Geochemistry of peat over kimberlites in the Attawapiskat area, James Bay Lowlands, northern Canada

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ABSTRACT

The James Bay Lowlands, which is the SE part of the Hudson Bay Lowlands, Canada, and within the Paleozoic limestone terrane, is covered mostly by peatlands. Peat samples were examined in the Attawapiskat area, a region of discontinuous permafrost, where more than 19 kimberlite pipes have been found beneath a cover of peat (2–4 m thick) and Quaternary sediments (up to 20 m thick) of Tyrell Sea clay beds and glacial tills. Pore water at a depth of 40 cm in the peat has a consistently low pH, <4, and high Eh, ~290 mV, in the areas over limestones far from kimberlites. On the other hand, peat pore water close to kimberlites has a high pH, up to 6.7, and low Eh, down to 49 mV; the values of pH and Eh are inversely correlated. The high pH and low Eh close to kimberlites suggest active serpentinization of olivine in the underlying kimberlites. The bulk compositions of peat indicate precipitation of secondary CaCO3 and Fe–O–OH. The secondary carbonate contains high concentrations of kimberlite pathfinder elements, such as Ni, rare earth elements (REE) and Y. The ratios of metal concentrations extracted by ammonium acetate solution at pH 5 (AA5) to those in a total digestion confirm that a majority of the divalent cations are hosted by the secondary carbonate, whereas tri-, tetra- and penta-valent cations are not. As these charged cations are not leached in Enzyme Leach, they are most likely adsorbed on Fe–O–OH.

The compositions of peat show spatial variation with the distribution of kimberlites, suggesting that they are influenced by the underlying rocks even through there are thick layers of tills and sediments between the bedrocks and peat. However, elevated concentrations of pathfinder elements of kimberlites in bulk peat samples and AA5 leach are not necessarily directly above kimberlites. The diffused metal anomalies around kimberlites are attributed to the dissolution–precipitation of secondary phases (carbonates and Fe–O–OH) in acidic and reduced waters in peat, and the movement of waters through peat. This pilot study suggests that peat compositions do reflect the underlying bedrock compositions. For kimberlite exploration, a geochemical survey of peat is useful to discriminate concealed kimberlites from other anomalies defined by geophysical and other techniques; however, such a geochemical survey is not suitable for delineating the shapes of the concealed kimberlites due to broad dispersed anomalies.

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1. Introduction

Metals in ombrotrophic peat are considered by many to be contributed from atmospheric fall-out; thus, the vertical concentration profiles of metals have been used to document historical trends in metal deposition due to industrial and other anthropogenic sources (e.g., Jones and Hao, 1993; Cortizas et al., 2002; Steinnes et al., 2005). A geochemical study of peat was conducted in the Attawapiskat area of the James Bay Lowlands, in the SE part of the Hudson Bay Lowlands on the Hudson Platform, the third largest wetland in the world after the Siberian Lowlands and the...
Amazon River floodplain. The principle question in this study was whether underlying bedrocks influence the composition of the overlying peat. The area is mostly underlain by flat-lying Paleozoic limestones that cover the Archean basement (Fig. 1). At about 170 Ma, explosive kimberlite magmas intruded the limestone (Webb et al., 2004). These kimberlites hosted by limestones are covered by a total thickness of 10–30 m of Quaternary sediments, both tills and clayey beds. Kimberlites have distinct chemical compositions compared to most crustal rocks as they contain high alkalis, alkali-earth elements, light rare earth elements (REE), Y and Mg. Furthermore, the bedrocks of the study area are Paleozoic limestones that contain mostly CaCO₃ with low REE (e.g., Liu et al., 1988). This setting makes a sharp contrast in chemical compositions between kimberlites and hosting carbonates. Among the 19 known kimberlite pipes within the study area, the Victor pipe is being developed for mining but the rest have yet to be disturbed, except for a few drill holes. Therefore, the study area provides an ideal location to evaluate the geochemical signatures of bedrock kimberlites in overlying peat. This paper also discusses the possible use of peat compositions in kimberlite exploration.

2. Study area

2.1. Surface features and climate

The surface in the Attawapiskat area is covered by bogs, open water and streams. The precipitation in the area is ~650 mm/a, based on 2005 records of 637 mm/a in Moose-neee, 250 km south of the study area, and 670 mm/a at Kuujjuarapik, 450 km NE of the study area (http://www.climate.weatheroffice.ec.gc.ca/climate_normals/index_e.html). Precipitation is high during summer months, ~100 mm/month, and low in the winter. The combination of high precipitation and cold temperatures results in a low rate of evaporation that maintains the area in a waterlogged condition, and which led to the development of this extensive wetland.

The area lies within the discontinuous permafrost region (Fig. 1; Smith and Burgess, 2002). Although the surface water temperatures reach over 20 °C, the peat at a depth of 60 cm was frozen at several sites in summer months. The cover of sphagnum moss and peat appears to act as a good thermal insulator of the underlying permafrost.

2.2. General geology

The study area is within the Paleozoic Platform where vast flat-lying Paleozoic limestones averaging 250 m in thickness, locally up to 300 m, cover the area. These limestones are mostly composed of calcite (CaCO₃) with very minor Ca–Mg carbonate (Johnson et al., 1992). The limestones overlie ~3.0 Ga Archean granite-greenstone belts (Fowler et al., 2001; Fig. 1). Kimberlite magmas intruded the Archean rocks and the overlying limestones at ~170 Ma, producing pyroclastic rocks and fall-back pipes (Webb et al., 2004). Subsequent erosion removed the pyroclastic rocks and the upper parts of pipes. The remaining hyperabyssal portions of the pipes were later covered by Quaternary glaciers and glacial sediments (Fig. 2). The retreat of the Laurentide Ice Sheet allowed the incursion of sea water and the deposition of the Tyrell Sea clay sediments at 8–4.4 ka bp (Fig. 2). Isostatic rebound of the continent has resulted in exposure of the area; uplift continues to occur (e.g., von Mörs and Bégìn, 1993). The poor drainage in the slowly uplifted area and the cold temperatures promoted the formation of thick peat (2–4 m) surrounded by bogs, e.g., Glaser et al. (2004).

Most kimberlites are concealed, except for the Uniform kimberlite, part of which is exposed on the north shore of the Attawapiskat River. The exploration history including geophysical surveys leading to the discovery of kimberlite pipes in the area is described in Kong et al. (1999) and Fowler et al. (2001). The Victor kimberlite pipe has a projected surface area of 15 ha, as delineated by magnetic anomaly and confirmed by drilling. Of the 19 kimberlites found on the DeBeers property, within which the study area is located, 17 are diamondiferous (Fowler et al., 2001). Small scale open-pit mining of the Victor kimberlite pipe commenced in spring 2008.

2.3. Access to the study area

The Victor mine site is located 90 km west of Attawapiskat, Ontario. With abundant bogs and muskegs in the area, surface access to the Victor site is possible only along ice roads in winter months. The mine site has daily chartered flights from Thunder Bay and Timmins. The mine site itself is surrounded by bogs. Therefore, field work over different kimberlite pipes requires a helicopter.

2.4. Description of study sites

Peat samples were collected along traverses over the Golf, Yankee and Alpha kimberlite pipes, as well as at the Control site (background samples). The country rocks of kimberlites are all limestones. The Golf kimberlite, ~11 km from the mine site, is covered by ~9 m of overburden of tills and Tyrell Sea clay bed. It has a surface area of 4.0 ha and its longest axis is 260 m (Fig. 3a, Fig. 4a). The Yankee pipe, located ~5.2 km from the mine site, has a surface area of 3.9 ha and its longest axis is 270 m. It is covered by ~10 m of overburden, that consists of tills and Tyrell Sea clayey sediments. The northern and southern areas over the Yankee kimberlite are slightly elevated and covered by trees and shrubs, so the sampling traverse was located between the raised areas (Fig. 4b). The Alpha kimberlite, ~16 km from the mine site, has a surface area of 7.6 ha with a long axis of 350 m. It is overlain by 2–12 m of overburden. The Alpha kimberlite consists of two pipes, and the study site traversed the Alpha South pipe. All studied kimberlites are composed of a hypabyssal facies of macrocrystic kimberlites with large crystals of olivine, Cr-diopside and garnet. The kimberlite pipes display prominent positive magnetic anomalies compared to their non-
magnetic limestone host. Therefore, the outlines of pipes are well defined.

The Control site, ~6 km from the mine site, has no known occurrences of kimberlite with no magnetic anomalies. Furthermore, the area has a similar surface condition and topography as the other sites.

3. Sampling and analysis

3.1. Sample collection

Peat samples were collected along traverses over the kimberlites and into background areas so that each traverse provide samples of local background areas in limestones (Fig. 4a–d). The traverses were selected to allow collection of similar surface media over a similar topography. Among the four traverses, the Yankee site (Fig. 4b) contains shrubs and small spruce trees, <2 m in size, but the ground between trees and shrubs is covered by sphagnum moss, similar to the other sites. The Golf, Alpha and Control sites contain bogs with open water (Fig. 3a, c and d).

Peat samples were collected at a depth of ~40 cm using a hand-held Dutch auger, and placed in plastic freezer bags. The water table in the study areas was at or near the surface and all samples were saturated with water. The movement of water is not obvious in most parts, but groundwaters have slow movements towards rivers and streams. Discharge of groundwater is apparent along river banks. Field work for sample collection was carried out in July and September, 2006.

Peat samples varied from partially decomposed, fibrous light to medium brown to extensively decomposed soft homogeneous dark-brown peat. Fibrous light-brown peat commonly contains soft stems and roots of live plants. Some are spongy with wood pieces, but highly decomposed peat does not contain any distinguishable plant remains. These samples likely originated from sphagnum moss judging from the extensive sphagnum cover in the area. Sedges were rare in the study area.
3.2. Field measurements

At each station, the texture and color of peat were recorded, and a peat sample weighing at least \( \frac{1}{2} \) kg was placed into a freezer plastic bag. Grit was not found in any samples. Immediately after collection, the plastic bag with peat inside was squeezed from the outside to drain the pore water into a disposable plastic cup (30 mL) for measurements of pH, conductivity and Eh. The plastic cup was rinsed with a small fraction of sample water before the measurements. The Eh of water increases during interaction with atmospheric O\(_2\). Therefore, the Eh value was recorded once the reading stabilized within 3–5 min after immersing the probe into the waters. Both pH and Eh values are similar to those obtained from waters collected through Piezometers at similar depths and filtered through a 0.45-\(\mu\)m Whatmann GD/X sterile syringe-type filter by Brauneder (Brauneder et al., 2007).

3.3. Laboratory analysis

Peat samples were dried at temperatures below 60 °C, gently disaggregated, and sieved to minus 80 mesh (<0.19 mm). The loss on ignition (LOI) of samples was recorded at 105 °C, 350 °C, 550 °C and 900 °C, and expressed as LOI\(_{105}\), LOI\(_{350}\), LOI\(_{550}\) and LOI\(_{900}\). The values of LOI\(_{550}\) represent the content of organic matter, whereas the LOI\(_{900}\) represents the carbonate content as CO\(_2\) (Heiri et al., 2001).

The samples were subjected to total digestion in hot HF–HCl–HNO\(_3\)–HClO\(_4\), plus a partial extraction using ammonium acetate leach at pH 5 (AA5) at Acme Analytical Laboratories Ltd. in Vancouver (e.g., Cave and Harmon, 1997). In addition, samples were also processed with another partial extraction using the Enhanced Enzyme Leach (Clark, 1993) at Activation Laboratories Ltd. in Ancaster, Ontario.

4. Results

4.1. Field data

The pH values of interstitial waters in peat at the Control site range from 3.6 to 3.9. The pH values at a distance from kimberlites are similar to background values. For example, the southern parts of traverses at Golf, Yankee, and Alpha all have pH values close to 4, whereas many samples within 100 m of kimberlites have higher pH values, up to 6.7 (Fig. 5a–c).

Eh values of waters in peat at the Control site are approximately 290 mV, similar to those of background areas of traverses over kimberlites. The southern part of the traverse at Golf has Eh values near 290 mV. Low Eh val-
ues occur close to kimberlites (Fig. 5b and c). Higher pH values tend to be inversely correlated with lower Eh, particularly over Golf and Alpha (Fig. 5a and c).

4.2. Laboratory data

The total ash contents vary from 12 to 25 wt%, similar to those of typical peat samples (e.g., Chagué-Goff and Fyfe, 1997). The amounts of CO$_2$, determined from LOI$_{900}$C, vary from 0.07 to 2.5 wt%. Samples from the Alpha traverse contain overall low contents of CO$_2$, up to 0.52 wt%. These values indicate the formation of secondary carbonates in peat (Fig. 5). A good correlation between Ca and LOI$_{900}$C suggests that carbonates are mostly CaCO$_3$, and confirmed by similar contents of CaCO$_3$ calculated from LOI and Ca.

The contents of secondary carbonates are high on the margin of the Golf kimberlite (Fig. 5a), in the centre of the Yankee kimberlite (Fig. 5b), and on the northeastern part of the Alpha traverse (Fig. 5c); the latter was meant to be background, but its location is adjacent to the elongated Alpha North kimberlite (Fig. 4c). The pattern from Alpha suggests that the samples are likely affected by the broad anomaly associated with the Alpha North kimberlite.

The contents of Ca and Fe correlate directly with an increase in pH (Fig. 6), as do the contents of Mn (Fig. 7). The data suggest that CaCO$_3$, Fe–O–OH and minor Mn–O–OH occur in peat at a relatively high pH. Aluminum is a significant component of mineral soils and its contents are commonly controlled by pH (e.g., Dahlgren and Walker, 1993), but Al is not significant in these peat samples. Aluminum contents in all samples are low, below 0.2 wt% in total digestion of most samples (Fig. 7).

Kimberlites contain high alkalis, REE, refractory elements such as Mg and Ni, and high field strength elements (HFSE) (e.g., Mitchell, 1986). For example, Ce contents of Type I kimberlites, to which Attawapiskat kimberlites belong, are over 200 ppm, whereas the content of bulk continental crust is 33 ppm (Taylor and McLennan, 1985). These kimberlite pathfinder elements show an anomalous concentration in peat samples near kimberlites of this study. Rubidium contents show large concentration peaks over the Golf kimberlite (Fig. 8a), near the edge of the Yankee kimberlite (Fig. 8b) and around the Alpha kimberlite (Fig. 8c). The northeastern part of the Alpha traverse shows high Rb and K, suggesting again that the area is influenced by the Alpha North kimberlite (Fig. 8c).

Nickel is high in olivine in kimberlites and other mafic igneous rocks, but low in crustal rocks and limestone. Therefore, the contents are different between kimberlites...
and country rocks. Nickel occurs as Ni²⁺ in solution and is expected to behave similarly to other divalent cations, such as Ca²⁺ and Sr²⁺. Therefore, the concentrations were examined in AA5 digestions. The concentrations of Ni in AA5 were all below the detection limit, 0.05 ppb, at the Control site, but samples from sites over kimberlites show significant concentrations of Ni (Fig. 9a–c).

Rare earth elements (REE) and Y show anomalous concentrations near kimberlites in comparison to those at the Control site (Fig. 10a–c), but the anomalies are broad and not restricted to positions near the kimberlites.

The concentrations of HFSE, such as Nb and Ta, are very low in crustal rocks but high in kimberlites, which should make HFSE good pathfinder elements. Their contents in AA5 are all low, below the detection limit of 5 ppb. The concentrations of HFSE in the Enzyme Leach from the Yankee traverse show detectable concentrations compared to the Control site, but the values are still very low, only up to 3 ppb Nb + Ta (Fig. 11). The sums of Nb + Y at the Alpha site are all below or close to the detection limits. The concentrations of most metals in Enzyme Leach are all low. The highest concentration of total REE + Y is 8 ppb at the Yankee site.
5. Discussion

5.1. Eh and pH in water

The pH values of peat interstitial waters in the Control site and far from kimberlites are low ranging from 3.6 to 3.9. The values are similar to those for ombrotrophic sphagnum peat waters in many northern countries (e.g., Kuhry et al., 1993). For example, pH values range from 3.9 to 5.7 in peat in Ireland (Talbot and Ryan, 1988) and from 3.7 to 4.3 in southwestern Switzerland (Zaccone et al., 2008).

The pH values of peat pore waters are high near kimberlites compared to the Control site and the high pH values...
Fig. 6. The contents of Fe and Ca in the total digestion vs. pH. Solid symbols are for sites within 50 m of kimberlites.

Fig. 7. The contents of Mn and Al in the total digestion vs. pH. Solid symbols are for sites within 50 m of kimberlites.
are correlated with low Eh values (Fig. 5). This is most prominent at the Golf site (Fig. 5a). Although this inverse correlation is evident at all sites, the ranges of values in the Alpha traverse are small (Fig. 5c). Alkaline waters and low Eh are explained by the hydration of olivine in kimberlites. Waters reacting with olivine-rich rocks produce alkaline pH values because H⁺ is consumed during the hydration of olivine to form serpentine. This has been well documented in groundwater seeps in California serpentine belts (Barnes et al., 1967), and in waters from drill holes that intersected kimberlites in the Kirkland Lake area (Sader et al., 2007). Low Eh values are also explained by the alteration of olivine because serpentinization of olivine commonly produce H₂ and/or CH₄ gases (e.g., Charlou et al., 1998a,b; Sleep et al., 2004). Reduced gases form from CO₂ and H₂O that react with Fe²⁺ released from olivine dur-

Fig. 8. The contents of K (left axis) and Rb (right axis) for the (a) Golf, (b) Yankee and (c) Alpha traverses. The gray squares indicate the first and third quartile values from the Control site, with the median values as the horizontal bars.
ing its serpentinization. Therefore, waters reacting with the olivine of kimberlites become relatively alkaline and low in Eh.

Higher pH and lower Eh closer to kimberlites suggests that kimberlites are being actively weathered below the surface. This proposed interpretation is supported by bubbling CH$_4$ gas from drill holes that intersect kimberlites, with the gas igniting to form blue flames (field observation in September, 2006). Additional support for a reduced oxidation state around kimberlites is provided by abundant heterotrophic bacteria over the studied kimberlites in contrast to the concentration of aerobic bacteria (unpublished data by L. Donkervoort and G. Southam, 2008). Abundant anaerobic bacteria have been noted elsewhere near active serpentinization of olivine in ultramafic rocks (e.g., Kelly et al., 2001).

Fig. 9. The concentration of Ni in AA5 are plotted for the (a) Golf, (b) Yankee and (c) Alpha traverses. The values at the Control sites are shown beside the axes. The gray square indicates the first and third quartile values from the Control site, with the median value as the horizontal bar.
The finding of active chemical weathering is surprising, considering that the kimberlites in the study area are below the surface and water table, without contact with atmospheric O₂. However, it is documented that atmospheric O₂ is not essential for the hydration of olivine to produce serpentine and H₂ gas (e.g., Sleep et al., 2004).

Chemical weathering is sluggish at cold temperatures, especially in an environment with little liquid water. The

**Fig. 10.** The sum of (REE + Y) along the (a) Golf, (b) Yankee and (c) Alpha traverses. The values at the Control site are shown by grey squares, defined by the upper and lower quartile values. The horizontal bar represents the median value.
mean daily temperatures of the study area are below freezing point from the end of October to the beginning of April (http://www.climate.weatheroffice.ec.gc.ca/climate_normals/index_e.html). Furthermore, the area is within the discontinuous permafrost region (Fig. 1), and ice has been encountered at a depth of ~60 cm below the surface in August. It appears that much of the groundwater is frozen most of the time. This is not the first report to document the chemical weathering of rocks in a cold climate. Active weathering of sulphide minerals has been described in continuous permafrost regions (e.g., Coker et al., 1991) and even under glaciers (e.g., Grasby et al., 2003). The presence of thin films of liquid water has been documented in permafrost regions, probably because the freezing point of water is depressed by the presence of solutes (e.g., Torrance and Schellekens, 2006). Bacterial activity has also been reported at temperatures below 0 °C (e.g., Rivkina et al., 2000).

In the Alpha traverse, pH values increase and Eh values decrease towards the north. This is most likely due to the proximity to the north-trending Alpha North kimberlite. At the Yankee site, the inverse correlation between pH and Eh is apparent SW of the kimberlite, but not above the kimberlite. There are several possible causes for the displacement, such as the lateral movement of groundwater.

5.2. Metals in peat

5.2.1. Source of metals

The compositions of ombrotrophic peat have been used to evaluate historic deposition of metals from the atmosphere via rainfall (e.g., Jones and Hao, 1993; Steinnes et al., 2005). This study shows that there are geographic variations in compositions and strong spatial correlation between metal anomalies and underlying kimberlites. The data suggest that the composition of bedrocks affect the composition of peat even through there are thick layers of glacial sediments between the rocks and peat. This study shows that an evaluation of the metal sources in peat must consider the degree of contribution from bedrocks and sediments underlying the peat.

The vertical transfer of metals has been well documented from buried metal sulphide deposits to the surface through thick soil or overburden including thick clay beds in many locations (e.g., Goldberg, 1998; Cameron et al., 2004). The mechanism of vertical transport of elements is beyond the scope of this paper as it has been hotly debated (e.g., Cameron et al., 2004; Hamilton et al., 2004; Mann et al., 2005; Kelley et al., 2006). The vertical transfer of elements from kimberlites to peat in the Attawapiskat area is most likely similar to that for concealed metal sulphide deposits.

5.2.2. Hosts of metals in peats

Metals are present in a variety of forms in peat (e.g., Twardowska et al., 1999; Syrovetnik et al., 2007). Some metals are incorporated into organic matter by organo-metallic complexes, such as Cu (e.g., Sobolewski, 1996) and Pd (Hattori and Cameron, 2004). Small amounts of REE and Y may possibly be incorporated in organic matter in peat, but the amounts are probably very low, judging from the low concentrations of REE in plants that grow in REE-rich soil (e.g., Dunn and Hoffman, 1986: Xu et al., 2003) and waters (e.g., Markert and Li, 1991). Therefore, the amounts of metals in organic matter in the samples are most likely insignificant.

Metals may reside in the secondary minerals, such as carbonates and sulphides. The contents of CaCO3 are calculated using two methods; based on Ca contents in the total digestion and CO2 contents in LOI900°C. The CaCO3 contents evaluated by the two methods are similar, indicating that authigenic CaCO3 is likely to be present in peat samples, and that most Ca forms CaCO3. The presence of sulphides is discounted because of the low contents of S in all samples, below 0.1 wt%.

Rare earth elements and Y3+ have a strong affinity with CO32− and can be incorporated into the secondary carbonates (e.g., Luo and Byrne, 1998). Ammonium acetate solution dissolves carbonates and leaches other exchangeable metals (e.g., Cave and Harmon, 1997; Syrovetnik et al., 2007). A high recovery of Ca in AA5, with a median value of 92% at the Golf site (Fig. 12), confirms that Ca is indeed present as CaCO3. The recovery is calculated by the concentration of Ca in AA5 divided by its concentration in the total digestion. The recoveries of other divalent cations, Sr2+
in particular, are also high, which also confirms its residence in CaCO₃. The valence of Mn ranges from +2 to +7. The high recovery of Mn in AA5 (Fig. 12), comparable to that of Sr²⁺, suggests that significant fractions are present as Mn²⁺ in the CaCO₃.

Nickel is divalent, but Ni²⁺, unlike Ca²⁺ and Sr²⁺, has an affinity for Mn–Fe–O–OH (e.g., Peacock and Sherman, 2007). This may explain the observed low recovery of Ni in AA5 leach.

The recovery rates of REE³⁺, Y³⁺ and other charged cations are low in the AA5 leach (Fig. 12); the median values of recoveries are 3.4% for Nd and 3.3% for Y³⁺. The median value for Ce⁴⁺, 2.2%, is even lower than those for REE³⁺ and Y³⁺. The concentrations of Nb⁵⁺ and Ta⁵⁺ in AA5 are all below the detection limit, 10 ppb. Low recovery rates of these penta-valent cations in the AA5 leach suggest that they are not in carbonate. The inverse relationship between lower recovery rates and higher valences suggests that these highly charged cations are hosted by other phases.

Higher charged cations have stronger affinities with oxides than less charged cations, since the surface of Fe–O–OH is negatively charged. Therefore, the low recoveries of penta-valent and tetra-valent cations in AA5 leach compared to less charged cations (Fig. 12) suggests that the higher charged elements are likely adsorbed on Fe–O–OH in peat.

Clays and Al(OH)₃ are likely not important in the samples because of the low concentrations of Al, <0.1 wt%, in the total digestion of peat. Furthermore, the solubility of Al is relatively high at low pH, <4. For example, water can dissolve more than 0.2 mol/L of Al at pH 3 at 25 °C. Therefore, it is unlikely that Al will precipitate as Al(OH)₃ in peat.

Enzyme Leach aims to dissolve amorphous Mn oxides, thus releasing cations adsorbed onto Mn oxides (Clark, 1993). The recovery rates of Ce⁴⁺ and other charged cations in the leachate from this study are very low. The recovery of Ce⁴⁺ (Ce in Enzyme Leach)/(Ce in total digestion), varies from 0.02% to 0.11%. The maximum content of Nb in Enzyme Leach is 2.8 ppb, although the contents in total digestion vary from 0.07 to 0.5 ppm. The highest Ta content in Enzyme Leach is 0.1 ppb, the detection limit of the element, but the contents in the total digestion are up to 1 ppb. The comparison of elemental concentrations suggests that Enzyme Leach dissolves very small fractions of elements associated with the peat samples. These metals are likely with Fe oxides, as discussed for results from the AA5 leach. As the bulk concentrations of metals are low in peat, even in the areas close to kimberlites, their concentrations in Enzyme Leach are too low to be useful in defining anomalous areas.

There are several possible explanations for low concentrations of metals in the Enzyme Leach. The leach only dissolves amorphous Mn oxides, but Mn in peat is mostly present as Mn²⁺ in carbonates, as it dissolved in the AA5 extraction (Fig. 12). In addition, this leach uses an oxidizing agent, H₂O₂. Abundant organic matter in peat may have consumed H₂O₂, thus reducing the effectiveness of the leach.

5.3. Diffused and displaced metal anomalies

Surface media over concealed mineral deposits commonly show sharp anomaly patterns (e.g., Goldberg, 1998; Kelley et al., 2003). The pattern is produced by the contrast in the concentrations of pathfinder elements between the area overlying deposits and areas outside the deposits. Peat samples in this study did not show such a prominent anomaly pattern along traverses over kimberlites. The diffused patterns of metal anomalies in peat are explained by several possibilities.

In most areas, surficial geochemical anomalies are produced as exogenic metal ions adsorbed or incorporated into the secondary minerals (e.g., Cameron et al., 2004). Among the secondary minerals, Fe–O–OH species are important in controlling the behaviour of exogenic ions, since they are abundant and effective in adsorbing a variety of cations. In some areas under arid environments and carbonate terranes, secondary carbonates are equally important.

An acidic water in peat is not favourable for the precipitation of carbonates. The acidic and reduced state of peat is also not conducive for the precipitation of Fe–O–OH. The stability of Fe species (pH–Eh diagram, Fig. 13) shows that Fe–O–OH may precipitate as a result of an increase in pH, Eh (interaction with air), or Fe concentrations. The concentrations of Fe in the pore water of the peat range from 0.03 to 0.5 μg/L in most samples (Brauneder et al., 2007), and the Eh–pH conditions of the background site are close to the boundary of stability fields for aqueous Fe²⁺ and goethite (α-FeOOH) or hematite (Fe₂O₃)(Fig. 13). This suggests that Fe–O–OH may precipitate, but will re-dissolve again in the solution with a small change in pH or Eh.

The Eh and pH of waters in peat vary over a short distance, <20 cm (Hamilton et al., 2005) and show seasonal changes (e.g., Koretsky et al., 2006). Waters in peat are
commonly more acidic in the dry months of August–September than in the wet months of May–June (e.g., Braekke, 1981). This means that the secondary phases are not stable in peat and the ions adsorbed on the secondary phases are not securely fixed in peat. Instability of the secondary minerals likely contributes to the dispersion of metals since they can be remobilized during the dissolution–precipitation processes.

An additional contributing factor for dispersion of metal anomalies is the physical movement of water in peat. Although the movement of water is slow, it is apparent on the river banks where groundwaters are drained. In addition, the seasonal freezing and thawing in the area may also contribute to the dispersion of metals because metals in solution are expelled from ice as liquid water freezes.

5.4. Fractionation of pathfinder elements

The plots of pathfinder elements along traverses show a variety of behaviours at different sites along traverses over kimberlites. For example, Rb concentrations along the Golf and Alpha traverses show prominent peaks over the kimberlites (Fig. 8a and b), whereas the sums of (REE + Y) display broad anomalies near kimberlites, or peaks that are offset up to a few 100s m (Fig. 10a–c). Concentrations of Ni show anomalies in the area above the Golf kimberlites, but stronger anomalies NE of the kimberlite (Fig. 9a).

There are several possible reasons for the displacement of anomalies of different pathfinder elements. Although they are collectively called kimberlite pathfinder elements, the source minerals in kimberlites are different. The alkalis are mostly present in phlogopite mica, whereas REE and Y are present in clinopyroxene and garnet, and Ni is mostly in olivine. Depending on the degrees of weathering of kimberlites, different minerals may be hydrated and altered to release different pathfinder elements. For example, olivine is likely the first mineral to be altered during the weathering of kimberlites, releasing Ni, whereas mica is less readily weathered. Therefore, alkalis are likely released later than Ni from kimberlites. Garnet hosts heavy REE, whereas clinopyroxene contains light REE. Since garnet is more resilient to weathering than clinopyroxene, the release of heavy REE may occur late in kimberlite weathering.

Once metals are released from kimberlites, their behaviours differ in surface media. Some will be held by the secondary carbonate and others are adsorbed on Fe–Mn–O–OH. These differences result in the fractionation of kimberlite pathfinder elements as they migrate away from their weathered source.

6. Summary of peat compositions

Peat pore water overlying concealed kimberlites has an unusually high pH and low Eh due to serpentinization of olivine at depth, despite the area being in the discontinuous permafrost region. Furthermore, peat displays anomalous concentrations of kimberlite pathfinder elements, such as REE, Y and Ni. These elements migrate from kimberlites toward the surface, passing through tills and clayey sediments. Comparisons of element concentrations in the total digestion, AA5 and Enzyme Leach suggest that divalent cations are in the secondary carbonates and that highly charged cations are likely adsorbed on Fe oxides.

Although small fractions of REE (3+, 4+) and Ni2+ are in carbonates, their concentrations leached in AA5 show anomalies near kimberlites, but the anomalies can be dispersed and broad, most likely due to the precipitation–dissolution of secondary minerals and the movement of groundwater.

Metals in ombrotrophic peat have previously been assumed to be derived from the atmosphere, mainly via rainfall (e.g., Jones and Hao, 1993; Steinnes et al., 2005). This study demonstrates that the compositions of peat are influenced by the underlying rocks even through there are thick layers of tills and sediments between the bedrocks and peat. Therefore, an evaluation of the metal sources in peat must consider the degree of contribution from bedrocks and sediments underlying the peat.

7. Geochemical survey of peat during kimberlite exploration

Large areas in the northern countries, such as the West Siberian Lowlands and the Hudson Bay Lowlands, likely contain significant kimberlites, since they are underlain by thick subcontinental lithospheric mantle; however, exploration for kimberlites is hampered by the extensive cover of till and wetlands. In the northern countries, exploration for diamonds most commonly uses two techniques; a survey of indicator minerals followed by geophysical surveys (e.g., Fipke et al., 1995; McClenaghan, 2005). The dis-
distribution of indicator minerals in basal till and streams provides a vector for diamondiferous rocks, but the potential areas could be huge, more than several hundred kilometers wide, in the upstream direction of ice flow. Magnetic surveys may identify buried kimberlites, but many rocks unrelated to kimberlites yield similar signals. Furthermore, significant numbers of diamondiferous kimberlites do not show magnetic anomalies (e.g., Power and Belcourt, 2004).

Large areas in the northern countries are covered by peat, and this study demonstrates that peat geochemistry can provide useful information to discriminate areas of kimberlites from other features defined by geophysical and other techniques. Anomalies in peat do not necessarily occur directly over kimberlites. Therefore, it is essential to collect samples over a concealed target along a traverse, typically several 100 m or more in length, in similar surface media.

The recommended analysis of peat samples is a partial extraction, such as AA5, in order to leach carbonates. An oxidizing leach, such as Enzyme Leach, is not as effective as AA5 for peat samples. Among the typical pathfinder elements for kimberlites, Ni, REE, Y and alkalis are useful. Niobium and Ta are also good pathfinder elements for kimberlites, but they are not concentrated in carbonates and therefore do not appear in AA5 leach.

Geochemical anomalies in peatlands can be used to determine the presence of kimberlites, but the diffuse anomalies do not allow the shape or exact position of the underlying intrusion(s) to be determined.

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Appendix A. Supplementary material


References


