

# Preliminary Results of a Vegetation, Ah-Horizon Soil and Charcoal Geochemical Investigation at the Kwanika Central Zone, North-Central British Columbia (NTS 093N/19)

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#### Introduction

In 2009, as part of Geoscience BC project 2009-019, a soil orientation survey was carried out over the Kwanika Central zone in north-central British Columbia (Heberlein, 2010; Heberlein and Samson, 2010). The aim of this survey was to investigate the effectiveness of a suite of commonly used chemical digestions, combined with a range of sample media, at detecting deeply buried porphyry Cu-Au mineralization through Quaternary glaciofluvial and postmineralization sedimentary cover. A total of nine digestions were used, including laboratory specific (proprietary and nonproprietary) methods as well as generic methods. Soil material was collected from the upper 50 cm of the profile; specifically from Ah, upper B, lower B and C horizons. In addition, samples for Mobile Metal Ion (MMI<sup>®</sup>) analysis were collected from a constant depth interval of 10 to 25 cm below the top of the mineral soil following the recommended protocol of SGS Mineral Services (Lakefield, Ontario).

Results showed that soil geochemistry is an effective technique for detecting deeply buried mineralization. Best results were obtained from the Ah horizon using an aquaregia digestion. This combination of sample media and digestion resulted in convincing multi-element anomalies for Cu, Au, W, As, Ag and Mo directly over the surface projection of the mineralized zone. Most convincing responses were obtained over the parts of the mineralized body that are present at more than 300 m below the surface. Of the generic methods, a sodium pyrophosphate leach on Ah horizon samples was also effective in producing credible anomalies for Cu, Au, Ag, W, U As, Sb and Mn. Laboratory specific methods applied to upper B, lower B and C horizons for the most part did not produce credible anomalies. Of the laboratory specific methods only ALS Chemex's (Vancouver, BC) ionic leach technique convincingly identified the deeper parts of the mineralized body but did not produce a response over shallower mineralization. MMI<sup>®</sup>, bioleach and Enzyme Leach<sup>SM</sup> failed to detect the zone. A conclusion of the study therefore was that there was no advantage to using these more expensive proprietary methods in this environment.

The current study builds on the results documented in Geoscience BC Report 2010-3 (Heberlein and Samson, 2010) by investigating the geochemical response to the Kwanika Central zone in surficial organic materials. It further investigates the effectiveness of the Ah horizon as a sample medium by testing three different chemical digestions (distilled water leach, sodium pyrophosphate leach and aqua regia) on an offset 100 by 100 m grid over the mineralization. It also examines the relationship between the metal contents of vegetation and the Ah horizon and attempts to determine whether metal anomalies detected in Ah horizon material are formed by accumulation from shed plant tissues or by entrapment of mobile metal ions by organic matter in the soil. In addition, charcoal debris in the Ah horizon is investigated as a potential sample medium. Charcoal is a common component of boreal and sub-boreal forest soils. It is formed by the thermochemical decomposition of wood by fire (DeLuca and Aplet, 2008). This highly porous material is known to have a strong metal sorption capacity (Johns et al., 1993; McMahon, 2006) and therefore should behave as an effective trap for mobile metal ions in the near-surface environment. It is potentially a useful sampling medium in areas of recent forest fires and logged areas where the vegetation and the Ah horizon may have been damaged or completely destroyed.

This paper describes the field sampling program carried out by the authors in late August to early September, 2010, and discusses the preliminary results of the charcoal sampling. A complete synthesis of the results of this study, including a

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discussion of the vegetation and Ah horizon geochemistry, will be published in a separate Geoscience BC report and presented at Mineral Exploration Roundup 2011.

# **Benefits to the Mining Industry**

This study is designed to provide the mineral exploration community with a better understanding of different organic sampling media that can be used for geochemical exploration in regions with thick glacial sedimentary cover. It provides comparisons of metal concentrations between vegetation, Ah horizon and charcoal debris and assesses the relative capabilities of each for isolating the secondary geochemical dispersion patterns related to a blind mineral deposit. It also provides guidelines about appropriate sampling media in a number of forest cover situations that are commonly encountered in north-central BC. These include pristine forest, clear-cut logged areas, beetle kill and burned areas.

# **Study Area**

Geoscience BC Report 2010-3 (Heberlein and Samson, 2010) provides a detailed description of the study area. The Kwanika project area is situated in the Omineca Mining Division, approximately 140 km northwest of Fort St. James (55°30'N, 125°18'W; Figure 1). It is accessible by well-maintained Forest Service roads from Fort St. James via the community of Takla Landing. Serengeti Resources Inc. holds the title to 28 contiguous mineral claims covering an area of 8960 ha (Rennie and Scott, 2009).

The Kwanika Central zone is one of two mineralized centres located at the northern end of the Kwanika property.



Figure 1. Location of the study area, north-central British Columbia.

Together with the Southern zone, it forms a linear, northtrending, Cu-Au porphyry system hosted in several small monzonite intrusions along the western margin of the multiphase Hogem batholith (Rennie and Scott, 2009). Monzonite intrudes diorite, quartz monzonite and granite of the Hogem batholith as well as andesitic volcanic rocks of the Upper Triassic Takla Group. Intrusive and volcanic hostrocks are truncated to the west by the Pinchi fault—a major terrain boundary juxtaposing Cache Creek terrane rocks to the west.

Mineralization at the Central zone is associated with a strong core of intense, texturally destructive albite alteration associated with a variable multiphase stockwork of quartz veinlets. Surrounding the albitic core is a broad zone of weak to strong, pervasive and fracture-controlled potassic alteration characterized by K-feldspar and secondary biotite (Rennie and Scott, 2009). Potassic alteration grades laterally into propylitic assemblages. Dominant sulphide minerals include pyrite, which is ubiquitous to the deposit, chalcopyrite and bornite. Molybdenite is also commonly present. Supergene enrichment consisting of an upper oxide zone with native copper and a lower sulphide zone with secondary chalcocite occurs on the upper surface of the hypogene mineralization beneath a package of younger conglomerate, sandstone and mudstone that buries the mineralization to the west. These sedimentary rocks are interpreted to be part of a younger sedimentary basin formed against the Pinchi fault. Quaternary glaciofluvial sediments, consisting of sand, gravel and local conglomerate, cover the study area.

# **Surficial Environment**

The Kwanika Central zone lies in a broad, flatbottomed valley containing an extensive cover of glacial till and outwash sediments. Local relief is 40 m within an area where elevations range from 900 to 1200 m asl. Drift cover over the deposit varies in thickness from a few metres to over 50 m (D. Moore, pers. comm., 2009) and bedrock outcrops occur only at the bottom of the deeply incised Kwanika Creek valley (Rennie and Scott, 2009). Away from the river valley, the surface is well drained with gently sloping topography. The forest is sub-boreal and typical of large areas of the gently rolling plateaus of central interior BC. The dominant trees are lodgepole pine (Pinus contorta), white spruce (Picea glauca) and subalpine fir (Abies lasiocarpa). In the boggy swamps, which occur locally in the Kwanika Creek valley, there are thick tangles of willow (Salix spp.), and on the drier plains the undergrowth is relatively sparse with mostly soopolallie (Shepherdia canadensis; also known as buffaloberry or soapberry), occasional shrub alder (Alnus spp.) and ferns.



Three types of soil profile are present in the study area. These are, for the most part, developed on a substrate of cobble-rich sand and gravel. Podzols (Orthic Ferro-Humic; soil nomenclature based on the Canadian System of Soil Classification [Canada Soil Survey Committee, Subcommittee on Soil Classification, 1978])) are the most widespread soil type, occurring on well-drained, gentle slopes within the pine and spruce forest. Brunisol, the second soil type, is common at the base of slopes adjacent to boggy areas. A typical example has a surficial LF (a surface organic layer formed by the accumulation of organic matter derived from leaves, needles, twigs and woody materials [L] and partly decomposed organic matter [F]) and Ah horizon up to 4 cm thick overlying an undifferentiated olive-brown Bm horizon. The third soil type is represented by Organic soils. These occur in depressions and boggy areas and consist of an upper thick, peaty Of or Om horizon that can be tens of centimetres thick, overlying a lower grey or bluegrey C horizon. All occurrences of Organic soils were water saturated.

# Sampling and Analysis

Samples were collected from 82 stations at 100 m intervals along offset lines. Numbers and types of samples collected are summarized in Table 1 and illustrated in Figures 2, 3 and 4. Limitations on the availability of sample media at some sample stations meant that not all media could be collected at every site. This was especially true in areas of ground dis-

 Table 1. Numbers and types of samples collected, Kwanika Central zone, north-central British Columbia.

Sample medium	No. of samples	Field duplicates	Control samples
Ah horizon (Ah 1)	81	7	
Ah horizon (Ah 2)	81	7	
Charcoal	58	5	
Lodgepole pine bark	82	7	10
White spruce bark	9	1	1
Subalpine fir twigs	82	7	10
Other	2		

turbance caused by road-building and drilling activities as well as in swamps and major drainage areas.

#### Soil and Charcoal

Ah horizon sampling involved rolling back the surface moss-mat and leaf-litter layer (LF horizon) and handpicking the black humic material from the lower surface and the top surface of the mineral soil profile. In order to obtain enough material (50-75 g) and to create a composite sample to reduce within-site variability, at least five areas were sampled at each sample station. Samples were placed in heavy-duty, double-seal Ziploc® plastic bags. Two Ah horizon samples (Ah 1 and Ah 2) were collected at each site. Charcoal fragments (where present) were hand-picked from the Ah horizon and placed in Ziploc<sup>®</sup> plastic bags. The amount and size of fragments present was found to be highly variable from station to station. At some locations, only minute chips were present and a large number of places had to be sampled in order to obtain enough material. At other sample sites, carbonized twigs, bark or wood could be sampled relatively easily.

Ah horizon and charcoal samples were shipped to Acme Analytical Laboratories Ltd. (Vancouver, BC) where they were oven dried at 80°C for 24 hours. Charcoal samples were manually pulverized using a pestle and mortar prior to analysis. Analysis was done by inductively coupled plasma–mass spectrometry (ICP-MS) following a modi-

> fied aqua-regia digestion (HNO<sub>3</sub>-HCl-H<sub>2</sub>O). Ah horizon samples were screened to -80 mesh and the +80 mesh fraction milled to -100 mesh. Ah horizon samples were digested using three different methods: aqua regia, sodium pyrophosphate leach and distilled water leach. In each case, the analytical finish was by ICP-MS. In addition, loss on ignition (LOI) was determined to assess the C content of the samples. Table 2 summarizes the analytical methods used for each sample type.

Table 2.	Sample	media	and	analytical	methods	employed,	Kwanika	Central	zone,	north-central	
British Co	olumbia.										

Sample medium	Aliquot weight (g)	Analytical code	Analytical method
Ah (-80 mesh fraction)	15.0	Group 1F15	Ultratrace agua-regia digestion <sup>1</sup>
	1.0	1SLO	Sodium pyrophosphate leach <sup>1</sup>
	1.0	1SLW	Distilled water leach <sup>1</sup>
	2.0	2A05	Loss on ignition
Ah (+80 mesh fraction <sup>2</sup> )	15.0	Group 1F15	Ultratrace aqua-regia digestion <sup>1</sup>
. ,	1.0	1SLO	Sodium pyrophosphate leach1
	1.0	1SLW	Distilled water leach <sup>1</sup>
	2.0	2A05	Loss on ignition
Charcoal	1.0	Group 1F	Ultratrace aqua-regia digestion <sup>1</sup>
Vegetation	0.5	Group 1VE2-MS	Dissolution in nitric acid followed

<sup>1</sup> followed by inductively coupled plasma-mass spectrometry

<sup>2</sup> only 10 randomly selected samples of the +80 mesh fraction were analyzed



Figure 2. Sample locations for different sampling media, Kwanika Central zone, north-central British Columbia: a) Ah 1 horizon and b) Ah 2 horizon. Surface projection of mineralized zone (Central zone) is outlined in red for 0.6% Cu equivalent and blue for 0.2% Cu equivalent.



Figure 3. Sample locations for different sampling media, Kwanika Central zone, north-central British Columbia: a) charcoal and b) subalpine fir twigs. Surface projection of mineralized zone (Central zone) is outlined in red for 0.6% Cu equivalent and blue for 0.2% Cu equivalent.



Figure 4. Sample locations for different sampling media, Kwanika Central zone, north-central British Columbia: a) lodgepole pine bark and b) spruce bark. Surface projection of mineralized zone (Central zone) is outlined in red for 0.6% Cu equivalent and blue for 0.2% Cu equivalent.



## Vegetation

The outer bark from lodgepole pine was obtained by scraping the scales from around the circumference of two neighbouring trees using a hardened-steel paint scraper, and pouring the scales into a standard kraft paper soil bag (approximately 50 g, a fairly full bag; Figure 5). At a few sites, bark from both lodgepole pine and white spruce was collected for chemical comparisons. Analysis of the two types of bark will permit levelling of the spruce bark data to a 'pine equivalent'.

Twigs and foliage of subalpine fir, comprising the most recent 5-7 years of growth, were collected. In central BC, this amount of growth is typically about a hand-span in length, at which point, the twig diameter is 4–5 mm. This diameter is quite critical because many 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. For the current survey, the potential problems that might ensue were not of particular significance because the foliage was used for analysis, not the twigs. However, as a general principle it is wise to follow this practice of consistency in sampling in order to minimize factors, such as plant growth, that might control metal accumulations. The twig with foliage samples (5-7 lengths) were snipped from around the circumference of a single tree and were placed into porous polypropylene bags (Hubco Inc.'s Sentry II). The use of plastic bags is to be avoided because samples soon release their moisture and become very soggy. If there is any delay in processing, they develop moulds and lose their integrity.

In the laboratory, all vegetation samples were thoroughly dried at 80°C in an oven for 24 hours to remove moisture.



Figure 5. Sampling procedure for white spruce and lodgepole pine bark, Kwanika Central zone, north-central British Columbia.

The foliage was then separated from the twigs. In preparation for chemical analysis, each foliage and bark sample was then milled to a powder using a Wiley mill. Analyses were carried out at Acme Analytical Laboratories Ltd. (Vancouver, BC) using their 1VE2-MS method (Table 2). This involves dissolution of a 0.5 g aliquot of milled material in nitric acid, followed by aqua-regia digestion, heating on a hot plate then diluting to a constant weight with deionized water. The analytical finish is by ICP-MS and data were obtained for 53 elements.

# **Quality Control**

Quality control measures employed for this study included the collection of field duplicate samples for each sample type. Up to seven field duplicates were collected for each sample type at randomly selected sample sites (Table 1). At each site, material was collected using exactly the same procedures as the original and from within 5 m of the original sample. 'Blind' control samples (milled vegetation of similar matrix and known composition) were inserted in the vegetation analysis. Control samples for the vegetation were inserted at a frequency of one in every ten field samples (Table 1).

### Results

Preliminary results for selected elements from the charcoal samples are presented in this section. Table 3 summarizes the relative standard deviations (RSD or % coefficient of variation) for the field duplicate results. RSD is a measure of the precision or reproducibility of the analytical results. It provides an estimate of how representative the sampling is at a given location. For low-level geochemical analyses, values of less than 20% are considered to be good, values of between 20 and 50% acceptable, and values of over 50% marginal. Of the elements presented in this report, only Zn has an RSD value in the good range (18.59%). The other elements have higher values, with Mo (46.04%), Cu (34.08%), Pb (40.75%) and Ag (25.09%) falling within the acceptable range. Gold is the only element with a higher RSD (74.77%). These results suggest that the data is usable but caution should be exercised when interpreting the Au results. Generally results for elements with RSD values of

Table 3. Rel	ative stand	dard deviat	ion estimate	s for
selected ore	elements in	n charcoal s	amples, Kwa	anika
Central zone	, north-cen	tral British (	Columbia.	

Element	Relative standard deviation (%)
Мо	46.04
Cu	34.08
Pb	40.75
Zn	18.59
Ag	25.09
Au	74.77



>50% should be assessed based on the geological significance of the results (i.e., whether they make geological sense).

## Charcoal

Figures 6 to 8 illustrate the results for Au, Cu, Ag, Mo, Pb and Zn in charcoal fragments. Dots represent log (10) transformed values with increasing size and hotter colours representing more anomalous values. Raw values are also plotted next to the symbols for comparison.

Gold results (Figure 6a) are relatively flat across the grid area with background concentrations ranging between 0.1 and 0.9 ppb. Two highly anomalous samples (3.6 and 6.1 ppb) are present in the west-central part of the grid. These fall within the surface projection of the Central zone mineralization as defined by the 0.6% Cu equivalent outline (red line), an area where the top of the mineralization lies some 300 m below the surface (Heberlein and Samson, 2010). The westernmost sample also lies close to the surface projection of the Pinchi fault.

Copper (Figure 6b) has a similar pattern to Au. Background values are extremely flat, ranging from 2.1 to 6.5 ppm. The two samples that were highly anomalous for Au are also anomalous for Cu. These have values of 44.04 and 63.72 ppm or approximately 5 to 10 times background values. In addition, two moderately anomalous samples (26.44 and 19.39 ppm) occur close to the Pinchi fault, to the north (and outside) of the limits of the mineralization. A second cluster of moderately to highly anomalous samples is present at the northeast corner of the grid. The anomalous values (69.03 and 36.51 ppm) have a similar magnitude to those over the surface projection of the Central zone. There is no known source for Cu in this area.

Results for Ag and Mo are presented in Figures 7a and b. Silver (Figure 7a) displays a convincing anomalous pattern coinciding with the western part of the Central zone. Four highly anomalous samples occur close to the surface projection of the mineralization: two inside (597 and 674 ppb) and two just outside to the north (1333 and 606 ppb). In addition, two moderately anomalous samples coincide with the eastern edge of the mineralized body (409 and 498 ppb). Away from the surface projection of the mineralization, values are subdued and define a background value averaging approximately 120 ppb. One highly anomalous (1688 ppb) and two moderately anomalous samples (553 and 537 ppb) occur at the southern limit of the grid. There is no obvious source for these anomalies.

Patterns for Mo (Figure 7b) are less clear than those for Cu and Au. Moderately anomalous values (0.76 to 1.26 ppm) are scattered over much of the grid within both background and mineralized areas. Maximum values, however, occur over the western limit of the Central zone at the surface projection of the Pinchi fault (22.09 ppm) and at the northeast corner of the grid (3.73 ppm), coincident with the maximum Cu value.

Lead (Figure 8a) has quite a different distribution to the elements described so far. All except two of the moderately anomalous (11.68 ppm) and highly anomalous values (16.71 ppm) fall outside the surface projection of the Central zone and appear to form a halo around the deposit. Highest values occur on the north side where concentrations reach 15.95 ppm. Isolated highly anomalous values also occur on the northeast and southeast margins of the zone (13.3 and 16.71 ppm, respectively). Outside this anomalous zone, background values are relatively flat and range between 1.7 and 5.5 ppm.

A less coherent pattern is shown by Zn (Figure 8b). Five highly anomalous samples are scattered across the central part of the grid. One occurs within the surface projection of the Central zone on the Pinchi fault (109.1 ppm) and three others (83.5, 113.6 and 88.0 ppm) lie peripheral to the zone near its north, east and south edges. An isolated highly anomalous value (96.6 ppm) occurs due east of the zone on the easternmost grid line. Four of these anomalous samples have one thing in common; they lie either at the base of slope or on the slope leading down to the Kwanika Creek drainage. This suggests that the charcoal may be concentrating hydromorphically dispersed Zn. There is no obvious anomaly associated with the surface projection of the Central zone mineralization.

### Discussion

Results of the charcoal sampling show convincing patterns that suggest this material is acting as a repository for mobile metal ions in the near-surface environment. Coincident anomalies for the ore elements, Au, Cu, Ag and Mo, directly over the highest grade part of the Central zone suggest that ions migrating from the mineralization to the surface (by whatever mechanism) are being trapped in the charcoal to form detectable anomalies. Several anomalous samples lie on or close to the surface trace of the Pinchi fault, which intersects the mineralization at depth. Therefore one likely scenario is that some of the metals concentrated in the charcoal may have migrated to the surface along the permeable fault zone. There is also evidence that the charcoal is concentrating hydromorphically dispersed metals, such as Zn. The presence of Zn anomalies along the base of slope on the north side of the Kwanika Creek drainage could be related to seepage zones where groundwater carrying dissolved Zn is emerging at surface. Another possibility is that the charcoal contains metals that were in the original plant tissues. Results from the vegetation samples will help to determine if this is the case.

The spotty nature of the Cu and Au responses over the mineralized zone is interesting. Only two of six sample sites oc-



Figure 6. Analytical results for charcoal samples, north-central British Columbia: a) Au and b) Cu. Scaled symbols represent log (10) transformed values; raw values (Au in ppb and Cu in ppm) are plotted next to each symbol. Surface projection of mineralized zone (Central zone) is outlined in red for 0.6% Cu equivalent and blue for 0.2% Cu equivalent. Green dots indicate 2009 transects.



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Figure 7. Analytical results for charcoal samples, north-central British Columbia: a) Ag and b) Mo. Scaled symbols represent log (10) transformed values; raw values (Ag in ppb and Mo in ppm) are plotted next to each symbol. Surface projection of mineralized zone (Central zone) is outlined in red for 0.6% Cu equivalent and blue for 0.2% Cu equivalent. Green dots indicate 2009 transects.



Figure 8. Analytical results for charcoal samples, north-central British Columbia: a) Pb and b) Zn. Scaled symbols represent log (10) transformed values; raw values (in ppm) are plotted next to each symbol. Surface projection of mineralized zone (Central zone) is outlined in red for 0.6% Cu equivalent and blue for 0.2% Cu equivalent. Green dots indicate 2009 transects.



curring within the 0.6% Cu equivalent outline have anomalous concentrations for these elements. This may be a function of the quantity and quality of the charcoal at each site, which was found to be highly variable. At most sites only the coarsest charcoal fragments were collected by hand-picking. This sampling method may not be providing a truly representative or consistent sample. This conclusion is supported by the relatively high RSD values for these elements. Better results may be obtained by using a more effective sampling technique that would concentrate charcoal particles from the finer fractions of the soil. Such a method is described by McMahon (2006). This involves floating the charcoal particles (specific gravity  $< 1.0 \text{ g/cm}^3$ ) in deionized water and concentrating them by filtering. More experimentation is needed in order to perfect the sampling technique.

### Conclusions

The following conclusions can be drawn from results obtained to date for this study:

- charcoal is a potentially effective sampling medium—it has the capability of preserving the geochemical signal from a deeply buried mineral deposit;
- coincidental anomalies for the ore elements Au, Cu, Ag and Mo directly over the surface projection of the deposit suggest the metals are derived from the underlying mineralization;
- Pb anomalies in charcoal appear to form a partial halo around the Cu-Au mineralization—highest values are developed on the north side of the zone;
- charcoal appears to be sensitive to hydromorphic dispersion as illustrated by anomalous Zn values along the break of the slope south of the Central zone; and

Cu and Mo define a separate anomaly at the northeast corner of the grid where there is no known source of mineralization.

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