# Water chemistry and noble gases in perennial springs at Bear Cave Mountain, Fishing Branch River, Yukon


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## Field Area

The field site is located on the Fishing Branch River at Bear Cave Mountain in Yukon, Canada (see Map 1). The site is at located at 66°25'N and 139°20'W. The closest town and weather station is at Old Crow which is s 121 km to the north-west. Old Crow which has average temperature -8.9°C and receives 265.5mm of precipitation (Calculated from Environment Canada, 2003). With the cold air temperature the area is underlain by continuous permafrost (90-100% permafrost)(The atlas of Canada: Permafrost, 2003).

**Bear Cave Mountain Sampling Sites**

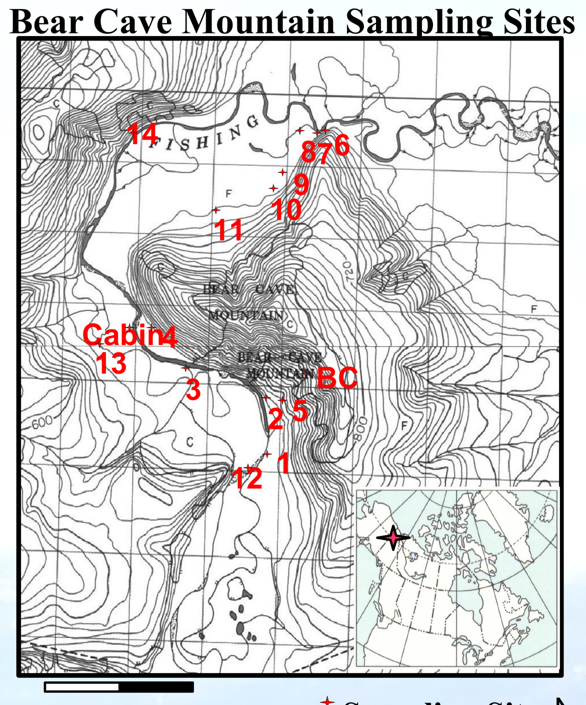



Image from Energy, Mines and Resources Topographic maps, 116J/11 and 116J/6 Yukon Territory and Canada Map from Geological Survey of Canada Map 1522A, Porcupine River, Yukon Territory

**Map 1:** Sampling Sites: Sites labeled R are on the River, S are springs and C creeks.

## Regional Geology

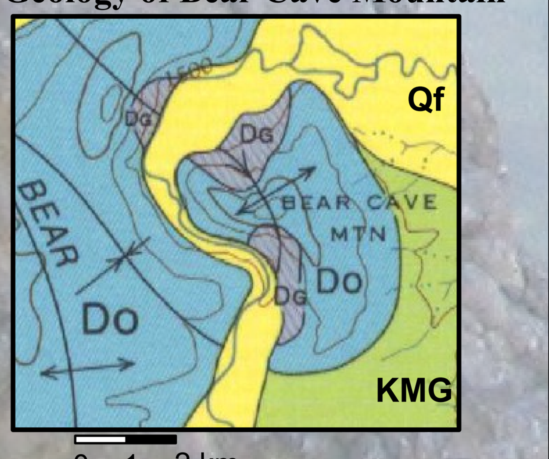
The Fishing Branch watershed is dominated by folded and faulted Cambrian and Devonian Carbonates and Cretaceous silisiclastics (Map 2) (Norris, 1978). Bear Cave Mountain is a tightly folded anticline of Devonian Carbonates. The eastern dipping limb has a shallow dip of ~20°, while the western limb nearly vertical. The Fishing Branch River valley is filled with Quaternary unconsolidated fluvial silts, sands and gravels.

## Hydrology and Water Chemistry

Perennial springs along the Fishing Branch River at Bear Cave Mountain stop the river from freezing over during the winter. There are perennial springs which discharge from the karsted limestone and there are also other springs discharging through the quaternary sediments. From site 12 to site 6 (see sampling site map) the river gains over 10 $m^3/s$ of flow.

Water samples were analyzed for dissolved ions, isotopes of $^{13}C$ from dissolved organic and inorganic carbon (see Table 1) and for isotopes of oxygen and hydrogen (Figure 1) . All waters had a pH between 7.5 and 8.5. The primary dissolved Ions are $Ca^{2+}$, $Mg^{2+}$, $Na^+$ $SO_4^{2-}$ and $HCO_3^-$. Inorganic carbon $\delta^{13}C$ ranged from -5‰ to -11‰, and organic carbon around 26‰. Samples s for $\delta^{18}O$ and $\delta^2H$. Springs at site 5 and 4 are around 1-2 °C, while springs at site 6, 7 and 8 are between 5 - 7 °C. Springs at site 6, 7 and 8 are interpreted to be from a deeper source, while springs from site 5 and 4 are likely from active layer melting. Springs from 6, 7 and 8 don't fall on the average trend line.

**Geology of Bear Cave Mountain**




**LEGEND**

Qf — **Quaternary** Fluvial silt, sand and gravel

KMG — **Lower Cretaceous** **Mount Goodenough Formation:** Shale, siltstone and sandstone

**Lower and Middle Devonian**

Do — **Ogilvie Formation:** Fine grained limestone dark grey, may include Gossage Formation

Do — **Gossage Formation:** Fine grained limestone grey or brown

**Anticline**

**Syncline**

**Map 2** Image from Geological Survey of Canada Map 1522A, Porcupine River, Yukon Territory

| Sample Labels | pH | T °C | $Ca^{2+}$ | $K^+$ | $Mg^{2+}$ | $Na^+$ | $Si^{2+}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | DIC | DOC | $\delta^{13}C_{DOC}$ | $\delta^{13}C_{DIC}$ | Log (SI) Calcite |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ppm | | | | | | | | | | ‰ VPDB | | |
| **River** | | | | | | | | | | | | | | | |
| R-12 | 8.01 | 7.0 | 42 | 0.3 | 8.5 | 2.9 | 1.3 | 1.6 | <0.5 | 10.2 | 30.0 | 4.5 | -26.9 | -10.7 | 0.12 |
| R-1 | 8.07 | 10.8 | 36 | 0.3 | 7.3 | 2.5 | 1.1 | 1.7 | <0.5 | 13.6 | 27.6 | 4.6 | -27.1 | -10.1 | 0.15 |
| R-2 Upper | 8.21 | 8.9 | 37 | 0.4 | 7.6 | 2.6 | 0.9 | 2.0 | <0.5 | 14.0 | 28.3 | 4.5 | -26.7 | -9.6 | 0.28 |
| R-2 Hole | 8.46 | 10.8 | 37 | 0.3 | 7.6 | 2.6 | 1.0 | 2.5 | <0.5 | 17.4 | 26.7 | 4.4 | -26.7 | -9.9 | 0.53 |
| R-2 Hole-2 | 8.07 | 6.9 | 41 | 0.3 | 8.3 | 3.0 | 1.2 | 2.7 | <0.5 | 16.6 | 30.2 | 4.9 | -26.7 | -10.1 | 0.17 |
| Cabin River | 8.09 | 6.7 | 47 | 0.3 | 10 | 3.6 | 1.6 | 1.4 | <0.5 | 11.7 | 34.4 | 2.7 | -26.4 | -11.0 | 0.30 |
| R-7 | 7.88 | 6.5 | 42 | 0.3 | 11 | 5.6 | 1.4 | 3.7 | <0.5 | 7.7 | 33.4 | 2.9 | -26.2 | -9.6 | 0.02 |
| R6-2 | 8.47 | 11.4 | 42 | 0.3 | 8.8 | 3.0 | 1.1 | 1.6 | <0.5 | 13.9 | 29.1 | 4.4 | -26.9 | -9.8 | 0.63 |
| R-6 | 8.14 | 7.8 | 41 | 0.3 | 9.2 | 3.9 | 1.2 | 2.7 | <0.5 | 11.3 | 31.8 | 3.4 | -26.8 | -10.1 | 0.28 |
| **Springs and Creeks** | | | | | | | | | | | | | | | |
| S-1 Lower | 7.69 | 4.1 | 44 | 0.4 | 9.9 | 4.4 | 1.5 | 4.8 | 1.32 | 12.2 | 35.6 | 3.9 | -26.4 | -11.0 | -0.20 |
| S-1 Upper | 7.71 | 4.2 | 44 | 0.4 | 9.9 | 4.4 | 1.5 | 4.0 | 1.01 | 9.4 | 35.2 | 3.8 | -26.4 | -11.0 | -0.15 |
| S-5 | 7.90 | 0.9 | 43 | 1.0 | 3.3 | 0.3 | 0.9 | <1.0 | 1.96 | 2.6 | 28.0 | 10.2 | -26.3 | -6.0 | -0.10 |
| C-3 | 7.96 | 11.0 | 47 | 0.6 | 9.4 | 3.5 | 1.5 | 2.2 | 0.82 | 12.9 | 35.4 | 3.4 | -26.5 | -11.1 | 0.24 |
| S-4 | 7.60 | 2.3 | 47 | 0.3 | 9.4 | 2.9 | 1.6 | 1.7 | 0.89 | 12.0 | 35.2 | 3.1 | -26.5 | -11.7 | -0.28 |
| S-13 | 7.78 | 4.7 | 47 | 0.3 | 10 | 4.0 | 1.7 | 3.1 | 0.78 | 21.1 | 34.8 | 2.6 | -26.3 | -10.9 | -0.06 |
| S-13-2 | 7.78 | 4.7 | 47 | 0.3 | 10 | 3.9 | 1.7 | 2.4 | 0.63 | 18.3 | 34.7 | 2.6 | -26.1 | -10.8 | -0.05 |
| C-11 | 8.14 | 3.9 | 31 | 0.1 | 2.6 | 0.2 | 0.2 | <1.0 | <0.5 | 2.1 | 22.2 | 4.2 | -26.4 | -5.7 | -0.03 |
| C-10 | 8.12 | 2.8 | 36 | 0.2 | 2.2 | 0.3 | 0.6 | <1.0 | <0.5 | 1.1 | 25.5 | 7.5 | -26.3 | -7.4 | 0.05 |
| S-9 | 7.91 | | 34 | 2.6 | 8.0 | 4.7 | 1.1 | 3.7 | <0.5 | 61.2 | 25.7 | 11.4 | -26.9 | -7.8 | -0.21 |
| S-8 | 7.89 | 6.8 | 39 | 0.3 | 10 | 5.2 | 1.4 | 3.4 | <0.5 | 6.7 | 33.2 | 3.5 | -26.3 | -9.7 | 0.01 |
| S-7 | 7.86 | 5.6 | 39 | 0.3 | 10 | 5.4 | 1.4 | 4.4 | 0.71 | 8.8 | 34.7 | 3.5 | -26.2 | -9.8 | -0.03 |
| S-6 | 7.73 | 5.7 | 39 | 2.4 | 10 | 6.5 | 1.3 | 6.7 | 0.84 | 13.0 | 32.6 | 3.0 | -26.2 | -9.7 | -0.19 |

**Table 1:** Samples organized from upstream to downstream. R denotes river samples, S for spring samples and C for creeks. Calcite saturation determined using WATEQ software (logSI > 0 = calcite over saturation)

**Bear Cave Mountain:** Photo taken looking north into hinge of anticline, red line indicates approximate bedding attitude. Approximately 1km of mountain in view.

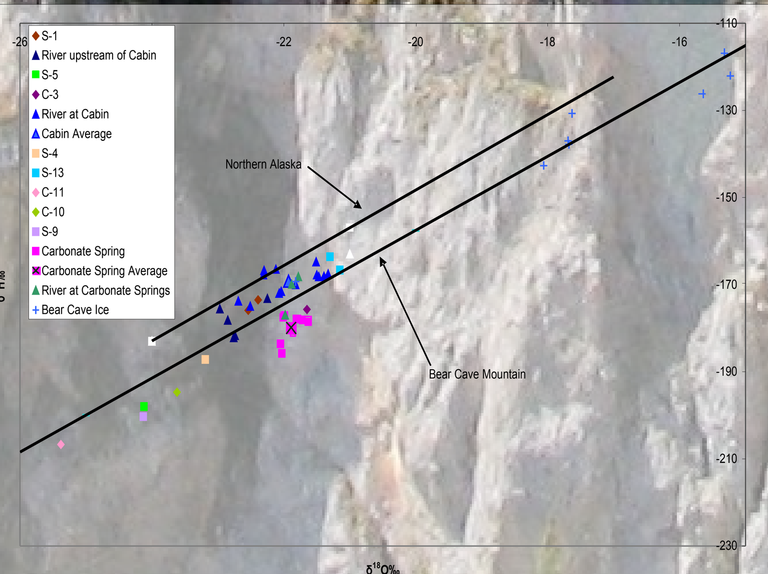



**Figure 1:** $\delta^{18}O$‰ vs. $\delta^2H$‰. Samples labeled carbonate spring are from sites S-6 through S-8, where the springs discharge out of carbonate bed rock, samples labeled Bear Cave Ice are samples of ice taken within caves on Bear Cave Mountain (see BC on map). Bear Cave Mountain line is a average trend line, Northern Alaska meteoric water line from (Cooper *et al.* 1993)

## Noble Gases

### Background

Noble gases are being used to better determine the recharge temperature and groundwater residence time. The solubility of noble gases is temperature dependent, so they can be used to determine recharge temperature. Helium can be used to determine mean groundwater residence time. Atmospheric testing of nuclear warheads released large amount of tritium into the atmosphere. Tritium decays to $^3He$, with a half life of 12.43 yrs (Clark and Fritz, 1997). Several elements may decay to $^4He$, including $^{232}Th$, $^{235}Ur$, $^{238}Ur$ and $^{40}K$ (Lippmann *et al.*, 2003). If the $(^3He/^4He_{sample})/(^3He/^4He_{air})$ ratio is greater than 1 it suggests that tritium decay is predominant, while if the ratio is less than 1 is suggests more decay of Th, U and K. If there is excess $^4He$, this suggests that the water may have a deeper flow path, where it may pass through rock rich in these elements, it may also be indicative of a longer residence time. The $Ne_{sample}/Ne_{air}$ is a indicator of excess air. Excess air refers to when the concentration of air in the samples is greater than there should be in a air equilibrated water. Excess air enters water by bubbles, and gaps in the rock.

### Sampling

Diffusion samplers were used to collect gas samples. These samplers have two copper tubes at the ends, separated by a semi permeable silicon tube (Figure 2) These samplers are installed and left for a week for them to reach equilibrium, the sampler is them clamped closed. To date analysis has only been conducted for Helium and Neon.

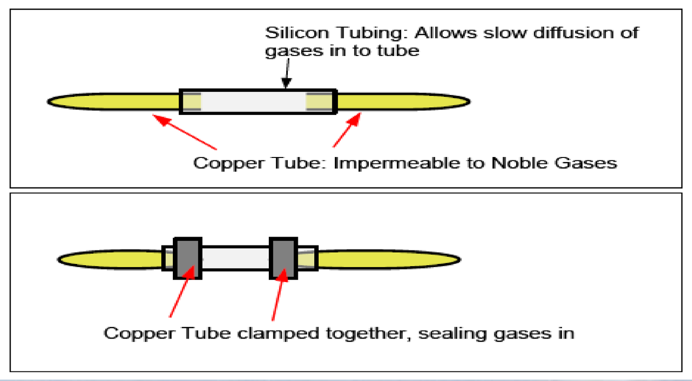



**Figure 2:** Diagram of diffusion Sampler, top shows a diffusion sampler in sampling mode. The sampler is left for a week, then clamped off, as is shown at the bottom.

| Sample | $\frac{^3He/^4He_{(sample)}}{^3He/^4He_{(air)}}$ | | $^{20}Ne/^{22}Ne$ | | $^{21}Ne/^{22}Ne$ | | Total Ne | | $Ne_{Sample}/Ne_{Air}$ | | Sample Runs |
|---|---|---|---|---|---|---|---|---|---|---|---|
| S-6-2 | 0.89 ± | 0.03 | 10.1 ± | 0.10 | 0.00135 ± | 0.00026 | 8.26E-07 ± | 8.5E-08 | 5.41 ± | 0.56 | 4 |
| S-6-1 | 0.85 ± | 0.01 | 10.4 ± | 0.01 | 0.00114 ± | 0.00004 | 7.25E-07 ± | 5.1E-08 | 4.75 ± | 0.34 | 3 |
| S-7 | 0.86 ± | 0.03 | 10.3 ± | 0.03 | 0.00122 ± | 0.00003 | 5.78E-07 ± | 9.2E-08 | 3.79 ± | 0.61 | 4 |
| S-1 | 0.91 ± | 0.03 | 10.1 ± | 0.01 | 0.00144 ± | 0.00010 | 3.02E-07 ± | 6.1E-08 | 1.98 ± | 0.40 | 3 |
| R-2 | 1.39 ± | | 9.5 ± | | 0.00215 ± | | 8.21E-09 ± | | 0.05 ± | | 1 |
| S-4 | 1.17 ± | 0.03 | 10.3 ± | 0.06 | 0.00104 ± | 0.00009 | 6.99E-07 ± | 1.9E-07 | 4.58 ± | 1.23 | 4 |
| S-13 | 1.20 ± | 0.10 | 10.3 ± | 0.04 | 0.00113 ± | 0.00016 | 5.81E-07 ± | 2.9E-07 | 3.81 ± | 1.89 | 2 |

**Table 2:** Preliminary Helium and Neon results. Error estimate is 95% confidence interval. No error calculate for R-2 as only 1 analyses could be conducted of this sample.

### Results

Table 3 shows the results from samples which have been analyzed to date. In the gas samples from S-6, S-7 and S-1 the ratio of $(^3He/^4He_{sample})/(^3He/^4He_{air})$ is less than 1. This suggests that the flow path may be deeper, or that there is a high amount of U, T, of K in the rocks in the area. If there is little tritium in the water it suggests that the water is older than 50 yrs. The samples from sites S-4 and S-13 have more 3He than air. The flow systems associated with these spring may be shallower with more recent water. Water samples were collected for tritium analysis, however this analysis has yet to be conducted. The gas samples will also be analyzed Argon, Krypton and Xenon. These gases will be used in determining the recharge temperature of the springs. The recharge temperature will be compared with the discharge temperature. This will provide a better understanding of the spring flow dynamics.

## Conclusion and Further Work:

- Noble gas results suggest that perennial springs at Bear Cave Mountain may have a deep flow path, with water older than 50 yrs.
- River water chemistry moving towards that of S-13 as we move downstream. Water of the type discharging at S-6, S-7, S-8 may be less important.
- Measure tritium in samples where noble gases have been collected
- Analyze samples for Argon, Krypton and Xenon.

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