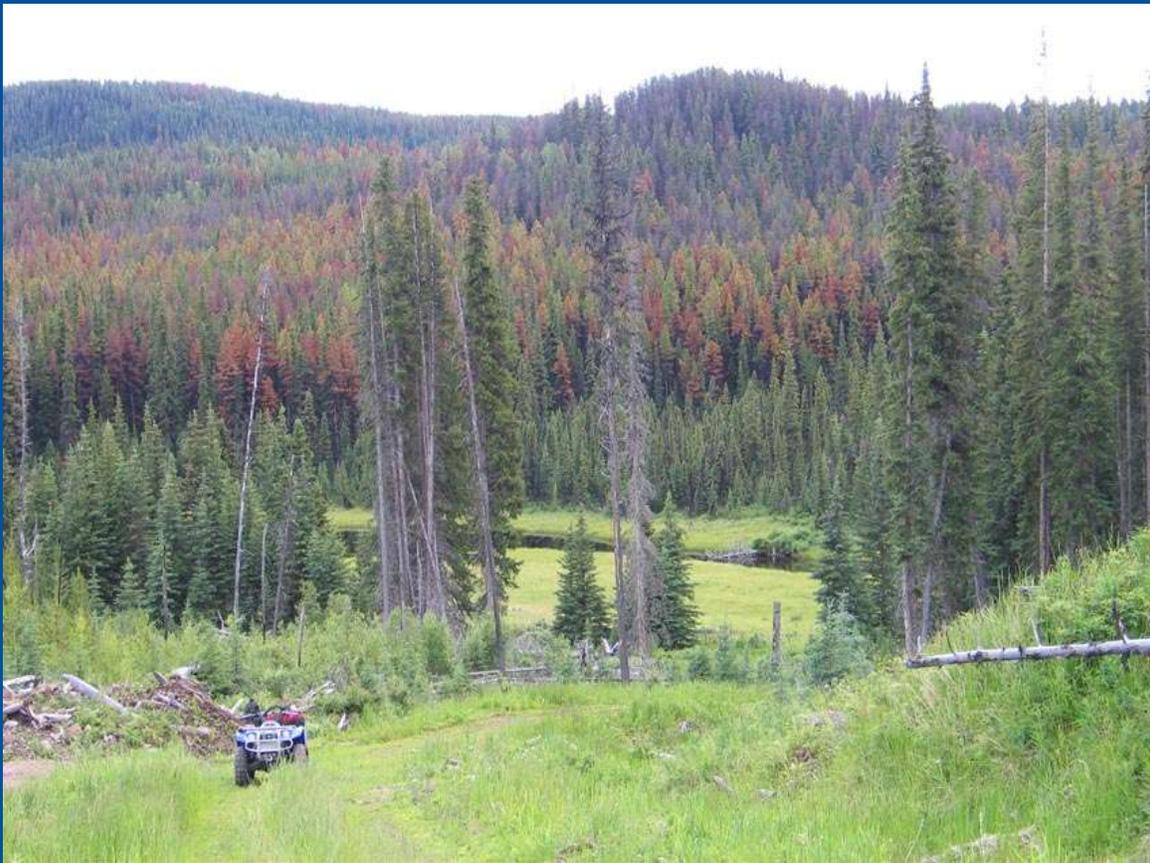# Geoscience BC

Geoscience BC Report 2007-10

Final Report for Geoscience BC Project 2005-008

**Halogens in Surface Exploration Geochemistry:
Evaluation and Development of Methods
for Detecting Buried Mineral Deposits**

By Colin E. Dunn, Stephen J. Cook and Gwendy E.M. Hall

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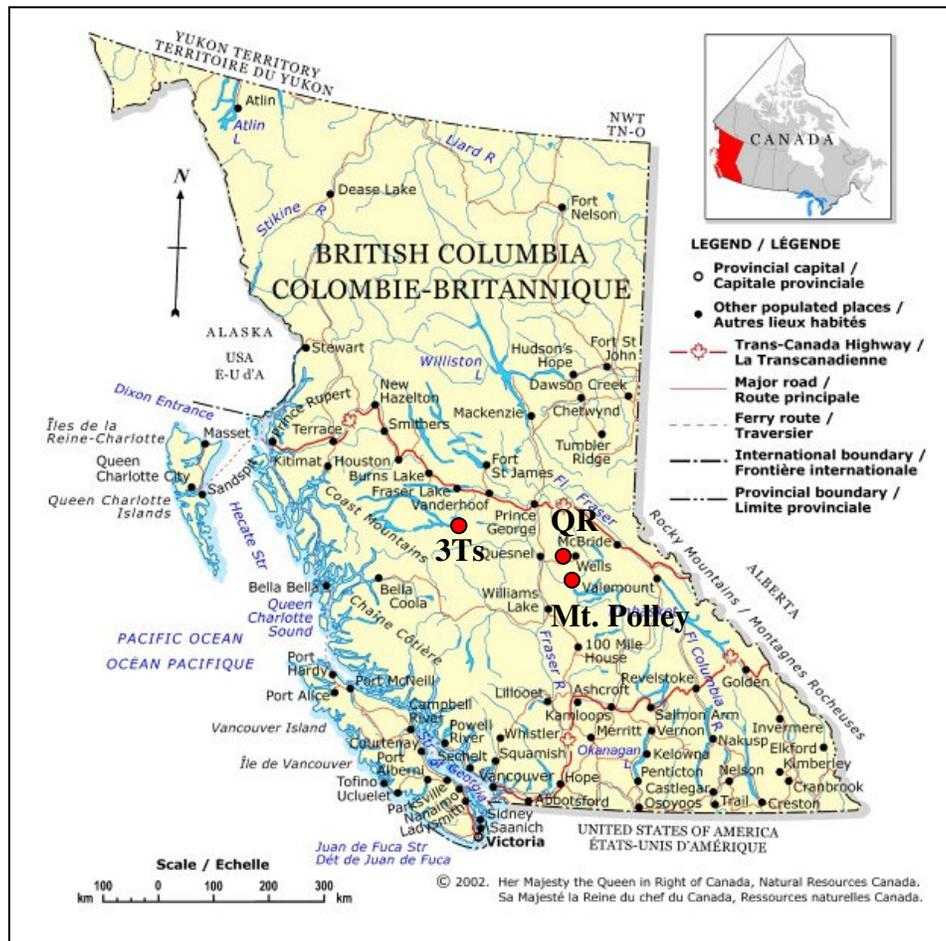
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Executive Summary

Much of the bedrock in central British Columbia has a cover of Quaternary deposits and/or volcanic rocks, yet few mineral discoveries. Given the fact that the area is underlain by the generally 'fertile' Quesnellia Terrane, there is good reason to be optimistic that significant buried mineralization may be present. The challenge is, therefore, to develop a method for detecting mineralization hidden beneath this cover. To address this challenge, the Geoscience BC program, in collaboration with three industry partners, has funded a major portion of a geochemical project aimed at enhancing the discovery of concealed mineral deposits. These studies are focused on soil and common vegetation from three target areas: Mount Polley (Imperial Metals Corp.; Cu-Au-Ag porphyry); QR (Cross Lake Minerals Ltd.; Au skarn and other Au targets); and 3Ts (Silver Quest Resources Ltd.; epithermal Au-Ag).

The halogen elements (F, Cl, Br, I) are commonly associated with the emplacement of mineral deposits. They are contained within the structure of many minerals and in saline fluid inclusions that are typical of a wide range of mineral deposits. Their volatility renders them good candidates to examine as 'pathfinder elements' in surface geochemical media, where they may be captured on soil particles and taken up by vegetation. Russian workers have demonstrated the exceptional migrational abilities of I and Br in different geological settings, and found these elements to be highly effective in exploring for orebodies at depths of up to 1000 m.

A prime objective of this program is to investigate the distribution of halogens that might be derived from concealed mineralization; hence, it is the labile (readily leached) portion of any halogens that may have emanated from a mineral deposit that are of principal interest, and not the halogens structurally bound in crystal lattices (e.g., in apatite, mica and rock-forming minerals). With this objective in mind, in order to ascertain the optimal analytical method(s) for the halogens, 35 test samples of soil and vegetation were selected for analysis at several laboratories using a variety of methods. Based upon information derived from these tests, a method was selected by which all of the newly collected samples from the three properties would be analyzed. Consideration was given to the precision and accuracy of the method(s), the appropriate level of sensitivity for the concentrations of labile elements present in the soil and vegetation, and the cost of analysis. Given these objectives, the optimal procedures for determining the halogen levels at this time are

- a water digestion of the sieved soil and milled vegetation samples, with instrumental finish by high resolution inductively coupled plasma mass spectrometry (ICP-MS) for Br, Cl and I; and
- the same solution by ion selective electrode (ISE) for F.

By these methods, detection levels are 0.02 ppm for Br, 1 ppm for Cl, 0.001 ppm for I and 0.4 ppm for F, such that most samples yielded values above detection.

In order to compare the halogen signatures with those of commodity metals, all samples were also analyzed for 53 elements by ICP-MS following an aqua regia digestion.

The suite of samples involved in this study comprised 35 test samples (20 vegetation and 15 soil), and, excluding field duplicates, there were 196 B-horizon soil samples and 581

vegetation samples of various common species collected from the three survey areas. In total, approximately 60,000 analytical determinations were obtained. The digital data are presented in the appendices arranged in tables by survey area and sample media. Each table shows UTM coordinates, halogen concentrations from a warm water leach, then the multielement analyses after an aqua regia digestion, sorted alphabetically by element symbol. The digital data are arranged in sequence along each individual sample traverse with a chart embedded for scrolling across the elements. The patterns observed in these charts are summarized in the text. Key observations are

- **Mount Polley:** Two forested areas were sampled. Quaternary deposits, overlying volcanic rocks and monzonite, range from zero to several metres in thickness:

    - *Boundary zone extension:* Data from dry cedar foliage (*Thuja plicata*) show some enrichment in Au, Cu and Mo; notable concentrations in the soil include Ag, As, Au, Cu, Hg and V. Iodine provides the best signature among the halogens with respect to the zone of mineralization. Multielement and halogen data show that highest concentrations of several elements (including I) in cedar occur directly over mineralization, whereas in soil multielement (including F and I) enrichment is displaced 50 to 100 m downslope to the south.
    - *Pond zone:* Elements that exhibit enrichment in subalpine fir (*Abies lasiocarpa*) needles include Au, Cu, (Mo), Zn and most notably Re with local concentrations more than 100 times background. Notable concentrations in the soil include As, Au and Cu; Re is also slightly elevated in the soil. The strongest halogen signatures are F in soil at the eastern end of both traverses, and I in fir near the assumed location of mineralization. Along with other data, local subtle enrichment of Au, Cd, Cu, Cs, Hg, Ni, Rb, Se and Tl in fir needles provides an indication that mineralization may trend northwestward, and three zones of element enrichments are outlined.

- **QR:** Three areas were sampled, each with variable Quaternary cover (up to several metres thick) over volcanic rocks:

    - *Main zone:* Dry Douglas-fir needles were collected in 1988. Analyses confirm a previously identified Au anomaly in twig ash. The halogens in these needles do not clearly outline known mineralization, yielding only a modest enrichment of I close to the Main and North zones of mineralization.
    - *Eastern IP zone:* To the northeast of the Main zone, there is an induced polarization (IP) anomaly in an area with little outcrop. Analysis of soil, spruce (*Picea engelmannii*) needles and pine (*Pinus contorta*) bark from over this area show a peak of I and Cl at the site of a magnetic anomaly, whereas F values are higher over breccia than the basalt. Thickness of volcanic cover is unknown.
    - *Cariboo zone:* This third Au target has rare outcrop. Soil chemistry indicates three zones of multielement enrichment involving Ag, Au, Bi, Cu and Hg. Only the northern zone includes a Mo signature. Iodine and Br in the soil clearly delineate the three zones of multielement enrichments, whereas Cl delineates only the north and south zones and F only responds at the central

zone with a very subtle signature. Halogens in the vegetation are less definitive.

- **3Ts:** Two transects were conducted in forested areas with minor outcrop and a Quaternary cover up to several metres in thickness, although less than 1 m for the most part. Locally, the glacial deposits are underlain by Middle Jurassic volcanic rocks of variable thickness:

  - *Tommy vein*: Over mineralization with a veneer of Quaternary cover, soil and vegetation yield a positive response of Ag and Au and of Br and I, but not of either Cl or F (Cook and Dunn, 2007). Spruce (*Picea glauca*) needles and pine (*Pinus contorta*) bark yield subtle multielement signatures over many of the vein systems with I and F in the bark providing the best biogeochemical signatures among the halogens. There is a strong Mo and F signature over the Ringer showing, at the eastern end of the Tommy-vein traverse.
  - *Ted vein:* The principal known vein system (Ted vein) has a veneer of Quaternary cover, and yields a good response of Br, Cl and I from pine bark, whereas the I from soil indicates a 'rabbit ears' anomaly on either side of the Ted vein. At the eastern end of the traverse, near the Adrian West boulders, there is a strong F and Mo signature in both soil and vegetation. A similar anomaly at the east end of the Tommy-vein traverse (Ringer showing) suggests a north-south stratigraphic continuity.

Principal outcomes of this project are:

- For the first time, the levels of labile halogens that can be expected in soil and vegetation from central BC have been defined. This information can be used as a basis for evaluating halogen concentrations elsewhere in Canada and in similar environments around the world.
- A strong acid (aqua regia) leach of the sample media to establish the multielement signatures has provided insight as to the nature of concealed bedrock enrichments of metals.
- Optimum cost-effective digestion and analytical procedures for determining labile components of halogens in soil and vegetation have been established after evaluating many methods and identifying considerable analytical complications.
- It has been shown that, from a water leach of the various media, the halogens exhibit a clear response to most zones of mineralization that have been tested. Depth to mineralization varies from a thin veneer of Quaternary and/or volcanic cover, to possibly tens of metres.
- Numerous analytical problems have been identified and further analytical research is required to better define the methods required for obtaining improved analytical precision and accuracy at the low levels of halogen elements typically present in a water leach of soil and vegetation, and at the costs acceptable to mineral exploration.
- Halogen signatures vary according to the nature of the mineralization: whereas I may provide the best signature in one area, F may be best in another. This indicates that each style of mineralization is likely to generate a different suite of positive halogen responses that have yet to be clearly defined; hence analysis for all four halogens is advisable.

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- Tests conducted along one traverse show that after reducing pine bark samples to ash by controlled ignition, a residual halogen component remains that relates to known zones of mineralization. This suggests that ashing may be a viable procedure to adopt, because analysis of ash eliminates complications that arise from the presence of organic compounds in dry tissues.
- Pine bark is the vegetation medium that best concentrates I, and gives good contrast for the other halogens. Since outer bark is dead tissue, it makes no difference to the analyses if pine has been killed by mountain pine beetle infestation, and it is therefore a viable exploration medium.

This project has established for the public record a fundamental new database of typical concentrations of 53 elements in B horizon soil and several species of vegetation from an aqua regia digestion, and determined the levels of halogens (from a water leach) that can be expected both in background areas and over zones of mineralization. As such, the study is unique and provides a yardstick by which future surveys can be measured. Now that a clear response of labile halogens in soil and vegetation to known mineralization has been established, targets concealed by thick overburden (both Quaternary and volcanic) need to be tested. Such targets are probably best identified by close collaboration with geophysicists.

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Introduction

A striking feature of the current MINFILE (2007) mineral occurrence map of BC is that a significant part of central BC has very few mineral discoveries (Figure 1). Much of this area has a cover of Quaternary deposits and/or volcanic rocks and, given the fact that it is underlain by the generally 'fertile' Quesnellia Terrane, there is good reason to be optimistic that significant buried mineralization may be present. The challenge is, therefore, to develop a method for detecting mineralization hidden beneath this cover. This study aims at augmenting the suite of geochemical techniques currently available to assist in the search for buried mineralization in BC by testing and developing new methodology. A preliminary account of this study was presented by Dunn et al. (2006).
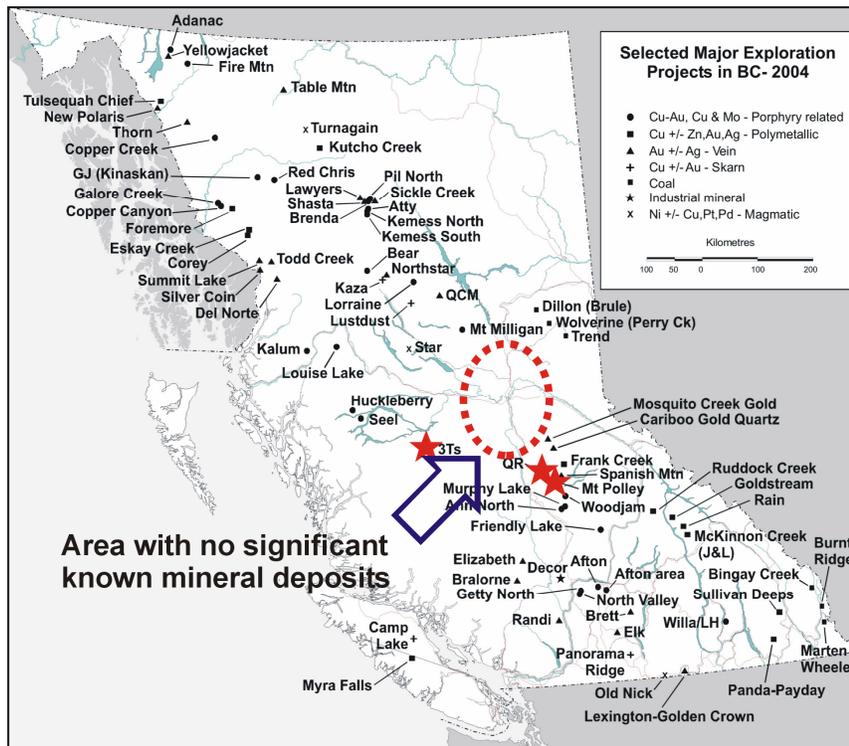
Figure 1: *Area outlined for focusing on halogen geochemistry method development. Red stars indicate areas of focused studies: Mount Polley, QR and 3Ts.*

The primary focus of the study is the analysis for halogens because they are commonly associated with the emplacement of mineral deposits, as witnessed by their presence in many minerals and in saline fluid inclusions that are typical of many mineral deposits. Halogens comprise five nonmetallic elements whose compounds form salts. The term 'halogen' means 'salt-former' and, at room temperature, they exist in all three states of matter: solid (iodine, astatine), liquid (bromine), gas (fluorine, chlorine). However, they all form diatomic molecules that are gases at normal temperatures and pressures, and therefore are mobile and play significant roles in the atmosphere, hydrosphere and biosphere. They are the most organophilic elemental family, such that they react with

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organic compounds on contact and are therefore readily absorbed by plants. Their volatility renders them good candidates to examine as 'pathfinder elements' in surface geochemical media, where they may be captured on soil particles and taken up by vegetation. Of the five halogens, astatine is radioactive and not considered in this study.

Fluorine-rich minerals are characteristic of late-stage hydrothermal systems. Fluid inclusions associated with mineral deposits are commonly rich in NaCl (e.g., ~50% NaCl in inclusions within Cu porphyries), attesting to the highly saline environment of many ore-forming processes. In recent years, fluid inclusion studies have included determinations of Br and I. Furthermore, some styles of mineralization, such as the Broken Hill Sedex deposits in Australia, have high levels of F and Cl in fluorite, apatite and amphiboles. During the degradation of these mineral deposits, whether due to the reaction with subsurface waters, subtle changes in pressure or fracturing by slight seismic activity, some of the halogen component may be released.

The high contents of Br, Cl and I in seaweed have long been known. Relatively little information is available on the distribution of these elements within and among land plants, and their relationships to mineralization have received little attention except in Russia, from where detailed information is difficult to obtain. Some published and personal observations are that

- pine needles are good indicators of F;
- spruce needles can contain >1000 ppm Cl (C.E. Dunn, unpublished data);
- Br levels are commonly elevated in vegetation growing over Au deposits (Dunn, 1985);
- unpublished scanning electron microscope investigations by the senior author have revealed chlorides of K and Bi formed in the trunk wood of trees growing on the epithermal Au system at Mt. Washington (Vancouver Island), demonstrating the metal complexing of halogens within plant tissues; and
- iodine enrichment occurs in plants growing over porphyry deposits (Al Ajely et al., 1985).

Outside of the former Soviet Union, halogens have been little used in mineral exploration; this is partly because of inadequate easily accessible analytical methodology for determinations at low concentrations. An account of the significance of I and Br for indicating deep ore deposits has recently been made available as an English translation of a classic Russian work (Trofimov and Rychkov, 2004). They demonstrate the exceptional migrational abilities of I and Br in different geological settings, and "show these elements to be highly effective in exploring for deeply buried endogenous ore bodies and using this technique has resulted in finding new highly prospective ore bodies….up to 1,000 m depth". They stated that "within all deposits studied, iodine and bromine occupy the position most distant from ore bodies. This extreme zonal position makes it possible to use these elements as very effective indicators of hidden ore deposits". They concluded that "secondary geochemical haloes ….are still insufficiently studied, and biogeochemical halos of these elements have yet to be found [because there are no reported studies]. These problems must be the primary focus of further studies. We must improve the analytical determinations of iodine and bromine and then transfer this understanding to the analytical instrumentation".

An example provided by Trofimov and Rychkov (2004) is from the Karatas deposit of eastern Kazakhstan. They showed concentrations of I in soil developed on sandy loam that blankets a porphyry system containing Cu ore. Figure 2 indicates I anomalies more than an order of magnitude over background levels of 10 to 30 ppb I, occurring directly over the locations of the two thick sequences of ore, with only weak anomalies over the thinner, central part of the orebody.
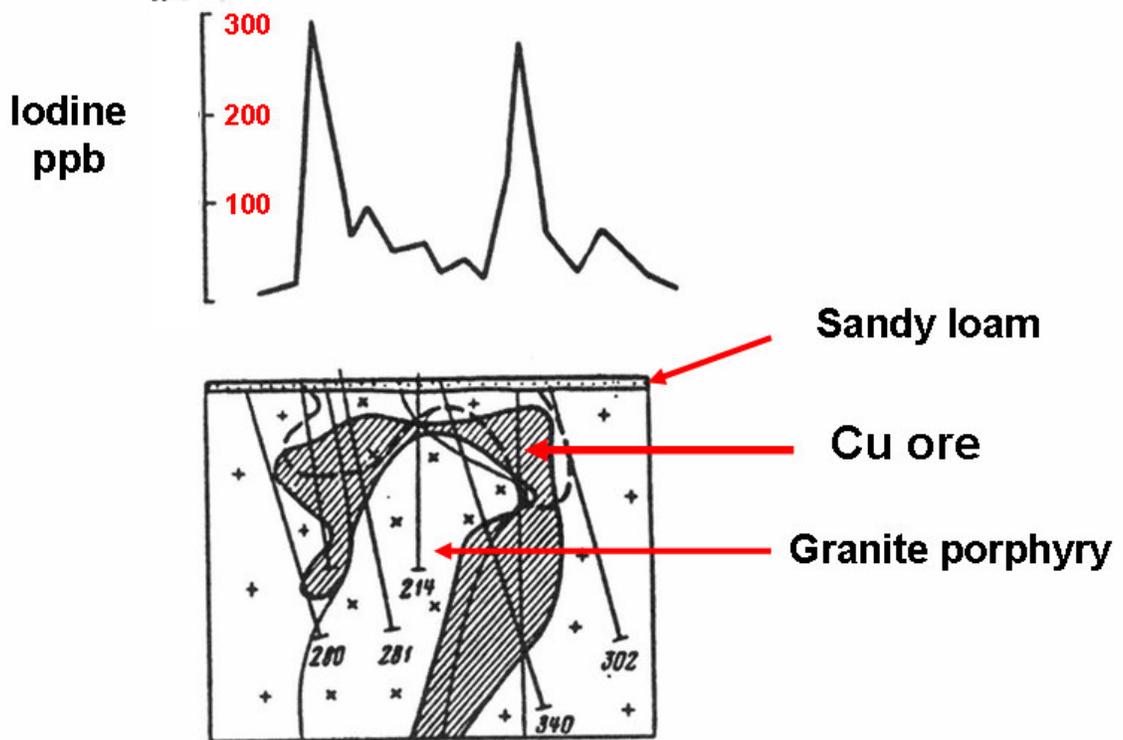
Figure 2: *Iodine in soil over the Karatas Cu porphyry deposit, Kazakhstan (annotated after Trofimov and Rychkov, 2004).*

Analysis of Test Samples

In order to ascertain the optimal analytical method for the halogens, a set of 35 test samples was selected for analysis by several laboratories using a variety of methods. In the final selection of the method by which all of the newly collected samples would be analyzed, consideration was to be given to the appropriate level of sensitivity, accuracy and precision, and the cost of analysis.

The vegetation test samples were Douglas-fir (*Pseudotsuga menziesii*) needles and lodgepole pine (*Pinus contorta*) outer bark collected in 1988 and 1989, respectively, from the vicinity of the QR deposit and archived at the Geological Survey of Canada (GSC) in Ottawa. Ten samples of needles and five samples of bark were chosen from sites that spanned the Au biogeochemical anomaly (Figure 3). This anomaly was defined by the concentrations of Au in ash of the top stems of Douglas-fir collected by helicopter.
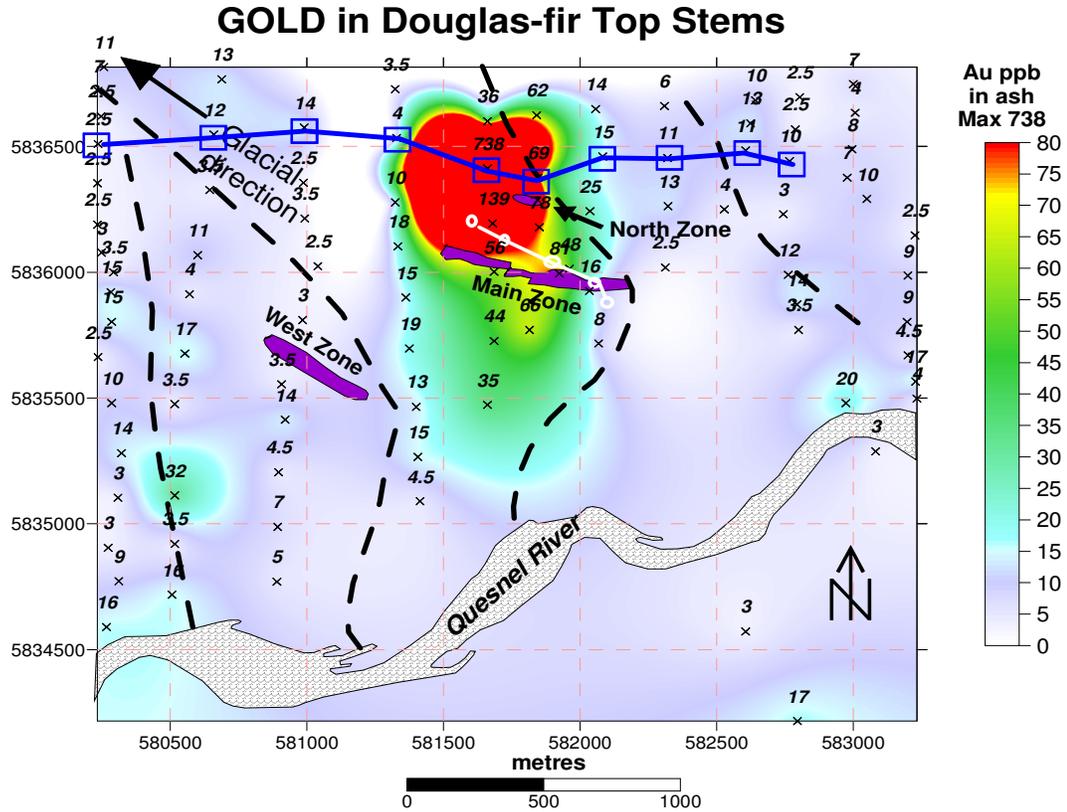
Figure 3: *Gold in the ash of Douglas-fir top stems, collected and analyzed in 1988, prior to mine development. Test samples of Douglas-fir foliage recovered from the archived collection are shown as blue squares; test samples of lodgepole pine bark are shown as white circles. Figure modified after Dunn and Scagel (1989).*

In addition to the archived samples, five vegetation controls of known composition were included. They were two samples of V6, a composite of pine twigs and needles developed in 1990 by the senior author, using CANMET facilities in Ottawa; two samples of CLV-2, CANMET spruce needles (certified values); and one sample of V13, mountain hemlock needles developed recently by the senior author and Acme Analytical Laboratories Ltd. The suite of archived samples represented suitable test material in that prior analysis had shown there to be elevated levels of Au in these samples from sites over or adjacent to known Au deposits (Figure 3). Furthermore, some halogens have been shown to accumulate in foliage, and some limited halogen data (Cl and Br) were available for V6. Nothing was known about the halogen content of bark; however, since bark is known to accumulate many metals that are surplus to plant metabolism, the tests should determine if this would be a suitable sample medium for the halogens.

No appropriate soil was available from over known mineralization, so tests were performed on five splits each of GSC controls that had certified values for many elements, with recommended values for F and Cl. They were STSD-1 and STSD-4 (both stream sediment) and TILL-4.

Table 1 lists the suite of methods for which analyses were requested at various Canadian laboratories. A more comprehensive set of spreadsheets with details of the analyses is appended as Table 1-1 in Appendix 1. At the start of this project, it was not known if

optimal results would be from a total halogen analysis (e.g., instrumental neutron activation analysis [INAA] or X-ray fluorescence [XRF]) or from an analysis involving a partial extraction (e.g., leaching by water or pH-controlled ammonium acetate). With regard to the vegetation, it was considered that a partial extraction might yield similar results to a 'total' analysis, because of the high solubilities of the halogens. However, for soil, there may be greater differences, because some halogens may be structurally bound in crystal lattices and therefore not readily extracted by a weak leach (e.g., Cl in biotite and amphiboles; F and/or Cl in apatite). However, since the objective of this program was to investigate the distribution of halogens that might be derived from concealed mineralization, it was the labile (readily leached) portion of any halogens that would be of principal interest, and not the structurally bound halogens.

INAA: epithermal instrumental neutron activation analysis for Cl, Br and I
ICP-MS   water leach: approximately 50 elements
ICP-MS   2% nitric acid leach: approximately 50 elements
ICP-MS   ammonium acetate pH 7 leach: approximately 50 elements
ICP-MS   nitric acid and aqua regia: approximately 50 elements
ICP-ES   water leach: approximately 10 elements
ICP-ES   2% nitric acid leach: approximately 10 elements
ICP-ES   ammonium acetate pH 7 leach: approximately 10 elements
Ion chromatography (IC - Dionex)   water leach: all available anions
Ion chromatography (IC - Dionex)   ammonium acetate pH 7 leach: all available anions
F_water leach   ion selective electrode (ISE)
Cl_water leach   ion selective electrode (ISE)
F_fusion (Teflon bomb)   ion selective electrode (ISE)
Enzyme Leach[SM]: full suite of elements including I, Br and semiquantitative Cl
XRF (high resolution): halogens

Table 1: Analytical methods to which the test samples were subjected at various laboratories: 20 samples of milled vegetation and 15 soil samples.

Results of Determinations on Test Samples

Analyses for Total Halogen Contents

Although a principal aim of the project was to determine the readily leachable component of halogens present in soil and vegetation, some tests were conducted to establish, as a starting point, their total contents in test materials and controls. Table 2 shows some comparisons of results obtained by XRF (high resolution 'Axios') and epithermal INAA for short-lived isotopes.

Sample#	Material	F XRF ppm	Target* ppm	Br XRF ppm	Br INAA ppm	Target* ppm	Cl XRF ppm	Cl INAA ppm	Target* ppm	I XRF ppm	I INAA ppm
DFN_04	Fir needles	75		0.7	0.7		199	131		1.1	0.1
DFN_08	Fir needles				1.2			72			0.1
DFN_14	Fir needles	78		1.1	1.3		217	105		0.9	-0.1
DFN_22	Fir needles	86		0.9	0.6		137	57		1.8	-0.1
DFN_33	Fir needles	63		1.1	0.3		228	99		2.0	-0.1
DFN_45	Fir needles	72		1.1	1.5		189	76		0.9	-0.1
DFN_60	Fir needles	72		0.3	0.2		214	147		0.8	-0.1
DFN_65	Fir needles	68		3.0	3.6		254	172		1.3	-0.1
DFN_70	Fir needles	65		1.9	2.4		279	225		2.2	-0.1
DFN_74	Fir needles	83		1.8	0.3		198	76		1.6	0.2
V6	Veg.Control	96		2.8	4.0	2.2**	355	313	286***	1.9	0.8
V6	Veg.Control	81		2.8	3.0	2.2**	357	227	286***	1.0	0.5
CLV-2	Veg.Control	-25		4.4	-0.1	4.2**	493	415		1.1	-0.1
CLV-2	Veg.Control	80		1.0	6.0	4.2**	133	407		1.2	0.4
V13	Veg.Control	-42		0.9	-0.1		281	98		1.6	-0.1
STSD-1	Stream sed.	1001	950*	34.6	23.4	40*	319	700		17.2	15.1
STSD-4	Stream sed.	413	380*	11.3	14.9	13*	178	138		6.0	4.2

* values previously published, method not specified (Govindaraju, 1994)
** values obtained previously by INAA (C.E. Dunn, unpublished data)
*** values obtained previously by ion chromatography (C.E. Dunn, unpublished data)

Table 2: *Comparisons of data received for the total contents of halogens in test samples, determined by X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA).*

The data in Table 2 show that the few published data for stream sediment samples STSD-1 and STSD-4 are in good agreement with the values obtained for F and Br by both XRF and INAA. There are no known published data for Cl or I in these materials. Data for the vegetation samples show greater variability but controls are in moderate agreement with data previously obtained. We were advised that the results of the XRF analyses of the vegetation for F were only semiquantitative and that further refinement of the methodology was required.

Multielement Determinations by Inductively Coupled Plasma Mass Spectrometry after Different Leaches

Bromine, Cl and I can be determined simultaneously with other elements by inductively coupled plasma mass spectrometry (ICP-MS) and/or inductively coupled plasma emission spectroscopy (ICP-ES) after leaching with various leachates. Fluorine cannot be determined by these methods. In accordance with the protocols outlined in Table 2, test vegetation and soil samples were leached in water, dilute nitric acid and pH-controlled (pH 7) ammonium acetate.

Table 1-2 in Appendix 1 shows a comparison of results obtained from the three leachates. For some elements (e.g., Rb shown in Figure 4), the amount extracted by each leachate is virtually identical.

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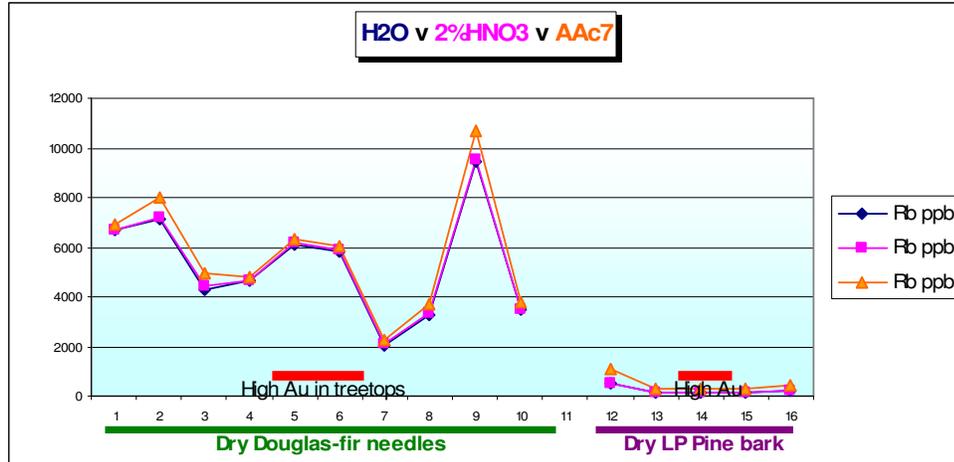
Figure 4: Rubidium extracted from fir needle and lodgepole (LP) pine bark test samples by three leachates: water, dilute nitric acid and ammonium acetate (colour-coded in the title). Note the virtually identical amounts by each dilute leach. Bottom axis is west to east sequence (see Figure 3).

In general, there is little difference in the amount of each element extracted by a water leach and a dilute (2%) nitric acid leach. The pH 7–controlled ammonium acetate leach (AAc7) extracts higher quantities of some elements but less of others. For each leach, the detection limit varies. Figure 5 shows similar amounts of Cu extracted by the three leaches, but with the AAc7 leach extracting a little more from the fir needles than from the pine bark.
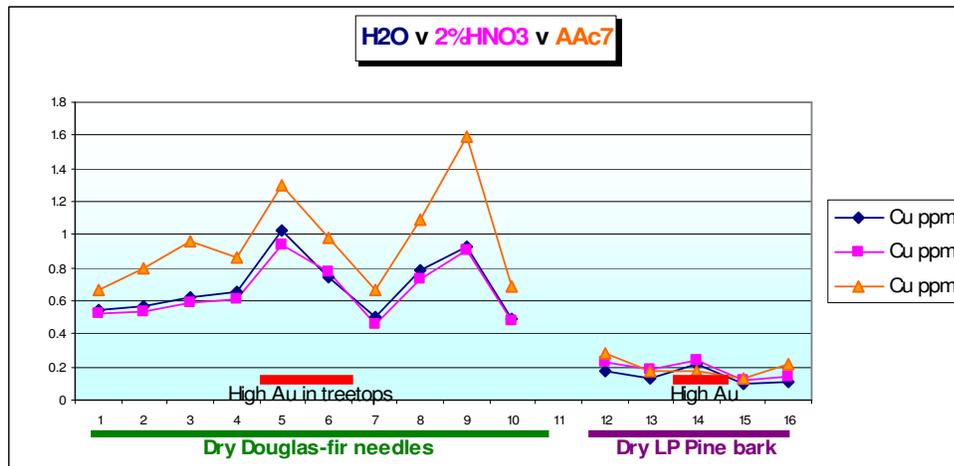
Figure 5: Copper extracted from fir needle and lodgepole (LP) pine bark test samples by three leachates: water, dilute nitric acid and ammonium acetate (colour-coded in the title). Bottom axis is west to east sequence (see Figure 3).

This demonstrates that in the case of weak leaches there is a need to select an appropriate leach for each individual plant species and plant tissue. However, also of importance, is the fact that the relative amounts of each element extracted remain much the same: that is, the *patterns* of relative concentrations are very similar. This is evident from the plot of Zn (Figure 6), with AAc7 yielding more Zn than the other two leachates but with appreciably more extracted from the bark than from the needles. Note, however, that the

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element profiles across the sampling profile remain almost identical, so any of the leaches would provide the same patterns of element distributions but different absolute concentrations.
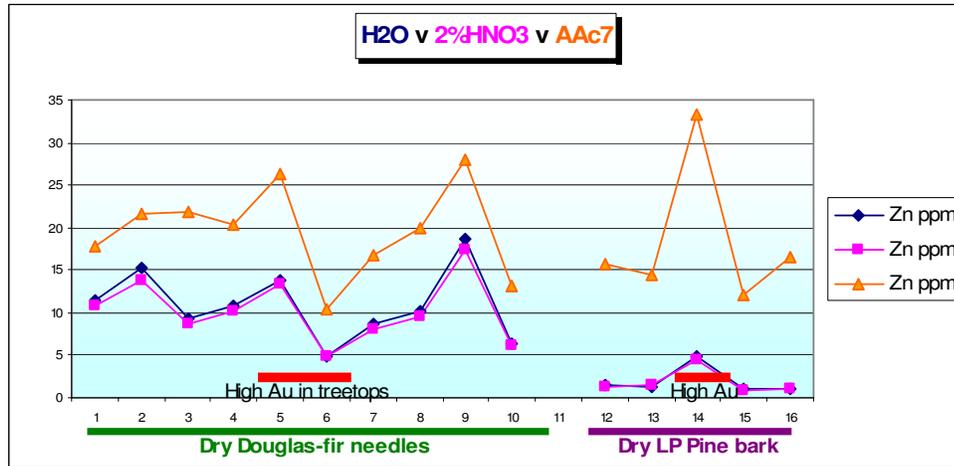
Figure 6: Zinc extracted from fir needle and lodgepole (LP) pine bark test samples by three leachates: water, dilute nitric acid and ammonium acetate (colour-coded in the title). Bottom axis is west to east sequence (see Figure 3).

For other elements, such as K (Figure 7), the AAc7 leach extracts proportionally far less of the element from the needles than from the bark.
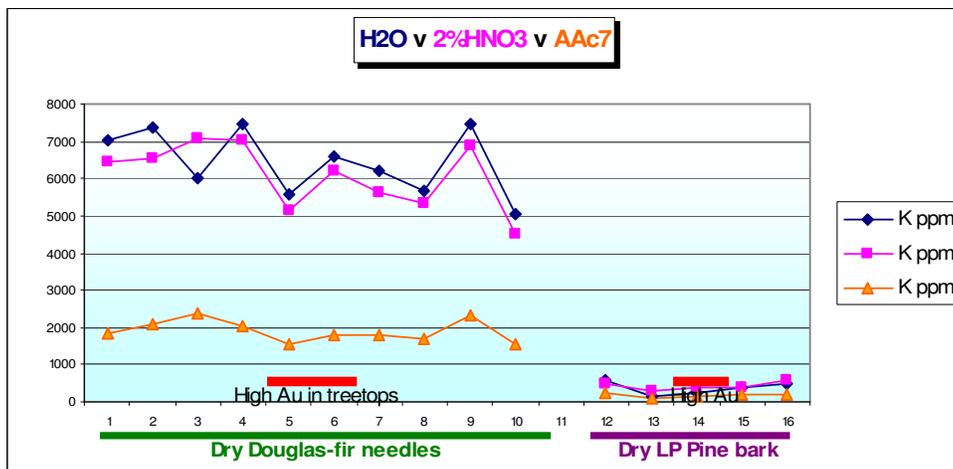
Figure 7: Potassium extracted from fir needle and lodgepole (LP) pine bark test samples by three leachates: water, dilute nitric acid and ammonium acetate (colour-coded in the title). Bottom axis is west to east sequence (see Figure 3).

Each element has its own characteristics and there is a wealth of information that can be extracted from Table 1-2 (Appendix 1) by dragging the embedded chart across each set of digestions for each element and observing the differences. The procedure for scrolling across the elements is described in detail in Appendix 3. Bromine, Cl and I could not be determined by the AAc7 leach so there are only comparative data for the water and dilute nitric acid leaches (Figure 8).
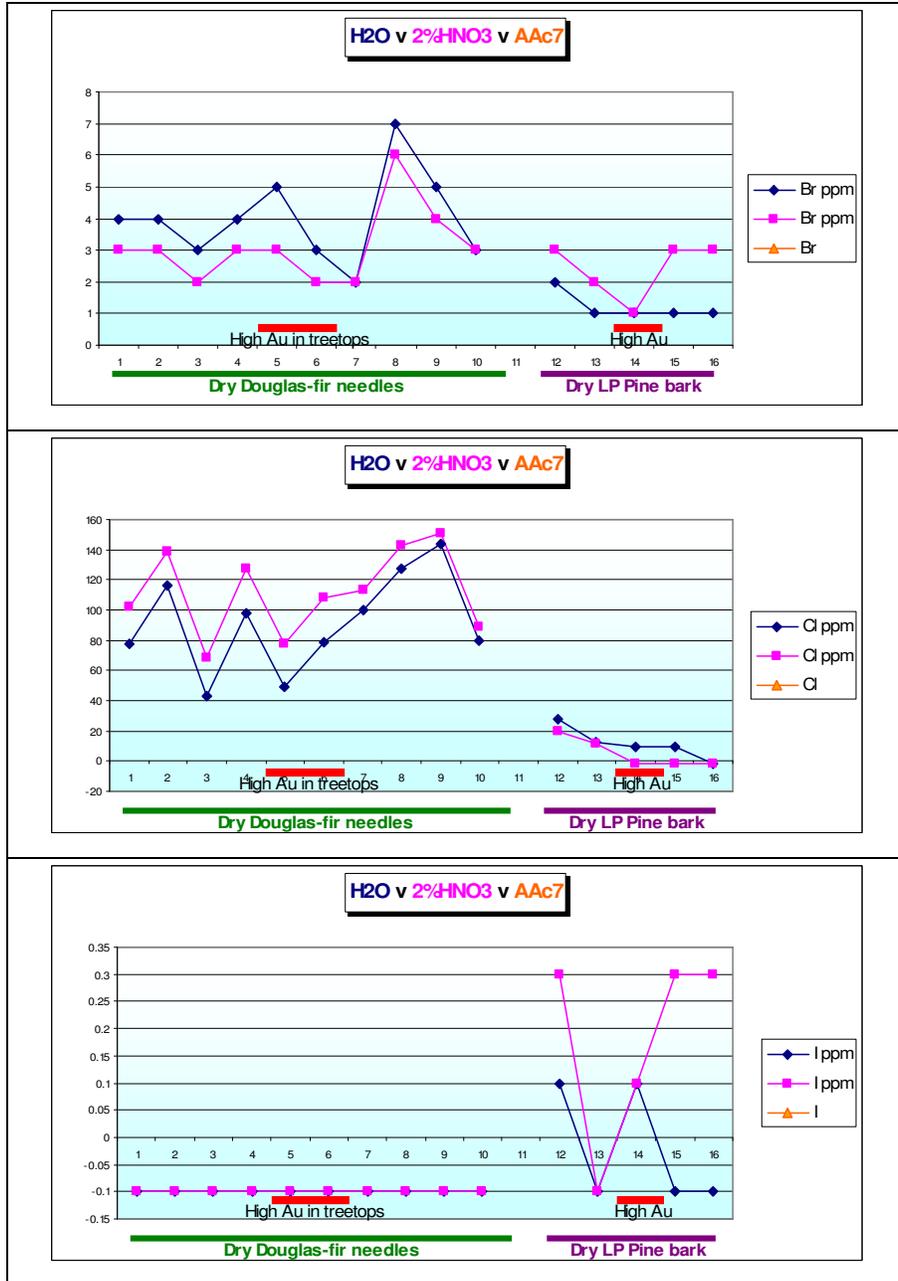
Figure 8: *Bromine, Cl and I in fir needle and lodgepole (LP) pine bark test samples, determined by ICP-MS after leaching in water and dilute nitric acid. These elements could not be determined from the ammonium acetate leach (i.e., no orange line shown). Bottom axis is west to east sequence (see Figure 3).*

From Figure 8 it can be seen that there is little difference in the amount of Br and Cl that is extracted by the water and dilute nitric acid leaches; either would be suitable. Of interest, is the phenomenon that compared to the dilute nitric acid, the water leach removes more Br from the needles than from the bark. Conversely, the dilute nitric acid leach removes more Cl from the needles than the water leach does, and the reverse is true for the bark. This provides a first insight as to how the halogens may be complexed in the

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different types of tissue: the needles represent an active repository whereas the bark is dead tissue in which many elements are sequestered.

Iodine cannot be readily detected by these three leachates and instrumental determinations (ICP-MS) because concentrations are mostly below detection levels.

In summary, the results of these tests demonstrate that Br and Cl can be determined in the dry vegetation by ICP-MS following a weak leach of either water or dilute nitric acid. However, alternative methods are required for F and I.

Comparisons of Multielement Determinations by ICP-MS after Strong and Weak Digestions

To provide further insight into the degree by which elements are bound within plant tissues, an additional strong leach was carried out, using concentrated nitric acid followed by aqua regia. This leach provides a near total extraction of almost all elements in plant tissue. The strong digestion does not provide results for any of the halogens. Results for the other elements were compared to those obtained from the water and AAc7 leaches, and they are shown in Table 1-3 (Appendix 1). Again, an embedded chart can be scrolled across each element to observe the relationships. For most elements, the amount of each element extracted by the aqua regia leach is, as expected, considerably greater than from the weak leaches, however the relative amounts of each element extracted remain much the same, such that the patterns are consistent. Note that in these plots a secondary axis is shown (right axis) with different units because concentrations from the weak leaches are expressed mostly in ppb, whereas concentrations from the aqua regia leach are mostly in ppm. Again, it is the relative concentrations that are of interest. In the case of Ni (Figure 9), the patterns are almost identical; concentrations from the aqua regia leach are in ppm along the right axis and those from the other leaches are in ppb along the left axis. The situation is similar for, amongst others, Sr and Zn.
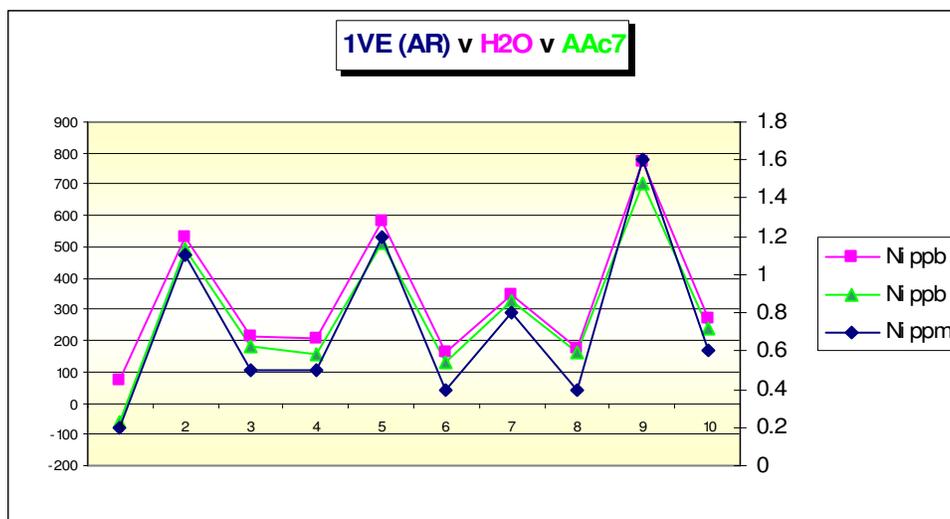
Figure 9: *Nickel in dry fir needle test samples determined by ICP-MS after three types of leach, one strong (concentrated nitric acid followed by aqua regia) and two weak (water and ammonium acetate).*

Highly soluble elements, such as Rb, are mostly extracted by just a simple water leach. Figure 10 shows that more than 80% of Rb is removed by the water leach.
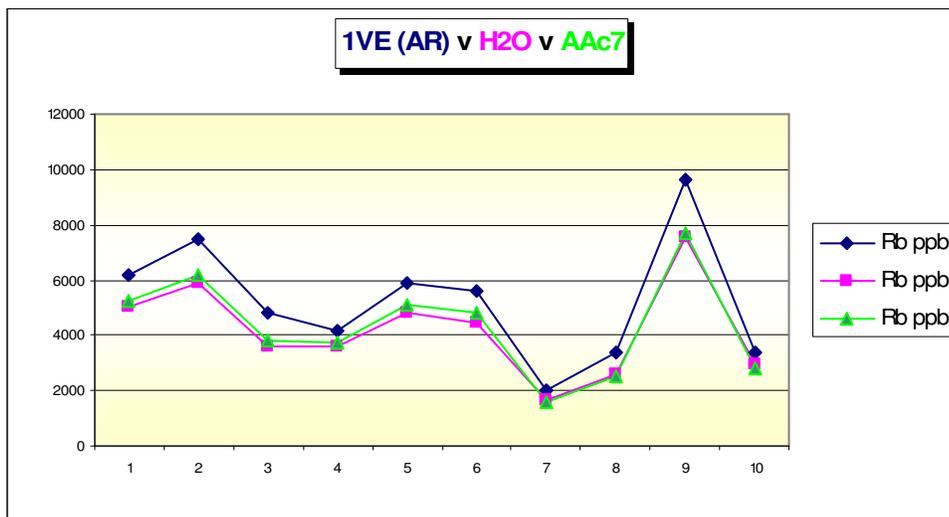
Figure 10: *Rubidium in dry fir needle test samples determined by ICP-MS after three types of leach, one strong (concentrated nitric acid followed by aqua regia) and two weak (water and ammonium acetate).*

Specific Tests for Halogens

Results showed some significant complications with regard to obtaining consistent and accurate data. Some datasets are clearly inadequate and/or inaccurate, emphasizing the need to develop appropriate analytical methodologies. For example, total F in vegetation obtained by one method yielded concentrations of 60 to 80 ppm F, whereas by another method values were <10 ppm F; furthermore, analysis by a partial (water) leach returned values for the same samples mostly in excess of 1000 ppm F! A selection of these differences is shown in Table 3.

In the analysis of vegetation samples by ion chromatography (Dionex), F^- is the first halogen to be evolved. Whereas it may appear that F^- gives a clean positive signature, a variety of unknown organic compounds greatly enhance the presumed fluoride signature generating a false analysis. It appears that there are so many organic compounds dissolved in both water and AAc7 leaches, with more in the AAc7, that the chromatogram is so complex that it is impossible to read. This is a significant analytical problem that would need to be resolved before ion chromatography would be a viable option for analysis of vegetation materials. To quote the analyst directly:

"The Dionex analysis of Colin's sample by the water leach was ugly. The samples had over 26 peaks... Some of the peaks are mislabelled such as Br as it is a small peak under peaks 14 and 15. The only element that was relatively easy to read was the PO_4 peak although it tends to move around when it gets large. None of the peaks are easily resolved. I originally started with an isocratic analysis, which quickly got switched to a gradient elution after seeing the results for a few samples. I tried direct and diluted with two different gradient elutions to try and get better resolution but I am still not comfortable with trying to report any nitrate or bromide by Dionex on these samples. I did try standard addition on one of the samples to confirm whether I had the correct peak or not but for both Br and NO_3, larger peaks seemed to overlap completely with the actual peak of interest and could not be easily seen. Even with manual

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Sample #	Dionex (IC)	Dionex (IC)	Dionex (IC)	XRF	NaOH fusion	Ion Sel. Electrode	Ion Sel. Electrode
	Water Leach	Water leach	Water leach	Total	Total	Water leach	Water leach 2hrs.
	F-Lab A1	F-Lab B	F-Lab C	F-Lab D	F-Lab A3	F-Lab A2	F-Lab B2
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Needles_45	1429	45	1623	72	<10	0.23	< 0.4
Needles_33	1383	16	1613	63	<10	0.15	< 0.4
Needles_22	839	24	1168	86	<10	0.24	< 0.4
Needles_14	1324	27	1476	78	<10	0.2	< 0.4
Needles_08	1529	35	1776		20	0.34	0.4
Needles_04	1241	27	1380	75	<10	0.36	0.4
Needles_60	1121	26	1255	72	<10	0.21	< 0.4
Needles_65	1253	33	1393	68	<10	0.15	0.4
Needles_70	1616	18	2028	65	<10	0.19	< 0.4
Needles_74	1170	20	1318	83	<10	0.2	< 0.4
Pine Bark_11	64	18	109		<10	0.11	< 0.4
Pine Bark_09	74	15	124		<10	0.14	< 0.4
Pine Bark_73	88	24	115		<10	0.22	0.5
Pine Bark_28	99		128		<10	0.14	< 0.4
Pine Bark_68	63	24	102		<10	0.09	< 0.4
Controls							
V6	70	0.75	83	96	<10	1.17	2.0
V6	77	0.92	83	81	<10	0.6	1.7
CLV-2	774	21.2	900	<25	<10	0.34	< 0.4
CLV-2	1022	10.9	906	80	<10	0.34	0.5
V13	2284	33.8	2666	<42	<10	0.17	< 0.4

Table 3: Vegetation samples analyzed for F by several different methods at different laboratories. No certified values available for partial leaches of the controls.

data manipulation I could not resolve the data for these two elements. The large amount of organic [material] present in the sample after the 20 hour shake also resulted in a shift in the peak elution time (loss of column capacity) when analysed directly. Not great to analyse. Difficult to get the data to be comparable to ES and MS as well as between direct and dilutions."

GSC tests permitted the comparison of elements extracted from the vegetation by a water leach with those by an AAc7 leach and generated data from an ICP-MS finish for Br and I by this method, but not Cl and F. By AAc7 leach, the standard method of extracting 1 g of vegetation in 30 ml of solute provided detection levels of 15 ppb I and 150 ppb Br. Whereas such detection levels proved satisfactory for Br in the field samples, the I detection was somewhat too high and required lowering by an order of magnitude to see relief in the data that has subsequently proved to be informative. Further testing of this is warranted, especially for the Br and I since there was insufficient material available for further testing. The tests indicated that the AAc7 leach is sensitive to subtle differences in pH and the time of leaching, such that future extractions with ammonium acetate at pH 7 require very close control of the pH and, after dilution, analysis should be immediate. Time, therefore, becomes a critical factor.

Data from test samples indicated some positive associations of F and I with the location of the Au-in-treetops anomaly (Figure 3). Figure 11 shows ion selective electrode (ISE) determinations of fluoride in a water leach of 1 g samples of dry vegetation. From these and other data it appears that there are typically higher concentrations of F in foliage than bark, although subsequently there is some doubt with regard to the detection levels that

were provided for these test samples and the values reported are probably low by about an order of magnitude. Regardless, the relative concentrations by ISE are similar and so the patterns of F distribution remain similar.
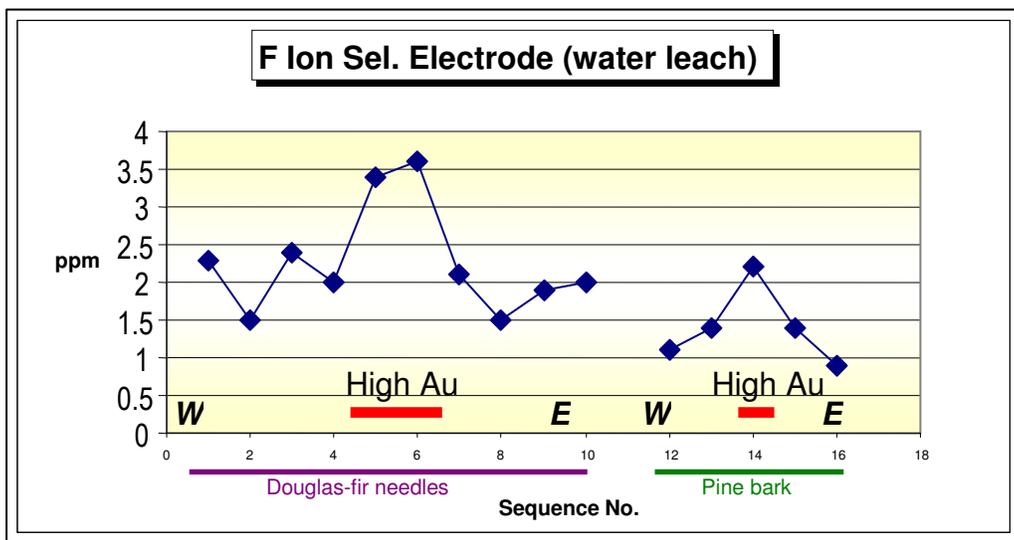
Figure 11: *Concentrations of fluoride in dry Douglas-fir needles and pine bark test samples with respect to the Au-in-treetops anomaly. Determinations by ion selective electrode on water leach (uncertainty with regard to absolute values). Samples collected in 1988 and 1989 prior to mine development.*

Determinations of I in the same materials by several methods have generated results with a range of values. However, there is a reasonable correspondence between I determined by INAA and by Enzyme Leach[SM], although the detection level for I is 100 ppb by INAA and only two samples were slightly above detection, giving the illusion in Figure 12 that INAA is superior.

There was insufficient archived bark material available for running all samples by all methods; however, test sample data from several analytical methods indicate that I is considerably more concentrated in the bark than in the foliage.

With regard to halogen anomalies associated with mineralization, although Figures 11 and 12 show some increased values where there are elevated levels of Au in treetops, it should be noted that such a relationship may not always occur, depending on the nature of the mineralization, depth of burial, and faulting and fracturing of overlying bedrock. Trofimov and Rychkov (2004) note that an I and/or Br halo may occur marginal to a halo of other pathfinder elements (e.g., As, Hg) that are themselves marginal to an orebody. As a result, the spatial relationship of the halogens may form a broad halo anomaly at the surface over a deeply buried ore deposit, with peak values surrounding the deposit. Along transects over mineralization, the appearance would be the classic 'rabbit ears' type of anomaly. Data for Cl and Br show similar substantial variability among the various analytical methods that were tested, and neither element shows the positive response over the Au-in-treetops anomaly noted for F and I.

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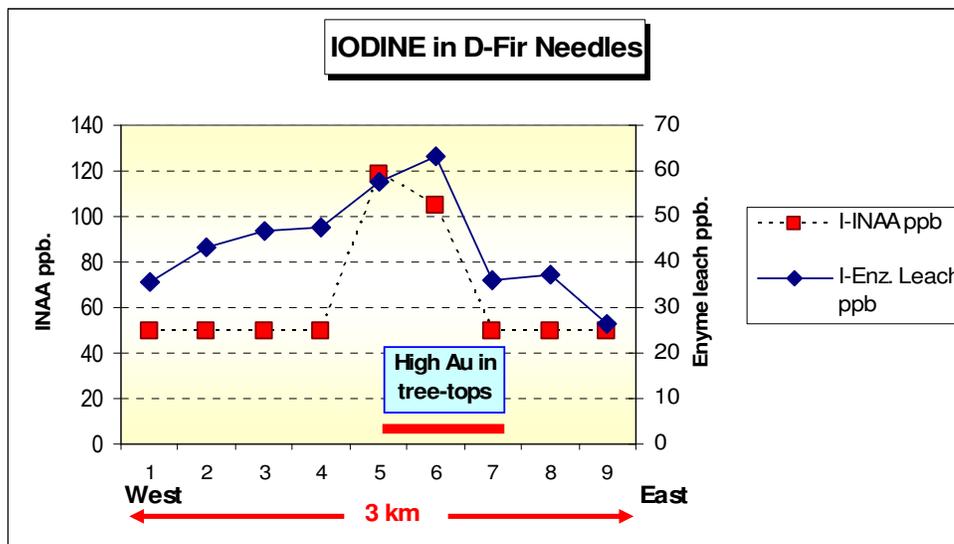
Figure 12: *Concentrations of I in dry fir needle test samples. Comparison of results from an Enzyme Leach[SM] and by INAA. Detection level by INAA was 100 ppb; values below detection are shown as half detection (50 ppb).*

Sediment Tests

In general, data for the sediment standards (two stream sediment and one till) were more consistent than those for the vegetation because fewer interferences from organic compounds were experienced. However, a number of samples were resubmitted because of spurious data. Even after some re-analysis, there clearly remain some analytical problems, although these are mostly isolated discrepancies, such as Br by ion chromatography (Table 4). As would be expected, only a small percentage (mostly <10%) of the halogens is released from the sediment during a weak leach (water and enzyme leach) compared to a total analysis.

Sed. Std.	Br	Br	Br_H2O	Br		Cl	Cl	Cl	F		I-EL	I-H2O-MS	I-INAA
	EL	IC	ICP-MS	INAA		EL	IC	INAA	ISE		EL	ICP-MS	INAA
	ppb	ppb	ppb	ppm		ppm	ppm	ppm	mg/L		ppb	ppb	ppm
STSD-1	2820	-30	2280	23.4		48	2.91	700	0.89		678	560	15.1
STSD-1	2840	1136	2290	38.1		50	3.40	417	0.29		688	538	14.5
STSD-1	2740		2330	25.5		50		469			660	553	14.6
STSD-1	2630		2250	37.2		48		337			651	566	13.1
STSD-1	2640		2540	33.7		47		213			639	549	15.4
TILL-4	807	1132	715	16.3		-2	1.71	81	1.03		93	94	3.4
TILL-4	834	1136	725	20.3		-2	1.83	168	0.84		99	93	3.6
TILL-4	817		731	12.8		-2		125			96	86	5.3
TILL-4	798		692	12.7		-2		40			91	86	4.2
TILL-4	804		748	14.9		-2		138			94	90	4.2
STSD-4	1100	-30	901	10.9		19	2.98	109	0.95		329	267	4.2
STSD-4	1210	-30	1070	13.0		19	3.05	185	1.41		343	267	5.1
STSD-4	1210		930	13.1		19		69			357	262	5.0
STSD-4	1130		901	19.8		18		305			343	266	4.9
STSD-4	1190		974	7.9		19		271			344	266	5.0

Table 4: *Comparison of halogen concentrations extracted from sediment standards by various leaches. Abbreviations: EL, Enzyme Leach[SM]; IC, ion chromatography (Dionex); ICP-MS, inductively coupled plasma mass spectrometry; INAA, instrumental neutron activation analysis (epithermal); ISE, ion selective electrode.*

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Analysis of samples by ion chromatography can simultaneously yield concentrations of other anions (NO_2, NO_3, PO_4 and SO_4). These results are included, along with the quality control data from the analytical laboratory in Table 1-4 (Appendix 1). Determinations by pyrolysis at the GSC (Table 1-5, Appendix 1) provide yet another dataset for comparison, although detection levels for F and Cl are mostly too high by this method to be of value for the current project.

Summary of Analytical Methods

There are many problems involved in obtaining accurate and precise data for the labile components of halogen elements in soil and vegetation, in part because of the low levels typically present. After examination of a broad spectrum of possible methods, no single method has been identified that can produce the required results. The best compromise at this time is to digest finely ground material in water at $30^{o}C$ and determine the concentrations of Br, Cl and I by high resolution (HR) ICP-MS and take an aliquot of the same solution and determine the F^- content by ISE. Time and temperature appear critical for obtaining consistent interbatch results and further analytical research is required to ascertain the optimum parameters for further improving on the analytical methodologies.

Field Studies

Introduction

The focus of the field studies was to obtain suitable vegetation and soil samples for analysis and to investigate their geochemical signatures over a range of mineral deposit styles typically found in central BC: a Cu-Au porphyry (Mount Polley) with some basalt and till cover; a Au skarn (QR) and nearby Au-Mo mineralization associated with diorite overlain by andesite (Cariboo zone); and a Au-Ag epithermal system (3Ts) with a till cover. The aims of the studies were to

- determine the geochemical response of volatile elements (halogens) to known mineralization;
- compare these responses to trace element signatures of the same samples;
- assess the potential value of halogen geochemistry to the exploration for minerals concealed by volcanic rocks and glacial deposits;
- evaluate and compare commercially available analytical methods and thus identify gaps in analytical methodology and develop new analytical techniques (in a subsequent year) most suited to the geological and physiographic environments of central BC; and
- develop new technology and methods for passing on to Canadian analytical laboratories and to the exploration community at large.

A summary of the samples collected in each of the three survey areas is given in Table 5. The table shows that considerably more vegetation samples were collected than soil samples. This is partly because two or three different plant tissues could be collected in the same time that was required to collect one soil sample and record the relevant observations, and partly because at the time of collection it was unknown which plant species would be the most suitable for accumulating the halogens. The samples that were submitted for analysis are shown in bold italics in Table 5. The budget was insufficient to

Location	Areas Sampled	Soil Sites		Vegetation Sites	
		*n**	*Horizon*	*Species*	*n**
Mt. Polley	Boundary Zone	45	B	***Western redcedar foliage***	***46***
	Boundary Zone			Engelmann spruce outer bark	41
	Pond Zone	60	B	***Subalpine fir foliage***	***54***
	Pond Zone			Western redcedar foliage	58
	Pond Zone			Engelmann spruce outer bark	21
QR	Main and West Zones**	0		***Douglas-fir needles (crowns)****	***100***
	Northern extension	0		Douglas-fir needles (low branches)	10
	Northern extension			Lodgepole pine outer bark	21
	Eastern IP' transect	32	B	***Engelmann spruce foliage***	***32***
	Eastern IP' transect			***Lodgepole pine outer bark***	***31***
	Cariboo Zone	24	B	***Engelmann spruce foliage***	***23***
	Cariboo			Lodgepole pine outer bark	13
3Ts	Tommy vein transect	20	B***	***White spruce foliage***	***43***
	Tommy vein transect			***Lodgepole pine outer bark***	***40***
	Ted vein transect	15	B***	***White spruce foliage***	***24***
	Ted vein transect			***Lodgepole pine outer bark***	***24***

* Excluding field duplicates
** Archived samples from collection made in 1988, prior to site development
*** Multi-horizon samples collected

Table 5: *Summary of soil and vegetation samples collected at each location. All soil samples were analyzed and the vegetation samples sent for analysis are shown in bold italics.*

analyze all samples, so the samples not analyzed remain in storage for possible future analysis.

Russian literature has indicated that halogens tend to concentrate in the foliage, so at each of the present survey areas the prime sample medium was foliage of the most common species, with pine bark as a secondary collection and local collection of a few samples of a third species. No single species was present at all of the desired sample locations. Lodgepole pine was the most common species, but its foliage could not be collected because most trees were dead from mountain pine beetle infestation. Bark remained the only feasible choice. Whereas this might have proved to be an optimal sample medium, because of its ubiquity and ease of collection, it was desirable to obtain information on additional species (including spruce bark) because there is the likelihood that millions of acres of central BC will have sparse pine populations once the dead trees have been felled. Figure 13 shows the vast extent of mountain pine beetle infestation in western Canada, and Figure 14 shows a close-up of the beetle. Figure 15 is a photograph of a lodgepole pine with the dried sap residue that bears witness to the pine beetle.
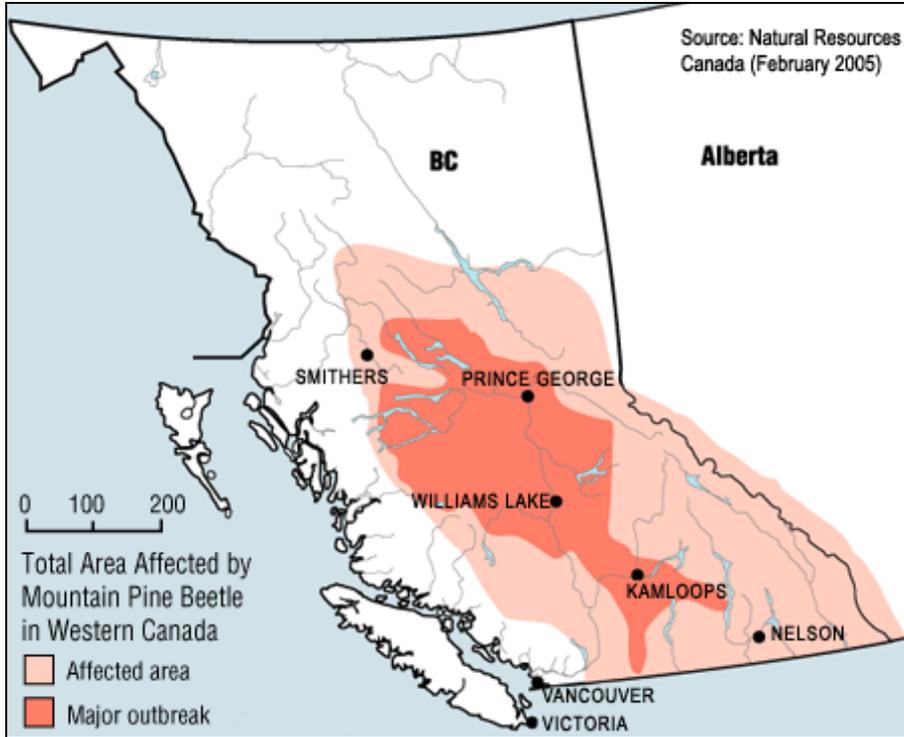
Figure 13: *Extent of mountain pine beetle infestation.*

Figure 14: *Mountain pine beetle. Photo by Dion Manastyrski,Ministry of Forests, southern Interior Forest Region (* http://www.for.gov.bc.ca/hfp/mountain_pine_beetle/ *[April 2006]).*

Figue 15: *Bark of lodgepole pine (Pinus contorta) showing 'pitch tubes' from a mountain pine beetle infestation. Photo by L. Rankin, BC Ministry of Forests, southern Interior Forest Region (http://www.for.gov.bc.ca/hfp/mountain_pine_beetle/ [April 2006])*

Geology and Mineralization

Mount Polley (Imperial Metals Corporation)

Located 56 km northeast of Williams Lake in central BC, the Mount Polley mine lies between Polley and Bootjack lakes. Mount Polley is a Late Triassic alkalic porphyry Cu-Au deposit located within the Quesnel Trough. It is described by Fraser et al. (1995) as a "silica-saturated intrusive complex…assumed to be coeval with volcanic rocks of similar composition in the Nicola Group in which it was emplaced. The Mount Polley deposit is characterized by multiple intrusions that vary from diorite to crowded plagioclase porphyry to monzonite. Abundant hydrothermal breccias occur on the margins and above plagioclase porphyry intrusions. These breccias provide the main host for mineralization and are associated with the highest concentrations of copper and gold." Dating of the

rocks demonstrated an age of 202 to 200 Ma (Mortensen et al., 1995) and new unpublished data clearly indicate ages that predate 200 Ma (J. Logan, pers. comm.). Recent geological and lithogeochemical studies are described in Logan and Mihalynuk (2004).

The Mount Polley open pit Cu-Au mine was commissioned in 1997 and ore from the Cariboo and Bell pits was mined until September 2001 when, due to low metal prices, the mine was idled. Subsequent increases in metal prices resulted in reopening of the mine in March of 2005. While the mine was closed, exploration continued and significant new zones of mineralization were discovered. Two recently discovered zones, the Boundary and Southeast, are surrounded by areas that have undergone little surface disruption, the Boundary zone extension and Pond zone. These sites proved suitable for focusing the sampling program of the present study (Figure 16).
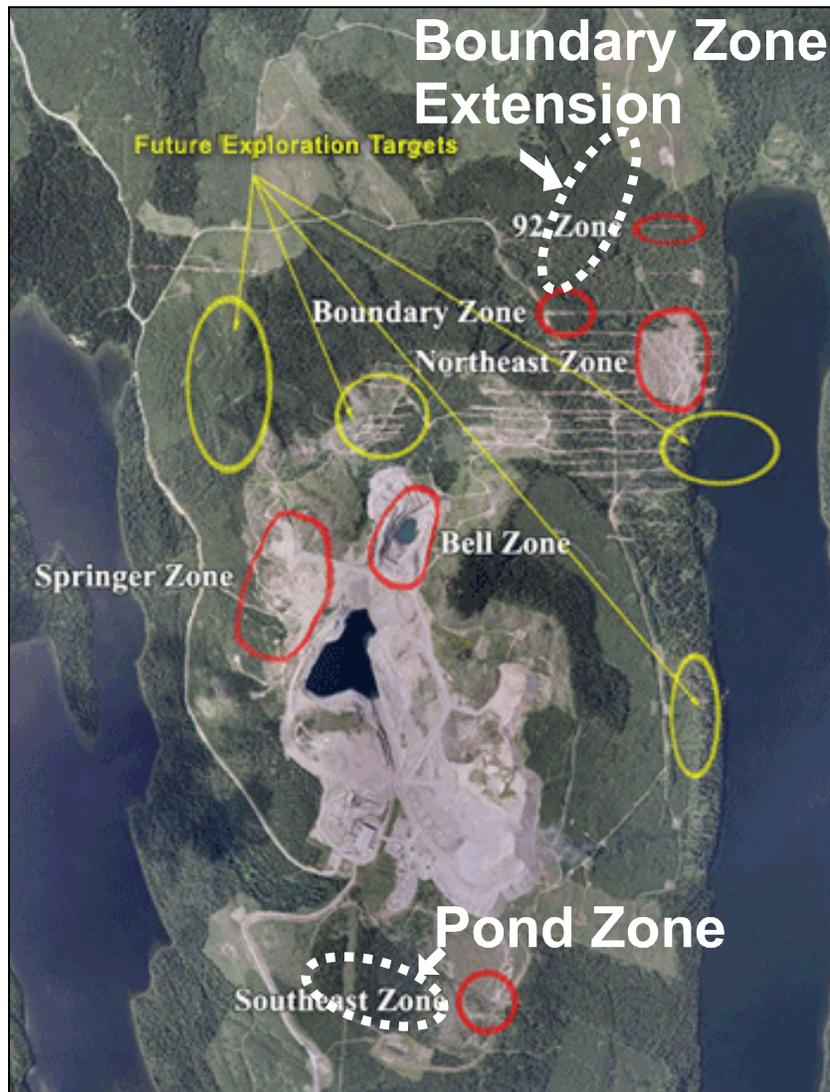
Figure 16: *Locations of principal ore zones at Mount Polley and the two little-disturbed areas selected for this study, Boundary zone extension and Pond zone (annotated aerial photograph from Imperial Metals, 2005).*

QR (Cross Lake Minerals Ltd.)

Located 58 km southeast of Quesnel, the QR is a Au skarn situated near the eastern edge of the northwesterly trending assemblage of Late Triassic-Early Jurassic volcanic rocks of the Quesnel Trough (Fox et al., 1987). The deposits occur in association with propylitized and carbonatized fragmental mafic volcanic rocks. Micrometre-size particles of Au occur with Ag along pyrite and chalcopyrite boundaries in stockworks and in massive basaltic tuffs. Associated minerals include epidote, chlorite, anhydrite and carbonate. Details of the geology and mineralogy are given in Fox et al. (1987) and Melling and Watkinson (1988).

Biogeochemical studies were conducted over the QR deposit in the late 1980s, prior to mine development (Dunn, 1989; Dunn and Scagel, 1989). Vegetation samples were collected from an area now stripped of vegetation and the area of the dominant Au-in-vegetation anomaly is occupied largely by the mine tailings pond. These archived samples were made available by the GSC to complement this geochemical investigation. This unique material offered a valuable opportunity to determine the halogen and multielement metal signatures prior to any mine development. Figure 17 shows the original survey area and two of the sampling zones selected for this study, the Northern Extension and Eastern IP zones.

The Northern Extension zone was selected in order to determine if the treetop Au anomaly that was originally identified (Figure 3) extended farther to the north into areas of thicker volcanic rocks. On arrival in the field, it was apparent that sampling could only be conducted within a fairly small block, since it was constrained by the tailings pond (constructed in the 1990s) in the south and a recent clear-cut to the north. Another constraint on sample collection was the lack of helicopter support to collect samples from the tops of the 20 to 40 m tall Douglas-fir. Since some test samples indicated that foliage from lower limbs has different concentrations of some elements compared to foliage at treetops, only a few samples of Douglas-fir foliage were collected in the Northern Extension zone (Figure 17).

A second area sampled was a geophysical induced polarization (IP) anomaly to the east of the tailings pond, the Eastern IP zone, where Douglas-fir was rare (Figure 17). It represented a target that exploration personnel from Cross Lake Minerals considered worth examining from a geochemical standpoint. Including controls, 32 sites at 50 m intervals were sampled northward along two parallel lines, set 100 m apart. Sample media were B horizon soil, foliage from Engelmann spruce and outer bark from lodgepole pine.

The third target area, situated 6 km to the east of the area depicted in Figure 17, is the Cariboo zone (Au, Cu, Mo associated with diorite and mafic volcanic rocks). The area is not disturbed by any mining activities and a single north-south line was sampled at 50 m intervals over a distance of 1250 m. The same sample media were collected as those at the Eastern IP zone.
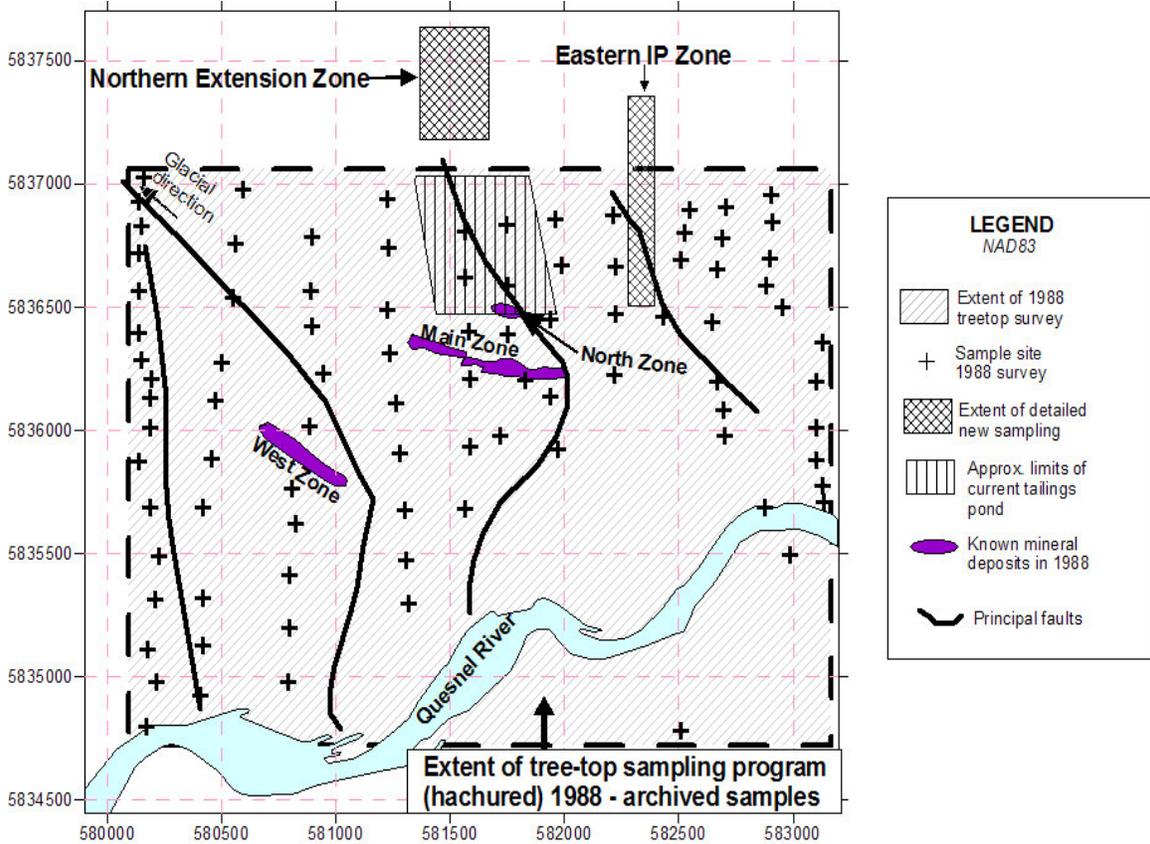
Figure 17: *QR deposit: location of 1988 survey and areas surveyed in 2005.*

3Ts (Silver Quest Resources Ltd., formerly Southern Rio Resources Ltd.)

The 3Ts Au-Ag prospect is located in the Fawnie Creek map area (NTS 93 F/3), approximately 125 km south of Vanderhoof, in the southern Nechako Plateau region of the Interior Plateau of central BC. The 3Ts is a low-sulphidation epithermal Au-Ag prospect of the Late Jurassic (144.7 ±1.0 Ma, Bottomer, 2003a). The Tommy and Ted veins are the best explored of at least nine parallel veins and stockworks, which make up the 3Ts quartz veins system (Figure 18) that extends over an approximately 2 km^2 area within the host felsic tuffs of the Entiako Formation. In general, subvertically dipping mineralized quartz-calcite-potassium feldspar veins on the property strike north-northwesterly and exhibit typical epithermal textures including vein breccia fragments, crustiform banding and comb crystal structures consistent with a shallow depth of formation (Pawliuk, 2005). They are associated with potassium feldspar-quartz-sericite-pyrite alteration haloes of variable thickness. Gold in quartz veins has also been intersected below the crosscutting microdiorite sill at both the Tommy and Ted veins and each remains open at depth. The Tommy vein is considered to represent a higher level in the hydrothermal system than the Ted vein based on differences in the Ag:Au ratio, base metal content and the extent of wall rock alteration (Bottomer, 2003b).

The Tommy and Ted Au-bearing quartz veins were the prime targets over which the sampling transects were designed for this study (Figure 18). In total 55 B-horizon soil

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samples (including control samples) were collected along the entire length of the Ted
vein traverse and along the western third of the Tommy vein traverse. At the same time, a
significant number of multihorizon soil samples were collected for another study (Cook
and Dunn, 2006, 2007). Vegetation was considerably easier to collect than the soil;
approximately 150 samples (including field duplicates) were collected, comprising equal
collections of white spruce (*Picea glauca*) foliage and outer bark from lodgepole pine.
Vegetation sampling extended across the Tommy vein eastward to the Ringer boulder
showing; and eastward across the Ted vein to the Adrian West boulder showing.
Geological details of this area are given in Bottomer (2003a, b) and Cook and Dunn
(2006, 2007).
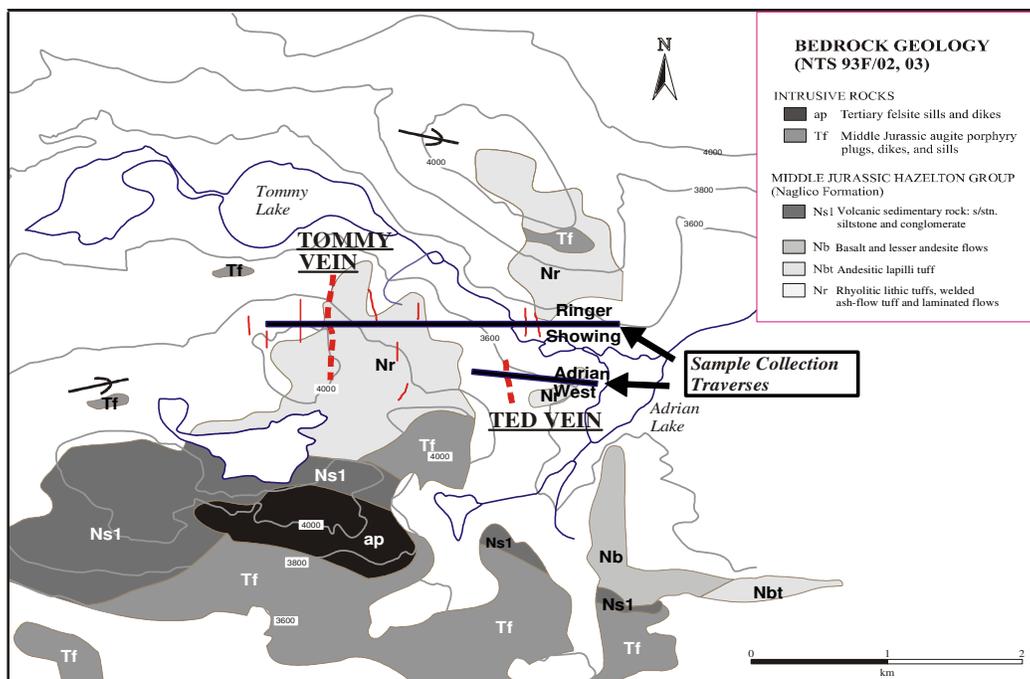
Figure 18: 3Ts: general geology, topography and location of traverses across the mineralized
veins and boulder occurrences (Ringer showing and Adrian West). Geology modified after
Diakow and Webster (1994) and Diakow et al. (1994, 1995a,b). Note also that Unit Tf has
recently been dated by J. Mortensen to be a Late Cretaceous microdiorite intrusion (L. Bottomer,
pers. comm., 2005).

Sample Collection, Preparation and Analysis

Sample Collection and Preparation

At each sample location (mostly at 50 m intervals) a B-horizon soil sample was collected
from the typical Brunisol profile, placed into a plastic bag and securely fastened with a
plastic strap. In addition, five to seven samples of twigs and foliage, comprising the most
recent five to seven years of growth, were collected. At Mount Polley, the species
sampled were western redcedar[1] (*Thuja plicata*) and subalpine fir (*Abies lasiocarpa*); at

_____

[1] Nomenclature: In February 1988 *Thuja plicata* was designated the official tree of British Columbia.
Although commonly referred to as 'cedar', it is not a true cedar (genus *Cedrus*) and belongs to the cypress
family. In order to avoid confusion with a true cedar, botanists spell the popular name 'redcedar' rather
than 'red cedar'. Douglas-fir is hyphenated, because it is not a true fir.

QR, Engelmann spruce (*Picea engelmannii*) and Douglas-fir (*Pseudotsuga menziesii)*; and at 3Ts, white spruce. In the environment of central BC, for these species this amount of twig growth is typically about a handspan in length, at which point along the twig the diameter is 4 to 5 mm. This diameter is quite critical, because many of trace elements concentrate in the bark part of the twig, while 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 bark. Such inconsistency in sampling can be likened to mixing populations of A horizon and B horizon soil and expecting to obtain meaningful data. For the current survey the potential problems that might ensue were not of particular significance because the foliage and not the twigs was to be targeted for analysis. However, as a general principle it is wise to follow this practice of consistency in sampling in order to minimize factors controlling metal accumulations that might simply be related to plant growth.

Figure 19 shows typical growth of subalpine fir in the Mount Polley area, five to seven years of growth is at about the point along the twig where the colour changes from pale to medium brown.

Figure 19: *Typical subalpine fir foliage (approximately seven years of growth).*

Each unseparated twig and foliage sample was placed into a porous polypropylene bag (Hubco Sentry II). In addition, on most traverses, where available, outer bark of lodgepole pine and/or spruce was scraped using a hardened steel paint scraper, and poured into a standard 'kraft' paper soil sample bag (approximately 50 g, which half-filled a bag). Many of the pines were dead or dying because of the rampant mountain pine beetle. However, this was not a problem for the sample integrity and quality because outer bark scales are dead tissue even when a tree is alive. Figures 20 and 21 show the

utensils used in collecting outer scales of conifer bark, and the resultant sample. Detailed accounts of sampling procedures are described in Dunn (2007).

Figure 20: *Hardened steel paint scraper used for collection of pine outer bark. Photo shows the tree after removal of outer bark.*

Figure 21: *Collection of pine outer bark. Modified pan used to collect the bark; the hardened steel paint scraper used for the collection; and the standard 'kraft' paper soil sample bag into which the scrapings are poured.*

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In the laboratory, soil samples were dried at 40°C and sieved to -80 ASTM (180 μm). Vegetation samples were dried at 70°C in an oven for 24 hours to remove all moisture. The foliage could then be separated from the twigs. Each foliage and bark sample was then milled to a powder in preparation for chemical analysis.

Airborne Contamination

An aspect of potential concern with regard to the vegetation samples was the possibility of contamination by airborne dust derived from the mine workings at Mount Polley. Whereas this should not be a problem with respect to the halogens, it could influence the results for the commodity metals that are currently being mined. The issue of whether or not to wash samples prior to analysis is complex because rigorous washing removes surface organic particles as well as any adhering dust, and can therefore modify the analytical results that are obtained (Dunn, 2007).

In order to address this situation, eight samples of subalpine fir were each split into two portions prior to drying and separation. The samples selected were from the area considered most likely to be subjected to airborne dust; that is the traverses north of the assumed extension of the Pond zone, located only a few hundred metres from the southern extremity of the open pit (Figure 16). One portion of each sample was rinsed by swirling it in a container of tap water; the second portion was not washed.

Table 1-6 (Appendix 1) shows a spreadsheet with an embedded chart for scrolling across the elements, each paired with unwashed needles first (black font and line) followed by washed (red font and line). At the right side of each chart, two symbols show the average value for each element.

The washing tests show that there is little or no contamination of most elements. However, there appears to be some contamination of Ag (in just two samples), Au, Fe, Li, REE, Ti and Zr. Contamination increased the concentrations of these elements by approximately 20%, with higher levels for Au and Li. Conversely, washing of the samples has actually increased the concentrations of Cd, Cu, Mo, Ni, Pb and Zn. This implies that dust adhering to the needles is primarily composed of silicates present in sufficient concentration to dilute the content of these metals when the vegetation is analyzed.

Since the Pond zone samples are considered a worst case scenario for dust contamination among the various survey areas of this project, and since there is minimal likelihood of airborne contamination by the halogens, it was decided that the extra step of washing all samples was not warranted. The extra washing could in fact introduce complications by removing cuticle from the plant tissues that might contain trace elements, especially the labile components of the halogens for which a water leach of the milled material was one of the tests to be conducted.

Multielement ICP-MS

Soil samples were submitted to Acme Analytical Laboratories, Vancouver, BC, for 53 element ICP-MS analysis by method 1F (aqua regia digestion) and pH determinations. Vegetation samples were analyzed at Acme Analytical Laboratories by method 1VE-MS (nitric acid followed by aqua regia digestion). A portion of each sieved soil and milled

vegetation sample was set aside for later analysis for the halogens, once a suitable method(s) had been identified.

The results of the multielement ICP-MS on the B horizon soil and the principal sets of vegetation (foliage) were obtained within a few weeks of the field samples being submitted for analysis. The multielement data for these samples were required for comparison of the commodity elements (especially Au, Ag, Cu) with the data subsequently to be obtained for the halogens. Data were acquired, also, for some of the bark samples, in light of the relative enrichment of I (in bark compared to foliage) revealed from the test samples. A total of approximately 60,000 analytical determinations were made on the full set of field and test samples.

Halogen Analysis

Analysis for the halogens was undertaken at Activation Laboratories, Ancaster, Ont. Soil and vegetation samples were subjected to a water leach by placing a 1 g sample in 10 mL deionized water which was then vortexed and allowed to sit for 1 hour at 30°C in an incubator. Samples were then centrifuged and filtered through a 0.45 µm filter. Analysis for Br, Cl and I was by high resolution ICP-MS (Finnigan Element2 instrumentation). For F, an aliquot of each solution was taken for determination by ISE.

Quality Control of ICP-MS (multielement)

Field duplicates were collected at every 10th sample site and appropriate quality control samples were inserted at a minimum of 1 in every 20 samples. Control samples for the soil were portions of the same GSC stream sediment standards (STSD-1 and STSD-4) that were used for the test samples. The vegetation data quality was monitored by the insertion of controls: V6 (pine needles), CLV-2 (spruce needles), V13 (mountain hemlock needles) and the Standard Reference Material NIST 1575a (pine needles). Tables 1-7, -8, -9 and -10 (Appendix 1) summarize the analytical quality control for the field duplicates, laboratory duplicates and control samples. For the vegetation determinations by ICP-MS (53 element suite by method 1VE-MS), data are presented in Tables 1-7 and -8 (Appendix 1) for the standards and duplicates, respectively. Each work order (i.e., batch) from the analytical laboratory has the quality control (QC) presented as a separate worksheet. QC data for soil determinations (53 element suite by method 1F) are presented in Tables 1-9 and -10 (Appendix 1). These tables all have a similar format. Elements are arranged in alphabetical order, and for the controls the detection limits are inserted and bar charts are embedded for scrolling across the elements. The field duplicates are presented as paired sets of analyses, again with respect to each of the individual work orders. There are in these four tables a total of 18 worksheets, each with 53 elements. In short, the precision and accuracy of the final datasets that were received fall within the normal range of quality and precision that can be expected for analysis by these methods. Precision is better for some elements than others and this is partly a function of elemental concentrations and partly the analytical methodology. All data are provided for close scrutiny of any particular method.

Two additional tables of QC data are presented as Tables 1-11 and -12 (Appendix 1). These show results from a water leach of pine bark from QR. This was the only dataset for which results for all 53 elements (plus Br and Cl by ICP-MS and F by ISE) were determined on a water leach. Iodine by this instrumentation (i.e., not high resolution)

could not be determined and not only were most Br and many Cl values below detection levels by this method but clearly the precision for these elements by this method was unsatisfactory. The remaining Br, Cl and I analyses were obtained by high resolution ICP-MS and F by ISE.

Quality Control, Halogens

As noted above, Activation Laboratories provided data for Br, Cl and I by high resolution ICP-MS (HR-ICP-MS) and F by ISE. These were the only practical methods for obtaining data at the low levels present in the sample materials.

The QC data obtained for the halogens are presented in Tables 1-13, -14, -15 and -16 (Appendix 1) and, because of their significance to this project, these results are discussed in more detail than those for the multielement analyses.

No prior data for soil and vegetation control samples were available for a water leach. Given that a water leach is only a partial leach, accuracy could not be determined but precision on control samples and on field duplicates could be established.

Table 6 shows the values obtained from the water leach described above (see Halogen Analysis), for three different dry vegetation controls and one ash control (V6a). Ash determinations were obtained on only one small test batch of pine bark ash from 3Ts. Of note is that the concentrations tended to vary by analytical batch. This is addressed in Section 3 but of importance to the present study and the interpretation of results is that for each individual survey area all samples were run at the same time. Therefore, values relative to one another along a single profile should be meaningful.

Sample#	Batch #	Control	n	Cl	Br	I	F
				ppm	*ppm*	*ppm*	*ppm*
Approx. d.l.				*1*	*0.02*	*0.001*	*0.4*
Average	3807	1575a	n=2	406	2.1	0.017	1.51
Average	3806	1575a	n=4	400	2.5	0.020	0.77
Average	3807	CLV-2	n=5	361	2.6	0.013	1.36
Average	3806	CLV-2	n=3	380	2.4	0.009	-0.40
Average	3807	V6	n=15	227	0.5	0.015	2.42
Average	3806	V6	n=7	235	0.4	0.015	1.14
Average	3806	V6a	n=2	1250	21.3	0.135	2.74

Table 6: Average concentrations of halogens in vegetation controls after a water leach (see Table 1-15, Appendix 1 for details).

Figure 22 shows the halogen data obtained on all vegetation field duplicate samples. There is a moderate amount of variability, with R^2 varying from 0.45 for Br to 0.81 for F. For I there are a few high values that weight the data and once these are removed (Figure 22, second I plot) R^2 is appreciably lower, but adequate given that values are in the low ppb range. Given the very low levels of I, Br and F present, this overall precision is acceptable and it is of note that where one sample provides a relatively high value, its paired field sample also is relatively high.

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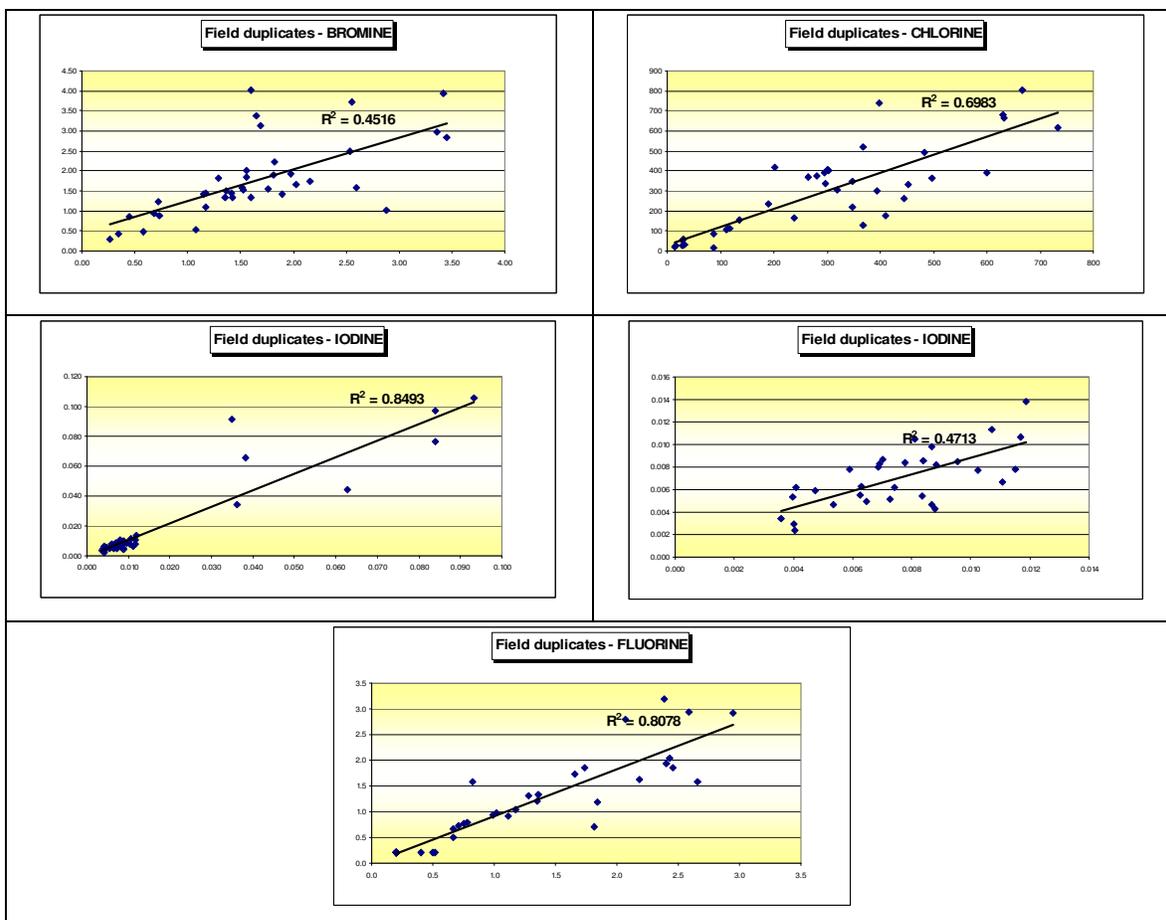
Figure 22: *Halogens in vegetation field duplicates after water leach (see Table 1-16, Appendix 1, for details).*

Data for the soil are presented in the same manner as for the vegetation. Table 7 shows that after a water leach of the sediment controls, including a bulk field sample from 3Ts, Br, I and F levels are similar to those in the vegetation but Cl concentrations are far lower in the soil. In general, there was less between-batch variation in the soil samples than in the vegetation. From consultation with the analyst, it appears that the digestion procedure described above was consistent but the between-batch variability is due to differing times from samples digestion to introduction of the solutes into the analytical equipment. Clearly, this is an area for future testing in order to optimize the stability of the solutions.

Figure 23 shows that reproducibility of results from field soil duplicates was substantially less precise than vegetation for Br and Cl but similar for I and F. With regard to the Cl, the poorer precision is probably a reflection of the much lower concentrations of Cl in the soil.

	Batch #	Control	n	Cl	Br	I	F
				ppm	ppm	ppm	ppm
Approx. d.l.				*1*	*0.02*	*0.001*	*0.4*
Average	A3807	STSD-1	7	48	2.20	0.526	1.2
Average	A3806	STSD-1	5	35	2.01	0.365	0.9
Average	A3807	STSD- 4	4	23	0.95	0.260	0.9
Average	A3806	STSD-4	3	23	1.17	0.393	1.8
Average	A3806	Bulk Field control	5	10	0.12	0.018	-0.40

Table 7: *Average concentrations of halogens in soil controls after water leach (see Table 1-13, Appendix 1, for details).*
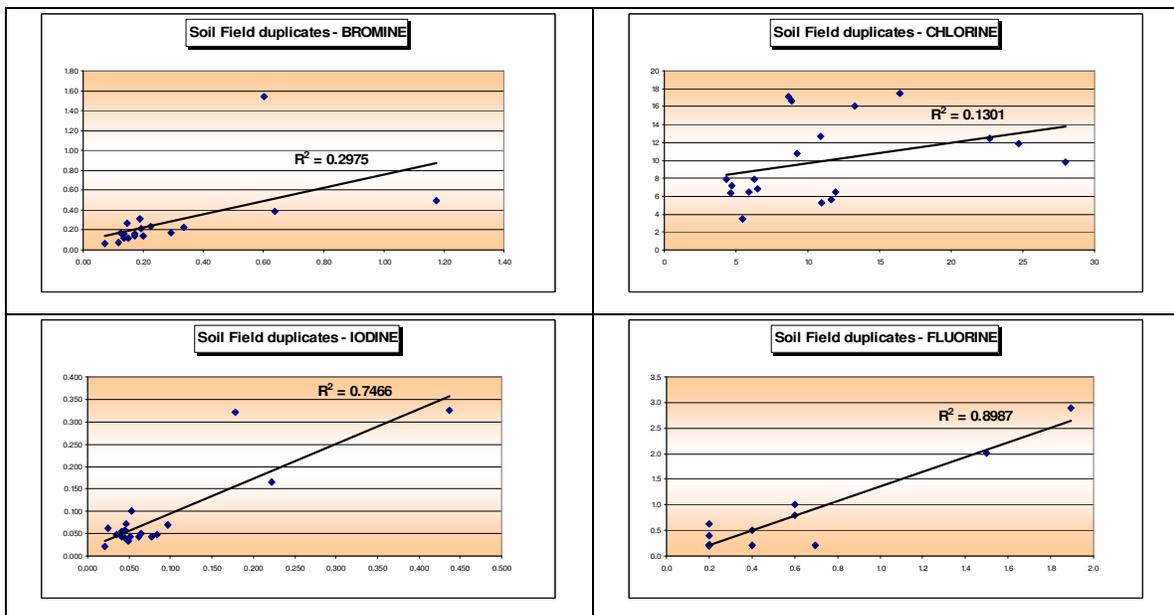
Figure 23: *Halogens in soil field duplicates after a water leach (see Table 1-14, Appendix 1, for details).*

Summary of Analytical Results

Data Presentation

This section emphasizes the halogen data and highlights some of the multielement data by presenting selected plots for each of the survey areas. Appendix 2 (Tables 2-1 to 2-18) contains all of the analytical data for these areas, each with an embedded chart for scrolling across the individual elements. Each of the 18 tables is organized in the same manner:

- UTM (NAD 83) eastings and northings are arranged sequentially, by south to north for northerly traverses and west to east for easterly traverses. The only exception is Table 2-5 where samples were taken in a grid pattern at QR, therefore there is no embedded chart. Sample numbers are not necessarily sequential, since sampling on some traverses started in the middle of a line which was later infilled.

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- The distance between sample stations and the cumulative distance along each line are shown as separate columns.
- Elements are arranged so that the halogens (all water leach) are shown first, highlighted in blue, followed by an alphabetical listing of elements determined from a strong acid leach (nitric acid followed by aqua regia digestion for vegetation; aqua regia digestion for soil).
- Concentrations below detection are shown at half the detection limit (Tables 1-7 to -16, Appendix 1, all show the detection limits).
- Zones of known or inferred mineralization are shown highlighted in yellow or orange on the spreadsheets and as red bars or arrows on the embedded charts.
- Note that several of the tables contain multiple sheets (e.g., Tables 2-1 and -2 show data for each sample line on a separate tabbed Excel sheet).
- For detailed instructions on how to scroll the charts across the elements, refer to Appendix 3.

Mount Polley

Boundary Zone Extension

Including field duplicates, 55 samples were collected north of the Boundary zone, mostly at 50 m intervals along two north-south parallel lines (100 m apart). Figure 16 shows the location of the Boundary zone and the area sampled, the Boundary zone extension. Sampling extended from till-covered brecciated monzonite in the south, northward to Jurassic volcanic cover of unknown thickness. The collection, detailed in Table 5, comprised B horizon soil, foliage of western redcedar and subalpine fir and outer bark from Engelmann spruce. For simplicity, the western redcedar will be referred to as 'cedar', since this is the name commonly used by those working in the forests of BC. Sample sites are superimposed on a simplified sketch of the underlying geology in Figure 24.

At the time of writing (April 2006), Imperial Metals indicate that there is a circular area of mineralization with a 30 m radius, as shown on Figure 24. Drilling to date indicates that the zone extends from surface to a depth of approximately 110 m. It is hosted in magnetite breccia, mineralized with chalcopyrite and pyrite, with alteration products that include magnetite, calcite and garnet.

Table 8 is a statistical summary of element concentrations in dry cedar foliage. Table 9 shows the same statistical parameters for the soil samples. These tables are provided for general information on element levels encountered in this environment, and serve as a yardstick against which to compare data from future surveys. In general, elements considered somewhat concentrated in the cedar foliage are Au, Cu and Mo; notable concentrations in the soil include Ag, As, Au, Cu, Hg and V.
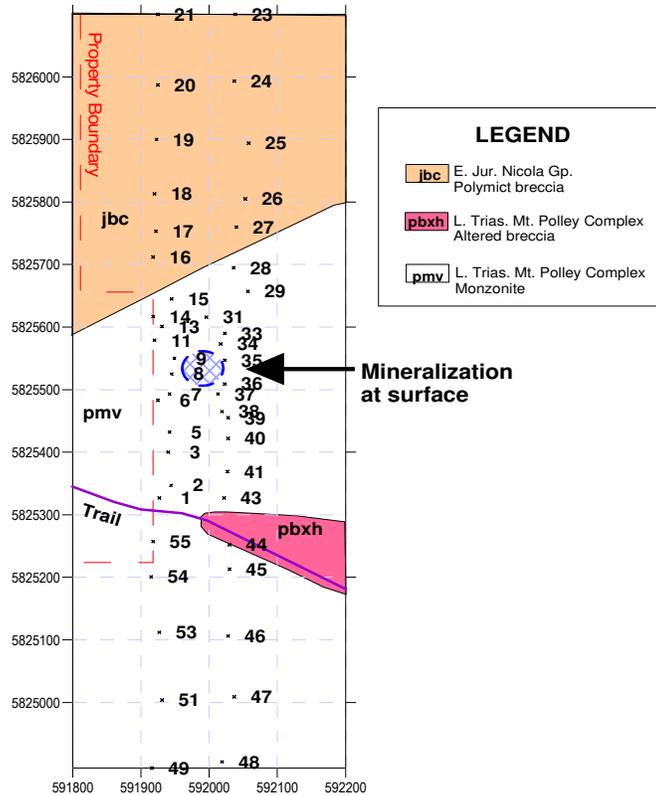
Figure 24: Boundary zone extension: simplified geology showing location of known mineralization and the vegetation and soil samples collected along two traverses.

A comparison of several commodity elements in the soil with those in the cedar foliage is instructive, in that anomalous concentrations appear at different localities (Figures 25 to 28). Previous studies of concentrations in soil versus vegetation in glaciated terrain, at Beaver Dam, Nova Scotia (Dunn et al.*,* 1991) and Mount Milligan, BC (Dunn et al.*,* 1996), have found that vegetation anomalies tend to be more directly situated over mineralization than the soil anomalies.

The implication from the above comparisons is that the zone of mineralization occurs in the centre of the survey area, as indicated by the vegetation, rather than downslope to the south where most of the soil anomalies lie. This is in accordance with the zone of mineralization defined by Imperial Metals (Figure 24). To explain this spatial discrepancy between the vegetation and soil anomalies, it is considered that a significant local concentration of a metal is required in order to be reflected in the plant chemistry: there is insufficient concentration of metals in a soil anomaly (even though it constitutes a geochemical anomaly) to be reflected in the vegetation. The soil anomaly is commonly displaced by down-ice or downslope dispersion or dispersal, or perhaps downslope via groundwater, whereas a biogeochemical anomaly typically occurs directly over a mineralized source.

		N	Mean	Std. Dev.	Minimum	Percentiles				Maximum
						50	70	80	90	
Ag	ppb	46	3	1	1	3	4	4	4	6
Al	%	46	0.005	0.001	0.005	0.005	0.005	0.005	0.006	0.010
As	ppm	46	0.09		<0.1	<0.1	0.10	0.10	0.13	0.30
Au	ppb	46	0.9	1.1	0.1	0.5	0.9	1.5	2.7	5.0
B	ppm	46	17	4	11	16	18	20	23	29
Ba	ppm	46	29	15	7	25	38	44	51	63
Be	ppm	46	0.1		<0.1	<0.1	<0.1	<0.1	<0.1	0.1
Bi	ppm	46	<0.02		<0.02	<0.02	<0.02	<0.02	<0.02	0.0
Ca	%	46	1.177	0.192	0.850	1.150	1.229	1.310	1.530	1.660
Cd	ppm	46	0.03	0.02	0.01	0.03	0.04	0.05	0.06	0.07
Ce	ppm	46	0.06	0.02	0.03	0.06	0.07	0.08	0.10	0.11
Co	ppm	46	0.06	0.02	0.02	0.06	0.07	0.08	0.08	0.10
Cr	ppm	46	2.1	0.2	1.7	2.1	2.2	2.3	2.3	2.5
Cs	ppm	46	0.019	0.013	0.007	0.016	0.020	0.022	0.035	0.065
Cu	ppm	46	5.5	1.5	2.2	5.3	5.9	6.8	7.6	11.0
Fe	%	46	0.013	0.004	0.006	0.012	0.014	0.015	0.020	0.023
Ga	ppm	46	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ge	ppm	46	<0.01		<0.01	<0.01	<0.01	0.01	0.01	0.01
Hf	ppm	46	0.0		<0.002	0.002	0.003	0.003	0.004	0.006
Hg	ppb	46	24	7	14	23	27	28	33	42
In	ppm	46	<0.02		<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
K	%	46	0.533	0.105	0.300	0.530	0.589	0.620	0.679	0.770
La	ppm	46	0.04	0.02	0.02	0.04	0.05	0.05	0.07	0.08
Li	ppm	46	0.05	0.06	0.01	0.03	0.07	0.09	0.11	0.38
Mg	%	46	0.101	0.020	0.059	0.102	0.112	0.119	0.126	0.147
Mn	ppm	46	176	97	34	159	208	248	345	412
Mo	ppm	46	1.5	1.4	0.4	1.2	1.5	1.8	2.5	10.1
Na	%	46	0.002		<0.002	0.002	0.002	0.002	0.002	0.003
Nb	ppm	46	0.01	0.01	<0.01	0.01	0.02	0.02	0.03	0.07
Ni	ppm	46	1.4	0.7	0.2	1.2	1.6	1.8	2.2	3.6
P	%	46	0.125	0.026	0.066	0.123	0.137	0.144	0.163	0.187
Pb	ppm	46	0.11	0.08	0.05	0.09	0.12	0.12	0.14	0.58
Pd	ppb	46	<2		<2	<2	<2	<2	<2	<2
Pt	ppb	46	<1		<1	<1	<1	<1	<1	1.0
Rb	ppm	46	2.4	1.6	0.6	2.1	2.9	3.3	3.9	9.5
Re	ppb	46	<2		<2	<2	<2	<2	<2	2.0
S	%	46	0.073	0.041	0.005	0.070	0.100	0.116	0.130	0.160
Sb	ppm	46	0.04	0.05	<0.02	0.02	0.04	0.05	0.06	0.34
Sc	ppm	46	0.2	0.1	<0.2	0.2	0.3	0.3	0.3	0.3
Se	ppm	46	0.2	0.1	<0.2	0.2	0.2	0.2	0.2	0.3
Sn	ppm	46	0.04	0.05	0.01	0.03	0.05	0.06	0.08	0.32
Sr	ppm	46	62	24	24	60	78	86	92	117
Ta	ppm	46	<0.002		<0.002	<0.002	<0.002	<0.002	<0.002	0.0
Te	ppm	46	<0.02		<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Th	ppm	46	<0.01		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ti	ppm	46	8.2	1.5	5.0	8.0	8.9	9.0	10.3	12.0
Tl	ppm	46	<0.02		<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
U	ppm	46	<0.01		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
V	ppm	46	<2		<2	<2	<2	<2	<2	<2
W	ppm	46	0.1		<0.1	<0.1	<0.1	<0.1	<0.1	0.3
Y	ppm	46	0.03		0.01	0.03	0.03	0.04	0.05	0.06
Zn	ppm	46	11.6	2.9	5.9	12.1	12.7	13.8	15.1	20.8
Zr	ppm	46	0.06	0.09	0.02	0.05	0.05	0.05	0.07	0.68

Table 8: *Mount Polley Boundary zone extension: statistical summary of data obtained after digestion of dry cedar foliage in nitric acid and aqua regia with analysis by ICP-MS (Acme Analytical Laboratories method 1VE-MS).*

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| | | N | Mean | Std. Dev. | Minimum | Percentiles | | | | Maximum |
						50	*70*	*80*	*90*	
Ag	ppb	45	262	303	35	189	248	295	565	1545
Al	%	45	2.4	0.84	1.21	2.16	2.606	2.858	3.426	6.16
As	ppm	45	6.6	3.0	2.7	5.9	7.9	8.3	10.8	15.9
Au	ppb	45	5.7	8.8	0.2	2.1	5.0	8.8	16.8	40.2
B	ppm	45	4.3	2.7	2	4	4	4	8	16
Ba	ppm	45	173	80	80	155	199	218	306	429
Be	ppm	45	0.5	0.41	0.2	0.4	0.5	0.58	0.64	3.1
Bi	ppm	45	0.15	0.12	0.07	0.12	0.14	0.15	0.21	0.83
Ca	%	45	0.54	0.252	0.24	0.47	0.58	0.67	0.90	1.37
Cd	ppm	45	0.29	0.23	0.06	0.27	0.31	0.38	0.43	1.55
Ce	ppm	45	16.3	6.4	6.5	15.4	17.8	20.5	24.7	39.3
Co	ppm	45	13.3	2.9	8.2	13.6	14.7	15.4	15.7	25
Cr	ppm	45	51	21	4.2	56	65	72	75	80
Cs	ppm	45	2.3	1.8	0.62	1.73	2.19	2.81	4.48	11.42
Cu	ppm	45	118	198	8.07	52	91	145	269	1106
Fe	%	45	3.8	0.53	2.72	3.87	4.082	4.186	4.356	5.92
Ga	ppm	45	7.4	1.7	5.1	6.7	8.1	8.5	10.0	13.8
Ge	ppm	45	-0.1		-0.1	-0.1	-0.1	-0.1	-0.1	0.1
Hf	ppm	45	0.075	0.047	0.02	0.06	0.08	0.106	0.13	0.29
Hg	ppb	45	81	91	16	45	66	106	202	469
In	ppm	45	0.03	0.009	0.02	0.03	0.03	0.03	0.04	0.06
K	%	45	0.106	0.045	0.06	0.1	0.11	0.118	0.14	0.3
La	ppm	45	9.6	4.6	3.5	8.8	10.1	11.1	14.5	28.1
Li	ppm	45	23	12.4	11.5	20	22	24	29	92
Mg	%	45	0.65	0.19	0.21	0.66	0.732	0.75	0.854	1.34
Mn	ppm	45	670	330	323	604	782	879	1040	1932
Mo	ppm	45	1.09	0.88	0.2	0.72	1.29	1.56	2.38	4.01
Na	%	45	0.011	0.004	0.006	0.01	0.013	0.014	0.016	0.028
Nb	ppm	45	0.8	0.25	0.2	0.79	0.88	1.01	1.17	1.45
Ni	ppm	45	28	14	3.1	31	35.2	38.3	42.8	73.3
P	%	45	0.122	0.073	0.026	0.105	0.156	0.178	0.217	0.422
Pb	ppm	45	10.5	13.2	4.91	7.14	9.5	11.7	14.9	94.3
Pd	ppb	45	-10		-10	-10	-10	-10	-10	-10
Pt	ppb	45	-2		-2	-2	2	2	2	2
Rb	ppm	45	10.6	3.1	6.3	10	11	12	13	25
Re	ppb	45	-1		-1	-1	1	1	1	2
S	%	45	0.002	0.014	-0.01	-0.01	0.01	0.01	0.02	0.04
Sb	ppm	45	0.26	0.1	0.14	0.24	0.26	0.3	0.44	0.58
Sc	ppm	45	4.6	2.4	2.6	4.1	4.74	5.08	6.18	18.4
Se	ppm	45	0.2	0.2	-0.1	0.1	0.2	0.3	0.64	0.7
Sn	ppm	45	0.5	0.10	0.3	0.5	0.5	0.5	0.6	0.8
Sr	ppm	45	56	21	26.2	51	59	64	86	127
Ta	ppm	45	-0.05	0	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Te	ppm	45	0.025	0.04	-0.02	0.02	0.04	0.058	0.09	0.11
Th	ppm	45	1.95	0.82	0.7	1.8	2.12	2.5	2.92	5.5
Ti	%	45	0.10	0.03	0.073	0.1	0.1	0.1	0.2	0.2
Tl	ppm	45	0.06	0.04	0.04	0.05	0.05	0.06	0.064	0.27
U	ppm	45	0.57	0.39	0.3	0.5	0.5	0.6	0.82	2.8
V	ppm	45	113	20	67	117	124.4	128	137.8	155
W	ppm	45	0.09	0.17	-0.1	0.1	0.1	0.2	0.2	0.9
Y	ppm	45	4.8	5.8	2.1	3.2	3.9	4.8	6.6	37.2
Zn	ppm	45	100	30	53	94	121	130	142	176
Zr	ppm	45	3.75	2.16	1.5	3.2	3.62	5.32	6.9	11.9
pH		45	5.47	0.5	4.4	5.4	5.7	5.8	6.24	6.7

Table 9: Mount Polley Boundary zone extension: statistical summary of data obtained from aqua regia digestion of –80 mesh B-horizon soil samples (30 g) with analysis by ICP-MS (Acme Analytical Laboratories method 1-F).
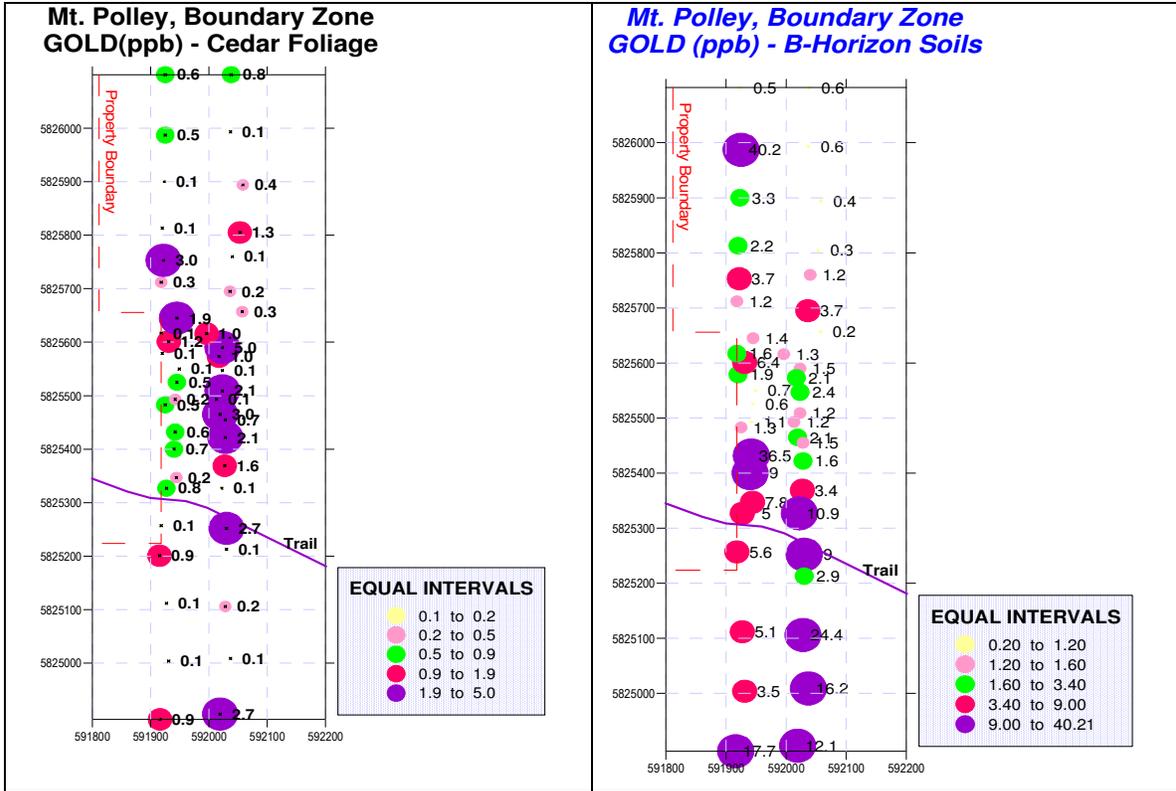
Figure 25: *Mount Polley Boundary zone extension: Au in dry cedar foliage compared to B horizon soil.*

Figure 26: *Mount Polley Boundary zone extension: Hg in dry cedar foliage compared to B horizon soil.*
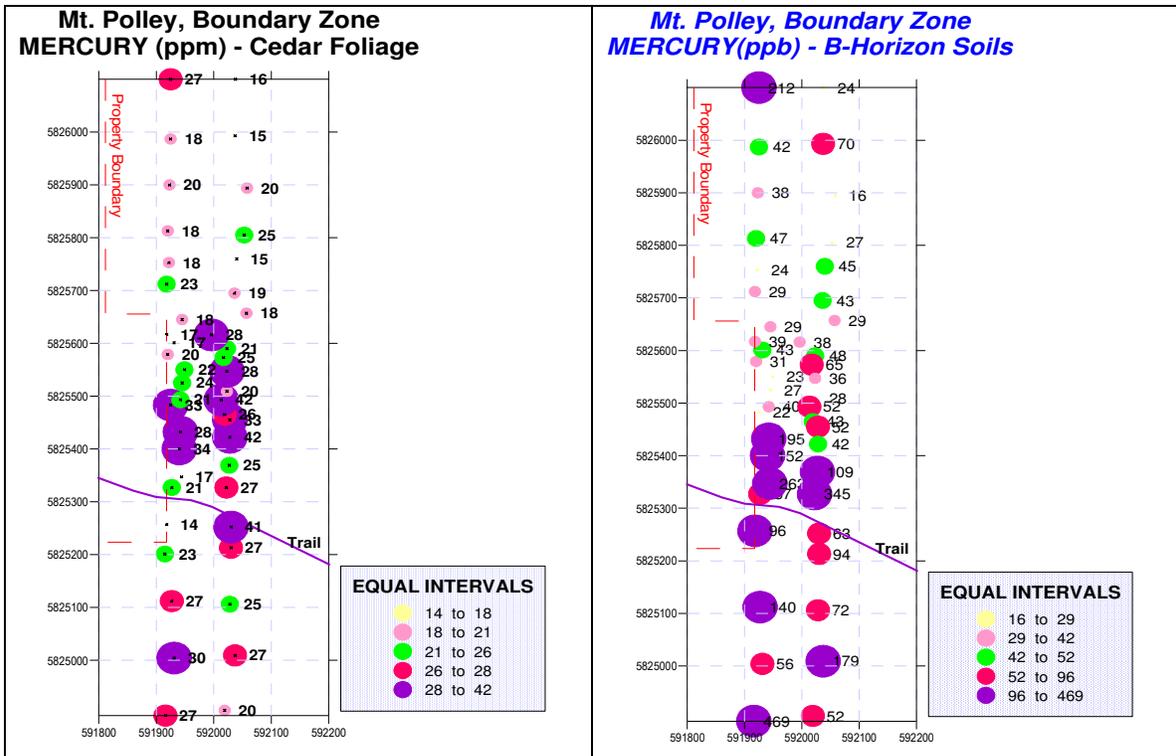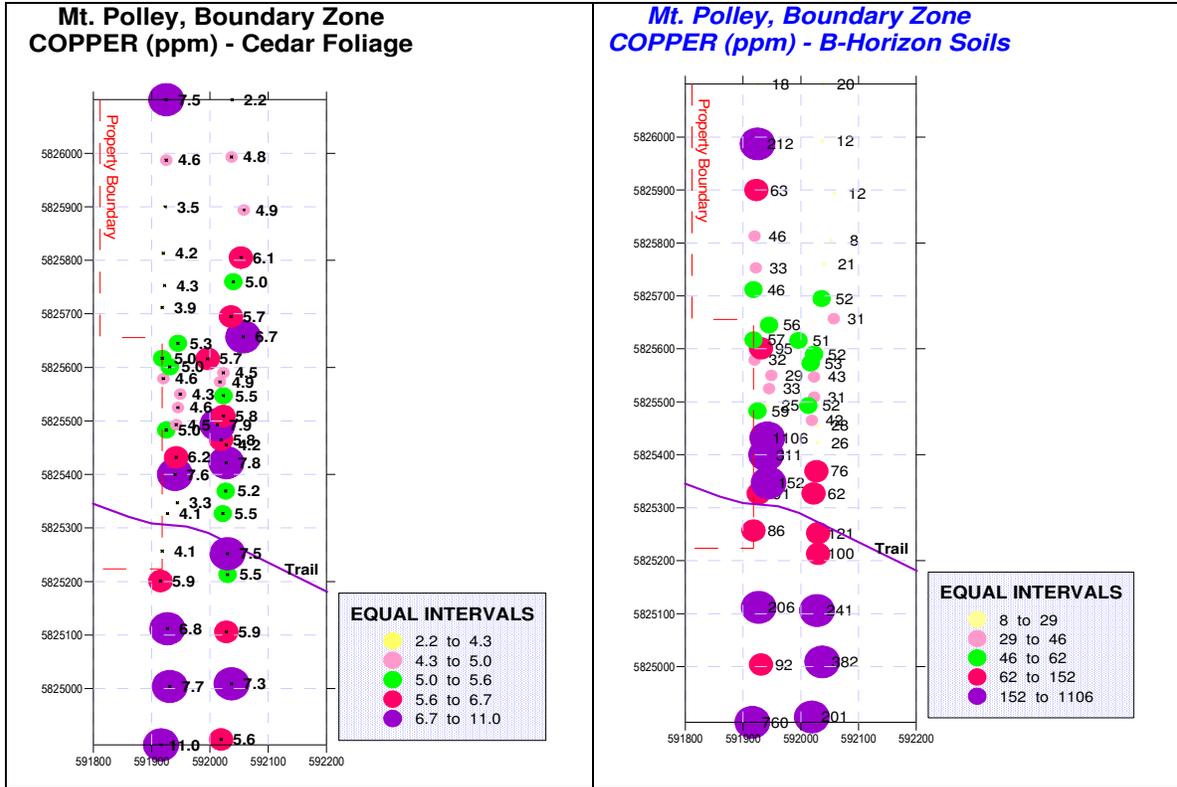
Geoscience BC

Figure 27: *Mount Polley Boundary zone extension: Cu in dry cedar foliage compared to B horizon soil.*

Figure 28: *Mount Polley Boundary zone extension: Mo in dry cedar foliage compared to B horizon soil.*
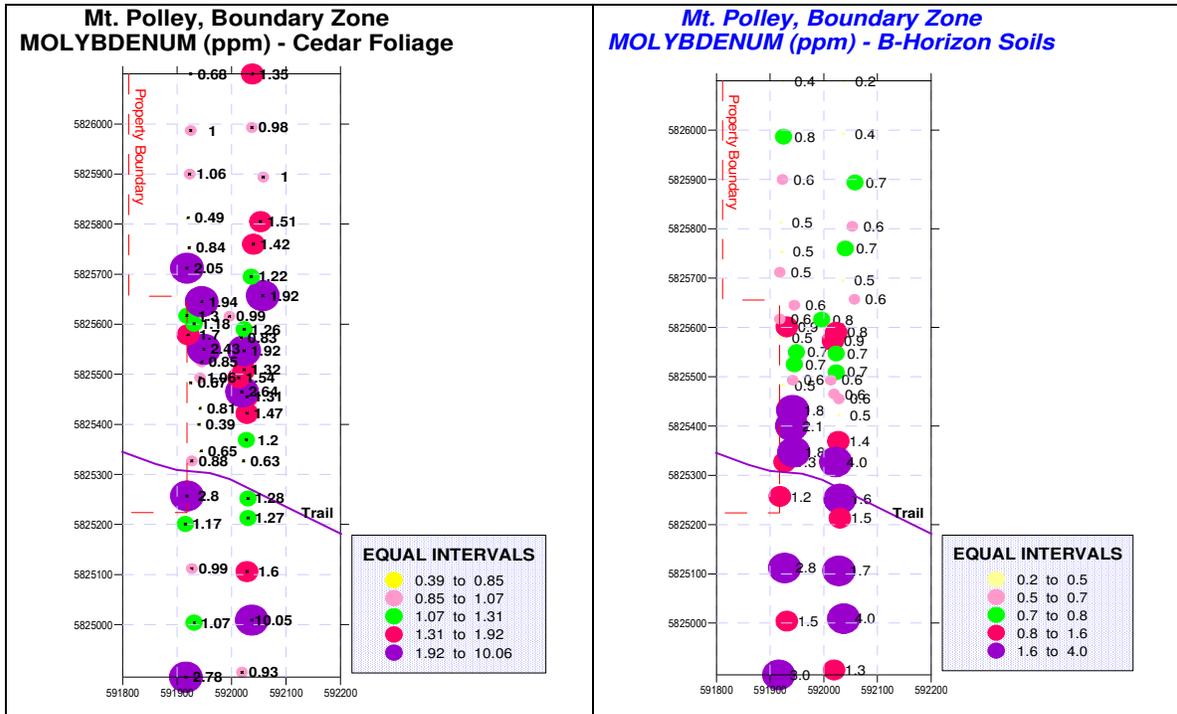
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An examination of the halogen data from the western traverse (sample sites 1 to 21 and 49 to 55, Figure 24) further confirms this observation since I concentrations are highest at the sites of the highest Au, Cu, Hg and Mo concentrations in the cedar (Figures 29 and 30).
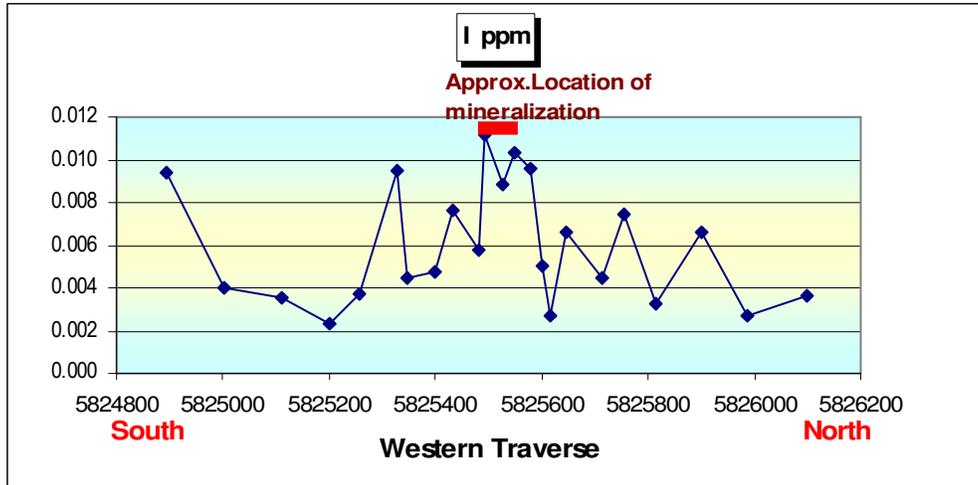
Figure 29: Mount Polley Boundary zone extension: I in cedar foliage sampled along western traverse.

The eastern traverse (Figure 30) is located 100 m to the east of the above western traverse (sample sites 23 to 48, Figure 24).
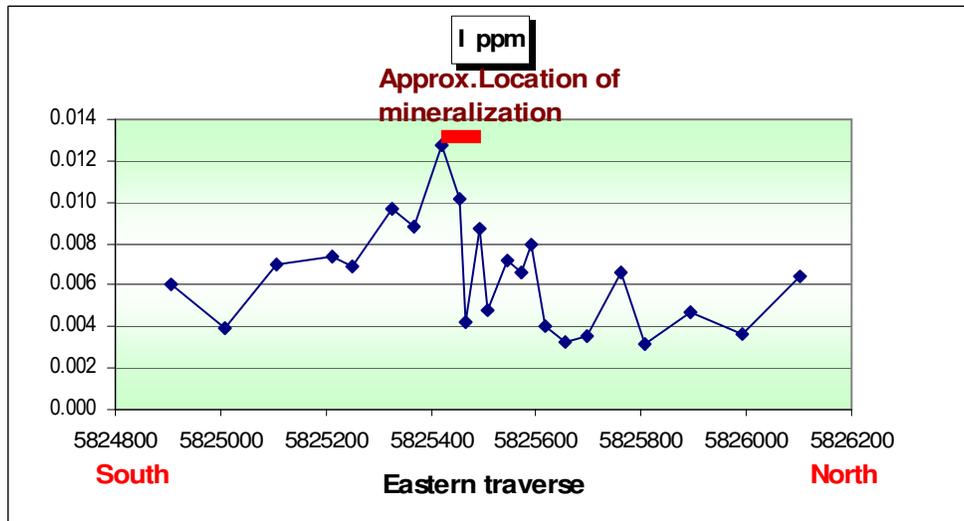
Figure 30: Mount Polley Boundary zone extension: I in cedar foliage sampled along eastern traverse.

The cedar data suggest a southeast strike to the mineralization, intersecting at 5825520 to 5825550N along the western traverse, and at about 5825400N on the eastern traverse.

In the soil, the I enrichment occurs at a single site (5825400N) on the western traverse but is not anomalous along the eastern traverse. However, F levels are elevated at and south of this location on both traverse lines (Figures 31 and 32).
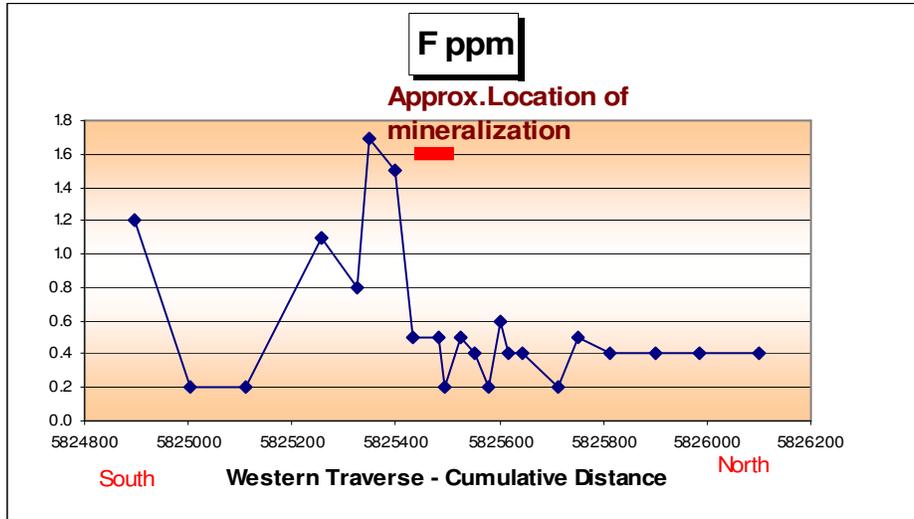
Figure 31: Mount Polley Boundary zone extension: F in soil sampled along western traverse.

The eastern traverse gives the best F signature around 5825350N (Figure 32).
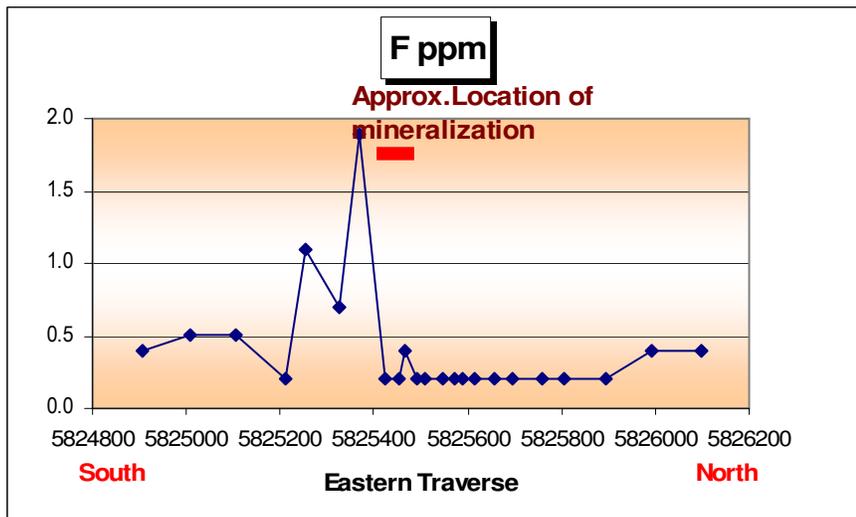
Figure 32: Mount Polley Boundary zone extension: F in soil sampled along eastern traverse.

Based on the overall geochemical patterns, it appears that mineralization may trend southeast and dip fairly steeply to the south or southwest. If this proves to be the case, the combined halogen and multielement data, especially from the vegetation, could be important information for providing fine focus to locating drill targets, with the implication that drilling costs might be reduced. Figure 33 shows the extent of the I biogeochemical anomaly. The soil anomaly (based on metal data, F values and a single I value) occurs 50 to 100 m downslope to the south.
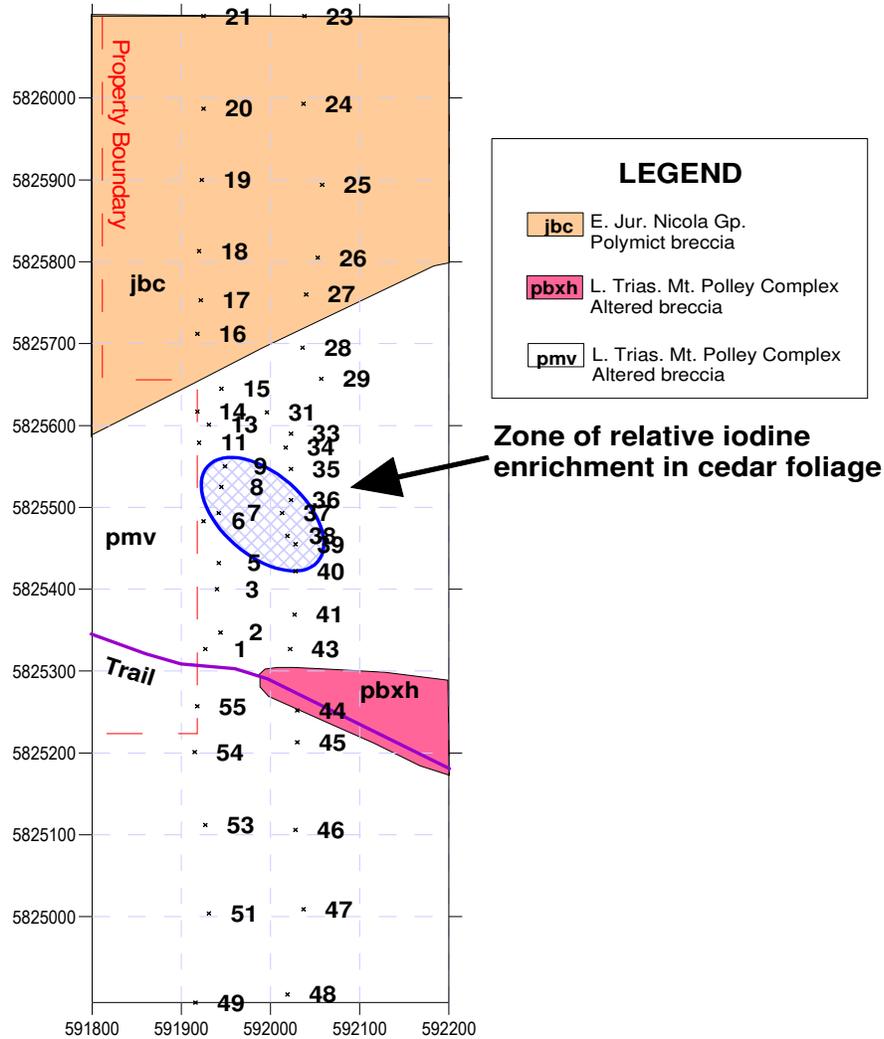
Figure 33: *Mount Polley Boundary zone extension: zone of relative enrichment of I in cedar foliage.*

Pond Zone

At the Pond zone (Figure 34), sampling was undertaken at 75 sites at 50 m intervals, along two parallel east-west lines 100 m apart. The sampling covered an area of brecciated monzonite and mineralized Triassic basalt that hosts the monzonite. The Pond zone is a garnet-magnetite skarn, mineralized with chalcopyrite, pyrite, copper, gold, silver, and geochemically anomalous levels of arsenic, cadmium and zinc. The trenched showing (Figure 34) is currently known to be 40 by at least 50 m and extends beneath a veneer of till (<1 to 3 m) to a depth of at least 110 m. To the east, geological indications are that the zone appears to be cut off by a north-trending vertical fault. Farther east, shortly past the eastern extension of the traverses, lies the Southeast zone of proven mineralization.

No vegetation remains above and immediately surrounding the trench at the Pond zone showing and the soil is disturbed, so sampling was undertaken along parallel transects above a cliff to the north of this zone The sample collection comprised B horizon soil and

foliage of subalpine fir and cedar. Spruce was rare, so relatively few samples of Engelmann spruce outer bark were collected and they have not been submitted for analysis (details in Table 5). At this time, the cedar has not been analyzed. It was considered desirable to obtain data on an additional species (the fir) since the cedar had been sampled over the Boundary zone extension.
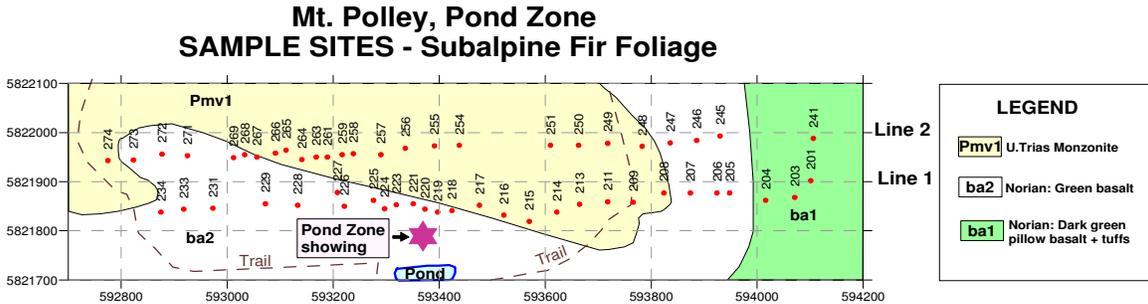
Figure 34: *Mount Polley Pond zone: simplified geology and location of subalpine fir foliage samples collected along two traverses. B-horizon soil samples were collected at the same sites, plus a few more where gaps appear between cedar samples.*

Figure 35 shows a typical soil at a site about 150 m north and 600 m east of the Pond zone showing (see sample site 206 on Figure 34 for location).

Figure 35: *Soil profile 150 m north of the Pond zone showing, Mount Polley.*

Figure 36 shows a soil profile on colluviated till near the edge of the monzonite, 400 m to the east of the Pond zone showing (sample site 209, Figure 34).

Figure 36: *Rubbly soil 400 m east of the Pond zone showing, Mount Polley.*

Table 10 presents a statistical breakdown of the analysis of the subalpine fir foliage and Table 11 gives the information from –80 mesh B horizon soil from the same sites. Elements in the fir needles that are enriched for conifer foliage in general include Au, Cu, Zn and, most notably, Re. Notable concentrations in the soil include As, Au and Cu; Re, too, is slightly elevated in the soil.

Figure 37 presents plots of selected elements along the northernmost of the two traverses. Soil is shown on the left and vegetation on the right. Of note are the peaks at the eastern end of the line: Au, Mo and Re in both media, with F in soil but not in the vegetation. A peak of Cu occurs in the soils and levels of Cu in vegetation are anomalous in the eastern area (background is usually around 8 ppm, and there is up to 14 ppm Cu present), but far less so than in the west (around 593000 to 593350E), where Cu is coincident with Au in the vegetation. The inference is that there are two different styles of mineralization present: a Cu, Au, Fe association with Cs, REE and Cd at the western anomaly, which is displaced, like that indicated at the Boundary zone extension, approximately 50 m west of the principal multielement soil anomalies (Ag, Bi, Mo, Pb, Sb, Se, Te); and a second zone of Au enrichment in the east, where the association from the soil (Co, Cr, Ni, Mg and REE, with an associated Hg and U signature) indicates a mafic substrate. The vegetation signature is predominantly Au, Mo, Pb, Li, Rb and Re.

Of note in Figure 37 are modest signatures of the commodity metals where mineralization is assumed to occur, but strong enrichments of Au, Cu, Mo and especially Re (associated with Mo) at the eastern end of the traverses. In the east, approaching the Southeast zone, there is dense cedar and fir forest but no trenching or drilling activity. The strongest halogen signatures are F in soil at the eastern end of both traverses, and I in fir near the assumed location of mineralization.

		N	Mean	Std. Dev.	Minimum	50	70	80	90	Maximum
						Percentiles				
Ag	ppb	54	7.815	5.356	3	6	7	8	14.5	36
Al	%	54	0.02	0.009	0.005	0.02	0.02	0.02	0.03	0.05
As	ppm	54	0.261	0.585	0.05	0.1	0.2	0.2	0.4	3.7
Au	ppb	54	1.363	1.275	<0.2	0.9	1.6	2.2	3.05	5.5
B	ppm	54	14.352	5.209	5	13.5	17	20	22.5	25
Ba	ppm	54	81	38	3	73	93	105	134	208
Ca	%	54	0.858	0.244	0.43	0.835	0.935	1.04	1.19	1.68
Cd	ppm	54	0.059	0.037	0.01	0.05	0.065	0.08	0.115	0.17
Ce	ppm	54	0.074	0.029	0.02	0.075	0.09	0.09	0.11	0.2
Co	ppm	54	0.117	0.046	0.04	0.11	0.135	0.15	0.17	0.28
Cr	ppm	54	1.956	0.133	1.7	2	2	2.1	2.15	2.2
Cs	ppm	54	0.065	0.113	0.006	0.032	0.056	0.078	0.154	0.779
Cu	ppm	54	11.6	4.6	4.1	10.5	12.8	14.4	16.8	33.6
Fe	%	54	0.018	0.008	0.006	0.017	0.021	0.024	0.027	0.056
Ga	ppm	54	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ge	ppm	54	<0.01	0.004	<0.01	<0.01	<0.01	0.01	0.015	0.02
Hf	ppm	54	0.002		<0.002	0.002	0.002	0.003	0.003	0.005
Hg	ppb	54	26	8	11	26	31	32	37	51
In	ppm	54	<0.02		<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
K	%	54	0.509	0.082	0.35	0.52	0.555	0.57	0.605	0.74
La	ppm	54	0.044	0.016	0.01	0.04	0.05	0.06	0.06	0.11
Li	ppm	54	0.156	0.34	0.01	0.075	0.095	0.11	0.205	2.23
Mg	%	54	0.096	0.023	0.038	0.097	0.108	0.119	0.125	0.154
Mn	ppm	54	1253	751	346	1151	1573	1894	2150	4536
Mo	ppm	54	0.139	0.09	0.05	0.125	0.145	0.17	0.21	0.54
Na	%	54	0.002		0.001	0.002	0.002	0.002	0.003	0.003
Nb	ppm	54	0.011		<0.01	0.01	0.01	0.01	0.03	0.06
Ni	ppm	54	0.717	0.292	0.3	0.7	0.8	0.9	1.05	2
P	%	54	0.152	0.025	0.099	0.15	0.163	0.168	0.18	0.233
Pb	ppm	54	0.163	0.074	0.06	0.15	0.19	0.21	0.265	0.46
Rb	ppm	54	5.3	2.4	1.1	4.8	6.15	6.9	9.45	10.9
Re	ppb	54	2.9		<1	<1	1	1	4.5	77
S	%	54	0.084	0.024	0.005	0.09	0.1	0.1	0.115	0.12
Sb	ppm	54	0.027	0.013	<0.02	0.02	0.03	0.04	0.045	0.07
Sc	ppm	54	0.235	0.059	<0.2	0.2	0.3	0.3	0.3	0.3
Se	ppm	54	0.191	0.092	<0.2	0.2	0.2	0.2	0.2	0.6
Sn	ppm	54	0.025	0.019	<0.02	0.02	0.03	0.04	0.05	0.1
Sr	ppm	54	25.961	9.05	5.6	25.05	28.1	32.8	40.15	52.2
Th	ppm	54	<0.01		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ti	ppm	54	9.907	2.467	5	10	11	12	12.5	20
Tl	ppm	54	0.024	0.016	<0.02	0.02	0.03	0.04	0.05	0.07
U	ppm	54	<0.01		<0.01	<0.01	<0.01	<0.01	<0.01	0.01
Y	ppm	54	0.045	0.017	0.013	0.043	0.052	0.058	0.066	0.116
Zn	ppm	54	47	16	12	47	55	58	66	90
Zr	ppm	54	0.037	0.013	0.02	0.03	0.04	0.05	0.05	0.09

Table 10: *Mount Polley Pond zone: statistical summary of data obtained from digestion of dry subalpine fir foliage in nitric acid and aqua regia with analysis by ICP-MS (Acme Analytical Laboratories method 1-VE-MS).*

		N	Mean	Std. Dev.	Minimum	Percentiles				Maximum
						50	70	80	90	
Ag	ppb	60	282	235	67	227	287	392	486	1732
Al	%	60	1.766	0.518	0.92	1.71	1.987	2.242	2.536	2.98
As	ppm	60	5.9	3.0	2.2	4.9	6.7	7.5	11.4	16.3
Au	ppb	60	15	22	-0.2	7.4	15.4	21	41	149
B	ppm	60	2.3	0.9	1	2	3	3	4	5
Ba	ppm	60	107	39	41	107	118	131	160	238
Be	ppm	60	0.42	0.15	0.2	0.4	0.5	0.6	0.6	0.9
Bi	ppm	60	0.17	0.12	0.07	0.13	0.17	0.21	0.26	0.7
Ca	%	60	0.388	0.196	0.17	0.34	0.407	0.478	0.629	1.36
Cd	ppm	60	0.22	0.11	0.09	0.2	0.25	0.28	0.39	0.59
Ce	ppm	60	17	4	10.2	16.7	18.2	19.5	21.3	33.1
Co	ppm	60	10.2	3.5	4.5	9.7	10.8	11.7	16.5	21.6
Cr	ppm	60	31	9	18	29	33	38	45	57
Cs	ppm	60	2.8	2.6	0.76	1.89	2.75	3.22	6.37	15.30
Cu	ppm	60	72	102	11	41	63	85	152	652
Fe	%	60	3.053	0.783	1.86	2.875	3.308	3.75	4.083	5.65
Ga	ppm	60	6.2	1.5	3.8	6.1	6.8	7.5	8.7	10.0
Ge	ppm	60			-0.1	-0.1	-0.1	-0.1	-0.1	0.1
Hf	ppm	60	0.048	0.022	-0.02	0.049	0.06	0.068	0.08	0.11
Hg	ppb	60	39	19	9	39	47	51	61	119
In	ppm	60	0.02	0.02	-0.02	0.02	0.02	0.03	0.03	0.04
K	%	60	0.084	0.031	0.04	0.08	0.1	0.1	0.119	0.19
La	ppm	60	9.6	1.6	6.2	9.5	10.4	11.1	11.7	13.8
Li	ppm	60	18.6	5.2	7.9	18.2	20.1	22.1	27.2	30.9
Mg	%	60	0.482	0.215	0.17	0.45	0.524	0.598	0.767	1.22
Mn	ppm	60	620	374	237	479	701	851	1165	1881
Mo	ppm	60	1.7	1.6	0.5	1.1	1.5	2.3	4.2	7.2
Na	%	60	0.008	0.004	0.005	0.007	0.008	0.009	0.01	0.031
Nb	ppm	60	0.83	0.17	0.50	0.80	0.92	0.98	1.10	1.25
Ni	ppm	60	18.4	8.4	6.6	17	21	23	31	51
P	%	60	0.104	0.057	0.032	0.089	0.111	0.134	0.204	0.292
Pb	ppm	60	7.0	2.1	4.5	6.5	7.1	8.0	10.6	13.9
Pd	ppb	60	-10	0	-10	-10	-10	-10	-10	-10
Pt	ppb	60	-2		-2	-2	-2	-2	2	2
Rb	ppm	60	13.4	4.1	7.1	13.3	14.5	16.2	20.3	23.8
Re	ppb	60		1.9	-1	-1	-1	-0.39	1.9	7
S	%	60	0.011	0.045	-0.01	0.01	0.01	0.018	0.03	0.31
Sb	ppm	60	0.29	0.08	0.15	0.28	0.33	0.36	0.41	0.52
Sc	ppm	60	3.2	1.4	1.6	2.9	3.3	3.68	4.27	10.7
Se	ppm	60	0.36	0.39	-0.1	0.2	0.387	0.48	0.7	2.2
Sn	ppm	60	0.45	0.14	0.3	0.4	0.5	0.5	0.6	1.2
Sr	ppm	60	58	39	19	44	57	77	109	232
Ta	ppm	60		0	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Te	ppm	60	0.013	0.029	-0.02	0.02	0.03	0.03	0.05	0.09
Th	ppm	60	2.06	0.50	0.7	2.08	2.4	2.5	2.69	3.1
Ti	%	60	0.103	0.039	0.049	0.094	0.112	0.123	0.148	0.276
Tl	ppm	60	0.07	0.03	0.03	0.07	0.08	0.10	0.11	0.18
U	ppm	60	0.42	0.12	0.2	0.4	0.4	0.5	0.5	1
V	ppm	60	84	22	49	80	88	99	111	158
W	ppm	60	0.14	0.16	-0.1	0.1	0.2	0.2	0.39	0.6
Y	ppm	60	3.4	1.7	1.6	3.0	3.4	3.9	4.7	12.9
Zn	ppm	60	98	38	49	86	120	131	152	197
Zr	ppm	60	2.1	0.7	0.8	1.9	2.3	2.5	3.0	5.2
pH		59	5.1	0.5	4.3	5.1	5.2	5.4	5.8	6.4

Table 11: *Mount Polley Pond zone: statistical summary of data obtained from aqua regia digestion of –80 mesh B-horizon soil samples (30 g) with analysis by ICP-MS (Acme Analytical Laboratories method 1-F).*
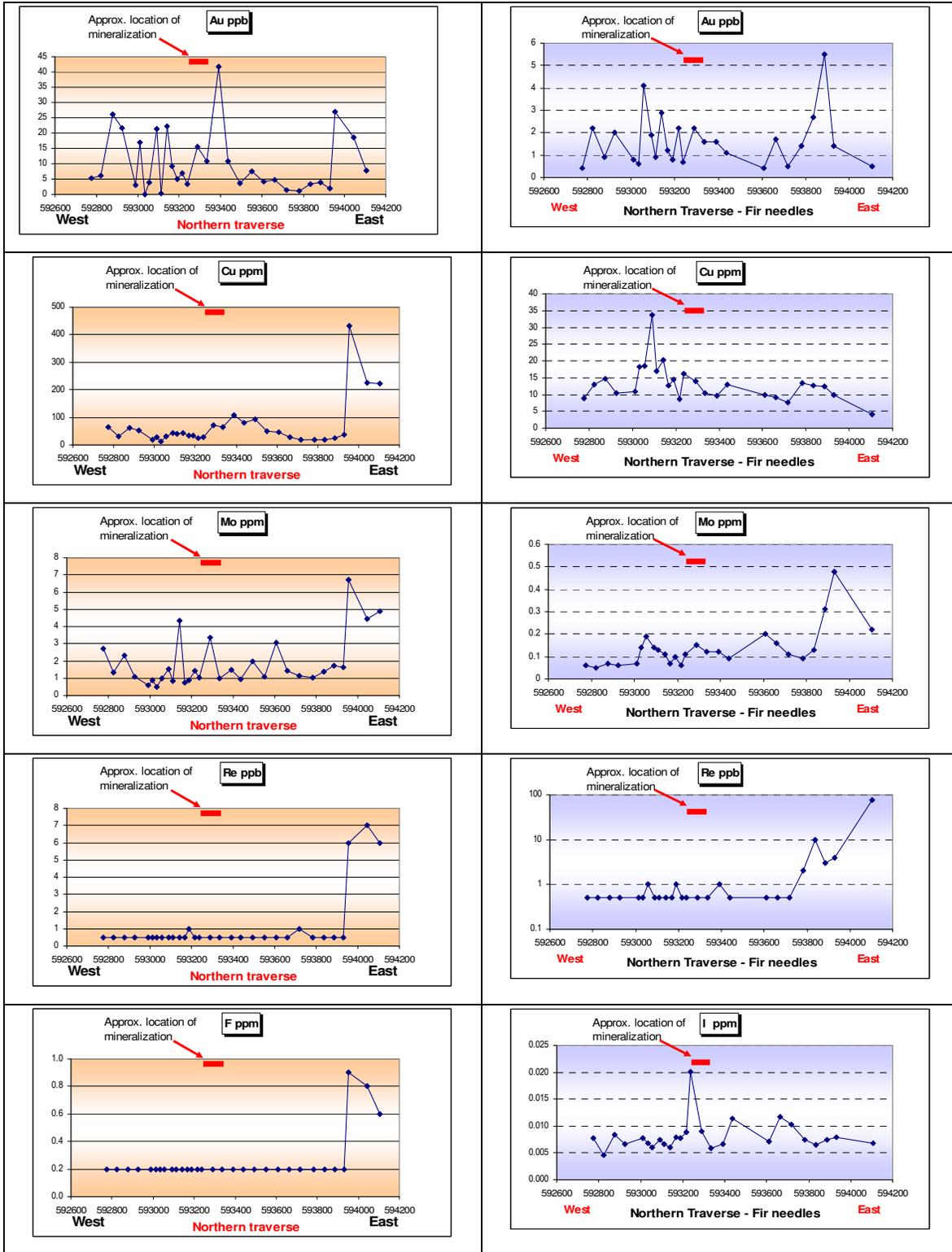
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Figure 37: *Mount Polley Pond zone: concentrations in soil and foliage of subalpine fir along the northern west-east traverse (soil in left column, subalpine fir needles in right column). Note that Re in fir is shown on a log scale because of the strong background/anomaly contrast (maximum of 77 ppb Re with background of <1 ppb Re).*

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Based upon these patterns, there is an indication that mineralization may trend northwestward. Figure 38 shows the interpreted zones of mineralization, based primarily on a combination of data from soil and fir, considering both the halogen and multielement data. The western ellipse, with the dashed line, is outlined because of Cu-Au enrichment in the fir foliage, coincident with Cl and subtle F anomalies and some subtle enrichment of Cd, Cs, Hg, Ni, Rb, Se and Tl in the fir at about 593200E on the northern traverse. This element assemblage suggests a different style of mineralization from that at the Pond zone showing.
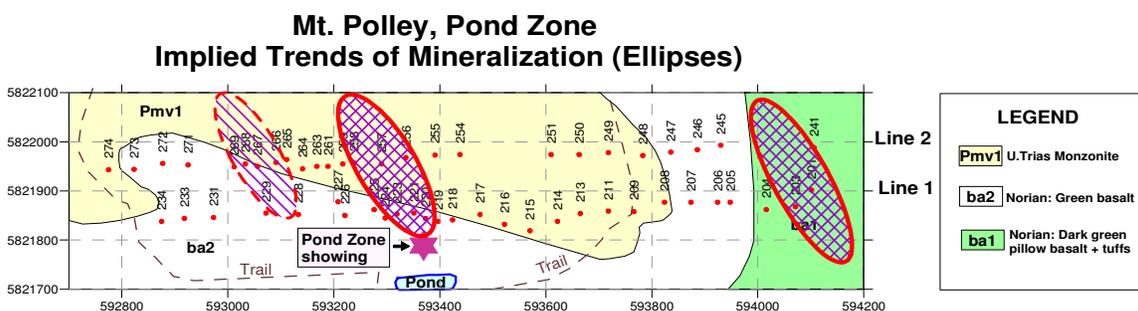
Figure 38: *Mount Polley Pond zone: trends of mineralization interpreted from the geochemical data.*

QR Deposit

Three areas of the QR deposit were sampled, each with variable Quaternary cover (up to several metres thick) over volcanic rocks:

- *Main zone:* Douglas-fir needles and top stems were collected in 1988. Analyses of the dry needles confirm a previously identified Au anomaly in stem ash. The halogens in these needles do not clearly outline known mineralization, yielding only a modest enrichment of I close to the Main and North zones of mineralization.

- *Eastern IP zone:* To the northeast of the Main zone, there is an induced polarization (IP) anomaly in an area with little outcrop. Analysis of soil, spruce (*Picea engelmannii*) needles and pine (*Pinus contorta*) bark from over this area show a peak of I and Cl at the site of a magnetic anomaly, whereas F values are higher over breccia than the basalt. The thickness of the volcanic cover is unknown.

- *Cariboo zone:* This third Au target has rare outcrop. Soil chemistry indicates three zones of multielement enrichment involving Ag, Au, Bi, Cu and Hg. Only the northern zone includes a Mo signature. Iodine and Br in the soil clearly delineate the three zones of multielement enrichments, whereas Cl delineates only the north and south zones and F only responds at the central zone with a subtle signature. Halogens in the vegetation are less definitive.

Analysis of Archived Needles from Douglas-fir Treetops

Analysis of the dry needle tissue confirmed and refined the original anomalies identified from analysis of the top stems (Dunn and Scagel, 1989). Previously, data were obtained from only a few samples of the needles. The correspondence of the anomalies in the dry needles (Figure 39; by ICP-MS) compared to the ashed top stems (Figure 3; by INAA) confirms and validates the robustness of the geochemical signature, and in fact enhances the relationship of the biogeochemical signature to the subcropping mineralization at

either end of the West zone. New data from the northern extension of the principal anomaly does not indicate an extension to the north. However, the multielement dataset shows that, in general, there are quite substantial differences between needles from the treetops collected in 1988 and those from the lower branches that were collected in 2005. There is no systematic increase or decrease of elements that might be attributed to either contamination from mining activities or long-term natural variations in plant chemistry. The complications arising from trying to compare needles from the tops of trees with those from lower branches collected 17 years later and at a different time of the year appear to be quite substantial. As a result, no further consideration is given here to the few samples of needles collected in 2005 from the area to the north of the 1988 sample collection.
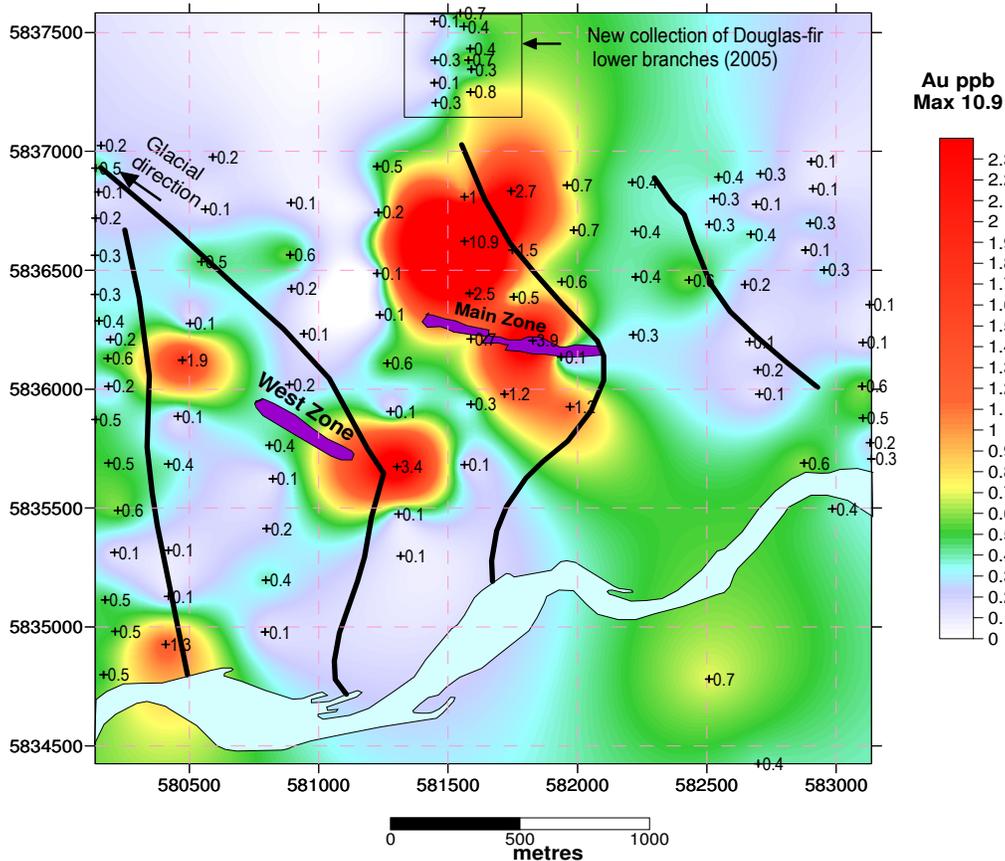
Figure 39: *QR: Au in dry Douglas-fir needles from treetops, with cluster of samples in the north showing results of new data from lower branches.*

The archived collection of needles was analyzed for the multielement and halogen content (Table 2-5, Appendix 2). As with the original analysis of treetop stem data in 1988, Au remains the only element to present a clear anomalous pattern of enrichment with respect to the zones of known mineralization. The halogens do not clearly outline known mineralization: there is a modest enrichment of I close to the Main and North zones (Figure 40) but with anomalies of similar magnitude in the northwest and northeast parts of the survey area. No further consideration is given to these data in this report.

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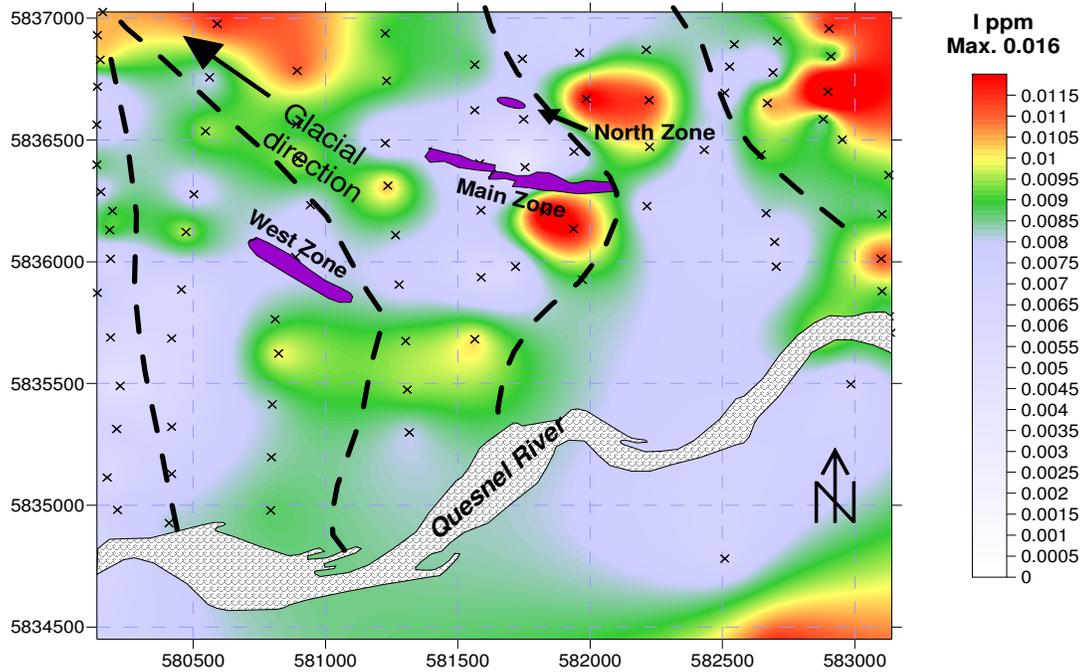## QR - Treetops
IODINE in Douglas-fir Needles

Figure 40: *QR: I in Douglas-fir needles (1988 archived collection).*

Eastern IP Zone

Two traverses were conducted to collect soil and spruce foliage from north-south lines approximately 500 m east of the Main zone anomaly (Figures 3, 17 and 39). These lines were selected because of the presence of an IP anomaly of unknown origin. Company maps indicate an approximate contact between breccia, south of about 10500, with basalt to the north, but no mineralization is known to occur. There is little outcrop and the only other mapped features are small magnetic anomalies between 10700 and 10800 on each transect. The breccia-basalt contact (red dashed line) and magnetic anomalies (red box) are shown on the charts embedded in the spreadsheets of Tables 2-6, -7, -8 and -9 (Appendix 2).

Figure 41 shows plots of I, Cl and F in soil, spruce needles and pine bark. Most media show a peak of I and Cl at the site of the magnetic anomaly, whereas F values are mostly higher over the breccia rather than basalt.

Of the trace metals, the soil has Au enrichment at 10600, and Cu enrichment close to the breccia/basalt contact about 100 m to the south. The pine bark indicates subtle Au, Cu and Bi enrichment in the same area (Figure 42), but the spruce needles (not shown), because of their lesser ability to absorb most trace metals, have levels close to background.
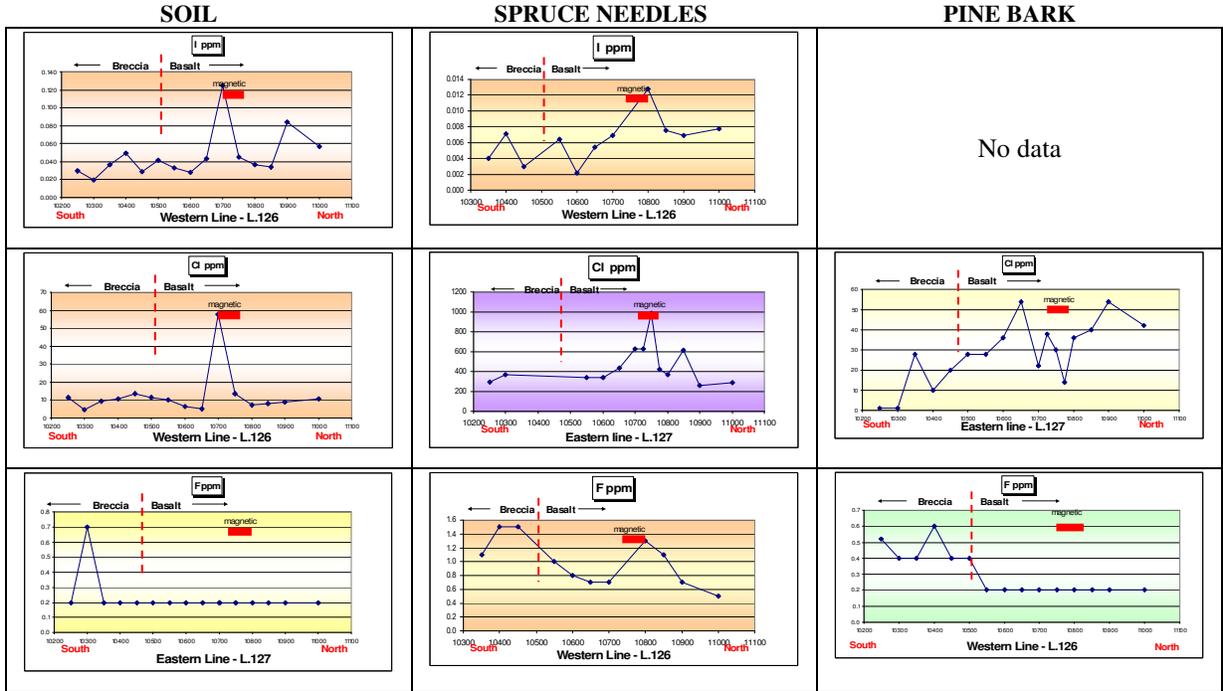
Figure 41: *QR Eastern IP zone: I, Cl and F in soil, spruce needles and pine bark.*
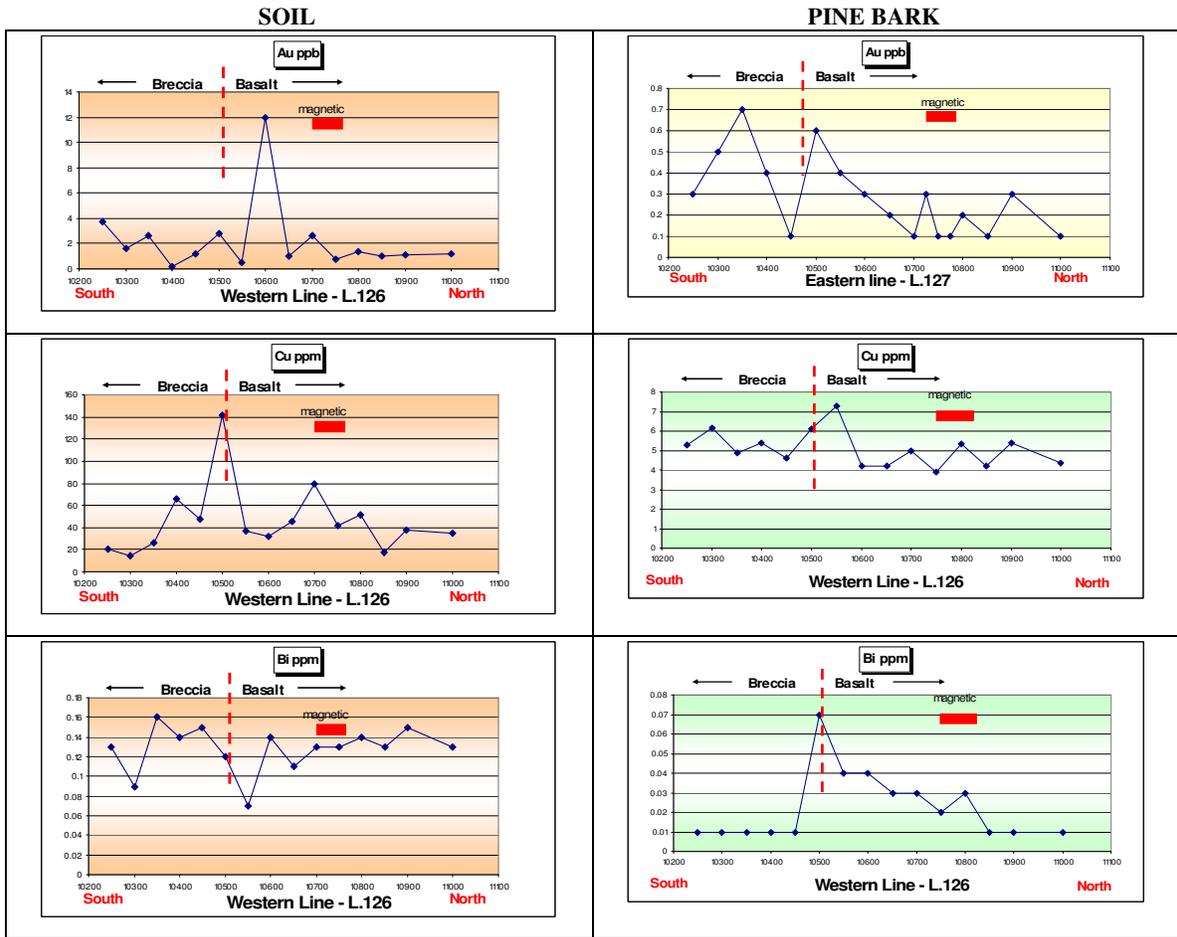

Figure 42: *QR Eastern IP zone: Au, Cu and Bi in soil and pine bark.*

Several elements in the various sample media indicate enrichments over the magnetic zones, notably Au with unusually high levels of Hg in pine bark (Figure 43).
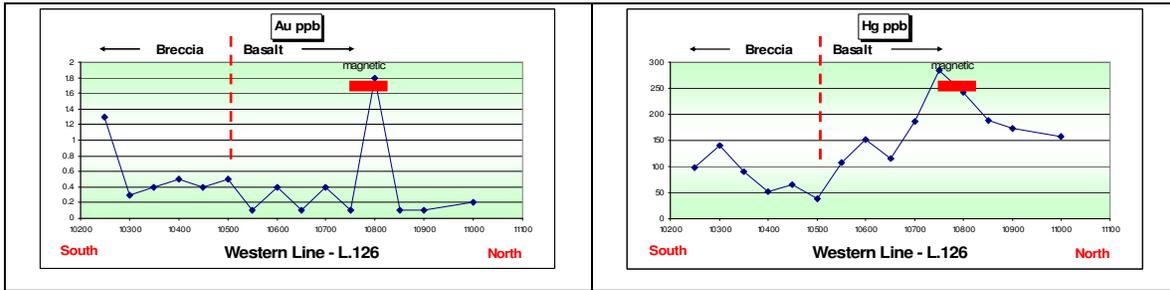

Figure 43: QR Eastern IP zone: Au and Hg in pine bark.

Data from the spruce needles show the usual quite low levels of trace metals. They were selected for this project because spruce was the only common species from which foliage could be collected in this area, and because the literature has indicated that foliage is more likely than woody tissue to yield enrichments of the halogens. This study has shown, however, that except for Cl this is not necessarily the case.

Cariboo Zone

The third area of study in the vicinity of the QR deposit lies 6 km to the east. Since this area has undergone little disturbance, it was selected for a single 1400 m north-south traverse along line 58E (588140E, 5832000 to 5833400N). The area is dominated by Engelmann spruce with scattered lodgepole pine and a dense understorey with thimbleberry (*Rubus parvifloris*) and alder (*Alnus sitchensis*) shrubs (Figure 44). In addition to the soil, the media selected for sampling were spruce needles and pine bark. Pine was only present at 13 of the 23 sample sites, and so the pine bark samples have not been processed.
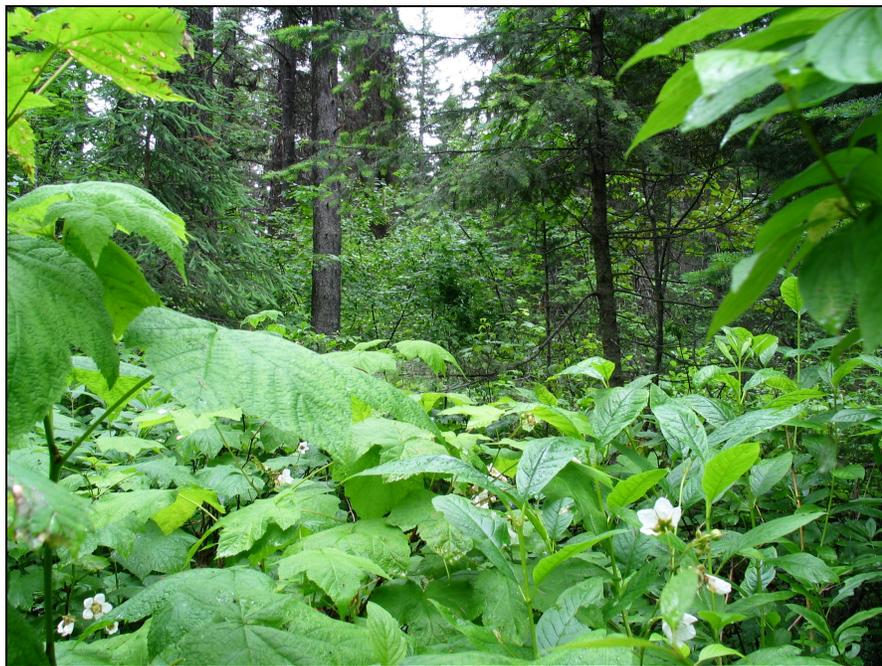

Figure 44: View of spruce and pine along 58E in Cariboo zone, with dense understorey.

Outcrop in this area is rare and along the line selected for sampling just three very small dioritic outcrops are mapped. Cross Lake Minerals has outlined coincident geochemical and geophysical anomalies at three zones along the line selected for sampling (58E), and they report that Au mineralization may occur in two modes: the first in quartz veins and shears within mafic tuff; the second as Cu-Au-Mo in an intrusive body (probably dioritic or gabbroic). They indicate that in the survey area, a cover of basalt is intruded by mafic plutons and there is an extensive veneer of till.

Profiles of selected soil data are shown in Figure 45. In accordance with the studies by Cross Lake Minerals, the soil data indicate three zones of multielement enrichment involving Ag, Au, Bi, Cu and Hg, among others. The central zone is subtle with respect to Ag, Au and Bi, but has a strong Hg and Cu signature. Only the northern zone includes a Mo signature and enrichment is spatially marginal to the peaks of concentration for the other metals.
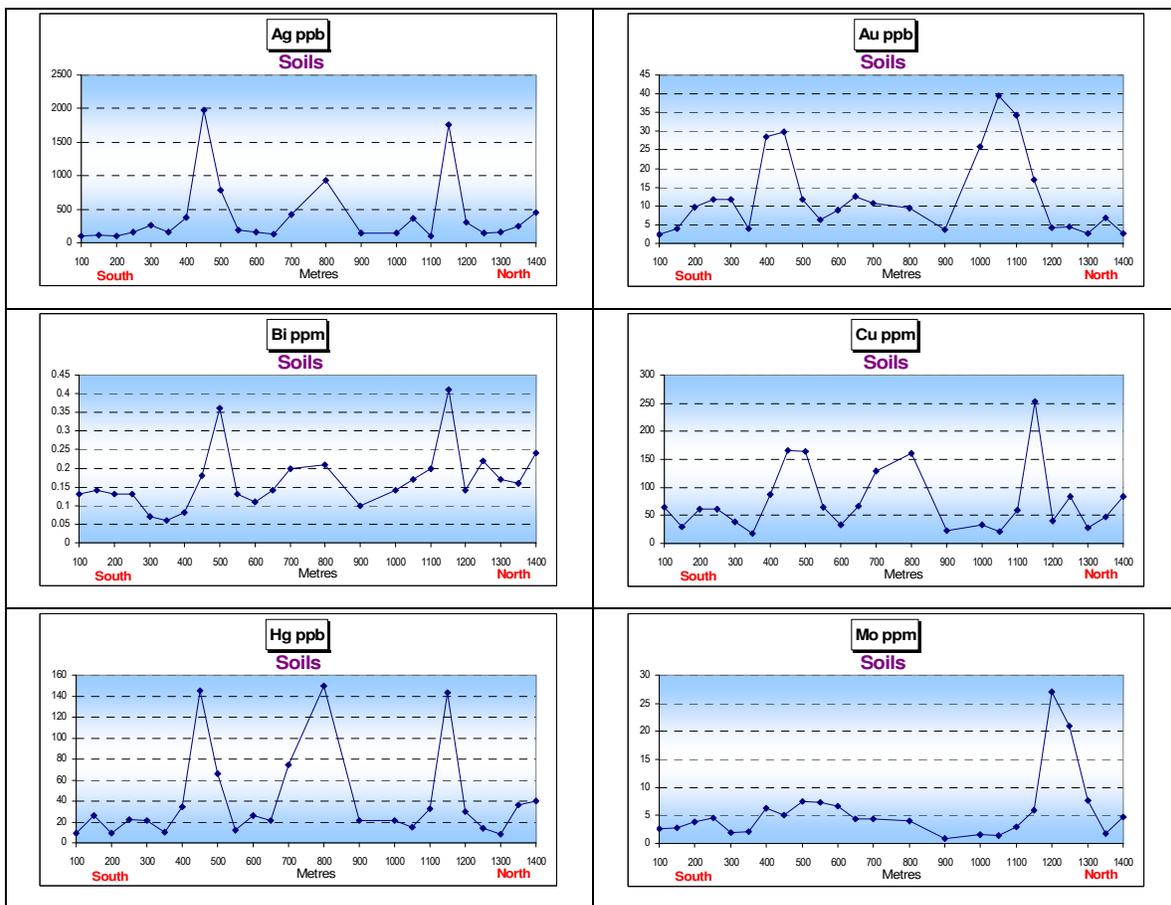
Figure 45: *QR Cariboo zone: examples of multielement signatures in B horizon soil.*

The multielement signatures in the spruce needles are mostly more subtle than those from the soil, and the anomalies that do occur are displaced from those of the soil by approximately 50 m. Figure 46 presents examples of a few elements.
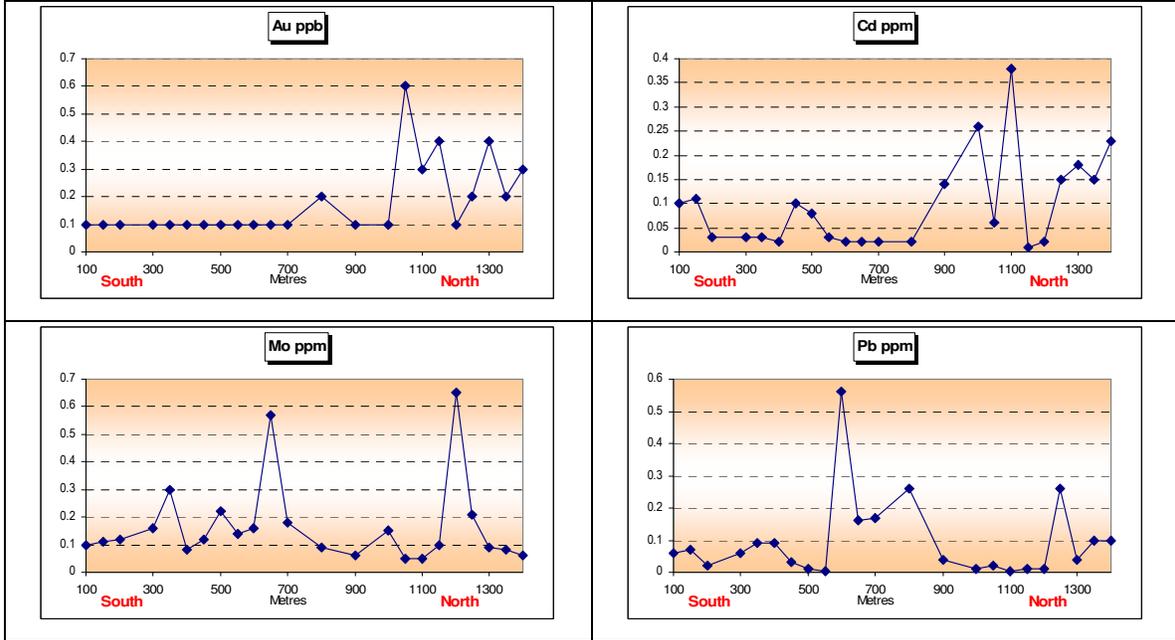
Figure 46: *QR Cariboo zone: Au, Cd, Mo and Pb concentrations in dry spruce needles.*

Iodine and Br in the soil clearly delineate the three zones of multielement enrichments, whereas Cl delineates the north and south anomalies and F only delineates the central anomaly with a very subtle signature (0.5 ppm F compared to a background level of <0.4 ppm; all other samples plot as 0.2 ppm, half the detection limit; Figure 47).
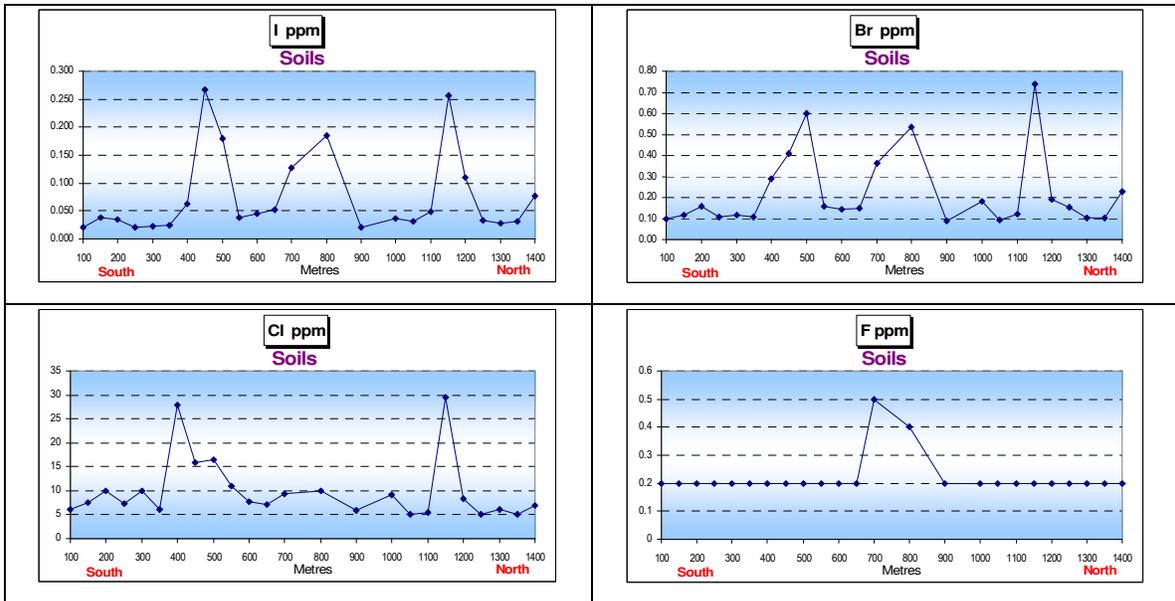

Figure 47: *QR Cariboo zone: halogens in soil.*

Halogens in the spruce needles do not display clear patterns, with Cl providing the best signatures over the central zone, and I giving only a weak and diffuse response (Figure 48).
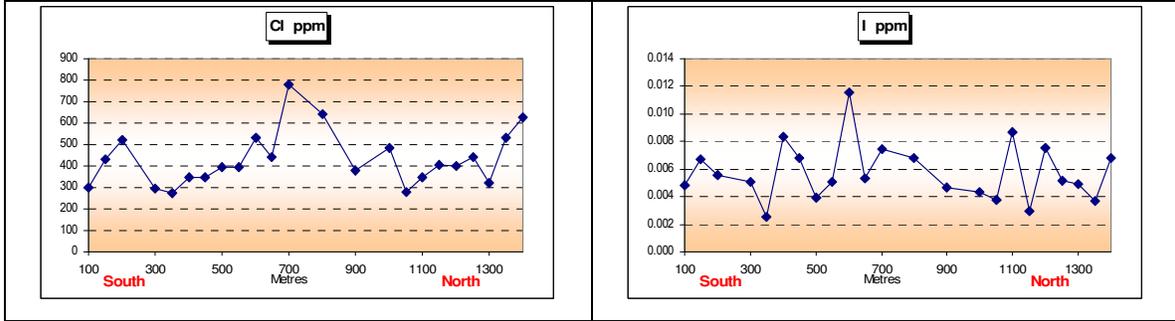
Figure 48: *QR Cariboo zone: Cl and I in spruce needles.*

3Ts Prospect

As noted above, the 3Ts prospect was the focus for another Geoscience BC project involving detailed soil studies of all soil horizons and their analysis by a broad range of methods (Cook and Dunn, 2006, 2007). With regard to the halogen project, in addition to B horizon soil, white spruce needles and lodgepole pine bark were selected for multielement and halogen analysis. Fieldwork at 3Ts was complicated by the fact that just prior to conducting the sampling program, easy access to the field area had been made impossible by decommissioning of the only good quality trail. Minor trails required the use of all-terrain vehicles.

It is an area of rolling hills, small lakes, ponds and minor wetland areas ranging in elevation from 1065 to 1250 m asl. Quartz veining and associated alteration systems are relatively resistant to weathering and locally form small but prominent ridges between Tommy Lake to the northwest and Adrian Lake to the southeast (Figure 49). The geological substrate to the two sample collection traverses is Middle Jurassic Hazelton Group rhyolitic pyroclastic rocks over which there is a till and/or colluvial cover that is generally less than 1 m thick. Figure 49 shows the lithological contacts as mapped by Diakow and Webster (1994) and Diakow et al. (1994, 1995a, b). Subsequent work has suggested that the lowermost unit of the Naglico Formation (felsic volcanic rocks shown as 'Nr' on Figure 49) should be ascribed to the underlying Entiako Formation, Hazelton Group (Diakow and Levson, 1997).

Tommy Vein to the Ringer Showing

The Tommy traverse extends from west of the Tommy vein eastward to the Ringer showing (Figure 49). As noted, soil samples were only collected along the western third of the traverse (i.e., to about 200 m east of the Larry vein). Details of their multifaceted analyses are in Cook and Dunn (2006, 2007). Details of the B-horizon soil analysis discussed in the present account are shown in Table 2-12 (Appendix 2). The soil response of the four halogens to the mineralized veins is shown in Figure 50. Whereas there is a positive response for Br and I, this is not present for either Cl or F. Fluorine shows highest values to the west of the Ian vein where there is bedrock alteration.
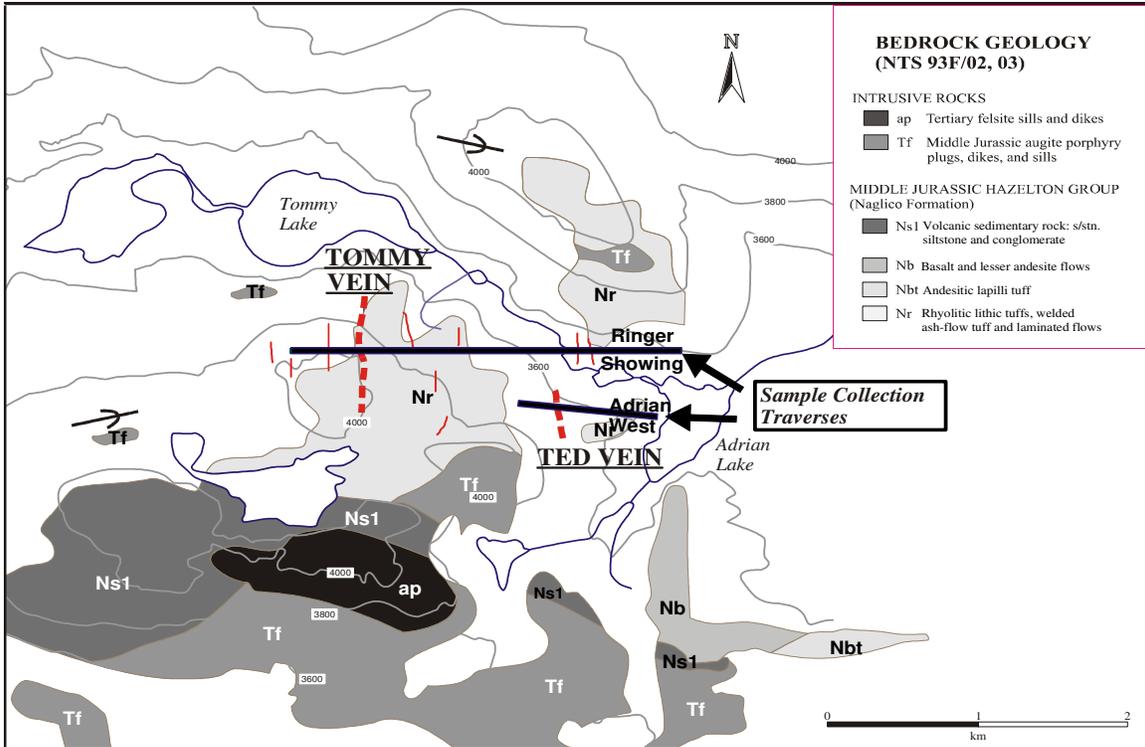
Figure 49: *3Ts: general geology, topography and location of the traverses for the vegetation sample collection (geology modified after Diakow and Webster, 1994 and Diakow et al., 1994, 1995a, b). The soil transect along the Tommy vein extended only along the western one-third of that line. Note also that Unit Tf has recently been dated by J. Mortensen to be a Late Cretaceous microdiorite intrusion (L. Bottomer, pers. comm., 2005).*
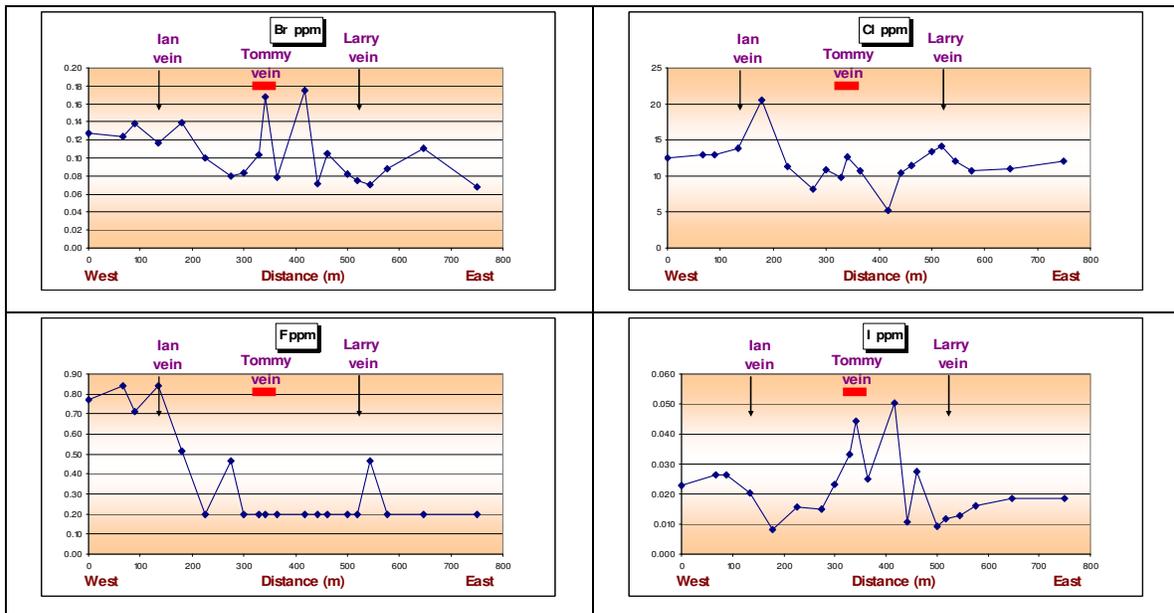

Figure 50: *3Ts Tommy traverse: halogens in soil.*

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Vegetation coverage is primarily white spruce and lodgepole pine that has suffered from mountain pine beetle kill. Typical forest is shown in Figure 51. Both the spruce needles and outer bark of the pine have been analyzed and results are contained in Tables 2-13 and -14 (Appendix 2), respectively. The foliage was originally selected as the priority medium for the halogens, but subsequent data on test samples of bark have yielded relatively high concentrations of I, so the bark samples were also submitted for analysis.

Figure 51: *3Ts Tommy traverse: typical spruce and pine forest.*

Near the west end of the Tommy traverse, a number of veins have been recognized and both the pine bark and spruce needles indicate subtle enrichment of several elements throughout this zone in general, with some elevated levels closely related to the principal veins (Tommy and Larry) and, to a lesser extent, the narrower Ian vein. Farther east, the Mint vein was traversed and it, too, generates a subtle multielement biogeochemical signature. Figure 52 shows Ag in both vegetation media, with a plot of Li in spruce, and Ba, Sr and Sb in bark. These elements are relatively enriched at sites just east of the Mint vein where there are also enrichments of Ba, Sr, Pb and Ni (Tables 2-13 and -14, Appendix 2), of which the Ba and Sr suggest the presence of carbonate rocks.

Iodine and F in the pine bark are both slightly enriched east of the Mint vein with a more prominent F peak at the Ringer showing (Figure 53). The I peaks help pinpoint the potential target at between 1800 and 1850 m along the traverse (365120 and 365170E; Table 2-13, Appendix 2). Spruce needle data for Ba and Sr (Table 2-13, Appendix 2) also suggest another zone of carbonate rocks at around 2075 m (365370E). Whereas the source of the boulders that constitute the Ringer showing has yet to be identified, these sites of multielement enrichments between the Mint vein and the Ringer showing could be indicating a source of mineralization.
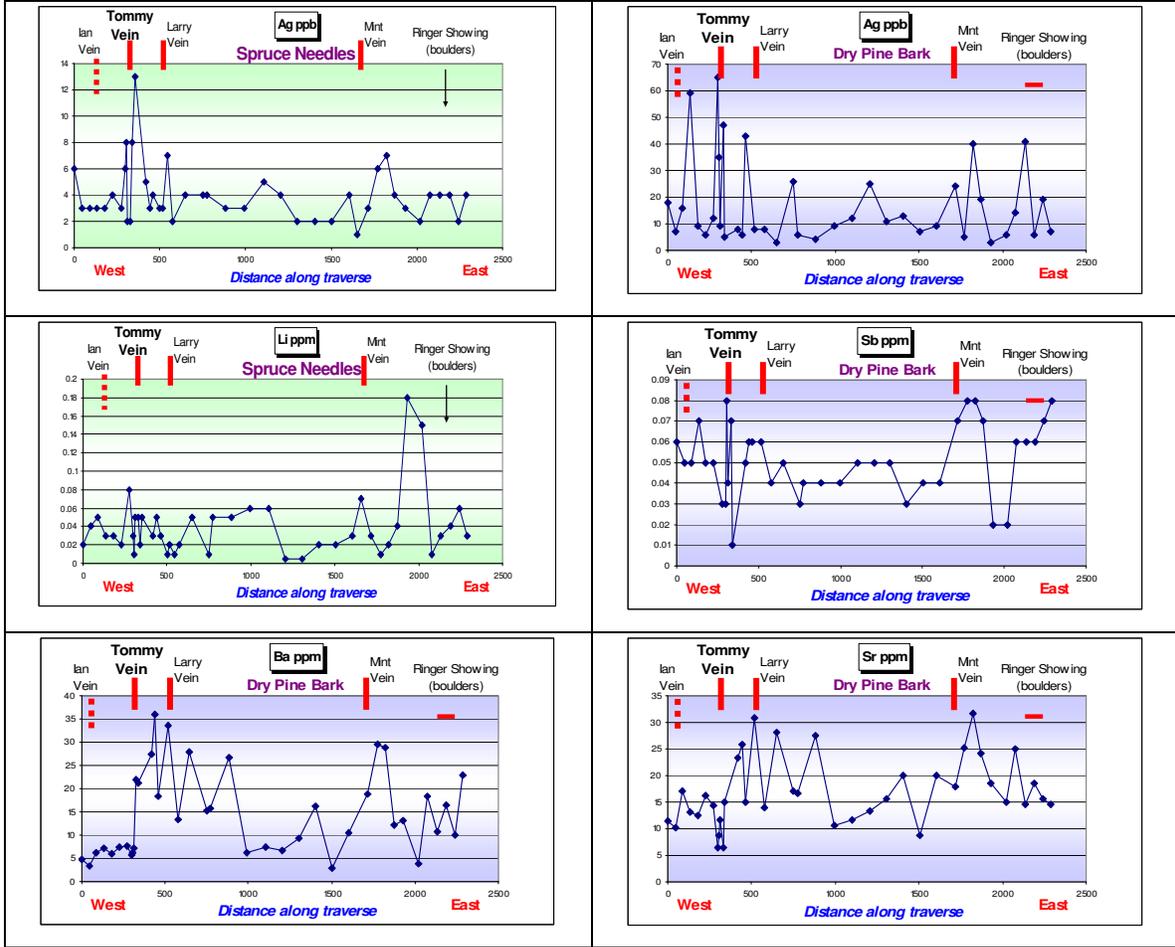
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Figure 52: *3Ts Tommy traverse: concentrations of selected elements in dry spruce needles and pine bark.*
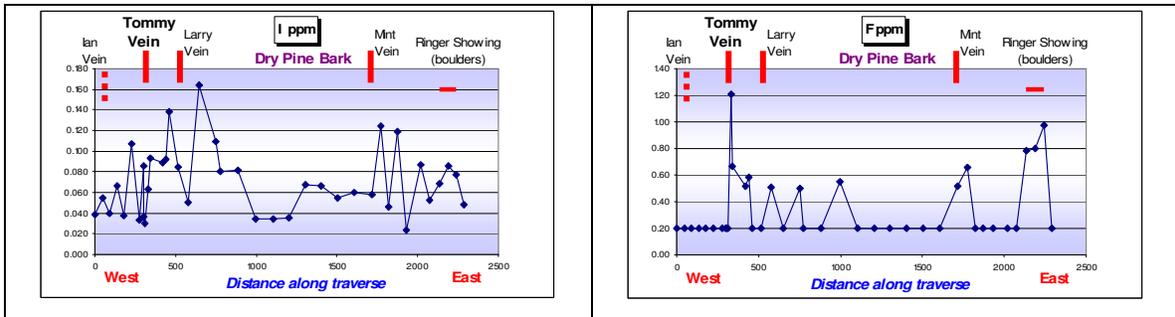

Figure 53: *3Ts Tommy traverse: I and F in dry pine bark.*

Of interest is a sharp increase in Mo at the eastern extremity of the traverse. This is evident from both the spruce foliage and the pine bark (Figure 54), but with the bark yielding almost an order of magnitude more Mo. In this area, other elements showing strong enrichment in the bark include Cr, Ni, REE, Sb, U and Zn (Tables 2-13 and -14, Appendix 2). The enrichment suggests either a change in bedrock or, given the high

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concentrations in the bark, Mo mineralization. The Ted traverse to the south also shows Mo enrichment at the eastern end of the traverse, near Adrian Lake (see section below).
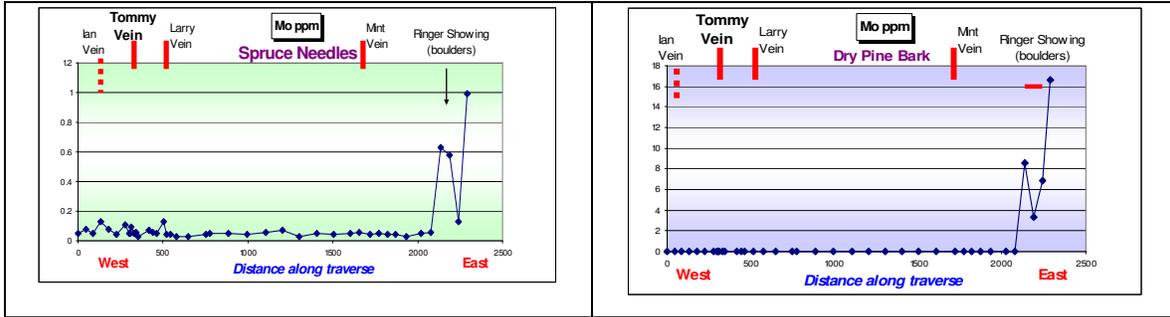

Figure 54: *3Ts Tommy traverse: Mo in spruce needles and pine bark.*

Ted Vein to Adrian West Boulders

Soil and the same plant species and tissues as those from along the Tommy vein traverse were collected along the Ted traverse extending from just west of the Ted vein to the southern edge of the boulder showing near Adrian Lake (Figure 49). The halogens in soil are shown in Figure 55, from which it can be seen that, except for I, there is generally a rather diffuse response to the Ted vein, and F is only elevated at the eastern end of the line along strike from the F anomaly of the Tommy traverse (Figure 53).
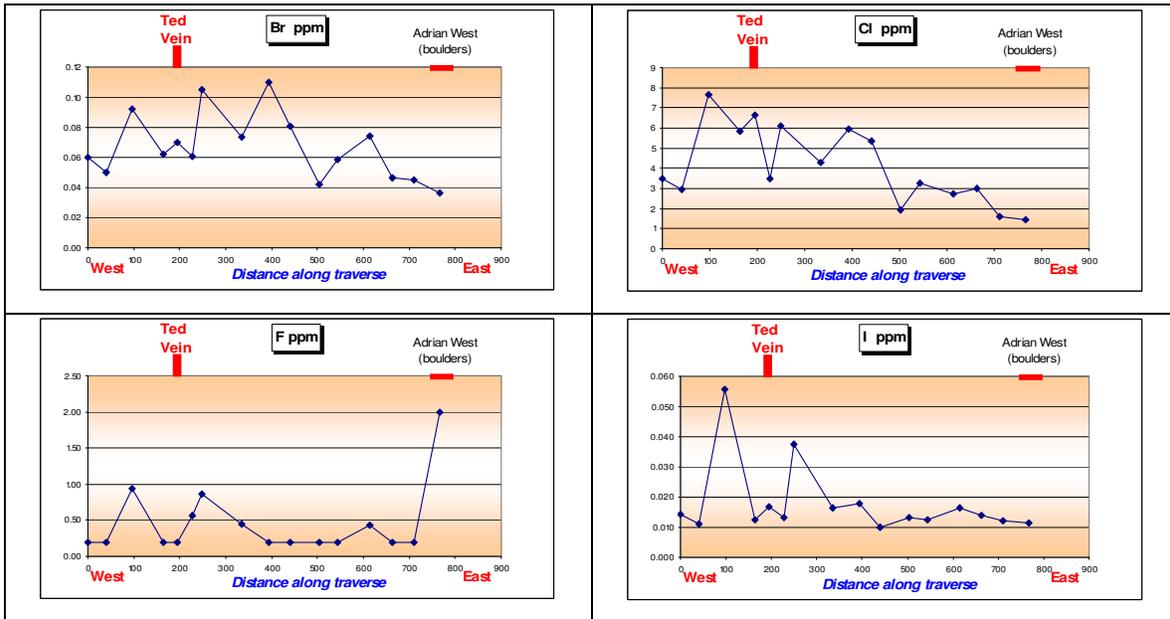

Figure 55: *3Ts Ted traverse: halogens in soil.*

At the Ted vein, the soil shows a strong response in Ag, Au, Cd, Mn, Pb, Sb, Tl and Zn (Table 2-15, Appendix 2). Copper is enriched about 100 m to the west of the Ted vein (Table 2-15, Appendix 2) yielding the highest levels of Cl and I. Around the Ted vein, I in particular exhibits a classic 'rabbit ears' signature of anomalous values on either side of the vein (Figure 55). Farther to the east, at a distance of 500 m from the start of the traverse, the soil has anomalous levels of As, Cs, Pb, S and Sb (Table 2-15, Appendix 2).

The halogens Br, Cl and I in pine bark indicate a positive response to mineralization at the Ted vein (Figure 56) but F shows the same response as the soil samples, with enrichment at the far eastern end of the line near the Adrian West boulders.
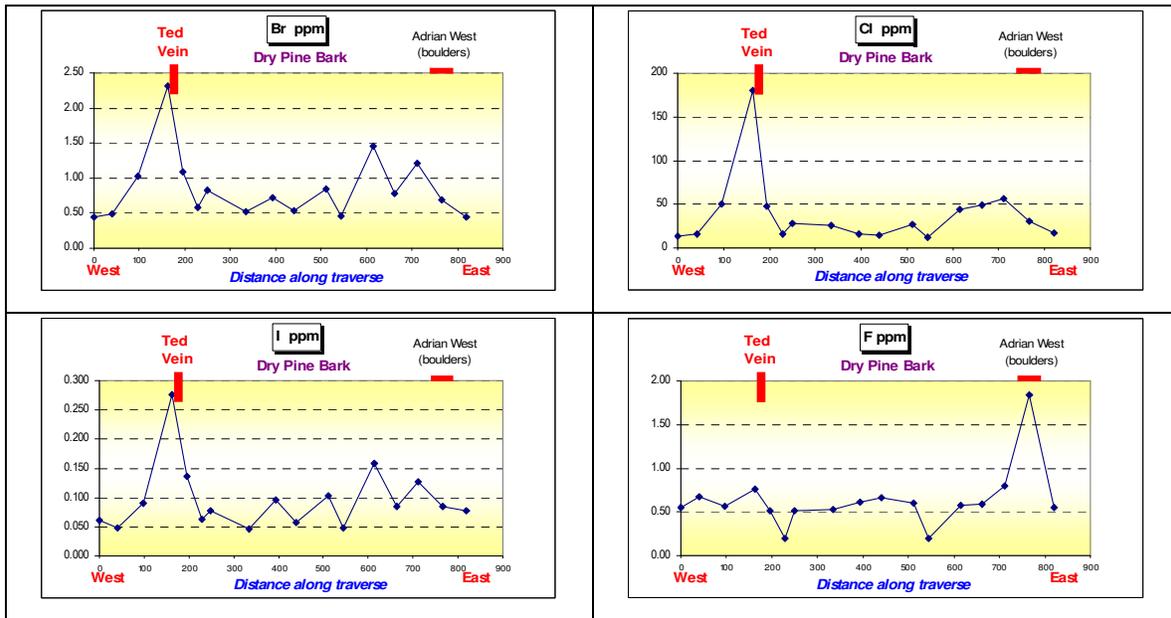

Figure 56: *3Ts Ted traverse: halogens in pine bark.*

Figure 57 shows the concentrations of S, Zn, Cd and Mo in spruce needles and pine bark along the Ted traverse. Molybdenum enrichment at the eastern end of the line suggests some stratigraphic continuity with the end of the line to the north, in the vicinity of the Ringer showing (Figure 49).

The geochemical indications are that the boulders at the Ringer showing and those at Adrian West are likely to be from the same source, and their geochemical response in the soil and especially in the vegetation suggests that they are not related to the epithermal vein systems, but represent a different style of mineralization that can be recognized from its Mo, Zn, Ag, Sn, U and F signature, with a possible source related to carbonate rocks, as witnessed by Ba and Sr in the vegetation. For an unknown reason, Sr enrichment is not evident to the west of the Adrian West showing but there are strong Ba anomalies.
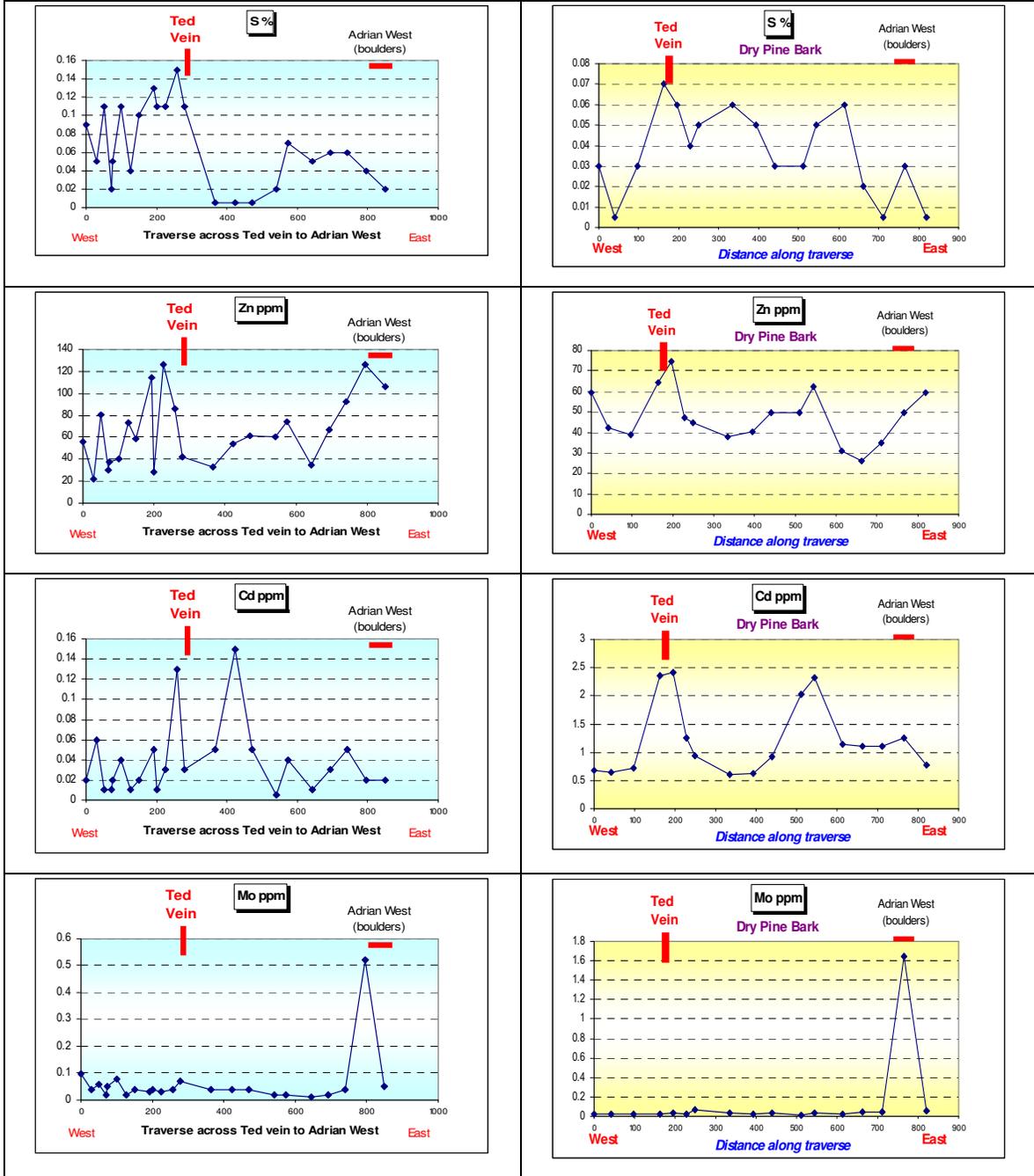
Figure 57: *3Ts Ted traverse: S, Zn, Cd and Mo in spruce needles (left column) and pine bark (right column).*

In order to assess what residual halogen content may be left after reducing the vegetation to ash, the pine bark samples were ignited at 470°C and submitted for analysis. Figure 58 shows that there is a residual amount of each halogen in the samples, and that in spite of some losses due to volatilization, there is still a positive response to mineralization.
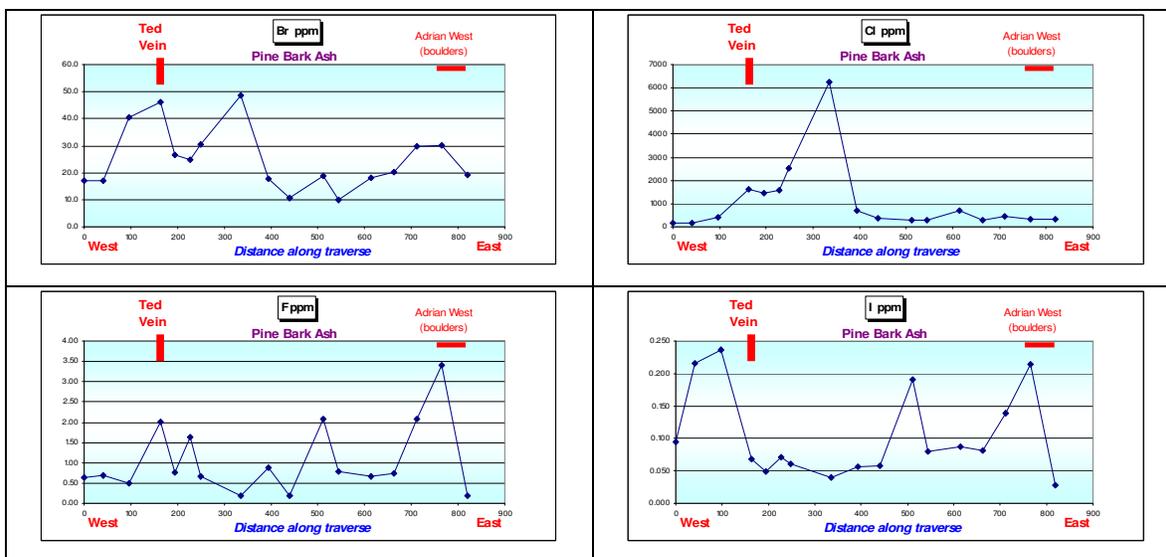
Figure 58: *3Ts Ted traverse: halogens in pine bark ash.*

The fact that some of each halogen remains in the ash of the vegetation, and profiles of their concentrations remain similar, could be of significance for further development of the halogens as pathfinders to mineralization. Residual concentrations in the ash are substantially above detection levels, and the ash does not suffer from the complications encountered in determining halogens in organic samples.

Summary and Conclusions

Gold-rich Douglas-fir needles and lodgepole pine bark archived from GSC surveys over the QR deposit in the late 1980s have served as samples for testing and developing various methods to determine the concentrations of halogen elements: F, Cl, Br and I. In addition, splits of three standard sediment samples (STSD-1, STSD-4 and TILL-4) were used for developing methods appropriate for analyzing soil.

Multielement analyses (aqua regia digestion with an ICP-MS finish for 53 elements) provided data on the distribution of elements in soil and vegetation with respect to known mineralization at the three survey areas. A few points of note are some unusually high Re results from Mount Polley (east of the Pond zone); high Mo results near two mineralized boulder occurrences at 3Ts (Adrian West and Ringer showing); enrichment of base and precious metals at the Cariboo zone (east of the QR deposit). In general, both soil and vegetation provided positive geochemical responses to known zones of mineralization, and locally indicate anomalies where mineralization might exist. Of note is that vegetation anomalies appear to be more directly located over concealed mineralization than anomalies present in the soil because the latter are displaced either downslope or down-ice from mineralization.

For determining the halogen elements, 16 different analytical methods were tested at commercial laboratories in Canada and at the GSC, of which some methods were duplicated at several of the laboratories. The test data indicate widely divergent results, in part due to differences between 'total' and 'partial' analyses, but problems mostly lie in selecting appropriate digestions and instrumentation. Whereas the ion chromatograph

would appear to be suitable for halogen determinations, the problems in obtaining accurate and precise data at low concentrations are at present sufficiently significant, especially for the vegetation, that this is not the recommended technique. With regard to measurements of F⁻ by ISE, there are indications there may be a stability issue for F in the leach solution that needs to be addressed.

Halogen elements that are structurally bound in crystal lattices of minerals contained within soil are unlikely to represent a good indication of concealed mineralization. Of greater significance to exploration is the labile fraction of the halogens that may emanate from concealed mineralization and become adsorbed on to soil particles and absorbed by plant roots. Research of methods has indicated that this readily soluble fraction is best determined after leaching samples with water. In order to obtain data at the low halogen concentrations present, the preferred digestion at this time is a water leach at 30°C of both the soil and vegetation samples, with a finish by high resolution ICP-MS for I, Br and Cl, and by ISE for F. These methods have permitted, for the first time, quantification of halogens in soil and common tree species of central BC. No comparable database is known from anywhere else in the world.

Average halogen concentrations in the various media from the three survey areas are presented in Table 12. With respect to the vegetation, this shows that I is more concentrated in bark than in the foliage, whereas Br and Cl are more concentrated in the foliage, with an order of magnitude more for Cl. The readily leachable halogens in the soil are present at lower concentrations than in the plant tissues except for I, which was higher in the soils than in the foliage but still lower in the soils than in the bark.

			QR		Mt. Polley		3Ts
			Cariboo	QR	Boundary	Pond	
F	ppm	Soil	<0.4	<0.4	0.5	<0.4	<0.4
Cl	ppm	Soil	10.0	10.9	8.5	8.2	8.5
Br	ppm	Soil	0.22	0.21	0.24	0.16	0.09
I	ppm	Soil	0.075	0.049	0.078	0.046	0.019
			Spruce	Spruce	Cedar	Fir	Spruce
F	ppm	Foliage	1.1	0.8	2.4	1.8	<0.4
Cl	ppm	Foliage	425	431	390	305	337
Br	ppm	Foliage	1.4	2.0	2.4	1.7	1.7
I	ppm	Foliage	0.006	0.006	0.006	0.009	0.006
				Pine			Pine
F	ppm	Bark		0.4			0.5
Cl	ppm	Bark		23			30
Br	ppm	Bark		<0.1			0.659
I	ppm	Bark					0.080

Table 12: *Average halogen content in sample media, after water leach, from the three survey areas.*

In both soil and vegetation, at each of the survey areas, the halogens have provided a positive response to concealed mineralization. There are however, different halogen responses at some occurrences (e.g., I at the Boundary zone extension, Mount Polley) than at others (e.g., F at 3Ts boulder showings). The halogens have, therefore, the

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potential to assist in fingerprinting the type of mineralization that may be present. Of note is that pine bark is the vegetation medium that best concentrates I, and gives good contrast for the other halogens. Since outer bark is dead tissue, it makes no difference to the analyses if the pine has been killed by mountain pine beetle infestation, and it is therefore a viable exploration medium which would not suffer the vagaries of potential seasonal variation of chemistry.

Although current analytical technology is adequate for halogen determinations, problems exist and further improvement of analytical methodology will expand the potential of using readily leached halogens in soil and vegetation to assist in locating mineralization concealed beneath glacial overburden and/or volcanic cover. A current limitation is that only a few commercial laboratories have high resolution ICP-MS instrumentation. Results from this orientation and demonstration project in areas of known mineralization are encouraging for extending the methodology to areas of thicker cover in central BC, concentrating on locations considered to have good potential from geological and geophysical indications.

Acknowledgments

References

Al Ajely, K.O., Andrews, M.J. and Fuge, R. (1985): Biogeochemical dispersion patterns associated with porphyry-style mineralization in the Coed Y Brenin forest, north Wales; *in* Prospecting in Areas of Glaciated Terrain, Institution of Mining and Metallurgy, London, v. 6, p. 1–10.

Bottomer, L. (2003a): Epithermal gold-silver mineralization in the Nechako plateau, central British Columbia; *in* North West Mining Association, Annual Meeting, Program with Abstracts, December 2003.

Bottomer, L. (2003b): The 3Ts epithermal gold-silver project, Nechako region, central B.C.; *in* Cordilleran Round-Up 2003, Program with Abstracts, January 2003.

Cook, S.J. and Dunn, C.E. (2006): Preliminary results of the Cordilleran geochemistry project: a comparative assessment of soil geochemical methods for detecting buried

mineral deposits, 3Ts Au-Ag prospect (NTS 093F/03), central British Columbia; *in* Geological Fieldwork 2005, BC Ministry of Energy, Mines and Petroleum Resources, Paper 2006-1 and Geoscience BC, Report 2006-1, p. 238–258.

Cook, S.J. and Dunn, C.E. (2007): Final report on results of the Cordilleran geochemistry project: a comparative assessment of soil geochemical methods for detecting buried mineral deposits – 3Ts Au-Ag prospect, central British Columbia; Geoscience BC, Paper 2007-7, 224 p.

Diakow, L. and Levson, V.M. (1997): Bedrock and surficial geology of the southern Nechako plateau, central British Columbia (NTS 93F/2,3,6,7); BC Ministry of Energy, Mines and Petroleum Resources, Geoscience Map 1997-2.

Diakow, L. and Webster, C. (1994): Geology of the Fawnie Creek map area; *in* Geological Fieldwork 1993, BC Ministry of Energy, Mines and Petroleum Resources, Paper 1994-1, p. 15–26.

Diakow, L.J., Webster, I.C.L., Levson, V.M. and Giles, T.R. (1994): Bedrock and surficial geology of the Fawnie Creek map area (NTS 93F/3); BC Ministry of Energy, Mines and Petroleum Resources, Open File 1994-2.

Diakow, L.J., Webster, I.C.L., Whittles, J. and Richards, T.A. (1995a): Stratigraphic highlights of bedrock mapping in the Southern Nechako Plateau, Northern Interior Plateau Region; *in* Geological Fieldwork 1994, BC Ministry of Energy, Mines and Petroleum Resources, Paper 1995-1, p. 171–176.

Diakow, L.J., Webster, I.C.L., Whittles, J., Richards, T.A., Giles, T.R. and Levson, V.M. (1995b): Bedrock and surficial geology of the Tsacha Lake map area (NTS 93F/2); BC Ministry of Energy, Mines and Petroleum Resources, Open File 1995-16.

Dunn, C.E. (1985): Biogeochemical exploration for gold in the La Ronge Belt, 1985; *in* Summary of Investigations 1985, Saskatchewan Geological Survey, Saskatchewan Energy and Mines, Miscellaneous Report 85-4, p. 37–49.

Dunn, C.E. (1989): Airborne and surface biogeochemical surveys for precious metals in the Cordillera; *in* Cordilleran Geology and Exploration Roundup, Geological Survey of Canada, Open File, 3 p.

Dunn, C.E. (2007): Biogeochemistry in mineral exploration; Handbook of Exploration and Environmental Geochemistry 9, M. Hale (ed.), Elsevier, Amsterdam, 462 p.

Dunn, C.E., Balma, R.G. and Sibbick, S.J. (1996): Biogeochemical survey using lodgepole pine bark: Mount Milligan, central British Columbia (parts of NTS 93N/1 and 93O/4); Geological Survey of Canada, Open File 3290 and BC Ministry of Energy, Mines and Petroleum Resources, Open File 1996-17.

Dunn, C.E., Cook, S.J. and Hall, G.E.M. (2006): Halogens in surface exploration geochemistry: evaluation and development of methods for detecting buried mineral deposits (NTS 93F), central British Columbia; *in* Geological Fieldwork 2005, BC Ministry of Energy, Mines and Petroleum Resources, Paper 2006-1 and Geoscience BC, Report 2006-1, p. 259–280.

Dunn, C.E., Coker, W.B. and Rogers, P.J. (1991): Reconnaissance and detailed geochemical surveys for gold in eastern Nova Scotia using plants, lake sediment, soil and till; Journal of Geochemical Exploration, v. 40, p. 143–163.

Dunn, C.E. and Scagel, R.K. (1989): Tree-top sampling from a helicopter – a new approach to gold exploration; Journal of Geochemical Exploration, v. 34, p. 255–270.

Fox, P.E., Cameron, R.S. and Hoffman, S.J. (1987): Geology and soil geochemistry of the Quesnel River gold deposit, British Columbia; *in* GEOEXPO '86, Association of Exploration Geochemists and Cordilleran Section, Geological Association of Canada, Vancouver, BC, p. 61–71.

Fraser, T.M., Stanley, C.R., Nikic, Z.T., Pesalj, R. and Gore, D. (1995): The Mount Polley copper-gold alkalic porphyry deposit, south-central British Columbia; *in* Porphyry Deposits of the Northwestern Cordillera of North America, T.G. Schroeter (ed.), Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume 46, p. 609–622.

Govindaraju, K. (1994): Special issue on analytical standards; Geostandards Newsletter, v. 18, July.

Imperial Metals (2005): Aerial photo of Mount Polley area; Imperial Metals, URL <http://www.imperialmetals.com/s/MountPolley.asp> [October 2005].

Logan, J.M. and Mihalynuk, M.G. (2004): Regional geological setting of the Cariboo, Bell, Springer and Northeast porphyry Cu-Au zones at Mount Polley, south-central British Columbia; *in* Geological Fieldwork 2004, BC Ministry of Energy, Mines and Petroleum Resources, Paper 2005-1, p. 249–270.

Melling, D.R. and Watkinson, D.H. (1988): Alteration and fragmental basaltic rocks: the Quesnel River gold deposit, central British Columbia; *in* Geological Fieldwork 1987, BC Ministry of Energy, Mines and Petroleum Resources, Paper 1988-1, p. 325–348.

MINFILE (2007): MINFILE BC mineral deposits database; BC Ministry of Energy, Mines and Petroleum Resources, URL <http://www.em.gov.bc.ca/Mining/Geolsurv/Minfile/> [March 2007].

Mortensen, J.K., Ghosh, D. and Ferri, F. (1995): U-Pb geochronology of intrusive rocks associated with copper-gold deposits in the Canadian Cordillera; *in* Porphyry Deposits of the Northwestern Cordillera of North America, T.G. Schroeter (ed.), Canadian Institute of Mining, Metallurgy and Petrology, Special Volume 46, p. 142–158.

Pawliuk, D.J. (2005): Summary report on the Ted vein diamond drilling program – November 2004, Tam property, 3Ts project, Omineca Mining Division; report prepared for Southern Rio Resources, April 2005, filed on SEDAR July 8 2005, 28 p.

Trofimov, N.N. and Rychkov, A.I. (2004): Iodine and bromine: geochemical indicators of deep ore deposits; Colorado Mountain Publishing House, Denver, Co., 205 p.

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