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Evidence of geothermal activity near the Nazko volcanic cone, British Columbia, Canada, from ground and surface water chemistry

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Introduction

Water-rock and water-mineral interactions, aquifer geology, solution residence times, environmental factors and reaction rates are all factors that affect ground and surface water geochemistry. In areas where there is evidence of geothermal activity, variations of surface and ground water chemistry can also reflect accelerated rock weathering, changes in mineral solubility with increasing temperature and the mixing of hot and cold ground water. For example, Pasvanoğlu (2013) interpreted high dissolved CO_2, Si, Li, As, Hg and B concentrations in the thermal waters from wells in Eastern Turkey to be the result of reactions between hot water and silica-rich volcanic rocks and by mixing of hot and cold solutions during the ascent of water through rock fractures to the surface. Hence, the solubility of alteration minerals in surface and ground water may be a guide to water temperature.

Here we describe evidence of geothermal activity from a study of the water chemistry in two wetlands, informally named the North and South Bogs, near the Nazko volcanic cone, British Columbia, Canada (Fig. 1). The bog water chemical data are interpreted by their comparison to other geothermal areas, from a thermodynamic simulation with the PHREEQC software (Parkhurst & Appelo 2013) and from the results of stable isotope (δD, $\delta^{18}O$, $\delta^{13}C$) analysis of bog water.

There has been past interest in the geothermal potential of the area because of the presence of scattered travertine deposits on the wetland surface, calcium carbonate-rich organic bog soil and many carbon CO_2-rich gas seepages. Although the Nazko cone last erupted in 7200 ka BP (Souther *et al.* 1987) there is geophysical evidence of more recent seismic activity. An earthquake swarm 20 km west the Nazko cone in 2007 (Cassidy *et al.* 2011) and an interpretation of seismic data by Kim *et al.* (2014) suggested that magma, a potential geothermal heat source, has accumulated in the lower crust beneath the cone. While there is an anecdotal report that the wetlands are snow-free in winter, indicating near-surface heat, the highest bog water temperature measured by the authors is 23° C.

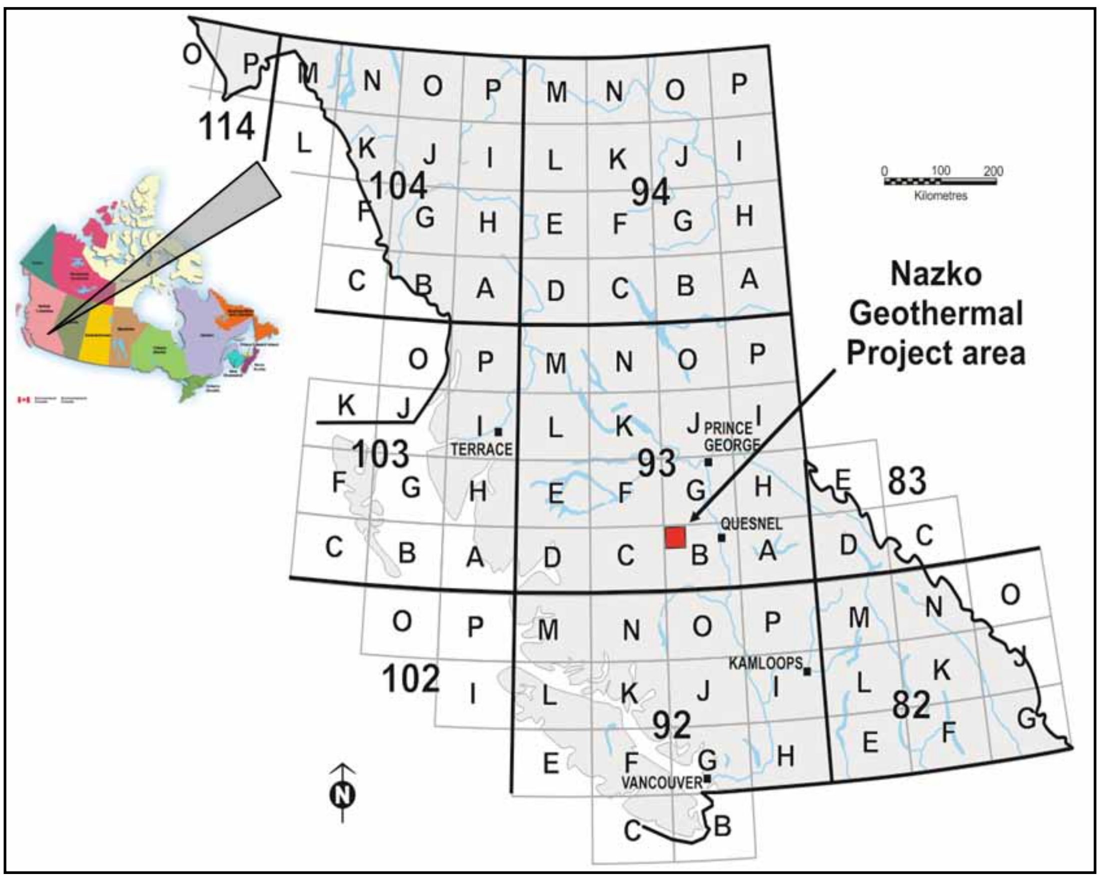

Figure 1. Geothermal project area location in western Canada.

Background to the study

Located on the glaciated Fraser Plateau 95 km west of Quesnel, British Columbia, Canada, the Nazko cone is the youngest and most easterly of several Pleistocene-Holocene volcanoes that

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together form the east-trending Anahim volcanic belt in Central British Columbia (Kuehn *et al.* 2015). The youngest rocks are the Miocene to Holocene Anahim Volcanics that form the Nazko cone. Souther *et al.* (1987) proposed that the Nazko cone formed from pyroclastic ash, lapilli and volcanic bombs ejected periodically after the Fraser Glaciation (9,000 ka BP). An ash layer deposited between 7100 and 7200 ka BP is the most recent evidence of local volcanic activity and the ash covers much of the area around the cone including the North and South bogs. Older volcanic and sedimentary rocks in the area include the Miocene to Pliocene Chilcotin Group, the Eocene Ootsa Lake Group and the Cretaceous Skeena Group. Recent geological mapping and an interpretation of airborne geophysical survey data by Angen *et al.* (2015) identified several new faults crossing the area (Fig. 2). Bedrock is largely concealed beneath Pleistocene deposits including till and glaciofluvial sediments, and there are several eskers and outwash features on the north side of the Nazko cone.

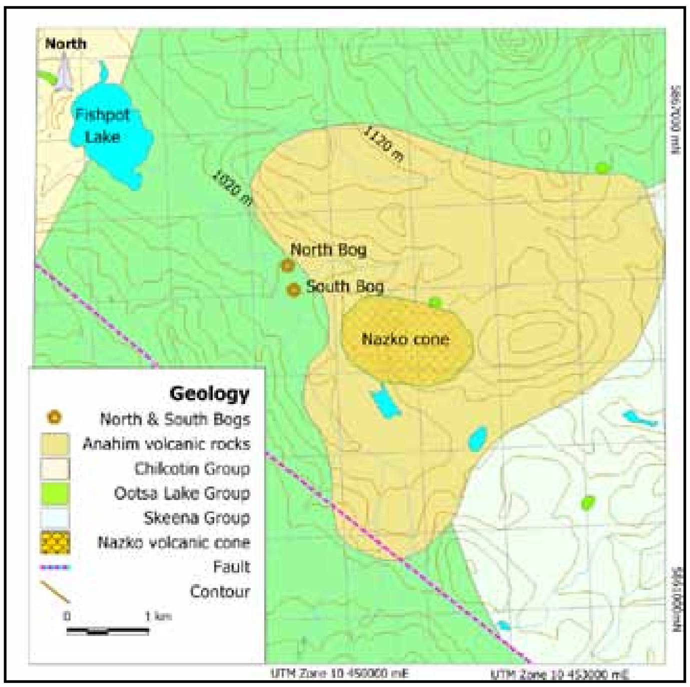

Figure 2. Bedrock geology of the area around the Nazko volcanic cone (modified from Angen *et al.* 2015).

Features typical of the North and South Bog are sedge and scattered wetland shrubs intersected by areas of calcium carbonate-rich mud, stagnant pools or slow moving streams, small, isolated areas of travertine, forest dominated bog, small ponds and meandering streams (Fig. 3). Vegetation ranges from scattered willow and spruce stands in the wetland to a second-growth lodge pole pine *(Pinus contorta)* canopy on the surrounding upland. Luvisolic and brunisolic soils have developed on glacial deposits that cover bedrock on the hill slopes surrounding the bogs, whereas gleyoslic and organic soil form along the poorly drained bog margin. The wetlands contain more than 3 m of peat mixed with a calcium carbonate-rich mud. Travertine, typically a rusty to white coloured rubble, forms small, isolated mounds on the

Figure 3. South view across part of the South Bog towards the Nazko volcanic cone. The white coloured surface area is carbonate mud and travertine deposits. Carbon dioxide seeps through surface water pools in this area are common.

bog surface. A small, 35 cm high cone-shaped travertine deposit on the northern edge of the North bog has a partially water-filled vent from through which there is a steady flow of CO_2-rich gas (Fig. 4).

Figure 4. Water filled travertine cone in the North Bog with associated CO_2-rich gas seepage.

Methodology

Sampling

During field visits between 2013 and 2015, 19 ground and 27 surface water samples were collected by Lett & Jackaman (2015) in the North and South Bogs from pits, pools and streams (Fig. 5). At each site the following water samples were collected: (1) filtered (0.45 µ) and acidified (HNO_3) for trace metal analysis, (2) unfiltered for laborato-

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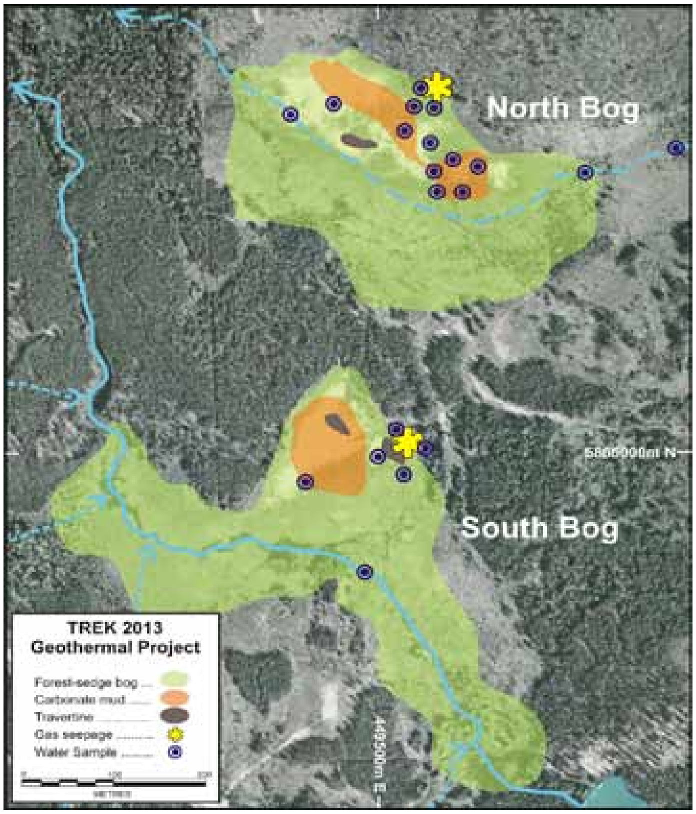

Figure 5. Location of water samples and CO_2-rich gas seepages in the North and South Bogs.

ry anion and alkalinity analysis, (3) for field determined dissolved CO_2 and alkalinity, and (at selected sites) (4) filtered, acidified (HCl) sample for dissolved Hg analysis. Water pH, conductivity, total dissolved solids and salinity were measured with an Oakton Model PCSTestr 35 meter and site characteristics recorded. Deionized water was also filtered and acidified in the field to detect contamination during sample processing. Five of the water samples collected were analysed for δD, $\delta^{18}O$ and $\delta^{13}C$.

Sample Analysis

All of the water samples were analysed by ALS Environmental, Vancouver. Filtered, acidified water samples, water blanks and the NRCC (National Research Council Canada) standard SLRS 3 were analysed for Ag, Al, As, Ag, Ba, Be, Bi, B, Cd, Ca, Cs, Cr, Co, Cu, Ga, Fe, Pb, Li, Mn, Mo, Ni, Na, P, K, Re, Rb, Sb, Se, Si Sr, Sn, Te, Tl, Ti, U, V, Y, Zn and Zr by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Unfiltered water samples were also analysed for hardness, total alkalinity by titration and for F^-, Cl^-, Br^-, NO_3^{2-}, NO_2^- and SO_4^{2-} by ion chromatography. Selected water samples were analysed for dissolved Hg by cold vapour-ICP-MS. Instrument detection limits for trace elements (e.g. Cu, Li, Zn) ranged from 0.05 to 1 parts per billion (ppb) and for minor elements (e.g. Ca, Mg, Na, K, Br^-) from 1 to 0.5 parts per million (ppm). Only traces of Ca, Li and Sr (less than twice the detection limit) were detected in water blank samples. Five of the water samples from the North Bog were analysed at the University of

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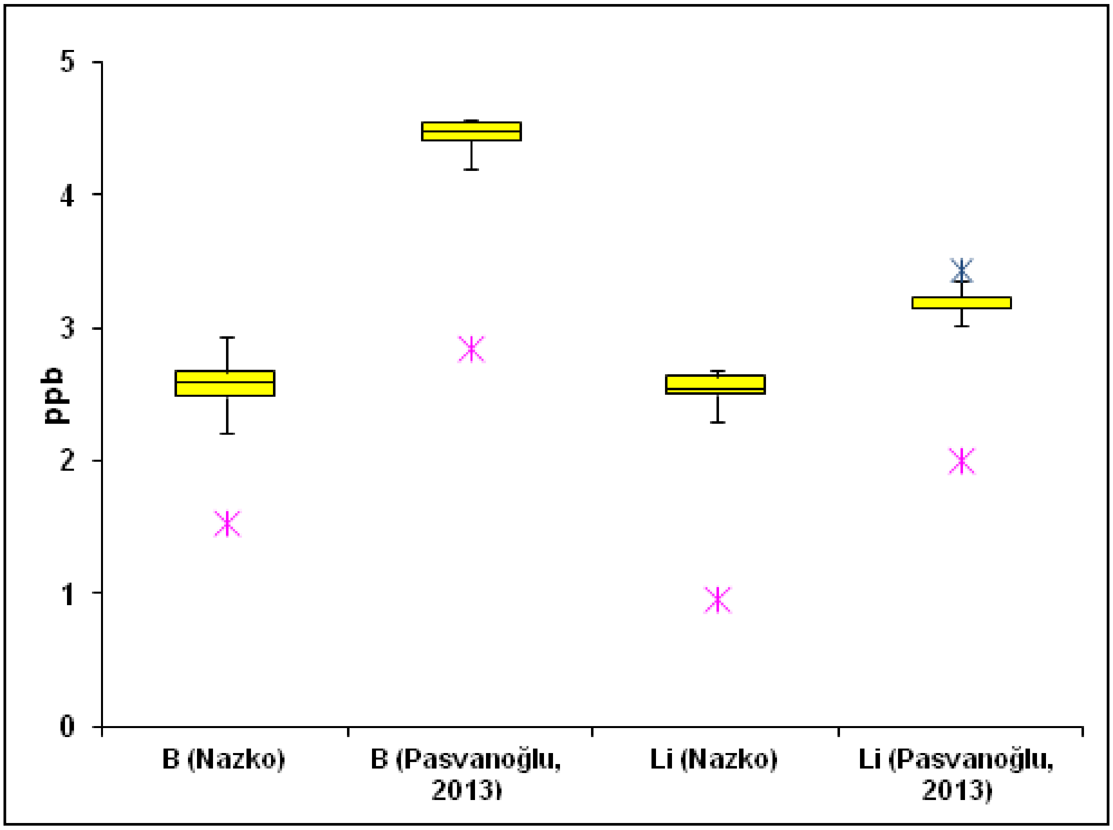

Figure 6. Lithium and B contents in Nazko (N) ground water and thermal well water (P) sampled by Pasvanoğlu (2013). Units in parts per billion (ppb).

Calgary for $\delta^{18}O$ by CF-GasBench-IRMS (Continuous Flow – Isotope Ratio Mass Spectrometry), δD by TCEA-CF-IRMS (Thermal Conversion Continuous Flow – Isotope Ratio Mass Spectrometry) and $\delta^{13}C$ and dissolved inorganic carbon (DIC) by CF-GasBench-IRMS. The Department of Earth Ocean Atmospheric Sciences, University of British Columbia, analysed the travertine samples for modal mineralogy by X-ray diffraction.

Results

Water chemistry

Lithium, B, As, Rb, Sr and Hg, are among known geochemical pathfinders for geothermal activity and may reach several hundred parts per million (ppm) in hot springs (Pasvanoğlu (2013). For example, the thermal bore holes and springs in Eastern Turkey sampled by Pasvanoğlu (2013) have water temperatures reaching 78°C and water that has up to 762 ppm Ca, 104 ppm Mg, 138 ppm Si, 2.7 ppm Li, 37 ppm B, 2820 ppm Sr, 5070 ppb As and 0.3 ppb Hg. By contrast, the Nazko bog waters only have up to 637 ppb B (ground water; Fig.6); 547 ppb Li (surface water; Fig 6); 2.6 ppb As (ground water); 56.1 ppb Rb and 15.9 ppm Sr (surface water), 383 ppm dissolved Ca (ground water); 850 ppm dissolved CO_2 (surface water) and up to 18.7 ppm Si (Table 1).

The highest Ni (44 ppb), As (2.4 ppb) and Fe (3920 ppb) concentrations are found in the water from the small travertine cone - CO_2-rich gas vent on the edge of the North Bog. No Hg or Cl^- was detected in this water and the highest temperature measured was 5.9°C. The travertine cone - CO_2-rich vent water was sampled several times in 2013, 2014 and 2015 to monitor seasonal changes in the water geochemistry and the results indicate that water temperature, pH, and most element concentrations (except Fe) are very similar from year to year and from month to month.

Sympathetic geochemical associations in ground water may reflect a common source for the elements. Major to trace element ratios can compensate for spurious fluctuations in water chemistry such as those caused by seasonal variations. For example, the ratio of Li to Ca vs. Ca to Mg

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Table 1. Median and range for analytes in ground water (GW) and surface water (SW) samples from the North and South Bogs and surrounding area.

Analyte	Median GW	Median SW	Range GW	Range SW
pH	6.53	7.76	5.85 - 7.03	6.58 - 9.06
Temp °C	13.5	14.5	5.9 - 15.3	7.2 - 23.0
Alk. ppm	2200	140	55 - 3000	60 - 3000
TDS	2490	205	285 - 3380	2 -3080
CO_2 ppm	300	40	150 - 750	3 - 850
Al ppb	1	3	0.5 - 14.2	0.5 - 49.3
As ppb	0.25	0.49	0.05 - 2.56	0.05 - 0.85
B ppb	343	13	12 - 637	5.4 - 430
Ca ppm	218	34	43 - 383	6 - 358
Co ppb	0.134	0.07	0.05 - 6.73	0.05 - 0.44
Fe ppb	106	65	30 - 5240	30 - 1290
Li ppb	327	7.7	3 - 475	0.2 - 547
Mg ppm	239	18	23 - 393	5 - 390
Na ppm	250	10.4	6 - 412	6.2 - 311
Ni ppb	0.8	0.3	0.4 - 44.0	0.24 - 6.73
Rb ppb	39.6	4.2	2.8 - 52.4	1.4 - 56.1
Si ppm	13.7	13.4	6.89 - 18.7	6.58 - 18.5
Sr ppm	7.53	0.41	0.24 - 15	0.05 - 15.9

(Fig. 7) reveals that the ground and surface water chemistry is similar and a cluster of North Bog samples, including the travertine cone - CO_2 - rich vent water, plot on a common trend suggesting a similar source for the Li and major elements. The Li to major element ratios also display two diverging geochemical trends for the stream water and a different composition to the North Bog ground and surface water (Fig. 7). The Li to Ca versus Li to Rb plots (Fig 8) shows a similar difference between the stream and the surface-ground water chemistry.

Mineral solubility

Table 2 lists pH, temperature, bicarbonate alkalinity, SO_4 and element concentrations in the water sampled at six North Bog locations labelled on Figure 9. The sample sites are from the stream flowing into the bog, the stream leaving

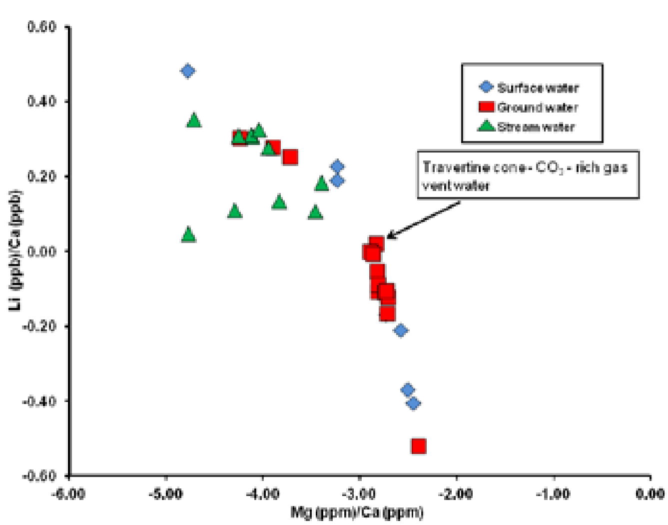

Figure 7. Lithium/Ca versus Mg/Ca in water samples collected in this study.

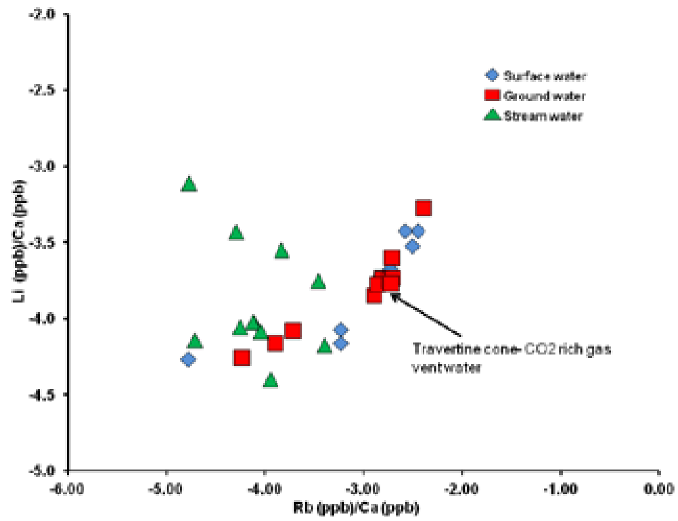

Figure 8. Lithium/Ca versus Rb/Ca in water samples collected in this study.

Table 2. Chemistry and mineral saturation indices for ground, surface pool and stream water sites in the North Bog. Ground* indicates the chemistry of the travertine cone-CO_2 vent water. HCO_3^- ppm = ppm $CaCO_3$. Temp. °C** is calculated for chalcedony equilibrium by Log SiO_2 = 4.69-(1.32/t°C +273.15) (Pasvanoğlu 2013).

Analyte	142006	132009	142002	142004	142003	142007
Type	Stream	Pool	Ground	Ground*	Ground	Stream
pH	7.14	7.8	6.5	6.37	5.76	8.12
Temp. °C	14.3	19.3	5.8	5.9	11.26	11.2
Temp. °C**	67.6	35.2	30.6	27.5	66.9	47.6
HCO_3^- ppm	375	1590	2670	2410	249	123
Al ppb	8.5	0.5	1.1	0.5	30.7	2.12
Ca ppm	65.1	90.8	231	235	47.1	25.2
Mg ppm	42.6	213	306	239	26.3	11.9
Fe ppb	6390	65	1750	3920	15	15
Ni ppb	2.62	0.34	37.3	44	12	0.26
B ppb	44	234	429	343	34	21
Li ppb	26.4	283	450	323	9	2.27
Si ppm	21.6	10.4	9.26	9.63	21.3	14
Sr ppm	1.05	3.6	8.05	9.37	0.278	0.149
SO_4 ppm	1	1	19	18	10.3	4
Aragonite	-0.27	1.02	0.42	0.04	-1.97	-0.15
Calcite	-0.12	1.17	0.57	0.18	-1.82	0.01
Chalcedony	0.24	-0.14	-0.12	-0.04	0.27	0.08
Dolomite	-0.23	2.99	1.19	0.49	-0.45	-0.17

the bog, the travertine cone - CO_2 - rich vent water, a typical bog surface pool, and ground water sampled in two pits adjacent to the travertine cone - CO_2 vent. Minerals that could be expected to precipitate or dissolve in the water and their saturation indices calculated from the water data with a PHREEQC thermodynamic simulation are listed with the chemistry in Table 2. There is an increase in the pH and in the concentrations of Ca, Mg, B, Li, Fe, Ni, HCO_3^- and SO_4^{--} from the ground water sampled upslope from the bog (sample 142003) to the travertine cone - CO_2 - rich vent water (sample 142004) and the water sampled closer to the

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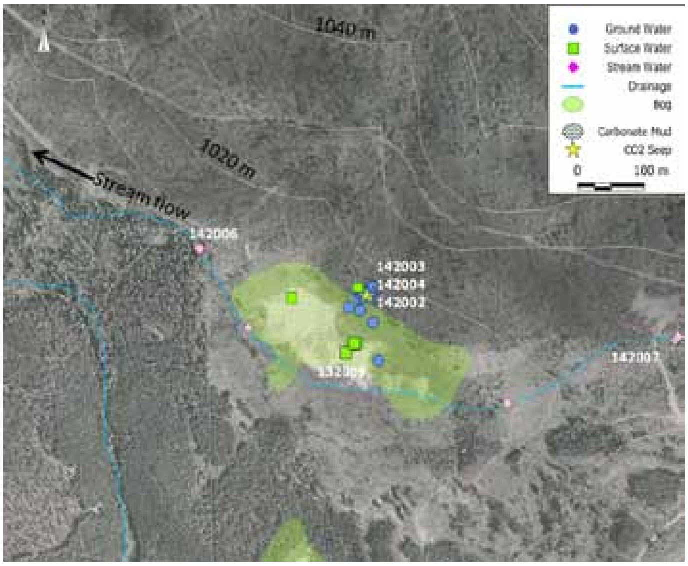

Figure 9. Location of North Bog water sample sites with geochemical data used for PHREEQC mineral solubility modelling.

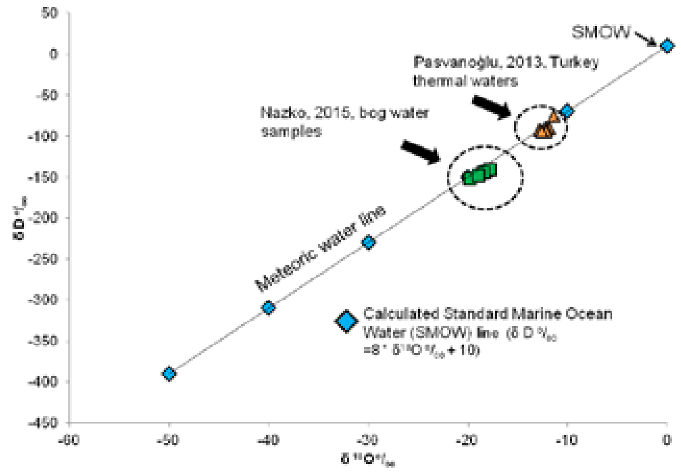

Figure 10. δD and δ^{18}O values for North Bog water samples (green square) compared to δD and δ^{18}O values for thermal waters samples reported by Pasvanoğlu (2013) (orange triangle). The sigma error for the North and South Bog water sample δD determinations is 1 and the sigma error for δ^{18}O determinations is 0.1.

bog center (samples 14002 and 13009). Stream water pH decreases whereas most element concentrations increase from the North Bog inflow (sample 142007) to the stream outflow (sample 142006).

Positive saturation indices predict that aragonite, calcite, magnesite and dolomite should precipitate from the North Bog surface and the travertine cone-CO_2-rich vent ground water, but not from the stream water and from the ground water upslope from the bog. Conversely, the saturation indices predict that chalcedony and illite should precipitate from the stream water and in the upslope ground water reflecting higher dissolved silica. Oversaturation of $Fe(OH)_3$ predicted for several water samples explains the visible iron oxide deposits around several of the seeps including the travertine cone-CO_2-rich vent.

Stable isotope chemistry

The δD vs. δ^{18}O in water from five North Bog sites and in the thermal water at five sites sampled by Pasvanoğlu (2013) are compared in Figure 10. The ratios are also compared to the meteoric water line plotted from a relationship $\delta D = 8 * \delta^{18}O + 10$ (Faure 1998). Depending on the sample latitude, δ^{18}O values of meteoric water range from - 20‰ to - 25‰ whereas isotopic values of around 0‰ for geothermal water are closer to those of sea water. Because the water samples from the Nasko North Bog have δ^{18}O values ranging from - 17.8‰ to - 19.8‰ with a mean of - 18.62‰ and a standard deviation of - 0.77‰ it is likely the water is meteoric rather than from a deeper ground water source. The DIC δ^{13}C values in the five North Bog water samples range from - 1.6 to -7.1‰ with a mean of - 4.6‰ and a standard deviation of - 2.2‰.

Discussion

Variations in the Nazko ground and surface water chemistry could reflect (1) cold water flowing into the bogs from the surrounding uplands, (2) thermal water upwelling from bedrock, and (3) mixing of hot and cold water in bedrock and overburden aquifers. The low temperature of the water in the travertine cone-CO_2 -rich vent on the edge of the North Bog compared to surface and other ground water temperatures indicates an absence of hot water. However, the net enthalpy for the formation of carbonic acid from CO_2 and water is + 1.76 kcal mol^{-1} (Faure 1998) predicting that the reaction is endothermic. Consequently, bubbling CO_2 through the water could absorb heat and lower the water temperature. Alternatively, water upwelling from depth could dissipate heat to cooler aquifer rocks along the flow path to the surface. While Li, B and Sr concentrations measured in the North Bog ground water are lower than levels reported by Pasvanoğlu (2013) they are higher than those detected in stream water. The Li, Sr, and Si may therefore be the soluble products of volcanic rock - ground water and/or overburden - ground water reactions whereas higher B could be the product of diluting a concentrated solution of this element in upwelling thermal water.

Mineral solubility predictions can help with the interpretation of water chemistry, but the results of the PHREEQC simulation need to be applied with caution because computer thermodynamic modelling can oversimplify the complexity of natural water systems (Leybourne & Cameron 2010). The abundant mineral carbonate mud and travertine in the North and South Bogs are predicted by oversaturation of calcite and aragonite carbonate. These minerals precipitate when the CO_2 seeping from beneath the bogs reacts with dissolved Ca and Mg weathered from vesicular basalt outcropping near streams flowing into the wetlands. While saturation indices suggest calcite forms in preference to aragonite, X-ray diffraction analysis of rock from the wall of the travertine cone -CO_2-rich vent reveal that the mineral is predominately aragonite (> 80 percent).

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A higher temperature and a faster carbonate precipitation rate will favour formation of aragonite rather than calcite (Faure 1998).

Thermal water temperature can be predicted from the degree of silica saturation assuming that SiO_2 is in equilibrium with the water. A PHREEQC simulation predicts that chalcedony would, ideally, precipitate from the North Bog ground water and Pasvanoğlu (2013) has proposed an equation for predicting temperature from chalcedony equilibrium. The equation is:

$$\text{Log } SiO_2 = 4.69 - (1.32/t\ ^{o}C + 273.15)$$

The SiO_2 geo-thermometer temperatures listed in Table 2 are clearly much higher than those actually measured in the water and are likely unrealistic since only trace amounts of quartz were detected in travertine samples by X-ray diffraction analysis. However, the predominance of aragonite in the travertine and the higher Si content of the water suggest that higher water temperatures may have existed in the past.

Probable sources for the North Bog ground water and the CO_2 are suggested by results of the stable isotope analyses. The North Bog $\delta^{18}O$‰ and δD‰ values fall close to the meteoric water line and are more negative than the values reported for thermal water by Pasvanoğlu (2013). Hence, the North Bog ground water is unlikely to have upwelled from a thermal source and are likely meteoric in origin. Minissale et al. (2013) interpreted the $\delta^{13}C$ values between - 7‰ to + 3‰ in central Yemen thermal well water to be the result of CO_2 from either magmatic source or from limestone dissolution. Because the North Bog $\delta^{13}C$ values range from - 1.6 to -7.1‰ the CO_2 could have been generated from a mantle magma.

Conclusions

Higher Li, B, Sr in bog waters and an existence of CO_2 seeps may be surface geochemical indicators for deeper geothermal activity although the trace element concentrations are lower than usually found in thermal springs. The North Bog water chemistry may be a product of bedrock-ground water reactions and mixing at depth of cool and warm waters. Stable isotope analyses suggest a meteoric source for the ground water and a magmatic source for the CO_2. Travertine and calcium carbonate organic mud deposits form where high concentrations of dissolved Ca and Mg in bog waters reacts with CO_2. The travertine in the Nazko bogs is predominantly aragonite suggesting that the carbonate was deposited from warm water. A SiO_2 geo-thermometer based on chalcedony solubility suggests that in the past bog water temperatures could have been higher than those at present.

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