Tracing the Source of Anomalous Geochemical Patterns in Carbonate-Rich Bog Soils near the Nazko Volcanic Cone, Central British Columbia (NTS 093B/13)

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Introduction

Two wetlands, informally named the North and South bogs, near the Nazko volcanic cone in central British Columbia have CO_2 gas seepages, travertine deposits and organic soil mixed with abundant $CaCO_3$ (Figure 1). In 2013, soil, water and rock samples were collected in the bogs and in the surrounding area to identify the possible surface geochemical expression of concealed geothermal activity (Lett and Jackaman, 2014). Previous sampling by Alterra Power Corp. of seepage gas in the bogs revealed that CO_2 had negative $\delta^{13}C$ values in addition to traces of CH_4 and He, suggesting a magmatic and possibly geothermal source for the gas (Hickson, pers. comm., 2013; Vigouroux, pers. comm., 2013). However, median bog-water temperatures of 14.5°C, measured in 2013, suggested that surface upwelling of thermal water from depth is unlikely. Sampling in 2013 found that bog water is typically alkaline and has high concentrations of dissolved Ca and CO_2. Trace-element analysis of samples also measured higher dissolved Li and B in bog surface water and groundwater compared to levels in wetland streams, but concentrations of these elements are lower than those reported in springs sampled at known geothermal fields. The source of the Li and B in the Nazko bog water is unknown, but it may be in the soil and rock surrounding the bogs. Concentrations of Si and Sr in bog waters, two other potential geothermal indicators, are less than 18 ppm. Calcium carbonate mixed with organic soil and travertine deposits on the surface of the North and South bogs is likely the result of mineral precipitation when dissolved Ca in streamwater mixes with CO_2 seeping through the bog water. During the 2013 fieldwork, a vigorous CO_2 flow from the base of a small travertine cone was discovered on the edge of the North bog. A probable source for up to 44 ppb Ni and 2.4 ppb As dissolved in the water in the bottom of the travertine cone is the groundwater solution draining soil and glacial sediment surrounding the bog, rather than upwelling deeper thermal water.

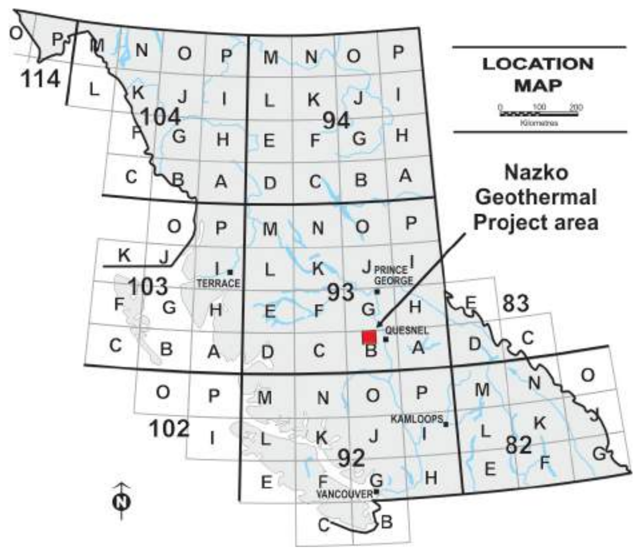

Figure 1. Location of the Nazko geothermal project area.

Boron and Li levels are less than 65 ppm in soil and show little variability along profiles extending from well-drained mineral-rich soils developed on glacial deposits surrounding the bogs to $CaCO_3$–rich organic soil. However, As, Ni, Ag, Cu and Hg increase sharply at the bog margin, where well-drained soils give way to water-saturated organic soil. The highest Hg values measured during the 2013 study are in the water-saturated organic soil near the travertine cone–CO_2 vent. Cinnabar grains have been identified in a till heavy-mineral concentrate at a TREK regional till-survey site 2 km from the vent, so the cinnabar could be a source for the high Hg found in the soil (Jackaman and Sacco, 2014). Other trace metals (e.g., Cu, Ni, Ag) weathered from the surrounding glacial sediments and transported in solution by groundwater could be concentrated in the organic soil or precipitated in the alkaline (pH >8) $CaCO_3$ deposits.

Travertine samples were found to have an average 48.34% CaO, equivalent to more than 88% calcite assuming that the travertine is mainly calcite and aragonite. The remaining 12% of the mineral content is most likely to be $MgCO_3$, Fe-

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carbonates, strontianite and trace elements. Most travertine samples have low trace-element concentrations, except for a sample from the wall of the travertine cone in the North bog that has anomalously high Fe, As, Hg and Ni.

This paper reports the results of resampling and analysis of groundwater and streamwater in the North bog to confirm results of the 2013 study. Also described here are the soil and tree-bark sampling around the travertine cone–CO_2 vent in the North bog to better establish the size of the geochemical patterns. Proposed collection of CO_2 seepage gas for ^3He:^4He isotope analysis, to identify if there is a possible magmatic source for the gas, and the analysis of water samples for stable isotopes are also mentioned in the paper.

Geology and Surface Environment

The North and South bogs lie in the Anahim volcanic belt, an east-trending cluster of Pleistocene–Holocene volcanoes, the most easterly of which is the Nazko cone. Much of the surrounding area is underlain by Eocene Ootsa Lake Group, Miocene Endako Group and Pleistocene–Holocene volcanic rocks, and by clastic sedimentary rocks of the Cretaceous Taylor Creek formation (Riddell, 2011; Talinga and Calvert, 2014). Glacial deposits covering the bedrock are till and glaciofluvial sediments.

Souther et al. (1987) estimated that Nazko volcanism began during the Fraser Glaciation. Later, in the Holocene, ejection of red pyroclastic ash, lapilli and volcanic bombs formed the cone. An ash layer, found in a bog near the cone, was interpreted by these authors to have been the result of an eruption around 7200 years BP when, in addition to the ash fall, olivine basalt lava flowed from the volcano to the south and west. Although there has been no volcanic activity since the original eruption, an earthquake swarm in 2007 near the Nazko cone (Cassidy et al., 2011) and an interpretation of seismic data by Kim et al. (2014) suggest that there is magma in the lower crust at a depth of 22–36 km.

Sedge and scattered wetland shrubs, $CaCO_3$–rich mud, stagnant pools or slow moving streams, small isolated areas of travertine, forest-dominated bog, small ponds and meandering streams are characteristic of the North and South bogs. Vegetation ranges from scattered willow and spruce stands in the wetland to a second-growth pine canopy on the surrounding upland. Luvisolic and brunisolic soils have formed on the hill slope above the wetland and gleysolic soil has formed along the poorly drained bog margin. Peat mixed with a $CaCO_3$–rich mud is the most common bog deposit. Travertine, typically a rust- to white-coloured rubble, forms small isolated mounds on the bog surface. The small (35 cm high) inverted cone–shaped travertine deposit discovered in 2013 on the northern edge of the North bog has a partially submerged vent from which there is a steady flow of CO_2 though water filling the bottom of the cone.

Fieldwork

In August 2014, fieldwork in the Nazko bogs and surrounding area included

- sampling water from the travertine cone–CO_2 vent, shallow dug pits and the stream flowing through the North bog. An Oakton PCSTestr 35 meter was used to measure the pH, temperature, salinity and conductivity of the water at each site. Water flow, water-table depth and other site features were recorded. Eight water samples were collected.
- sampling Ah (humus), B and C soil horizons and pine-tree bark at intervals along several profiles extending from the edge of the North bog into the surrounding upland. A total of 20 bark and 67 soil samples was collected. At each site, the pH of a –2 mm fraction of the mineral soil beneath the humus was measured on a slurry of soil and distilled water (1:1 vol:vol) with an Oakton PCSTestr 35 meter. The slurry pH was measured again after addition of 0.1 ml of 10% HCl.
- sampling travertine deposits in the North and South bogs (five samples).
- resampling bulk till at seven sites where TREK regional till samples had been taken in 2013 (Jackaman and Sacco, 2014). Soil profiles and tree bark were also sampled in addition to the bulk till collected for later heavy-mineral preparation.

The water, soil, bark and bulk-till sample locations are shown on Figures 2 and 3.

Sample Preparation and Analysis

Four water samples were collected in high-density polyethylene (HDPE) bottles at each site for the following analysis:

- Within 6 hours of collection, one of the water samples was analyzed using Hach portable test kits for total alkalinity and dissolved CO_2.
- A second sample was stored at 4°C for later analysis by ALS Environmental (Vancouver) for hardness; total alkalinity by titration; and Fl^-, Cl^-, Br^-, NO_3^-, NO_2^- and SO_4^{-2} by ion chromatography.
- A third sample was filtered through a Phenex™ polyethersulfone 0.45 µm membrane filter, acidified with ultrapure HNO_3 to pH 1 and later analyzed by ALS Environmental for Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mn, Mo, Na, Ni, P, Pb, Rb, Rh, Sb, Se, Si, Sn, Sr, Te, Th, Ti, Tl, U, V, Y, Zn and Zr by mass spectrometry. One blank sample of distilled–deionized water and one sample of the National Research Council Canada (NRCC) riverwater standard SLRS 3 were analyzed with the field samples.
- A fourth sample, filtered through a Phenex™ polyethersulfone 0.45 µm membrane filter and acidified with ultrapure HCl to pH 1, was stored in a glass vial for later

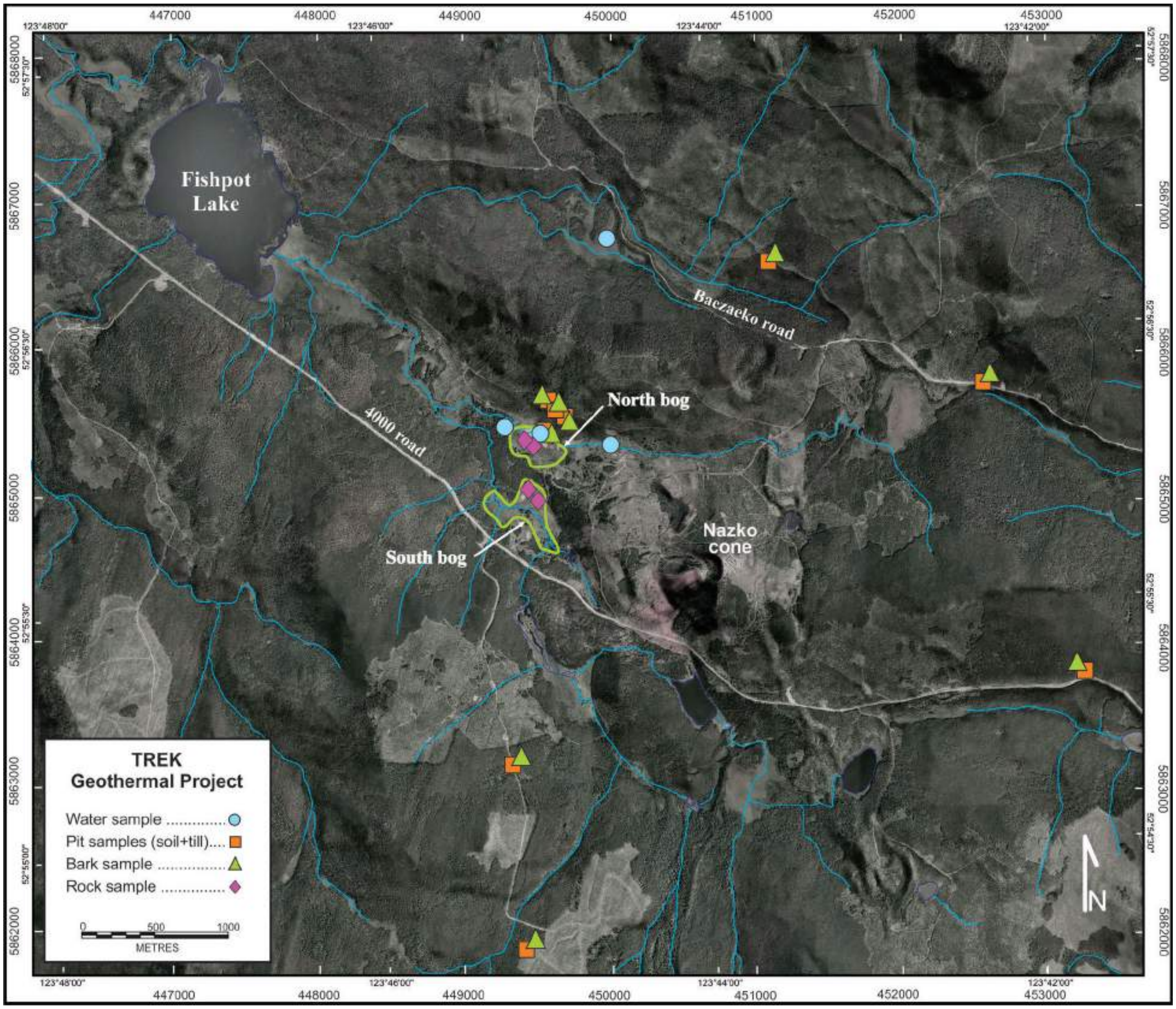

Figure 2. Soil, till, rock, water and tree-bark sample sites in the area surrounding the Nazko cone. Digital elevation model from Canadian Digital Elevation Data (CDED; GeoBase®, 2007).

analysis for dissolved Hg by ALS Environmental (Vancouver).

Soil and tree-bark samples were air dried at <30°C and sieved to –80 mesh (<0.177 mm). Travertine samples were also air dried and milled to –150 mesh (<0.050 mm). The –80 mesh fraction of the soil and the –150 mesh fraction of the travertine were analyzed at Bureau Veritas Commodities Canada Limited (Vancouver; formerly Acme Analytical Laboratories Ltd.) for the trace and minor elements Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mn, Mo, Na, Ni, P, Pb, Rb, Rh, Sb, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, Y, Zn and Zr by aqua-regia digestion and inductively coupled plasma–mass spectrometry (ICP-MS); for the major oxides (Al_2O_3, SiO_2, Fe_2O_3, CaO, MgO, MnO, P_2O_5) and minor elements Ba, Ce, Co, Cu, Nb, Ni, Sc, Sr, Y, Zn and Zr by lithium borate–ICP-MS; for loss-on-ignition at 1100°C; and for C and S by LECO combustion.

Preliminary Geochemistry Results

Table 1 lists element detection limits, reported values for the distilled–de-ionized water blank, the reported values for water standard SLRS 3 and the NRCC-reported element values for SLRS 3. No element concentrations were found to be above the instrument detection limits in the filtered water blank. Where the NRCC reported a value for an element in SLRS 3, the detected concentration is within 20% of the recommended value. Table 2 lists the pH, temperature, total alkalinity (mg $CaCO_3$), dissolved CO_2 and element concentrations measured in water samples collected from the North bog, including data for water from the bottom of the travertine cone–CO_2 vent sampled in August 2013, June 2014 and August 2014. Also listed in Table 2 are analyses of groundwater samples from pits within 3 m of the CO_2 vent and surface water from the stream flowing through the North bog.

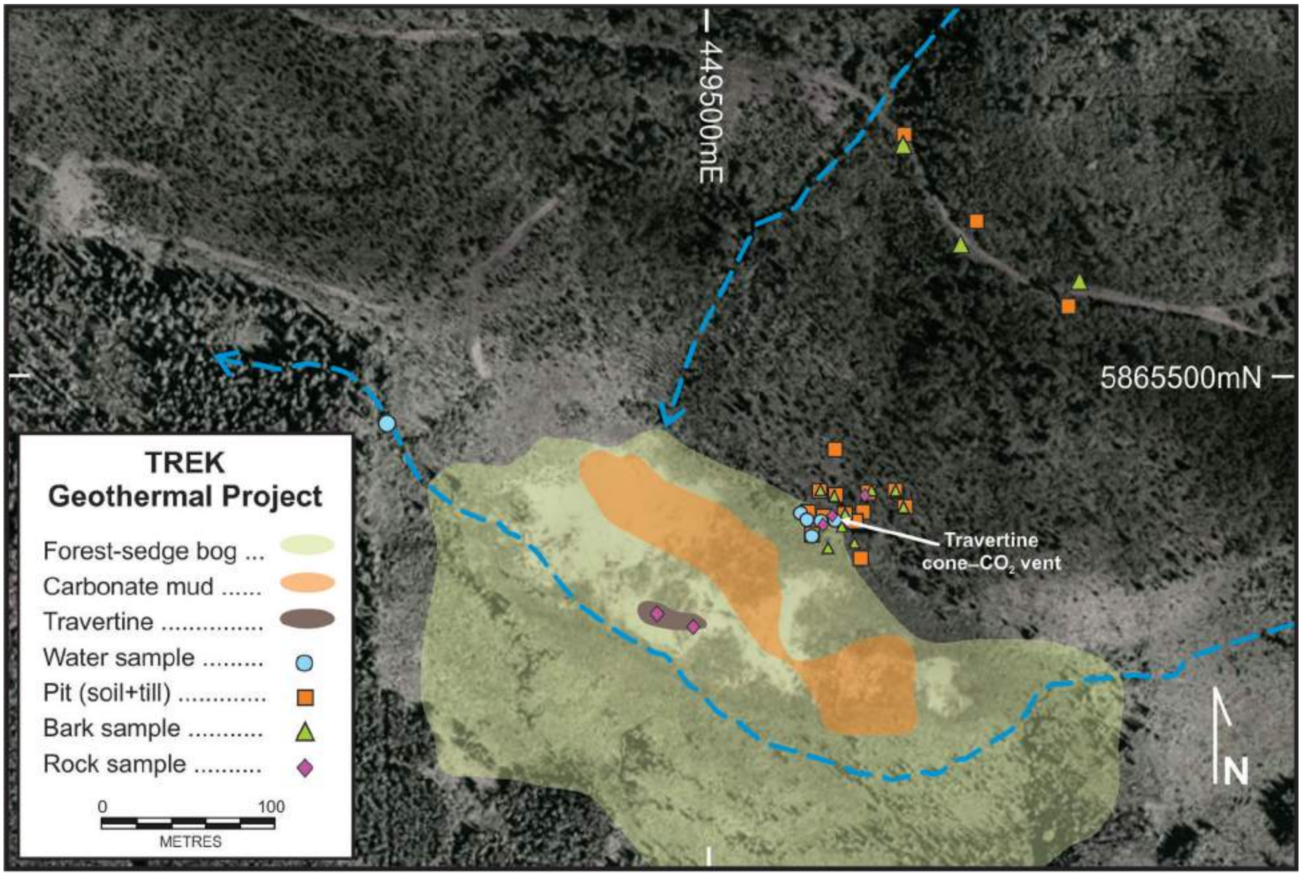

Figure 3. Soil, till, rock, water and tree-bark sample sites in the North bog. Digital elevation model from Canadian Digital Elevation Data (CDED; GeoBase®, 2007).

Table 2 reveals that temperature, pH, sulphate and most element concentrations in the water from the travertine cone–CO_2 vent sampled in August 2013 are very similar to those of water collected in June 2014 and in August 2014. There are, however, large differences in alkalinity, dissolved CO_2 and dissolved Fe concentrations measured in this water sampled on the three dates. Alkalinity and dissolved CO_2 differences may reflect a change in the CO_2 flux though the water over the vent. A large difference in the dissolved Fe could be explained by changes in the deeper groundwater circulation through different bedrock. Boron (343–369 ppb), Li (323–346 ppb), Ni (37–44 ppb) and As (1.71–2.56 ppb) are elevated in the travertine cone–CO_2 vent water compared to levels in surface water, and the concentrations are similar in samples collected on the three dates. However, B, Li, Ni, As, dissolved Fe and Ca are much lower in the groundwater from a pit that is 3 m north of the vent, suggesting a nearby source for the mineralized water. Table 2 also shows that there are differences in the chemistry of the streamwater flowing into the bog compared to that of the water draining the bog. For example, water pH increases from 7 to 8 along the stream, but As, Fe and Ca concentrations decrease. No dissolved Hg was detected in any of the water samples.

The geochemical analyses of the soil, tree-bark and travertine samples are still in progress. Soil pH was measured during sampling, and soil pH variation is shown in Figure 4 as inverse difference hydrogen ion (IDH) values, calculated by a method developed by Smee (2009). The IDH is calculated from the difference between the pH of the initial soil–distilled water slurry and that of the soil–distilled water slurry measured after addition of 1 drop of 10% HCl. Inverse difference hydrogen ion values compensate for the buffering effect on pH of high $CaCO_3$ in the soil and allow the display of a wider range of values compared to the conventional pH units. Although the IDH results for the North bog soils show no clear trends in soil pH, the integration of IDH values with the results of the geochemical analysis may reveal more significant relationships among the trace elements.

Future Work

Completion of this project will involve

- preparation and geochemical analysis of the soil, bark and travertine samples;
- analysis of the travertine samples by X-ray diffraction for amounts of calcite and aragonite;

Table 1. Analytical detection limits, results of National Research Council Canada (NRCC) riverwater standard SLRS 3, and NRCC-reported SLRS 3 'best values'.

Analyte	Detection limit	201493B2010 (SLRS 3)	NRCC SLRS 3 best values
Total alkalinity (ppm)	0.5	nd	
Br (ppm)	0.05	nd	
Cl (ppm)	0.5	nd	
F (ppm)	0.02	nd	
NO_3 (ppm)	0.005	nd	
NO_2 (ppm)	0.001	nd	
SO_4 (ppm)	0.5	nd	
Al (ppb)	1	30.6	31
Ag (ppb)	0.005	–0.005	
As (ppb)	0.05	0.97	0.72
B (ppb)	5.00	13.10	
Ba (ppb)	0.1	15.6	13.4
Be (ppb)	0.005	0.0077	0.005
Bi (ppb)	0.05	–0.05	
Ca (ppm)	0.050	6.28	6
Cd (ppb)	0.005	0.0152	0.013
Co (ppm)	0.05	–0.05	0.027
Cr (ppb)	0.5	–0.5	0.3
Cs (ppb)	0.005	0.0065	
Cu (ppb)	0.2	1.55	1.35
Fe (ppb)	30.0	104.0	100
Ga (ppb)	0.05	–0.05	
Hg (ppb)		–0.05	
K (ppm)	2	–2	0.7
Li (ppb)	0.2	0.85	
Mg (ppm)	0.1	1.69	1.6
Mn (ppb)	0.2	4.05	3.9
Mo (ppb)	0.05	0.188	0.19
Na (ppm)	2	2.6	2.3
Ni (ppb)	0.2	0.77	0.83
P (ppm)	0.3	–0.3	
Pb (ppb)	0.05	0.070	0.068
Rb (ppb)	0.02	1.72	
Re (ppb)	0.005	–0.005	
Sb (ppb)	0.01	0.17	0.12
Se (ppb)	0.2	–0.2	
Si (ppm)	0.05	1.80	
Sn (ppb)	0.2	–0.2	
Sr (ppm)	0.001	0.0325	0.028
Te (ppb)	0.010	–0.01	
Th (ppb)	0.005	0.037	
Ti (ppb)	0.2	0.68	
Tl (ppb)	0.002	0.007	
U (ppb)	0.002	0.044	0.045
V (ppb)	0.05	0.301	0.3
W (ppb)	0.01	–0.01	
Y (ppb)	0.005	0.122	
Zn (ppb)	1.00	1.70	1.04
Zr (ppb)	0.05	0.118	

- analysis of the travertine samples for $^{16}O/^{18}O$ and $^{13}C/^{12}C$ isotopes;
- preparation of heavy-mineral concentrates of the till samples and identification of indicator minerals, including cinnabar, in the concentrates;
- sampling of groundwater and surface water for stable isotopes (^{1}H, ^{2}D, ^{16}O, ^{18}O);
- analysis of soil samples for Hg using selective extractions and aqua regia–cold vapour atomic absorption spectroscopy;
- sampling of soil gas from CO_2 seepage sites and analysis for ^{3}He and ^{4}He isotopes;
- interpretation of the water, soil and sediment data; and
- final reporting, scheduled for the spring of 2015.

Summary

Geology, seismic-data analysis, travertine-deposit analysis, numerous CO_2 seepages and anecdotal evidence (e.g., snow-free wetland areas) of a thermal anomaly beneath the Nazko bogs and the results of seepage-gas analysis all suggest the existence of a geothermal resource. However, there is only tenuous evidence for geothermal activity from water and soil geochemistry, and the absence of thermal springs may reflect capping of the upwelling water by the wetland sediments. Additional field studies to detect other signs of geothermal activity will include resampling of groundwater in the bogs near a travertine cone–CO_2 seep, analysis of the water for O and C isotopes, and analysis of the seepage gas for He isotopes. High Hg levels in soil near the North bog travertine cone–CO_2 vent may reflect the presence of glacially transported cinnabar in till from a mineralized bedrock source rather than migration of Hg vapour to the surface with the escaping CO_2. A practical application of this study to support future exploration for geothermal resources is the development of baseline geochemical data for such indicator elements as B and Li in soils, vegetation, water and rock. The study also aims to improve existing methods for sampling and isotope analysis of seepage-gas samples, and techniques designed to distinguish surface geochemical patterns caused by a geothermal source from those that reflect sulphide mineralization in bedrock.

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Table 2. Analytical results for North bog travertine cone–CO_2 vent water sampled in 2013 and 2014, and groundwater from pits close to the vent and streamwater. Chloride, bromide, Cr, Ga, P, Th, Sn and Pb are not reported because values in all samples were below detection limit. Abbreviation: nd, not determined.

Sample	2013-1038	2014-1003	2014-2002	2014-2003	2014-2004	2014-2006	2014-2007
Date	6-Aug-13	23-Jun-14	24-Aug-14	24-Aug-14	26-Aug-14	26-Aug-14	26-Aug-14
UTM easting	449580	449580	449569	449881	449580	449328	450046
UTM northing	5865428	5865428	5865420	5865428	5865428	5865493	5865431
Notes	CO_2 vent water	CO_2 vent water	3 m south of CO_2 vent	3 m north of CO_2 vent	CO_2 vent water	Stream into North bog	Stream leaving North bog
Temp	5.9	5.80	14.1	11.26	5.5	14.3	11.2
pH	6.37	6.31	6.46	5.76	6.44	7.14	8.12
CO_2	600	1450	990	660	1210	80	30
Total alkalinity (ppm)	2410	4600	2670	249	2720	375	123
F (ppm)	0.45	nd	0.57	0.159	0.57	0.240	0.194
NO_3 (ppm)	–0.1	nd	–0.1	–0.005	–0.1	0.0058	0.0212
SO_4 (ppm)	18	nd	19	10.3	19	–0.5	3.98
Ag (ppb)	–0.005	–0.005	–0.005	–0.005	–0.005	0.027	–0.005
Al (ppb)	–1	–30	1.1	30.7	2.4	8.5	2.2
As (ppb)	2.56	1.79	1.17	0.21	2.51	4.73	0.66
B (ppb)	343	369	429	34	353	44	21
Ba (ppb)	187	159.0	241.0	29.2	232.0	99.9	61.5
Be (ppb)	0.044	0.054	–0.005	0.025	0.059	0.006	–0.005
Ca (ppm)	235	207	231	47.1	231	65.1	25.2
Cd (ppb)	0.0376	0.044	0.007	0.219	0.025	–0.005	–0.005
Co (ppb)	2.24	1.95	5.16	1.03	2.07	2.51	–0.05
Cs (ppb)	1.73	1.73	2 58	0 01	2 18	0.08	0 01
Cu (ppb)	–0.2	0.50	0.47	2.79	–0.2	–0.2	0.23
Fe (ppb)	3920	1330	1750	–30	5240	6390	–30
Hg (ppb)	nd	nd	–0.05	–0.05	–0.05	–0.05	–0.05
K (ppm)	31.5	30	31.8	3.9	32.1	4.2	3.0
Li (ppb)	323	378	450	9	436	26	2
Mg (ppm)	239	267	306	26.3	295	42.6	11.9
Mn (ppb)	193	142	471	60	194	1400	1
Mo (ppb)	0.459	0.38	0.0990	0.6310	0.4210	1.7500	1.2600
Na (ppm)	307	275	303	8.0	304	18.9	7.2
Ni (ppb)	44	36.5	37.3000	12.0000	40.8000	2.6200	0.2600
Rb (ppb)	39.3	37.1	42.7000	3.9300	39.1000	4.3700	2.0800
Re (ppb)	0.0064	0.007	–0.005	0.0152	–0.005	–0.005	0.0308
Sb (ppb)	0.039	0.05	0.0280	0.4900	0.0320	0.0420	0.0640
Se (ppb)	–0.2	–0.2	–0.2	0.5500	–0.2	0.7200	3.2200
Si (ppm)	9.63	9.3	9.26	21.3	8.54	21.6	14.0
Sr (ppm)	7.68	7.16	8.05	0.278	9.37	1.05	0.149
Te (ppb)	–0.01	–0.01	0.014	–0.01	0.013	–0.01	–0.01
Ti (ppb)	0.23	0.3	2.3200	1.3700	0.3700	0.5400	–0.2
Tl (ppb)	0.323	0.36	0.3180	0.5940	0.3400	0.0028	–0.002
U (ppb)	0.12	0.125	0.2200	0.2550	0.1590	0.1240	0.1500
V (ppb)	1.08	0.81	0.1190	0.3740	1.5600	1.4500	1.6900
Y (ppb)	0.358	0.185	0.0167	0.8390	0.4780	0.0514	0.0103
Zn (ppb)	10.5	12	5	10	11	–1	–1
Zr (ppb)	1.73	0.38	0.9600	0.5150	1.7300	0.2270	–0.05

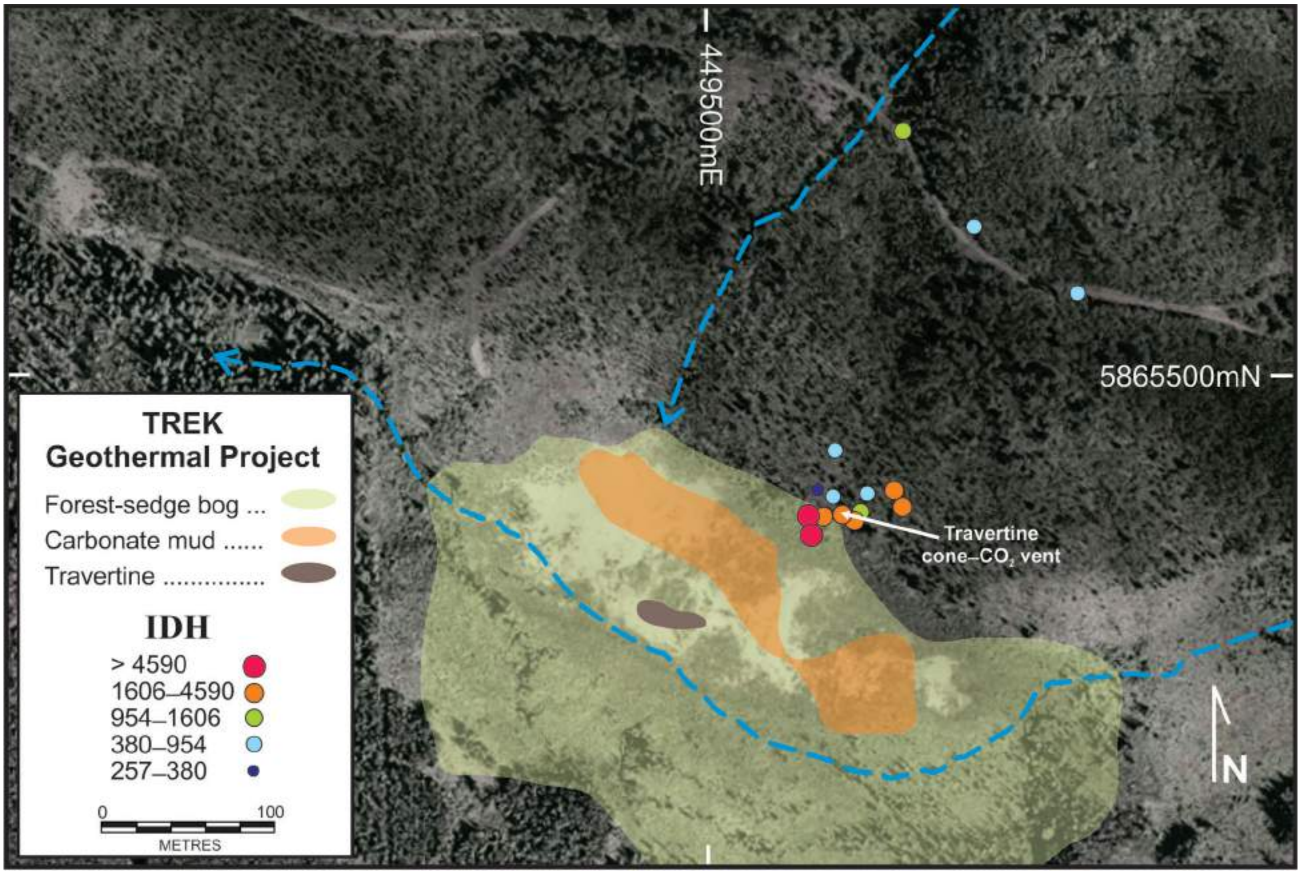

Figure 4. Inverse difference hydrogen ion (IDH) values for soil samples taken around the North bog. Digital elevation model from Canadian Digital Elevation Data (CDED; GeoBase®, 2007).

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