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Use of Organic Media in the Geochemical Detection of Blind Porphyry Copper-Gold Mineralization in the Woodjam Property Area, south-central BC (NTS 093A/03, /06)

by

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## EXECUTIVE SUMMARY

Plant exudates can contain metals translocated from underlying mineralization. These materials (saps, transpired fluids, salts and particulates on leaf surfaces) may provide simple and cost-effective sample media for detecting mineralization through transported cover. A 'proof of concept' study carried out at the Woodjam project in central BC tested the geochemical response of exudates and spruce tissues collected over the blind Deerhorn and Three Firs porphyry Cu-Au systems, concealed beneath glacial cover and/or basalt. HR-ICP-MS was required to obtain low ppb and ppt detection limits for some ore and pathfinder elements in the exudates. Results are compared with data from Ah horizon and soil charcoal samples.

Over mineralization spruce twig samples showed elevated levels of Au, Cu, S and Sb. Cesium and Rb anomalies appeared to indicate the position of potassic alteration associated with mineralized zones. Similar results were obtained in charcoal samples collected from the Ah horizon, notably for Rb, Ca, As and Cu.

An experiment to vacuum the particulates from the leaf surfaces was unsuccessful, probably because recent heavy rain had washed off surface salts and spalling particulates. This method is likely to only be appropriate in hot and arid environments.

The fluids that transpire through the plant stomata on a sunny day can be readily collected into plastic bags tied around a branch, but little fluid accumulates on cloudy days. The limited sampling provided some encouraging results implying that 'toxic' elements (such as Hg, Tl, W and As) as well as nutritional elements in excess of the plants' requirements (such as Cu, Mo and S) appear to be flushed through the plant and readily exuded with the fluids.

Congeaed sap collected from the surface of spruce trees was enriched in a number of elements including Cu and Mo, and the pathfinder elements As, Hg, Sb, Tl and W. Although quite a rapid but delicate procedure, care must be taken to ensure that sap samples exclude traces of plant tissues.

Leaves of alder and new growth of white spruce needles were collected in order to strip off the surface waxes and salts using chloroform. Limited data indicate enrichments of Cu, Mo and Zn in the leachates, but concentrations of the pathfinder elements As, Hg, Sb, Tl and W were mostly below the levels of detection precluding any meaningful interpretation.

It is concluded that non-essential and potentially toxic elements commonly associated with mineralization, such as As, Hg, Tl and W, can enter plants via their roots and be translocated through the plant. Analysis of plant tissues shows that a portion of these elements precipitates in plant cells, but a portion continues through the plant in solution to be exuded with sap and transpired fluids. These exudates then fall to the forest floor and contribute their chemical signatures to the surface soil layers.

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## INTRODUCTION

This paper covers activities conducted under a Geoscience BC project entitled “Evaluation of plant exudates to assist in mineral exploration and the development of simple and cost effective field procedures and analytical methods”. Large areas prospective for porphyry and epithermal-style mineralization in central BC are covered by either glaciofluvial sediments or young basalt units. In areas where the cover is unconsolidated material of glacial origin, recently completed Geoscience BC-funded projects have significantly advanced the understanding of the underlying bedrock geology and have demonstrated means of ‘seeing through’ this type of cover using geochemistry (e.g., Cook and Dunn, 2007; Dunn et al., 2007; Barnett and Williams, 2009; Heberlein, 2010; Heberlein and Samson, 2010; Heberlein and Dunn, 2011). However, geochemistry is not commonly used to investigate the underlying geology in those areas covered by young basalt flows (Bissig et al., 2013a, b). The present study is aimed at establishing a geochemical strategy to see through glacial drift and young basalt cover, using a variety of analytical techniques on a variety of organic or organically-derived sample media to test what works best.

## OBJECTIVES

This project set out to address the following questions:

1. Are plant exudates such as sap, transpired fluids, leaf surface particulates and surface waxes practical to collect, and do they provide information of value to the exploration for porphyry Cu/Au deposits that are concealed by overburden and basalt cover?
2. What levels of detection are required to see the geochemical signatures of these exudates?
3. Which of these media gives the most definitive surface signature of blind copper-gold porphyry-style mineralization through transported cover?
4. How do these geochemical signatures compare to signatures from an aqua regia digestion of organic-rich soils (Ah horizon) and are they more definitive of underlying mineralization?
5. How do these signatures compare to the analysis of charcoal from forest fires?
6. How do these signatures compare to signatures derived from the analysis of spruce bark and spruce twigs and do they provide different (and more definitive) spatial signatures of this buried mineralization?
7. Which of the methods tested provides the most useful geochemical signatures to explore for this style of mineralization in this terrain?
8. What are the recommended sampling strategies of the media tested?

## BENEFITS TO THE MINING INDUSTRY

This study is designed to provide the mineral exploration community with a better understanding of different organic sampling media that can be used for biogeochemical exploration in regions with thick glacial sediment or Tertiary basalt cover. It provides comparisons of metal concentrations in vegetation, Ah-soil horizon and charcoal debris, and assesses the relative capabilities of each medium for preserving the secondary geochemical dispersion patterns related to a blind mineral deposit. The study also examines metal concentrations in saps, leaf coatings and transpired fluids to determine whether direct

sampling of these 'exudates' is an effective way of detecting blind mineralization. If successful, exudate geochemistry could provide the exploration community with an alternative sampling medium for local- and regional-scale geochemical sampling programs in areas where conventional soil-sampling methods are found to be ineffective.

## PREVIOUS STUDIES

Kyuregyan and Burnutyanyan (1972) demonstrated that plant saps could be used in exploration for Au, because the sap Au content was significantly higher than that of other aqueous extracts of the plant material or of the underlying soil. Saps from birch are the most studied, both because of the ubiquity of birch in the boreal forests (especially Siberia and Finland) and of their strong sap flow in the spring. Krendelev and Pogrebnyak (1979) conducted a sampling program in an area of permafrost over an intensively fractured and hydrothermally-altered Au-mineralized stockwork in Transbaikal, where most of the Au is associated with pyrite and there is a 0.5–4 m cover of unconsolidated sediments. The mean Au content from analysis of 73 samples was reported as 0.011–0.33 ppb; Zn concentrations in fresh sap from trees growing over Zn-rich ore reached 17.2 ppm. The authors observed that, in the vascular system of the birch species studied (*Betula platyphylla*), there is no biological barrier against the absorption of Zn and concluded that the best anomaly to background contrast was obtained by calculating the  $Zn/(K+Ca+Mg)$  ratio. Harju and Huldén (1990) conducted an exhaustive survey in southern Finland, where they collected sap samples from many species of birch (mostly *Betula verrucosa*) over a 10-year period. Sap samples collected along transects over a zone of base-metal mineralization revealed clear anomalies of Ag, Cd, Zn and Pb above the orebody (Fig. 1). More details of the use of saps in exploration are summarized in Dunn (2007).

Collection of cuticle and salt particulates on leaf tissues as a possible sample medium was tested by Barringer (1977), who compared the geochemical expression in soil, conifer vegetation and vegetation particulates sampled over Zn mineralization in Ontario. Later, some interesting positive results were recorded over Cu/Pb/Zn sulphides in the United Kingdom by Horler et al. (1980).

## LOCATION AND ACCESS

Test sites selected for this study lie within Gold Fields Canada Exploration (Vancouver) and Consolidated Woodjam Copper Corp.'s (Vancouver) Woodjam property, which is located in the Cariboo Mining District of central BC (NTS map areas 093A/03, /06; Fig. 2). The property, which consists of 178 mineral claims totalling 58 470 ha, is located about 65 km to the northeast of Williams Lake. Horsefly, the nearest settlement and logistical base for the fieldwork, lies within the property boundary and is accessible by a paved road from Williams Lake. The two test sites, known as Deerhorn and Three Firs (formally known as Megalloy; Fig. 2), lie 8 and 12 km respectively to the southeast and south of Horsefly; both are readily accessible via a network of well-maintained logging roads.

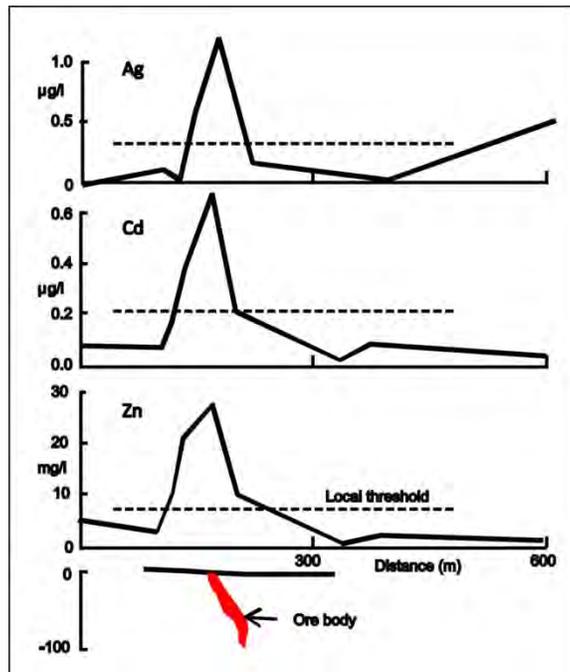


FIGURE 1. TRANSECT ACROSS A SKARN-TYPE POLYMETALLIC SULPHIDE DEPOSIT IN FINLAND. CONCENTRATIONS IN BIRCH SAP (*BETULA VERRICOSA*) OF SILVER, CADMIUM AND ZINC (AFTER HARJU AND HULDÉN, 1990).

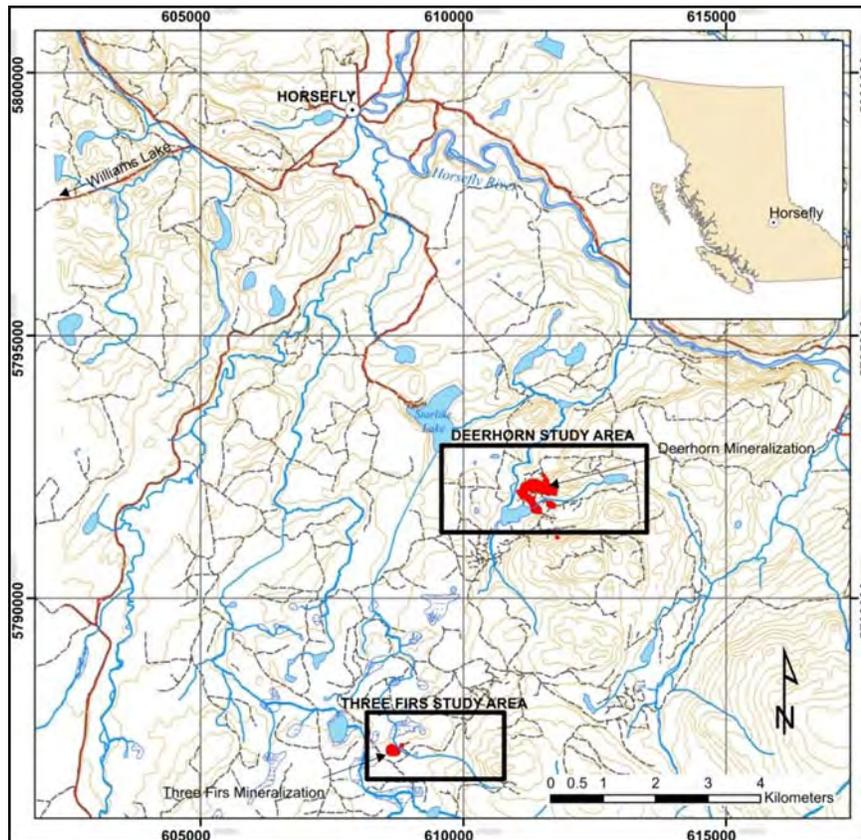


FIGURE 2. LOCATION OF THE STUDY AREAS AT THE WOODJAM PROPERTY. RED SHAPES REPRESENT THE SURFACE PROJECTION OF MINERALIZATION DEFINED BY THE +0.20 G/T AU-EQUIVALENT CUTOFF (BLACKWELL ET AL., 2012).

## SURFICIAL ENVIRONMENT

The project area lies at the boundary between the Fraser Plateau and Quesnel Highland physiographic regions of central BC (Holland, 1964). The terrain in the study areas has characteristics of both regions. The Deerhorn test site lies at a fairly sharp transition between relatively flat rolling topography typical of the Fraser Plateau on the western side of the mineralized zone, to low hills of the Quesnel Highland to the east (Fig. 2). Elevations across the Deerhorn sample traverse, which crosses the transition, vary from 900 m at the western end to 1030 m at the highest point, close to the eastern end. A number of small lakes and ponds are scattered throughout the area and are linked by small streams and boggy depressions, which form part of a dendritic drainage pattern connecting with the Horsefly River, some 5 km to the northeast of Deerhorn.

The Three Firs test site lies in a similar physiographic setting to Deerhorn (Fig. 2). More than half of the Three Firs sample traverse crosses relatively flat terrain typical of the Fraser Plateau, where elevations range from 975 to 1000 m. At these lower elevations, a number of swamps and small creeks define a northwest-flowing dendritic drainage pattern, which merges with Woodjam Creek, some 8 km to the

northwest. The terrain gradually rises eastward into the rounded hills of the Quesnel Highland, where the maximum elevation at the eastern end of the line is 1140 m.

Quaternary glacial deposits cover of mineralization at both study areas (Levson, 2010). To the east of Deerhorn, surficial deposits consist of an intermittent till veneer, which mantles the hillsides and becomes thicker in topographic depressions. The maximum thickness of the till is unknown but the presence of outcrops on the northern flank of the hillside east of Deerhorn suggests that it is likely to be no more than a few metres thick. Glacial landforms, such as drumlinoid features, are present in this area and east of the sample traverse. Their long axes indicate a west-northwesterly ice-flow direction. Cover thickens rapidly westward onto the lowlands and drilling at Deerhorn has shown that the bedrock surface is buried beneath up to 60 m of till and glaciofluvial sediments (Skinner, 2010; del Real et al., 2013). Surficial deposits at the southern limit of the projected mineralized zone consist of well-sorted sand and gravel of probable glaciofluvial origin; the distribution of these deposits is unknown.

At Three Firs, the cover environment is complicated by the presence of a Tertiary basalt unit (Chilcotin Group?) beneath the glacial deposits. Drilling has shown that the basalt probably obscures a part of the mineralized zone. It consists of fresh, black, highly vesicular lava ranging from 2 to 20 m thick (A. Rainbow, pers. comm., 2012). Nicola Group rocks at its lower contact are intensely weathered over several metres in what is likely to be a paleoregolith. This clay- and oxide-rich zone is alternatively interpreted as a fault-gouge zone by Gold Fields Canada Exploration geologists (A. Rainbow, pers. comm., 2012). The extent of volcanic cover is unknown, although its distribution is most likely restricted to paleo-valleys rather than forming a continuous cap over the mineralized area. This would be typical of other occurrences of Chilcotin Group flows in the region (Dohaney, 2009). Surficial deposits at Three Firs consist predominantly of till, which forms a blanket 40 to 100 m thick over the Nicola Group and basalt unit (A. Rainbow, pers. comm., 2012). There is no outcrop in the vicinity of the mineralization. Till cover appears to thin gradually eastward and outcrops of distinctive 'turkey-track' feldspar porphyry become widespread in the east-central part of the sample traverse. On the hillside, at the eastern end of the traverse, till cover is present as a thin veneer no more than a metre or two thick.

The Woodjam area is situated at the transition between the sub-boreal spruce biogeoclimatic zone to the west, dominated by white spruce and/or Engelmann spruce hybrids, and the interior cedar-western hemlock biogeoclimatic zone to the east. Douglas-fir occurs in the drier areas, with some large trees, and some lodgepole pine and western redcedar. Birch and poplar, scattered throughout, are the most common deciduous species. The understory has shrub alder and birch. Typical sample site and soil profiles are shown in Figures 3-5.



FIGURE 3. A TYPICAL SAMPLE LOCATION AT DEERHORN



FIGURE 4. A TYPICAL PODZOL PROFILE FOR CENTRAL BC

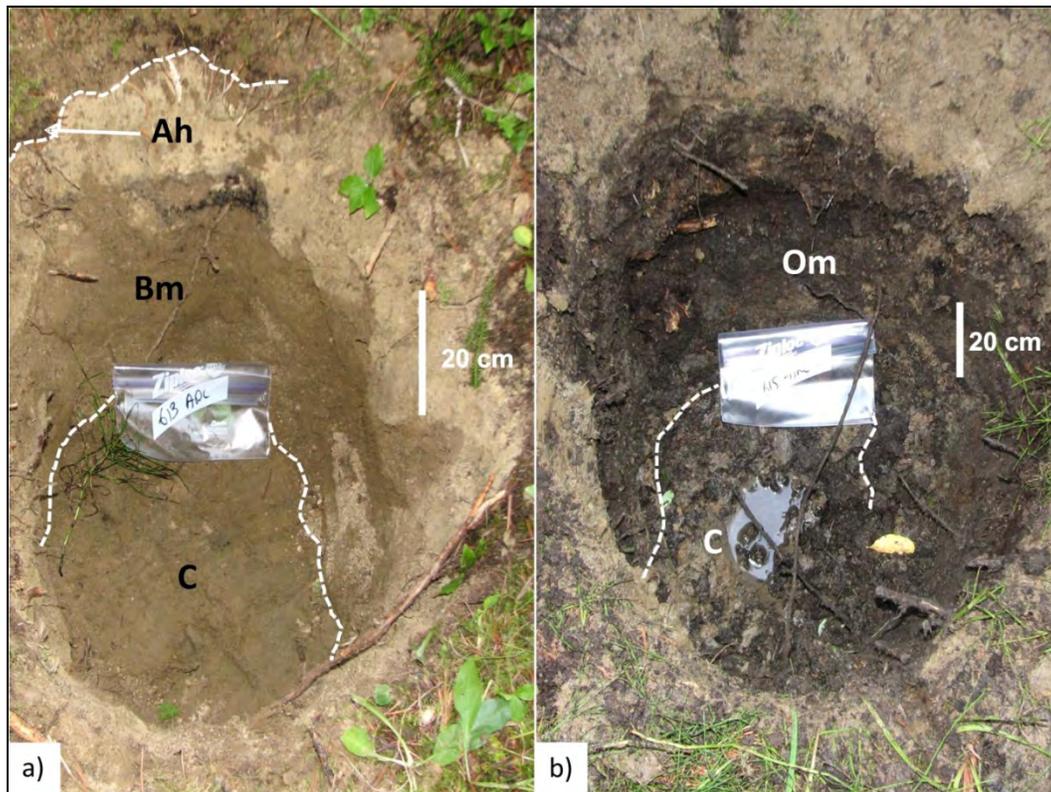


FIGURE 5. BRUNISOL (A) AND ORGANIC SOIL (B) PROFILES TYPICAL OF CENTRAL BC

## GEOLOGY

### REGIONAL SETTING

The Woodjam property area lies in the southern part of the highly prospective Quesnel terrane: a Late Triassic to Early Jurassic magmatic arc complex, which extends for most of the length of the Canadian Cordillera. It is flanked to the east by assemblages of Proterozoic and Paleozoic carbonate and siliciclastic rocks of ancestral North American affinity, but is separated from them by a sliver of oceanic basalt and chert of the Slide Mountain terrane (Schiarizza et al., 2009). Oceanic rocks of the Late Paleozoic to Early Mesozoic Cache Creek terrane bound the Quesnel terrane to the west (Fig. 6). The southern part of the Quesnel terrane hosts a number of important Cu-Au porphyry deposits; nearby examples include Gibraltar and Mount Polley.

In the Woodjam property area, the Quesnel terrane is represented by Middle to Upper Triassic volcano-sedimentary rocks of the Nicola Group (Fig. 6). Locally this consists of a shallow northwest-dipping sequence of volcanic and volcanic-derived sedimentary rocks, which include augite-phyric basalt flows and polymictic breccias containing latite, trachyte and equivalent volcanic clasts (Skinner, 2010). Sandstones and conglomerates are intercalated with the volcanic units. A suite of more or less coeval intrusions of alkaline to calcalkaline affinity intrudes the volcanic and sedimentary sequence. These

intrusions include the Early Jurassic Takomkane batholith, located to the south and east of the project area, and a number of smaller syenite, monzonite, quartz monzonite and monzodiorite stocks and dikes within the Woodjam property itself; many of these are associated with Cu-Au mineralization (J. Blackwell, pers. comm., 2012).

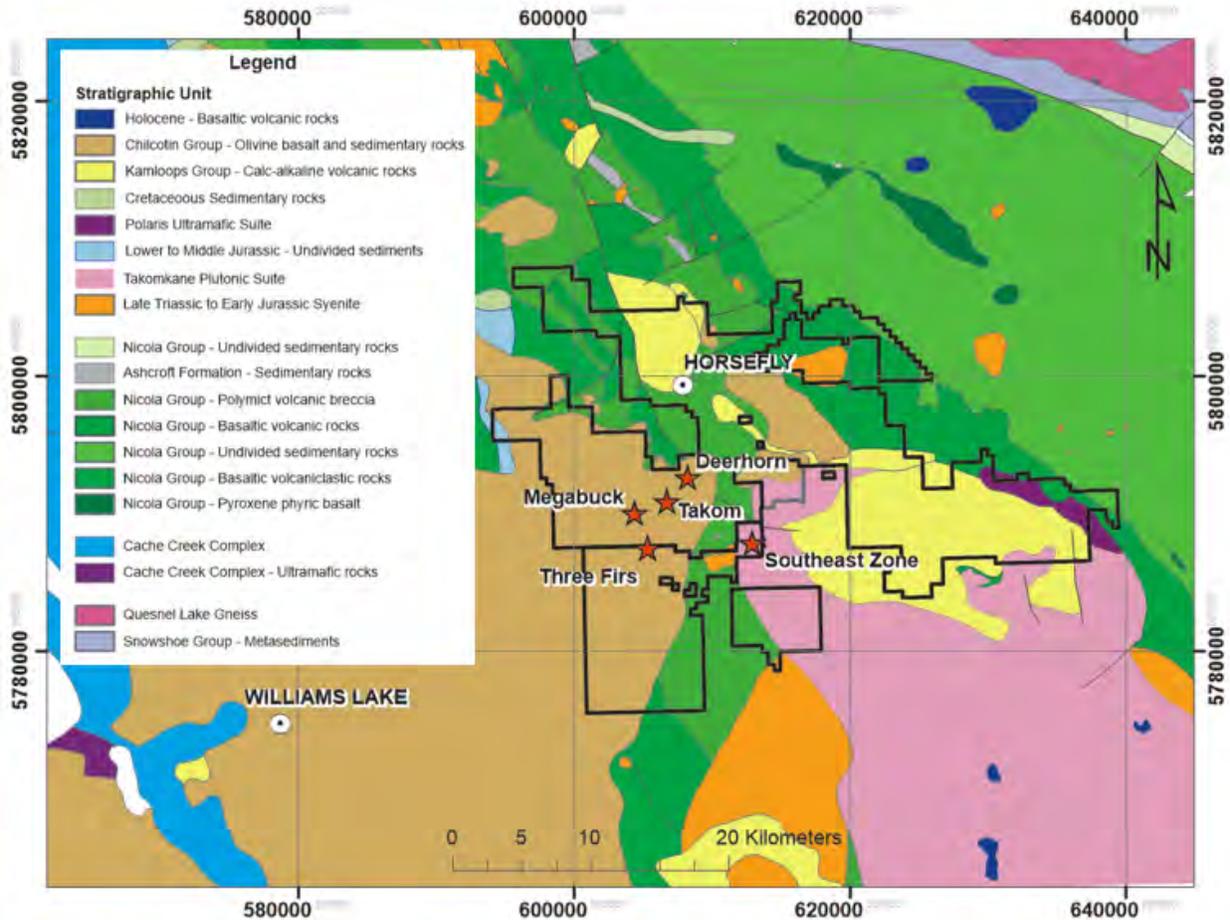


FIGURE 6. REGIONAL GEOLOGY OF THE WOODJAM PROPERTY AREA, SOUTH-CENTRAL BC (AFTER BLACKWELL ET AL., 2012); BLACK OUTLINES DENOTE THE PROPERTY BOUNDARY; RED STARS INDICATE THE MINERAL DEPOSITS AND PROSPECTS

The Woodjam South property contains several centres of Early Jurassic porphyry-style Cu-Mo-Au mineralization (Schiarizza et al., 2009). Style of mineralization, host rocks and metal association vary from one mineralized centre to another; these include the Southeast, Takom, Megabuck, Deerhorn and Three Firs prospects (Figs. 2, 6 and 7). The Southeast zone is currently at the most advanced stage of exploration and has an inferred, pit-constrained resource of 146.5 Mt grading 0.33% Cu (Sherlock et al., 2012). Copper-Mo mineralization is hosted in intrusive rocks, which form part of the Takomkane batholith. Deerhorn is the next most advanced prospect and is currently undergoing exploration drilling. It is characterized by Cu-Au mineralization hosted in Nicola Group volcanic rocks and a series of small porphyry stocks and dikes (see below). The remaining prospects are all at the exploratory drilling stage. Three Firs represents a new discovery that was made early in 2012 (Consolidated Woodjam Copper

Corp., 2012a); it is currently in the initial drill-testing stage. Nicola Group rocks in much of the western part of the Woodjam South property area and an area to the east of Deerhorn are covered by younger Cenozoic rocks belonging to the Chilcotin Group (Bevier, 1983; Dohaney, 2009). These consist of olivine basalt lavas, tuffs and sedimentary units, including sandstone, siltstone, shale and conglomerate. This younger volcanic and sedimentary rock cover masks prospective areas of the underlying Nicola Group.

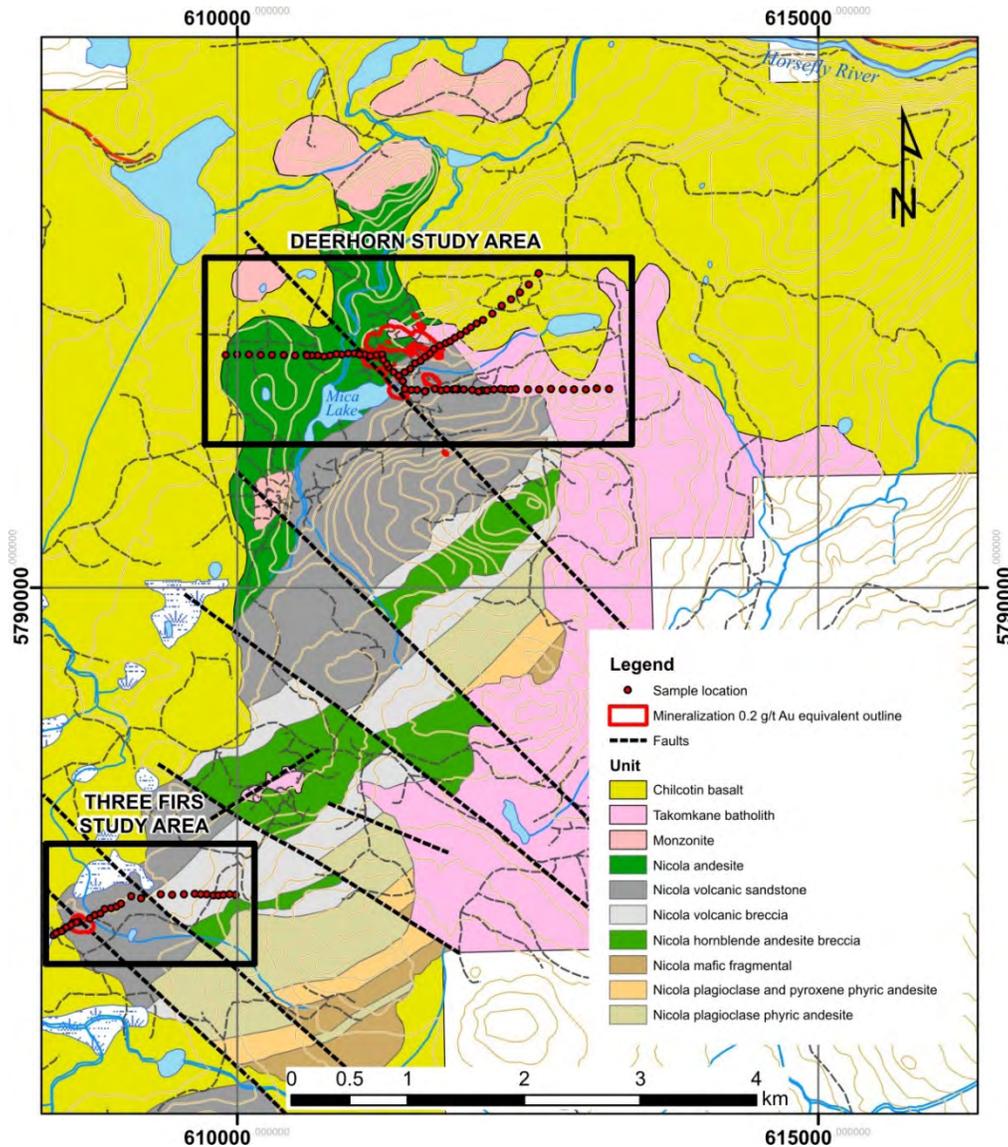


FIGURE 7. BEDROCK GEOLOGY OF THE WOODJAM SOUTH PROPERTY AREA (AFTER BLACKWELL ET AL., 2012). RED DOTS INDICATE SAMPLE STATIONS, INCLUDING A NORTHEASTERLY LINE AT DEERHORN FOR WHICH SELECTED SAMPLES WERE FOR A COMPLEMENTARY GEOSCIENCE BC PROJECT (BISSIG ET AL., 2013)

## DEERHORN

Deerhorn is a blind zone of porphyry Cu-Au-style mineralization, which was discovered by drilling a large chargeability anomaly in 2007 (Skinner, 2010). The mineralization, shown by the red +0.20 g/t Au equivalent outline in Figures 2 and 7, is the surface projection of a pipe-like body containing a higher-grade shoot, which plunges at a moderate angle to the southeast (J. Blackwell, pers. comm., 2012). Its dimensions are approximately 350 m in strike, 100 m in width and 200 m in depth (Consolidated Woodjam Copper Corp., 2012b). Higher grade mineralization is enclosed within a much more extensive lower-grade envelope defined by quartz and magnetite stockwork, veinlets and disseminated chalcopyrite mineralization. Low-grade mineralization is locally associated with a chargeability anomaly that extends northwest of the Deerhorn drilling and continues south and west to the Megabuck prospects, which suggests that the prospects are likely part of a single larger mineralized system.

Geological mapping and reconstruction of the bedrock geology from drilling by Gold Fields Canada Exploration (J. Blackwell, pers. comm., 2012; Fig. 7) indicates that the mineralization is hosted in a northeast-striking, northwest-dipping package of Nicola Group andesite and volcanic sandstone. Higher-grade mineralization is associated with a number of northwest-striking dike-like monzonite bodies 30–75 m wide, which cross the contact between volcanic-derived sandstone units in the southeast and andesitic rocks in the northwest of the mineralized zone. The intrusion and volcano-sedimentary units are offset by sets of west-northwest- and northeast-striking faults (J. Blackwell, pers. comm., 2012). Copper-Au mineralization subcrops beneath a variable cover of Quaternary glacial and glaciofluvial deposits. The deposits consist of a till blanket up to 60 m thick over the mineralization and a sequence of overlying glaciofluvial sand and gravel exposed in road cuts near the southeastern shore of Mica lake. The distribution of these deposits is unknown but they are not likely to be extensive.

## THREE FIRS

Bedrock geology of the Three Firs study area is not exposed. Mineralization was discovered at this prospect during the early spring of 2012. At the time of sampling for this study, only three holes had encountered significant Cu and Au mineralization. What makes this study area appealing from a deep-penetrating-geochemistry standpoint is the presence of a basalt unit, inferred to be part of the Chilcotin Group, which overlies at least part of the mineralized zone. The extent of the basalt is unknown and it is difficult to determine from the interpretation of ground and airborne magnetic data. A basalt cap at least 30 m thick covering the underlying altered and mineralized Nicola Group rocks has been intersected by drilling. Figures 6 and 7 illustrate the known distribution of basalt and the surface projections of the mineralized drill intersections.

Quaternary glacial sediments overlie the basalt; where observed in drill road exposures, the sediments appear to consist of a boulder till containing abundant large rounded clasts (up to 1 m in diameter) of distinctive 'turkey-track' andesite porphyry that is known to outcrop near the eastern end of the sample traverse and immediately to the southeast. The size and composition of the boulders indicate that the till is locally derived and possibly forms only a thin veneer across the survey area.

## FIELD METHODS

### SAMPLING PROCEDURES

Samples were collected along traverses across the surface projections of the known Cu-Au mineralization (Fig. 8). The Deerhorn traverse (Fig. 8a) is 3500 m long with sample sites spaced at 100 m intervals in background areas and at 50 m intervals over the projected Cu-Au mineralization. The eastern and western thirds of the traverse have east-west orientations, while the central part over the mineralized zone is oriented northwest-southeast in order to avoid a small lake.

At Three Firs (Fig. 8b), the traverse line is 1650 m long. The western half over the Cu-Au mineralization has a north-easterly orientation and the eastern half is aligned east-west. Again sample sites were spaced at 50 m intervals over the inferred position of the mineralization and at 100 m intervals in inferred background areas; background could only be achieved at the eastern end of the line. Sampling was not possible to the west of the mineralization due to the proximity of the property boundary.

Samples were collected on two occasions. The bulk of the sampling was completed in early July 2012 in conjunction with a complementary Geoscience BC project involving the soil and rock geochemistry (Bissig et al., 2013). Initial results indicated that the lines sampled should be extended in order to reach well into 'background' areas. Furthermore, the quality of some of the foliar samples from the exudate component might have been compromised; therefore some additional sampling was warranted. This follow-up phase was undertaken during a two-day period at the beginning of September 2012.

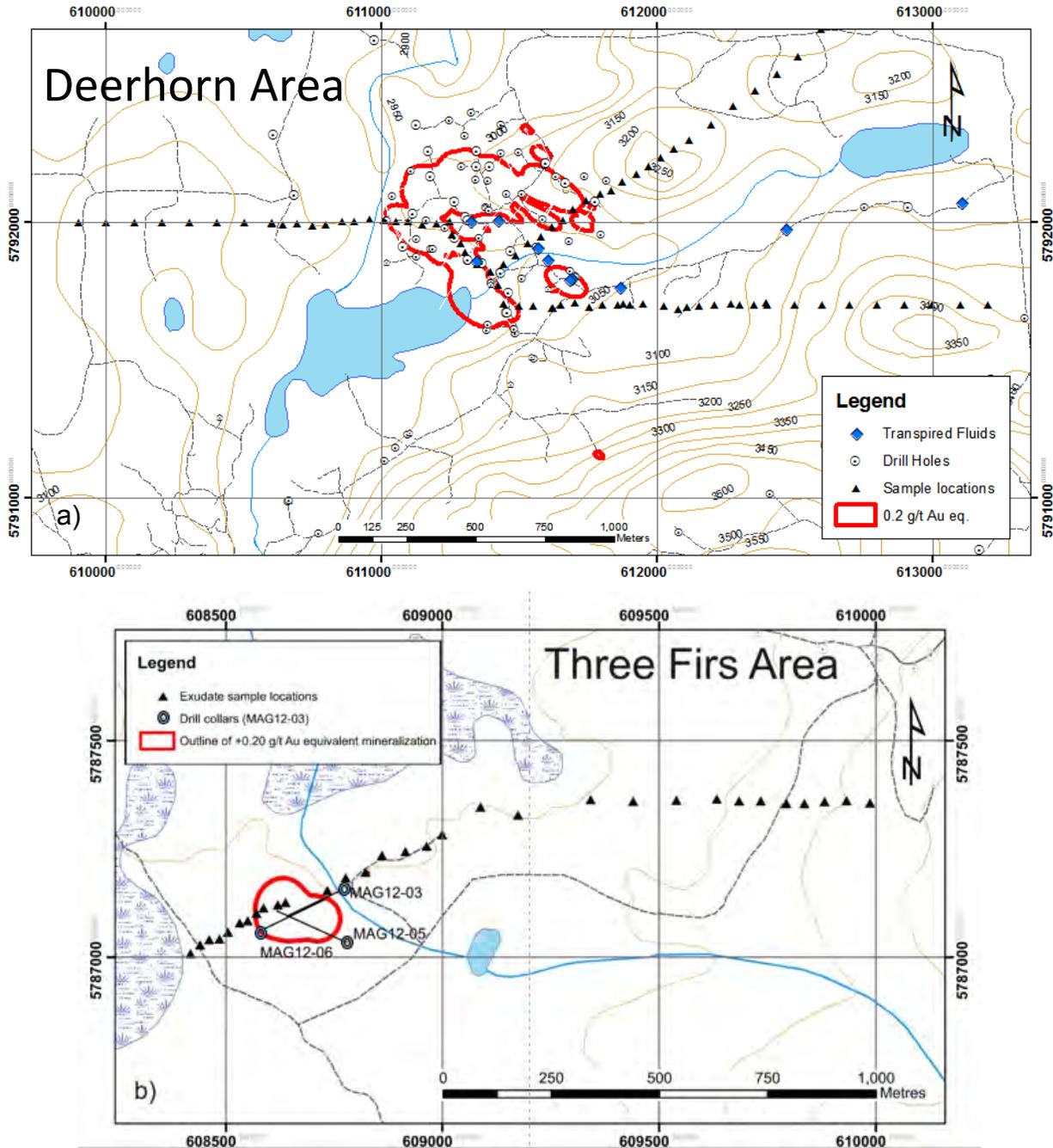


FIGURE 8. LOCATION OF SAMPLE SITES: A) DEERHORN TRAVERSE; B) THREE FIRS TRAVERSE. RED OUTLINES DENOTE THE SURFACE PROJECTION OF >0.2 G/T AU EQUIVALENT MINERALIZATION.

## AH SOIL HORIZON AND CHARCOAL SAMPLES

Ah-soil horizon sampling involved rolling back the surface moss-mat and leaf-litter layer (LF and LFH horizons) and scraping the black humic material accumulated on top of the mineral soil profile (Fig. 4a). In order to obtain enough material (50–75 g) and to create a composite sample to reduce within-site variability, several patches were sampled at each station and put in Kraft paper sample bags. An Ah horizon sample and a charcoal sample (where present) were collected at each site. Charcoal fragments were hand-picked from the Ah horizon and placed in Ziploc® plastic bags. The amount and size of fragments present were found to be quite variable from station to station. At some locations, only minute chips (<1 mm) were obtained and it was necessary to collect charcoal from several spots within a 10 m radius of the sample location in order to obtain sufficient material for analysis (approximately 5 g). At other sample sites, carbonized twigs, bark or wood could be sampled relatively easily.

## VEGETATION

For the vegetation sampling, the dominant tree species proved to be spruce, and was therefore the focus for the biogeochemical sampling. Both twigs and outer bark were sampled, and the spruce trunks proved to be good sources for the collection of congealed sap. Alder were sufficiently abundant that leaves could be readily collected for some of the surface-wax tests.

The outer bark from spruce (*Picea glauca*) was obtained by scraping the scales from around the circumference of a single large tree using a hardened-steel paint scraper, and pouring the scales into a standard Kraft paper soil bag (a fairly full bag contained approximately 50 g; Fig. 9a).



FIGURE 9. SAMPLING PROCEDURES FOR A) WHITE SPRUCE BARK; AND B) TWIGS

Samples of twigs and needles of spruce comprising the most recent 5–7 years of growth were snipped from around the circumference of a single tree. In central BC, this amount of growth is typically about a hand-span in length, at which point the twig diameter is 4–5 mm (Fig. 9b). A consistent diameter is quite critical because many trace elements concentrate in the bark part of the twig, whereas the woody tissue (the cortex) has lower concentrations of most elements. Consequently, unless there is a consistency in the diameters of the twigs that are collected, any analysis of twig tissue can result in variability among

samples simply because of the differing ratios of woody tissue to twig bark. The twig with needles samples were placed into porous polypropylene bags ('Hubco' Inc.'s Sentry II). The use of plastic bags is to be avoided because samples soon release their moisture and become very soggy; if there is any delay in processing they develop moulds and lose their integrity.

At the laboratory, vegetation samples were thoroughly dried at 80°C in an oven with a forced-air fan for 24 hours to remove moisture. The needles were then separated from the twigs. In preparation for chemical analysis, each bark sample was milled to a powder using a Wiley mill. The spruce twigs, less the needles, were weighed in aluminum trays, which were placed in a kiln dedicated to plant tissues, and reduced to ash by controlled ignition at 475°C for 24 hours.

## PLANT EXUDATES

Several different types of plant exudates were collected (Figs. 10, 11, 12):

White spruce sap, the congealed material that accumulates on the surface of tree trunks at the site of wounds, insect borings, dead branches or damaged surfaces (e.g., grazed by falling trees) was collected. A pocket knife or paint scraper was used (Fig. 10a) to delicately pick or scrape off a sufficient amount of the congealed sap (1-5 g; Fig. 10b) to fill a small polyethylene vial. At most sites material was collected from several trees and two or three minutes were usually sufficient to collect the required amount.



**FIGURE 10. COLLECTION OF SPRUCE SAP: A) EXTREME EXAMPLE OF CONGEALED SAP ON TREE TRUNK; B) TYPICAL SAMPLE SIZE (APPROXIMATELY 1 TO 5G)**

Alder leaves were collected and the surface waxes were stripped off using chloroform. During the first phase of the survey they were stuffed into 250 mL polyethylene bottles and the lids screwed on tightly. This proved not to be the optimal procedure, since the leaves soon turned brown and started to decompose unless they were refrigerated on the day of collection. During the second phase, they were put into Kraft paper sample bags.

The current year's growth of spruce twigs and needles was snipped from several branches following the same procedures as those used for the alder leaves. Although these did not deteriorate like the alder, they were nevertheless put into Kraft paper sample bags during the second phase of sampling.

During a hot summer's day, plants transpire fluids through the stomata on their foliage. Gold has been reported in these fluids from studies in Siberia (Kyuregyan and Burnutyan, 1972). In order to collect this material (referred to here as 'transpired fluids'), plastic bags were tied over the twigs of several spruce trees over mineralized and background areas and left in the hot sunshine for a day (Fig. 11a). At the end of the day, the sites were revisited and the accumulated liquid was poured from the plastic bags into plastic vials and sealed (Fig. 11b). On a cool day no fluids accumulated, whereas on a hot day more than 50 mL was obtained from each twig. During the first phase of sample collection, more than 50 mL of fluid was collected in a single sunny day. During the second phase, when it was cool and cloudy, no fluids accumulated and the bags were left for a week (including some sunny days) before there was sufficient fluid for collection.



**FIGURE 11. COLLECTION OF EXUDATE SAMPLES: A) AND B) TRANSPIRED FLUIDS; C) AND D) SURFACE PARTICULATES USING A VACUUM AND CYCLONE SYSTEM**

Horler et al. (1980) experimented with the collection of plant-surface particles from gorse bushes in southwestern England and concluded that the analysis of these particulates provided a useful geochemical indicator. Attempts were made to collect these particulates using the same type of cyclone (with a similar vacuum attachment) as that described in the paper by Horler et al. (1980; Figs. 11c and

d). Unfortunately, because there had been substantial rain just prior to both field visits, no particulates could be collected; all plant surfaces (mostly alder and spruce in the field area) failed to produce any particulate material. Figure 12 shows the range of samples collected at each sample station.



FIGURE 12. MEDIA COLLECTED FOR STUDY (EXCEPT CHARCOAL)

## SOIL pH AND ELECTRICAL CONDUCTIVITY MEASUREMENTS

Samples for soil pH and electrical conductivity (EC) measurements were collected from both study areas (Fig. 8). Where possible, approximately 100 g of material was collected from the top centimetre of the leached Ae horizon (e.g., in podzol profiles; Fig. 4) or from the top of the B horizon, where the Ae horizon was either absent or poorly developed (e.g., in brunisol profiles; Fig. 5). At sample sites with poor drainage, where organic material comprises the upper part of the profile, no sample was collected. Samples were placed in heavy-duty double-seal Ziploc® plastic bags, which were kept refrigerated prior to measuring.

Conductivity measurements were made on 1:1 slurry of soil in distilled water using a VWR® conductivity meter. Soil pH readings were taken on the same slurry using a double-junction pHTestr® 30 handheld pH meter manufactured by Oakton® Instruments. The instrument was calibrated using standard pH buffer solutions at pH 4.00, 7.00 and 10.00. Two pH measurements were taken on each sample: the first one taken 20 seconds after immersion of the electrode into the slurry, and a second taken 20 seconds after adding one drop of 5% acetic acid (white vinegar) and stirring. Readings were recorded into an Excel® spreadsheet and converted to H<sup>+</sup> concentrations for interpretation.

A discussion of these results is included Bissig et al. (2013).

## QUALITY CONTROL

Quality control measures employed for this study included the collection of field duplicate samples for each sample type, as well as the insertion of 'blind' control samples (milled or ashed vegetation of similar matrix and known composition) for the vegetation analysis. A total of seven field duplicates were collected for each sample type at randomly selected sites. At each site, material was collected using exactly the same procedures as the original sample and from within 5 m of the original sample. Control samples for the vegetation were inserted at a frequency of approximately 1 per 10 field samples.

## LABORATORY METHODS

### SAMPLE PREPARATION AND ANALYSIS

Table 1 provides a summary of the types of materials collected for the exudate study and the analytical protocols used. Analysis of the milled dry bark samples was carried out at Acme Analytical Laboratories Ltd. (Vancouver) using their 1VE2-MS method. This involves dissolution of a 1 g aliquot of milled material in nitric acid followed by aqua-regia digestion, heating on a hot plate, then diluting to a constant weight with de-ionized water; the analytical finish is by inductively coupled plasma–mass spectrometry (ICP-MS).

TABLE 1. SAMPLE MEDIA AND ANALYTICAL METHODS EMPLOYED ON AH HORIZON SOILS, CHARCOAL PLANT TISSUES AND EXUDATES

Medium	No. of samples	Process	Analysis	Survey area
White spruce twigs	69	Needles separated and twigs reduced to ash	Acme method 1F04	Deerhorn and Three Firs
White spruce outer bark	68	Milled to powder - analysis of dry tissue	Acme method 1VE2	Deerhorn and Three Firs
Alder leaves	41	Leached in chloroform to remove surface waxes	QFIR - HR-ICP-MS <sup>1</sup>	Deerhorn
First year white spruce twigs with needles	41	Leached in chloroform to remove surface waxes	QFIR - HR-ICP-MS	Deerhorn
Spruce sap (congealed)	43	Microwave digestion in concentrated nitric acid	QFIR - HR-ICP-MS	Deerhorn
Transpired fluids	10	Analysis by direct aspiration after spiking with 4 mL of sample with 80 µL of ultrapure nitric acid	QFIR - HR-ICP-MS	Deerhorn
Leaf surface particulates	0	Unsuccessful - no samples	None	Deerhorn
Ah	72	Dried, sieved and digested in modified aqua regia	Acme method 1F04	Deerhorn and Three Firs
Charcoal	72	Dried, milled and digested in modified aqua regia	Acme method 1F04	Deerhorn

<sup>1</sup> Queen's University Facility for Isotope Research (QFIR), Kingston, Ontario, in collaboration with W. Macfarlane Acme Analytical Laboratories Ltd., Vancouver, BC; all analyses by inductively coupled plasma-mass spectrometry (ICP-MS), supplemented by inductively coupled plasma-emission spectrometry, except those at QFIR done using high resolution (HR) ICP-MS

Ah-horizon, charcoal and ashed spruce twig samples were also analysed at Acme Analytical Laboratories Ltd., where 0.5 aliquots (or 0.25 g of ash) were dissolved in modified aqua regia (method code Group 1F) and analyzed by ICP-MS and inductively coupled plasma–emission spectrometry (ICP-ES) for 53 elements and REE's. Saps were analyzed at Queen's University Facility for Isotope Research (QFIR) by digesting 1.0 g of sample in 6 ml of concentrated nitric acid using a microwave digestion system manufactured by Anton Paar. Microwave power was set at 1400W and the total cycle time was 40 minutes, including power ramp up and cool down. In most instances, clear solutions with no solid residues were obtained and analyzed for 55 elements on an Element2 sector field ICP-MS manufactured by Thermo Fisher

Scientific Inc. Transpired fluids were analyzed directly on the sector field ICP-MS at QFIR for the same suite of elements as the saps. Minimum dilutions were achieved by spiking 4 mL of sample with 80 µL of ultrapure concentrated nitric acid to provide a matrix with maximum instrumental sensitivity: the combination of minimum dilution and maximum sensitivity was necessary to effectively assess this very low-concentration medium. Alder and spruce foliage were placed in ultrapure chloroform and processed for 5 minutes in an ultrasonic bath to remove surface waxes and crystallized exudates. The leachate was then transferred into clean Teflon® beakers and allowed to evaporate to dryness in a Class 1000 cleanroom. The residue was then taken up in 2% nitric acid and analyzed on the sector field ICP-MS at QFIR.

## DATA PROCESSING

In order to prepare the analytical results for interpretation, a number of steps were taken. First the analytical results were merged with the sample location and field observational data using Geosoft's Target™ Geochemistry software and then exported to an Excel spreadsheet. During this procedure, "less than" detection limit symbols (< and -) were automatically replaced with a value equal to half the detection limit. Next, results for field and analytical duplicates were extracted from the dataset for QA/QC evaluation. The completed datasets were then compared with the original laboratory certificates to ensure that no merging errors had occurred. X-Y plots of the northings and eastings were also prepared so that location errors could be identified and corrected.

Merged results were then ported into ioGAS™ software where histograms were generated for each element. This was done to assess the type of distribution (i.e. log normal or normal) and to determine which elements require transformation prior to interpretation. Next, box and whisker plots were generated for each element using various field parameters as classification variables. This step assesses whether sample site characteristics such as slope, soil moisture etc. affect element concentrations and whether levelling is necessary to remove their effects from the dataset.

## DATA QUALITY

### FIELD DUPLICATE RESULTS

For the purpose of this report, data quality is assessed using the average percent relative standard deviation or average %RSD (also known as the % coefficient of variation), as an estimate of precision or reproducibility of the analytical results. Average %RSD is calculated in an Excel spreadsheet using the field duplicate results. This value represents the cumulative uncertainty related to field sampling, sample preparation and analysis. Field duplicate results provide important information about the homogeneity of the sample medium and the representivity of the sampling method employed.

Average %RSD is determined from the duplicate results by first determining the mean and standard deviation of each duplicate pair and then calculating the %RSD value using the formula:

$$\%RSD = (\text{standard deviation}/\text{mean}) \times 100$$

The average %RSD is then determined by averaging the %RSD values for the duplicate pairs. This is done for each element and analytical method. Spreadsheets with the calculations are included in Appendix 1. In the following discussions, average %RSD values below 30% are considered to indicate good data quality (precision); between 30 and 50% marginal quality, and over 50%, poor quality. The higher an average %RSD value is, the less likely it is to be able distinguish real patterns from noise. Noise is considered as the cumulative effect of geological background variation plus sampling and analytical error.

Table 2 shows the %RSD values calculated from field duplicate results. Results are colour coded to indicate data quality with green representing good data quality (%RSD <30%), yellow marginal data quality (%RSD 30-50%) and pink poor data quality (%RSD >50%).

For the ore related elements Mo, Cu, Pb, Zn and Ag, the duplicate results fall mostly within the good quality range for all media. Exceptions include Mo and Zn in charcoal and Ah horizon soil and Ag in spruce bark and twigs where precision is marginal.

Gold has good precision in charcoal and Ah horizon duplicates and poor precision in spruce twigs. A %RSD value could not be calculated for spruce bark because only detection limit concentrations were reported for the duplicate samples.

Of the pathfinder elements, As has the poorest precision with unacceptably high %RSD values calculated for charcoal and spruce bark and marginal values in spruce twigs and Ah horizon soil. Antimony results are much better. %RSD values indicating good quality are shown by charcoal, spruce twigs and bark but only a marginal value was obtained for Ah horizon soil. Mercury quality varies considerably across the different sample media. Spruce bark duplicate results show good data quality for this element. Results for charcoal are of marginal quality and in the Ah horizon soils the data quality is poor. Thallium has duplicate results above detection limit for only spruce twigs and Ah horizon soil where the %RSD values are marginal and poor, respectively.

Potentially important major and minor elements such as Ca, Sr, K, Rb, Cs, Mg, Fe and Mn have quite variable precisions across the sample media. Of this group of elements, Ca and Sr both have good data quality for charcoal, spruce bark and twigs but only marginal quality for Ah horizon soils. Potassium has good data quality for all media except spruce twigs, which only report detection limit values for the duplicate analyses. The related elements Rb and Cs have variable data quality. Cesium shows good precision for charcoal and Ah horizon and moderate precision for spruce bark and twigs. Rubidium results are not quite as good. This element has poor quality %RSD results for spruce bark and twigs and only moderate quality in charcoal and Ah horizon results.

Iron and Mn duplicate results indicate moderate data quality for most media. Exceptions include Fe in spruce twigs, which has good precision, and Mn in Ah soils where precision is poor.

Precision results for the transpired fluids (Tr. Fluids) field duplicates are also included in Table 3. These results are not directly comparable with the other sample media. Whereas the sample pairs were collected from the same trees, the duplicates were actually collected several weeks after the original samples under considerably different environmental conditions. The original samples represent a single day's fluid collection under warm summer sunshine; the duplicates were collected under gloomy and wet autumnal weather conditions over the course of several days. Not surprisingly the results show

considerable differences between the duplicate pairs that likely reflect seasonal differences in the activity of the spruce trees as well as the dramatically different weather conditions affecting transpiration rates. Consequently most elements show poor precisions. Arsenic and W are exceptions. These elements have good precisions. Uranium, Cd and La have %RSD values indicating marginal precision.

Comparing the overall precision of the different sample media, Table 2 shows normal scores at the bottom of each column. These are calculated by summing scores (good = 3, moderate = 2 and poor = 1) and normalizing the totals by the number of elements represented. Transpired fluids with a normal score of 1.32, has by far the worst overall precision of the media tested. Of the other sample media, spruce sap has the best overall precision (N-Score = 2.88) and Ah horizon the worst (N-Score = 2.37), however the difference between the best and worst performers is very slight.

**TABLE 2. SUMMARY OF AVERAGE %RSD VALUES FOR SELECTED ELEMENTS AND SAMPLE MEDIA**

%RSD - Field Duplicates						
	Charcoal (N=4)	Sp-Bk (N=3)	Sp-Tw (N=4)	Sp Sap (N=1)	Ah (N=1)	Tr. Fluids
Ag	10.63%	32.59%	30.80%		28.61%	
As	60.24%	51.85%	31.91%	53.50%	46.92%	15.92%
Au	18.74%		85.78%		21.21%	
Ba	43.05%	17.40%	36.24%	14.18%	56.42%	72.55%
Bi	64.57%		23.24%	69.04%	31.71%	71.53%
Ca	11.76%	20.73%	13.60%	6.82%	37.29%	76.60%
Cd	8.92%	75.79%	66.05%	13.29%	30.96%	45.01%
Co	35.55%	30.30%	45.27%	0.60%	32.44%	70.70%
Cr	41.19%	11.91%	25.66%	34.23%	20.59%	65.23%
Cs	20.44%	37.91%	58.02%	11.67%	20.24%	17.82%
Cu	12.34%	8.47%	13.53%	7.38%	21.57%	88.15%
Fe	41.67%	45.05%	20.56%	17.12%	37.82%	71.58%
Hg	31.56%	21.59%		10.12%	50.73%	71.91%
K	8.86%	29.77%		8.53%	11.44%	67.61%
La	45.38%	47.14%	28.15%	27.02%	40.40%	40.89%
Mg	22.28%	15.47%	19.52%	6.45%	9.81%	69.27%
Mn	48.13%	36.02%	36.84%	2.19%	84.56%	80.39%
Mo	33.95%	29.46%	26.04%	60.84%	47.70%	81.21%
Na	55.00%		18.43%	2.03%	9.43%	90.12%
Ni	41.82%	42.43%	47.92%	11.89%	22.90%	80.15%
Pb	7.57%	25.00%	29.93%	15.64%	24.22%	85.61%
Rb	30.09%	51.40%	58.40%	4.45%	34.42%	65.53%
S	26.19%	23.57%	11.17%	0.46%	61.02%	50.30%
Sb	15.71%	6.73%	20.07%		34.57%	100.17%
Se	11.79%		83.28%		11.79%	
Sr	22.00%	24.95%	13.67%	6.78%	34.98%	93.79%
Tl			37.71%	4.09%	23.76%	140.14%
U	23.57%			90.20%	31.43%	38.16%
V	40.95%		17.14%	19.48%	37.77%	51.35%
W	31.43%			134.83%		9.25%
Zn	37.37%	24.40%	33.37%	8.45%	48.37%	74.52%
Score	73	59	69	75	71	33
N	30	23	28	26	30	25
N-Score	2.43	2.57	2.46	2.88	2.37	1.32
Score						
3	Good quality					
2	Marginal quality					
1	Poor quality					
<DL						

Colours represent: good precision – green; marginal precision – yellow; and poor precision - red. Blanks represent elements with values at or below detection limit. Abbreviations: Sp-Bk – spruce bark; Sp-Tw – spruce twigs, Ah – Ah horizon soil.

For details on the precision estimations the reader is referred to Appendix 1 where calculations for each medium are presented.

## CONTROL SAMPLES

In addition to the field duplicate samples summarized above, control reference material (CRM) P5 (spruce twigs) was inserted after every 10<sup>th</sup> dry bark sample. Acme Labs also inserted their own vegetation CRM samples (CDV-1 and V16) after every 20<sup>th</sup> sample. The average, standard deviations and RSD percentages are shown in Table 3. Many elements have RSD values below 20%, and some are <10%. The precision for Au is poor (although biased strongly by 1 anomalous value) and elements with inferior precision (>20%) include As, Bi, some REE's (close to detection), Hf, Li, Mo, Nb, Pt, S, Sc and Sn. Most of the elements in this list had concentrations close to the detection limit. Elements for which no RSD values are shown were all at or mostly below the detection level.

TABLE 3. CONTROL REFERENCE MATERIAL P5 INCLUDED WITH THE BARK SAMPLES

Dry Spruce Control P5 (n=5)						Dry Spruce Control P5 (n=5)					
		Accepted value	Average	Std. Dev.	RSD%			Accepted value	Average	Std. Dev.	RSD%
Ag	ppb	164	132	8.438	6	Na	%	0.002	<DL	<DL	<DL
Al	%	0.02	0.02	<DL	<DL	Nb	ppm	0.03	0.026	0.005	21
As	ppm	0.1	0.23	0.058	25	Nd	ppm		0.24	0.059	25
Au	ppb	5.9	7.6	6.259	82*	Ni	ppm	28.6	29	1.306	4
B	ppm	10	17	3.647	21	P	%	0.059	0.061	0.003	5
Ba	ppm	26	29	1.343	5	Pb	ppm	1.43	1.4	0.011	1
Be	ppm	0.1	<DL	<DL	<DL	Pd	ppb	47	40	5.857	15
Bi	ppm	0.13	0.12	0.032	26	Pr	ppm		0.062	0.008	13
Ca	%	0.43	0.40	0.015	4	Pt	ppb	1	2.6	0.894	34
Cd	ppm	0.10	0.092	0.016	18	Rb	ppm	3.09	3.1	0.114	4
Ce	ppm	0.48	0.52	0.031	6	Re	ppb	1	<DL	<DL	<DL
Co	ppm	0.7	0.65	0.059	9	S	%	0.05	0.043	0.017	40
Cr	ppm	4.31	4.1	0.259	6	Sb	ppm	0.02	0.032	0.004	14
Cs	ppm	0.043	0.04	0.002	4	Sc	ppm	0.2	0.18	0.050	29
Cu	ppm	41.02	36	1.938	5	Se	ppm	0.5	0.35	0.058	16
Dy	ppm		0.023	0.006	25	Sm	ppm		0.042	0.008	20
Er	ppm		<DL	<DL	<DL	Sn	ppm	0.03	0.043	0.015	35
Eu	ppm		<DL	<DL	<DL	Sr	ppm	10	9.4	0.277	3
Fe	%	0.225	0.21	0.012	6	Ta	ppm	0.001	<DL	<DL	<DL
Ga	ppm	0.1	<DL	<DL	<DL	Tb	ppm		<DL	<DL	<DL
Gd	ppm		0.038	0.015	40	Te	ppm	0.07	0.074	0.015	20
Ge	ppm	0.01	<DL	<DL	<DL	Th	ppm	0.06	0.064	0.005	9
Hf	ppm	0.004	0.006	0.001	24	Ti	ppm	10	10.2	0.447	4
Hg	ppb	51	52	7.563	15	Tl	ppm	0.04	0.038	0.004	12
Ho	ppm		<DL	<DL	<DL	Tm	ppm		<DL	<DL	<DL
In	ppm	0.02	<DL	<DL	<DL	U	ppm	0.03	0.022	0.004	20
K	%	0.23	0.24	0.005	2	V	ppm	2	<DL	<DL	<DL
La	ppm	0.25	0.23	0.015	6	W	ppm	0.1	<DL	<DL	<DL
Li	ppm	0.26	0.25	0.065	26	Y	ppm	0.112	0.10	0.013	12
Lu	ppm		<DL	<DL	<DL	Yb	ppm		<DL	<DL	<DL
Mg	%	0.086	0.087	0.003	3	Zn	ppm	28.7	27	1.756	6
Mn	ppm	430	422	17.306	4	Zr	ppm	0.14	0.14	0.020	14
Mo	ppm	0.04	0.038	0.008	22						

\*RSD = 25% with 1 anomalous value excluded

The control used for the ashed samples was V6e – ashed pine twigs and needles. This material suffers from the occasional high value for Au and Cu, presumably because of a slight lack of homogeneity. The material was collected near some gossanous boulders more than 20 years ago, and serves as a good control on most elements (Table 4).

TABLE 4. CONTROL ASH REFERENCE MATERIALS V6E INCLUDED WITH THE SPRUCE TWIG ASH SAMPLES

Ash Control V6e (n=7)					Ash Control V6e (n=7)				
		Average	Std.Dev	RSD%			Average	Std.Dev	RSD%
Ag	ppb	334	22	7	Nb	ppm	0.11	0.03	29
Al	%	1.1	0.16	15	Nd	ppm	12.6	0.93	7
As	ppm	6.1	0.76	13	Ni	ppm	73	53	71***
Au	ppb	10.2	7.6	73*	P	%	0.74	0.024	3
B	ppm	195	19	10	Pb	ppm	199	27	14
Ba	ppm	175	10	6	Pd	ppb	<DL		
Be	ppm	0.3	0.13	37	Pr	ppm	3.4	0.27	8
Bi	ppm	0.3	0.05	17	Pt	ppb	8.0	1.7	22
Ca	%	13.3	1.8	14	Rb	ppm	22.0	1.2	5
Cd	ppm	3.4	0.57	17	Re	ppb	6.4	3.3	51
Ce	ppm	30.2	2.6	9	S	%	0.57	0.08	14
Co	ppm	6.5	0.59	9	Sb	ppm	0.64	0.12	19
Cr	ppm	34.6	3.4	10	Sc	ppm	2.3	0.34	15
Cs	ppm	0.6	0.04	7	Se	ppm	0.51	0.28	55
Cu	ppm	153	82	53**	Sm	ppm	2.2	0.24	11
Dy	ppm	1.6	0.20	13	Sn	ppm	2.3	0.41	17
Er	ppm	0.7	0.07	10	Sr	ppm	568	20	4
Eu	ppm	0.5	0.06	12	Ta	ppm	<DL		
Fe	%	1.3	0.09	7	Tb	ppm	0.28	0.02	6
Ga	ppm	3.4	0.34	10	Te	ppm	0.05	0.03	68
Gd	ppm	2.0	0.30	15	Th	ppm	2.3	0.38	17
Ge	ppm	<DL			Ti	%	0.03	0.003	10
Hf	ppm	<DL			Tl	ppm	0.11	0.013	12
Hg	ppb	<DL			Tm	ppm	0.10	0.013	12
Ho	ppm	0.3	0.02	6	U	ppm	1.04	0.08	8
In	ppm	0.03	0.01	37	V	ppm	29.4	2.1	7
K	%	1.7	0.06	4	W	ppm	0.26	0.10	38
La	ppm	14.9	1.1	7	Y	ppm	7.4	0.28	4
Li	ppm	6.7	0.61	9	Yb	ppm	0.65	0.06	9
Lu	ppm	0.08	0.02	19	Zn	ppm	578	18	3
Mg	%	2.0	0.08	4	Zr	ppm	0.53	0.67	126
Mn	ppm	783	82	10	*31% excluding 1 anomalous value				
Mo	ppm	4.7	0.23	5	**14% excluding 1 anomalous value				
Na	%	0.18	0.02	13	***19% excluding 1 anomalous value				

In general the precision is better than that for the dry bark shown in Table 3. The worst elements are Au, Cu and Ni, but the statistics for these elements are biased by single anomalous values that are probably a function of the control material itself, rather than analytical precision. Other elements with poor precision returned concentration levels that were very close to the lower detection limits – Be, In, Lu, Nb, Pt, Re, Se, Te, W and Zr.

## RESULTS

In this section the results for selected ore and pathfinder elements are presented for each sample medium. The order of presentation is from the ground up, beginning with the top of the soil profile (Ah horizon and charcoal) and progressing upwards into the vegetation and concluding with the plant exudates. Results are presented as profile plots of element concentration versus distance along the sample transect onto which the position of the mineralized zone, swamps and surface projections of geological units are superimposed for reference. The bars representing the position of the blind mineralization are based on the envelope of > 0.2 g/t Au eq. intercepts from exploration drill holes. Lower grade material is known to be present between the bars (pers. comm., Gold Fields, 2012). Jogs in the sample line (Fig. 8a) are indicated by vertical dashed lines.

Summary statistics for selected elements for each sample medium are included in Appendix 2.

## DEERHORN

### AH HORIZON

The Ultratrace digestion is strong enough to dissolve Fe and Mn oxides and break down organic matter (humic and fulvic acids) while at the same time non-selectively desorbing metal ions from all components of the soil; it is not strong enough to completely dissolve any fibrous plant material, silicate or resistate minerals. Therefore, if introduced ions from blind mineralization are present in the sample (i.e. an exogenic signal) this digestion should be able to isolate it from the bulk (endogenic) component of the sample as has been documented by Heberlein and Samson (2010) and Heberlein and Dunn (2011) at the Kwanika project in north-central BC.

### COMMODITY ELEMENTS

Silver results are shown in Figure 13. This element displays a relatively flat background of about 200 ppb away from the surface projection of the mineralized zone (red bars). Elevated concentrations occur as a series of peaks located directly over mineralization. The highest value (847 ppb) occurs over a lower grade part of the zone situated between the main body of the deposit to the west and a small outlier of higher grade mineralization to the east. A strong single sample response of 1188 ppb near to the western end of the sample line is unexplained.

Copper (Fig. 14) has a much less convincing response than Ag. This element shows little variation along most of the line with background concentrations maintaining fairly stable levels of about 10 ppm. Over the Deerhorn mineralization a single peak (77.7 ppm) occurs over the western part of the zone. There is no contrast between samples over mineralization and background sites over the rest of the zone.

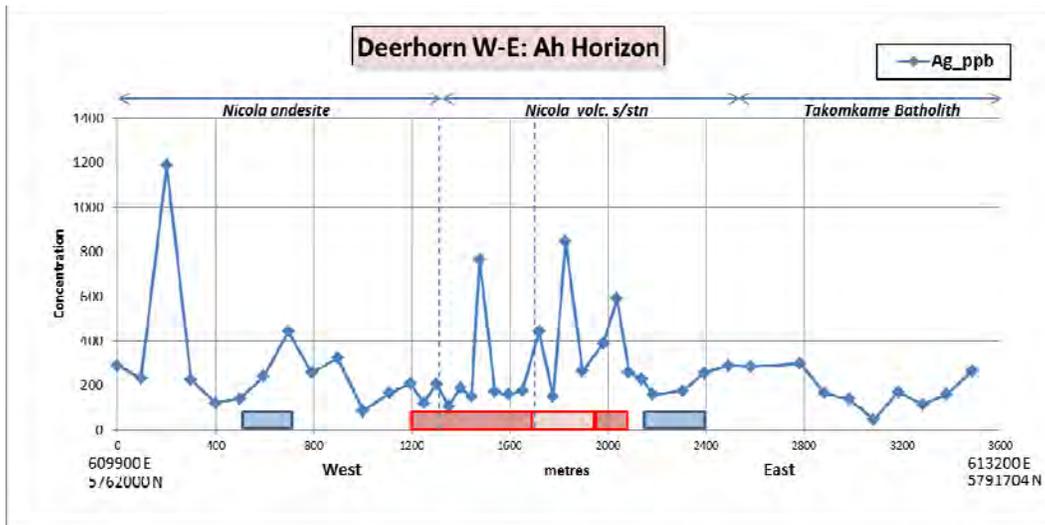


FIGURE 13. DEERHORN - SILVER IN AH HORIZON SOILS: THE RED BAR INDICATES THE MINERALIZED ZONE AND THE BLUE BARS SWAMPS

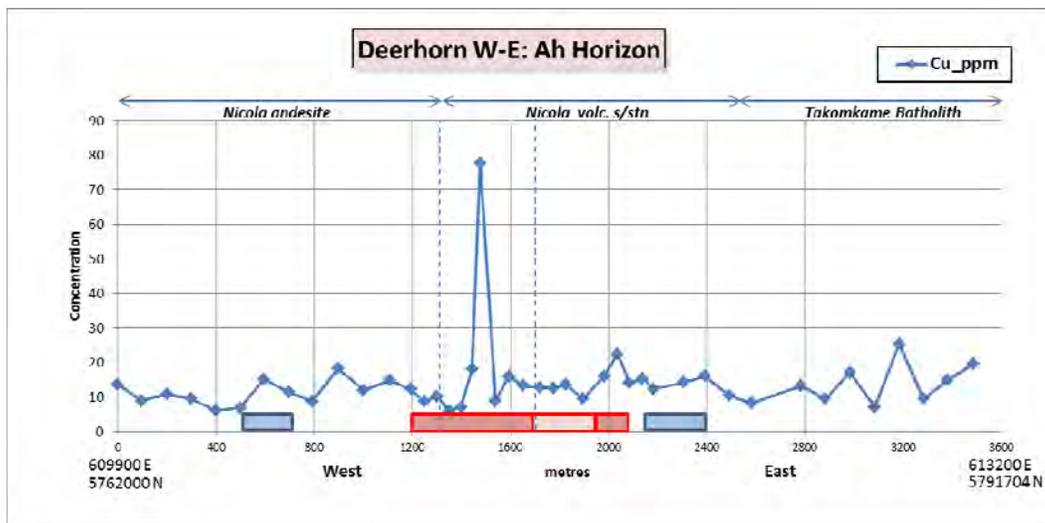


FIGURE 14. DEERHORN - COPPER IN AH HORIZON SOILS

Molybdenum results (Fig. 15) also have very little contrast. Values over background areas at the east and west ends of the line vary between 1 and 4 ppm. There is a slight difference in background concentration between samples overlying the Takomkame batholith in the east and Nicola andesites in the west. The former samples average less than 2 ppm while the latter reach 4 ppm near the west end of the line. A subtle increase in concentration is noted over the Deerhorn mineralization where individual samples reach concentrations up to 4.9 and 5.3 ppm respectively. A single elevated sample (4.8 ppm) corresponds with an area of boggy ground (blue bar) located immediately east of the mineralized zone and is interpreted to represent hydromorphic concentration of this element.



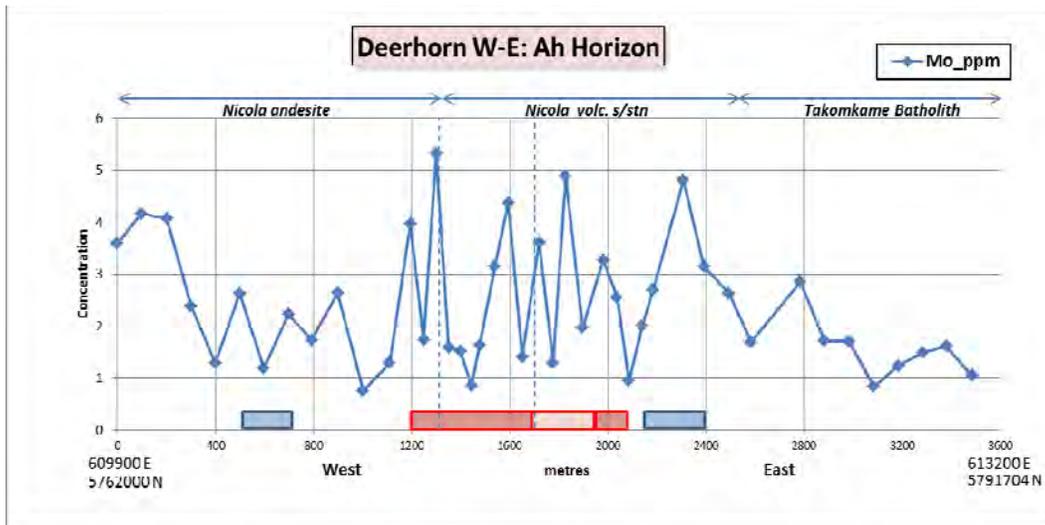


FIGURE 15. DEERHORN - MOLYBDENUM IN AH HORIZON SOILS

Gold results (Fig. 16) are somewhat similar to Ag. At the east end of the line over the Takomkame batholith, background levels vary between 0.5 and 1.5 ppb. Higher background concentrations are observed over the Nicola andesites at the west end of the line. In this area elevated values form a broad feature with a maximum concentration on 3.5 ppb. Patterns over the mineralization are quite different from background areas; rather than gradual changes in concentration, elevated Au values define two single sample peaks (5.9 and 3.9 ppb) located directly over the western part of the zone. These resemble a rabbit-ear response but are not at the margins of the mineralized zone, as would be expected. A single sample peak lying to the east of the mineralization occurs within a swamp filled depression that appears to be a former river valley. It is likely that elevated gold concentrations in this area are related to alluvial gold in the drainage channel rather than underlying mineralization.

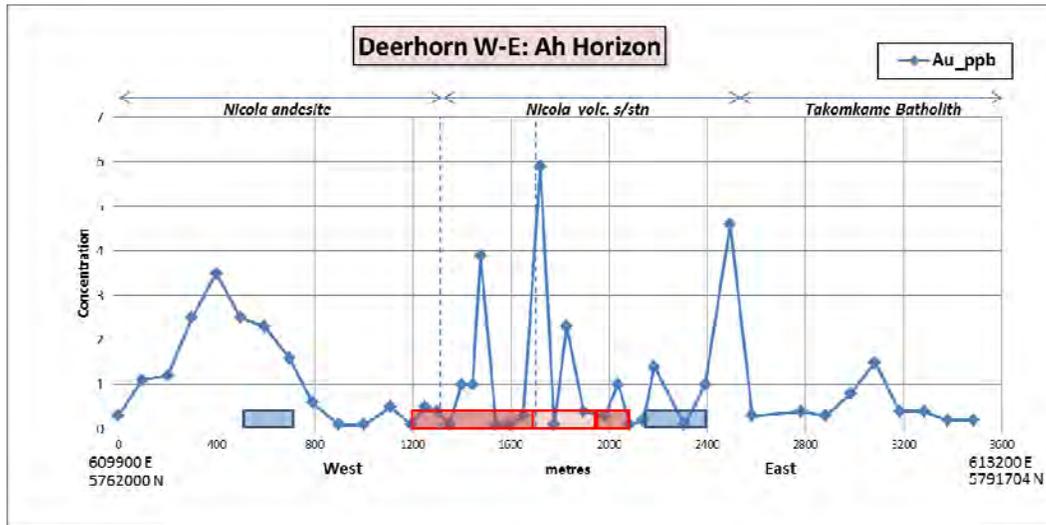


FIGURE 16. DEERHORN - GOLD IN AH HORIZON SOILS

#### PATHFINDER ELEMENTS

The pathfinder elements for Au generally have very low concentrations in the Ah soils. Nevertheless, patterns reflecting the Deerhorn mineralization are recognized for As, Sb, Hg and W.

Figure 17 shows the results for As. The profile for this element is quite noisy with background variation ranging between 0.3 and 0.8 ppm. Concentrations appear to increase towards the mineralization, particularly to the west where a subtle increase in As values is detected about 600 metres away from the western edge of the Cu-Au zone. This response may be reflecting an As enriched halo around the Cu-Au mineralization. Over the zone itself, As values define a possible asymmetrical rabbit-ear response with a western peak of 3.4 ppm and a shorter eastern peak of 1.3 ppm located within the surface projection of the zone. Between the peaks values seem to be depressed slightly below background levels.

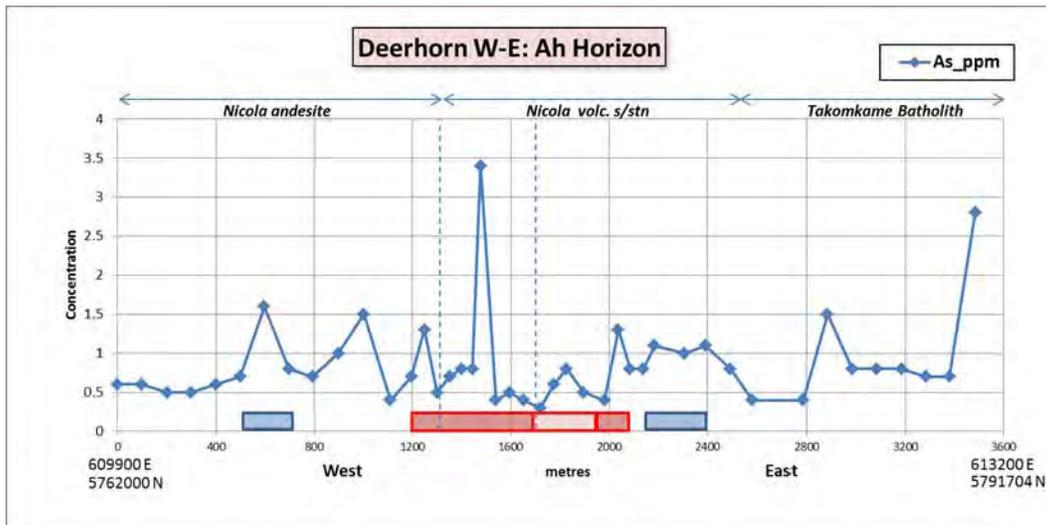


FIGURE 17. DEERHORN - ARSENIC IN AH HORIZON SOILS

Antimony contrast is very low (about 2-3 times background; Fig. 18). Background concentrations for this element vary consistently between 0.8 and 1.6 ppm over the length of the line with only a hint of an increase in the vicinity of the Deerhorn mineralization. A single peak with a value 0.35 ppm occurs over the western part of the zone. It is coincident with the western rabbit ear peak observed in the As results. Samples immediately adjacent to this feature to the west have values below background levels (0.16 - 0.17 ppm). A similar but more subtle low occurs over the eastern part of the mineralized zone. Together these features give the impression of a negative rabbit-ear pattern, but the response is very subtle.

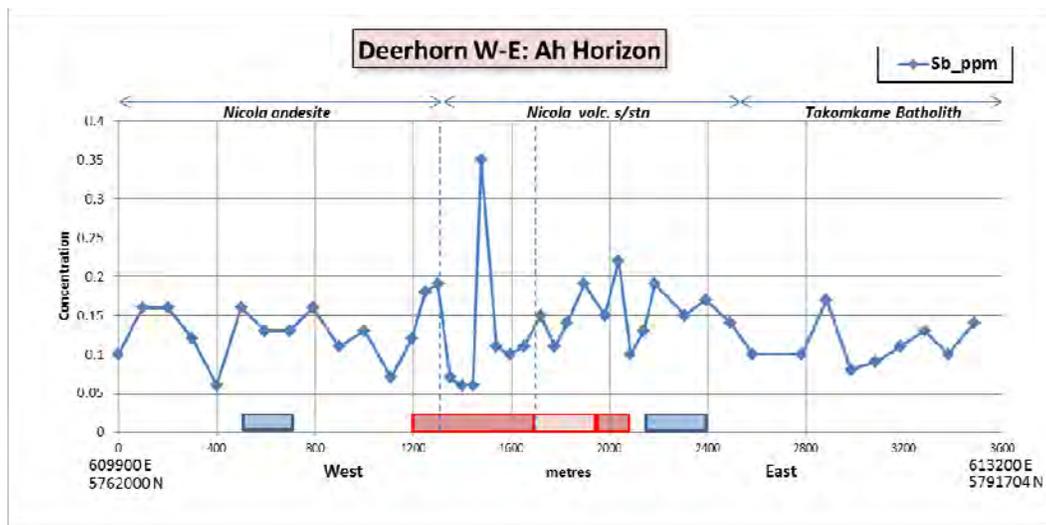


FIGURE 18. DEERHORN - ANTIMONY IN AH HORIZON SOILS

Mercury results (Fig. 19) show little contrast between mineralized and background locations. On the east side of the mineralized zone over the Takomkame Batholith the background is relatively flat with



values ranging between 62 and 143 ppb. Near to the eastern end of the line there is a single anomalous sample with a value of 262 ppb. The cause of this elevated value is not apparent. West of the mineralized zone background is relatively noisy. Here concentrations range between 46 and 309 ppb with no obvious pattern. Similar variations occur over the mineralization where abrupt changes between adjacent samples distinguish the area from background locations. There is a suggestion of a rabbit-ear pattern over the western part of the Deerhorn zone. This is defined by two samples with elevated concentrations of 289 and 261 ppb located close to the edges of the surface projection of the > 0.2 g/t Au equivalent mineralization.

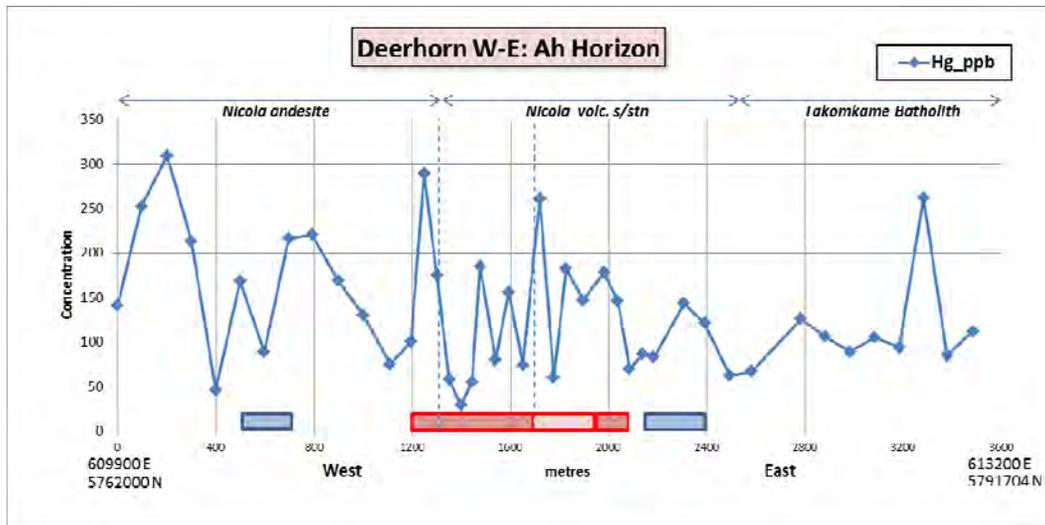


FIGURE 19. DEERHORN - MERCURY IN AH HORIZON SOILS

With the exception of a single anomalous sample (2 ppm) over the western part of the mineralized zone, W shows values at or close to detection limit over most of the line (Fig. 20). While not generally recognized as a porphyry pathfinder element, W has been observed to be significantly concentrated in Ah horizon soils above deeply buried porphyry style mineralization at Kwanika (Heberlein and Samson, 2010; Heberlein and Dunn, 2011).

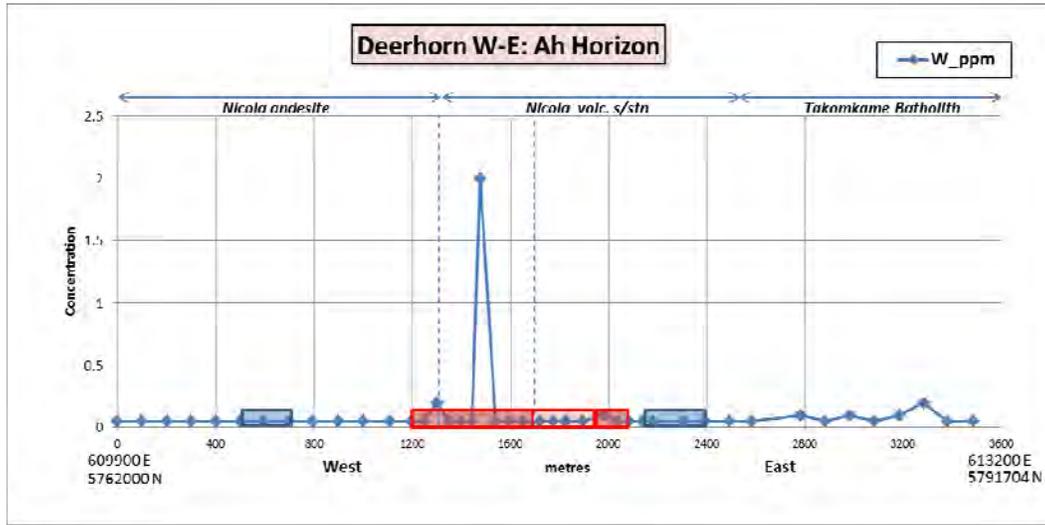


FIGURE 20. DEERHORN - TUNGSTEN IN AH HORIZON SOILS

### RARE EARTH ELEMENTS (REE)

REEs display recognizable responses to the Deerhorn mineralization. Figure 21 shows that La, Nd and Y all display rabbit-ear-like patterns with moderate contrast peaks over the mineralized zone. Neodymium has the highest concentration response with maximum a value of 13.5 ppm over the western part of the Deerhorn zone. Background concentrations for this element are quite noisy, ranging from a low of 0.9 to a high of 6.8 ppm. Yttrium has the highest contrast response with the highest concentration peak having a contrast of 7 times background.

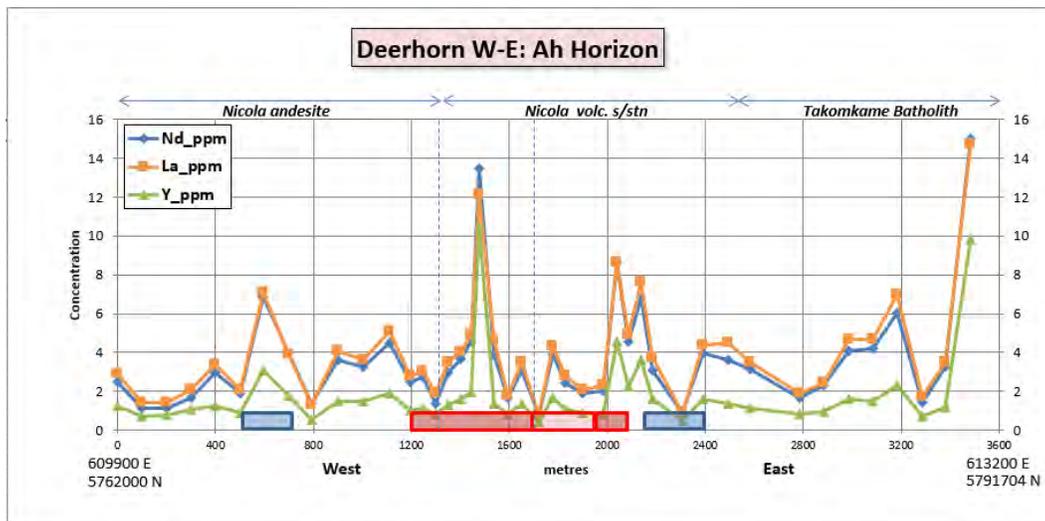


FIGURE 21. DEERHORN - LANTHANUM, NEODYMIUM AND YTTRIUM IN AH HORIZON SOILS

## PH SENSITIVE ELEMENTS

Results for the pH sensitive elements Ca and Sr are shown in Figure 22. These elements are sensitive to changes in near surface pH conditions in response to the release of hydrogen ions from oxidizing sulphide minerals at depth (Smee, 1998). Smee's model (Smee, 1997 and 1998) predicts peaks for Ca and Sr over the edges of the mineralized zone formed by re-precipitation of carbonate minerals around the edges of an acid zone located directly above the sulphide source.

Results show no conspicuous peaks for these elements. Variations in concentration over the Deerhorn mineralization are similar to those in background areas. Over the western part of the mineralized zone there is a hint of a rabbit-ear pattern defined more by very low values in the centre of the zone than conspicuous peaks.

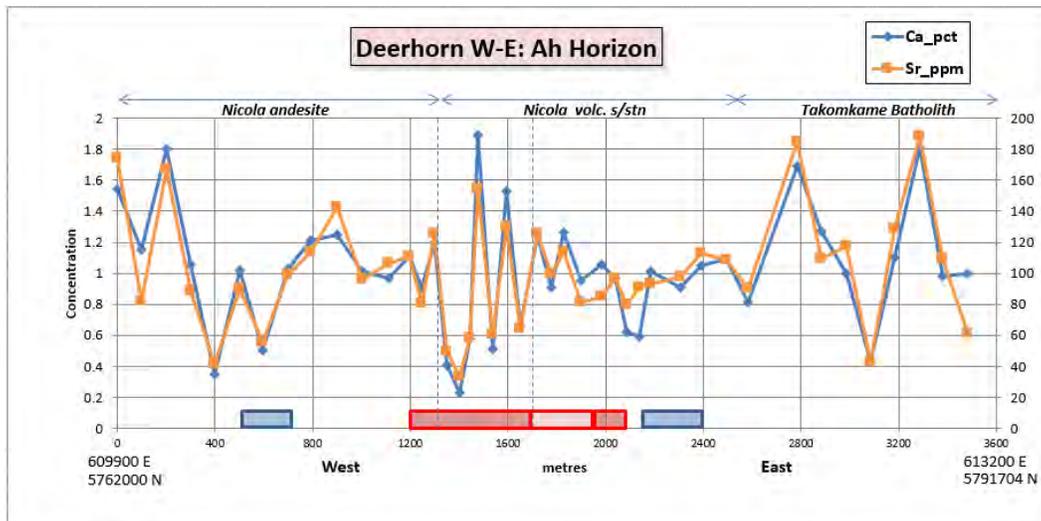


FIGURE 22. DEERHORN - CALCIUM AND STRONTIUM IN AH HORIZON SOILS

## CHARCOAL

Charcoal is a common component of boreal and sub-boreal forest soils derived from periodic forest fires. It is highly porous material that is known to have a strong metal sorption capacity (Johns et al., 1993; McMahon, 2006) and therefore should behave as an effective trap for mobile metal ions in the near-surface environment. It is potentially a useful sampling medium in areas of recent forest fires and logged areas where the vegetation and the Ah horizon may have been damaged or completely destroyed. In more mature forests charcoal debris can be readily obtained from the A horizon, either as small fragments or dust or as larger pieces of carbonized wood. Fine particles of this material most likely make up a significant component of the black organic-rich Ah horizon.

## COMMODITY ELEMENTS

Charcoal results for Cu, Mo Ag and Au are shown in Figures 23 to 26.

Copper results (Fig. 23) display a reasonable contrast between background and mineralized areas. In the background area to the west of the mineralization Cu varies between 2.68 and 6.89 ppm. Similar variation is noted on the east side close to the edge of the mineralized zone. Further away

concentrations gradually increase to a maximum of 16.0 ppm at the east end of the line. These elevated values in a supposedly background area are attributed to weak Cu mineralization in the Takomkame Batholith. Over the Deerhorn mineralization Cu forms a moderate contrast triple peak anomaly. Two of the peaks (13.3 and 16.3 ppm) define a rabbit ear over the western part of the mineralized zone. The third peak, defined by two anomalous samples (13.8 and 17.1 ppm), overlies the smaller eastern body of mineralization.

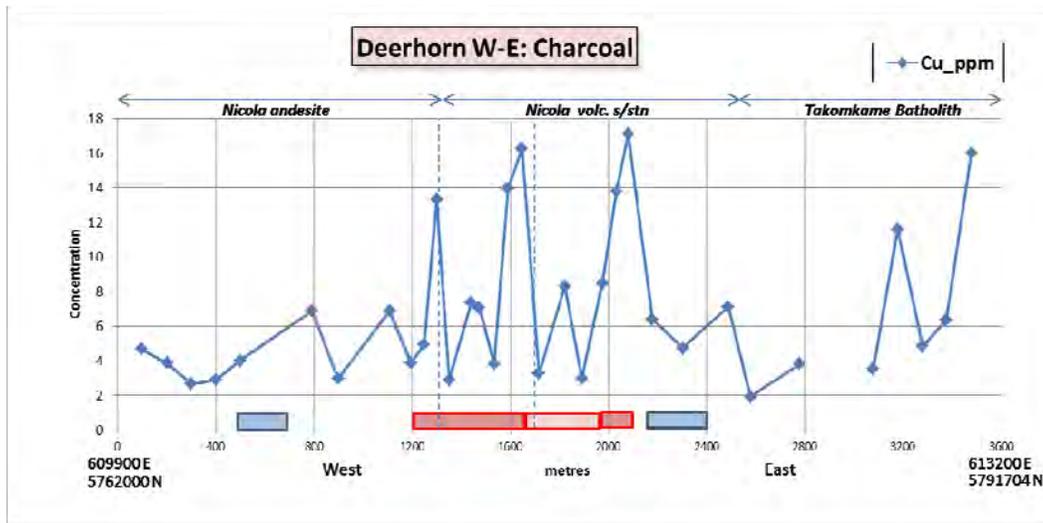


FIGURE 23. DEERHORN - COPPER IN CHARCOAL

A much broader and lower contrast response to the mineralization is shown by Mo. Figure 24 shows that background levels are generally less than 1 ppm but values increase to over 2 ppm over the mineralization to form a broad but erratic response. Rather than the rabbit-ear pattern seen in Cu, the position of the mineralized zone is defined by series of peaks separated by lower, sometimes sub-background values. While the contrast is quite low, the position of the highest concentration samples is unmistakably over the mineralized zone.

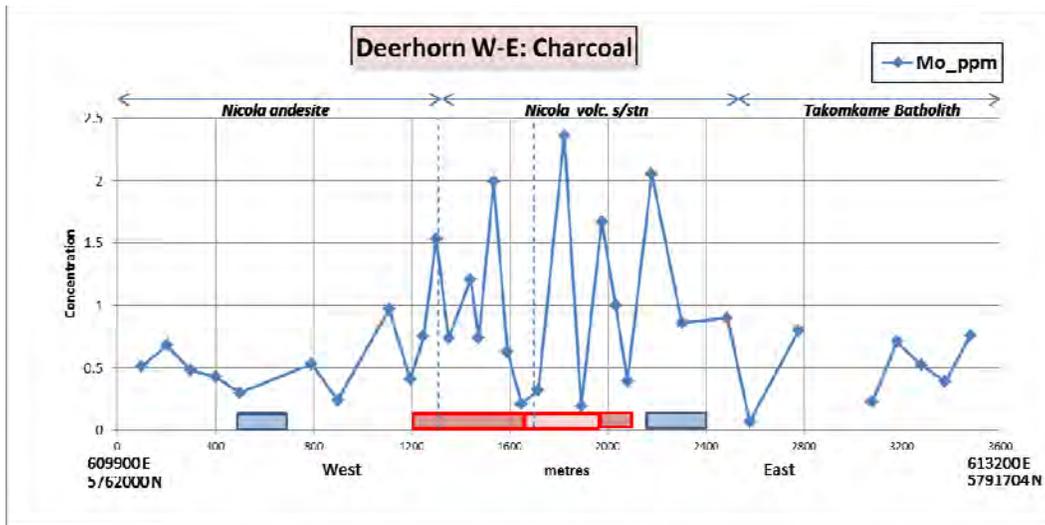


FIGURE 24. DEERHORN - MOLYBDENUM IN CHARCOAL

Silver displays a somewhat similar pattern to Mo. Figure 25 shows that this element forms a broad high contrast response over the central and eastern parts of the Deerhorn zone. The maximum concentration of 583 ppb occurs over the lower grade part of the mineralization defined by the > 0.2 g/t Au equivalent envelope (darker red bars). Elevated values also cover parts of the higher grade zones adjacent to a swampy area immediately to the east (blue bar). Elevated values around the swamp most likely indicate hydromorphic concentration of this element and may not represent a direct expression of the underlying mineralization. Away from the mineralized zone background concentrations are consistently below 200 ppb. The one exception is a single anomalous sample of 981 ppb near the west end of the line. The cause of this high value is not known but it correlates with an isolated high Ag values in the Ah horizon soil (Fig. 13).

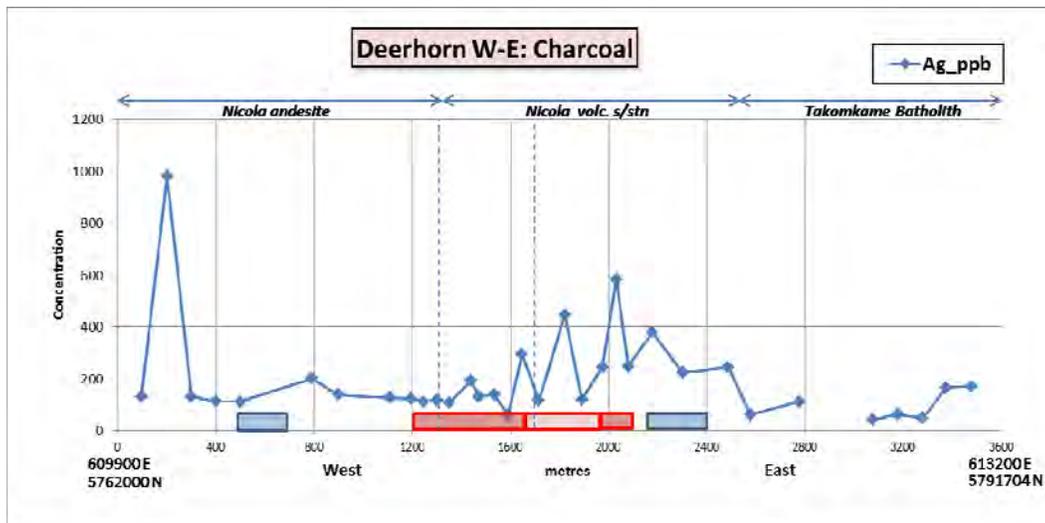


FIGURE 25. DEERHORN - SILVER IN CHARCOAL

There is no recognizable expression of the Deerhorn mineralization in the Au results (Fig. 26). Values across the sample line appear to only reflect background variation (detection limit to 1.3 ppb) at both mineralized and background sample locations.

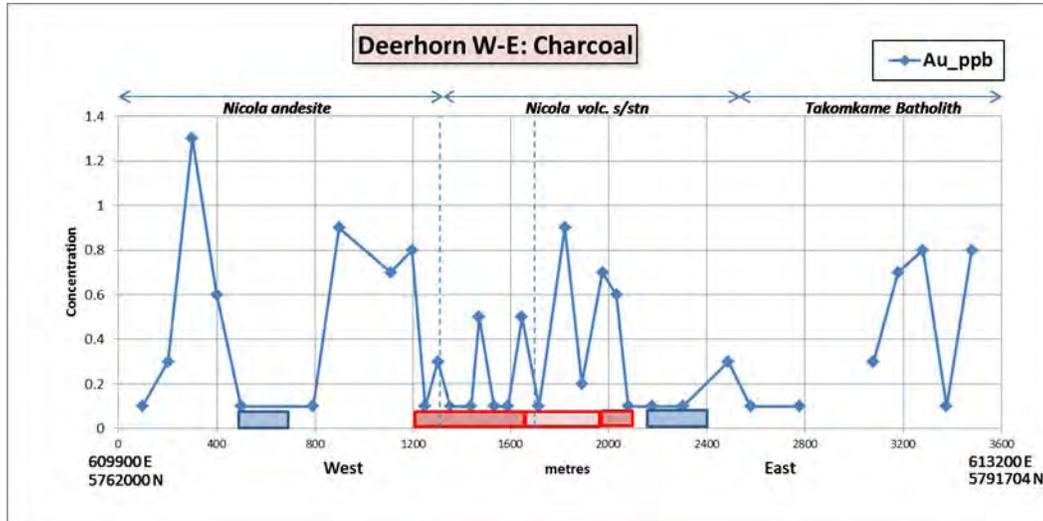


FIGURE 26. DEERHORN – GOLD IN CHARCOAL

#### PATHFINDER ELEMENTS

Several of the pathfinder elements display recognizable responses to the Deerhorn mineralization. Arsenic (Fig. 27) displays an interesting triple peaked pattern over the mineralization. The outer peaks, with values of 0.7 and 0.9 ppm, appear to form broad rabbit ears located over the edges of the zone. The maximum concentration occurs in the centre of the projected mineralization where two adjacent samples define a high contrast peak reaching 13.3 ppm. Concentrations at background sites east and west of the zone are very low with values between 0.1 and 0.4 ppm. A single peak response is also present near the west end of the line. This corresponds with similar features identified in Ag, Au and As.

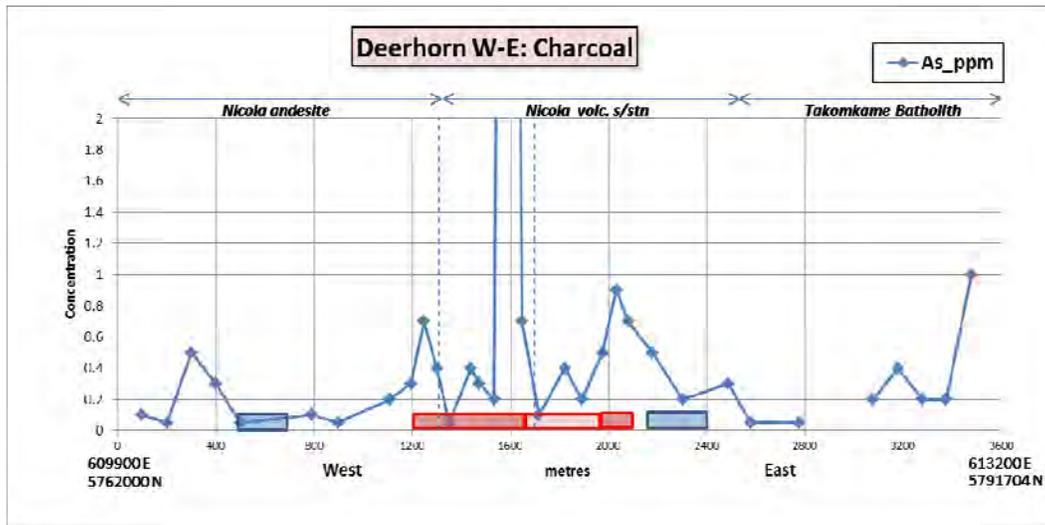


FIGURE 27. DEERHORN - ARSENIC IN CHARCOAL

Antimony displays an apical response similar to those observed for Mo and As (Figs 24 and 27). Values show a subtle increase above background levels (< 0.05 ppm) over the projected mineralization with one sample reaching a maximum concentration of 0.21 ppm over the western higher grade zone. While concentrations are very low, the contrast of this response is reasonably good: the maximum concentration is almost 7 times the background level.

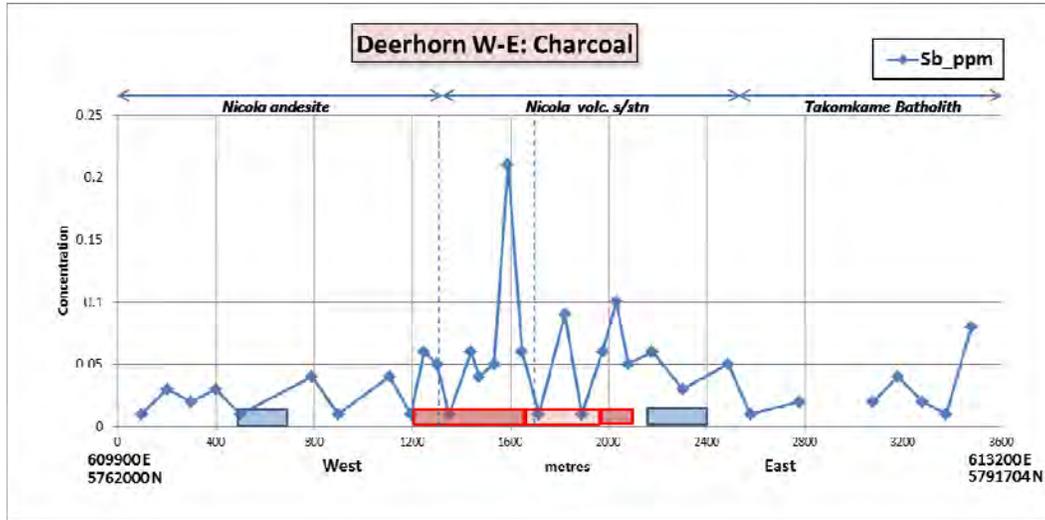


FIGURE 28. DEERHORN - ANTIMONY IN CHARCOAL

Other pathfinder elements with recognizable responses to the mineralization include Re and W. As shown in Figure 29 these two elements only have detectable values in samples located directly over the mineralization. Rhenium has two results above detection limit located between the higher grade parts of the mineralized zone. This element is an important indicator of mineralization as it is commonly



concentrated in the ore mineral molybdenite (McCandless et al., 1993). Tungsten has six results above detection limit, all occurring within the surface projection of the mineralized zone. As mentioned earlier in the discussion of the Ah horizon results, this element is known to produce significant anomalies in the upper part of the soil profile over blind or buried porphyry systems (Heberlein and Dunn, 2011).

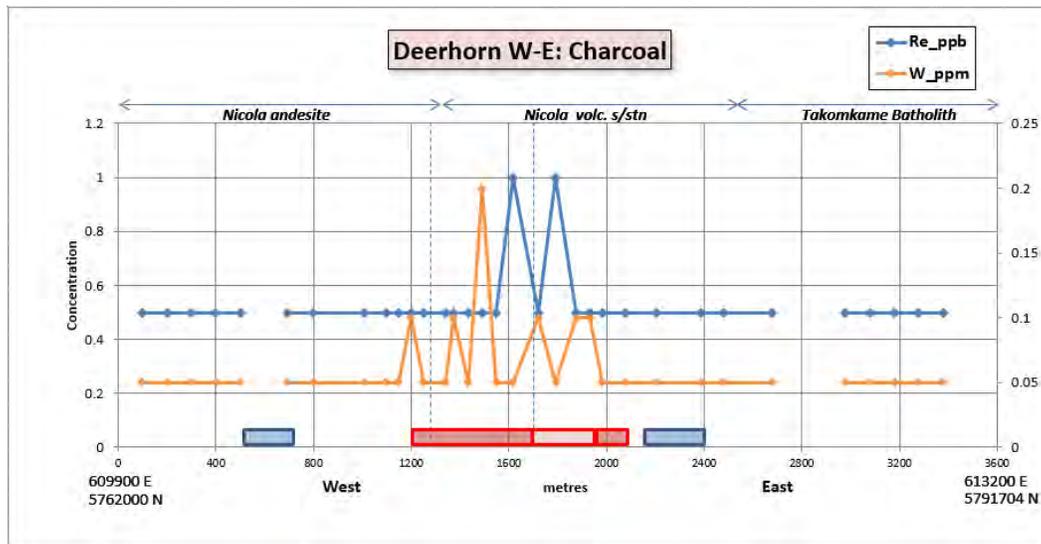


FIGURE 29. DEERHORN - TUNGSTEN AND RHENIUM IN CHARCOAL

#### RARE EARTH ELEMENTS

Patterns for the REE are similar to those observed in the Ah horizon soil results. Not surprisingly most of the REE display similar profiles across the mineralization with large differences in absolute concentrations between the individual elements. Neodymium has the highest concentration results. Figure 30 shows that this element produces a very high contrast response occurring as a series of individual peaks over the entire width of the mineralized zone. Most of these peaks have values of between 1.63 and 2.54 ppm (or about 10 times background). The highest concentration of 5.37 ppm forms part of a two sample peak located near to the eastern edge of the zone. Away from the surface projection of the mineralization values fall rapidly to background values at or slightly over the analytical detection limit (0.02 ppm).

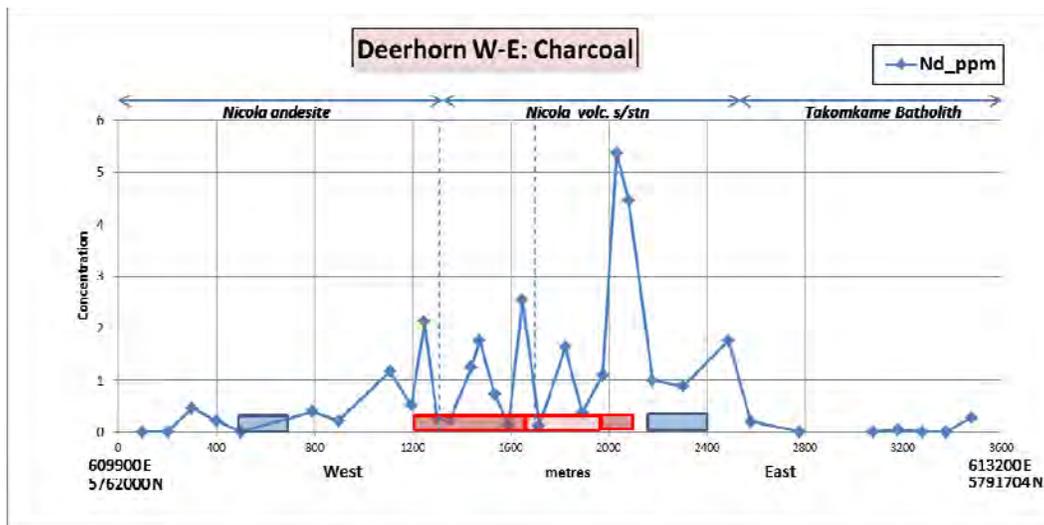


FIGURE 30. DEERHORN - NEODYMIUM IN CHARCOAL

#### OTHER ELEMENTS

There are a number of other elements displaying recognizable responses to the mineralization. Of these Rb and Fe are noteworthy and merit discussion. Rubidium results (Fig. 31) show a clear spatial relationship to the surface projection of the Deerhorn mineralization. This element forms a pronounced rabbit-ear pattern centred on the zone. The peaks reach concentrations of 6.1 and 5.3 ppm respectively, with the larger one occurring over the western zone of higher grade mineralization. Background variation is very flat to the west of the zone where values are less than 1.0 ppm. On the east side there is more variation (up to 4.9 ppm), particularly over the Takomkane Batholith where the K feldspar bearing granitic rocks are likely to be the main influence of Rb concentration. The observed patterns over the mineralization may be an expression of potassic alteration associated with the porphyry mineralization.

Iron results display a similar pattern to Cu, Mo, Rb and REE. Figure 32 shows that this element has generally elevated concentrations over the projected mineralization defined by a series of peaks separated by background or below background values. On the west side of the zone background concentrations are less than 0.13%. Over mineralization the peaks vary between 0.35 and 0.6%: or up to 4.6 times the background concentration. Background levels to the east of the mineralized zone are quite erratic.

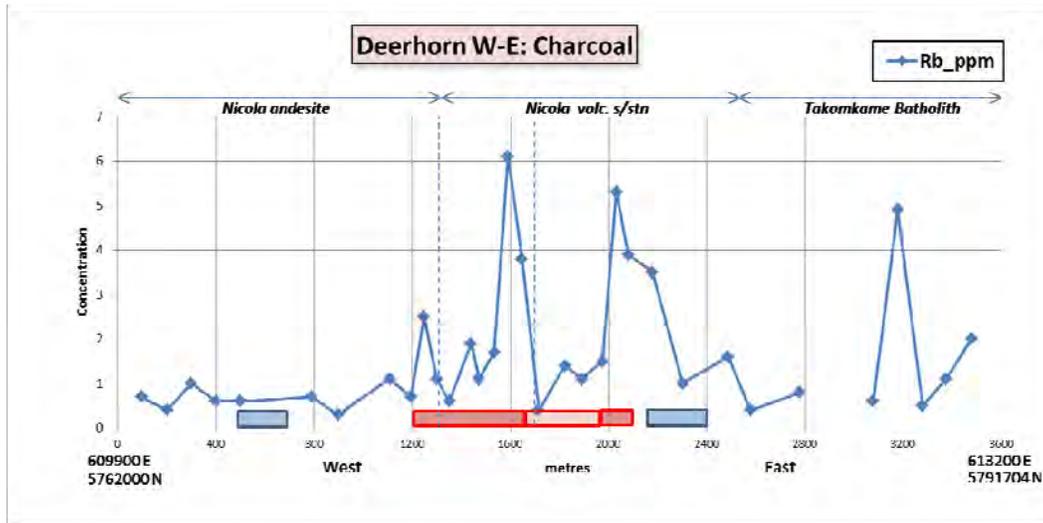


FIGURE 31. DEERHORN - RUBIDIUM IN CHARCOAL

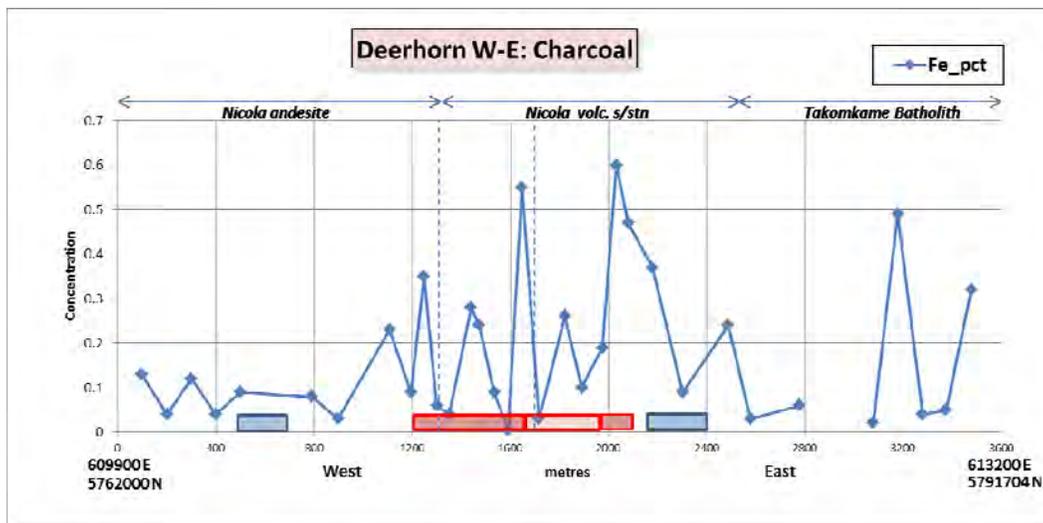


FIGURE 32. DEERHORN - IRON IN CHARCOAL

## SPRUCE BARK

The nitric acid then aqua regia digestion of the dry vegetation tissues is nearly a total digestion for all elements. The precision of the analytical method is good to excellent for most elements except for Au and some of the high field strength elements (e.g. Hf, Nb, Ti, Zr) which generally have inferior precision (Table 3).

The dataset indicates no unusually high concentrations of any element either at Deerhorn or Three Firs.

Many elements returned concentrations below or close to the detection limits. Each plant species and type of tissue (i.e. bark, twigs, needles etc.) has a different capability to absorb and store elements.

Copper is an element that is required for a plant's metabolism and so concentrations of a few ppm Cu are typical and only excesses to those levels are likely to be attributable to any concealed mineralization. In situations where a geochemical signature is subtle, it is commonly difficult to distinguish a 'mineralization' from a 'metabolic' signature. This is the case at Deerhorn where the highest Cu concentration is located over mineralization, but at only one sample station so it is not a conclusive response to mineralization (Fig. 33).

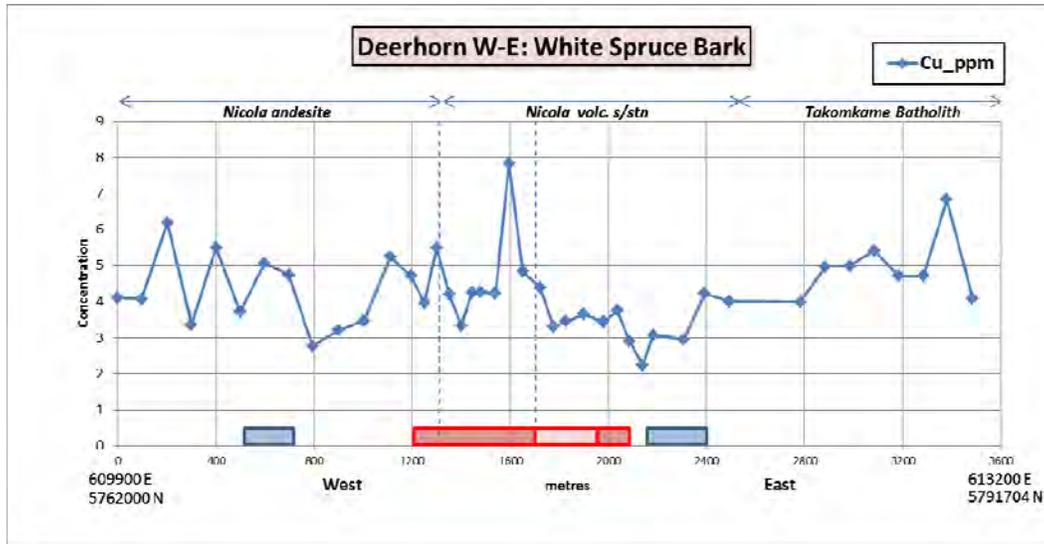


FIGURE 33. DEERHORN – COPPER IN DRY SPRUCE BARK. RED BARS SHOW THE LOCATION OF THE MINERALIZATION; BLUE BARS INDICATE SWAMPY AREAS

In the general vicinity of the buried mineralization, As concentrations were above detection in a number of samples, but the response is subtle (Fig. 34) and analytical precision poor. Other elements with slightly elevated concentrations in this area include Cd, Li, Mg, Sb, Y and Zn. Of particular note are the positive responses of Cs, Rb, Hg and Pb above the zones of mineralization (Figs. 35-38)

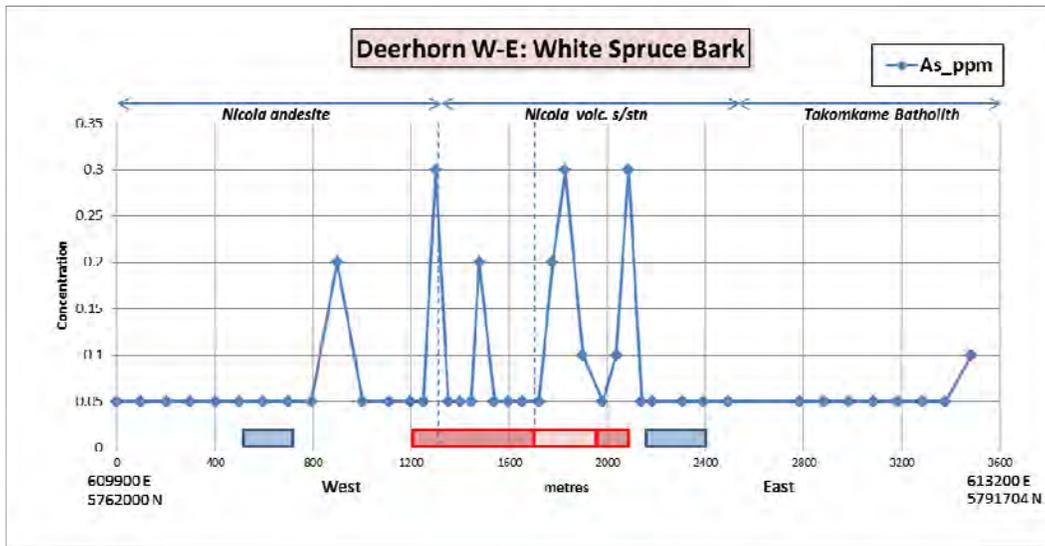


FIGURE 34. DEERHORN – ARSENIC IN DRY SPRUCE BARK.

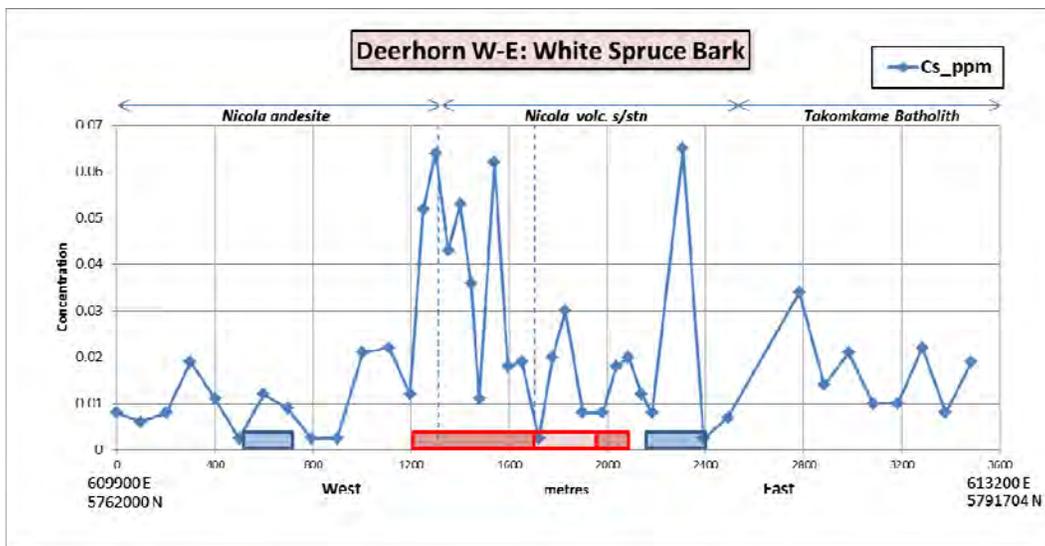


FIGURE 35. DEERHORN – CESIUM IN DRY SPRUCE BARK.

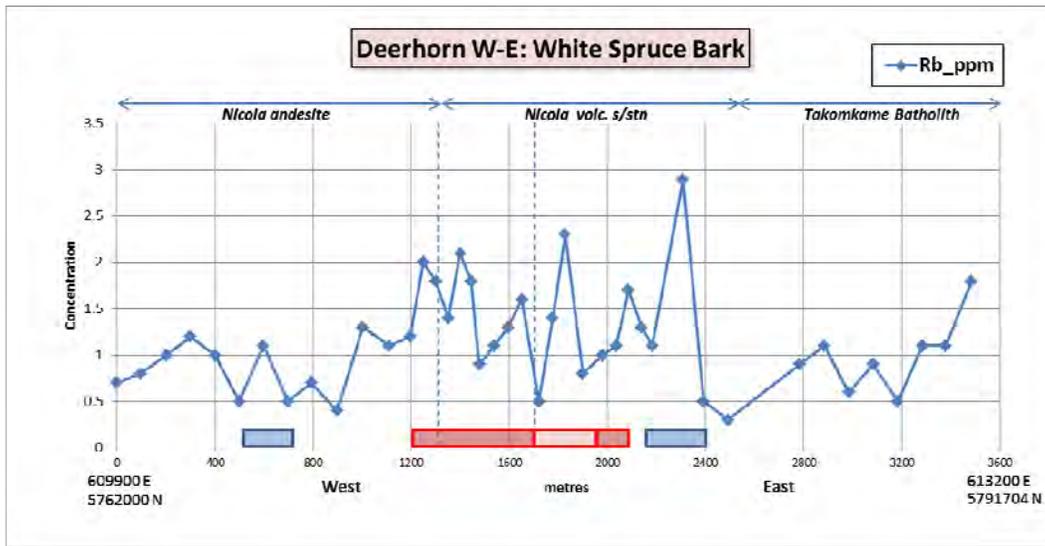


FIGURE 36. DEERHORN – RUBIDIUM IN DRY SPRUCE BARK.

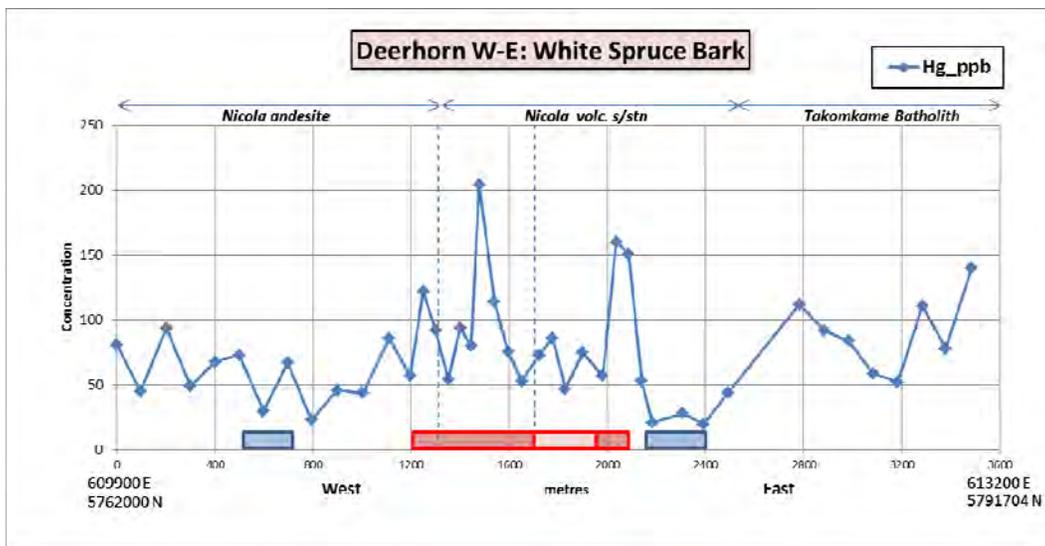


FIGURE 37. DEERHORN – MERCURY IN DRY SPRUCE BARK.



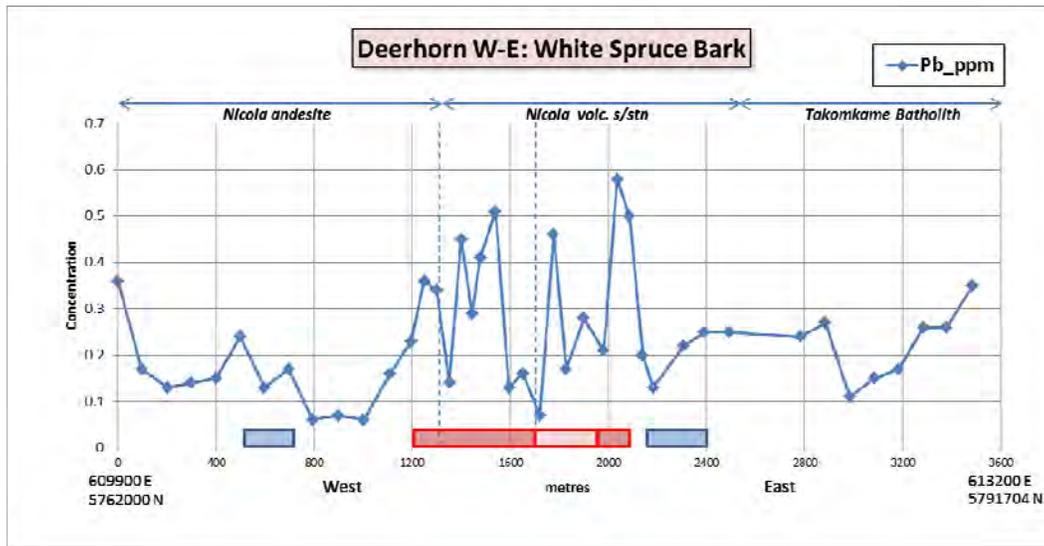


FIGURE 38. DEERHORN – LEAD IN DRY SPRUCE BARK.

## SPRUCE TWIG ASH

By reducing the spruce twigs to ash prior to analysis, elements are concentrated about 30-fold, since the ash yield is approximately 3%. Consequently, the numbers reported from the analysis are substantially higher than for the dry spruce bark and concentrations of more elements are well above detection levels. However, there is the drawback that some elements volatilize during the ashing process – notably all the Hg, and some of the Cr and possibly As, S, Sb and Se. However, provided ashing conditions are similar, the proportion of any element loss is fairly consistent and so element distribution patterns can be meaningful. There is a little variation among samples in the ash yield (about 2.6 to 3.4%), and although this makes negligible difference to the overall patterns the data have been levelled to a dry-weight basis prior to plotting the data, hence the low concentrations shown on the following charts.

Whereas the Au determinations from analysis of the dry spruce bark were mostly below DL, the concentration of the inorganic components by ashing has revealed the ‘texture’ of the data, and all sites with slightly elevated levels of Au occur over and adjacent to the zone of buried mineralization (Fig. 39). Similarly, the As concentrations are slightly higher over this zone, but the contrast is subtle (Fig. 40). Copper concentrations are erratic and non-definitive (Fig. 41), perhaps because Cu is an essential element and taken up and sequestered in the concentrations that are required by the spruce twigs with excess concentrations moving elsewhere in the tree.

Other elements exhibiting relative enrichments over the mineralized zone include Be, Bi, Cs, Pt, Rb and Te. Figures 42-44 show the patterns of Cs, Rb and Pt.

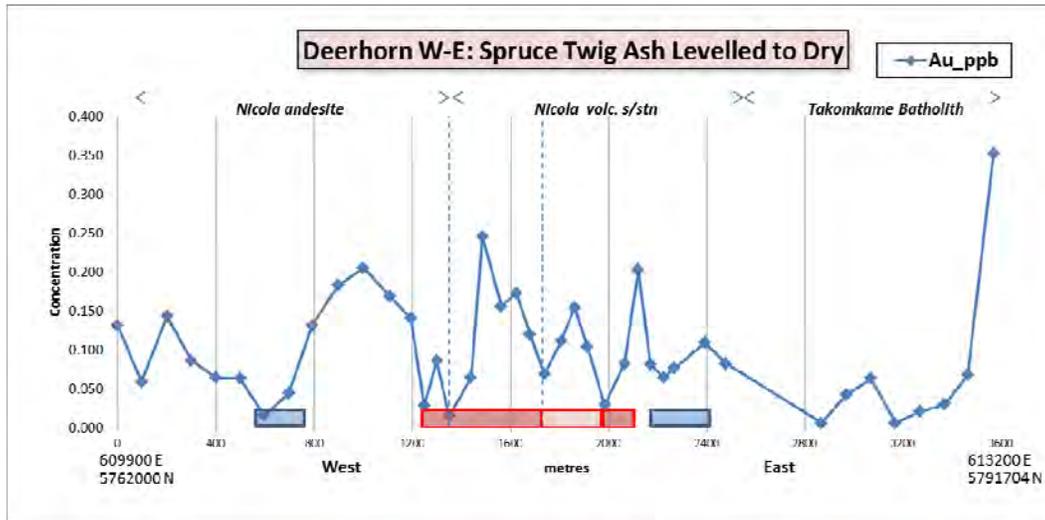


FIGURE 39. DEERHORN – GOLD IN DRY SPRUCE BARK.

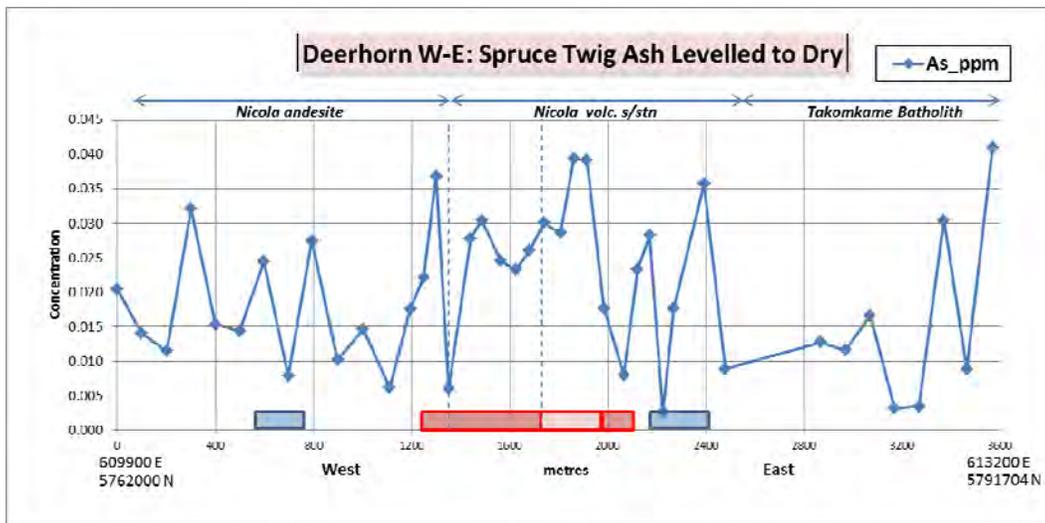


FIGURE 40. DEERHORN – ARSENIC IN DRY SPRUCE TWIGS

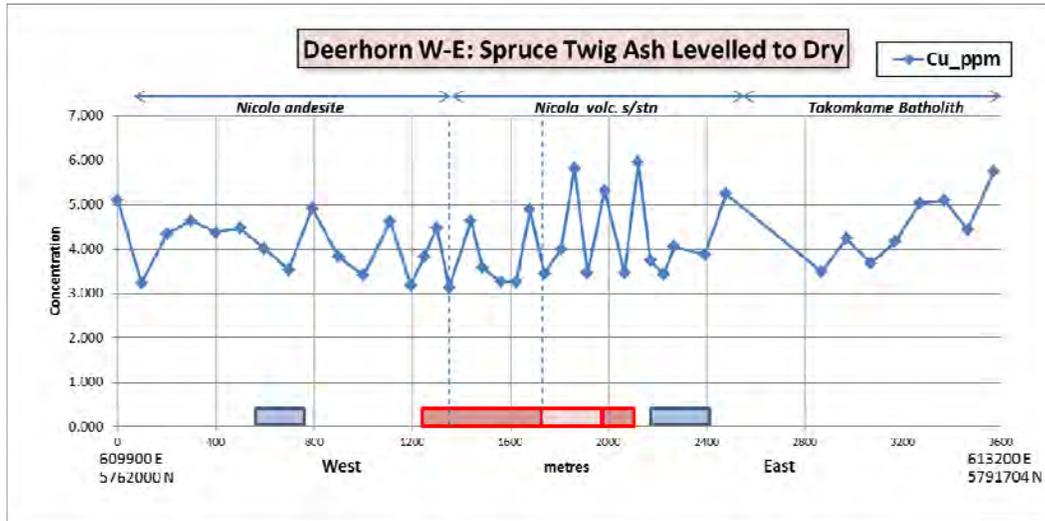


FIGURE 41. DEERHORN – COPPER IN DRY SPRUCE TWIGS

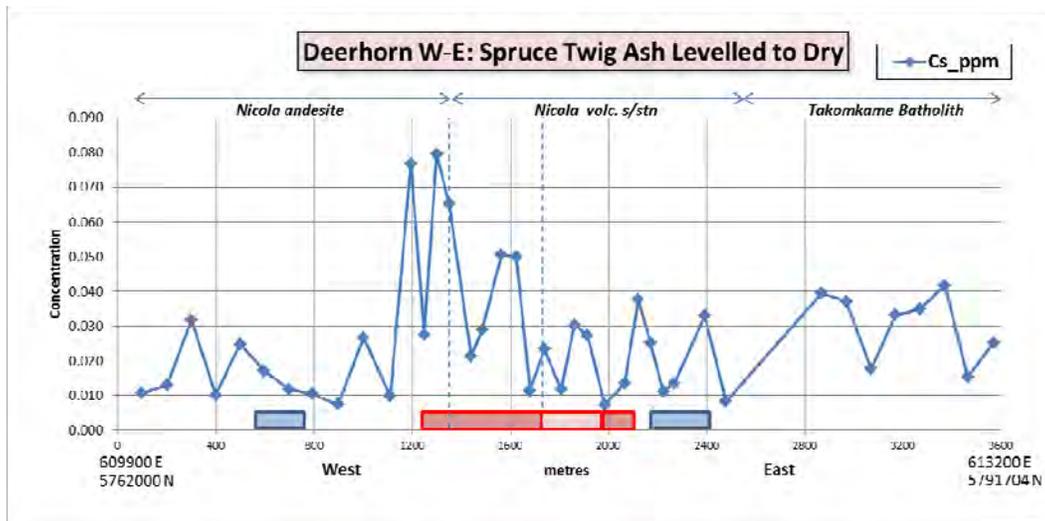


FIGURE 42. DEERHORN – CESIUM IN SPRUCE TWIGS. ANOMALOUS SAMPLE AT WESTERNMOST SITE OMITTED TO EMPHASIZE CENTRAL AREA



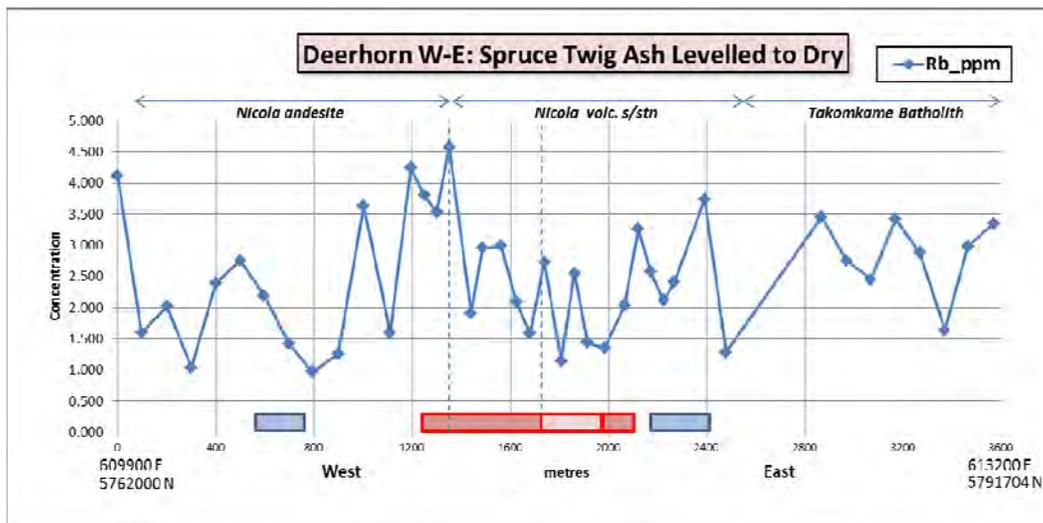


FIGURE 43. DEERHORN – RUBIDIUM IN DRY SPRUCE TWIGS



FIGURE 44. DEERHORN – PLATINUM IN DRY SPRUCE TWIGS

## EXUDATE GEOCHEMISTRY

### SPRUCE SAP

This section discusses primarily only the samples that were collected during the initial survey in July. Since the dissolution and analysis of 1 g samples at QFIR proved somewhat problematic, 0.3 g aliquots of samples from the September collection were dissolved and analyzed. Results showed that there was a substantially increased detection limit (DL) for a number of elements, such that it was not possible to integrate the two datasets even after attempts at data levelling. Later reanalysis of a 0.3 g portion of the original samples provided results that were not comparable with those from the original dataset.

This may be the result of significant sample inhomogeneity or analytical problems that remain to be resolved. The smaller samples returned DL that were better for some elements but worse for others. At the time of writing these various issues have not been resolved. Consequently, results described in this section are restricted to the analysis of samples from the first sampling campaign.

#### COMMODITY ELEMENTS

There was no detectable response for Au or Ag in this medium. All values were below detection limit. Copper however, did produce a high contrast pattern with the maximum concentration of 1.47 ppm, representing an order of magnitude above background, located over the area between the two zones of mineralization (Fig. 45). Patterns for Mo are less convincing. This element displays a single anomalous sample located over the western mineralized zone (Fig. 46).

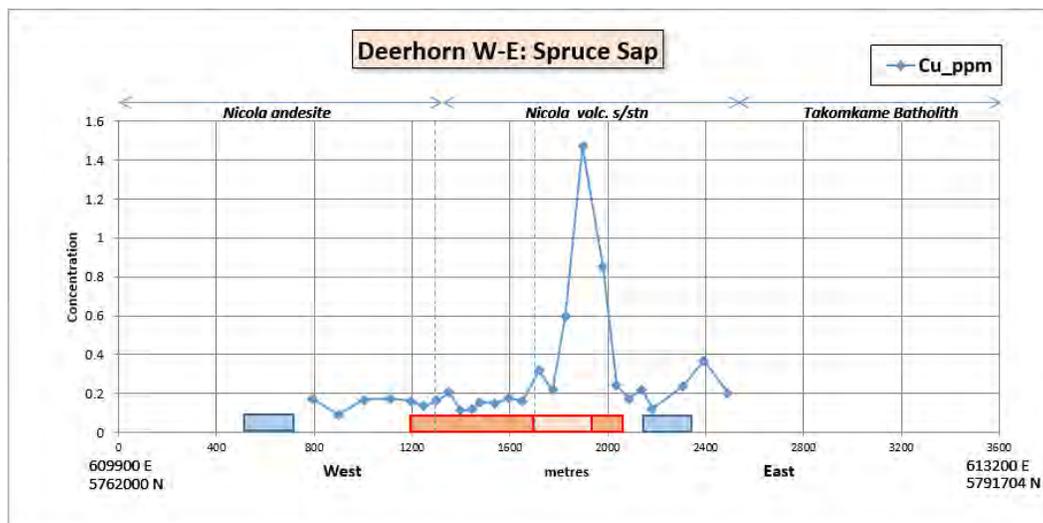


FIGURE 45. DEERHORN – COPPER IN SPRUCE SAP.

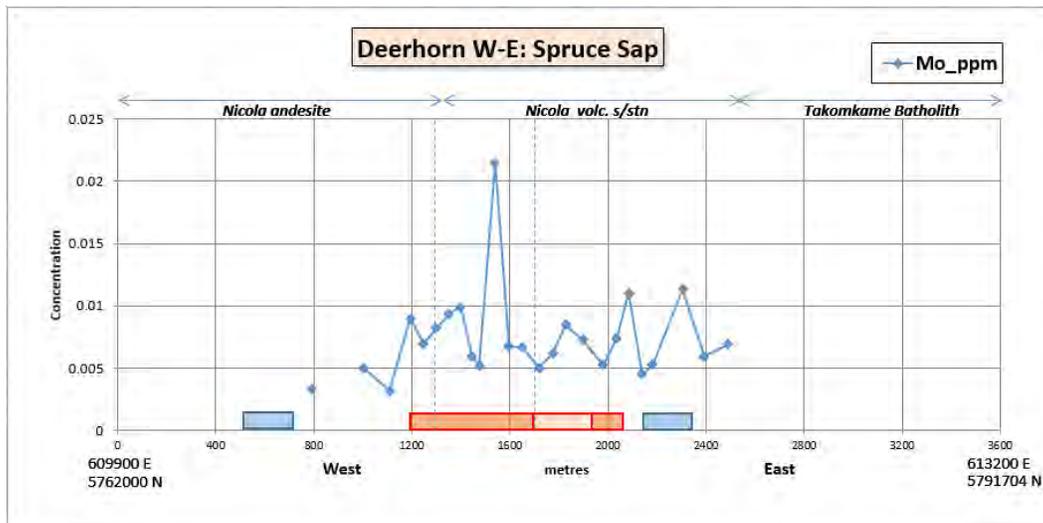


FIGURE 46. DEERHORN – MOLYBDENUM IN SPRUCE SAP.

## PATHFINDER ELEMENTS

Results for the pathfinder elements As, Sb, Hg, W and Tl are illustrated in Figures 47 to 51. Arsenic displays a noisy response over the mineralized zone with the highest concentration samples occurring close to the edges of the mineralization, forming what appears to be a rabbit ear pattern. Samples falling outside the mineralized zone in interpreted background areas have very low values. On the east side As concentrations are close to detection limit, while on the west side values are significantly lower than those over the mineralized zone, suggesting that the rabbit ear peaks occur within a broader zone of elevated concentrations.

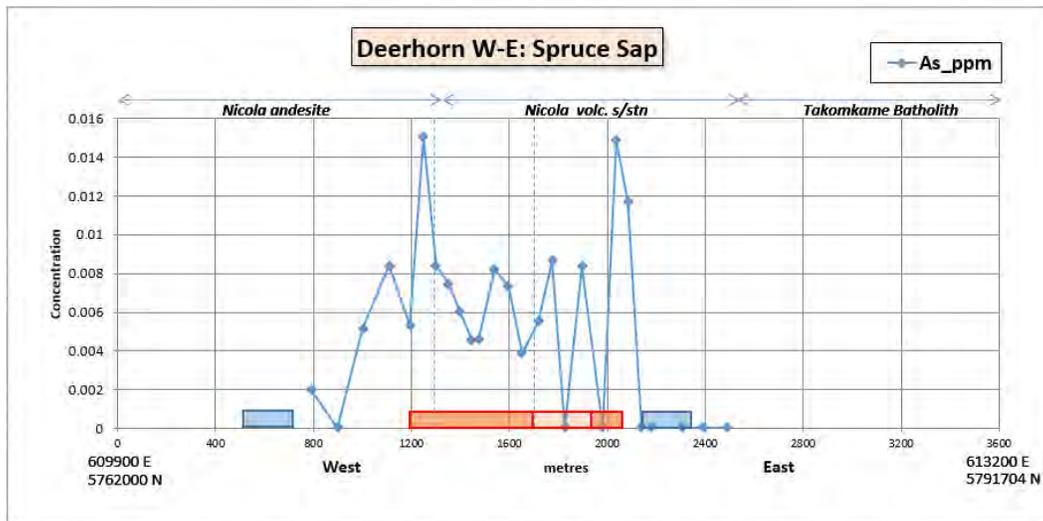


FIGURE 47. DEERHORN – ARSENIC IN SPRUCE SAP.

Antimony (Fig. 48) displays almost the reverse pattern to As. Highest concentrations occur outside the areas of stronger mineralization, particularly on the east side, where erratic values appear to increase towards background. Values over the western part of the mineralized zone are at or close to detection limit.

A much more robust response is shown by Hg (Fig. 49). Highest values highlight the position of the two mineralized bodies. The response over the wider western body appears to have a rabbit ear pattern enclosed within a zone of generally elevated concentrations. The smaller eastern body of mineralization is defined by two adjacent highly anomalous samples. Maximum contrast (6 times background) occurs over the western part of the mineralized zone but contrast over the eastern part is almost as high (5.4 time background).

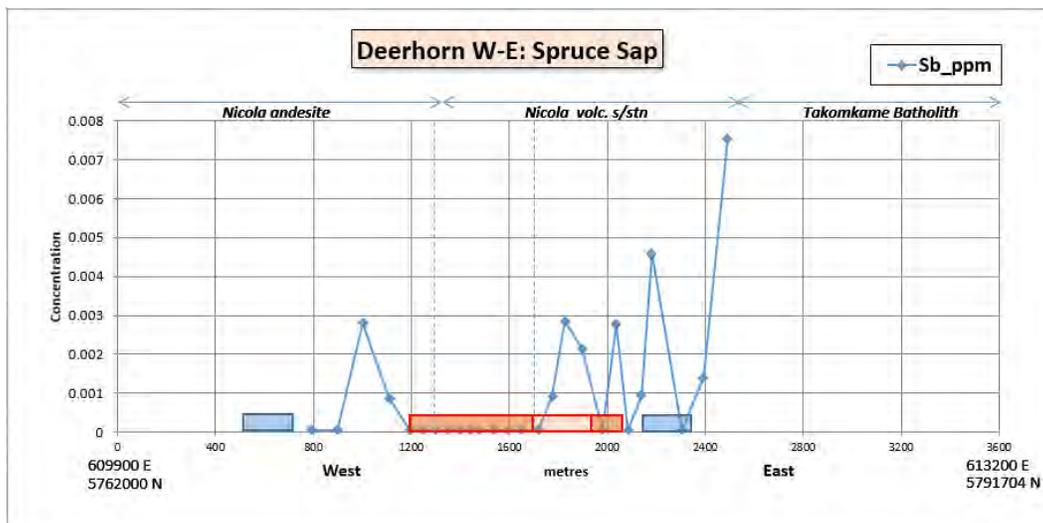


FIGURE 48. DEERHORN – ANTIMONY IN SPRUCE SAP.

The plots for W and TI show data from both sets of samples – the first batch, which extended over the zone of mineralization, and the second batch collected 2 months later, that involved the collection of samples from extension of the lines to the west and east in order to reach background sites. It should be noted that the detection levels were higher for the second batch and so these signatures into ‘background’ are not definitive. The plots do, however, give an indication of relatively well defined signals over the zones of mineralization. Further work is required to establish the authenticity of these patterns.

Tungsten shows an interesting asymmetrical pattern (Fig. 50). The western mineralized body is highlighted by three non-contiguous highly elevated W values defining a triple peak pattern. Maximum concentration of 0.13 ppm (or 13 time background) overlies the middle of the zone. The eastern mineralized body has no recognizable response. Outside the mineralized zone, background values are generally less than 0.02 ppm but one sample near to the west end of the line has a concentration of 0.07 ppm. This feature is unexplained.

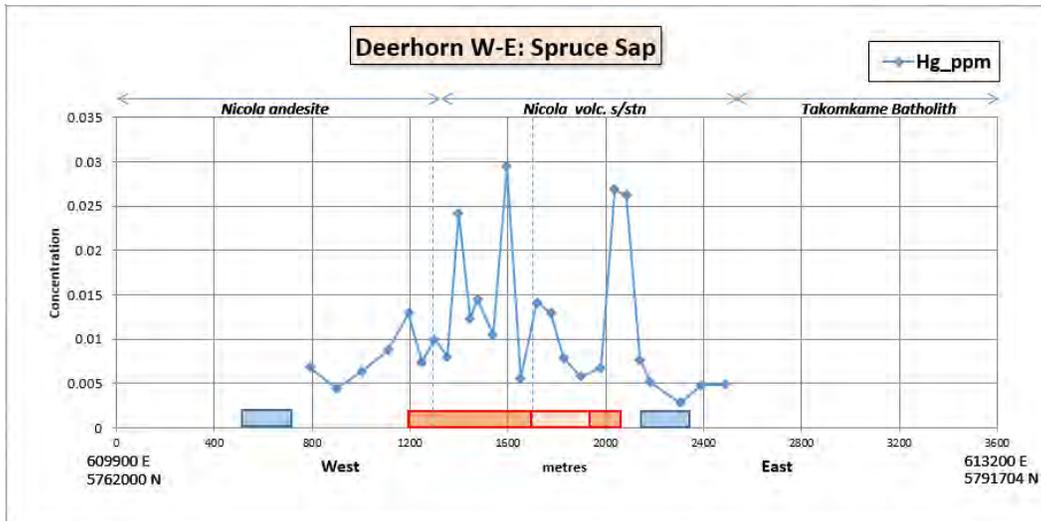


FIGURE 49. DEERHORN – MERCURY IN SPRUCE SAP.

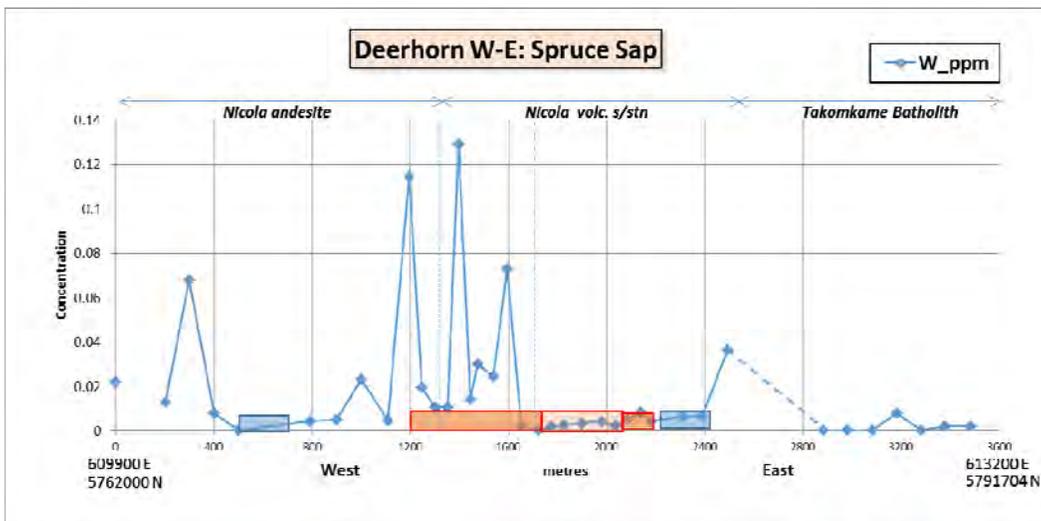


FIGURE 50. DEERHORN – TUNGSTEN IN SPRUCE SAP.

A robust pattern is displayed by Tl (Fig. 51). This element defines a broad zone of generally elevated values that extends a short distance beyond the mineralized zones in both directions. Within this area, discrete peaks highlighting the positions of the mineralized bodies can be seen. The eastern body is clearly indicated by three adjacent higher concentration samples that reach a maximum 0.00024 ppm (0.24 ppb or 8 times background). The western mineralized body has a slightly lower contrast double peak or rabbit ear-like pattern with a maximum concentration of 0.22 ppb or 7 times background.

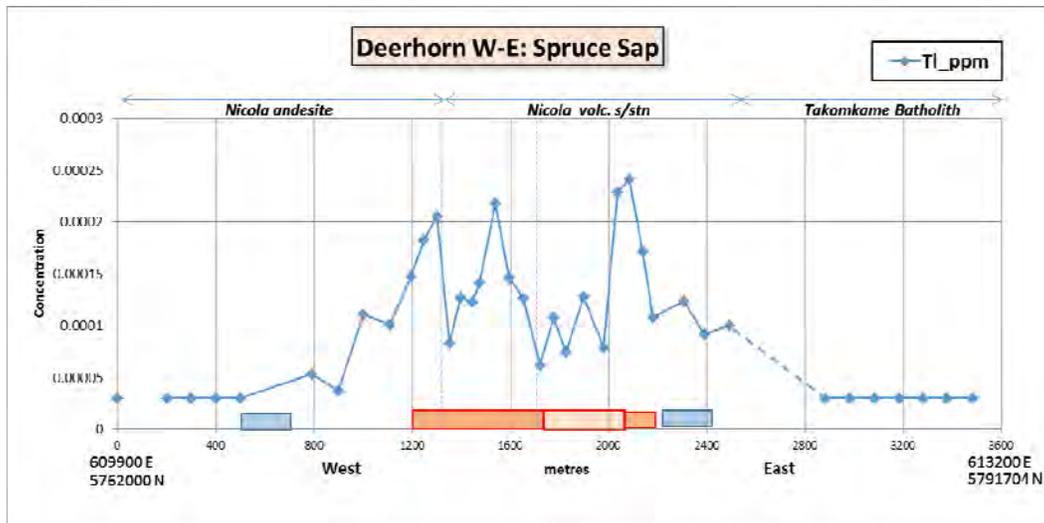


FIGURE 51. DEERHORN – THALLIUM IN SPRUCE SAP.

#### OTHER ELEMENTS

In addition to the ore and pathfinder elements, several other elements display recognizable patterns over the mineralization. Yttrium (Fig. 52) shows a broad zone of erratically elevated concentrations over the mineralized body. The lack of background samples for this element makes it difficult to estimate the contrast of this feature. Rubidium and Cs show similar responses to each other (Figs. 53 and 54). Rubidium defines a wide zone of higher values over the mineralized zone with concentrations peaking in the gap between the western and eastern mineralized bodies. Again, a lack of background samples makes it difficult to determine contrast but the highest concentration sample has approximately nine times the Rb content of the lowest sample. The Cs response appears to be more discriminating than that of Rb (Fig. 53). The element defines a broad zone of elevated values over the mineralization with higher contrast rabbit ear peaks highlighting the position of the western mineralized body. Once again contrast of the response is difficult to establish due to limited background data but the difference between the highest and lowest samples is approximately 14 times. Rubidium and Cs are elements that occur within potassium bearing minerals and as such likely indicate potassic alteration associated with the Cu-Au mineralization at Deerhorn.

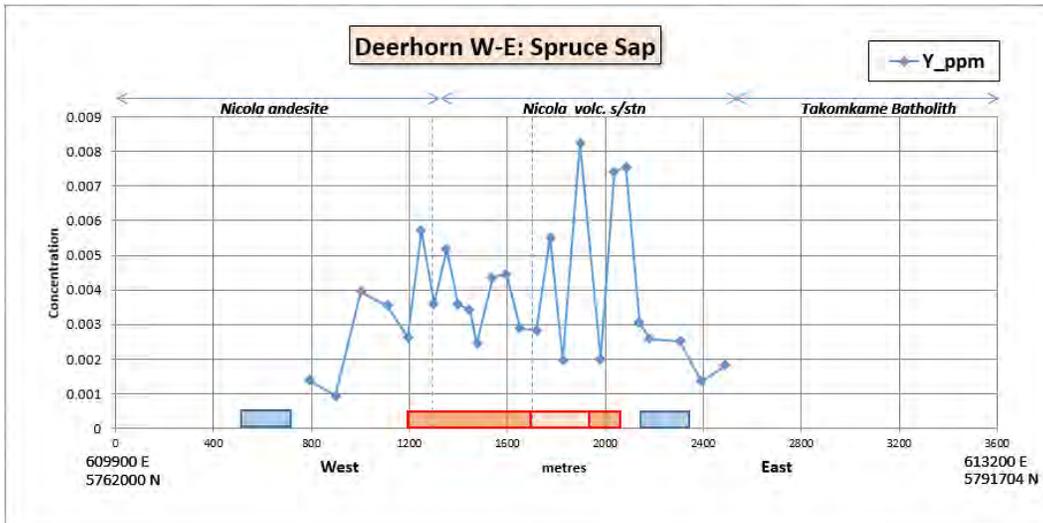


FIGURE 52. DEERHORN – YTTRIUM IN SPRUCE SAP.

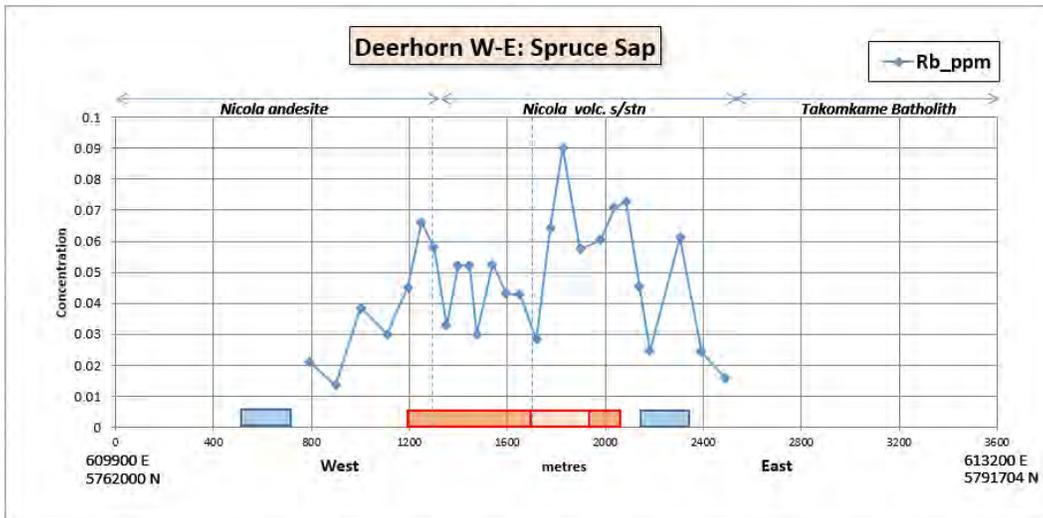


FIGURE 53. DEERHORN – RUBIDIUM IN SPRUCE SAP



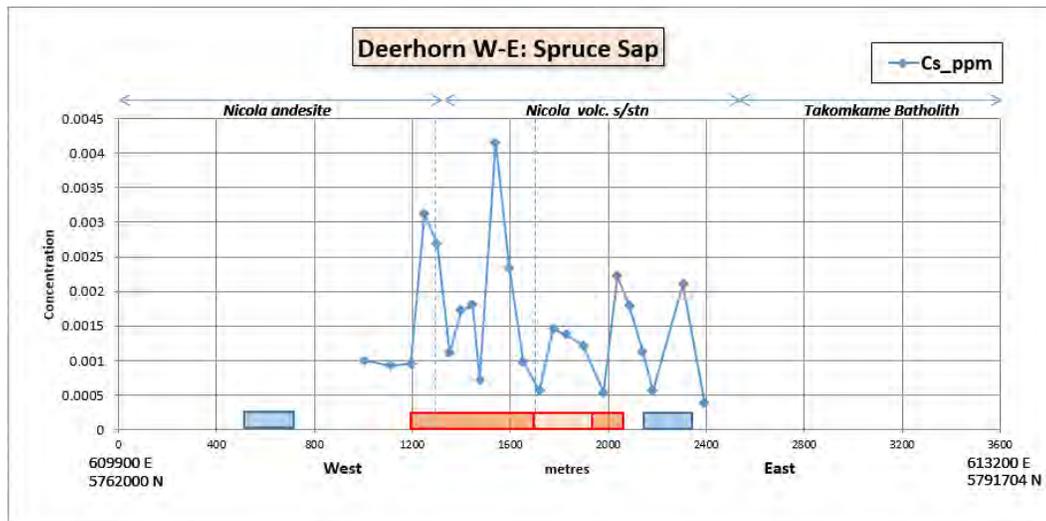


FIGURE 54. DEERHORN – CESIUM IN SPRUCE SAP.

## CHLOROFORM LEACHATES – SURFACE WAXES

Alder and spruce foliage were placed in ultrapure chloroform to remove surface waxes and crystallized exudates (see 'Field Methods' – Exudates). The leachate was evaporated to dryness then taken up in 2% nitric acid and analyzed on the sector field ICP-MS at QFIR. In order to merge the datasets from the two sets of samples (analyzed at different times), the data were levelled using a response ratio approach – the median of each dataset for each element was calculated and the relative enrichment recorded as a multiple of this median value.

## SPRUCE FOLIAGE

Samples comprised several snipped lengths of the most recent 2 years of twig and needle growth. Most of each sample comprised needles, with just a small percentage being new green twig growth. The two tissues were not separated.

## COMMODITY ELEMENTS

Copper (Fig. 55) appears to exhibit a combination of an apical and rabbit ear response over the mineralization, with peaks about 2.5 times background. The strongest anomaly, however, is located farther to the east and is of unknown source.

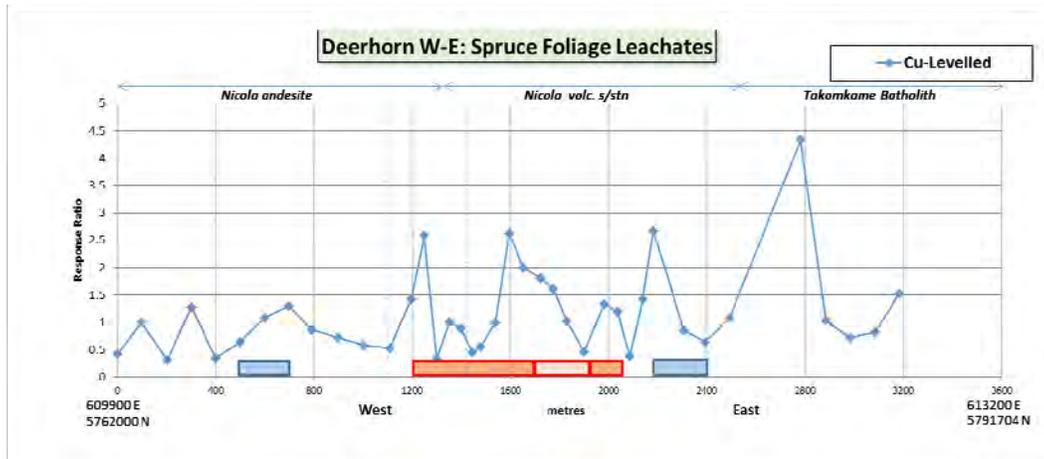


FIGURE 55. DEERHORN –LEVELLED COPPER IN SPRUCE FOLIAGE LEACHATES

Molybdenum (Fig. 56) has a single strongly anomalous value (25 times background) and a second at 5 times background over the main zone of mineralization. Anomalies (x2) on either of the zone of mineralization could be interpreted as constituting a rabbit ear response.

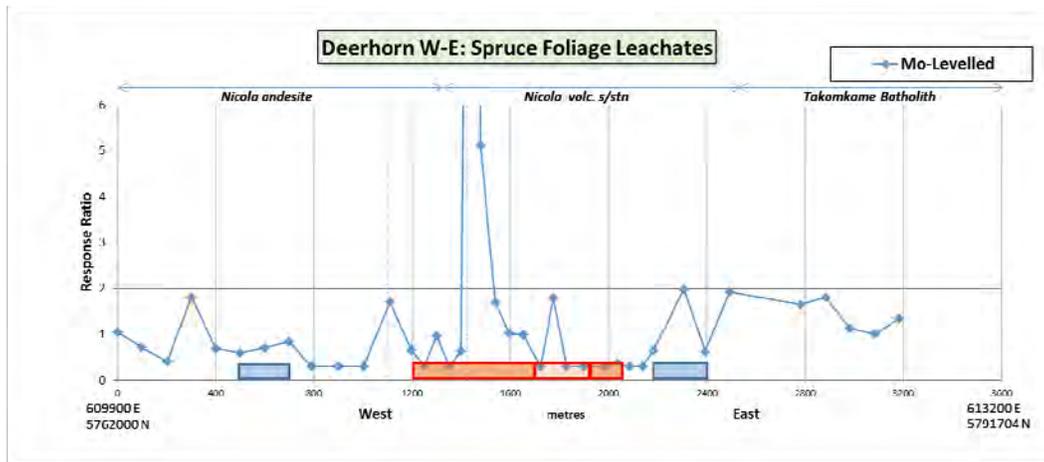


FIGURE 56. DEERHORN – LEVELLED MOLYBDENUM IN SPRUCE FOLIAGE LEACHATES

Zinc (Fig. 57) shows the strongest response of two sites with >3 times background directly over mineralization, and slightly weaker anomalies at several other locations – notably adjacent to the western extent of mineralization at two sample stations. This area is of note in that the leachates of both spruce and alder indicate multi-element enrichments and might be reflecting a possible asymmetric rabbit ear anomaly.

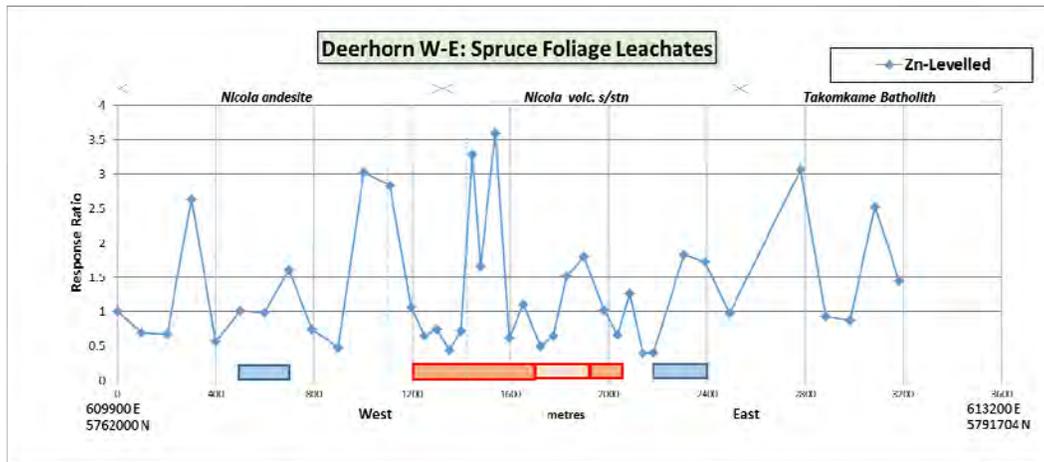


FIGURE 57. DEERHORN –LEVELLED ZINC IN SPRUCE FOLIAGE LEACHATES

### PATHFINDER ELEMENTS

Concentrations of As, Hg, Sb, Tl and W were mostly below the levels of detection precluding any meaningful plots.

### OTHER ELEMENTS

The highest anomaly to background site in the plots of Fe, K, Ca and Sr (Figs. 58 to 60) occurs over mineralization at the same sites as enrichments of Mo and Zn. Iron results have quite low contrast between mineralized and background sites. Furthermore, changes in the characteristics of the background profile for this element between the west and east ends of the line may indicate some unresolved analytical issues or batch effects in the data, which were not removed by levelling. Contrast for K, Ca and Sr is also very low making it difficult to make any meaningful conclusions from the results.

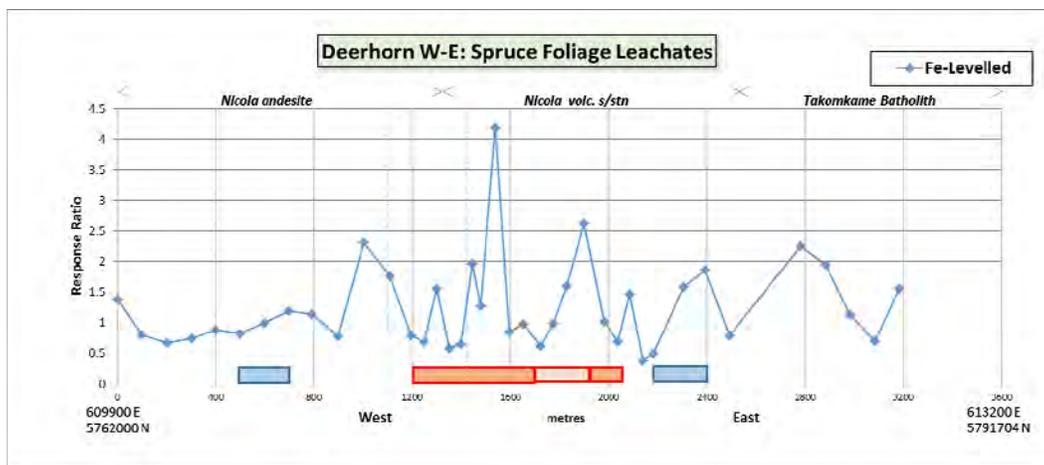


FIGURE 58. DEERHORN – LEVELLED IRON IN SPRUCE FOLIAGE LEACHATES

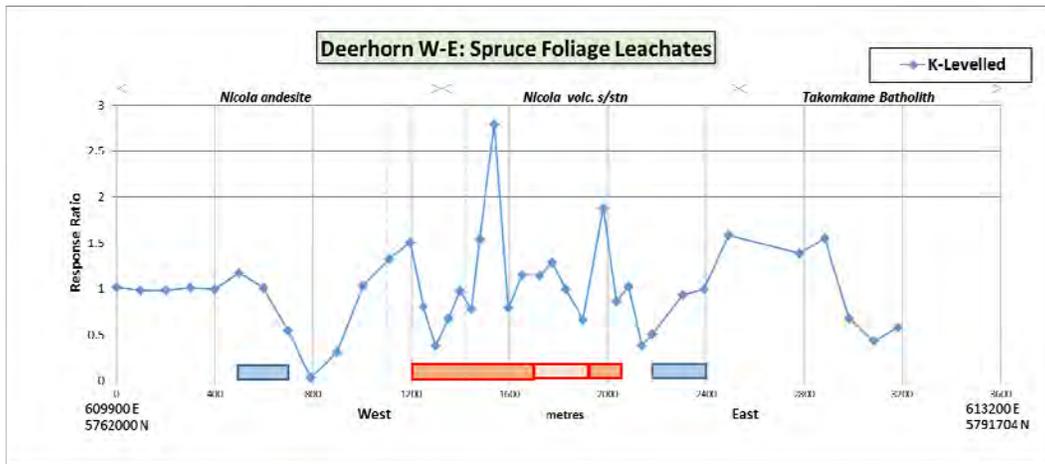


FIGURE 59. DEERHORN – LEVELLED POTASSIUM IN SPRUCE FOLIAGE LEACHATES

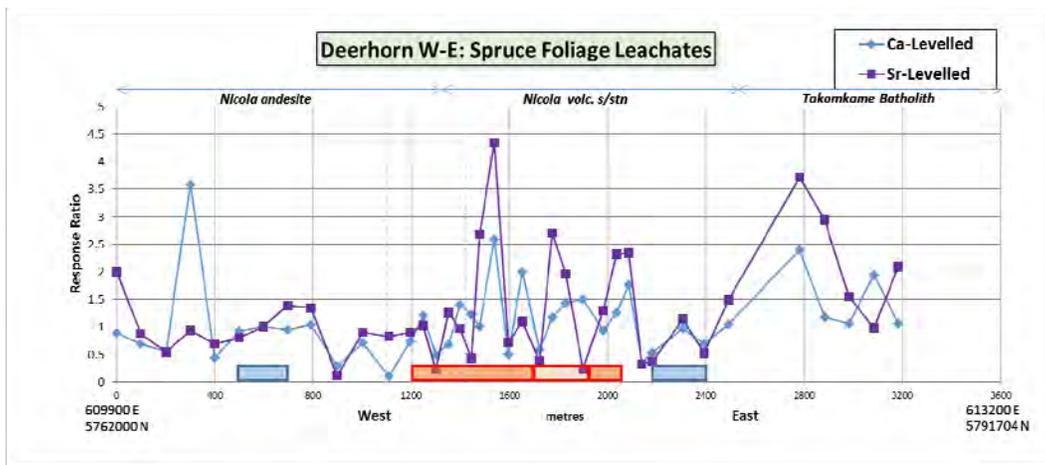


FIGURE 60. DEERHORN – LEVELLED CALCIUM AND STRONTIUM IN SPRUCE FOLIAGE LEACHATES

### ALDER FOLIAGE (PRELIMINARY DATA)

As noted earlier, during the first phase of the survey (July, 2012), alder leaves rapidly started to decompose unless they were refrigerated on the day of collection. Therefore, the integrity of some of the samples was compromised and results from this section should be treated with extreme caution and no conclusions should be drawn from this experimental phase of the survey. During the second phase of sampling the leaves were put into Kraft paper sample bags and did not decompose. Results from the two surveys were levelled prior to plotting, but should be treated as preliminary since further research is required. Plots of selected elements are presented 'for information only', since there are some interesting coincidences with some positive responses present at the same locations as found with other sample media. The following diagrams indicate some blank areas at the west end of the line where alder was not present.

## COMMODITY ELEMENTS

Copper shows relative enrichment at a single location west of the zone of mineralization and directly above it, but contrast is erratic and quite low – mostly only 2-3 times background levels (Fig. 61). By contrast Mo (Fig. 62) shows a strong response at the western margin of the mineralization and near the edge of the swamp located to the east. It is noteworthy that at the sites of the Mo anomalies are coincident enrichments of Ca, Sr and Ba – all carbonate-related elements that are typically enriched at the margins of electrochemical cells (Fig. 63). Zinc exhibits a similar response (Fig. 64), whereas Pb is enriched only at the western part of the mineralization (Fig. 65) and Ni only at the eastern swamp (Fig. 66).

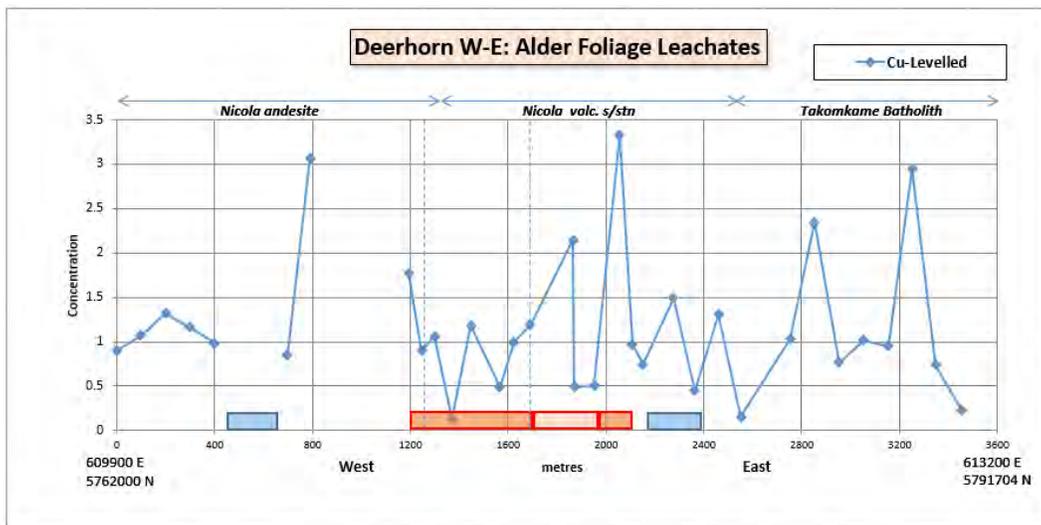


FIGURE 61. DEERHORN – LEVELLED COPPER IN ALDER FOLIAGE LEACHATES

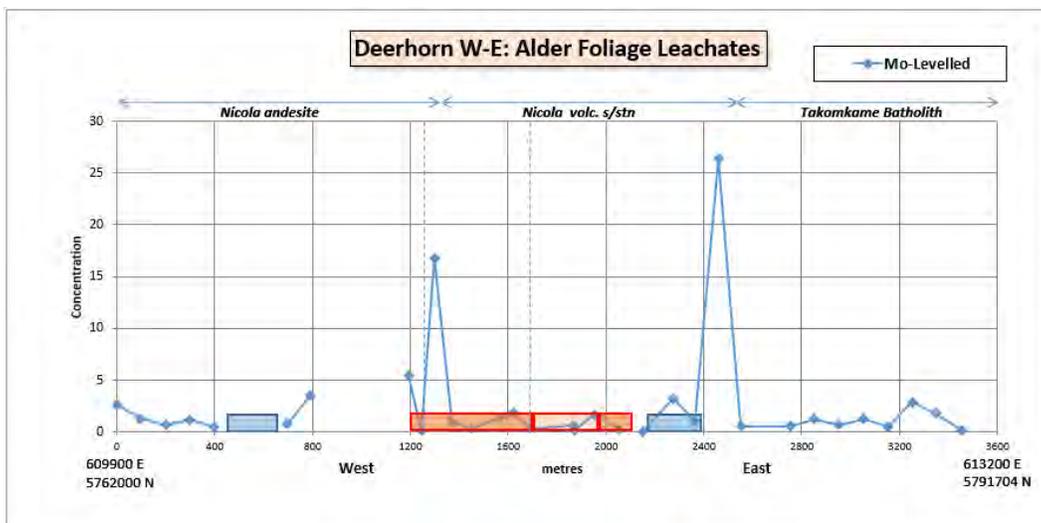


FIGURE 62. DEERHORN – LEVELLED MOLYBDENUM IN ALDER FOLIAGE LEACHATES

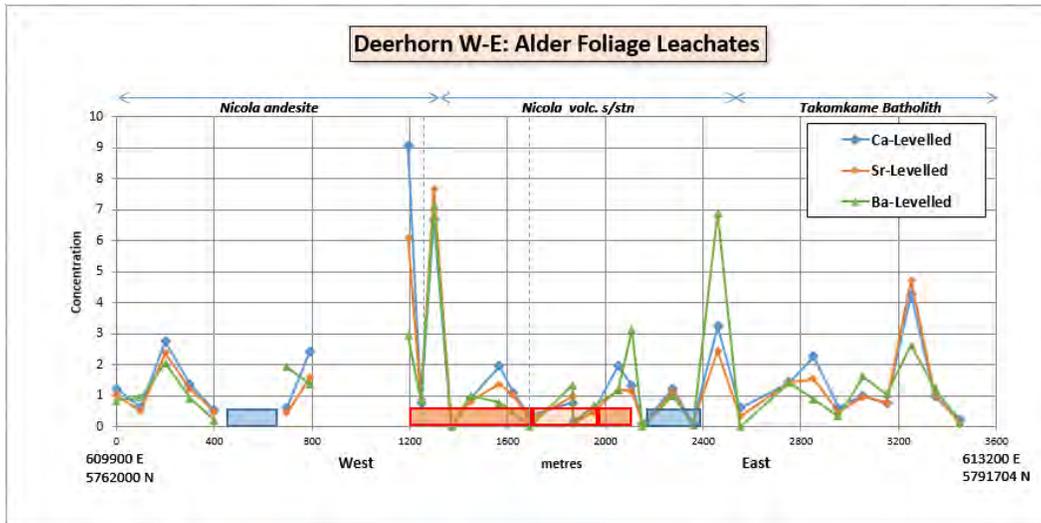


FIGURE 63. DEERHORN – LEVELLED CALCIUM, STRONTIUM AND BARIUM IN ALDER FOLIAGE LEACHATES

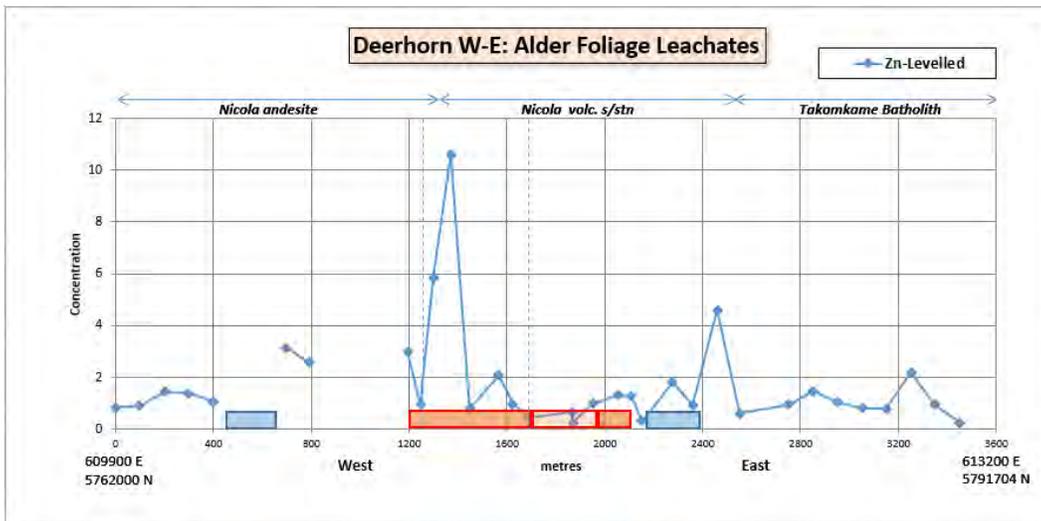


FIGURE 64. DEERHORN – LEVELLED ZINC IN ALDER FOLIAGE LEACHATES



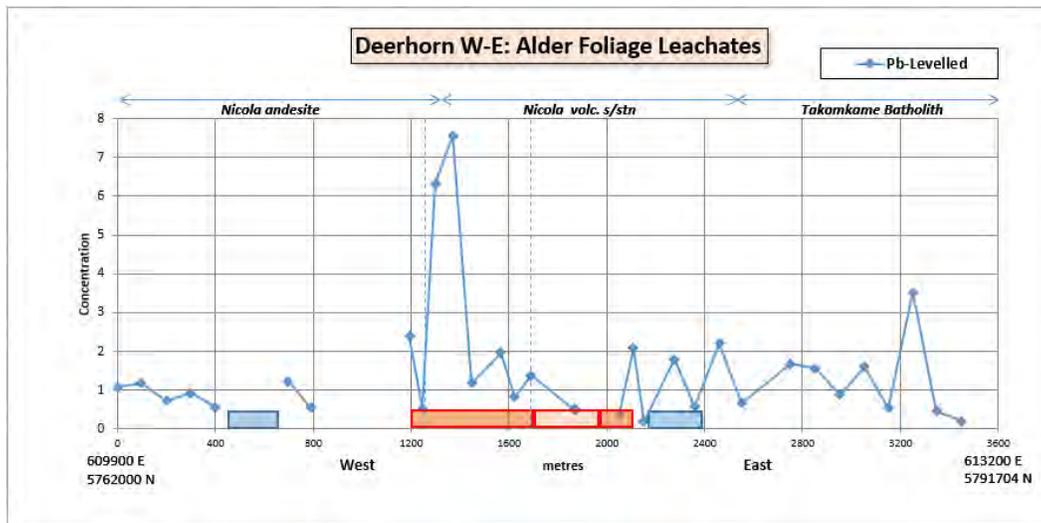


FIGURE 65. DEERHORN – LEVELLED LEAD IN ALDER FOLIAGE LEACHATES

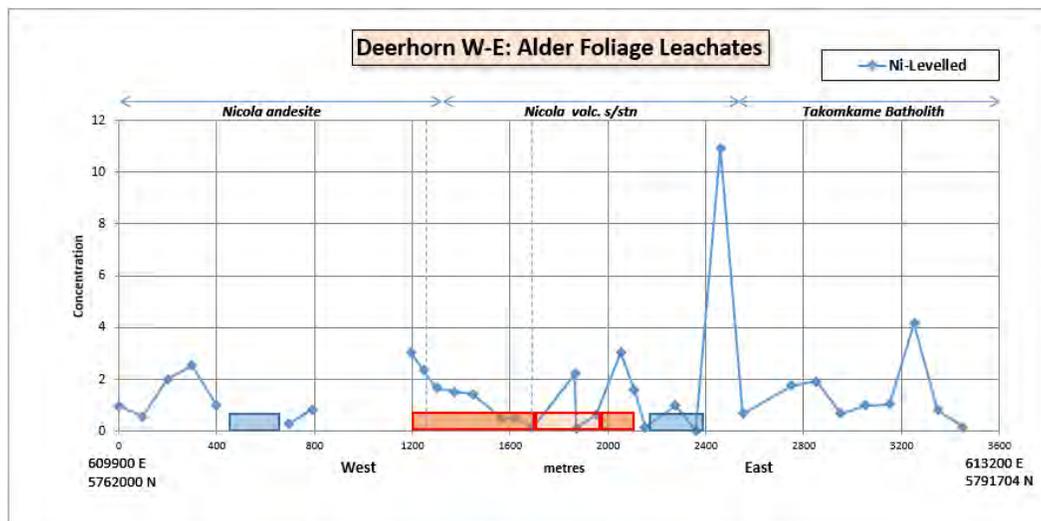


FIGURE 66. DEERHORN – LEVELLED NICKEL IN ALDER FOLIAGE LEACHATES

#### PATHFINDER ELEMENTS

Of the pathfinder elements shown for the other sample media (As, Hg, Sb, Tl and W) all were below DL in most samples of the alder leachates, such that no meaningful patterns could be discerned

#### OTHER ELEMENTS

The major elements Fe, Mg, K, Na, P and S (and the minor element Rb) all yielded anomalously high values close to the western margins of the mineralized zone, and most were elevated, too, immediately east of the eastern swamp (Figs. 67 to 72). The results have a rabbit ear appearance but, since these patterns are mostly (but not entirely) inconsistent with other sample media, this response may be

fortuitous or perhaps an analytical artifact because of the poor state of some of the samples by the time they were delivered to the laboratory for analysis.

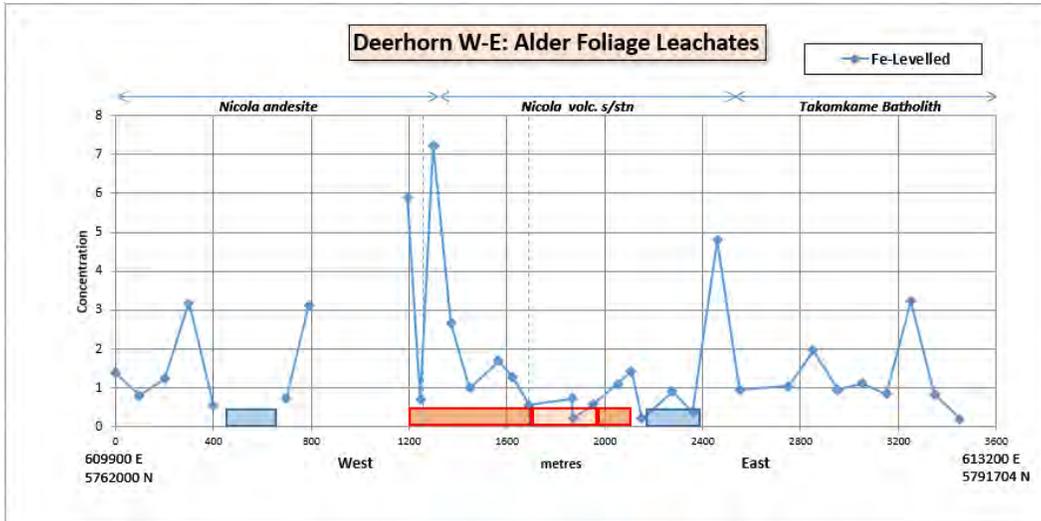


FIGURE 67. DEERHORN – LEVELLED IRON IN ALDER FOLIAGE LEACHATES

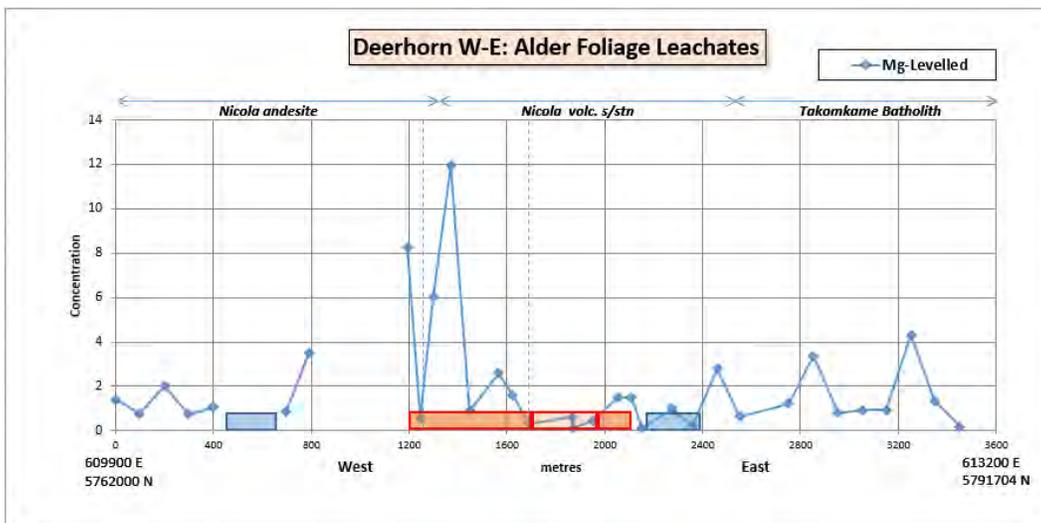


FIGURE 68. DEERHORN – LEVELLED MAGNESIUM IN ALDER FOLIAGE LEACHATES

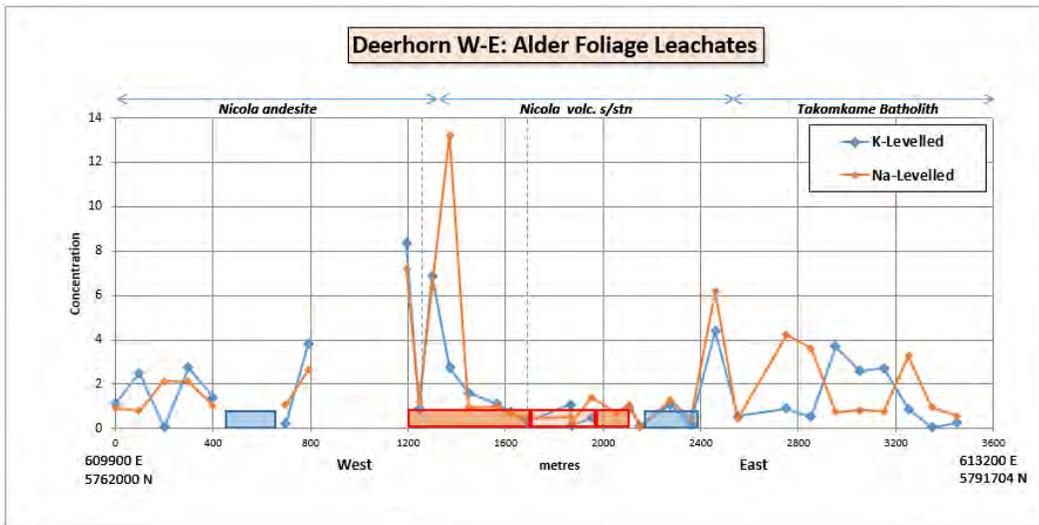


FIGURE 69. DEERHORN – LEVELLED SODIUM AND POTASSIUM IN ALDER FOLIAGE LEACHATES

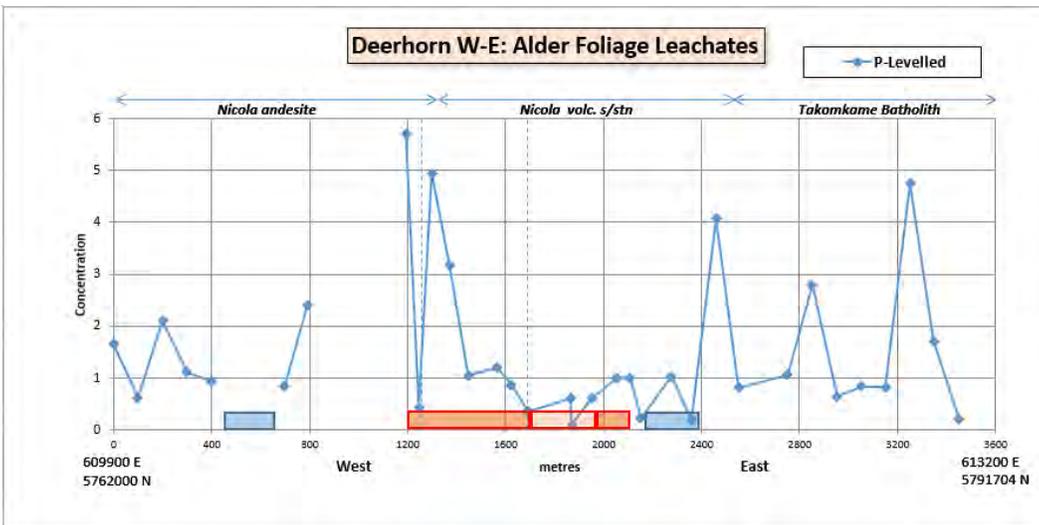


FIGURE 70. DEERHORN – LEVELLED PHOSPHORUS IN ALDER FOLIAGE LEACHATES



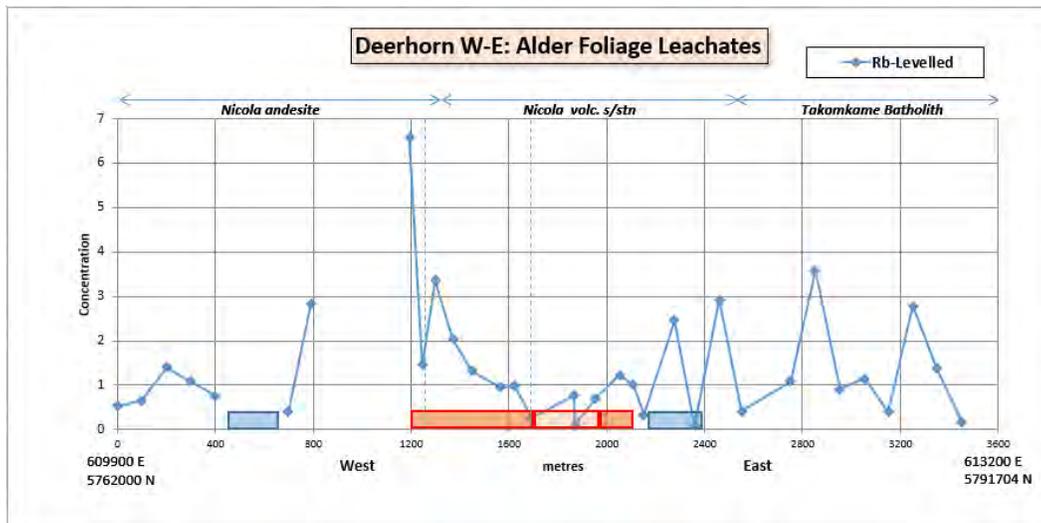


FIGURE 71. DEERHORN – LEVELLED RUBIDIUM IN ALDER FOLIAGE LEACHATES

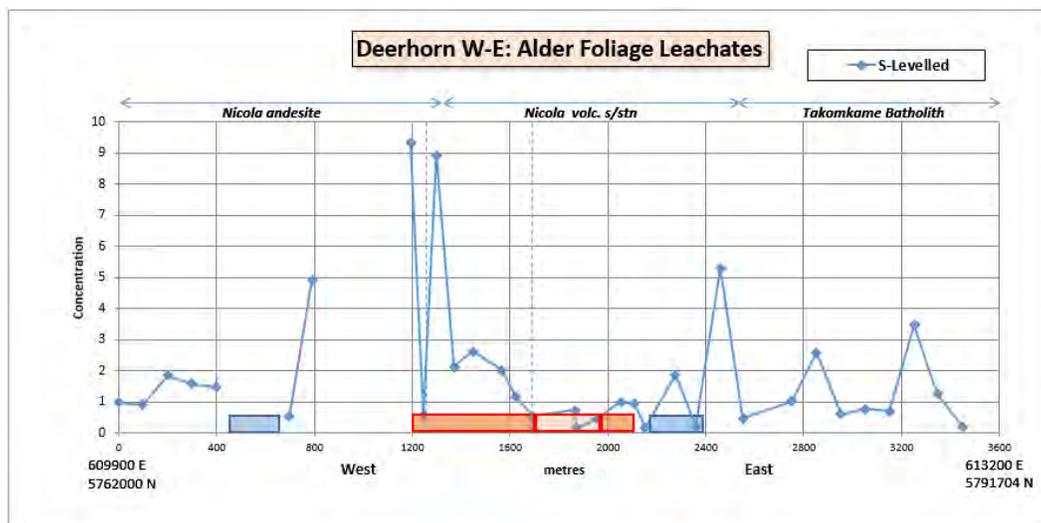


FIGURE 72. DEERHORN –LEVELLED SULPHUR IN ALDER FOLIAGE LEACHATES

## TRANSPIRED FLUIDS

Results for the transpired fluid geochemistry are treated slightly differently from the other media. Rather than representing a continuous traverse across the deposit, samples were collected from strategic locations over mineralization and in supposed background locations along the main access road. Ten samples were collected: four from what were deemed to be background sites and seven from over or immediately adjacent to the mineralized bodies and three in background locations at varying distances from the mineralized zone. Sample locations are shown in Figure 73.

Very low concentrations in the low ppb or ppt range are reported for most elements. Despite the extremely low absolute concentrations high contrast patterns are evident for some of the ore and

pathfinder elements. Table 5 shows comparative statistics between mineralized and background site for a selection of elements.

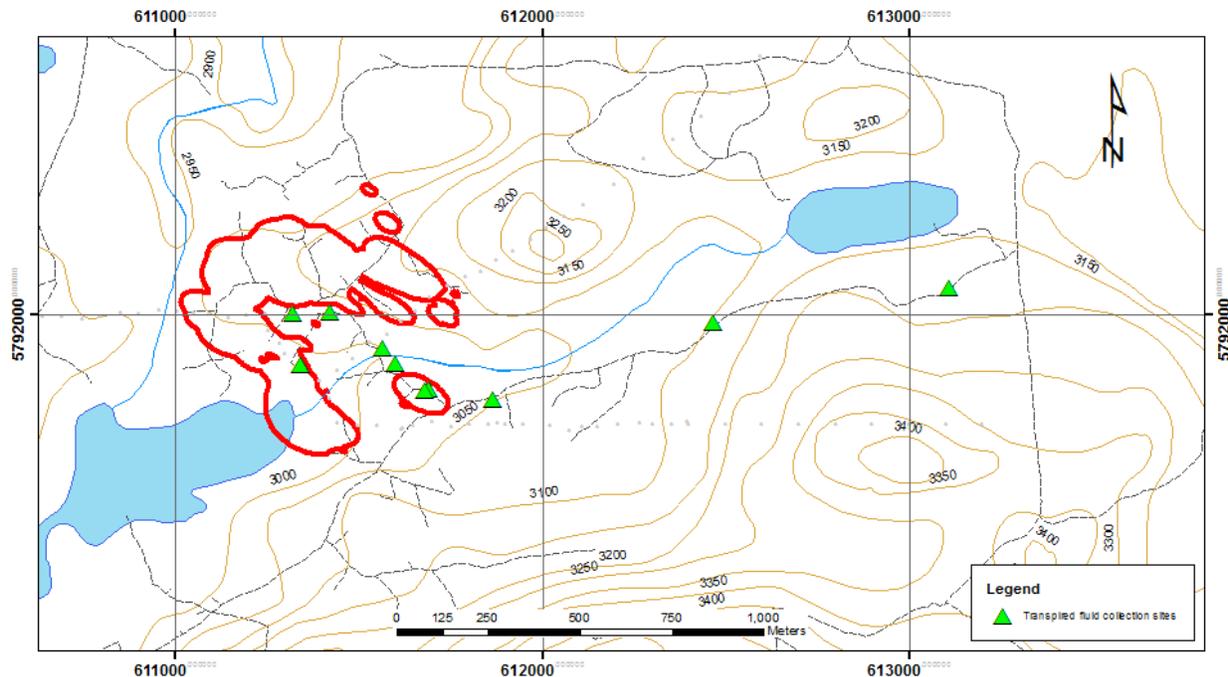


FIGURE 73. TRANSPIRED FLUID COLLECTION SITES. RED OUTLINE SHOWS THE SURFACE PROJECTION OF THE >0.2 G/T AU EQ. MINERALIZATION

#### COMMODITY ELEMENTS

Of the ore elements, Cu and Mo yielded results above detection limit. Copper (Fig. 74) shows a good response over the mineralized zone with highest concentrations (up to 48.1 ppb) overlying the projected mineralization. Not all samples in close proximity to the mineralized zone are anomalous. However, two samples have values similar to background levels and both of these correspond to trees in locations with relatively poor exposure to direct sunshine. Contrast for this element, defined as the ratio of the mean of the mineralized sites to that of background sites is 4 times background, which makes it a credible response.

Molybdenum (Fig. 75) displays four anomalous values with a maximum concentration of 0.44 ppb in the vicinity of the mineralization. Four of the seven sites classified as mineralized however, have very low concentrations just above the detection limit. Furthermore, one of the three background sites (the one closest to the eastern mineralized body) has an elevated value of 0.27 ppb. While visually presenting a recognizable response to the mineralization, the contrast is reduced to 0.9 times background by the presence of background values at mineralized sites and vice versa. Nevertheless it is encouraging that the samples with highest concentrations overlie mineralization.

## PATHFINDER ELEMENTS

Several pathfinder elements, including As, Bi, Hg, Tl and W produced recognizable responses to the mineralization.

TABLE 5. SUMMARY STATISTICS FOR SELECTED ELEMENTS IN TRANSPIRED FLUIDS

	Cu_ppb		Mo_ppb		S_ppb		Fe_ppb	
	Bkgr	Min'zd	Bkgr	Min'zd	Bkgr	Min'zd	Bkgr	Min'zd
N	3	7	3	7	3	7	3	7
Minimum	2.4	1.7	0.1	0.0	0.05	0.04	2.5	5.1
Maximum	4.1	48.1	0.3	0.4	0.06	0.58	40.9	144.1
Mean	3.1	12.4	0.1	0.1	0.05	0.20	15.5	29.7
Median	3.0	9.0	0.1	0.1	0.05	0.12	3.1	12.3
Stdev	0.9	16.5	0.1	0.1	0.01	0.20	22.0	50.7
IQR	1.7	12.9	0.3	0.1	0.01	0.31	38.4	11.3
Range	1.7	46.4	0.3	0.4	0.01	0.54	38.4	139.0
Contrast	4.0		0.9		3.8		1.9	
	As_ppt		Tl_ppt		W_ppb		Hg_ppb	
	Bkgr	Min'zd	Bkgr	Min'zd	Bkgr	Min'zd	Bkgr	Min'zd
N	2	4	2	7	0	2	3	6
Minimum	44.5	62.3	1.6	2.2	0.3	0.3	0.0	0.1
Maximum	46.7	470.1	1.7	10.1	0.3	7.7	1.7	1.0
Mean	45.6	176.4	1.6	5.6	0.3	4.0	0.6	0.4
Median	45.6	86.5	1.6	4.3	0.3	4.0	0.0	0.4
Stdev	1.6	196.2	0.0	3.0	0.3	5.2	1.0	0.3
IQR	2.2	308.4	0.1	5.9	0.3	7.3	1.7	0.6
Range	2.2	407.9	0.1	7.9	0.3	7.3	1.7	0.9
Contrast	3.9		3.4		13.4		0.7	

Arsenic results (Fig. 76) show six samples above detection limit: four at mineralized sites and two in background. Three of the four mineralized sites show elevated values with maximum concentrations reaching 470 ppt and a relatively high contrast at 3.9 times background. Sulphur (Fig. 77) has a similar contrast of 3.8 times background. Above detection limit results for this element were returned for all samples. Highest concentrations occur in samples directly overlying mineralization. Interestingly two samples located between the east and west mineralized bodies have background concentrations suggesting that this element is an effective discriminator of mineralization in this medium.

A very robust response is shown by Tl (Fig. 78). Despite having very low concentrations in the low ppt range, this element yielded above detection limit results for all but one of the background samples. Elevated values between 3 and 10 ppt occur in three of the seven sites over mineralization while at background sites concentrations reach only 1.7 ppt. Contrast is quite good at 3.4 times background.

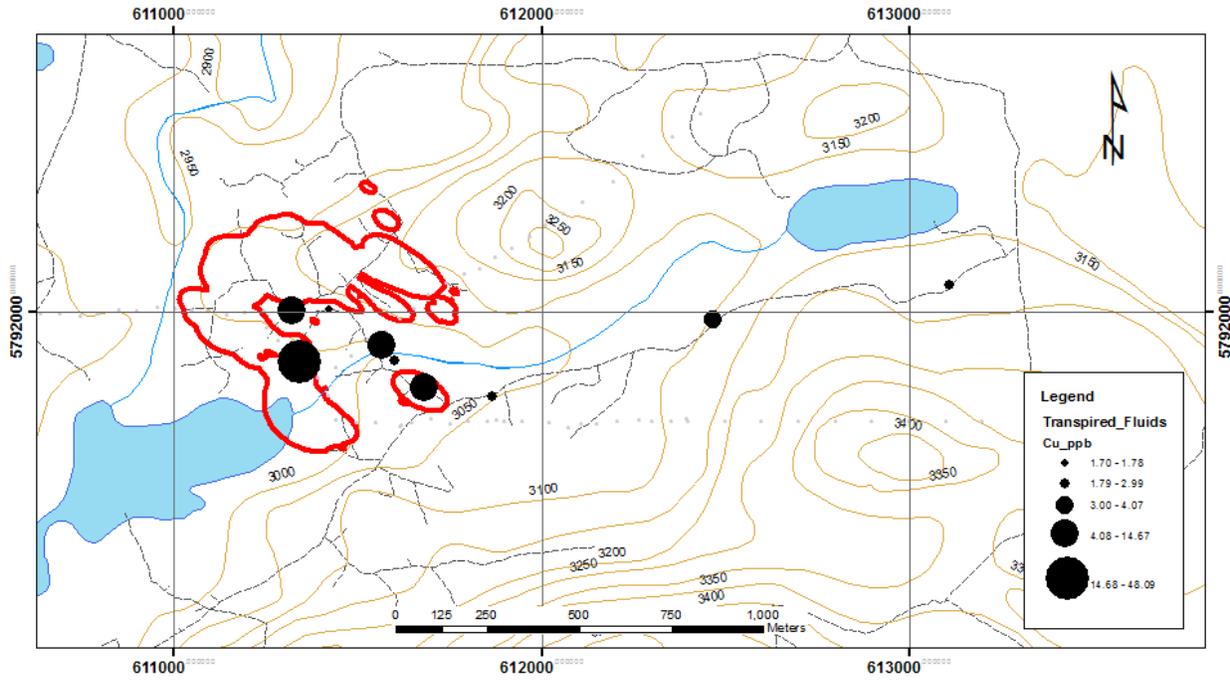


FIGURE 74. COPPER (PPB) IN TRANSPIRED FLUIDS

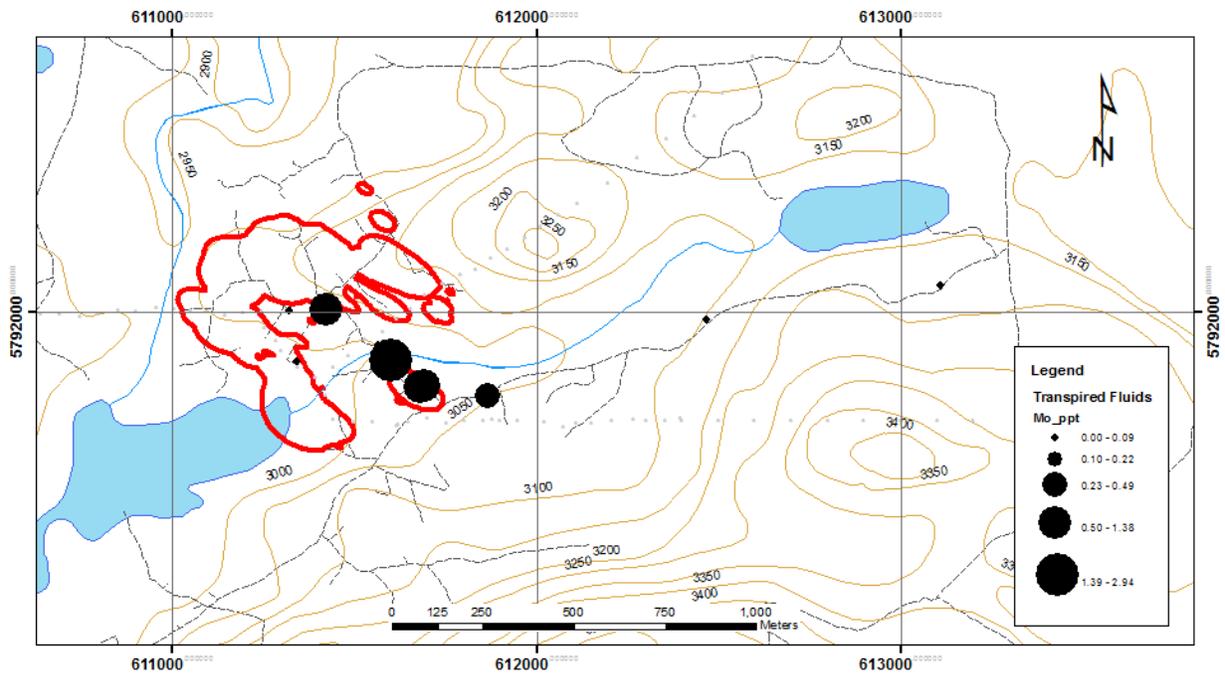


FIGURE 75. MOLYBDENUM (PPT) IN TRANSPIRED FLUIDS

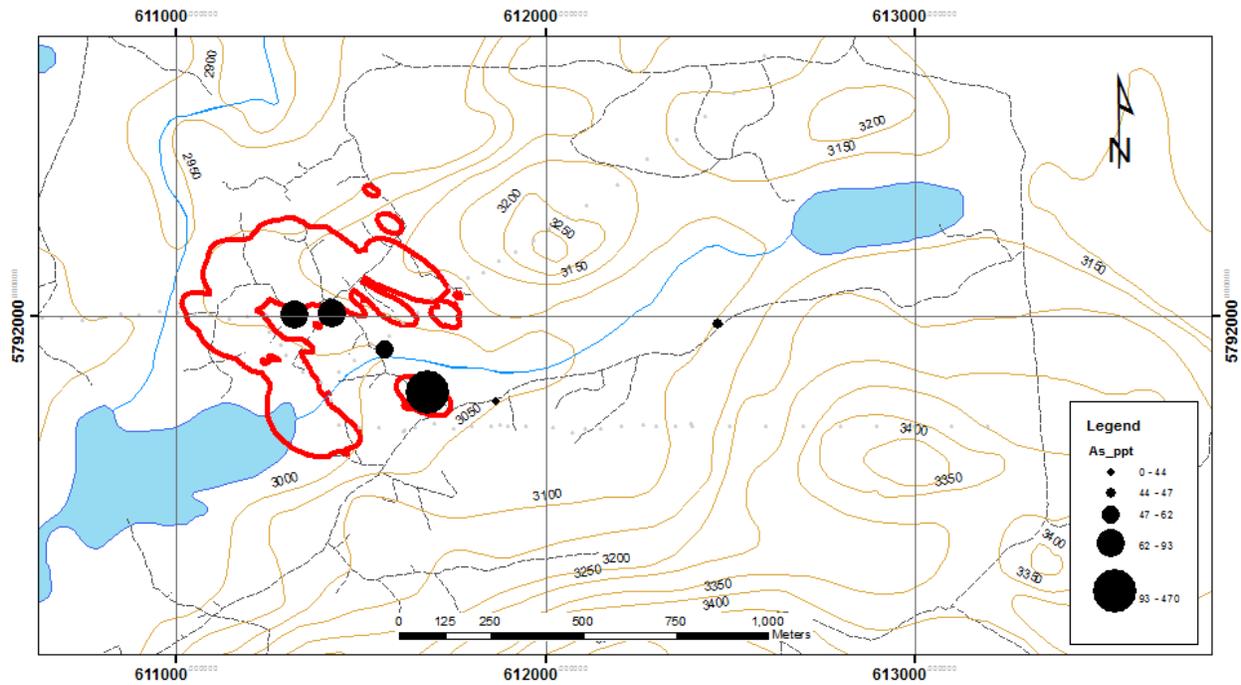


FIGURE 76. ARSENIC (PPT) IN TRANSPIRED FLUIDS

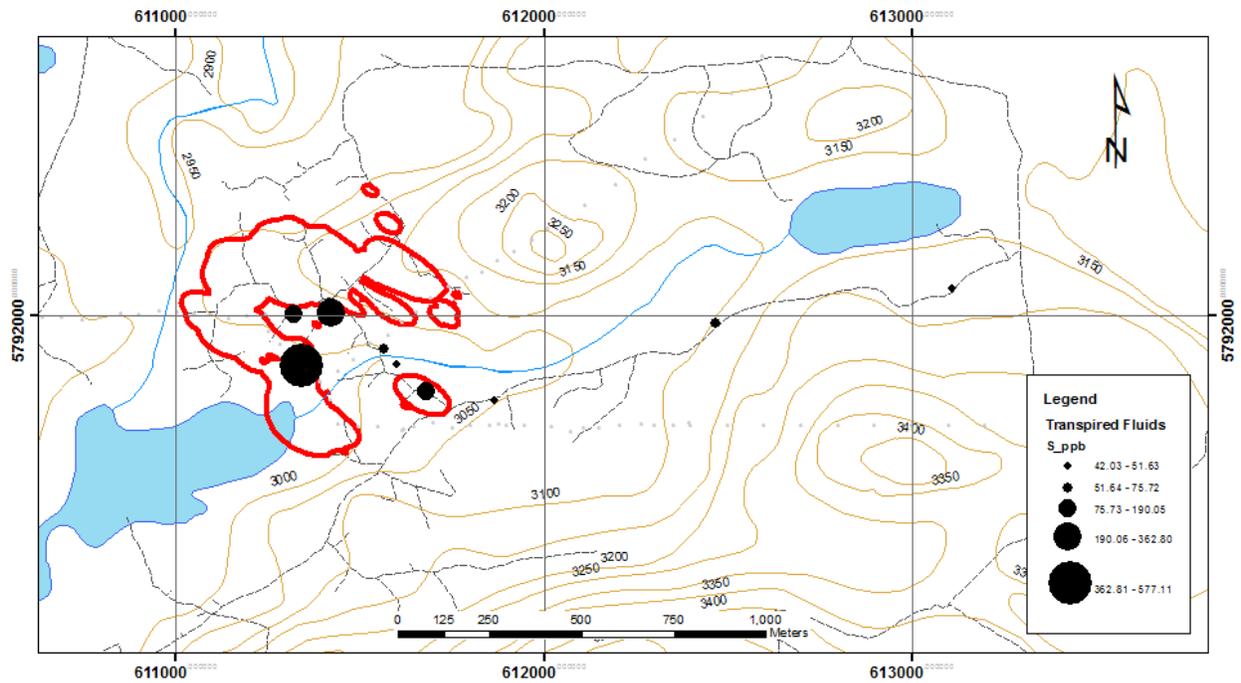


FIGURE 77. SULPHUR (PPB) IN TRANSPIRED FLUIDS

Tungsten, an element that is known to highlight blind mineralization in other media (e.g. Ah, charcoal) also appears to have a signal in transpired fluids. Figure 79 shows that two samples yielded values above detection limit. Both of them are located at mineralized sites. The maximum concentration of 7.68 ppt occurs over the eastern mineralized body. The other detectable concentration (3.44 ppt) occurs adjacent to the western body.

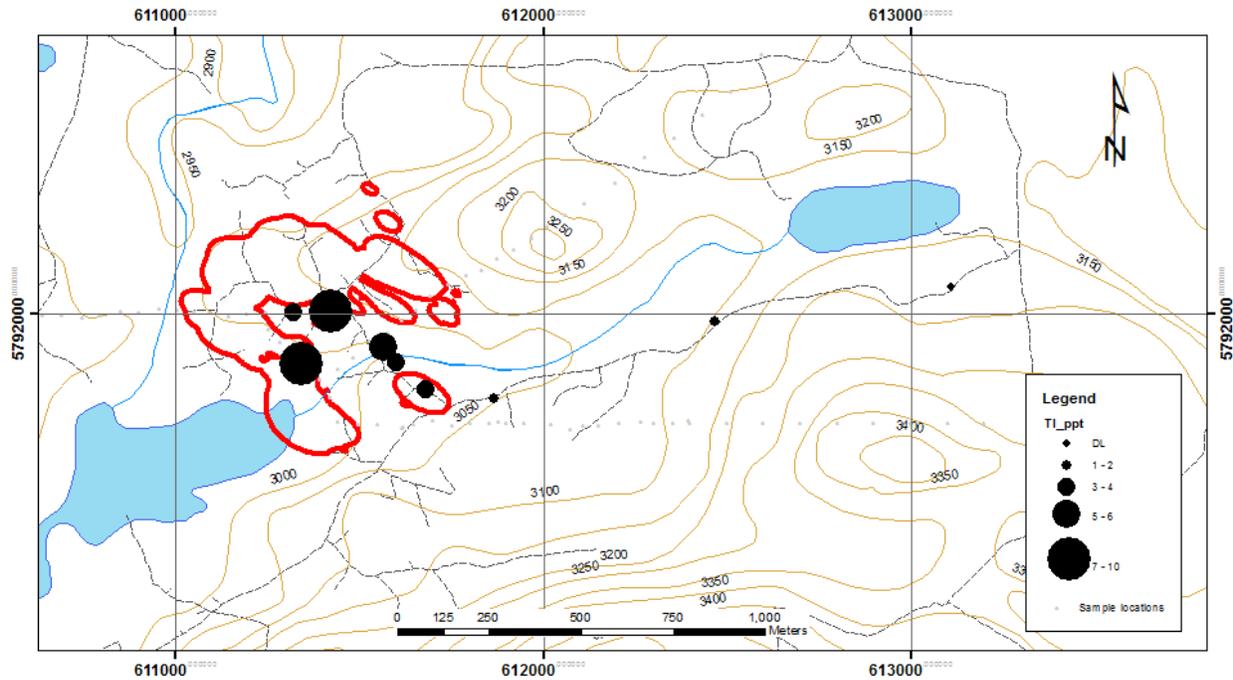


FIGURE 78. THALLIUM (PPT) IN TRANSPIRED FLUIDS

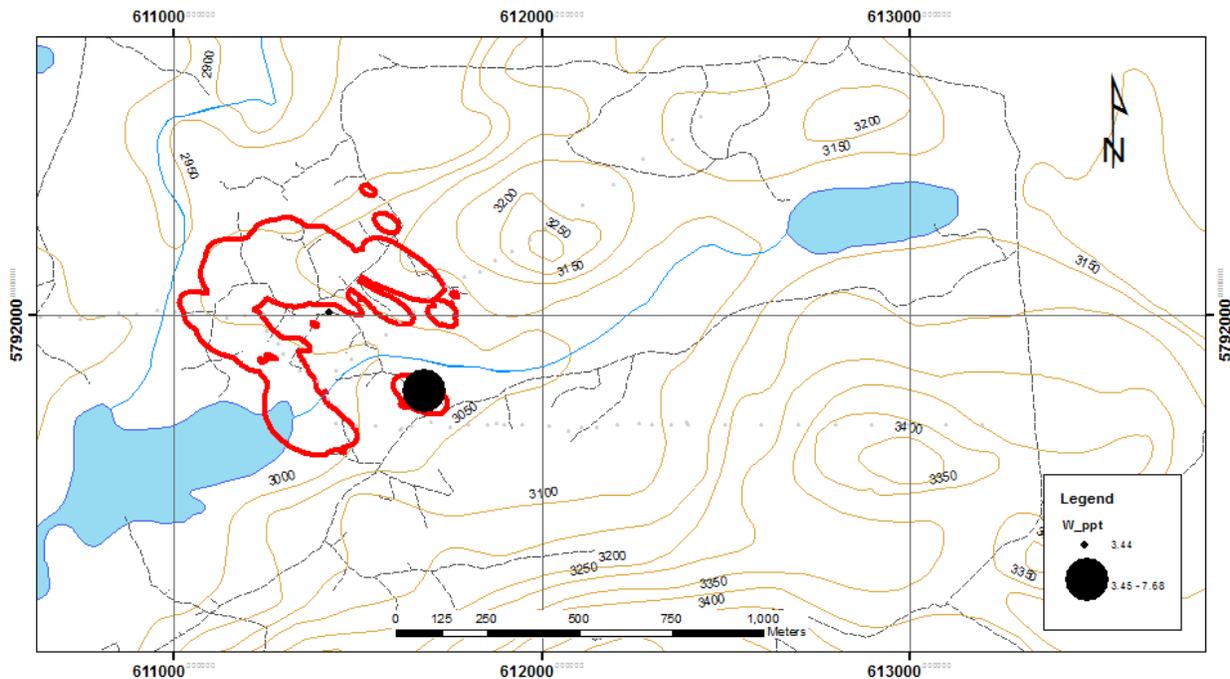


FIGURE 79. TUNGSTEN (PPB) IN TRANSPIRED FLUIDS

## THREE FIRS

### AH HORIZON

#### COMMODITY ELEMENTS

The commodity elements Cu, Mo, Au and Ag have slightly elevated values over the known zone of mineralization, but also have significantly higher concentrations at differing locations farther east on the line where there is no known mineralization. These responses may also be due to as yet undiscovered mineralization or in some cases attributed to hydromorphic processes.

Copper (Fig. 80) displays a subtle enrichment (20 ppm) over the known mineralization. Contrast of this feature is only two times background. It is suppressed by stronger responses located at the east and west ends of the line. The westernmost sample has a concentration of 49 ppm and lies at the edge of a boggy area suggesting that it may be caused by hydromorphic enrichment. At the eastern end of the line, there is a multi-peak or possible rabbit ear anomaly with contrast of 6 times background. Samples comprising this feature lie in a well-drained hilly area and are therefore unlikely to represent hydromorphic concentration. The cause of this response has not been established.

Figure 81 shows that Mo also has a subtle response that is subdued by much higher concentrations at the east end of the line. The response over the known mineralization appears to have a rabbit ear form with reasonable contrast of 3.5 times the local background. Values almost twice as high occur near the east end of the line. A gradual rise in Mo concentration from the mid part of the line eastwards may reflect a lithological change and/or thinning cover in that direction. However the general coincidence of

the elevated Mo values with higher Cu concentrations means that an unknown mineralized source is also a possible explanation.

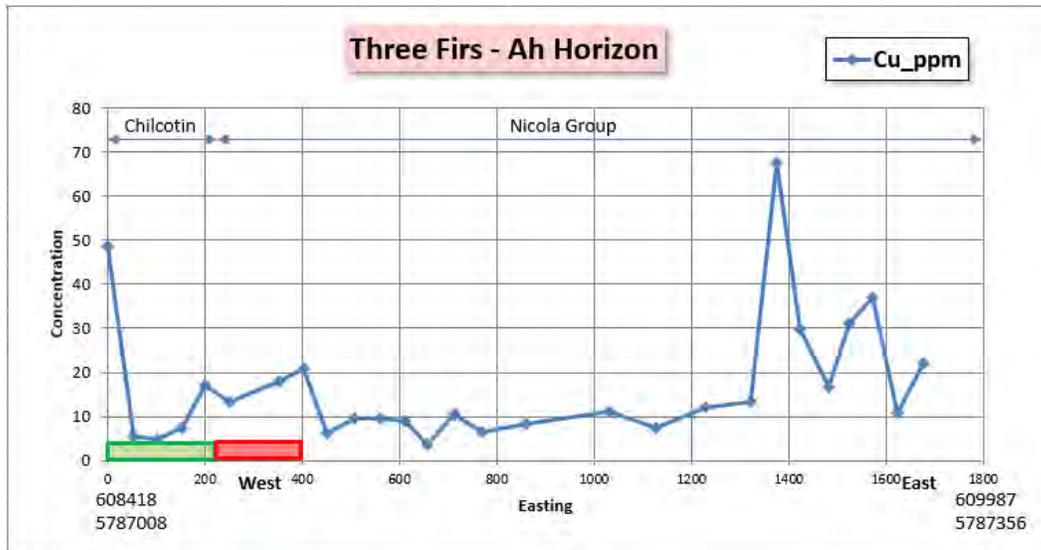


FIGURE 80. THREE FIRS - COPPER IN AH HORIZON SOIL. THE GREEN BAR INDICATES THE INFERRED POSITION OF SUBCROPPING CHILCOTIN BASALT AND THE RED BAR HIGHLIGHTS THE POSITION OF CU=AU MINERALIZATION ENCOUNTERED BY DRILLING



FIGURE 81. THREE FIRS - MOLYBDENUM IN AH HORIZON SOILS

Neither Ag nor Au has a recognizable response over the Three Firs mineralization (Figs. 82 and 83). Silver concentrations are anomalously low over the known mineralization and increase rapidly away in both directions. Much of the line east of the mineralized zone is characterized by a noisy elevated background defined by concentrations ranging between 200 and 800 ppb. A subtle peak, or possible rabbit ear, is present on the west side of the zone over the contact between the Nicola and Chilcotin groups.

However the contrast of this feature is overwhelmed by much higher values (over 600 ppb) at the west end of the line where boggy conditions suggest hydromorphic concentration. Patterns for Au are somewhat clearer than those for Ag. This element shows a very subtle elevation in concentration over the known mineralization but this is overwhelmed by a much stronger response from the central part of the line. As most of the values are quite close to the analytical detection limit (0.2 ppb), these patterns may have no geological meaning whatsoever and may be the result of noise.

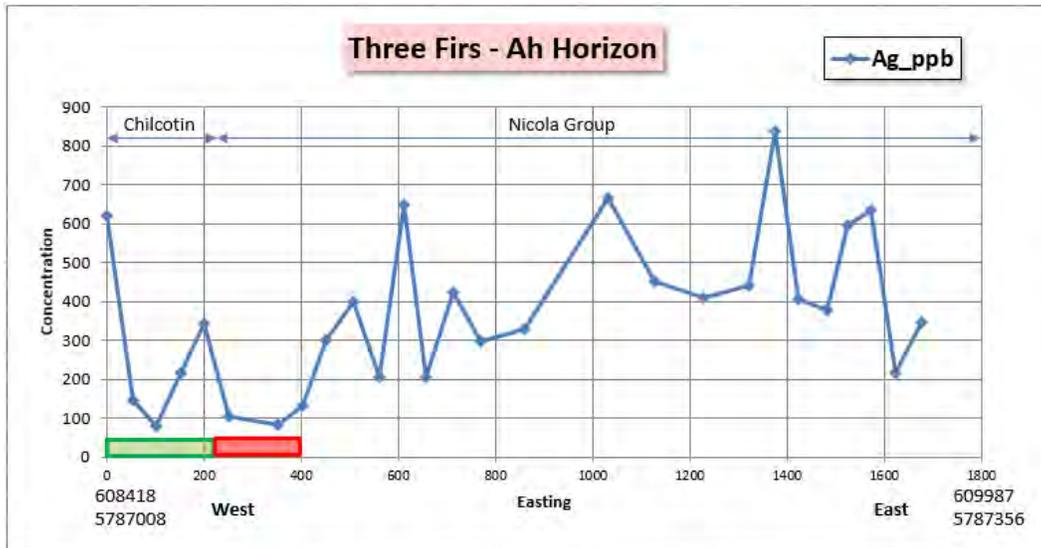


FIGURE 82. THREE FIRS - SILVER IN AH HORIZON SOIL

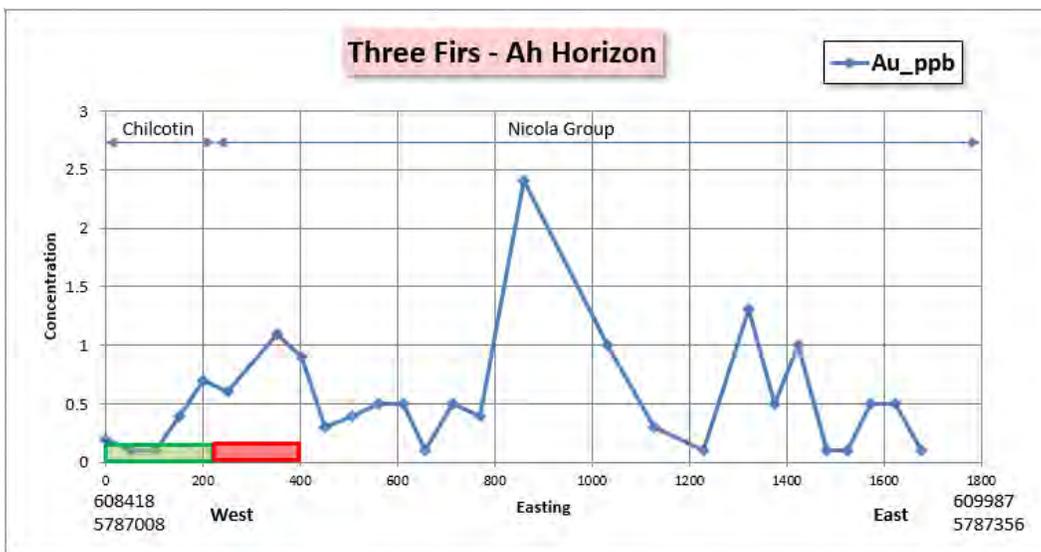


FIGURE 83. THREE FIRS – GOLD IN AH HORIZON SOIL

### PATHFINDER ELEMENTS

Arsenic, Hg, Sb and W follow similar patterns to the Cu and Mo, with no compelling responses over mineralization, and a general trend of increasing values eastward.

### OTHER ELEMENTS

Iron, Ga, Mg, Na, Nb, Sr, Te, and Ti have highest concentrations over the known zone of mineralization. The reader is referred to Appendix 1 for profiles of these elements. Some of the highest concentrations of Ca and REE occur at the contact between mineralization and the Chilcotin basalt cover. A feature of this line of samples is, however, that most elements, including the commodity and pathfinder elements are considerably more enriched near the eastern end of the line than over known mineralization. At this time it is unknown why this should be.

### SPRUCE BARK

There are few elements of note that exhibit enrichments over, or adjacent to, the zone of known mineralization. It has been noted that mineralization appears to extend beneath the basalt cover to the west (Bissig et al., 2013). Highest Cs and Rb concentrations occur right at this contact and over the basalt (Figs. 84 and 85). No other element exhibits a distinct pattern of enrichment in the bark from stations along this line.

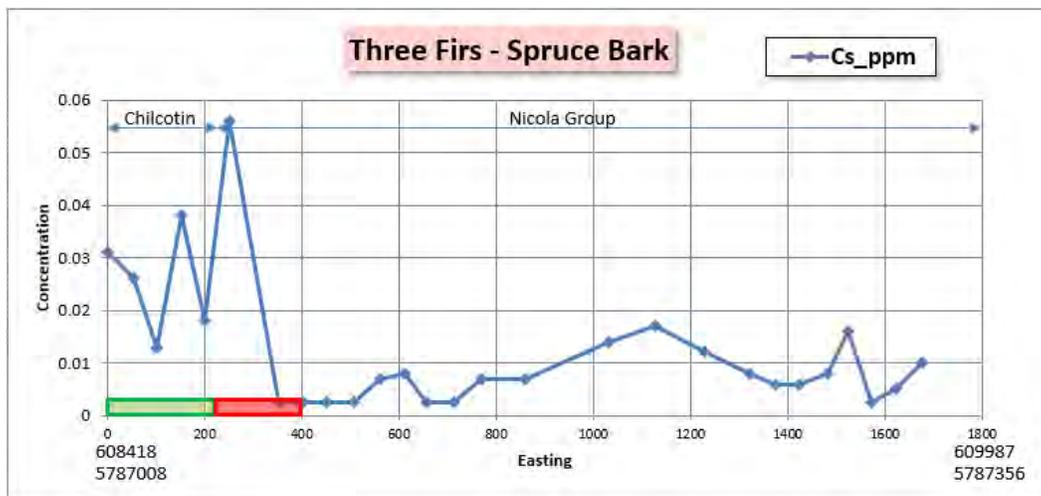


FIGURE 84. THREE FIRS – CESIUM IN SPRUCE BARK

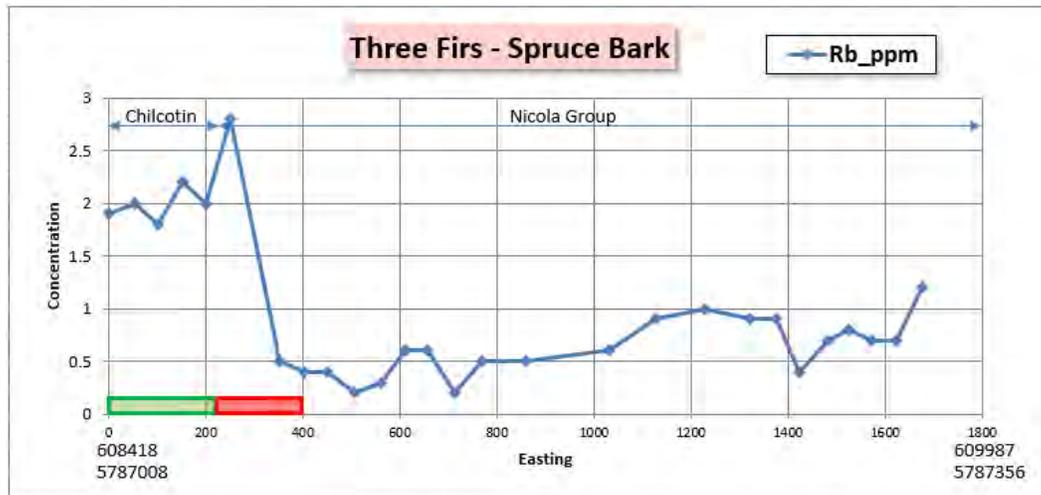


FIGURE 85. THREE FIRS – RUBIDIUM IN SPRUCE BARK

## SPRUCE TWIGS

Ash yields from the spruce twigs collected at Three Firs were similar. Comparative plots of concentrations in ash and concentrations in ash levelled to a dry weight basis showed there to be no significant differences in the profiles of elements; however, to add an extra level of precision, ash values have been levelled to a dry-weight equivalent prior to plotting the data.

## COMMODITY ELEMENTS

Whereas the dry spruce bark yielded such low concentrations for many elements that many values were below DL, the ashing of the twigs has permitted variations at low concentrations to be revealed. Copper and Ag do not display recognizable responses over the Three Firs mineralization. The highest Au value however (10 ppb), occurs directly over the known mineralization (Fig. 86). This single peak apical response has a contrast of about 3.3 times background. East and west of the highest concentration, Au values show a noisy background variation between 2 and 4 ppb. The erratic nature of the profile is likely due to the very low concentrations that in some places approach the analytical detection limit.

Molybdenum displays a similar profile to Au (Fig. 87). Highest concentrations occur over the known mineralization and appear to define a low contrast (3.0 times background) rabbit ear pattern. A single sample peak is also present near the mid-point of the line and values show a gradual increase towards the east end. It is unknown if any mineralization occurs in those areas to explain the elevated concentrations but the higher values at the east end of the line occur in the same general area as elevated values observed for Cu and Mo in the Ah horizon results (Figs. 80 and 81)

## OTHER ELEMENTS

Figures 88 to 91 illustrate profiles of Li, Se, Pb and Nd, which all appear to show responses to the Three Firs mineralization.

Lithium (Fig. 88) appears to have a moderate contrast (4.2 times background) rabbit ear response. The western rabbit ear directly overlies the known mineralization but the eastern one occurs 300 m east suggesting that the mineralized zone may be of greater extent than previously thought. A similar pattern is shown by Se (Fig. 89). This element is more indicative of potential sulphide mineralization than Li. The rabbit ear peaks coincide with Li and suggest that sulphides may continue east of the known zone.

Lead, shows a broad zone of enrichment (to 3.5 times background) extending over the known mineralization and encompassing the Li and Se rabbit ears (Fig. 90). The highest value, however, occurs at the east end of the line in the same area as the elevated Cu and Mo mentioned above.

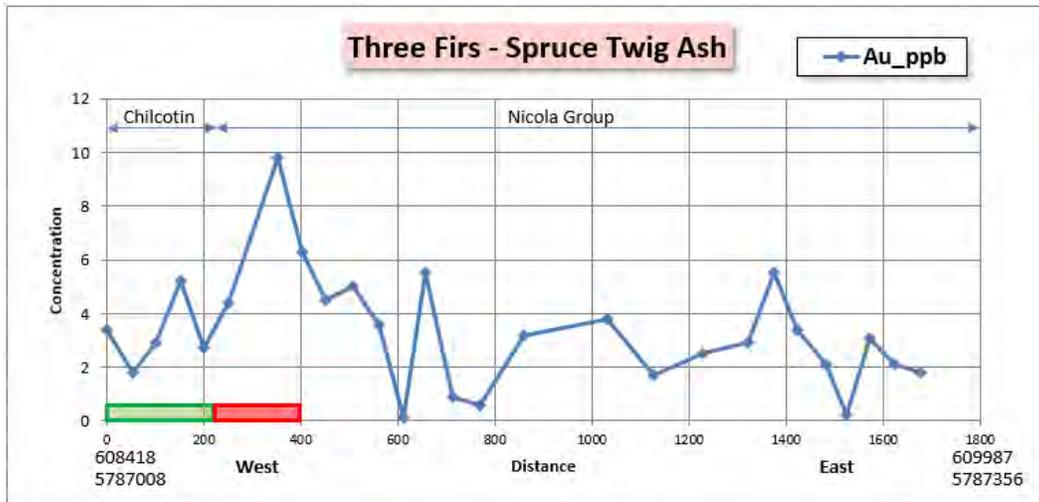


FIGURE 86. THREE FIRS – GOLD IN SPRUCE TWIG ASH

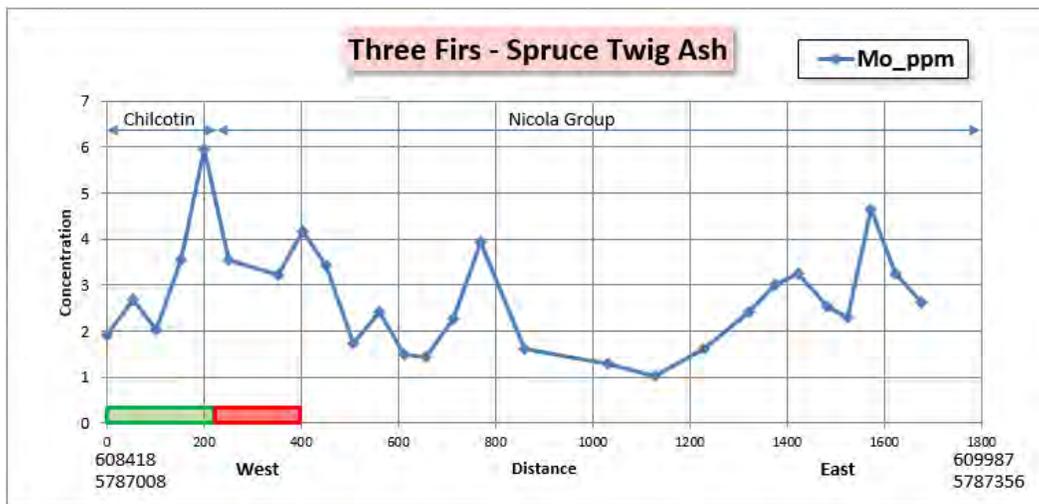


FIGURE 87. THREE FIRS – MOLYBDENUM IN SPRUCE TWIG ASH

REE profiles for Ce, Nd and Y show a broad zone of enrichment over the mineralized zone and extending for over 300 m eastwards (Fig. 91). It coincides with the Pb response. Cerium has the highest contrast

response (2.4 response ratio) of the three REE with the maximum concentrations again occurring at the east end of the sampled line.

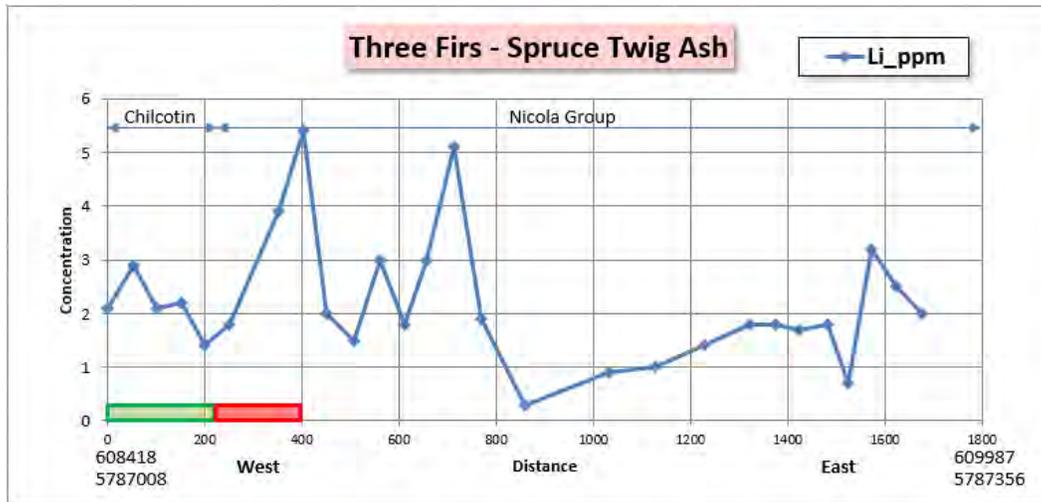


FIGURE 88. THREE FIRS – LITHIUM IN SPRUCE TWIG ASH

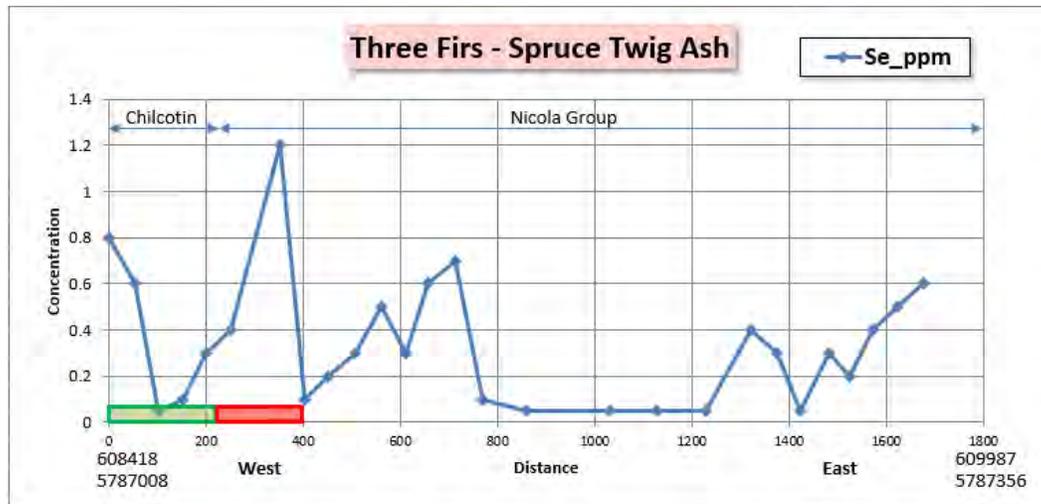


FIGURE 89. THREE FIRS – SELENIUM IN SPRUCE TWIG ASH

Antimony (Fig. 92) displays a single elevated value located near to the eastern margin of the Three Firs zone. Signatures of Cs and Rb are mostly highest over the basalt suggesting a possible lithological control (Fig. 93 and 94). Other elements with elevated values over the known mineralization include Cr, Fe, and Sr. The latter displays a low contrast rabbit ear pattern similar to those observed for Li and Se.

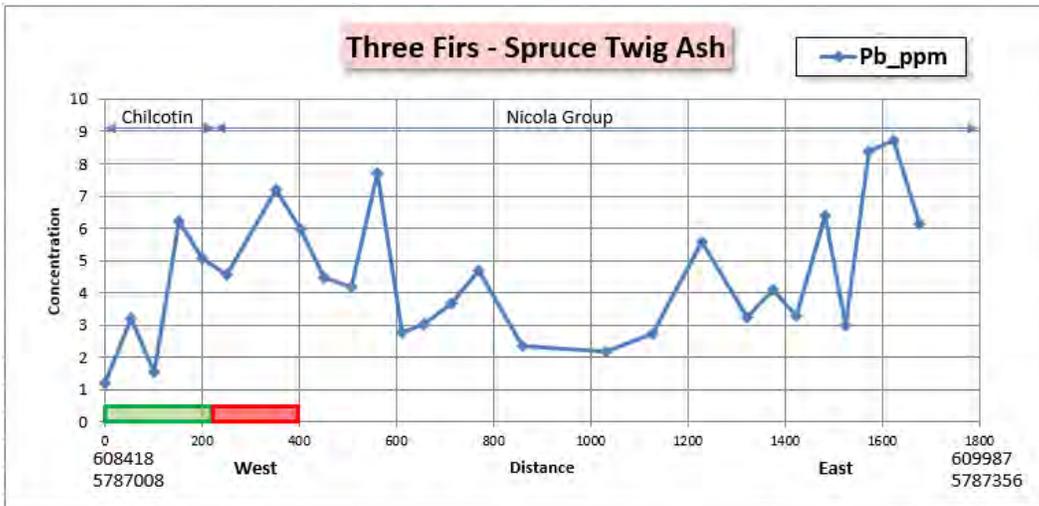


FIGURE 90. THREE FIRS – LEAD IN SPRUCE TWIG ASH

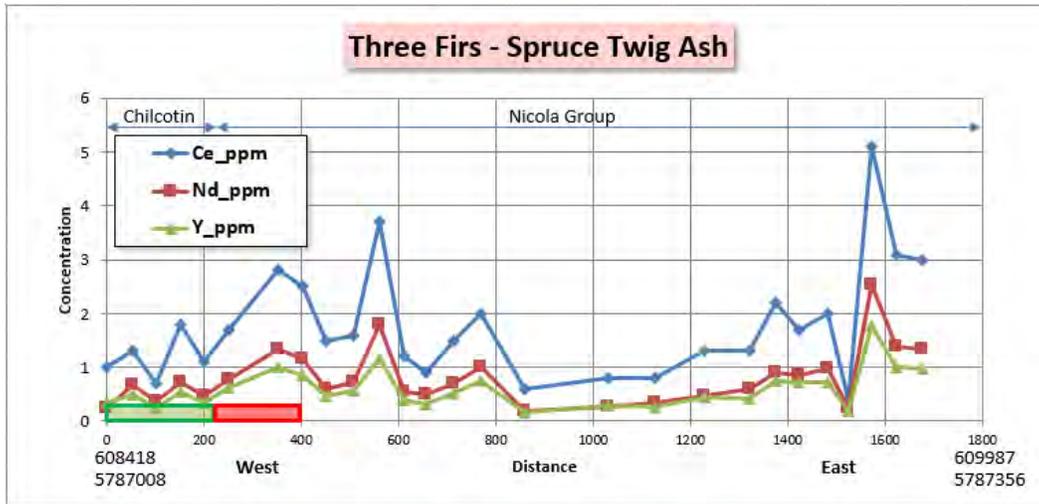


FIGURE 91. THREE FIRS – REE REPRESENTED BY CERIUM, NEODYMIUM AND YTTRIUM IN SPRUCE TWIG ASH



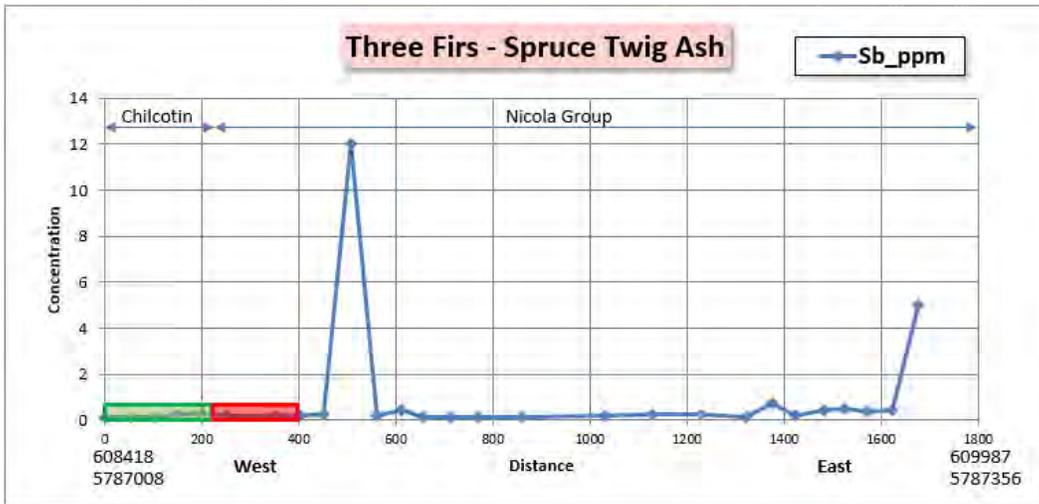


FIGURE 92, THREE FIRS – ANTIMONY IN SPRUCE TWIG ASH



FIGURE 93. THREE FIRS – RUBIDIUM IN SPRUCE TWIG ASH



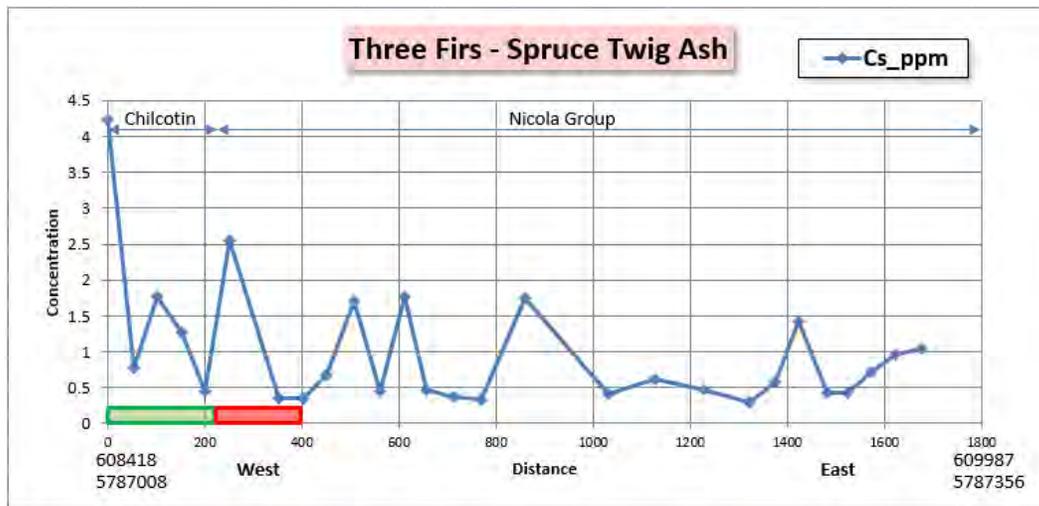


FIGURE 94. THREE FIRS – CESIUM IN SPRUCE TWIG ASH

## DISCUSSION

A procedure has been designed to summarize the diversity of data obtained from analysis of all sample media tested at the Deerhorn and Three Firs areas. The approach explained below describes element responses in terms of contrast and anomaly form so that results can be presented as a concise summary table. Contrast is defined as a response ratio (RR), which is an estimate of the relative magnitude of anomalies over mineralization compared to background sites. Anomaly form refers to the type of pattern an element presents over the mineralization. It can have apical (single peak or multiple peak) responses or rabbit ear forms.

Figure 95 is taken from Bissig et al. (2013), using the Three Firs transect as an example. The procedure used to calculate RR is as follows:

1. Samples collected above mineralization are highlighted yellow in Fig. 95 and by the red box on the accompanying chart.
2. The median element concentrations of the five 'mineralized' sites ("Med Anom") are shown in blue font on line 25. These are compared to the median of all other sites along the transect ("Med Bck"), which are shown in red font on line 24. The latter value is taken as the background concentration for the line.
3. The maximum value of the 5 'mineralized sites' is shown in green font on line 26.
4. The value on line 25 is then divided by that on line 24 (i.e. maximum anomaly divided by background) to produce the RR shown in line 29.
5. Finally, the maximum RR was calculated by dividing the maximum concentration of the 'mineralized sites' in line 26 by the median background value in line 24. Maximum RR values are then summarized in Table 6.

This procedure was followed for all elements described in the preceding discussion of results for each medium and the results shown in Table 6. Maximum response ratios that exceed 2x the background are highlighted according to the following colour scheme:

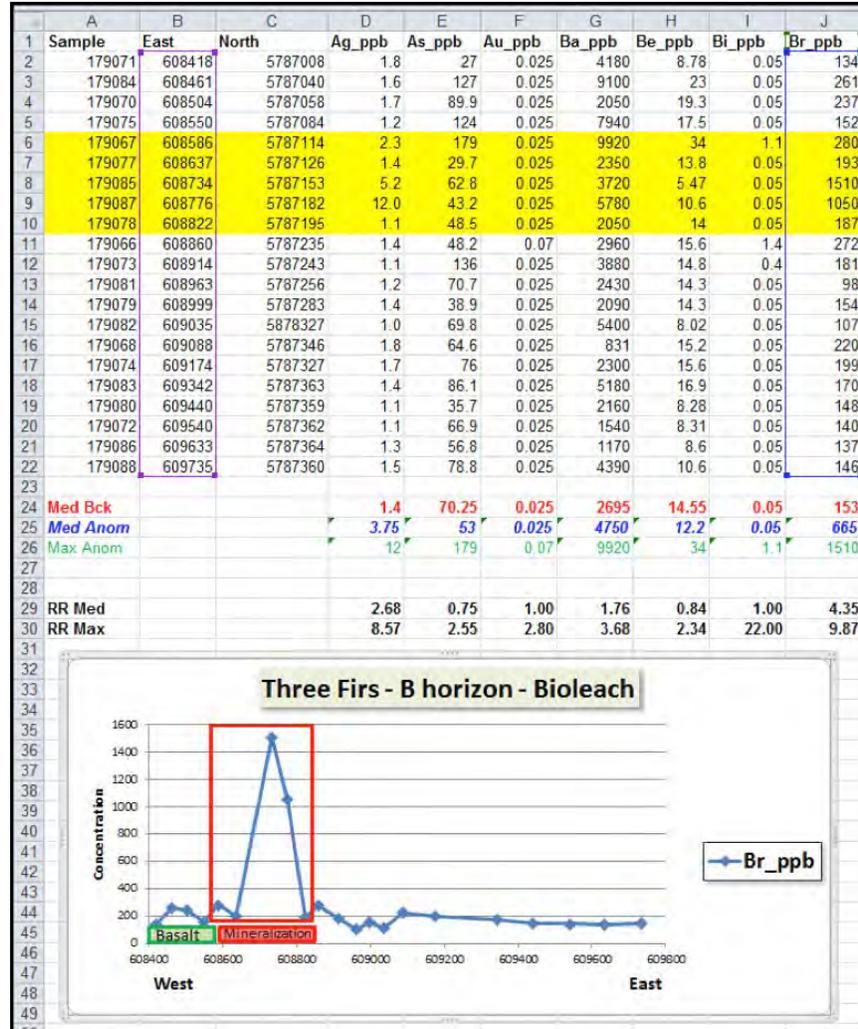


FIGURE 95. AN EXAMPLE OF THE CALCULATION OF RELATIVE CONCENTRATIONS OR RESPONSE RATIOS USING BUILT IN STATISTICAL FUNCTIONS IN MICROSOFT EXCEL SOFTWARE. SEE TEXT FOR DESCRIPTION

1. **Green - Apical multiple peak signatures** – several sites with anomalous concentrations located directly over known mineralization.
2. **Pink - Single point anomalies** – these should be considered with some caution since they are not always reproducible.
3. **Blue – “Rabbit Ear” signatures** – adjacent to the margins of the buried mineralization.
4. **Yellow** - Signatures that may be influenced by underlying lithologies.

5. **Bold boxes around coloured box** – Additional peaks beyond limits of known mineralization (i.e. potential false anomalies).
6. **Bold number with no colour** – Anomaly form undetermined
7. **Blank** - No recognizable response

The reader is referred to the digital files provided in Appendix 1 to explore these data further and to view responses for other elements not included in the table.

TABLE 6. SUMMARY OF GEOCHEMICAL RESPONSES TO MINERALIZATION FOR TESTED MEDIA

	DEERHORN									Three Firs		
	Ah Horizon	Charcoal	Spruce Bark	Spruce Twig Ash	Spruce Sap	Spruce foliage leachate	Alder foliage leachate	Transpired Fluids	Ah Horizon	Spruce Bark	Spruce Twig Ash	
	RR Max	RR Max	RR Max	RR Max	RR Max	RR Max	RR Max	RR Max	RR Max	RR Max	RR Max	
Ag	4.2	3.3										
As	3.8	33.3	6.0	2.9	2.5			3.9				
Au	3.2			5.0							3.3	
Ba							7.0					
Be												
Ca						4.3	4.3		2.7			
Ce											2.4	
Cs			4.3	4.0	4.5					5.6	5.7	
Cu	7.9	4.3	1.9		7.9	3.2		4.0	2.0			
Fe		6.0				4.2	7.2	1.9				
Hg					6.0							
K						2.8	8.2					
La	4.0											
Li											4.2	
Lu							12.0					
Mg							12.0					
Mo	1.8	5.9				3.14	8.0	0.9			3.0	
Na												
Nd	4.6	9.0									3.6	
P												
Pb			3.6								3.5	
Pt				3.3								
Rb		11.0	3.4	2.3	4.5		5.8			4.7	4.6	
Re		2.00										
S								3.8				
Sb	2.3	6.7			3.0						24.0	
Se											4.0	
Sr						4.4	9.3				2.2	
Tl					2.4			3.4				
W	20	4.5			13.0			13.4				
Y	6.5				8.2							
Zn							11.0					

**LEGEND**  
 Apical multiple peak  
 Rabbit Ear  
 Single peak  
 Lithology/Adjacent peak  
 No Recognizable Response  
 Peaks also beyond limits of mineralization  
**4.0** Anomaly form undetermined



## OBSERVATIONS

The following observations can be made from the compiled results in Table 6:

1. Robust responses to mineralization are apparent in all media tested especially at Deerhorn where a significant body of sub-economic mineralization has been defined by drilling.
2. Responses at Three Firs are less impressive. This is possibly due to the uncertain extent and grade of the mineralization.
3. Of the commodity elements, Cu and Mo responses were detected by most media. Highest contrast responses for Cu are in the Ah horizon (RR 7.9) and spruce sap (RR 7.9) but good responses are also seen in Charcoal (RR 4.3), spruce foliage leachates (RR 4.2) and transpired fluids (RR 4). The presence of Cu in soil, plant tissues and exudates suggests that this element is being cycled through the spruce trees, despite its role as an essential micronutrient, and presumably represents excess amounts over those required for the plant metabolism.
4. At Deerhorn, Mo responses were detected in all media except spruce bark and twig ash. Molybdenum is usually present in much lower concentrations in spruce bark than in alder tissues where the maximum contrast (RR 13) occurs in alder foliage leachate. Alder is known to be an accumulator of Mo since it is an essential element for fixing N in the nodules that form on its roots, and plays a role in enzymatic processes within the plant. Important responses are also observed in spruce foliage leachate (RR 8) and charcoal (RR 5.9). The type of Mo response differs between media. Alder foliage leachate shows a classic rabbit ear pattern over the edges of the mineralized zone suggesting that it is responding to an electrochemical or ionic dispersion in the underlying substrate. In other media the profiles are apical with either single or multiple peak forms. At Three Firs only spruce twig ash showed elevated values over the mineralized zone occurring as a broad moderate contrast (RR 3.3) apical response.
5. Arsenic is detectable over mineralization in all media except the spruce and alder foliage leachates. In the Ah soil and charcoal, which are intimately associated, As has a single peak apical pattern over the western Deerhorn zone. Charcoal has by far the highest contrast of the soil media (RR 33). Spruce bark displays a multi-peak apical response over the Deerhorn zone with maximum contrast of RR 6.9. Contrast in spruce twig ash and sap is slightly lower (RR 2.9 and 2.5). Saps show a rabbit ear form, while the twigs have a more apical pattern. Interestingly, As is also detectable in the transpired fluid where it has a response ratio of 3.9. At Three Firs, As does not display anomalous values over the known mineralization in any of the media.
6. Of the pathfinder elements, Sb and W show recognizable responses in the most media, although the contrast is quite subtle in some. At Deerhorn Sb has the highest contrast response in charcoal (RR 6.7) where it defines a multi-peak apical anomaly. A lower contrast rabbit ear pattern is present in spruce sap (RR 3.0) and a single peak apical response (RR 2.3) is noted in Ah horizon. Spruce and alder tissues and leachates do not show recognizable patterns for this element. Tungsten has very high contrast responses in Ah horizon (RR 20) and spruce foliage leachate (RR 13), where the profiles consist of single sample peaks over the western part of the Deerhorn mineralization. In charcoal it displays a multi-peak pattern (RR 4.5) extending over the

entire width of the zone. There is also a suggestion of a response in transpired fluids at Deerhorn but this is based on very few samples above detection limit.

7. Other elements that appear to indicate the presence of the blind Deerhorn mineralization include Au, Ag, Cs, Fe, K, Nd, Rb, Tl and Y. Gold has strongest responses in the Ah horizon (RR 3.2) and spruce twig ash (RR 5.0) where it forms multi-peak apical anomalies. Silver patterns are only present in Ah horizon and charcoal (RR 4.2 and 3.3 respectively).
8. The alkali elements K, Cs and Rb all define robust patterns over the mineralization. These elements are probably detecting the potassic alteration associated with the Cu-Au porphyry mineralization at depth. Cesium and Rb responses occur in spruce bark (RR 4.3), twig ash (RR 4.0) and sap (RR 4.5), where they define multi-peak apical anomalies. Potassium responses are only detected in the spruce and alder leachates, where it forms a low contrast single peak apical anomaly in spruce leachate (RR 2.8) and a high contrast rabbit ear response in alder leachate (RR 8.2). Potassium is an essential and mobile element in leaves which regulates the opening and closing of the pores (stomata) through which leaves exchange CO<sub>2</sub>, water vapour and O<sub>2</sub>. Leaf surfaces are, therefore, very sensitive to K such that an enhanced flux from a sub-surface source might result in its enhanced expression in the leaf epidermis. REE responses are observed principally in the Ah horizon samples at Deerhorn where La, Nd and Y display rabbit ear patterns with contrasts of RR 4.0, 4.6 and 6.5 respectively.
9. The medium with the largest number of elements with recognizable patterns over the Deerhorn mineralization is alder foliage leachate, with 14. This result should be regarded with caution because, as mentioned earlier, many of the samples were significantly degraded before analysis. Sample degradation may have contributed to the extractability of certain elements by the chloroform leach. Ah horizon and charcoal have very similar results with 10 elements each. Both media have good anomalies for commodity elements and pathfinders including As, Sb, and W. Media with the fewest number of elements exhibiting strong response ratios were the spruce bark and twig ash with 5 each elements responding; however, responses for these elements were quite strong and apical. Responses were in Au (twig ash only), the pathfinder elements As, Pb (bark only) and showed compelling patterns for Cs and Rb. The spruce twig ash returned slightly anomalous levels of Pt over the mineralization, but the data quality for Pt is doubtful and so the response cannot be considered definitive.
10. Spruce sap as an experimental medium performed quite well from the initial set of analyses, detecting recognizable patterns in 10 elements, including the commodity elements Cu and Mo and pathfinder elements As, Hg, Sb, Tl and W. Since congealed spruce sap on trunk surfaces is widespread and easy to sample, it could potentially be an important sample medium for both regional and local geochemistry if sufficiently low detection limits could be attained at commercial laboratories. Most of the elements detected have low ppb levels.
11. The Cu pathway from mineralization to its final resting place in the soil is open to speculation. Direct tapping of Cu-bearing groundwater in proximity to the mineralization is unlikely. At Deerhorn, the top of the mineralization is tens of metres below the maximum depth of root penetration. White spruce is known to be a shallow rooting species (<3 metres).

## IMPLICATIONS FOR ANOMALY FORMATION

The process by which elements migrate through exotic overburden from deeply buried mineralization is not well understood. However, the presence of commodity and pathfinder element patterns in surficial materials reflecting the position of underlying mineralization is undeniable. Results from this study illustrate that similar patterns in plant tissues, exudates and the soil Ah horizon suggest that the geochemical pathway from primary environment to surface may well be quite complex. Uptake of metals by vegetation directly from groundwater is unlikely because the species tested by this study are shallow rooting. Therefore uptake of metals into plants means that the metals must have migrated to within reach of the root systems by another process or processes. The most likely mechanism in this environment is a reduced chimney.

Hamilton (1998) proposed the existence of reduced chimneys above reduced bedrock features and suggested a mechanism for their formation based in the transfer of charge between the negatively charged bedrock source and the positively charged surface. According to Hamilton's model, overburden reduction occurs through the migration of reduced anionic species between the top of the reduced bedrock feature (i.e. sulphides) and the ground surface. Charge is transferred by the reaction with oxidized cationic species migrating in the opposite direction. This process results in the formation of a redox front that propagates to the surface to form a reduced column or chimney. Lateral redox gradients at the edges of a chimney cause polarizable particles (such as clay particles and bacterial cells) to become aligned so that their negative poles point outwards towards more oxidizing conditions and their positive poles point inwards towards the more reduced centre of the chimney. The cumulative effect of this charge alignment is to produce a potential difference across the edge of the chimney; a phenomenon termed RISP or redox induced spontaneous potential. These localized potential fields in combination with the Earth's potential field provide electrochemical gradients along which cations and anions can migrate. Cations migrate outwards and upwards from the source, while anions migrate inwards and downwards, thereby balancing the charge. In other words the redox changes produce a voltaic cell.

If such a process is operating at Deerhorn, it could explain how metals are available for uptake by white spruce and alder. This raises another possibility about the accumulation of metals observed in charcoal and Ah horizon. Instead of the humic acids and charcoal trapping the upward migrating ions directly, perhaps these media are capturing metals that have been cycled through the vegetation and exuded or otherwise expelled from the plants by exudation in transpired fluids and saps or physically expelled by tissue shedding (i.e. in leaves, needles and cuticles). Another possible mechanism for transporting metals from plants to the soil is rainwater washing soluble salts that have crystallized on the undersides of leaves and on needle surfaces from evaporating transpired fluids. A great deal more research is required to fully understand these geochemical pathways. A proposed model for what may be happening at Deerhorn is illustrated in Figure 96.

## SAMPLING AND ANALYSIS – LESSONS LEARNED

Sampling protocols for the Ah soils, charcoal and the spruce bark and twigs are well established and offered no surprises during the field sampling program. Analysis, too, followed well-defined protocols of predominantly an aqua regia digestion and presented no surprises. The dry spruce bark proved to have concentrations of many elements that were below the detection of the analytical instrumentation. New generation ICP-MS technology promises to offer lower detection levels thereby revealing the low-level texture of the geochemical data. At present, the options for obtaining lower levels of detection are to make use of the more expensive high-resolution ICP-MS, or, as employed for the spruce twigs, reduce the tissues to ash by controlled ignition prior to analysis. This effectively concentrates the inorganic components of the bark and twigs by 30-50 fold. The only drawback is that all of the Hg volatilizes

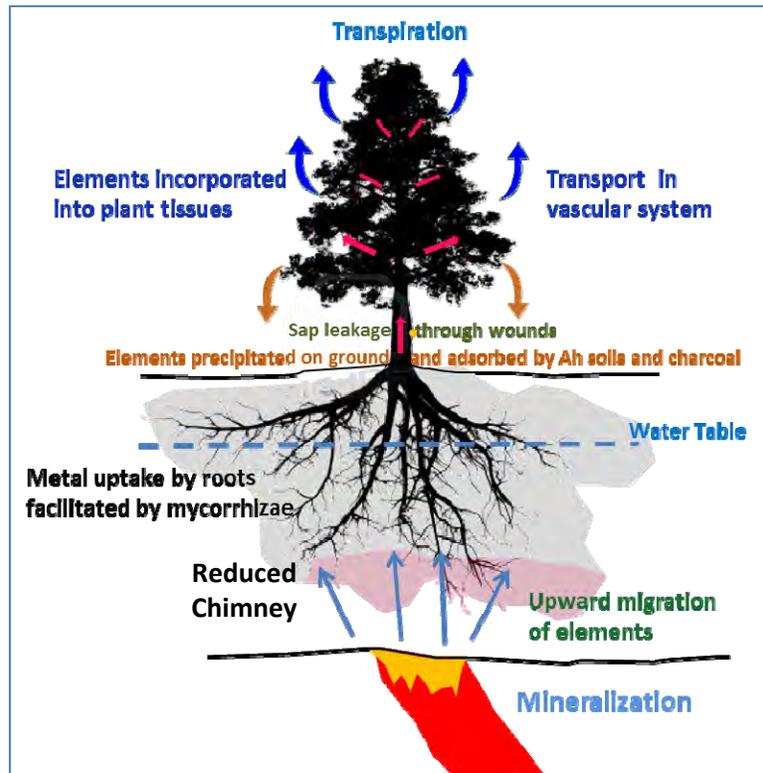


FIGURE 96. PROPOSED ELEMENT MIGRATION MODEL

during ashing, and some of the As, Cr, Sb and S are lost, but in general the percentage of those elemental losses is quite consistent and so meaningful patterns can still be obtained.

The experiment to vacuum the particulates from the leaf surfaces proved fruitless. This is probably because recent heavy rain had washed off surface salts and spalling particulates. This method could be tried again after a dry period, but will probably only be appropriate in a hot and arid environment. Analysis of any fine particulate material that might be collected would probably require HR-ICP-MS instrumentation.

The fluids that transpire through the plant stomata on a sunny day can be readily collected into plastic bags tied around a branch. The plant must be a species that has abundant pores (stomata) through which the fluids can pass and tests showed that the warm sunshine is a prerequisite since bags left out on a cloudy day failed to accumulate any fluid. In an arid environment plants develop mechanisms to help retain fluids and so this method is unlikely to be effective. Clearly, plant morphology must be a consideration for the possible application of this technique. This is unfortunate because the limited sampling conducted in the present survey provided some encouraging results that implied that 'toxic' elements (such as Hg, Tl, W and As) as well as nutritional elements in excess of the plants' requirements (such as Cu, Mo and S) appear to be flushed through the plant and readily exuded with the fluids. Concentrations are, however, at such very low levels (parts per trillion for Hg, Tl, W and others) that detailed and careful analysis by HR-ICP-MS would be a requirement for some time to come.

As an alternative to the transpired fluids there is tree sap. In the Woodjam area the tree species that presented the best opportunity for collecting congealed sap from the bark surface was white spruce. A little careful searching revealed trees with sap on the trunk surfaces at each of the desired sample stations. Sample collection was quite delicate and involved picking off a few grams of small globules of hardened sap. After a microwave digestion in nitric acid of 1 g of sap and HR-ICP-MS analysis of the solutions some meaningful patterns of element concentrations were obtained. However, a subsequent dissolution of another portion of each sap sample (using 0.3 g) failed to give a good correlation with the earlier dataset. Some additional experimentation is required to ascertain the optimum sample size and to test the homogeneity of each sap sample. Experience has taught that the sap collected should be as devoid of plant tissue material (i.e. bark) as possible.

The other test for this study was to collect leaves of alder and new growth (2 years) of white spruce needles (with the small amount of green twig still attached), and strip off the surface waxes and salts. A problem encountered was that the alder foliage soon degraded when kept in plastic bottles, so it is important that they should be kept in paper or porous cloth bags until ready for analysis. The spruce needles maintained their integrity much better, but again paper or cloth bags are advisable. Chloroform proved a suitable solvent for releasing the waxes and salts. The solute was evaporated to dryness and the residue dissolved in 2% nitric acid prior to HR-ICP-MS finish. Results appear to be quite promising, but more detailed work is required to assess the usefulness of the technique since the integrity of some samples was compromised by the partial degradation of some samples.

## IMPLICATIONS TO MINERAL EXPLORATION

Many of the plant exudate tests are not yet practical or economical for routine mineral exploration. The sampling procedures are simple and this study has identified a number of protocols that would need to be followed in conducting a survey. Of particular interest is that some of the vagaries of the geochemical cycling of elements appear to be avoided by sampling just the fluids that are left after a plant has extracted those elements that are essential to its metabolism, or can be readily tolerated in plant structures. It seems that a portion of some of the more toxic (As, Hg, Tl, W) and commodity (Cu, Mo) elements might be flushed through the plant to provide a good signature of underlying mineralization, from which metals have migrated to the surface, and the elements in solution may provide a cleaner and more definitive signature of the nature of the mineralized body.

Further experimentation to define processes and protocols and analysis using ultra-sensitive instrumentation might ultimately offer the exploration community simple, informative and low-impact exploration tools to assist in locating zones of buried mineralization.

The use of charcoal as a possible alternative to Ah or B horizon sampling in a boreal forest environment has been highlighted by the results of this study and previous work by the authors at Kwanika (Heberlein and Dunn, 2011). Charcoal fragments are very easy to collect by hand picking from the A horizon and only a few grams of material are required for an aqua regia digestion and low level ICP-MS analysis. Charcoal can be a useful medium in areas like recent clear cuts or burns where the Ah horizon has been heavily disturbed or removed all together.

## CONCLUSIONS

Main conclusions from this study are:

- 1 Each sample medium appears to have a signature that can be related to the buried porphyry mineralization. However, although there are several 'responsive' elements that are common to most sample media, they are not always the same. This is probably because each medium is collecting, storing and discarding a different component of the geochemical cycle. Moving upward these are:
  - a. Ah Horizon soils: Ag, As, Au, Cu, Mo, REE, Sb, W. This signature appears to be a composite of elements that have been transported from depth and adsorbed on soil particles, and those that have migrated through the geochemical cycle and have been added to the organic rich soil via the decaying vegetation components.
  - b. Charcoal: Ag, As, diffuse Au, Cu, Mo, REE, Sb, W; also Fe, Rb and a very weak Re component. This signature is similar to that of the Ah soils.
  - c. Spruce bark (many values < detection): As, Cs, Cu, Hg, Pb and Rb.
  - d. Spruce twigs (ash): As, Au, Cs, Rb, and Pt.
  - e. Spruce sap: As, Cs, Cu, Hg, Mo, REE, Rb, (possibly Sb), Tl, W.
  - f. Spruce foliage - Surface waxes and salts: Cu, Mo, Zn, (also Ca, Fe, K and Sr)
  - g. Alder foliage – Surface waxes and salts (N.B. poorly preserved samples, so signatures doubtful) Mo, Pb, Rb, Zn (Ba, Ca, K, Mg, P, Rb, S, Sr)
  - h. Transpired fluids (only 10 samples) – As, Cu, Mo, S, Tl, W.
- 2 The various fluid components that have been exuded or leached from the plants can provide multi-element signatures of concealed mineralization at depth, but highly sensitive instrumentation is required to determine the very low element levels that are present.

More detailed work is required to determine the processes that cause elements to move through the geochemical cycle and be deposited at certain stages or continue through the cycle. It seems that some of the more toxic elements (As, Hg, Pb, Tl, and W) are partially precipitated in the trees, but a significant proportion tends to pass through the tree still in solution to generate a high contrast

signature. This observation needs further testing, but if validated it could be a process of value to the exploration community.

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APPENDIX 1

DATA

APPENDIX 2

SUMMARY STATISTICS

APPENDIX 3

QUALITY CONTROL