



GEOLOGICAL SURVEY OF CANADA
OPEN FILE 2951

**Biogeochemical survey, Baie Verte area,
Newfoundland: black spruce twigs
(parts of NTS 12H/16 and 12I/1)**

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

1995



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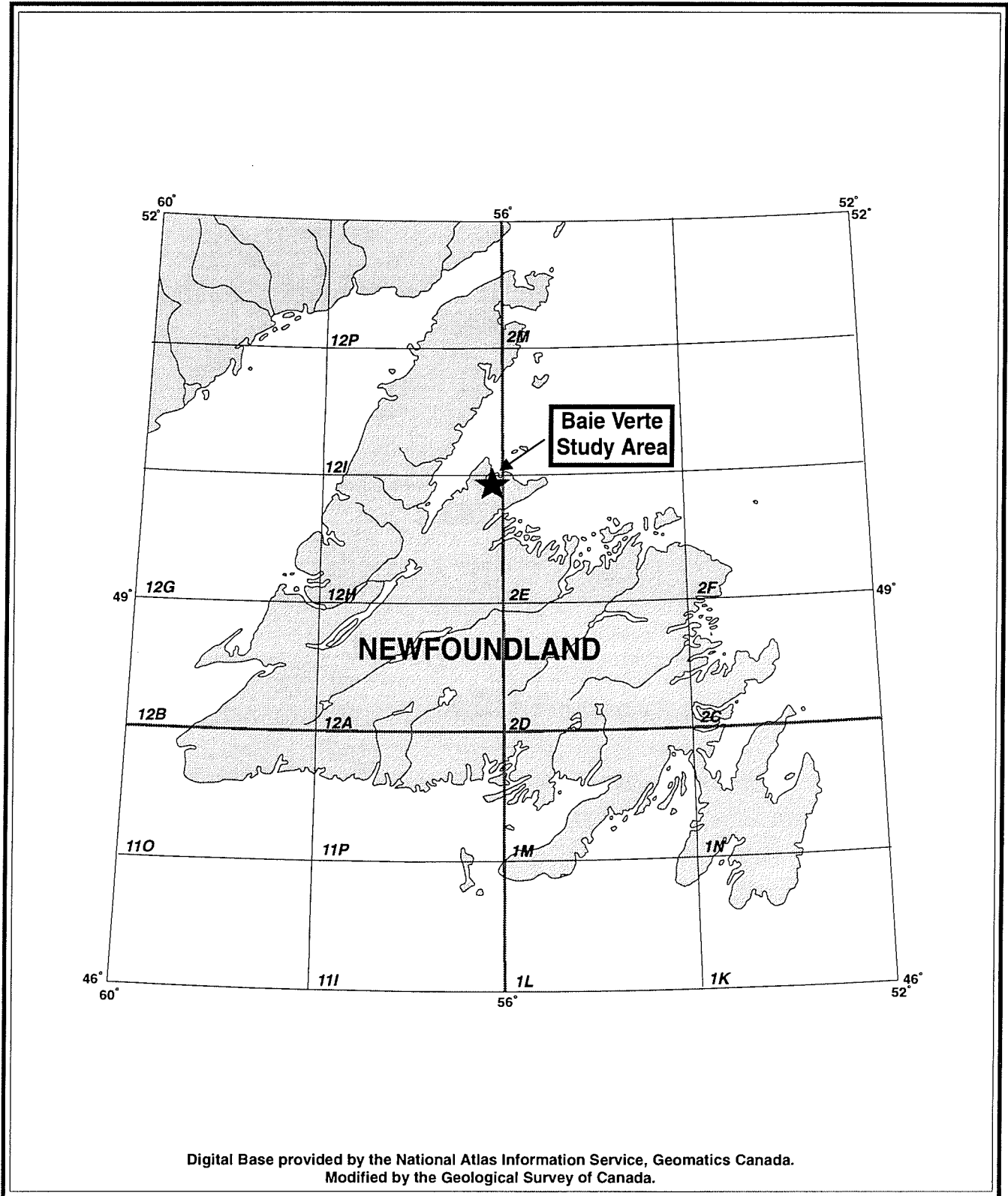
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**Survey area with respect to
National Topographic System (NTS) map sheets**

BIOGEOCHEMICAL SURVEY, BAIE VERTE AREA, NEWFOUNDLAND: BLACK SPRUCE TWIGS

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

INTRODUCTION

This Open File contains data from a biogeochemical survey in the Baie Verte area of northern Newfoundland. The survey was conducted in conjunction with a hydrogeochemical survey (Hall *et al.*, in prep.), in June, 1992, by the Geological Survey of Canada under the Canada - Newfoundland Cooperation Agreement on Mineral Development (1990 - 1994). It contains results of the first reconnaissance-style biogeochemical survey to be undertaken in Newfoundland. Field observations, data listings, statistical summaries, a geology and sample location map, and element distribution maps are presented. The maps show element concentrations in the ash of twigs from black spruce (*Picea mariana*). Instrumental neutron activation analysis (INAA) was used for determining 35 elements, of which 27 were in sufficient concentration to be detected and quantified. In addition, data are included for 15 elements determined by inductively-coupled plasma emission spectrometry (ICP-ES) and for 4 elements by other methods. All data reported are concentrations in ash remaining after controlled ignition at 470°C. For black spruce, the ashing process concentrates the elements with little or no loss of elements except for a few 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. Several reconnaissance biogeochemical survey similar to that reported here, but at lower sample density, have been conducted in Nova Scotia (e.g. Dunn *et al.*, 1989; Dunn *et al.*, 1994), and interpretive accounts are given in Dunn (1988, 1990), Rogers and Dunn, 1989, Dunn et al. (1991), and Rogers and Dunn (1993).

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 than significant differences in the chemistry of the substrate. However, major differences in Zn concentrations may reflect the presence of Zn mineralization.

The Zn example illustrates that biogeochemical data should be interpreted with caution and the text notes provided for each element should be considered. Biogeochemistry is a complex science involving the interaction of organic and inorganic processes that are controlled by many physicochemical parameters. However, despite these complexities, careful and systematic collection and preparation of vegetation samples can provide cost-effective new insight, not readily obtainable by other means, to the chemistry of the substrate and its groundwaters.

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

GSC Bookstore
Geological Survey of Canada
601 Booth St.
Ottawa
Ontario, K1A 0E8 Tel: (613) 995-4342 Fax: (613) 943-0646

The data will be supplied on an MS-DOS (IBM-PC) 3.5" 1.44 Mb diskette, as a .DBF file, which can be read by any DBASE-compatible software, and as an ASCII comma delimited file.

SURVEY DESCRIPTION AND METHODOLOGY

Scope of Survey

In the early summer of 1991 an orientation survey was conducted in the Baie Verte region to collect samples of tissues from common trees and shrubs. The analytical data obtained from these samples indicated that the most suitable tree in this area for a biogeochemical survey would be the ubiquitous black spruce. At several locations the metal concentrations were extraordinarily high in both twigs and outer bark. Therefore, during a two week period in June, 1992, samples of twigs and bark were collected from 145 sites within an area of approximately 200 km² to the east of the town of Baie Verte (Fig. 1). The reason for collecting both tissue types was that although they provide similar information, there are subtle differences for a few elements because of the ability of spruce to fix elements in different tissue types. Data from the spruce bark will be reported in a separate GSC Open File.

Sample Collection

The preferred sample spacing was one site per 1 km², but logistical limitations to sample collection resulted in an average sample density of approximately 1 per 1.5 km². Traverses were made along roads, driveable trails, and on foot through the forest. Access to a few locations around the peninsula was gained by boat. 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 in order to minimize roadside contamination.

Live twigs and needles were snipped from the limbs using standard anvil-type, teflon-coated, garden pruning snips, and placed in heavy-duty brown paper hardware bags (approximately 25 x 35 cm) and secured with masking tape. Usually 5 - 7 twigs, each comprising approximately 10 years of growth, provided the required 200 g of material. Within the survey area this amount of growth was commonly a twig length of 25 - 30 cm. Although there is annual variation in uptake and storage of many chemical elements (some accumulating near the twig ends), and it is important to maintain moderate consistency in the amount of growth collected, the over-riding factor for consideration is the *diameter* of the twig. It is important to maintain a consistent ratio of twig bark to twig wood, because many of the heavy metals are located in the bark, and not in the woody tissue of the twig. If this ratio changes

substantially, then variations in element content may be attributable to mixing thick with thin twigs, providing false anomalies. For the spruce survey the twig diameter at most locations was approximately 5 mm where twig growth was 10 years old.

Sample Preparation and Analysis

After the samples were air-dried for several weeks in a greenhouse, the needles were separated from the twigs by simply shaking the bags. Spruce needles have a different chemical composition from the twigs, with substantially lower levels of most heavy and base metals in the needles. The ratio of needle to twig may vary among sample locations, so if twigs are not separated from needles some false anomalies may be generated which are simply a function of different twig to needle ratios.

The 200 g samples of fresh limbs yielded approximately 50 g of dry twigs. These were weighed into aluminum trays and placed in a pottery kiln. The temperature was raised slowly (over 2 - 3 hours) to 470°C. After a further 12 hours no charcoal remained, and the twigs were reduced to approximately 1 g of ash. Half was weighed accurately 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 27 of these elements - concentrations of Ag, Hg, Ir, Sn, and Tb were all below the detection levels of 2 ppm, 1 ppm, 2 ppb, 100 ppm, and 0.5 ppm, respectively); reproducibility of data was poor for Ni (detection level of 50 ppm), and for Mo and Se at the low levels present (mostly <2 ppm), therefore no maps of these elements determined by INAA are included and instead there are maps by the wet chemical methods. Appropriate vegetation ash standards and duplicates were inserted to ensure quality control. The precision obtained varied among 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 +/- 10 percent.

The remaining half of the ash sample was submitted for multi-element ICP-ES analysis, following an aqua regia digestion. This solution was analyzed also for Hg by cold vapour AAS (atomic absorption spectrometry) and for elements that form hydrides - As, Bi, Sb, Se, and Te. Data for As and Sb by this method are similar to those obtained by INAA, therefore results by hydride generation are not repeated for these two elements. For most elements this extraction is 'total', although for some (e.g. Al, B) it is only partial. However, the analytical precision was good for most elements, such that the relative element distribution patterns are meaningful even if the absolute concentrations are only partial.

Analytical Quality Control

Included within each block of 20 samples prepared for analysis there was one standard ash sample (V6a or V5) to determine analytical accuracy, and one duplicate ash sample for assessing the analytical precision obtained from the field samples. These two samples are similar in composition (jack pine twigs). Data on mean values and standard deviations for each element in samples of V6a are given in Tables 1 and 2. Tables 3 and 4 contain the raw data from which these determinations were made. Tables 5 and 6 list the analytical data obtained on the duplicate pairs. Reproducibility is good except at very low concentrations. Tables 7 and

8 show the determination (detection) limits quoted for each element by the analytical laboratories, and the substitution values used for statistical calculations where analyses were below these levels.

Table 1: Mean and Standard Deviation for Standard V6a Analyzed by INA (N=9)

Element			Mean	Standard Deviation
Gold	ppb	Au	12	2
Arsenic	ppm	As	6.1	0.9
Barium	ppm	Ba	437	20
Bromine	ppm	Br	21	5
Calcium	%	Ca	15.5	1.3
Cobalt	ppm	Co	8	1
Chromium	ppm	Cr	58	5
Cesium	ppm	Cs	1.1	0.6
Iron	%	Fe	1.87	0.14
Hafnium	ppm	Hf	4.9	0.4
Potassium	%	K	3.31	0.65
Sodium	ppm	Na	10281	740
Rubidium	ppm	Rb	44	11
Antimony	ppm	Sb	1.3	0.2
Scandium	ppm	Sc	4.6	0.2
Strontium	ppm	Sr	1020	286
Thorium	ppm	Th	2.9	0.4
Uranium	ppm	U	1.5	0.3
Tungsten	ppm	W	*	*
Zinc	ppm	Zn	927	85
Lanthanum	ppm	La	20.0	1.6
Cerium	ppm	Ce	42	5
Neodymium	ppm	Nd	22	3
Samarium	ppm	Sm	3.7	0.3
Europium	ppm	Eu	0.77	0.11
Ytterbium	ppm	Yb	1.51	0.09
Lutetium	ppm	Lu	0.28	0.02

* all values below determination limit

**Table 2: Mean and Standard Deviation for V6a
Analyzed by ICP-ES (N=7)**

Element			Mean	Standard Deviation
Silver	ppm	Ag	0.4	0.2
Aluminum	%	Al	0.98	0.23
Boron	ppm	B	216	49
Beryllium	ppm	Be	*	*
Bismuth	ppm	Bi	0.4	0.1
Cadmium	ppm	Cd	2.8	0.7
Copper	ppm	Cu	113	34
Mercury	ppb	Hg	*	*
Lithium	ppm	Li	8	2
Magnesium	%	Mg	2.27	0.50
Manganese	ppm	Mn	801	255
Molybdenum	ppm	Mo	4	2
Nickel	ppm	Ni	44	12
Phosphorus	%	P	0.580	0.130
Lead	ppm	Pb	208	53
Selenium	ppm	Se	0.5	0.2
Tellurium	ppm	Te	**	**
Titanium	%	Ti	0.03	0.01
Vanadium	ppm	V	26	7

* all values below determination limit

** 71% of values below determination limit

Table 3: Standards V6a and V5 - concentrations in ash determined by INAA

	As ppm	Au ppb	Ba ppm	Br ppm	Ca %	Co ppm	Cr ppm	Cs ppm	Fe %	Hf ppm	K %	Na ppm	Rb ppm	Sb ppm	Sc ppm	Sr ppm	Th ppm	U ppm	W ppm	Zn ppm	La ppm	Ce ppm	Nd ppm	Sm ppm	Eu ppm	Yb ppm	Lu ppm
V6a	5.4	9	470	24	16.7	8	58	<0.5	1.83	4.5	3.17	10100	43	1.2	4.5	690	3.2	1.5	<1	930	21.0	42	27	3.6	0.82	1.61	0.28
V6a	5.0	15	420	23	15.5	9	54	1.2	1.82	4.8	3.17	9980	38	1.1	4.5	390	2.5	1.7	<1	970	18.0	39	22	3.5	0.79	1.59	0.26
V6a	6.9	13	430	30	15.7	7	64	<0.5	2.12	4.7	3.25	10000	38	1.7	4.5	1200	2.9	1.2	<1	1000	20.0	44	24	3.9	0.61	1.39	0.29
V6a	5.7	12	400	21	12.8	7	60	1.3	1.77	4.3	2.37	9620	53	1.1	4.3	1100	2.5	1.0	<1	870	18.0	33	19	3.4	0.63	1.37	0.26
V6a	5.7	12	450	22	15.8	7	51	1.2	1.68	5.0	3.30	12100	54	1.2	4.4	1100	2.7	1.3	<1	760	20.0	40	21	3.2	0.70	1.58	0.29
V6a	7.7	12	440	16	14.3	10	56	1.1	1.86	5.1	3.08	10100	29	1.6	4.4	1200	3.0	1.4	<1	840	20.0	45	17	3.7	0.80	1.55	0.28
V6a	5.7	11	430	16	15.5	7	55	1.8	1.79	5.3	2.80	9730	32	1.2	4.6	1200	2.6	1.5	<1	970	19.0	38	22	3.7	0.92	1.49	0.28
V6a	7.0	9	440	16	16.4	8	61	<0.5	2.02	5.2	4.29	10600	56	1.2	4.8	1200	3.1	2.2	<1	1000	21.0	41	25	4.0	0.88	1.52	0.30
V6a	6.2	16	450	17	16.9	8	66	2.0	1.96	5.2	4.40	10300	57	1.3	5.0	1100	3.8	1.5	<1	1000	23.0	52	24	4.1	0.82	1.48	0.32
V5	7.4	17	330	27	16.0	10	19	4.9	1.28	1.6	2.22	3260	38	2.0	1.9	1400	1.6	<0.1	<1	2200	18.0	25	15	2.1	<0.02	0.61	0.11
V5	9.3	22	530	35	19.6	13	29	5.0	1.44	2.1	2.49	3900	58	2.8	2.4	1700	1.8	<0.1	<1	2400	22.0	30	19	2.5	0.46	0.88	0.15
V5	9.6	19	520	29	18.1	14	29	4.5	3.23	2.0	2.98	4440	52	2.5	2.2	1300	1.7	<0.1	<1	2100	19.0	26	10	1.9	0.38	0.84	0.12

Table 4: Standards V6a and V5 - concentrations in ash determined by ICP-ES (Hg by Cold Vapour AAS)

	Ag ppm	Al %	B ppm	Be ppm	Bi ppm	Cd ppm	Cu ppm	Hg ppb	Li ppm	Mg %	Mn ppm	Mo ppm	Ni ppm	P %	Pb ppm	Se ppm	Te ppm	Ti %	V ppm
V6a	0.6	1.16	246	<0.3	0.5	3.4	133	<10	9	2.54	933	5	54	0.644	255	0.9	<0.2	0.03	31
V6a	0.5	1.09	234	<0.3	0.3	3.0	114	<10	8	2.57	1205	5	51	0.607	230	0.4	<0.2	0.03	29
V6a	0.3	0.93	214	<0.3	0.5	2.9	162	<10	7	2.36	833	5	45	0.595	217	0.4	0.2	0.03	27
V6a	0.5	1.12	242	<0.3	0.3	3.1	116	<10	8	2.57	802	5	50	0.660	220	0.4	0.4	0.03	29
V6a	0.3	1.07	240	<0.3	0.5	3.1	107	<10	10	2.44	776	6	43	0.660	238	0.3	<0.2	0.04	31
V6a	0.4	1.00	230	<0.3	0.6	2.7	109	<10	7	2.26	708	4	44	0.581	202	0.6	0.6	0.03	25
V6a	0.4	1.00	214	<0.3	0.3	2.6	96	<10	8	2.36	706	4	38	0.564	190	0.7	0.2	0.04	24
V5	0.9	1.08	340	<0.3	0.9	11.0	245	<10	7	2.32	2846	3	71	1.000	395	0.7	0.2	0.02	22
V5	0.5	0.97	369	<0.3	0.8	11.1	252	15	7	2.21	2282	3	55	1.033	403	0.8	<0.2	0.02	20
V5	0.7	1.05	333	<0.3	0.6	10.6	191	15	6	2.26	2606	3	57	1.127	388	1.0	0.8	0.02	20

Table 5: Laboratory Duplicates - concentrations in ash determined by INAA

Sample Number	As ppm	Au ppb	Ba ppm	Br ppm	Ca %	Co ppm	Cr ppm	Cs ppm	Fe %	Hf ppm	K %	Na ppm	Rb ppm	Sb ppm	Sc ppm	Sr ppm	Th ppm	U ppm	W ppm	Zn ppm	La ppm	Ce ppm	Nd ppm	Sm ppm	Eu ppm	Yb ppm	Lu ppm
AL92/1099	4.7	<5	870	39	11.7	13	90	<0.5	2.66	3.6	6.28	22700	59	2.1	12.0	550	3.7	2.0	<1	2100	21.0	34	26	4.0	0.67	1.65	0.30
AL92/1100	4.2	8	960	39	8.8	13	87	1.4	2.58	3.1	4.92	22400	64	0.6	12.0	1000	3.4	2.1	<1	1800	22.0	38	19	4.1	1.02	1.68	0.33
AL92/1139	29.0	18	660	28	9.5	51	450	<0.5	5.63	2.4	8.50	20300	62	1.4	30.0	920	1.0	1.3	<1	1300	11.0	26	15	3.5	0.86	2.50	0.45
AL92/1140	27.0	19	670	30	8.5	50	470	<0.5	5.70	2.2	7.20	20700	75	1.4	31.0	<300	1.5	1.0	<1	1300	11.0	26	15	3.6	0.87	2.49	0.43
AL92/1170	200	810	2400	24	9.8	27	140	2.4	5.18	2.7	7.24	14800	85	26.0	17.0	<300	1.9	3.9	8	9500	12.0	20	11	2.6	0.63	2.00	0.38
AL92/1171	200	620	2600	28	10.3	26	130	2.9	5.00	3.1	8.09	14800	86	26.0	17.0	<300	1.7	3.4	6	9900	11.0	22	11	2.5	0.69	1.86	0.40

Table 6: Laboratory Duplicates - concentrations in ash determined by ICP-ES (Hg by Cold Vapour AAS)

Sample Number	Ag ppm	Al %	B ppm	Be ppm	Bi ppm	Cd ppm	Cu ppm	Hg ppb	Li ppm	Mg %	Mn ppm	Mo ppm	Ni ppm	P %	Pb ppm	Se ppm	Te ppm	Ti %	V ppm
ICP92/1099	0.6	1.00	295	<0.3	0.3	1.0	131	<10	7	2.66	15763	<2	73	1.069	77	1.1	<0.2	0.07	32
ICP92/1100	0.6	1.03	305	<0.3	0.4	1.1	135	10	7	2.73	15956	<2	75	1.094	73	1.1	0.2	0.08	32
ICP92/1139	0.9	2.47	213	<0.3	0.3	1.8	206	<10	12	4.25	5894	<2	195	0.885	32	0.6	0.5	0.09	69
ICP92/1140	0.9	2.51	200	<0.3	0.5	1.6	199	<10	12	4.26	5227	<2	194	0.749	35	0.6	0.6	0.10	72
ICP92/1170	9.6	1.27	310	<0.3	1.2	12.7	8609	110	7	2.14	8879	12	83	1.410	2533	<0.2	0.6	0.04	35
ICP92/1171	9.4	1.25	307	<0.3	1.4	12.5	8413	115	7	2.15	9357	11	86	1.421	2323	<0.2	0.2	0.04	34

Table 7: Determination Limits and Substitution Values for Elements Analysed by INAA

Element		Units of Measure	Determination Limit	Substitution Value
Gold	Au	ppb	5	3.125
Arsenic	As	ppm	0.5	0.3125
Barium	Ba	ppm	10	*
Bromine	Br	ppm	1	*
Calcium	Ca	%	0.2	*
Cobalt	Co	ppm	1	*
Chromium	Cr	ppm	1	*
Cesium	Cs	ppm	0.5	0.3125
Iron	Fe	%	0.05	*
Hafnium	Hf	ppm	0.5	0.3125
Potassium	K	%	0.05	*
Sodium	Na	ppm	10	*
Rubidium	Rb	ppm	5	*
Antimony	Sb	ppm	0.1	*
Scandium	Sc	ppm	0.1	*
Strontium	Sr	ppm	300	187.5
Thorium	Th	ppm	0.1	0.0625
Uranium	U	ppm	0.1	0.0625
Tungsten	W	ppm	1	0.625
Zinc	Zn	ppm	20	*
Lanthanum	La	ppm	0.1	*
Cerium	Ce	ppm	3	1.875
Neodymium	Nd	ppm	5	3.125
Samarium	Sm	ppm	0.1	*
Europium	Eu	ppm	0.01	0.00625
Ytterbium	Yb	ppm	0.05	0.03125
Lutetium	Lu	ppm	0.05	0.03125

* all values above the determination limit

Table 8: Determination Limits and Substitution Values for Elements Analysed by ICP-ES

Element		Units of Measure	Determination Limit	Substitution Value
Silver	Ag	ppm	0.2	*
Aluminum	Al	%	0.01	*
Boron	B	ppm	2	*
Beryllium	Be	ppm	0.3	0.1875
Bismuth	Bi	ppm	0.2	0.125
Cadmium	Cd	ppm	0.2	*
Copper	Cu	ppm	1	*
Mercury	Hg	ppb	10	6.25
Lithium	Li	ppm	2	1.25
Magnesium	Mg	%	0.01	*
Manganese	Mn	ppm	1	*
Molybdenum	Mo	ppm	2	1.25
Nickel	Ni	ppm	1	*
Phosphorus	P	%	0.001	*
Lead	Pb	ppm	3	*
Selenium	Se	ppm	0.2	0.125
Tellurium	Te	ppm	0.2	0.125
Titanium	Ti	%	0.02	0.0125
Vanadium	V	ppm	2	*

* all values above the determination limit

GEOLOGY

Bedrock

The survey area lies within the Dunnage tectono-stratigraphic Zone, near its western margin with the Fleur de Lys Belt of the Humber Zone (Hibbard, 1983). Dimmell and Hartley (1991) note that 'the peninsula is bisected into contrasting lithostratigraphic terranes by the Baie-Verte-Brompton Line (BVBL), a north-northeast trending, steeply dipping, structural zone that separates oceanic rocks of the Dunnage Zone to the east from the ancient continental margin of the Humber Zone to the west'. The 'Baie Verte Belt' was informally named by Hibbard (1983) to denote the mostly Cambro-Ordovician assemblage of volcanic and intrusive rocks that occur on the east side of the Baie Verte Peninsula. The survey area is dominated by ophiolites of the Point Rousse Complex and the Pacquet Harbour Group. These were intruded by the Burlington Granodiorite during the Early Ordovician (ca. 460 Ma). To the west of the Burlington Granodiorite there is a small region within the survey area where there are mafic volcanic and volcanoclastic rocks of the Lower Silurian Flatwater Pond Group. In the southwest of the survey area Siluro-Devonian quartz-feldspar porphyry of the Cape Brule Porphyry underlie a few of the biogeochemical sample sites.

The Cambro-Ordovician Point Rousse Complex comprises mostly pillow lava, mafic and ultramafic volcanic and volcanoclastic rocks, and diabase dykes. Included are minor amounts of iron formation, marble and chert, and there are intrusions of feldspar porphyry diabase dykes. It is a dismembered but complete ophiolite suite, mostly steeply dipping, that occurs in structural blocks that have been metamorphosed to lower greenschist facies. Locally, at the margins of the Burlington Granodiorite they attain amphibolite facies.

Rocks of the Pacquet Harbour Group are also Cambro-Ordovician in age and comprise a similar suite of rocks to the Point Rousse Complex, but with the addition of gabbro, and mafic epiclastic and felsic volcanoclastic rocks. Gale (1971, 1973) determined from geochemical studies that the lavas of the Group fall into two groups - tholeiitic and komatiitic basalt. The stratigraphic relationships of the Pacquet Harbour Group lithologies is uncertain because of poor exposure and complex relationships. Felsic volcanoclastic rocks (keratophyres) predominate in the centre of the survey area around the Rambler mine.

There is a major tectonic contact known as the Scrape Thrust which transects the survey area. Rocks of the Pacquet Harbour Group have been thrust northward over the Point Rousse Complex.

For the purpose of this report, the complex range of lithologies have been grouped into three main units: Burlington Granodiorite, Pacquet Harbour Group, Point Rousse Complex. A few sample sites were over younger rocks of the Flatwater Pond Group and the quartz feldspar rocks that form the Cape Brule Porphyry in the east and the King Point Complex in the south; both are identified on the maps as Unit 4 'Quartz Feldspar Porphyry'.

Mineralization

Exploration of the Baie Verte peninsula for base and precious metals commenced in 1864. The main activity has centred around the Rambler area. Sulphide mineralization was first found in 1903, but a mine was not brought into production until 1964. From 1964-1982 Consolidated Rambler Mines Limited mined the Main, East, Ming and Big Rambler Pond massive sulphide deposits. A total of 4.75 million tons was produced grading mostly 1 - 1.3% Cu. The relatively small Rambler Main deposit (440,000 short tons), yielded also 2.16% Zn, 0.15 oz/t Au and 0.85 oz/t Ag. Several small gold deposits have been worked within the survey area (e.g. Goldenville, and Deer Cove), and within the past 10 years the area has received renewed interest. New gold deposits and showings associated with quartz veining and pyrite have been discovered in the ophiolites of the Point Rousse Complex - Stog'er Tight, Romeo, Juliet, and Pine Cove. The most important of these is the Pine Cove deposit in which gold is associated with pyrite in quartz veins and in sheared and altered host rocks. Dimmell and Hartley (1991) describe the mineralized zones as 'silicified, chloritized (basalt and massive, fine-grained pyroclastic rocks), oxidized and sulphidized (basalts and hematitic arenite)'.

Several gold showings have been found recently in the southeastern part of the survey area within rocks of the Pacquet Harbour Group - notably the Brass Buckle quartz vein hosted mineralization, and massive native gold at the Krissy showing approximately 2 km south of Rambler Main (P. Dimmell, pers. communication, 1993).

Throughout the survey area the metallic mineral occurrences are mostly pyrite and chalcopyrite, with some pyrrhotite, sphalerite, galena, bornite, and native gold. Tellurium is associated with the Au at the Brass Buckle deposit.

PHYSIOGRAPHY, VEGETATION AND QUATERNARY DEPOSITS

The coastline of the Baie Verte peninsula is rugged and with steep cliffs that rise more than 100 m to the forested hilly topography of the Peninsula. Southward the topography is less severe. Ponds, small lakes and streams are common, and there is an increasing incidence of bogs toward the south. The entire area is forested with black spruce (*Picea mariana*) with some white spruce (*Picea glauca*), jack pine (*Pinus banksiana*) and balsam fir (*Abies balsamea*). Interspersed are paper birch (*Betula papyrifera*), trembling aspen (*Populus tremuloides*) and shrub alder (*Alnus rugosa* and *Alnus crispa*). Reafforestation (mostly black spruce and jack pine) of the southern half of the survey area over the past 20 years followed extensive clear-cutting.

The area is covered with a veneer of sandy till, mostly less than 1 m thick, upon which a podzol has developed. Studies have indicated that the displacement of metal-rich zones by glaciation is only minor (Dimmell and Hartley, 1991).

MAP PRODUCTION AND DATA HANDLING

Maps were drawn using the Universal Transverse Mercator (UTM) projection, with a central meridian of 56° (Zone 21). The coastline and drainage were digitized from maps at a scale of 1:50,000.

Data for the study area were compiled using Microsoft Access relational database software. Separate tables for the INAA, ICP-ES, field 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.

Statistics were generated for each element using SPSS software (Statistical Package for the Social Sciences). 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. For samples with duplicate analyses, the analysis from the first of each duplicate pair was plotted.

The element distribution, sample site and geology maps were created using Arc/Info v. 6.1.1 software, running on a SUN workstation. 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 beneath the percentile values on the right hand of each map) in order to provide an appropriate visual impact. For output, Arc/Info maps 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

General Comments

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. This 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) which are arranged according to convention in order of increasing atomic weight - i.e. La, Ce, Nd, Eu, Sm, Yb. For determinations by ICP-ES,

elements are arranged alphabetically by chemical symbol.

Effects from Rambler (Blue Maps)

Results indicate that there is high enrichment of many elements in the vegetation around the Rambler area. In view of the wide extent of tailings from the Rambler and Ming deposits, it is probable that the chemistry of trees from this area is a mixed signature of metals that were absorbed through the root systems, and air-borne particulates from the mine tailings that have lodged on the plant surfaces. As a result, regardless of the origin of these element enrichments, the effects of mineralization in the Rambler area dominate the distribution patterns of many elements, such that the map plots do not reveal subtle variations in plant chemistry that may occur throughout the rest of the survey area. In an attempt to eliminate the effects of airborne particulates from Rambler, 23 sites from that area were excluded from the original data set, and new maps plotted. These sites are location numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 59, 63, 108, 110, 114, 508, 524, 527, 529, 534, 535, 536, 543, 544. Consequently, for some elements there are two maps: the first shows relative concentrations of an element for all sites, whereas the second shows relative concentrations with the presumed effects of Rambler excluded. To assist in comparing the two data sets, the maps with the reduced number of samples are plotted on blue paper, and a suffix of RE (i.e. Rambler Excluded) is inserted alongside the element symbol at the top right-hand corner of each map.

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. The background concentration of Au in the ash of black spruce twigs is commonly less than 10 ppb Au. Because of the low (ppb) traces of Au that are present, the precision of the INAA on duplicate pairs is not as good as that of most other elements determined by this method, and at concentrations below 10 ppb Au the reproducibility of analyses is poor. Gold concentrations in spruce twigs from the survey area are moderately high (median of 17 ppb - see p.B1), and unusually enriched in samples from around the Ming and Rambler deposits where there is a maximum of 810 ppb Au. Because the Pacquet Harbour Group hosts these deposits, the statistical breakdown of the data according to underlying rock Group shows strong Au enrichment in the Pacquet Harbour (mean 81 ppb Au; median 19 ppb Au). There is no notable Au enrichment in samples from the Burlington Granodiorite.

The map of Au distribution that excludes the Rambler area shows there to be subtle enrichment around the Brass Buckle and Pine Cove deposits, and at a few isolated locations. Two sites 1 km southwest of Deer Cove show moderate Au enrichment. Several sites to the east of Rambler are weakly enriched in Au. These anomalies may be due to airborne contamination, but it is noteworthy that they are up-drainage from Rambler. Similarly, the anomaly close to Highway 414 west of Rambler is not in the Rambler drainage system, and is down drainage from source waters on the Burlington granodiorite. The source of the Au at an isolated site 3 km west of Brass Buckle is unknown.

Arsenic (As)

Arsenic is renowned for its toxicity, yet some species of tree (especially Douglas-fir) can accumulate extraordinary amounts without exhibiting any visible harmful effects (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 is highly enriched around the Rambler and Ming deposits (maximum of 210 ppm As) and relative to the other rock groups is enriched throughout the Pacquet Harbour Group (mean 25 ppm As; median 6.7 ppm As). The map that excludes data from the Rambler area shows mostly isolated occurrences of As enrichment of which the most noteworthy are those which are coincident with Au enrichment in the twigs - south of Deer Cove; west of Rambler (Hwy 414); and near Hwy 418, close to the Scrape Thrust.

Barium (Ba)

All samples yielded substantially more barium than the INAA detection limit of 10 ppm Ba. Black spruce twigs commonly contain up to 2000 ppm Ba. Some unusually high concentrations occur within the map area, with up to 8,000 ppm in a samples east of Rambler. From a comparison with the maps of Au and Cu distributions it is evident that Ba is not associated with the Au and base metal deposits of the survey area. There is a general depletion of Ba in samples from the mafic rocks of the Point Rouse Complex where the median concentration of 940 ppm Ba is less than half that of either the Burlington Granodiorite or the Pacquet Harbour Group. There is a general southward increase in Ba content of the spruce twigs, with notable enrichment to the east of Rambler, and near the contact between the Burlington Granodiorite and the Pacquet Harbour Group.

Bromine (Br)

Bromine is a volatile element that is present in most, if not all terrestrial plants, but it is not known to be an essential element. It can occur in many forms as complexes within plants. Some Br complexes volatilize during the ashing process, causing losses of 30 - 90 percent of the Br contained within the plant tissues. Although there is sometimes a Au/Br association in plant ash from zones of mineralization (Dunn, 1986), this is not apparent in the survey area although there is moderate enrichment at Pine Cove, south of Deer Cove, and at a few isolated locations.

It might be expected that Br enrichment would occur in shoreline samples, due to the influence of Br-bearing salt spray from the ocean. However, most high concentrations of Br occur as isolated anomalies inland. It is likely that Br from the salt spray volatilized during the ashing process, and that the zones of Br enrichment are related to local chemistry and physicochemical conditions.

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 twigs are greater than is usual for a population of spruce twigs. Slight enrichment in trees from the Point Rouse Complex in part reflects the relative enrichment of Ca that is characteristic of mafic volcanic rocks. However, there is also enrichment near known zones of mineralization within the Point Rouse Complex, suggesting that the alteration associated with mineralization may have encouraged Ca uptake by the trees.

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 (Kabata-Pendias and Pendias, 1984), but conifer twigs commonly have approximately 5 ppm Co. Within the survey area the median content of Co in the spruce twigs is 19 ppm. 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). Cobalt enrichment occurs within the Pacquet Harbour Group to the south of the Rambler deposit where there are unusual concentrations of up to 110 ppm Co. This enrichment could reflect a zone of lithogeochemical enrichment related to the Rambler mineralization. The mafic nature of the Point Rouse Complex has resulted also in Co enrichment, but to a lesser degree than in the Pacquet Harbour Group except for an isolated site of Au enrichment south of Deer Cove.

Chromium (Cr)

Chromium is a non-essential element for which precise INAA data are obtained at low ppm levels. Concentrations are unusually high with respect to the normal range of values for black spruce twigs (10 - 20 ppm Cr), especially in samples from over the Point Rouse Complex where the median concentration is 120 ppm Cr and the maximum is 510 ppm Cr. Concentrations of this order are characteristic for plants growing over ultramafic rocks. Within the Pacquet Harbour Group there are high concentrations (maximum of 190 ppm Cr), especially northward from Rambler. Even samples from the Burlington Granodiorite are locally enriched in Cr, attesting to the high background concentrations in the Baie Verte area.

Cesium (Cs)

This alkali metal performs no known essential function in plant tissues, and is usually present at less than 3 ppm Cs in conifer twig ash. Within the survey area Cs concentrations are mostly close to normal background levels, with only a few sites showing moderate, but not exceptional Cs concentrations.

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. Statistical analysis of many biogeochemical data sets has revealed the presence of an 'iron factor' (Dunn, Ch. 20 'Biogeochemical Prospecting for Metals' in Brooks *et al.*, 1995), represented by a close association among Fe, Hf, Sc, Th, and the rare-earth elements. There are similarities in the distribution patterns of these elements in the Baie Verte area, but there is a strong overprint of the elements that occur with iron in the major zone of mineralization around the Rambler and Ming deposits - namely Au, Ag, As, Cd, Cu, Hg, Mo, Pb, Sb, U, and Zn. Locally there is unusually high enrichment of Fe in both the Pacquet Harbour Group (up to 7.17% Fe) and the Point Rouse Complex (up to 5.63% Fe), especially when compared to common background concentrations of < 1% Fe in black spruce twigs. Once the influence of Rambler is excluded the strong relative enrichment of Fe in the Point Rouse Complex is apparent, especially on the eastern side of the peninsula.

Hafnium (Hf)

Ash of conifer twigs usually contains 1 - 2 ppm Hf. Hafnium levels are higher where Fe concentrations are high because the two elements are commonly associated in plants. The uptake of Hf by plants may also be controlled by Zr, because of their close geochemical affinities. The weak, but relatively high enrichment of Hf over the Burlington Granodiorite may be due to a Hf/Zr association.

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. The moderate concentrations present in the black spruce twigs (median of 14.2%) are normal to low for this species because of the low K content of the mafic rocks.

Sodium (Na)

The effect of salt-spray from the sea may be contributing to the high concentrations of Na in the trees, especially around the shores of the peninsula. Relative enrichment of Na on the Burlington Granodiorite probably reflects the higher Na concentration of this lithology relative to rocks of the ophiolitic suite.

Rubidium (Rb)

There is an antagonism between K and Rb in plants (Kabata-Pendias and Pendias, 1984) because of their competition for the same binding sites, often resulting in differences in the distribution patterns of the two elements. Cesium, too, is involved, but the strong correlation commonly shown between Rb and Cs in trees is not apparent in the survey area. Background levels of Rb in black spruce twigs are usually in excess of 200 ppm, such that the biogeochemical data indicate a Rb depletion resulting from the generally mafic nature of the substrate, since Rb occurs mostly in granitic rocks. Twig samples from sites on the Burlington Granodiorite have relatively high concentrations of Rb (median of 170 ppm Rb).

Antimony (Sb)

Excellent analytical precision is obtained for Sb by INAA down to sub-ppm levels in ash. 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. In black spruce twigs background concentrations are commonly about 1 ppm Sb, as is the case in the Baie Verte area where the median concentration is 0.9 ppm Sb (p. B 19). The map of Sb distribution shows a strong anomaly around the Rambler and Ming deposits with a maximum concentration of 47 ppm Sb. When samples from around these deposits are removed from the data set (map of 'Antimony - Rambler Excluded') there remain few sites where concentrations exceed 2 ppm Sb. Several sites of relative enrichment to the southwest of Rambler could be showing the effects of contamination from the mine site. However, this area is not within the path of the dominant wind direction nor is it down-drainage from Rambler, and therefore these anomalies may indicate some Sb enrichment in the substrate. There is weak Sb enrichment at Pine Cove.

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 twigs is controlled essentially by the chemistry of the substrate and by the distribution of other elements. In particular, there is a high correlation between Sc and Fe. Background concentrations in black spruce twigs are commonly 2 - 3 ppm Sc, rarely exceeding this amount where there is no Fe enrichment although there can be Fe enrichment without Sc. At Rambler the high levels of Fe are derived from Fe sulphides with which Sc levels are not elevated. Outside of the Rambler area there is a strong similarity between the distribution patterns of Fe and Sc, with the highest concentrations occurring over mafic rocks of the Point Rouse Complex to the west of Ming's Bight.

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 well above detection limits in most samples, such that the areas of Sr enrichment depict significant regional variations.

Strontium is 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, but within the survey area there is a broad similarity between the distribution patterns of the two elements. The mean concentration of 1300 ppm Sr is identical to that obtained for a suite of over 300 black spruce twig samples from southeastern Cape Breton Island (Dunn *et al.*, 1994). Samples from over the mafic rocks of the Point Rouse Complex are relatively enriched in Sr, notably in the Pine Cove and Deer Cove areas, containing a median concentration of 1600 ppm Sr and a maximum of 3600 ppm Sr.

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). In the Baie Verte area the Th concentrations are anomalously low (median of 0.7 ppm Th), reflecting the low Th concentrations typical of mafic rocks. There is no appreciable enrichment of Th associated with the Rambler mineralization. Concentrations in trees from the Burlington Granodiorite are typical of those growing on felsic plutons.

Uranium (U)

Although U₃O₈ 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 black spruce twigs near the Athabasca uranium deposits locally contain over 2000 ppm U (Dunn, 1983). In the Baie Verte area 76% of the samples yielded U concentrations below the determination limit of 0.1 ppm U (p. B 26). With respect to the survey area in general there is clearly enrichment of U associated with the Ming, but not the Rambler deposits, indicating the presence of U with the fluids from which the massive sulphides of the Ming deposits were

derived. As would be expected, concentrations are slightly higher over the Burlington Granodiorite because of the relatively high U content of felsic plutons.

Tungsten (W)

Tungsten is not known to perform any useful function in plant metabolism. The detection limit for W by INAA is 2 ppm in ash, which is above the usual concentrations in tree tissues, and analytical precision at this level is poor. In the survey area only 8 samples yielded more than 2 ppm W, with all but one occurring in the Pacquet Harbour Group. Of these the most notable is an unusually high 37 ppm W to the east of Rambler.

Zinc (Zn)

Zinc is essential for carbohydrate and protein metabolism, therefore 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. Black spruce twigs commonly contain 2000 - 2500 ppm Zn, therefore the trees in the Baie Verte area are moderately enriched in Zn (median 2900 ppm Zn), and highly enriched around the Rambler and Ming deposits where a maximum of 9500 ppm Zn is recorded. The Pacquet Harbour Group has a high median concentration of 3200 ppm Zn. Once the effects of Rambler have been excluded it becomes evident that there is moderate enrichment of Zn associated with the Brass Buckle deposit; east of Rambler; and the various deposits around Pine Cove.

Rare-Earth Elements (REE)

Because of their chemical coherence, these elements are considered as a single group. Included in standard INAA multi-element packages are determinations for lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), europium (Eu), terbium (Tb), ytterbium (Yb), and lutetium (Lu). Of these elements, excellent precision is obtained for all except Nd, and Tb. Terbium consistently yields concentrations below the detection level (0.5 ppm) and therefore no map of Tb is included. The overall concentrations of the REE are quite low for black spruce twigs. Although there are broad similarities in their distribution patterns, the REE show some distinct differences. In particular, the light rare-earth elements (LREE - La, Ce, Nd and, to a lesser degree, Sm) are relatively enriched over the Burlington Granodiorite, whereas the heavier REE (Eu, Yb and Lu) are more enriched over mafic rocks of the Point Rousse Complex. All REE are weakly enriched in the Ming area. There is commonly a close association between the REE and Fe in tree tissues, and a comparison with the map of Fe distribution shows broad similarities. There remains, however, an underlying control on the REE patterns which is attributable to the REE signatures of the different rock types.

Distribution Maps of Elements Determined by ICP-ES

Silver (Ag)

Silver is not known to be essential to plant life, and can become toxic to plants by substituting for K in membranes and thereby inhibiting the absorption of other cations by roots (Hendrix and Higinbotham, 1974). However, at the few ppm concentrations present within the study area (and most natural environments) the inhibiting effects of Ag on the uptake of other

elements is insignificant. The 50th percentile value of 2.6 ppm Ag is high for black spruce twigs indicating a high regional background of Ag in the Baie Verte area. The map of Ag distribution shows clearly the enrichment of Ag associated with the Ming deposits where there is a maximum of 14 ppm Ag. The map excluding sites around the Rambler and Ming deposits shows a few isolated occurrences of Ag enrichment, and weak enrichment associated with the Brass Buckle deposit.

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 undertaken to compare data obtained on an ash standard 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. With respect to the rest of the survey area there is notable depletion of Al in samples from over the Burlington Granodiorite suggesting that Al is more tightly bound into crystal lattices in this area than in areas of mafic and altered rocks.

Boron (B)

Borosilicate test tubes were used for the acid digestion of the ash samples. Test studies at Acme Analytical Laboratories indicate that this digestion may release 5 - 10 ppm B from the borosilicate, but this amount is insignificant in comparison with the 100s ppm B present in the ash. Tests indicate that the analytical procedure provides data which represent about 50% of the true concentrations of B in the samples. Precision, however, is excellent.

Boron is essential for plant growth, and it is believed to play an important role in the translocation of sugars. The median concentrations of B show little variation from one substrate to the next.

Beryllium (Be)

There is usually less than 2 ppm Be in soils, and because it is a non-essential element for plant growth (in high concentrations it is toxic), its presence in the substrate is reflected in the black spruce twigs by concentrations of less than 1 ppm Be at all but three sites. With the exception of a single site east of Ming's Bight where there is weak Be enrichment, all sites with more than 0.5 ppm Be occur over, or close to the margin of the Burlington Granodiorite. Analytical precision is good above 0.5 ppm Be.

Bismuth (Bi)

The map of Bi distribution shows clearly the association with mineralization at the Rambler and Ming deposits. With the effects of these deposits excluded there remain few sites with concentrations above 1 ppm Bi. The patterns indicate that there may be a little Bi associated with the Brass Buckle, Romeo, Juliet, and Pine Cove deposits.

Cadmium (Cd)

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 easily absorbed by plants and may therefore be expected to reflect relative Cd concentrations in soil and groundwater. Absolute concentrations differ among plant species because Cd can be captured by a variety of organic compounds in cell walls and therefore not all will be transported to the tree extremities. Although concentrations are not high for spruce twigs, there is notable relative enrichment of Cd in samples from over the Pacquet Harbour Group, especially around the Ming and Brass Buckle deposits.

Copper (Cu)

Data obtained by ICP-ES from the aqua regia leach are both precise and accurate. Copper plays a fundamental role in plant metabolism. It assists in respiration, photosynthesis, nitrogen fixation and valence changes, and it 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 black spruce twigs is high compared to many trace elements, and commonly over 200 ppm Cu.

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 significant differences in the Cu content of the substrate than the relatively small differences attributable to micronutrient functions.

A statistical breakdown of the data set shows that the over all median concentration is 237 ppm Cu, and that there is notable enrichment in the Pacquet Harbour Group (median 330 ppm Cu), with quite remarkable enrichment of up to 1.2% Cu near the Ming deposits. The high levels in this area are interpreted to reflect some contamination from airborne particulates, some uptake of Cu dissolved in water derived from acid rock drainage of tailings, and also a natural background component. On replotting the data (map of 'Cu - Rambler Excluded') there remain several sites with high Cu concentrations to the east of Rambler, and one adjacent to the Scrape thrust.

Mercury (Hg)

Although most Hg volatilizes during ashing of twigs, it has been suggested that there is sometimes residual Hg in plant ash (in the form of a carbide) in the vicinities of some mineral deposits (Kovalevskii, 1986). Around Rambler, and for a distance of 3 - 4 km to the southeast, spruce twigs yielded anomalously high concentrations of Hg in ash coincident with enrichment of Au, As, Mo, Sb, Se, and Fe. It is tempting to assign these coincident anomalies to new and undiscovered zones of gold mineralization. However, a more probable explanation is that the metals are associated with fine particles of wind-blown sulphide-rich dust, derived from the large open area of mine tailings at Rambler, that have become lodged in the tree tissues. Analysis of these tailings shows that most of the Hg, Au, As, Se, and Mo is associated with the < -250

mesh particles (Table 9). Not all the Hg volatilized during ashing because it was tightly locked within the crystal lattices of the sulphide grains. Despite careful washing of vegetation samples, it is not always possible to remove all dust because some becomes firmly embedded and with time tissue may grow around and over some grains, such that they become incorporated within the plant structure.

Table 9: Metal Concentrations in Different Size Fractions of Tailings from the Consolidated Rambler Mine

	Hg ppb	Au ppb	As ppm	Mo ppm	Se ppm	Sb ppm	Cr ppm
Coarse: > -32 mesh (> 500 μ)	110	200	33	2	8	18	170
-32 to -80 (500-180 μ)	175	300	70	8	15	31	160
-80 to -150 (180-106 μ)	195	700	390	19	87	28	95
-150 to -250 (106-63 μ)	485	750	600	26	120	19	45
Fine: < -250 mesh (< 63 μ)	1170	1700	670	41	120	37	190

The source of Hg enrichment in the sample from between the Stog'er Tight and Pine Cove deposits is unknown.

Lithium (Li)

Lithium commonly follows Rb and Cs in nature. In black spruce twigs it is less abundant than Rb but enriched with respect to Cs. Background levels are commonly in the range of 4 - 8 ppm Li. 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 readily reflected in plant tissues. Samples with the highest Li content are from the Pacquet Harbour Group, although the median Li value is slightly lower than that of the Point Rouse Complex.

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 high concentrations in samples from the mafic rocks of the Point Rouse Complex are notable, with up to 7.2% Mg and a median value of 4.07%

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 affinity for Fe. Samples from the southern part of the survey area are markedly enriched in Mn with up to 7.7% Mn over the Pacquet Harbour Group

and a median concentration of 3.25%. By contrast spruce twigs from the Point Rouse Complex have a median concentration of only 1.2% Mn.

Molybdenum (Mo)

Molybdenum in trace amounts is required by most plants for nitrogen fixation and nitrate reduction. Concentrations are usually <2 ppm Mo in conifer twigs, although over highly alkaline soils the trees are able to absorb Mo more readily, and therefore slightly higher levels may be expected. Although no high concentrations of Mo are present in samples from the survey area, there is relative enrichment of Mo associated with the Ming and Rambler deposits.

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 twigs is 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 a few ppm Ni.

Background concentrations of Ni in black spruce twigs are commonly 30 - 40 ppm Ni, therefore the survey area has a relatively high background level (median of 76 ppm Ni). The effect of the mafic to ultramafic rocks comprising the Point Rouse Complex is seen north of the Scrape Thrust, where the median level is 226 ppm Ni and there is a maximum of 664 ppm.

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 which, from the maps showing distribution patterns of Ca and P, appears to take place in the black spruce twigs from sites underlain by the Pacquet Harbour Group and Point Rouse Complex. However, this association does not occur on the more acidic and relatively P-rich terrain of the Burlington Granodiorite. 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. The Pb content of the spruce twigs (median 85 ppm Pb) is similar to background levels in pristine forests elsewhere in northern Canada. Notable enrichment occurs only around the Ming (2533 ppm Pb) and, to a lesser extent, the Rambler deposits. With samples from this area removed from the data set (map of 'Lead - Rambler Excluded') there are no sites with unusually high concentrations of Pb. Relative enrichment occurs near Pine Cove and to both the east and west of Rambler.

Selenium (Se)

Traces of Se are essential for some plants. 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 twig ash is not proportional to the total content of the dry tissue. Analytical precision by INAA at low ppm levels of Se is poor, therefore the samples were analyzed for Se by hydride generation with an ICP-ES finish. Typically, Se concentrations in ashed vegetation are less than 2 ppm Se. The median value for the spruce twigs is 1.9 ppm Se, with relative enrichment of up to 10.5 ppm Se in trees from around the Ming and Rambler deposits (median 2.5 ppm Se) with which the Se is associated and concentrated in the -250 mesh fraction (Table 9). The map of Se (Rambler Excluded) shows that elsewhere in the survey area there are no significant zones of Se enrichment except for two sites to the east and two sites to the south of Rambler.

Tellurium (Te)

There are few data on the Te content of conifers and its essentiality is unknown. Tellurium has a geochemical affinity for Se, and its most renowned association is with Au as tellurides. The map shows there to be some Te enrichment associated with Rambler, the Romeo and Juliet deposits, and at a site of unknown source 1.5 km northwest of Ming W. Elsewhere within the survey area there are isolated sites of weak Te enrichment (e.g. Brass Buckle), but at levels below 0.5 ppm Te the precision of the data are poor, therefore their validity is in doubt.

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. The pattern of Ti distribution in the survey area shows no clear association with other elements or mineralization. Concentrations are within the normal range for conifer twigs.

Vanadium (V)

The essentiality of V for plant metabolism, other than that of 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 concentrations are within the normal range for spruce twigs, ranging from 5 - 94 ppm V with a median value of 18 ppm V. Except for the area immediately surrounding the Ming and Rambler deposits, V appears closely associated with Fe.

NOTES ON THE BIOGEOCHEMICAL DATA LISTINGS (APPENDICES A and B)

Appendix A lists field data and all analytical data obtained for the balsam fir twig ash. Appendix B provides 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. Abbreviations used in the appendices are explained in Tables 10 and 11.

Table 10: Abbreviations Used in Appendix A

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.
Twig Min Age Twig Max Age	The minimum age of each length of twig collected. The maximum age of each length of twig collected.
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.
Remarks	More detail about the sample site.

Table 11: Abbreviations Used in Appendix B

Rock Type	Underlying bedrock lithology (derived from published geological maps): BG - Burlington Granodiorite PH - Pacquet Harbour Group PR - Point Rouse Complex QP - Quartz-Feldspar Porphyry (Cape Brule Porphyry in east, King's Point Complex in south) FP - Flatwater Pond Group
N dl Cum %	N = number of samples dl = determination limit Cum % = cumulative frequency (as a percentage)

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