Maximizing Beryllium Anomalies for Successful Emerald Exploration

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Introduction

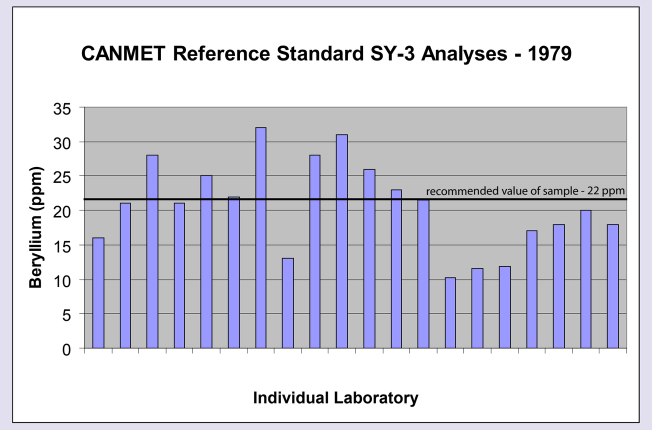
Since the discovery of emeralds in the Yukon in 1998, beryllium (the defining element in beryl - $Be_3Al_2Si_6O_{18}$) has become an element of interest for exploration geochemistry. However, gemstone exploration is in its infancy in the Yukon and the effectiveness of sampling for geochemistry and analytical techniques for beryllium is not well-established.

This study evaluates various commercially available analytical techniques for determining beryllium and assesses the effectiveness of soil sampling as an exploration tool for discovering gem beryl and emerald.

Analytical Variability

Large variability can be seen in analytical results for beryllium from different laboratories. This graph shows beryllium results from selected, high-quality laboratories for the CANMET reference standard SY-3 syenite.

This sample yielded values between 13 and 32 ppm, which indicates poor analytical accuracy. The wide range of results illustrates the difficulties in establishing a "true value" for beryllium in a given sample.

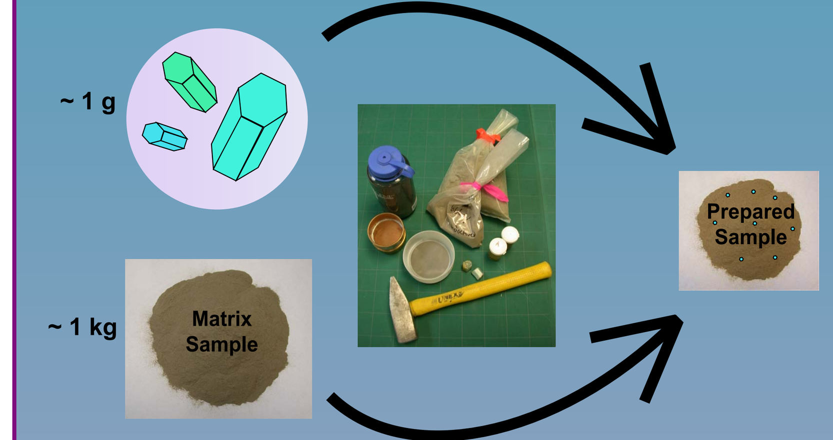


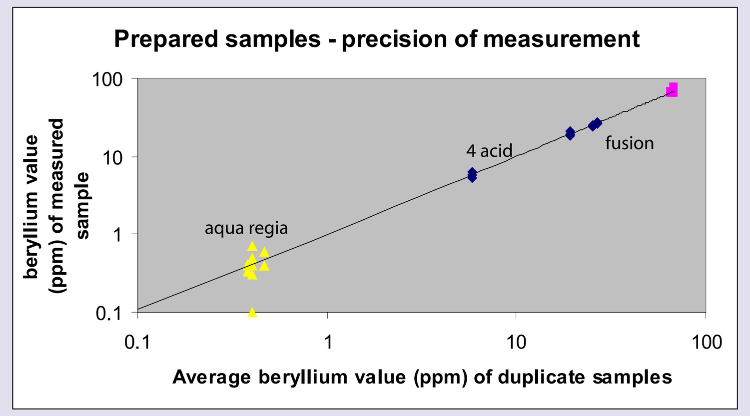
Methodology

In order to evaluate the geochemical responses of the different analytical techniques, a beryl-enriched samples was prepared.

A silt/clay "matrix" sample was sieved to -100 mesh and spiked with crushed, sieved aquamarine crystals to achieve a beryllium concentration of approximately 60 ppm. This is the "prepared sample".

Samples of prepared and matrix materials were sent to four labs. Triplicate analyses were requested on prepared and matrix samples. A reference standard (CANMET Reference Standard SY-3) was also sent for analysis.





Reproducible results for duplicate samples show that homogenization of beryl within the prepared sample was achieved.

These results also indicate excellent precision, even at low levels, for each of the analytical techniques. The apparent widespread results for aqua regia are due to the use of the log scale and one outlier result.

Analytical Methods

Techniques among the labs used for the study are fairly similar. The greatest variation is in the sample digestions. Measurement in all cases is by ICP methods.

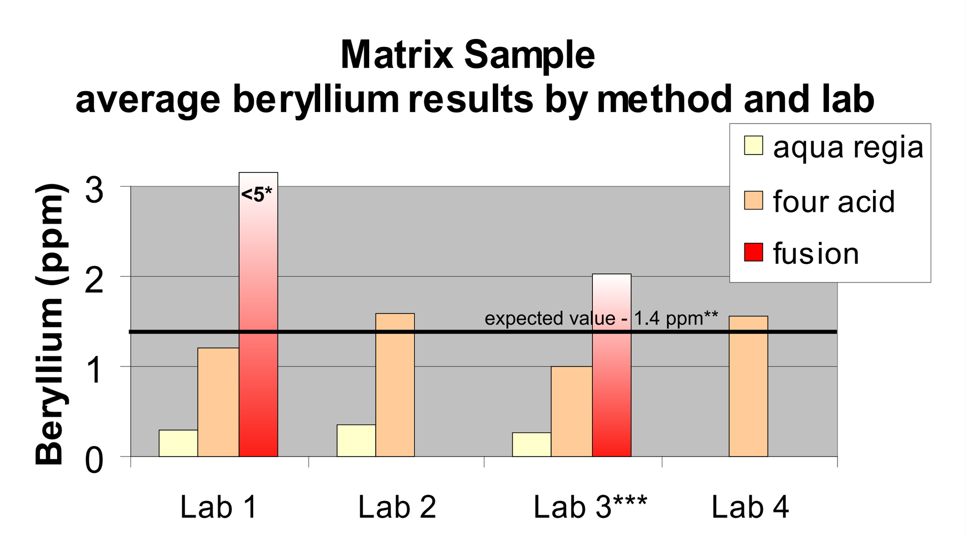
Aqua Regia - ICP-MS/AES
Sample is digested with aqua regia (hydrochloric acid and nitric acid) in a heated water bath. After cooling, the solution is diluted with distilled water and analyzed by ICP-MS/AES. This method is considered a partial digestion, especially for refractory silicate minerals, but gives the lowest levels of detection.

Four acid - ICP-MS/AES
Sample is digested with perchloric, nitric and hydrofluoric acids , after which hydrochloric acid is added. The solution is then analyzed by ICP-MS/AES. This method is more effective at breaking down silicate minerals than simple aqua regia due to the addition of hydrofluoric acid.

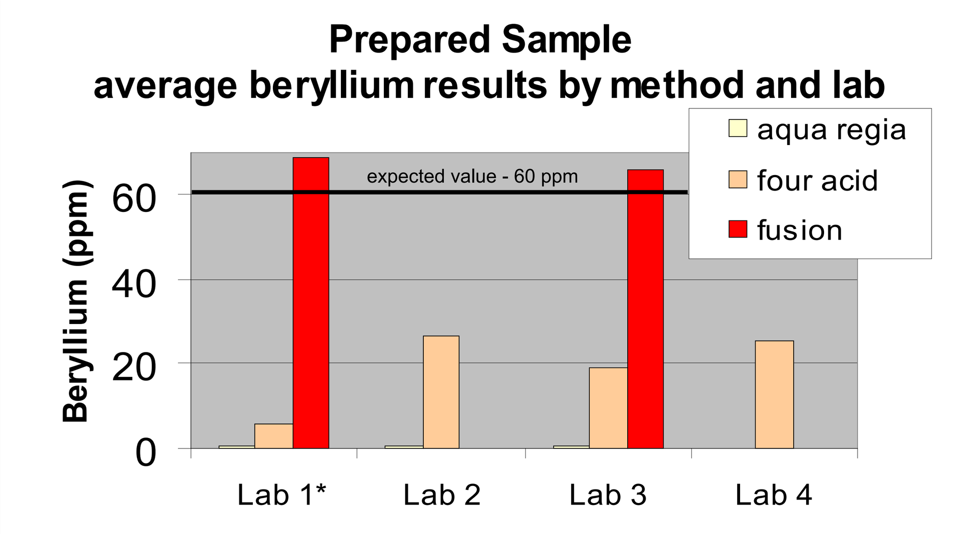
Fusion
Sample is dissolved in a hot flux. For **lithium metaborate ($LiBO_2$) fusion**, the sample is fused at 900°C with $LiBO_2$, dissolved in nitric acid and then analyzed by ICP-ES.

For **sodium peroxide (Na_2O_2) fusion**, Na_2O_2 and sodium hydroxide are added to the sample. The sample is heated to 550°C, distilled water and nitric acid are added, and then the solution is analyzed by ICP-ES. Fusion methods generally give better results for silicates than multi-acid digestion because the high temperature makes the sample more digestible.

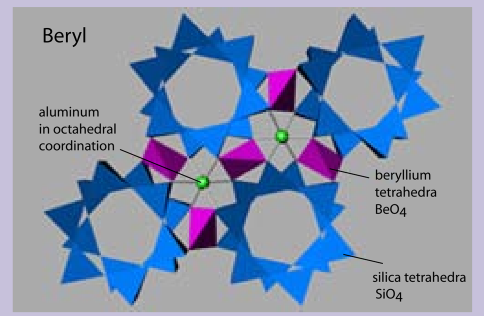
Results



*the sodium peroxide fusion method has a high lower detection limit for beryllium (5 ppm), all three results were below detection
**value is the average of 12 four acid analyses and the two LiBO2 fusion results above detection
***lithium metaborate fusion method gave imprecise results (1, <1, 3 ppm)



*lab 1 results for four acid are much lower than the other labs. This may be due to loss of volatilized sample in an open system or to poor digestion. The ratio of sample to solution, duration of digestion and temperature of extraction are all factors that may have affected these results.



Since beryllium is such a light element, it comprises only ~5% (by weight) of the beryl mineral structure. Therefore, even anomalous geochemical results tend to be low. For example, a sample with 0.1% beryl will have only 50 ppm Be.

Aqua Regia

· Aqua regia is a poor digestion method for beryl and beryllium-containing silicate minerals like those in the matrix sample (feldspars, micas, etc.) and yields values that are lower than the expected value.

Four Acid

· Beryllium values in the prepared samples were up to **70 times higher for four acid than aqua regia** digestion.

· Beryllium values in the matrix samples were up to **4.4 times higher for four acid digestion than aqua regia**.

· Determinations for the prepared samples are considerably (33%) lower than the expected value. This suggests that even four acid digestions do not dissolve all the beryl.

Fusion

· Beryllium values in the prepared sample were up to **178 times higher for fusion digestion than aqua regi**a and almost **three times higher than four acid**.

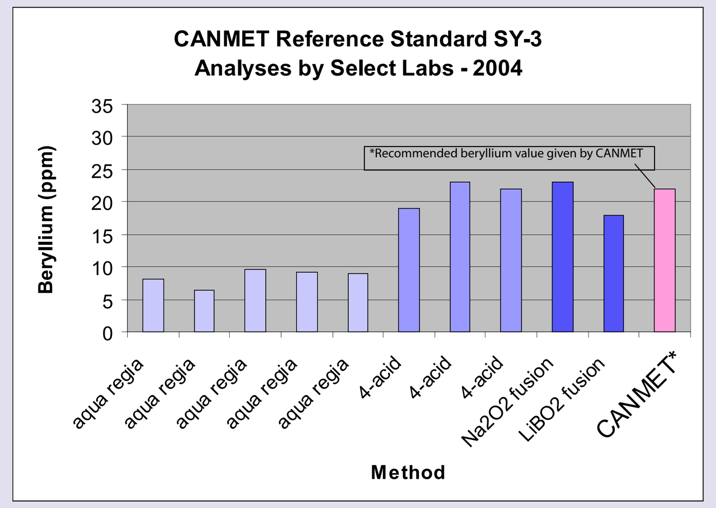
· Beryllium values in the matrix sample were below detection limit for sodium peroxide fusion and imprecise for the lithium metaborate fusion method.

Reference Standard

To independently check the analyses of the laboratories used, a reference standard was submitted (SY-3 syenite, CANMET Report 79-35). These results confirm the importance of multi-acid digestion in beryllium determinations.

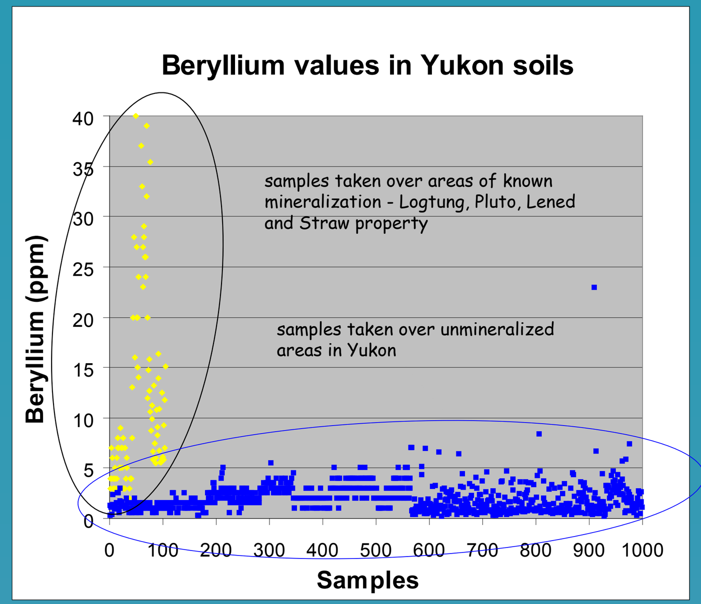
The reference sample has a recommended value of 22 ppm. Aqua regia digestion gave a maximum result of 9.6 ppm and an average result of 8.4 ppm. This is half the result of the fusion and four acid digestion methods.

The four acid digestion was as effective as the fusion methods in determining beryllium concentration. This is likely because the beryllium is bound up in minerals other than beryl. Unlike our matrix sample that had low beryllium values (close to lower detection limit (LDL)), beryllium concentration in SY-3 is well above detection and not subject to the imprecision of analyses near LDL. As well, the reference sample has been pulverized to -200 mesh, which might allow better digestion of silicates than the matrix sample which was sieved to only -100 mesh.

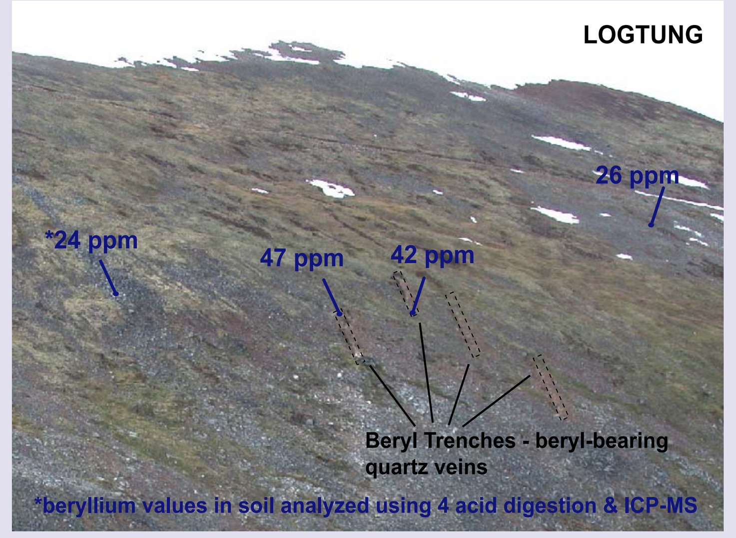


Emerald Exploration

Beryllium in Rocks and Soils



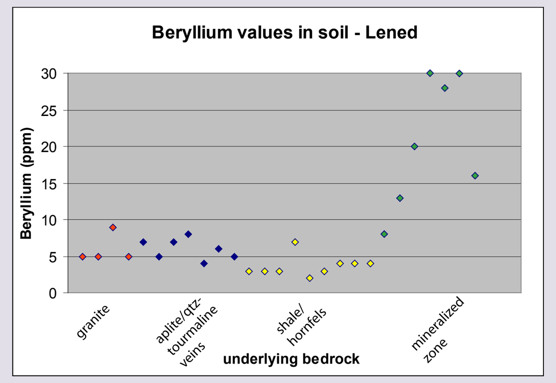
Yukon soils range from 0.1 ppm over unmineralized areas to >50 ppm over beryl-bearing veins. A plot of 1170 soil samples analyzed using three (hydrochloric, hydrofluoric and nitric acid) and four acid digestion across Yukon shows that most samples over unmineralized areas are <5 ppm beryllium.

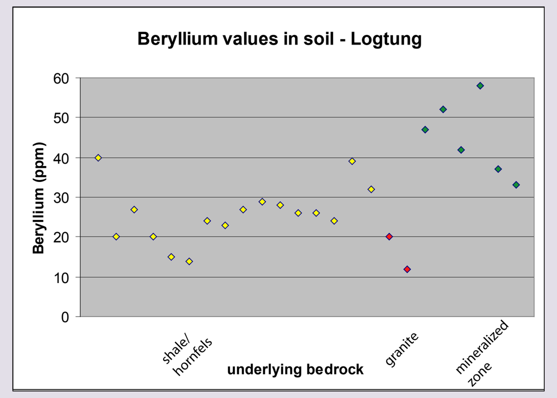


The beryllium content of most rocks and rock-forming minerals is low. Granitic rocks in Yukon range between 2 and 20 ppm beryllium.

Naturally occurring beryllium is not very mobile in the environment since it is bound up in resistant silicate minerals. Beryllium values in soil above bedrock should closely mirror beryllium values in underlying rock.

Beryllium values for Lened granite are 3 - 10 ppm. Soil values over the granite range from 5 to 9 ppm.





Emerald Exploration - the difficulties

Granitic rocks associated with emerald mineralization in Yukon and NWT have low beryllium values, however, establishing the level that constitutes a geochemical enrichment is the necessary starting point to identify beryl-mineralizing granites.

Geochemical data for rocks, silts and soils across Yukon is available from some mining assessment reports. Unfortunately, beryllium analysis was often not part of the package of elements analyzed, and when it was included, aqua regia rather than four acid digestion was typically used.

It is still possible to use this aqua regia data. Firestone Ventures Inc., which ran 103 silts and 35 soil samples from their beryl-mineralized Straw property using aqua regia and then later using four acid digestion, found the four acid digestion results to be approximately double those of the aqua regia.

Rocks and soils may be enriched in beryllium but the system may not have had the right conditions to form beryl. Beryllium-in-soil values >5 ppm define areas of beryllium enrichment, but may not necessarily indicate beryl mineralization.

Most beryl occurrences are localized (pockets, veins, miarolitic cavities, pegmatites, etc.) and therefore, highly anomalous beryllium values (>20 ppm) may be erratic and spatially restricted to beryl-mineralized areas

Conclusions

· Background beryllium values in Yukon soils are low, typically below 5 ppm (as determined using four acid digestion).

· Beryllium values in soils will reflect underlying bedrock. Beryllium is not geochemically mobile in the surficial environment since it is bound up in resistant silicate minerals.

· Beryllium soil anomalies (>5 ppm) will reflect a beryllium-rich system, but not necessarily beryl mineralization. Soils over areas of beryl mineralization may have spatially restricted high anomalies.

· Aqua regia digestion is a partial digestion method that is ineffective for dissolving beryl and only moderately effective at dissolving silicate mineral phases containing Be. It can be used as a first pass analytical method because a beryllium-enriched system will tend to have beryllium enrichments in different silicate minerals such as micas and feldspars.

· Four acid digestion method gives more accurate beryllium results, which is more effective at highlighting anomalies.

· Fusion methods give the most accurate results for beryllium, especially if it is bound up in a refractory mineral such as beryl, however, detection limits may be too high to outline weak anomalies.

Further Information

Ribbe, P.H. (editor), 2002. Beryllium - Mineralogy, Petrology, and Geochemistry. Reviews in Mineralogy & Geochemistry, Volume 50. Mineralogical Society of America., Washington, D.C., 2002.
Franklin, J.M., Duke, J.M., Shilts, W.W., Coker, W.B., Friske, P.W.B., Maurice, Y.T., Ballantyne, S.B., Dunn, C.E., Hall, G.E.M. and Garrett, R.G., 1991. Exploration Geochemistry Workshop. Geological Survey of Canada Open File 2390.
London D. and Evensen, J.M., 2002. Beryllium in Silicic Magmas and the Origin of Beryl-Bearing Pegmatites. In: Beryllium - Mineralogy, Petrology, and Geochemistry. Reviews in Mineralogy & Geochemistry, Volume 50. Mineralogical Society of America. P.H. Ribbe, Series Editor. Washington, D.C., 2002.
Reedman, J.H., 1979. Techniques in Mineral Exploration. Applied Science Publishers, London.
Vesely, J., Norton, S.A., Skrivan, P., Majer, V., Kram, P., Navratil, T. and Kaste, J.M., 2002. Environmental Chemistry of Beryllium. In: Beryllium - Mineralogy, Petrology and Geochemistry. E.S. Grew (editor), Reviews in Mineralogy & Geochemistry, vol. 50.

Acknowledgements

Special thanks to Lori Walton and Bill Wengzynowski for providing geochemical data.