible (meta) sedimentary intercalations • Pay particular attention to the early recognition of present late stage magmatic/ hydrothermal mineral associations (e.g. greisen, spessartine garnet, muscovite, coltan, ilmenorutile)
PLAN	4. Evaluate SS sampling strategies and protocols taking into account the project scope, area, logistics, budget and timeframe 5. Develop a customised sampling plan	• Reflect on learnings from orientation study and design a sampling programme that meets the technical and logistical requirements • Develop databases and workflows for sampling personnel, e.g. BGS G-BASE. • Ensure the project team understands the link between sampling-geochemistry-mineralogical response-lithological controls	• Ensure that the database takes into account granite/ LCT pegmatite mineralisation system characteristics • Consider requirements for minimum sample size/ fraction/ analytical geochemistry and mineralogy equipment available on site or in a nearby laboratory (e.g. sodium peroxide fusion).
TEST	6. Conduct the survey	• Ensure that sample protocols and workflows are followed • Conduct detailed observations and record available outcrops/ SS material in order to improve understanding of catchment geology and likely geochemical and mineralogical responses • Collect and send samples for geochemical and mineralogical analysis	• Pay particular attention to possible mixing of SS from different sources that may have an impact on geochemical and mineralogical responses • Beware of secondary dispersion processes that may affect pathfinder element abundances and ratios, e.g. winnowing, heavy element traps, etc.
EVALUATE **AND REFLECT**	7. Analyse the results 8. Interpret and integrate geochemical, mineralogical and source lithological responses to improve the understanding of catchment and mineralisation processes 9. Consider how the sampling campaign supported the evaluation of the project area and how it can be improved 10. Finalise target generation and test using advanced methods	• Conduct data cleaning/ treatment, QAQC, levelling against bedrock (e.g. Z-score), if required • Conduct uni- and multivariate statistical anomaly analysis and lithological fingerprinting • Relate geochemical signatures to mineralogical and geological observations to help explain the nature of the former and vice versa • Identify scope for further mineral-chemistry studies to better understand target mineralogy, identified in SS HMCs • Reflect and evaluate on the interpretation process and use feedback loops to improve the understanding of geology and target generation	• Apply characteristic petrogenetic fractionation element and ratio plots • Identify target mineralogy as described above • Explain variations in pathfinder geochemistry by variations in mineralogy, e.g. presence of Nb minerals vs. changes in Nb/Ta ratio. • Target generation should lead to the definition of prospective local areas, possible outcrops or locations for additional soil sampling, pitting or trenching

Figure 2. Suggested considerations for a stream sediment (SS) workflow integrating an orientation study, catchment analysis, multi-element geochemistry and mineralogy.

As mineralogical and mineral-chemistry data is often time consuming and relatively expensive to obtain, careful selection of a sub-set of samples for analysis is required at this stage. For example, Paper 3 related variations in local magma evolution to Nb/Ta pathfinder geochemistry and an increasing abundance of columbite and Ilmenorutile in the stream sediment samples. Following an evaluation of the physico-chemical and mineralogical processes defining watersheds, the overall interpretation of the survey results, and therefore the exploration targeting process, can be improved, contextualised, and feedback loops developed in order to improve current and future stream sediment sampling campaigns.

5.2. New evidence and data for Variscan magmatic-hydrothermal mineralisation systems of the Vosges Mountains

This PhD research resulted in the delineation of new evidence for granite-related magmatic-hydrothermal mineralisation systems in the comparably underexplored Vosges Mountains. Stream sediment geochemistry and mineralogy successfully outlined lithologically-controlled Li-Nb-Ta-Sn-W mineralisation occurrences in both enrichedmantle-derived metaluminous-peraluminous CVMg-K granites of the central Vosges, and S-type peraluminous Kagenfels Granite of the northern Vosges (Figure 3). Furthermore, the research demonstrated a spatial coincidence of prospective drainages along regional shear zones and splays. The presence of structures is therefore interpreted as a major control for the movement and emplacement of fractionated melts and hydrothermal fluids, leading to mineralisation.

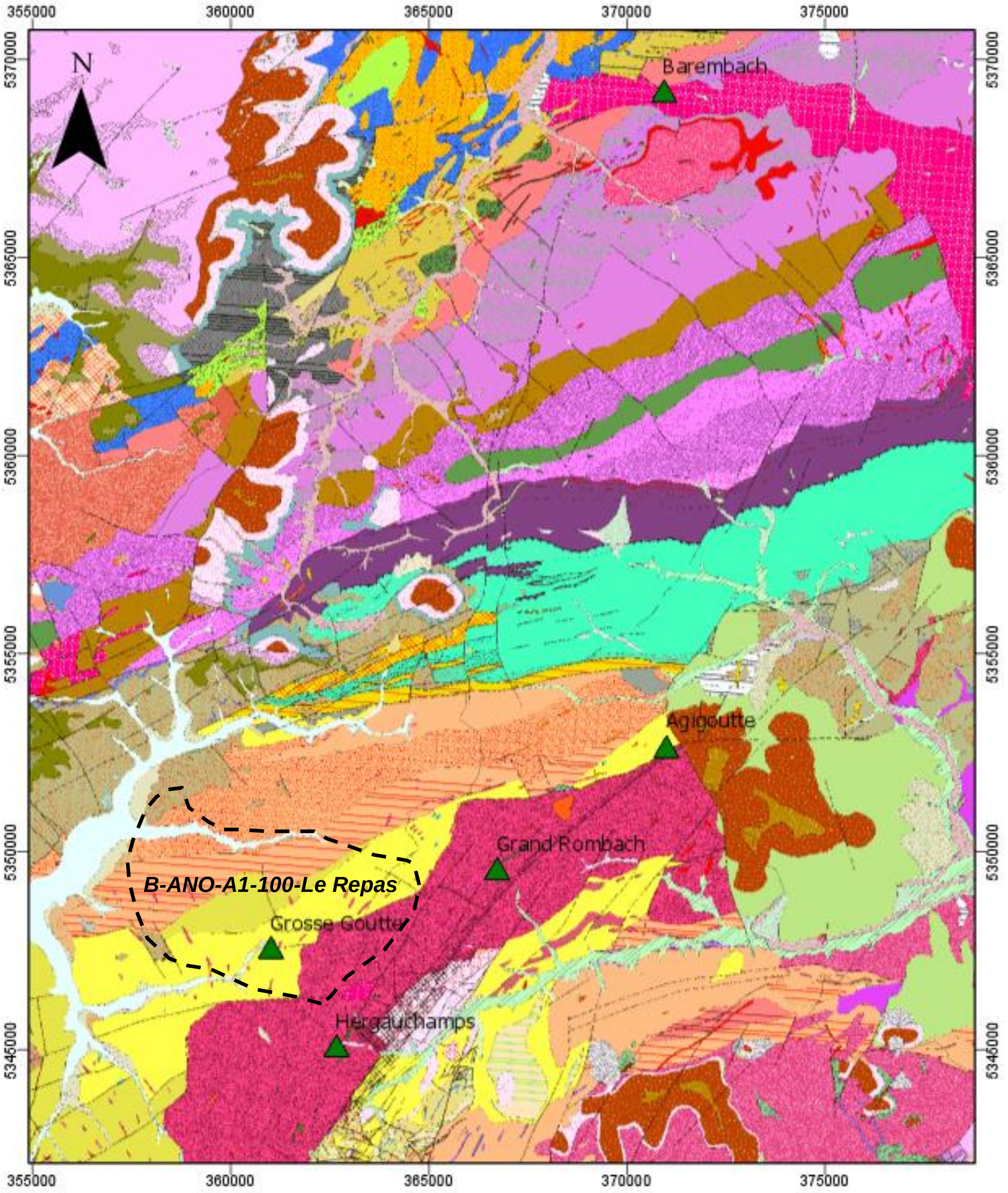

Figure 3. Summary map of streams with Li-Nb-Ta and Sn-W geochemical signatures outlined during the Vosges Exploration Campaign 2017-2019. The Agigoutte, Grand Rombach, Hergauchamps and Grosse Goutte streams (Paper 2) are related to highly fractionated felsic rocks occurring along NE-SW trending regional shear zones within or downstream of the CVMg-K Granite. The Barembach Stream (Paper 3), which drains the Kagenfels Granite, contains grains of columbite, ilmenorutile, wolframite and tourmaline-chlorite-muscovite (greisen assemblage). In late 2019, buried pegmatitic quartz(-feldspar) veins were observed in the catchment. The Grosse Goutte target is located in the previously identified low priority target area 'B-ANO-A1-100-Le Repas' (Billa et al., 2016). The background map is taken from BRGM WMS server (http://geoservices.brgm.fr/geologie?).

The geochemical and mineralogical (cassiterite, ilmenite, ilmenorutile, columbite, wolframite, quartz-muscovite-tourmaline-chlorite greisen) assemblages described in Papers 2 and 3 are characteristic not only for rare metal granite mineralisation in the central part of the European Variscan Belt, but also for phenomena related to late magmatic fractionation, hydrothermal alteration and overprinting of rare metal granites comparable to other metallogenic districts worldwide (Černý and Ercit, 2005; Gourcerol et al., 2019).

In the central Vosges, mineralisation occurs in biotite-amphibole-titanite-ilmenite CVMg-K granites, representing granites characterised by an enriched and contaminated mantle signature, described as metaluminous-peraluminous 'A2-type' granites elsewhere (Ballouard et al., 2020). A2-type granites are known to contain critical metals and to be present in the Erzgebirge (Breiter, 2012) and the Lachlan Fold Belt (Collins et al., 1982), whereby Nb-Ta signatures are related to the preferred early fractionation of Nb into primary mafic minerals, such as biotite and ilmenite, during muscovite breakdown (Ballouard et al., 2020). This process, however, would require higher temperatures to enable biotite melting, mixing with crustal melts and fractionation and hydrothermal alteration in order to explain the occurrence of Ta, Sn, W and Li anomalies in the study area (Romer and Kroner, 2016).

Such an interpretation is supported by the presence of primary mafic minerals, proximal strongly metamorphosed and exhumed granulites and metasedimentary rocks, leucogranitic and pegmatitic float encountered in drainages characterised by an anomalous critical metal signature, along with distinct structural weakness zones (shear zones) providing pathways for melts and hydrothermal fluids generated by internal heating of the CVMg-K granite. On the other hand, Sn-W-Nb-Ta mineralisation in the peraluminous S-type Kagenfels Granite (northern

Vosges) is interpreted to be a result of the late stage magmatic-hydrothermal evolution of a peraluminous rare metal granite, with critical metal enrichment due to greisenisation. This mineralisation style and the close spatial occurrence of S-, I-S-, and 'A2-type' granites in the northern Vosges is similar to other Variscan provinces, such as the Erzgebirge (Förster et al., 1999; Breiter, 2012).

Whilst a pegmatitic origin of the critical metal assemblage has not been confirmed yet, evidence in the form of pegmatitic and leucogranitic float along prospective drainages (Paper 2) and subcropping pegmatitic quartz-feldspar veins in the Barembach stream, along with historical descriptions of pegmatites in the Kagenfels Granite (Weil, 1936; Paper 3), at least imply the presence of pegmatites and pegmatite-related metasomatic rocks in both study areas. Further research will be required, however, to increase the understanding and possible relationship to the encountered mineralisation occurrences.

6. Conclusions and outlook

The principal conclusions of this thesis are:

1. Regional, low-resolution stream sediment geochemical surveys (1 sample per 4 km^2) allow the narrowing down of target zones for rare metal granite and LCT pegmatite exploration. The investigation and mapping of applicable trace and pathfinder elements may provide information on magmatic fractionation and hydrothermal alteration patterns related to parent granites further upstream. This was evidenced by the delineation of several prospective catchments in the Grosse Goutte, Hergauchamps, Grand Rombach, Agigoutte (Paper 2) and Barembach (Paper 3) areas. At a commercial analytical rate of US$30 per sample (2019), excluding field staff costs, prospective areas at Barembach were delineated at a cost of

US$600 during this study, representing a very competitive cost considering commercial exploration budgets.

2. The application of geochemical magmatic fractionation indicator elements and ratios, previously established in mineral and litho-geochemical studies, can also be used in surface geological materials affected by secondary dispersion, if the regional and catchment geology is taken into account and integrated into the geochemical interpretation. For example, detailed field and mineralogical observations in the catchments studied in Papers 2 and 3 have allowed the linking of stream sediment geochemical signatures to those in float and outcrop. This has significant implications for the (re-)evaluation of stream sediment datasets to determine the prospectively of certain pegmatites and granites.
3. The application of automated mineralogical analysis to regional stream sediment sample sets, linking geochemistry and mineralogy, can significantly improve exploration workflows and an understanding of regional geology. For example, automated mineralogy can be used to reliably determine the modal mineralogy of the <75 µm fraction of regional stream sediments. The results can be used to interpret the effects of fractionation and hydrothermal alteration/mineralisation, which may have impacted the granite magmas during their evolution, therefore providing exploration indicators (Paper 3).
4. The prospectivity of the Variscan basement complex in the Central and Northern Vosges Mountains was re-evaluated and evidence was obtained for the presence of previously unrecognised magmatic-hydrothermal mineralisation systems. The occurrence of rare and critical metal mineralisation is interpreted to be a result of late-stage hydrothermal

alteration in evolved granites, focused along existing regional structural weakness zones, which facilitated the movement of felsic melt and hydrothermal fluids. Maps showing prospective catchments are included in Papers 2–4.

5. Regional and local critical metal exploration strategies for granites and pegmatites need to be based on a combined and mutually informed geological, geochemical and mineralogical approach. This approach must link geochemical and mineralogical signatures to visual rock observations, particularly when geologists struggle to correctly identify the silicate mineralogy of micas, feldspars and Li-bearing pyroxenes.
6. A long overdue summary review paper on grassroots LCT pegmatite exploration has been published (Paper 4), which provides a synthesis of LCT pegmatite genesis, applicable exploration techniques, and a systematic ‘cookbook’ approach to commercial exploration targeting and related investigations.

In order to better constrain the mineralisation patterns encountered in the northern and central Vosges (Paper 2), future research will benefit from applying geochronological, isotope geochemical and mineral chemistry techniques to rock and stream sediment samples. Mineralised float and outcrop samples should primarily be dated using zircon and monazite U/Pb dating techniques as constraining an age interval for the mineralising fluids will primarily allow the observed mineralisation to be placed in the context of known magmatic pulses in the Vosges Mountains. This should help confirm whether the mineralisation is genetically related to intrusion of the CVMg-K or W-CVG granites (Paper 2), which have different chemical compositions, geochemical source reservoirs and intrusion ages. Furthermore, the determination of initial Sr and Nd isotope ratios will support the determination of the source of the leucogranites and enable a comparison with published results from the CVMg-K and CVG granites. From an exploration point of view, obtaining isotope ratios will determine the source reservoir(s) the target lithologies belong to, and therefore guide the selection of prospective lithologies and target areas.

Further genetic studies involving the analysis of stream sediment mineral grains, and any internal chemical zonation and preserved paragenetic relationships, can be applied to determine how mineralisation patterns and conditions in the Vosges samples compare with economic, rare metal granites or pegmatites from other districts at Leinster and in the Variscan belt, such as the Erzgebirge or Cornwall. In addition, mineral chemistry will highlight the evolutionary trends of the studied granites. K/Rb ratios in K-feldspar and muscovite, along with the enrichment of Li, Cs, Mn, Ta and other key incompatible elements in muscovite, usually provide a good indication for rare metal granite and pegmatite prospectivity (Selway et al., 2005), particularly in stream sediments that show minor evidence of weathering. Mn/(Mn+Fe) ratios in spessartine garnet, along with Fe/Mn and Nb/Ta ratios in columbite-tantalite, will provide additional indicators for the magmatic-hydrothermal transition and sub-solidus alteration in granitic and pegmatitic systems (Shaw et al., 2016; Kaeter et al., 2021a).

In a more general sense, this PhD thesis has shown that further detailed research is required to understand the sedimentological and secondary dispersion processes leading to the accumulation and loss of stream sediment and its characteristic geochemical signature. Furthering our knowledge of these processes will support the analysis and interpretation of geochemical and mineralogical datasets. Future research should therefore consider a detailed evaluation of the lithological and chemical compositional variability of stream sediments in a watershed, relating the acquired information to geological and erosional processes. Such a study would make use of detailed sediment and outcrop descriptions, followed by automated mineralogical analysis, multi-variate geochemical modelling (e.g., PCA), and spatial representation of data in compositional pie charts and genetic diagrams (e.g., the Nb/Ta vs. K/Rb plot as outlined in this thesis). A study area should be selected that not only offers access to abundant outcrops, therefore providing the required geological baseline information, but that also contains mineralised rare element granites and/or pegmatites, which were eroded and their minerals dispersed. Stream sediments from different catchments across the wider area should be analysed using geochemical and mineralogical techniques. It is likely that these conditions would be satisfied in mountainous areas with abundant outcrops, such as the European Alps or the North and South American Cordillera.

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8. Appendix A: Analytical and QC Procedures

Geochemical laboratory analysis

Samples obtained for Papers 2 and 3 were dried gently in an oven at 40°C for a few days and then prepared and analysed at Camborne School of Mines, University of Exeter (UK). As part of an orientation and sampling optimisation study in Paper 2, the samples were sieved using a certified Pascal sieve stack (1 mm, 600 µm, 125 µm, 75 µm) and a Pascal Sieve Shaker to isolate the <75 µm fraction which was identified to contain the highest concentration of W and Cu. Individual fraction weights were determined to assess if sample loss had occurred by comparing these to the sample weight before sieving.

142 (Paper 2) and 20 (Paper 3) samples underwent standard four acid digestion (HCl-HF-HNO_3-$HClO_4$) and the resulting sample solutions were then analysed using an Agilent 7700 ICP-MS instrument (Agilent Technologies, Santa Clara, CA, USA), so that, compared to historic studies, a wider range of trace and pathfinder elements, including Nb, Ta, Li, Hf, could be analysed for, aiding the determination of magmatic fractionation trends. A full suite of 41 elements was determined (Uren and Rollinson, 2014).

In addition, an Olympus DP 6000 pXRF analyser was used for the analysis of the samples noted in Paper 2, but not for the samples noted in Paper 3, and was used to carry out an initial orientation study (applying ‘soil mode’ and 60s recording/ beam time) on homogenised sample pulps in XRF sample cups covered by Prolene® 4.0 µm film to determine which of the sediment grain size fractions had the highest target element concentrations. It was also decided that, due to the likelihood of incomplete dissolution of Sn- and W-bearing minerals (mainly cassiterite and wolframite, respectively; Figure 4) using the four acid digestion method, followed by ICP-MS analysis (Table 2), their determination would be by pXRF. Therefore, Sn and W pXRF data were used in Paper 2, whilst ICP-MS data were used for the remaining trace elements. As Nb and Hf were not routinely recorded on the pXRF device, but these elements are essential for providing Nb/Ta and Zr/Hf, which are important in petrogenetic studies, Nb, Ta, Zr and Hf data obtained from the ICP-MS instrument were utilised. Upon critical reflection, it is extremely important to ensure total digestion of refractory minerals containing these important indicator elements, for example by using the sodium peroxide fusion, rather than four acid digestion, method (Lemière, 2018). However, at the time of study this was not available, and therefore a combination of pXRF and near-total, four acid digestion was employed.

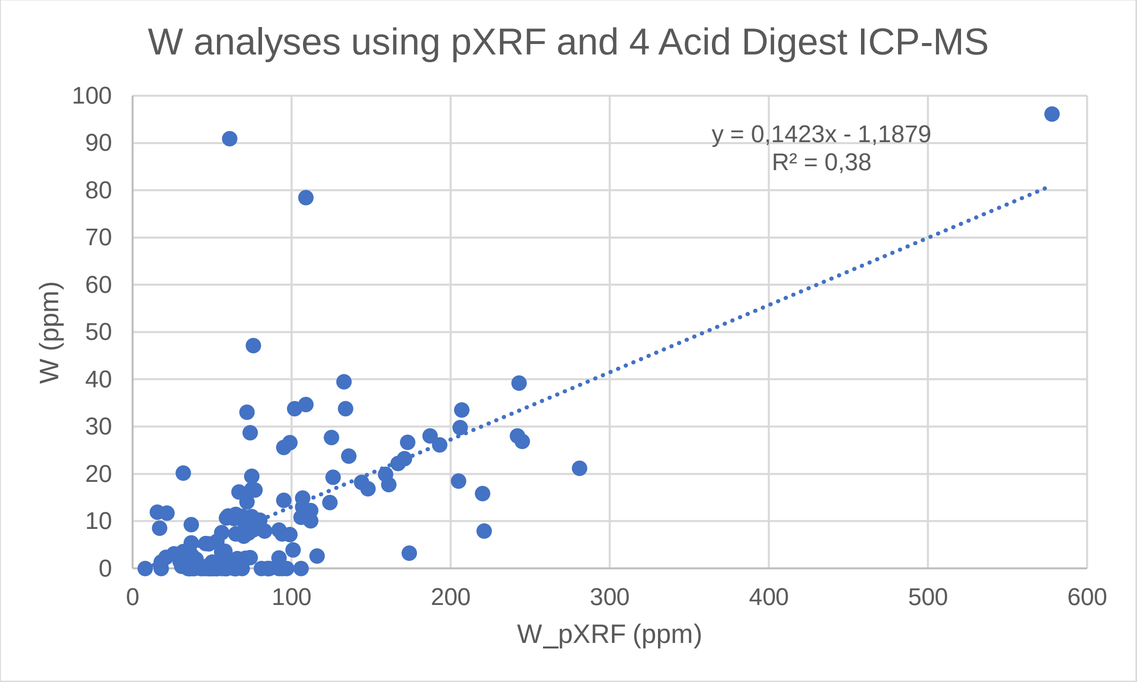

Figure 4. Comparison of ICP-MS and pXRF concentrations for W. Note the poor correlation between four acid digest and XRF, which is explained by incomplete digestion of resistate minerals.

Geochemical Quality Control (QC)

A range of quality control measures were adopted during the process of pXRF, XRF and ICP-MS analysis, detailed in Papers 1-3 and summarised below.

Knights and Heath (2016) described and evaluated the GSI analytical procedures and quality control measures completed as part of the XRF and Fire Assay (FA) ICP-MS analysis of archived stream sediment samples used in Paper 1. A short summary is provided here and the reader is referred to the GSI document for further information. Analytical blanks, laboratory in-house reference materials, internal GSI reference materials and secondary certified reference materials (CRMs) were randomly inserted into the sample stream in order to assess accuracy, precision and bias in the geochemical analyses. The archived pulp samples did not contain enough sample material to produce replicate samples, and therefore it was not possible to quantitatively describe the analytical or within sample variance. The QC analysis revealed that a number of sample batches failed the blank test for Pt implying an unknown contamination issue at the analytical laboratory. Pt, however, was not used for geochemical interpretations in Paper 1. Reference materials showed no quality control failure for FA ICP-MS analysis. Analyses conducted by XRF instruments showed a minimal number of standard failures and generally had a pass rate of 99.99%. The magnitude of the failures/exceedances was considered very low and are emphasised by the data being pixelated or rounded when reported. Furthermore, no analytical trend was observed occurring on the same day or in adjacent runs of samples, and therefore the random errors were considered acceptable.

As part of the geochemical analyses of Papers 2 and 3, several quality control tests have been applied. Pulp duplicates, low grade standards/ blanks (OREAS 22e) and certified reference materials OREAS 147 and OREAS 148 (sourced from Australian LCT pegmatites) were randomly inserted at a rate of 1:20 (Abzalov, 2008; Mazzuchelli, 2011; Table 1) into the sample stream for further ICP-MS analysis. Certified elemental values for four acid digestion and ICP-MS/ -OES were used for QC purposes. Six blanks, duplicates, three OREAS 147 and three OREAS 148 were inserted into the sample stream for Paper 2 samples. However, as only 20 samples were analysed for Paper 3, two OREAS 147 and two OREAS 751 CRMs, two OREAS 22e, and two blanks were inserted into the sample batch in order to get quality control results from a variety of grade ranges (Abzalov, 2016). CRM results were plotted in "QC Mine", a macro-enabled MS Excel worksheet developed by Analytical Solutions Ltd. and OREAS, allowing statistical analysis and visualisation of CRM samples. QC Mine produces summary statistical values, such as the observed mean, standard deviation (SD), relative standard deviation (RSD) and z-score (number of SDs by which the value of a data point is above or below the certified mean value of the CRM), along with a measure of the percentage of samples falling inside of 1 SD, 2 SD and 3 SD of the certified mean. In addition, the worksheet reports on the number of 'failures' (values greater than mean ± 3 SD or z > ± 3) and 'outliers' (values greater than mean ± 2 SD or z > ± 2). Results are represented in control charts allowing the visualisation of CRM performance and outliers or failures (Figure 5).

Summary of Quality control materials used	
Paper 2	OREAS 147
	OREAS 148
	OREAS 22e
Paper 3	OREAS 147
	OREAS 751
	OREAS 22e

Table 1. Summary of certified reference materials used for Papers 2 and 3.

	OREAS 147				OREAS 148			
	4AD		**SPF**		**4AD**		**SPF**	
Element	CV	SD	CV	SD	CV	SD	CV	SD
Sn	503*	-	699	37	837*	-	1157	80
W	4.88*	-	6.46*	-	6,45	0,373	6,42	1,32
Zr	105	7	194	29	79	4,8	153	25
Hf	2,99	0,32	5,45	0,84	2,16	0,22	4,15	0,53
Nb	1110	80	1150	70	1690	100	1680	110
Ta	17,8	23	17,8	1,9	23,1	2,9	22.2*	-
Li	2260	120	2270	110	4650	90	4760	110
Th	93	5,5	95	3,4	48,2	3,62	51	2

Table 2. Summary table of four acid digest (4AD) and sodium peroxide fusion (SPF) element certifications (CV = certified value; SD = 1 standard deviation) for OREAS 147 and 148.

QC was conducted for key elements used in the study, and examples of K, Rb, Nb, Ta, Zr, Hf, Sn, W, Li and Cu worksheets have been included in Electronic Appendix A and B. All elements considered had statistically acceptable error boundaries of $z < \pm 3$. However, the determination of some elements, such as Zr, Hf and also Li, likely contained in refractory minerals, resulted in a constant negative bias of up to – 1 SD from the certified element concentration (Figure 5). This is explained by the incomplete dissolution of refractory minerals using the four acid digest. Whilst the results are still within acceptable error boundaries, the absolute concentrations might be underestimated.

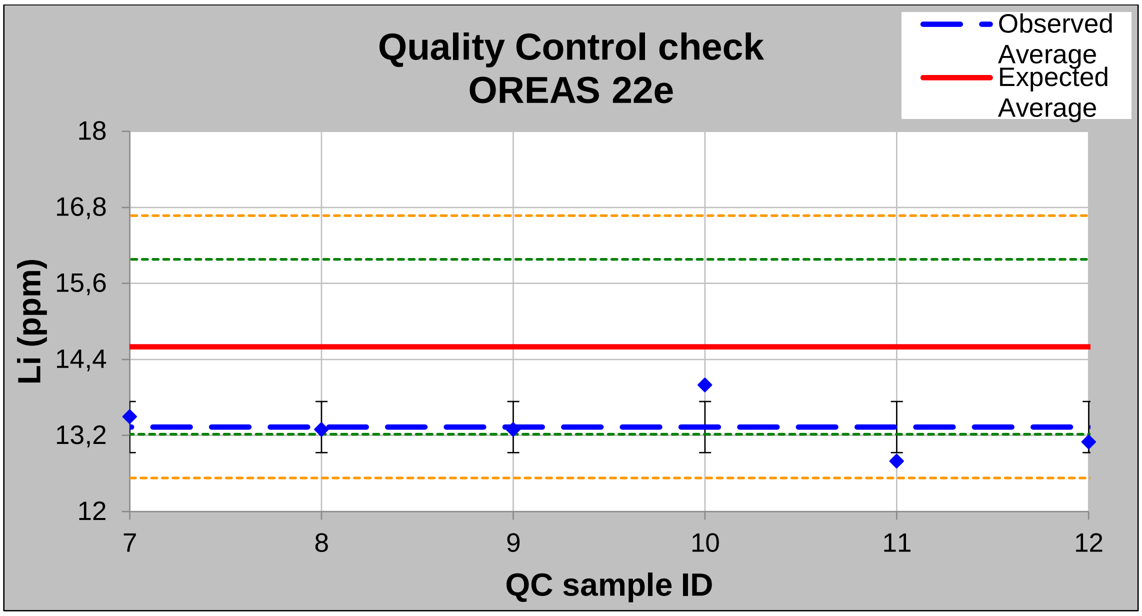

Figure 5. Li quality control chart for low-grade standard/ blank OREAS 22e produced for Paper 2. The analysis of OREAS 22e demonstrated that low Li concentrations are within an acceptable error window of z < -2.6. However, a reasonable constant negative bias is prevalent which might be a result of incomplete dissolution of host minerals.

Pulp duplicates were assessed by calculating the mean absolute percentage difference (MAPD) and mean for duplicate pairs (Abzalov, 2016). MAPD values for Papers 2 and 3 are generally lower than 20% (Figure 6), with occasional outliers of up to 66% in sub-ppm concentrations of Be and Ta. The precision of the analysis was generally deemed acceptable and fit for purpose.

Possible contamination in the sample preparation and homogenisation phase was assessed by including certified low-grade standard/ blank OREAS 22e (Figures 5 and 7). The results of the low-grade analysis confirmed, depending on the element analysed, results at sub-ppm level or below average crustal abundance concentrations (Mazzuchelli, 2011).

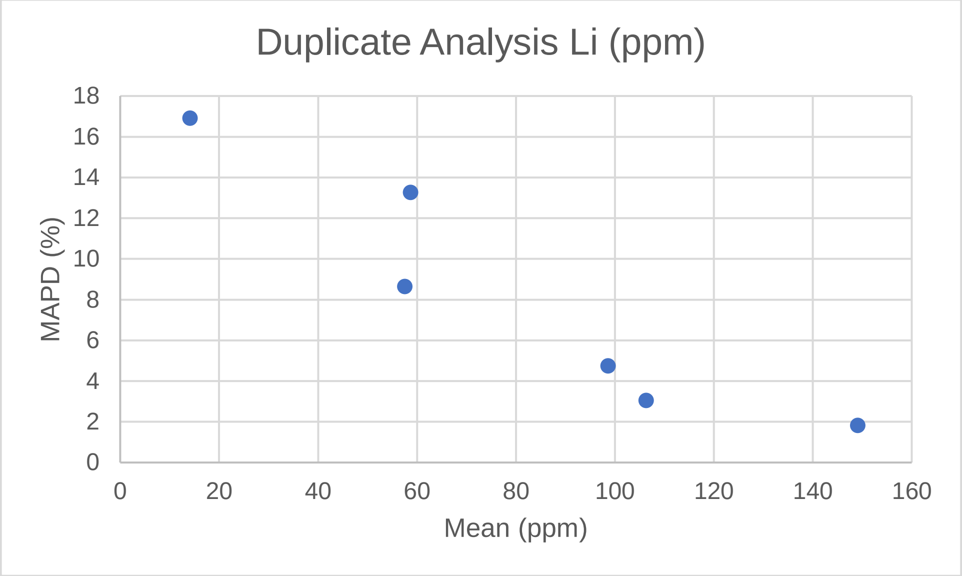

Figure 6. Duplicate quality control chart for Li produced for Paper 2. The Mean Absolute Percentage Difference (MAPD) is generally less than 20% and decreases with increasing concentrations. This implies that the precision of the analysis, particularly at increasing concentrations, is good.

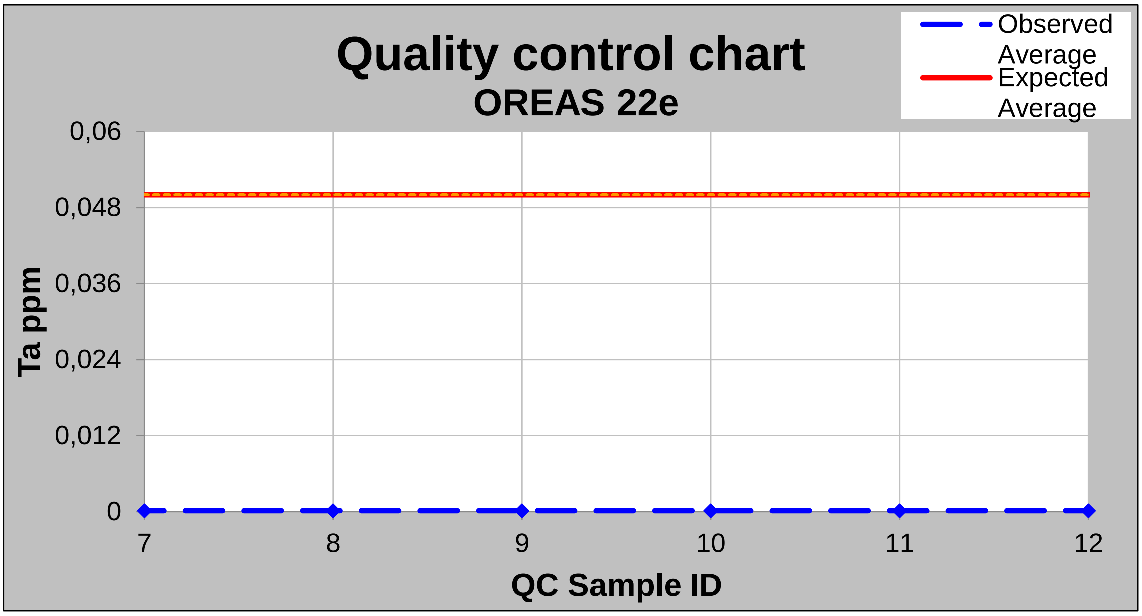

Figure 7. Ta quality control chart for low-grade standard/ blank OREAS 22e produced for Paper 2. The analysis confirmed that the samples contained no noteworthy Ta, and therefore imply that no inter-sample contamination occurred during the sample preparation stage.

In order to ensure quality control on pXRF analyses in Paper 2, a series of replicate and pulp CRM measurements have been conducted following suggestions by Lemière (2018). In order to improve the signal to noise ratio, each sample was consecutively analysed three times for a total of 60 s per analysis, without moving or lifting the samples between measurements, and an average calculated. The reproducibility was generally good with an average relative standard deviation (RSD) of 11.85% (W) and 13.75% (Sn), respectively. The average RSDs were affected by outliers during the warm-up phases of the instrument. Similar to ICP-MS analyses, four OREAS 147, four OREAS 148 CRM and silica blank materials were analysed as part of routine QC procedures (Electronic Appendix C). W concentrations are certified for OREAS 148, but are indicative for OREAS 147, despite a reported concentration difference of 0.04 ppm. However, whilst the W z-score for OREAS 147 was not calculated, both were plotted to enable the construction of a linear regression line, which requires a minimum of two sets of data points. Due to the non-availability of elemental certifications for pressed pellet XRF samples, certified elemental values from sodium peroxide fusion - ICP-MS analyses were used, which covered a comprehensive range of trace elements. However, XRF and ICP-MS/ -OES analytical techniques are fundamentally different in nature, the former using an X-ray beam to obtain a point chemical analysis of a fused bead or pressed powder sample, and the latter employing chemical sample digestion followed by ionisation of the sample solution and mass spectrometry. pXRF calibration was based on a linear regression of the signal from the standard against its certified elemental concentrations, which increased the reliability and usability of the obtained numerical values.

The statistical quality control results for Sn and W demonstrate that throughout the analytical campaign, both elements, compared to the used CRMs, had a consistent, minor positive bias averaging $z = 0.39$ for Sn and $z = 1.75$ for W. This means that a minor, local calibration issue affected the pXRF analyser, however overall the pXRF concentration values fall in a commonly accepted error envelope of certified mean +1 SD or z > + 1, and therefore represent reasonably accurately the values certified for sodium peroxide fusion. Linear regression and calibration of the pXRF against the CRM values led to correction equations of $y = 0.98x - 1.40$ for Sn, and $y = 0.72x$ for W (Figures 8 and 9). The graphs show that Sn performed very well during linear regression, with a very high R^2 value of 0.9914. The standard deviation increases from 16 (OREAS 147) to 31 (OREAS 148) indicating a higher spread of concentration values for Sn > 1,000 ppm, and therefore possibly a percentage error in the data. The standard deviations of the pXRF analysis, however, are more than half less than the standard deviations listed for the OREAS certified analysis, and are therefore interpreted to be well within analytical error range. W is characterised by a good correlation of $R^2 = 0.9989$ and a moderate bias towards higher concentrations. A possible reason might be an overestimation due to a device calibration error and therefore requires correction. The use of an additional reference material with higher certified concentrations, i.e. covering the range of obtained results particularly between 100-250 ppm, is clearly desirable in order to improve the correction, however such a standard was not available at the time of analysis. The subsequently calibrated pXRF concentration values of the original stream sediment samples were then used in the following geochemical analysis and interpretation. Detailed QC and linear calibration sheets can be found in Electronic Appendix C.

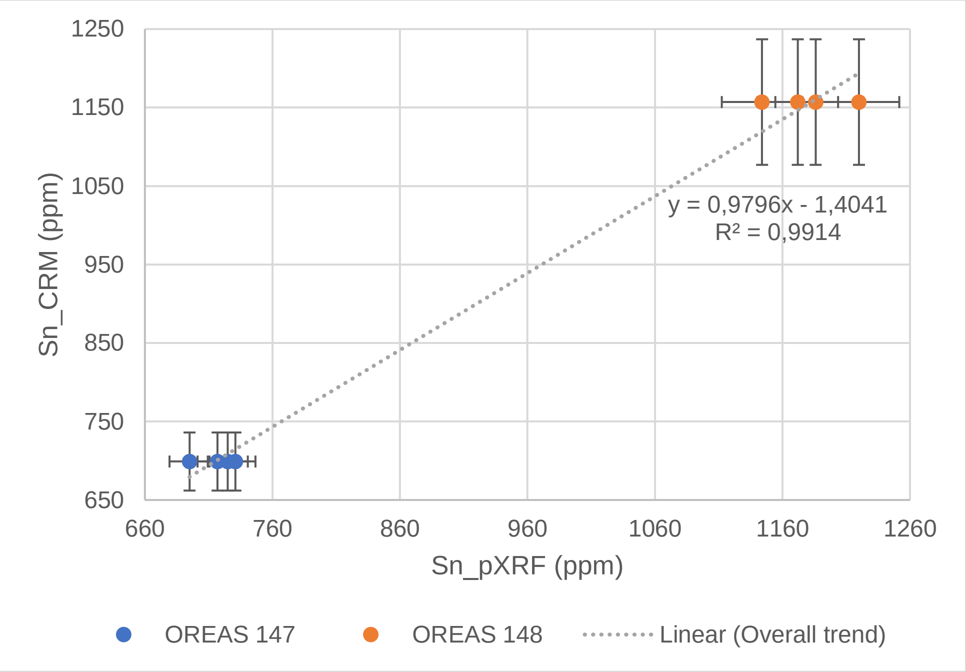

Figure 8. Linear regression analysis of Sn concentrations using pXRF. OREAS 147 and 148 certified reference materials were used to calculate a linear function to adjust Sn concentrations. Error bars (1 SD) are calculated as one standard deviation from the mean of multiple analyses of OREAS 147 and 148, respectively. Note that no CRM was available for low range (< 500 ppm) and mid-range (900 ppm) Sn concentrations, however the linear correlation achieved by the two CRMs is deemed very good.

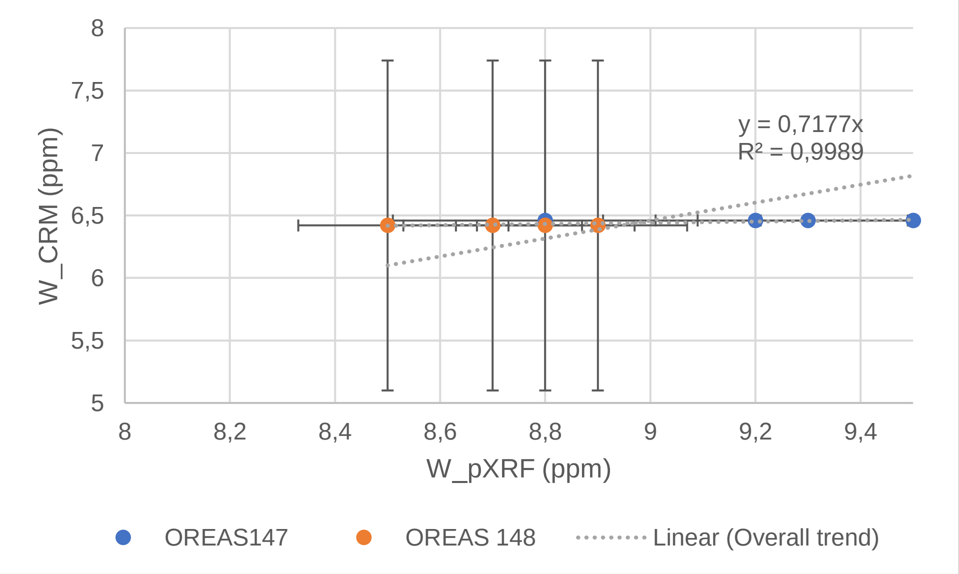

Figure 9. Linear regression analysis of W concentration using pXRF. Only OREAS 148 contained certified W concentrations of 6.42 ppm. Indicated W concentrations for OREAS 147 are reported to be 6.46 ppm and show a higher data spread in the diagram.

Mineralogical laboratory analysis

Of the 20 stream sediment samples that underwent ICP-MS analysis as part of Paper 3, nine samples of the < 75 μm fraction, considered homogenous, were selected for mineralogical analysis (QEMSCAN®). In addition, two rock samples (17A and 18A) were collected within a 10 m distance upstream of their corresponding stream sediment sample locations. The sediment samples were prepared as 30 mm diameter polished epoxy resin mounts. To produce these, each sample of the < 75 μm fraction was mixed with pure graphite powder in the ratio 1:1.5, to reduce settling bias and to separate particles, and then with epoxy resin. The sample surface of the cured mounts was carefully ground to expose the particles and then polished to a 1 μm finish using a 6 stage polishing process (200 and 1200 grit, 9 μm, 6 μm, 3 μm and 1 μm) using diamond media. The rock samples were prepared as uncovered polished thin sections (approx. 47 x 25 mm) of these samples. The resin blocks and polished thin sections were then carbon-coated to a 25 nm thickness.

Samples were analysed using a QEMSCAN® 4300 at Camborne School of Mines, University of Exeter, UK. Sample measurement used iMeasure version 4.2SR1 software for data collection and iDiscover 4.2SR1 and 4.3 software for data processing. The Particle Mineral Analysis (PMA) measurement mode was used to map particles at a resolution (pixel spacing) of 2 μm, field size of 600 μm (300 × 300 square, magnification of ×111), default of 1000 X-ray counts per analysis point and a target of 10,000 particles per sample. The final number of particles mapped per sample was higher than this (up to 14,556) due to the system completing the particles in the field it was on when it reached its 10,000 particle target. The number of analysis points per sample varied from 900,000 to 4 million. The data collected during measurement were processed using a modified version of the standard LCU5 SIP (database), following and building upon details outlined in section 7 of Rollinson et al. (2011). The SIP is a hierarchical list of mineral entries that ED data are checked against during classification, thus the order of this list is critical as it is not best match (it starts at the top of the list and stops when it reaches a match). Each entry contains the elements that should be present for a mineral using the 1000 count x-ray spectra range and BSE signal data from 0 to 255 (greyscale range). A mineral can have multiple entries to account for variations in chemistry and edge effects with other mineral and the mounting media. The SIP list itself is grouped into mineral folders to create a shorter list call the 'primary list', which contains the theoretical chemistry and density of the mineral (added by the user). The primary list is then further grouped into a shorter list of folders called the secondary list, for reporting purposes and to keep the list focussed to the batch of samples being examined. For this job, an existing SIP that was close to the mineralogy of the samples was used as a starting point, and was checked and developed to match the samples. This involved checking every entry against the ED data (from pixels) to ensure it correctly identified the mineral (examination of elemental abundance, elemental ratios, BSE range). A mineral group name or a chemical name after the dominant elements/ minerals, e.g. mica or feldspar group minerals, is used for a class where there is a range in the elemental composition data such that a specific mineral member cannot be separately identified, or, the low abundances of the grouped minerals make a group more meaningful with regards to the expected outcomes of the project. For example, primary or secondary Fe-oxides, usually comprising magnetite, hematite, goethite, siderite, were grouped and summarised in the Fe-Ox (Mn)/CO_3 class, as their significance for the outcomes of this study, focusing primarily on exotic minerals such as columbite, cassiterite and wolframite, was deemed limited. Both mineral area-% (volume %) and mineral mass-% (density weighted) data were produced, and it was decided to use the mineral mass-% data as they better reflect the economic mineral content of the samples. However, all data acquired is from 2D sections of 3D particles. Mass values are derived from the measurement of particle / grain areas that are stated to be corrected for stereological error via the iDiscover software, with an assumed mineral density added manually to each mineral in the primary mineral list based on the average theoretical density of that mineral (Williamson et al., 2013; FEI, 2018). As these were stream sediments, the focus was on both the major minerals (e.g. quartz, feldspar, mica) and trace or unusual minerals (e.g. ilmenorutile, ilmenite, cassiterite, spessartine), with the SIP customised to reflect the mineralogy of samples.

Quality Control

Quality checks followed in-house procedures that have been developed over 15 years (Rollinson, 2019a, 2019b, Electronic Appendix D) and included mineral identification not just from the measured chemical spectra, but also against in-house mineral reference standards which have been used to validate and develop the database (SIP) over many previous projects. For example but not limited to, silicates such as quartz, plagioclase feldspar, K-feldspar, muscovite, biotite, phlogopite and schorl, with all the common sulphides chalcopyrite, sphalerite and galena. Data is also examined to ensure that it makes sense in a geological context and also against any other data such as bulk stream sediment ICP-MS geochemistry to check for enrichment of incompatible and accessory elements/ minerals. In addition, quality checks were also completed for possible Li minerals following the method developed at Camborne School of Mines during the FAME EU Horizon 2020 project (Simons et al., 2018). In the case of identified

Ta-Nb minerals, independent point analysis SEM-EDS checks, as illustrated in Paper 3, were conducted to confirm the composition of associated minerals and intergrowths. A selected number of K-feldspar grains per sample were cross-checked for possible alteration to muscovite or illite using their morphological appearance on QEMSCAN® mineral maps along with K-feldspar and muscovite standards. Similarly, the morphology of muscovite particles was regularly cross-checked against illite. Due to the size of the stream sediment sample particles (< 75 μm) and the generally low abundance of muscovite in the samples (average of 0.98% in the studied samples), no further optical petrography or XRD study was undertaken. It was determined that the assigned K-feldspars generally form either large, massive monomineralic particles (> 20 μm) or occur in association with plagioclase and biotite, and therefore reflect a genuine granitic source mineral association. The assigned muscovite particles are characterised by a long, platy habit (e.g. Figure 10), as opposed to fine-grained (< 2 um) illite mineral particles. The samples do not appear to have weathering rims, i.e. they are unweathered products of erosion. Due to the way QEMSCAN® operates, and the fine-grained nature of the <75 μm fraction stream sediment samples (excluding the thin sections), the QC checks outlined above and previous QC of the system (outlined in Rollinson 2019), duplicate analyses were not deemed necessary.

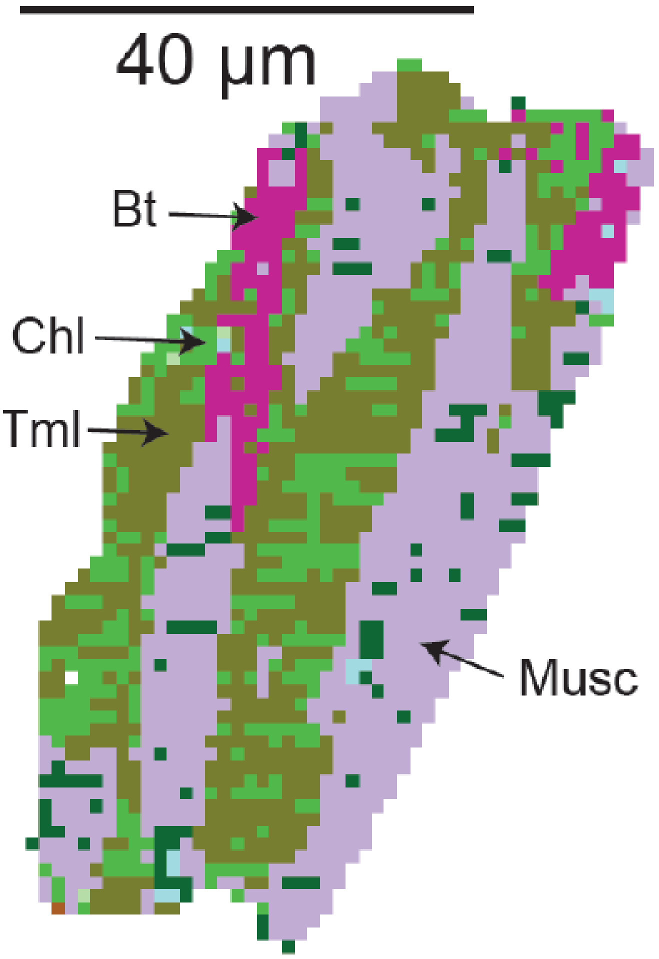

Figure 10. QEMSCAN® mineral map of stream sediment particle (sample 18) showing the intergrowth of chlorite (chl)–tourmaline (tml)–muscovite (musc)–biotite. This mineral association is interpreted to represent evidence of granite-related magmatic–hydrothermal alteration (similar to greisenisation, see below); the nature of the protolith is unclear. From Steiner et al. (2019).

9. Electronic Appendices

Data obtained for this PhD study has been compiled in Electronic Appendices A-D. The content of the appendices is summarised here:

- **Appendix A**: Contains geochemical data in MS Excel format utilised in Paper 2. In addition, QC standard and blank graphs for key elements (Be, Cr, Cs, Cu, Hf, K, Li, Nb, Rb, Sn, Ta, Th, Zr), along with duplicate (MAPD vs. Mean) plots are included. The four acid ICP-MS operating procedure (Uren and Rollinson, 2014) is included.
- **Appendix B**: Contains QC standard and blank graphs for key elements (Be, Cr, Cs, Cu, Hf, K, Li, Nb, Rb, Sn, Ta, Th, W, Zr), along with duplicate (MAPD vs. Mean) plots are included. Note: Raw geochemical data for the stream sediment samples is listed in Table A2 in Paper 3.
- **Appendix C**: Contains QC standard plots for Sn and W, along with linear regression plots, utilised in Paper 2.
- **Appendix D**: Contains raw automated mineralogy data utilised in Paper 3, such as QEMSCAN modal mineralogy and mineral association data. In addition, the QEMSCAN quality control procedures developed and utilised at CSM (Rollinson, 2019b) are included.

10. Original Papers

This section contains links to the original papers as listed in preamble i.

Paper 1: https://www.jstor.org/stable/10.3318/ijes.2018.36.45?seq=1

Paper 2: https://www.sciencedirect.com/science/article/pii/S037567421830428X

Paper 3: https://www.mdpi.com/2075-163X/9/12/750/htm

Paper 4: https://www.mdpi.com/2075-163X/9/8/499