



GEOLOGICAL SURVEY OF CANADA

OPEN FILE 2558

Reconnaissance Biogeochemical Survey Southeastern Cape Breton Island Nova Scotia Part 1 - Black Spruce Bark Parts of NTS 11F,G,J,K

Colin E. Dunn, Stephen W. Adcock, Wendy A. Spirito

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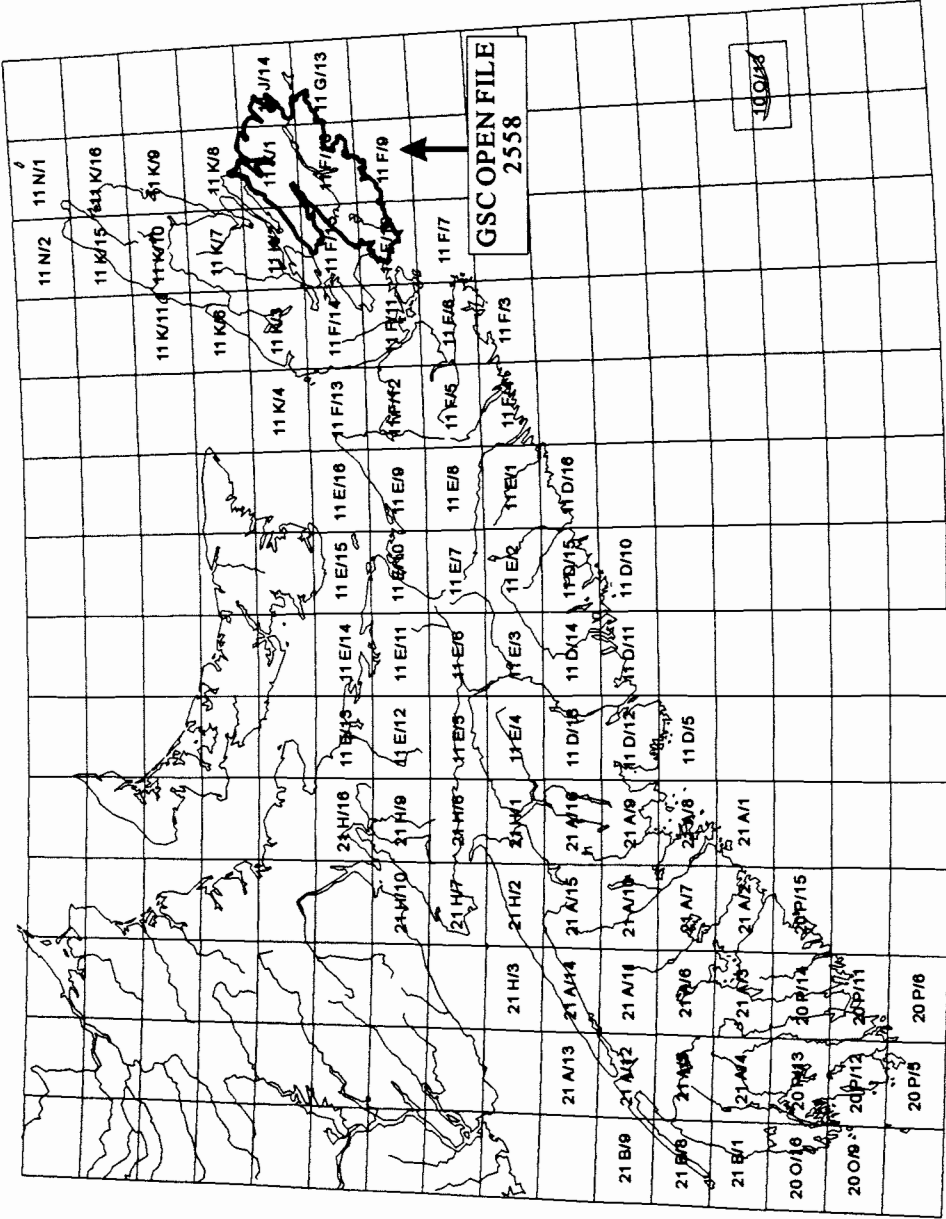
1992

RECONNAISSANCE BIOGEOCHEMICAL SURVEY, SOUTHEASTERN CAPE BRETON ISLAND, NOVA SCOTIA: PART 1 - BLACK SPRUCE BARK

C.E.Dunn, S.W. Adcock, and W.A. Spirito

COOPERATION	COOPERATION AGREEMENT ON MINERAL DEVELOPMENT	ENTENTE DE COOPERATION SUR L'EXPLOITATION MINÉRALE
	Contribution to Canada-Nova Scotia Cooperation Agreement on Mineral Development 1990-1992, a subsidiary agreement under the Economic and Regional Development Agreement. Project funded by the Geological Survey of Canada.	
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		 Province of Nova Scotia

GSC OPEN FILE 2558



Survey area with respect to National Topographic System (NTS) map sheets

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South East Cape Breton

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Geographic Features

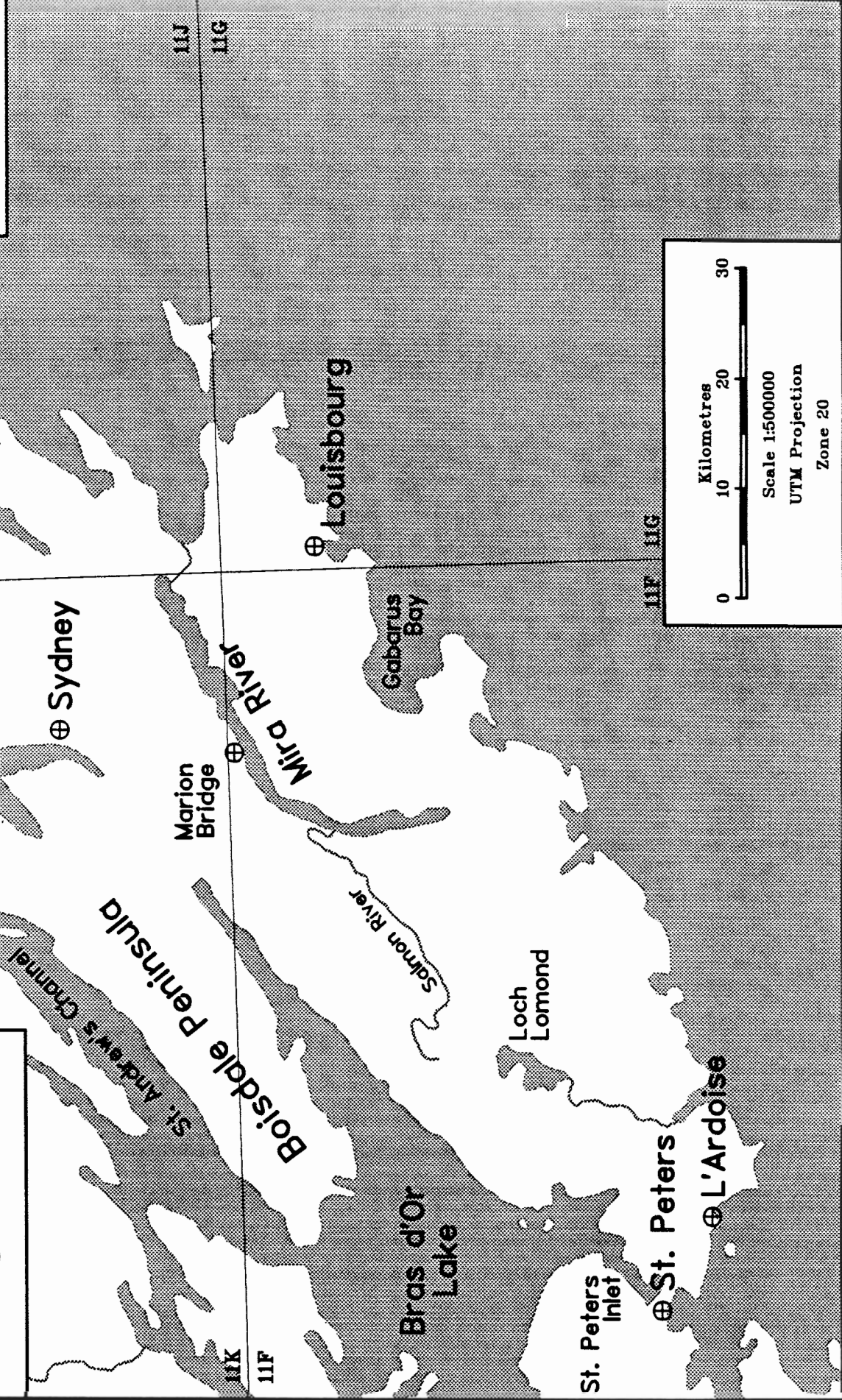


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Introduction

This Open File contains data from a reconnaissance biogeochemical survey in southeastern Cape Breton Island. The survey was conducted in late May to mid-June, 1991, by the Geological Survey of Canada under the Canada - Nova Scotia Cooperation Agreement on Mineral Development (1990 - 1992). It represents the first of a series of biogeochemical Open Files of different tree tissues from several species in the same area. Included are field observations, data listings, statistical summaries, a geology and sample location map, and element distribution maps. The maps show the ash yield of outer bark from black spruce (*Picea mariana*), and the concentrations of 31 elements determined by instrumental neutron activation (INA) analysis, and of 14 elements determined by inductively-coupled plasma emission spectrometry (ICP-ES). All data quoted are concentrations in ash remaining after controlled ignition at 470°C. The ashing process concentrates the elements with little or no loss of elements except those of high volatility (e.g. Br and Hg).

The value to exploration of reconnaissance geochemical surveys that involve the collection of lake or stream sediments and waters, has been extensively tried, tested and documented. However, reconnaissance-level biogeochemical surveys received little attention until a survey of similar magnitude to that reported here was conducted in southeastern Nova Scotia in 1987. Results were published as an Open File (Dunn et al., 1989), and interpretive accounts are given in Dunn (1988, 1990), Rogers and Dunn (1989), Dunn et al. (1991), and Rogers and Dunn (in prep.). In May, 1991 another survey was undertaken in southwestern Nova Scotia. The first of several Open File reports from that area is published by Dunn et al. (1992).

Unlike other geochemical sample media, plants require certain elements for their existence. Zinc, for example, is needed for plant metabolism. Therefore, subtle differences in Zn concentrations between sample sites are more likely to reflect the health of the plant rather than significant differences in the chemistry of the substrate. However, major differences in Zn concentrations may reflect the presence of Zn mineralization.

In light of the Zn example, interpretation of biogeochemical data should be treated with caution. Text notes are provided for each element for assistance. Biogeochemistry is a complex science involving the interaction of organic and inorganic processes that are controlled by many physicochemical parameters. Notwithstanding these complexities, careful and systematic collection and preparation of vegetation samples can provide cost-effective new insight, not readily obtainable by other means, into the chemistry of the substrate and its groundwaters.

The data listed in Appendix A are available in digital form from:

Publications Distribution
Geological Survey of Canada
601 Booth Street
Ottawa
Ontario
K1A 0E8

Tel (613) 995-4342

The data will be supplied on MS-DOS (IBM-PC) 3.5" 1.44 Mb diskettes, as both an RBASE UNLOAD file (ASCII format; can be read by any text editing software; can be imported directly into an RBASE database), and as a .DBF file, which can be read by any DBASE-compatible software.

Credits

Survey design, direction, and sampling methodology: C.E.Dunn.

Field party leader: S.W. Adcock.

Sub-party leaders: E.H.W. Hornbrook, C. Logan, and S. Alvarado, assisted by W.A. Spirito, R.D. Cardinal, S. Lambert, K. Ruhland and S. Phaneuf.

Sample Preparation: undertaken and supervised by R.D. Cardinal, with the assistance of S. Lambert, C. Logan, S. Alvarado, and M. Peters.

Data Management: W.A. Spirito and S.W. Adcock.

Computer Programming: S.W. Adcock developed a program to operate on a VAX computer for plotting the maps.

Instrumental Neutron Activation Analysis: by contract to Activation Laboratories Ltd., Ancaster, Ontario.

Inductively-Coupled Plasma Emission Spectrometry: by contract to Min-En Laboratories Ltd., Vancouver, B.C.

Survey Description and Methodology

Scope of Survey

During a three week period, commencing late in May, 1991, tree tissue samples were collected from approximately 550 sites within a 4000 km² area of southeastern Cape Breton Island. The southeastern boundary of the survey area was St. Peters Inlet. The northwestern boundary was St. Andrew's Channel. Black spruce were present at only 244 of these sites. Therefore, this Open File contains data from bark samples collected at an average density of 1 per 15 km². The sampling grid was irregular because of difficulty in accessing some areas. Where available, samples were collected at 2 km intervals along driveable roads and tracks, with helicopter access to a few remote sites. Three trucks were used, each with a crew of two. At each sample location vegetation samples were selected from a site at least 50 m from a highway, or 10 m from a little-used track.

Sample locations

The 1:10000 LRIS (Land Registration Information Service) maps were used for almost all of the field work. The only exceptions were a handful of sites for which the 1:10000 maps were not available at the time of the survey. For these sites, 1:50000 NTS maps were used. The 1:10000 maps use the Nova Scotia modified transverse Mercator (MTM) projection, in conjunction with the NAD27 datum. A program (CONV27) was purchased from LRIS to convert MTM coordinates to UTM coordinates, based on the NAD27 datum.

Sample Collection

An orientation survey of the area conducted in October, 1990, showed that the most common species are balsam fir (*Abies balsamea*), black spruce (*Picea mariana*), white spruce (*Picea glauca*), and tamarack (*Larix laricina*). Chemical analysis of twigs from these species and the outer bark of the spruce and tamarack indicated that each was sensitive to a particular range of elements, but that black spruce bark had generally higher concentrations of trace metals than the other tissues that were collected. The chemistry of white spruce is appreciably different from that of black spruce (Dunn, 1991); therefore samples from the two species could not be interchanged. White spruce has a lower content than black spruce of many trace elements (especially those associated with Fe), and in most parts of the survey area white spruce is the less common of the two species (except around Bras d'Or Lake). Consequently, black spruce bark was selected as one of the principal sample media, but in addition, samples of tamarack bark and the twigs of black spruce, balsam fir and tamarack were collected at those survey sites where they were available. Data from these species will be presented in future open file releases.

The outer bark of the spruce was collected by scraping about 50 g of loose scales into a plastic pan, and transferring samples to a standard 'kraft' paper soil bag. A paint scraper proved to be an effective tool for removing the bark scales. Care was taken to select only black spruce trees. Also, care was taken *not* to include the inner bark for the same reason.

There are seasonal variations in the chemistry of twigs, but outer bark is dead tissue, and therefore its composition does not change during the course of the year. However, since twigs were also collected the survey was completed as quickly as possible.

Sample Preparation and Analysis

Approximately 50 g of dry bark was weighed into aluminium trays. The trays were placed in a pottery kiln, and the temperature slowly raised (over 2 - 3 hours) to 470°C. After a further 12 hours at this temperature, no charcoal remained and the bark was reduced to approximately 1 g of ash. Half was accurately weighed and compacted into small polyethylene vials, suitable for instrumental neutron activation analysis (INAA), and submitted for the determination of 35 elements. Maps are provided for 31 of these elements. Concentrations of

Hg, Ir, and Tb were all below the detection levels of 1 ppm, 2 ppb, and 0.5 ppm, respectively. Determination levels for Sn by INAA vary with the matrix composition of the sample, and are commonly between 50 and 100 ppm Sn. Only two samples yielded concentrations above detection by this method and, because further tests did not substantiate the analytical data, the data for Sn by INAA are omitted from the listings.

The remaining half of the ash sample was submitted for multi-element analysis by inductively coupled plasma emission spectrometry ICP-ES, following an aqua regia digestion. For most elements this extraction is 'total', although for some (e.g. Al, B) it is only partial. However, the analytical precision was extremely good for most elements, such that the relative element distribution patterns are meaningful even if the absolute concentrations are only partial.

Appropriate standards and duplicates were inserted to ensure quality control. The precision obtained varied between elements and with element concentration. Of the elements reported here, most samples contained levels substantially higher than detection limits, thereby providing analytical precision of better than $\pm 10\%$.

Data on mean values and standard deviations obtained for each element in a standard ash sample (V2) are given in Tables 1 and 2. Examples of the reproducibility of the data on two sample splits are presented graphically for Au, As, Zn, Ni, Cu, and Pb in Figure 1. Tables 3 and 4 show the determination (lowermost detection) limits quoted for each element by the analytical laboratories, and the substitution values used for statistical calculations where analyses yielded concentrations below detection.

Table 1: Mean and Standard Deviation for Standard V2 (N=14) analyzed by INA

Element		Mean	Standard Deviation
Gold	Au	13	1
Silver	Ag	14	0.5
Arsenic	As	1.7	0.3
Barium	Ba	2650	191
Bromine	Br	17	2
Calcium	Ca	26.2	2.2
Cobalt	Co	4	0.5
Chromium	Cr	29	2
Caesium	Cs	2.8	0.3
Iron	Fe	1.33	0.38
Hafnium	Hf	1.4	0.2
Potassium	K	6.86	0.48
Molybdenum	Mo	4	1
Sodium	Na	5757	443
Rubidium	Rb	193	13
Antimony	Sb	1.1	0.1
Scandium	Sc	1.0	0.1
Selenium	Se	*	*
Strontium	Sr	1221	153
Tantalum	Ta	*	*
Thorium	Th	1.2	0.3
Uranium	U	0.5	0.3
Tungsten	W	*	*
Zinc	Zn	2371	216
Lanthanum	La	4.1	0.6
Cerium	Ce	7	1
Neodymium	Nd	*	*
Samarium	Sm	0.5	0.1
Europium	Eu	*	*
Ytterbium	Yb	0.20	0.06
Lutetium	Lu	*	*

* all values below the determination limit

Table 2: Mean and Standard Deviation for standard V2 (N=14) analyzed by ICP-ES

Element		Mean	Standard Deviation
Aluminium	Al	7992	426
Boron	B	172	8
Beryllium	Be	*	*
Cadmium	Cd	1.7	0.6
Copper	Cu	168	65
Lithium	Li	2	0.5
Magnesium	Mg	33164	1239
Manganese	Mn	17945	644
Nickel	Ni	41	3
Phosphorus	P	10753	382
Lead	Pb	415	107
Titanium	Ti	537	34
Vanadium	V	16.2	0.6
Tin	Sn	47	2

* all values below the determination limit

Figure 1: Scatterplots of analytical duplicate pairs for Au, As, Zn (INAA), Cu, Pb, Ni (ICP-ES)

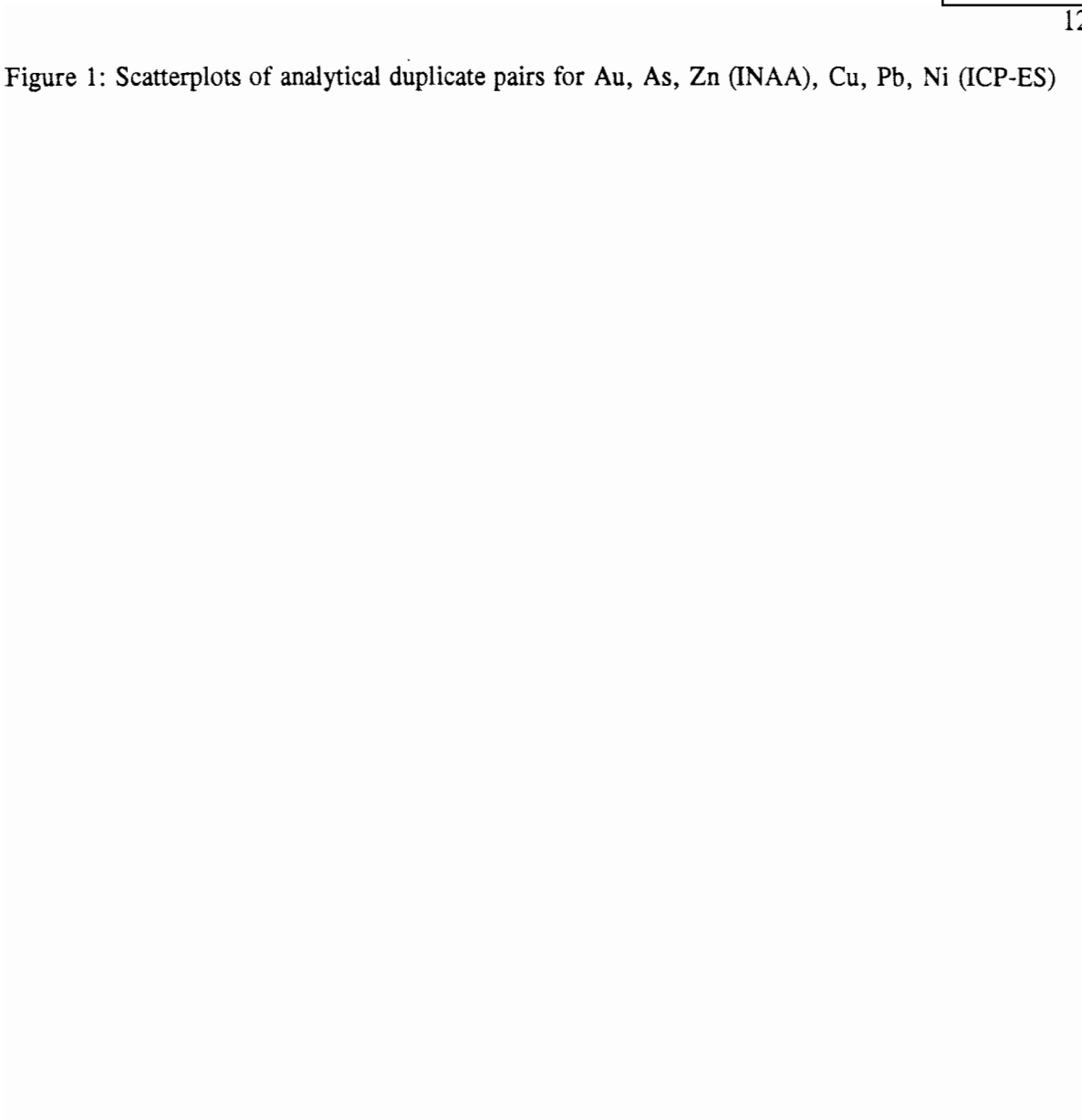


Figure 1: Scatterplots of analytical duplicate pairs for Au, As, Zn (INAA), Cu, Pb, Ni (ICP-ES)

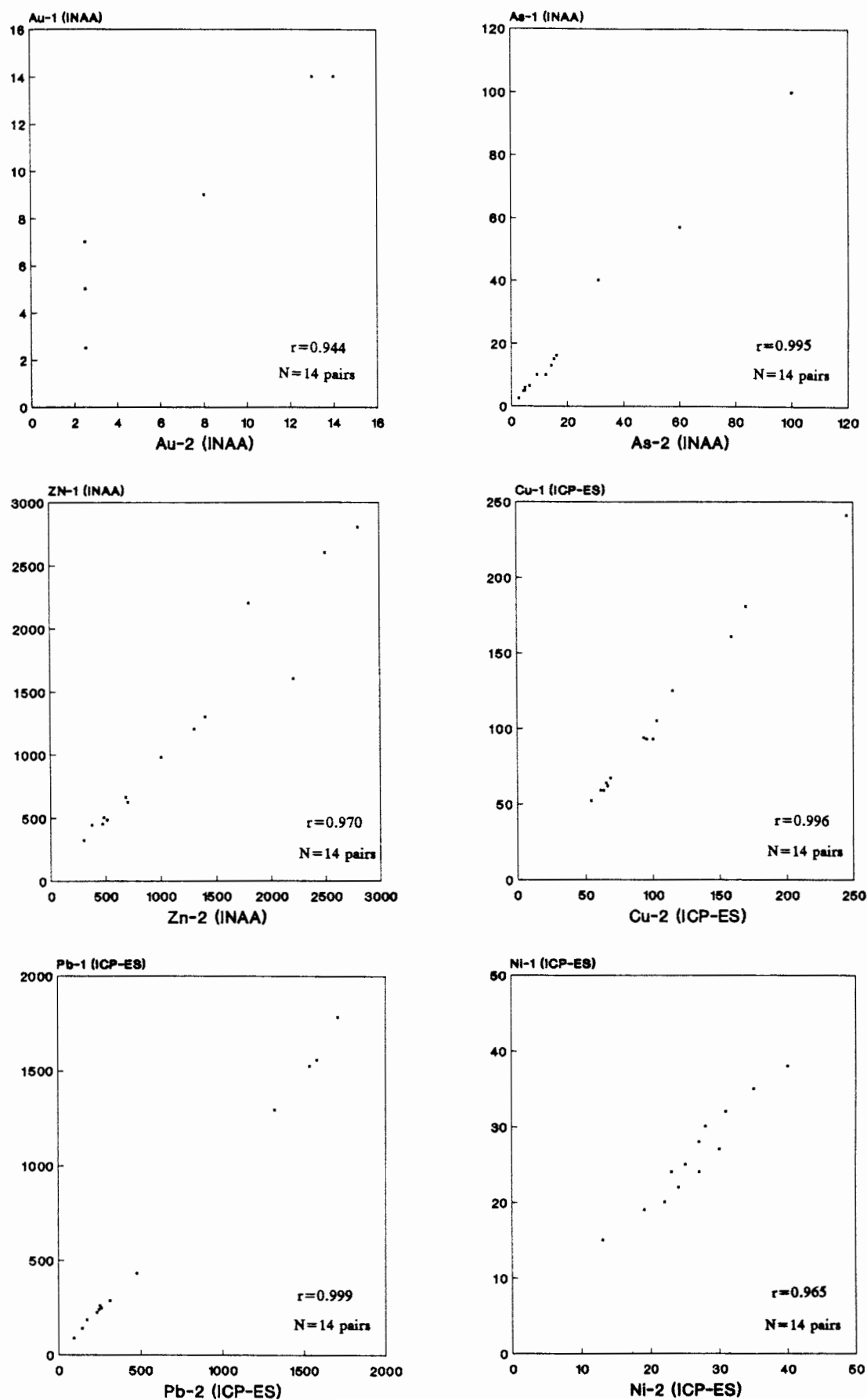


Table 3: Determination Limits and Substitution Values for Elements Analysed by INAA

Element		Units of Measure	Determination Limit	Substitution Value
Gold	Au	ppb	5	2.5
Silver	Ag	ppm	2	1
Arsenic	As	ppm	0.5	*
Barium	Ba	ppm	10	*
Bromine	Br	ppm	1	*
Calcium	Ca	%	0.2	*
Cobalt	Co	ppm	1	*
Chromium	Cr	ppm	1	*
Caesium	Cs	ppm	0.5	0.25
Iron	Fe	%	0.05	*
Hafnium	Hf	ppm	0.5	0.25
Potassium	K	%	0.05	*
Molybdenum	Mo	ppm	2	1
Sodium	Na	ppm	10	*
Rubidium	Rb	ppm	5	2.5
Antimony	Sb	ppm	0.1	*
Scandium	Sc	ppm	0.1	*
Selenium	Se	ppm	2	1
Strontium	Sr	ppm	300	150
Tantalum	Ta	ppm	0.50	0.25
Thorium	Th	ppm	0.1	*
Uranium	U	ppm	0.1	0.05
Tungsten	W	ppm	1	0.5
Zinc	Zn	pm	20	*
Lanthanum	La	ppm	0.1	*
Cerium	Ce	ppm	3	1.5
Neodymium	Nd	ppm	5	2.5
Samarium	Sm	ppm	0.1	*
Europium	Eu	ppm	0.01	0.005
Ytterbium	Yb	ppm	0.05	0.025
Lutetium	Lu	ppm	0.05	0.025

* all values above the determination limit

Table 4: Determination Limits and Substitution Values for Elements Analysed by ICP-ES

Element		Units of Measure	Determination Limit	Substitution Value
Aluminium	Al	ppm	1	*
Boron	B	ppm	1	*
Beryllium	Be	ppm	0.2	0.1
Cadmium	Cd	ppm	0.2	0.1
Copper	Cu	ppm	1	*
Lithium	Li	ppm	1	*
Magnesium	Mg	ppm	10	*
Manganese	Mn	ppm	1	*
Nickel	Ni	ppm	1	*
Phosphorus	P	ppm	10	*
Lead	Pb	ppm	1	*
Titanium	Ti	ppm	10	*
Vanadium	V	ppm	0.1	*
Tin	Sn	ppm	2	1

* all values above the determination limit

Geology

Bedrock and Mineralization

The geology of southeast Cape Breton Island is very complex. The area is heavily faulted, and correlating stratigraphic units is very difficult (c.f. Barr and Raeside, 1989; Keppie, 1990).

The late Precambrian rocks have been divided into three major groups. Weeks (1954) identified the George River Group and Fourchu Group. Barr et al. (1989) re-assigned part of the Fourchu Group to a new unit, which they termed the Main-à-Dieu sequence. The George River Group is a metasedimentary sequence of quartzites and marbles. The Fourchu Group is a predominantly metavolcanic sequence, with minor metasediments. It outcrops in a series of fault-bonded blocks, with a pronounced northeast-southwest orientation. The Main-à-Dieu sequence is distinguished from adjacent Fourchu Group rocks by a predominant sedimentary component and weaker cleavage.

Overlying the Precambrian rocks is a sequence of sedimentary and minor volcanic rocks of late Precambrian to Ordovician age. South of Marion Bridge, Barr et al. (1992) identified two distinct sequences separated by a major fault running along the Mira River.

The Devonian-Carboniferous L'Ardoise Block is an allochthonous sedimentary unit. The poorly exposed McAdam Lake Formation is of similar age and lithology.

Carboniferous sediments occur throughout the area. Gibling et al. (1987) recognised two fining-upward megasequences. The Horton, Windsor and Canso Groups comprise the lower sequence. The coal-bearing Morien Group comprises the upper sequence.

Plutonic rocks occur throughout the area. The majority of the plutons are late Precambrian to Cambrian in age. The Salmon River, Gillis Mountain and Deep Cove plutons are Devonian. Compositionally, the larger plutons are acidic (granite, granodiorite), and the smaller plutons range from acidic to basic (gabbro).

There are three large abandoned mines in the area - the Mindamar Mine at Stirling (Zn-

Pb-Cu massive sulphide deposit), the Yava Mine on the Salmon River (sandstone-hosted Pb; Sangster and Vaillancourt, 1990; MacDonald et al., 1991) and the Coxheath Mine (porphyry Cu; Oldale, 1967). Other notable deposits include the polymetallic Cu-Mo prospects at Deep Cove, Blue Mountain and Gillis Mountain (Macdonald, 1989). Northeast of Loch Lomond, there are several open pits producing celestine (SrSO_4).

Geological base map compilation

The transparent geological overlay map provided in the pocket, and the coloured 1:125000 sample location map are digitized computer-plotted compilations derived from the following sources:

Barr, S.M., Macdonald, A.S. and White, C.E. (1988). The Fourchu Group and associated granitoid rocks, Coxheath Hills, East Bay Hills, and southwestern Stirling and coastal belts, southeastern Cape Breton Island, Nova Scotia. GSC Open File 1759.

Barr, S.M., Macdonald, A.S. and White, C.E. (1989). Geological maps of the coastal and Stirling belts, southeastern Cape Breton Island, Nova Scotia. GSC Open File 1988.

Barr, S.M., O'Reilly, G.A. and O'Beirne, A.M. (1982). Geology and geochemistry of selected granitoid plutons of Cape Breton Island. N.S. Dept. Mines and Energy, Paper 82-1.

Barr, S.M. and Setter, J.R.D. (1984). Geological map of the Boisdale Peninsula, central Cape Breton Island. N.S. Dept. Mines and Energy, Map 84-2.

Barr, S.M. and Setter, J.R.D. (1986). Petrology of granitoid rocks of the Boisdale Peninsula, central Cape Breton Island, Nova Scotia. N.S. Dept. Mines and Energy, Paper 84-1.

Boehner, R.C. and Giles, P.S. (1986). Geological map of the Sydney Basin, Cape

- Breton Island. N.S. Dept. Mines and Energy, Map 86-1.
- Boehner, R.C. and Prime, G. (1985). Geology, Loch Lomond basin and Glengarry half graben. N.S. Dept. Mines and Energy Map 85-2.
- Donohoe, H.V. Jr. and Grantham, R.G. (1989). Geological Highway Map of Nova Scotia, second edition, Atlantic Geoscience Society, Halifax, AGS Special Publication No. 1.
- Keppie, J.D., Dostal, J. and Murphy, J.B. (1979). Petrology of the late Precambrian Fourchu Group in the Louisbourg area, Cape Breton Island. N.S. Dept. Mines, Paper 79-1.
- Keppie, J.D. and Smith, P.K. (1978). Age of igneous rocks along the Lennox Passage - St. Peters lineament, southern Cape Breton Island. N.S. Dept. Mines Paper 78-2.
- Macdonald, A.S. (1989). Metallogenic studies, southeastern Cape Breton Island. N.S. Dept. Mines and Energy Paper 89-1.
- Smith, P.K. (1978). Geology of the Giant Lake area, southeastern Cape Breton Island, Nova Scotia. N.S. Dept. Mines, Paper 78-3.
- Weeks, L.J. (1954). Framboise map sheet. GSC Map 1037A.
- Weeks, L.J. (1958). Mira map sheet. GSC Map 1056A.
- Weeks, L.J. (1964). St. Peters map sheet. GSC Map 1083A.

Quaternary Deposits

The chemistry of trees is influenced partly by the bedrock, but primarily by the chemical composition of groundwaters and surficial deposits. Therefore, consideration of the physical and chemical nature of the glacial deposits is relevant to interpretation of the biogeochemical patterns.

Grant (1988) recognized four periods of Wisconsinan ice flow in the study area. The oldest was toward the south, followed by flows to the east, then north, and finally toward the south once more. Most of the survey area is covered by a veneer of sandy and silty red or grey tills. Recent work by McClenaghan et al. (1992) presents comprehensive summaries of till geochemical data and pebble lithologies within approximately 50% of the biogeochemical survey area.

Map Production and Data Handling

The maps are all drawn using the Universal Transverse Mercator projection, with a central meridian of 63° (Zone 20). This projection is the same as that used for the 'Geological Map of the Province of Nova Scotia' (Keppie, 1979). Map plots in this Open File were produced by VAXMAP geochemical mapping software used by the Applied Geochemistry Subdivision of the GSC. Computations were performed on a VAX minicomputer, with output to a Hewlett-Packard Laserjet printer (for the small maps) and to a Synergy electrostatic printer (large coloured map).

The coastline and drainage were obtained in digital form from Surveys, Mapping and Resource Sector of the Dept. of Energy, Mines and Resources. For the small scale maps, the digital data were purchased from the National Atlas Information Service. These data were derived from 1:2000000 scale original maps. Features are accurate to about 200m. This led to some samples which were collected near lakes or the ocean being plotted in the water. The 1:125000 map was plotted from data purchased from the Canada Centre for Geomatics. These data were derived from the 1:250000 NTS map sheets, and therefore are much more accurate than the NAIS data. There is too much detail for them to be useful as base maps at a scale of

1:500000.

Element concentrations below analytical detection limits were reduced to half of the determination limit for data plotting and statistical calculations. For samples with duplicate analyses, data from the first of each duplicate pair were used in the statistical analysis.

The dot maps are based on a method first developed by Bjorklund and Gustavsson (1987). It was used as the primary data presentation method for the Nordkalott project (Bolviken et al., 1986), and since then has become a popular technique at the GSC (Thorleifson and Kristjansson, 1990; McClenaghan, DiLabio and Laurus, 1992; Coker et al., in preparation).

The dot size is proportional to the analytical value, according to the following formula (in FORTRAN notation):

$$\text{RADIUS} = \text{RSYM} * (\text{RA} ** \text{RFOPT} / \text{RV} ** \text{RFOPT})$$

RSYM: the maximum dot radius, defined by the user in millimetres.
RA: the analytical value to be plotted
RV: the analytical value at a specified percentile
RFOPT: an exponent

If RA is greater than RV, then RA is set equal to RV. RV is generally set equal to the analytical value corresponding to the 95th or 98th percentile. All samples with values greater than RV will therefore be plotted with a constant dot size equal to RSYM. If the calculated value of RADIUS drops below a certain minimum radius, as defined by the user, then a dot of that minimum radius is plotted. This ensures that dots do not become minuscule. RFOPT is defined by the user, and is usually set in the range 1 to 2. Increasing RFOPT emphasises those samples with high values.

Element Distribution Maps

Before interpreting the element distribution maps, the reader is advised to note the comments provided under each of the element headings. These notes are organized alphabetically by element symbol, dealing first with those elements determined by INAA, followed by those determined by ICP-ES (except for the rare earth elements, which are grouped together after Zn). This sequence is the same as the element listings in Appendix A and the statistical summary in Appendix B.

Transparent Overlay

A transparent overlay at the same scale as the element distribution maps is provided to help in locating individual samples (identified by sample number on the folded 1:125 000 scale colour map), and in relating their positions to main communities, bedrock geology, mineral deposits and showings.

Ash Yield

The map of ash yield from the twigs is presented because Russian workers (Chukhrov et al., 1979) have noted that high ash yield of plants can be related to areas of intensely weathered bedrock. If this association occurs in Cape Breton Island there may be exploration significance to the patterns observed, since zones of alteration (often related to mineralization) are subject to relatively intense weathering. It should be noted, however, that the ash yield varies according to the nature of the underlying rock *type* (p. B1), presumably because of the relative ease of weathering of some lithologies.

Distribution Maps of Elements Determined by ICP-ES

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 spruce bark are commonly less than 10 ppb Au. The median value obtained for the current data set is 5 ppb Au, although the median values

are slightly higher for samples from over the Fourchu Group and the Devono-Carboniferous sediments. 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 (see Figure 1). In general, Au concentrations in the study area are low, and local clusters of samples with Au enrichment are few. Highest concentrations occur near the abandoned Stirling mine.

Silver (Ag)

The analytical detection limit for Ag in plant ash is 2 ppm Ag. Ninety-five percent of the samples yielded less than this concentration, and the map of Ag distribution shows that there are just a few single point anomalies. These are not considered to be of particular relevance to mineral exploration.

Arsenic (As)

Arsenic is known for its toxicity, yet some tree species 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. Compared to other areas of Canada, the As concentrations are relatively high for black spruce bark (median is 10 ppm As) reflecting moderately high background levels of As in rocks of the area. Of note is the relative enrichment of As in samples from over the Morien Group, indicating either elevated levels in the bedrock or contamination from the industry on the east coast between Sydney and Glace Bay.

Barium (Ba)

All samples yielded substantially more barium than the INAA detection limit of 10 ppm Ba. Spruce bark commonly contains 1000 -2000 ppm Ba, but concentrations within the map area range up to 8500 ppm. Highest concentrations occur in samples from over the Devono-Carboniferous sediments (p. B.5)

Bromine (Br)

Bromine is a volatile element, present in most, if not all terrestrial plants, but it is not known to be an essential element. It can form many different complexes within plants. Some complexes volatilize during the ashing process, causing losses of 30 - 90 percent of the Br contained within the plant tissues. However, it has been noted (Dunn, 1986) that where gold mineralization exists, there is sometimes enrichment of Br in plant ash, indicating that a stable Br compound is retained. Within the survey area this association is not apparent, and the median Br concentrations are similar for all underlying rock formations..

Calcium (Ca)

Calcium is a major 'building block' element, essential for the rigidity of cell walls in most plants. The variations in Ca content of the bark may influence the distribution of some trace elements. For example, a statistical analysis of multi-element data sets commonly reveals a strong association of Ca with Ba and Zn. The median Ca content of bark samples from trees growing over Morien Group rocks is appreciably lower than elsewhere in the study area.

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 the vicinities of gold mineralization in northern Saskatchewan (Dunn, 1986). Throughout southeastern Cape Breton Island the Co concentrations in spruce are generally low, with the median value at only 8 ppm Co, and the 98th percentile at 16 ppm Co. Clusters of relative Co enrichment occur over sediments of the Morien Group to the east of Glace Bay, and southwest of Loch Lomond on the southern margin of the L'Ardoise Block.

Chromium (Cr)

Chromium is a non-essential element for which precise INAA data are obtained at low ppm levels. Concentrations are commonly higher than the 10 - 20 ppm Cr that is characteristic of conifer bark ash. Enrichment is particularly noticeable over sediments of the Morien Group with up to 290 ppm Cr in samples from north of Sydney. There is a striking similarity between

the distribution patterns of Cr and those of Fe and Pb.

Caesium (Cs)

This alkali metal performs no known essential function in plant tissues, and is usually present at less than 3 ppm Cs in spruce bark ash. The median value for this data set is 3 ppm Cs, and no zones of unusual enrichment are present. Clusters of relative enrichment occur in bark samples collected over the Proterozoic and Cambro-Ordovician sediments and volcanic rocks between Marion Bridge and Gabarus Bay. There is a close geochemical affinity between Cs and Rb in most rock types, but in plant tissues the two elements behave differently. Consequently, there are appreciable differences between the distribution patterns shown in the Cs and Rb maps.

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 map of Fe distribution closely parallels that of Cr and to a lesser extent Pb. The strong influence of Morien Group sediments on the Fe content of the spruce bark is particularly noticeable.

Hafnium (Hf)

The content of Hf in the ash of spruce bark is commonly 1 - 2 ppm Hf, and there is usually a strong association with Fe. The maps show, however, that in the study area the elements are behaving differently, and that most sites with Hf enrichment occur in a northeasterly trend which follows the contact between rocks of the Canso and Morien groups. The reason for this unusual enrichment of Hf is unknown.

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. Lower concentrations are present in bark than in most other plant tissues, with less than 3% as the median value. In environments where there is an abundance of K, trees may excrete unwanted amounts into the outer bark. If this is the case, sites with relatively high levels of K in bark may reflect a potassic-rich substrate (e.g. K-rich clays or felsic rocks).

Molybdenum (Mo)

Molybdenum is required in trace amounts by most plants for nitrogen fixation and nitrate reduction. Concentrations are usually < 2 ppm Mo in spruce bark, although over highly alkaline soils the trees more readily absorb Mo and therefore slightly higher levels may be expected. Concentrations of Mo are unusually high for spruce bark in samples from over clastic rocks of the Morien Group in the northeastern part of the survey area.

Sodium (Na)

The effect of salt-spray from the sea is evident on the Na map, since most of the elevated Na concentrations occur in trees from sites near the shore.

Rubidium (Rb)

Although Rb may substitute for K in rock-forming minerals, there is an antagonism between K and Rb in plants (Kabata-Pendias and Pendias, 1984). This results from their competition for the same binding sites, thereby causing different distribution patterns for the two elements. Samples from over the Carboniferous sediments are more enriched in Rb than elsewhere in the survey area.

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. Moderate enrichment of Sb occurs in bark from sites scattered throughout the survey area. In general samples from over rocks of the Fourchu, Windsor and Morien groups are relatively enriched in Sb, although the highest concentration (88 ppm Sb) is from a site (#5114) with coincident enrichment of As, overlying Cambro-Ordovician sediments.

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 bark is controlled essentially by the chemistry of the substrate and by the distribution of other elements. In particular, there is commonly a near perfect correlation between Sc and Fe in plant tissues, and it is therefore surprising that the Sc and Fe maps exhibit such disparate patterns. It appears that an unknown factor is controlling the distribution of Sc in this area.

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 bark ash does not represent the total content of the dry tissue. Despite this, the residual Se commonly bears a significant relationship to zones of Au mineralization. This was particularly notable in southeastern Nova Scotia (Dunn, 1988). The dominant feature of the Se map is the relative enrichment that occurs in samples from over the Proterozoic rocks.

Strontium (Sr)

INAA has poor sensitivity to traces of Sr, and analytical precision is inferior to that for most other elements considered in this study. However, Sr concentrations are significantly above detection limits in over 80 percent of the samples, such that the areas of Sr enrichment depict significant regional variations.

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. However, interactions between Ca and Sr are complex and, as demonstrated by the distribution maps for these elements, they do not closely follow one another.

Tantalum (Ta)

Bark rarely contains more than 1 ppm Ta in ash. Within the survey area the median value for the data set is below the determination limit for Ta, and the 95th percentile is only 1.7 ppm Ta. The few sites that exhibit weak Ta enrichment are mostly from over clastic rocks of the Morien Group.

Thorium (Th)

Thorium has low solubility and is not essential for plant growth. Its concentration in plant ash is typically < 2 ppm Th, 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 map of Th distribution shows that there is a pronounced northeasterly trend of relative Th enrichment extending from Loch Lomond to Glace Bay in samples from over the sediments of the Windsor and Morien groups.

Uranium (U)

Although U_3O_8 has high solubility, it rarely exceeds concentrations of more than 2 ppm in plant ash. There are a number of notable exceptions, particularly in northern Saskatchewan where enrichments in spruce twigs are locally more than three orders of magnitude (Dunn, 1983). In southeastern Cape Breton the median value for U in spruce bark ash is 1.2 ppm U and, although concentrations do not exceed 5 ppm U, there is a northeasterly trend (similar to that of Th) of relative U enrichment that is confined mostly to subcropping rocks of the Windsor and Morien groups.

Tungsten (W)

The detection limit for W by INAA is 2 ppm in ash, which is above the usual concentrations in tree tissues. This accounts for the simple pattern of W distribution on the map, except for the area of enrichment in the northeast over sediments of the Morien Group.

Zinc (Zn)

Because 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. However, the Zn map shows a range in concentration of over 5000 ppm Zn; therefore, the regional pattern of Zn distribution is reflecting broad differences across the area. Data on p. B26 show that there is relative enrichment of Zn in bark samples from over the Devono-Carboniferous and Morien Group sediments.

Rare-Earth Elements (REE)

Because of their chemical coherence, these elements are considered as a single 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). Of these elements, only Tb consistently yields concentrations below the detection level of 0.5 ppm and therefore no map of Tb is included. Maps of these elements show very similar distribution patterns, with relatively high concentrations over rocks of the Morien Group to the east of Glace Bay. There is a similarity in the distribution of the REE with the patterns observed for Th, U, Hf and to a lesser degree Pb.

Distribution Maps of Elements Determined by ICP-ES

Aluminium (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 and the high levels of Al in the samples 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 undertaken to compare data obtained on the ash internal standard (V2) by ICP-ES (aqua regia digestion) with some INAA data (determinations for short-lived isotopes) indicate that the acid digestion releases approximately 50% of the Al.

Boron (B)

Borosilicate test tubes were used for the acid digestion of the ash samples, from which the analysts suggest 5 - 10 ppm B may be released. This is an insignificant amount in comparison with the concentrations of B present in the ash. Tests indicate that the analytical procedure used provides data which represent about 50% of the true concentrations of B in the samples. Precision, however, is excellent.

Boron is an element that is essential for plant growth, and it is believed to play an important role in the translocation of sugars. In general, B uptake is low from Ca-rich soils, and there is a general similarity between the maps of these two elements suggesting that Ca may play a role in controlling the distribution of B. There is a relative deficiency of B in samples collected over rocks of the Morien Group.

Beryllium (Be)

Russian workers have found that conifer bark is effective in concentrating Be in the vicinity of Be mineralization (Kovalevskii, 1978). Only a few ppm Be is present in soils, and because it is a non-essential element to plant growth (in high concentrations it is toxic), its presence in the substrate is reflected in the spruce bark by anomalies of only a few ppm. Analytical precision is extremely good to the 0.5 ppm Be level, but almost 90% of the samples yielded Be concentrations below this level. The subtle anomalies that are present are mostly located over sedimentary rocks of the Morien Group to the east and southeast of Glace Bay.

Cadmium (Cd)

Although there is a strong geochemical association between Cd and Zn in many geochemical environments, this is always 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 may therefore be expected to reflect relative Cd concentrations in the soils and groundwaters whether they are due to mineral deposits or environmental contamination. 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.

Within the survey area there are some high concentrations of Cd but they are not

restricted to any one rock unit. Multi-site enrichment occurs between the Stirling and Yava deposits.

Copper (Cu)

Data obtained by ICP-ES from the aqua regia leach are both precise and accurate (see Figure 1). Copper plays a fundamental role in a plant's metabolism. It assists in such processes as respiration, photosynthesis, nitrogen fixation and valence changes, and is present in many micro-components of plants (small and large molecules, chloroplasts, mitochondria etc.). As a consequence, the 'background' concentration of Cu in ash of the bark (median value of 150 ppm Cu) is high compared to many trace elements.

The interpretation of Cu distribution patterns in tree tissues should be approached with caution, since laboratory studies report numerous antagonistic and synergistic interactions with both major and minor elements. These are reviewed briefly by Kabata-Pendias and Pendias (1984). However, despite 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. Several sites of Cu enrichment are coincident with those of Cd between the Stirling and Yava deposits, and near the contact between the Fourchu and Main-à-Dieu groups from Gabarus Bay northward where up to 701 ppm Cu in the bark is recorded.

Lithium (Li)

Lithium commonly follows Rb and Cs in nature. In spruce bark it is less abundant than Rb but enriched with respect to Cs. It is not known to be essential to plant metabolism. Its high solubility (except where firmly bonded to clay minerals) causes Li enrichment in soils and waters to be readily reflected in plant tissues. Most of the sites where the spruce bark shows relative enrichment in Li occur over rocks of the Morien Group.

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. The data on p. B40 show that there is relative depletion of Mg in samples from over the Cambro-Ordovician and Morien sediments.

Manganese (Mn)

Red and black spruce contain considerably more Mn than most other species. 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 affinity for Fe. Unusually high Mn concentrations occur in samples from over the felsic igneous complexes.

Nickel (Ni)

The presence of Ni may assist in the translocation of nitrogen in some plants, but its general essentiality is unproven. When in solution, Ni is readily taken up by plants, therefore it may be expected that the Ni content of the bark 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 down to the minimum level (8 ppm) recorded for this data set. Throughout the survey area the concentrations of Ni are not high, although zones of relative Ni enrichment occur between the Stirling and Yava deposits, and southwest of Loch Lomond.

Phosphorus (P)

Phosphorus plays a vital role in plant energy metabolism, and it is extremely important as a structural part of many organic compounds. Its uptake by trees may be antagonized by excess Ca but, from the maps showing distribution patterns of Ca and P, this antagonism is not apparent in the black spruce bark. 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 chemistry of the substrate.

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. Kovalevskii (1979) showed that in Dahurian larch, which is chemically similar in many respects to black spruce, there is a strong correlation between the Pb content of soil and that of bark. As a result of these processes, the natural background levels of Pb in the spruce bark ash are high (median of 311 ppm Pb), and local concentrations of almost 7000 ppm Pb occur in the northeastern part of the survey area. Lead enrichment occurs near the Yava deposit, supporting the findings of Fortescue and Hornbrook (1969). Smaller concentrations occur around the abandoned Stirling mine. In general, samples from over the Windsor and Morien groups are relatively enriched in Pb.

Tin (Sn)

Tin was determined by INAA and as part of a routine scan of elements by ICP-ES. Analysis by INA has poor sensitivity and yields variable detection levels because of spectral interferences from other elements: no sample returned an analysis above the detection limits which were in general about 100 ppm Sn. Tin analysis by ICP-ES provides a substantially lower determination limit (2 ppm Sn) than by INAA, but the aqua regia digestion and the simultaneous determination of Sn from the ICP-ES scan provides data that are much lower, indicating that the acid leach is only partial. Little significance should be attributed to the few samples on the map of Sn distribution which yielded detectable concentrations.

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)

Although V is detectable in all of the bark samples, its essentiality 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. In general, the V concentrations are moderately high for black spruce bark, with highest concentrations occurring over the Fourchu and Morien groups.

Other Elements

Each sample was analyzed for iridium and mercury. All Ir analyses showed concentrations of less than 2 ppb, indicating that no obvious platinum-group elements occur in the area. All samples contained less than 1 ppm Hg, suggesting that there are no strong associations of Hg with mineralization. Although most Hg volatilizes during ashing of the twigs, it has been shown that there is sometimes residual Hg in plant ash (in the form of a carbide) in the vicinities of some mineral deposits (Kovalevskii, 1986). In our experience these concentrations rarely exceed 100 ppb Hg, whereas remote from mineralization concentrations are < 20 ppb Hg.

Notes on the Biogeochemical Data Listings (Appendices A and B)

Appendix A lists field data and all analytical data obtained for the spruce bark ash. Appendix B provides some simple statistical analyses of the data by treating the data set as a whole, and by dividing the data according to the underlying bedrock geology (according to stratigraphic formation for the sediments, or lithology for intrusions). Abbreviations used in the appendices are explained in Tables 5 and 6.

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Table 5: Abbreviations Used in Appendix A

RS	Replicate Status; an integer (1 or 2) that follows the Site ID and indicates two splits from the same sample.
Map Sheet	National topographic system (NTS): First three characters refer to 1:250,000 scale quadrangle; remaining two characters identify the 1:50,000 scale map sheet within the quadrangle.
Zone, Easting and Northing	The Universal Transverse Mercator (UTM) zone followed by easting and northing co-ordinates in metres.
Bark	The coarseness of the bark collected (i.e. Fine (F), Medium (M) or Coarse (C)).
Slope	0 = flat ground 1 = slight incline followed by downward compass direction (e.g. 1N = slight downward incline to the north) 2 = moderate incline 3 = steep incline
Forest Type	Type of vegetation cover and degree of surface water saturation.

Table 6: Abbreviations Used in Appendix B

Rock Type	<p>Underlying bedrock lithology (derived from published geological maps):</p> <p>ign - igneous plutons Cm - Carboniferous Morien Group Cw - Carboniferous Windsor and Canso Groups Ch - Carboniferous Horton Group D-C - Devono-Carboniferous C-O - Cambro-Ordovician Hmd - Hadrynian Main-à-Dieu Group Hf - Hadrynian Fourchu Group</p>
<p>N dl Cum %</p>	<p>N = number of samples dl = determination limit Cum % - cumulative frequency (as a percentage)</p>

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