Using Tellus stream sediment geochemistry to fingerprint regional geology and mineralisation systems in Southeast Ireland.

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Abstract

Regional stream sediment geochemistry provides a useful tool for screening relatively large areas for anomalous metal concentrations. Large, open-source governmental datasets represent an affordable option for smaller companies to prioritise areas for follow-up. Equally, such datasets are useful in applied geochemical research.

This study investigates recently released Tellus regional stream sediment analyses for Southeast Ireland, focusing on counties Wicklow, Wexford, and parts of Kildare, Carlow, Kilkenny and Waterford. The aim is to: i) apply trace element ratios and vectors to define and confirm key lithologies and types of mineralisation previously mapped in the study area, ii) provide a tool to reconstruct the geological setting at a 1:500k regional scale and iii) outline follow-up areas from a mineral exploration point of view.

I demonstrate that governmental geochemical datasets can not only define anomalous areas per se, but also support the recognition of regional geological trends and the definition of a number of ore deposit styles. The Tellus dataset for Southeast Ireland, despite its low-density and regional nature, confirmed the regional geological setting albeit in limited detail. Geochemical vectors for Li-Cs-Ta (LCT) pegmatites in the Leinster Granite as well as Volcanogenic Massive Sulphide (VMS) mineralisation in the Copper Coast and Avoca areas, were established and support previous univariate anomaly detection studies.

The workflow will be particularly beneficial in remote and poorly mapped areas where geochemical surveys can add additional value to support ongoing definition of stratigraphy, lithologies and anomalous metal abundances.

Keywords: stream sediments, Tellus, southeast Ireland, trace elements, geochemistry, exploration

Introduction

Ireland has long been known to host world-class lead-zinc and gold deposits, which are currently mined by a number of mineral companies. Smaller mineral deposits associated with volcanogenic massive sulphide (VMS) and fractionated LCT-pegmatite mineralisation occur in southeast Ireland, and although less well-known, are important in their own right (Minerals Ireland 2018).

In 2016, the Geological Survey of Ireland (GSI) released the Tellus regional stream sediment geochemical survey of southeast Ireland. The advent of affordable routine analytical techniques in the 2000s, such as laser ablation ICP-MS and portable XRF, allowed geoscientists to employ trace elements to map mineralising systems in order to effectively aid exploration targeting. The definition of lithological and alteration characteristics of mineral deposits has successfully been demonstrated in porphyry copper (Halley *et al.* 2015) and sedimentary-hosted base metal systems (Halley *et al.* 2016). Both studies prove the usefulness of trace element assays, particularly in the delineation of hydrothermal mineral systems, aiding an understanding of fluid sources and pathways, redox barriers, stratigraphy and alteration features. Using immobile element and principal component analysis, Kirkwood *et al.* (2016) interpreted British Geological Survey (BGS) Geochemical Baseline Survey of the Environment (G-BASE) data to characterise rock types and their lithostratigraphically constrained distributions in southwest England. This led to a detailed comparison between stream sediment geochemical signatures and bedrock geology on a regional scale. Similarly, this Tellus southeast Ireland dataset was interrogated using geochemical trace element ratios and indices described by Sweetman (1987), McConnell *et al.* (1991), Breheny (2010) and Ballouard *et al.* (2016). The aim of this paper is to fingerprint regional mineralisation systems and to present information about prospective metallogenic areas in southeast Ireland.

Geological Setting

Fig. 1

Sharing much of its geological history with Britain, Ireland primarily consists of two major domains: the Peri-Gondwanan-Ganderia Terrane with associated arcs in the south, and Laurentia in the north. Southeast Ireland features a diverse Precambrian and Palaeozoic-Mesozoic geology (Brück *et al.* 1979; Pollock *et al.* 2012). This paper focuses on the Leinster Granite, the Caradocian volcanic belt of the Irish Caledonides and associated mineralisation (Fig. 1).

Leinster Granite and Caledonides of SE Ireland

The Leinster Granite comprises a ~400 Ma Caledonian granite encompassing a surface area of ~1500 km^2, which was intruded into Lower to Middle Ordovician metasediments of the Ribband Group (Roycroft 1989). Due to intense shearing and intrusion, fringing metasedimentary rocks have been subjected to high-strain metamorphism (Reavy 2013). The intrusion is described as a two-mica, two-feldspar, peraluminous, S-type granite and consists of five main units: the Northern Unit, Upper Liffey Unit, Lugnaquilla Unit, Tullow Lowlands Unit and Blackstairs Unit (Brück and O’Connor 1977; Sweetman 1987; Reavy 2013). The Leinster Granite is located on both sides of the Iapetus Suture, separating peri-Laurentian from peri-Gondwanan terranes (Murphy *et al.* 1991; Soper *et al.* 1992). The mechanics of magma emplacement involved deep-crustal shear zones that dilated in a southeastward direction, enabling magma and fluid movement as the structure developed (Roycroft 1989). Fritschle *et al.* (2018) demonstrated that the Northern Unit intruded incrementally over a time span of up to 16.8 million years during the Lower Devonian, and was derived from Mid- to Upper Ordovician peri-Gondwanan arc-related magmatic and Lower to Mid-Ordovician Ribband Group metasedimentary rocks, followed by assimilation of wall rock. The principal granite types have variable compositions, however all are characterised by an ubiquitously low Th/U ratio (generally < 1), especially the Blackstairs Unit, resulting from early fractionation of Th into zircon, allanite and monazite during magma evolution at lower crustal levels (Sweetman 1987).

A southwest-northeast trending belt of Upper Ordovician felsic volcanic and sedimentary rocks, known as the Caradocian volcanic belt, is a result of extensional tectonics within a continental margin volcanic arc setting prior to closure of the Iapetus Ocean (Stillman *et al.* 1974; McConnell 2000). The lithologies encountered are principally arc-related subaqueous mafic and felsic extrusive rocks, shallow-level intrusive rocks, and tuffs representing gravity flows of pyroclastic or epiclastic origin (Breheny *et al.* 2016). Detailed geochemical and mineralogical studies of the Avoca and Copper Coast areas have highlighted the bi-modal character of the volcanic arc system, expressed by a distinct fractionation trend from basalt to rhyolite. The rhyolites are enriched in High Field Strength (HFS) elements, such as Nb, Zr and Y, and are characterised by a Th/U ratio of 3.5-8 (McConnell *et al.* 1991; Breheny 2010). Similar in nature to the Upper Ordovician rhyolites described in Snowdonia and Anglesey (Leat *et al.* 1986) and other bi-modal volcanic provinces (Ferrara and Treuil 1974), the Caradocian rhyolites are peralkaline in composition. In this paper, the contrasting bi-modal geochemical signature is considered as a significant tool to establish a vector towards lithological classification and mineralisation.

Quaternary Geology

Alternating periods of glaciation throughout the Pleistocene produced widespread glaciogenic deposits and related geomorphological features. Although glacial influence is limited in the study area, localised occurrences of glacial and glaciofluvial deposits exist on the western flank of the Leinster Granite, along with the glacial erosion of cirques within the granites (Hegarty

2004; MacCarthy 2013). This limited glacial drift in a southeasterly direction may influence the distribution of sediments, and should be considered when interpreting the Tellus dataset.

Mineralisation Potential

Southeast Ireland hosts significant mineralisation within widespread Proterozoic to Lower Palaeozoic metasediments and metavolcanics. O'Connor and Reimann (1993) previously used univariate anomaly detection tools, such as box-and-whisker diagrams, to determine anomalous populations of base and precious metals in stream sediments. This led to the preliminary definition of prospective areas over a large part of the Leinster Granite and the Irish Caledonides. Extensive low-grade VMS Cu-Pyrite deposits, granite-related W-Li mineralisation, and vein-type Cu, Pb, and Au deposits, are associated with the Leinster Granite and surrounding sediments and volcanic rocks. Li-Cs-Ta (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; Barros and Menuge 2016). Sulphide mineralisation is associated with Ordovician-age volcano-metasediments of the Caradocian volcanic belt. This Kuroko-style mineralisation formed during rifting, producing Cu-Pb-Zn-Au massive sulphide orebodies at Avoca and in the Copper Coast area with the potential for future discoveries along the volcanic belt (McConnell *et al.* 1991; Breheny 2010; Breheny *et al.* 2016).

Methodology

As part of the Tellus regional geochemical survey, GSI re-analysed sediment samples obtained between the years 1986 and 1990 (Tellus 2018). A total of 1851 archived samples were collected over a 7544 km^2 area (1 per 4 km^2) from first, second and third order streams, and analysed for 56 elements (Fig. 1). All samples were wet sieved at the collection site, retaining the <150 μm fraction. A 12g milled fraction of each sample was analysed by X-Ray Fluorescence (XRF) and Fire Assay Inductively Coupled Plasma Mass Spectroscopy (FA-ICP-MS) for precious metals (Knights and Heath 2016). The use of XRF excluded the detection of

Li, which is potentially a drawback in the assessment of LCT pegmatite prospects. Stream sediment sampling relies upon the premise that collected sediments are the product of local erosion and weathering processes, thus representing the catchment area of a stream drainage network (Hale and Plant 1994). The measured sediment composition pertains to the catchment bedrock geology, overburden, and mineralisation.

Table 1

An initial literature study involved the compilation of major and trace element concentrations and ratios (Table 1) from regional geochemical case studies of the Leinster Granite (Sweetman 1987), Avoca and Copper Coast bimodal volcanic rocks (McConnell *et al.* 1991; Breheny 2010), and the Geochemical Atlas of Europe (Salminen 2005). The elemental concentrations and ratios should be considered as guidance values only, as the 1980-1990s studies employed XRF whereas the 2010 study used four-acid digest ICP-MS analytical instrument procedures, resulting in potentially variable measurements of resistate elements. Table 1 was utilised to map and distinguish the dominant lithology for each sample point in the Tellus dataset. The workflow involved initial classification of lithological units by mapping population clusters in bivariate plots, which were then refined to better represent the subclasses of geochemically similar lithologies, such as 'greywacke' and 'Zr-rich greywacke' (Table 2). Each sample point was assigned a lithology, however, if data was lacking or a clear interpretation could not be made, lithological units were not assigned. However, in many cases assumptions using nearby clustering data points were made in order to define a lithological association.

Table 2

Areas prospective for Cu, Ta and Au were identified by investigating anomalous elemental levels in cumulative frequency and scandium binary plots. Anomalies were defined by determining the 99th percentile followed by visual inspection of breaks in cumulative frequency plots.

Usually obtained through airborne geophysical measurements, an RGB image of elemental K_2O-Th-U was produced from the assays and subsequently scrutinised for distinctive radiometric signatures and trends. A similar approach was applied to map key exhalative VMS Cu-Pb-Zn base metal districts of the Copper Coast and Avoca areas.

Litho-geochemical populations and associations

Ratios of major and trace elements have been used to distinguish mafic, felsic and sedimentary lithologies using the Tellus dataset. Table 1 and 2 list the general occurrence and distribution of elements used in this study as well as their applicability to geochemical mapping.

Felsic and mafic lithologies

Fig. 2

Elements employed in this study to distinguish 'basalt or dolerite' from granites are predominantly SiO_2 and Sc (Fig. 2). Scandium, a transition row element that substitutes for Fe^{3+} in oxides such as pyroxenes, plays a key role in mapping mafic signatures due to increased abundances in basalts and other mafic rocks (Salminen 2005). Sc and SiO_2 values form a population cluster ranging from 23-28 ppm and 1-3%, respectively, and therefore indicate the presence of 'basalts and dolerites'. The Leinster Granite has previously been described as depleted in Th with a characteristically low Th/U ratio due to fractionation of Th-rich minerals during the early stages of magma evolution (Sweetman 1987). Sub-populations can consequently be delineated using bivariate plots of Th/U vs. Ti/Zr and K/Rb vs. Na_2O+K_2O, indicative of fractional crystallisation processes and the presence of feldspar and zircon (Figs 3a and b; Table 2). The Th/U < 1 and 12 < Ti/Zr < 45 population is classified as 'Leinster Granite Population 1', adhering to average values obtained from Sweetman (1987). Th/U < 1 and Ti/Zr < 12 values ('Leinster Granite Population 2') indicate a high content of Zr and potentially represent an earlier product of fractionation in the batholith. 'Leinster Granite Population 3' has a higher Th content (1 < Th/U < 3.5), whilst 'Leinster Granite Population 4' is characterised by high values of Zr (up to 900 ppm), Y (up to 30 ppm) and 1 < Th/U < 8, suggesting varying degrees of fractionation within the Leinster Granite. It is apparent from Fig. 3b that decreasing K/Rb and increasing Na_2O+K_2O allow a distinction to be made between relatively unfractionated (Leinster Granite Populations 2 and 3), moderately fractionated (Leinster Granite Population 4) and strongly fractionated (Leinster Granite Population 1) groups. A distinct population cluster in the W vs. K/Rb plot ranging from 8-19 ppm W (Fig. 5a) and 42.5-62% SiO_2 (Fig. 2), suggest a tungsten-rich intermediate rock and was therefore called a 'W-rich tonalite'.

The stream sediments were not assayed for Li, therefore LCT pegmatite populations were described using petrogenetic ratios outlined by Ballouard *et al.* (2016). Characteristic values of K/Rb < 150, Nb/Ta < 7, 28 < Zr/Hf < 47, 12 < Cs < 47 ppm , Ta < 7.5 ppm, W < 10 ppm and Sn of up to 50 ppm in previously classified granitic populations (Figs 4 and 5), imply the interaction of fractional crystallisation and magmatic-hydrothermal alteration processes (Ballouard *et al.* 2016) that locally altered the chemistry of the Leinster granite and led to the enrichment of incompatible elements. As a result, this population was classified as a 'LCT pegmatite with Sn-W signature'.

Figs 4 and 5

Immobile High Field Strength (HFS) elements (Zr, Nb) and Rare Earth Elements (REE) such as Y are enriched in Avoca and Campile Formation rhyolites (McConnell *et al.* 1991; Breheny 2010), and therefore form particularly useful petrogenetic indicators. 'Avoca and Campile Rhyolites' show distinctive population clusters characterised by 3.5 < Th/U < 8, 15 < Ti/Zr < 70, 35 < Y < 115 ppm, and 15 < Nb < 45 ppm (exemplified by the Th/U vs. Y plot in Fig. 6). However, the mean Zr concentration of interpreted rhyolite populations is 310 ppm, with outliers of 790 ppm, and thus is not as high as stated in McConnell *et al.* (1991).

Figs. 3a-c

Carbonate sedimentary lithologies

A CaO+MgO vs. Al_2O_3 plot allows the differentiation between pure and impure carbonates, or predominantly clastic sediments. In Fig. 7a 'calcium carbonates' form a population between 21 < CaO+MgO < 28% and Al_2O_3 < 4.5%.

Fig. 6

Figs 7a-d

Clastic sedimentary lithologies

The principal elements used to map and subdivide clastic sediments were K_2O, SiO_2, Al_2O_3, Fe_2O_3 and Zr. ‘Argillaceous sandstones or quartzites’ have a distinct SiO_2 content of >70% (Fig. 2). ‘Shales and siltstones’ display characteristic value ranges of Si/Al < 5 and K_2O > 2% due to variable clay content (Fig. 7b). The Duncannon Group ‘greywackes’ represent an erosional product of the Caradocian volcanic arcs and therefore are characterised by Zr values of up to 1,000 ppm in a Si/Al vs. Zr plot along with a ‘Zr-rich greywacke’ variety with Zr > 1,000 ppm (Fig. 7b). ‘Calcareous siltstones and litharenites’ clustering in the northwestern part of the study area are K_2O-poor (< 1.5%) and demonstrate a typical impure carbonate signature of 8 < CaO+MgO < 19% and 3.5 < Al_2O_3 < 11.5 % (Figs 7a and b). The $\frac{Fe_2O_3}{K_2O}$ vs. $\frac{SiO_2}{Al_2O_3}$ diagram provides an additional tool to differentiate sandstones from shales and greywackes which has been achieved with reasonable success (Fig. 7d; Herron 1988).

Sulphide enrichment and anomalies

‘Red-Green-Blue’ (RGB) ternary plots of Cu-Pb-Zn and Fe_2O_3-MnO-Ba, the latter indicating exhalative processes, illustrate prominent occurrences of elevated base metal associations in the Copper Coast area, the southwest-northeast trending Caradocian volcanic belt and the Northern Unit of the Leinster Granite (dashed lines in Fig. 8a and b). This confirms the presence of a volcano-sedimentary base metal district and structurally-controlled base metal mineralisation in the Leinster Granite.

Figs. 8a-b

Sc, previously employed to determine mafic rocks, is used to discriminate sulphide and oxide metal enrichment, and therefore enrichment and depletion processes, as scandium is predominantly hosted in oxide, and not sulphide, minerals (Salminen 2005). A binary plot of Sc vs. Cu shows sulphide enrichment where base metal values significantly lie above the regression line (Fig. 9a, Halley *et al.* 2016). Further anomaly detection using cumulative frequency plots demonstrate that Au and Ta do not always spatially correlate with this copper sulphide signature (Figs 9b-d). Clusters of anomalous Au is found in the Gorey-Ballycarney area and elevated Ta is clearly associated with the Leinster Granite, in line with O'Connor and Reimann (1993), whereas base metal sulphide enrichment principally occurs in Duncannon and Ribband Group deep-marine siliciclastic and felsic volcanic rocks along the Caradocian volcanic belt.

Correlation of multi-element geochemistry and bedrock geology

At regional scale, the ternary K_2O-Th-U (RGB) plot defines the internal architecture of the Leinster Granite and surrounding felsic volcanics and sediments, particularly the Caradocian volcanic belt, extending from Wicklow to Tramore (dashed lines in Fig. 10). The Leinster Granite has a distinctive radiometric signature and shows internal heterogeneities resulting from varying abundances of Th, in particular, indicating variations in fractional crystallisation (Sweetman 1987). The plot also highlights areas of strong potassic alteration, such as the Avoca VMS region and the eastern peripheries of the Leinster Granite.

Fig. 10

Overall the 'litho'-geochemical interpretation shows a strong correlation to the GSI bedrock geology (Fig. 11) and univariate anomaly maps by O'Connor and Reimann (1993). The geochemical analyses demonstrate that the Leinster granite can be accurately outlined using trace element geochemistry and this technique can be used to specifically pinpoint areas of increased magmatic fractionation and LCT pegmatite potential. This is particularly evident in the southwestern part of the Tullow Lowlands Unit, where 'LCT pegmatites with Sn-W signature' were identified in the Borris-Muine Bheag-Fennagh triangle. This finding implies that additional LCT pegmatite bodies may be present along the western flank of the unit, in addition to previously described occurrences further east (O'Connor and Reimann 1993). Furthermore, the results demonstrate that the Leinster Granite is a compositionally heterogeneous granite batholith that experienced significant geochemical evolution over time through fractional crystallisation processes.

Fig. 11

‘Leinster Granite Population 1’ granite was mapped throughout the batholith, with a significant clustering throughout the Blackstairs Unit, the eastern margin of the Tullow Lowlands Unit and the central-western portion of the Northern and Upper Liffey Valley Units. ‘Leinster Granite Population 2’ predominantly occurs in the central-western half of the Tullow Lowlands Unit, potentially indicating early stage fractionates similar in nature to the Graiguenamanagh Granite of the Blackstairs Unit described by Sweetman (1987). Signatures of ‘Leinster Granite Population 3’ can be found throughout the Leinster Granite exhibiting a trend towards the western margin of the Tullow Lowlands Unit. The same geochemical signature is found to the north of Castlebridge in Ribband Group sediments. This population may indicate poorly exposed Ballynamuddagh Granite, which has been described to extend at depth (Tietzsch-Tyler and Sleeman 1994). ‘Leinster Granite Population 4’ (anomalous Zr and Y) geochemical signatures trace the eastern margin of the Tullow Lowlands, Lugnaquillia and Northern Units. Similar geochemical occurrences located outside the main intrusion are related to the 454 Ma Croghan Kinshelagh Granite, described by Gallagher *et al.* (1994) as geochemically comparable with subalkaline varieties of the Caradocian volcanic rocks. ‘W-rich tonalites’ form a northeast-southwest linear trend along the eastern flank of the Tullow Lowlands Unit, and resemble the scheelite-rich greisen veins hosted by microtonalite sheets that were intruded into Ribband Group metasediments (O’Connor and Reimann 1993).

The geochemical signature of ‘basalts and dolerites’ principally trace the mafic lithologies between Ballyfad and Coolboy, and mafic-intermediate intercalated rocks of the Campile Formation at Enniscorthy. However, the mapped population does not identify basalts and other mafic rocks of the Bunmahon Formation further southwest along the Copper Coast. Instead, the predominant signature appears to be ‘shales and siltstones’, which can be explained by the proximal occurrence of Dunbrattin Formation shales and the large scale interfingering with Campile Formation shales (Sleeman and McConnell 1995; Breheny 2010).

As a result of the prominent HFS element-enriched signature, 'Avoca and Campile Rhyolites' correlate well with known rhyolite occurrences of the Caradocian volcanic belt between Avoca and the Copper Coast. Population clusters located outside known occurrences either indicate undescribed rhyolites in the Duncannon Group, or are related to hydrothermal enrichment of HFS elements along prominently north-south striking fault systems, for example in Silurian slates near Boolyglass.

'Calcium carbonates', interpreted from a generally trace element depleted MgO-CaO-Al_2O_3 signature, occur mainly along the northwestern flank of the Leinster Granite and are likely to be linked to Carboniferous limestones of the Central Ireland Basin. 'Calcareous siltstones and litharenites' along the northwestern flank of the Leinster Granite likely represent calcareous metasediments of the Ordovician-Silurian Kilcullen Group. An alternative explanation is the presence of Carboniferous carbonate material in stream sediment that was transported and re-deposited by glacial or glaciofluvial processes in a south-easterly direction, particularly on the western flank of the Leinster Granite (MacCarthy 2013).

The classification of clastic metasedimentary populations into 'Zr-rich greywackes', 'greywackes', 'shales and siltstones' and 'arkoses' using major and trace element geochemistry correlates with the existing 500k GSI geological map and the intercalated metasedimentary nature of the Duncannon and Ribband Groups. The occurrence of these populations within the northern part of the Tullow Lowlands Unit demonstrates the influence of glacial and glaciofluvatile processes reworking sediments in a southeasterly direction. 'Greywackes' and 'argillaceous sandstones or quartzites' in particular trace known occurrences of immature clastic lithologies of the Bray, Ribband and Kilcullen Groups, whereas 'shales and siltstones' predominantly trace intercalated Duncannon Group shales/ schists and rhyolites. This geochemical mapping approach can locally achieve a high level of detail as exemplified by the ability to trace the thin sliver of metamorphosed schists of the Butter

Mountain and Maughlin Formations that are located between the Northern and Lugnaquillia units of the Leinster Granite (Laragh-Donard area).

Conclusion

The Tellus SE Ireland survey is a low-density, regional geochemical dataset made available through the Geological Survey of Ireland (GSI). This study has proven the validity and utility of using regional stream sediment geochemistry as a fingerprinting tool in early stage regional reconnaissance programmes and as a good starting point for regional target generation. Whilst metallogenic districts were previously outlined using univariate anomaly detection tools (O'Connor and Reimann 1993), the application of petrogenetic vectors to mineralisation and the production of a 'litho'-geochemical interpretation has demonstrated that regional stream samples can reflect larger geological and metallogenic domains in southeast Ireland and outline new areas of interest. It is therefore anticipated that the approach presented here will encourage geoscientists to use governmental surveys effectively when conducting exploration elsewhere in remote and underexplored areas.

Despite the nature and limitations of the Tellus survey, the samples provide useful pathfinder signatures over a large area. It is evident that the survey area is enriched in a variety of metals, and most of these are thought to be related to igneous activity and other hydrothermal processes. This preliminary work supports the generation of prospective areas which subsequently require more detailed sampling and geophysical surveys:

1. LCT pegmatites around the northern and southern periphery of the Leinster Granite, particularly the Blackstairs Unit, where fractionation indices indicate enrichment of Cs-Ta-Rb.
2. Clusters of smaller VMS deposits of the Avoca District, Copper Coast and Waterford, as well as throughout the deformed volcanic belt of the Ordovician Duncannon Group. The felsic and pelitic lithologies within this group are thought to be prospective for Cu, Pb, Zn

and Au. Considering the extent of the volcanic belt, the potential for further VMS discoveries is considered to be high.

3. Au is widespread in the surveyed region, but has thus far seen limited exploitation from small placer deposits.

The future integration of high-resolution GSI airborne geophysical datasets (radiometrics, magnetics and electromagnetics) to accompany the stream sediment data would greatly enhance the understanding and permit a more focused follow-up in highlighted areas.

Acknowledgements

Benedikt Steiner would like to thank Matthew Parkes, James Barnet and an anonymous reviewer for thorough and constructive reviews that have significantly improved the paper.

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Figures and Tables

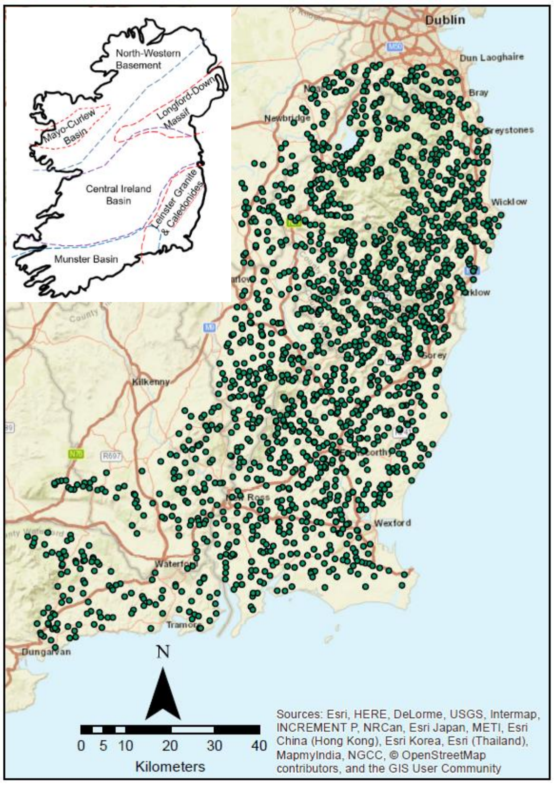


Fig. 1. Locations of GSI stream sediment samples overlying Open Street Map (ESRI ArcGIS Online feature of Open Street Map 2018). The inset map illustrates the mineral provinces of Ireland (modified from Minerals Ireland 2018). The Tellus dataset used in this study covers the Leinster Granite and the Irish Caledonides of southeast Ireland.

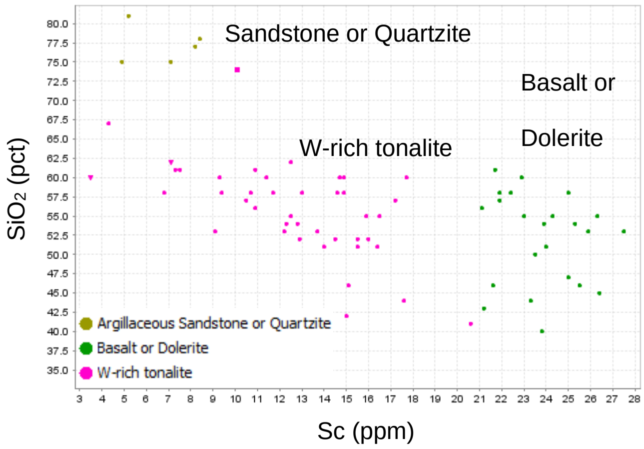


Fig. 2. Bivariate plot of Sc vs. SiO_2 defining characteristic elemental signatures of 'basalt or dolerite' (23-28 ppm Sc and 42.5-62% SiO_2), 'W-rich tonalite' (7-20 ppm Sc and 42-62% SiO_2) and 'argillaceous sandstone or quartzite' (SiO_2 >70%).

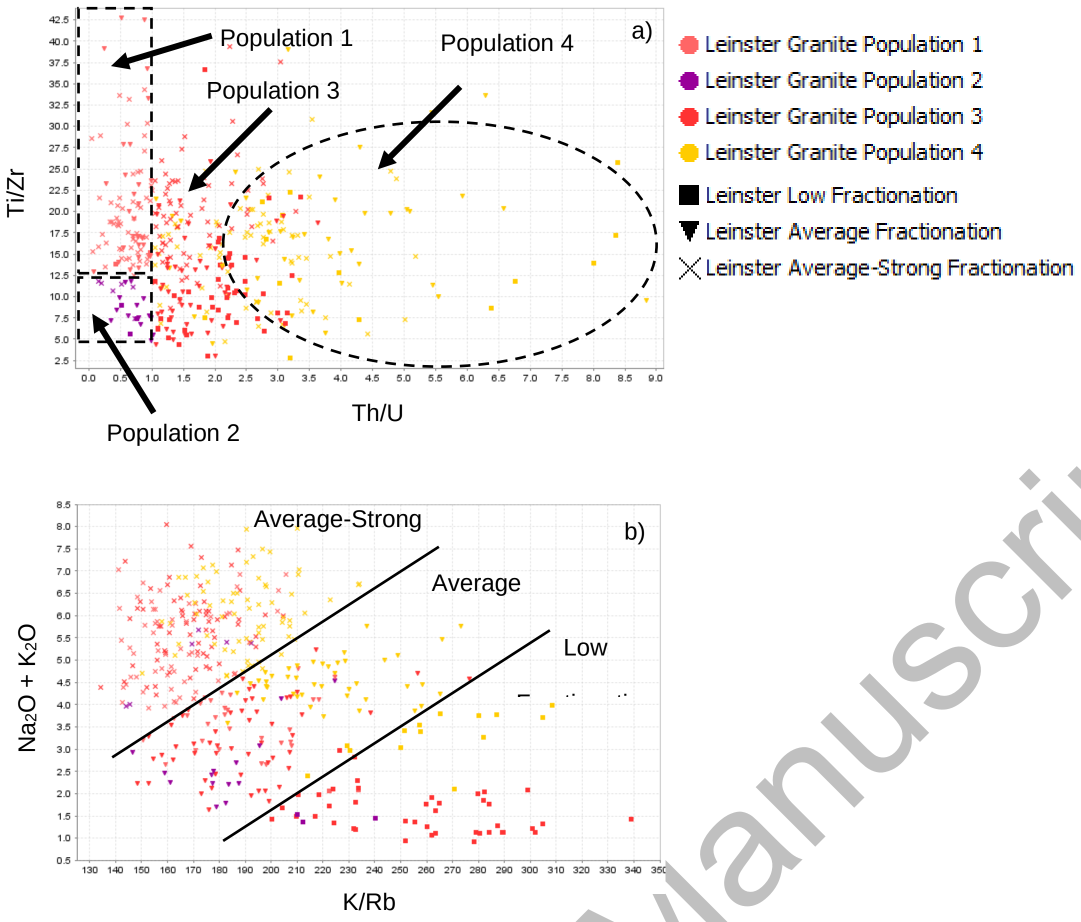


Fig. 3. Bivariate plots of a) Th/U vs. Ti/Zr and b) K/Rb vs. Na_2O+K_2O defining the heterogeneous nature of the Leinster Granite both in terms of chemical composition and degree of fractionation. Four Leinster Granite sub-populations and three fractionation grades have been defined using the Tellus dataset. The Leinster Granite has previously been described as a Th and Zr-poor batholith with considerable variation in mineralogical composition (Sweetman 1987).

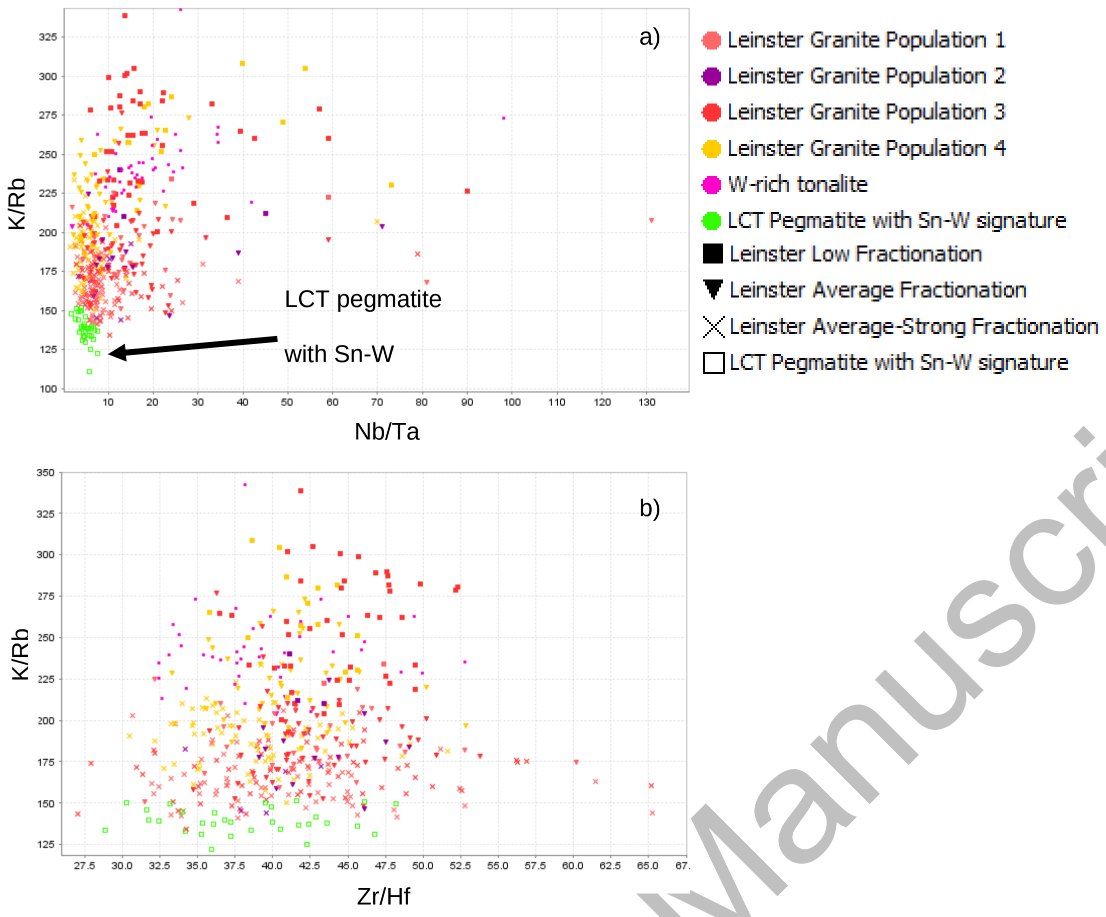


Fig. 4. LCT pegmatite fractionation ratios after Ballouard et al. (2016) using bivariate plots of a) K/Rb vs. Nb/Ta and b) K/Rb vs. Zr/Hf. Value ranges of K/Rb < 150, Nb/Ta < 7 and 28 < Zr/Hf < 47 indicate the influence of magmatic fractionation coupled with hydrothermal alteration in the Leinster Granite. This population was therefore called 'LCT pegmatite with Sn-W signature' in line with previous comparative studies by Ballouard et al. (2016).

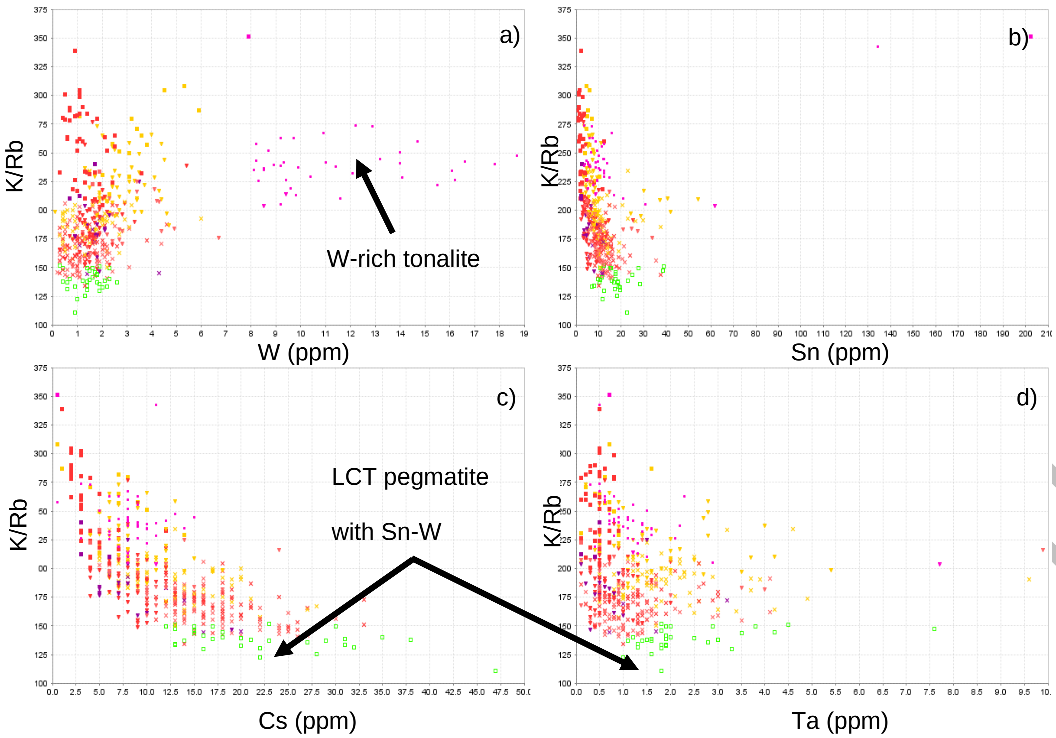


Fig. 5. Bivariate plots of K/Rb vs. a) W, b) Sn, c) Cs and d) Ta indicate the enrichment of incompatible elements in late-stage fractionates whereby a ratio of) imply increasing magmatic fractionation (Ballouard et al. 2016). 'LCT pegmatite with Sn-W signature' and 'W-rich tonalite' are distinctively clustering populations. Symbols as for Fig. 4.

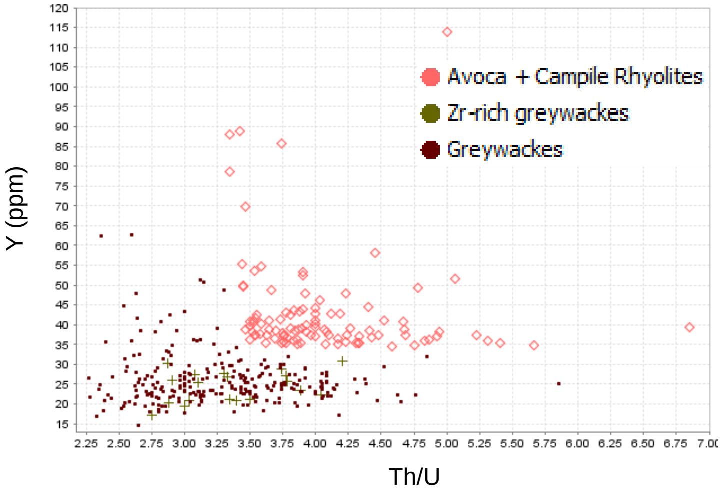


Fig. 6. Th/U vs. Y bivariate plot exemplifying the enrichment of HFS elements in rhyolitic volcanic rocks of the Avoca and Copper Coast areas (McConnell et al. 1993; Breheny 2010). A Y concentration of 35-115 ppm was determined characteristic of this dataset.

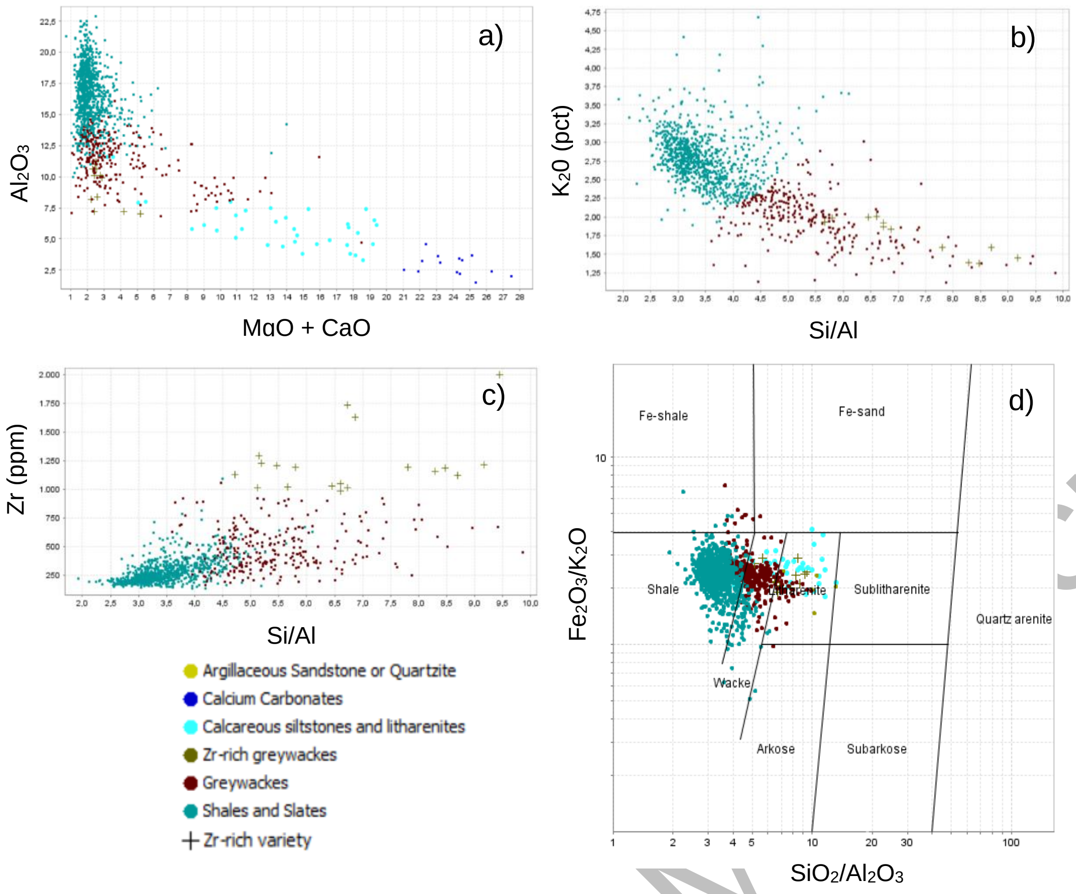


Fig. 7. Bivariate plots used in conjunction to support the mapping of sedimentary lithologies. a) CaO+MgO vs. Al_2O_3 outline ‘carbonates’ (21 < CaO+MgO < 28% and Al_2O_3 < 4.5%) and ‘Calcareous siltstones and litharenites’ (8 < CaO+MgO < 19% and 3.5 < Al_2O_3 < 11.5 %). b) Si/Al vs. K_2O show ‘shales and siltstones’ (Si/Al < 5 and K_2O > 2%) and ‘greywackes’ (Si/Al > 4 and K_2O < 2%). c) Si/Al vs. Zr indicate ‘greywackes’ (Zr < 1,000 ppm) and ‘Zr-rich

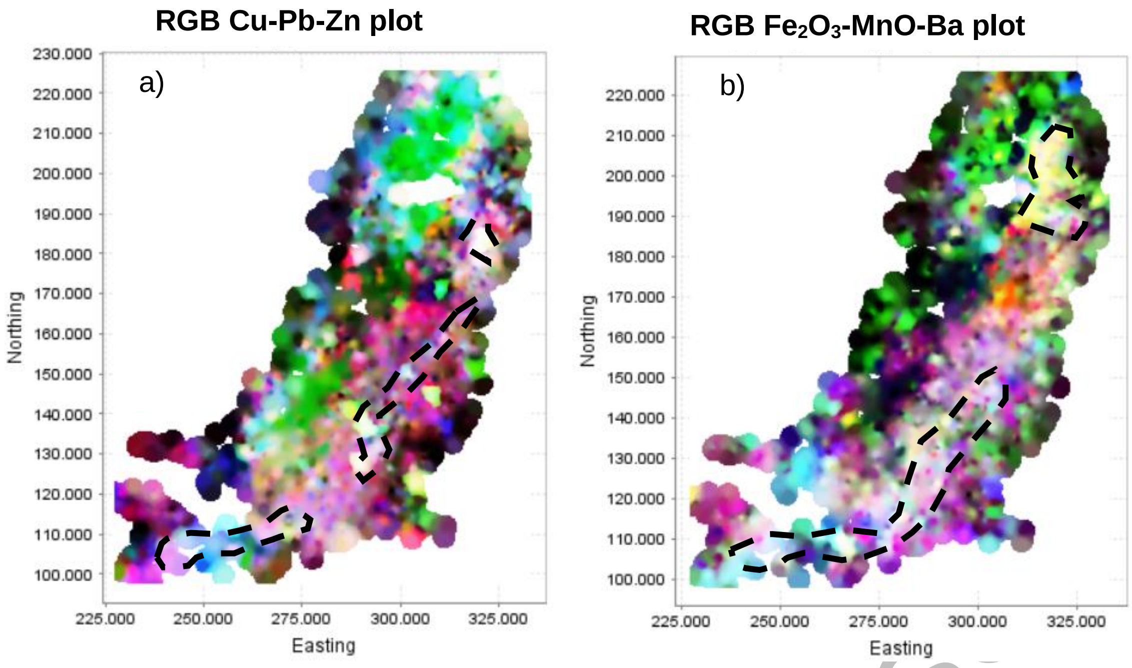


Fig. 8. Ternary mineralisation and alteration RGB plots of a) red=Cu, green=Pb and blue=Zn and b) red=Fe_2O_3, green=MnO and blue=Ba. A co-existence of a base metal and exhalative indicators (dashed lines) can be observed in the Copper Coast area and the southwest-northeast trending Caradocian volcanic belt.

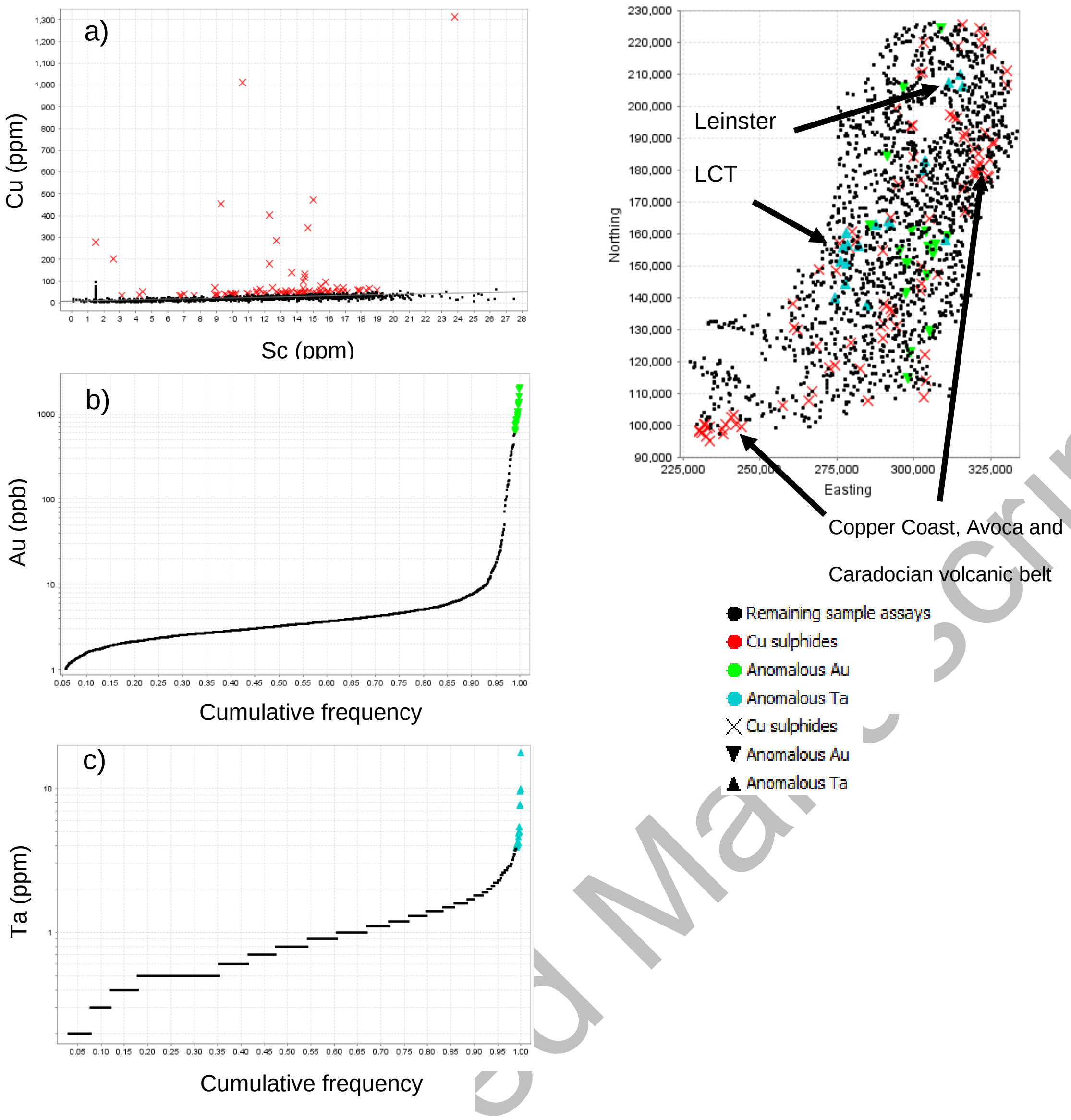


Fig. 9. a) A Sc vs. Cu binary plot reveals anomalous samples associated with sulphide mineralisation above the regression line. Anomalous b) Au and c) Ta were determined by the 99^{th} percentile in a cumulative frequency plot, d) relates the metal anomalies to the overall survey area showing clusters in the Copper Coast area (base metals), Gorey-Ballycarney area (Au) and Leinster Granite (Ta).

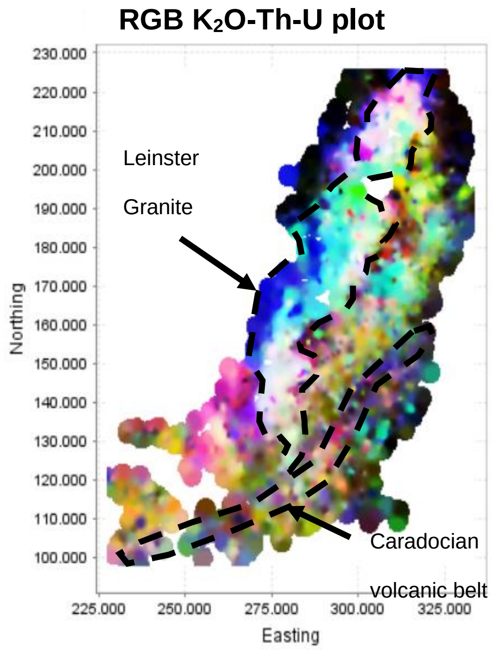
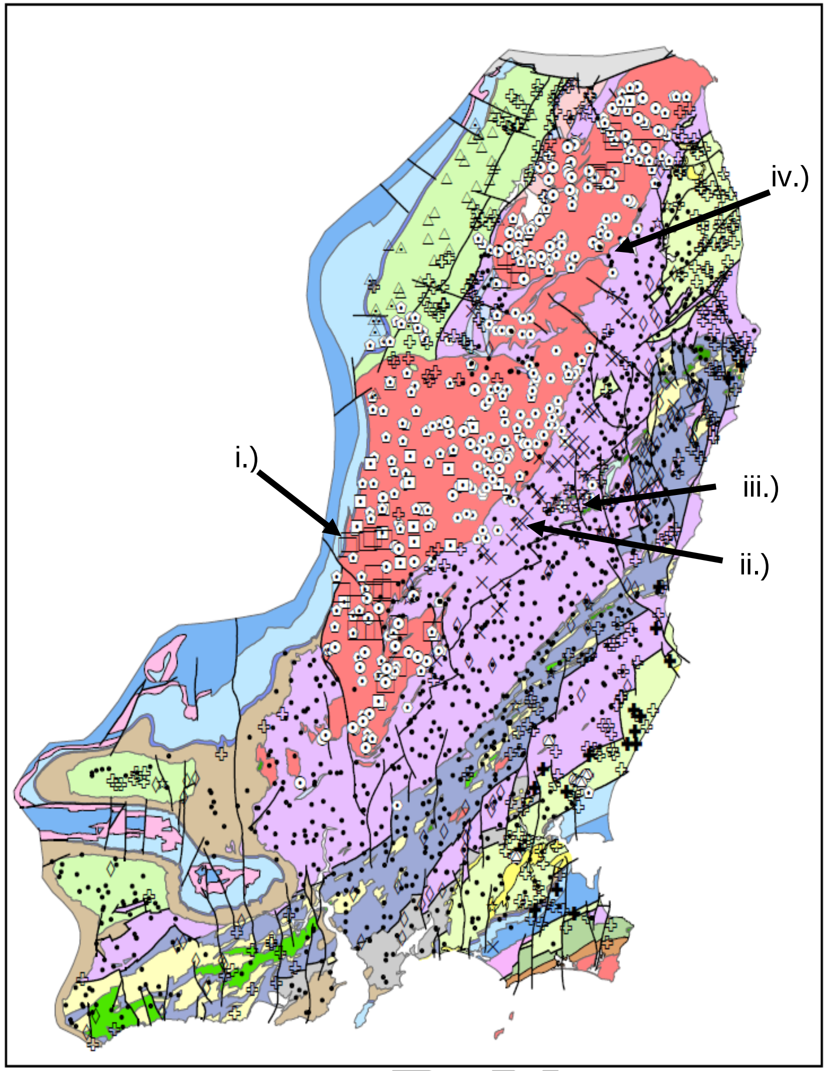


Fig. 10. Ternary radiometric RGB plot in which red=K_2O, green=Th and blue=U. The Leinster Granite and Caradocian volcanic belt have distinctive radiometric signatures (annotated dashed lines) whereby the former shows internal heterogeneities resulting from varying abundances of Th, in particular, indicating variations in fractional crystallisation (Sweetman 1987). The 'ballooning effect' observed around the margins of the surveyed area is due to widely spaced sample with spacings larger than the cell size of 150 used for this interpolation.



Southeast Ireland: Interpretation of stream sediment geochemistry

- ◊ Avoca + Campile Rhyolites
- ☆ Basalt or Dolerite
- □ LCT Pegmatite with Sn-W signature
- ⊙ Leinster Granite Population 1
- ⊡ Leinster Granite Population 2
- Leinster Granite Population 3
- Leinster Granite Population 4
- × W-rich tonalite
- Calcium Carbonates
- △ Calcareous siltstones and litharenites
- Argillaceous Sandstone or Quartzite
- Greywackes
- ✚ Zr-rich greywackes
- • Shales and Slates

N

0 5 10 20 30

Kilometers

Fig. 11. Interpreted lithologies overlying GSI 500k geological map (Department of Communications, Climate Action and Environment 2018). Legend to map can be found in Appendix 1. Selected examples discussed in the paper that demonstrate the validity of the geochemical mapping workflow are i.) LCT pegmatites in the Borris-Muine Bheag-Fennagh triangle, ii.) ‘W-rich tonalites’ along the northeastern flank of the Tullow Lowlands Unit, iii.) dolerites and Croghan Kinshelagh Granite between Ballyfad and Coolboy and iv.) thin sliver of schists of the Butter Mountain and Maughlin Formations located between the Northern and Lugnaquillia units of the Leinster Granite (Laragh-Donard area).

	Zr_ppm	TiO_2_pct	Ti/Zr	Y_ppm	Ce_ppm	Sc_ppm	Cr_ppm	Nb_ppm	K/Rb	Th/U
Leinster Granite	15-140	0.05-0.4	23-33	1-9	12-50	-	1-15	3-15	105-185	0.2-0.3
Avoca Rhyolites	750-2,000	0.25-0.45	1.6-6.3	97-208	50-315	0.12-5.5	<2	42-117	345-480	3.5-8
Avoca Basalts	220-310	1.75-2.35	64.5-107.3	30-55	41-49	31-39	17-98	15-19	364	0.9-15.9
Campile Rhyolites	85-270	0.13-0.58	5.2-63.7	18-63	35-117	-	-	5-17	275-400	1.7-5.5
Bunmahon Mudstones	130-175	0.85-1.2	48-80	3-38	6-96	-	-	13-61	230-490	1.77-2.97
Bunmahon Volcanics	65-350	0.14-1.24	90-147	16-62	11-100	-	-	2-12	230-520	1.5-3.1

Table 1. Guidance values for trace element concentrations obtained during comprehensive geochemical studies of the Leinster Granite (Sweetman 1987), Avoca bi-modal volcanic rocks (McConnell et al. 1991) and Copper Coast bi-modal volcanic rocks (Breheny 2010). The 1980-1990s studies employed XRF analytical techniques, whilst the 2010 study relied on four-acid digest ICP-MS.

Lithological Classification	Geochemical Plot	Elemental signature	Relation to 500k GSI map
Basalt or Dolerite	Sc:TiO_2	Sc (23-28 ppm); TiO_2 (1-3%)	Trace the mafic rocks between Ballyfad and Coolboy, and mafic-intermediate intercalated rocks of the Campile Formation at Enniscorthy. The population does not identify basalts and other mafic rocks of the Bunmahon Formation further southwest along the Copper Coast.
Leinster Granite Population 1	Th/U:Ti/Zr	Th/U < 1; 12 < Ti/Zr < 45	Occurs throughout the Leinster Granite, with a prominent clustering throughout the Blackstairs Unit, the eastern margin of the Tullow Lowlands Unit and the central-western portion of the Northern and Upper Liffey Valley Units.
Leinster Granite Population 2	Th/U:Ti/Zr	Th/U < 1; Ti/Zr < 12	Predominantly clusters in the central-western half of the Tullow Lowlands Unit, potentially indicating early stage fractionates similar in nature to the Graiguenamanagh Granite of the Blackstairs Unit (Sweetman 1987).
Leinster Granite Population 3	Th/U:Ti/Zr	1 < Th/U < 3.5; 3 < Ti/Zr < 40	Found across the Tullow Lowlands Unit with further occurrences to the north of Castlebridge indicating poorly exposed Ballynamuddagh Granite.
Leinster Granite Population 4	Th/U: Zr and Y	Zr (up to 900 ppm); Y (up to 30 ppm)	Traces NE flank of Tullow Lowlands Pluton and coincides with Croghan Kinshelagh Granite.
W-rich tonalite	Th/U:Y	1 < Th/U < 8; Y (up to 60 ppm)	Constitutes a northeast-southwest linear trend along the eastern flank of the Tullow Lowlands Unit. Resembles scheelite-rich greisen veins hosted by microtonalite sheets (O'Connor and Reimann 1993)
LCT Pegmatite with Sn-W signature	K/Rb:Nb/Ta, Nb/Ta:Zr/Hf, K/Rb:Ta and Sn	K/Rb < 150; Nb/Ta < 7; Zr/Hf < 28-47; Ta < 7.5 ppm and Sn up to 50 ppm	Clusters across Leinster Northern Unit and Blackstairs Unit. Previously unrecognised areas near the Borris-Muine Bheag-Fennagh triangle.
Avoca and Campile Rhyolites	Th/U: Y and Ce	3.5 < Th/U < 8; 35 < Y < 115 ppm; 15 < Nb < 45 ppm	Correlate well with known rhyolite occurrences of the Caradocian volcanic belt. Population clusters located outside known occurrences either indicate undescribed rhyolites in the Duncannon Group or are related to hydrothermal enrichment of HFS elements along prominently north-south striking fault systems in the Bray and Ribband Groups.
Calcium Carbonates	Al_2O_3: CaO+MgO	21 < CaO+MgO < 28%; Al_2O_3 < 4.5%	Occur along the northwestern flank of the Leinster Granite linked to Carboniferous limestones of the Central Ireland Basin.
Calcareous siltstones and litharenites	Si/Al: K_2O	5 < Si/Al < 13; 0.7 < K2O < 1.5%	Similar to 'Carbonates', this population occurs along the northwestern flank of the Leinster Granite and likely represent calcareous metasediments of the Ordovician-Silurian Kilcullen Group.
Greywacke	Si/Al: K_2O	4 < Si/Al < 9; 1.5 < K2O < 2.6%	Trace known occurrences of immature clastic lithologies of the Bray, Ribband and Kilcullen Groups.
Zr-rich greywacke	Si/Al: K_2O, Th/U: Zr	As greywackes, but with Zr>1000 ppm	Trace known occurrences of immature clastic lithologies of the Bray, Ribband and Kilcullen Groups.
Shales and Siltstones	Si/Al: K_2O	Si/Al < 5; K_2O > 2%	Predominantly trace intercalated shales/ schists and rhyolites of the Duncannon Group. Glacial and glaciofluvatile reworking of sediments has moved the geochemical signature in a southeasterly and northerly direction.
Argillaceous Sandstone or Quartzite	SiO_2: Al_2O_3	SiO_2 >70%	Trace known occurrences of immature clastic lithologies of the Bray, Ribband and Kilcullen Groups.

Table 2. Lithological classification of geochemical populations in the Tellus SE Ireland dataset. The range of characteristic major and trace element concentrations is provided for each population along with a summary of the relation between mapped populations and the GSI 500k geological map.

Legend

GSI Bedrock Map 1:500k

UnitName

- 16, Kilmore Quay Group; Paragneiss, schist
- 17, Greenore Point Group; Schistose amphibolite
- 2, Serpentinite, Neoproterozoic (NE Ox Mts) & Lower Ordovician (Clew Bay, Carnew)
- 30, Marine; Quartzite & minor slate
- 31, Marine; Slate
- 32, Marine; Greywacke & shale
- 33, Basalt - andesite, tuff & shale
- 34, Rhyolite and rhyolitic tuff
- 35, Deep marine; Slate, schist & minor greywacke
- 36, Deep marine; Greywacke, shale, sandstone & conglomerate
- 37, Basalt - andesite, tuff, slate & mudstone
- 38, Rhyolite, rhyolitic tuff & slate
- 39, Deep marine; Slate, shale, minor sandstone & siltstone
- 4, Granodiorite, tonalite, dacite, granite
- 49, Deep marine turbidite sequence; Mudstone, greywacke & conglomerate
- 5, Gabbro, dolerite & diorite
- 54, Continental redbed facies; Sandstone, conglomerate & siltstone (in places extends into the Carboniferous)
- 58, Shallow marine ("Lower Limestone Shale"); Shale, sandstone & thin limestone
- 6, Microgranite & porphyry
- 61, Marine shelf & ramp facies; Argillaceous dark-grey bioclastic limestone, subsidiary shale
- 62, Waulsortian mudbank; Pale-grey massive limestone
- 64, Marine shelf facies; Limestone & calcareous shale
- 65, Marine basinal facies (Tobercolleen & Lucan Fms - "Calp"); Dark-grey argillaceous & cherty limestone & shale
- 7, Appinite Suite
- 74, Continental redbed facies (Permo-Triassic, Wexford); Sandstone, conglomerate & siltstone
- 8, Granite, granodiorite

Appendix 1. Legend for the 1:500k Geological Map of SE Ireland (Department of Communications, Climate Action and Environment 2018).