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Characterising dispersed metal plumes in surficial soils and sediments in the Irish Midlands: Using isotope fingerprints to develop vectors in mineral exploration

Ph.D. Thesis

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Summary

This thesis deals with the enhancement of geochemical and isotopic methods for mineral exploration through surficial soil and till at the Ballinalack Zn-Pb deposit, in the Irish Midlands, Ireland. This carbonate hosted Zn-Pb deposit is currently sub-economic in nature, but has been the focus of exploration and thus accessible for sampling. The thesis builds on the geochemistry of the sulphides for a better understanding of which elements may be transported upwards towards the surface. Soil and surficial sediments have been further investigated using various geochemical and isotopic approaches to examine the prevailing reduced chimney model for element dispersion, based on an orientation study conducted by Teck Ireland Ltd in 2007. The reduced chimney model explains a vertical element transport from sulphide mineralisation through overburden towards the surface, induced by changes in the redox potential.

Using laser ablation ICP-MS provides insights into the chemistry of sphalerite and pyrite, that together with galena, marcasite and arsenopyrite comprise the sulphide mineralisation at Ballinalack. Samples were collected from two drill holes throughout the mineralised zone to understand proximal-distal changes in chemistry within the deposit (Chapter 3). Interestingly, only minor macroscopic differences occur between the samples. However, at the microscopic scale, sulphide minerals exhibit marked zonation, notably micro-inclusions of pyrite in sphalerite and similarly sphalerite-galena inclusions in pyrite. Furthermore, the highest reported (published) Ni concentrations in pyrite were detected within this study, which have implications for the source of metals. The analyses of the sulphides reveal an elemental pool of Ag, As, Co, Fe, Ga, Hg, Mo, Ni, Pb, Sb and Zn that may be transported within the system.

Based on the sulphide geochemistry and the orientation study, a survey with 163 soil and till samples provides a good comparison between shallowly and deeply buried sulphide mineralisation within an area affected by glaciation and anthropogenic land use. Analyses do not support the prevailing reduced chimney model for element migration in soil and till over the Ballinalack Zn-Pb deposit. However, a proximal geochemical fingerprint featuring elevated concentrations of Pb, Cd, As, Ag, Tl, Zn, Sb and Ba in soil and till (Chapter 4) coincides with element signatures within the sulphides and thus demonstrates that the geogenic signature from the sulphide mineralisation has not been obliterated by glaciogenic and anthropogenic chemical influences.

To further investigate the buried mineralisation for subtle chemical signatures, which could not be detected using conventional lithogeochemistry, stable metal isotopes, i.e., Cu and Zn isotopes were applied to a selection of 15 of the soil and till samples. Furthermore, five sphalerite samples were also analysed for Zn isotopes to investigate the source of the Zn soil signature. The total digested samples were analysed using MC ICP-MS and provide a signature of heavy $\delta^{65}\text{Cu}$ and light $\delta^{66}\text{Zn}$ isotopic signatures above the shallow mineralisation as a result of sulphide weathering (Chapter 5). Although the deeply buried mineralisation cannot be detected using these isotope systems, additional insight can be provided for the shallow mineralisation. Copper and Zn isotopes clearly demonstrate that the sub-surface weathering of sulphide mineralisation are the source of anomalies measured in soil and till.

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Abstract

The enhancement of mineral exploration is essential for the growing demand of base metals in the world. Successful geochemical surveys in soil and till have led to numerous discoveries. However, most of these deposits are shallow and situated in areas unaffected by anthropogenic activities. Exploring for more deeply buried mineralisation, and in areas such as anthropogenic influenced lands offer new challenges for mineral exploration.

This thesis demonstrates geochemical investigations to advance mineral exploration tools and their implications, using the example of the Ballinalack carbonate-hosted Zn-Pb deposit in the Irish Midlands, Ireland. Sulphide samples (sphalerite and pyrite) were texturally characterised using SEM imaging technique and afterwards analysed by in situ laser ablation ICP-MS to understand proximal-distal fingerprints within the mineralisation lens and their elemental pool. Furthermore, a trace element as well as Cu and Zn isotope approach have been applied to surficial sediments (soil and till) to understand how elevated concentrations of trace elements can be detected and transported above a shallowly (1.5 m) and deeply buried (150 m) sulphide lens in an area affected by former glaciation and modified by agricultural practices.

The trace element signature of the sulphides at Ballinalack consists of Ag, As, Co, Fe, Ga, Hg, Mo, Ni, Pb, Sb and Zn, among others, which broadly coincide with elevated concentrations of Pb, Cd, As, Ag, Tl, Zn, Sb and Ba in soil and till above the shallowly buried sulphide mineralisation. Any overprint from glaciation or active agriculture-pasture, would seem to be minimal; however, the deeply buried mineralisation was not detected by trace-element analyses of the overlying soil/till. These findings contradict the prevailing reduced chimney model for the transport of elements towards the surface. The anomalous soil and till concentrations of trace elements mentioned above can be spatially associated by heavy $\delta^{65}\text{Cu}$ and light $\delta^{66}\text{Zn}$ isotope signatures; the heavy Cu isotope signatures reflect direct weathering of the sulphides resulting in the soil anomaly. The Zn isotope signature may indicate that sphalerite is also a source of the trace-elemental anomaly and hence the mineralisation in the underlying bedrock is the source of the fingerprint in the soil and till. Accordingly, this approach confirms the feasibility of stable metal isotopes for use as an additional tool in mineral exploration.

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Chapter 1: Introduction

1 Motivation of this research study

Metals such as lead and zinc are important for manufacturing, galvanising, and chemical industries. Ireland is an important Zn producer (Singer, 1995), due chiefly to Tara Mines, which is Europe's largest Zn producer. For this reason, understanding Irish-type carbonate-hosted Zn-Pb deposits with respect to their genesis and history is important. New research approaches using state of the art geochemical and isotopic methods can help in the exploration for new deposits.

First, laser ablation ICP-MS is widely used for characterising sulphide minerals, such as pyrite and sphalerite. The character of a particular sulphide mineral can provide insights into ore formation and physiochemical conditions (Large et al., 2009), and their trace-element signatures could be used as a proximal-distal indicator in addition to conventional lithogeochemical approaches.

Second, geochemical investigations of overlying sediments, soils and natural waters have been successful in the exploration for Zn-Pb deposits (e.g., Hoagland, 1962, DeGeffroy et al., 1967, Cameron, 1975, Cox and Curtis, 1977). Soil anomalies can indicate not only shallow mineralisation, but also deeply buried sulphide mineralisation in varied settings and climates, including arid and glaciated terrains (Cameron et al., 2004). This has been applied to great success in pristine areas, but targets can be extended into more challenging regions, such as agriculturally developed areas.

It is anticipated that the transport of elements can take place from mineralisation upwards through cover rock and overburden into the surficial environment which commonly consists of soil and till. In glaciated terrains, the reduced chimney model after Hamilton (1998, 2000) is widely accepted as a model to explain this geochemical process (Fig. 1). The model is based on an electric self-potential (Sato and Mooney, 1960) in which four prerequisite conditions are required to develop such a self-potential:

1. The ore body must be a good conductor of electricity.
2. The sulphide minerals need to be in direct connection with the ground water of different potential.
3. The sulphides have to be chemically inert.
4. No occurrence of an insulating cap on top of the sulphide body.

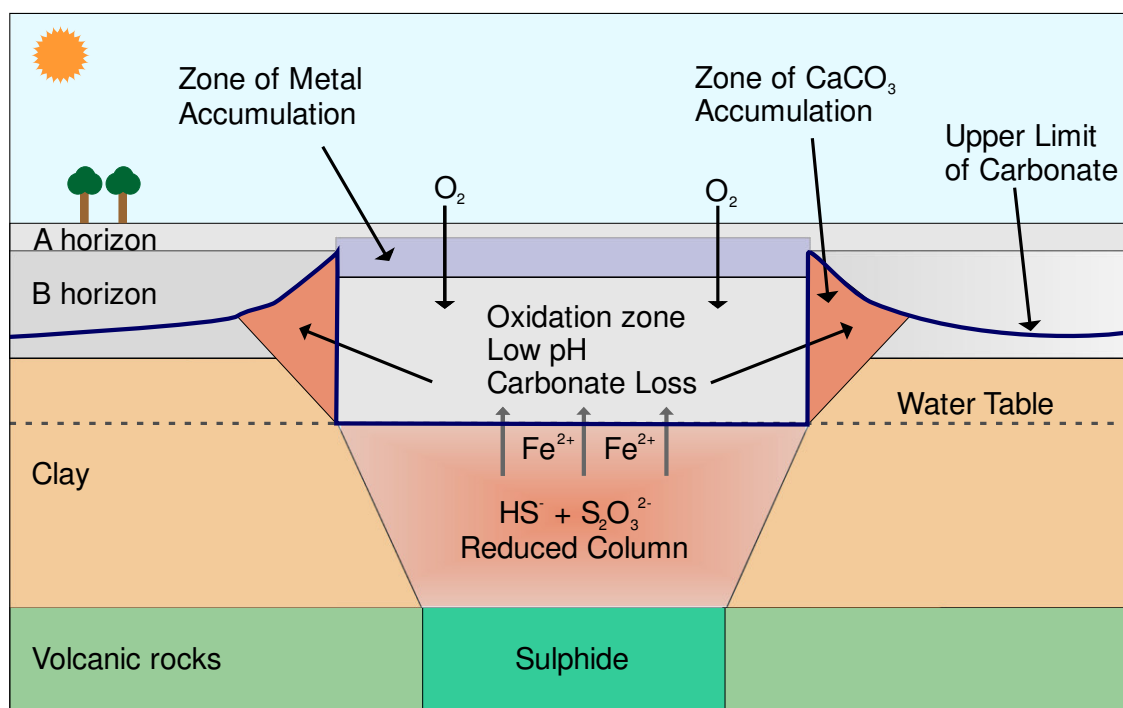


Fig. 1 Idealised model of a reduced chimney halo (Hamilton, 1998) illustrating elemental transport from sulphide mineralisation through overburden in glaciated terrains (after Cameron et al., 2004).

Consequently, the sulphide body can consist of pyrite, pyrrhotite or lesser chalcopyrite, covellite, graphite and anthracite. Galena behaves differently, although it is a good conductor and oxidises easily, it does not produce a noticeable self-potential. Sphalerite does not produce a self-potential behaviour due to its low conductivity. Notably, Poldini (1938) reports a lack of self-potential in areas where the sulphide body is overlain by peat horizons. Arguably, the pH value is mainly acidic pH 2–5 (Sato and Mooney, 1960) in sections above the water table overlying ore bodies.

In the case of a sulphide ore body, that developed a self-potential, underlying a thick overburden with an upward-increasing redox gradient, a more reduced environment should develop above the mineralisation. Likewise, the redox characteristics in a voltaic cell model (Hamilton, 1998) include a deeper reduced zone of a mineralisation overlain by more oxidising upper parts (Fig. 1). Hence, the consumption of oxidising agents in the upper part results in a reduced environment over time. This redox front propagates upwards and outwards until it encounters a continuous source of oxidising agents, which is commonly a function of depth from surface. Subsequently, a permanent reduced chimney is developed. With respect to the higher redox gradient between the sulphides and the ground surface, at the edges of the reduced column relative to its centre, an ionic current is typically concentrated at the flanks. Predictably,

twin-peak (rabbit ear) anomalies form by upward movement of reduced anions at the edges and an inward movement of oxidised cations. Thus, a higher pH value develops at surface along the flanks, and influences element mobilisation and precipitation. Consequently, due to their higher mobility, Fe and Mn, as well as co-precipitated elements, are depleted at surface over the centre of the sulphide body (Hamilton, 1998, 2000).

Third, with improvements in analytical techniques, especially multi-collector inductively-coupled plasma mass spectrometry (MC ICP-MS), isotope ratios of transition metals like Fe, Zn, Cu and Cd, among others can now be measured (overview in Eiler et al., 2014). These developments and mass bias corrections have helped to develop a new field of isotope geochemistry, which is being applied in the field of economic geology. With the application of novel stable isotope analyses in ore systems, the cycle of aqueous fluids (hydrothermal and meteoric) and the mobility of elements could provide new insights into the genesis of Zn-Pb deposits; in addition, the movement and enrichment of elements in overlying sediments can be used as potential markers (fingerprints) of mineralisation. For this reason, modern isotopic tools may refine exploration models, allowing a full understanding of geochemical (trace and isotopic) processes in the formation of ore deposits and wall rock alteration, as well as secondary weathering in overlying sediments and soils and the source of the geochemical anomalies.

In terms of Irish-type Zn-Pb deposits, a closer examination of the trace-element geochemistry and stable metal isotopes may provide new insights into the mobility of elements above a blind deposit. Historically, exploration using elevated Zn concentrations in soil have been successfully applied in the Irish Midlands, contributing to the discovery of the sub-cropping Lisheen (Hitzman et al., 1992, Fusciardi et al., 2003) and Navan (Tara Mines) Zn-Pb deposits (O'Brien and Romer, 1971).

In this research, the emphasis will be placed on the Ballinalack deposit, which is situated in the Irish Midlands, west of the Navan Zn-Pb deposit (Tara Mines). Ballinalack was discovered in the late 1960s through a regional geochemical survey based on wide-spaced stream sediment and soil sampling (Holman, 2000), and is currently held by Teck Ireland Ltd. (60 %) and Nonfemet (40 %). The deposit is presently sub-economic, hence the objective of this study is to help refine exploration models and expand resources in the region.

Teck Ireland Ltd. provided trace- and major-element data (Appendix A) for soil samples collected in a NW to SE trending line (Fig. 2) with a 25 m spacing above the northern sulphide mineralisation, which is situated at approximately 150 m depth and is covered by barren stratigraphic units and overburden; a 50 m spacing is used for background samples away from

mineralisation. Soil samples (23 locations) were collected and prepared for ICP-MS analyses using an aqua regia (partial) digestion. Each site location consisted of three mineral soil horizons: 1) the A-horizon, at 0–10 cm of depth (upper Ah), 2) the lower Ah horizon at 15–30 cm depth that can be referred as plough sole, and 3) the BC horizon that is a transitional horizon of the subsoil at 45–65 cm of depth (Clarke and Reed, 2009, Cook, 2010).

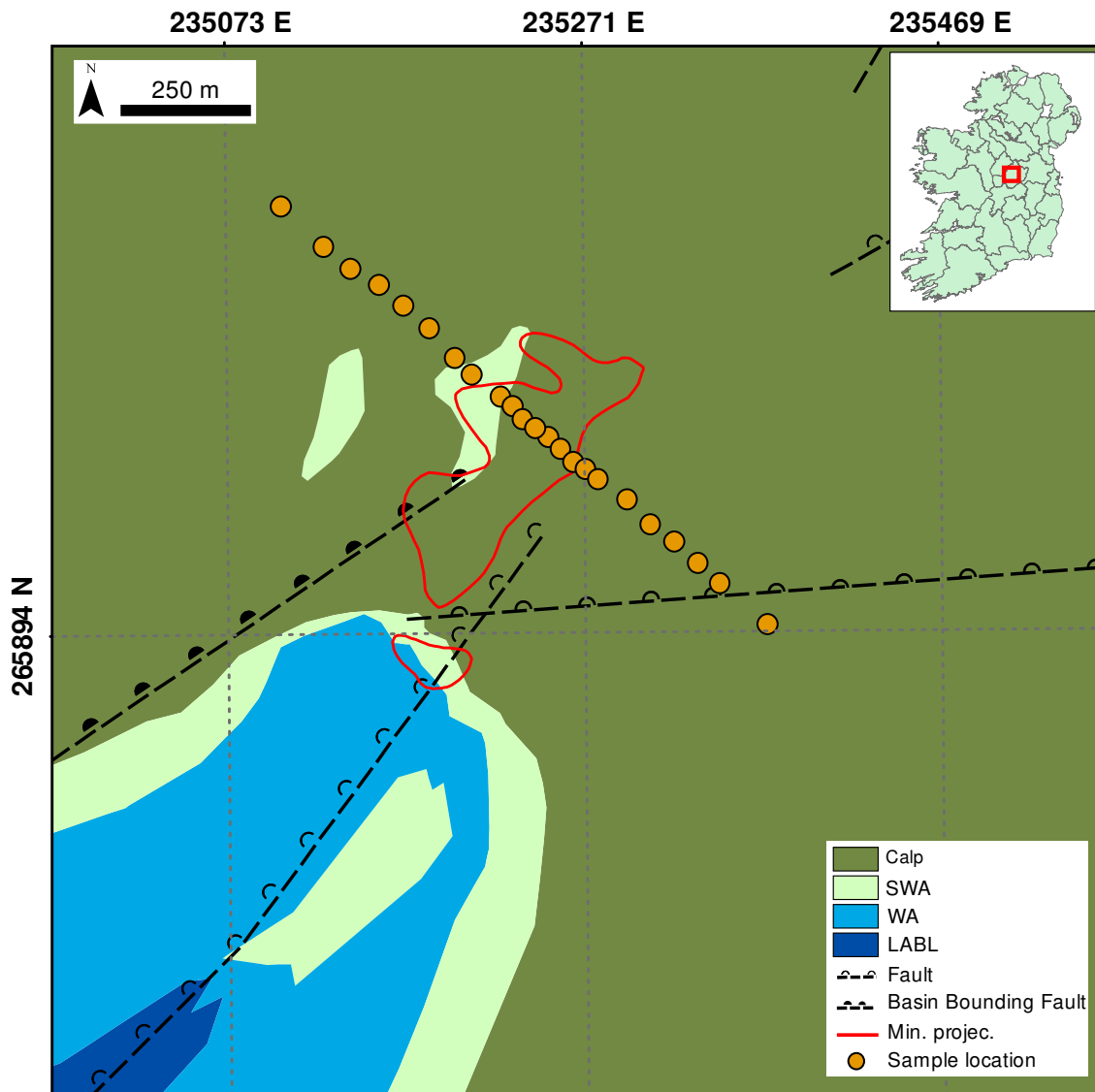


Fig. 2 Geological map of Ballinalack area, showing sulphide mineralisation as a projection to surface (red line) and soil sample locations of the Teck Ireland Ltd. orientation study. SWA = Supra Waulsortian Limestone, WA = Waulsortian Limestone, LABL = Lower Argillaceous Bioclastic Limestone, Min. projec. = Mineralisation projection, Irish grid TM 65 coordinates.

The results of the analyses display the spatial differences between the soil horizons. The B and BC horizons are well defined in terms of element signatures, with the following results illustrated based on the BC-horizon (Fig 3). Although the background geochemical signatures are variable (noisy), the response ratio RR ($\text{concentration}_{\text{value}}/\text{concentration}_{\text{median}}$ - median of all values for an element) of As, Mo and Sb show apical anomalies over the mineralisation (Fig. 3). All elements may occur in varying proportions as trace elements in sphalerite (Cook et al., 2009, Palero-Fernandez and Martin-Izard, 2005). Arsenic and Mo may also occur as trace elements in pyrite and galena; Sb is often substituted for Pb in galena (Palero-Fernandez and Martin-Izard, 2005, George et al., 2015). The response ratio of Ca and Sr are up to 20 times higher compared to the background signature on the flanks of the mineralised body, resulting in a twin-peak (rabbit ear) anomaly. According to Cook (2010) the pH value (Fig. 3) reports the same tendency, likely due to carbonate remobilisation and precipitation, which would seem to confirm the reduced chimney model after Hamilton (1998, 2000). Furthermore, the west flank peak is much more significant than the east flank peak (Fig. 3). This could be either due to less overburden in the west or due to the change of underlying geology from the Calp unit to Supra-Waulsortian carbonates in the west or a combination of both.

In addition to galena and sphalerite, which are the main ore minerals in carbonate-hosted Irish-type Zn-Pb deposits, pyrite and marcasite are also abundant; these represent sulphides formed as primary and secondary minerals during diagenesis and ore-forming processes. Since the Ballinalack sulphide body is separated into a major deeply buried and a minor sub-cropping sulphide body, it serves as an example to compare two differing exploration scenarios. This complex mineralogy and history must be taken into account in any trace element or isotopic (Cu and Zn isotopes) study. The characterisation of this distribution could help elucidate the behaviour of fluids distal to an ore-system and provide new insights into mineral exploration, and current research.

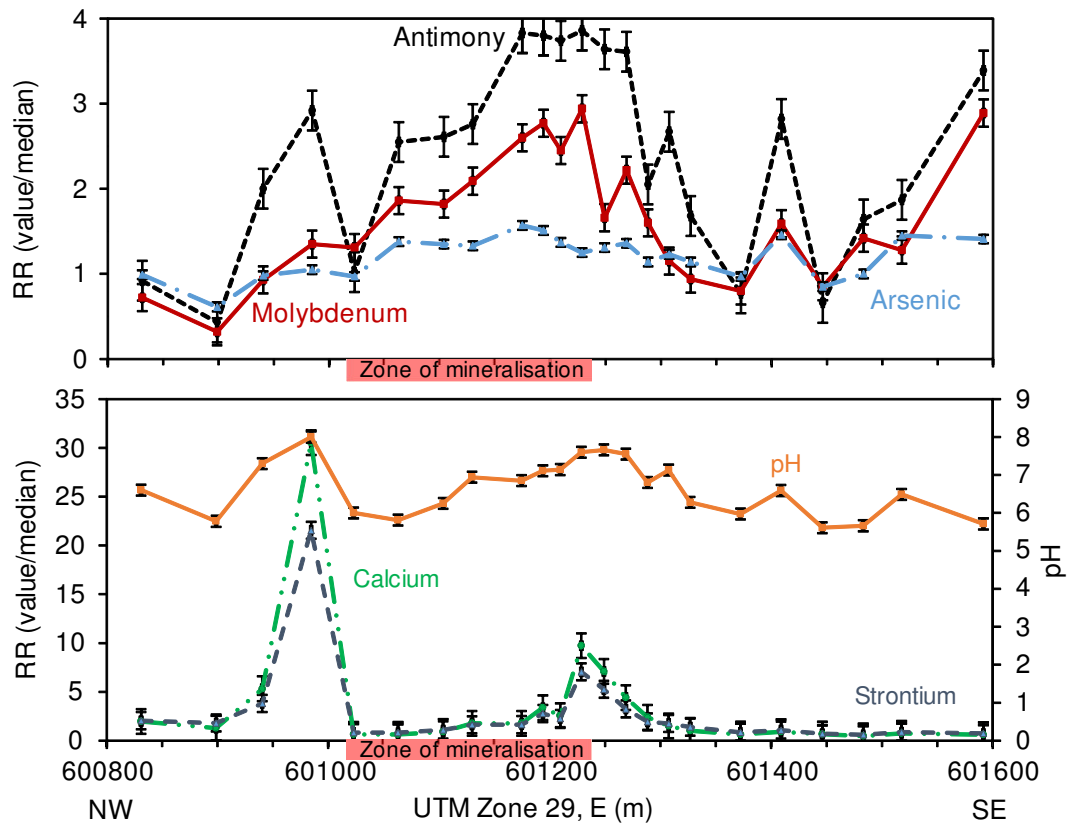


Fig. 3 Geochemical profiles based on a Teck Ireland Ltd. orientation study, NW to SE line above the northern buried (150 m) sulphide mineralisation. Top: Single peak (apical) anomaly of Sb, As, and Mo above the mineralised zone in BC horizon. Bottom: Two peaks (rabbit-ear) anomaly of Ca, Sr, and pH in BC horizon (after Cook, 2010). RR = Response Ratio ($\text{concentration}_{\text{value}} / \text{concentration}_{\text{median}}$), error bars based on 2 % of the value.

2 Layout and Themes of the Thesis

In this study, a literature review and three research topics will provide insight into the Ballinalack deposit and its elemental and isotopic behaviour, which could be of use for mineral exploration. The objectives are addressed as independent studies, each forming chapters of the thesis. The chapters are in a manuscript format, accordingly, the reader will explore variations of the introduction to each manuscript.

Chapter 2 provides a literature review, for an understanding of the widespread topics covered in the proceeding chapters. It provides a summary of trace elements in sulphides and soils and the behaviour of Cu and Zn isotopes. The chapter focuses on elemental mobility as well as isotopic fractionation processes. After each section, a case study illustrates how it can be applied in mineral exploration.

Chapter 3 provides a summary of the sulphide geochemistry of the Ballinalack Zn-Pb deposit in the Irish Midlands, targeting the following question: What are the trace-element

characteristics of the sulphide body at the Ballinalack Zn-Pb deposit? In order to better understand how Irish Zn-Pb deposits were formed, sulphide samples have to be investigated for their petrography using reflected light microscopy as well as SEM images and for their trace-element signatures using in situ micro-analytical techniques (i.e., SEM and laser ablation ICP-MS - spots and line rasters) on sphalerite and pyrite. A better understanding of the Ballinalack sulphides could help to improve the knowledge in general of Irish-type deposits and thus for further exploration targets within the Irish Midlands. Also, the elemental signatures within the sulphides will help in the follow-up study to understand element mobility within surficial sediments and whether the sulphides are an actual source of geochemical anomalies.

Chapter 4 illustrates the investigation of elemental haloes for mineral exploration in pasture land in glaciated terrains. It focuses on answering the following questions: Which elements exhibit anomalies within the soil and till cover above the Ballinalack Zn-Pb deposit? And further, what would be the mechanisms and fluid pathways leading to these observed geochemical signatures? How are these processes affected by differences in soil and till over deeply-buried and shallowly sub-cropping sulphide bodies? As presented above, Teck Ireland Ltd. has undertaken an orientation study to evaluate surface responses in mineral soils at Ballinalack. In order to confirm or modify their model of a reduced chimney (Hamilton, 1998, 2000), a total of 163 soil and till samples were collected over the main and minor sulphide bodies. Aqua regia (partial) digestion for geochemical analyses (ICP-OES/MS) will provide mainly mobile elements within the soil and till. Finally, if there are elemental haloes above the sulphide bodies, it will be explained how the elements were transported vertically and/or with the glacial dispersion (horizontally). The results are essential to understanding the influence of pasture land on soil geochemistry for mineral exploration. Further, it will test the element transport model, which can further be applied in other carbonate-hosted mineral deposit settings.

Chapter 5 focuses on the innovative use of metal stable isotopes in the surficial environment to aid mineral exploration, and addresses the following questions: Will Zn and Cu isotopes show systematic variation in the surficial environment and can this be attributed to systematic weathering or transport of Zn-Pb mineralisation? Will stable metal isotopes provide a useful tool for mineral exploration? To date, there are no known studies investigating Cu and Zn isotopes in surficial sediments above a mineral deposit for mineral exploration. If there are systematic variations of Cu and Zn isotopes and they are related to the underlying sulphide bodies (in this study represented by sphalerite), it may be possible to delineate proximal-distal relationships in the surficial environment. This could be a useful tool as an addition to the

common selective leach/partial digestion methodology. In this study, in particular, Cu isotopes might provide a new vector for mineral exploration, also for other sulphide deposits, as they showed a clear change above the mineralisation compared to the background. The results provide a good orientation study for further research to track more cryptic signatures induced by sulphide mineralisation.

In Chapter 6 a comprehensive conclusion is presented about the insights presented in the individual chapters from this research. Further, the implications of the results of the trace-element study on sulphides, soil and till, as well as, the new isotopic findings will be presented for mineral exploration and future research.

3 Contributors

All three core research chapters (chapters 3–5) consist of manuscripts prepared for submission to peer-reviewed journals. The potential co-authors provided assistance in understanding the geology and their geochemical context; advice and guidance in analytical work, as well as general discussion and interpretation. The detailed roles are explained below.

Dr. Daniel A. Frick, German Research Centre for Geosciences Potsdam, Germany, provided guidance for the femtosecond LA-ICP-MS analyses and data reduction (Chapter 3).

Stephen Cook, Teck Resources Limited, Vancouver, Canada, provided advice and guidance through the Teck orientation study of Ballinalack, as well as discussion for the soil survey of this study (Chapter 4).

Dr. Damien Guinoiseau, Max Planck Institute for Chemistry Mainz, Germany, provided guidance throughout the sample preparation and measurements of Cu and Zn isotopes, as well as discussion of Chapter 5.

Dr. Seán H. McClenaghan and Professor Dr. Balz S. Kamber, Trinity College Dublin, Ireland, developed the project design and provided guidance through the implementation of the study.

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Chapter 2: Literature Review

1 Trace elemental composition of sulphides

1.1 Sulphide mineralisation in the Irish Midlands

Zinc-lead mineralisation in the Irish Midlands is hosted in Lower Carboniferous rocks. Ore minerals are sphalerite, galena, pyrite and marcasite with minor chalcopyrite and tennantite. The sulphides are found in association with hydrothermal dolomite, calcite, minor barite and quartz. They occur in economic settings in massive form with complex structure and in rather sub-economic settings in massive, laminated, disseminated and vein- and breccia-filling forms (e.g., Boast et al., 1981, Anderson et al., 1998, Hitzman et al., 2002, Fusciardi et al., 2003, Wilkinson et al., 2005a).

1.2 Trace elemental composition of sulphides

In the following, a summary is given of the most relevant elements hosted by the minerals sphalerite and pyrite, including their behaviour and mechanism of incorporation. For more details, Cook et al. (2009) provide an excellent overview on sphalerites; comprehensive reviews on pyrite chemistry can be found in Abraitis et al. (2004) and Large et al. (2014). Notably, earlier studies on mineral chemistry employed electron microprobe, which is still used for the generation of high-resolution element maps (major elements > 0.1%), but this has been supplanted by laser ablation ICP-MS capable of determining the trace-element composition of the sulphide minerals.

1.2.1 Sphalerite

Sphalerite ZnS incorporates a wide range of trace elements, and most notably Fe, Mn and Cd through a tetrahedral coordinated substitution governed by the size and the charge of the metal ion. Iron occurs commonly in sphalerite up to 15 wt.%, without any structural distortion (Pring et al., 2008). The element is often used as geological barometer to identify the formation conditions regarding metamorphism and metamorphogenic ore formation (e.g., Scott, 1973, Lusk and Ford, 1978, Lusk et al., 1993, Martín and Gil, 2005). However, Cook et al. (1994) have pointed out some of the limits in this methodology.

Concentrations of > 2 wt.% Mn can occur in sphalerite through simple substitution of $Mn^{2+} \leftrightarrow Zn^{2+}$. For instance, Graeser (1969) noted the correlation of the surrounding environment and the enriched Mn content in sphalerite. Further, Di Benedetto et al. (2005) illustrate the influence of Cd on the distribution of Fe and Mn in sphalerites and its inverse correlation to both Fe and Mn caused by the competitive mineral-fluid interface. At high

temperatures, Cd is often enriched in sphalerites (Chen et al., 1988) and in many deposits could serve as a source of Cd, with concentrations ranging from 0.1–0.5 wt.%. Notably, sphalerites at the Red Dog deposit in Alaska contain up to 0.6 wt.% Cd (Kelley et al., 2004). The ratio of Zn/Cd could be used to determine and distinguish different genetic deposit types (Qian, 1987) or to track ore fluid interactions in a deposit (Gottesmann and Kampe, 2007, Gottesmann et al., 2009). Sphalerite is a well-known host for Hg in a wide range of ore deposits. At Eskay Creek in Canada, Hg has been measured to be between 0.08–16.35 wt.% in sphalerite (Grammatikopoulos et al., 2006). These exceptionally high Hg concentrations are most likely associated with micro-inclusions of Hg-bearing minerals, notably in sphalerite that has low concentrations of Fe.

Although in theory high amounts of Co could easily substitute for Zn in sphalerite (Becker and Lutz, 1978), it is rarely documented in studies. Cobalt in sphalerite leads to a change in colour to greenish; in rare cases concentrations were analysed of up to 840 ppm (Hofmann and Henn, 1984). Nickel can occur in higher concentrations in sphalerite than Co with reported values of up to 2,000 ppm in an Australian VHMS deposit (Huston et al., 1995). However, these values were associated with micro inclusions of a Co mineral rather than incorporated as trace element.

Concentrations of up to 100 ppm and rarely up to 700 ppm of Ag are reported in sphalerite (Cabri et al., 1985, Huston et al., 1996, Kelley et al., 2004). It is still not clear if Ag is incorporated in the crystal lattice (Taylor and Radtke, 1969) or if these concentrations are largely derived from micro-inclusions. Two studies (Huston et al., 1995, Orberger et al., 2003) display Mo concentrations of 15 to 95 ppm within sphalerites; Huston et al. (1995) claim that Mo^{3+} replaces Zn^{2+} ; Orberger et al. (2003) report 5,000 ppm Mo in sphalerites hosted by black shales in the Selwyn Basin, Canada. And Krämer et al. (1987) illustrate that higher Ga concentrations are associated with low-temperature carbonate-hosted replacement deposits. They also claim that Ga occurs as micro-inclusions of Ga sulphides. In MVT deposits, Ga concentrations are about 50 ppm (Moskalyk, 2003); in a rare occurrence, low Fe-bearing sphalerite at Khusib Springs ranges from 2,000 to 3,120 ppm Ga (Melcher et al., 2006).

Indium is a common trace element in sphalerite and is reported by many studies (e.g., Burke and Kieft, 1980, Patrick et al., 1993, Schwarz-Schampera and Herzig, 2002, Ishihara and Endo, 2007). It can be incorporated into sphalerite through a coupled substitution of $Cu^+In^{3+} \leftrightarrow Zn^{2+}Fe^{2+}$. Seifert and Sandmann (2006) observed a negative correlation between In and Fe, confirming the coupled substitution mechanism. Sinclair et al. (2006) measured In of up to 6.9 wt.% in sphalerites from the Mount Pleasant deposit with a mean concentration of

1.23 wt.%. Copper can be incorporated into sphalerite as part of a coupled substitution with In (see above). Further, it may occur as so-called “chalcopyrite disease”, where micrometer-scale inclusions (blebs) of chalcopyrite appear in sphalerite (e.g., Barton and Bethke, 1987); it is still not clear whether this process is due to exsolution, replacement or co-precipitation processes.

Thallium is a typical by-product of the smelting and refining of Zn (sphalerite). Murao et al. (1996) and Kelley et al. (2004) among others reported Tl contents in sphalerite below 37 ppm, incorporated as a $Tl_{0.5}^{+}As_{0.5}^{3+}S$ solid solution in sphalerites (Xiong, 2007). Arsenic was reported in low-temperature pink sphalerite from the Alacran deposit in Chile with 1.7 wt.% As (Clark, 1970). Also, little data is reported on Sb in sphalerite, which was determined by Beaudoin (2000) with 0.55 wt.%, whereas Kelley et al. (2004) report 0.4–2,400 ppm of Sb in sphalerite from the Red Dog district, Canada. Germanium, Au, Sn, Se, Te may occur within sphalerites but are not of relevance for this research study due to the low reported contents in sphalerite.

1.2.2 Pyrite

Pyrite FeS_2 has a simple cubic structure, equivalent to $NaCl$, in which Fe has the face-centered position. Each Fe atom is surrounded by six S atoms in an octahedral coordination. It is assumed that due to the electronegativity and the short Fe–S bond distance, covalent bonding exists. Notably, pyrite usually occurs in stoichiometric form with a 1:2 Fe to S ratio. Doyle and Mirza (1996) confirmed this assumption with a variation of ± 1 % based on the S/Fe ratio of 2. Nevertheless, natural pyrite incorporates minor and trace elements regularly. Stoichiometric replacement into the lattice of pyrite commonly takes place with Co^{2+} and (or) Ni^{2+} for Fe^{2+} and further Se and (or) Te for S. Nonstoichiometric replacements result in a change of electrical properties in the mineral, including As for S in form of AsS^{3-} or As_2^{4-} . Early studies by Fleischer (1955) and Vaughan and Craig (1978) report As, Pb, V, Sb, Ti, Sn, Tl, Se, Ag, Au, Ga, Bi, Ge, Mo, Cd, In and Hg in decreasing concentrations within pyrites. However, these studies did not validate if these high concentrations of trace elements are derived from incorporation into the pyrite lattice or if they are derived from micro inclusions within the pyrite grains.

A correlation between As and Au is well documented in pyrite from diverse settings (e.g., Wells and Mullens, 1973, Cook and Chrysosoulis, 1990, Arehart et al., 1993, Fleet et al., 1993). The presence of As as an incorporated element in pyrite is confirmed by experiments conducted by Clark (1970), who determined 0.1 wt.% of As in pyrite in equilibrium with arsenopyrite at 600 °C. In natural pyrite, the concentration of As varies between 6 and 96,000 ppm (Cook and Chrysosoulis, 1990). In assemblages with pyrite in different habits, it is

reported that the highest accumulation of As is within colloform or fine-grained pyrite grains (Cook and Chrysosoulis, 1990, Huston et al., 1995). Note, in arsenopyrites, which adopts the orthorhombic crystal structure of marcasite, the concentration of As is about 43 wt.% (Klein and Hurlbut Jr., 1993). Oscillatory zoning of both Au and As in a single pyrite grain was observed by Arehart et al. (1993), and Fleet et al. (1993). Both associate this zoning with rapid fluid composition changes during the growth of the pyrite grain. The pyrite structure is retained when As-bearing Co and Ni phases, as cobaltite $CoAsS$ and gersdorffite $NiAsS$, are in solid solution with pyrite (Tossell et al., 1981). However, Co and Ni are also typical elements occurring as minor and trace elements within pyrites, respectively. In theory, a solid solution between pyrite and the Co and Ni-bearing mineral phases could be the reason for the incorporation for As and Sb. However, a correlation between Co and Ni with As is not reported in these studies (Griffin et al., 1991, Huston et al., 1995). Following the same principles, Sb-bearing Co ($CoSbS$) and Ni ($NiSbS$) minerals could be incorporated within pyrite (Tossell et al., 1981). It is assumed that As substitutes for S in the pyrite by forming AsS^{3-} dianion. The same processes may incorporate Sb as well as SbS^{3-} dianion (Huston et al., 1995). Furthermore, the AsS^{3-} dianion could be compensated by Au^{3+} replaced for Fe^{2+} within the mineral lattice explaining the positive correlation between these two elements. This coupled substitution may affect other elements as well, such as Tl^{3+} and Mo^{3+} , which enter the pyrite lattice similar to Au^{3+} (Huston et al., 1995). Molybdenum ranges between 2.2–790 ppm and Tl between 1.3 and 7,830 ppm within pyrites. Huston et al. (1995) also document that higher Tl concentration are associated with rapid precipitation of As-rich pyrites.

Cobalt and Ni ions Co^{2+} and Ni^{2+} easily replace Fe^{2+} , due to its similar ionic radii; moreover, CoS_2 and NiS_2 would adopt the analogous structure of pyrite (Vaughan and Craig, 1978, Tossell et al., 1981). In contrast to CoS_2 , NiS_2 does not form a complete solid solution with FeS_2 (Vaughan and Craig, 1978), resulting in a bond difference between Ni–S and Fe–S and might be metastable. Cobalt concentrations vary from 26 ppm to 2.2 wt.% and Ni between 106 ppm and 0.2 wt.%. The ratio of Co/Ni in pyrites has been applied to understand the origin of the pyrite (Brill, 1989). Commonly, Co is more abundant in high-temperature environments, but Ni tends to dominate sedimentary systems (Huston et al., 1995).

The elements Pb, Zn and Cd form one group in pyrites. They range from 27 to 9,000 ppm (Pb), 9 to 9,000 ppm (Zn) and 14 to 52 ppm (Cd) (Huston et al., 1995). According to Huston et al. (1995), the concentrations, in particular, the higher values, are associated with micro-inclusions of Zn- and Pb-bearing minerals such as sphalerite and galena. Notably, the highest concentrations were within colloform pyrites, leading to the assumption that the

inclusions were formed during rapid precipitation of pyrite. This theory was confirmed by Griffin et al. (1991) and supported by the studies from Oberthuer et al. (1997), who investigated mineral assemblages free of Pb and Zn minerals with a low concentration of 96 ppm for Pb and 9 ppm for Zn in pyrite. Also, the pyrites with micro-inclusions of Pb and Zn minerals have higher As levels.

After Huston et al. (1995), Ag is also present in the form of mineral inclusions within pyrite, these minerals could be tetrahedrite or galena; whereas Cabri et al. (1985) determined Ag in pyrites of 0.04 to 0.12 wt.%. Generally, concentrations for Ag vary between 8 and 656 ppm. It can be assumed that a coupled substitution similar to the Au^{3+} replacement of Ag^{3+} can take place. Few data reveal concentrations of mercury within pyrites (Wells and Mullens, 1973, Griffin et al., 1991), but Griffin et al. (1991) determined Hg of 22–3,000 ppm within pyrite grains. Remarkably, the highest Hg concentrations, analysed by Wells and Mullens (1973), were measured in gold bearing pyrites in a mineral assemblage with cinnabar (HgS).

1.2.3 Case study - sulphide geochemistry for mineral exploration

Trace elements in pyrites are used to understand the genesis of ore deposits. For instance, Large et al. (2009) report that with trace element zonation in pyrites of sediment-hosted gold-arsenic deposits, different timings of ore formation can be identified. At a syn-sedimentary stage, Au, As, Ni, Pb, Zn, Ag, Mo, Te, V and Se were enriched in the diagenetic pyrites; whereas, the later hydrothermal pyrites are typically depleted in Ni, V, Zn, Pb and Ag and enriched in Co, Ni and As in cyclic zonation. Further, they use the trace elemental pattern of the outermost zonation to distinguish between moderate to low-grade (Co-Ni rich and As-Au poor) such as the Sukhoi Log and Spanish Mountains deposits and moderate to high-grade (As-Au rich) deposits, like in the Carlin and Bendigo deposits.

2 Elemental behaviour and mobility within soils

In order to understand how anomalous concentrations can be formed above mineralisation within soil and till, an overview of the relevant elements used within this thesis is provided in the following section. A focus is on the elemental behaviour and mobility, more specifically their predicted behaviour in different environmental conditions. Unless stated differently the behaviour is described for a moderate climate zone.

In the Irish Midlands, an annual average rainfall of 925 mm (MetÉireann, 2016) occurs, that highly influenced the formation of the soil type in this area. The predominant soil types are grey brown podzol, gley soil and peat soil in the Irish Midlands (Gardiner and Radford, 1980, Fay et al., 2007). In general, podzols form when leaching from the surface takes place. A translocation of nutrients and fine particles initiates towards the subsurface. As a result Ca and Mg are leached from the surface, thus an acidification of the soil results in a mobilisation of Fe. Also Al is deficient at the surface due to its accumulation in the fine particles that are translocated in the subsurface (Schachtschabel et al., 1976, Fay et al., 2007). A grey brown podzol is formed from calcareous parent material. An alkaline front derived from the parent material accentuates the leaching effect from the surface. This results in a leaching of only fine particles, mainly clay, thus a translocation of predominately Al takes place (Fay et al., 2007). Gley soils form when drainage is poor, due to a high clay content or when the bedrock is impermeable. A prerequisite is a permanent or intermittent water supply (Schachtschabel et al., 1976, Fay et al., 2007). It is referred to as surface-water gley when the water supply is precipitation and cannot further drain through the soil (Fay et al., 2007, Teagasc, 2014). Peat soil consists of high organic matter and may, depending on the organic matter content, be referred to as organic soil. It is further characterised by poorly drained conditions due to high rainfall (Schachtschabel et al., 1976, Fay et al., 2007, Teagasc, 2014).

2.1 Silver in soils

Silver usually occurs in small concentrations within soils, but, since it is associated with sulphide minerals it can be elevated in soils near mines (Guseva, 1996, Davies and Ginnever, 2009). Below pH 4, Ag is mobile and occurs as cations and complex anions Ag^+ , Ag^{2+} , AgO^+ , $AgCl_2^-$, $Ag(SO_4)_2^{3-}$ (Cappel, 1997, Kabata-Pendias and Sadurski, 2008). In addition to its high affinity for Fe and Pb sulphides, Mn oxides can also adsorb Ag easily (Bodek et al., 1988). Additionally, organic matter, namely humic material governs the behaviour of Ag in soil (Sikora and Stevenson, 1988, Jones et al., 1990). After Jones and Peterson (1986), the absence

of organic matter leads to toxic levels for plants and high amounts of Ag_2S that reduces the growth of meso- and microbiota (Kabata-Pendias, 2011).

2.2 Arsenic in soils

Ferric hydroxides influence the As concentration in soil and soil solution. (Kabata-Pendias and Sadurski, 2008). A good review on As and its behaviour in the environment is provided by Bhattacharya (2007). Arsenic minerals and compounds are highly soluble, in particular, arsenopyrite which can be easily oxidised by O_2 and Fe^{3+} . However, As is mainly controlled by adsorption onto clay minerals, hydroxides and soil organic matter. Most As is fixed by the clay granulometric fraction < 0.001 mm. Furthermore, in many soils, As exhibits a positive correlation with Fe_2O_3 (Manaka, 2006), confirmed by Deschamps et al. (2003) showing that Fe and Mn minerals absorb As. The complex anions AsO_2^- , AsO_4^{3-} , $HAsO_4^{2-}$, $H_2AsO_4^-$ are the most mobile forms, however, they are sorbed at pH between 7 and 9. After Crecelius et al. (1986), As^{5+} is most stable species under near surface environmental conditions; whereas, only under low pH and low Eh conditions is As^{3+} stable. Organic matter adsorbs As under reduced and reoxidised soil conditions, though, clay adsorption is a stronger mechanism (Ghosh and Bhattacharyya, 2004). Arsenates and arsenides are mainly sorbed at the reactive sites of the mineral in the form of metal oxides and aluminosilicates (Violante et al., 2008).

To conclude, As ions are readily fixed by Fe and Al hydroxides, clay fractions, P and Ca compounds and soil organic matter. The hydroxy-Al compounds on the external surfaces of micaceous minerals are significant contributors to the fixation of As (Huang, 1975). According to Norrish (1975) and Woolson et al. (1973), As behaves much like phosphates, and in acid soils, Fe or Al arsenates are the most common forms. Overall, complexation of As with P, Fe, Al and Mn strongly influences the mobility of As (Lund and Fobian, 1991).

In gley soils, As is accumulated in surficial horizons and leached from the subsurface with a high reduction potential; an opposite behaviour is observed in well-drained soils. Several bacteria can accelerate the oxidation of arsenates. Studies by Boyle and Jonasson (1973), Jernelöv (1975), and Weinberg (1977) report that microbiota influence the migration, precipitation and volatilisation of As.

2.3 Barium in soils

Generally, Ba is not highly mobile during weathering; when released it easily precipitates as sulphates, carbonates or becomes adsorbed by clays. However, the sorption by oxides and hydroxides is also very strong. Its mobility is highly dependent on the pH of the

soil; the more acidic the soil, the more mobile is Ba. Moreover, due to the similar character of alkaline earth elements, it can easily be substituted by those. Whereas if Ba is adsorbed onto Al_2O_3 it can be released due to a substitution of Ba by Be or Sr (Bodek et al., 1988). In arid soils, Ba migrates upwards and becomes enriched in the surface layer, where Ba occurs in the form of the easily soluble mineral hollandite. The contrary is observed in humid climate soils, where Ba is immobilised by Fe and Mn hydrous oxides. Also, mica has a great affinity of sorbing Ba in temperate humid climates (Lee et al., 2007). The element Ba is also present in aerosol form as a pollutant and phosphate fertiliser, so an increase of Ba in the top soil can occur due to anthropogenic processes (Kabata-Pendias, 2011).

2.4 Cadmium in soils

Cadmium is easily mobilised and goes into soil solution during weathering as a complex ion and organic chelates such as $CdCl^{3-}$, $Cd(OH)^{3-}$, $CdCl^+$, $CdOH^+$, $CdHCO_3^+$ (Kabata-Pendias and Sadurski, 2008); moreover, Welch and Norvell (1999) illustrate that organic acids with humic and fluvic acids result in the mobility of Cd. According to Taylor and Percival (2001), 55 to 90 % of Cd is within soil solution and readily available for plants. Also, the soil texture governs the Cd concentration, as Cd is accumulated up to 10 % in the soil clay fraction (Farrah and Pickering, 1977, Tiller et al., 1979, Soon, 1981). Another key factor for the Cd distribution is the occurrence of Fe and Mn oxides, which can absorb Cd under acidic conditions. Under alkaline conditions, Cd is only soluble in the form of $CdCO_3$ and $Cd_3(PO_4)_2$ and it preferentially sorbs onto soil organic matter. Under oxidising conditions, Cd forms oxides and is mainly immobilised in phosphates (Matusik et al., 2008). Under reducing conditions, Cd readily precipitates with sulphides (Christensen and Haung, 1999), whereas Martin-Garin et al. (2002) claim that Cd is mobile in the presence of calcite and can be sorbed to carbonate minerals. Generally, Cd's mobility greatly depends on pH in all soils, moreover, in acidic soils, soil organic matter as well as sesquioxides govern the soil solubility and in alkaline soils Cd precipitates easily in Cd compounds (Gadde and Laitinen, 1974, Forbes et al., 1976, Lamy et al., 1993). In addition, soil microbes are able to accumulate Cd (Ledin et al., 1999), a natural advantage used for soil remediation (Burd et al., 2000).

2.5 Cobalt in soils

The variation of Co in a soil profile depends on soil formation and therefore on the climatic conditions. In reducing and acidic soils, Co is mobilised from the precipitates or the adsorbed form. While during oxidising conditions, reactions with Mn oxides lead to the formation of hydroxyl species $Co(OH)_2$, which can precipitate on oxide surfaces (Fleming,

1983). The high capacity of Fe and Mn hydrous oxides to sorb Co in most kinds of soils, increases with increasing pH. Therefore, the Co concentration mainly correlates with an accumulation of Fe as well as Mn. In addition to oxide minerals, clay minerals also have a great affinity to sorb Co, but they also release Co easily.

Besides soil texture, organic matter governs the character of Co as well. As mentioned above, the mobility depends greatly on the pH and organic compounds. In general, organic rich soil layers have a relatively low concentration of Co; some organic species such as organic chelates support the sorption of Co on Fe-coated silica compounds, but if these Fe species are absent, Co is easily mobilised (Brooks and Herman, 1998). Soil solution is often depleted in Co, due to its low mobility; species found in soil solution are Co^{2+} , Co^{3+} , $CoOH^+$, $Co(OH)^{3-}$ and $Co(OH)_2$ (Kabata-Pendias and Sadurski, 2008). Contamination of Co in soils can occur near metal processing industries (Smith and Carson, 1981), near sludge farm soil or at the roadside.

2.6 Chromium in soils

Chromium in soils is rather complex and has been investigated by several studies (Groth III, 1975, Bartlett and Kimble, 1976, Cary et al., 1977, Bartlett and James, 1979, Bloomfield and Pruden, 1980, Bartlett, 1999, James, 2001).

In soils, the mobility of chromium depends highly on the oxidation state and pH conditions. Although more than 80 % of chromium is fixed within soils, Cr^{3+} is slightly mobile in acidic environments, whereas Cr^{6+} is easily mobilised under both acidic and alkaline conditions. Moreover, the silty and loamy soil fraction is generally richer in chromium than are sandy soils. Peat soils have an especially high sorption of Cr, in which it forms insoluble metal-organic complexes (e.g., Kyziol, 2002, Priyantha et al., 2016).

In soils, chromium is found as anionic (e.g., CrO_4^{2-} , $Cr(OH)_4^-$), cationic (e.g., $CrOH^{2+}$), and organic complexes. Generally, Cr^{6+} is more mobile than Cr^{3+} . Therefore, organic matter controls the reduction of chromium and modifies the chromium behaviour with the soil profile. Moreover, according to Chung and Sa (2001), the oxidation of chromium seems to be directly related to the Mn content within the soil. In mineral soils, chromium has a high sorption affinity to clays and minor to Fe hydroxides and soil organic matter (Barnhart, 1997, James et al., 1997, Bartlett, 1999, James, 2001).

2.7 Copper in soils

Copper content in soils is highly dependent on soil texture; light sandy soils generally display lower contents with loamy soils exhibiting the highest Cu contents (Kabata-Pendias, 2011). Higher levels of Cu in soils are usually governed by parent material, soil formation processes and to a lesser extent clay fractions, Fe and Mn oxides and degree of base saturation.

The most common form of Cu in soils is the hydrous ion $Cu(H_2O)_6^{2+}$, which is easily adsorbed on clay minerals or co-precipitated on other minerals and soil organic matter compounds. Other predominant ionic and solid forms are hydroxides and carbonates that strongly depend on the pH including Cu^+ , Cu^{2+} , $Cu(Cl_2)^-$, $CuSO_4^0$, $Cu(OH)_2^0$, $CuCO_3^0$ and $CuCl^0$ (McBride, 1994, Alloway, 1995). In soil solution, Cu^{2+} , $CuOH^+$, $Cu_2(OH)_2^{2+}$ and $Cu(OH)^{3-}$, $Cu(OH)_4^{2-}$ and $Cu(CO_3)_2^{2-}$ are the most common ions, their mobility also highly depends on pH, soil compounds and species (Kabata-Pendias and Sadurski, 2008). According to Ponizovsky et al. (2006), only 1 % of Cu ions remain in soil solutions in dry soil systems, the majority is sorbed on soil components. Also, they claim that its mobility depends on soil organic matter, dissolved organic matter, pH and soil Cu content. At a pH below 7 hydrolysis products, $CuOH^+$ and $Cu_2(OH)_2^{2+}$ are most common, while above pH 8 hydroxyl complexes become dominant; the solubility of $CuCO_3$ is independent of pH (Kabata-Pendias, 2011). The most common forms (80 %) of Cu in soil solution are soluble organic chelates (Hodgson et al., 1965). According to McBride and Blasiak (1979) organic complexing of Cu is stable over a wider range of pH and therefore has an impact on the bioavailability and migration of Cu in soils.

The mobility of Cu is reduced significantly when large mineral colloids with Fe-Al oxyhydroxide coatings are present consisting of oxyhydroxide particles of Al, Mn, Fe and organic matter (Kabata-Pendias and Sadurski, 2008). Dissolved organic matter inhibits Cu sorption to other soil components, by forming immobile Cu-organic complexes (Zhou and Wong, 2003). In mineral soils, Ca in calcite can be substituted by Cu in calcareous soils, but, in other soils $Cu(OH)_2$ and/or $Cu_2(OH)_2CO_3$ can precipitate (Ma et al., 2006). Wei et al. (2009) illustrate the low mobility of Cu in mineral soils. They studied a Cu-fertilised area and observed a Cu accumulation within the surface soil (0–15 cm), where Cu was fixed in the mineral soil fractions. It has been claimed by numerous studies that the greatest amount of adsorbed Cu is associated with Fe and Mn oxides (see Kabata-Pendias, 2011); however, soil organic matter is also known to bond Cu^{2+} in particular to humic acids and fluvic acids (Stevenson and Fitch, 1981).

2.8 Iron in soils

Iron in soils controls the soil colour, which is a function of the Fe content, form and type of Fe compounds present. After Stucki et al. (1988), the investigation of Fe within a soil profile can provide information about the soil type and properties. For instance, lepidocrocite, which occurs in humid temperate climates and poorly drained soils, mainly forms under acidic pH, low temperatures and the absence (non-appearance) of Fe^{3+} . The behaviour of Fe is mainly controlled by its change in oxidation state and is linked to the O, S and C cycle. Also, Fe is fixed under alkaline and oxidising conditions, whereas it is mobile under acid and reducing conditions. Apart from the precipitation of oxides after its release, Fe also substitutes for Mg and Al in other minerals and replaces metals in complexes with organic ligands. Again, the most common forms in soils are oxides and hydroxides in small grain sizes or in amorphous forms as an adsorbed ion. By contrast, in layers rich in soil organic matter, Fe occurs in the form of chelates. Further, microorganisms have an impact on the formation of Fe oxides and their form (Megonigal et al., 2003).

Significantly, Fe influences the soil properties, and the mobility of other elements; Kabata-Pendias (2011) provides a brief overview of which metals can bond to Fe, e.g., crystalline Fe-oxide bond usually about 5–29 % Cu, 3–53 % Pb, 15–34 % Zn and 5–46 % As of the available element. The hydrolysis and formation of complexed species has one of the highest impacts on the solubility of Fe and therefore the mobility of Fe within the soil profile. More details about Fe in soils and its characterisation have been investigated by e.g., Krauskopf (1951), Norrish (1975), Schwertmann and Taylor (1977), Lindsay (1979) and Bloomfield and Pruden (1980).

2.9 Magnesium in soils

During weathering, free Mg and Mg-compounds are very soluble and therefore readily mobile under all environmental conditions. In soil solution, Mg mainly occurs as a Mg^{2+} cation. For soils in humid climate, Mg^{2+} becomes more mobile in solution with increasing clay contents (Schachtschabel et al., 1976).

2.10 Nickel in soils

Depending on the soil type, the Ni distribution is strongly related to organic matter content or the amorphous oxides of Fe and Mn within the soil profile. Further, Senwo and Tazisong (2004) observed a relationship of Ni to the clay content.

During weathering, Ni is easily mobilised and stable in the aqueous phase, so it can be transported more easily within the soil profile. Norrish (1975) illustrates that only 15–30 % of Ni is associated with Fe and Mn oxides in soils, making it easily available for plants. The sorption to Fe and Mn oxides depends on the pH; Ni concentrations in soil decrease with increasing pH (Bodek et al., 1988, Ponizovsky et al., 2006, Siebielec and Chaney, 2006). Moreover, Dähn et al. (2004) provide evidence for the high affinity of Ni for montmorillonite clay minerals.

In top soils, Ni is mainly bound to organic compounds, which are easily soluble chelates. Notwithstanding, the bonding of Ni to organic ligands is very strong. Nickel can be remobilised from solid phases in the presence of fluvic and humic acids, meaning Ni still is mobile in soils which can form strong complexes (Tejada et al., 2008). Also, Rajaie et al. (2008) observed that Ni as sulphate transforms in calcareous soil into oxides and minor to the other fraction within soil.

2.11 Lead in soils

The accumulation of Pb in soil strongly depends on the granulometric fraction; in loamy soils Pb can be accumulated up to 50 % more than in sandy soils. As soon as Pb is released from sulphides during weathering, it oxidises and either forms carbonates or becomes immobilised by clay minerals, hydroxides and (or) soil organic matter. According to Li and Shuman (1996), the fixation by soil organic matter is stronger than hydrous oxides. Further Basta et al. (2005) confirmed this strong fixation, as a result of its inner-sphere complexing with organic matter and the strength of fixation increasing towards alkaline conditions and moreover the degree of adsorption as well. Therefore, surface soils may display an accumulation of Pb (Sipos et al., 2005). Nevertheless, the sorption effects of clay minerals are stronger than organic matter in the fixation of Pb. Still, investigation of natural soils reveals that Pb can also be accumulated in deeper horizons, such as in podzolic soils in Norway (Steinnes and Friedland, 2005). Due to its similarity to the alkaline-earth elements Ba, Sr and Ca, it can substitute or be sorbed in association with these elements. In soil solution, Pb is present as Pb^{2+} , $PbCl^+$, $PbOH^+$, $PbCl^{3-}$ and $Pb(CO_3)_2^{2-}$ (Kabata-Pendias and Sadurski, 2008); in these anions and cations, it can easily be transported within the soil profile. Moreover, microbial activity can induce Pb in soil solution instead of bonding to Fe-minerals (Perelomov and Kandeler, 2006). According to Vega et al. (2007), Pb is one of the least mobile elements in soils; however, its sorption is lower compared to Zn and Cu and therefore it may migrate more easily. Lead soil pollution is not rare since the start of the industrial age and thus the surface

soils can be affected the most (e.g., Gough et al., 1988, Wixson and Davies, 1993, Davies, 1997).

2.12 Antimony in soils

During weathering, Sb often is present in soluble form; however, investigations on antimony in soils are generally poor and inconclusive. The sorption of antimony on clay minerals and hydrous oxides is high. Also, Ashley et al. (2003) illustrate that Sb is more mobile in the absence of Fe-free or low-Fe systems. According to Jones et al. (1990), and based on an isotopic study, Sb can migrate downwards through the soil profile. Other studies display the mobility of Sb even after its fixation to Fe, Mn and Al compounds (Brannon and Patrick, 1985); further, Sb correlates with amorphous species within the soil (Manaka, 2006). Hou et al. (2006) determined that up to 34 % Sb is associated with the residual fraction and 6 % with carbonaceous species in soil. Because Sb also occurs as a sulphide species, it is available for uptake in plants; Hammel et al. (2000), and Jones et al. (1990) claim that this could affect the behaviour of Sb in soils.

2.13 Thallium in soils

Elevated Tl concentrations in soils correlates with the clay and soil organic matter content. Moreover, due to its similar behaviour to K, it is associated with micaceous minerals (Frantz and Carlson, 1987). During weathering, Tl follows the alkaline elemental pathways and is readily mobilised; however, it is also easily immobilised by the surrounding clays, and Mn and Fe hydroxides, or it may be oxidised and fixed by sulphides (Sager, 1998). In general, the mobility of Tl in soils is limited because of the strong fixation; nevertheless, acidic rain can mobilise Tl. Soil pollution with Tl could be caused by coal combustion, metal smelting, refining processes and the cement industry (e.g., Scholl, 1980, Schoer, 1984, Sager, 1998).

2.14 Vanadium in soils

Vanadium does not vary significantly within the soil profile, and the concentration is highly dependent on the parent rock. Therefore, the highest concentration is expected where the soil is derived from mafic rocks; lowest concentrations are within peat soils (Kabata-Pendias, 2011). Moreover, its accumulation depends on the soil texture. In general, V has an affinity for Fe hydrous oxides and soil organic matter and becomes mobile in association with clay minerals (Kabata-Pendias, 2011). The behaviour of V varies in different environments; in acidic soils the vanadyl cation VO^{2+} is most abundant and forms complexes with organic acids, whereas under alkaline conditions VO_3^- , VO_4^{2-} and $H_2VO_4^-$ anionic metal complexes form (Kabata-Pendias and Sadurski, 2008), which then become easily adsorbed on clay minerals in

combination with Fe cations. Therefore, the presence of Fe might explain the accumulation of V in mainly Fe- and Mn-rich nodules. Nevertheless, according to Berrow et al. (1978), fixation of V is stronger on organic acids binds than sorption with Fe oxides. Aerosol input of V can cause soil pollution (Belsare, 1986, Tyler, 1976, Morrell et al., 1986); typical release of V occurs through industrial processing of ore minerals and coal burning.

2.15 Zinc in soils

The Zn content in soil is governed by parent material, soil formation processes and organic matter. Vega et al. (2007) have shown that the clay fraction, and high amounts of vermiculite and gibbsite influence the Zn concentrations within soils. A strong sorption capacity of soil organic matter leads to an enrichment of Zn in the surface soil. Generally, agricultural land use increases the Zn concentration in surface soils, but Huang and Jin (2008) show that there are small variations regarding the different type of use. The atmospheric input of Zn exceeds the output, because of leaching processes and the production of biomass within the soil; for instance, in Sweden, unpolluted forest areas can have a higher output than atmospheric input of Zn (Tyler, 1981).

As stated above, in general, Zn is very mobile in soils, mostly as free Zn and complex ions in soil solution. In soil solution, Zn commonly occurs as Zn^{2+} , $ZnCl^+$, $ZnOH^+$, $ZnHCO^{3+}$, ZnO_2^{2-} , $Zn(OH)_3^-$, $ZnCl_3^-$ as well as Zn organic species (Kabata-Pendias and Sadurski, 2008). Additionally, some species which adsorb Zn cations, can also be very mobile. Factors controlling Zn mobility are comparable to those of Cu, except that Zn is generally more readily soluble and does not undergo redox reactions. A detailed review about Zn adsorption and retention is given in Lindsay (1972), and the fixation is well described in Smolders and Degryse (2006). The process of Zn fixation is relatively slow and depends highly on soil pH and speciation. Moreover, experiments show a release of Zn from TiO_2 at increasing temperature from 5 °C to 40 °C (Li et al., 2008). According to Peganova and Eder (2008), Zn is strongly accumulated in most soils within the clay fraction and soil organic matter under neutral to mildly alkaline pH conditions. In the neutral pH range (7–7.5), dissolved soil organic matter is the main factor governing the mobility of Zn (Wong et al., 2007).

Kumpiene et al. (2008) report a fixation of Zn controlled by phosphorous and clays, supported by Kabata-Pendias and Krakowiak (1995), who modelled that the clay fraction hold up to 60 % of Zn in soil. Two different mechanisms arise depending on the pH: in an acidic regime, cation exchange takes place and in an alkaline regime, chemisorption and organic ligands have to be taken into account. To a lesser extent, Al, Fe and Mn oxides and hydroxides

can hold Zn in some soils as well. However, microorganisms reduce the sorption capacity, because they store Zn in their living cells (Perelomov and Kandeler, 2006). After Kabata-Pendias (2011), Zn is mainly associated with clay minerals (24–63 %), Fe and Al oxides (14–38 %), readily mobile fractions (1–20 %) and organic complexes (1.3–2.3 %) on average considering all soil types.

The nucleation of Zn hydroxide on clay surfaces might be the reason for the pH-dependent immobilisation of Zn (McBride and Blasiak, 1979). Through competition, cations at lower pH regimes could decrease the affinity of Zn^{2+} to be adsorbed and therefore be mobile and leached. At alkaline pH regimes, more organic soil compounds exist within the soil, but soluble Zn organic complexes may account for the mobility of Zn. In sandy soil with acidic pH conditions, Zn is immobilised in the soil organic matter.

In general, Zn is readily mobile and available in acid mineral soils, whereas the retention of Zn commonly takes place in Ca and P-rich, well-aerated soils with S compounds and soils with Ca-saturated minerals and hydrous oxides (Kabata-Pendias, 2011).

2.16 Case studies - Soil geochemistry in mineral exploration

Cameron et al. (2004) investigated soil geochemistry and elemental transport in three different study areas, a) above porphyry deposits in an arid climate in Chile, b) above Au-Cu deposits in a semi-arid climate, in the Carlin district in Nevada, and c) above volcanogenic massive sulphide bodies that are covered by glacial sediments in a cool humid climate in the Abitibi greenstone belt in Ontario. In all cases, enrichments of elements were detected in soils above the mineralised areas.

In the Ontario study area, the soil is separated by 30 m of varved clay with silty laminae overlying the Zn-Cu-Ag VMS deposit. Anomalous concentrations of Zn and Cd, as well as Cu, Ag, Pb, Au, Mn, Hg, Co, Bi, and Se occur within the soil. Here, elemental transport upwards is proposed by van Geffen et al. (2012), as a result of groundwater advection induced under remnant hydrostatic pressure from the retreating ice sheet.

This example highlights that deeply buried mineralisation can be detected successfully with surficial geochemistry. It also provides alternative transport models besides the reduced chimney model (Hamilton, 1998, 2000) for the translocation of the elements towards the surface environment.

3 Zinc and Copper isotopes

After Maréchal et al. (1999, 2000) had published the first articles on Zn and Cu isotopes, it was followed by a chapter from Albarède (2004) providing a first review. Further improvements were summarised in Cloquet et al. (2008), more in Wiederhold (2015) and finally, the most recent review is given by Moynier et al. (2017) for both Zn and Cu isotopes and another review for Cu isotopes in Wang et al. (2017). Ranges of isotope ratios for Zn and Cu and typical values for different environments are given in Figure 1.

3.1 Methodology used for Zn and Cu isotopes

Zinc and Cu isotopes were difficult to measure until recently due to their low thermal ionisation signals; the first investigations of Cu were made by Walker et al. (1958), Shields et al. (1964, 1965), and Rosman (1972) and for Zn by Gawinowski et al. (1989), Loss and Lugmair (1989, 1990), and Völkening and Papanastassiou (1990) using Thermal-Ionisation Mass-Spectrometry (TIMS). However, these analyses had low analytical precision and high uncertainty of 2 %/amu for Cu (Shields et al., 1964, 1965). For Zn, it was possible to correct for instrumental bias by using double spike methods, but the precision was still poor compared to other isotopic systems of 0.1–0.2 %/amu (Ghidan and Loss, 2011). With advances in inductively-coupled plasma - mass spectrometry (ICP-MS) technology and the further introduction of the multi-collector (MC) ICP-MS, for the first time it was possible to successfully report on these isotope systems, using standard sample bracketing (e.g., Maréchal et al., 1999, Mason et al., 2004a, b, Weiss et al., 2005, Bermin et al., 2006, Viers et al., 2007, Balistrieri et al., 2008, Peel et al., 2008, Vance et al., 2008, Savage et al., 2015a, Sossi et al., 2015) or a double spike method for Zn (e.g., Bermin et al., 2006, Arnold et al., 2010b, Conway and John, 2015).

Maréchal et al. (1999) showed for the first time a combination of standard bracketing and elemental doping of Cu for Zn and Zn for Cu, with which they reach an accuracy of 0.1 %/amu using a VG Elemental Plasma 54 MC ICP-MS. The follow-up work by Zhu et al. (2000, 2002) and Archer and Vance (2002, 2004) confirmed and extended the method. Additionally, Larner et al. (2011) illustrate that Ni doping for Cu isotopes is a good alternative for using Zn as doping. For difficult matrixes such as seawater or organic materials, the double spike method for Zn has been successful more recently. It also eliminates isotopic fractionation effects during the chemical separation (Bermin et al., 2006, Arnold et al., 2010b, Zhao et al., 2014, Conway and John, 2015, Vance et al., 2016a).

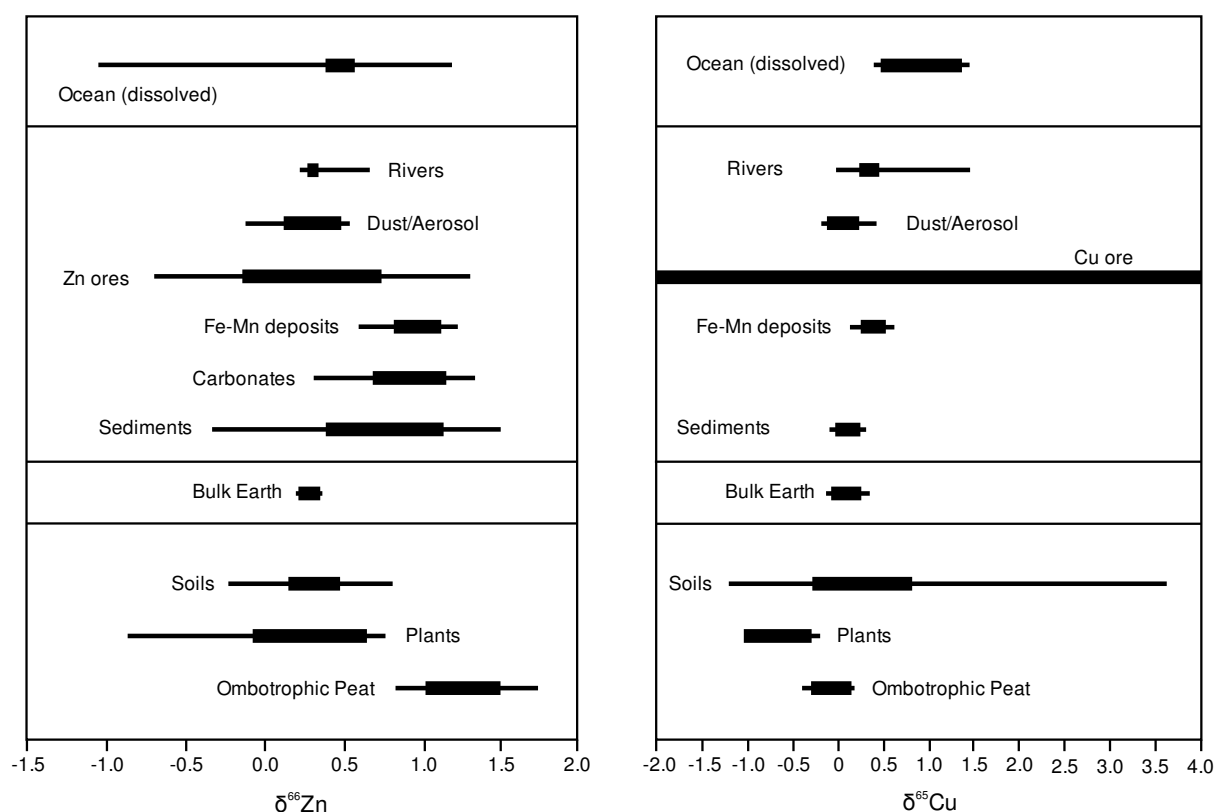


Fig. 1 Zinc and Cu isotope variations for different terrestrial environments, modified after Moynier et al. (2017).

The thick lines indicate the range of the majority of samples, the thin lines illustrate the outlier samples, including 2 S.D. Note, Cu ore samples have a much wider range than displayed $\delta^{65}\text{Cu}$ from -16.5 to +9.98 ‰. *Bulk Earth*: Othman et al. (2006), Li et al. (2009), Lee et al. (2012), Chen et al. (2013), Ikehata and Hirata (2013), Savage et al. (2015b). *Ocean*: Bermin et al. (2006), Vance et al. (2008), Boyle et al. (2012), Conway and John (2014,2015), Takano et al. (2014), Thompson and Ellwood (2014), Zhao et al. (2014). *River*: Vance et al. (2008), Ilina et al. (2013), Little et al. (2014b), Guinoiseau et al. (2017). *Dust/aerosol*: Maréchal et al. (2000), Li et al. (2009), Bigalke et al. (2010b), Dong et al. (2013), Little et al. (2014b), Takano et al. (2014). *Ore minerals*: Maréchal et al. (1999), Larson et al. (2003), Albarède (2004), Mason et al. (2005), Mathur et al (2005, 2009, 2010), Wilkinson et al. (2005b), Markl et al. (2006), Asael et al. (2007), Sonke et al. (2008), Kelley et al. (2009), Gagnevin et al. (2012), Pasava et al. (2014), Duan et al. (2016) *Fe-Mn deposits*: Maréchal et al. (2000), Little et al. (2014a). *Carbonates*: Pichat et al. (2003). *Sediments*: Maréchal et al. (1999, 2000), Asael et al. (2007), Bentahila et al. (2008), Sonke et al. (2008), Chen et al. (2009), Bigalke et al. (2010b), Andersen et al. (2011), Gagnevin et al. (2012), Mathur et al. (2012), Hendry and Andersen (2013), Little et al. (2016), Vance et al. (2016a). *Soils and plants*: Viers et al. (2007), Bigalke et al. (2010b, 2011), Mathur et al. (2012), Liu et al. (2014), Vance et al. (2016b), Opfergelt et al. (2017). *Ombrotrophic peat*: Weiss et al. (2007).

During the chemical separation using ion-exchange chromatography Cu and Zn isotopes can easily fractionate (Maréchal and Albarède, 2002), therefore either a double-spike has to be added before column introduction, or a control using a quantitative yield is needed. The double-spike method is based on adding a trace solution with a known specific isotopic composition (Dodson, 1963, Rudge et al., 2009) to each sample before ion-exchange chromatography.

Absolute abundances of Zn isotopes can also be investigated by analysing synthetic isotope mixtures (Tanimizu et al., 2002, Ponzevera et al., 2006).

The chemical separation of Cu and Zn is done using ion-exchange chromatography in 6-10 M HCl with the resins AG-MP1 or AG1-X8 (Maréchal et al., 1999, Archer and Vance, 2004, Conway and John, 2015, Sossi et al., 2015). Savage et al. (2015a), and Vance et al. (2016b) among others have reported a repetition step for Cu purification and an additional step using HBr/HNO₃ on a micro column (0.1 µl) using the AG1-X8 resin for Zn purification (Luck et al., 2005, Moynier et al., 2006, Moynier and Le Borgne, 2015).

Potential isobaric interferences can occur with $(^{23}\text{Na}^{40}\text{Ar})^+$ and $(^{23}\text{Na}^{16}\text{O}^2\text{H})^+$ for ^{63}Cu and $(^{25}\text{Mg}^{40}\text{Ar})^+$ for ^{65}Cu (Zhu et al., 2000, Archer and Vance, 2004, Larner et al., 2011, Savage et al., 2015a). Zinc has two potential interferences, first ^{64}Zn can interfere with ^{64}Ni , therefore the intensity of ^{62}Ni is reported as well and can be corrected for afterwards; the second interference is ^{70}Zn with ^{70}Ge . However, ^{70}Zn has a low abundance and thus in most cases is either not measured or not reported.

After measurement using MC ICP-MS, a mass bias correction has to be performed. Maréchal et al. (1999) and Larner et al. (2011) discussed the method when using elemental doping. The correction is based on the exponential laws for both Cu and Zn isotopes.

$$\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}}\right)_{\text{Measured}} = \left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}}\right)_{\text{True}} \times \left(\frac{M_{66}}{M_{64}}\right)^{f_{\text{Zn}}} \quad (1)$$

$$\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{Measured}} = \left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{True}} \times \left(\frac{M_{65}}{M_{63}}\right)^{f_{\text{Cu}}} \quad (2)$$

With M_{63} , M_{64} , M_{65} , M_{66} are the atomic masses of ^{63}Cu , ^{64}Zn , ^{65}Cu and ^{66}Zn , respectively and f_{Zn} and f_{Cu} are mass-independent fractionation factors. When using the double-spike method, the mass discrimination is done after Bermin et al. (2006). Here, the three measured isotope ratios $^{66}\text{Zn}/^{64}\text{Zn}$, $^{67}\text{Zn}/^{64}\text{Zn}$ and $^{68}\text{Zn}/^{64}\text{Zn}$, the exponential mass discrimination law and the natural mass dependent fractionation relative to a standard are used to calculate the final isotopic ratio of the sample.

The results are given in the delta notation for both Cu and Zn:

$$\delta^{65}\text{Cu}_{\text{NIST 976}} = \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST 976}}} - 1 \right] \cdot 10^3 [\text{‰}] \quad (3)$$

and

$$\delta^{66}\text{Zn}_{JMC} = \left[\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{JMC}} - 1 \right] \cdot 10^3 [\text{‰}] \quad (4)$$

Zinc isotopic behaviour follows the mass-dependent law for terrestrial samples, meaning $\delta^{70}\text{Zn}/3 = \delta^{68}\text{Zn}/2 = \delta^{67}\text{Zn}/1.5 = \delta^{66}\text{Zn}$. For Cu isotopes in terrestrial samples, no such a behaviour can be concluded, due to the fact it has only two isotopes.

Results should be reported similar to the pioneering study of Maréchal et al. (1999) relative to the JMC Lyon standard (Zn) and NIST SRM 976 (Cu) for consistency and comparability. Note, Larson et al. (2003) named NIST SRM 976 = NBS 976, which is the same standard. For Zn different reference standards exists and their conversion to JMC Lyon standard is given in Table 1.

Tab. 1 Overview of other reference standards used for Zn isotopes and their $\delta^{66}\text{Zn}$ values relative to JMC Lyon.

Name	Positive shift to JMC Lyon	References
IMC 12053	0.09 ‰	Gagnevin et al. (2012)
IMP Zn	0.044 ± 0.035 ‰	Mason et al. (2004a) Wilkinson et al. (2005b)
SRM NIST 683	0.07 ‰	Cloquet et al. (2008) Pasava et al. (2014)
IRMM 3702	0.30 ‰	Cloquet et al. (2008) Moeller et al. (2012) Matthies et al. (2014) Sossi et al. (2015)

3.2 Fractionation processes

In this study Cu and Zn isotopes were investigated in a low-temperature environment; therefore this review focuses on processes taking place in this environment.

The main variation of Cu and Zn isotopes is within a range of and -1 to 1.7 ‰ (Zn) and -1.2 to 3.6 ‰ (Cu), except Cu isotopes in supergene ore mineralisation, which can vary between -16.5 to +9.98 ‰. Four main processes lead to the fraction of Cu and Zn isotopes: I) This applies only to Cu isotopes, the isotopic equilibrium between Cu in oxidation states, II) Isotopic equilibrium distribution between Zn and Cu ions in dissolution, III) A combination of equilibrium and kinetic fractionation due to interactions of solids, aqueous solutions, abiotic and living cells, including processes like sorption and precipitation, IV) The uptake of isotopes into cells of living microbes and plants, namely kinetic and equilibrium fractionation. However, it is often not possible to make a sharp distinction between these fractionation processes. Due to a lack of changes in oxidation state of Zn and its small range, a combination with Cu provides a good description of an environment.

In the same way as discussed in the section on *Cu and Zn mobility in soils*, organic complexing is a key process in soils for these elements, likewise, it is for isotopic fractionation process of Cu and Zn. The ion Cu^{2+} forms preferentially strong inner sphere complexes in organic matter (McBride, 1981, Grybos et al., 2007, Ryan et al., 2014). Copper, as well as Zn, are up to 98 % complexed by organic ligands, despite being “dissolved” in natural waters (McBride, 1981, Coale and Bruland, 1988, Bruland, 1989, Moffett and Brand, 1996, Wells et al., 1998, Shank et al., 2004, Grybos et al., 2007, John et al., 2007, Vance et al., 2008, Ryan et al., 2014). According to Grybos et al. (2007), the elements Cu and Zn either bind to organic complexes in condensed organic matter or in aqueous phases or they become adsorbed to surfaces of secondary minerals, for instance, Fe and Mn oxyhydroxides or clays. Follow-up investigations confirm that these processes contribute mainly to the isotopic distribution within soil and dissolved phases (Vance et al., 2008, Bigalke et al., 2010a, 2010c, 2011, Little et al., 2014a, Vance et al., 2016a).

3.2.1 Fractionation processes during chemical reactions and interactions of solids

Copper serves as an ideal tracer for redox reactions, which take place at the Earth’s surface, and it occurs in reduced and oxidised forms. Zhu et al. (2002) documented for the first time the large isotopic fractionation of $\Delta^{65}Cu_{Cu(II)-Cu(I)} = 4 \text{ ‰}$ for an aqueous reduction of Cu(II) to Cu(I) iodide precipitation, which was confirmed by Ehrlich et al. (2004) in similar experiments. They also reported a small fractionation in redox experiments of $\Delta^{65}Cu_{Cu(II)aq-Cu(II)(OH)_2} = 0.27 \pm 0.02 \text{ ‰}$. Likewise, Marechal and Sheppard (2002), as well as Mathur et al. (2005), and Wall et al. (2011), observed small fractionations in redox experiments. In natural systems, reduction of Cu can also take place while uptake of Cu into bacteria or yeast cells (Zhu et al., 2002). Generally, the light Cu isotopes are preferentially taken up by bacteria and higher plants and include a reduction by reductase proteins (Navarrete et al., 2011, Weinstein et al., 2011, Jouvin et al., 2012, Ryan et al., 2013).

Copper and Zn are essential nutrients for plants and animals, therefore a sorption, bonding or uptake for the metabolism is required, though in higher concentrations the elements can be toxic (e.g., Anderson and Morel, 1978, Flemming and Trevors, 1989, Moffett and Brand, 1996, Sold and Behra, 2000, Bruland and Lohan, 2003, Peers and Price, 2006, Yruela, 2009, Marschner, 2011). The interaction of the elements with plants and animals causes large isotopic fractionation of both Cu and Zn isotopes. Bonding and sorption to biological surfaces prefer the heavy isotopes of both elements. Uptake of the elements in the metabolism has to be divided into three major processes: I) a kinetic transport-limited process (John et al., 2007), II) reduction of Cu (Zhu et al., 2002, Navarrete et al., 2011) and III) an active uptake by phytosiderophores

(Arnold et al., 2010a). Processes I) and II) prefer light isotopes and process III) also favour the heavy isotopes.

Pokrovsky et al. (2005) observed in Cu sorption experiments that light Cu isotopes get sorbed onto cells of soil bacteria at acidic conditions pH 1.8–3.3. This sorption is an outer-sphere monodentate complexation, in which, Cu forms complexes with phosphoryl groups at the surface of the cell at low pH. This bonding differs from the inner-sphere complexation by a longer bond distance, apparently leading to a preference for light isotopes. Another important observation has been made by Navarrete et al. (2011) who compared the Cu uptake into living and dead cells of *E. coli* and *B. subtilis* in experiments. Heavy Cu isotopes remain in the solution while living cells are present at different pH values. This light isotopic uptake might be due to either kinetic fractionation or an equilibrium fractionation by the reduction of Cu within the cell. Just a slight difference of light Cu isotopes in a solution of about 0.4 ‰ was observed when dead cells are present compared to a lack of dead cells. Similar to Gélabert et al. (2004), (2006) who documented a small isotope fractionation of Zn in experiments between marine and freshwater diatoms, a complexation of Zn and Cu to organic functional groups caused the fractionation (Bigalke et al., 2010a, Ryan et al., 2014).

In general, a few observations have shown that all plants have a lighter Cu isotope signature than the surrounding pool (Navarrete et al., 2011) mostly due to the Cu reduction during uptake. In contrast, Zn isotope signatures are either heavy or light in bulk samples compared to the external pool. Most likely, this phenomenon depends on whether the Zn was taken up as free Zn or as a Zn complex. The transport within the plants reveals a preference for light Zn isotopes (Moynier et al., 2009, Caldelas et al., 2011, Fujii and Albarède, 2012, Jouvin et al., 2012, Tang et al., 2012), while Cu isotopes can be either heavy or light (Jouvin et al., 2012, Ryan et al., 2013, 2014).

To understand the fractionation processes during plant uptake, the different uptake strategies have to be taken into account. A useful comparison can be made to the pioneering work of Guelke and von Blanckenburg (2007) who investigated the uptake of Fe isotopes into higher plants and separated them into two strategies. Strategy I): free metal Fe has to be reduced before uptake, in which the lighter isotopes are preferred, resulting in an uptake of the lighter isotopes of Fe. Copper undergoes this process in soil as well, where Cu(II) is reduced to Cu(I) by reductase enzymes (Sancenon et al., 2004, Jouvin et al., 2012). Whereas free Zn, which only occurs in one oxidation state, follows another strategy. Strategy II takes place when the soil is deficient in metal, then given the example of Fe, the plant roots can complex the soil Fe (III) to a phytosiderophore, no reduction is required in this process, leading to an uptake of slightly

heavier isotopes (Guelke and von Blanckenburg, 2007, Moynier et al., 2013). Jouvin et al. (2012) further specify the plant uptake of Zn are: I) low and II) high-affinity uptake. Low-affinity uptake takes place when Zn is in excess in the external pool that involves diffusive transport through ion channels and electrogenic pumps through the cell membrane; both processes prefer light isotopes. High-affinity uptake binds Zn from a low Zn bearing external pool using Zn-Fe-permease (ZIP) proteins at the cell membrane (Tang et al., 2012), and consequently make uptake through the transmembrane feasible, this process favours heavy isotopes (Arnold et al., 2010a).

Among organic complexation within a dissolved free metal pool, sorption to abiotic species has also been experimentally determined. Pokrovsky et al. (2005) obtained the preference of light Zn isotope sorption to goethite $FeO(OH)$ and birnessite $\delta - MnO_2$ and heavy Zn isotope sorption to pyrolusite $\beta - MnO_2$ and Al oxides in experiments. With decreasing pH from 5.5, the highest fractionation occurs when Zn becomes adsorbed to hematite $\Delta^{66}Zn_{sorbed-free} = 0.61 \text{ ‰}$. However, the follow-up work shows irregularities, according to Bryan et al. (2015) due to kinetic effects in short duration experiments. Peacock and Sherman (2004), Schauble (2004), Balistrieri et al. (2008), and Juillot et al. (2008) suggest that the heavy isotope is preferred by the lower coordinate covalent bond of the metal on that it gets sorbed as well. They all conclude that heavy Cu and Zn preferentially sorbed to oxides (Balistrieri et al., 2008, Juillot et al., 2008, Bryan et al., 2015). Moreover, Balistrieri et al. (2008) provide an example from nature where drained mining water was mixed with river water. They observed a decreasing concentration of Cu and Zn in river water, with decreasing pH in aqueous solution due to the fact that they both underlie sorption processes $\Delta_{sorbed-solution} = +0.73 \pm 0.08 \text{ ‰}$ for Cu and $= +0.52 \pm 0.04 \text{ ‰}$ for Zn.

Generally, in many soil systems, the most important process is the equilibrium partitioning of Cu and Zn and their isotopes between organic complexes in the soil solution and the sorption of the elements to secondary minerals (Grybos et al., 2007). While Fe oxides are present in the soil, most likely heavy Cu and also Zn isotopes are transferred into aqueous organic complexes, therefore a sorption of light isotopes takes place on Fe oxides (Bigalke et al., 2010c, 2011, Vance et al., 2016b). However, this requires that the organic complexing of heavy Cu isotopes is greater than the sorption onto oxides (Chen et al., 2008, 2009, Vance et al., 2008, Little et al., 2014a, Ryan et al., 2014).

3.2.2 Cu and Zn isotopes during weathering and in ore deposits

The release of Cu and Zn from primary minerals during weathering can be predicted based on several experiments (e.g., Pokrovsky et al., 2008, Fernandez and Borrok, 2009, Wall et al., 2011, Ryan et al., 2014). Fernandez and Borrok (2009) investigated fluids after oxidative leaching of sulphide-bearing rocks. At pH 2 and 5, the Cu is up to 2 ‰ heavier in the fluid than in the rock, most likely due to a change of oxidation state, and Zn can be both heavier and lighter depending on the rock and mineral, the highest difference being 0.2 ‰. Another study from Weiss et al. (2014) obtained an isotopic signature from leaching experiments of biotite granite with weak acids. A kinetic fractionation takes place, displayed by an early light isotope release (-1.2 ‰), which equilibrated to 0.1 to 0.3 ‰ over time.

The experiments described above can only provide ideas to interpret field data. Although the experiments of Fernandez and Borrok (2009) display clear trends, in an open system it is not only sulphide minerals that release Cu and Zn, with natural field settings being much more complex. As a result, the interaction of aqueous phases and soil particles influences the signature significantly as well. To understand the release of Cu and Zn into the system Mathur et al. (2012) introduced for a Cu isotope study in soils a factor τ , which describes the gain (positive) and loss (negative) of an element in soil compared to the host rock/mineral, similar to the enrichment factor used in environmental sciences (Loska et al., 1997, Reimann and de Caritat, 2005, Reimann et al., 2009, Sucharovà et al., 2012, Barbieri, 2016).

$$\tau_{i/j} = \left[\frac{(C_i/C_j)_h}{(C_i/C_j)_p} - 1 \right] \quad (5)$$

With C as concentration, i is the element of interest, j an immobile element such as Nb, Al, Zr and h stand for the soil horizon and p for parent material.

To understand the processes fractionating isotopes in ore systems and their production, first, an understanding of the signature (Mason et al., 2005) within the ore is necessary. For Cu, it depends on the environment in which it formed (Graham et al., 2004, Mason et al., 2005, Markl et al., 2006, Asael et al., 2007, 2009, Mathur et al., 2009, 2010). Primary sulphide ores are around $\delta^{65}\text{Cu} = 0 \pm 0.5$ ‰, whereas ores within the supergene environment range between -16.5 to +10 ‰. The latter fractionation might be caused due to several stages of redox reactions, in open system behaviour, Rayleigh fractionation or some combination of processes. The range of Zn isotopes is rather small compared to Cu isotopes. In volcanic-hosted massive sulphide ore deposits, a range of $\delta^{66}\text{Zn}$ of 0.63 ‰ has been measured and in Irish type sphalerites, a range of -0.17 to +1.33 ‰ (Wilkinson et al., 2005b, Gagnevin et al., 2012).

3.2.3 Atmospheric and anthropogenic impact of Cu and Zn isotope signatures

Not many studies deal with the atmospheric aerosol input to soils and their isotopic change. Thus far, it is well known that dust can influence the elemental soil signature and so it does also for isotopes. Vance et al. (2016b) studied the impact of Asian desert dust, deposited on Hawaiian soils, illustrating a change related to dust of 0 ‰ for Cu and +0.3 ‰ for Zn. Whereas in Finland, higher impact is documented of +0.9 ‰ for Zn (Weiss et al., 2007) and a more detailed investigation of Asian dust, shows that samples of size fraction of $>63\ \mu\text{m}$ can change Cu isotope ratios of up to 0.5 ‰ (Dong et al., 2013). Generally, the upper organic-rich horizon at the surface reveals light signatures in Cu and Zn (Weiss et al., 2007, Bigalke et al., 2010a, 2011, Liu et al., 2014, Vance et al., 2016b). However, it is not clear how this signature has formed. In addition to aerosol dust deposition, the uptake by plants and the decay of plant material could be other potential processes. The pioneering study of Viers et al. (2007) pointed out the importance of Zn in the plant cycle. Light Cu isotope signatures are most likely associated with plant activity in the surface soil horizon (Bigalke et al., 2011, Liu et al., 2014).

Zn and Cu are elements that are typically released through human activities such as agriculture, manufacturing and waste disposal (Rauch and Pacyna, 2009). Copper mainly is derived from non-ferrous metal production and fossil fuel combustion. Zinc is derived from the same processes, however to a less extent, rather steel and cement production, as well as waste disposal, are significant (see review in Fekiacova et al., 2015). Zinc metal produced has a low variation compared to the initial ores of $+0.19 \pm 11\ \text{‰}$ (2 S.D., $n=14$) (Wilkinson et al., 2005b) and +0.15 ‰ (Mason et al., 2005). Several studies investigated the trace emissions of Zn to the atmosphere (Cloquet et al., 2006, Gioia et al., 2008, Mattielli et al., 2009) after mining and smelting, which could overprint natural signatures of plants (Dolgoplova et al., 2006), ombrotrophic peats (Weiss et al., 2007), soils and sediments from rivers and lakes (Juillot et al., 2008, Sivry et al., 2008, Sonke et al., 2008, Aebischer et al., 2015). In general, heavy isotopes of Zn are found within slag residues and tailings, whereas light isotopes occur within the emitted aerosols (Dolgoplova et al., 2006, Juillot et al., 2008, Sivry et al., 2008, Sonke et al., 2008); the influences were investigated in an area of up to 5 km from the smelter. However, one study after Ochoa Gonzalez and Weiss (2015) claim that heavier isotopes were within the aerosols compared to the residues in the bottom ash after coal combustion. Moreover, agriculturally used fertiliser are enriched in heavy Zn isotopes +0.19 to +0.42 ‰ (Chen et al., 2008).

3.3 Case studies for mineral exploration

Several case studies exist about non-traditional stable metal isotopes in mineral exploration and its related fields, which are presented in the following.

Mathur et al. (2014) present Cu isotopes as a tool for the exploration of Cu deposits. Samples of chalcopyrite and chalcocite were selected from open pit and underground mines of porphyry Cu systems, one massive sulphide system and an epithermal gold and a skarn system. Samples of ore were compared to samples of groundwater proximal to the deposit. As expected, Cu isotope values are enriched in ^{65}Cu at the surface, resulting from oxidation of the Cu minerals.

Kelley et al. (2009) focus on base-metal (Zn-Pb) deposits in the Red Dog District, Northern Alaska. It is a shale-hosted massive sulphide deposit consisting of predominantly sphalerite mineralisation; the study addresses an underlying vein breccia deposit. $\delta^{66}\text{Zn}$ isotope values range from 0.0 to 0.6 ‰, which are inversely correlated to the Fe/Mn ratio of sphalerites; generally, these sphalerite crystals have low Cu concentrations. The report suggests a model of Zn isotopes as a tracer for flow paths in hydrothermal systems, due to their variation in Zn isotope signatures between the main deposit and the proximal footwall vein breccias. Furthermore, this work assumes that Zn isotopes can be used as a tracer to distinguish between the proximal core and the distal part of a large hydrothermal system.

A recent study from Pasava et al. (2014) presents Zn and S isotopes applicable to sphalerite compositions from the Picos de Europa (Lower Carboniferous) Mine as well as sphalerite and hydrozincite samples from the La Florida Mine (Lower Cretaceous). Both carbonate-hosted Zn-Pb deposits (mines) are Mississippi Valley-type (MVT) deposits in northern Spain. Samples from Picos de Europa exhibit two generations of mineralisation, mirrored by Zn and S isotope signatures. In addition, the trace-element patterns vary considerably. In the earlier phase, Pb, As, Mn and Sb are strongly enriched and Ag, Ni and Cu are slightly enriched, whereas Co, Ga, Tl, Te, Ge and Sn are depleted. The study suggests that a heavy Zn isotope value may be an indicator of rapid precipitation of sphalerite under conditions of high temperature and low pH; whereas, light Zn isotope values reflect a slow precipitation of sphalerite in a low temperature and high-pH system. A completely different conclusion can be made for the La Florida deposit; Zn may be from higher-temperature fluids that precipitated after the fluid mixing. In general, the $\delta^{66}\text{Zn}$ value of sphalerite is light in both deposits.

These three examples illustrate how Cu and Zn isotopes has been used for mineral exploration using the isotopic fingerprint of the sulphide or try to compare the ore with surficial samples to detect a source or a mineral exploration tool.

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Chapter 3: Characterising zonation of the trace-elemental pattern of sphalerite and pyrite at the Ballinalack Zn-Pb deposit in the Irish Midlands, Ireland

Abstract

The Ballinalack deposit is one of the numerous carbonate-hosted Zn-Pb deposits that occurs in the Irish Midlands, which is an established base-metal province in Ireland. Sulphide lenses comprising sphalerite, pyrite-marcasite and galena occur mainly in the Lower Carboniferous Waulsortian Limestone and in a stratigraphically lower calcareous unit known as the Pale Beds. In addition to several studies on larger Irish type deposits such as Navan, Lisheen and Silvermines, characterisation of Irish type sulphides still needs further work. This study is the first documentation using femtosecond laser ablation ICP-MS on sulphides from Irish type deposits. Samples from the Lower Argillaceous Bioclastic Limestone, as well as Waulsortian Limestone, were investigated from the centre of the mineralisation and on the flanks to the east. The data provides a closer insight into the zonation within Irish type mineralisation hosted by Waulsortian Limestone. Sphalerite chemistry illustrates that these deposits do not display much variation in their trace-elemental pattern, apart from high Ga concentrations in the centre of mineralisation. However, sub-microscopic inclusions of pyrite and galena characterise the sphalerites, reflected in enrichments of Co, Ni, Mo and Ag, Hg, respectively. Trace-element signatures of pyrites reveal elevated concentrations of As, Ni, Co, Mn and Mo within the centre of Irish type mineralisation. Remarkably, the Ni concentrations (max. 81,367 ppm) are some of the highest reported values for pyrite, suggesting a high Ni rich source in the Lower Palaeozoic basement. This characterisation forms an orientation study that will provide additional insights for mineral exploration through a better understanding of the formation of mineralisation and its trace-element signatures.

1 Introduction

Irish-type carbonate-hosted Zn-Pb mineralisation is typically composed of massive sphalerite, galena and pyrite accompanied by lesser marcasite, chalcopyrite and arsenopyrite. While sphalerite and galena are the principal and most important ore minerals for the base metals Zn and Pb, Fe sulphides are of no economic value and considered gangue. Nevertheless, the geochemical character of pyrite can provide much information about the sulphide genesis and environment of deposition (e.g., Bralía et al., 1979, Roberts, 1982, Griffin et al., 1991, Craig et al., 1998, Abraitis et al., 2004, Deditius et al., 2008, Large et al., 2009, 2014, 2017, Chappaz et al., 2014). Although sphalerite (ZnS) and pyrite (FeS₂) are chemically simple, the minor and trace elements contained within their crystal structure can vary significantly (Chapter 2). A better understanding of the minor and trace-element chemistry of sulphide minerals is critical for mineral exploration. The trace-element signature of sulphide minerals may provide insights into the genesis of a deposit. In addition, bulk litho-geochemistry applied to drill core, detailed petrography can provide data concerning deposit zonation and proximal-distal relationships.

Numerous contributions have been published regarding trace-elemental patterns within sulphides using bulk sulphides and laser ablation techniques. Past studies of various sphalerites (Cook et al., 2009, Ye et al., 2011, Barrie et al., 2009, Gagnevin et al., 2014, Grammatikopoulos et al., 2006, Kuhlemann and Zeeh, 1995, Palero-Fernandez and Martin-Izard, 2005, Pfaff et al., 2011, Kelley et al., 2009, Pasava et al., 2014) provide an overview of the elements and their behaviour and incorporation in sphalerites and how the elements can enter into the lattice, including base metals such as, Fe, Cd, Mn, Cu, Pb, etc. (e.g., Burke and Kieft, 1980, Kuhlemann and Zeeh, 1995, Bernardini et al., 2004, Cook et al., 2009, Ye et al., 2011, Gagnevin et al., 2014). Pyrites are less often investigated for their trace elements in the characterisation of sulphide deposits, however, Craig et al. (1998), Abraitis et al. (2004), and Large et al. (2009), (2014) provide a review of the occurrence of trace elements and their reported concentrations measured in natural pyrite samples and their substitution into the pyrite lattice, e.g., As, Co and Ni (for more details, see Chapter 2).

In this work, I report on the trace-element variations in sphalerite and pyrite within the Ballinalack Zn-Pb deposit in the Irish Midlands, Ireland. Herein, femtosecond laser ablation ICP-MS data is presented from Irish type sphalerites and pyrites detailing their trace-element zonation. The aim of this study is to document the trace-element variation of sphalerite and pyrite crystallised in one deposit and how it relates to former studies of Zn-Pb deposits, in particular, Irish type deposits (Wilkinson et al., 2005b, Gagnevin et al., 2014). With the aid of

this data, deposit genesis can be better understood and a supplementary guide for mineral exploration is provided. These results can also be used as trace element indicators for soil geochemical prospecting. Anomalies in soils may help to locate blind ore deposits and their subsurface outline. Knowing what type of deposits are characterised and for which element signatures are crucial, will be echoed within the overlying soils and offer insight into the proximal-distal relationship, both vertically and horizontally.

1.1 Deposit Geology of Ballinalack

The Ballinalack carbonate-hosted Zn-Pb deposit is situated in the Irish Midlands, approximately 50 km west of the Navan Zn-Pb deposit. The deposit's resources are currently sub-economic and estimated to contain 7.71 Mt grading 6.33 % Zn and 0.95 % Pb (The Robertson Group Plc, 1991).

The Ballinalack area is mainly characterised by a fault bound inlier of Pale Beds, referred to as the Ballynacarrigy inlier. At the margin of the Ballinacarrigy inlier, northeast striking extensional faults are present across the Irish Midlands. At Ballinalack, another northeast trending fault system exists, termed the Ballinalack Fault Zone (Fig. 1). This fault zone is regionally extensive and further extends beyond the Ballinalack deposit. These faults are locally covered by late Courceyan and Chadian rocks, Supra Waulsortian and Calp (Bradfer, 1982, Jones and Bradfer, 1982, Hitzman and Large, 1986, Jones and Brand, 1986, Hitzman and Beaty, 1996). The sulphide mineralisation occurs in Lower Carboniferous carbonates of the Pale Beds and the Waulsortian Limestone (Fig. 2), with the highest grades occurring within the latter.

The Pale Beds unconformably overlies the Lower Palaeozoic basement comprising micaceous, quartz sandstones that can be partly metamorphosed. The younger calcareous Pale Beds sequence is of Courceyan age and alternates between coarse-grained packstone/grainstone and finer-grained bituminous lime mudstones; fossils and bioturbation occur rarely. With a thickness between 150–200 m, it was deposited in a basal marine transgressive environment. The stratigraphically higher Shaley Pales (Courceyan) are composed of two units: I) a non-fossiliferous carbonate packstone that is interbedded with black lime mudstone, and II) a mixture of thinly alternating crinoidal wackestone, packstone and lime mudstone. With a thickness of 50–60 m in the area of Ballinalack, it was deposited in a transitional environment to marine basin slope. The Lower Argillaceous Bioclastic Limestone (Lower ABL) is described as dark grey, argillaceous, bioclastic wackestone and floatstone with nodules of light grey lime mudstone; it is widely described to contain fossils and bryozoan (Hitzman and Beaty, 1996).

This unit is deposited in an open marine basinal environment with a thickness of 150–200 m (Clarke and Reed, 2009).

Above this unit, the Waulsortian Limestone was deposited, which is a light bluish-grey calcareous mudstone and mud-boundstone with sparry calcite-filled stromatactis cavities (Bradfer, 1982, Jones and Bradfer, 1982). Three knolls occur within this unit, which are related to the northeast-trending Ballinalack Fault Zone (Bradfer, 1982). Accordingly, the thickness of the Waulsortian Limestone varies with the occurrence of the knoll resulting in thickness ranging from 150 to 250 m. It was deposited in an open marine environment at about 200–300 m depth (Lees et al., 1977, Lees, 1982).

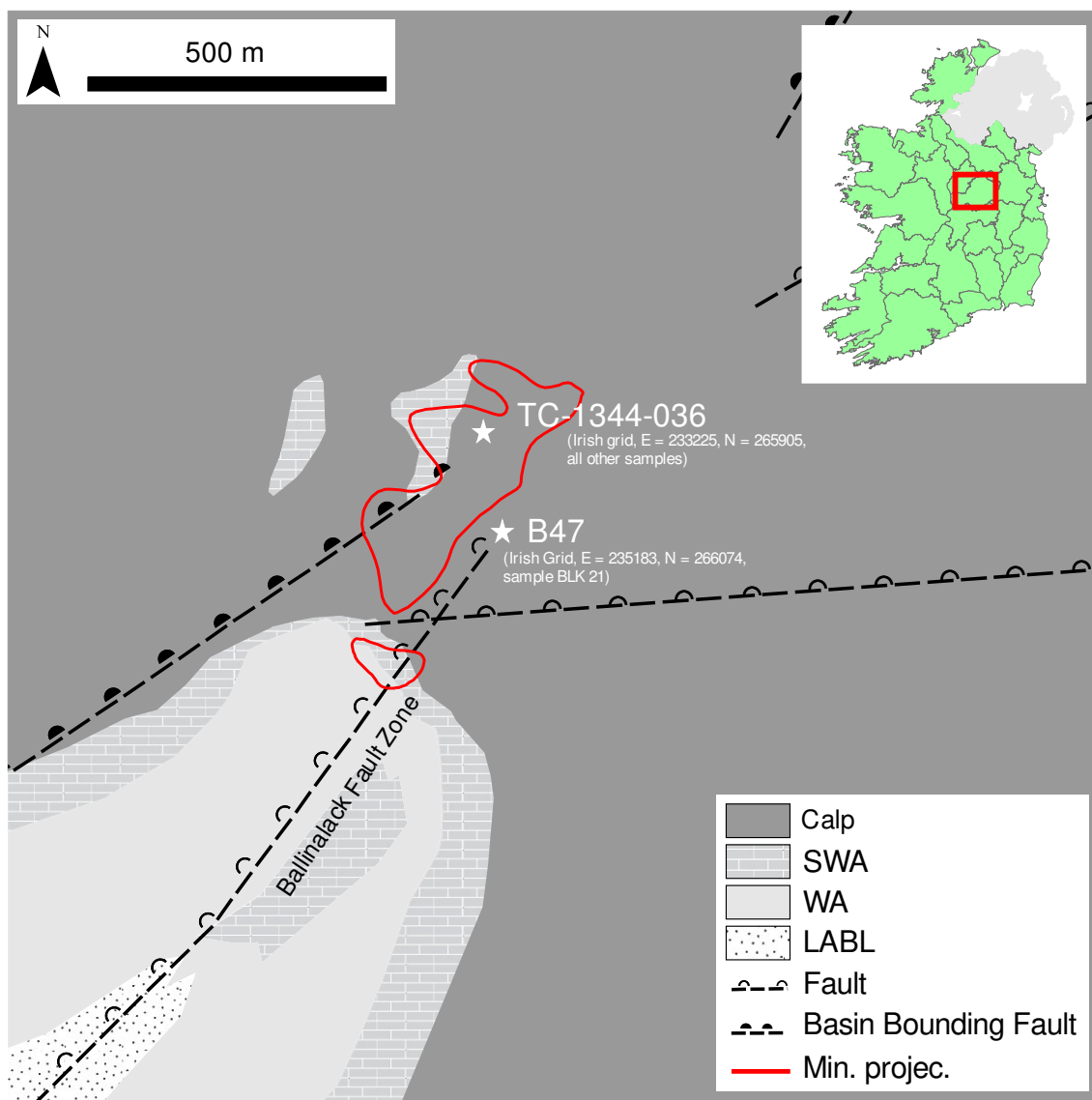


Fig. 1 Geological setting of Ballinalack. The Ballinalack setting consists of two sulphide lenses. The major one in the north and the minor sulphide body in the south. Star = drill collar location, SWA=Supra Waulsortian Limestone, WA=Waulsortian Limestone, LABL= Lower Argillaceous Bioclastic limestone, Min projec. = Mineralisation projection.

1.2 Mineralisation

Mineralisation at the Ballinalack deposit occurs within both the Pale Beds and the Waulsortian Limestone (Fig. 2). Samples in this study are only from the Waulsortian Limestone mineralisation (Fig. 2, 3), in the following it is simply referred to as the Waulsortian mineralisation only. According to Jones and Bradfer (1982) the age of the mineralisation is pre-Hercynian and early Carboniferous (Late Courceyan to Arundian). No fluid inclusion data is available to estimate the temperature of the mineralising fluid. However, based on Finlow-Bates (1984), the Ag content in galena can indicate the formation temperature, Jones and Brand (1986) suggest that the fluid temperature at Ballinalack may have been approximately 150 °C.

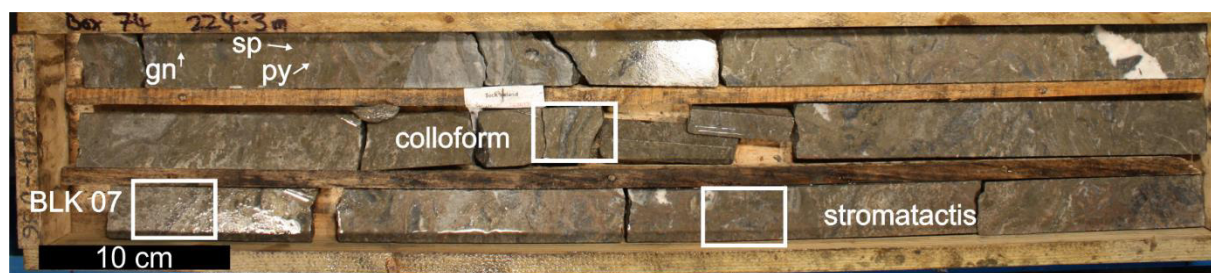


Fig. 3 Drill core picture of TC-1344-036, showing the section of Waulsortian Limestone 224.3–227.0 m, clearly, the stromatactitic filling, as well as colloform mineralisation, are visible. Mineralisation consists of brown sphalerite, golden pyrite and silvery galena. White boxes show sample location BLK 07 taken at 225.54 m, example for colloform mineralisation and stromatactis structure. Enlarged picture in Appendix B. Source photo: Teck, Ireland Ltd.

The sulphide lenses are composed of sphalerite, pyrite and galena and to a lesser extent marcasite, arsenopyrite and chalcopyrite in the form of cavity- and fracture-lining to massive veins and further as breccia and fracture fills (hand specimen-scale). One of the most common mineralisation forms at Ballinalack is as a lining along stromatactis cavities (Fig. 3). The banded sulphides occur in the stromatactis cavities alternating in pyrite, sphalerite and galena. The centre is often filled with carbonate minerals, i. e., calcite, ferroan carbonate and dolomite. Further, the mineralisation along stylolites are mainly composed of pyrite with minor sphalerite and rare galena, with colloform textures exhibited (Fig. 3). This texture can occur in open cavities with mainly pyrite and sphalerite and lesser galena and carbonate minerals.

Both mineral textures, massive (Fig. 4a) and colloform (Fig. 4b, d) sulphides are also evident on micro scale (<1000 µm). The massive mineralisation is composed of fine grained discrete sulphide minerals and is the prevalent form of mineralisation, similar to those observed in Wilkinson et al. (2005b). The micro-textural observations suggest a general sequential precipitation of calcite, pyrite, sphalerite, and galena (Fig. 4a, c). The described sequence of

mineralisation agrees with the paragenesis for Ballinalack (Fig. 5) as proposed by Jones and Brand (1986). In this study sphalerite occasionally occurs as inclusions within pyrite, indicating later precipitation of pyrite followed by sphalerite. The textural observations further suggest different stages of replacement. In an early stage carbonate minerals are replaced by pyrite (Fig. 4e) and sphalerite (Fig. 4a-d, f), resulting in residual calcite as inclusions in larger (up to 500 μm) sulphide grains. This can also be observed in the rare colloform sphalerites within this study that replace carbonate minerals (Fig. 4d). The bands are separated by thin carbonate films, also indicating a replacement feature. In a later stage, the pyrite grains were replaced by sphalerite leading to the formation of typical replacement textures and pyrite inclusions within sphalerite (Fig. 4a-c). Meanwhile, galena grains are often intergrown with sphalerite grains (Fig. 4c), but also occur as inclusions within later precipitated sphalerite grains (Fig. 4f). This also supports the paragenesis (Fig. 5) established by Jones and Brand (1986) as they proposed a short galena mineralisation event within the main sphalerite precipitation stage. Note, zonation within the sphalerites was not detectable petrographically using transmitted light microscopy (Appendix B).

Further images of the thin sections (reflected and transmitted light) used within this study are given in Appendix B, but a more detailed evaluation of the mineral textures and paragenesis was beyond the scope of this study. However, the discussed formation mechanisms (replacement and contemporary precipitation of phases) result in two important textures. Firstly, sulphides formed by mineral replacement containing residual grains as inclusions of the replaced mineral phase. The size of the inclusions vary from approximately 100 μm to sub- μm level. Secondly, contemporary precipitation of phases results in textures characterised by intergrowth of the two mineral phases. In particular, those sub- μm level textures greatly influence the results of the LA ICP-MS data, discussed in the following sections.

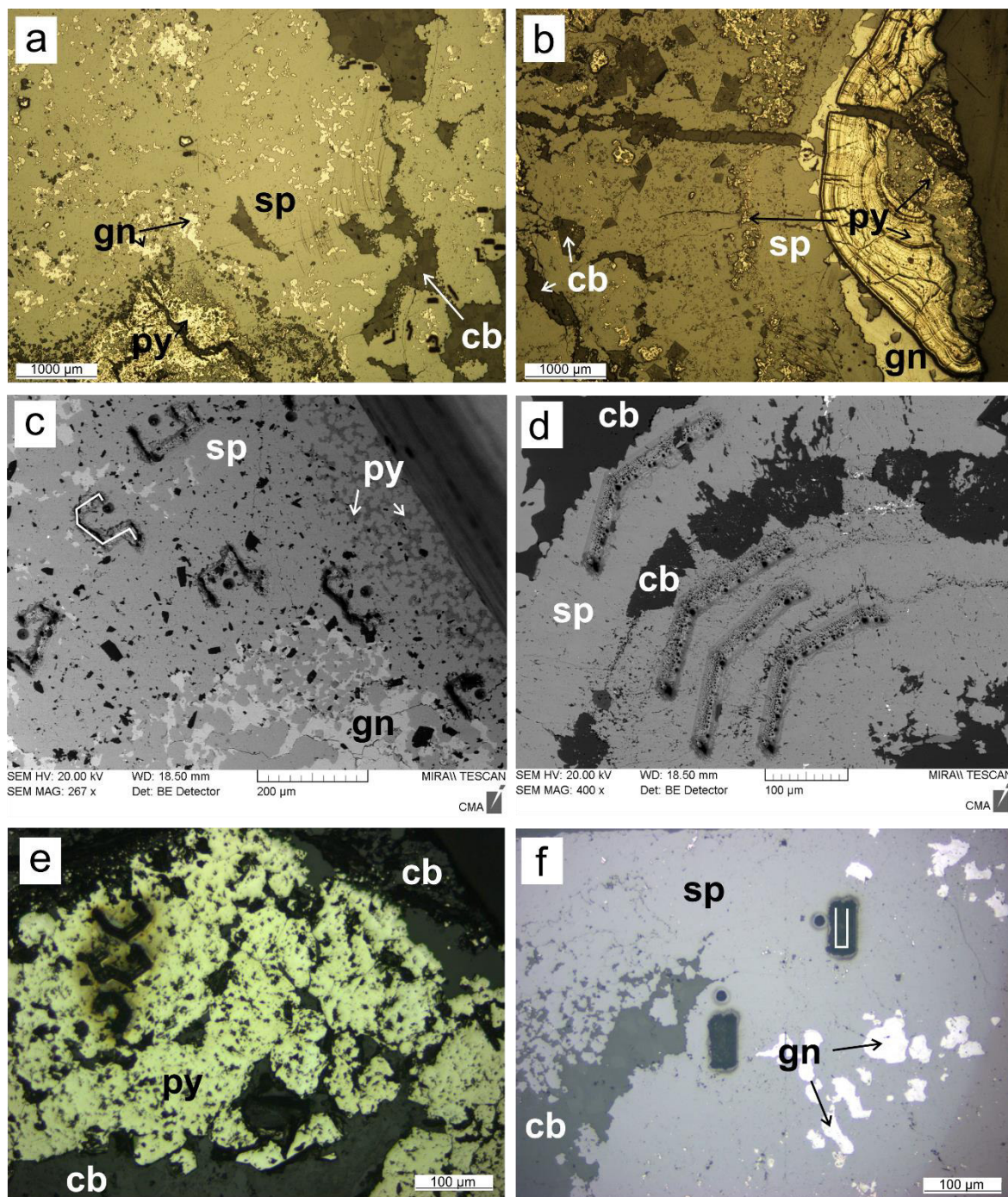


Fig. 4 SEM and reflected light images from sulphide mineralisation at Ballinalack: a.) Sample BLK 08 illustrates typical massive sulphide mineralisation, with replacement structures; b.) sample BLK 12, colloform sulphide mineralisation; c.) SEM image sample BLK 08 same area as a.), white line highlights a pathway for line analysis; d.) SEM image: rare banded sphalerite in more detail, from BLK 11; e.) sample BLK 05, massive pyrite with residual carbonate minerals as a result of replacement; f.) massive sphalerite replaces galena and carbonate minerals, in BLK 08, white line shows an exemplary raster line analysis pathway. cb = carbonate mineral, gn = galena, py = pyrite, sp = sphalerite.

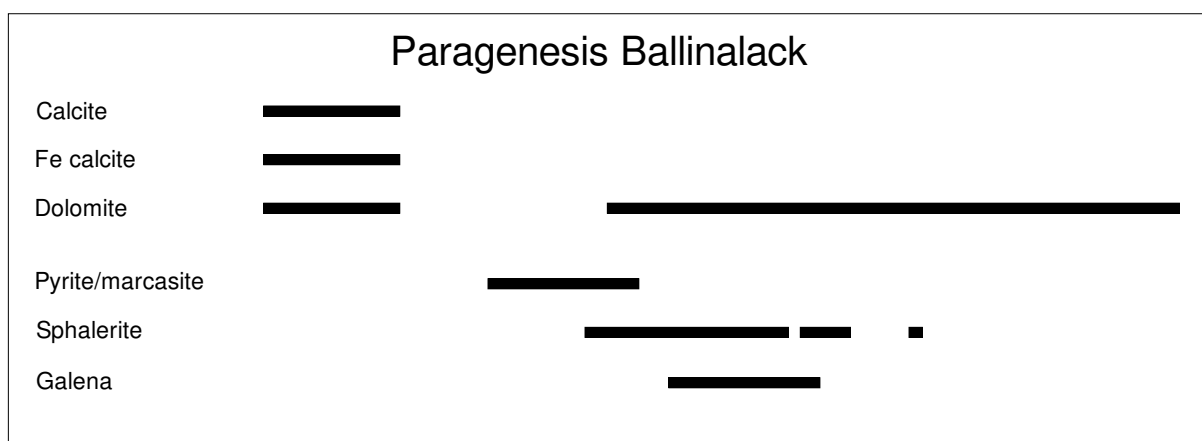


Fig. 5 Paragenesis of Ballinalack after Jones and Brand (1986).

2 Methodology

Samples consisted of 10 cm portions of quartered drill core from two drill holes intersecting the Ballinalack deposit: drill hole TC-1344-036 (Irish grid, E = 233225, N = 265905) with eight samples collected between 245.78 and 161.49 m (Tab. 1), and one sample from drill hole B 47 (Irish Grid, E = 235183, N = 266074) east of the mineralisation to compare with the main sulphide lens (Fig. 1, Tab. 1). The main focus of this sampling was for analysis of sphalerites and pyrites to characterise the stratigraphic variation and distribution of trace elements in sphalerite and pyrite.

Tab. 1 Overview of thin sections related to their drill core, lithology and depth, as well as their sulphide mineralisation.

	Drill hole	Depth	Lithology	Mineralisation
BLK 05	TC-1344-036	270.48	Lower ABL	py
BLK 06	TC-1344-036	245.78	Lower ABL	py
BLK 07	TC-1344-036	225.54	Waulsortian	sp, gn, py
BLK 08	TC-1344-036	214.49	Waulsortian	sp, py
BLK 09	TC-1344-036	206.4	Waulsortian	sp, py
BLK 10	TC-1344-036	195.1	Waulsortian	sp, py
BLK 11	TC-1344-036	169.84	Waulsortian	py, gn
BLK 12	TC-1344-036	161.49	Waulsortian	sp, gn, py
BLK 21	B 47	145.5	Waulsortian	sp, gn, py

Laser ablation ICP-MS analyses were carried out on colloform and massive (subhedral) forms of sphalerites (n = 99) and pyrite (n = 63). The analyses were obtained using a custom built ultraviolet (UV, $\lambda = 193$ nm) femtosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA ICP-MS) at the German Research Centre for Geosciences (GFZ) in Potsdam. The laser ablation system uses ultra-fast laser pulses (in the range of 150 fs) to reduce non-stoichiometric ablation conditions, which can be observed when using nanosecond laser

ablation systems. For the analysis of sphalerites and pyrites, the use of femtosecond LA ICP-MS has proven to be advantageous (Glaus et al., 2010, Shaheen et al., 2012). More details about the LA ICP-MS set up and its performance can be reviewed in Schuessler and von Blanckenburg (2014). The conditions consisted of a spot/line size of 20 μm in diameter, a frequency of 20 Hz and a laser power of 7 mW. Calibration was performed against the MASS-1 sulphide standard (Wilson et al., 2002). Additionally, NIST610 (Jochum et al., 2011) and BHVO-2G (Jochum et al., 2005) standards were used as unknown samples for control. The areas analysed were chosen as relatively clean areas (no inclusions), however, due the sub- μm structures described in the mineralisation, complete avoidance of the inclusions could not be assured. The ablation path (Fig. 4c, d, f) was either a spot, line or a raster. Raster analyses are ‘back and forth’ traverses covering a small area of the mineral (Fig. 4f), no elemental maps were measured. Each path has been repeated two times for one measurement. Data evaluation was carried out in StalQuant - a Python based program to reduce large numbers of point-by-point quantification data (Fricker, 2012). For the sulphides, MASS-1 was used as an external standard for the following isotopes ^{51}V , ^{52}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{67}Zn , ^{69}Ga , ^{75}As , ^{76}Se , ^{95}Mo , ^{107}Ag , ^{111}Cd , ^{115}In , ^{118}Sn , ^{121}Sb , ^{124}Te , ^{137}Ba , ^{182}W , ^{202}Hg , ^{205}Tl , ^{207}Pb , and ^{209}Bi . The choice of elements was restricted to the elements given by the standard MASS-1, nevertheless, the standard provides all elements of interest expected within the sulphide minerals pyrite and sphalerite. An accuracy of ± 10 to 15 % was determined, based on the repetition of standards. Prior to LA ICP-MS analysis, major-element data was obtained for use as an internal standard on a scanning electron microscope (SEM) Tescan Mira XMU with energy dispersive X-ray microanalysis at the Centre for Microscopy and Analysis of Trinity College Dublin. The average of Zn and Fe for each sample (thin section), respectively, was calculated and used as an internal standard: Zn for ^{67}Zn in sphalerites and Fe for ^{57}Fe in pyrites (note the StalQuant software requires to choose an isotope instead of an element, the isotopes with low abundances were selected) for the evaluation of laser ablation ICP-MS analyses. Prior to the SEM work, the thin sections were coated with carbon (Cressington 208Carbon, high-resolution carbon coater). Analytical parameters during measurements were performed at a current of 20 kV and 60 s counting and 30 % dead time, with a spot size of 5.2 μm . Analysis of sphalerite and pyrite grains were conducted for S, Fe, Zn, Ni, Co, Pb, and As (Appendix B) and calibrated against the standard 2277 BioRad A 1876. The lower detection limit was approximately 1,000 ppm for all elements. The INCA software was used for calibration of the SEM, and Mira TC was used to process and evaluate the measurements.

Note, all results of SEM-EDX and LA ICP-MS and discussion are based on a limited number of samples and further studies with a more detailed sampling is required to draw a definite conclusion. This investigation can rather be seen as orientation study.

3 Results

SEM-EDX analyses can be seen in Appendix B, as well as a detailed table of the LA ICP-MS results. A summary of the trace element concentrations determined by LA ICP-MS on sphalerite and pyrite grains is shown in Tables 2 and 3, respectively. A total of 89 raster analyses for sphalerites, and 16 single spots, as well as 51 raster analyses on pyrites were evaluated, each obtained from nine independent polished thin sections. Apart from BLK 05, with only pyrite and BLK 08 with only sphalerite analyses, all samples were analysed for both pyrite and sphalerite. Although laser ablation lines were chosen carefully to avoid any inclusions, this was not always possible due to the sub- μm inclusions at the surface and directly underneath and the encroachment of host material is included in a number of analyses. Obviously high concentrations, were removed during data evaluation and described within each of the results section for sphalerite and pyrite to ensure representative analyses. The results provide an overview of the variation of trace elements within sphalerite and pyrite in the Ballinalack deposit. The differences are still clear, even considering a large error of $\pm 10\text{--}15\%$.

3.1 Sphalerite

High Ba concentrations, which are not known as a trace element substitution in sphalerite occur in detectable concentrations from 3–6,077 ppm (Fig. 6a), in the range of the 75th percentile, Ba can be up to 318 ppm, the few higher concentrations are mainly in samples BLK 07, 10 and sparsely in BLK 06 (Fig. 8). These samples are taken into careful consideration in the following data treatment. Analyses with concentrations above 14,000 ppm of Ba are not further considered in the evaluation, due to the fact that Ba is not a known trace element within sphalerite and it cannot be assumed that only sphalerite was ablated in those analyses. Iron concentrations were obtained by both SEM and LA ICP-MS analysis. Due to the fact that the more pure homogeneous areas are chosen for analysis by SEM than by laser ablation, the SEM data are more reliable. The SEM provides a higher resolution and although the areas chosen with alleged homogenous areas, it could not be completely avoided to ablate inhomogeneous areas (replacement structures). The highest concentrations of Fe are 1.3 wt.% ± 0.42 determined by SEM-EDX. Also, to assure that only sphalerite grains were ablated, all concentrations above Fe 1.7 wt.% (including standard deviation) are neglected for the evaluation of sphalerite (Fig. 6b).

For a general overview histograms (Fig. 7), and for further understanding box and whisker plots, divided into the thin sections (Fig. 8) are provided. These plots of Fe, Pb, Sb, Cd, Mn, As, Mo, Cu, Hg, Ni, Ag, Co, Tl and Ga exhibit that the sample BLK 21 (from core B-47 outside of the major mineralisation) is very similar to samples from the main sulphide lens from core TC-1344-036. In the sphalerites from BLK 21, Hg is the only element exhibiting a significant variation, with concentrations up to 718 ppm that is approximately four times higher than the mean Hg concentration of 190 ppm (Figs. 7, 8) obtained by other sphalerite samples. In addition, sphalerites in sample BLK 21 are rather low in concentrations of Co and relatively high in mean contents of Cu (518 ppm), Cd (2,376 ppm), Ga (26 ppm) and Ag (65 ppm) in comparison to the other samples. In general, high Spearman Rank correlations (R_s) and Pearson correlations (R_p) can be observed and are displayed in Figure 6, for example Tl:Sb ($R_s = 0.74$, $n = 72$, Fig. 6c) and Hg:Ga ($R_s = 0.81$, $n = 72$ (Fig. 6d). Further high correlations are observed in Co:Ni ($R_p = 0.93$, $n = 98$, Fig. 6h), and further in As:Fe ($R_p = 0.81$, $n = 99$, Fig. 6e), As:Co ($R_p = 0.80$, $n = 99$, Fig. 6f), As:Ni ($R_p = 0.83$, $n = 98$, Fig. 6g).

Although the sphalerites of all samples from drill core TC-1344-036 reveal a similar pattern in histograms, they are slightly different in their composition with a vertical trend (Fig 8). This may be reflected in the bimodal distribution of Fe, Cd, Sb, As, Cu, Hg, Ag and Ga illustrated in Figure 7. Sample BLK 06, which consists of Lower Argillaceous Bioclastic Limestone, and not from Waulsortian Limestone appears to have a typical signature (Fig. 8) of high Fe (max. 17,685 ppm), Mn (max. 663 ppm), Cd (max. 2,274 ppm) and Hg (max. 388 ppm) concentrations, whereas Co (max. 25 ppm), Tl (max. 20 ppm) and Pb (max. 1,544 ppm) are relatively depleted.

In sample BLK 07 Ga has a maximum concentration of 40 ppm, within an overall occurrence between 3–40 ppm at Ballinalack. The highest concentrations of Mo (823 ppm) are obtained from sample BLK 09, which also host the highest concentrations of Pb of 19,662 ppm (Fig. 8). Silver can be used to distinguish sample BLK 12 which is the stratigraphically highest sample. Notable is the overall trend of Cd; the concentration tends to decrease upwards within the section in drillhole TC-1344-036.

Tab. 2 Summary statistics of sphalerite from Ballinalack. <LOR = below limit of reporting, all concentrations in ppm.

Sample	Mn	Fe	Co	Ni	Cu	Ga	As	Mo	Ag	Cd	Sb	Ba	Hg	Tl	Pb
All															
n	52	72	72	71	72	72	72	27	72	72	72	60	72	72	72
Min	36.6	2253	1.8	1.5	26	3.3	5.3	0.2	2.1	323	60	3.5	63	1.9	491
Max	1130.3	17685	115.1	503.7	739	40.4	1694.8	823.3	144.6	3829	3610	6077.4	718	154.0	19662
Mean	207.9	9529	19.7	99.6	269	12.4	399.5	84.7	60.0	1341	1257	373.8	191	54.8	3904
Median	159.4	9447	13.0	61.7	205	10.5	325.1	5.6	50.3	1274	1139	21.7	146	46.1	3221
Std. Dev.	183.8	3750	19.8	108.8	224	7.6	332.5	190.9	38.8	674	815	1085.7	133	37.7	3496
BLK 06															
n	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Min	36.6	10886	3.7	15.7	87	12.6	288.2	1.7	66.3	1489	614	208.0	217	17.3	1156
Max	662.7	17685	24.9	177.3	114	21.6	715.0	23.4	77.1	2274	852	2162.8	388	20.0	1544
Mean	295.0	14658	13.3	89.8	101	16.4	452.0	10.0	72.1	1993	727	888.5	284	18.2	1331
Median	185.6	15404	11.3	76.4	103	15.0	352.8	4.8	73.1	2216	715	294.6	246	17.4	1292
Std. Dev.	327.0	3460	10.7	81.6	14	4.7	230.1	11.7	5.5	438	120	1104.5	92	1.5	197
BLK 07															
n	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Min	55.6	5753	41.6	88.1	47	12.5	219.3	31.4	25.8	2186	348	318.7	140	22.1	612
Max	101.4	15449	77.5	503.7	61	40.4	410.6	138.6	31.0	2509	896	6077.4	238	42.4	981
Mean	76.3	8984	54.1	201.0	54	22.4	310.7	60.8	29.0	2264	517	2459.9	168	29.5	754
Median	76.5	7189	46.7	114.5	54	14.1	321.2	39.2	29.5	2207	420	462.5	147	27.5	742
Std. Dev.	17.0	4058	14.7	173.8	5	12.8	70.8	45.1	1.9	138	221	2886.6	41	7.7	139
BLK 08															
n	0	20	20	20	20	20	20	6	20	20	20	8	20	20	20
Min	<LOR	4224	6.3	35.8	186	3.6	121.2	0.2	19.4	746	828	8.8	66	46.6	1552
Max	<LOR	13200	55.1	484.5	729	11.3	1694.8	6.1	75.6	2005	3116	16.6	131	154.0	11359
Mean	<LOR	10171	17.4	118.8	474	7.7	459.4	1.4	49.4	1440	2089	11.8	99	94.6	4274
Median	<LOR	10074	14.3	92.3	452	7.5	336.8	0.5	49.5	1501	2245	11.2	97	88.0	3934
Std. Dev.	<LOR	2244	12.0	108.2	149	2.1	383.7	2.3	15.5	384	599	2.9	20	31.4	2137

Tab. 2 continued.

Sample	Mn	Fe	Co	Ni	Cu	Ga	As	Mo	Ag	Cd	Sb	Ba	Hg	Tl	Pb
BLK 09															
n	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Min	148.6	2253	18.2	96.6	151	7.5	227.7	155.3	24.2	671	404	11.9	77	34.2	4167
Max	196.5	4890	29.4	300.7	230	10.5	393.5	823.3	54.7	825	564	75.8	125	42.0	19662
Mean	170.4	3877	22.9	214.4	198	9.2	330.3	471.1	41.4	727	469	48.8	99	38.6	12195
Median	168.2	4183	21.9	230.2	205	9.5	350.0	452.9	43.3	706	454	53.7	96	39.1	12475
Std. Dev.	20.0	1205	4.7	95.0	33	1.3	73.8	273.8	12.8	67	74	26.8	23	3.2	7069
BLK 10															
n	7	7	7	7	7	7	7	4	7	7	7	7	7	7	7
Min	154.3	5087	12.5	30.3	27	4.5	126.4	0.9	2.1	498	60	16.1	145	13.9	679
Max	1130.3	16620	115.1	433.1	185	15.2	1287.5	40.5	21.4	1441	1842	2023.9	205	134.2	4884
Mean	478.2	10709	48.6	176.4	100	10.8	610.8	12.9	12.0	959	730	633.8	171	64.3	2561
Median	421.7	9460	41.4	137.7	98	11.4	525.0	5.1	12.5	807	511	79.0	170	53.9	1872
Std. Dev.	351.6	4783	34.4	144.6	59	3.7	487.5	18.5	8.1	333	667	846.1	21	46.6	1778
BLK 11															
n	8	8	8	8	8	8	8	2	8	8	8	8	8	8	8
Min	137.0	4350	4.6	1.5	119	3.3	5.3	1.5	8.4	424	66	3.5	63	1.9	921
Max	291.7	17360	21.9	10.8	537	11.9	722.8	6.4	35.8	1449	3610	19.9	135	97.7	4235
Mean	193.6	9630	12.6	4.1	371	6.6	237.9	4.0	25.1	699	1359	9.8	102	47.5	2534
Median	185.6	5947	12.8	3.2	386	6.3	165.8	4.0	24.9	539	1491	8.9	108	47.9	2744
Std. Dev.	52.9	6021	7.1	2.9	133	2.9	231.8	3.4	8.7	361	1212	6.0	23	34.0	1151
BLK 12															
n	17	17	17	17	17	17	17	2	17	17	17	17	17	17	17
Min	84.7	6722	2.8	5.2	26	9.7	65.0	0.3	59.2	323	403	4.2	132	10.2	2035
Max	237.4	16620	17.3	99.9	52	14.0	1049.3	0.4	144.6	1470	2039	152.5	242	72.3	14027
Mean	156.3	9931	8.9	45.1	43	11.9	513.4	0.3	117.8	957	1071	43.1	207	44.9	4814
Median	151.5	9350	8.5	44.0	46	12.0	529.9	0.3	118.7	927	970	19.4	218	45.6	3544
Std. Dev.	37.7	2538	3.8	22.9	8	1.4	281.8	0.1	19.7	316	414	48.8	32	16.0	3331

Tab. 2 continued.

Sample	Mn	Fe	Co	Ni	Cu	Ga	As	Mo	Ag	Cd	Sb	Ba	Hg	Tl	Pb
BLK 21															
n	8	8	8	7	8	8	8	1	8	8	8	8	8	8	8
Min	56.8	4089	1.8	14.2	303	16.9	16.3	0.5	34.5	1828	349	4.7	424	3.8	491
Max	285.8	10691	37.3	178.0	739	34.4	112.0	0.5	91.6	3829	1514	1518.1	718	21.6	5596
Mean	164.0	7181	9.7	75.6	518	26.4	54.9	0.5	65.3	2376	985	240.9	516	13.3	2375
Median	171.9	6815	4.6	52.7	503	26.3	41.8	0.5	71.7	2136	1067	56.1	487	13.2	2109
Std. Dev.	69.6	2427	11.9	70.9	159	6.1	32.7	0.0	21.4	673	423	518.2	95	6.2	1592.4

Tab. 3 Pyrites from Ballinalack, <LOR = below limit of reporting, all concentrations in ppm.

Sample	Mn	Zn	Co	Ni	Cu	As	Mo	Ag	Cd	Sb	Hg	Tl	Pb	Co/Ni
All														
n	59	44	57	59	53	59	59	58	25	59	55	59	59	57
Min	4	2	0.2	1.7	0.6	9	0.3	0.0	0.3	0.6	0.2	0.2	9	0.02
Max	263	46078	10451.9	81367.0	1284.0	44925	753.6	84.3	223.1	1809.1	15.6	1044.7	235551	0.81
Mean	69	6829	669.1	5730.8	75.9	12634	79.0	7.9	27.7	420.0	3.4	277.5	15013	0.10
Median	63	61	28.1	283.7	25.7	11482	35.8	2.2	4.6	340.9	2.2	185.5	4463	0.09
Std. Dev.	62	13008	2081.5	16488.5	182.1	11941	147.9	15.6	46.7	472.7	3.6	297.6	36747	0.11
BLK 05														
n	15	9	15	15	15	15	15	15	3	15	15	15	15	15
Min	4	28	3.0	102.3	15.3	9	0.3	0.2	1.3	0.6	0.6	0.2	9	0.03
Max	253	443	43.7	687.7	237.2	655	7.7	2.3	2.4	10.3	2.8	2.0	106	0.15
Mean	28	122	17.3	214.0	105.4	199	2.5	0.6	1.7	3.1	1.6	0.8	34	0.09
Median	11	40	13.1	172.7	87.2	47	2.7	0.4	1.4	1.9	1.5	0.7	30	0.09
Std. Dev.	63	169	11.4	156.0	77.6	238	2.1	0.6	0.6	2.6	0.7	0.5	24	0.03
BLK 06														
n	6	4	6	6	6	6	6	6	2	6	6	6	6	6
Min	66	22	6.6	108.3	11.7	8253	18.8	16.8	1.5	526.9	3.8	150.0	13090	0.05
Max	168	21249	116.8	1197.4	46.6	25118	56.9	84.3	69.8	1753.4	11.6	386.5	42774	0.29
Mean	107	5342	39.4	345.0	23.9	18892	40.9	37.7	35.6	903.6	6.6	283.0	29213	0.12
Median	101	48	20.3	196.1	21.7	19752	42.8	31.6	35.6	744.0	5.3	315.1	29068	0.09
Std. Dev.	36	10605	43.8	419.8	12.3	5690	13.1	23.8	48.3	448.4	3.3	90.2	10890	0.09

Tab. 3 continued.

Sample	Mn	Zn	Co	Ni	Cu	As	Mo	Ag	Cd	Sb	Hg	Tl	Pb	Co/Ni
BLK 07														
n	3	3	3	3	3	3	3	3	2	3	3	3	3	3
Min	61	71	51.0	760.2	5.3	17554	70.3	5.6	29.5	142.3	2.0	683.1	3930	0.07
Max	101	43809	159.5	1562.7	11.6	19177	125.6	8.7	223.1	280.6	2.5	1044.7	7354	0.10
Mean	78	16968	96.2	1168.3	8.1	18370	92.3	7.7	126.3	214.4	2.4	838.8	5679	0.08
Median	71	7025	78.1	1181.9	7.5	18379	81.1	8.7	126.3	220.2	2.5	788.7	5754	0.07
Std. Dev.	21	23503	56.5	401.4	3.2	812	29.3	1.8	136.9	69.3	0.3	185.9	1713	0.02
BLK 09														
n	7	6	7	7	6	7	7	7	6	7	6	7	7	7
Min	51	26	4.2	280.0	4.5	10010	7.7	1.1	1.3	488.7	0.5	104.0	1950	0.02
Max	194	33904	8704.8	81367.0	16.5	18377	432.4	10.8	49.0	1032.0	4.2	270.9	235551	0.15
Mean	114	12177	2229.0	19223.7	9.5	15083	179.0	4.8	17.9	798.4	2.5	204.6	52570	0.10
Median	111	5481	352.6	2364.9	9.0	16970	204.1	4.6	9.2	850.8	2.8	203.4	8646	0.11
Std. Dev.	51	14963	3499.7	31150.9	5.0	3573	145.2	3.1	20.2	196.2	1.6	63.1	84334	0.05
BLK 10														
n	4	4	4	4	3	4	4	4	3	4	4	4	4	4
Min	82.1	20	52.5	430	5.9	11482	126.7	0.3	17.0	35.9	1.1	203.4	4463	0.11
Max	262.6	46078	10451.9	62193	31.6	44925	753.6	2.6	64.6	546.0	10.9	992.3	21306	0.18
Mean	141.5	24297	4348.7	31017	18.4	28334	462.3	1.5	44.6	380.7	7.0	754.7	11333	0.13
Median	110.7	25546	3445.2	30723	17.7	28465	484.5	1.5	52.1	470.6	8.0	911.5	9782	0.12
Std. Dev.	83.9	19145	5103.5	34526	12.9	17161	331.7	1.1	24.7	238.6	4.6	369.7	8079	0.03
BLK 11														
n	5	3	3	5	3	5	5	4	0	5	2	5	5	3
Min	7.6	4	0.2	2	0.6	2120	41.7	0.1	<LOR	7.0	1.0	208.8	83	0.02
Max	24.0	55	1.5	33	1.3	6062	83.0	0.7	<LOR	91.0	2.0	623.1	2338	0.81
Mean	13.6	31	1.0	11	1.1	4036	62.0	0.3	<LOR	42.0	1.5	411.4	1402	0.34
Median	11.9	33	1.3	8	1.3	3582	62.8	0.3	<LOR	20.4	1.5	368.6	1303	0.20
Std. Dev.	6.2	26	0.7	13	0.4	1872	19.3	0.3	<LOR	40.3	0.7	181.6	952	0.42

Tab. 3 continued.

Sample	Mn	Zn	Co	Ni	Cu	As	Mo	Ag	Cd	Sb	Hg	Tl	Pb	Co/Ni
BLK 12														
n	7	6	7	7	5	7	7	7	3	7	7	7	7	7
Min	84.0	25	8.4	193	2.5	11708	32.8	3.8	1.0	340.9	1.0	147.3	5375	0.04
Max	108.3	34328	68.3	1107	5.2	16764	41.6	11.0	43.9	621.4	8.8	219.8	9213	0.08
Mean	96.5	6952	29.4	502	3.9	13981	35.9	6.4	21.5	466.4	3.5	173.5	6868	0.05
Median	94.0	253	20.6	428	4.2	13592	35.1	5.8	19.5	493.1	2.6	165.2	6709	0.05
Std. Dev.	10.3	13663	22.1	308	1.2	1791	3.1	2.5	21.5	117.6	2.7	23.3	1382	0.01
BLK 21														
n	6	3	6	6	6	6	6	6	2	6	6	6	6	6
Min	43.6	40	54.9	1027	13.1	26984	38.1	2.1	4.6	480.8	1.7	534.2	6330	0.04
Max	76.2	14645	2029.1	37928	248.3	39219	110.6	66.2	50.0	1809.1	15.6	886.4	143785	0.14
Mean	59.7	4960	667.6	10933	91.5	33428	69.0	18.7	27.3	1188.4	7.2	662.0	36368	0.08
Median	59.9	194	251.1	2571	41.6	35599	66.9	5.2	27.3	1181.2	3.9	633.2	9636	0.06
Std. Dev.	13.2	8388	817.3	15136	98.6	5073	24.8	25.6	32.2	549.1	6.5	130.8	54351	0.04

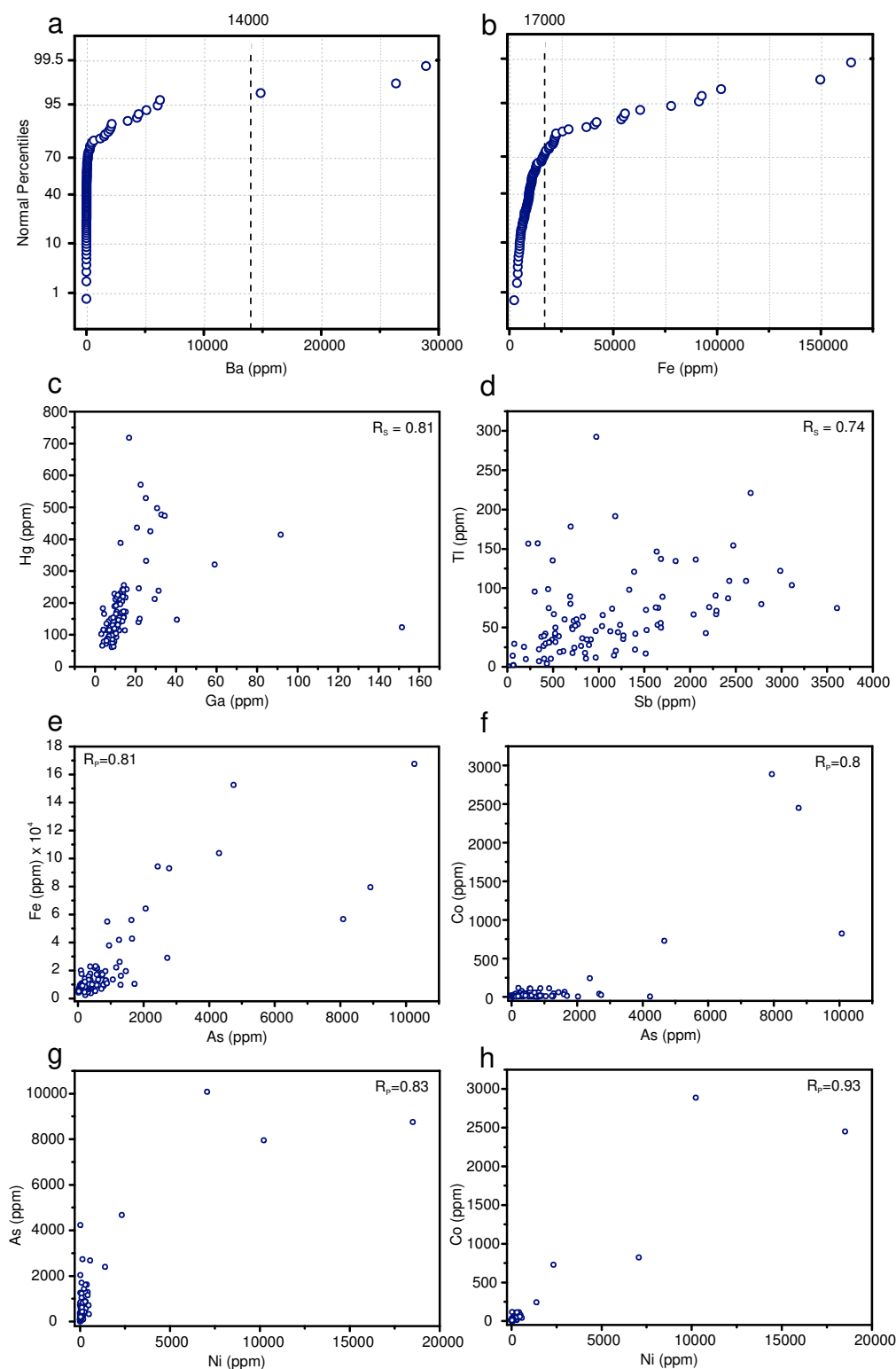


Fig. 6 a.) and b.): Normal probability plots of Ba and Fe in sphalerite determined by LA ICP-MS. a.) Barium concentrations in sphalerite, showing which sample most likely include barite ablation above 14,000 ppm, which are not considered in the following evaluation and interpretation (further explained in main text); b.) Iron concentrations illustrate a wide range, known from SEM data, that Fe concentrations are most likely not above 1.7 wt.%, therefore those analyses are neglected for the evaluation (further explained in main text); c.) through h.) show strong correlations within sphalerite.

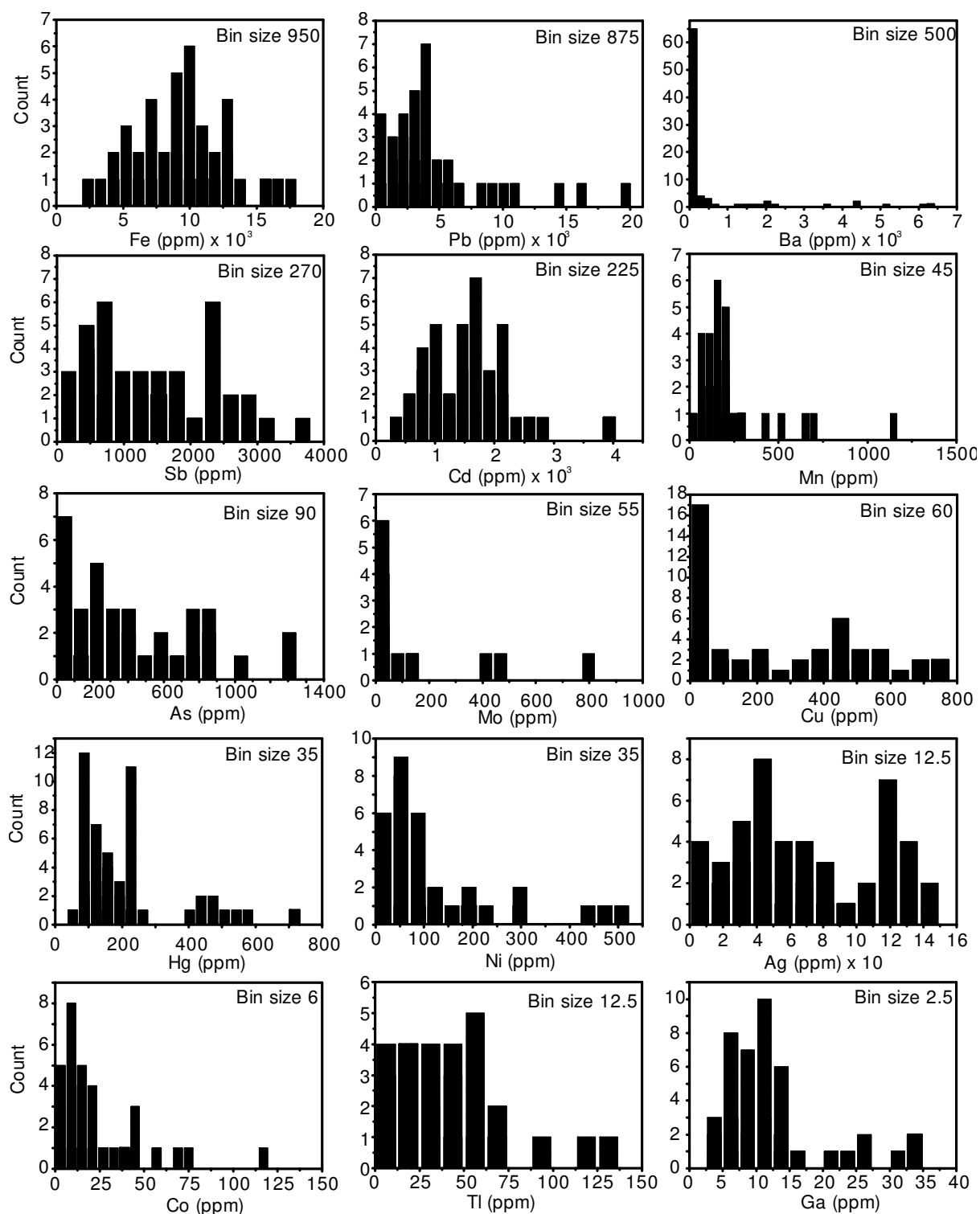


Fig. 7 Histograms for all elements in sphalerite. Bin size was kept between $\frac{1}{2}$ to $\frac{1}{4}$ of standard deviation for each element (Sinclair, 1986).

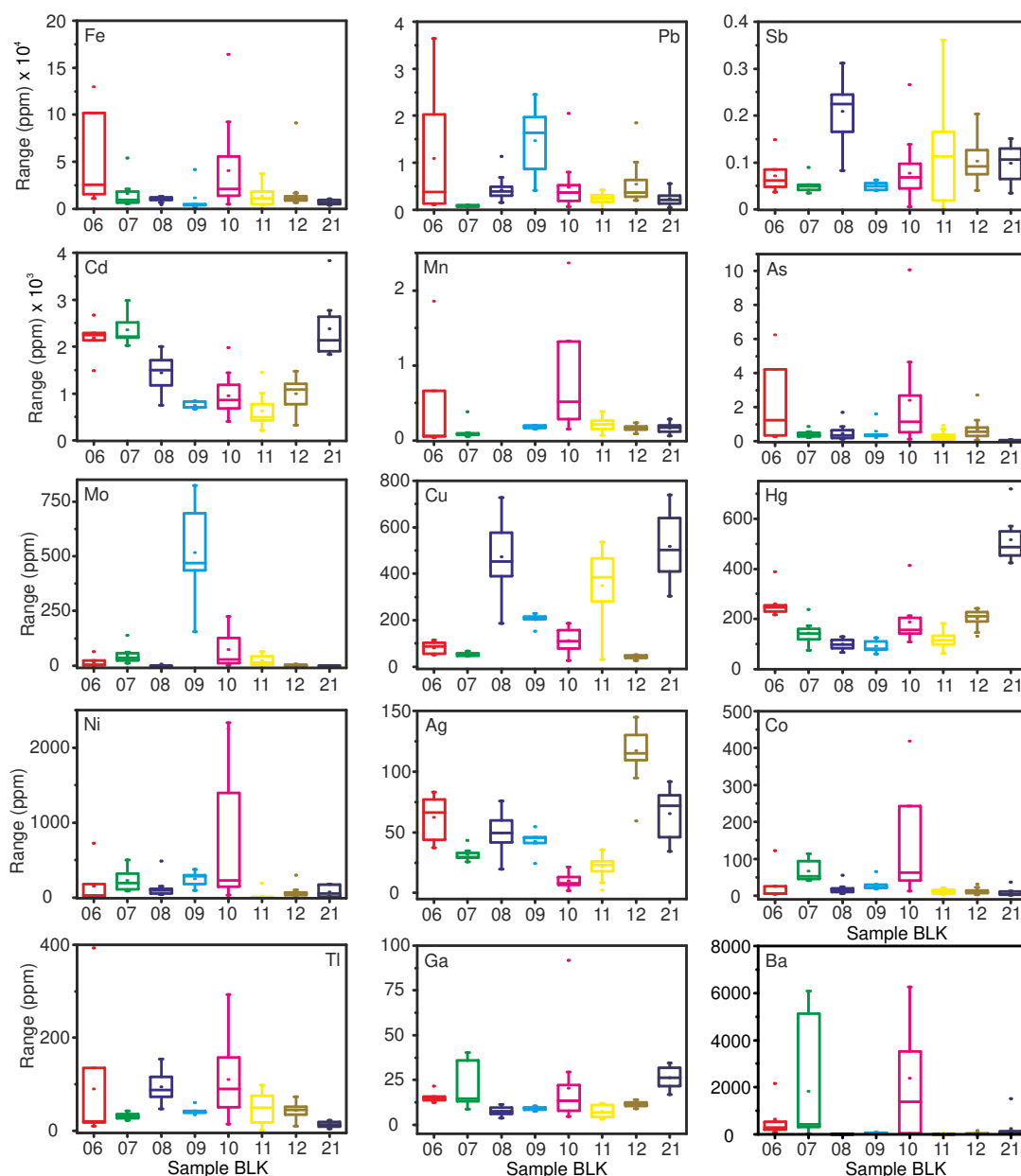


Fig. 8 Box and whisker plots (based on the median for each element) for sphalerite samples at Ballinalack. Note, BLK 6, is not part of the main mineralisation in the Lower Argillaceous Bioclastic Limestone and other samples from Waulsortian Limestone. BLK 07 comprised petrographically, the highest mineralisation.

Petrographically, the highest level of mineralisation is within sample BLK 07, which also is characterised geochemically by high maxima of Co (77 ppm), Ni (503 ppm), Ga (40 ppm) and Cd (2,508 ppm) concentrations and depletions in Mo (max. 138 ppm), Hg (max. 238 ppm) and Mn (max. 101 ppm).

In general, Mn has a significant signature in sphalerites at Ballinalack, its concentration ranges from 37–1,130 ppm (Fig. 7, 8). Clearly, the highest concentrations occur within sample BLK 06 and 10. Copper, Tl and Sb exhibit relatively high concentrations in sample BLK 08.

The analysed colloform sphalerite bands (Fig. 4d) in BLK 11 displays a variation of trace elements, however, without any coherence between each other.

3.2 Pyrite

In this study, pyrites were also analysed in two different drill cores, TC-1344-036 within the mineralisation lens, B 47 east of and slightly outside the defined mineralisation lens (BLK 21). The latter drill core does not have a unique signature compared to other samples, however, upon closer examination, it is relatively high in Sb (max. 1,809 ppm), Hg (max. 76 ppm) and Ag (max. 66 ppm), slightly enriched in Tl (max. 886 ppm) and Pb (max. 14,644 ppm) as well. Furthermore, it displays the third largest Ni and Co concentrations of the samples measured in this study. Bimodal distributions occur clearly in Sb, Tl, Cd, Ag and Hg considering all samples. Nickel and Co are widely distributed (Fig. 9), whereas, As reveals a multi-modal distribution pattern, in the samples from drill hole TC-1344-036 (Fig. 8, 9, 10). Sample BLK 05 represents a low-level group from 9–655 ppm, which is the stratigraphically lowest sample. Medium level groups exhibit concentrations between 2,120 and 20,013 ppm and a high-level group 21,766–44,925 ppm. The high-level group is represented by BLK 21 with minor contributions from BLK 06 and BLK 10.

Other trace elements that typically can occur in high concentrations within pyrites are Co and Ni. Here, Co concentrations vary between the detection limit and 10,452 ppm and Ni between 2 and 82,367 ppm; Ni and Co exhibit a strong Spearman Rank correlation (R_s) with a value of $R_s=0.9$ (Fig. 12). The highest Co and Ni contents are found in samples BLK 09, 10 and 12 (Fig. 11), notably these sections reflect the centre of the mineralisation. A total of 14 analysis exhibit Ni concentrations higher than 2,289 ppm. Apart from one analysis, all Co/Ni ratios are lower than one: median 0.09, mean 0.1 (Fig 10).

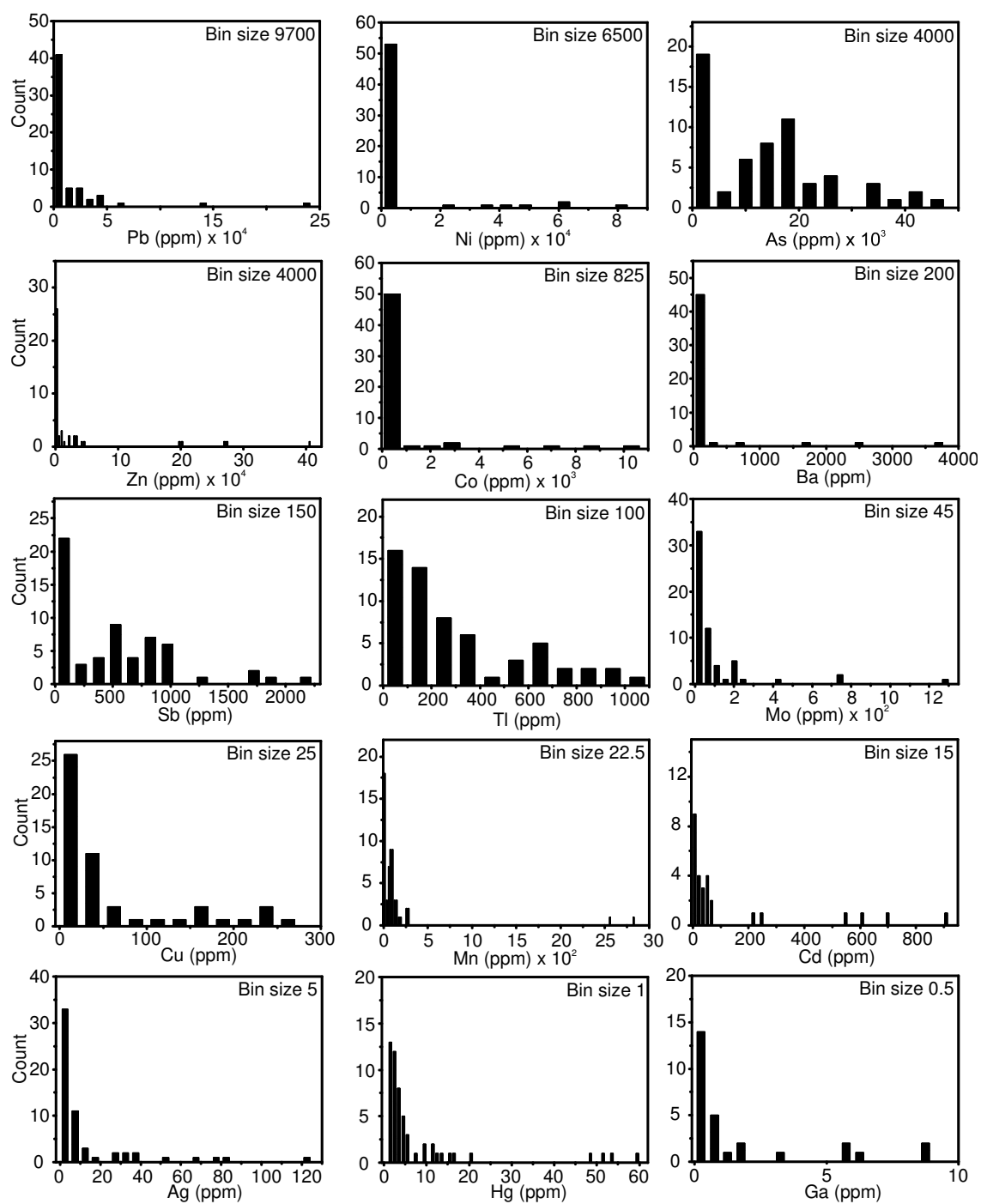


Fig. 9 Histograms showing the variability of elements within pyrites from Ballinalack. Bin size was kept between $\frac{1}{2}$ to $\frac{1}{4}$ of standard deviation for each element (Sinclair, 1986).

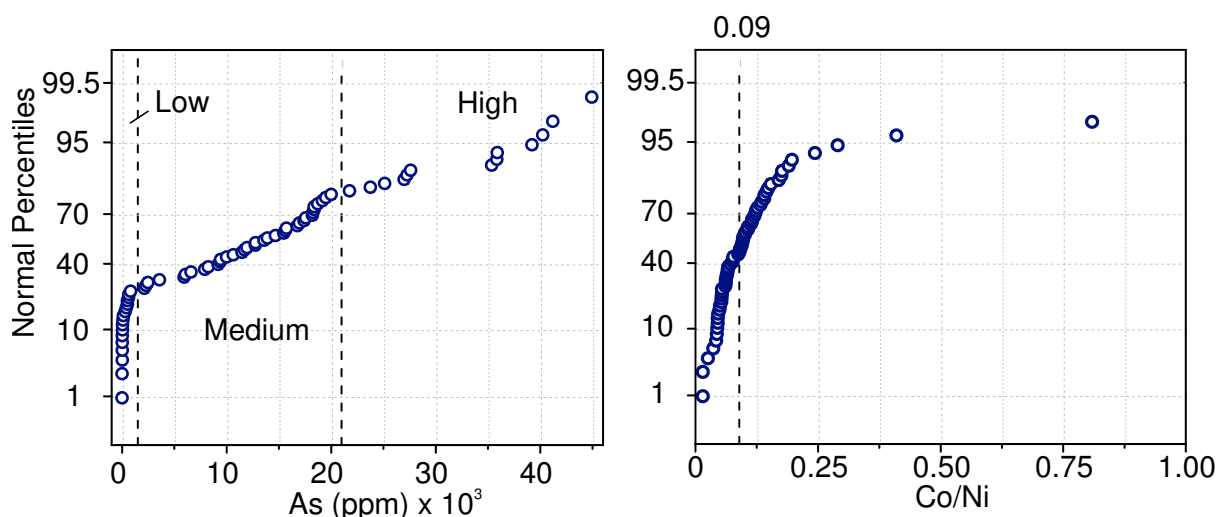


Fig. 10 Probability plot for As and Co/Ni ratio within pyrites of Ballinalack. Left) Arsenic distribution that displays a separation (based on change in slope of normal distribution) into low-, medium- and high-level As concentrations within pyrites. Right) Normal distribution of Co/Ni ratio within pyrites, the median is at 0.09.

Molybdenum varies between 0.3 and 1,275 ppm within pyrite at Ballinalack. The distribution is similar to Co and Ni, one of the lowest concentrations of Mo is within sample BLK 05, with the highest contents found in samples from the centre of the mineralisation. Thallium concentrations exhibit a wide range in values (0.2–1,600 ppm). As stated before, the stratigraphically lowest sample BLK 05 exhibits the lowest concentrations (0.2–12.5 ppm) of Tl, the highest concentrations (886–1,600 ppm) are within sample BLK 07, 10, 11 and 21. Copper concentrations vary between 0.6 and 270 ppm with one analysis measured at 6,984 ppm. Significantly high concentrations of Zn (197,979–404,900 ppm) and Pb (65,647–554,787 ppm) at Ballinalack are associated with sub-microscopic intergrown sphalerite and galena, respectively (Fig. 4a, c). In pyrite at Ballinalack, Ag concentrations are within a range of 0.1 to 124 ppm, and except for one outlier that reaches concentrations of 349 ppm; this outlier is also reflected by higher concentrations of Sn (22 ppm) and Hg (1293 ppm) compared to the other samples (Sn 0.5–4.9 ppm and Hg 0.5–59 ppm). In addition, this analysis line has the highest Ga concentration (104 ppm), the higher concentrations of the elements Sn, Hg and Ga only in one sample, indicates that the ablation includes, apart from pyrite, most likely another phase.

Another notable element is Mn that has concentrations between 4 and 3,423 ppm in pyrites. Three significantly high Mn concentrations between 2,563 and 3,423 ppm come from samples comprising the centre of mineralisation (Fig. 9, 11).

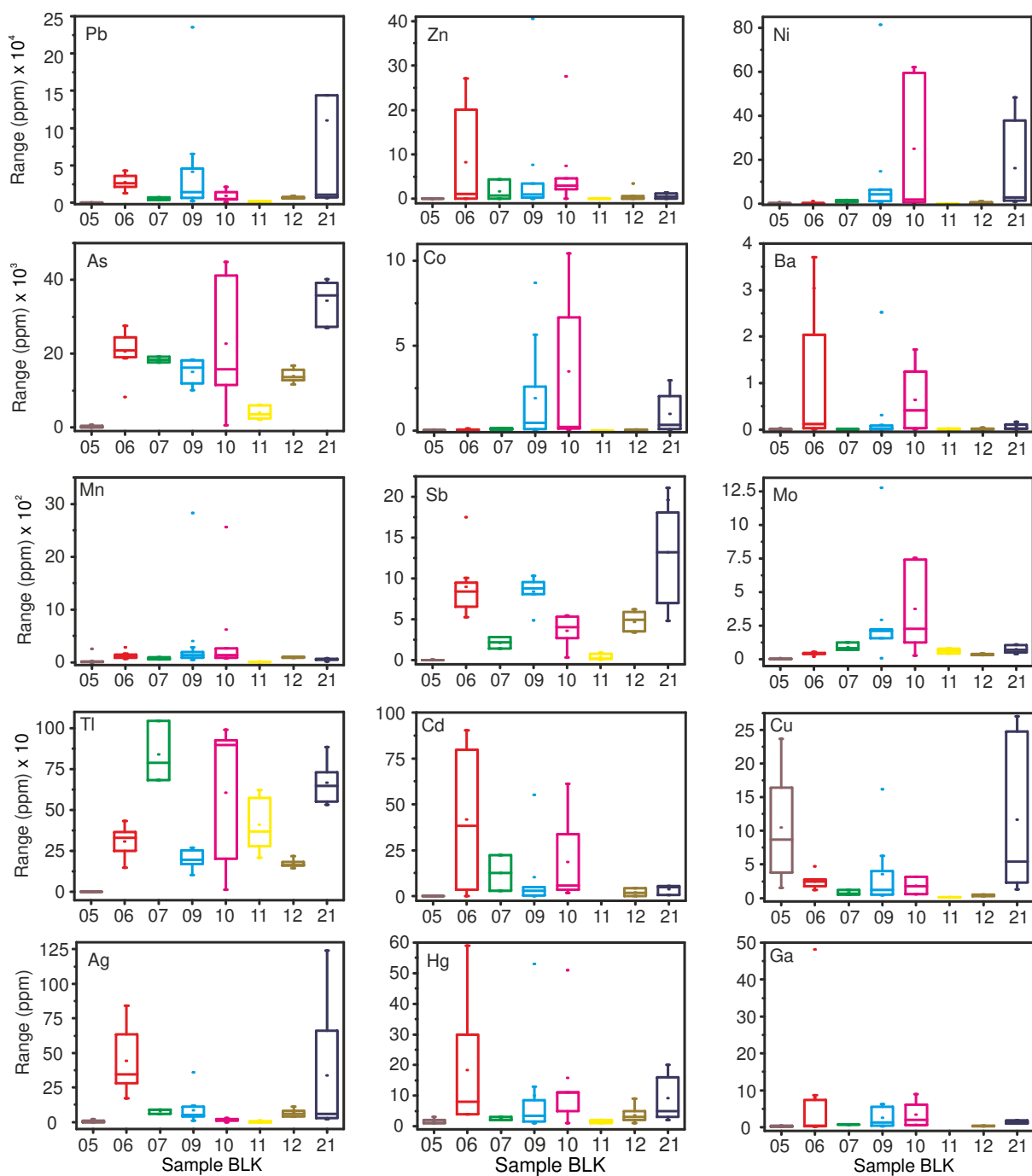


Fig. 11 Box and whisker plots (based on the median for each element) from pyrites at Ballinalack. Note, BLK 06 is not part of the main mineralisation Lower Argillaceous Bioclastic Limestone, other samples from Waulsortian Limestone. BLK 07 comprised petrographically, the highest mineralisation

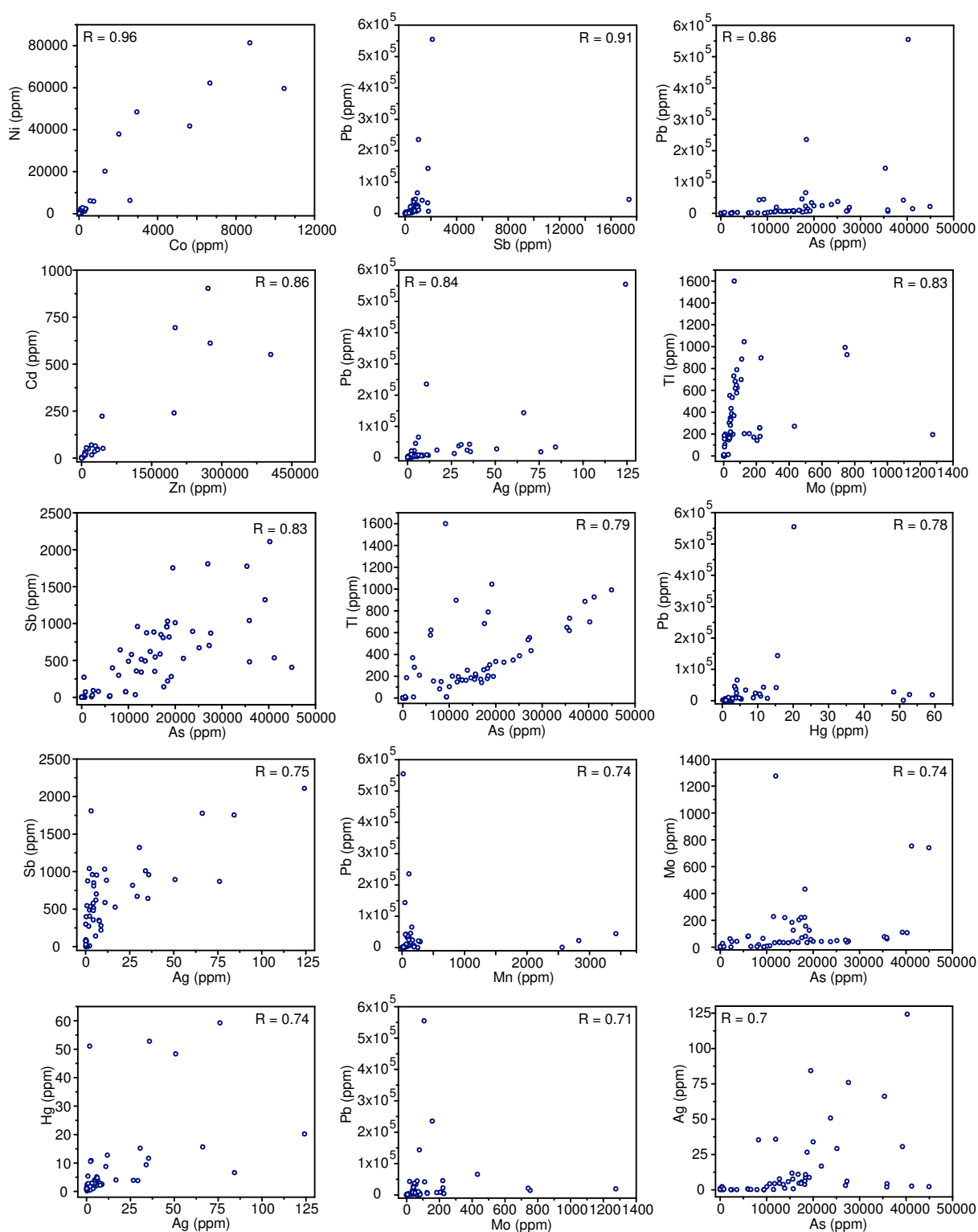


Fig. 12 Pearson correlations of elements within pyrites. Note, correlation of Ni and Co within pyrites, Pearson correlation (R_p) 0.96, Spearman correlation (R_s) 0.93 ($n = 57$).

4 Discussion

4.1 Sphalerite trace-elemental signature

Two different drill cores were compared in this study: TC-1344-036 within the sulphide lens (proximal) and B-47 east (distal) of the defined sulphide lens (Fig. 1), in which sulphide minerals still occur. Interestingly, there is no major difference between these two spatial separated sulphide lenses in terms of sphalerite composition. However, Hg is relatively high in the sample BLK 21. Notwithstanding, Hg has to be treated critically since it is volatile and usually does not occur homogeneously in neither the standard nor the sample. Assuming that Hg is measured in a representative concentration, the following discussion could apply. Usually, higher Hg concentrations correlate with low Fe concentrations (Cook et al., 2009), which cannot be confirmed at Ballinalack. George et al. (2016) also observed Hg in sphalerite, in a mineral assemblage with galena. They claim, that solid solution with Hg-bearing minerals, although a complete solid solution has yet to be determined. Due to the fact that Hg has a high correlation to Cd $R_p=0.81$ and to Ag $R_p=0.77$ ($n = 72$), it may be that Hg is hosted in another phase, like galena. Nevertheless, in the case Hg is a trace element within sphalerite, it may be used as an indicator for a fluid temperature window of between 80 and 150 °C for sulphide mineralisation (Krauskopf, 1951, Tunell, 1964). This observation coincides with temperatures determined in the Waulsortian Limestone hosted Irish Type Zn-Pb deposits; Hitzman and Beaty (1996) provide an overview of Lisheen (Thompson et al., 1992), Silvermines (Andrew, 1986, Greig et al., 1971) and Tynagh (Banks and Russell, 1992, Boast et al., 1981), Garrycam (Slowey et al., 1995) and Derrykearn based on fluid inclusion studies. These studies reveal that fluids leading to sphalerite mineralisation experienced average temperatures between 130 and 280 °C. Wilkinson (2014) summarises that a majority are within 130 and 240 °C. Consequently, these samples from both drill cores offer the same elemental pattern, concluding that they were likely formed at the same time and hydrothermal fluids are from similar sources.

Mineral textures (>100 µm–cm scale) do not show any trend with respect to their chemical character. Also the banded sphalerite (Fig. 4d), that was analysed in each band, does not provide a chemical trend. Notably, this may also be related to the ablation of sub-µm inclusions of the carbonate minerals.

Higher Ga concentrations in sphalerites are also reported within the Lisheen deposit with a reported mean concentration of 600 ppm (Wilkinson et al., 2005b). Remarkably, the sphalerite in Lisheen can also be colloform or fine grained and intergrown with pyrite and galena. Krämer et al. (1987) and George et al. (2016) have also demonstrated that higher Ga

concentrations can occur within sphalerites following substitution processes in low-temperature carbonate-hosted replacement deposits, such as the Ballinalack deposit.

The behaviour and incorporation of Mo in sphalerite is still not completely understood, however, several studies (Huston et al., 1995, Orberger et al., 2003, Cook et al., 2009) show similar and even higher concentrations of Mo in sphalerites, for instance, 5,000 ppm Mo in sphalerite from a black shale-hosted deposit, in the Yukon Territory of Canada (Orberger et al., 2003); these studies suggest that Mo is associated with micro-inclusions within the ablated sample material, that could also be the case for Ballinalack, for instance the ablation of pyrite.

High concentrations of Fe, Ni and Co in sphalerite are likely caused due to a mixed ablation signal (Fig. 4a, c) most likely from pyrites. Although Fe and Co might be elevated in sphalerites as well (Cook et al., 2009, Gagnevin et al., 2014, Kuhlemann and Zeeh, 1995, Ye et al., 2011) it is more likely that Fe, Ni and Co are hosted within pyrites (Roberts, 1982, Koglin et al., 2010, Gregory et al., 2015), hence measured as sub- μm inclusion of pyrite within sphalerite. Also the ablation of ferroan carbonate, could cause higher Fe concentrations, but the strong correlation of Fe to As (Fig. 6e) confirm that this elevated Fe concentration are rather associated with pyrite. Moreover, the intensity profile of the laser ablation ICP-MS measurement (Fig. 13) reveals an oscillating signal of both Fe and As throughout the measurement. At a first glance, the intensity profile of Fe and As within sphalerite may indicate an non-discernible petrographical zonation within the sphalerite, but this is unlikely, due to three reasons: a.) the intensity profile is based on a raster pathway of the laser beam, b.) the repetition of the same pathway twice, c.) the shape of the intensity peaks. If the signals were caused by zonation, a mirrored intensity peak would occur, when the pathway changes its direction backwards; further, the signal peak would be longer. The peak appears to be sharp followed by a decreasing shallow slope, caused by the remaining signal (indicated by dashed arrow in Fig. 13), similar to the signal after the ablation ends before background. Therefore, it could be interpreted as inclusions within the sphalerite.

Cook et al. (2009) argues, based on several studies (Taylor and Radtke, 1969, Cabri et al., 1985, Chrysosoulis and Surges, 1988, Huston et al., 1995, Huston et al., 1996, Kelley et al., 2004) from different mineral deposits with sphalerites that Ag is rarely incorporated into the lattice of sphalerite and rather occurs as sub- μm inclusion minerals, as no correlation between Pb and Ag can be observed galena is the likely host for Ag in the sphalerites from Ballinalack.

Sparse data exists on Tl in sphalerite, however, Murao et al. (1996), Kelley et al. (2004), and Xiong (2007) report Tl within sphalerite grains. Strikingly, Kelley et al. (2004) illustrate that the highest concentrations of Tl are in the youngest (late) form of sphalerite in the Red Dog

Zn-Pb-Ag district, Alaska. However, Wilkinson et al. (2005b) measured Tl within sphalerites from Lisheen using microprobe with a mean concentration of 2200 ppm Tl in sphalerite, displaying much higher signatures than at Ballinalack.

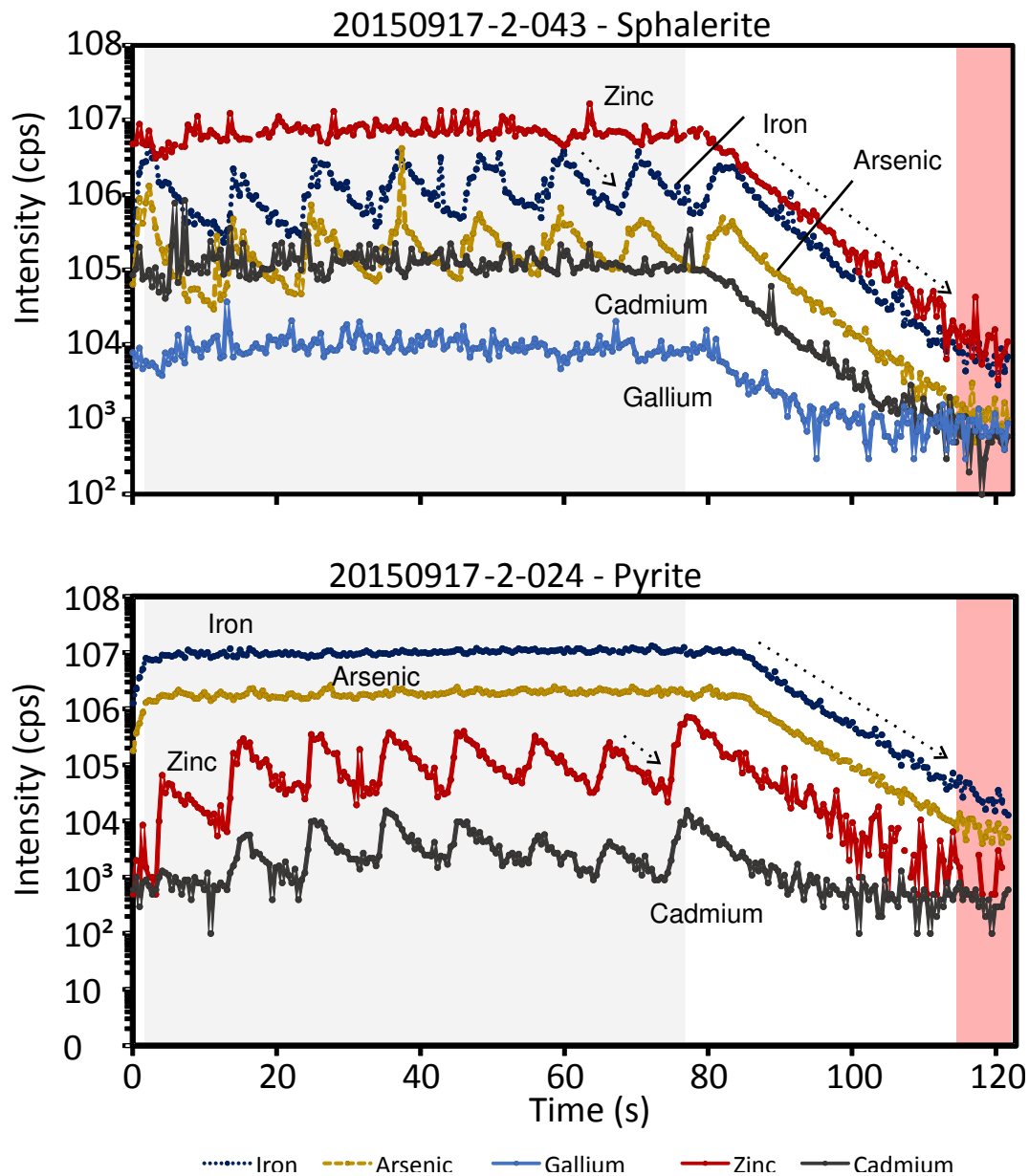


Fig. 13 Intensity plot of laser ablation ICP-MS signal in counts per second logged (y-axes) for a line ablation of Top: sphalerite sample and Bottom: pyrite sample. Top: Showing the oscillation of the Fe and similarly As intensity within the sphalerite grain. Due to a lack of visible zonation in this sphalerite, this is most likely caused by pyrite sub- μ m inclusion. Bottom: Showing the oscillation of the Zn and Cd intensity within the pyrite grain. Due to a lack of visible zonation in this pyrite, this is most likely caused by sphalerite sub- μ m inclusion. Grey background displays ablation signal used as integration box, red box defines background, dashed-arrows indicate the shallow decrease of the remaining signal before reaching background intensities.

Although indium is a very common trace element in sphalerites (e.g., Burke and Kieft, 1980, Pattrick et al., 1993, Schwarz-Schampera and Herzig, 2002, Ishihara and Endo, 2007), this element could not be detected (the signal lower than the limit of reporting) within the sphalerites in Ireland.

In general, elemental variation of sphalerites can be observed within drill core TC-1344-036. Where the highest level of visual massive sulphide is located, BLK 07 is characterised by high Ni, Co, Ga and Cd concentrations, note that even Ni and Co occur as pyrite inclusions. The stratigraphically higher samples BLK 09 and 12 reveal the highest concentrations of Mo and Ag, respectively. Additionally, the comparison to B-47 illustrates opposite trends of high Hg concentrations indicating that these sulphides may be distal signatures. Fusciardi et al. (2003) and Wilkinson et al. (2005b) report high concentrations proximal of Cu, As, Ni and Pb in all sulphides precipitated during the main ore stage at Lisheen, Ireland. This trend can be roughly observed at Ballinalack as well. Paradoxically, Fe-rich pyrite zones (caps) occurring at the top and fringes of the ore zone within Irish type deposits (Fusciardi et al., 2003, Wilkinson et al., 2005b) cannot be demonstrated at Ballinalack (Fig. 8).

4.2 Pyrite trace-elemental signature

Similar to the sphalerite interpretation, a distinction between pyrites from the two drill holes cannot be made. Nevertheless, Hg, Sb, and Ag exhibit some enrichment within sample BLK 21 compared to other samples at Ballinalack.

Also pyrite does not exhibit any chemical trend regarding the different mineral textures (>100 μm –cm scale). All pyrites reveal a similar S (53 wt.%) and Fe (45 wt.%) concentration, close to its stoichiometric composition, which was determined at Ballinalack by SEM-EDX. These concentrations confirm the assumption that most of the high concentrations of Fe, Ni and Co within the sphalerites, in particular, in sample BLK 10, are associated with sub- μm inclusions of pyrite.

Arsenic concentrations can vary significantly, reported values range between 6 and 96,000 ppm (Abraitis et al., 2004). The lower concentrations of As in pyrite can be observed in the stratigraphically lowest samples measured in the Lower Argillaceous Bioclastic Limestone. The zonation of high As concentrations within the centre of the deposit decreases towards distal mineralisation. Similar to As^{3+} , Tl^{3+} and Mo^{3+} can enter the pyrite lattice (Huston et al., 1995). At Ballinalack a strong Pearson correlation ($R_P=0.83$, $n=59$) between Mo and Tl (Fig. 12) suggests that both elements are occurring as substitutions within the lattice of pyrite. The maximum value reported for Mo is as high as 2.8 wt.% (Chenery et al., 1995); however, the

usual range is between 2 and 790 ppm (Abraitis et al., 2004). Relating the Mo concentrations of pyrites with the sphalerite concentrations, the measured Mo concentrations within the sphalerites might have been sub- μm inclusions of Mo-bearing pyrites. Thallium concentrations exhibit a wide range (0–1,600 ppm), which is within the reported concentration in the literature (1–7,830 ppm, Abraitis et al., 2004).

As stated in the results above, the highest concentrations of Ni and Co occur within the samples, which form the centre of the mineralisation. In general Ni in pyrite from Ballinalack is elevated, in this study reaching a maximum of 81,367 ppm, whereas Lisheen reaches up to 19,200 ppm (Wilkinson et al., 2005b), and exceeds the highest reported values measured in pyrites outside Ireland in the North Carlin Trend (9,601 ppm, Large et al., 2009). According to Wilkinson et al. (2011), the significantly high Ni concentrations proximal to the most massive sulphide mineralisation could reflect structural conduits for hydrothermal fluids. This high concentration of Ni in pyrite at Ballinalack requires a Ni-rich source, for instance a mafic source. Generally, Ni is more abundant than Co in most environments. The source could be similar as for Zn and Pb, which is most likely derived from leaching of a deep-seated source, such as the Lower Palaeozoic Basement (e.g., Caulfield et al., 1986, LeHuray et al., 1987, Dixon et al., 1990, Everett, 1999, Everett et al., 2003, Walshaw et al., 2006, Wilkinson and Hitzman, 2010, Wilkinson et al., 2005a, further description later in this chapter). At Ballinalack, this deep-seated source of Ni could be taken into account to explain the high Ni concentrations. Also, these high concentrations of Ni in pyrite could be derived from solid solutions with pentlandite (Shewman and Clark, 1970, Craig, 1973), and (or) vaesit NiS_2 however, further studies are required to understand the high Ni concentrations, for instance, separation of pyrite and detailed X-ray diffraction spectroscopy.

In contrast to other studies on pyrite (Einaudi, 1968, Griffin et al., 1991) no correlation of As and Cu-bearing pyrites can be observed, leading to the conclusion that the high Cu concentrations may be related to a sub- μm inclusions of chalcopyrite (Oberthuer et al., 1997) and (or) tetrahedrite.

Lead, Zn and Cd form a group of elements, which may occur as sub- μm inclusions in the pyrite grain (Huston et al., 1995, Griffin et al., 1991). However, according to Oberthuer et al. (1997) they could be hosted within the pyrite lattice. Nevertheless, lower concentrations could originate from those inclusions as well. A closer look into the ablation intensity of Zn and Cd within some pyrite grains, that do not reveal zonation within the pyrite, display an oscillation pattern of Zn and Cd (Fig. 13), indicating that it is not a pure pyrite grain (further explanation regarding the intensity profile is described in the discussion below). In addition, its

strong correlation between Zn and Cd ($R_p=0.91$, $n=25$) leads to the assumption that Cd is likely associated with sub- μm inclusions of sphalerite in the pyrite grains.

It is unclear if Ag occurs within the pyrite lattice (Cabri et al., 1985) or if higher concentrations are caused by ablation of sub- μm inclusions of argentiferous galena, tetrahedrite or tennantite (Huston et al., 1995). In fact, Ag correlates strongly with Pb ($R_s=0.81$, $n=58$), since Ag also correlates with Hg $R_p=0.74$ (Fig. 12), and Hg is also an element which incorporates into the lattice of galena (Bethke and Barton, 1971, Foord et al., 1988, Tauson et al., 2005). Therefore inclusions of galena most likely influence the pyrite signature at Ballinalack.

Reported Mn concentrations within pyrite vary between 7 and 36 ppm (Nickel, 1954). However, recent LA ICP-MS analyses on sedimentary pyrites reveal concentrations of Mn between 0 and 16,503 ppm (Large et al., 2014) and marine pyrites of 0–13,500 ppm (Large et al., 2017). The high concentrations at Ballinalack (3,423 ppm) might be due to ablation of host rock minerals (ferroan carbonate or dolomite), sub- μm inclusions of carbonates, a substitution of Mn^{2+} with Fe^{2+} or as isomorphous substitution of Mn in pyrites (Fleischer, 1955). According to Large et al. (2017), who conducted elemental mapping of zoned pyrites using images of LA ICP-MS element distribution, Mn most likely occurs in both pyrites and matrix/inclusions. Also, sphalerite sub- μm inclusions are present within the pyrites. As stated above, Mn is a common trace element within sphalerite and galena (Bethke and Barton, 1971). Therefore, a combination of all theories could cause the higher Mn concentrations within pyrites at Ballinalack.

A stratigraphic variation of pyrites from Ballinalack can be characterised by an enrichment of Mo, Co, Ni, Mn and As in samples BLK 09 and 10 (Fig. 14) that is stratigraphically above the highest mineralised zone within the Waulsortian Limestone.

A general trend is illustrated within the sulphides of the same element enrichment at Ballinalack. Nickel, Co, Mo and Mn are relatively high within these sulphides. The similar elemental pattern reveals that they are from the same hydrothermal source and event. The characterisation and combination of both sphalerite and pyrite may be used as a proximal-distal indicator within mineral exploration, after an extensive study of more samples and other Irish-type deposits.

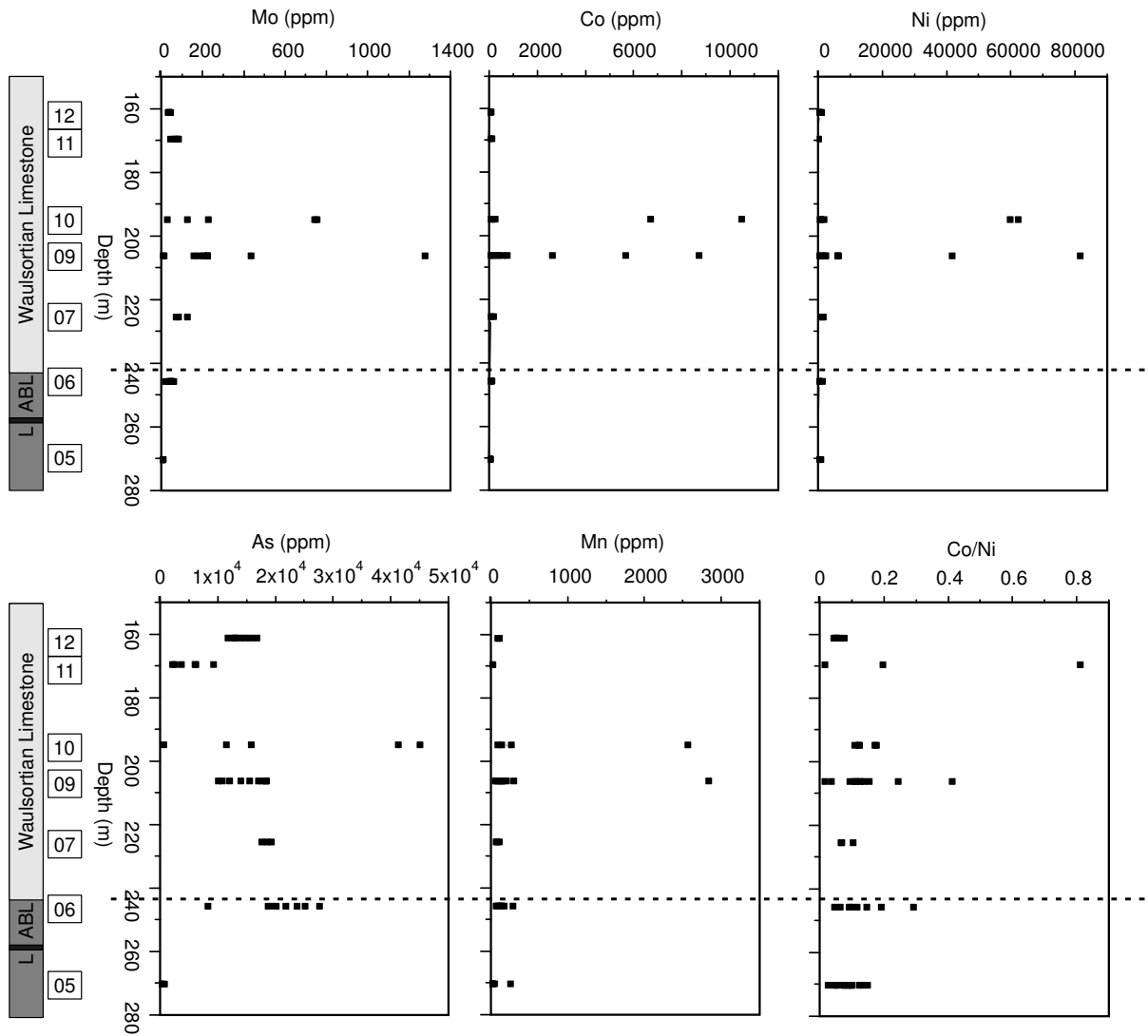


Fig. 14 Stratigraphic variation in pyrites within drill core TC-1344-036 from Ballinalack. The elements Mo, Co, Ni and Mn exhibit the same pattern with an enrichment in the centre of the mineralisation. Arsenic is similar to those elements as well. The Co/Ni ratio does not vary greatly, apart from one sample in BLK 11, in which many inclusions occur within the pyrites, therefore this ratio is most likely not a pure pyrite signature. Area beneath dashed line displays zone not part of the main mineralisation. BLK 07 is petrographically the highest mineralisation.

4.3 Pyrite Co/Ni implications

The ratio of Co/Ni is empirically used as an indicator to help understand the ore genesis. Early studies by Loftus-Hills and Solomon (1967), Price (1972) and later confirmed by e.g., Bralía et al. (1979), Bajwah et al. (1987), Rimmer (2004). They suggest a distinction of I) sedimentary or diagenetic origin in shales with high Co and Ni concentrations and $\text{Co/Ni} < 1$, II) volcanic origin or hydrothermal origin without associated Pb and Zn minerals and $\text{Co/Ni} > 1$,

and III) volcanic origin with association of Pb and Zn minerals with low Co and Ni concentrations and $\text{Co/Ni} < 1$ (Loftus-Hills and Solomon, 1967).

At Ballinalack, the ratio of Co/Ni is lower than one with a maximum of 0.81 in pyrites that would indicate according to the model presented above, that they are derived from either a sedimentary origin or diagenetic origin, or a combination of both. As stated, Ballinalack is formed in a sedimentary system and based on previous alteration studies (Byrne, 2006), the sediments also underwent diagenetic processes, therefore the pyrite is most likely associated with sedimentary and diagenetic processes. But petrographic investigations clearly reveal hydrothermal textures of the pyrites (e.g. Fig. 4b). Thus an implication of the genesis of the pyrite drawn by only the Co/Ni ratio can be misleading. Irish type mineralisation is thought to have formed from fluid mixing of metal-rich fluids from the basement that encountered S-rich fluids from the former sea floor and then precipitated rapidly. Sulphur isotopic studies at Navan reveal two major signatures of $\delta^{34}\text{S}$ around -15 ± 10 ‰, representing bacteriogenic sulphides within an open system, where bacterial reduction of Lower Carboniferous seawater sulphate took place and $\delta^{34}\text{S}$ around $+10 \pm 10$ ‰ values that reflect diagenetic pyrites (Boyce et al., 1983, Anderson et al., 1998, Fallick et al., 2001, Wilkinson et al., 2005a), similarly S isotope studies reveal the same trend for Ballinalack (Caulfield et al., 1986). More important, as stated already above, the metal source, also for Ni, is possibly situated in the Palaeozoic basement. This theory has been supported by Pb isotopes (Caulfield et al., 1986, O'Keeffe, 1986, LeHuray et al., 1987, Dixon et al., 1990), as well as Sr, C and O isotopes (Everett, 1999, Wilkinson, 2003, 2005a). Isotopes of Nd (Walshaw et al., 2006) and H isotopes (Wilkinson and Hitzman, 2010) indicate an interaction with the crystalline basement. The Palaeozoic basement most likely have been mafic or ultramafic to explain such high Ni concentrations observed at Ballinalack and it explains also the very low Co/Ni ratio. Thus the Co/Ni ratio after Rankama and Sahama (1952) is not applicable for the sulphides at Ballinalack.

Interestingly, Wilkinson et al. (2005b) measured Co and Ni within pyrites as well (by electron-microprobe) and their mean concentrations result in a Co/Ni ratio of 0.57. This is slightly higher than at Ballinalack that can be explained by the very high concentration of Ni occurring in the pyrites at Ballinalack. Further, it could be caused due to a wider sampling from four different ore zones.

5 Conclusion

The sulphide mineral investigation of sphalerite and pyrite displays that most sulphide minerals contain other inclusions, for instance, pyrite in sphalerite and vice versa. In addition, galena is a common sulphide inclusion, therefore, it is evident that sulphides in the Ballinalack deposit are not homogeneous (sub- μm inclusions) and are intergrown with each other. Iron, Co and Ni within the sphalerites are therefore ablated pyrite sub- μm inclusions; Pb, Ag and Hg are associated with galena ablation in both sphalerites and pyrites. Zinc within pyrite is most likely due to ablated sphalerite sub- μm inclusions. Neither in Lisheen (Wilkinson et al., 2005b) nor in Navan (Gagnevin et al., 2014) are such sulphide inclusions reported (caused by mineral replacement processes), which could be an indicator of deposit grade; further investigations of other deposits are necessary.

The following observations can be used for the characterisation of the sulphides at Ballinalack:

- Comparison of sphalerites and pyrites illustrates that the mineralisation in drill hole B-47, outside of the main sulphide lens, is associated with the main mineralisation and reflected in the same elemental pattern; however, the highest Hg concentrations in sphalerites and to lesser extent in pyrites are within the samples of B-47, distal to the centre of the main sulphide lens.
- Pyrite samples exhibit a very low median Co/Ni ratio of 0.09, mainly caused by very high Ni concentrations derived from the Lower Palaeozoic basement. Further analyses of pyrites from different Irish type deposits could provide more insight into the source of Irish Type deposits.
- Cadmium concentrations of sphalerites tend to increase with increasing stratigraphic depth, and the highest Ga concentration in sphalerite in sample BLK 07 mirrors the most mineralised area within drill core TC-1344-036. Pyrites are characterised by high Ni, Co and Mo concentrations within sample BLK 09 and 10. The element As is elevated in pyrites in sample BLK 10. These samples are stratigraphically higher than BLK 07 and form the centre of the mineralisation lens.
- To complement the studies of Fusciardi et al. (2003), and Wilkinson et al. (2005b), a distinct signature for sulphides and pyrites can be added with the results from Ballinalack. Proximal fingerprints are characterised by high Ga signatures in sphalerite and for pyrite corresponds to elevated As, Ni, Co, Mn and Mo values. Distal sphalerites may be enriched with Hg, whilst the distal pyrites may be characterised by low Tl concentrations. However, distal characterisation has to be taken with caution, as it is only based on one drill core and one sample.

- Moreover, these results will help guide soil geochemists in the targeting proximal mineralisation signatures.

Further investigation of other Irish type deposits, in particular, pyrites but also galena, could reveal further insight into the nature of this type of deposits.

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Chapter 4: Trace-element patterns within soil BC horizons and top of the till above the Ballinalack, Zn-Pb deposit, Ireland: implications for mineral exploration

Abstract

Metals such as Zn, Fe, As and Pb are commonly found in lower concentrations in soils, but may exhibit higher anomalous concentrations in areas prospective for mineral deposits. These signatures can occur as a result of natural dispersion from metal-bearing geological formations and (or) from anthropogenic sources. As a result, soil and till sampling is a common mineral exploration tool to detect these blind (buried) base-metal deposits. The sub-economic Ballinalack Zn-Pb deposit in the Irish Midlands provides an excellent example to test such surveys in pasture land on glacial soil/till. In addition, it provides two geological case settings, a shallowly buried (1.5 m deep) sulphide lens and a deeper buried (150 m deep) sulphide lens within an area of approx. 1.1 km². The sulphide mineralisation is composed of sphalerite, pyrite and galena, with lesser marcasite, arsenopyrite and trace phases. The BC horizon of the soil profile and the top horizon of glacial till were collected above the two sulphide lenses considering the change from the lithologies from Calp to Supra Waulsortian Limestone to Waulsortian Limestone in underlying bedrock geology. Elevated concentrations within both soil and till were compared to and validated using background-control sites. Principal component analysis and enrichment factors (EF) were employed to exclude the influence of underlying bedrock geology. This method disconfirms an anticipated geochemical enrichment of Fe (2,800 ppm, EF = 0.3), Ni (64 ppm, EF = 0.26), Co (11 ppm, EF = 0.27) as well as Cr (42 ppm, EF = 0.5), Mg (3,700 ppm, EF = 0.04) and V (53 ppm, EF = 0.5) in the top of the till above the deeper buried sulphide body. However, the enrichment factor and the single location occurrence disprove their trueness. Whereas, Pb (soil, max. 6,430 ppm, EF = 58), Cd (soil, max. 68 ppm, EF = 38), As (soil, max. 295 ppm, EF = 4), Ag (soil, max. 20 ppm, EF = 32), Tl (soil, max. 9 ppm, EF = 17), Zn (till, max. 13,150 ppm, EF = 17), Sb (till, max. 197 ppm, EF = 14) and Ba (soil, max. 1,230 ppm, EF = 3) anomalies reflect the underlying shallow sulphide lens in both soil and till. Due to soil formation from limestone as parent material, larger calcareous clasts buffer the pH of the host soil and till. A constant higher pH above the shallow sulphide lens is related to the thin overburden and thus more interaction with calcareous lithologies in the underlying bedrock. Hence, the pH, which is also often used as an indicator for mineral exploration, must be carefully applied in calcareous systems like the Irish Midlands. Furthermore, the effects of a reduced chimney model cannot be confirmed after

a survey of 163 soil BC horizon and top of the till samples with a high sample resolution of 25 m spacing. Even though the geochemical signature is mixed within the soil and till at Ballinalack, the shallow mineralisation is still detectable by concentration measurements at a sample depth of 20 cm. Despite the anthropogenic (mainly agricultural) use of the area, minor impact from pasture land use can be observed in the results. The glacial movement also had a minor impact on the soil and till geochemistry for mineral exploration. This study provides new insights into mineral exploration on pasture lands in areas of mineralisation hosted by calcareous lithologies.

1 Introduction

The need for exploration of base metal deposits is continually expanding, but how do we continue to discover new ore bodies, when many of the shallowly occurring deposits have been found using conventional techniques? Among exploration methodologies (review of geophysical methods in Hoover et al., 1995 and references therein), a very common and successful technique is soil geochemistry (e.g., Cameron et al., 2004, Hamilton et al., 2004a, b, Fabris et al., 2009, Plouffe and Ferbey, 2016). These studies are mainly focused on mineral exploration in glaciated terrains, and are summarised in more detail in Hamilton (2007). Further, Cohen et al. (2010) outlines its general development and use in geochemical mineral exploration. Soil geochemical surveys above blind (buried) deposits do not only consider geochemical signatures, they also include investigations of spontaneous potential, pH and redox variation within soil and/or till horizons. Moreover, they provide guidance to soil sample surveys, including the choice of digestion method (i.e., aqua regia versus selective leaches like distilled water, Enzyme Leach, Na-pyrophosphate and Mobile Metal IonTM) and varying the sample depth, as well as additional soil techniques such as soil hydrocarbon methodology (e.g., Carter and Cazalet, 1984, Fletcher et al., 1986, Cameron et al., 2004, Hamilton et al., 2004b, Hamilton, 2007).

Most of these case studies in glacial terrains were performed in pristine areas such as in North America or Scandinavia, rarely in Great Britain. In actual fact, there are likely many other studies, conducted by exploration companies who have compiled data in unpublished internal reports. Early studies for deeply buried sulphide deposits successfully applied organic carbon, hydrocarbon and conductance in the soil B horizon above sulphide deposits (e.g., Key Anacon, White Lake) in glaciated terrains in Canada (Govett and Chork, 1977). Cameron et al. (2004) summarised trace-elemental case studies in detecting buried sulphide deposits in soils of a volcanogenic massive sulphide (VMS) deposit in a glaciated terrain in Ontario covered by 30 to 240 m of overburden. It is revealed that anomalous concentrations in soils are present above the mineralised zones. It is suggested that over time the metals were transferred and incorporated into secondary minerals within the soil. Interestingly, the soil anomaly above the VMS deposit in Ontario, must have formed within a few thousand years, after the glacial sediments were deposited. Their observations reveal elevated concentrations of Pb, Zn and Cd in the soil above the sulphide bodies, but their transport process could not be explained completely by using the reduced chimney model (Hamilton, 1998, Hamilton et al., 2004b). Moreover, van Geffen et al. (2012) further investigated buried VMS mineralisation of the Talbot prospect in Ontario. In the till (30 cm underneath surface), which covers the sulphide

mineralisation (100 m depth) and that is composed of dolomite and glacial till, anomalies of Zn, Cu, Ag, Pb, Au, Mn, Hg, Cd, Co, Bi and Se occur and their upward transport towards surface was explained using the hypothesis of advection of groundwater under remnant hydrostatic pressure from a retreating ice sheet, for more details see Chapter 2.

A few soil geochemical studies were conducted in Great Britain, in areas similar to Irish Midlands, which also experienced glaciation. For instance, Al Ajely et al. (1984) investigated among plant samples, soil B horizon samples in the Coed y Brenin forest above a 6–30 m buried porphyry-style Cu mineralisation in North Wales. Elevated concentrations of Cu and Mo within the soil were associated with hydromorphic processes and groundwater flow. In Scotland, Coats et al. (1984) studied soil, till and peat samples associated with stratabound mineralised (base metals) horizons in the Dalradian Supergroup. They conclude that the anomalous concentrations of Cu and Zn that are displaced several 10 m can successfully be used only in combination with geophysics. These elevated concentration are formed due to soil fluctuation and hydromorphic transport.

Till geochemical sampling revealed a Pb dispersion train following the former down-ice direction in West Ireland, Lough Derg, as a result of post-glacial weathering and hydromorphic dispersion (Miller, 1984). Mobile elements, such as Zn and Cu were mixed and too dispersed as indicator elements. Also Sb was used as indicator element in till geochemical studies in Ireland (Keel, Avoca, Glendinning). As a trace element within sphalerite, galena as well as arsenopyrite, Sb was found as an anomaly caused by hydromorphic processes in till (2 m of overburden) and peat (Moon and Hale, 1984).

In Ireland, other surficial exploration surveys successfully discovered mineral deposits. Boulders along field boundaries lead to the discovery of lithium pegmatites in the Caledonian Leinster granite, followed by successful stream-sediment and soil geochemical surveys in the form of Li anomalies (Steiger, 1977). In the same area between Aughrim and Tinahely, stream sediments indicated scheelites drained from the Leinster granite. The follow-up shallow soil sample survey revealed anomalous concentrations of W and As, with that a more precise source was known (Steiger, 1977).

Here I present the results of a soil and till geochemical survey over an undisturbed carbonate hosted Zn-Pb deposit in reworked pasture lands of the Irish Midlands. The prospective Ballinalack Zn-Pb deposit in the Irish Midlands has been affected by the Midlandian glaciation and to a greater extent anthropogenic land use, in particular agriculture; both overprint the soil and till geochemical signatures. Various influences can be characterised in this area, and summarised in three groups; I) geogenic: parent material including underlying

geological units, fault systems, and possibly sulphide minerals, II) Quaternary geogenic: the soil and till system itself with soil and till thickness, topography, water table and its lithological composition (including its abundance of clasts), and III) anthropogenic: surface influences from dust pollution, peat cuts, former farm houses, fertiliser, drainage systems, agriculture and pasture land. Moreover, this sulphide deposit can be divided into two geological case settings; a) shallowly buried sulphide mineralisation with approximately 1.5 m overburden without cover rock and b) deeply buried sulphide mineralisation with up to 150 m of cover rock and overburden. The direct comparison of the shallowly and deeply buried setting provides new insights into the soil geochemical techniques employed by mineral exploration and its feasibility in testing of deeper sulphide mineralisation as well as the impact from the last glaciation and more recent land use. Furthermore, this study verifies the sample media of soil and till for mineral exploration in the Irish Midlands. The investigation uses an aqua regia digestion for elemental concentration analysis, as well as pH, and loss-on-ignition measurements on both soil and till samples. An anticipated reduced chimney model after Hamilton (1998, 2000), which has guided the current licence holder Teck Ireland Limited for orientation studies (Clarke and Reed, 2009, Cook, 2010), was tested by the study presented herein. These results may offer a new understanding of the impacts of glaciation and agriculture (pasture land) on surficial geochemical anomalies.

1.1 Reduced chimney model

The reduced chimney model (Fig. 1) after Hamilton (1998, 2000) is a widely accepted model to explain elemental transport from a sulphide mineralisation through overburden towards the surface, where anomalous concentrations can be detected and used for mineral exploration. Some prerequisite conditions are necessary and further described in Chapter 1. Most importantly is that the sulphide mineralisation serves as good conductor and is in direct contact with the groundwater. In case, the setting of a sulphide mineralisation reveal an upward-increasing redox gradient, a self-potential of the sulphide mineralisation may develop, comparable with a voltaic cell. A continuous release of electron would take place above the sulphide mineralisation, leading towards a more reduced environment at the top of the sulphide body. Due to the consumption of oxidising agents, an excess of electrons shift the reduced zone upwards. Simultaneously, the electrons following the shift including its self-potential and thus are translocated among the direct upwards direction also towards the sides of the system. As soon as the electrons encounter an oxygen rich water table, an increase of pH affects the environmental conditions and element mobility, such as Fe, Mn, etc. are mobilised. The mobilised elements become translocated following perpendicular the potential lines. Typically,

this results in a two-peak (rabbit-ear) anomaly at the flanks of sulphide mineralisation at the surface in form of reduced anions (Fig. 1). And an inward movement of oxidised cations are found in the centre, above the sulphide mineralisation at the surface, leading to a one-peak (apical) anomaly.

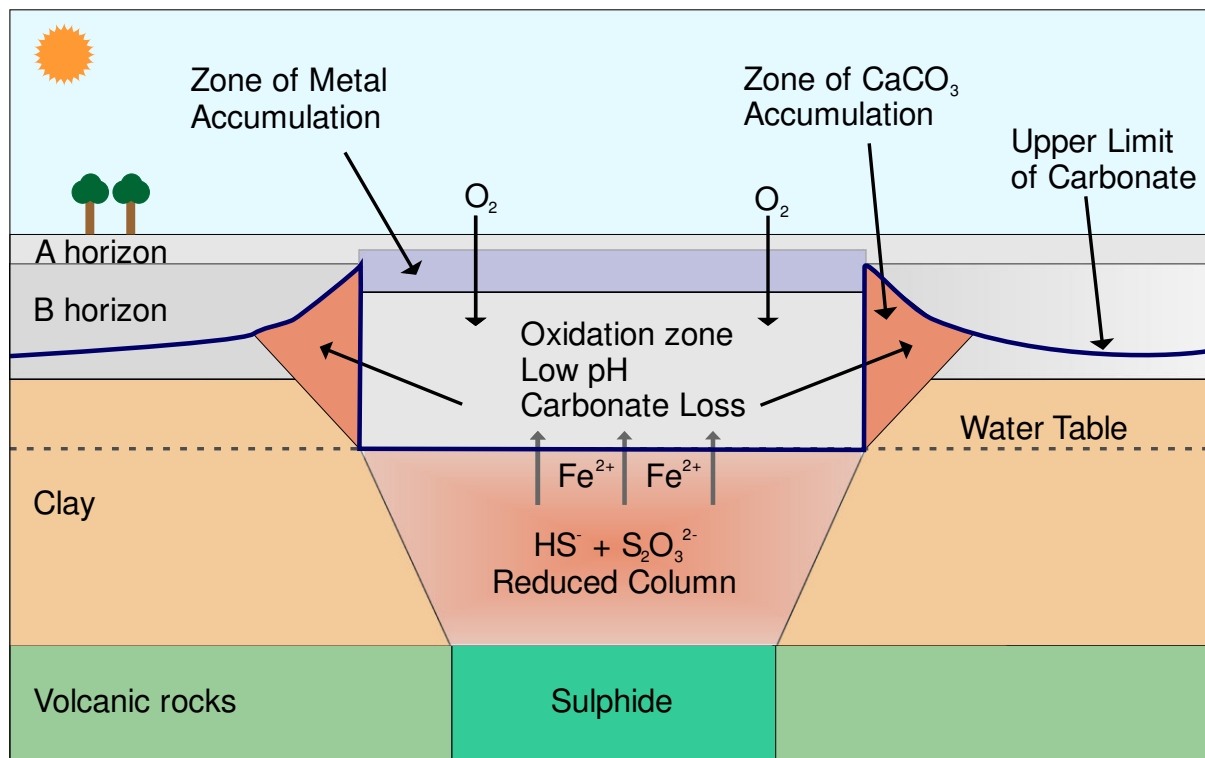


Fig. 1 Reduced chimney model after Hamilton (1998, 2000) to explain elemental transport from a sulphide mineralisation towards the surface through overburden.

1.2 Background - Element mobility in soils

In order to understand processes affecting geochemical signatures within soil profiles over the Ballinalack Zn-Pb deposit, it is important to draw upon what work has been carried out in a number of terrains; a short summary of element mobility is provided for selected elements of interest (for more information see Chapter 2).

Broadly, Shacklette and Boerngen (1984), have shown that organic-rich soils tend to hold more Ag than mineral soils. The organic matter along with pH-Eh conditions within the soil controls the element behaviour (Jones et al., 1990). Humic substances within the organic matter are responsible for the adsorption of metals, therefore an accumulation can occur within the near surface soil environment.

The behaviour of Pb and its reaction with soil compounds is still inconclusive in terms of which components adsorb Pb. However, Norrish (1975), Riffaldi et al. (1976), Tidball (1976), and Schnitzer and Kerndorff (1981) report that Pb mainly interacts with clay minerals,

Mn oxides, Fe and Al hydroxides as well as soil organic matter. Li and Shuman (1996) point out that metal adsorption by soil organic matter is higher than by hydroxides. Furthermore, Basta et al. (2005) illustrate that the soil organic matter sorption of Pb increases with increasing pH; whereas, Sipos et al. (2005) report a stronger fixation by clay minerals rather than soil organic matter. In general, Pb can accumulate in surface soils associated with soil organic matter (Jin et al., 2005) or in deeper soil horizons as shown for podzolic soils in the forests of Norway (Steinnes and Friedland, 2005).

During weathering, Tl can be mobilised and transported with other alkaline elements, although it is often fixed by clays as well as Mn and Fe hydroxides. It also exhibits similar behaviour to K and has a strong affinity for layered silicates and mica minerals (Frantz and Carlson, 1987).

The behaviour of Sb during weathering is not fully understood, however, it can occur as a soluble form or mixed with humates. In general, the element is known to be easily adsorbed in minerals and would therefore be easily accommodated in clay minerals and hydrous oxides (Kabata-Pendias, 2011).

Zinc content within soils strongly depends on constituents of the soil; low concentrations can be expected in sandy soil, whereas, high concentrations usually occur within calcareous and organic soils. In addition, agricultural practices can also increase the Zn content of the surface soils (e.g., Huang and Jin, 2007); mobilised Zn can be trapped strongly in the lattice of clay minerals (Vega et al., 2007, Peganova and Eder, 2008).

Near-surface soils are generally low in As, although it can be more concentrated in organic-rich layers or when soil is acidic and contains sulphates (Dudas, 1987). According to Kabata-Pendias and Sadurski (2008) ferric hydroxides mainly control the behaviour of As within soil, in addition, it correlates strongly to Fe oxides (Manaka, 2006, Deschamps et al., 2003). Moreover, its strong adsorption by clays and hydroxides, as well as soil organic matter limits the mobility of As. Remarkably, up to 90 % of the As can be fixed within the clay granulated fraction (Kabata-Pendias, 2011).

Cadmium is highly mobile in both acidic and near-neutral pH environments. Consequently, during weathering it is readily mobile and forms complex ions as well as chelates, which can be either cationic or anionic species (Kabata-Pendias and Sadurski, 2008). Further, Cd has a strong affinity to soil organic matter (Basta et al., 2001); John (1972) adds that Cd is even more likely adsorbed by organic matter than by clay minerals. Soon (1981)

supports the trends, showing that with increasing pH, the sorption of Cd by soil organic matter increases.

1.3 Geology

The sub-economic Ballinalack Zn-Pb deposit is situated in the Irish Midlands, Ireland, approximately 50 km west of the Navan Zn-Pb deposit and 80 km west of Dublin. Its resources are estimated at 7.71 Mt with 6.33 % Zn and 0.95 % Pb (The Robertson Group Plc, 1991).

The main character of the Ballinalack area is a fault bound inlier of Pale Beds, referred to as Ballynacarrigy inlier. At the inlier's margin, also northeast striking, extensional faults are present, which extend across the Irish Midlands. At Ballinalack itself, an additional northeast trending fault system is present, the Ballinalack Fault Zone. Regionally, this fault zone is extensive and spreads beyond the Ballinalack deposit. These faults are overlain by the late Courceyan and Chadian Supra Waulsortian and Calp units (Fig. 2, Bradfer, 1982, Jones and Bradfer, 1982, Hitzman and Large, 1986, Jones and Brand, 1986, Hitzman and Beaty, 1996). The sulphide mineralisation is hosted by Lower Carboniferous calcareous units (Fig. 3), with the highest grades occurring within the Waulsortian Limestone and to a lesser extent in the Pale Beds (Chapter 3).

The Lower Argillaceous Bioclastic Limestone (Lower ABL) is composed of dark grey, argillaceous, bioclastic wackestone and floatstone with nodules of light grey lime mudstone. It is fossiliferous and bryozoan-rich (Jones and Brand, 1986, Hitzman and Beaty, 1996). These open marine basal sediments have a thickness of 150–200 m.

This unit is overlain by the Waulsortian Limestone, which can be described as light bluish-grey lime mudstone and mud-boundstone with abundant sparry calcite-filled stromatactis cavities and was deposited in an open marine environment (Bradfer, 1982, Jones and Bradfer, 1982). Due to three northeast trending knoll systems, the thickness of the Waulsortian Limestone varies significantly ranging from 150 to 250 m; these knolls are related to the northeast trending Ballinalack Fault (Bradfer, 1982).

Waulsortian Limestone is overlain by the Supra Waulsortian Limestone, also referred to as Upper Argillaceous Bioclastic Limestone. These cover rocks are similar to the Lower Argillaceous Bioclastic Limestone, however, they do not consist of any dark argillaceous lime mudstone, but a thick, clean lime mudstone instead. This mudstone is interbedded by shallow water bioclastic, wispy argillaceous bands and coarse nodules of light grey mudstone as deposition in an open and deep marine environment (Jones and Brand, 1986, Hitzman and

Beaty, 1996). The thickness of this sequence varies as a function of the underlying Waulsortian Limestone.

Also the overlying Calp was formed in a deep marine environment and is a complex sequence comprising the Tober-Colleen and the Striped Unit (Fig. 3), which can reach a thickness of up to 300 m. These calcareous rocks are mainly deposited in the Dublin Basin as well-bedded and graded carbonate turbidites. The Calp varies between moderately to highly argillaceous content. Turbidites occur in the form of several structures: elongated, slumps, ball and pillows as well as beds in the form of coarse grainstone and local olistostromes (Jones and Brand, 1986, Hitzman and Beaty, 1996). The Tober Colleen unit is generally poor in bioclastic material and forms a thin black mudstone with a thickness varying between 20 and 50 m. It has been interpreted as a medium to thick deep water carbonate turbidite; whereas the Striped Unit consists of alternating planar bedded packstones and mudstones (Clarke and Reed, 2009, Clarke et al., 2010).

Ireland was affected by two main glaciation events during the Irish Pleistocene (e.g., Mitchell, 1973, Bowen et al., 1986, McCabe, 1987, review in Knight et al., 2004). The older Munsterian glaciation, is associated with the European Saalian glaciation during 302–132 ka BP (Mitchell, 1973, Coxon, 1993). The younger and most recent glaciation in Ireland is the Midlandian cold stage, associated with the continental Weichselian period 117–10 ka BP (Mitchell, 1973, Bowen et al., 1986, Bowen, 1992). The recent glacial landforms and sediments are older than the Middle Midlandian organic sediments (Colhoun et al., 1972), thus they are correlated to the Late Midlandian (ca. 25–10 ka BP); Bowen et al. (1996) suggest a first ice drawback northwards after ca. 40 ka BP.

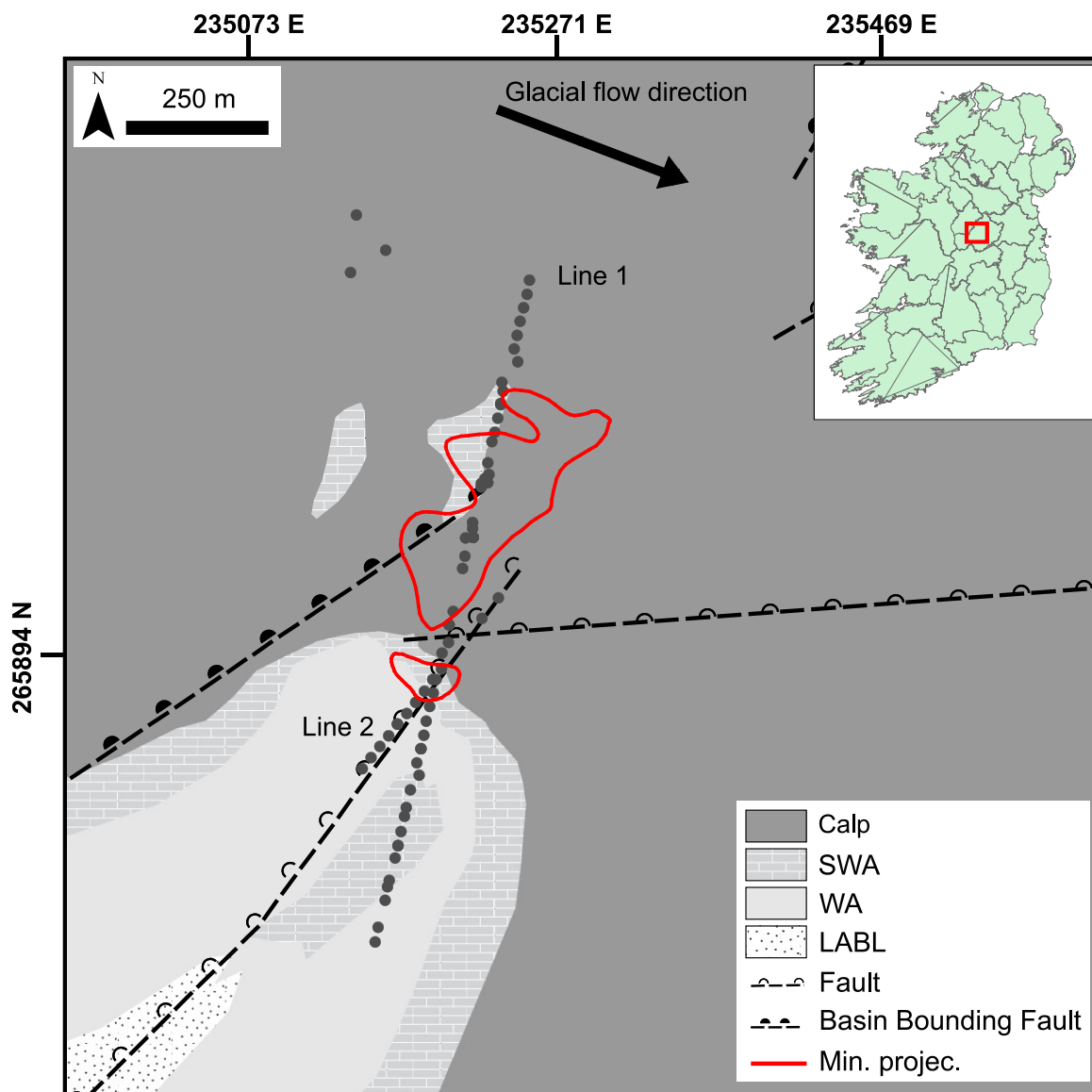


Fig. 2 Geology of Ballinalack with sample locations (grey dots) for the soil survey. The Red line represents the projection of mineralisation to surface. In the North, the major sulphide lens is overlain by cover rocks of the Supra Waulsortian and Calp. The minor sulphide lens to the south is overlain by Supra Waulsortian. SWA = Supra Waulsortian Limestone, WA = Waulsortian Limestone, LABL = Lower Argillaceous Bioclastic Limestone, Min. project. = Mineralisation projection; Irish Grid TM65 coordinates.

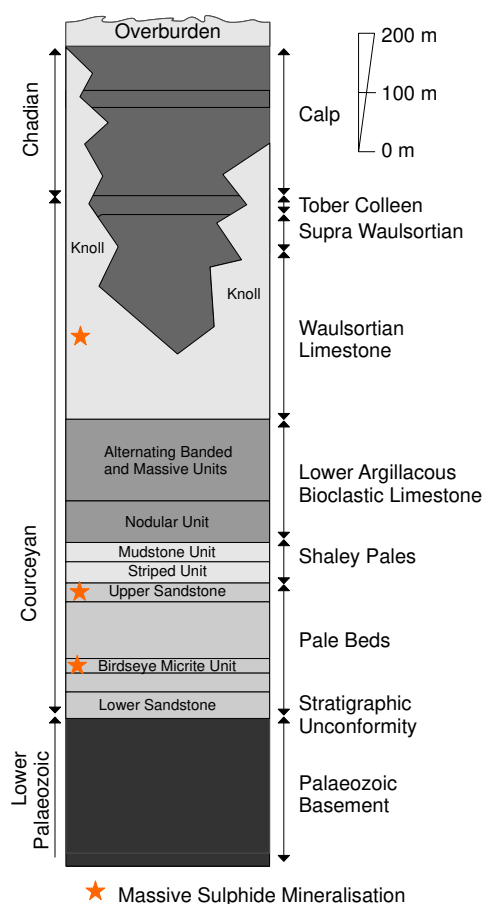


Fig. 3 Stratigraphy of the Ballinalack area (after Jones and Brand, 1986). Major massive sulphide mineralisation occurs within the Waulsortian Limestone, which can be sub-cropping in some areas, due to its knoll system (for more details see Chapter 3).

The Late Midlandian is represented by the uppermost till facies (Maguiresbridge Till of the Glenavy Stadial). Based on chronostratigraphy, the Late Midlandian ice most likely formed over 30 ka BP ago (McCabe, 1987). The landforms formed during that time consist of drumlins and isolated end-moraine belts with a focus on central and northern part of Ireland (Synge, 1969, McCabe, 1987, 1993). More recent studies suggest major changes in the subglacial environment 25–18 ka BP, which mobilised and remoulded the sediments in ridge forms and preserved as landforms. These ridges indicate the regional-scale ice flow direction (Lundqvist, 1989, Hättestrand, 1997). At a later stage of the Late Midlandian 18–17 ka BP, a main drumlin formation phase took place (Synge, 1969, 1979). The drumlins are associated to ice flows towards terrestrial (Irish Midlands) and marine ice (coastal low lands) margins. These drumlins align with the former ice flow direction and internal sediment structures (Knight and McCabe, 1997, Knight, 1999). The Irish Midlands were mainly shaped by an ice flow direction from NW to SE (Synge and Stephens, 1960, McCabe, 1985, Warren and Ashley, 1994, Fig.2). Locally, at Ballinalack the surrounding drumlins Lough Owel and Lough Derravaragh, as well as

subglacial lineations, follow the main trend from NW to SE (Meehan, 2013), hence indicating the local glacial flow direction NW to SE.

Depending on the local conditions, different soil types formed on the glacial sediments after the retreat of the ice sheet. Therefore, soil developed on the glacial sediments and underwent gleisation throughout the Irish Midlands. However, its parent material is mainly composed of the calcareous Calp unit. According to Finch (1977) peat extraction has taken place over wide areas of the Irish Midlands, nonetheless, the area is reclaimed and recently also used as pasture land. With an annual rainfall of on average 925 mm (MetÉireann, 2016), the area is classified as a humid climate. A general description of soil characteristic of the Ballinalack area can be found in Teagasc (2014a). Mostly, the Ballinalack area is divided into two main mineral soil groups a) peaty soil and cuts in the northern part of the sample area and b) surface water gleys (pseudogleys) in the southern part of the sample area within the top 40 cm, described as fine loamy drift with siliceous stones (Simo et al., 2008, Teagasc, 2014a). The peaty soil is poorly drained with a peaty topsoil (Teagasc, 2014b). Surface-water gleys consist of poorly-drained mineral soils (Teagasc, 2014b). Subgroups are not further defined by the Teagasc Group in this research area.

2 Sampling & Methodology

2.1 Sampling

In total, 163 samples were collected from the Ballinalack prospecting area (PL-1344) in the Irish Midlands. Respectively, soil and till samples were extracted at each site using a Dutch Auger along NE to SW trending lines at a 25 m sample spacing (Fig. 2). Two lines were chosen to include soil and till material overlying different underlying stratigraphy, as well as transecting the surface projection of mineralisation. In addition, anthropogenic influences were avoided by shifting sample locations away from paths, drainage and former drilling locations to ensure natural vertical profiles. From NNE to SSW, Line 1 covers both the northern sulphide lens and smaller southern sulphide lens, whereas Line 2 is above the southern lens only. Locally, two additional soil profiles were collected above the major mineralisation where elevated concentrations were reported to verify anomalies and assess any nugget effects on bulk geochemistry.

Typical soil BC horizon samples were collected at a depth of 15–25 cm. They are dark brown (Fig. 4), silty, moist to dry and contain black gravels of a 5 mm size fraction (originating from the cover rock Calp). Rarely, traces of red oxidation can be observed, which are likely due to an accumulation of Fe-oxides in the form of pore linings (Vepraskas and Sprecher, 1997).

Top of the till samples, hereafter, simply referred to as till, were collected at depths of 40–60 cm, and infrequently to depths of 80 cm. The till is moist to wet and has hydromorphic features at most locations in the form of mottled colour changes (Fig. 4) mainly black, grey and light brown, and sometimes green to orange caused by Fe and Mn reduction (Vepraskas and Sprecher, 1997, Mitsch and Gosselink, 2015, Schoeneberger et al., 2017); this is most likely due to a varying water table. The gravels within the till are approximately 2–3 cm in size and vary from grey to black (similar to soil-hosted clasts). The parent material of the black clasts is likely the Calp, with the grey clasts originating in the Supra Waulsortian or Waulsortian Limestone units. Pictures of each a soil and a till sample collected by a Dutch auger is in Appendix C. To ensure consistent sampling at each location, a test hole was examined (also using a Dutch Auger) to verify if the soil profile was naturally occurring and free of any visible anthropogenic influences as well as verifying the depth of various horizons of interest. Note, nomenclature for soil differs from the Teck Ireland Ltd. orientation study, the soil BC horizon in this study is comparable to the B horizon in the orientation study.

Samples above the major sulphide mineralisation include TCS 20604–20629 and 20755–20761 with flanking samples designated as TCS 20041–20046, 20049–20603 and 20631–20636. Samples above minor sulphide mineralisation include TCS 20644–20645 and 20741–20743 with flanking samples designated as TCS 20641–20643 and 20647–20648. All sample locations are provided in the supplementary table and map (Appendix C).

Additionally, 12 rock samples were collected from the underlying stratigraphy (Calp, Supra Waulsortian Limestone and Waulsortian Limestone) at various depths and analysed for the calculation of enrichment factors.

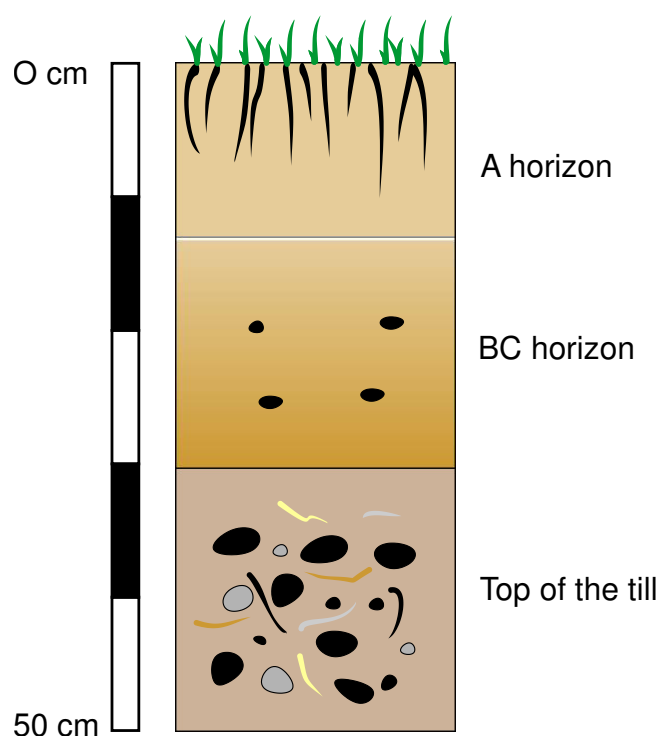


Fig. 4 Typical vertical soil profile from Ballinalack. Soil sample is brown, no colour change and rarely black clasts of Calp occur. The till sample changes its colour due to redoximorphic processes from brown, to light brown/ grey and black.

2.2 Sample preparation

All samples of soil and till were submitted to ALS Loughrea Laboratories Limited in Ireland for preparation and geochemical analysis. For each sample, 0.5 g of sample material was dried in an oven at $< 60^{\circ}\text{C}$ and sieved to $180\ \mu\text{m}$ / 80 mesh (PREP-41). The rock samples were crushed and pulverised to $< 75\ \mu\text{m}$ (methods CRU-31, PUL-32). Material was digested using the partial digestion aqua regia (3:1 ratio of 12 N HCl: 16 N HNO_3) followed by analysis using ICP-MS and -OES, providing low detection limits (Tab. 1) for 51 elements (method ME-MS41). To prove the measurements accuracy conducted by ALS Loughrea, Ireland, field and laboratory duplicates, blanks, and standards were included. In addition, ALS Loughrea conducted loss on ignition (LOI) analysis at 550°C using the OA-GRA05a method.

Field duplicates are expected to be within $\pm 30\%$ (Fig. 5). Considering this limit, several elements had to be treated carefully. Elements exceeding the accepted range (twice) are Ag, Al, As, Cu, Mo, Na, Pb, Sc, W, Y and Zn, notably Ca varies significantly up to 129 % in six samples. The variations of elements within the field duplicates point out the variation within the soil and till at a small scale. The major variations are mainly within the till, due to the different coarse gravels, composed of limestones, which can cause nugget effects and thus different geochemical signatures can be expected. In particular Ca (max. 129 %) and Sr

(max. 99 %) are expected to vary considerably as result of deriving from limestones, resulting in a change in pH, hence the mobility of elements and their abundance can change easily within tens of centimetres. Very carefully treated have to be Au, Ca, Sr, S, Mn, Hg and Na.

Tab. 1 Limits of detection for each element (method ME-MS41 conducted by ALS Loughrea).

Analyte	Units	Lower Limit	Upper Limit	Analyte	Units	Lower Limit	Upper Limit
Ag	ppm	0.01	100	Mo	ppm	0.05	10000
Al	%	0.01	25	Na	%	0.01	10
As	ppm	0.1	10000	Nb	ppm	0.05	500
Au	ppm	0.2	25	Ni	ppm	0.2	10000
B	ppm	10	10000	P	ppm	10	10000
Ba	ppm	10	10000	Pb	ppm	0.2	10000
Be	ppm	0.05	1000	Rb	ppm	0.1	10000
Bi	ppm	0.01	10000	Re	ppm	0.001	50
Ca	%	0.01	25	S	%	0.01	10
Cd	ppm	0.01	1000	Sb	ppm	0.05	10000
Ce	ppm	0.02	500	Sc	ppm	0.1	10000
Co	ppm	0.1	10000	Se	ppm	0.2	1000
Cr	ppm	1	10000	Sn	ppm	0.2	500
Cs	ppm	0.05	500	Sr	ppm	0.2	10000
Cu	ppm	0.2	10000	Ta	ppm	0.01	500
Fe	%	0.01	50	Te	ppm	0.01	500
Ga	ppm	0.05	10000	Th	ppm	0.2	10000
Ge	ppm	0.05	500	Ti	%	0.005	10
Hf	ppm	0.02	500	Tl	ppm	0.02	10000
Hg	ppm	0.01	10000	U	ppm	0.05	10000
In	ppm	0.005	500	V	ppm	1	10000
K	%	0.01	10	W	ppm	0.05	10000
La	ppm	0.2	10000	Y	ppm	0.05	500
Li	ppm	0.1	10000	Zn	ppm	2	10000
Mg	%	0.01	25	Zr	ppm	0.5	500
Mn	ppm	5	50000				

Ten laboratory duplicates were analysed and their deviation limit is acceptable between ± 10 %. The elements Ag, As, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, La, Mg, Mn, Mo, Ni, P, Pb, Rb, Sb, Sr, Th, U, V, Y, Zn and Zr are within the range. Aluminium (-25.9 %), Cs (-10.5 %), K (-16.7 %), Li (11.5 %), Nb (10.3 %), S (-50 %), Sc (-13 %), Ti (50 %), Th (10.4 %) exceed the limit once. Tungsten is two times higher than the accepted limit (-20.0 and 26.2 %). Beryllium (10.4, 11.6 and 12.5 %), and Sn (11.1, 14.3 and 27.3 %) three times. Hafnium exceeds the range four times (10.3, 10.9, 12.0 and -13.0 %), as well as Hg (12.0, 19.5, -11.1, 13.6 %) and Se (-11.1, 18.2, -18.5 and -22.2 %). However, Au exceeds the limits in five duplicates (11.8, -16.1, -25.0, -38.5, 41.2 and -70.0 %). Sodium is six times higher than 10 % (-14.3, 16.7, -20.0, -20.0, -25.0, -25.0 and -50.0 %). Indium does not match the range in 7 of 10 laboratory duplicates (17.6, -19.0, 22.7, -24.0, 37.5 and 42.9 %).

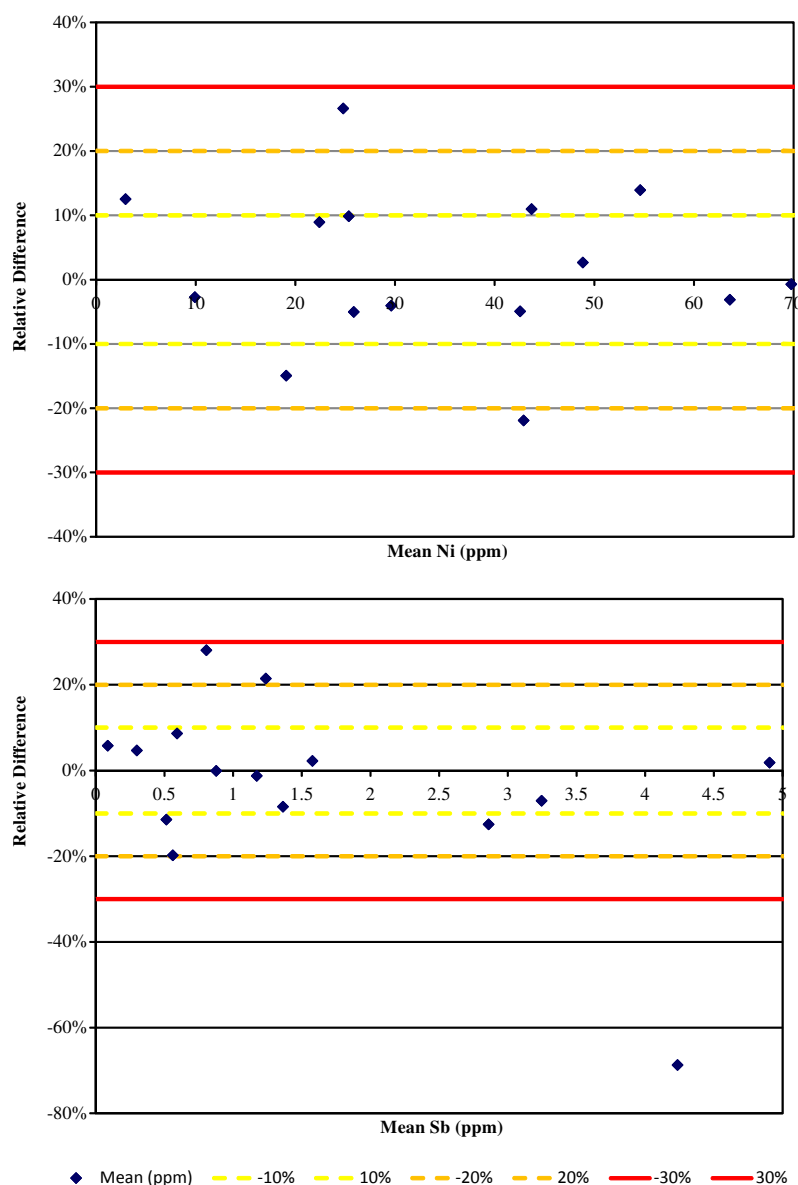


Fig. 5 Relative difference plot for field duplicates with the example of Ni and Sb. A relative difference of up to 30 % is acceptable, Sb has one outlier derived from clasts weathering within the till sample.

Every 10th sample an internal certified reference material was added in the sample order. It is a A-horizon soil standard collected in the Irish Midlands, named Limerick 2011, the results also are based on aqua regia digestion. Note, the standard does not provide a value for the elements Au, B, Be, Bi, Cs, Ge, Hf, In, K, La, Li, Na, Nb, P, Pd, Pt, Re, Se, Ta, Te, Ti and W. The limits are expected to be within $\pm 10\%$. Apart from Hg (99.91 %), Sc (10.21 %) and Zr (98.78 %), all elements are within this range.

ALS Loughrea, Ireland provided the following standards OREAS-45d, GBM908-10, GEOMS-03, MRGeo08, GBM399-5, MP-1b, OREAS-133a and GIOP-26, -28, 30, used as external standard. Remarkably, Au, Al, Bi, Cd, Ge, Hg, Nb, and Se are mostly a bit lower than the given range. Notably, not all elements are listed in the official certificates, hence, Bi and

Nb in GB908-10 are not certified or mentioned in this standard. No free available certificate exist for GEOMS-03, in which Au and Nb are exceeding the range, therefore no control is possible here. The same is for Cd, Ge and Hg in OREAS-45d. Standards used for Loss on ignition values are within the acceptable range. Based on the external standards and the target range given by ALS Loughrea and considering the official certified values, the analysis are reliable.

Distributed over the batches, nine blanks were conducted during the analysis by ALS Loughrea, Ireland. All blanks are within the expected range.

Based on standards and duplicate evaluation, some elements have to be treated carefully and cannot be used for further investigations; the following elements are excluded for the interpretation Au, B, Be, Bi, Hf, Hg, In, Na, Pd, Pt, Re, Ta and Te.

ALS Minerals, Loughrea, Ireland calibrates the instruments that the relative standard deviation (% RSD) is less than 2 %, therefore ± 2 % of each concentration provides the error bar limits:

$$\%RSD = \frac{\text{Standard Deviation (population)}}{\text{Average (population)}} * 100 \quad (1)$$

Precision is < 2 % and the accuracy 2 %.

Measurements of pH were performed in a 1:2 soil to 0.01 M CaCl_2 solution for soil and till samples at Trinity College Dublin using methods outlined by Hendershot et al. (2008) for each sample. The pH-value is based on both field and laboratory measurements and for interpretation only laboratory values are considered. Due to the accuracy of the pH-meter, a deviation of ± 0.1 can be expected.

Determination of mineral phases was obtained by x-ray diffraction (XRD) of powdered samples at the Trinity College Dublin facilities. For soil and till samples the fraction sieved to $180 \mu\text{m}$ (through 80 mesh), and for drill core samples rock was pulverised to less than $75 \mu\text{m}$ prior to analysis. Selected and representative samples for all soil types, till as well as from the background, at flanks and above mineralisation were analysed on a Bruker D5000 XRD; its Cu long line focus is 2.2 kW (0.4 x 12 mm filament) with the following optical configuration: 2.5° primary soller, 1 mm aperture diaphragm, 1 mm scattered radiation diaphragm, no secondary soller, 0.2 mm detector diaphragm and a secondary curved graphite monochromator ahead of the scintillation counter. Each sample was scanned from 5 to 70° (2θ) with a speed of 2 s per 0.02° step. The tube voltage was 40 kV and the current 40 mA. In general, sample rotation was used during analysis.

The evaluation and interpretation of data was performed using BRUKER AXS, Diffrac.Eva software (2012 Release, Version 3.0) and all peaks were referenced to a database of XRD lines in the International Centre for Diffraction Data, Pennsylvania; PDF-4 3+. Sietronics SiroQuant software (version 4.0, Release 5, with database v3.0g) was used to perform semi-quantitative analysis. The χ^2 factor was kept at < 3 and the residual or reliability factor (R-factor) < 0.3 .

The detection of mineral phases is relatively accurate, however, minor phases could still be difficult to detect by XRD. Preferred orientation of mineral phases was avoided, but cannot be assured. During the quantitative determination using the Rietveld method, it is difficult to predict an accuracy as it highly depends on the crystallinity of the mineral phases, the amorphous contents as well as the degree of overlapping peaks, in particular in complex samples with many phases. The software Sietronics Siroquant (Version 4.0, Release 5) suggest that the merit of the fit is quantified by χ^2 and the R-factor and it will be accurate to 10 % relative.

2.3 Background definition

Due to the varying underlying geology, it is crucial to treat the data in a systematic manner to allow for sample comparison and elucidation of trends. In this study, an enrichment factor is used, which is a common methodology for the assessment of anomalous geochemical behaviour in environmental or soil sciences (e.g., Atteia, 1994, Berg et al., 1994, Loska et al., 1997, Getty et al., 1999, Reimann and de Caritat, 2005, Veyseyre et al., 2001). The enrichment factor (EF) is a simple formula to diminish influence factors, and in this study decrease the impact of the change in the underlying geology and clasts within soil and till. The formula is as follows:

$$EF = \frac{X_{sample}/Y_{sample}}{X_{rock}/Y_{rock}} \quad (2)$$

Where X is the element of interest, for instance, Zn, Pb or Co, and Y is the constant element which is considered to be relatively immobile during weathering and pedogenesis, for instance, Al, Nb, Sc, Ti or Zr, in this study Nb is the immobile element chosen for normalisation of the data (the EF can be calculated according the equation above and the data provided of soil and till, as well as rock samples in Appendix C, respectively). Note, in most environmental studies, the reference background rock is based on data from the continental crust (e.g., Négrel et al., 2015). In this study, the concentration for the underlying bedrock is based on an average of aqua regia digested Calp, Supra Waulsortian Limestone and Waulsortian Limestone samples. As the change of bedrock is based on geological interpretations, it has to be noted that, in

particular in the transition area of bedrock, the enrichment factor can be slightly over- or underestimated. Theoretically, every sample revealing $EF > 1$ is enriched; therefore for instance, Barbieri (2016) suggests that enrichment factors above 2 indicate minimal enrichment of an element, whereas values above 5 can be counted as a significant enrichment of an element. Note, Ca concentrations exceeded the upper limit of detection during rock samples measurements (see Appendix C), therefore an enrichment factor for Ca could not be calculated.

3 Results of soil and till sample survey

3.1 Mineralogy of soil and till at Ballinalack

Results of the mineralogy are presented in Table 2 and visually in Figure 6. For all samples, quartz is the predominant mineral phase (Fig. 6), followed by muscovite and chlorite (notably, due to the software used chlorite stands also for clay minerals; clay minerals themselves were not determined in this study) as well as albite and calcite. Soil samples reveal generally higher proportions of the mineral phase muscovite and less chlorite than the till samples, which are rather comprised of chlorite instead of muscovite phases. In moist to wet soils goethite is also a dominant mineral phase. Minor phases are dolomite and feldspar. In rare samples, in particular in till samples, manganite and hydrozincite can be identified. Sphalerite might also occur in the till sample TCS 20645, directly located above the southern (shallow) mineralisation. More minor phases might be within the soil and till samples that could not be identified with the XRD methodology used within this study. Specifically the minor phases have large influences to the trace elemental pattern with respect to anomalies. For instance, sphalerite may release more Zn and weathers easily compared to clay minerals fixing Zn, leading to elevated concentrations within the soil/ till sample.

Tab. 2 XRD results for selected soil and till samples from Ballinalack. TCS 20645 may also display a sphalerite peak. Note, method used is quantitative, thus suggested percentages are indicative and not absolute. Chlorite comprises also all clay minerals. Srfc-wtr Gl. = Surface-water Gley, bckgr = background, min = mineralisation, S min = southern mineralisation.

Sample ID	Soil-till type	Quartz	Muscovite	Chlorite	Calcite	Albite	Dolomite	Feldspar	Goethite	Manganite	Hydrozincite	Chi^2	R-Factor	Location
TCS20028	Peaty Gley	79.3	2.9	10.8		7						2.23	0.246	bckgr
TCS20041	Peaty Gley	78.5	0.3	11.1	1.5	8.5						2.28	0.269	flank
TCS20608	Peaty Gley	90.6	8			0.7			0.7			2.12	0.257	flank
TCS20611	Peaty Gley	73.2	3.4	9.1	5.6	8.7						2.08	0.272	min
TCS20613	Peaty Gley	59.9	15.5	4.8		4.7			15.1			2.05	0.296	flank
TCS20622	Srfc-wtr Gl.	81.4	2.1	10		6.6						2.26	0.266	bckgr
TCS20624	Srfc-wtr Gl.	66.9	3.5	6.7	13.9	9						2.07	0.252	bckgr
TCS20631	Srfc-wtr Gl.	72.1	2.8	9	3.8	12.3						2.38	0.234	bckgr
TCS20637	Srfc-wtr Gl.	79.5	8.2	6.4	0.7	4.5		0.7				2.84	0.257	bckgr
TCS20644	Srfc-wtr Gl.	68.7	0	13.8	9.2	5.6	2.6				0.1	2.5	0.35	S min
TCS20646	Srfc-wtr Gl.	31.9	44	2.4		0			21.7			2.7	0.33	bckgr
TCS20681	Srfc-wtr Gl.	79.9	2.4	10.4		7.4						2.71	0.297	bckgr
TCS20696	Srfc-wtr Gl.	69.4	22.6		0.3	7.7						2.89	0.414	bckgr
TCS20713	Srfc-wtr Gl.	71.3	20.9	1.5		6.3						2.63	0.334	bckgr
TCS20734	Srfc-wtr Gl.	66.6	29.2	0.3		3.9						2.31	0.325	bckgr
TCS20029	till	77.7	0	13.2	0.7	8.4						2.12	0.26	
TCS20042	till	67.7	0.1	8	17.4	6.9						2.03	0.277	flank
TCS20609	till	76.2	4.4	0		5.5		13.7	0.3			2.41	0.276	min
TCS20614	till	19.9	9.3	17.2	32	10.9	0.2			10.5		2.22	0.252	flank
TCS20623	till	79.3	0.6	12.5	6.4	1.3						2.61	0.268	bckgr
TCS20625	till	78	3.1	7.2	2.1	9.7						2.06	0.239	bckgr
TCS20632	till	68.5	13.2	2.3	7.8	8.3						2.47	0.274	bckgr
TCS20638	till	77.1	12	10.2		0.8						2.1	0.373	S min
TCS20645	till	53.7	8.2	5.9	20.4	4.4	5.7		1.2		0.4	2.23	0.291	bckgr
TCS20647	till	79.7	6	7.1		5.4			1.9			2.57	0.299	bckgr
TCS20682	till	68.6	4.3	15.1	6.6	5.3						2.88	0.391	bckgr
TCS20714	till	70.6	16.6	4	2.9	5.8						2.52	0.328	bckgr
TCS20735	till	62.6	28.2	6		3.2						2.56	0.36	bckgr
TCS20746	till	79.7	5.6	5.2	0.6	4.4		2.2	0	2.1	0.2	2.63	0.314	bckgr

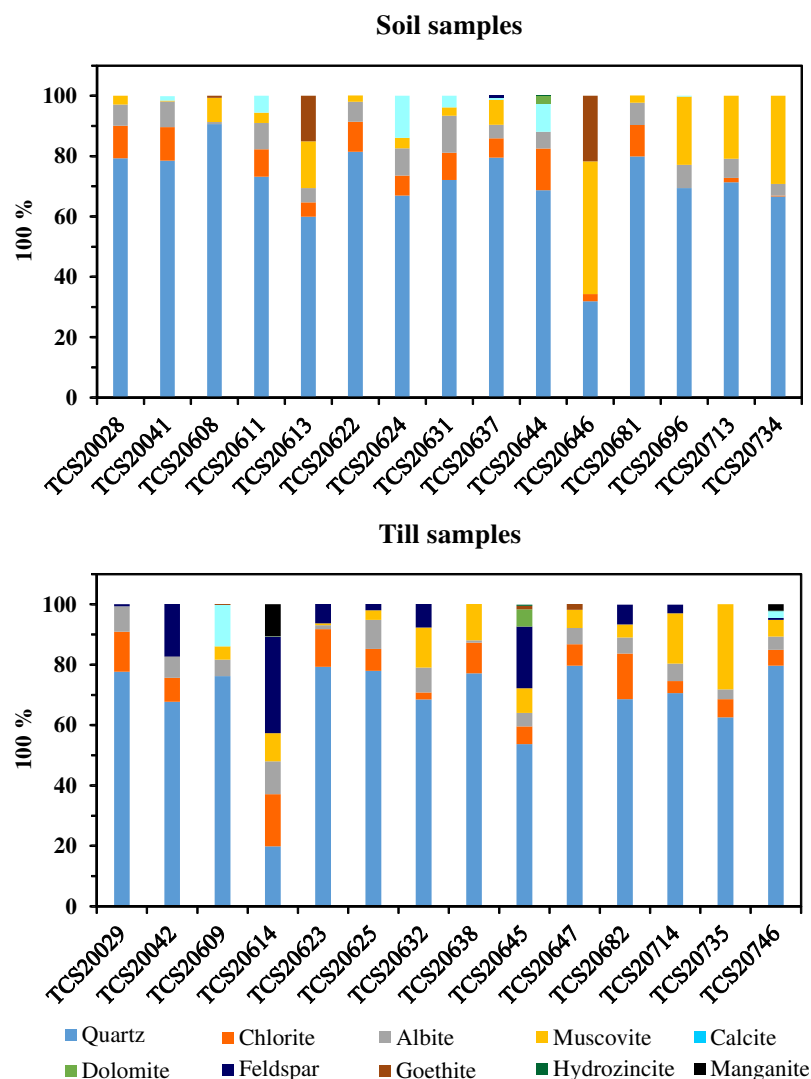


Fig. 6 Comparison and overview of soil and till mineralogy at Ballinalack; normalised to 100 %. Predominant phases are quartz, muscovite, albite and chlorite. Note, till is more enriched in chlorite than the soil samples.

3.2 Trace elemental pattern in soil and till

The soil BC horizon as well as till samples exhibit a characteristic trace-elemental pattern above the Ballinalack Zn-Pb deposit. Concentrations for the soil and till samples, are summarised in Table 3 and all results as well as a map with sample locations are found in Appendix C. In Figure 7, a normalised 100 % ternary plot was devised to illustrate the geochemical characteristics of soil and till samples, with respect to their carbonate (Ca as major element in calcite and dolomite), clay minerals (Rb as representative trace element in clay minerals) and organic matter (LOI) contents. This ternary plot displays easily the variations of the soil and till samples with respect to their major components. Till samples are much lower in organic matter than soil samples.

Tab. 3 Concentration for all samples, soil BC and top of the till. Unless stated differently, concentrations are given in ppm.

All samples	Ag	As	Ba	Ca	Cd	Co	Cr	Cs	Cu	Fe	Ga	In	Li
n	193	193	193	193	193	193	193	193	193	193	193	193	193
Min	0.04	1.43	10	800	0.20	0.52	3.94	0.06	2.77	5000	0.32	0.00	0.30
Max	19.90	362.00	1230	134000	67.80	22.00	62.50	1.32	42.10	52300	7.60	0.04	35.60
Mean	0.41	21.53	68	12919	3.35	7.49	21.59	0.51	17.72	18919	2.76	0.02	7.56
Median	0.12	7.72	40	2800	1.52	7.32	20.20	0.47	17.25	17900	2.44	0.02	6.70
Std. Dev.	1.74	46.53	110	23028	7.59	3.08	7.21	0.19	7.27	6961	1.05	0.01	3.67

All samples	Mg	Mn	Mo	Nb	Ni	Pb	Rb	S	Sb	Sc	Se	Sn	Sr
N	193	193	193	193	193	193	193	193	193	193	193	193	193
Min	300	24	0.43	0.07	2.77	1.92	0.38	50	0.08	0.48	0.40	0.03	5.44
Max	9000	1620	8.43	0.37	134.00	6430.00	14.40	9600	196.50	8.66	16.60	1.32	543.00
Mean	1688	465	2.73	0.16	40.30	131.28	7.93	379	4.99	3.86	1.63	0.46	47.53
Median	1300	461	2.59	0.16	37.40	15.70	7.86	200	1.18	3.63	1.40	0.44	14.95
Std. Dev.	1127	256	1.39	0.06	20.05	581.97	2.69	901	20.56	1.55	1.56	0.15	77.12

All samples	Th	Tl	U	V	Y	Zn	Zr	LOI (%)	pH
N	193	193	193	193	193	193	193	193	193
Min	0.19	0.02	0.44	15.80	1.89	27	0.70	1.0	4.4
Max	4.86	8.56	19.30	70.80	89.70	13150	14.85	80.6	7.5
Mean	1.75	0.58	1.17	38.53	22.22	570	2.48	6.1	6.1
Median	1.53	0.32	0.93	37.50	20.20	104	2.28	5.1	5.9
Std. Dev.	0.76	0.93	1.69	8.83	11.71	1593	1.48	6.6	0.9

Tab. 3 Continued.

Soil BC - All	Ag	As	Ba	Ca	Cd	Co	Cr	Cs	Cu	Fe	Ga	In	Li
N	97	97	97	97	97	97	97	97	97	97	97	97	97
Min	0.05	1.43	21	1000	0.36	0.98	3.94	0.06	3.69	5000	0.32	0.00	0.30
Max	19.90	295.00	669	95500	67.80	11.05	36.60	1.14	31.00	36500	5.29	0.04	11.00
Mean	0.44	22.78	67	6813	2.94	6.33	19.70	0.54	15.40	16496	2.69	0.02	6.78
Median	0.11	6.67	41	2300	1.22	6.69	19.80	0.53	14.70	16400	2.49	0.02	6.80
Std. Dev.	2.08	47.44	86	13455	7.71	2.19	3.71	0.17	5.67	4488	0.72	0.01	1.32

Soil BC - All	Mg	Mn	Mo	Nb	Ni	Pb	Rb	S	Sb	Sc	Se	Sn	Sr
N	97	97	97	97	97	97	97	97	97	97	97	97	97
Min	400	38	0.45	0.07	5.34	1.92	0.38	100	0.16	0.48	0.40	0.03	5.48
Max	4100	1040	5.62	0.27	75.40	6430.00	14.40	9600	187.00	6.23	11.90	0.81	312.00
Mean	1311	465	2.37	0.16	30.08	157.88	8.86	456	4.79	3.01	1.51	0.50	25.36
Median	1200	486	2.50	0.17	26.60	16.20	9.05	300	0.88	3.01	1.30	0.47	11.75
Std. Dev.	508	246	1.05	0.03	13.37	700.95	2.86	958	20.10	0.99	1.30	0.12	42.47

Soil BC - All	Th	Tl	U	V	Y	Zn	Zr	LOI (%)	pH
N	97	97	97	97	97	97	97	97	97
Min	0.19	0.02	0.50	15.80	2.52	28	0.77	1.0	4.5
Max	2.48	8.56	19.30	57.20	43.70	9990	4.79	80.6	7.5
Mean	1.36	0.62	1.16	36.88	17.26	471	2.37	7.0	5.8
Median	1.34	0.28	0.91	36.80	16.80	104	2.41	5.8	5.6
Std. Dev.	0.37	1.06	1.90	6.39	7.71	1324	0.68	8.2	0.8

Tab. 3 Continued.

Top of the till - All	Ag	As	Ba	Ca	Cd	Co	Cr	Cs	Cu	Fe	Ga	In	Li
N	96	96	96	96	96	96	96	96	96	96	96	96	96
Min	0.04	2.02	10	800	0.20	0.52	8.19	0.17	2.77	5100	1.05	0.01	3.10
Max	9.39	362.00	1230	134000	52.50	22.00	62.50	1.32	42.10	52300	7.60	0.04	35.60
Mean	0.38	20.27	69	19088	3.76	8.67	23.49	0.48	20.06	21367	2.84	0.02	8.35
Median	0.13	8.33	38	4800	1.82	8.64	21.35	0.44	20.08	19800	2.40	0.02	6.65
Std. Dev.	1.32	45.80	130	28501	7.49	3.41	9.16	0.21	7.95	8096	1.30	0.01	4.92

Top of the till - All	Mg	Mn	Mo	Nb	Ni	Pb	Rb	S	Sb	Sc	Se	Sn	Sr
N	96	96	96	96	96	96	96	96	96	96	96	96	96
Min	300	24	0.43	0.07	2.77	6.19	2.86	50	0.08	0.57	0.50	0.13	5.44
Max	9000	1620	8.43	0.37	134.00	3420.00	12.20	8300	196.50	8.66	16.60	1.32	543.00
Mean	2069	464	3.09	0.17	50.62	104.40	6.98	302	5.20	4.71	1.75	0.42	69.93
Median	1550	454	2.89	0.14	47.65	14.48	6.71	200	1.42	4.52	1.40	0.38	29.25
Std. Dev.	1419	266	1.59	0.07	20.43	431.92	2.13	838	21.11	1.56	1.77	0.17	95.86

Top of the till - All	Th	Tl	U	V	Y	Zn	Zr	LOI (%)	pH
N	96	96	96	96	96	96	96	96	96
Min	0.60	0.11	0.44	21.40	1.89	27	0.70	1.0	4.4
Max	4.86	5.39	13.65	70.80	89.70	13150	14.85	39.3	7.5
Mean	2.14	0.54	1.18	40.20	27.23	670	2.60	5.1	6.4
Median	1.89	0.33	0.96	39.40	25.95	105	2.11	4.4	6.7
Std. Dev.	0.86	0.79	1.46	10.53	12.91	1826	1.98	4.1	0.9

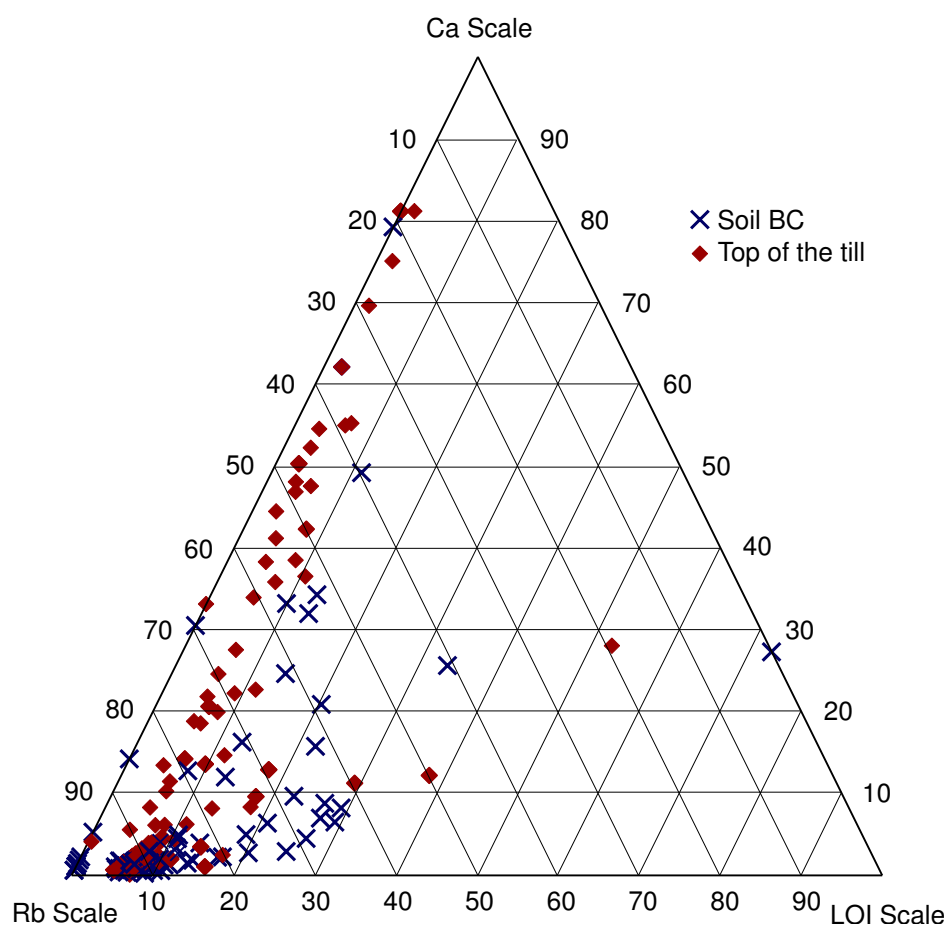


Fig. 7 Ca-Rb-LOI ternary plot (normalised to 100 %) displaying compositions for all soil and till samples (n=163) collected during this study. The Ca apex represents calcareous minerals, whereas Rb reflects clay minerals and LOI mirrors organic matter. Red diamonds = top of the till, blue crosses = soil BC. Clearly till samples have higher clay and calcareous contents, soil samples can contain higher amounts of organic matter.

In general, strong to very strong correlations (Fig. 8) can be identified in the dataset when considering all samples. A very strong correlation ($R > 0.9$) is exhibited for Ag:Pb, Ag:Sb, As:Tl, Ba:Sb, Ba:Zn, Ca:Sr, and S:LOI as well as strong correlations ($0.8 < r < 0.89$) for Ag:Cd, Ba:Pb, Cd:Pb, Cd:Zn, Co:Fe, Co:Ni, Cr:Th, and Cu:Ni.

No clear pattern can be discerned for pH and LOI (apart from LOI:S, $R = 0.91$, Fig. 8); however, soil samples display mildly alkaline conditions (pH up to 7.35) above the smaller sulphide lens (Fig. 9). Remarkably, the pH of most soil samples exhibit values either around 5 or near 7 (Fig. 9).

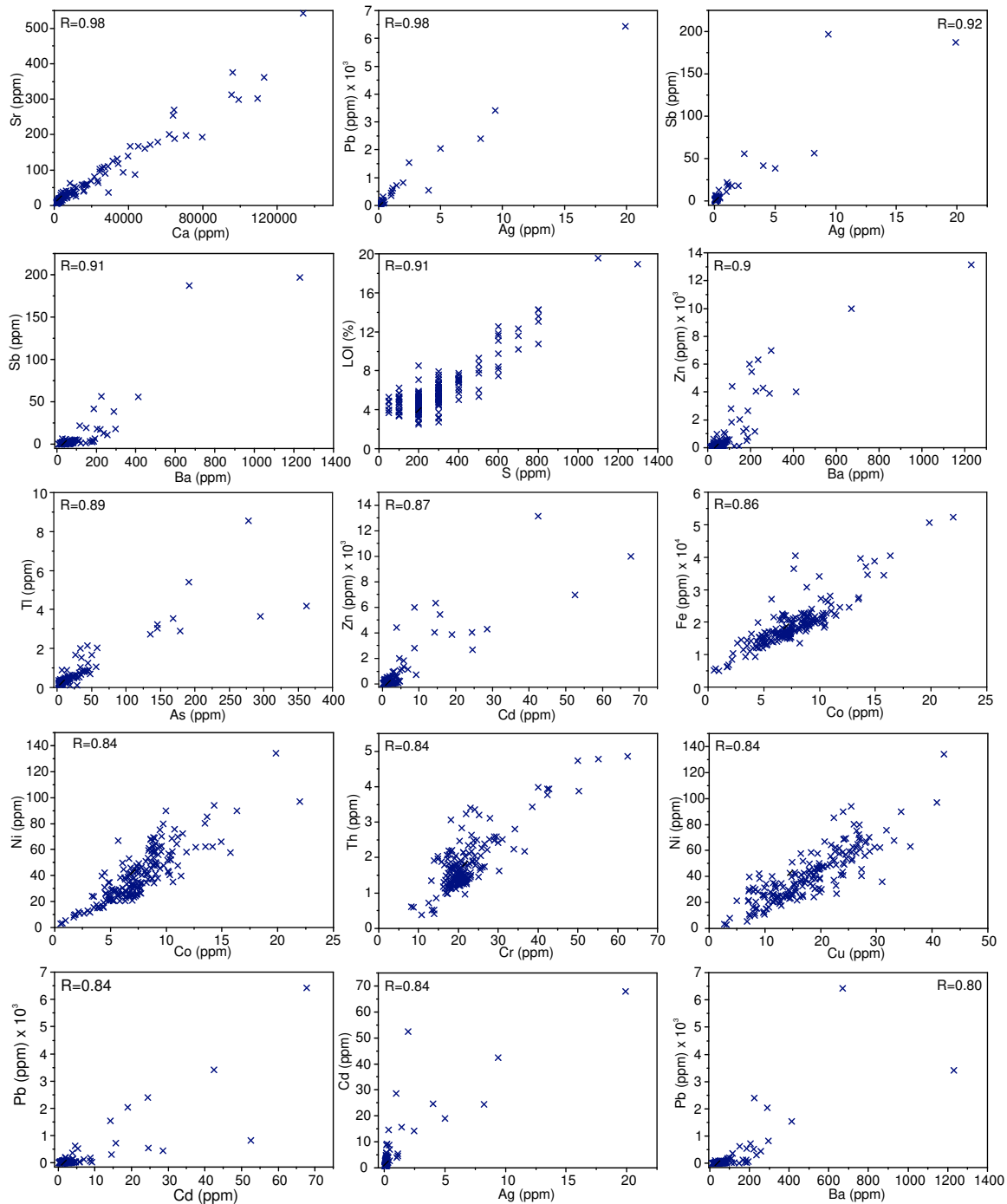


Fig. 8 Correlation based on both soil and till samples ($n = 163$). For instance, strong correlation of Pb to Ag is probably associated with galena, that Ba correlate to Zn indicates that Ba is associated with the fluid leading to mineralisation. Strontium represents a typical substitution within carbonate minerals and S has a high affinity to the soil organic matter. More information in the main text.

The elements Cr, Mg, and V show elevated concentrations between the two sulphide lenses in samples TCS 20633–TCS 20641, including both soil and till with mean concentrations of Cr (29 ppm, Fig. 10), Mg (2,375 ppm, Fig. 11) and V (45 ppm, Fig. 12). However, the most distinct anomalous concentrations are within soil. Moreover, loss on ignition in these samples is also higher (up to 14 %) than in the sample flanking the anomalies and the background control

samples (mean: 5.5 %). However, after converting these element concentrations into enrichment factors, none of the elements display true enrichments ($EF < 0.5$).

For the following treatment, the data is separated into the two settings: I) above the major sulphide lens in the north, which is buried beneath approximately 150 m of cover rock and overburden; and II) above the minor sulphide lens in the south, which is covered by approximately 1.5 m overburden.

3.3 Results - Major sulphide lens

Elements occurring in soil and till above the major sulphide lens are not elevated apart from one location (sample TCS 206013) within the till. Here, Fe (52,300 ppm, Fig. 9), Co (22 ppm, Fig. 11), Ni (97 ppm, Fig. 10), and to a lesser extent, Cr (42 ppm, Fig. 10), Mg (3,700 ppm, Fig. 11) and V (53 ppm, Fig. 12) are elevated compared to the other samples with a mean of 20,294 ppm (Fe), 8 ppm (Co), 44 ppm (Ni), 42 ppm (Cr), 1,894 ppm (Mg), 41 ppm (V). Taking into consideration the enrichment factors, these samples ($EF < 2$) do not actually appear to be significantly elevated (Fig. 10, 11, 12). Notably, close to this location TCS 20608 (soil) and TCS 20609 (till) are slightly enriched in Ba ($EF = 2$). Calcium is randomly enriched in places, buffering the pH locally (Fig. 9).

3.4 Results - Minor sulphide lens

In both soil and till above the minor sulphide lens, elevated concentrations occur of Ag, As, Ba, Cd, Pb, Sb, Tl, and Zn (Fig. 9-12). Lead is one of the elements, which exhibits very high concentrations in both soil (max. 6,430 ppm) and till (max. 3,420 ppm), mainly above the minor mineralisation, but also south of it on the flanks with up to 200 ppm Pb (TCS 20739). These locations exhibit an enrichment factor for Pb of up to $EF = 4$ south of the minor sulphide lens, which increases up to $EF = 58$ in soil and $EF = 34$ in till directly above the mineralisation (Fig. 10). Thallium does not exhibit such clear anomalous concentrations, 8.5 ppm in soil and 5.3 ppm in till, yet the enrichment is high with $EF = 17.1$ and 8.6 in soil and till, respectively (Fig. 11). Remarkably, the enrichment factors show non-predictable elevated concentrations on the flanks of the minor sulphide lens.

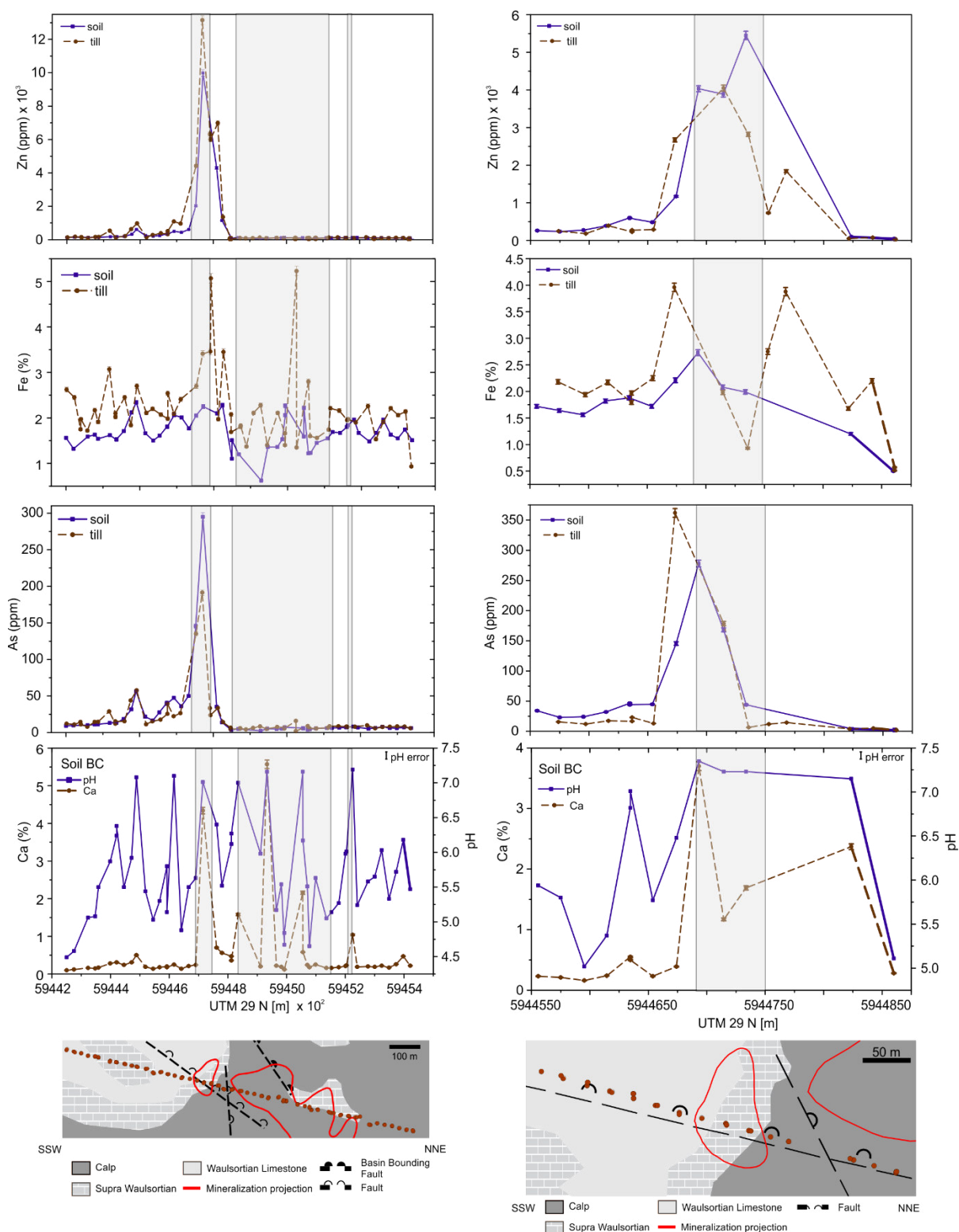


Fig. 9 Horizontal and vertical distribution of element concentrations within soil and till. Left: Line 1, Right: Line 2. Grey boxes within plots indicate the mineralisation projection. Zinc, Fe and As are elevated above the minor sulphide lens, further, Fe is also elevated in till above the major sulphide lens. Here, pH is buffered by elevated Ca concentrations and provides an inconclusive pattern, however in Line 2, pH close to neutral is consistent above the minor sulphide lens.

Silver exhibits concentrations up to 20 ppm in soil and 9.5 ppm in till above the minor mineralisation. The Ag enrichment factor is very high for both soil and till, up to 32.5 and 25 (EF), respectively (Fig. 11). The highest concentrations of As are found within the soil with 295 ppm above the minor lens (Fig. 9), as well as to a lesser extent south of the lens above the Waulsortian Limestone and Supra Waulsortian limestone in sub-cropping areas. In the till, As does not vary as much as within the soil compared to the background; however, it is still distinct above the minor lens and to the south, where the Waulsortian Limestone sub-crops. Their enrichment factors are up to EF = 25 and EF = 33 in soil and till, respectively (TCS 20648–20656, 20724–20725 and 20732–20739).

The concentration of Ba is elevated above the minor sulphide lens and its flanks in both horizons, confirmed by a low enrichment factor of EF = 3 in soil and EF = 3.4 in till (Fig. 12). Cadmium is particularly enriched above the minor sulphide lens as well as to the north between the minor and major sulphide lens in both soil and till. Its significantly high enrichment factor in soils up to EF = 38 and in till up to EF = 22 (Fig. 10) above the centre of mineralisation and still up to EF = 8 further south of the mineralisation (TCS 20738 and 20739), confirms that this represents a true anomaly. However, analyses also reveal some locations with slightly enriched Cd concentrations in the background-control sites and at the flanks of major mineralisation (TCS 20665, 20732) in both soil and till. Such a distinct anomaly is revealed by Zn concentrations as well, in soil with a maximum of 9,990 ppm and in till with a maximum of 13,150 ppm (Fig. 9), above the minor sulphide lens as well as at the flanks north (TCS 20639) and south (TCS 20648–20652, 20732–20739 and 20665). Generally, Zn is reflected in relatively lower enrichment factors than Pb, up to EF = 12 in soil and EF = 17 in till. In addition, slightly enriched locations north and south of the minor mineralisation are characterised by EF = 2. Antimony reveals the same distribution pattern in both concentration and enrichment factors as Zn. Concentrations of Sb within soil reach up to 187 ppm and within till up to 197 ppm above the minor sulphide lens, and the EF totals to EF = 13.5 and EF = 9.4, respectively (Fig. 12).

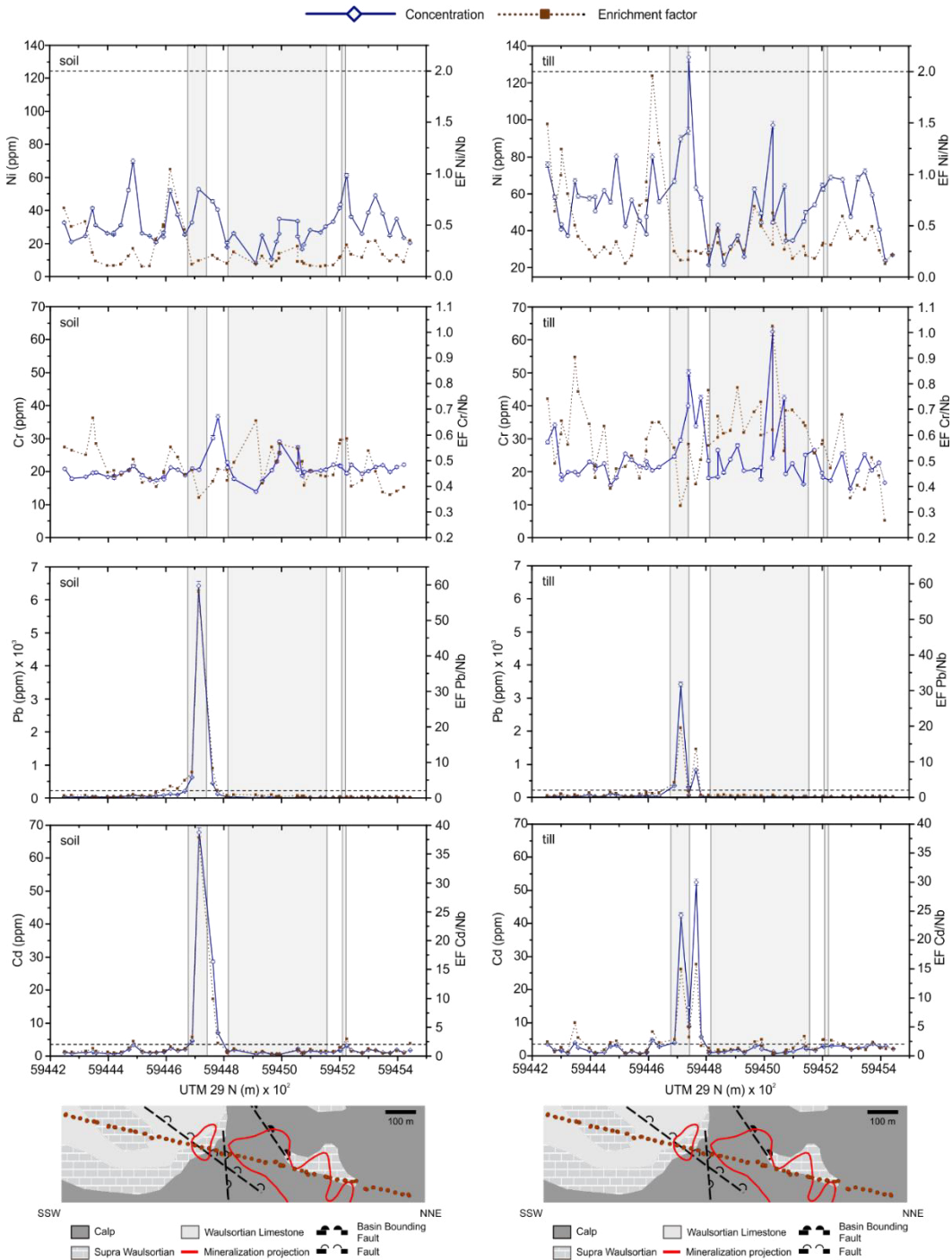


Fig. 10 Concentrations and enrichment factors for Line 1. Left: Soil, Right: Till. Grey boxes within plots indicate the mineralisation projection. Although Ni and Cr seem to be elevated in till above the major and minor sulphide lens, the enrichment factor disproves this assumption. The false anomaly might be caused by hydromorphic dispersion. Lead reveals clear elevated concentrations and enrichment factors. Chromium displays an enrichment in concentration between the two sulphide lenses within the soil, but is not valid when taking into consideration the enrichment factor ($EF < 1$). Cadmium reveals enrichment factors of up to 4 above the minor mineralisation, as well as, randomly distributed, meaning that Cd is not a clear indication for sulphide mineralisation and a combination of elements is needed.

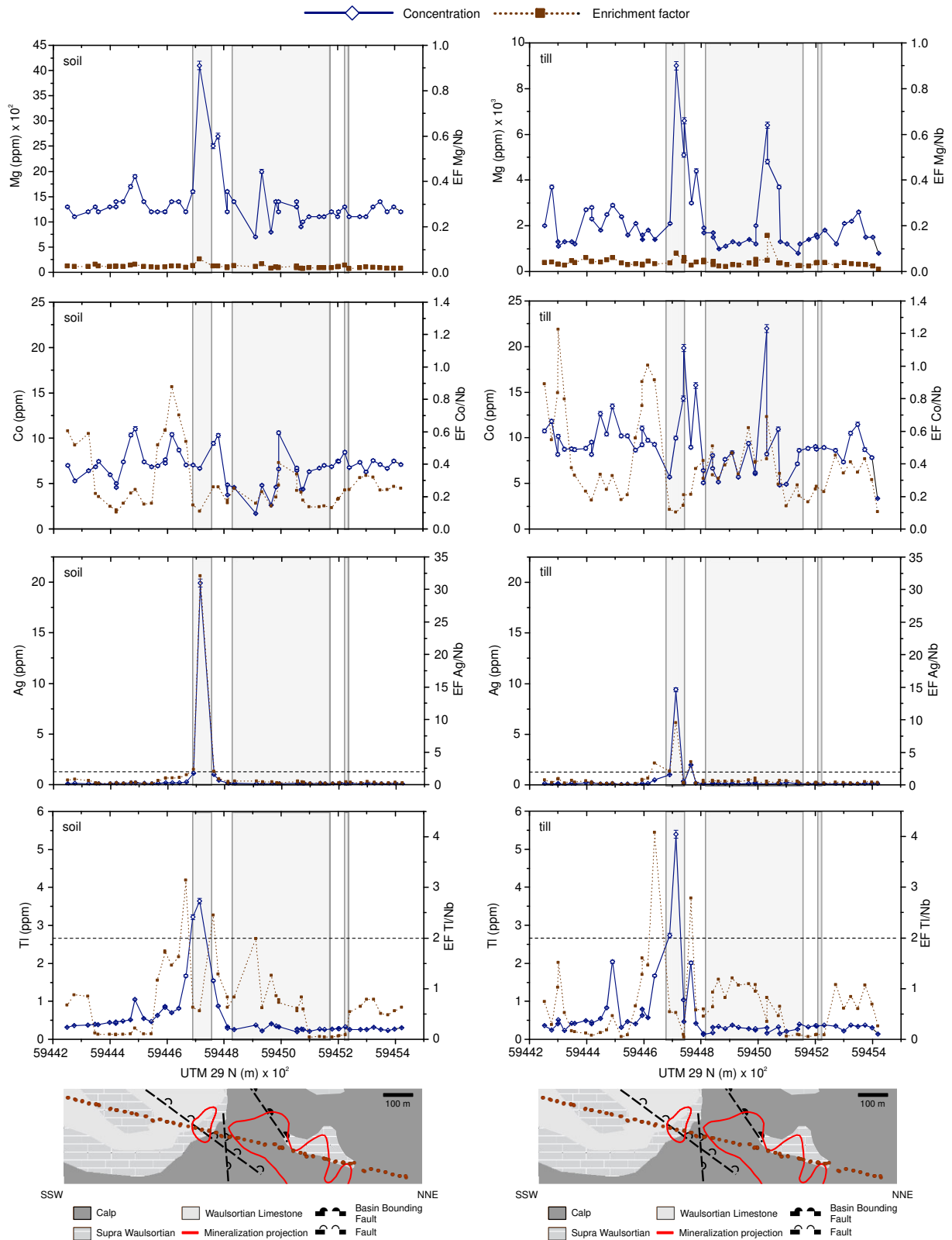


Fig. 11 Concentrations and enrichment factors for Line 1. Left: Soil, Right: Till. Magnesium and Co do not reveal true enrichments; their elevated concentrations might be related to a higher content of oxides. Silver and Ti reflect the shallow mineralisation significantly.

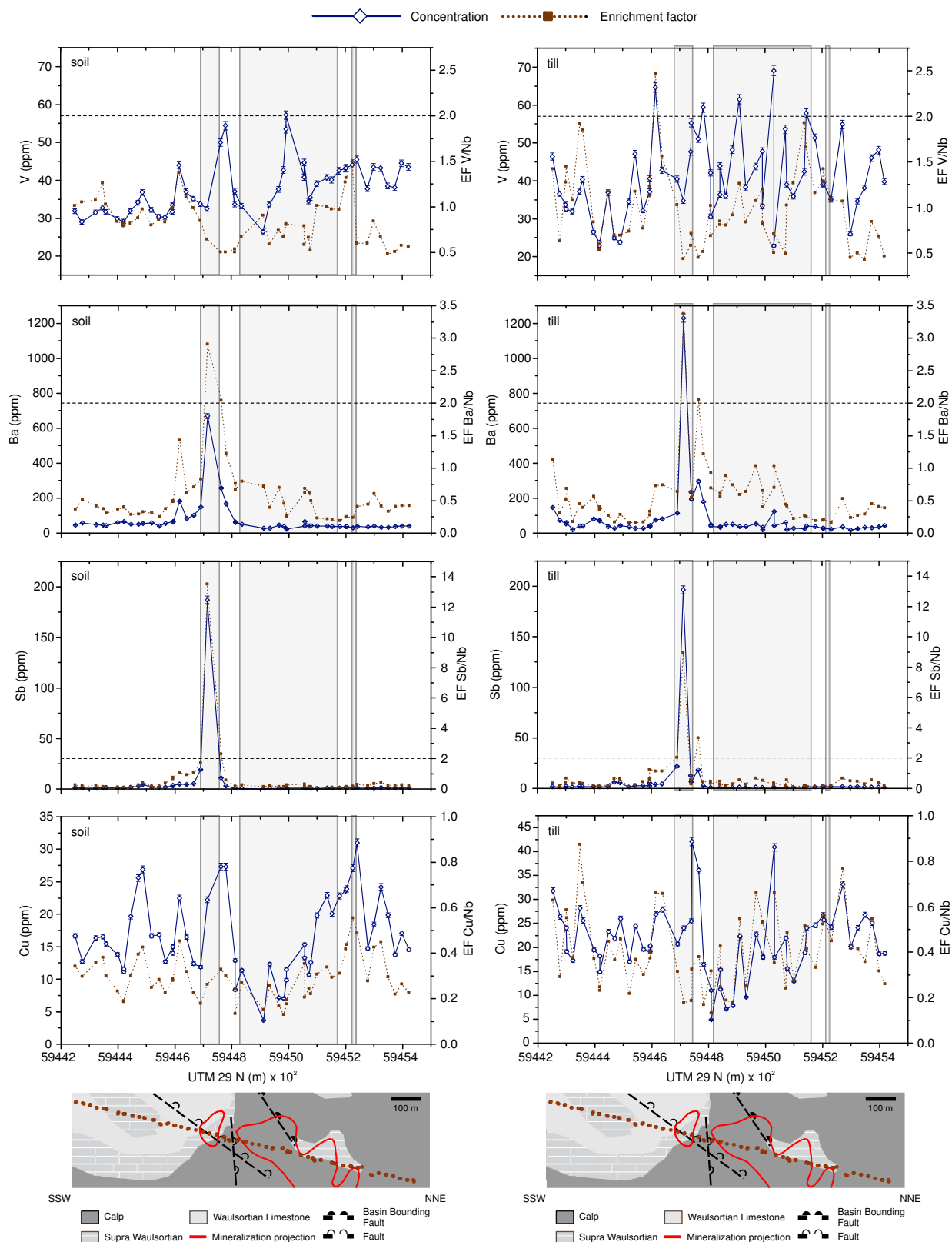


Fig. 12 Concentrations and enrichment factors for Line 1. Left: Soil, Right: Till. Grey boxes within plots indicate the mineralisation projection. Vanadium display that no enrichment exists in soil and till above the major sulphide lens. Barium and Sb display the minor mineralisation lens, supported by the enrichment factor. Cu does not reveal neither in concentration nor through enrichment factors anomalous values.

4 Discussion

4.1 General observations

Element correlation patterns in soil and till are a first indication to validate sulphide mineralisation beneath the overburden (Fig. 9). Iron, Ni and Co in overburden positively correlate with each other and likely reflect pyrite signatures (Abraitis et al., 2004, and references therein, Chapter 3). Zinc, As, Cd and Tl are associated with sphalerite (Cook et al., 2009, and references therein) and Ag, Sb and Cd with galena (George et al., 2015, and references therein). Barium correlates with Sb, Pb and Zn (Fig. 8), which may represent the occurrence of barite associated with sulphide minerals. Despite these indicators for sulphide mineralisation, the S content itself is strongly associated with soil organic matter. The positive correlation of S with loss on ignition values (Fig. 8) provides an approximation of soil organic matter (Schachtschabel et al., 1976, Brady, 1984). A correlation between Ca and Sr (Fig. 8) reflects the substitution of Sr in carbonate minerals in the parent material of the limestones.

Principal Component Analysis (PCA) of both soil and till data clearly illustrates three element groups (Fig. 13), details of the PCA scores are in Appendix C. Group (I) represents the major elements S, Mn, Mg, Fe and Ca, which reflect carbonate and oxide minerals occurring within the soil and till; note that Si, K, and Al were not included in the evaluation due to the incomplete digestion of silicate phases using the aqua-regia digestion method. Group (II) represents elements typically associated with sulphides Zn, Pb, Ba, As, Cd, Tl, Ag, and Sb (Chapter 3, Abraitis et al., 2004, Cook et al., 2009, George et al., 2015). Barium is known to occur as barite in Irish type deposits often intimately associated with sulphides, up to 10 % in the Tynagh and Navan deposits, minor amounts in Lisheen, Galmoy and Ballinalack (e.g. Schultz, 1968, Hitzman and Beaty, 1996, Anderson et al., 1998, Wilkinson, 2014) and within K-silicates in the Irish carbonates (Riegler and McClenaghan, 2017). Group (III) represents elements, which do not vary systematically and are not anomalous in their behaviour. Overall, the PCA results corroborate with results of the correlation analysis.

The variation in pH can be linked to the compositional variation in soil and till. Most of the samples were near a pH of 5, which is relatively low when considering that the soil developed on limestone, where an alkaline pH of around 7 or 8 would be expected. Similar to many other regions within Europe, soil acidification is common and caused by low pH precipitation (acid rain), NH_4^{4+} from sludge and ferrolyse, soil respiration, plant roots and soil organisms that release organic acids to make cations available, as well as microbial decomposition of organic matter (Schachtschabel et al., 1976).

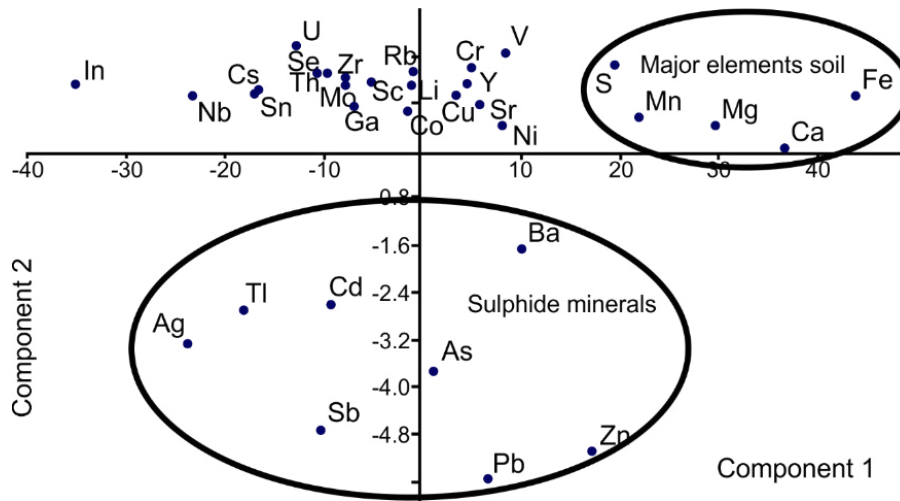
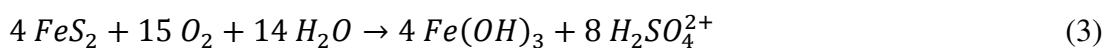
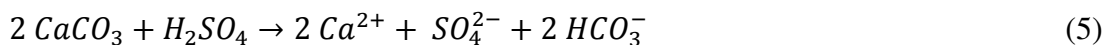
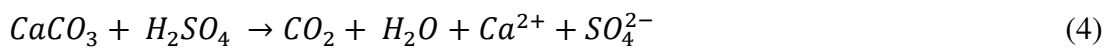


Fig. 13 Principal component analysis for both soil and till, showing three groups: soil forming minerals, sulphide minerals and mixed.

In addition, during the last glaciation soils became mixed and were transported in a broad NW to SE trend carrying bedrock debris (mainly Calp in the Irish Midlands) and materials to form a well-developed till horizon across the Irish Midlands. Weathering of carbonate minerals (at Ballinalack clasts within till) buffer the pH, leading to the given higher pH of 7 within the soil and till samples (Schachtschabel et al., 1976). This is reflected in a strong correlation between Ca and pH ($R = 0.98$; $n = 163$, Fig. 8) at Ballinalack. Furthermore, the pH above the minor sulphide lens is consistently higher ($\text{pH} = 7.5$, Fig. 9) compared to the surrounding samples. Strikingly, as soon as sulphide minerals have access to oxygen, an oxidation process should occur, which leads to the release of hydronium ions and accordingly acidification (Torres et al., 2014), e.g.,:



The release of hydronium ions can further react with carbonate minerals neutralising the pH and acting as a buffer; two reactions may take place:



Meaning that water and sulphides may produce an acid environment which can be neutralised by the occurrence of carbonate minerals. Another influencing factor on pH could be caused by the fact that the samples above the minor mineralisation were generally wet and dense, however, the samples between the two sulphide lenses exhibit similar boggy conditions (TCS 20633–TCS 20641), where no higher pH occurs. By comparing these similar setting, the wet and dense character may not be the reason for the increase of pH above the minor sulphide lens. Nevertheless, a slight change in the mineralogy, meaning more carbonate minerals in

conjunction with the presence of sulphide minerals, could lead to a higher pH (Tab. 2, Fig. 6) above the minor sulphide mineralisation, following equations 3–5. Furthermore, high Ba concentrations also occur within these samples above the minor sulphide lens, however, Ba most likely occurs in form of barite, which at near surface conditions would be insoluble and could not induce a pH buffer (Kabata-Pendias, 2011). The use of CaCl_2 in the pH measurements, could affect the pH, but the concentration of 0.01 M of CaCl_2 would not be sufficient to start a reaction, and this would not result in the generation of OH^- anions. Another variable to consider is that at this particular location the bedrock was intersected; this area has the lowest overburden depth of all sample locations. In addition, large (mm-scale) calcite and dolomite grains could be identified visually in these samples above the minor sulphide lens. The proximity to the bedrock comprising Supra Waulsortian and Waulsortian Limestone, as well as the calcareous clasts within the till, most likely buffered the pH more strongly, such that reactions 3 and 4 resulted in the neutral pH above the minor sulphide lens. Therefore, pH is not necessarily an indicator for the underlying sulphide lens (but sulphide can also drive the neutralisation reaction presented above in moist conditions), it merely correlates with a thin overburden at Ballinalack and can most likely be extended for carbonate hosted sulphide deposits.

As stated in the results, the area between the two sulphide lenses (TCS 20633–TCS 20641) is characterised by higher concentrations of Cr, Mg, and V in soils (Fig. 10–12). Since there is no true enrichment observed in the calculated enrichment factors; these higher concentrations may be explained by surface environmental changes. Topographically, the area is characterised by low ground, which is moist to wet (boggy) at the surface, indicating an elevated water table. Hamilton (2007) states that wet samples could cause false anomalies. Additionally, the high LOI estimates indicate that Cr, Mg, and V might be adsorbed by organic matter and clay minerals under reducing conditions and thus fixed. Chromium is relatively immobile within soils, and only occurs at higher concentrations in connection with silty and loamy soils. Its oxidised form of Cr^{6+} is more mobile than the Cr^{3+} form (Kabata-Pendias, 2011). These samples can be described as very dense and exhibiting some oxidation features in the soil and hydromorphic features in the till. Vanadium is associated with Fe hydrous oxides and organic matter. Also, Mg is associated with clay fractions e.g. chlorite group and organic matter (Schachtschabel et al., 1976). Therefore, this location is enriched in Cr, Mg, and V due to differing surface conditions, high organic matter content and a higher clay fraction (Fig. 6).

Even though Cu occurs up to several hundred ppm in the sulphide minerals (Chapter 3), no elevated concentrations (Fig. 12), nor the enrichment factor display anomalous values. This

might be due to the strong aqua regia digestion, leading to a diffuse signal compared to the background.

4.2 Major sulphide lens

Although Fe, Ni and Co, as well as Cr, Mg and V seem to be elevated in TCS 20613 (Fig. 9–12), this is only one sample at one location and it would require careful consideration in mineral exploration. In addition, the calculated enrichment factor ($EF < 2$) reveals signatures that do not represent a true enrichment (Fig. 10, 11); none of the other elements measured show true enrichments. Additional sampling (TCS 20755–20761) around this vertical soil profile, did not confirm any enrichment in Cr, Mg, V, Fe, Ni, Co or any other element. Chromium, Mg and V anomalies are inconclusive at Ballinalack. They might be introduced in the soil system through the bedrock, glacially or anthropogenically. Thus the elements Cr, Mg and V should not be used as a mineral exploration tool for Zn-Pb sulphide deposits within the Irish Midlands.

The mineralogy of sample TCS 20613 (soil) and 20614 (till) reveals that among the common minerals, quartz, albite, muscovite and chlorite, the mineral goethite occurs as a minor phase (Fig. 6), that could explain the slightly elevated concentrations, because in any other sample oxides could have been detected. At Ballinalack, no elevated elements could be detected above the major sulphide lens. Strikingly for the orientation study, neither an apical anomaly of Sb, As and Mo, nor a rabbit-ear anomaly of Ca and pH could be confirmed. Therefore, the anticipated reduced chimney model (see Chapter 1 and Reduced Chimney model section within this Chapter) after Hamilton (1998, 2000), above the buried sulphide deposit at Ballinalack should not be considered. Nevertheless, in general the geological conditions do not support the development of a reduced chimney. Poldini (1938) observed that a development of self-potential of the sulphide body is missing near peat layers; at Ballinalack some soils are described as peaty soil and approximately 1 km north of the mineralisation a peat area is located. Furthermore, neither galena nor sphalerite produce a self-potential. Galena serves as a good conductor and is easily oxidised, however, it does not produce a noticeable self-potential, whereas sphalerite exhibits too low of a conductivity response (Sato and Mooney, 1960). Pyrite alone may not produce such a strong self-potential in assemblages with sphalerite and galena. Furthermore, the model after Hamilton (1998, 2000) is based on an overburden between the sulphide mineralisation and surface in contact with groundwater, at Ballinalack overburden and cover rocks (Calp and Supra Waulsortian) separates the surface from the mineralisation, a connection between those through groundwater is not known. In particular the cover rock Calp may prevent an elemental transport towards the surface. It is intersected by the Tober-Colleen,

a black carbonate mudstone. This fine-grained rock might serve as a cap (aquitard) and hinder or prevent a geochemical transport.

Based on all these facts, even though a change of digestion method to selective leach displaying anomalous concentrations above the major sulphide body, a reduced chimney model could not explain the elemental transport at Ballinalack.

4.3 Minor sulphide lens

The elements Ag, As, Ba, Cd, Pb, Sb, Tl, and Zn all illustrate a distinct anomalous zone within the soil as well as in the till above the minor sulphide lens. Its centre is found above the minor sulphide lens as projected to the surface (Fig. 9-12) and on the flanks of the lens. Expecting that the concentrations would be higher within the till, which is closer to the underlying limestones and sulphide mineralisation, there is no obvious geochemical link (pattern) between the till and mineralisation in bedrock at Ballinalack. Strikingly, the elements do not even exhibit the same vertical distribution within the small area above the minor mineralisation. Overall, apart from Zn and As, all elements of interest are more elevated in soil than in the till. This phenomenon may be explained by referring to the soil and till constitution and thus their capacity of fixing elements in for example organic matter, however, since it varies locally, this vertical pattern is inconclusive. Moreover, as stated above, each soil and till horizon consists of various clasts that affect pH values locally, resulting in variability. However, any variations caused by glacial movement from NW to SE can be considered minimal since the enrichment in soil and till is directly above the sulphide projection. A transport based on an advection of groundwater model under remnant hydrostatic pressure from a retreating ice sheet as proposed by van Geffen et al. (2012) should not be excluded. The Ballinalack setting was also influenced by an ice sheet, and a retreating ice sheet may also have released pressure, changing the groundwater conditions. As the overburden of 1.5 m is relatively shallow, the groundwater may have been in contact to the sulphide mineralisation. Dust pollution could play a minor role, but contributions from dust are negligible as prevailing winds in the Irish Midlands come from the west, where no known smelters or Zn-Pb metal refining industries exist.

According to George et al. (2015), among Pb as a major element, Sb and Tl are typical minor and trace elements of galena. Gagnevin et al. (2014) report Zn, Fe, Cd, Sb and As in Irish type sphalerites from the Navan deposit in Ireland that were also detected in sulphides at Ballinalack (Chapter 3). Furthermore, Co and Tl are common trace elements in sphalerites (Cook et al., 2009, Murciego et al., 2010, Kuhlemann and Zeeh, 1995, Ye et al., 2011 and Chapter 3). Pyrites mainly consist of Fe and S, however, Ni, Co, As, Cd, Sb and rarely Pb are

associated with pyrite forms (Roberts, 1982, Gregory et al., 2015, Koglin et al., 2010 and Chapter 3). Barium is not known to be a trace element in these sulphides, however, laser ablation ICP-MS analysis do reveal high Ba concentrations (Chapter 3). These are not likely from the sulphides themselves, but it indicates as mentioned above the presence of Ba micro-inclusions occurring as barite or Ba bearing feldspar and mica (Riegler and McClenaghan, 2017) and as elevated concentrations in carbonate minerals. Furthermore, analysis of host and cover rock by aqua regia digestions for ICP-MS (Appendix C) shows that Ba is enriched in the host rock, however, their concentrations in the host rock are too low (50 ppm) to form an anomaly in a soil with 1,230 ppm. Hence, the elevated Ba concentrations likely come from the altered and sulphide bearing host Waulsortian sequence. As stated above, Ba is largely immobile in the form of barite. Even if Ba was mobilised, it would be readily adsorbed and immobilised by Fe and Mn oxides, clays and hydroxides under humid conditions (Kabata-Pendias, 2011).

Silver is more enriched in the soil than in the till (Fig. 11), although its source is from sulphide minerals in Waulsortian Limestone bedrock. Despite no organic soils at Ballinalack, the organic matter within the soil controls pH-Eh conditions, element behaviour and subsequent distribution (Jones et al., 1990). Lead is also more elevated in the soil than in the till (Fig. 10). At Ballinalack, although the source for Pb is originating in the underlying sulphide mineralisation, Pb is most likely fixed by soil organic matter within the soil and therefore exhibits higher concentrations than in the underlying till. Similar to Ag and Pb, Tl is more enriched in the soil (Fig. 11); however, Tl broadly correlates with K and has an affinity for mica minerals (Frantz and Carlson, 1987). At Ballinalack, it is most likely associated with muscovite in the soil. Furthermore, Sb also is more enriched within the soil horizon (Fig. 12). Typical enrichments of clay minerals (Kabata-Pendias, 2011) are not reflected in the soil data from Ballinalack (Tab. 2), here sulphide grains within the soil horizon itself may explain strong enrichments.

Based on the Irish Soil Atlas after Fay et al. (2007) it is known, that the background levels of Zn are relatively high (> 80 ppm) in the Irish Midlands, due to sulphides in the underlying limestones. Simple weathering of the sphalerite will release Zn into the system and results in an enrichment in soil and the clay bearing till. Like Zn, As is higher in the till than in the soil (Fig. 9), most likely due to its strong adsorption to the clay fraction, after being mobilised due to weathering of sulphide minerals at Ballinalack.

Apart from the soil and till above the minor sulphide lens, other locations reveal elevated concentrations as well, in particular, south of the minor lens, TCS 20681–20682, where

sulphide minerals likely occur as grains (particles) within the samples. This could originate from the till clasts (Waulsortian Limestone) within the vertical profile, which can bear sulphides such as sphalerite, pyrite and galena.

Since elevated Cd enrichment factors (up to $EF = 4$; Fig. 10) seem to occur on the flanks of the minor mineralisation, and no correlation to other elements at these locations can be made, the enrichment factor under $EF = 4$ is inconclusive for Cd as there are many locations, for instance at the northern flank of the major sulphide mineralisation above Calp, (i.e., TCS 20041, 20041, 20679), which reveal such enrichment factors for Cd without any pattern (link) as well. However, directly above the minor sulphide lens, it forms a clear anomaly and correlates strongly with Pb ($R = 0.85$, $n = 163$) and Zn ($R = 0.87$, $n = 163$), indicating that Cd is associated with the sulphide minerals sphalerite and galena. Although Cd exhibits similar behaviour to Zn, it is more enriched in the soil than in the till, which could be explained by Cd's affinity to soil organic matter (Basta et al., 2001). Due to the fact that Cd is more likely to be adsorbed by organic matter than by clay minerals (John, 1972); unlike Zn it is transported into the soil fraction and not trapped by the clay fraction in the till. The inconclusive enrichment of Cd within the soil and till at Ballinalack, emphasises the importance of using a robust element suite as opposed to a single element as an exploration tool.

Compared to the case study of the buried VMS bodies in Ontario (Cameron et al., 2004, Hamilton et al., 2004b), not only Zn and Pb are expected, also associated trace elements of sulphides (Chapter 1, 2, 3) seem to be very important for the mineral exploration of Zn-Pb sulphides bodies. Both Cd and Zn do not change their oxidation state, and thus cannot be transported upwards by redox reactions, also downplaying the reduced chimney model in element transport upwards to the surface. They could only be transported as compounds such as oxides. Further, van Geffen et al. (2012) also report an enrichment of a variety of elements, in their study Zn, Ag, Pb, and Cd in till above the Talbot VMS Cu-Zn prospect. Therefore, a combination of elements can help in identifying buried sulphide mineralisation and avoid interpretation of false anomalies.

5 Conclusion

Geochemical soil surveys for mineral exploration are feasible within pasture land in the Irish Midlands. The investigations of soil BC horizon and top horizon of the till above the Zn-Pb sulphide deposit at Ballinalack illustrate the differences between shallow and deeply buried sulphide mineralisation at a small scale. The following aspects have to be considered:

- Contrary to the published reduced chimney model (Hamilton, 1998, 2000), the pH value should be used with extreme caution as an indicator of sulphide mineralisation at depth in the Irish Midlands and other carbonate hosted deposits, where soils have formed on limestone and naturally neutral to alkaline pH would be expected. However, due to soil acidification, the average soil pH is around 6, and locally clasts of limestone or thin overburden buffer the pH of the soil and till, resulting in random elevated pH values (local) within soil and till samples. Therefore, elevated pH values that could be interpreted as rabbit-ear anomalies can be linked to the limestone clasts rather than the sulphide mineralisation and in soil and till derived from calcareous sediments.
- Elevated metal concentrations should be tested for their accuracy, with comparison to background levels and enrichment factors to validate the data, in particular in environments with changing underlying geology and anthropogenic impacts.
- At Ballinalack, anticipated elevated Fe, Ni and Co and suspect Cr, Mg and V concentrations, above the major sulphide lens, could not be observed and thus do not reflect the underlying mineralisation. However, enrichments occur above the minor sulphide lens as reflected in Pb, Cd, As, Ag, Tl, Zn, Sb and Ba concentrations with decreasing relevance (Fig. 14). These elements were most likely released from the sulphide minerals sphalerite, pyrite and galena, whereas Ba as an accessory element indicates that it originates from the sulphide mineralisation as well.
- An upwards transport following a reduced chimney should not be applied at Ballinalack due to a thick overburden in combination with cover rock, nearby peat fields and disturbed environments with respect to pH, as indicated by elevated concentrations of the elements Cd and Zn, which do not undergo changes in oxidation states and accordingly cannot be transported upwards by redox reactions.
- Both soil as well as till samples are useful in showing elevated concentrations above the minor sulphide lens, indicating that they are directly associated with the minor sulphide lens at Ballinalack and could be used individually in the mineral exploration in the Irish Midlands.

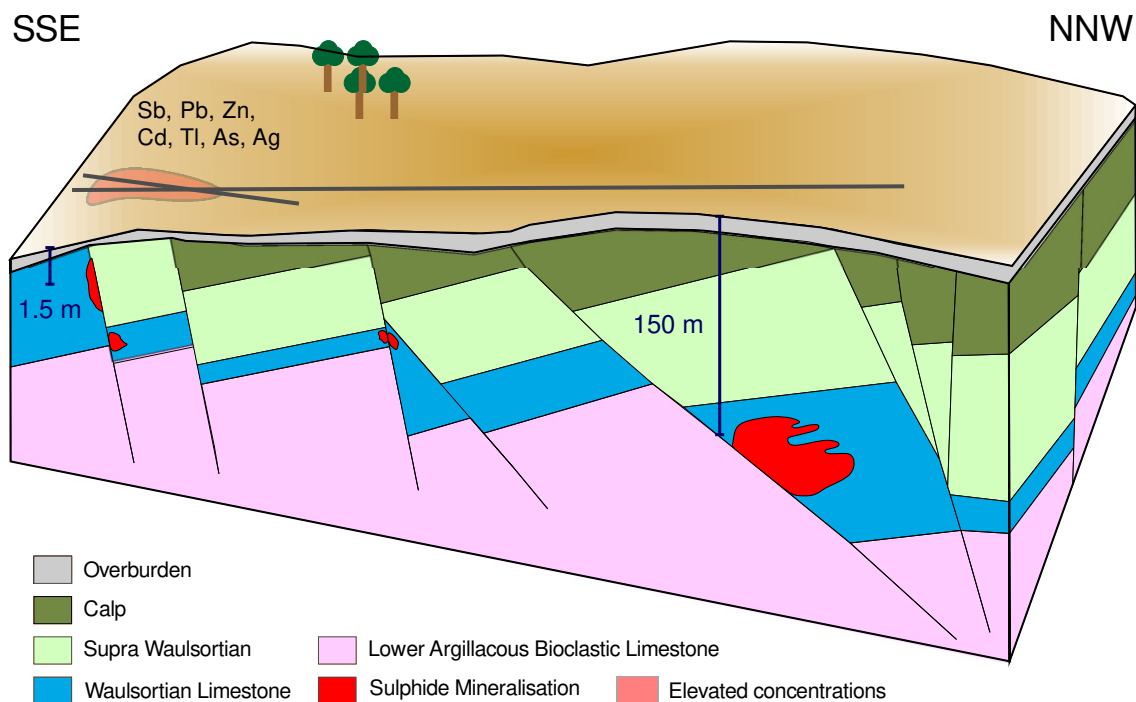


Fig. 14 Geology of Ballinalack after The Robertson Group Plc (1991) with sample line (black) and the occurring elevated elements above the shallow sulphide mineralisation at Ballinalack.

The example of Ballinalack in the Irish Midlands provides that the deeper buried sulphide lens at 150 m depth cannot be discovered with soil geochemistry alone, whereas the shallow sulphide lens (1.5 m depth) is readily detected. Interestingly, the minor sulphide lens is detected not only by Pb and Zn, but also by trace elements, which confirms that they might have been geogenic in source. Despite the anthropogenic influences of the pasture land, the geochemical character of the soil and till signature is still easy detectable. Also, no considerable impact for the mineral exploration can be confirmed from glaciation in this area. It cannot be detected whether soil anomalies have been deposited before the glaciation, certainly it is still at the place even after the glaciation. It may that till has not moved far from the mineralisation; this could be tested by additional sampling according the glaciation flow direction NW to SE. The results reveal that soil geochemical surveys should be used for targeting only areas with sub-cropping or shallowly buried Waulsortian rocks with a potential for Zn-Pb mineralisation, however, they can still be used in environments affected by anthropogenic impacts. The deeply buried sulphide lens might induce an upward transport of elements, which are within the background concentrations. Other methods, such as an application of metal stable isotopes could identify more subtle changes within the soil and till chemistry.

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Chapter 5: Isotope geochemistry in soil and till at Ballinalack Zn-Pb deposit, Ireland - An orientation study

Abstract

The demand for base metals, including Pb, Zn and Cu increases every year. However, locating new deposits is getting more difficult. Thus, innovative exploration methodologies and ideas are required to supply future needs. Soil and till geochemical prospecting is a widely used tool in mineral exploration. With partial digestion or selective leaches, elevated element concentrations can indicate the presence of buried sulphide mineralisation. This has mainly been applied in pristine areas and in areas with shallow mineral deposits. To improve present exploration tools, its application in anthropogenically influenced areas, such as pasture land, and/or deeply buried mineral deposits is of great interest. This orientation study presents a novel approach to soil and till geochemical prospecting using Cu and Zn isotopes, assessing whether stable metal isotopes can be used as an exploration tool. Soil and till samples, as well as sphalerite samples, from the carbonate-hosted Zn-Pb deposit at Ballinalack in the Irish Midlands, were analysed for both Cu and Zn isotopes. The area is dominated by pasture land, which sits upon Quaternary glacial tills, resulting in mixed geochemical signatures. Adding to this complexity, the Ballinalack deposit can be separated into two mineralised settings comprising shallow (1.5 m) and deeply buried (150 m) sulphide mineralisation. At eight locations, both soil BC and top of the till samples were analysed for Cu and Zn isotopes and further five sphalerite samples were investigated for their Zn isotope signatures. Where $\delta^{66}\text{Zn}$ isotopic values (relative to JMC Lyon 3702) are inconclusive and exhibit partly light signatures ($0.07 \pm 0.02 \text{ ‰}$) above the shallow mineralisation compared to the average soil and till samples ($0.28 \pm 0.04 \text{ ‰}$); $\delta^{65}\text{Cu}$ (relative to NIST SRM 976) reveals significantly heavier signatures ($0.25 \pm 0.04 \text{ ‰}$) directly above the shallow mineralisation, compared to the average $\delta^{65}\text{Cu}$ signature ($0.08 \pm 0.04 \text{ ‰}$). The heavier $\delta^{65}\text{Cu}$ signature is likely associated with the release of heavier Cu isotopes from the weathering of sulphide minerals. Notably, the fractionation processes induced by redox-reactions are a key mechanism for the shift towards heavy $\delta^{65}\text{Cu}$ isotopes above the mineralisation. Most remarkably, simple Cu concentrations measured in till and soil are unable to detect buried sulphide mineralisation at depth and can be related to the isotopic signature above the shallow mineralisation. A general trend of heavier isotopes in soil rather than till is observed for both the Cu and Zn isotope systematics. Light isotopes are likely fixed by bacteria and plant-soil interactions in the A-horizon. It would appear that heavier isotopes are washed downwards in the sampled BC horizon, where heavy isotopes are fixed by

organic matter and oxides, leaving lighter isotopes (relative to the BC horizon) for further transport downwards in the soil profile. Overall, Cu isotopes would appear to be promising for shallow mineral exploration despite minor influences from pasture land and variations induced by glaciated materials. This observation will need to be investigated further, however, it has already provided new insights into isotopic tools for geochemical vectoring in mineral exploration.

1 Introduction

Mineral exploration using soil geochemistry is a common exploration tool and has been successfully used to detect buried sulphide deposits (e.g., Cameron et al., 2004, Hamilton et al., 2004, van Geffen et al., 2012, Chapter 4). In these studies, major as well as trace-element patterns were used in soil and till to locate sulphide mineralisation. Exploration tools for buried mineral deposits have gained more interest in recent years, as most shallow near-surface deposits have already been found using conventional exploration methods. Trace elemental studies, such as Cameron et al. (2004) and van Geffen et al. (2012), illustrate that buried (30–240 m) ore deposits can be detected in different pristine environments, such as in arid, semi-arid climates or glaciated terrains. In addition, more challenging areas, such as pastureland, offer unique challenges to exploration due to anthropogenic factors (Chapter 4). At Ballinalack, the buried (150 m) sulphide body cannot be detected using trace elements; however, a shallow sulphide body (1.5 m) was detected through elevated concentrations of Pb, Cd, As, Ag, Tl, Zn, Sb and Ba in soil and till samples (Chapter 4). It is proposed that the trace-element signature is detectable although the anthropogenic land use in soil has been taken place above the shallow sulphide body. However, the buried sulphide body may be undetectable because of anthropogenic alteration of pasture soil and till or the element signatures attributed to the mineralisation have not been transmitted through the cover rock. Thus non-pristine areas require more focussed studies and supplemental geochemical tools that go beyond trace-element geochemistry.

Metal stable isotopes, which have gained more attention and use in recent years, could help to detect more subtle chemical processes in soil and till than trace-element geochemistry alone. In mineral exploration, non-traditional isotopes are already used to characterise base metal deposits, to understand their genesis and implications for mineral exploration. Typical isotope systems used are Cd (Wen et al., 2016, Zhu et al., 2017), Cu (Mathur et al., 2010, Mathur et al., 2014, Mathur et al., 2005, Mathur et al., 2009, Wilson et al., 2016) and Zn (Wilkinson et al., 2005b, Kelley et al., 2009, Gagnevin et al., 2012). Gagnevin et al. (2012) illustrate the change in Zn isotopes in zoned sphalerites from the Navan Zn-Pb deposit in Ireland. In general, with increasing growth of sphalerite, the $\delta^{66}\text{Zn}$ ratio becomes heavier due to kinetic fractionation. Small variations can be explained by source heterogeneity; however, Gagnevin et al. (2012) support that the metal bearing fluids vary by less than 0.2 ‰ in $\delta^{66}\text{Zn}$. Further, during oxidative leaching experiments of sulphide-rich rocks (pyrite, chalcopyrite and sphalerite), Fernandez and Borrok (2009) observed variations in Cu (0.0 to +2.0 ‰) as well as Zn isotopes (0.0 to +0.2 ‰) towards heavier isotopes in the fluid compared to the rock. Similar

experiments, mainly conducted for Cu isotopes, reveal similar results (Ehrlich et al., 2004, Pokrovsky et al., 2008, Kimball et al., 2009, Wall et al., 2011, Mathur et al., 2014).

In soil systems, Cu and Zn isotopes are often used individually or in combination to understand soil processes and elemental mobility within vertical soil profiles (e.g., Viers et al., 2007, Bigalke et al., 2010a, 2010c, 2011, Moeller et al., 2012, Mathur et al., 2012, Vance et al., 2016). Zinc is widely used in environmental studies to trace pollution sources in natural environments (Weiss et al., 2007, Sivry et al., 2008, Bigalke et al., 2010a); more recently, Cd has been used as tool to trace sources of pollution (Wen et al., 2016, Zhang et al., 2016). So far it is known that within soils, heavy Zn isotopes are adsorbed onto oxides, such as Mn oxides (Bryan et al., 2015) or Fe-oxides (Juillot et al., 2008, Balistrieri et al., 2008, Pokrovsky et al., 2008) and phyllosilicates (Li et al., 2015, Guinoiseau et al., 2016). Also, organic matter within soil can fractionate Zn isotopes (Opfergelt et al., 2017) and Cu isotopes (Ryan et al., 2014, Bigalke et al., 2010b); for instance, Opfergelt et al. (2017) report light Zn isotopes in organic carbon rich soil. Further knowledge about these fractionation processes in mineralised settings could help to identify anomalous processes within soil and may help to locate sulphide mineralisation or to define the source of anomalies in soil.

To assess such a novel technique for surficial mineral exploration, we have conducted an orientation study, in which Cu and Zn isotope analyses were applied to soil and till over an undisturbed Zn-Pb deposit to test a methodology that can be used as an exploration tool in glaciated terrains. Soil and till geochemical anomalies were verified and modelled with respect to their underlying Zn-Pb mineralisation which is located in shallowly and deeply buried sulphide zones. Furthermore, it is discussed whether soil or till or both are useful sample media for stable metal isotope analyses. In addition to targeting mineral deposits, Cu and Zn isotopes could help to further understand soil and till interactions with groundwater and soil formation processes.

The sample area is the well-defined and previously investigated Ballinalack Zn-Pb deposit in the Irish Midlands, Ireland (Bradfer, 1982, Caulfield et al., 1986, Clarke et al., 2010, Halls, 1971, Jones and Bradfer, 1982, Jones and Brand, 1986, Chapter 4). As described in Chapter 4, the area was affected by glaciation and is overlain by variable till and soil thicknesses as well as managed pastureland. This area also provides a good comparison between shallowly (1.5 m) and deeply buried (150 m) sulphide mineralisation. Trace-element signatures did not explicitly indicate the presence of deeply buried sulphide mineralisation. More significant to this isotopic study, Cu concentrations in soil and till did not reveal any geochemical response (low enrichment factors <1 , Fig. 7) to the presence of the shallow or deep sulphide

mineralisation; the study includes both mineralised settings for the testing of Cu and Zn isotopic signatures. In addition to soil and till samples, sphalerite was investigated to test the mineralisation as an end member for the Zn isotopic signature. Cu isotopes could not have been measured in sulphides from Ballinalack, due to their low Cu concentrations in combination with small sample masses. The aim of this isotope orientation study is to help guide the direction of future investigations using stable metal isotopes in surficial environments concealing base-metal mineralisation.

1.1 Geology of Ballinalack deposit

The carbonate-hosted Ballinalack Zn-Pb deposit is located in the Irish Midlands, Ireland. Detailed geology is provided in the preceding Chapters 3 and 4. Mineralisation at Ballinalack is hosted by Lower Carboniferous carbonates, occurring within two stratigraphic horizons: minor pyrite as well as galena and sphalerite, mineralisation in the lower Pale Beds and more significant Zn-Pb mineralisation within the overlying Waulsortian Limestone (Jones and Brand, 1986). The Zn-Pb sulphide mineralisation within the Waulsortian Limestone occurs in the form of lenses and pods, which have accumulated in two significant zones (Fig. 1): I) a larger sulphide zone in the north, deeply buried by 150 m of carbonate cover rocks (Calp, and (or) Supra Waulsortian Limestone) as well as overburden, and II) a smaller sulphide lens to the south that is sub-cropping with an overburden cover of approximately 1.5 m (no cover rock intersects the surface from the mineralisation).

Soil in the Ballinalack area can be described as fine loamy drift with siliceous stones (Teagasc, 2014), as well as surface water gley. Widespread peat excavation has taken place in the area surrounding Ballinalack, which have been reclaimed and also used as pasture land (Finch, 1977). After the last glaciation (Midlandian, Knight et al. 2004) soil developed on the till and underwent widespread gleisation in the Irish Midlands (Chapter 4). Its parent material is mainly composed of the calcareous Calp unit. More details are within Chapter 4, note, anomalous concentrations were clearly detectable directly above the sulphide mineralisation. The investigated area is located in a humid climate with an average annual rainfall of ca. 925 mm (MetÉireann, 2016).

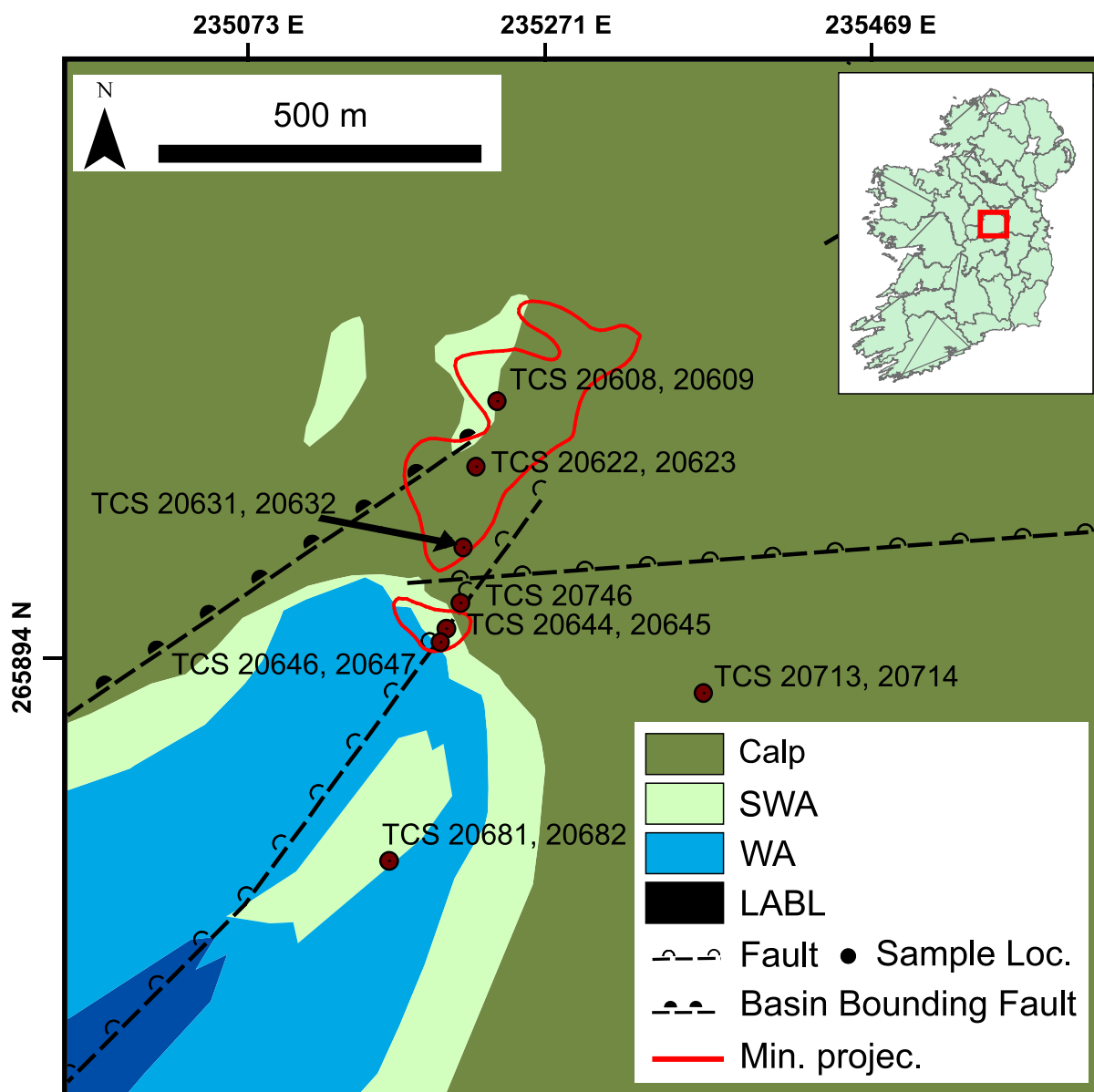


Fig. 1 Geological map of Ballinalack with sample locations used for isotope analysis. Except for TCS 20746 (till), all locations consist of a vertical profile of a soil and a till sampling. The first number defines soil sample number, the last number till samples. SWA = Supra Waulsortian Limestone, WA = Waulsortian Limestone, LABL = Lower Argillaceous Bioclastic Limestone, Min. projec. = Mineralisation projection; Irish Grid TM65 coordinates.

2 Sample material & Methodology

2.1 Sample material

Soil and till samples were collected as part of a soil survey for mineral exploration (Chapter 4). Due to the soil use as pasture land, and the root system of the grass, the top soil A horizon was not sampled. Soil BC horizon samples are brown and relatively devoid of clasts and redox alteration features, range from 15 to 30 cm in average depth-thickness and herein are

referred to as soil (Fig. 2). Top of the till samples are from a depth of 40 to 60 cm, herein referred as till and contain 2–3 cm clasts composed of Calp and Supra Waulsortian Limestone bedded in a silt to clay matrix (Fig. 2). The till commonly varies in colour, these hydromorphic features are a change of redox conditions caused by Fe and Mn reduction (Vepraskas and Sprecher, 1997, Mitsch and Gosselink, 2015, Schoeneberger et al., 2017), most likely due to a varying water table at Ballinalack. A selection ($n = 15$) of those soil and till samples covering the shallow and the buried deposit, as well as background samples, were analysed for Zn and Cu isotopes in the current study; a picture of a vertical profile taken by a Dutch Auger is in Appendix C.

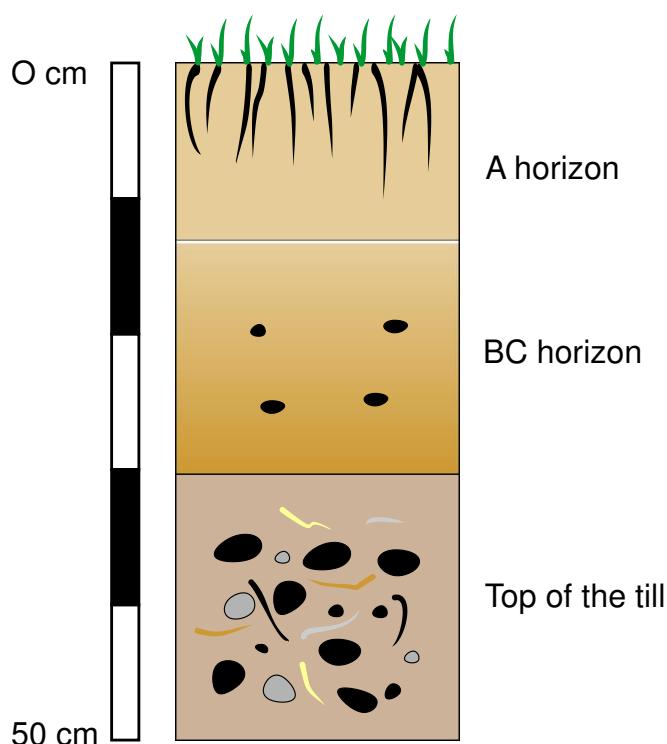


Fig. 2 Schematic picture of typical vertical profile at Ballinalack (Chapter 4). The soil is homogenous and does not show any features produced by redox processes; rarely 1 cm black cobbles derived from the underlying bedrock (Calp) occur. The till can contain various 2-3 cm black (Calp derived) and grey (Supra Waulsortian Limestone derived) clasts. Also, variations in colours (illustrated as wisps in the cartoon) from hydromorphic process are common within the till.

Additionally, five sphalerite separates were collected for Zn isotopes using a New Wave computer-controlled micromill at University College of Dublin (pictures of all samples are within Appendix D in reflected and transmitted light; exemplary BLK 21 is shown in Figure 3). Sample weights vary between 0.12 and 0.42 mg. Copper isotope analyses were not possible, due to the low Cu concentrations within the sphalerites (Chapter 3) in combination with the light sample weight. Sample BLK 21 is distal from the centre of mineralisation (for more details

see Chapter 3) from core B 47, all other samples are from core TC-1344-036 directly through the centre of the major mineralisation. Samples BLK 10a, 12 and 21 were collected from colloform sphalerites, a replacement of carbonate minerals. Samples BLK 08 and 10b were collected from massive sphalerites that is an assemblage of small discrete grains, also as a result of carbonate replacement.

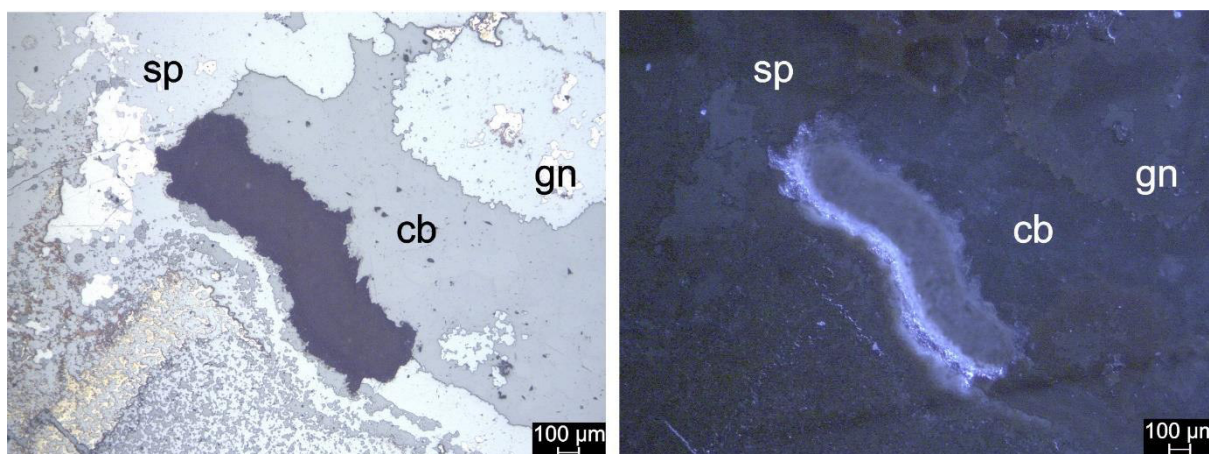


Fig. 3 Photomicrograph of a polished thick section, showing a microdrill path in sphalerite for sample BLK 08. Right in reflected light; left in transmitted light; sp = sphalerite, gn = galena, py = pyrite, sd = siderite, cb = carbonate mineral.

2.2 Sample digestion and analysis

Soil and till samples (100–250 mg) were dissolved in 16 M HNO_3 and 27 M HF followed by 70 % HClO_4 on a hotplate at temperatures varying between 100 and 130 °C. For three samples an additional aqua regia digestion step was necessary due to co-precipitation of crystalline phases (fluorides) during digestion. Sphalerite samples underwent a simple aqua regia digestion on a hot plate at 110 °C. Some difficulties were encountered during the sample digestion and two protocols were applied, the detailed digestion protocol and development for soil, till and sphalerite samples are given in Appendix D.

The Zn and Cu separation protocol was adopted from Maréchal et al. (1999) and Guinoiseau et al. (2016) and can be examined in detail in Table 1. Columns of 12 ml were used filled with 2 ml of Biorad AG-MP1 200-400 mesh resin. For both Zn and Cu fractions, a second separation was conducted (Tab. 2). For Cu the same columns were used with only 0.8 ml of resin. For Zn isotopes, the second separation took place differently using a 0.8 x 4 cm micro-column, filled with ca. 0.2 ml resin (column preparation is provided in Appendix D).

Tab. 1 Ion exchange chromatography protocol of 1st step for Cu and Zn.

Step	Volume	Reagent	Comment
Washing	8 ml	HNO ₃ 1M	
Washing	8 ml	MilliQ water	
Conditioning	6 ml	HCl 6 M	
Sample introduction	1 ml	HCl 6 M	
Elution matrix	9 ml	HCl 6 M	
Elution Cu	21 ml	HCl 6 M	
Elution Fe	10 ml	HCl 2 M	Discard
Elution Zn	10 ml	HNO ₃ 0.5M	2ml/8ml steps

Tab. 2 Ion exchange chromatography protocol for 2nd step for Cu (left) and Zn (right).

Cu			Zn		
Step	Volume	Reagent	Step	Volume	Reagent
Washing	4 ml	HNO ₃ 1 M	Soak sample	1 ml	HBr 1.5 M
Washing	4 ml	MilliQ water	Clean	Full tank ¹	MilliQ water
Washing	4 ml	HNO ₃ 1 M	Clean	Full tank ¹	HNO ₃ 0.5 M
Washing	4 ml	MilliQ water	Clean	Full tank ¹	MilliQ water
Conditioning	3 ml	HCl 6 M	Clean	Full tank ¹	HNO ₃ 0.5 M
Sample introduction	1 ml	HCl 6 M	Clean	Full tank ¹	MilliQ water
Matrix elution	2 ml	HCl 6 M	Clean	Full tank ¹	HNO ₃ 0.5 M
Cu elution	7 ml	HCl 6 M	Clean	1/3 tank	MilliQ water
Washing	10 ml	MilliQ water	Condition	1/2 tank	HBr 1.5 M
			Sample introduction	1 ml	
			Rinse	Full tank ¹	HBr 1.5 M
			Rinse	Full tank ¹	HBr 1.5 M
			Zn elution	Full tank ¹	HNO ₃ 0.5 M
			Zn elution	Full tank ¹	HNO ₃ 0.5 M
			Discard Resin		

¹Full tank, approx. 3 ml

For the Cu and Zn fractions, an Alfa Aesar stock (AAS) solution (Chen et al., 2009) was added as doping with $^{66/64}\text{Zn} = 0.565055 \pm 0.000004$ (2σ) and $^{65/63}\text{Cu} = 0.44574 \pm 0.000004$ (2σ), respectively, achieving a ratio of $\text{Zn}/\text{Cu} = 2$. The doping leads to a better detection (empirically tested) of the isotopes in the ratio $\text{Zn}/\text{Cu} = 2$ at the instrument used. The samples were processed and analysed using a Neptune Plus (ThermoFinnigan) multi-collector inductively-coupled plasma mass spectrometer (MC ICP-MS) with sample standard bracketing at the Institute de Physique du Globe du Paris. The doping stock solutions AAS were also used as an in-house standard. Zinc and Cu isotopes are expressed using the following notation:

$$\delta^{66}\text{Zn}_{\text{JMC}} = \left[\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{JMC}}} - 1 \right] \cdot 10^3 (\text{‰}) \quad (1)$$

and

$$\delta^{65}\text{Cu}_{\text{NIST 976}} = \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST 976}}} - 1 \right] \cdot 10^3 (\text{‰}) \quad (2)$$

The samples were analysed three times, each bracketed with standards. The resulting standard deviation is calculated by the average of the repeated analysis and sample standard bracketing.

The in-house standards were calibrated to IRMM 3702 (Zn) and NIST SRM 976 (Cu). For Zn, results are further transformed to JMC Lyon 3702. All data are expressed for Zn relative to JMC Lyon 3702 and for Cu relative to NIST SRM 976 (Cloquet et al., 2006, Moeller et al., 2012, Chen et al., 2009); deviations are reported as 2σ based on three repetitive analysis of each sample. The laboratory duplicate (Tab. 3) reflects a reproducibility for Zn isotopes of 0.01 ‰, 2σ and for Cu isotopes of 0.03 ‰, 2σ . Nevertheless, the general reproducibility of IRMM 3702 and NIST SRM 976 are 0.04 ‰, 2σ . Prior to and after chromatography, Zn and Cu concentrations were analysed for yield control using ICP-MS and -OES. Blanks were acceptable with less than 0.5 and 0.3 % compared to lowest concentrations for Zn and Cu, respectively. Also, BCR-2 was processed for additional control on the method and gave results of $\delta^{66}\text{Zn}_{\text{JMC}}$ of $0.24 \pm 0.04 \text{ ‰}$ (2σ) and $\delta^{65}\text{Cu}_{\text{NIST 976}} = 0.24 \pm 0.03 \text{ ‰}$ (2σ) that are in agreement with the values reported in literature (Bigalke et al., 2010a, Bigalke et al., 2011, Liu et al., 2014, Sossi et al., 2015, Guinoiseau et al., 2016). For more details about mass dependent fractionation, blanks, standards and recovery of this study see Appendix D.

3 Results

A summary displaying the overall variation in $\delta^{66}\text{Zn}$ for soil, till and sphalerite samples, and for $\delta^{65}\text{Cu}$ for soil and till samples is shown in Table 3 and Figure 4. In general, $\delta^{66}\text{Zn}$ sphalerite samples vary between $0.06 \pm 0.03 \text{ ‰}$ and $0.35 \pm 0.04 \text{ ‰}$. Surficial samples including both soil and till vary from $\delta^{66}\text{Zn} = 0.07 \pm 0.02$ to $0.41 \pm 0.02 \text{ ‰}$ and $\delta^{65}\text{Cu}$ from -0.19 ± 0.01 to $0.25 \pm 0.01 \text{ ‰}$.

Tab. 3 Results for trace elements (in ppm), Cu and Zn isotopes (in ‰), $\delta^{66}\text{Zn}$ is relative to JMC Lyon 3702 and $\delta^{65}\text{Cu}$ is relative to NIST SRM 976. Sphalerite Zn concentrations are obtained from SEM-EDX analysis (see Chapter 3). In grey samples above shallow mineralisation, sp = sphalerite.

Sample name	Type	As ²	Cd ²	Cu	Fe ²	Pb ²	Sb ²	Zn	$\delta^{66}\text{Zn}$	2 σ	$\delta^{65}\text{Cu}$	2 σ
Sphalerite 08	sp							666600	0.21	0.04		
Sphalerite 10a	sp							664800	0.20	0.03		
Sphalerite 10b	sp							664800	0.08	0.03		
Sphalerite 12	sp							670200	0.35	0.04		
Sphalerite 21	sp							681200	0.06	0.03		
TCS 20608	soil	4	1	8	12200	15	0	93	0.41	0.02	0.07	0.01
TCS 20609	till	9	1	18	28000	16	1	97	0.30	0.03	-0.19	0.01
TCS 20622	soil	5	1	5	13600	23	0	139	0.36	0.05	0.14	0.03
TCS 20623	till	8	3	19	21100	11	1	101	0.34	0.01	0.07	0.04
TCS 20631	soil	5	2	10	12000	24	1	173	0.32	0.04	0.09	0.03
TCS 20632	till	6	1	13	18000	13	1	105	0.34	0.03	-0.19	0.04
TCS 20644	soil	295	68	12	22500	6430	187	9376	0.16	0.06	0.25	0.01
TCS 20645	till	192	43	13	34100	3420	197	12150	0.07	0.02	0.08	0.04
TCS 20646	soil	146	5	9	20500	627	19	2221	0.27	0.04	0.23	0.03
TCS 20647 ¹	till	135	4	15	27000	359	22	4341	0.32	0.05	0.25	0.03
TCS 20647 (a)	till								0.31	0.05	0.28	0.03
TCS 20647 (b)	till								0.32	0.05	0.22	0.03
TCS 20681	soil	11	1	14	16300	24	1	165	0.29	0.01	0.08	0.01
TCS 20682	till	15	4	23	21700	34	2	163	0.27	0.02	0.11	0.03
TCS 20713	soil	5	1	10	13500	12	1	87	0.37	0.03	0.17	0.01
TCS 20714	till	7	3	16	17800	12	1	97	0.33	0.02	0.06	0.01
TCS 20746	till	12	9	28	27500	39	4	1585	0.19	0.04	0.09	0.03

¹ Laboratory duplicate, reported for interpretation as average of both values

²Based on aqua regia digestion

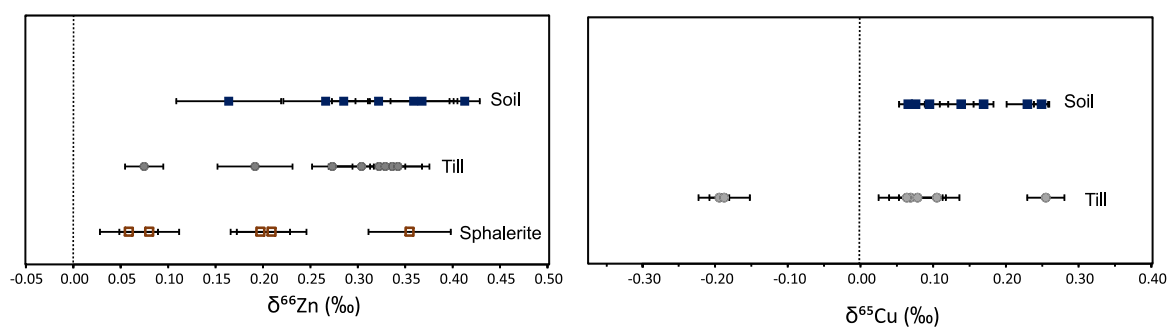


Fig. 4 Isotope variation in different media at Ballinalack in comparison to the literature values.

3.1 Zinc isotope variations

A Pearce (R) correlation for soil and till between isotopic values and bulk element concentrations reveal distinct patterns (Tab. 4, Fig. 5, 6). In general, all significant correlations for $\delta^{66}\text{Zn}$ are negative. Considerably strong negative correlations occur with Cd (R = -0.92), Pb (R = -0.84), Zn (R = -0.79) and Fe (R = -0.79) in till (n = 8, Fig. 6); in soils, As (R = -0.88), Pb (R = -0.82), Zn (R = -0.85) and Fe (R = -0.9), as well as with $\delta^{65}\text{Cu}$ (R = -0.78); n = 8, Fig. 5. Note, no correlation can be observed in till between $\delta^{66}\text{Zn}$ and $\delta^{65}\text{Cu}$.

Tab. 4 Correlation (R > 0.5 and R < -0.5) of element concentration to $\delta^{66}\text{Zn}$ and $\delta^{65}\text{Cu}$ in each soil and till at Ballinalack. Note, concentrations are based on partial aqua regia digestion; n = 7 for soil and n = 8 for till samples.

Till	$\delta^{66}\text{Zn}$	Soil	$\delta^{66}\text{Zn}$	Soil	$\delta^{66}\text{Zn}$	Till	$\delta^{65}\text{Cu}$	Soil	$\delta^{65}\text{Cu}$
Cd	-0.92	Ni	-0.91	Sn	-0.6	Mo	0.58	$\delta^{66}\text{Zn}$	-0.69
Mg	-0.91	Fe	-0.9	Cr	-0.57			Ca	0.52
Ba	-0.9	Mg	-0.9	LOI (%)	-0.56			Cr	0.52
U	-0.88	As	-0.88	S	-0.53			In	0.55
Se	-0.87	Y	-0.86	V	0.64			Zr	0.58
Ag	-0.84	Ba	-0.85					Ag	0.65
Pb	-0.84	Zn	-0.85					Cd	0.65
Sb	-0.84	Cu	-0.83					Mg	0.66
Nb	-0.8	Sb	-0.83					Pb	0.67
Zn	-0.8	Tl	-0.83					Sb	0.68
Fe	-0.79	Pb	-0.82					Ba	0.71
Ga	-0.79	Ag	-0.81					Zn	0.73
Ni	-0.79	Cd	-0.81					Sn	0.74
LOI (%)	-0.74	In	-0.79					Ga	0.75
Tl	-0.72	Sc	-0.79					Fe	0.81
Li	-0.7	Ca	-0.77					As	0.83
Ca	-0.67	Co	-0.71					Tl	0.87
As	-0.63	$\delta^{65}\text{Cu}$	-0.69					Nb	0.91
Sr	-0.61	Ga	-0.68						
S	-0.56	Nb	-0.68						
Cu	-0.54	Sr	-0.68						
Sn	-0.54	Mo	-0.63						
Co	-0.52	Se	-0.62						

Surficial samples display a general trend of heavier isotopic signatures in soil than in till samples (Fig. 8); the heaviest $\delta^{66}\text{Zn}$ signatures are above the Calp unit over the buried sulphide mineralisation (TCS 20608) with 0.41 ± 0.02 ‰, similar to background samples (e.g. TCS 20713) with 0.37 ± 0.03 ‰. The lightest $\delta^{66}\text{Zn}$ values are mainly above the shallow sulphide body (TCS 20644, 20645, 20646) with 0.07 ± 0.02 ‰ to 0.27 ± 0.04 ‰ and slightly north of the sulphide body (TCS 20746) of 0.19 ± 0.05 (Fig. 7).

High Zn concentrations already show an anomaly above the shallow sulphide mineralisation that is confirmed by a high enrichment factor. This can be further validated by light Zn isotope signatures in both soil and till (Fig. 7, 9). The direct comparison of the $\delta^{66}\text{Zn}$ values to the concentrations of sulphide bearing elements (Fe, Cd, Zn, Pb, Cd; Fig. 8, 9, 13), reveal a correlation between the isotopic and element signatures. Even though the Zn isotopes mirror the shallow mineralisation, the deeply buried mineralisation cannot be detected by either the element concentrations or Zn isotopes.

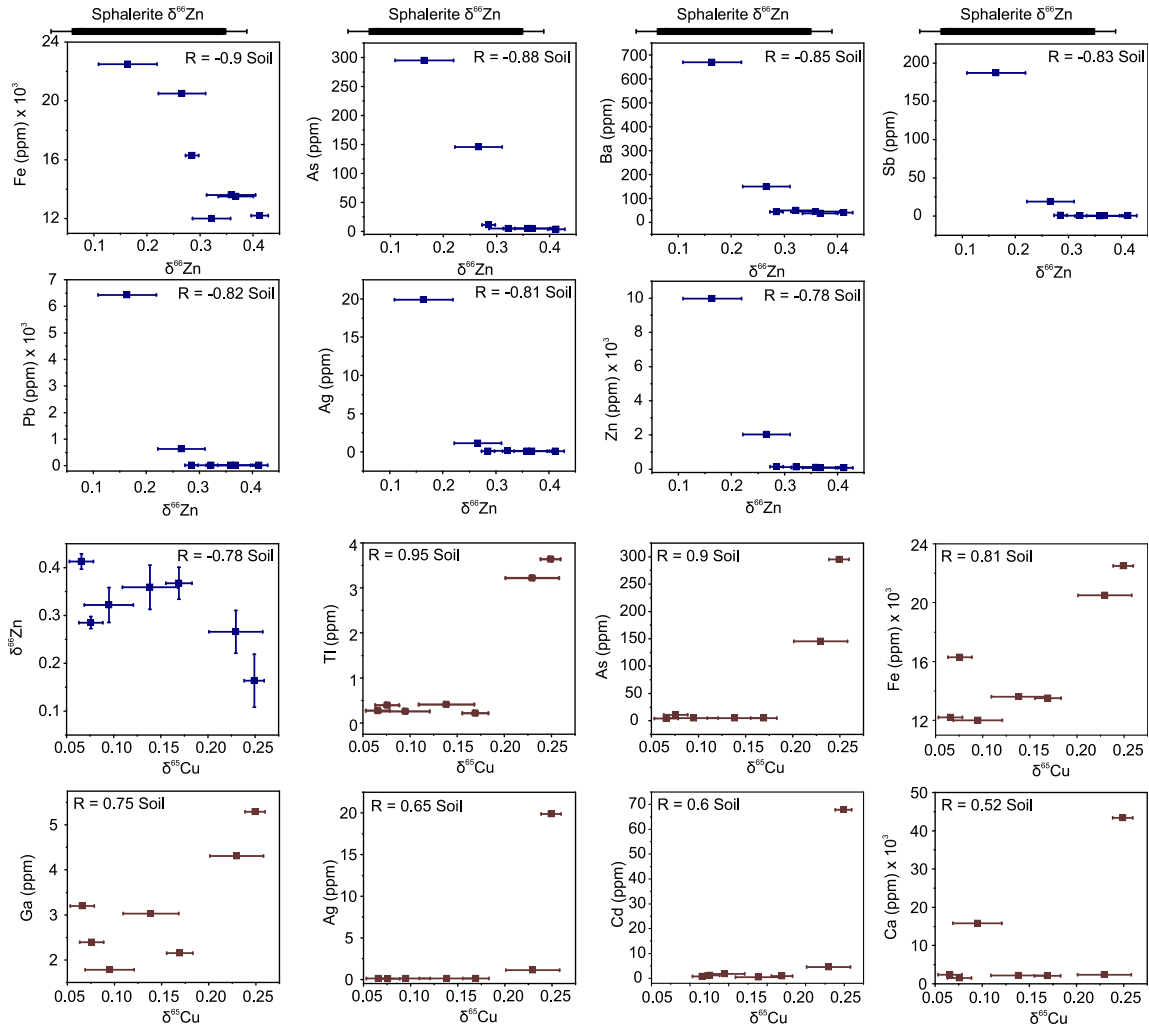


Fig. 5 Selection of correlations of soil samples at Ballinalack, soil n = 7. Strong correlations exist to elements associated with sulphide minerals. Those plots display in particular the strong correlation of high concentrations of those elements with the lightest $\delta^{66}\text{Zn}$ and highest $\delta^{65}\text{Cu}$ ratio.

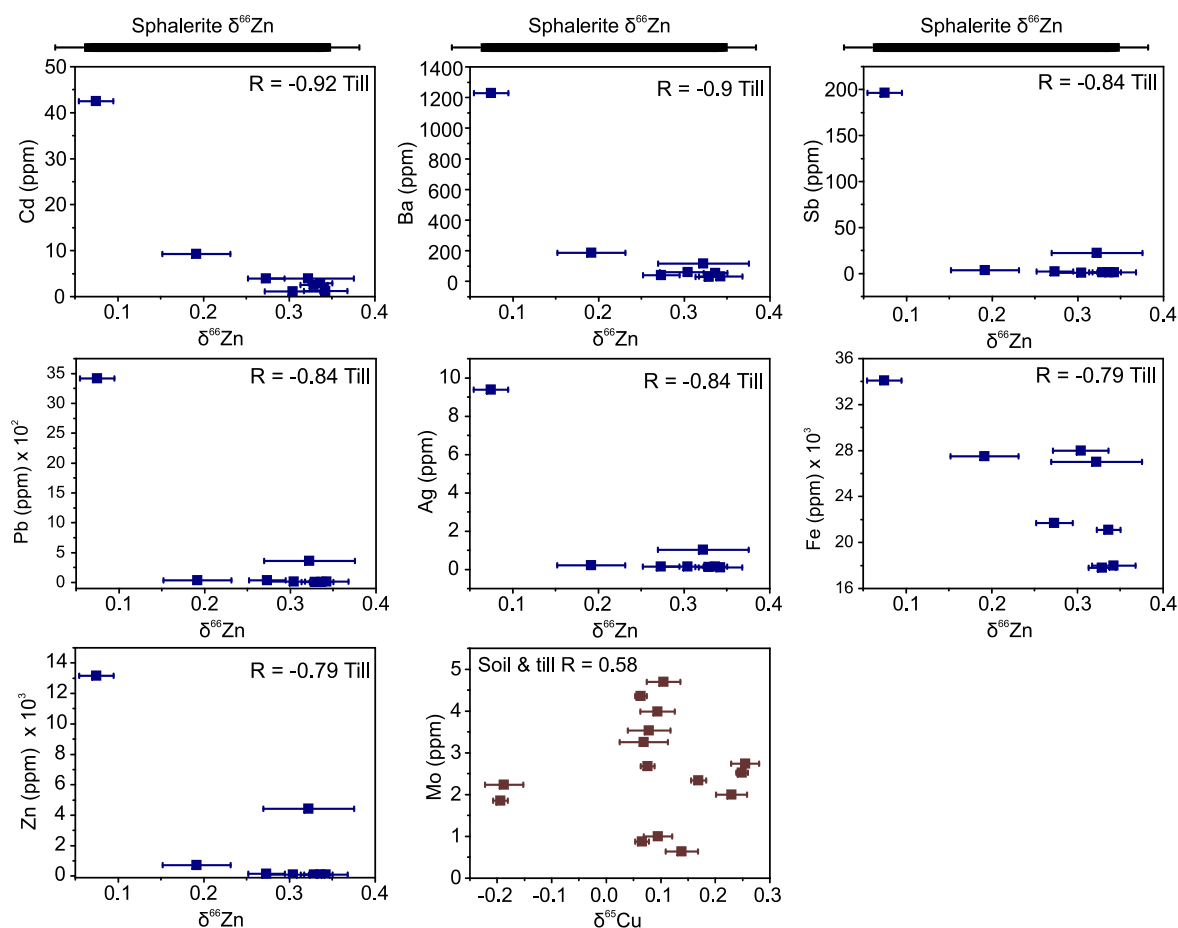


Fig. 6 Correlation of elements with isotopes in till at Ballinalack; $n = 8$. Strong correlations exist to elements associated with sulphide minerals. Those plots display in particular the strong correlation of high concentrations of those elements with the lightest $\delta^{66}\text{Zn}$ ratio.

3.2 Copper isotope variations

In till samples, a Pearce (R) correlation between $\delta^{65}\text{Cu}$ and bulk element concentrations are moderate, the highest with Mo ($R = 0.58$, $n=8$, Fig. 6). However, in soil samples, strong positive correlations exist with other elements, for instance Tl ($R = 0.95$), Fe ($R = 0.88$) and As ($R = 0.9$, Tab. 4 and Fig. 5). Remarkably, a strong negative correlation occurs with $\delta^{66}\text{Zn}$ ($R = -0.78$). An overview of all strong correlations is illustrated in Table 4.

Copper isotopes do not reveal the same trend as the Zn isotope signatures (Fig. 7). The light $\delta^{65}\text{Cu}$ signatures in tills above the deeply buried mineralisation above the Calp unit are quite distinctive (Fig. 7, 8) with samples TCS 20609 and TCS 20632 both showing $\delta^{65}\text{Cu} = -0.19 \pm 0.04$ ‰. However, they are still close to the background signature. The heaviest $\delta^{65}\text{Cu}$ signatures of both soil and till occur above the shallow mineralisation (TCS 20647, 20644 and 20646) ranging between 0.23 ± 0.03 ‰ and 0.25 ± 0.03 ‰ (Fig. 7).

Remarkably, Figure 7 shows that the Cu concentrations and their corresponding enrichment factors do not indicate the presence of underlying sulphide lenses. However, Cu isotope signatures in soil and till samples do exhibit anomalies that reflect the shallow mineralisation, easily seen when compared to the Zn concentration (Fig. 7).

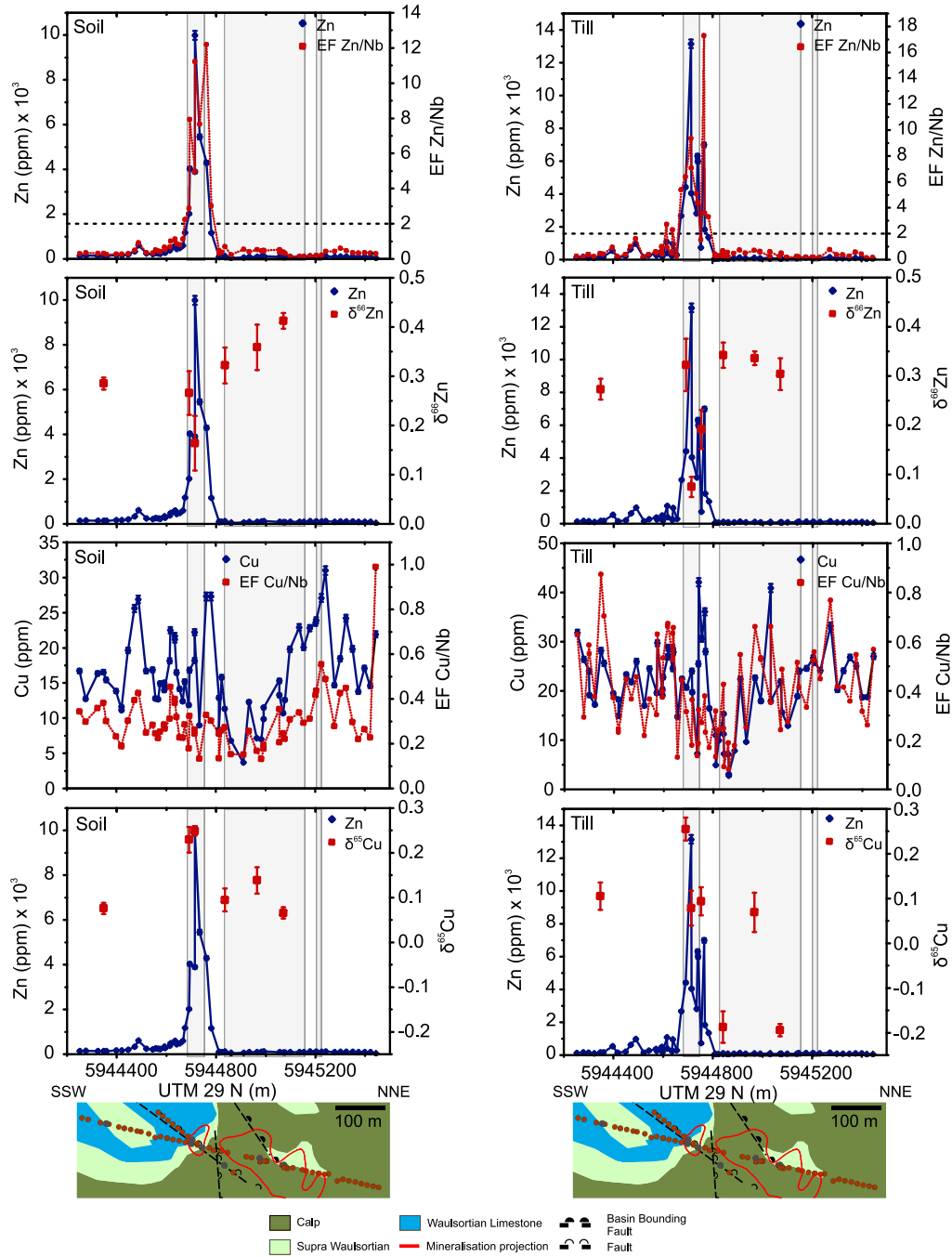


Fig. 7 Overview of concentrations compared to Cu and Zn isotopes. Elements Cu and Zn in comparison to their enrichment factor (see Chapter 4); Cu does not reveal anomalous concentrations, however, Cu and Zn isotopes compared with Zn concentrations show that the shallow mineralisation may be reflected by both isotopes. The grey shade in the graphs indicate the projected sulphide mineralisation.

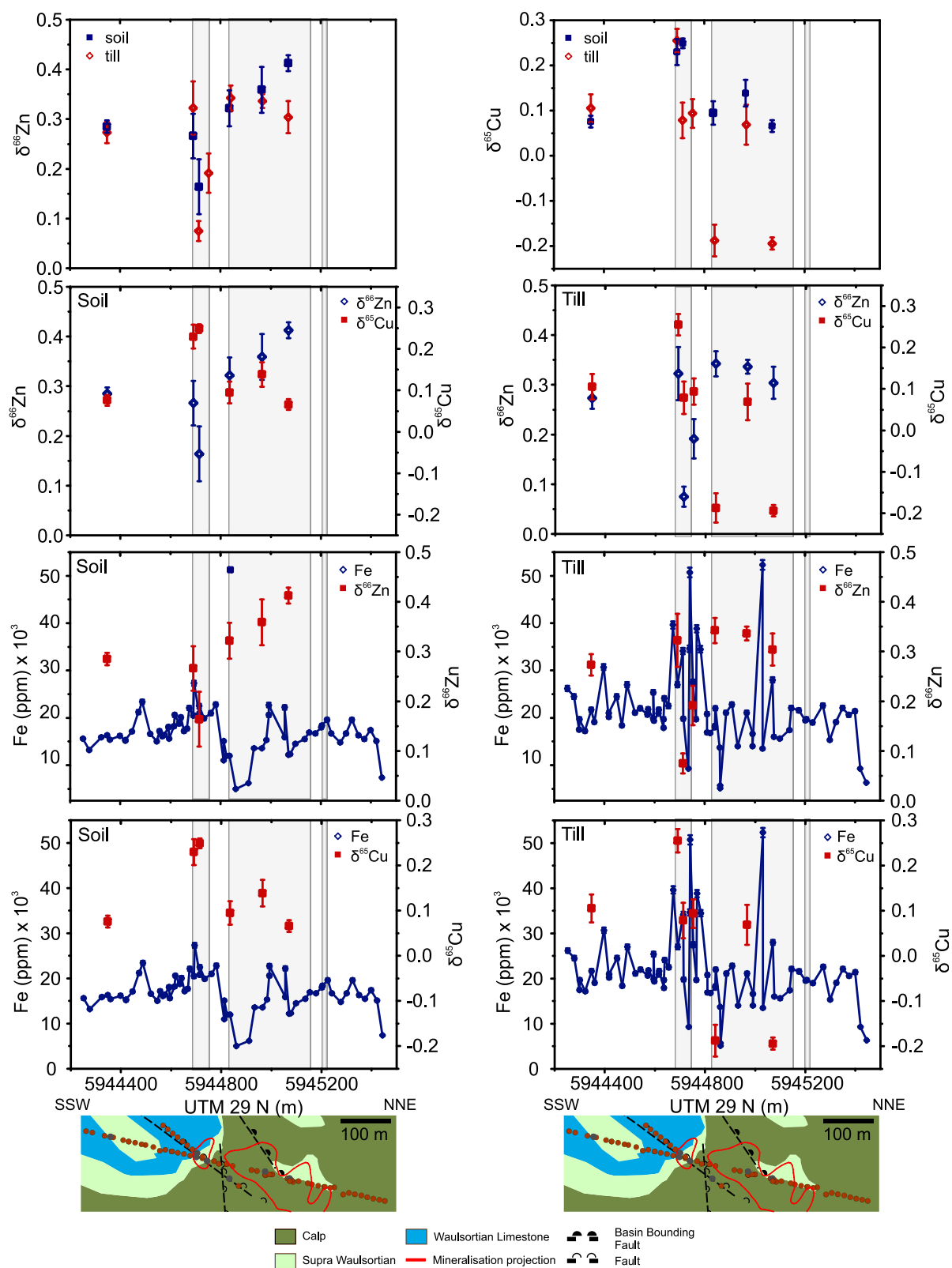


Fig. 8 Overview of Cu and Zn isotopes for each soil and till; comparison of both isotopes showing their opposing behaviour. Also both isotopes compared with Fe, showing light correlation (compare Fig. 5, 6). The grey shade in the graphs indicate the projected sulphide mineralisation.

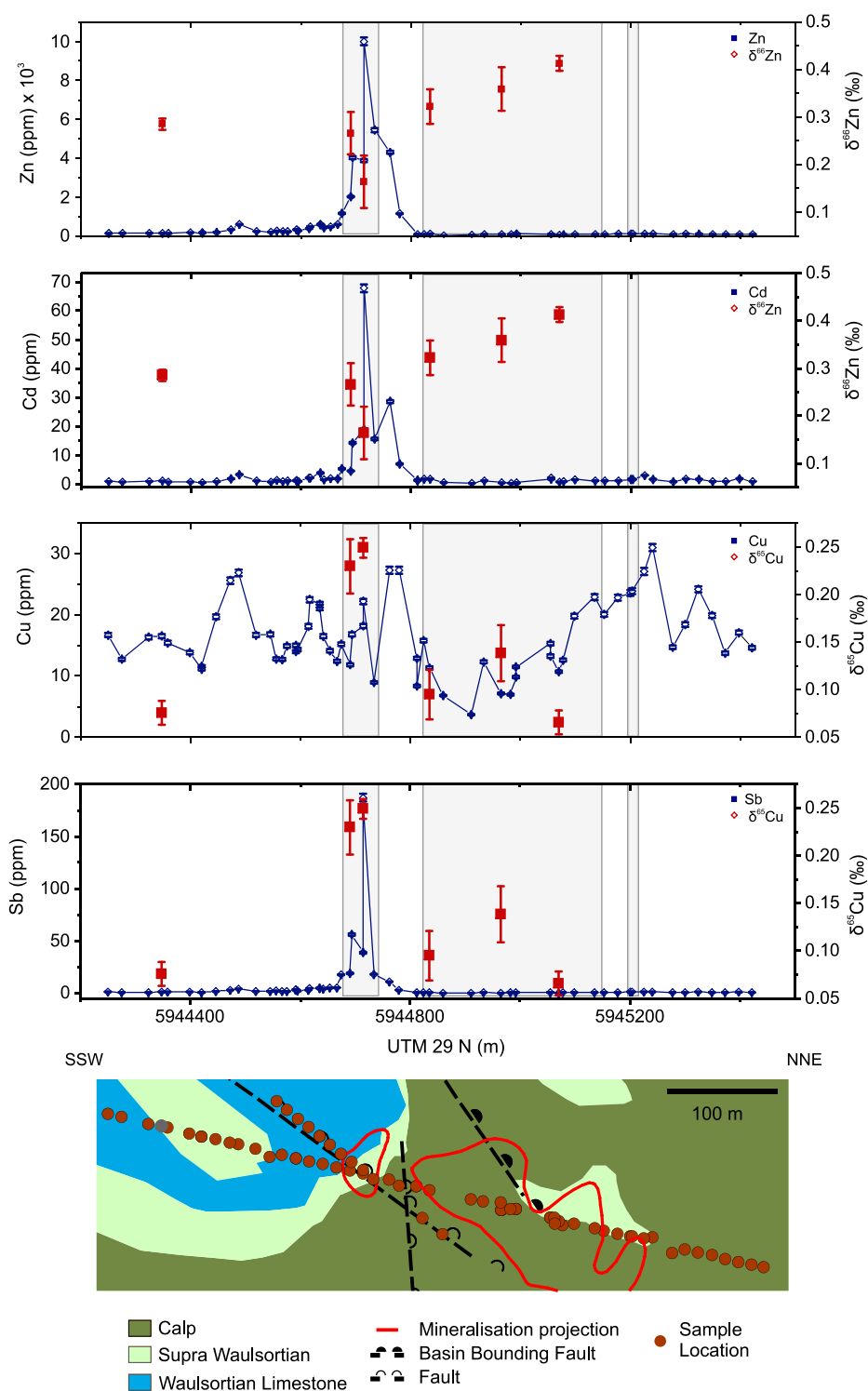


Fig. 9 Enlarged overview of soil Zn and Cu concentrations as well as their isotope ratios in association with its lateral distribution and trace elements in soils. The grey shade in the graphs indicate the projected sulphide mineralisation. Notably, both Cu and Zn isotopes may indicate the underlying shallow mineralisation in heavy and light signature, respectively. The strong association with sulphide bearing elements such as Cd and Sb indicate that most likely the sphalerites are the source causing the signature in the soil.

4 Discussion

4.1 Sphalerite samples

The $\delta^{66}\text{Zn}$ signatures ($\delta^{66}\text{Zn} = 0.06 - 0.35 \text{ ‰} \pm 0.04$) for the five sphalerite samples are within the average range (Fig. 10) for measured Irish-type sphalerite samples ranging from -0.23 to +1.33 ‰ (Gagnevin et al., 2012, Wilkinson et al., 2005b). This broad variation is associated with different stages of precipitation. Wilkinson et al. (2005b) explain that the lightest $\delta^{66}\text{Zn}$ signatures might be due to kinetic isotopic fractionation during rapid precipitation, caused by a fluid mixing of metalliferous and sulphur-rich fluids. Those sphalerites are associated with feeder vein zones beneath the main sulphide bodies, whereas major sulphide bodies are characterised by slightly heavier $\delta^{66}\text{Zn}$ signatures. This is caused by Rayleigh fractionation with a precipitation of sphalerites from Zn-depleted fluids.

This trend can be confirmed by Kelley et al. (2009) on sphalerites from the Red Dog district, Alaska. Accordingly, the sphalerites at Ballinalack may have also underwent Rayleigh fractionation during precipitation from a Zn depleted fluid. However, basement samples of the Lower Palaeozoic beneath the nearby Navan orebody have a range of $\delta^{66}\text{Zn} = -0.02$ to $+0.23 \text{ ‰}$ (Gagnevin et al., 2012), encompassing roughly the range of sphalerites from Ballinalack $\delta^{66}\text{Zn} = 0.06$ to 0.35 ‰ . Sphalerite samples at Ballinalack, with metals derived from the Palaeozoic basement (e.g., Caulfield et al., 1986, LeHuray et al., 1987, Dixon et al., 1990, Everett, 1999, Everett et al., 2003, Walshaw et al., 2006, Wilkinson and Hitzman, 2010, Wilkinson et al., 2005a), may simply reflect the source rock and have not undergone further isotopic fractionation. Furthermore, Gagnevin et al. (2012) demonstrates the variation of Zn isotopes on a small scale by investigating colloform textured growth bands. They observed a $\delta^{66}\text{Zn}$ signature range of 0.33 ‰ showing a trend from lighter to heavier signatures towards the growth direction. A similar trend was reported in an experimental study conducted by Archer et al. (2004). It is proposed that varying precipitation regimes during formation of the sulphides as well as surface reactions and diffusion caused by varying fluid mixing rates, lead to the variations in the $\delta^{66}\text{Zn}$ signature within the sphalerites. The variations are also most likely caused by kinetic fractionation through a change in mixing rate and thus their varying precipitation rate as proposed by Gagnevin et al. (2012) for the nearby Navan Zn-Pb deposit. However, as stated above, the isotope ratio might also reflect the source rock itself, as a transported isotope ratio without experiencing isotope fractionation.

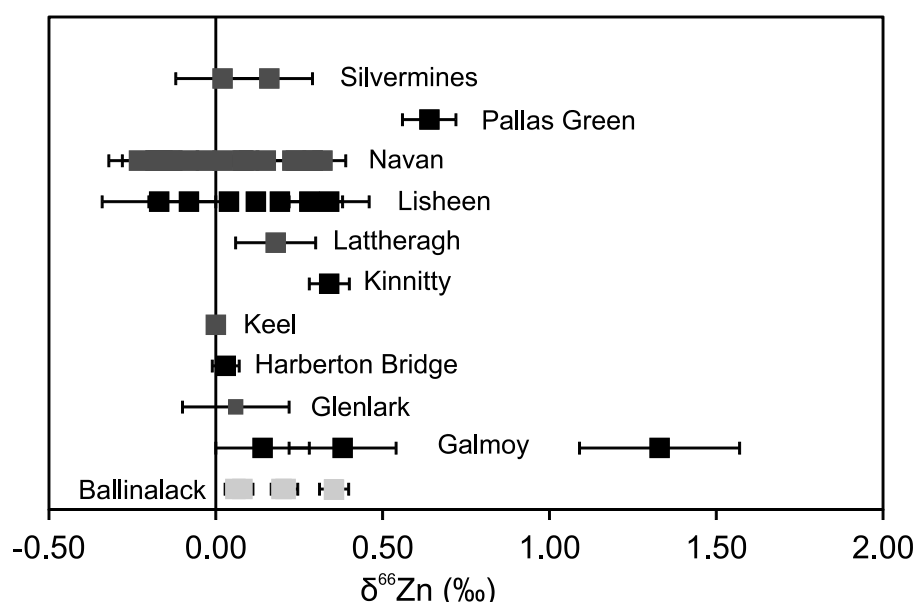


Fig. 10 Comparison of Zn isotopes between Irish-type sphalerites (Wilkinson et al., 2005b, Gagnevin et al., 2012) and sphalerites from Ballinalack (this study).

The sphalerite samples were analysed to understand the source of Zn isotope signatures in soil and till over the Ballinalack deposit, and the degree of fractionation resulting from fluid migration towards surface. Ideally, the lightest isotopic signature exists within the sulphides; during weathering slightly lighter 0.2 ‰ could be released (Fernandez and Borrok, 2009), which shifts during mobilisation towards heavier isotopes, e.g. adsorption onto clay minerals, Fe-oxides and organic matter (e.g., Pokrovsky et al., 2005, Jouvin et al., 2009, Guinoiseau et al., 2016). Sphalerites from Ballinalack appear slightly lighter in $\delta^{66}\text{Zn}$ signatures than the soil and till samples (Fig. 4). However, sphalerite sample BLK 12 exhibits a heavy $\delta^{66}\text{Zn}$ isotope signature of 0.35 ± 0.04 ‰ equivalent to the highest till signature recorded at 0.34 ± 0.03 ‰. It cannot be excluded, that sphalerite grains (nugget effect) that could not be detected in the mineralogy (Fig. 11, more details in Chapter 4) of the soil and till, may occur within the surficial sediment samples and furthermore, an average Zn isotopic signature of the sphalerite responsible for the till signatures. Therefore, the $\delta^{66}\text{Zn}$ signature can still be used as an end member in the Ballinalack system to understand the origin of the anomalous geochemical (bulk) signatures within the overlying soil and till.

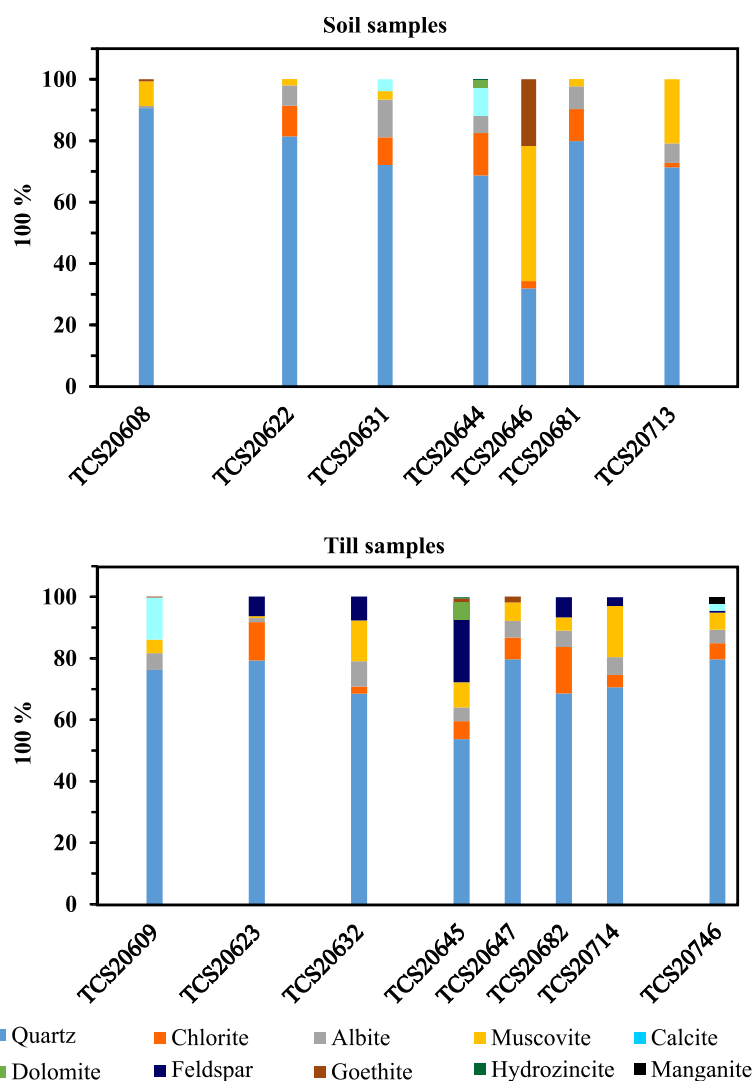


Fig. 11 Comparison and overview of soil and till mineralogy at Ballinalack; normalised to 100 % (modified after Chapter 4). Predominant phases are quartz, muscovite, albite and chlorite 9 (as representative form of clay minerals). Note, till is more enriched in chlorite than the soil samples.

4.2 Soil and till samples

Both Cu and Zn isotopes show strong correlations with element concentrations in soil as well as in till samples. These correlations can be an indication of associated soil formation processes and their element origins. Fractionation processes in soil and till for Cu and Zn isotopes could originate from a combination of redox processes (only for Cu isotopes) (Zhu et al., 2002, Ehrlich et al., 2004, Mathur et al., 2005) and (or) complexing with soil organic matter (Ban et al., 2002, Jouvin et al., 2009, Bigalke et al., 2010b, Ryan et al., 2014), and sorption onto clay minerals and (or) (hydr-) oxides (Pokrovsky et al., 2005, 2008, Gélabert et al., 2006, Balistrieri et al., 2008, Juillot et al., 2008, Navarrete et al., 2011, Kafantaris and Borrok, 2014, Bryan et al., 2015, Coutaud et al., 2014, Guinoiseau et al., 2016).

One of the most important isotopic fractionation soil processes was first observed and described by Grybos et al. (2007), and involved the distribution of isotopes following equilibrium of Cu and Zn between aqueous organic complexes and adsorption onto oxides. In general, both fractionation processes lead to a shift towards heavier isotopic signatures in adsorbed metal. However, in any competition the heavier isotopes are preferentially bound by organic complexes and lighter isotopes are accommodated by adsorption onto Fe-oxides (e.g., Vance et al., 2008, Vance et al., 2016, Bigalke et al., 2010b, 2011, Ryan et al., 2014). In addition, the sorption to microbes increases towards the soil surfaces, notably, in a sorption of heavier isotopes of both Cu and Zn (Arnold et al., 2010, Navarrete et al., 2011). For soil samples at Ballinalack, a strong correlation $R = 0.81$ exists between $\delta^{65}\text{Cu}$ and Fe (Fig. 5, 8); two options could explain this correlation: (1) this could reflect the sulphide source associated with Fe rich minerals, e.g., chalcopyrite and pyrite; and (2) the more Fe is accumulated within the soil, the heavier is the signature of Cu isotopes, corresponding that Fe oxides adsorb preferentially the heavy Cu isotopes in natural systems (Balistrieri et al., 2008, Bigalke et al., 2010c, Fernandez and Borrok, 2009, Mathur et al., 2005), indicating the organic matter may play a minor role within the setting of Ballinalack. A fixation of heavier isotopes (Cu and Zn) in the topsoil would lead to a washing out of lighter isotopes towards deeper soils and more specifically till at the Ballinalack deposit. Consequently, all these processes could explain the slightly heavier $\delta^{65}\text{Cu}$ signature in soil compared to till for Cu and Zn isotopes (Fig. 8), except for samples occurring directly above the shallow mineralisation, in the vertical profiles at Ballinalack (Fig. 7, 8, 13).

In theory, anthropogenic aerial dust could also lead to an increase in heavy isotopes towards the soil surface. However, the location of Ballinalack was chosen to avoid any aerial dust input. The prevailing westerly winds diminish the aerial dust input and no former nor recent industrial smelter has been established close to the sample area or upwind of the prevailing wind direction. Agriculturally used fertiliser would shift the isotope ratio towards a heavier signature (Chen et al., 2008), which could also lead a role in soils at Ballinalack. Although the fields are mainly used as pasture land, a fertilisation in the past cannot be excluded. After Bigalke et al. (2010a), ash from smelting would introduce isotopically lighter $\delta^{66}\text{Zn}$ signatures in the soils. Also, fractionation processes caused by plant-soil interaction are minimised by sampling 10 cm underneath the sward; however, it could still have a minor influence on the underlying BC horizon. According to Weiss et al. (2005, 2007) the lighter Zn isotope is preferentially taken up by the plants, leaving the heavy isotopes within pore waters. However, these processes might have taken place above the samples used in this study, which can still be

influenced by a wash down of the remaining heavy isotope pool caused by plant-soil processes (Fig. 12). This pool of heavier Cu and Zn isotopes could then have been fixed in the soil horizon due to the fractionation processes with organic matter and oxides and thus is not further washed downwards in the profile (Fig. 12).

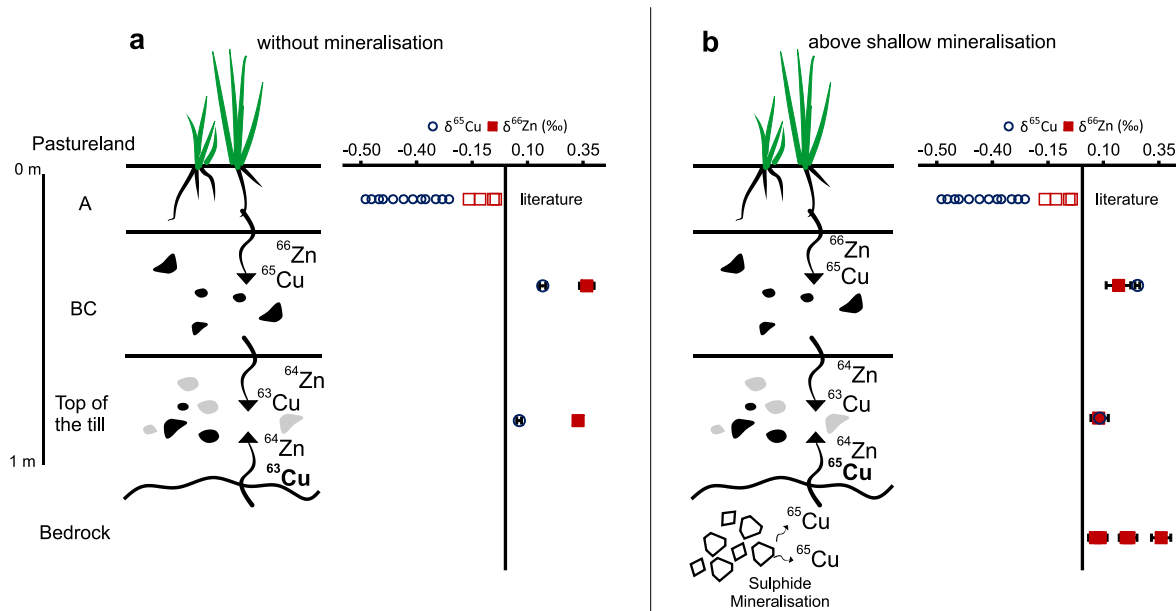


Fig. 12 Schematic isotopic signature within a soil profile above shallow mineralisation (TCS 20644 - soil, 20645 - till) and without (TCS 20713 - soil, 20714 - till) sulphide mineralisation at Ballinalack. Cu and Zn isotope signatures within the A horizon were not determined, here given by literature (e.g., Zhu et al., 2002, Weiss et al., 2005, John et al., 2007, Pokrovsky et al., 2008, Moynier et al., 2009, Jouvin et al., 2012, Conway and John, 2014, Moynier et al., 2017). The significant difference in isotopes is marked in bold within the till.

For Cu isotopes, another process takes place within the till samples that may lead to a shift towards lighter isotope signatures. This would have implications for fractionation of Cu in the till, which does not fractionate Zn isotopes. As Zn does not change its oxidation state at surficial conditions, where Cu does, redox-processes most likely influenced the isotopic signature of till at Ballinalack. Till samples exhibited a hydromorphic character in the field (Fig. 2), noticeable by the change in colour toward grey to black (Chapter 4). As reported by Zhu et al. (2002), Ehrlich et al. (2004), and Mathur et al. (2005), redox reactions result in a lighter Cu isotope pool in the soil that can be confirmed by studying the isotopic range at Ballinalack. Cu isotopes reveal a significantly broader range (0.45 ‰) than Zn isotopes (0.27 ‰) within the till samples, whereas an opposite trend exists between the range of Cu (0.18 ‰) and Zn (0.24 ‰) in soil samples. Thus, among the already lighter isotopic pool of Cu and Zn washed downwards through the soil profile, an additional shift towards lighter Cu isotopes is likely caused by redox processes.

4.2.1 Above mineralisation

The samples above the shallow sulphide mineralisation show anomalously light $\delta^{66}\text{Zn}$ in the profile TCS 20644 and 20645, as well as the nearby profile TCS 20646 and 20647. For the same samples the opposite effect of a heavy $\delta^{65}\text{Cu}$ anomaly occurs in soils at both locations and also in till at TCS 20647. This is most likely related to sulphide weathering. Borrok et al. (2009), Kimball et al. (2009), Vance et al. (2008), and Mathur et al. (2005) reported a release of heavy Cu isotopes into surrounding fluids compared to the initial mineral after sulphide weathering. Borrok et al. (2009) verified these results with modelling and leaching experiments. An electron exchange governed by mineral surface reactions leads to an accumulation of heavy Cu isotopes in the surface layer, which then becomes leached, causing the release of heavy isotopes (0.0 to +2.0 ‰) into the surrounding fluid. The heavy Cu isotope signature directly above the shallow sulphide deposit likely reflects this oxidative weathering process affecting the sulphides. Whereas, Zn isotopes do not undergo such a large fractionation, although, Fernandez and Borrok (2009) reported a slight release of 0.2 ‰ lighter Zn isotopes into the environment, which would coincide with the lightest Zn signature above the shallow sulphide mineralisation.

The vertical profile with samples TCS 20646 and 20647 representing the mineralised area directly, are similar to the overall average $\delta^{66}\text{Zn}$ signature and thus do not distinctively reflect the underlying mineralisation. Contrary soil profiles TCS 20644 and 20645, also directly above the shallow sulphide mineralisation, display distinct light Zn signatures. In addition, one sample (TCS 20746), which is not associated directly with the mineralisation projection above the Calp and outside the mineralisation area, has a similarly light Zn isotope signature, as described for the sample above the shallow mineralisation (TCS 20644 and 20645). Although the sample outside the mineralised area (TCS 20746) is not directly associated with the sulphide mineralisation, it is close to the deposit flanks (the projection of mineralisation is an interpretation and could also be shifted). Therefore, the $\delta^{66}\text{Zn}$ signature could also be associated and derived from the underlying sulphides. Although, XRD analyses did not reveal sulphides within the soil and till at Ballinalack (Fig. 11, Chapter 4), small sulphide grains (nugget effect) may influence the isotopic signature, which is supported by strong correlations of light Zn ratios to sulphide hosted elements, such as Pb, Zn, Sb, Cd, Tl, and Ag (Figs. 6, 12).

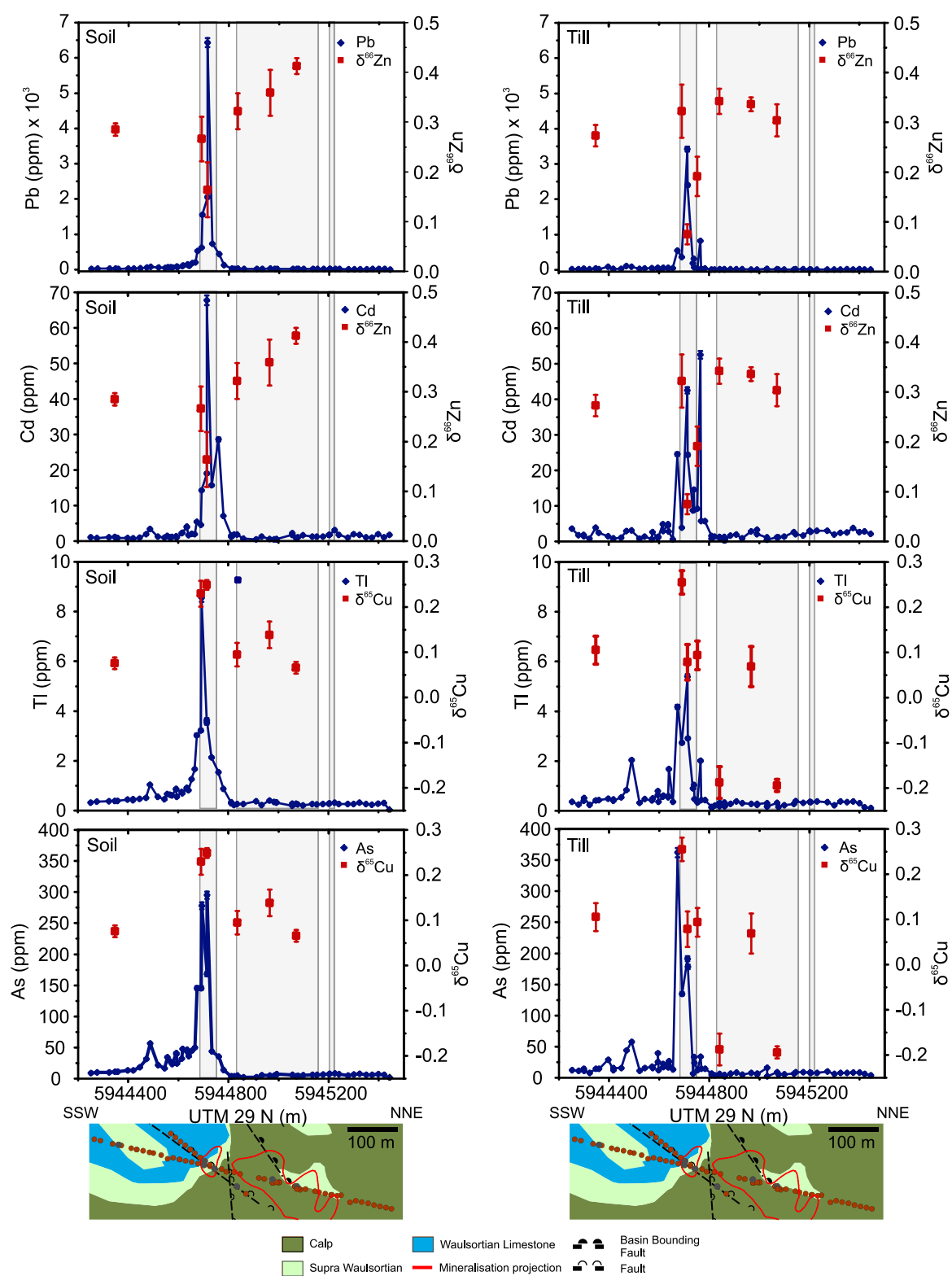


Fig. 13 Overview of sulphide hosted element concentrations compared to Cu and Zn isotopes, showing that the isotopic signatures are most likely related to the underlying sulphide mineralisation. The grey shade in the graphs indicate the projected sulphide mineralisation.

Also, the isotope signatures for sulphides are highly variable, demonstrated by the broad range in values for sphalerite from this study (Fig. 4), as well as from the studies conducted by Wilkinson et al. (2005b), and Gagnevin et al. (2012). Both profiles including the samples TCS 20644 - 20647, even those revealing average $\delta^{66}\text{Zn}$ signatures, could be related to the underlying sulphide mineralisation. Also here, minor sulphide nuggets might occur within the soil and (or) till, which would be supported by the strong correlations of $\delta^{66}\text{Zn}$ with the major and trace elements within the sulphides detected (see Chapter 3); e.g., Cd ($R = -0.92$), Ba ($R = -0.9$), Ag, Sb and Pb (all elements $R = -0.84$), and Zn ($R = -0.8$), Figures 5-9, 13.

In fact, the Zn isotopic signature above the shallow sulphide mineralisation, differs slightly from the other soil and till signatures, also it is within the same range of the sphalerite signature. Nevertheless, due to the broad range of Zn isotope signatures within sphalerites and the only small shifts caused by fractionation processes in soil and till, would generally mean that measured Zn isotopes are equivocal at Ballinalack.

Interestingly, as illustrated in Figure 7 the Cu concentration does not reflect the underlying sulphide mineralisation at either the deeply-buried (north) or the shallow (south) mineralisation (Chapter 4), which can be related to lower Cu concentrations within the sulphides at Ballinalack (Chapter 3). Although, no correlation exists between the Cu concentration and the $\delta^{65}\text{Cu}$ values within the till samples, the heaviest $\delta^{65}\text{Cu}$ of 0.25 ± 0.03 ‰ lies directly above the shallow sulphide mineralisation. Correspondingly, in soils a positive correlation between $\delta^{65}\text{Cu}$ and Zn ($R = 0.72$, Fig. 5) is observed; the higher the Zn concentration, the heavier the $\delta^{65}\text{Cu}$ ratio in both soil and till, that can be further observed for other elements associated with the sulphides, e.g., As, Cd, Fe and Tl (Figs. 5-9, 13).

These findings, indicate that Cu isotopes, in fact, reflect the underlying sulphide mineralisation. This approach appears to show that shallow mineralisation can be detected through the use of stable Cu isotopes, in which in situ weathering of sulphide minerals can take place. It is important to bear in mind, that the deeply buried mineralisation to the north is neither reflected in the trace element geochemistry (Chapter 4) nor in $\delta^{65}\text{Cu}$ or $\delta^{66}\text{Zn}$ signatures (this study). Also, both sample media, soil and till provide a distinct signature of the underlying sulphide mineralisation. Soil BC horizon samples are not as clear as till samples, likely due to less clasts within the soil, meaning that minor changes (mineralogy, environment) within the samples can highly influence the isotopic signature. Most likely sulphide particles within the till induced the indicative concentration and isotopic signatures at Ballinalack.

Although the Ballinalack landscape is dominated by pasture land and former glaciation, the geogenic signature caused by the underlying geology still is detectable (Chapter 4), this is the same for the isotopic signature of Cu and Zn.

Nevertheless, these results should be interpreted with caution, as the sample number is low and therefore should be treated as an orientation study and a guide for further research. An increase in the number of samples, focussing on the shallow mineralisation and background samples, above all types of lithology (Calp, Supra Waulsortian Limestone and Waulsortian Limestone) would improve any further investigations. Additional sampling of the A horizon, kettle facies and a deeper sample taken underneath the top of the till, would provide more insights of the mobility and fractionation of the elements within the vertical soil profiles at Ballinalack.

5 Conclusion

The application of Cu and Zn isotopes for surficial geochemical prospecting reveals new insights into mineral exploration in glaciated terrains. This study exhibits different behaviour for Cu and Zn isotopes in natural soil and till systems, highlighting the importance of redox sensitive fractionation processes for Cu isotopes. Where $\delta^{66}\text{Zn}$ signatures do not necessarily reflect sulphide mineralisation due to the lack of oxidation during weathering as well as their small compositional range, Cu isotopes seem to be promising as a mineral exploration tool in soil and till samples. Although Cu concentrations do not indicate any sulphide mineralisation in either soil or till samples, Cu isotopes do exhibit fractionation towards heavy $\delta^{65}\text{Cu}$ signatures. However, the sulphide mineralisation can only be associated when in situ weathering within or directly underneath the sample takes place. Notably, the isotopic signature is still associated with the sulphide mineralisation although many influence factors, such as glacial impact (clasts) and pasture lands overprint the entire area at Ballinalack. Therefore, Cu isotopes might also be a useful tool for exploration in anthropogenically influenced areas prospective for base metal mineralisation.

For this orientation study, it is difficult to explain the fractionation processes with absolute certainty; moreover, Cu and Zn species and organic carbon determination would be required. Further investigations are recommended with additional samples of the vertical profiles, as well as, lateral distribution focusing on the shallow sulphide mineralisation. Samples from host rock lithologies and other sulphide minerals could help to define the origin of the isotopic signatures measured in soil and till.

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Chapter 6: Conclusion

Mineral exploration is necessary for discovering new resources essential for growing economies and quality of human life. Surficial geochemistry is used successfully in the exploration industry for near surface base-metal deposits in accessible areas, although some organisations may have given up this exploration technique (e.g., Hamilton, 2007 and references therein). Deeply buried mineral deposits in more complex regions comprise many of the new exploration targets; with the help of geophysics (e.g., Hoover et al., 1995) and geochemical techniques (e.g., Hamilton et al., 2004), these areas can now be considered for exploration and delineation of resources. Mineral deposits at depths of up to several hundreds of meters can be discovered from surface through the identification of geochemical haloes using soil geochemistry and understanding transport mechanisms in a variety of different climates (e.g., Cameron et al., 2004, van Geffen et al., 2012). In addition to lithogeochemistry, microanalysis of sulphide minerals, have been used to characterise ore systems and understand the conditions in which mineralisation formed (e.g., Large et al., 2009). Nevertheless, the exploration for base metal deposits is more challenging in glaciated terrains; a full understanding of the elemental transport processes from the sulphides toward the surface environment (till and soil) is often lacking full comprehension. This is complicated further in non-pristine areas, where the distinction between elements derived from blind mineralisation and those derived from anthropogenic sources (land-use) in soils requires further consideration.

In order to address challenges in tracing geochemical processes in the surficial environment, it is important to understand the geochemistry of sulphide mineralisation and the incorporation of trace elements in host sulphide minerals (e.g., Abraitis et al., 2004, Cook et al., 2009, Large et al., 2014, George et al., 2015). Understanding the overall trace-element systematics of the mineralisation will allow for predictions as to the anticipated element signatures in the overlying soil and till; furthermore, a model could be drawn to help understand their migration from bedrock to surface. For instance, redox-sensitive elements such as Fe could be mobilised towards the surface within a reduced chimney (Hamilton, 1998, 2000), whereas both Zn and Cu might be transported by groundwater or fluids along faults. This thesis offers a discussion about mineral exploration techniques in the form of sulphide geochemistry and transport models for both shallow and buried sulphide bodies in pasture land in the Irish Midlands. Furthermore, the applicability of stable metal isotopic methods to mineral exploration are assessed at the Ballinalack deposit. The main conclusions and contributions of the thesis can be summarised in the following four findings:

- 1) In situ analyses of sphalerite and pyrite (Laser Ablation ICP-MS) can provide new insights into the evaluation of sulphide deposits in the Irish Midlands. Compared to other deposits in the Irish Midlands, the Ballinalack Zn-Pb deposit exhibits characteristic sub μm -level inclusions within the sulphides, that have not been fully characterised in other studies on Irish-Type Zn-Pb systems (Wilkinson et al., 2005b, Gagnevin et al., 2014). Sphalerites contain abundant fine-grained inclusions of pyrite and similarly, pyrite displays in addition to the incorporation of trace elements into the pyrite lattice trace-element variations due to the presence of fine-grained sub μm -level inclusions. These geochemical signatures could serve as a vector towards higher-grade mineralisation at Ballinalack. Furthermore, the highest reported Ni concentrations are observed within pyrites at Ballinalack. Their source still is not identified, however, it is anticipated that nickel derived from a very Ni-rich source, namely Lower Palaeozoic basement (e.g., Caulfield et al., 1986, LeHuray et al., 1987, Dixon et al., 1990, Everett, 1999, Everett et al., 2003, Walshaw et al., 2006, Wilkinson and Hitzman, 2010, Wilkinson et al., 2005a). Elements that could be derived from the sulphide and mobilised within overlying surficial sediments include Ag, As, Co, Fe, Ga, Hg, Mo, Ni, Pb, Sb and Zn.

In situ measurements of trace elements have revealed new insights into the genesis of sulphide deposits and although it may have posed more questions than answers, it will help to better understand ore deposits. Local raster LA ICP-MS elemental analysis of sulphide minerals, provides new insights into the mineral growth and accordingly the fluid chemistry and conditions. Moreover, it could serve as another tool in mineral exploration. Subtle changes in the chemistry of the sulphides can indicate their proximal-distal relationship and further, they could indicate the fertility (grade) of the sulphide deposit.

- 2) The soil/till survey attempted to understand soil geochemical anomalies in pasture land above a shallow sub-cropping and buried Zn-Pb mineralisation at the Ballinalack deposit in the Irish Midlands. This area has been affected by past glaciation and more recent agricultural use primarily as pasture land. While the deeply buried sulphide bodies do not appear to affect the trace-element signature of the overlying soil and till, the shallow sulphide body clearly displays a geochemical halo in soils and till. The elements Pb, Cd, As, Ag, Tl, Zn, Sb and Ba (in order of decreasing relevance) display enrichments in soils and till (Fig. 1); these elements are primarily associated with sulphide mineralisation (sphalerite, pyrite and galena) and indicate that any geochemical effects from past glaciation or agricultural activity have not removed the signature of

the sulphide minerals. Validity of anomalies was verified by defining background concentrations and calculating enrichment factors, based on the underlying bedrock.

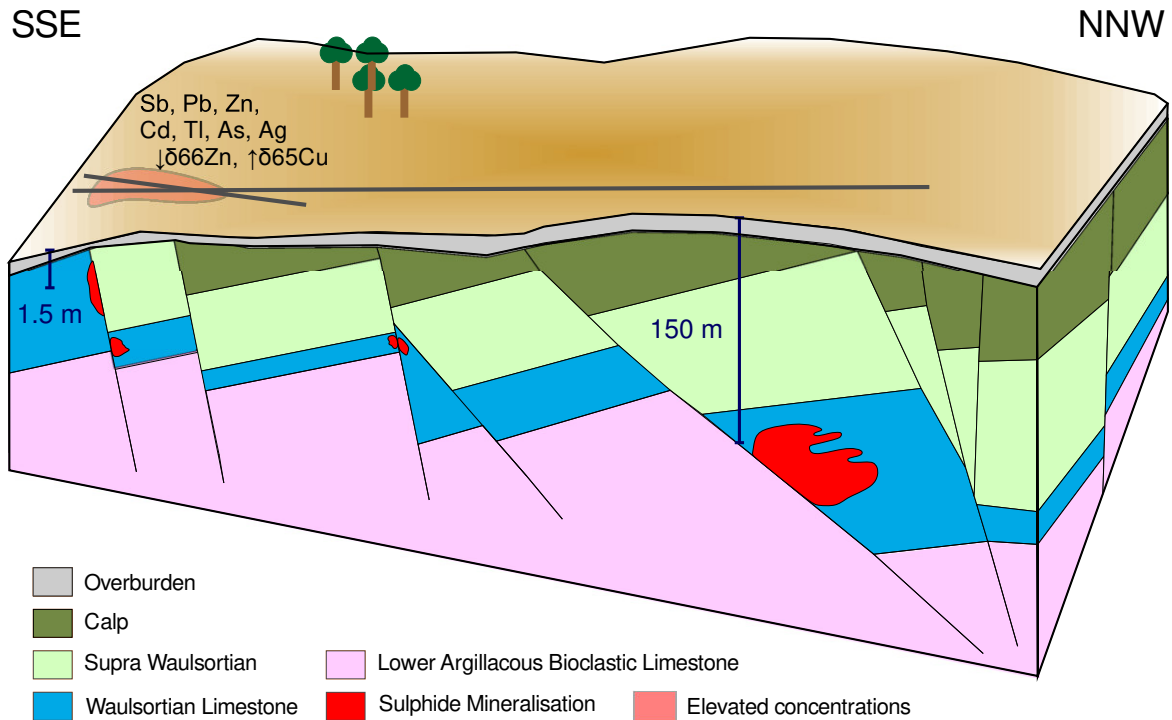


Fig. 1 Schematic cross section of the Ballinalack deposit. The carbonate-hosted Zn-Pb deposit is divided into a deeper and a shallow sulphide lens. The black line indicates the soil and till sample lines and the red lens at the surface indicates the anomalous signature within soil and till (interpretation of The Robertson Group Plc, 1991, Chapter 4).

- 3) The reduced chimney transport model for mobile elements (Hamilton, 1998, 2000) could not be confirmed at Ballinalack with data collected for this thesis. Calcareous clasts within soil and till buffer the pH locally and cannot be used as an indicator for a twin-peak (rabbit ear) anomaly, which was the main reasoning, historically, behind applying the reduced chimney model at Ballinalack. Furthermore, conditions in the Irish Midlands diminish the chance of a development of a reduced chimney, including a nearby peat cut (Poldini, 1938) and the major sulphide minerals sphalerite and galena which do not necessarily induce a self-potential (Sato and Mooney, 1960). Also the presence of an additional cover rock to the overburden, may further prevent an upwards translocation of elements. Simple weathering of sulphide minerals likely caused the anomalous concentrations above the shallow sulphide body at Ballinalack. Generally, it is difficult to apply the reduced chimney model in carbonate-hosted geological settings, due to significant local shifts in pH.

The investigation of glaciogenic and anthropogenic influenced terrains offer challenging target areas for mineral exploration. Deeply buried sulphide deposits are still difficult to detect; however, in different geological settings they may be easier to follow than in the Irish Midlands where a thick cover sedimentary rock sequence consisting of mudstone separate the surficial sediments from the sulphide lens. Also, the limitations of the reduced chimney model (Hamilton, 1998, 2000) where applied to the Ballinalack deposit can most likely be extended to the rest of the Irish Midlands and other carbonate-hosted Pb-Zn systems, worldwide, to guide exploration teams to look for other elemental anomalies and can be misguided by pH values. Further investigations of other buried deposits could help to understand which characteristics prevent a translocation of elements or which techniques might be better for detecting fingerprints in the surficial sediments, such as other stable isotope systems. Nevertheless, shallow sulphide deposits can be detected in anthropogenically affected soils. The chemistry of pasture land in the Irish Midlands does not appear to prevent the detection of the geogenic sulphide signature within the soils/tills, and surficial geochemical surveys can still be a very useful mineral exploration technique in agriculturally affected areas.

- 4) The feasibility of stable metal isotopes as a mineral exploration tool on soil/till surveys was tested over the Ballinalack soil anomaly. This orientation study illustrates that Cu, as well as Zn, isotopes show a distinct response above the shallow sulphide mineralisation in both soil and till. Where Zn concentrations are anomalously high, $\delta^{66}\text{Zn}$ exhibits lighter isotopic signatures above the shallow mineralisation. Further, its comparison to the $\delta^{66}\text{Zn}$ signature of the sulphides confirms that the signature originates from the underlying sulphides. Interestingly, bulk copper concentrations do not indicate the presence of any sulphide mineralisation; however, $\delta^{65}\text{Cu}$ signatures exhibit clearly higher ratios in response to the underlying shallow sulphide mineralisation (Fig. 1). The fractionation of both isotopic systems are likely caused by sulphide weathering processes; therefore, they are only detectable above the shallow mineralisation. Note, that due to redox-reactions during the weathering process, Cu isotopes are fractionated by an additional process compared to Zn; thus the Cu isotope signature is potentially more indicative of mineralisation. In areas, where anomalous concentrations in soil and till are inconclusive, an investigation using combined Zn and Cu isotopes could reveal the presence of blind mineralisation.

Metal stable isotopes can be helpful to mineral exploration. These methods will not replace conventional lithogeochemical investigations of bedrock, soil and till; however,

they could serve as an additional tool in the targeting of geochemical anomalies. Further empirical and orientation studies, in addition to laboratory experiments, will help to understand fractionation processes better and how to apply these techniques in more complex systems. Accordingly, a better understanding will improve knowledge on mobilisation of metals in soils and tills, and their bedrock sources. This study illustrates its feasibility in the field and reveals additional useful information on the use of trace elements for surficial geochemistry programmes across the Irish Midlands. Although the analysis of stable metal isotopes is time-consuming and expensive, further research and development could bring the approach forward to be applied economically in the mineral exploration sector.

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Appendix

Structure of Appendix

Appendix A

Map with sample locations - Teck Ireland Orientation Study 2007 (p. 221).

Raw data - Teck Ireland Limited Orientation Study 2007 (p. 222).

Appendix B

Images of thin sections in reflected and transmitted light (p. 233).

Image of drill core (enlarged, p. 247).

Raw data laser ablation ICP-MS of pyrite and sphalerite (p. 248)

Average concentrations for pyrite and sphalerite obtained using SEM (p. 258).

Appendix C

Map of sample location (p. 263).

Soil profile representative for Ballinalack (p. 264).

Raw data trace elements of soil BC horizon and top of the till from Ballinalack (this study, p. 265).

Raw data - Drill core raw data based on aqua regia digestion (p. 314).

Principal component analysis scores (p. 316).

Appendix D

Thin section images of micro-drilled sphalerite (p. 319).

Soil and till sample digestion (p. 322).

Sphalerite sample digestion (p. 323).

Column preparation (p. 324).

Blanks - isotope analysis (p. 324).

Standards for isotopic analysis (p. 325).

Isotope laboratory duplicate (p. 326).

Elemental recovery during ion exchange chromatography.

Mass dependent fractionation of isotopes (p. 328).

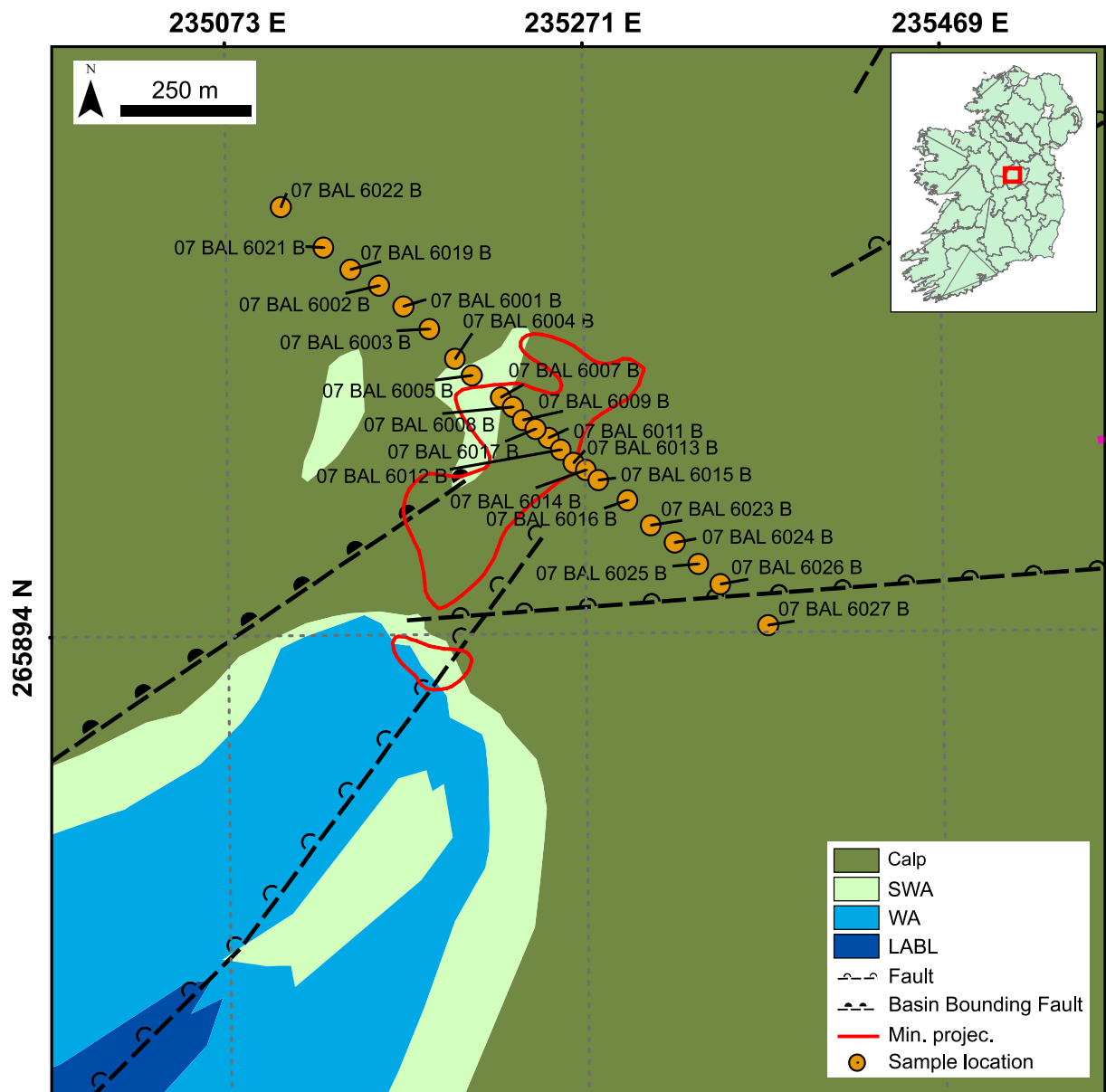
References (p. 329).

Appendix A

Map with sample locations - Teck Ireland Orientation Study 2007.

Raw data - Teck Ireland Limited Orientation Study 2007.

Map with sample locations - Teck Ireland Orientation Study 2007



Sample location of Teck orientation study 2007. SWA = Supra Waulsortian Limestone, WA = Waulsortian Limestone, LABL = Lower Argillaceous Bioclastic Limestone, Min. Projec. = Mineralisation Projection. Coordinate system Irish Grid TM65.

Raw data Teck orientation study Ballinalack. Trace elements of soil samples, digested using aqua regia

Sample ID	Project	Horizon	ING_TM65_X	ING_TM65_Y	UTM Zone	Analysis_Method	Soil_Samplers	Soil_From (m)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)
07 BAL 6001 A	BLK	A	234986.96	266401.96	29N	Aqua Regia	SteveCook	0.1	0.11	1.13	4.22	7.96	35.64	0.49
07 BAL 6001 B	BLK	BC	234986.96	266401.96	29N	Aqua Regia	SteveCook	0.25	0.14	1.12	5.38	37.11	36.53	0.61
07 BAL 6001 C	BLK	C	234986.96	266401.96	29N	Aqua Regia	SteveCook	0.8	0.11	1.21	6.02	8.45	36.83	0.76
07 BAL 6002 A	BLK	A	234949.09	266434.65	29N	Aqua Regia	SteveCook	0.1	0.10	1.12	3.94	7.73	37.87	0.56
07 BAL 6002 B	BLK	BC	234949.09	266434.65	29N	Aqua Regia	SteveCook	0.27	0.16	1.25	4.83	14.13	42.28	0.73
07 BAL 6002 C	BLK	C	234949.09	266434.65	29N	Aqua Regia	SteveCook	0.75	0.16	1.49	3.73	7.87	48.78	0.80
07 BAL 6003 A	BLK	A	235026.57	266367.53	29N	Aqua Regia	SteveCook	0.1	0.13	1.04	4.16	7.60	33.08	0.48
07 BAL 6003 B	BLK	BC	235026.57	266367.53	29N	Aqua Regia	SteveCook	0.3	0.19	1.21	5.08	12.02	37.11	0.73
07 BAL 6003 C	BLK	C	235026.57	266367.53	29N	Aqua Regia	SteveCook	0.6	0.14	1.02	5.98	8.73	27.76	0.86
07 BAL 6004 A	BLK	A	235066.73	266321.53	29N	Aqua Regia	SteveCook	0.1	0.10	1.05	6.16	7.74	30.69	0.66
07 BAL 6004 B	BLK	BC	235066.73	266321.53	29N	Aqua Regia	SteveCook	0.3	0.15	1.11	5.70	10.75	35.28	0.77
07 BAL 6004 C	BLK	C	235066.73	266321.53	29N	Aqua Regia	SteveCook	0.85	0.07	0.69	6.38	8.95	19.69	0.69
07 BAL 6005 A	BLK	A	235092.45	266295.78	29N	Aqua Regia	SteveCook	0.1	0.09	0.99	5.15	6.77	35.46	0.50
07 BAL 6005 B	BLK	BC	235092.45	266295.78	29N	Aqua Regia	SteveCook	0.3	0.16	1.06	4.69	9.46	39.58	0.53
07 BAL 6005 C	BLK	C	235092.45	266295.78	29N	Aqua Regia	SteveCook	0.85	0.10	1.12	5.89	7.37	31.65	0.78
07 BAL 6007 A	BLK	A	235136.75	266262.18	29N	Aqua Regia	SteveCook	0.1	0.08	0.96	4.64	6.78	30.09	0.49
07 BAL 6007 B	BLK	BC	235136.75	266262.18	29N	Aqua Regia	SteveCook	0.3	0.09	1.11	5.71	8.90	32.80	0.56
07 BAL 6007 C	BLK	C	235136.75	266262.18	29N	Aqua Regia	SteveCook	0.75	0.10	0.98	8.38	7.68	30.55	0.99
07 BAL 6008 A	BLK	A	235155.71	266247.75	29N	Aqua Regia	SteveCook	0.1	0.09	0.91	5.20	7.07	37.58	0.56
07 BAL 6008 B	BLK	BC	235155.71	266247.75	29N	Aqua Regia	SteveCook	0.3	0.10	1.09	6.13	9.68	37.59	0.70
07 BAL 6008 C	BLK	C	235155.71	266247.75	29N	Aqua Regia	SteveCook	0.7	0.11	1.17	8.21	8.01	35.89	1.21
07 BAL 6009 A	BLK	A	235171.14	266227.15	29N	Aqua Regia	SteveCook	0.1	0.11	0.96	6.55	7.41	41.93	0.61
07 BAL 6009 B	BLK	BC	235171.14	266227.15	29N	Aqua Regia	SteveCook	0.3	0.10	1.09	7.99	9.24	34.43	0.77
07 BAL 6009 C	BLK	C	235171.14	266227.15	29N	Aqua Regia	SteveCook	0.7	0.13	0.93	8.07	8.05	27.88	1.16
07 BAL 6011 A	BLK	A	235210.23	266199.5	29N	Aqua Regia	SteveCook	0.1	0.09	0.98	6.75	7.65	30.45	0.64
07 BAL 6011 B	BLK	BC	235210.23	266199.5	29N	Aqua Regia	SteveCook	0.3	0.10	1.05	6.94	9.66	31.60	0.73
07 BAL 6011 C	BLK	C	235210.23	266199.5	29N	Aqua Regia	SteveCook	0.6	0.13	1.03	9.57	9.57	32.21	1.24
07 BAL 6012 A	BLK	A	235229.76	266181.06	29N	Aqua Regia	SteveCook	0.1	0.09	0.97	6.89	7.75	29.55	0.69
07 BAL 6012 B	BLK	BC	235229.76	266181.06	29N	Aqua Regia	SteveCook	0.3	0.19	0.92	8.49	8.06	28.23	0.75
07 BAL 6012 C	BLK	C	235229.76	266181.06	29N	Aqua Regia	SteveCook	0.7	0.14	0.88	9.19	8.61	30.36	1.34
07 BAL 6013 A	BLK	A	235249.09	266161.28	29N	Aqua Regia	SteveCook	0.1	0.10	0.99	7.34	7.96	31.88	0.79
07 BAL 6013 B	BLK	BC	235249.09	266161.28	29N	Aqua Regia	SteveCook	0.3	0.10	1.09	6.65	9.25	33.16	0.84
07 BAL 6013 C	BLK	C	235249.09	266161.28	29N	Aqua Regia	SteveCook	0.75	0.12	0.84	8.36	9.32	29.26	1.16
07 BAL 6014 A	BLK	A	235268.01	266150.18	29N	Aqua Regia	SteveCook	0.1	0.09	0.81	6.80	7.47	28.29	0.67
07 BAL 6014 B	BLK	BC	235268.01	266150.18	29N	Aqua Regia	SteveCook	0.3	0.12	0.93	7.25	9.04	32.02	0.88
07 BAL 6014 C	BLK	C	235268.01	266150.18	29N	Aqua Regia	SteveCook	0.6	0.12	0.84	7.59	9.89	25.36	0.98

Raw data Teck orientation study Ballinalack (continued).

Sample ID	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)	Ge (ppm)	Hg (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)
07 BAL 6001 A	0.06	0.15	0.77	19.96	4.09	20.41	9.12	1.28	2.80	0.13	0.08	0.07	13.44	6.82	0.13	293.76	1.53	0.01
07 BAL 6001 B	0.10	0.14	0.89	22.93	4.72	23.69	10.06	1.10	2.74	0.13	0.09	0.06	15.68	20.80	0.13	305.75	1.30	0.01
07 BAL 6001 C	0.05	0.47	1.16	26.75	5.79	24.76	12.20	1.45	2.73	0.19	0.05	0.08	19.62	8.55	0.14	338.04	1.54	0.01
07 BAL 6002 A	0.05	0.24	1.15	19.67	4.17	19.88	9.10	1.26	2.79	0.13	0.07	0.07	13.55	6.93	0.14	300.71	1.02	0.01
07 BAL 6002 B	0.08	0.19	1.36	25.90	5.47	26.97	11.63	1.38	3.60	0.15	0.09	0.06	18.03	10.25	0.15	353.66	1.19	0.01
07 BAL 6002 C	0.06	0.31	1.42	28.53	5.40	29.59	10.40	1.10	3.47	0.15	0.06	0.08	19.90	10.40	0.19	290.24	0.67	0.01
07 BAL 6003 A	0.05	0.17	0.94	19.41	4.10	20.55	9.88	1.28	2.61	0.12	0.08	0.09	13.37	6.49	0.13	350.17	1.59	0.01
07 BAL 6003 B	0.09	0.19	0.86	25.87	4.85	26.68	12.24	1.23	3.07	0.16	0.10	0.07	18.33	9.10	0.14	265.02	1.47	0.01
07 BAL 6003 C	0.05	1.27	1.20	28.79	6.26	23.67	15.35	1.58	2.54	0.14	0.07	0.09	23.52	7.00	0.15	265.63	1.98	0.01
07 BAL 6004 A	0.05	0.19	1.06	25.14	4.89	22.22	18.36	1.64	2.49	0.16	0.11	0.09	17.59	6.50	0.14	285.94	1.78	0.01
07 BAL 6004 B	0.09	0.19	1.07	29.45	6.25	26.32	21.29	1.46	2.84	0.16	0.12	0.08	21.40	7.25	0.15	504.95	1.97	0.01
07 BAL 6004 C	0.03	7.31	2.07	26.70	6.44	17.13	18.32	1.48	1.41	0.05	0.05	0.09	21.46	5.03	0.19	409.18	2.86	0.01
07 BAL 6005 A	0.06	0.17	0.87	20.34	5.30	20.49	15.02	1.30	2.45	0.14	0.07	0.09	12.61	6.32	0.13	610.17	2.06	0.01
07 BAL 6005 B	0.10	0.14	0.75	21.08	5.32	24.21	15.34	1.22	3.10	0.13	0.06	0.07	13.50	7.28	0.12	610.18	2.27	0.01
07 BAL 6005 C	0.05	0.15	0.70	33.74	6.02	23.17	11.80	1.65	2.20	0.16	0.07	0.08	21.97	8.23	0.12	475.02	2.78	0.01
07 BAL 6007 A	0.05	0.15	0.73	19.91	4.59	20.77	15.99	1.28	2.32	0.12	0.08	0.10	12.42	6.53	0.13	384.31	1.86	0.01
07 BAL 6007 B	0.05	0.13	0.57	21.33	5.39	23.24	12.85	1.32	2.47	0.13	0.06	0.07	13.86	7.79	0.14	567.74	2.47	0.01
07 BAL 6007 C	0.06	0.15	1.47	35.47	7.91	24.58	19.67	1.96	2.53	0.20	0.08	0.10	28.43	7.24	0.17	532.45	3.96	0.01
07 BAL 6008 A	0.05	0.24	1.01	20.83	5.22	21.60	18.84	1.40	2.12	0.16	0.08	0.13	13.88	5.53	0.14	617.91	2.19	0.01
07 BAL 6008 B	0.07	0.20	1.05	24.42	6.14	24.33	24.51	1.48	2.45	0.13	0.07	0.09	16.65	7.66	0.14	741.27	2.45	0.01
07 BAL 6008 C	0.06	0.22	1.38	38.53	8.11	29.11	19.64	2.13	3.32	0.20	0.08	0.10	31.50	7.98	0.16	628.80	3.88	0.01
07 BAL 6009 A	0.05	0.21	1.02	23.21	5.94	20.87	15.12	1.51	2.28	0.18	0.07	0.09	15.41	5.69	0.13	521.63	2.61	0.01
07 BAL 6009 B	0.06	0.18	0.82	25.87	6.25	25.65	15.50	1.51	2.78	0.19	0.08	0.08	17.93	7.12	0.13	583.85	2.87	0.01
07 BAL 6009 C	0.06	0.42	1.76	35.16	7.88	25.09	19.33	2.01	2.35	0.20	0.08	0.08	30.04	5.58	0.13	590.86	4.45	0.01
07 BAL 6011 A	0.05	0.22	1.03	24.17	6.57	21.00	22.55	1.68	2.25	0.20	0.06	0.11	16.76	5.66	0.13	660.02	2.87	0.01
07 BAL 6011 B	0.06	0.18	0.88	23.92	5.66	24.43	25.98	1.46	2.60	0.19	0.06	0.07	18.90	6.58	0.13	461.08	3.10	0.01
07 BAL 6011 C	0.07	0.43	2.34	34.06	8.60	26.55	24.64	2.42	2.43	0.27	0.10	0.10	32.75	6.47	0.16	550.21	5.53	0.01
07 BAL 6012 A	0.06	0.22	1.20	26.62	6.19	21.11	25.57	1.67	2.20	0.18	0.09	0.11	18.51	5.83	0.13	532.55	3.10	0.01
07 BAL 6012 B	0.06	0.18	0.96	25.88	5.49	22.87	24.63	1.38	2.04	0.19	0.07	0.07	19.76	5.71	0.12	435.52	3.08	0.01
07 BAL 6012 C	0.07	0.81	3.14	35.99	8.61	24.34	23.62	2.13	2.32	0.27	0.08	0.09	32.07	5.47	0.13	538.80	5.89	0.01
07 BAL 6013 A	0.06	0.24	1.42	29.21	7.01	21.88	21.90	1.86	2.30	0.20	0.07	0.10	19.70	5.88	0.14	620.56	3.59	0.01
07 BAL 6013 B	0.09	0.18	1.10	31.30	6.65	26.28	23.69	1.67	2.81	0.18	0.07	0.08	22.08	6.95	0.13	517.16	3.70	0.01
07 BAL 6013 C	0.05	0.61	3.31	31.94	8.22	20.94	21.65	2.05	1.84	0.21	0.08	0.10	25.07	5.31	0.14	545.40	5.22	0.01
07 BAL 6014 A	0.05	0.26	1.48	23.24	5.76	19.91	14.30	1.66	1.84	0.21	0.07	0.14	17.86	4.80	0.13	578.56	3.19	0.01
07 BAL 6014 B	0.06	0.23	1.51	27.03	6.54	23.59	16.48	1.56	2.36	0.16	0.08	0.09	21.88	6.11	0.13	583.83	3.15	0.01
07 BAL 6014 C	0.06	2.33	2.56	32.71	7.28	20.64	19.78	2.02	1.77	0.13	0.07	0.09	26.94	5.50	0.15	558.03	6.25	0.01

Raw data Teck orientation study Ballinalack (continued).

Sample ID	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)
07 BAL 6001 A	0.14	16.44	0.09	13.87	11.96	0.00	0.07	0.09	2.60	0.58	0.51	10.56	0.01	0.01	1.43	43.95	0.32	0.62
07 BAL 6001 B	0.17	19.83	0.05	14.13	12.91	0.00	0.03	0.29	3.57	0.59	0.50	11.27	0.01	0.05	2.34	45.96	0.43	0.71
07 BAL 6001 C	0.12	29.17	0.06	12.19	15.01	0.00	0.02	0.37	3.65	0.50	0.37	26.21	0.01	0.01	1.88	57.49	0.38	0.56
07 BAL 6002 A	0.11	16.50	0.09	16.13	10.12	0.00	0.08	0.08	2.43	0.93	0.43	13.19	0.01	0.03	1.18	40.94	0.30	0.55
07 BAL 6002 B	0.41	25.19	0.05	14.41	12.00	0.00	0.04	0.40	4.18	1.26	0.43	13.36	0.01	0.04	1.82	46.14	0.40	0.86
07 BAL 6002 C	0.12	25.95	0.05	15.36	13.64	0.00	0.03	0.17	3.98	0.80	0.40	23.06	0.01	0.01	2.07	48.98	0.39	0.80
07 BAL 6003 A	0.15	16.89	0.10	12.94	13.23	0.00	0.07	0.12	2.41	0.63	0.42	11.56	0.01	0.01	1.12	43.10	0.30	0.66
07 BAL 6003 B	0.18	24.34	0.05	12.72	14.47	0.00	0.03	0.35	3.70	0.91	0.48	12.82	0.01	0.02	1.90	48.54	0.39	0.87
07 BAL 6003 C	0.09	41.49	0.06	11.27	12.57	0.00	0.02	0.80	4.46	0.49	0.29	48.66	0.01	0.01	1.61	51.48	0.38	0.89
07 BAL 6004 A	0.14	23.20	0.12	16.01	12.21	0.00	0.07	0.36	3.05	0.77	0.56	10.96	0.01	0.01	1.45	44.90	0.27	1.07
07 BAL 6004 B	0.48	28.60	0.06	15.29	16.64	0.00	0.03	0.57	4.56	0.88	0.56	13.43	0.02	0.01	1.70	53.73	0.39	1.07
07 BAL 6004 C	0.10	44.70	0.06	9.08	8.58	0.00	0.02	1.18	3.89	0.60	0.22	275.24	0.01	0.01	1.68	51.56	0.36	1.11
07 BAL 6005 A	0.15	16.56	0.12	17.11	14.76	0.00	0.06	0.21	2.27	0.60	0.56	10.20	0.01	0.03	1.20	47.30	0.31	1.16
07 BAL 6005 B	0.42	18.55	0.06	14.10	22.55	0.00	0.02	0.28	3.60	0.62	2.79	10.37	0.02	0.01	1.18	52.60	0.40	1.18
07 BAL 6005 C	0.11	26.43	0.05	10.67	16.63	0.00	0.01	0.41	3.99	0.66	0.27	10.76	0.01	0.02	1.86	47.59	0.35	0.95
07 BAL 6007 A	0.14	16.79	0.13	14.11	13.66	0.00	0.06	0.17	2.16	0.62	0.47	8.65	0.01	0.01	1.02	45.73	0.28	0.84
07 BAL 6007 B	0.15	19.59	0.07	12.62	18.96	0.00	0.03	0.28	2.65	0.65	0.52	8.14	0.01	0.01	1.27	56.91	0.35	0.72
07 BAL 6007 C	0.12	50.13	0.05	12.63	13.13	0.00	0.01	1.03	4.57	0.95	0.29	10.50	0.01	0.03	1.81	66.10	0.43	0.92
07 BAL 6008 A	0.20	19.93	0.17	16.33	13.20	0.00	0.07	0.25	2.43	0.59	0.48	11.09	0.01	0.01	1.09	49.27	0.26	0.88
07 BAL 6008 B	0.16	24.43	0.08	16.91	17.59	0.00	0.04	0.44	3.10	0.71	0.49	9.92	0.01	0.01	1.53	54.70	0.34	0.87
07 BAL 6008 C	0.41	42.79	0.05	14.10	18.30	0.00	0.02	1.05	6.08	0.95	0.35	14.08	0.05	0.03	1.85	58.33	0.44	1.03
07 BAL 6009 A	0.15	22.31	0.14	19.76	14.23	0.00	0.08	0.39	2.73	0.69	0.41	11.31	0.01	0.01	1.20	45.19	0.31	0.84
07 BAL 6009 B	0.16	26.18	0.06	14.54	17.54	0.00	0.03	0.50	3.39	0.78	0.44	9.41	0.01	0.01	1.50	51.06	0.36	0.90
07 BAL 6009 C	0.11	45.18	0.07	12.13	12.83	0.00	0.02	1.11	5.41	0.88	0.26	20.80	0.01	0.01	1.69	50.38	0.42	1.01
07 BAL 6011 A	0.17	22.46	0.13	16.70	12.38	0.00	0.07	0.47	2.64	0.74	0.48	9.57	0.01	0.01	1.31	52.10	0.29	0.87
07 BAL 6011 B	0.15	26.20	0.06	15.14	16.16	0.00	0.03	0.62	3.42	0.73	0.42	8.58	0.01	0.03	1.79	57.83	0.34	0.89
07 BAL 6011 C	0.12	56.05	0.05	13.44	14.03	0.00	0.02	1.54	5.33	1.20	0.32	20.94	0.01	0.04	1.71	63.92	0.47	1.01
07 BAL 6012 A	0.14	24.63	0.14	16.29	13.22	0.00	0.07	0.55	3.03	0.85	0.43	10.59	0.01	0.01	1.27	44.00	0.30	1.07
07 BAL 6012 B	0.13	26.54	0.06	15.10	14.36	0.00	0.03	0.67	3.46	0.92	0.41	8.29	0.01	0.01	1.61	47.09	0.33	1.01
07 BAL 6012 C	0.12	55.10	0.06	13.71	12.68	0.00	0.02	1.53	5.79	1.16	0.34	35.53	0.01	0.06	1.62	48.58	0.50	1.07
07 BAL 6013 A	0.14	28.34	0.13	16.90	13.30	0.00	0.07	0.63	3.29	0.77	0.46	12.52	0.01	0.01	1.35	44.26	0.30	1.05
07 BAL 6013 B	0.31	33.24	0.06	15.70	18.47	0.00	0.03	0.84	4.51	1.04	0.41	10.49	0.01	0.02	1.46	48.28	0.39	1.20
07 BAL 6013 C	0.10	53.75	0.05	12.12	10.36	0.00	0.01	1.51	5.22	0.86	0.21	29.03	0.01	0.04	1.70	57.97	0.49	0.95
07 BAL 6014 A	0.11	27.38	0.14	16.94	11.65	0.00	0.07	0.63	2.97	0.77	0.40	13.36	0.01	0.04	1.16	40.24	0.25	0.88
07 BAL 6014 B	0.13	34.98	0.06	21.66	13.16	0.00	0.03	0.91	3.98	0.90	0.42	13.44	0.01	0.01	1.46	44.23	0.33	0.87
07 BAL 6014 C	0.08	47.25	0.07	16.07	11.90	0.00	0.02	1.55	4.94	1.07	0.28	89.99	0.01	0.03	1.85	41.06	0.50	1.09

Raw data Teck orientation study Ballinalack (continued).

Sample ID	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
07 BAL 6001 A	36.59	0.05	10.10	81.20	1.62
07 BAL 6001 B	36.06	0.05	12.33	86.61	2.77
07 BAL 6001 C	43.52	0.05	16.51	100.95	2.22
07 BAL 6002 A	32.11	0.05	10.50	71.08	1.63
07 BAL 6002 B	40.59	0.05	14.78	80.38	3.12
07 BAL 6002 C	40.82	0.05	15.19	89.61	3.63
07 BAL 6003 A	36.58	0.05	10.63	75.10	1.55
07 BAL 6003 B	40.27	0.05	15.00	83.94	2.44
07 BAL 6003 C	40.72	0.05	21.91	85.83	0.94
07 BAL 6004 A	37.55	0.05	15.23	88.09	2.55
07 BAL 6004 B	40.46	0.05	18.30	99.66	3.17
07 BAL 6004 C	32.53	0.05	21.11	81.70	0.74
07 BAL 6005 A	35.62	0.05	9.31	95.12	1.70
07 BAL 6005 B	41.07	0.05	9.57	95.49	3.33
07 BAL 6005 C	40.05	0.05	20.88	115.17	1.82
07 BAL 6007 A	34.46	0.05	9.32	81.65	1.56
07 BAL 6007 B	36.65	0.05	10.17	95.54	1.29
07 BAL 6007 C	39.76	0.05	23.79	101.40	1.56
07 BAL 6008 A	42.59	0.16	11.57	90.19	2.11
07 BAL 6008 B	41.28	0.05	13.77	100.64	2.44
07 BAL 6008 C	53.33	0.05	29.79	107.30	3.35
07 BAL 6009 A	38.10	0.05	13.22	102.97	1.94
07 BAL 6009 B	41.16	0.05	15.10	99.46	2.18
07 BAL 6009 C	48.65	0.05	30.56	107.99	1.55
07 BAL 6011 A	43.24	0.05	14.60	94.37	1.88
07 BAL 6011 B	42.42	0.05	16.63	103.70	1.91
07 BAL 6011 C	51.05	0.05	33.56	104.51	1.07
07 BAL 6012 A	40.62	0.05	16.61	97.15	2.15
07 BAL 6012 B	39.12	0.11	17.37	98.65	2.25
07 BAL 6012 C	55.56	0.05	35.01	118.22	0.93
07 BAL 6013 A	42.35	0.05	17.44	108.53	2.21
07 BAL 6013 B	46.93	0.05	19.63	117.39	2.62
07 BAL 6013 C	48.51	0.05	27.44	110.18	0.70
07 BAL 6014 A	37.67	0.05	17.33	95.50	2.28
07 BAL 6014 B	42.95	0.05	21.20	111.89	2.37
07 BAL 6014 C	48.50	0.05	28.50	122.10	1.54

Raw data Teck orientation study Ballinalack (continued).

Sample ID	Project	Horizon	ING_TM65_X	ING_TM65_Y	UTM Zone	Analysis_Method	Soil_Samplers	Soil_From (m)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)
07 BAL 6015 A	BLK	A	235287.25	266134.62	29N	Aqua Regia	SteveCook	0.1	0.10	0.91	6.41	7.99	31.23	0.62
07 BAL 6015 B	BLK	BC	235287.25	266134.62	29N	Aqua Regia	SteveCook	0.3	0.11	1.04	6.64	10.47	34.24	0.79
07 BAL 6015 C	BLK	C	235287.25	266134.62	29N	Aqua Regia	SteveCook	0.55	0.12	1.01	7.95	11.62	31.13	0.84
07 BAL 6016 A	BLK	A	235332.2	266103.03	29N	Aqua Regia	SteveCook	0.1	0.09	0.87	5.68	9.19	34.91	0.53
07 BAL 6016 B	BLK	BC	235332.2	266103.03	29N	Aqua Regia	SteveCook	0.3	0.10	0.98	4.87	8.91	32.77	0.58
07 BAL 6016 C	BLK	C	235332.2	266103.03	29N	Aqua Regia	SteveCook	0.7	0.12	0.75	8.26	9.33	34.77	0.83
07 BAL 6017 A	BLK	A	235190.03	266212.93	29N	Aqua Regia	SteveCook	0.1	0.10	1.01	6.10	7.88	33.34	0.65
07 BAL 6017 B	BLK	BC	235190.03	266212.93	29N	Aqua Regia	SteveCook	0.3	0.09	1.08	6.38	9.08	32.91	0.75
07 BAL 6017 C	BLK	C	235190.03	266212.93	29N	Aqua Regia	SteveCook	0.6	0.10	0.99	6.93	8.45	28.84	0.80
07 BAL 6019 A	BLK	A	234905.2	266459.59	29N	Aqua Regia	SteveCook	0.1	0.16	1.14	3.49	7.31	48.82	0.58
07 BAL 6019 B	BLK	BC	234905.2	266459.59	29N	Aqua Regia	SteveCook	0.25	0.11	1.12	4.75	8.69	41.63	0.74
07 BAL 6019 C	BLK	C	234905.2	266459.59	29N	Aqua Regia	SteveCook	0.6	0.24	1.05	7.49	9.06	34.91	0.85
07 BAL 6021 A	BLK	A	234864.01	266493.56	29N	Aqua Regia	SteveCook	0.1	0.09	1.31	3.61	7.39	42.11	0.52
07 BAL 6021 B	BLK	BC	234864.01	266493.56	29N	Aqua Regia	SteveCook	0.2	0.11	1.35	4.41	8.99	47.51	0.55
07 BAL 6021 C	BLK	C	234864.01	266493.56	29N	Aqua Regia	SteveCook	0.55	0.12	1.35	6.92	7.93	42.99	0.97
07 BAL 6022 A	BLK	A	234797.15	266555.62	29N	Aqua Regia	SteveCook	0.1	0.08	1.18	4.29	8.16	36.76	0.46
07 BAL 6022 B	BLK	BC	234797.15	266555.62	29N	Aqua Regia	SteveCook	0.15	0.09	1.26	4.22	8.69	39.48	0.54
07 BAL 6022 C	BLK	C	234797.15	266555.62	29N	Aqua Regia	SteveCook	0.5	0.07	1.26	5.90	7.44	35.42	0.83
07 BAL 6023 A	BLK	A	235368.32	266064.34	29N	Aqua Regia	SteveCook	0.1	0.15	1.01	5.21	8.64	34.47	0.56
07 BAL 6023 B	BLK	BC	235368.32	266064.34	29N	Aqua Regia	SteveCook	0.15	0.09	0.99	5.25	9.50	35.94	0.61
07 BAL 6023 C	BLK	C	235368.32	266064.34	29N	Aqua Regia	SteveCook	0.5	0.12	1.19	8.86	7.53	37.69	1.33
07 BAL 6024 A	BLK	A	235405.29	266038.56	29N	Aqua Regia	SteveCook	0.1	0.07	0.88	4.06	7.72	31.20	0.37
07 BAL 6024 B	BLK	BC	235405.29	266038.56	29N	Aqua Regia	SteveCook	0.13	0.09	0.95	5.38	8.29	33.56	0.47
07 BAL 6024 C	BLK	C	235405.29	266038.56	29N	Aqua Regia	SteveCook	0.4	0.11	1.00	5.16	6.20	31.77	0.49
07 BAL 6025 A	BLK	A	235441.79	266005.56	29N	Aqua Regia	SteveCook	0.1	0.07	0.93	4.26	6.93	26.69	0.37
07 BAL 6025 B	BLK	BC	235441.79	266005.56	29N	Aqua Regia	SteveCook	0.17	0.10	1.02	4.88	8.67	29.73	0.39
07 BAL 6025 C	BLK	C	235441.79	266005.56	29N	Aqua Regia	SteveCook	0.55	0.07	1.06	6.07	6.45	26.42	0.57
07 BAL 6026 A	BLK	A	235475.96	265974.31	29N	Aqua Regia	SteveCook	0.1	0.09	0.98	4.78	8.85	31.28	0.40
07 BAL 6026 B	BLK	BC	235475.96	265974.31	29N	Aqua Regia	SteveCook	0.2	0.08	1.07	5.00	9.69	32.56	0.48
07 BAL 6026 C	BLK	C	235475.96	265974.31	29N	Aqua Regia	SteveCook	0.6	0.07	1.09	8.84	6.37	27.68	0.96
07 BAL 6027 A	BLK	A	235548.93	265910.18	29N	Aqua Regia	SteveCook	0.1	0.09	0.98	4.56	7.82	27.60	0.46
07 BAL 6027 B	BLK	BC	235548.93	265910.18	29N	Aqua Regia	SteveCook	0.25	0.10	1.14	5.45	8.99	28.91	0.53
07 BAL 6027 C	BLK	C	235548.93	265910.18	29N	Aqua Regia	SteveCook	0.65	0.09	0.99	8.60	6.79	27.74	1.31

Raw data Teck orientation study Ballinalack (continued).

Sample ID	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)	Ge (ppm)	Hg (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)
07 BAL 6015 A	0.06	0.29	1.28	22.36	5.33	19.10	20.18	1.56	2.17	0.18	0.07	0.10	16.18	5.41	0.13	407.86	2.34	0.01
07 BAL 6015 B	0.06	0.27	1.04	24.05	5.13	25.15	28.37	1.38	2.87	0.17	0.07	0.08	18.63	6.55	0.14	371.46	2.29	0.01
07 BAL 6015 C	0.07	1.70	1.81	28.29	8.03	22.70	21.98	1.83	2.33	0.15	0.08	0.11	21.31	6.43	0.16	490.17	3.53	0.01
07 BAL 6016 A	0.05	0.57	1.11	19.04	4.75	17.55	14.37	1.33	2.15	0.14	0.06	0.14	13.32	5.47	0.14	461.39	1.81	0.01
07 BAL 6016 B	0.04	0.27	0.94	19.06	4.84	21.89	12.50	1.16	2.51	0.13	0.05	0.11	14.09	6.16	0.13	473.45	1.67	0.01
07 BAL 6016 C	0.05	1.06	3.43	27.08	9.18	18.47	24.50	1.86	1.87	0.10	0.07	0.08	23.84	4.74	0.13	1098.09	4.73	0.01
07 BAL 6017 A	0.05	0.19	0.97	23.54	5.55	21.07	15.92	1.56	2.38	0.18	0.07	0.11	16.88	6.01	0.14	490.94	2.84	0.01
07 BAL 6017 B	0.05	0.15	0.87	25.01	5.43	23.95	15.97	1.52	2.55	0.14	0.08	0.08	19.34	6.84	0.14	450.68	3.08	0.01
07 BAL 6017 C	0.04	0.57	1.21	27.52	6.82	22.35	14.51	1.62	2.48	0.17	0.07	0.07	20.47	6.35	0.13	554.72	3.41	0.01
07 BAL 6019 A	0.05	0.40	1.86	23.00	3.39	20.60	10.67	0.98	2.85	0.12	0.09	0.08	16.53	6.90	0.13	162.18	0.86	0.01
07 BAL 6019 B	0.05	0.49	2.14	25.38	4.59	23.85	11.47	1.21	3.05	0.15	0.10	0.07	18.31	7.83	0.14	190.21	1.17	0.01
07 BAL 6019 C	0.05	0.36	2.09	31.71	8.89	27.00	14.49	1.99	2.64	0.20	0.12	0.09	25.56	7.43	0.18	159.23	2.45	0.01
07 BAL 6021 A	0.06	0.37	1.09	19.44	2.88	22.23	8.48	1.05	3.49	0.15	0.07	0.07	13.33	7.60	0.13	161.00	0.76	0.01
07 BAL 6021 B	0.07	0.37	1.17	21.60	3.41	26.82	8.65	1.16	3.58	0.13	0.07	0.07	14.75	8.46	0.13	161.54	0.82	0.01
07 BAL 6021 C	0.08	0.25	1.16	32.47	7.43	31.99	11.57	2.20	3.71	0.24	0.08	0.08	23.86	8.95	0.21	273.99	2.01	0.01
07 BAL 6022 A	0.06	0.27	0.75	18.52	4.16	21.43	10.45	1.28	3.04	0.13	0.06	0.09	12.44	7.10	0.14	282.48	1.22	0.01
07 BAL 6022 B	0.05	0.23	0.76	21.32	4.65	24.40	9.47	1.17	3.16	0.13	0.04	0.08	14.52	8.42	0.14	268.07	1.19	0.01
07 BAL 6022 C	0.04	0.15	0.88	28.88	7.06	27.26	10.78	1.61	3.26	0.19	0.08	0.09	21.26	8.92	0.17	569.48	1.71	0.01
07 BAL 6023 A	0.06	0.43	1.02	21.87	5.28	20.07	12.89	1.38	2.41	0.16	0.07	0.11	14.59	5.89	0.14	421.60	1.93	0.01
07 BAL 6023 B	0.06	0.38	1.02	23.31	5.74	23.12	13.51	1.30	2.71	0.13	0.07	0.09	15.70	6.33	0.13	393.87	1.94	0.01
07 BAL 6023 C	0.08	0.22	2.04	44.17	11.16	31.53	27.04	2.14	3.12	0.30	0.11	0.10	38.07	7.59	0.18	723.66	3.38	0.01
07 BAL 6024 A	0.04	0.32	0.91	16.38	4.00	17.10	10.78	1.10	2.14	0.14	0.06	0.12	10.46	5.05	0.13	380.52	1.50	0.01
07 BAL 6024 B	0.05	0.22	0.91	18.73	4.85	20.24	11.47	1.31	2.24	0.12	0.07	0.08	11.88	6.06	0.12	349.00	1.52	0.01
07 BAL 6024 C	0.03	0.16	0.72	19.46	5.73	21.07	9.80	1.34	2.31	0.17	0.05	0.06	12.09	6.34	0.12	588.20	1.81	0.01
07 BAL 6025 A	0.06	0.23	0.61	15.59	3.76	18.88	9.35	1.14	2.51	0.14	0.09	0.08	9.44	5.41	0.11	219.71	1.43	0.01
07 BAL 6025 B	0.06	0.18	0.67	18.37	4.65	21.76	9.57	1.31	2.39	0.10	0.07	0.07	11.14	6.23	0.12	259.65	1.77	0.01
07 BAL 6025 C	0.05	0.11	0.61	25.26	6.98	23.40	13.27	1.54	2.53	0.14	0.06	0.08	14.49	6.60	0.13	516.46	3.03	0.01
07 BAL 6026 A	0.05	0.45	0.91	18.43	5.09	18.94	10.80	1.37	2.33	0.11	0.05	0.09	10.86	5.78	0.13	488.61	1.62	0.01
07 BAL 6026 B	0.04	0.36	0.76	19.94	5.53	22.18	9.99	1.32	2.65	0.11	0.06	0.07	12.04	6.67	0.13	511.26	1.55	0.01
07 BAL 6026 C	0.06	0.18	1.20	40.73	8.63	26.45	16.29	2.02	2.63	0.23	0.09	0.08	29.50	7.33	0.18	710.49	2.73	0.01
07 BAL 6027 A	0.06	0.30	0.83	19.98	4.66	20.39	11.46	1.25	2.43	0.15	0.11	0.10	12.13	5.78	0.15	354.78	2.47	0.01
07 BAL 6027 B	0.06	0.18	0.73	22.57	5.15	27.00	11.87	1.40	2.59	0.13	0.16	0.10	14.06	7.34	0.15	336.16	2.82	0.01
07 BAL 6027 C	0.05	0.14	1.97	38.95	7.99	25.24	21.23	2.09	2.10	0.30	0.14	0.08	38.65	6.22	0.15	548.62	6.15	0.01

Raw data Teck orientation study Ballinalack (continued).

Sample ID	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)
07 BAL 6015 A	0.11	23.72	0.13	18.06	12.38	0.00	0.08	0.55	2.84	0.68	0.46	15.16	0.01	0.01	1.29	41.28	0.29	0.89
07 BAL 6015 B	0.13	30.39	0.07	17.15	15.77	0.00	0.04	0.77	3.76	0.84	0.46	15.14	0.01	0.01	1.63	47.39	0.34	0.76
07 BAL 6015 C	0.20	51.71	0.06	15.24	15.15	0.00	0.02	1.47	4.55	0.72	0.37	67.16	0.01	0.03	1.74	55.87	0.49	0.86
07 BAL 6016 A	0.12	20.22	0.20	15.66	14.62	0.00	0.10	0.27	2.48	0.72	0.43	24.42	0.01	0.01	1.17	41.05	0.29	0.58
07 BAL 6016 B	0.13	23.52	0.07	10.89	15.56	0.00	0.04	0.31	2.97	0.51	0.34	12.73	0.01	0.01	1.32	43.80	0.33	0.79
07 BAL 6016 C	0.08	53.91	0.07	10.40	11.30	0.00	0.02	1.45	4.47	0.67	0.26	41.47	0.01	0.06	1.86	39.41	0.33	0.85
07 BAL 6017 A	0.15	22.87	0.13	17.89	13.80	0.00	0.07	0.67	2.84	0.64	0.50	11.17	0.01	0.01	1.22	47.55	0.31	0.84
07 BAL 6017 B	0.27	26.38	0.06	15.00	17.78	0.00	0.03	1.13	3.69	0.77	0.43	10.08	0.01	0.04	1.27	50.87	0.39	0.88
07 BAL 6017 C	0.11	30.44	0.06	12.65	14.88	0.00	0.02	0.83	3.61	0.88	0.32	24.63	0.01	0.01	1.52	50.09	0.36	0.75
07 BAL 6019 A	0.09	17.26	0.11	16.78	9.78	0.00	0.09	0.09	2.68	1.71	0.49	17.11	0.01	0.01	1.22	33.39	0.28	1.22
07 BAL 6019 B	0.13	21.59	0.09	18.24	12.49	0.00	0.09	0.29	3.07	1.98	0.50	17.10	0.01	0.03	1.36	38.29	0.31	1.03
07 BAL 6019 C	0.12	45.03	0.07	12.16	9.92	0.00	0.02	1.08	4.69	0.68	0.27	22.53	0.01	0.01	2.24	54.02	0.33	0.61
07 BAL 6021 A	0.19	12.70	0.10	16.36	11.05	0.00	0.09	0.03	2.54	0.69	0.45	14.88	0.01	0.01	1.64	39.67	0.34	1.17
07 BAL 6021 B	0.34	14.32	0.08	22.68	13.16	0.00	0.09	0.03	3.21	0.94	0.48	15.45	0.01	0.01	1.44	54.52	0.41	1.38
07 BAL 6021 C	0.16	30.23	0.04	15.37	12.72	0.00	0.02	0.68	4.81	0.64	0.33	17.91	0.01	0.01	2.37	68.70	0.38	0.70
07 BAL 6022 A	0.17	15.54	0.12	14.22	15.28	0.00	0.07	0.08	2.53	0.59	0.42	10.39	0.01	0.01	1.41	41.77	0.34	0.79
07 BAL 6022 B	0.19	16.76	0.07	13.15	17.63	0.00	0.05	0.07	2.84	0.58	0.40	9.74	0.01	0.01	1.31	49.50	0.39	0.88
07 BAL 6022 C	0.13	29.17	0.04	11.48	16.64	0.00	0.02	0.31	4.04	0.66	0.31	10.98	0.01	0.01	1.78	57.70	0.35	0.88
07 BAL 6023 A	0.13	20.93	0.15	16.12	15.39	0.00	0.08	0.27	2.61	0.55	0.47	17.61	0.01	0.01	1.43	42.43	0.32	0.69
07 BAL 6023 B	0.21	22.77	0.11	16.21	17.65	0.00	0.07	0.36	3.12	0.68	0.40	17.03	0.03	0.01	1.40	43.82	0.38	0.75
07 BAL 6023 C	0.14	54.64	0.05	16.01	16.46	0.00	0.02	1.14	5.90	1.06	0.40	13.83	0.01	0.03	2.05	54.38	0.46	1.02
07 BAL 6024 A	0.11	13.86	0.16	14.01	12.95	0.00	0.09	0.09	1.87	0.43	0.41	11.55	0.01	0.01	1.06	41.53	0.29	0.79
07 BAL 6024 B	0.14	15.64	0.12	16.65	14.43	0.00	0.07	0.18	2.20	0.56	0.40	9.98	0.01	0.01	1.19	46.78	0.32	0.90
07 BAL 6024 C	0.11	18.13	0.06	12.14	15.08	0.00	0.02	0.27	2.53	0.58	0.32	9.09	0.01	0.01	1.46	47.34	0.31	0.72
07 BAL 6025 A	0.11	13.35	0.11	13.96	13.23	0.00	0.07	0.11	1.98	0.62	1.44	8.91	0.01	0.01	1.11	41.51	0.31	0.87
07 BAL 6025 B	0.24	15.62	0.09	15.43	16.97	0.00	0.05	0.22	2.55	0.60	0.40	8.35	0.08	0.01	1.00	47.71	0.36	0.96
07 BAL 6025 C	0.23	28.04	0.05	11.83	16.63	0.00	0.02	0.66	3.24	0.71	0.32	7.76	0.01	0.01	1.10	55.37	0.35	0.88
07 BAL 6026 A	0.12	16.45	0.14	14.59	12.16	0.00	0.09	0.12	2.00	0.72	0.49	14.87	0.01	0.01	1.10	43.65	0.28	0.95
07 BAL 6026 B	0.13	18.54	0.08	14.63	14.35	0.00	0.06	0.23	2.38	0.69	0.44	13.39	0.01	0.01	1.18	49.60	0.35	1.04
07 BAL 6026 C	0.13	41.11	0.04	14.09	12.59	0.00	0.01	0.75	4.85	0.90	0.27	11.25	0.01	0.03	1.56	63.58	0.36	0.95
07 BAL 6027 A	0.11	18.45	0.14	14.13	14.67	0.00	0.08	0.22	2.10	0.74	0.48	11.68	0.01	0.01	1.09	46.67	0.31	0.97
07 BAL 6027 B	0.14	21.65	0.09	14.06	18.06	0.00	0.06	0.37	2.68	0.89	0.42	9.76	0.01	0.01	1.31	53.90	0.38	1.04
07 BAL 6027 C	0.09	44.56	0.05	11.58	11.58	0.00	0.02	1.37	5.84	1.23	0.28	9.44	0.01	0.02	1.56	41.87	0.45	1.11

Raw data Teck orientation study Ballinalack (continued).

Sample ID	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
07 BAL 6015 A	34.14	0.05	14.71	90.32	2.50
07 BAL 6015 B	41.78	0.05	17.15	106.65	3.25
07 BAL 6015 C	42.33	0.05	20.32	106.61	1.77
07 BAL 6016 A	32.83	0.05	11.53	93.15	2.09
07 BAL 6016 B	34.14	0.05	12.34	91.97	2.01
07 BAL 6016 C	44.43	0.11	24.28	109.44	2.00
07 BAL 6017 A	39.14	0.05	14.75	90.02	1.82
07 BAL 6017 B	41.85	0.05	17.02	96.57	2.01
07 BAL 6017 C	41.39	0.05	18.89	94.04	1.84
07 BAL 6019 A	29.95	0.05	13.01	71.99	2.23
07 BAL 6019 B	37.02	0.05	14.93	88.86	2.19
07 BAL 6019 C	43.46	0.05	22.05	76.45	2.19
07 BAL 6021 A	36.19	0.05	9.46	78.62	1.59
07 BAL 6021 B	45.70	0.05	10.41	88.15	2.08
07 BAL 6021 C	51.28	0.05	19.91	87.52	2.02
07 BAL 6022 A	35.95	0.05	9.05	86.50	1.58
07 BAL 6022 B	39.65	0.05	10.60	97.17	1.62
07 BAL 6022 C	40.36	0.05	19.04	97.64	1.94
07 BAL 6023 A	35.62	0.05	12.06	94.01	1.92
07 BAL 6023 B	39.83	0.05	12.80	97.34	2.24
07 BAL 6023 C	46.37	0.05	39.43	111.07	2.04
07 BAL 6024 A	29.71	0.05	7.71	82.90	1.59
07 BAL 6024 B	36.68	0.05	8.74	88.22	1.72
07 BAL 6024 C	34.96	0.05	8.53	82.90	1.93
07 BAL 6025 A	31.74	0.05	6.14	76.58	1.63
07 BAL 6025 B	37.75	0.05	7.13	85.75	2.13
07 BAL 6025 C	39.45	0.05	10.49	94.22	1.43
07 BAL 6026 A	32.08	0.05	7.81	87.00	1.82
07 BAL 6026 B	37.00	0.05	8.56	91.39	1.89
07 BAL 6026 C	44.97	0.05	24.50	104.25	1.24
07 BAL 6027 A	33.48	0.05	8.77	85.32	1.56
07 BAL 6027 B	41.03	0.05	10.39	96.54	1.86
07 BAL 6027 C	52.30	0.05	35.20	118.47	1.35

Appendix B

Images of thin sections in reflected and transmitted light.

Image of drill core (enlarged).

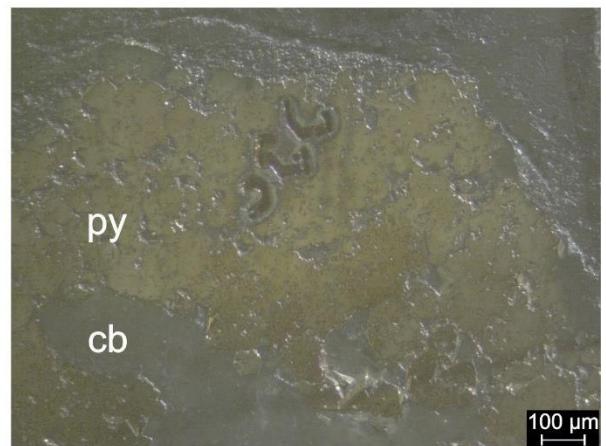
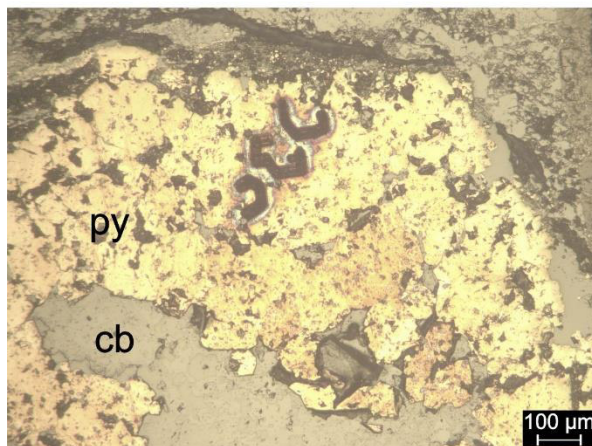
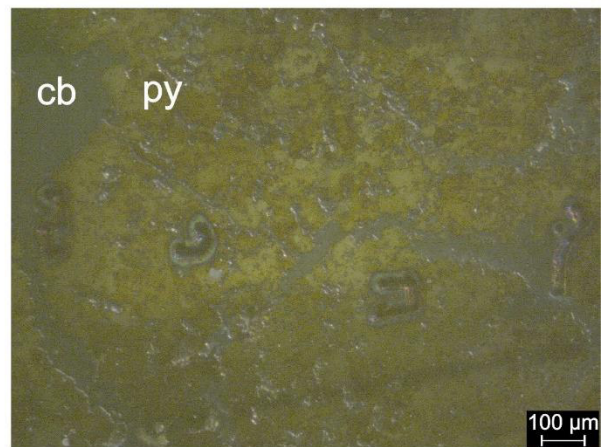
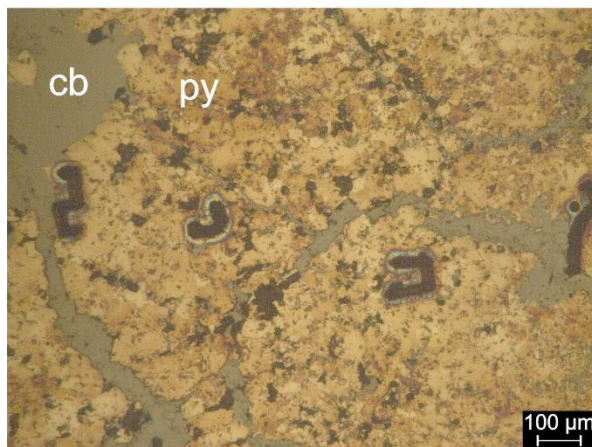
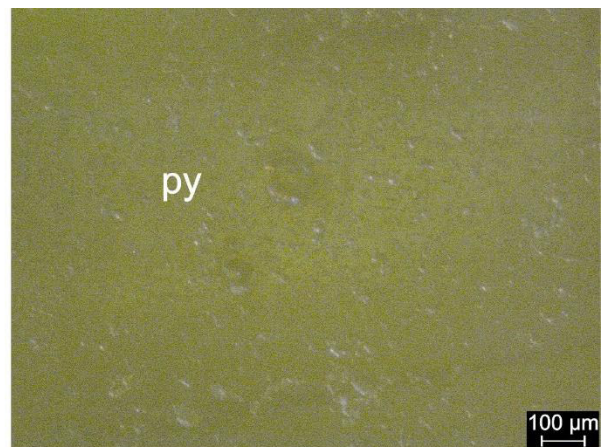
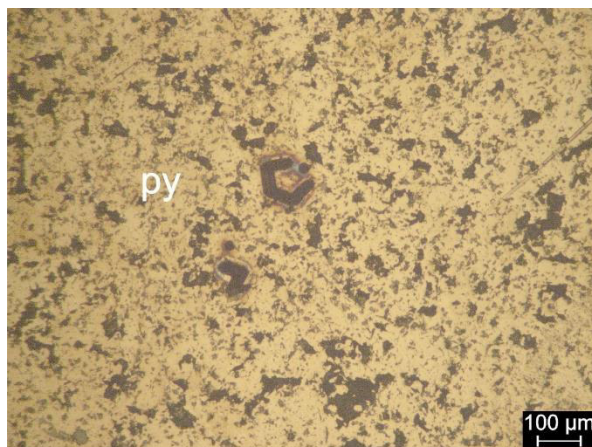
Raw data laser ablation ICP-MS of pyrite and sphalerite.

Average concentrations for pyrite and sphalerite obtained using SEM.

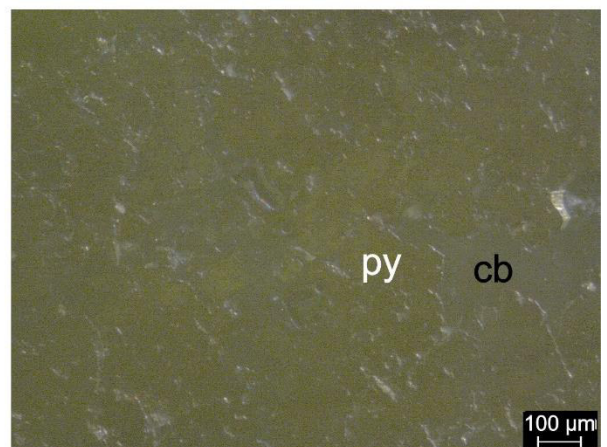
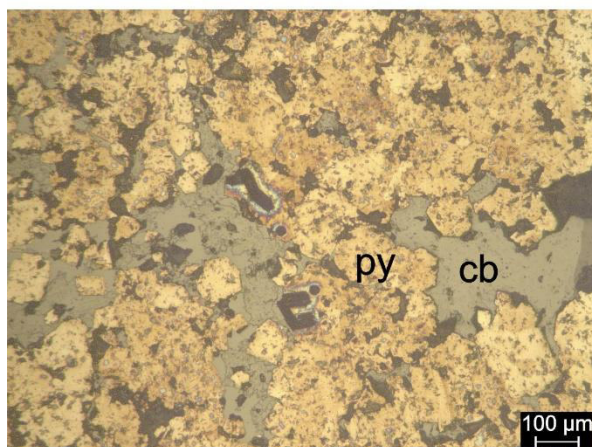
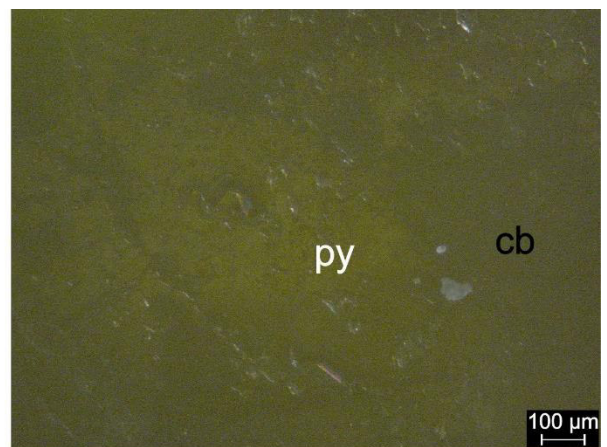
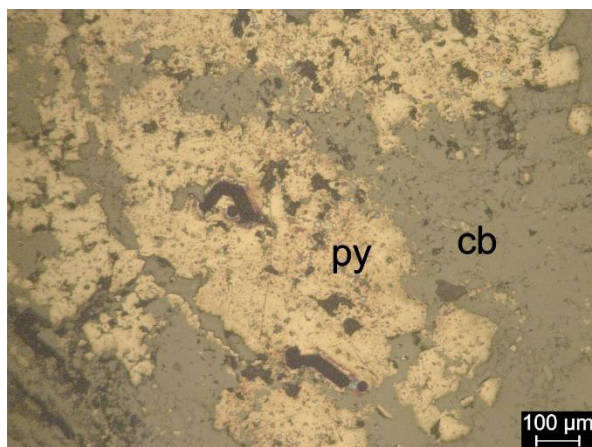
Images of thin sections in reflected and transmitted light

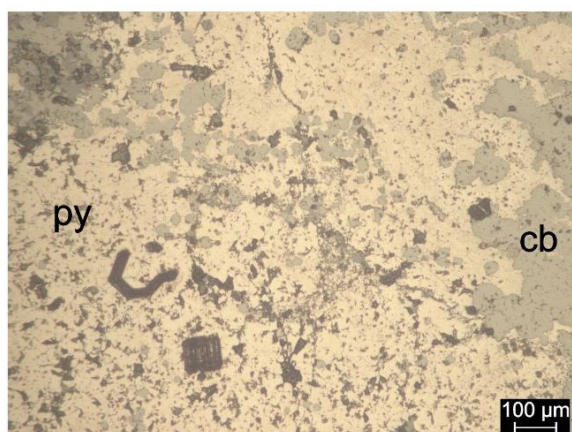
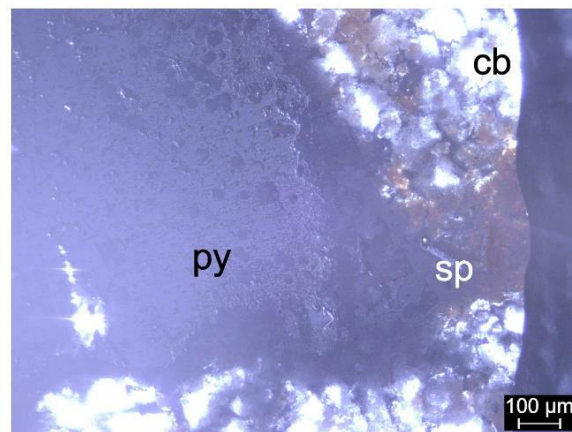
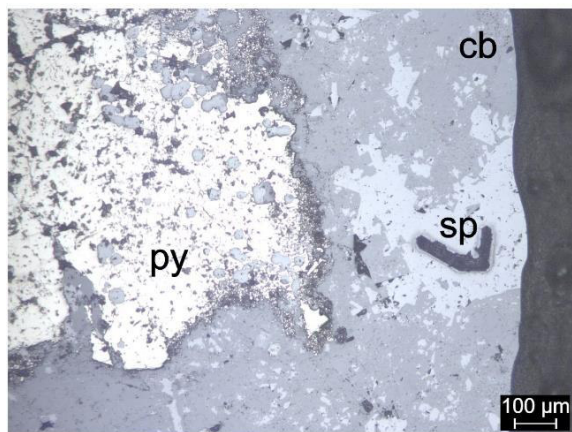
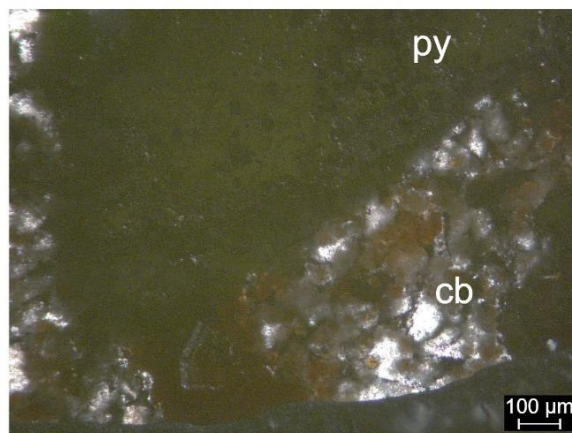
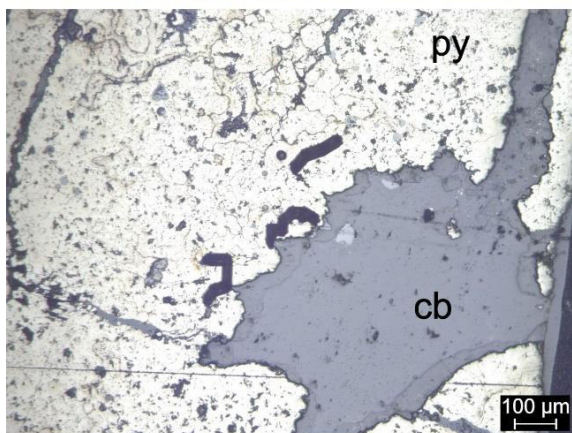
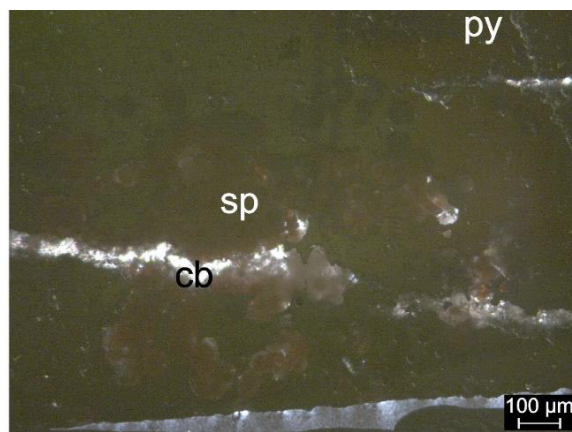
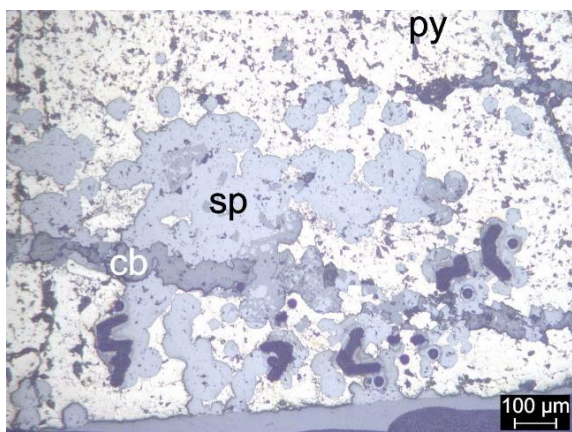
Thick section photographs in reflected (left) and transmitted (right) light for analysed sphalerite and pyrite. Notably, the thickness of the sections were $\sim 80\text{ }\mu\text{m}$, that influenced the transmitted light images. Using the microscope, transmitted light images, mainly appeared black; most of the transmitted light images only showed structures with an increase of length of exposure.

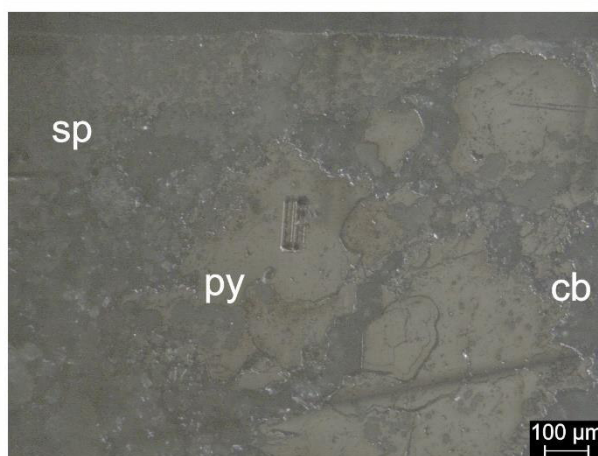
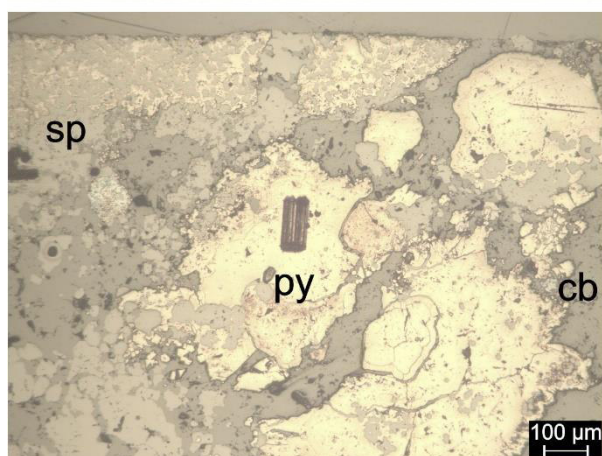
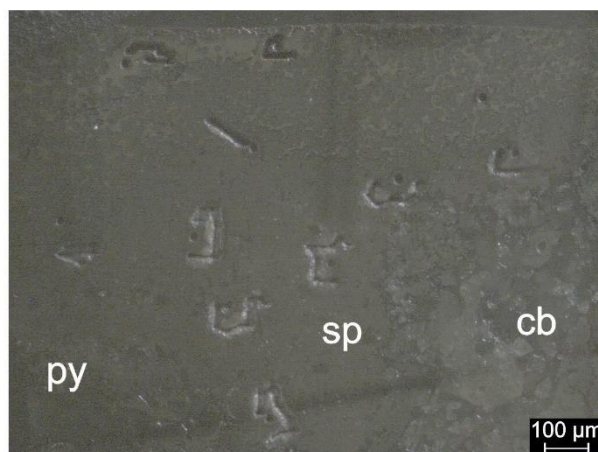
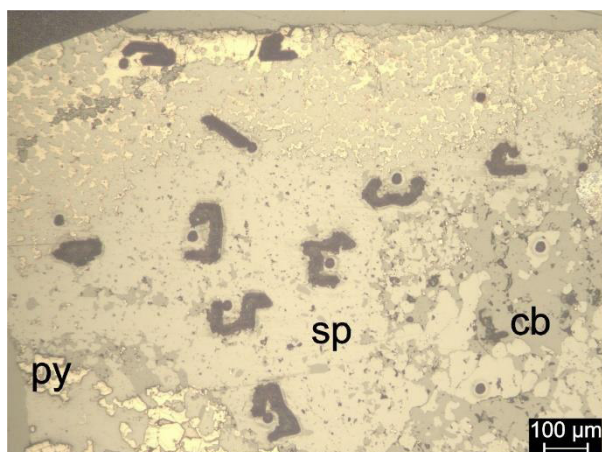
BLK 05

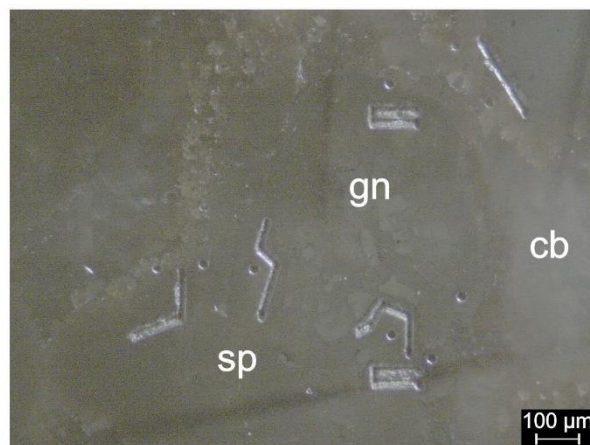
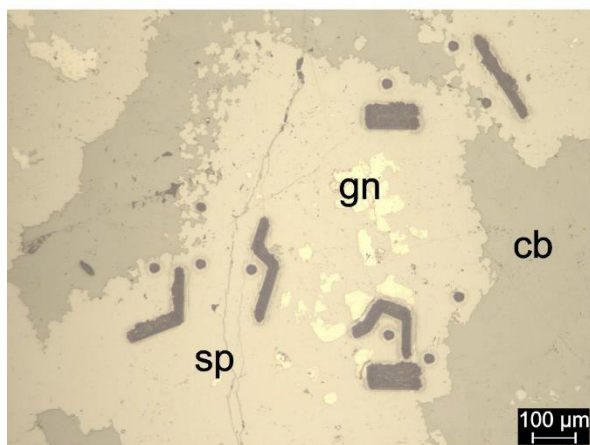
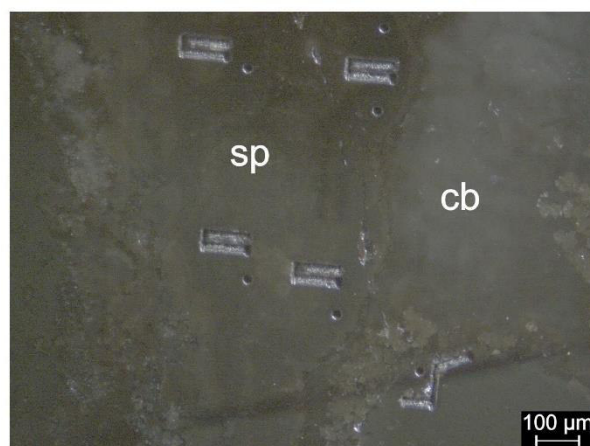
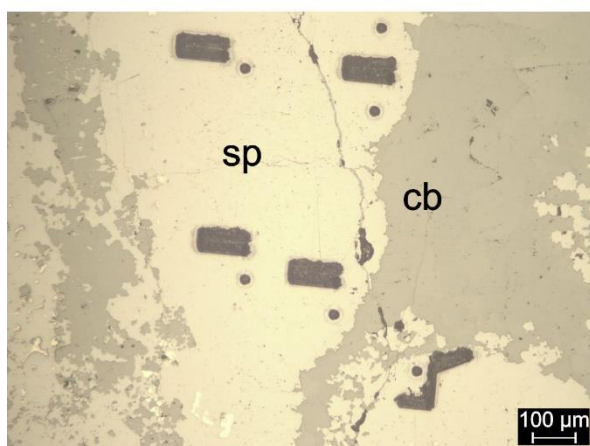
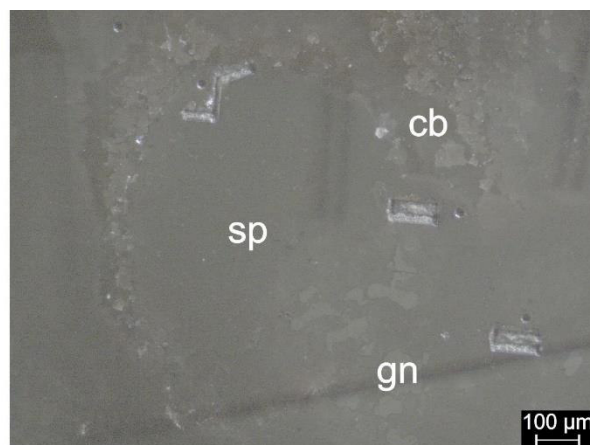
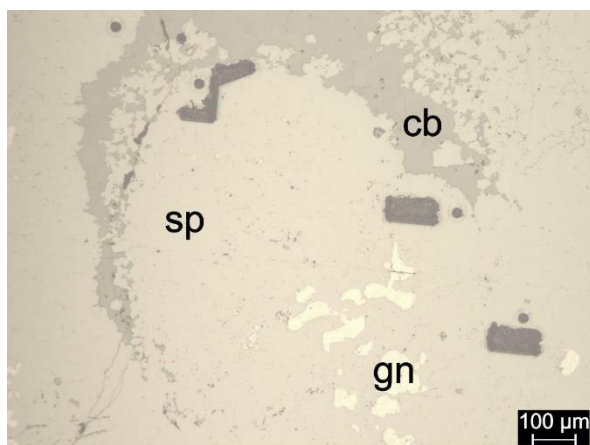


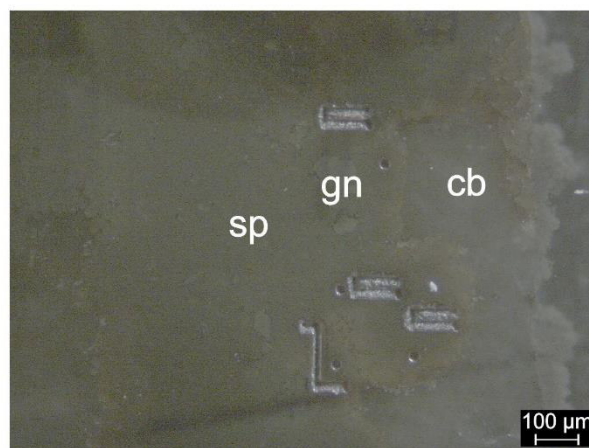
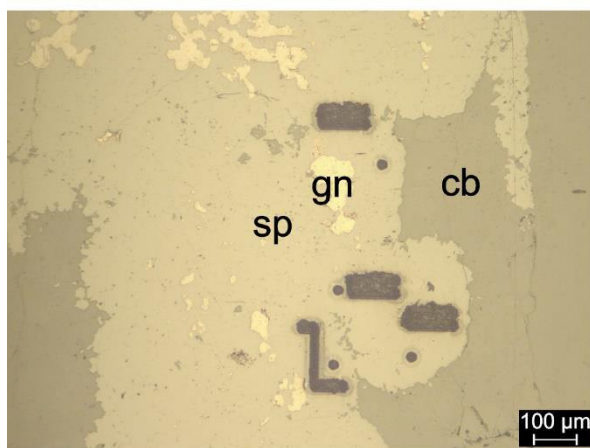
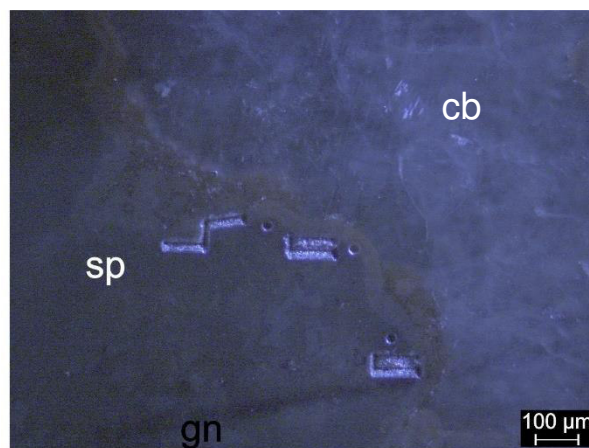
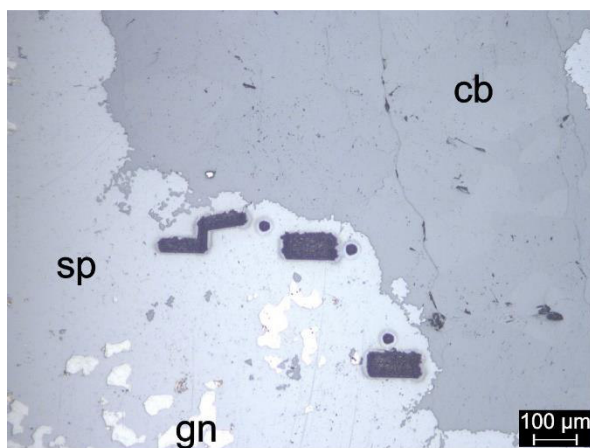
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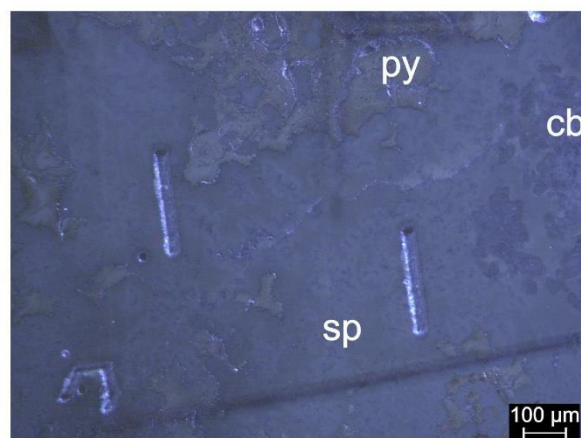
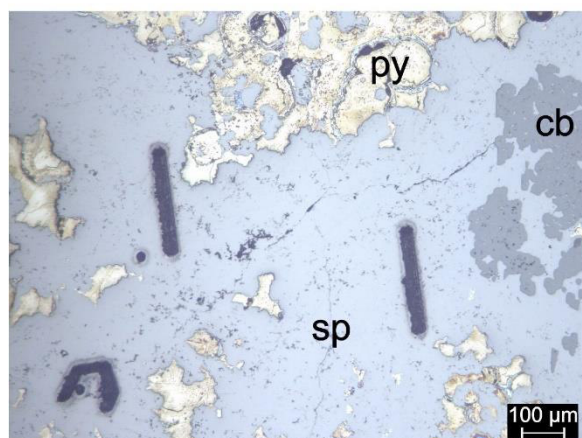
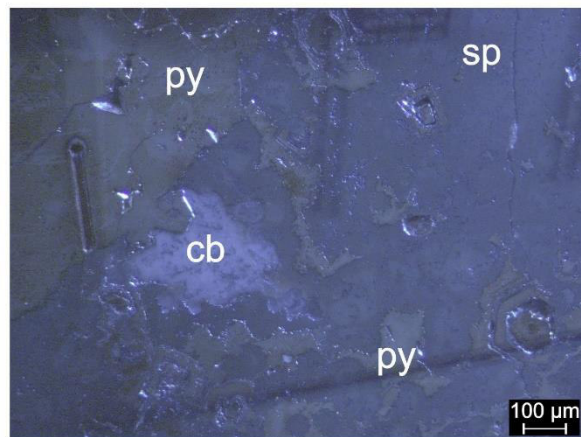
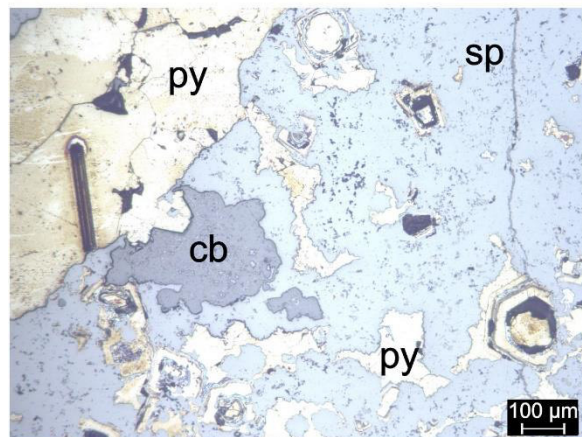
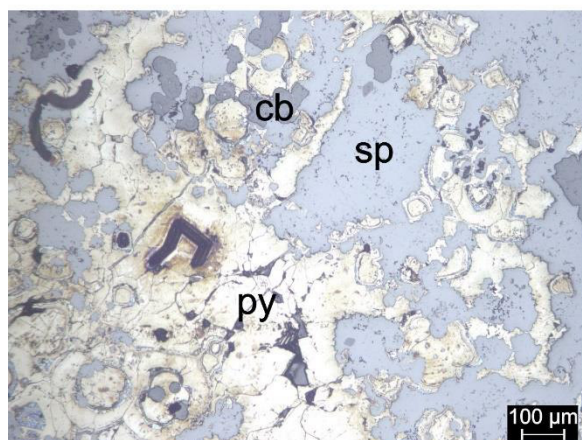
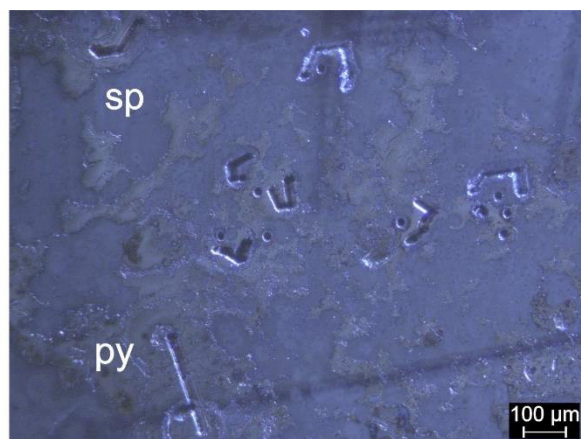
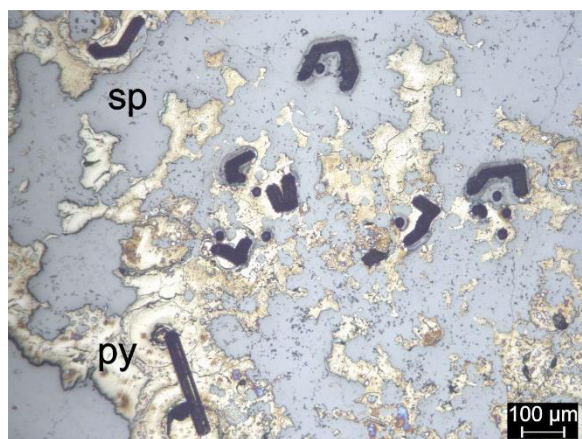


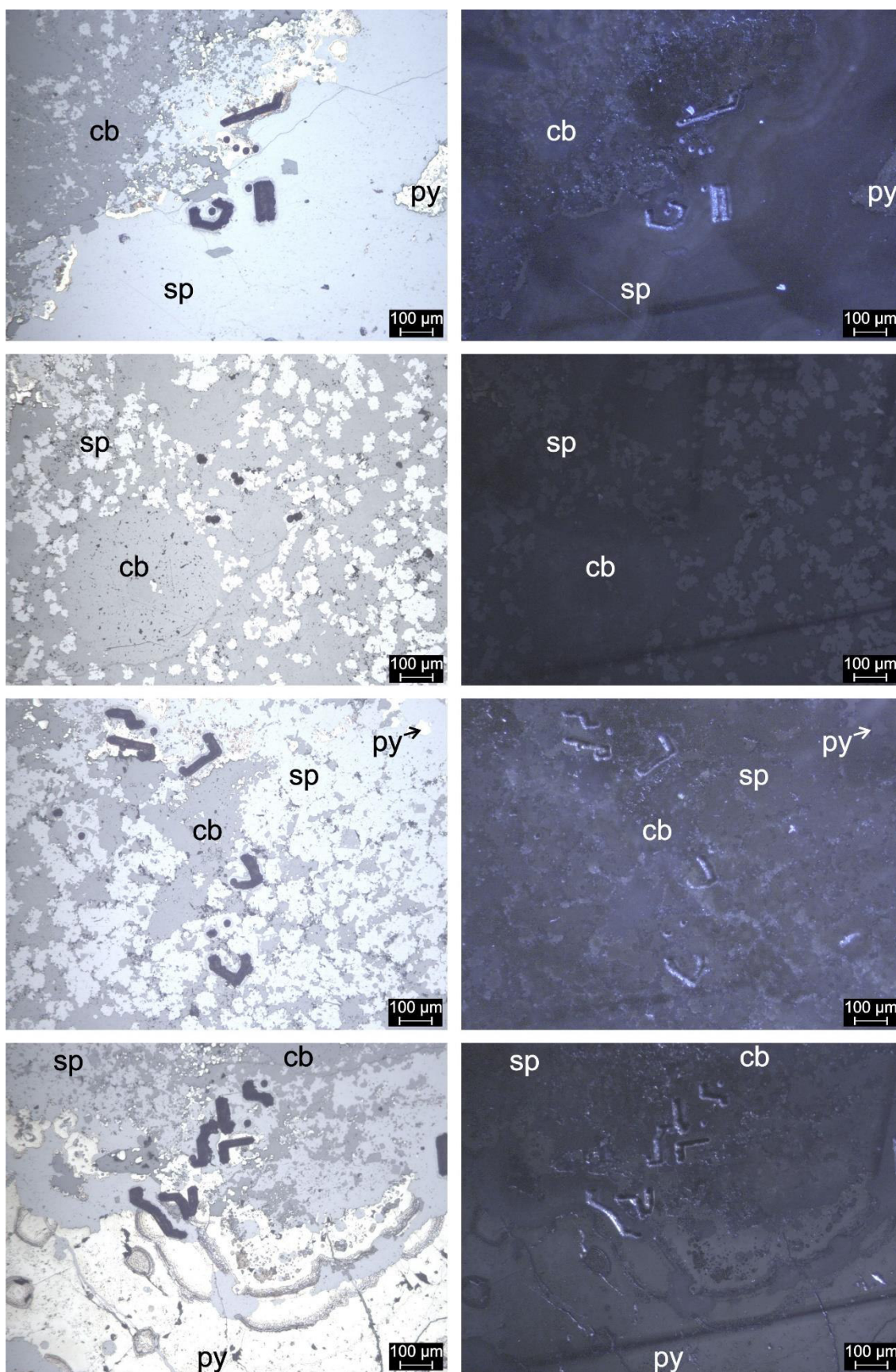


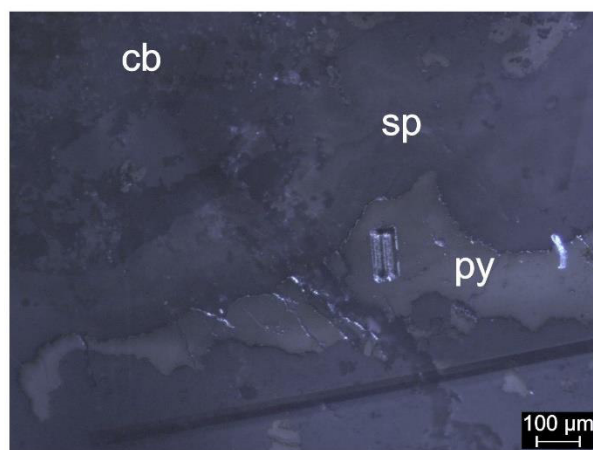
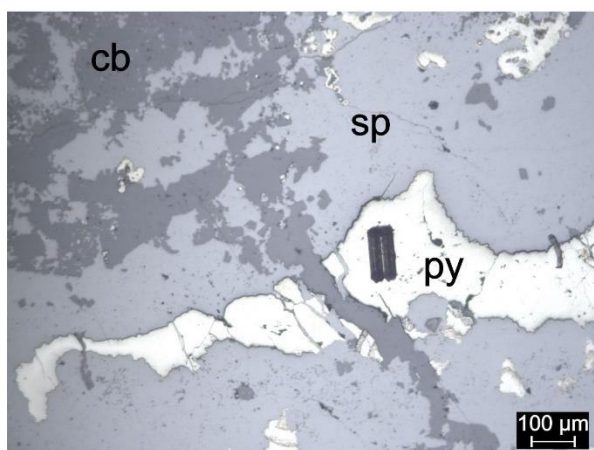
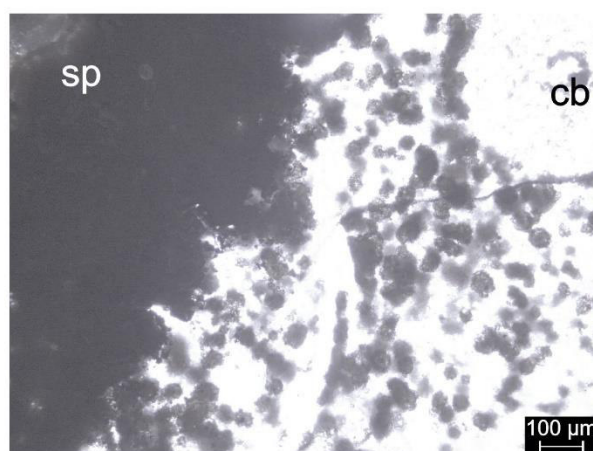
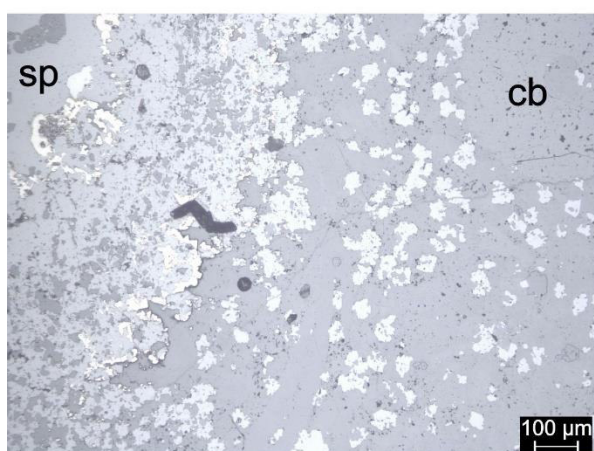
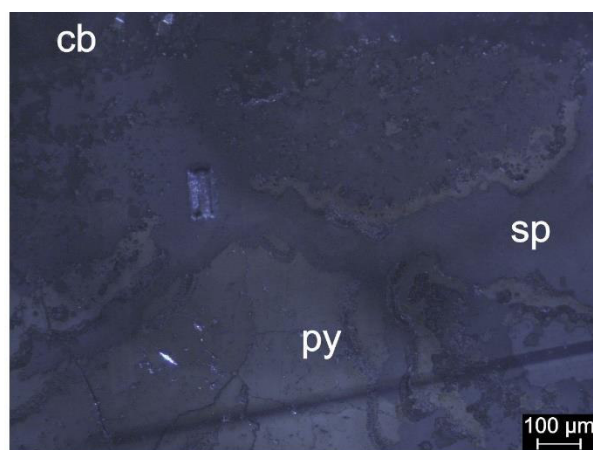
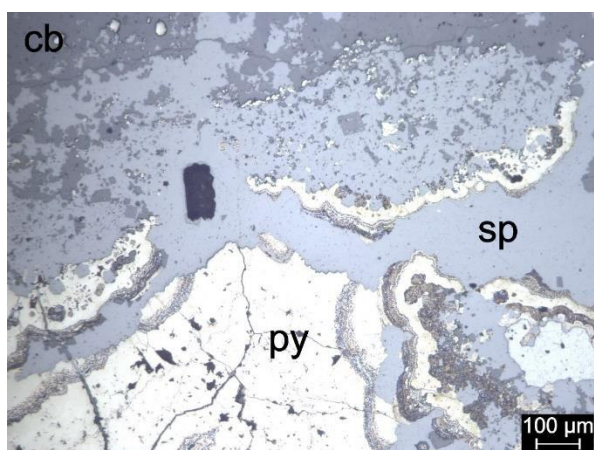


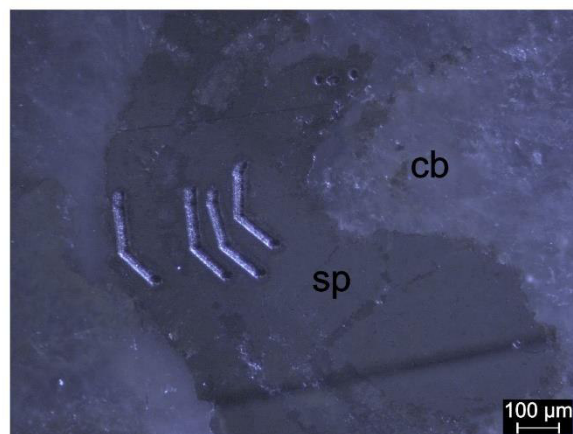
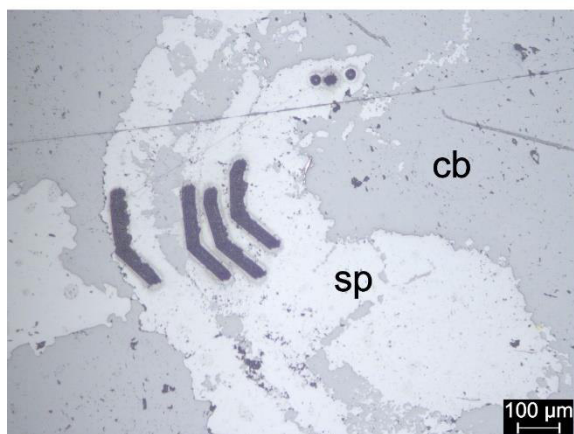
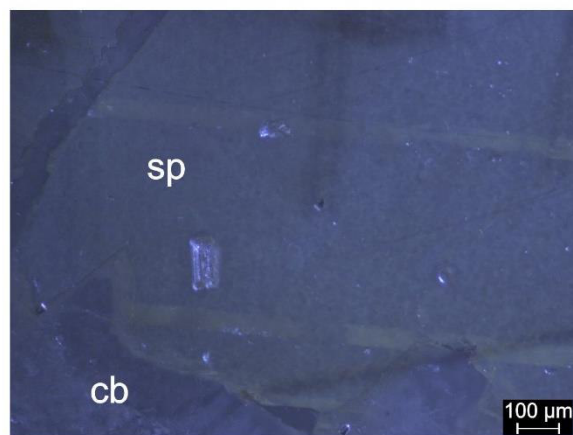
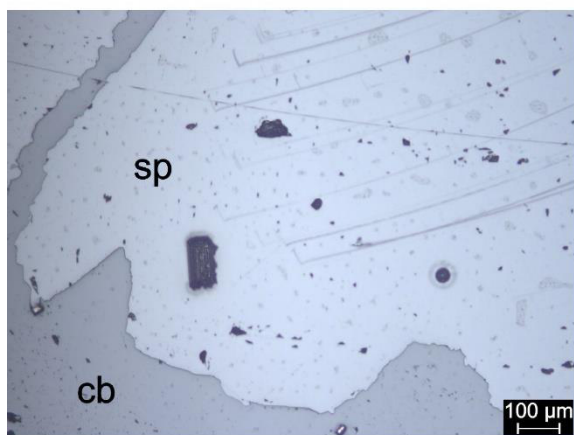
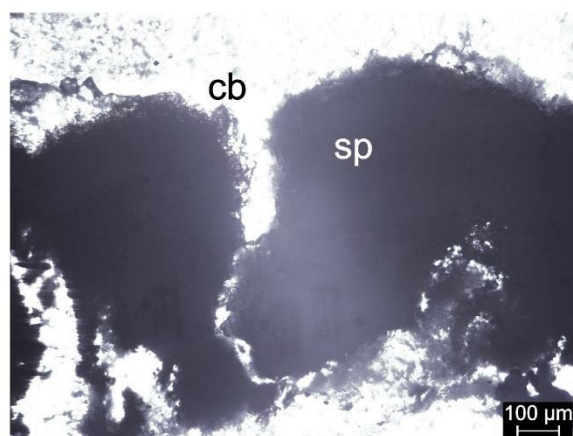
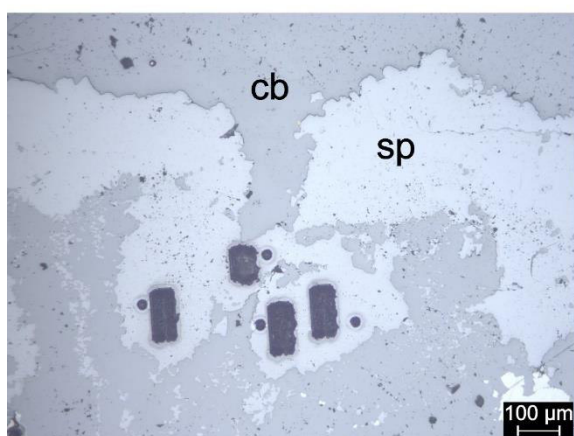
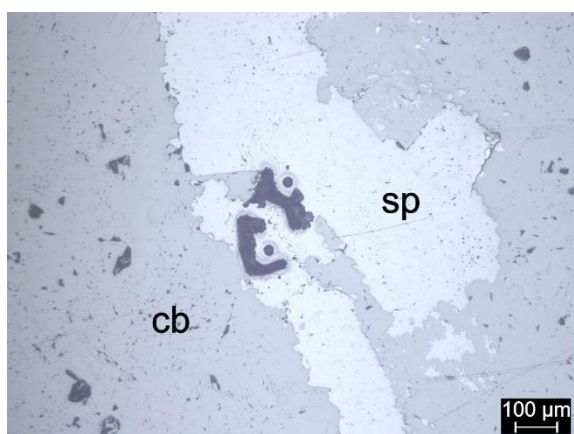


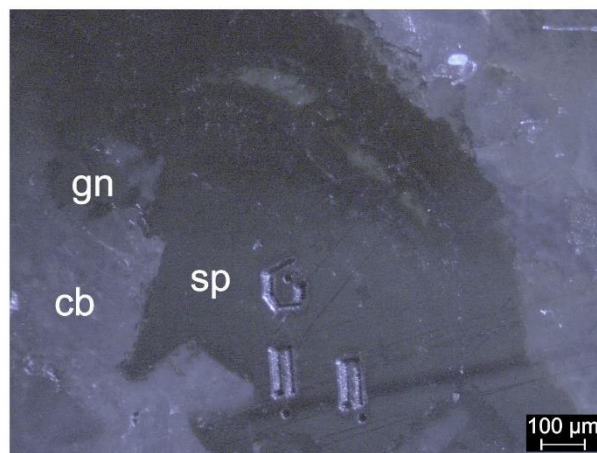
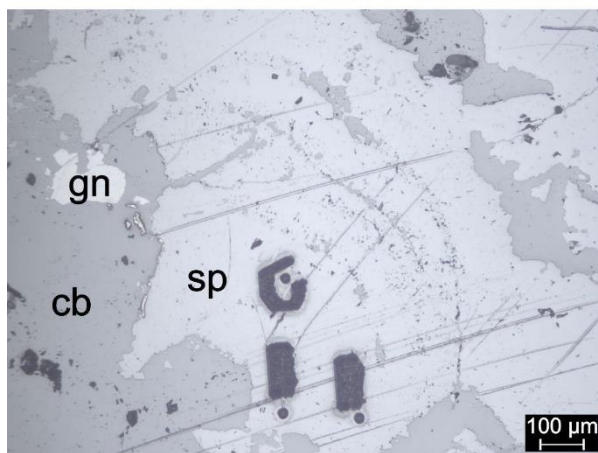
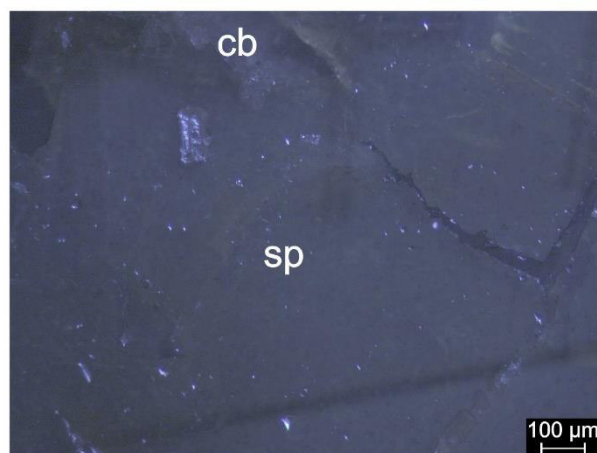
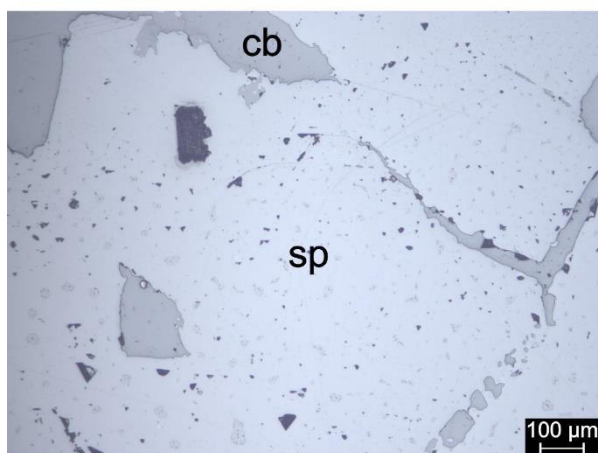
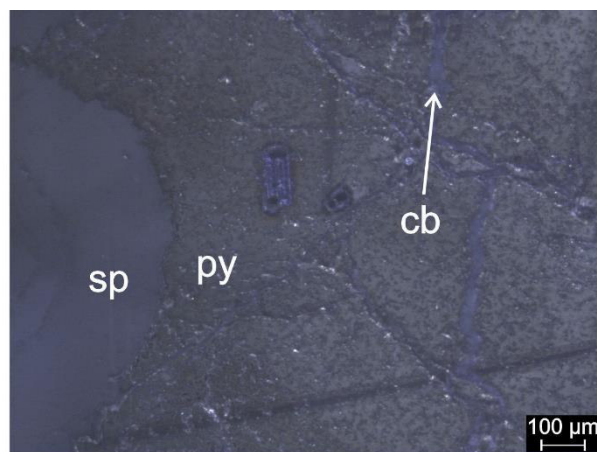
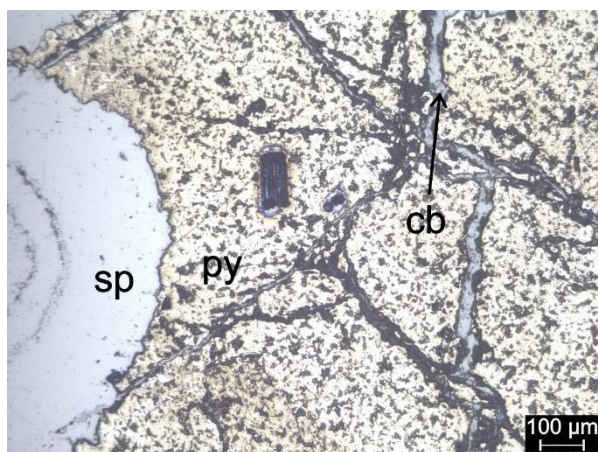


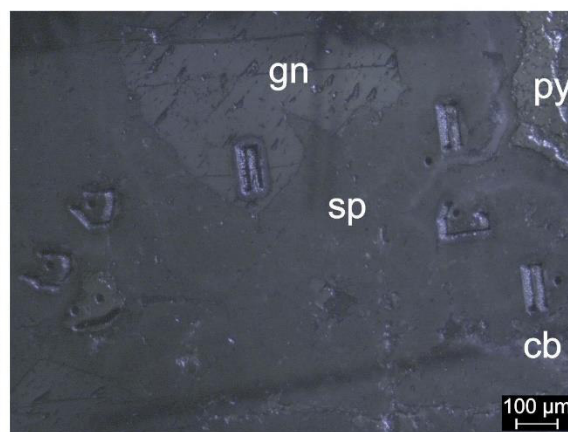
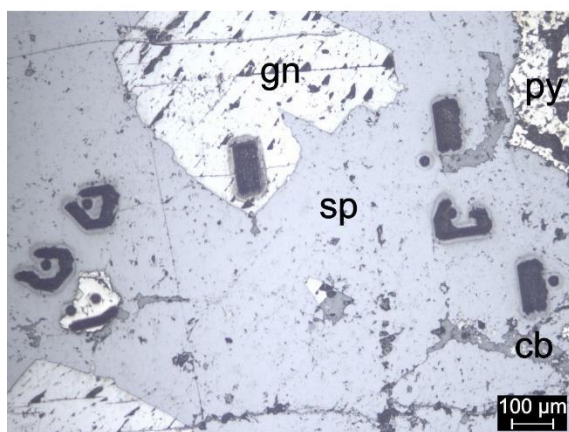
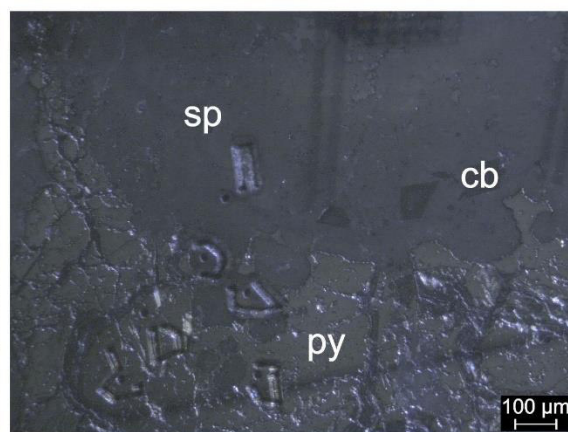
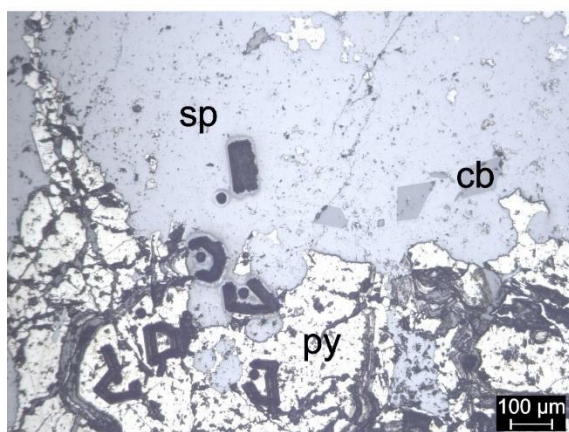
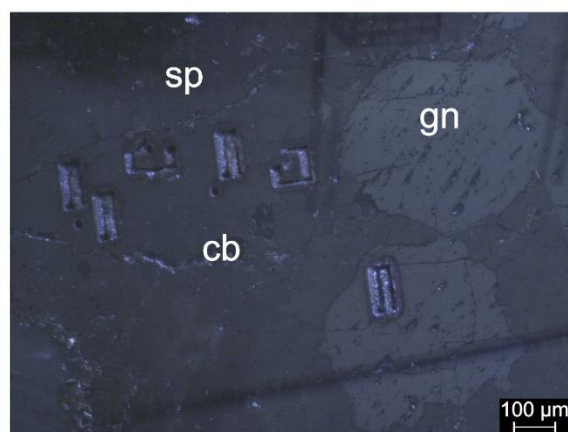
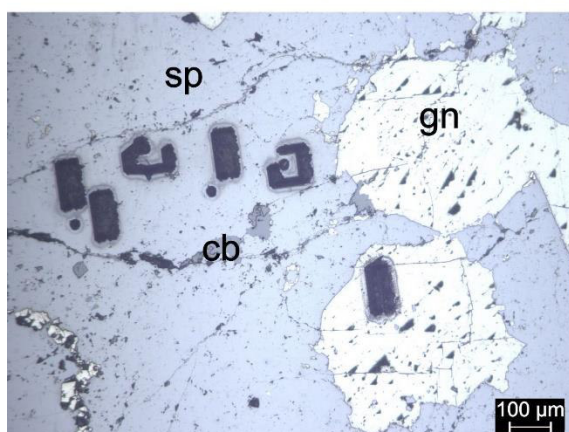
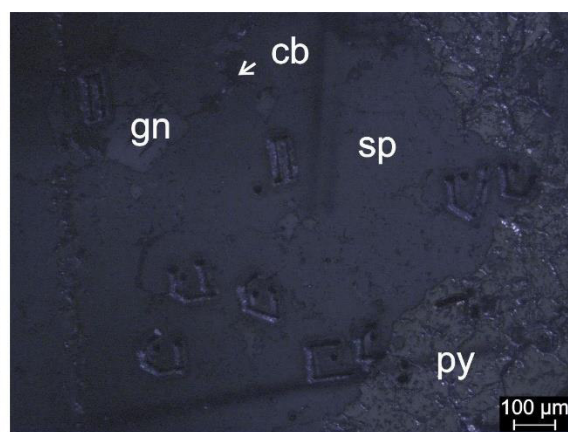
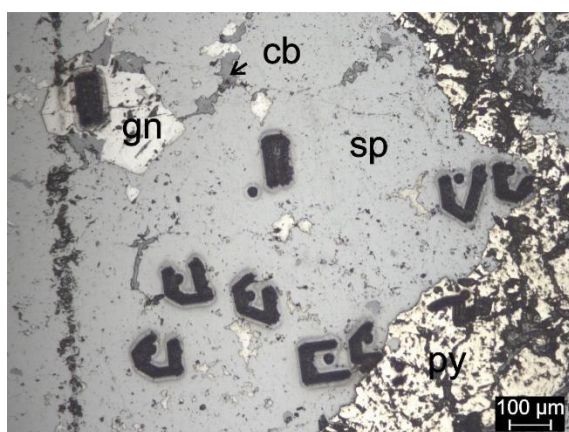


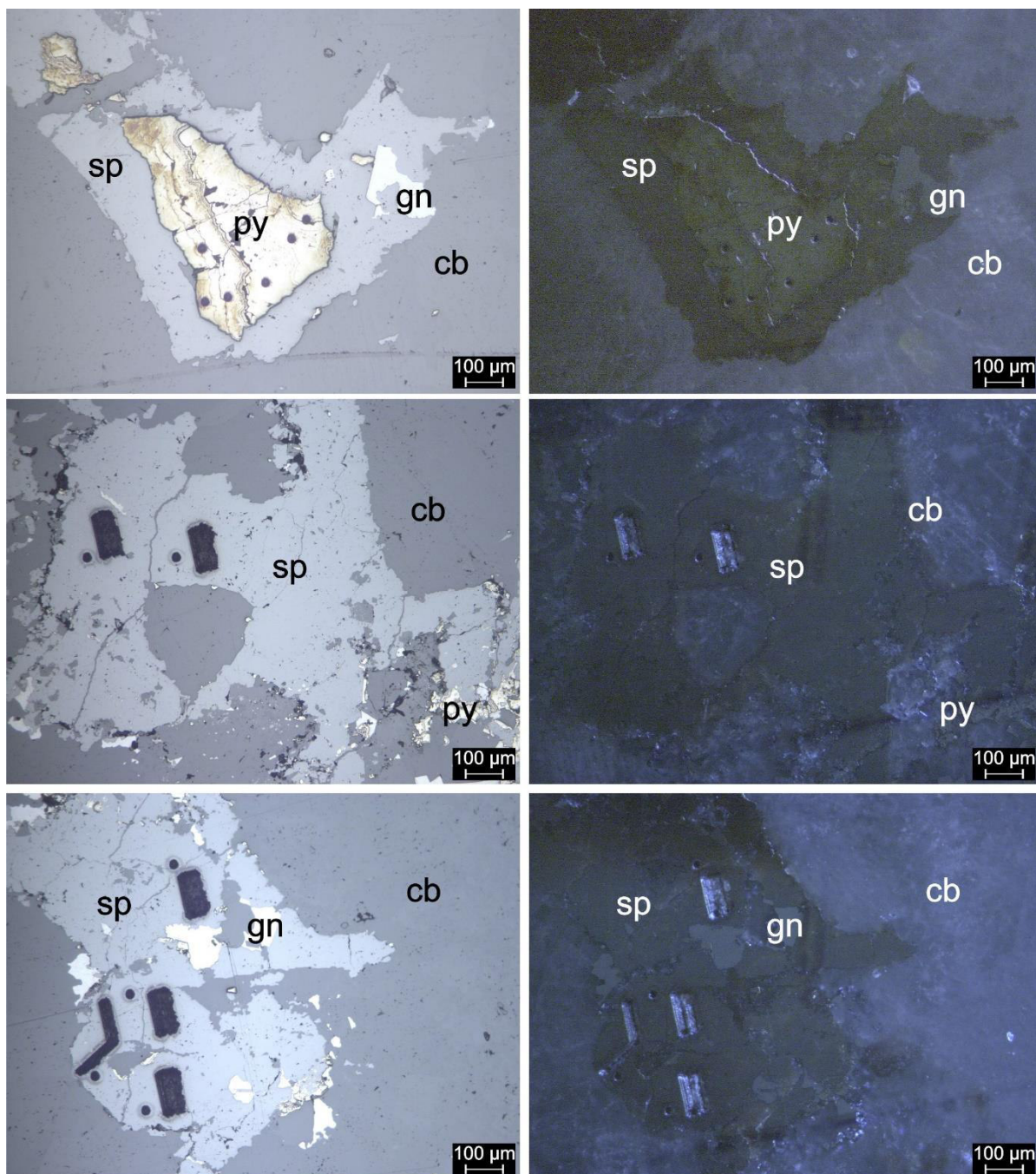












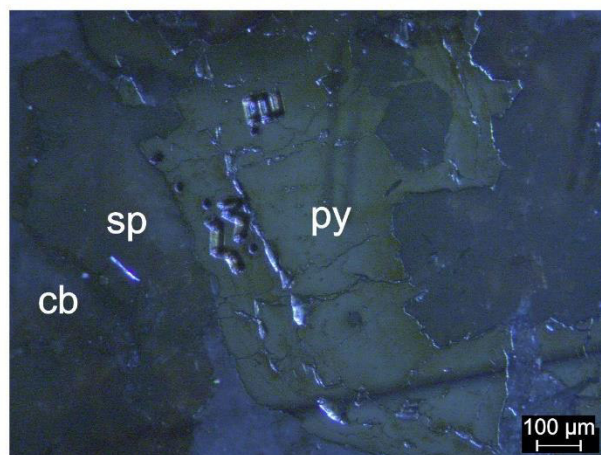
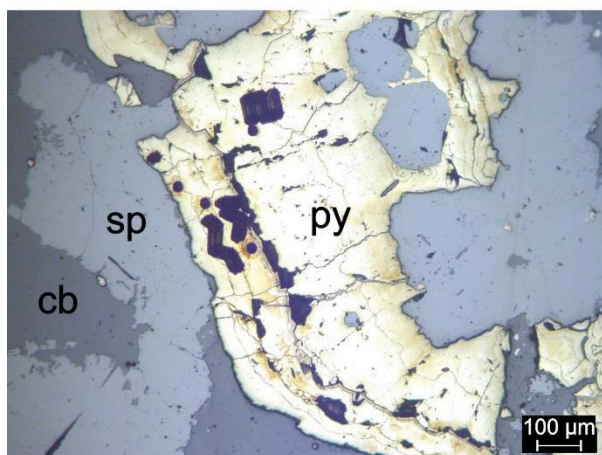
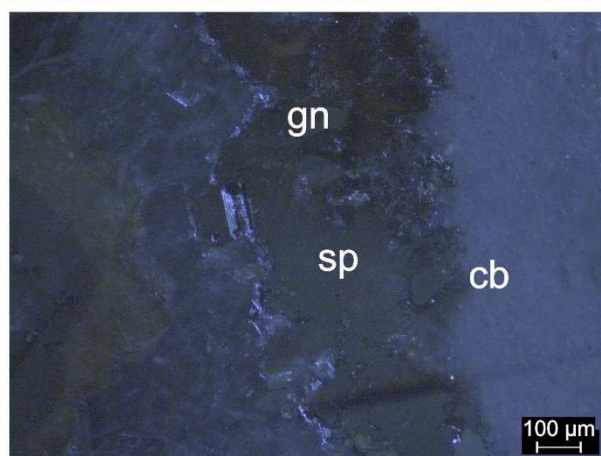
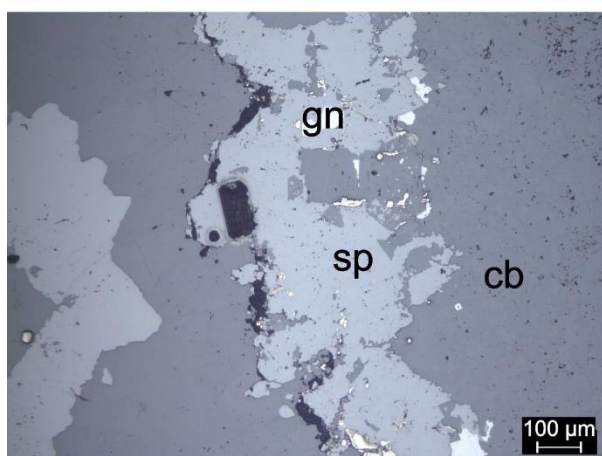
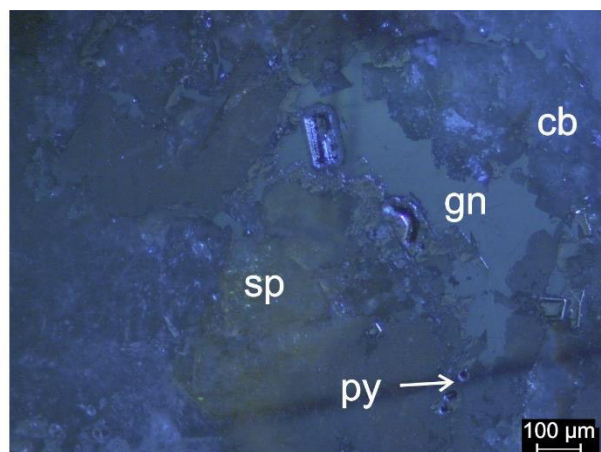
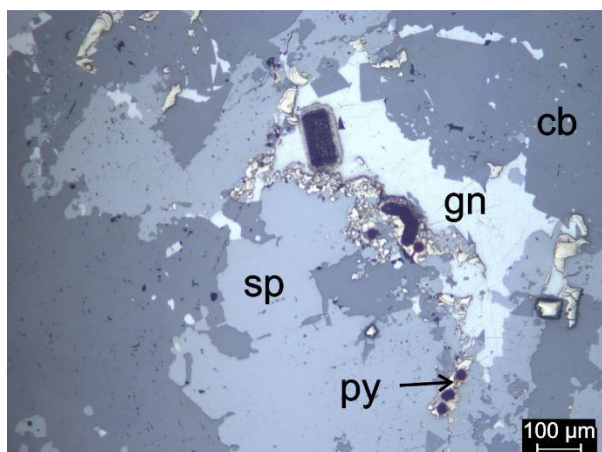


Image of drill core (enlarged)



Drill core picture of TC-1344-036, showing the section of Waulsortian Limestone between 224.3–227.0 m. The stromatolite filling, as well as colloform mineralisation, are visible. Mineralisation consists of brown sphalerite, golden pyrite and silvery galena. Sample BLK 07 was taken at 225.54 m. White boxes show sample location BLK 07, example for colloform mineralisation and stromatolite structure. Source photo: Teck, Ireland Ltd.

Raw data laser ablation ICP-MS of pyrite and sphalerite. - indicated values under limit of reporting.

Sample ID	Sample	Thin Section	V (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Mo (ppm)	Ag (ppm)
20150918-5_014.csv	Pyrite	BLK05	-	-	7	458,800	10	113	15	-	-	32	1	0
20150918-5_015.csv	Pyrite	BLK05	0	-	5	458,800	3	116	46	30	-	9	0	0
20150918-5_016.csv	Pyrite	BLK05	1	1	11	458,800	13	173	44	-	0	32	0	0
20150918-5_017.csv	Pyrite	BLK05	-	-	12	458,800	10	134	50	-	-	619	1	0
20150918-5_018.csv	Pyrite	BLK05	0	-	15	458,800	23	251	32	-	0	655	1	0
20150918-5_019.csv	Pyrite	BLK05	0	-	11	458,800	34	688	32	443	-	520	3	0
20150918-5_020.csv	Pyrite	BLK05	0	-	15	458,800	21	143	38	33	-	300	1	0
20150918-5_022.csv	Pyrite	BLK05	1	1	15	458,800	17	175	164	36	-	143	3	1
20150918-5_023.csv	Pyrite	BLK05	2	2	253	458,800	44	433	235	40	0	417	8	2
20150918-5_024.csv	Pyrite	BLK05	-	-	20	458,800	8	185	134	28	-	97	5	1
20150918-5_025.csv	Pyrite	BLK05	0	1	5	458,800	32	261	150	396	-	47	5	1
20150918-5_026.csv	Pyrite	BLK05	1	2	38	458,800	8	156	87	46	-	26	3	0
20150918-5_027.csv	Pyrite	BLK05	0	-	7	458,800	10	102	237	43	-	45	3	0
20150918-5_028.csv	Pyrite	BLK05	0	-	4	458,800	13	176	204	-	0	25	2	1
20150918-5_029.csv	Pyrite	BLK05	0	-	8	458,800	14	104	111	-	0	15	3	0
20150918-4_018.csv	Pyrite	BLK06	1	3	132	449,900	43	224	28	200,353	48	23,747	41	51
20150918-4_019.csv	Pyrite	BLK06	2	-	286	449,900	25	173	27	270,720	9	27,612	45	76
20150918-4_023.csv	Pyrite	BLK06	-	-	168	449,900	7	144	26	21,249	0	20,013	43	34
20150918-4_024.csv	Pyrite	BLK06	0	-	123	449,900	7	108	19	-	0	18,711	35	27
20150918-4_025.csv	Pyrite	BLK06	0	-	79	449,900	117	1197	47	22	0	19,490	57	84
20150918-4_027.csv	Pyrite	BLK06	1	-	66	449,900	66	228	16	-	6	8,253	19	35
20150918-4_028.csv	Pyrite	BLK06	1	-	110	449,900	23	203	12	67	1	21,766	42	17
20150918-4_029.csv	Pyrite	BLK06	-	-	92	449,900	17	189	24	30	0	25,118	49	29
20150918-4_014.csv	Sphalerite	BLK06	1	2	663	15,404	11	76	103	652,800	22	353	5	77
20150918-4_015.csv	Sphalerite	BLK06	0	-	37	17,685	4	16	87	652,800	15	715	2	66
20150918-4_016.csv	Sphalerite	BLK06	5	24	11,921	673,420	122	726	92	652,800	15	34,934	65	83
20150918-4_017.csv	Sphalerite	BLK06	1	-	54	63,020	5	24	66	652,800	14	2,033	2	56
20150918-4_020.csv	Sphalerite	BLK06	-	-	59	101,982	6	28	56	652,800	14	4,225	7	44
20150918-4_021.csv	Sphalerite	BLK06	0	0	61	25,625	5	27	51	652,800	16	1,255	3	37
20150918-4_026.csv	Sphalerite	BLK06	1	4	186	10,886	25	177	114	652,800	13	288	23	73
20150917-3_008.csv	Pyrite	BLK07	-	-	61	452,600	51	760	5	7,025	-	17,554	70	6
20150917-3_009.csv	Pyrite	BLK07	-	-	71	452,600	78	1182	12	43,809	1	18,379	81	9
20150917-3_016.csv	Pyrite	BLK07	0	-	101	452,600	160	1563	7	71	-	19,177	126	9
20150917-3_005.csv	Sphalerite	BLK07	2	2	56	15,449	60	192	54	657,600	31	328	61	29

LA ICP-MS raw data (continued)

Sample ID	Cd (ppm)	In (ppm)	Sn (ppm)	Sb (ppm)	Ba (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)
20150918-5_014.csv	-	-	1	1	9	1	0	14
20150918-5_015.csv	-	-	1	1	4	2	1	9
20150918-5_016.csv	-	-	1	2	31	1	1	19
20150918-5_017.csv	-	-	1	2	3	1	0	13
20150918-5_018.csv	-	-	1	1	7	1	0	14
20150918-5_019.csv	1	-	1	6	4	2	0	54
20150918-5_020.csv	-	-	1	4	3	1	0	28
20150918-5_022.csv	-	-	1	6	10	2	1	49
20150918-5_023.csv	-	-	1	10	27	3	2	106
20150918-5_024.csv	-	0	1	2	9	2	1	39
20150918-5_025.csv	2	-	1	3	6	1	1	42
20150918-5_026.csv	-	0	2	3	11	1	1	30
20150918-5_027.csv	-	0	1	2	8	2	0	21
20150918-5_028.csv	1	-	2	3	6	3	1	39
20150918-5_029.csv	-	-	2	1	15	1	1	32
20150918-4_018.csv	694	0	3	894	19,998	48	347	27,814
20150918-4_019.csv	903	-	5	869	371	59	435	18,499
20150918-4_023.csv	70	-	1	1,010	32	9	334	23,663
20150918-4_024.csv	-	-	1	818	10	4	303	13,090
20150918-4_025.csv	-	-	1	1,753	26	7	197	33,950
20150918-4_027.csv	-	-	2	643	3,706	12	150	42,774
20150918-4_028.csv	-	-	1	527	199	4	327	24,187
20150918-4_029.csv	1	0	1	671	29	4	386	37,617
20150918-4_014.csv	2,274	0	3	715	2,163	246	17	1,156
20150918-4_015.csv	2,216	0	2	614	295	217	20	1,292
20150918-4_016.csv	2,131	0	12	1,492	535	252	393	36,477
20150918-4_017.csv	2,245	-	3	479	-	229	10	3,754
20150918-4_020.csv	2,670	-	2	497	-	256	135	20,297
20150918-4_021.csv	2,294	0	3	373	84	242	38	11,485
20150918-4_026.csv	1,489	0	3	852	208	388	17	1,544
20150917-3_008.csv	30	-	1	142	-	2	683	3,930
20150917-3_009.csv	223	-	1	220	1	2	789	5,754
20150917-3_016.csv	-	-	1	281	6	3	1,045	7,354
20150917-3_005.csv	2,228	-	3	348	5,122	238	22	679

LA ICP-MS raw data (continued).

Sample ID	Sample	Thin Section	V (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Mo (ppm)	Ag (ppm)
20150917-3_006.csv	Sphalerite	BLK07	2	2	68	10,430	77	504	54	657,600	14	321	139	31
20150917-3_007.csv	Sphalerite	BLK07	2	2	81	5,753	42	88	47	657,600	12	219	39	26
20150917-3_010.csv	Sphalerite	BLK07	2	2	85	21,277	109	324	46	657,600	15	580	53	29
20150917-3_012.csv	Sphalerite	BLK07	1	3	77	6,101	47	107	61	657,600	14	274	31	29
20150917-3_013.csv	Sphalerite	BLK07	2	-	101	7,189	45	115	55	657,600	40	411	34	30
20150917-3_014.csv	Sphalerite	BLK07	1	2	105	7,860	45	191	67	657,600	152	375	12	43
20150917-3_015.csv	Sphalerite	BLK07	1	2	88	53,870	114	306	47	657,600	9	884	17	35
20150916-3_018.csv	Sphalerite	BLK08	-	-	-	12,734	20	101	648	666,600	8	379	0	63
20150916-3_019.csv	Sphalerite	BLK08	-	-	-	13,200	20	107	703	666,600	9	611	-	73
20150916-3_020.csv	Sphalerite	BLK08	-	-	-	9,584	9	67	291	666,600	6	131	-	27
20150916-3_021.csv	Sphalerite	BLK08	0	-	-	10,795	13	36	668	666,600	11	857	-	71
20150916-3_022.csv	Sphalerite	BLK08	-	-	-	10,125	12	96	729	666,600	9	1,695	-	76
20150916-3_023.csv	Sphalerite	BLK08	-	-	-	12,633	17	153	571	666,600	9	832	-	63
20150916-3_024.csv	Sphalerite	BLK08	-	-	-	6,706	55	485	434	666,600	10	705	-	52
20150916-3_025.csv	Sphalerite	BLK08	-	-	-	12,276	14	99	441	666,600	10	327	-	49
20150916-3_026.csv	Sphalerite	BLK08	-	-	-	10,694	18	296	574	666,600	9	876	-	54
20150916-3_027.csv	Sphalerite	BLK08	-	-	-	9,755	42	235	377	666,600	11	409	1	39
20150916-3_030.csv	Sphalerite	BLK08	-	-	-	12,927	14	89	489	666,600	7	324	0	49
20150916-3_031.csv	Sphalerite	BLK08	-	1	-	10,023	25	77	425	666,600	10	347	-	42
20150916-3_032.csv	Sphalerite	BLK08	0	-	-	8,154	9	62	232	666,600	5	121	6	19
20150916-3_033.csv	Sphalerite	BLK08	-	-	-	11,236	6	44	462	666,600	4	192	-	50
20150916-3_034.csv	Sphalerite	BLK08	-	-	-	9,927	10	68	401	666,600	7	181	-	42
20150916-3_035.csv	Sphalerite	BLK08	-	-	-	11,666	20	104	373	666,600	6	212	1	41
20150916-3_036.csv	Sphalerite	BLK08	0	-	-	9,643	16	129	579	666,600	7	428	-	57
20150916-3_037.csv	Sphalerite	BLK08	-	-	-	8,166	11	47	473	666,600	6	217	-	51
20150916-3_038.csv	Sphalerite	BLK08	-	-	-	8,959	7	36	423	666,600	6	141	0	48
20150916-3_039.csv	Sphalerite	BLK08	-	-	-	4,224	8	45	186	666,600	4	203	-	23
20150918-3_014.csv	Pyrite	BLK09	-	-	63	441,600	86	2365	5	26	-	10,658	11	4
20150918-3_015.csv	Pyrite	BLK09	1	-	2,830	441,600	2596	6331	-	9,787	6	18,197	222	4
20150918-3_016.csv	Pyrite	BLK09	-	-	111	441,600	8705	81367	-	-	-	18,377	157	11
20150918-3_017.csv	Pyrite	BLK09	0	-	194	441,600	68	602	6	2,837	-	13,898	220	1
20150918-3_020.csv	Pyrite	BLK09	0	-	88	441,600	749	5924	13	28,027	1	16,970	204	5
20150918-3_022.csv	Pyrite	BLK09	-	-	155	441,600	353	2289	17	33,904	0	18,244	432	6
20150918-3_024.csv	Pyrite	BLK09	-	-	139	441,600	568	6092	63	197,980	2	15,460	185	12

LA ICP-MS raw data (continued).

Sample ID	Cd (ppm)	In (ppm)	Sn (ppm)	Sb (ppm)	Ba (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)
20150917-3_006.csv	2,207	-	2	896	463	173	28	755
20150917-3_007.csv	2,186	-	2	398	319	140	26	612
20150917-3_010.csv	2,524	-	3	525	426	114	40	780
20150917-3_012.csv	2,192	-	3	420	319	142	29	742
20150917-3_013.csv	2,509	-	2	523	6,077	147	42	981
20150917-3_014.csv	2,027	-	2	527	28,928	124	31	1,017
20150917-3_015.csv	2,988	-	2	458	14	76	31	1,001
20150916-3_018.csv	1,756	-	4	3,116	17	124	104	4,073
20150916-3_019.csv	1,485	-	3	2,987	14	86	122	4,613
20150916-3_020.csv	746	-	2	1,680	-	83	55	2,234
20150916-3_021.csv	1,489	-	2	2,063	-	92	136	3,961
20150916-3_022.csv	1,754	-	2	2,473	-	100	154	5,675
20150916-3_023.csv	1,513	-	3	2,432	-	99	109	3,744
20150916-3_024.csv	1,653	-	3	1,637	-	104	147	3,467
20150916-3_025.csv	1,692	-	3	1,701	-	128	89	11,359
20150916-3_026.csv	1,934	-	3	1,683	-	130	137	6,895
20150916-3_027.csv	1,615	-	2	1,150	-	131	74	2,307
20150916-3_030.csv	1,308	-	3	2,416	-	113	87	3,772
20150916-3_031.csv	1,713	-	3	1,627	-	119	75	2,581
20150916-3_032.csv	800	-	2	1,528	14	72	47	2,329
20150916-3_033.csv	975	-	3	2,782	12	78	80	5,067
20150916-3_034.csv	1,443	-	3	2,286	-	96	67	5,948
20150916-3_035.csv	1,037	-	3	2,290	-	88	71	3,907
20150916-3_036.csv	2,005	-	2	2,614	10	115	109	4,176
20150916-3_037.csv	1,713	-	2	2,279	9	86	91	4,359
20150916-3_038.csv	1,390	-	2	2,211	9	81	76	3,471
20150916-3_039.csv	771	-	1	828	9	66	64	1,552
20150918-3_014.csv	1	-	1	580	5	2	199	3,875
20150918-3_015.csv	29	-	3	961	2,520	-	178	22,304
20150918-3_016.csv	3	-	2	1,032	101	-	203	235,551
20150918-3_017.csv	3	0	1	875	5	1	255	6,632
20150918-3_020.csv	36	-	1	851	4	4	142	8,646
20150918-3_022.csv	49	0	1	954	13	4	271	65,647
20150918-3_024.csv	240	-	2	884	15	13	171	7,527

LA ICP-MS raw data (continued).

Sample ID	Sample	Thin Section	V (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Mo (ppm)	Ag (ppm)
20150918-3_026.csv	Pyrite	BLK09	1	4	291	441,600	292	1198	162	404,900	6	11,952	1276	36
20150918-3_027.csv	Pyrite	BLK09	-	-	51	441,600	4	280	4	140	-	10,010	8	2
20150918-3_029.csv	Pyrite	BLK09	-	-	138	441,600	5639	41739	12	8,125	0	17,424	221	5
20150918-3_018.csv	Sphalerite	BLK09	0	1	196	4,683	18	281	207	654,500	7	373	155	41
20150918-3_019.csv	Sphalerite	BLK09	0	-	164	4,890	21	179	151	654,500	10	327	436	24
20150918-3_023.csv	Sphalerite	BLK09	0	1	200	42,002	65	373	216	654,500	8	1,621	696	46
20150918-3_025.csv	Sphalerite	BLK09	0	1	149	3,683	29	301	230	654,500	10	394	823	55
20150918-3_028.csv	Sphalerite	BLK09	-	-	172	2,253	23	97	204	654,500	9	228	470	46
20150918-1_015.csv	Pyrite	BLK10	5	5	2,563	440,900	109	640	-	275,293	9	519	28	2
20150918-1_018.csv	Pyrite	BLK10	0	-	133	440,900	6670	62193	32	46,078	1	41,198	754	3
20150918-1_020.csv	Pyrite	BLK10	-	2	263	440,900	10452	59606	18	29,589	3	44,925	741	2
20150918-1_026.csv	Pyrite	BLK10	-	-	88	440,900	53	430	-	20	-	11,482	228	0
20150918-1_040.csv	Pyrite	BLK10	1	1	82	440,900	220	1840	6	21,503	1	15,732	127	1
20150918-1_016.csv	Sphalerite	BLK10	-	-	516	15,923	44	433	155	664,800	10	1,288	6	12
20150918-1_017.csv	Sphalerite	BLK10	0	-	1,322	164,574	823	7064	161	664,800	8	10,073	153	13
20150918-1_019.csv	Sphalerite	BLK10	-	-	283	77,937	2450	18505	186	664,800	7	8,756	220	12
20150918-1_021.csv	Sphalerite	BLK10	-	1	149	28,509	40	572	117	664,800	7	2,682	22	13
20150918-1_022.csv	Sphalerite	BLK10	21	10	1,030	149,726	726	2334	161	664,800	22	4,665	210	8
20150918-1_025.csv	Sphalerite	BLK10	-	-	255	9,460	13	288	185	664,800	8	1,284	-	20
20150918-1_027.csv	Sphalerite	BLK10	-	-	158	5,464	33	94	98	664,800	13	267	-	21
20150918-1_028.csv	Sphalerite	BLK10	-	-	154	5,087	24	138	124	664,800	11	525	-	19
20150918-1_030.csv	Sphalerite	BLK10	101	46	9,077	21,923	107	184	94	664,800	59	557	101	7
20150918-1_031.csv	Sphalerite	BLK10	28	4	9,624	20,923	62	145	94	664,800	25	576	30	7
20150918-1_032.csv	Sphalerite	BLK10	5	-	1,130	8,563	41	47	36	664,800	13	126	5	2
20150918-1_033.csv	Sphalerite	BLK10	24	3	1,077	21,571	51	170	91	664,800	30	516	17	6
20150918-1_036.csv	Sphalerite	BLK10	103	158	16,700	92,631	242	1393	57	664,800	92	2,390	91	7
20150918-1_037.csv	Sphalerite	BLK10	13	5	406	19,114	59	220	62	664,800	14	831	23	7
20150918-1_038.csv	Sphalerite	BLK10	10	7	1,319	19,013	61	226	115	664,800	14	1,436	3	7
20150918-1_039.csv	Sphalerite	BLK10	10	3	712	16,620	70	205	79	664,800	15	566	40	6
20150918-1_041.csv	Sphalerite	BLK10	5	2	336	55,671	2888	10226	156	664,800	12	7,944	224	14
20150918-1_042.csv	Sphalerite	BLK10	9	5	351	21,810	113	423	109	664,800	22	1,152	25	9
20150918-1_043.csv	Sphalerite	BLK10	2	3	422	13,846	115	30	27	664,800	5	220	1	3
20150917-4_021.csv	Pyrite	BLK11	-	8	3,423	464,500	113	25	6,984	11,429,531	105	9,195	65	349
20150917-4_031.csv	Pyrite	BLK11	-	-	8	464,500	-	3	1	55	-	2,120	63	-

LA ICP-MS raw data (continued).

Sample ID	Cd (ppm)	In (ppm)	Sn (ppm)	Sb (ppm)	Ba (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)
20150918-3_026.csv	551	-	3	959	85	53	194	19,297
20150918-3_027.csv	-	-	1	489	-	1	104	1,950
20150918-3_029.csv	15	-	1	809	25	3	258	45,690
20150918-3_018.csv	671	-	2	418	51	125	42	8,632
20150918-3_019.csv	709	-	2	404	12	111	39	4,167
20150918-3_023.csv	836	-	3	628	78	61	60	24,507
20150918-3_025.csv	825	-	2	564	76	77	39	19,662
20150918-3_028.csv	703	-	2	491	57	82	34	16,318
20150918-1_015.csv	612	-	4	272	1,721	51	13	1,076
20150918-1_018.csv	52	0	2	536	10	11	926	14,492
20150918-1_020.csv	65	0	1	406	779	11	992	21,306
20150918-1_026.csv	-	0	1	36		1	897	4,463
20150918-1_040.csv	17	-	1	546	44	5	203	5,072
20150918-1_016.csv	498	-	3	1,842	79	189	134	4,581
20150918-1_017.csv	596	-	4	2,663	57	108	221	10,287
20150918-1_019.csv	406	-	3	974	13	123	292	8,069
20150918-1_021.csv	811	-	2	229	24	143	157	2,926
20150918-1_022.csv	1,981	-	5	712	3,520	140	50	2,807
20150918-1_025.csv	785	-	2	1,390	43	151	121	4,884
20150918-1_027.csv	1,441	0	2	459	16	170	32	1,207
20150918-1_028.csv	1,241	-	2	772	23	145	54	1,872
20150918-1_030.csv	992	-	8	528	14,843	321	50	1,495
20150918-1_031.csv	891	-	8	453	4,452	332	75	2,287
20150918-1_032.csv	760	-	7	60	1,609	205	14	679
20150918-1_033.csv	1,238	-	5	690	6,273	212	80	3,080
20150918-1_036.csv	678	-	21	696	26,369	414	178	6,963
20150918-1_037.csv	1,102	-	3	446	2,103	156	98	5,081
20150918-1_038.csv	658	-	4	335	1,861	154	157	4,365
20150918-1_039.csv	1,182	-	3	511	2,024	172	67	3,686
20150918-1_041.csv	860	-	3	1,183	1,174	114	192	20,501
20150918-1_042.csv	1,109	-	3	688	4,306	150	89	5,222
20150918-1_043.csv	807	-	5	77	642	165	29	1,019
20150917-4_021.csv	6,113	-	22	17,398	485	1,293	1,600	44,505
20150917-4_031.csv	-	-	0	7	9	2	369	83

LA ICP-MS raw data (continued).

Sample ID	Sample	Thin Section	V (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Mo (ppm)	Ag (ppm)
20150917-4_032.csv	Pyrite	BLK11	-	-	24	464,500	2	8	1	33	-	3,582	43	0
20150917-4_033.csv	Pyrite	BLK11	-	-	14	464,500	1	2	-	4	-	2,479	42	0
20150917-4_034.csv	Pyrite	BLK11	-	-	12	464,500	-	33	1	-	-	5,937	79	1
20150917-4_035.csv	Pyrite	BLK11	-	-	11	464,500	0	11	-	-	-	6,062	83	0
20150917-4_015.csv	Sphalerite	BLK11	-	-	225	17,360	12	3	491	665,500	12	371	6	26
20150917-4_016.csv	Sphalerite	BLK11	-	-	213	6,295	5	3	537	665,500	7	215	-	36
20150917-4_017.csv	Sphalerite	BLK11	-	-	67	4,023	4	-	31	665,500	12	-	-	2
20150917-4_018.csv	Sphalerite	BLK11	0	0	137	4,350	18	3	342	665,500	4	309	-	25
20150917-4_020.csv	Sphalerite	BLK11	-	-	221	15,989	5	11	398	665,500	7	723	2	24
20150917-4_022.csv	Sphalerite	BLK11	-	-	378	37,074	12	190	401	665,500	4	935	64	18
20150917-4_025.csv	Sphalerite	BLK11	-	-	228	22,458	12	6	486	665,500	11	377	23	22
20150917-4_026.csv	Sphalerite	BLK11	-	-	292	5,599	14	4	446	665,500	6	85	-	36
20150917-4_027.csv	Sphalerite	BLK11	0	-	152	4,922	20	5	266	665,500	4	78	-	21
20150917-4_028.csv	Sphalerite	BLK11	-	1	300	19,611	8	2	299	665,500	11	96	-	18
20150917-4_029.csv	Sphalerite	BLK11	-	-	159	17,214	5	3	374	665,500	9	117	-	24
20150917-4_030.csv	Sphalerite	BLK11	0	-	152	5,312	22	1	119	665,500	3	5	-	8
20150917-2_020.csv	Pyrite	BLK12	-	-	94	459,500	18	356	-	343	0	11,708	33	4
20150917-2_024.csv	Pyrite	BLK12	-	-	108	459,500	68	1107	3	6,693	-	14,670	33	6
20150917-2_033.csv	Pyrite	BLK12	-	1	106	459,500	52	686	-	34,328	0	16,764	36	11
20150917-2_036.csv	Pyrite	BLK12	-	-	85	459,500	15	284	4	161	0	15,625	42	8
20150917-2_039.csv	Pyrite	BLK12	-	-	84	459,500	21	461	5	25	-	12,750	38	8
20150917-2_040.csv	Pyrite	BLK12	-	-	92	459,500	23	428	3	163	-	13,592	35	4
20150917-2_041.csv	Pyrite	BLK12	-	-	106	459,500	8	193	5	-	-	12,759	35	5
20150917-2_014.csv	Sphalerite	BLK12	-	-	154	8,917	7	46	39	670,200	12	629	-	119
20150917-2_015.csv	Sphalerite	BLK12	0	1	186	11,694	7	40	49	670,200	12	328	-	133
20150917-2_016.csv	Sphalerite	BLK12	0	-	205	13,129	9	82	45	670,200	10	1,049	0	124
20150917-2_017.csv	Sphalerite	BLK12	-	-	143	16,620	6	52	49	670,200	10	737	-	115
20150917-2_018.csv	Sphalerite	BLK12	-	-	188	10,986	3	26	26	670,200	10	811	-	59
20150917-2_019.csv	Sphalerite	BLK12	-	1	182	8,724	6	100	38	670,200	11	767	-	107
20150917-2_021.csv	Sphalerite	BLK12	0	-	185	10,396	5	50	49	670,200	12	530	-	134
20150917-2_022.csv	Sphalerite	BLK12	-	-	152	8,473	9	33	46	670,200	13	326	-	140
20150917-2_023.csv	Sphalerite	BLK12	-	1	116	10,693	9	34	46	670,200	14	358	-	115
20150917-2_027.csv	Sphalerite	BLK12	0	1	144	22,505	21	69	38	670,200	14	526	1	112
20150917-2_028.csv	Sphalerite	BLK12	-	-	124	7,247	11	44	46	670,200	14	219	0	127

LA ICP-MS raw data (continued).

Sample ID	Cd (ppm)	In (ppm)	Sn (ppm)	Sb (ppm)	Ba (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)
20150917-4_032.csv	-	-	1	80	6	1	209	2,338
20150917-4_033.csv	-	-	-	91	-	-	281	2,310
20150917-4_034.csv	-	-	1	11	16	-	576	977
20150917-4_035.csv	-	-	2	20	-	-	623	1,303
20150917-4_015.csv	518	-	2	1,654	4	114	75	3,234
20150917-4_016.csv	1,449	-	2	3,610	10	94	75	4,235
20150917-4_017.csv	830	-	2	16	3	153	0	42
20150917-4_018.csv	559	-	2	184	9	114	25	922
20150917-4_020.csv	438	-	2	1,336	18	77	98	3,141
20150917-4_022.csv	210	-	1	301	39	183	95	2,996
20150917-4_025.csv	443	-	1	1,044	12	131	66	2,309
20150917-4_026.csv	1,012	-	1	2,175	20	135	43	3,049
20150917-4_027.csv	469	-	1	204	5	115	10	921
20150917-4_028.csv	405	-	1	1,211	8	120	44	2,491
20150917-4_029.csv	424	-	1	1,645	9	63	53	2,440
20150917-4_030.csv	722	-	1	66	4	103	2	2,332
20150917-2_020.csv	1	-	1	356	-	2	147	5,375
20150917-2_024.csv	19	0	1	621	6	5	185	6,775
20150917-2_033.csv	44	-	1	588	23	9	171	9,213
20150917-2_036.csv	-	0	-	351	42	3	220	8,152
20150917-2_039.csv	-	-	1	341	5	2	164	6,290
20150917-2_040.csv	-	-	1	493	-	1	161	5,561
20150917-2_041.csv	-	-	1	515	5	3	165	6,709
20150917-2_014.csv	850	-	3	970	20	212	46	3,208
20150917-2_015.csv	721	-	3	1,684	51	197	50	4,080
20150917-2_016.csv	927	0	3	729	34	212	58	4,105
20150917-2_017.csv	720	-	3	746	5	193	52	2,654
20150917-2_018.csv	323	-	3	1,520	4	132	72	3,380
20150917-2_019.csv	517	-	3	1,234	14	172	53	3,688
20150917-2_021.csv	674	-	3	2,039	121	146	66	3,105
20150917-2_022.csv	912	0	3	1,403	14	196	42	2,542
20150917-2_023.csv	1,385	-	2	822	15	239	36	2,035
20150917-2_027.csv	1,267	-	3	575	16	232	19	4,039
20150917-2_028.csv	1,171	-	3	1,268	19	242	35	3,544

LA ICP-MS raw data (continued).

Sample ID	Sample	Thin Section	V (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	As (ppm)	Mo (ppm)	Ag (ppm)
20150917-2_029.csv	Sphalerite	BLK12	-	-	130	12,504	7	55	51	670,200	10	841	-	130
20150917-2_030.csv	Sphalerite	BLK12	0	-	160	9,350	10	61	50	670,200	11	571	-	145
20150917-2_031.csv	Sphalerite	BLK12	0	1	141	9,199	12	19	44	670,200	13	251	-	114
20150917-2_032.csv	Sphalerite	BLK12	-	-	237	7,363	14	43	36	670,200	12	254	-	121
20150917-2_034.csv	Sphalerite	BLK12	-	-	85	6,722	17	5	27	670,200	14	65	-	95
20150917-2_035.csv	Sphalerite	BLK12	0	0	145	91,309	23	135	27	670,200	10	2,733	6	103
20150917-2_038.csv	Sphalerite	BLK12	0	-	150	9,455	6	57	52	670,200	11	758	-	109
20150917-2_042.csv	Sphalerite	BLK12	-	-	174	40,978	13	85	45	670,200	9	1,234	2	140
20150917-2_043.csv	Sphalerite	BLK12	-	1	155	54,990	32	299	40	670,200	10	1,606	4	104
20150917-2_044.csv	Sphalerite	BLK12	-	-	119	7,348	14	21	39	670,200	14	232	-	114
20150917-1_014.csv	Pyrite	BLK21	2	-	47	452,800	2029	37928	248	14,645	1	35,348	78	66
20150917-1_015.csv	Pyrite	BLK21	1	2	20	452,800	2951	48435	270	10,492	2	40,247	107	124
20150917-1_026.csv	Pyrite	BLK21	-	-	54	452,800	1322	20199	181	194	-	39,219	111	31
20150917-1_028.csv	Pyrite	BLK21	-	-	71	452,800	324	2305	54	40	-	27,265	38	6
20150917-1_029.csv	Pyrite	BLK21	-	-	44	452,800	178	2837	29	-	-	35,899	62	4
20150917-1_030.csv	Pyrite	BLK21	0	-	76	452,800	97	1027	23	-	-	26,984	53	3
20150917-1_031.csv	Pyrite	BLK21	-	-	65	452,800	55	1300	13	-	-	35,850	72	2
20150917-1_016.csv	Sphalerite	BLK21	-	-	57	4,089	3	14	303	681,200	31	16	-	34
20150917-1_017.csv	Sphalerite	BLK21	-	-	181	7,316	12	74	498	681,200	27	40	-	67
20150917-1_018.csv	Sphalerite	BLK21	0	-	202	6,315	5	14	739	681,200	21	43	-	92
20150917-1_019.csv	Sphalerite	BLK21	-	-	194	5,311	2	25	508	681,200	33	40	-	78
20150917-1_021.csv	Sphalerite	BLK21	-	-	112	4,909	2		491	681,200	34	28	-	56
20150917-1_024.csv	Sphalerite	BLK21	-	1	162	9,378	5	53	549	681,200	25	70	-	77
20150917-1_025.csv	Sphalerite	BLK21	-	-	117	10,691	37	171	330	681,200	17	112	0	36
20150917-1_027.csv	Sphalerite	BLK21	-	-	286	9,439	12	178	730	681,200	23	89	-	83
20150918-2_005.csv	Pyrite	BLK344	1	0	193	467,800	28	604	120	50	0	810	4	0
20150918-2_006.csv	Pyrite	BLK344	1	0	6	467,800	6	55	28	2	0	9,375	2	0
20150918-2_007.csv	Pyrite	BLK344	0	0	46	467,800	10	187	27	35	0	6,597	6	0
20150918-2_008.csv	Pyrite	BLK344	1	1	5	467,800	51	287	86	24	0	2,305	1	0
20150918-2_009.csv	Pyrite	BLK344	0	1	6	467,800	34	240	47	42	0	9,434	2	0
20150918-2_010.csv	Pyrite	BLK344	0	0	24	467,800	10	158	1,284	32	0	7,914	5	0

LA ICP-MS raw data (continued).

Sample ID	Cd (ppm)	In (ppm)	Sn (ppm)	Sb (ppm)	Ba (ppm)	Hg (ppm)	Tl (ppm)	Pb (ppm)
20150917-2_029.csv	1,093	-	3	758	18	229	60	2,375
20150917-2_030.csv	1,188	-	2	1,128	36	218	45	14,027
20150917-2_031.csv	1,090	-	2	915	152	229	35	6,294
20150917-2_032.csv	1,085	-	3	809	151	223	26	9,559
20150917-2_034.csv	1,365	-	3	403	17	220	10	10,150
20150917-2_035.csv	1,206	-	2	715	18	165	48	2,726
20150917-2_038.csv	771	-	2	1,037	19	225	52	2,755
20150917-2_042.csv	809	-	3	1,271	4	154	40	18,514
20150917-2_043.csv	1,267	-	3	870	9	191	35	7,439
20150917-2_044.csv	1,470	-	2	733	42	241	24	4,338
20150917-1_014.csv	50	1		1,776	163	16	648	143,785
20150917-1_015.csv	55	0	4	2,110	104	20	698	554,787
20150917-1_026.csv	5	-	1	1,322	16	15	886	41,895
20150917-1_028.csv	-	-	1	702	-	5	553	8,519
20150917-1_029.csv	-	-	2	481	-	3	732	6,330
20150917-1_030.csv	-	0	1	1,809	6	3	534	6,925
20150917-1_031.csv	-	-	2	1,041	22	2	619	10,752
20150917-1_016.csv	3,829	-	3	434	5	497	4	491
20150917-1_017.csv	2,207	-	3	967	126	424	12	2,099
20150917-1_018.csv	2,065	-	3	1,514	41	436	17	2,583
20150917-1_019.csv	2,507	-	3	1,167	1,518	477	15	5,596
20150917-1_021.csv	2,776	-	4	863	12	473	10	1,017
20150917-1_024.csv	1,828	-	3	1,189	71	529	20	1,616
20150917-1_025.csv	1,924	-	3	349	128	718	7	3,482
20150917-1_027.csv	1,875	-	3	1,400	26	571	22	2,118
20150918-2_005.csv	1	0	2	74	3	1	186	2,596
20150918-2_006.csv	0	0	2	76	6	1	8	206
20150918-2_007.csv	1	0	2	399	2	0	155	1,770
20150918-2_008.csv	1	0	2	28	7	1	8	149
20150918-2_009.csv	-	0	2	77	20	1	11	262
20150918-2_010.csv	0	0	2	299	2	1	83	1,352

Average concentrations of pyrite and sphalerite obtained using SEM-EDX

Sphalerite average concentrations in %, <LOR = under limit of reporting, note Pb was not analysed in all samples, due to its low concentrations under limit of reporting.

Sample	S	Fe	Co	Ni	Zn	As	Pb	Total
BLK 07								
BLK 07-1	32.98	1.29	0.03	0.05	64.93	1.80	<LOR	100.00
BLK 07-2	32.85	0.66	0.02	0.08	65.52	1.90	<LOR	100.00
BLK 07-3	32.59	0.11	0.02	0.02	66.55	1.85	<LOR	99.99
BLK 07-4	32.79	0.82	0.00	0.02	65.59	1.82	<LOR	100.00
BLK 07-5	32.94	1.68	0.03	0.00	64.57	1.74	<LOR	100.01
BLK 07-6	32.94	0.51	<LOR	0.02	66.14	1.75	<LOR	100.01
BLK 07-7	32.83	0.63	<LOR	0.06	65.83	1.70	<LOR	100.01
BLK 07-8	32.94	0.50	0.08	0.07	66.04	1.61	<LOR	100.01
BLK 07-9	32.70	0.17	0.06	0.05	66.62	1.61	<LOR	99.99
BLK 08								
BLK08-1	33.36	1.14	<LOR	<LOR	66.51	0.23	<LOR	100.00
BLK 08-2	32.93	0.54	0.05	<LOR	66.93	0.23	<LOR	100.00
BLK 08-3	32.83	0.48	0.02	<LOR	66.98	0.26	<LOR	100.00
BLK 08-4	33.07	0.17	0.05	<LOR	67.27	0.29	<LOR	100.01
BLK 08-5	32.81	0.28	0.01	0.00	67.11	0.31	<LOR	100.00
BLK 08-6	33.03	0.63	0.02	<LOR	66.56	0.48	<LOR	100.00
BLK 08-7	33.08	0.65	0.01	0.05	66.81	0.33	<LOR	100.00
BLK 08-8	33.24	0.65	0.00	<LOR	66.90	0.26	<LOR	100.00
BLK 08-9	33.21	1.27	0.01	0.05	65.73	0.26	<LOR	100.00
BLK 08-10	33.34	1.37	0.05	0.02	65.76	0.24	<LOR	99.99
BLK 06								
BLK 06-4	32.36	0.86	0.00	0.05	64.19	0.27	<LOR	96.68
BLK 06-5	32.94	0.31	<LOR	<LOR	66.46	0.20	<LOR	98.72
BLK 6-6	32.29	0.61	<LOR	<LOR	65.13	0.35	<LOR	97.51
BLK 06-8	32.91	0.87	0.06	0.02	65.35	0.17	<LOR	98.10
BLK 09								
BLK 09-5	32.47	0.85	0.00	0.04	65.61	0.37	<LOR	98.01
BLK 09-06	32.28	0.71	0.02	0.01	65.07	0.56	<LOR	98.09
BLK 09-10	32.61	0.48	0.00	0.03	65.66	0.28	<LOR	98.25
BLK 10								
BLK 10-1	32.96	0.74	0.01	<LOR	66.08	0.24	<LOR	98.89
BLK 10-2	32.74	0.85	<LOR	0.02	65.27	0.28	<LOR	98.18
BLK 10-1	33.69	2.51	0.03	0.29	65.87	0.27		102.66
BLK 10-4	33.05	0.69	<LOR	0.03	68.31	0.14		102.21
BLK 10-5	33.34	0.57	<LOR	0.00	68.19	0.23		102.31
BLK 10-6	33.22	0.78	0.02	<LOR	68.40	0.22		102.63
BLK 10-7	33.20	1.54	0.00	<LOR	67.15	0.18		102.04
BLK 10-8	33.20	1.84	0.07	<LOR	67.33	0.18		102.61
BLK 10-9	32.84	1.78	0.09	0.19	65.40	0.77		101.06
BLK 10-10	33.00	0.77	<LOR	<LOR	67.65	0.23		101.60

Sphalerite average concentrations (continued).

Sample	S	Fe	Co	Ni	Zn	As	Pb	Total
BLK 11								
BLK 11-1	33.17	0.88	0.04	0.03	67.95	0.32		102.39
BLK 11-2	33.32	3.74	0.06	0.05	64.50	0.50		102.17
BLK 11-3	32.98	3.86	0.02	<LOR	64.87	0.46		102.17
BLK 11-4	33.04	0.86	<LOR	<LOR	67.75	0.28		101.88
BLK 11-5	32.84	0.73	0.06	0.06	66.40	0.34		100.43
BLK 11-6	33.09	0.77	0.07	<LOR	66.80	0.31		101.04
BLK 11-7	33.11	0.62	<LOR	<LOR	68.58	0.38		102.65
BLK 11-9	33.14	0.43	0.00	<LOR	67.96	0.18		101.70
BLK 11-10	32.90	0.70	0.02	0.02	67.39	0.30		101.33
BLK 11-11	32.84	0.31	0.01	<LOR	68.37	0.39		101.88
BLK 11-12	32.64	2.63	0.02	0.04	64.79	0.30		100.43
BLK 11-13	33.01	2.72	0.05	0.03	65.03	0.31		101.15
BLK 11-14	33.15	3.42	0.01	0.03	64.91	0.31		101.83
BLK 11-15	33.41	0.97	0.04	0.05	67.93	0.27		102.66
BLK 11-16	32.87	1.00	0.01	<LOR	66.37	0.57		100.79
BLK 11-17	33.08	0.63	<LOR	0.01	68.18	0.18		102.08
BLK 11-18	33.40	0.54	<LOR	<LOR	68.67	0.30		102.87
BLK 11-19	33.07	0.59	0.03	<LOR	67.17	0.26		101.09
BLK 11-21	33.89	7.68	0.04	0.07	60.87	0.32		102.85
BLK 21								
BLK 21-1	33.11	0.62	<LOR	0.02	67.74	0.24		101.72
BLK 21-4	33.28	1.05	0.01	<LOR	67.69	0.28		102.27
BLK 21-6	33.61	0.19	0.06	<LOR	69.49	0.3		103.63
BLK 21-7	33.03	0.75	0.06	<LOR	67.56	0.33		101.69
BLK 12								
BLK 12-1	32.52	1.55	0.06	0.05	65.91	0.60		100.69
BLK 12-3	32.53	1.47	0.01	0.04	66.48	0.49		101.02
BLK 12-4	32.44	1.51	0.03	0.01	66.07	0.39		100.46
BLK 12-5	32.88	2.36	0.04	0.01	66.32	0.39		101.99
BLK 12-6	32.49	1.09	0.03	0.01	66.70	0.47		100.79
BLK 12-7	32.74	1.05	<LOR	<LOR	67.24	0.40		101.39
BLK 12-8	33.30	0.93	0.07	0.01	68.64	0.40		103.35
BLK 12-9	33.29	0.96	0.06	0.02	67.93	0.34		102.61
BLK 12-10	33.04	0.98	0.05	<LOR	67.68	0.48		102.21
BLK 12-11	33.07	1.11	<LOR	0.03	67.24	0.34		101.74

Pyrite average concentrations concentrations in %, <LOR = under limit of reporting, note Pb was not analysed in all samples, due to its low concentrations under limit of reporting.

Sample	S	Fe	Co	Ni	Zn	As	Pb	Total
BLK 05								
BLK 05-07	53.94	46.21	0.17	0.04	0.02	<LOR	<LOR	98.61
BLK 05-08	53.93	46.47	0.11	0.02	<LOR	0.07	<LOR	98.29
BLK 05-09	53.80	46.14	0.18	0.03	0.09	0.06	<LOR	98.08
BLK 05-2	52.40	45.27	0.18	0.19	0.00	0.25	<LOR	96.60
BLK 05-4	52.73	45.57	0.21	0.05	0.05	0.05	<LOR	96.91
BLK 05-6	52.63	45.54	0.09	<LOR	<LOR	0.15	<LOR	95.93
BLK 05-7	52.83	45.69	0.22	0.01	<LOR	0.12	<LOR	96.82
BLK 05-8	52.67	45.40	0.15	0.05	<LOR	0.13	<LOR	96.28
BLK 06								
BLK 06-02	52.50	45.54	0.15	0.02	0.05	0.34	<LOR	97.14
BLK 06-03	52.19	45.31	0.18	0.04	0.07	0.40	<LOR	96.53
BLK 06-07	50.76	43.77	0.25	0.03	0.06	2.58	<LOR	96.76
BLK 06-09	52.60	45.34	0.13	0.05	0.27	0.29	<LOR	96.69
BLK 07								
BLK07-10	53.07	45.75	0.29	0.01	<LOR	2.98	<LOR	100.00
BLK07-11	52.93	44.76	0.14	0.42	0.00	3.28	<LOR	100.02
BLK 07-12	53.22	45.30	0.11	0.19	0.05	2.72	<LOR	100.00
BLK 07-13	52.81	44.97	0.26	0.10	0.22	3.34	<LOR	100.00
BLK 07-14	52.87	45.50	0.21	0.07	0.58	1.88	<LOR	100.01
BLK 09								
BLK 09-01	51.40	44.36	0.17	0.08	0.18	1.44	<LOR	96.37
BLK 09-04	51.92	43.14	0.14	1.20	0.20	1.28	<LOR	96.25
BLK 09-07	52.33	45.03	0.13	<LOR	0.15	1.02	<LOR	96.73
BLK 09-09	51.33	44.10	0.23	0.02	0.42	1.99	<LOR	96.96
BLK 10								
BLK 10-03	51.05	43.23	0.17	0.16	0.10	4.16	<LOR	97.65
BLK 10-04	50.09	41.74	0.28	1.19	0.35	4.86	<LOR	97.61
BLK 10-3	52.63	45.51	0.17	0.10	1.28	1.22		100.91
BLK 10-2	53.02	45.83	0.20	0.17	1.27	0.90		101.39
BLK 10-11	51.48	45.68	0.13	0.09	0.26	1.02		98.66
BLK 10-12	51.44	45.63	0.17	0.14	0.28	1.04		98.69
BLK 10-13	52.42	45.85	0.19	0.10	0.51	0.80		99.88
BLK 11								
BLK 11-22	53.91	46.37	0.17	0.02	<LOR	0.35		100.72
BLK 11-23	53.67	46.60	0.18	0.07	<LOR	0.36		100.85
BLK 11-24	52.69	46.37	0.24	0.04	0.07	0.82		100.22
BLK 12								
BLK 12-2	52.76	45.70	0.15	0.03	0.31	1.77		100.74
BLK 12-12	52.98	46.17	0.21	0.09	0.36	1.31		101.13
BLK 12-13	52.98	46.12	0.16	0.04	0.41	1.99		101.70
BLK 12-14	52.54	46.05	0.21	0.02	0.30	1.44		100.56
BLK 12-15	52.35	45.69	0.16	0.12	<LOR	1.55		99.86
BLK 21								
BLK 21-8	51.03	44.32	0.15	0.28	0.47	4.05		100.29
BLK 21-9	51.47	44.64	0.19	0.12	0.36	3.89		100.66
BLK 21-10	51.76	45.51	0.23	0.1	0.06	2.46		100.12
BLK 21-11	51.86	45.32	0.18	0.16	<LOR	3.55		101.02
BLK 21-12	52.98	46.24	0.16	0.12	0.17	2.96		102.63
BLK 21-13	51.8	45.64	0.06	0.04	0.54	3.71		101.79

Appendix C

Map of sample location.

Soil profile representative for Ballinalack.

Raw data of trace elements from soil BC horizon and top of the till from Ballinalack (this study).

Raw data - Drill core raw data based on aqua regia digestion.

Principal component analysis scores.

Sample locations for soil BC and top of the till samples at Ballinalack. Coordinate system Irish Grid TM65.



Soil profile representative for Ballinalack



Pictures of soil and till collected with a Dutch Auger at Ballinalack. Typical soil and till samples at Ballinalack. A) Sample TCS 20028 representing the top of BC horizon; typically brown with 1 cm black gravels. B) Sample TCS 20684; typical till with mottled areas in greyish and black, indicating hydromorphic processes.

Raw data of trace elements from soil BC horizon and top of the till from Ballinalack (this study). x = no duplicate exists, comp = composition.

Sample name	Project	Soil_Horizon	ING_TM65_X	UTM 29 E	ING_TM65_Y	UTM 29 N	Location	Duplicate	Clasts
TCS 20022	IsoNose	BC	235220	601253	266575	5945444	Outside	x	mm gravels
TCS 20023	IsoNose	Top of till	235218	601251	266576	5945445	Outside	x	1 cm gravels
TCS 20024	IsoNose	BC	235215	601249	266553	5945422	Outside	x	mm gravels
TCS 20025	IsoNose	Top of till	235212	601246	266551	5945420	Outside	x	no gravels
TCS 20026	IsoNose	BC	235211	601245	266529	5945398	Outside	x	barely gravels
TCS 20027	IsoNose	Top of till	235210	601244	266531	5945400	Outside	x	crumbly 1-2 cm gravels
TCS 20028	IsoNose	BC	235205	601239	266505	5945373	Outside	x	no roots, mm gravels
TCS 20029	IsoNose	top of till	235204	601238	266506	5945374	Outside	x	2-3 cm gravels
TCS 20031	IsoNose	BC	235198	601233	266481	5945349	Outside	x	mm gravels
TCS 20032	IsoNose	Top of till	235196	601231	266481	5945349	Outside	x	2-3 cm gravels
TCS 20033	IsoNose	BC	235193	601228	266456	5945324	Outside	x	mm gravels
TCS 20034	IsoNose	top of till	235193	601228	266456	5945324	Outside	x	2-3 cm gravels
TCS 20035	IsoNose	BC	235188	601223	266432	5945300	Outside	x	1 cm gravels
TCS 20036	IsoNose	Top of till	235188	601223	266431	5945299	Outside	x	2-3 cm gravels
TCS 20037	IsoNose	BC	235194	601230	266409	5945277	Outside	x	mm gravels
TCS 20038	IsoNose	Top of till	235192	601228	266404	5945272	Outside	x	2-3 cm gravels
TCS 20039	IsoNose	BC	235166	601202	266373	5945241	Outside	x	1 cm gravels
TCS 20041	IsoNose	BC	235168	601205	266357	5945225	Flank	x	1 cm gravels
TCS 20042	IsoNose	Top of till	235168	601205	266363	5945231	Flank	x	2-3 cm gravels
TCS 20043	IsoNose	BC	235164	601201	266333	5945201	Flank	x	mm gravels
TCS 20044	IsoNose	Top of till	235166	601203	266337	5945205	Flank	x	chips - black and grey weathered
TCS 20045	IsoNose	BC	235164	601201	266336	5945204	Flank	Dup of 20043	mm gravels
TCS 20046	IsoNose	top of till	235163	601200	266334	5945202	Flank	Dup of 20044	chips - black and grey weathered
TCS 20047	IsoNose	BC	235159	601196	266310	5945178	Outside	x	mm gravels
TCS 20048	IsoNose	Top of till	235161	601198	266307	5945175	Outside	x	2-3 cm gravels
TCS 20049	IsoNose	BC	235154	601192	266285	5945153	Flank	x	mm gravels
TCS 20601	IsoNose	Top of till	235153	601191	266277	5945145	Flank	x	2-3 cm gravels
TCS 20602	IsoNose	BC	235149	601187	266268	5945136	Flank	x	1 cm gravels
TCS 20603	IsoNose	Top of till	235152	601190	266271	5945139	Flank	x	2-3 cm gravels
TCS 20604	IsoNose	BC	235141	601179	266231	5945099	Mineralisation	x	mm gravels
TCS 20605	IsoNose	Top of till	235143	601181	266232	5945100	Mineralisation	x	1-2 cm gravels
TCS 20606	IsoNose	BC	235144	601183	266210	5945078	Mineralisation	x	mm gravels
TCS 20607	IsoNose	Top of till	235143	601182	266209	5945077	Mineralisation	x	2 cm gravels
TCS 20608	IsoNose	BC	235136	601175	266203	5945071	Mineralisation	x	mm gravels
TCS 20609	IsoNose	Top of till	235133	601172	266203	5945071	Mineralisation	x	1 cm gravels
TCS 20611	IsoNose	BC	235130	601169	266188	5945055	Mineralisation	x	mm gravels

Soil and till samples results (aqua regia digestion, continued).

Sample name	Characteristics	Moisture	Parent_Material	Line	Physiography	Contamination	Comp_Silt
TCS 20022	-	wet	CALP	Line 2	Pastureland	Possible	X
TCS 20023	brownish layers	wet	CALP	Line 2	Pastureland	Possible	X
TCS 20024	-	moist	CALP	Line 2	Pastureland	Possible	-
TCS 20025	interlayers brownish	wet	CALP	Line 2	Pastureland	Possible	X
TCS 20026	-	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20027	loose	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20028	-	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20029	-	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20031	-	moist	CALP	Line 2	Pastureland	Possible	-
TCS 20032	-	saturated	CALP	Line 2	Pastureland	Possible	XX
TCS 20033	gravels black and flat = chips	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20034	Fe+Mn weathering (black and grey)	saturated	CALP	Line 2	Pastureland	Possible	X
TCS 20035	black (weathered, low level)	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20036	10 % of till gravels, all barely weathered	wet	CALP	Line 2	Pastureland	Possible	-
TCS 20037	-	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20038	gravels all weathered (black)	wet	CALP	Line 2	Pastureland	Possible	X
TCS 20039	low oxidation, cannot go deeper	dry	CALP	Line 2	Pastureland	Possible	X
TCS 20041	black weathered chips	moist	SWA	Line 2	Pastureland	Possible	-
TCS 20042	cannot go deeper	wet	SWA	Line 2	Pastureland	Possible	-
TCS 20043	black unweathered chips	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20044	-	moist	SWA	Line 2	Pastureland	Possible	-
TCS 20045	black unweathered chips	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20046	-	moist	SWA	Line 2	Pastureland	Possible	-
TCS 20047	black chips	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20048	weathering in black, grey, lt brown	moist	SWA	Line 2	Pastureland	Possible	-
TCS 20049	black chips	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20601	weathering, lt brown, grey, orange; green and red clasts	moist	SWA	Line 2	Pastureland	Possible	-

Soil and till samples results (aqua regia digestion, continued).

Sample name	Comp_Sand	Comp_Organic	Comp_Clay	Sampling_Method	Slope	Year_Collected	Soil_Colour	Soil_From (m)	Soil_To (m)	Au (ppm)
TCS 20022	-	-	X	Auger	flat 0-5 ⁰	2015	dark brown	0.3	0.6	0.0036
TCS 20023	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	1.05	1.3	0.0032
TCS 20024	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.25	0.6	0.0021
TCS 20025	-	-	X	Auger	flat 0-5 ⁰	2015	blackish	0.65	0.94	0.0018
TCS 20026	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.15	0.38	0.0018
TCS 20027	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.38	0.45	0.002
TCS 20028	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.07	0.4	0.0015
TCS 20029	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.98	1.2	0.0017
TCS 20031	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.2	0.5	0.0015
TCS 20032	-	-	X	Auger	flat 0-5 ⁰	2015	lt. Brown	0.75	1	0.0019
TCS 20033	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.45	0.0023
TCS 20034	-	-	XX	Auger	flat 0-5 ⁰	2015	lt. Brown	0.63	0.9	0.0014
TCS 20035	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.23	0.6	0.0019
TCS 20036	-	-	XX	Auger	flat 0-5 ⁰	2015	lt. Brown	0.9	1.15	0.0016
TCS 20037	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.1	0.3	0.0014
TCS 20038	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.45	0.65	0.0025
TCS 20039	X	roots	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0018
TCS 20041	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.2	0.4	0.0022
TCS 20042	-	-	XX	Auger	flat 0-5 ⁰	2015	brown/grey	0.6	0.7	0.0015
TCS 20043	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.25	0.5	0.0018
TCS 20044	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.5	0.7	0.0018
TCS 20045	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.25	0.5	0.002
TCS 20046	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.5	0.7	0.0019
TCS 20047	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.1	0.3	0.0013
TCS 20048	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.3	0.6	0.0012
TCS 20049	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.15	0.3	0.0014
TCS 20601	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.45	0.65	0.0022

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)
TCS 20022	0.049	0.12	1.43	10	23.6	0.12	0.011	5.07	1.71	3.0	1.9	3.9	0.059	21.9	0.74	0.32
TCS 20023	0.092	0.37	3.99	10	22	0.47	0.04	3.49	2.11	16.6	3.1	11.2	0.193	27	0.63	1.05
TCS 20024	0.104	1	6.27	5	41	0.54	0.091	0.22	1.05	28.3	7.1	22.1	0.689	14.6	1.51	2.77
TCS 20025	0.138	0.79	6.06	5	42	0.49	0.069	1.07	2.86	21.2	3.4	16.7	0.409	18.75	0.93	2.28
TCS 20026	0.132	0.93	7.25	5	41.1	0.82	0.108	0.47	1.96	31.6	7.5	21.4	0.449	17.1	1.74	2.64
TCS 20027	0.139	0.86	8.23	10	36.3	0.88	0.109	2.57	2.65	32.1	7.8	22.7	0.398	18.7	2.14	2.63
TCS 20028	0.095	0.91	6.03	5	39	0.58	0.101	0.26	1.01	27.0	6.7	20.0	0.55	13.75	1.55	2.70
TCS 20029	0.129	0.78	8.4	5	31.3	1.01	0.102	0.5	3.74	36.4	8.7	20.4	0.356	25.1	2.06	2.42
TCS 20031	0.084	0.91	6.17	5	33.8	0.7	0.098	0.17	1.04	35.9	7.1	21.9	0.468	19.85	1.63	2.51
TCS 20032	0.077	1.02	7.97	5	33.4	1	0.102	0.8	2.55	39.8	11.5	25.2	0.515	26.8	2.21	3.33
TCS 20033	0.111	0.89	7.97	5	33.8	1.11	0.101	0.22	1.78	37.4	7.6	21.4	0.399	24.2	1.96	2.56
TCS 20034	0.089	0.76	7.71	5	24.2	0.78	0.097	6.44	2.46	30.6	10.5	20.3	0.477	24.1	1.91	2.13
TCS 20035	0.124	0.84	6.42	5	39.5	0.78	0.096	0.19	1.91	33.4	6.3	20.2	0.43	18.45	1.67	2.25
TCS 20036	0.094	0.54	5.98	5	17.6	0.5	0.071	9.61	1.92	24.1	7.3	14.9	0.377	20.2	1.53	1.54
TCS 20037	0.08	0.86	5.22	5	35.2	0.53	0.09	0.2	0.95	25.7	7.4	19.4	0.503	14.7	1.48	2.33
TCS 20038	0.109	0.86	9.94	5	34.6	1.23	0.117	0.25	3.03	50.8	8.6	25.5	0.311	33.2	2.26	2.30
TCS 20039	0.12	0.83	7.06	5	38.9	0.86	0.107	0.19	1.76	34.4	6.8	22.0	0.318	31	1.67	2.35
TCS 20041	0.145	0.75	8.22	5	31.4	1.05	0.099	1.04	3.10	36.3	8.5	19.5	0.287	27.1	1.96	2.19
TCS 20042	0.109	0.66	8	10	23.2	0.74	0.093	6.39	3.05	29.4	8.9	17.4	0.356	24.2	1.90	1.76
TCS 20043	0.109	0.87	7.23	5	37.4	0.87	0.104	0.21	1.75	38.0	7.5	21.8	0.344	23.6	1.80	2.32
TCS 20044	0.125	0.71	7.85	5	26.6	0.87	0.102	3.14	2.72	33.8	8.8	18.2	0.321	25.8	1.97	1.90
TCS 20045	0.114	0.87	7.58	5	37.7	0.86	0.113	0.23	1.78	38.0	7.4	21.6	0.365	23.9	1.84	2.31
TCS 20046	0.132	0.75	8.21	10	27.4	0.84	0.104	4.09	2.98	34.5	9.0	19.6	0.389	26.7	1.95	2.05
TCS 20047	0.097	0.89	6.67	5	37.9	0.67	0.111	0.18	1.26	34.5	6.9	22.1	0.481	22.8	1.67	2.26
TCS 20048	0.093	1.03	8.68	5	38	0.89	0.112	0.19	1.69	52.9	8.8	26.6	0.402	24.6	2.16	2.14
TCS 20049	0.087	0.88	6.3	5	38.3	0.71	0.098	0.16	1.26	32.3	7.0	20.5	0.461	20.1	1.69	2.48
TCS 20601	0.149	0.92	8.67	5	39.7	1.27	0.113	0.22	2.01	42.5	8.6	25.1	0.395	24	2.21	2.44

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Pd (ppm)
TCS 20022	0.101	0.032	0.044	0.0025	0.01	1.785	0.3	0.04	61.7	3.81	0.009	0.067	20.4	0.032	1.92	0.004
TCS 20023	0.077	0.086	0.076	0.01	0.02	10.9	3.1	0.09	46.1	7.31	0.006	0.144	26.8	0.042	6.19	0.001
TCS 20024	0.045	0.076	0.041	0.021	0.04	13.7	7.5	0.12	525	2.92	0.006	0.195	23.5	0.054	16.1	0.0005
TCS 20025	0.04	0.104	0.051	0.014	0.03	10.55	4.5	0.08	197	2.01	0.006	0.218	24.1	0.055	11.35	0.002
TCS 20026	0.064	0.096	0.048	0.018	0.05	17.45	7.1	0.13	657	2.88	0.007	0.196	35	0.066	16.9	0.001
TCS 20027	0.066	0.1	0.062	0.02	0.05	18.35	7.3	0.15	576	3.85	0.008	0.179	40.6	0.066	15.6	0.002
TCS 20028	0.041	0.081	0.039	0.02	0.04	11.6	7.5	0.12	615	2.5	0.004	0.19	24.8	0.055	14.15	0.002
TCS 20029	0.087	0.06	0.064	0.023	0.06	21.9	7.1	0.15	618	4.3	0.005	0.139	59.5	0.063	12.85	0.002
TCS 20031	0.044	0.063	0.056	0.017	0.05	15	7.6	0.14	421	2.89	0.002	0.203	38.1	0.038	12.5	0.0005
TCS 20032	0.083	0.055	0.039	0.023	0.08	21.4	10.4	0.26	588	2.72	0.004	0.227	72.2	0.049	14.7	0.001
TCS 20033	0.087	0.061	0.067	0.024	0.06	25.3	7.2	0.13	573	3.88	0.004	0.163	49.1	0.037	12.95	0.001
TCS 20034	0.054	0.04	0.044	0.019	0.08	16	6.5	0.22	447	3.5	0.008	0.176	68.5	0.055	12.2	0.006
TCS 20035	0.058	0.07	0.035	0.018	0.05	19.8	5.8	0.11	629	2.91	0.006	0.131	38.6	0.052	11.8	0.001
TCS 20036	0.045	0.03	0.034	0.011	0.06	12.2	4.6	0.21	332	2.7	0.01	0.147	47.6	0.052	9.29	0.007
TCS 20037	0.04	0.069	0.055	0.017	0.04	11.55	6.3	0.11	798	2.39	0.004	0.16	25.9	0.055	12.25	0.0005
TCS 20038	0.11	0.055	0.088	0.024	0.06	37.6	5.9	0.12	534	4.5	0.005	0.131	67.7	0.073	12.1	0.001
TCS 20039	0.064	0.093	0.091	0.022	0.07	21.5	6.3	0.11	614	3.83	0.006	0.192	36.1	0.068	17.2	0.0005
TCS 20041	0.081	0.063	0.054	0.022	0.07	25.1	5.9	0.13	634	4.36	0.005	0.133	61.2	0.055	13.85	0.001
TCS 20042	0.056	0.037	0.049	0.02	0.07	16.15	4.9	0.18	461	3.92	0.011	0.147	68.9	0.06	11.6	0.005
TCS 20043	0.063	0.073	0.08	0.016	0.06	21.7	6.3	0.11	625	3.68	0.006	0.154	41.5	0.049	14.75	0.0005
TCS 20044	0.062	0.04	0.068	0.022	0.07	20.1	5.4	0.15	488	4.18	0.008	0.126	62.6	0.054	12.8	0.001
TCS 20045	0.065	0.077	0.057	0.023	0.06	21.7	6.2	0.12	606	3.84	0.008	0.149	43.6	0.05	14.65	0.001
TCS 20046	0.06	0.041	0.063	0.02	0.07	19.95	5.8	0.16	485	4.21	0.009	0.139	64.6	0.059	12.75	0.002
TCS 20047	0.048	0.082	0.073	0.021	0.06	16.85	6.3	0.12	528	3.5	0.005	0.199	33.2	0.066	14.95	0.0005
TCS 20048	0.068	0.067	0.081	0.027	0.06	25.6	6.5	0.14	478	4.74	0.005	0.201	54.1	0.04	14.25	0.002
TCS 20049	0.051	0.076	0.062	0.017	0.05	16.3	6.9	0.11	638	3.3	0.005	0.187	30.2	0.056	14.9	0.0005
TCS 20601	0.094	0.068	0.092	0.027	0.06	36.1	6.6	0.12	645	5.82	0.007	0.158	50.1	0.046	13.7	0.003

Soil and till samples results (aqua regia digestion, continued).

Sample name	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)	V (ppm)
TCS 20022	0.008	0.384	0.022	0.96	1.99	0.478	11.9	0.03	191	0.0025	0.01	0.191	0.001	0.024	19.3	15.8
TCS 20023	0.005	2.86	0.046	0.83	1.495	2.12	16.6	0.13	118.5	0.0025	0.01	1.04	0.003	0.108	13.65	27
TCS 20024	0.002	10.95	0.001	0.03	0.734	2.79	1.4	0.6	11.2	0.0025	0.02	1.26	0.003	0.309	1.28	43.5
TCS 20025	0.001	4.66	0.004	0.11	0.727	2.15	2.5	0.55	53.1	0.0025	0.01	1.14	0.004	0.144	7.01	39.8
TCS 20026	0.001	9.1	0.001	0.05	1.015	3.4	1.5	0.54	23.6	0.0025	0.02	1.26	0.003	0.274	0.909	44.5
TCS 20027	0.001	8.51	0.0005	0.04	1.25	4.04	1.6	0.47	106	0.0025	0.02	1.415	0.003	0.308	0.997	48.1
TCS 20028	0.001	10.5	0.001	0.04	0.699	2.24	1.2	0.47	12.45	0.0025	0.03	1.235	0.003	0.229	0.968	38.1
TCS 20029	0.001	6.72	0.001	0.02	1.43	5.22	1.6	0.3	27.9	0.0025	0.03	1.585	0.004	0.37	0.882	46
TCS 20031	0.001	9.74	0.0005	0.02	0.942	3.37	1.3	0.42	13.05	0.0025	0.04	1.4	0.004	0.258	0.926	38.5
TCS 20032	0.002	6.57	0.0005	0.01	1.27	5.38	1.3	0.32	39.7	0.0025	0.03	3.2	0.01	0.344	0.796	38.1
TCS 20033	0.001	8.01	0.001	0.02	1.39	4.53	1.9	0.33	14.3	0.0025	0.04	1.34	0.003	0.32	1.08	43.2
TCS 20034	0.001	6.07	0.001	0.02	1.565	4.61	1.4	0.25	270	0.0025	0.02	2.46	0.006	0.369	1.065	34.6
TCS 20035	0.001	10.4	0.001	0.03	0.89	3.55	1.2	0.42	12	0.0025	0.02	1.23	0.003	0.259	1.095	43.5
TCS 20036	0.001	4.49	0.001	0.02	1.365	3.39	1	0.2	376	0.0025	0.03	2.03	0.006	0.225	1.075	26
TCS 20037	0.001	9.58	0.0005	0.03	0.683	2.53	0.9	0.47	8.94	0.0025	0.02	1.425	0.003	0.258	0.841	37.8
TCS 20038	0.001	8.39	0.0005	0.02	1.65	6.35	1.6	0.37	17.05	0.0025	0.04	1.71	0.003	0.352	1.33	54.9
TCS 20039	0.001	9.15	0.0005	0.04	1.055	3.68	1.4	0.61	11.35	0.0025	0.02	1.305	0.003	0.262	1.3	45.5
TCS 20041	0.001	6.69	0.001	0.02	1.51	4.58	1.9	0.4	43.2	0.0025	0.04	1.46	0.003	0.323	1.17	44.1
TCS 20042	0.001	5.52	0.001	0.03	1.65	4.31	1	0.22	255	0.0025	0.05	1.955	0.004	0.368	1.105	35.1
TCS 20043	0.001	9.13	0.0005	0.03	1.165	3.93	1.4	0.4	11.75	0.0025	0.02	1.365	0.003	0.282	1.105	43.1
TCS 20044	0.001	6.14	0.0005	0.02	1.595	4.48	1.4	0.32	126	0.0025	0.03	1.76	0.003	0.346	0.919	39.4
TCS 20045	0.001	9.19	0.0005	0.03	1.18	4.13	1.3	0.41	12.5	0.0025	0.05	1.495	0.003	0.285	1.125	43.3
TCS 20046	0.001	6.66	0.001	0.02	1.56	4.79	1.4	0.31	167	0.0025	0.04	1.81	0.003	0.358	1.025	39
TCS 20047	0.001	11.05	0.001	0.04	0.936	3.07	1.3	0.52	10.5	0.0025	0.02	1.375	0.003	0.27	1.21	42.5
TCS 20048	0.001	8.84	0.0005	0.02	1.43	4.55	1.4	0.34	11.75	0.0025	0.04	1.74	0.003	0.322	1.215	51.3
TCS 20049	0.001	11.05	0.001	0.03	0.823	3.09	1.2	0.54	9.3	0.0025	0.03	1.28	0.003	0.253	0.974	40.1
TCS 20601	0.001	9.14	0.0005	0.03	1.62	5.4	2	0.4	12.2	0.0025	0.05	1.45	0.003	0.393	1.2	57.8

Soil and till samples results (aqua regia digestion, continued).

Sample name	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH (lab)	LOI (%)
TCS 20022	0.019	2.52	28	1.27	-	80.6
TCS 20023	0.033	13.9	31.7	3.66	7	39.3
TCS 20024	0.042	14.2	88.6	2.11	5.47	6.58
TCS 20025	0.042	10.7	40.7	3.48	5.35	19.55
TCS 20026	0.046	22.6	98.7	3.07	6.18	9.33
TCS 20027	0.054	25.7	103.5	3.09	7.41	7.03
TCS 20028	0.04	11.55	90.3	2.5	5.72	7.09
TCS 20029	0.066	31.5	110.5	1.91	6.93	4.02
TCS 20031	0.043	15.45	99.5	1.97	5.33	4.82
TCS 20032	0.05	25.1	87.5	2.8	7.48	3.76
TCS 20033	0.041	33.5	107	1.8	6.03	5.2
TCS 20034	0.046	22	88.9	2.21	7.45	3.45
TCS 20035	0.042	25.5	110.5	2.31	5.65	4.79
TCS 20036	0.039	15.25	75.4	1.98	7.47	2.52
TCS 20037	0.039	12.2	97.9	2.17	5.58	6.28
TCS 20038	0.067	54.5	141.5	1.98	6.32	4.3
TCS 20039	0.081	28.2	116	3.16	5.24	7.11
TCS 20041	0.053	35.3	112	2.05	7.19	4.59
TCS 20042	0.048	21.8	96.7	1.38	7.38	3.25
TCS 20043	0.047	28	110	2.28	5.98	5.14
TCS 20044	0.049	27	95	1.5	7.19	3.95
TCS 20045	0.04	28.3	111	2.43	6.01	5.12
TCS 20046	0.048	27.1	98	1.47	7.37	4.01
TCS 20047	0.055	19.7	116	2.68	5.27	6.86
TCS 20048	0.049	32.3	133.5	2.2	5.52	5.06
TCS 20049	0.056	19.35	98.7	2.45	5.14	6.25
TCS 20601	0.067	51.4	123	2.37		5.02

Soil and till samples results (aqua regia digestion, continued).

Sample name	Project	Soil_Horizon	UTM 29		UTM 29		Location	Duplicate	Clasts
			ING_TM65_X	E	ING_TM65_Y	N			
TCS 20602	IsoNose	BC	235149	601187	266268	5945136	Flank	x	1 cm gravels
TCS 20603	IsoNose	Top of till	235152	601190	266271	5945139	Flank	x	2-3 cm gravels
TCS 20604	IsoNose	BC	235141	601179	266231	5945099	Mineralisation	x	mm gravels
TCS 20605	IsoNose	Top of till	235143	601181	266232	5945100	Mineralisation	x	1-2 cm gravels
TCS 20606	IsoNose	BC	235144	601183	266210	5945078	Mineralisation	x	mm gravels
TCS 20607	IsoNose	Top of till	235143	601182	266209	5945077	Mineralisation	x	2 cm gravels
TCS 20608	IsoNose	BC	235136	601175	266203	5945071	Mineralisation	x	mm gravels
TCS 20609	IsoNose	Top of till	235133	601172	266203	5945071	Mineralisation	x	1 cm gravels
TCS 20611	IsoNose	BC	235130	601169	266188	5945055	Mineralisation	x	mm gravels
TCS 20612	IsoNose	BC	235130	601169	266188	5945056	Mineralisation	x	no gravels
TCS 20613	IsoNose	C?	235124	601163	266163	5945030	Mineralisation	x	mm gravels
TCS 20614	IsoNose	Top of till	235125	601164	266163	5945030	Mineralisation	x	2 cm gravels
TCS 20615	IsoNose	BC	235114	601154	266125	5944992	Mineralisation	x	mm gravels
TCS 20616	IsoNose	Top of till	235112	601152	266124	5944991	Mineralisation	x	mm gravels
TCS 20617	IsoNose	BC	235114	601154	266125	5944992	Mineralisation	x	mm gravels
TCS 20618	IsoNose	Top of till	235112	601152	266124	5944991	Mineralisation	x	mm gravels
TCS 20619	IsoNose	BC	235114	601154	266115	5944982	Mineralisation	x	mm gravels
TCS 20621	IsoNose	Top of till	235111	601153	266116	5944841	Mineralisation	x	2-3 cm gravels
TCS 20622	IsoNose	BC	235102	601142	266098	5944965	Mineralisation	x	mm gravels
TCS 20623	IsoNose	Top of till	235100	601140	266100	5944967	Mineralisation	x	2-3 cm gravels
TCS 20624	IsoNose	BC	235101	601142	266066	5944933	Mineralisation	x	2 cm gravels
TCS 20625	IsoNose	Top of till	235104	601145	266064	5944931	Mineralisation	x	larger gravels up to 5 cm
TCS 20626	IsoNose	BC	235097	601138	266044	5944911	Mineralisation	x	mm gravels
TCS 20627	IsoNose	Top of till	235097	601138	266042	5944909	Mineralisation	x	-
TCS 20628	IsoNose	Top of till	235090	601131	266018	5944885	Mineralisation	x	3cm gravels
TCS 20629	IsoNose	Top of till	235085	601127	265994	5944861	Mineralisation	x	3cm gravels

Soil and till samples results (aqua regia digestion, continued).

Sample name	Characteristics	Moisture	Parent_Material	Line	Physiography	Contamination	Comp_Silt
TCS 20602	rarely orange weathered gravels	moist	SWA	Line 2	Pastureland	Possible	-
TCS 20603	weathering ochre and black	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20604	no weathering	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20605	weathering black, orange, grey	moist	SWA	Line 2	Pastureland	Possible	-
TCS 20606	-	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20607	weathering ochre, black; parts sandy; overlain by brown weathered soil (2 cm)	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20608	unweathered, dense	moist	CALP	Line 2	Pastureland	Possible	-
TCS 20609	very dense	moist	CALP	Line 2	Pastureland	Possible	-
TCS 20611	barely weatered	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20612	dense	moist	CALP	Line 2	Pastureland	Possible	-
TCS 20613	dense	moist	CALP	Line 2	Pastureland	Possible	-
TCS 20614	gravels in red, green; hit water table	wet	CALP	Line 2	Pastureland	Possible	-
TCS 20615	-	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20616	black stripes (weathering)	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20617	-	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20618	black stripes (weathering)	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20619	-	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20621	high concentration of gravels	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20622	no weathering	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20623	black weathering lines	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20624	high concentration of gravels	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20625	weathering black, ochre, orange, one red chip	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20626	gravels distributed (a few), no weathering	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20627	weathering grey, black, orange	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20628	weathering black, grey, orange	moist	CALP	Line 2	Pastureland	Possible	X
TCS 20629	weathering black, grey, orange	moist	CALP	Line 2	Pastureland	Possible	XX

Soil and till samples results (aqua regia digestion, continued).

Sample name	Comp_Sand	Comp_Organic	Comp_Clay	Sampling_Method	Slope	Year_Collected	Soil_Colour	Soil_From (m)	Soil_To (m)	Au (ppm)
TCS 20602	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.1	0.3	0.0012
TCS 20603	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.55	0.7	0.0014
TCS 20604	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.2	0.5	0.0014
TCS 20605	-	-	XX	Auger	flat 0-5 ⁰	2015	brown/black	0.65	0.75	0.0017
TCS 20606	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.15	0.35	0.0013
TCS 20607	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.6	0.7	0.0018
TCS 20608	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.2	0.4	0.001
TCS 20609	-	-	XX	Auger	flat 0-5 ⁰	2015	lt. brown	0.55	0.75	0.0024
TCS 20611	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.4	0.0017
TCS 20612	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0012
TCS 20613	-	-	XX	Auger	flat 0-5 ⁰	2015	brown/grey	0.4	0.6	0.0022
TCS 20614	-	-	XX	Auger	flat 0-5 ⁰	2015	grey	0.8	0.9	0.0014
TCS 20615	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0014
TCS 20616	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.45	0.7	0.0026
TCS 20617	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.35	0.0011
TCS 20618	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.45	0.7	0.0019
TCS 20619	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.4	0.001
TCS 20621	-	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.45	0.65	0.0017
TCS 20622	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.3	0.0009
TCS 20623	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.4	0.55	0.0014
TCS 20624	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.45	0.0013
TCS 20625	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.5	0.75	0.0013
TCS 20626	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.3	0.0015
TCS 20627	-	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.45	0.6	0.0022
TCS 20628	X	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.2	0.45	0.0015
TCS 20629	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.45	0.0012

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)
TCS 20602	0.121	0.89	6.18	5	40.4	0.59	0.097	0.16	1.22	29.5	6.7	20.3	0.5	22.9	1.55	2.35
TCS 20603	0.146	0.55	6.58	5	26.3	0.76	0.081	0.51	2.61	32.1	7.2	16.2	0.258	18.9	1.74	1.56
TCS 20604	0.108	0.88	5.7	5	40.9	0.63	0.093	0.25	1.65	31.1	6.3	20.2	0.38	19.8	1.45	2.66
TCS 20605	0.214	0.8	5.59	5	28.6	0.73	0.094	0.37	1.36	34.7	4.9	22.5	0.26	12.95	1.56	2.24
TCS 20606	0.111	0.99	4.54	5	42.6	0.5	0.091	0.18	1.06	28.0	4.4	19.9	0.633	12.6	1.23	2.66
TCS 20607	0.121	0.61	5.72	5	20	0.78	0.089	3.38	1.14	28.6	4.8	19.4	0.279	15.6	1.60	1.82
TCS 20608	0.097	0.98	3.95	5	41.5	0.57	0.082	0.24	0.83	26.1	4.3	18.8	0.694	10.7	1.22	3.20
TCS 20609	0.135	1.69	8.96	5	60.7	1.06	0.134	0.37	1.14	43.1	11.0	42.4	0.766	21.9	2.80	4.40
TCS 20611	0.128	0.89	6.28	5	40.9	0.75	0.1	2.16	1.79	31.6	6.5	20.5	0.323	15.3	1.59	2.49
TCS 20612	0.139	1.38	5.76	5	66.5	0.85	0.095	0.58	2.23	33.6	6.7	27.2	0.725	13.25	2.22	4.13
TCS 20613	0.107	2.63	15.95	5	123	1.57	0.157	0.85	1.18	56.6	22.0	62.5	0.974	40.9	5.23	7.60
TCS 20614	0.081	1.04	2.02	5	42.4	0.56	0.078	6.2	0.53	35.9	8.2	24.1	0.628	17.9	1.35	3.13
TCS 20615	0.072	1.22	6.56	5	22.4	0.51	0.111	0.12	0.47	23.2	6.6	25.6	0.558	9.88	2.06	2.73
TCS 20616	0.197	0.74	6.71	5	33.4	1.42	0.087	0.84	3.27	55.0	6.1	21.3	0.254	18	1.66	1.98
TCS 20617	0.07	1.28	7.41	5	22.7	0.63	0.114	0.12	0.59	29.3	10.6	29.0	0.496	11.5	2.27	2.56
TCS 20618	0.124	0.65	5.58	5	20.8	0.95	0.087	4.87	2.04	49.5	6.2	17.7	0.373	17.95	1.40	1.63
TCS 20619	0.09	1.19	5.22	5	36.9	0.41	0.089	0.19	0.51	20.3	4.6	23.0	0.75	6.99	1.53	3.01
TCS 20621	0.17	1.09	6.04	5	38.9	0.99	0.086	0.16	1.15	45.9	6.7	26.6	0.439	11.25	1.83	2.36
TCS 20622	0.105	1.09	4.74	5	45.2	0.5	0.079	0.22	0.55	26.3	2.6	20.4	0.835	7.16	1.36	3.03
TCS 20623	0.147	0.73	7.72	5	53.7	0.74	0.097	2.89	2.86	32.2	9.4	20.6	0.34	22.7	2.11	1.74
TCS 20624	0.105	0.71	5.43	5	28.6	0.41	0.073	5.57	1.28	22.0	4.8	17.1	0.368	12.3	1.36	2.03
TCS 20625	0.106	0.98	4.88	5	37	0.58	0.085	1.05	0.89	30.2	5.7	20.3	0.481	9.62	1.40	2.67
TCS 20626	0.076	0.85	2.32	5	26.6	0.24	0.061	0.2	0.51	15.1	1.7	13.9	0.719	3.69	0.62	2.52
TCS 20627	0.151	1.01	8.5	5	36.9	1.48	0.12	0.25	1.90	57.7	8.4	27.9	0.45	22.4	2.28	2.53
TCS 20628	0.131	1.02	6.44	5	49.7	0.87	0.097	0.19	1.69	37.8	7.6	23.7	0.447	7.84	2.11	2.64
TCS 20629	0.125	1.02	4.36	5	50.4	0.62	0.084	0.28	1.24	28.9	5.2	19.8	0.649	7.12	1.37	2.85

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Pd (ppm)
TCS 20602	0.047	0.087	0.058	0.019	0.05	15.75	6.4	0.11	652	2.99	0.005	0.184	26.7	0.061	15	0.001
TCS 20603	0.069	0.063	0.054	0.019	0.04	21.5	4	0.08	770	3.68	0.004	0.1	45.1	0.066	12.75	0.003
TCS 20604	0.051	0.097	0.042	0.017	0.05	16.25	7.3	0.11	605	2.09	0.004	0.175	28.1	0.058	15.7	0.0005
TCS 20605	0.066	0.09	0.11	0.022	0.05	19.65	6.6	0.12	245	1.92	0.005	0.129	34.7	0.064	11.1	0.001
TCS 20606	0.040	0.083	0.064	0.016	0.04	14	6.5	0.1	278	1.16	0.006	0.172	19.3	0.049	16.1	0.0005
TCS 20607	0.060	0.047	0.063	0.021	0.04	18.25	4.9	0.13	193	2.23	0.006	0.097	34.6	0.078	9.04	0.0005
TCS 20608	0.039	0.083	0.045	0.015	0.04	13.25	7.2	0.09	239	0.88	0.005	0.132	16.5	0.034	14.8	0.0005
TCS 20609	0.065	0.102	0.073	0.031	0.09	28	12.9	0.37	364	1.85	0.007	0.275	64.2	0.029	16.1	0.001
TCS 20611	0.049	0.103	0.06	0.026	0.05	18.2	6.6	0.13	351	1.52	0.008	0.131	33.5	0.061	15.95	0.002
TCS 20612	0.060	0.146	0.104	0.021	0.04	18.5	8.5	0.14	456	0.63	0.006	0.194	24.3	0.058	21.9	0.002
TCS 20613	0.092	0.167	0.08	0.036	0.1	31.8	22.2	0.64	884	2.41	0.01	0.351	97.1	0.045	25.5	0.0005
TCS 20614	0.059	0.117	0.029	0.019	0.07	18.9	13.2	0.48	174.5	0.47	0.008	0.082	44.5	0.042	11.55	0.003
TCS 20615	0.036	0.068	0.081	0.029	0.04	11.95	8.1	0.12	208	2.65	0.004	0.169	26	0.03	16.2	0.001
TCS 20616	0.119	0.034	0.095	0.024	0.04	58.8	4.6	0.12	347	2.14	0.004	0.102	49.6	0.041	10.1	0.002
TCS 20617	0.044	0.071	0.093	0.03	0.04	14.4	8.4	0.14	317	2.83	0.004	0.179	35	0.027	16.2	0.0005
TCS 20618	0.086	0.024	0.067	0.017	0.05	37.7	4.6	0.2	276	2.61	0.007	0.103	44.5	0.043	9.49	0.002
TCS 20619	0.033	0.07	0.065	0.02	0.03	10.35	8.8	0.14	220	1.54	0.005	0.162	21	0.036	13.85	0.0005
TCS 20621	0.073	0.057	0.106	0.033	0.04	31.5	6.5	0.15	331	1.86	0.007	0.138	40.2	0.024	9.64	0.001
TCS 20622	0.034	0.073	0.056	0.016	0.03	14.9	6.4	0.08	73.1	0.64	0.005	0.129	10.75	0.048	23.4	0.0005
TCS 20623	0.053	0.049	0.06	0.022	0.05	20.8	4.3	0.14	1150	3.25	0.008	0.104	62.4	0.07	10.95	0.003
TCS 20624	0.039	0.066	0.057	0.019	0.05	12.85	5.4	0.2	201	2	0.008	0.145	24.9	0.081	14.3	0.002
TCS 20625	0.046	0.07	0.062	0.02	0.06	17.9	6.6	0.12	230	1.42	0.006	0.116	25.9	0.043	14.35	0.0005
TCS 20626	0.025	0.038	0.044	0.011	0.03	7.9	5.7	0.07	38.3	0.45	0.003	0.074	7.83	0.035	13.85	0.0005
TCS 20627	0.091	0.04	0.118	0.03	0.05	45.5	5.9	0.13	170	3.33	0.005	0.124	37.3	0.038	14.4	0.0005
TCS 20628	0.050	0.048	0.091	0.022	0.05	21.3	5.6	0.11	306	2.15	0.005	0.134	31.2	0.017	14.55	0.001
TCS 20629	0.041	0.069	0.068	0.015	0.03	16.85	6.3	0.1	395	1.09	0.006	0.114	21.6	0.027	18.55	0.0005

Soil and till samples results (aqua regia digestion, continued).

Sample name	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)	V (ppm)
TCS 20602	0.001	11	0.001	0.03	0.729	2.82	1	0.57	9.71	0.0025	0.01	1.285	0.002	0.266	0.972	40.7
TCS 20603	0.001	6.74	0.001	0.03	1.13	3.97	1.4	0.28	29.2	0.0025	0.03	1.18	0.002	0.274	0.888	42.4
TCS 20604	0.001	8.62	0.001	0.03	0.618	3.24	1.3	0.47	14.75	0.0025	0.02	1.48	0.002	0.213	0.804	39.1
TCS 20605	0.001	6.05	0.001	0.02	0.692	4.89	0.9	0.27	23.3	0.0025	0.03	1.775	0.003	0.215	0.666	35.9
TCS 20606	0.001	8.12	0.0005	0.04	0.454	2.8	1.1	0.48	10.95	0.0025	0.005	1.48	0.002	0.255	0.964	35.4
TCS 20607	0.001	4.96	0.002	0.02	1.025	4.14	1.6	0.27	131.5	0.0025	0.05	2.06	0.003	0.157	0.829	39.1
TCS 20608	0.001	8.38	0.0005	0.03	0.333	2.64	1.4	0.51	14.1	0.0025	0.02	1.52	0.002	0.274	0.866	34.5
TCS 20609	0.001	11.1	0.001	0.02	0.842	6.49	1.3	0.5	35	0.0025	0.03	3.93	0.009	0.322	0.96	53.6
TCS 20611	0.001	5.84	0.001	0.06	0.782	3.63	1.8	0.48	80.9	0.0025	0.03	1.505	0.002	0.2	0.818	40.8
TCS 20612	0.001	4.27	0.018	0.07	0.562	4.22	5.2	0.49	34.7	0.0025	0.04	2.22	0.003	0.272	1.555	44.7
TCS 20613	0.002	8.25	0.003	0.02	1.495	8.44	6.1	0.59	62.8	0.0025	0.05	4.86	0.013	0.305	0.998	69.1
TCS 20614	0.001	6.38	0.007	0.02	0.532	3.45	2	0.23	201	0.0025	0.03	3.35	0.006	0.168	0.75	22.8
TCS 20615	0.001	8.11	0.001	0.03	0.745	2.76	2	0.42	7.07	0.0025	0.02	2.05	0.002	0.33	0.815	53.5
TCS 20616	0.001	6.15	0.001	0.02	1.01	7.17	2.2	0.3	31.9	0.0025	0.03	2.15	0.003	0.242	1.175	47.8
TCS 20617	0.001	7.86	0.001	0.02	0.869	3.8	2.5	0.43	7.69	0.0025	0.03	2.48	0.002	0.324	0.944	57.2
TCS 20618	0.001	5.45	0.001	0.02	1.02	6.56	1.7	0.28	161	0.0025	0.03	2.09	0.003	0.278	1.33	33.3
TCS 20619	0.001	5.94	0.001	0.03	0.466	2.12	1.4	0.43	10.65	0.0025	0.02	1.455	0.003	0.347	0.707	42.7
TCS 20621	0.001	7.5	0.001	0.02	0.718	5.4	1.4	0.36	11.1	0.0025	0.03	2.39	0.002	0.319	0.983	43.9
TCS 20622	0.001	5.85	0.001	0.04	0.325	2.71	1.5	0.46	11.2	0.0025	0.02	1.205	0.002	0.407	0.898	37.6
TCS 20623	0.001	5.09	0.002	0.03	1.355	4.76	1.2	0.34	111	0.0025	0.05	1.92	0.003	0.284	0.941	43.8
TCS 20624	0.001	5.04	0.001	0.06	0.631	2.31	2	0.37	180	0.0025	0.02	0.986	0.003	0.224	0.872	33.6
TCS 20625	0.001	5.55	0.001	0.03	0.547	2.93	1.5	0.38	38.5	0.0025	0.02	1.215	0.002	0.311	0.793	38.3
TCS 20626	0.001	5.17	0.0005	0.03	0.218	1.09	1.1	0.35	9.88	0.0025	0.01	0.406	0.001	0.368	0.674	26.4
TCS 20627	0.001	8.19	0.001	0.02	1.275	8.07	2.2	0.39	18.35	0.0025	0.03	3.11	0.002	0.375	1.17	61.5
TCS 20628	0.001	5.71	0.001	0.02	0.763	4.56	1.4	0.39	12.6	0.0025	0.03	2.34	0.002	0.275	0.774	48.2
TCS 20629	0.001	5.49	0.001	0.04	0.451	3.08	1.5	1.11	16.3	0.0025	0.02	1.57	0.002	0.336	1.305	36

Soil and till samples results (aqua regia digestion, continued).

Sample name	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH (lab)	LOI (%)
TCS 20602	0.05	18.85	97.1	2.41	5.05	6.54
TCS 20603	0.05	30.9	93.4	2.15	6.8	4.55
TCS 20604	0.117	19.3	93.3	2.96	5.63	6.23
TCS 20605	0.063	30.6	77.6	2.6	6.66	4.27
TCS 20606	0.042	15.1	75.4	2.74	4.65	6.75
TCS 20607	0.046	25.8	67.5	2.05	7.15	3.21
TCS 20608	0.035	12.4	70.4	2.51	5.51	5.33
TCS 20609	0.049	30.2	90.4	4.6	6.25	5.4
TCS 20611	0.077	21.9	97.4	3.25	7.16	8.11
TCS 20612	0.046	19.8	98.4	4.61	6.17	10.2
TCS 20613	0.052	30.9	113	8.97	7	8.53
TCS 20614	0.02	12.8	68.4	5.24	7.46	3.09
TCS 20615	0.053	10.4	107	2.29	4.67	6.31
TCS 20616	0.059	89.7	82.2	1.38	7.01	3.55
TCS 20617	0.057	13.05	121.5	2.65	4.84	5.65
TCS 20618	0.049	48.5	91.6	1.13	7.19	3.15
TCS 20619	0.044	7.91	100	1.98	5.54	6.26
TCS 20621	0.05	36.7	91.3	1.53	5.28	4.01
TCS 20622	0.047	14.4	96.5	2.16	5.17	7.76
TCS 20623	0.054	28	105	1.97	7.09	4.38
TCS 20624	0.062	13.7	84.2	2.12	7.16	8.44
TCS 20625	0.044	19.8	81.8	2.38	7	5.58
TCS 20626	0.031	4.77	56.2	1.05	5.98	6.68
TCS 20627	0.067	52.1	126.5	2.31	5.91	4.38
TCS 20628	0.053	26.3	88.2	2.11	5.03	4.92
TCS 20629	0.041	17.8	86.8	2.11	5.98	6

Soil and till samples results (aqua regia digestion, continued).

Sample name	Project	Soil_Horizon	ING_TM65_X	UTM 29 E	ING_TM65_Y	UTM 29 N	Location	Duplicate	Clasts
TCS 20631	IsoNose	BC	235080	601122	265968	5944835	Flank	x	mm gravels
TCS 20632	IsoNose	Top of till	235080	601122	265974	5944841	Flank	x	3 cm gravels
TCS 20633	IsoNose	BC	235073	601115	265945	5944812	Flank	x	mm gravels
TCS 20634	IsoNose	Top of till	235076	601118	265942	5944809	Flank	x	2-3 cm gravels
TCS 20635	IsoNose	BC	235073	601115	265945	5944812	Flank	Dup of 20633	mm gravels
TCS 20636	IsoNose	Top of till	235076	601118	265942	5944809	Flank	Dup of 20634	2-3 cm gravels
TCS 20637	IsoNose	BC	235072	601115	265913	5944780	Outside	x	no gravels
TCS 20638	IsoNose	Top of till	235074	601117	265916	5944783	Outside	x	2cm gravels
TCS 20639	IsoNose	BC	235061	601104	265895	5944762	Outside	x	-
TCS 20641	IsoNose	Top of till	235061	601104	265899	5944766	Flank	x	3 cm gravels
TCS 20642	IsoNose	Top of till	235056	601099	265872	5944739	Flank	x	3 cm gravels
TCS 20643	IsoNose	Top of till	235053	601096	265874	5944741	Flank	x	2 cm gravels
TCS 20644	IsoNose	BC	235050	601094	265848	5944715	Mineralisation	x	mm gravels
TCS 20645	IsoNose	Top of till	235053	601097	265846	5944713	Mineralisation	x	2-3 cm gravels
TCS 20646	IsoNose	BC	235045	601089	265824	5944691	Flank	x	mm gravels
TCS 20647	IsoNose	Top of till	235044	601524	265825	5944691	Flank	x	2-3 cm gravels
TCS 20648	IsoNose	BC	235039	601083	265800	5944666	Flank	x	mm gravels
TCS 20649	IsoNose	BC	235033	601078	265775	5944641	Outside	x	1-2 cm gravels
TCS 20651	IsoNose	Top of till	235036	601081	265772	5944638	Outside	x	1-4 cm gravels
TCS 20652	IsoNose	BC	235028	601073	265750	5944616	Outside	x	mm gravels
TCS 20653	IsoNose	Top of till	235027	601072	265749	5944615	Outside	x	1-3 cm gravels
TCS 20654	IsoNose	BC	235023	601068	265726	5944592	Outside	x	mm gravels
TCS 20655	IsoNose	Top of till	235023	601068	265728	5944594	Outside	x	2 cm gravels
TCS 20656	IsoNose	BC	235023	601068	265726	5944592	Outside	Dup of 20654	mm gravels
TCS 20657	IsoNose	Top of till	235023	601068	265728	5944594	Outside	Dup of 20655	2 cm gravels
TCS 20658	IsoNose	BC	235016	601062	265701	5944567	Outside	x	mm gravels

Soil and till samples results (aqua regia digestion, continued).

Sample name	Characteristics	Moisture	Parent_Material	Line	Physiography	Contamination	Comp_Silt
TCS 20631	-	moist to dry	CALP	Line 2	Pastureland	Possible	X
TCS 20632	weathering black, grey, orange	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20633	-	moist to dry	CALP	Line 2	Pastureland	Possible	X
TCS 20634	weathering grey, black, orange, red	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20635	-	moist to dry	CALP	Line 2	Pastureland	Possible	X
TCS 20636	weathering grey, black, orange, red	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20637	still some roots	moist	CALP	Line 2	Pastureland	Possible	XX
TCS 20638	weathering black, grey, brown, red, orange; dense	wet	CALP	Line 2	boggy	Possible	X
TCS 20639	very shallow, low oxidation	moist	CALP	Line 2	boggy	Possible	XX
TCS 20641	dense; weathering black, grey, orange, red	wet	CALP	Line 2	boggy	Possible	-
TCS 20642	dense; weathering black, grey, orange, red	wet	SWA	Line 2	boggy	Possible	-
TCS 20643	in situ weathering of pyrite; and in grey, black, orange; very dense	wet	SWA	Line 2	boggy	Possible	-
TCS 20644	rarely white weathering	moist	SWA	Line 2	boggy	Possible	X
TCS 20645	dense	moist to wet	SWA	Line 2	boggy	Possible	X
TCS 20646	black chips	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20647	dense, weathering in black, grey	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20648	at bottom fresh calcite crystals	moist to dry	WA	Line 2	Pastureland	Possible	X
TCS 20649	gravels are black and with fossils	moist to dry	WA	Line 2	Pastureland	Possible	X
TCS 20651	weathering black, grey, orange, green	moist	WA	Line 2	Pastureland	Possible	XX
TCS 20652	black chips, barely weathered	moist	WA	Line 2	Pastureland	Possible	XX
TCS 20653	weathering black in layers	moist to wet	WA	Line 2	Pastureland	Possible	XX
TCS 20654	black chips, barely weathered	moist	WA	Line 2	Pastureland	Possible	X
TCS 20655	black weathering	moist to wet	WA	Line 2	Pastureland	Possible	X
TCS 20656	black chips, barely weathered	moist	WA	Line 2	Pastureland	Possible	X
TCS 20657	black weathering	moist to wet	WA	Line 2	Pastureland	Possible	X
TCS 20658	black chips	moist	WA	Line 2	Pastureland	Possible	XX

Soil and till samples results (aqua regia digestion, continued).

Sample name	Comp_Sand	Comp_Organic	Comp_Clay	Sampling_Method	Slope	Year_Collected	Soil_Colour	Soil_From (m)	Soil_To (m)	Au (ppm)
TCS 20631	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.3	0.0012
TCS 20632	-	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.3	0.66	0.0015
TCS 20633	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0032
TCS 20634	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.38	0.45	0.0234
TCS 20635	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.35	0.002
TCS 20636	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.38	0.6	0.0024
TCS 20637	-	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.1	0.21	0.0065
TCS 20638	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.24	0.5	0.0049
TCS 20639	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.1	0.2	0.0036
TCS 20641	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.22	0.6	0.0026
TCS 20642	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.4	0.6	0.0023
TCS 20643	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.6	0.8	0.0021
TCS 20644	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.28	0.005
TCS 20645	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.3	0.6	0.0021
TCS 20646	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.25	0.38	0.0018
TCS 20647	-	-	-	Auger	flat 0-5 ⁰	2015	grey	0.4	55	0.0036
TCS 20648	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.3	0.48	0.0013
TCS 20649	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.45	0.0008
TCS 20651	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.6	0.78	0.0011
TCS 20652	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.38	0.0012
TCS 20653	-	-	X	Auger	flat 0-5 ⁰	2015	lt.. Brown	0.55	0.75	0.0015
TCS 20654	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.45	0.0006
TCS 20655	-	-	X	Auger	flat 0-5 ⁰	2015	brown/black	0.63	0.77	0.0013
TCS 20656	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.45	0.001
TCS 20657	-	-	X	Auger	flat 0-5 ⁰	2015	brown/black	0.63	0.77	0.0026
TCS 20658	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.45	0.0007

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)
TCS 20631	0.131	0.9	4.91	5	50.4	0.4	0.089	1.58	1.84	28.1	4.6	17.8	0.379	11.35	1.20	1.79
TCS 20632	0.109	0.69	5.51	5	33.4	0.89	0.086	2.74	1.26	35.1	8.1	18.5	0.267	15.35	1.80	2.02
TCS 20633	0.147	1.13	3.54	5	61	0.63	0.088	0.47	1.56	30.5	3.8	21.2	0.777	12.9	1.10	3.44
TCS 20634	0.134	0.91	6.55	5	48.6	0.97	0.088	1.19	1.59	32.4	6.4	23.3	0.373	11	2.08	2.96
TCS 20635	0.109	1.14	3.82	5	63.2	0.57	0.081	0.36	1.19	27.7	4.9	22.8	0.774	8.37	1.51	3.32
TCS 20636	0.083	0.76	4.62	5	39.3	0.53	0.058	0.32	0.78	23.7	5.1	18.1	0.277	4.93	1.69	2.28
TCS 20637	0.448	1.81	13.95	5	168	0.97	0.126	0.56	7.05	41.3	10.3	36.6	1.14	27.3	2.28	4.85
TCS 20638	0.157	2.02	14.2	5	179	1.07	0.116	0.55	5.76	41.8	15.8	42.3	0.981	16.45	3.45	5.63
TCS 20639	0.989	1.66	35.3	5	257	0.94	0.128	0.7	28.60	36.2	9.4	30.3	0.797	27.3	2.10	4.82
TCS 20641	1.955	1.83	33.8	5	297	1.01	0.118	0.85	52.50	39.4	9.0	33.9	0.916	36.1	1.97	5.03
TCS 20642	0.345	2	33.5	5	236	1.09	0.12	1.07	14.55	47.9	14.3	40.1	0.821	25.5	3.46	6.34
TCS 20643	0.168	2.36	23.8	5	194	1.13	0.135	2.33	8.83	54.8	19.9	50.0	0.745	42.1	5.07	6.26
TCS 20644	19.9	1.33	295	10	669	0.63	0.088	4.34	67.80	29.0	6.7	20.5	0.597	22.2	2.25	5.29
TCS 20645	9.39	1.57	191.5	10	1230	0.78	0.101	7.08	42.50	32.7	10.0	29.5	0.76	24	3.41	5.82
TCS 20646	1.125	1.65	145.5	5	150	0.61	0.094	0.24	4.60	29.1	7.0	20.9	0.727	11.85	2.05	4.31
TCS 20647	1.015	1.11	135	5	115	0.76	0.094	0.3	3.90	34.7	5.7	24.6	0.527	20.7	2.70	3.72
TCS 20648	0.263	1.31	50	5	100	0.51	0.087	0.21	1.98	26.7	7.1	18.9	0.822	12.4	1.77	3.81
TCS 20649	0.18	1.86	36	5	83.5	0.69	0.09	0.14	1.70	35.9	8.7	20.6	0.474	16.5	2.01	4.01
TCS 20651	0.461	0.82	26.6	5	81.4	1.08	0.114	0.27	2.78	37.9	9.3	21.4	0.409	27.9	2.41	2.42
TCS 20652	0.161	1.38	47.5	5	183	0.86	0.103	0.25	2.34	42.8	10.4	21.2	0.429	22.5	2.06	3.38
TCS 20653	0.137	0.45	22.4	5	76.1	1.28	0.109	1.79	4.82	39.1	9.7	20.4	0.366	26.9	2.09	2.91
TCS 20654	0.164	1.35	40.8	5	65.4	0.45	0.084	0.2	1.38	27.8	7.6	18.4	0.769	15	1.81	3.49
TCS 20655	0.11	1.39	25.6	5	36.8	0.64	0.104	0.14	0.98	43.0	9.3	21.2	0.45	19.1	1.98	3.46
TCS 20656	0.159	1.22	39.4	5	64	0.43	0.09	0.18	1.18	27.0	7.2	17.7	0.681	14	1.80	2.72
TCS 20657	0.136	0.8	39.5	5	44.1	0.89	0.108	0.16	1.29	50.1	11.1	23.1	0.491	20.3	2.54	3.52
TCS 20658	0.116	0.94	27.7	5	54.4	0.42	0.081	0.18	1.04	24.8	7.0	17.4	0.648	12.7	1.61	3.26

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Pd (ppm)
TCS 20631	0.032	0.081	0.084	0.018	0.04	16	4.7	0.14	183	1	0.007	0.126	26.1	0.056	23.5	0.001
TCS 20632	0.059	0.054	0.042	0.022	0.05	20.9	5.6	0.17	267	2.23	0.007	0.109	43.1	0.072	13.2	0.001
TCS 20633	0.045	0.078	0.13	0.02	0.04	17.75	7.5	0.12	123.5	0.56	0.005	0.16	17.65	0.06	25.7	0.001
TCS 20634	0.054	0.05	0.055	0.023	0.04	18.7	7.2	0.19	303	2.18	0.006	0.105	28.1	0.077	13.4	0.0005
TCS 20635	0.048	0.067	0.081	0.021	0.04	15.6	8	0.16	134.5	0.93	0.006	0.188	20.5	0.053	22	0.0005
TCS 20636	0.041	0.038	0.04	0.02	0.04	13.15	6.8	0.17	237	1.61	0.005	0.113	21.5	0.061	10.85	0.001
TCS 20637	0.060	0.146	0.221	0.033	0.04	23.9	11	0.27	489	0.92	0.01	0.274	40.7	0.063	123	0.001
TCS 20638	0.064	0.145	0.093	0.029	0.05	23.4	14.6	0.44	667	1.48	0.009	0.293	57.7	0.048	41.2	0.0005
TCS 20639	0.060	0.117	0.584	0.031	0.04	21.4	11	0.25	316	0.86	0.008	0.252	45.6	0.079	443	0.0005
TCS 20641	0.06	0.155	1.25	0.027	0.04	22.7	11.7	0.3	145.5	0.43	0.01	0.289	63.3	0.071	825	0.0005
TCS 20642	0.083	0.154	0.191	0.025	0.07	24.9	18.6	0.51	190	3.89	0.009	0.373	94	0.057	315	0.003
TCS 20643	0.092	0.313	0.096	0.037	0.11	29.1	20.4	0.66	242	7.4	0.009	0.354	134	0.046	70.3	0.002
TCS 20644	0.066	0.098	11.6	0.021	0.05	15.5	7.3	0.41	362	2.52	0.014	0.23	52.9	0.08	6430	0.003
TCS 20645	0.099	0.059	8.41	0.026	0.09	16.6	12.9	0.9	288	3.53	0.02	0.364	89.7	0.055	3420	0.003
TCS 20646	0.05	0.09	1.04	0.024	0.05	15.9	7.4	0.16	606	2	0.006	0.181	32.7	0.042	627	0.0005
TCS 20647	0.06	0.062	0.981	0.023	0.06	20.7	7.9	0.21	240	2.74	0.007	0.179	66.9	0.053	359	0.0005
TCS 20648	0.039	0.09	0.131	0.022	0.05	13.3	7.2	0.12	736	2.48	0.006	0.177	25.2	0.055	202	0.0005
TCS 20649	0.06	0.097	0.156	0.019	0.07	18.25	7.4	0.14	820	3.4	0.006	0.167	37.4	0.047	102	0.002
TCS 20651	0.071	0.049	0.324	0.026	0.06	27.2	6.1	0.14	686	4.23	0.008	0.137	55.8	0.042	41.1	0.0005
TCS 20652	0.072	0.081	0.147	0.026	0.06	27	6.9	0.14	817	4.31	0.006	0.16	52.1	0.041	121	0.0005
TCS 20653	0.072	0.03	0.095	0.028	0.06	24.1	6.8	0.18	567	5.81	0.005	0.131	80	0.047	34.8	0.0005
TCS 20654	0.038	0.094	0.145	0.021	0.06	13.3	6.7	0.12	943	2.98	0.007	0.169	26.6	0.061	82.5	0.001
TCS 20655	0.056	0.078	0.166	0.03	0.06	23.8	7	0.14	738	3.28	0.006	0.165	38.2	0.044	36.3	0.0005
TCS 20656	0.035	0.084	0.137	0.025	0.05	13.25	6	0.12	875	2.97	0.007	0.161	24.1	0.058	80.2	0.001
TCS 20657	0.07	0.091	0.37	0.023	0.07	24	8.1	0.16	1320	3.58	0.006	0.165	47.6	0.051	56.8	0.0005
TCS 20658	0.033	0.068	0.069	0.017	0.05	11.35	6.8	0.12	806	2.6	0.005	0.182	20.7	0.055	63.5	0.0005

Soil and till samples results (aqua regia digestion, continued).

Sample name	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)	V (ppm)
TCS 20631	0.001	4.84	0.002	0.06	0.628	3.1	1.5	0.42	57.6	0.0025	0.02	1.515	0.002	0.261	0.808	33.2
TCS 20632	0.001	4.25	0.001	0.03	0.99	4.22	1.4	0.28	90	0.0025	0.04	2.2	0.003	0.174	0.776	36.4
TCS 20633	0.001	4.49	0.001	0.07	0.505	3.63	2.3	0.48	22.1	0.0025	0.02	1.75	0.002	0.331	1.94	33.7
TCS 20634	0.001	3.79	0.004	0.02	0.918	4.45	1.5	0.33	50.7	0.0025	0.05	2.63	0.002	0.156	1.115	42.1
TCS 20635	0.001	4.96	0.001	0.04	0.616	3.27	1.8	0.44	20.3	0.0025	0.02	2.12	0.003	0.297	1.765	37.1
TCS 20636	0.001	3.78	0.002	0.02	0.692	2.85	1.1	0.24	18.4	0.0025	0.04	2.18	0.003	0.128	0.779	30.5
TCS 20637	0.001	5.2	0.001	0.07	3.02	5.04	4.9	0.68	26.1	0.0025	0.03	2.18	0.003	0.879	2.89	54.4
TCS 20638	0.002	4.8	0.005	0.03	2.41	5.96	4.4	0.58	32.6	0.0025	0.04	3.77	0.005	0.426	1.245	59.3
TCS 20639	0.001	5.4	0.002	0.08	11	3.85	4.7	0.69	29.5	0.0025	0.04	1.625	0.003	1.545	3.07	50
TCS 20641	0.001	4.69	0.004	0.08	18.2	5.01	4.9	0.61	36.7	0.0025	0.02	2.23	0.004	2.01	3.13	51.1
TCS 20642	0.001	6.3	0.001	0.01	12.7	6.71	2.1	0.66	39.7	0.0025	0.03	3.99	0.01	1.035	0.816	47.7
TCS 20643	0.002	8.76	0.001	0.01	6.45	8.26	4.1	0.69	69.9	0.0025	0.04	4.73	0.02	0.466	1.135	55.3
TCS 20644	0.001	7.27	0.001	0.08	187	3.25	2.2	0.61	86.7	0.0025	0.04	1.33	0.003	3.64	0.733	32.5
TCS 20645	0.002	7.62	0.001	0.05	196.5	5.08	2.3	0.57	198	0.0025	0.03	2.59	0.01	5.39	1.29	34.7
TCS 20646	0.001	9.94	0.0005	0.03	19.05	3.53	1.1	0.68	9.78	0.0025	0.03	1.515	0.003	3.22	0.844	33.8
TCS 20647	0.002	6.86	0.001	0.01	22.1	4.99	1.4	0.59	16.1	0.0025	0.03	2.5	0.004	2.73	0.899	40.4
TCS 20648	0.001	13.85	0.001	0.02	5.26	2.87	0.7	0.65	10.65	0.0025	0.03	1.37	0.003	1.67	0.768	35.1
TCS 20649	0.002	9.81	0.0005	0.02	4.24	3.49	1.2	0.64	8.07	0.0025	0.03	1.37	0.003	0.815	0.887	37
TCS 20651	0.001	7.78	0.0005	0.02	4.31	5.08	1.7	0.34	13.65	0.0025	0.07	1.815	0.004	1.675	1.015	42.8
TCS 20652	0.001	8.46	0.001	0.02	4.6	4.71	1.6	0.64	12.15	0.0025	0.04	1.46	0.002	0.7	0.922	44
TCS 20653	0.001	6.36	0.001	0.02	4.07	5.99	1.6	0.56	59.2	0.0025	0.04	1.72	0.003	0.574	1.11	64.6
TCS 20654	0.001	14.4	0.001	0.03	3.13	2.82	0.9	0.7	11.1	0.0025	0.04	1.235	0.003	0.868	0.896	33.4
TCS 20655	0.001	10.55	0.001	0.02	2.78	4.24	1.4	0.59	9.59	0.0025	0.06	1.395	0.004	0.632	1.06	37.1
TCS 20656	0.001	13.6	0.0005	0.03	3.36	2.58	0.6	0.67	8.2	0.0025	0.03	1.24	0.003	0.841	0.889	31.7
TCS 20657	0.001	11.3	0.001	0.02	5.69	4.43	2	0.56	10.2	0.0025	0.05	1.495	0.004	0.794	1.02	40.6
TCS 20658	0.001	14.3	0.002	0.02	1.955	2.35	0.8	0.61	7.79	0.0025	0.04	1.16	0.003	0.634	0.864	30.3

Soil and till samples results (aqua regia digestion, continued).

Sample name	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH (lab)	LOI (%)
TCS 20631	0.045	17.4	123.5	2.41	7	9.77
TCS 20632	0.045	25.3	104	2.53	7.18	4.46
TCS 20633	0.05	19.6	105	2.53	6.12	11.6
TCS 20634	0.045	22.1	62.3	2.46	7.16	4.33
TCS 20635	0.038	14.8	81.9	2.05	6.27	7.51
TCS 20636	0.03	12.45	45.6	1.59	7.32	3.58
TCS 20637	0.055	26.4	1155	4.79	5.52	12.3
TCS 20638	0.047	22.3	1355	5.81	5.61	7.09
TCS 20639	0.07	23.4	4300	3.87	6.4	14.25
TCS 20641	0.049	25.4	6990	5.11	6.49	13.05
TCS 20642	0.056	25.9	6320	7.75	7.01	5.25
TCS 20643	0.051	31.4	6000	14.85	7.3	5.34
TCS 20644	0.054	18.05	9990	2.58	7.01	10.75
TCS 20645	0.043	17.6	13150	2.3	7.18	6.03
TCS 20646	0.045	17.1	2020	2.63	5.63	5.79
TCS 20647	0.055	26	4420	2.19	5.82	3.88
TCS 20648	0.04	12.55	603	2.5	5.5	4.96
TCS 20649	0.047	20.2	438	2.42	4.88	5.05
TCS 20651	0.067	39.6	960	1.76	5.91	4.44
TCS 20652	0.059	31.2	495	2.29	7.1	5.55
TCS 20653	0.056	37.4	1085	1.29	7.38	3.74
TCS 20654	0.041	12.5	339	2.48	5.8	5.95
TCS 20655	0.049	24.8	325	2.36	5.33	3.92
TCS 20656	0.045	12.35	328	2.41	5.14	5.38
TCS 20657	0.061	26.6	508	2.72	5.24	4.69
TCS 20658	0.036	9.36	247	2.07	5.3	5.29

Soil and till samples results (aqua regia digestion, continued).

Sample name	Project	Soil_Horizon	ING_TM65_X	UTM 29 E	ING_TM65_Y	UTM 29 N	Location	Duplicate	Clasts
TCS 20659	IsoNose	Top of till	235015	601061	265705	5944571	Outside	x	5 cm gravels
TCS 20661	IsoNose	BC	235020	601066	265679	5944545	Fault	x	mm gravels
TCS 20662	IsoNose	Top of till	235018	601064	265677	5944543	Fault	x	2 cm gravels
TCS 20663	IsoNose	BC	235005	601051	265653	5944519	Fault	x	1-2 cm gravels
TCS 20664	IsoNose	Top of till	235004	601050	265656	5944522	Fault	x	2 cm gravels
TCS 20665	IsoNose	BC	234997	601044	265622	5944488	Outside	x	mm gravels
TCS 20666	IsoNose	Top of till	234999	601046	265624	5944490	Outside	x	2 cm gravels
TCS 20667	IsoNose	BC	234994	601041	265606	5944472	Outside	x	mm gravels
TCS 20668	IsoNose	Top of till	234994	601041	265604	5944470	Outside	x	2 cm gravels
TCS 20669	IsoNose	BC	234988	601036	265580	5944446	Outside	x	mm gravels
TCS 20671	IsoNose	Top of till	234990	601037	265583	5944449	Outside	x	1-2 cm gravels, rarely 4 cm
TCS 20672	IsoNose	BC	234983	601031	265555	5944421	Outside	x	mm gravels
TCS 20673	IsoNose	Top of till	234982	601030	265552	5944418	Outside	x	1-2 cm gravels
TCS 20674	IsoNose	BC	234983	601031	265555	5944421	Outside	Dup of 20672	mm gravels
TCS 20675	IsoNose	Top of till	234982	601030	265552	5944418	Outside	Dup of 20673	1-2 cm gravels
TCS 20676	IsoNose	BC	234978	601026	265533	5944399	Outside	x	mm gravels
TCS 20677	IsoNose	Top of till	234981	601029	265531	5944397	Outside	x	-
TCS 20678	IsoNose	BC	234967	601016	265493	5944359	Outside	x	mm gravels
TCS 20679	IsoNose	Top of till	234966	601443	265491	5944359	Outside	x	up to 5 cm gravels
TCS 20681	IsoNose	BC	234964	601013	265482	5944348	Fault	x	mm gravels
TCS 20682	IsoNose	Top of till	234963	601012	265482	5944348	Fault	x	2 cm gravels
TCS 20683	IsoNose	BC	234960	601009	265458	5944323	Fault	x	mm gravels
TCS 20684	IsoNose	Top of till	234961	601010	265457	5944322	Fault	x	2 cm gravels
TCS 20685	IsoNose	BC	234953	601003	265434	5944299	Outside	x	mm gravels
TCS 20686	IsoNose	Top of till	234952	601002	265435	5944300	Outside	x	1-2 cm gravels
TCS 20687	IsoNose	BC	234947	600997	265410	5944275	Outside	x	mm gravels

Soil and till samples results (aqua regia digestion, continued).

Sample name	Characteristics	Moisture	Parent_Material	Line	Physiography	Contamination	Comp_Silt
TCS 20659	weathering in black, with layers of low level of weathering	moist	WA	Line 2	Pastureland	Possible	XX
TCS 20661	black chips	dry to moist	SWA	Line 2	Pastureland	Possible	X
TCS 20662	weathered	wet to moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20663	black, no weathering	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20664	-	dry to moist	SWA	Line 2	Pastureland	Possible	-
TCS 20665	black chips, one weathered green gravel	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20666	weathering in black, orange, red, grey (WA and CALP)	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20667	-	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20668	black weathered	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20669	-	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20671	dense; weathering in black, brown, orange, green, white	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20672	black chips; very deep; dense; rarely lines of oxidation (red)	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20673	dense; weathering in black, grey, orange	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20674	black chips; very deep; dense; rarely lines of oxidation (red)	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20675	dense; weathering in black, grey, orange	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20676	schlieren of brown/red oxidation	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20677	weathering in black, orange	moist	SWA	Line 2	Pastureland	Possible	XX
TCS 20678	black chips; lines of brown/red oxidation, getting less with depth	moist	SWA	Line 2	Pastureland	Possible	X
TCS 20679	weathering in black, yellow; dense	wet	SWA	Line 2	Pastureland	Possible	X
TCS 20681	brownish lines (schlieren)	dry to moist	SWA	Line 2	stable grass	Possible	X
TCS 20682	weathering in ochre, black, orange	moist	SWA	Line 2	stable grass	Possible	X
TCS 20683	-	dry to moist	WA	Line 2	Pastureland	Possible	XX
TCS 20684	weathering in black, orange, grey	moist	WA	Line 2	Pastureland	Possible	XX
TCS 20685	-	moist	WA	Line 2	Pastureland	Possible	XX
TCS 20686	weathering in light brown	moist	WA	Line 2	Pastureland	Possible	XX
TCS 20687	black chips	moist	WA	Line 2	boggy	Possible	XX

Soil and till samples results (aqua regia digestion, continued).

Sample name	Comp_Sand	Comp_Organic	Comp_Clay	Sampling_Method	Slope	Year_Collected	Soil_Colour	Soil_From (m)	Soil_To (m)	Au (ppm)
TCS 20659	-	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.65	0.85	0.0008
TCS 20661	XX	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.001
TCS 20662	-	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.4	0.75	0.0013
TCS 20663	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.4	0.0013
TCS 20664	XX	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.45	0.6	0.0011
TCS 20665	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.38	0.0015
TCS 20666	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.4	0.6	0.0009
TCS 20667	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.22	0.32	0.0021
TCS 20668	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.43	0.55	0.0013
TCS 20669	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.45	0.0014
TCS 20671	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.45	0.7	0.0011
TCS 20672	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.45	0.0014
TCS 20673	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.6	0.75	0.0019
TCS 20674	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.45	0.0008
TCS 20675	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.6	0.81	0.002
TCS 20676	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.35	0.55	0.0008
TCS 20677	-	-	-	Auger	flat 0-5 ⁰	2015	lt.brown	0.7	0.85	0.0021
TCS 20678	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.3	0.0024
TCS 20679	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.4	0.7	0.0038
TCS 20681	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.4	0.0022
TCS 20682	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.45	0.7	0.0033
TCS 20683	-	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.4	0.0019
TCS 20684	-	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.5	0.65	0.0017
TCS 20685	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.15	0.25	0.0026
TCS 20686	-	-	X	Auger	flat 0-5 ⁰	2015	lt. brown	0.55	0.7	0.0016
TCS 20687	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.15	0.4	0.0015

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)
TCS 20659	0.042	1	17.75	5	28.1	0.94	0.107	0.12	0.65	41.3	8.7	21.6	0.444	19.6	2.07	4.47
TCS 20661	0.097	0.72	16.6	5	40.8	0.42	0.085	0.14	0.92	24.8	6.8	17.5	0.581	16.85	1.50	3.19
TCS 20662	0.082	0.75	15.3	5	29	1.01	0.115	0.14	1.34	48.3	10.2	23.6	0.348	24.5	2.20	3.23
TCS 20663	0.116	1.65	21.7	5	57.9	0.53	0.085	0.19	1.22	26.1	7.4	19.0	0.712	16.7	1.66	3.78
TCS 20664	0.048	1.74	11.35	5	34.7	0.54	0.084	0.15	0.74	34.3	10.2	25.4	0.446	17	2.11	4.17
TCS 20665	0.172	1.35	56.4	5	55.9	1	0.111	0.5	3.42	39.7	11.1	21.7	0.511	26.9	2.34	3.75
TCS 20666	0.127	1.55	57.8	10	44	1.01	0.138	7.97	3.14	41.9	13.5	18.2	1.315	26	2.70	3.53
TCS 20667	0.159	1.33	31.9	5	51.6	0.77	0.123	0.31	1.98	37.8	10.4	20.4	0.253	25.6	2.12	2.90
TCS 20668	0.094	0.8	44	5	27.2	0.56	0.084	9.92	2.88	28.8	10.4	15.9	0.528	21.8	1.84	2.55
TCS 20669	0.092	1.75	18.55	5	50.2	0.56	0.107	0.24	0.97	30.8	7.4	19.7	0.696	19.65	1.71	3.64
TCS 20671	0.066	1.17	15.55	5	39.1	1.34	0.136	0.18	1.09	55.4	12.7	22.5	0.622	23.3	2.45	3.24
TCS 20672	0.114	1.33	13.4	5	64.6	0.58	0.094	0.31	0.74	27.4	5.0	18.7	0.677	11.15	1.52	3.51
TCS 20673	0.157	1.93	12.1	5	74.6	0.98	0.14	0.71	0.85	48.2	9.5	21.9	0.699	18.25	2.02	4.13
TCS 20674	0.12	0.91	13.35	5	64.9	0.61	0.092	0.31	0.66	28.0	4.6	18.1	0.706	11.6	1.53	3.58
TCS 20675	0.2	1.83	15.35	5	70.4	0.99	0.127	1.61	0.74	41.7	8.2	20.9	0.662	14.9	2.10	4.02
TCS 20676	0.098	0.8	13.2	5	59.6	0.66	0.101	0.28	0.88	29.3	6.0	18.4	0.76	13.85	1.62	3.60
TCS 20677	0.224	1.16	28.9	5	81.3	1.17	0.145	1.15	1.44	47.7	8.9	23.0	0.786	19.5	3.07	3.28
TCS 20678	0.08	0.96	11.25	5	43.3	0.61	0.108	0.17	0.92	31.7	7.4	19.8	0.681	15.45	1.54	2.45
TCS 20679	0.102	0.78	14.65	5	39.4	1.08	0.114	0.2	2.41	40.6	8.7	19.1	0.499	25.6	1.91	1.96
TCS 20681	0.087	0.94	11.05	5	44.3	0.69	0.101	0.15	1.19	33.2	6.8	19.7	0.62	16.55	1.63	2.39
TCS 20682	0.156	0.72	14.55	5	39.4	1.05	0.11	2.45	3.90	37.5	8.8	19.9	0.392	28.2	2.17	1.90
TCS 20683	0.09	0.94	10.15	5	48.6	0.5	0.1	0.16	1.09	26.7	6.4	18.5	0.677	16.35	1.59	2.66
TCS 20684	0.04	0.86	7.97	5	21.3	0.59	0.098	0.1	0.81	39.7	8.7	20.0	0.432	17.25	1.72	2.04
TCS 20685	0.121	0.89	14.6	5	53.7	0.82	0.118	0.19	1.80	35.5	8.2	19.1	0.53	24	1.75	2.38
TCS 20686	0.107	0.83	11.2	5	61.9	0.96	0.127	0.21	1.43	38.7	10.2	17.6	0.468	19.15	1.97	2.24
TCS 20687	0.112	0.92	9.88	5	57.1	0.47	0.097	0.12	0.84	26.0	5.3	17.9	0.531	12.75	1.32	2.50

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Pd (ppm)
TCS 20659	0.078	0.041	0.093	0.017	0.07	21.5	11.5	0.21	529	2.64	0.004	0.209	45.5	0.021	48.5	0.0005
TCS 20661	0.027	0.067	0.058	0.018	0.04	10.6	6.8	0.12	583	2.54	0.003	0.162	24.6	0.048	46.3	0.002
TCS 20662	0.078	0.056	0.103	0.019	0.06	28.4	7.5	0.16	582	4.22	0.005	0.182	56.7	0.028	34	0.001
TCS 20663	0.04	0.1	0.068	0.024	0.06	12.45	8	0.14	762	2.48	0.006	0.183	26.1	0.06	57.1	0.001
TCS 20664	0.036	0.055	0.04	0.022	0.06	11.85	10.9	0.24	452	2.36	0.007	0.213	42.5	0.025	23.6	0.001
TCS 20665	0.071	0.112	0.143	0.022	0.09	24	8.9	0.19	830	3.25	0.007	0.172	69.9	0.052	79.9	0.002
TCS 20666	0.07	0.049	0.183	0.028	0.13	21.4	9.1	0.29	570	3.46	0.01	0.155	80.2	0.058	86.5	0.005
TCS 20667	0.06	0.118	0.103	0.021	0.16	23	7.2	0.17	863	2.77	0.008	0.177	52.3	0.061	57.2	0.002
TCS 20668	0.066	0.043	0.195	0.016	0.09	14.75	5.9	0.25	449	2.47	0.011	0.162	55.5	0.056	104	0.005
TCS 20669	0.048	0.101	0.081	0.022	0.06	14.4	7.9	0.14	509	2.55	0.007	0.177	31.1	0.052	37.2	0.002
TCS 20671	0.094	0.047	0.101	0.033	0.08	37.1	8.6	0.18	675	2.97	0.006	0.142	61.7	0.025	26.5	0.0005
TCS 20672	0.046	0.111	0.031	0.02	0.06	15.85	8.7	0.13	256	1.37	0.006	0.162	25.2	0.042	30.1	0.001
TCS 20673	0.073	0.098	0.052	0.036	0.12	26.1	12.1	0.28	766	1.49	0.007	0.202	58.4	0.073	23	0.001
TCS 20674	0.05	0.099	0.047	0.021	0.06	15.55	8.3	0.14	206	1.43	0.006	0.165	26.5	0.044	31.7	0.0005
TCS 20675	0.068	0.1	0.076	0.028	0.1	26.1	10.3	0.23	503	1.34	0.006	0.175	50.8	0.063	24.9	0.001
TCS 20676	0.056	0.1	0.061	0.023	0.06	15.35	8.4	0.13	371	1.65	0.006	0.162	26.1	0.045	32.5	0.001
TCS 20677	0.065	0.09	0.208	0.03	0.11	30.7	13.5	0.27	873	1.92	0.005	0.143	57.6	0.05	83.5	0.002
TCS 20678	0.043	0.071	0.077	0.023	0.05	14.5	7.4	0.12	492	2.61	0.005	0.14	31.1	0.041	22.3	0.0005
TCS 20679	0.065	0.034	0.088	0.024	0.05	28.3	5.7	0.12	580	4.22	0.004	0.099	58.8	0.03	19	0.0005
TCS 20681	0.044	0.068	0.081	0.021	0.05	17	7.4	0.13	491	2.68	0.004	0.118	41.3	0.041	23.8	0.001
TCS 20682	0.073	0.044	0.085	0.028	0.06	29.3	5.5	0.13	494	4.7	0.006	0.088	67	0.038	33.7	0.0005
TCS 20683	0.039	0.072	0.056	0.019	0.05	13.3	8	0.12	580	2.32	0.005	0.147	24.4	0.053	24.6	0.001
TCS 20684	0.044	0.027	0.065	0.018	0.04	15.75	7.7	0.13	467	3.2	0.003	0.148	37.4	0.024	14.9	0.001
TCS 20685	0.058	0.1	0.097	0.022	0.05	21.8	7.2	0.13	736	2.8	0.004	0.132	40.8	0.051	30.5	0.0005
TCS 20686	0.052	0.071	0.067	0.02	0.06	23.5	6.8	0.11	1050	3.29	0.004	0.112	43.5	0.03	23.4	0.0005
TCS 20687	0.031	0.075	0.041	0.025	0.08	13.7	7	0.11	494	2	0.004	0.138	21	0.054	26	0.001

Soil and till samples results (aqua regia digestion, continued).

Sample name	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)	V (ppm)
TCS 20659	0.001	7.88	0.0005	0.01	2.48	4.5	1.5	0.55	9.81	0.0025	0.04	2.03	0.005	0.414	0.879	32.2
TCS 20661	0.001	11.45	0.001	0.02	1.72	2.16	0.9	0.62	6.76	0.0025	0.04	1.27	0.003	0.462	0.886	30.4
TCS 20662	0.001	7.34	0.0005	0.01	2.53	5.48	1.9	0.58	9.4	0.0025	0.04	1.89	0.004	0.468	1.08	47.1
TCS 20663	0.001	14.3	0.001	0.03	1.775	2.39	0.8	0.78	8.25	0.0025	0.03	1.185	0.003	0.553	0.892	32.2
TCS 20664	0.001	8.14	0.001	0.02	1.26	3.07	0.9	0.52	8.05	0.0025	0.04	1.65	0.006	0.315	0.76	34.5
TCS 20665	0.001	10	0.001	0.03	4.21	4.65	1.4	0.64	20.8	0.0025	0.04	1.625	0.003	1.045	0.917	36.8
TCS 20666	0.001	10.2	0.001	0.02	5.78	5.48	1	0.7	193.5	0.0025	0.04	3.06	0.005	2.04	0.912	23.7
TCS 20667	0.001	8.26	0.001	0.04	2.83	4.04	1.5	0.79	13.05	0.0025	0.04	1.485	0.003	0.516	0.933	34.1
TCS 20668	0.002	6.32	0.001	0.03	6.24	3.82	0.9	0.51	299	0.0025	0.05	1.89	0.005	0.831	1.05	24.9
TCS 20669	0.001	13.05	0.001	0.03	1.6	3.01	1	0.76	9.87	0.0025	0.04	1.535	0.003	0.473	0.892	31.9
TCS 20671	0.001	10.45	0.001	0.02	1.83	7.15	1.9	0.59	11.05	0.0025	0.06	2.35	0.003	0.545	1.115	36.9
TCS 20672	0.001	13.9	0.001	0.03	0.876	3.47	0.7	0.71	14.3	0.0025	0.01	1.65	0.003	0.416	0.56	29.1
TCS 20673	0.001	11.25	0.001	0.02	1.305	5.87	1	0.61	24.9	0.0025	0.05	3.23	0.006	0.451	0.695	23.7
TCS 20674	0.001	13.95	0.001	0.03	0.877	3.36	1	0.66	13.75	0.0025	0.01	1.685	0.003	0.459	0.747	28.7
TCS 20675	0.001	10.25	0.001	0.02	1.42	5.87	0.8	0.58	43.4	0.0025	0.03	2.83	0.005	0.406	0.683	22.9
TCS 20676	0.001	13.65	0.002	0.03	1.025	3.27	0.8	0.71	9.96	0.0025	0.02	1.735	0.003	0.443	0.863	29.8
TCS 20677	0.001	12.2	0.0005	0.005	1.82	5.54	1.4	0.5	33.3	0.0025	0.02	3.4	0.004	0.491	0.774	26.4
TCS 20678	0.001	11.45	0.0005	0.01	1.105	2.62	1.3	0.54	8.72	0.0025	0.01	1.4	0.003	0.387	1.095	31.7
TCS 20679	0.002	6.94	0.0005	0.005	1.93	4.94	1.4	0.43	12.95	0.0025	0.03	1.74	0.003	0.425	1.065	40.3
TCS 20681	0.001	11.6	0.0005	0.01	1.135	3.18	1.3	0.47	10.4	0.0025	0.01	1.385	0.003	0.395	1.15	32.8
TCS 20682	0.001	7.46	0.0005	0.005	2.05	4.96	1.8	0.39	94.9	0.0025	0.02	1.735	0.003	0.415	1.14	37.2
TCS 20683	0.001	12.8	0.0005	0.01	0.91	2.17	1.2	0.53	8.79	0.0025	0.02	1.25	0.004	0.375	0.989	31.5
TCS 20684	0.001	6.76	0.0005	0.005	1.245	2.69	1.2	0.33	8.45	0.0025	0.03	1.56	0.004	0.233	0.782	31.9
TCS 20685	0.001	11.3	0.0005	0.01	1.47	3.48	1.6	0.57	10.9	0.0025	0.02	1.46	0.003	0.407	1.19	33.7
TCS 20686	0.001	9.09	0.0005	0.005	2.05	4.17	1.3	0.4	12.15	0.0025	0.03	1.825	0.003	0.509	0.955	32.5
TCS 20687	0.001	12.4	0.0005	0.01	0.815	2.31	1	0.54	6.94	0.0025	0.01	1.32	0.002	0.364	1.07	29

Soil and till samples results (aqua regia digestion,
continued).

Sample name	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH (lab)	LOI (%)
TCS 20659	0.045	21.1	380	1.33	5.26	3.4
TCS 20661	0.039	8.9	207	1.92	5.03	5.18
TCS 20662	0.059	33.1	279	1.44	5.12	3.81
TCS 20663	0.052	10.9	241	2.22	5.44	5.83
TCS 20664	0.103	8.65	146.5	1.36	7.01	3.77
TCS 20665	0.053	29.1	604	2.85	7.08	6.59
TCS 20666	0.039	19.95	972	1.48	7.44	4.16
TCS 20667	0.046	27.3	329	3.1	5.92	7.15
TCS 20668	0.045	17.45	626	1.5	7.33	3.12
TCS 20669	0.047	12.9	196	2.94	5.5	6.26
TCS 20671	0.048	41.8	212	1.67	5.6	4.23
TCS 20672	0.035	14.6	168	2.68	6.24	5.14
TCS 20673	0.041	23.7	126.5	2.6	7.17	4.02
TCS 20674	0.039	14.3	175	2.8	6.38	5.31
TCS 20675	0.038	24.5	136.5	2.82	7.35	4.16
TCS 20676	0.038	13.55	174	2.71	5.87	5.31
TCS 20677	0.084	29.1	533	2.56	7.19	5.31
TCS 20678	0.042	13.95	140	1.97	5.5	5.71
TCS 20679	0.055	37.6	163	1.21	5.73	3.97
TCS 20681	0.052	17.5	144.5	1.97	5.08	5.07
TCS 20682	0.05	42.7	160	1.4	7.19	4.35
TCS 20683	0.033	12.25	142.5	1.89	5.06	5.68
TCS 20684	0.043	14.1	102.5	0.91	5.1	3.66
TCS 20685	0.041	26.2	154	2.92	5.04	6.24
TCS 20686	0.043	25.4	134	2.05	5.8	3.97
TCS 20687	0.032	12.9	148	2.18	4.58	5.1

Soil and till samples results (aqua regia digestion, continued).

Sample name	Project	Soil_Horizon	ING_TM65_X	UTM 29 E	ING_TM65_Y	UTM 29 N	Location	Duplicate	Clasts
TCS 20688	IsoNose	Top of till	234949	600999	265413	5944278	Outside	x	2 cm gravels
TCS 20689	IsoNose	BC	234942	600992	265385	5944250	Outside	x	mm gravels
TCS 20691	IsoNose	Top of till	234939	600989	265387	5944252	Outside	x	2-3 cm gravels
TCS 20692	IsoNose	BC	235271	601314	265896	5944766	Outside	x	mm gravels
TCS 20693	IsoNose	Top of till	235271	601314	265894	5944764	Outside	x	2-3 cm gravels
TCS 20694	IsoNose	BC	235271	601314	265896	5944766	Outside	Dup of 20692	mm gravels
TCS 20695	IsoNose	Top of till	235271	601314	265894	5944764	Outside	Dup of 20693	2-3 cm gravels
TCS 20696	IsoNose	BC	235281	601324	265881	5944751	Outside	x	mm gravels
TCS 20697	IsoNose	Top of till	235279	601322	265876	5944746	Outside	x	2-3 cm gravels
TCS 20698	IsoNose	BC	235325	601369	265850	5944720	Outside	x	-
TCS 20699	IsoNose	Top of till	235328	601372	265852	5944722	Outside	x	2cm gravels
TCS 20701	IsoNose	BC	235340	601384	265839	5944710	Outside	x	mm gravels
TCS 20702	IsoNose	Top of till	235339	601383	265839	5944710	Outside	x	2-3 cm gravels
TCS 20703	IsoNose	BC	235359	601403	265824	5944695	Outside	x	mm gravels
TCS 20704	IsoNose	Top of till	235354	601398	265824	5944695	Outside	x	2 cm gravels
TCS 20705	IsoNose	BC	235372	601416	265813	5944684	Outside	x	mm gravels
TCS 20706	IsoNose	Top of till	235368	601412	265809	5944680	Outside	x	2-3 cm gravels
TCS 20707	IsoNose	Top of till	235401	601445	265787	5944659	Outside	x	-
TCS 20708	IsoNose	BC	235416	601461	265776	5944648	Fault	x	mm gravels
TCS 20709	IsoNose	Top of till	235416	601461	265777	5944649	Fault	x	2-3 cm gravels
TCS 20711	IsoNose	BC	235436	601481	265760	5944632	Outside	x	mm gravels
TCS 20712	IsoNose	Top of till	235435	601480	265762	5944634	Outside	x	2-3 cm gravels
TCS 20713	IsoNose	BC	235454	601499	265745	5944617	Outside	x	mm gravels
TCS 20714	IsoNose	Top of till	235457	601502	265745	5944617	Outside	x	2-3 cm gravels
TCS 20715	IsoNose	BC	235454	601499	265745	5944617	Outside	Dup of 20713	mm gravels
TCS 20716	IsoNose	Top of till	235457	601502	265745	5944617	Outside	Dup of 20714	2-3 cm gravels

Soil and till samples results (aqua regia digestion, continued).

Sample name	Characteristics	Moisture	Parent_Material	Line	Physiography	Contamination	Comp_Silt
TCS 20688	dense; weathering in black, grey, green	wet to moist	WA	Line 2	boggy	Possible	XX
TCS 20689	black chips	moist	WA	Line 2	Pastureland	Possible	XX
TCS 20691	weathering in black, grey	moist	WA	Line 2	boggy	Possible	X
TCS 20692	black chips	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20693	weathering in lt. brown, gravels are mainly black, orange Schlieren	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20694	black chips	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20695	weathering in lt. brown, gravels are mainly black, orange Schlieren	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20696	black chips	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20697	weathering in lt. brown, orange, barely black	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20698	oxidised in brownish, orange, grey	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20699	very weathered in grey, orange, black	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20701	grey, orange Schlieren	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20702	weathering in grey, l. brown, orange, black	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20703	black chips	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20704	dense; low level of weathering, a few lines in brown, orange, crumbling while augering	wet to moist	CALP	Line 4	Pastureland	Possible	X
TCS 20705	black chips; lines of brown, orange	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20706	weathering in black, orange, lt. brown, red	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20707	no BC, weathering in grey, orange	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20708	black chips	dry to moist	CALP	Line 4	Pastureland	Possible	X
TCS 20709	weathering in grey, lt. brown, black	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20711	black chips	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20712	weathering in black, lt. brown	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20713	black chips	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20714	weathering in black, orange	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20715	black chips	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20716	weathering in black, orange	moist	CALP	Line 4	Pastureland	Possible	XX

Soil and till samples results (aqua regia digestion, continued).

Sample name	Comp_Sand	Comp_Organic	Comp_Clay	Sampling_Method	Slope	Year_Collected	Soil_Colour	Soil_From (m)	Soil_To (m)	Au (ppm)
TCS 20688	-	-	X	Auger	flat 0-5 ⁰	2015	very lt. brown	0.45	0.7	0.0063
TCS 20689	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.08	0.25	0.0055
TCS 20691	-	-	X	Auger	flat 0-5 ⁰	2015	lt. brown	0.42	0.7	0.0035
TCS 20692	-	roots	-	Auger	flat 0-5 ⁰	2015	brown	0.12	0.25	0.0026
TCS 20693	X	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.32	0.5	0.0024
TCS 20694	-	roots	-	Auger	flat 0-5 ⁰	2015	brown	0.12	0.25	0.0022
TCS 20695	X	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.32	0.5	0.002
TCS 20696	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.08	0.2	0.0021
TCS 20697	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.25	0.45	0.0019
TCS 20698	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.08	0.2	0.0028
TCS 20699	-	-	X	Auger	flat 0-5 ⁰	2015	lt. brown	0.35	0.5	0.0019
TCS 20701	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.8	0.15	0.002
TCS 20702	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.35	0.5	0.0026
TCS 20703	-	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.5	0.002
TCS 20704	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.7	1	0.002
TCS 20705	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.08	0.23	0.0015
TCS 20706	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.3	0.5	0.0023
TCS 20707	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.4	0.65	0.0019
TCS 20708	XX	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.2	0.4	0.0017
TCS 20709	X	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.45	0.6	0.0025
TCS 20711	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.3	0.0024
TCS 20712	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.5	0.7	0.0025
TCS 20713	X	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.2	0.45	0.0014
TCS 20714	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.6	0.75	0.0025
TCS 20715	X	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.2	0.45	0.0019
TCS 20716	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.6	0.75	0.0022

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)
TCS 20688	0.095	1.48	11.05	5	72.1	0.87	0.127	0.29	1.70	43.3	11.8	34.2	0.577	26.4	2.45	3.90
TCS 20689	0.109	0.9	9.11	5	46.4	0.69	0.104	0.1	1.08	35.1	7.0	20.8	0.596	16.7	1.56	2.26
TCS 20691	0.119	1.2	12.15	5	147.5	1.45	0.135	0.2	3.58	51.7	10.8	29.0	0.501	31.8	2.62	3.23
TCS 20692	0.092	0.74	3.36	5	23.3	0.25	0.074	0.66	0.61	15.3	1.7	14.0	0.456	7.27	0.63	2.34
TCS 20693	0.054	1.24	6.36	5	23.9	0.44	0.094	0.2	0.35	25.1	5.5	23.3	0.539	7.07	1.70	2.76
TCS 20694	0.077	0.73	2.99	5	26.4	0.26	0.072	1.02	0.67	15.4	1.8	13.4	0.427	8.19	0.69	2.22
TCS 20695	0.052	1.16	6.54	5	27.8	0.57	0.087	0.2	0.43	29.1	7.7	23.8	0.383	8.28	1.97	2.71
TCS 20696	0.078	0.66	3.54	5	23.4	0.31	0.075	1.57	0.79	16.0	2.2	12.6	0.34	9.77	0.86	2.10
TCS 20697	0.106	1.29	7.32	5	21.1	0.8	0.101	0.45	0.79	32.8	5.9	25.9	0.493	9.01	2.16	2.40
TCS 20698	0.124	1.02	4.47	5	46.9	0.55	0.094	0.38	1.10	28.0	3.0	20.0	0.734	9.84	1.45	2.73
TCS 20699	0.093	0.55	4.55	5	22.1	0.51	0.062	13.4	1.75	21.5	4.5	14.0	0.277	12	1.33	1.39
TCS 20701	0.126	1	3.84	5	43.2	0.47	0.103	0.3	0.95	28.3	2.2	18.4	0.561	9.91	1.04	2.61
TCS 20702	0.186	0.75	3.99	5	25.6	0.7	0.085	4.51	1.48	30.6	3.5	19.0	0.231	12.15	1.44	1.97
TCS 20703	0.115	0.79	5.18	5	34.5	0.61	0.094	1.7	1.78	29.8	5.5	18.2	0.28	15.6	1.50	2.00
TCS 20704	0.117	0.71	4.28	5	32.6	0.51	0.095	3.97	1.84	27.2	5.1	16.8	0.279	14.4	1.32	1.76
TCS 20705	0.106	0.89	3.44	5	38.3	0.52	0.083	0.2	0.89	26.0	3.5	18.0	0.645	8.53	1.27	2.42
TCS 20706	0.137	0.78	5	5	35.6	0.71	0.096	0.23	1.44	29.3	5.2	19.5	0.322	8.8	1.65	2.01
TCS 20707	0.074	1.3	10.05	5	37.8	1.26	0.144	0.14	1.46	69.8	10.6	30.0	0.474	23.9	2.67	2.93
TCS 20708	0.081	0.89	4.6	5	24	0.36	0.084	0.11	0.36	20.9	3.9	16.8	0.63	10.35	1.42	2.27
TCS 20709	0.11	1.1	8.25	5	34.9	1.2	0.124	0.08	2.10	57.5	9.2	26.0	0.401	19.7	2.30	2.29
TCS 20711	0.074	0.91	5.64	5	31.5	0.47	0.091	0.17	1.04	29.0	5.2	19.1	0.609	14.25	1.52	2.17
TCS 20712	0.126	0.64	8.53	10	26.5	1.17	0.104	0.33	2.95	43.6	8.4	19.7	0.316	25.7	1.87	1.60
TCS 20713	0.092	0.85	4.87	10	38.4	0.46	0.092	0.21	0.98	24.9	5.0	17.6	0.41	12.15	1.35	2.15
TCS 20714	0.126	0.7	6.86	10	30.1	0.9	0.09	1.48	2.54	34.7	6.8	17.5	0.318	19.3	1.78	1.81
TCS 20715	0.085	0.94	4.52	10	41.7	0.51	0.076	0.23	1.02	23.6	4.9	17.8	0.441	11.85	1.39	2.35
TCS 20716	0.151	0.74	6.32	10	32.1	0.64	0.091	0.32	2.11	31.9	6.7	16.9	0.326	17.9	1.70	1.81

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Pd (ppm)
TCS 20688	0.047	0.096	0.052	0.024	0.08	24.5	13.2	0.37	611	1.69	0.005	0.291	58.2	0.033	22.6	0.0005
TCS 20689	0.045	0.069	0.086	0.022	0.05	19.45	7	0.13	386	2.57	0.003	0.157	32.6	0.053	22.8	0.0005
TCS 20691	0.096	0.057	0.124	0.027	0.08	38.4	9.3	0.2	652	2.98	0.005	0.163	75.8	0.034	19.1	0.0005
TCS 20692	0.024	0.044	0.075	0.016	0.09	8.15	6.5	0.09	138.5	0.98	0.004	0.178	9.78	0.107	15.2	0.0005
TCS 20693	0.035	0.052	0.064	0.022	0.08	11.7	12.6	0.19	104.5	1.33	0.005	0.222	29	0.02	13.7	0.0005
TCS 20694	0.024	0.037	0.069	0.013	0.11	8.21	5.7	0.1	159.5	1.06	0.008	0.151	10.05	0.127	15.5	0.0005
TCS 20695	0.037	0.051	0.068	0.02	0.08	14.4	10.1	0.2	207	1.38	0.004	0.214	30.2	0.015	12.55	0.0005
TCS 20696	0.029	0.044	0.069	0.01	0.12	8.47	5	0.1	159	1.68	0.008	0.136	12.2	0.122	13.55	0.0005
TCS 20697	0.048	0.084	0.086	0.022	0.12	18.2	35.6	0.25	166	2.5	0.007	0.192	38.5	0.03	12.85	0.0005
TCS 20698	0.042	0.076	0.091	0.024	0.04	15.85	5.6	0.1	100.5	0.84	0.005	0.169	12.95	0.076	18.2	0.001
TCS 20699	0.043	0.047	0.048	0.015	0.04	12.6	3.7	0.24	234	1.83	0.014	0.099	30.8	0.05	20.1	0.005
TCS 20701	0.039	0.097	0.098	0.019	0.05	15.9	5.2	0.09	121	0.81	0.007	0.164	11.05	0.081	18.1	0.0005
TCS 20702	0.041	0.072	0.116	0.018	0.04	19.2	4.9	0.15	145.5	1.77	0.009	0.093	23.7	0.075	10.2	0.002
TCS 20703	0.045	0.098	0.073	0.018	0.08	16.55	5.5	0.13	419	2.38	0.009	0.152	28.5	0.101	15.35	0.0005
TCS 20704	0.039	0.094	0.076	0.016	0.06	15.05	5.2	0.15	331	1.88	0.009	0.113	29	0.081	13.6	0.002
TCS 20705	0.033	0.076	0.062	0.017	0.04	14.4	5.5	0.1	201	1.21	0.004	0.121	15.45	0.051	14.7	0.0005
TCS 20706	0.046	0.06	0.102	0.019	0.04	21.7	4.7	0.09	504	1.97	0.004	0.12	28.3	0.025	10.5	0.0005
TCS 20707	0.094	0.067	0.093	0.033	0.07	40.1	9.1	0.17	515	6.76	0.003	0.182	58.5	0.027	18.45	0.0005
TCS 20708	0.03	0.048	0.043	0.016	0.04	9.36	6.5	0.09	210	2.53	0.006	0.128	15	0.048	12.05	0.0005
TCS 20709	0.071	0.063	0.102	0.029	0.05	29.8	6.5	0.11	564	4.42	0.004	0.118	48.1	0.035	13.75	0.0005
TCS 20711	0.026	0.062	0.051	0.019	0.04	12.05	6.2	0.1	321	2.78	0.005	0.132	29.6	0.043	12.1	0.0005
TCS 20712	0.075	0.029	0.07	0.019	0.04	32.4	4.2	0.09	449	5.48	0.002	0.101	53.4	0.038	11.6	0.001
TCS 20713	0.039	0.077	0.047	0.016	0.05	12.8	5.8	0.09	342	2.34	0.007	0.178	23.4	0.043	11.9	0.001
TCS 20714	0.064	0.059	0.058	0.02	0.04	22.8	5	0.11	394	4.36	0.007	0.132	46.1	0.043	11.5	0.002
TCS 20715	0.035	0.084	0.04	0.017	0.05	11.75	6.3	0.1	398	2.2	0.01	0.169	21.4	0.045	11.95	0.0005
TCS 20716	0.055	0.074	0.043	0.016	0.04	18.15	5.8	0.1	398	3.92	0.009	0.118	41.3	0.053	11.05	0.001

Soil and till samples results (aqua regia digestion, continued).

Sample name	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)	V (ppm)
TCS 20688	0.001	9.2	0.0005	0.005	1.44	4.53	0.9	0.52	20	0.0025	0.04	2.8	0.011	0.25	0.681	36.6
TCS 20689	0.001	12.25	0.0005	0.03	1.105	2.91	1.4	0.51	6.98	0.0025	0.01	1.29	0.003	0.319	1.085	31.9
TCS 20691	0.001	7.65	0.0005	0.005	1.575	7.28	2.1	0.47	14.1	0.0025	0.04	2.59	0.004	0.366	1.24	46.4
TCS 20692	0.001	7.43	0.0005	0.06	0.306	0.937	1	0.42	22	0.0025	0.005	0.52	0.002	0.169	0.621	28.4
TCS 20693	0.001	7.14	0.0005	0.01	0.485	2.13	1	0.33	12.9	0.0025	0.005	2.18	0.004	0.188	0.59	30.5
TCS 20694	0.001	7.38	0.0005	0.08	0.292	1.03	1	0.46	28.9	0.0025	0.005	0.518	0.002	0.174	0.606	26.3
TCS 20695	0.001	6.33	0.0005	0.01	0.544	3.06	1	0.33	11.95	0.0025	0.005	2.48	0.004	0.163	0.63	28.5
TCS 20696	0.001	6.58	0.001	0.08	0.402	1.175	1.3	0.44	39.1	0.0025	0.01	0.722	0.002	0.166	0.496	27.8
TCS 20697	0.001	8.89	0.0005	0.02	0.698	3.63	1.5	0.39	15.95	0.0025	0.02	2.26	0.003	0.238	0.737	45.8
TCS 20698	0.001	5.29	0.0005	0.06	0.498	2.9	1.6	0.54	17.8	0.0025	0.02	1.475	0.002	0.277	1.02	41.3
TCS 20699	0.001	3.34	0.001	0.02	0.965	3.38	0.7	0.25	543	0.0025	0.01	1.92	0.004	0.151	1.265	25.3
TCS 20701	0.001	7.07	0.0005	0.06	0.409	2.48	1.2	0.61	13.65	0.0025	0.005	1.255	0.002	0.237	1.24	37.5
TCS 20702	0.001	3.58	0.0005	0.02	1.03	3.78	1.2	0.36	167.5	0.0025	0.02	1.795	0.002	0.128	0.932	35.1
TCS 20703	0.001	7.84	0.0005	0.05	0.696	2.89	1.5	0.81	59.2	0.0025	0.01	1.22	0.002	0.193	0.666	36.7
TCS 20704	0.001	6.32	0.001	0.05	0.723	2.87	1.6	1.32	139.5	0.0025	0.01	1.365	0.002	0.165	0.722	29.2
TCS 20705	0.001	8.04	0.0005	0.03	0.422	2.51	1.1	0.5	11.55	0.0025	0.005	1.325	0.002	0.223	0.738	33.3
TCS 20706	0.001	6.16	0.0005	0.01	0.759	4	1.3	0.37	15.1	0.0025	0.01	1.83	0.002	0.173	0.561	35.5
TCS 20707	0.001	9.69	0.0005	0.01	1.24	6.34	2.5	0.48	9.73	0.0025	0.04	2.42	0.003	0.436	1.445	48.5
TCS 20708	0.001	10.25	0.0005	0.02	0.473	1.66	1	0.4	5.48	0.0025	0.02	1.005	0.003	0.226	0.99	30.5
TCS 20709	0.001	9.19	0.0005	0.01	1.18	4.99	2	0.4	6.59	0.0025	0.02	1.73	0.002	0.354	1.285	52.2
TCS 20711	0.001	9.99	0.0005	0.02	0.737	2.35	1.4	0.43	10.2	0.0025	0.02	1.395	0.003	0.275	1.1	34.4
TCS 20712	0.001	6.4	0.001	0.01	1.525	5.74	2	0.32	19.4	0.0025	0.05	1.445	0.002	0.354	1.25	51.9
TCS 20713	0.002	7.69	0.0005	0.03	0.617	2.6	0.9	0.45	9.18	0.0025	0.02	1.27	0.002	0.218	1.15	37
TCS 20714	0.001	5.72	0.0005	0.02	1.37	4.48	1.1	0.32	57.8	0.0025	0.03	1.435	0.002	0.313	0.912	43.2
TCS 20715	0.001	8.54	0.001	0.03	0.566	2.46	1.1	0.44	9.46	0.0025	0.04	1.19	0.003	0.222	1.285	36.8
TCS 20716	0.001	5.79	0.001	0.02	1.105	3.78	1.1	0.34	19.55	0.0025	0.03	1.485	0.002	0.275	0.839	40.7

Soil and till samples results (aqua regia digestion, continued).

Sample name	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH (lab)	LOI (%)
TCS 20688	0.051	23.6	171	3.47	5.09	4.89
TCS 20689	0.038	21.1	139.5	2.17	4.49	7.59
TCS 20691	0.057	55.1	131.5	2	4.91	4.78
TCS 20692	0.085	5.19	54.1	1	6.61	12.55
TCS 20693	0.036	5.92	66.5	1.88	6.33	4.76
TCS 20694	0.07	5.83	59.3	1.12	6.82	14.25
TCS 20695	0.037	9.99	60	1.87	6.54	4.19
TCS 20696	0.054	7.04	61.4	1.34	7.13	13.6
TCS 20697	0.05	20	96.5	2.59	6.89	5.92
TCS 20698	0.048	17.4	63.9	2.28	5.6	11.8
TCS 20699	0.03	15.9	58.2	2.57	7.2	2.65
TCS 20701	0.06	17.2	57.9	2.68	5.48	11.1
TCS 20702	0.036	25	48.1	2.37	7.19	4.3
TCS 20703	0.073	20	87.2	2.93	7.18	8.71
TCS 20704	0.049	18.6	79.5	3.08	7.29	7.73
TCS 20705	0.048	15.5	66.3	2.11	5.03	7.92
TCS 20706	0.053	27.8	57.3	2.07	5.5	4.5
TCS 20707	0.053	48.7	131.5	2.06	5.01	5.31
TCS 20708	0.039	8.28	69.4	1.23	4.8	5
TCS 20709	0.05	40.1	131	2.31	4.4	4.84
TCS 20711	0.038	11.7	88.7	2.22	5.04	5.3
TCS 20712	0.038	44.9	109.5	1.28	6.66	3.9
TCS 20713	0.035	13.35	74.9	2.38	5.92	5.44
TCS 20714	0.041	30.2	94.2	2.04	7.24	4.38
TCS 20715	0.032	11.55	76.2	2.23	6.04	5.12
TCS 20716	0.033	23.1	80.7	2.28	6.42	4.16

Soil and till samples results (aqua regia digestion, continued).

Sample name	Project	Soil_Horizon	ING_TM65_X	UTM 29 E	ING_TM65_Y	UTM 29 N	Location	Duplicate	Clasts
TCS 20717	IsoNose	BC	235474	601519	265729	5944602	Outside	x	mm gravels
TCS 20718	IsoNose	Top of till	235473	601518	265728	5944601	Outside	x	2-3 cm gravels
TCS 20719	IsoNose	BC	235494	601539	265713	5944586	Outside	x	mm gravels
TCS 20721	IsoNose	Top of till	235496	601541	265714	5944587	Outside	x	2-3 cm gravels
TCS 20722	IsoNose	BC	235513	601559	265697	5944570	Outside	x	mm gravels
TCS 20723	IsoNose	Top of till	235516	601562	265695	5944568	Outside	x	2-3 cm gravels
TCS 20724	IsoNose	BC	234919	600965	265691	5944556	Outside	x	mm gravels
TCS 20725	IsoNose	BC	234935	600981	265710	5944575	Outside	x	mm gravels
TCS 20726	IsoNose	Top of till	234931	600977	265709	5944574	Outside	x	2-3 cm gravels
TCS 20727	IsoNose	BC	234951	600996	265730	5944595	Outside	x	mm gravels
TCS 20728	IsoNose	Top of till	234948	600993	265732	5944597	Outside	x	2-3 cm gravels
TCS 20729	IsoNose	BC	234966	601011	265749	5944614	Outside	x	mm gravels
TCS 20731	IsoNose	Top of till	234968	601013	265751	5944616	Outside	x	1-2 cm gravels
TCS 20732	IsoNose	BC	234982	601027	265769	5944635	Outside	x	mm gravels
TCS 20733	IsoNose	Top of till	234978	601023	265771	5944637	Outside	x	2-3 cm gravels
TCS 20734	IsoNose	BC	234982	601027	265769	5944635	Outside	Dup of 20732	mm gravels
TCS 20735	IsoNose	Top of till	234978	601023	265771	5944637	Outside	Dup of 20733	2-3 cm gravels
TCS 20736	IsoNose	BC	234998	601043	265788	5944654	Flank	x	mm gravels
TCS 20737	IsoNose	Top of till	234999	601044	265789	5944655	Flank	x	2 cm gravels
TCS 20738	IsoNose	BC	235014	601058	265808	5944674	Flank	x	mm gravels
TCS 20739	IsoNose	Top of till	235016	601060	265807	5944673	Flank	x	2-3 cm gravels
TCS 20741	IsoNose	BC	235029	601073	265827	5944693	Mineralisation	x	bedrock gravels
TCS 20742	IsoNose	BC	235044	601088	265848	5944714	Mineralisation	x	mm gravels
TCS 20743	IsoNose	Top of till	235046	601090	265848	5944715	Mineralisation	x	2-3 cm gravels
TCS 20744	IsoNose	BC or C	235060	601103	265867	5944734	Flank	x	up to 3 cm gravels
TCS 20745	IsoNose	Top of till	235061	601104	265869	5944736	Flank	x	3 cm gravels

Soil and till samples results (aqua regia digestion, continued).

Sample name	Characteristics	Moisture	Parent_Material	Line	Physiography	Contamination	Comp_Silt
TCS 20717	black chips, weathering in grey	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20718	weathering in black, lt.brown, white	moist	CALP	Line 4	Pastureland	Possible	XX
TCS 20719	low level of grey weathering	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20721	weathering in black, orange	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20722	low level of oxidation in grey	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20723	weathering in black, orange	moist	CALP	Line 4	Pastureland	Possible	X
TCS 20724	no till	dry	WA	Line 3	Pastureland	Possible	XX
TCS 20725	-	dry to moist	WA	Line 3	Pastureland	Possible	XX
TCS 20726	weathering in dark brow to light brown	dry to moist	WA	Line 3	Pastureland	Possible	X
TCS 20727	black chips	dry to moist	WA	Line 3	Pastureland	Possible	XX
TCS 20728	weathering in black, lt. brown, green	dry to moist	WA	Line 3	Pastureland	Possible	X
TCS 20729	black chips	dry to moist	WA	Line 3	Pastureland	Possible	XX
TCS 20731	weathering in black	dry to moist	WA	Line 3	Pastureland	Possible	X
TCS 20732	black chips	dry to moist	WA	Line 3	Pastureland	Possible	XX
TCS 20733	weathering in black, lt. brown, white	moist	WA	Line 3	Pastureland	Possible	X
TCS 20734	black chips	dry to moist	WA	Line 3	Pastureland	Possible	XX
TCS 20735	weathering in black, lt. brown, white	moist	WA	Line 3	Pastureland	Possible	X
TCS 20736	black chips	dry to moist	WA	Line 3	Pastureland	Possible	XX
TCS 20737	low level of weathering	dry to moist	WA	Line 3	Pastureland	Possible	XX
TCS 20738	black chips	dry to moist	WA	Line 3	Pastureland	Possible	X
TCS 20739	gravels black, white; weathering in black and white	dry	WA	Line 3	Pastureland	Possible	XX
TCS 20741	hitting bedrock (weathered): WA	dry	WA	Line 3	Pastureland	Possible	X
TCS 20742	bedrock gravels	dry to moist	SWA	Line 3	Pastureland	Possible	XX
TCS 20743	weathering black, white, orange lines	moist	SWA	Line 3	Pastureland	Possible	XX
TCS 20744	black chips, weathered dolomite (yellowish)	moist	SWA	Line 3	Pastureland	Possible	XX
TCS 20745	weathering in grey, black, orange (dolomite)	moist	SWA	Line 3	Pastureland	Possible	X

Soil and till samples results (aqua regia digestion, continued).

Sample name	Comp_Sand	Comp_Organic	Comp_Clay	Sampling_Method	Slope	Year_Collected	Soil_Colour	Soil_From (m)	Soil_To (m)	Au (ppm)
TCS 20717	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0015
TCS 20718	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.5	0.7	0.0018
TCS 20719	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.002
TCS 20721	-	-	X	Auger	flat 0-5 ⁰	2015	lt. brown	0.67	0.75	0.0019
TCS 20722	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0009
TCS 20723	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.35	0.7	0.0017
TCS 20724	-	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.45	0.0015
TCS 20725	-	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.55	0.0013
TCS 20726	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.9	1.1	0.0024
TCS 20727	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0013
TCS 20728	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.55	0.75	0.0018
TCS 20729	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0017
TCS 20731	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.6	0.75	0.0021
TCS 20732	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.3	0.0021
TCS 20733	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.45	0.6	0.0019
TCS 20734	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0018
TCS 20735	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.45	0.55	0.0021
TCS 20736	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.2	0.35	0.0022
TCS 20737	-	-	-	Auger	flat 0-5 ⁰	2015	lt. brown	0.5	0.65	0.0019
TCS 20738	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.3	0.3	0.0024
TCS 20739	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.6	0.75	0.0018
TCS 20741	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.35	0.0019
TCS 20742	X	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.2	0.35	0.0031
TCS 20743	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.65	0.8	0.0063
TCS 20744	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.22	0.35	0.0012
TCS 20745	-	-	X	Auger	flat 0-5 ⁰	2015	lt. brown to grey	0.32	0.58	0.0018

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)
TCS 20717	0.077	0.92	4.61	10	33.9	0.29	0.08	0.19	0.52	19.2	4.0	17.3	0.7	10.2	1.21	2.28
TCS 20718	0.063	0.97	6.96	10	26.3	0.87	0.103	0.15	1.04	49.2	9.0	24.1	0.404	20.5	1.93	2.18
TCS 20719	0.072	0.99	5.51	10	27.7	0.37	0.098	0.15	0.62	19.6	5.7	20.2	0.632	12.4	1.68	2.36
TCS 20721	0.105	1	9.13	5	36.7	1.65	0.113	0.15	2.35	60.1	8.6	24.5	0.46	27	2.28	2.37
TCS 20722	0.068	0.85	3.4	5	25.3	0.24	0.074	0.17	0.37	15.6	3.2	14.4	0.556	8.17	1.15	2.29
TCS 20723	0.062	1.08	7.58	10	28.6	0.74	0.11	0.14	0.89	43.1	9.8	22.8	0.482	20.4	2.03	2.10
TCS 20724	0.13	1.01	34.2	10	69.8	0.56	0.094	0.23	1.45	27.4	7.3	17.5	0.71	12.8	1.72	2.63
TCS 20725	0.124	0.93	23.1	10	53.4	0.45	0.1	0.21	1.19	28.8	7.4	18.7	0.655	14.9	1.64	2.24
TCS 20726	0.103	0.95	15.7	10	53.7	1.24	0.122	0.25	2.66	42.4	9.6	22.4	0.444	29.7	2.18	2.86
TCS 20727	0.137	0.9	24.2	5	56.7	0.47	0.092	0.16	1.03	27.1	6.4	18.2	0.634	14.35	1.56	2.32
TCS 20728	0.07	0.84	12.1	5	28.7	0.84	0.116	0.13	1.26	50.5	9.1	20.5	0.345	22.8	1.94	1.98
TCS 20729	0.195	0.94	32.1	5	73.2	0.65	0.111	0.24	2.21	34.0	8.2	20.2	0.564	18.15	1.82	2.43
TCS 20731	0.258	0.8	17.45	5	78.7	1.03	0.112	0.25	2.95	38.5	8.9	21.4	0.433	28.8	2.17	2.19
TCS 20732	0.311	0.89	46.5	10	92	0.73	0.107	0.55	4.04	36.6	9.1	20.9	0.482	21.7	1.88	2.36
TCS 20733	0.169	0.72	16.7	10	52.7	0.65	0.102	5.16	4.82	32.9	8.8	17.4	0.374	24.5	1.79	1.71
TCS 20734	0.29	0.9	44.1	5	88.9	0.8	0.105	0.5	3.92	34.3	8.8	19.8	0.478	21.2	1.88	2.51
TCS 20735	0.25	0.84	23.1	5	65.9	0.8	0.114	1.75	4.43	37.3	9.6	20.1	0.41	28.7	1.97	2.16
TCS 20736	0.299	1	44.8	5	91.2	0.52	0.097	0.23	2.01	28.7	7.7	19.7	0.729	14.15	1.72	2.61
TCS 20737	0.053	1.33	13.1	5	43.7	0.6	0.114	0.12	0.54	38.1	11.4	27.8	0.664	14.75	2.25	3.69
TCS 20738	1.115	0.97	145.5	5	221	0.71	0.102	0.39	5.39	30.6	8.9	18.7	0.596	15.2	2.21	2.77
TCS 20739	4.03	0.72	362	5	186.5	0.94	0.107	2.91	24.60	35.7	13.7	17.8	0.371	22.4	3.96	2.56
TCS 20741	2.44	0.81	278	5	412	0.66	0.1	3.7	14.30	30.6	10.1	18.1	0.343	16.8	2.73	2.60
TCS 20742	5.01	1.01	168	5	289	0.64	0.109	1.17	19.00	30.8	7.3	20.3	0.554	18.2	2.08	3.16
TCS 20743	8.22	0.74	178.5	5	225	0.53	0.09	6.49	24.40	26.2	7.5	16.4	0.436	19.75	1.98	2.62
TCS 20744	1.43	1.04	44	5	205	0.71	0.063	1.69	15.70	27.9	4.5	21.3	0.46	8.98	1.99	3.05
TCS 20745	0.373	0.82	6.56	5	109.5	0.44	0.057	10.95	8.77	26.9	4.2	17.6	0.403	7.22	0.93	2.01

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Pd (ppm)
TCS 20717	0.028	0.046	0.033	0.013	0.04	9.54	6.3	0.09	226	2.1	0.007	0.16	15.2	0.042	12.95	0.0005
TCS 20718	0.067	0.026	0.096	0.019	0.06	24.6	6.3	0.14	300	3.22	0.007	0.196	47.7	0.017	12.3	0.002
TCS 20719	0.032	0.046	0.063	0.016	0.05	8.71	8.1	0.11	266	2.83	0.007	0.195	24.6	0.039	12.85	0.0005
TCS 20721	0.101	0.038	0.084	0.029	0.06	39.6	6.7	0.12	428	4.76	0.005	0.157	68.3	0.024	12.85	0.001
TCS 20722	0.029	0.039	0.044	0.007	0.06	7.44	6.7	0.09	178.5	1.77	0.007	0.143	11.8	0.045	11.3	0.001
TCS 20723	0.055	0.044	0.063	0.021	0.06	18.65	7.2	0.12	317	3.79	0.007	0.198	47.6	0.024	13.45	0.001
TCS 20724	0.04	0.07	0.088	0.016	0.05	13.65	7.2	0.12	995	2.77	0.007	0.168	25.4	0.057	64.8	0.0005
TCS 20725	0.035	0.064	0.084	0.015	0.05	14.15	6.6	0.12	761	3.07	0.008	0.189	25.6	0.054	62.4	0.0005
TCS 20726	0.089	0.041	0.096	0.022	0.07	29.7	8.4	0.15	730	4.24	0.007	0.152	62.8	0.05	30.4	0.002
TCS 20727	0.035	0.071	0.084	0.013	0.05	12.7	6.9	0.12	537	2.59	0.006	0.173	23	0.053	68.7	0.0005
TCS 20728	0.075	0.025	0.093	0.019	0.05	27.2	6.4	0.13	583	3.98	0.006	0.138	48.8	0.031	26.3	0.001
TCS 20729	0.051	0.083	0.133	0.022	0.05	19	6.9	0.13	829	3.05	0.008	0.188	34.6	0.058	98.4	0.001
TCS 20731	0.07	0.061	0.193	0.022	0.06	24.4	6.1	0.13	681	5.71	0.005	0.138	59.5	0.045	58.2	0.001
TCS 20732	0.056	0.095	0.162	0.021	0.05	21.8	6.9	0.15	785	3.18	0.006	0.183	49.5	0.058	141	0.0005
TCS 20733	0.05	0.052	0.098	0.015	0.06	18.2	5.8	0.19	493	3.56	0.008	0.15	69.5	0.057	40.2	0.002
TCS 20734	0.063	0.086	0.214	0.022	0.05	20.5	7.1	0.16	769	3.01	0.008	0.171	48.2	0.055	139	0.0005
TCS 20735	0.06	0.067	0.129	0.02	0.06	22.5	6.9	0.17	589	3.79	0.007	0.146	70	0.057	53.5	0.002
TCS 20736	0.045	0.08	0.207	0.015	0.04	14.05	7.2	0.14	816	2.9	0.007	0.201	26.2	0.055	188	0.001
TCS 20737	0.045	0.028	0.068	0.018	0.07	14.55	15	0.37	453	1.62	0.006	0.366	39.7	0.017	45.9	0.002
TCS 20738	0.049	0.094	0.5	0.02	0.05	17	7	0.13	1040	3.16	0.009	0.172	34.1	0.06	530	0.0005
TCS 20739	0.072	0.064	2.26	0.02	0.05	22.5	5.9	0.14	1620	5.32	0.008	0.163	85.3	0.051	544	0.003
TCS 20741	0.069	0.081	1.755	0.02	0.05	17.85	6.6	0.32	790	3.96	0.012	0.167	52	0.074	1550	0.0005
TCS 20742	0.055	0.107	2.99	0.018	0.04	16.9	7.1	0.19	486	2.1	0.009	0.203	42.9	0.064	2050	0.003
TCS 20743	0.049	0.056	4.21	0.017	0.04	13.65	6.1	0.38	393	2.33	0.01	0.148	45.6	0.056	2400	0.003
TCS 20744	0.053	0.053	0.631	0.016	0.04	17.3	7.8	0.24	79	0.85	0.008	0.184	42.2	0.057	730	0.002
TCS 20745	0.047	0.026	0.25	0.017	0.05	15.3	7.4	0.44	129	0.51	0.016	0.144	39.7	0.055	184.5	0.003

Soil and till samples results (aqua regia digestion, continued).

Sample name	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)	V (ppm)
TCS 20717	0.001	10.6	0.0005	0.02	0.463	1.81	0.8	0.42	6.95	0.0025	0.01	0.984	0.003	0.267	1.26	34.3
TCS 20718	0.001	6.64	0.0005	0.01	1.21	5.57	1.4	0.33	8.16	0.0025	0.04	2.05	0.004	0.32	0.925	41.9
TCS 20719	0.001	9.95	0.001	0.02	0.765	1.985	1.1	0.45	6.5	0.0025	0.03	1.255	0.003	0.273	1.03	38.3
TCS 20721	0.001	7.37	0.0005	0.01	1.43	8.66	2	0.4	11.1	0.0025	0.04	1.895	0.003	0.39	1.355	49.6
TCS 20722	0.001	8.77	0.0005	0.03	0.385	1.26	0.7	0.37	5.51	0.0025	0.03	0.854	0.002	0.208	0.829	27.5
TCS 20723	0.001	7.03	0.001	0.02	1.355	4.28	1.3	0.34	7.89	0.0025	0.06	1.84	0.003	0.304	1.155	40
TCS 20724	0.001	11.9	0.0005	0.03	2.17	2.22	0.8	0.52	10.05	0.0025	0.03	1.15	0.003	0.671	0.717	33.6
TCS 20725	0.001	11.95	0.0005	0.03	1.92	2.46	0.8	0.47	9.36	0.0025	0.05	1.235	0.003	0.607	0.973	35.6
TCS 20726	0.001	8.48	0.0005	0.02	2.09	4.48	1.9	0.41	14.05	0.0025	0.05	1.415	0.003	0.505	0.997	46.3
TCS 20727	0.001	10.8	0.0005	0.03	2.18	2.3	1.1	0.52	6.97	0.0025	0.02	1.165	0.003	0.561	0.742	32.8
TCS 20728	0.002	6.7	0.001	0.01	2.01	4.51	1.9	0.3	7.93	0.0025	0.06	1.485	0.003	0.359	1.1	39.4
TCS 20729	0.001	10.7	0.0005	0.03	3.2	3	1.6	0.57	10.35	0.0025	0.04	1.28	0.003	0.746	0.863	38.1
TCS 20731	0.002	8.16	0.001	0.02	2.96	4.36	1.7	0.4	14.25	0.0025	0.05	1.495	0.003	0.607	1.005	49.5
TCS 20732	0.001	9.01	0.001	0.04	4.95	3.68	1.4	0.52	20.6	0.0025	0.06	1.35	0.003	0.917	0.636	40.4
TCS 20733	0.001	5.97	0.001	0.03	2.68	4.04	1.1	0.29	171.5	0.0025	0.05	1.565	0.003	0.535	0.956	34.1
TCS 20734	0.001	8.87	0.001	0.04	4.86	3.63	1.6	0.43	21.3	0.0025	0.05	1.3	0.003	0.873	0.597	39.1
TCS 20735	0.001	7.49	0.001	0.02	3.04	4.69	1.2	0.36	60.9	0.0025	0.05	1.56	0.003	0.596	0.811	39.8
TCS 20736	0.001	11.7	0.0005	0.03	5.05	2.46	1.2	0.5	9.61	0.0025	0.04	1.27	0.003	1.265	0.913	36.2
TCS 20737	0.001	8.41	0.0005	0.01	1.725	3.51	0.9	0.34	10.2	0.0025	0.03	2.52	0.011	0.359	0.827	32.2
TCS 20738	0.001	10.55	0.001	0.04	17.6	3.12	1.3	0.62	10.6	0.0025	0.04	1.35	0.003	3.03	0.703	37.3
TCS 20739	0.002	7.53	0.0005	0.04	42	4.05	1.8	0.33	36.6	0.0025	0.06	1.695	0.003	4.17	0.726	33.6
TCS 20741	0.001	6.92	0.001	0.06	56.1	3.17	1.2	0.36	93.5	0.0025	0.05	1.255	0.003	8.56	0.691	33.1
TCS 20742	0.002	7.6	0.0005	0.05	38.8	3.34	1.5	0.48	26.2	0.0025	0.05	1.41	0.003	3.53	0.519	35.7
TCS 20743	0.001	5.14	0.001	0.05	56.2	2.97	1.5	0.3	189	0.0025	0.03	1.295	0.003	2.91	0.794	27.1
TCS 20744	0.001	3.29	0.001	0.02	18.1	3.69	1.7	0.35	57	0.0025	0.03	2.15	0.003	2.14	0.81	39.4
TCS 20745	0.001	3.87	0.001	0.03	4.64	3.25	0.7	0.23	302	0.0025	0.02	2.19	0.003	0.898	0.927	27.5

Soil and till samples results (aqua regia digestion, continued).

Sample name	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH (lab)	LOI (%)
TCS 20717	0.033	7.81	69	1.25	5.99	5.05
TCS 20718	0.04	29	96.1	1.1	5.78	3.46
TCS 20719	0.039	6.6	79.2	1.34	5.29	5.55
TCS 20721	0.051	53.2	113	1.3	5.21	4.49
TCS 20722	0.028	4.92	57	1.01	5.41	6.02
TCS 20723	0.045	19.9	108	1.55	5.31	4.34
TCS 20724	0.038	12.5	261	1.81	5.94	5.64
TCS 20725	0.05	13.05	234	1.87	5.8	5.21
TCS 20726	0.059	39.6	245	1.43	6.27	4.35
TCS 20727	0.039	11.4	271	2.15	5.02	5.93
TCS 20728	0.059	26.9	180	0.93	5.08	3.81
TCS 20729	0.042	21	387	2.77	5.37	6.78
TCS 20731	0.06	32.5	389	2.06	5.74	4.9
TCS 20732	0.056	26.9	600	3.18	6.82	7.23
TCS 20733	0.044	23.3	226	1.7	7.17	3.71
TCS 20734	0.04	25.5	590	2.96	7.01	7.15
TCS 20735	0.049	29.9	273	2.09	7.32	4.58
TCS 20736	0.04	13.2	482	2.21	5.77	5.96
TCS 20737	0.047	6.96	287	1.06	5.58	3.37
TCS 20738	0.043	18.65	1170	2.61	6.48	6.27
TCS 20739	0.05	28.1	2670	2.21	7.35	4.99
TCS 20741	0.044	22.1	4030	2.55	7.35	7.46
TCS 20742	0.04	18.8	3890	2.95	7.23	8.08
TCS 20743	0.032	15.85	4050	1.88	7.44	5.36
TCS 20744	0.041	17.65	5450	1.7	7.23	4.99
TCS 20745	0.022	14.6	2820	1.75	7.31	2.75

Soil and till samples results (aqua regia digestion, continued).

Sample name	Project	Soil_Horizon	ING_TM65_X	UTM 29 E	ING_TM65_Y	UTM 29 N	Location	Duplicate	Clasts
TCS 20746	IsoNose	Top of till	235075	601118	265886	5944753	Outside	x	3 cm gravels
TCS 20747	IsoNose	Top of till	235087	601130	265901	5944768	Outside	x	2-3 cm gravels
TCS 20748	IsoNose	BC	235131	601173	265956	5944824	Outside	x	mm gravels
TCS 20749	IsoNose	Top of till	235128	601170	265954	5944822	Outside	x	2 cm gravels
TCS 20751	IsoNose	Top of till	235145	601187	265974	5944842	Outside	x	2-3 cm gravels
TCS 20752	IsoNose	BC	235160	601202	265992	5944860	Outside	x	mm gravels
TCS 20753	IsoNose	Top of till	235159	601201	265993	5944861	Outside	x	2-3 cm gravels
TCS 20754	IsoNose	Top of till	235159	601201	265993	5944861	Outside	Dup of 20753	2-3 cm gravels
TCS 20755	IsoNose	BC	235130	601169	266195	5945063	Mineralisation	x	mm gravels black
TCS 20756	IsoNose	Top of till	235130	601169	266195	5945063	Mineralisation	x	cm gravels black
TCS 20757	IsoNose	Top of till	235130	601169	266195	5945063	Mineralisation	x	cm gravels black
TCS 20758	IsoNose	BC	235141	601180	266196	5945064	Mineralisation	x	mm gravels black
TCS 20759	IsoNose	Top of till	235141	601180	266196	5945064	Mineralisation	x	cm gravels black
TCS 20761	IsoNose	Top of till	235141	601180	266196	5945064	Mineralisation	x	mm gravels black
TCS 20762	IsoNose	BC	234909	600941	266669	5945533	Outside	x	mm gravels black
TCS 20763	IsoNose	Top of till	234909	600941	266669	5945533	Outside	x	cm gravels black
TCS 20764	IsoNose	BC	234961	600994	266606	5945471	Outside	x	mm gravels black
TCS 20765	IsoNose	Top of till	234961	600994	266606	5945471	Outside	x	cm gravels black
TCS 20766	IsoNose	BC	234899	600933	266567	5945431	Outside	x	cm gravels black
TCS 20767	IsoNose	Top of till	234899	600933	266567	5945431	Outside	x	cm gravels black

Soil and till samples results (aqua regia digestion, continued).

Sample name	Characteristics	Moisture	Parent_Material	Line	Physiography	Contamination	Comp_Silt
TCS 20746	no BC here; weathering in grey, black	moist	CALP	Line 3	boggy	Possible	X
TCS 20747	no BC here; weathering in lt. brown, grey, black, white, green	moist	CALP	Line 3	boggy	Possible	X
TCS 20748	gravels in black and white	dry	CALP	Line 3	Pastureland	Possible	X
TCS 20749	gravels in black and white; weathering in grey, lt. brown, black	moist	CALP	Line 3	Pastureland	Possible	XX
TCS 20751	Bc only 5 cm; weathering in lt. brown, black, grey	moist	CALP	Line 3	Pastureland	Possible	-
TCS 20752	low level of weathering: orange Schlieren, gravels only rarely	dry	CALP	Line 3	Pastureland	Possible	X
TCS 20753	weathering in grey, lt. brown, orange	moist	CALP	Line 3	Pastureland	Possible	X
TCS 20754	weathering in grey, lt. brown, orange	moist	CALP	Line 3	Pastureland	Possible	X
TCS 20755	rarely minor brownish blackish feature	dry to moist	CALP	No line	Pastureland	Possible	xx
TCS 20756	brown, grey, orange features	moist	CALP	No line	Pastureland	Possible	x
TCS 20757	very dense; grey, brown features	moist	CALP	No line	Pastureland	Possible	x
TCS 20758	few yellow, orange spots	dry to moist	CALP	No line	Pastureland	Possible	xx
TCS 20759	brown, black, features; very dense	moist	CALP	No line	Pastureland	Possible	x
TCS 20761	brown, black, features; very dense	moist	CALP	No line	Pastureland	Possible	
TCS 20762	few red pore lines	dry to moist	CALP	No line	Pastureland	Possible	xx
TCS 20763	few brown black feature	dry to moist	CALP	No line	Pastureland	Possible	x
TCS 20764	clear	dry to moist	CALP	No line	Pastureland	Possible	xx
TCS 20765	grey orange features	moist	CALP	No line	Pastureland	Possible	x
TCS 20766	rarely orange pore lines	dry to moist	CALP	No line	Pastureland	Possible	xx
TCS 20767	orange features	dry to moist	CALP	No line	Pastureland	Possible	x

Soil and till samples results (aqua regia digestion, continued).

Sample name	Comp_Sand	Comp_Organic	Comp_Clay	Sampling_Method	Slope	Year_Collected	Soil_Colour	Soil_From (m)	Soil_To (m)	Au (ppm)
TCS 20746	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.2	0.4	0.002
TCS 20747	-	-	XX	Auger	flat 0-5 ⁰	2015	brown	0.2	0.55	0.0013
TCS 20748	X	-	-	Auger	flat 0-5 ⁰	2015	brown	0.15	0.23	0.0002
TCS 20749	-	-	-	Auger	flat 0-5 ⁰	2015	brown	0.32	0.5	0.0008
TCS 20751	-	-	XX	Auger	flat 0-5 ⁰	2015	lt. brown	0.2	0.4	0.0005
TCS 20752	-	-	-	Auger	flat 0-5 ⁰	2015	dark brown	0.07	0.2	0.0005
TCS 20753	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.27	0.42	0.0004
TCS 20754	-	-	X	Auger	flat 0-5 ⁰	2015	brown	0.27	0.42	0.0003
TCS 20755	-	-	-	Auger	flat 0-5 ⁰	2016	brown	0.2	0.37	0.0013
TCS 20756			x	Auger	flat 0-5 ⁰	2016	light brown	0.45	0.6	0.0011
TCS 20757			xx	Auger	flat 0-5 ⁰	2016	light brown	0.7	1	0.0011
TCS 20758			-	Auger	flat 0-5 ⁰	2016	brown	0.2	0.33	0.0010
TCS 20759			xx	Auger	flat 0-5 ⁰	2016	very light brown	0.4	0.63	0.0011
TCS 20761			xx	Auger	flat 0-5 ⁰	2016	light brown, yellowish	0.67	0.9	0.0020
TCS 20762				Auger	flat 0-5 ⁰	2016	brown	0.2	0.35	0.0014
TCS 20763			xx	Auger	flat 0-5 ⁰	2016	brown	0.4	0.65	0.0011
TCS 20764				Auger	flat 0-5 ⁰	2016	brown	0.2	0.35	0.0006
TCS 20765			x	Auger	flat 0-5 ⁰	2016	light brown to brown	0.45	0.65	0.0013
TCS 20766				Auger	flat 0-5 ⁰	2016	brown	0.18	0.35	0.0006
TCS 20767			x	Auger	flat 0-5 ⁰	2016	brown	0.4	0.65	0.0015

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)
TCS 20746	0.213	1.68	12	5	186.5	1.17	0.116	0.81	9.24	48.3	13.5	38.6	0.794	30.6	2.75	4.78
TCS 20747	0.188	1.86	14.5	5	110.5	1.38	0.141	0.64	5.74	49.3	15.0	42.7	0.919	28	3.88	5.43
TCS 20748	0.132	0.85	4.02	10	65	0.62	0.092	2.37	1.82	25.0	4.9	17.9	0.342	15.8	1.20	2.47
TCS 20749	0.123	0.89	4.06	5	58.7	0.64	0.088	3.45	1.34	26.7	6.7	19.1	0.422	9.95	1.68	2.38
TCS 20751	0.148	1.45	5.13	5	68.2	0.83	0.114	0.24	0.97	35.7	7.0	31.0	0.875	7.21	2.20	4.03
TCS 20752	0.099	0.63	2.07	5	25.1	0.15	0.067	0.28	0.64	11.6	1.0	10.8	0.506	6.82	0.50	2.24
TCS 20753	0.056	0.59	2.07	5	13.1	0.12	0.058	0.18	0.25	10.6	0.7	8.8	0.547	2.77	0.57	1.97
TCS 20754	0.062	0.57	2.05	5	10.4	0.09	0.062	0.12	0.20	9.7	0.5	8.2	0.474	3.12	0.51	1.80
TCS 20755	0.110	0.93	5.00	5	47.4	0.58	0.086	0.31	1.30	29.0	5.2	19.2	0.560	11.60	1.29	2.59
TCS 20756	0.108	1.02	4.57	5	44.8	0.66	0.082	0.36	1.22	31.4	5.6	21.4	0.578	9.96	1.45	2.86
TCS 20757	0.095	0.96	4.89	10	37.9	0.66	0.084	1.02	1.05	30.4	6.2	20.8	0.605	9.76	1.66	2.42
TCS 20758	0.096	1.05	3.73	5	46.6	0.50	0.075	0.27	0.84	24.5	4.4	19.8	0.802	8.33	1.42	3.01
TCS 20759	0.060	2.06	10.40	10	73.2	1.05	0.129	0.36	0.88	43.3	14.2	50.3	1.010	26.40	3.71	5.90
TCS 20761	0.115	2.12	12.55	5	84.2	1.36	0.141	0.46	1.42	52.4	16.4	55.1	0.836	34.40	4.05	6.24
TCS 20762	0.134	0.88	5.97	5	43.5	0.77	0.095	0.29	1.59	33.9	6.3	21.0	0.342	17.35	1.65	2.35
TCS 20763	0.139	0.75	6.98	10	34.3	0.77	0.092	1.98	2.55	31.6	7.4	19.8	0.286	19.40	1.66	2.15
TCS 20764	0.100	0.83	6.27	5	39.9	0.68	0.089	0.26	1.63	31.9	7.0	19.2	0.460	18.60	1.67	2.27
TCS 20765	0.093	0.90	7.84	10	38.5	0.92	0.097	0.26	1.72	39.9	8.4	21.9	0.464	18.85	2.04	2.39
TCS 20766	0.115	0.89	5.80	5	40.6	0.70	0.095	0.23	1.55	32.3	7.2	20.7	0.469	13.25	1.67	2.49
TCS 20767	0.146	0.86	6.91	5	37.4	0.78	0.099	0.26	1.58	33.6	7.0	21.7	0.348	14.45	1.87	2.35

Soil and till samples results (aqua regia digestion, continued).

Sample name	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Pd (ppm)
TCS 20746	0.079	0.119	0.119	0.025	0.05	27.3	14.8	0.36	372	3.99	0.007	0.342	62.4	0.047	39.2	0.004
TCS 20747	0.09	0.133	0.105	0.033	0.05	30	16.3	0.38	454	4.13	0.01	0.366	66.1	0.072	31.2	0.0005
TCS 20748	0.05	0.089	0.088	0.018	0.04	14.65	6.5	0.24	323	0.98	0.01	0.184	21.6	0.115	18	0.002
TCS 20749	0.048	0.065	0.067	0.015	0.04	16.1	7	0.18	276	1.66	0.009	0.125	31.2	0.055	10.95	0.003
TCS 20751	0.049	0.094	0.084	0.019	0.05	20.9	10.7	0.2	357	1.18	0.009	0.237	29.9	0.025	16.6	0.001
TCS 20752	0.021	0.028	0.07	0.009	0.03	6.67	3.7	0.06	73.3	0.6	0.005	0.135	5.34	0.074	14.35	0.0005
TCS 20753	0.019	0.026	0.034	0.008	0.02	5.76	4.3	0.04	23.6	0.46	0.003	0.102	3.14	0.027	9.19	0.0005
TCS 20754	0.017	0.026	0.02	0.01	0.03	5.11	4.3	0.03	23.9	0.59	0.003	0.115	2.77	0.029	7.93	0.0005
TCS 20755	0.05	0.09	0.05	0.02	0.04	14.70	6.30	0.09	348	1.19	0.004	0.09	20.50	0.04	13.95	0.001
TCS 20756	0.05	0.08	0.06	0.02	0.04	16.05	7.40	0.11	224	1.16	0.005	0.13	24.20	0.04	12.85	0.0005
TCS 20757	0.05	0.05	0.05	0.02	0.04	14.65	7.00	0.11	168	1.62	0.005	0.09	25.40	0.03	11.45	0.0005
TCS 20758	0.04	0.08	0.05	0.01	0.04	11.55	7.70	0.10	286	0.81	0.005	0.10	15.50	0.03	12.80	0.0005
TCS 20759	0.08	0.09	0.07	0.03	0.09	21.00	19.00	0.45	500	1.91	0.007	0.28	62.10	0.01	17.25	0.0005
TCS 20761	0.11	0.16	0.08	0.04	0.10	34.00	19.40	0.50	523	2.27	0.005	0.23	90.00	0.03	17.70	0.00
TCS 20762	0.07	0.14	0.06	0.02	0.06	21.30	6.50	0.12	436	1.85	0.005	0.12	37.20	0.06	11.90	0.0005
TCS 20763	0.07	0.11	0.06	0.02	0.06	18.65	6.10	0.14	578	2.25	0.005	0.13	46.80	0.07	11.95	0.00
TCS 20764	0.06	0.08	0.06	0.02	0.05	16.25	6.20	0.11	607	2.38	0.004	0.11	32.70	0.05	12.50	0.0005
TCS 20765	0.08	0.07	0.08	0.02	0.06	25.10	6.50	0.12	633	3.21	0.005	0.11	41.30	0.04	12.15	0.0005
TCS 20766	0.06	0.09	0.09	0.02	0.06	17.60	6.80	0.12	658	2.07	0.005	0.16	31.60	0.04	12.15	0.00
TCS 20767	0.07	0.09	0.07	0.02	0.06	20.90	6.50	0.13	487	2.33	0.004	0.10	42.70	0.04	10.80	0.0005

Soil and till samples results (aqua regia digestion, continued).

Sample name	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)	Tl (ppm)	U (ppm)	V (ppm)
TCS 20746	0.002	4.53	0.002	0.02	3.61	6.6	2.5	0.44	39.2	0.0025	0.04	3.43	0.007	0.332	1.055	51.8
TCS 20747	0.001	4.86	0.003	0.03	3.39	7.32	4.6	0.55	41.4	0.0025	0.06	3.93	0.007	0.43	1.25	70.8
TCS 20748	0.001	4.23	0.002	0.13	0.561	2.62	2.6	0.43	65.1	0.0025	0.01	1.14	0.002	0.22	0.997	35.5
TCS 20749	0.001	4.57	0.001	0.03	0.842	3.85	1.2	0.31	118	0.0025	0.03	1.975	0.003	0.208	1.175	33
TCS 20751	0.001	9.93	0.0005	0.04	0.499	5.25	1.4	0.46	17.15	0.0025	0.005	2.52	0.004	0.306	0.917	44.7
TCS 20752	0.001	5.76	0.0005	0.06	0.157	0.764	1.1	0.47	11.65	0.0025	0.005	0.384	0.002	0.261	0.64	26.2
TCS 20753	0.001	3.89	0.0005	0.02	0.089	0.771	0.8	0.3	8.18	0.0025	0.01	0.597	0.002	0.213	0.446	21.7
TCS 20754	0.001	4.04	0.0005	0.02	0.084	0.569	0.8	0.28	5.44	0.0025	0.005	0.611	0.002	0.18	0.446	21.4
TCS 20755	0.001	6.68	0.0005	0.04	0.57	3.23	1.00	0.47	17.40	0.0025	0.03	1.39	0.002	0.24	0.78	34.80
TCS 20756	0.001	6.17	0.0005	0.03	0.66	3.79	0.70	0.43	21.50	0.0025	0.04	1.57	0.003	0.25	0.52	37.20
TCS 20757	0.001	5.90	0.0005	0.02	0.78	3.68	0.50	0.38	42.90	0.0025	0.03	1.89	0.002	0.25	0.44	39.90
TCS 20758	0.001	7.92	0.0005	0.03	0.37	2.87	0.80	0.45	14.75	0.0025	0.03	1.57	0.002	0.26	0.72	34.30
TCS 20759	0.001	10.40	0.001	0.02	1.11	6.61	1.20	0.55	29.30	0.0025	0.07	3.88	0.009	0.30	1.22	53.70
TCS 20761	0.001	9.55	0.0005	0.02	1.52	8.61	0.80	0.51	38.60	0.0025	0.07	4.78	0.012	0.26	1.28	58.60
TCS 20762	0.001	9.75	0.0005	0.03	0.86	4.16	0.40	0.41	14.95	0.0025	0.04	1.56	0.003	0.20	0.82	38.30
TCS 20763	0.001	8.43	0.001	0.02	1.03	3.89	0.70	0.36	69.60	0.0025	0.01	1.53	0.004	0.25	0.81	37.60
TCS 20764	0.001	9.94	0.0005	0.03	0.86	3.45	0.70	0.48	12.50	0.0025	0.06	1.35	0.003	0.22	0.83	36.70
TCS 20765	0.001	9.65	0.0005	0.02	1.18	4.57	0.80	0.47	14.90	0.0025	0.08	1.47	0.003	0.27	0.82	43.30
TCS 20766	0.001	10.40	0.0005	0.03	0.84	3.83	0.80	0.45	14.35	0.0025	0.06	1.55	0.003	0.23	0.77	40.20
TCS 20767	0.001	7.89	0.0005	0.02	1.13	4.63	0.60	0.37	19.75	0.0025	0.05	1.83	0.003	0.25	0.62	39.50

Soil and till samples results (aqua regia digestion, continued).

Sample name	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH (lab)	LOI (%)
TCS 20746	0.042	29	731	5.82	7	7.08
TCS 20747	0.067	35.1	1840	6.38	6.78	7.29
TCS 20748	0.083	17	97	2.73	7.15	18.95
TCS 20749	0.041	19.1	50.4	2.19	7.4	4.71
TCS 20751	0.051	21.1	75.1	2.85	5.15	7.03
TCS 20752	0.067	3.82	44.6	0.77	5.11	11.6
TCS 20753	0.025	2.37	26.9	0.7	5.21	5.32
TCS 20754	0.021	1.885	28.2	0.81	4.92	4.98
TCS 20755	0.30	16.80	74.60	2.70	5.2	5.7
TCS 20756	0.05	18.60	70.70	2.43	6.0	5.06
TCS 20757	0.05	16.75	73.40	1.85	6.8	3.72
TCS 20758	0.04	10.65	81.90	2.87	5.2	4.84
TCS 20759	0.06	17.70	91.30	3.98	5.6	5.77
TCS 20761	0.07	38.40	82.20	8.67	5.9	5.67
TCS 20762	0.05	28.00	96.30	4.23	5.4	5.61
TCS 20763	0.05	26.50	87.00	3.28	6.3	4.44
TCS 20764	0.05	20.10	85.00	2.48	5.7	5.22
TCS 20765	0.08	31.50	96.00	2.14	5.6	4.62
TCS 20766	0.06	22.20	83.60	2.82	5.3	5.11
TCS 20767	0.06	26.40	84.40	2.32	6.0	3.94

Raw data - Drill core raw data based on aqua regia digestion

SAMPLE	Core	From (m)	To (m)	Unit	Ag (ppm)	Al (%)	As (ppm)	Au (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cd (ppm)
BLK-DC-AKK-029	TC-1344-013	187.12	187.26	ABL	0.23	0.37	3.4	0.1	10	10	0.51	0.04	22.4	0.64	16.15	4.5	16
BLK-DC-AKK-001	TC-1344-027	42.15	42.24	CALP	0.01	0.01	0.4	0.1	5	5	0.17	0.005	50	0.04	2.71	0.7	1
BLK-DC-AKK-017	TC-1344-036	19.57	19.73	CALP	0.05	1.4	4.3	0.1	10	30	0.91	0.19	17.85	0.24	37.1	11.3	20
BLK-DC-AKK-018	B47	38.45	38.58	CALP	0.03	0.24	2.8	0.1	5	10	0.28	0.04	50	0.14	15.2	2.9	4
BLK-DC-AKK-027	TC-1344-013	54.6	54.66	CALP	0.07	0.41	2.5	0.1	10	20	0.48	0.04	50	1.13	19.55	3.7	9
BLK-DC-AKK-028	TC-1344-013	101.69	101.8	CALP	0.12	0.37	3.1	0.1	10	10	0.52	0.04	20	0.17	12.75	3.2	9
BLK-DC-AKK-014	TC-1344-036	109.87	110	SWA	0.05	0.3	5.2	0.1	5	20	0.57	0.03	50	0.17	17.6	3.8	5
BLK-DC-AKK-015	TC-1344-036	68.87	69.16	SWA	0.04	0.19	4.3	0.1	5	50	0.29	0.02	50	0.53	13.25	7.7	5
BLK-DC-AKK-016	TC-1344-036	50.9	51.04	SWA	0.15	0.5	8.2	0.1	5	20	0.48	0.1	17.85	0.03	22.8	10	8
BLK-DC-AKK-019	B47	81.16	81.31	SWA	0.03	0.44	3.2	0.1	5	10	0.54	0.03	50	0.05	22.9	5.1	7
BLK-DC-AKK-013	TC-1344-036	148.6	148.72	WA	0.03	0.1	2.6	0.1	5	30	0.31	0.01	50	0.35	11.25	1.1	3
BLK-DC-AKK-031	TC-1344-013	369.83	369.95	WA	0.02	0.54	0.8	0.1	10	10	0.35	0.02	50	0.1	12.35	2.6	9

SAMPLE	Cs (ppm)	Cu (ppm)	Fe (%)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
BLK-DC-AKK-029	0.76	24.5	0.9	1.07	0.05	0.27	0.005	0.009	0.16	10.4	3.3	1.07	93	3.91	0.03	0.025	36.1
BLK-DC-AKK-001	0.025	2.6	0.09	0.05	0.025	0.05	0.01	0.0025	0.005	2.4	0.2	0.34	496	0.19	0.02	0.05	1.1
BLK-DC-AKK-017	1.19	20.1	2.6	3.47	0.05	0.25	0.005	0.033	0.32	19.2	27.6	1.37	409	1.06	0.04	0.025	69
BLK-DC-AKK-018	0.43	6.1	0.7	0.69	0.025	0.1	0.005	0.009	0.1	11.1	3.3	0.67	436	0.3	0.02	0.025	15.9
BLK-DC-AKK-027	0.79	10.7	0.92	1.09	0.025	0.19	0.005	0.017	0.15	10.1	2.1	1.16	134	4.54	0.03	0.025	21.3
BLK-DC-AKK-028	0.57	10	0.8	0.94	0.025	0.17	0.005	0.012	0.14	7.3	2.1	2.02	115	1.63	0.03	0.025	23.7
BLK-DC-AKK-014	0.63	7.9	0.5	0.86	0.025	0.13	0.04	0.008	0.17	12	4	0.36	590	0.7	0.02	0.025	20.3
BLK-DC-AKK-015	0.38	8.4	2.18	0.65	0.025	0.07	0.03	0.009	0.07	9.4	3.6	0.68	754	2.24	0.03	0.025	47.5
BLK-DC-AKK-016	0.62	12.9	1.54	1.37	0.025	0.26	0.02	0.01	0.2	15.4	7.8	0.91	282	1.3	0.02	0.025	58.9
BLK-DC-AKK-019	1.07	7.5	1.17	1.16	0.025	0.11	0.01	0.015	0.17	14.2	7.9	1.15	458	0.43	0.03	0.025	24
BLK-DC-AKK-013	0.46	4	0.18	0.3	0.025	0.04	0.02	0.0025	0.06	8.2	1.8	0.36	916	1.37	0.03	0.025	3.3
BLK-DC-AKK-031	0.72	11.5	0.91	1.42	0.025	0.08	0.005	0.006	0.18	9.9	10	1.2	233	0.34	0.03	0.025	12.3

Drill core samples trace elements (continued).

SAMPLE	P (ppm)	Pb (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)	Tl (ppm)	U (ppm)	V (ppm)
BLK-DC-AKK-029	1510	4.6	8.9	0.026	0.94	1.42	3.5	6.3	0.1	969	0.005	0.02	1.5	0.0025	0.07	2.23	45
BLK-DC-AKK-001	150	2.1	0.2	0.001	0.04	0.025	0.3	0.2	0.1	898	0.005	0.01	0.1	0.0025	0.02	0.43	4
BLK-DC-AKK-017	290	13.5	16	0.007	0.9	0.34	6.8	1.5	0.3	699	0.005	0.1	3.7	0.0025	0.09	1.12	18
BLK-DC-AKK-018	330	5.7	5.1	0.001	0.17	0.78	2.6	0.7	0.1	576	0.005	0.01	1.3	0.0025	0.05	0.85	3
BLK-DC-AKK-027	220	4	9	0.007	0.62	0.95	4.1	2	0.2	1150	0.005	0.02	2	0.0025	0.16	1.76	15
BLK-DC-AKK-028	220	6.4	7.9	0.006	0.81	0.75	3.2	2.6	0.1	1150	0.005	0.03	1.7	0.0025	0.05	1.18	19
BLK-DC-AKK-014	740	11.5	8.3	0.006	0.26	1.46	2.6	0.4	0.1	321	0.005	0.03	1.3	0.0025	0.12	1.43	4
BLK-DC-AKK-015	260	15.7	4.1	0.006	2.01	1.85	1.8	0.7	0.1	894	0.005	0.01	0.9	0.0025	2.54	2.48	6
BLK-DC-AKK-016	510	11.8	10.2	0.008	0.99	2.18	5.2	1.3	0.1	552	0.005	0.04	2.5	0.0025	0.1	1.11	7
BLK-DC-AKK-019	360	9.2	8.9	0.002	0.31	0.53	3	0.4	0.1	619	0.005	0.005	1.6	0.0025	0.07	0.96	5
BLK-DC-AKK-013	180	8.9	3.3	0.001	0.06	1.31	0.9	0.3	0.1	342	0.005	0.01	0.6	0.0025	0.06	2.32	3
BLK-DC-AKK-031	240	2.7	9.9	0.001	0.19	0.06	2.2	0.4	0.2	876	0.005	0.005	1	0.0025	0.09	0.59	7

SAMPLE	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	LOI (%)
BLK-DC-AKK-029	0.025	12.45	18	9.8	2.27
BLK-DC-AKK-001	0.025	4.21	5	5.5	0.48
BLK-DC-AKK-017	0.025	23.7	130	8.8	2.41
BLK-DC-AKK-018	0.025	10.15	31	2.8	0.82
BLK-DC-AKK-027	0.025	13.2	35	7.5	2.15
BLK-DC-AKK-028	0.025	12.2	9	6	2.17
BLK-DC-AKK-014	0.025	10.9	89	4.5	0.87
BLK-DC-AKK-015	0.025	8.98	262	2.2	0.92
BLK-DC-AKK-016	0.025	14.3	10	7.3	1.69
BLK-DC-AKK-019	0.025	11.7	26	2.9	1.08
BLK-DC-AKK-013	0.025	8.15	111	1.6	0.6
BLK-DC-AKK-031	0.025	8.59	41	2.5	2.06

Principal component analysis scores

	PC 1	PC 2	PC 3	PC 4
Eigenvalue	302.61	4.72	2.83	1.32
% variance	96.27	1.50	0.90	0.42
Ag	-23.83	-3.22	-1.59	0.63
As	0.98	-3.60	1.40	-0.57
Ba	9.88	-1.61	0.61	1.12
Ca	36.60	0.01	-5.38	-0.21
Cd	-9.39	-2.52	-1.87	-0.98
Co	-1.61	0.88	0.86	-1.34
Cr	4.87	1.53	0.84	0.38
Cs	-16.80	1.15	0.59	1.40
Cu	3.46	1.07	0.23	-1.04
Fe	43.81	1.04	1.96	0.06
Ga	-7.01	0.93	0.74	1.00
In	-35.25	1.30	-0.26	-0.40
Li	-1.34	1.29	1.07	0.70
Mg	29.62	0.54	0.57	0.32
Mn	21.68	0.79	2.52	-1.39
Mo	-7.86	1.29	0.44	-1.83
Nb	-23.32	1.04	-0.06	0.69
Ni	7.93	0.62	0.32	-1.86
Pb	6.55	-5.46	0.84	1.42
Rb	-1.07	1.48	1.80	0.61
S	19.35	1.34	-1.47	3.33
Sb	-10.40	-4.60	-0.42	-1.49
Sc	-5.37	1.32	0.26	-1.21
Se	-10.76	1.35	-1.05	0.54
Sn	-17.44	1.11	0.72	1.01
Sr	5.65	0.79	-5.23	-0.83
Th	-9.86	1.48	0.06	-0.51
Tl	-18.12	-2.58	0.49	0.27
U	-12.79	1.83	-1.07	0.57
V	8.26	1.72	0.70	0.43
Y	4.38	1.34	0.44	-1.71
Zn	17.14	-4.97	1.13	0.25
Zr	-7.98	1.34	-0.19	0.65

Appendix D

Thin section images of micro-drilled sphalerite.

Soil and till sample digestion.

Sphalerite sample digestion.

Column preparation.

Blanks - isotope analysis.

Standards for isotopic analysis.

Isotope laboratory duplicate.

Elemental recovery during ion exchange chromatography.

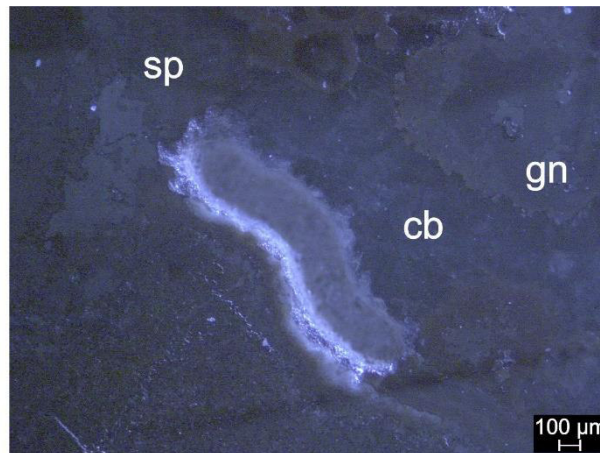
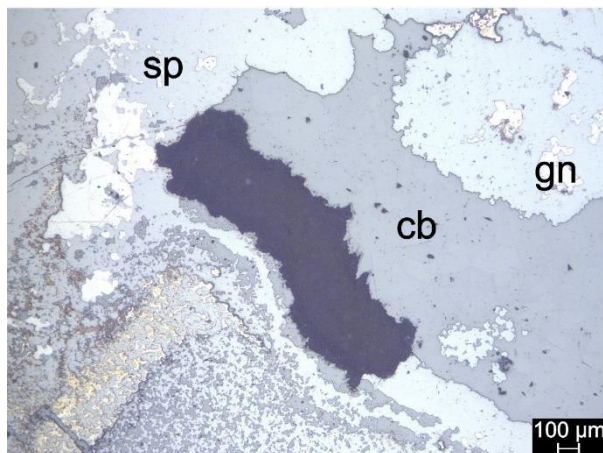
Mass dependent fractionation of isotopes.

References.

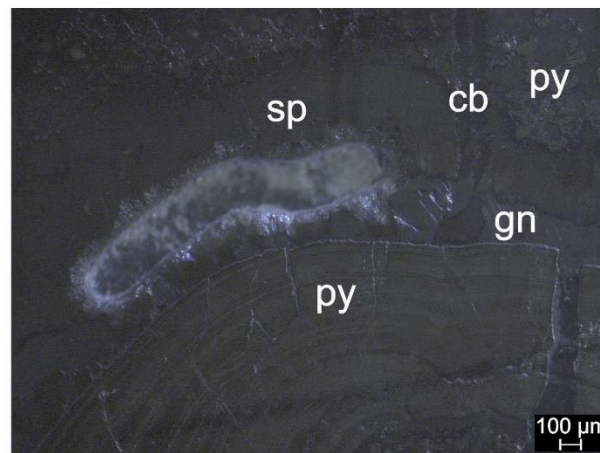
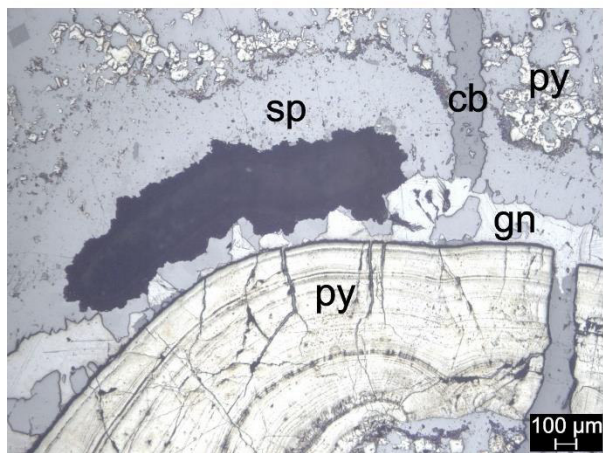
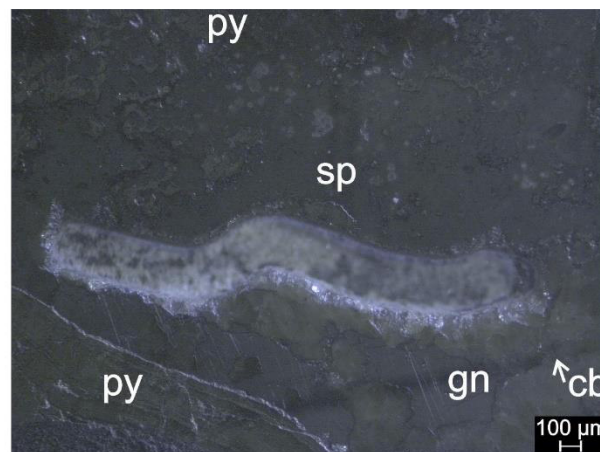
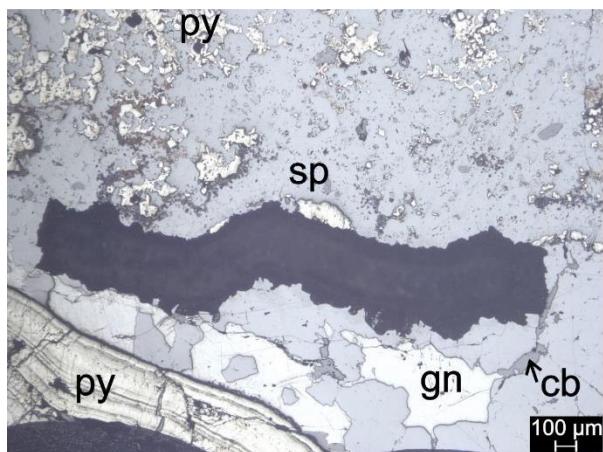
Thin section images of micro-drilled sphalerite

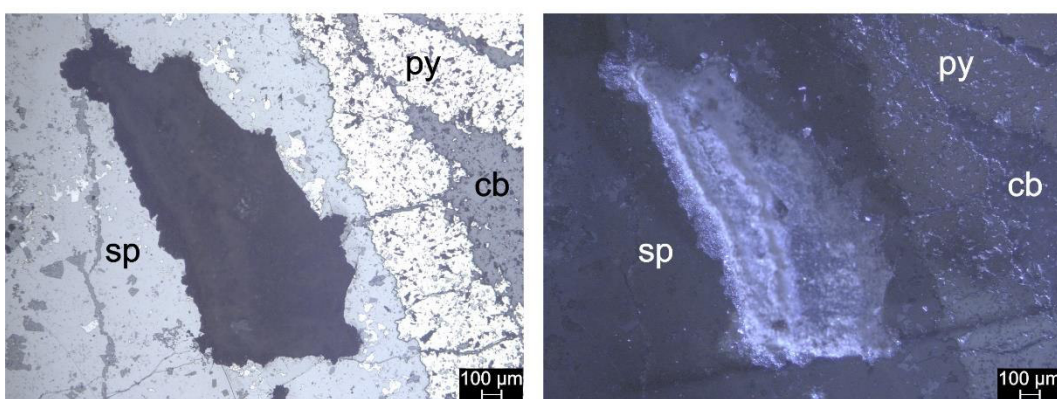
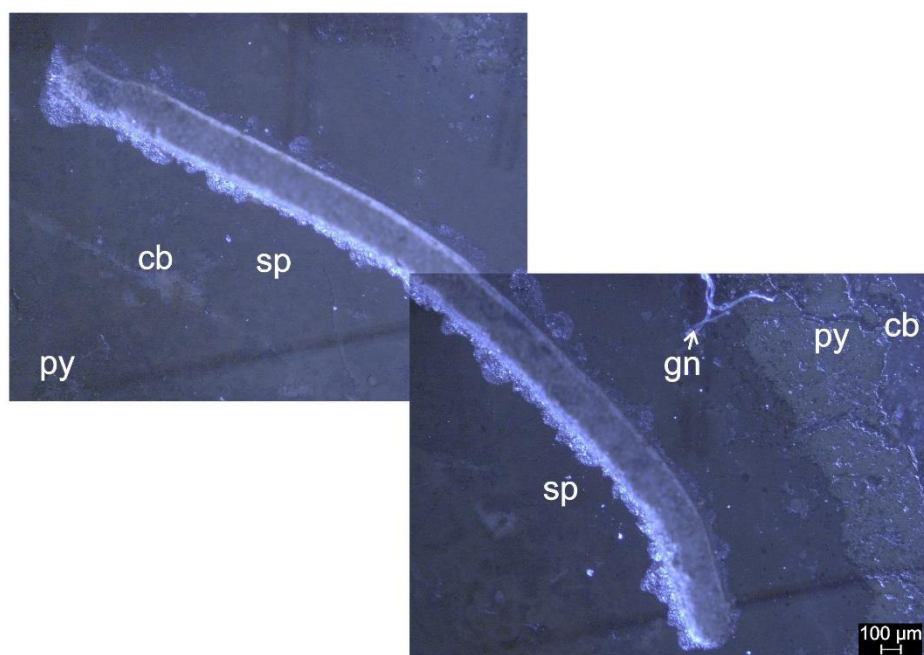
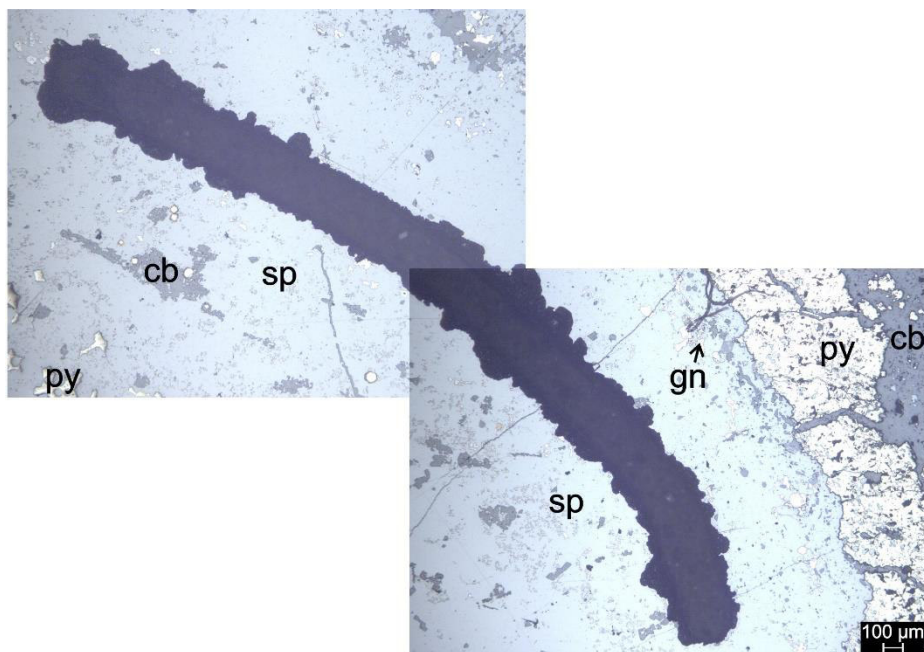
Note, transmitted light images are taken from ~80 μm thick thin sections.

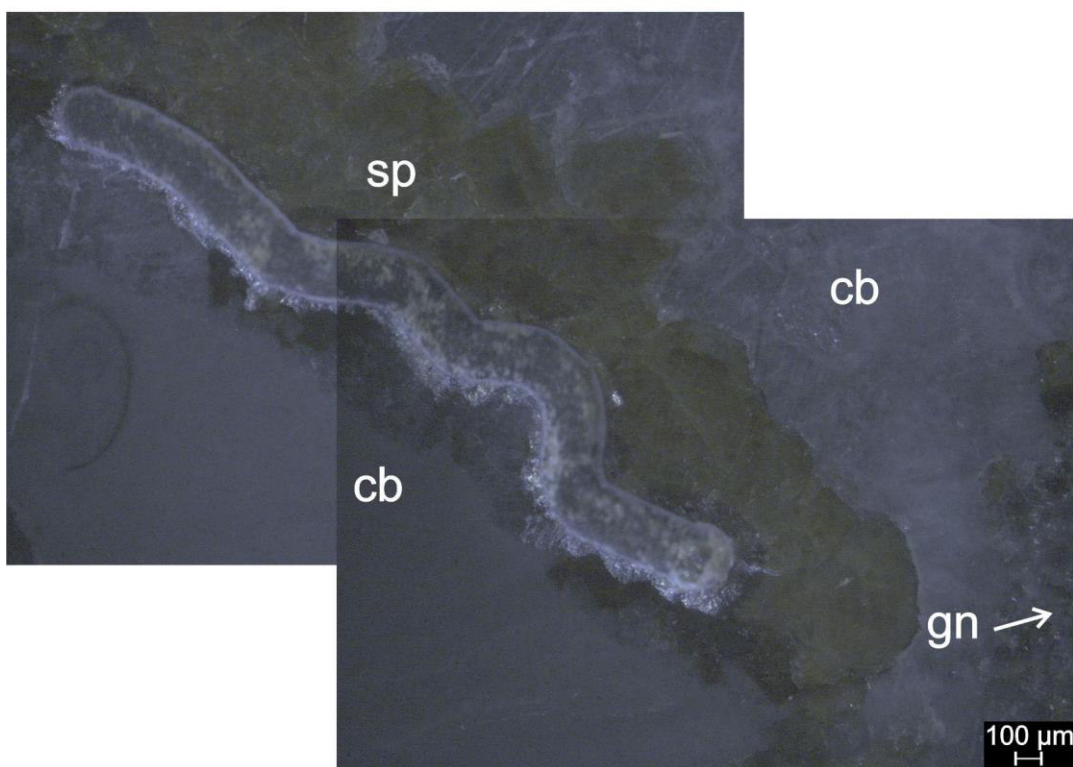
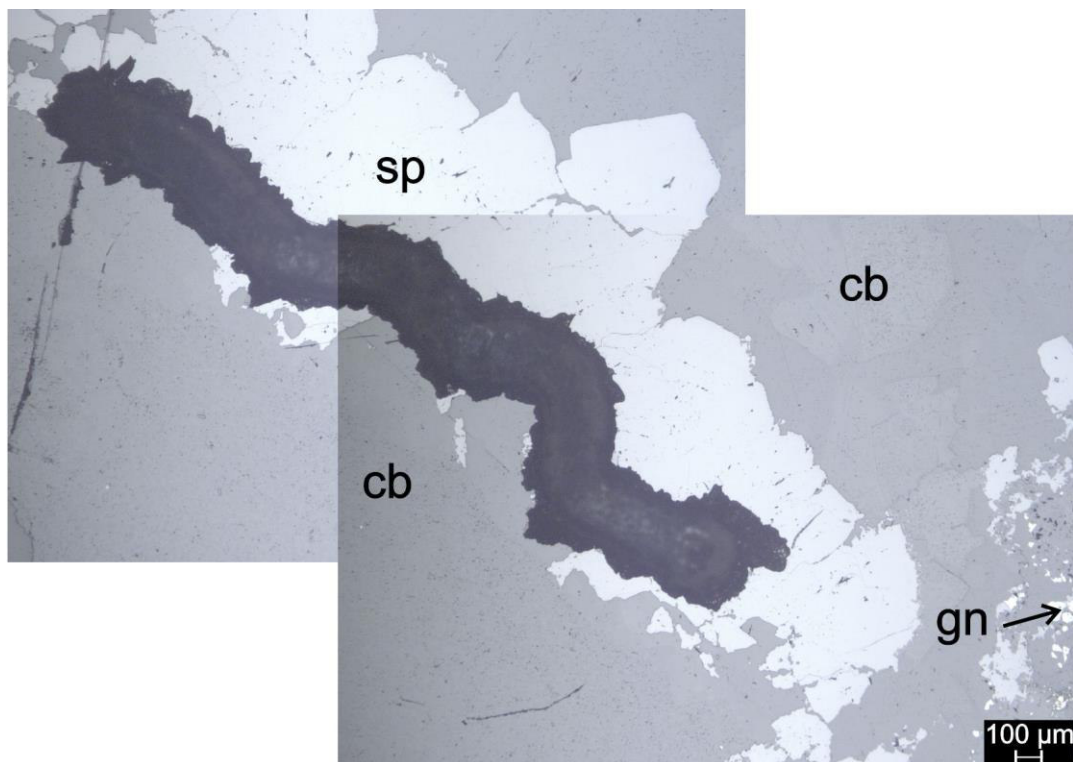
BLK 08



BLK 12







Soil and till sample digestion

Two trials to digest the soil and till samples are presented in the following:

1st trial

- Aliquots of the samples with 100 to 250 mg were prepared depending on the Cu concentration from the aqua regia method (Chapter 4).
- 2 ml of H₂O₂ 30 % were added to all samples rinsing the dust from the inner beaker wall. The cap was loosely fastened allowing for degassing during reaction. In the case of a strong initial reaction H₂O₂ was added dropwise. Digestion of slow reacting samples was enhanced by moderate heating. After the main reaction, 1 ml of H₂O₂ 30 % was added and the sample was stored overnight under fume hood to ensure the completion of the reaction.
- The digestion fluid was evaporated.
- One ml HNO₃ 16 N and 0.5 ml HF were added followed by heating at 120 °C for at least 24 h using a hotplate.
- A pale brown residue indicated the presence of undigested organic matter inside. In this case, the beaker were carefully opened, the droplets of the cap were rinsed in the beaker and the inner beaker wall was cleaned with 0.5 ml HClO₄ 70 %.
- Alternatively 0.5 ml HNO₃ 16 N and then 0.5 ml HClO₄ 70 % were added after evaporation.
- In the next step, the sample was placed in an EvapoClean and the beaker was slightly unscrewed, contact between digestion fluid and the potentially contaminated outer surface of the beaker was voided.
- If brown residues disappeared from the beaker wall and no particles were observed the fluid was evaporated.
- In the next step, 1 to 2 ml HNO₃ 16 N were added and the sample was again heated followed by the inspection for any remaining particles (complete digestion).
- If particles remained in the solution, the following step was decided based on their colour. White particles were probably CaF from the HF acid attack (evaporation and addition of 0.6 ml HBrO₃ and 0.5 ml HNO₃ 16 N followed by overnight heating at 130 °C). Black particles indicated rock material and/or organic matter requiring an additional acid treatment (HClO₄).

Unfortunately, during the handling of some samples, small amounts (droplets) were lost in the first step using H₂O₂ (a few samples reacted too strong). Also during the HF digestion, a

few droplets were lost. High reaction pressure within the Teflon beakers led to a leakage. To ensure, that no sample material was lost and no fractionation was artificially induced, the digestion of affected samples has been repeated using a different method.

2nd trial to digest soil and till samples:

- Aliquots of the samples with 100 to 250 mg were prepared depending on the Cu concentration from the aqua regia method (Chapter 4).
- 4 ml HNO₃ 16 M were added to the samples, drop by drop to avoid strong reaction. The digestion beaker was carefully closed and heated overnight on hotplate at 100 °C. In the case of strong reactivity, the beaker was left open at room temperature until the release of further yellow steam stopped.
- Further 2 ml HF 27 M were added and the closed beaker was left for at least 3 days on a hotplate at 130 °C until the colour changed to less dark.
- Then, 1 ml HClO₄ 70 % was added and the sample was transferred into the Evapocleaner. The procedure was started with 100 °C to digest remaining organic components (indicated by brown colour) and increased to 130 °C until no liquid was left in the sample beaker. Adhesive material from the wall could be removed easily.
- In the last step, 2 ml HNO₃ 16 M were added and the sample was heated overnight on a hotplate at 110 °C. The absence of remaining crystals indicated that the sample was successfully digested. Otherwise, the sample was treated 1 hour in an ultrasonic bath to minimise the crystals and 6 ml HCl 6 M were added, followed by overnight heating on hotplate (120 °C).

Sphalerite sample digestion

- Sphalerite samples were stored in polypropylene containers for 3 days in contact with 1 ml HNO₃ 6 M.
- The resulting solution was transferred into a Teflon beaker (15 ml) and the polypropylene container was rinsed 3 times with MilliQ water to ensure complete transfer of the sample.
- The fluid was evaporated using a hotplate at 120 °C and subsequently cooled to room temperature.
- In the next step, 0.5 ml HNO₃ 16 N were added and the sample was inspected for total digestion (transfer to chromatography).
- In the case of incomplete digestion, 1.5 ml HCl 6 N were added and the closed beakers were heated on hotplate at 120 °C for at least 12 h.

Column preparation

- The remaining resin within the columns from previous studies was removed by adding distilled H₂O and shaking until the whole resin is dissolved.
- A plastic spoon cleaned with distilled water was used to transfer about 35 ml resin (BioRad Ag MP-1M 200 - 400 mesh) in a 50 ml tube. Afterwards distilled H₂O was added to reach 45 ml. The tube was vertically fixated in a beaker to allow settling of the resin. The water was replaced several times to remove unwanted particles.
- For the first separation step of both Cu and Zn and for the second Cu separation, 12 ml columns were filled with 2 ml and 0.8 ml BioRad AG MP-1M 200 - 400 mesh, respectively. For the second Zn separation a 3 ml column was filled with 1 ml Biorad AG-MP-1M 200-400 mesh resin.
- The columns were labelled from 1 to 12 and positioned in the suitable rack.
- Then the column was rinsed with 1 M HCl to remove droplets sticking to the inner wall, followed by rinsing with 6 M HCl. Finally, the column was filled with 1 M HNO₃, closed at both ends and stored overnight.

Blanks - isotope analysis

In total, 15 blanks were used during the isotopic measurement using MC ICP-MS. One of the blanks underwent all steps including digestion. All other blanks only underwent the chromatographic exchange procedure. Assuming the highest blank compared with the lowest concentration of the samples, the highest Zn contamination is 0.54 % and for Cu 0.03 %.

Blank measurements conducted by MC ICP-MS; - = not determined

Sample	approx. Cu mass (ng)	approx. Zn mass (ng)
Washing	-	-
ZnT1 03/08	-	52.9
ZnT3 03/08	-	29.1
ZnT5 03/08	-	15.0
ZnT10 03/08	-	16.9
ZnT9 03/08	-	30.1
CuT1 03/08	0.5	2.9
CuT3 03/08	0.5	4.0
CuT5 03/08	0.5	6.2
CuT9 03/08	0.7	4.4
CuT10 03/08	0.5	8.1
CuT7s 19/08	3.1	-
ZnT9s 22/08	0.1	21.3
CuT8s 26/08	0.2	3.3
ZnT8s 28/08	-	24.5

Standards for isotopic analysis

A small fractionation occurs for the in-house standard (IPG AAS) during the analysis, however, it is not high for Zn isotope data and the values are still trustful. For Cu values, the in-house standard fractionation is of 0.1 ‰ in three samples (CuT2_0308, CuT4_0308, CuT6_0308).

The certified standards IRMM 3702 and NIST SRM 976 for Zn and Cu were used during the MC ICP-MS measurement. After conversion from the in-house standard to JMC Lyon, the standard IRMM 3702 has a signature of $\delta^{66}\text{Zn}_{\text{JMC}} = 0.23 \pm 0.04 \text{ ‰}$ (2σ). Considering the standard deviation, the result is close to the reported value of $\delta^{66}\text{Zn}_{\text{JMC}} = 0.32 \pm 0.03 \text{ ‰}$ (2σ) (Petit et al., 2008). During one measurement block, the IRMM 3702 revealed very low values and after preparing a new solution, the values matched again. If those anomalous values are rejected from the calculation, $\delta^{66}\text{Zn}_{\text{JMC}} = 0.30 \pm 0.04 \text{ ‰}$ (2σ) matches well the reported values. The standard for Cu NIST SRM 976 reported to the in-house standard $\delta^{65}\text{Cu}_{\text{NIST}} = -0.02 \pm 0.03 \text{ ‰}$ (2σ) is in well agreement with the reported values (Moeller et al., 2012).

Furthermore, the basalt BCR-2 standard was processed through each step to have an additional control related to fractionation during samples digestion and separation. For Cu and Zn, the signatures are in agreement with the reported isotopic signatures $\delta^{66}\text{Zn}_{\text{JMC}} = 0.24 \pm 0.04 \text{ ‰}$ (2σ) and $\delta^{65}\text{Cu}_{\text{NIST}} = 0.24 \pm 0.03 \text{ ‰}$ (2σ).

Comparison between isotopic standards of this study to literatures.

Standard		measured this study	2σ	Literature	2σ	Source
IRMM 3702	$\Delta^{66}\text{Zn}_{\text{JMC}}$	0.30	0.04	0.32	0.03	Petit et al. (2008)
	$\Delta^{66}\text{Zn}_{\text{JMC}^*}$	0.23	0.04	0.32	0.03	Petit et al. (2008)
NIST 976	$\Delta^{65}\text{Cu}_{\text{NIST}}$	-0.02	0.03	-0.01	0.5	Moeller et al. (2012)
BCR-2	$\Delta^{66}\text{Zn}_{\text{JMC}}$	0.24	0.04	0.23	0.02	Bigalke et al. (2010), Sossi et al. (2015), Chen et al. (2016), Guinoiseau et al. (2016)
BCR-2	$\Delta^{65}\text{Cu}_{\text{NIST}}$	0.24	0.03	0.2	0.05	Bigalke et al. (2010), Bigalke et al. (2011), (2014)

Isotope laboratory duplicate

One duplicate sample TCS 20647 (original) and TCS 20647 D (duplicate) was conducted during the isotope treatment for both Cu and Zn isotopes. Considering the standard deviations, the isotopic values are acceptable (see following table). For the interpretation, the average was calculated and used for indicating a reproducibility of ± 0.03 .

Laboratory duplicate sample TCS 20647.

Sample	$\delta^{66}\text{Zn}$	2σ	$\delta^{67}\text{Zn}$	2σ	$\delta^{68}\text{Zn}$	2σ
TCS 20647	0.23	0.03	0.27	0.10	0.46	0.06
TCS 20647 D	0.24	0.07	0.35	0.12	0.48	0.10

Sample	$\delta^{65}\text{Cu}$ by $^{66}/^{64}\text{Zn}$ ratio	2σ	$\delta^{65}\text{Cu}$ by $^{67}/^{64}\text{Zn}$ ratio	2σ	$\delta^{65}\text{Cu}$ by $^{68}/^{64}\text{Zn}$ ratio	2σ
TCS 20647	-0.34	0.02	-0.41	0.02	-0.39	0.03
TCS 20647 D	-0.41	0.03	-0.45	0.06	-0.42	0.01

Elemental recovery during ion exchange chromatography

Various processes fractionate Cu and Zn isotopes, see review by Moynier et al. (2017), and hence isotopic fractionation during sample preparation might affect the isotopic ratio. After Maréchal and Albarède (2002), Cu and Zn isotopes can also fractionate in contact with the

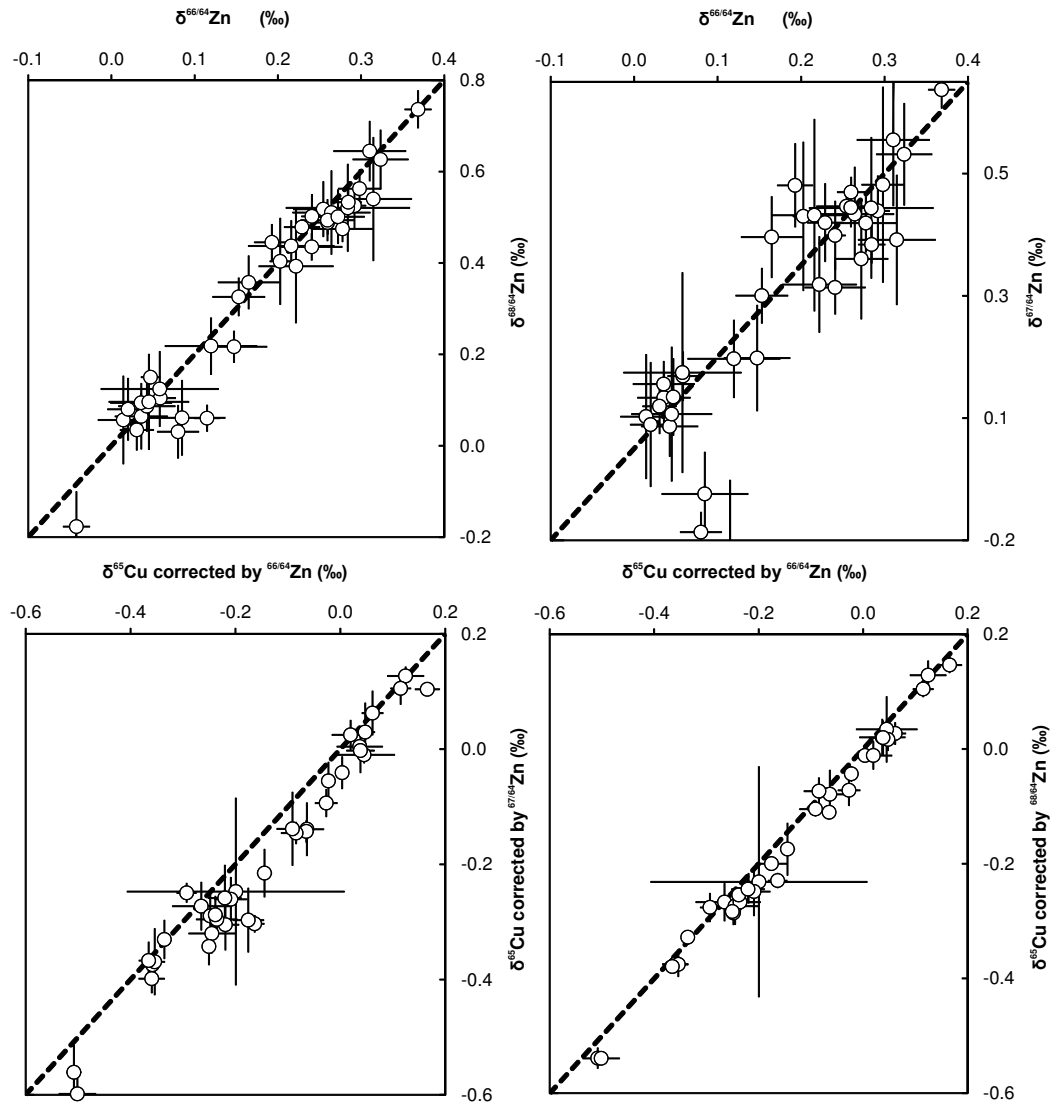
resin, leading to a shift in the ratios (Chapman et al., 2006). To evaluate the effects of such processes, the recovery of Cu and Zn was checked for each sample; Zn concentrations were obtained by ICP-OES and Cu by ICP-MS analysis. The recovery of Zn is in an acceptable range of 100 ± 10 %, however 4 samples exceed the limits towards 128 %. The recovery of Cu ranges from 99 to 132 %. The recoveries show that neither Zn, nor Cu is lost during chemical separation. The values exceeding 100 % indicate an addition of Zn and Cu, however, due to low blanks of both Cu and Zn, a contamination is unlikely to be responsible for the concentration increase. Here, most likely a matrix effect shifts the determined concentration values artificially during analysis. Noticeable, sample TCS 20623 has to be carefully evaluated, as it shows high recoveries for both Zn and Cu.

Recoveries for Zn and Cu fractions determined by ICP-OES and ICP-MS, respectively. Red = exceeding the acceptable rang.

Sample name	Batch	Zn yield [%]	SD [%]	Cu yield [%]	SD [%]
SP08	1	100.3	1.0		
SP10a	1	101.6	0.8		
SP10b	1	101.8	1.4		
SP12	1	101.3	1.4		
SP21	1	100.8	1.2		
TCS 20608	1	106.5	1.5	115.5	0.2
TCS 20609	1	106.9	1.2	110.7	1.5
TCS 20622	2	108.9	1.3	107.5	1.0
TCS 20623	2	128.4	1.3	132.2	0.6
TCS 20631	2	95.0	1.1	98.9	0.6
TCS 20632	2	111.5	1.2	99.5	1.4
TCS 20644	1	102.8	0.4	128.7	0.2
TCS 20645	1	105.5	0.3	122.1	0.3
TCS 20646	2	108.4	1.2	110.0	0.8
TCS 20647	2	112.8	1.3	112.4	0.5
TCS 20647D	2	102.5	1.0	101.9	1.0
TCS 20681	1	97.5	1.1	112.2	1.4
TCS 20682	1	100.7	1.1	108.1	0.1
TCS 20713	2	104.8	1.1	113.0	1.1
TCS 20714	2	109.4	0.9	106.1	0.9
TCS 20746	2	111.5	1.3	115.4	0.9

Mass dependent fractionation of isotopes

All samples experienced mass dependent isotope fractionation. There are outliers within the Zn isotopes, which are related to the IRMM 3702 standard and most likely contaminated (those samples where repeated).



Mass dependent fractionation for standard IRMM 3702 measured.

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