GEOLOGICAL SURVEY OF CANADA

OPEN FILE 2839

Reconnaissance biogeochemical survey using Lodgepole pine tops: Fish Lake area (NTS 92 O), west-central British Columbia

C.E. Dunn, R.G. Balma, W.A. Spirito

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RECONNAISSANCE BIOGEOCHEMICAL SURVEY USING LODGEPOLE PINE TOPS: FISH LAKE AREA (NTS 92 O), WEST-CENTRAL BRITISH COLUMBIA

C.E. Dunn, R.G. Balma, and W. Spirito

INTRODUCTION

In May, 1993, a contract was issued to Pacific Phytometric Consultants (Surrey, B.C.) to collect, by helicopter, tree tops from the Fish Lake area on the Fraser Plateau (Fig. 1; Plates 1 and 2). Previously, GSC/Pacific Phytometric studies at the QR gold deposit (east of Quesnel, B.C.) had determined the viability of tree top sampling as a means of revealing concealed mineralization. A strong gold signature was found in the tree tissues (Dunn and Scagel, 1989).

A ground-based orientation survey was conducted in 1992 around the Fish Lake zones of mineralization. Lodgepole pine (*Pinus contorta*) tops yielded weak enrichments of Au, Mo, Cu, Cs, Ni and Na. The pine bark showed some enrichment of Cu, As, and up to 67 ppb Au in ash, representing an order of magnitude of enrichment compared to background concentrations for the area.

This is the first airborne reconnaissance survey of its kind to be undertaken. The objective was to establish regional geochemical patterns of element concentrations, and thereby assist in the exploration for concealed mineral deposits through the recognition of element associations that are characteristic of these deposits. The technique is a method of rapidly screening an area to provide focus for more detailed ground studies.

Biogeochemical data should be interpreted differently from data obtained by more conventional geochemical sample media (rocks, soils, lake and stream sediments). Plants require certain elements for their survival, and they have the ability to concentrate metals by scavenging them from the substrate. For example, zinc is needed for plant metabolism. Therefore, moderate differences in zinc concentrations between sample sites may simply reflect the health of a tree rather than significant differences in the chemistry of the substrate. However, major differences in zinc concentrations may reflect the presence of zinc mineralization. By contrast, plants also have the ability to exclude those
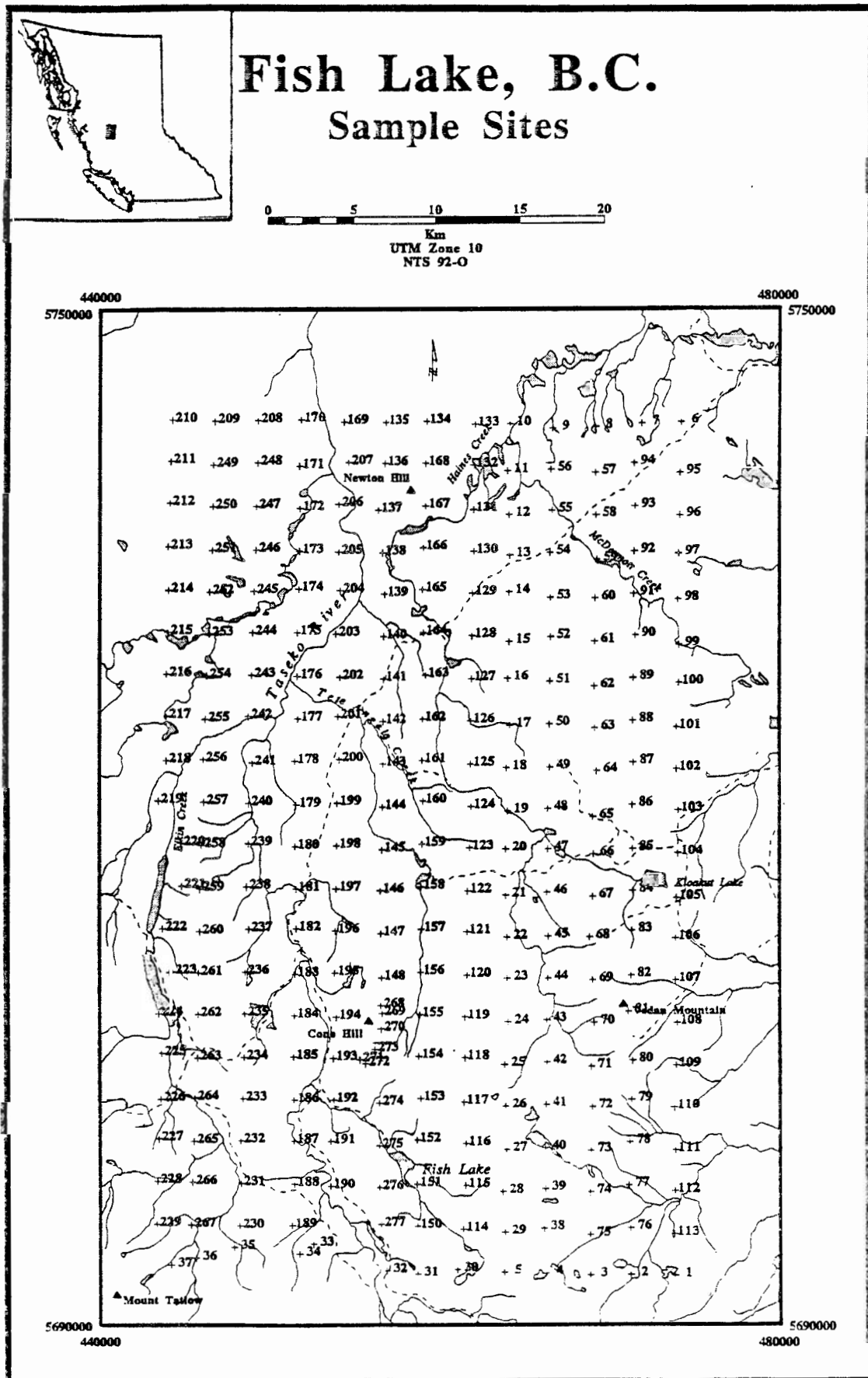
Fig. 1: Location map and sample sites

Plate 1a: Tree Top Sampling from a Helicopter

Plate 1b: Lodgepole pine top - amount collected for analysis (above hand)

elements that would have a detrimental effect on their growth or health. This 'barrier' mechanism may result in only weak enrichment of an element in a tree from an environment where that element may be enriched in the substrate. As a consequence, there is no simple relationship between the chemistry of a tree tissue and the chemistry of the ground. Brief discussion is provided on the role of each element in plant function in order to assist in data interpretation. Biogeochemistry is a complex science involving the interaction of many organic and inorganic processes. However, careful and systematic collection and preparation of plant samples can provide cost-effective new insight into the chemistry of the substrate.

SURVEY AREA

Figure 2 shows the geological contacts, drainage, the main topographic features and place names, and locations of the sample sites. The highest point is Mount Tatlow at 3061 m in the southwestern corner. Throughout much of the survey area the topography is flat or gently undulating as a result of flooding by Tertiary basalt. Locally, hills of plutonic rock rise above the basalt (Cone Hill, Newton Hill, Vedan Mountain), and there are steep-sided valleys where rivers have cut through the basalt into underlying Mesozoic strata. Much of the surface water drains northerly into the incised valley containing the fast-flowing Taseko River. Farther east, surface run-off is into streams which drain into the more gently flowing Haines Creek. In the south-eastern part of the survey area (Vedan Mt.) drainage is toward the east.

The veneer of glacial cover which masks much of the area has developed an immature soil (mostly thin podsol) which supports a forest cover dominated by Lodgepole pine (*Pinus contorta*). Locally, there are stands of Douglas-fir (*Pseudotsuga menziesii*), white spruce (*Picea glauca*), and Engelmann spruce (*Picea engelmannii*). The stands of Lodgepole pine are at least 80 years old, and the area is suffering from pine beetle kill, especially in the east and at higher elevations

GEOLOGICAL SUMMARY

H.W. Tipper published a geological map of NTS 92 O in 1978. Recently, mapping has been completed in the southern part of the survey by Riddell et al. (1993), and the adjacent area to the north by Hickson and Higman (1993). These studies have allowed the earlier mapping to be revised and refined. The geological contacts shown in Fig. 2 are based upon the published results, and comments by C. Hickson (personal communication).

The region is largely drift covered and thick glacio-fluvial deposits occupy the valleys. Laterally extensive flows of Miocene to Pleistocene basalt (Chilcotin Group), mostly less than 30 m thick, cover large tracts of the survey area. These overlie Eocene volcanic rocks that range in composition from picritic basalt to rhyolite. Small Cretaceous to Tertiary

granodioritic plutons occur 8 km north of Fish Lake at Cone Hill, in the east at Vedan Mountain, and in the north at Newton Hill. Cretaceous strata are mostly clastic sediments with some acid volcanic rocks. Clastic sedimentary rocks of Jurassic age crop out in the southwestern corner of the survey area, overlying Upper Triassic calcareous clastic beds of the Hurley Formation.

A major steeply-dipping fault system, named the Yalakom fault by Leech (1953) has brought Triassic to Cretaceous strata in the southwest into juxtaposition with rocks ranging in age from Cretaceous to Pleistocene. Northeast of this fault the flood basalts and glacial deposits obscure the structure, but north and northeasterly striking faults have been recognized (e.g. Elkin Creek and Taseko Valley).

Mineralization has been found at Fish Lake, Newton Hill, and Cone Hill. The Fish Lake deposit is by the far the largest known in the survey area. A recent report (Northern Miner 27th December, 1993) estimated the deposit to contain minable reserves totalling 960 million tons grading 0.23% Cu and 0.0125 oz. gold per ton at a strip ratio of just under 2 to 1. The deposit is oval in plan, 1.5 km long, up to 800 m wide, and extends to a depth of 880 m. Mineralization is disseminated chalcopyrite with bornite associated with potassic metasomatism, and has a halo of pyrite to the north and east that coincides with a zone of phyllic alteration.

SURVEY METHODS

Pacific Phytometric Consultants (Surrey, B.C.) was contracted to collect tree top samples from a helicopter, at sites identified on 1:50 000 scale topographic maps. The contract specified that, wherever possible, a tree top should be sampled within a 200 m radius of the preferred site. The only departures from the preassigned grid were due to recent burns, pine beetle kill, bogs, and complex multi-storied, multi-species stands.

During a three-day period in early May, 1993, a 1625 km^2 area was surveyed along 715 km of grid lines at a spacing of 2.5 km between sample sites. The top 0.5 m, comprising 2 - 3 years of growth was snipped from a Lodgepole pine at each of 276 sites (Plate 2: portion above where the top is being held). A single top (stem, branches, needles, and cones) from a healthy tree was collected at each sample station. Rounded top Lodgepole pines have thick branches and abundant cones making them difficult to cut with hand shears. In some cases it was possible to break the top of the trees by bending the top and finishing the cut with the hand shears. The fresh weight of each sample varied from 500 g to 1 kg,

Scale 1 : 320 000

0   5   10   15   20

Km
UTM Zone 10
NTS 92-O

LEGEND

MIOCENE AND PLIOCENE

MPcv   Basalt (olivine +/- plag.)

EOCENE

Ev   Picritic basalt; andesite; rhyolite

CRETACEOUS TO TERTIARY

KTmg   Granodiorite and tonalite

CRETACEOUS

Kgd   Granodiorite and diorite (porphyritic)
UKpc   *(Powell Ck. Fm)* Volcanic flows and tuffs (andesitic)
LKtc   *(Taylor Ck. Gp)* Clastic sediments
LKsq   *(Silverquick Fm)* Sandstone and conglomerate
LKv   Volcanic lavas and tuffs (rhyolite to andesite)

Jackass Mtn. Gp.
LKJMy   *(Yalakom Mtn. Facies)* Clastic sediments
LKJMcc   *(Churn Ck. Facies)* Marine sediments and conglom.
LMJlc   *(Last Ck. Fm)* Clastic sediments

TRIASSIC

UTrch   *(Hurley Fm)* Clastic and carbonate sediments

Fig. 2 Simplified geology compiled from Tipper (1978), Hickson and Higman (1993) and Riddell et al. (1993).

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to give a total weight for the survey shipment of over 200 kg. The total flying time was 15.9 hours to provide an overall productivity of 17.5 samples/hour (3.4 minutes/sample). Production was 22 sites/hour (2.75 minutes/sample) when flying along preset grid lines.

The survey crew consisted of the pilot, a navigator (who also bagged the samples), and a sampler, secured with a safety belt by two lanyards, who leaned out of the hovering helicopter to snip off the tree tops. Once the helicopter was positioned, the actual sample

retrieval time was usually 5 - 10 seconds. Constant intercom communication amongst the flight crew is essential for safety and efficiency of sampling. More details of the sampling methods are given in Dunn and Scagel (1989), with modifications described in a second paper (Dunn and Scagel, in prep.). Site locations were located with an accuracy of 15 m using a GARMON GPS-100 global positioning system receiving signals from at least five satellites

SAMPLE PREPARATION AND ANALYSIS

All samples were returned to the GSC laboratories in Ottawa where they were left to air dry for four weeks. Cones and needles were removed from the stems and retained for later analysis. This procedure is quite time consuming, especially if the samples have not been thoroughly dried. The drying can be accelerated by placing the samples in large ovens for 24 hours, or in a microwave oven for a few minutes. However, mercury may volatilize from the samples at 40°C and, since the mercury content of the *needles* was to be determined, air-drying was the preferred method. The needles had to be plucked from the stems, and in order to twist the sharp cones from the stems leather gloves had to be worn. Separation of plant tissues is required because the chemistry of the various tissue types is different.

Stems were reduced to ash in a kiln (470°C for 12 hours), and samples of 0.25 and 0.5g were weighed accurately into vials and sent for 35 element analysis by instrumental neutron activation analysis (INAA) at Activation Laboratories Ltd., Ancaster, Ont. Most samples yielded sufficient ash for a second split (0.25 - 0.5 g) to be submitted for 35 element analysis by inductively-coupled plasma emission spectrometry (ICP-ES) on an aqua regia digestion (Acme Laboratories Ltd., Vancouver). A minimum sample weight of 0.25 g is required in order to obtain good analytical precision without having to resort to more laborious procedures. Accuracy and precision were monitored by inserting within each batch of 20 samples one vegetation ash of known composition (V6c - prepared at the GSC), and a duplicate of one of the ash samples.

Tables 1 - 4, at the beginning of Appendix A, list data obtained for the analytical controls, and the detection limits for each element. Table 1 lists the duplicate pairs of analyses by INAA for 15 samples, and by ICP-ES for 3 samples. Insufficient ash was available for ICP-ES analyses on all 15 of the samples determined by INAA, therefore the an extra 12 pairs of the V6c standard were inserted. All data obtained on V6c are listed in Table 2. Table 3 lists the determination limits of elements measured by INAA, and lists the 'substitution value' used in statistical calculations for data below the detection limit. All substitution values are 5/8 of the detection limit. Table 4 provides the same information as Table 3, but for elements determined by ICP-ES.

DATA PROCESSING AND MAP PRODUCTION

Data for the study area were compiled using Microsoft Access relational database software. Separate tables for the INAA, ICP-ES and location data were created. These tables were linked through a primary site-id key. Data listings for all field samples are presented in Appendix A. Control references and duplicates are listed in Tables 1 and 2.

Statistics were generated for each element, using SPSS. Statistical summaries provided in Appendix B were generated using software developed in the Applied Geochemistry Subdivision of the Geological Survey of Canada. For computing purposes, analytical results less than detection were assigned a value 5/8 the determination limit. Since the 75 percent of the sample sites were over the Tertiary basalt, no attempt was made to provide statistical summaries of the tree chemistry with respect to underlying lithology. Differences do occur (e.g. Cr enrichment in trees over Cretaceous sediments in the valley striking northward from Fish Lake), but these can best be seen by placing the transparent overlay (showing geological units) over the element distribution maps.

The element distribution, sample site and geology maps were created using ARC/INFO software. Site specific location and analytical point data were transferred from the relational database into ARC/INFO point attribute tables. Geology, faults, hydrography, roads and other topographic features were digitized manually and stored in separate ARC/INFO polygon, arc and point coverages. In order to partially automate the mapping process an ARC/INFO macro was written, prompting users to enter all variables necessary to create the element distribution maps. The maps show percentile values of the data, and dots of increasing size that correspond to relative concentrations of elements according to an exponential function. Different functions were used (as shown in the top right hand corner of each map) in order to provide the best visual impact. For output, ARC/INFO map compositions were first converted into graphics files and then converted to PostScript files. These were subsequently printed at 600 dots per inch on a laser printer and appear in Appendix C.

ELEMENT DISTRIBUTION MAPS

Interpretation of the element distribution maps requires some consideration of the role of chemical elements in plant function. Some comments are given in this section to assist in this interpretation. These notes deal first with those elements determined by INAA, followed by those determined by ICP-ES. The sequence is the same as the element listings in Appendix A and the statistical summary in Appendix B.

For determinations by INAA, elements are arranged alphabetically by chemical symbol, except for the rare earth elements (REE) arranged in order of increasing atomic weight - i.e. La, Ce, Nd, Eu, Sm, Yb, as is conventional for REE listings. For determinations by ICP-ES, elements are arranged alphabetically by chemical symbol. There is some repetition of element determinations (e.g. Ca, Co, Cr, Fe, K, Mo, Na, Zn by both INAA and ICP-ES). This is done either:

a)   to reaffirm the validity of the geochemical patterns (i.e. are anomalous concentrations detected by both analytical methods?). A question often asked is 'how accurate are the data by the two different analytical methods?'. These comparisons help to answer this question; or

b)   because one analytical method may provide more precise data than the other (e.g. Ni, Ba, and Sr data are more precise by ICP-ES than INAA; whereas the opposite is true for Au, As, Cr, Sb, U and La); or

c)   in some cases to demonstrate the differences in the analytical methods. INAA is a total analysis, whereas ICP-ES following an aqua regia digestion is only partial for some elements (e.g. Na). The differences between total and partial analyses are of significance for most geochemical sample media because the data provide information that can be related to the manner in which some elements are bound to or within crystal lattices. For biogeochemical data these differences are of lesser significance since the aqua regia leach prior to ICP-ES determinations releases most, if not all, of an element from an ash sample. However, after an aqua regia leach of an ash sample there commonly remains a gelatinous residue which may trap a portion of some elements. Further research may show that this difference between total and partial analyses may have a bearing on data interpretation, and therefore the two data sets for a single element are presented for the sake of completion.

Transparent Overlay
    A transparent overlay, at the same scale as the element distribution maps, is provided to show the underlying geology, drainage, trails and main place names.

Distribution Maps of Elements Determined by INAA

Gold (Au)
    Gold is not known to be essential for plant growth and health. Consequently, patterns of Au distribution reflect zones of relative gold enrichment in soils, groundwaters and near-surface rocks. Background levels of Au in the ash of pine twigs and stems are commonly less than 10 ppb Au. The median value obtained for the current data set is 8 ppb Au. Because of the low (ppb) traces of Au that are present, the precision of the INAA on

duplicate pairs, although acceptable, is not as good as that of most other elements determined by this method. In general, Au concentrations in the study area are low, but local clusters of samples with relative Au enrichment occur in several areas.

Arsenic (As)

Arsenic is renowned for its toxicity, yet plants (especially Douglas-fir) can accumulate extraordinary amounts without exhibiting any visible harmful affects (Warren et al., 1964; Dunn and Scagel, 1989). Arsenic is an essential element for the metabolism of carbohydrates in fungi and algae, and a few ppm As in most conifer tissues is to be expected. Arsenic concentrations in samples from the study area are low, yet clusters of relative enrichment occur in the northwest, and northeast of Tete Angela Creek.

Barium (Ba)

Over 80 percent of the samples yielded less than the INAA detection limit of 40 ppm Ba, and the precision of the data at concentrations less than 200 ppm Ba is commonly poor. Consequently, the INAA for Ba have been excluded, and determinations by ICP-ES are presented.

Bromine (Br)

Bromine is not known to be an essential element, although it is present in most, if not all, terrestrial plants. It can form many complexes within plants. Some complexes volatilize during the ashing process, causing losses of 30 - 90 percent of the Br contained within the plant tissues. Concentrations in the pine tops are consistently lower than the 10 - 50 ppm Br typically found in plant ash. Although there is commonly a Au/Br association in plant ash from zones of Au mineralization, this is not apparent in the survey area.

Calcium (Ca)

Calcium is a major 'building block' element, essential for the rigidity of cell walls in most plants. Variations in Ca content of tree tissues have not been found to be related to mineralization.

Cobalt (Co)

Traces of Co are required by some plants to assist in the fixation of major nutrients (e.g. N, S). One ppm Co in ash is all that is required by most plants, but conifer twigs usually have 5 - 10 ppm Co. Plant tissues commonly contain elevated levels of Co over ultramafic rocks, and it has been observed that some plants exhibit Co enrichment in areas of gold mineralization in northern Saskatchewan (Dunn, 1986). The map of Co in the survey area does not indicate an association with Au, nor are there unusually high concentrations of Co in the tree tops.

Chromium (Cr)

Chromium is a non-essential element for which precise INAA data are obtained at low ppm levels. Local concentrations up to 190 ppm Cr are much higher than background

values (median of 8 ppm), especially in the eastern part of the survey area, and east of the valley extending from Fish Lake to Cone Hill.

Cesium (Cs)

This alkali metal performs no known essential function in plant tissues, and is usually present at less than 3 ppm Cs in the ash of conifer stems (thick), twigs and bark. By dissecting a whole Lodgepole pine it has been found that maximum concentrations of Cs occur in the top stems (Dunn, 1994). Commonly, there is a spatial relationship of Cs in plant tissue to epithermal Au deposits with highest concentrations occurring peripherally to zones of Au enrichment. It is noteworthy that most of the highest Cs concentrations occur in the southeast, to the west of a zone of relative Au enrichment over Vedan Mountain.

Iron (Fe)

Iron is essential for photosynthesis and is a major constituent of chlorophyll. In addition, there is a residual content of Fe which reflects the composition of the substrate. The levels of Fe in the pine ash are consistent with those to be expected in areas dominated by mafic rocks.

Hafnium (Hf)

The content of Hf in the ash of conifer twigs is commonly 1 - 2 ppm Hf, and it is not known to perform any useful role in plant growth. Hafnium in plants commonly exhibits a close relationship to Fe, such that where Fe concentrations are high (3 - 4% Fe) there may be 5 - 10 ppm Hf. The uptake of Hf by plants may also be linked to Zr, due to their close geochemical affinities. Unlike the distribution pattern of Fe, Hf shows subtle enrichment in the eastern half of the survey area.

Potassium (K)

Potassium has no structural role in plants, but it serves a number of catalytic roles and is required in large amounts (Bidwell, 1979). It is very important in the overall metabolism of plants. In environments where there is an abundance of K, trees may concentrate unwanted amounts in their extremities. When this occurs, sites with relatively high levels of K in pine tops may reflect potassium-rich substrate (e.g. K-rich clays or felsic rocks). An area of relative K enrichment occurs in the centre of the survey area.

Molybdenum (Mo)

Molybdenum in trace amounts is required by most plants for nitrogen fixation and nitrate reduction. Concentrations are usually <2 ppm Mo in woody conifer tissues.)ver highly alkaline soils the trees are able to absorb Mo more readily resulting in slightly higher levels. In general, however, concentrations of more than a few ppm Mo may be expected to reflect some Mo enrichment in the substrate (e.g. Cone Hill).

Sodium (Na)

Sodium concentrations between 0.1 and 1 percent are common in conifer tissues and

may reach several percent over zones of Na enrichment in the substrate. Some Na enrichment commonly occurs in association with Fe. In the survey area the sample with the highest Na (8 km south of Newton Hill) also contains the highest amount of Fe.

Rubidium (Rb)

Although in rocks there is a geochemical affinity between Rb and K, in plants there is an antagonism between these elements (Kabata-Pendias and Pendias, 1984). This arises from competition for the same binding sites, causing different distribution patterns for the two elements. Cesium is also involved, but the strong correlation commonly shown between Rb and Cs in trees (cf. maps of Cs and Rb distributions) indicates that antagonism does not occur at the levels of concentration normally present.

Antimony (Sb)

Excellent analytical precision is obtained for traces of Sb by INAA, so that variations in the sub-ppm concentrations are real, and not an artifact of the analytical technique. Although Sb can be readily taken up by plants in soluble forms, it is considered a non-essential element (Kabata-Pendias and Pendias, 1984) and is usually present at low ppm levels. With the exception of one site northwest of Kloakut Lake that yielded 9 ppm Sb (confirmed by ICP-ES analysis of a second split), the only site to yield over 1 ppm Sb was at Cone Hill.

Scandium (Sc)

Data on the essentiality of Sc in biologic systems are inconclusive (Horovitz, 1988). If required, Sc is needed only in 'ultra-trace' amounts, and therefore its presence in pine tops is controlled essentially by the chemistry of the substrate and by the distribution of other elements. In particular, there is a near perfect correlation between Sc and Fe.

Selenium (Se)

Traces of Se are essential for some plants and for human health. Selenium occurs in combination with many compounds, some of which break down to release volatile chemical species of Se during the ashing process. Consequently, it is probable that the Se content of the pine ash does not represent the total content of the dry tissue. There is, however, a residual amount of Se in ash that commonly bears a significant relationship to zones of Au mineralization. This was particularly notable in southeastern Nova Scotia (Dunn, 1988). In the survey area the 'spotty' enrichment of Se at the few sites where it was detectable cannot be related to zones of known mineralization.

Tantalum (Ta)

Plant tissues rarely contain more than 1 ppm Ta in ash, and Ta is not known to be essential for plant health. However, over the Ta deposit at Bernic Lake, Manitoba, Ta-rich mineral phases occur within the structure of bark, attesting to the accumulation of Ta by

absorption through the root systems. The few determinations of detectable Ta from the survey area are not considered to be of significance

Thorium (Th)

Thorium has low solubility and is not essential for plant growth. Its concentration in plant ash is typically < 2 ppm, and even over zones of Th-rich mineralization (e.g. allanite with > 5000 ppm Th in northern Saskatchewan) only a few ppm accumulate in the tissues (Dunn and Hoffman, 1986). The low Th levels in samples from the survey area are unlikely to assist in defining zones of mineralization.

Uranium (U)

Although U_3O_8 has high solubility, it rarely exceeds concentrations of more than 2 ppm in plant ash unless there are significant U deposits in the vicinity. Concentrations of U in the survey area are slightly higher in the west than the east, but all values must be considered 'background'.

Zinc (Zn)

Since Zn is essential for carbohydrate and protein metabolism, differences of a few 100 ppm Zn in ash are probably related to the health of the tree rather than subtle changes in substrate chemistry.

Rare-Earth Elements (REE)

Because of their chemical coherence, the REE are considered as a group. INAA can be used to readily determine lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), europium (Eu), terbium (Tb), ytterbium (Yb), and lutetium (Lu).   Terbium consistently yields concentrations below the detection level of 0.5 ppm and therefore no map is included. In plants, there is commonly a strong correlation between the REE and Fe. Comparison of the La and Fe maps confirms this association in the survey area.

REE concentrations are low. The median value for La of 1.1 ppm is an order of magnitude lower than the value commonly obtained from plant tissue. Maps of the light REE (La, Ce, Nd, Sm) show similar distribution patterns, particularly La and Sm. At the low concentrations present, the poorer analytical precision obtained for Nd and Ce probably accounts for most of the differences observed on these maps. Distribution patterns of the heavier REE suggest that there may be some partitioning from the light REE.

Distribution Maps of Elements Determined by ICP-ES

Silver (Ag)

Silver concentrates in the trunk wood of conifers, and it is therefore important that stem samples be of similar diameter for data comparison.   If the diameter varies

substantially, the bark:stem wood ratio will vary as will the Ag content. Silver is not known to perform any useful function in plants. Ninety percent of the samples contained detectable levels of Ag (>0.2 ppm), with most of the higher concentrations occurring in the northern part of the survey area indicating a regional geochemical enrichment.

Aluminum (Al)

All dry vegetation samples were placed in Al trays for ashing. Therefore a certain amount of contamination from this source is inevitable. However, the wide range in Al concentrations, the high levels of Al in the samples, and the similarity of Al distribution patterns to those of Fe suggest that areas of *relative* Al enrichment are significant. The aqua regia extraction used is not 'total', but good precision was obtained for duplicate samples. Tests to compare data obtained from a total analysis with those by ICP-ES (aqua regia digestion) indicate that the acid digestion releases approximately 50% of the Al.

Relatively high Al concentrations in the southeastern part of the survey area may reflect greater availability of Al to the trees, perhaps from a greater abundance of clay minerals derived from alteration of the bedrock. The available literature does not indicate that this area was subjected to relatively intense alteration.

Boron (B)

Borosilicate test tubes were used for the acid digestion of the ash samples, from which 5 - 10 ppm B may be released. This is an insignificant amount in comparison with the concentrations of B present in the ash.

Boron is an element that is essential for plant growth, and it is believed to play an important role in the translocation of sugars. It is more highly concentrated at the top of Lodgepole pine than elsewhere in the tree. In general, B uptake is low from Ca-rich soils, but since the study area is not noted for its Ca enrichment the variations in B concentrations are not attributable related to Ca.

Barium

In many trees and shrubs Ba concentrations are commonly 100s or 1000s ppm Ba in ash. By comparison the Lodgepole pine tops are depleted in Ba. ICP-ES provides Ba data of variable quality, but comparison with the detectable levels of Ba by INAA suggests that Ba data are close to the total concentrations. The highest values, occurring at the north end of the survey area, coincide broadly with sites of Sr and Ca enrichment.

Beryllium (Be)

Beryllium is a non-essential element to plant growth, and in high concentrations it is toxic. Typical concentrations in plant ash are less than 1 ppm Be, which is in accord with the values obtained from these samples. In general, there is relative enrichment of Be in the southeastern part of the survey area.

Cadmium (Cd)

Absolute concentrations of Cd differ among plant species because Cd can be captured by a variety of organic compounds in cell walls and therefore not all of it will be transported to the tree extremities.

Although there is a strong geochemical association between Cd and Zn in many geochemical environments, this is not evident in plant tissues because of the *requirement* that plants have for Zn but not for Cd. However, Cd is extremely easily absorbed by plants and Cd enrichment in plant tissues may be expected to reflect relative Cd enrichment in soil and groundwater. In southeastern British Columbia levels of 10 - 50 ppm Cd in pine ash correlate well with zones of base metal mineralization. In the Fish Lake survey area Cd is not strongly enriched in the pine tops. There is a broad zone of relative enrichment in the south.

Calcium (Ca)

ICP-ES determinations of Ca yielded values about 20 percent lower than those by INAA. There is a high correlation between the two data sets, and most sites identified as Ca-rich by INAA were confirmed by the ICP-ES analysis.

Cobalt (Co)

Distribution patterns and yields of Co were similar by ICP-ES and INAA.

Chromium (Cr)

Distribution patterns and yields of Cr were similar by ICP-ES and INAA.

Copper (Cu)

Perhaps more is known about the role of Cu in plant health than any other trace element. Copper plays a fundamental role in a plant's metabolism. It assists in such processes as respiration, photosynthesis, nitrogen fixation and valence changes, and it is present in many micro-components of plants (small and large molecules, chloroplasts, mitochondria etc.). The interpretation of Cu distribution patterns in tree tissues should be approached with caution, since laboratory studies on Cu in plants report numerous antagonistic and synergistic interactions with both major and minor elements. These are reviewed briefly by Kabata-Pendias and Pendias (1984). Notwithstanding the essentiality of Cu and the complex metabolic roles that it may play, substantial differences among the survey samples are more likely to reflect major differences of Cu in the substrate than the relatively small differences attributable to micronutrient functions.

The 'background ' concentration of Cu in the pine stems (median value of 244 ppm Cu) is high compared to many trace elements due to its essentiality. Relatively high Cu levels occur in the west of the survey area, but nowhere are concentrations clearly indicative of near-surface Cu mineralization. Data obtained by ICP-ES from the aqua regia leach are both precise and accurate.

Iron (Fe)

Iron determinations by ICP-ES are approximately 20 percent lower than those obtained by INAA, but the distribution patterns are consistent.

Potassium (K)

Distribution patterns and yields of K were similar by ICP-ES and INAA.

Lithium (Li)

Lithium commonly follows Rb and Cs in nature, but shows a markedly different distribution pattern in the survey area. In pine tops it is less abundant than Rb but, with local exceptions, enriched relative to Cs. It is not known to be essential to plant metabolism, and its high solubility (except where firmly bonded to clay minerals) causes Li enrichment in soils and waters to be reflected in plant tissues. The precision of the data is good, but standard samples indicate that the aqua regia leach is partial for Li.

Magnesium (Mg)

Magnesium is a macronutrient which plays several important roles in plant health, including photosynthesis and numerous enzymic reactions. From a biogeochemical prospecting perspective, major differences in Mg concentrations in plants can indicate significant differences in the underlying lithology, but smaller differences are not known to be of value in delineating zones of mineralization.

Manganese (Mn)

Manganese is an essential element which is readily taken up by plants, especially where the acidity of the ground is high. In acidic environments there is a Mn/Fe antagonism, which is extended to elements with a broad Fe association.

Molybdenum (Mo)

Distribution patterns and yields of Mo were similar by ICP-ES and INAA. Analytical precision was better by ICP-ES than INAA at concentrations below 5 ppm Mo.

Sodium (Na)

At the concentrations of Na present in the ash samples, determinations by ICP-ES yield appreciably lower results than those by INAA, and the correlation between the two data sets is poor. Since the INAA analysis is total (and accuracy determined by standard samples was good) it must be assumed that the aqua regia digestion is partial for Na. For data interpretation, the INAA results are preferred.

Nickel (Ni)

The presence of Ni may assist in the translocation of nitrogen in some plants, but its essentiality is unproven. When in solution, Ni is taken up easily by plants, therefore the Ni content of the pine tops may be positively correlated with Ni concentrations in groundwaters.

INAA has low sensitivity to Ni (detection limit of 50 ppm Ni in ash). In contrast,

excellent precision and accuracy are obtained by ICP-ES throughout the range of concentrations of this data set. Nickel is an element that concentrates at tree extremities - especially pine tops and cones (Dunn and Scagel, 1989; Dunn, 1994). There is a relative abundance of Ni in the western part of the study area with a maximum of 435 ppm Ni south of Newton Hill, suggesting that the underlying bedrock may be more mafic than elsewhere.

Phosphorus (P)

Phosphorus plays a vital role in plant metabolism, and it is extremely important as a structural part of many organic compounds. Its uptake by trees may be impeded by excess Ca but, from the maps showing distribution patterns of Ca and P, this antagonism is not apparent in the pine tops. Similarly, high levels of P may influence the uptake of numerous trace metals, although this effect appears to be subordinate to the over-riding effect of the substrate chemistry. Highest P concentrations occur in the southwestern part of the survey area.

Lead (Pb)

Despite the known toxic effects of Pb, it occurs naturally in all plants, and in small traces Pb may even be an essential element (Broyer et al., 1972). It is taken up mainly by root hairs and stored as a pyrophosphate in cell walls.

Within Lodgepole pine, Pb is stored mostly in the roots with lesser amounts in the outer bark and lower twigs. Relatively little makes its way to the top stem, as indicated in this data set which shows a median value of 7 ppm Pb and the 98th percentile to be only 22 ppm Pb. The source of the Pb enriched sample (#229) in the southeastern corner of the survey area is unknown.

Tin (Sn)

The quality of the data obtained for Sn is doubtful, and probably random below 3 ppm Sn. These values were from a multi-element ICP-ES scan with no special treatment to extract all of the Sn. Concentrations are almost certainly partial, and clusters of relative Sn enrichment may or may not prove significant.

Strontium (Sr)

Strontium is known to be essential for some plant species, but its general essentiality still needs confirmation. It performs a function similar to Ca in plants, and may be incorporated into their structural components. Interactions between Ca and Sr are complex and they do not always closely follow one another. However, in the survey area the two elements show broadly similar distribution patterns, although there is greater geochemical relief in the Sr data.

Titanium (Ti)

The essentiality of Ti for plant growth is uncertain, but it may play a role in photosynthesis. The ICP-ES analysis is probably not 'total', although it is likely that most of the Ti in the ash goes into solution during the aqua regia digestion.

Vanadium (V)

The essentiality of V for plants other than green algae has not been proven. Soluble V is easily taken up by roots, and it may play a similar role to Mo in fixing nitrogen. Vanadium in the tree tops is mostly present at concentrations below the detection level of 2 ppm. The single high value of 16 ppm V is from an Fe-rich sample.

Tungsten (W)

The precision of the W data below 5 ppm is poor by both INAA and ICP-ES, hence the validity of the data is doubtful. There is a cluster of sites in the eastern part of the area which yielded 3 - 6 ppm by ICP-ES, but these data were not corroborated by the INAA.

Zinc (Zn)

The Zn yield by ICP-ES is generally 20 - 25 percent lower than determinations by INAA. There are differences in the distribution patterns of Zn determined by ICP-ES and by INAA. Some of the relatively high values obtained by INAA were in the northeast at sites for which insufficient ash was available for ICP-ES determinations. The sample in the southwest corner that yielded the highest Zn content by INAA was confirmed by ICP-ES as being rich in Zn.

Other Elements

Iridium determinations by INAA were all less than the detection limit of 2 ppb Ir, indicating that no obvious platinum-group elements occur in the area. Determinations by ICP-ES for bismuth (<2 - 7 ppm) and thallium (<1 - 8 ppm) yielded such poor precision that they were excluded from the data set. Similarly, a problem was encountered with As and Sb determinations by ICP-ES and the data are not reported.

No sample yielded more mercury than the detection limit by INAA of 1 ppm. Although most Hg volatilizes during ashing of the twigs, it has been suggested that there is sometimes residual Hg in plant ash (in the form of a carbide) from near some mineral deposits (Kovalevskii, 1986). In our experience concentrations are typically <20 ppb Hg, rising to approximately 100 ppb Hg in mineralized areas, whereas remote from mineralization concentrations are < 20 ppb Hg. Mercury determinations on the ash by ICP-ES (cold vapour) yielded <5 - 45 ppb Hg, which may be ambient atmospheric levels of Hg in the analytical laboratory. Mercury concentrates more in foliage than in woody tissues. Consequently, pine needles were macerated and analyzed for Hg. Results were a similar order of magnitude to determinations of Hg in ash, yet relatively high concentrations clustered in an area of weak gold enrichment in the pine tops, suggesting that there may be a natural gold/mercury association rather than an artifact (Fig. 3).
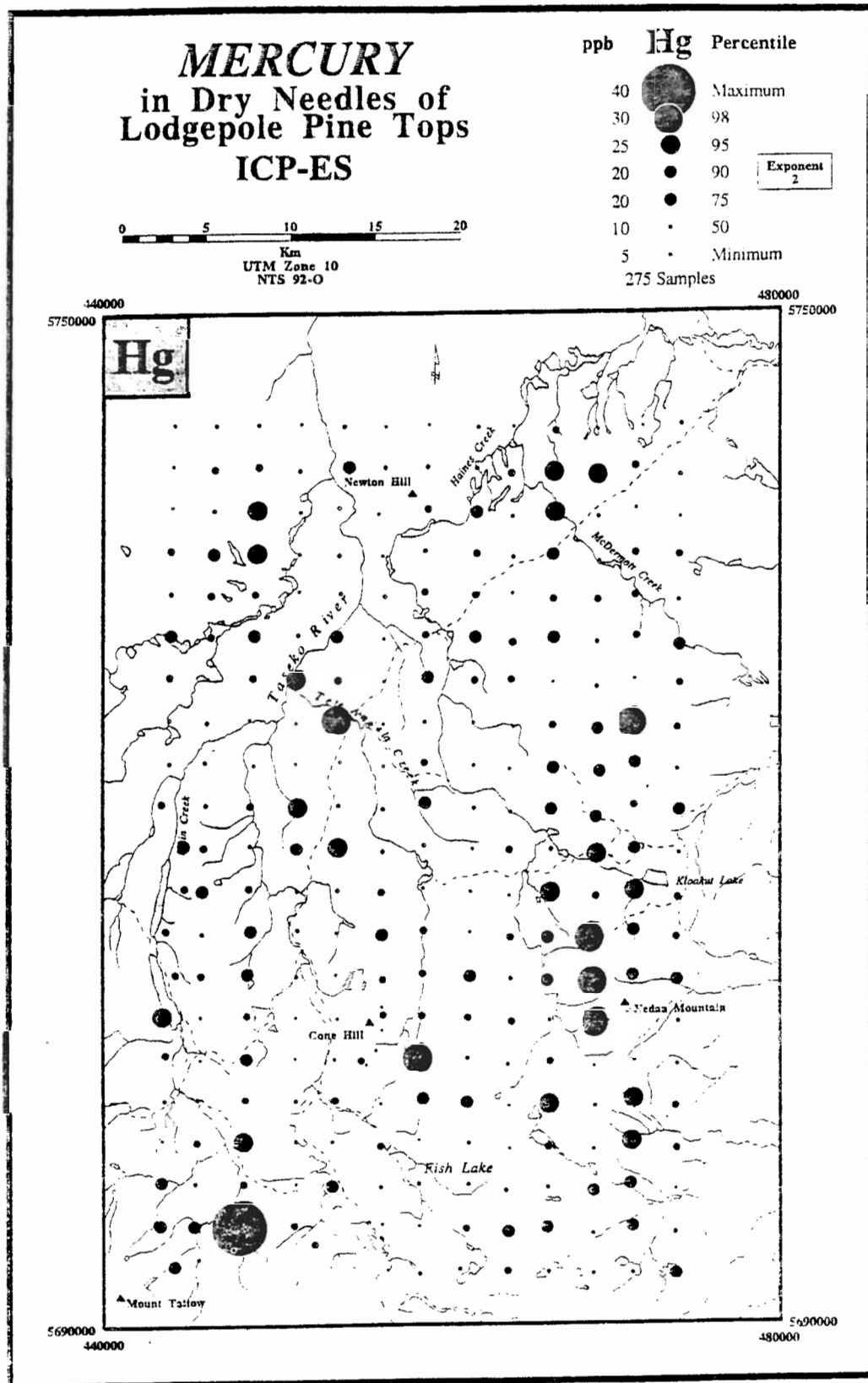
Dunn, Balma, Spirito

Fig. 3: Mercury in Dry Lodgepole Pine Needles

DISCUSSION

In general, element concentrations in tree tops from the survey area are low. However, the low density sampling shows regional trends in geochemical patterns and spatial relationships can be sen. Factors to note are:

a) Chromium is the most strongly concentrated element over the zones of Au mineralization at Fish Lake and Cone Hill;

b) Sample density was too low to outline the low-grade gold mineralization at Fish Lake. However, several areas of *relative* enrichment of Au occur, and there is a northerly trend to some zones of enrichment;

c) In the eastern part of the survey area, near Vedan Mountain, there is relative enrichment of Au, Cs, Rb, W and, to a lesser degree Cd. These elements are amongst those enriched in vegetation from zones of modern epithermal Au mineralization in New Zealand. A similar pattern is exhibited by Al, possibly reflecting an increased level of alteration in the rocks from this area;

d) Copper, Mo, Li, Ni, P and Ag are more enriched in the western part of the study area than in the east.

Helicopter-borne tree top sampling programs at a reconnaissance level provide an extremely rapid means of conducting geochemical surveys in forested terrain, regardless of topography and access. At a between-site spacing of 2.5 km an area of 100 km^2 can be sampled in an hour of flying. This sample density permits recognition of major geochemical trends in the substrate, and the spatial relationships of zones of relative metal enrichment which may reflect lithogeochemical zonation of metals. Data need to be viewed along with those of other data sets (e.g. gamma-ray spectrometry; Quaternary studies) to help in determining their significance. The technique is a method of rapidly screening an area to provide focus for more detailed ground studies.

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