

# Geochemical responses in peat groundwater over Attawapiskat kimberlites, James Bay Lowlands, Canada and their application to diamond exploration

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**ABSTRACT:** Peat groundwater compositions at depths of 0.4 and 1.1 m below ground surface in the Attawapiskat region of the James Bay Lowlands are evaluated for diamond exploration applications. Samples were collected along transects that typically extended at least 200 m beyond the margins of Yankee, Zulu, and Golf kimberlites. Locations of upwelling groundwater usually occur at or near kimberlite margins based on hydrogeological measurements and variations in peat groundwater geochemical parameters (pH and EC are high, and the Eh is low relative to ombrotrophic peat groundwaters). Concentrations of the kimberlite pathfinder metals Ni, Cr, light rare earth elements (LREEs), Ba, Mg/Ca, and alkalis are commonly elevated at sample sites at or near kimberlite margins and where groundwaters are upwelling. The presence of elevated kimberlite pathfinders at these sites suggests that fractures along the boundaries between kimberlites and limestone formed during kimberlite emplacement provide dilation for upward movement of groundwater with elevated kimberlite pathfinder metals. Typically, Ni, Cr, LREE, and Ba behave similarly and thus high concentrations of these metals are found at similar locations along transects. On the other hand, locations of elevated alkalis and Mg/Ca vary. The spatial variations among pathfinder metals in peat groundwaters are possibly due to geochemical processes in the peat, such as metal binding to dissolved organic material, adsorption to insoluble organics or Fe-oxyhydroxides, and incorporation into secondary mineral precipitates, which can act to increase or decrease metal solubility. The findings of this study are readily applicable in diamond exploration in wetlands elsewhere.

**KEYWORDS:** *surficial geochemical exploration, groundwater geochemistry, kimberlite, diamond, James Bay Lowlands, metal migration, dispersion*

**SUPPLEMENTARY MATERIAL:** Krigged water table data for Yankee and Zulu locations are available at <http://www.geolsoc.org.uk/SUP18488>.

The James Bay Lowlands in northern Ontario, Canada represents one of the largest continuous peat bogs on Earth with an area of *c.* 300 000 km<sup>2</sup> (Sjors 1963). In addition to the Attawapiskat kimberlite field, there are several kimberlites that make up the Kyle Lake kimberlite field in the James Bay Lowlands. It is likely that there are additional kimberlites that have not been discovered at these two fields. On a global scale, there have been numerous kimberlite discoveries in other northern regions such as Russia and Finland (Janse & Sheahan 1995; O'Brien & Tyni 1999; Lehtonen *et al.* 2005) where peat bog terrain is common (Frenzel 1983). Due to the lack of mineral soil at surface, the most common exploration methods used in the

James Bay region are geophysical. However, kimberlites are not always magnetic, and magnetic geophysical anomalies are not necessarily kimberlite. To gain further information as to whether a geophysical response concealed by sediment cover may be kimberlite, surficial geochemical exploration in glaciated terrains commonly utilize tills and soils (Mann *et al.* 1998; Cameron *et al.* 2004; McClenaghan *et al.* 2006; Hattori *et al.* 2009; Sader *et al.* 2009) and recently peat (Hattori & Hamilton 2008).

In wetlands, conventional mineral soil sampling is not feasible in geochemical exploration due to the dominance of sphagnum peat at surface. As the James Bay Lowland region is

dominantly composed of water-saturated peat, peat groundwaters may be useful as a medium for surficial geochemical exploration. Groundwater geochemistry has been shown to provide information related to underlying rock types in wetlands (Syrovetskii *et al.* 2004) and has also been used to effectively vector to mineral deposits in a variety of settings (Leybourne & Cameron 2010). Anomalous geochemical responses in near-surface media are typically the result of water – ore interactions due to weathering processes at depth (Leybourne & Cameron 2006; Sader *et al.* 2007a).

This study was conducted to examine whether shallow peat groundwater may be used to identify buried kimberlites in wetlands. The results present evidence to suggest that peat groundwaters have metal anomalies due to underlying kimberlites. Kimberlites easily undergo low temperature serpentinization (Sader *et al.* 2007a, b), which results in an unusual groundwater geochemistry relative to waters flowing through a host of other rock types (Leybourne & Cameron 2010). The geochemical contrast with waters whose origin is limestone or Tyrell Sea sediment may be used for diamond exploration in wetlands. Geochemical results, coupled with hydrogeological parameters, are used to discuss metal transport mechanisms in wetlands.

#### LOCATION, GEOLOGICAL SETTING AND MINERALOGY

The kimberlites in this study are located in the James Bay Lowlands *c.* 90 km west of the community of Attawapiskat and within 15 km of the DeBeers Victor diamond mine (Fig. 1a & b). These mid Jurassic (*c.* 170 Ma) kimberlites are emplaced into Ordovician and Silurian limestone, dolostone, clastic sedimentary rocks, and Archean basement igneous and metamorphic rocks (Norris 1993; Webb *et al.* 2004) (Fig. 2). Host rock to kimberlites at the bedrock surface is the Upper Attawapiskat Formation limestone (Fig. 2), which also locally outcrops in the form of bioherms up to 2 m above the surrounding ground surface. Bioherms are reef cores composed of coral and skeletal remains of other marine organisms (Cowell 1983). They generally represent locations of groundwater recharge, as bioherms contain abundant void spaces and karstic textures.

A thin till layer (< 1 m in thickness) was deposited on the glacially eroded bedrock surface during the Quaternary. Tyrell Sea sediment (TSS) (2.1–21 m in thickness) is composed of varying fractions of silt and clay that are grey in colour. Small 10 to 20 cm thick sand lenses and small pebbles are occasionally observed. This sediment was deposited between 10 and 5 Ka following the end of the last glaciation when the shoreline of James Bay (referred to as the Tyrell Sea during that period) extended inland *c.* 300 km west and southwest of its present location. Isostatic rebound resulted in ground surface elevation increases of 100–300 m since the retreat of the Laurentide ice sheet in the Attawapiskat region (Shilts 1986). Peat (2.5–3.4 m in thickness) is located at the surface and has been accumulating since the retreat of the Tyrell Sea *c.* 5 000 years BP. The peat is dominantly composed of sphagnum and becomes progressively more decomposed with depth. All kimberlites are buried by Quaternary sediment, with the exception of the Zulu kimberlite, which outcrops at one location at the south margin.

The Yankee kimberlite is located in a shallow bowl-shaped depression and bioherms are located southwest and northeast of the kimberlite (Fig. 3a). The Zulu kimberlite is located on the east part of a lobate raised bog and there is a small bioherm beside the south margin of the kimberlite (Fig. 3b). Ground surface at the Golf kimberlite is similar to that of Zulu, as they both slope gently from west to east. However, no bioherm

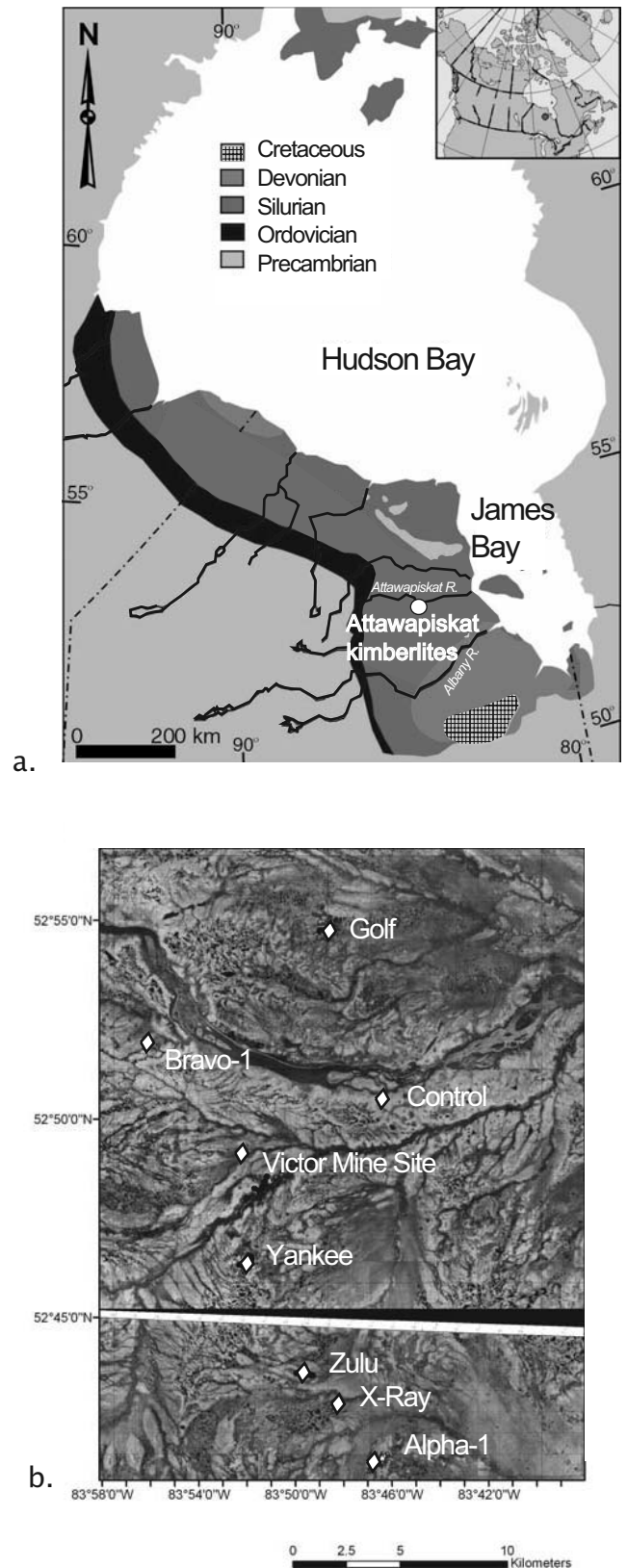


Fig. 1. (a) Regional geology of the James Bay Lowlands; from Bellefleur *et al.* (2005); and (b) the locations of Attawapiskat kimberlites and the Control site in this study.

was noted in the areas adjacent to Golf (Fig. 3c). The ground surface at the Control site grades gently towards the Attawapiskat River *c.* 600 m to the north (Fig. 3d). Geophysical

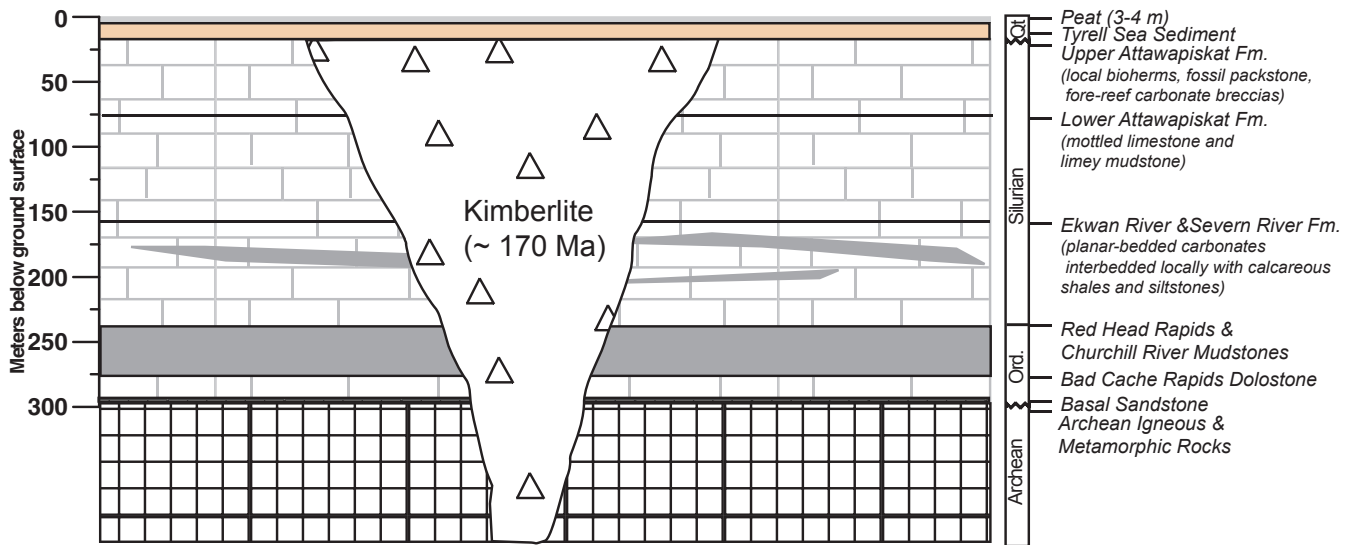


Fig. 2. A schematic vertical section of rocks and sediment into which Attawapiskat kimberlites are emplaced. The kimberlite and host rocks are overlain by a thin basal till layer (not shown), Quaternary Tyrell Sea sediment (12–4 Ka), and peat (4 Ka–present). Figure modified from Webb *et al.* (2004); geology from Norris (1993).

data (DeBeers, unpublished) suggest that there is no kimberlite in the vicinity of the Control site.

#### Attawapiskat kimberlite mineralogy and geochemistry

Detailed mineralogical descriptions of each kimberlite were made by Sage (2000a). To summarize his work: Yankee kimberlite is hypabyssal with mantle and crustal xenoliths. It contains macrocrysts of garnet, ilmenite, phlogopite, clinopyroxene, and olivine in no particular order of abundance. Diamond has not been found in this kimberlite. Zulu kimberlite is diamondiferous and is composed of hypabyssal and brecciated facies with limestone, basement, and mantle xenoliths. It contains macrocrysts of olivine, phlogopite, ilmenite, and chrome diopside with minor garnet, chromite, and clinopyroxene. Golf kimberlite is hypabyssal with xenocrysts composed of mantle olivine, pyroxene, and xenoliths of limestone. It also contains, ilmenite, and clinopyroxene, minor garnet and, minor chromite. It is unknown whether the kimberlite is diamondiferous or barren. The Alpha-1 and Alpha-1 North kimberlites are hypabyssal with limestone, basement, and mantle xenoliths. Olivine, pyroxene, phlogopite, ilmenite, minor chromite and minor chrome diopside have been identified. It is unknown whether the kimberlite is diamondiferous or barren. The X-Ray kimberlite consists of hypabyssal facies and contains limestone and other crustal xenoliths. The mineralogy includes olivine, ilmenite, chrome diopside, and garnet, and the kimberlite is diamondiferous. The Bravo-1 kimberlite consists of hypabyssal facies with fresh and altered olivine, clinopyroxene, ilmenite, chromite, and rarely garnet. This kimberlite is diamondiferous. Carbonate, spinel, phlogopite, apatite, and perovskite are common groundmass mineral in Attawapiskat kimberlites (Kong *et al.* 1999; Armstrong *et al.* 2004).

The whole rock geochemical compositions of Attawapiskat kimberlites (DeBeers, unpublished data) are comparable to other Jurassic kimberlites along the Timiskaming fault such as those from Kirkland Lake and New Liskeard (Sage 2000b) and other kimberlites worldwide (Mitchell 1986).

## METHODS

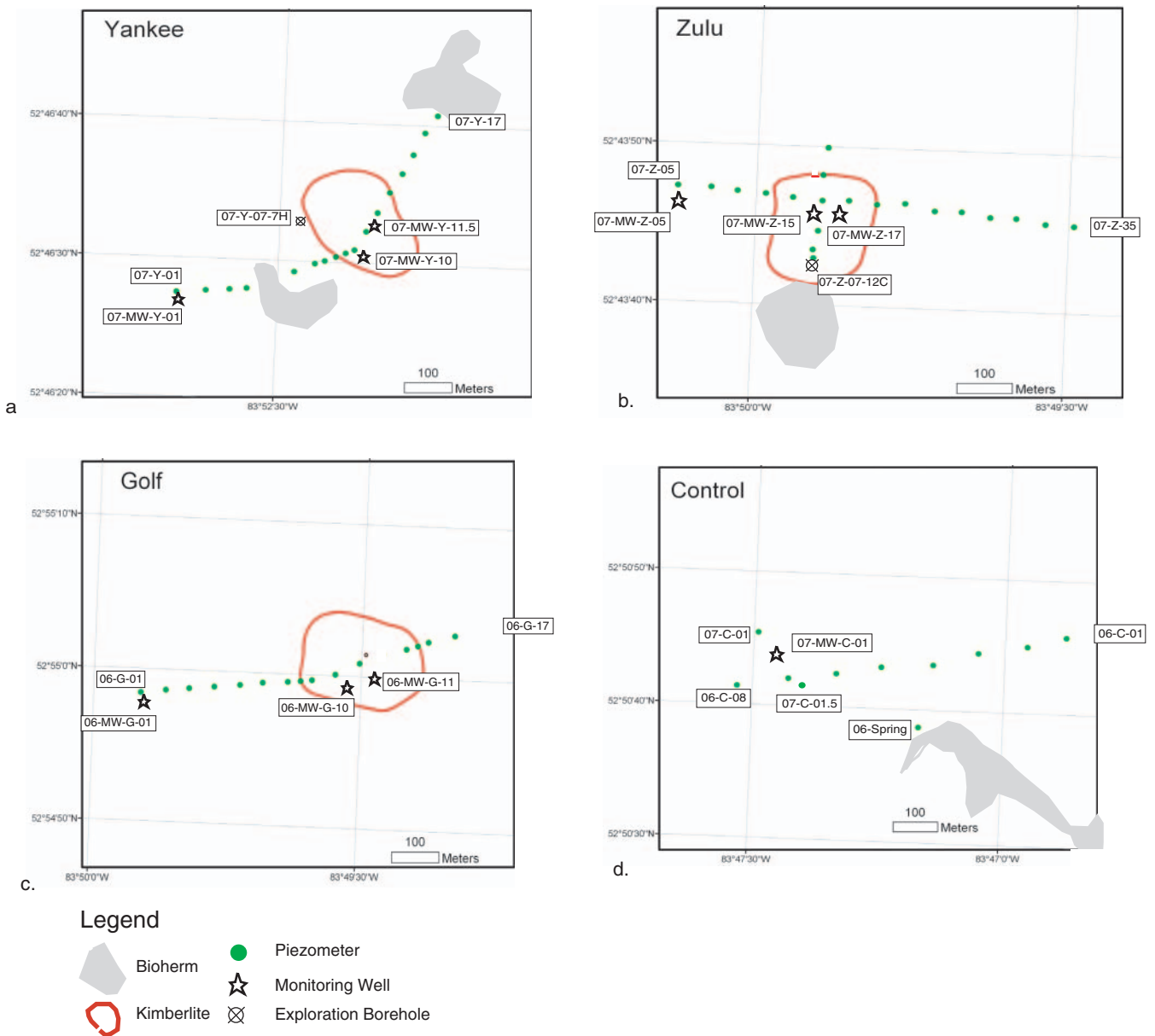
### Field procedures

#### Water sampling

Water samples were collected in the summer (August 14–23) and autumn (October 14–18) of 2007, and in the summer (early August) and autumn (late September) of 2006. Samples collected in 2006 and 2007 are denoted by the prefixes 06 and 07, respectively, and samples collected in fall are denoted by the suffix *F*. Samples along Yankee, Zulu, and Golf transects are denoted by the prefixes of Y, Z, and G, respectively. All water samples from 2006 were reported by Braunerder (2007). Compositions of water samples collected in 2007 are presented in Table 1.

Peat groundwaters were collected using piezometers with an internal diameter of 19 mm, made of 1.5-m long white environmental grade polyvinyl chloride (PVC) or grey PVC. Piezometers function as a method to collect groundwater from a desired depth with minimal influence of waters from shallower zones within an aquifer. In this study they were installed 1.1 m below ground surface (mbgs) into the peat at the Zulu, Yankee, and Control locations in 2007, and to 0.4 mbgs along the transect at Golf and Control in 2006. Piezometers were pushed into the peat with a loosely fitting plastic champagne cork at the end to prevent peat from entering the pipe while it was being installed. The pipe was then pulled up  $\approx$  0.1 m so that the cork did not impede water from flowing into the piezometer. Piezometers were installed approximately every 25–50 m along each transect and at least 200 m beyond the kimberlite margins (where conditions permitted).

Monitoring wells were installed below the peat/TSS interface at each kimberlite location (two over the kimberlite and one outside the kimberlite margin) to collect deeper groundwater. Monitoring wells 07-MW-Y-10 and 11.5 at Yankee (Fig. 3a), 07-MW-Z-15 and 17 at Zulu (Fig. 3b), 06-MW-G-10 and 11 at Golf (Fig. 3c), 07-A-MW-11 and 12 at Alpha-1, and 07-B-MW-01 and 03 at Bravo-1 were installed over the kimberlites. Wells 07-MW-Y-01 at Yankee, 07-MW-Z-05 at Zulu, 06-MW-G-01 at Golf, 07-A-MW-01 at Alpha-1, and 07-B-MW-02 at Bravo-1 were installed outside kimberlite margins. One well (07-MW-C-01) was installed at the Control site



**Fig. 3.** Locations of piezometer transects, monitoring wells, and boreholes at (a) Yankee; (b) Zulu; (c) Golf; and (d) Control Site. Outlines of kimberlites were determined by geophysics and drilling by DeBeers Canada.

(Fig. 3d). Each monitoring well was installed within 30 cm of the piezometer with the same identification (i.e. 07-MW-Z-17 and 07-Z-17) with the exception of 07-MW-Y-11.5. Wells were installed 70 cm below the peat/TSS interface except for 07-MW-Z-15, which could only be advanced 13 cm below the peat.

Groundwater samples were collected at a depth of  $\approx 14$  mbgs from five exploration boreholes. All boreholes are cased through Quaternary units. They are located south of center at the Zulu kimberlite (07-Z-07-12C) (Fig. 3b),  $\approx 10$  m outside and up-gradient of the Yankee kimberlite margin (07-Y-07-7H) (Fig. 3a), and near the centers of Alpha-1 (06-A-BH-06), X-ray (07-X-07-014C) and Bravo-1 (07-B1-07-08C) kimberlites. In addition, a spring discharging from limestone near the Attawapiskat River and the Control Site was sampled (Fig. 3d).

#### Field measurements

The water levels were recorded for all piezometers and monitoring wells from Yankee and Zulu. The top of piezometers

and monitoring well casings were surveyed using a theodolite and a surveying rod to determine the water table elevation, the general direction of horizontal groundwater flow, and sites of upwelling groundwater.

The pH, oxidation-reduction potential (ORP), electrical conductivity (EC), dissolved oxygen content (DO), and temperature were measured on-site with a Hanna HI-9828 multi probe. The pH, DO, and EC probes were calibrated daily. Oxidation-reduction potential values have been corrected to the standard hydrogen electrode (SHE) for waters at 10°C by adding 207 mV to the ORP values, and are reported as Eh. Water samples were filtered through 0.45- $\mu\text{m}$  Sterivex-HV filters (Millipore Corporation) into Nalgene high-density polyethylene bottles for cation and anion analysis. Samples for dissolved inorganic carbon (DIC) were collected in 40-ml brown tinted borosilicate bottles with a silicone-Teflon septum cap. A polytetrafluoroethylene-rubber septum manufactured by Chromatographic Specialties Inc. was inserted underneath the septum cap to prevent DIC loss, as silicone is gas-permeable.

**Table 1.** The geochemistry of groundwaters in peat, TSS, and boreholes from the Atamapitsikeat kimberlite region. Na, not analysed; bd, below detection

Sample	07-Y-01	07-Y-02	07-Y-03	07-Y-04	07-Y-05	07-Y-06	07-Y-07	07-Y-08	07-Y-09	07-Y-10	07-Y-11	07-Y-12	07-Y-13	07-Y-14	07-Y-15	07-Y-16	07-Y-17
Distance along transect	0	64	116	153	255	299	324	349	370	393	443	489	539	589	639	689	739
water type	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat	peat
Lat	52.8455	52.7743	52.7743	52.7744	52.7747	52.7749	52.7750	52.7751	52.7751	52.7752	52.7756	52.7760	52.7764	52.7768	52.7771	52.7776	52.7779
Long	-83.7915	-83.8772	-83.8765	-83.8759	-83.8745	-83.8739	-83.8735	-83.8732	-83.8729	-83.8726	-83.8723	-83.8720	-83.8716	-83.8712	-83.8709	-83.8706	-83.8702
Temp °C	8.7	9.8	9.0	9.5	8.8	8.1	7.9	7.7	6.3	7.4	6.7	8.2	10.4	8.0	7.2	7.6	4.2
pH	5.49	5.87	5.89	7.71	6.41	5.59	5.77	7.15	6.53	6.21	7.37	6.83	5.71	6.40	6.11	6.21	7.10
Eh (mV)	332	316	316	260	303	317	316	240	299	316	224	258	325	266	303	294	302
EC (uS/cm)	29	56	55	264	92	55	47	218	78	30	301	71	35	45	30	41	54
DO (mg/L)	1.24	2.23	3.11	4.47	4.48	4.39	2.56	2.72	1.72	1.90	2.66	1.19	4.00	1.97	0.77	8.00	3.13
DIC (mg/L)	7.36	na	15.31	36.00	22.67	na	11.68	30.30	20.37	9.82	47.88	25.61	10.14	13.66	19.05	12.95	na
	Method																
	Detection Limit																
mg/L																	
Ca	2.91	7.07	8.12	60.54	17.89	9.15	5.75	26.18	21.12	5.49	63.91	14.01	2.52	3.43	3.36	6.50	9.54
Mg	0.24	0.33	0.31	0.88	0.68	0.81	0.59	12.55	2.04	0.38	2.84	0.45	0.34	0.49	0.46	0.48	0.44
K	0.35	0.36	0.00	0.00	0.26	0.00	0.00	0.00	0.31	0.00	0.00	0.00	0.25	0.45	0.26	0.19	0.27
Na	0.34	0.44	0.36	0.42	0.80	0.52	0.39	0.66	0.47	0.26	0.85	0.33	0.34	0.33	0.44	0.43	0.50
SO <sub>4</sub> <sup>2-</sup>	0.36	na	0.21	0.39	0.04	na	0.29	1.09	0.09	0.15	0.07	0.12	0.39	0.38	3.97	0.33	0.50
Cl <sup>-</sup>	0.59	na	0.76	0.63	0.12	na	1.24	0.71	0.89	0.71	0.87	0.22	2.05	1.2	0.73	1.68	0.50
ug/L																	
Fe	155	409	258	25	302	256	171	400	586	111	4052	4726	119	140	151	448	1428
Mn	18	23	7	65	6	14	33	78	34	17	74	129	19	12	14	36	26
S	318	bd	bd	510	bd	348	bd	467	bd	bd	433	bd	341	bd	358	373	394
Cr	0.32	0.11	0.14	0.09	0.09	0.19	0.24	4.23	0.20	0.18	0.24	0.13	0.25	0.22	0.35	0.48	0.34
Ba	2.80	2.62	2.69	3.11	4.25	3.04	3.26	58.06	8.65	2.41	8.57	6.41	1.71	2.11	2.00	3.05	2.92
Ni	0.40	0.40	0.42	0.66	0.51	0.46	0.87	60.76	1.22	0.56	1.87	0.40	0.35	0.42	0.51	1.18	0.64
Rb	0.717	1.009	0.193	0.240	0.670	0.363	0.176	0.553	1.002	0.446	0.481	0.260	0.498	0.624	0.540	0.599	0.586
Cs	0.0215	0.0352	0.0087	0.0010	0.0130	0.0122	0.0031	0.0038	0.0251	0.0107	0.0130	0.0046	0.0131	0.0168	0.0134	0.0154	0.0202
La	0.030	0.037	0.033	0.092	0.032	0.053	0.050	1.715	0.071	0.036	0.032	0.010	0.029	0.032	0.046	0.072	0.052
Ce	0.059	0.069	0.068	0.150	0.047	0.097	0.109	2.386	0.123	0.077	0.075	0.017	0.063	0.065	0.102	0.132	0.100
Pr	0.0071	0.0098	0.0089	0.0215	0.0058	0.0127	0.0134	0.2467	0.0148	0.0095	0.0095	0.0020	0.0081	0.0076	0.0122	0.0158	0.0102
Nd	0.031	0.035	0.031	0.092	0.026	0.051	0.054	0.823	0.056	0.040	0.039	0.009	0.032	0.028	0.048	0.064	0.034
Sm	0.007	0.006	0.007	0.016	0.005	0.009	0.011	0.126	0.013	0.008	0.009	0.003	0.008	0.009	0.011	0.011	0.006



Table 1. continued

Sample	07MW-A-01	07MW-A-01F	07MW-A-11	07MW-A-11F	07MW-A-12	07MW-A-12F	07MW-C-01F	07MW-Y-01	07MW-Y-01F	07MW-Y-10	07MW-Y-10F	07MW-Y-11.5	07MW-Y-11.5F	07MW-Z-05	07MW-Z-05F	07MW-Z-15	07MW-Z-15F	07MW-Z-17F	07MW-B-01F	07MW-B-02F	07MW-B-03F
Distance along transect	0	469	518	518	518	518	na	0	0	393	393	466	466	0	0	250	250	300	na	na	na
water type	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS	TSS
over/outside kimberlite	outside	over	over	over	over	over	outside	outside	outside	over	over	over	over	outside	outside	over	over	over	over	outside	outside
Lat	52.6907	52.6938	52.6938	52.6939	52.6939	52.6939	52.8455	52.7743	52.7752	52.7752	52.7752	52.7759	52.7759	52.7298	52.7298	52.7296	52.7296	52.7296	52.8651	52.8656	52.8651
Long	-83.7810	-83.7810	-83.7769	-83.7762	-83.7762	-83.7762	-83.7915	-83.8781	-83.8781	-83.8781	-83.8725	-83.8725	-83.8721	-83.8354	-83.8354	-83.8316	-83.8316	-83.8309	-83.9387	-83.9387	-83.9395
Temp °C	13.3	14.5	8.8	7.6	11.5	8.5	16.5	8.4	6.2	18.4	5.4	16.8	6.5	16.4	16.4	7.1	7.1	6.5	9.6	6.2	15.1
pH	7.12	7.51	7.53	6.24	6.71	7.19	7.44	8.25	6.98	9.06	7.40	8.92	8.17	6.57	7.67	7.24	7.24	7.66	6.77	6.71	7.54
Eh (mV)	103	263	101	244	209	279	276	60	192	210	237	224	411	102	175	281	241	241	341	306	303
EC (µS/cm)	481	474	524	377	448	248	285	440	410	409	475	407	411	479	304	440	440	474	977	600	600
DO (mg/L)	0.32	1.42	0.38	2.45	6.64	4.91	5.42	0.60	0.84	1.02	4.15	6.52	2.87	0.00	1.95	2.72	2.72	0.56	6.82	7.69	1.90
DIC (mg/L)	68.33	76.52	77.93	62.93	70.99	61.28	73.90	na	64.64	57.70	68.85	53.62	56.41	126.16	32.06	78.14	84.00	153.36	61.46	130.06	70.22
Method																					
Detection Limit																					
mg/L																					
Ca	110.94	112.39	85.65	25.34	78.02	50.90	na	103.17	102.94	116.19	112.86	94.91	87.84	103.89	43.62	82.21	82.60	150.65	64.42	179.63	107.80
Mg	0.03	2.21	10.01	6.45	21.40	15.28	na	7.91	8.63	6.03	5.86	4.27	3.98	3.09	2.49	27.35	24.45	41.85	15.62	10.84	8.36
K	0.18	1.08	1.64	3.06	0.45	0.38	na	0.48	0.29	0.58	0.55	0.68	0.88	2.37	3.21	0.22	0.00	11.96	0.64	5.34	1.40
Na	0.05	3.21	5.06	27.62	1.75	1.30	na	1.56	1.04	1.88	1.42	2.55	2.23	3.38	8.26	1.24	0.89	38.14	3.00	15.40	4.46
SO <sub>4</sub> <sup>2-</sup>	0.04	1.20	0.46	4.74	12.97	0.49	na	2.16	0.35	0.16	0.21	0.27	0.27	0.20	0.97	0.16	0.04	1.24	0.49	1.28	0.57
Cl <sup>-</sup>	0.03	1.89	4.28	10.31	3.70	1.02	na	1.64	1.64	1.76	1.34	1.53	1.39	2.15	1.34	0.93	0.93	3.74	2.63	8.85	2.46
ug/L																					
Fe	90.35	54.28	2.430	256	4.794	7063	na	836	672	1044	490	526	589	1981	224	5997	5863	111	130	105	43
Mn	181	172	94	32	148	109	na	47	43	80	70	166	185	180	46	149	155	223	63	328	203
S	626	465	1218	2804	584	334	na	679	591	671	606	500	483	886	336	612	547	bd	492	bd	474
Cr	0.02	1.33	0.29	0.51	0.42	6.89	na	1.21	0.91	1.65	1.16	0.22	0.24	2.09	0.80	18.05	14.96	0.36	0.43	0.28	0.23
Ba	8.83	15.58	5.29	8.60	14.86	13.06	na	8.19	14.68	17.95	16.80	15.46	19.90	28.57	10.82	314.24	269.03	45.96	15.43	31.25	27.41
Ni	12.51	5.65	9.40	18.15	41.88	38.81	na	9.75	4.63	18.45	5.08	29.38	7.65	28.34	20.90	5.01	2.86	25.08	82.37	11.48	15.19
Rb	1.372	1.396	3.143	4.261	2.901	2.404	na	1.184	0.895	1.425	1.018	0.746	0.749	2.844	2.161	0.787	0.600	4.996	1.686	3.821	1.923
Cs	0.0005	0.0127	0.0104	0.0139	0.0260	0.0166	na	0.0094	0.0069	0.0060	0.0060	0.0044	0.0036	0.0385	0.0103	0.0174	0.0101	0.0086	0.0115	0.0104	0.0115
La	0.0019	0.0006	0.0015	0.007	0.795	0.984	na	0.067	0.101	0.098	0.126	0.011	0.012	0.387	0.197	0.663	0.599	0.007	0.350	0.004	0.056
Ce	0.002	0.034	0.012	0.037	1.408	1.831	na	0.133	0.208	0.205	0.261	0.021	0.023	0.695	0.371	1.281	1.106	0.011	0.682	0.007	0.102
Pr	0.0040	0.0015	0.0043	0.018	0.1603	0.2033	na	0.0167	0.0268	0.0260	0.0328	0.0030	0.0030	0.0759	0.0435	0.1223	0.1041	0.0016	0.0783	0.0010	0.0120
Nd	0.0180	0.0050	0.0260	0.0080	0.5720	0.7610	na	0.0650	0.1060	0.1220	0.1320	0.0150	0.0120	0.2950	0.1510	0.4810	0.4160	0.0190	0.2910	0.0110	0.0460
Sm	0.003	0.001	0.007	0.001	0.106	0.127	na	0.014	0.023	0.020	0.026	0.004	0.004	0.051	0.028	0.078	0.085	0.001	0.050	0.002	0.010

Table 1. continued

Sample	07-B1-07-08C-F	07-X-07-014C	07-Z-07-12C	07-Z-07-12C-F	07-Y-07-7H	07-Y-07-7H-F	07-07-C-01.5F	07-07-C-01F
Distance along transect								
water type	na	na	na	na	na	na	na	na
limestone or kimberlite	borehole kimberlite	borehole kimberlite	borehole kimberlite	borehole kimberlite	borehole limestone	borehole limestone	peat	peat
Lat	52.8649 -83.9393	52.7960 -83.8537	52.7290 -83.8317	52.7290 -83.8317	52.7756 -83.8737	52.7756 -83.8737	52.8449 -83.7905	52.8455 -83.7915
Long	9.6	9.0	12.4	16.9	7.5	16.9	14.8	16.4
Temp °C	8.55	7.76	7.51	8.04	8.06	7.29	5.54	4.93
pH	226	23	68	136	-4	95	276	290
Eh (mV)	597	198	945	247	377	na	69	29
EC (uS/cm)	2.48	bd	bd	1.26	bd	1.27	2.79	2.05
DO (mg/L)	74.12	37.96	76.14	23.34	49.53	53.02	20.58	32.41
DIC (mg/L)								
Method								
Detection Limit								
mg/L								
Ca	25.19	25.18	47.99	17.94	68.25	72.37	5.99	3.23
Mg	68.25	21.64	39.91	13.70	5.74	6.04	0.60	0.48
K	5.33	0.40	9.47	1.28	0.46	0.46	bd	bd
Na	7443.23	832.83	117766.12	9572.27	1172.30	999.68	430.72	429.12
SO <sub>4</sub> <sup>2-</sup>	0.24	0.67	13.09	3.92	0.43	0.04	0.38	0.19
Cl <sup>-</sup>	6.00	0.50	158.31	14.98	1.00	0.77	0.94	0.89
ug/L								
Fe	73	299	444	1370	12373	12799	104	252
Mn	20	19	16	20	116	122	8	6
S	bd	537	939	823	462	382	428	301
Cr	0.17	1.56	0.64	1.29	0.13	0.14	0.25	0.35
Ba	654.57	1455.47	127.74	566.93	30.13	24.60	2.83	2.48
Ni	1.79	6.18	29.65	18.41	0.36	0.47	0.48	0.48
Rb	5.488	8.050	3.330	2.654	0.494	0.464	0.160	0.397
Cs	0.0119	0.0991	0.0579	0.0302	0.0011	0.0005	0.0087	0.0124
La	0.026	0.102	0.060	0.925	0.009	0.005	0.026	0.030
Ce	0.012	0.120	0.090	1.276	0.015	0.007	0.050	0.069
Pr	0.0009	0.0120	0.0091	0.1209	0.0022	0.0011	0.0071	0.0091
Nd	0.006	0.038	0.030	0.402	0.011	0.000	0.028	0.032
Sm	0.004	0.016	0.005	0.050	0.002	0.001	0.006	0.009

na = not analysed

bd = below detection



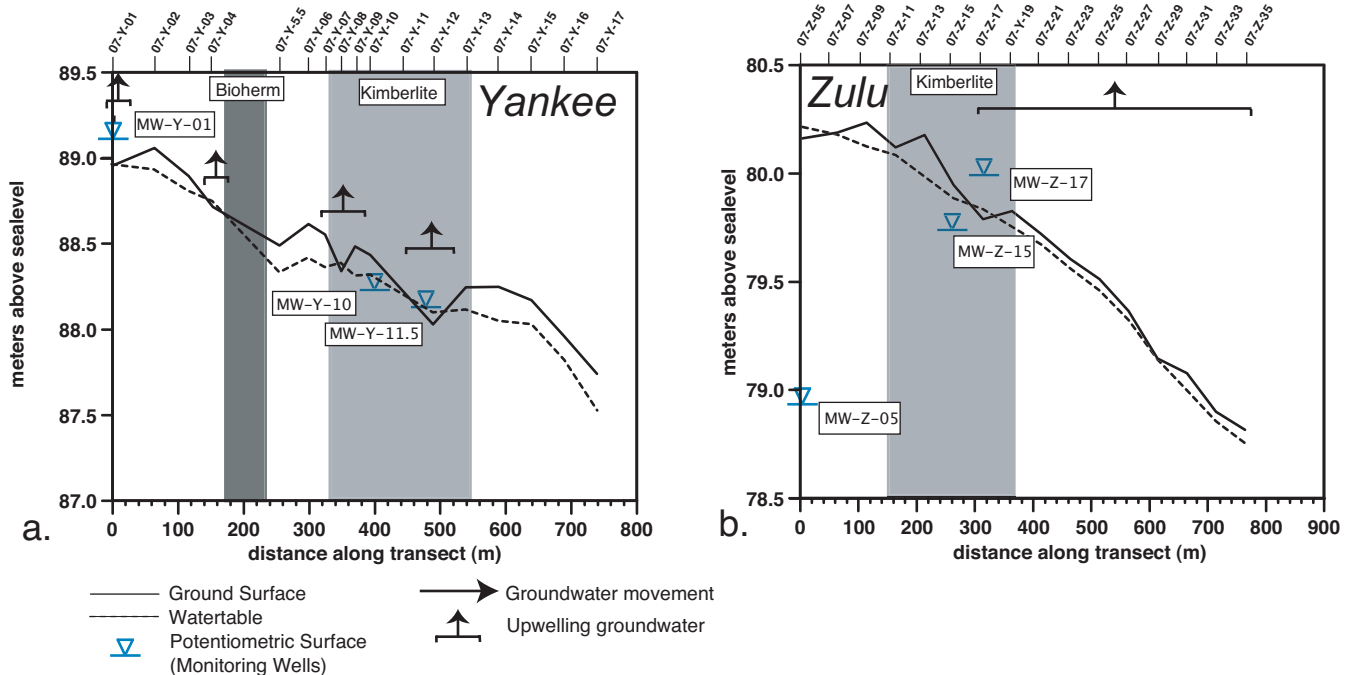


Fig. 4. Profiles of the ground surface, the water table, and potentiometric surfaces along the transects at (a) Yankee and (b) Zulu kimberlites. Sites with potentiometric surfaces greater than the water table indicate upwelling groundwater.

All water samples were kept cool in ice-packed coolers or refrigerated until they were analysed.

### Laboratory procedures

The elemental composition data of groundwaters were measured at the Geoscience Laboratories of the Ministry of Northern Development of Mines, Sudbury, Ontario, Canada. Waters were analysed for Ca, K, Mg, Na, and S using a Spectro inductively coupled plasma emission spectrometer (ICP-ES). Analysis of certified references FP83MI1 and FP83TE1 before, during, and after the run indicate a precision, calculated in terms of relative standard deviation (RSD), of better than 5% for all metals except K (14%). The concentrations of Fe, Mn, Cr, Ni, Rb, Cs, Ba, and LREEs were determined using an inductively-coupled plasma mass spectrometer (ICP-MS). Analysis of certified reference SLRS-4 from the National Research Council of Canada before, during, and after the run indicate a precision of better than 5% RSD for all metals except Mn (7%) and Cs (7%). Prior to analysis, water samples analysed for cations were acidified to 1% concentration using Baseline-grade  $\text{HNO}_3$  from Seastar Chemicals. Anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) were determined using a Dionex ion chromatograph. The RSDs for internal references, which were included during the runs, are less than 5% for both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . Waters were analysed for DIC concentrations at the University of Ottawa G.G. Hatch Stable Isotope Laboratory using a Finnigan-Mat Delta Plus mass spectrometer. The  $2\sigma$  analytical precision is  $\pm 0.002$  ppm.

## RESULTS

### Hydrogeology and groundwater movement

The lateral velocity ( $v$ ) of peat groundwater movement down-gradient was calculated using Darcy's Law:

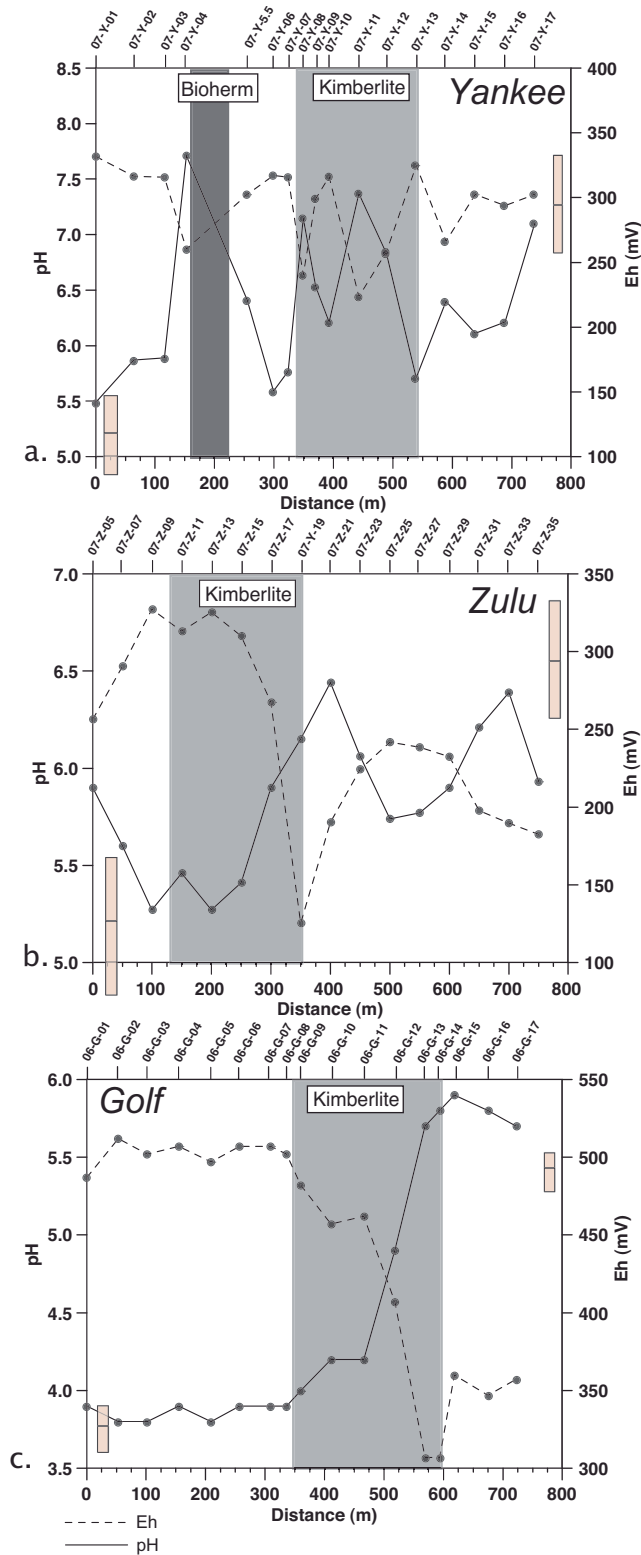
$$v = (-Ki)/n$$

where  $K$  is the hydraulic conductivity of the peat,  $i$  is the gradient, and  $n$  is peat porosity. The calculation used a hydraulic

conductivity value of  $0.001$  cm/s based on measurements from northern sphagnum bogs and spring fens (Chason & Siegel 1986). This  $K$  value is in the upper range for the catotelum (peat zone deeper than 0.3–0.5 mbgs), as  $K$  typically ranges from  $10^{-2}$ – $10^{-6}$  cm/s (Ingram 1983; Hoag & Price 1995; Price 2003) in this zone. An active peat porosity ( $n$ ) value of 0.3 was used based on measurements of the catotelum from sphagnum peat bogs (Hoag & Price 1995, 1997).

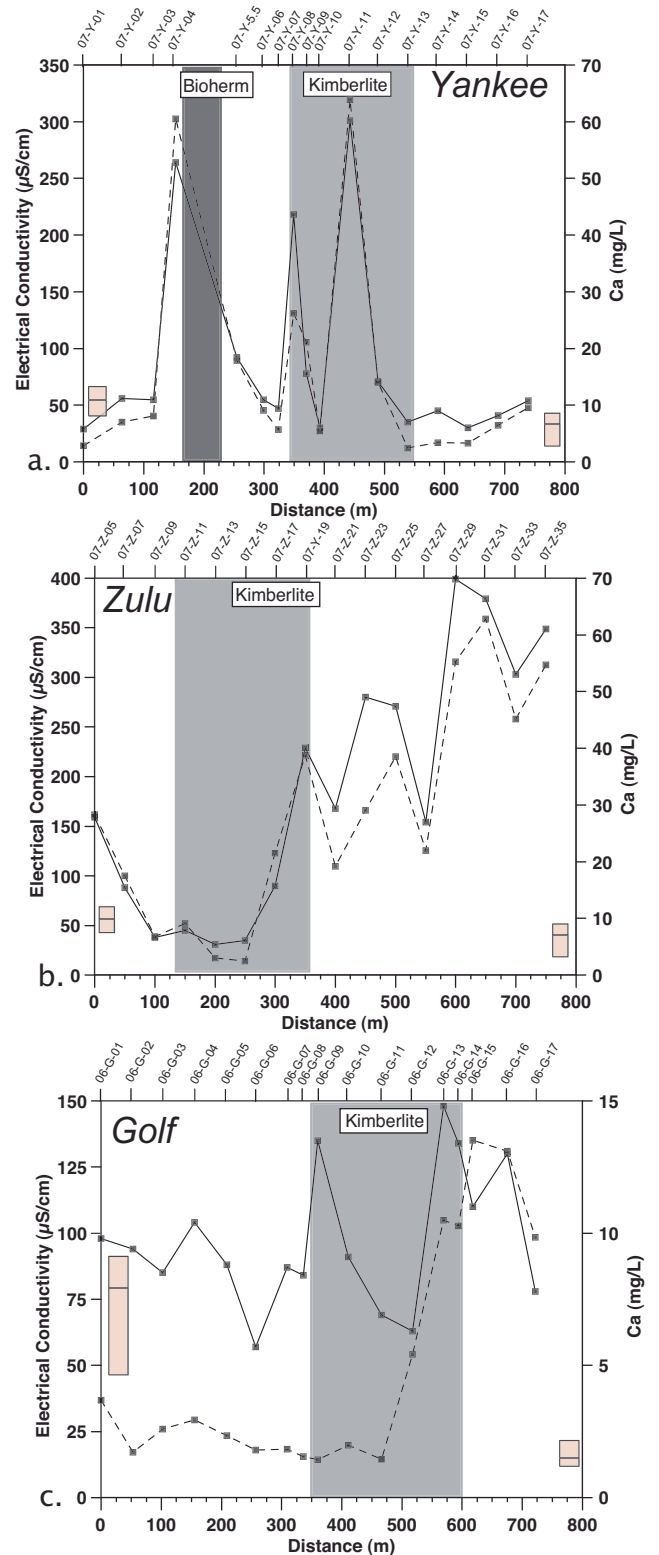
Peat groundwaters along the Yankee transect flow from approximately SW–NE with a gradient ( $i$ ) of  $-1.66 \times 10^{-3}$ . The water table is virtually horizontal between 07-Y-5.5 and 10 ( $i = -1.46 \times 10^{-5}$ ), and between 07-Y-12 and 15 ( $i = -4.67 \times 10^{-5}$ ) (Fig. 4a). The calculated velocity of peat groundwater is  $5.53 \times 10^{-6}$  cm/s for the entire length of the Yankee transect. However, the calculated velocity is significantly lower for the segment between 07-Y-5.5 and 10 ( $4.82 \times 10^{-8}$  cm/s), and for the segment between 07-Y-12 and 15 ( $1.56 \times 10^{-7}$  cm/s) along the transect. Upwelling of deep minerotrophic groundwater was detected at sites 07-Y-01, 04, 08, 09 and 12 where the saturated zone is close to or above the ground surface. Additionally, the potentiometric surface of monitoring wells suggests upwelling in the vicinity of 07-MW-Y-01 and 07-MW-Y-11.5 (Fig. 4a). At Zulu, peat groundwater flows from west to east with a horizontal gradient of  $-1.95 \times 10^{-3}$  and is generally parallel to the ground surface (Fig. 4b). The calculated velocity of peat groundwater along the length of the Zulu transect is  $6.50 \times 10^{-6}$  cm/s. Upwelling deep groundwater is noted at 07-MW-Z-17 based on the potentiometric surface in the monitoring well and likely extends to the end of the probable transect.

At Golf, geochemical data are used to evaluate sites of upwelling groundwater, as hydrogeological surveying was not conducted at this location. Elevated relative values of pH and low Eh (Fig. 5c), and elevated Ca and EC (Fig. 6c) suggest upwelling of deep groundwater along the transect between sites 06-G-08 (near the western margin of the kimberlite) to the eastern end of the transect. Elevated values of Ca, EC, and pH, and low values of Eh are commonly used to identify



**Fig. 5.** Profiles of pH and Eh along transects over: (a) Yankee; (b) Zulu; and (c) Golf kimberlites. Typically, pH and Eh indicate sites of upwelling groundwater and a shift from ombrotrophic to minerotrophic peat groundwater conditions. Box plots represent the mean, first and third quartile values for baseline ombrotrophic peat groundwaters.

contrasts between upwelling minerotrophic and ombrotrophic groundwaters in wetlands (Ingram 1983; Hill & Siegel 1991; Hoag & Price 1995). Regional drainage patterns of the area



**Fig. 6.** Profiles of electrical conductivity and Ca along transects over: (a) Yankee; (b) Zulu; and (c) Golf kimberlites. Electrical conductivity and Ca correlate well and indicate sites of upwelling minerotrophic groundwaters. Box plots represent the mean, first and third quartile values for baseline ombrotrophic peat groundwaters.

surrounding Golf observed in aerial photography suggest that regional groundwater movement is from west to east.

**Geochemistry of groundwaters from kimberlite, limestone and Tyrell sea sediment**

The pH values in water samples collected from exploration boreholes within Attawapiskat kimberlites vary from 7.5–8.5 and the Eh varies from 23–272 mV. Concentrations of pathfinder metals such as LREE, Ni, Cr, Ba, Mg, Rb, and Cs in kimberlite groundwaters are typically greater than those in groundwaters collected from limestone (Table 1). On average, the majority of these pathfinder metals are also elevated in kimberlite borehole groundwaters relative to waters in TSS that are directly above kimberlites. However, in TSS waters over kimberlites Ni and Cr have average concentrations of 26.5 and 4.5 µg/l, respectively, which is twice the concentration in kimberlite borehole groundwaters (Table 1).

The pH values of groundwater in TSS vary between 6.5–8.5; however, at 06-G-MW-11F and 07-Y-MW-10 the pH values are as high as 9.25 and 9.05, respectively. The Eh values in TSS groundwaters (average = 217 mV) are typically more elevated compared with Eh values in kimberlite groundwaters (average = 90 mV). Concentrations of LREEs, Ni, Cr, Ba, Mg, and Rb in TSS groundwaters are an average of 1.8, 1.7, 3.9, 2.8, 2.3, and 1.2 times greater, respectively, over kimberlites compared to samples collected outside their margins (Table 1). Additionally, the Mg/Ca weight ratios in TSS groundwaters are an average of 3.9 times greater over compared to outside kimberlites. However, Cs concentrations in TSS waters over kimberlites are only 0.8 times the concentration of TSS waters outside kimberlite margins.

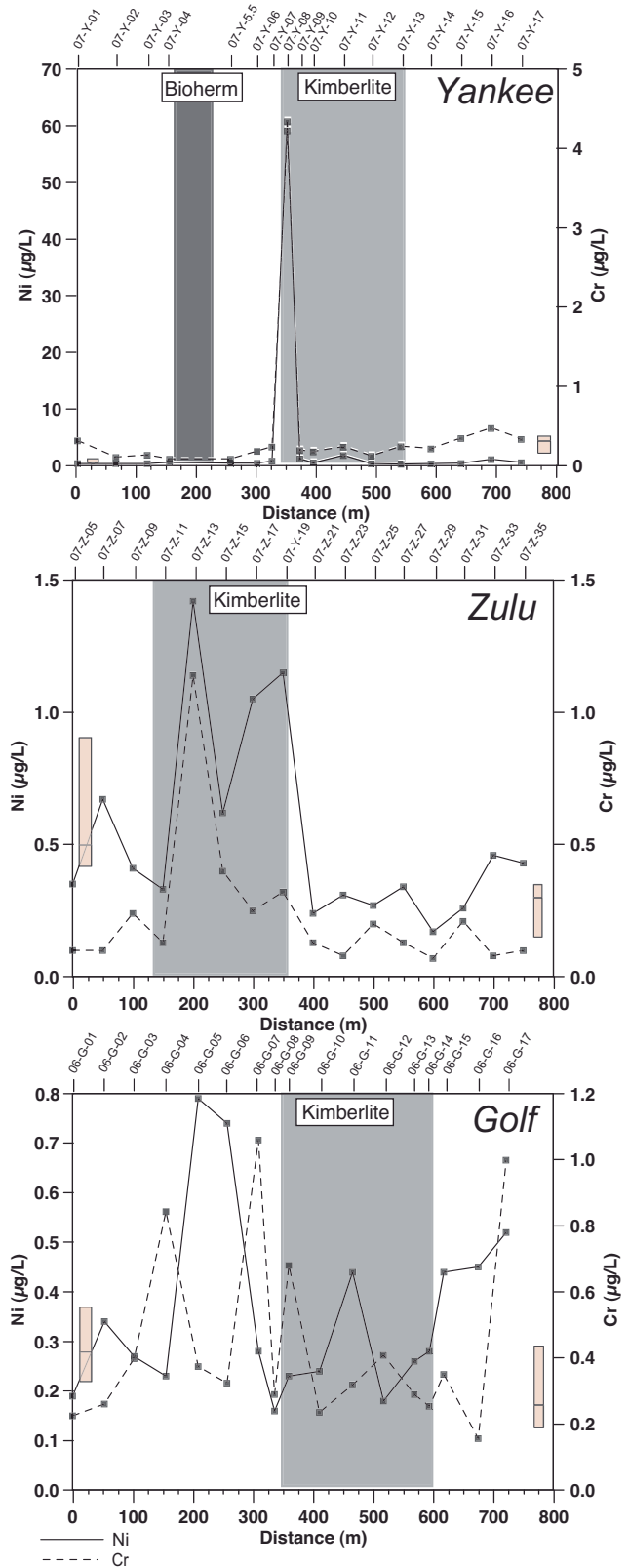
**Peat groundwater geochemistry**

In peat groundwater samples, the pH values vary from 3.8–7.1 and Eh values range from 125–512 mV (Fig. 5a, b, c). The highest pH and lowest Eh values are generally observed at sites of upwelling minerotrophic groundwater along each transect. Of Yankee, Zulu, and Golf peat groundwaters, samples from Golf have the lowest pH and highest Eh values. This may be explained by the shallower collection depth of water at Golf (0.4 mbgs).

Ombrotrophic peat groundwaters are indicated by low EC (< 100 µS/cm) and Ca concentrations (< 8 mg/l) (Ingram 1983; Hill & Siegel 1991; Hoag & Price 1995). Conversely, high EC values (> 100 µS/cm) and Ca concentrations (up to 70 mg/l) suggest contributions of minerotrophic groundwaters and are observed at sites of groundwater upwelling along the transects (Fig. 6a, b, c). High EC and Ca are accompanied by elevated DIC (Table 1). Dissolved organic carbon (DOC) concentrations vary between 3.30 and 158 mg/l, have a broad negative correlation ( $r = -0.61$ ) with EC, and are typically low at sites where hydrogeological and geochemical measurements indicate upwelling.

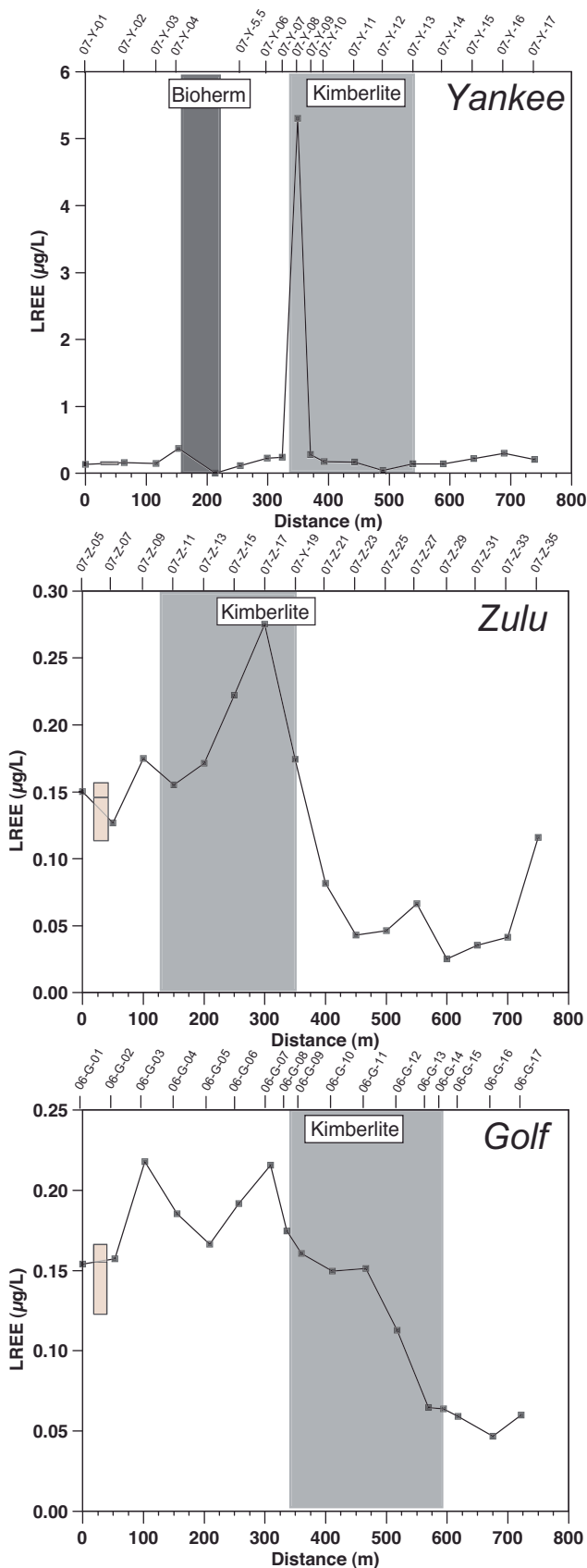
Baseline values are derived for metals (Ni, Cr, LREE, Ca, Mg, Mg/Ca, Ba, Rb, and Cs) and for pH, Eh, and EC from peat groundwaters that were collected at 1.1 mbgs greater than 200 m from kimberlite margins and from Control Site. As Golf peat groundwaters were collected from a more shallow depth of 0.4 mbgs, baseline values are those of waters collected 200 m beyond the Golf, Yankee, Alpha-1 kimberlite margins and Control Site during 2006 sampling events (Brauneder 2007). All waters used to obtain baseline values are ombrotrophic with EC values of < 100 uS/cm.

Transition metals consisting of Ni, Cr, and LREE (La-Sm) are consistently elevated along transects at sites near kimberlite margins. Although the Yankee transect shows four sites of upwelling (07-Y-01, 04, 08–09, and 12), only site 07-Y-08 (west kimberlite margin) has significantly elevated Ni and Cr (Fig.



**Fig. 7.** Concentrations of Cr and Ni in peat groundwater along transects over: (a) Yankee; (b) Zulu; and (c) Golf kimberlites. Ni and Cr are typically observed at sites of upwelling at kimberlite margins. Box plots represent the mean, first and third quartile values for baseline ombrotrophic peat groundwaters.

7a), and LREE (Fig. 8a) concentrations. These metals are between 1.5 and 2.5 orders of magnitude greater than the baseline concentrations and are similar to concentrations



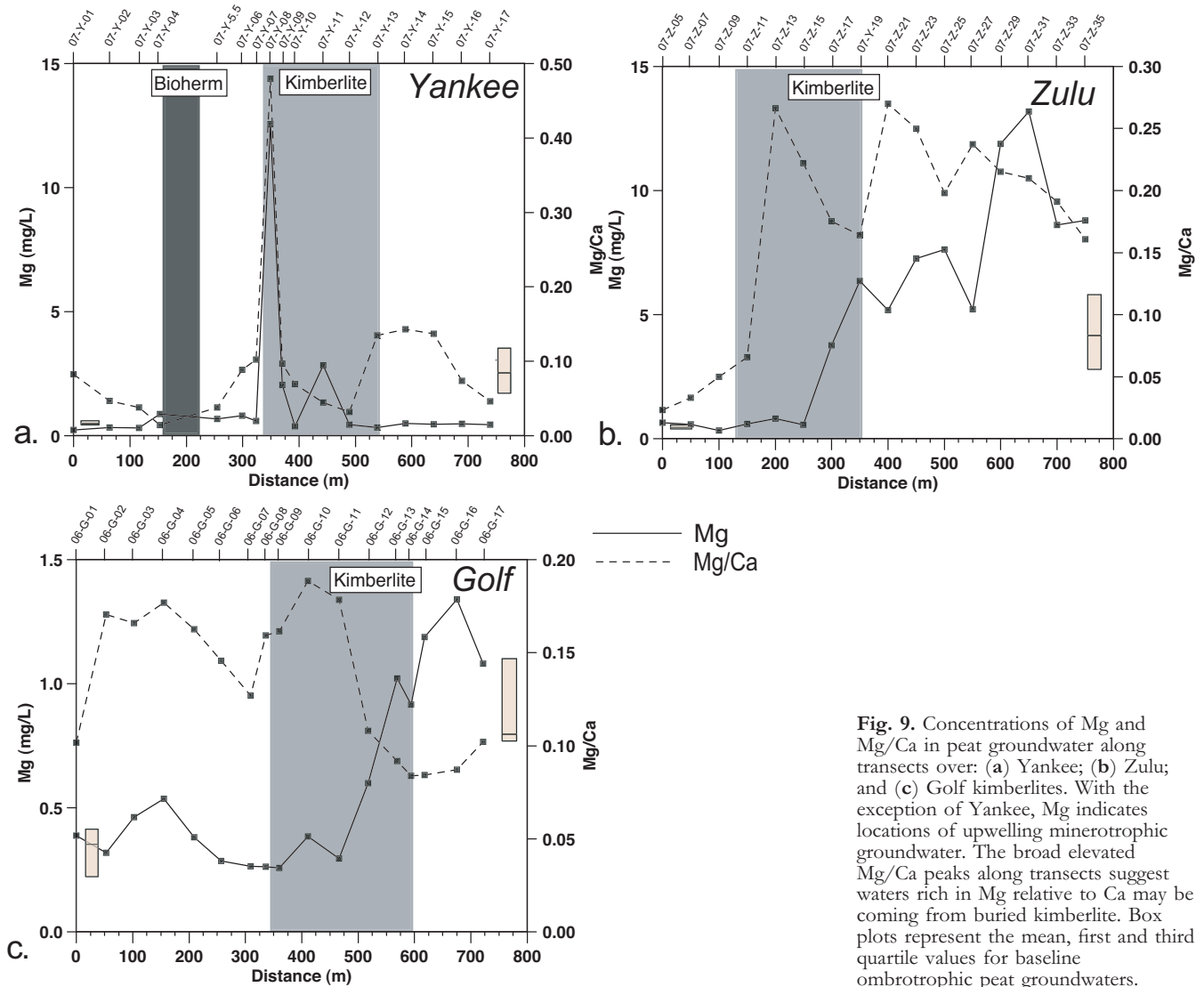
**Fig. 8.** Concentrations of LREEs (La-Sm) in peat groundwater along transects over: (a) Yankee; (b) Zulu; and (c) Golf kimberlites. Light REEs have similar profiles to Ni and Cr and are typically observed at the kimberlite margins. Box plots represent the mean, first and third quartile values for baseline ombrotrophic peat groundwaters.

observed in groundwaters from exploration boreholes in kimberlites (Table 1). Nickel, Cr and LREE are low at 07-Y-12 (near the east kimberlite margin) (Figs 7a, 8a). Elevated Ni, Cr, and LREE concentrations in peat groundwaters from Zulu and Golf are typically 2–3 times greater than mean baseline values. At Zulu, Ni is elevated near the east kimberlite margin (07-Z-15 to 19); however, Cr is only elevated at sites 07-Z-13 and to a lesser extent at 07-Z-15 (Fig. 7b). Light REEs are significantly greater than baseline concentrations at the east kimberlite margin (07-Z-15 and 17; Fig. 8b). The location of Ni, Cr and LREE concentration profiles along the transect at Golf are similar to those of Zulu except that the highest concentrations of these metals are located at the west margin of Golf kimberlite (between 06-G-04 and 08) (Figs 7c, 8c). However, elevated concentrations of Ni occur at 06-G-11 and at the east margin from 06-G-15 to 17 and elevated Cr is located at 06-G-17 (Fig. 7c). At both Zulu and Golf, the highest metal concentrations usually coincide with a small contribution of upwelling minerotrophic water. Nickel, Cr, and LREE concentrations are typically lower than baseline values at sites down-gradient at both Zulu and Golf, and at 07-Y-12 (Yankee) where minerotrophic waters are more dominant. Collectively, Ni, Cr, and LREEs are referred to as ‘Group 1 metals’ due to the similarity of their spatial distribution along the transects in this study.

Peat groundwaters along the Yankee transect show elevated Mg concentrations at 07-Y-08 and 11 (Fig. 9a). The Mg/Ca ratios are high at 07-Y-08 and between 07-Y-13 and 15, but are low at 07-Y-11 (Fig. 9a). Elevated concentrations of Ca (Fig. 6b, c), and Mg (Fig. 9b, c) observed along Zulu and Golf transects are consistent with upwelling minerotrophic groundwaters. However, the Mg/Ca ratios are highest at sites of upwelling near kimberlite margins (Fig. 9b & c). Elevated ratios are also detected at some sites where groundwater is not upwelling such as 07-Z-13 and 15 at Zulu and 07-G-02 to 05 at Golf.

Concentrations of Ba in peat groundwaters are 1–1.5 orders of magnitude higher relative to the baseline concentrations at or near Yankee and Zulu kimberlite margins. The Ba profile along the Yankee transect (Fig. 10a) is consistent with other alkaline earth metals. The profile is almost identical to that of Mg (Fig. 9a), with elevated concentrations at 07-Y-08, 11 and 12. However, Ba is low at 07-Y-04 even though Ca is high. The Ba concentration profiles along at Zulu and Golf sampling transects are not consistent with other alkaline earth metals, but are more similar to the profiles of Group 1 metals. Barium is highest along the Zulu transect near the eastern margin of the kimberlite between sites 07-Z-17 and 21 (Fig. 10b). Along the Golf transect, Ba is elevated at the up-gradient margin of the kimberlite (between 06-G-06 and 09; Fig. 10c). Note that the Ba concentrations at Golf are 2 orders of magnitude greater than Yankee or Zulu. All waters collected from this sampling event (summer 2006) have high Ba values. We have ruled out the possibility of contamination, and analytical artifact. Because of these high concentrations, we have revised the baseline data for Ba to reflect only waters collected during summer 2006 for consistency.

Concentration profiles of alkali metals (Rb and Cs) in peat groundwaters differ from those of Group 1 and alkaline earth metals along transects and are typically displaced 50 to 100 m from sites of elevated Group 1 metals and Ba. The highest alkali metal concentrations at Yankee are at 07-Y-02, 08, and 09 (Fig. 11a). Along the Zulu transect, alkalis are elevated at sites of upwelling from 07-Z-19 to 29, but sharply decrease farther east along the transect even though upwelling appears to continue (Fig. 11b). At Golf, the highest alkali concentrations



**Fig. 9.** Concentrations of Mg and Mg/Ca in peat groundwater along transects over: (a) Yankee; (b) Zulu; and (c) Golf kimberlites. With the exception of Yankee, Mg indicates locations of upwelling minerotrophic groundwater. The broad elevated Mg/Ca peaks along transects suggest waters rich in Mg relative to Ca may be coming from buried kimberlite. Box plots represent the mean, first and third quartile values for baseline ombrotrophic peat groundwaters.

are observed at 06-G-05, in waters considered ombrotrophic (Fig. 11c). At Golf and Yankee alkali concentrations are only slightly higher than baseline values.

Sulphate concentrations are low at all sites (mean = 0.35, median = 0.3, max = 3.97 mg/l) (Table 1) and total sulphur concentrations in waters are also low (mean = 0.4, max = 0.9, many samples less than the detection limit of 0.3 mg/l) (Table 1). Chloride concentrations are low and range from 0.12–25.43 mg/l with mean and median concentrations of 3.6 and 2.0 mg/l, respectively (Table 1).

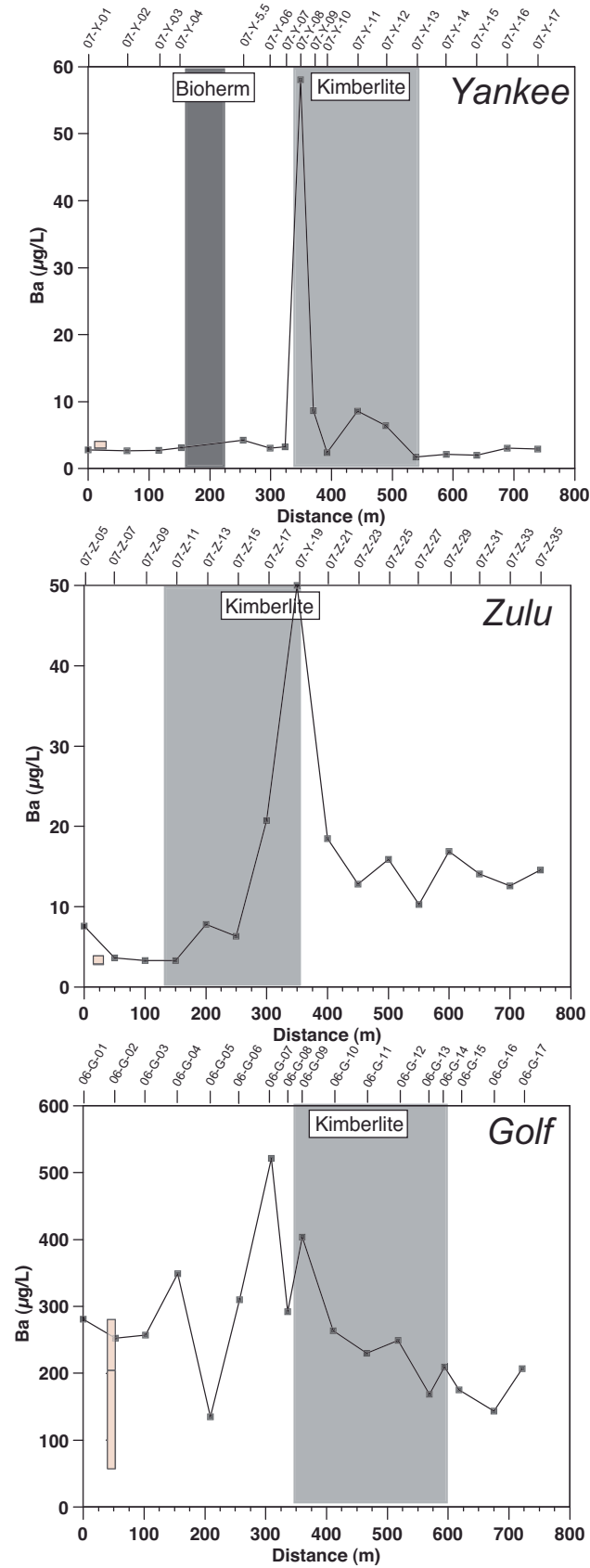
## DISCUSSION

### Metal sources in peat groundwaters

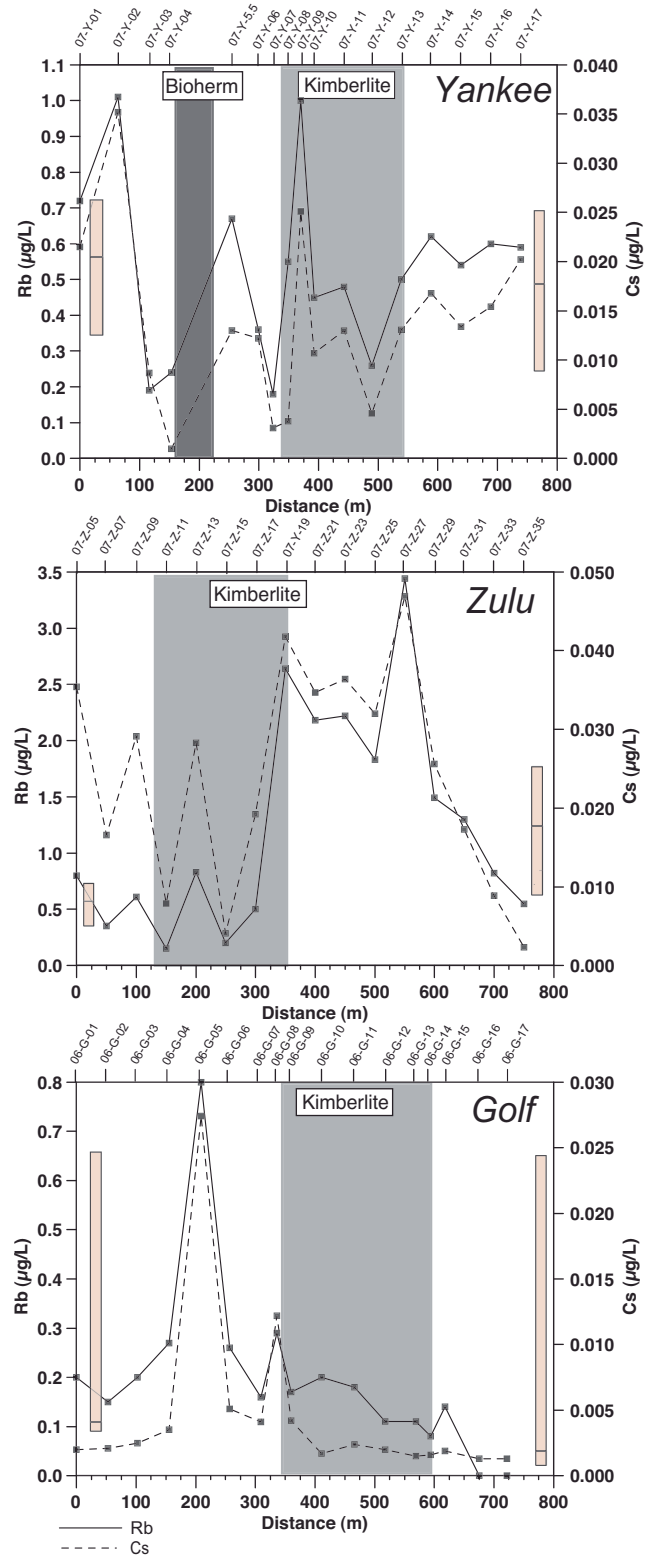
There are only three possible sources of metals in the study area that could contribute to elevated pathfinder metals in peat groundwaters: (1) host rock (dominantly Attawapiskat Formation limestone); (2) TSS; or (3) kimberlite. A limestone source for the elevated metals can be discounted because the concentrations of Group 1, Ba, Mg/Ca and alkali metals in peat, TSS, and kimberlite groundwaters are always greater than concentrations in limestone groundwater (sometimes by more than one order of magnitude). Additionally, the Upper Attawapiskat Formation limestone is typically much lower in minerals that host high concentrations of Group 1, Ba, or alkali metals

(Norris 1993), especially compared to the mineral composition of kimberlites (Mitchell 1986). Plots of kimberlite and limestone groundwaters from this study, together with groundwaters from Kirkland Lake kimberlites (Sader *et al.* 2007a) (Fig. 12) highlight the differences in pathfinder metal concentrations between kimberlite and limestone sources. The elevated pathfinder metals observed in Attawapiskat and Kirkland Lake kimberlite groundwaters in slightly alkaline conditions (pH = 7–8.5) are due to the chemical weathering of olivine, pyroxene, and phlogopite in kimberlites (Sader *et al.* 2007a). Elevated Mg/Ca ratios are due to the serpentinization of olivine, which often results in an Mg-HCO<sub>3</sub><sup>-</sup> waters in ultramafic rock (Barnes & O’Neil 1969; Palandri & Reed 2004). In kimberlite waters that have circum-neutral pH (7–9) and bicarbonate alkalinity Mg/Ca ratios are typically 0.5–0.8 (Sader *et al.* 2007a) and are comparable to kimberlite waters in this study (Fig. 12).

Elevated metal concentrations at or near the kimberlite margins are most likely due to geochemical influences from kimberlite rather than TSS. Of the TSS groundwaters, concentrations of Group 1, Ba, and alkalis are 1.2 to 4 times greater (with the exception of Cs) for those waters collected over kimberlites versus those collected outside the margins. The Mg/Ca ratios in TSS groundwaters over kimberlites support a kimberlite origin as they are *c.* 4 times greater than TSS

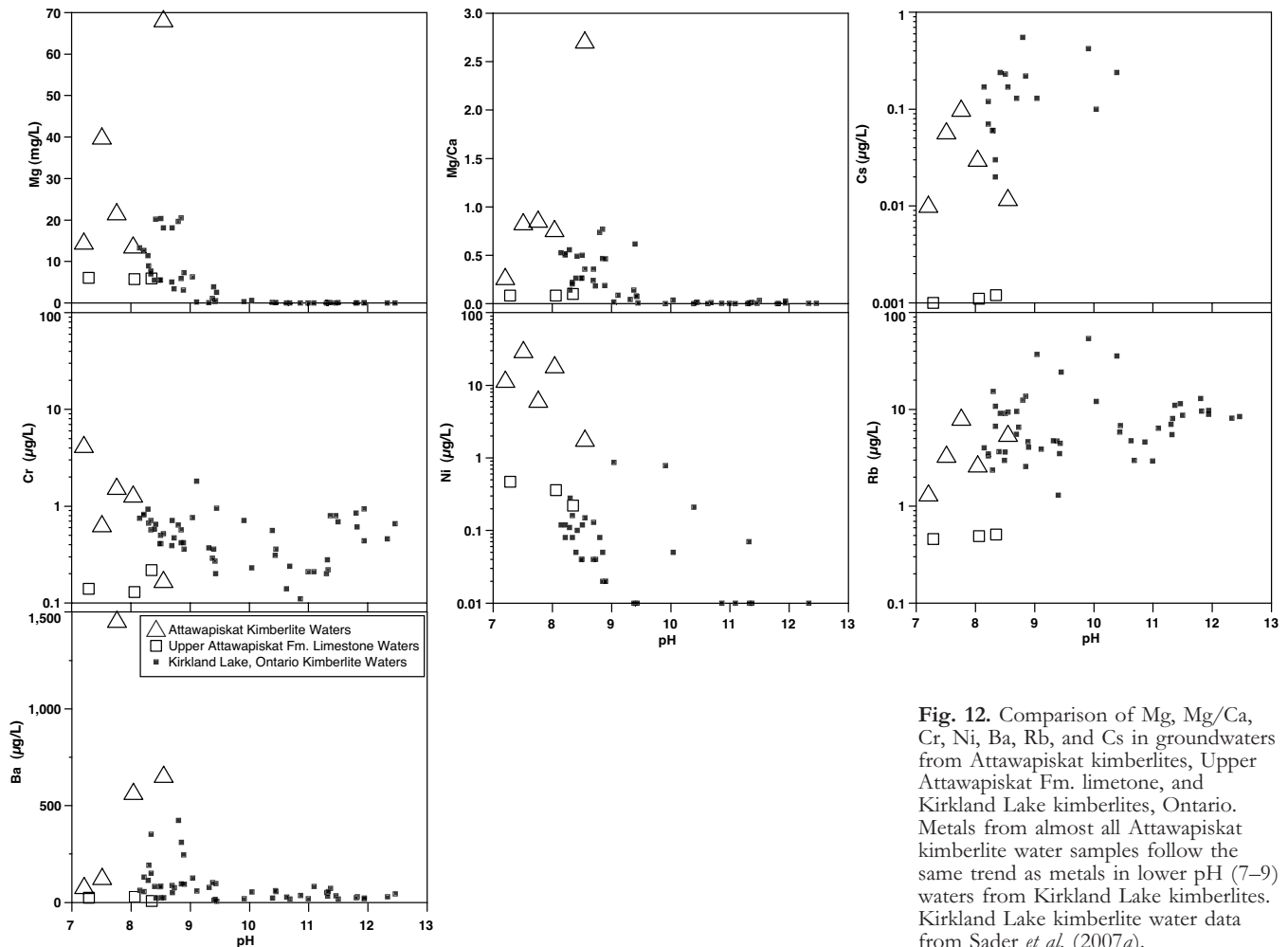


**Fig. 10.** Concentrations of Ba in peat groundwater along transects over: (a) Yankee; (b) Zulu; and (c) Golf kimberlites. Barium is typically elevated only a kimberlite margins and their profiles differ compared with other alkaline earth metals (i.e. Ca and Mg) at Zulu and Golf. Box plots represent the mean, first and third quartile values for baseline ombrotrophic peat groundwaters.



**Fig. 11.** Concentrations of Rb and Cs in peat groundwater along transects over: (a) Yankee; (b) Zulu; and (c) Golf kimberlites. Although alkalis at Golf are marginally elevated relative to baseline values at 06-G-08 the concentration was prominent relative to other sites along the transect. Box plots represent the mean, first and third quartile values for baseline ombrotrophic peat groundwaters.

groundwaters collected outside kimberlites and 10 times greater than ratios in groundwaters from limestone. Although there is a dolomite unit within the host Palaeozoic rock, it is 200 m below the Upper Attawapiskat Formation and is likely of little



**Fig. 12.** Comparison of Mg, Mg/Ca, Cr, Ni, Ba, Rb, and Cs in groundwaters from Attawapiskat kimberlites, Upper Attawapiskat Fm. limestone, and Kirkland Lake kimberlites, Ontario. Metals from almost all Attawapiskat kimberlite water samples follow the same trend as metals in lower pH (7–9) waters from Kirkland Lake kimberlites. Kirkland Lake kimberlite water data from Sader *et al.* (2007a).

influence on the shallow groundwater geochemistry in this study.

### Spatial distribution of kimberlite pathfinder metals in peat groundwaters

#### *Hydrogeological controls on vertical metal movement*

The most likely pathway for the upward migration of pathfinder metals from kimberlites is along kimberlite–limestone margins. Group 1, Ba, Mg/Ca, and alkalis are commonly found at peat groundwater sample sites that have evidence of upwelling and that are also within 200 m of kimberlite margins. Conversely, upwelling at other sites such as near bioherms (07-Y-04 at Yankee), or sites that are greater than 200 m from kimberlites did not usually indicate elevated pathfinder metals.

The location of upwelling deep groundwaters to peat near the margins of kimberlites could be due to elevated hydraulic conductivity in fractured rocks near the boundary between kimberlite and the host rock. During kimberlite emplacement in various geological settings, the margins of kimberlite pipes and adjacent host rocks are commonly fractured due to the explosive release of volatiles (Mitchell 1986; Wilson & Head 2007). These fractures likely represent preferential pathways for upward groundwater movement from kimberlite. With respect to Attawapiskat kimberlites, the highly fractured zone surrounding the Victor kimberlite forms a ring up to 150 m wide and has a hydraulic conductivity of  $5.79 \times 10^{-3}$  cm/s (Hydrologic Consultants 2004). In contrast, non-fractured host Attawapiskat Formation limestone had a moderately lower

lateral hydraulic conductivity ( $1.16 \times 10^{-3}$  cm/s), and a much lower vertical hydraulic conductivity ( $1.16 \times 10^{-5}$  cm/s), (Hydrologic Consultants 2004). Additionally, the less common occurrence of elevated pathfinder metal concentrations directly over kimberlites in this study could be explained by their lower relative hydraulic conductivities. The K values in several brecciated kimberlites such as Diavik in Canada (Kuchling *et al.* 2000), and Lethakane, The Oaks and Venetia in South Africa (Morton & Mueller 2003) are  $4 \times 10^{-5}$ ,  $1.97 \times 10^{-6}$ ,  $1.62 \times 10^{-7}$ , and  $5.8 \times 10^{-8}$  cm/s respectively.

#### *Hydrogeological controls on lateral peat groundwater movement*

Profiles of geochemical parameters (i.e. EC, pH, Eh) along transects do not have a characteristic dispersion plume pattern down-gradient, such as those observed in streams (Leybourne *et al.* 2003), or aquifers (Freeze & Cherry 1979). This suggests limited lateral movement of metals within peat groundwaters and is consistent with low hydraulic conductivity of peat within the catotelum (Ingram 1983; Chason & Siegel 1986; Fraser *et al.* 2001; Price 2003). The profiles likely indicate the presence of mixing as peat groundwaters grade from dominantly ombrotrophic to minerotrophic. The portion of water from deep sources increases relative to ombrotrophic peat groundwater at sites along transects at Zulu (07-Z-17 to 29) and Golf (06-G-08 to 15).

The combination of the hydraulic conductivity of peat and the very small water table gradient suggest that at the depth of sample collection (1.1 mbs), peat groundwater will migrate

laterally between 0.2–200 cm/year. It could also be less if the peat freezes to sample depth during winter. There is a greater potential for metals to migrate laterally at Golf, as samples were only collected at 0.4 m, and may be in a zone of higher hydraulic conductivity (i.e. the acrotelm); however, a dispersion-plume profile of geochemical parameters was not observed.

#### *Peat geochemical controls*

It is likely that geochemical processes within the peat exert considerable controls on kimberlite pathfinder metals in peat groundwaters and may explain the spatial variability between metals and/or groups of metals along transects. Although it is assumed the suite of pathfinder metals originates from buried kimberlite, their displacement relative to each other and relative to sites of upwelling suggests adsorption, binding and mineral precipitation may play a role in controlling their solubility in peat groundwaters.

Variable DOC concentrations may influence metal concentrations in ombrotrophic and minerotrophic peat groundwaters. Where DOC concentrations are elevated (low contributions from upwelling groundwaters), pathfinder metals such as Group 1 may preferentially bind to dissolved organic matter (DOM) and result in enhanced metal solubility. Metals bound to DOM are typically inhibited from adsorption or precipitation processes (Cornell & Schwertmann 2003). Conversely, where waters are strongly minerotrophic and DOC concentrations are low, Group 1 metals may be less likely to form complexes with DOM. Decreases in metal-DOM complexes typically result in greater concentrations of free ions, which could easily be scavenged from solution by adsorption or secondary mineral precipitation (Tang & Johannesson 2005; Syrovetsnik *et al.* 2008). In this study, Group 1 metals are usually lower than baseline values at sites of strong upwelling such as 07-Y-12, at Yankee, 07-Z-21 to 35 at Zulu, and 07-G-10 to 17 at Golf. At these sites, Group 1 metals may adsorb to Fe-oxyhydroxides or be incorporated into their structure. Fe contents in Attawapiskat peat along Yankee and Golf transects (Hattori & Hamilton 2008) increase with increasing upwelling groundwater contributions observed in this study.

In comparison to Group 1 metals, alkaline earth and alkalis have lower affinities to bind to dissolved organics, or to adsorb to insoluble organics (Stevenson 1994) and they have almost no affinity to adsorb onto Fe-oxyhydroxides at pH values in this study (Kinniburgh *et al.* 1976). Elevated Mg/Ca ratios are typically observed at sites of other elevated pathfinder metals in this study (Group 1, Ba, and alkali metals). Because both Mg and Ca behave similarly in peat groundwaters with respect to adsorption or binding to organic substances and because Mg/Ca is a ratio and not an absolute metal concentration, Mg/Ca ratios may be less susceptible to variable geochemical processes in peat.

#### **Contrasts between peat and peat groundwater geochemistry**

The peat groundwater hydrogeological and geochemical data suggest that metal anomalies in peat at Yankee and Golf (Hattori & Hamilton 2008) are the result of upward movement of deep groundwater from kimberlites. Peat samples of Hattori and Hamilton (2008) were collected at the same sites as peat groundwater samples of this study, but at 0.6 mbgs. Good correlations were observed between the results of ammonia acetate leach at pH 5 (AA5) of peat (Hattori & Hamilton 2008) and alkaline earth metals in peat groundwaters. As AA5

typically leaches metals weakly adsorbed and metals that co-precipitate with carbonates, Mg/Ca ratios in peat and peat groundwaters are positively correlated ( $r = 0.76$ ).

Elevated LREEs, Ni, and Rb in peat (by AA5) and peat groundwater correlated well at Yankee sites 07-Y-08 and 09. Light REEs are also high in concentration at similar locations in both peat (AA5) and peat groundwaters at the Golf kimberlite. However, the elevated LREE and Ni concentrations in peat at 07-Y-11 at Yankee and Ni at Golf are coupled with groundwater concentrations that are the same as or less than baseline values. The elevated metals in peat groundwaters are instead observed at locations where peat (AA5) concentrations are low. There are a number of possibilities as to why discrepancies between the locations of elevated LREE, Ni, and Rb concentrations in peat (AA5) and peat groundwaters exist at some sites. It is possible that they are related to the affinity of these pathfinder metals to remain in solution, or to be removed from solution via precipitation or adsorption. It is also possible that AA5 is not the optimum leach for some metals. The recovery of Ni, LREEs, and Rb in AA5 compared to total peat concentration was only 30, 4, and 17%, respectively (Hattori & Hamilton 2008), as AA5 is not favored to leach metals strongly adsorbed to insoluble humic substances or Fe-oxyhydroxides. Differences in the spatial distribution of elevated Ni, LREEs, and Rb in peat (AA5) and peat groundwaters may also be related to different sampling depths of media. Peat groundwaters were collected at 1.1 mbgs at Yankee and 0.4 mbgs at Golf. Redox conditions, metal concentrations, concentrations of dissolved organic material, and the degree of peat humification vary significantly with small changes in depth (Clymo 1983; Syrovetsnik *et al.* 2004; Beer & Blodau 2007).

## **PEAT GROUNDWATERS IN GEOCHEMICAL EXPLORATION**

### **Application to exploration**

Groundwaters from peat and other geological units are excellent media for geochemical surveys (Leybourne *et al.* 2003; Sader *et al.* 2007a; Leybourne & Cameron 2010). This study shows that kimberlite pathfinder metals in peat groundwaters are likely reliant on the presence of upwelling groundwater from kimberlites. Pathfinder metals in these groundwaters contrast with dilute ombrotrophic peat groundwaters and groundwaters that have upwelled from limestone or TSS. The limestone host rock in this study does not contain minerals that host high concentrations of kimberlite pathfinder metals. Furthermore, at locations where the kimberlite host rock is igneous or metamorphic crystalline such as the Superior, the Slave, and the Churchill cratons in Canada, kimberlite pathfinder metals are typically released to groundwater more readily from kimberlites due to the relatively rapid weathering of ultramafic minerals such as olivine and pyroxene (Sader *et al.* 2007a). Therefore, groundwaters influenced by kimberlite-water interactions are likely distinguishable from upwelling groundwaters that passed through different rock types.

Large cratonic regions in the northern hemisphere have high potential for the existence of undiscovered diamondiferous kimberlite occurrences (Janse & Sheahan 1995). As these regions commonly have vast wetlands, shallow groundwater has the potential to be utilized as a geochemical exploration tool to mitigate the greater challenges involved in implementing more established exploration methods such as geophysics. Other intrusive bodies such as syenite and mafic dykes may show geophysical features similar to kimberlites. Surficial water geochemical methods can assist by providing evidence as to



whether a geophysical anomaly is a kimberlite before the commencement of drilling.

### Survey design

This study suggests that sampling of groundwaters should be combined with a hydrogeological survey of the areas near a potential buried kimberlite body. A hydrogeological survey provides information on the flow direction of groundwaters and sites of upwelling deep waters. Installation of monitoring wells is useful to confirm upwelling and they are typically more precise at locating sites of upwelling in peat groundwaters compared with the detection of variations in geochemical parameters such as EC, Eh, and pH. For example, the 07-Z-MW-17 (Zulu) monitoring well hydrogeological data indicate upwelling; however, there are only low to moderate geochemical upwelling indicators in peat groundwaters at that site relative to sites farther east along the transect. The disadvantage of monitoring wells is that installation is physically demanding and time-consuming. As it is not feasible to install monitoring wells at each site that a piezometer is installed at to identify sites of upwelling, it is important to rely on variations in geochemical parameters in conjunction with hydrogeology to detect groundwater upwelling. One alternative to the installation of many monitoring wells would be to install piezometer nests that are only within the peat zone. Hydrogeological data from piezometers beside each other at various depths in the peat would permit the construction of flow nets and better indications of peat groundwater movement.

Peat groundwater samples should be collected at least 200 m beyond the suspected kimberlite margins where possible, as fractured host rock may extend as far as 150 m from the margin. If upwelling of deep groundwater is present, a transect may be extended longer than 200 m to gauge possible geochemical differences in peat groundwaters from different sources. Additionally, the data from samples > 200 m from the suspected kimberlite body provide local baseline values. Peat and soil sampling well beyond the margin of targets was also suggested in exploration surveys for kimberlites in wetlands (Hattori & Hamilton 2008). Depending on site conditions, it is likely that grid sampling would provide an enhanced portrait of peat groundwater geochemistry associated with a potential buried kimberlite.

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Figure A-1.

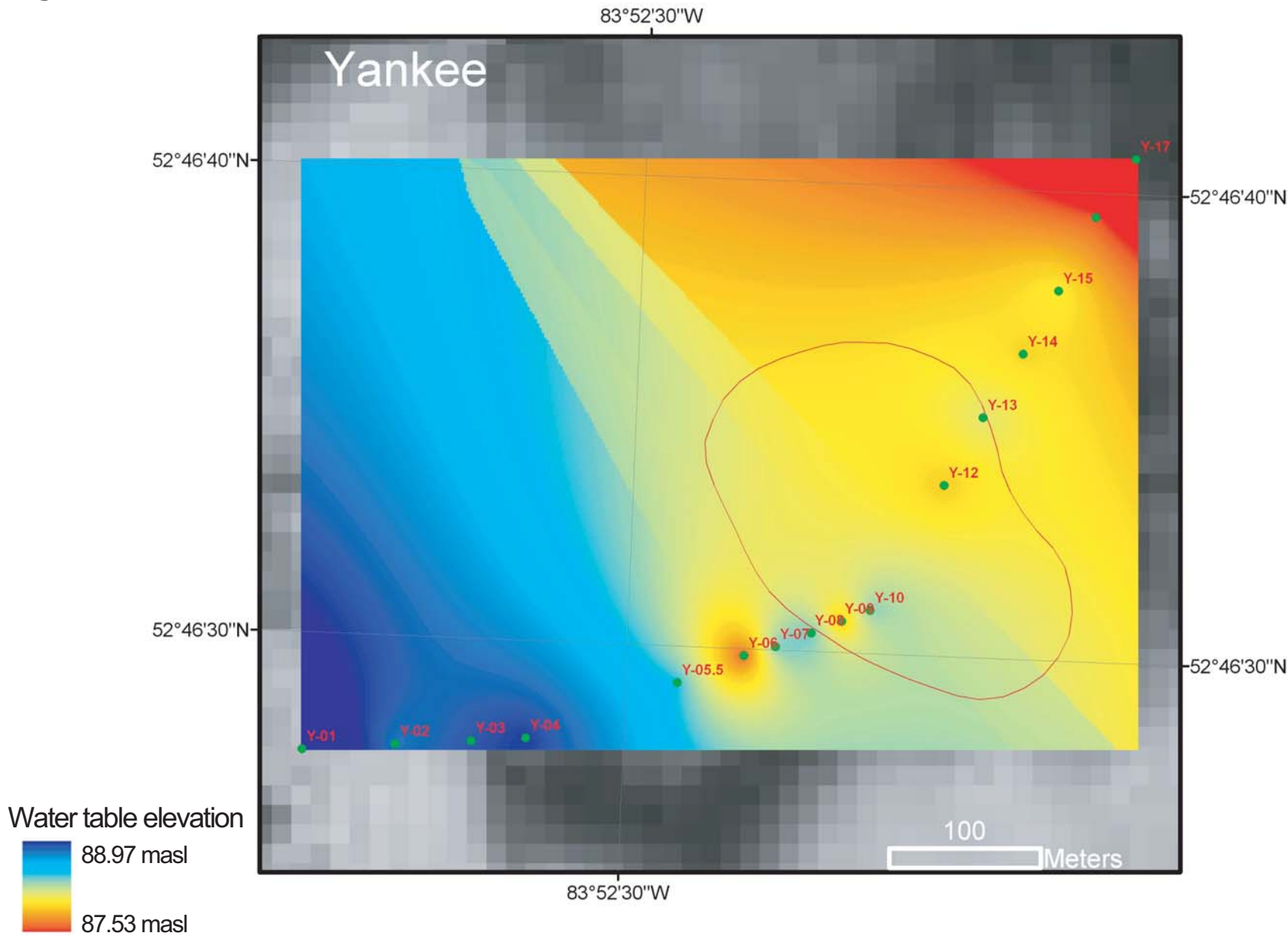


Figure A-1. Peat groundwater flow direction at Yankee based on kriging of water table data.

Figure A-2.

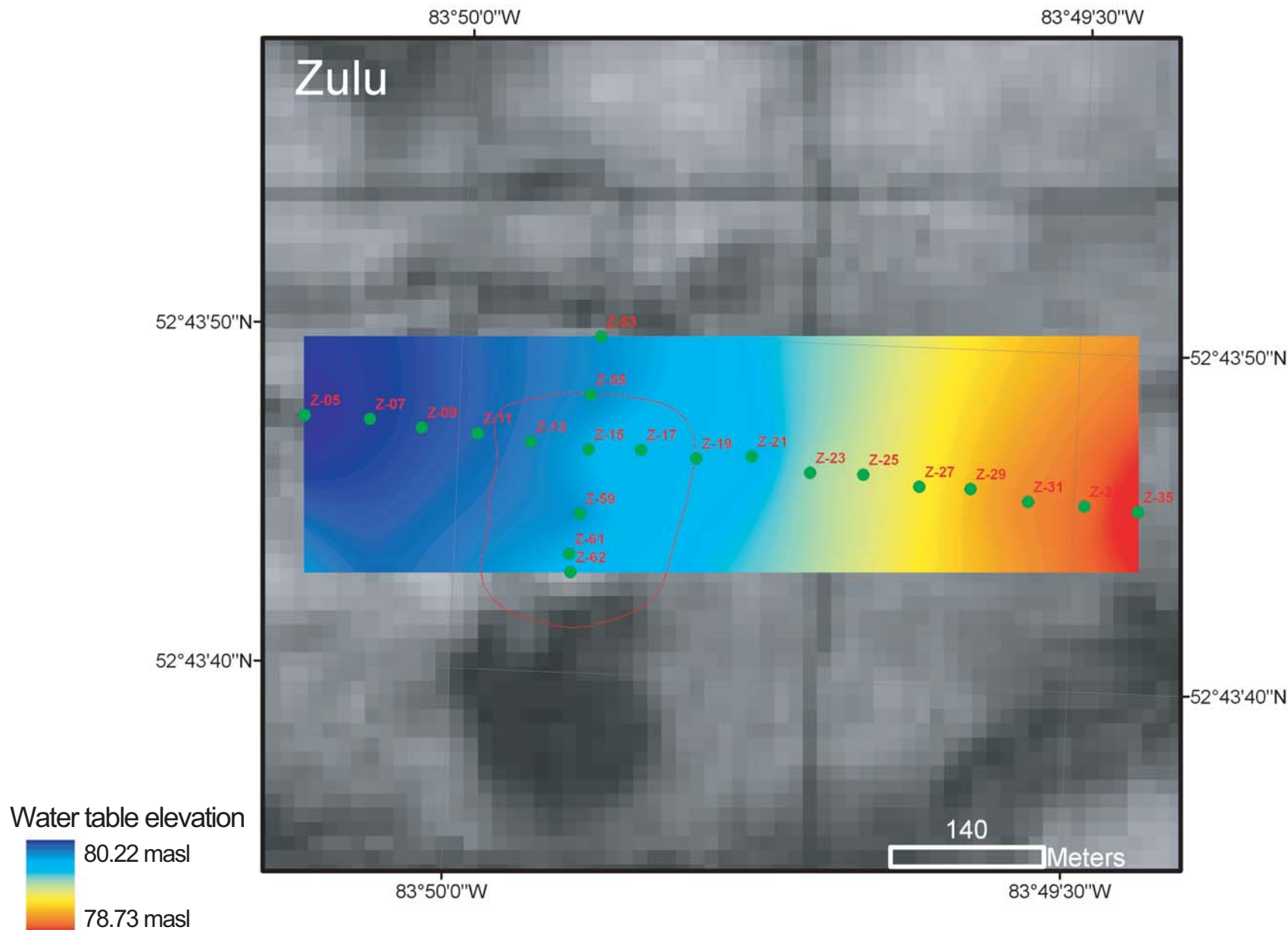


Figure A-2. Peat groundwater flow direction at Zulu based on kriging of water table data.